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The construction of rigid supramolecular polymers in water through the self-assembly of rod-like monomers and cucurbit[8]uril[†]

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Two new types of supramolecular polymers have been constructed *via* the self-assembly of rigid rod-like monomers and cucurbit[8]uril (CB[8]) in water. These supramolecular polymers possessed rigid backbones and further aggregated into stick-like bunched fibres.

Synthetic polymers are some of the most widely produced materials made by human beings. With the development of supramolecular chemistry, supramolecular polymers, in which the monomers are connected by noncovalent interactions such as hydrogen bonding,¹ aromatic stacking,² C-H··· π interactions,³ metal-ligand bonds,⁴ donor-acceptor interactions,⁵ and host-guest interactions⁶ instead of covalent bonds as found in classic polymers, have drawn considerable attention in the past few decades because of their important applications in fabricating smart materials. Although currently a myriad of supramolecular polymers have been fabricated by means of molecular selfassembly, their structural diversity is quite limited compared with traditional polymers whose morphologies are much more diversified. For example, very recently a new type of polymeric structures named rod-rod block copolymers which possess rigid backbones have been fabricated that display unique properties owing to their rigid conformation.⁷ With respect to their supramolecular counterparts, however, there were just very few examples reported for supramolecular polymers with rigid backbones.⁸ In this context, this niche remains to be further explored. We herein report the construction of two types of stick-like supramolecular polymers in water driven by cucurbit[8]uril (CB[8])-encapsulation-enhanced stacking of 4,4'-bipyridin-1-ium (BP) units.9 These supramolecular polymers have even more rigid

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backbones than those reported previously,⁸ which were visualized by TEM and AFM microscopies.

It was reported that BP units could also adopt head-to-head stacking in the cavity of CB[8].¹⁰ Therefore, in order to prevent the monomers from forming [2+2] head-to-head dimers with CB[8], two isopropyl groups were introduced into the skeleton of monomer **T1** to provide steric hindrance (**T1**), and in the structure of monomer **T2** a viologen segment was incorporated to increase electrostatic repulsion of the monomer (Scheme 1). Both strategies should facilitate the formation of supramolecular polymers with linear backbones.

The binding behaviour between monomers T1-T2 and CB[8] was investigated by the ¹H NMR titration experiment. As can be seen in Fig. 1, successive addition of CB[8] into a solution of T1 in D_2O resulted in a decrease of the intensities of the peaks corresponding to free T1 and growth of a new set of signals which were assigned to CB[8]-encapsulated T1 on the fact of the upfield shifts of the signals. The peaks of free T1 significantly diminished when the molar ratio of T1 and CB[8] reached 1:1.



Scheme 1 Chemical structures of monomers T1–T2 and CB[8].

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Thus a 1:1 binding stoichiometry was suggested for them and further corroborated by Job's plot (Fig. S1, ESI⁺). Furthermore, it was also observed that the resolution of the peaks decreased upon the addition of CB[8], suggesting the formation of polymeric aggregates. In the case of ¹H NMR titration of T2 with CB[8], the peaks became broad and shifted upfield upon the addition of CB[8], also indicating the formation of polymeric structures (Fig. S2, ESI[†]). A 1:1 binding stoichiometry for T2 and CB[8] was also confirmed by Job's plot (Fig. S3, ESI⁺). The binding behaviour between CB[8] and T1 and T2 were further investigated by the isothermal titration calorimetry (ITC) experiment (Fig. S4 and S5, ESI⁺), which again revealed a 1:1 binding model for the monomers and CB[8] and generated apparent binding constants to be $(2.1 \pm 0.36) \times 10^7$ and $(8.3 \pm 1.8) \times 10^5 \text{ M}^{-2}$ for CB[8] and T1, and CB[8] and T2, respectively. The lower binding constant of the latter might be attributed to the competitive binding resulting from the interaction between CB[8] and the viologen unit of T2.11

An attempt to grow single crystals of supramolecular polymers fabricated from a 1:1 mixture of T1 or T2 and CB[8] for X-ray crystallographic analysis was not successful. However, the crystals of monomer T1 were successfully grown by slow evaporation of a solution of T1 in ethanol. Crystallographic analysis revealed that two BP units were stacked upon each other in a head-to-tail manner in the solid state which further led to one dimensional extension of **T1** molecules (Fig. 2, top).¹² The BP units adopted an offset face-to-face stacking with an average distance being 3.73 Å, a typical distance for aromatic stacking. Thus, in the presence of CB[8], the encapsulation of two stacked BP units in the cavity of a CB[8] molecule, just as that found in the crystal structure of complex 1-phenyl-BP-CB[8] we reported previously,⁹ could be expected. It would lead to the formation of linear supramolecular polymers (Fig. 2, bottom). This expectation was confirmed by 2D ¹H NMR NOESY of a 1:1 mixture of **T1** and CB[8] in D_2O . The spectrum displayed intermolecular NOE connections between H_a and H_d, and H_b and H_d, clearly indicating that two BP units were stacked upon each other and aligned in a head-to-tail manner in the cavity of CB[8] (Fig. S6, ESI⁺). Similar NOE contacts were also observed for a solution of T2 and CB[8] (Fig. S7, ESI⁺), suggesting a similar host-guest binding between CB[8] and BP units of T2. These results clearly indicated that the rigid monomers and CB[8] self-assembled into linearly polymeric structures in water. Since the monomers are fully rigid, the resulting supramolecular polymers could be expected to possess a rigid rod-like conformation.

The formation of supramolecular polymers were further evidenced by 2D ¹H NMR diffusion ordered spectroscopy (DOSY), which is a technique widely used to characterize supramolecular structures in solution by correlating chemical resonances with diffusion coefficients (*D*).¹³ While a solution of **T1** alone in D₂O (1.0 mM) gave a *D* value of 2.9×10^{-10} m² s⁻¹, the *D* value of the solution of a mixture of **T1** and CB[8] (1:1, 1.0 mM) was determined to be 1.6×10^{-10} m² s⁻¹ and further decreased to 8.5×10^{-11} m² s⁻¹ when the concentration of the mixture was increased to 6.0 mM (Fig. S8–S10, ESI[†]). For **T2**, the *D* values were determined to be 4.0×10^{-10} , 1.6×10^{-10} , and 1.1×10^{-10} m² s⁻¹



Fig. 2 The packing structure of **T1** in the single crystal, highlighting the linearly extending of **T1** molecules through stacking of BP units (top), and illustration of the formation of rigid linear supramolecular polymers after the encapsulation of the stacked BP units in the cavity of CB[8] generated by Hartree–Fock/3-21G on the basis of the crystal structure of **T1** (bottom). The hydrogen atoms and counter anions were omitted for clarity.

for the solution of T2 alone (1.0 mM) and a mixture of T2 and CB[8] (1:1) at 1.0 and 5.0 mM in D₂O, respectively (Fig. S11-S13, ESI⁺). These results strongly suggested the formation of supramolecular polymers in solution. In addition to DOSY, the dynamic light scattering (DLS) experiment also revealed the existence of supramolecular polymers in solution. Upon the addition of 1 equiv. of CB[8] to the solutions of monomers in water, the hydrodynamic diameters $(D_{\rm h})$ of the aggregates formed were found to increase with an increase in the concentration of mixtures of the monomers and CB[8] (1:1), which was attributed to a higher degree of polymerization of the supramolecular polymers at higher concentrations (Fig. S14 and S15, ESI[†]). Furthermore, no ¹H NMR signals of free monomers were observed when concentrated solutions of the supramolecular polymers were diluted, suggesting that no significant dissociation of the supramolecular polymers occurred even in very dilute solutions, indicating a high stability of the supramolecular polymers (Fig. S16 and S17, ESI[†]). The variable-temperature ¹H NMR experiment was performed for the supramolecular polymers. No apparent disassociation of the supramolecular polymers was observed even at 75 °C, suggesting again that the polymeric structures were highly stable (Fig. S18 and S19, ESI[†]).

The morphology of the as-prepared supramolecular polymers was investigated by transmission electron microscopy (TEM). In the TEM images straight stick-like objects can be observed (Fig. 3), which is consistent with the expectation for rigid linear polymeric chains. Their widths were estimated to be dozens of nanometers while their lengths were several hundred nanometers. The atomic force microscopy (AFM) study also revealed the formation of stick-like structures (Fig. S20, ESI⁺). Since the diameter of the backbone of a single supramolecular polymer chain should be close to the diameter of CB[8] (ca. 1.75 nm),¹⁴ the stick-like objects observed under the microscopes should be bundles of individual polymers produced by the aggregation of the linear chains, as illustrated in Fig. 4. The aggregation of the polymer chains was attributed to outer-surface interactions occurring through the convex face of CB[8].15 In contrast, monomers T1 and T2 generated ill-defined aggregates under similar conditions, as revealed by scanning electron microscopy (SEM) (Fig. S21, ESI[†]). These results further confirmed that the stick-like objects were generated from supramolecular polymers.



Fig. 3 TEM images of linear supramolecular polymers fabricated from (a) T1 + CB[8] (1:1, 6.0 mM), and (b) T2 + CB[8] (1:1, 1.0 mM).



Fig. 4 Cartoon representation of the formation of rigid linear supramolecular polymers and their further aggregation into bundles.

In summary, two new types of supramolecular polymers with rigid backbones have been constructed in water through the self-assembly of rigid rod-like monomers and CB[8], driven by CB[8]-encapsulation-enhanced dimerization of 4,4'-bipyridin-1ium units. The use of rigid supramolecular monomers has some advantages over their flexible counterparts. Firstly, it removes the obstacle of cyclization of flexible monomers, which seriously hampers the polymerization of supramolecular polymers. Furthermore, the resulting supramolecular polymers with a rigid conformation offer accurate control over the spatial distance of substituents on their backbones because random coiling or folding of the backbones can be eliminated for these rigid linear polymers. This should be crucial for the fabrication of functional materials which requires fine control over the spatial distance of functional units. The potential of these advantages is currently being explored.

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