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A fluorescent cross-linked supramolecular network formed by orthogonal metal-coordination and host–guest interactions for multiple ratiometric sensing†

Luonan Xu,‡[a] Dong Chen,‡[a] Qian Zhang,[a] Tian He,[a] Chenjie Lu,[a] Xi Shen,[a] Danting Tang,[a] Huayu Qiu,[a] Mingming Zhang *[b] and Shouchun Yin *[a]

A cross-linked supramolecular network was prepared by the orthogonal self-assembly of metal-coordination and host–guest interactions. Due to the incorporation of two fluorophores, coumarin and tetraphenylethene, into the network as well as the abundant stimuli-responsiveness of the two non-covalent interactions, it can be used for the ratiometric sensing of pH, cyclen and Cl$^-$.

Cross-linked supramolecular networks are used to describe polymer networks cross-linked by non-covalent interactions (*e.g.*, hydrogen bonding, host–guest interactions, π–π stacking, and metal-coordination interactions).[1] Various functions, such as stimuli-responsiveness, self-adaptability, self-healing and shape-memory properties, are expected for these networks due to the reversibility of these non-covalent interactions.[2] Compared with supramolecular networks cross-linked by only one type of non-covalent interaction, the introduction of two or more orthogonal non-covalent interactions is even more interesting, especially for fluorescent sensing because the incorporation of more interactions will bring more stimuli-responsiveness into the system, making the networks good candidates for multiple sensing.[3]

In recent years, fluorescent supramolecular polymers and polymer networks have received much attention and some of them have already been used for chemical sensing.[4] For example, Huang and co-workers reported a supramolecular cross-linked network using a conjugated polymer as the fluorophore for multiple sensing.[3c] However, the conjugated polymer backbones normally present aggregation-caused quenching (ACQ) properties,[5] which means that their fluorescence was often weakened or quenched at high concentrations, thus limiting their application as solid fluorescent sensors. In 2001, a different type of fluorophore (such as tetraphenylethene (TPE) and hexaphenylsilole (HPS)) which is non-emissive in dilute solution but highly emissive in the aggregation state was reported by Tang and coworkers.[6] This phenomenon was termed as aggregation-induced emission (AIE). Recently, we prepared a fluorescent supramolecular polymer containing TPE which could be used as a chemosensor for Pd^{2+} ions.[7] It is worth mentioning that the fluorescence of the above sensors was often monitored at a single wavelength, so the measuring accuracy would be easily affected by the microenvironment, sensor concentration, illumination intensity and so on.[8] Therefore, it is of great importance to develop ratiometric fluorescent sensors to eliminate the ambiguities by self-calibration from two emission bands.[9] Herein, we introduced two different fluorophores, coumarin with ACQ properties and TPE with AIE properties, to prepare a supramolecular network with two emission bands. In dilute solutions, the supramolecular network is expected to mainly give the fluorescence of coumarin, while the emission of TPE should dominate the fluorescence at high concentrations. Due to the abundant responsiveness derived from the orthogonal metal-coordination and host–guest interactions, the supramolecular network can be easily disassembled and reassembled by multiple stimuli, together with varied fluorescence intensity at two wavelengths from the ACQ and AIE chromophores, making it suitable for multiple ratiometric fluorescent sensing.

Polymer **P1** with polystyrene as the backbone with coumarin moieties and dibenzylammonium salt (DBAS) units as pendant groups was prepared by the copolymerization of styrene, a coumarin derivative **7** and a DBAS derivative **9** (Scheme S2†). **H1** was synthesized by linking dibenzo-24-crown-8 (DB24C8) and terpyridine to each side of a bi-functional TPE. The mixture of **P1** and **H1** (1 : 1 DBAS/DB24C8 in molar ratio) mainly exhibited two fluorescent peaks at 390 and

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[a] *College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, P. R. China. E-mail: yinsc@hznu.edu.cn; Fax: +86-571-28867899; Tel: +86-571-28867897*

[b] *State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, P. R. China. E-mail: mingming.zhang@xjtu.edu.cn*

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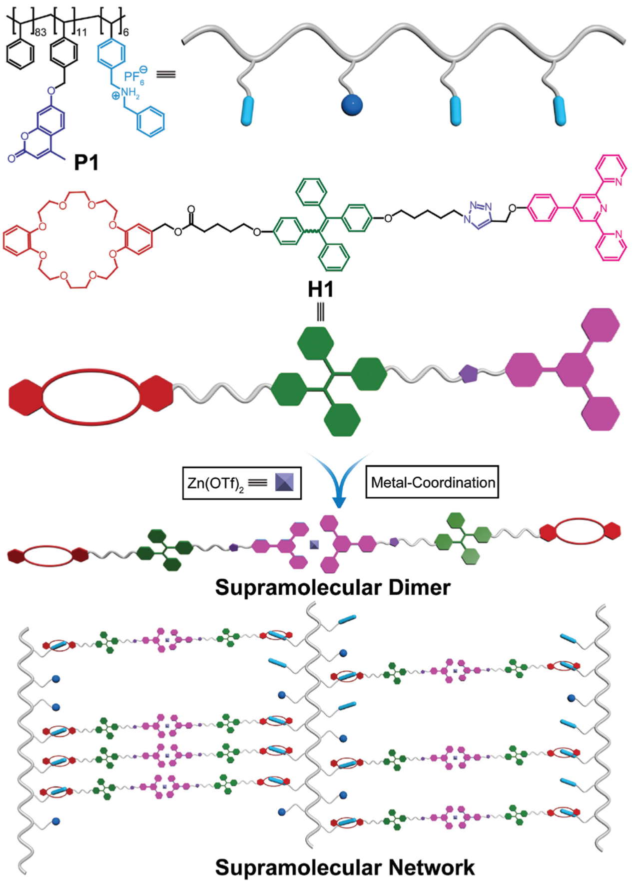
‡ These authors contributed equally to this work.

460 nm derived from the emission of coumarin and TPE, respectively. The supramolecular polymer network was prepared by subsequently adding $Zn(OTf)_2$ to the above mixture, along with an increased emission at 460 nm and a decreased emission at 390 nm. This is because the addition of $Zn(OTf)_2$ would combine **P1** and **H1** to form networks, making the whole system aggregate and thus the emission from the AIE fluorophore (TPE) would play a more significant role than that from the ACQ fluorophore (coumarin).[7,10] The addition and removal of cyclen, Cl^- or a base would disassemble and reassemble the network, accompanied by the changes of the fluorescence intensities at these two wavelengths, making the network work as a multiple ratiometric fluorescent sensor. Moreover, the supramolecular polymer network would form supramolecular gels at high concentrations, which possess macroscopic self-healing properties as bulk materials (Scheme 1).

The metal-coordination interactions between $Zn(OTf)_2$ and terpyridine were studied by UV-Vis spectroscopy (Fig. S19†). A clear isosbestic point at 315 nm was observed by gradually adding $Zn(OTf)_2$ to the solution of **H1**, indicating the existence of metal–ligand interactions. The absorbance at 327 nm hardly changed when the molar ratio of $Zn(OTf)_2$/**H1** reached 0.5, suggesting that the stoichiometry between $Zn(OTf)_2$ and **H1** is 1 : 2 in this system.[11] ^1H NMR provided insights into the complexation between DB24C8 and DBAS in the networks. Clear chemical shift changes were observed for both benzyl protons of DBAS and ethyloxy protons of DB24C8 and all of them split into two sets of signals, which are the characteristic properties of the DB24C8/DBAS recognition motif. All these pieces of evidences are consistent with previously reported results,[1d,2e] indicating the orthogonal metal-coordination and host–guest interactions.



Scheme 1 Cartoon representations of **P1**, **H1**, the supramolecular dimer formed by **H1** and $Zn(OTf)_2$ and the supramolecular network.

To confirm the formation of supramolecular polymer networks, two-dimensional diffusion-ordered NMR (DOSY), viscosity measurements, and concentration-dependent ^1H NMR were performed. The diffusion coefficients decreased considerably from 10.01×10^{-11} to 0.45×10^{-11} m^2 s^{-1} as the concentration of the system increased from 0 to 21 mM (Fig. 1). The correlation between the specific viscosity and the concentration of **P1** was almost linear at a concentration of 1.35–32.40 mM, while the specific viscosity of the mixture of **P1**, **H1** and $Zn(OTf)_2$ increased exponentially with the increase in DBAS concentration. The concentration-dependent ^1H NMR spectra further proved the formation of the supramolecular polymer networks because the original uncomplexed methylene peaks gradually decreased while the complexed peaks increased as the concentration increased from 0 to 15 mM (Fig. S21†).[2e,3b] All these data suggest the formation of the cross-linked supramolecular network.

Fluorescence spectroscopy was conducted to study the emission properties of the networks. The UV/Vis and fluorescence spectra of individual **H1** and **P1** were first recorded

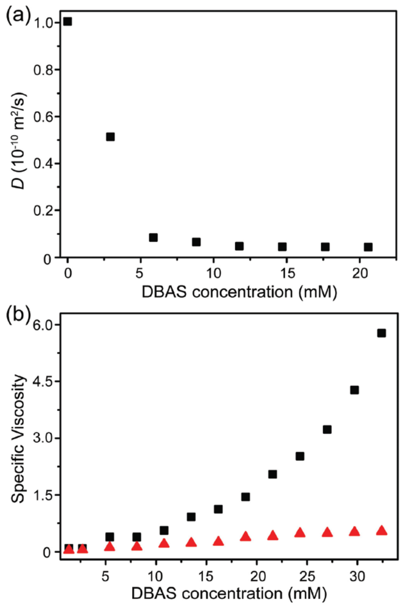


Fig. 1 (a) Concentration-dependent diffusion coefficient *D* (500 MHz, 1 : 1 $CDCl_3/CD_3CN$, 293 K) of the supramolecular network. (b) Specific viscosity (1 : 1 $CHCl_3/CH_3CN$, 298 K) of **P1** (▲) and the supramolecular network (■) *versus* DBAS concentration. Here, the concentration of DBAS was used as the monomer concentration.

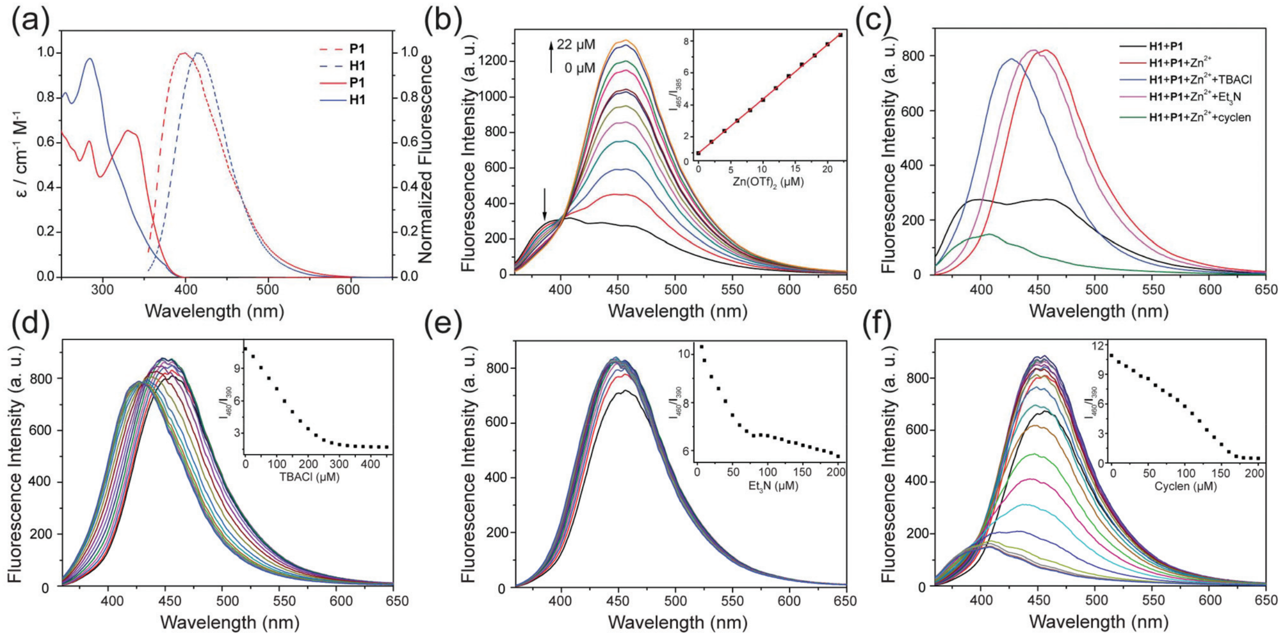


Fig. 2 (a) Normalized UV/Vis and fluorescence spectra of **H1** (100 μM) and **P1** (18.6 μM). (b) Fluorescence spectra of the mixture of **H1** (100 μM) and **P1** (18.6 μM) with increasing amount of $Zn(OTf)_2$. Inset: Ratio of the fluorescence intensities at 460 nm and 390 nm as a function of the $Zn(OTf)_2$ concentration. (c) Fluorescence spectra of the mixture of **H1** (100 μM) and **P1** (18.6 μM) and the addition of $Zn(OTf)_2$ (50 μM), TBACl (450 μM), Et_3N (200 μM) or cyclen (200 μM). Fluorescence spectra of the network (**H1**: 100 μM, **P1**: 18.6 μM and $Zn(OTf)_2$: 50 μM) with increasing amount of (d) TBACl, (e) Et_3N and (f) cyclen. The insets are the plots of the fluorescence intensity ratio (I_{460}/I_{390}) as a function of the concentration of (d) TBACl, (e) Et_3N and (f) cyclen. λ_{ex} = 350 nm.

(Fig. 2a and S22†). **H1** showed one absorption band centered at 285 nm while **P1** exhibited two absorption bands centered at 283 nm and 329 nm. An emission at 390 nm derived from coumarin was observed for **P1**. **H1** emitted at 415 nm, which should come from the emission of terpyridine moieties as indicated by the fluorescence spectra of a terpyridine derivative in Fig. S23† because TPE units are nearly non-emissive in dilute solutions.[12] There was little overlap between the absorption of **H1** and the emission of **P1**, indicating that no obvious Förster resonance energy transfer (FRET) would take place between the two species and the changes of the fluorescence were mainly due to the changes of the aggregation densities of the networks. The mixture of **P1** (18.6 μM) and **H1** (100 μM) exhibited two main fluorescent peaks at 390 and 460 nm arising from the emission of the coumarin and TPE units, respectively, while the emission at 415 nm from the terpyridine group was covered by the strong emission from the coumarin groups. Gradual addition of $Zn(OTf)_2$ into the mixture of **P1** and **H1** (DBAS/DB24C8 = 1/1 in molar ratio) increased the emission at 460 nm and decreased that at 390 nm and the ratio I_{460}/I_{390} fits linearly proportional to the concentration of $Zn(OTf)_2$ (Fig. 2b and Fig. S22†). This is because the addition of $Zn(OTf)_2$ will cross-link **P1** and **H1** to form networks, which will force the aggregation of TPE to give a bright emission at 460 nm, accompanying the decrease in emission at 390 nm from coumarin.

Since both metal-coordination and host–guest interactions were incorporated into the network structure, the degradation of the network should be easily induced by the destruction of either metal-coordination or host–guest interactions, thereby inducing the changes of fluorescence. The fluorescence changes based on the addition of competitive ligands (TBACl, Et_3N or cyclen) were sequentially studied in detail. As seen in Fig. 2c, a blue shift (from 460 nm to 420 nm) was observed by the addition of TBACl to the network, indicating that the network was totally destroyed as the emission of individual **H1** located at *ca.* 420 nm. The addition of Et_3N also resulted in a blue shift of the emission band (from 460 nm to 445 nm), meaning that the addition of a base would also influence the emission of **H1** to a certain extent. The addition of cyclen dramatically decreased the emission of the network, along with a blue shift from 460 nm to 410 nm.

The different fluorescence responses inspired us to explore the network for sensing Cl^-, pH and cyclen. Quantitative titration experiments were performed upon the addition of TBACl, Et_3N or cyclen to the network and the fluorescence spectra at varied concentrations of the competitive ligands were recorded (Fig. 2d–f). When the concentration of TBACl increased from 0 to 450 μM, the ratio between the emission intensities at 460 and 390 nm (I_{460}/I_{390}) decreased dramatically from 10.8 to 1.7. Similar results were also observed when Et_3N or cyclen was used as competitive ligands. The detection limits of the network for Cl^-, Et_3N and cyclen were calculated to be 24.9, 18.6 and 14.5 μM, respectively (Fig. S24†). It is worth mentioning that although the addition of the three ligands all induces a decrease in the emission, their influences on the maximum emission are different, providing a possible route to distinguish the three stimuli by fluorescence experiments. Therefore, the supramolecular polymer network could be used as a multiple ratiometric fluorescent sensor to detect Cl^-, Et_3N and cyclen.

With the increase in concentration, the cross-linked networks formed supramolecular gels, which were characterized by rheological experiments and scanning electron microscopy (SEM). The storage modulus (G') was larger than the loss modulus (G''), and both were independent of the angular frequency (ω) (Fig. 3a), indicating the formation of organogels. Besides, interconnected network structures (Fig. 3b) were observed by SEM, which were the characteristics for gel structures. Moreover, owing to the reversibility of the non-covalent interactions, the gels showed both stimuli-responsive gel–sol transition (Fig. 4) and self-healing behaviors (Fig. 3c, d and S25†). The gels would form sols by heating or adding KPF_6, Et_3N or cyclen, and the reverse process could be triggered by cooling or adding B18C6, CH_3COOH or Zn^{2+}, respectively. The gels recovered to their original G' and G'' values in less than 10 s, showing good self-healing properties as our previous supramolecular gel systems.[2e,13]

In conclusion, we have prepared a supramolecular polymer network based on orthogonal DB24C8/DBAS and terpyridine-Zn^{2+} interactions. By the incorporation of the TPE and coumarin units as the fluorophores, the network shows ratiometric fluorescent sensing towards Cl^-, Et_3N and cyclen due to the stimuli-responsiveness of the two non-covalent interactions. Moreover, the network forms supramolecular gels at high concentrations and shows the stimuli-responsiveness and good self-healing properties. This work offers a method for using supramolecular networks towards multiple ratiometric fluorescent sensing and enriches the development of advanced sensor materials.

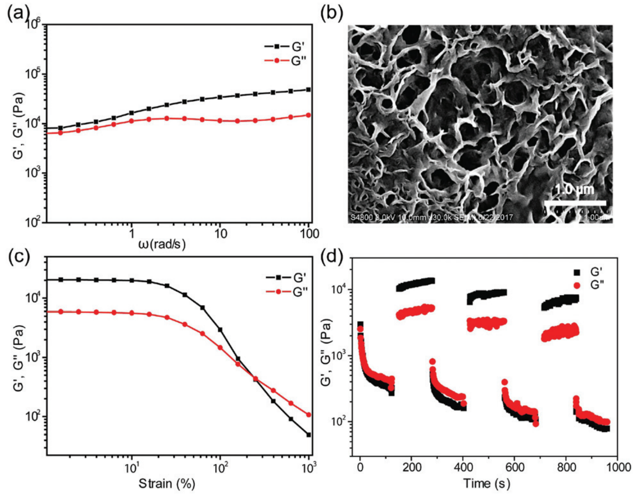


Fig. 3 (a) Storage (G', ■) and loss (G'', ●) moduli *versus* frequency (ω) of the supramolecular gel. (b) SEM image of the xerogel prepared using the freeze-drying method. (c) G' and G'' of the gel on strain sweep. (d) G' and G'' of the gel in continuous step strain measurements. The gel was first subjected to 100% strain for 120 s, then the strain was stopped for 40 s, and the gel was again subjected to 1% strain for 120 s. The process was repeated 3 times. The scanning frequency was 10 rad s^{-1}. Concentration of different species in the gel: **P1**: 10 mM, **H1**: 54 mM and $Zn(OTf)_2$: 27 mM. The concentration of DBAS and DB24C8 was used as the concentration of **P1** and **H1**, respectively.

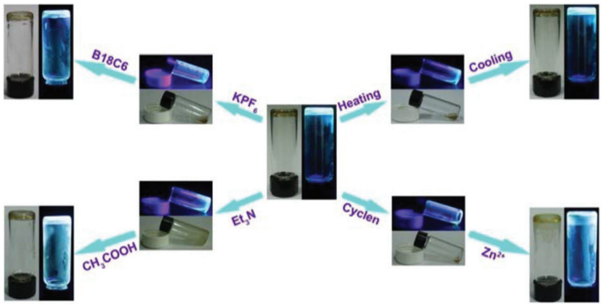


Fig. 4 Optical and fluorescent photographs of the reversible gel–sol transition.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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