

Article

Physical Mechanisms of Linear and Nonlinear Optical Responses in Ferrocene-Embedded Cycloparaphenylenes

Gang Zhang , Qianqian Wang, Yi Zou *, Ying Jin * and Jingang Wang * 

College of Science, Liaoning Petrochemical University, Fushun 113001, China; zhanggang0308@163.com (G.Z.); wangqian9802@163.com (Q.W.)

* Correspondence: happylele1989@126.com (Y.Z.); jinying@lnpu.edu.cn (Y.J.); jingang_wang@lnpu.edu.cn (J.W.)

Abstract

This study employs molecular orbital (MO) analysis, density of states (DOS) analysis, and advanced techniques such as charge density difference (CDD), transition density matrix (TDM), transition electric dipole moment density (TEDM), and transition magnetic dipole moment density (TMDM) to systematically investigate the electronic structure characteristics of Fc-[8]CPP and Fc-[11]CPP. Using density functional theory (DFT) and time-dependent DFT (TD-DFT), the π -electron delocalization properties and optical behaviors of these molecules were analyzed. Furthermore, their responses to external electromagnetic fields were explored through electronic circular dichroism (ECD) and Raman spectroscopy, comparing chiral optical responses and electron–vibration coupling effects to elucidate their photophysical properties. The results reveal that the HOMO-LUMO energy gaps of Fc-[8]CPP and Fc-[11]CPP are 5.81 eV and 5.95 eV, respectively, with a slight increase as ring size grows; Fc-[8]CPP exhibits a stronger chiral response, while Fc-[11]CPP shows reduced chirality due to enhanced symmetry. Finally, TD-DFT calculations demonstrate that their optical absorption is dominated by localized excitations with partial charge transfer contributions. These findings provide a theoretical foundation for designing conjugated macrocyclic materials with superior optoelectronic performance.

Keywords: ferrocene-embedded conjugated macrocycles; cycloparaphenylenes (CPPs); electronic structure; chiral response; photophysical properties



Academic Editor: Valentine Vullev

Received: 26 June 2025

Revised: 18 August 2025

Accepted: 20 August 2025

Published: 25 August 2025

Citation: Zhang, G.; Wang, Q.; Zou, Y.; Jin, Y.; Wang, J. Physical Mechanisms of Linear and Nonlinear Optical Responses in Ferrocene-Embedded Cycloparaphenylenes. *Chemistry* **2025**, *7*, 136. <https://doi.org/10.3390/chemistry7050136>

Correction Statement: This article has been republished with a minor change. The change does not affect the scientific content of the article and further details are available within the backmatter of the website version of this article.

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Cycloparaphenylenes (CPPs) are a class of macrocyclic compounds featuring a cyclic π -conjugated structure, which have garnered significant attention in materials science due to their unique molecular nanorings and exceptional electronic and optical properties [1–3]. The radial π -conjugation system of CPPs endows them with remarkable charge transport capabilities and pronounced optical responsiveness, rendering them highly promising for applications in organic electronics, host–guest chemistry, and as discrete building blocks for structurally uniform carbon nanotubes [4–6]. Their distinctive toroidal topology not only provides a stable π -electron framework but also imparts significant potential for molecular recognition and supramolecular chemistry [7]. Recent advancements in synthetic methodologies have markedly enhanced the preparation of CPPs, enabling the synthesis of homologues ranging from the smallest [5] CPP to larger, topologically complex structures [8–10]. Novel synthetic strategies, such as transition-metal-catalyzed cyclization and template-directed synthesis, have significantly improved yields and structural diversity [11]. These developments have facilitated systematic investigations into the

size-dependent electronic structures, optical transitions, and intermolecular interactions of CPPs, laying a robust foundation for the design of functional materials [12–14].

Building on the unique architecture of CPPs, researchers have developed a variety of functionalized CPP derivatives, significantly expanding their structural versatility and application scope [15–17]. For instance, nitrogen-heterocycle-doped CPPs (e.g., pyridine-, pyrazine-, or carbazole-doped CPPs) enhance electron-accepting properties and molecular recognition capabilities through heteroatom incorporation, making them suitable for high-efficiency molecular sensing, catalysis, and supramolecular assembly [18,19]. Sulfur-doped CPPs (e.g., thiophene- or benzothiophene-substituted CPPs) exhibit superior photoluminescence and electrochemical stability, showing great promise for organic light-emitting diodes (OLEDs), photoelectrochemical devices, and photocatalysis [20–22]. Alkyl-chain-functionalized CPPs, by modulating intermolecular π - π stacking and solubility, optimize performance in organic thin-film transistors and flexible electronic devices [23,24]. Additionally, CPPs functionalized with aromatic substituents (e.g., naphthalene, anthracene, or pyrene units) enhance light absorption and fluorescence emission through extended conjugation, making them ideal for optoelectronic devices and energy transfer studies [25–27]. Other functionalization strategies, such as the incorporation of electron-donating or electron-withdrawing groups, further tune the electronic structure and photophysical properties, offering diverse options for tailored functional materials [28–31]. These functionalized CPP derivatives not only retain the intrinsic π -conjugation of pristine CPPs but also achieve specific optoelectronic, catalytic, or molecular recognition functionalities through structural modifications, providing a versatile platform for next-generation functional nanomaterials.

In this context, Lingyun Zhu and coworkers successfully synthesized a novel hybrid macrocyclic compound, Fc-[n]CPP, by incorporating ferrocene (Fc) units into the CPP framework [32]. Fc, a prototypical organometallic compound with excellent chemical stability and reversible redox behavior, is widely utilized in catalysis, sensing, and molecular electronics [33–38]. Employing an efficient “one-step, two-component burst synthesis” approach, Zhu et al. prepared Fc-[n]CPP macrocycles (e.g., Fc-[8]CPP and Fc-[11]CPP with reference to the structure in Supplementary Information Figure S1), which combine the redox properties of Fc with the π -conjugated system of CPPs, exhibiting multi-responsive luminescence and electrochemically tunable properties [32,39]. The size-dependent electronic structures and optical responses of these macrocycles make them highly promising for applications in molecular electronics, photonics, and enantioselective sensing [40–42]. Using density functional theory (DFT) and time-dependent DFT (TD-DFT), we conducted a comprehensive analysis of the ground and excited states, as well as the optical properties of Fc-[8]CPP and Fc-[11]CPP, providing a theoretical framework for the development of next-generation functional nanosystems.

2. Materials and Methods

All quantum-chemical computations were carried out with the Gaussian 16 (Rev. A.03) program package; molecular models were constructed and visualized using GaussView 6.0.16 [43,44]. Ground-state geometries were optimized at the B3LYP [45] level of theory employing a mixed basis set: 6-31G(d) for C and H atoms, and the MDF10 Stuttgart–Dresden effective-core-potential basis set for the Fe center. We employed the B3LYP functional with D3 dispersion correction (B3LYP-D3) to optimize the structure of ferrocene-embedded conjugated macrocycles [46]. B3LYP-D3 accurately describes the molecular geometry of ferrocene-containing and conjugated systems, with dispersion correction effectively accounting for weak interactions, making it suitable for this study [32]. This method balances computational efficiency and accuracy. Harmonic frequency analyses confirmed

that all optimized geometries correspond to true minima on the potential-energy surface, exhibiting no imaginary frequencies. Excited-state properties were computed by means of time-dependent density-functional theory (TD-DFT) using the CAM-B3LYP functional together with the identical mixed basis set [47]; this combination provides an accurate description of long-range electronic interactions inherent to conjugated macrocycles. The CAM-B3LYP functional was employed to strike an optimal balance between computational cost and accuracy for the electronically and structurally intricate Fc-[n]CPP systems. Wave-function analyses were performed with Multiwfn 3.8 [48] to generate natural-bond-orbital (NBO) [49] populations, CDD maps, TEDM distributions, and TMDM distributions; three-dimensional visualizations were rendered with VMD 1.9.3 [50]. Total and projected density-of-states (TDOS and PDOS) curves, UV-visible (UV-Vis) spectra, TDM [51], ECD spectra [52,53], as well as Raman and resonance-Raman profiles were plotted using Origin 2024b. Vibrational modes were characterized on the basis of harmonic frequencies obtained at the same B3LYP/mixed-basis level and visualized with GaussView [54]. All calculations were conducted under vacuum conditions to isolate intrinsic molecular properties.

3. Results

3.1. Electronic Structure

This study focuses on two ferrocene-embedded conjugated macrocycles of different sizes, Fc-[8]CPP and Fc-[11]CPP (as shown in Figure 1). From the figure, the inner diameters of Fc-[8]CPP and Fc-[11]CPP can be observed to be 3.566437 Å and 5.653819 Å, respectively.

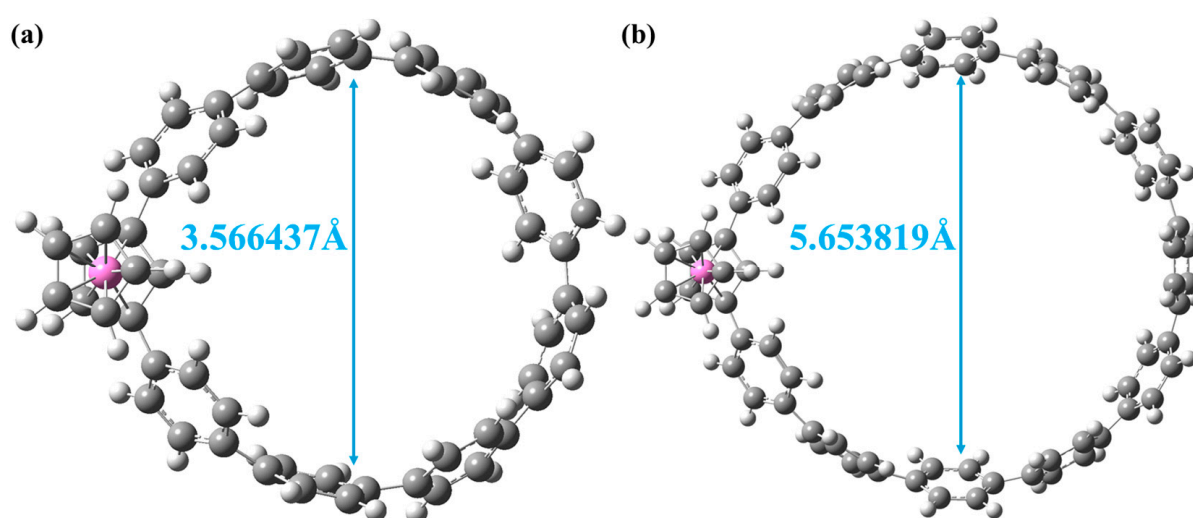


Figure 1. Three-dimensional structural schematic of Fc-[8]CPP (a) and Fc-[11]CPP (b). Gray represents carbon atoms, white represents hydrogen atoms, and purple represents +2 valence iron.

3.2. HOMO and LUMO Analysis

Figure 2 presents the calculated energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for Fc-[8]CPP and Fc-[11]CPP, along with their corresponding HOMO-LUMO energy gaps. Accordingly, the HOMO and LUMO energies of Fc-[8]CPP are −6.32 eV and −0.51 eV, respectively, with a HOMO-LUMO energy gap of 5.81 eV. In contrast, the HOMO and LUMO energies of Fc-[11]CPP are −6.44 eV and −0.46 eV, respectively, with an energy gap of 5.95 eV. The HOMO-LUMO gap in Fc-[n]CPP macrocycles widens with increasing ring size, rising from 5.81 eV in Fc-[8]CPP to 5.95 eV in Fc-[11]CPP. This inversion stems from the electron-donating character of the ferrocenyl (Fc) moiety. In the smaller Fc-[8]CPP, strong d- π coupling between the Fe d orbitals and the CPP π manifold destabilizes the HOMO, whereas in the

larger Fc-[11]CPP the extended π -conjugation preferentially lowers the LUMO, leading to an enlarged gap. A larger HOMO-LUMO gap increases the energy required for electronic transitions from HOMO to LUMO; therefore, the transition of Fc-[11]CPP is more difficult to occur than that of Fc-[8]CPP.

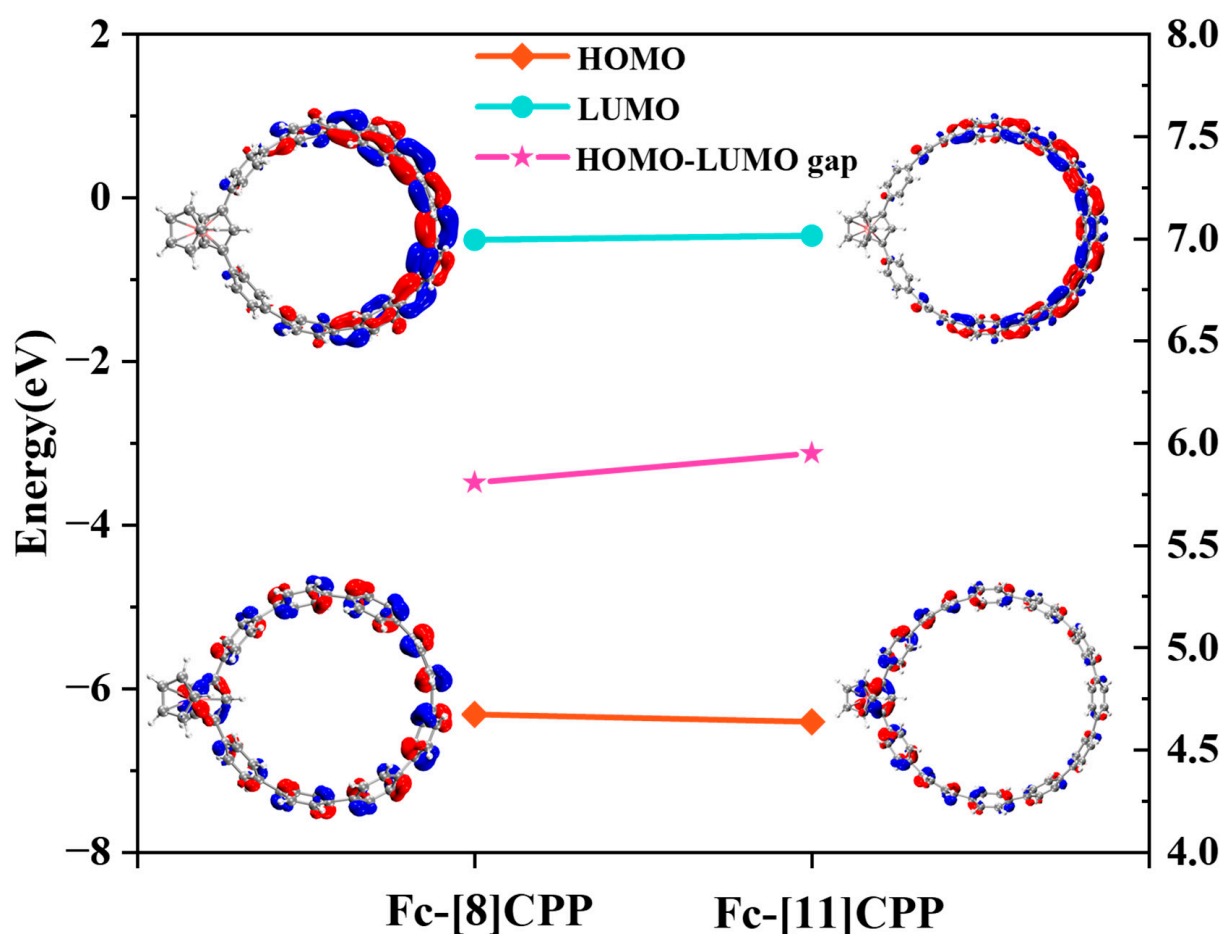


Figure 2. HOMO and LUMO energies, along with the HOMO-LUMO gap, for Fc-[8]CPP and Fc-[11]CPP.

3.3. MO and DOS Analyses

MO character analysis reveals that both Fc-[8]CPP and Fc-[11]CPP possess three distinct classes of valence-occupied orbitals: radial π_{in} -MOs, peripheral π_{out} -MOs, and σ -type MOs. Figure 3 presents the cumulative contributions of all occupied MOs to the total density of states (TDOS) together with the partial density of states (PDOS) arising from selected frontier orbitals for each system. For Fc-[8]CPP (Figure 3a), the low-energy region below -10 eV exhibits mixed contributions from σ -MOs, π_{in} -MOs, and π_{out} -MOs. Between -10 eV and -4.4 eV, the DOS is dominated by the joint contribution of π_{in} -MOs and π_{out} -MOs, while the energy window from -0.5 eV to 4.2 eV corresponds to formally unoccupied (virtual) orbitals. In Fc-[11]CPP (Figure 3b), the lowest-lying states are almost exclusively σ -MOs. The energy span from -14.2 eV to -3.1 eV is characterized by overlapping contributions of π_{in} -MOs and π_{out} -MOs. Analogous to Fc-[8]CPP, the region extending from -0.5 eV to 4.2 eV remains unoccupied.

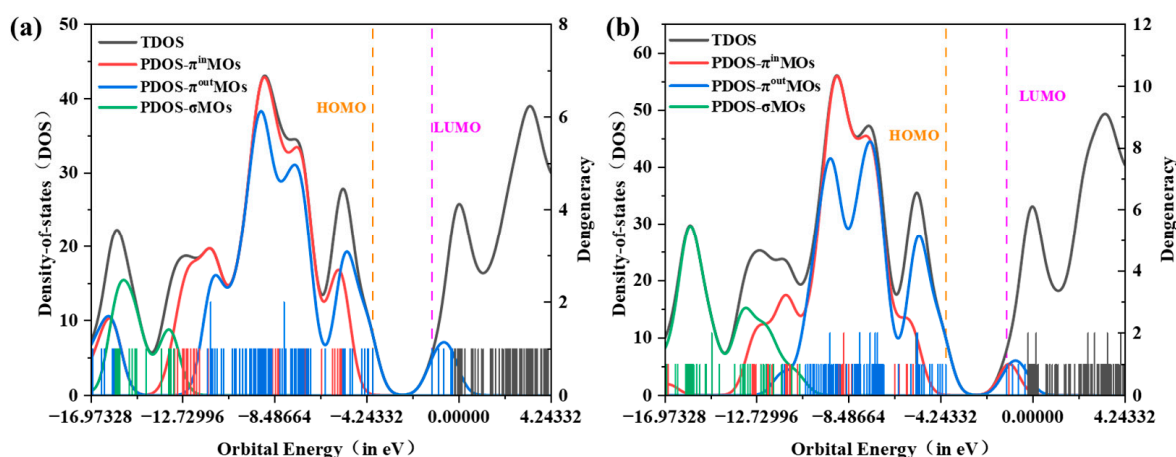


Figure 3. (a) PDOS and TDOS profiles of Fc-[8]CPP; (b) PDOS and TDOS profiles of Fc-[11]CPP.

3.4. Natural Bond Orbital (NBO) Analysis

To elucidate the electronic interactions in Fc-[8]CPP and Fc-[11]CPP, natural bond orbital (NBO, Figure 4) analyses were performed, focusing on the Fe–Cp bond and the C–C bonds within the CPP macrocycles. In Fc-[8]CPP the Fe $d(xz)$ and $d(yz)$ orbitals accept electron density from the Cp π orbitals. The C–C bonds of the [8]CPP ring display moderate π -type interactions, consistent with the limited conjugation imposed by the small ring size. By contrast, the Fe–Cp interaction in Fc-[11]CPP is slightly attenuated owing to diminished electronic overlap between the ferrocenyl unit and the expanded macrocycle. Concurrently, the C–C π interactions are markedly enhanced, reflecting both extended π -conjugation and increased planarity. These electronic disparities manifest spectroscopically the lowest-energy absorption band shifts from 340 nm in Fc-[8]CPP to 350 nm in Fc-[11]CPP, corroborating the UV–visible data and underscoring the role of extended π -conjugation in narrowing the HOMO–LUMO gap.

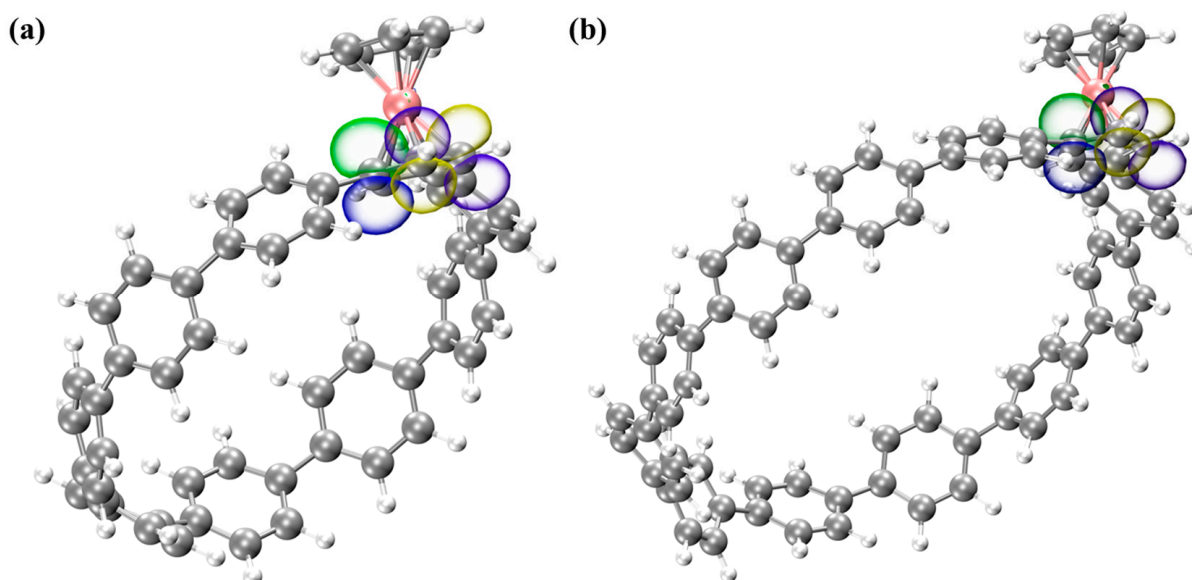


Figure 4. (a,b) Donor and acceptor orbitals arising from second-order perturbative interaction analyses for (a) Fc-[8]CPP and (b) Fc-[11]CPP, computed at the B3LYP level with a mixed basis set (6-31G(d) for C and H, MDF10 for Fe) under vacuum conditions. Regions of positive phase are rendered in green–yellow, while negative phase regions are shown in blue–purple.

3.5. OPA and TPA Analyses of Fc-[8]CPP and Fc-[11]CPP

3.5.1. OPA Analyses

To assess the photostability of the electronically excited states, the S_1 geometries of Fc-[8]CPP and Fc-[11]CPP were fully optimized at the TD-DFT level employing the CAM-B3LYP functional in conjunction with the mixed basis set 6-31G(d) for C and H and the MDF10 effective-core-potential basis set for Fe. Relative to their respective ground-state structures, the S_1 geometries exhibit only minor distortions, with all bond-length deviations remaining below 0.05 Å and no discernible structural reorganization, thus confirming the robust stability of the photoexcited states. This study systematically analyzes the OPA spectra of Fc-[8]CPP and Fc-[11]CPP to elucidate the relationship between their electronic transition mechanisms and molecular structures. The OPA spectrum of Fc-[8]CPP (Figure 5a) exhibits three prominent absorption peaks in the 150–400 nm range, located at 347.77 nm, 306.30 nm, and 190.45 nm, corresponding to the excited states S_6 , S_8 , and S_{77} , respectively. In contrast, the spectrum of Fc-[11]CPP (Figure 5b) in the same range displays two main absorption peaks at 314.30 nm and 189.98 nm, corresponding to S_8 and S_{93} , with oscillator strengths of 3.6081 and 1.7844, respectively.

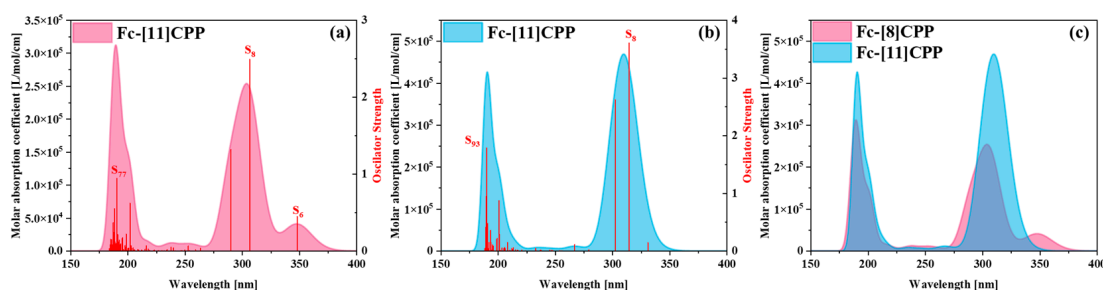


Figure 5. One-photon absorption spectra of Fc-[8]CPP and Fc-[11]CPP (a,b) and a combined one-photon absorption spectrum (c).

This study analyzes the electronic transition characteristics of Fc-[8]CPP during the one-photon absorption (OPA) process using CDD and TDM analyses (Figure 6). The OPA spectrum of Fc-[8]CPP is primarily dominated by the S_8 and S_{77} excited states. For the S_8 excited state (Figure 6a), the TDM shows transition density concentrated in the upper right corner of the diagonal, with minimal off-diagonal density. In the top view of the CDD, electrons (red) and holes (blue) are uniformly distributed along the carbon-carbon bonds of the CPP framework, with a small amount scattered in other regions, indicating a high overlap between electrons and holes characteristic of localized excitation. For the S_{77} excited state (Figure 6b), the TDM reveals that the transition density is primarily concentrated in the lower left corner of the diagonal, accompanied by a small amount of off-diagonal distribution. In the top view of the CDD, electrons and holes remain concentrated on the CPP framework, but their spatial separation is more pronounced, with electrons and holes distributed in different regions, indicating a charge transfer characteristic.

The OPA spectrum of Fc-[11]CPP is primarily dominated by the S_8 and S_{93} excited states. The TDM of S_8 (Figure 7a) shows a high concentration of transition density along the diagonal, with a minor amount of off-diagonal density. In the top view of the CDD, electrons and holes are uniformly distributed across the CPP framework without significant regional separation, confirming the localized excitation characteristic, consistent with the diagonal features of the TDM. The TDM of S_{93} (Figure 7b) reveals that the transition density is mainly concentrated along the diagonal with a relatively uniform distribution, while the CDD shows electrons and holes distributed in different parts of the CPP framework, indicating a charge transfer-dominated behavior.

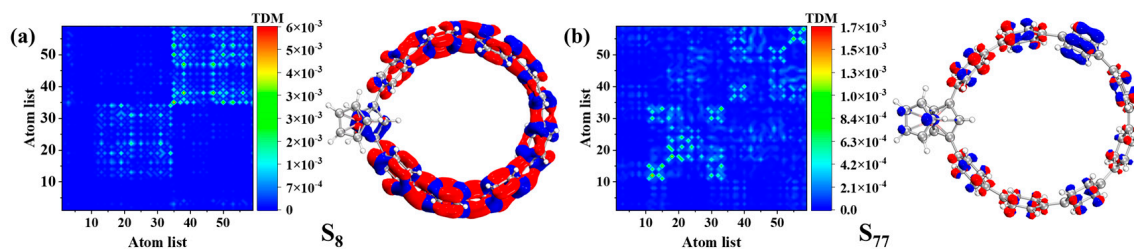


Figure 6. (a) TDM and CDD plots for Fc-[8]CPP in the 8th excited state; (b) TDM and CDD plots for Fc-[8]CPP in the 77th excited state. In the CDD plots, blue represents holes, red represents electrons, with an isosurface value of 0.0005.

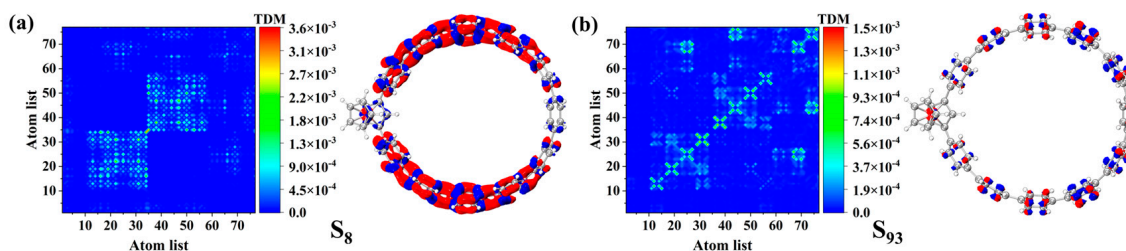


Figure 7. (a) TDM and CDD plots for Fc-[11]CPP in the 8th excited state; (b) TDM and CDD plots for Fc-[11]CPP in the 93rd excited state. In the CDD plots, blue represents holes, red represents electrons, with an isosurface value of 0.0005.

To further elucidate the electronic excitation character of Fc-[n]CPP macrocycles, we performed a comprehensive wave-function analysis and defined a set of transition indices. Sr(electrons and holes overlap index) larger values indicate stronger electron–hole overlap, characteristic of a local excitation. D(electron–hole distance, nm) smaller magnitudes denote more localized excitations. H(spatial extent of the electron–hole pair, nm). T(relative displacement between electron and hole centroids, nm) negative values are typically associated with locally confined excitations.

Table 1 lists the excited-state transition indices of Fc-[8]CPP and Fc-[11]CPP at their main absorption peaks.

$$(f = \frac{2}{3} \Delta E | \langle i | r | j \rangle |^2), \quad (1)$$

Table 1. Transition indices of the dominant excited states for Fc-[n]CPP near the main absorption peaks in the 150–200 nm range.

Molecule	Excited States	Oscillator Strength	Excited Energy (eV)	H(Å)	D(Å)	t (Å)	Sr
Fc-[8]CPP	S8	2.4957	4.048	6.191	0.223	−3.922	0.70482
Fc-[8]CPP	S77	0.9466	6.510	6.449	0.830	−3.607	0.27158
Fc-[11]CPP	S8	3.6081	3.945	8.216	0.060	−4.490	0.73501
Fc-[11]CPP	S93	1.7844	6.526	8.371	0.092	−5.180	0.34518

The oscillator strength increases with molecular size n, indicating enhanced absorption capacity with larger sizes.

$$(H_{\text{index}} = \frac{|\sigma_{\text{ele}}| + |\sigma_{\text{hole}}|}{2}), \quad (2)$$

The H index increases with n , reflecting a broader electron–hole distribution.

$$(D_{\text{index}} = \sqrt{D_X^2 + D_Y^2 + D_Z^2}), \quad (3)$$

$$(S_r = \int \sqrt{\rho^{\text{hole}}(r)} dr), \quad (4)$$

Analysis of the D index and S_r index shows that Fc-[8]CPP's S8 ($S_r = 0.70482$, $D = 0.223 \text{ \AA}$) and Fc-[11]CPP's S8 ($S_r = 0.73501$, $D = 0.060 \text{ \AA}$) exhibit high overlap and low separation, characteristic of localized excitation. In contrast, Fc-[8]CPP's S77 ($S_r = 0.27158$, $D = 0.830 \text{ \AA}$) and Fc-[11]CPP's S93 ($S_r = 0.34518$, $D = 0.092 \text{ \AA}$) are dominated by charge transfer.

$$(t_{\text{index}} = D_{\text{index}} - H_{\text{CT}}), \quad (5)$$

The t index values for Fc-[8]CPP and Fc-[11]CPP's S8 are $-3.922 \text{ \AA}$ and $-4.490 \text{ \AA}$, respectively, with large negative values confirming the dominance of localized excitation.

3.5.2. TPA Analyses

As shown in Figure 8a, the two-photon absorption (TPA) spectrum of Fc-[8]CPP exhibits three absorption peaks within the 300–800 nm range, located at 696.97 nm, 613.84 nm, and 418.22 nm, corresponding to the excited states S6, S8, and S46, respectively. The strong absorption peak S8 indicates that the molecule exhibits a significant nonlinear optical response at this wavelength. As shown in Figure 8b, the TPA spectrum of Fc-[11]CPP displays two absorption peaks within the 300–800 nm range, located at 629.88 nm and 424.50 nm, corresponding to the excited states S8 and S50, respectively. The strong absorption peak S8 suggests that this molecule also exhibits a notable nonlinear optical response at this wavelength.

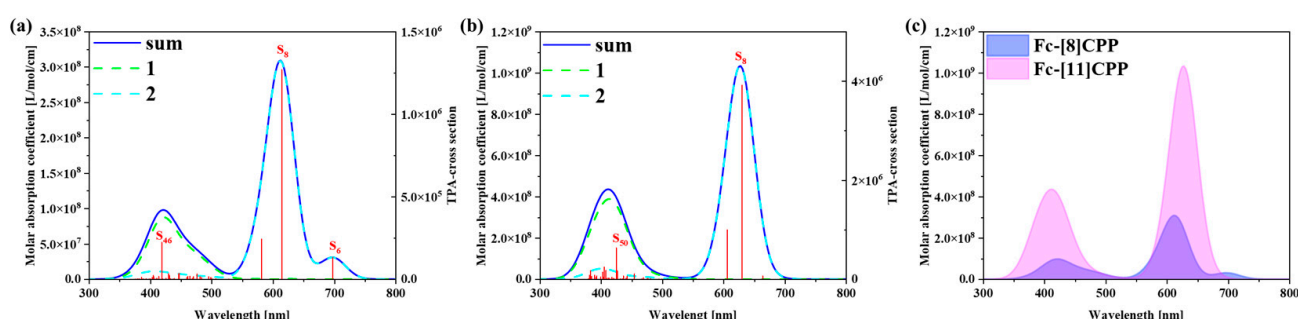


Figure 8. Two-photon absorption spectra of Fc-[8]CPP and Fc-[11]CPP (a,b) and a combined two-photon absorption spectrum (c).

Figure 9 illustrates the two-step TPA process of Fc-[8]CPP for the S6, S8, and S46 excited states, revealing electronic transition characteristics through the TDM and CDD. For the S6 excited state, the first step transition ($S_0 \rightarrow S_1$) shows transition density concentrated in the upper left and lower right, with the CDD indicating that electrons and holes are distributed across the five-membered rings of the Fc unit, exhibiting significant charge transfer from Fc to the CPP framework. The second step transition ($S_1 \rightarrow S_6$) features transition density distributed on both sides of the diagonal, with the CDD showing electrons and holes extending across the entire molecule, a pronounced electron–hole separation, and enhanced charge transfer. For the S8 excited state (maximum TPA cross-section), the first step transition ($S_0 \rightarrow S_6$) shows transition density primarily along the diagonal, with minor distribution in the upper left and lower right. The CDD indicates that electrons and holes are concentrated on the CPP ring, reflecting localized excitation characteristics. The second

step transition ($S_6 \rightarrow S_8$) has transition density focused along the diagonal, with the CDD showing electrons and holes confined to the CPP ring, exhibiting significant separation and characteristic of charge transfer excitation. For the S_{46} excited state, the first step transition ($S_0 \rightarrow S_8$) shows transition density concentrated in the upper right and lower left, with the CDD indicating that electrons and holes are distributed across the CPP ring, suggesting a mix of localized excitation and charge transfer. The second step transition ($S_8 \rightarrow S_{46}$) has transition density focused along the diagonal, with the CDD showing electrons and holes confined to the CPP ring, characteristic of charge transfer.

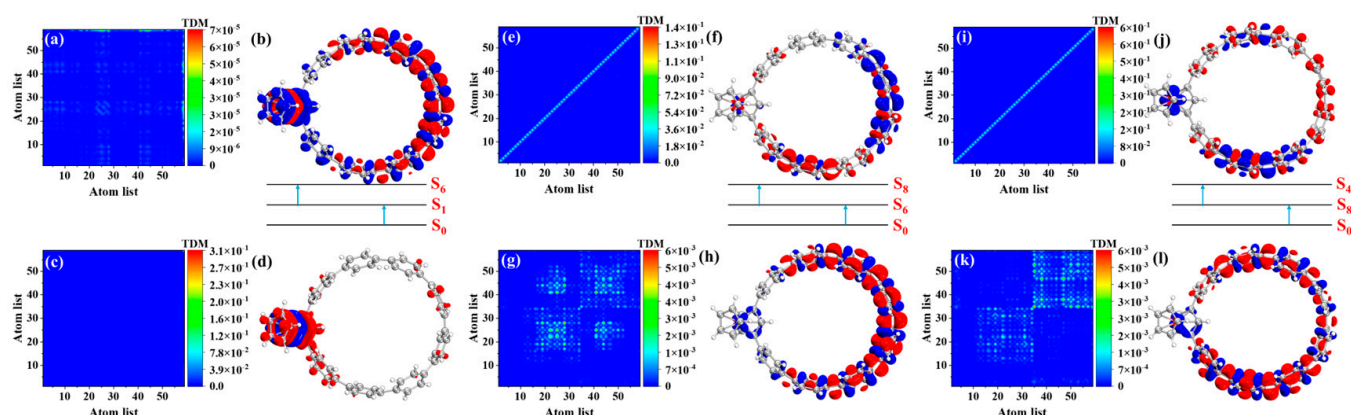


Figure 9. (a–f) Two-step TPA process of Fc-[8]CPP for the S_6 state, showing TDM and electron–hole pair density from the ground state to the intermediate state (c) and from the intermediate state to the final state (a) with electron–hole pair densities (b,d); two-step TPA process for the S_8 state, showing TDM and electron–hole pair density from the ground state to the intermediate state (g) and from the intermediate state to the final state (e) with electron–hole pair densities (h,f); two-step TPA process for the S_{46} state, showing TDM and electron–hole pair density from the ground state to the intermediate state (k) and from the intermediate state to the final state (i) with electron–hole pair densities (j,l). In the CDD plots, blue represents holes, red represents electrons, with an isosurface value of 0.0005.

Figure 10 illustrates the two-step TPA process of Fc-[11]CPP for the S_8 , S_{50} excited states, revealing electronic transition characteristics through the TDM and CDD. For the S_8 excited state (maximum TPA cross-section), the first step transition ($S_0 \rightarrow S_7$) shows transition density primarily along the diagonal, with minor distribution in the upper left and lower right, indicating dominant localized excitation with weak charge transfer. The CDD reveals that electrons and holes are concentrated on the CPP ring, confirming localized excitation as the primary mechanism with a minor charge transfer component. The second step transition ($S_7 \rightarrow S_8$) has transition density focused along the diagonal, with a small amount distributed in the upper left and lower right. The CDD shows electrons and holes distributed on the CPP ring phenyl units away from Fc, with significant separation, characteristic of charge transfer. For the S_{50} excited state, the first step transition ($S_0 \rightarrow S_8$) exhibits transition density primarily along the diagonal, with weaker distribution in the upper right and lower left. The CDD shows electrons and holes located on the upper and lower phenyl rings of the CPP ring, indicating a mix of localized excitation and charge transfer. The second step transition ($S_8 \rightarrow S_{50}$) has transition density concentrated along the diagonal, with the CDD revealing electrons and holes distributed in the CPP ring region away from Fc, where charge transfer diminishes, presenting pure localized excitation.

Table 2 reveals the transition dipole moments for each transition during two-photon excitation. The magnitude of the transition dipole moment is closely correlated with the intensity of the two-photon absorption cross-section.

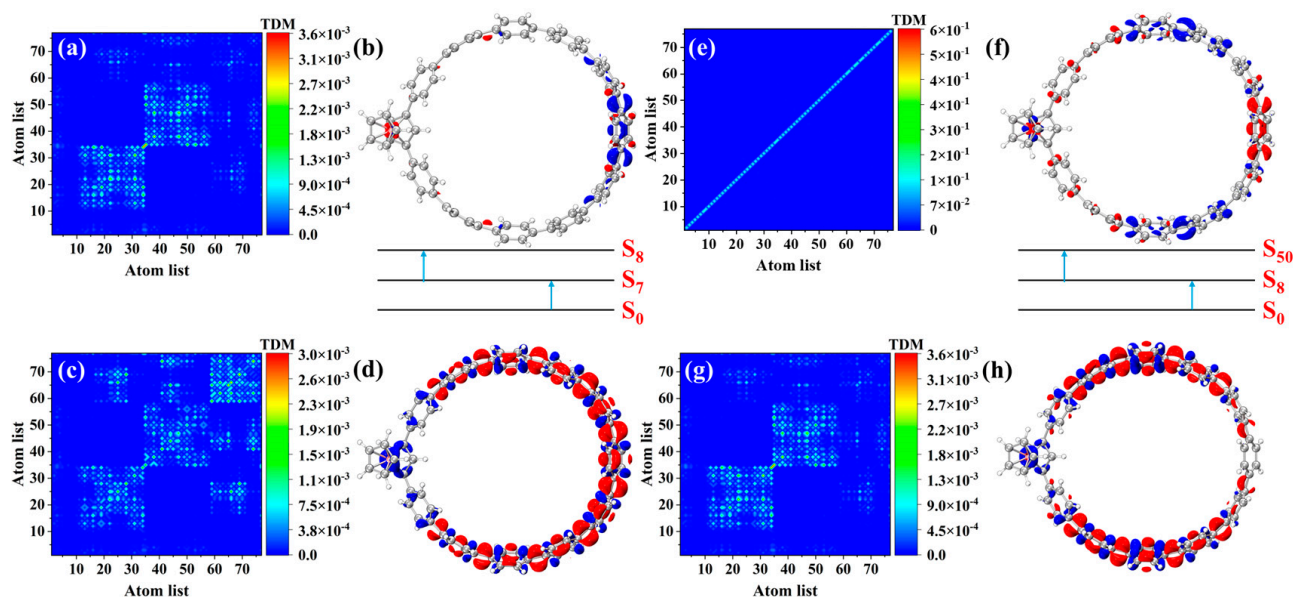


Figure 10. (a–h) Two-step TPA process of Fc-[11]CPP for the S8 state, showing TDM and electron-hole pair density from the ground state to the intermediate state (c) and from the intermediate state to the final state (a) with electron-hole pair densities (b,d); two-step TPA process for the S50 state, showing TDM and electron-hole pair density from the ground state to the intermediate state (g) and from the intermediate state to the final state (e) with electron-hole pair densities (h,f). In the CDD plots, blue represents holes, red represents electrons, with an isosurface value of 0.0005.

Table 2. Transition dipole moments and absorption cross-sections for the dominant two-photon absorption excited states of Fc-[n]CPP.

Molecule	State	Process	Integral Value (Debye)
Fc-[8]CPP	S6	$\langle \phi_{s0} \mu \phi_{s1} \rangle \times \langle \phi_{s1} \mu \phi_{s6} \rangle$	0.016×0.038
Fc-[8]CPP	S8	$\langle \phi_{s0} \mu \phi_{s6} \rangle \times \langle \phi_{s6} \mu \phi_{s8} \rangle$	4.473×139.474
Fc-[8]CPP	S46	$\langle \phi_{s0} \mu \phi_{s8} \rangle \times \langle \phi_{s8} \mu \phi_{s46} \rangle$	21.156×536.952
Fc-[11]CPP	S8	$\langle \phi_{s0} \mu \phi_{s7} \rangle \times \langle \phi_{s7} \mu \phi_{s8} \rangle$	1.492×0.299
Fc-[11]CPP	S50	$\langle \phi_{s0} \mu \phi_{s8} \rangle \times \langle \phi_{s8} \mu \phi_{s50} \rangle$	31.987×861.072

3.6. ECD Analysis of Fc-[8]CPP and Fc-[11]CPP

ECD is a crucial tool for studying the optical properties of chiral molecules, elucidating the relationship between molecular structure and light absorption [40,41]. In this study, the ECD spectra of Fc-[8]CPP and Fc-[11]CPP were calculated using time-dependent density functional theory (TD-DFT) (Figure 11), and their chirality mechanisms were analyzed by combining TEDM and TMDM. For Fc-[8]CPP (Figure 11a), the ECD spectrum in the 150–450 nm range exhibits four positive peaks and three negative peaks, with the spectral y-axis indicating a strong chiral response. For Fc-[11]CPP (Figure 11b), the spectrum in the 150–650 nm range shows five positive peaks and one negative peak, with the chiral signal on the y-axis significantly weakened. The comparison reveals that Fc-[8]CPP has a much stronger chiral intensity than Fc-[11]CPP, as the latter's higher symmetry leads to a reduced chiral response. To elucidate the chiral origin of the ECD spectra, TEDM and TMDM analyses were conducted for the excited states corresponding to the strongest positive and negative peaks.

To further investigate the ECD characteristics of Fc-[8]CPP, we calculated the TEDM and TMDM for the S67 excited state corresponding to the strongest positive absorption peak. Figure 12 shows that the TEDM in the X component is primarily distributed on the left and right sides of the molecule, while the Y component of TEDM is mainly distributed

on the upper and lower sides, with the positive and negative isosurfaces of both X and Y components being symmetrically distributed, and minimal TEDM distribution in the Z component. The distribution of TMDM is, to some extent, complementary to that of TEDM, with TMDM isosurfaces appearing in regions where TEDM isosurfaces are absent, reflecting the perpendicular relationship between electric and magnetic field directions in electromagnetic waves. The remaining TEDM and TMDM distributions are provided in the Supplementary Information, Figure S3 illustrates the distribution of TEDM and TMDM for the S₆₈ excited state, corresponding to the strongest negative absorption peak of Fc-[8]CPP, across different directions (in conjunction with Figure S3a–f). The TEDM in the X component is primarily distributed on the left and right sides of the molecule, while the Y component of TEDM is mainly distributed on the upper and lower sides, with the positive and negative isosurfaces of both X and Y components being symmetrically distributed, and minimal TEDM distribution in the Z component. The distribution of TMDM is, to some extent, complementary to that of TEDM, with TMDM isosurfaces appearing in regions where TEDM isosurfaces are absent. Figure S4 illustrates the distribution of TEDM and TMDM for the S₆₃ excited state, corresponding to the strongest positive absorption peak of Fc-[11]CPP, across different directions (in conjunction with Figure S4a–f). The TEDM in the X and Y components is primarily distributed on the upper and lower sides of the molecule, with the positive and negative isosurfaces being symmetrically distributed, and minimal TEDM distribution in the Z component. The distribution of TMDM is, to some extent, complementary to that of TEDM, with TMDM isosurfaces appearing in regions where TEDM isosurfaces are absent. Figure S5 illustrates the distribution of TEDM and TMDM for the S₆₄ excited state, corresponding to the strongest negative absorption peak of Fc-[11]CPP, across different directions (in conjunction with Figure S5a–f). The TEDM in the X component is primarily distributed on the left and right sides of the molecule, while the Y component of TEDM is mainly distributed on the upper and lower sides, with the positive and negative isosurfaces of the XY components being symmetrically distributed, and minimal TEDM distribution in the Z component. The distribution of TMDM is, to some extent, complementary to that of TEDM, with TMDM isosurfaces appearing in regions where TEDM isosurfaces are absent.

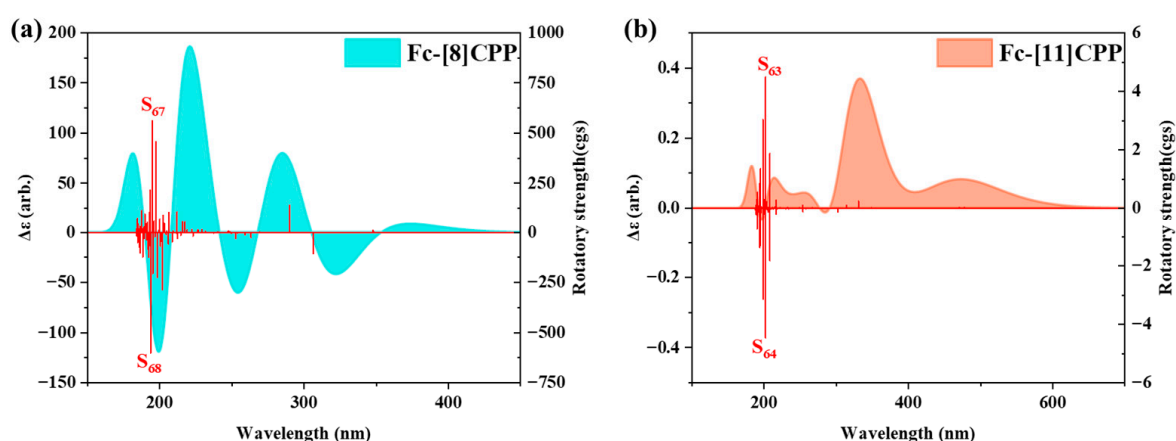


Figure 11. ECD spectra of Fc-[8]CPP and Fc-[11]CPP (a,b).

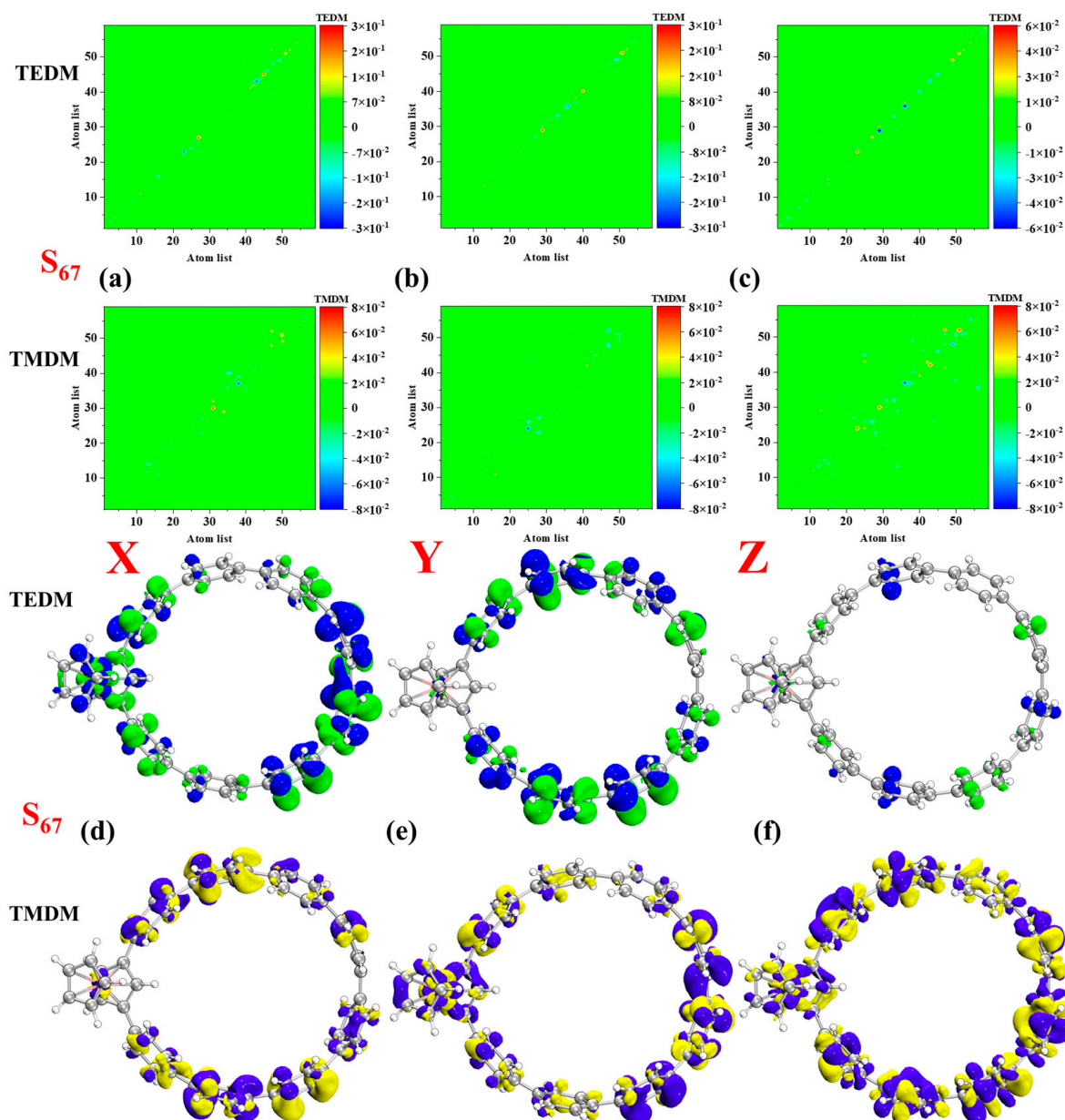


Figure 12. (a–f) Electric/magnetic dipole moment density matrices (top) and isosurface plots (bottom) for the S_{67} state of Fc-[8]CPP. In the TEDM plots, green represents positive values, blue represents negative values; in the TMDM plots, yellow represents positive values, purple represents negative values, with an isosurface value of 0.02.

3.7. Raman Spectra and Resonance Raman Spectra of Fc-[8]CPP and Fc-[11]CPP

Raman spectroscopy, which characterizes molecular vibrations and structural features by measuring the frequency shift of scattered light (Raman shift), is of significant value in molecular structure analysis. The ultraviolet-visible spectra of Fc-[8]CPP and Fc-[11]CPP exhibit prominent absorption peaks at 325 nm and 355 nm, respectively, located on the long-wavelength side of the absorption band, making them suitable for resonance Raman experiments. We employed 325 nm and 355 nm lasers to excite Fc-[8]CPP and Fc-[11]CPP, respectively, enhancing the vibrational mode signals coupled with electronic transitions, thereby increasing Raman intensity and reducing fluorescence background. Figure 13 presents the static and resonance Raman spectra of Fc-[8]CPP and Fc-[11]CPP. The static Raman spectrum of Fc-[8]CPP exhibits strong peaks concentrated in the 1500–1600 cm^{-1} range, with additional peaks appearing in the 750–1400 cm^{-1} region, and peak intensities

increase with molecular size. The resonance Raman spectrum shows strong peaks in the 700–1300 cm^{-1} range, with weaker peaks at 3000–3250 cm^{-1} . The peak positions in the resonance spectrum differ from those in the static spectrum, with intensities enhanced by approximately three orders of magnitude. The 325 nm laser for Fc-[8]CPP and the 355 nm laser for Fc-[11]CPP significantly enhance the Raman signals. To elucidate the assignment of characteristic peaks, we calculated the vibrational modes, and vector arrow diagrams reveal the direction and intensity of atomic vibrations, providing a microscopic basis for the spectral features (Figure 13).

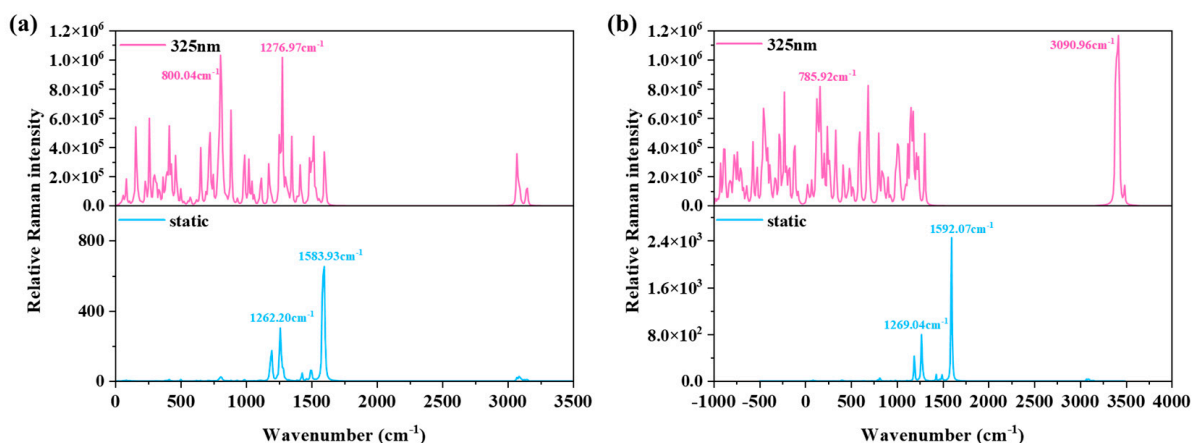


Figure 13. Raman and resonance Raman spectra of Fc-[8]CPP and Fc-[11]CPP (a,b).

The vibrational-mode diagrams for Fc-[8]CPP and Fc-[11]CPP are provided in the Supplementary Information, Figure S6 illustrates the vibrational modes of Fc-[8]CPP at different frequency bands. In the 325 nm resonance Raman spectrum, the vibrational mode at 800.04 cm^{-1} (Figure S6a) corresponds to the contraction of the central phenyl ring of the CPP and the vibrations of surrounding hydrogen atoms. The vibrational mode at 1276.97 cm^{-1} (Figure S6b) manifests as the transverse vibration of hydrogen atoms on the CPP ring and the vibrations of surrounding hydrogen atoms. In the Raman spectrum, the vibrational mode at 1262.20 cm^{-1} (Figure S6c) represents the vibrations of hydrogen atoms and the stretching vibrations of carbon atoms on the CPP ring. Similarly, the vibrational mode at 1583.93 cm^{-1} (Figure S6d) indicates the vibrations of hydrogen atoms and the stretching vibrations of carbon atoms on the CPP ring. Figure S7a,b displays the vibrational modes of Fc-[11]CPP across different frequency ranges. In the 355 nm resonance Raman spectrum, the vibrational mode of Fc-[11]CPP at 785.92 cm^{-1} (Figure S7a) is identified as the radial contraction vibration of the central phenyl ring of the CPP, accompanied by cooperative motion of the H atoms. This frequency exhibits a slight red shift compared to the lower frequency mode of Fc-[8]CPP at 800.04 cm^{-1} (Figure S6a), reflecting the influence of increased ring size. The 3060.96 cm^{-1} mode (Figure S7b) originates from the transverse C-H stretching vibration of H atoms, located in the high-frequency region. The 1269.04 cm^{-1} mode (Figure S7c) involves in-plane vibrations of H atoms and stretching vibrations of C atoms on the CPP ring, similar to the 1262.20 cm^{-1} mode of Fc-[8]CPP (Figure S6c). The 1592.07 cm^{-1} mode (Figure S7d) corresponds to H atom vibrations and C=C bond stretching vibrations of the CPP ring, with a slightly higher frequency than the 1583.93 cm^{-1} mode of Fc-[8]CPP (Figure S7d), indicating a fine-tuning effect due to ring size adjustment.

4. Discussion

This study systematically investigates the electronic structure and photophysical properties of Fc-[8]CPP and Fc-[11]CPP, employing a suite of analytical methods including

MO, DOS, NBO, CDD, TDM, TEDM, and TMDM analyses. MO and DOS analyses reveal partial overlap between the d-orbitals of the Fc unit and the π -system of the CPP ring, resulting in partial conjugation between Fc and CPP. NBO analysis reveals that Fc-[8]CPP exhibits stronger Fe-Cp interactions, leading to enhanced conjugation between the Fc unit and the CPP ring, while the C-C conjugation within the CPP ring remains moderate. In contrast, Fc-[11]CPP shows weaker Fe-Cp interactions due to its larger ring size, but the C-C conjugation within the CPP ring is significantly enhanced, resulting in a more pronounced conjugated structure in the CPP framework. This indicates that the smaller ring size of Fc-[8]CPP strengthens Fc-Cp-related conjugation, facilitating electronic transitions (Figure 3). The HOMO-LUMO energy gap increases with ring size, from 5.81 eV in Fc-[8]CPP to 5.95 eV in Fc-[11]CPP, reflecting the interplay between ring size and conjugation effects. Specifically, the HOMO of Fc-[8]CPP shows significant contributions from both the Fc unit and the CPP ring, indicating strong electronic coupling, whereas Fc-[11]CPP exhibits slightly reduced electronic coupling due to the larger ring size.

OPA and TPA analyses reveal that the primary transitions are localized excitations within the CPP framework, accompanied by weak charge transfer from Fc to CPP (Figures 5 and 8). The OPA peak of Fc-[11]CPP (314.3 nm) is red-shifted compared to that of Fc-[8]CPP (306.3 nm). Similarly, the TPA peak of Fc-[11]CPP (629.88 nm) is slightly red-shifted relative to Fc-[8]CPP (613.84 nm). The S8 state dominates both OPA and TPA processes due to its large transition dipole moment and significant electron-hole pair overlap (Table 1). Additionally, a deep ultraviolet absorption peak at ~190 nm (Figure 5) provides theoretical insights into high-energy excited states, although experimental UV-visible spectra are typically limited to wavelengths above 200 nm due to instrumental constraints. Computational results indicate that the primary OPA peak of [8]CPP is located at 304.78 nm, while that of [11]CPP is at 309.61 nm. The primary OPA peaks of Fc-[n]CPP (306.30 nm for Fc-[8]CPP and 314.30 nm for Fc-[11]CPP) exhibit a slight red-shift compared to their respective [n]CPP counterparts (Figure S8), attributed to the enhanced conjugation induced by the Fc unit. Compared to experimental results, the calculated OPA peak for Fc-[8]CPP is located at 347.77 nm, while the experimental primary absorption peak is approximately 340 nm, resulting in a difference of about 7 nm. For Fc-[11]CPP, the calculated primary OPA peak is at 341.3 nm, with the experimental primary absorption peak at approximately 340 nm. (Figure S11).

To further elucidate the photophysical properties of Fc-[n]CPP, this study compares their TPA and ECD characteristics with those of [n]CPP. The results show that the TPA cross-section of Fc-[n]CPP is higher than that of [n]CPP, indicating that the introduction of Fc enhances nonlinear optical efficiency (Figure S9). Notably, Fc-[8]CPP exhibits a stronger TPA response than Fc-[11]CPP (Figure 8). ECD spectra demonstrate that pristine [n]CPP exhibits a higher ECD cross-section than Fc-[n]CPP (Figure S10), indicating a stronger overall circular dichroism signal, likely due to its higher molecular symmetry. However, Fc-[8]CPP displays a significantly stronger chiral response than Fc-[11]CPP (Figure 8), as the Fc unit in the smaller ring induces greater disruption of molecular symmetry, leading to enhanced configurational distortion and amplified chiral signals. TEDM and TMDM analyses further clarify the electromagnetic interaction mechanisms underlying the chiral signals (Figures 12 and S3–S5).

Raman and resonance Raman spectroscopy analyses indicate that radial vibrations of the CPP ring and C-H bond motions are strongly coupled with electron-vibration interactions (Figures S6 and S7), providing critical insights into the relationship between molecular vibrations and optical properties.

5. Conclusions

In summary, a combined DFT/TD-DFT protocol was employed to elucidate the electronic structures, linear and nonlinear optical responses, and chiroptical characteristics of Fc-[8]CPP and Fc-[11]CPP. Partial d- π conjugation between the Fc moiety and the cycloparaphenylene (CPP) ring engenders a ring-size-dependent HOMO-LUMO gap that widens from 5.81 eV (Fc-[8]CPP) to 5.95 eV (Fc-[11]CPP), thereby modulating the associated electronic transitions. Natural bond orbital (NBO) analysis reveals that the more compact Fc-[8]CPP benefits from pronounced Fe-Cp interactions that enhance structural stability, whereas Fc-[11]CPP exhibits reinforced C-C π -delocalization, red-shifting the dominant absorption from 340 nm to 350 nm. Both OPA and TPA transitions are primarily localized on the CPP scaffold with a minor Fc $\rightarrow$ CPP charge-transfer component; the tighter geometry of Fc-[8]CPP confers a superior nonlinear optical response. ECD spectra further demonstrate that Fc-[8]CPP displays markedly stronger chiroptical signatures than Fc-[11]CPP, an effect ascribed to differential molecular symmetry. Resonance Raman profiles establish a clear correlation between CPP-ring vibrational modes and electron-vibration coupling. Collectively, these findings furnish a robust theoretical foundation for deploying Fc-[n]CPP scaffolds in nonlinear optical materials, enantioselective sensors, and molecular electronic devices. Future work may extend to coordination studies with alternative transition-metal centers and experimental validation of the predicted deep-UV absorption features, thereby broadening the utility of these macrocycles in functional nanomaterials.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemistry7050136/s1>, Figure S1: Optimized geometries of Fc-[8]CPP and Fc-[11]CPP; Figure S2: 3D structures of Fc-[8]CPP and Fc-[11]CPP; Figures S3–S5: TEDM and TMDM distributions of selected excited states; Figures S6 and S7: Vibrational modes of Fc-[8]CPP and Fc-[11]CPP; Figures S8 and S9: One- and two-photon absorption spectra; Figure S10: ECD spectra; Figure S11: UV-Vis spectra of Fc-[8]CPP and Fc-[11]CPP.

Author Contributions: Conceptualization, Y.Z. and Y.J.; methodology, J.W.; software, G.Z.; formal analysis, Y.Z.; investigation, Y.J.; resources, Y.Z.; data curation, Q.W.; writing—original draft preparation, G.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Basic Scientific Research Project of the Education Department of Liaoning Province, grant number JYTMS20231431 and JYTS20231432.

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding authors.

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

References

1. Segawa, Y.; Ito, H.; Itami, K. Structurally Uniform and Atomically Precise Carbon Nanostructures. *Nat. Rev. Mater.* **2016**, *1*, 15002. [CrossRef]
2. Lewis, S.E. Cycloparaphenylenes and Related Nanohoops. *Chem. Soc. Rev.* **2015**, *44*, 2221–2304. [CrossRef] [PubMed]
3. Jasti, R.; Bhattacharjee, J.; Neaton, J.B.; Bertozzi, C.R. Synthesis, Characterization, and Theory of [9]-, [12]-, and [18] Cycloparaphenylene: Carbon Nanohoop Structures. *J. Am. Chem. Soc.* **2008**, *130*, 17646–17647. [CrossRef]
4. Van Raden, J.M.; White, B.M.; Zakharov, L.N.; Jasti, R. Nanohoop Rotaxanes from Active Metal Template Syntheses and Their Potential in Sensing Applications. *Angew. Chem. Int. Ed.* **2019**, *58*, 7341–7345. [CrossRef]
5. Otteson, C.E.; Levinn, C.M.; Van Raden, J.M.; Pluth, M.D.; Jasti, R. Nanohoop Rotaxane Design to Enhance the Selectivity of Reaction-Based Probes: A Proof-of-Principle Study. *Org. Lett.* **2021**, *23*, 4608–4612. [CrossRef]
6. Hermann, M.; Wassy, D.; Esser, B. Conjugated Nanohoops Incorporating Donor, Acceptor, Hetero- or Polycyclic Aromatics. *Angew. Chem. Int. Ed. Engl.* **2021**, *60*, 15743–15766. [CrossRef]
7. Yamago, S.; Kayahara, E.; Iwamoto, T. Organoplatinum-Mediated Synthesis of Cyclic π -Conjugated Molecules: Towards a New Era of Three-Dimensional Aromatic Compounds. *Chem. Rec.* **2014**, *14*, 84–100. [CrossRef] [PubMed]

8. Darzi, E.R.; Jasti, R. The Dynamic, Size-Dependent Properties of [5]–[12] Cycloparaphenylenes. *Chem. Soc. Rev.* **2015**, *44*, 6401–6410. [[CrossRef](#)]
9. Zirakzadeh, A.; Herlein, A.; Groß, M.A.; Mereiter, K.; Wang, Y.; Weissensteiner, W. Halide-Mediated *Ortho*-Deprotonation Reactions Applied to the Synthesis of 1,2-and 1,3-Disubstituted Ferrocene Derivatives. *Organometallics* **2015**, *34*, 3820–3832. [[CrossRef](#)]
10. Kayahara, E.; Kouyama, T.; Kato, T.; Yamago, S. Synthesis and Characterization of [n] CPP (N = 5, 6, 8, 10, and 12) Radical Cation and Dications: Size-Dependent Absorption, Spin, and Charge Delocalization. *J. Am. Chem. Soc.* **2016**, *138*, 338–344. [[CrossRef](#)]
11. Zou, L.; Gao, Y.; Zhang, Q.; Ye, X.Y.; Xie, T.; Wang, L.W.; Ye, Y. Recent Progress in Asymmetric Domino Intramolecular Cyclization/Cascade Reactions of Substituted Olefins. *Chem. Asian J.* **2023**, *18*, e202300617. [[CrossRef](#)] [[PubMed](#)]
12. Xu, Y.; von Delius, M. The Supramolecular Chemistry of Strained Carbon Nanohoops. *Angew. Chem. Int. Ed.* **2020**, *59*, 559–573. [[CrossRef](#)] [[PubMed](#)]
13. Ren, Y.; Shang, W.; Sun, H.; Liang, Q.; Kayahara, E.; Yamago, S.; Li, Y.; Zhang, D. Synthesis of Octatrimethylsilyl-[8]cycloparaphenylene for Multifunctionalized Cycloparaphenylene. *J. Org. Chem.* **2025**, *90*, 8959–8965. [[CrossRef](#)] [[PubMed](#)]
14. Lovell, T.C.; Colwell, C.E.; Zakharov, L.N.; Jasti, R. Symmetry Breaking and the Turn-on Fluorescence of Small, Highly Strained Carbon Nanohoops. *Chem. Sci.* **2019**, *10*, 3786–3790. [[CrossRef](#)]
15. Zhang, H.; Lin, J. Syntheses and Properties of Heteroatom-Doped Conjugated Nanohoops. *Chin. J. Org. Chem.* **2022**, *42*, 3437–3455. [[CrossRef](#)]
16. Wu, D.; Cheng, W.; Ban, X.; Xia, J. Cycloparaphenylenes (CPPs): An Overview of Synthesis, Properties, and Potential Applications. *J. Org. Chem.* **2018**, *7*, 2161–2181. [[CrossRef](#)]
17. Wang, L.; Nogami, J.; Nagashima, Y.; Tanaka, K. Enantioselective Synthesis of Axially Chiral Figure-Eight Spirocycloparaphenylenes via Rh-Catalyzed Intermolecular [2 + 2 + 2] Cycloaddition. *Asian J. Org. Chem.* **2018**, *7*, 2161–2181.
18. Hines, D.A.; Darzi, E.R.; Hirst, E.S.; Jasti, R.; Kamat, P.V. Carbon Nanohoops: Excited Singlet and Triplet Behavior of Aza [8]CPP and 1,15-Diaza [8]CPP. *J. Phys. Chem. A* **2015**, *119*, 8083–8089. [[CrossRef](#)]
19. Brouillac, C.; McIntosh, N.; Heinrich, B.; Jeannin, O.; Sagazan, O.D.; Coulon, N.; Rault-Berthelot, J.; Cornil, J.; Jacques, E.; Quinton, C.; et al. Grafting Electron-Accepting Fragments on [4]cyclo-2,7-carbazole Scaffold: Tuning the Structural and Electronic Properties of Nanohoops. *Adv. Sci.* **2024**, *11*, 2309115. [[CrossRef](#)]
20. Kiciński, W.; Szala, M.; Bystrzejewski, M. Sulfur-doped porous carbons: Synthesis and applications. *Carbon* **2014**, *68*, 1–32. [[CrossRef](#)]
21. Ito, Y.; Cong, W.; Fujita, T.; Tang, Z.; Chen, M. High Catalytic Activity of Ni-trogen and Sulfur Co-Doped Nanoporous Graphene in the Hydrogen Evolution Reaction. *Angew. Chem. Int. Ed.* **2015**, *54*, 2131–2136. [[CrossRef](#)] [[PubMed](#)]
22. Van Raden, J.M.; Louie, S.; Zakharov, L.N.; Jasti, R. 2, 2'-Bipyridyl-Embedded Cycloparaphenylenes as a General Strategy to Investigate Nanohoop-Based Coordination Complexes. *J. Am. Chem. Soc.* **2017**, *139*, 2936–2939. [[CrossRef](#)] [[PubMed](#)]
23. Darzi, E.R.; Hirst, E.S.; Weber, C.D.; Zakharov, L.N.; Lonergan, M.C.; Jasti, R. Synthesis, Properties, and Design Principles of Donor–Acceptor Nanohoops. *ACS Cent. Sci.* **2015**, *1*, 335–342. [[CrossRef](#)]
24. Peters, G.M.; Grover, G.; Maust, R.L.; Colwell, C.E.; Bates, H.; Edgell, W.N.; Jasti, R.; Kertesz, M.; Tovar, J.D. Linear and Radial Conjugation in Extended π -Electron Systems. *J. Am. Chem. Soc.* **2020**, *142*, 2293–2300. [[CrossRef](#)]
25. Van Raden, J.M.; Louie, S.; Zakharov, L.N.; Jasti, R. Noncovalent Modification of Cycloparaphenylene by Catenane Formation Using an Active Metal Template Strategy. *Angew. Chem.* **2023**, *62*, e202310613.
26. Chen, M.; Unikela, K.S.; Ramalakshmi, R.; Li, B.; Darrigan, C.; Chrostowska, A.; Liu, S.Y. A BN-Doped Cycloparaphenylene Debuts. *Angew. Chem.* **2021**, *60*, 1556–1560. [[CrossRef](#)]
27. Lu, C.; Chen, P.; Sheng, H.; Li, C.; Wang, J. Physical Mechanism on Linear Spectrum and Nonlinear Spectrum in Double Helical Carbon Nanomolecule-Infinite. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2022**, *282*, 121674. [[CrossRef](#)]
28. Nakanishi, Y.; Omachi, H.; Matsuura, S.; Miyata, Y.; Kitaura, R.; Segawa, Y.; Itami, K.; Shinohara, H. Size-selective Complexation and Extraction of Endohedral Metallofullerenes with Cycloparaphenylene. *Angew. Chem.* **2014**, *126*, 3166–3170. [[CrossRef](#)]
29. Chang, X.; Xu, Y.; von Delius, M. Recent Advances in Supramolecular Fullerene Chemistry. *Chem. Soc. Rev.* **2024**, *53*, 47–83. [[CrossRef](#)]
30. Paul, A.; Borrelli, R.; Bouyanfif, H.; Gottis, S.; Sauvage, F. Tunable Redox Potential, Optical Properties, and Enhanced Stability of Modified Ferrocene-Based Complexes. *ACS Omega* **2019**, *4*, 14780–14789. [[CrossRef](#)]
31. Gray, H.B.; Sohn, Y.S.; Hendrickson, N. Hendrickson, Electronic structure of metallocenes. *J. Am. Chem. Soc.* **2002**, *93*, 3603–3612. [[CrossRef](#)]
32. Zhu, L.; Xu, J.; Lan, B.; Chen, X.; Kono, H.; Xu, H.; Yan, J.; Li, W.; Yagi, A.; Yuan, Y. Ferrocene-Based Conjugated Macrocycles: Shotgun Synthesis, Size-Dependent Properties and Tunable Fluorescence Intensity. *Org. Chem. Front.* **2024**, *11*, 5130–5137. [[CrossRef](#)]
33. Lan, B.; Xu, J.; Zhu, L.; Chen, X.; Kono, H.; Wang, P.; Zuo, X.; Yan, J.; Yagi, A.; Zheng, Y. Side-Chain Type Ferrocene Macrocycles. *Precis. Chem.* **2024**, *2*, 143–150. [[CrossRef](#)] [[PubMed](#)]

34. Astruc, D. Why Is Ferrocene so Exceptional? *Eur. J. Inorg. Chem.* **2017**, 2017, 6–29. [\[CrossRef\]](#)
35. Cullen, W.R.; Woollins, J.D. Ferrocene-Containing Metal Complexes. *Coord. Chem. Rev.* **1981**, 39, 1–30. [\[CrossRef\]](#)
36. Inkpen, M.S.; Scheerer, S.; Linseis, M.; White, A.J.; Winter, R.F.; Albrecht, T.; Long, N.J. Oligomeric Ferrocene Rings. *Nat. Chem.* **2016**, 8, 825–830. [\[CrossRef\]](#)
37. Hisatome, M.; Yoshihashi, M.; Yamakawa, K.; Iitaka, Y. X-Ray Crystal Structure of 7, 16, 24, 33-Tetrathia [3] Paracyclo [3](1, 3) Ferrocene [3] Paracyclo [3](1, 3) Ferrocenophane. *Bull. Chem. Soc. Jpn.* **1987**, 60, 3474–3476. [\[CrossRef\]](#)
38. Zhang, R.; Wang, Z.; Wu, Y.; Fu, H.; Yao, J. A novel redox-fluorescence switch based on a triad containing ferrocene and perylene diimide units. *Org. Lett.* **2008**, 10, 3065–3068. [\[CrossRef\]](#)
39. Segawa, Y.; Omachi, H.; Itami, K. Theoretical Studies on the Structures and Strain Energies of Cycloparaphenylenes. *Org. Lett.* **2010**, 12, 2262–2265. [\[CrossRef\]](#)
40. Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S. Selective and Random Syntheses of [n] Cyclopara-phenylenes (N = 8–13) and Size Dependence of Their Electronic Properties. *J. Am. Chem. Soc.* **2011**, 133, 8354–8361. [\[CrossRef\]](#)
41. Kamin, A.A.; Clayton, T.D.; Otteson, C.E.; Gannon, P.M.; Krajewski, S.; Kaminsky, W.; Jasti, R.; Xiao, D.J. Synthesis and Metalation of Polycatechol Nanohoops Derived from Fluorocycloparaphenylenes. *Chem. Sci.* **2023**, 14, 9724–9732. [\[CrossRef\]](#)
42. Li, K.; Xu, Z.; Deng, H.; Zhou, Z.; Dang, Y.; Sun, Z. Dimeric Cycloparaphenylenes with a Rigid Aromatic Linker. *Angew. Chem. Int. Ed.* **2021**, 60, 7649–7653. [\[CrossRef\]](#)
43. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H. *Gaussian 16*; Revision A. 03; Gaussian, Inc.: Wallingford, CT, USA, 2016.
44. Dennington, R.; Keith, T.A.; Millam, J.M. *GaussView*, Version 6.0. 16; Semichem, Inc.: Shawnee Mission, KS, USA, 2016.
45. Stephens, P.J.; Devlin, F.J.; Chabalowski, C.F.; Frisch, M.J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, 98, 11623–11627. [\[CrossRef\]](#)
46. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **2010**, 132, 154104. [\[CrossRef\]](#) [\[PubMed\]](#)
47. Yanai, T.; Tew, D.P.; Handy, N.C. A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, 393, 51–57. [\[CrossRef\]](#)
48. Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. *J. Comput. Chem.* **2012**, 33, 580–592. [\[CrossRef\]](#)
49. Glendening, E.D.; Reed, A.E.; Carpenter, J.E.; Weinhold, F. *NBO*, Version 3.1; Gaussian, Inc.: Pittsburgh, PA, USA, 2003.
50. Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual Molecular Dynamics. *J. Mol. Graph.* **1996**, 14, 33–38. [\[CrossRef\]](#)
51. Chen, X.; Lu, C.; Wang, L.; Wang, J. Angle-Resolved One and Two-Photon Absorption Spectrum in Twisted Bilayer Graphene Quantum Dots. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2022**, 271, 120894. [\[CrossRef\]](#)
52. Li, N.; Zhang, L.; Wang, J. Modulation of chiral spectral deflection by van der Waals force-induced molecular electropolarization in catenane oligomers. *RSC Adv.* **2023**, 13, 11055–11061. [\[CrossRef\]](#)
53. Li, Y.; Gai, X.; Zhao, B.; Wang, J. Chiral Nonlinear Luminescence Study of Pentaosonium Salt Molecules Driven by Internal Electric Field Induced by Orbital Polarization. *J. Petrochem. Univ.* **2025**, 38, 65.
54. Liu, Z.; Lu, T.; Chen, Q. Vibrational Spectra Molecular Vibrational Behaviors of All-Carboatomic Rings cy-clo [18]carbon Its Analogues. *Chem. Asian J.* **2021**, 16, 56–63. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.