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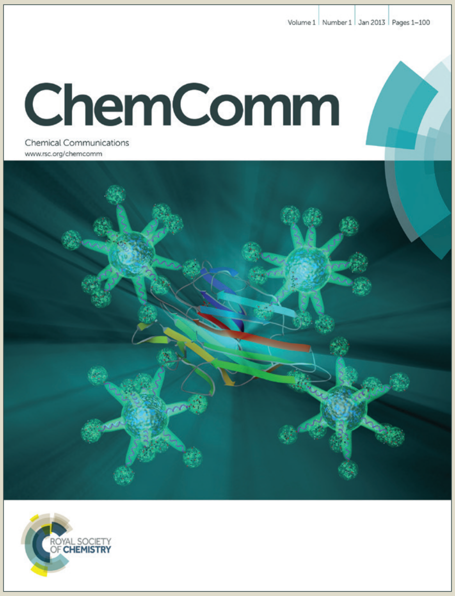

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COMMUNICATION

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

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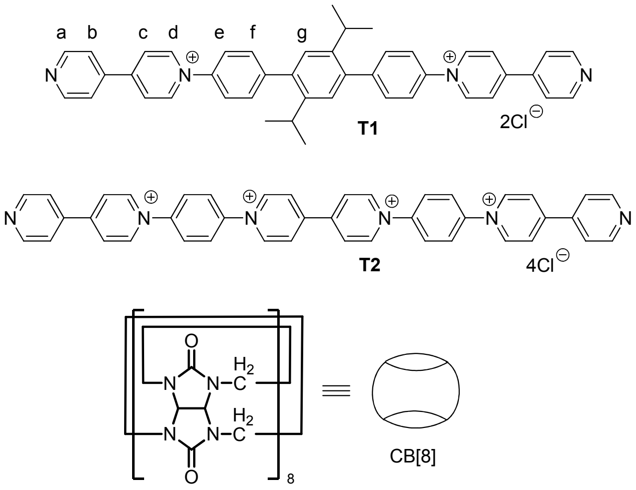
Two new types of supramolecular polymers have been constructed via the self-assembly of rigid rod-like monomers and cucurbit[8]uril (CB[8]) in water. These supramolecular polymers possessed rigid backbones and further aggregated into stick-like bunched fibres.

Synthetic polymers are one 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 interactions[6] instead of the formation of covalent bonds as that of classic polymers, have drawn considerable attention in the past decades because of their important applications in fabricating smart materials. Although currently a myriad of supramolecular polymers have been fabricated by means of molecular self-assembly, their structural diversity are 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 possessed rigid backbones have been fabricated and displayed 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 backbones than those reported previously,[8] which was 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 *iso*propyl groups were introduced to 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 the monomers **T1**-**T2** and CB[8] was investigated by ^{1}H NMR titration experiment. As can be seen in Figure 1, successively adding CB[8] into a solution of **T1** in D_2O resulted in 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** were significantly diminished when the molar ratio of **T1** and CB[8]



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

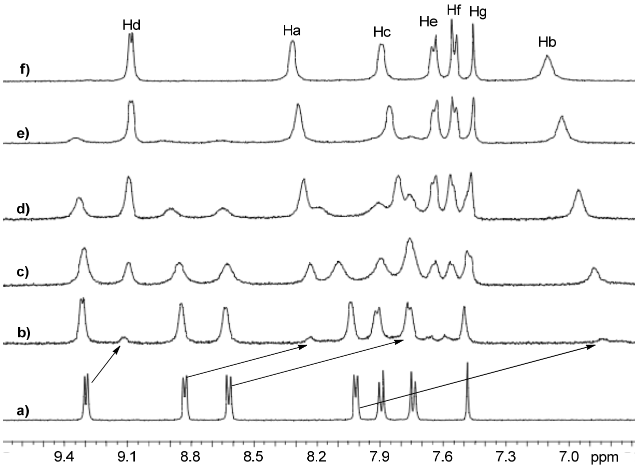


Fig. 1 Partial ^{1}H NMR spectra of (a) **T1**, (b) **T1** + CB[8] (1:0.2), (c) **T1** + CB[8] (1:0.4), (d) **T1** + CB[8] (1:0.6), (e) **T1** + CB[8] (1:0.8), and (f) **T1** + CB[8] (1: 1) in D_2O at 25 °C. The concentration of **T1** was 2.0 mM.

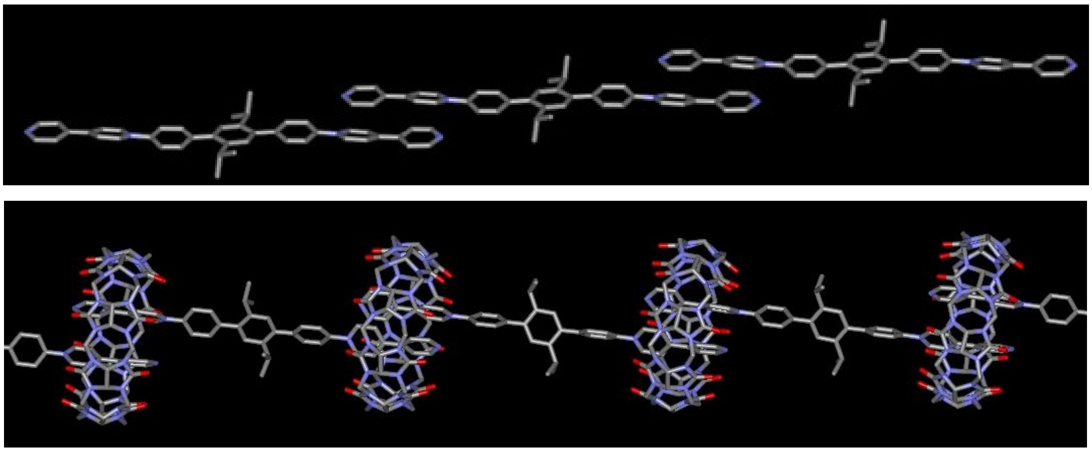


Fig. 2 The packing structure of **T1** in the single crystal, highlighting the linearly extending of **T1** molecules through stacking of BP units (top), and illustration for the formation of rigid linear supramolecular polymers after the encapsulation of the stacked BP units in the cavity of CB[8] generated 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.

reached 1:1. Thus a 1:1 binding stoichiometry was suggested for them and further corroborated by a Job's plot (Figure 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 ^{1}H NMR titration of **T2** with CB[8], the peaks become broad and shifted upfield upon the addition of CB[8], also indicating the formation of polymeric structures (Figure S2, ESI). A 1:1 binding stoichiometry for **T2** and CB[8] was also confirmed by a Job's plot (Figure S3, ESI). The binding behaviour between CB[8] and **T1** and **T2** were further investigated by isothermal titration calorimetry (ITC) experiment (Figure S4-5, 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 $(8.3 \pm 1.8) \times 10^5$ 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 coming from the interaction between CB[8] and the viologen unit of **T2**.[11]

Attempt to grow single crystals of supramolecular polymers fabricated from 1:1 mixture of **T1** or **T2** and CB[8] for X-ray crystallography 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 stacked each other in a head-to-tail manner in solid state which further led to one dimensionally extending of **T1** molecules (Figure 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 in the crystal structure of the complex 1-phenyl-BP—CB[8] we reported previously,[9] could be expected. It would lead to the formation of linear supramolecular polymers (Figure 2, bottom). This expectation was confirmed by 2D ^{1}H 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 stacked each other and aligned in a head-to-tail manner in the cavity of CB[8] (Figure S6, ESI). Similar NOE contacts were also observed for a solution of **T2** and CB[8] (Figure S7, ESI), suggesting 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 rigid rod-like conformation.

The formation of supramolecular polymers were further evidenced by 2D ^{1}H 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 D_2O (1.0 mM) gave a *D* value of 2.9×10^{-10} m^2/s, 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} m^2/s and further decreased to 8.5×10^{-11} m^2/s when the concentration of the mixture increased to 6.0 mM (Figures S8-10, ESI). As to **T2**, the *D* values were determined to be 4.0×10^{-10}, 1.6×10^{-10}, and 1.1×10^{-10} m^2/s for solutions of **T2** alone (1.0 mM), mixture of **T2** and CB[8] (1:1) at 1.0 and 5.0 mM in D_2O, respectively (Figures S11-13, ESI). These results strongly suggested the formation of supramolecular polymers in solution. In addition to DOSY, 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_h) of the aggregates formed were found to increase with the increasing 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 concentration (Figure S14-15, ESI). Furthermore, no ^{1}H 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 (Figures S16-17, ESI). Variable-temperature ^{1}H NMR experiment has been 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 (Figures S18-19, ESI).

The morphology of the as-prepared supramolecular polymers was investigated by transmission electron microscopy (TEM). On the TEM images straight stick-like objects were observed (Figure 3), which was in 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. Atomic force microscopy (AFM) study also revealed the formation of stick-like structures (Figure 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 by the microscopes should be bundles of individual polymer producing by the aggregation of the linear chains, as illustrated in Figure 4. The aggregation of the polymer chains was attributed to outer-surface interactions occurring through the convex face of CB8].[15] In contrast, monomers **T1** and **T2** generated ill-defined aggregates under similar conditions, as revealed by scanning electron microscopy (SEM) (Figure S21, ESI). This result further confirmed that the stick-like objects were generated from supramolecular polymers.

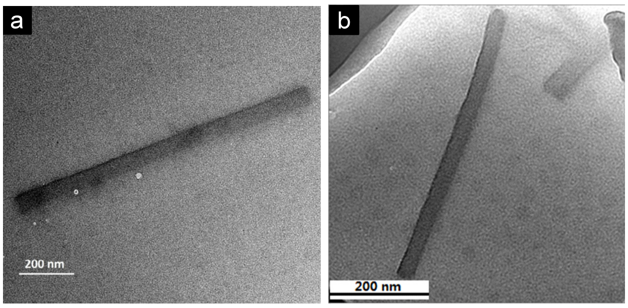


Fig. 3 TEM images of linear supramolecular polymers fabricated from (a) **T1** + CB[8] (1:1, 6.0 mM), and (b) **T2** + CB[8] (1:1, 1.0 mM).

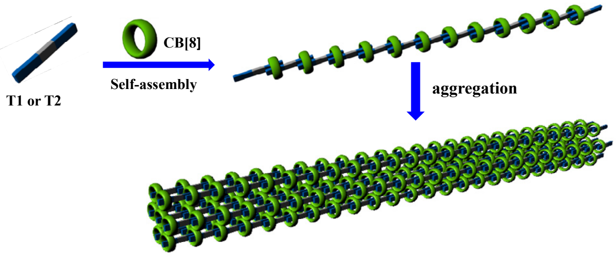


Fig. 4 Cartoon representation of the formation of rigid linear supramolecular polymers and their further aggregating into bundles.

Conclusions

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-1-ium units. The use of rigid supramolecular monomers should bring 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 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 require fine control over the spatial distance of functional units. The potentials of these advantages are currently being explored.

Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis and characterizations, additional ^{1}H NMR spectra, ITC profiles, 2D NOESY spectra, DOSY profiles, AFM and SEM images. See DOI: 10.1039/b000000x/

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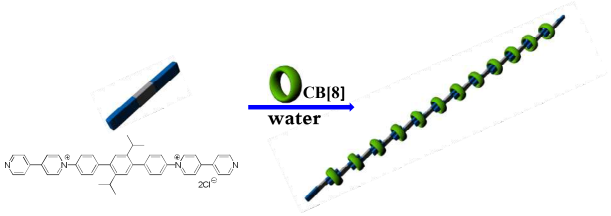

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