Review

Anthracene-Containing Metallacycles and Metallacages: Structures, Properties, and Applications

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Abstract: Due to its highly conjugated panel-like structure and unique photophysical and chemical features, anthracene has been widely used for fabricating attractive and functional supramolecular assemblies, including two-dimensional metallacycles and three-dimensional metallacages. The embedded anthracenes in these assemblies often show synergistic effects on enhancing the desired supramolecular and luminescent properties. This review focuses on the metallasupramolecular architectures with anthracene-containing building blocks, as well as their applications in host-guest chemistry, stimulus response, molecular sensing, light harvesting, and biomedical science.

1. Introduction

The construction of discrete supramolecular metallacycles and metallacages with well-defined sizes, shapes, and geometries has attracted considerable attention [1–6]. Based on the coordination-driven self-assembly strategy, the spontaneous formation of metal-ligand coordination bonds between Lewis-basic organic donor and Lewis-acidic metal acceptor fabricates a large number of two-dimensional (2D) and three-dimensional (3D) metallasupramolecular architectures, such as molecular triangles, squares, hexagons, polygons, polyhedrons, etc., [7–11]. The high directionality and relative strong strength of coordination bonds offer the possibility of introducing multiple functional units into metallasupramolecular structures with precise stoichiometric and spatial arrangement of individual moieties [12,13]. The incorporation of functional building blocks with favorable photophysical/chemical properties into these metallasupramolecular structures remains an effective means to pursue desired behavior and applications.

Among various functional blocks, anthracene derivatives have been extensively utilized in the fabrication of supramolecular coordination assemblies [14,15]. The large conjugated π-system and panel-like structure of anthracene endow robust photophysical and photochemical behavior, such as rich absorption and emission spectra, high fluorescence quantum yields, and ordered aromatic-aromatic interactions [16,17]. In order to incorporate anthracene into metallasupramolecular structures, the chemical modification of the anthracene core is usually required. In general, in line with the coordination-driven self-assembly methodology, the incorporation of anthracene moieties into metallasupramolecular structures can be achieved with either an anthracene-containing ligand as a Lewis-basic organic donor or a transition-metal moiety as a Lewis-acidic metal acceptor. It represents a facile way to develop anthracene-based organic donors by integrating anthracene with diverse organic ligands such as pyridyl [18], pyrazolyl [14,19], imidazolyl [20], or *N*-heterocyclic carbene (NHC) ligand [21]. The functionalized organic donors can subsequently react with

metal salts or organometallic motifs to afford target metallasupramolecules. In addition, some efforts have been devoted to preparing the anthracene-functionalized transition metal acceptors, which are capable of directly reacting with corresponding organic ligands to form coordination assemblies [22,23]. The anthracene-incorporated metallasupramolecular structures are featured by tunable cavity enclosure, favorable aromatic interactions, and appealing photoluminescent properties, resulting in a wide range of potential applications in host-guest chemistry, stimulus response, molecular sensing, light harvesting, and biomedical aspects [14,24–34].

In this review, we focus on the recent advance of the structural modifications, properties, and potential applications of anthracene-containing metallacycles and metallacages. Specifically, the anthracene-functionalization strategies for constructing metallasupramolecules and the representative advance in exploring the properties and applications of these metallasupramolecules are discussed.

2. Constructions of Anthracene-Containing Metallacycles and Metallacages

In order to construct discrete supramolecular metallacycles and metallacages via the coordination-driven self-assembly, the introduction of the direction-controlled metal–ligand interactions between complementary precursors is necessary. The precursors with pre-defined angles and symmetries react in a specific ratio to produce the well-defined supramolecular assemblies. The anthracene group can be incorporated into metallacycles and metallacages by using either the anthracene-containing organic donor or organometallic acceptor building blocks.

2.1. Anthracene-Containing Organic Donor Building Blocks

The combination of the anthracene moiety with organic coordination groups affords the rigid and versatile functional building blocks. After reacting with the complementary metallic reagents, a number of anthracene-based coordination assemblies have been documented including metallacycles and metallacages. In general, the nitrogen-based coordination linkers have been mostly employed in constructing discrete supramolecular structures compared to the metal–carbon or metal–oxygen coordination-driven self-assembly. For instance, ligand 1,8-bis(4-pyridylethynyl)anthracene (**1**) has been used as a rigid nitrogen-based organic "clip" to construct both rectangles and trigonal prisms (Figure 1). Considering the flexible coordination sphere of the 3d-metal ions, the equimolar reactions of **1** with 3d-metal acetate linear linkers such as Mn(II), Zn(II), or Cu(II) acetates result in the formation of either rectangular (**2**) or zigzag polymeric (**3**) structures [35]. However, after changing the metal linkers to 1,4-bis[*trans*-Pd(PEt$_3$)$_2$(NO$_3$)(ethynyl)]benzene (**7**), it only affords the rectangle product **4** due to the rigid square planar coordination environment of Pd(II) [36,37]. The similar phenomenon was also observed for the other square planar coordination metal linkers such as Pt(II) complexes [38,39]. The half-sandwiched Ru$^{II}_2$ metal precursor [Ru$_2$(μ-η^4-C$_2$O$_4$)(MeOH)$_2$(η^6-p-cymene)$_2$](O$_3$SCF$_3$)$_2$ (**8**) has also been demonstrated to react with **1** in 1:1 molar ratio to form the 2D metallacycle **5** [40]. Moreover, the 3D nanoscopic prismatic cage **6** with tunable shape, size, and properties was fabricated by mixing the tritopic Pt(II) linker 1,1,1-tris[4-(*trans*-Pt(PEt$_3$)$_2$(NO$_3$))phenyl]ethane (**9**) with **1** in 2:3 molar ratio [41,42]. Recently, Jin, Hahn, and co-workers presented a series of iridium(III) metalla[2]catenanes prepared from a non-linear but rigid dipyridyl donor ligand 1,5-bis(4-pyridylethynyl)anthracene [43]. Due to the nonlinear structure and aromatic π–π and C–H···π interactions of the ligand, the controlled transformations between tetranuclear metallarectangles and metalla[2]catenanes were realized in solution by changing the solvent, concentration, or guest species. In addition, the incorporation of halogen atoms into the dinuclear metal complex bridge led to interlocked metalla[2]catenanes with two different topological configurations in the solid state.

Besides the nitrogen-based organic donor ligands, the strong σ-donating NHC can form stable metal–carbon bonds to generate supramolecular structures. The NHC coordination complexes exhibit unusual chemical-physical properties and show promising

applications in catalysis [44–46], sensing [47], and medicine chemistry [48]. Zhang and co-workers integrated NHCs with supramolecular host calixarene fragments to synthesize the dinuclear Ag(I) metallamacrocycles functionalized with multi-anthracene groups [49]. As shown in Figure 2a, the anthracene-capped NHC ligand precursor **10** reacted with Ag$_2$O to afford metallacycle **11**. X-ray diffraction analysis indicated that 2D supramolecular layer (Figure 2b) and 3D supramolecular network (Figure 2c) were observed by viewing along the different axis of **11**. The 3D network was assembled by the π–π interactions of the intermolecular anthracene rings with a face-to-face separation of 3.367 Å and the C–H···F interactions among PF$_6^-$ anions and various proton atoms. The configurations of the metallacycle structures can also be modulated by changing the upper-rims of calixarenes or the *N*-substituents of the carbene ligand [49].
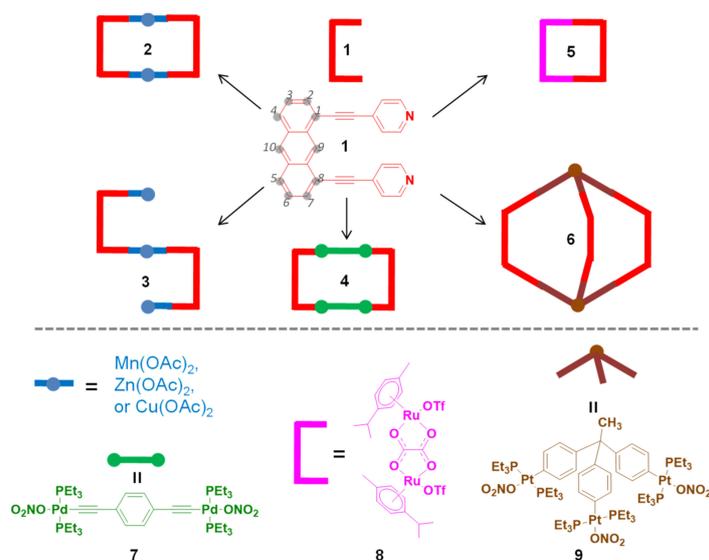

Figure 1. Nitrogen-based anthracene-containing ligand **1** for constructing coordination self-assemblies. The numbering scheme for the carbon atoms in anthracene is displayed along with the structure of ligand **1**.
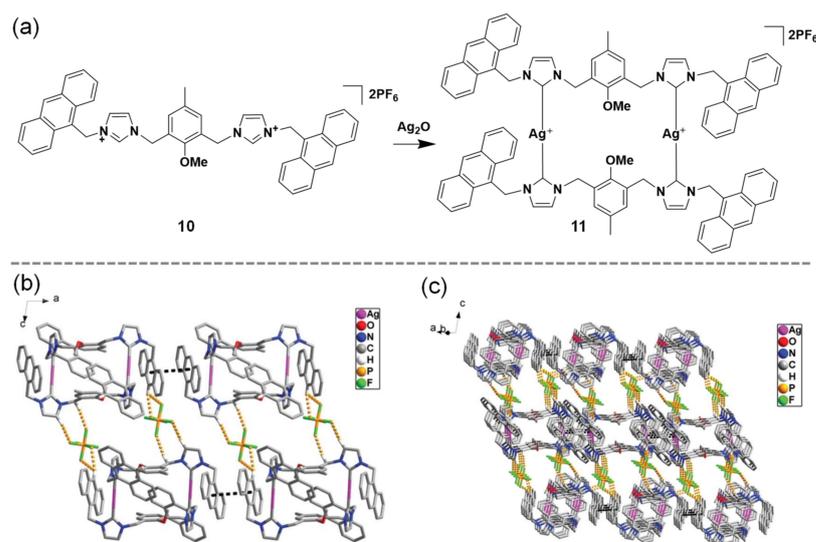

Figure 2. *N*-heterocyclic carbene-based anthracene-containing ligand precursor **10** for constructing coordination self-assemblies. (**a**) Synthesis of metallacycle **11**. (**b**) The 2D supramolecular layer of **11** viewed along the *b* axis. (**c**) The 3D supramolecular network of **11** viewed along the *a* axis. Reprinted with permission from Ref. [49]. Copyright 2013 Royal Society of Chemistry.

2.2. Anthracene-Containing Organometallic Acceptor Building Blocks

As an alternative approach to the organic donor linkers, anthracene has also been modified as the organometallic acceptor building blocks to construct coordination assemblies. The combination of metals with organic ligands usually simplifies the multi-component self-assembly. A handful of research interests have been focused on the 1,8-metalated anthracene congeners due to their parallel coordination environment [50–52]. By using bridging linkers with nitrogen- to oxygen-based organic coordination ligands, both supramolecular rectangles and cages have been developed via two-component self-assembly as discussed below.

Based on the dipyridyl-based coordination linkers, as shown in Figure 3, the Stang group fabricated the first series of 2D molecular rectangles via the assembly of a 1,8-diplatinum(II)-functionalized anthracene organometallic "clip" (**12**) with the linear ligand **15** or **16** [22]. Scanning tunneling microscopy investigations indicated that the long edge of the rectangle **13** stood on the surface and exhibited a 2D molecular network on pyrolytic graphite, while the rectangle face of **13** laid flat on the Au(111) surface showing linear chains [53]. The same group also reported a family of the propeller-type 3D supramolecular cages **14** with dimensions of 1×2 nm to 1×4 nm by the use of the tritopic pyridyl subunit **17** or **18** [54]. The size- and shape-selective self-sorting process in both 2D rectangles and 3D cages was also unveiled [55,56]. Mukherjee and co-workers extended the above methodology by incorporating the ethynyl unit into a new anthracene-containing organometallic Pt^{II}_2 "clip" molecule. They further introduced the four-imine-containing dipyridyl blocks to synthesize molecular rectangles, which showed reversible fluorescent responses to $Fe^{3+}/Cu^{2+}/Ni^{2+}$ via the metal coordination-triggered photo-induced electron transfer mechanism [34].
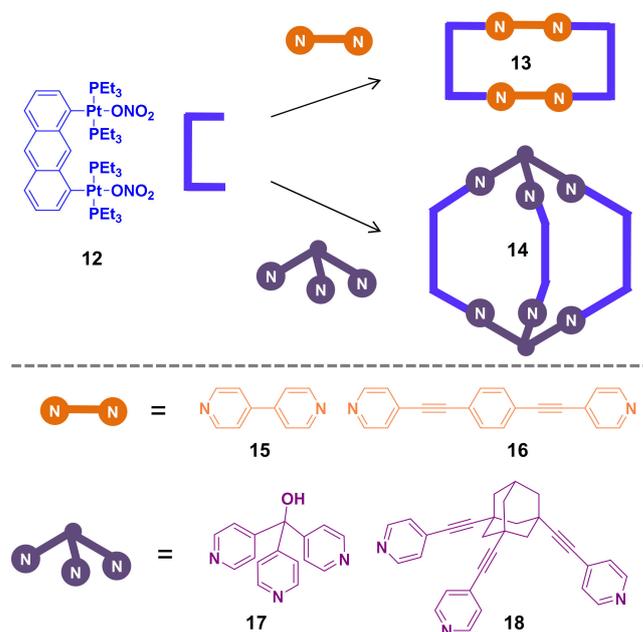

Figure 3. Diplatinum(II)-based anthracene-containing linker **12** for constructing nitrogen-based 2D and 3D coordination self-assemblies.

Anionic oxygen donors represent another type of simple coordination building blocks, which have been widely used to prepare supramolecular structures. As shown in Figure 4a, the 1:1 stoichiometric reactions of the 1,8-diplatinum(II) "clip" **12** with the linear dicarboxylate-based oxygen linker **19** or **20** produced the corresponding rectangles **21** and **22**. Single crystal X-ray analysis of the obtained assemblies confirmed the formation of the Pt-O bonds (Figure 4b) [57]. Inspired by this pioneering work, a number of functionality-directed metal-oxygen-bond-containing macrocycles were reported by incorporating various functional groups into the dicarboxylate linkers such as ferrocene [58], carborane [59], crown ether [60], and chiral species [61]. The modulation of the organometallic Pt^{II} "clip" to Pd^{II} architectures

has also been demonstrated by forming Pd–O bonds [62,63]. Moreover, Pluth and co-workers described an asymmetrical pyridyl quinolone ligand that was able to form hybrid metal–oxygen and metal–nitrogen bonds in the self-assembled macrocycle, which further expanded the library of metal−ligand-derived supramolecular architectures [64].
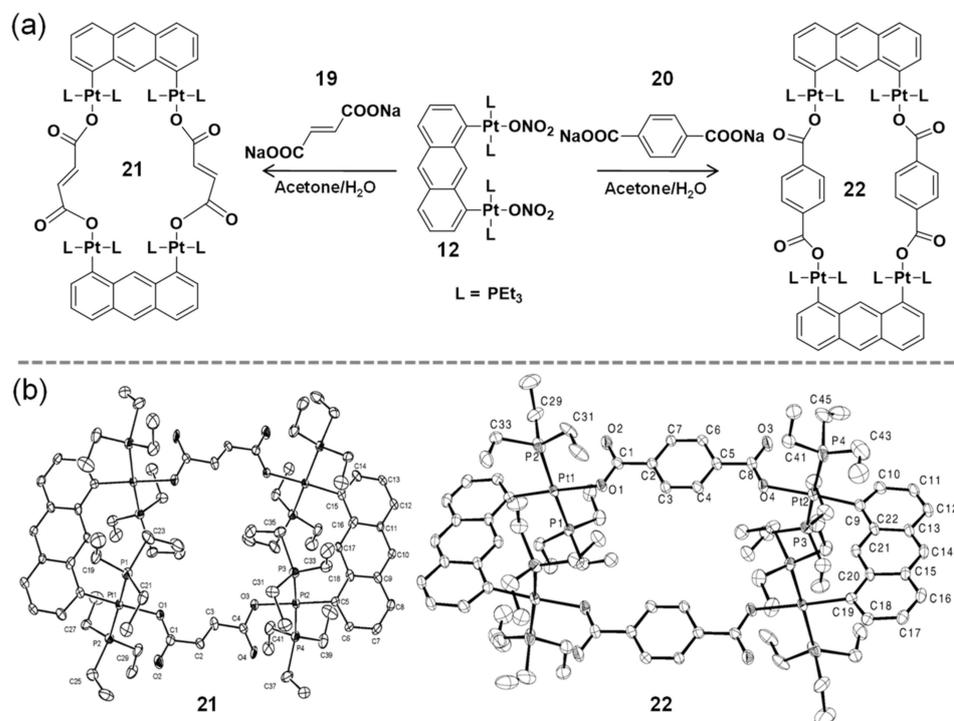

Figure 4. Diplatinum(II)-based anthracene-containing linker **12** for constructing oxygen-based rectangles. (**a**) The formation of molecular rectangles **21** and **22**. (**b**) ORTEP diagrams of **21** and **22**. Reprinted with permission from Ref. [57]. Copyright 2003 American Chemical Society.

3. Properties and Applications of Anthracene-Containing Metallacycles and Metallacages

The anthracene-containing metallacycles and metallacages combine multi-functional units into the well-defined discrete supramolecular architectures with extended π-surfaces and modifiable cavities and shapes. The resulting assemblies not only display the diversity of structural aspects, but also endow a wide range of intriguing properties and applications. In this section, we discuss the representative properties and potential applications of some recently developed anthracene-based supramolecules in the fields of host-guest chemistry, stimulus response, molecular sensing, light harvesting energy transfer, and biomedical science.

3.1. Host-Guest Chemistry

Host-guest chemistry represents one of the most important features of supramolecular assemblies. The construction of unique host-guest structures initiates numerous fundamental investigations and applied explorations in the fields of fluorescence, catalysis, drug delivery, etc., [65–69]. Among various supramolecular hosts, anthracene-containing 2D metallacycles and 3D metallacages have been well-explored because of their rigid aromatic surfaces and unique photophysical and photochemical properties.

As shown in Figure 5, Chi and co-workers disclosed the reversible structural transformations between monorectangle and metalla[2]catenane via guest- and solvent-dependent self-assembly [70]. The assembly of the tetracene-based diruthenium(II) acceptor **23** and the anthracene-functionalized dipyridyl donor **24** afforded multiple stimulus-responsive supramolecular structures. Specifically, the [M_2L_2] monorectangle structure **25** was obtained in an equivalent molar mixing of the donor and acceptor linkers in nitromethane (CH_3NO_2). After changing the solvent to methanol (CH_3OH), an interlocked [M_2L_2]$_2$

metalla[2]catenane **26** with strong π–π interactions was formed. Interestingly, the addition of pyrene into the identical reaction in methanol generated the pyrene-encapsulated host−guest complex [(pyrene)$_2$⊂**25**]. X-ray crystal structure studies indicated that two pyrene guests were bound in the aromatic cavity of **25** via host−guest interactions.
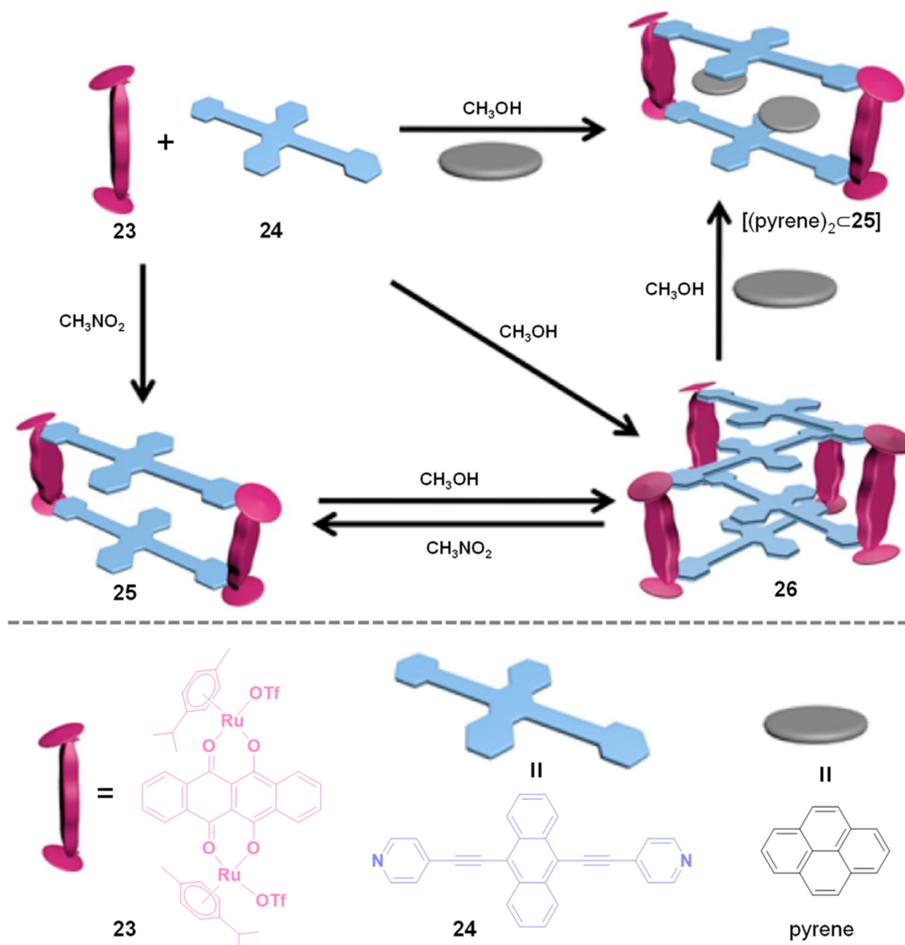

Figure 5. The reversibly fine-tuned self-assembly among monorectangle and catenane structures. Reprinted with permission from Ref. [70]. Copyright 2015 American Chemical Society.

Compared to metallacycle-based hosts, metallacages or capsules can introduce more tight and selective binding affinity for large guest substrates. For example, the Nitschke group employed a C_2-symmetric 1,5-diaminoanthracene **27** building block to generate the anthracene-edged Fe$^{II}_4$L$_6$ tetrahedral cage **28** (Figure 6a) [24]. The Diels−Alder cycloadditions of the six anthracene panels of **28** with the electron-deficient dienophile reagent such as tetracyanoethylene (TCNE) yielded the new cage **29**. The modified cage **29** possessed an enclosed cavity suitable for the encapsulation of the fullerene C$_{60}$ to give the host–guest complex [C$_{60}$⊂**29**]. In contrast, the treatment of the original cage **28** with C$_{60}$ formed a covalent adduct [C$_{60}$·**28**] through the Diels−Alder cycloadditions of three of its anthracene ligands with C$_{60}$. The remaining three anthracene ligands of [C$_{60}$·**28**] can further react with TCNE to give a new product (structure not shown) by post-assembly modification. These topologically controlled modifications would be unable to access if the reaction components were added together before assembly. As shown in Figure 6b, X-ray diffraction analysis of [C$_{60}$·**28**] and [C$_{60}$⊂**29**] confirmed the tetrahedral cage structure and the covalent Diels−Alder cycloaddition reactions of TCNE and C$_{60}$ with the iron cage.
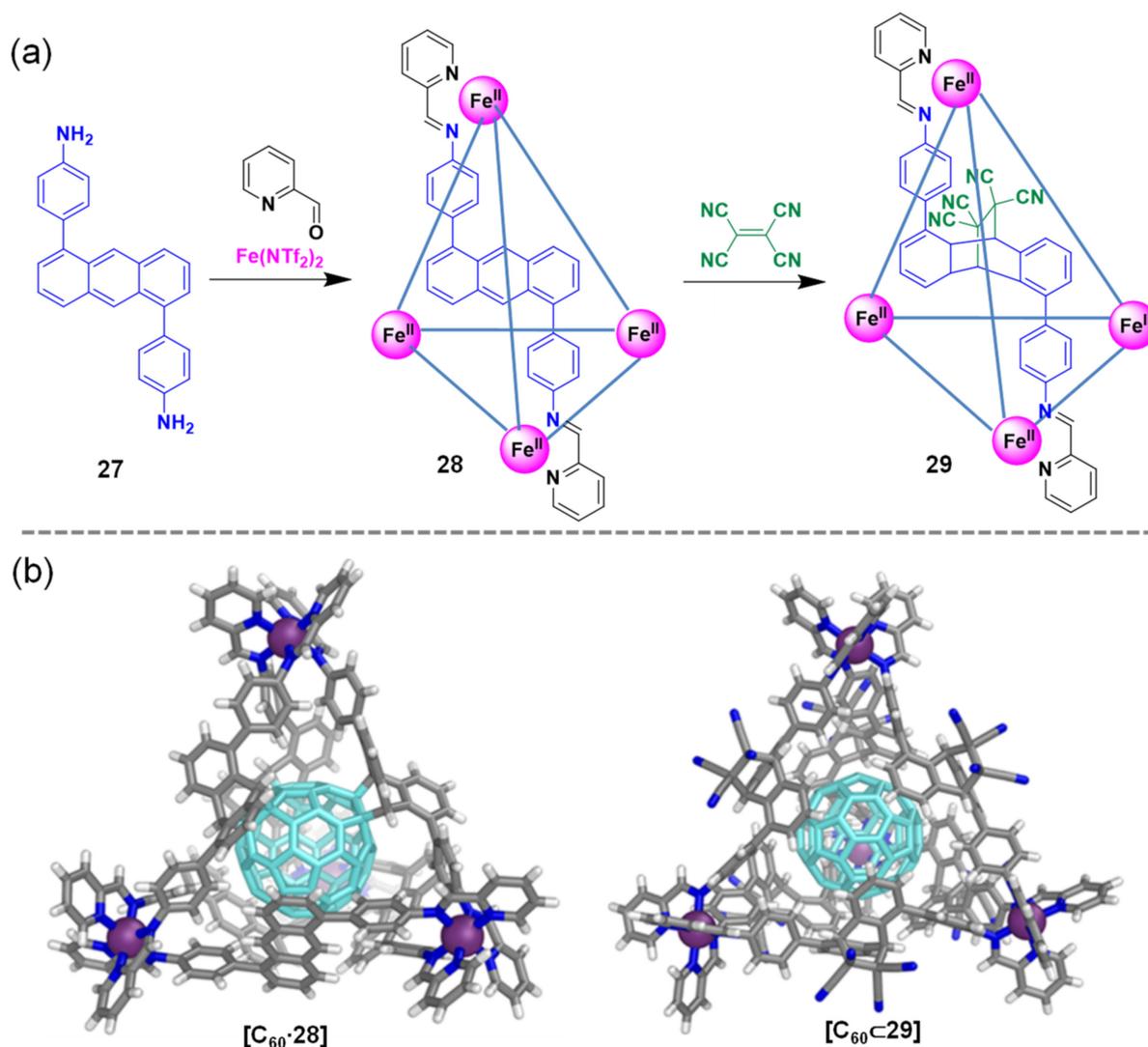
Figure 6. Anthracene-edged iron cages. (**a**) Formation of cage **28** and its post-modification with tetracyanoethylene to give **29**. (**b**) The crystal structures of the covalent adduct **[C$_{60}$·28]** and the host-guest complex **[C$_{60}$⊂29]**. Reprinted with permission from Ref. [24]. Copyright 2016 American Chemical Society.

Yoshizawa and co-workers designed a new bent bispyridine-anthracene linker **30** with an orthogonal conformation of the aromatic sub-units [30]. The combination of Pd(II) ions and **30** in a 1:2 molar ratio afforded the formation of a M$_2$L$_4$ capsule **31** possessing a cavity with a diameter around 1 nm (Figure 7a). The encapsulations of the medium-sized spherical guest [2,2]paracyclophane **32** and the planar guest 1-methylpyrene **33** were monitored by ^{1}H NMR techniques (Figure 7b–d). The X-ray crystal structure of the host-guest scaffold **[(33)$_2$⊂31]** further demonstrated that the cavity of **31** was able to encapsulate two guest molecules of **33**. Moreover, the larger molecule fullerene (C$_{60}$) also formed host-guest complexes with **31** in quantitative yields. The same group expanded the above platform to Pt(II)-linked coordination capsules using the same bispyridine-anthracene skeleton with different metal ions and substitutes [71]. The highly emissive host–guest complexes with fluorescence quantum yields up to 0.5 were successfully obtained by the encapsulation of various molecular dyes such as 4,4′-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) and coumarin derivatives.
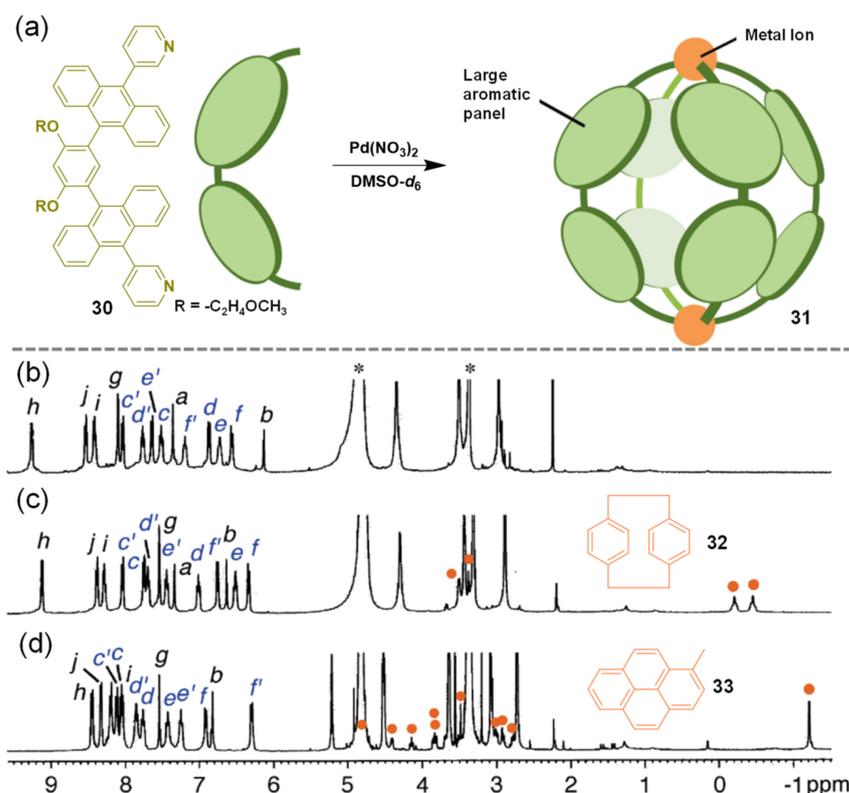
Figure 7. Self-assembly and host-guest chemistry of molecular capsule **31**. (**a**) Schematic representation of the formation of **31**. (**b–d**) ^{1}H NMR spectra of (**b**) **31**, (**c**) [**32**⊂**31**], and (**d**) [(**33**)$_2$⊂**31**]. Orange signals are from the encapsulated guest **32** or **33**. *: solvent signals. Reprinted with permission from Ref. [30]. Copyright 2011 American Chemical Society.

3.2. Stimulus Response

Stimulus response can be defined as the phenomenon that the substrates are capable of altering their structural and/or physical–chemical properties in response to external stimulus such as temperature, light irradiation, pressure, chemicals, solvent, and so on. The development of stimulus-responsive materials has attracted extensive research interests in order to mimic bioprocesses and explore functional materials [72–75]. Anthracene-based supramolecular architectures with intriguing photophysical, photochemical, and host-guest behavior represent a promising category of stimulus-responsive material candidates. For instance, three or six freely rotating anthracene groups have been incorporated into organoplatinum(II) hexagonal metallacycles to show temperature-responsive behavior (Figure 8). The treatment of the 120° anthracene-functionalized triarylamine ligand **34** with the 120° diplatinum(II) acceptor **35** or the 180° diplatinum(II) acceptor **36** generated the [3 + 3] or [6 + 6] hexagonal metallacycles **37** and **38**, respectively [76]. The resulting assemblies exhibited reversible fluorescent response in tetrahydrofuran (THF) upon temperature variation from −20 to 60 °C (Figure 8b). However, in coordinating solvent such as dimethyl formaldehyde (DMF), they showed two-stage responses (Figure 8c). In the lower temperature range (below 30 °C), the emission spectral changes were similar to those observed in THF. At higher temperatures, the metallacycles were destroyed by the solvents and exhibited ratiometric fluorescent response. The further development of a dianthracene-based rhomboidal organoplatinum(II) metallacycle showed both temperature and mechanical-force dependent fluorescence [77]. Very recently, Wang, Xu and co-workers studied the luminescence properties of the platinum(II) metallacycles with inner- and outer-modified 9,10-distyrylanthracene units, indicating that the modified position of fluorophores played a vital role in modulating the properties of supramolecular assemblies [78].
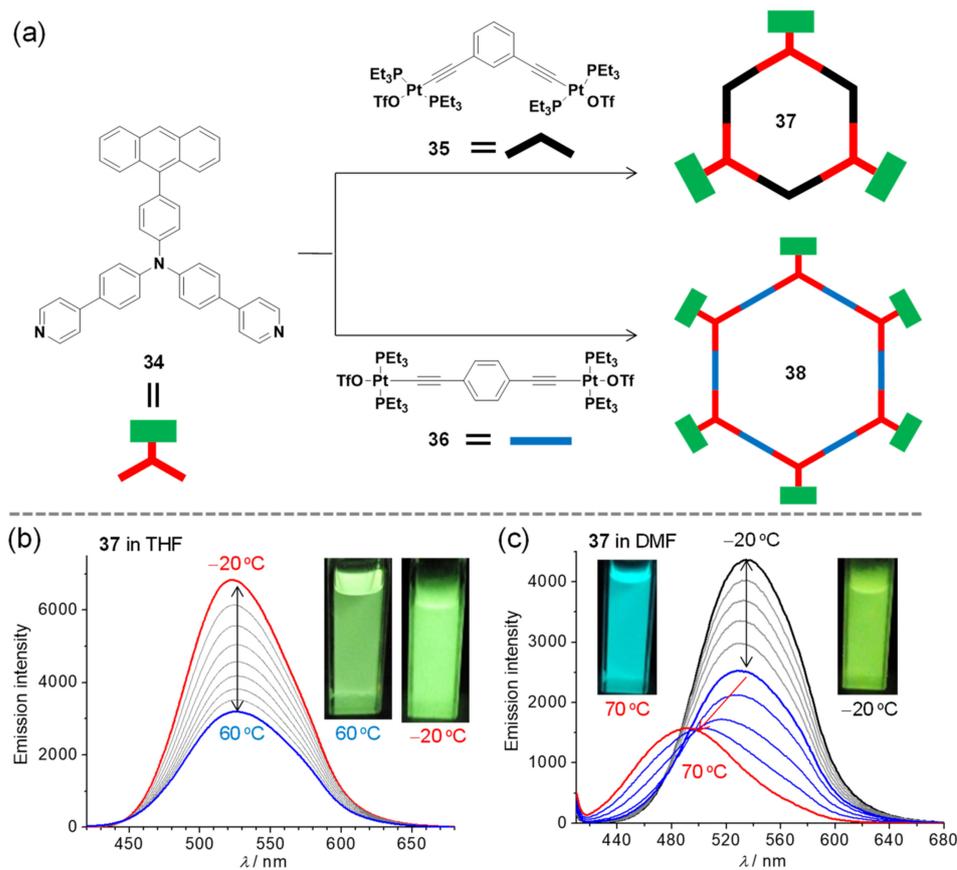
Figure 8. Temperature-responsive fluorescent metallacycles **37** and **38**. (**a**) Scheme of the syntheses of **37** and **38**. (**b**,**c**) Emission spectral changes of **37** in (**b**) THF and (**c**) DMF, respectively. The inset images show the solution under UV irradiation at specific temperature indicated. Reprinted with permission from Ref. [76]. Copyright 2018 American Chemical Society.

　　　Photo-driving chemical transformations have been widely investigated in modern organic synthesis and materials science [79,80]. Anthracene-based derivatives usually show interesting photochemical reactions of anthracene at 9,10 positions, including [4 + 4] photodimerization and [4 + 2] oxygenation [81]. The integration of anthracene units into supramolecular architectures provides a versatile platform to achieve chemo- and region-selective photochemical transformations. The Han group reported the rhodium-based photoactive metallarectangle **39** containing the 2,6-di(1*H*-imidazol-1-yl) anthracene linker (Figure 9). The photochemical [4 + 4] cycloaddition of **39** regioselectively occurred to afford the *syn*-dimeric photo-addition product **40** in quantitative yield under irradiation at 365 nm, which could be clearly discerned from the ^{1}H NMR spectral changes [82]. The reversible transformation was further observed by thermal- or photo-induced (254 nm) cleavage reaction. Moreover, the pure organic photodimer **41** could be readily released from the metallarectangle in high yield (Figure 9d), which was difficult to access via conventional organic ligand-based reactions. Another rhodium-rectangle with a 2,7-bis(4-pyridyl)anthracene linker showed similar photo- and thermal response. The same group also employed the supramolecular templating strategy to other kinds of metallasupramolecular assemblies. For example, *N*-heterocyclic carbene- or azole-2,6-disubstituted anthracenes have been used to react with Ag(I) or Au(I) metallic reagents to generate metallacycles, which showed appealing regio- and stereo-selectivity on the photochemical [4 + 4] cyclodimerization [83].
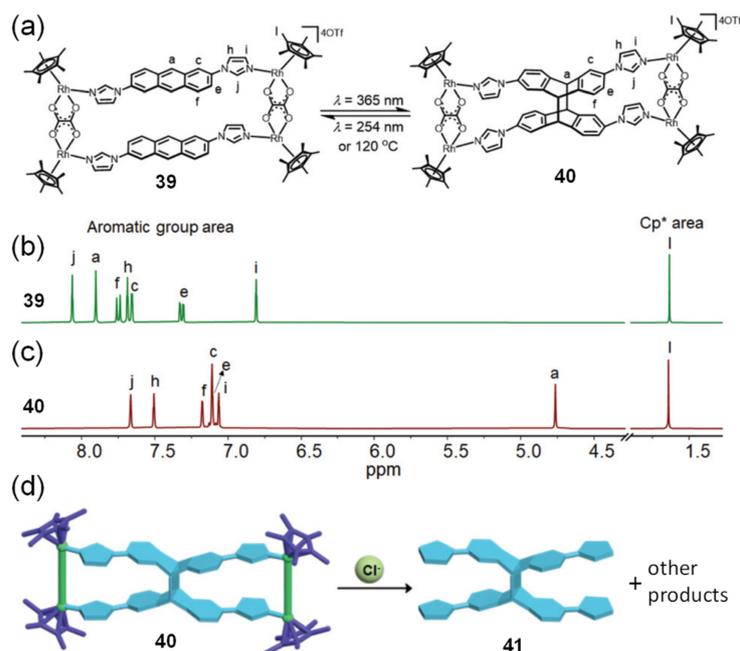
Figure 9. Stimulus-responsive rhodium-based metallarectangles. (**a**) Photochemical [4 + 4] cycloaddition of **39** and reversible transformation. (**b**,**c**) Partial ^{1}H NMR spectra in CD$_3$CN of (**b**) **39** and (**c**) **40**. (**d**) Schematic representation of the dissociation of **40** into **41**. Reprinted with permission from Ref. [82]. Copyright 2022 Royal Society of Chemistry.

The photochemical [4 + 2] oxygenation of anthracene-based supramolecular assemblies has also been demonstrated. Shionoya and co-workers reported the photosensitized oxygenation reactions in both liquid and solid conditions of a metallacycle containing multiple anthracene structures. As a result, the phase-dependent reactivity and host-guest interactions have been disclosed. Specifically, the photosensitized oxygenation reaction of metallacycle resulted in the fully oxygenated product in solution, whereas a mono-oxygenated C_s-symmetrical complex was provided in an amorphous solid state [84]. Our group introduced the reaction of a linear 9,10-bis(4-pyridyl)anthracene donor with a ~120° Pt(II) complementary acceptor to prepare a hexagonal metallacycle via the [6 + 6] coordination-driven self-assembly. The reversible capture and release of singlet oxygen in the resulting metallacycle were realized via combining photooxygenation with thermolysis processes [85].

3.3. Molecular Sensing

Molecular sensing can be generally considered as a sensor that interacts with an analyte to generate a detectable signal variation. The sensor molecule usually consists of two (or more) subcomponents that perform the recognition and signaling function, respectively. Selective and precise detection of target analytes is indispensable in a wide range of chemical, material, biological, environmental, and medical sciences [86–88]. Among these efforts, anthracene-containing metalla-supramolecular systems can incorporate multiple functional components into well-defined structures, providing the appropriate structural and chemical features for molecular sensing. Stang and co-workers developed a series of platinum(II)-based metallacycles for the selective and sensitive fluorescent detection of chemicals such as ammonia, nitroaromatics, amino acids, and so on [89,90]. As shown in Figure 10a, they employed the 9,10-di(4-pyridylvinyl)anthracene ligand (**42**) to react with dicarboxylates (**20** or **43**) and *cis*-(PEt$_3$)$_2$Pt(OTf)$_2$ linkers for fabricating two near-infrared (NIR) emissive platinum(II) metallacycles **44** and **45** [91]. The resulting assemblies not only showed aggregation-induced emission (AIE) and solvatochromism behavior, but also exhibited NIR fluorescent detection of ammonia gas in the solid state (Figure 10b). The reversible

forming and breaking of the Pt-N coordination bonds was proposed for the observed emissive sensing properties. In addition, Mukherjee and co-workers synthesized a ditopic 180° Pt-ethynyl-based acceptor, which could react with the 1,8-bis(4-pyridylethynyl)anthracene (**1**) organic donor to yield an emissive metallamacrocycle [38]. The emission intensity of the metallamacrocycle was selectively and efficiently quenched in solution by the addition of picric acid, which is a common component in many chemical explosives. The charge-transfer processes between the electron-rich Pt-ethynyl-anthracene backbones and the electron-deficient nitroaromatic molecules were believed to be responsible for the resulting fluorescence quenching behavior.
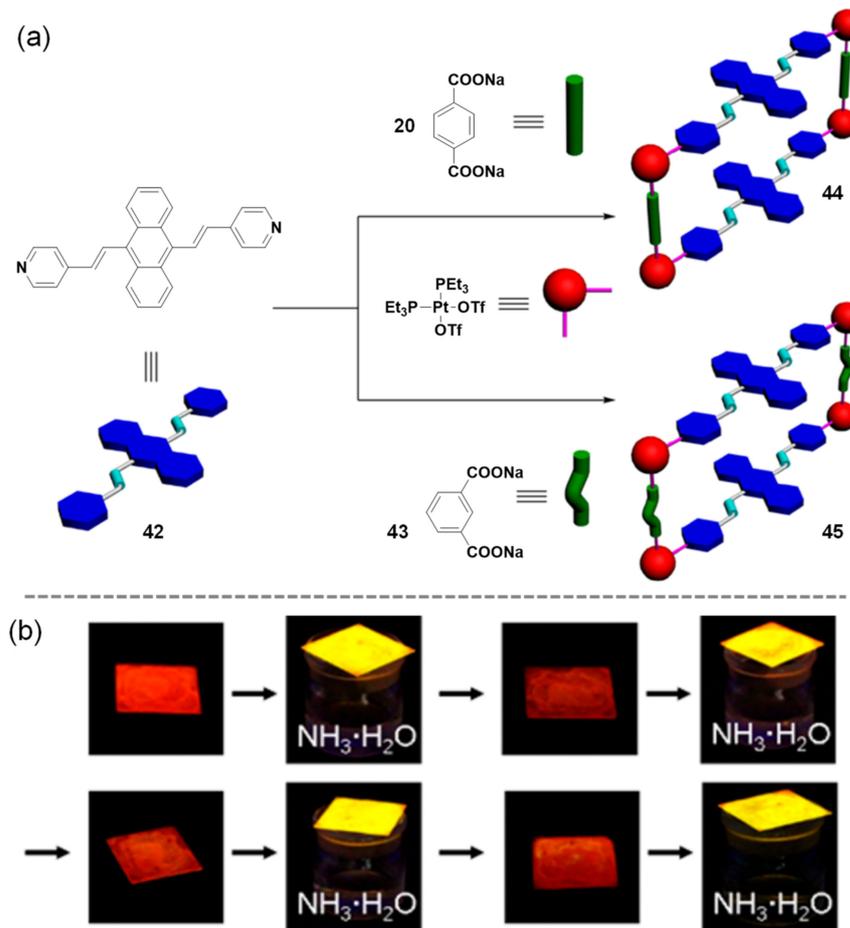

Figure 10. Near-infrared emissive discrete platinum(II) metallacycles. (**a**) Synthesis of metallacycles. (**b**) Photographs of films of **44** when exposed to or removed from ammonia under a UV lamp at 365 nm. Reprinted with permission from Ref. [91]. Copyright 2017 American Chemical Society.

Since 2008, the Yoshizawa group has continually worked on the bent anthracene dimer-based supramolecular capsules via the coordination-driven self-assembly approach to form M_2L_4-type structures [15]. One of these examples, capsule **31**, has been discussed in Figure 7 [30]. The multiple anthracene panels of these capsules lead to a rigid spherical polyaromatic cavity. Various synthetic molecules and biomolecules have been successfully encapsulated in the cavity of the capsules through host-guest interactions. In particular, they have achieved the selective recognition of D-sucrose from natural saccharide mixtures in water with 100% selectivity and >85% yield using a Pt(II)-based multi-anthracene capsule [92]. The theoretical calculations and control experiments demonstrated that the multiple CH-π interactions and complementary shapes between the capsule and guest molecules contributed to the unique recognition properties.

3.4. Light Harvesting and Biomedical Applications

Due to the well-resolved absorption and strong emission properties of anthracene fluorophores, anthracene-based metallacycles and metallacages have ensured promising photo-active applications including light harvesting energy transfer and biomedical science [93,94]. Yang, Xu, and co-workers incorporated multiple anthracene, coumarin, and BODIPY fluorophores into a discrete hexagonal metallacycle with precise distances and locations based on the coordination-driven self-assembly and host−guest interactions [95]. The prepared assembly showed two-step fluorescence-resonance energy transfer (FRET) behavior, which resulted in a higher photosensitization efficiency of generating singlet oxygen and an enhanced photooxidation activity of a sulfide substrate compared to the corresponding one-step FRET system.

Very recently, Li and co-workers fabricated two trigonal prismatic metallacages **48** and **49** via a three-component self-assembly of two molecules of the trianthracene−triphenylamine-based tripyridyl ligand **46**, three molecules of dicarboxylate **20** or **47**, and six molecules of the 90° Pt(II) linker *cis*-(PEt₃)₂Pt(OTf)₂ (Figure 11a) [96]. Being beneficial from the well-organized multi-anthracene−triphenylamine moieties, the obtained cages displayed unique absorption and emission properties with high emission quantum yield and stimulus-responsive fluorescence (solvent polarity, temperature, and concentration). Moreover, the efficient FRET between the cage energy donor and the Nile Red (NR) energy acceptor was realized with an energy transfer efficiency of >93% at an acceptor/donor ratio of 15/1 (Figure 11b,c). The apparent static quenching mechanism was proposed for the efficient energy transfer process.
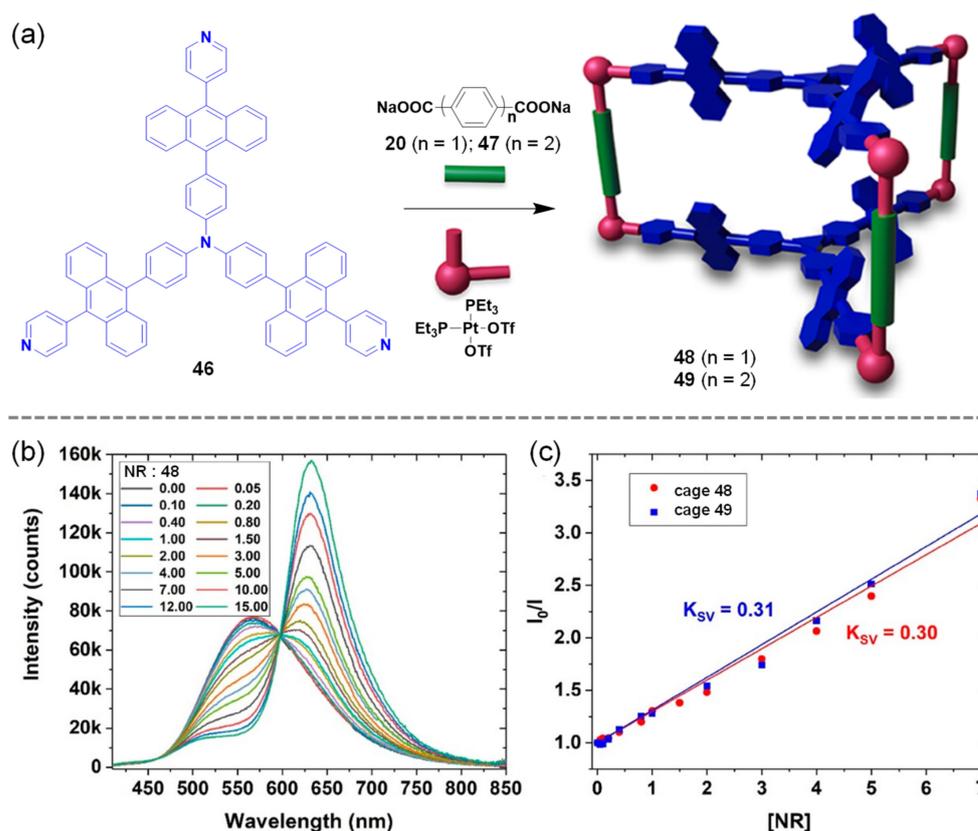
Figure 11. Trianthracene−triphenylamine-based platinum(II) metallacages **48** and **49** for light harvesting energy transfer. (**a**) Schematic representation of the syntheses of metallacages. (**b**) Emissive titration of **48** with varying amounts of Nile Red (NR). (**c**) The corresponding Stern−Volmer analyses of **48** and **49** in the presence of different concentration ratios of NR. Reprinted with permission from Ref. [96]. Copyright 2021 American Chemical Society.

　　　　Huang et al., reported a dual-emissive Pt(II) metallacage for in vivo hypoxia imaging and imaging-guided chemotherapy (Figure 12) [97]. In the molecular design, Pt(II)-meso-tetra(4-carboxyphenyl)porphine (**50**) was employed as an oxygen concentration responsive red phosphorescence unit, while the anthracene-based ligand **51** was selected as a blue fluorophore and *cis*-(PEt$_3$)$_2$Pt(OTf)$_2$ was selected as the 90° Pt(II) linker for the coordination-driven assembly. The absorption and emission studies of the obtained cage **52** presented the blue/red ratiometric emission changes corresponding to the variation of the oxygen (O$_2$) or nitrogen (N$_2$) atmosphere (Figure 12b–d). The encapsulation of cage **52** into an amphiphilic polymer methylpoly(ethyleneglycol)-block-poly(g-benzyl-l-glutamate) provided the metallacage-loaded nanoparticles with a loading efficiency of 65%, which could be further applied to detect the hypoxia environment both in vitro and in vivo (Figure 12e,f). In vivo studies indicated that the nanoformulations not only showed radiometric imaging of the tumor hypoxia condition, but also were capable of effectively suppressing the tumor growth.
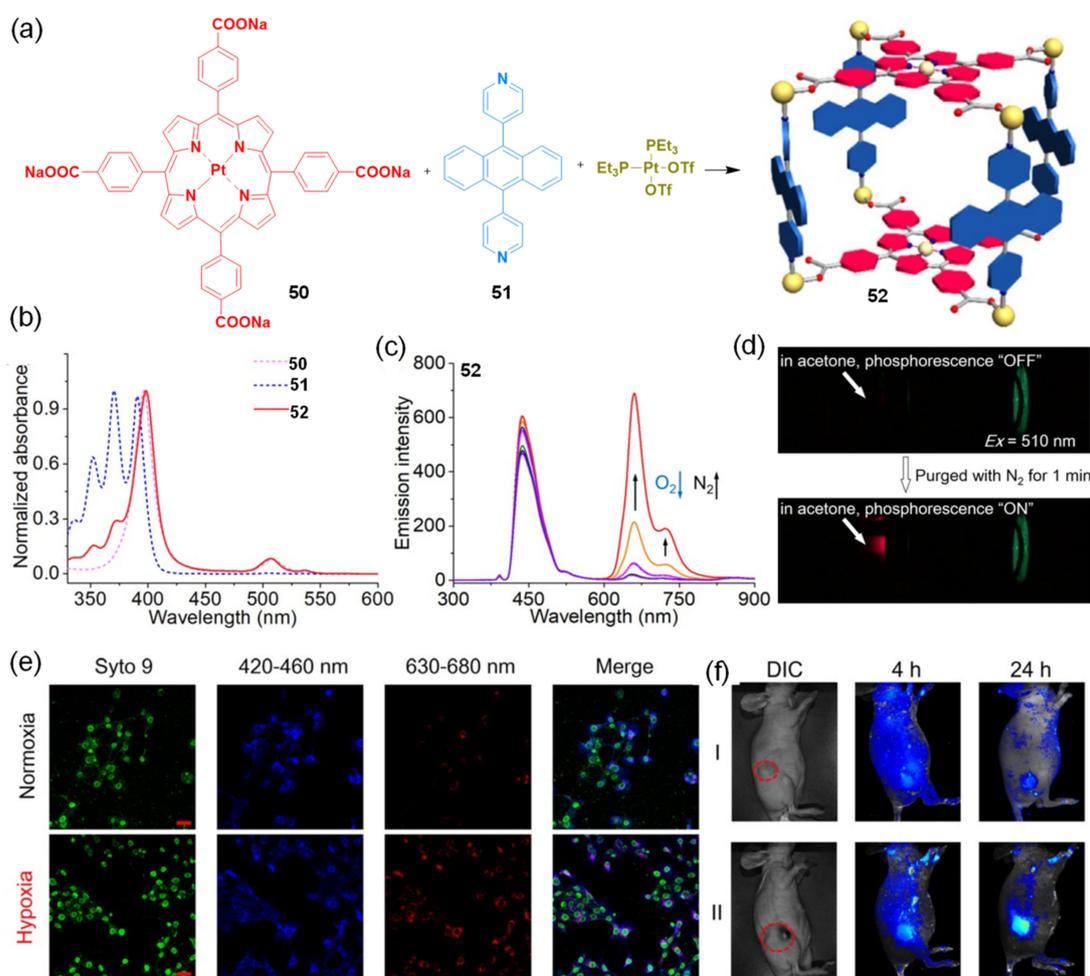

Figure 12. Dual-emissive Pt(II) metallacage and properties. (**a**) Synthesis of metallacage **52**. (**b**) Normalized absorption spectra of **50**, **51**, and **52**. (**c**) Emission spectra of **52** excited at 390 nm under O$_2$ or N$_2$ condition. (**d**) Photos of the emissions of an acetone solution of **52** in a quartz cuvette. (**e**) Confocal laser scanning microscopy of 4T1 cells stained by Syto 9 and the metallacage loaded nanoparticles. (**f**) In vivo fluorescent images. Reprinted with permission from Ref. [97]. Copyright 2020 John Wiley and Sons.

4. Conclusions and Outlook

　　　　Though the assemblies and functions of metallacycles and metallacages have been reviewed on many occasions [3,4,6–8,18], the specific topic on the anthracene-containing met-

allacycles and metallacages has not been surveyed in the literature. This review article summarizes for the first time the anthracene-containing metallacycles and metallacages with diverse shapes and sizes that are constructed by the facile and controllable coordination-driven self-assembly methodology. The modification of the anthracene backbone with different functional and/or directional moieties leads to the formation of corresponding supramolecular architectures with unique photophysical and photochemical behavior and a variety of confined cavities. In line with these properties, many of these structures have been explored in various applications such as host–guest chemistry, stimulus response, molecular sensing, light harvesting energy transfer and biomedical science. These results are expected to give insightful information to stimulate the design and preparation of functional coordination supramolecular assemblies.

Regarding the future development of the structural diversity and potential applications in this field, some aspects may be considered. On the one hand, the current functionalization of anthracene mainly focuses on the monomer-based derivatives. The construction of supramolecular scaffolds with ligands containing an anthracene dimer, or even a trimeric structure, remains under-explored, though a few of examples have proven that the anthracene dimer-based supramolecular scaffolds can exhibit sensitive stimulus-responsive fluorescence properties due to their expanded large aromatic conjugation and inter/intra molecular stackings. On the other hand, upgrading the current platforms toward practical applications is highly desired. For instance, in the case of the singlet oxygen-capture and -release systems, it is still challenging to achieve these functions under physiological condition, which is critical to the oxygen-independent photodynamic therapy of hypoxic tumors.

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