Light-Emitting Self-Assembled Metallacages

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ABSTRACT: Coordination-driven self-assembly of metallacages have garnered significant interest because of their three-dimensional layout and cavity-cored nature. The well-defined, highly tunable metallacage structures render them particularly attractive for investigating the properties of luminophores, as well as for inducing novel photophysical characters that enable widespread applications. In this review, we summarize the recent advances in synthetic methodologies for light-emitting metallacages, and highlight some representative applications of these metallacages. In particular, we focus on the favorable photophysical properties—including high luminescence efficiency in various physical states, good modularity in photophysical properties, and stimulus responsiveness—that have resulted from incorporating ligands displaying aggregation-induced emission (AIE) into metallacages. These features show that the synergy between carrying out coordination-driven self-assembly and using luminophores with novel photophysical characteristics like AIE could stimulate the development of supramolecular luminophores for applications in fields as diverse as sensing, biomedicine, and catalysis.

Keyword: supramolecular coordination complexes; coordination-driven self-assembly; aggregation-induced emission; metallacages; organometallic materials

1 INTRODUCTION

Molecular self-assembly is a ubiquitous process in nature and involves molecules with predefined recognition elements spontaneously forming well-defined ensembles through noncovalent interactions such as hydrogen bonds, van der Waals forces, hydrophilic and hydrophobic interactions, and coordination interactions [1,2]. Inspired by the elegant self-assembly processes found in nature, many efforts have been devoted to designing and synthesizing novel supramolecular ensembles for practical applications. Coordination-driven self-assembly, which relies on the spontaneous formation of coordination bonds between Lewis-acidic “acceptor” and Lewis-basic “donor” molecular building blocks, has evolved into a powerful methodology for carrying out rational, pre-designed self-assemblies of discrete supramolecular coordination complexes (SCCs) [3-5]. Functional SCCs can be readily prepared by introducing functional groups through pre- or post-self-assembly modifications [6-8]. Out of the plethora of reported SCCs, metallacages have shown particularly significant potential for various applications because of their favorable inherent properties. First, the modular nature of coordination self-assembly enables the precise spatial control over multiple and hetero functional groups within the three-dimensional supramolecular architecture, promoting new properties as a result of the synergy between the functional groups. Second, the presence of cavities in metallacages facilitates host-guest chemistry and has inspired the development of separation, sensing, delivery,
and catalysis applications of metallacages [9,10].

The development of luminophores with favorable photophysical properties is the basis for their applications in the areas of chemical probing [11], biological sensing and imaging [12], optoelectronic materials [13], and stimuli-responsive materials [14]. Studies on light-emitting SCCs stem from the use of rigid organic molecules as the building blocks for coordination-driven self-assembly. Many of these molecules have large conjugated systems and are inherently photophysically active, thus endowing the resulting SCCs with light-emitting properties. After these properties were first recognized, experimental and theoretical investigations that elucidated the photophysics of these SCCs were then conducted [15,16]. These results have provided the basis for preparing novel light-emitting metallacages that utilize their unique, tunable three-dimensional structures. The stoichiometries, spatial positions, and orientations of luminophores can be precisely modified and controlled when they are incorporated as components of self-assembled metallacages. Such modularity is highly challenging to realize using conventional covalent synthesis, but is nevertheless a goal worth striving for as it would promote the formation of interactions between the various components of the metallacages that may lead to the emergence of features and consequent applications that are not obtainable for an unincorporated luminophore. In addition, the almost limitless structural versatility of metallacages provides modularity over the photophysical profiles of the incorporated luminophore. These benefits are exemplified by studies on metallacages comprising luminophores with aggregation-induced emission (AIE) character.

AIE is a photophysical phenomenon displayed by some luminophores containing freely-rotating groups. These luminophores, often referred to as AIEgens, are weakly emissive or nonemissive in dilute solutions but become highly emissive upon aggregating. Discovered by Tang and colleagues in 2001 [17], this phenomenon is in sharp contrast to aggregation-caused quenching (ACQ), a photophysical phenomenon widely observed for conventional luminophores and in which luminescence efficiency significantly decreases in the aggregated state owing to excited-state interactions. Mechanistic studies on luminophores displaying AIE revealed that their low luminescence efficiency in dilute solutions could be attributed to the intramolecular motions of the freely-rotating groups that non-radiatively dissipate the excitation energy. This decay pathway is inhibited in the aggregated state, and thus a higher luminescence efficiency is observed for the AIEgens [18]. Manipulation of the intramolecular motions of the rotor units in AIEgens can be achieved both physically (by adjusting viscosity, temperature, or pressure) and chemically (by forming covalent or noncovalent bonds). In 2015, Huang, Stang, and coworkers observed that incorporating AIEgens into self-assembled metallacages resulted in high luminescence efficiency levels in both dilute solutions and in the aggregated states, thereby bridging the gap between the distinct AIE and
ACQ phenomena [19]. This uncommon photophysical phenomenon, in combination with the unique tunable structures of metallacages, has inspired further studies to be carried out on self-assembled AIE-active metallacages. They have emerged as new platforms for fabricating light-emitting materials for applications in molecular probing and sensing, energy conversion, bioimaging, and fabricating theranostic agents [20-27].

In this review, we summarize the current developments of light-emitting metallacages. The strategies used to prepare such metallacages are discussed, as well as their properties and consequent applications, which are enabled by the formation of metallacages through metal–ligand coordination interactions. Subsequently, AIE-active metallacages are highlighted. We expect that the illustrations provided here of their designs and applications should create more interest in this field, stimulate additional ideas from researchers, and further advance the development of light-emitting metallacages by the synergistic combination with AIE and other photophysical phenomena.

2 NON-AIE-ACTIVE LIGHT-EMITTING METALLACAGES

Studies on light-emitting SCCs originated from the use of rigid organic molecules as the building blocks for coordination-driven self-assembly. Many of these molecules include large conjugated systems and are inherently photophysically active, thus endowing the resulting SCCs with light-emitting properties. These early results motivated experimental and theoretical investigators to elucidate the photophysics of these SCCs, and provide the basis for developing light-emitting metallacages that display emerging photophysical properties. To date, researchers have employed luminophores as donor [28] or acceptor building blocks [29], or encapsulated guest molecules [30,31] inside the cavity of the metallacages (Table 1). The formation of a three-dimensional cage structure brings various molecular building blocks into proximity and thus facilitates their interactions. This feature can be exploited for energy transfer schemes, which are beneficial for sensing, delivery, and catalytic applications. However, it may also introduce low-lying dark states that decrease the luminescence efficiency and decrease the lifetime of the excited state. As a result, careful selection and arrangement of the molecular building blocks for self-assembly reactions are required to obtain metallacages with desired properties.

2.1 Luminophores as the donor building blocks

As a consequence of their straightforward nature and well-established photophysical properties, well-known luminophores are strongly considered for synthesizing light-emitting metallacages [32-34]. They are often modified...
with electron-rich recognition motifs and directly used as structural components for metallacages. Nitschke et al. selected and decorated widely used fluorescent dyes, such as BODIPY and pyrene with diamine and aldehyde motifs to afford metallacage building blocks [29]. Combining them was found to form metallacage 1 via the simultaneous formations of both dynamic covalent and metal-coordination bonds with Fe(II). Metallacages 1 exhibited fluorescence originating from BODIPY with a quantum yield ($\Phi_F$) value of 1.5% in acetonitrile. Adding acetate to the solution of 1 was found to lead to a 28-fold enhancement in fluorescence, which was probably due to the binding of the acetate anion inside the cavity of the cage, with this binding driven by electrostatic and anion-π interactions. Meanwhile, the presence of anion-π interactions could have perturbed the π orbitals of the ligand, which would explain the bathochromic shift of the absorption peak of 1. Based on this guest-responsiveness, Nitschke et al. further developed a white-light-emitting system by introducing perylene into the cavity of 1, which was shown to emit white light with a $\Phi_F$ value of 11% and CIE coordinates of (0.30, 0.36).
Table 1. Constituent building blocks and cartoon representations of non-AIE-active light-emitting metallacages.
In addition to organic luminophores, organometallic complexes have also been exploited as donor building blocks for self-assembling metallacages [35-37]. These complexes offered sophisticated structures and properties not displayed by pure organic ligands. Su and coworkers described a self-assembled Ru–Pd heterometallic coordination cage 2, wherein the Ru-containing donor was shown to endow the metallacage with light-emitting character [38]. Metallacage 2 was found to exhibit an emission band peak at 610 nm, corresponding to the Ru-centered triplet MLCT state. The intramolecular transfer of charge from Ru coordination complexes to Pd(Pyridine)₄ moieties enable metallacage 2 to be a light-harvesting system, endowing 2 with catalytic properties for photochemical hydrogen production.

Luminophores can also be introduced as pendant functional groups attached to the rigid structural components via covalent bonds [33,39-41]. Recently, Yang and coworkers prepared, via coordination-driven self-assembly, a new alkynylplatinum(II) bzimpy (3) containing metallacage 4. This metallacage displayed emitted light of different colors, from pale-yellow to orange-red, when placed in mixtures of water/DMF with different ratios [42]. Further investigation revealed this solvent-induced emission switch to be accompanied by an enhancement of the intensity of the emitted light as a result of changes in intermolecular Pt···Pt and π−π interactions.

2.2 Incorporation of rare-earth metals as the acceptor building blocks

Electron-deficient metal ions or metal complexes are necessary structural elements for coordination-driven self-assembly. In many cases, they induce the formation of a significant number of low-lying dark states, such as those resulting from ligand-to-metal charge transfer (LMCT) and that perturb the photophysical properties of the luminophores within the metallacages. In contrast, lanthanides display inherent light-emitting properties such as specific emission wavelengths, large Stokes shifts, and peripheral 4f electrons [43]. As a result, lanthanides are promising candidates for use in preparing light-emitting metallacages. A series of fluorescent molecular tetrahedrons were synthesized wherein the ligands with large absorption coefficients could act as efficient sensitizers for lanthanide ions via the "antenna effect" [44]. In 2011, Duan, He, and coworkers developed a neutral molecular tetrahedron 5, composed of Ce⁴⁺ ions and triphenylamine ligands, and observed an emission band for 5 at a wavelength 470 nm with a $\Phi_F$ value of 1% when excited at 350 nm in DMF [28]. Additionally, the well-defined cavity of 5 was shown to allow the encapsulation of 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxide (PTIO), a spin-labeling probe specific for NO only in living cells. The fluorescence of 5 could be quenched by PTIO but “turned on” in the presence of NO. Therefore, this work presents an example of the development of light-emitting metallacages and to explore their potentials as bioimaging agents.

To prepare metallacages that display long-wavelength absorption and emission, which are favorable for
biomedical applications, Sun, Han, and coworkers developed a europium tetrahedral cage 6, whose fluorescence could be induced by visible light through intraligand charge-transfer sensitzation (ILCT) [45]. The electron-deficient triazine unit within the ligand leads to high photosensitization efficiency, thus enabling the photoexcitation using light spanning from 280 nm to 430 nm with an emission $\Phi_F$ value of 10.2%. Furthermore, tetrahedral 6 was responsive toward $I^-\text{ and } Cu^{2+}$. $I^-$ behaved as a fluorescence quencher for 6 through the formation of H-bonding, which locked the cavity of 6 and thus hindered the exchange of the endohedral OTf$^-$ counterions. In contrast, owing to the weak cation–π interaction between triazine rings of ligands and $Cu^{2+}$, $Cu^{2+}$ enhanced the emission intensity by disturbing the ILCT process.

2.3 Constructions of host–guest systems

The cavity-cored nature of self-assembled metallacages endows them with guest-binding properties. By encapsulating guests with inherent photophysical properties, light-emitting supramolecular systems are obtained, wherein the metallacage provides a confined environment distinct from the bulk solution, leading to the emergence of novel photophysical phenomena. Careful design is often required to avoid undesirable interactions, both spatially and electronically, that quench the emission of light from the system. Fujita and coworkers designed an efficient light-emitting host-guest system ($\Phi_F = 17\%$) comprising the electron-deficient guest fluorophore 8 and metallacage 7 based on Pt(II) and triazine ligands [30]. The electron-deficient nature of 8 avoided the transfer of energy to the metallacage 7, thus preserving the light-emitting character. Moreover, the host-guest complex was found to be highly soluble in water and to prevent the aggregation of 8, hence prevent quenching of its emission by excited-state interactions. This pioneering work revealed the potential of metallacages to serve as hosts for fluorescent dye molecules. The work also paved a way to use metallacage-based host–guest systems for designing smart fluorescent materials.

To prepare supramolecular systems that emit light of various colors and with high efficiency, Yoshizawa and colleagues developed a host–guest system consisting of the Pt(II)-based metallacage 10 and various fluorescent dyes [31]. Their pioneering work demonstrated that the metallacages composed of an anthracene-cored ligand and Ni(II) or Zn(II) exhibited weak to strong emissions of blue light [34]. Based on this result, a range of well-known hydrophobic fluorescence dyes, including a BODIPY derivative (11), coumarin 153 (12), and Nile red (13), were chosen as guest molecules, and the host-guest encapsulation behaviors in water were examined. The resultant aqueous solution of 10ꞏ11 showed strong green fluorescence with a high $\Phi_F$ value of 48%, while 10ꞏ12 and 10ꞏ(13)$_2$ showed bluish-green ($\Phi_F = 25\%$) and red fluorescence ($\Phi_F = 32\%$), respectively. Moreover, the emission
behaviors of $\textbf{10} \geq \textbf{11}$ could be finely tuned upon co-encapsulation of anthracenes, phenanthrene, and pyrenes. This study represented a new approach for modulating the emission profile of metallacage-based host–guest systems [46].

3. METALLACAGES DISPLAYING AGGREGATION-INDUCED EMISSION PROPERTIES

3.1 Structural chemistry

Tetraphenylethylene (TPE) and its derivatives can be easily synthesized and can also be modified in various ways, and are hence widely used in constructing light-emitting materials with AIE properties [47,48]. In addition, to induce compact aggregation of the TPE molecules, various strategies have been developed to restrict the intramolecular motions of TPE molecules and thus activate their fluorescence emission. Covalent modifications of the TPE structure, such as those accomplished by adding bulky chemical groups and performing cyclization reactions, are extensively used to constrain the intramolecular motions [49]. Alternatively, noncovalent interactions such as hydrogen bonding, host–guest interactions, hydrophobic/hydrophilic interactions, and coordination interactions have also been employed [50-52]. Compared to other self-assembly approaches that often generate polymeric materials with limited solvent processability, such as metal-organic frameworks (MOFs), the self-assembly of metallacages provides structural rigidity that impedes the intramolecular motions of embedded AIEgens, yet yields a retention of good solubility due to their discrete nature. This unique feature allows for solvent-phase characterization and solution-based modularity over photophysical properties.
Table 2. Constituent building blocks and cartoon representations of AIE-active light-emitting metallacages.
The structures of representative AIE-active self-assembled metallacages are summarized in Table 2. Initial studies in this area focused on examining their “turn-on” luminescence in both solutions and aggregated states and their levels of responsiveness towards different solvents. Stang and coworkers designed and prepared a poly(ethylene glycol) (PEG)-decorated tetragonal prismatic platinum(II) metallacage 17 driven by the [2+4+8] self-assembly of tetra-(4-pyridylphenyl)ethylene (TPPE) 14, poly(ethylene glycol) (PEG)-decorated dicarboxylate ligand 15, and cis-(PEt3)2Pt(OTf)2 16 [19]. The multi-pyridyl ligand TPPE 14 was observed to not emit light in CH2Cl2 due to the free intramolecular motions of the TPPE group. However, embedding the nonfluorescent ligand into the rigid metallacages turned on the bright yellow fluorescence with a \( \Phi_F \) value of 10.8% in the CH2Cl2 solution. This sharp contrast between the emission behaviors of free TPPE ligands and metallacage 17 indicated that immobilizing the group within the metallacages is an efficient way to suppress the intramolecular motions, thus triggering the fluorescence. Moreover, as the relative amount of hexane in the solution was increased, the metallacage 17 gradually aggregated, and the \( \Phi_F \) value continuously increased from 10.8% to 51.3%, accompanied by a change in the emission color from yellow to pale blue. This observation suggested that metallacage 17 remained AIE-active, hence preserving emission behavior at high-concentration regimes through further restrictions on the conformational changes of 14 as a result of the aggregation. In addition, the decorated PEG chains were observed to endow metallacage 17 with high levels of solubility in a wide range of solvents from the relatively apolar CCl4 to the highly polar MeOH and water, leading to diverse visible emission colors. Notably, metallacage 17 exhibited an unusual emission of white light upon partially aggregating at room temperature in THF. The coordinates (0.313, 0.344) for this light in the CIE diagram were found to be close to those of pure white light (0.333, 0.333). The underlying mechanism of this partial AIE of white light from the discrete metallacages differs from that of conventional white-light-emitting materials, which in most cases require a mixture of two or more components. As a result, this scheme complements the current design for white-light-emitting materials and represents a promising approach for developing advanced optoelectronic materials. Overall, TPE-based metallacages with efficient emissions at both low and high concentrations and facile fluorescence tunability were demonstrated, which provides an emerging platform for light-emitting materials with modular photophysical properties.

The almost limitless modularity and tunability of the metallacage structures without significant synthetic penalty enable the incorporation of TPE with diverse structures into metallacages. Zhang and coworkers prepared highly emissive tetragonal prismatic metallacages 22a-c by carrying out a coordination-driven self-assembly of
benzoate-decorated TPE-core donors 18, platinum(II) acceptors 16, and three different dipyridyl pillars 19–21 [22]. Metallacages 22a and 22b showed strong emission bands centered at 493 nm, which originated from the TPE units, while 22c displayed two such bands, at 472 and 544 nm, which were assigned to TPE and BODIPY groups, respectively. All three of these metallacages strongly emitted light in polar aprotic solvents such as DMSO, with the highest $\Phi_F$ values of 25, 20, and 13%, respectively, suggesting that their emission behavior could be precisely tuned by altering the dipyridyl building block.

Instead of integrating dicarboxylate- or dipyridyl-containing ligands as pillars for metallacages, a series of drum-shaped metallacages with different counter anions (NO$_3^-$, OTf$^-$, and PF$_6^-$) were achieved by employing both AIE-active donor and acceptor building blocks [20]. Two TPE-core ligands 14 adopted a cofacial arrangement while the eight exterior freely rotating phenyl rings of four TPE-based organoplatinum donors 23 aligned around the prismatic core. Both donor and acceptor building blocks exhibited weak levels of fluorescence in CH$_2$Cl$_2$ solution. In comparison, structurally similar but counter anion diverse metallacages 24a–c displayed enhanced levels of emission relative to those of the precursors in dilute CH$_2$Cl$_2$ solution with the $\Phi_F$ values of 1.79, 3.07, and 3.36%, respectively, which could be assigned to the locking of nonemissive TPE ligands within the rigid metallacages. Moreover, upon modular aggregation, the emission intensities increased considerably as the hexane fraction was gradually increased to 90% in the mixed solutions, with the quantum yields reaching 8.87, 10.6, and 10.9% respectively. Scanning electron microscopy analysis of the aggregates in mixed solutions containing CH$_2$Cl$_2$ and hexane in a 1:9 ratio revealed well-defined nanospheres with average diameters between 150 and 250 nm. Therefore, the compact aggregation of these metallacages restricted the free intramolecular motions of the TPE moiety, explaining the aggregation-induced enhanced emission (AIEE) phenomena.

In addition to the tetragonal prismatic metallacage structures, a lantern-type emissive TPE-based metallacage 26 was synthesized by Sun and colleagues through a [4+2] self-assembly of ditopic TPE-based pyridinyl ligand 25 and Pd(NO$_3$)$_2$ [53,54]. These metallacages showed negligible emission in DMSO, probably resulting from the quenching effect induced by palladium and the nitrate counterion. However, upon addition of toluene, a rather inadequate solution for 26, the fluorescence of 26 showed an approximately 10-fold increase in intensity with a redshift of the maximal emission, indicating its AIE properties and the change of ligand conformation during aggregation. Moreover, the fluorescence of 26 can be turned on by encapsulating HCO$_3^-$ anions in its cavity, indicating an encapsulation-induced emission behavior. The formation of strong hydrogen bonding between the encapsulated anions and the inner surface of 26 was responsible for restricting the motions of the otherwise freely rotating TPE units, thus inducing their emission behavior.
Multiple luminophores can be introduced into a single metallacage system to induce sophisticated photophysical behaviors that originate from their interactions. Wang and coworkers described another elaborate design of light-emitting metallacages that integrated TPE and terpyridine (tpy) as ligands [25]. The final two types of metallacages, 29a and 29b, formed via the coordination-driven self-assembly of three TPE-based tpy ligands (27 or 28) and six Zn(II) ions. Compared to 29a, the constituent ligands of 29b contained an additional alkyne unit between the TPE and tpy units, increasing the ligand rigidity and extending the conjugation of the structure. The fluorescence spectrum of ligand 27 showed a single emission band centered at ~425 nm, which stemmed from the tpy units. In contrast to ligand 27, ligand 28 displayed two such bands, peaking at 430 nm and 550 nm, ascribed to the tpy and the TPE units, respectively, suggesting that the ligand with enhanced rigidity efficiently suppressed the rotation of the TPE units and thus triggered their AIE behavior. After coordinating with Zn(II), cages 29a and 29b each showed only a single emission band centered at 510 nm, attributed to TPE units. The emission of light from the tpy units was quenched because of the nonradiative decays through an MLCT process wherein the excited-state energy was transferred to the Zn(II) centers. The quantum yield of metallacage 29b in dilute acetonitrile solution (1.00 μM) reached 20.79%, 4.5-fold higher than that of 29a (4.67%) under the same conditions. This highly light-emitting nature of metallacage 29b originated from the structural rigidity that limited the rotation of TPE units in discrete modules rather than having originated from partial aggregation, hence representing a new strategy to exploit metallacages with strong emissions in dilute solutions.

The above examples describe the light-emitting metallacages prepared by locking the AIEgens within their rigid skeletons to constrain their intramolecular rotation, turning on their fluorescence. Besides this approach, another strategy inspired by the green fluorescent protein was designed to realize light-emitting metallacages by anchoring AIEgens within the confined cavities of metallacages to turn on their fluorescence [24]. Through coordination-driven self-assembly, 24 TPE units were precisely distributed either on the outer surface of each of metallacages 32a and 32b by exo-functionalizing the ligands, or within the inner confined space of each of 33a and 33b by preforming endo-functionalization. The absorption profiles showed lower absorption bands for the Pt12L24 self-assemblies than for their corresponding ligands, but similar intensities of the bands for the Pd12L24 self-assemblies and their corresponding ligands. This distinction may stem from the enrichment of the \( \pi \)-system by the comparatively strong \( \pi \) backbonding from the Pt center to the nitrogen \( \pi^* \), which lowers the excitation energy of donors in the Pt12L24 self-assemblies. Regarding their emission properties, both endo- and exo-functionalized metallacages showed fluorescence enhancements compared to their constituent ligands, attributed to the locally increased concentration of the TPE units. However, suffering from strong metal-to-ligand charge transfer, the
Pd_{12}L_{24} metallacage displayed a lower fluorescence enhancement than its Pt analogs. Notably, in dilute solution, the emission of the endohedral functionalized metallacage 33b was found to be much stronger than was that of the exohedral metallacage 32b. The endohedral functionalization induced a much higher local concentration of the 24 TPE units in the confined cavities than did the exohedral functionalization, and resulted in more restrictions on the intramolecular rotations of the TPE units and thus strengthened the emission.

3.2 Factors that influence the emission properties of AIE-active metallacages

The structural diversity and facile tunability of metallacage structures enable the systematic investigation of the factors that affect their photophysical profiles, including emission wavelength and intensity. These factors include external ones, such as solvents, temperature, and pressure, as well as internal ones stemming from the design of the metallacages, such as structural rigidity, counterions, and interactions with other components in the metallacage.

3.2.1 Solvent

The solubility of an AIE-metallacage in a particular solvent determines the physical states of the metallacage, and thus significantly influences its light-emitting properties. In general, addition of poor solvents leads to aggregation of metallacages, which can be visualized using microscopic techniques [19,20]. For instance, the average $D_h$ of metallacage 17 increased from 12.54 nm to 255 nm upon increasing the hexane content to 40%. Further elevating the hexane content to < 60% caused the aggregation of 17 into nanoparticles, which then evolved into regular nanospheres for hexane contents > 60% [19]. These morphology changes represented a tighter modular packing, imposing further restrictions on the conformational changes that can be made by the TPE moieties compared to the discrete rigid metallacages. As a result, the emission increased in intensity and was blue-shifted (Fig. 1a). At the same time, the $\Phi_f$ value at a hexane content of 90% was nearly 4.8-fold higher than that of the discrete entity in pure CH$_2$Cl$_2$, suggestive of their inherent AIE properties. An enhancement was also observed for 33b [24]. Increasing the hexane content in the CH$_2$Cl$_2$ solutions of these metallacages gradually enhanced the fluorescence, which was caused by the further suppression of the intramolecular motions of these TPE units upon their having undergone solvent-induced aggregation.
Figure 1. (a) Photographs of metallacage 17 in CH$_2$Cl$_2$/hexane mixtures with different fractions of hexane on excitation at 365 nm at 298 K ($c = 10.0 \mu$M). (b) Photographs of metallacage 17 in different solvents. Tol toluene, EA ethyl acetate, BA butyl acetate, Dio dioxane. Adapted with permission from [19]. (c) Plots of maximum emission intensity of 24a-c versus hexane fraction in CH$_2$Cl$_2$/hexane mixtures on excitation at 365 nm at 298 K ($c = 10.0 \mu$M). (d) Quantum yields of 24a-c versus hexane fraction in CH$_2$Cl$_2$/hexane mixtures. Adapted with permission from [20].

In addition to the molecular aggregation caused by poor solvents, the different conformations adopted in different solvents could vary the degree of conjugation of the TPE motifs, thereby changing the emission wavelength and intensity. Liu et al. observed that when gradually adding water to the acetone solution of metallacage 17 (but replacing eight OTf$^-$ groups with eight NO$_3^-$ groups to increase the solubility of the
metallacage in water and acetone), a stronger emission and a blue shift in the emission maximum occurred [55]. These changes are attributed to the hydrophobicity of TPPE ligands, which become twisted in water, reducing their degree of conjugation.

The solvent polarity is another key factor affecting the photophysical properties of AIE-active metallacages because of its influence on the many energy transfer processes between the components of the metallacages, especially those involving the transfer of charge between AIEgens and the metal centers. For example, metallacage 17 showed irregular differences in emission intensities and maximal emission wavelengths between solvents ranging from the relatively apolar CCl$_4$ to the highly polar MeOH and water (Fig. 1b) [19]. A comprehensive investigation revealed the mechanism behind these changes: the solubility of metallacage 17 in a specific solvent controls the photophysical properties. When the different solvent equally well dissolve 17, the solvent polarity is the dominating factor for the light-emitting behavior, due to this polarity influencing the MLCT processes within the metallacages. In this way, the higher polarity leads to a stronger MLCT process, thereby providing poorer fluorescence efficiency.

However, altering the building blocks of metallacages alters the fluorescence response to solvents of different polarities. Regarding metallacages 22a–c, they all were observed to exhibit strong emissions in polar aprotic solvents (DMF, DMSO, and acetonitrile), but moderate ones in less-polar aprotic solvents (acetone, CH$_2$Cl$_2$, and CHCl$_3$) as well as a polar protic solvent (MeOH) [22]. Although the two cases above were concluded to afford different fluorescent changes and mechanisms with respect to solvents of different polarities, it was confirmed that the emission properties of TPE-based metallacages can be efficiently tuned by changing the solvent.

3.2.2 Temperature

Temperature affects the intramolecular motions of TPE units and changes the fluorescence intensity stemming from their AIE behavior. In general, lowering the temperature of a TPE-based metallacage solution significantly limits the rotation of the TPE motifs, reducing the nonradiative decay and enhancing the emission of light. For example, when freezing acetonitrile solutions of 29a and 29b with liquid nitrogen to 77 K, their fluorescence intensities both increased [25]. However, a gradual increase in temperature was observed to lead to a decrease in the emission intensity of 17, but to no change in the emission wavelength. The partial dissociation of the metal-coordination bonds at elevated temperatures might be responsible for the weaker fluorescence [19,26].

3.2.3 External hydrostatic pressure

One prominent feature of TPE-based metallacages is their strong emission in the solid state, with this feature attributed to the full inhibition of intramolecular motions. However, upon imposing an external hydrostatic pressure,
the molecular packing changes and alters the fluorescence behaviors [26]. For metallacage 29b, its emission intensity increased as the pressure was increased from 0 to 1.10 GPa, but became quenched as the pressure was gradually increased further to 6.32 GPa [25]. Hence, increasing the pressure at low-pressure ranges may further suppress the intramolecular motion of the TPE units, but excessive pressures eventually leads to quenching because of the enhanced dipole-dipole interactions. This mechanical response of emission properties opens a promising route to creating highly emissive materials for applications as mechanochromic sensors.

3.2.4 Structural rigidity

The structural rigidity of an AIE-active metallacage is a major internal factor that influences its photophysical behavior [56]. For example, benefiting from the enhanced ligand rigidity resulting from introducing an additional alkyne group into 28, metallacage 29b showed a stronger fluorescence in dilute solutions than 29a [25]. Moreover, by mixing ligand 27 and 28 to fabricate hybrid metallacages, a series of assemblies with different ratios of 27 to 28 were furnished and followed a statistical distribution. The fluorescence profiles suggested the stronger emissions from the metallacages predominantly made up of 28, verifying the greater favorability of a higher degree of structural rigidity for the fluorescence of TPE motifs.

Another strategy for imposing a higher degree of structural rigidity is to shorten the distance between discrete metallacages in the aggregated state, where the TPEE units are fixed in a twisted, less conjugated state, and exhibit higher energy emissions [57].

3.2.5 Anion effects

In most cases, self-assembled metallacages are cationic in nature due to the use of metal ions or organometallic complexes as structural components. As a result, anions are necessary to balance the overall charge of the metallacage. Anions have been observed to significantly affect the solubility levels of SCCs, and in some cases even determine the structural outcome of the self-assembly. In the aggregated states, anions also influence the packing of supramolecular ensembles. For light-emitting metallacages, the effect of anions on the photophysical properties was examined. The fluorescence profiles for metallacages 24a–c (Fig. 1c), made of the same cage structure but different anions (NO$_3^-$, OTf$^-$, and PF$_6^-$), were investigated [20]. Although all of them displayed typical AIE behavior in a CH$_2$Cl$_2$/hexane mixture, the molar absorption coefficients, fluorescence emission intensities, and quantum yields of these metallacages followed the order of PF$_6^->$OTf$->$NO$_3^-$ (Fig. 1d). This phenomenon is attributed to the difference between the solubilities of the cages as a result of different counterions they have in their structures.
3.3 Applications of AIE-active metallacages

The versatile chemical designs of ligands have enabled researchers to produce structurally complex and functionally diverse metallacages. Regarding AIE-active fluorescent metallacages, extensive efforts have been devoted to developing such metallacages with novel photophysical properties and exploiting their potential applications as chemical sensors [19,22,25], functional emissive materials [22,58-60], light-harvesting systems [61,62], and theranostic agents [21,63,64]. In this section, the development and advances in the applications of AIE-active metallacages in diverse states ranging from discrete entities to multidimensional supramolecular materials are highlighted.

3.3.1 Sensors

Luminescence is a readily available spectroscopic approach for sensing applications. The fluorescence “turn on” behavior of many AIEgens provides the basis for their sensing applications, and incorporating AIEgens into metallacages not only preserves their desirable photophysical features but may also induce novel responsiveness due to the interplay between AIEgens and constituent building blocks [19,26,54]. For example, 17 exhibited a distinct emission color in the visible region when dissolved in structurally similar esters [19], and this emission was attributed to the inherent aggregation behaviors and charge transfer properties of 17 in the different solvents.

Apart from mechanisms involving the sensitivity of metallacages to solvent solubility and polarity, a mechanism involving a self-destruction of a metallacage was reported to operate for its sensing of amino acids (Fig. 2a). Since metallacage 22b is nearly nonemissive in MeOH/water (1/1, v/v), it can be used as a turn-on fluorescence sensor for thiol-containing amino acids through a self-destructive reaction [22]. The Pt-N coordination bonds of the metallacage can be disrupted by adding thiol-containing amino acids to the metallacage due to the Pt-S bonds they would form in this case being stronger than the relatively dynamic Pt-N bonds. Such a reaction was shown to release a TPE-based benzoate acid building block, which is highly emissive in MeOH/water (1/1, v/v) because of its poor solubility in this mixture. Specifically, upon gradual addition of glutathione or cysteine, the emission intensities linearly increased with the amino acid concentration in the range 0–80 μM (Fig. 2b and 2c), with detection limits of $1.87 \times 10^{-7}$ and $2.78 \times 10^{-7}$ M (S/N=3) for glutathione and cysteine, respectively. Furthermore, the metallacages can be regenerated by further adding Pt(II) acceptors. Therefore, metallacage 22b can be used as a “turn-on” sensor for amino acids. Such an interesting case provides a stimuli-responsive destruction mechanism and endows the cages with great potential for applications in controlled drug release and other bio-related systems.
Figure 2. (a) Cartoon representation of the self-destructive reaction for amino acid sensing. The emission intensities at 500 nm of 22b after 5 min upon the addition of increasing concentrations of (b) glutathione (Glu) and (c) cysteine (Cys) as a function of glutathione and cysteine concentration. Adapted with the permission from [22]. (d) Cartoon representation of the supramolecular fusion process and (e) time-dependent changes in the emission profiles of the mixture of 34 and square 35 (2:3 molar ratio) in DMSO. Adapted with the permission from [65]. (f) The metal-coordination self-assembly processes and the photoinduced supramolecule-to-supramolecule transformations. (g) Fluorescence emission spectra and (h) photographs of 38c after UV irradiation for different periods of time. Adapted with the permission from [66].
3.3.2 Monitoring the transformations of supramolecular structures

Inspired by natural processes such as molecular recognition, signal transduction, and allostERIC regulation, scientists are constructing synthetic supramolecular systems to mimic the biomolecular transformations with the aim of elucidating the mechanisms of these processes as well as fabricating materials with functions similar to those of biomolecules. However, the complexity of supramolecular systems presents a significant challenge for efficiently tracking their transformation processes in real time. Therefore, it has been considered highly desirable to develop a method to address the issue. For this purpose, Yan and coworkers proposed an efficient supramolecular transformation system: a TPE-containing trigonal prism 34 and its supramolecular fusion with a two-component molecular square 35 into a three-component molecular metallacage 36 (Fig. 2d) [65]. The entire process can be readily monitored by measuring the changes in the fluorescence signals of the supramolecular systems, due to the trigonal cage 34 exhibiting strong fluorescence via the restriction of TPE intramolecular motions upon coordination, but the transformation to the three-component cage as a result of heteroligation of the platinum center partially quenching the fluorescence as well as the redshifts in the emission maximum (Fig. 2e). According to the theoretical computations, the observed fluorescence quenching was attributed to the photo-induced electron transfer between the TPE and 4,4’-bipyridine motifs as the LUMO of the cage 36 are located on the bipyridine rings. Therefore, the results demonstrated the feasibility of real-time tracking of the supramolecular cage-to-cage transformation via the AIE phenomenon. This work showed an elegant synergy between AIE and supramolecular chemistry and can be used to provide unique avenues and perspectives for the efficient design, tracking, and characterization of complex, dynamic supramolecular systems with favorable photophysical properties for broad applications.

Recently, Han et al. explored the coordination chemistry of TPE-bridged tetrakistriazolylidene ligands and Ag metal centers as building blocks for the construction of supramolecular tetranuclear ([Ag₄L₂](PF₆)₄) 37a–b and octanuclear ([Ag₈L₄](PF₆)₈) metallacages 38c–f (Fig. 2f) [66]. The metallacages showed enhanced fluorescence due to the restriction of the TPE motifs upon coordination bond formation. Upon being exposed to UV irradiation in air, 37a–b and 38c–f underwent oxidative photocyclizations at the tetrakisarylethylene unit to yield complexes 39a–f, respectively. Note that all six of the products, i.e., 39a–f, shared the same tetranuclear metallacage structural plan despite the overall structures of the reactants 37a–b being quite different from the reactants 38c–f. These products 39a–f all included the 9,10-phenyl-substituted phenanthrene bridge, a feature responsible for immobilizing the tetrakistriazolylidene ligands and thereby quenching the fluorescence. Hence, due to the nonemissivities of the resulting metallacages, this in situ conformational transformation was monitored by the
having the fluorescence tracked, where the fluorescence continually weakened with prolonged irradiation time until it became fully quenched within 6 hours (Fig. 2g and 2h).

3.3.3 Multidimensional light-emitting materials

The above examples presented the promising fluorescence properties of the AIE-active metallacages in the discrete state. Given their unique photophysical properties, TPE-based metallacages have been regarded as building blocks for the fabrications of multidimensional superstructures or supramolecular soft materials with fluorescence tunability. These features have paved the way to exploiting highly emissive light-emitting materials. Sun, Stang, and colleagues reported such complex architectures with multicolor emissions based on the TPPE-core metallacages [59]. The metallacages were furnished by combining dicarboxylate ligand derivatives with various substituents (-sodium sulfonate, -nitro, -methoxyl, and -amine), TPPE, and cis-(PEt$_3$)$_2$Pt(OTf)$_2$. Finally, the obtained metallacages were used as building blocks and further assembled to form 1D, 2D, and 3D superstructures with broad emission wavelengths ($\lambda_{max}$ ranging from 451 to 519 nm) and tunable fluorescence features [60]. By using the “phase-transfer” co-assembly process, lysine-modified perylene was incorporated into metallacage-based microflowers, broadening the library of light-emitting superstructures. Similarly, chlorophyll-a and vitamin B$_{12}$ were introduced into the microflowers during the assembly process, and such procedures might be exploited in studies of energy capture and nerve repair in the future.

At the same time, the integration of fluorescent metallacages into supramolecular gels has attracted significant attention due to the well-defined hierarchical order and tunable emission properties of the resultant materials [58]. Yin and coworkers designed a fluorescent metallacage-cored supramolecular gel by achieving orthogonal metal-ligand coordination and host-guest interactions between the 21-crown-7 (21C7) and dialkylammonium salts [23]. The crown-ether-decorated tetragonal prismatic metallacage 40 was prepared by carrying out a metal-coordination-driven self-assembly of 18, 16 and linear dipyridyl ligands 41 (Fig. 3a). Subsequent addition of a bisammonium linker to 42 delivered a supramolecular polymer network (Fig. 3b). As a result, and specifically due to the incorporation of metallacages with AIE properties, the gel was highly emissive. Responsiveness to multiple stimuli involving heat and addition of KPF$_6$ as well as good self-healing properties were also observed here because of the dynamic natures of the metal coordination and host–guest interactions. Furthermore, the gel with metallacage cores displayed 10-fold higher storage and loss moduli than that without cores, indicating that the rigid metallacage enhanced the stiffness of the gel. This work not only enriched the functionalization approaches of fluorescent metallacages, but also paved the way for preparing dynamic yet robust supramolecular light-emitting materials.
Figure 3. (a) Self-assembly of 21C7-decorated metallacage 40 and (b) the formation of cross-linked supramolecular polymer network from metallacage 40 and bisammonium salt 42. Adapted with permission from [23]. (c) Self-Assembly of metallacages 45 and 46 with reverse FRET behavior. Adapted with permission from [26]. (d) Self-assembly of the metallacages 48 and (e) the formation of the artificial light-harvesting system with 48 and its application in a photocatalytic reaction. Adapted with permission from [61].

3.3.4 Light-harvesting system

Photosynthesis is widespread in living systems for the conversion of light energy to chemical energy. Fluorescence resonance energy transfer (FRET) represents the energy transfer behavior between different
chromophores through a nonradiative dipole-dipole coupling pathway. An efficient FRET system requires a favorable distance between energy donors and acceptors, and a good overlap in the fluorescence spectra between the emission of energy donors and the absorption of acceptors. In this regard, metallacages are good candidates for investigating FRET to mimic the natural energy harvesting process, due to their well-defined structures that precisely organize the constituent luminophores. Zhang and coworkers prepared two metallacages comprised of TPE-core benzoate 18 and two different dipyridyl pillars 43 and 44 by carrying out a coordination-driven self-assembly (Fig. 3c) [26]. Compared to pillar 43, 44 was functionalized with rhodamine B. The photophysical characterizations revealed a good overlap between the absorption band of 18 and the emission band of ligand 43. As a result, metallacage 45 exhibited a FRET from the 43-containing pillar building blocks to 18. In contrast, cage 46 showed FRET from 18 to the pillar 44, due to the adequate spectral overlap between the emissions of 18 and 44. Due to 45 and 46 being inherently emissive in dilute solution as a result of the restriction on the motions of the TPE-based ligands within the rigid skeletons, the reverse FRET process within the two cages led to distinct photophysical properties, which derived from the different solubilities as well as the distinct FRET efficiencies of the solvents. As such, these investigators demonstrated an efficient FRET system for metallacages wherein the fluorescence was finely tuned by altering the FRET behavior, providing a promising platform for developing artificial light-harvesting systems via mimicking the natural photosynthesis process. Therefore, they further constructed an artificial light-harvesting system in water based on FRET by making use of the light-emitting poly(ethylene glycol)-decorated tetragonal prismatic Pt(II) metallacage 48 as the energy donor molecule and eosin Y as the energy acceptor [61] (Fig. 3d). Note that eosin Y is a well-known photosensitizer used to catalyze C-H arylation of heteroarenes and cross-coupling. Metallacage 48 could self-assemble into micelles because of the hydrophilicity of the lateral poly(ethylene glycol) chains and hydrophobicity of the internal cavities of the metallacage (Fig. 3e). Because of the rigidity of the TPE units, metallacage 48 displayed a strong emission at 511 nm with a 23.8% quantum yield; this emission showed good spectral overlap with the absorption of eosin Y. As a result, an efficient light-harvesting system was achieved. This light-harvesting system exhibited a higher photocatalytic activity for the cross-coupling hydrogen evolution reaction than did eosin Y alone because of the additional utilization of light energy in the UV regions by metallacage 48 and the subsequent activation of eosin Y through the FRET process. This work represented an elaborate design of metallacages with complex structures and functions, and opened the avenue to constructing artificial photosynthesis systems with highly emissive TPE-cored metallacages.
3.3.5 Targeted theranostic agents

So far, platinum-based compounds such as cisplatin, oxaliplatin, and carboplatin have constituted a mainstay of clinical chemotherapeutics used to treat many solid tumors. However, severe side effects, poor specificity, and an inability to track the process of translocation have called for new agents that combine a targeting ability, diagnostic capabilities, and therapeutic functions. AIE-active metallacages show excellent potential as theranostic agents because metal ions, which are necessary elements in their structure, provide anticancer effects. Moreover, the high fluorescence efficiency levels of AIE-active metallacages in various environments allow for facile tracking and imaging [64] of their activities in biological systems.
Figure 4. (a) The self-assembly of metallacage 50 and the mPEG-DSPE and biotin-PEG-DSPE agents used for MNPs formation. (b) In vivo fluorescence imaging of nude mice bearing HeLa cancer xenograft following in vivo injection of MNPs. (c) In vivo tumor growth inhibition curves for PBS, oxaliplatin, carboplatin, cisplatin, or MNPs on the HeLa tumor model. (d) Scheme of MNPs transportation within blood vessels and accumulation in tumor tissue, followed by receptor-mediated endocytosis. Adapted with the permission from [21].
By carrying out multicomponent coordination-driven self-assembly, Huang, Stang, and coworkers prepared the highly emissive TPE-based metallacage 50 and utilized it as a theranostic platform for cancer therapy (Fig. 4a) [21]. Two variants of the 1,2-distearoyl-phosphatidylethanolamine/polyethylene glycol conjugate, mPEG–DSPE and biotin–PEG–DSPE, were used to form nanoparticles embedded in the metallacage to improve its circulation time and accumulation in tumors by taking advantage of the enhanced permeability and retention (EPR) effect. In vitro studies have shown the metallacage-loaded nanoparticles (MNPs) exhibiting excellent targeting capability and selectively delivering MNPs to biotin-receptor-overexpressing cancer cells via receptor-mediated endocytosis. In vivo fluorescence imaging (Fig. 4b) identified strong fluorescence signals that originated from the highly emissive MNPs in tumor tissues, confirming their diagnostic capability. Moreover, as shown in Fig. 4c, in vivo experiments demonstrated that the MNPs exhibited higher anti-tumor efficacy with lower toxicity than did free platinum anticancer drugs (oxaliplatin, carboplatin, and cisplatin), attributed to their EPR effect and active targeting ability (Fig. 4d).

Apart from physical encapsulation, modification of ligands for achieving specific recognition is another effective way to endow metallacages with targeting capacities. By introducing extra biotin moieties into the pillars of TPE-containing metallacages, Zhang and coworkers developed a light-emitting metallacage as a cancer-targeting theranostic that was specifically processed to selectively target cancer cells that overexpress biotin receptors [63]. Owing to the presence of biotin receptors on the HepG2 cells, metallacages with eight biotin groups easily attached to HepG2 cells, which further enhanced their endocytosis, as shown by the bright green fluorescence inside the cells. An MTT assay revealed that although their levels of cytotoxicity toward cancer cells were lower than that of the commercial anticancer drug cisplatin, they displayed a higher selectivity towards cancer cells that overexpress biotin receptors.

SUMMARY AND OUTLOOK

In this review, the recent achievements in the field of light-emitting metallacages have been summarized, including the principles for their rational design and efforts to explore their applications. The well-defined, tunable structures of metallacages have provided a versatile platform for taking advantage of their photophysical properties. Notably, combining metallacage chemistry with AIE has led to the development of AIE-active metallacages displaying favorable photophysical properties such as high luminescence efficiency and good modularity and having impressive relevance to a wide variety of areas such as sensing, energy conversion, and the development of
theranostic agents [15,67-69].

Nonetheless, many challenges remain, while several aspects are crucial for the future development of light-emitting metallacages. Current examples of light-emitting metallacages mainly involve noble metals and lanthanides. While the use of these metals is beneficial for establishing the scope and limitations of light-emitting metallacages, developing strategies for light-emitting metallacages constructed from abundant metals would be highly desirable for their scale-up and practical applications. Computational methods are expected to play an increasingly prominent role not only for predicting the structural outcomes of the self-assembly reactions but also for investigating the spatial and electronic interactions between the components within the metallacage structures. Systematic investigations of these interactions provide the basis for rationally designing metallacages with sophisticated photophysical behaviors that require a precise and synergistic combination of multiple photophysically active building blocks. Specifically with respect to the AIE-active metallacages, the rapid development of AIE offers continuous inspirations for the use of advanced AIE-active metallacage materials. The use of AIEgens with properties such as multiphoton absorption, red/near-infrared emission, enhanced solubility, and biocompatibility — that is, properties more desirable than those of the extensively studied TPE — is expected to result in the development of supramolecular luminophores with broader potentials. Combining AIEgens with metallacage-cored supramolecular polymers might lead to dynamic polymer materials that respond to diverse chemical and physical stimuli by emitting light. The possibilities of using AIEgens in photodynamic, photoacoustic, and photothermal therapies would permit an expansion of the range of biomedical applications of AIE-active metallacages. Overall, with the rapid advances of both coordination-driven self-assembly and luminophores with favorable photophysical properties such as AIE, it is expected that research on light-emitting self-assembled metallacages will continue to flourish.

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**CONFLICT OF INTEREST**

Conflict of interest statement. None declared.
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