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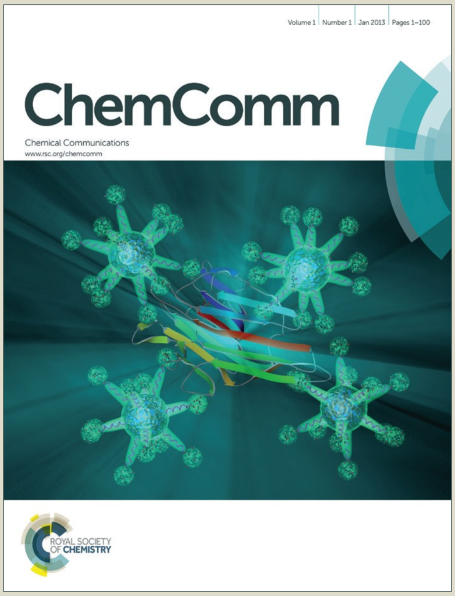

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COMMUNICATION

A novel supramolecular polymer gel constructed by crosslinking pillar[5]arene-based supramolecular polymers through metal–ligand interactions

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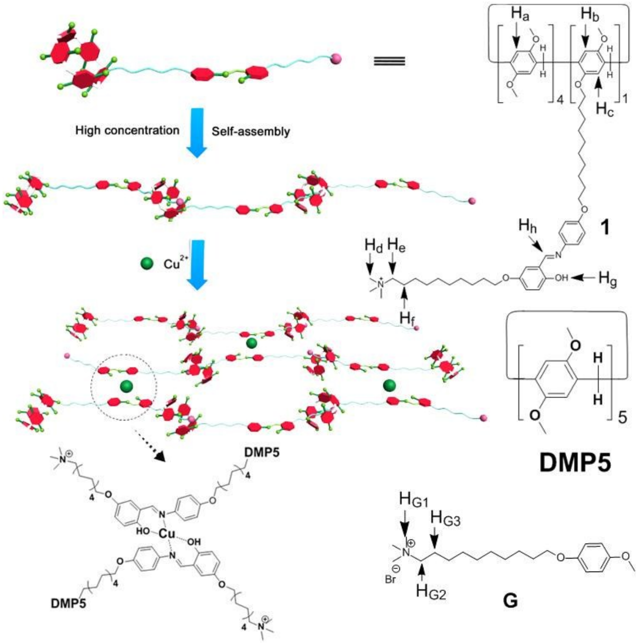
A novel heteroditopic A-B monomer is synthesized and used to construct linear supramolecular polymers utilizing pillar[5]arene-based host–guest interactions. Specifically, upon addition of Cu^{2+} ion, the supramolecular polymer chains are crosslinked through metal–ligand interactions, resulting in the formation of a supramolecular polymer gel. Interestingly, this self-organized supramolecular polymer can be used as a novel fluorescent sensor for detecting Cu^{2+} ion.

Polymer gels are three-dimensional structures of crosslinked macromolecules, and are usually classified as chemical or physical gels.[1] The chains of chemical gels are crosslinked by permanent covalent bonds, while those of physical gels are interconnected by non-covalent interactions. Because of the reversibility and stimuli-responsiveness, physical gels, namely supramolecular polymer gels, exhibit fascinating properties such as facile processing, recycling, stimuli-responsiveness, self-healing, and shape-memory.[2] Supramolecular polymer gels are commonly formed by two types of strategies: 1) the side-chain cross-linking of covalently joint polymers through non-covalent interactions;[3] 2) supramolecular bonds serve to construct the gels totally from non-covalently associating low molecular weight monomers.[4] In the former strategy, the initial design and preparation of traditional polymer backbones require time-consuming organic synthesis. However, in the later one, the functional groups in the low molecular weight monomers are well-organized, and traditional polymerization for the synthesis of polymer backbones is avoided. Therefore, it is important to construct supramolecular polymer gels from non-covalently associating low molecular weight monomers.

It is efficient and convenient to combine different types of non-covalent interactions to construct supramolecular polymer gels, resulting in the formation of systems with a high degree of complexity.[5] Pillararenes,[6] born after crown ethers, cyclodextrins, calixarenes, and cucurbiturils, are a new class of macrocyclic hosts for supramolecular chemistry.[7,8] Their repeating units are connected by methylene bridges at the *para*-positions, forming a special rigid pillar-like architecture. It is the unique structures and easy functionalization property of pillararenes that endow them with outstanding abilities to selectively bind different kinds of guests and further make pillararene-based host–guest chemistry widely used in constructing various interesting supramolecular systems.[9] In addition, metal–ligand coordination, a kind of strong, directional, and highly versatile driving force, has been widely used in the preparation of functional supramolecular systems.[10] Moreover, this kind of non-covalent interaction may bring unique magnetic, redox, optical, and electrochromic properties, benefitting the applications in the fields of heterocatalysis, electronics, and gas storage.

Herein, we present the design and synthesis of a heteroditopic A-B monomer **1** which further self-organize into linear supramolecular polymers at high concentration utilizing pillar[5]arene-based host–guest interactions (Scheme 1), and the synthesis and characterrzation of **1** and **G** were shown in ESI (Figs. S1–S15, ESI†). Furthermore, due to the presence of mesogenic bidentate Schiff base group in the middle of monomer **1**, the supramolecular polymer chains were crosslinked through metal–ligand interactions upon the addition of Cu^{2+} ions, resulting in the formation of a supramolecular polymer gel. Interestingly, we found that the fluorescence of the solution of monomer **1** could be quenched after adding Cu^{2+} ions, so this self-organized supramolecular polymer can be used as a novel fluorescent sensor for detecting Cu^{2+} ions.

Initially, the formation of a high-molecular-weight polymeric structure utilizing pillar[5]arene-based host-guest interactions was investigated. At first, 1,4-dimethoxypillar[5]arene (**DMP5**) and **G** were selected as model host and guest to study the binding strength between monomer **1** during supramolecular polymerization. The ability of **DMP5** to bind **G** was evaluated by ^{1}H NMR titration of **DMP5** into a 1.00 mM solution of **G** in $CDCl_3$ (Fig. S16, ESI†). A molar ratio plot confirmed that the complexation between **DMP5** and **G** was of 1:1 stoichiometry in $CDCl_3$ (Fig. S17, ESI†). Accordingly, the association constant (K_a) was determined to be 1.25×10^3 M^{-1} (Fig. S18, ESI†). Figure 1 showed the concentration-dependent ^{1}H NMR spectra of monomer **1** (500 MHz, $CDCl_3$, 298 K) in the range of 15.0–220 mM which provided further insight into the self-organization behavior of monomer **1**. As the monomer concentration increased, the peak splitting of the aromatic protons, such as $H_{a–c}$, and the alkyl chain protons disappeared along with broadening, which confirmed the formation of high molecular weight aggregates driven by the host-guest interactions between the pillar[5]arene host units and trimethylammonium units. This process was observed to be fast at first (Figs. 1j–1g) and then slow (Figs. 1f–1a), in accordance with the two-dimensional diffusion-ordered NMR (DOSY) characterization and viscosity measurements discussed below (Figs. S19–S25, ESI†). The assignment and correlation of the protons at high concentration were further validated by a 2D-NOESY NMR spectrum of monomer **1** (Fig. S26, ESI†).



Scheme 1. Cartoon representation of the self-assembly process of monomer **1** and the formation of supramolecular polymer gel driven by metal-ligand interactions.

Two-dimensional diffusion-ordered NMR (DOSY) experiments were also performed to investigate the self-assembly process of monomer **1** to form the linear supramolecular polymers. As the monomer concentration increased from 15.0 to 250 mM in CDCl$_3$, the measured weight-average diffusion D values decreased considerably from 1.90×10^{-5} to 9.20×10^{-7} m^{2}s^{-1}, indicating the concentration dependence of supramolecular polymerization of monomer **1** (Figs. S20–S25, ESI†). It can be explained by the fact that the extended, high molecular weight polymeric structures have greater obstacles in molecular motion and further lead to a lower measured weight average diffusion coefficient. Furthermore, viscometry is a convenient method to test the propensity of monomers to self-assemble into large aggregates. Therefore, viscosity measurements were carried out in CHCl$_3$ using a Cannon Ubbelohde semi-microdilution viscometer. As presented in Figure S26, the linear supramolecular polymer assembled from monomer **1** exhibited a viscosity transition that was characterized by a change in the slope in the double logarithmic plots of specific viscosity *versus* concentration. In the low concentration range, the slopes approximated unity, which is characteristic of cyclic oligomers with constant size. When the concentration exceeded the critical polymerization concentration (CPC; approximately 57.0 mM), a sharp increase in the viscosity was observed (slope = 1.69, at 298 K), indicating the formation of supramolecular polymers with the increasing concentration (Fig. S26, ESI†). The average degree of polymerization, n, is easily derived as being related to the equilibrium constant K_a and the initial monomer concentration (Table S1, ESI†).

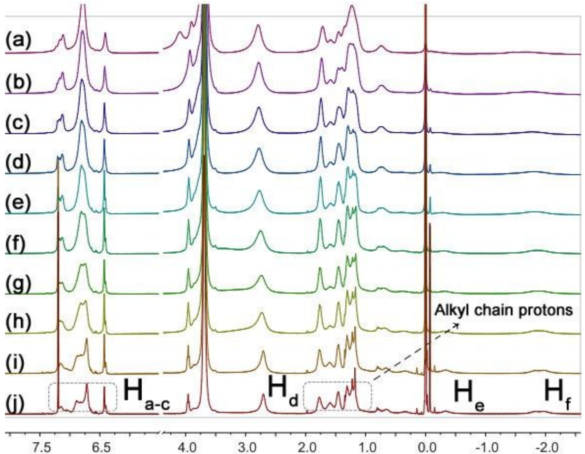


Fig. 1 Partial ^{1}H NMR spectra (500 MHz, CDCl$_3$, 298 K) of monomer **1** at different concentrations: (a) 227 mM; (b) 182 mM; (c) 151 mM; (d) 130 mM; (e) 113 mM; (f) 91.1 mM; (g) 75.8 mM; (h) 65.0 mM; (i) 30.0 mM; (j) 15.0 mM.

Encouraged by the above-mentioned results, we envisioned that the mesogenic bidentate Schiff base group in monomer **1** might show typical aggregation-caused quenching (ACQ) phenomenon when increasing the concentration of monomer **1**.[11] As shown in Fig. 2a, the significant quenching of the fluorescence intensity was found upon gradually increasing the concentration of monomer **1**. Due to the formation of the extended, high molecular weight polymeric structures, the collisional interactions between the aromatic molecules in the excited and ground states were caused which promoted the formation of sandwich-shaped excimers and exciplexes.[12] This observation proved the formation of supramolecular polymers with the increasing concentration in another way.

The conversion from linear to cross-linked supramolecular polymer was then accomplished by forming a disubsituted copper(II) complex between Cu(OAc)$_2$ and mesogenic bidentate Schiff base moieties, and this brought about the sol to gel transition. Since the formation of the copper(II) complex between Cu(OAc)$_2$ and mesogenic bidentate Schiff base moiety may cause the quenching of the fluorescence of the solution of monomer **1** at a relative low concentration, a fluorescent experiment was performed to confirm the formation of the metal-ligand complexes. As shown in Fig. 2b, upon adding successive Cu^{2+} ions to the CHCl$_3$ solution of monomer **1** at 60.0 mM, at which the linear supramolecular polymer still have strong fluorescence intensity, a significant quenching of the fluorescence intensity was found which was accordance with our expect. Besides, ^{1}H NMR was also used to investigate this process. Upon progressive addition of a saturated CD$_3$CN solution of Cu(OAc)$_2$·H$_2$O to the CDCl$_3$ solution of monomer **1** at 80.0 mM, it was found that the resonance for the phenolic hydroxyl H$_g$ proton gradually disappeared with increasing the amount of Cu^{2+} ions (Fig. 3), indicating preferential complexation between the mesogenic bidentate Schiff base moieties and the copper atom and the formation of a cross-linked supramolecular polymers. The minimum concentration of Cu(II) ions to be added to obtain a gel was 20.0 mM when **1** at a concentration of 80.0 mM. DLS experiments were then conducted to study the size distributions of the assemblies (Fig. S27, ESI†).

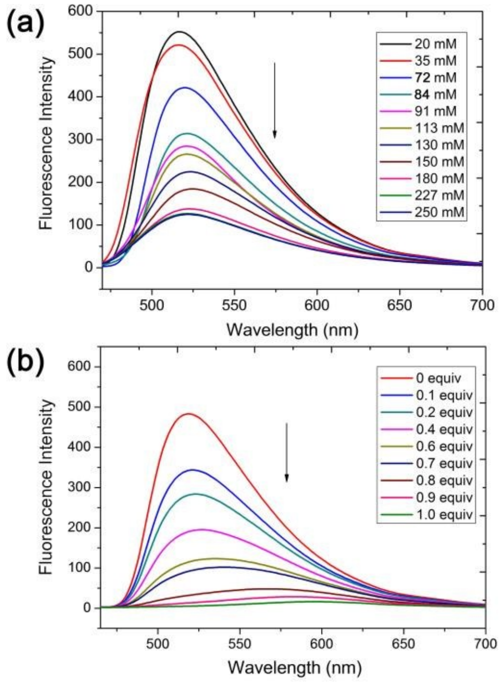


Fig. 2 (a) The changes of the fluorescence of a $CHCl_3$ solution of **1** upon increasing its concentration (20.0-250 mM). (b) The changes of the fluorescene of a $CHCl_3$ solution of monomer **1** (60.0 mM) upon the addition of Cu^{2+} ions (0–1.10 equiv).

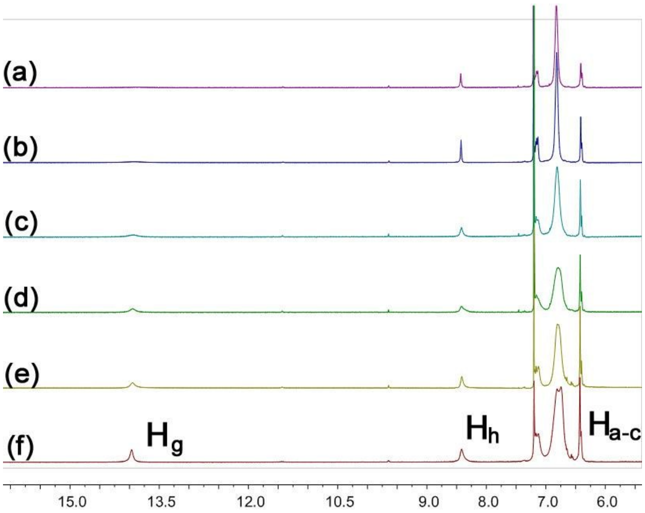


Fig. 3 Partial ^1H NMR spectra (500 MHz, $CDCl_3$, 298 K) of **1** at a concentration of 80.0 mM with successive addition of $Cu(OAc)_2{\cdot}H_2O$: (a) 0.50 equiv; (b) 0.40 equiv; (c) 0.30 equiv; (d) 0.20 equiv; (e) 0.10 equiv; (f) 0.00 equiv.

Furthermore, the morphology transition from linear supramolecular polymers to the cross-linked supramolecular gel was investigated. As shown in Fig. 4a, a rod-like extended fiber was observed by scanning electron microscopy (SEM) from a high concentration solution (150 mM) of monomer **1**, which provided direct evidence for the formation of linear supramolecular polymers. After an equimolar Cu^{2+} ions was added, a denser, three-dimensional network was obtained by entangling and crosslinking (Fig. 4b). This morphology transition showed that the metal-coordination interactions between the linear supramolecular polymers and Cu^{2+} ions not only achieved the conversion from linear supramolecular polymers to the 3D supramolecular polymeric network, but also made an impact on the microscopic nature of the resultant supramolecular polymer gel.

Fig. 4c showed the sol-glue-gel transition of this system: the solution of monomer **1** at low concentration exhibited good fluidity (Fig. 4c, left); when the concentration of monomer **1** was increased, the high concentration supramolecular polymers turned to glue-like viscous liquids (Fig. 4c, middle), but not gel; after the addition of Cu^{2+} ions, a supramolecular polymer gel was finally obtained (Fig. 4c, right).

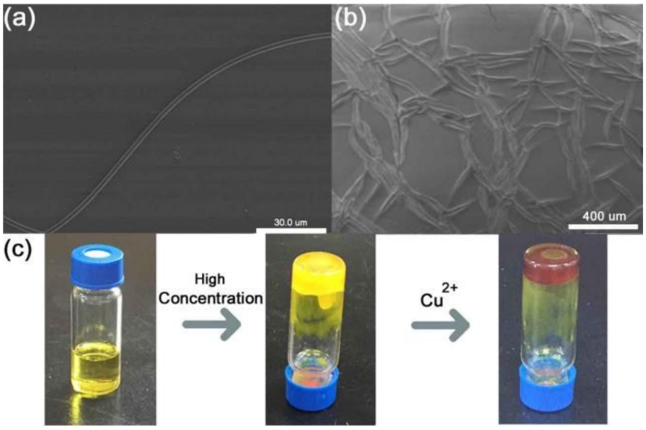


Fig. 4 (a) SEM image of the polymeric aggregates prepared from self-organization of 80.0 mM **1** in $CHCl_3$. (b) SEM image of the polymeric aggregates prepared from self-assembly of 80.0 mM **1** and 40.0 mM Cu^{2+} in $CHCl_3$. (c) Photos to show the sol-glue-gel transition of this system.

Considering the fluorescence quenching phenomenon after adding Cu^{2+} ions to the 60.0 mM $CHCl_3$ solution of monomer **1**, we wondered whether our system could be used in detecting Cu^{2+} ions. In order to investigate this, a thin film of linear supramolecular polymer formed by self-organization of monomer **1** at 60.0 mM in $CHCl_3$ was prepared by spin-casting solution onto glass slides. Fig. S28 showed that the thin film displayed a visually clear fluorescence quenching after adding one drop of $Cu(OAc)_2{\cdot}H_2O$ solution in CH_3CN. Therefore, this self-organized supramolecular polymer can be used as a novel fluorescent sensor for detecting Cu^{2+} ions, which showed excellent stability, reversibility, as well as repeatability (Fig. S29, ESI†).

In conclusion, we have synthesized a novel heteroditopic A-B monomer which could self-organize into linear supramolecular polymers at high concentration utilizing pillar[5]arene-based host–guest interactions. Due to the presence of mesogenic bidentate Schiff base group in the middle of the monomer, the supramolecular polymer chains could be crosslinked through metal–ligand interactions upon the addition of Cu^{2+} ions, resulting in the formation of a supramolecular polymer gel. Interestingly, since this Schiff base group has special recognition to Cu^{2+} ion, this self-organized supramolecular polymer can be used as a novel fluorescent sensor for detecting Cu^{2+} ions. This new type of pillar[5]arene- and copper-based supramolecular polymer gel is of high importance for developing novel functional fluorescent materials and molecular devices in the future.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures, characterizations, association constant determination, and other materials. See DOI: 10.1039/c0xx00000x.

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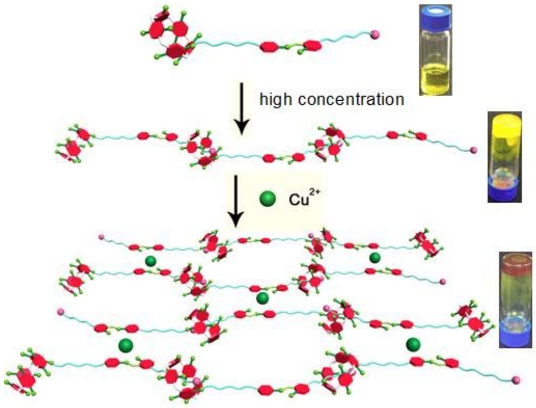

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