Neutral linear supramolecular polymers constructed by three different interactions†

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Neutral linear supramolecular polymers were efficiently constructed by the combination of quadruple hydrogen bonding, pillar[5]arene-based molecular recognition and π–π donor–acceptor interactions. The disassembly of the supramolecular polymers can be effectively controlled by adding the competitive adiponitrile guest.

Supramolecular polymers, in which non-covalent interactions are always employed to hold the monomeric units together, not only exhibit polymer-like properties, but also possess new structures with unique functions such as stimuli-responsiveness, recyclability, self-healing and degradability.1 Therefore, supramolecular polymers are expected to provide a wide range of potential applications as functional adaptive materials.2 As we know, nature commonly utilizes the combination of different non-covalent interactions to create complicated and functionally ordered architectures such as DNA and so on.3 Motivated by this, scientists have been trying to fabricate supramolecular polymers with unprecedented properties and intriguing functions by self-assembly of multiple non-covalent interactions.4 For instance, Huang’s group constructed a homogeneous linear supramolecular copolymer by orthogonal coordination-driven self-assembly, crown-ether-based 2 rotaxane host–guest interactions and quadruple hydrogen bonding of ureidopyrimidinone (UPy) in 2016.5 Recently, based on the unification of quadruple hydrogen bonding and crown-ether-based bistable [2]daisy chain rotaxane molecular recognition, Giuseppone’s group constructed a molecular-machine-based supramolecular polymer which could exhibit reversible sol–gel transitions, controlled by pH actuation.6

Pillararenes7 have captured more and more attention and provided a useful platform for the construction of supramolecular polymers8 because of their unique symmetrical pillar architecture, facile functionalization and adjustable host–guest properties.9 Until now, lots of pillararene-based neutral supramolecular polymers have been constructed by employing two kinds of non-covalent interactions.10 For example, Li’s group provided a new strategy for the construction of neutral linear supramolecular polymers by the marriage of endo-cavity and exo-wall complexation of a pillar[5]arene in 2015.11 Recently, Shi’s group constructed a novel linear supramolecular polymer by orthogonal pillar[5]arene-based molecular recognition, Eu(III)-coordination and π–π donor–acceptor interactions.12 However, to the best of our knowledge, pillar[5]arene-based neutral supramolecular polymers constructed by combining the themes of three non-covalent interactions are rare. Herein, we report novel neutral linear supramolecular polymers constructed by three kinds of non-covalent recognition motifs including quadruple hydrogen bonding, pillar[5]arene-based molecular recognition and π–π donor–acceptor interactions. Firstly, we designed an unsymmetrical guest 1 possessing a UPy unit and a carbamate moiety, which can dimerize to form an unusual homoditopic AA-type supramonomer. According to Li’s report, pillar[5]arene 2 binds with molecule 3 to form a 2 : 1 sandwich-type exo-wall complex driven by π–π donor–acceptor interactions, which was seen as a homoditopic BB-type supramonomer.13 As a result, neutral linear supramolecular polymers were successfully constructed in the A2B2 form as suggested in Scheme 1.

A well-designed guest molecule 1, which bears a UPy unit and a carbamate moiety, was obtained in a moderate yield using commercially available starting materials according to the reported methods.14 Initially, the host–guest interaction between 1 and 2 was investigated by 1H NMR spectroscopy (Fig. 1, and S5, ESI†). As shown in Fig. 1a, in the spectrum of individual 1, the Upy N–H signals showed large downfield shifts (between 10 and 13.5 ppm), which gave direct evidence for the dimerization of UPy units to form an unusual homoditopic AA-type supramonomer.15 After mixing 1 and 2, an evident upfield chemical

† Electronic supplementary information (ESI) available: Synthetic procedures, characterizations, NMR spectra, and the calculation of binding constants. See DOI: 10.1039/c7ra05351g
Cavity of Paper RSC Advances were clearly observed, indicating that neutral linear supramolecular polymers (by this, we investigated the possibility of constructing the can be seen as a homoditopic BB-type supramonomer. Inspired of non-covalent recognition motifs. Initially, when mixing I, 2, and 3 in a 2 : 2 : 1 molar ratio in CHCl₃ at low concentration,

shift and a broadening effect of the methylene protons (H₃–d) on I were clearly observed, indicating that 1 threaded into the cavity of 2.

Subsequently, two-dimensional ¹H NOESY was also carried out to study the self-assembly of 1 and 2 in CDCl₃ solution. Correlation signals were observed between the methylene protons (H₃–d) of guest I and H₂ of host 2, indicating the formation of a host–guest inclusion complex between 1 and 2 (Fig. S6, ESIf). In addition, a Job plot based on the ¹H NMR data demonstrated that the complex had 1 : 1 stoichiometry (Fig. S7, ESIf). By using a nonlinear curve-fitting analysis based on the ¹H NMR titration experiments, the association constant (Ka) of 2 \( \supset \) 1 was determined to be 85 ± 4.1 M⁻¹ (Fig. S9, ESIf).

As above-mentioned, the 2 : 1 sandwich-type complex between 2 and 3 formed via \( \pi–\pi \) donor–acceptor interactions can be seen as a homoditopic BB-type supramonomer. Inspired by this, we investigated the possibility of constructing the neutral linear supramolecular polymers (1₂–2₂·3) by three kinds of non-covalent recognition motifs. Initially, when mixing 1, 2, and 3 in a 2 : 2 : 1 molar ratio in CHCl₃ at low concentration,

a pale red color from \( \pi–\pi \) stacking between 2 and 3 appeared immediately. As the concentration increased, the color of the solution gradually became dark red (Fig. S10, ESIf). Thereafter, concentration-dependent ¹H NMR spectroscopy was performed to reveal the possibility of generating the expected supramolecular polymers. As shown in Fig. 2, the large downfield chemical shifts and lower intensities observed on UPy N–H indicated the dimerization of the UPy motifs. With increasing concentration, the signals of protons Hd of 1 and proton Hb of 3 underwent substantial upfield shifts (Fig. 2, and S11, ESIf). Moreover, all the signals became broad at a high concentration, which confirmed the formation of aggregates with a high molecular weight. Diffusion-ordered ¹H NMR spectroscopy (DOSY) was further employed to confirm the formation of a concentration-dependent supramolecular polymer. As the concentration of the mixtures of 3 with 2 equiv. of 1 and 2 increased from 4.00 mM to 50.0 mM, the measured weight average diffusion coefficient decreased significantly from \( 5.33 \times 10^{-10} \) m² s⁻¹ to \( 2.65 \times 10^{-10} \) m² s⁻¹, suggesting the gradual formation of high-molecular-weight polymeric aggregates (Fig. 3). To further study the self-assembly process of 1, 2, and 3 to form the neutral linear supramolecular polymers, viscosity measurements were carried out in CHCl₃ using a micro-Ubbelohde viscometer. As presented in Fig. 4, the aggregates assembled from the monomers presented a viscosity transition, which was characterized by a change in the slope of the double logarithmic plots of the specific viscosity versus the concentration. In the low concentration range, the curve slope was 0.71, which indicates the predominance of cyclic oligomers in dilute solutions. When the concentration exceeded the critical polymerization concentration (CPC, 7 mM), an obvious increase in the viscosity was observed (slope = 1.10), suggesting a transition from small oligomers to larger linear supramolecular polymers. Moreover, large spherical aggregates were distinctly observed in the TEM image, which may have originated from further assembly of the linear supramolecular polymers (Fig. S12, ESIf).
supramolecular polymers with rationally designed structures, by self-assembly of multiple non-covalent interactions.

Acknowledgements

This work was supported by the National Natural Science Foundation of China [Grant No. 21602112] and the China Postdoctoral Science Foundation [Grant No. 2017M611876], and sponsored by the Scientific Starting Fund from Nanjing University of Posts and Telecommunications (NUPTSF) [Grant No. NY215057] and the Natural Science Foundation of the Jiangsu Higher Education Institutions [Grant No. 16KJB150031].

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