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A water-soluble supramolecular polymer constructed by pillar[5]arene-based molecular recognition

**Bingbing Shi, Danyu Xia and Yong Yao***

A water-soluble linear supramolecular polymer was efficiently constructed driven by pillar[5]arene-based host–guest molecular recognition.

Supramolecular polymers,[1] the perfect combination of
10 supramolecular chemistry and traditional polymer chemistry, consist of the same or different kinds of monomers held together by reversible and directional non-covalent interactions. Benefiting from the dynamic nature of non-covalent interactions, supramolecular polymers not only show traditional polymeric
15 functions, but also exhibit fascinating stimuli-responsive properties which can be used for the construction of intelligent materials that respond to external stimuli, such as temperature, photons, and pH variation.

In recent years, non-covalent interactions, such as multiple
20 hydrogen bonding,[2] metal–ligand coordination,[3] hydrophobic interactions[4] and π–π stacking[5] have been introduced to fabricate linear or cross-linked supramolecular polymers. Host–guest interactions,[6] another kind of fascinating non-covalent driving forces, have been widely employed to construct macrocyclic
25 host-based supramolecular polymers because they endow supramolecular polymers with unique mechanical and stimuli-responsive properties.

Pillararenes are a new class of supramolecular hosts after crown ethers,[7] cyclodextrins,[8] calixarenes,[9] and cucurbiturils[10]
30 since they were found in 2008.[11] Their syntheses, functionalizations, conformations, host–guest properties and applications in different areas have been actively investigated.[12] Previously, Huang and coworkers found that a pillar[5]arene could form a complex with a hexane molecule resulting in a
35 [2]pseudorotaxane-type threaded structure with host–guest interactions.[13] With this important finding, a series of pillararene-based supramolecular polymers driven by host–guest interactions were successfully prepared. For instance, Huang and coworkers reported that based on the new pillar[5]arene⊃linear alkyl chain
40 molecular recognition motif, a supramolecular polymer was successfully prepared in solution and in the solid state.[14] Moreover, Wang and coworkers prepared supramolecular polymers including polypseudorotaxanes and polyrotaxanes based on the combination of quadruple hydrogen bonding
45 interactions and pillar[5]arene-based host–guest interactions.[15] Although there are so many good examples of supramolecular polymers constructed by pillararene-based molecular recognitions, these supramolecular polymers were usually obtained in pure

organic solutions.[16] This would greatly impede the application of
50 the supramolecular polymers, and pillararene-based supramolecular polymers in water have not been reported. Therefore, water-soluble supramolecular polymers constructed by pillararene-based molecular recognitions are extremely needed.
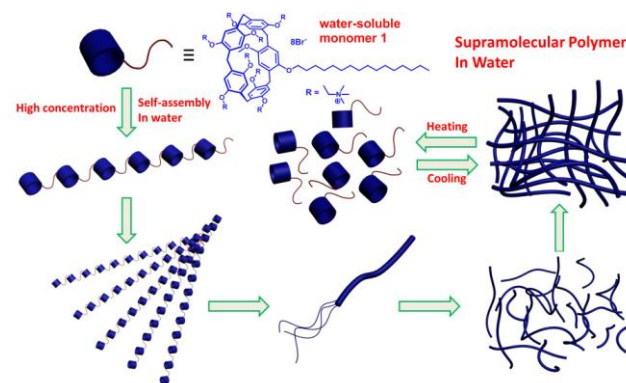
Hence, we attempted to prepare pillararene-based supramolecular polymers driven by host–guest interactions in water. First, we synthesized a water-soluble pillar[5]arene (**1**,
60 Scheme 1). **1** contains one 1-methoxy-4-cetylbenzene unit and four 1,4-bis(2-ethyoxyl-trimethylammonium)benzene units. We incorporated the long alkyl group as the guest part and eight trimethylammonium moieties as the water-soluble parts to get an A–B type monomer. We could easily obtain supramolecular
65 polymers from self-organization of **1** in water. Moreover, reversible phase transitions of the supramolecular polymer can be realized by subsequent alteration of heating and cooling (Scheme 1). Particularly, this is the first type of pillar[5]arene-based supramolecular polymers which can be obtained in 100 %
70 aqueous solution.

Linear supramolecular polymers were first envisioned to be driven by host–guest interactions in water. Then these linear supramolecular polymers self-assembled into bundles, which subsequently self-organized to form a cross-linked network. Thus
75 three-dimensional networks were constructed via the entanglement of the supramolecular bundles (Scheme 1).[14]

The self-assembly of the A–B monomer **1** was investigated by ^{1}H NMR, 2D NMR, viscosity measurements and scanning electron microscopy (SEM). ^{1}H NMR spectra of **1** (D$_2$O, 400

MHz, 293 K) at concentrations in the range of 0.460–184 mM were recorded (Fig. 1). As expected, the proton NMR spectra of **1** are concentration dependent, which reflects the involvement of
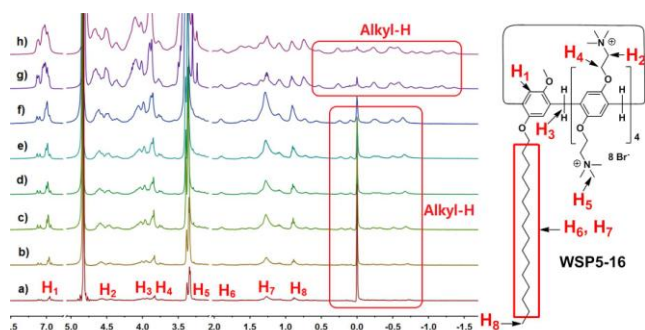
Fig. 1 ^{1}H NMR spectra (400 MHz, D$_2$O, 298K) of **1** at different concentrations: (a) 0.460 mM; (b) 0.920 mM; (c) 4.58 mM; (d) 9.18 mM; (e) 25.9 mM; (f) 61.9 mM; (g) 138 mM; (h) 184 mM.

fast-exchanging non-covalent interactions in solution. As shown in Fig. 1, the peaks related to protons H$_7$–H$_8$ shifted upfiled (ESI, Fig. S10†) and H$_1$–H$_6$ shifted downfield (ESI, Fig. S7, S8, S9†), demonstrating that the percentage of complexed cetyl groups increased when the concentration of **1** increased. Compared with the ^{1}H NMR spectra of 1-methoxy-4-(cetyl)benzene at a concentration of 1.00 mM, the cetyl protons of monomer **1** at the same concentration revealed significant upfield shift. This phenomenon indicates that the flexible cetyl groups tend to form intramolecular cyclic species at low
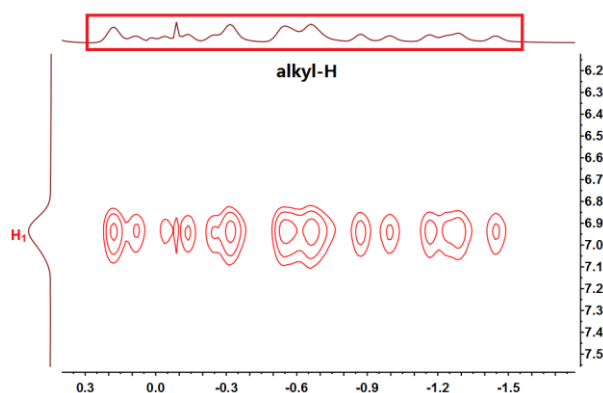

Fig. 2 Partial NOESY NMR spectrum (500 MHz, D$_2$O, 298K) of **1** at a concentration of 150 mM.

concentrations (ESI, Fig. S11†). On the other side, The transmission electron microscope (TEM) images of the monomer at low concentration (1.5×10^{-4} M) were provided (Fig. S14†). These TEM images showed that monomer **1** could also form micelles at low monomer concentration. And the critical aggregation concentrations were measured to be 0.62×10^{-4} M for monomer **1** by using the concentration-dependent conductivity measurements (Fig. S15 †). The assignment and correlation of the protons at high concentration were further validated by a 2D–NOESY NMR spectrum of **1** (Fig. 2, ESI, Fig. S12, S13†): Strong correlations were observed between the cetyl protons H$_7$–H$_8$ and the aromatic protons H$_1$, the bridging methylene protons H$_4$, as well as methyl proton H$_5$ on the trimethylammonium groups on the water-soluble pillar[5]arene unit, suggesting that the cetyl group deeply threaded into the

cavity of the pillararene moiety. Thus, the current measurements indicated the formation of an extended, high-molecular-weight polymeric structure through host–guest interactions, as shown in Scheme 1.

Viscometry is a convenient method to test the propensity of monomers to self-assemble into large aggregates. Therefore, viscosity measurements were carried out in water using a Cannon Ubbelohde semi-microdilution viscometer. As presented in Fig. 3, the linear supramolecular polymer assembled from **1**
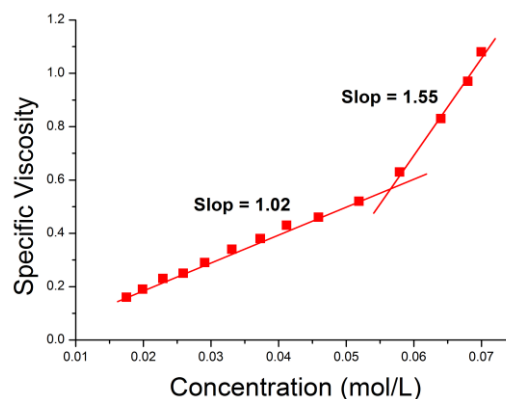
Fig. 3 Specific viscosity of the supramolecular polymer versus the concentration of monomer **1** in water at 25.0 °C.

exhibited a viscosity transition that is characterized by a change in slope in the double logarithmic plots of specific viscosity versus concentration. In the low concentration range, the slopes approximated unity, which is characteristic for cyclic oligomers with constant size. When the concentration exceeded the critical polymerization concentration (CPC; approximately 60.0 mM), a sharp rise in the viscosity was observed (slope = 1.55, at 298 K).
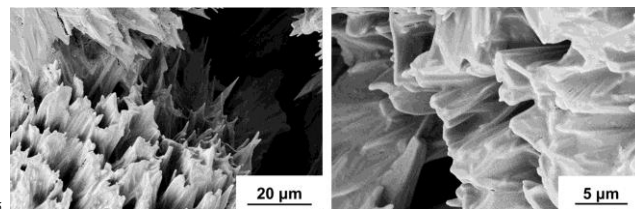

Fig. 4 SEM images of three-dimensional networks drawn from a highly concentrated solution of **1** in water.

Furthermore, the morphology of the supramolecular polymers was investigated. As show in Fig. 4, three-dimensional network were obtained from a highly concentrated solution and observed by scanning electron microscopy (SEM), these images provided direct evidence that monomer **1** self-assembled at nanoscale through host–guest interactions to form the bundles with high molecular weight. Then a denser, three-dimensional network was obtained by entangling and crosslinking.

The macroscopic properties of the high concentration supramolecular polymers were also investigated. The supramolecular polymers were prepared by dissolving the monomers in water at 80.0 °C followed by cooling to room temperature. Upon increasing the concentration of the monomers, the high concentration supramolecular polymers finally formed at phase-transition temperature of approximately 52.0 °C∼56.0 °C for **1** at the concentration of 600 mM. In addition, the high concentration supramolecular polymers showed reversible glue–

sol phase transitions by heating and cooling. Moreover, rod–like micro fiber was drawn from the high concentration supramolecular polymers (600 mM) of **1**, which showed very good stretchability of the supramolecular polymers (Fig. 5). This can provide direct evidence for the formation of the linear supramolecular polymers.
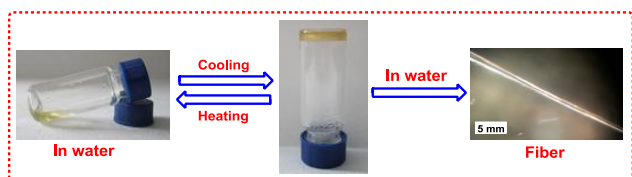
Fig. 5 Photos to show glue–sol transitions of supramolecular polymers triggered by the temperature stimulus and a rod–like micro fiber drawn from a highly concentrated solution of **1** in water.

In conclusion, with the easily available water-soluble pillararene monomer **1**, linear supramolecular polymers were efficiently constructed driven by host–guest interactions in water. By combination of various techniques, including ^{1}H NMR, 2D–NOESY, SEM and viscometry, it was demonstrated that the formation of the supramolecular polymer was highly dependent on the monomer concentration. Moreover, a rod–like fiber was drawn from a high-concentration solution, providing direct evidence for the formation of a linear supramolecular polymer. Furthermore, the supramolecular polymers showed reversible glue–sol phase transitions by heating and cooling. Considering the easy availability and good water-soluble properties of the **1** monomer, the present study provided a new and simple method to fabricate water-soluble supramolecular polymeric materials.

Acknowledgements

Notes and references

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Colour Graphic:

water-soluble monomer 1

Supramolecular Polymer In Water

8Br⁻

R =

Heating

Cooling

5 mm

Text:

A water-soluble linear supramolecular polymer was efficiently constructed driven by pillar[5]arene-based host–guest molecular recognition.