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Jiang Bo, Zhang Chang-Wei, Shi Xue-Liang, Yang Hai-Bo

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AIE-active Metal-organic Coordination Complexes Based on Tetraphenylethylene Unit and Their Applications

Bo Jiang, Chang-Wei Zhang, Xue-Liang Shi*, and Hai-Bo Yang*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China

Abstract Tetraphenylethylene (TPE) and its derivatives, as the widely used aggregation-induced emission (AIE) fluorophores, have attracted rapidly growing interest in the fields of material science and biological technology due to their unique light-emitting mechanism—they are nearly non-emissive in dilute solution but emit brilliant fluorescence in the aggregate state because of the restriction of intramolecular motion. Coordination-driven self-assembly, which provides a highly effective method to put the individual chromophores together, is consistent with the AIE mechanism of TPE. During the past few years, some AIE-active metal-organic coordination complexes have been successfully constructed *via* coordination-driven self-assembly, and their AIE properties and applications have been investigated. In this review, we survey the recent progress on TPE-based metal-organic coordination complexes and their applications in fluorescence sensors, cell imaging, and light-emitting materials. We will introduce them from three different types of structures: metallacycles, metallacages, and metal-organic frameworks (MOFs).

Keywords Aggregation-induced emission; Self-assembly; Metal-organic coordination complexes; Tetraphenylethylene; Sensor

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INTRODUCTION

Coordination-driven self-assembly has been demonstrated to be a well-established methodology for preparing various supramolecular architectures with well-defined shapes and sizes in recent decades.^[1–15] Due to the directional and predictable features of metal-ligand bonds, the desired metal-organic coordination complexes (MOCCs) could be constructed by the self-assembly of elaborately selected organic donors and metal acceptors. Moreover, owing to the diversity of the ligand precursors and metal salts, various functional groups can be easily incorporated into the resulting MOCCs. In the past few years, a great number of functional MOCCs have been successfully obtained, some of which have shown potential applications in the fields of catalysis, sensing, light-emitting materials, and so forth.^[16–31] These studies have demonstrated that the functional MOCCs usually exhibit unique properties which are not available in their individual building blocks. Moreover, the dynamic and reversible natures of metal-ligand bonds endow the resulting MOCCs with stimuli-response properties, which have been used for designing and constructing smart materials.^[32]

Aggregation-induced emission (AIE), first reported by Tang and co-workers in 2001,^[33] has attracted great atten-

tion in various fields.^[34–37] In general, the AIE-active fluorophores are usually non-emissive at low concentrations but emit brilliant fluorescence in the condensed state due to the restriction of intramolecular rotations.^[34] Tetraphenylethylene (TPE), as a well-known AIE chromophore, has been widely used to prepare light-emitting materials due to its facile synthesis and easy modification.^[38–40] Recently, the incorporations of TPE units into MOCCs, namely AIE-active metal-organic coordination complexes, have received considerable attention. By the rational design of TPE-based ligands, some AIE-active MOCCs have been successfully constructed, and some of them show intriguing photophysical properties and wide applications.^[41–64] Herein, we review the recent works on TPE-based MOCCs and their applications. We will introduce them from three different types of structures: metallacycles, metallacages, and metal-organic frameworks (MOFs).

AIE-ACTIVE METALLACYCLES

Due to the intriguing photophysical properties of TPE and its derivatives, a lot of TPE-based fluorescent sensors have been designed and successfully constructed to detect the various environmental pollutants and explosives.^[34–40] Among them, AIE-active metallacycles constructed *via* coordination-driven self-assembly have attracted considerable attention because it provides an effective method to put the multi-TPE units in a single entity with controllable structures. Moreover, due to the formation of metal-ligand bonds, the metallacy-

* Corresponding authors: E-mail xlshi@chem.ecnu.edu.cn (X.L.S.)
E-mail hbyang@chem.ecnu.edu.cn (H.B.Y.)

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cle skeleton is positively charged, which could potentially interact with the negatively charged compounds *via* electrostatic interactions. By taking advantage of these characteristics, Yang and co-workers have recently reported a discrete organoplatinum(II) metallacycle **1** functionalized with tris-TPE units, which could be used as a turn-on selective probe for heparin detection (Fig. 1).^[44] The tris-TPE hexagonal metallacycle **1** was easily prepared through the self-assembly of 120° TPE-containing donor and 120° diplatinum(II) acceptor. Notably, there are six positive charges distributed in the core skeleton of metallacycle **1**. When the negatively charged heparin was added into the mixed solvents of acetone and water of metallacycle, obvious fluorescence enhancement at 486 nm was observed in the emission spectral, which was attributed to the aggregation emission of TPE units (Fig. 1b). Moreover, the solution of a mixture of metallacycle **1** and heparin showed blue luminescence upon excitation at 365 nm, which was not observed in their individual components (Fig. 1c). These results strongly supported that multiple electrostatic interactions between the positively charged metallacycle **1** and the negatively charged heparin induced the aggregation of hexagonal metallacycle and then restricted the intramolecular motion of TPE units. Furthermore, the atomic force microscopy (AFM) images of a mixture of metallacycle **1** and heparin showed some single bead-like chains with a height distribution ranging between 1.0 and 4.0 nm, which was higher than that of individual metallacycle **1** or heparin (Fig. 1d). This result further supported the complexation of metallacycle **1** and heparin driven together by electrostatic interactions. Interestingly, the metallacycle **1** selectively responded to heparin, *e.g.*, when adding other biomolecules,

such as sucrose, glucose, lactose, human serum albumin, bovine serum albumin, to the solution of metallacycle **1**, no obvious change of emission intensity was observed, indicating the good selectivity of metallacycle **1** toward heparin. Thus, metallacycle **1** could act as a turn-on selective probe for heparin detection.

Subsequently, Stang and co-workers reported a pure TPE-based metallacycle **2** (Fig. 2), which could form a novel metal-organic biohybrid material with tobacco mosaic virus (TMV) *via* multiple electrostatic interactions.^[50] The biohybrid complex TMV/metallacycle **2** was prepared by simply mixing the TMV/H₂O solution with metallacycle **2**/DMSO solution, accompanied with the marked fluorescence enhancement. Transmission electron microscopy (TEM) showed that a discrete one-dimensional (1D) rod-like TMV transformed into three-dimensional (3D) micrometer-sized bundle-like superstructures, which derived from the tight TMV alignment after the addition of metallacycle **2**. This result indicated that metallacycle **2** could act as a positively charged molecular glue to connect the monodispersed TMV together to form well-ordered arrays *via* multiple electrostatic interactions. Moreover, by taking advantage of the dynamic nature of metal-ligand bonds, the TMV/metallacycle **2** biohybrid complexes could be reversibly disassembled to release the viruses by treating them with tetrabutylammonium bromide (TBAB), which could damage both the metallacycle skeleton and the positive charges of metallacycle **2**. These results suggested that metallacycle **2** could be used not only as a turn-on AIE-based fluorescence sensor to probe the hierarchical self-assembly processes but also to prepare the stimuli-responsive biohybrid materials.

The construction of multi-TPE units in a single entity still

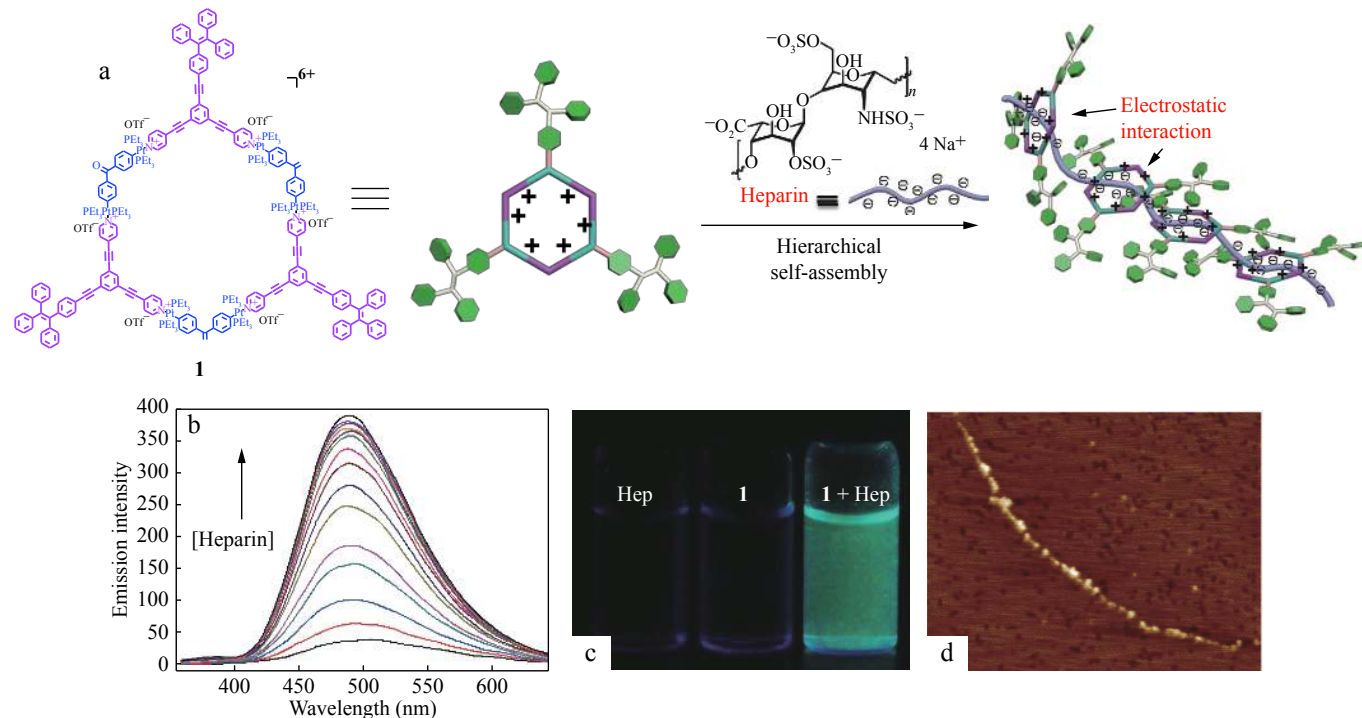


Fig. 1 (a) Schematic showing the possible binding mode of metallacycle **1** and heparin; (b) Emission spectral changes of **1** with the addition of heparin; (c) Photographs showing the emission change of **1** after adding heparin; (d) AFM images of a mixture of metallacycle **1** and heparin (Reprinted with permission from Ref. [44]; Copyright (2015) American Chemical Society)

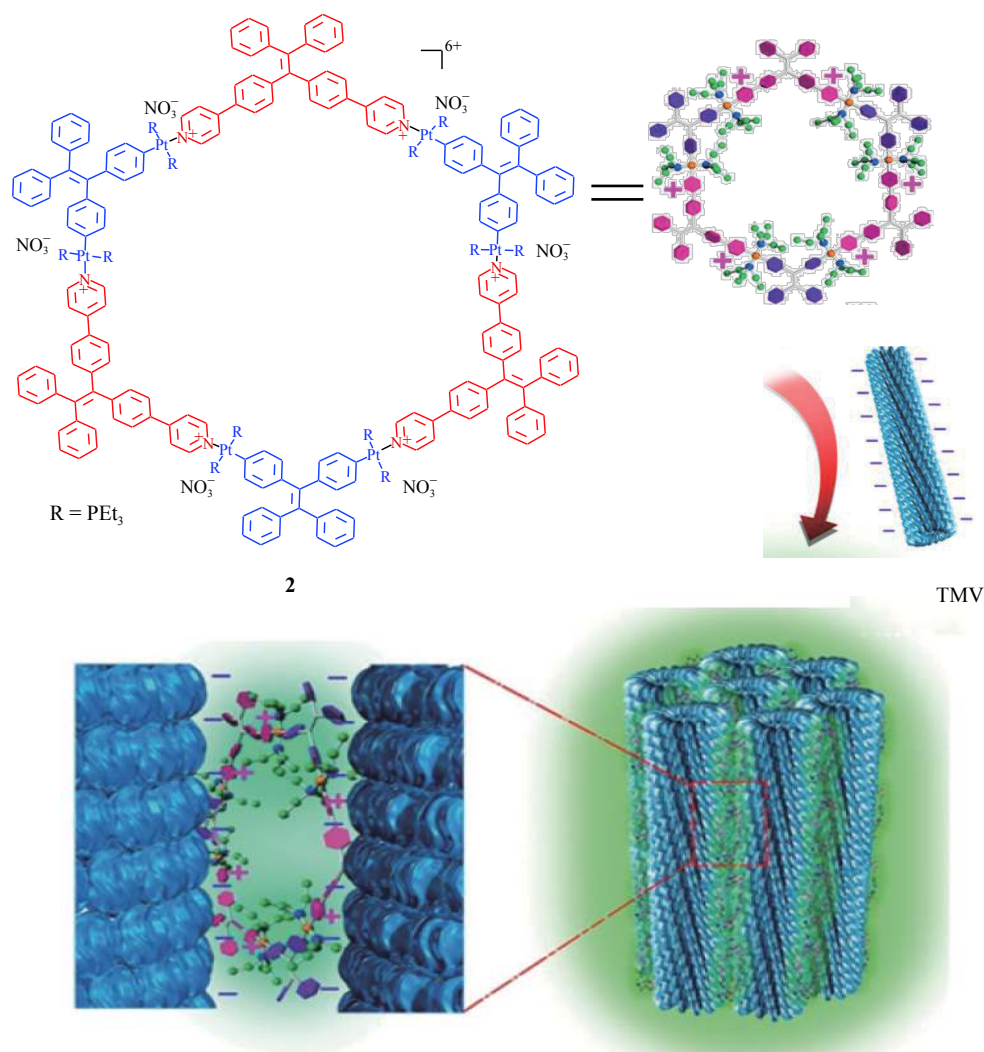


Fig. 2 Schematic representation of the formation of a metal-organic biohybrid material TMV/metallacycle **2** via multiple electrostatic interactions (Reprinted with permission from Ref. [50]; Copyright (2016) American Chemical Society)

remains a big challenge because the traditional covalent synthesis often suffers from the complicated synthetic route, tedious purification, and low yield. Coordination-driven self-assembly has been demonstrated to be a powerful tool to connect individual building block together at high efficiency to construct supramolecular coordination complexes with controlled shapes and sizes. In 2015, Stang and co-workers designed and synthesized a 120° TPE-based dipyrindyl ligand **3**, in which two phenyl rings in TPE unit were unrestricted.^[47] With the ligand **3** in hand, a new family of multi-TPE metallacycles with different shapes and sizes has been successfully constructed in high yield *via* coordination-driven self-assembly (Fig. 3). The study of AIE properties showed that both the rhomboid **9** and hexagons **10–13** displayed marked fluorescence enhancement when increasing the hexane content in CH₂Cl₂/hexane mixed solutions, indicating that they were AIE-active metallacycles. Notably, the TPE-based ligand **3** showed no obvious change of emission intensity under the same condition. Further investigation revealed that the light-emitting properties of these multi-TPE metallacycles were closely related to their structural factors,

including size, shape, distribution, and distance between AIE-active ligands. For example, the tris-TPE hexagons **10** and **11** have higher quantum yield values than those of hexa-TPE hexagons **12** and **13** in the aggregated state, which could be explained by that the larger metalacyclic skeletons of hexa-TPE hexagons might hinder the close stacking of TPE units. Interestingly, the rhomboid **9** has been proven to be a turn-off fluorescent probe, which has high selectivity toward picric acid. Except the structural factors, counterions also have an important influence on the photophysical properties of AIE-active metallacycles. According to the relative research, the quantum yield values of AIE-active metallacycles follow the order PF₆[−] > OTf[−] > NO₃[−] both in solution and in the aggregated state.^[48]

Stimuli-responsive supramolecular polymers have attracted great attention in the past few years due to their potential applications in the field of material science. Yang and co-workers have recently reported a new family of AIE supramolecular polymer gels with multiple stimuli-responsive behaviors *via* hierarchical self-assembly.^[41] The authors designed a new 120° TPE-cored ligand **14** (Fig. 4), which car-

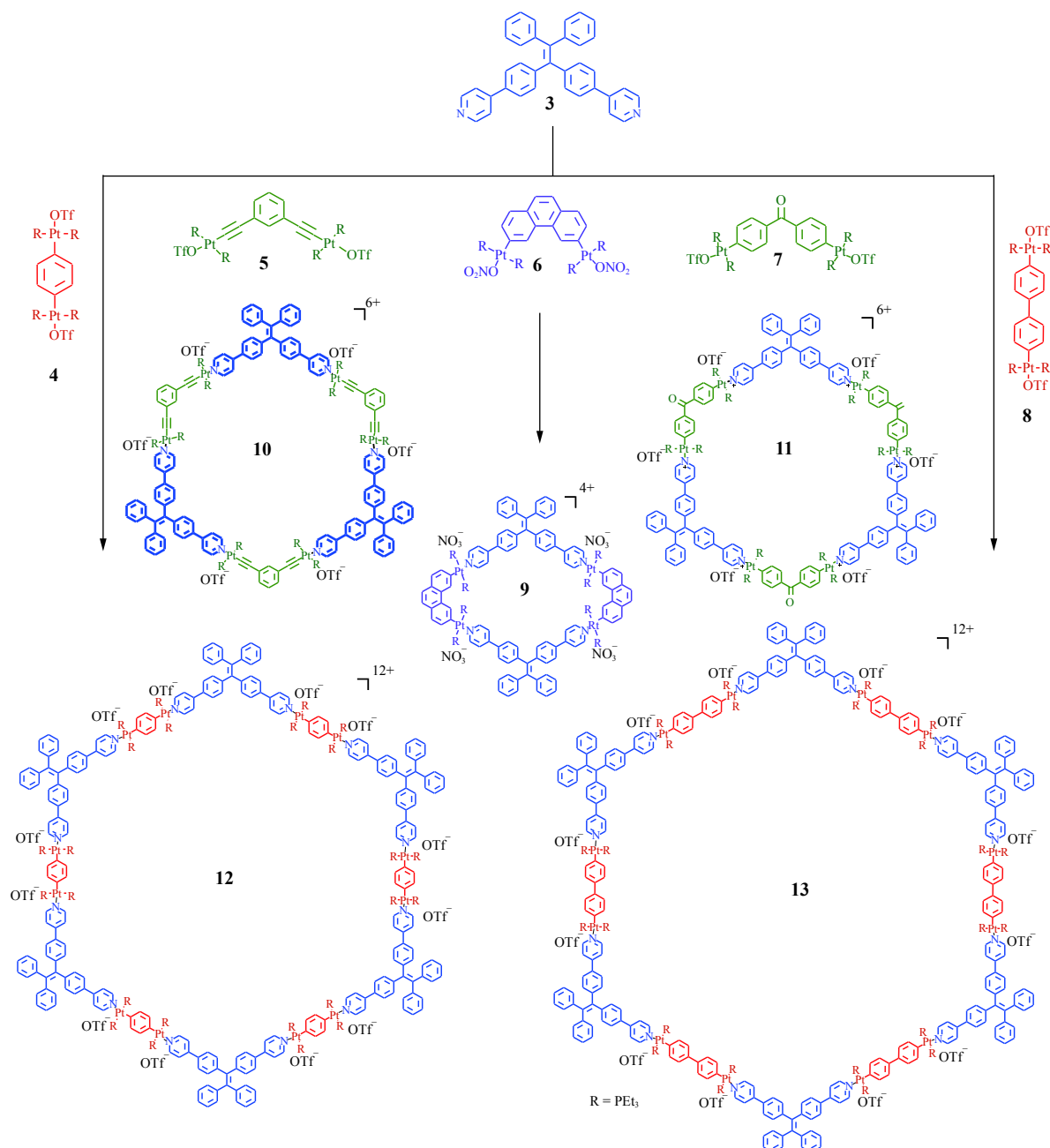


Fig. 3 The construction of multi-TPE metallacycles with different shapes and sizes *via* coordination-driven self-assembly (Reprinted with permission from Ref. [47]; Copyright (2015) American Chemical Society)

ried two binding sites for multiple noncovalent interactions: the pyridine could be used as a donor to coordinate with metal salts and the pillar[5]arene moieties could form host-guest complexes with a variety of guests. From the self-assembly of ligand **14** with 60° acceptor **15** or 120° acceptor **7**, respectively, the rhomboidal metallacycle **16** and hexagonal metallacycle **17** were successfully prepared (Fig. 4a). The investigation on photophysical properties showed that the metallacycles **16** and **17** exhibited approximately 18-fold and 50-fold fluorescence enhancement over the starting value, indicating that they were AIE-active. Taking advantage of pillar[5]arene moieties, supramolecular polymers were formed through host-guest interactions when the neutral dinitrile molecule was added. Interestingly, when the concentrations

were higher than $45.2 \text{ mmol} \cdot \text{L}^{-1}$, the supramolecular polymers could transform into stable gels with strong fluorescence intensity. Importantly, the AIE supramolecular polymer gels could respond to multiple external stimuli, such as temperature, competitive guest molecules, and halides, along with the “on-off” of fluorescence (Fig. 4b).

The water-soluble light-emitting materials are very interesting because of their good biocompatibility and potential to be used as biomaterials. However, most well-known TPE-based metallacycles are water-insoluble, which limits their further applications in biological labeling, cell imaging, and diagnostics. Yang and co-workers reported a new strategy, which included both the exo-functionalization and post-assembly polymerization methods, for the preparation of TPE-

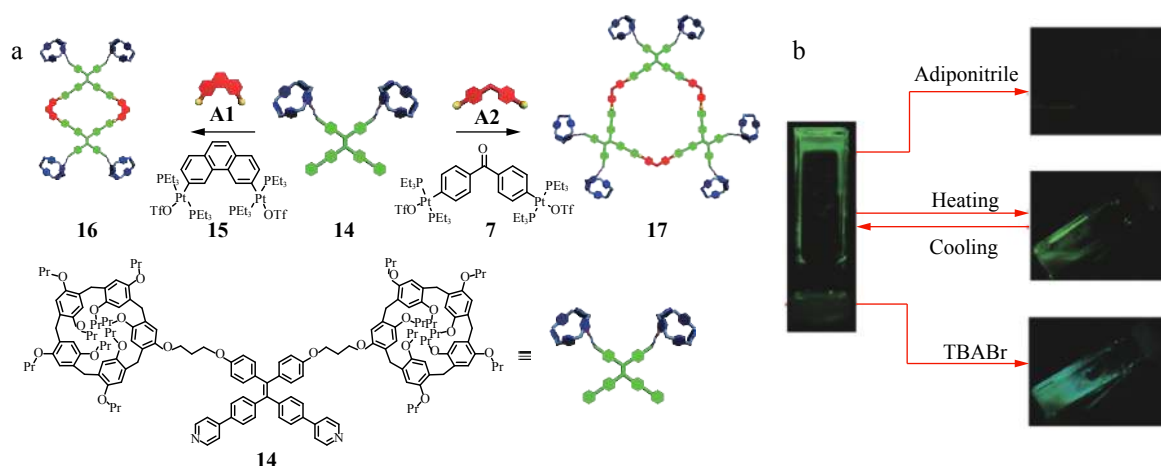


Fig. 4 (a) The construction of self-assembled metallacycles **16** and **17**; (b) AIE supramolecular polymer gel with multiple stimuli-responsive behaviors (Reprinted with permission from Ref. [41]; Copyright (2018) The Royal Society of Chemistry)

based supra-amphiphilic organoplatinum(II) metallacycle **20** (Fig. 5a).^[43] First, the exo-functionalization strategy was used to construct the supramolecular metallacycle **19**, which contained TPE and chain transfer agents (CTAs) moieties with controllable number and position. Subsequently, post-assembly controlled radical polymerization of (*N*-isopropylacrylamide) (NIPAAM) was performed to produce a supra-amphiphilic organoplatinum(II) metallacycle **20** with three water-soluble polymeric arms. The metallacycle **20** displayed approximately 30-fold fluorescence enhancement compared to the original state in a mixed THF/water solvent system, suggesting that metallacycle **20** held typical AIE characteristics. Furthermore, based on the intriguing AIE properties and good biocompatibility of metallacycle **20**, its potential application in cell imaging was studied by confocal laser scanning microscopy (CLSM). The investigation revealed that metallacycle **20** could be taken up by bone mes-

enchymal stem cells with a concentration of $1.0 \text{ mg} \cdot \text{mL}^{-1}$ and tended to accumulate in the cell nucleus.

Design and construction of new supramolecular architectures with increasing complexity and functionality *via* coordination driven self-assembly have attracted great attention in the past few years. Li and co-workers have done a lot of works in this field. Recently, Li and Yang have reported a new family of rosette-like metallo-supramolecules with tunable emissive properties.^[45] They designed and synthesized three generations of TPE-cored ligands, which contained multiple terpyridine (TPY) units. The large conjugation and bulky size of TPY substituents could help to restrict intramolecular rotations of TPE units. Thus, the ligands **22** and **23** (Fig. 6) displayed strong emission in dilute solution and also showed AIE effect with high efficiency. When these ligands were assembled with Cd^{2+} in $\text{CHCl}_3/\text{MeOH}$ mixed solvent, three generations of supramolecular rosettes **24**, **25**,

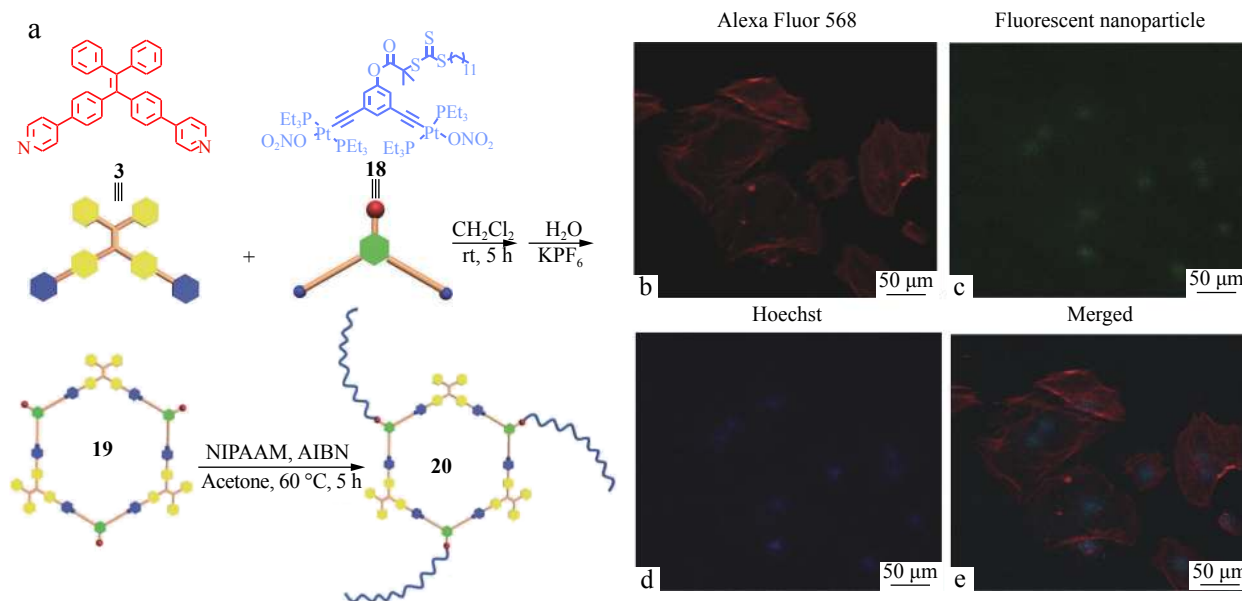


Fig. 5 (a) The synthesis of TPE-based supra-amphiphilic organoplatinum(II) metallacycle **20**; (b–e) Confocal microscopy images of bone mesenchymal stem cells incubated with the fluorescent nanoparticles of metallacycle **20** (Reprinted with permission from Ref. [43]; Copyright (2017) The Royal Society of Chemistry)

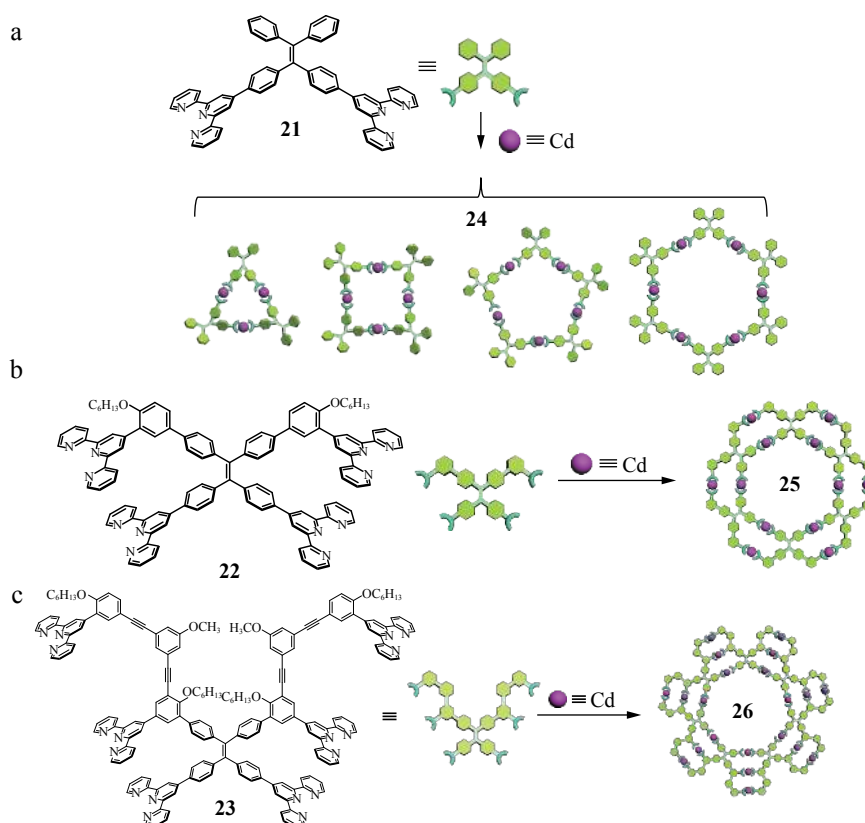


Fig. 6 The formation of (a) a mixture of trimer, tetramer, pentamer, and hexamer macrocycles, (b) double-layered hexamer **25**, and (c) triple-layered heptamer **26** (Reprinted with permission from Ref. [45]; Copyright (2018) Nature Publishing Group)

and **26** were obtained in high yields (Fig. 6). Notably, when treating ligand **21** with Cd^{2+} , a mix of trimer, tetramer, pentamer, and hexamer macrocycles rather than a single product was formed (Fig. 6a). However, the self-assembly of ligands **22** or **23** with Cd^{2+} led to the formation of double-layered hexamer **25** and triple-layered heptamer **26**, respectively, as the sole assembly (Figs. 6b and 6c). It is presumably because multitopic TPY units could provide more geometric constraints in the self-assembly through multivalent interactions, thus resulting in the formation of more thermodynamically favorable structures. Interestingly, due to the formation of rigid supramolecular scaffold, the rotation of TPE groups was further restricted and the supramolecular rosettes exhibited some intriguing photophysical properties that were not observable in their individual building blocks. For example, the double-layered hexamer **25** showed rare room temperature white-light emission in CH_3CN /water mixed solvent, which made it applicable in the field of white-light emission or as color-tunable optoelectronic materials.

AIE-ACTIVE METALLACAGES

In 2015, Stang and co-workers designed and synthesized a novel TPE-cored multi-pyridyl ligand **27** (Fig. 7), which was non-emissive in CH_2Cl_2 because of non-radiative decay via the effective intramolecular rotations.^[52] Through the self-assembly of ligand **27** with dicarboxylate ligands **28** or **29**,

and 90° Pt(II) acceptor **30** in a 1:2:4 ratio, two tetragonal metallacages, **31** and **32**, which is the first example of AIE-active discrete supramolecular coordination metallacage, were successfully obtained (Fig. 7a). Both **31** and **32** displayed bright-yellow fluorescence in CH_2Cl_2 at room temperature and showed more than 20-fold fluorescent enhancement over the free ligand at a concentration of $10.0 \mu\text{mol}\cdot\text{L}^{-1}$. Interestingly, the emission colors of metallacycle **31** changed from yellow to blue to cyan accompanied with the remarkable fluorescent enhancement by simply increasing the proportion of hexane in CH_2Cl_2 /hexane mixture. Moreover, the metallacycle **32** exhibited various emission colors in different polar solvents, including white-light emission in tetrahydrofuran (Fig. 7b). It is well known that light-emitting materials, especially the white-light emission materials, have received much attention due to their potential applications in fluorescent probes, bioimaging agents, optoelectronic devices, and so on. However, in most cases, the white-light emission materials require a mixture of two or more components. The single complex with room-temperature white-light emission is relatively rare. Thus, this study represented a rare example that a single metallacage showed white-light emission in a single solvent at room temperature, which made it an outstanding candidate for optoelectronic materials.

Subsequently, the same research group constructed another tetragonal prismatic cage **35** via the similar multicomponent self-assembly strategy (Fig. 8a).^[54] Different from the previous works, the functional group 21-crown-7 (21C7),

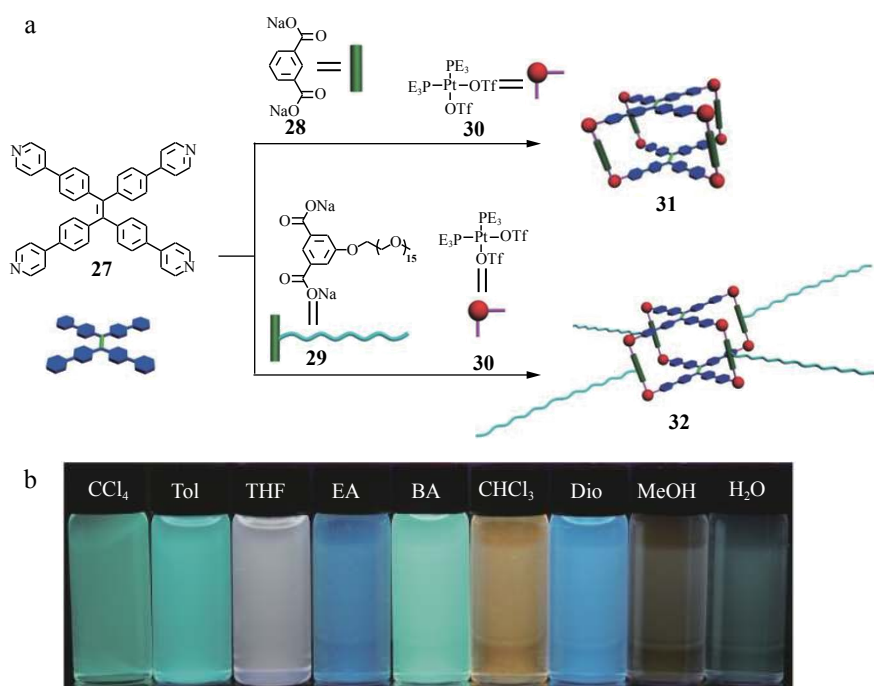


Fig. 7 (a) The construction of TPE-containing metallacages **31** and **32** through a multi-component self-assembly strategy; (b) Photographs of metallacage **32** in different solvents (Reprinted with permission from Ref. [52]; Copyright (2015) Nature Publishing Group)

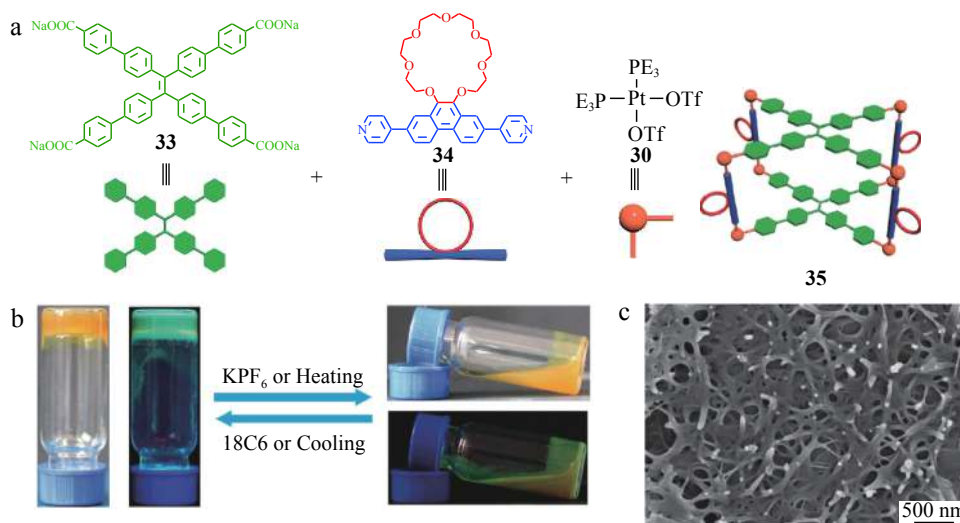


Fig. 8 (a) Self-assembly of 21C7-functionalized metallacage **35**; (b) Optical and fluorescence photographs of the reversible gel-sol transition of supramolecular polymer network; (c) SEM image of the supramolecular polymer network (Reprinted with permission from Ref. [54]; Copyright (2018) American Chemical Society)

which could form host-guest complexes with bisammonium, was incorporated into the resulting metallacage **35** in this case. The four 21C7 moieties were appended in the pillar parts of metallacage **35**, thus endowing the metallacage **35** with the ability to form supramolecular polymer network (SPN). Concentration-dependent $^1\text{H-NMR}$ experiments confirmed the existence of host-guest complexation between metallacage **35** and bisammonium, suggesting the formation of SPN at high concentration. Scanning electronic microscopy of SPN displayed an interconnected porous structure with entangled nanofibers (Fig. 8c), which further supported the formation of cross-linked networks. When the metalla-

cage **35** and bisammonium were mixed in acetone at $160\text{ mmol}\cdot\text{L}^{-1}$ in crown ether/ammonium salt, a metallacage-core supramolecular gel formed immediately through orthogonal metal coordination and host-guest interactions (Fig. 8b). Notably, the supramolecular gel had a higher quantum yield value than that of metallacage **35** because the formation of SPN would further restrict intramolecular rotation of ligand **33**. Interestingly, the gel showed visual gel-sol transitions induced by temperature or the addition of KPF_6 . Moreover, due to the dynamic and reversible nature of metal coordination and host-guest interactions, the metallacage-core gel also exhibited self-healing properties, which could recover to

the initial state when the gel was broken.

AIE-ACTIVE METAL-ORGANIC FRAMEWORKS

Metal-organic frameworks (MOFs) are a class of microporous materials with tunable properties and facile characterization, which have various applications in gas storage, catalysis, and gas separation. In 2011, Dincă and co-workers reported a TPE-based MOF **37** constructed by the self-assembly of ligand **36** with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in a mixture of *N,N*-diethylformamide (DEF) and ethanol at 75 °C (Fig. 9a).^[57] X-ray analysis of a crystal of MOF **37** revealed a structure in which paddlewheel shaped $\text{Zn}_2(\text{O}_2\text{C}-)$ ₄ secondary building units were bridged by ligand **36** to form staggered two-dimensional sheets. More importantly, the closest intermolecular phenyl...phenyl contact was 0.4753 nm for MOF **37**, which was more than 0.1 nm larger than the shortest phenyl...phenyl contacts of approximately 0.34 nm observed for common TPE derivatives, indicating that the TPE moieties were not close-packed in **37**. However, MOF **37** was luminescent, so these results demonstrated that tight packing of the TPE units was probably not necessary for turn-on fluorescence. Interestingly, MOF **37** displayed temperature-persistent luminescence, which could maintain its fluorescence even the temperature was up to 350 °C (Fig. 9b).^[58] The study on the temperature-dependent luminescence of MOF **37** showed that it only lost 50% of its initial fluorescence intensity at 190 °C. This result is dramatically different from the behavior of most TPE-based materials, which are often non-emissive at high temperature. Furthermore, the unique feature of MOF **37**

endowed it with the capacity of selectively detecting gaseous ammonia at 100 °C. When the activated MOF **37** was exposed to different vapors at 100 °C, including vapors of ammonia, triethylamine, ethylenediamine (en), DEF, and water, only ammonia vapor induced a significant shift of the emission maximum, suggesting that MOF **37** was selective probe for NH_3 detection.

Zhou and co-workers reported a new luminescent MOF **39** constructed by the self-assembly of a new extended TPE-based linker **38** with ZrCl_4 in the presence of benzoic acid and DEF (Fig. 10a).^[61] The study on photophysical properties revealed that the TPE-based linker **38** showed yellow emission with 30.0% quantum yield (Φ) in the solid state at room temperature under ambient atmosphere. However, due to the rigid structure of fluorescent linker in MOF **39**, the emission color transformed from yellow to blue. Moreover, the Φ value of MOF **39** increased to 99.9% (Fig. 10b) at room temperature under argon atmosphere, which was extremely high compared to the values of all reported fluorescent MOFs. Interestingly, when trifluoroacetic acid (TFAA) rather than benzoic acid was used as the competing reagent, another new TPE-based MOF **40** was successfully prepared even though the same ligand and metal salt were used. The original MOF **40** was white powder (referred to as **40-W**) and emitted bright blue light measured at 470 nm. However, when compressed with a glass slide or treated with 6.0 mol·L⁻¹ HCl solution, which could induce the loss of TFA groups coordinated to Zr_6 clusters, the color of **40-W** changed from white to yellow (referred to as **40-Y**). **40-Y** emitted green light at 538 nm, which was almost 70 nm red-shifted compared to **40-W**. Moreover, both the color and luminescence changes were completely reversible. When **40-Y**

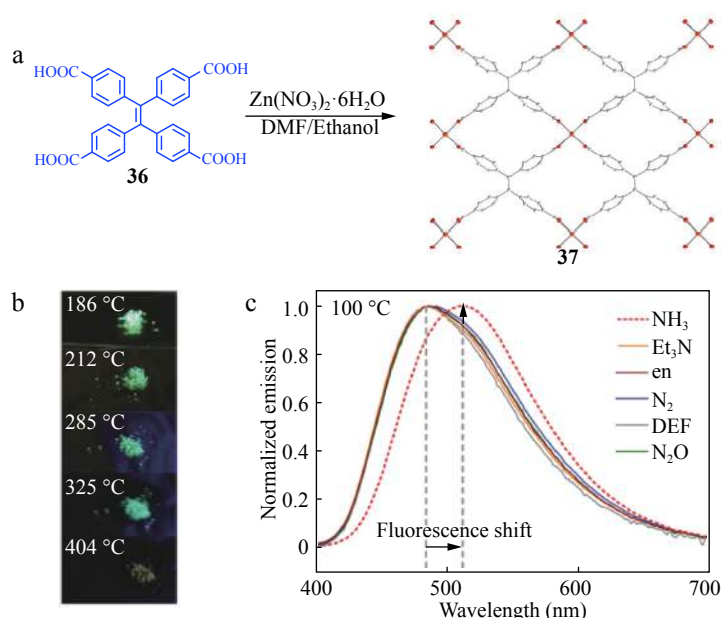


Fig. 9 (a) TPE-based MOF **37** formed by reacting ligand **36** with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in a mixture of *N,N*-diethylformamide and ethanol; (b) The optical micrographs showing fluorescent MOF **37** upon heating at various temperatures in air; (c) Normalized emission spectra of MOF **37** when exposed to various analytes at 100 °C (Reprinted with permission from Ref. [57]; Copyright (2011) American Chemical Society)

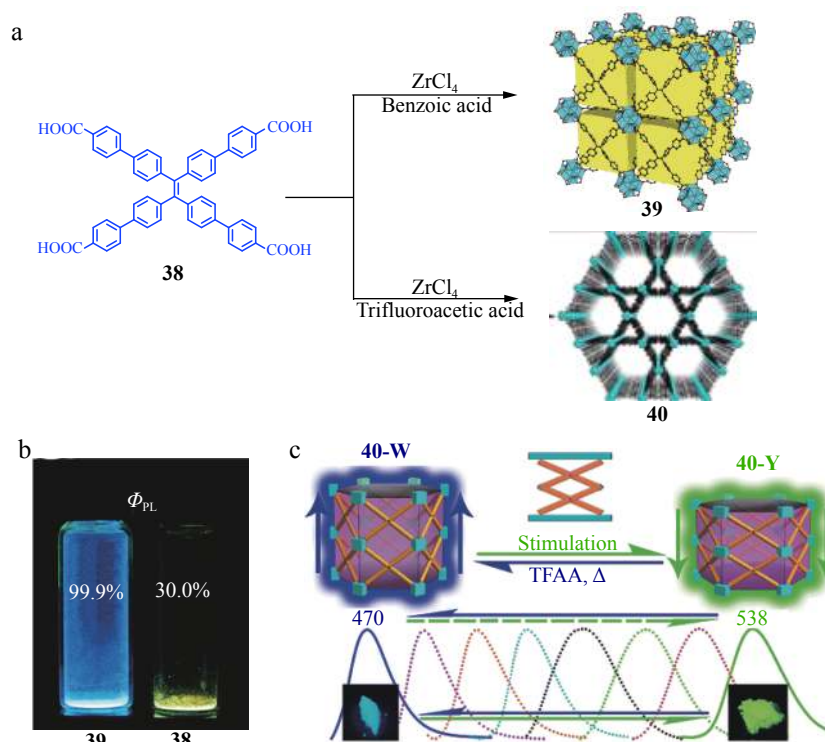


Fig. 10 (a) Two new TPE-based MOFs **39** and **40** constructed from ligand **38**; (b) Photos of MOF **39** and ligand **38** shown under UV light; (c) Reversible piezofluorochromic behavior of MOF **40** (Reprinted with permission from Ref. [61]; Copyright (2015) American Chemical Society)

was treated with TFAA in DMF at elevated temperature, **40-W** was reproduced. All these results indicated that **40** was a reversible 3D piezofluorochromic MOF, which have potential applications in photocatalysis and sensing.

In addition, Zhao and co-workers reported a 2D layered MOF constructed from a novel TPE-based ligand, in which two dangling phenyl rings without carboxylate groups could be restricted through molecular interactions with analytes.^[63] Thus, the 2D MOF showed responsive turn-on fluorescence to various volatile organic compounds. Li and co-workers designed and synthesized a new luminescent MOF, which could be used as a chemical sensor for the selective optical detection of mycotoxins *via* a luminescence quenching mechanism.^[64]

CONCLUSIONS AND PERSPECTIVES

In this review, we have mainly summarized the research progress of AIE-active metal-organic coordination complexes based on TPE units and their applications in fluorescence sensors, cell imaging, and light-emitting materials. During the past few years, some TPE-based metallacycles, metallacages, and MOFs have been successfully constructed by the self-assembly of TPE-cored ligands with metal salts, and their AIE properties and applications have been detailedly investigated. Generally, the formation of metal-ligand bonds could help to restrict intramolecular rotations of TPE units, thereby endowing the resulting metal-organic coordination complexes with some unique photophysical properties, such as white-light emission, piezofluorochromic behavior, high quantum yield, and so on, which are not observed for the free TPE-based ligands. Furthermore, the

potential applications of these AIE-active metal-organic coordination complexes have been preliminarily explored in the field of fluorescent sensors.

However, despite burgeoning advances aforementioned, some problems and challenges still exist and need to be addressed in this area. On the one hand, the ligands used to construct the AIE-active metal-organic coordination complexes are almost limited to TPE units. More AIE-active ligands, which may introduce unique properties into the resulting coordination complexes, should be explored. On the other hand, the interaction between metals and TPE units in AIE-active metal-organic coordination complexes has rarely been studied, and their influence on AIE and advantages over traditional small AIE molecules are still not disclosed. Last but not least, the reported applications of AIE-active metal-organic coordination complexes are mainly focused on the fluorescent sensors. Thus, more research effort should be devoted to exploring their applications in various areas.

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