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Concentration and acid–base controllable fluorescence of a metallosupramolecular polymer†

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A metallosupramolecular polymer (MP-Zn) bearing dibenzo-24-crown-8 (DB24C8) arms is constructed by coordinating Zn²⁺ with a conjugated bis-terpyridine ligand, which indicates concentration-dependent emissions from cyan to white to yellow. Successively, reversible emissions are realized by acid–base controllable recognition of DB24C8 moieties in MP-Zn with dialkylammonium ion centers.

By utilizing multiple nonvalent interactions, living systems can self-assemble into hierarchical nanostructures with desired multifunctional properties, which has inspired fabrication of multimodal artificial supramolecules.¹ Typical examples are supramolecular polymers that are fabricated by binding monomeric units *via* reversible non-covalent and/or dynamic covalent interactions. Because of the dynamic nature, they usually respond to a diverse range of external stimuli, such as pH values, temperatures, and chemical reactions.² These types of polymers are being developed for potential applications in the fields of molecular devices, healable materials, and drug delivery.² Of particular note is that the combination of two or more kinds of non-covalent interactions together can endow supramolecular polymers with more complicated topological structures and unique functions.³ Recent research studies focus on topological structures³ and sol–gel transition of supramolecular polymers^{3d,g,o} constructed by multiple non-covalent interactions. Comparatively, little effort has been made to investigate their photophysical properties and controllable transformations.^{2d,3i} Such supramolecular polymers are expected to hold great promise for applications in developing luminescence soft materials and their resulting optoelectronic devices.

It is well-known that dibenzo-24-crown-8 (DB24C8) can form a steady 1 : 1 threaded structure with its complementary guest dibenzylammonium salts (DBAs) by means of a cooperative combination of [N⁺–H··O] and [C–H··O] hydrogen bonds and π – π stacking interactions. Such host–guest assemblies are responsive to ions, pH values, or temperatures.⁴ On the other hand, metal–ligand coordination interactions have tunable binding strength and various coordination modes. Metallosupramolecular polymers can be accordingly fabricated with metal-centered features, such as unique catalysis, redox, and photophysical properties.⁵ The above-mentioned two interactions are independent of each other.^{3h,i,n} Therefore, the combination of the DB24C8-based host–guest interaction with the metal–ligand complexation could facilitate the construction of novel stimuli-responsive supramolecular materials.^{3h,i,n} Herein, we report the fabrication of a light-emitting supramolecular polymer (MP-Zn) by complexing Zn²⁺ with a conjugated bis-terpyridine ligand bearing two DB24C8 groups (Scheme 1). MP-Zn shows concentration and acid–base controllable emissions.

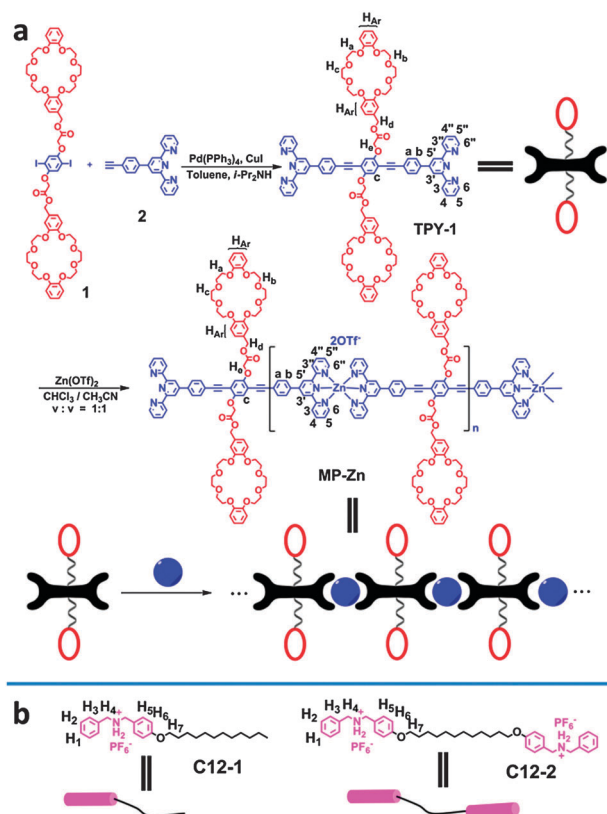
Compounds **1** and **2** were synthesized according to ref. 7c and 5d, respectively. Sonogashira coupling of **1** with **2** resulted in the formation of a bis-terpyridine ligand with two DB24C8 groups (TPY-1) as depicted in Scheme 1. TPY-1 was characterized by high resolution electrospray ionization mass spectrometry (ESI-MS) and ¹H and ¹³C NMR spectroscopies (Fig. S1 and S2, ESI†). An acetonitrile solution of Zn(OTf)₂ was added to an isovolumetric chloroform solution of TPY-1 at room temperature with vigorous stirring, where their final molar ratio was controlled at 1/1. This mixture was stirred for 30 min prior to further analyses.

The resulting ¹H NMR spectrum of MP-Zn (1.25 mM) showed two typical features (Fig. S3, ESI†). (a) The resonance proton signals of TPY-1 were broadened significantly and no signals for the uncoordinated TPY-1 were detected. (b) The (3',5'), (3,3''), (4,4''), and (5,5'')-terpyridine proton signals were shifted toward downfield regions, while the upfield shift of the (6,6'')-terpyridine signals was clearly observed. These signal changes indicated the formation of the desired metallosupramolecular polymer, MP-Zn.^{5d,e} A diffusion-ordered NMR spectroscopy (DOSY) experiment was also employed to investigate the coordination

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Scheme 1 Synthetic approach of (a) TPY-1 and MP-Zn; (b) chemical structures of the guest molecules, C12-1 and C12-2.

between TPY-1 and $\text{Zn}(\text{OTf})_2$ (Fig. S8 and S9, ESI[†]). As shown in Fig. S10 (ESI[†]), the diffusion coefficient D values decreased from 3.42×10^{-9} to $2.10 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ after the complexation with $\text{Zn}(\text{OTf})_2$, which indicated the formation of a high molecular-weight polymer. The UV-vis absorption spectrum of TPY-1 revealed that the band due to a $\pi\text{-}\pi^*$ charge-transfer transition appeared at 365 nm (Fig. S11, ESI[†]). This absorption band showed a red-shift to 380 nm upon Zn^{2+} complexation with TPY-1 in the chloroform/acetonitrile mixture solvent ($v/v = 1$, Fig. S12, ESI[†]). As already addressed for Zn^{2+} -based supramolecular polymers, such an absorption red-shift originated due to Zn^{2+} coordination with bis-terpyridine ligands.^{5d,e} Therefore, the ^1H NMR, DOSY NMR and UV-vis spectra confirmed that the coordination binding occurred between TPY-1 and Zn^{2+} ions, leading to the formation of a metallosupramolecular polymer, MP-Zn.

The sizes of TPY-1 and MP-Zn in the chloroform/acetonitrile mixture solvents ($v/v = 1:1$) were determined experimentally through DLS measurements at room temperature (Fig. S13, ESI[†]). The DLS plot of a solution of TPY-1 (1.25 mM) showed a peak at a hydrodynamic diameter (D_h) of $3.1 \pm 0.4 \text{ nm}$, which was consistent with its molecular size (*ca.* 3.0 nm). At a concentration of 1.25 mM of MP-Zn, a DLS signal appeared at 158 nm, indicating the presence of a supramolecular polymer with a high molecular weight. At 125 μM , the DLS plot revealed two signal modes at 32 and 160 nm. The former was accordingly assigned to the supramolecular oligomer of MP-Zn, whereas the latter was consistent with the DLS signal at 1.25 mM. When the concentration of MP-Zn

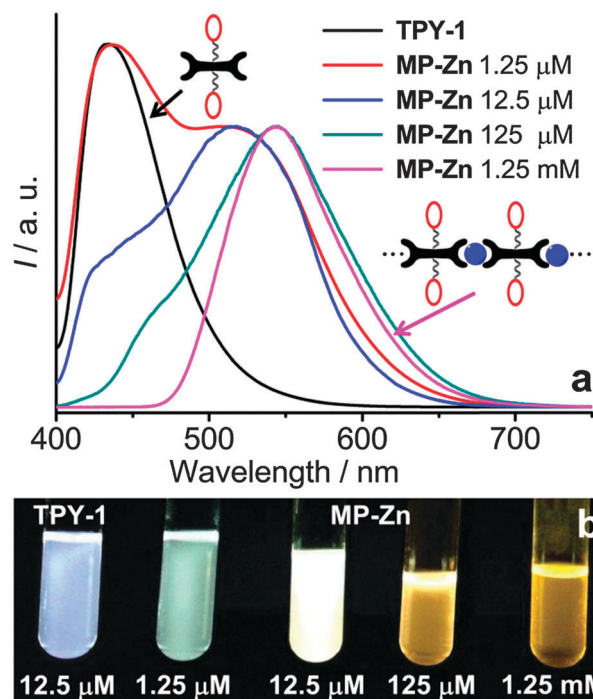


Fig. 1 (a) Fluorescence emission spectra of TPY-1 and MP-Zn in $\text{CHCl}_3/\text{CH}_3\text{CN}$ ($v/v = 1/1$). (b) Photographs of TPY-1 and MP-Zn under UV irradiation. The concentrations referred to the monomer concentrations.

decreased to 12.5 μM , three broad bands were clearly centered at 5, 15, and 132 nm. The first band directly corresponded to the sizes of the monomer, the dimer, and the trimer. The latter two values clearly originated from the supramolecular oligomer and polymer, respectively. A further decrease in the concentration led to a large error because of the detection limit. These DLS situations were of similarity with the reported supramolecular polymers prepared from terpyridine-Zn coordination^{3h} and [60]fullerene host-guest recognition.^{6a}

Upon excitation at 380 nm, TPY-1 showed a strong emission band at 435 nm (Fig. 1a). After TPY-1 was coordinated with Zn^{2+} ions, MP-Zn showed up concentration controllable fluorescence. At a concentration of 1.25 μM , two emission bands were clearly recognized at 435 and 516 nm with comparable intensities. Under UV illumination at 365 nm, this solution indicated a cyan emission (Fig. 1b). When the concentration was increased to 12.5 μM , the relative intensities of the two emission bands increased and decreased to an appropriate degree, respectively. However, nearly white emission occurred at this moment. A further increase in the concentration to 125 μM led to clear red shifts of the emission bands from 435 and 516 nm to 460 and 545 nm, respectively. And the emission band at 460 nm decreased significantly in its relative intensity. When the concentration reached 1.25 mM, the high-energy shoulder disappeared totally and only a band at 545 nm was observed. The latter two solutions showed a yellow emission under UV illumination at 365 nm. In conjugated polymers, an increase in repeating units generally results in the red shift of the emission band. When the repeating units were increased to an appropriate degree, the emission bands did not red shift

any more.⁸ Therefore, the red shift from 516 nm to 545 nm was derived from the increasing degree of polymerization at the high concentrations of 125 μM and 1.25 mM. The emission band centered at 435 nm was assigned to an excited state of free TPY-1. Accordingly, it was reasonable that the emission band at 460 nm corresponded to an excited state of the oligomers of MP-Zn at a concentration of 125 μM . These spectral assignments were consistent with the DLS results at different concentrations.

As discussed above, the coordination of Zn^{2+} ions by terpyridine-like ligands is relatively weak and highly labile in solution specifically under dilution conditions. Accordingly, it is reasonable to believe that the Zn^{2+} -coordinated supramolecular polymers form linear oligomers at low concentrations and linear polymers with a high degree of polymerization at high concentrations. This conjecture is completely consistent with the situation of supramolecular polymers formed by other nonvalent interactions.^{3h,k,6} In the present case, it is not strange that the oligomers and free TPY-1 ligands appeared in the solution at the low concentrations. On the basis of these considerations, the emission bands at 516 and 435 nm were tentatively assigned to $\pi-\pi^*$ excited states of the oligomers and uncoordinated TPY-1, respectively. The band centered at 545 nm was accordingly attributed to a $\pi-\pi^*$ excited state of linear polymers with a high degree of polymerization at high concentrations. This latter assignment agreed well with the previously reported results of other Zn^{2+} -coordinated supramolecular polymers.^{5d,e} To the best of our knowledge, this is the first example for concentration and thus polymerization degree controllable fluorescence of metallosupramolecular polymers.

Next, we examined host-guest recognition of MP-Zn with the guest molecules, C12-1 and C12-2 (Fig. 2). They have one and two DBA groups, respectively. Upon addition of C12-2 to a solution of MP-Zn ($\text{CDCl}_3/\text{CD}_3\text{CN}$, $v/v = 1:1$), the resulting ^1H NMR spectrum became really complicated and key changes were described as follows (Fig. 2b). The resonance signals of C12-2 and DB24C8 groups split uncomplexed and complexed moieties. Among these signals, the benzyl protons H_4 of C12-2 shifted downfield

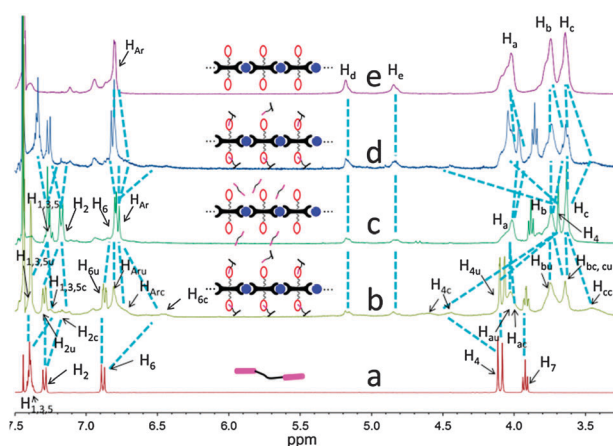


Fig. 2 Partial ^1H NMR spectra (400 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$, 1/1) of (a) guest C12-2, (b) 1.25 mM MP-Zn (monomer concentration) with 1.0 equivalent of C12-2 (DBA/DB24C8 1:1 molar ratio), (c) obtained by adding 2.4 equivalents of $\text{P}_1\text{-tBu}$ to (b), (d) obtained by adding 2.8 equivalents of CF_3COOH to (c), and (e) 1.25 mM MP-Zn. Here "u" and "c" denote uncomplexed and complexed moieties, respectively.

from $\delta = 4.1$ to 4.6 ppm together with the significant broadening, while the other signals of C12-2 and DB24C8 groups shifted upfield. These chemical shifts indicated that the partial crown ether moieties were threaded by the dialkylammonium ions. Subsequent addition of 2.4 equivalents of base (*N-tert-butyl- N',N',N'',N'',N''',N''' -hexamethyl-phosphorimidic triamide*, $\text{P}_1\text{-tBu}$) resulted in the absence of complexed signals (Fig. 2c). The obtained ^1H NMR spectrum was consistent with the combined one of MP-Zn and deprotonated C12-2, indicating that the host-guest recognition was completely dissociated. When 2.8 equivalents of CF_3COOH were subsequently added, the ^1H NMR spectrum was restored completely, where the complexed signals were clearly observed again (Fig. 2d). Upon addition of C12-1 the solution of MP-Zn resulted in almost the same ^1H NMR spectral changes as described above (Fig. S14, ESI †).

With these results in mind, we further investigated fluorescence responsiveness of MP-Zn by performing acid-base reactions. Upon titration of MP-Zn (1.25 μM) with C12-2, the fluorescence bands centered at 435 and 516 nm showed a stepwise decrease in their intensities (Fig. 3a). After 2.4 equivalents of $\text{P}_1\text{-tBu}$ were subsequently added to the above mixture of MP-Zn and C12-2, the emission intensities of both bands reverted back to the original level. Upon addition of 2.8 equivalents of CF_3COOH , the fluorescence intensity decreased again (Fig. 3b). When MP-Zn was treated with C12-1, similar emission changes in the fluorescence intensities were also observed (Fig. S15, ESI †). Such fluorescence reversibilities were accordingly attributed to the threading and dethreading of DBAs in the host moieties of MP-Zn under the acid-base reactions. Generally, conjugated polymers show strong fluorescence in solution, which can be quenched or weakened by their aggregation induced by non-covalent interactions.⁷ In our case, the host-guest recognition between DB24C8 and DBA groups may result in the more rigidity and/or polarity and thus aggregation of the resulting complexes in the solutions.

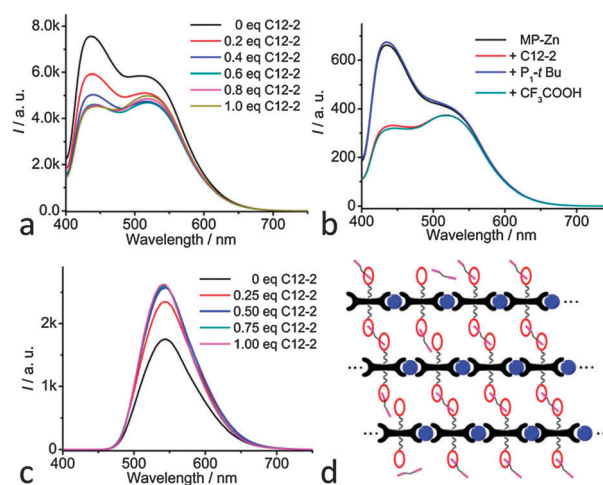


Fig. 3 (a) Fluorescence spectra of MP-Zn in $\text{CHCl}_3/\text{CH}_3\text{CN}$ ($v/v = 1:1$, 1.25 μM) upon titration with C12-2. (b) Fluorescence responsiveness of MP-Zn by performing acid-base reactions. (c) Fluorescence spectra of MP-Zn in $\text{CHCl}_3/\text{CH}_3\text{CN}$ ($v/v = 1:1$, 1.25 mM) upon titration with C12-2. (d) Schematic representation of cross-linked MP-Zn.

Upon titration of MP-Zn with C12-2 at a concentration of 1.25 mM, however, the fluorescence band centred at 545 nm showed a significant increase in its intensity (Fig. 3c). Of difference was that only slight fluorescence enhancement was observed when the solution of MP-Zn was treated with C12-1 (Fig. S16, ESI†). According to the aggregation-enhanced emission,⁹ when the intra- and/or inter-molecular rotations of non-planar luminogenic molecules are restricted, the non-radiative pathway is blocked and the radiative channel is opened, both of which cause an enhanced emission. Due to the host-guest recognition between DB24C8 and DBA groups, the intramolecular rotations were partly restricted at the molecular level, which induced the emission enhancement. These phenomena were in agreement with the reported organometallic luminogens.^{9b-f} As shown in the DLS plots (Fig. S17, ESI†), upon addition of C12-1, the size distribution of the resulting complex became broad. Comparatively, the addition of C12-2 resulted in a sharp increase in the D_h from 158 to 5450 nm, indicating the presence of larger aggregates in the resulting solution. The TEM image showed that an interconnected film was formed (Fig. S18, ESI†). This cross-linked network further restricted the intermolecular rotations (Fig. 3d) and thus the resulting fluorescence was significantly enhanced. At the intermediate concentrations of 12.5 and 125 μ M, no significant changes were detected in their fluorescence intensities (Fig. S16, ESI†).

In summary, we have constructed a supramolecular polymer MP-Zn bearing DB24C8 arms by coordinating Zn(OTf)₂ with a ditopic TPY-1 *in situ*. This metallosupramolecular polymer shows concentration-dependent and acid-base controllable emissions. Such dual responsiveness is highly important to develop a new kind of fluorescence materials and molecular devices.

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