Giant Concentric Metallo-Supramolecule with Aggregation-Induced Phosphorescent Emission

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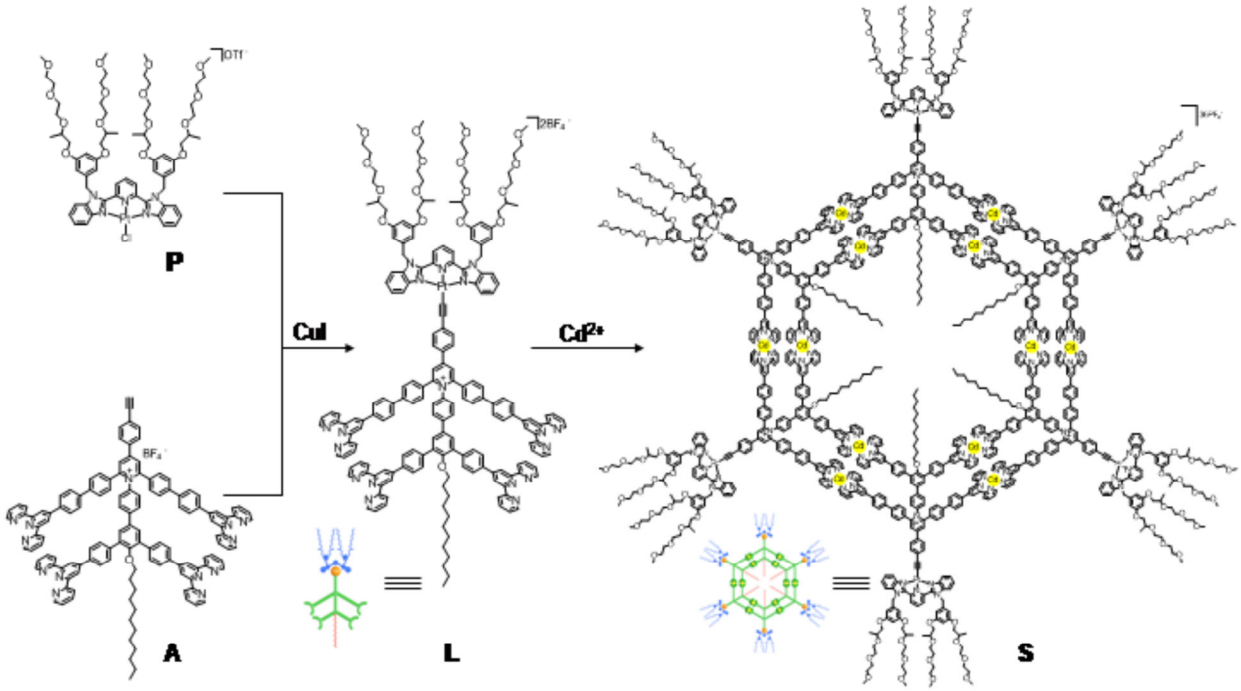
ABSTRACT: Fluorescent metallo-supramolecules have received considerable attention due to their precisely-controlled dimensions as well as the tunable photophysical and photochemical properties. However, phosphorescent analogues are still rare, and limited to small structures with low-temperature phosphorescence. Herein, we report the self-assembly and photophysical studies of a giant, discrete metallo-supramolecular concentric hexagon functionalized with six alkynylplatinum(II) bzimpy moieties. With a size larger than 10 nm and molecular weight higher than 26,000 Da, the assembled terpyridine-based supramolecule displayed phosphorescent emission at room temperature. Moreover, the supramolecule exhibited enhanced aggregation-induced phosphorescent emission compared to the ligand by tuning the aggregation states through intermolecular interactions, and significant enhancement of emission to CO_2 gas.

Introduction

Discrete metallo-supramolecules obtained via coordination-driven self-assembly have emerged as a class of materials to bridge the gap between small molecules and polymers,[1] on account of the precisely-controlled dimensions that provide an ideal platform for investigations of structure-property-function relationships.[2] Among the various functions, the luminescence of metallo-supramolecules has a wide range of applications in sensing,[3] photocatalysis,[4] bioimaging,[5] light-harvesting,[6] phototherapy[7] and so on.[8] Emissive metallo-supramolecules have been constructed mainly through the following three strategies: (i) introducing the luminophores into the scaffolds;[9] (ii) attaching the luminophores on the backbone as accessories;[7c, 10] (iii) encapsulating luminophores in the cavity of the structures through host-guest chemistry.[8f, 11] Generally, the luminophores include small organic motifs, such as tetraphenylethylene,[12] boron-dipyrromethene (BODIPY),[5b, 13] triphenylamine,[14] pyrene,[15] and perylene diimide,[16] as well as emissive metal complexes containing Ru(II),[17] Eu(III),[18] Ir(III),[6a, 10, 19] Pt(II),[20] and Au(I).[21] Among these emissive metallo-supramolecules, however, phosphorescent analogues are still rare, and mainly limited to small structures with low-temperature phosphorescence.[18d, 20a, 21a, 22]

2,2':6',2''-terpyridine (tpy) as one of the most intensively investigated building blocks, has been widely used in constructing sophisticated metallo-supramolecular architectures with well-defined sizes, shapes and geometries.[23] With weak luminescence, tpy has been functionalized with many luminophores to tune the emissive properties of corresponding metal complexes.[24] For instance, Cd(II) was frequently assembled with tpy to construct fluorescent supramolecules,[25] among which characteristic aggregation-induced emission (AIE)[12a, 26] was observed. Recent examples further employed tpy building blocks to construct phosphorescent metallo-polymers.[27] Among the luminophores, square-planar Pt(II) motifs have received considerable attention because of their unique photophysical and electrochemical properties.[28] These complexes exhibit phosphorescence brought by the heavy-atom effect with tunable emission wavelengths and lifetimes.[28b, 29] Also, Pt(II) luminophores are prone to have strong intermolecular Pt···Pt interaction,[30] which can manipulate their aggregations and enable emission through aggregation-induced phosphorescent emission (AIPE) effect,[31] a variant of AIE. More importantly, Pt(II) complexes are thermodynamically stable and kinetically inert.[28a] Thus, such features facilitate the synthesis

of tpy building blocks with Pt(II) luminophores for further coordination-driven self-assembly.



Scheme 1. Synthesis of ligand **L** and self-assembly of metallo-supramolecule **S**.

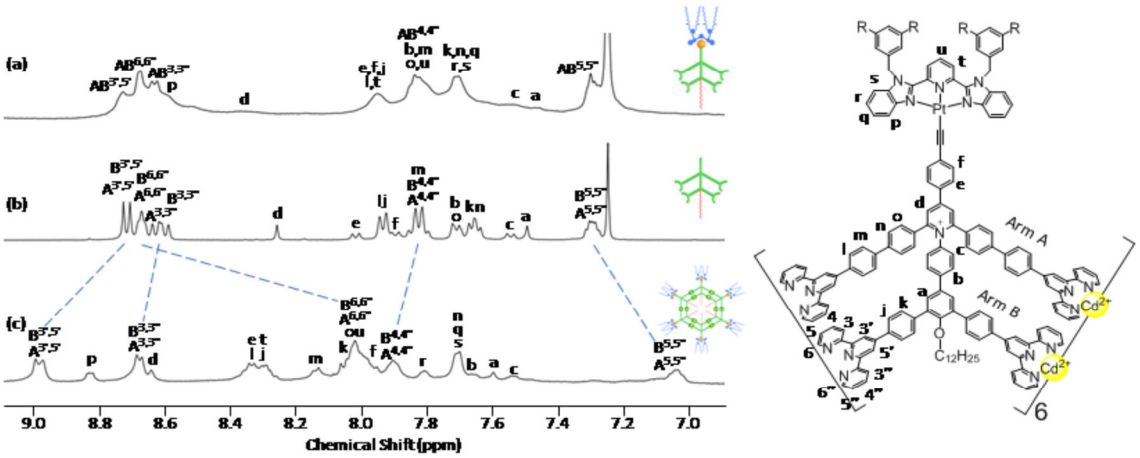


Figure 1. ^{1}H NMR spectra of (a) **L** in $CDCl_3$ (b) **A** in $CDCl_3$, and (c) **S** in CD_3CN. The broad signals of **L** were attributed to the strong aggregation in solution.

On the basis of previous study, we speculated the combination of AIPE-active Pt(II) components with tpy-based emissive supramolecules could create a synergy, by which the emissive properties of individual components could be retained, and the hybrid supramolecular architectures could even display superior AIPE compared to the individual components. According to this speculation, we designed a giant but discrete metallo-supramolecular concentric hexagon (**S**) functionalized with six Pt(II) bzimpy (bzimpy=2,6-bis(benzimidazole-2'-yl) pyridine) motifs. In the design, a terminal alkynyl group was employed to install the Pt(II) motif with a stable and rigid Pt(II)-alkynyl bond for further self-assembly. Also, we introduced multiple hydrophilic ethylene glycol chains into bzimpy moieties on the periphery, and long alkyl chain (C12) into the interior to tune the aggregation through balancing the overall hydrophobicity/hydrophilicity. With a size larger than 10 nm and a molecular weight higher than 26,000 Da, the assembled tpy-based supramolecule containing six Pt(II) centers displayed phosphorescent emission with a lifetime of 218 ns at room temperature. By synergistically combining AIPE from Pt(II) luminophores and AIE features from Cd(II)-tpy assemblies, the functionalized supramolecule **S** exhibited significantly enhanced AIPE compared to the ligand **L**. Via tuning the aggregation states of the functionalized ligand **L** and **S**, their AIPE behaviors were carefully investigated. More interestingly, further enhancement of phosphorescent emission was observed in both **L** and **S** when purged by CO_2 gas. As such, this system is expected to find practical applications, such as gas sensing.

Results and Discussion

In the synthesis of building block **L**, tetratopic tpy-pyridinium salt precursor **A** was synthesized using a modified procedure as previously reported.[23h] A terminal alkynyl group

was introduced into the backbone of **A** in order to further functionalize the metallo-supramolecule, including the installation of the following Pt(II) motif with the stable and rigid Pt(II)-alkynyl bond. The detailed synthesis procedure for **A** and chloroplatinum(II) bzimpy precursor **P** (Scheme S1) is described in the Supporting Information (SI). The final alkynylplatinum(II) bzimpy ligand **L** was synthesized by bridging **P** and **A** in the presence of a catalytic amount of copper(I) iodide and triethylamine in DMF solution under N_2 atmosphere.

All of the ligand and precursors were fully characterized by multi-dimensional nuclear magnetic resonance (NMR), including ^{1}H, ^{13}C, 2D correlation spectroscopy (2D COSY), and/or Nuclear Overhauser Effect Spectroscopy (NOESY), as well as electrospray ionization mass spectrometry (ESI-MS) (See details in SI). It is noteworthy that the proton resonance of ligand **L** showed very broad signals in $CDCl_3$ (Figure 1a), as well as in CD_3CN (Figure S38). In contrast, the proton resonance for the Pt(II) free precursor **A** displayed sharp signals (Figure 1b). All these results suggested that **L** was highly prone to aggregate in solutions through intermolecular Pt···Pt and π-π interactions [32].

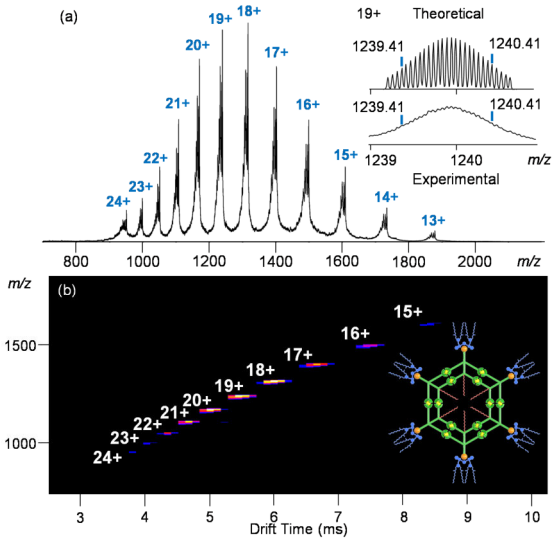


Figure 2. (a) ESI-MS and (b) TWIM-MS plots of **S**.

The self-assembly of **S** was achieved by treating **L** with $Cd(NO_3)_2$ in a stoichiometric ratio of 1:2, followed by counter-ion exchange with excess NH_4PF_6 to give **S** as a yellow precipitate in a high yield. The ^{1}H NMR spectrum of the supramolecule (Figure 1c) showed much sharper signals compared with the spectrum of **L**, indicating weaker aggregation of **S** owing to the bulky size of the octahedral coordination of <tpy-Cd(II)-tpy> unit that reduced the intermolecular Pt···Pt interactions. Two characteristic singlets with an integration ratio of 1:1 were observed at 9.00 ppm and 8.97 ppm, respectively, which were assigned to the tpy-$H^{3',5'}$ protons of the inner and outer layer, excluding the formation of polymeric species. Compared with those of **A**, the tpy-$H^{3',5'}$ signals of **S** showed a diagnostic downfield shifted (*ca.* 0.3 ppm), while the tpy-$H^{6,6''}$ peaks exhibited a significantly upfield shift (*ca.* 0.7 ppm), indicating the complexation of tpy units with Cd(II). Diffusion Ordered Spectroscopy (DOSY) NMR of **S** revealed a narrow band with diffusion coefficient log D = -9.20 at 298 K (Figure S50), suggesting the formation of a discrete structure. All the assignments were further supported by 2D COSY and NOESY spectra (Figures S45-S49).

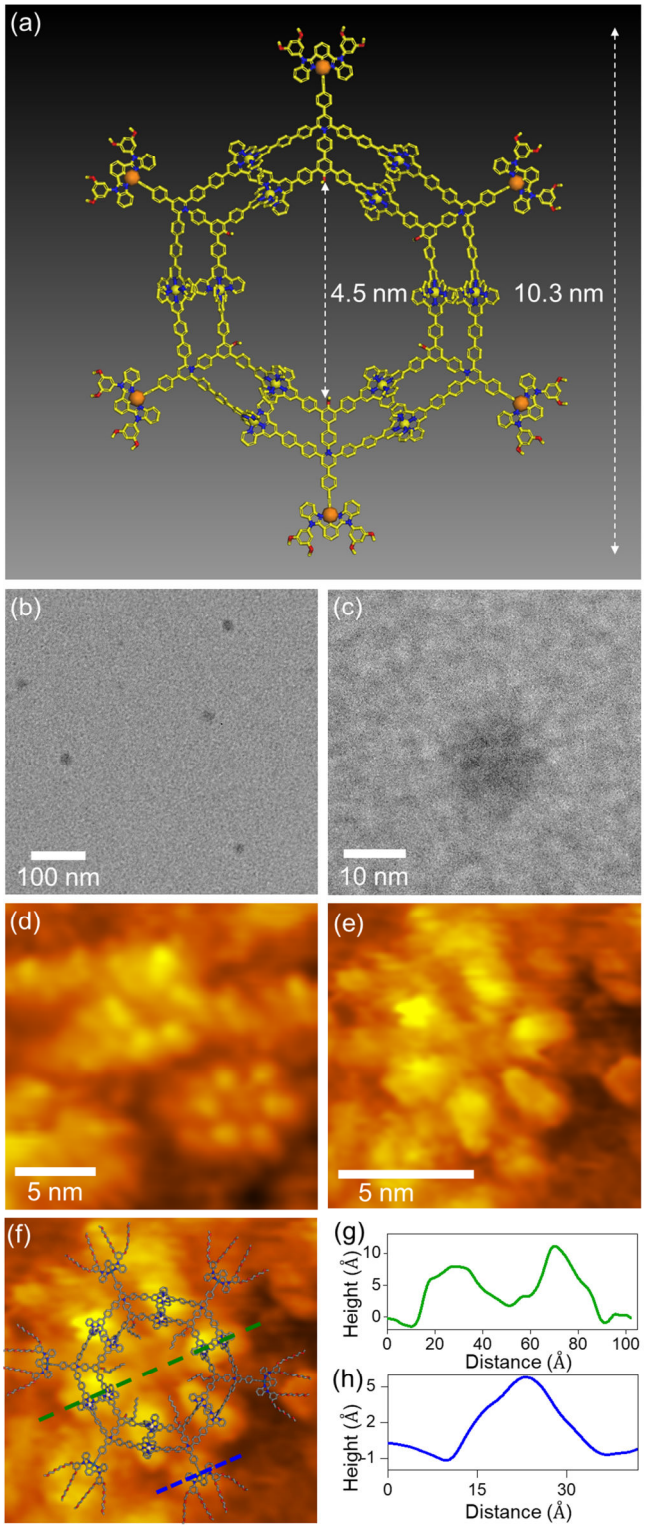


Figure 3. TEM and STM imaging of **S**. (a) Molecular modeling of **S** (Ethylene glycol and alkyl chains were omitted for clarity.) (b) TEM image of **S**. (c) Magnified TEM image of **S**. (d) A large area STM image of **S** showing the presence of two supramolecules, [Imaging parameters: V_t = 2.5 V, and I_t = 35 pA]. (e) Magnified image of a single supramolecule. (f) STM image of **S** with molecular modeling overlay [Imaging param-

eters: V_t = 2.5 V, and I_t = 29 pA]. (g and h) STM line profiling measurements made along the green and blue dashed lines shown in (f).

In addition, electrospray ionization-mass spectrometry (ESI-MS) and traveling wave ion mobility-mass spectrometry (TWIM-MS) [33] were used to characterize the functionalized supramolecule. A series of peaks with continuous charges from 13+ to 24+ was observed in ESI-MS (Figure 2a), due to the successive loss of PF_6^- counterions. After deconvolution, the molecular weight was calculated as 26,301 Da, corresponding to the chemical composition of $C_{1188}H_{1152}N_{108}O_{102}Pt_6Cd_{12}P_{36}F_{216}$. The experimental isotope pattern of each charge state agreed well with the corresponding simulated peak (Figure 2a inset, Figure S63). Moreover, only one set of signals was observed from TWIM-MS, indicating that there was no other structural conformer or isomer for the assembled structure (Figure 2b).

To further study the structure of the supramolecule, transmission electron microscope (TEM) was utilized to verify the size and shape of **S**. The supramolecules were observed as a dispersion of individual uniform dots (Figure 3b). The average size of the particles was in good agreement with the theoretical diameter calculated by molecular modeling (Figure 3a and c). In order to directly visualize the structure of the metallo-supramolecules with high resolution, ultrahigh vacuum-low temperature-scanning tunneling microscope (UHV-LT-STM) was also applied.[23k, 34] Ultrahigh vacuum provided a clean and neat environment to minimize noise, and low temperature would reduce thermal motion, thus leading to a higher resolution. A very dilute solution of **S** was drop-casted on a Ag(111) substrate followed by cooling down to 4 K. Due to the octahedral coordination and high electron density around the metal center, the STM imaging showed six elliptic bright dots corresponding to <tpy-Cd(II)-tpy> units, which depicted the framework of hexagonal structure (Figure 3d-f). Within the magnified image, the shape and direction of each elliptic-shaped lobe can be distinctly observed. Note that each dot was attributed as the fusion of signals from two <tpy-Cd(II)-tpy> units in the two layers because of the short distance between them. Moreover, the double-layered scaffold without Pt(II) motifs was measured to have a diameter of ~8 nm and a height of ~10 Å (Figure 3f-h), which agreed well with the theoretical modeling (Figure 3a). In sharp contrast to the bright lobes of <tpy-Cd(II)-tpy> units in STM measurement, Pt atoms did not exhibit strong signals. We speculated that the bulky <tpy-Cd(II)-tpy> unit with octahedral coordination geometry might lift the entire organic moieties off the substrate, as well as the end groups of alkynyl-Pt bzimpy. Therefore, the square planner Pt(II) center could have less contact with the surface, leading to the loss of tunneling current.

After the structural characterization, the emission properties of **S**, **L** and the precursors **A** and **P** were investigated in acetonitrile solutions (mixed with 5% CH_2Cl_2 for **A**) at room temperature. The normalized emission spectra are shown in Figure 4a and the emission parameters, including emission wavelengths and lifetimes are listed in Table S1. The emissions of **P**, **L**, and **S** exhibited large Stokes shifts (> 200 nm) with respect to their corresponding absorption bands (Figure S64),[35] and were prone to oxygen quenching. Additionally, the recorded emission lifetimes of **L** and **S** deduced from the decay traces were 270 and 218 ns, respectively (Figure 4b and c) which are longer than those of general fluorescence. These features implied a nature of room-temperature phosphorescence through the emission from the triplet excited states.

The emission spectra of **P**, **L**, and **S** resembled each other with essentially the same energy and similar vibronic progressions, indicating the same/similar original emitting excited states. The vibronic spacing between the band maxima (*ca.* 567 nm) and the shoulder (*ca.* 606 nm) was approximately 1135 cm^{-1}, which is in accordance with the stretching mode of the aromatic rings.[35] Also, broad tails were observed in **L** and **S** compared to **P** due to the metal–metal-to-ligand charge transfer (^{3}MMLCT) excited states from the Pt···Pt and π-π stacking interactions.[32] In view of the similar structural component in these three complexes, *i.e.*, bzimpy, as similar $[(N^N^N)PtCl]^+$ complex reported in the literature, we attribute the observed emission originating from the metal-perturbed $^3\pi,\pi^*$ emission of the bzimpy.[36] Pt(II)-contained precursor **P** exhibited short-lived emission of 18 ns (Figure S65). This phenomenon could be ascribed to the presence of thermally accessible low-lying metal-centered non-emissive $^3d,d$ state, which provided an additional decay pathway and quenched the ligand-localized $^3\pi,\pi^*$ emission. This is a common feature in many other $[(N^N^N)PtCl]^+$ complexes.[37] When the Cl ligand in **P** was replaced by the acetylide ligand in **L**, the electron-donating ability of the acetylide ligand lifted up the $^3d,d$ state with a negligible impact on the energy of the $^3\pi,\pi^*$ state. This separated the non-emissive $^3d,d$ state from the emitting $^3\pi,\pi^*$ state further, and consequently improved the emission in **L**. The introduction of heavy-atom Cd(II) during the self-assembly of **L** into **S** could induce intersystem crossing (a competing nonradiative thermal process with the radiative decay path) from the T_1 to S_0. Meanwhile, the weak ligand field strength of Cd(II) ion would narrow the energy gap between the nonemissive $^3d,d$ state and the emitting $^3\pi,\pi^*$ state, which would decrease the lifetime of **S**. Interestingly, **S** still retained a relatively long lifetime of 218 ns. It is worth noting that these phosphorescent properties are quite unique for such a giant supramolecule with a diameter of 10 nm.

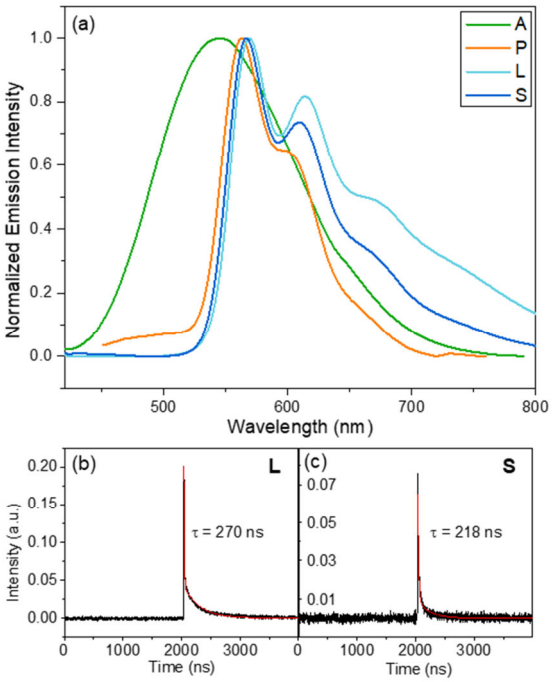


Figure 4. (a) Normalized emission spectra of **P** and **A** (λ_{ex} = 390 nm), **L** and **S** (λ_{ex} = 370 nm) in N_2 deoxygenated acetonitrile (with 5% CH_2Cl_2 for **A**) at room temperature ($c = 1 \times 10^{-5}$ mol/L). Emission lifetime decay traces of (b) **L** and (c) **S**.

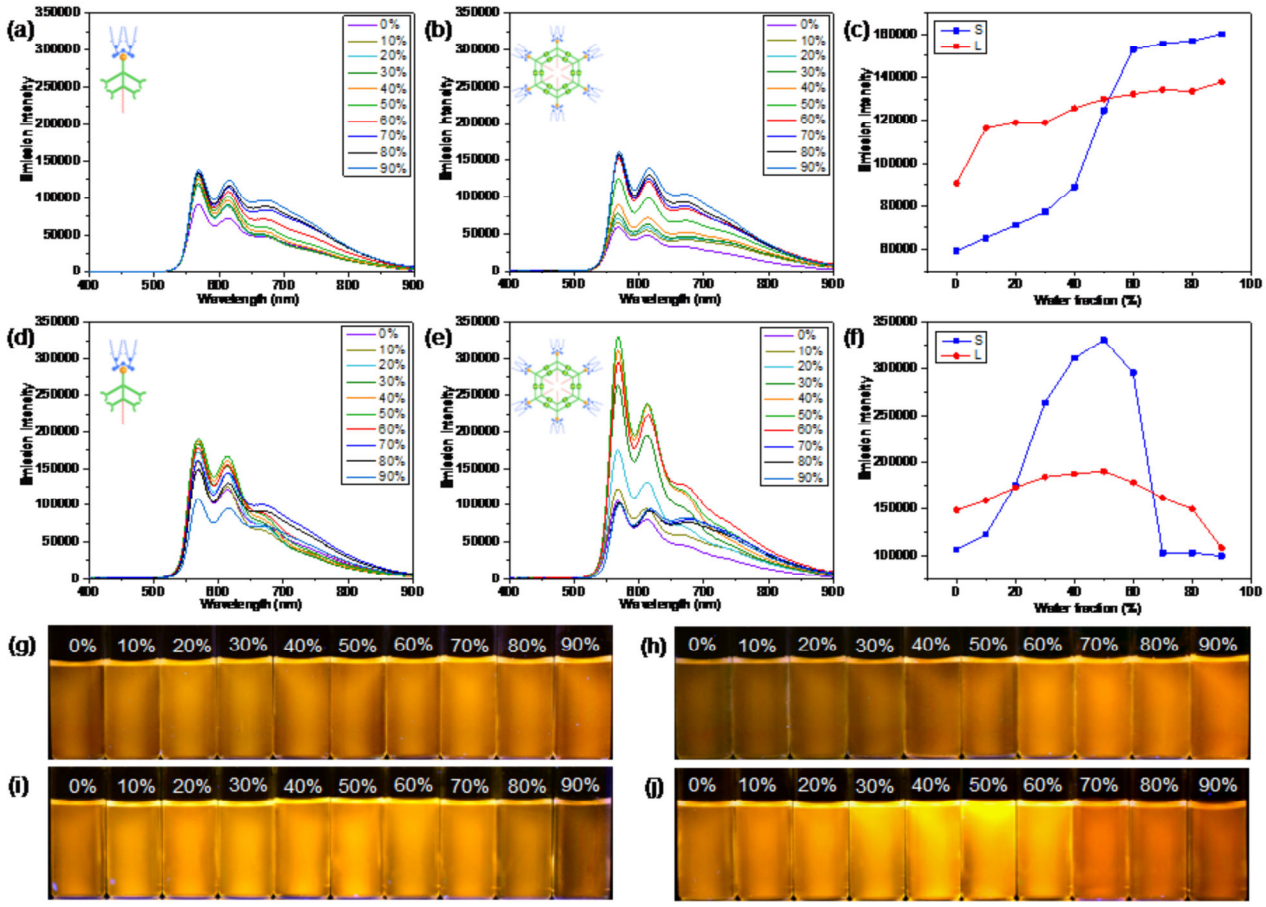


Figure 5. Emission spectra of **L** and **S**. (a) Emission spectra of ligand **L** in non-deoxygenated acetonitrile/water solvent (λ_{ex} = 370 nm, c = 3.5 μM). (b) Emission spectra of **S** in non-deoxygenated acetonitrile/water solvent (λ_{ex} = 370 nm, c = 0.6 μM). (c) Emission intensity of **L** and **S** at 567 nm with different fraction of water in non-deoxygenated acetonitrile/water solution (d) Phosphorescent emission spectra of **L** with N_2 deoxygenated acetonitrile/water solvent (λ_{ex} = 370 nm, c = 3.5 μM). (e) Phosphorescent emission spectra of **S** with N_2 deoxygenated acetonitrile/water solvent (λ_{ex} = 370 nm, c = 0.6 μM). (f) Emission intensity of **L** and **S** at 567 nm with different fraction of water in N_2 deoxygenated acetonitrile/water solution. (g) Emission photographs of **L** in non-deoxygenated acetonitrile/water with various water fractions. (h) Emission photographs of **S** in non-deoxygenated acetonitrile/water with various water fractions. (i) Emission photographs of **L** in N_2 deoxygenated acetonitrile/water with various water fractions (under 365 nm UV lamp). (j) Emission photographs of **S** in N_2 deoxygenated acetonitrile/water with various water fractions (under 365 nm UV lamp).

To investigate the intermolecular interactions within ligands and supramolecules, temperature-dependent emission studies were performed (Figure S66). The spectra of both **L** and **S** showed that with the elevation of the temperature, the intensity of the emission decreased dramatically as the non-covalent interactions could become negligible at high temperature.[38] These results suggested the existence of Pt···Pt interactions in both ligand **L** and supramolecule **S** at room temperature. Indeed, the formation of aggregations by Pt···Pt interactions brought the restriction of intramolecular rotation (RIR) effect at low temperature[26d, 26e], and immobilized the luminophores on the molecules, leading to the enhancement of emission.

Further detailed photophysical studies of **L** and **S** were performed in acetonitrile/water mixed solvents with various fractions of poor solvent (i.e., water), to investigate the AIPE effects. Since both **L** and **S** have installed multiple ethylene glycol chains for enhanced solubility in aqueous solutions, they did not show immediate precipitation with high fraction of water. When the fraction of water was increased, the UV−vis absorption spectra of both **L** and **S** (Figure S67) displayed a rise in the absorption tail around 480 nm, indicating the growth of ^{3}MMLCT transition due to Pt·· Pt interaction[30d, 39]

Both the ligand **L** and the supramolecule **S** showed weak emission in pure acetonitrile, with increasing the fraction of water as the poor solvent, **S** exhibited stronger emission in its aggregation state due to the cooperative effect from Pt(II) motif and <tpy-Cd(II)-tpy> units(Figure 5a and b). Furthermore, in the deoxygenated solvent without oxygen-quenching for the phosphorescence, supramolecule **S** exhibited significantly enhanced AIPE compared to ligand **L**, *i.e.*, the maximum in emission intensity reached 3.1-fold enhancement for **S** but only 1.3-fold increase for **L** (Figure 5b and 5e). In addition, the AIPE behavior was well maintained along with the increasing fraction of water from 0% to 50%. However, further

increasing the poor solvent fraction (60% to 90%) resulted in a decrease of phosphorescent intensity. Due to the poor solubility of **L** and **S** in water, we observed large aggregates formed in the solutions with high water fractions after the deoxygenating process.

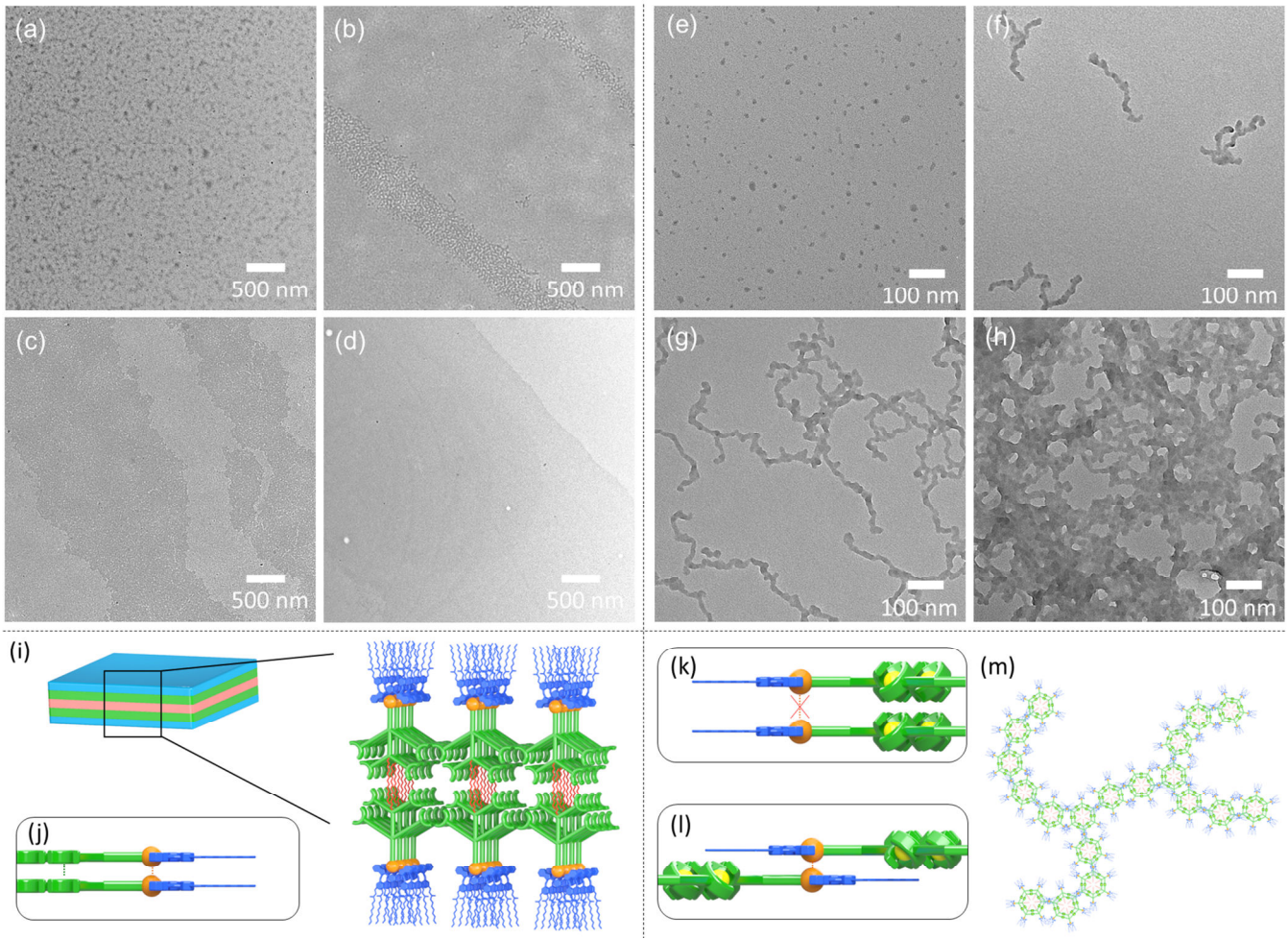


Figure 6. TEM images of **L** and **S** aggregates. TEM images of the aggregates of **L** formed in acetonitrile/water mixtures containing (a) 20%, (b) 40%, (c) 60%, and (d) 80% water, and aggregates of **S** formed in acetonitrile/water mixtures containing (e) 20%, (f) 40%, (g) 60%, and (h) 80% water. (i) Proposed formation of sheet-like aggregates by **L**. (j) Proposed Pt···Pt interaction and π-π stacking between ligands with face-to-face direction. (m) Worm-like aggregates of **S**. (k) Unfavourable face-to-face stacking. (l) Proposed head-to-tail Pt···Pt interaction bridging supramolecules without ring stacking.

And the precipitation formation caused the decrement of phosphorescent intensity.

For further comparison and investigation of the AIPE mechanism, supramolecule **C** without Pt(II) motif was constructed (see detailed characterizations in Figures S39-S44, S61 and S62) by assembling **A** and Cd(II) directly (Scheme S4). The emission enhancement was also observed by increasing the fraction of water (Figure S69a), suggesting the AIE feature of Cd(II)-tpy based supramolecules. However, **C** exhibited short-lived emission less than 5 ns and no further enhancements were observed with deoxygenated solvent (Figure S69b), indicating that this emission was fluorescence only.

Interestingly, variations in emission spectra were observed by using different gases to deoxygenate the solvent (Figure S70). It was found that CO_2 can further trigger substantial enhancements in emission intensity compared with the results in non-deoxygenated solvent (*ca*. 5.5-fold increase in case of **S**, and 1.8-fold increase in case of **L**). As a comparison, N_2 brought weaker enhancement for **L** and **S**, *i.e.*, 3.3- and 1.3-fold increase, respectively. We speculated that CO_2 might have weak interactions with Pt(II)[40], since CO_2 has a kinetic diameter of 3.3 Å, which is very close to the ideal distance between Pt atoms in Pt···Pt interaction (3.5 Å). As such, CO_2 might strengthen the Pt···Pt interactions between supramolecules with a higher RIR effect, leading to an increased emission. In addition, **S** exhibited more significant responses to different gases than **L**, perhaps due to the cooperative effect of multiple Pt(II) centers within the large supramolecular architectures. This property may lead to a potential application for gas sensing[41].

Morphology studies of aggregates were generally used for evaluating aggregation behaviors and investigating AIE or AIPE mechanism. Dynamic light scattering (DLS) and TEM were utilized to further elucidate the relationship between luminescent properties and aggregation of the ligand **L** and supramolecule **S**. The DLS results (Figure S71) showed the average hydrodynamic diameters (D_h) of the aggregations of **L** and **S** were increased with the increment of the water fraction. Also, the TEM images (Figure 6a-6d) showed that **L** aggregated into layered nanosheet structure in acetonitrile/water, and the size of the sheet was increased with the increment of water portion. In contrast, **S** aggregated into worm-like structures

(Figure 6e-6h). With the increase of the water fraction, the length of the worm-like aggregates extended and finally became a cross-linked structure. These results agreed well with the AIPE effect observed in acetonitrile/ water solvent.

It is interesting to observe the tremendously different aggregation morphologies of **L** and **S**. To further gain insight of the aggregation mechanism, different solvent mixtures were used to investigate their aggregation behaviors. Comparing with the layered structure observed in CH_3CN/water system, **L** formed spherical aggregates with diameters around 100 nm in DMF/Et_2O solution, and larger spherical structures could be observed in DMF/i-Pr_2O system (Figure S72). The difference between the sheet and sphere is possibly due to the long hydrophobic/hydrophilic chains decorated on the inner and outer rims of the ligand performing differently in aqueous/nonaqueous solutions. According to the observation, we postulated that both Pt···Pt interaction and π-π stacking might work simultaneously to organize ligand **L** with a face-to-face direction (Figure 6j).

In a sharp contrast, after coordinating with Cd(II), the metallo-supramolecule **S** did not aggregate into spherical/layered morphologies as **L**, or a tubular structure as the unfunctionalized concentric hexagons.[23h] Instead, the amorphous worm-like structure was the only morphology observed in several different solvent systems (Figure S73). We speculated that the entire concentric hexagon core played an essential role in regulating the aggregating behavior of Pt-Pt interaction and determining the final morphology of the hierarchical self-assembly. Since the ideal distance between Pt atoms in Pt···Pt interaction is reported around 3.5 Å,[42] the bulky octahedral coordination of <tpy-Cd(II)-tpy> with height of 10 Å as measured from STM can effectively prohibit the formation of π-π stacking and block the Pt-Pt interaction from face-to-face orientation (Figure 6k), but force the Pt-Pt interaction to a head-to-tail way (Figure 6l). The emissive behavior of individual components (Pt and tpy) was retained in supramolecule **S**, which even displayed enhanced phosphorescent properties during aggregation than individual components.

Conclusions

In summary, a giant but discrete concentric metallo-supramolecule with six well-arrayed alkynyl-platinum(II) bzimpy groups was assembled through rational design to enrich the library of phosphorescent metallo-supramolecules, which still remain in the infancy. The cyclic structure was clearly visualized by STM imaging at the submolecular resolution. With the Pt(II) motifs installed, functionalized ligand and metallo-supramolecule exhibited room-temperature phosphorescence with lifetimes of 270 ns and 218 ns, respectively. With the AIE enhancement from the <tpy-Cd(II)-tpy> coordination, supramolecule **S** exhibited conspicuously stronger AIPE compared to ligand **L**. In addition, both ligand and supramolecule exhibited significant responses to CO_2 gas, indicating the potential existence of weak interaction between gas molecules and aggregates. Regarding the aggregation behaviors driven by intermolecular interactions, the ligand could aggregate into layered and spherical structures in different solvent systems, while the supramolecule could only aggregate into worm-like structure and gel at high concentration. Our endeavors expand the scope of discrete phosphorescent materials into the dimensions beyond 10 nm, and will shed lights on the development of novel phosphorescent materials that combine the advantages from small molecules and polymers, i.e., precise functions, high level of sophistication and facile device fabrication.

ASSOCIATED CONTENT

Supporting Information

Synthetic details, ligands and complexes characterization including ^{1}H NMR, ^{13}C NMR, 2D COSY, 2D NOESY, ESI-MS, TWIM-MS , UV-Vis, TEM are included in supporting information. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interests.

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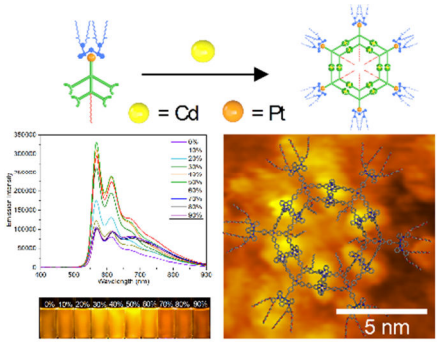
Table of Contents



A new discrete metallo-supramolecular concentric hexagon functionalized with six alkynylplatinum(II) bzimpy moieties was prepared. With a size larger than 10 nm and molecular weight higher than 26,000 Da, the assembled supramolecule displayed phosphorescent emission at room temperature. Moreover, the supramolecule exhibited enhanced aggregation-induced phosphorescent emission compared to the ligand.