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Special Issue Reprint

Research on Metallofullerenes

Edited by
Filip Uhlík, Takeshi Akasaka, Zdeněk Slanina and Xing Lu

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Guest Editors

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Contents

About the Editors	vii
Preface	ix
Zdeněk Slanina, Filip Uhlík, Takeshi Akasaka, Xing Lu and Ludwik Adamowicz	
La ₂ C ₂ @D ₅ (450)-C ₁₀₀ : Calculated High Energy Gain in Encapsulation	
Reprinted from: <i>Inorganics</i> 2024 , 12, 196, https://doi.org/10.3390/inorganics12070196	1
Martina Vrankić, Takeshi Nakagawa, Melita Menelaou, Yasuhiro Takabayashi, Naoya Yoshikane, Keisuke Matsui, et al.	
On the Structural and Vibrational Properties of Solid Endohedral Metallofullerene Li@C ₆₀	
Reprinted from: <i>Inorganics</i> 2024 , 12, 99, https://doi.org/10.3390/inorganics12040099	9
Yabei Wu, Zhonghao Zhou and Zhiyong Wang	
Stability and Electronic Properties of 1D and 2D Ca@C ₆₀ Oligomers and Polymers	
Reprinted from: <i>Inorganics</i> 2024 , 12, 45, https://doi.org/10.3390/inorganics12020045	22
Dong Liu, Yuan Shui and Tao Yang	
Geometries, Electronic Structures, Bonding Properties, and Stability Strategy of Endohedral Metallofullerenes TM@C ₂₈ (TM = Sc ⁻ , Y ⁻ , La ⁻ , Ti, Zr, Hf, V ⁺ , Nb ⁺ , Ta ⁺)	
Reprinted from: <i>Inorganics</i> 2024 , 12, 40, https://doi.org/10.3390/inorganics12020040	34
Yunpeng Xia, Yi Shen, Yang-Rong Yao, Qingyu Meng and Ning Chen	
Synthesis and Characterization of a Novel Non-Isolated-Pentagon-Rule Isomer of Th@C ₇₆ :Th@C ₁ (17418)-C ₇₆	
Reprinted from: <i>Inorganics</i> 2023 , 11, 422, https://doi.org/10.3390/inorganics11110422	46
Xinyi Zhou, Yang-Rong Yao, Yajing Hu, Le Yang, Shaoting Yang, Yilu Zhang, et al.	
Reactivity of Open-Shell Metallofullerene Anions: Synthesis, Crystal Structures, and Electrochemical Properties of Benzylated Gd@C _{2v} -C ₈₂	
Reprinted from: <i>Inorganics</i> 2023 , 11, 349, https://doi.org/10.3390/inorganics11090349	57
Huichao Zhang, Jinpeng Xin, Huaimin Jin, Wenhao Xiang, Muqing Chen, Yang-Rong Yao and Shangfeng Yang	
TmCN@C ₈₂ : Monometallic Clusterfullerene Encapsulating a Tm ³⁺ Ion	
Reprinted from: <i>Inorganics</i> 2023 , 11, 323, https://doi.org/10.3390/inorganics11080323	71
Zdeněk Slanina, Filip Uhlík, Takeshi Akasaka, Xing Lu and Ludwik Adamowicz	
Pr@C ₈₂ Metallofullerene: Calculated Isomeric Populations	
Reprinted from: <i>Inorganics</i> 2023 , 11, 313, https://doi.org/10.3390/inorganics11070313	84
Yaoxiao Zhao, Wangqiang Shen, Weixing Chen and Xing Lu	
Lu-Lu Bond in Lu ₂ @C ₆₀ Metallofullerenes	
Reprinted from: <i>Inorganics</i> 2023 , 11, 277, https://doi.org/10.3390/inorganics11070277	93
César Martínez-Flores and Vladimir A. Basiuk	
DFT Analysis of the Electronic and Structural Properties of Lanthanide Nitride Cluster Fullerenes Ln ₃ N@C ₈₀	
Reprinted from: <i>Inorganics</i> 2023 , 11, 223, https://doi.org/10.3390/inorganics11050223	102
Jordan Burkhardt, Hayden Prescott and Wan-Lu Li	
Metalloborospherene Analogs to Metallofullerene	
Reprinted from: <i>Inorganics</i> 2024 , 12, 193, https://doi.org/10.3390/inorganics12070193	117

Yameng Hou and Xianglei Kong

Endometallofullerenes in the Gas Phase: Progress and Prospect

Reprinted from: *Inorganics* **2024**, *12*, 68, <https://doi.org/10.3390/inorganics12030068> **138**

Fupin Liu and Alexey A. Popov

Capturing Unstable Metallofullerenes

Reprinted from: *Inorganics* **2024**, *12*, 48, <https://doi.org/10.3390/inorganics12020048> **156**

Sapna Sinha, Karifa Sanfo, Panagiotis Dallas, Sujay Kumar and Kyriakos Porfyraakis

Process Parameter Optimisation for Endohedral Metallofullerene Synthesis via the Arc-Discharge Method

Reprinted from: *Inorganics* **2024**, *12*, 38, <https://doi.org/10.3390/inorganics12020038> **171**

Song Wang, Xianming Zhang, Xi Tan, Hongzhen Li, Songxin Dai, Bin Yao, et al.

Recent Progress on the Functionalization of Endohedral Metallofullerenes

Reprinted from: *Inorganics* **2023**, *11*, 346, <https://doi.org/10.3390/inorganics11080346> **191**

About the Editors

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Preface

The 40th anniversary is approaching of the first experimental observation of fullerenes in a laser-vaporized graphite cluster beam mass spectrum, which was made by H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley in 1985. This will be the anniversary not only for fullerenes and buckminsterfullerene in particular, but also for the first endohedral metallofullerene observed, La@C₆₀, just a few days later. There has been tremendous progress in the field since then, documented by tens of thousands of publications. The production of fullerenes in macroscopic quantities, i.e., hundreds of observed and isolated new species, has influenced their characterization both experimentally and theoretically, determining their various applications as MRI and X-ray contrast agents, radiotracers, photovoltaic cells, nanoelectronics, superconductors, and more.

The field of metallofullerene research is leading, with hundreds of new publications each year; therefore, this Reprint on Metallofullerenes in Inorganics, discussing the chemical and physical properties of metallofullerenes studied both experimentally and theoretically, is very timely.

Filip Uhlík, Takeshi Akasaka, Zdeněk Slanina, and Xing Lu

Guest Editors



Article

La₂C₂@D₅(450)-C₁₀₀: Calculated High Energy Gain in Encapsulation

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Abstract: The structure and energetics of the clusterfullerene La₂C₂@D₅(450)-C₁₀₀ are calculated at the B3LYP/6-31G*~SDD level (including counterpoise correction for the basis set superposition error), and the observed features are confirmed. Its stability is explained by substantial energy gain connected with the encapsulation, viz. 140 kcal/mol per atom of the encapsulate, actually higher than previously found for comparable systems.

Keywords: metallofullerenes; clusterfullerenes; La₂C₂@D₅(450)-C₁₀₀; theory-experiment comparisons; quantum-chemical calculations

1. Introduction

In fullerene and metallofullerene research, calculations have from the beginning helped experimental search and understanding of new nanocarbons [1–4], more recently even with species containing around one hundred carbons [5–7]. In the group of such large metallofullerenes [8–18], another giant system has recently been characterized [14] by X-ray crystal diffraction, namely La₂C₂@D₅(450)-C₁₀₀. In this study, the giant clusterfullerene is calculated using the density functional theory (DFT) in order to further enhance knowledge of its structure and encapsulation energetics.

2. Calculations

The D₅(450)-C₁₀₀ fullerene is one of the 450 isolated-pentagon-rule (IPR) cages of C₁₀₀ [19] (if enantiomers are considered as equivalent, 862 IPR isomers if enantiomers are regarded as distinct). Interestingly, the total number of all C₁₀₀ isomeric cages (i.e., IPR and non-IPR cages) is 285,913 if enantiomers are considered equivalent [4]. The D₅(450)-C₁₀₀ fullerene exhibits D₅ topological symmetry which is however reduced owing to the Jahn-Teller distortion. At our computational level the topological symmetry is in geometry optimization lowered to the C₂ point group of symmetry (Figure 1, one can speak on a near D₅-symmetry). Interestingly enough, there are other C₁₀₀ IPR cages with a higher topological symmetry like D_{5d} or T.

The La₂C₂@D₅(450)-C₁₀₀ geometrical structure was optimized with the Becke's three parameter DFT functional with the non-local Lee-Yang-Parr correlation functional [20–22], the approach is conventionally labeled as B3LYP. The DFT calculations were at first performed in a combined atomic basis set: the standard 3-21G basis for C atoms while for La atoms the SDD basis set with the SDD effective core potential [23] (B3LYP/3-21G~SDD). The geometry optimization started from the X-ray structure [14] and was further refined with the B3LYP/6-31G*~SDD treatment using an extended 6-31G*~SDD basis set, followed by the GF harmonic vibrational analysis. The vibrational analysis allows for a check of the nature of the stationary points found, i.e., if local energy minima were really

found (and not activated complexes or even higher types of hypersurface stationary points). Moreover, the analysis can also be used for simulations of the IR and Raman vibrational spectra. For numerical integrations with the DFT functional the so called ultrafine grid was used. Moreover, the tight SCF (self consistent field) convergency criterion was applied. Finally, the wavefunction stability was tested throughout in order to eliminate unstable SCF solutions (without a real physical significance).

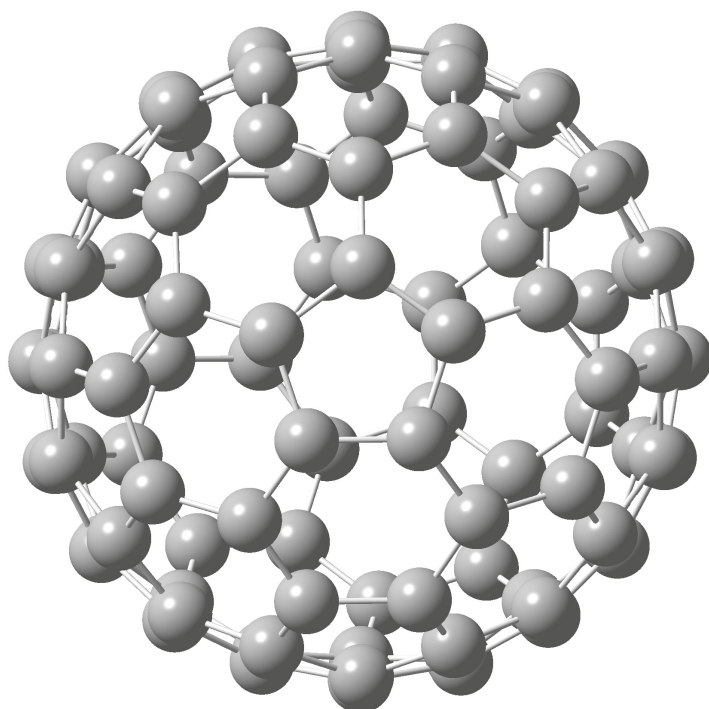


Figure 1. The B3LYP/6-31G* optimized structure of $D_5(450)-C_{100}$.

The so-called basis set superposition error (BSSE) was considered accordingly, namely by application of the approximative Boys-Bernardi counterpoise method (also known as CP2, or CPn, depending on the number of the reaction components in the treated association process) [24], since recently considered [25] also with metallofullerenes. The Boys-Bernardi approach to the BSSE correction term is an approximative treatment that ensures that every reaction component of a studied chemical process is formally described by the same number of the atomic basis set functions (so that the calculated energies are directly comparable). The required basis-set consistence is realized by rather formal, artificial atoms (thus also called ghost) possessing no electrons. The BSSE problem essentially originates in the fact that the considered basis sets are always finite. In other words, the BSSE correction would disappear in a situation of a basis set with infinite number of atomic basis functions (of course, such an infinite scheme cannot practically be handled). The BSSE correction term represents an important addition also to the energetics of any encapsulation process. Without the BSSE correction the energy gain created by encapsulation would be exaggerated (so that endohedrals would artificially be over-stabilized). Thus, the BSSE consideration is needed for reliable predictions of energetics, indeed.

All the reported calculations were performed with the program package Gaussian 09 [26]. The calculations were carried out with computers operating in parallel regime, mostly with 8–24 processors (with computational frequency up to 3 GHz each and with the available operational memory up to 60 GB).

3. Results and Discussion

The B3LYP/6-31G*~SDD optimized structure of $\text{La}_2\text{C}_2@D_5(450)-C_{100}$ shown in Figure 2 basically agrees with the X-ray results [14]. The calculated C-C bond length in the La_2C_2

encapsulate is 1.26 Å while the C-La bond 2.44 Å, the La-C shortest contact with the cage 2.64 Å. The B3LYP/3-21G SDD computed Wiberg bond index for the C-C bond is 2.58 (i.e., between double and triple bond), for C-La bond 0.69 (B3LYP/6-31G*~SDD values C-C 2.59, C-La 0.63). It should be realized that the calculated values are obtained for the gas-phase free (isolated) endohedral. Moreover, the calculated terms correspond to the equilibrium geometries with motionless nuclei. The X-ray values are however obtained for the crystal-state endohedral.

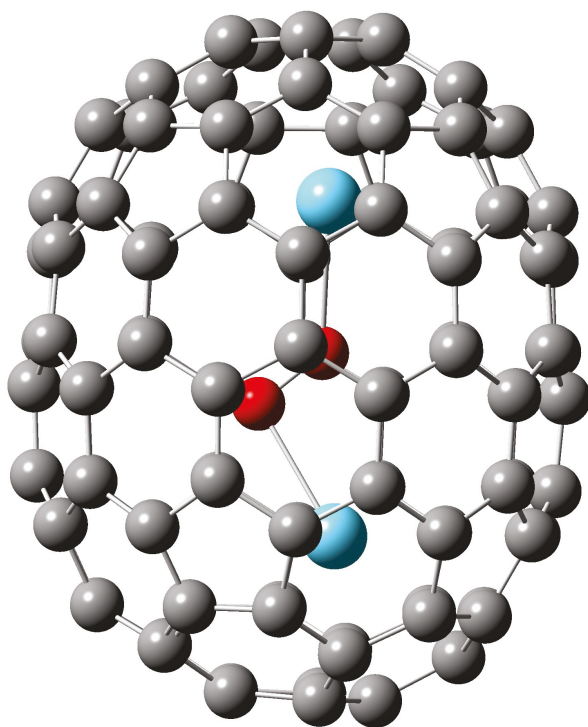


Figure 2. The B3LYP/6-31G*~SDD optimized structure of $\text{La}_2\text{C}_2@D_5(450)\text{-C}_{100}$ (carbons of La_2C_2 are in red).

The Mulliken atomic charges on atoms are (owing to their historical introduction) to be constructed at a simpler level, i.e., B3LYP/3-21G~SDD. The Mulliken charges on atoms calculated with the 3-21G basis set are known [27] to produce for metallofullerenes a good agreement with the available observed charges [28]. Moreover, there are also general methodological reasons [29,30] why some larger basis sets should not be applied in the calculations of the Mulliken atomic charges on atoms—as they can sometimes produce rather unphysical values. The Mulliken charges on the La atoms are 2.41 and 2.47 (of the electron elementary charge) while on the carbons of the La_2C_2 encapsulate the charges are -0.32 and -0.34 . Hence, the total charge on the encapsulate is 4.22. In overall, the charge transfer from the encapsulate to the cage amounts to 4.22 electrons. Thus, energetics of tetra-anions of empty cages could serve for stability estimations with encapsulations of La_2C_2 by other C_{100} cages.

Although the ground state of $\text{La}_2\text{C}_2@D_5(450)\text{-C}_{100}$ is singlet electronic state, the first electronic triplet state is rather low lying. At the B3LYP/6-31G*~SDD level the triplet state is located only about 1.88 kcal/mol above the ground-state singlet.

The energy change connected with the (formal thermodynamic) gas-phase encapsulation process:

$$2\text{La}(\text{g}) + 2\text{C}(\text{g}) + D_5(450) - \text{C}_{100}(\text{g}) = \text{La}_2\text{C}_2@D_5(450) - \text{C}_{100}(\text{g}) \quad (1)$$

is a useful characteristics known as encapsulation energy. Calculated reaction thermodynamic changes are mostly treated as the reaction potential-energy change $\Delta E_{\text{pot,enc}}$.

However, a more adequate description refers to the enthalpy change at absolute zero temperature $\Delta H_{0,enc}^0$, i.e., the potential energy change corrected for the vibrational zero-point energies upon encapsulation ΔZPE_{enc} :

$$\Delta H_{0,enc}^0 = \Delta E_{pot,enc} + \Delta ZPE_{enc}. \quad (2)$$

The encapsulation potential-energy change corrected $\Delta E_{pot,enc}$ is to be refined by inclusion of the basis set superposition error [24,26] (BSSE/CP5) and so-called steric correction [25] that reflects the cage distortion upon encapsulation [31]. Table 1 presents the energy terms for reaction (1) considered as reduced or relative values, i.e., per one atom of the La_2C_2 encapsulate (thus in the units of kcal/mol/atom). Such reduced values are convenient for comparisons with encapsulations of species with different numbers of atoms. For example, the reduced $\Delta H_{0,enc}^0$ term of -138.4 kcal/mol/atom from Table 1 represents the encapsulation-energy gain larger by 21.1 kcal/mol/atom than found [18] for $\text{Y}_2\text{C}_2@C_{1(1660)}-C_{108}$ at the same computational level. Similarly, the reduced $\Delta E_{pot,enc}$ term of -140.2 kcal/mol/atom in Table 1 gives by 3.7 kcal/mol/atom better energy gain than calculated [32] at the same level for $\text{Ti}_3\text{C}_3@I_h-C_{80}$. In overall, $\text{La}_2\text{C}_2@D_5(450)-C_{100}$ is a new interesting member of the family of metallofullerenes with relatively large energy gains upon encapsulation.

Table 1. The B3LYP/6-31G*~SDD computed ^a encapsulation energetics for $\text{La}_2\text{C}_2@D_5(450)-C_{100}$.

Energy Term	(kcal/mol/atom)
$\Delta E_{pot,enc}$ without BSSE	−148.7
$\Delta E_{pot,enc}$ with BSSE	−143.2
$\Delta E_{pot,enc}$ with BSSE & steric	−140.2
$\Delta H_{0,enc}^0$	−138.4

^a See process (1), the BSSE correction evaluated with the CP5 approach.

The encapsulation enthalpy $\Delta H_{0,enc}^0$ (enhanced by the related entropic contributions) allows for statistical thermodynamic evaluations of the equilibrium concentrations [33,34], in our case by means of the encapsulation equilibrium constant for process (1):

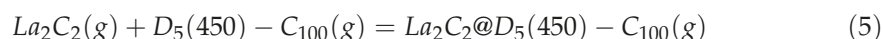
$$K_{p,enc}(1) = \frac{p_{\text{La}_2\text{C}_2@D_5(450)-C_{100}}}{p_{\text{La}}^2 p_{\text{C}}^2 p_{D_5(450)-C_{100}}} \quad (3)$$

defined by the partial pressures p of the individual reaction components in reaction (1). The encapsulation equilibrium constant from Equation (3) can indeed be expressed [34, 35] by a compact formula using the molecular (or atomic) partition functions q_i^0 (the partition functions have to correspond to the selected standard state, e.g., ideal gas phase at 1 atm = 101,325 Pa pressure) and the standard encapsulation enthalpy change at the absolute zero temperature $\Delta H_{0,enc}^0$:

$$K_{p,enc}(1) = \frac{\frac{q_{\text{La}_2\text{C}_2@D_5(450)-C_{100}}^0}{N_A}}{[\frac{q_{\text{La}}^0}{N_A}]^2 [\frac{q_{\text{C}}^0}{N_A}]^2 \frac{q_{D_5(450)-C_{100}}^0}{N_A}} \exp\left[-\frac{\Delta H_{0,enc}^0}{RT}\right], \quad (4)$$

where symbol N_A stands for the Avogadro number. The molecular partition functions q_i^0 primarily consist of the rotational-vibrational partition functions based on the molecular parameters from the GF harmonic vibrational analysis.

In principle, the encapsulation energy can also be defined [34] by a more straightforward encapsulation stoichiometry, namely:



when the basis set superposition error [24,26] is evaluated by the simpler BSSE/CP2 approach which at the B3LYP/6-31G*~SDD level yields the reduced energy gain of -58.7 kcal/mol/atom (-62.5 kcal/mol/atom without the BSSE correction). Obviously, the energy gain must be now smaller than with the BSSE/CP5 approach as in the latter case the formation of the bonds of the encapsulate is included.

However, if one is interested in the thermodynamic-equilibrium populations of non-isomeric endohedrals [33], approach according to Equation (1) should be preferred. Incidentally, in addition to our starting system $La_2C_2@D_5(450)-C_{100}$ another pertinent species is known [10], viz. $La_2@D_5(450)-C_{100}$. The relative populations of the two non-isomeric endohedrals can be described using the equilibrium constant $K_{p,enc}(1)$ defined by Equation (3) and its equivalent $K_{p,enc}(6)$ for parent process in Equation (6):



The population ratio of the two endohedrals is given by formula [33]:

$$\frac{p_{La_2C_2@D_5(450)-C_{100}}}{p_{La_2@D_5(450)-C_{100}}} = p_C^2 \frac{K_{p,enc}(1)}{K_{p,enc}(6)}. \quad (7)$$

Obviously, the relative equilibrium populations of such non-isomeric nanocarbons represent distinctly more complex problem compared to the situation of just isomeric species [34–37]. The equilibrium constant $K_{p,enc}(6)$ can again be evaluated by the partition functions and calculated molecular parameters as in Equation (4). The partial pressure of carbon p_C can be approximated by the carbon saturated pressure [34]. However, the actual carbon pressure p_C depends on particular experimental setup and thus varies from case to case. This aspect is one of the reasons why the population ratio of the two endohedrals can be different in different experiments, too. The interesting relative stability problem for non-isomeric nanocarbons should further be calculated in future.

The encapsulation of La_2C_2 into the $D_5(450)-C_{100}$ cage creates six new vibrational modes, actually with rather low frequencies—at the B3LYP/6-31G*~SDD level between 24 and 73 cm^{-1} . The low frequencies basically belong to motions of the whole La_2C_2 encapsulate inside the cage, they could roughly be viewed as relatively free rotations. Such low frequency motions would particularly be important for the endohedral thermodynamics [35,36]. The new vibrational frequencies created by the encapsulation also contribute to the reaction change ΔZPE_{enc} of the vibrational zero-point energy for process (1). On the other hand, the highest computed vibrational frequency has a value of 1926 cm^{-1} and belongs to the bond stretching of the C-C bond in La_2C_2 (though the vibrational mode exhibits rather negligible IR intensity as well as Raman activity). Let us note that the gas-phase C_2 molecule has [38] in the singlet ground state observed vibrational frequency of 1855 cm^{-1} (the C_2 lowest triplet state lies higher only by 2.05 kcal/mol). For another comparison, the highest vibrational frequency of the empty $D_5(450)-C_{100}$ cage at the B3LYP/6-31G* level has value of 1615 cm^{-1} . Figure 3 presents the B3LYP/6-31G*~SDD calculated harmonic IR and Raman spectra of $La_2C_2@D_5(450)-C_{100}$. The spectra should be useful in identification of the species.

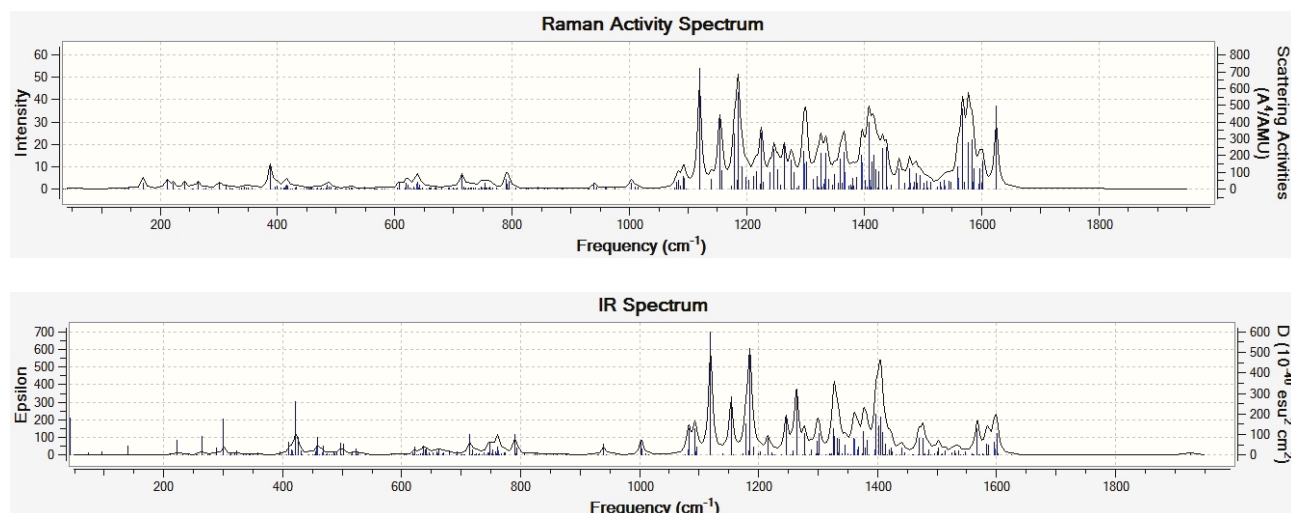


Figure 3. The B3LYP/6-31G*~SDD calculated IR (**bottom**) and Raman (**top**) spectra of $\text{La}_2\text{C}_2@D_5(450)\text{-C}_{100}$.

4. Conclusions

The structure and energetics of the metallofullerene (or clusterfullerene) $\text{La}_2\text{C}_2@D_5(450)\text{-C}_{100}$ are evaluated using the DFT approach at the B3LYP/6-31G*~SDD level with inclusion of the correction for the basis set superposition error calculated by the counterpoise method. The calculated encapsulation potential-energy change $\Delta E_{\text{pot,enc}}$ amounts to a sizeable value of -140.2 kcal/mol/atom (i.e., per atom of the encapsulate), or at the $\Delta H_{0,\text{enc}}^0$ level to -138.4 kcal/mol/atom. The found energy gains connected with encapsulation are larger than previously reported for other clusterfullerene systems like $\text{Y}_2\text{C}_2@C_{1(1660)}\text{-C}_{108}$ or $\text{Ti}_3\text{C}_3@I_h\text{-C}_{80}$. Possible descriptions of encapsulation energetics are discussed and a thermodynamically consistent evaluation of the relative equilibrium populations of non-isomeric metallofullerenes is suggested with an aim to compare the $\text{La}_2\text{C}_2@D_5(450)\text{-C}_{100}$ equilibrium population with that of a related observed species $\text{La}_2@D_5(450)\text{-C}_{100}$. The approach can be of a use also for studies of other interesting complex nanocarbon systems [39–45].

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Article

On the Structural and Vibrational Properties of Solid Endohedral Metallofullerene Li@C₆₀

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Abstract: The endohedral lithium fulleride, Li⁺@C₆₀^{•−}, is a potential precursor for new families of molecular superconducting and electronic materials beyond those accessible to date from C₆₀ itself. Solid Li@C₆₀ comprises (Li@C₆₀)₂ dimers, isostructural and isoelectronic with the (C₅₉N)₂ units found in solid azafullerene. Here, we investigate the structural and vibrational properties of Li@C₆₀ samples synthesized by electrolytic reduction routes. The resulting materials are of high quality, with crystallinity far superior to that of their antecedents isolated by chemical reduction. They permit facile, unambiguous identification of both the reduced state of the fulleride units and the interball C-C bonds responsible for dimerization. However, severe orientational disorder conceals any crystal symmetry lowering due to the presence of dimers. Diffraction reveals the adoption of a hexagonal crystal structure (space group *P*6₃/*mmc*) at both low temperatures and high pressures, typically associated with close-packing of spherical monomer units. Such a situation is reminiscent of the structural behavior of the high-pressure Phase I of solid dihydrogen, H₂.

Keywords: endofullerenes; dimerization; vibrational spectroscopy; synchrotron X-ray diffraction; high pressure

1. Introduction

Following the serendipitous discovery of the fullerene family of molecular carbon nearly 40 years ago, research on the chemical, physical, and materials properties of its members and those of their derivatives has proceeded unabated. In brief, there are four distinct ways of manipulating the molecular and crystalline forms of the fullerenes. Firstly, direct chemical functionalization of the π -electron molecular framework leads to a rich organic chemistry, affording numerous derivatives of both C₆₀ and its higher fullerene antecedents that have applications in diverse fields from molecular electronics to solar cells [1].

Secondly, reductive intercalation of metal ions into the voids of the crystalline structures of fullerenes—most prominently, that of C_{60} —leads to sensitively modifying the electronic structure and has resulted in a plethora of fulleride salts with M_xC_{60} stoichiometry and x ranging from a low value of 1 (e.g., in RbC_{60}) to a high value of 12 (e.g., in $Li_{12}C_{60}$). In particular, exohedrally modified fulleride materials with A_3C_{60} (A = alkali metal) stoichiometry have provided examples of high- T_c molecular superconductors with transition temperatures as high as 38 K and with the zero-resistance performance surviving to record high magnetic fields (exceeding 90 T). Of significance is also the unconventional, highly correlated nature of superconductivity, which is proximate to an antiferromagnetic Mott insulating state out of which it emerges upon lattice contraction via the application of chemical and/or physical pressure [2–5].

Thirdly, the electronic structure can be tuned by on-ball substitution of heteroatoms such as B or N. The most prominent derivative has been the azafullerene radical, $C_{59}N^\bullet$, which dimerizes to afford the non-magnetic $(C_{59}N)_2$ moiety [6]. Further manipulation of the properties of such heterofullerenes can be achieved by exohedral metal intercalation, resulting in salts such as $K_6C_{59}N$, in which electron doping is achieved synergistically both by on- and in-between-the-balls donors [7].

Finally, a large family of fullerene derivatives can be accessed by endohedral encapsulation of atomic or molecular units to afford $A@C_n$ moieties. For a long while, this field of fullerene research was dominated by metal encapsulation of higher fullerenes [8,9], with bulk availability of endohedral C_{60} units remaining elusive. This situation has changed dramatically following two significant discoveries: (a) the development of the “molecular surgery” synthetic technique [10], which has led to numerous endohedral C_{60} fullerenes incorporating noble gas atoms (e.g., He, Ne, Ar, Kr) or small molecules (e.g., H_2 , HF, CO, H_2O , CH_4) [11,12] and (b) the successful synthesis of fullerene salts, $(Li^+@C_{60})X^-$ ($X^- = PF_6^-, SbCl_6^-$), which comprise $Li^+@C_{60}$ endohedral molecular ions and X^- spacer units, which serve a charge-balancing role [13–15]. Remarkably, both chemical and electrochemical reduction of the $Li^+@C_{60}$ cation lead to the formation of the neutral radical anion, $Li^+@C_{60}^{\bullet-}$ [16,17], which, in analogy with the on-ball-substituted azafullerene $C_{59}N^\bullet$ radical, dimerizes to afford $(Li@C_{60})_2$, isostructural and isoelectronic with the $(C_{59}N)_2$ molecule [18,19].

Structural and electronic characterization of the $(Li@C_{60})_2$ solid obtained by chemical reduction confirmed its dimeric structure in the solid state [17]. However, the as-obtained material lacked good crystallinity, resulting in moderate quality diffraction and spectroscopic data. Attempts to sublime the material led to the escape of the metal ion from the endofullerene space, precluding any improvement in crystallinity, in contrast to its azafullerene antecedent [19]. Here, we report on the structural and vibrational properties of the $(Li@C_{60})_2$ solid obtained by electrochemical reduction—this is a highly crystalline material, which permits detailed study of the structural and electronic properties. While vibrational spectroscopy readily identifies the vibrational signatures of interball C-C bond formation consistent with dimerization, the material is shown to adopt a highly symmetric hexagonal-close-packed crystal structure—typically associated with monomer sphere packing—as a result of disorder both at ambient pressure down to 3.4 K and at ambient temperature up to 13.1 GPa.

2. Results and Discussion

2.1. Vibrational Properties

The Raman spectrum of $(Li@C_{60})_2$ obtained by electrochemical reduction of the $(Li^+@C_{60})(PF_6^-)$ precursor, along with those of monomeric C_{60} , $(Li@C_{60})(PF_6)$, and dimeric $(C_{59}N)_2$ solids, is illustrated in Figure 1—the corresponding molecular units are generated by VESTA [20]. The frequencies of the observed Raman peaks are summarized in Table S1. In the case of the monomeric C_{60} and $(Li@C_{60})(PF_6)$ fullerene materials, the 785 nm laser line was used for excitation to prevent photoinduced polymerization upon illumination with visible or ultraviolet light [21]. On the other hand, owing to the stability of the dimeric

(Li@C₆₀)₂ and (C₅₉N)₂ fullerenes against photoinduced polymerization, the 633 nm line of a He-Ne laser was used for their excitation to take advantage of the improved throughput of the Raman spectrometer in the corresponding spectral region. The Raman spectra of C₆₀ solid and (Li@C₆₀)(PF₆) are nearly identical to each other with small frequency shifts (≤ 3 cm⁻¹) between the corresponding peaks and are compatible with the monomeric nature of the C₆₀ units. Both spectra are dominated by the ten Raman-active intramolecular C₆₀ modes, attributed to the two totally symmetric A_g(1) and A_g(2) modes and the eight fivefold-degenerate H_g(1)–H_g(8) of the C₆₀ molecule in icosahedral I_h symmetry [22]. The weak crystal field in solid C₆₀ causes only the splitting of the radial H_g(1) mode into two components (at 266 and 272 cm⁻¹), while the appearance of a weak peak at 1458 cm⁻¹ can be attributed to the presence of traces of polymerized C₆₀ (A_g(2) mode of polymeric chains [23]).

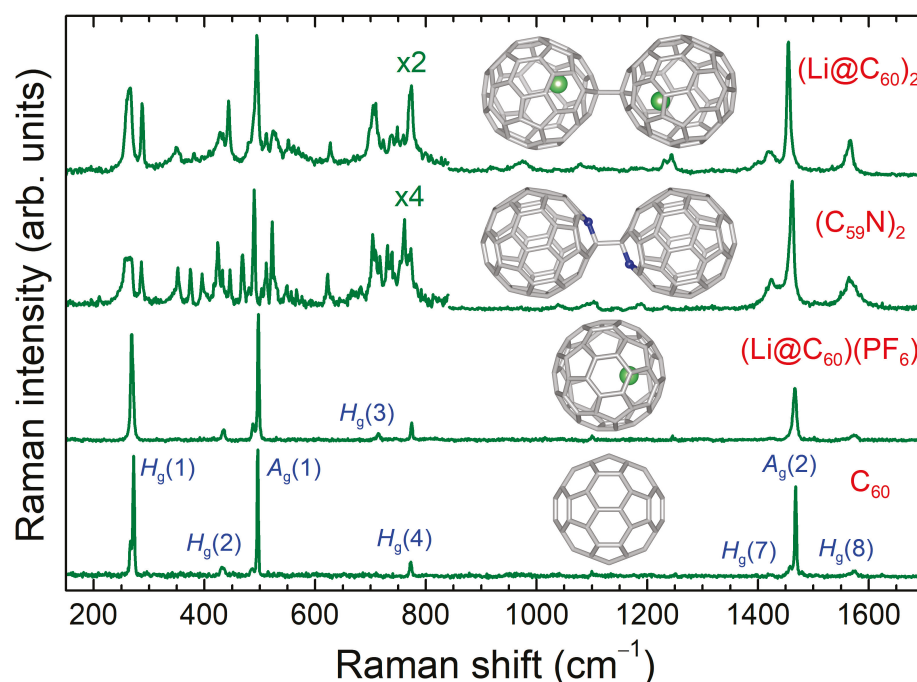


Figure 1. The Raman spectrum of the (Li@C₆₀)₂ sample prepared by electrochemical reduction ($\lambda_{\text{exc}} = 633$ nm) is displayed together with those of C₆₀ ($\lambda_{\text{exc}} = 785$ nm), monomeric (Li@C₆₀)(PF₆) ($\lambda_{\text{exc}} = 785$ nm), and dimeric (C₅₉N)₂ ($\lambda_{\text{exc}} = 633$ nm) solids. The low-frequency spectral region in the dimeric molecular solids has been suitably enhanced to improve visibility. The mode assignment refers to the irreducible representations of the C₆₀ molecule in I_h symmetry. Each spectrum is accompanied by the structure of the corresponding molecular unit drawn by VESTA [20].

The Raman spectrum of dimeric (C₅₉N)₂ solid is far richer in structure compared to the monomeric systems, as the cage distortion and the concomitant lowering of the molecular symmetry upon dimerization cause the appearance of additional Raman peaks. These originate from the splitting of the degenerate H_g modes and the activation and splitting of inactive vibrational modes of the C₆₀ molecule in I_h symmetry [24,25]. The plethora of Raman split components appearing in the spectrum of (C₅₉N)₂ is in fair agreement with those earlier reported in the literature and assigned to intramolecular C₆₀ modes in I_h symmetry [24]. The same assignment of the observed Raman peaks in the present work was also adopted in Table S1. As inferred from Figure 1 and Table S1, the similarity of the Raman spectrum profile and the frequencies of the constituent Raman peaks of (Li@C₆₀)₂ obtained by electrochemical reduction with those of dimeric (C₅₉N)₂ is evident, establishing its dimeric nature unambiguously. Moreover, comparison of the overall Raman spectrum profile of the present (Li@C₆₀)₂ sample with that of the neutral Li@C₆₀ obtained by chemical reduction of the Li⁺@C₆₀ cation by decamethylferrocene (Figure S1) clearly illustrates the

stronger intensities and narrower lineshapes of the split Raman components in $(\text{Li}@\text{C}_{60})_2$ obtained by electrochemical reduction—this is in addition to the similarities regarding the appearance of the Raman peaks associated with the dimerization of the C_{60} cages. The present results are compatible with the superior crystallinity of the present material, in accordance with its powder XRD data (*vide infra*), contrary to the situation encountered in $(\text{Li}@\text{C}_{60})_2$ obtained by chemical reduction, where a small fraction of monomers is also present [17].

The frequency of the $A_g(2)$ pentagonal pinch mode of the C_{60} molecule deserves further attention. In particular, the $A_g(2)$ frequency in C_{60} -based materials is extremely sensitive to both doping and intermolecular covalent bonding [23–28]. In monomeric alkali fullerenes, it downshifts quasi-linearly by $6\text{--}7\text{ cm}^{-1}$ per electron transferred from the metal atoms to the C_{60} units [26–28], due to the elongation of the intramolecular bonds induced by the charge transfer process and the resulting softening of the force constants [29,30]. Moreover, in neutral polymeric C_{60} -based fullerene materials—including dimerized systems—the $A_g(2)$ mode also softens due to the intermolecular covalent bond formation and the concomitant decrease in the mean intramolecular bond strength. The observed softening depends strongly on the number of the sp^3 -like coordinated carbon atoms per molecular cage [31]. Accordingly, and as evident in Table S1 (numbers in bold), there is a softening of the $A_g(2)$ peak in neutral $(\text{C}_{59}\text{N})_2$ compared to that in C_{60} solid by $\sim 6\text{ cm}^{-1}$, which is attributed to the formation of the intermolecular covalent bond due to dimerization [25]. In the case of $(\text{Li}@\text{C}_{60})_2$, the softening of this peak is even larger, ~ 13 and $\sim 10\text{ cm}^{-1}$ relative to monomeric C_{60} and $(\text{Li}@\text{C}_{60})(\text{PF}_6)$, respectively. This can be understood in terms of the combined effect of covalent intermolecular bonding and uptake of one electron by the C_{60} cage in $(\text{Li}@\text{C}_{60})_2$ —here, electrons are more delocalized over the radical carbanion cage than in the case of $(\text{C}_{59}\text{N})_2$, where the electron pairs are localized on the nitrogen atoms [17].

The dimeric nature of $(\text{Li}@\text{C}_{60})_2$ obtained by electrochemical reduction is further supported by its IR transmission spectrum illustrated in Figure 2 in comparison with that of monomeric C_{60} solid. More specifically, the IR spectrum of C_{60} solid is dominated by the four IR active modes of the C_{60} molecule in I_h symmetry $\{F_{1u}(1)\text{--}F_{1u}(4)\}$, appearing at 525, 576, 1182, and 1428 cm^{-1} , in excellent agreement with the literature [32]. The additional weaker spectral features are due to forbidden fundamentals, activated by the distortion of the molecular I_h symmetry in the C_{60} crystal. As in the case of the corresponding Raman spectrum, in the IR spectrum of $(\text{Li}@\text{C}_{60})_2$, several split components appear due to intercage bonding and symmetry lowering, similar to the case of $(\text{C}_{59}\text{N})_2$ [33]. Despite similarities of the IR spectrum with that of monomeric C_{59}HN , the appearance of characteristic features in the frequency region $800\text{--}850\text{ cm}^{-1}$ (marked accordingly in Figure 2) provides a fingerprint of the dimerization of the molecular cages [33].

2.2. Structural Properties at Ambient Pressure

The synchrotron X-ray powder diffraction patterns of the $(\text{Li}@\text{C}_{60})_2$ sample recorded at 300 and 3.4 K at ambient pressure are shown in Figure 3. An immediate observation is that they appear strikingly similar to those reported for as-prepared solid $(\text{C}_{59}\text{N})_2$, in terms of both the position and the relative intensity of the diffraction peaks present [18,34]. As-prepared $(\text{C}_{59}\text{N})_2$ crystallizes in a hexagonal lattice (space group $P6_3/mmc$) with lattice constants at ambient temperature, $a = 9.97\text{ Å}$ and $c = 16.18\text{ Å}$ [18]. In a remarkable analogy, the patterns of $(\text{Li}@\text{C}_{60})_2$ prepared by electrochemical reduction are also consistent with the material adopting an isostructural hexagonal closed-packed (*hcp*) arrangement of the fullerene units with a somewhat smaller (c/a) anisotropy (space group $P6_3/mmc$, at 300 K: $a = 10.04374(10)\text{ Å}$ and $c = 16.13451(19)\text{ Å}$; at 3.4 K: $a = 9.9560(3)\text{ Å}$ and $c = 16.0317(5)\text{ Å}$). Excellent refinements of the diffraction profiles are achieved by the LeBail pattern–decomposition technique using the GSAS suite (at 300 K: $R_{\text{wp}} = 1.88\%$, $R_{\text{exp}} = 1.48\%$; at 3.4 K: $R_{\text{wp}} = 2.23\%$, $R_{\text{exp}} = 1.43\%$) (Figure 3).

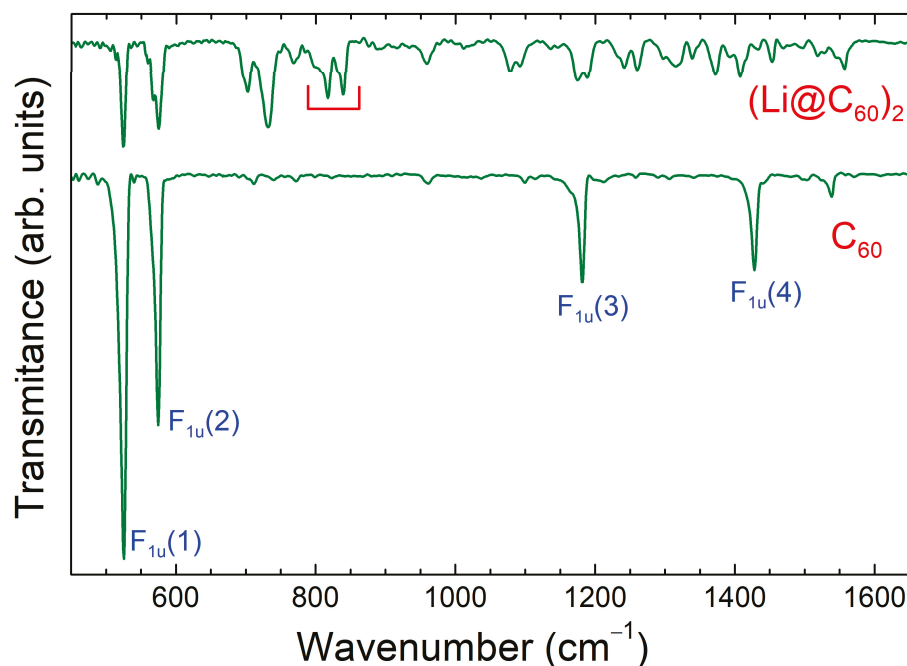


Figure 2. IR transmission spectrum of the $(\text{Li}@\text{C}_{60})_2$ sample prepared by electrochemical reduction and compared to that of solid C_{60} . Characteristic “dimer peaks” in the frequency region $800\text{--}850\text{ cm}^{-1}$ are indicated. The mode assignment refers to the irreducible representations of the C_{60} molecule in I_h symmetry.

On the other hand, the measured profiles of the present $(\text{Li}@\text{C}_{60})_2$ sample contrast sharply with those of both $(\text{Li}@\text{C}_{60})_2$ prepared by chemical reduction route [17] and sublimed $(\text{C}_{59}\text{N})_2$ [19]. The former displays a powder pattern, which can be indexed on a pseudo-cubic unit cell with a lattice size of $\sim 14.15\text{ \AA}$ (interfullerene separation $\sim 10.01\text{ \AA}$) [17], whereas the latter provides clear evidence of a dimerized molecular structure and a lowering of crystal symmetry to monoclinic [19].

The apparent *hcp* crystal structure (Figure 3a inset) of $(\text{Li}@\text{C}_{60})_2$ prepared by electrochemical reduction is an archetypal packing arrangement of monomer units. Therefore, it is counterintuitive and contrasts sharply with the dimerization of the molecular units that has been unambiguously established by vibrational spectroscopy (*vide supra*). In the $P6_3/mmc$ space group, the $\text{Li}@\text{C}_{60}$ balls reside in the $2d$ positions, $(2/3, 1/3, 1/4)$ and $(1/3, 2/3, 3/4)$. As a result, their center-to-center distance at ambient temperature is $9.94\text{ \AA}$, implicit of the absence of interball bond formation. Due to the translational symmetry of the hexagonal unit cell, there are six nearest neighbors at this distance of $9.94\text{ \AA}$, together with six additional ones in the *ab* plane at $10.04\text{ \AA}$. These are close to the $\text{C}_{60}\text{—C}_{60}$ distances in monomeric C_{60} ($\sim 10\text{ \AA}$) and are longer than those ($\sim 9.34\text{ \AA}$) in typical dimerized C_{60} structures like that of RbC_{60} [35–37].

The inconsistency with the vibrational results may be resolved if we introduce orientational disorder of the dimer units residing on the *hcp* sites. To this effect, we recall a much-celebrated analogous situation—namely, that of the Phase I of solid dihydrogen, H_2 [38]. At room temperature, this phase is stable between 5 and 190 GPa and comprises freely rotating dihydrogen molecules, forming an *hcp* crystal structure (space group $P6_3/mmc$). We therefore attempted Rietveld refinements of the diffraction data by modeling the pronounced orientational disorder of the fullerene moieties in terms of spherical shell scatterers placed at the $2d$ sites of $\bar{6}m2$ symmetry in the *hcp* lattice. In the course of the refinements, we found it necessary to also introduce scattering density at the $2a$ sites of $\bar{3}m$ symmetry, presumably reflecting the presence of residual CH_2Cl_2 solvent molecules intercalated during the electrochemical synthetic protocol. Rietveld refinements now proceeded smoothly, resulting in a stoichiometry of $(\text{Li}@\text{C}_{60})_2 \cdot (\text{CH}_2\text{Cl}_2)_{0.81(2)}$ for the material. We note

that an analogous situation was encountered in the Rietveld refinements of the diffraction data of as-prepared *hcp*-structured azafullerene solid, whose stoichiometry was established as $(\text{C}_{59}\text{N})_2 \cdot (\text{CS}_2)_{1.0}$ [34]. The refinement results are shown in Figure 4 and Table S2.

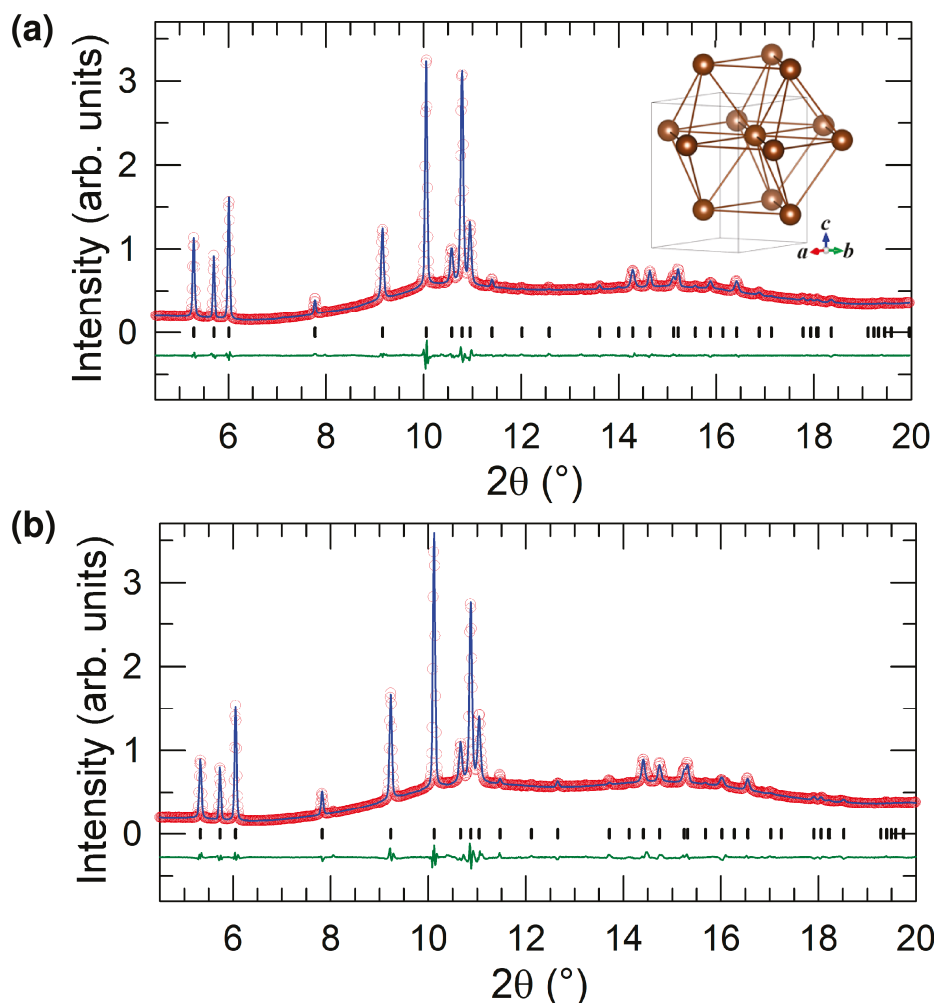


Figure 3. LeBail refinements (using the GSAS suite of programs) of the synchrotron X-ray ($\lambda = 0.80031 \text{ \AA}$) powder diffraction profiles of $(\text{Li}@\text{C}_{60})_2$ at (a) 300 K and (b) 3.4 K. The red open circles represent the measured intensity, and the blue solid line shows the calculated intensity. The lower green solid line shows the difference profile, and the tick marks show the reflection positions in space group $P6_3/mmc$. The inset in (a) shows a schematic diagram of the apparent hexagonal close-packing motif of solid spheres, consistent with the space group symmetry.

Figure 5a,b shows the temperature dependence of the unit-cell volume and the lattice parameters a and c , as extracted from the LeBail analyses of the diffraction data. The smooth evolution in lattice size confirms the absence of any structural phase transition down to 3.4 K. The only apparent effect is a decrease in the lattice anisotropy, as measured by the (c/a) ratio, which monotonically increases with decreasing temperature, approaching a value just larger than 1.61 at 3.4 K (Figure 5c). This is still smaller than the ideal value of 1.633 in perfect hexagonal close-packed architectures, but the decreased anisotropy on cooling may reflect a partial freezing out of the orientational disorder of the fullerene units.

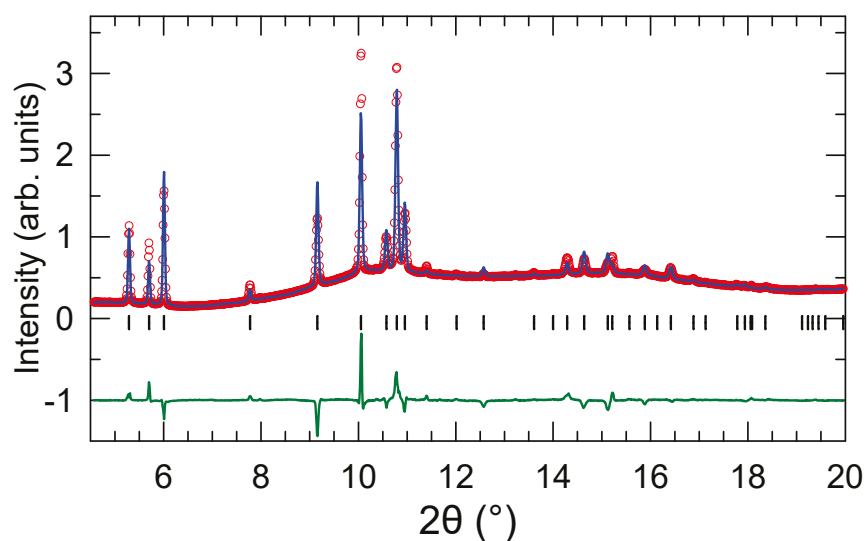


Figure 4. Rietveld analysis result (space group $P6_3/mmc$) using the Fullprof suite of programs—final observed (red circles) and calculated (blue solid line) synchrotron X-ray ($\lambda = 0.80031 \text{ \AA}$) powder diffraction profiles for the $(\text{Li@C}_{60})_2$ sample at 300 K. The lower solid line shows the difference profile, and the tick marks show the reflection positions. Refined parameters and agreement indices are provided in Supplementary Information, Table S2.

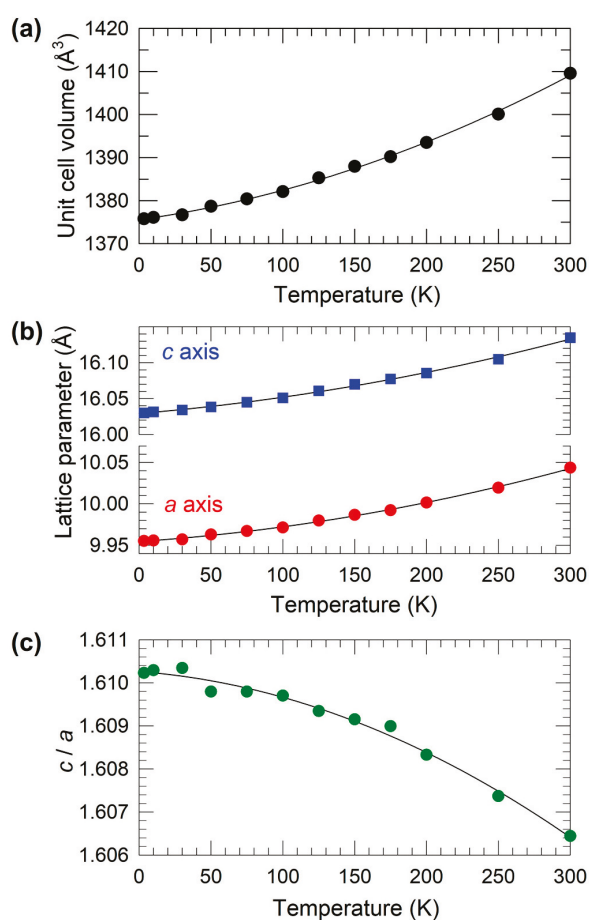


Figure 5. Temperature dependence of (a) the unit cell volume, (b) the hexagonal lattice constants, a and c , and (c) the (c/a) ratio in $(\text{Li@C}_{60})_2$ at ambient pressure. The lines through the points are guides-to-the-eye.

2.3. Structural Properties at High Pressure

Synchrotron X-ray powder diffraction data of $(\text{Li}@\text{C}_{60})_2$ were collected at ambient temperature and at selected pressures between 0.5 and 13.1 GPa. As the pressure increases, the diffraction profiles show gradual Bragg peak shifting towards higher 2θ angles consistent with unit cell contraction; this is accompanied by some peak broadening due to increasing inhomogeneities upon pressurization (Figure 6). No evidence of the occurrence of any structural phase transition is found in the pressure range of the present experiments. All diffraction patterns index with the same hexagonal unit cell (space group $P6_3/mmc$) found at all temperatures at ambient pressure. Representative LeBail refinements at base and highest pressures are included in Figure 6 (at 0.5 GPa: $a = 9.89824(18)$ Å and $c = 15.9333(3)$ Å; $R_{\text{wp}} = 0.35\%$, $R_{\text{exp}} = 4.60\%$; at 13.1 GPa: $a = 9.2495(5)$ Å and $c = 15.0437(11)$ Å; $R_{\text{wp}} = 0.29\%$, $R_{\text{exp}} = 4.94\%$). The evolution of the $(\text{Li}@\text{C}_{60})_2$ unit cell dimensions upon pressurization was investigated by LeBail refinements of the diffraction profiles (Figure 7a,b). Some spurious weak peaks, which were present in the diffraction datasets when the sample was introduced into the diamond anvil cell (DAC)—but were absent for the same sample batch outside the pressure cell—were excluded from the refinements. Figure 7c displays the change in the lattice anisotropy of the *hcp* structure, as monitored by the evolution of the (c/a) ratio. Upon pressurization, c/a increases monotonically at the beginning but eventually saturates above ~ 10 GPa towards a value of ~ 1.626 , close to the ideal value of 1.633 expected for perfect *hcp* stacking of solid spheres. Comparable behavior was also observed before for the isostructural dimeric $(\text{C}_{59}\text{N})_2$ solid, in which the (c/a) ratio approached ~ 1.633 at ~ 6.5 GPa [18]. Such behavior implies that, at these elevated pressures, the intradimer and interdimer C-C distances in the compressed material have become comparable. Notably, this occurs in the same pressure range that the interdimer center-to-center separations in $(\text{Li}@\text{C}_{60})_2$ have decreased to values on the order of ~ 9.2 – 9.3 Å. Such close interball contacts have provided the signature of single C-C bond formation in fullerene-derived polymers [35–37] before.

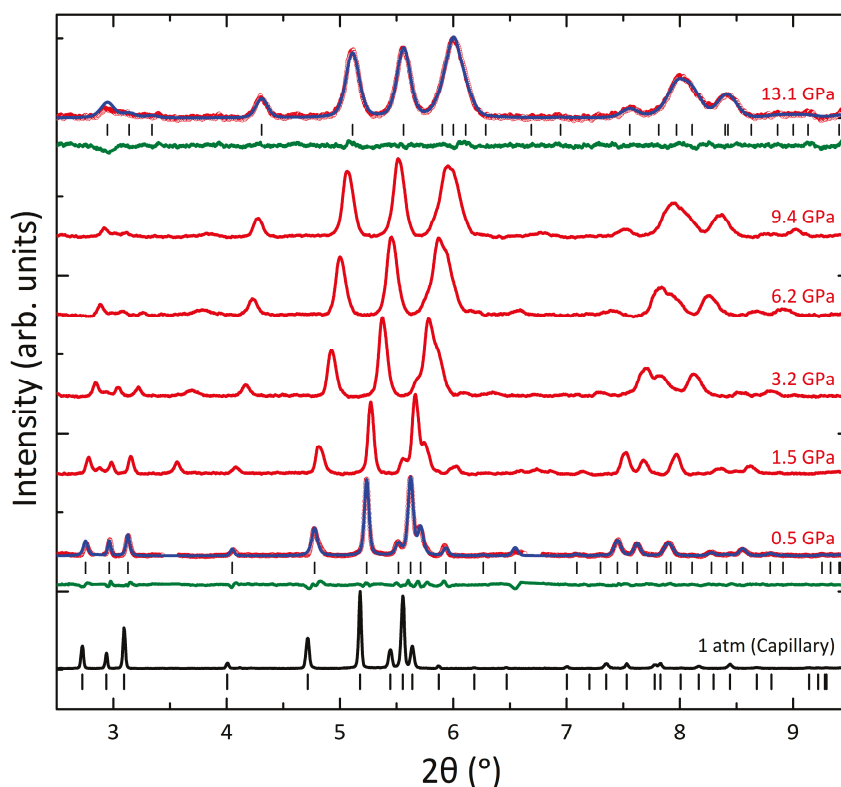


Figure 6. Representative high-pressure synchrotron X-ray powder diffraction profiles after background subtraction ($\lambda = 0.4128$ Å) of $(\text{Li}@\text{C}_{60})_2$ (red solid lines and open circles) at elevated pressures.

The corresponding diffraction profile at 1 atm (capillary) from Figure 5 is also displayed for comparison after conversion to the same wavelength (black solid line). The LeBail refinement results for base (0.5 GPa) and highest (13.1 GPa) pressure are also included (blue solid lines: calculated, red circles: observed). Tick marks label the reflections of the hexagonal lattice (space group $P6_3/mmc$), and the green solid lines are the difference profiles between observed and calculated profiles. Some spurious weak peaks present in the high-pressure data with the sample inside the diamond anvil cell (DAC) are excluded from the refinements.

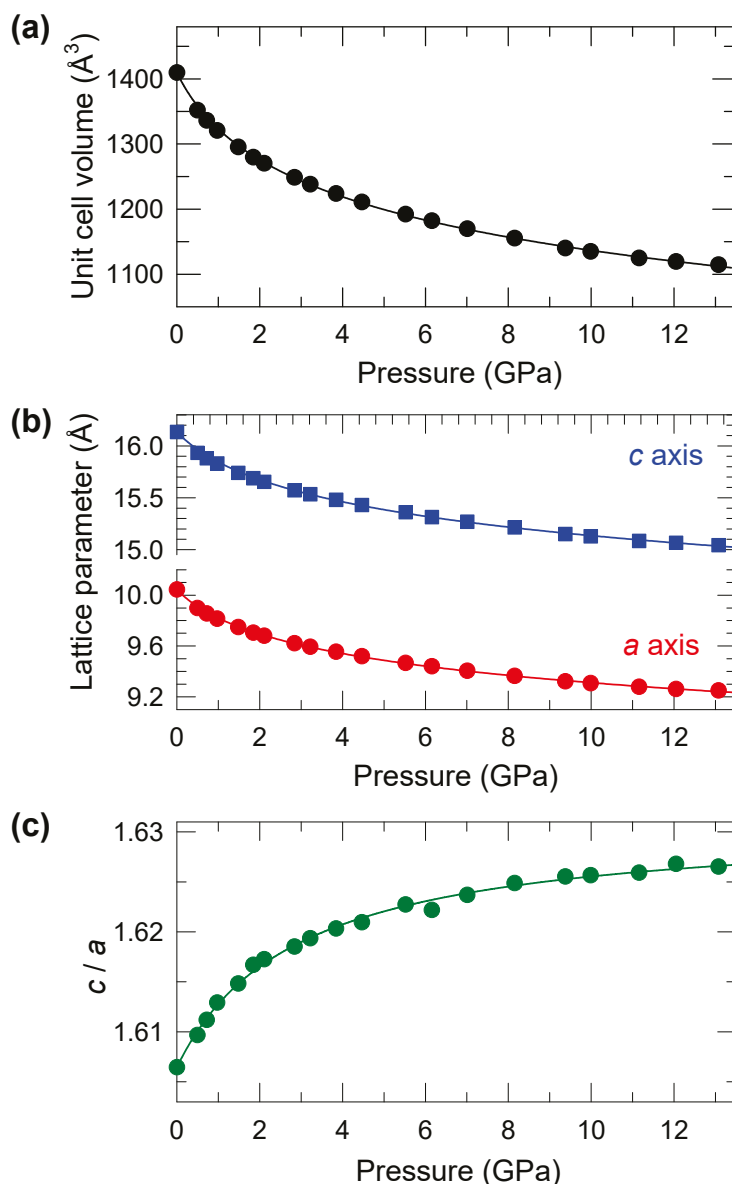


Figure 7. Pressure dependence of (a) the unit cell volume, (b) the hexagonal lattice constants, *a* and *c*, and (c) the (*c/a*) ratio in $(Li@C_{60})_2$ at ambient temperature. The solid lines in (a,b) are the results of least-squares fits to the semi-empirical 2nd-order Murnaghan equation-of-states (EoS) and its axial compressibility variants, respectively. The line through the points in (c) is a guide-to-the-eye.

The pressure dependence of the unit cell volume of $(Li@C_{60})_2$ was next investigated using the semi-empirical second-order Murnaghan equation-of-state (EoS):

$$P = \left(\frac{K_0}{K_0'} \right) \left[\left(\frac{V_0}{V} \right)^{K_0'} - 1 \right] \quad (1)$$

where K_0 is the atmospheric pressure isothermal bulk modulus, K_0' is its pressure derivative ($\equiv dK_0/dP$) _{$P=0$} , and V_0 is the unit-cell volume at zero pressure (approximated by the ambient pressure datum at 1 atm; here, $V_0 = 1409.58 \text{ \AA}^3$). The EoS fit to the $V(P)$ data (see Equation (S1) in the Supplementary Materials) of $(\text{Li@C}_{60})_2$ up to a pressure of 13.1 GPa results in values of $K_0 = 10.8(3) \text{ GPa}$ (leading to an initial volume compressibility, $\kappa = -d\ln V/dP = 0.093(3) \text{ GPa}^{-1}$) and of $K_0' = 11.4(2)$ (Figure 7a). The measured volume compressibility of $(\text{Li@C}_{60})_2$ is higher than those of $(\text{C}_{59}\text{N})_2$ ($\kappa = 0.046(2) \text{ GPa}^{-1}$) and of the monomeric C_{60} ($\kappa = 0.055 \text{ GPa}^{-1}$) and $(\text{Li}^+\text{@C}_{60})(\text{PF}_6)$ ($\kappa = 0.0571(4) \text{ GPa}^{-1}$) [15,18,39] solids, implying more flexible nearest-neighbor bonds and somewhat less tight crystal packing. Modified EoS equations, in which K_0 and its pressure derivative, K_0' , were replaced by K_x and K_x' ($x = a$ or c) parameters, were used to fit the corresponding lattice axes data to extract initial axial compressibilities, β_x ($= 1/(3K_x) \text{ GPa}^{-1}$, $x = a$ or c) (Figure 7b). As anticipated by the earlier discussion on the pressure dependence of the (c/a) ratio, we find that the compressibility along the c -axis ($\beta_c = 0.0086(2) \text{ GPa}^{-1}$) is smaller than that along the a -axis ($\beta_a = 0.0112(3) \text{ GPa}^{-1}$). Such a pressure response was also observed for $(\text{C}_{59}\text{N})_2$ and was then interpreted as a consequence of the intradimer bonds being oriented along the $(1/3, 2/3, 1/2)$ direction and therefore inclined at a larger angle to the basal plane than to the c -axis [18].

3. Materials and Methods

The $(\text{Li}^+\text{@C}_{60})(\text{PF}_6^-)$ sample used as a precursor in the present work was purchased from Idea International Corporation. Its electrochemical reduction to afford $(\text{Li@C}_{60})_2$ was performed according to the experimental protocol described in the literature before [16].

Raman spectra of $(\text{Li@C}_{60})_2$ were recorded in backscattering geometry using a LabRam HR (HORIBA, Kyoto, Japan) micro-Raman spectrometer, equipped with a Peltier cooled CCD detector. Laser lines at 633 and 785 nm were alternatively used for excitation, focused on the samples by means of a $100\times$ objective at a power lower than 0.3 mW to avoid any laser-heating-induced effects.

Infrared (IR) transmission spectra of the samples under argon atmosphere were collected by means of a JASCO (Tokyo, Japan) FT-IR 6200 spectrometer.

Synchrotron X-ray powder diffraction measurements of $(\text{Li@C}_{60})_2$ at various temperatures between 3.4 and 300 K at ambient pressure were performed with the high-resolution powder diffractometer on beamline BL44B2 at SPring-8, Hyogo, Japan using a helium-flow cryostat [40]. The powder sample was sealed in a 0.5 mm diameter thin-wall glass capillary under He gas. The wavelength was $0.800312(1) \text{ \AA}$. LeBail and Rietveld analyses were performed with the GSAS and Fullprof suites of refinement programs [41–43].

Synchrotron X-ray powder diffraction measurements of $(\text{Li@C}_{60})_2$ up to 13.1 GPa at ambient temperature were conducted at the BL10XU beamline, SPring-8, Hyogo, Japan. The powder X-ray diffraction data (monochromatized beam with $\lambda = 0.41277(5) \text{ \AA}$, beam size = $40 \text{ }\mu\text{m}$) were collected on an image plate detector (Rigaku (Tokyo, Japan) R-Axis IV⁺⁺, $300 \times 300 \text{ mm}^2$, and 0.10 mm pixel size) while oscillating the sample [44]. Masking of the Bragg reflections of the DAC and integration of the 2D diffraction images to afford one-dimensional diffraction profiles were processed with the IPanalyzer software [45]. LeBail analysis of the diffraction profiles was performed with the GSAS suite of refinement programs [41,42]. A DAC [46,47], equipped with single-crystal diamonds of $500 \text{ }\mu\text{m}$ culet diameter and with an $80 \text{ }\mu\text{m}$ -thick stainless-steel gasket, was used for pressure generation. Powder samples were introduced into $250 \text{ }\mu\text{m}$ diameter holes made at the center of the gasket, together with a ruby sphere and helium gas (solidification pressure $\sim 12.1 \text{ GPa}$ at room temperature, pressure uncertainty less than 0.5% at the highest pressure of the present experiment [48]) as pressure marker and pressure medium, respectively. The applied pressure was measured by the ruby-fluorescence method [49]. All measured pressure values are quoted to one decimal point.

4. Conclusions

In conclusion, we have presented a detailed structural and vibrational characterization of the dimerized endohedral metallofullerene, $(\text{Li}@\text{C}_{60})_2$, in the solid state. The material used in the present work was obtained by electrochemical reduction of the trifluoromethanesulfonyl imide precursor salt, $(\text{Li}^+\text{C}_{60})(\text{TFSI}^-)$ [16]. Its highly crystalline nature permits facile identification of spectroscopic features related to interfullerene C-C bonding. Remarkably, the crystal structure of the material remains hexagonal close-packed (space group $P6_3/mmc$) both at low temperatures and ambient pressure and at high pressures and ambient temperature, concealing the effects of dimerization and the anticipated lowering in symmetry. High orientational disorder (together with the presence of some residual dichloromethane solvent) can account for the apparent high symmetry. A comparable orientational disorder scenario has been used to rationalize the *hcp* Phase I of solid dihydrogen (H_2) at high pressures.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics12040099/s1>, Figure S1: Comparison of Raman spectra of $(\text{Li}@\text{C}_{60})_2$ obtained by chemical and electrochemical reduction; Table S1: Assignment of observed Raman peaks and their frequencies for C_{60} , $(\text{Li}@\text{C}_{60})(\text{PF}_6)$, $(\text{C}_{59}\text{N})_2$, and $(\text{Li}@\text{C}_{60})_2$; Table S2: Refined parameters of the Rietveld analysis of the synchrotron X-ray powder diffraction data of $(\text{Li}@\text{C}_{60})_2$; Equation (S1): $V(P)$ form of the Murnaghan equation-of-state.

Author Contributions: Synthesis, M.V., T.N. and K.K. (Ken Kokubo); synchrotron X-ray diffraction—data collection and analysis, M.V., T.N., M.M., Y.T., K.K. (Kenichi Kato) and K.P.; high-pressure synchrotron X-ray diffraction—data collection and analysis, N.Y., K.M., S.K.-I., H.K. and K.P.; vibrational spectroscopy, J.A.; conceptualization and overall conclusions, J.A., Y.K. and K.P.; project supervision, K.P.; writing—review and editing, K.P. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: All data supporting the reported results in this paper can be obtained from the authors.

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Conflicts of Interest: The authors declare no conflicts of interest.

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Article

Stability and Electronic Properties of 1D and 2D Ca@C₆₀ Oligomers and Polymers

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Abstract: The polymerization of fullerenes is a significant method for obtaining fullerene-based materials that possess intriguing properties. Metallofullerenes, as a notable type of fullerene derivatives, are also capable of undergoing polymerization, potentially resulting in the creation of metallofullerene polymers. However, there is currently limited knowledge regarding the polymerization process of metallofullerenes. In this study, we have selected Ca@C₆₀ as a representative compound to investigate the polymerization process of metallofullerenes. The objective of this research is to determine whether the polymerization process is energetically favorable and to examine how the electronic properties of the metallofullerene are altered throughout the polymerization process. Ca@C₆₀ is a unique metallofullerene molecule that exhibits insolubility in common fullerene solvents like toluene and carbon disulfide but is soluble in aniline. This behavior suggests a potential tendency for Ca@C₆₀ to form oligomers and polymers that resist dissolution. However, the structures and properties of polymerized Ca@C₆₀ remain unknown. We employed density functional theory calculations to investigate the stability and electronic properties of one-dimensional and two-dimensional Ca@C₆₀ oligomers and polymers. Our findings indicate that the coalescence of Ca@C₆₀ monomers is energetically favorable, with a significant contribution from van der Waals interactions between the fullerene cages. The polymerization process of Ca@C₆₀ also involves the formation of covalent linkages, including four-atom rings and C-C single bonds. The increase in the number of the Ca@C₆₀ units to three and four in the oligomer leads to a significant decrease in the HOMO-LUMO gap. In the two-dimensional polymerized Ca@C₆₀, the organization of the monomers closely resembles the spatial configuration of carbon atoms in graphene. With a direct bandgap of 0.22 eV, the polymerized Ca@C₆₀ holds potential for utilization in optoelectronic devices.

Keywords: fullerenes; metallofullerenes; density functional theory calculations

1. Introduction

Fullerenes, which typically consist of several tens of carbon atoms, are carbon allotropes with a cage-like structure. These structures possess conjugated electronic configurations and display intriguing optical, electrical and electrochemical properties [1–6]. C₆₀, the most prominent member of the fullerene family, has been extensively researched for several decades. Its derivatives have found wide-ranging applications in photovoltaic devices and have shown potential for disease treatment [7–10]. Alongside the C₆₀ monomer, there has been significant interest in studying the polymerized form of C₆₀. Reports suggest that when exposed to photo irradiation or high pressure treatment, C₆₀ molecules can polymerize into oligomers and polymers [11,12]. The properties of the C₆₀ polymers have been explored through theoretical and experimental studies [3,13–16]. During the polymerization process, the reaction between two neighboring C₆₀ molecules typically occurs via a [2 + 2] cycloaddition mechanism, leading to the formation of a cyclobutane ring that connects two fullerene cages. Subsequent to polymerization, the resulting products usually

exhibit high insolubility in solvents that can dissolve C_{60} [16]. The structural composition of the products derived from C_{60} sample is determined by the reaction conditions. The formation of polymers and metastable materials occurs when the pressure exceeds several GPa and the temperature surpasses several hundred degrees Celsius. At higher pressures and temperatures, the C_{60} cage can rupture, leading to the production of diamond-like materials [16,17]. Sabirov utilized density-functional theory to examine the polarizability of fullerene oligomers $(C_{60})_n$ ($n = 1-5$) [18]. The study findings demonstrated that the average polarizability of $(C_{60})_n$ is not linearly correlated with the number of fullerene cores in the molecules, suggesting a violation of additivity. This phenomenon, referred to as the exaltation of polarizability, arises from the interaction between the π -electronic systems of the fullerene cores in $(C_{60})_n$ and becomes increasingly significant as the distance between them increases. Quantum chemical calculations of fullerene oligomers are expensive because of the large size of the oligomers. Sabirov investigated energy, topology, and information theoretic descriptors, and obtained a ternary energy-topology-symmetry law. The findings indicate that topological indices are effective in identifying the most and least reactive atoms within the fullerene dimer structure [19].

Recently, the synthesis of monolayer and few-layer two-dimensional fullerene networks has been reported [20,21]. In the polymeric C_{60} monolayer, the C_{60} molecules are covalently bonded, showcasing excellent crystallinity and thermodynamic stability. Measurements of the electronic band structure of the polymeric C_{60} monolayer indicate a bandgap of approximately 1.6 eV. The two-dimensional crystalline polymer of C_{60} has been coined “graphullerene” and serves as a bridge between molecular and extended carbon materials. The synthesis of graphullerene involves the growth of single crystals of layered polymeric Mg_4C_{60} , followed by the removal of magnesium atoms [20,21]. Theoretical studies reveal that graphullerene is a meta-stable semiconductor with an indirect band gap [22].

Metallofullerenes, as a notable type of fullerene derivatives, may also have the ability to polymerize and form metallofullerene polymers. However, there is currently limited knowledge regarding the polymerization process of metallofullerenes. The aim of this study is to investigate the stability and electronic properties of polymerized metallofullerenes, a previously unexplored area of research. A variety of metal elements can be accommodated within the interior cavity of fullerene cages. Metallofullerene molecules have been extensively studied in terms of their synthesis, structures, and properties [23–33]. The arc-discharge technique is commonly employed for the synthesis of various metallofullerenes. While some metallofullerenes are soluble in organic solvents like toluene and carbon disulfide, others are not. One notable metallofullerene, $Ca@C_{60}$, is soluble in aniline but insoluble in toluene and carbon disulfide [34]. This can be attributed to its reactivity towards polymerization and its lack of solubility in non-polar organic solvents. The solubility in aniline may be due to the formation of a charge-transfer complex. Currently, the understanding of the structure and characteristics of polymerized $Ca@C_{60}$ is very limited. To address this gap, our study focuses on examining the stability and electronic properties of $Ca@C_{60}$ oligomers and polymers using density functional theory (DFT) calculations. We also analyze the interactions between individual $Ca@C_{60}$ monomers.

2. Results and Discussion

In a previous study by Kubozono and co-workers, endohedral metallofullerene $Ca@C_{60}$ was prepared and extracted [34]. The preparation involved arc-heating graphite rods containing CaO, followed by extraction with aniline under an air atmosphere. The laser desorption time-of-flight mass spectra of the extracted solutions showed prominent peaks attributed to $Ca@C_{60}$, demonstrating the stability of $Ca@C_{60}$. We conducted DFT calculations on $Ca@I_h-C_{60}$. Figure 1a illustrates the DFT-optimized structure of $Ca@C_{60}$. Upon encapsulation of a Ca atom, the molecule’s symmetry is reduced from I_h to C_{2v} . The Ca atom is positioned adjacent to a carbon-carbon bond, with a distance of 2.45 Å between the Ca atom and the carbon atom in the bond. In some metallofullerenes, the metal

atom resides in close proximity to the center of a six-member carbon atom ring, while the coordination occurring at a carbon-carbon bond results in an increase in energy. Regarding Ca@C_{60} , it is observed that the Ca atom is situated near a carbon-carbon bond and remains in an off-center position. If the Ca atom were to shift towards the center of the molecule, there would be a noticeable increase in the overall energy.

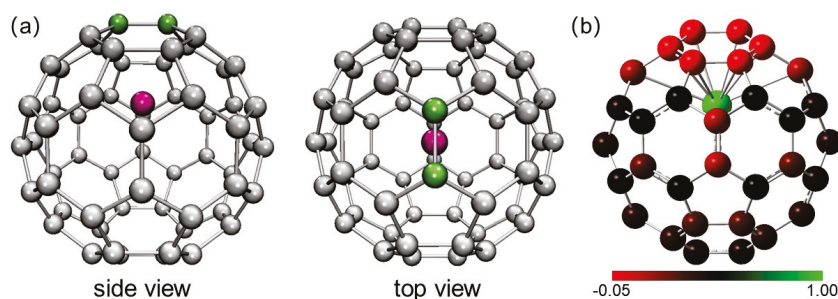


Figure 1. (a) Two views of the optimized structure of Ca@C_{60} . The carbon atoms adjacent to the Ca atom are indicated with a green color. (b) The charge distribution on the atoms of Ca@C_{60} . The green and red color indicates positive and negative charges, respectively. The black color indicates neutral atoms.

The HOMO-LUMO gap of Ca@C_{60} is calculated to be 1.14 eV. To assess the charge distribution, we conducted a natural population analysis (NPA), revealing a NPA charge of 1.8 for the Ca atom. Considering that the Ca atom possesses two valence electrons, the calculated NPA charge signifies a transfer of two electrons to the fullerene cage. Therefore, the formal charge of Ca atom can be regarded as +2. The charge distribution of Ca@C_{60} is illustrated in Figure 1b. It is evident that the negative charges on the fullerene cage are distributed unevenly. In particular, the carbon atoms in close proximity to the Ca atom exhibit a greater concentration of negative charges.

The C_{60} cage contains two types of C-C bonds. One type corresponds to the hexagon-hexagon ring junction, known as the (6,6) bond, while the other corresponds to the pentagon-hexagon ring junction, known as the (5,6) bond. In our previous research, we investigated the reactivity of the (5,6) and (6,6) bonds in Ca@C_{60} towards Diels-Alder cycloaddition reactions using density functional methods [35]. For the pristine C_{60} , the reactivity of the (6,6) bond is much higher than that of the (5,6) bond. We found that for the Diels-Alder mono-addition reaction, the unreactive (5,6) bond in C_{60} can be effectively activated by encapsulating a Ca atom. The enhancement of reactivity is attributed to both electron transfer from the metal atom to the fullerene cage and the interaction between the metal cation and the cage. The functionalization of Ca@C_{60} leads to significant increases in the HOMO-LUMO gap, which can improve the chemical stability of Ca@C_{60} . For the formation of oligomers of Ca@C_{60} , both the (5,6) and (6,6) bonds could serve as reaction sites. Consequently, various structures of Ca@C_{60} oligomers were considered in this study.

It has been reported that the metallofullerene Li@C_{60} can form dimers in solid states [36]. In the dimer of Li@C_{60} , the fullerene cages are connected by a single C-C bond. In our study on the dimer $[\text{Ca@C}_{60}]_2$, four possible isomers were considered. Isomer 1, referred to as $[\text{Ca@C}_{60}]_2$ -1, consists of two fullerene cages connected by a single C-C bond (Figure 2a). Isomers 2–4, on the other hand, involve the linkage of the fullerene cages through a four-atom ring (Figure 2b–d). Isomers 2–4 can be seen as the result of $[2 + 2]$ cycloaddition reactions between two Ca@C_{60} molecules. Three products were considered from the $[2 + 2]$ cycloaddition reactions between two Ca@C_{60} molecules. The product formed by connecting two (6,6) bonds is labeled as $[\text{Ca@C}_{60}]_2$ -2 (Figure 2b). The product formed by connecting two (5,6) bonds is labeled as $[\text{Ca@C}_{60}]_2$ -3 (Figure 2c). Finally, the product formed by connecting a (6,6) bond and a (5,6) bond is labeled as $[\text{Ca@C}_{60}]_2$ -4 (Figure 2d). Our DFT calculations revealed that $[\text{Ca@C}_{60}]_2$ -3 has the lowest energy, indicating that the dimerization of Ca@C_{60} prefers to occur at the (5,6) bond of the fullerene cage. This situation

is different from the C_{60} dimer. In the case of C_{60} dimer, the fullerene cages are connected by cycloaddition reaction between two (6,6) bonds. Once metal atoms are encapsulated, the cage's reactivity is altered due to electron transfer from the metal atom to the fullerene cage. As previously discussed, the unreactive (5,6) bond in C_{60} can be effectively activated by encapsulating a Ca atom in the context of the Diels-Alder mono-addition reaction. It is a common trend that the reactivity of the (5,6) bond towards Diels-Alder reactions is heightened in the case of metallofullerenes compared to empty fullerenes.

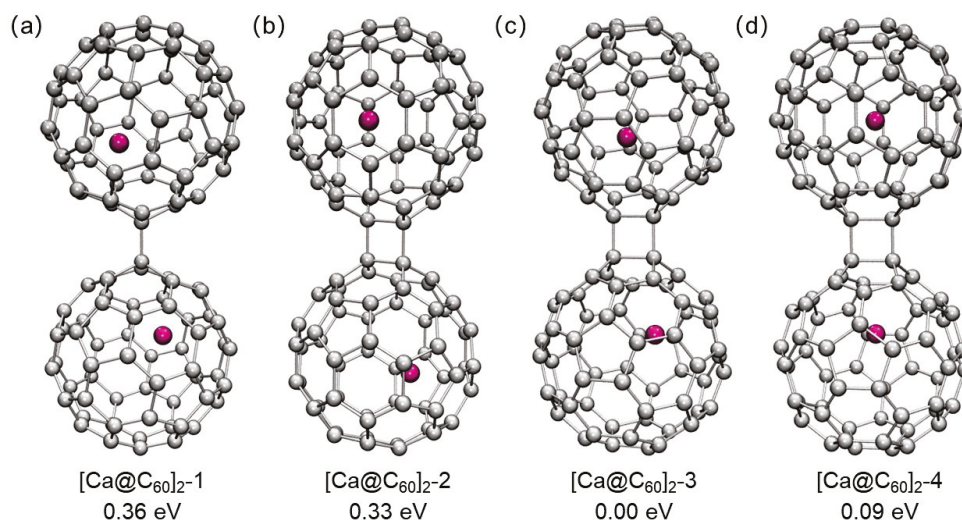


Figure 2. The optimized structures of the dimers $[Ca@C_{60}]_2$. The calculated relative energies are shown.

We examined five isomers of the trimers $[Ca@C_{60}]_3$. The first isomer, $[Ca@C_{60}]_3$ -1, is formed by linking three $Ca@C_{60}$ molecules with C-C single bonds (Figure 3a). Isomers 2–4 can be regarded as the product of $[2 + 2]$ cycloaddition reactions between three $Ca@C_{60}$ molecules. In $[Ca@C_{60}]_3$ -2, only (6,6) bonds are involved in the cycloaddition reactions (Figure 3b), while in $[Ca@C_{60}]_3$ -3, only (5,6) bonds are involved (Figure 3c). In $[Ca@C_{60}]_3$ -4, the four-atom ring connecting the fullerene cages is formed by a (6,6) bond and a (5,6) bond (Figure 3d). In $[Ca@C_{60}]_3$ -5, the three fullerene cages are arranged in a triangular shape and connected by a four-atom ring and two C-C single bonds (Figure 3e). The four-atom ring is formed by cycloaddition reaction between two (5,6) bonds. DFT calculations indicate that $[Ca@C_{60}]_3$ -5 has the lowest energy, making the triangular trimer more thermodynamically stable than the linear isomers.

For the tetramers $[Ca@C_{60}]_4$, we considered six isomers. Isomers 1–4, which are linear molecules (Figure 4a–d), have a bonding pattern similar to isomers 1–4 of the trimers. The fifth isomer, $[Ca@C_{60}]_4$ -5, has a rectangular shape, with four fullerene cages connected by two four-atom rings and two single bonds (Figure 4e). In the sixth isomer, $[Ca@C_{60}]_4$ -6, the fullerene cages form a rhombus shape (Figure 4f). DFT calculations show that $[Ca@C_{60}]_4$ -5 and $[Ca@C_{60}]_4$ -6 have significantly lower energy compared to the other isomers. The arrangement of the fullerene cages in $[Ca@C_{60}]_4$ -6 is similar to the reported two-dimensional monolayer C_{60} polymer “graphullerene” [20–22]. The computed charge distribution of the atoms in $[Ca@C_{60}]_4$ -5 and $[Ca@C_{60}]_4$ -6 is depicted in Figure 4e,f. It is evident that the negative charges on the fullerene cage are concentrated in close proximity to the Ca atom. Consequently, there exists a robust electrostatic attraction between the negatively charged fullerene cage and the Ca cation.

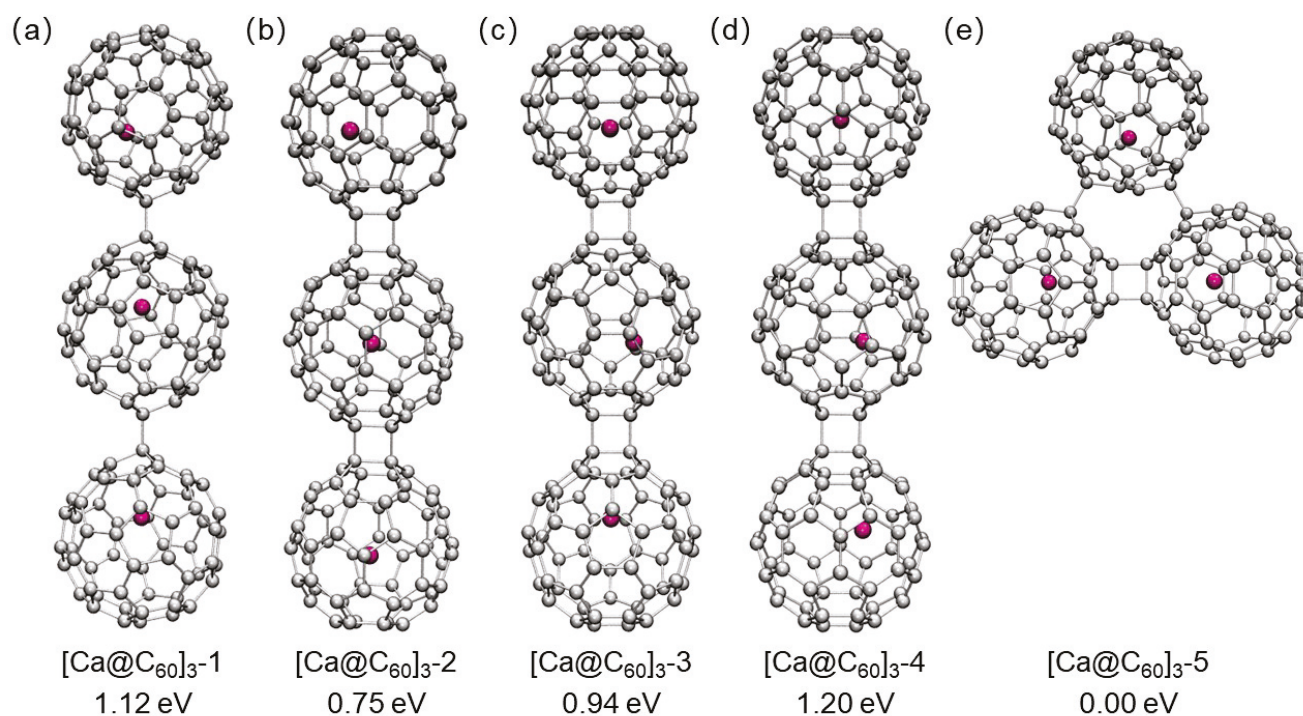


Figure 3. The optimized structures of the trimers [Ca@C₆₀]₃. The calculated relative energies are shown.

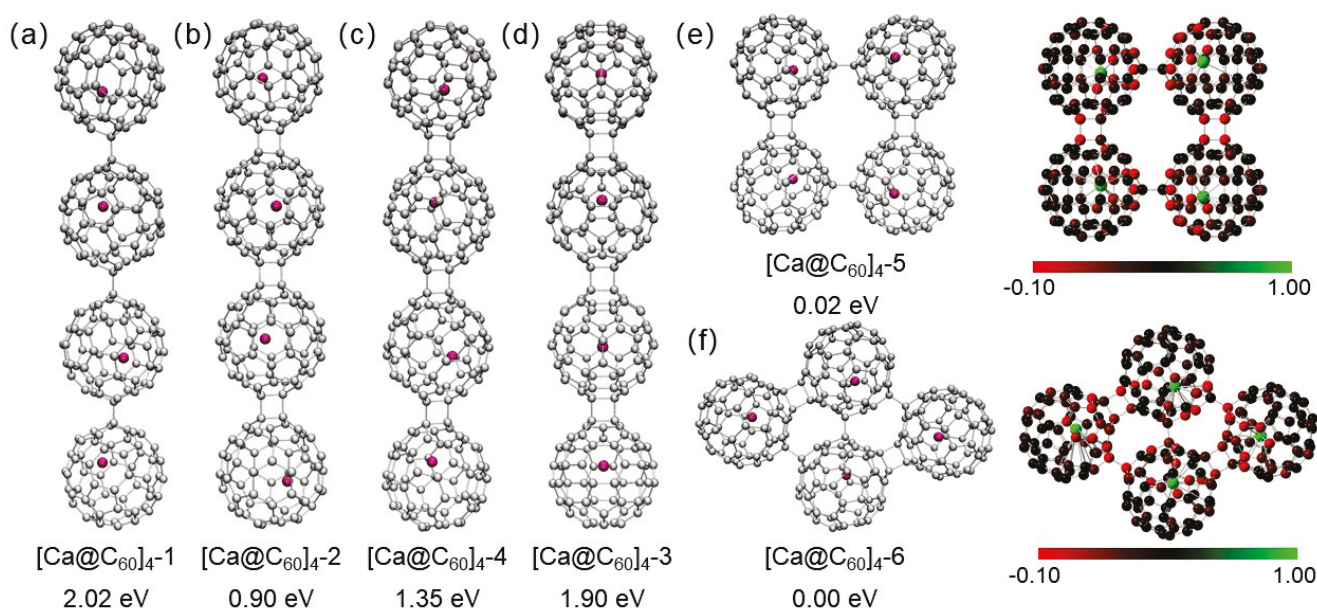


Figure 4. The optimized structures of the tetramers [Ca@C₆₀]₄. The calculated relative energies are shown.

Figure 5 depicts the molecular orbital diagrams for Ca@C₆₀, [Ca@C₆₀]₂-3, [Ca@C₆₀]₃-5 and [Ca@C₆₀]₄-6. DFT calculations reveal a significant alteration in the HOMO-LUMO gap of the oligomers [Ca@C₆₀]_n compared to the monomer Ca@C₆₀. The HOMO-LUMO gaps for Ca@C₆₀, [Ca@C₆₀]₂-3, [Ca@C₆₀]₃-5 and [Ca@C₆₀]₄-6 are 1.14, 1.36, 0.60 and 0.27 eV, respectively. The dimer [Ca@C₆₀]₂-3 shows an enlarged HOMO-LUMO gap in comparison to Ca@C₆₀. For the trimer and tetramers, the HOMO-LUMO gap substantially decreases as the number of Ca@C₆₀ units increases. The HOMO-LUMO gaps for other isomers of the oligomers are summarized in Table 1. In the case of empty C₆₀, the HOMOs and LUMOs

are degenerate, with the HOMOs being five-fold degenerate and the LUMOs being triply degenerate. However, when a Ca atom is encapsulated, two electrons occupy the LUMO of C_{60} , resulting in the HOMO of $Ca@C_{60}$ having a similar shape to the LUMO of C_{60} . Additionally, the LUMO and LUMO+1 of $Ca@C_{60}$, which are derived from the LUMOs of C_{60} , are almost degenerate. Similarly, the HOMO-6 to HOMO-1 of $Ca@C_{60}$, which are derived from the five-fold HOMOs of C_{60} , have very close energies.

In the case of the dimer $[Ca@C_{60}]_{2-3}$, both the HOMO and LUMO are observed to be spread across two fullerene cages. Additionally, the HOMO is also observed to be present at the C-C bridge that connects the fullerene cages. Moving on to the trimer $[Ca@C_{60}]_{3-5}$, it can be observed that the HOMO and LUMO are primarily distributed at the two fullerene cages that are connected by a four-atom ring. In the case of the tetramers $[Ca@C_{60}]_{4-6}$, the HOMO and LUMO are distributed across the two fullerene cages, which are separated by a significant distance.

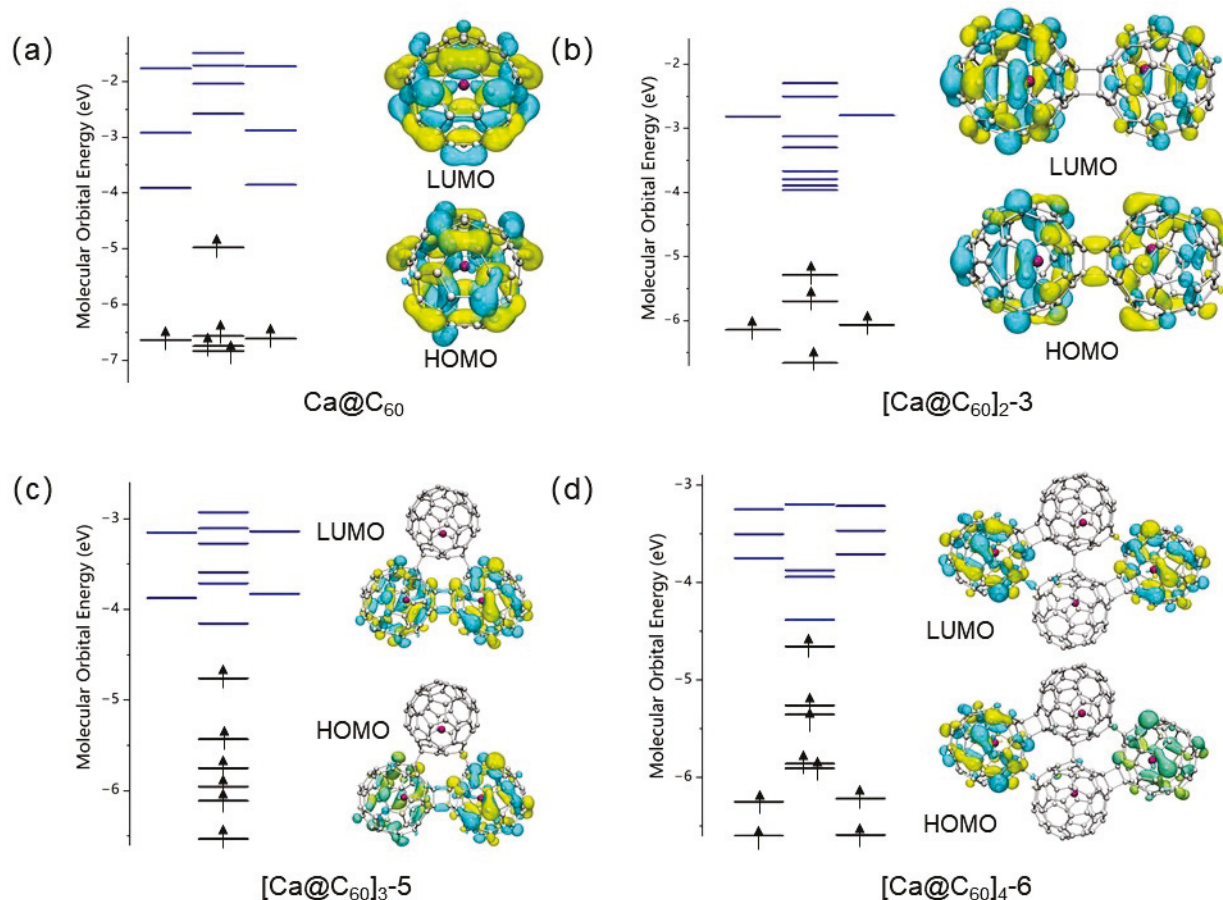


Figure 5. The calculated molecular orbital diagrams for (a) $Ca@C_{60}$, (b) $[Ca@C_{60}]_{2-3}$, (c) $[Ca@C_{60}]_{3-5}$ and (d) $[Ca@C_{60}]_{4-6}$. The occupied and unoccupied molecular orbitals are denoted in black and blue, respectively.

Table 1. The DFT-calculated HOMO-LUMO gaps (in eV) of $Ca@C_{60}$ and its oligomers.

	HOMO-LUMO Gap
$Ca@C_{60}$	1.14
2-1	0.50
2-2	1.07
2-3	1.36
2-4	0.94

Table 1. Cont.

	HOMO-LUMO Gap
3-1	0.22
3-2	1.02
3-3	1.21
3-4	0.79
3-5	0.60
4-1	0.14
4-2	1.05
4-3	1.14
4-4	0.80
4-5	0.38
4-6	0.27

The UV-vis-NIR absorption spectra for Ca@C_{60} , $[\text{Ca@C}_{60}]_{2-3}$, and $[\text{Ca@C}_{60}]_{3-5}$ are presented in Figure 6. It is observed that both Ca@C_{60} and $[\text{Ca@C}_{60}]_{2-3}$ exhibit an absorption onset at approximately 1000 nm, with a prominent absorption peak at around 800 nm. Notably, $[\text{Ca@C}_{60}]_{3-5}$ displays a broad absorption peak spanning the range of 1400–3000 nm, which can be attributed to its small HOMO-LUMO gap. This characteristic suggests potential applications in the fields of biomedicine and optoelectronic devices. On the other hand, the TDDFT calculations for $[\text{Ca@C}_{60}]_{4-6}$ were unsuccessful due to the high computational cost.

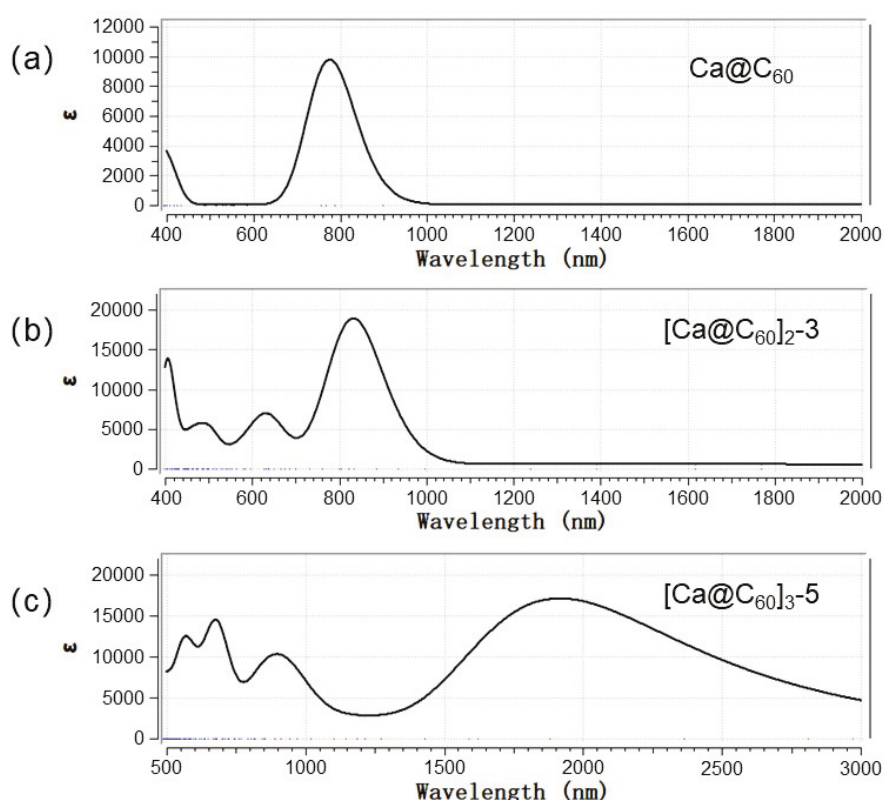


Figure 6. The calculated UV-vis-NIR absorption spectra for (a) Ca@C_{60} , (b) $[\text{Ca@C}_{60}]_{2-3}$ and (c) $[\text{Ca@C}_{60}]_{3-5}$ by using the TDDFT method.

On the basis of DFT calculations, we compared the energy between the oligomers $[\text{Ca@C}_{60}]_n$ and the monomer Ca@C_{60} . The results indicate that the formation of oligomers is an exothermic process. We calculated the relative energies for $[\text{Ca@C}_{60}]_n$ per Ca@C_{60} unit using the monomer Ca@C_{60} as a reference. The calculated values for $[\text{Ca@C}_{60}]_{2-3}$,

$[\text{Ca@C}_{60}]_{3-5}$, $[\text{Ca@C}_{60}]_{4-5}$ and $[\text{Ca@C}_{60}]_{4-6}$ per Ca@C_{60} unit are -0.54 , -0.67 , -0.69 and -0.70 eV, respectively, revealing significantly lower energies compared to the monomer Ca@C_{60} . Remarkably, the relative energy decreases with an increase in the number of Ca@C_{60} units. Consequently, the process of polymerizing Ca@C_{60} exhibits a favorable energy profile.

The stability of the oligomers $[\text{Ca@C}_{60}]_n$ can be attributed to two factors. Firstly, the covalent bonding between the fullerene cages plays a crucial role. Secondly, the van der Waals interaction between the fullerene cages also contributes to the stability. To illustrate this, we examined the dimer $[\text{Ca@C}_{60}]_{2-3}$ as a representative compound and calculated the dispersion energy between the two fullerene units. This was achieved by performing energy decomposition using dispersion corrected density functional theory (DFT-D3). The calculated dispersion energy was found to be 0.49 eV, indicating that the dispersion energy significantly contributes to the dimer formation. To visualize the weak interactions between the fullerene cages, we conducted an analysis using the Independent Gradient Model based on Hirshfeld partition (IGMH) for $[\text{Ca@C}_{60}]_{2-3}$, $[\text{Ca@C}_{60}]_{3-5}$, and $[\text{Ca@C}_{60}]_{4-6}$. The results are presented in Figure 7. The isosurface of δg indicates the region where dispersion interaction is present. It is evident that dispersion interaction exists between the fullerene cages.

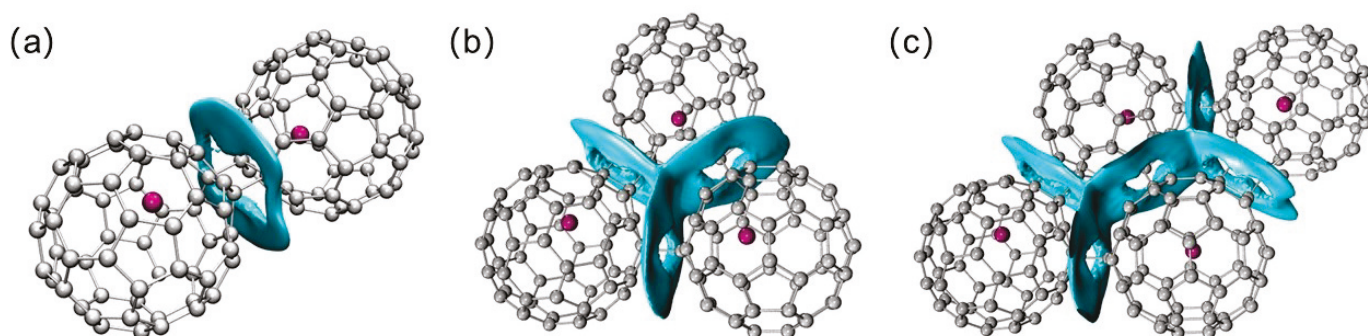


Figure 7. IGMH- δg isosurface (isovalued = 0.001 a.u.) showing the dispersion interaction between the Ca@C_{60} fragments for (a) $[\text{Ca@C}_{60}]_{2-3}$, (b) $[\text{Ca@C}_{60}]_{3-5}$ and (c) $[\text{Ca@C}_{60}]_{4-6}$.

For the two-dimensional polymers $[\text{Ca@C}_{60}]_{\infty}$, we considered two possible structures. The first one, $[\text{Ca@C}_{60}]_{\infty-1}$, is constructed by extension of the Ca@C_{60} units in $[\text{Ca@C}_{60}]_{4-6}$. The second one, $[\text{Ca@C}_{60}]_{\infty-2}$, is constructed by extension of the Ca@C_{60} units in $[\text{Ca@C}_{60}]_{4-5}$. Figure 8 displays the optimized structures of these polymers. In $[\text{Ca@C}_{60}]_{\infty-1}$, each fullerene cage is connected to six adjacent cages, resembling a “graphullerene” structure [20–22]. In $[\text{Ca@C}_{60}]_{\infty-2}$, each fullerene cage connects with four adjacent cages. DFT calculations indicate that $[\text{Ca@C}_{60}]_{\infty-1}$ is thermodynamically more stable than $[\text{Ca@C}_{60}]_{\infty-2}$. The energy difference for the unit cell containing two Ca@C_{60} units is 1.08 eV. Figure 9 shows the band structure for $[\text{Ca@C}_{60}]_{\infty-1}$, with a direct bandgap of 0.22 eV. Notably, this bandgap is significantly smaller in comparison to that of “graphullerene” [20,22]. This reduction in bandgap can be attributed to the transfer of electrons from Ca atoms to the fullerene cage. As a result, a portion of the conduction band of “graphullerene” is occupied by these transferred electrons. Consequently, the polymer $[\text{Ca@C}_{60}]_{\infty-1}$ exhibits distinct electronic characteristics in comparison to “graphullerene”. The band structure of $[\text{Ca@C}_{60}]_{\infty-1}$ reveals that the wave vectors corresponding to the Conduction band minimum (CBM) and Valance band maximum (VBM) are both situated at the high symmetry point G in the Brillouin zone. The electron transition mode displays vertical transitions, while the band structure itself demonstrates direct bandgap characteristics. Notably, since the CBM and VBM coincide at the same momentum point, the transition from the valence band to the conduction band in $[\text{Ca@C}_{60}]_{\infty-1}$, upon absorption of photons by electrons, only requires adherence to the energy conservation constraint, without necessitating additional phonon

interaction. In comparison with indirect bandgap materials, $[\text{Ca@C}_{60}]_{\infty-1}$ exhibits superior quantum efficiency, rendering it a promising contender for optoelectronic devices.

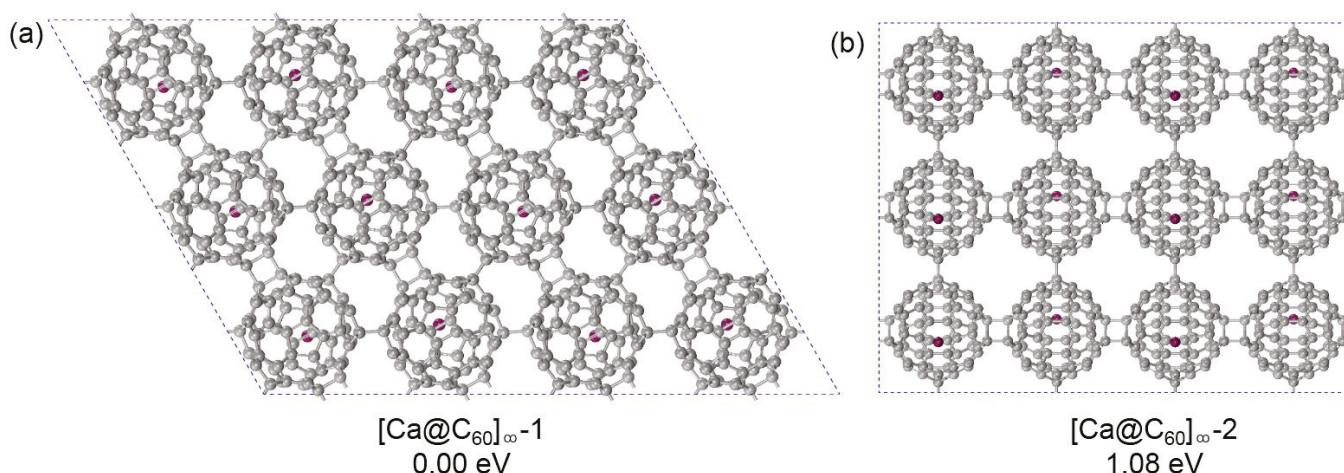


Figure 8. The optimized structures of $[\text{Ca@C}_{60}]_{\infty-1}$ and $[\text{Ca@C}_{60}]_{\infty-2}$. The calculated relative energies for a unit cell are shown.

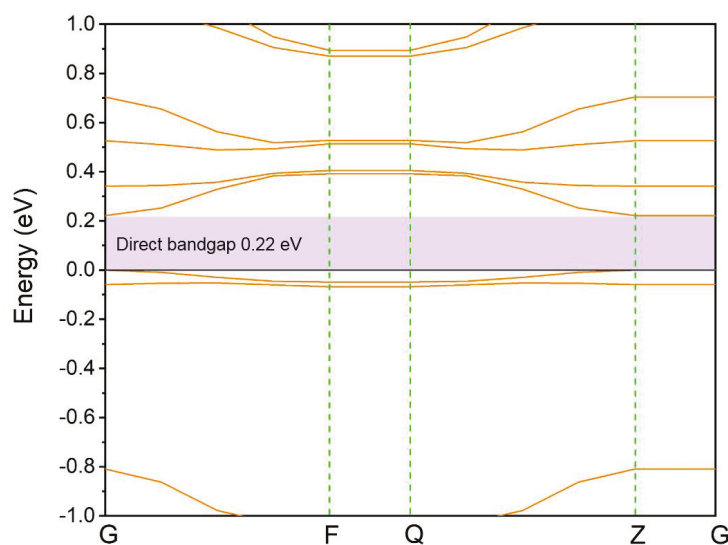


Figure 9. The calculated band structure of $[\text{Ca@C}_{60}]_{\infty-1}$.

3. Computational Details

DFT calculations were conducted on Ca@C_{60} and its oligomers and polymers. The oligomers included the dimer $[\text{Ca@C}_{60}]_2$, the trimer $[\text{Ca@C}_{60}]_3$ and the tetramer $[\text{Ca@C}_{60}]_4$. The polymers were referred to as $[\text{Ca@C}_{60}]_{\infty}$. Gaussian16 version A03 [37] was used for the calculations on the oligomers, with the PBE0 functional employed [38]. To account for the significant van der Waals interaction between the fullerene cages, the dispersion correction D3(BJ) was applied [39]. The geometric optimization utilized the def2SVP basis set for the carbon and calcium atoms [40], while the def2-TZVP basis set was used for single-point energy calculations [41]. The counterpoise method of Boys and Bernardi was employed to correct the basis set superposition error (BSSE) [42]. The interaction between Ca@C_{60} monomers was investigated using the MULTIWFN program [43], specifically the analysis of independent gradient model based on Hirshfeld partition (IGMH) [44,45]. The visualization of the calculation results was achieved using the Visual Molecular Dynamics (VMD, version 1.9.3) software [46].

We utilized the Dmol3 package [47,48] to perform calculations on the polymers $[\text{Ca}@\text{C}_{60}]_{\infty}$ within periodic models. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [49] was applied to simulate the electron exchange correlation interaction. Electron-ion interactions were described using the DFT Semi-core Pseudopotentials (DSPP) [50]. The wave function is expanded by Double Numerical plus polarization (DNP) basis set, and the Brillouin zone is used by $2 \times 4 \times 1$ K-point grid for $[\text{Ca}@\text{C}_{60}]_{\infty}-1$, $4 \times 2 \times 1$ for $[\text{Ca}@\text{C}_{60}]_{\infty}-2$. The van der Waals interaction was described using the Tkatchenko-Scheffler method [51]. In order to prevent interlayer interaction between the same research objects, a 15 Å vacuum layer was applied.

4. Conclusions

We conducted a comprehensive investigation into the stability and electronic properties of oligomers and polymers of $\text{Ca}@\text{C}_{60}$ through DFT calculations. In the most stable $\text{Ca}@\text{C}_{60}$ dimer, the fullerene cages are connected through a four-atom ring, with each fullerene cage utilizing a (5,6) bond to form the four-atom ring. The trimer of $\text{Ca}@\text{C}_{60}$ exhibits a most stable isomer with a triangular structure. For $\text{Ca}@\text{C}_{60}$ tetramers, two thermodynamically stable isomers exist—one with a rectangular shape and the other with a rhombus shape. Our findings indicate a decreasing HOMO-LUMO gap as the number of $\text{Ca}@\text{C}_{60}$ units increases to three and four in the oligomers. Furthermore, our study reveals that the oligomer formation is an exothermic process, with van der Waals interactions between fullerene cages playing a crucial role. In the case of the two-dimensional polymer of $\text{Ca}@\text{C}_{60}$, we observe structural similarities with graphullerene. This polymer functions as a semiconductor, featuring a direct bandgap of 0.22 eV. Given the solubility of the $\text{Ca}@\text{C}_{60}$ monomer in aniline, future experimental studies on the polymerization of $\text{Ca}@\text{C}_{60}$ are deemed feasible.

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Article

Geometries, Electronic Structures, Bonding Properties, and Stability Strategy of Endohedral Metallofullerenes TM@C_{28} ($\text{TM} = \text{Sc}^-$, Y^- , La^- , Ti , Zr , Hf , V^+ , Nb^+ , Ta^+)

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Abstract: We performed quantum chemical calculations on the geometries, electronic structures, bonding properties, and stability strategy of endohedral metallofullerenes TM@C_{28} ($\text{TM} = \text{Sc}^-$, Y^- , La^- , Ti , Zr , Hf , V^+ , Nb^+ , Ta^+). Our calculations revealed that there are three different lowest-energy structures with C_{2v} , C_{3v} , and T_d symmetries for TM@C_{28} . The HOMO–LUMO gap of all these structures ranges from 1.35 eV to 2.31 eV, in which $[\text{V@C}_{28}]^+$ has the lowest HOMO–LUMO gap of 1.35 eV. The molecular orbitals are mainly composed of fullerene cage orbitals and slightly encapsulated metal orbitals. The bonding analysis on the metal–cage interactions reveals they are dominated by the Coulomb term ΔE_{elstat} and the orbital interaction term ΔE_{orb} , in which the orbital interaction term ΔE_{orb} contributes more than the Coulomb term ΔE_{elstat} . The addition of one or two CF_3 groups to $[\text{V@C}_{28}]^+$ could increase the HOMO–LUMO gap and further increase the stability of $[\text{V@C}_{28}]^+$.

Keywords: fullerenes; quantum-chemical calculations; chemical bonding; stability

1. Introduction

Fullerenes, structurally unique closed hollow carbon cages, are composed of exactly 12 pentagons and a certain number of hexagons. Among them, buckminsterfullerene C_{60} stands out as the most symmetrical and chemically inert member [1–3]. The smallest fullerene, C_{20} , presents a singular dodecahedral structure but is theoretically predicted to be highly reactive [4]. The reason why these small fullerenes are highly reactive is their high curvature. Thus, there are two main strategies to stabilize these fullerenes. On the one hand, there is the encapsulation of metal inside fullerenes, which gives rise to endohedral metallofullerenes (EMFs), which could lead to a charge transfer from metal to fullerenes and stabilize the high curvature motifs [5]. On the other hand, exohedral derivatization on high curvature motifs could release the curvature directly and make them transform from sp^2 hybridization to sp^3 hybridization [6,7].

EMFs, which encapsulate metal atoms or clusters within fullerene cages [5,8,9], represent an innovative class of metal–carbon clusters. These EMFs combine the structural merits of fullerene frameworks with the photoelectromagnetic advantages of metals. Particularly, C_{28} has been observed to exhibit one remarkable peak in the domain of supersonic carbon cluster beam experiments [4,10]. However, the isolation of C_{28} has been challenging due to its open-shell electronic nature. EMFs not only improve the stability of reactive fullerenes such as C_{28} [11,12] but also introduce novel functionalities. For instance, the encapsulation of tetravalent metals like titanium (Ti), zirconium (Zr), and uranium (U) culminates in the formation of stable endohedral metallofullerenes, namely Ti@C_{28} , Zr@C_{28} , and U@C_{28} [4,13–17]. $\text{U}^{2+}\text{@C}_{28}$ has been theoretically predicted to adhere to the 32-electron principle [18], of which central f-block metals like uranium have their s-, p-, d-, and f-type valence shells completely filled and exhibit remarkable stability. U@C_{28} also

follows the 32-electron rule and accommodates two valence electrons within the peripheral cage structure [19].

The synthesis of EMFs involves various experimental methods [20], including electric arc discharge [21], which generates EMFs by vaporizing graphite rods and metal oxides in an inert atmosphere, and laser ablation [22], where a high-power laser vaporizes a carbon-rich target and metal oxides to facilitate EMF formation. Chemical vapor deposition (CVD) methods [23,24], involving the thermal decomposition of hydrocarbon gases on metal catalysts, contribute to fullerene production. Additionally, the surgery approach [25] is often employed to open fullerene cages, put transition metals inside, and close fullerene cages.

The presence of a fullerene can also modify the physical and chemical properties of encapsulated atoms. Recently, one theoretical study showed that in ${}^7\text{Be}@C_{28}$, the electron capture decay rate of ${}^7\text{Be}$ could become slower because of the metal–cage interactions [26]. Wang and Gao revealed that a hyperhydrogenated water species, H_4O , can be easily formed using H_2 and H_2O if they are put inside small-sized fullerenes like C_{28} as nanoreactors [27]. Spano and coworkers theoretically studied the $\text{Cr}@C_{28}$ and found there are two stable sites of Cr metal in C_{28} , leading to two different measurable currents in single-molecule devices [28]. The bonding, electron affinity, optical, and magnetic properties of $\text{M}@C_{28}$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{U}$) have been investigated theoretically [29]. However, the element effect on the geometries and electronic structures is rarely discussed. Moreover, the chemical bonding between the encapsulated metal and fullerene cage C_{28} has been explored.

In the present study, we studied the geometries, electronic structures, bonding properties, and stability strategy of endohedral metallofullerenes $\text{TM}@C_{28}$ ($\text{TM} = \text{Sc}^-, \text{Y}^-, \text{La}^-, \text{Ti}, \text{Zr}, \text{Hf}, \text{V}^+, \text{Nb}^+, \text{Ta}^+$) by using quantum chemical calculations. The chemical bonding between metal and C_{28} was studied using the energy decomposition analysis. The stability strategy of the highly reactive EMFs is discussed using trifluoromethyl groups.

2. Computational Methods

The structural search was started from two fullerene cages, including $C_{28}\text{-D}_2(1)$ and $C_{28}\text{-T}_d(2)$. The positions of transition metal atoms were generated randomly within a geometric sphere centered on the fullerene cages and with a radius smaller than that of the fullerene cage. In total, over 1000 initial structures were randomly generated. Clustering of these structures was conducted using the ISOSTAT module within the Molclus program [30] with two criteria: (a) an energy difference of less than 0.25 kcal/mol and (b) a geometric deviation of less than 0.1 Å. The geometric deviation was defined by calculating a distance matrix based on the atomic coordinates of the structures and converting its nondiagonal elements into a one-dimensional array. The calculations start from the semiempirical GFN-xTB method [31,32] and follow density functional theory (DFT) calculations at the PBE-D3(BJ)/def2-SVP level [33]. The final optimizations were performed at the PBE-D3(BJ)/def2-TZVPPD level [34–41]. The wave function stability and frequency analysis were subsequently verified, confirming these structures as local minima on the potential energy surface. The atomic charge distribution was computed using natural bond orbital (NBO7.0) [42] at the PBE-D3(BJ)/def2-TZVPPD level to gain electron distribution and bonding interactions. NBO analysis offers a comprehensive view of molecular bonding by translating electron densities into more chemically intuitive patterns like bonds and lone pairs, thus aiding in the understanding of intrinsic molecular interactions. All these DFT calculations were performed using Gaussian 16 software [43].

The energy decomposition analysis (EDA) developed by Ziegler and Rauk [44] is one of the most powerful methods to study the nature of chemical bonds. Here, the bonding nature between the metal dimer and fullerene cage was studied via EDA. Scalar relativistic effects and zeroth-order regular approximation (ZORA) [45] were considered. In EDA calculations, the molecule AB divides into two fragments, A and B, and the kernel is put on the intrinsic interaction between fragments that hold a specified electronic reference state in the frozen geometry [46,47]. The EDA approach decomposes the instantaneous

interaction energy ΔE_{int} of the A–B bond into four energy terms, of which the first three are the main components:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}} \quad (1)$$

The term ΔE_{elstat} is the *quasi*-classical electrostatic interaction between the unperturbed charge distributions of the prepared atoms and is usually an attractive term. The Pauli repulsion ΔE_{Pauli} is the energy change in the transformation from the superposition of the unperturbed electron densities $\rho_A + \rho_B$ of the isolated fragments to the wave function $\Psi^0 = N\hat{A}[\Psi_A\Psi_B]$, which properly obeys the Pauli principle through explicit antisymmetrization ($\hat{A}$ operator) and renormalization ($N = \text{constant}$) of the product wavefunction. ΔE_{Pauli} comprises the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction ΔE_{orb} derives from charge transfer, electron-pair bonding, and polarization effects. The EDA calculations were performed with the ADF2019 [48,49] package using the BP86 [50,51] functional with Grimme's dispersion correction D3(BJ) [33] and TZ2P+ basis set [52]. The zeroth-order regular approximation (ZORA) Hamiltonian was adopted to include the relativistic effect [45]. All these EDA calculations were performed based on the PBE-D3(BJ)/def2-TZVPPD-optimized structures.

3. Results and Discussion

There are two isomers of C_{28} , including $D_2(1)$ and $T_d(2)$. Our calculations show that all these metals prefer to be encapsulated inside the $T_d(2)$, giving rise to $\text{TM}@T_d(2)-C_{28}$. Figure 1 presents the calculated structural models of optimized $\text{TM}@T_d(2)-C_{28}$ ($\text{TM} = \text{Sc}^-, \text{Y}^-, \text{La}^-, \text{Ti}, \text{Zr}, \text{Hf}, \text{V}^+, \text{Nb}^+, \text{Ta}^+$). All these structures have a singlet as the ground state. However, the optimized structures are quite different for the different metals and slightly depend on the charge state. In the case of $[\text{Y}@C_{28}]^-, [\text{La}@C_{28}]^-,$ and $[\text{Hf}@C_{28}]$, the metal could stay in the center of the fullerene cage, leading to the T_d symmetry of the whole endohedral metallofullerenes. The metal in $\text{TM}@C_{28}$ ($\text{TM} = \text{Sc}^-, \text{Ti}, \text{V}^+, \text{Ta}^+$) is positioned off-center and close to the carbon atom along the C_3 axis, giving rise to the C_{3v} symmetry of this EMF. In contrast, $[\text{Zr}@C_{28}]$ and $[\text{Nb}@C_{28}]^+$ exhibit the lowest symmetry (C_{2v}) due to the off-center positioning of the metal. Despite the Zr and Ti metals having the same d-electron configuration, $\text{Zr}@C_{28}$ (C_{2v}) and $\text{Ti}@C_{28}$ (C_{3v}) exhibit different symmetries and structures.

The Root Mean Square Deviation (RMSD) serves as an essential quantitative index for analyzing alterations in the symmetry and structural integrity of molecular frameworks. In Figure 2, visualized with the aid of VMD software [53], a structure from each symmetry class is presented, with concomitant structures co-aligned through strategic translation and rotation. Subsequent calculations of RMSD values between disparate structures (expressed in angstrom units) were conducted. RMSD values in Figure 2a,b primarily stem from the locomotion of the encapsulated transition metal atoms, while in Figure 2c, the RMSD is attributable to the dimensional augmentation of the carbon cage. Consequently, in the lower portion of Figure 2c, a line representation is adopted, where the central atoms of varying systems are overlaid in a spatial context, with lines in diverse hues representing the different structural configurations. This representational approach succinctly delineates the subtle disparities in atomic positioning and cage structural modifications resulting from the incorporation of distinct transition metals.

The RMSD values for the C_{2v} symmetry systems with Zr and Nb^+ encapsulation are notably low (0.000 and 0.076, respectively), suggesting minor structural deviations due to the movement of the transition metals along the C_2 axis. For the C_{3v} symmetry systems encompassing $\text{V}^+, \text{Sc}^-, \text{Ta}^+,$ and Ti, there is an observed increment in RMSD values (0.000, 0.144, 0.164, and 0.181, respectively), indicating structural adaptations associated with the distribution of transition metals along different C_3 axes. In the T_d symmetry systems containing $\text{Y}^+, \text{Hf},$ and La^- , the RMSD changes (0.000, 3.950, and 3.981, respectively) denote significant structural changes, principally due to the global expansion or contraction of the carbon cage. This behavior could be a direct consequence of the larger atomic radii of these encapsulated metals, which may enforce a more dramatic spatial rearrangement of

the carbon atoms, altering the fullerene cage dimensions. These observed RMSD variations between different metals underscore the influence of atomic size, electronic configuration, and oxidation state on the resulting symmetry and structural modifications within the fullerene cage. The complexity of these interactions suggests a nuanced interplay between metal properties and fullerene adaptability.

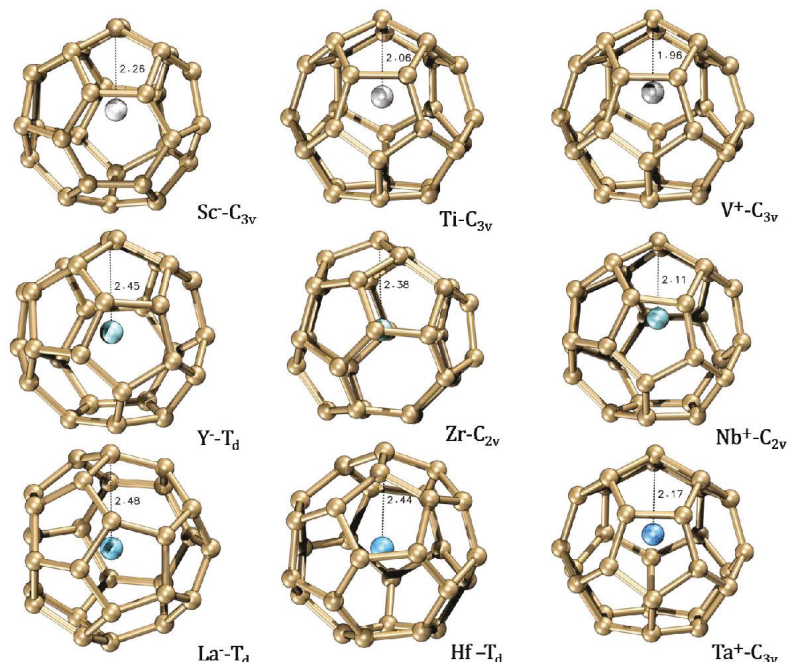


Figure 1. The optimized structures of TM@ C_{28} (TM= Sc⁻, Y⁻, La⁻, Ti, Zr, Hf, V⁺, Nb⁺, Ta⁺) with the shortest TM-C bond length.

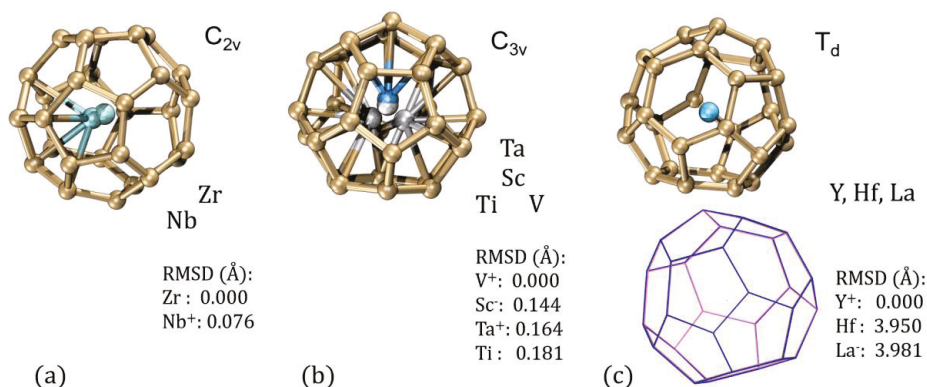


Figure 2. Visualization of transition metal-doped C_{28} fullerenes exhibiting varied symmetry classes, analyzed using VMD software [53]. Panel (a) illustrates the C_{2v} symmetric structure with Zr and Nb⁺ encapsulation, panel (b) displays the C_{3v} symmetric structure with V⁺, Sc⁻, Ta⁺, and Ti encapsulation, and panel (c) represents the T_d symmetric structure with Y⁺, Hf, and La⁻ encapsulation. The calculated RMSD values (in angstroms) highlight the structural deviations due to the specific movements of the embedded atoms and the expansion or contraction of the carbon cage. Panel (c) also features a line representation for clarity in structural differentiation, with superimposed central atoms from different systems and color-coded lines to distinguish between the structures.

The RMSD values derived from structural analysis provide a quantitative reflection of the divergence in geometric structures among different endohedral metallofullerenes. This divergence can be partially rationalized by applying the Hard and Soft Acids and Bases (HSAB) principle [54], which suggests a preferential interaction between “hard” acids and “hard” bases, as well as “soft” acids with “soft” bases. The HSAB principle is predicated on

the notion that the chemical behavior of atoms and molecules during bond formation is influenced by their electronic properties, specifically the polarizability and the relative size of their orbitals.

Within the context of the periodic table, these properties are not constant; they demonstrate notable variation. For instance, as transition metal changes from titanium (Ti) to hafnium (Hf), there is an observed increase in the size of the metal ions. According to HSAB theory, this increment in size correlates with an increase in softness, which implies a greater capacity for deformation or polarization upon interaction with a base, which is the fullerene cage in this case. The softness of the metal ion can enhance the degree of distortion or expansion of the cage structure, as softer ions can form more malleable and adaptable bonds, accommodating themselves within the confines of the fullerene lattice.

Furthermore, this interaction is not merely a function of size or electronic softness; other chemical and physical parameters also play important roles. Steric effects, for example, pertain to the spatial arrangement of atoms and can drastically affect how a metal ion is incorporated into the fullerene cage. The specific nature of the metal–fullerene interaction, dictated by the unique chemistry of each metal, further contributes to the resultant geometric configuration. Additionally, the overall stability of the resulting complex is an aggregate effect of these individual interactions and properties.

It is also worth noting that while elements such as Ti, Zr, and Hf may share similar d-electron configurations, which suggests comparable chemical reactivity, the subtle differences in their ionic radii, softness, and other chemical properties can lead to distinct geometric structures within the fullerene framework. The HSAB concept provides a framework to understand these variations. A holistic understanding of the geometric forms adopted by these complexes necessitates an integrated approach, considering not only HSAB theory but also delving into quantum mechanical explanations, electron density distribution, and the dynamics of bond formation and breaking. Only by encompassing these multifaceted chemical and physical factors can one begin to fully elucidate the reasons behind the observed structural diversity in these endohedral metallofullerenes.

Table 1 presents the optimized shortest TM–C bond lengths of all nine EMFs. The TM–C distances range from 1.96 Å to 2.48 Å. It is not surprising that the shortest TM–C distance for the same group metal increases monotonically. For instance, the shortest TM–C distance for TM@T_d(2)-C₂₈ (TM = Sc[−], Y[−], La[−]) increases from 2.26 to 2.48 Å. On the other hand, the TM–C distance decreases for the same period element. Particularly, the shortest V–C distance is only 1.96 Å. The calculations on the singlet–triplet splitting energy (ΔE_{S-T}) revealed that all those values are larger than 1.04 eV, suggesting that the ground state for all these EMFs is a singlet.

Table 1. Symmetry (Sym.), the singlet–triplet splitting energy (ΔE_{S-T}), the shortest TM–C bond length (d_{TM-C}) of TM@C₂₈ (TM = Sc[−], Y[−], La[−], Ti, Zr, Hf, V⁺, Nb⁺, Ta⁺).

EMFs	Sym.	ΔE_{S-T} (eV)	d_{TM-C} (Å)
[Sc@C ₂₈] [−]	ca. C _{3v}	1.87	2.26
[Y@C ₂₈] [−]	ca. T _d	1.98	2.45
[La@C ₂₈] [−]	ca. T _d	1.93	2.48
[Ti@C ₂₈]	ca. C _{3v}	1.56	2.06
[Zr@C ₂₈]	ca. C _{2v}	2.01	2.38
[Hf@C ₂₈]	ca. T _d	2.03	2.44
[V@C ₂₈] ⁺	ca. C _{3v}	1.04	1.96
[Nb@C ₂₈] ⁺	ca. C _{2v}	1.86	2.11
[Ta@C ₂₈] ⁺	ca. C _{3v}	1.64	2.17

To assess the kinetic stabilities of the EMFs, Figure 3 presents the gap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO). Except Ti@C₂₈, [V@C₂₈]⁺, and [Ta@C₂₈]⁺, all the other EMFs hold a large HOMO–LUMO gap above 2.0 eV, indicating that these EMFs could be isolated experimentally.

Particularly, both Zr@C_{28} and Hf@C_{28} have the highest HOMO–LUMO gap of 2.31 eV. On the other hand, the HOMO–LUMO gap of $[\text{V@C}_{28}]^+$ is as small as 1.35 eV, suggesting that this EMF is reactive and might not be isolated easily. Particularly, the HOMO–LUMO gap results are in agreement with the above the singlet–triplet splitting energy $\Delta E_{\text{S-T}}$ results; the larger the HOMO–LUMO gap, the larger $\Delta E_{\text{S-T}}$. Figure 4 presents the frontier molecular orbitals (FMOs) of three EMFs with different symmetries. Cage orbitals which are from the 2p atomic orbitals obviously contribute to all these FMOs. On the other hand, the metal orbitals show slight contributions. Particularly, the metal d orbitals show some contributions to the HOMO-1 and HOMO-2 of $[\text{Ta@C}_{28}]^+$ and HOMO of $[\text{La@C}_{28}]^-$.

To further analyze the electronic structures of TM@C_{28} , an NBO analysis was performed, and the results of the metals are shown in Table 2. The charges of metals range from -0.18 to $+1.81$. Although TM@C_{28} ($\text{TM} = \text{Sc}^-, \text{Y}^-, \text{La}^-$) is negatively charged, the charge is mainly localized on the cage rather than on the metal, which is in line with the above molecular orbitals results. The highly positive charge ($+1.34$) of Y metal in $[\text{Y@C}_{28}]^-$ may come from the fact that the NBO analysis does not treat (n)p functions as valence orbitals of transition metals [55]. For the other six EMFs, the metal is positively charged, with the positive charge ranging from 0.53 to 1.81.

The formation energy of EMFs, which is defined by the energy difference from total energy minus the sum of neutral fullerene and neutral/charged transition metals, is important to assess the stability of EMFs. The formation energy of TM@C_{28} was calculated and is shown in Table 2. All the formation energy falls in the range of -5.91 to -10.63 eV, indicating that these EMFs could form in the experiments. Particularly, Ti@C_{28} , which was observed experimentally, has a formation energy of -8.18 eV.

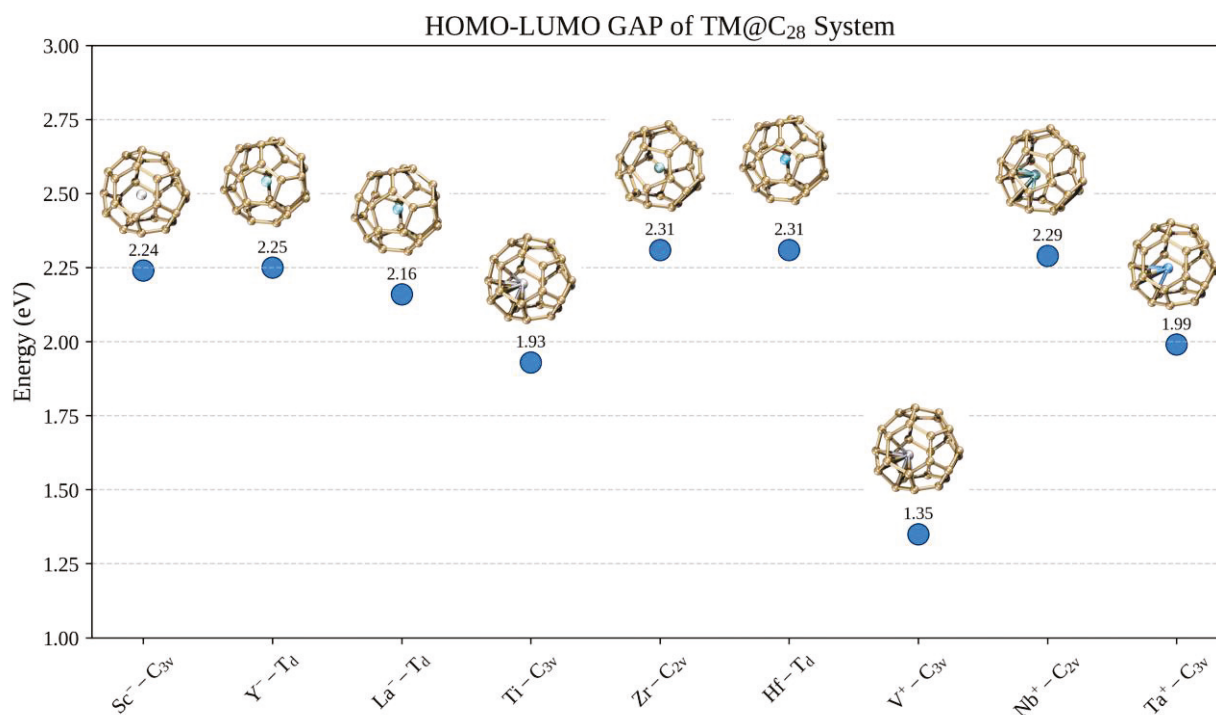


Figure 3. The HOMO–LUMO gap of TM@C_{28} ($\text{TM} = \text{Sc}^-, \text{Y}^-, \text{La}^-, \text{Ti}, \text{Zr}, \text{Hf}, \text{V}^+, \text{Nb}^+, \text{Ta}^+$).

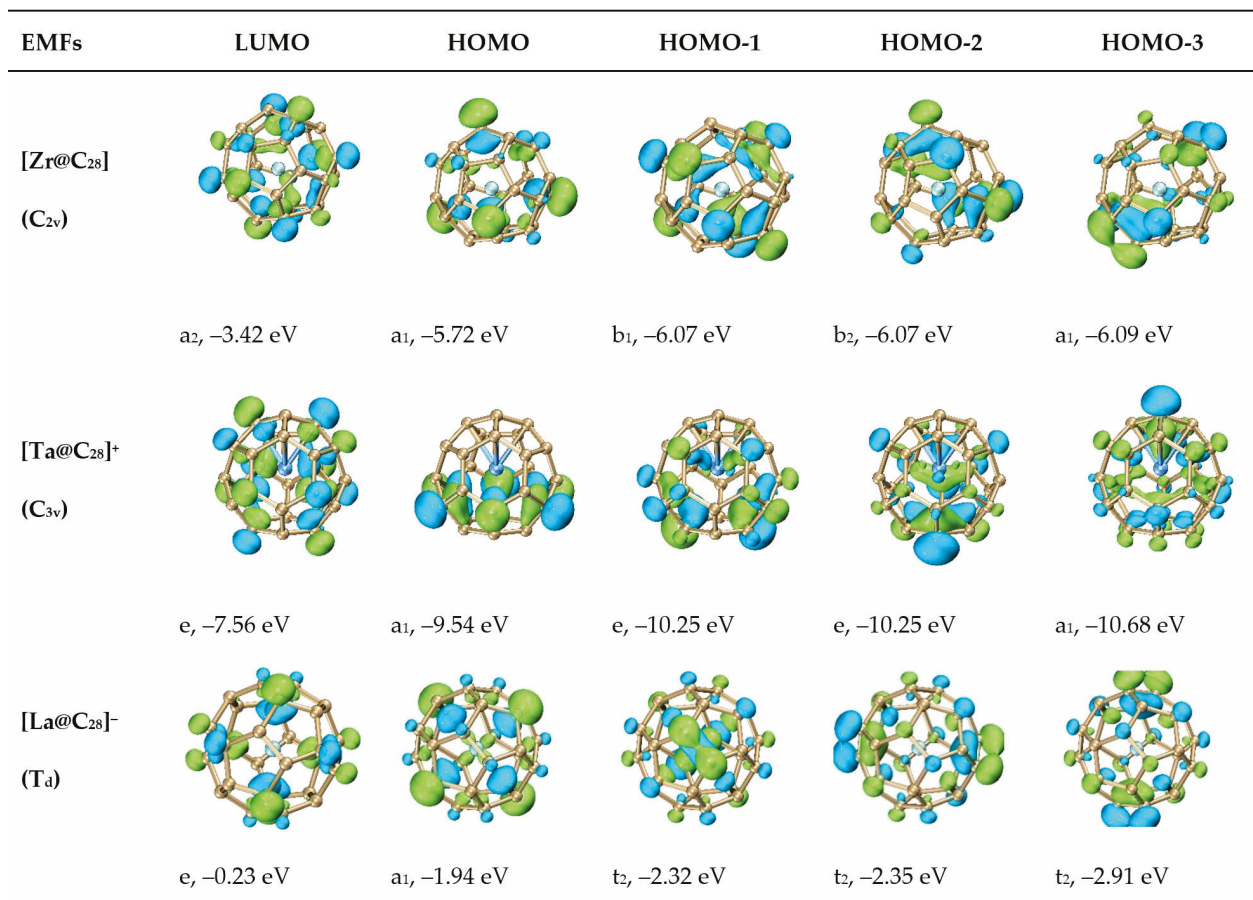


Figure 4. Selected molecular orbitals (isovalue = 0.05) of [TM@C₂₈] at the PBE-D3(BJ)/def2-TZVPPD level.

Table 2. NBO partial charges, the formation energy from the carbon cage C₂₈ and transition metal atoms, and the first excitation energies and corresponding oscillator strengths of TM@C₂₈ (TM = Sc[−], Y[−], La[−], Ti, Zr, Hf, V⁺, Nb⁺, Ta⁺). The T and Q represent the triplet and quintet states, respectively.

EMFs (Singlet)	Fragment	Natural Charge (TM)	Formation Energy (eV)	Excitation Energies (eV)	Oscillator Strengths (nm)
[Sc@C ₂₈] [−]	Sc [−] (T) + C ₂₈ (Q)	−0.18	−10.63	2.31	537.7
[Y@C ₂₈] [−]	Y [−] (T) + C ₂₈ (Q)	1.34	−10.13	2.30	539.5
[La@C ₂₈] [−]	La [−] (T) + C ₂₈ (Q)	0.19	−5.91	2.22	559.0
[Ti@C ₂₈]	Ti(Q) + C ₂₈ (Q)	0.53	−8.18	2.05	605.8
[Zr@C ₂₈]	Zr(Q) + C ₂₈ (Q)	1.68	−9.02	2.37	523.7
[Hf@C ₂₈]	Hf(T) + C ₂₈ (Q)	1.64	−8.66	2.37	523.9
[V@C ₂₈] ⁺	V ⁺ (Q) + C ₂₈ (Q)	1.38	−6.66	1.48	837.6
[Nb@C ₂₈] ⁺	Nb ⁺ (Q) + C ₂₈ (Q)	1.33	−8.00	2.38	521.5
[Ta@C ₂₈] ⁺	Ta ⁺ (Q) + C ₂₈ (Q)	1.81	−8.47	2.13	582.9

The excitation energies and corresponding oscillator strengths, which are related to the electron excitation from the HOMO to LUMO, were calculated using time-dependent density functional theory (TDDFT), as shown in Table 2. The excitation energies range from 1.48 to 2.38 eV, with oscillator strengths ranging from 837.56 to 521.49 nm. The smaller the excitation energy, the larger the oscillator strength. The excitation energy also agrees well with the above HOMO–LUMO gap. The [V@C₂₈]⁺ needs the smallest excitation energy.

Although the electronic structures of TM@C₂₈ like Ti@C₂₈ have been discussed in previous papers [13–16], the bonding nature between the metals and C₂₈ has not been analyzed.

Recently, we found that the EDA analysis could describe the bonding nature of EMFs [56] and Zintl clusters [57,58] well. Thus, to study the bonding nature between the encapsulated metal and fullerenes C_{28} , we performed the EDA analysis on $TM@C_{28}$. Because the EDA results strongly depend on how to divide a whole EMF into two interacting fragments, we first carried out the EDA analysis on the $TM@C_{28}$ by using different models. According to the criterion that the bonding model that has the smallest absolute orbital interactions $|\Delta E_{orb}|$ is usually determined as the best bonding model, the EDA results with the best bonding models are shown in Table 3, with the remaining models in the Supporting Information. As shown in Table 3, the bonding energy ranges from -331.9 kcal/mol to -851.5 kcal/mol, suggesting that all these EMFs are stable. The attractive interaction terms, including the Coulomb term ΔE_{elstat} and the orbital interaction term ΔE_{orb} , compensate for the repulsive terms ΔE_{Pauli} . In general, the Coulomb term ΔE_{elstat} contributes less than the orbital interaction term ΔE_{orb} . Particularly, for $[Nb@C_{28}]^+$, the contribution from the orbital interaction term ΔE_{orb} to the total attractive energy is as high as 76.9%. The dispersion interactions contribute slightly to the total bonding strength with a range of -2.8 to -6.9 kcal/mol.

Table 3. EDA results (in kcal/mol) of the $[TM@C_{28}]$ with TM^{m+} and C_{28}^{n-} as interacting fragments at the BP86-D3(BJ)/TZ2P+ level. The interaction energies (ΔE_{int}), Pauli repulsion (ΔE_{Pauli}), electrostatic interactions (ΔE_{elstat}), orbital interactions (ΔE_{orb}), and dispersion (ΔE_{disp}) are presented with the percentages showing the contribution of orbital interactions or electrostatic attractions to the total attractive interactions.

EMFs	$[Sc@C_{28}]^-$	$[Y@C_{28}]^-$	$[La@C_{28}]^-$
Fragments	$Sc^+ (4s^0 3d^2) + [C_{28}]^{2-}$	$Y^+ (5s^0 4d^2) + [C_{28}]^{2-}$	$La^+ (6s^0 5d^2) + [C_{28}]^{2-}$
ΔE_{int}	−552.3	−361.4	−308.7
ΔE_{Pauli}	+472.3	+752.4	+1160.2
ΔE_{elstat}^a	−363.7 (35.6%)	−522.8 (47.1%)	−703.7 (48.1%)
ΔE_{orb}^a	−658.1 (64.4%)	−588.3 (52.9%)	−760.8 (51.9%)
ΔE_{disp}	−2.8	−2.8	−4.3
EMFs	$[Ti@C_{28}]$	$[Zr@C_{28}]$	$[Hf@C_{28}]$
Fragments	$Ti^+ (4s^1 3d^2) + [C_{28}]^-$	$Zr^+ (5s^1 4d^2) + [C_{28}]^-$	$Hf^+ (6s^1 5d^2) + [C_{28}]^-$
ΔE_{int}	−423.0	−331.9	−559.6
ΔE_{Pauli}	+908.5	+848.4	+1053.6
ΔE_{elstat}^a	−464.5 (35.0%)	−485.7 (41.3%)	−585.9 (36.4%)
ΔE_{orb}^a	−861.3 (65.0%)	−689.4 (58.7%)	−1024.4 (63.6%)
ΔE_{disp}	−5.7	−5.2	−2.8
EMFs	$[V@C_{28}]^+$	$[Nb@C_{28}]^+$	$[Ta@C_{28}]^+$
Fragments	$V^{2+} (4s^0 3d^3) + [C_{28}]^-$	$Nb^{2+} (5s^0 4d^3) + [C_{28}]^-$	$Ta^{2+} (6s^0 5d^3) + [C_{28}]^-$
ΔE_{int}	−851.5	−508.0	−622.1
ΔE_{Pauli}	+831.1	+1003.9	+690.4
ΔE_{elstat}^a	−463.1 (27.6%)	−348.2 (23.1%)	−388.8 (29.7%)
ΔE_{orb}^a	−1214.1 (72.4%)	−1156.9 (76.9%)	−918.8 (70.3%)
ΔE_{disp}	−5.4	−6.9	−4.9

^a The percentages corresponding to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb}$) are in parentheses.

The HOMO–LUMO gap of $[V@C_{28}]^+$ is as small as 1.35 eV, which is less than the average HOMO–LUMO gap (2.09 eV) in the nine EMFs, suggesting the relatively lower kinetic stability of $[V@C_{28}]^+$. Previous studies have shown that electronegative organic groups like trifluoromethyl can enhance the stability of EMFs by increasing the HOMO–LUMO gap [59,60]. In these previous studies, $La@C_{60}$, which has an open-shell structure and is difficult to isolate experimentally, is theoretically predicted to be able to be stabilized by introducing CF_3 groups [56]. Then, this theoretical proposal was verified by the experimental

single-crystal structure of the CF_3 -adduct of La@C_{60} [57]. In the present study, we studied the addition of the trifluoromethyl group to $[\text{V@C}_{28}]^+$ to enhance its stability and facilitate its future experimental isolation.

We focused on the single addition and double addition of the trifluoromethyl group to $[\text{V@C}_{28}]^+$. For the lowest-energy $[\text{V@C}_{28}]^+$ (C_{3v}), we tried all 28 configurations (C_{28}^1) of single CF_3 addition and 378 configurations (C_{28}^2) of two CF_3 additions at the PBE-D3(BJ)/def2-SVP level. After optimizations, only 7 structures and 51 structures exist for $[\text{V@C}_{28}]^+-\text{CF}_3$ and $[\text{V@C}_{28}]^+-(\text{CF}_3)_2$, respectively. Figure 5 shows the seven possible adducts of $[\text{V@C}_{28}]^+-\text{CF}_3$ with the relative reaction energies and HOMO–LUMO gaps, and the remaining results are shown in Supporting Information. The two lowest-energy structures of $[\text{V@C}_{28}]^+-\text{CF}_3$ have almost the same reaction energy of 68.3 kcal/mol and 69.2 kcal/mol, respectively. The HOMO–LUMO gaps of these two structures are 1.72 and 1.84 eV, obviously higher than that of $[\text{V@C}_{28}]^+$.

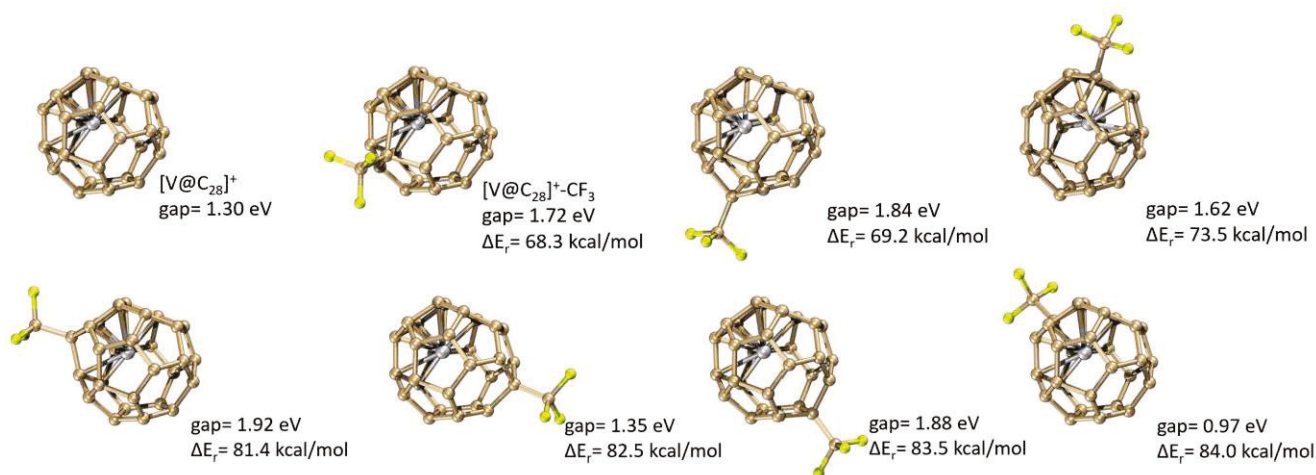


Figure 5. The HOMO–LUMO gaps and reaction energies of $[\text{V@C}_{28}]^+$ and $[\text{V@C}_{28}]^+-\text{CF}_3$ isomers at the PBE-D3(BJ)/def2-SVP level.

Further addition of one more CF_3 group to $[\text{V@C}_{28}]^+-\text{CF}_3$ gives rise to lots of possible $[\text{V@C}_{28}]^+-(\text{CF}_3)_2$ isomers. Figure 6 only presents four isomers with relative energy between $[\text{V@C}_{28}]^+$ and two CF_3 groups. The lowest-energy isomer has the two CF_3 group additions on the two carbon atoms connected by one C–C bond with a reaction energy of 152.5 kcal/mol. The HOMO–LUMO gap then increases to 2.18 eV. The reaction energy of the second isomer is only 1.20 kcal/mol higher than that of the first one, but its HOMO–LUMO gap is only 1.78 eV, indicating its lower kinetic stability. Therefore, it is clear from the above discussion that the addition of CF_3 groups to $[\text{V@C}_{28}]^+$ will increase its stability, which will assist future experimental isolation of $[\text{V@C}_{28}]^+-(\text{CF}_3)_2$.

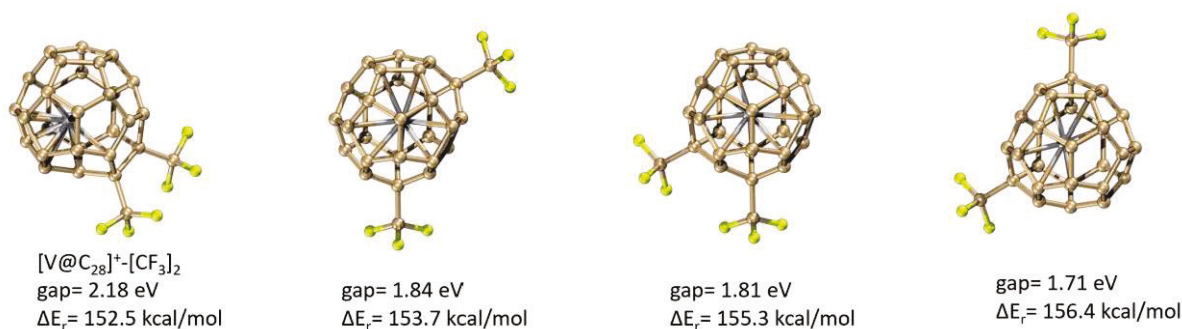


Figure 6. The HOMO–LUMO gaps and reaction energies of low-energy $[\text{V@C}_{28}]^+-(\text{CF}_3)_2$ isomers at the PBE-D3(BJ)/def2-SVP level.

4. Conclusions

By using quantum chemical calculations, we studied the geometries, electronic structures, bonding properties, and stability strategy of endohedral metallofullerenes $\text{TM}@\text{C}_{28}$ ($\text{TM} = \text{Sc}^-, \text{Y}^-, \text{La}^-, \text{Ti}, \text{Zr}, \text{Hf}, \text{V}^+, \text{Nb}^+, \text{Ta}^+$). $\text{TM}@\text{C}_{28}$ has three different structures with C_{2v} , C_{3v} , and T_d symmetries. The HOMO–LUMO gap ranges from 1.35 eV to 2.31 eV, with $[\text{V}@\text{C}_{28}]^+$ having the lowest HOMO–LUMO gap of 1.35 eV. The trend of singlet–triplet splitting energy and first excitation energy is in line with the HOMO–LUMO gap. The frontier molecular orbitals analysis revealed that the molecular orbitals are mainly from fullerene cage orbitals, with a slight contribution from the encapsulated metals. The bonding interactions between encapsulated metal and fullerene cages are dominated by the Coulomb term ΔE_{elstat} and the orbital interaction term ΔE_{orb} , in which the orbital interaction term ΔE_{orb} contributes more than the Coulomb term ΔE_{elstat} . The addition of one or two CF_3 groups to $[\text{V}@\text{C}_{28}]^+$ could increase the HOMO–LUMO gap, giving rise to the possible isolation of $[\text{V}@\text{C}_{28}]^+$.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/inorganics12020040/s1>, Figure S1: The HOMO–LUMO GAP after attaching a CF_3 group to $[\text{V}@\text{C}_{28}]^+$ and the energy differences between different isomers, at the PBE–D3(BJ)/def2–SVP level.; Table S1: The atomic (ionic) energies (in eV) calculated using PBE–D3(BJ)/def2–TZVPPD.; Figure S2: After the addition of two CF_3 groups, the HOMO–LUMO GAP and the energy relationships among different isomers, at the PBE–D3(BJ)/def2–SVP level; Table S2: The EDA results (in kcal/mol) of the $[\text{TM}@\text{C}_{28}]$ with TM^{m+} and C_{28}^{n-} as interacting fragments at the BP86–D3(BJ)/TZ2P+ level.

Author Contributions: For the author contributions in our manuscript: D.L. was responsible for the majority of the computations, analysis, and original draft preparation. Y.S. contributed to parts of the data discussion and analysis. T.Y., as the corresponding author, provided project management, funding acquisition, supervision, and was involved in the review and editing of the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: We emphasize open data sharing and hereby provide the following data availability statement: All research data have been meticulously recorded and are stored in a trusted data repository. Some essential data are attached in the Supplementary Materials of this paper for reference. We encourage interested researchers to contact us for further details on data availability.

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Conflicts of Interest: The authors declare no conflict of interest.

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Article

Synthesis and Characterization of a Novel Non-Isolated-Pentagon-Rule Isomer of Th@C_{76} : $\text{Th@C}_1(17418)\text{-C}_{76}$

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Abstract: A novel Non-Isolated-Pentagon-Rule (non-IPR) isomer of thorium-based endohedral mono-metallofullerenes (mono-EMFs), $\text{Th@C}_1(17418)\text{-C}_{76}$, was successfully synthesized and characterized using MALDI-TOF mass spectroscopy, single-crystal X-ray diffraction, UV-vis-NIR spectroscopy, and Raman spectroscopy. The molecular structure of this non-IPR isomer was determined unambiguously as $\text{Th@C}_1(17418)\text{-C}_{76}$ using a single-crystal X-ray diffraction analysis. The crystallographic results further revealed that the optimal Th site resided at the intersection of two adjacent pentagons, similar to that of $\text{U@C}_1(17418)\text{-C}_{76}$. Additionally, the UV-vis-NIR spectra of $\text{Th@C}_1(17418)\text{-C}_{76}$ exhibited distinct differences compared to the previously reported $\text{U@C}_1(17418)\text{-C}_{76}$, highlighting the distinctive electronic structure of actinium-based endohedral metallofullerenes (EMFs). The Raman spectrum of $\text{Th@C}_1(17418)\text{-C}_{76}$ exhibited similarities to that previously reported for thorium-based EMFs, indicating the analogous strong metal–cage interactions of thorium-based EMFs.

Keywords: endohedral metallofullerenes; mono-metallofullerenes; thorium; X-ray crystallography

1. Introduction

Endohedral metallofullerenes (EMFs) are a specialized type of carbon nanomaterial featured by the encapsulation of metal atoms or metal clusters within the carbon cage of the fullerenes [1–3]. In 1991, Smalley et al. achieved the isolation of the first EMF, La@C_{82} , which initiated the exploration of the structure and properties of EMFs [4]. Subsequently, numerous types of mono-EMFs and endohedral clusterfullerenes have been synthesized and reported by researchers [5–8]. Depending on the differences between endohedral species, EMFs can be further classified as mono-metallofullerenes, di-metallofullerenes, tri-metallofullerenes, and clusterfullerenes [9–13]. The electron transfer and host–guest interactions between the endohedral metal units and fullerene carbon cages contribute to the intriguing electronic structures and physicochemical properties of these EMFs, thereby presenting immense potential in various cutting-edge fields, including biomedicine, organic photovoltaic devices, and single-molecule devices [14–17].

Mono-EMFs represent the most extensively studied type of EMF, with the majority of reported mono-EMFs being based on lanthanide metals. These metals are embedded within the carbon cage of the fullerene in the form of M@C_{2n} ($\text{M} = \text{Ce}$ [18], Pr [19], Nd [20], Sm [21], Eu [22], Gd [23], Tb [24], Dy [25], Ho [26], Er [27], Yb [28], and Lu [29]). In recent years, research on actinium-based mono-EMFs has also been reported, primarily focused on uranium (U) and thorium (Th). Among them, the characterization of $\text{Th@C}_{3v}(8)\text{-C}_{82}$ [30] marked the beginning of the investigation into actinium-based mono-EMFs. In

monometallic thorium-based EMFs, thorium usually exhibits an oxidation state of a +4 oxidation state. For example, $\text{Th}@T_d(19151)\text{-C}_{76}$ [31], $\text{Th}@D_{5h}(6)\text{-C}_{80}$ [32], $\text{Th}@C_{2v}(9)\text{-C}_{82}$, $\text{Th}@C_2(5)\text{-C}_{82}$ [33], and $\text{Th}@C_1(11)\text{-C}_{86}$ [34] have been discovered in previous research. All of them demonstrate a four-electron charge transfer from the metal atom to the fullerene cage. Conversely, uranium's oxidation state displays a remarkable flexibility. In $\text{U}@C_{2v}(9)\text{-C}_{82}$, the endohedral uranium transfers three electrons to the C_{82} carbon cage, while in $\text{U}@C_2(5)\text{-C}_{82}$, the endohedral uranium transfers four electrons to the C_{82} fullerene cage [35]. Because of the contributions from f-orbital electrons, the unique characteristics and variability of oxidation states in actinide metals lead to more complex electron configurations in actinide-based EMFs compared to lanthanide-based EMFs. Actinide-based EMFs also exhibit stronger metal–cage interactions than those of lanthanide-based EMFs, and actinide metal ions have a more significant influence on the properties of actinide-based EMFs than previously observed for lanthanide-based EMFs. For example, previously reported mono-EMFs based on uranium, known as $\text{U}@C_1(28324)\text{-C}_{80}$, and mono-EMFs based on thorium, labeled as $\text{Th}@C_1(28324)\text{-C}_{80}$, possess the same fullerene carbon cage, and both of them undergo a four-electron charge transfer process. They demonstrate distinct electronic properties, as evidenced by significant differences in their UV-vis-NIR spectra [36].

Based on extensive research on actinium-based mono-EMFs, it is clear that the remarkable charge transfer and strong engagement between actinide metal ions and fullerene carbon cages are essential for stabilizing previously unstable fullerene cage structures. Thus, in addition to the experimentally verified isomers, there are numerous isomers that have only been predicted and researched theoretically in actinium-based mono-EMFs. Consequently, further experimental investigations are of paramount importance to exploring actinium-based mono-EMFs, as they will reveal the distinct electronic properties and carbon cage structures that differentiate them from traditional lanthanide-based mono-EMFs.

Recently, two independent computational studies proposed two possible isomeric structures of $\text{Th}@C_{76}$, one is referred to as $\text{Th}@T_d(19151)\text{-C}_{76}$, while the other is referred to as $\text{Th}@C_1(17418)\text{-C}_{76}$. [37,38]. Nevertheless, only the existence of $\text{Th}@T_d(19151)\text{-C}_{76}$ [31] has been experimentally confirmed. Further experimental investigation of $\text{Th}@C_1(17418)\text{-C}_{76}$ would contribute to a deeper understanding of the unique carbon cage structures, electronic properties, and host–guest interactions exhibited by actinide-based EMFs.

In this study, we present the synthesis and characterization of a novel non-IPR isomer of thorium-based mono-EMFs, $\text{Th}@C_1(17418)\text{-C}_{76}$. $\text{Th}@C_1(17418)\text{-C}_{76}$ was successfully synthesized by using a modified Krätschmer–Huffman direct-current DC arc-discharge method. It was thoroughly characterized through various techniques, including MALDI-TOF mass spectroscopy, single-crystal X-ray diffraction, UV-vis-NIR spectroscopy, and Raman spectroscopy. The crystallographic results revealed that the optimal Th site resided at the intersection of two adjacent pentagons, and the presence of a single Th ion played a crucial role in stabilizing the non-IPR C_{76} fullerene cage.

2. Results and Discussion

2.1. Synthesis and Isolation of $\text{Th}@C_{76}$

Thorium-based EMFs were produced using a modified Krätschmer–Huffman direct-current DC arc-discharge method. Hollow graphite rods, packed with ThO_2 and graphite powder (molar ratio of Th: C = 1:24), were vaporized in an arcing reactor chamber under a 200 Torr helium atmosphere. The resulting soot was then collected and extracted with CS_2 for 12 h. Multistage high-performance liquid chromatography (HPLC) separation processes were employed to isolate and purify the $\text{Th}@C_{76}$ (Figure S1). The purity of the $\text{Th}@C_{76}$ was confirmed by the observation of single peaks with HPLC and positive-ion-mode matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry, as exhibited in Figure 1. The mass spectra of the isomer of $\text{Th}@C_{76}$ exhibited

a peak at 1143.975 m/z , and the experimental isotopic distribution of the sample agrees well with the empirical projection.

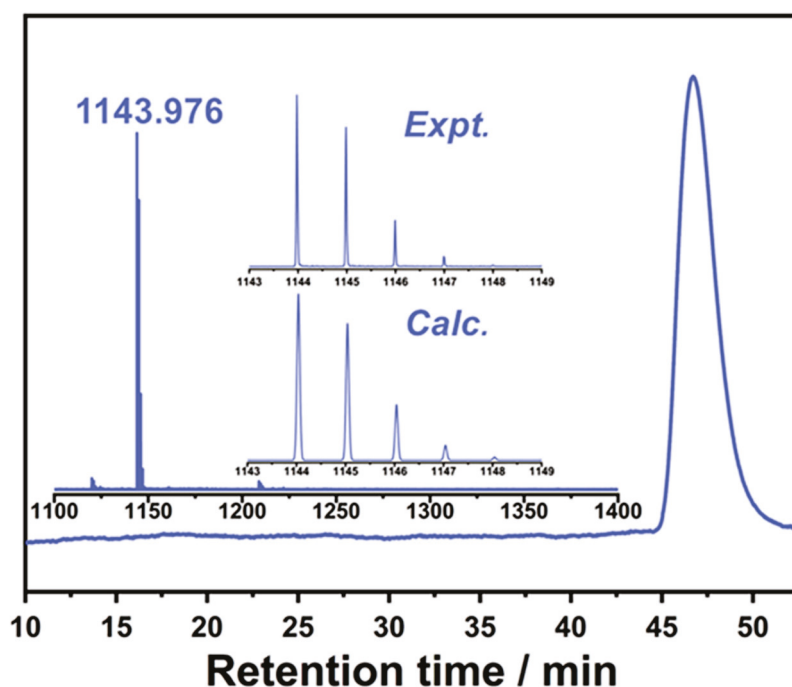


Figure 1. HPLC chromatogram of purified Th@C₇₆ on a Buckyprep column using toluene as the eluent, with a 4 mL/min flow rate. The mass spectra of Th@C₇₆ and associated empirical and hypothetical isotopic profiles of the sample are shown in the inset.

2.2. Molecular Structure of Th@C₁(17418)-C₇₆

The molecular configuration of Th@C₇₆ was unequivocally ascertained through single-crystal X-ray diffraction analyses. Th@C₇₆ and Ni^{II}-OEP (OEP = 2, 3, 7, 8, 12, 13, 17, 18-octaethylporphyrin dianion) were co-crystallized by slowly diffusing the benzene solution of Ni^{II}-OEP into the carbon disulfide solution of the purified compounds. The structure of Th@C₇₆ was resolved and refined in the C2/c (No. 15) space group. The experimental results clearly showed that this new isomer of Th@C₇₆ showed a different structure from the reported Th@T_d(19151)-C₇₆ [31]. It shares the same carbon cage structure with U@C₁(17418)-C₇₆, which possesses a low-symmetry C₁(17418)-C₇₆ cage and one adjacent pentagon pair [36]. Interestingly, crystallographic investigations of the C₁(17418)-C₇₆ carbon cage have primarily been limited to actinide metallofullerenes, and no previous studies have reported the observation of or noticed the same cage in lanthanide-based EMFs. This indicates that a stronger interaction between U or Th and fullerene cages may facilitate the stabilization of these unconventional fullerene cage isomers. On the other hand, Th@C₁(17418)-C₇₆ was also predicted to be the most advantageous product in experiments at elevated temperatures due to its dominant molar fraction [38]. This result verifies the theoretical predications.

Figure 2 shows the molecular structure of Th@C₁(17418)-C₇₆ and its relationship to the co-crystallized Ni^{II}(OEP) molecule. The Th@C₁(17418)-C₇₆ moiety is close to the adjacent Ni^{II}(OEP), with a short Ni-to-cage carbon distance (Ni1-C12) of 2.875 Å, demonstrating a characteristic interplay between the carbon cage and Ni^{II}(OEP). There are five crystallographic sites for the Th atoms with occupancies of 0.50 for Th1, 0.30 for Th2, 0.14 for Th3, 0.03 for Th4, and 0.025 for Th5 (see Figure S2). Th1 (occupancy 0.50) is situated at the intersection of two adjacent pentagons with the shortest Th–C distance in the range of 2.359–2.449 Å (Table S2), as shown in Figure 3. The shortest Th–C distances of the Th@C₁(17418)-C₇₆ are similar to those in Th@T_d(19151)-C₇₆, demonstrating similar interactions between the Th atom and the carbon cage [31]. In comparison to two examples

of lanthanide-based non-IPR monometallic C_{76} ($M@C_{2v}(19138)-C_{76}$, $M = Eu$ [39], Sm [40]), although the major metal sites are all located at the intersection of two adjacent pentagons, there are large differences in the shortest Th–cage distances. This discrepancy suggests that the interaction between the metal and cage in $Th@C_{76}$ could potentially possess a greater strength when compared to its lanthanide counterparts.

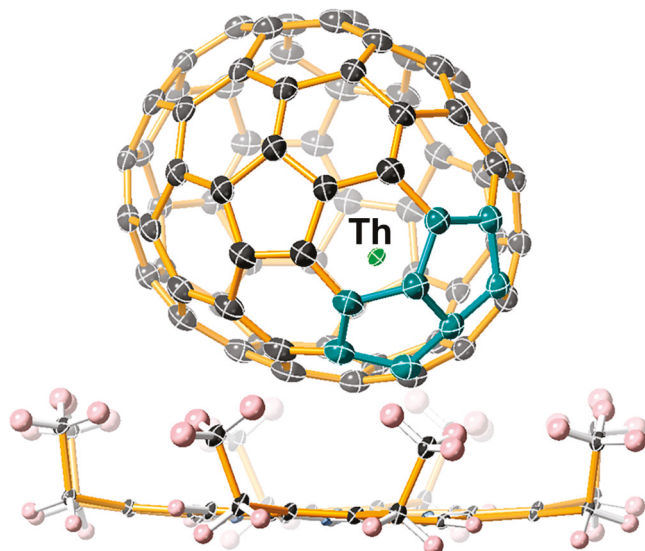


Figure 2. ORTEP drawings showing the relationship between the EMF and porphyrin moieties for $Th@C_1(17418)-C_{76} \cdot [Ni^{II}(OEP)]$ with 15% thermal ellipsoids. Only the major cage orientation and predominant thorium sites are shown.

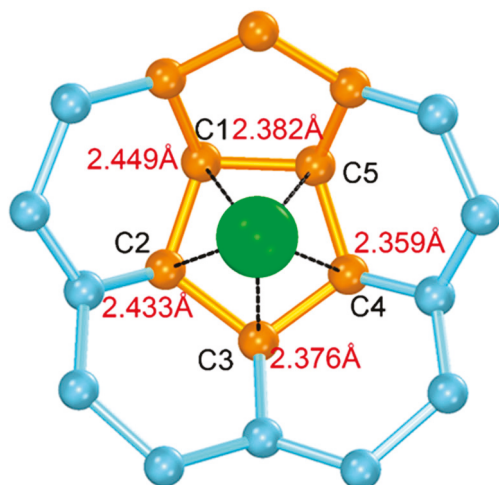


Figure 3. Perspective drawings showing the interaction of the major thorium closest cage portion in $@C_1(17418)-C_{76}$.

2.3. Spectroscopic Characterizations

UV-vis-NIR absorption is a useful technique that can help us to determine the electronic structures of EMFs. Normally, EMFs sharing the same cage and charge transfer exhibit almost identical absorption spectra [1]. The UV-vis-NIR absorption spectrum was utilized in this study to characterize the pure sample dissolved in a CS_2 solution, as depicted in Figure 4. This allowed for further analysis. $Th@C_1(17418)-C_{76}$ exhibits five characteristic peaks at 490, 602, 755, 930, and 1078 nm. The absorption onset occurs at approximately 1230 nm, indicating an optical band of 1.01 V. The absorption spectrum of $U@C_1(17418)-C_{76}$ [36], which shares the same cage isomer and charge transfer, though showing some similarity to that of the $Th@C_1(17418)-C_{76}$, only exhibits one absorption

at 593 nm (Figure 4a). This result shows a notable influence of the actinide metal on the electronic structures of $M@C_1(17418)-C_{76}$ ($M = U, Th$). A similar phenomenon can also be observed in $M@C_1(28324)-C_{80}$ [36] ($M = U, Th$), revealing that the endohedral metal itself also plays a significant role in the electronic structure of the EMFs. On the other hand, the spectrum of $Th@T_d(19151)-C_{76}$ [31] shows different characteristic peaks compared to those of the $Th@C_1(17418)-C_{76}$ (Figure 4b). This agrees with the crystallographic results that the $Th@C_{76}$ identified in this work is a novel isomer. To delve deeper into the electronic structure of $Th@C_1(17418)-C_{76}$, we conducted electrochemical tests on the compound. The cyclic voltammogram of $Th@C_1(17418)-C_{76}$ presents two oxidation peaks and three reduction peaks. However, the cyclic voltammogram of $U@C_1(17418)-C_{76}$ only presents one oxidation peak and three reduction peaks [36]. In addition, compared to the first oxidation potential of $U@C_1(17418)-C_{76}$ (0.14 V), the first oxidation potential of $Th@C_1(17418)-C_{76}$ (0.37 V) shows a significant positive shift. This result shows the notable influence of the actinide metal on the electronic structures of $M@C_1(17418)-C_{76}$ ($M = U, Th$).

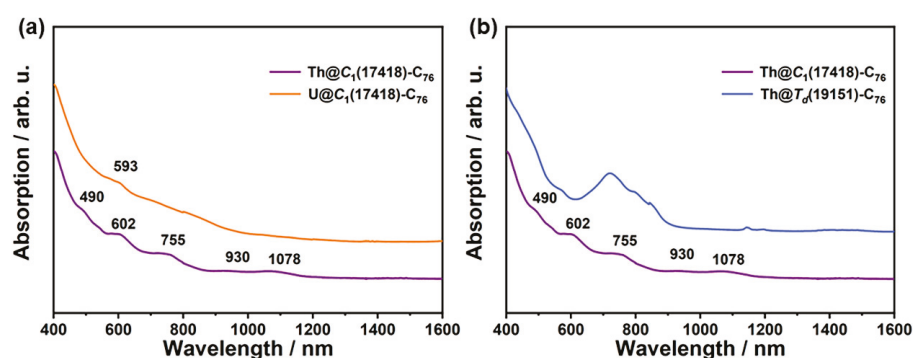


Figure 4. UV-vis-NIR absorption spectra of $Th@C_1(17418)-C_{76}$ and (a) $U@C_1(17418)-C_{76}$ and (b) $Th@T_d(19151)-C_{76}$ in CS_2 .

$Th@C_1(17418)-C_{76}$ was also characterized using low-energy Raman spectroscopy, as shown in Figure 5. Sharp peaks at 149, 218, and 479 cm^{-1} are observed for the Raman spectrum of $Th@C_1(17418)-C_{76}$. Similar frequencies also can be observed in $Th@D_{5h}(6)-C_{80}$ [32] (150 and 219 cm^{-1}), $Th@C_{2v}(9)-C_{82}$ (151 and 216 cm^{-1}), and $Th@C_2(5)-C_{82}$ [33] (152 and 215 cm^{-1}), indicating that thorium-based mono-EMFs have similar metal–cage interactions. Though the UV-vis-NIR absorption spectra of $Th@C_1(17418)-C_{76}$ differ from those of $U@C_1(17418)-C_{76}$, the vibrational frequencies on the Raman spectrum of $U@C_1(17418)-C_{76}$ are at 153, 219, and 359 cm^{-1} [36], showing notable similarities to those of the $Th@C_1(17418)-C_{76}$. This phenomenon can also be observed in $Th@C_1(28134)-C_{80}$ and $U@C_1(28134)-C_{80}$ [36], which also share the same carbon cage. This may indicate that the cage isomers play a major role on the metal–cage interaction of the corresponding EMFs.

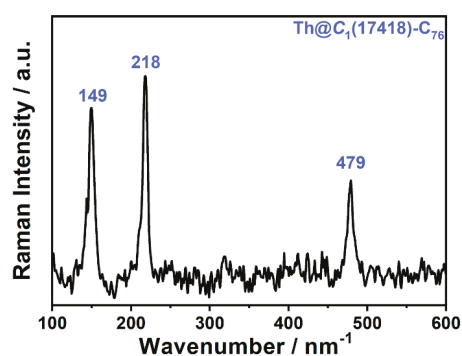


Figure 5. Low-energy Raman spectra of $Th@C_1(17418)-C_{76}$ at 633 nm excitation.

3. Materials and Methods

Materials. The chemicals employed in this research were Th₂O₃ (99.9%, School of Radiation Medicine and Protection of Soochow University, Suzhou, China), CS₂ (99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), toluene (99%, Sinopharm Chemical Reagent Co., Ltd.), hexane ethanol (99%, Sinopharm Chemical Reagent Co., Ltd.), hexane (99%, Sigma Aldrich Co., St. Louis, MO, USA), benzene (99%, Sigma Aldrich Co.), trichloromethane (99%, Sinopharm Chemical Reagent Co., Ltd.), ferrocene (99.8%, Beijing Bailing Wei Technology Co., Ltd., Beijing, China), Octaethylnickel porphyrin (99.8%, Beijing Bailing Wei Technology Co., Ltd.), tetrabutylammonium hexafluorophosphate (electrochemical-grade, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China), 1,2-dichlorobenzene (99%, Shanghai Aladdin Biochemical Technology Co., Ltd.), and graphite rods and graphite powder (Shanghai Fengyi Carbon Co., Shanghai, China).

Synthesis of Th@C₁(17418)-C₇₆. Th@C₁(17418)-C₇₆ was synthesized using the direct-current arc discharge method. ThO₂ powders and graphite powder were mixed in an atomic molar ratio of Th:C = 1:24 (equivalent to a mass ratio of ThO₂:C = 1:1.09). The resulting mixture was then uniformly filled into a hollow graphite rod and compacted to achieve dense packing. The filled graphite rod was placed into a tube furnace and subjected to a 12 h reduction process at 1000 °C under a nitrogen atmosphere, aiming to convert the metal oxide into a metal carbide.

After the reduction process, the compaction graphite rod containing the reduced material was utilized as the anode, while a solid graphite rod served as the cathode within a vacuum arc furnace. The furnace was evacuated to a pressure of 4 Pa and then filled with 200 Torr of helium gas. The distance between the electrodes was maintained at approximately 1 cm, and the current was set to 90 A using an electric welding machine. Plasma evaporation took place during the arc discharge process. The anode was manually rotated with the left hand to achieve the optimal evaporation positioning, while the cathode was rotated with the right hand to push the solid graphite rod towards the consumed mixture graphite rod. When the mixture rod was nearly depleted, the cathode was retracted rapidly to prevent any damage to the metallic target on the anode. Subsequently, the power supply of the electric welding machine was switched off. Once the furnace temperature cooled down to room temperature, air was introduced into the furnace to reach atmospheric pressure. The furnace cover was opened, and the carbon ash accumulated on the furnace wall was collected using tools like a test tube brush. The collected carbon ash was soaked in a solution of carbon disulfide and left to stand for 12 h. Once the first immersion was completed, the obtained carbon ash was immersed twice with the same operation, so that as much of the obtained fullerene sample as possible was extracted. The extraction of fullerene samples needs to be carried out in a glove box with specific filtration devices.

The carbon disulfide solution was separated from the solid carbon residues using a vacuum filtration device equipped with a 0.45 µm organic membrane, resulting in a carbon disulfide filtrate. The carbon disulfide solvent was then evaporated using rotary evaporation until no liquid remained, and an appropriate quantity of toluene solution was added to dissolve the residue. The resulting reddish brown solution underwent another round of filtration to eliminate the solid particles of fullerenes, resulting in a saturated crude extract solution of fullerenes, which could be further utilized for High-Performance Liquid Chromatography (HPLC) separation in subsequent steps.

Isolation of Th@C₁(17418)-C₇₆. The separation and purification of Th@C₁(17418)-C₇₆ was achieved using multi-stage HPLC procedures. The HPLC was performed with toluene as the mobile phase and a UV detector with a detection wavelength of 310 nm. A 10 mL chromatographic injector was used to inject samples of fullerenes dissolved in toluene into a preparative HPLC system for separation. Prior to injection, a disposable syringe filter was employed to filter the fullerene sample, mitigating the interference caused by solid particles during the chromatographic separation. Distinct chromatographic columns were employed for the separation at various stages of the process.

Multiple HPLC columns, including a Buckyprep-M column (25 × 250 mm, Cosmosil, Nacalai Tesque Inc., Kyoto, Japan), a Buckprep column (10 × 250 mm, Cosmosil, Nacalai Tesque, Kyoto, Japan), and a 5PBB column (10 × 250 mm, Cosmosil, Nacalai Tesque, Kyoto, Japan), were utilized in the procedures. The purity of the target fractions was monitored by using MALDI-TOF during the separation process. In our mass spectrometry analysis, numerous signals corresponding to monometallic fullerenes based on thorium (Th), including Th@C₇₆, Th@C₈₀, Th@C₈₂, Th@C₈₄, Th@C₈₆, and Th@C₈₈, were observed. Among them, in particular, the isomer of Th@C₇₆ reported in this study has not been experimentally documented before. Therefore, in subsequent separation steps, our focus was solely on the purification and characterization of Th@C₇₆.

Th@C₁(17418)-C₇₆ was subjected to purification utilizing a four-stage high-performance liquid chromatography (HPLC) process, as shown in Figure S1. Initially, the compound was passed through a Buckyprep-Mcolumn (25 mm × 250 mm, Cosmosil, Nacalai Tesque) at a flow rate of 10 mL/min during the first stage of separation. Subsequently, the fraction eluted between 26 and 27.5 min (indicated by the color blue) was collected and reinjected into the Buckyprep column (10 mm × 250 mm, Cosmosil, Nacalai Tesque) for the second stage of separation, utilizing toluene as the eluent with a flow rate of 4 mL/min. The fraction containing Th@C₁(17418)-C₇₆ was obtained between 46 and 49.5 min (highlighted in red) and isolated accordingly. Moving on to the third stage of the separation, the 5PBB column (10 mm × 250 mm, Cosmosil, Nacalai Tesque) was employed, delivering a flow rate of 4 mL/min. The desired fraction, marked in orange, appeared within the 65 to 73 min range and specifically contained Th@C₁(17418)-C₇₆. Finally, the last stage involved passing the sample through the Buckyprep column (10 mm × 250 mm, Cosmosil, Nacalai Tesque) at a flow rate of 4 mL/min, bringing forth the achievement of pure Th@C₁(17418)-C₇₆. Notably, the confirmation of the extracted Th@C₁(17418)-C₇₆'s purity was impeccably established through the utilization of MALDI-TOF in positively charged mode, as visually exemplified in Figure 1.

Spectroscopic Studies of Th@C₁(17418)-C₇₆. The positive-ion mode matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) (Bruker, Karlsruhe, Germany) was employed for the mass characterization. A rotary evaporator was used to spin dry the fullerene sample under investigation. The substance was dissolved in carbon disulfide and the sample was transferred onto a mass spectrometry target using a pipette. A mass spectrometry analysis proceeded after the solvent evaporated. The purified Th@C₁(17418)-C₇₆ fullerene sample was dissolved in CS₂ and the carbon disulfide solution of the fullerene was transferred into a 2 mL quartz cuvette. A control experiment was prepared by adding blank carbon disulfide to another quartz cuvette. The Cary 5000 UV-vis-NIR spectrophotometer (Agilent, Santa Clara, CA, USA) was used to measure the ultraviolet-visible-near-infrared absorption wavelengths of the sample in the detection range of 400–1600 nm. After completing the measurements, the carbon disulfide solution was collected from the sample in a glass vial and the quartz cuvette was rinsed with clean carbon disulfide solution. The Raman spectra were obtained using a Horiba Lab RAM HR Evolution Raman spectrometer using a laser at 633 nm.

Electrochemical Studies of Th@C₁(17418)-C₇₆. The cyclic voltammetry was performed using a conventional three-electrode system consisting of a glassy carbon electrode as the working electrode, a silver wire as the reference electrode, and a platinum wire as the counter electrode. A 0.05 M (n-Bu)₄NPF₆ solution was prepared by adding ortho-dichlorobenzene to the electrolyte, which contained tetrabutylammonium hexafluorophosphate. Subsequently, the purified sample of monometallic fullerene was dissolved in the solution for a cyclic voltammetry analysis using a CHI-660E electrochemical workstation. The reference material used for calibration was ferrocene, and the scan rate was set at 100 mV/s.

X-ray Crystallographic Study. Single crystals of Th@C₇₆ were obtained, employing a solvent diffusion method characterized in a gradual process. A supersaturated solution of benzene (0.2 mL), encompassing Ni^{II}(OEP) (0.18 mg), was meticulously diffused into

an impeccably concocted carbon disulfide solution (0.1 mL) of Th@C₁(17418)-C₇₆ (0.1 mg). Prior to the crystal growth procedure, the fabricated fullerene sample underwent a comprehensive purification and cleaning step utilizing n-hexane. Filtering and cleaning devices were obtained by using a rubber-tipped dropper. The filter paper was folded to obtain a filter core approximately 1 cm in size, precisely filling the neck of the pipette. The fullerene sample requiring filtration and cleaning was dissolved in carbon disulfide, followed by drying with nitrogen gas. A small amount of hexane was added, and ultrasonication was applied to suspend the fullerene sample in the hexane solution. Using a pipette, the mixture of hexane and fullerene samples was transferred to a prepared filtration pipette, with the rate of filtration controlled at one drop per second. As fullerene samples are insoluble in hexane, they remained on the filter core. The filter core was then rinsed with carbon disulfide, and the cleaning solution was collected, resulting in a fully cleaned fullerene sample.

In explicit detail, the carbon disulfide solution of Th@C₁(17418)-C₇₆ and the benzene solution of Ni^{II}(OEP) were introduced into a precisely maintained 5 mm inner diameter nuclear magnetic resonance (NMR) tube, adhering to an exact volumetric ratio of 1:2. Prior to crystal growth, the NMR tube necessitated a series of sequential cleansing steps. The NMR tube was thoroughly filled with solutions of soap, ethanol, n-hexane, and carbon disulfide in a successive manner. The subsequent cleansing process involved subjecting the NMR tube to ultrasonic irradiation for a duration exceeding 30 min, with three cycles of ultrasonic treatment for each solution. To ensure a meticulously controlled and hermetically sealed environment, the aperture of the NMR tube was securely enclosed using a specialized sealing film. This meticulously prepared assembly was subsequently transferred to a refrigerated environment, maintaining a constant temperature of 4 °C, and left undisturbed, allowing for a designated duration of one month.

After the designated duration, we used an optical microscope to observe the NMR tubes, black prism-shaped crystals, exhibiting a remarkable specular gleam, precipitated within the NMR tube. The meticulous selection of appropriately sized and shaped black prism-shaped crystals was conducted to facilitate a subsequent single-crystal X-ray diffraction analysis. These selected crystals were subjected to thorough testing and characterization employing a cutting-edge single-crystal diffractometer; the model was the Bruker D8 Venture with metaljet. The single-crystal X-ray data of Th@C₁(17418)-C₇₆ were collected at 120 K, respectively, on a diffractometer (APEX II; Bruker Analytik GmbH, Karlsruhe, Germany) equipped with a CCD collector. The multiscan method was used for absorption correction. The structures were solved using direct methods and refined on F² using full-matrix least-squares using the SHELXL2014 crystallographic software packages. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters.

Crystal data for Th@C₁(17418)-C₇₆·[Ni^{II}(OEP)]·2C₆H₆: *Mr* = 1892.47, 0.1 mm × 0.08 mm × 0.06 mm, monoclinic, C2/*c* (No. 15), *a* = 44.778(2) Å, *b* = 14.9844(11) Å, *c* = 25.431(22) Å, $\alpha = 90^\circ$, $\beta = 121.405(3)^\circ$, $\gamma = 90^\circ$, *V* = 14564(22) Å³, *Z* = 8, $\rho_{\text{calcd}} = 1.756 \text{ g cm}^{-3}$, $\mu(\text{Ga K}\alpha) = 6.129 \text{ mm}^{-1}$, $\theta = 2.756\text{--}58.099$, *T* = 120.0 K, *R*₁ = 0.1339, *wR*₂ = 0.2547 for all data; *R*₁ = 0.0901, *wR*₂ = 0.2256 for 10155 reflections (*I* > 2.0σ(*I*)) with 1220 parameters. Goodness-of-fit indicator 1.074. The Maximum residual electron density was 1.429 e Å^{−3}.

4. Conclusions

In conclusion, a novel non-IPR isomer of thorium-based mono-EMFs, the synthesis and characterization of Th@C₁(17418)-C₇₆ were accomplished through mass spectroscopy, single-crystal X-ray diffraction, Raman spectroscopy, and UV-vis-NIR spectroscopy. The crystallographic characterization unambiguously demonstrated that this isomer possesses a pair of adjacent pentagons, sharing the same carbon cage as the one previously reported for U@C₁(17418)-C₇₆. The major metal sites in U@C₁(17418)-C₇₆ and Th@C₁(17418)-C₇₆ are all situated at the intersection of two adjacent pentagons. Currently, the stabilization of the C₁(17418)-C₇₆ cage is only achieved by the encapsulation of U and Th, suggesting

that the unique 5f electrons present in actinide metals enable them to stabilize uncommon carbon cage structures. In addition, despite similarity of their Raman vibrational spectra, the UV-vis-NIR absorption spectra of $\text{U@C}_1(17418)\text{-C}_{76}$ and $\text{Th@C}_1(17418)\text{-C}_{76}$ exhibit notable differences. This work introduces a novel addition to the group of thorium-based mono-EMFs, enhancing the comprehension of the distinctive carbon cage structure, electronic properties, and interactions exhibited by actinium-based EMFs.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/2304-6740/11/11/422/s1>, Figure S1: HPLC isolation procedures of $\text{Th@C}_1(17418)\text{-C}_{76}$ and the pure sample's MALDI-TOF mass spectrum.; Figure S2: Ball and stick representation of disordered Th sites inside $\text{Th@C}_1(17418)\text{-C}_{76}$, five positions (Th1, Th2, Th3, Th4, and Th5) are observed.; Figure S3: Cyclic voltammograms of $\text{Th@C}_1(17418)\text{-C}_{76}$ in *o*-dichlorobenzene.; Table S1: Occupancies of disordered thorium sites in $\text{Th@C}_1(17418)\text{-C}_{76}$.; Table S2: Closest Th-Cage distances (Å) in $\text{Th@C}_1(17418)\text{-C}_{76}$.; Table S3: Crystallographic information of $\text{Th@C}_1(17418)\text{-C}_{76}$.

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Data Availability Statement: The crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre with the CCDC numbers 2295545 via www.ccdc.cam.ac.uk/data_request/cif (accessed on 18 September 2023). The other data are available upon reasonable request from the corresponding authors.

Conflicts of Interest: The authors declare no conflict of interest.

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Article

Reactivity of Open-Shell Metallofullerene Anions: Synthesis, Crystal Structures, and Electrochemical Properties of Benzylated $\text{Gd@C}_{2v}\text{-C}_{82}$

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Abstract: The reactivity of the open-shell $\text{Gd@C}_{2v}\text{-C}_{82}$ with different charge states towards benzyl bromide was investigated. $[\text{Gd@C}_{2v}\text{-C}_{82}]^{3-}$ exhibited enhanced activity relative to $\text{Gd@C}_{2v}\text{-C}_{82}$ and $[\text{Gd@C}_{2v}\text{-C}_{82}]^{-}$. The structural characterizations, including MALDI-TOF MS, UV-vis-NIR, and single crystal X-ray diffraction, indicate the formation of isomeric benzyl monoadducts of $\text{Gd@C}_{2v}\text{-C}_{82}$. All three monoadducts contain 1:1 mirror-symmetric enantiomers. Additionally, the addition of the benzyl group and its specific position result in distinct electrochemical behavior of the products compared to the parent $\text{Gd@C}_{2v}\text{-C}_{82}$. Theoretical studies demonstrate that only $[\text{Gd@C}_{2v}\text{-C}_{82}]^{3-}$ has a HOMO energy level that matches well with the LUMO energy level of the PhCH_2 radical, providing a rationalization for the observed significantly different reactivity.

Keywords: endohedral metallofullerene; open shell; electrosynthesis; fullerene anion; $\text{Gd@C}_{2v}\text{-C}_{82}$

1. Introduction

Endohedral metallofullerenes (EMFs) have garnered substantial attention from scientists due to their exceptional chemical and physical properties [1–9]. Since the discovery of the first solvent-extractable EMF, La@C_{82} [10], there has been a boom in interest in EMFs. According to the electronic structure, EMFs are categorized into two main groups: closed-shell EMFs and open-shell EMFs. Closed-shell EMFs possess completely filled electron shells, meaning that all the molecular orbitals are paired with electrons. Consequently, they exhibit a stable and relatively non-reactive structure. In contrast, open-shell EMFs have partially filled electron shells, resulting in the presence of unpaired electrons in their molecular orbitals. This characteristic makes them more reactive and prone to chemical reactions [11–13]. Nevertheless, compared with closed-shell EMFs, the reaction of open-shell EMFs is relatively less studied.

The physical and chemical properties of open-shell EMFs can be altered by functionalization [11,14–17]. By introducing trifluoromethyl, phenyl, or dichlorophenyl groups into the Er@C_{82} cages, the derived products exhibit distinct photoluminescent properties [18]. Additionally, multi-hydroxylated Pr@C_{82} [19], Gd@C_{82} [20–23], and $\text{Ho}_x\text{@C}_{82}$ [24] show enhanced solubility, rendering them suitable for use in biomedicine as novel biological radical scavengers, radiographic agents, magnetic resonance imaging agents, and “missile” drugs [20].

Gd@C_{2v}-C₈₂, with the inner Gd atom capable of transferring three electrons to the C₈₂ cages, represents a typical open-shell molecule. The electronic states of this system can be described as Gd³⁺@C₈₂³⁻ [25–27]. Gd@C_{2v}-C₈₂ has magnetic properties stemming from the interaction between the spin of the metal atom and the electron spin of the cage [28]. Gd@C_{2v}-C₈₂ has found widespread use in various biomedical applications, including MRI contrast [20,29,30], antitumor therapeutics [31–33], adjuvant therapeutic agents [34,35], metabolic disease modulation [22,36,37], and so forth. Indeed, the diverse range of applications for Gd@C_{2v}-C₈₂ in biomedicine can be attributed to appropriate derivatization. The process of modifying its chemical structure through derivatization allows for tailoring its properties to suit specific biomedical applications, thereby enhancing its effectiveness and versatility in various medical contexts. In addition, the carbon cage encasing the Gd ion serves as a protective barrier, preventing the release of Gd³⁺ and thereby eliminating potential toxicity concerns. Therefore, expanding the variety of Gd@C_{2v}-C₈₂ derivatives holds great significance as it allows for a more comprehensive exploration of their potential properties and applications.

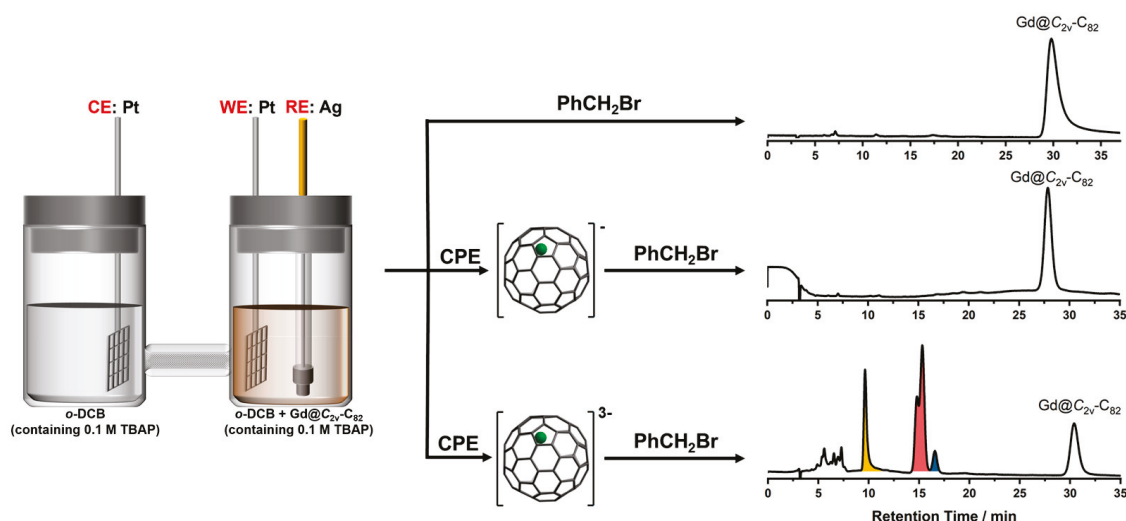
In this work, we utilized the electrochemical method to produce Gd@C_{2v}-C₈₂ anions, which were then subjected to the benzylation reaction. Interestingly, this reaction has been demonstrated to be ineffective for the neutral form of the molecule. The reduction of Gd@C_{2v}-C₈₂ to its trianions resulted in a notable increase in reactivity towards the benzylation reaction. Three benzylated Gd@C_{2v}-C₈₂ isomers (**2a**, **2b**, and **2d**) are isolated and characterized. The structures are confirmed through X-ray single crystal diffraction, revealing that they are monoadducts with a benzyl group attached to the [5,6,6] junction of the C₈₂ cage. In addition, each isomer exists in a mirror-symmetric form. The electrochemical properties of the benzylated Gd@C_{2v}-C₈₂ isomers show distinct characteristics compared to the pristine Gd@C_{2v}-C₈₂. Through density functional theory (DFT) calculations, the reactivity of the Gd@C_{2v}-C₈₂ trianion towards the benzyl group was unveiled.

2. Results and Discussion

Despite Gd@C_{2v}-C₈₂ having an unpaired electron, it does not exhibit reactivity towards benzyl bromide (PhCH₂Br) as shown in Scheme 1. As previously known, Gd@C₈₂ demonstrates its capability as an excellent electron acceptor, with the capacity to accept up to seven electrons [38,39]. Electrochemical reduction can be used to selectively synthesize fullerene anions by controlling the applied potential. To enhance the reactivity, Gd@C_{2v}-C₈₂ was subjected to electrochemical reduction, specifically to its monoanion, using controlled potential electrolysis (CPE). The resulting Gd@C_{2v}-C₈₂ monoanion was then subjected to the benzylation reaction. However, it was observed that the monoanion also shows no reactivity toward PhCH₂Br (Scheme 1), indicating that the nucleophilicity of the Gd@C_{2v}-C₈₂ monoanion is not sufficiently strong to attack the carbon cation (C⁺) of PhCH₂Br. Therefore, additional electrons were added to the Gd@C_{2v}-C₈₂ cage through the CPE process. According to the cyclic voltammogram of Gd@C_{2v}-C₈₂, the second reduction is a simultaneous two-electron transfer process [27,39]; therefore, it is rational to consider the anions obtained via CPE to be trianions. Once the electrogeneration of [Gd@C_{2v}-C₈₂]³⁻ was completed, PhCH₂Br was added to the solution in one portion and stirred for 3 h. High performance liquid chromatography (HPLC) observation confirms the occurrence of the reaction between [Gd@C_{2v}-C₈₂]³⁻ and PhCH₂Br (Scheme 1). It is evident that [Gd@C_{2v}-C₈₂]³⁻ shows enhanced reactivity toward PhCH₂Br.

As observed in Figure 1a, the HPLC results show the synthesis of multiple products through the reaction of [Gd@C_{2v}-C₈₂]³⁻ with PhCH₂Br. To separate and purify the products from the crude mixture, a three-stage HPLC procedure was performed. Initially, the reaction mixtures in toluene were separated using a Buckyprep column to isolate the main fractions 1, 2, and 3 (Figure 1a). Subsequent chromatography employing a Buckyprep column (Figure 1b) and a 5PBB column (Figure 1c) revealed that fraction 2 comprises four compounds: **2a**, **2b**, **2c**, and **2d**. (Figure 1c). Notably, as we only succeeded in getting

single crystal structures of **2a**, **2b**, and **2d**, the subsequent discussion in this study was only focused on these three products. Electrosynthesis has been commonly recognized as an effective strategy for the highly selective synthesis of fullerene derivations. The production of multiple adducts is likely ascribed to the delocalization of charges caused by the low symmetry of the C_{82} cage and the high reactivity of trianionic $Gd@C_{2v}-C_{82}$.



Scheme 1. Benzylation reactions of $Gd@C_{2v}-C_{82}$, $[Gd@C_{2v}-C_{82}]^-$, and $[Gd@C_{2v}-C_{82}]^{3-}$, and the corresponding HPLC profiles of the reaction crude. Conditions: Buckyprep ($\varphi 4.6 \times 250$ mm), toluene, 1 mL/min. (colors indicate the areas of each fraction).

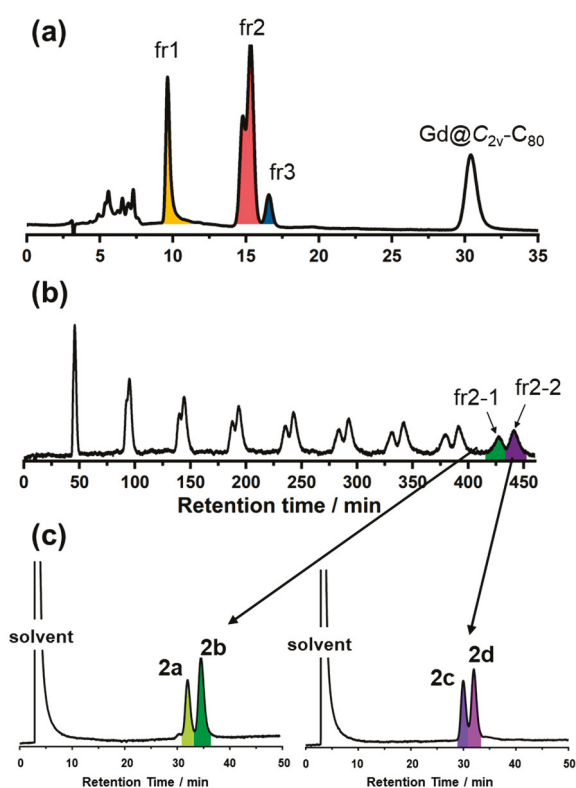


Figure 1. (a) HPLC profile of the reaction mixture (colors indicate the areas of each fraction). Conditions: Buckyprep ($\varphi 4.6 \times 250$ mm), toluene, 1 mL/min. (b) Recycling HPLC profile of fraction 2. Conditions: Buckyprep ($\varphi 20 \times 250$ mm), toluene, 7 mL/min. (c) HPLC profiles of fractions 2-1 and 2-2. Conditions: 5PBB ($\varphi 4.6 \times 250$ mm), toluene, 1 mL/min.

The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry gave preliminary speculation on the structure of the three products (Figure 2). The mass spectra of **2a**, **2b**, and **2d** reveal very similar molecular ion peaks, positioned around $m/z = 1233$. This observation indicates that they are isomers, each featuring a single benzyl group ($\text{CH}_2\text{C}_6\text{H}_5$) attached to the $\text{Gd@C}_{2v}\text{-C}_{82}$ cage, i.e., $\text{Gd@C}_{2v}\text{-C}_{82}(\text{CH}_2\text{C}_6\text{H}_5)$ (theoretical $m/z = 1232.979$). The addition pattern is consistent with that of the reported open-shell EMFs derivatives [12,40–44]. This can be attributed to the paramagnetic behavior of $\text{Gd@C}_{2v}\text{-C}_{82}$, which leads to specific addition patterns of functional groups in its derivatives.

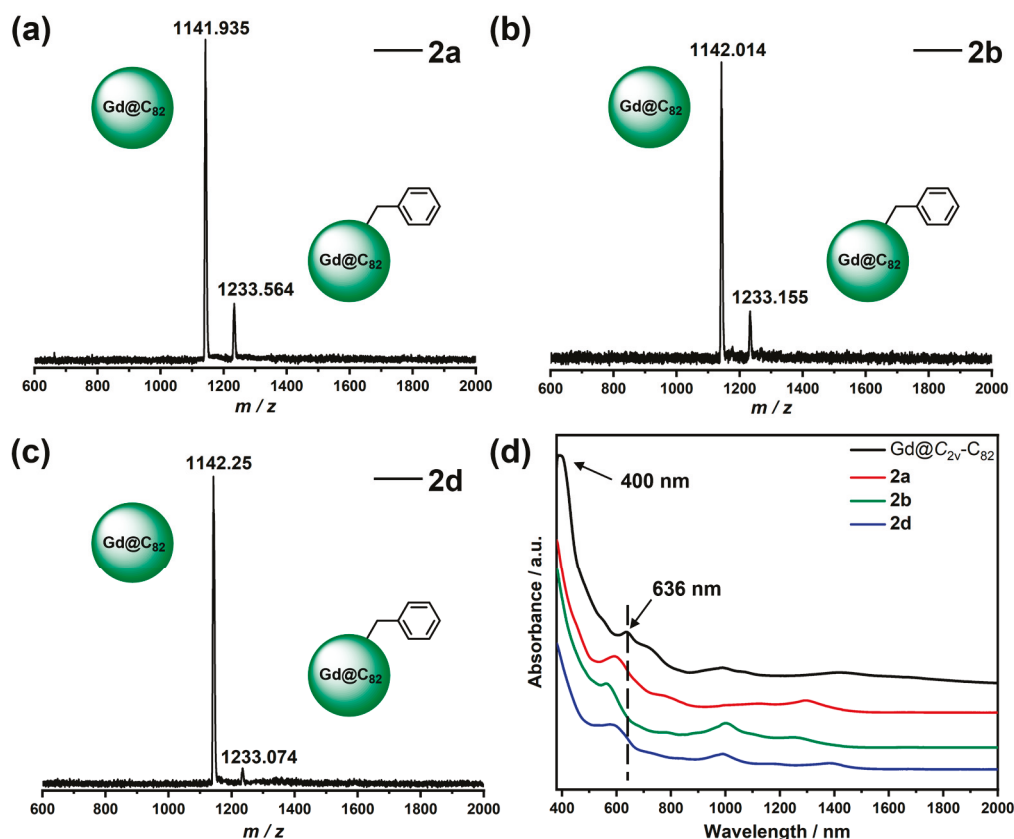


Figure 2. MALDI-TOF mass spectra of **2a** (a), **2b** (b), and **2d** (c) with TPB as the matrix. (d) UV-vis-NIR spectra of **2a**, **2b**, **2d**, and $\text{Gd@C}_{2v}\text{-C}_{82}$ in CS_2 solution.

The optical properties that can provide crucial insights into the electronic structures were studied through the analysis of the UV-vis-NIR absorption spectra. As shown in Figure 2, the UV-vis-NIR spectra of **2a**, **2b**, and **2d** show remarkably different behavior compared to that of the parent $\text{Gd@C}_{2v}\text{-C}_{82}$, which is attributed to the changes in the electronic structure of the cage caused by the addition of the benzyl groups [45]. The characteristic absorption of $\text{Gd@C}_{2v}\text{-C}_{82}$ at $\lambda = 636$ nm undergoes a blue shift upon the addition of the benzyl groups, which can be explained by the reduction of the π -conjugated region in the molecule [44]. The characteristic band of Gd@C_{82} at 400 nm disappears in all benzyl adducts, which is ascribed to the quenching of unpaired electrons by the odd number of benzyl groups on the Gd@C_{82} cage. A similar phenomenon was observed in the absorption of Gd@C_{82} morpholine derivatives [44].

Single crystal X-ray diffraction measurement is widely accepted as the most reliable technique for analyzing the structure of isomers [46–49]. It provides solid evidence for the structure confirmation of **2a**, **2b**, and **2d**. We made efforts to obtain single crystals for all the products, unfortunately, only products **2a**, **2b**, and **2d** were successfully crystallized. Figure 3 displays the single crystal structures of the three isomers, namely, **2a**, **2b**, and **2d**.

Notably, **2a** and **2b** were co-crystallized with decapyrrylcorannulene (DPC) molecules [50]. The DPC molecules were found to form a V-shaped structure when combined with **2a** and **2b**, with the angle between the DPC molecules being 64.9° and 64.8° , respectively. The arrangement of these two molecules is very similar to other reported structures [51–54]. In **2a**·2DPC, the distances between the centroid of the C_{82} cage and the central five-membered rings of DPC molecules are 7.361 Å and 7.394 Å, while they are 7.439 Å and 7.474 Å in **2b**·2DPC. From there, it can be deduced that the distance between the carbon cage and the DPC is approximately 2.8–3.2 Å, indicating the presence of π - π interactions between the carbon cage and DPC molecules. These π - π interactions play a significant role in stabilizing the co-crystallized structure of **2a** and **2b** with DPC molecules. All three crystals feature a monoclinic $P2_1/c$ space group. The carbon cages and embedded Gd atoms (in cyan color) display varying degrees of disorder. An interesting observation is that, irrespective of the location of the benzyl addition, the Gd atoms with major occupancy are consistently found underneath a hexagonal ring along the C_2 axis of the C_{2v} - C_{82} cage (marked in orange in Figure 3). And, the distances between Gd and the adjacent carbon atoms, ranging from 1.9 Å to 2.4 Å, indicate a strong interaction between the endohedral Gd and the outer C_{2v} - C_{82} cage.

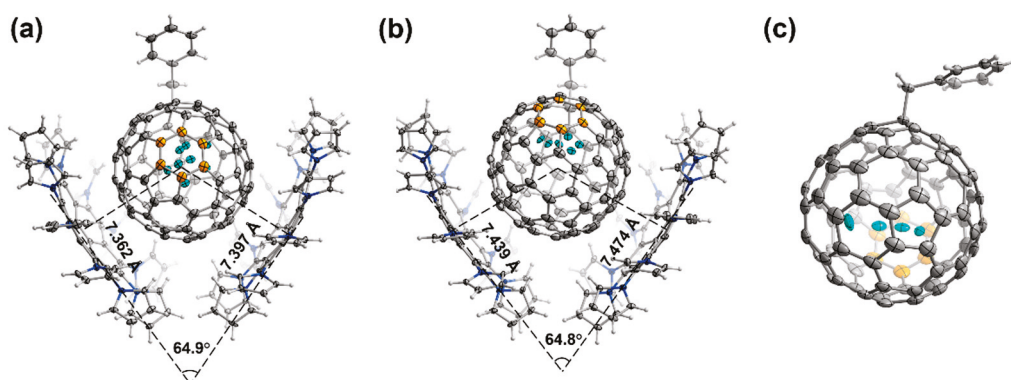


Figure 3. Single crystal structures of **2a**·2DPC (a), **2b**·2DPC (b), and **2d** (c) with thermal ellipsoids set at the 20% probability level. The solvent molecules are omitted and only one cage orientation is shown.

As depicted in Figure 3, the benzyl group was added in the form of a single bond at the [5,6,6]-ring junction of the C_{2v} - C_{82} cage. Despite the addition, the C_{2v} symmetry of the cage is preserved, indicating that the attachment of the benzyl group did not disrupt the overall symmetry of the molecule (Figure 4). Interestingly, all three crystal structures of **2a**, **2b**, and **2d** contain mirror-symmetric enantiomers, suggesting that each compound exists in a pair of structures that are mirror images of each other. To gain a better understanding of the addition sites and the arrangement of the benzyl groups in each enantiomer, a Schlegel diagram of the C_{2v} - C_{82} cage was mapped. In this diagram, the addition sites of the benzyl groups in each enantiomer are marked (1–2 for **2a**, 3–4 for **2b**, and 5–6 for **2d**) (Figure 4a), providing valuable insights into the spatial orientation and symmetry of the derivatives. It can be observed that the addition sites in structures that are mutually enantiomeric are mirror-symmetric. The denoted sites 1 and 2 refer to cage 1 and cage 2 of **2a**, sites 3 and 4 refer to cage 1 and cage 2 of **2b**, and sites 5 and 6 refer to cage 1 and cage 2 of **2d**. Figure 4b displays the mirror-symmetric enantiomers for **2a**, **2b**, and **2d**. For every isomer, there is an identical structure that is a mirror image of the original isomer. Owing to the existence of the C_2 axis, the addition sites labeled as 1' to 6' on the cage are equivalent to the corresponding sites of 1 to 6.

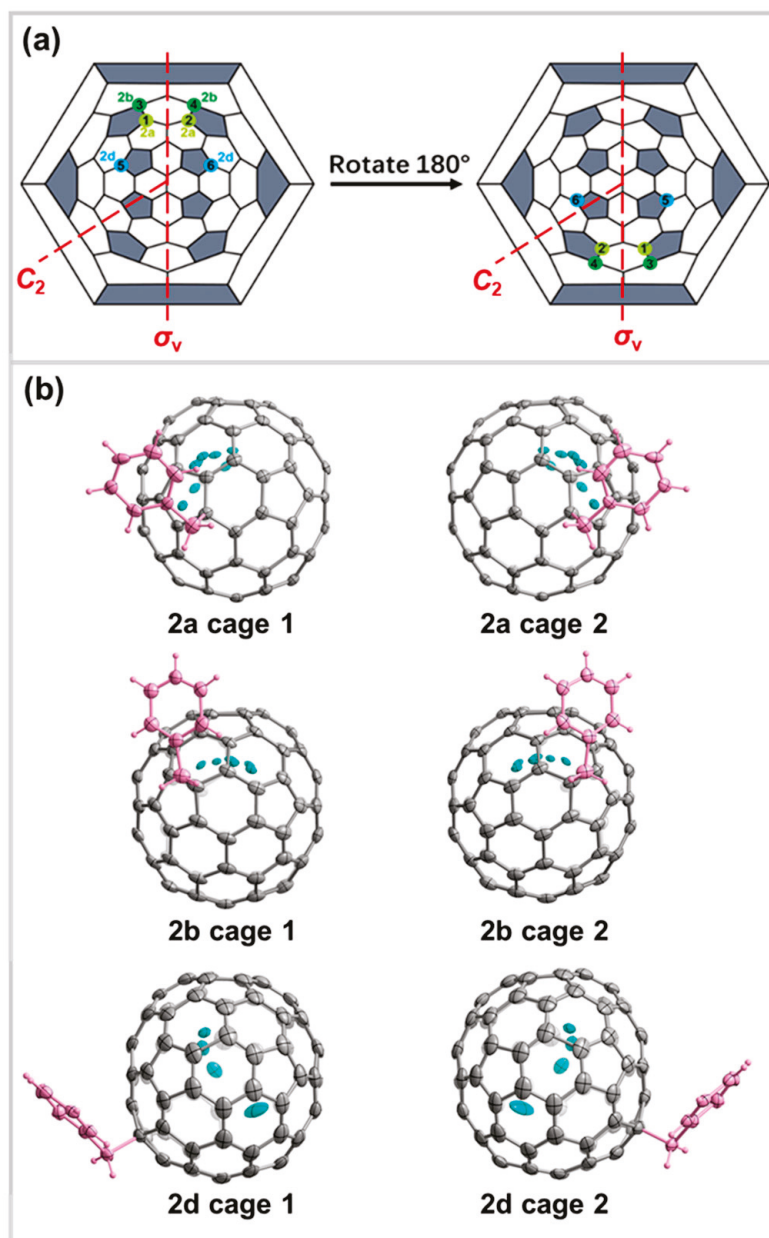


Figure 4. (a) Schlegel diagram showing the addition sites of **2a**, **2b**, and **2d**. (b) Structures of enantiomers of **2a**, **2b**, and **2d** with 20% thermal probability. Internal disordered sites of gadolinium atoms were also shown. Benzyl groups are labeled in pink. The co-crystallization and solvent molecules were omitted for clarity.

The crystal packing and molecular organization for each isomer were studied. As shown in Figure 5, the smallest asymmetric unit for the three products consists of four fullerene cages. Furthermore, **2a** and **2b** are arranged in a head-to-tail mode with DPC molecules along the *b*-axis. Additionally, the DPC molecules adopt an S-shape configuration along the *c*-axis. The distances between the two back-to-back DPC molecules are in the range of 3.4–3.8 Å, indicating the existence of π - π interactions. These interactions lead to favorable π -electron overlap and stabilize the crystal packing. The crystal structure of **2d** without DPC co-crystallization reveals the formation of a one-dimensional zigzag supramolecular chain along the *b*-axis. The detailed crystallographic data for these compounds can be found in the experimental section.

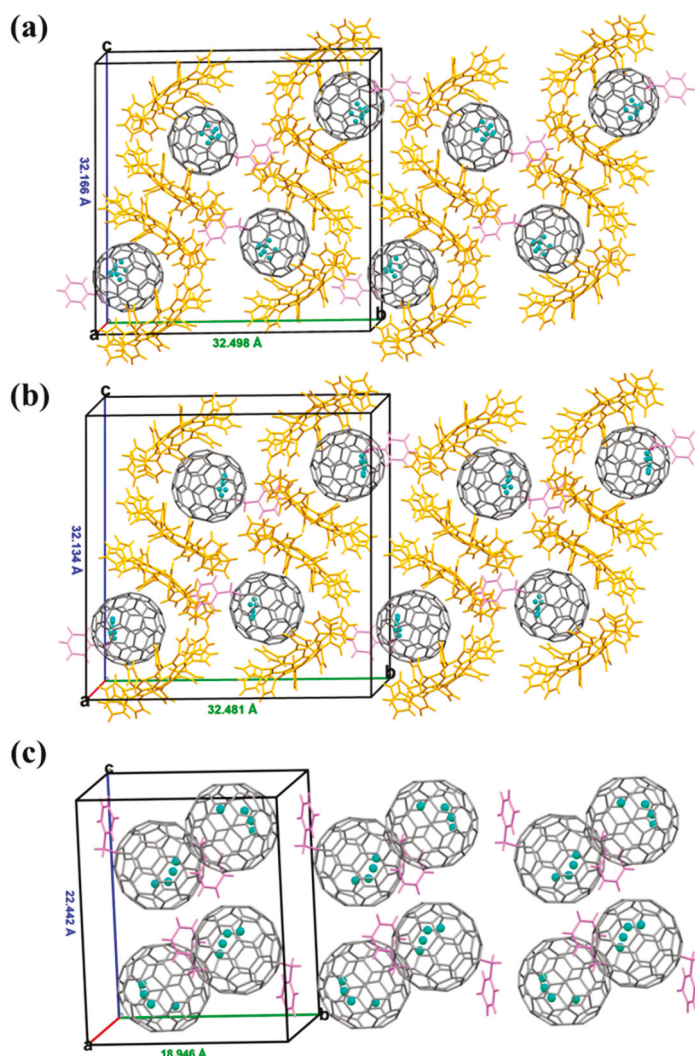


Figure 5. The packing structures of (a) **2a**·2DPC, (b) **2b**·2DPC, and (c) **2d**. The solvent molecules are omitted and only one cage orientation is shown.

The addition of functional groups on the fullerene cages can greatly alter the electrochemical properties of the compounds. Cyclic voltammetry (CV) measurements were conducted for each isomer and compared with the CV curves of the pristine $\text{Gd@C}_{2v}\text{-C}_{82}$ [27]. As reported in the literature, the pristine $\text{Gd@C}_{2v}\text{-C}_{82}$ shows three pairs of reversible redox peaks and two irreversible redox processes in its CV curves, and the second and the fourth reduction are two-electron processes [27]. However, the addition of the benzyl group to form isomers **2a**, **2b**, and **2d** has led to changes in the electrochemical characteristics of the compounds. Moreover, the addition position of the benzyl group was found to have effects on the electrochemical behavior [46,55]. As illustrated in Figure 6, the CV curves of **2a**, **2b**, and **2d** exhibit more redox signals compared with the pristine $\text{Gd@C}_{2v}\text{-C}_{82}$, suggesting the presence of distinct electron transfer processes, which is attributed to the addition of the benzyl group and its influence on the electronic structure of $\text{Gd@C}_{2v}\text{-C}_{82}$. In the case of **2a**, the CV curves display irreversible cathodic electrochemical behavior, with peak potential (E_{pc}) values observed at -0.97 , -1.51 , -1.66 , -1.93 , and -2.39 V vs. Fc/Fc^+ (Table 1). On the other hand, **2a** also shows one quasi-reversible oxidation peak with an E_{pa} value of $+0.14$ V vs. Fc/Fc^+ and two irreversible oxidations with E_{pa} values of $+0.74$ and $+1.03$ V vs. Fc/Fc^+ . For compound **2b**, there are three quasi-reversible reductions with E_{pc} values of -1.06 , -1.89 , and -2.11 V vs. Fc/Fc^+ , while the second reduction is found to be irreversible, with an E_{pc} value of -1.58 V vs. Fc/Fc^+ . The electrochemically anodic behavior of **2b** exhibits irreversible characteristics. CV measurements

for **2d** show two irreversible reductions with E_{pc} values of -0.86 and -1.52 V vs. Fc/Fc^+ and two quasi-reversible reductions with E_{pc} values of -1.77 and -2.04 V vs. Fc/Fc^+ . Moreover, compound **2d** exhibits electrochemically irreversible anodic behavior, which is similar to the behavior observed for **2d**. The distinct electrochemical characteristics of **2a**, **2b**, and **2d** may be attributed to the specific addition position of the benzyl group and its influence on the electronic structure of the $Gd@C_{2v}-C_{82}$ cage. In addition, compared to the redox behavior of $Gd@C_{2v}-C_{82}$, the first reduction potentials of **2a**, **2b**, and **2d** show negative shifts, and the first oxidation potentials show positive shifts, which indicates a decrease in electron-donating/accepting properties after modification with the benzyl group. The enlarged electrochemical gaps in the derivatives **2a**, **2b**, and **2d** demonstrate the enhanced stability of the derivatives relative to the parent $Gd@C_{2v}-C_{82}$. The redox potentials for $Gd@C_{2v}-C_{82}$ and its benzylated products are summarized in Table 1.

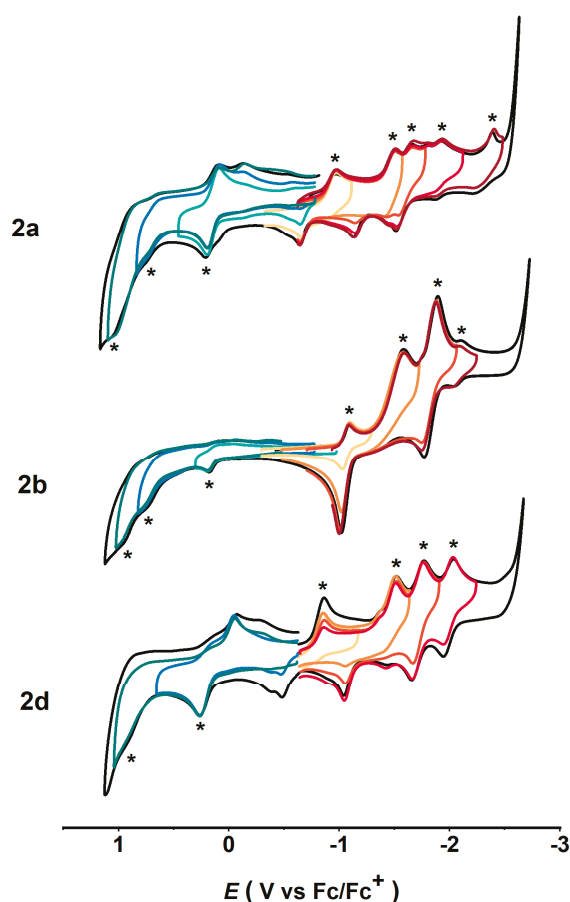


Figure 6. Cyclic voltammograms of **2a**, **2b**, and **2d** recorded in a 0.05 M solution of TBAPF₆ in *o*-DCB at a scan rate of 100 mV s^{−1}. (The redox processes are labeled with a star and each process is indicated in different colors).

Table 1. Redox potentials (V vs. Fc/Fc^+) of $Gd@C_{2v}-C_{82}$ and **2a**, **2b**, and **2d**.

	$E^{2+/3+}$	$E^{+/2+}$	$E^{0/+}$	$E^{0/-}$	$E^{-/2-}$	$E^{2-/3-}$	$E^{3-/4-}$	$E^{4-/5-}$	E_{gap}
$Gd@C_{2v}-C_{82}$ ^a		+1.08 ^b	+0.09 ^c	−0.39 ^c	−1.38 ^{c,d}		−2.22 ^{b,d}		0.48
2a	+1.03 ^b	+0.74 ^b	+0.14 ^c	−0.97 ^b	−1.51 ^b	−1.66 ^b	−1.93 ^b	−2.39 ^b	1.11
2b	+0.94 ^b	+0.73 ^b	+0.19 ^b	−1.06 ^c	−1.58 ^b	−1.89 ^c	−2.11 ^c		1.25
2d		+0.94 ^b	+0.26 ^b	−0.86 ^b	−1.52 ^b	−1.77 ^c	−2.04 ^c		1.12

^a From reference [21]; ^b peak potentials; ^c quasi-reversible process; and ^d two-electron process.

Density functional theory calculations at the M06-2X/6-31G*~SDD level were then carried out to disclose the underlying reactivity of Gd@C_{2v}-C₈₂ and its anions. Figure 7 illustrates the optimized structures of **2a**, **2b**, and **2d**, which are consistent with the corresponding single crystal structures. For pristine Gd@C_{2v}-C₈₂, it is well known that it has an unpaired electron distributed on the outer cage due to the 3e[−] transfer from the internal metal to the cage. However, our calculations with different spin multiplicities reveal that all three monoadducts have the octet ground state completely stemming from the Gd-4f⁷ electron configuration of their internal Gd³⁺ cation (Table 2). Clearly, the unpaired electron (spin) on the outer cage of Gd@C_{2v}-C₈₂ has been effectively quenched as a result of the formation of a single bond with the benzyl group, which thus leads to the excellent stability of the adducts.

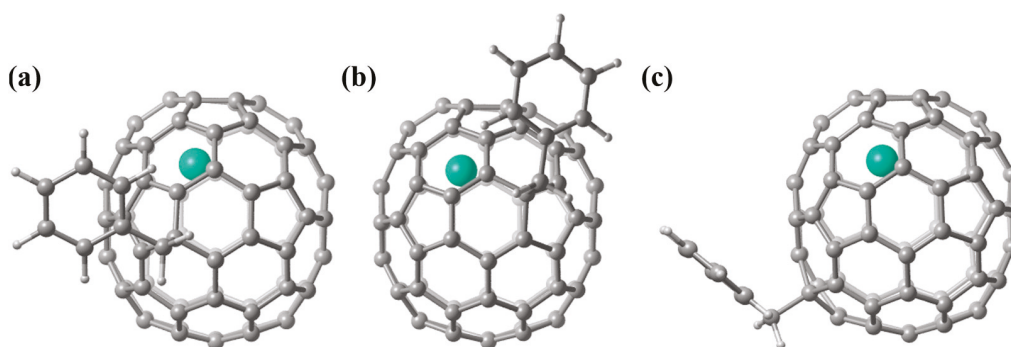


Figure 7. Optimized structures of (a) **2a**, (b) **2b**, and (c) **2d**.

Table 2. Relative energies (kcal/mol) of **2a**, **2b**, and **2d** as well as [Gd@C_{2v}-C₈₂][−] and [Gd@C_{2v}-C₈₂]^{3−} with different spin multiplicities (*M*).

<i>M</i>	6	8	10
2a	21.0	0.0	20.9
2b	17.0	6.8	14.9
2d	22.1	1.8	22.2
[Gd@C _{2v} -C ₈₂] [−]	58.3	0.0	17.8
[Gd@C _{2v} -C ₈₂] ^{3−}	0.0	18.3	26.7

In addition, the reactivity of different charged forms of Gd@C_{2v}-C₈₂ was elaborated through DFT simulations. Figure 8 shows the calculated energy levels of frontier molecular orbitals of Gd@C_{2v}-C₈₂ with various charge states (0, −1, −3). Consistent with our experimental findings, only [Gd@C_{2v}-C₈₂]^{3−} demonstrates HOMO (highest occupied molecular orbital) energy levels that are comparable to the LUMO (lowest unoccupied molecular orbital) of PhCH₂ radical, thus enhancing the orbital interactions and charge transfer during the addition reaction. Through the process of electrochemical reduction, the orbital energy levels of Gd@C_{2v}-C₈₂ are greatly elevated, resulting in a significant improvement in its reactivity.

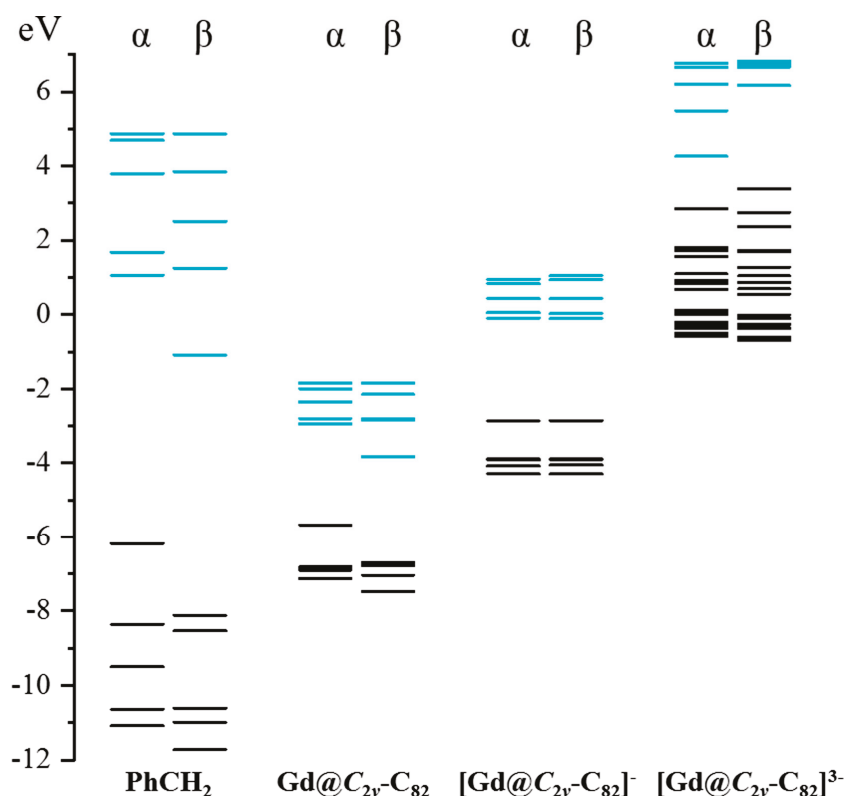


Figure 8. Frontier molecular orbital energy levels of PhCH_2 radical and $\text{Gd@C}_{2v}\text{-C}_{82}$ in different charge states (occupied: black; unoccupied: cyan).

3. Materials and Methods

$\text{Gd@C}_{2v}\text{-C}_{82}$ was purchased from Xiamen Funano New Material Technology Company LTD, Xiamen, China. PhCH_2Br , anhydrous *o*-DCB, 1,1,4,4-Tetraphenyl-1,3-butadiene (TPB), toluene, CDCl_3 , and CS_2 were purchased from Aladdin and used as received. Tetra-butylammonium perchlorate (TBAP) and Tetra-*n*-butylammonium hexafluorophosphate (TBAPF_6) were recrystallized from absolute ethanol and dried under vacuum before use. The purity of the products was verified by HPLC (LaboACE LC-5060, Japan Analytical Industry Co., Ltd., Tokyo, Japan) equipped with Buckyprep and 5PBB columns, with toluene used as the eluent. UV-vis-NIR spectra were recorded using a SHIMADZU UV-3600 spectrophotometer (Shimadzu Corporation, Kyoto, Japan). MALDI-TOF MS measurements were conducted using a Bruker autoex speed mass spectrometer. CV studies were conducted in a solution of *o*-DCB containing 0.05 M TBAPF_6 in a one-compartment cell connected to a CHI 760E workstation, Shanghai, China. A 2 mm diameter glassy carbon disk, a Pt wire, and a Ag wire were used as the working, counter, and pseudoreference electrodes, respectively. Ferrocene (Fc) was introduced into the solution at the end of each experiment as an internal standard. All reactions were carried out inside a glove box under Ar protection.

3.1. Synthesis of **2a**, **2b**, and **2d**

A 2 mg (1.75 mmol) sample of $\text{Gd@C}_{2v}\text{-C}_{82}$ was electrochemically reduced at -1.36 V versus a silver wire reference electrode in 8 mL of *o*-DCB containing 0.1 M TBAP as the supporting electrolyte under an argon atmosphere. The potentiostat was turned off once the electrogeneration of $[\text{Gd@C}_{2v}\text{-C}_{82}]^{3-}$ was completed. Subsequently, 100 equivalents of PhCH_2Br (21.5 μL) were added into the solution in one portion under stirring. The reaction was allowed to proceed for 2 h with stirring, and, finally, it was electrochemically oxidized at a potential of 0 V. The solvent was evaporated under a vacuum, and the crude was washed with plenty of methanol to remove the unreacted PhCH_2Br and the

supporting electrolyte. The slurry was separated by filtration. The residue was dried at 70 °C under a vacuum and dissolved in toluene. The soluble fraction was then purified by HPLC using Buckyprep and 5PBB columns.

3.2. Single Crystal X-ray Crystallography

The single crystals of **2a** and **2b** were obtained by co-crystallization with DPC molecules. In a 5.0 mL centrifuge tube, 0.5 mg of **2a** was dissolved in 0.5 mL of carbon disulfide. Then, a toluene solution containing DPC was added to the tube, with a molar ratio of DPC to fullerene in the mixed solution being 2:1. After around three weeks, black sheet-like crystals were formed. A crystal of 0.4 mm × 0.25 mm × 0.03 mm dimension was mounted in the 100 K nitrogen cold stream on an XtaLAB PRO MM007HF diffractometer with Cu-K α radiation ($\lambda = 1.5406$ Å). The CrystalClear software package (Rigaku) was used for data collection, cell refinement, and data reduction. The crystal structures were solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXLTL software package. All the non-hydrogen atoms were refined anisotropically, and the positions of the hydrogen atoms were generated geometrically.

Crystal data of **2a**·**2DPC**: C₂₁₆H₉₅Gd_{0.88}N₂₀, $M_w = 3108.89$ amu, monoclinic, $P2_1/C$, $a = 14.6998$ (1) Å, $b = 32.4984$ (3) Å, $c = 32.1664$ (3) Å, $\alpha = 90^\circ$, $\beta = 102.071$ (1)°, $\gamma = 90^\circ$, $V = 15,026.8$ (2) Å³, $T = 100$ K, $Z = 4$, R indices (all data) $R_1 = 0.0896$ (23,666), $wR_2 = 0.2647$ (29,671), GOF = 1.054.

Black sheet-like crystals of **2b** were obtained through the same procedures as for **2a**. Crystallographic characterization of a piece of co-crystal (0.12 mm × 0.1 mm × 0.08 mm) was performed at 100 K by using synchrotron radiation (0.65250 Å) with a MarCCD detector at the beamline BL17B station of Shanghai Synchrotron Radiation Facility.

Crystal data of **2b**·**2DPC**: C₂₁₆H₉₅Gd_{0.87}N₂₀, $M_w = 3106.92$ amu, monoclinic, $P2_1/C$, $a = 14.6857$ (4) Å, $b = 32.4812$ (11) Å, $c = 32.1342$ (9) Å, $\alpha = 90^\circ$, $\beta = 101.791$ (1)°, $\gamma = 90^\circ$, $V = 15,004.9$ (8) Å³, $T = 100$ K, $Z = 4$, R indices (all data) $R_1 = 0.1054$ (20,309), $wR_2 = 0.3207$ (29,611), GOF = 1.052.

The crystal of **2d** was grown through solvent diffusion in which a near-saturated carbon disulfide solution was injected into the glass tube followed by slow injections of hexane, and the fullerene solution was layered at a height of about 5 cm. At this point, a clear delamination between hexane and carbon disulfide solution appears, creating a diffusion interface that provides favorable conditions for crystal growth. The tube is closed with a cap and left at a low temperature for several weeks until the solvent diffusion is complete and several crystals are attached to the tube walls. The crystal of **2d** (0.1 mm × 0.08 mm × 0.06 mm) was tested using the same instruments and methods as **2b**.

Crystal data of **2d**: C₈₇H₇Gd_{0.91}, $M_w = 1233.20$ amu, monoclinic, $P2_1/C$, $a = 10.891$ (2) Å, $b = 18.946$ (4) Å, $c = 22.442$ (5) Å, $\alpha = 90^\circ$, $\beta = 96.45$ (3)°, $\gamma = 90^\circ$, $V = 4601.4$ (16) Å³, $T = 100$ K, $Z = 4$, R indices (all data) $R_1 = 0.1409$ (6211), $wR_2 = 0.3370$ (8277), GOF = 1.069.

The supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre with CCDC numbers 2281483, 2283118, and 2283119 via www.ccdc.cam.ac.uk/data_request/cif (accessed on 1 July 2023).

3.3. Computational Details

The calculations were carried out at the DFT level with the M06-2X [56] function, the 6-31G* all-electron basis set of C and H atoms, the SDD basis set, and the corresponding effective core potentials of Gd [57–59]. All the above DFT calculations were performed using the Gaussian 09 software package [60]. The results were visualized with CYLview [61] and VMD [62] software.

4. Conclusions

In summary, this study presents the first successful synthesis of open-shell Gd@C_{2v}-C₈₂ benzyl monoadducts using the electrochemical synthesis method. Three Gd@C_{2v}-

C₈₂(PhCH₂) isomers (**2a**, **2b**, and **2d**) were synthesized, isolated, and characterized. The crystal structures revealed that the benzyl group is attached to the [5,6,6] junction of the cage through a single bond and each isomer contains a mirror-symmetric enantiomer. The addition of the benzyl group and its specific position have notable effects on the electrochemical behavior. DFT calculations reveal that [Gd@C_{2v}-C₈₂]^{3−} has a HOMO energy level that aligns effectively with the LUMO energy levels of the PhCH₂ radical, rationalizing the higher reactivity towards benzyl. The electrochemical method shows great potential in regulating the chemical reactivity of fullerenes, opening up possibilities for creating a wide range of new fullerene products.

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Article

TmCN@C₈₂: Monometallic Clusterfullerene Encapsulating a Tm³⁺ Ion

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Abstract: Metal cyanide clusterfullerenes (CYCFs) are formed via the encapsulation of a single metal atom and a cyanide unit inside fullerene cages, endowing them with excellent properties in various applications. In this work, we report the synthesis, isolation, and characterizations of the first cases of thulium (Tm)-based CYCFs with the popular C₈₂ carbon cages. The structural elucidation of the two TmCN@C₈₂ isomers was achieved via diverse analytical techniques, including mass spectrometry, Vis-NIR spectroscopy, single-crystal X-ray crystallography, and cyclic voltammetry. The crystallographic analyses unambiguously confirmed the molecular structures of the two TmCN@C₈₂ isomers as TmCN@C_s(6)-C₈₂ and TmCN@C_{2v}(9)-C₈₂. Both TmCN clusters adopt a well-established triangular configuration, with the Tm ion located on the symmetrical plane of the carbon cages. The electronic structures of both TmCN@C₈₂ isomers adopt a Tm³⁺(CN)[−]@(C₈₂)^{2−} configuration, exhibiting characteristic spectral and electrochemical properties reminiscent of divalent endohedral metallofullerenes (EMFs). Intriguingly, unlike the divalent Tm²⁺ ion observed in the mono-metallofullerenes Tm@C_{2n}, a higher oxidation state of Tm³⁺ is identified in the monometallic TmCN cluster due to bonding with the cyanide anion. This result provides valuable insight into the essential role of the non-metallic endo-units in governing the oxidation state of the metal ion and the electronic behaviors of EMFs.

Keywords: endohedral metallofullerenes; cyanide clusterfullerenes; thulium; X-ray crystallography

1. Introduction

Fullerene is an allotropic carbon with a great number of family members differentiated by the number of carbon atoms and structural isomerism [1]. A pristine fullerene comprises 12 pentagons and several hexagons according to the number of carbon atoms, forming a cage-like structure with a hollow cavity. Based on the unique structures of fullerenes, three strategies, including exohedral [2–4], cage skeletal [5–7], and endohedral [8–10] modifications, have been widely employed for the chemical functionalization of fullerenes. In particular, the hollow cavity can serve as a nanoscale container to encapsulate various metal atoms or metal clusters, resulting in the formation of endohedral metallofullerenes (EMFs), which have attracted significant interest due to their unique structures and excellent physical and chemical properties, which are different from those of empty fullerenes, in versatile research fields [11–13].

The exploration of EMFs began with the discovery of La@C₆₀ in 1985 [14], which sparked a surge of enthusiasm among researchers in understanding the structures, properties, and potential applications of EMFs. Over the past three decades, remarkable progress has been made, particularly with the identification of the first clusterfullerene, Sc₃N@C₈₀, in 1999, which opened doors to the encapsulation of various cluster species [15]. Subsequently, clusterfullerenes have developed dramatically as the most important branch

of EMFs, with various clusters, such as metal nitride [15–17], carbide [18–21], oxide [22–25], sulfide [26–29], and cyanide [30–39]. Among them, metal cyanide clusterfullerenes (CYCFs), which feature a distinctive mono-metallic cluster with flexible configurations, provide ideal models for regulating properties in applications such as single-molecule magnets [30,32].

To date, a wide range of CYCFs have been successfully synthesized and characterized [30–39], including MCN@C₇₆ (M = Y [30], Tb [30], Lu [35]) and MCN@C₈₂ (M = Y [31,38], Tb [32,37], Dy [33], Lu [35], U [34]), and MCN@C₈₄ (M = Y [36,39], Tb [36], and Dy [36]). Notably, the oxidation state of uranium in the UCN cluster remains ambiguous as it can exhibit U(I) or U(III) due to the significant donation bonding from the fullerene cage and CN[−] cluster to uranium [34]. In contrast, cyanide clusters based on yttrium (Y), terbium (Tb), dysprosium (Dy), and lutetium (Lu) uniformly adopt a fixed oxidation state of +3. However, little is known about tunable lanthanide metals with variable oxidation states, such as thulium (Tm), which generally exhibit +2 or +3 oxidation states in fullerenes [40–44]. In addition, compared to the extensively studied rare earth metals, there have been limited reports on Tm-based EMFs, despite their promising applications as fluorescent probes. For example, Shinohara and co-workers demonstrated that the divalent Tm²⁺ in Tm@C₈₈ isomers and trivalent Tm³⁺ in Tm₂C₂@C₈₂ isomers exhibit characteristic photoluminescence at 1200 and 1300–2000 nm, respectively, owing to their distinct energy level transitions [45]. Hence, it is highly desirable to explore novel Tm-based EMFs to gain insights into their bonding, structures, and applications based on their variable oxidation states.

Herein, we report the synthesis, isolation, and characterizations of the first Tm-based EMFs, TmCN@C_s(6)-C₈₂ and TmCN@C_{2v}(9)-C₈₂, which, to the best of our knowledge, represent the first isolated Tm-based CYCFs. These two compounds were characterized well via mass spectrometry, single-crystal X-ray diffraction, visible-near-infrared (Vis-NIR) spectroscopy, and cyclic voltammetry. The crystallographic analysis revealed a triangular configuration of the TmCN cluster within both fullerene cages. The electronic structures of both TmCN@C₈₂ isomers are proposed to exhibit a Tm³⁺(CN)[−]@(C₈₂)^{2−} configuration, displaying characteristic spectral and electrochemical properties reminiscent of divalent EMFs. Notably, a higher oxidation state of Tm³⁺ in the mono-metallic TmCN cluster, in contrast to the divalent Tm²⁺ observed in mono-metallofullerenes Tm@C_{2n}, can be attributed to the presence of the encapsulated cyanide anion.

2. Results and Discussion

Soot containing Tm-based cyanide clusterfullerenes was synthesized utilizing a modified Krätschmer–Huffman direct current (DC) arc discharge method [46]. Briefly, graphite rods were densely packed with graphite powder, Tm₂O₃, and TiO₂, which acts as a catalyst to enhance the yields of the Tm-based cyanide clusterfullerenes. The molar ratio of C/Tm/Ti was maintained at 15/1/1, and the arc-discharge synthesis was performed under a low-vacuum atmosphere with 200 mbar He and 10 mbar N₂. The two targeted TmCN@C₈₂ isomers were extracted from the carbon soot samples using the Soxhlet extraction method, followed by isolation via multiple-stage high-performance liquid chromatography (HPLC). The high purity of the isolated TmCN@C₈₂ isomers was verified by observing a solitary peak in the HPLC chromatograms via an analytical Buckyprep column, as depicted in Figure 1. The inserted mass spectra of the two TmCN@C₈₂ isomers also exhibited a solitary peak at *m/z* = 1179, further confirming their high purity. In addition, the experimental isotopic distributions of the two TmCN@C₈₂ isomers show good agreement with the theoretical predictions.

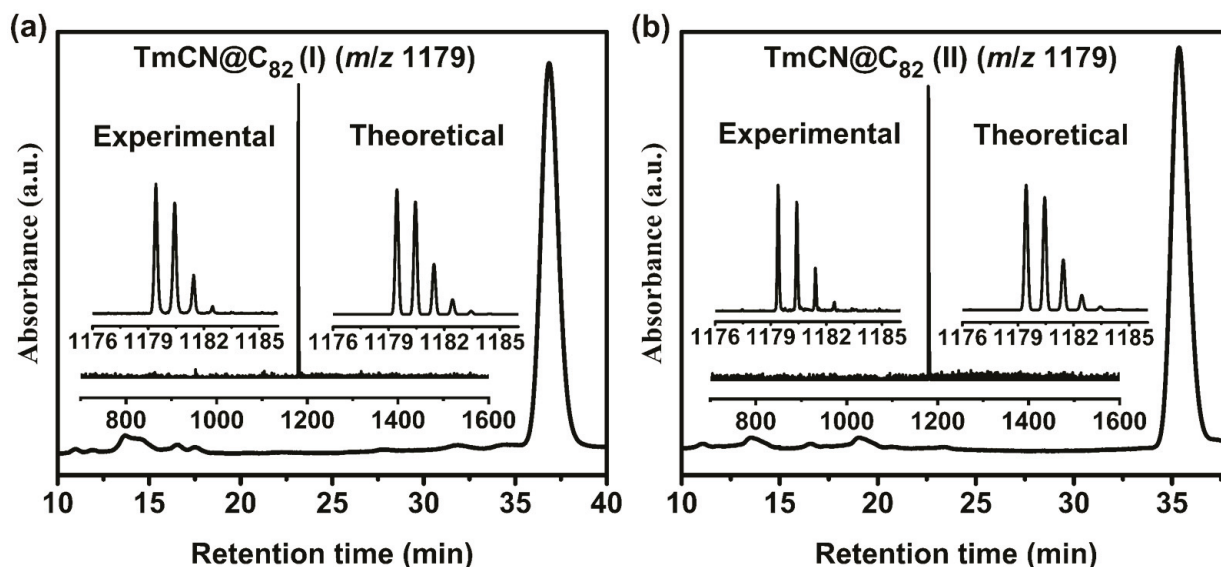


Figure 1. HPLC chromatograms of purified (a) TmCN@C₈₂ (I) and (b) TmCN@C₈₂ (II), obtained using an analytical Buckyprep column with toluene as the eluent and a flow rate of 1 mL/min. The inserts show the mass spectra of two TmCN@C₈₂ isomers with experimental versus theoretical isotopic distributions.

The molecular structures of the TmCN@C₈₂ (I) and TmCN@C₈₂ (II) were precisely characterized as TmCN@C_s(6)-C₈₂ and TmCN@C_{2v}(9)-C₈₂, respectively, via single-crystal X-ray diffraction and through their co-crystallization with decapyrrylcorannulene (DPC) molecules, which enhance the crystallinity of EMFs [47]. Both co-crystals were found to crystallize in P2₁/c, a space group of No. 14, which is commonly seen in the EMF-DPC co-crystallization systems, and the utilization of the low-symmetry primitive lattice for the EMF-DPC co-crystals could effectively circumvent the “crystallographic mirror dilemma” that generally appears in the EMF-Ni^{II}(OEP) co-crystals crystallized in the C2/m space group [48]. As shown in Figure 2a,b, the TmCN@C₈₂ isomers were co-crystallized with two DPC molecules, exhibiting a distinctive V-shaped configuration with a dihedral angle of about 65°. The closest C⋯C distances between both TmCN@C₈₂ isomers and the DPC molecules were measured to be ~3.37 Å; this is close to the interlayer spacing observed in graphite (3.35 Å), suggesting their π - π stacking interactions.

The encapsulated TmCN cluster, with a CN non-metallic unit supported by a mono-metallic Tm ion, adopts a triangular configuration inside both C₈₂ isomers, similar to their analogs MCN@C_s(6)-C₈₂ and MCN@C_{2v}(9)-C₈₂ (M = Y, Tb, Dy, Lu). Due to the larger electronegativity of nitrogen versus carbon, the distance of the Tm-N bond is significantly shorter than that of the Tm-C bond, and the C-N bond lengths fall in the range of typical C-N triple bonds, as shown in Figure 2c,d. The encapsulated Tm ion shows some slight disorder which is probably caused by thermal vibration. The dominant Tm site, with the most significant occupancy, is located over an s-indacene-type hexagon of the carbon cages, exhibiting Tm-cage distances in the range of 2.23–2.49 Å and 2.23–2.68 Å inside the C_s(6)-C₈₂ and C_{2v}(9)-C₈₂ carbon cages, respectively. Interestingly, the dominant Tm location is aligned with the symmetrical plane of both the C_s(6)-C₈₂ and C_{2v}(9)-C₈₂ cages, which is in perfect agreement with the recent finding of the “mirror observation” for mono-metallofullerenes, suggesting that the mono-metallic cyanide clusterfullerenes display some structural characteristics that are similar to those of mono-metallofullerenes [48].

The crystallographic results suggest the preference of the TmCN cluster for encapsulation inside the cages of C_s(6)-C₈₂ and C_{2v}(9)-C₈₂, which can be inferred from our previous work on TbCN@C₈₂ isomers [32]. TbCN@C_{2v}(9)-C₈₂ is the most stable isomer among all TbCN@C₈₂ isomers, followed by TbCN@C_s(6)-C₈₂, which is similar to the relative energy order found for the YCN@C₈₂ isomers. The results reveal that the cage cavity volumes of C_s(6)-C₈₂ and C_{2v}(9)-C₈₂ are suitable for encapsulation of a metal

cyanide cluster; this is in agreement with the theoretical studies on C_{84} isomers [49], which provided insights into the relationship between the stability of an encapsulated endo-unit and the volume of a specific carbon cage.

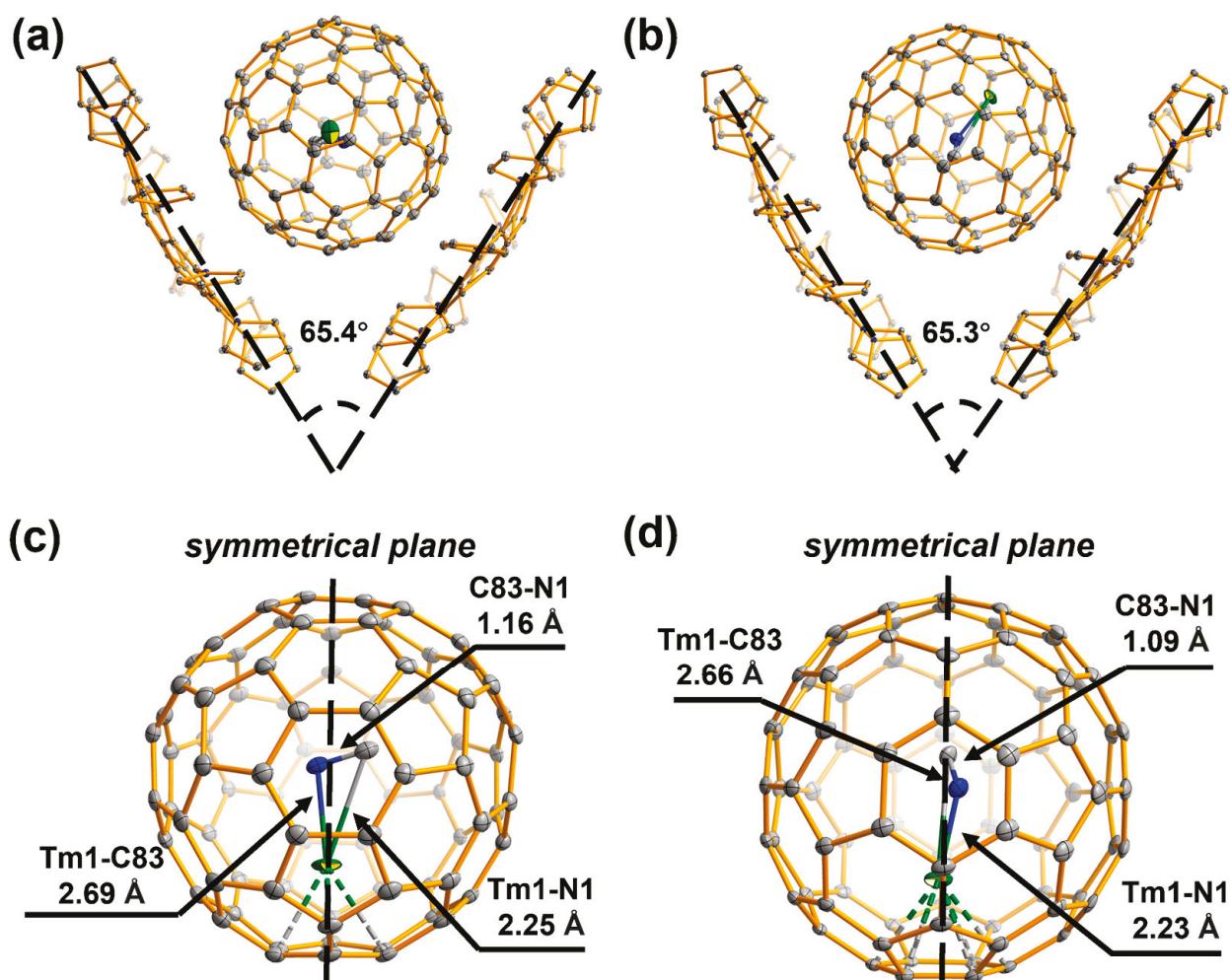


Figure 2. Oak Ridge thermal ellipsoid plot (ORTEP) drawings of crystallographic structures of the two co-crystals. (a,b) The relative orientations between two DPC molecules and (a) $TmCN@C_s(6)-C_{82}$ and (b) $TmCN@C_{2v}(9)-C_{82}$. (c,d) The relative orientations between the encapsulated TmCN cluster with detailed structural information and the (c) $C_s(6)-C_{82}$ and (d) $C_{2v}(9)-C_{82}$ cages. The Tm, N, and C atoms are presented as green, blue, and gray, respectively.

The electronic properties of $TmCN@C_s(6)-C_{82}$ and $TmCN@C_{2v}(9)-C_{82}$ were investigated via visible-near infrared (Vis-NIR) spectroscopy. It is well-established that the absorption spectra of EMFs are primarily governed by the $\pi-\pi^*$ excitations of the carbon cages; thus, Vis-NIR spectroscopy is commonly employed to study the electronic structures of EMFs [12]. As shown in Figure 3, $TmCN@C_s(6)-C_{82}$ exhibits a distinct spectrum with absorptions at 510, 758, 1016, 1134, and 1334 nm, while $TmCN@C_{2v}(9)-C_{82}$ displays a strong absorption at 1338 nm, accompanied by relatively weak absorptions at 524, 622, 706, 770, 1016, and 1168 nm. The measured optical bandgap of $TmCN@C_s(6)-C_{82}$ is 0.76 V, slightly larger than that of $TmCN@C_{2v}(9)-C_{82}$ (0.71 V). The absorption features and optical bandgaps of both $TmCN@C_s(6)-C_{82}$ and $TmCN@C_{2v}(9)-C_{82}$ resemble those of Y-, Tb-, Dy-, and Lu-CYCFs (Table 1) [31–35], which share the same cage isomerism and exhibit a divalent electronic configuration. Consequently, the formal electronic configurations of the two Tm-based CYCFs can be described as $Tm^{3+}(CN)^-@C_s(6)-C_{82})^{2-}$ and $Tm^{3+}(CN)^-@C_{2v}(9)-C_{82})^{2-}$, respectively. Notably, compared to $TmCN@C_s(6)-C_{82}$ and $TmCN@C_{2v}(9)-C_{82}$, $Tm@C_s(6)-C_{82}$ and $Tm@C_{2v}(9)-C_{82}$ display distinct absorption

spectra [50–52] despite sharing the same cage isomerism. In addition, previous X-ray absorption spectroscopy (XAS) and ultraviolet photoelectron spectroscopy (UPS) studies [53,54] demonstrated that the Tm atoms prefer an oxidation state of +2 in mono-metallofullerenes. Therefore, the obtained results indicate that on one hand, the Tm ion or the TmCN cluster significantly contributes to the molecular orbitals. On the other hand, the higher oxidation state (+3) of the Tm atom in the TmCN cluster is identified due to bonding with the non-metallic CN unit.

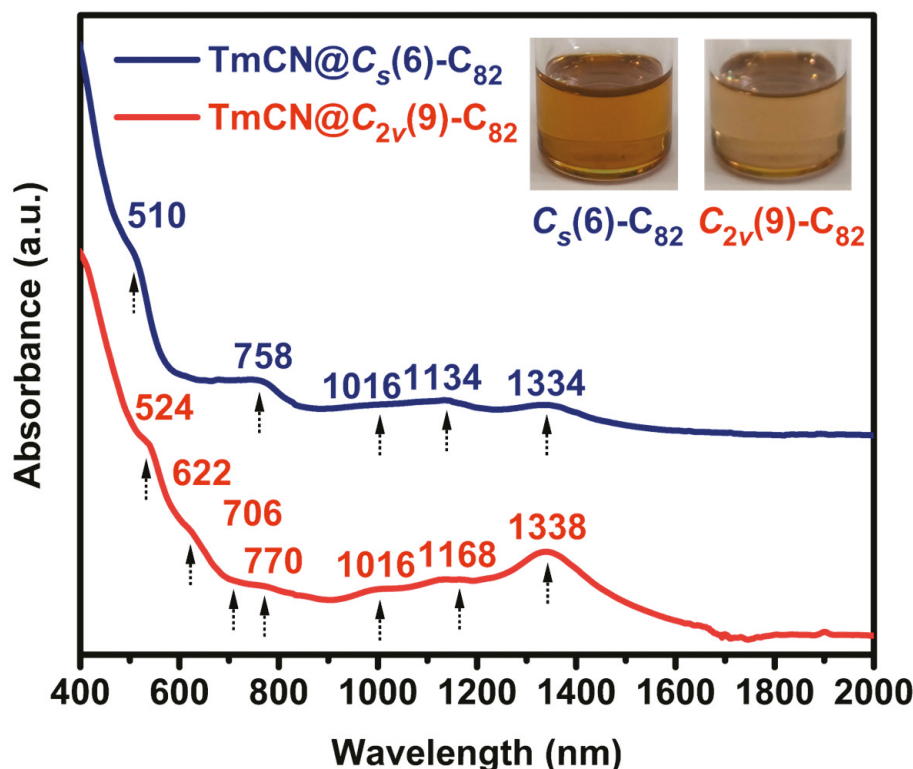


Figure 3. The Vis-NIR absorption spectra of TmCN@C_s(6)-C₈₂ (in blue) and TmCN@C_{2v}(9)-C₈₂ (in red). The inserts are photographs of the two CYCFs dissolved in CS₂. The spectra of the two TmCN@C₈₂ isomers are shown together by shifting one along the ordinate axis, and the absorption peaks are indicated by black arrows.

Table 1. Vis-NIR absorption spectral data of two TmCN@C₈₂ isomers as well as Y-, Tb-, Dy-, and Lu-CYCFs for comparison.

Compounds	Absorption Peaks (nm)	λ_{onset} (nm)	ΔE_{gap} (eV) ¹	Note
TmCN@C _s (6)-C ₈₂	510, 758, 1016, 1134, 1334	1624	0.76	this work
TbCN@C _s (6)-C ₈₂	491, 744, 1072, 1132, 1318	1620	0.77	Ref [32]
DyCN@C _s (6)-C ₈₂	497, 744, 1024, 1140, 1339	1656	0.75	Ref [33]
LuCN@C _s (6)-C ₈₂	494, 596, 744, 1069, 1131, 1345	1638	0.76	Ref [35]
YCN@C _s (6)-C ₈₂	491, 741, 1064, 1123, 1318	1620	0.77	Ref [31]
TmCN@C _{2v} (9)-C ₈₂	524, 622, 706, 770, 1016, 1168, 1338	1740	0.71	This work
TbCN@C _{2v} (9)-C ₈₂	518, 618, 710, 772, 1144, 1320	1770	0.70	Ref [32]
DyCN@C _{2v} (9)-C ₈₂	536, 627, 1144, 1342	1785	0.69	Ref [33]
LuCN@C _{2v} (9)-C ₈₂	512, 621, 697, 782, 1096, 1296	1680	0.74	Ref [35]

¹ $\Delta E_{\text{gap}} = 1240/\lambda_{\text{onset}}$.

Figure 4 shows the electrochemical behaviors of TmCN@C_s(6)-C₈₂ and TmCN@C_{2v}(9)-C₈₂, determined using cyclic voltammetry (CV) with tetrabutylammonium hexafluorophosphate (TBAPF₆) and ferrocene (Fc) as the supporting electrolyte and internal standard, respectively. Both show four reversible reduction steps and one reversible oxidation step, recorded as +0.55, −0.67, −0.90, −1.72, and −2.16 V for TmCN@C_s(6)-C₈₂ and +0.64, −0.45, −0.79, −1.60, and −1.94 for Tm@C_{2v}(9)-C₈₂. The full reduction

potentials of $\text{TmCN@C}_s(6)\text{-C}_{82}$ are also more negatively shifted to about 0.1–0.2 V than those of $\text{Tm@C}_{2v}(9)\text{-C}_{82}$; thus, $\text{TmCN@C}_s(6)\text{-C}_{82}$ is more accessible for oxidation than $\text{Tm@C}_{2v}(9)\text{-C}_{82}$. Notably, the electrochemical gap of $\text{TmCN@C}_s(6)\text{-C}_{82}$ (1.22 V) is larger than that of $\text{Tm@C}_{2v}(9)\text{-C}_{82}$ (1.09 V), which results from the relatively more significant difference in their first reduction potentials.

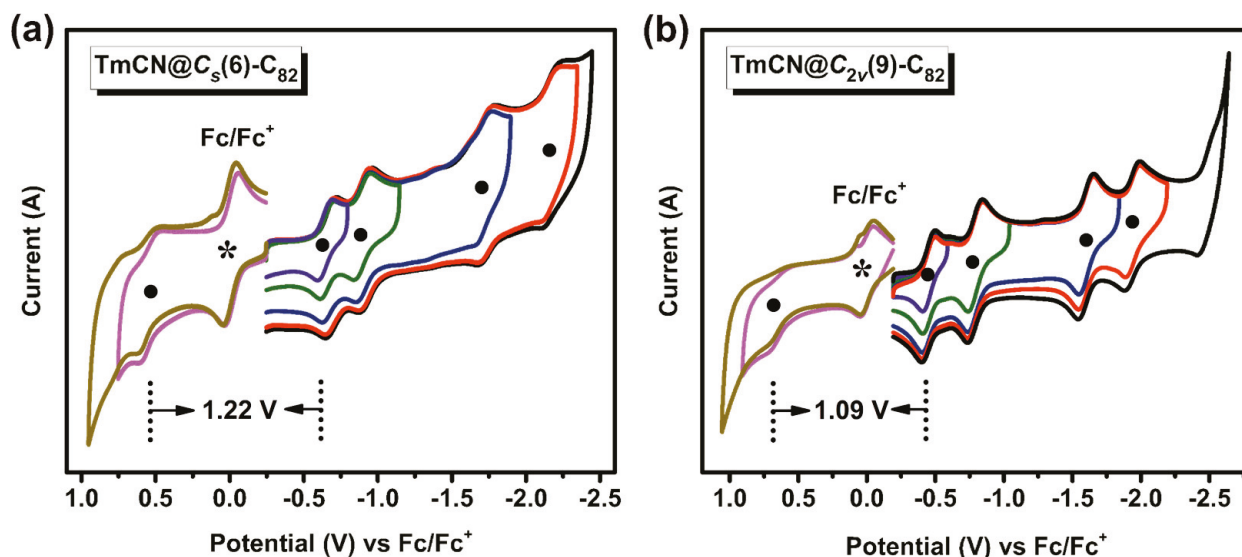


Figure 4. Cyclic voltammograms of (a) $\text{TmCN@C}_s(6)\text{-C}_{82}$ and (b) $\text{TmCN@C}_{2v}(9)\text{-C}_{82}$ in a *o*-DCB solution with a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$. TBAPF_6 and Fc were employed as the internal standard and supporting electrolyte, respectively. Black circles and asterisks are presented to show the redox and the Fc/Fc^+ peaks.

The comparison of the two TmCN@C_{82} isomers and other mono-metallic EMFs based on $\text{C}_s(6)\text{-C}_{82}$ and $\text{C}_{2v}(9)\text{-C}_{82}$ was also studied, as shown in Table 2. The redox behaviors of $\text{TmCN@C}_s(6)\text{-C}_{82}$ and $\text{TmCN@C}_{2v}(9)\text{-C}_{82}$ are fairly similar to those of the corresponding Y-, Tb-, Dy-, and Lu-CYCF counterparts [31–35], suggesting that both TmCN@C_{82} isomers bear a divalent electronic configuration of $\text{Tm}^{3+}(\text{CN})^-@(\text{C}_s(6)\text{-C}_{82})^{2-}$, which is in agreement with the spectroscopic result. Similar redox behaviors between divalent M@C_{82} isomers, such as $\text{Yb@C}_s(6)\text{-C}_{82}$ and $\text{Yb@C}_{2v}(9)\text{-C}_{82}$ [55] and TmCN@C_{82} isomers further confirm the electronic configurations of $\text{Tm}^{3+}(\text{CN})^-@(\text{C}_{82})^{2-}$ for both $\text{C}_s(6)$ and $\text{C}_{2v}(9)$ isomerisms. In comparison, trivalent mono-metallofullerenes ($\text{M}^{3+})@(\text{C}_{82})^{3-}$ ($\text{M} = \text{Y}$ [56], La [57,58], Pr [59], Er [60], and U [61], etc.) based on $\text{C}_s(6)$ and $\text{C}_{2v}(9)$ cage isomerism exhibit sharply different redox potentials with much more negatively shifted first oxidation potentials and much smaller electrochemical gaps. These phenomena originate from the three-electron charge transfer of $(\text{M}^{3+})@(\text{C}_{82})^{3-}$, which results in an open-shell electronic structure, while $\text{TmCN@C}_s(6)\text{-C}_{82}$ and $\text{TmCN@C}_{2v}(9)\text{-C}_{82}$ have a closed-shell electronic structures due to the two-electron transfer from the encapsulated TmCN cluster to the carbon cages.

Table 2. Redox potentials (V vs. Fc/Fc⁺) and electrochemical gaps of TmCN@C_s(6)-C₈₂ and TmCN@C_{2v}(9)-C₈₂ and the corresponding cyanide metallofullerenes MCN@C₈₂ and mono-metallofullerene M@C₈₂ isomers.

Compounds	ox E_1	red E_1	red E_2	red E_3	red E_4	ΔE_{gap} (eV)	Note
TmCN@C _s (6)-C ₈₂	0.55	−0.67	−0.90	−1.72	−2.16	1.22	This work
TbCN@C _s (6)-C ₈₂	0.55	−0.59	−0.84	−1.77	−1.92	1.14	Ref [32]
DyCN@C _s (6)-C ₈₂	0.56	−0.58	−0.84	1.77	−1.92	1.14	Ref [33]
LuCN@C _s (6)-C ₈₂	0.52	−0.58	−0.90	−1.69	−1.86	1.10	Ref [35]
YCN@C _s (6)-C ₈₂	0.56	−0.59	−0.84	−1.76	−1.92	1.15	Ref [31]
La@C _s (6)-C ₈₂	−0.07	−0.47	−1.40	−2.01	−2.40	0.40	Ref [57]
Pr@C _s (6)-C ₈₂	−0.07	−0.48	−1.39	−1.99	/	0.41	Ref [59]
Er@C _s (6)-C ₈₂	−0.09	−0.44	−1.46	−2.04	−2.46	0.35	Ref [60]
Y@C _s (6)-C ₈₂	−0.07	−0.43	−1.43	−2.05	/	0.36	Ref [56]
Yb@C _s (6)-C ₈₂	0.34	−0.62	−0.92	−1.81	−2.01	0.94	Ref [55]
TmCN@C _{2v} (9)-C ₈₂	0.64	−0.45	−0.79	−1.60	−1.94	1.09	This work
TbCN@C _{2v} (9)-C ₈₂	0.55	−0.46	−0.81	−1.78	−1.96	1.01	Ref [32]
DyCN@C _{2v} (9)-C ₈₂	0.56	−0.45	−0.81	−1.78	−1.96	1.01	Ref [33]
LuCN@C _{2v} (9)-C ₈₂	0.50	−0.54	−0.96	−1.71	−1.93	1.04	Ref [35]
La@C _{2v} (9)-C ₈₂	0.07	−0.42	−1.37	−1.53	−2.26	0.49	Ref [58]
Pr@C _{2v} (9)-C ₈₂	0.07	−0.39	−1.35	−1.46	−2.21	0.46	Ref [59]
Er@C _{2v} (9)-C ₈₂	0.08	−0.42	−1.40	−2.18	/	0.50	Ref [60]
U@C _{2v} (9)-C ₈₂	0.10	−0.43	−1.42	−1.76	−1.77	0.53	Ref [61]
Y@C _{2v} (9)-C ₈₂	0.10	−0.34	−1.34	−2.22	/	0.44	Ref [56]
Yb@C _{2v} (9)-C ₈₂	0.61	−0.46	−0.78	−1.60	−1.90	1.07	Ref [55]

3. Materials and Methods

Materials. The reagents used in this work were Tm₂O₃ (99.99%, Suzhou Rare Earth New Materials Co., Suzhou, China), TiO₂ (99%, Sinopharm Chemical Reagent Co., Ltd., Ningbo, China), CS₂ (99%, Sinopharm Chemical Reagent Co., Ltd.), toluene (99%, Sinopharm Chemical Reagent Co., Ltd.), tetrabutylammonium hexafluorophosphate (electrochemical-grade, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China), 1,2-dichlorobenzene (99%, Shanghai Aladdin Biochemical Technology Co., Ltd.), and graphite rods and graphite powder (Sinosteel Shanghai New Graphite Material Co., Shanghai, China).

Synthesis of TmCN@C₈₂ isomers. Soot containing TmCN@C₈₂ isomers was synthesized using a modified Krätschmer–Huffman DC arc discharge method. Graphite rods packed with graphite powder, Tm₂O₃, and TiO₂, with a C/Tm/Ti molar ratio of 15/1/1, were preheated in a tube furnace at 1000 °C for 20 h under a nitrogen atmosphere. Subsequently, the preheated graphite rods were installed in a VDK-250 arc discharge reactor (Beijing Technol Science Co., Ltd., Beijing, China) under a low-vacuum atmosphere with 200 mbar He and 10 mbar N₂, followed by vaporization in a DC of 120 A. The two TmCN@C₈₂ isomers were extracted from the carbon soot with CS₂ using the Soxhlet extraction method. The resulting fullerene solution in CS₂ was evaporated and then dissolved again in toluene, followed by concentration for the following multi-stage HPLC procedures [62,63].

Isolation of TmCN@C₈₂ isomers. As illustrated in Figure 5, a four-stage HPLC process was employed to purify the two TmCN@C₈₂ isomers, and toluene was employed as the eluent in all stages. The first stage was performed on a preparative 5PYE column (20 × 250 mm) with a 15 mL/min flow rate, and fraction A, which contained the two TmCN@C₈₂ isomers and other fullerenes, was collected, concentrated, and then re-injected into the HPLC. In the second stage, a recycling mode was employed on a preparative Buckyprep-M column (20 × 250 mm) with a 12 mL/min flow rate. After three runs of recycling, fraction A-4, which contained the TmCN@C₈₂ isomers, was collected for the next stage. A semi-preparative 5PBB column (10 × 250 mm, 4 mL/min flow rate) was used in the third separation stage to remove the other mixed fullerenes in the A-4 fraction. Fraction A-4-3 was found to contain only two TmCN@C₈₂ isomers, and all the impurity fullerenes had been removed. In the last stage, a recycling HPLC process was employed to purify the two isomers, using a semi-preparative Buckyprep column (10 × 250 mm)

with a 4 mL/min flow rate. After 13 recycling runs, purified $\text{TmCN@C}_s(6)\text{-C}_{82}$, labeled as A-4-3-1, and $\text{TmCN@C}_{2v}(9)\text{-C}_{82}$, labeled as A-4-3-2, were individually collected for further characterizations. The detailed fraction information for each stage is shown in Table 3.

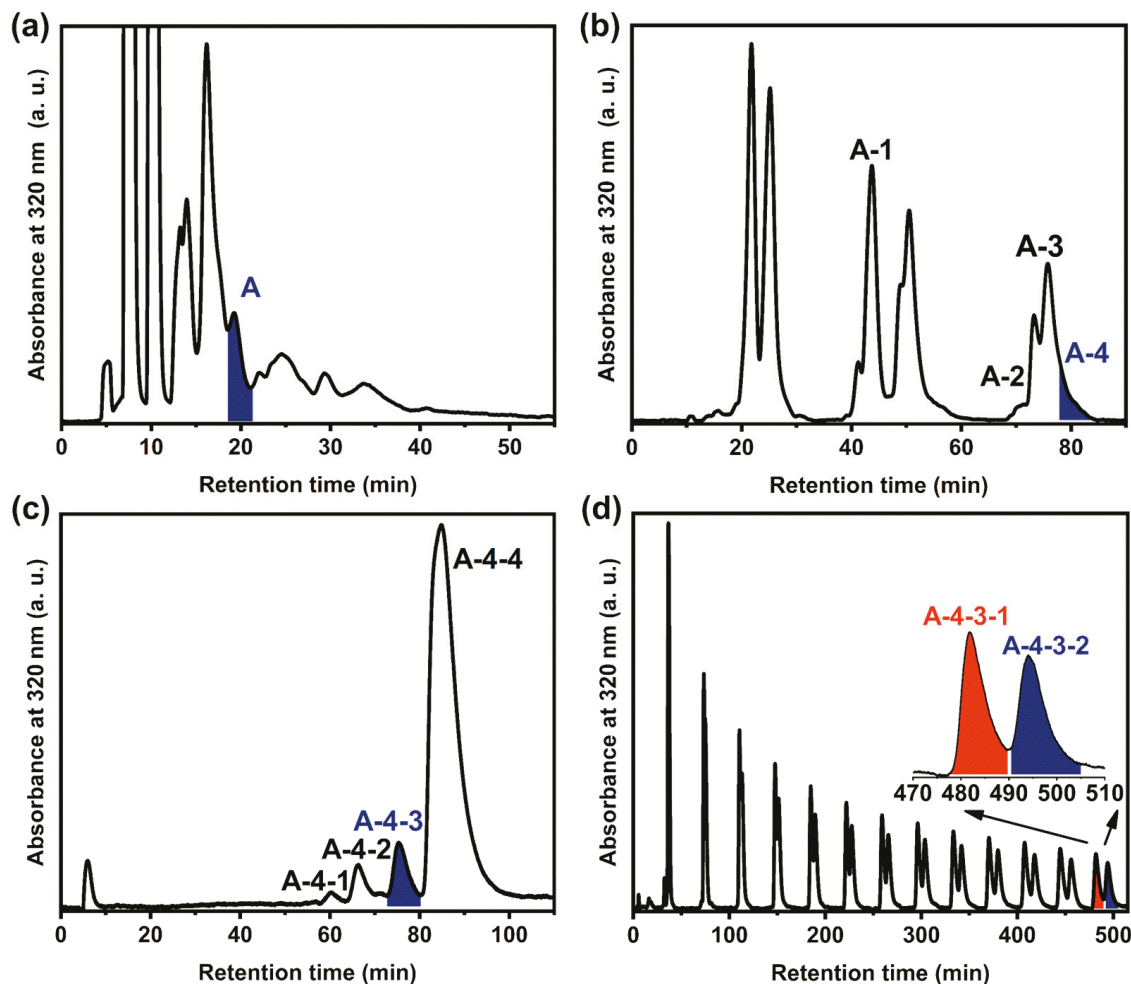


Figure 5. HPLC isolation procedure for $\text{TmCN@C}_s(6)\text{-C}_{82}$ and $\text{TmCN@C}_{2v}(9)\text{-C}_{82}$. (a) the first stage of HPLC isolation procedure on a preparative 5PYE column (20 × 250 mm). (b) the second stage of HPLC isolation procedure on a preparative Buckyprep-M column (20 × 250 mm). (c) the third stage of HPLC isolation procedure on a semi-preparative 5PBB column (10 × 250 mm). (d) the fourth stage of HPLC isolation procedure on a semi-preparative Buckyprep column (10 × 250 mm). The insert in (d) shows the recycled fractions of A-4-3-1 (red) and A-4-3-2 (blue), which represent the purified $\text{TmCN@C}_s(6)\text{-C}_{82}$ and $\text{TmCN@C}_{2v}(9)\text{-C}_{82}$, respectively.

Table 3. The major eluted components in each HPLC fraction and their relative abundances.

Fraction	Subfraction	Major Component	Relative Abundance
A	A-1	C_{84-86}	46.1%
	A-2	$\text{Tm@C}_{82}/\text{TmC}_{77}\text{N}$	3.4%
	A-3	$\text{Tm@C}_{80-84}/\text{TmC}_{83}\text{N}$	36.7%
	A-4	$\text{Tm@C}_{80,84}/\text{Ti}_2\text{C}_{80}/\text{TmCN@C}_{82}$	13.8%
A-4	A-4-1	Ti_2C_{80}	2.2%
	A-4-2	Tm@C_{80}	6.5%
	A-4-3	$\text{TmCN@C}_{82}(\text{C}_s(6), \text{C}_{2v}(9))$	8.7%
	A-4-4	Tm@C_{84}	82.6%
A-4-3	A-4-3-1	$\text{TmCN@C}_s(6)\text{-C}_{82}$	52.1%
	A-4-3-2	$\text{TmCN@C}_{2v}(9)\text{-C}_{82}$	47.9%

Spectroscopic studies. The mass spectra of the two TmCN@C₈₂ isomers were recorded on an Autoflex III matrix-assisted laser desorption ionization time-of-flight mass spectrometer (MALDI-TOF-MS, Bruker, Germany) under positive mode. The Vis-NIR spectra of the purified samples were measured using a UV-3600 spectrometer (Shimadzu, Japan).

Electrochemical analysis. The electrochemical study was performed in a CHI 660 potentiostat (CH Instrument, USA) using a three-electrode system, including a glassy carbon working electrode, a platinum (Pt) wire counter electrode, and a silver (Ag) wire reference electrode. Tetrabutylammonium hexafluorophosphate (TBAPF₆) and ferrocene (Fc) were employed as the supporting electrolyte and the internal standard, respectively. TBAPF₆, Fc, and the samples were all dissolved in 1,2-dichlorobenzene (*o*-DCB).

X-ray crystallographic study. The co-crystals of the DPC molecules and EMF samples were obtained by slowly laying a DPC toluene solution onto an EMF CS₂ solution in a nuclear magnetic resonance (NMR) tube. Black block co-crystals of a suitable size for X-ray diffraction analysis were observed on the wall or in the bottom after 10–15 days. The crystallographic data were collected in the BL17B beamline station at Shanghai Synchrotron Radiation Facility. The crystallographic structures were solved using SHELXT-2014 via the intrinsic phasing method and then refined with SHELXL-2018 via the full-matrix least-squares method based on F^2 within the software Olex2 [64,65]. The SQUEEZE program [66] included in the PLATON program was employed to calculate the contribution of the disordered toluene solvents. The detailed crystallographic data of the two co-crystals are shown in Table 4.

Table 4. Crystallographic information of two TmCN@C₈₂ co-crystals.

Crystal	TmCN@C _s (6)-C ₈₂	TmCN@C _{2v} (9)-C ₈₂
Empirical formula	C ₂₁₀ H ₈₈ N ₂₁ Tm	C ₂₁₀ H ₈₈ N ₂₁ Tm
Formula weight	3073.94	3073.94
Habit	Block	Block
Temperature, K	100	100
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a , Å	14.669	14.724
b , Å	32.146	32.032
c , Å	32.213	32.215
α , deg	90	90
β , deg	101.74	101.91
γ , deg	90	90
Volume, Å ³	14,872.3	14,866.8
Z	4	4
D_x , g/cm ³	1.373	1.373
$F(000)$	6256	6256
Crystal Size, mm ³	0.06 × 0.03 × 0.01	0.12 × 0.08 × 0.03
2θ max, °	20.499	24.712
R_1/wR_2 ($I > 2\sigma(I)$) ¹	0.1193/0.2831	0.0937/0.2531
GOF	1.116	1.052
Completeness	0.972	0.987
Obs reflects	5752	14,863
Total reflects	14,478	25,026
Parameters	2131	2162
metal disorder	Tm1(0.60)/Tm2(0.08)/Tm3(0.17)/ Tm4(0.11)/Tm5(0.04)	Tm1(0.25)/Tm2(0.14)/Tm3(0.09)/Tm4(0.04)/ Tm5(0.08)/Tm6(0.13)/ Tm7(0.20)/Tm8(0.07)

$$^1R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

4. Conclusions

In conclusion, we report the synthesis, isolation, and characterization of the first Tm-based CYCFs with the popular C₈₂ carbon cages via mass spectrometry, single-crystal X-ray crystallography, UV-vis-NIR spectroscopy, and cyclic voltammetry. The molecular structures of these two TmCN@C₈₂ were unambiguously determined to be TmCN@C_s(6)-C₈₂ and TmCN@C_{2v}(9)-C₈₂. The TmCN cluster bears a popular triangular configuration, and the Tm ion is located in one symmetrical plane of the carbon cage for both C_s(6)-C₈₂ and C_{2v}(9)-C₈₂. In addition, the two TmCN@C₈₂ isomers feature the characteristic spectral and electrochemical properties of divalent EMFs, suggesting a closed-shell electronic structure described as Tm³⁺(CN)[−]@(C₈₂)^{2−}. Compared to the Tm@C₈₂ isomers, which contain a divalent Tm²⁺ ion, the 3+ oxidation state of the Tm atom in the mono-metallic TmCN cluster is identified due to bonding with the encapsulated cyanide anion.

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Data Availability Statement: The crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre with the CCDC numbers 2253745 and 2253746 via www.ccdc.cam.ac.uk/data_request/cif (accessed on 31 August 2022). The other data are available upon reasonable request from the corresponding authors.

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Article

Pr@C₈₂ Metallofullerene: Calculated Isomeric Populations

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Abstract: Relative equilibrium populations of the five lowest-energy isolated-pentagon-rule (IPR) isomeric structures of Pr@C₈₂ under high-temperature fullerene synthesis conditions were calculated with the Gibbs energy terms based on molecular characteristics derived using density functional theory (DFT) treatments (B3LYP/6-31+G*~SDD energetics and B3LYP/6-31G*~SDD entropy). Two leading isomers were identified, major Pr@C_{2v};9-C₈₂ and minor Pr@C_s;6-C₈₂. The calculated isomeric relative equilibrium populations agreed with observations.

Keywords: metallofullerenes; evaluations of isomeric populations; theory–experiment comparisons; quantum-chemical calculations

1. Introduction

Endohedral metallofullerenes have been pursued as not only targets of fundamental research but also promising species for nanoelectronics, as well as for energy conversions, superconductive properties, and applications in medicine. Such studies have also dealt with praseodymium-encapsulating metallofullerenes, in particular with Pr@C₈₂ [1–8] (a field-effect transistor was also fabricated [7] with one of its isomers). Actually, just two Pr@C₈₂ isomers (Figure 1) have been observed [3–6], namely the major species with the carbon cage obeying the isolated pentagon rule (IPR), conventionally labeled Pr@C_{2v};9-C₈₂, and the minor isomer Pr@C_s;6-C₈₂ (or Pr@C_s(c;6)-C₈₂). Presently, there are two labeling or coding systems [9] for the IPR C₈₂ cages considered in this research. The older system works only with the symmetries of the cages (namely, the highest topological symmetries, regardless of possible symmetry reductions): C_{3v}(a), C_{3v}(b), C_{2v}, C₂(a), C₂(b), C₂(c), C_s(a), C_s(b), and C_s(c). The second labeling system employs serial numbers from the enumeration spiral algorithm [10]; these symbols are: C_{3v}(a);7, C_{3v}(b);8, C_{2v};9, C₂(a);3, C₂(b);1, C₂(c);5, C_s(a);2, C_s(b);4, and C_s(c);6. Numerous metals can be encapsulated in C₈₂ cages, frequently producing at least two isomers [4–6,9,11–16]. In the present report, the isomeric relative equilibrium populations (or the relative concentrations) were evaluated for the isomeric system of the five lowest-potential-energy Pr@C₈₂ IPR species, as such stability information is needed for the interpretation of some observations.

The relative stabilities of isomeric nanocarbons are mostly evaluated by simply using potential-energy terms. Nevertheless, several examples have been reported [17–26] showing that the Gibbs energy should be applied instead, as its entropy component becomes increasingly important at elevated temperatures. Consequently, an isomer that is not the lowest on the potential-energy scale can still exhibit the highest populations at the high temperatures needed for nanocarbon syntheses. Moreover, other higher-energy structures can in some cases exhibit relative stability interchanges with increasing temperature. Clearly enough, it is not possible to predict such relative stability interchanges

simply from the potential-energy terms alone. Hence, computations were performed in this report for the high-temperature relative equilibrium populations of the five Pr@C₈₂ IPR isomers with the lowest potential energy, employing both the enthalpy and entropy parts of the Gibbs energy in simulations of the isomeric equilibrium populations under supposed fullerene synthesis conditions.

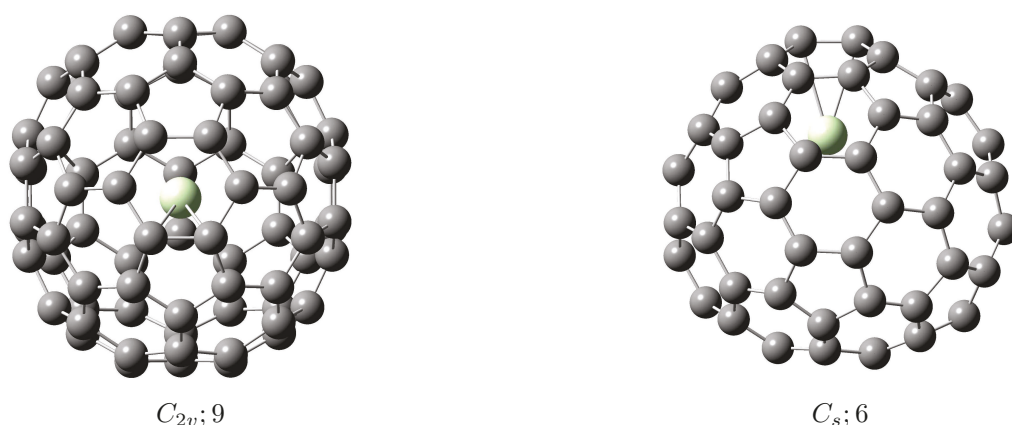


Figure 1. The B3LYP/6-31G*~SDD-optimized structures of the two most populated Pr@C₈₂ isomers, Pr@C_{2v};9-C₈₂ (**left**), Pr@C_s;6-C₈₂ (**right**) (the shortest Pr-C contact is indicated by a link).

2. Calculations

The calculations started with the molecular geometry optimization of the considered isomers, which was performed in a combined atomic basis set—the standard 3-21G basis [27] for carbon atoms and the SDD basis [28] with the SDD effective core potential for praseodymium (labeled 3-21G~SDD). We applied density functional theory (DFT) treatments employing Becke’s three-parameter functional [29] combined with the Lee–Yang–Parr non-local correlation functional [30]—the unrestricted B3LYP/3-21G~SDD treatment. Moreover, the B3LYP/3-21G~SDD pre-optimized structures were improved further with the standard 6-31G* basis set [31] for carbon atoms—the B3LYP/6-31G*~SDD approach. The calculations were carried out for the quartet electronic state, as the multiplicity produced significantly lower energy at the considered computational levels than the doublet and sextet electronic states. The geometry optimizations were carried out with the analytical energy gradient. All nine [9] IPR C₈₂ cages were subjected to geometry optimizations. The geometry optimizations with both the B3LYP/3-21G~SDD and B3LYP/6-31G*~SDD treatments identified five isomers (Table 1) with sufficiently low potential energy. All other Pr@C₈₂ IPR isomers were, according to the B3LYP/6-31G*~SDD treatment, located 19 kcal/mol or more higher than the lowest-energy species Pr@C_{2v};9-C₈₂. Their energy separation (in combination with the entropy terms) produced already insignificant relative equilibrium concentrations. Further on, the inter-isomeric energetics was still improved by applying a yet more advanced B3LYP/6-31G*~SDD approach (still using the B3LYP/6-31G*~SDD geometries). For the optimized B3LYP/6-31G*~SDD geometries, the vibrational analysis was performed using the harmonic GF scheme with the analytical force–constant matrix F in order to simulate the IR vibrational spectra (Figure 2) and, in particular, to construct the partition functions of the harmonic vibrations for the stability evaluations. The SCF wavefunction stability [32,33] was systematically tested throughout in order to prevent misleading unstable SCF solutions that could produce a physically unsound picture. The calculations were performed with the Gaussian 09 suite of programs [34].

Table 1: Pr@C₈₂ relative potential energies $\Delta E_{pot,rel}$ for the five lowest-energy isomers calculated in the B3LYP/6-31G*~SDD-optimized structures.

Species	$\Delta E_{pot,rel}/\text{kcal}\cdot\text{mol}^{-1}$	
	B3LYP/6-31G*~SDD	B3LYP/6-31+G*~SDD
C ₂ ; 5	17.9	17.3
C _{3v} ; 7	13.0	14.2
C _{3v} ; 8	7.54	7.37
C _s ; 6 ^a	3.46	3.47
C _{2v} ; 9 ^a	0.0	0.0

^a See Figure 1.

The relative equilibrium concentrations of m isomers are described as mole fractions x_i that can be expressed [35,36] through their partition functions q_i and the enthalpies at a temperature of absolute zero or ground-state energies $\Delta H_{0,i}^0$ (i.e., the relative potential energies corrected for the vibrational zero-point energies) by a master formula:

$$x_i = \frac{q_i \exp[-\Delta H_{0,i}^0 / (RT)]}{\sum_{j=1}^m q_j \exp[-\Delta H_{0,j}^0 / (RT)]} \quad (1)$$

where R is the gas constant and T is the absolute temperature. Equation (1) is a rigorous formula that can be obtained [35] using statistical thermodynamics with the standard isomeric Gibbs energies under the conditions of the inter-isomeric thermodynamic equilibrium. The rotational-vibrational components of the partition functions were approximated [36] by the conventional rigid-rotor and harmonic-oscillator (RRHO) approach. Frequency scaling was not applied as it was not significant for the x_i values at high temperatures [37]. Moreover, the chirality contribution [38] was considered accordingly (the partition function q_i for a pair of enantiomers was doubled). The temperatures at which fullerene or metallofullerene electric-arc synthesis takes place are not precisely known; however, recent observations [39] suggest that it takes place somewhere around a temperature of 1500 K. Hence, the values discussed in this report were calculated for this particular temperature region.

Moreover, an adjusted [23,40] RRHO treatment for the description of the metal motions was applied, considering findings [41] suggesting that the encapsulated metal atoms can exercise large-amplitude vibrational motions, in particular at higher temperatures (if the motions are not restricted by derivatizations of cages [42]). It could be expected that if the metal was relatively free, then, at sufficiently elevated temperatures, its motions in different endohedral cages would provide a similar contribution to the overall partition functions. Such similar contributions would consequently be mutually canceled out in Equation (1). This approximation has been called [23,40] the floating, fluctuating, or free encapsulation model (FEM). The FEM treatment consists of two steps. The first step is the suppression of the three lowest vibrational frequencies (which belong to the metal vibrations inside the cage). The second step deals with the symmetries of the cages—they should be taken as the highest topologically possible terms, reflecting the averaging influence of the large-amplitude motions upon the symmetries. For example, with the Pr@C₈₂ IPR isomer related to the C_{2v}; 9 cage (Table 1), the C_{2v} symmetry is indeed applied in the FEM treatment, in spite of the fact that its static [43] symmetry (i.e., derived from the geometry optimization) is only C_s or even C₁ (Figure 1). The FEM approach is generally known to produce better agreement [23,40] with observed data than the simple RRHO treatment. The FEM approach was thus also applied in this report.

Table 2: The selected characteristics of the five lowest-energy Pr@C₈₂ isomers—the closest Pr-C contact ^a r_{Pr-C} , the Mulliken charge ^b on Pr q_{Pr} , and the lowest vibrational frequency ^a ω_{low} .

Species	$r_{Pr-C}/\text{\AA}$	q_{Pr}	$\omega_{low} / \text{cm}^{-1}$
C _{2v} ;5	2.512	2.449	39.3
C _{3v} ;7	2.516	2.293	17.6
C _{3v} ;8	2.476	2.462	22.3
C _s ;6 ^c	2.500	2.337	20.5
C _{2v} ;9 ^c	2.549	2.364	15.8

^a B3LYP/6-31G*~SDD terms. ^b B3LYP/3-21G~SDD terms. ^c See Figure 1.

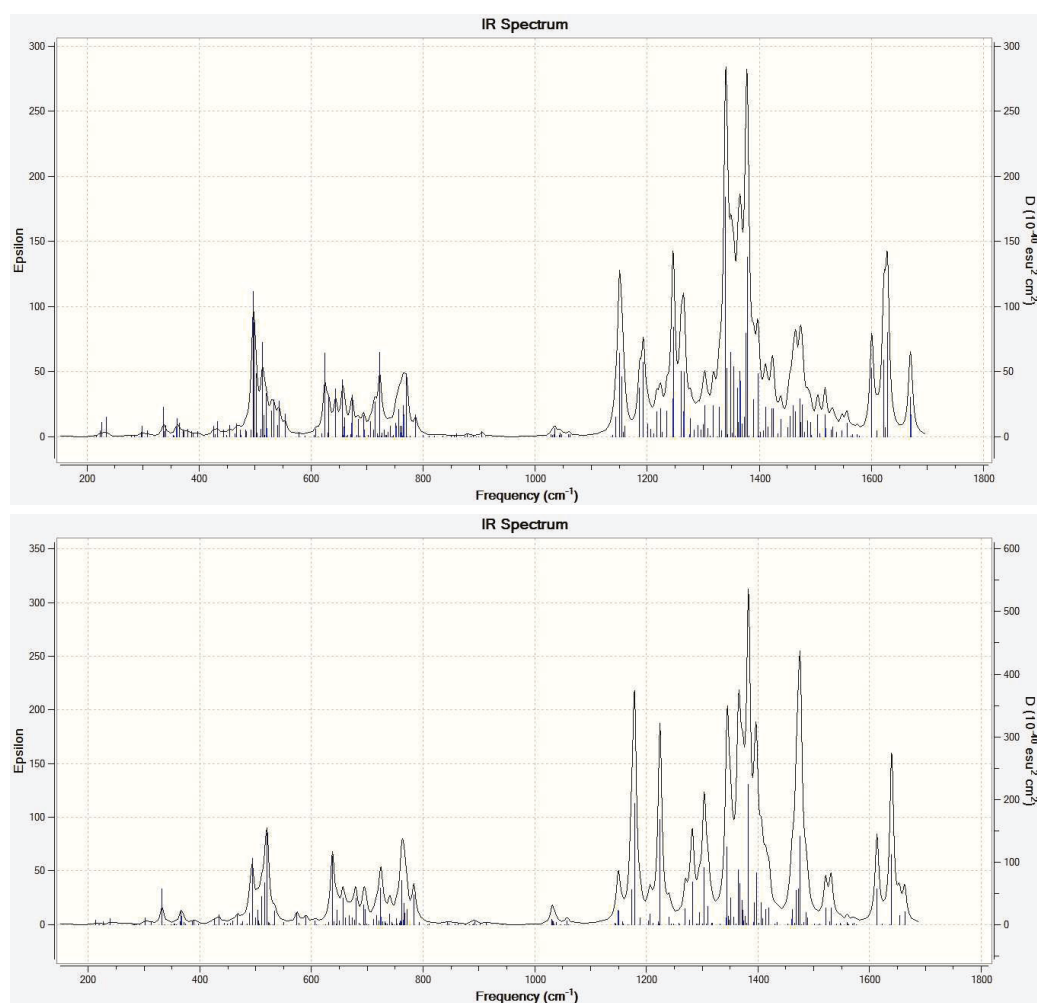


Figure 2. B3LYP/6-31G*~SDD-calculated IR spectrum of the Pr@C_{2v};9-C₈₂ (bottom) and Pr@C_s;6-C₈₂ (top) isomers.

3. Results and Discussion

The Pr@C₈₂ relative isomeric energetics calculated in the two selected approaches (namely, the relative potential energy without the inclusion of the zero-point vibrational energies) for the five lowest-energy isomers selected from the nine [9,44] IPR-satisfying C₈₂ cages are presented in Table 1. The lowest-energy Pr@C₈₂ isomer was the C_{2v};9 species, followed at 3 kcal/mol higher by the C_s;6 endohedral species (Figure 1). Then, C_{3v};8 and C_{3v};7 were located about 7 and 14 kcal/mol above the C_{2v};9 stabilomer, respectively. It should be noted that the B3LYP/6-31G*~SDD and B3LYP/6-31+G*~SDD relative energies were similar. The five species from Table 1 were subjected to equilibrium thermodynamic analysis.

Table 2 presents selected calculated molecular parameters for the five lowest-potential-energy $\text{Pr}@\text{C}_{82}$ species. The B3LYP/6-31G*~SDD calculated shortest distances $r_{\text{Pr}-\text{C}}$ between Pr and the carbon cages at around 2.5 Å, which were thus similar to those previously reported for other C_{82} -based endohedrals [9,15,44]. Interestingly, the calculated position of the Pr atom in $\text{Pr}@\text{C}_{2v};9-\text{C}_{82}$ (i.e., under a hexagonal ring) is also known for other systems [9]. The lowest harmonic vibrational frequencies ω_{low} in Table 1 reflect the relatively free motions of the encapsulated metals in metallofullerenes. B3LYP/3-21G~SDD produced Mulliken atomic charges q_{Pr} on Pr are close to 2.4 (electron elementary charge). It should be stressed that the Mulliken atomic charges from the 3-21G~SDD basis are known to produce [25] for metallofullerenes good agreement with experimental charges [45] (which is not the case for, e.g., the 6-31G*~SDD level). In addition, there are deeper physical reasons [46–49] why extended bases should not be used for Mulliken charges (as the latter can sometimes produce rather unphysical charges [47]). As for yet another basis-set effect, let us also mention that, as we were only dealing with isomers, there was no need to consider the basis set superposition error (BSSE) [49]. The BSSE correction is indeed important for association processes in order to assure that all the components are treated in the same basis set. In a set of isomers, however, the basis set used is the same for all the species, and therefore the total energies do not require a correction of the BSSE type. If such a treatment was still performed, there would be a relatively constant additive term that would then cancel out in Equation (1).

Figure 3 gives the key results of this report—the temperature dependencies of the relative equilibrium concentrations for the five lowest-potential-energy $\text{Pr}@\text{C}_{82}$ isomers at moderate and high temperatures. The presented relative isomeric populations were obtained with the FEM approach. In any case, at very low temperatures, the species with the lowest $\Delta H_{0,i}^0$ had to be the most populated, i.e., the $\text{Pr}@\text{C}_{2v};9-\text{C}_{82}$ isomer. However, the second ($\text{Pr}@\text{C}_s;6-\text{C}_{82}$) and, somewhat, the third ($\text{Pr}@\text{C}_{3v};8-\text{C}_{82}$) lowest-potential-energy isomers showed a rapid increase in their relative populations, while the remaining isomers were negligible. At the suggested [39] representative temperature of 1500 K for fullerene synthesis, the relative equilibrium populations were 59.3, 34.9, 4.8, 0.3, and 0.8% for the $\text{C}_{2v};9$, $\text{C}_s;6$, $\text{C}_{3v};8$, $\text{C}_{3v};7$, and $\text{C}_2;5$ isomers, respectively. Interestingly, in a stability evaluation without the entropic part (i.e., when just the simple Boltzmann factors [35,36] were considered), the relative isomeric populations were rather different: 71.0, 22.2, 6.0, 0.6, and 0.2% for the $\text{C}_{2v};9$, $\text{C}_s;6$, $\text{C}_{3v};8$, $\text{C}_{3v};7$, and $\text{C}_2;5$ species, respectively.

Overall, the calculations agreed with the observations [3–6] for two isomers, major $\text{Pr}@\text{C}_{2v};9-\text{C}_{82}$ and minor $\text{Pr}@\text{C}_s;6-\text{C}_{82}$. Their observed [6] population ratio has been reported as $\text{Pr}@\text{C}_{2v};9-\text{C}_{82} : \text{Pr}@\text{C}_s;6-\text{C}_{82} = 2.5$. In our calculations, the population ratio was achieved at a quite reasonable synthetic temperature of 1130 K. Still, it is not known how close the experiments were to the inter-isomeric equilibrium predicted by the thermodynamic treatment. For the interpretation of the observations, it is also of interest that the calculations predicted just two significant isomers, while the populations of the other species were rather negligible. The calculated IR spectra (Figure 2) should also be of use for the identification of the two isomers.

The reported results presented similarities with the previous calculations [12,23,50–54] for other C_{82} -based metallofullerenes with a similar metal-to-cage charge transfer—in particular [12,23], $\text{La}@\text{C}_{82}$. The similarities originated from the fact that metallofullerenes are not stabilized by some new covalent bond but instead formed by an ionic bond [55–59]. It should be mentioned that experimental populations can depend on the metal sources used [60]. This aspect can be related to catalytic and kinetic factors [61–63] and indicates the variable levels to which the expected inter-isomeric thermodynamic equilibrium could actually be obtained in the synthesis. Yet another factor is the solubility [64–66] of individual isomers in the selected extraction solvents. In conclusion, the $\text{Pr}@\text{C}_{82}$ results provide more evidence of the good applicability of the Gibbs energy approach to isomeric populations, thus supporting further studies of this type into yet more complex nanocarbon isomeric sets [67–71].

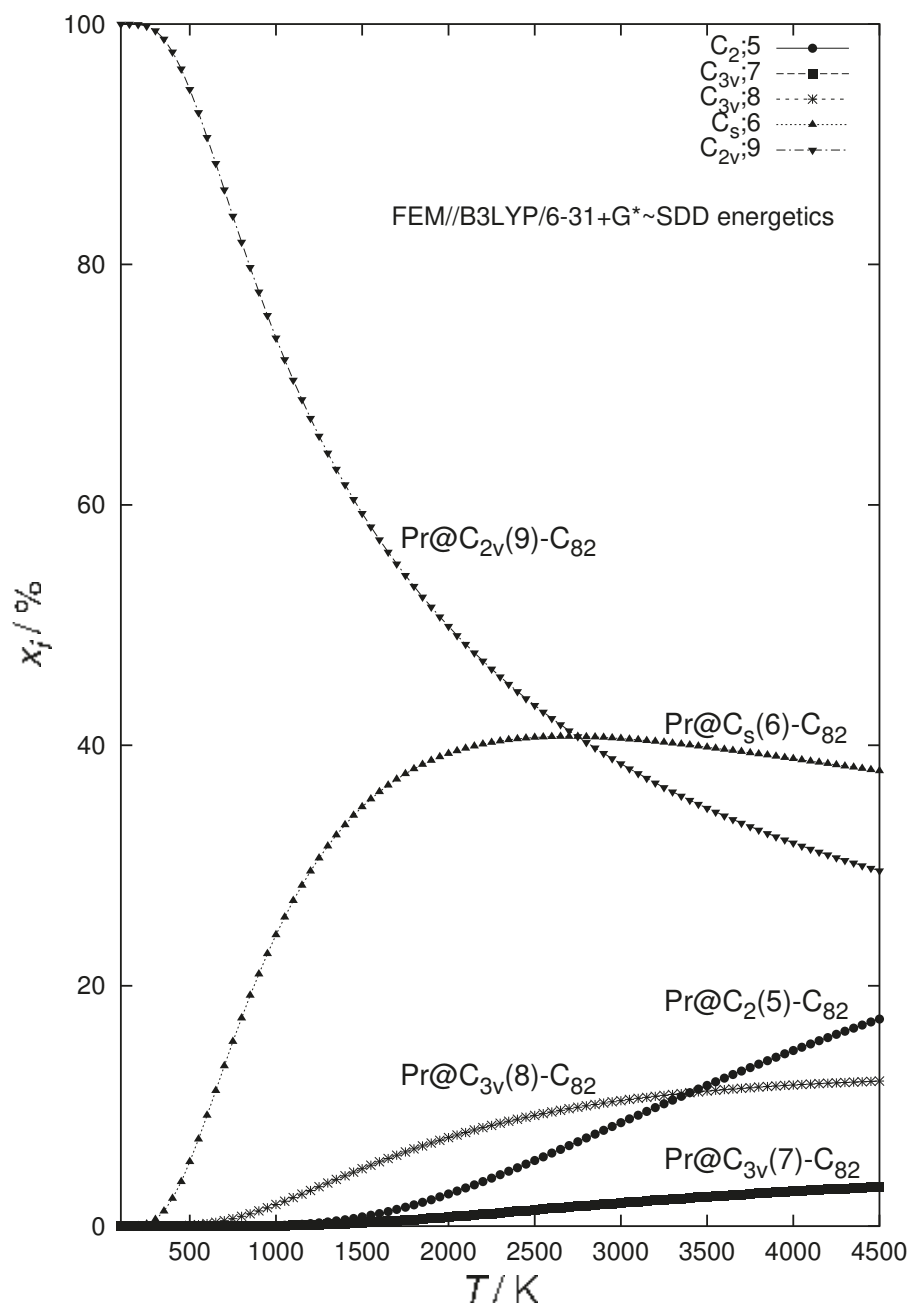


Figure 3. The relative populations of the Pr@C_{82} isomers based on the FEM treatment with the B3LYP/6-31+G*~SDD energetics and B3LYP/6-31G*~SDD entropy.

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Article

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Abstract: This study on $\text{Lu}_2@C_{60}$ isomers provides insights into the metal–metal bond through the confinement effect of fullerene cages. Density functional theory calculations were used to study the nature of the Lu-Lu bond in two stable endohedral metallofullerenes (EMFs), $\text{Lu}_2@C_{2v}\text{-}C_{60}$ and $\text{Lu}_2@I_h\text{-}C_{60}$, both with negative endohedral energy. These two isomers are geometrically connected through a simple Stone–Wales (SW) transformation. The electronic configuration of $(\text{Lu}_2)^{4+}@C_{60}^{4-}$ was also confirmed, leading to the formation of a two-center two-electron (2c–2e) Lu-Lu σ single bond. By comparing the Lu-Lu bonds in $\text{Lu}_2@C_{60}$ with those in acknowledged $\text{Lu}_2@C_{2n}$, the smaller C_{60} fullerene compressed the geometry of Lu_2 resulting in a much shorter Lu-Lu bond length. However, the Lu-Lu bond strength is slightly weaker in $\text{Lu}_2@C_{60}$ than that in large fullerenes, as the Lu-Lu bond in C_{60} is likely a p-p σ bond with an above the 40% contribution of p orbital and a strong metal–cage interaction. Additionally, the vis-NIR spectra of $\text{Lu}_2@C_{2v}\text{-}C_{60}$ and $\text{Lu}_2@I_h\text{-}C_{60}$ were simulated, which could provide valuable information for future experimental studies on Lu-based EMFs.

Keywords: endohedral metallofullerenes; metal–metal bond; size effect

1. Introduction

Metal–metal bonds have been a subject of significant research interest in past decades, which show important roles in catalysis and biology [1,2]. Metal–metal bonds provide a large perturbation in electronic structure and the unique properties of these dinuclear fragments can be harnessed in a broad range of applications [3]. Since the synthesis and characterization of $\text{Re}_2\text{Cl}_8^{2-}$ [4], there is growing evidence for the formation of metal–metal bonds under specific conditions [5,6], and growing research interest in understanding the nature of the metal–metal bonds. Generally, the transition metals could form multinuclear complexes with direct metal–metal interactions, but a complex coordination environment makes it difficult to understand the nature of metal–metal interaction [7].

Luckily, endohedral dimetallofullerenes (di-EMFs), i.e., fullerenes with two metal atoms trapped inside are considered as the ideal model to study the metal–metal bond [8]. In 2014, di-EMF $\text{Sc}_2@C_1(4059)\text{-}C_{66}$ was determined as the geometry of Sc_2C_{66} molecule by the single-crystal X-ray diffraction (XRD) [9]. $\text{La}_2@C_{94}$ are also proposed with experimental and theoretical methods [10], and later, theoretical study revealed that the La–La bond plays a key role in the stability of dimetallofullerenes $[\text{La}_2@C_{2n}]^-$ ($2n = 92\text{--}96$) [11]. Recently, Chen et al. have studied Sc–Y σ^2 bond in $\text{ScY}@C_{3v}(8)\text{-}C_{82}$ [12].

Additionally, the previous reports clarified strong confinement effects of fullerene size on the metal–metal bond in EMFs [7,13–15]. For example, Poblet et al. theoretically reveal a U–U triple bond in $\text{U}_2@C_{60}$ with the effective bond order of 2.52, singly

occupied molecular orbitals (MOs) with metal–metal bond characters in $\text{U}_2@\text{C}_{80}$, non-negligible $\text{U}\cdots\text{U}$ interaction in $\text{U}_2@\text{C}_{78}$, but the metal–metal interaction almost disappears in $\text{U}_2@\text{C}_{104}$ [8]. In 2017, di-EMFs $\text{Lu}_2@\text{C}_{2n}$ ($2n = 82, 84$, and 86) were synthesized and characterized with the single-crystal XRD method, which gives the crystallographic evidence of direct Lu–Lu bond between two divalent lutetium ions inside fullerenes [16]. Later, additional Lu_2C_{2n} ($2n = 76\text{--}90$) molecules were reported with a wide range cage size, and the successful isolation and unambiguous crystallographic assignment of a series of lutetium-containing EMFs, Lu_2C_{2n} ($2n = 76, 78, 80, 84, 86, 88$, and 90), reveal an unrecognized decisive effect of the cage size on the configuration of the encapsulated clusters [17]. Following theoretical studies reveal a stable two-center two-electron (2c–2e) Lu–Lu σ bond in $\text{Lu}_2@\text{C}_{84}$ and $\text{Lu}_2@\text{C}_{86}$ [18,19]. However, experimental and theoretical study focused on the Lu-containing di-EMFs with medium- or large-size fullerene cages and Lu–Lu bond in small fullerene cages is still unclear.

Herein, Lu–Lu bond is studied in the smaller C_{60} fullerene cage with the highest yield in the fullerene family by using density functional theory calculations and bonding analysis. The aim is to evaluate the confinement effect of fullerene size on the Lu–Lu bond. Two isomers, $\text{C}_{2v}\text{-C}_{60}$ and $I_h\text{-C}_{60}$, which have been previously verified as the stable host cage of C_{60} fullerene to encage inner moieties, were selected as they have well-established thermodynamic stability and were used to encapsulate the Lu_2 dimer. The bonding features of the Lu–Lu in the C_{60} were evaluated via frontier molecular orbital (FMO), natural bond orbital (NBO), and bond orders analyses. Additionally, the visible-near-infrared (vis-NIR) spectra of $\text{Lu}_2@\text{C}_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$ were simulated to study their electronic features and gain a better understanding of the Lu–Lu bonds both in theory and experiment.

2. Results and Discussion

2.1. Stability and Geometries of $\text{Lu}_2@\text{C}_{60}$

The good stability of fullerenes $\text{C}_{2v}\text{-C}_{60}$ and $I_h\text{-C}_{60}$, connected through a single-step Stone–Wales transformation, has been previously reported [20], and they have been characterized as suitable isomers of C_{60} fullerenes to encage metal atoms or clusters [8,21]. In this work, we focus on both $\text{Lu}_2@\text{C}_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$ to generally elucidate the confinement effect of the fullerene on metal–metal bond.

Figure 1 shows the optimized geometries of $\text{Lu}_2@\text{C}_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$. The lowest frequencies for $\text{Lu}_2@\text{C}_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$ are calculated to be 36 and 45 cm^{-1} , respectively, suggesting their possible existence, as shown in Figures S1 and S2. The single-point energy calculations showed that the $\text{Lu}_2@\text{C}_{2v}\text{-C}_{60}$ possessed energy of $5.3\text{ kcal}\cdot\text{mol}^{-1}$ higher than the energy of $\text{Lu}_2@I_h\text{-C}_{60}$, of which results are confirmed by the hybrid functional PBE0 (PBE0/6-311G(d,p)~SDD//PBE0/6-31G(d)~CEP-4G) showing $\text{Lu}_2@\text{C}_{2v}\text{-C}_{60}$ with energy of $0.7\text{ kcal}\cdot\text{mol}^{-1}$ higher than the energy of $\text{Lu}_2@I_h\text{-C}_{60}$.

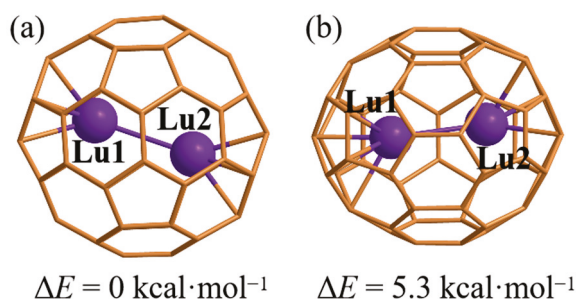


Figure 1. Geometries of optimized $\text{Lu}_2@I_h\text{-C}_{60}$ (a) and $\text{Lu}_2@\text{C}_{2v}\text{-C}_{60}$ (b) on the PBE/6-31G(d)~CEP-4G, including the relative energy (ΔE) on the theoretical level of PBE/6-311G(d,p)~SDD with single-point calculations.

In order to evaluate the effect of temperature, the Boltzmann distribution has been calculated for $\text{Lu}_2@C_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$. The results indicate that the Boltzmann distribution of $\text{Lu}_2@I_h\text{-C}_{60}$ is about 97%, 84%, 75%, 70%, 66%, and 63% at 500, 1000, 1500, 2000, 2500, and 3000 K, respectively, which is higher than $\text{Lu}_2@C_{2v}\text{-C}_{60}$ with the Boltzmann distribution values of about 4%, 16%, 25%, 30%, 34%, and 37% at 500, 1000, 1500, 2000, 2500, and 3000 K, respectively. The energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are 0.19 and 0.35 eV for $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$, respectively, which are larger than the DFT-computed HOMO-LUMO gaps of $\text{Lu}_2@C_s(17,490)\text{-C}_{76}$ and $\text{Lu}_2@C_{2v}(19,138)\text{-C}_{76}$ [22].

The formation energy for $\text{Lu}_2@C_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$ has been calculated by basis set superposition error (BSSE) correction with a counterpoise calculation on the PBE/6-311G(d,p)~SDD considering the Grimme's dispersion with the original D3 damping function. The formation energy for $\text{Lu}_2@C_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$ are -179.7 and -156.4 kcal·mol $^{-1}$, indicating the possible synthesis and isolation in experiment. On the other hand, the much negative formation energy indicates their good stability. The similar stability for $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$ might be explained by the geometrical connection with only the single-step Stone–Wales transformation, and this case is similar to the hollow cage of $C_{2v}\text{-C}_{60}$ and $I_h\text{-C}_{60}$ isomers.

The Lu-Lu bond length in $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$ are 3.04 and 3.14 Å, respectively, which are much smaller than the previously reported Lu-Lu bond length (~ 3.50 Å) in $\text{Lu}_2@C_{2n}$ ($2n \geq 76$) [17–19,22]. This suggests that there is a confinement effect of fullerenes on the Lu-Lu bond length. The bond length of Sc-Sc and Y-Y in C_{82} are 3.201 and 3.695 Å, respectively, and bond length of La-La in C_{80} is 3.826 Å, indicating the presence of a metal–metal single bond, which has been verified in both theory and experiment [22]. Based on the geometry, further study into the confinement effect of fullerenes on the Lu-Lu bond is warranted.

2.2. Electronic Structures of $\text{Lu}_2@C_{60}$

The electronic structure of $\text{Lu}_2@C_{60}$ was further investigated through NBO calculations. The results in Table 1 show that there is charge transfer from inner Lu_2 dimer to the C_{60} fullerenes, and in combination with the Lu-Lu σ bond in C_{60} , the 6s orbitals of Lu atoms lose four electrons in $\text{Lu}_2@C_{60}$. Therefore, the electronic configurations of both $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$ can be expressed as $(\text{Lu}_2)^{4+}@(C_{60})^{4-}$.

Table 1. Natural population analysis (NPA) on $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$, and the NPA charges (*e*) for metal atoms on the PBE/6-311G(d,p)~SDD.

Molecules	Atoms	Populations	NPA Charges
$\text{Lu}_2@I_h\text{-C}_{60}$	Lu1	5d ^{0.37} 6s ^{0.29} 6p ^{0.48} 6d ^{0.88} 7p ^{0.29}	0.78
	Lu2	5d ^{0.36} 6s ^{0.37} 6p ^{0.46} 6d ^{0.85} 7p ^{0.28}	0.78
$\text{Lu}_2@C_{2v}\text{-C}_{60}$	Lu1	5d ^{0.36} 6s ^{0.30} 6p ^{0.41} 6d ^{0.97} 7p ^{0.39}	0.65
	Lu2	5d ^{0.34} 6s ^{0.30} 6p ^{0.32} 6d ^{0.89} 7p ^{0.40}	0.83

In addition, the location of fractional charge on 6p, 6d, and 7p orbitals of Lu atoms implies the occurrence of back-donation, similar to that observed in other EMFs [23–37]. This is further supported by the presence of electrostatic interaction between the Lu_2 dimer and fullerene cages, as depicted in Figure 2. These observations are consistent with the ionic model of EMFs [13,38,39].

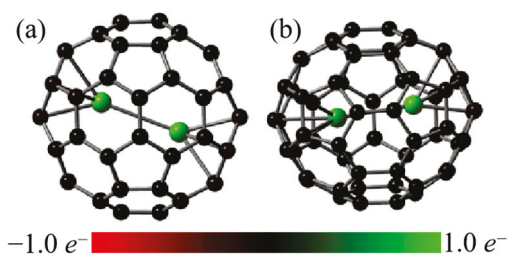


Figure 2. NPA charges for $\text{Lu}_2@I_h\text{-C}_{60}$ (a) and $\text{Lu}_2@C_{2v}\text{-C}_{60}$ (b) on the PBE/6-311G(d,p)-SDD, in which the atoms are colored by corresponding NPA charges.

Furthermore, the FMOs have been mapped as shown in Figure 3, in which the C_{60} fullerenes based on single-point calculations are obtained from the optimized $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$. The highest occupied molecular orbitals (HOMOs) of $\text{Lu}_2@C_{60}$ are contributed by the Lu_2 dimer, presenting the Lu-Lu bond. It is clear that the LUMO and LUMO + 1 of the C_{60} fullerenes become the HOMO-1 and HOMO-2 of the $\text{Lu}_2@C_{60}$ indicating the four-electron transfer from inner moiety to fullerene cage, and this result is in line with the natural bond order analysis again confirming the electronic configuration of $(\text{Lu}_2)^{4+} @ (\text{C}_{60})^{4-}$. This electronic configuration has been verified in the previous report on $\text{Lu}_2@C_{2n}$ ($2n \geq 76$) [17–19,22]. Additionally, the t_{1u} LUMO has been split after encapsulation of Lu_2 dimer. As shown in Figure 3, after encapsulation of Lu_2 dimer in $I_h\text{-C}_{60}$, its energy level of LUMO + 1 and LUMO is equal, but the energy level of LUMO + 2 is -4.22 eV. This is derived from the distortion of C_{60} fullerene. The symmetry of $I_h\text{-C}_{60}$ and $C_{2v}\text{-C}_{60}$ have reduced to D_{3d} and C_1 , respectively, after encapsulation, and the calculated distortion energies of $I_h\text{-C}_{60}$ and $C_{2v}\text{-C}_{60}$ are 35.4 and 29.6 kcal·mol $^{-1}$, respectively, on the theoretical level of PBE/6-311G(d,p)-SDD.

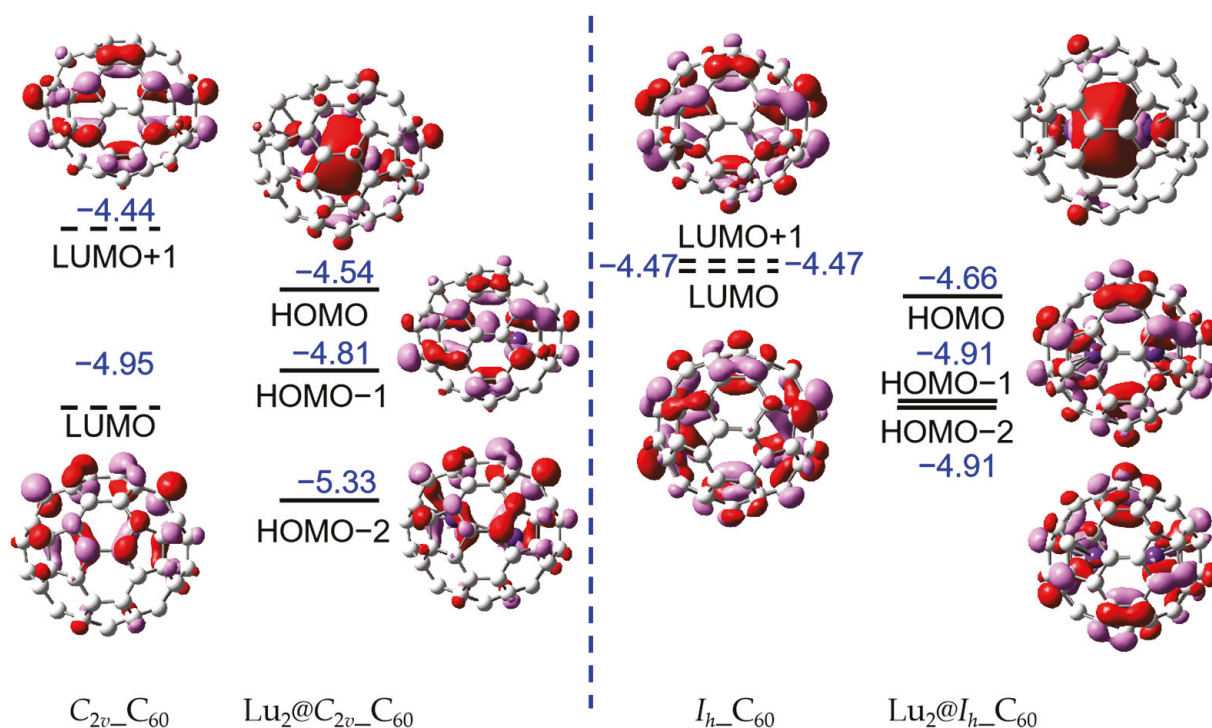


Figure 3. FMOs for stable $C_{2v}\text{-C}_{60}$, $I_h\text{-C}_{60}$, $\text{Lu}_2@I_h\text{-C}_{60}$, and $\text{Lu}_2@C_{2v}\text{-C}_{60}$ molecules with isovalue of 0.03 a.u. for the surface with the PBE functional, 6-311G(d,p) basis set for carbon atoms, and SDD basis set for Lu atoms. The highest occupied molecular orbitals (HOMO) represented the Lu-Lu bond in C_{60} . The blue numbers represent the energies of orbitals.

2.3. Bonding Features of $\text{Lu}_2@\text{C}_{60}$

Figure 3 illustrates the presence of a clearly localized bonding molecular orbital between two Lu atoms in $\text{Lu}_2@\text{C}_{60}$, which has been reported in previous studies [16–19]. The energy level of the bonding molecular orbitals is -4.66 and -4.54 eV for $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$, respectively. However, due to the confinement effect of the smaller fullerene cage size, such as C_{60} , further investigation is needed to determine the strength of the Lu-Lu bond. The LUMOs are shown in Figure S3, which display both a metal–metal antibonding orbital and a π antibonding orbital.

To study the nature of the Lu-Lu bond in small fullerene sizes, we calculated the Mayer bond order (MBO) and Wiberg bond order (WBO) and the results are presented in Table 2. Despite the much shorter bond length of Lu-Lu in fullerene C_{60} , the MBO for Lu-Lu bond in C_{60} is smaller than that in larger fullerenes. For example, in $\text{Lu}_2@\text{C}_{2n}$ ($2n = 84$ and 86), the MBO is a little larger than 1 for Lu-Lu bond with a larger bond length [18,19]. The WBOs for Lu-Lu bond in C_{60} are also smaller than 1. To gain further insights into this abnormal phenomenon, the hybrid compositions of M-M bond in $\text{Lu}_2@\text{C}_{60}$ were studied with NBO calculations. As shown in Table 2, the p orbital contributes more than 40% to the Lu-Lu bond, while the rest of the contributions come from the s and d atomic orbitals. Thus, the Lu-Lu σ bond in C_{60} is likely a p-p σ bond. Previous studies have shown that the Lu-Lu bond is mainly contributed by s orbitals [18,19], in which the metal–metal bond is more like a s-s σ bond. Generally, the overlap of s orbitals is more effective than that of p orbitals, meaning that the s-s σ bond is much stronger than the p-p σ bond. On the other hand, the interaction between Lu_2 dimer and fullerene cage C_{60} is stronger with MBO values of 4.19 and 4.82 for $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$, respectively.

Table 2. Mayer bond order (MBO) and Wiberg bond order (WBO) of Lu-Lu bond, and hybrid compositions of M-M bond in the $\text{Lu}_2@\text{C}_{60}$ at the theoretical level of PBE/6-311G(d,p)-SDD.

Molecules	MBO	WBO	Atoms	Hybrid Composition
$\text{Lu}_2@I_h\text{-C}_{60}$	0.99	0.73	Lu1	s(26%)p(46%)d(28%)
			Lu2	s(36%)p(43%)d(21%)
$\text{Lu}_2@C_{2v}\text{-C}_{60}$	0.84	0.67	Lu1	s(26%)p(44%)d(30%)
			Lu2	s(28%)p(45%)d(27%)

In $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$, the Lu-Lu σ bond is mainly derived from p orbitals, for which the bond strength is related to the bond length. The Lu-Lu bond in $I_h\text{-C}_{60}$ with higher values of bond orders (0.99 for MBO and 0.73 for WBO, Table 2) show stronger bond strength than that in $C_{2v}\text{-C}_{60}$, because the shorter bond length in $I_h\text{-C}_{60}$ than that in $C_{2v}\text{-C}_{60}$.

2.4. Simulated Spectra of $\text{Lu}_2@\text{C}_{60}$

Figure 4 illustrates that the excitation energies of the first excited state of $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$ are 0.49 eV (2542 nm) and 0.47 eV (2637 nm), respectively, which are smaller than the first excitation energy of approximately 0.90 eV (1384 nm) for $\text{Lu}_2@\text{C}_{86}$ in both theory and experiment [16,19]. The excitation from S_0 to S_1 is primarily derived from the transition of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of $\text{Lu}_2@\text{C}_{60}$, and the energy required for this transition is $0.78 e^-$ and $0.61 e^-$ for $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$, respectively. As demonstrated in Figure 3 and Figure S3, the HOMO corresponds to the metal–metal bonding orbital and the LUMO corresponds to the metal–metal antibonding orbital and the π antibonding orbital in $\text{Lu}_2@\text{C}_{60}$, which is potential reason why their first excitation energy is low. The much lower first excitation energy and the ease of electron transition suggest the poor photochemical stability of $\text{Lu}_2@\text{C}_{60}$.

In addition, although the absorption peaks of $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$ isomers have similar shapes (Figure 4), there is a clear difference in their absorption strength,

which can be useful for distinguishing them in the future experiments. Specifically, $\text{Lu}_2@I_h\text{-C}_{60}$ exhibits a much stronger absorption peak at around 750 nm compared to $\text{Lu}_2@C_{2v}\text{-C}_{60}$. The absorption band at 200–700 nm for $\text{Lu}_2@C_{2v}\text{-C}_{60}$ is slightly wider than that of $\text{Lu}_2@I_h\text{-C}_{60}$. Furthermore, the IR spectra of $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$ were simulated (Figure S4) to evaluate their vibration models. These characterized absorption peaks in the vis-NIR and IR spectra can be beneficial for future characterization of $\text{Lu}_2@C_{60}$ in experiments.

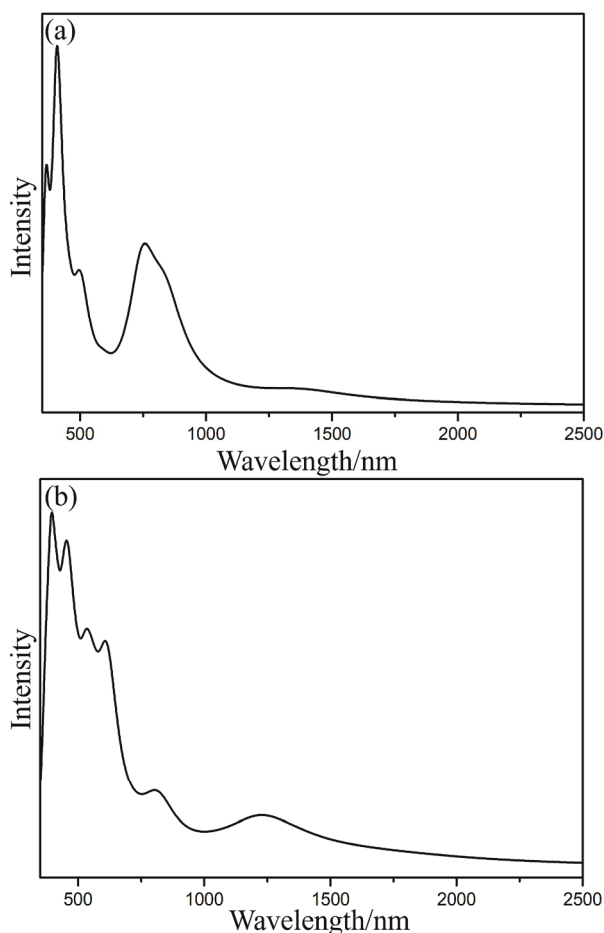


Figure 4. Simulated vis-NIR spectra of the $\text{Lu}_2@I_h\text{-C}_{60}$ (a) and $\text{Lu}_2@C_{2v}\text{-C}_{60}$ (b) isomers. The broadening function is Lorentzian and full width at half maximum is 0.30 eV.

3. Computational Methods

The optimizations of $\text{Lu}_2@C_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$ were carried out on the PBE/6-31G(d)~CEP-4G theoretical level [40,41], in which the basis function 6-31G(d) was used for the carbon atom and CEP-4G containing pseudopotential was used for the lutetium atom with valance electronic configuration of $4f^{14}5d^16s^2$. The frequencies were calculated on the same theoretical level for the optimized geometries of $\text{Lu}_2@C_{60}$, and all of them are free from imaginary frequency meaning the existence of local minima point for $\text{Lu}_2@C_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$. The PBE has been previously proved to be the suitable functional for the lutetium-based EMFs [18,19,42,43]. To obtain accurate energy and frontier molecular orbitals (FMOs), a single-point calculation was performed on the PBE/6-311G(d,p)~SDD theoretical level, in which a larger basis set 6-311G(d,p) [40] with polarization functions and SDD with effective core pseudopotential were used for the carbon and lutetium atoms, respectively. In order to confirm the calculated results on PBE, the hybrid functional PBE0 (PBE0/6-311G(d,p)~SDD//PBE0/6-31G(d)~CEP-4G) calculations were also carried out for both $\text{Lu}_2@C_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$. In order to

evaluate the effect of temperature, the Boltzmann distribution has been calculated for $\text{Lu}_2@C_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$. The formation energy for $\text{Lu}_2@C_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$ was calculated based on basis set superposition errors via counterpoise corrections on the theoretical level of PBE/6-311G(d,p)~SDD. NBO [44] analyses were also conducted on the PBE/6-311G(d,p)~SDD theoretical level. The vis-NIR spectra were simulated on the PBE/6-311G(d)~CEP-4G theoretical level. All the above calculations were carried out by Gaussian16 software package [45]. In addition, Mayer bond order (MBO) [46] together with localized molecular orbitals (LMOs) [47,48] analyses for $\text{Lu}_2@C_{60}$ were performed with the Multiwfn program [49].

4. Conclusions

Based on the $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$ which are related by a single-step Stone–Wales transformation, we provide insight into the confinement effects of fullerene on the metal–metal bonding. Although, in the $\text{Lu}_2@C_{60}$, there is a much shorter Lu–Lu bond length, its bond strength is a little weaker than the Lu–Lu bond in large fullerenes, because the Lu–Lu σ bond in C_{60} is likely a p–p σ bond with the contribution p orbital above 40% and a strong metal–cage interaction. Clearly, the confinement effects of fullerene play important roles in the geometry of the inner cluster, especially the bond length in the present work, and the electronic effect is more important for the bonding nature. Furthermore, the electronic configurations of $(\text{Lu}_2)^{4+}@C_{60}^{4-}$ were confirmed. Additionally, the vis-NIR spectra of $\text{Lu}_2@C_{2v}\text{-C}_{60}$ and $\text{Lu}_2@I_h\text{-C}_{60}$ were simulated, which could give some valuable information for the future experimental study on Lu-based EMFs.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/2304-6740/11/7/277/s1>, Figure S1: Several selected displacement vectors of $\text{Lu}_2@I_h\text{-C}_{60}$ with vibration frequencies, including the lowest vibration one; Figure S2: Several selected displacement vectors of $\text{Lu}_2@C_{2v}\text{-C}_{60}$ with vibration frequencies, including the lowest vibration one; Figure S3: Lowest unoccupied molecular orbitals (LUMO) with localization of $\text{Lu}_2@I_h\text{-C}_{60}$ (a) and $\text{Lu}_2@C_{2v}\text{-C}_{60}$ (b) with isovalue of 0.03 a.u. for the surface; Figure S4: IR vibration spectra for $\text{Lu}_2@I_h\text{-C}_{60}$ (a) and $\text{Lu}_2@C_{2v}\text{-C}_{60}$ (b). The broadening function is Gaussian function and full width at half maximum is 12 cm^{-1} ; coordinates for optimized geometries: $\text{Lu}_2@I_h\text{-C}_{60}$ and $\text{Lu}_2@C_{2v}\text{-C}_{60}$.

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Article

DFT Analysis of the Electronic and Structural Properties of Lanthanide Nitride Cluster Fullerenes $\text{Ln}_3\text{N@C}_{80}$

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Abstract: We have undertaken a DFT study of the nitride cluster fullerenes (NCFs) $\text{Ln}_3\text{N@C}_{80}$ for the complete series of fourteen lanthanides plus lanthanum by using the PBE functional with the Grimme's dispersion correction (PBE-D2). We tested the DN and DND basis sets, which are equivalent to 6-31G and 6-31G(d) Pople-type basis sets, respectively. Due to the known convergence problems when treating lanthanide-containing systems, only with the DN basis set was it possible to complete the calculations (geometry optimization and analysis of selected electronic parameters) for all the fifteen NCFs. We found that the bending of the Ln_3N cluster increases as the ionic radius increases, in general agreement with the available X-ray diffraction data. The Ln_3N cluster becomes more planar as the Ln–N bond length is contracted, and the C_{80} cavity slightly deforms. The HOMO–LUMO energies and distribution, as well as the charge and spin of the encapsulated metal ions, are analyzed.

Keywords: nitride cluster fullerenes; lanthanides; density functional theory; geometry; electronic parameters

1. Introduction

At the end of the last century, it was discovered experimentally that it was possible to trap atoms or molecules (A) inside fullerene cages (C_n): the resulting complexes are referred to as endohedral fullerenes (EFs or endohedral metallofullerenes, EMFs, when A species contains metals) of the general formula A@C_n . The new structures were related to promises of application in many areas of medicine as magnetic resonance imaging contrast agents, single-molecule magnets, electron-spin quantum computing, etc. [1–3]. This was the logical next step in the chemistry of carbon nanoclusters after the experimental discovery of the C_{60} molecule via mass spectrometry in 1985 [4,5], when the efforts to obtain new related systems with unique geometrical and electronic properties dramatically increased [6,7]. The A@C_n structures described until present are based on the combination of different atoms/molecules and fullerenes of variable size. In 1999, Dorn and collaborators [8] reported on the synthesis of $\text{Sc}_3\text{N@I}_h(7)\text{-C}_{80}$, a member of a new family of EFs named nitride clusterfullerenes (NCFs). The NCFs encapsulate an M_3N cluster where M usually is a rare-earth metal (Sc, Y or lanthanide), and the fullerene C_{2n} cage comprises different sizes ($60 < 2n < 88$) [9]. The M_3N cluster is made up of M^{3+} ions located at the vertices of a triangle, with the nitride N^{3-} in its center. Neither the M_3N cluster nor the $\text{C}_{2n}\text{-I}_h$ cage can be synthesized separately due to their lability, whereas their combination leads to the stabilization of NCF via the electron transfer of six electrons from the cluster to the carbon cage as it is suggested by experimental and theoretical data [10–12].

One of the most interesting NCF types is the one where the lanthanide (Ln) species are present in the internal cluster (Ln_3N) due to the presence of 4f-electrons in their electronic configuration. The Ln-based combinations exhibit long spin relaxation lifetimes [13–15] and intriguing geometrical characteristics [16–18]. In some cases, the encapsulated Ln_3N

cluster suffers deformation from planar topology, depending on the Ln metal and cavity size. In addition, changes can be observed in the Ln–N bond length, the Ln–N–Ln angle between Ln and N species, as well as the C_{2n} cage geometry. Such changes have been reported for a broad variety of cavity sizes and species [2,3,9].

A particularly interesting and important family is $Ln_3N@C_{80}$ NCFs. Here, one should emphasize that the previous experimental and theoretical research reports were limited to consideration of a few selected members of this family. The topology of the inner cluster has been analyzed both experimentally and theoretically. For example, this is the case for X-ray studies of Ln_3N bending in $Gd_3N@C_{80}$ [19], $Tb_3N@C_{80}$ [20], $Ho_3N@C_{80}$ [21] and $Er_3N@C_{80}$ [21,22]. For $Lu_3N@C_{80}$ [23], the encapsulated species has a planar structure, explained by the fact that Lu has the smallest ionic radius of all lanthanides. Interestingly, the X-ray structural analysis turns out to be a very challenging task, since until now it has been impossible to crystallize pure $Ln_3N@C_{80}$ NCFs; the ‘trick’ which is used to obtain experimental geometries is to co-crystallize NCF with nickel (II) octaethylporphyrin [19–23]. The interaction between the two interacting units is very strong, so one cannot be totally sure whether it does not alter the $Ln_3N@C_{80}$ geometry. In this regard, theoretical calculations within the framework of density functional theory (DFT) on isolated NCFs have an evident advantage in terms of excluding the external influence of the above sort. Within this area, one should mention several efforts to characterize the geometrical and electronic properties of NCFs. For example, Aparicio-Anglès et al. [16] showed for $M_3N@C_{80}$ (where $M = Sc, Y, La-Nd, Gd, Tb, Er, Tm$ and Lu), as well as for some other NCFs, that the bending of the M_3N cluster increases as the atomic radius increases. Additionally, Schlesier et al. [24] used DFT calculations to analyze the geometrical features of some $M_3N@C_{80}$ members (namely, mixed dysprosium–lanthanide $DyM_2N@C_{80}$ and $Dy_2MN@C_{80}$, where $M = Gd, Er, Tm$ and Lu), with a similar conclusion that the N atom is pushed out of the plane of Ln ions. On the other hand, to the best of our knowledge, the information on the frontier molecular orbital and spin density distribution in NCFs is rather scarce [7,25,26], with no published information on how they change during the step-by-step adding of 4*f*-electrons from La to Lu.

The changes in Ln–N bond lengths were analyzed previously both experimentally [21,27,28] and theoretically [16,24,29,30] for several NCFs. In particular, Olmstead et al. [21], Yang et al. [27] and Zuo et al. [28] reported the relevant experimental data for the Ho, Er, Dy and Tm NCFs. Aparicio-Anglès et al. [16] presented the DFT-calculated values for the Ln–N bond length for selected lanthanides including La–Nd, Gd, Tb and Er–Lu, and found it shortened as the ionic radius decreased. Both the above values and the ones reported by Schlesier et al. [24] and Gan et al. [29] for Gd, Dy, Er and Lu NCFs are in good agreement with the experimental parameters. On the other hand, again, there are no published DFT-calculated values comprising the complete lanthanide series.

In the present work we made an attempt to trace how the main geometrical and electronic properties of $Ln_3N@C_{80}$ NCFs change for the complete series from lanthanum to lutetium, that is, during the step-by-step addition of 4*f*-electrons. The DFT functional of choice was PBE, same as in the most systematic related study by Aparicio-Anglès et al. [16] (though, periodic plane wave calculations instead of cluster calculations were employed in their work). Nevertheless, our approach has an important difference from the latter, where for Tb, Er, Tm and Lu ions, having very deep 4*f* orbitals, the *f* electrons were considered for simplicity to be in the core (that is, included in the pseudopotential); in our case, to fulfill our goal, all the 4*f* electrons had to be included explicitly.

2. Results and Discussion

Selected geometrical parameters, orbital energies and other electronic properties for $Ln_3N@C_{80}$ NCFs were calculated by using the DN and DND basis sets (Tables 1–4 and Figures 1–7). We considered the complete series of lanthanides with the purpose of tracing the effect of a step-by-step adding of 4*f*-electrons on the selected geometrical and electronic

parameters of NCFs. It was also important to verify to what degree the results can vary when using the basis sets of different sizes.

Table 1. Three Ln–N bond lengths (in Å), Ln–N–Ln angles (in °), the pyramidalization (θ) angle of the Ln₃N cluster (in °), Ln···Ln distances (in Å), and the N···C_{C80} distance between N and the nearest C₈₀ aromatic ring (in Å) were calculated by using the DN basis set.

NFC	Ln–N (Å)	Ln–N–Ln (°)	θ (°)	Ln···Ln (Å)	N···C _{C80} (Å)
La ₃ N@C ₈₀	2.247, 2.260, 2.265	94.6, 95.8, 96.0	31.3	3.325, 3.345, 3.352	2.949
Ce ₃ N@C ₈₀	2.179, 2.223, 2.242	90.6, 93.5, 95.2	33.0	3.174, 3.206, 3.266	2.962
Pr ₃ N@C ₈₀	2.068, 2.082, 2.165	111.1, 113.5, 117.1	14.5	3.503, 3.540, 3.540	3.597
Nd ₃ N@C ₈₀	2.079, 2.086, 2.090	115.5, 116.7, 117.9	10.6	3.533, 3.550, 3.568	3.758
Pm ₃ N@C ₈₀	2.076, 2.085, 2.086	115.7, 117.0, 118.0	10.2	3.532, 3.550, 3.568	3.770
Sm ₃ N@C ₈₀	2.058, 2.059, 2.084	117.7, 118.8, 119.9	6.4	3.543, 3.564, 3.566	3.925
Eu ₃ N@C ₈₀	2.064, 2.065, 2.068	118.3, 119.2, 119.7	5.6	3.548, 3.564, 3.569	3.948
Gd ₃ N@C ₈₀	2.064, 2.065, 2.066	118.2, 119.1, 119.5	5.9	3.546, 3.56, 3.567	3.957
Tb ₃ N@C ₈₀	2.090, 2.108, 2.126	107.8, 109.4, 112.0	19.2	3.422, 3.441, 3.481	3.443
Dy ₃ N@C ₈₀	2.097, 2.112, 2.116	109.2, 109.2, 111.2	18.4	3.431, 3.446, 3.477	3.461
Ho ₃ N@C ₈₀	2.081, 2.128, 2.132	105.4, 109.3, 112.2	20.0	3.433, 3.496, 3.889	3.423
Er ₃ N@C ₈₀	2.069, 2.084, 2.086	112.0, 112.7, 115.3	15.3	3.444, 3.472, 3.508	3.617
Tm ₃ N@C ₈₀	2.056, 2.065, 2.092	110.8, 110.9, 118.6	15.1	3.415, 3.423, 3.543	3.593
Yb ₃ N@C ₈₀	2.022, 2.086, 2.088	109.0, 114.9, 116.7	15.0	3.398, 3.464, 3.497	3.543
Lu ₃ N@C ₈₀	2.047, 2.049, 2.050	118.8, 119.8, 120.0	3.9	3.528, 3.545, 3.548	3.985

Table 2. Three Ln–N bond lengths (in Å), Ln–N–Ln angles (in °), the pyramidalization (θ) angle of the Ln₃N cluster (in °), Ln···Ln distances (in Å), and the N···C_{C80} distance between N and the nearest C₈₀ aromatic ring (in Å) were calculated by using the DND basis set.

NFC	Ln–N (Å)	Ln–N–Ln (°)	θ (°)	Ln···Ln (Å)	N···C _{C80} (Å)
La ₃ N@C ₈₀	2.236, 2.251, 2.252	95.6, 97.0, 97.2	30.4	3.360, 3.366, 3.337	2.983
Ce ₃ N@C ₈₀	2.177, 2.223, 2.246	88.9, 92.7, 94.0	33.9	3.126, 3.184, 3.235	2.933
Pr ₃ N@C ₈₀	2.048, 2.120, 2.129	111.1, 114.2, 115.7	14.8	3.503, 3.508, 3.530	3.563
Nd ₃ N@C ₈₀	2.054, 2.310, 2.310	78.3, 99.8, 99.8	32.5	2.917, 3.343, 3.343	2.998
Eu ₃ N@C ₈₀	2.039, 2.090, 2.223	105.6, 109.3, 118.4	17.6	3.446, 3.487, 3.548	3.462
Gd ₃ N@C ₈₀	2.078, 2.093, 2.096	115.1, 115.3, 115.3	12.8	3.520, 3.526, 3.539	3.692
Dy ₃ N@C ₈₀	1.984, 2.304, 2.477	63.3, 93.8, 99.4	35.9	3.275, 3.277, 2.513	2.935
Tm ₃ N@C ₈₀	2.060, 2.123, 2.132	104.8, 107.8, 110.2	21.3	3.370, 3.388, 3.429	3.366
Yb ₃ N@C ₈₀	2.014, 2.084, 2.086	117.0, 117.1, 108.0	14.4	3.373, 3.494, 3.497	3.551
Lu ₃ N@C ₈₀	2.054, 2.054, 2.054	119.1, 119.6, 119.8	4.2	3.541, 3.550, 3.554	3.994

From La to Lu, the Ln₃N cluster shows geometrical changes in Ln–N bond lengths, Ln–N–Ln angles, Ln···Ln distances, N···C_{C80} distances (between N and the nearest C₈₀ ring), and the bending degree. These changes are due to the electrostatic repulsion between the fullerene cage and the Ln₃N unit, which depends on the size of the metal ion (Tables 1 and 2; Figures 1 and 2). In the case of Ln–N bond lengths, the DN results are close to the ones obtained previously experimentally [19–22,27,28,31] and theoretically [22–24,29,32,33], with the present DFT values tending to be slightly higher (except for Nd [16], Gd and Lu [16,24,33] NCFs). The average calculated values for La and Ho NCFs reach a maximum

discrepancy of 4.4% and 3.7% in comparison with the computational results of Gan et al. [29] and experimental values of Olmstead et al. [21], respectively. In general, the trend in Ln–N bond length changes can be described as follows: a notable contraction is observed from $\text{La}_3\text{N@C}_{80}$ (2.247–2.265 Å; Table 1 and Figure 1) to $\text{Gd}_3\text{N@C}_{80}$ (2.064–2.066 Å), then an increase for $\text{Tb}_3\text{N@C}_{80}$ (2.090–2.126 Å), followed by a gradual decrease until the end of the series, that is, $\text{Lu}_3\text{N@C}_{80}$ (2.047–2.05 Å). The largest span of Ln–N bond lengths was found for Pr (0.097 Å). The experimental values by Olmstead et al. [21], Yang et al. [27] and Zuo et al. [28] showed a similar reduction in Ln–N bond length in the series of Dy–Tm NCFs, as with the DFT-computed data reported previously [22–24,29,32,33]. In the present study, with the DN basis set, within the entire series two general situations can be observed: in most cases, only two Ln–N bonds have the same (or almost the same) length (La, Pr–Sm and Dy–Tm NCFs), whereas for the Eu, Gd and Lu NCFs, all three bond lengths are almost exactly equal.

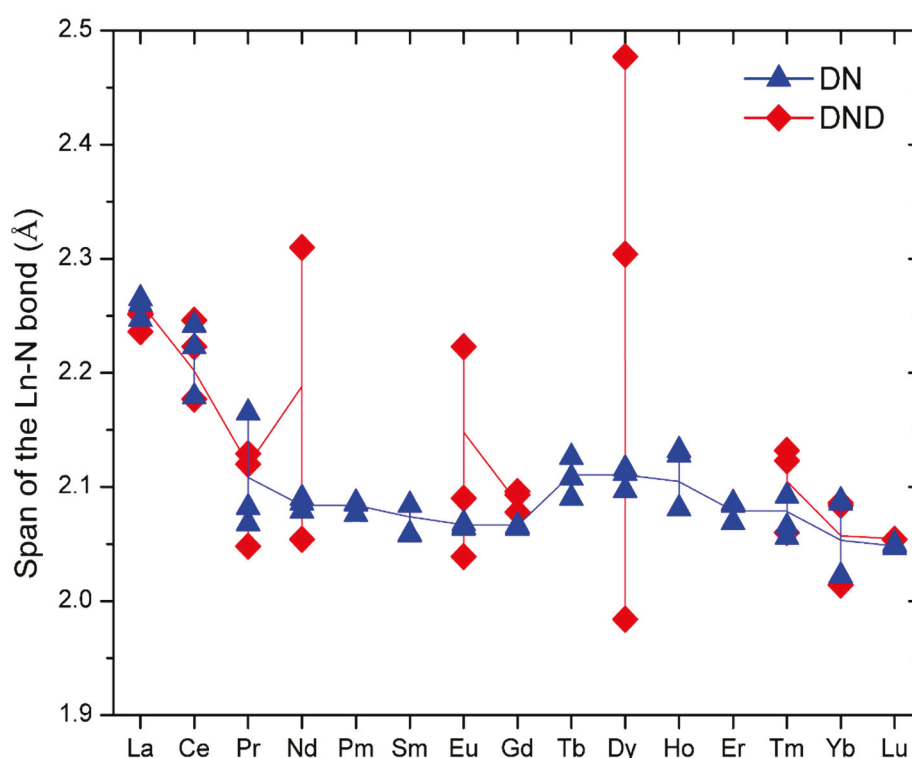


Figure 1. Comparison of the three Ln–N bond lengths in $\text{Ln}_3\text{N@C}_{80}$ NCFs calculated by using the DN and DND basis sets.

Regarding the geometries obtained with the DND basis sets (Table 2 and Figure 1), the general trend of Ln–N bond contraction can be seen in two (incomplete) series: La–Gd and especially Dy–Lu. However, this conclusion is not as straightforward as the one made for the DN basis set. The reason is that the use of the DND basis set results in too-rampant differences between the three Ln–N bond lengths, which are supposed to be more uniform, according to the experimental geometries ([21] and references therein). An especially ‘conflictive’ case is $\text{Dy}_3\text{N@C}_{80}$, for which the difference span reaches 0.493 Å, with the Dy–N bond lengths being 1.984, 2.304 and 2.477 Å; whereas the experimental ones are 2.017, 2.087 and 2.059 Å [21]; and the ones obtained with the DN basis set are 2.097, 2.112 and 2.116 Å (Table 1). The comparison of the two sets of results leads to a clear conclusion that, despite the prevailing idea that the use of a larger basis guarantees more realistic geometries (among other computed parameters), in the present case the smaller DN basis set is preferred to DND. In other words, for $\text{Ln}_3\text{N@C}_{80}$ NCFs we observe the same tendency as in the case of lanthanide ‘double-decker’ bisphthalocyanines that have been reported recently [34]. Taken together with the results of another study on Ln@C_{60}

endohedral fullerenes [35], where no substantial effect of the basis set (DN vs. DND) on the calculated parameters was found, one can strongly suggest the use of DN for further theoretical investigations of lanthanide-containing NCFs, polyazamacrocyclic and probably some other classes of Ln compounds (at least when using the DMol³ module). Hereafter in this section we will place emphasis on the parameters obtained with the DN basis set for the same reasons. Coming back to the Ln–N bond lengths (Figure 1), one final observation to mention is that a reasonably good match between the DN and DND-computed values was obtained only for five lanthanides: La, Ce, Gd, Yb and Lu.

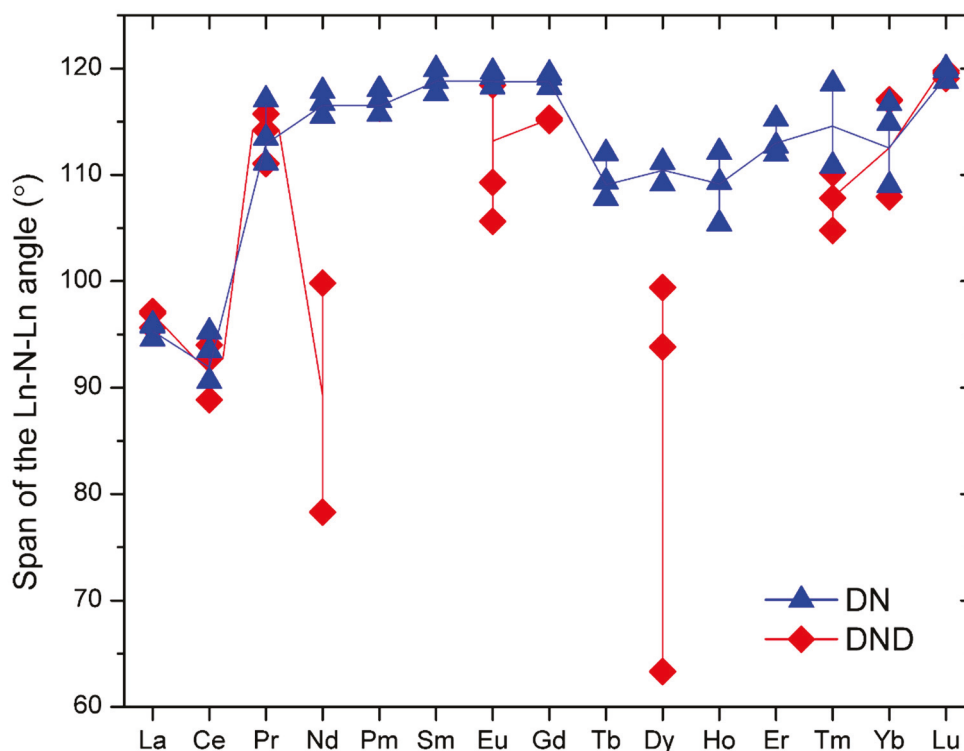


Figure 2. Comparison of the three Ln–N–Ln angles in Ln₃N@C₈₀ NCFs calculated by using the DN and DND basis sets.

Another important and closely related geometric parameter is the Ln–N–Ln angle (Tables 1 and 2; Figure 2), which directly reflects the effect of Ln₃N confinement within the C₈₀ cage. In the case of the DN basis set, the NCFs studied can be classified into two groups (though the difference between them is rather subtle): the three Ln–N–Ln values are notably different for Ce–Sm, Tb, Ho, Er and Yb; whereas for La, Eu, Gd, Dy, Tm and Lu, one value is different from the other two. The phenomenon of lanthanide contraction manifests itself in the general trend of increasing Ln–N–Ln angles in two separate series: Pr–Gd and Tb–Lu; in other words, the effect is not continuous from Pr to Lu. In addition, with the values for La and Ce NCFs, which have the largest Ln³⁺ ionic radii, the angles are much smaller than for all other Ln₃N@C₈₀ species, due to the strongest confinement. As a whole, this behavior correlates with the trends in the changes of Ln–N bond length; the larger Ln–N–Ln angles match the smaller Ln–N values. In the case of the DND basis set (Table 2; Figure 2), the changes in Ln–N–Ln angles from La to Lu are much more rampant, with very big differences between the three values for most NCFs, which is no surprise considering the results of the Ln–N bond length analysis presented above.

When comparing our results (obtained with the more reliable DN basis set) with that reported by other authors, for Er₃N@C₈₀ we found an average Er–N–Er angle of 113.3°, which differs from the experimental value [22] by 6%. In the case of Tb₃N@C₈₀ and Tm₃N@C₈₀, we obtained the average angles of 109.7° and 113.4°, respectively, which are up to 7% smaller than the values calculated by Aparicio-Anglès et al. [16], who used a

very different theoretical approach (periodic calculations without inclusion of a dispersion correction and explicit consideration of the 4*f*-electrons).

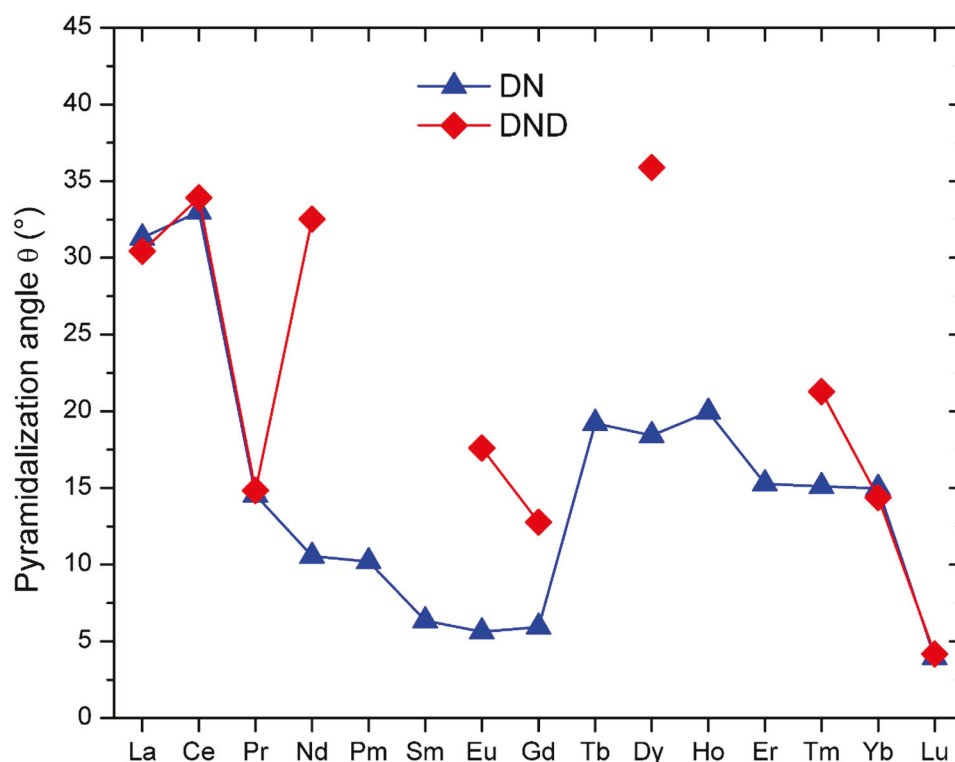


Figure 3. Pyramidalization (θ) angle in Ln_3N endohedral species calculated by using the DN and DND basis sets.

The bending of the Ln_3N cluster caused by the confinement within the C_{80} cage can also be characterized by the pyramidalization angle θ , which is referred to as one of the most important geometric parameters for NCFs [36]. Several experimental [19–21,23,37] and theoretical [6,16,24,33] reports showed that the Ln_3N cluster can acquire a planar or bent shape depending on the Ln metal and the size of the C_{2n} cavity. In most cases, large fullerene cages favor planar geometry [24]. The θ values obtained are summarized in Tables 1 and 2 and Figure 3. The ones obtained with the DN basis set exhibit more uniform behavior compared to the rampant ones calculated with DND, in particular, a more uniform decrease, which is split into two series of Ce–Gd and Tb–Lu. Only for La, Ce, Yb and Lu did the DN and DND values approximately coincide, with the lowest θ values of 3.9 and 4.2°, respectively, found for the Lu_3N cluster. As a whole, the θ angles presented here are larger compared to the experimental [19–21,28] and DFT-calculated ones [16–20,28] reported by other authors, and again, the DN basis set yields more realistic results. On the other hand, it is difficult to explain why the experimental θ values for the central lanthanides Gd, Tb and Dy uniformly decrease (14.6, 12.6 and 7.4°, respectively; [21] and references therein), but the DN-computed angles jump from 5.9° for Gd to 19.2° and to 18.4° for Tb and Dy, respectively. One should remember, however, that the experimental values were obtained for NCF–Ni(II) octaethylporphyrin co-crystals (where solvent molecules are present as well), and it remains unclear how the solid-state environment can influence the geometry of encapsulated Ln_3N species.

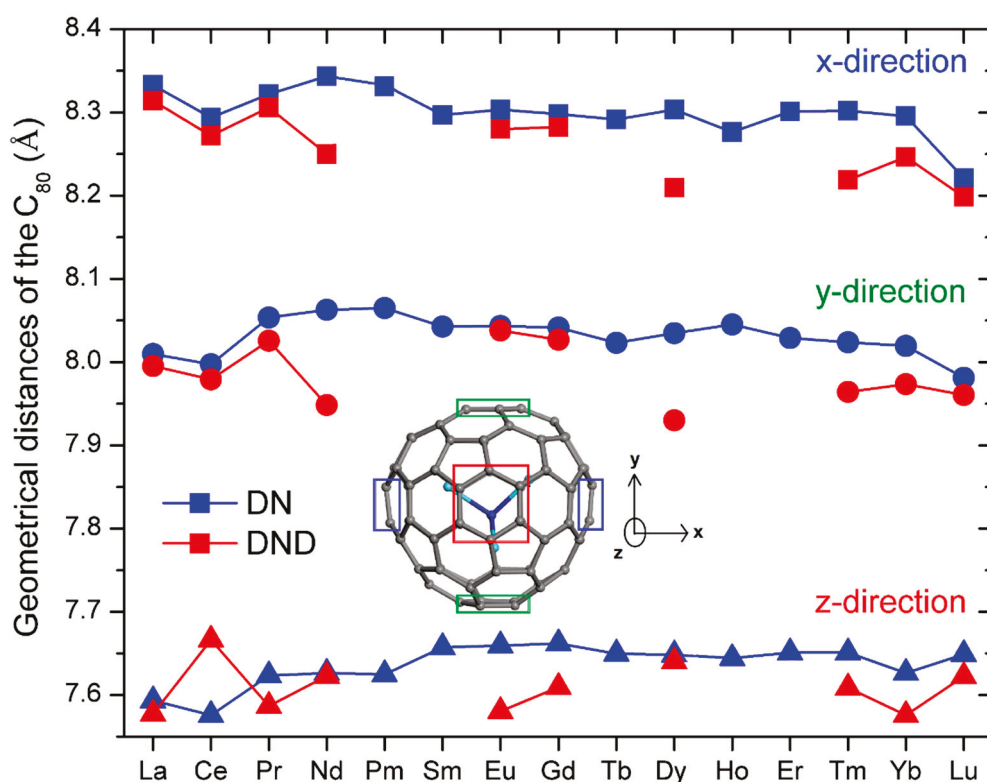


Figure 4. Average distances between opposite aromatic rings of fullerene cage in $\text{Ln}_3\text{N}@\text{C}_{80}$ NCFs calculated by using the DN and DND basis sets. The x - (horizontal), y - (vertical) and z -directions (into the plain of view) are considered, as explained by the inset.

Other geometric parameters of interest are the $\text{Ln} \cdots \text{Ln}$ and $\text{N} \cdots \text{C}_{80}$ distances (between the N atom and the nearest hexagon/pentagon ring of C_{80} cage) [16,29], which directly depend on the bending of the Ln_3N cluster (Tables 1 and 2; Figures S1 and S2 of the Electronic Supplementary Information). For example, the $\text{N} \cdots \text{C}_{80}$ distances exhibit behavior opposite to the behavior of the θ values, since the increase in pyramidalization results in a closer approach of the N atom to the fullerene cage.

The presence of encapsulated bulky Ln_3N clusters leads to slight geometrical changes in the geometry of the C_{80} cage. It can be expressed in different ways. As Figure 4 explains, the way we did it is to measure average distances between two opposite C–C bonds in the x -direction, between two opposite pentagonal rings in the y -direction, and between two opposite hexagons in the z -direction. As calculated with the DN basis set, the C_{80} cage exhibits relatively stable geometry with variations of 0.12 (x -direction), 0.08 (y -direction) and 0.09 Å (z -direction) between the maximum (La and Nd for x -; Pm for y -; Sm–Gd for z -direction) and minimum (Lu for x - and y -directions; Ce for z -direction) distances. As a general trend, the cage is compressed in the x - and y -directions, and at the same time slightly elongates in the z -direction, as the atomic number of lanthanides increases. Like for all the above parameters analyzed, the use of the DND basis sets yields very rampant values without clear trends.

Table 3. HOMO, LUMO and HOMO-LUMO gap energies (in eV), as well as the charge and spin values (in *e*; formal spin of Ln atom in parenthesis) for Ln₃N@C₈₀ NCFs calculated by using the DN basis set.

NFC	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	Charge (<i>e</i>)		Spin (<i>e</i>) ^a	
				Ln	N	Ln	N
La ₃ N@C ₈₀	−6.012	−4.640	1.371	0.447, 0.467, 0.486	−0.925	0, 0, 0 (0)	0
Ce ₃ N@C ₈₀	−5.818	−4.956	0.862	0.397, 0.415, 0.439	−0.809	0.948, 0.992, 1.044 (1)	0.042
Pr ₃ N@C ₈₀	−5.500	−4.798	0.702	0.303, 0.352, 0.353	−0.453	2.063, 2.072, 2.103 (2)	0.051
Nd ₃ N@C ₈₀	−5.923	−4.983	0.941	0.160, 0.178, 0.180	−0.634	3.147, 3.162, 3.179 (3)	0.179
Pm ₃ N@C ₈₀	−5.976	−5.248	0.728	0.054, 0.070, 0.080	−0.696	4.223, 4.256, 4.268 (4)	0.066
Sm ₃ N@C ₈₀	−5.956	−5.660	0.296	0.424, 0.434, 0.463	−0.837	5.441, 5.446, 5.474 (5)	0.446
Eu ₃ N@C ₈₀	−5.940	−5.868	0.072	0.426, 0.441, 0.469	−0.857	6.646, 6.649, 6.661 (6)	0.627
Gd ₃ N@C ₈₀	−6.046	−4.589	1.457	0.496, 0.512, 0.527	−0.992	6.899, 6.934, 6.935 (7)	0.028
Tb ₃ N@C ₈₀	−5.979	−5.791	0.189	0.409, 0.430, 0.454	−0.827	5.519, 5.520, 5.530 (6)	0.198
Dy ₃ N@C ₈₀	−5.974	−5.900	0.074	0.412, 0.412, 0.435	−0.824	4.338, 4.387, 4.409 (5)	0.109
Ho ₃ N@C ₈₀	−5.952	−5.882	0.070	0.457, 0.499, 0.505	−0.862	3.350, 3.360, 3.384 (4)	0.058
Er ₃ N@C ₈₀	−5.961	−5.872	0.089	0.467, 0.487, 0.542	−0.878	2.377, 2.393, 2.421 (3)	0.083
Tm ₃ N@C ₈₀	−5.960	−5.835	0.125	0.368, 0.375, 0.420	−0.822	1.263, 1.268, 1.273 (2)	0.005
Yb ₃ N@C ₈₀	−5.942	−5.859	0.083	0.417, 0.420, 0.445	−0.855	0.012, 0.099, 0.110, (1)	0.053
Lu ₃ N@C ₈₀	−6.034	−4.506	1.528	0.557, 0.584, 0.595	−1.074	0, 0, 0 (0)	0

^a Absolute values.

Tables 3 and 4 summarize the calculated HOMO, LUMO and HOMO-LUMO gap (E_{gap}) energies, as well as the charge and spin (from Mulliken population analysis) of Ln and N atoms as calculated with the DN and DND basis sets. For the frontier orbital energies, obtained with either the DN or DND basis set, no clear trend is observed (Tables 3 and 4), with La, Gd and Lu NCFs having similar values for LUMO energies with both basis sets. The DN-calculated E_{gap} energies (Table 3) tend to decrease in the entire NCF series, with the exception of the ‘jumping-back’ values for Nd, Gd and Lu derivatives. These species with totally empty (La), half-filled (Gd) and totally filled (Lu) 4*f* orbitals exhibit the highest gap values of 1.371, 1.457 and 1.528 eV, respectively; these results are in good agreement with the DFT-calculated values by Zhu et al. [38]. As a whole, E_{gap} spans from 0.070 (Ho₃N@C₈₀) to 1.528 eV (Lu₃N@C₈₀) with DN, and from 0.084 (Dy₃N@C₈₀) to 1.485 eV (La and Lu₃N@C₈₀), with no clear trend, when the DND basis set is used (Table 4). Here, it is appropriate to mention that the GGA functionals (including PBE) tend to underestimate HOMO-LUMO gap energies, and we present the values obtained simply to illustrate their relative behavior from La to Lu.

Table 4. HOMO, LUMO and HOMO-LUMO gap energies (in eV), as well as the charge and spin values (in *e*; formal spin of Ln atom in parenthesis) for Ln₃N@C₈₀ NCFs calculated by using the DND basis set.

NFC	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	Charge (<i>e</i>)		Spin (<i>e</i>) ^a	
				Ln	N	Ln	N
La ₃ N@C ₈₀	−5.769	−4.284	1.485	0.962, 0.962, 0.962	−1.021	0, 0, 0 (0)	0
Ce ₃ N@C ₈₀	−5.459	−4.695	0.764	0.829, 0.837, 0.838	−0.889	1.052, 1.079, 1.101 (1)	0.116
Pr ₃ N@C ₈₀	−5.214	−4.537	0.677	0.050, 0.082, 0.086	−0.758	2.047, 2.047, 2.065 (2)	0.051
Nd ₃ N@C ₈₀	−5.579	−5.140	0.438	0.060, 0.164, 0.174	−0.545	3.185, 3.220, 3.297 (3)	0.127
Eu ₃ N@C ₈₀	−5.649	−5.558	0.090	0.888, 0.907, 0.907	−0.933	6.567, 6.608, 6.703 (6)	0.243

Table 4. Cont.

NFC	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	Charge (e)		Spin (e) ^a	
				Ln	N	Ln	N
Gd ₃ N@C ₈₀	−5.739	−4.365	1.373	0.854, 0.857, 0.857	−1.136	6.866, 6.910, 6.913 (7)	0.031
Dy ₃ N@C ₈₀	−5.634	−5.550	0.084	0.696, 0.867, 0.901	−0.742	4.175, 4.159, 4.446 (5)	0.261
Tm ₃ N@C ₈₀	−5.673	−5.573	0.100	0.819, 0.823, 0.832	−0.964	1.266, 1.282, 1.288 (2)	0.114
Yb ₃ N@C ₈₀	−5.650	−5.563	0.088	0.845, 0.862, 0.862	−1.012	0.014, 0.114, 0.122 (1)	0.085
Lu ₃ N@C ₈₀	−5.758	−4.272	1.485	0.882, 0.884, 0.884	−1.215	0, 0, 0 (0)	0

^a Absolute values.

As we mentioned in Introduction, the I_h -C₈₀ fullerene is a very reactive molecule per se [1,3], but its combination with some other species (M₃N, M₂, etc.) gives stable complexes [1,2,9,10,39,40]; this stabilizing effect is due to electron transfer from the encapsulated species to the carbon cage. Formally, in the case of rare-earth derivatives M₃N@C₈₀, the M₃N cluster is supposed to donate six electrons to C₈₀. Nevertheless, it turns out that the “actual” charges are very different from “formal” charges, which are integers and imply that the cluster–cage bonding is purely ionic. This aspect was addressed in several theoretical studies (on representative Sc₃N@C₈₀), which found that the calculated net Sc₃N charges are also much smaller than the values expected for the purely ionic bonding [41,42]; for example, around +1, either from the Mulliken or Hirshfeld population analysis [42]. This effect is referred to as “back-donation” [43,44]. Additionally, in our calculations, the actual positive charge on Ln atoms (Tables 3 and 4; from the Mulliken population analysis) was much lower than the “formal” charge of +3; in particular, it spans from 0.054–0.080 e (Pm₃N) to 0.557–0.595 e (Lu₃N) with the DN basis set, and from 0.050–0.086 e (Pr₃N) to 0.962 e (La₃N) with DND. For the N atom, the values vary from −0.453 e (Pr₃N) to −1.074 e (Lu₃N) with DN, and from −0.545 e (Nd₃N) to −1.215 e (Lu₃N) with DND. The DN-calculated absolute values are generally lower than the DND ones. It is interesting and important to mention the observation that the use of a smaller basis set produces more reliable results for the Mulliken population analysis [45–47].

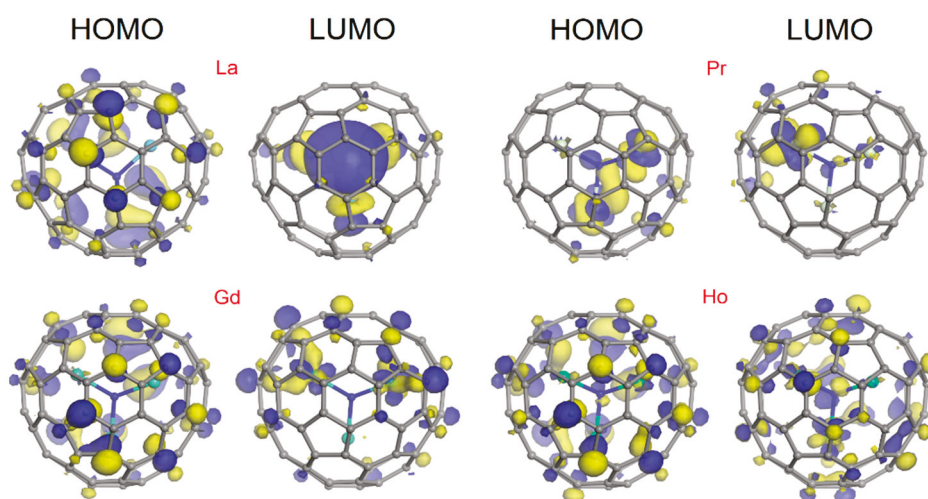


Figure 5. Selected patterns of HOMO-LUMO distributions (isosurfaces at 0.03 a.u.) in Ln₃N@C₈₀ NCFs calculated by using the DN basis set.

Figure 5 shows the selected patterns of the HOMO and LUMO distribution obtained with the DN basis set. After analyzing these plots for the complete NCF series, it was not possible to classify them in a simple way due to a large variability in the results (with both basis sets). Here, we show the four most distinctive cases (La, Pr, Gd and Ho NCFs) obtained with the DN basis set (the reader can find all the plots for the fifteen NCFs in

Electronic Supplementary Information, in Figures S3–S6; with the aim of completeness of the graphical presentation, both the front and the side views are included.) As can be seen in Figure 5, the HOMO lobes in the case of La and Gd NCFs are very similar: they are localized on the C₈₀ cage, with no apparent contribution from the Ln₃N cluster. In the case of Ho NCF, the HOMO distribution on fullerene cage is rather similar to the one found for La and Gd complexes, but a minor contribution from the Ho₃N cluster can be observed as well. For Pr₃N@C₈₀, the HOMO lobes are localized mostly on two Pr atoms, whereas the contribution from the C₈₀ cage is minimal. For the LUMO density, the lobes on Ln and N atoms are of highly variable size; of the ones presented in Figure 5, the largest ones can be seen for the La₃N cluster. The LUMO lobes on the fullerene cage almost vanish for La, Ce, Nd, Pm, Sm and Tb NCFs. The results obtained with DND (Figures S5–S6) only partially match the ones calculated by using the DN basis set.

As compared to the formal spin for isolated Ln³⁺ ions, the results obtained with the DN and DND basis sets (Tables 3 and 4; Figure 6) show the possibility of spin transfer both to and from lanthanide species. In the DN data set (Table 3), spin depletion from Ln can be observed for Ce (but from two cerium atoms only) and the late lanthanides Gd–Yb (by up to 0.890–0.988 *e* for Yb, compared to to the formal spin of 1 *e* for isolated Yb³⁺); this can be also seen from Figure 6 (here we plotted the average values for simplicity). The early lanthanides Pr–Eu tend to acquire additional spin, with the strongest increase by 0.646–0.661 *e* observed for Eu (compared to the formal spin of 6 *e* for isolated Eu³⁺). For La and Lu ions with totally empty and totally filled 4*f* orbitals, respectively, the spin remains to be zero. The limited available values calculated by using the DND basis set (Table 4 and Figure 6) follow a similar trend.

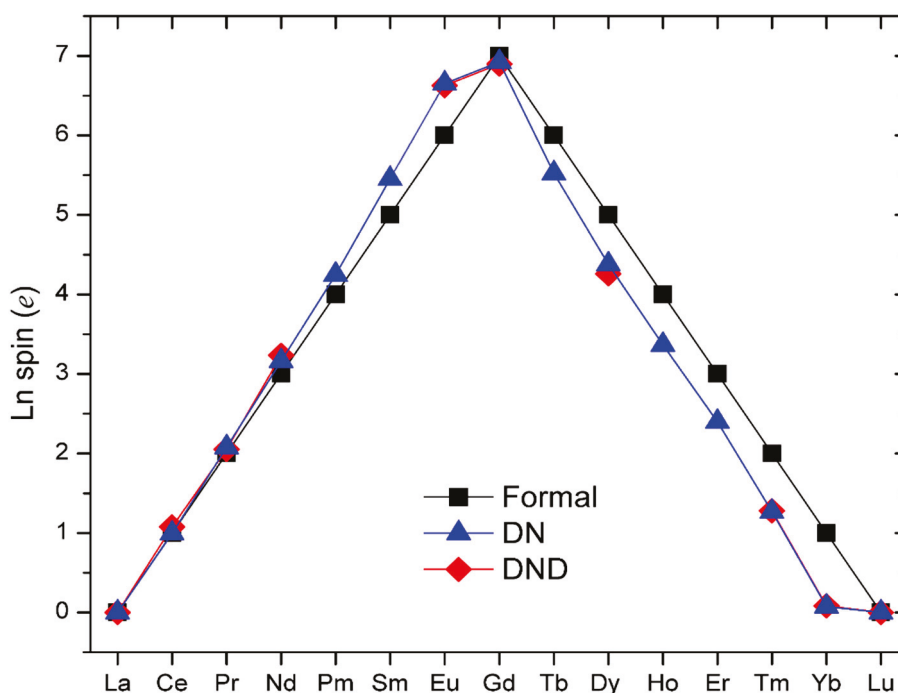


Figure 6. Comparison of the average spin of three Ln ions in Ln₃N@C₈₀ NCFs calculated by using the DN and DND basis sets with the formal spin of isolated Ln³⁺ ions.

The spin density plots for Ln₃N@C₈₀ NCFs presented in Figure 7 (the DN data set) cannot serve as a similar quantitative measure of spin transfer, but instead are more illustrative, especially in order to show variability in spin alignment. In the most simplistic terms of spin distribution, they can be classified into three general cases. The first one includes La and Lu NCFs (with the closed-shell electronic configuration of Ln species), where no unpaired electrons can be found on either the Ln₃N cluster or C₈₀ cage (the corresponding side views are shown in Figure S7). In the case of Ce–Nd and Gd NCFs, the main contribu-

tion comes from the Ln_3N cluster, where the largest lobes are localized on metal species. For the remaining NCFs (Pm–Eu, Tb–Yb), spin density can be found on both the cluster and fullerene cage. In the calculations with the DND basis set, qualitatively similar spin density plots were obtained (Figures S8 and S9 of the Electronic Supplementary Information).

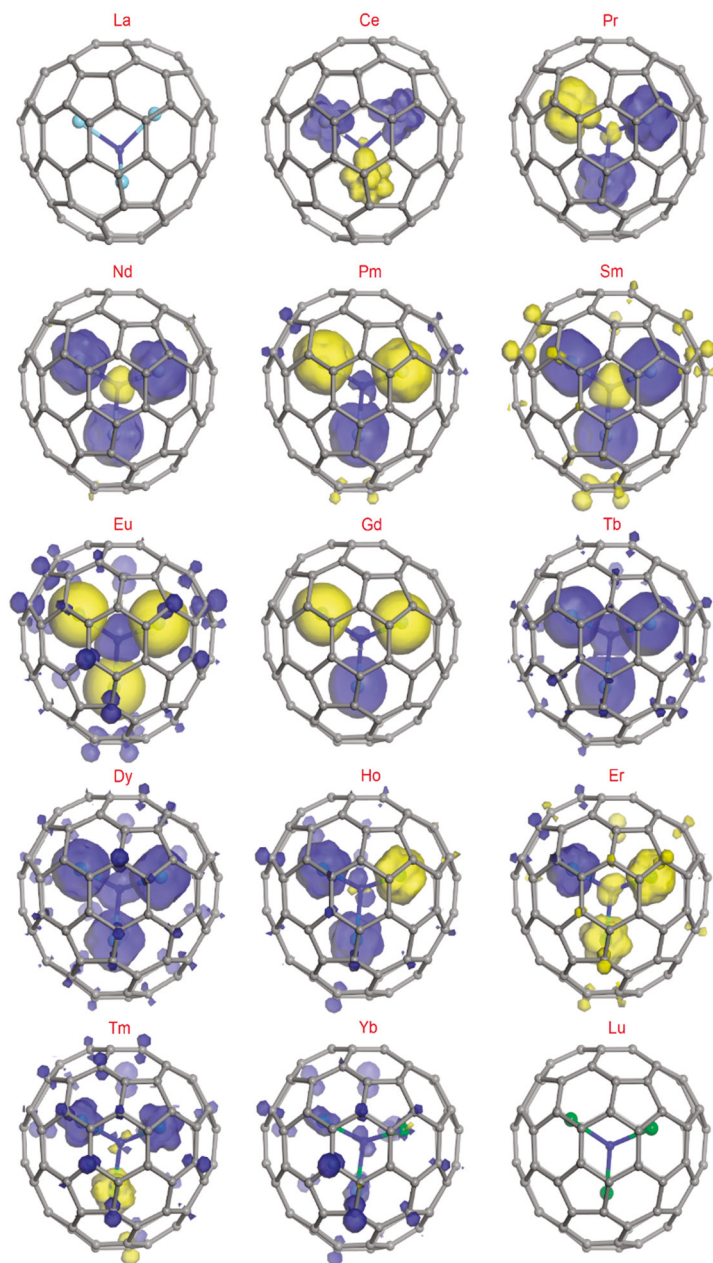


Figure 7. Spin density plots (isosurfaces at 0.02 a.u.) for $\text{Ln}_3\text{N}@C_{80}$ complexes as calculated by using the DN basis set. Blue and yellow lobes correspond to spin-up and spin-down electrons, respectively.

As regards the spin-up and spin-down directions, they turned out to be broadly variable as well. When considering Ln_3N cluster only, all the NCFs can be classified into the following groups: (1) the spin directions of all four atoms coincide (spin-up) for Tb, Dy and Yb; (2) the spin directions of three Ln atoms coincide, but for the N atom it is the opposite, which is observed for Nd, Sm and Eu; (3) the spin directions of Ln atoms differ (2 + 1) for all the remaining NCFs (Ce, Pr, Pm, Gd, Ho, Er and Tm). One should also note that in three cases of Tb, Dy and Yb derivatives, the spin directions of Ln_3N atoms (spin-up) are the same as those of the small lobes found on the carbon atoms of the C_{80} cage.

3. Computational Methods

The theoretical analysis of the geometries and electronic properties of $\text{Ln}_3\text{N@C}_{80}$ NCFs was performed by using the numerical-based DFT module DMol³, which is a part of the Materials Studio 8.0 software package [48–51]. The Perdew–Burke–Ernzerhof (PBE) general gradient approximation functional [52] was employed in combination with the empirical dispersion correction developed by Grimme [53], usually referred to as PBE-D (or PBE-D2). The previous computational method was successfully used in our previous studies involving C_{80} -based dyads [25,54], as well as in numerous studies by other research groups on systems that include metal species and carbon nanoclusters.

The DN (with no polarization functions added) and DND (with a polarization *d*-function added on all non-hydrogen atoms) double-numerical basis sets were employed, which are equivalent to the 6-31G and 6-31G(d) Pople-type basis sets. The full geometry optimization and the calculation of the electronic parameters were performed with the DFT semi-core pseudopotentials (DSPPs), including relativistic and spin-orbit coupling effects, whose account is important due to the presence of the lanthanide species. In the calculations with the DN basis set, the real space cutoff (defined by the presence of lanthanide species) was 4.3 Å and a DND of 5.0 Å. The convergence criteria were as follows: For the DN basis set, an energy gradient of 10^{-4} Ha/Å, maximum force of 0.02 Ha/Å, maximum displacement of 0.05 Å, and SCF tolerance of 10^{-4} Ha; for the DND basis set, an energy gradient of $2 \cdot 10^{-5}$ Ha/Å, maximum force of 0.004 Ha/Å, maximum displacement of 0.005 Å, and SCF tolerance of 10^{-5} Ha.

The existence of 4*f* orbitals results in a high number of degenerate states near the Fermi level, which has a serious negative impact on the self-consistent field (SCF) convergence. Thermal smearing was employed as an indispensable tool to solve the (almost always inevitable) SCF convergence problems according to the general protocol explained in the previous studies [55,56]. It was found that the use of a very low value of 0.0001 Ha (equivalent temperature of 31.6 K) yields stable and consistent results. At the same time, even with the use of thermal smearing tools, only for the DN basis set was a successful convergence afforded for all $\text{Ln}_3\text{N@C}_{80}$ NCFs. With DND, we were unable to finish the calculations for Pm-, Sm-, Tb-, Ho- and Er-containing systems.

4. Conclusions

The most important results can be summarized as follows.

(1) The geometry optimization and electronic parameter calculation for the series of fifteen $\text{Ln}_3\text{N@C}_{80}$ NCFs ($\text{Ln} = \text{La-Lu}$) was possible to complete only with the DN basis set. The use of DND basis sets leads to SCF convergence problems, due to which it was impossible to obtain the results for Pm-, Sm-, Tb-, Ho- and Er-containing systems. Furthermore, within the NCFs for which the computations seemed to be successful, too-rampant behavior was observed for most important geometric parameters (including the Ln–N bond lengths, Ln–N–Ln angles, and pyramidalization angle θ), which is supposed to be more uniform and logical.

(2) For the frontier orbital energies, obtained with either the DN or DND basis set, no clear trend is observed. The DN-calculated E_{gap} energies tend to decrease in the entire NCF series, with the exception of the ‘jumping-back’ values for Nd, Gd and Lu derivatives. These species with totally empty (La), half-filled (Gd) and totally filled (Lu) 4*f* orbitals exhibit the highest gap values of 1.371, 1.457 and 1.528 eV, respectively, which are in good agreement with the DFT results reported elsewhere. The corresponding HOMO and LUMO distribution patterns are highly variable.

(3) The calculated “actual” positive charge on Ln atoms, as estimated from the Mulliken population analysis, is much lower than the “formal” charge of +3; it spans from 0.054–0.080 *e* (Pm_3N) to 0.557–0.595 *e* (Lu_3N) with the DN basis set, and from 0.050–0.086 *e* (Pr_3N) to 0.962 *e* (La_3N) with DND. Similarly, for the N atom, the values vary from −0.453 *e* (Pr_3N) to −1.074 *e* (Lu_3N) with DN, and from −0.545 *e* (Nd_3N) to −1.215 *e* (Lu_3N) with DND. These results are in good agreement with the known effect of “back-donation”.

(4) As compared to the formal spin for isolated Ln^{3+} ions, the results obtained show the possibility of spin transfer both to and from lanthanide species. In the DN data set, spin depletion from Ln can be observed for Ce (but from two cerium atoms only) and the late lanthanides Gd–Yb, with it being up to 0.890–0.988 e for Yb. The early lanthanides Pr–Eu tend to acquire additional spin, with the strongest increase by 0.646–0.661 e observed for Eu. For La and Lu ions with totally empty and totally filled $4f$ orbitals, respectively, the spin remains to be zero. The spin density plots reveal interesting features in terms of localization of unpaired electrons, as well as spin alignment.

Supplementary Materials: Supplementary data associated with this article can be found in the online version at <https://www.mdpi.com/article/10.3390/inorganics11050223/s1>. Figure S1: Comparison of the $\text{Ln} \cdots \text{Ln}$ distance (Å) in $\text{Ln}_3\text{N}@\text{C}_{80}$ NCFs calculated by using the DN and DND basis sets; Figure S2: Comparison of the $\text{N} \cdots \text{C}_{\text{C}_{80}}$ distance (Å) of the $\text{Ln}_3\text{N}@\text{C}_{80}$ complexes calculated by using the DN and DND basis sets; Figure S3: Complete patterns of HOMO–LUMO distribution (front views with isosurfaces at 0.03 a.u.) in $\text{Ln}_3\text{N}@\text{C}_{80}$ NCFs calculated by using the DN basis set; Figure S4: Complete patterns of HOMO–LUMO distribution (isosurfaces at 0.03 a.u.) in $\text{Ln}_3\text{N}@\text{C}_{80}$ NCFs but rotated at an angle of 90° to the left (side view) with respect to Figure S3; Figure S5: Patterns of HOMO–LUMO distribution (front views with isosurfaces at 0.03 a.u.) in $\text{Ln}_3\text{N}@\text{C}_{80}$ NCFs calculated by using the DND basis set; Figure S6: Patterns of HOMO–LUMO distribution (isosurfaces at 0.03 a.u.) in $\text{Ln}_3\text{N}@\text{C}_{80}$ NCFs but rotated at an angle of 90° to the left (side views) with respect to Figure S5; Figure S7: Spin density plots (isosurfaces at 0.02 a.u.) for $\text{Ln}_3\text{N}@\text{C}_{80}$ NCFs calculated by using the DN basis set but rotated an angle of 90° to the left (side views) with respect to Figure 7. Blue and yellow lobes correspond to spin-up and spin-down electrons, respectively; Figure S8: Spin density plots (isosurfaces at 0.02 a.u.) for $\text{Ln}_3\text{N}@\text{C}_{80}$ NCFs were calculated by using the DND basis set. Blue and yellow lobes correspond to spin-up and spin-down electrons, respectively; Figure S9: Spin density plots (isosurfaces at 0.02 a.u.) for $\text{Ln}_3\text{N}@\text{C}_{80}$ NCFs calculated by using the DND basis set but rotated an angle of 90° to the left (side views) with respect to Figure S8.

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Metalloborospherene Analogs to Metallofullerene

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Abstract: Boron, the neighbor element to carbon in the periodic table, is characterized by unique electron deficiency that fosters multicenter delocalized bonding, contributing to its diverse chemistry. Unlike carbon cages (fullerenes), which preserve their structural integrity under endohedral or exohedral doping, larger boron cages (borospherenes) exhibit diverse structural configurations. These configurations can differ from those of pure boron cages and are stabilized by various metals through unique metal–boron bonding, resulting in a variety of metalloborospherenes. Due to boron’s electron deficiency, metalloborospherenes exhibit fascinating chemical bonding patterns that vary with cluster size and the type of metal dopants. This review paper highlights recent advancements in metalloborospherene research, drawing comparisons with metallofullerenes, and focuses on the use of transition metals, lanthanides, and actinides as dopants across various cage dimensions.

Keywords: fullerene; borospherene; metal-containing cages; analogs; clusters

1. Introduction

The discovery and characterization of fullerenes, a class of carbon cage structures, have profoundly impacted various fields of chemistry and materials science. Fullerenes, composed predominantly of pentagonal and hexagonal carbon rings, exhibit remarkable stability due to their unique sp^2 hybridization and delocalized π -electron system [1,2]. Among these, C_{60} , known as buckminsterfullerene, is the most well-known and stable fullerene, characterized by a structure comprising 12 pentagons and 20 hexagons [3,4]. This stability is attributed to the Isolated Pentagon Rule (IPR), which states that no two pentagons should share an edge, minimizing strain in the carbon network [5].

Boron, a neighbor of carbon in the periodic table, forms analogous cage-like structures known as borospherenes, first discovered in the B_{40}^- cage [6]. Unlike carbon, boron is electron-deficient, which gives rise to the formation of multicenter bonds to stabilize its structures [7,8]. This electron deficiency leads to diverse bonding patterns, including delocalized σ and π bonds, which stabilize planar or quasi-planar clusters for boron clusters up to B_{38}^- [6,9]. This delocalized bonding scheme imparts extraordinary stability to planar boron clusters due to multiple aromaticities, where the number of delocalized electrons satisfies the $(4n + 2)$ Hückel rule, analogous to hydrocarbons [10]. However, larger boron cages, such as the seashell-like chiral B_{28} cluster and the B_{40}^- , adopt fullerene-like structures [6,11] that are stabilized through delocalized multicenter bonding to maintain the structural integrity despite their larger size.

The unique electronic properties of boron make it an excellent candidate for forming stable metalloborospherenes through metal doping [7]. These structures can be stabilized by incorporating various metals, leading to significant changes in their geometrical and electronic configurations. Metalloborospherenes exhibit a range of fascinating bonding patterns and structural motifs that evolve with cluster size and metal composition. This review compares recent advancements in metalloborospherene research with metallofullerene

studies, focusing on transition metals, lanthanides, and actinides as dopants in various cage dimensions.

Metallofullerenes are formed by encapsulating metal atoms within fullerene cages, such as C_{60} or its analogs, using methods like arc discharge, laser ablation, and chemical vapor deposition [12,13]. The encapsulated metal atoms significantly influence the properties of fullerenes, leading to various applications in materials science, medicine, and catalysis. For example, in materials science, metallofullerenes are used to enhance the mechanical and electronic properties of composite materials. In medicine, they are explored for drug delivery systems and diagnostic imaging due to their ability to encapsulate therapeutic agents or contrast materials [14–16]. By comparison, metalloborosphenes, though less understood, involve substantial interactions between the metal atoms and the boron framework. These interactions result in unique structural and electronic properties that differ significantly from those of metallofullerenes. Metalloborosphenes exhibit complex bonding patterns and structural motifs that evolve with cluster size and the type of metal dopant. The incorporation of different metals can lead to a variety of electronic properties, making metalloborosphenes potentially valuable for applications in catalysis, electronics, and nanotechnology [7,17]. Understanding these properties requires further research, but the potential for discovering new materials with tailored functionalities is significant.

Recent studies have explored the incorporation of lanthanide atoms within borosphenes; $La_3B_{18}^-$ was the first observed metalloborospherene [18], and exhibits distinctive bonding interactions due to charge transfer and significant $(d-p)\pi$ and $(d-p)\delta$ bonding [19,20]. These interactions lead to novel structural motifs, including inverse-sandwich and trihedral configurations, which are not commonly observed in other types of boron clusters [18,21]. Similarly, transition-metal-based and actinide-based metalloborosphenes have been theoretically predicted, revealing complex electronic structures and unique bonding patterns that differ from those of their lanthanide counterparts [22,23]. These theoretical predictions indicate the possibility of forming stable complexes with actinides, which could have implications for both fundamental chemistry and potential applications. Although the study of metalloborosphenes is still in its early stages and lacks extensive experimental evidence, the initial findings suggest that both fullerene and borospherene cages have the potential to stabilize unconventional metal clusters, paving the way for new materials with advanced properties. These materials could find applications in various fields, including catalysis, electronic devices, and materials science, due to their unique structural and electronic characteristics. The exploration of these novel metalloborosphenes and metallofullerenes opens up exciting avenues for future research, highlighting the need for further experimental and theoretical investigations to fully understand their potential and to harness their properties for practical applications.

2. Structures of Fullerene and Borospherene

Fullerenes are enclosed cages of carbon molecules composed of many adjacent rings, with rings of size $n = 5$ or $n = 6$ being more prevalent than other ring sizes, suggesting that fullerenes consisting of pentagons and hexagons exhibit increased stability [1,2]. The smallest fullerene that satisfies these requirements is C_{60} , as shown in Figure 1 [3]. This cage structure is a network of sp^2 -hybridized carbon atoms, where paired valence electrons from the 2s orbitals collectively inhabit molecular orbitals arranged in triangular units centered around each carbon atom individually, forming a delocalized σ network [4]. The triangular sp^2 hybrid orbitals of every adjacent carbon atom then overlap from end to end to form pentagonal rings, which constitute the faces of the “soccer ball” structure of the fullerene [4]. This concept is referred to as the Isolated Pentagon Rule (IPR), which asserts that the most stable state of a purely carbon or metal-doped fullerene is a network with the minimum number of separate pentagons required for the carbon atom count, with every bonding electron being fully delocalized over the σ molecular orbital [5]. The remaining two valence 2p electrons in carbon inhabit a fully occupied 2p state, overlapping in a π formation,

where the lobes (amplitudes) of the 2p wavefunctions conjoin to cover a continuous π (2p) orbital over the full carbon cage surface [5]. In these carbon fullerenes, the presence of two electrons in the 2p state enhances stability by resulting in occupancy of one electron in both the degenerate $2p_x$ and $2p_y$ orbitals of carbon in accordance with Hund's rule. This results in a sufficient number of electrons being distributed throughout both delocalized molecular orbitals [5].

Boron fullerenes, known as borospherenes [6], are analogous to carbon fullerenes. Figure 1 summarizes the reported borospherene structures validated by theoretical studies and photoelectron spectroscopy (PES) [24]. Unlike carbon, boron is electron-deficient, possessing only one 2p electron, which leads to the formation of delocalized σ and π bonds [6–9]. This electron deficiency necessitates a more complex bonding scheme to achieve stability. Boron clusters often adopt planar or quasi-planar structures (up to B_{38}^-) [7] to maximize electron delocalization and minimize electronic repulsion, a stark contrast to the spherical structures of carbon fullerenes that adhere to a $2(n + 1)^2$ π -electron counting rule to determine spherical aromaticity [25]. In borospherenes, more electrons need to be delocalized over the structure to mitigate the electron deficiency effect, resulting in unique bonding characteristics and stability [26]. The presence of delocalized σ and π bonds in borospherenes allows for a double delocalization pattern, which is observed less frequently in carbon fullerenes. This double delocalization leads to increased stability and distinct chemical properties. Additionally, boron's propensity for forming multicenter bonds contributes to the diversity in structural motifs observed in borospherenes, ranging from planar to tubular and cage-like structures, depending on the size and composition of the cluster [8,9].

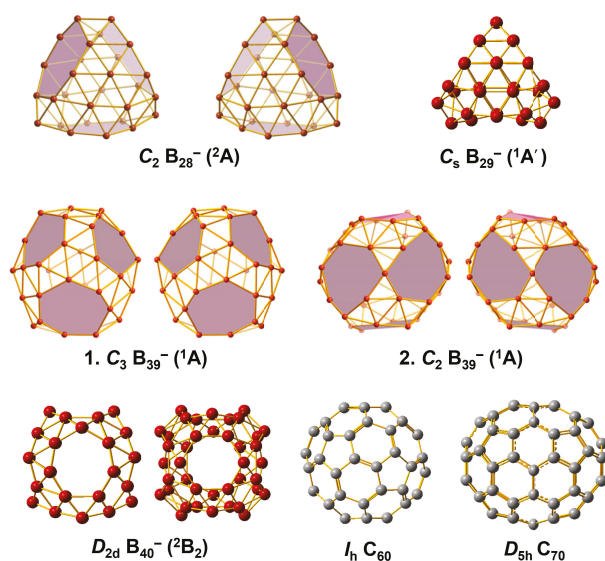


Figure 1. Known borospherene structures of B_{28}^- [11,27], B_{29}^- [28], B_{39}^- [29], and B_{40}^- [6] validated by PES and quantum chemistry calculations compared with I_h -C₆₀ and D_{5h} -C₇₀. Here, B_{28}^- and B_{39}^- systems demonstrate chiral enantiomers.

The first borospherene structure experimentally and theoretically reported was neutral B_{40} [6], as shown in Figure 1. This structure consists of eight B_6 quasi-planar triangle faces with two B_6 rings on the top and bottom and two B_7 rings on the sides in between the triangle faces. The anion counterpart, B_{40}^- , has two coexisting degenerate isomers with planar and cage-like shapes, respectively. In the B_{39}^- cluster [29], two distinct chiral borospherene isomers with C_2 and C_3 symmetry were discovered through PES and theoretical studies, both derived from the B_{40} borospherene. The C_3 isomer can be formed by replacing a B_7 heptagon in the B_{40} cage with a B_6 hexagon, followed by structural reorganization. The C_2 B_{39}^- isomer, on the other hand, can be created by removing a single boron atom from the waist of the B_{40} borospherene, resulting in a narrowed boron double chain and

the formation of a “defect” site. The seashell-like B_{28}^- has been identified as the smallest borospherene, featuring chiral enantiomers with C_2 point-group symmetry [11,27], as shown in Figure 1. The PES of B_{29}^- [28] exhibits a complex pattern, indicating the presence of low-lying isomers. Global minimum searches and extensive theoretical calculations have revealed a complicated potential energy surface for B_{29}^- , with multiple low-lying isomers contributing to the experimental spectrum. Among these, the global minimum is a three-dimensional seashell-like C_s ($^1A'$) borospherene isomer, characterized by two heptagons on the waist and one octagon at the bottom. This is followed by a planar C_1 (1A) isomer with a hexagonal hole and a stingray-shaped planar C_s ($^1A'$) isomer featuring a pentagonal hole.

Ab initio calculations suggest that B_{44}^- may be the next negatively charged borospherene, although extensive global minima searching has not been conducted [30]. Additionally, theoretical studies have predicted a variety of borospherene structures. The global minimum structures of several positively charged boron clusters have been identified as borospherene configurations, including B_{29}^+ , B_{31}^+ , B_{35}^+ , B_{38}^+ , B_{38}^{2+} , B_{39}^+ , B_{40}^+ , B_{41}^+ , and B_{42}^+ [26,30–35]. To date, no borospherene clusters larger than B_{42} have been identified through global minimum searches [36]. Nevertheless, numerous stable structures for large borospherenes have been predicted with high stability [36,37]. For larger clusters such as B_{80} , a buckminsterfullerene template was used as the starting structure, adding one boron atom to the center of each hexagon face [38]. Subsequent studies have revealed that core-shell structures, where additional atoms are incorporated inside the cage, are more stable than their hollow counterparts [39].

3. Metallofullerene and Metalloborospherene

Metallofullerenes are formed by trapping metal atoms inside the hollow cages of fullerenes [12,13], such as C_{60} or larger fullerenes like C_{70} . The encapsulation process can occur through methods like arc discharge, laser ablation, and chemical vapor deposition. Their ability to encapsulate metal atoms opens up numerous possibilities for advancements in materials science, medicine, and catalysis, making them a significant area of study in nanotechnology and materials chemistry [14–16]. Metalloborospherenes, unlike metallofullerenes, involve significant interactions between the metal atoms and the boron cage structures [7,17]. These interactions often result in substantial changes to the boron framework, leading to the formation of unique metalloborospherene structures through metal-boron ring chemical bonding.

3.1. Lanthanide-Doped Fullerene and Borospherene Clusters

Endohedral metallofullerenes (EMFs) offer a unique platform for studying otherwise unstable metallic clusters due to the protective environment provided by fullerene cages. Lanthanide atoms can be encapsulated within these cages, forming various structures such as monometallofullerenes, dimetallofullerenes, carbide clusterfullerenes with an M_2C_2 unit encapsulated inside the fullerene cages, and nitride clusterfullerenes [40,41]. The interaction between the lanthanide atoms and the coordinated carbon rings facilitates charge transfer, leading to unusual valence states and chemical bonding patterns. For example, single-electron lanthanide–lanthanide bonds can form within C_{80} fullerenes, resulting in robust redox-active molecular magnets [42,43]. Crystallographic analysis of typical carbide clusterfullerenes has revealed a relationship between the ionic radius of encapsulated metal ions and the size of the fullerene cage. Using Shannon ionic radii [44], it has been observed that larger cages accommodate larger metal ions. For example, Sc_2C_2 is typically found within C_{72-88} cages, Er_2C_2 within C_{80-92} cages, and La_2C_2 within C_{90-104} cages, respectively (Figure 2) [40].

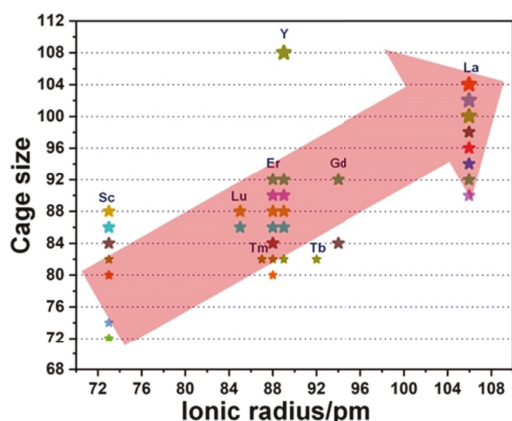


Figure 2. The relationship between the ionic radius of encapsulated metal ions and the fullerene cage size for typical Ln_2C_2 carbide clusterfullerenes. Each star in the diagram may represent more than one compound [40].

Due to the electron deficiency of boron, lanthanide elements usually form dative bonds with boron group ligands. Recent findings show that lanthanide-doped boron clusters exhibit unique structures due to charge transfer interactions and significant (d-p) π and (d-p) δ bonding [19,20]. Unlike transition metal-doped boron clusters, which often form borometallic molecular wheels, lanthanide-doped clusters create distinct inverse-sandwich-type structures, particularly evident in Ln_2B_n^- clusters ($n = 7-9$) [21]. Furthermore, the latest research suggests that these inverse-sandwich configurations can extend to form lanthanide–boron nanowires. The first experimentally observed tri-metal-doped inverse triple-decker, $\text{La}_3\text{B}_{14}^-$ with C_{2v} point group, exhibits a unique structure where three lanthanum atoms are positioned between two conjoined $\eta^8\text{-B}_8$ rings that share a B–B unit on one edge, resulting in a tilted La–B₈–La–B₈–La configuration [45]. With increasing cluster size, recent studies have identified the first perfect spherical trihedral metalloborosphenes, D_{3h} $\text{Ln}_3\text{B}_{18}^-$ ($\text{Ln} = \text{La}, \text{Tb}$) [18], through joint PES and first-principles theory investigations. These metalloborosphenes are notable for their distinct geometry, featuring three deca-coordinate lanthanide centers that are integral to the cage surface. These centers are coordinated within three equivalent $\eta^{10}\text{-B}_{10}$ decagons, which share two eclipsed triangular B₆ units connected by three B₂ units, as shown in Figure 3. Due to the 4f electrons of lanthanides, this configuration gives these metalloborosphenes unique magnetic and catalytic properties.

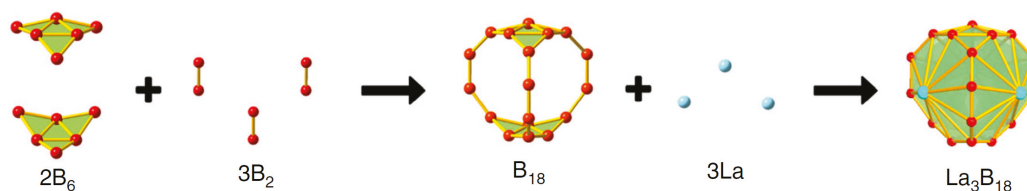


Figure 3. Preferable pathway for the B₁₈ construction and its bonding scheme with three La atoms to form D_{3h} $\text{Ln}_3\text{B}_{18}^-$ metalloborospherene [18].

Following the discovery of the first lanthanide-doped borospherene, $\text{La}_3\text{B}_{18}^-$, a series of theoretical studies have emerged, predicting the existence of other lanthanide-doped borospherene structures with varying numbers of lanthanide atoms. Two core–shell-like metalloborosphenes, C_{2v} $\text{La}_3\& [\text{B}_2\text{@B}_{17}]^-$ and D_{3h} $\text{La}_3\& [\text{B}_2\text{@B}_{18}]^-$ have been identified, featuring a transition-metal-like B₂ core at the center of the $\text{La}_3\text{B}_{17}^-$ and $\text{La}_3\text{B}_{18}^-$ cages [46]. These structures exhibit unique donor–acceptor duality within the $\text{La}_3\&\text{B}_n^-$ spherical trihedral shells ($n = 17, 18$). The B₂ core acts as a donor–acceptor entity, contributing to the stability and electronic properties of the metalloborosphenes. Unlike the tri-lanthanide-doped metalloborospherene, which typically exhibits in-plane coordination with boron

atoms, the tri-lanthanide-doped metallofullerene $\text{Ln}_3\text{@C}_{80}^+$ cation features an endohedral structure [47]. In this configuration, the Ln_3 cluster is situated inside the carbon cage and interacts through a three-center two-electron (3c-2e) σ bond. Lu et al. theoretically proposed a T_d La_4B_{24} cluster featuring a tetrahedral cage structure [48]. This cluster consists of four interconnected B_6 triangles on the surface and four nona-coordinate lanthanum atoms embedded within four conjoined $\eta^9\text{-B}_9$ nonagonal ligands. This configuration represents a boron-based counterpart to the experimentally observed T_d C_{28} tetrahedral carbon fullerene [49].

Theoretically, as the number of boron atoms increases, the resulting boron cages become sufficiently large to accommodate endohedral doping. For instance, M@B_n ($\text{M} = \text{Eu}, \text{Gd}$; $n = 38, 40$) clusters have been predicted to form spherically symmetric endohedral metalborosphenes [50], which is a derivative of the B_{40} borosphenene structure [6].

3.2. Transition Metal-Containing Fullerene and Borosphenene

In this section, we focus on transition metal-containing EMFs to compare their structures with metalborosphenes. Over the past two decades, rare-Earth metals, such as Group-3 elements (Sc, Y) and many lanthanides, have been successfully encapsulated within fullerene cages. The exploration of EMFs with d-block transition metals began in 1992 with the detection of Ti@C_{28} [51]. The macroscopic synthesis of Ti-containing EMFs, such as Ti_2C_{80} and Ti_2C_{84} , was first reported by Shinohara et al. [52,53]. In 2013, Echegoyen et al. identified $\text{Ti}_2\text{S@C}_{78}$, which features a near-linear Ti_2S cluster inside the fullerene cage [54]. Recently, Lu and colleagues prepared $\text{Ti}_3\text{C}_3\text{@I}_h(7)\text{-C}_{80}$ [55], which displays a unique cyclopropane-like geometry. The use of Group-3 metals in mixed-metal clusters has also led to the creation of nitride and carbide clusterfullerenes [56]. Synthesizing V-only EMFs has proven to be challenging. However, inspired by the successful synthesis of the M-Ti system, researchers used Sc to facilitate the encapsulation of vanadium. This approach led to the synthesis of mixed-metal nitride and carbide cluster fullerenes, such as $\text{VSc}_2\text{N@I}_h(7)\text{-C}_{80}$ and $\text{VSc}_2\text{C@I}_h(7)\text{-C}_{80}$ [57]. Unlike Ti-clusterfullerenes, V-containing clusters can host one or two V atoms, highlighting their unique chemical properties. This distinction underscores the complexity and diversity of transition metal-containing EMFs, as the incorporation of different metals can lead to varied structural and electronic characteristics.

Since the isolation of the first EMFs in the early 1990s, their electronic structures have been of significant interest due to their correlation with stability. The high electron affinity of fullerenes suggests an ionic structure for EMFs, with metal cations encapsulated within negatively charged carbon cages (e.g., $\text{Y}^{3+}\text{@C}_{82}^{3-}$) [58]. This was confirmed by ESR spectroscopy and molecular orbital analysis, which indicated that spin density and frontier MOs are localized on the fullerene cage. This ionic model applies to monometallofullerenes and complex species like dimetallofullerenes, nitride clusterfullerenes, and carbide clusterfullerenes, including Ti-containing EMFs such as Ti_2C_{80} and Ti_2C_{84} . Various spectroscopic and computational studies [59–61] support this ionic nature, with XPS, UV-vis-NIR, and electrochemistry showing similar properties for isostructural EMFs. However, studies reveal a covalent contribution to metal–cage bonding, evident in smaller computed atomic charges and detailed electron density analyses [62].

Compared with metallofullerene, doping boron nanoclusters with transition metals results in significant structural transformations. As illustrated in Figure 4 and reported in our recent review paper [7], joint experimental and computational studies have observed structures including wheel-like clusters such as $\text{D}_{8h} \text{Co@B}_8^-$, $\text{D}_{9h} \text{M@B}_9^-$ ($\text{M} = \text{Rh}, \text{Ir}, \text{Re}$), and $\text{D}_{10h} \text{M@B}_{10}^-$ ($\text{M} = \text{Ta}, \text{Nb}$) [63–65], half-sandwich clusters like $\text{C}_{3v} \text{CoB}_{12}^-$ and IrB_{12}^- [66], and tubular clusters such as $\text{D}_{8d} \text{CoB}_{16}^-$ [67], MnB_{16}^- [68], RhB_{18}^- [69], $\text{C}_s \text{B}_2\text{-Ta@}_{18}^-$, and $\text{D}_{10d} \text{Ta@B}_{20}^-$, with Ta@B_{20}^- exhibiting the highest coordination number ($\text{CN} = 20$) among tubular species [70]. The metal-centered tubular boron clusters exhibit multiple aromaticities due to the delocalized bonding, which results from the efficient overlap between the orbitals of the metal center and the surrounding boron group orbitals. It should be noted that no ex-

perimental evidence for the transition metal-containing metalloborospherene structures has been reported. Table 1 lists the predicted structures along with their corresponding doping patterns and symmetries, which await validation through experimental characterization. More recent theoretical predictions include spherical trihedral metalloborospherenes and endohedral complexes $B_{20}TM_n$ (TM = Sc, Y; $n = 3, 4$) [71], Ta-centered metalloborospherenes such as $Ta@B_{22}^-$ and $Ta@B_n^q$ ($n = 23-28$, $q = -1-3$), the smallest trihedral metalloborospherene D_{3h} $Ta_3B_{12}^-$ with $\sigma + \pi + \delta$ aromaticity, and the spherical tetrahedral metalloborospherene T_d Ta_4B_{18} with four nonacoordinate Ta centers [72,73]. For larger boron sizes, theoretical studies have previously proposed the existence of metalloborospherenes, specifically for MB_{40} ($M = Be, Mg$) and Ni_nB_{40} ($n = 1-4$) [74–76], which feature seven-coordinate metal centers on the B_{40} cage surface. These structures are related to the corresponding metalloborophenes, serving as precursors with similar coordination environments for the metal centers.

Table 1. Theoretically Predicted Transition Metal-Containing Borospherenes.

Species	Symmetry	Doping Mechanism
$Ta_3B_{12}^-$ [75]	D_{3h}	exohedral
$Zr_3B_{15}^+$ [77]	D_{3h}	exohedral
Zr_3B_{15} [77]	D_{3h}	exohedral
$Zr_3B_{15}^-$ [77]	D_{3h}	exohedral
$Hf_3B_{15}^+$ [77]	D_{3h}	exohedral
Hf_3B_{15} [77]	D_{3h}	exohedral
$Hf_3B_{15}^-$ [77]	D_{3h}	exohedral
$V_3B_{16}^-$ [78]	C_{2v}	endohedral
$Cr_3B_{16}^-$ [78]	C_{4v}	endohedral
$Mn_3B_{16}^-$ [78]	C_{4v}	endohedral
$Fe_3B_{16}^-$ [78]	D_{8d}	endohedral
$Co_3B_{16}^-$ [78]	D_{8d}	endohedral
$Ni_3B_{16}^-$ [78]	C_s	endohedral
$Ta_4B_{18}^-$ [79]	T_d	exohedral
$Nb_4B_{18}^-$ [79]	T_d	exohedral
$Sc_3B_{20}^-$ [71]	D_{3h}	exohedral
$Y_3B_{20}^-$ [71]	D_{3h}	exohedral
$Ti_3B_{20}^-$ [71]	D_{3h}	exohedral
$Zr_3B_{20}^-$ [71]	D_{3h}	exohedral
$Hf_3B_{20}^-$ [71]	D_{3h}	exohedral
$Sc_3B_{20}^{3-}$ [71]	D_{3h}	exohedral
$Y_3B_{20}^{3-}$ [71]	D_{3h}	exohedral
$Sc_4B_{20}^-$ [71]	D_{3h}	exohedral
$Y_4B_{20}^-$ [71]	D_{3h}	exohedral
ScB_{24}^- [80]	D_2	endohedral
TiB_{24}^- [80]	D_{3h}	endohedral
VB_{24}^- [80]	C_{2v}	endohedral
CrB_{24}^- [80]	C_s	endohedral
MnB_{24}^- [80]	C_s	endohedral

Table 1. Cont.

Species	Symmetry	Doping Mechanism
FeB ₂₄ [−] [80]	C _s	endohedral
CoB ₂₄ [−] [80]	C _s	endohedral
SrB ₄₀ [−] [76,81]	D _{2d}	endohedral
CaB ₄₀ [−] [76,81]	C _{2v}	endohedral
BeB ₄₀ [−] [76,81]	C _s	exohedral
MgB ₄₀ [−] [76,81]	C _s	exohedral
LiB ₄₀ [82]	C _s	exohedral
NaB ₄₀ [82]	C _{2v}	endohedral
KB ₄₀ [82]	C _s	exohedral
BaB ₄₀ [82]	D _{2d}	endohedral
TlB ₄₀ [82]	C _s	exohedral
TiB ₄₀ [83]	C ₁	endohedral
Ti ₂ B ₄₀ [83]	C _s	endohedral

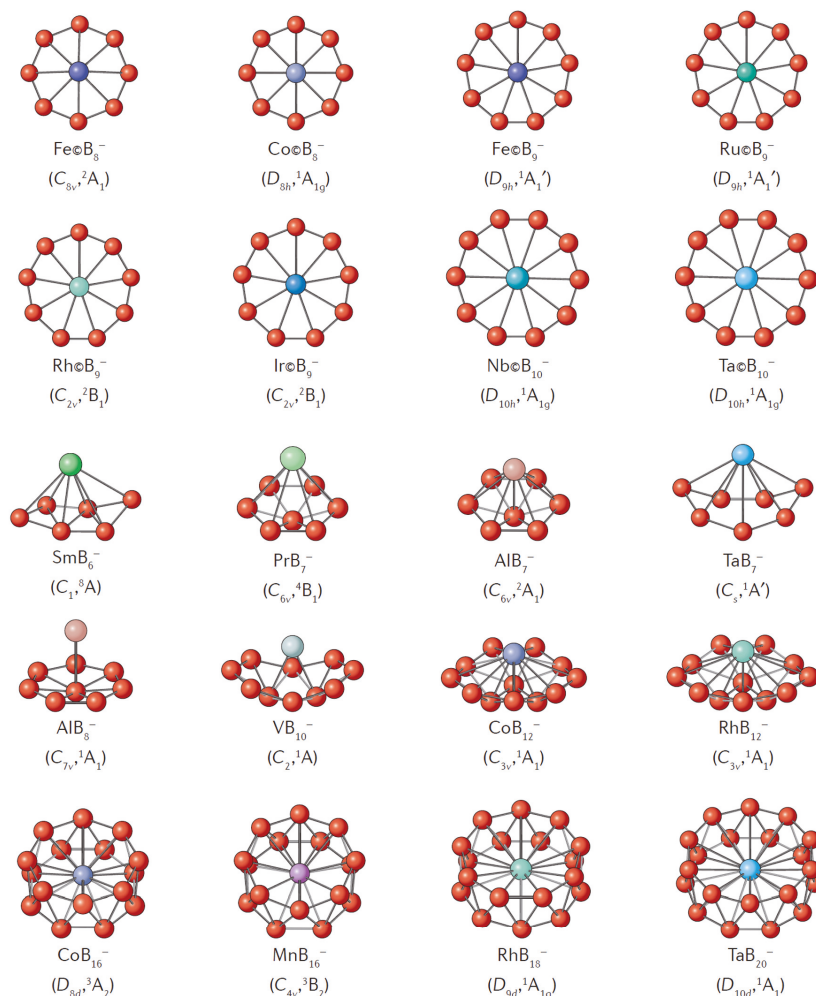


Figure 4. Three classes of metal-doped boron clusters have been observed experimentally: metal-centered monocyclic rings, half-sandwich type structures, and metal-centered tubular structures. The point group symmetry and electronic state are reported for each structure [7].

3.3. Actinide-Containing Fullerene and Borospherene

Actinide-based EMFs have recently garnered interest, compared with the extensively researched lanthanide-based EMFs [22]. Due to the diverse valence electron shells of actinide elements, actinide EMFs have revealed intricate electronic structures and novel bonding configurations not present in lanthanide counterparts [23], suggesting that the unique actinide clusters encapsulated within fullerene cages offer a valuable platform to examine the nature of actinide–ligand interactions within a controlled, inert environment, thereby unveiling new dimensions of actinide chemistry.

A defining characteristic of actinide EMFs is the substantial charge transfer from the metal to the fullerene cage, influencing both their stability and reactivity. Early actinides, such as thorium (Th), plutonium (Pu), and uranium (U), are notably redox-active and exhibit a wide range of oxidation states [84]. For instance, U can be present in various oxidation states, from U(III) to U(VI), in contrast to the limited oxidation states of lanthanides [85,86]. The high chemical activity of the 5f orbitals in actinides results in unique cage isomer preferences and novel electronic structures [85,87]. Although the radioactivity of actinides has traditionally restricted their study to theoretical calculations and limited spectroscopy, recent experimental advancements have significantly deepened our understanding, exemplified by the first crystallographic analysis of Th@C_{3v}(8)-C₈₂ and the identification of a formal U⁵⁺ charge state in U₂C@I_h(7)-C₈₀ [49,88]. Additionally, UCU@I_h(7)-C₈₀ represents the first actinide metallic cluster EMF, showcasing unsupported U=C double bonds [89]. Recent advancements have expanded our knowledge of actinide clusterfullerene families with the synthesis and characterization of U₂C₂@I_h(7)-C₈₀ and UCN@C_s(6)-C₈₂ [90–92]. U₂C₂@I_h(7)-C₈₀ features two uranium atoms bridged by a carbon–carbon triple bond (C ≡ C), while UCN@C_s(6)-C₈₂ contains a triangular UCN cluster with η² (side-on) coordination of uranium by cyanide. These discoveries underscore the potential of fullerene cages to stabilize unconventional actinide clusters, offering profound insights into actinide bonding and paving the way for the development of advanced materials.

Although various metal-doped boron clusters have been reported, actinide (An)-doped boron clusters remain relatively unexplored due to significant challenges in both experimental and computational approaches. Similar to other metal atoms, doping boron clusters with actinides can enhance their stability and lead to diverse geometrical structures. Notable computational examples include the half-sandwich structures AnB₁₂ (An = Th to Cm) [93], the double-ring tubular structures An@B₂₀ [94], An@B₂₄ (An = Th, Pu, and Am) [95], and the actinide-centered borane An(BH)₂₄ (An = Th to Cm) [96]. Inspired by the discovery of monovalent lanthanides in the LnB₈[−] system through PES and quantum chemistry calculations [97], we investigated the AnB₈[−] system and identified the potential for monovalent actinide elements in later actinides such as BkB₈[−], MdB₈[−], and NoB₈[−] [98]. Despite significant interest in metalloborospherenes, there is limited evidence for the stabilization of boron cages by actinide metal atoms, with the notable exception of the recently theoretically reported boron cluster U@B₄₀. This discovery raises intriguing questions about the viability of other actinide metal-doped borospherenes. Theoretical calculations have demonstrated the existence of actinide endohedral borospherenes such as An@B_n (An = U and Th; n = 36, 38, and 40) [99,100] and the chiral actinide endohedral borospherenes Ac@B₃₉, [Ac@B₃₉]²⁺, Th@B₃₉, and [Th@B₃₉]³⁺ [101]. Additionally, global searches have revealed that U@B₂₄ possesses a unique half-cage structure [96]. These findings highlight the potential for a broader range of actinide-doped boron clusters, suggesting new avenues for research into their stability, electronic properties, and geometric configurations. The continued exploration of these systems could provide valuable insights into the bonding characteristics and chemical behavior of actinides, further expanding the understanding of actinide chemistry in novel boron-based materials. Actinide metallofullerenes and actinide metalloborospherenes exhibit significant differences in their structural, electronic, and stability characteristics. Actinide metallofullerenes, composed of actinide atoms encapsulated within highly symmetric carbon-based fullerene cages, rely on substantial metal-to-cage charge transfer interactions for stability that are rarely observed in other systems where a

single metal ion is positioned within a carbon cage, and exhibit unique redox properties influenced by the interaction of actinide 5f orbitals with the carbon π -system [22,87,88]. In contrast, actinide metalloborospherenes, consisting of actinide atoms within boron-based cages [102], present a broader range of geometrical configurations due to boron's ability to form multicenter bonds. The study of these actinide-doped clusters provides valuable insights into the complex chemistry of actinides, with metallofullerenes offering stable environments and metalloborospherenes presenting versatile and reactive platforms for further exploration.

4. Theoretical and Computational Methods

Theoretical and computational methods are crucial for studying metalloborospherene, as they enable the prediction of stable geometries and electronic structures that are challenging to investigate experimentally. Additionally, simulating spectroscopy and comparing it to experimental observations can provide evidence of the true global minimum structures. These methods offer detailed insights into the bonding patterns and aromaticity of metalloborospherene. We recently proposed the novel concept of “cluster-assembly materials” [98], wherein highly symmetric stable clusters serve as the foundational building blocks for derivative materials. This approach guides experimental efforts and enhances our understanding of these advanced materials.

4.1. Global Minimum Search

Global minimum searching can be performed using several different algorithms. One of the earliest methods for this purpose is the Basin Hopping (BH) algorithm [103]. This method randomly perturbs the current structure, performs a geometry optimization, and then accepts the new structure if the energy is lowered, or based on a probability determined from the ratio of the population of the previous structure to that of the new structure as determined by the canonical ensemble partition function (Equation (1)). This strategy was implemented in the TGMIn package, which allows acceptance of higher energy structures, enabling the BH algorithm to avoid becoming trapped in local minima that are not the global minimum [103–106]. The pure BH algorithm has been successfully used to identify the structures of B_{40}^- [6], MnB_{16}^- [68], etc.

$$p < e^{\frac{E(X_0) - E(X_{new})}{k_B T}} \quad (1)$$

A modified version of the BH method was developed in TGMIn 2.0 [107], enhancing efficiency through several modifications: checking displaced structures for low-coordination numbers, freezing some atoms to reduce search dimensions, adjusting unreasonable structures before ab-initio calculations, and preventing the revisiting of prior structures. TGMIn 2.0 has successfully identified the global minimum structures of $La_3B_{18}^-$, $Tb_3B_{18}^-$, MnB_{16}^- , and $La_3B_{14}^-$ [45,68,77].

In addition to the BH method, the Stochastic Surface Walking (SSW) method [108,109] enhances global minimum searching by adding random displacements to the current local minima structure and performing a biased dimer rotation to incorporate information about transition states between isomers, followed by geometry optimization [110]. This method has been successfully used to determine the global minimum structure of B_{40}^- [6]. Similarly, the Coalescence Kick algorithm [111–113], which was employed to find the global minimum structure of MnB_{16}^- , involves displacing each atom within a spherical radius R of its prior position, akin to the displacement strategies used in BH, TGMIn, and SSW.

Another advanced technique is the CALYPSO (Crystal Structure Analysis by Particle Swarm Optimization) package [114], which predicts structures by generating random structures with symmetry constraints followed by geometry optimization. Each structure is assigned a geometric parameter similar to a genetic code, and position adjustments are made through particle swarm optimization [115,116]. This method was used to predict the structures of AnB_{36} ($An = Pa, Np, Pu, Am, Cm, Bk, \text{ and } Cf$) clusters [102].

For the energy calculation, *ab initio* methods need to be employed using quantum chemistry software such as Gaussian (16) [117] and ADF (2024.1) [118,119]. These calculations are essential for accurately determining the electronic structure and properties of the systems under investigation. However, as the number of atoms in a system increases, the computational cost of *ab initio* calculations becomes a significant bottleneck. This necessitates the use of faster, less accurate basis sets and functionals for initial global minimum searches, followed by more precise calculations at higher levels of theory for the most promising structures.

To address these computational challenges, the development of machine learning (ML) potentials is becoming increasingly important. ML potentials can significantly accelerate energy and geometry optimizations by learning from a subset of high-quality *ab initio* calculations and then predicting the properties of new configurations with high accuracy. This approach has been successfully applied in various fields, demonstrating its potential to handle large systems efficiently [120–123]. For example, Behler–Parrinello neural networks [120] and Gaussian approximation potentials [124] are among the techniques that have been developed to create accurate and transferable potential energy surfaces based on machine learning.

Furthermore, integrating ML potentials with traditional quantum chemistry methods can create hybrid approaches that balance accuracy and computational efficiency. This integration allows for initial rapid screening of large configurational spaces using ML models, followed by detailed *ab initio* calculations on a select number of configurations. This hybrid strategy has shown promise in materials science and chemistry, making it a valuable tool for studying complex systems such as metalloborospherenes and other large clusters [125–127]. By leveraging the strengths of both *ab initio* methods and machine learning, researchers can more effectively explore the vast configurational landscapes of complex molecular systems, leading to a deeper understanding and more accurate predictions of their properties.

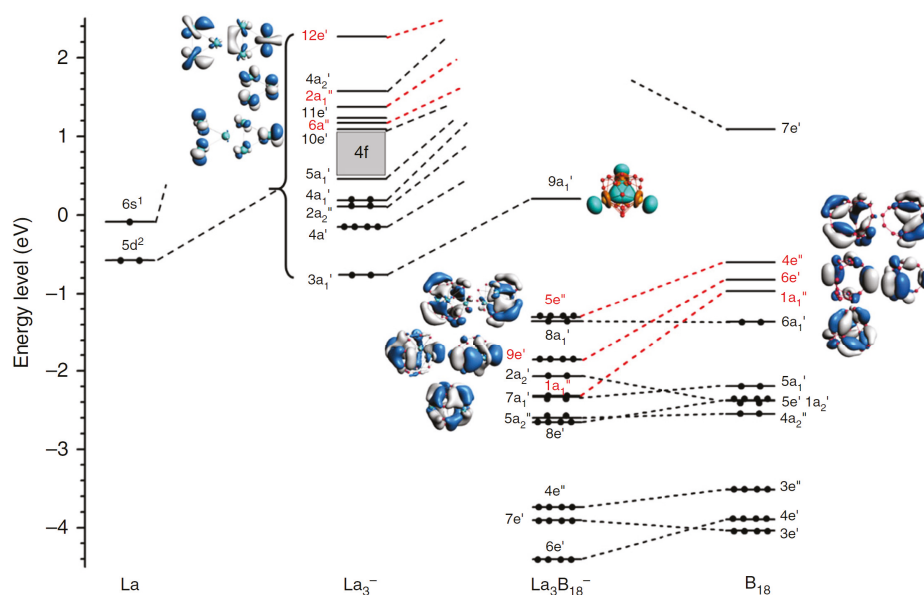
4.2. Photoelectron Spectroscopy Simulation

The PES can be simulated using the Δ SCF-TDDFT method [128]. In this approach, the adiabatic detachment energy (ADE), which also refers to the electron affinity of the neutral species, is calculated as the energy difference between the neutral molecule at its optimized geometry and the anion at its optimized geometry, defining the onset of the first band in the PES. The peak of the first band, known as the first vertical detachment energy (VDE1), is determined as the energy difference between the neutral molecule and the anion, both at the anion geometry [129]. Higher VDEs are obtained by simulating the excitations of the neutral molecule at the anion geometry using time-dependent DFT (TDDFT) methods for systems without strong electron correlations, while for systems with strong electron correlation or spin–orbit (SO) coupling effects, single-electron VDEs from the anion ground state to the corresponding ground and excited states of the neutral cluster are calculated using the CASSCF/CCSD(T)/SO approach [130], where CCSD(T) energy values replace the diagonal elements of the CASSCF matrix with SO effects treated as a perturbation. Excitations with the electron detached from occupied molecular orbitals to the corresponding molecular orbital of the anion are selected, and the first VDE energy is added to these excitations to produce higher VDEs, corresponding to the peaks of subsequent bands in the PES.

The method of statistical average of different orbital model potentials (SAOP) [131] is typically preferred for the calculation of the excitation energies in metalloborophenes due to its accurate long-range behavior, which is essential for calculating charge transfer excitations in systems with significant charge separation in excited states, such as between metal fragments and boron clusters [18]. In pure boron fullerenes, such as B_{40}^- , the time-dependent DFT formalism [6,129] is used at the PBE0 level to achieve similar accuracy.

4.3. Molecular Orbitals and Chemical Bonding Analysis

The analysis of molecular orbitals (MOs) in metalloborophenes is vital for understanding their structural stability and the interactions between the metal atoms and the borospherene framework [132]. Moreover, determining the oxidation states of the encapsulated metals is crucial, which can be achieved through appropriate fragment analysis. As illustrated in Figure 5, the MO plot for $\text{La}_3\text{B}_{18}^-$ reveals that the $6e''$, $12e'$, and $2a_1'$ irreducible representations associated with the La_3 moiety exhibit La 5d character, whereas the $4e''$, $6e'$, and $1a_1'$ irreducible representations associated with the B_{18} framework exhibit B 2p character. Consequently, the $5e''$, $9e'$, and $1a_1''$ MOs demonstrate significant bonding interactions between La 5d and B_{18} 2p orbitals. This bonding pattern indicates that the La atoms are in their favored +III oxidation state in $\text{La}_3\text{B}_{18}^-$, which can be approximately represented as $(\text{La}^{3+})_3[\text{B}_{18}^{10-}]$.



ring tubular structure of the boron framework, which consists of two B_{12} tubular subunits connected by B_6 rings and capped by beryllium atoms. This method also illustrates the charge transfer and orbital mixing between the fragments, highlighting the role of Be to form strong covalent bonds, which is crucial for the stability and unusual geometry of the metalloborospherene.

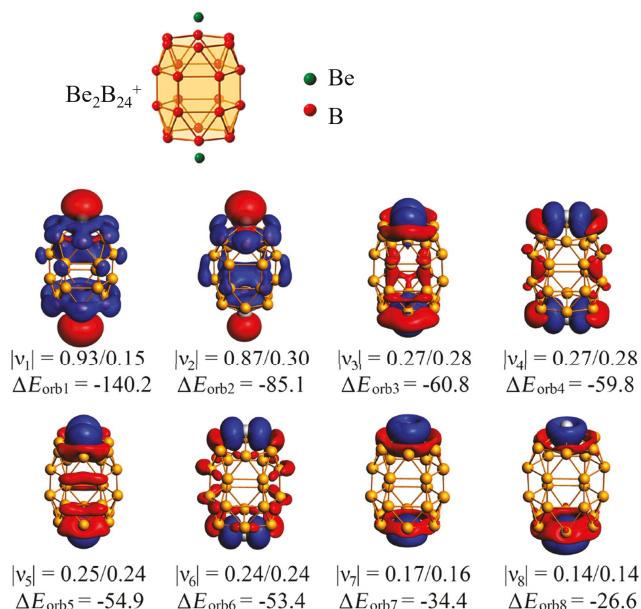


Figure 6. $Be_2B_{24}^+$ structure alongside plots of deformation densities $\Delta\rho_{1-8}$ for the pairwise orbital interactions in $Be_2B_{24}^+$ [136]. The associated interaction energies (ΔE_{orb} in kcal/mol) and eigenvalues (v) are also shown. Eigenvalues (v) represent the magnitude of charge transfer, with the direction of charge transfer illustrated from red to blue.

Bader's Quantum Theory of Atoms in Molecules (QTAIM) [137] provides a refined method for analyzing electron density and thereby understanding metal–cage interactions in EMFs [62]. Instead of focusing on individual molecular orbitals, QTAIM assesses the overall electron density, identifying natural boundaries between atoms via surfaces with zero flux in the gradient vector field. These boundaries, or atomic basins, allow for the integration of scalar properties, such as electron density, to specific atoms. Critical points (CPs) where the density gradient vanishes are classified by their rank (number of nonzero Hessian eigenvalues) and signature (sum of Hessian eigenvalue signs). Different types of CPs (nuclear, bond, ring, and cage) provide insights into bonding characteristics. Bond critical points (BCPs) are particularly crucial, as their presence between atoms signifies bonding. The electron density at BCPs (ρ_{bcp}) and its Laplacian ($\nabla^2\rho_{bcp}$) help distinguish between covalent (high ρ_{bcp} , negative $\nabla^2\rho_{bcp}$) and noncovalent (low ρ_{bcp} , positive $\nabla^2\rho_{bcp}$) interactions. Studies on EMFs using QTAIM, such as those by Kobayashi and Nagase [138,139], reveal the ionic character of metal–cage bonds through small ρ_{bcp} values and positive $\nabla^2\rho_{bcp}$, alongside high bond ellipticity, indicating delocalized metal–cage interactions. Despite QTAIM's robustness, its application in EMF studies has been limited, primarily focusing on atomic charges rather than a comprehensive analysis of bonding indicators. This approach can provide a more detailed understanding of bonding in various EMF classes, including mono- and dimetallofullerenes, nitride cluster fullerenes, and carbide cluster fullerenes (Figure 7).

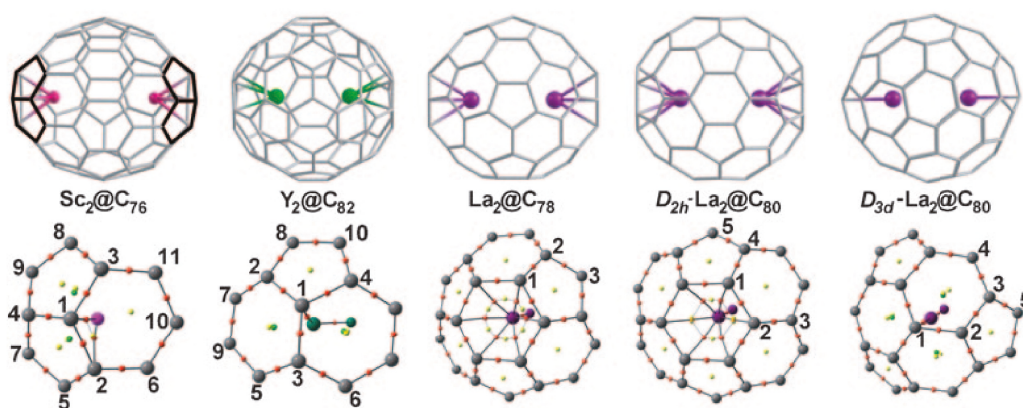


Figure 7. Molecular structures and fragments of molecular graphs in the vicinity of the metal atoms of $\text{Sc}_2\text{@C}_{76}$ -Cs(17,490), $\text{Y}_2\text{@C}_{82}$ - C_{3v} (8), $\text{La}_2\text{@C}_{78}$ - D_{3h} (5), D_{2h} - $\text{La}_2\text{@C}_{80}$ - I_h (7), and D_{3d} - $\text{La}_2\text{@C}_{80}$ - I_h (7). Atoms are colored as follows: carbon (gray), bond critical points (BCP, red), ring critical points (RCP, yellow), and cage critical points (CCP, green) [62].

QTAIM has also been widely used to analyze the chemical bonding in metalloborospherenes. For example, in Th@B_{36} metalloborospherene as shown in Figure 8 [140], QTAIM provides a detailed topological analysis of the electron density, highlighting critical points that reveal the nature of boron–boron (B–B) and metal–boron (Th–B) interactions. The analysis identifies BCPs for B–B bonds, indicating a significant covalent character due to high ρ_{bcp} and negative $\nabla^2\rho_{bcp}$. Additionally, ring critical points (RCPs) and cage critical points (CCPs) indicate the presence of multicenter bonding, a characteristic feature of boron clusters. For Th–B interactions, QTAIM reveals smaller electron density and positive Laplacian values at the BCPs, suggesting a closed-shell interaction with partial covalent character, further supported by negative values of the energy density ($H(r)$) at these points.

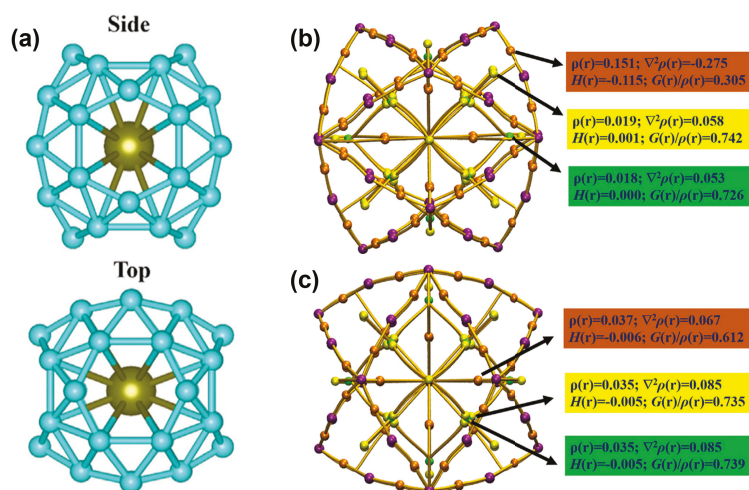


Figure 8. (a) Geometry of Th@B_{36} from different views. Critical points (CPs) associated with boron–boron and metal–boron bonding in (b,c), respectively. The color scheme is purple for atoms, orange for bond critical points (BCPs), yellow for ring critical points (RCPs), and green for cage critical points (CCPs). Key parameters for different critical points are also provided [140].

The Adaptive Natural Density Partitioning (AdNDP) [141] analysis, which integrates Lewis theory with canonical molecular orbital theory, provides a powerful approach for describing the bonding in complex molecular systems. This method assigns each molecular orbital as an n -center (1,2)–electron bond, where n can range from 1 to the total number of

atoms in the molecule, indicating a spectrum of bonding scenarios from localized to fully delocalized electrons.

AdNDP analysis is particularly effective in visualizing bonding patterns that are not easily represented by traditional two-center, two-electron bonds. For instance, in systems with delocalized bonding, such as the $\text{La}_3\text{B}_{18}^-$ system as shown in Figure 9, AdNDP can reveal multicenter bonds that involve three or more atoms sharing electron pairs. This capability is essential for understanding the electronic structure of such molecules, where conventional bonding models fall short.



Figure 9. AdNDP analyses of $\text{La}_3\text{B}_{18}^-$ cluster [18].

Moreover, AdNDP analysis can also provide insights into the aromaticity of certain compounds by demonstrating the presence of delocalized electron clouds that contribute to the stability and reactivity of the molecule. All these advanced computational techniques collectively provide a comprehensive understanding of the electronic structure, bonding, and stability of metalloborophenes, facilitating the design and synthesis of new materials with tailored properties.

5. Conclusions and Perspectives

In summary, metalloborosphenes represent a fascinating and rapidly evolving class of materials that parallel the well-studied metallofullerenes. The unique electron-deficient nature of boron leads to diverse and complex bonding patterns, enabling the formation of stable boron cages when doped with various metals. These metalloborosphenes exhibit a range of intriguing structural motifs and electronic properties that differ significantly from their carbon-based counterparts.

Recent advancements have demonstrated the ability of metalloborosphenes to stabilize novel metal clusters, particularly those involving transition metals, lanthanides, and actinides. These studies have provided deep insights into the electronic structure, bonding characteristics, and potential applications of these materials. For instance, the stabilization of actinide clusters within borospherenes and fullerenes has revealed complex electronic configurations and bonding interactions not observed in lanthanide-doped systems.

The potential applications of metalloborosphenes are vast, spanning catalysis, materials science, and nanotechnology. The unique bonding and structural properties of these clusters offer opportunities for designing new materials with tailored electronic and

catalytic properties. Moreover, the ability to encapsulate and stabilize actinide elements opens up new avenues for research in actinide chemistry, with implications for nuclear science and advanced materials.

Future research should continue to explore the synthesis, characterization, and theoretical modeling of metalloborosphenes. Advanced computational methods, such as global minimum searches and machine learning potentials, will play a crucial role in predicting and understanding the properties of these complex systems. Additionally, experimental techniques such as photoelectron spectroscopy and crystallography will be essential for validating theoretical predictions and uncovering new structural motifs. The practical application of metalloborosphenes relies heavily on the feasibility of their macroscale synthesis. Current research in this area is predominantly theoretical and experimental at the nanoscale. However, advancements in synthetic techniques for boron-based nanostructures and metallofullerenes provide a promising foundation for scaling up production. One potential method for macroscale synthesis involves chemical vapor deposition (CVD), which has been successfully employed for producing other boron-rich nanomaterials [142,143]. By optimizing the parameters of CVD, such as temperature, pressure, and precursor composition, it may be possible to achieve controlled synthesis of metalloborosphenes on a larger scale. Another promising approach is the use of solution-based synthesis methods, including solvothermal and hydrothermal processes [144,145]. These methods can facilitate the formation of boron cages and their subsequent doping with metal atoms in a controlled environment. The development of suitable solvents and reaction conditions will be crucial for this approach. Additionally, template-assisted synthesis [146], where preformed templates guide the assembly of boron and metal atoms into the desired structures, could provide a pathway for producing metalloborosphenes at scale. This method has been used successfully for other complex nanostructures and could be adapted for metalloborosphenes. Overall, while the macro-scale synthesis of metalloborosphenes presents challenges, ongoing advancements in nanomaterial synthesis techniques hold promise for overcoming these obstacles, making the large-scale production of these materials feasible in the near future.

Overall, the study of metalloborosphenes is a dynamic and promising field that bridges the gap between boron chemistry and nanomaterials science. The insights gained from this research will not only advance our understanding of boron-based clusters but also pave the way for the development of innovative materials with unique properties and wide-ranging applications.

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Endometallofullerenes in the Gas Phase: Progress and Prospect

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Abstract: This review describes the progress of the gas-phase study of endometallofullerenes (EMFs) by mass spectrometry and theoretical calculation over the past 15 years. The attention herein focuses on the gas-phase syntheses, reactions, and generation mechanisms of some novel EMF ions, along with their structures and properties. The highlighted new species include EMFs with small-size carbon cages of C_{2n} ($n < 60$), multiple metal atoms ($M_x@C_{2n}$, $x \geq 3$), late transition metals, and encaged ionic bonds. Furthermore, the gas-phase experimental and calculational supports for top-down or bottom-up models are summarized and discussed. These gas-phase results not only provide experimental evidence for the existence of related novel EMF species and possible synthesis methods for them, but they also provide new insights about chemical bonds in restricted space. In addition, the opportunities and further development directions faced by gas-phase EMF study are anticipated.

Keywords: endometallofullerenes; gas phase; electronic properties; mass spectrometry

1. Introduction

Interestingly, the history of endometallofullerenes (EMFs) is almost as long as that of fullerene [1,2]. Just one week after the wonderful experiment on the magic cluster ion of C_{60}^+ , ions of LaC_{2n}^+ ($2n = 46-70$) were observed in the laser ablation mass spectrum of the La-loaded graphite by Smalley and his co-workers. The endohedral structure proposal was further supported by the “shrink wrapping” experiment and reaction test with oxygen or ammonia gas [3,4]. About six years later, which is one year after the success of the synthezation of solid C_{60} [5], solid EMFs of $La@C_{82}$ and $La_2@C_{80}$ were also synthesized by the laser ablation method and the Krätschmer–Huffman method [4,6]. The number of known EMFs has been rapidly and constantly growing in the past twenty years, which is mainly attributed to the improvement of synthesis, separation, and analysis methods [7–10]. Carbon cages are now able to encapsulate metal atoms in different forms, such as metallic nitrides, oxides, sulfides, and carbides. Because the cage can serve as an ideal nanoscale container for research on exceptional structures and unique clusters or chemical bonds, EMFs have great potential for showcasing new physical and chemical properties, as well as molecular devices [11–14].

However, due to the great success and rapid development of solid-state synthesis technology for EMFs, there was a time when interest in gas-phase EMF studies decreased. Notably, progress in new materials such as graphene and mass spectrometry technology bring new opportunities for gas-phase research on EMFs [15]. It can be seen that in the past 15 years, gas-phase EMF study has mainly focused on two aspects. The first one is the discovery of novel EMFs, which are difficult to prepare using existing methods and are often considered very difficult or impossible to generate, such as EMFs with small cages, with multiple metal atoms, and with transition metals or ionic bonds. This type of research can inform researchers about the stability of these novel EMFs and provide methodological recommendations for their synthesis. The second one is the generation mechanism of EMFs, which helps us to understand the generation process of EMF in principle and provides

guidance for new methods aimed at EMF synthesis. Both aspects will be summarized and discussed in this review. In summary, we focus on the discovery of new endohedral species in gas-phase experiments, which is typically related to the method of laser ablation mass spectrometry. The structures and properties of important species, mostly based on theoretical calculations, are also included. The mechanisms of generation of these novel EMFs are summarized and discussed in the last section, and an outlook on the prospects of gas-phase EMF studies is presented, too.

2. Experimental Method

From both historical and practical perspectives, gas-phase EMF study is mainly performed with mass spectrometry technology, combined with different cluster ion sources. Considering the diversity of ion species generated and the isotopic distribution of ions, high-resolution mass spectrometry is necessary in these experiments. Although high-resolution time-of-flight mass spectrometers are also applied, more experiments are conducted on Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometers, which have higher resolution and stronger capabilities for ion trapping and manipulation [16]. For the generation of the EMF ions to be studied, the Smalley-type laser-vaporization supersonic expansion cluster beam source is widely used, and there are also many kinds of variations of this type of source [1,2,17]. Generally, a rotatable solid target disk is vaporized by a focused beam from a YAG laser at 532 nm. In the source, pulsed helium gas should be adjusted in timing and pressure to coincide with the laser shot. However, there are also other cluster sources based on laser ablation in vacuum without using the accompanying pulsed helium gas. Two typical experimental setups applied by Dunk et al. in Florida State University [18–20] and Kong et al. in Nankai University [21–23] are shown in Figure 1a,b, respectively. In Dunk et al.'s setup, the cluster source block (shown in the upper corner of Figure 1a) includes vertical channels for helium gas and the laser beam. The other channel, located downstream from the target, is aligned with the gas channel to fulfill the free jet expansion and introduction of clusters into octapoles after the skimmer [18]. Dissimilarly, Kong et al. directly applied a commercial-matrix-assisted laser desorption/ionization (MALDI) [24] source for the laser ablation experiments without modifying any hardware [23]. In their experiments, the precursor was deposited on a metal plate (the MALDI plate) in turn. A focused 355 nm YAG laser beam was applied. Although a pulsed valve is also used in the source chamber (Figure 1b), its function is mainly to help in the accumulation of the generated ions in the hexapole. It is worth noting that although both experimental devices were implemented on FT-ICR mass spectrometers, the EMF species produced and the dependence of their yields on experimental conditions vary in the two setups due to their different cluster source designs and precursor materials used. This will be reflected in the examples mentioned in the following sections. For the generated EMF ions, they can be mass selected in the cell with the method of stored waveform inverse Fourier transform (SWIFT) [25] and can be further studied by other tandem mass spectrometric methods, including collision-induced dissociation (CID), ultraviolet photodissociation (UVPD), or reaction tests with reactive gas molecules (for example, O₂) [3,4,26].

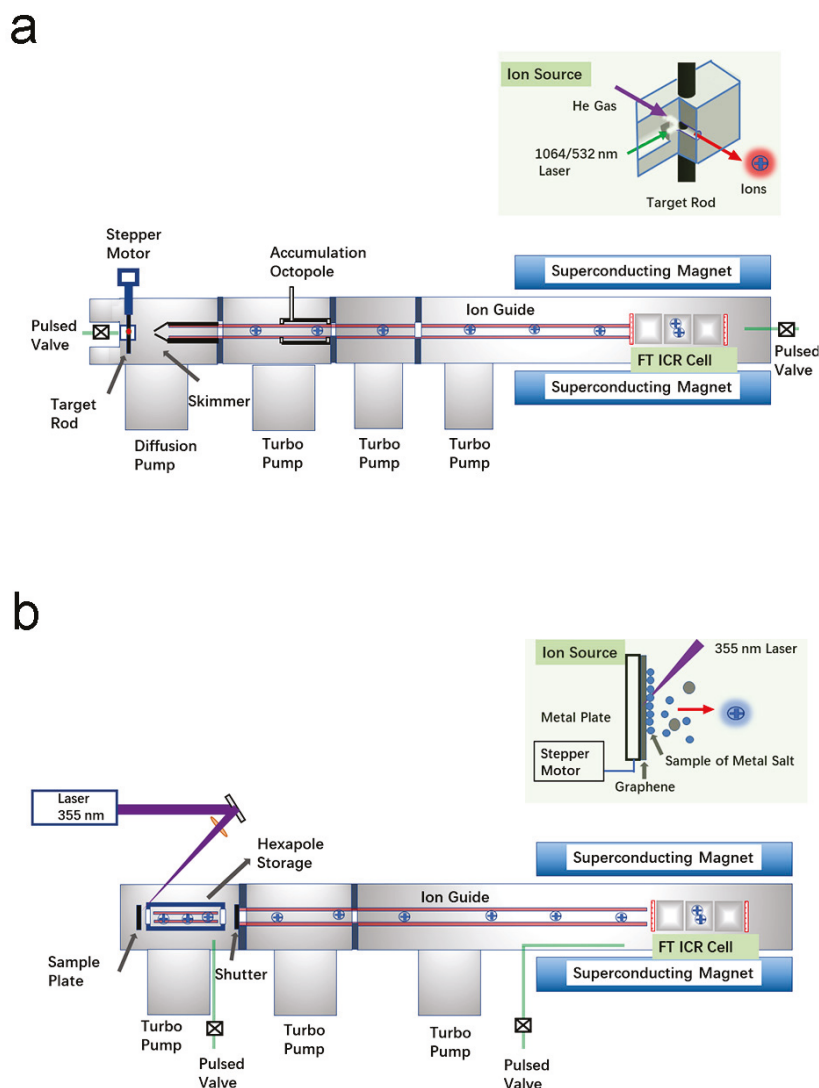


Figure 1. (a) Experimental setup for gas-phase EMF studies applied at Florida State University [18–20]. A 9.4 T FT-ICR mass spectrometer combined with a self-designed cluster source was applied. The cut-away view of the source block is shown in the upper right of the graph. The vaporization of target rods is achieved by laser shots at 532 nm, in conjunction with the opening of the pulsed valve. (b) Experimental setup for gas-phase EMF study applied in Nankai University [21–23]. A 7.0 T FT-ICR mass spectrometer with a commercial ion source (Varian IonSpec ProMALDI) was applied in these experiments without any modification. The precursor is deposited on the metal plate and irradiated by the 355 nm laser. The metal plate is controlled by a stepper motor and moves in the x–y plane during experiments.

3. Novel EMFs in the Gas Phase

3.1. EMFs with Small-Size Carbon Cages of C_{2n} ($n < 60$)

As closed-cage carbon molecules, the theoretically predicted smallest fullerene is C_{20} . However, for a very long time, questions regarding the existence of this structure have been raised due to its high curvature and reactivity. Prinzbach et al. reported the short-lived species $C_{20}Br_{20}$ in 1993 [27] and showed in 2000 that the fullerene C_{20} with a cage structure can be produced from $C_{20}HBr_{13}$ by gas-phase debromination [28]. Calculation examples show that doping the metal atoms in C_{20} can change its electronic structure [29–35]. On the other hand, Tomanek and Schluter predicted that closed carbon cages show a larger stability than other structures for clusters with sizes larger than 20, based on their theoretical calculations [36], and later Kent et al. predicted that the smallest

stable fullerenes should be the C_{26} and C_{28} clusters [37]. Thus, the possible stabilization of C_{28} by an endohedral species has been a very intriguing topic and has attracted the interest of many researchers [33,38–43]. The first experimental evidence in support of the idea was reported by Smalley et al. in 1992, in which they investigated the mass spectra of soot prepared by laser furnace and arc discharge methods [43]. Shrink-wrapping experiments indicated their endohedral structures, in which the fragmentation of larger endohedral uranofullerenes appeared to dissociate by only C_2 loss. The authors claimed that a tetravalent internal metal atom could donate four electrons to the fullerene to afford a closed-shell $M^{4+}@C_{28}^{4-}$ species with a large HOMO–LUMO gap and permit sufficient stabilization for such species [43].

By using a pulsed laser vaporization cluster source, Kroto and Marshal et al. have also reported that C_{28} fullerene could be stabilized by encapsulation with appropriate metal forms [44]. Impressively, for the first time, they reported the high-resolution mass spectrum of $Ti@C_{28}$ (Figure 2). For a long time, titanium has been one of the most attractive tetravalent candidates for C_{28} stabilization by encapsulation. However, its major isotope, ^{48}Ti , which is just 52 mDa different in mass from C_{44} , makes the ion of $Ti@C_{28}$ hard to resolve from the signal of empty-cage C_{32} with conventional mass spectrometers. Using a 9.0-T Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR) mass spectrometer, Kroto and Marshal et al. clearly identified the species, along with ions of $Ti@C_{2n}$ ($n = 19–23$), in the mass spectrum [44]. Collision-induced dissociation (CID) experiments on $Ti@C_{28}$ show that the ion can remain completely intact with neither the loss of Ti nor the loss of C_3 or C after many collisions, indicating the fact that the metal is not directly attached to the skeleton, which is neither linear nor cyclic. Further CID experiments on $Ti@C_{30}$ show that $Ti@C_{30}$ can fragment to $Ti@C_{28}$ by C_2 loss, demonstrating that both species are endohedral. They also investigated other metal elements in the periodic table and found that both $Zr@C_{28}$ and $U@C_{28}$ formed in abundance, but $Hf@C_{28}$ was much weaker.

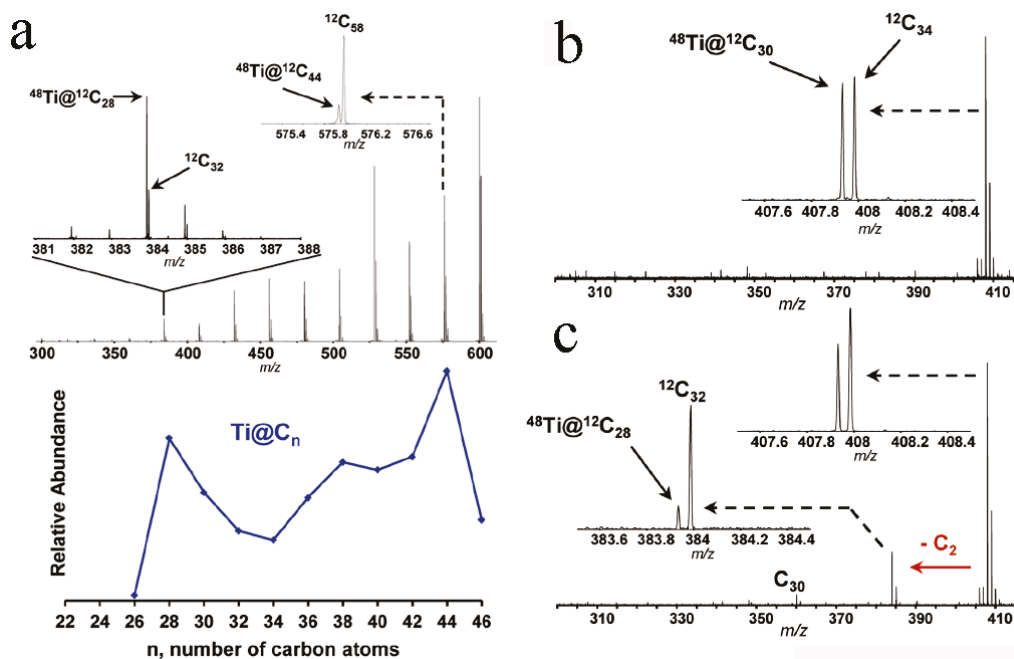


Figure 2. (a) Laser vaporization mass spectrum of a Ti-doped graphite target. Among the observed cations in the $Ti@C_{2n}$ family, $Ti@C_{28}$ is observed in great abundance without the accompany of the empty-cage C_{28} . (b) Isolated ions of $Ti@C_{30}$ and C_{34} , and (c) fragmentation pathway of $Ti@C_{30}$. Taken with permission from [44].

Dunk et al. have synthesized a series of uranium-endohedral fullerenes using the method of Krätschmer–Huffman arc discharge [45]. Several uranofullerenes were able

to be observed in experiments utilizing solvents with different polarities. Via extractions using pyridine and 1,2-Dichlorobenzene (o-DCB), species of $U@C_{2n}$ ($2n = 28, 60, 66, 68$, and 70) were observed in the FT-ICR mass spectra. The distribution of the series of uranium-endohedral fullerenes was found to be different from that obtained in the early experiment reported by Smalley and his colleagues [43]. Some missing species of uranium-endohedral fullerenes have been observed for the first time in Dunk et al.'s experiment [45].

Due to its primary oxidation state at +4, it was predicted that thorium could form $Th@C_{28}$ via the method described above. However, Dunk et al. found that the species $Th@C_{28}$ was absent and replaced by the species $Th@C_{36}$ in the resulting mass spectrum, which could be attributed to the larger ionic radius of Th^{4+} relative to U^{4+} [20]. For the purpose of creating mono-metallofullerene from metal-incorporated graphite, more than 80 components were examined separately in their experiment. The detectable species with the smallest carbon cages are $M@C_{50}$ for Group 1 elements (K, Rb, Cs), $M@C_{42}$ or $M@C_{44}$ for Group 2 elements (Ca, Sr, Ba), $M@C_{36}$ for trivalent rare earth metals (Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu), $M@C_{44}$ for divalent lanthanides (Sm, Eu, Yb), and $M@C_{50}$ for Ga and In. The results indicate that the oxidation states of the encapsulated metals (corresponding to the charge transfer to the carbon cage outside) and the ionic radius are determining factors that govern the size limits of the observed EMFs and the corresponding EMF formation.

Alternatively, Rodríguez-Forte et al. recently reported the cation species of $U@C_{2n-1}B$ ($2n - 1 = 27-59$) using their laser vaporization source [46]. As shown in Figure 3, mass spectrometric results identified the boron-doped $U@C_{27}B$ as the most prevalent borafullerene within the $U@C_{2n-1}B$ family. According to density functional theory (DFT) calculations, the U atom is positioned in the middle of the cage and interacts with every other atom there as though it were a 28-hapto ligand. This exotic radical shows us an intriguing example of unique host-guest chemistry in metallofullerenes.

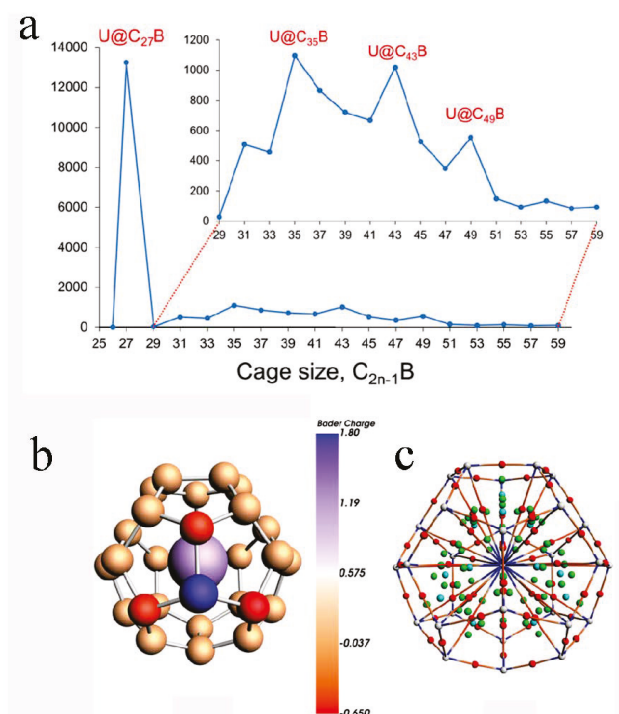


Figure 3. (a) Distribution of cations of $U@C_{2n-1}B^+$ formed by laser vaporization of U-containing graphite. The region $2n - 1 = 29$ to 59 is expanded in the inset for clarity. (b) Bader charges and (c) AIM critical points (CPs) and bond paths for $U@C_{27}B$. Atom CP in white, bond CP in red, ring CP in green, and cage CP in light blue. Taken with permission from [46].

The observed new EMF species in small carbon cages in the gas phase were also simulated using theoretical methods on their structure and properties [31–35,47–49]. For example, Rodríguez-Fortea, Kroto, and Poblet and have reported their theoretically calculated results of the Ti@C_{2n} ($2n = 26\text{--}50$) family [47]. The stability and unique electronic characteristics of the two main species, Ti@C_{28} and Ti@C_{44} , account for their abundance. It is demonstrated that all of the optimum isomers in the family are connected by a straightforward C_2 insertion, with the exception of a few cages that need an extra C_2 rearrangement. Da et al. studied the ground-state electronic structures of U@C_{28} in its neutral, monovalent, and bivalent cationic forms [41]. The findings indicate that, rather than the $(5f)^1$ (cage)¹ ground state with a D_2 symmetry, the neutral U@C_{28} is characterized by a (cage)² ground state with a Td symmetry [41]. Meng et al. studied the geometric and bonding properties of EMFs, including an f-block metal atom or ion enclosed in a C_{20} cage [48]. Muñoz-Castro investigated the availability of $\text{U}_2\text{@C}_{36}$ as an example for the small endohedral dimetallofullerene. The result indicates its neutral and dicationic forms can behave as plausible candidates with a U-U distance of 2.27 Å [49]. Zhou et al. reported the structures and properties of TM@C_n ($n = 20, 24, 28$) based on their DFT calculations, showing that after the embedding of TM atoms, the stability of TM@C_{20} is greatly enhanced [33]. Their recent results show that the general species of $\text{Mg}^{2+}\text{@[C}_{20}]^{n-2}$ can be classified as superatoms [35].

3.2. EMFs including Multiple Metal Atoms ($\text{M}_x\text{@C}_{2n}$, $x \geq 3$)

The Coulomb repulsion among the metal ions in EMFs with multiple metal atoms creates a barrier to their stabilities. As the number and size of metal atoms increase, this situation becomes more serious. There are two ways to solve the problem [50]. One is to introduce electronegative elements (such as N, S, and O) to compensate for the Coulomb repulsion; the other is to adopt fullerene cages with large sizes. For the generation and structure study of EMFs that include multiple metal atoms, gas-phase experiments provide a convenient and effective method, especially when combined with DFT calculations. Graphene has been found to be a powerful precursor for the generation of EMF ions that encage multiple metal atoms in the gas phase [23,51–58]. For example, the laser ablation of LaCl_3 /graphene can generate EMF ions of $\text{La}_n\text{@C}_{2m}^+$ with a long accumulation time in the cell of the FT-ICR mass spectrometer [53]. As shown in Figure 4a, compared to the wide distributions of $\text{La@C}_{58\text{--}194}^+$ and $\text{La}_2\text{@C}_{74\text{--}168}^+$, the distribution of trimetallofullerene ions is narrower ($2n = 96\text{--}160$), with a center located at $\text{La}_3\text{C}_{110}$. The primary products are the monometallofullerene ions; nonetheless, the species ranked second in abundance is La_3C_{2m} , instead of La_2C_{2m} . Other EMF ions of $\text{La}_4\text{C}_{112\text{--}160}$, La_5C_{2m} ($132 \leq 2m \leq 170$), and La_6C_{2m} ($152 \leq 2m \leq 180$) ions were also identified.

Although the diverse species generated in these experiments make the clear isolation of a special EMF ion difficult, the CID experiments have also been applied to some EMF ions, such as CaC_{60}^+ , SrC_{60}^+ , BaC_{60}^+ , BaC_{92}^+ , and BaC_{130}^+ [23]. For other EMF ions with more metal atoms or larger carbon cages, the gas-phase oxygen reaction test was applied to verify their endohedral structures. Nevertheless, since endohedral carbide cluster fullerene structures cannot be ruled out, it is not possible to properly identify their structures based solely on these mass spectrometric experiments.

The laser ablation of the mixture of graphene and LuCl_3 generated EMF ions with more metal atoms encaged (Figures 4b and 5) [54]. As shown in Figure 5, EMF ions of $\text{Lu}_n\text{C}_{2m}^+$ ($n = 1\text{--}9$, $50 \leq 2m \leq 198$) were observed in the mass spectrum. The gas-phase reaction test experiments confirmed their endohedral architectures. A few mono-EMF ions, such as LuC_{50}^+ and LuC_{66}^+ , exhibit appreciable relative intensities, suggesting that the encaged metal atom significantly stabilizes relative IPR-violating cages. Similar to the cases of La and Y, the yield of trimetallofullerene ions, $\text{Lu}_3\text{C}_{2m}^+$, is the highest among all of the multimetallic metallofullerene ions. The intensities of $\text{Lu}_4\text{C}_{2m}^+$ and $\text{Lu}_5\text{C}_{2m}^+$ are still strong, suggesting the potential of their practical synthesis. The more Lu atoms contained in the EMFs, the larger the required carbon cage size. It has been found that the cage's average size rises by 12 carbon atoms for every additional Lu atom within the fullerene.

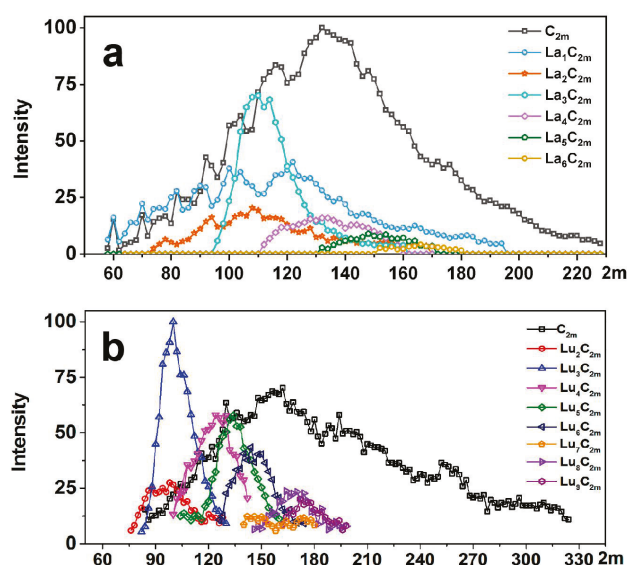


Figure 4. Intensity distributions of (a) $\text{La}_{1-6}\text{C}_{2m}^+$ and (b) $\text{Lu}_{2-9}\text{C}_{2m}^+$. (Figure 4b is taken with permission from [54]).

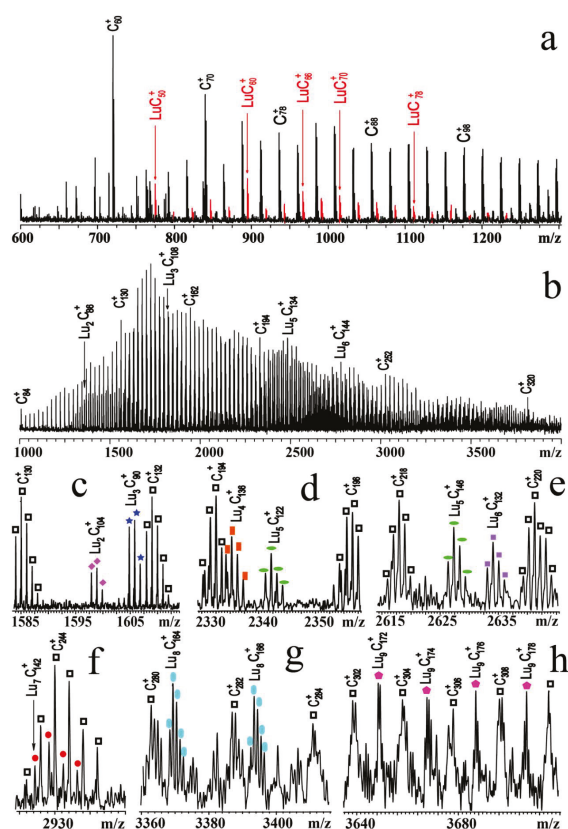


Figure 5. Laser ablation mass spectra of $\text{LuCl}_3/\text{graphene}$ (a) obtained in the m/z region of 600–1300, and (b) obtained in the m/z region of 1000–4000. Some metallofullerene ions of $\text{Lu}_{2-9}\text{C}_{2n}^+$ are further shown in (c–h) in detail. Taken with permission from [54].

Other rare earth metals were also considered in order to obtain a general understanding of the multi-metallofullerene ions generated by laser ablation. Together with the previous data for alkali metal and alkali earth metal species, Table 1 summarizes all the multi-metallofullerene species created under identical experimental conditions in such studies [23,52–55]. As shown here, EMF ions with numerous metal atoms ($n > 4$) are only

available in the cases of Y, La, Tb, Ho, and Lu. The increased number of encaged metal atoms also creates requirements for the size of carbon cages, but these requirements vary for different metals. For instance, the distribution of La_5C_{2m} falls between 132 and 170 in terms of $2m$, whereas the ranges for Tb, Ho, and Lu are 124 and 150, 114 and 160, and 104 and 160, respectively. The outcomes show the impacts of the metals' ionic radii in addition to the interaction of metal clusters with carbon cages. For the majority of these rare earth metals, it is possible to generate distinct multi-EMF ions ($n \geq 2$); however, Sm and Eu exhibit divergent outcomes, with no metallofullerene ions reported in the studies. For alkali metals and alkaline earth metals, only dimetallofullerene ions were observed in the examples of calcium and barium.

Table 1. Observed multi-metallofullerene ions of different metals in gas-phase laser ablation experiments.

M	Oxide States	Observed Multi-Metallofullerene Ions	Ref.
La	+3	$\text{La}_2\text{C}_{74-168}^+$, $\text{La}_3\text{C}_{96-160}^+$, $\text{La}_4\text{C}_{112-160}^+$, $\text{La}_5\text{C}_{132-170}^+$, $\text{La}_6\text{C}_{152-180}^+$	[53]
Ce	+3 +4	$\text{Ce}_2\text{C}_{88-106}^+$, $\text{Ce}_3\text{C}_{94-136}^+$, $\text{Ce}_4\text{C}_{100-150}^+$	[55]
Pr	+3 +4	$\text{Pr}_2\text{C}_{88-102}^+$, $\text{Pr}_3\text{C}_{94-134}^+$, $\text{Pr}_4\text{C}_{108-138}^+$	[55]
Nd	+3	$\text{Nd}_3\text{C}_{96-130}^+$	[55]
Sm	+2 +3	None	[55]
Eu	+2 +3	None	[55]
Gd	+3	$\text{Gd}_2\text{C}_{86-108}^+$, $\text{Gd}_3\text{C}_{90-128}^+$, $\text{Gd}_4\text{C}_{106-134}^+$	[55]
Tb	+3 +4	$\text{Tb}_2\text{C}_{80-112}^+$, $\text{Tb}_3\text{C}_{86-130}^+$, $\text{Tb}_4\text{C}_{100-144}^+$, $\text{Tb}_5\text{C}_{124-150}^+$, $\text{Tb}_6\text{C}_{134-164}^+$, $\text{Tb}_7\text{C}_{148-176}^+$	[55]
Dy	+3	$\text{Dy}_2\text{C}_{82-108}^+$, $\text{Dy}_3\text{C}_{90-128}^+$	[55]
Ho	+3	$\text{Ho}_2\text{C}_{74-104}^+$, $\text{Ho}_3\text{C}_{86-124}^+$, $\text{Ho}_4\text{C}_{98-112}^+$, $\text{Ho}_5\text{C}_{114-154}^+$, $\text{Ho}_6\text{C}_{132-162}^+$	[55]
Er	+3	$\text{Er}_2\text{C}_{82-96}^+$, $\text{Er}_3\text{C}_{90-114}^+$	[54]
Tm	+2 +3	$\text{Tm}_2\text{C}_{80-100}^+$, $\text{Tm}_3\text{C}_{88-122}^+$, $\text{Tm}_4\text{C}_{110-132}^+$	[54]
Yb	+2 +3	$\text{Yb}_3\text{C}_{90-110}^+$	[54]
Lu	+3	$\text{Lu}_2\text{C}_{76-128}^+$, $\text{Lu}_3\text{C}_{82-130}^+$, $\text{Lu}_4\text{C}_{100-142}^+$, $\text{Lu}_5\text{C}_{104-160}^+$, $\text{Lu}_6\text{C}_{126-174}^+$, $\text{Lu}_7\text{C}_{140-180}^+$, $\text{Lu}_8\text{C}_{146-198}^+$, $\text{Lu}_9\text{C}_{172-198}^+$	[54]
Y	+3	$\text{Y}_2\text{C}_{74-130}^+$, $\text{Y}_3\text{C}_{88-128}^+$, $\text{Y}_4\text{C}_{102-142}^+$, $\text{Y}_5\text{C}_{128-154}^+$, $\text{Y}_6\text{C}_{130-154}^+$	[53]
Li	+1	None	[52]
Na	+1	None	[52]
Rb	+1	None	[52]
Cs	+1	None	[52]
Mg	+2	None	[23]
Ca	+2	$\text{Ca}_2\text{C}_{96-160}^+$	[23]
Sr	+2	None	[23]
Ba	+2	$\text{Ba}_2\text{C}_{80-182}^+$	[23]

3.3. EMFs including Late Transition Metals

Although EMFs with rare earth metals and their adjacent elements (groups I–IV) have been investigated in the gas phase, those containing post-transition metals are very rarely experimentally studied. Entrapping these transition metals in fullerene cages is still a challenge [56]. There may be many reasons for this, but one of them is that these metal species usually exhibit high reactivity with carbon atoms during the generative process. Thus, it is suggested that the most performable way to make EMFs containing post-transition metals is to use heterometal clusters to reduce the reactivity of these metal species.

Recently, Kong's group successfully synthesized metal fullerene ions containing platinum atoms in the gas phase for the first time [56]. By laser ablation of a mixed sample of graphene/ LaCl_3 / PtCl_4 in vacuum, the EMF ions of $\text{La}_m\text{PtC}_{2n}^+$ were observed (Figure 6a) and verified with oxygen reaction tests [50,56]. An example is shown in Figure 6. Apart from the EMF ions of $\text{La}_2\text{C}_{2n}^+$ and $\text{La}_3\text{C}_{2n}^+$, $\text{La}_m\text{PtC}_{2n}^+$ ($m = 2-3$; $n = 43-65$) was also observed. The distributions of the observed EMF ions are compared and shown in Figure 6b. It can be found that EMF ions of $\text{La}_2\text{PtC}_{2n}^+$ have a distribution from $2n = 86$ to 114 centered on the $\text{La}_2\text{PtC}_{98}^+$, and those of $\text{La}_3\text{PtC}_{2n}^+$ have a distribution from $2n = 98$ to 130 centered on the $\text{La}_3\text{PtC}_{112}^+$.

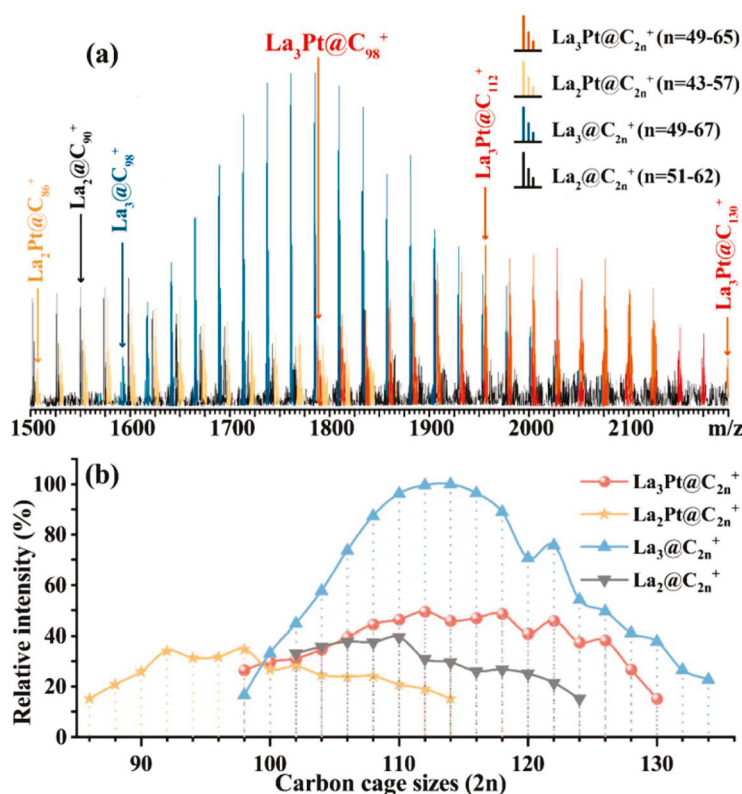


Figure 6. (a) Laser ablation MS spectrum of the mixture of graphene/LaCl₃/PtCl₄ in the region of 1500–2200 *m/z*. For convenience, the abundant fullerene ions of C_{2n}⁺ (*n* = 63–91) have been manually removed. (b) Intensity distributions of La_{*m*}Pt@C_{2n}⁺ (*m* = 2, 3) and La_{*m*}@C_{2n}⁺ (*m* = 2, 3) observed in the upper figure. Taken with permission from [50].

Extensive theoretical studies have been performed for the neutral forms of these two selected species, La₂PtC₉₀⁺ and La₃PtC₉₈⁺ [50,56]. For La₂PtC₉₀ (the neutral species of La₂PtC₉₀⁺), the two most stable structures are La₂Pt@C₂(99915)-C₉₀ and La₂Pt@C₂(99916)-C₉₀, with the energy of the latter being 8.1 kcal/mol greater than that of the former. Moreover, large HOMO-LUMO gaps of 1.28 and 1.13 eV have been found for the two isomers. Impressively, the most stable isomer of the corresponding metal carbide EMFs, which has been identified to be La₂PtC₂@D2(81738)-C₈₈, has a much higher energy (>89 kcal/mol) than La₂Pt@C₂(99915)-C₉₀. As shown in Figure 7a,b, the internal La₂Pt clusters in both structures exhibit a “V” shape, with La coordinating with the carbon cage and Pt located at the center of the La₂Pt cluster, serving as a connecting point to stabilize the EMFs. Within the triatomic cluster, the distances between La–La and La–Pt are ~4.01 and 2.73 Å, respectively, indicating the existence of the La–Pt bond.

The two most stable isomers of La₃Pt@C₉₈ were found to be La₃Pt@C₂(231010)-C₉₈ and La₃Pt@C₁(231005)-C₉₈ [50]. Their structures are shown in Figure 7c,d. In both isomers, the La₃Pt clusters form pyramidal tetrahedrons in carbon cages. The distances between two nearby La atoms are 4.18–4.40 Å, a little longer than those in the top two isomers of La₂Pt@C₉₀. The encaged clusters of La₃Pt in both isomers have typical La–Pt bonds with a length of about 2.80 Å, and La–Pt–La bond angles of ~100°, with a shape similar to the metal nitride clusters in M₃N@C₈₀ (*M* = Y, Tb, Gd), but different from planar triangles in the cases of M₃N@C₈₀ (*M* = Sc, Lu, Dy).

In order to explore the role of the encaged Pt atom, Mulliken charge distribution calculations were carried out for these structures [50,56]. Results show that the carbon cages and the endohedral La atoms are negatively and positively charged, respectively. Very interestingly, it is noted that Pt atoms within La₂Pt or La₃Pt clusters appear to have a negative valence and may mediate the interactions between two La or among three La

atoms. For $\text{La}_2\text{Pt}@C_2(99915)\text{-C}_{90}$, the charges of the two La atoms are +1.82 and +1.81, and the Pt atom is negatively charged (with a charge of -0.64). This role is similar to that of Pt in the embedded tetrametallic fullerene $\text{La}_3\text{Pt}@C_{98}$. For both $\text{La}_3\text{Pt}@C_1(231005)\text{-C}_{98}$ and $\text{La}_3\text{Pt}@C_2(231010)\text{-C}_{98}$, the La atoms present positive states (from 0.49 to 0.52), while the Pt atoms are negatively charged (around -0.24). In the case of $\text{La}_3\text{Pt}@C_{98}$, all three of the La atoms create 2c–2e bonds with the negatively charged Pt atom, which serves as a mediator. Interestingly, the entire molecule is stabilized by the 4c–2e tetrametallic bond, with the highest occupancy number in the unit of La_3Pt . It is noteworthy that seven electrons have transferred from the inner metal cluster to the outside fullerene cage in this instance, which is quite rare and has not been documented before. This is further evidenced by the adaptive natural density partitioning (adNDP) analysis, where Pt takes two electrons to fill its 5d-shell from La atoms and shares its $6s^2$ pair as a back-donation with La atoms, resulting in its unique electron distribution in a form of $[(\text{La}^{3+})_3\text{Pt}^{2-}]^{7+}@C_{98}^{7-}$.

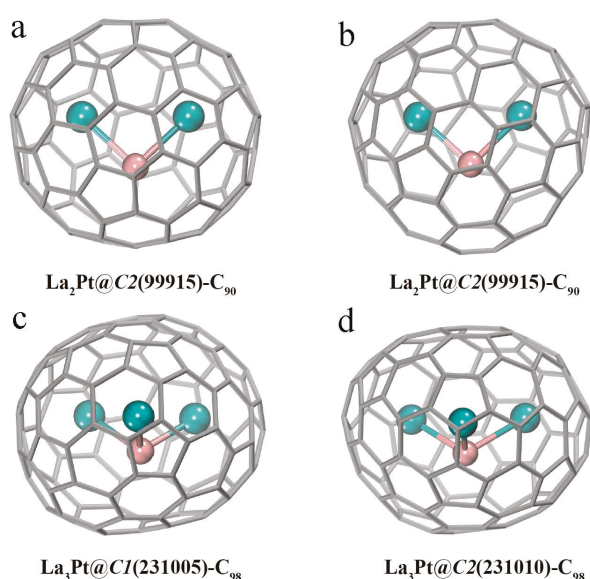


Figure 7. The calculated structures of two most stable isomers of $\text{La}_2\text{Pt}@C_{90}$: (a) $\text{La}_2\text{Pt}@C_2(99915)\text{-C}_{90}$, (b) $\text{La}_2\text{Pt}@C_2(99916)\text{-C}_{90}$. The calculated structures of the two most stable isomers of $\text{La}_3\text{Pt}@C_{98}$: (c) $\text{La}_3\text{Pt}@C_1(231005)\text{-C}_{98}$ and (d) $\text{La}_3\text{Pt}@C_2(231010)\text{-C}_{98}$.

3.4. EMFs including Ionic Bonds

There are still big challenges to encapsulating various ionic bonds in fullerenes (except for metal oxides) [57–61]. The confinement of an individual ionic bond is very difficult, since it has neither sharing electrons nor a fixed pairing relationship between the two ions. Due to the difficulty in generation, they have only very rarely been the subject of experimental research. Using a Smalley-type ion source, Martin et al. observed such fullerene ions in the gas phase in their pioneering works. They identified ions of $\text{CaCl}@C_{66}^+$ and $\text{HoCl}@C_{60}^+$ in the gas phase and gave a justification for the species' threshold sizes using the spherical approximation [61].

Recently, Kong's group reported the identification of endohedral ions of LuClC_{2n}^+ ($2n = 90\text{--}190$) with high-resolution laser ablation mass spectrometry [57]. In the experiments, a mixture of graphene/ LuCl_3 / LiCl was applied as the precursor, and oxygen gas was used as the reaction gas to verify their endohedral structures. Similarly, mixtures of graphene and sodium halides (NaX) ($X = \text{Cl}, \text{Br}, \text{I}$), EMF ions of $\text{NaCl}@C_{2n}^+$ ($2n = 120\text{--}244$), $\text{NaBr}@C_{2n}^+$ ($2n = 110\text{--}240$), and $\text{NaI}@C_{2n}^+$ ($2n = 116\text{--}198$) were also observed by the same group [58]. Interestingly, Li or K could not substitute for the encapsulated metal ion in these studies, indicating that the metal cation's effects on the EMFs outweigh those of halide anions.

To figure out the structures and properties of the endohedral ionic bond fullerenes, the species of LuCl@C_{90} was selected and studied systematically using DFT methods [57]. $\text{LuCl@C}_2(99917)\text{-C}_{90}$ and $\text{LuCl@C}_2(99914)\text{-C}_{90}$ were found to be the top two isomers (Figure 8), which have significant HOMO–LUMO gaps of 1.61 and 1.82 eV, respectively. Statistical thermodynamic analysis shows that the former prevails inside a small temperature range of 0 to 500 K. With the temperature increasing, it is exceeded by $\text{LuCl@C}_2(99914)\text{-C}_{90}$ at 650 K and by $\text{LuCl@C}_2(99913)\text{-C}_{90}$ at 3000 K. For all optimized isomers, it was found that the Lu atoms are situated between the Cl atoms and the cages, and the Cl atoms are found in the hubs of the cages. The potential curve of an encaged ionic bond is distinct from that of isolated ionic bonds, which are identified by their usual Morse or Morse long-range potentials. As shown in Figure 7, infinite potential wells exist due to the restriction of the carbon cages, and the wells are deeper than those of unprotected ionic species, clearly showing that they have different characteristics. In addition, the calculation shows that the equilibrium distances of the Lu–Cl bonds in both isomers is 2.49 Å, which is larger than that of LuCl_2^+ (2.30 Å) and a little smaller than that of LuCl (2.55 Å).

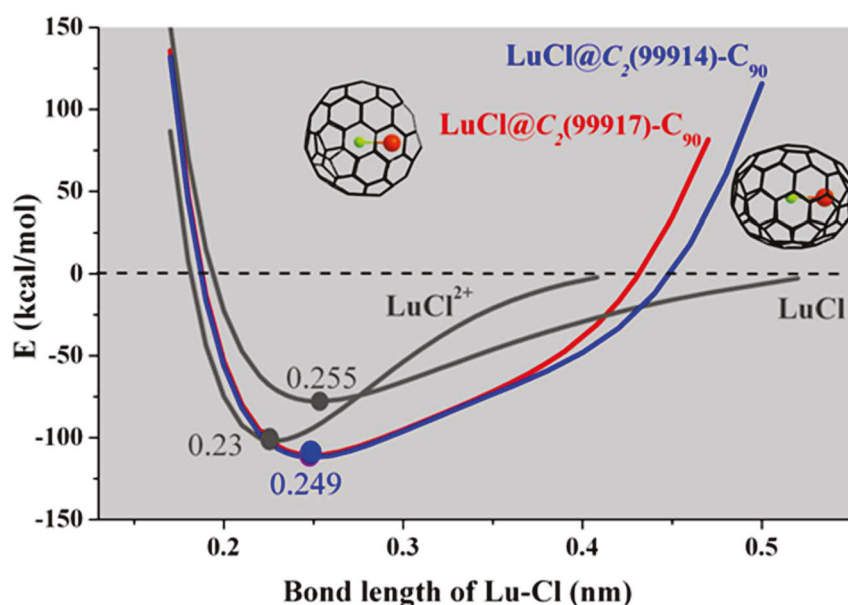


Figure 8. Potential curves of LuCl_2^+ , LuCl , $\text{LuCl@C}_2(99917)\text{-C}_{90}$, and $\text{LuCl@C}_2(99914)\text{-C}_{90}$. Taken with permission from Ref. [57].

An interesting effect of endohedral ionic bond fullerenes is that it is possible to rotate the bond inside the carbon cages. The energy barrier mainly depends on the interaction between the metal ion and the cage [57]. For instance, seven energy minima were discovered during the rotation of the Cl–Lu bond in the lowest energy isomer of $\text{LuCl@C}_2(99917)\text{-C}_{90}$, and the energy barriers were found in the range of 20–220 kcal/mol. However, the results depend very much on the selected plane for rotation. If the perpendicular rotation plane is selected, there are only four energy minima and the rotation energy barrier is considerably larger, reaching up to 600 kcal/mol.

In fact, the properties of encaged ionic bonds have previously been noticed by theoretical chemists and have always been a focus of their attention [62–65]. Foroutan-Nejad et al. proposed a single-molecule switch based on the neutral dipolar molecule that uses alkali metal halides contained in a C_{70} cage for data storage [65]. The encaged ionic bonds have two local energy minima separated by an energy barrier relative to the fullerene. Attractively, an external electric field can be used to manipulate the dipolar system inside the fullerene. This is possible with contemporary instruments like scanning tunneling microscopes. The ionic bond aligns along the main axis of C_{70} to minimize the steric clash. The conformations with the dipole moment along the electric field are more stable than the

others when the electric field is on. With an increasing electric field, the stabilization should lead to the reorientation of the encaged ionic bond. The same group has also proposed using a two- or four-electrode system to speed up the switching procedure, showing their potential in the application of random-access memories and memristors [64]. As illustrated in Figure 9, the dipolar MX causes the system to operate like a diode by polarizing the fullerene shell electrons. A series of species of MX@C_{70} (M = a metal or hydrogen, X = a halogen or a chalcogen) have been studied to be identified as possible molecular memristors by the same research group.

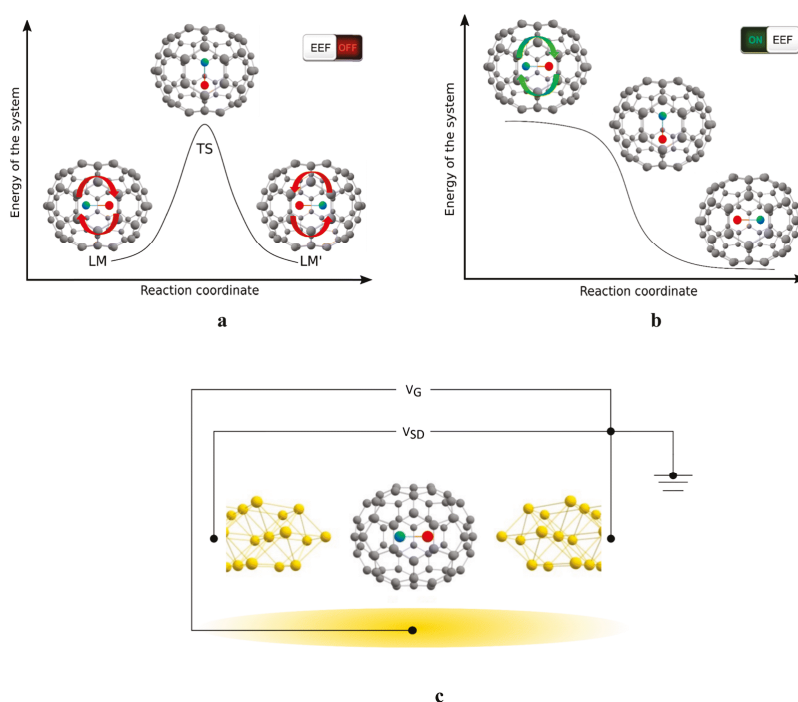


Figure 9. The principle of an MX@C_{70} molecular memristor (EEF stands for the external electric field). (a) MX@C_{70} with two local minima (LM and LM') separated by a transition state (TS) with an energy barrier. (b) Upon application of external voltage, one of the local minima becomes unstable. This leads to the rotation of MX between LM and LM' (or LM' and LM), and thus to the switching of the system's polarity and conductivity. (c) The four-electrode setup in which the source–drain voltage (VSD) is applied horizontally and the gate voltage (V_G) is perpendicular to the VSD. Taken with permission from Ref. [64].

Impressively, Gan et al. recently reported the preparation of an open-cage fullerene as a selective molecular trap for ionic bonds of $\text{LiF}/[\text{BeF}]^+$ [60]. They made use of a hydroxy group-containing open-cage C_{60} derivative. LiF and $[\text{BeF}]^+$ were encapsulated as a result of the hydroxy group's ability to coordinate lithium or beryllium cations, functioning as a bait or hook. The whole structures were clearly identified by single-crystal X-ray diffraction. A bright future lies ahead for the development of more cage-opening reactions for the prospective uses of fullerene-based molecular containers, especially in light of the recent advancements in the logic-in-memory operations of a two-terminal single-metallofullerene device at room temperature [62].

4. Mechanism Study

Similar to those of fullerenes, the suggested mechanisms for the formation of EMFs can be generally classified into two types: bottom-up or top-down [20,44,47,66–82]. For example, Dunk et al. demonstrated that U@C_{28} acts as a precursor for larger uranofullerenes while itself being formed through a bottom-up process [44]. They have identified the structures of Ti@C_{2n} ($2n = 26\text{--}50$) and uncovered essential features in their growth processes

by DFT calculations and molecular dynamics (MD) simulations [47]. Further studies by the same group show more proofs of the suggested bottom-up formation process of giant mono-EMFs from $\text{Pr}@C_{2v}\text{-C}_{82}$ [20]. They proposed that, under EMF synthesis circumstances, mono-metallofullerenes with small to giant sizes might form in the gas phase via a bottom-up mechanism. The extent of charge transferred to carbon cages appears to be determined by the elements' ionization energies during graphite/metal evaporation. It has been suggested that the unconventional small-sized EMFs could stabilize by charge transfer, although the existing strain energy resulted in the impeding of C_2 insertion and the inhibition of overall bottom-up formation of large-sized metallofullerenes. MD simulation also plays an important role in understanding the formation mechanisms of EMFs [83–87]. Using constructed multi-body potential functions, Yamaguchi et al. found that the clustering process of a system containing 500 isolated carbon atoms and five La atoms under a controlled temperature of 3000 K can result in lanthanum-containing caged clusters. For the Ni–C system, the Ni atom ultimately stayed on the face of caged structures [83]. Deng et al. investigated the effects of the inert cooling gas helium in the Sc-EMF forming process with the method of quantum chemical molecular dynamics. Their results show that Sc encapsulation involves nucleation of carbon clusters with Sc atoms at early stages, and the existence of He gas reduces the size of the self-assembled cages [84]. An extended simulation with an Fe atom shows no formation of such Fe-EMF, which is consistent with experimental results [71]. Fan et al. found that the growth patterns of Sc-EMFs resemble those of hollow cages, and the He gas could promote both the formation of carbon cages and the encapsulation of scandium atoms [86].

The bottom-up mechanism is suitable for the formation of mono-metallofullerenes from metal-incorporated graphite [20]. However, the generation of multiple metallofullerenes in some experiments, such as the examples shown in Figures 3–5, may have different mechanisms. The top-down mechanism offers another kind of possibility [71–78]. There is evidence to support the theory that giant fullerenes formed from large-size polycyclic aromatic hydrocarbons (PAHs), or graphene sheets shrunk into smaller ones, through interstellar and laboratory observations as well as theoretical calculations [71,77,78]. For example, Irlé et al. use a 'shrinking hot giant fullerene' mechanism in which giant carbon cages occur first, followed by multiple C_2 losses with self-assembly to appropriate symmetric fullerene cages, such as $I_h\text{-C}_{60}$ and $D_{5h}\text{-C}_{70}$ [71]. Moreover, the transformation of graphene to a fullerene cage was demonstrated by Chuvilin et al., based on their transmission electron microscopy and theoretical studies [74].

For EMFs, the top-down mechanism is also applied in some cases [23,48–56,79–82]. Dorn et al. isolated and characterized metal carbide metallofullerenes $\text{M}_2\text{C}_2@C_1(51383)\text{-C}_{84}$ ($\text{M} = \text{Y, Gd}$) and proposed that the cage with fused pentagons is a preserved 'missing link' in the top-down mechanism [80]. The unique asymmetric structure can form many symmetric fullerenes that account for some well-known solvent-extractable metallofullerenes using limited, well-established rearrangement steps. Lu et al. presented the identified $\text{La}_2\text{C}_2@C_2(816)\text{-C}_{104}$ as an origin formation of other known ideal tubular cages by removing the pyracylene motif, providing support for the top-down formation mechanism of such fullerenes [79]. Using the method of transmission electron spectroscopy, Sinitsa et al. proposed a method for synthesis of nickel EMFs, in which the formation was initiated by electron irradiation of a metal cluster surrounded by amorphous carbon inside a carbon nanotube [87]. Their MD simulations also rationalize the experimental observations. On the other hand, Kong et al. suggested the top-down mechanism to explain the multiple EMF ions produced in the process of laser ablation of graphene flakes mixed with metal salts [23,48–56]. It is proposed that the instantaneous process of wrapping metal atoms or clusters inside curved graphene flakes produced by laser irradiation can lead to the production of EMFs with large-sized cages and multi-metal atoms. Moreover, the mechanism can be used to interpret the generation of fullerenes with engaged ionic bonds in a similar way. It is important to notice the difference between the use of graphene and graphite as

precursors in these experiments, since their differently reported mass spectra indicate their different laser ablation processes and mechanisms.

5. Prospect

The gas-phase EMF study provides valuable information in many ways. The importance of gas-phase research on EMFs in their discovery can never be overstated, and they are going to remain essential in interdisciplinary investigations of new species in this big family. In this review, we summarized the progress of gas-phase EMF studies in the past 15 years, focusing on novel EMF species identified in the gas phase and the relative mechanism study, which provided valuable information for the structural research, synthesis, and design of such new molecules. Although the research undertaken in gas-phase EMF research is much less widespread compared to those engaged in the synthesis, separation, and application of EMFs, the gas-phase results still provide valuable clues for new members in the family of EMF. On the one hand, these novel EMF species observed in the gas phase provide direct experimental evidence for their existence and valuable clues for their solid-phase synthesis methods, which can promote the exploration and discovery of new synthesis methods for EMFs. On the other hand, the structural study of these new EMF species can provide insights into their novel structures and new chemical bonds, different properties, and potential applications.

Experimentally, high-resolution mass spectrometry is widely applied to qualitatively identify charged EMF species and their molecular compositions. The distributions of EMF ions related to different experimental conditions, precursors, and metal elements can provide valuable information on the mechanism of the generation of important and novel EMF species, especially when combined with theoretical calculations. Among them, the selection of precursors is found to be important, and it is worth noting that, in future research, the synthesis of specific novel EMFs can be more effectively achieved by selecting appropriate precursors. However, it should be pointed out that a great deal of essential work in gas-phase EMF study still needs to be done. First, new methods for the generation of new or novel EMF ions are necessary. Considering that the bottom-up mechanism dominates most laser ablation experiments, based on the Smalley-type source, different generation and ionization methods based on the top-down mechanism are needed for large-size or special EMF ions. Different precursors and new sample preparation methods are important, too. Second, the formation of EMFs encaging transition metals is one of the most fascinating topics in gas-phase EMF chemistry. It is also an important means of discovering novel EMFs. Considering the examples of $\text{La}_2\text{Pt}@C_{90}$, and $\text{La}_3\text{Pt}@C_{98}$, it is natural to assume that more types of embedded metal clusters or ionic bonds can be discovered or synthesized. On the other hand, the ionic bonds composed of different elements can provide new members for the EMF family and may be applied as crucial components of molecular devices. Third, it is expected that more methods of ion chemistry should be applied to the investigation of the structure and characteristics of gas-phase fullerene ions. In addition to the widely used method of CID, other methods, such as reaction mass spectrometry, collisional section measurement, UV photodissociation spectroscopy, etc., should be combined in tandem mass spectrometric study. Fourth, the gas-phase study of EMF anions, which may open up a different path for discovering new EMFs, is still very limited.

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Review

Capturing Unstable Metallofullerenes

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Abstract: Metallofullerenes are interesting molecules with unique structures and physicochemical properties. After they are formed in the arc-discharge process, they are first buried in the carbon soot, which requires solvent extraction to fish them out, normally followed by HPLC separation. In this minireview, we summarize the main procedures developed to obtain pure metallofullerenes, including well-established extraction with conventional fullerene solvents followed by HPLC (procedure **I**) as well as several methods developed for isolation and purification of unstable fullerenes insoluble in conventional fullerene solvents, including chemical modification followed by dissolution (**II.1**), chemical functionalization *during* extraction followed by HPLC (**II.2**), and chemical functionalization of ionic EMFs *after* redox-extraction followed by HPLC (procedure **II.3**). The main focus here is on procedure **II.3**, for which the current status and future perspective are discussed.

Keywords: endohedral metallofullerenes; extraction; open-shell electronic structure; electrophilic trifluoromethylation; benzylation

1. Introduction

Endohedral metallofullerenes (EMFs) are molecules with metal ions encapsulated in a fullerene cage, which are interesting because of their unique coordination between metal ions and the fullerene cage, resulting in fascinating physicochemical properties [1–52]. The pursuit of novel EMF structures has been a strong impetus in the field, not only for the discovery of a bizarre interplay between metal ions and fullerene cages, but also for their appealing application potentials endowed by this unique interaction. Metallofullerenes are usually prepared by direct current arc discharge of graphite rods embedded with a metal source. However, this process simultaneously produces EMFs, empty fullerenes, as well as other carbonaceous species, and the EMFs are then fished out of the carbon soot. The general procedure uses extraction with some organic solvents to dissolve metallofullerenes from the carbon soot, followed by separation procedures to obtain pure compounds (Procedure **I**, Figure 1). CS₂ is the most commonly used solvent during the extraction, although toluene, chlorobenzene and other aromatic solvents are also applied occasionally; we will refer to this group of solvents as **fullerene solvents** in the following discussion. Separation of the dissolved fullerenes is usually performed by high-performance liquid chromatography (HPLC), but may also include some non-HPLC steps.

Procedure **I** prevails in the EMF research because many fullerenes/metallofullerenes are well soluble in these solvents, and the extraction procedure is relatively straightforward. However, there is a certain fraction of fullerenes that show moderate to negligible solubility in fullerene solvents. These fullerenes therefore remain in the soot after extraction with fullerene solvents, but their formation in the arc-discharge synthesis could be demonstrated by extraction with other solvents or chemical functionalization, as will be discussed further in this review. In the following, we define **stable fullerenes** as those fullerenes that can be routinely obtained by Procedure **I**, while **unstable fullerenes** are those that cannot be obtained by this procedure due to poor solubility in fullerene solvents at the extraction and separation stages. The boundary between stable and unstable fullerenes is not clearly defined. Fullerenes are usually considered stable if their solution in

fullerene solvents remains intact for months, i.e., long enough to complete the separation and characterization procedures.

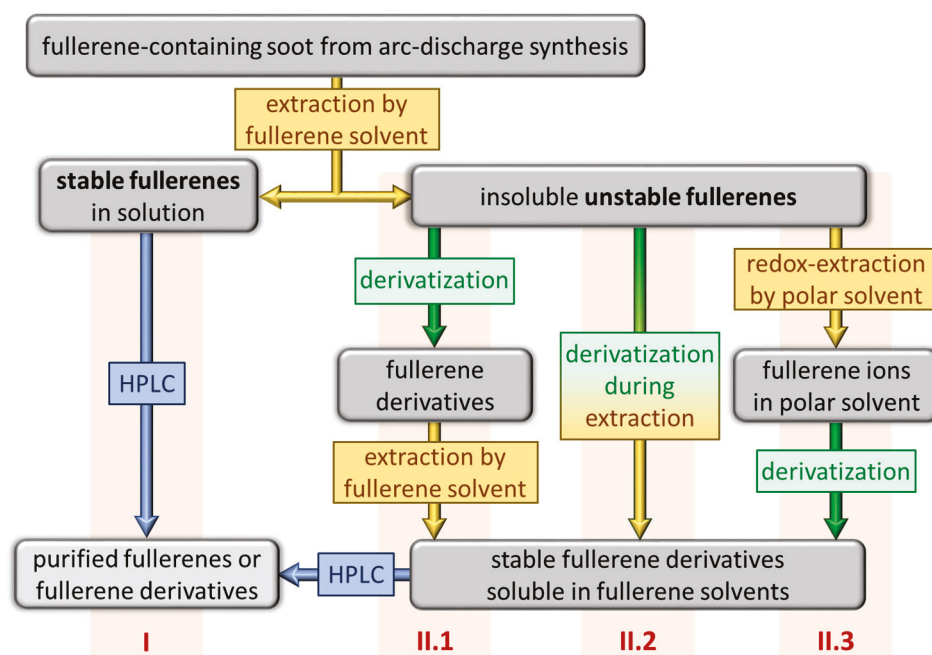


Figure 1. Schematic description of fullerene separation procedures discussed in this minireview.

2. Unstable Fullerenes

It should be emphasized that the stability discussed here is not stability in the thermodynamic sense. The **unstable fullerenes**, which are the focus of this review, are formed during synthesis, and if we assume that the yield of fullerenes in the arc-discharge process is controlled by thermodynamic factors, we should also assume **thermodynamic stability** of these unstable fullerenes. In other words, the relative energies of these structures with respect to different cage isomers should be low, and calculations of equilibrium concentration at the temperature of the synthesis will likely predict considerable concentration for these fullerenes. Therefore, it is their low **kinetic stability** or, equivalently, high reactivity, that poses the problem for their isolation and characterization. The high reactivity is usually related to the electronic structure and can be deduced from the analysis of the frontier orbital levels. Examples of frontier orbital situations in three types of fullerenes, which often have unstable structures among them, are shown in Figure 2:

- (1) Empty fullerenes. Soluble empty fullerenes have a large HOMO-LUMO gap and a closed-shell electronic structure with the singlet ground state. However, if the HOMO-LUMO gap is small, the triplet (biradical) state may be accessible or even become lower in energy than the singlet (Figure 2a). The molecule thus has an open-shell electronic structure, which is usually synonymous with enhanced reactivity. A typical example of an insoluble empty fullerene with a triplet ground state is D_{3h} - C_{74} [53].
- (2) Monometallofullerenes with trivalent metals, $M^{III}@C_{2n}$ (Figure 2b). Since endohedral metal atoms transfer their electrons to the fullerene cage, the M^{III} state implies that the fullerene cage accepts three electrons and thus has a radical nature with one unpaired electron. Interestingly, some monometallofullerenes, such as $M^{III}@C_{2v}(9)-C_{82}$, behave as stable fullerenes and can be obtained in pure form by procedure I, while the others, such as $M^{III}@C_{60}$ or $M^{III}@C_{2v}(5)-C_{80}$, are insoluble in fullerene solvents and require special procedures for extraction and isolation. $M^{III}@C_s(6)-C_{82}$ is a good example of a dual behavior as it shows reasonable solubility and can be obtained by conventional procedure I, but tends to form dimers upon crystallization [54,55]. The boundary

- between the two types is blurred, indicating that the peculiarities of the π -system distribution for a given carbon cage also play an important role.
- (3) Dimetallofullerenes of trivalent metals (Figure 2c). Their situation in some way resembles that of empty fullerenes since the transfer of six electrons from the metal dimer to the host fullerene should result in a closed-shell electronic structure. Indeed, dimetallofullerenes of early lanthanides, such as $\text{La}_2@C_{2n}$ and $\text{Ce}_2@C_{2n}$, are soluble in fullerene solvents and can be purified using procedure I. The difference from empty fullerenes is that the LUMO of dimetallofullerenes is usually a metal–metal bonding orbital, and its energy depends on the metal. For heavier lanthanides, starting with Nd, the energy of the metal-based LUMO becomes so low that the triplet state, in which one unpaired electron occupies the metal-based MO and one occupies the fullerene MO, becomes more stable than the closed-shell singlet [56,57].
 - (4) Clusterfullerenes, i.e., metallofullerenes with endohedral clusters such as M_3N , M_2C_2 , M_2O , M_2S , etc., usually have a closed-shell electronic structure of the carbon cage, and the vast majority of them can be obtained from the soot and separated by procedure I. It is certainly possible that some of them are unstable due to the small HOMO–LUMO gap of the carbon cage, similarly to insoluble empty fullerenes, but we are not aware of any experimentally characterized examples of clusterfullerenes that are not soluble in fullerene solvents but could be extracted and separated by other approaches. Clusterfullerenes are therefore not discussed further in this review.

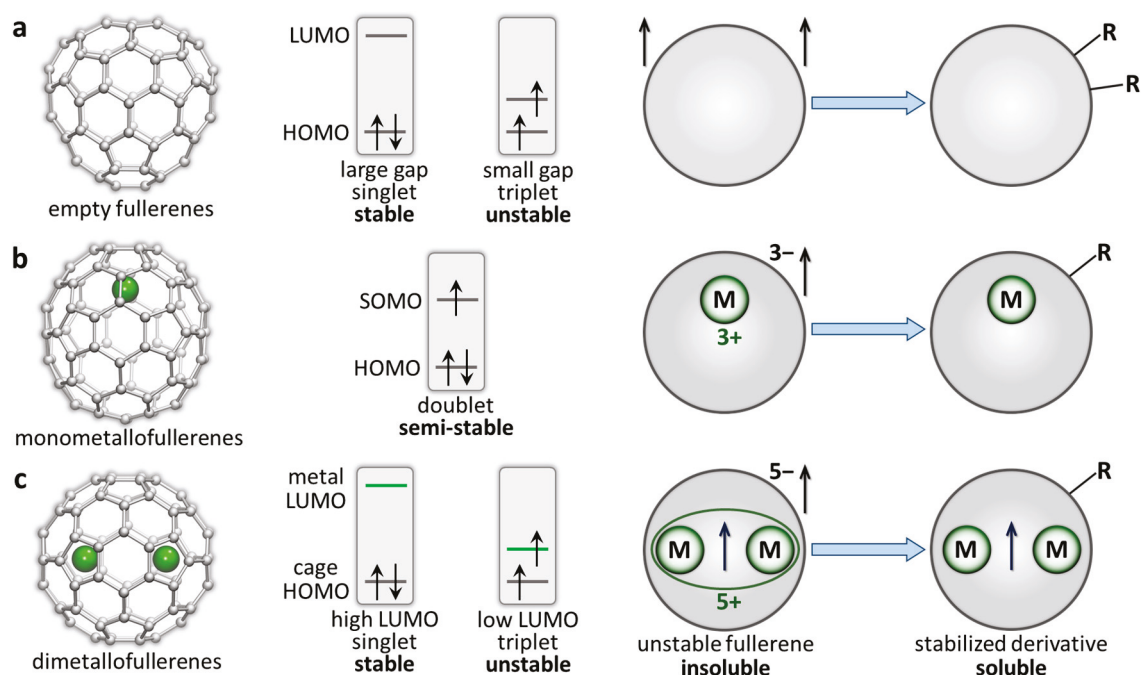


Figure 2. Major types of unstable fullerenes: (a) empty fullerenes, (b) monometallofullerenes with trivalent metals, (c) dimetallofullerenes with trivalent metals. For each type, the figure shows an example of a molecular structure (left), population of the frontier MOs (middle; fullerene MO levels are gray, metal-based MO levels are green), formal charge of the metal species and the cage (b,c) and stabilization of the open-shell electronic structure of the carbon cage by addition of radical groups (right). Vertical arrows denote unpaired electrons.

The low solubility of unstable fullerenes is likely caused by the tendency of fullerene cages to stabilize their open-shell structure by forming covalent bonds between fullerene molecules (dimerization/polymerization) or by forming bonds with other unidentified components of the soot. Either way, polymerization or binding to soot particles renders unstable fullerenes poorly soluble and causes them to remain in the soot during extraction with fullerene solvents. Importantly, it is the open-shell structure of the carbon cage

that is critical for kinetic stability and separation of EMFs. Endohedral species can also have an open-shell electronic structure, but it does not affect the kinetic stability if the fullerene cage has closed-shell electronic structure. For instance, dimetallo-azafullerenes $M_2@C_{79}N$ ($M = Y, Gd, Tb$) [58,59], trimetal-carbide clusterfullerenes $M_3C_2@C_{80}$ ($M = Sc, Dy, Er$) [60–62] or dimetallofullerenes derivatives $M_2@C_{80}(R)$ ($M = \text{rare earth elements}$) [63–67] have unpaired electrons localized on their endohedral species, but this does not hinder their solubility in fullerene solvents and their overall kinetic stability.

3. Redox Extraction

Extensive studies of metallofullerene synthesis in the late 1990s revealed that while the solubility of some metallofullerenes in fullerene solvents is low, it can be greatly enhanced if extraction is performed using polar nitrogen-containing solvents such as pyridine, *N,N*-dimethylformamide (DMF), or aniline [68–79]. Subsequent studies found that EMFs in these solvents adopt the negative charge state [80,81], suggesting that stabilization of insoluble EMFs, which allows their extraction, occurs via the electron transfer from the solvent. Indeed, since unstable metallofullerenes have an open-shell electronic structure in their pristine neutral form, the addition or removal of an electron can change the fullerene structure to the closed-shell, while endohedral metal species can still retain their spin structure. The process by which fullerenes are reduced or oxidized during extraction with a polar solvent is hereafter referred to as **redox extraction**. Redox extraction requires the presence of either reducing agents (amines [74–79], which can simultaneously be a solvent), or oxidizing agent (magic blue (BrC_6H_4)₃NSbCl₆, AgSbF₆) [82–85], or the use of electrolysis [70,86]. Ionic fullerenes are not soluble in most fullerene solvents and instead require the use of highly polar solvents, whereas uncharged fullerenes are conversely poorly soluble in many polar solvents. Therefore, redox extraction can be used not only for extraction of unstable fullerenes, but also for a partial separation of fullerenes based on their redox properties.

One of the most popular forms of redox extraction in EMF synthesis applies DMF [72,73,81,87–90], which undergoes partial thermal decomposition during extraction with the formation of amines. Hereby, amines act as mild reducing agents, facilitating the formation of EMF anions that are well soluble in DMF. Meanwhile, fullerenes with large HOMO-LUMO gap, including the majority of empty fullerenes, remain in the uncharged state. Since the solubility of neutral fullerenes in DMF is rather modest, extraction with hot DMF is quite efficient for dissolving of mono- and dimetallofullerenes and separating them from empty fullerenes [91,92].

Redox extraction helps to obtain unstable fullerenes from a soot as charged species, but their further separation is less straightforward. To date, $Li@C_{60}$ is the only unstable fullerene that has been isolated in a pure cationic form by redox methods [84,85]. HPLC procedures and column materials used for fullerene separation have been developed for uncharged fullerenes, and their efficiency for ionic species is not guaranteed. In addition, polar solvents normally used for unstable fullerenes, such as DMF or aniline, have high boiling points and are toxic, which adds obstacles for further separation by multi-step HPLC. Therefore, the separation of fullerenes extracted with DMF usually involves non-HPLC methods, such as electrochemical or chemical redox reactions, which change the charge state of the dissolved fullerenes and thus strongly affect their solubility [70,86,90,92,93]. The disadvantage of this strategy is that the redox reaction is not only controlled by the intrinsic redox potentials of the fullerenes, but also strongly affected by their concentrations. This means that very high purity separations can hardly be achieved by this method, and HPLC is still required in the final step. If dissolved anionic EMFs are also stable in the pristine form, they can be oxidized to the neutral form and then separated by HPLC [90]. However, if neutral EMFs are unstable, the oxidation of their anions will obviously produce open-shell species with ensuing low kinetic stability and solubility problems. For instance, attempts in our laboratory to obtain dimetallofullerenes of heavy lanthanides by oxidation

of their DMF-soluble anions immediately formed insoluble precipitates that could not be further processed.

4. Chemical Functionalization of Unstable Fullerenes

4.1. General Remarks

An alternative approach to stabilize fullerenes with open-shell electronic structure is their chemical derivatization by attachment of exohedral groups, which should quench unpaired electrons of the carbon cage. Obviously, each unpaired cage electron can be compensated by the addition of one radical group, and therefore, we will only consider derivatization with groups that form single bonds to the fullerene surface. Cycloaddition reactions, which usually introduce two bonds to a fullerene at once, are not suitable for stabilization of EMFs with the open-shell electronic structure of the fullerene cage. Figure 2 sketches the minimum number of groups that are required to stabilize different types of unstable fullerenes:

- (1) Empty fullerenes with triplet ground state require the addition of at least two radical groups to quench the cage biradical. However, it is not guaranteed that the bisadduct $C_{2n}(R)_2$ will have a large HOMO-LUMO gap. Depending on the MO structure of the molecule, the bisadduct may also have a small gap, thus requiring the addition of another pair of radical groups. However, regardless of how many pairs of radical groups are ultimately required to obtain a stable derivative, it is certain that the number of groups will be even.
- (2) Monometallofullerenes $M^{III}@C_{2n}$ have one unpaired electron, and therefore require the addition of at least one radical group. In general, the number of groups in the stable closed-shell $M^{III}@C_{2n}(R)_x$ derivative should be odd.
- (3) Open-shell dimetallofullerenes of trivalent metals are peculiar in that of the two unpaired valence electrons, one is localized on the fullerene cage and one on the metal dimer. The latter does not seem to be relevant for the kinetic stability, which means that only the unpaired electron of the cage should be quenched. Therefore, dimetallofullerenes require the addition of at least one and generally odd number of groups, similarly to monometallofullerenes.

Once unstable fullerenes are stabilized by derivatization, they can be processed akin to stable fullerenes, since derivatives are soluble in fullerene solvents and can be separated by conventional HPLC to achieve high-purity separation. This strategy will be referred to as Procedure II.

4.2. Derivatization Followed by Dissolution

Depending on the sequence of derivatization and extraction, three modifications of Procedure II can be distinguished, as shown in Figure 1. In method II.1, chemical derivatization is first applied to insoluble unstable fullerenes. A classic example is the thermal radical trifluoromethylation of a mixture of insoluble empty fullerenes (left after pre-extraction of stable fullerenes with *o*-dichlorobenzene) by CF_3I gas [94]. This procedure resulted in a series of $C_{2n}(CF_3)_{12}$ derivatives that exhibited high HOMO-LUMO gaps and good solubility in fullerene solvents. Separation of the mixture by HPLC and subsequent ^{19}F NMR and/or single-crystal X-ray diffraction studies of purified derivatives revealed the formation of some previously unreported empty fullerenes, such as D_{3h} - C_{74} , T_d - C_{76} , $D_{3h}(5)$ - C_{78} , $C_{2v}(5)$ - C_{80} , or $C_2(5)$ - C_{82} [94,95]. More recently, Shinohara et al. modified the method by adding polytetrafluoroethylene into the arc-discharge generator, thus performing the reaction in situ, before any extraction step [96]. Applying this procedure in the synthesis of Y, La, and Gd EMFs, they were able to isolate CF_3 derivatives of several elusive monometallofullerenes, including $M@C_{60}$, $M@C_{70}$, $M@C_{72}$, $M@C_{74}$, etc., and determine their molecular structures by single-crystal X-ray diffraction [96–99]. In situ chlorination [100–102] and hydrogenation [103–105] during fullerene formation, which allowed the capture of many unstable and nonclassical empty fullerenes in the form of chlorides and hydrides, can also be considered as a version of Procedure II.1, but its application to metallofullerenes has not

been very successful so far: halogenated EMF species have been detected in mass-spectra, but not yet isolated in bulk form [106].

4.3. *In Situ Derivatization during Extraction*

One notable breakthrough in the stabilization and isolation of unstable metallofullerenes by their chemical derivatization was made by Akasaka and colleagues (Procedure II.2 in Figure 1). They found that halogenated benzenes, such as 1,2,4-trichlorobenzene [25] or iodobenzene [107], which act as good fullerene solvents for stable fullerenes, can also be a source of aryl radicals that functionalize unstable fullerenes and make them soluble in the form of aryl monoadducts. The solvent thus plays a dual role, as a reactant in the addition reaction of unstable fullerenes and simultaneously as a solvent for stable fullerenes and stable derivatives of unstable fullerenes. Conventional HPLC can then be used in further separation steps. This in situ chemical functionalization during the extraction was successful in fishing out a number of unstable metallofullerenes, such as La@C₇₂ [108] La@C₇₄ [109,110], La@C₈₀ [111], and minor isomers of La@C₈₂ [112]. Since these EMFs could not be isolated in their pristine form by Procedure I, they were dubbed as “missing fullerenes” by the authors. A detailed review of this strategy can be found in Ref. [25]. The success of procedure II.2 is limited by the reactivity of the applied solvent/reactant to the targeted metallofullerenes. It has not been possible to identify a universal solvent/reactant for all types of metallofullerenes, because the reactivity of metallofullerenes varies so much based on the topology of the π -electron distribution and the energetics of the frontier orbitals. For example, we have found that the derivatization and isolation of highly interesting dimetallofullerenes with a single-electron metal–metal bond is not feasible via the in situ chemical functionalization strategy.

4.4. *Redox-Extraction and Derivatization of Anions*

The stabilization/separation strategy that appeared to be successful for unstable dimetallofullerenes is denoted in Figure 1 as Procedure II.3. In the first step, EMFs are redox-extracted from the soot with hot DMF, resulting in a mixture of EMF anions. As discussed above, the separation of the EMF anions is not straightforward. Instead, EMF anions can be chemically functionalized to produce stable neutral derivatives. For instance, thermal trifluoroalkylation of a dried Y-EMF mixture extracted with DMF gave a mixture of EMF-CF₃ derivatives, from which pure Y@C₈₂(CF₃)₅ was isolated by HPLC and characterized by NMR [113].

Recently, we have developed two versions of Procedure II.3, which involved the functionalization of the metallofullerene anions with the formation of neutral compounds. Hereby, the insoluble metallofullerenes are converted into derivatives that are soluble in fullerene solvents and can be further separated by HPLC to obtain the derivatives of desired metallofullerenes in high purity. In the first method, we successfully applied benzyl bromide PhCH₂Br to react with the metallofullerene anions in DMF [66]. The reaction required mild heating and presumably proceeded as a nucleophilic substitution of bromide with metallofullerene anions, producing benzyl monoadducts of metallofullerenes (see Figure 3a for details). An alternative mechanism, proposed in Ref. [114], involves the electron transfer from the EMF anion to benzyl bromide in the first step, followed by the radical coupling reaction. The benzyl derivatives of metallofullerenes are well soluble in fullerene solvents, allowing their subsequent HPLC separation to yield the high-purity compounds. Using this strategy, we have synthesized and isolated a series of dimetallofullerene derivatives M₂@I_h-C₈₀(CH₂Ph) (M₂ = Sc₂, Y₂, Gd₂, Tb₂, TbY, TbGd, Dy₂, Ho₂, Er₂), among which Tb₂@C₈₀(CH₂Ph) and Dy₂@C₈₀(CH₂Ph) show particularly remarkable single-molecule magnetic properties [20,65–67].

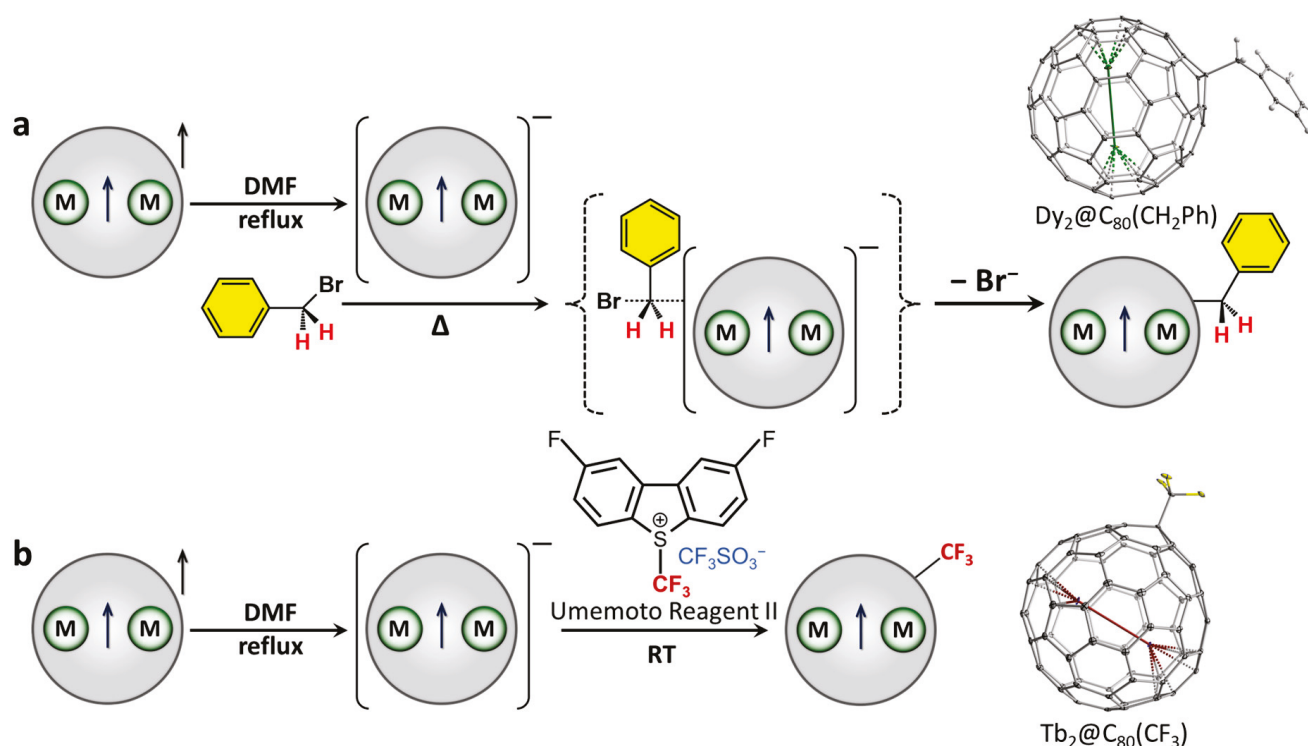


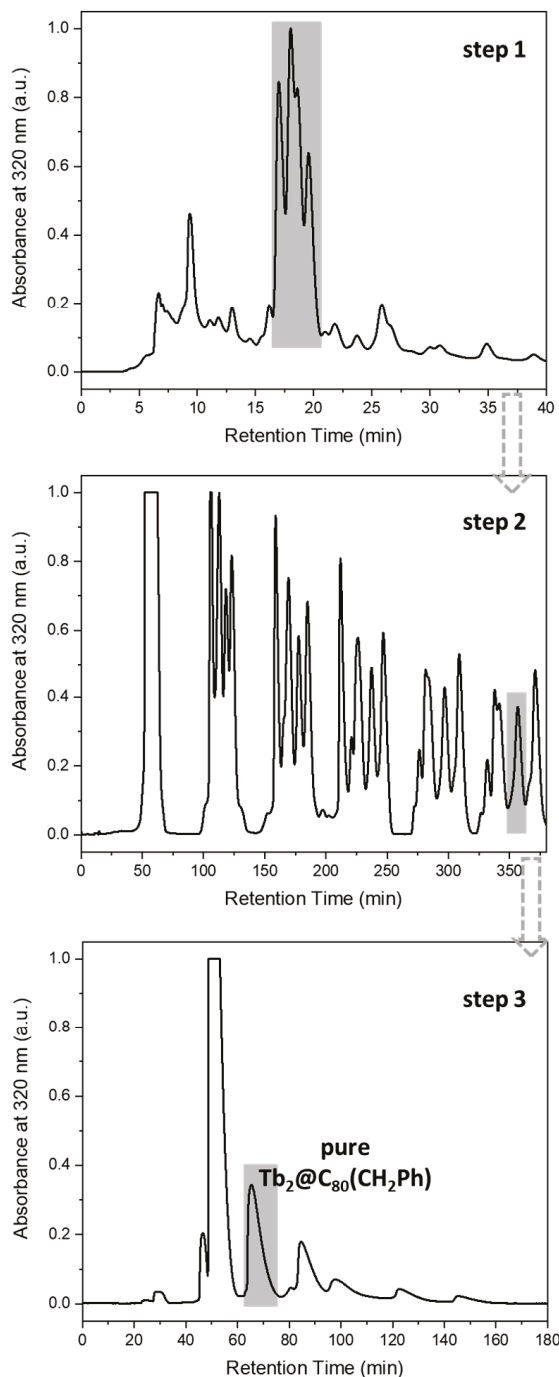
Figure 3. Two modifications of procedure II.3: (a) benzyl bromide route applied to stabilize $M_2@C_{80}$ in the form of $M_2@C_{80}(CH_2Ph)$; (b) CF_3 functionalization route leading to $M_2@C_{80}(CF_3)$. Also shown are molecular structures of $Dy_2@I_h-C_{80}(CH_2Ph)$ and $Tb_2@I_h-C_{80}(CF_3)$ determined by single-crystal X-ray diffraction in Refs. [66,115]. Vertical arrows denotes unpaired electron localized on the metal-metal bond.

The unusual magnetic properties are the reason why, until recently, the main focus in the exploitation of the anion functionalization strategy II.3 has been on the dimetallofullerenes $M_2@I_h-C_{80}$. However, $M_2@I_h-C_{80}$ with a single-electron metal-metal bond is not the only unstable EMF that can be solubilized in the anionic form during DMF extraction. In fact, the DMF extract contains anions of many monometallofullerenes, and, similarly to $M_2@C_{80}^-$, they also undergo mono-benylation in the reaction with benzyl bromide. This procedure can thus be used to fish out other unstable “missing” EMFs from the fullerene soot. Recently, Yang and colleagues used the benzyl bromide functionalization route to successfully isolate and structurally characterize $Dy@C_{80}(CH_2Ph)$ with the $C_{2v}(5)$ cage isomer [116]. Since $Dy@C_{2v}(5)-C_{80}$ is not soluble in fullerene solvents, it had never been properly characterized in the previous studies of Dy-EMFs. This example shows that the benzylation route can be very useful for the stabilization and structural elucidation of various unstable EMFs, and it is very likely that its exploration will help in the discovery of novel elusive fullerene structures.

The versatility of the thermal reaction with benzyl bromide in its application to EMF anions, while being very useful for exploratory studies, becomes a drawback when targeting a specific EMF derivative. The fact that the reaction works well with most of the known metallofullerene anions suggest that it has low selectivity to specific types of metallofullerenes. Furthermore, for EMFs with relatively low symmetry, benzylation does not show particularly high regioselectivity and can yield several isomers of adducts. Maeda et al. showed that the thermal reaction of $La@C_{2v}(9)-C_{82}$ anion with benzyl bromide produces two major and two minor isomers of $La@C_{82}(CH_2Ph)$ [114]. Thus, the benzylation of an anionic EMF extract that already contains many EMFs produces an even greater variety of benzyl adducts. The complexity of the product mixture then complicates the HPLC separation. Figure 4 illustrates that the isolation of $Tb_2@C_{80}(CH_2Ph)$ after benzylation

of the Tb-EMF anionic mixture is a rather tedious process, requiring three HPLC steps, including recycling HPLC [65].

a HPLC separation procedure of $\text{Tb}_2\text{@C}_{80}(\text{CH}_2\text{Ph})$



b HPLC separation procedure of $\text{Tb}_2\text{@C}_{80}(\text{CF}_3)$

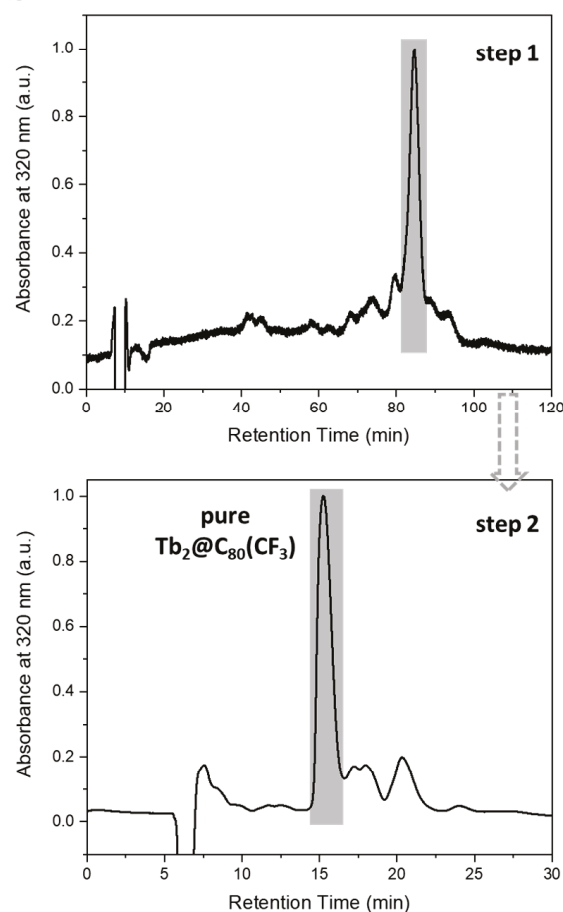


Figure 4. HPLC separation procedure of crude reaction products: (a) thermal benzylation of the Tb-EMF anionic extract in DMF, the target compound— $\text{Tb}_2\text{@C}_{80}(\text{CH}_2\text{Ph})$ [65]; (b) electrophilic trifluoromethylation of Tb-EMF anions in DMF at room temperature, the target compound— $\text{Tb}_2\text{@C}_{80}(\text{CF}_3)$ [115]. Shaded are the fractions containing the target compound and subjected to the next separation step. Note that $\text{Tb}_2\text{@C}_{80}(\text{CH}_2\text{Ph})$ is only a small fraction of the crude product in (a), while $\text{Tb}_2\text{@C}_{80}(\text{CF}_3)$ is the main component of the crude product in (b). Adapted with permission from Ref. [65]. Copyright 2019, Springer Nature. Adapted with permission from Ref. [115]. Copyright 2021 American Chemical Society.

Another possible source of complication in benzylation is that EMF monoanions do not react with benzyl bromide at room temperature, and the reaction requires heating to proceed. However, we have observed that even slight overheating changes the reaction mechanism from controllable monoaddition to uncontrolled polyaddition of benzyl groups. Presumably, heating facilitates homolytic cleavage of the C–Br bond and formation of benzyl radicals, which then react with fullerene anions by a radical addition mechanism. The latter appeared to be very unselective, and the resulting mixtures of benzyl multiadducts could not be separated into individual compounds. Lowering the reaction temperature requires an increase in the reactivity of EMF anions, which can be achieved by the reduction beyond the monoanionic state. Li et al. showed that benzyl bromide reacts with the $\text{Gd@C}_{2v}(9)\text{-C}_{82}^{3-}$ trianion already at room temperature to give several isomers of $\text{Gd@C}_{82}(\text{CH}_2\text{Ph})$ [117].

Seeking for a different functionalization reaction for EMF anions that would help to circumvent the drawbacks of the benzyl bromide route, we found that the electrophilic CF_3 addition can be particularly useful for the isolation of $\text{M}_2@I_h\text{-C}_{80}$ species [115]. Umemoto's Reagent II (Figure 3b), which can be formally described as a source of CF_3^+ , reacts with anionic EMF extract in DMF instantaneously and at room temperature. DMF is then removed under reduced pressure and the residue is extracted with toluene, in which neutral CF_3 derivatives are well soluble. The toluene solution can then be subjected to further analysis and HPLC separation. When the CF_3^+ reagent was taken in a large excess, the reaction gave CF_3 multiadducts. However, it showed remarkable selectivity toward $[\text{Tb}_2@I_h\text{-C}_{80}]^-$, and under an optimized reagent ratio, $\text{Tb}_2@I_h\text{-C}_{80}(\text{CF}_3)$ was obtained as the main toluene-soluble product. As a result, the time required to isolate the pure monoadduct was dramatically reduced compared to the isolation of $\text{Tb}_2@I_h\text{-C}_{80}(\text{CH}_2\text{Ph})$, since the HPLC isolation of $\text{Tb}_2@I_h\text{-C}_{80}(\text{CF}_3)$ required a much smaller number of injections and could be accomplished in two simple steps (see Figure 4, right panel for details). Electrophilic trifluoromethylation thus paves the way for further in-depth studies of the properties and applications of dimetallofullerenes $\text{M}_2@I_h\text{-C}_{80}$ with metal–metal bonds. The method is less efficient for EMFs with other carbon cages, as their trifluoromethylation is significantly less selective, and the yield of their monoadducts is considerably lower. Nonetheless, since CF_3 adducts crystallize easier than their benzyl analogs, the CF_3 route should be more efficient in the structural studies of unstable fullerenes.

In another recent work, we used electrophilic trifluoromethylation to elucidate the stability and molecular structures of Nd dimetallofullerenes [56]. A comparison of the extraction of arc-discharge soot containing Pr and Nd EMFs showed that while $\text{Pr}_2@\text{C}_{80}$ and other Pr dimetallofullerenes are soluble in CS_2 , Nd dimetallofullerenes could not be extracted by CS_2 , but were soluble in hot DMF. Thus, the boundary between stable and unstable lanthanide dimetallofullerenes was found to be between Pr and Nd. The anionic Nd-EMF extract in DMF was then reacted with Umemoto's Reagent II and showed similar selectivity toward $\text{Nd}_2@I_h\text{-C}_{80}$ as in the earlier study of Tb-EMFs. At the same time, analysis of minor HPLC fractions identified another isomer of $\text{Nd}_2@\text{C}_{80}(\text{CF}_3)$. Using single-crystal X-ray diffraction, the molecular structures of two isolated isomers were elucidated as $\text{Nd}_2@D_{5h}(6)\text{-C}_{80}(\text{CF}_3)$ and $\text{Nd}_2@I_h(7)\text{-C}_{80}(\text{CF}_3)$. Figure 5 illustrates the transition from unstable to stable forms of $\text{Nd}_2@\text{C}_{80}$ isomers by plotting the evolution of the spin density distribution from unstable $\text{Nd}_2@\text{C}_{80}$ to stable anion $[\text{Nd}_2@\text{C}_{80}]^-$ and stable neutral $\text{Nd}_2@\text{C}_{80}(\text{CF}_3)$. The presence of the single-electron Nd–Nd bond in all three forms is well evidenced by the spin density lobes localized between Nd atoms, while the spin density on the fullerene cage is present only in $\text{Nd}_2@\text{C}_{80}$, but is absent in the anion and CF_3 monoadduct.

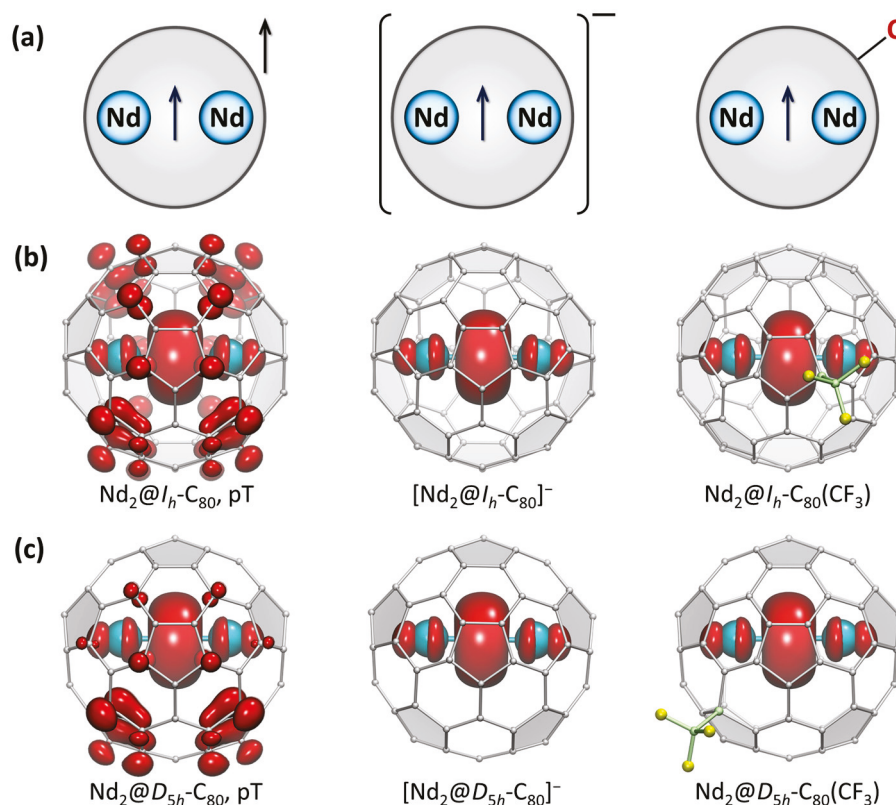


Figure 5. (a) Schematic description of neutral Nd₂@C₈₀ in pseudo-triplet (pT) state (two unpaired valence electrons), [Nd₂@C₈₀]⁻ anion with unpaired electron on the Nd–Nd bonding orbital, and Nd₂@C₈₀(CF₃) with unpaired electron on the Nd–Nd bonding orbital. (b) DFT-computed valence spin density distribution in Nd₂@C₈₀, [Nd₂@C₈₀]⁻ anion and Nd₂@C₈₀(CF₃) with I_h-C₈₀ cage. (c) DFT-computed valence spin density distribution in Nd₂@C₈₀, [Nd₂@C₈₀]⁻ anion and Nd₂@C₈₀(CF₃) with D_{5h}-C₈₀ cage. Adapted with permission from Ref. [56]. Copyright 2023 The Authors, published by Wiley-VCH GmbH.

5. Conclusions

In summary, we overviewed the general strategies to fish out metallofullerenes from the carbon soot, with the emphasis on the recently developed anion functionalization strategy (procedure II.3). The most appealing potential of this approach is that it specifically targets the novel structures missing in conventional separation routine (procedure I). This potential of the anion functionalization to stabilize and isolate “missing” metallofullerenes is not deeply exploited yet, and it is expected that many more novel metallofullerenes will be discovered with this strategy. The discovery of these novel structures will certainly renew our understandings to the coordination structures and physicochemical properties of metallofullerenes. It is worth noting that the chemical functionalization of metallofullerenes is a burgeoning field with a large variety of reactions already studied towards improved regioselectivity and physicochemical property modification [4,118–124]. In this regard, the PhCH₂ and CF₃ addition reactions merely exemplify a proof of concept, with the vast possibilities in this direction using the currently available versatile chemical functionalization methods yet to be explored.

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Review

Process Parameter Optimisation for Endohedral Metallofullerene Synthesis via the Arc-Discharge Method

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Abstract: Fullerenes have a unique structure, capable of both encapsulating other molecules and reacting with those on the exterior surface. Fullerene derivatives have also been found to have enormous potential to address the challenges of the renewable energy sector and current environmental issues, such as in the production of n-type materials in bulk heterojunction solar cells, as antimicrobial agents, in photocatalytic water treatment processes, and in sensor technologies. Endohedral metallofullerenes, in particular, can possess unpaired electron spins, driven by the enclosed metal atom or cluster, which yield valuable magnetic properties. These properties have significant potential for applications in molecular magnets, spin probes, quantum computing, and devices such as quantum information processing, atomic clocks, and molecular magnets. However, the intrinsically low yield of endohedral fullerenes remains a huge obstacle, impeding not only their industrial utilization but also the synthesis and characterization essential for exploring novel applications. The low yield and difficulty in separation of different types of endohedral fullerenes results in the usage of a large amount of solvents and energy, which is detrimental to the environment. In this paper, we analyse the methodologies proposed by various researchers and identify the critical synthesis parameters that play a role in increasing the yields of fullerenes.

Keywords: endohedral metallofullerenes; EMFs; arc discharge; bottom-up synthesis; in situ doping

1. Introduction

Carbon, the building block of life and the fourth most abundant element in the universe, is one of the most indispensable materials known to humankind. In addition to the two naturally occurring allotropes, graphite and diamond, carbon is also capable of taking several remarkable physical forms on the nanoscale. One such distinct allotrope in the family of carbon nanomaterials is the fullerene. Its discovery [1] sparked a great deal of curiosity and interest amongst the scientific community due to its unique closed, cage-like structure, composed solely from sp^2 hybridized carbon [2,3]. Within the first few years after the discovery of buckyball C_{60} , the term ‘fullerene’ achieved a uniform acceptance as the general name for these carbon cages. Fullerenes can have different numbers of carbon atoms, shapes, and symmetry; hence, the largely accepted notation system [4] is to subscript the number of carbon atoms to state the class of the fullerene. The structure of C_{60} , the most abundant buckyball, has been verified to consist of 12 five-membered rings and 20 six-membered rings [2]. Most of the fullerenes obey the isolated pentagon rule (IPR), where pentagons are exclusively surrounded by hexagons, which increases their stability. However, several fullerenes, especially a number of endohedral fullerenes (see next section),

do not follow the IPR rule [5]. Instead they follow the maximum pentagon separation rule, where they exhibit maximum pentagon separation for maximum stability [6].

Fullerenes are known to have different isomers, with C_{60} having 1812 theoretically different isomers [7,8]. These isomers can have different symmetry, form, and energetic stability. An example of the different structures of the six most stable isomers of C_{80} is shown in Figure 1, with D_{5d} and D_2 being the most stable and abundantly found isomers [9]. Fullerene isomers are also known to have different oxidation potential and chemical reactivity. For instance, the D_3 isomer of C_{78} is easier to oxidize than the C_{2v} isomer of the same fullerene by about 0.25 V [10]. Another very intriguing feature of the fullerenes is that they have a hollow space, which is large enough to encapsulate other atoms, ions, molecules, and various kinds of clusters, giving rise to a new class of hybrid materials called endohedral fullerenes.

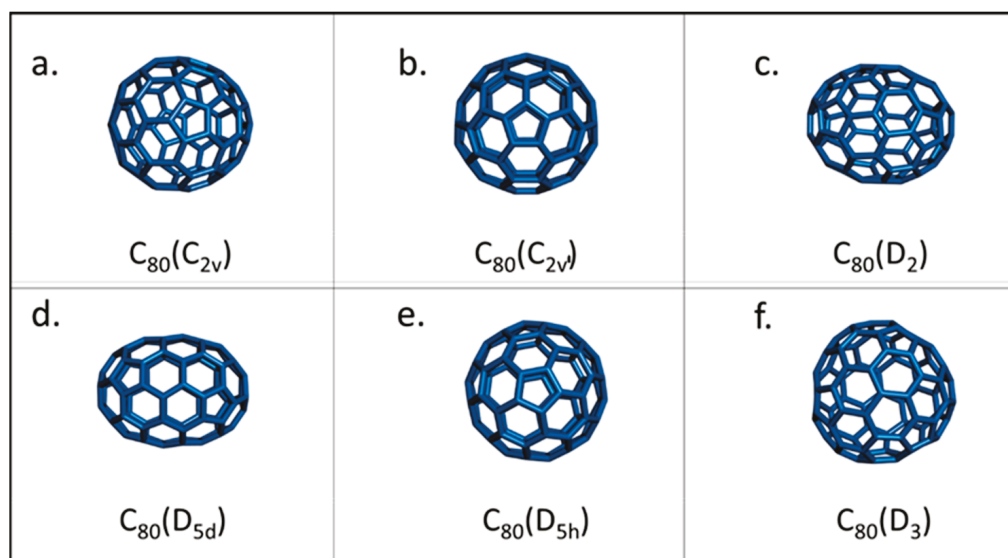


Figure 1. (a–f) Schematic representation of the different isomers of the C_{80} cage.

2. Structure of Endohedral Fullerenes

The ability of different sizes of fullerene cages to incorporate different types of metals and clusters can lead to the formation of materials with novel solid-state properties. The robust nature of the carbon cage plays a very important role in isolating the atoms from the exterior environment, while the electronic properties of the cage can be tuned by the selection of the atoms inside. $La@C_{82}$ was among the first discovered endohedral fullerene, where the symbol @ denotes the inclusion of a La atom inside a C_{82} cage. Since then, fullerenes encapsulating metallic [11], carbide [12,13], nitride [14], and many methano- [15] and oxide- [16] clusters have been synthesized and isolated over the years. In fact, fullerenes containing single atoms of elements that otherwise are not stable, such as noble gases [17–19] and non-metals [20] such as nitrogen [21], have also been synthesized. Transition metals and actinides were amongst the challenging elements to encapsulate within fullerenes, primarily due to their reactivity and the difficulties associated with their incorporation into the graphite rod for arc-discharge synthesis. However, over the past decade, significant progress has been made in also encapsulating various transition metals within fullerenes. [22] In these cases, while describing the diversity of the fullerene cages, prefixes and cage symmetries are also used. For instance, $Sc_4(\mu_3-O)_3@I_h(7)-C_{80}$ represents the endohedral cluster group, cage structure, and point-group symmetry, following the nomenclature of Fowler and Manolopoulos [4].

In 1991, researchers succeeded in encapsulating metal atoms, which opened a complete new set of possibilities in the field of material development, generally referred to as endohedral metallofullerenes [23]. Among the endohedral fullerenes, the trimetallic nitride-containing cages of the type $M_3N@C_{2n}$ (where $M = Sc, Gd$; $2n = 68–96$), shown in Figure 2,

have been one of the most studied materials since their discovery in 1999 [14] due to their high yields during synthesis and their appropriate HOMO-LUMO levels, desired for applications in solar cells. However, despite the comparable high yields, empty fullerenes still constituted as major product during the synthesis process. The yields of $M_3N@C_{2n}$ were further improved by Dunsch and Yang [24], who introduced ammonia during fullerene synthesis and produced an endohedral fullerene, $Sc_3N@I_h-C_{80}$, as the majority product for the first time. This family of fullerenes has an especially high yield because of the charge transfer from the encaged cluster, which results in a stable ion pair and stabilizes the higher fullerene cages of various isomeric structures. In addition, the large HOMO-LUMO gaps give further kinetic stability to the hybrid molecule.

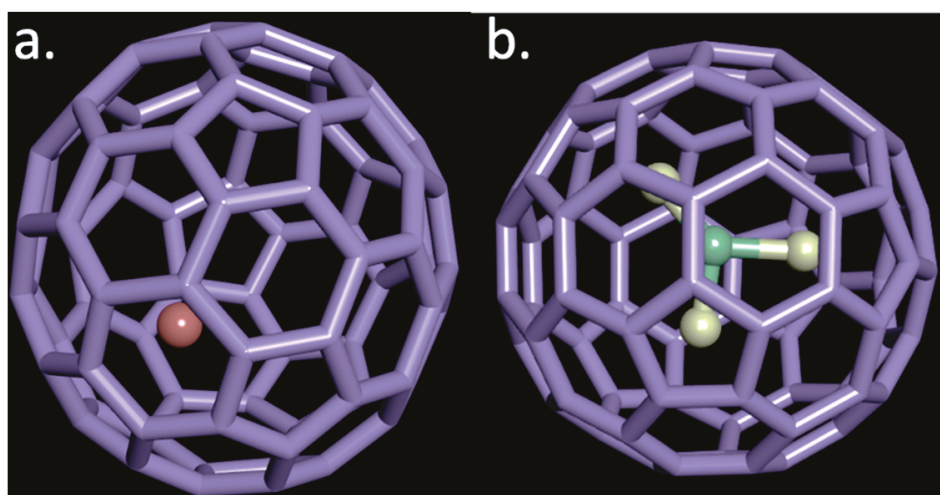


Figure 2. A representative figure of two endohedral metallofullerenes, (a) monometallic in a C_{82} cage and (b) trimetallic nitride encapsulated in a C_{80} fullerene cage. The red and the yellow balls correspond to the metal ion encapsulated in the carbon cage and the green to nitrogen.

2.1. Endohedral Metallofullerenes: EMFs

In the years following the discovery of C_{60} , the study of empty cage fullerenes heavily dominated the field of nanomaterials. The focus on empty cage buckyballs often resulted in the blind assumption that endohedral metallofullerenes (denoted as EMFs) possessed the same structural or chemical properties as the corresponding empty cages. However, over the years, after more studies were conducted on individual EMFs, it became established that they exhibit novel structural, chemical, and electronic properties, which were completely different to those of their parent empty cages. For instance, carbon cages of EMFs have different isomeric structures as compared to their parent fullerene cage, and they also show different solubility in individual solvents [25]. As for their electronic and chemical behaviour, their chemical reactions with radicals [26] and many other cyclo-addition [27] reactions show significantly different patterns and redox potentials [28]. For instance, the reduction potentials of $La@C_{82}$ and $La_2@C_{80}$ are 0.70 V and 0.81 V lower than that of C_{60} [29]. The reason for such a huge difference is largely attributed to the covalent interaction between the enclosed species and the carbon cage as well as the charge transfer phenomenon from the metallic species to the fullerene cage.

The most studied metallofullerenes involve rare earth metals, such as La, Sc, Dy, and Tm [23,30–35], and main group metals such as Li and Ca [36]. There is an extensive array of EMFs that have one, two, three, or even four metal atoms trapped inside them [37]. Alternatively, they can also contain M_3N [14] or M_2C_2 units [12], where M refers to metals. The key to understanding the electronic properties of these hybrid materials is through studying the degree of charge transfer from the metal species to the exterior cage, which alters its electronic state. While the number of electrons transferred from a majority of metal atoms to the cage is known and verified using X-ray diffraction, absorption, and

other spectroscopic methods [31–35], we observed that contradictory results still exist in the literature regarding the effect of the various parameters on the arc synthesis and the formation mechanism of these fullerenes. For instance, Dunk et al. claimed that the formation mechanism is governed by a charge transfer between the metal and the cage [38]. Through detailed mechanistic studies, they revealed that the C₂ insertion during the bottom-up synthesis becomes more difficult as the oxidation state of the metal increases. This charge transfer and the nature of the cluster inside the cage also dictates a series of properties, such as electrochemical behaviour and light emission. In fact, Ito et al. studied Er₂@C₈₂ and Er₂C₂@C₈₂, which showed nearly identical cage properties with a 6-negatively charged C₈₂^{6−}, using fluorescence spectroscopy [39]. Most notably, this cage charge contradicted an earlier publication by Wang et al. claiming that the Er₂@C₈₂ and Er₂C₂@C₈₂ compounds have a 4- negatively charged cage, i.e., C₈₂^{4−} [40]. Furthermore, Ito et al. showed that the characteristic emission of the erbium ions at 1520 nm was influenced by the symmetry of the cage, an observation later echoed by Plant et al. [41]. Until as recently as 2020, previously unknown factors, such as enantiomers and enthalpy, were discovered to play vital and evolving roles in the synthesis mechanism for fullerenes C_{2n} (50 ≤ 2n ≤ 70) [42]. After a critical analysis of research articles [43,44], it can be concluded that the complete mechanism of their formation, either through a bottom-up or top-down approach, and the charge transfer itself remains elusive and highly controversial [45]. In fact, the insights derived from experimental results have also been contradictory to theoretical results in the field. For instance, it has been suggested that factors such as the C₂ concentration and temperature may dictate the more favourable direction of the reversible C₂ injection/ejection reaction during the synthetic process [46]. However, theoretical studies have highlighted that the C₂ injection is more energetically favourable than its C₂ ejection counterpart, contradicting the experimental data on the importance of temperature and concentration [47,48]. The missing key links and low synthesis yield of fullerenes make it difficult to investigate the fullerene formation mechanism. Utilizing both experimental and theoretical frameworks is therefore necessary to answer some of the fundamental questions of this field.

As briefly mentioned in the previous section, the isomeric structures of the carbon cages encapsulating metals differ from their empty counterparts [34]. Further study of the positions and movements of the encapsulated atoms is also important in determining the chemical and physical properties of EMFs, including their magnetic behaviour, electron paramagnetic resonance (EPR), and electrochemical properties [49]. The structure of the EMFs themselves had long been speculated, but the first crucial evidence came through in 1995 when Shinohara et al. experimentally confirmed that the metal atom is indeed encapsulated within the fullerene cage [31]. The synchrotron X-ray powder diffraction patterns of Y@C₈₂ and the maximum entropy method (MEM) revealed that the yttrium atom was displaced from the centre and instead tightly bound to the cage [50]. The study also confirmed strong dipole–dipole and charge transfer interaction between the different molecules [49]. MEM/Rietveld analysis has long been used to determine the structures of metallofullerenes [31,50]. However, the results (structure and position of metals inside the carbon cage) obtained by this method have been in question in recent years. This started when Wang et al. [12] discovered that the scandium carbide endohedral fullerene, Sc₃C₂@C₈₀, was, in fact, what had long been considered to be a tri-metallofullerene Sc₃@C₈₂ [51]. These incoherences emphasize the importance of ¹³C NMR and synchrotron X-ray structural analysis in determining the structures and encapsulated cluster inside the fullerene cage and suggest the unreliability of the decades of results obtained exclusively using MEM/Rietveld analysis when determining the structures of metallofullerenes [52–54]. Consequently, the structures and positions of metals inside a fullerene have been re-examined in the past few years [55–58]. Furthermore, it was also observed that these metal clusters had motions and trajectories inside the cage [59], which also changed positions depending on the temperature [60,61].

2.2. Environmental Application

A massive number of publications in fullerene-related research show the possibility of using fullerenes for a variety of environmental and energy applications. The characteristics of fullerenes that give them an advantage over other materials include their robust carbon structure, absorption of light in the visible range, electron-accepting capabilities, and more recently, superconductivity [62]. All these properties make fullerenes especially sought-after materials for energy applications, especially organic solar cells [63]. They have become, and remain, an important part of high-performance organic solar cells.

2.3. Synthesis

Over the past few decades, EMFs have been proposed for a number of applications, including energy harvesting in organic solar cells [64] and MRI contrast agents [65–67]. EMFs have been synthesized through a range of different methodologies, such as laser ablation of graphite [23,68], arc discharge [30,33], ion bombardment [36,69], resistive heating [70], and electron initiation inside carbon nanotubes (CNTs) within aberration-corrected high-resolution transmission electron spectroscopy (AC-HRTEM) (CNT acts as a nanoreactor container to facilitate the formation of endohedral fullerenes from metals and the amorphous carbon atoms trapped inside. The process is energetically enabled under the presence of an electron beam inside an AC-HRTEM.) [71]. Some of these popular methods are summarized in Table 1 below.

Table 1. Advantages and disadvantages of different synthetic approaches.

EMF Synthesis Method	Advantages	Disadvantages
Arc discharge [72]	• Low setup and maintenance costs • Fewer structural defects • Access to the broadest catalogue of EMF	• Difficult to scale-up • Requires extensive purification • Low yield (1–30%)
Laser ablation [72]	• Higher purity of products • Useful for mechanistic studies	• High cost for reactor building and maintenance
Molecular surgery [72,73]	• Low energy impact • Simple HPLC purification	• Several synthetic steps required to open/close the fullerenes cage • Harmful synthetic solvents • Limited to non-metal and alkali-metal EMFs • Low yield (~0.1 to 1%)
Ion implantation [72]	• Lower pressure required (5–10 mbar) • Low-temperature process, where ions are accelerated towards the carbon cages • Simple HPLC purification possible	• Limited to non-metal and alkali-metal EMFs • Very low yield (10^{-5} to $10^{-4}\%$)

The Kratschmer–Huffman arc method has been widely used and accepted as the most efficient and cost-effective technique to produce EMFs and, hence, is the focus of this review. Figure 3a shows a schematic diagram of a typical standard direct current (D.C.) arc-discharge apparatus, and Figure 3b shows the actual image of one in the Porfyrakis laboratory in the Department of Materials at the University of Oxford.

While the Kratschmer–Huffman method immediately became the most popular choice of EMF synthesis, it was not exempt from certain limitations. Most notably, only 60–70% of the graphite electrode was transferred to the carbon condensate (CC) containing the fullerenes and EMF, while the remaining 30–40% was lost as graphite build-up on the cathode. This disadvantage has now been eliminated by utilizing a high frequency arc discharge to supply the arc. The symmetrical setup of the electrodes allowed reaching up to a 100% conversion of the electrode material into the fullerenes and EMF containing CC [74]. Additionally, high-frequency arc discharge can also be used for further mechanistic investigation of fullerene synthesis.

A metal oxide/graphite composite is used as the anode, whereas graphite is used as the cathode, and both of them are arced in the D.C. mode in the presence of an inert gas (usually helium). Despite three decades of extensive research and various proposed pathways, a well-established formation mechanism for the synthesis of fullerenes and EMFs is still missing. Their ambiguous reaction pathways, alongside the violent conditions involving the plasma formation, arc, and chemical ionization that are required for the synthesis, are a major drawback in studying the synthesis mechanisms of these unique carbon nanostructures. Furthermore, a few other drawbacks hinder the scaling-up of their synthesis and consequently the applications of endohedral metallofullerenes. The overall yield of the arc-discharge synthesis of EMFs is low, with the ratio of EMF-to-empty-cage typically at around 1% [49]. As a result, a mixture of empty cage and endohedral fullerenes is typically produced, thus limiting the applications of the existing chromatographic methodologies for their fast and efficient separation. This results in the use of excessive amounts of solvents to efficiently separate them, which is neither ecological nor environmentally friendly. Therefore, it becomes important to review the synthesis of fullerenes. Shinohara published the first detailed scientific review of EMF research in 2000 [75], followed by an extensive update on endohedral fullerenes by Popov et al. in 2012 [76]. Many other groups have addressed the synthesis and properties of endohedral fullerenes [76–79], including nitride fullerenes [24], carbide cluster fullerenes [80], and oxide cluster fullerenes. Herein, we focus primarily on critically discussing the key findings in the field for optimizing of synthesis parameters of endohedral metallofullerenes and the new chemically activated method, with a particular emphasis on the post-2000 science along with comparisons to the early methodologies. The yield of the EMF has been observed to be highly dependent on the pressure of He gas, the arc current, the arc gap, and the composition of anodes, among other factors [51,81]. Liu [82] and Bandow [83] have argued that other parameters, such as the presence of catalysts (Cu, Fe, etc.), the back-burning of anodes, and in situ activation during arc discharge, also have an effect on the EMF yield. However, the latter two parameters would not increase the yield by a huge fraction because they do not modify the arc conditions drastically or change/influence the synthesis chemistry, e.g., lower the activation energy of the formation of the endohedral metallofullerenes. However, in order to maximize the efficiency of the method, a balance between the time spent during the synthesis and increase in yield needs to be established. Predominant aspects of overcoming the above challenge are anode composition, ionization potential, catalysts, and helium pressure in synthesis [74].

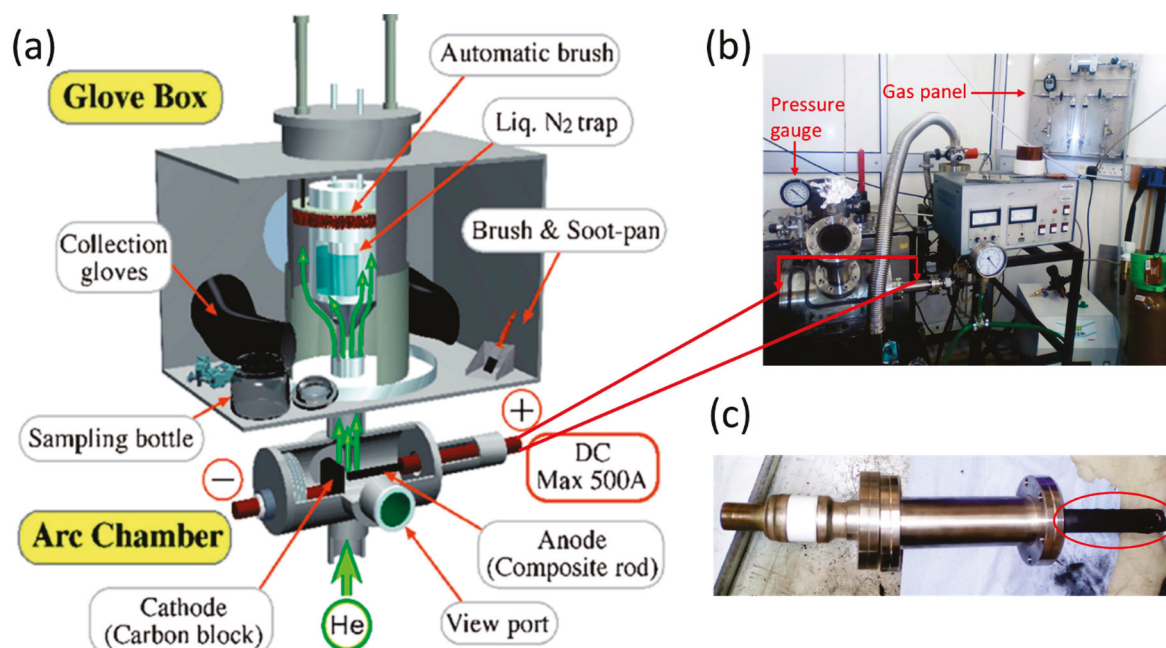


Figure 3. (a) A schematic diagram of a typical arc-discharge apparatus used for synthesizing fullerenes (Reprinted/adapted with permission from Ref. [84]. Copyright (c) 2007 The Japan Society of Applied Physics). (b) An image of an actual arc-discharge apparatus from the Porfyrakis laboratory at the University of Oxford. (c) Image of a metal oxide/graphite composite rod used during an arc-discharge process.

In recent years, the Kratschmer–Huffman arc design has also been modified mechanically in several ways to make it more environmentally friendly. For instance, the use of demineralized coal electrodes, minimizing the use of current and using direct current instead of high alternating current are a few ways in which the process has been made more efficient and less energy intensive [85]. Recently, Kyesmen et al. showed scaled-up production yield of fullerenes by employing such methods and including efficient energy usage by using resistive heating of one of the electrodes along its length [86]. Such green methodologies should be further explored for future research purposes and industrial-scale production of fullerenes to ensure an environment friendly approach towards using nanomaterials.

3. Reaction Parameters and Pathways

In this section, we will delve into the critical parameters that are essential for achieving the highest yield of EMFs, with a special focus on encapsulation in the C_{82} cage.

3.1. Anode Composition

Metal oxide (e.g., La_2O_3 , Y_2O_3 , etc.) mixed with graphite has generally been used as the anode material during the arc-discharge process. However, there has been no general consensus on the ratio of metal/carbon used in the metal. Inakuma et al. also showed that the abundance of different types of EMF present in the soot depends heavily on the metal/carbon mixing ratio in the composite rods [51,81]. The M/C ratio has varied widely over the years, also depending on the metals that are incorporated inside the graphite, as broadly summarized in Table 2. Furthermore, it has also been found that anodes made out of metal-carbide rods actually produce EMFs in a bigger yield than metal-oxide rods, which has been experimentally proved by several authors [82,83]. Using La as the example metal, the authors showed that the presence of LaC_2 in supersaturated carbon vapor plays an important role in generating the metallofullerenes. However, this conclusion is in contrast with the work published later by Lian et al. [87], who studied Ni-La alloy anode rods for the preparation of lanthanum-containing metallofullerenes ($La@C_{82}$ (I), $La@C_{82}$ (II), and $La_2@C_{80}$). It was found that $LaNi_2$ is a much better dopant than conventional La_2O_3 in the

anode rod, and the ratio of La:C is very important for increasing the yield. The absence of oxygen in the LaNi_2 dopant can partly be the reason for such observations as well as the possible catalytic effect of Nickel in the formation of fullerenes. The authors also found that the use of LaNi_2 instead of La_2O_3 enhanced the amount of raw soot produced from arc discharge. The authors attributed the results to reduction in the amount of formation of cathode deposits and debris. The optimum conditions increased the yield of La-EMF by almost 30% compared to conventional substrates. Comparing the existing literature in this field, as summarized in Table 2, it seems rather hard to deduce which single metal/carbon ratio in the anode would produce the best yields for different types of metallofullerenes. It surely is a huge determinant of the yield of a particular type of EMF, but more research, both experimental and theoretical, needs to be undertaken in this direction to test different combinations of metals for anodes and also to explore the chemistry involved.

3.2. Ionization Potential

The ionization potential (I.P.) of the EMFs has been known to play a very important role in EMF extraction and chemical reactivity, but it only recently came to light that the first ionization potential of the metal itself plays an important role in EMF synthesis. Ross et al. deduced that the I.P. of the metal atom not only influences the efficiency of the synthesis but may partly determine the metallofullerene formation [88]. Their group noted that when graphite anode rods were impregnated with Y/La atoms and with Sc/Y atomic composition in equal ratio, there was a greater abundance of La- and Y-containing metallofullerenes than Y or Sc, respectively. The results suggested that metals with lower I.P. ($\text{La} < \text{Y} < \text{Sc}$) tend to react more efficiently, i.e., the growth reaction of metal ions and fullerene precursor species plays an important role in the arc-discharge process. This is consistent with other experimental studies that show that lanthanides are easier to encapsulate inside a fullerene cage compared to other alkali earth metals or transition metals [89]. Comparing the yields of the synthesis of Pt-EMF [90,91], Fe-EMFs [92], and Sc-EMFs ($\text{Pt}_{\text{I.P.}} = 8.96 > \text{Fe}_{\text{I.P.}} = 7.90 > \text{Sc}_{\text{I.P.}} = 6.56$) [93], Pt-EMFs have the lowest yield, whereas the Sc-EMFs have the highest yield, even though the covalent radii of the metals are not very different ($\text{Pt} = 1.17 \text{ \AA}$; $\text{Fe} = 1.3 \text{ \AA}$; $\text{Sc} = 1.44 \text{ \AA}$). Since the overall yield of EMFs is generally low, and their synthesis is a very time-consuming process, it is important that the choice of the metal atom, which can potentially form EMFs, is based on their ionization potential and chemical nature of bonding with the carbon clusters.

3.3. Effect of Catalyst

The catalytic growth of carbon nanomaterials has long been known from the synthesis of carbon nanotubes [94], and more recently, graphene [95]. However, the use of catalysts for the synthesis of fullerenes was not developed until 2008, when Stevenson et al. [16] doped the graphite rods with copper nitrate in a modified arc chamber. They observed that the presence of metallic copper increased the overall yield of endohedral fullerenes. It still remains unclear if it also facilitates the formation of endohedral mono-metallofullerenes and if the ratio of metallofullerenes to other empty cages in the carbon soot is, in fact, higher than previously reported. Other groups have noted that using transition metal alloys (e.g., Ni) in the anode composition [87] increases the yield of the EMFs. But again, results published in the literature make it difficult to judge whether the transition metal plays an active role as a catalyst or if it just reduces the detrimental effects that oxygen has, whilst using metal oxide composite rods during the arc discharge. We deduce that catalysts have not been studied in depth largely because of the difficulty in producing homogeneous composite anode rods containing different catalysts such that they can be actually used systematically during the arc operation. The development of new methods for efficient dispersion of catalytic particles inside the electrodes during their fabrication could help solve these problems. Studying the effect of metal clusters or metal alloys as additives in the arc discharge, could be worthwhile not only for increasing the yield of EMFs but

also for elucidating the formation pathways for fullerenes and carbon nanotubes in the arc reactor chamber.

3.4. Effect of Helium Pressure

The presence of helium in the arc-discharge chamber is well known to be beneficial for the formation of endohedral fullerenes [96]. It is still not clear what the exact mechanism behind it is, but it is believed that He, being a small and inert species, facilitates collisions between carbon atoms without taking part in reactions. Therefore, it enhances the possibility of carbon–carbon bond formation. There is also a general consensus that varying the pressure of helium leads to different yields of the EMFs. A literature survey (Table 2) in the field shows that using lower pressures of helium (50–100 mBar) has been the standard arc-discharge parameter until recently, when researchers started using high He pressures (up to 500–700 mBar) for EMF synthesis. In 2017, Qian et al. [97] published the first theoretical study on how the self-assembly of fullerene during the arc-discharge process is influenced by the presence of helium. They also proposed how the concentration of helium can change the distribution of different fullerene formation in the arc. Similar results were shown for synthesizing fullerenes in a high-frequency arc-discharge system, as reported by Churilov et al. [74]. The authors experimented with a range of helium pressures (30–150 kPa) and their effect on the formation of different types of Y-EMFs, and concluded that 120 kPa results in the maximum yield for the EMF Y@C₈₂. Moreover, empty cages were found to increase with the helium pressure but not the EMFs. The effect of helium pressure in both the traditional arc discharge as well as high-frequency arc discharge suggests a difference in the mechanism of formation of the empty cages and the EMFs. Further studies in this area can help optimize the exact synthetic parameters for the desired type of fullerene. Another helium pressure-dependent study was reported by Chervyakova et al. [98], where they carried out a series of experiments by keeping all the variables constant and only changing the He pressure in the chamber from 30 to 360 mBar. The experiment was carried out for various EMFs, and they found that although 120 mBar helium pressure yields the optimal condition for synthesis of different M@C₈₂, there is a huge variation in the obtained optimal yield. For instance, although both Sc@C₈₂ and Gd@C₈₂ showed the best synthetic yields at 120 kPa He pressure, the yields were very different, with Sc@C₈₂ having 9.6 wt% ratio of all fullerenes, as compared to Gd@C₈₂, which had only 5.4 wt%. However, there is a massive variation in homemade arc-discharge apparatus as well as differences in the exact operational parameters used for experiments carried out at different places. Therefore, there is a need for a systematic study on a single apparatus, for synthesizing the range of EMFs and determining if the pressure conditions vary depending on the entrapped metals. Moreover, a wider pressure range should also be tested so that the exact reaction pathway behind the formation of different types of EMFs can be properly investigated.

Table 2. Summary of the parameters used over the years to synthesize different types of endohedral metallofullerenes.

Year	Anode	Fullerene	He Pressure (mBar)	Current	Extraction Solvent	References
1992	Sc ₂ O ₃	Sc-EMF	66.6	-	Toluene and Pyridine and CS ₂ ₁	[35]
1992	Sc ₂ O ₃	Sc-EMF	266.6	-	Toluene	[32]
1992	La ₂ O ₃	La-EMF	266.6	-	Toluene	[33]
1993	Sc ₂ O ₃ M/C = 2.3/100 atomic ratio	Sc-EMF	66	220 A	CS ₂	[81]
1993	8 wt% La ₂ O ₃	La@C ₈₂	133.3	2.3 A/mm ²	Toluene	[83]
1994	Sc ₂ O ₃ M/C = 1:10		66–133	500 A	CS ₂	[51]

Table 2. Cont.

Year	Anode	Fullerene	He Pressure (mBar)	Current	Extraction Solvent	References
1995	La ₂ O ₃ (La/C = 2:100)	La@C _{2n}	133	200 A	Toluene	[82]
1995	Gd ₂ O ₃ (1–2% atomic%)	Gd-EMF	60	250 A	TCB ²	[99]
1995	-	Y@C ₈₂	66	500 A	Toluene	[31]
1996	CeO ₂	Ce@C ₈₂	66		DMF	[100]
1996	Tm/C = 1:50	Tm@C ₈₂	200	175 A	Toluene	[34]
1996	Pr ₆ O ₁₁ (Pr/C = 1:100)	Pr@C ₈₂ , Pr ₂ @C ₈₀	66		DMF ³	[101]
1998	-	Sc@C ₈₂	66	300–400 A	Toluene	[93]
1999	Sc ₂ O ₃ Sc/C = 2.8/100	Sc ₃ @C ₈₂	66	500 A	CS ₂	[11]
2002	M/C = 1/100 (M = La, Y)	La@C _{2n} ⁴ , Y@C _{2n}	160	90 A	o-xylene+ DMF/DMA/DMSO	[102]
2002	Tm/C composite rod	Tm@C ₈₂	240	600 A	TCB	[103]
2002		Gd@C ₈₂	960	50 A	DMF	[104]
2003	Gd ₂ O ₃	Gd@C ₆₀	133	-	Dichlorobenzene DMF (~6–7%) CS ₂ (~1.5%) Pyridine (~1.5%) Aniline (~1%) ⁵	[105]
2004	MNi ₂	All EMF	960	50 A		[106]
2005	CeO ₂ (Ce/C = 2/100)	Ce ₂ @C ₈₀	66.6	70 A	TEA/acetone ⁶	[107]
2006	Sc ₂ O ₃ Sc/C = 2/100	Sc- EMF	66	150 A, 40 V	TCB	[108]
2010	Gd ₂ O ₃	Gd@C ₈₂	200	90 A	DMF liq./liq. extraction	[109]
2014	Gd ₂ O ₃	Gd@C ₈₂ , Gd@C ₈₄	506	110–120 A	o-xylene and DMF	[110]
2017	Gd ₂ O ₃ (M:C = 1:1) mass ratio	Gd@C ₈₂	1200	50–400 A	C ₅ H ₅ N	[98]
2017	Sc ₂ O ₃ (M:C = 1:1) mass ratio	Sc@C ₈₂	1200	50–400 A	C ₅ H ₅ N	[98]
2017	Er ₂ O ₃ (M:C = 1:1) mass ratio	Er@C ₈₂	1200	50–400 A	CS ₂	[98]
2017	TiO (M:C = 1:1) mass ratio	Ti@C ₈₂	600	50–400 A	CS ₂	[98]
2017	Y ₂ O ₃ O (M:C = 1:1) mass ratio	Y@C ₈₂ , Y ₂ @C ₈₂	600	50–400 A	CS ₂	[98]
2017	Y ₂ O ₃ O (M:C = 1:1) mass ratio	Y@C ₈₂	1200	50–400 A	C ₅ H ₅ N	[98]
2023	Tb ₄ O ₇ (M:C = 1:15) molar ratio	Tb@C ₈₂	400 mbar	100 A	of CS ₂ /toluene	[111]

¹ Carbon Disulfide; ² 1,2,4-Trichlorobenzene; ³ N,N-Dimethylformamide; ⁴ $68 \geq 2n \geq 96$; ⁵ Extraction yield by weight percent of (Tb, Y, La, Gd)-EMF to soot; ⁶ Triethylamine.

3.5. Chemically Activated Arc Discharge

3.5.1. In Situ Doping

Another way to address the low yield and the unwanted mixture of various types of fullerenes is by changing the reaction conditions through in situ doping of the graphite/metal electrodes, which are to be vaporized during the arc discharge. These methodologies require the incorporation of reactive gases and/or solid compounds that alter the conditions and influence the reaction equilibrium towards the formation of higher cages and, ideally, EMFs. One of the most typical examples is the use of reactive gases, e.g., NH₃ [112], whose incorporation leads to the scaled-up synthesis of trimetallic nitride fullerenes, for instance, making the Sc₃N@I_n-C₈₀ the third most abundant fullerene, after C₆₀ and C₇₀. Another alternative is the doping of the graphite electrodes themselves with solid organic compounds. Core drilled graphite rods have been repeatedly doped with active inorganic or organic compounds. These compounds could be calcium cyanamide [113], urea and, most importantly, inorganic nitrate compounds. In that direction, Stevenson et al. pioneered the CAPTEAR method (the name stands for “Chemically Adjusting Plasma Temperature, En-

ergy and Reactivity”) (Figure 4). They core-drilled and filled the graphite/ Sc_2O_3 electrodes with copper nitrate powder and in a later study with metallic Cu, in order to study the reactive species generated during the synthesis procedure [114,115]. The decomposition of copper nitrate led to an exothermic reaction and the generation of reactive nitrogen gases, oxygen, and vaporized copper. A detailed analysis of the decomposition products can be seen in the references herein. These factors influenced the temperature, energy, conductivity of the arc, and reactivity of the plasma. Stevenson et al. observed that this particular arc discharge reaction leads to the exclusive and highly selective formation of TNT-type metallofullerenes ($\text{Sc}_3\text{N}@I_h\text{-C}_{80}$) and that the empty cage fullerenes were formed with a low yield. In their pioneering 2007 publication, they observed that this preferential formation of EMFs, based on HPLC calculated yield, was about 80% wt as compared to standard yield of 5–30 wt%. They observed that from the 13 mg of extracted fullerenes, 12 mg were identified as $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$.

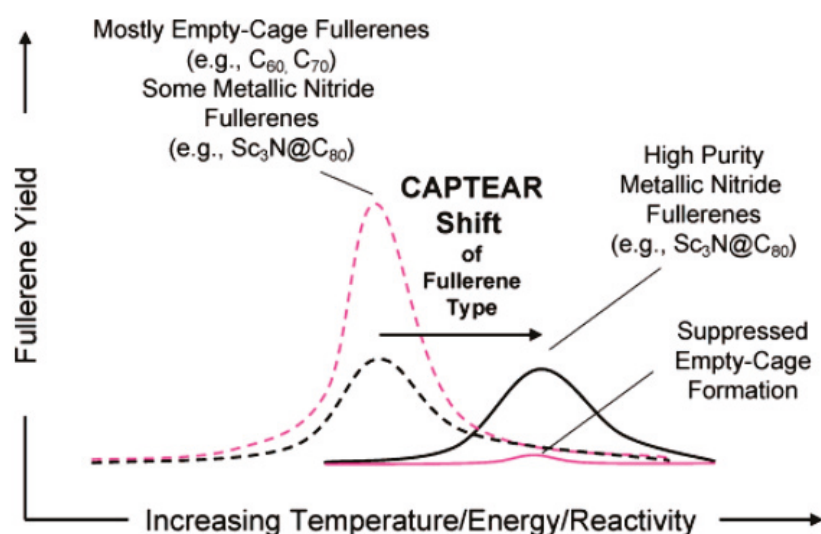


Figure 4. Parameter optimization of the CAPTEAR method to synthesize the desired endohedral fullerene. (Reprinted/adapted with permission from Ref. [114]. Copyright © 2007, American Chemical Society).

Expanding this method further, we recently developed a similar methodology for the study of the synthesis of gadolinium metallofullerenes and carbon nanotubes. We constructed phase diagrams regarding the effect of pressure and doping levels with copper nitrate on the overall yields. Figure 5 shows a phase diagram (reproduced from [116]) summarizing the ratio between the various fullerene families, depending on different reaction conditions. Another interesting aspect of this method is that when high doping with copper nitrate is applied, the yield of C_{60} and C_{70} appears to be inversed. During a conventional arc discharge reaction, the ratio of C_{60} to C_{70} is 3:1; however, under high levels of chemical doping, C_{70} appears to have a higher yield compared to C_{60} . The results can be attributed to the difference in thermodynamic stability of these two fullerenes.

The thermodynamic parameters for the formation of C_{60} were determined long after its initial discovery, mainly due to the early difficulties in producing sufficient amounts of the material and the low purity. Interestingly, despite the fact that the fullerene is a strained molecule and hence has much higher energy in free form as compared to diamond and graphite, it can still be formed in sufficient quantities. Higher cages than C_{60} have a different structure and symmetry, with C_{70} , the second most abundant fullerene to exceed C_{60} , has a binding energy per carbon atom of more than 0.02 eV greater than C_{60} , whose binding energy is 7.40 eV/C [117]. Despite the thermodynamic favour of C_{70} , C_{60} is kinetically favoured. According to previous reports, the heat of formation for C_{70} is 2555 kJ/mol, and 2327 kJ/mol for C_{60} [118]. The comparison between C_{60} and C_{70} is shown

in Figure 6. Similarly, fullerenes with more carbon atoms and EMFs themselves, which exhibit different isomers with different strains, will give a more complicated picture for determining the thermodynamic parameter of their synthesis [119].

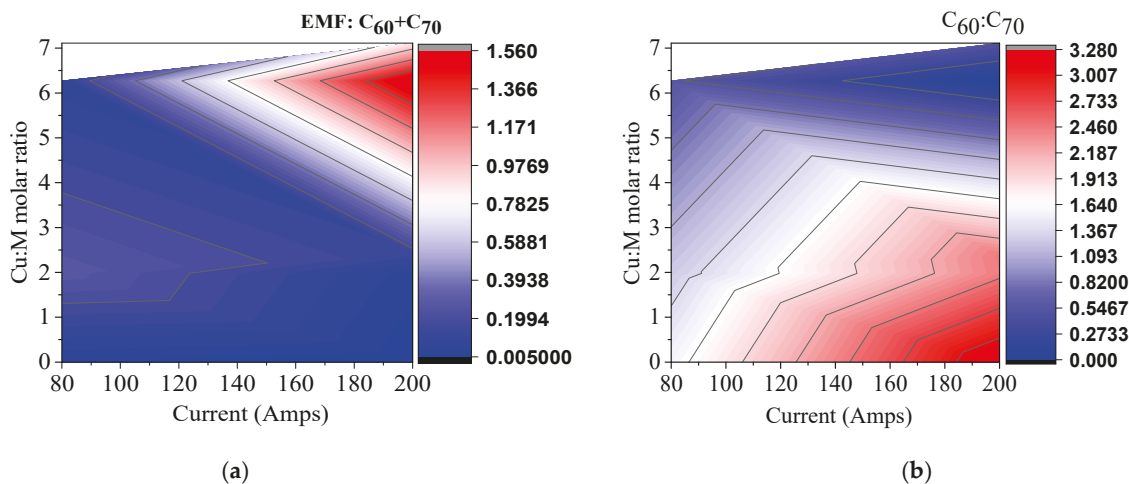


Figure 5. (a) The ratio of the higher fullerenes (>C₈₈) and EMF to the abundant C₆₀/C₇₀ vs. the current and Cu-to-rare-earth-metal molar ratio. (b) The ratio of C₆₀ to C₇₀ vs. the current and Cu-to-rare-earth-metal molar ratio (Reprinted/adapted with permission from [116]. Copyright 2006, Royal Society of Chemistry).

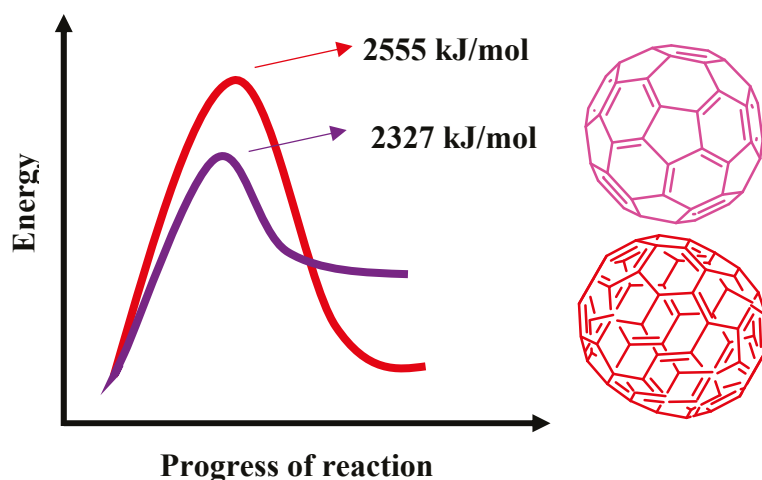


Figure 6. Kinetic vs. thermodynamic behaviour of the two most abundant fullerenes C₆₀ (in purple) and C₇₀ (in red). Reproduced from [118].

3.5.2. Effect of Reactive Gases: Methane and Ammonia

Chemically activated arc discharge presents a novel route not only for the control of the reaction pathway and hence the overall yield of the fullerenes, but also for the synthesis of novel EMFs with exciting properties, simply by carefully tailoring and studying the reaction conditions. Chen et al. [120] obtained different yields of dysprosium sulphite EMFs, a class of materials with interesting magnetic properties, by changing the levels of methane pressure used during synthesis. The dysprosium disulphide EMFs exhibit unique magnetic properties, with three energy barriers at 10.5, 48, and 1232 K. In general, a variety of magnetic behaviour can be observed in EMFs depending on the type of the incarcerated cluster. For example, the carbide Er₂C₂@C₈₂ behaves as a paramagnet, while the monometallic Er@C₈₂ shows an antiferromagnetic behaviour. An important dimetallic EMF, ErSc₂N@C₈₀, has even shown a long life of photoisomerization, which could be measured for 12 h at 20 K without any degradation. The synthesis of these EMFs is highly

important, as they hold promising applications as molecular memory elements [121] and materials for spintronics and telecommunications device applications. EMFs comprising erbium and scandium are of special interest, as erbium has important optical properties (1.52 μm emission at the telecommunications window), and scandium atoms have large nuclear spin ($I = 2/7$), which is suitable for spin probe and atomic clock applications.

For the efficient synthesis of dysprosium sulphide EMFs, methane has been a valuable addition during the arc-discharge synthesis of metallofullerenes as a reactive gas, similar to the use of ammonia during the synthesis of fullerenes containing trimetallic nitride [122,123]. Popov demonstrated that the simple addition of 20 mbar CH_4 led to significant reduction in the formation of empty cage fullerenes during the synthesis of dysprosium sulphide fullerenes. The reaction mechanism in both methane- and ammonia-mediated synthesis is dominated by the hydrogen atom present in the gases. Hydrogen suppresses the growth of empty cage fullerenes and enables the more selective synthesis of mixed-metal and trimetallic nitride EMFs. On the other hand, other additives may have detrimental effects on the empty cage/EMF ratio. For example, during the graphite/metal oxide arc evaporation in the presence of SO_2 , the empty fullerenes are the main products.

Furthermore, the nitrogen-containing atmosphere may lead not only to carbon cages but to a different class of fullerenes, the azafullerenes, where a nitrogen replaces a carbon atom and inherits other interesting properties. One of these azafullerenes, $\text{Gd}_2\text{@C}_{79}\text{N}$, exhibits a long spin relaxation time and a high magnetic spin state and is suitable for SQUID and pulsed EPR studies. In the case of dimetallic azafullerenes, gadolinium appears to have a higher yield compared to yttrium [124]. The gadolinium atoms couple in a ferromagnetic manner.

The formations of carbon nanotubes and metal carbides are two other reactions that take place during the arc vaporization and could be used as another observation to support either the bottom-up or the top-down mechanism for fullerene synthesis. Regarding the proposed mechanism of the charge transfer between the metal and the cage that stabilizes the EMF, see the work by Shinohara and Kroto [38].

In another example, Shinohara managed to isolate the missing low band gap endohedral metallofullerenes simply by adding Teflon tubes inside the arc reactor, in a short distance from the centre of the arc. During the arc-discharge process, the Teflon decomposed to CH_2 and CF_3 reactive groups that functionalize, in situ, the surface of the fullerenes. The resulting perfluorinated EMFs were more stable than their pristine counterparts, which are notoriously difficult to isolate with any common solvent [125]. Examples of the isolated fullerenes are $\text{Y@C}_{70}(\text{CF}_3)_3$, $\text{Y@C}_{72}(\text{CF}_3)$, $\text{Y@C}_{74}(\text{CF}_3)$ (I), $\text{Y@C}_{74}(\text{CF}_3)$ (II), and $\text{Y@C}_{74}(\text{CF}_3)_3$, as identified through MALDI-TOF analysis. The authors performed optical and DFT studies on these following analysis of other missing, small band gap EMFs. By further expanding the gallery of doping agents and mapping the temperature and pressure conditions, for example, by incorporating thermal and light sensors in the reactor and identifying the ideal molar ratio among the compounds, it is expected that the hindrances regarding the fullerene applications will be overcome. For example, in the case of nitrogen-based doping compounds, the reactivity in a CAPTEAR reaction appears to be based on the specific nitrogen anion, further demonstrating the complexity of the reaction [126].

4. Solvent Extraction

Solvent extraction is the next most important step in extraction of the EMFs from the carbon soot. Across much of the literature, the separation of fullerenes and/or EMFs from the soot is typically achieved by the Soxhlet extraction (SE) method [127]. Hence, the yield of extraction is dependent on the type of soot, the number of extraction cycles, and the solvents circulated through the sample. As discussed in the introduction, the metal inside the EMFs is not located in the centre of the carbon cage and is shifted towards one of the ends; therefore, this imparts a dipole moment to the EMF. Thus, the extraction of EMFs from the soot also requires a solvent of higher dipole moment, such as DMF, aniline, or

DMSO, instead of toluene or other solvents of low dipole moments that have traditionally been employed for extracting empty cages [110]. One of the common ways of extracting the maximum amount of fullerenes is by involving a two-step extraction method, where first a low-polarity solvent is used to extract the empty cages (>60%), followed by a high-polarity solvent for maximum extraction of the EMFs [110]. It is also important to note that different solvents work for different types of EMF. For instance, under constant parameters, Chervyakova et al. [98] showed that CS₂ could efficiently extract 11 wt% of Y@C₈₂ out of all fullerenes, compared to 5.0 wt % and 2.3 wt% yield of Sc@C₈₂ and Gd@C₈₂, respectively. Moreover, although CS₂ and C₅H₅N are both considered a good solvent for extracting EMFs, it was observed that the overall yield of M@C₈₂ could vary widely between the types of solvents used under different synthetic parameters. For instance, at 360kPa He pressure, CS₂ extraction yielded about 12 times more Sc@C₈₂ than the use of C₅H₅N. Whereas at 120kPa, CS₂ extraction resulted in a threefold decrease in the Sc@C₈₂ yield as compared to using C₅H₅N. The authors have not commented on these observations, but perhaps a detailed study in this direction could help understand the relationship between synthesis processes and the resultant complex reactions of fullerenes as well as the corresponding methods to extract them efficiently using a particular solvent.

It has also been reported that porous glass, used for holding the soot and the solvent, increases the area of contact of the soot with the solvents and thus leads to a two- to threefold increase in the efficiency of the extraction process [110].

The latest methods and devices for the extraction of fullerenes have seen a shifted focus, aiming to address the limitations of the Soxhlet extraction method instead of optimising its parameters. In fact, the typical solvent extraction can be time-consuming, with the extraction requiring up to 48 h and the need for constant monitoring of stability parameters. Additionally, an efficient SE is still wasteful and utilizes environmentally harmful solvents, as listed in the previous paragraph [128,129]. Recently, Churilov et al. [130] devised a new method of extraction for empty cage fullerenes, called the mechanical extraction method, where a rotating shaft is used to rotate and grind the fullerenes, thus breaking the van der Waals bonds between the fullerenes and insoluble carbon particles from the soot. This also helps in separating the soluble fullerenes from the insoluble fullerenes in the solvent, thus efficiently separating the two in the extraction process. The combination of the mechanical influence with the filtration led to a massive reduction in the time taken for extraction (~15 min) compared to the traditional Soxhlet extraction method, whilst maintaining a similar resultant weight percentage of fullerene-to-soot-extraction ratio. The same group went on to demonstrate the efficiency of the method with higher cage empty fullerenes and EMFs [131]. They showed that the mechanical extraction method could extract 0.4 wt% higher weight fullerenes, which consisted of about 25% EMFs. Although the authors showed this methodology to work well with both EMFs and empty cages, we believe that it is worth using the mechanical extraction method and Soxhlet extraction to efficiently extract empty cage fullerenes and subsequently EMFs, respectively. Moreover, improvements can be further made in the mechanical extraction process by introducing heating in the system. This could lead to increased breaking of the fullerene-carbon particle bond and their increased solubility in the solvent.

5. Conclusions

In conclusion, we summarized some of the important parameters needed to optimize the synthesis of endohedral metallofullerenes. It is important to increase the yield of these nanomaterials in order to carry out in-depth investigation of their synthesis mechanism as well as to ensure a sustainable use for future electronic and opto-electronic devices. Challenges still exist in scaling-up the synthesis of individual fullerene molecules and optimizing separation of individual fullerenes from the obtained soot. While the conventional arc-discharge method, based on the vaporization of graphite composites, seems to have some limitations, the doping of the rods, despite being a more tedious and uncontrollable process, can be further expanded and provide new insights and pathways. New doping

agents and optimized reaction conditions can be developed for further studying the role of different parameters during synthesis. Our ongoing research has a final aim of mapping the temperature and pressure conditions during the arc-discharge process by utilizing tailor-made arc-discharge reactors and carefully controlling and recording the reaction parameters and conditions. Incorporation of thermocouples inside the reactor to map the temperature during the synthesis will help in understanding the reaction conditions that are best suited for optimum synthesis yield of the endohedral fullerenes of interest [132]. This mapping is important not only for the scaled-up production of EMFs but also for the synthesis of new clusters, presenting either new properties or combining optical, optoelectronic, electrochemical, and magnetic properties. Examples of such materials are EMFs that incorporate erbium with gadolinium or dysprosium in different ratios, with the former providing the optical properties and the latter providing the magnetic behaviour. New advances, such as the construction of atomic clocks with N@C₆₀ [133], can provide new directions for the applications of endohedral fullerenes. In particular, EMFs of both well-known (such as Y@C₈₂, Sc@C₈₂, and La@C₈₂) or newly developed materials with different electron and nuclear spin numbers (such as phosphorous-containing endohedral fullerenes) could potentially be used for atomic clock applications. The incorporation of machine learning (ML) and artificial intelligence (AI) approaches for the synthesis of EMFs could revolutionize the industrial-scale production of these molecules by defining optimal process parameters and complementing traditional techniques such as the Design of Experiments (DoE) approach [134], favoured by engineers for many decades. This is a direction in which we plan to endeavour in the near future.

Finally, a combination of optical and paramagnetic properties [135–137] can also lead to new carbon nanotube–EMF peapods or EMF–graphene hybrid nanomaterials [138] with novel properties. Even in organic photovoltaics, fullerenes have recently been incorporated in ternary systems [139]. The incorporation of ternary systems including EMFs and non-fullerene acceptors could provide further avenues for higher-efficiency solar cells. Thus, the science and technology of EMFs will be a viable research topic for years to come.

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Review

Recent Progress on the Functionalization of Endohedral Metallofullerenes

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Abstract: Functionalization of endohedral metallofullerenes (EMFs) plays an important role in exploring the reactivity of EMFs and stabilizing missing EMFs, thus conferring tunable properties and turning EMFs into applicable materials. In this review, we present exhaustive progress on the functionalization of EMFs since 2019. Classic functionalization reactions include Prato reactions, Bingel–Hirsch reactions, radical addition reactions, carbene addition reactions, and so on are summarized. And new complicated multi-component reactions and other creative reactions are presented as well. We also discuss the structural features of derivatives of EMFs and the corresponding reaction mechanisms to understand the reactivity and regioselectivity of EMFs. In the end, we make conclusions and put forward an outlook on the prospect of the functionalization of EMFs.

Keywords: endohedral metallofullerenes; functionalization; reactivity; regioselectivity; derivatives; DFT calculation

1. Introduction

Endohedral metallofullerenes (EMFs) with the metallic atom(s) or cluster encapsulated inside the carbon cages exhibit unique molecular structure and physicochemical properties, conferring EMFs great potential application in biomedicine, optoelectronic, and spin devices [1,2].

Until now, hundreds of EMFs have been reported and it is found that metals from IA, IIA, IIIB, IVB, and VB groups can be entrapped in the carbon cage [1–3], especially Sc, Y, and lanthanides, and form various EMFs including conventional EMFs and cluster EMFs. In the past five years, Th- or U-based actinide EMFs become new family members, showing novel molecular structures [4–6].

Based on the entrapped metallic species, EMFs are usually divided into conventional EMFs including mono-metallofullerenes (e.g., La@C₈₂) [7], di-metallofullerenes (e.g., La₂@C₈₀) [7], tri-metallofullerenes (e.g., Sm₃@C₈₀) [8] and cluster metallofullerenes [2]. In 1999, Sc₃N@C₈₀, the first cluster metallofullerenes, was reported and also represented trimetallic nitride template (TNT) EMFs [9]. Later on, various cluster metallofullerenes such as carbides (e.g., Sc₂C₂@C₈₄ [10], TiLu₂C@C₈₀) [11], methano (e.g., Sc₃CH@C₈₀) [12], carbonitride (e.g., Sc₃CN@C₈₀) [13], oxide (e.g., Sc₄O₂@C₈₀) [14], sulfide (e.g., Sc₂S@C₈₂) [15] and cyano-clusters (e.g., YCN@C₈₂) [16] metallofullerenes have been successively reported. In particular, the embedded metallic species donates electrons (up to 6e) to the carbon cages [17,18], which significantly stabilizes EMFs and changes their electronic structures compared to that of pristine empty fullerenes.

EMFs show distinctive chemical properties compared to empty fullerenes due to the doping of embedded metallic species [1–3,19–21]. In 1995, Akasaka first reported the chemical reaction of La@C₈₂ [22], which starts to tune the properties of EMFs. Up to now, various kinds of methods have been developed for the functionalization of EMFs including photochemical reactions [23,24], Diels–Alder reactions [25,26], Prato reactions [27,28], Bingel–Hirsch reactions [29,30], radical addition reactions [31,32] and so on [1–3]. The inherent properties of EMFs are investigated via functionalization, which is essential access to the application of EMFs. In addition, the functionalization of EMFs is beneficial to acquiring high-quality crystals of EMFs and characterizing the structures of EMFs by forming derivatives that reduce the symmetry of EMFs [33,34]. Hence, the functionalization of EMFs is a popular direction and lots of reviews on the functionalization of EMFs have been published [1–3,19,35].

In this review, we focus on recent progress in the functionalization of EMFs from 2019. Classic functionalization reactions of EMFs with variable endohedral specials, different cage sizes, and isomers are summarized. And new complicated multi-component reactions and other creative reactions are also presented. The structural features of derivatives of EMFs and the corresponding reaction mechanisms are mainly discussed to understand the reactivity and regioselectivity of EMFs. Finally, we make conclusions and put forward an outlook.

2. Functionalization Reactions

The functionalization of EMFs since 2019 was summarized in Table 1.

2.1. Silylation and Germylation

The first exohedral functionalization of EMFs started from the organosilicon reaction of La@C_{2v}(9)-C₈₂ in 1995 [22]. Later on, the digermirane reaction of the La@C_{2v}(9)-C₈₂ was also introduced and showed high reactivity [36]. So far, silylation and germylation reactions of mono-EMFs [37], di-EMFs [38,39], and nitride cluster-fullerenes (NCFs) [40,41] have been realized and exhaustively summarized in Kako's and Jin's reviews [35,42].

Very recently, a novel method for the exclusive separation of *I_h* and *D_{5h}* isomers of Sc₃N@C₈₀ was proposed based on the different reactivity of photoreactions of Sc₃N@*I_h*-C₈₀ and Sc₃N@*D_{5h}*-C₈₀ with disilirane, silirane, and digermirane [43]. Specifically, under the same condition, Sc₃N@*I_h*-C₈₀ reacted readily with them to afford the corresponding 1:1 adducts, whereas Sc₃N@*D_{5h}*-C₈₀ was recovered without any adducts [43]. According to these results, the separation solution was put forward and involved three steps: selective derivatization of Sc₃N@*I_h*-C₈₀ with disilirane, silirane, and digermirane, facile high performance liquid chromatography (HPLC) separation of pristine Sc₃N@*I_h*-C₈₀ and Sc₃N@*D_{5h}*-C₈₀ derivatives, and thermolysis of corresponding derivatives to recovery pristine Sc₃N@*I_h*-C₈₀ [43]. Furthermore, the reaction mechanism has been studied by laser flash photolysis experiments [43]. Decay of the transient absorption of ³Sc₃N@*I_h*-C₈₀* was observed to be enhanced in the presence of disilirane, indicating the quenching process; however, the transient absorption of ³Sc₃N@*D_{5h}*-C₈₀* was much less intensive, which could not confirm the quenching of ³Sc₃N@*D_{5h}*-C₈₀* by disilirane [43]. Finally, based on the time-dependent density functional theory (TD-DFT) calculations, the poor electron acceptor property of ³Sc₃N@*D_{5h}*-C₈₀* might decrease the photochemical reactivity toward disilirane, silirane, and digermirane compared to ³Sc₃N@*I_h*-C₈₀* [43].

2.2. Prato Reaction (1,3 Dipolar Cycloaddition)

The Prato reaction via 1,3-dipolar cycloaddition of azomethine ylides with alkene is one of the most useful methods of fullerene functionalization due to its high selectivity and feasibility [1,2], which means easily connecting a wide range of addends and functional group to fullerenes. Prato reactions of mono-EMFs [44], di-EMFs [27,45], nitride EMFs [28,46], and carbide EMFs [47] have been reviewed in Dunsch's, Yang's, and Jin's reviews [1,2,35]. Herein, recent progress is summarized and some results are inspiring.

The pyrazole and the ring-fused pyrrole reaction of di-EMF $Y_2@C_{3v}(8)-C_{82}$ affords highly regioselective and quantitative mono-adduct [48]. Only one [6,6]-adduct out of the twenty-five different types of nonequivalent C-C bonds of $Y_2@C_{3v}(8)-C_{82}$ was got and its molecular structure was identified by the single crystal X-ray diffraction [48]. Theoretical results suggested that both the anisotropic distribution of p-electron density on the $C_{3v}(8)-C_{82}$ cage and the local strain of the cage carbon atoms lead to the formation of the highly regioselective and quantitative mono-adduct [48]. Additionally, electrochemical studies revealed that the reversibility of the reductive processes of $Y_2@C_{3v}(8)-C_{82}$ was significantly changed by exohedral functionalization, whereas the oxidative process was less influenced [48]. The reason for this phenomenon is that the reduction processes depend on the carbon cage, but the oxidation is mainly influenced by the endohedral Y_2 cluster [48].

In 2022, Chen et al. [49] reported the 1,3-dipolar cycloaddition photoreaction of $Sc_3N@D_{3h}-C_{78}$ with carbonyl ylide affords two isomeric mono-adducts **1a** and **1b** under light irradiation (see Figure 1a). The single crystal X-ray diffraction confirmed that both mono-adducts **1a** and **1b** have the same addition sites at a closed [6,6] bond and possess the same *cis*-conformation, namely, in which the hydrogen atoms of two methines situated at the same side of the tetrahydrofuran ring with parallel orientation [49]. However, two isomeric mono-adducts **3a** and **3b** were got when $Sc_3N@D_{3h}-C_{78}$ was replaced by C_{60} in a similar reaction under the same condition [49]. Surprisingly, the crystal structure of **3b** shows that the addition pattern is located at the closed [6,6]-bond and exhibits a *trans*-conformation, in which the hydrogen atoms of the two methines within the tetrahydrofuran ring located at the opposite sides (see Figure 1b) [49]. In contrast, **3a** has the *cis*-conformation based on the 1H NMR spectrum which has been previously reported by Wang and Yang [50,51]. Furthermore, the DFT calculation results indicated that the synergistic contributions of thermodynamics of adducts, the most reactive C-C bond, and the *cis*-dipole intermediate from *trans* **2**, result in the high regioselectivity of *cis*-conformations of **1a** and **1b** [49].

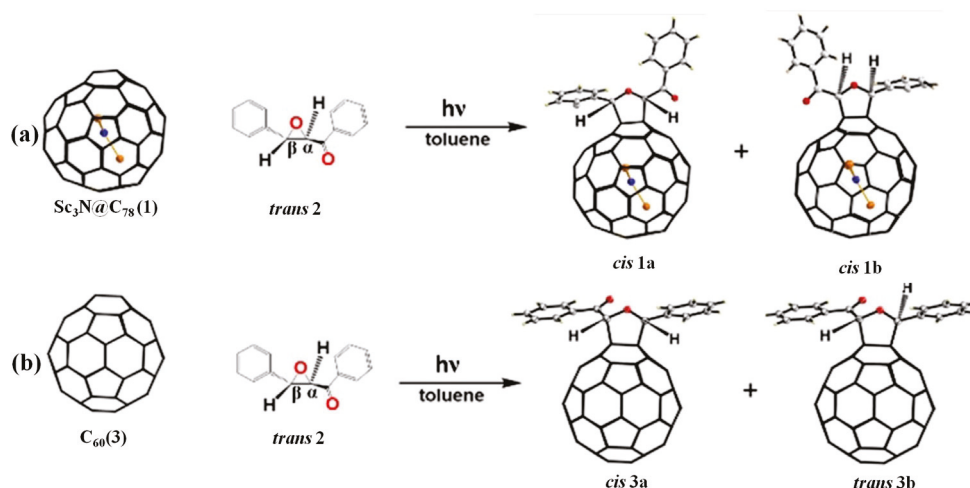


Figure 1. The 1,3-dipolar cycloaddition of *trans*-phenyl-(3-phenyl-oxiranyl)-methanone (*trans* **2**) with (a) $Sc_3N@D_{3h}-C_{78}$ and (b) C_{60} . Atom key: Sc (brown-yellow), N (blue), O (red). Reproduced from Ref. [49] with permission. Copyright 2021 John Wiley and Sons.

Though the mono-adducts of Prato reaction of $M_3N@C_{80}$ ($M = Sc, Y, Gd, Dy, Ho, Er, Lu$) have been widely reported [1,2], the corresponding bis-adducts are rare. Aroua et al. [52] synthesized the bis-adducts of the Prato reaction of $Gd_3N@I_h-C_{80}$ and $Y_3N@I_h-C_{80}$ in 2015. Later on, Cerón et al. [53] obtained 1,3-dipolar bis-additions of $Sc_3N@I_h-C_{80}$ and $Lu_3N@I_h-C_{80}$ using the tether-controlled multi-functionalization method, but the unambiguous crystal structure characterization of these reported Prato bis-adducts are missing. Fortunately, Semivrazhskaya et al. [54] reported one precise crystal structure of two bis-ethylpyrrolidinoadducts of $Gd_3N@I_h-C_{80}$ (**4**) obtained by regioselective 1,3-dipolar

cycloadditions; see Figure 2a. The crystal structure of the minor-bis-adduct (7) shows a C_2 -symmetric carbon cage with [6,6][6,6]-addition sites, as shown in Figure 2b and a strictly planar Gd_3N cluster, which is much less strained compared to a pyramidalized cluster of the pristine $Gd_3N@I_h-C_{80}$. Indeed, two interior Gd atoms coordinated to the C_{80} cage at two sp^3 addition sites, releasing the strain of the endohedral Gd_3N cluster in the minor-bis-adduct. However, the structure of major-bis-adduct was presumably asymmetric [6,6][6,6]-addition sites, because its visible - near infrared (vis-NIR) spectra are almost identical to that of the major bis-adduct of $Y_3N@C_{80}$ with an asymmetric [6,6][6,6]-structure. Moreover, it is experimentally observed that the symmetrical minor-bis-adduct of $Gd_3N@I_h-C_{80}$ isomerized to the asymmetrical major-adduct and based on the linear transit calculations, a pathway of the isomerization is through the formation of the [6,6][6,6]-bis-adduct, followed by [5,6][6,6]-bis-adduct [54].

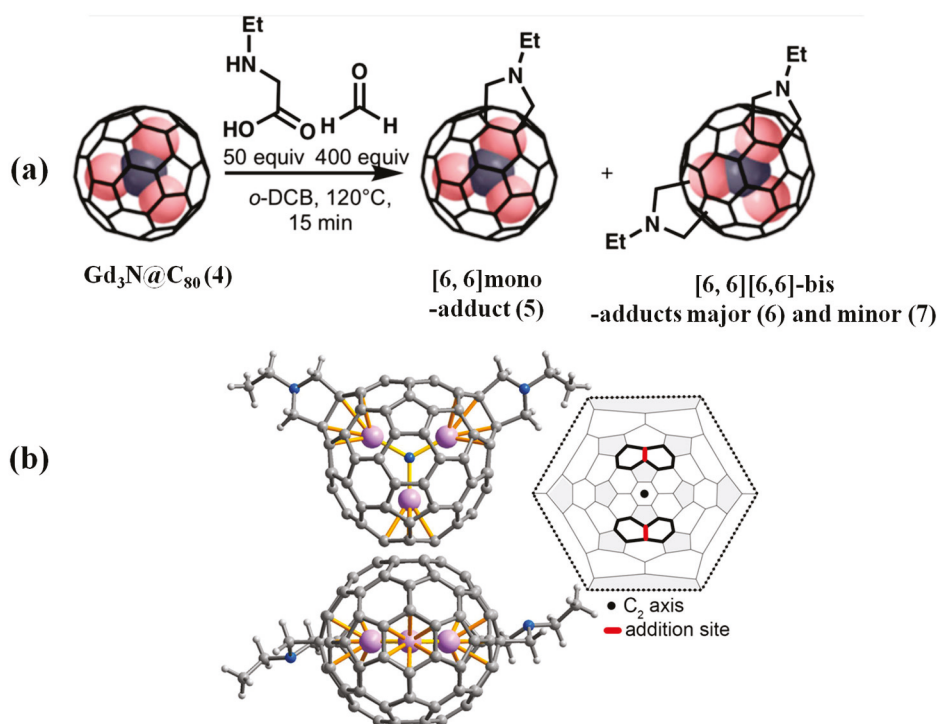


Figure 2. (a) Prato reactions of $Gd_3N@I_h-C_{80}$ (4) afford the mono-adducts (5) and bis-adducts (6) and (7). (b) X-ray crystal structure of minor-bis- $Gd_3N@C_{80}[C_4H_9N]_2$ 7 (side and top views) and the red thick bonds in the Schlegel diagram represent the additional sites. The black dot in the center of the Schlegel diagram indicates the C_2 axis. Reproduced from Ref. [54] with permission. Copyright 2019 American Chemical Society.

It is hard to get the Prato multi-additions of EMFs because of their huge isomers theoretically. Unexpectedly, four tris- and one tetra-isomers for both $Y_3N@I_h-C_{80}$ and $Gd_3N@I_h-C_{80}$ were obtained in a regioselective manner when $M_3N@I_h-C_{80}$ ($M = Y, Gd$) reacted with an excess of N-ethylglycine and formaldehyde [55]. Three of four tris-adducts of $Y_3N@I_h-C_{80}$ are [6,6][6,6][6,6] isomers and the remaining one is [6,6][6,6][5,6]-isomer confirmed by the NMR whereas the tetra-adduct is all [6,6] isomer which is similar to that of $Gd_3N@I_h-C_{80}$ [55]. And, mutual interconversions among all [6,6] tris-adducts of both $Y_3N@I_h-C_{80}$ and $Gd_3N@I_h-C_{80}$ are observed at room temperature. Density functional theory (DFT) calculations show that the most stable structures corresponded to adding at the most strained bonds by estimating the relative stabilities of tris- and tetra-adducts formed upon Prato functionalization of the most pyramidalized regions of the fullerene structure [55]. Electron resonance (ESR) measurements of pristine, bis-, and tris-adducts of $Gd_3N@I_h-C_{80}$ show that the rotation of the endohedral cluster slowed down as the addition numbers to C_{80} cage increased, which indicates the accommodating of Gd atoms of the relatively large

Gd₃N cluster inner space at the sp³ addition sites [55]. Therefore, the strain release of the Gd₃N@I_h-C₈₀ leads to the high regioselectivity of the Prato multi-addition reaction.

2.3. Bingel–Hirsch Reaction

Bingel–Hirsch reaction is one of the most used methods to synthesize derivations of EMFs [1,2]. The first Bingel–Hirsch reaction of Gd@C₆₀ affords multi-adducts Gd@C₆₀[C(COOH)₂]_n (n = 1–10) [56]. Surprisingly, the reaction of La@C_{2v}(9)-C₈₂ obtains four singly bonded adducts as well as one conventional cyclopropane adduct [29,57]. Recently, a highly regioselective Bingel–Hirsch reaction of Y@C_s(6)-C₈₂ induced by the metal encapsulation was reported by Shen et al. [58]. Three mono-adduct out of 44 possible isomers for the C_s(6)-C₈₂ cage have been thoroughly isolated, showing high regioselectivity [59]. The single-crystal X-ray diffraction crystallography analysis confirmed that the bromomalonate group was singly bonded to the [5,6,6]-cage carbon of Y@C_s(6)-C₈₂ in one isomer [59]. Meanwhile, further experimental and theoretical results indicate that three mono-adduct isomers may mutually be regioisomers with bromomalonate singly bonded to different cage carbon atoms having high spin density values caused by the encapsulation of a Y³⁺ ion into the low symmetric C_s(6)-C₈₂ cage [58].

Despite differences in activity, NCFs such as M₃N@I_h(7)-C₈₀ (M = Sc, Y, Gd, Lu) [59] and Gd₃N@C_{2n} (2n = 82, 84) [60], typically afford the methanofullerene adduct (via [2 + 1] cycloaddition). The Bingel–Hirsch reaction of Y₃N@I_h(7)-C₈₀ yields an unexpected [6,6]-open mono-adduct confirmed by a crystallographic study [30]. In contrast, the Bingel–Hirsch reaction of TiY₂N@I_h(7)-C₈₀, a Y³⁺ ion replaced by a Ti³⁺ ion compared to the Y₃N@I_h(7)-C₈₀, affords a singly bonded adduct, indicating that change the endohedral atom or clusters can manipulate the regioselectivity of EMFs as well as the addition pattern [61].

Notably, a new route to synthesize the Bingel–Hirsch derivative of EMFs via the cationic metallofullerenes was reported by Hu et al. recently, as shown in Figure 3 [62]. M₃N@I_h(7)-C₈₀ (M = Sc or Lu) cations were generated by both electrochemical and chemical oxidation and then the cations successfully underwent the typical Bingel–Hirsch reaction [62]. For Sc₃N@I_h(7)-C₈₀, both [5,6]-open (10) and [6,6]-open (11) adducts have been obtained whereas the former has never been synthesized via the neutral NCFs [62]. However, only a [6,6]-open adduct (12) was generated for Lu₃N@I_h(7)-C₈₀ [62]. DFT calculations implied that the cationic M₃N@I_h(7)-C₈₀ was much more reactive than the neutral compound for the Bingel–Hirsch reaction [62]. Furthermore, a new unusual mechanism for the Bingel–Hirsch reaction of the cationic NCFs is proposed, involving an outer-sphere single-electron transfer (SET) process [62]. Namely, the diethyl bromomalonate anion not only acts as a nucleophile, the same role in common Bingel–Hirsch reaction, but also as an electron donor, a new role to stable intermediate [M₃N@C₈₀(C₂H₅COO)₂CBr]⁺ [62]. Additionally, the energy profiles for the Bingel–Hirsch additions on M₃N@C₈₀⁺ cations for M = Sc and Lu were drawn out to explain the distinguished regioselectivity of M₃N@C₈₀⁺ cations, in which M = Sc (with the [6,6] and [5,6] products) and M = Lu (with only the [6,6] product) [62].

2.4. Carbene Addition

The carbene reactions are vital for the functionalization of EMFs as well as for determining the molecular structure of EMFs [3]. Up to now, photochemical carbene reactions of mono-EMFs [24], di-EMFs [63], carbide clusterfullerenes [64], and NCFs [65] have been reported and open fulleroid derivatives were usually achieved. Especially, the N-heterocyclic carbene (NHC) reaction of Sc₃N@I_h-C₈₀ afforded an abnormal carbene product with C5 as its active center singly connected to the inert [6,6,6] carbon atom of the C₈₀ cage [66]. In contrast, normal NHC products of M₃N@I_h-C₈₀ (M = Sc, Lu) were acquired by the introduction of a little oxygen in the same reaction [67]. Recent results of NHC reaction with Lu₃N@I_h(7)-C₈₀, Lu₂@C_{3v}(8)-C₈₂, and Lu₂@C_{2v}(9)-C₈₂ indicated that the high regioselectivity and preferential formation for mono-adducts mainly originated from the electronic

effect including molecular orbitals and electrostatic interactions of the fullerene cages in addition to the steric clash between the NHC and EMFs [68].

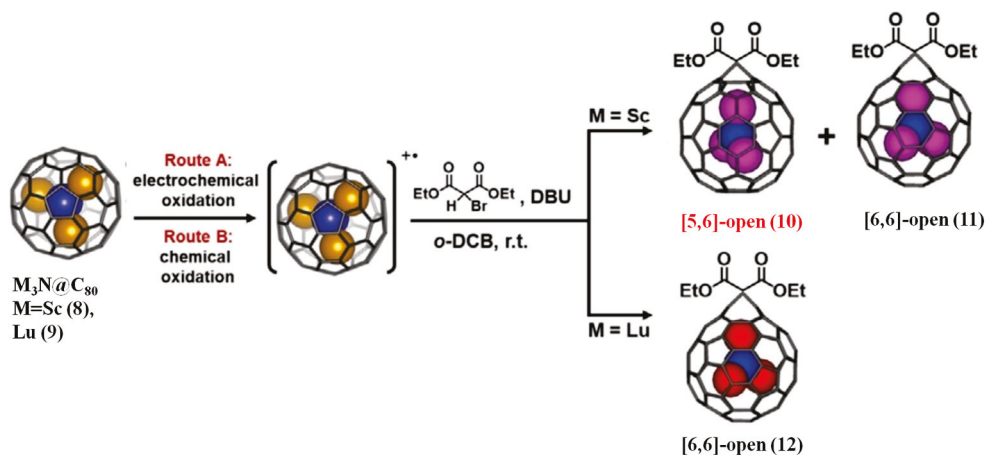


Figure 3. Bingel–Hirsch reaction of $M_3N@I_h-C_{80}$ ($M = \text{Sc}$ or Lu) radical mono-cation under conventional conditions. Reproduced from Ref. [62] with permission. Copyright 2020 John Wiley and Sons.

Recently, the carbene reaction was extended to the actinide EMFs, $\text{Th}@C_{3v}(8)\text{-C}_{82}$ and $\text{U}@C_{2v}(9)\text{-C}_{82}$, and the former afforded three mono-adducts, named $\text{Th}@C_{3v}(8)\text{-C}_{82}\text{Ad}$ (I, II, III) (Ad = adamantylidene), while four mono-adducts were acquired for the latter, named $\text{U}@C_{2v}(9)\text{-C}_{82}\text{Ad}$ (I, II, III, IV), presenting remarkably higher reactivity than lanthanide EMFs [69], as shown in Figure 4a. Both $\text{Th}@C_{3v}(8)\text{-C}_{82}\text{Ad}$ (I) and $\text{U}@C_{2v}(9)\text{-C}_{82}\text{Ad}$ (I) are [6,6]-open cage structures, which are unambiguously confirmed by single crystal X-ray crystallography [69]. Moreover, isomerization of $\text{Th}@C_{3v}(8)\text{-C}_{82}\text{Ad}$ (II) and $\text{Th}@C_{3v}(8)\text{-C}_{82}\text{Ad}$ (III) and $\text{U}@C_{2v}(9)\text{-C}_{82}\text{Ad}$ (II) and $\text{U}@C_{2v}(9)\text{-C}_{82}\text{Ad}$ (III) was observed at room temperature; however, $\text{Th}@C_{3v}(8)\text{-C}_{82}\text{Ad}$ (I) and $\text{U}@C_{2v}(9)\text{-C}_{82}\text{Ad}$ (I) showed high stability under the same condition [69]. DFT calculations suggested that carbon atoms with the largest negative charge density and POAV(p-orbital axis vector) values are the best sites toward the Ad addition [69]. Furthermore, compared to the lanthanide analogs, the unusually high reactivity of $\text{Th}@C_{3v}(8)\text{-C}_{82}$ and $\text{U}@C_{2v}(9)\text{-C}_{82}$ stemmed from much closer metal–cage distance, increased metal-to-cage charge transfer, and strong metal–cage interactions, which is due to the significant contribution of extending Th-5f and U-5f orbitals to the occupied molecular orbitals [69].

Very recently, the first carbene reaction of $\text{Dy}_2\text{TiC}@I_h-C_{80}$, the μ_3 -carbido cluster-fullerene ($\mu_3\text{-CCF}$) bearing central $\mu_3\text{-C}$ and Ti(IV) atoms forming a $\text{Ti}=\text{C}$ double bond, with 2-adamantane-2,3-[3H]-diazirine (AdN_2) was reported [70], see Figure 4b. Noteworthy, the photochemical carbene reaction of $\text{Dy}_2\text{TiC}@I_h-C_{80}$ with AdN_2 affords only one mono-adduct with a [6,6]-open addition pattern, which is unambiguously confirmed by single-crystal X-ray diffraction [70]. Meanwhile, the Ad moiety selectively attacks the [6,6]-bond which is adjacent to the Ti^{4+} ion instead of the two Dy^{3+} ions, thus the encapsulated Ti atom within $\text{Dy}_2\text{TiC}@I_h-C_{80}\text{-Ad}$ is fully ordered while the two Dy atoms are still disordered [70]. Theoretical calculations indicate that the [6,6]-open adduct is thermodynamic and the Ti(IV) ion plays a decisive role in the high regioselectivity [70]. In contrast, a different type of adduct with the additional sites adjacent to the Y^{3+} ion instead of the Ti^{3+} ion is predicted to be got when a similar reaction of $\text{Y}_2\text{TiN}@I_h-C_{80}$ containing a Ti(III) ion with AdN_2 is carried out [70]. Hence, the non-rare-earth metal Ti bearing a high oxidation state within the $\mu_3\text{-CCF}$ determines the peculiarity of the chemical properties of the $\mu_3\text{-CCF}$ [70].

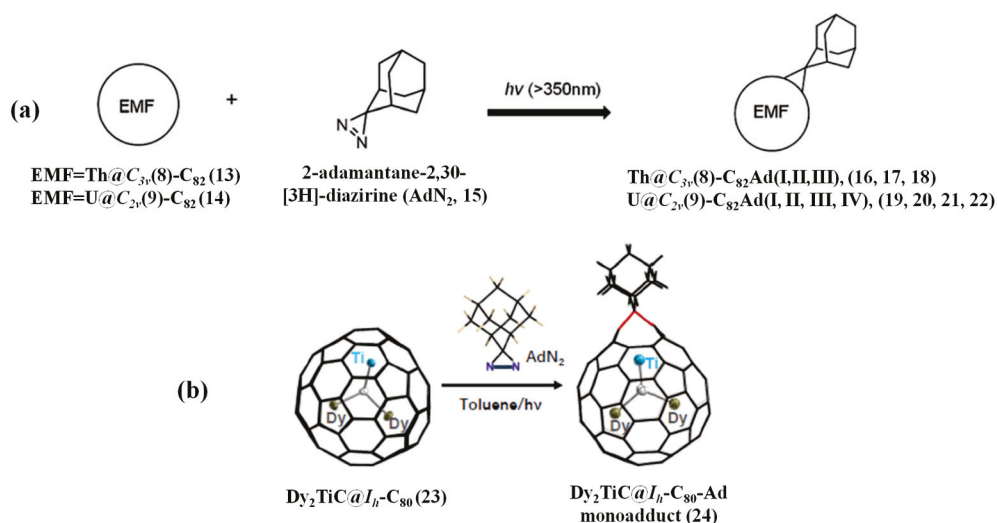


Figure 4. (a) Reaction of AdN₂ (AdN₂ = 2-adamantane-2,30-[3H]-diazirine) (15) with Th@C_{3v}(8)-C₈₂ (13) or U@C_{2v}(9)-C₈₂ (14). Reproduced from Ref. [69] with permission from the Royal Society of Chemistry. (b) Synthetic route of Dy₂TiC@I_h-C₈₀-Ad (24) through the photochemical reaction of Dy₂TiC@I_h-C₈₀ (23) with AdN₂ (15). Reproduced from Ref. [70] with permission from the Chinese Chemical Society (CCS), Peking University (PKU), and the Royal Society of Chemistry.

2.5. Radical Addition Reaction

Radical addition reactions of EMFs can generate a wide range of derivatives and especially capture the unstable EMFs to form stable derivatives with a closed-shell electronic configuration. Radical groups such as benzyl or trifluoromethyl were reacted with EMFs including mono-EMFs [71], di-EMFs [31], NFC [72], CCF [32], and cyano-clusters [73] EMFs.

Liu et al. reported that an array of air-stable dimetallofullerene Ln₂@C₈₀(CH₂Ph) (Ln₂ = Y₂, Gd₂, Tb₂, Dy₂, Ho₂, Er₂, TbY, TbGd) (25) was acquired by reacting metallofullerene anions with benzyl-bromide in DMF (N,N-Dimethylformamide) solution [74]. Single-crystal X-ray diffraction of Ln₂@C₈₀(CH₂Ph) shows that the benzyl is attached to the cage via a single bond, see Figure 5a [74]. Moreover, there is a covalent lanthanide–lanthanide bond in Ln₂@C₈₀(CH₂Ph) and a single electron residing on the metal–metal bonding orbital [74]. Thanks to very strong exchange interactions between 4f moments and the residing single electron, Tb₂@C₈₀(CH₂Ph) is a robust nanomagnet and shows a gigantic coercivity of 8.2 Tesla at 5 K and a high 100 s blocking temperature of magnetization of 25.2 K [74].

Recently, a long-sought dysprosium-based EMF Dy@C_{2v}(5)-C₈₀ was captured in the form of Dy@C_{2v}(5)-C₈₀(CH₂Ph)(Ph = -C₆H₅) (26) from carbon soot with various fullerenes [75]. On the basis of the single crystal X-ray diffraction, the carbon cage is confirmed as a rare C_{2v}(5)-C₈₀, which is the first case of an EMF composed of a mono-metal rare earth ion encapsulated within this C₈₀ cage, as shown in Figure 5b [75]. And, the benzyl group is grafted onto the [5,6,6]-carbon atom via a single bond, which verifies that Dy@C_{2v}(5)-C₈₀(CH₂Ph) has an open-shell electron configuration and its electron configuration is Dy³⁺@C_{2v}(5)-C₈₀³⁻ [75]. Meanwhile, the encapsulated Dy³⁺ ion is sited underneath the [6,6]-bond and deviated from the symmetry plan of C_{2v}(5)-C₈₀ [75]. Furthermore, based on theoretical calculations, the bandgap is enlarged from 1.11 eV to 1.86 eV and the LUMO energy level is obviously elevated to about 0.87 eV due to a benzyl radical addition to Dy@C_{2v}(5)-C₈₀, thus synergistically stabilizing the missing Dy@C_{2v}(5)-C₈₀ [75].

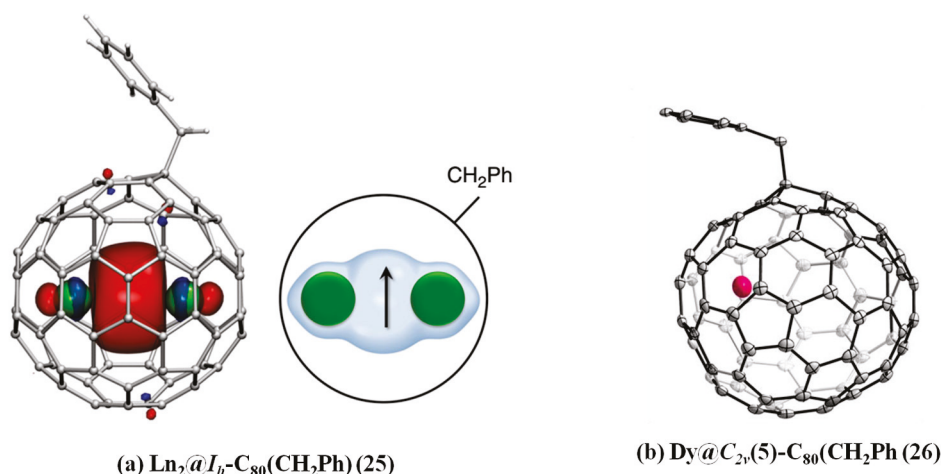


Figure 5. (a) Molecular structure of $\text{Ln}_2@I_h\text{-C}_{80}(\text{CH}_2\text{Ph})$ (25). Single-occupied Ln–Ln bonding molecular orbital (left; carbons are gray, hydrogens are white, lanthanides are green), and schematic depiction of the molecule (right; the arrow represents an unpaired electron residing on the Ln–Ln bonding orbital). (b) Drawing of $\text{Dy}@C_{2v}(5)\text{-C}_{80}(\text{CH}_2\text{Ph})$.

Xu et al. reported that using 1,2,4-trichlorobenzene or iodobenzene to extract the Er-based fullerene soot, $\text{Er}@C_{72}(\text{C}_6\text{H}_3\text{Cl}_2)$ and $\text{Er}@C_{76}(\text{C}_6\text{H}_5)$ were obtained by free radical addition [76]. In addition, a high-temperature trifluoromethylated reaction of $\text{Er}@C_{2n}$ and AgCOOCF_3 afforded several adducts, $\text{Er}@C_{76}(\text{CF}_3)_5$, $\text{Er}@C_{82}(\text{CF}_3)_3$, and $\text{Er}@C_{82}(\text{CF}_3)_5$ (I, II, III) [76]. Unexpectedly, all derivatives of $\text{Er}@C_{2n}$ ($2n = 72, 76, 82$) exhibit detectable characteristic NIR photoluminescence at around 1520 nm, which stems from the emission of Er^{3+} , but pristine $\text{Er}@C_{2n}$ ($2n = 76, 82$) show no photoluminescence [76]. Based on the UV-vis-NIR absorption spectrum, HOMO-LUMO gaps of the derivatives are remarkably enlarged compared to that of pristine $\text{Er}@C_{2n}$ [76]. And, odd-number addition groups result in a closed-shell electronic structure for the derivatives [76]. Hence, the enlarged HOMO-LUMO gap and the closed-shell electronic structure turn on the photoluminescence activity of Er^{3+} [76]. In addition, the photoluminescence mechanism study suggests that the photoluminescence of the Er^{3+} ion comes from the energy transfer from the fullerene cage to the Er^{3+} ion; however, the photoluminescence of pristine $\text{Er}@C_{2n}$ was quenched by energy transfer from the first excited state of Er^{3+} to the fullerene cage [76].

Li et al. reported a novel radical reaction of $\text{Y}@C_{2v}(9)\text{-C}_{82}$ with N-arylbezamidine catalyzed by silver carbonate [77]. The reaction is highly regioselective and affords only one mono-adduct with an imidazoline group. The theoretical calculation reveals the addition group is attached to a specific [5,6]-bond near the Y atom [77].

2.6. Electrophilic Trifluoromethylation

The lack of selectivity of the radical addition reactions results in multi-adducts and a complicated separation process. Unprecedentedly, the high selectivity of electrophilic trifluoromethylation of metallofullerene anions was reported very recently [78]. Specifically, reacting metallofullerene anions extracted by DMF with Umemoto reagent II affords $\text{M}_2@C_{80}(\text{CF}_3)$ ($\text{M} = \text{Tb}, \text{Y}$) mono-adducts as the major product, indicating higher selectivity of electrophilic trifluoromethylation than that of benzyl bromide reaction (see Figure 6a) [78]. The single-crystal X-ray diffraction analysis shows that the CF_3 group is attached to the pentagon/hexagon/hexagon junction ([5,6,6] position) of the $I_h\text{-C}_{80}$ cage via a single bond, as shown in Figure 6b [78]. Similarly, a single electron remains between two Tb ions, forming single-electron metal–metal bonds with the formal metal oxidation state of $\text{Tb}^{2.5+}$ [78]. As expected, $\text{Tb}_2@C_{80}(\text{CF}_3)$ is also a robust single-molecule magnet based on magnetic characterizations, which is comparable to the benzyl mono-adduct $\text{Tb}_2@C_{80}(\text{CH}_2\text{Ph})$ [78]. Therefore, electrophilic trifluoromethylation is a very excellent approach to stabilize metallofullerene anions $\text{M}_2@C_{80}$, which is a simple, fast

room-temperature reaction with high selectivity and needs less time for required HPLC separation compared to the benzylation reaction of $M_2@C_{80}$ [78].

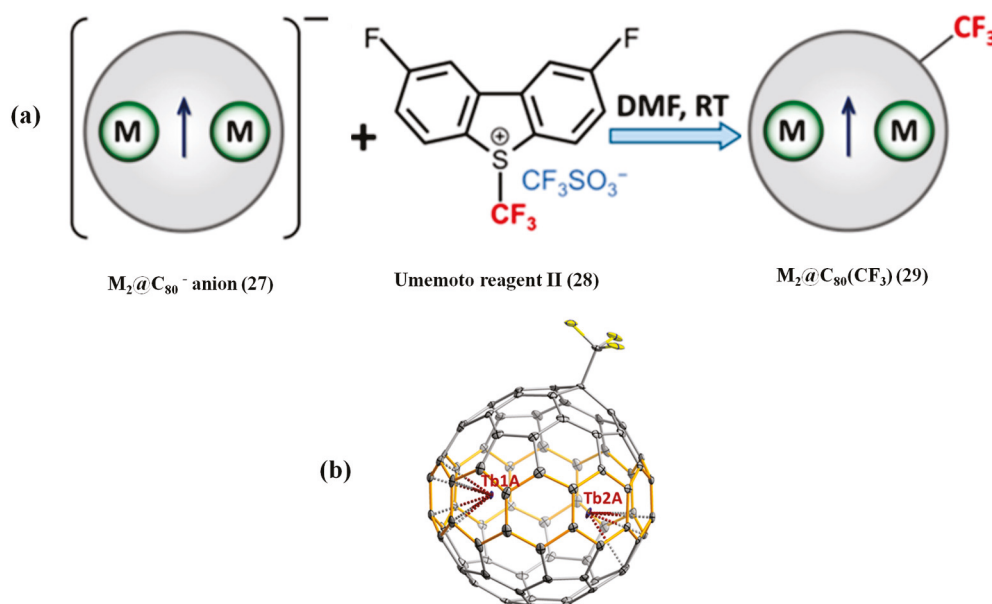


Figure 6. (a) Scheme of the reaction between $M_2@C_{80}^-$ anion and Umemoto reagent II with the formation of $M_2@C_{80}(CF_3)$. (b) $Tb_2@C_{80}(CF_3)$ molecule from the single crystal showing the main Tb sites Tb1A and Tb2A. Reproduced from Ref. [78] with permission. Copyright 2021 American Chemical Society.

2.7. Coordination Reaction

The organometallic complexes of EMFs usually bear the η^2 coordination fashion [79], and the η^1 -coordinated complexes of EMFs with only one metal–cage bond are very desirable. Until 2019, Xie et al. [80] reported a coordination reaction of $Re_2(CO)_{10}$ (31) to paramagnetic $Y@C_{2v}(9)-C_{82}$ (30) by an efficient radical coupling, and an unprecedented η^1 -coordinated complex: $Re(CO)_5-\eta^1-Y@C_{2v}(9)-C_{82}$ (32) was obtained, as shown in Figure 7a. Crystallographic results confirmed that the $Re(CO)_5$ moiety coordinates to a [5,6,6]-carbon atom of the C_{82} cage via a single Re–C σ bond [80]. Furthermore, Vis-NIR and ESR results verified that the $Re(CO)_5$ moiety transfers one electron to the EMF, resulting in a closed-shell electronic structure similar to anionic $(Y@C_{82})^-$ species with high stability [80]. In contrast, replacing with diamagnetic $Sc_3N@I_h(9)-C_{82}$ and $Lu_2@C_{2v}(9)-C_{82}$ in the same reaction, no product is yielded, further confirming a radical coupling process [80].

Bao et al. [81] reported that reacting mono-metallofullerenes, $Eu@C_2(5)-C_{82}$ (33) and $Eu@C_2(13)-C_{84}$ (34), with a tungsten complex $W(CO)_4(Ph_2PC_2H_4PPh_2)$ (35) afford the highly regioselective product; alternatively, only one product was acquired for each reaction. Single crystal X-ray crystallography shows that in both products (36, 37), the tungsten moiety coordinates to a [6,6]-bond of the cage with an η^2 -fashion, as shown in Figure 7b [81]. And, after the coordination of the tungsten moiety, the motion of the internal Eu ion in both adducts is restricted to a certain extent, which is due to changing the electrostatic potentials inside the cage supported by theoretical calculations [81]. Moreover, the observed high regioselectivity is explained by electron transfer from the endohedral Eu to the cage, which significantly changed the LUMO distribution on $C_2(5)-C_{82}/C_2(13)-C_{84}$ based on theoretical calculations [81]. Therefore, the interplay between the endohedral and the exohedral metallic moiety is achieved in a single molecule system via intramolecular charge transfer [81].

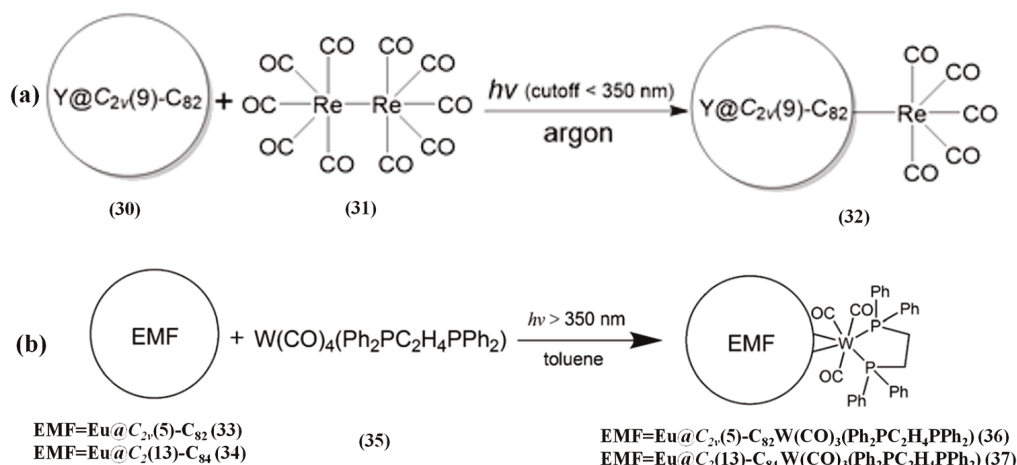


Figure 7. (a) Reaction scheme of $\text{Y}@C_{2v}(9)-C_{82}$ with $\text{Re}_2(\text{CO})_{10}$. Reproduced from Ref. [80] with permission from the Royal Society of Chemistry. (b) Reaction of $\text{W}(\text{CO})_4(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)$ with $\text{Eu}@C_2(5)-C_{82}$ or $\text{Eu}@C_2(13)-C_{84}$. Reproduced from Ref. [81] with permission. Copyright 2019 American Chemical Society.

2.8. Methoxide Reaction

Unexpected bis-methoxyl adducts of $\text{Sc}_3\text{N}@I_h-C_{80}$ were got for the first time when $\text{Sc}_3\text{N}@I_h-C_{80}$ reacted with/without $\text{Ph}_2\text{C}=\text{O}$, $\text{PhC}\equiv\text{CPh}$ or $\text{PhC}\equiv\text{N}$ in the presence of tetrabutylammonium hydroxide (TBAOH) stored in CH_3OH [82]. However, it was further observed that bis-methoxyl adducts of $\text{Sc}_3\text{N}@I_h-C_{80}$ form irrespective of the presence of other reagents, since TBAOH in CH_3OH efficiently boosts the $-\text{CH}_3\text{O}$ addition [82]. Furthermore, single crystal X-ray diffraction analysis unambiguously determines the molecular structures of the products as 1,4- and 1,2-bis-methoxyl adducts, and the conformations of the two $-\text{OCH}_3$ groups in both bis-methoxyl adducts are obviously different bis-methoxyl, as shown in Figure 8a,b [82]. And, the planar Sc_3N cluster in 1,4-bis-methoxyl adducts (38) is orthogonal with the plane crossing the addition sites, whereas the metal cluster in 1,2-bis-methoxyl adducts (39) is nearly parallel to the plane crossing the addition site, which indicates that exohedral modification is practical to control the orientation of the embedded cluster bis-methoxyl [82]. In addition, a possible mechanism related to an anion addition and a radical reaction was put forward (see Figure 8c), which opened up new horizons to the highly selective reactions between the methoxyl anion and EMFs [82]. Specifically, CH_3O^- generated by deprotonates CH_3OH via TBAOH prevailed over OH^- (from TBAOH) in the o-DCB (o-dichlorobenzene) solution and attached to $\text{Sc}_3\text{N}@C_{80}$ to form the mono-anion $[\text{Sc}_3\text{N}@C_{80}(\text{OCH}_3)]^-$ firstly [82]. Then, the mono-anion was oxidized to $[\text{Sc}_3\text{N}@C_{80}(\text{OCH})]^\bullet$ radical by I_2 , and the dimethoxyfullerene anion $[\text{Sc}_3\text{N}@C_{80}(\text{OCH}_3)_2]^-$ formed by accepting another CH_3O^- [82]. Finally, the ultimate 1,2- or 1,4-addition dimethoxyfullerene products were yielded through the oxidation of dimethoxyfullerene anion by I_2 [82].

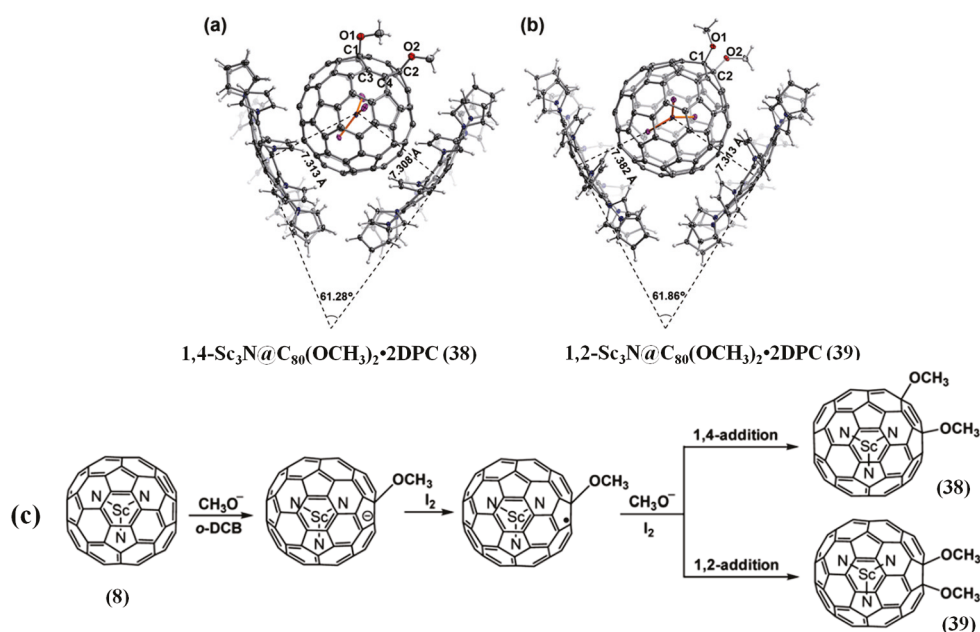


Figure 8. Single crystal X-ray structures of co-crystals $1,4\text{-Sc}_3\text{N@C}_{80}(\text{OCH}_3)_2 \cdot 2\text{DPC}$ (a) and (b) $1,2\text{-Sc}_3\text{N@C}_{80}(\text{OCH}_3)_2 \cdot 2\text{DPC}$ with thermal ellipsoids at the 10% probability level. (c) Plausible mechanism of the reaction between $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$ and TBAOH/ CH_3OH in *o*-DCB. Reproduced from Ref. [82] with permission from the Royal Society of Chemistry.

2.9. Multicomponent Reactions

Very recently, pyrazoline-fused metallofullerene derivative (**41**) as shown in Figure 9 was generated from a four-component cascade reaction of $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$ with 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazines (**40**), H_2O , and O_2 [83]. The [5,6] pyrazoline-fused structure is remarkably different from the reaction of a 1,2,4,5-tetrazine with $\text{Sc}_3\text{C}_2\text{@I}_h\text{-C}_{80}$ which provided a bis-fulleroid derivative [84]. Moreover, the reaction was extended to 3,6-bis(6-methylpyridin-2-yl)-1,2,4,5-tetrazine, and a similar [5,6] pyrazoline-fused derivative (**42**) was achieved [83]. Furthermore, a plausible formation mechanism of pyrazoline-fused metallofullerenes is proposed, which involved a complicated sequence of Diels–Alder reaction, retro Diels–Alder reaction with N_2 extrusion, hydration reaction, rearrangement reaction, and oxidative dehydrogenation reaction [83].

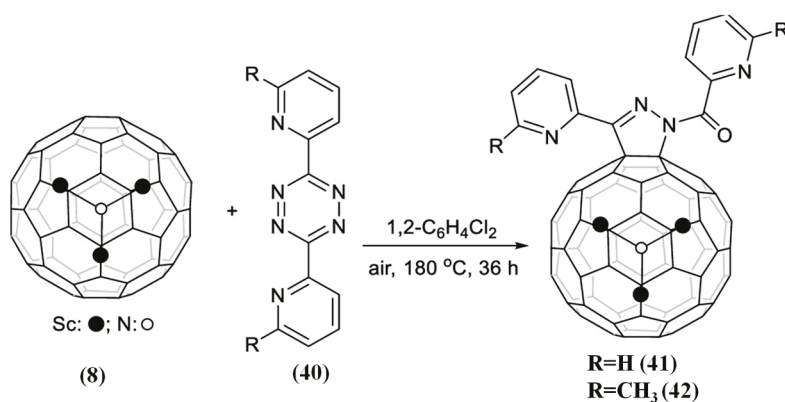


Figure 9. The reaction of $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$ with tetrazines (**40**). Reproduced from Ref. [83] with permission. Copyright 2022 American Chemical Society.

Table 1. An exhaustive list of functionalizations of EMFs reported from 2019 to date.

Reaction	Endohedral Metallofullerene	Reactants	Product	Addition Position	Number of Isomers	Ref.
Silylation and germylation	$\text{Sc}_3\text{N}@I_h\text{-C}_{80}$	Disilirane	$\text{Sc}_3\text{N}@C_{80}\text{Si}_2\text{Mes}_4$	[1,2], [1,4]	2	[40,43]
		Silirane	$\text{Sc}_3\text{N}@C_{80}\text{Si}(\text{Dep})_2\text{CH}_2\text{CHtBp}$	[5,6]diastereomers,[6,6]	3	[43]
		Digermirane	$\text{Sc}_3\text{N}@C_{80}\text{Ge}(\text{Dep})_4$	[1,4]	1	[43]
	$\text{Sc}_3\text{N}@D_{5h}\text{-C}_{80}$	Disilirane, silirane, digermirane	No product	non-reactive	0	[43]
Prato reaction (1,3 dipolar cycloaddition)	$\text{Y}_2@C_{3v}(8)\text{-C}_{82}$	Diphenylnitrimine ylide	$\text{Y}_2@C_{82}\text{N}_2(\text{C}_6\text{H}_5)_2$	[6,6]	1	[48]
		N-benzylazomethine ylide	$\text{Y}_2@C_{82}\text{NCH}_2(\text{C}_6\text{H}_5)$	[6,6]	1	[48]
		Trans-phenyl-(3-phenyl-oxiranyl)-methanone	$\text{Sc}_3\text{N}@C_{78}(\text{C}_6\text{H}_5)\text{CHOCHCO}(\text{C}_6\text{H}_5)$	cis-[6,6]	2	[49]
	$\text{Gd}_3\text{N}@D_{3h}\text{-C}_{78}$	N-ethylglycine, paraformaldehyde	$\text{Gd}_3\text{N}@C_{80}((\text{CH}_2)_2\text{NEt})_2$ $\text{Gd}_3\text{N}@C_{80}((\text{CH}_2)_2\text{NEt})_3$ $\text{Gd}_3\text{N}@C_{80}((\text{CH}_2)_2\text{NEt})_3$ $\text{Gd}_3\text{N}@C_{80}((\text{CH}_2)_2\text{NEt})_4$	[6,6] [6,6]-bis adduct [6,6] [6,6] [6,6] tris-adduct [6,6] [6,6] [5,6] tris-adduct all [6,6] tera-adduct	2 3 1 1	[54] [55] [55] [55]
Bingel–Hirsch reaction	$\text{Y}@C_s(6)\text{-C}_{82}$	Diethyl bromomalonate, DBU	$\text{Y}@C_{82}\text{CBr}(\text{CCOOCH}_2\text{CH}_3)_2$	[5,6,6]-single bond	3	[58]
	$\text{Sc}_3\text{N}@I_h(7)\text{-C}_{80}$	Diethyl bromomalonate, DBU	$\text{Sc}_3\text{N}@C_{80}\text{CBr}(\text{CCOOCH}_2\text{CH}_3)_2$	[5,6]-open, [6,6]-open	2	[62]
	$\text{Lu}_3\text{N}@I_h(7)\text{-C}_{80}$	Diethyl bromomalonate, DBU	$\text{Lu}_3\text{N}@C_{80}\text{CBr}(\text{CCOOCH}_2\text{CH}_3)_2$	[6,6]-open	1	[62]
	$\text{Th}@C_{3v}(8)\text{-C}_{82}$	2-adamantane-2,3,0-[3H]-diazirine(AdN ₂)	Th@C ₈₂ Ad	[6,6]-open, et al.	3	[69]
Carbene addition	$\text{U}@C_{2v}(9)\text{-C}_{82}$	2-adamantane-2,3,0-[3H]-diazirine(AdN ₂)	U@C ₈₂ Ad	[6,6]-open, et al.	4	[69]
	$\text{Dy}_2\text{TiC}@I_h\text{-C}_{80}$	2-adamantane-2,3,0-[3H]-diazirine(AdN ₂)	Dy ₂ TiC@C ₈₀ -Ad	[6,6]-open	1	[70]

Table 1. Cont.

Reaction	Endohedral Metallofullerene	Reactants	Product	Addition Position	Number of Isomers	Ref.
Radical addition reaction	$\text{Ln}_2\text{@C}_{80}$ ($\text{Ln}_2 = \text{Y}_2, \text{Gd}_2, \text{Tb}_2, \text{Dy}_2, \text{Ho}_2, \text{Er}_2, \text{TbY}, \text{TbGd}$)	BrCH_2Ph	$\text{Ln}_2\text{@C}_{80}(\text{CH}_2\text{Ph})$	[5,6,6]	1	[74]
	$\text{Dy@C}_{2v}(5)\text{-C}_{80}$	BrCH_2Ph	$\text{Dy@C}_{80}(\text{CH}_2\text{Ph})$	[5,6,6]	1	[75]
	Er@C_{72}	1,2,4-trichlorobenzene	$\text{Er@C}_{72}(\text{C}_6\text{H}_3\text{Cl}_2)$	Unknown	1	[76]
	Er@C_{76}	Iodobenzene	$\text{Er@C}_{76}(\text{C}_6\text{H}_5)$	Unknown	1	[76]
	Er@C_{82}	AgCOOCF_3	$\text{Er@C}_{76}(\text{CF}_3)_5$	Unknown	1	[76]
Electrophilic trifluoromethylation	$\text{Y@C}_{2v}(9)\text{-C}_{82}$	AgCOOCF_3	$\text{Er@C}_{82}(\text{CF}_3)_3$	Unknown	1	[76]
	$\text{Tb}_2\text{@C}_{80}^-$	N-arylbezamide	$\text{Y@C}_{82}\text{NPhCNPh}$	[5,6]	3	[77]
	$\text{Y}_2\text{@C}_{80}^-$	Umemoto reagent II	$\text{Tb}_2\text{@C}_{80}(\text{CF}_3)$	[5,6,6]	1	[78]
	$\text{Y@C}_{2v}(9)\text{-C}_{82}$	Umemoto reagent II	$\text{Tb}_2\text{@C}_{80}(\text{CF}_3)$	[5,6,6]	1	[78]
	$\text{Eu@C}_2(5)\text{-C}_{82}$	$\text{Re}_2(\text{CO})_{10}$	$\text{Re}(\text{CO})_5\text{-}\eta^1\text{-Y@C}_{2v}(9)\text{-C}_{82}$	[5,6,6]	1	[80]
Coordination reaction	$\text{Eu@C}_2(13)\text{-C}_{84}$	$\text{W}(\text{CO})_4(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)$	$\text{Eu@C}_{82}\text{W}(\text{CO})_3(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)$	$\eta^2\text{-}[6,6]\text{-bond}$	1	[81]
	$\text{Sc}_3\text{N@I}_h\text{-C}_{80}$	$\text{TBAOH}, \text{CH}_3\text{OH}$	$\text{Sc}_3\text{N@C}_{80}(\text{OCH}_3)_2$	$\eta^2\text{-}[6,6]\text{-bond}$	1	[81]
Methoxide reaction				[1,2], [1,4]	2	[82]

Table 1. Cont.

Reaction	Endohedral Metallofullerene	Reactants	Product	Addition Position	Number of Isomers	Ref.
Multicomponent reactions	Sc ₃ N@I _h -C ₈₀	3,6-di(pyridin-2-yl)-1,2,4,5-tetrazines, water, and oxygen	Sc ₃ N@C ₈₀ CN=NCO(C ₅ NH ₄) ₂	[5,6]-closed	1	[83]
		3,6-bis(6-methylpyridin-2-yl)-1,2,4,5-tetrazine, water, and oxygen	Sc ₃ N@C ₈₀ CN=NCO(C ₅ NCH ₃) ₂	[5,6]-closed	1	[83]
	Lu ₃ N@I _h -C ₈₀	tBuNC and EWG-bearing terminal alkynes	Lu ₃ N@C ₈₀ CCR ¹ CONHtBuCOR ²	[6,6]-open	1	[85]
		tBuNC and dimethyl acetylenedicarboxylate (DMAD)	Lu ₃ N@C ₈₀ C(COOMe)C(COOMe)CNtBu	[6,6]-open	1	[85]
Difluoromethylenation reaction	Sc ₃ N@I _h -C ₈₀	CF ₂ ClCOONa	Sc ₃ N@C ₈₀ (CF ₂)	[6,6]-open	1	[86]
	Sc ₃ N@C ₇₈	CF ₂ ClCOONa	Sc ₃ N@C ₇₈ (CF ₂)	[6,6]	1	[87]

Unexpected formation of metallofulleroids with [6,6]-open structure from the isocyanide-based multicomponent reactions of an isocyanide (e.g., *t*BuNC), various alkynes, and $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ have been reported recently [85]. A major product was obtained by using EWG (electron-withdrawing group)-bearing terminal alkynes, whereas no products were obtained by using disubstituted internal alkynes [85]; see Figure 10a. Notably, when $\text{Lu}_3\text{N}@I_h\text{-C}_{80}$ was replaced by C_{60} , there were no isolated products under any conditions [85]. Surprisingly, unlike internal alkynes, dimethyl acetylenedicarboxylate (DMAD) yielded a ketenimine metallofulleroid **45**, as shown in Figure 10b, while the addition pattern is greatly different from that of C_{60} reacting with the same reactants [85]. Strikingly, a variable temperature single-crystal study of metallofulleroid **46** showed that the motion of the embedded cluster is significantly hindered by the close interaction with the exohedral organic appendant of a neighboring molecule [85]. Furthermore, DFT calculations suggested that the reaction mechanism involved three main steps including a barrierless anionic attack of the dipole, 3-exo-trig ring closure, and final hydration [85].

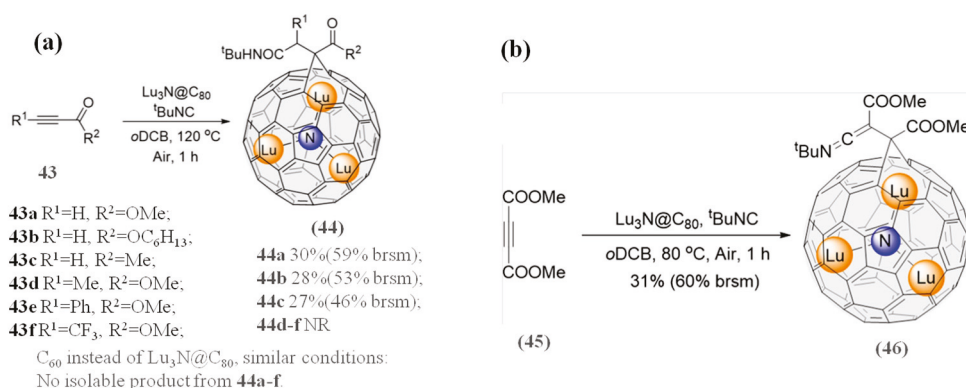


Figure 10. (a) Preparation of **44a–c** reacted from alkyl isocyanides and alkynes. Brsm = based on recovered starting material; NR = No reaction. (b) Synthesis of a ketenimine metallofulleroid **46**. Reproduced from Ref. [85] with permission. Copyright 2021 John Wiley and Sons.

2.10. Difluoromethylenation Reaction

Recently, difluoromethylenation of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$ reacting with $\text{CF}_2\text{ClCOONa}$ affords a sole C_s -symmetric $\text{Sc}_3\text{N}@C_{80}(\text{CF}_2)$ adduct [86]. Based on the ^{19}F , ^{13}C , and ^{45}Sc NMR spectroscopic, $\text{Sc}_3\text{N}@C_{80}(\text{CF}_2)$ was identified as the [6,6]-open structure with 2.2–2.3 Å between the bridgehead atoms, which is consistent with the DFT-optimized structure (see Figure 11) [86]. And the UV/vis spectra of $\text{Sc}_3\text{N}@C_{80}(\text{CF}_2)$ are similar to that of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$, thus indicating the [6,6]-open structure with weakly perturbed π -electron systems [86]. Furthermore, the electrochemical behavior of $\text{Sc}_3\text{N}@C_{80}(\text{CF}_2)$ resembles that of $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$, in which both the HOMO and LUMO level of $\text{Sc}_3\text{N}@C_{80}(\text{CF}_2)$ downshift 0.1 eV compared to the pristine $\text{Sc}_3\text{N}@I_h\text{-C}_{80}$, resulting in essentially unchanged HOMO–LUMO gap [86]. It is worth noting that in the experiment the absence of the [5,6]-conformer, the more energetically favorable one based on the theoretical analysis, suggests that the adduct is kinetical rather than thermodynamical [86]. In addition, the nucleophilic route, which involves nucleophilic addition of CF_2Cl^- anion followed by cyclopropanation via Cl^- displacement, is considered to be better than the route of [2 + 1]-cycloaddition of CF_2 carbene [86].

Very recently, the difluoromethylenation reaction was extended to $\text{Sc}_3\text{N}@C_{78}$ and it showed higher reactivity than $\text{Sc}_3\text{N}@C_{80}$, in which the reaction temperature is lower [87]. Mono-adduct $\text{Sc}_3\text{N}@C_{78}(\text{CF}_2)$ was identified by the mass spectrum, but, unfortunately, the $\text{Sc}_3\text{N}@C_{78}(\text{CF}_2)$ degraded rapidly, which was different from $\text{Sc}_3\text{N}@C_{80}(\text{CF}_2)$ and the CF_2 adducts of empty fullerenes [87]. And, only the UV-Vis spectrum of the $\text{Sc}_3\text{N}@C_{78}(\text{CF}_2)$ was recorded and showed high similarity with the spectra of the Bingel–Hirsch mono-adduct and that of the major Prato mono-adduct, indicating that $\text{Sc}_3\text{N}@C_{78}(\text{CF}_2)$ has the same bond type, bond 66-6 [87]. Moreover, DFT results suggested that the open [6,6]- $\text{Sc}_3\text{N}@C_{78}(\text{CF}_2)$

is more stable and the regioselectivity is controlled kinetically as well as the CF_2 addition mechanism resembles that of $\text{Sc}_3\text{N@C}_{80}$ [87].

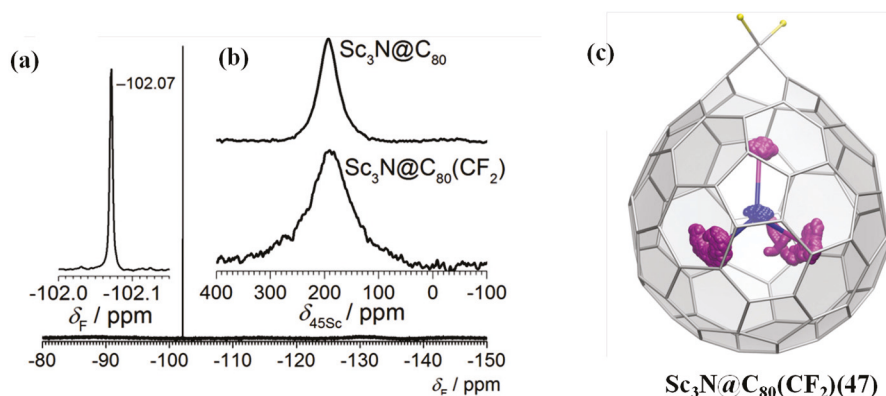


Figure 11. (a) ^{19}F NMR spectra of $\text{Sc}_3\text{N@C}_{80}(\text{CF}_2)$. (b) Room temperature ^{45}Sc NMR spectra of $\text{Sc}_3\text{N@I}_h\text{-C}_{80}$ (top) and $\text{Sc}_3\text{N@C}_{80}(\text{CF}_2)$ (bottom). (c) DFT molecular dynamics trajectories for $\text{Sc}_3\text{N@C}_{80}(\text{CF}_2)$ (100 ps), C atoms are magenta, and N is blue. Reproduced from Ref. [86] with permission from the Royal Society of Chemistry.

3. Conclusions and Outlook

In summary, EMFs exhibit active reactivities toward versatile functionalization reactions, which confer EMFs tunable properties. Prato reaction was extended to EMFs with low symmetry, such as $\text{Sc}_3\text{N@C}_{78}$ and $\text{Y}_2\text{@C}_{3v}(8)\text{-C}_{82}$; furthermore, the complicated bis-adducts and multi-adducts of Prato reaction were studied as well. Metal encapsulation induces a highly regioselective Bingel–Hirsch adducts of $\text{Y@C}_s(6)\text{-C}_{82}$ achieved and a new cationic metallofullerene route was put forward for Bingel–Hirsch reaction. Carbene additions of actinide EMFs and Ti-based EMFs were developed. A new non-cycloaddition of EMFs, methoxide reaction, was exploited. Furthermore, new complicated multi-component reactions instead of simple transplantation from empty fullerenes arise and acquire unexpected adducts, expanding new horizons in the functionalization of EMFs. Especially, besides radical reactions, new electrophilic trifluoromethylation was exploited to stabilize the missing EMFs.

High regioselectivity is frequently observed for EMFs due to strong metal–cage interactions. The endohedral cluster plays an important role in determining the regioselectivity and addition pattern. Furthermore, combined with calculated results, the regioselectivity of the reactions was plausibly interpreted by POAV, HOMOs/LUMOs, and charges. However, new credible, advanced, and reasonable theoretical calculation schemes are also expected. In turn, the addition groups affect the location, motion, orientation, and electronic state of the encapsulated clusters. As a result, the ultimate structures and properties of the derivatives of EMFs are together regulated by the intramolecular interplay of the cluster, carbon cage, and exohedral groups.

Recent functionalization reactions are mainly restricted to exploring the inherent chemical activities of EMFs or stabilizing EMFs. However, using reaction groups to modulate the magnetic, luminescence, or photovoltaic properties of EMFs is rarely reported. And it is not much clear whether and how the type or amount of reaction groups affects those properties of EMFs. Therefore, more efforts are needed to reveal the relationships between the reaction groups and those properties of EMFs and make metallofullerenes truly applicable materials. Functionalizations of EMFs are an attractive and popular area of fullerene research, which still holds great promise.

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