Metallacycles, metallacages, and their aggregate/optical behavior

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Abstract
Since the first metallacycle was prepared by Verkade in 1983, various metallacycles and metallacages with controllable nanoscale shapes and sizes have been created by modular design and synthesis, showing unique properties that enable applications in catalysis, sensors, and biomedicine. Everything from their photophysical properties to their antitumor activities and catalysis was found to be influenced by their suprastructures. Thus, it is necessary and helpful to develop a systematic understanding of the relationships among the micro/nanostructures, the resultant photophysical/chemical properties, and the corresponding applications. In this review, we summarized the latest progress in this area in approximately the past 5 years.

KEYWORDS
aggregation, coordination-driven assembly, emission

INTRODUCTION

Metal-organic complexes (MOCs), including metallacycles and metallacages, are discrete and well-defined molecular entities formed by the coordination-driven assembly (CDSA) of metal centers and ligands. By using platinum, palladium, iron, zinc, and silver as the metal centers, Stang, Fujita, Mirkin, Raymond, and others developed different strategies for constructing MOCs. As a result, MOCs with tunable geometry and size can be designed and synthesized. To date, two-dimensional triangular, square, rhomboidal, and hexagonal structures and three-dimensional tetrahedra, dodecahedra, and other polyhedron have been prepared. Compared with their precursors, the resultant MOCs have shown improved properties in terms of catalysis, sensing, emission, and host–guest behaviors and are more suitable for biomedical applications.

The concept of aggregation-induced emission (AIE) was first defined by Tang et al. in 2001. Since then, great advances have been made in this field, and AIE has been used in related systems, such as nucleic acids and cycloexetrins. Additionally, the AIE lumogen (AIE-gen) has been used in the construction of MOCs. With the development of this field, work concentrating on the optical behaviors of MOCs and their possible applications has attracted increasing attention. To improve the photophysical properties, various lumiphores have been used as functional units to construct coordination interaction-based suprastructures with tunable emissions. To date, anthracene, pyrene, phenanthrene, porphyrin, and tetra-(4-pyridylphenyl)ethylene (TPPE) have been used as skeletal or functional groups (Scheme 1), leading to the formation of MOCs with emission wavelengths ranging from blue to green to red and near-infrared regions. Normally, after CDSA, the resultant MOCs show a distinct redshift and lower quantum yield (compared to the precursor) in both the absorption and fluorescence spectra due to metal-ligand charge transfer (MLCT). The controllable optical properties also make MOCs good sensors. To enhance the stability of MOCs in vivo, an increasing number of MOC-based nanoparticles/micelles have been used in antitumor research. In contrast to the successful production of small molecules and macromolecule-based functional materials by aromatic interactions, hydrogen bonds, and other weak interactions the investigation of MOC-based functional materials is still in its infancy. For the purpose of broadening MOC applications, other functional building blocks materials formed by MOCs with tunable suprastructures were prepared. To date, MOC-based hollow nanospheres, micro/nanofibers, microneedles, octahedrons, gels, and liquid crystals have been prepared. Most recently, a macroscopic centimeter film was prepared from TPPE-based metallacages, representing a new strategy for MOC preparation.

In this review, the heavy-atom effect, ligand conformation, solvent polarity, substituent effects, geometry of MOCs, and other factors that play key roles in tuning the absorption and emission properties will be discussed in terms of recent progress.
By utilizing the relationships between these factors and the resultant optical properties, MOCs can be designed to serve as light-emitting materials, light-harvesting systems, information-encryption media, isomerization controllers, protein-delivery carriers, bacterial imaging materials and antibacterial agents (Scheme 2). Most importantly, as theranostic agents, MOCs have been applied in the fields of chemotherapy, photochemotherapy, photodynamic therapy, NIR-II theranostics, etc.

**AGGREGATE/OPTICAL BEHAVIOR OF PT-CONTAINING METALLACYCLES/CAGES**

The factors that influence photophysical properties

**Heavy-atom effect**

Normally, after coordination, metallacycles/cages show a red-shift compared with the corresponding precursors; for example, in platinum-containing anthracene/phenanthrene $\text{Pt}^{3/4}$ (Figure 1A,B), excitation can be realized in different ways, as shown in Figure 1C. Through a nonemissive process, $\text{Pt}^{3}$ can be excited to higher excited states and then can relax to the first excited state. Subsequently, by an irradiative process, $\text{Pt}^{3}$ can decay from the first excited state to the ground state. $\text{Pt}^{4}$ can be excited to $\text{S}_{n}$ (fluorescent states) through another pathway and decay to the ground state. Fluorescence spectra can be used to measure the decay of $\text{Pt}^{4}$ from the bright state to the ground state. $\text{Pt}^{4}$ decays from dark states to the ground state through the nonradiative transition pathway. Thus, the fluorescence lifetimes of $\text{Pt}^{4}$ are shorter than those of phenanthrene. Moreover, because of the introduction of Pt, the intersystem crossing (ISC) effect can be enhanced as the low-lying single excited states of $\text{Pt}^{3/4}$ move to the low-lying triplet state. Thus, compared with the precursor anthracene/phenanthrene, $\text{Pt}^{3/4}$ has short lifetimes. For example, the average fluorescence lifetime values of $\text{Pt}^{4}$ decreased with the increase in emission wavelength. For the precursor phenanthrene, the lifetime values remained constant with the increase in emission wavelength.
In dichloromethane (DCM), after the incorporation of Pt, the absorbance peaks of anthracene move from 326, 341, 359, 378 nm to 356, 375, 396, 418 nm (Pt 3), respectively. The corresponding emission peaks move from 381, 402, 426, 452 nm to 385, 404, 428, 453 nm (Pt 3), respectively. Moreover, Pt enhances the spin-orbital coupling effect of the ligands, increasing the ISC rate/intramolecular charge transfer (ICT) effect. Fluorescence quenching occurs as a result. The quantum yield changes from 0.17 ± 0.01 to 0.043 ± 0.008. A redshift can be observed in Pt-containing phenanthrene, and as reported, the absorbance peaks of phenanthrene move from 276, 283, and 295 nm to 291, 309, and 323 nm, respectively. The corresponding emission peaks move from 335, 353, and 369 nm to 390, 388, and 480 nm, respectively. Additionally, the quantum yield decreases from 0.13 ± 0.01 to 0.011 ± 0.002.50a

A similar redshift phenomenon can be observed in the TPE-based system (Figure 1D). As shown in Figure 1D, the maximum absorbance peak of L13 is located at 310 nm, and a redshift (ca. 23 nm) of the energy band is observed after the introduction of Pt (Pt5). The corresponding -NO3 (Pt6) and -OTf (Pt7) compounds show slight blueshifts (Figure 1E).50b In addition to the investigation of the heavy-atom effect after the introduction of Pt into the Pt acceptors, the optical property differences between the ligands and the as-prepared metallacycles are also revealed. Taking anthracene-containing ligands (L5) and metallacycles (M1, M2) as examples, M1 forms by the coordination between L5 and Pt 8 through [3+3] assembly, and M2 is obtained from the [6+6] assembly between L5 and Pt9 (Figure 1F). As shown in Figure 1G, L14 shows a broad absorption band at approximately 370 nm in tetrahydrofuran (THF). After metal-ligand bond formation, the absorption peaks of M1 and M2 show bathochromic shifts of approximately 50 nm. In addition, clear molar absorption coefficient enhancements are observed.28a In another example, a hexagonal prism (M3, M4) is formed by the integration of L14/9 with Pt(II) acceptors (Figure 1H). After the formation of the prism, redshifts of approximately 41 nm (M3) and 47 nm (M4) are observed in DCM (Figure i). Additionally, the emission peaks of M3/4 show bathochromic shifts. The emission maximums for L14 is 448 nm, for M3 is 535 nm. Compare with the ligand L9 (472 nm), the l_{em, max} of M4 is 517 nm.50c

Metallacycle/cage conformation, solvent, substituent, and geometric effects

The functional units in MOCs have been found to adopt different conformations from the free molecules (in solution)
because the geometric adjustment changes the photophysics of the functional unit; as a result, the orbitals involved in the transitions between ground and excited states can be changed.\textsuperscript{51a} Taking \textit{L15} as an example, as shown in Figure 2A, diphenyl sulfone moieties, phenothiazine, and pyridyl groups are used as the linkers for coordination. By using \textit{L15} as a building block, \textit{M5} and \textit{M6} were synthesized by CDSA. Then, the methylpyridinium salt \textit{L16} was prepared to compare the effects of connecting motifs on optical properties. Because of the free intramolecular motion of phenothiazine moieties, \textit{L15} exhibits the AIE phenomenon. However, in contrast to the lower radiative decay rate of free \textit{L15} or the non-self-assembled analog \textit{L16}, the corresponding MOCs display a high decay rate by the activation
of the emissive transition, which exhibits a higher radiative decay rate ($k_r$) than those in the free luminophore or in its non-self-assembled analog. The corresponding optimized geometry (Opt) and self-assembly geometry (SAGeo) of L15, Opt of M6 and L16 are shown in Fig. 2B.51a

The functional unit in MOCs has been found to adopt different geometries from the free molecule. In addition to the steric conformational effect, intermolecular hydrogen bonding also plays an important role in the ICT fluorescence of platinum complexes. As shown in Figure 2C, Pt12 was synthesized, and its optical properties in different solvents were investigated. The geometric and electronic structures of Pt12 in the ground and excited states and the corresponding complexes (formed by hydrogen bonds) were revealed by the density functional theory/time-dependent density functional theory (DFT/TDDFT) method. Figure 2D shows the optimized geometric structures of Pt12, Pt12/ethanol, and Pt12/hexanol complexes. Figure 2E displays the different fluorescence emission mechanisms of Pt12 in solvents with and without hydrogen bond formation. In non-hydrogen-bonding solvents, Pt12 can be excited directly to the S2 state (fluorescent state). In addition, through fluorescence emission, Pt12 can relax from the fluorescent state to the ground state. Moreover, by nonradiative transition, Pt12 can decay from the fluorescent state to the nonfluorescent state, which has a lower energy level. Hence, because the nonfluorescent state is lower in energy than the fluorescent state, the nonradiative transition competes with the fluorescence emission of Pt12 in hexane. Thus, the lifetime of Pt12 in hexane is short. In solvents that can form hydrogen bonds, the energy level of the ICT state can easily be lowered. Thus, the fluorescent state of Pt12 in hexanol and ethanol solvents is lowered, enabling direct excitement to the fluorescent state of the lowest energy level. Because of the competition between nonradiative
transitions (fluorescent state to the nonfluorescent state), the fluorescence lifetimes of Pt 12 in hexanol and ethanol are longer than in hexane. Figure 2F shows the orbital energy levels of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs), in addition to the energy gaps between these orbitals for Pt 12 and the hydrogen bond complexes. The intermolecular hydrogen bonds raise the HOMO energy level and lower the LUMO energy level. Thus, the energy gaps between the HOMOs and LUMOs are reduced from 4.49 eV to 4.28 (Pt 12/hexanol) and 4.27 eV (Pt12/ethanol).

The solvatochromic properties of M7 and M8 in different solvents can be examined as examples Figure 3A), and the two metallacycles show various emissions due to changes in the pillars and solvent polarities. The absorptions of M7 and M8 exhibit changes in intensities and shifts in wavelength. In addition, the emissions of the two metallacycles show irregular changes as the solvent polarity increases. The emission intensities of M10 in THF and dioxane are high, and the intensity decreases as the polarity increases (EA, methanol, and water). M8 shows similar photophysical properties except for the intensity differences in CCl4 and EA, which might be caused by polarity changes. As shown in Figure 3A (bottom), both M7 and M8 show long-wavelength emission with tunable colors upon changes in the solvent (polarity). In addition to the emission properties defined based on the anthracene-based rectangle, different photophysical properties can be observed by changing the geometry (from single metallacycles to bimetallic complexes) and the luminophores (from anthracene to AIE-active TPE). Likewise, M9 and M10 show distinct changes in emission and color with changes in solvent polarity and solubility. As described in Figure 3B, both the intramolecular rotation of the benzene rings in the ground state and the double bond in the excited state are restricted by the bicyclic structure; M9 shows high emission intensities in DCM, EA, CHCl3, MeOH, dioxane and THF (ΦF = 21.9-82.3%). It should be noted that in MeCN, M9 is brown in color with a peak ca. 606 nm (ΦF = 21.9%), and in EA, M9 shows a yellow color with a peak at 557 nm (ΦF = 59.9%). In DCM, MeOH, and MeCN, the M10 emission is similar to that of M9, whereas the intensity of M10 in THF is higher than that of M9.

This difference is most likely caused by differences in the pillars. Based on these observations, the optical properties of both M9 and M10 show regular changes as the solvent polarity increases. Depending on the solubility and aggregate behaviors, these bicyclic structures show green, yellow, and orange emissions. Taking the solubility effect as an example, the yellow emission with ΦF = 59.9% and 68.4% in poor solvents (EA and dioxane) decreases to a lower ΦF value in normal solvents and then weakens to ΦF = 21.9% (MeCN) in good solvents. In a complicated photophysical system, the steric geometry also plays a key role in tuning the emission (Figure 3C). By using triphenylamine and anthracene moi eties as functional units (L7), two trigonal prismatic metallacages (M11 and M12) were prepared. The photophysical properties of L7, M11, and M12 in acetone were compared, and they all showed characteristic π-π*-dominated transitions at 355, 378, and 395 nm, respectively. However, both cages showed higher absorption intensities than the ligand. Additionally, a slight redshift of a few nanometers was observed. These observations suggest that the chromophores in the cage may not produce a strong complexation system in the absorptive excited state. The unchanged absorption spectra in toluene, EA, THF, dimethyl sulfoxide (DMSO), and chloroform suggest that the excited state accessed through vertical excitation is similar to the ground state. In less polar solvents, the slight band broadening at approximately 395 nm may be caused by the weak low-energy transitions containing Pt. L7 shows distinct solvatochromism, and the emissive peak shifts to longer wavelengths from toluene (454 nm) to DMSO (543 nm). As a result, the color changes from dark blue to yellow (λmax = 365 nm). A similar effect is also observed in the corresponding cages, with a smaller redshift than those of the precursors. As shown in Figure 3C, only changes from blue to yellow changes are observed. The smaller redshift may be caused by the fact that the cage also exhibits a redshift (compared with L7) resulting from the restricted anthracene rotation in M11 and M12.

Tunable emission in binary systems

For TPE-based metallacages (Figure 4A), similar solvent effects are also observed in different solvents because of polarity changes and aggregation-induced electronic structure changes. Figure 4B shows color changes with the addition of solvents. In toluene, a cyan color is observed (ΦF = 81.6%). As the solubility increases, ΦF decreases significantly. In good solvents (methanol and chloroform), ΦF weakens to 29.8% (chloroform) and 7.79% (MeOH). Thus, it is deduced that for similar solubilities, the higher the polar environment is, the lower the light-emitting efficiency. Pillar modifications influence the spectra. In dioxane, M14 emits strong blue light, and M13 emits cyan light. It should be noted that M14 emits white light in THF. Time-dependent fluorescence was used to track the origin of this white color. M14 showed a yellow emission (550 nm) at the initial time (zero minutes), and the peak blueshifted to 450 nm after three minutes (aggregate state). During this color-change process, the band covered almost the whole visible spectral region, endowing the solution with an overall white-light emission. This experiment supports the idea that the white emission originates from the mixture of yellow and blue light. The CIE diagram shows that the white emission is close to that of pure white light (0.333, 0.333) (Figure 4C, right). Substituent effects also influence the tuning of the emission region of metallacages. In DCM, EtOH, MeOH, dioxane, EA, and THF, with substituents with varying electrical properties from –SO3Na to –NH2 (L21-24), the emissions of the corresponding metallacages showed changes to multicolor emissions (Figure 4D-E). As a result, wavelengths ranging from 35 nm (–SO3Na) to 83 nm (NH2) were observed. The color regions in the CIE diagrams changed from narrow to wide as the substituents changed (Figure 4F).

Applications of emissive MOCs

Emissive MOCs serve as sensors for detecting temperature, pressure, and halogen content

By utilizing various dicarboxylate pillars, metallacycles with tunable emissions at different temperatures can be observed.
At low concentrations (≤ 10 μM), because of monomeric emission, M19 and M21 show almost the same emissions as M20 recorded in acetone. At higher concentrations (> 600 mM), distinct emissions from M19-21 are observed. Figure 5A shows the longest emission wavelength for each of these MOCs. The longest-wavelength emission peaks of M19-21 shift sharply at concentrations from 10 μM to 200 μM but remain almost the same at higher concentrations. Metallacycles with different sizes show different aggregation behaviors, which might stem from the differences in free volume fractions in the aggregated state. A predictable emission profile range from 476 to 581 nm can be realized.
by tuning a rhomboid metallacyle (M22-26). With increasing electron-donating ability from –NO₂ to –NH₂, the emissions show a substantial redshift (Figure 5B). The effects of counteranions on the optical properties of the metallacycles/cages (M27-32) were investigated, and both the emission intensities and quantum yields of M27-29 in DCM followed the order PF₆⁻ > OTf⁻ > NO₃⁻. As displayed in Figure 5C, because rotations of the pendant phenyl rings lead to nonradiative decay, M27-29 each show weak emissions at 485 nm. In contrast, because of the locking of nonemissive TPE in metallacages, M30-32 show strong emissions at 500 nm. Based on this information about the emissions, the AIE characteristics can also be used to characterize the dynamic supramolecular
transformation. M33 shows strong fluorescence in dilute DCM because of the restriction of TPE after cage formation. The quantum yields of M33 and M34 were measured as 28.8% and 0.80%, respectively (Figure 5D). The steric position of TPE can also be used to tune the rotation restriction degree and thereby control the emission. As shown in Figure 5E, because of intramolecular rotations of the pyridyl and phenyl rings, L25 and L26 were nonradiative in DMSO. The emissions of M36 show a peak at 465 nm, whereas endohedral functionalization (M38) shows a different emission.

Changing the ratio of solvent in the binary system is another way to tune the emission of metallacycles/cages. Taking M39 in acetone/hexane solution as an example, the color can be tuned from blue to dark blue as the hexane content increases. As displayed in Figure 6A, the intensity shows no substantial change at hexane ratios from 0 to 50%. When the hexane content increases to 60%, the emission peak shows a blueshift from 445 to 437 nm; at the same time, the intensity decreases sharply. The dark blue emission is maintained as the hexane ratio increases to 90%. AIE-active 9,10-di(4-pyridylvinyl)anthracene (DPA) was locked into M7/M8, and M7 showed pale orange fluorescence with a peak at 576 nm in pure acetone, with a slight blueshift of ca. 6 nm as the hexane content increased to 50%. The emissions of both M7 and M8 in acetone with different hexane contents were also recorded (Figure 6B). During the corresponding change to 70%, a redshift of 16 nm was observed. Moreover, both the intensity and quantum yield increased (Figure 6B). Based on transmission electron microscopy (TEM) and dynamic light scattering (DLS) characterization, the formation of aggregates is proposed to be responsible for the wavelength shift. M8 shows similar properties in acetone/hexane mixtures. The other example is TPPE-containing metallacages in a DCM/hexane mixture. As shown in Figure 6C, both M13 and M14 show bright yellow emissions at peaks of 555 nm ($\Phi_F = 23.2\%$) in pure DCM. For M13, the peak blueshifts by approximately 25 nm when the hexane content increases to 30% and then substantially blueshifts from 555 to 458 nm when the hexane content increases to 50%; at the same time, the emission color changes from yellow to blue. When the hexane ratio is further increased to 90%, the color changes from blue to cyan, with a $\sim 50$ nm redshift. As a result, the emission region of M13 can be tuned from yellow to blue to cyan. For M14, the emission intensities are almost the same when the hexane content is 40%.

**FIGURE 5** (A) Plots of the maximum emission wavelengths for acetone solutions of M19-21 as functions of concentration; (B) chemical structures of M22-26 and emission profiles for M22 (blue), M23 (turquoise), M24 (green), M25 (yellow), and M26 (red); (C) fluorescence emission spectra of M27-32 in DCM; (D) fluorescence spectra of M33 and M34 in DCM; and (E) chemical structures of L25, L26, and M35-38 and fluorescence spectra of M35-38 in DMSO. Copyright 2013, 2019 American Chemical Society. Copyright 2020 Wiley-VCH.
However, the intensity increases sharply when the hexane content is above 50%. At the same time, the emissions undergo a blueshift of ca. 63 nm, and the color changes from yellow to yellowish green and then pale blue. With a hexane ratio of 90%, the quantum yield is almost 4.8-fold larger than that of the monomer. The difference between M13 and M14 might be caused by the introduction of polyethylene glycol (PEG) chains, which endow M14 with more tunability. Thus, the wavelength of M13 undergoes a blueshift and then a redshift as the hexane content increases (caused by the competition between AIE and MLCT), whereas M14 undergoes a blueshift as the hexane content increases. In addition to changing the modular parts (face and pillar), solvents, and geometries, the introduction of other molecules into the
system is another choice for manipulation.\textsuperscript{53a} Taking M9 and M10 as examples (Figure 6D), only changes in fluorescence intensities (no distinct wavelength shift) can be obtained by interactions with perylene, suggesting the absence of any ground-state interactions between bicyclic structures and perylene. These results imply that a photoinduced electron-transfer process or a nonradiative energy loss occurs in the coassembled system (M9/M10 and perylene). It should be noted that white-light-like emission is observed when the ratio of M9/M10 and perylene is equal to 2.

The CIE diagram shows that the emission in DCM is close to pure white light, indicating the potential for fabricating white-light materials. A host-guest system (formed by M40 and bis-ammonium salt G1) is another example with tunable emission upon concentration changes. At high concentrations (>0.5 mM), orange emission is observed, and at lower concentrations (<25 μM), blue emission is observed. This result most likely occurs because M40 serves as the AIE fluorophore and bis-ammonium salt is used as the aggregation-induced quenching (ACQ) unit. M40 shows orange emission because the AIE lumiphore plays a dominant role at high concentrations.\textsuperscript{56}

G1 shows a blue color due to the ACQ effect at low concentrations. Thus, at 29 μM, emission covering the entire visible wavelength region is realized based on orange and blue emission. As a result, white-light emission is observed (Figure 6E). M41 is decorated with six pillar\textsuperscript{2} arenes, which have been found to enhance the coaggregation between G2 and pillar\textsuperscript{2} arenes synergistically; this, in turn, results in a dramatic increase in intensity. The fluorescence intensity and quantum yield of M41\textsuperscript{2}G2 in acetone/water mixtures increase when the water content increases to 70%. The inset in Figure 6F shows a fluorescence photograph of an M41\textsuperscript{2}G2 complex in an acetone/water mixture (95% water).\textsuperscript{17a}

Temperature is another factor that can be used to tune emissions. As an example, the emission spectra of M20 are displayed in Figure 7A. Aggregation can be induced by decreasing the temperature; as a result, a redshift is observed in the emission, accompanied by the appearance of a new peak at a longer wavelength. As the temperature decreases from 50 to 10°C, the ratio I\textsubscript{543}/I\textsubscript{454} increases, which can be easily tracked by observing the emission color change from blue to green and then yellow. The above results indicate that aggregation in the ground state occurs as the temperature decreases.\textsuperscript{53b} M1 also shows temperature-responsive properties, as shown in Figure 7B. In DMF, the emission intensity of the hexagon at 520 nm decreases significantly when the temperature increases from -20 to 30°C.\textsuperscript{28a} However, the emission peak shifts from 530 to 490 nm when the temperature increases to 70°C. The changes can be tracked by observing the green to cyan color change. Rhomboidal M42 is sensitive to temperature. As shown in Figure 7C, M42 (1 μM) displays a broad emission band at 482 nm in acetone. Moreover, the emission color changes from cyan to yellow with a bathochromic shift as the temperature changes from 77 to 297 K.\textsuperscript{28b}

In addition to this temperature-responsive tuning, this emission can be tuned by adjusting the pressure, as shown in Figure 7D. Under ambient conditions, M43 and M44 show pale green and red emissions with peaks at 500 and 605 nm, respectively.\textsuperscript{53d} Then, the emissions redshift to 620 nm and 700 nm as the compression increases to 14.1 GPa and 12.1 GPa (Figure 7E), respectively.\textsuperscript{53d} The process can be reversed at least 10 times. This mechanochromic response might be caused by the molecular packing mode change that occurs during the pressure changes, resulting in pillar tilting and TPE moiety planarization and affecting the dipole-dipole coupling in the metallacages. The stimuli-responsive behaviors of the M45-based film (Figure 7F) are also tested using halogen ions.\textsuperscript{64}

As shown in Figure 7G, the emission color changes from yellow to blue within a few seconds of the addition of halogen ion to the film. It should be noted that the change can be reversed by the addition of AgOTf, which regenerates the metallacycles inside the film. It has been found that the switchable emission process can be repeated at least three times. In addition to the ability to detect halogen, the film is sensitive to picric acid, which is often used in explosives. Fluorescence experiments showed that the emission decreased with the addition of picric acid, a change that can be observed by the naked eye (Figure 7H). M46 (Figure 7I) has been used as a building block (photosensitizer) to form assemblies, exhibiting a cell-penetrating peptide-decorated virus coat protein.\textsuperscript{62}

The generation of reactive oxygen species (ROS) creates a strong membrane-intercalating capacity.\textsuperscript{62} The blue emission color supports the occurrence of abundant M46 uptake (Figure 7J). From TEM observations, it can be concluded that the M46-containing assemblies cause bacterial membrane perturbations under light irradiation and then induce structural membrane damage (Figure 7K). As shown in Figure 7L, M48-50-based supramolecular networks were prepared. The M48- and M49-based networks show a strong ability to lethally damage E. coli and S. aureus, indicating that these networks have broad-spectrum antibacterial activities (Figure 7L).

Emissive MOCs serve as building blocks for liquid crystalline, information-encryption, and light-harvesting systems

Rhomboid M51 (Figure 8A) has liquid crystalline C phases.\textsuperscript{47} The reconstructed electron density (ED) map confirms the formation of the Co\textsubscript{5}H\textsubscript{12}c2mm structure (Figure 8B). In the map, M51 is surrounded by terminal alky1 and tri(EG) groups of medium-to-average ED (blue) and has low-ED pores (red). The high-ED rim (purple) that surrounds each pore originates from platinum; orientational averaging makes this rim nearly circular. These observations indicate that mesophases can be induced by coordination interactions.\textsuperscript{47} In addition to aiding in liquid crystal preparation, the chiral unit can be incorporated into metallacycles/metallacages to produce functional materials.\textsuperscript{14} As shown in Figure 8C, M53-M56 with chiral ligands were constructed and can serve as circularly polarized luminescence units. Through circularly polarized luminescence (CPL), positive signals ranging from 380–400 nm were observed for M55 and M56; however, the CPL results for M53 and M54 show a mirror relationship (Figure 8D). The chirality of these triangles can induce CPL and provide a novel structure for constructing CPL materials.\textsuperscript{14} By using perylene as a building block, metallacages (M57 and M58) can be formed upon the coordination of the designed pillar (Figure 8E).\textsuperscript{58} The cavity is
FIGURE 7  (A) Fluorescence spectra of M20 in acetone at a concentration of 10 μM; (B) emission spectra changes in M1; (C) emission spectra of M42 recorded at different temperatures; (D) M43 and M44; (E) optical and fluorescent images of M43 and M44 under different pressures; (F) chemical structure of M45; (G) fluorescence photographs of a thin M45 film, taken before and after halogen addition; (H) reversible emission transitions; (I) chemical structure of M46 and the corresponding assemblies; (J) SIM images of E. coli treated with assemblies; (K) TEM image of E. coli incubated with M46-based assemblies; (L) M48-50 and their corresponding crosslinked supramolecular networks; and (M) colony-forming units of E. coli and S. aureus incubated with M48-50-based supramolecular networks. Copyright 2020, Royal Society of Chemistry, Copyright 2018, 2019, 2020 American Chemical Society, Copyright 2019, National Academy of Sciences (USA), Copyright 2020, Wiley-VCH
used to encapsulate G3, and then the cage, guest, and host-guest complex are used as inks in a tricolor inkjet cartridge to print a pattern. The region printed with the host-guest complexes is white. As shown in Figure 8f,58 the printed lantern pattern is dim under both natural and UV light57b; the pattern becomes bright when it is sprayed with MeCN vapor.

Zhang prepared M59 and used it as a donor, with eosin Y as an acceptor, to construct a light-harvesting system in aqueous solution. Benefiting from this combination, the catalytic activity was enhanced compared with that of eosin Y through the catalysis of the cross-coupling hydrogen-evolution reaction. The fluorescence resonance energy transfer (FRET)
process increases the number of excited photocatalysts (eosin Y*) that undergo a catalytic cycle to increase the catalytic activity. Moreover, hydrogen is produced by the combination of dissociated hydrogen radicals, offering a pathway for storing light energy (Figure 8G).57b

Emissive MOCs as antitumor agents

Because of the enhanced permeability and retention (EPR) effect, MOCs and platinum centers have excellent antitumor activities. Here, we will summarize the recent progress in this field, taking the example of M60, which has been designed to have oxygen-responsive red phosphorescence for hypoxia imaging and chemotherapy (Figure 9A).58a The combination of porphyrin and anthracene endows M60 with oxygen-responsive red phosphorescence and blue fluorescein.

Then, M60 is integrated into the nanoparticles to prolong their circulation times. The ratio between red and blue emissions can be used to provide a precise standard for hypoxia imaging and detection. As shown in Figure 9B, bright emissions were observed in tumor regions, confirming the capability of in vivo hypoxia imaging for both small and large tumors. In addition, large tumors possessed better tumor-to-normal-tissue ratios and stronger intensities than small tumors, suggesting that the nanoparticles have excellent
therapeutic performance. M61-63 were synthesized with a TPE-based dipyrindyl donor and 60- or 120-degree Pt acceptors (Figure 9C) and used as building blocks to construct the corresponding nanoparticles. These particles exhibited long-term fluorescence and tumor retention activities. M61-63 and the corresponding nanoparticles showed better anti-tumor properties than cisplatin. As shown in Figure 9D, and the corresponding nanoparticles showed better anti-tumor activities based on the smallest resulting tumor size. Wang prepared M64 and M65 with porphyrin derivatives (Figure 9E), and the single crystal in M64 implies that the structure inhibits both intramolecular and intermolecular stacking interactions in the porphyrin motifs, resulting in a higher ROS-generation efficiency than the precursor. By using an amphiphilic block polymer as a coassembly factor, M64- and M65-based nanoparticles were prepared with enhanced stabilities in physiological environments. The tumors were excised 3 weeks posttreatment, and the weights of the tumors were assessed. As shown in Figure 9F, the tumor growth inhibition ratio of the groups treated with M64-based nanoparticles was 98.4% with irradiation treatment, while the growth inhibition ratios for the other groups were all below 65%. Wang reported the use of adamantane-modified metallacage M66-based nanoparticles (Figure 9G) for protein delivery. The hierarchical assembly process maintains high efficiency in the presence of protein, realizing the integration of protein into the nanoparticles for intracellular protein delivery for therapeutic applications and CRISPR/Cas9 genome editing.

MOCs were used as building blocks to prepare multilevel suprastructures

As typical functional compounds, platinum-based MOCs have served as sensors, catalysts, and anticancer agents in recent years. However, in contrast to peptides, graphene-based suprastructures that extend the hierarchical order from the nanoscale to the macroscale lead to the generation of flexible supercapacitors, wearable devices, ultrasoft electronics, and so on.

Most of the reports about MOC-based suprastructures are limited on the nano or microscale. In addition, controlling the morphology at the nanoscale is still a challenge. To solve these problems, TPE- and porphyrin-based MOCs were used as model compounds to construct suprastructures with hierarchical order on a multilevel scale. As a result, porphyrin-containing MOC-based octahedra and TPE-containing MOC-based centimeter films were produced, which may serve as functional devices in further work. As shown in Figure 10A, M67 was synthesized as a model to investigate the assembly behavior of TPE-based metallacages. M67-based microneedles with nanometer-scale diameters and millimeter-scale lengths can be formed by the phase-transfer process; both the physical properties and size can be controlled by adjusting the ratios of DCM and EA (Figure 10B).

Fluorescence microscopy shows blue and green emissions from the microneedles. Importantly, these suprastructures can be used as platforms for the functional molecular loading of molecules such as vitamin B12 (Figure 10C). Compared to the structures formed by M67 alone, these structures are wider (Figure 10D). To broaden the library of MOC-based suprastructures and obtain more functional materials, M68 was synthesized as a model to study the behaviors of porphyrin-based metallacages (Figure 10E). As shown in Figure 10F, an M64-based uniform octahedral with ca. 520 nm sizes can be prepared by the interface-assembly process. To reveal the mechanism for the evolution of metallacages into octahedra, both experiments and theoretical simulations were performed in this study. The absorption band was slightly blueshifted and decreased in intensity (Figure 10G).

Latest progress

By using M69 (Figure 11A) as a building block, a centimeter film with a tunable size can be prepared. Figures 11B-C show images of thin films with diameters of 1.3 cm without and with UV-light irradiation, respectively; the diameter increases to 2.3 cm with increasing container size (Figures 11D-E). These materials can be used as carriers for riboflavin (Figures 10F-G) and shikonin (Figure 11H) loading. Figure 11I shows a fluorescence image of the shikonin-loaded film with a diameter of 1.3 cm. As the size of the container continues to increase, a centimeter film with a diameter of 6.5 cm can be obtained (Figures 10J-K). Figure 11L shows the film after gentle shaking. The observation of the microstructure confirms that it is composed of uniform and extralong nanofibers. Figure 11M shows the CLSM image of these fibers, proving that M69 is distributed uniformly across the whole film. Close observations based on TEM and scanning transmission electron microscopy (STEM) confirm the uniformity of these nanofibers.

CIE analysis shows that films with tunable emission colors have been obtained by adjusting the different emission molecules. As a new system, macroscopic assemblies not only amplify the excellent properties of individual units in advanced ensembles but also enable processability. As shown in Figures 11Q-T, the centimeter films coated on copper, silica, glass, and polyethylene all show uniform emissions under UV irradiation. In contrast, with more M69 covering these materials, weak emission is observed instead of uniform, strong (Figures 11U-X). Taking the comparison between centimeter films covered with polymers and nanofibers covered with polymers as an example, a 40-fold weight M69-based nanofiber is used, showing worse emission properties than the film in Figure 11T. Yang designed and synthesized rhombohedral metallacage M70 or hexagonal M71 decorated with mesogenic forklike dendrons (Figures 12A) that could form a liquid crystal phase at room temperature. Their liquid-crystalline behaviors could be tuned by the electrostatic interactions between the positive charges of metallacycles and negatively charged heparin. Based on these liquid-crystalline metallacycles, the holographic storage of colored images was successfully realized (Figures 12B-C). This work provides the first successful example of supramolecular liquid-crystalline metallacycles for holographic storage of colored images.

Qu organized photosensitive molecular motors into discrete metallacycles of different sizes by coordinating molecular-motor-based electron-rich donors with different di-Pt(II) acceptors. The photo- and thermoresponsive molecular motor units might render the system responsive to allow noninvasive control of such hierarchical aggregation (Figure 13A). Kinetic studies of the thermal isomerization steps
of metallacycles illustrated that the coordination of the free ligand donors and di-Pt(II) acceptors had no influence on the isomerization processes or the rotation speed of molecular motors. These findings demonstrated that coordination-driven self-assembly provides a facile approach to organize several single molecular motors and reveals a potential design strategy to implement collective motions.

Zhang prepared a series of TPE-based metallacages that exhibit good emission both in solution and in the solid state. One of the metallacages achieves a very high fluorescence quantum yield ($\Phi_F = 88.46\%$) in the solid state, which is further used as the coating of a blue LED bulb to achieve white-light emission (Figure 13B). Phillips synthesized Pt(II) tpy/bpy acetylide complexes with a TPE derivative as the ancillary ligand. The ultrafast photophysical dynamics of the TPE-based triplet excited states are examined systematically. Their findings provide insights into the characteristics of the triplet excited states of TPE and demonstrate that the lifetimes are predominantly governed by the phenyl rotation of TPE, which accelerates the nonradiative decay rate.

**CONCLUSION AND PERSPECTIVES**

Metallacycles and metallacages with controllable geometries, shapes, and sizes have been successfully designed and synthesized, confirming that they are excellent candidates for use in sensors, catalysts, and biomedical applications. To broaden the functional groups of these metallacycles and metallacages, lumiphores with various photophysical...
properties have been used as described above to modify MOCs. To date, MOCs have been successfully created and evaluated, although some challenges remain to be addressed for enabling further applications. In our previous work, a series of MOCs with two-dimensional triangular, rectangular, and so on structures to three-dimensional polyhedron were prepared. Among these MOCs, those with emissive characteristics show excellent photophysical properties and can be used in sensors, antitumor reagents, adhesive materials, and so on. However, there are also some significant issues that remain to be fully understood and need further investigations. In particular, the detailed, exact mechanism of these self-assembly processes is not yet well understood. The specific effect of aggregation on the photophysical properties as
well as the complex nature of the excitation process, energy transfer between singlet-triplet species, etc is far from clear. Most importantly almost nothing is known about the nature of the well established antitumor activity of these species. The exact interaction of these MOCs with DNA and RNA should be studied. Finally more in vivo animal experiments need to be carried out and carefully analysed. Hence, it is evident from this brief review that coordination driven self-assembly is a powerful and easy to use methodology to rationally predesign molecules for materials as well as biochemical and biomedical applications. Given the almost infinite variety of organic ligands and the diverse metals that have been and can be used by researchers worldwide it is evident that this field will continue to thrive, including many yet unforeseen discoveries as well as applications. Moreover, the possibility of hierarchical self-assembly, that is using more than one of nature’s relatively weak interacting processes such as hydrogen boning, or p–p stacking, and so on in conjunction with coordination and functional lumiphores, will provide a ready route to a near infinite variety of fascinating, novel, complex, molecular systems and hence uses.
FIGURE 13  (A) Schematic representation of the manipulated supramolecular aggregation of M72 and heparin; (B) tetraphenylethylene-based multi-component emissive metallacages as solid-state fluorescent materials. Copyright 2021, American Chemical Society. Copyright 2021 Wiley-VCH

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