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Formation of polypseudorotaxane networks by cross-linking the quadruple hydrogen bonded linear supramolecular polymers *via* bisparaquat molecules†

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The creation of novel crown ether–paraquat polypseudorotaxane networks, constructed by bisparaquat monomers threading into the cavity of the crown ether units of linear supramolecular polymers that are formed based on the quadruple hydrogen bonded unit ureidopyrimidinone (Upy) in the concentrated solution, is described.

Polypseudorotaxanes/polyrotaxanes[1] are mechanically interlocked compounds constructed by incorporating multiple pseudorotaxane/rotaxane moieties into the polymeric framework. They have attracted great attention in the past years owing to their potential applicability in the material chemistry, electrochemistry, life science, and biotechnology.[2] For most of the reported polypseudorotaxanes and polyrotaxanes, at least one covalent polymer was used as a component. Whereas, the threading efficiency of macrocycles or axes to the covalent polymers is relatively low and is significantly influenced by the affinity of the subunits, temperature, concentration, and polymer chain length.[3] While up to now, there is only one report using the non-covalent polymers as the polymeric backbones. In 2009, Huang and co-workers reported the formation of linear main-chain polypseudorotaxanes with supramolecular polymer backbones *via* two self-sorting host–guest motifs.[4] Generally, the supramolecular polymer backbones assembled from monomeric units are reversible and stimuli responsive, which can exhibit polymeric properties in solutions as well as in the bulk.[5] Therefore, this work provides an effective method to construct new polypseudorotaxanes which might be possessing some unique, adaptive properties.

The polypseudorotaxane/polyrotaxane networks[6] are the most fascinating class of cross-linked polymers due to their unique structure and specific properties. The combination of different non-covalent interactions is a convenient and efficient way for the creation of complicated supramolecular architectures.[7] Very recently, we have reported the formation of novel linear supramolecular polymers *via* the combination of two types of classical binding interactions: quadruple hydrogen bonding ureidopyrimidinone (UPy) and crown ether–paraquat recognition motifs in the main chain.[8] Therefore, we envisioned that bifunctional ureidopyrimidinone monomers can self-assemble into linear supramolecular polymers at high concentrations.[9] If bifunctional ureidopyrimidinone monomers are bridged with crown ether units, the quadruple hydrogen bonded linear supramolecular polymers which are constructed with crown ether units are formed, and if such formed linear supramolecular polymers are utilized as polymeric backbones, plus if bisparaquat is utilized as the axes, polypseudorotaxane networks might be obtained in the concentrated solution. In that respect, we synthesized two types of monomers: bifunctional Upys **P1** bridged with a crown ether unit and bisparaquat **D1**. Finally we investigated the polypseudorotaxanes formation in solution (Fig. 1). The reason to select the ester-containing crown ether is that the ester-substituted **BPP34C10** derivatives show an increased binding ability toward the electron-deficient bipyridinium unit in the form of pseudorotaxane.[10]

Firstly, ^{1}H NMR spectroscopy was used to investigate the formation of the linear supramolecular polymer and the cross-linked polypseudorotaxanes in acetonitrile-d_3–chloroform-d (1 : 1, v/v). For the individual **P1**, the Upy N–H signals showed a large downfield shift together with a little lower intensity (between 10 and 13.5 ppm), which gave direct evidence for the UPy unit dimerization in this mixed solvent.[7f,11] That indicated the linear polymer formation at relatively high concentrations (Fig. S2, ESI†). Upon mixing 0.5 equiv. **D1** to the **P1** solution, the UPy N–H signals shifted little compared with the individual **P1**. The proton signals of crown ether and paraquat subunits had only one set of signals and were concentration dependent, since the complexation between crown ether and paraquat shows a fast-exchange process. As the concentration of **P1** increased, the ethoxy protons, the aromatic protons of the crown ether, and the paraquat all shifted upfield progressively, which revealed the concentration dependent percentage of the complexed species of the crown ether–paraquat moieties (Fig. 2). The association ratios

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† Electronic supplementary information (ESI) available: Experimental details, ^{1}H NMR, DOSY, NOESY, and UV-Vis spectra of individual compounds or mixtures of **P1** and 0.50 equiv. **D1**, the association constant K_a of crown ether–paraquat. See DOI: 10.1039/c1cc14559b

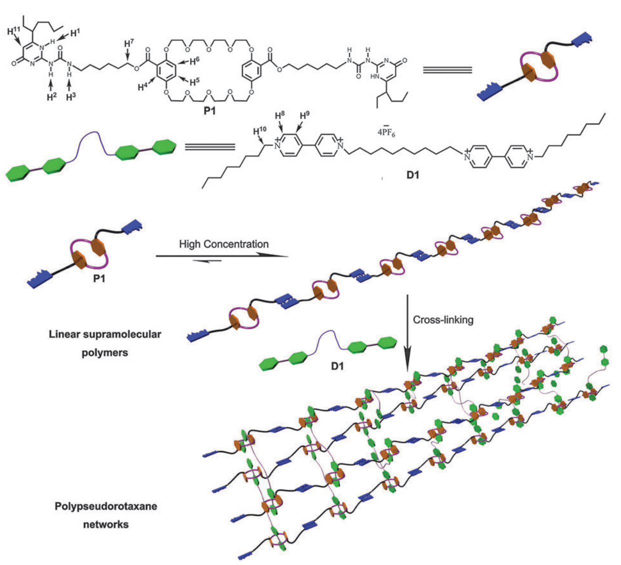

Fig. 1 Graphical representation of the construction of polypseudorotaxane networks from monomers **P1** and **D1**.

between the crown ether moieties and the paraquat groups of the **P1** and 0.50 equiv. **D1** were calculated under different concentrations (Table S1), which proves that the [3]pseudorotaxane structure had been incorporated leading to cross-linking (at least 70% based on the association ratio of 87.4% at 220 mM **P1**).[6e] The NOESY NMR spectrum of **P1** and 0.50 equiv. **D1** mixtures confirmed that the paraquat moieties threaded into the cavity of the crown ether (Fig. S4†). All evidence above supports the cross-linking of the hydrogen bonded linear supramolecular polymers *via* the bisparaquat to form the polypseudorotaxane networks at relatively high concentrations.

The formation of the large supramolecular polypseudorotaxane networks was also examined by the viscosity studies. Fig. 3a shows a change in slope at $\sim$40 mM for the double logarithmic plot of individual **P1**. At low concentrations, the curve slope is 1.48, while for the non-interacting assemblies of constant size, the slope should tend to 1,[12] this might be caused by the quite long, bulky linkage of bis-Upys **P1**. The cyclic structures formed in the diluted solutions, in the range of 4.0–40.0 mM, are predominantly multimeric macrocycles, which is deduced from the DOSY measurements (Fig. S5 and S6). The multimeric macrocycles are large, bulky and can associate with each other to some extent through the entanglement of the macrocycles. When the concentration increased to above 40 mM, a sharp rise of the slope (2.56) is observed, indicating a transition from the cyclic structures to the linear supramolecular polymers of increasing size.

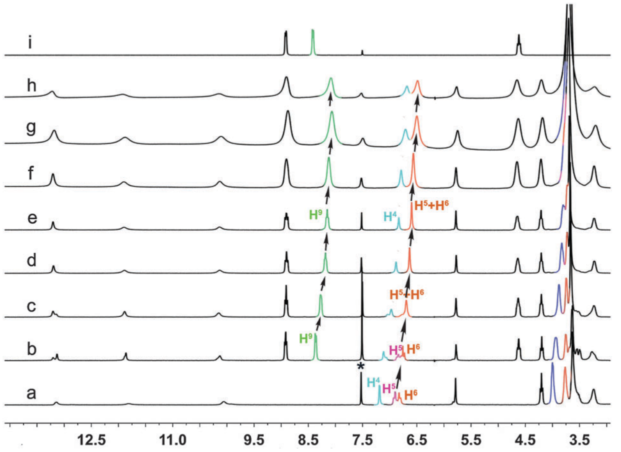

Fig. 2 Partial ^{1}H NMR spectra (300 MHz, 1 : 1 $CDCl_3$–CD_3CN, 297 K) of (a) **P1**; mixtures of **P1** and 0.50 equiv. **D1** at different **P1** concentrations: (b) 4.0, (c) 16.0, (d) 40.0, (e) 72.2, (f) 106.4, (g) 158.6, (h) 220 mM; and (i) **D1**. Signals affiliated with solvents are denoted by star symbols.

Furthermore, in order to investigate the cross-linking of the hydrogen bonded linear supramolecular polymers, the viscosity data of **P1** and **D1** varied from 0.1 to 0.5 equiv. mixtures at different concentrations were obtained. Firstly, we found that the reduced viscosity (V_R) of **P1** with addition of 0.5 equiv. **D1** varied nearly exponentially upon increasing the monomers concentration, suggesting formation of the polypseudorotaxane networks. While with the reducing amount of **D1** in the same **P1** solution, the reduced viscosity decreased gradually. By contrast, especially from 40 mM onward, individual **P1** samples showed a relatively much lower value at the same concentrations (Fig. 3b). This could be mainly due to the increased cross-linking ratio of the linear supramolecular polymer backbones with bisparaquat monomers by threading into the cavity of the crown ether units of linear supramolecular polymers above and the increased percentage of the complexed crown ether and paraquat units at higher concentrations. While below 40 mM, the reduced viscosity has similar values for the individual **P1** and the mixtures, indicating that the cyclic oligomers are the predominant species below 40 mM, which is in accordance with the double logarithmic plot of individual **P1**.

The diffusion ordered ^{1}H NMR spectroscopy (DOSY) is a useful technique to investigate the size of the aggregates in solution.[6c,13] Thus as shown in Fig. 4, the diffusion coefficient D of individual **P1** and mixtures of **P1** and 0.5 equiv. **D1** at different concentrations were measured. As the **P1** monomers concentration increased, the diffusion constant decreased to smaller values gradually. For the individual **P1**, the diffusion constant of the assemblies decreased $\sim$13 fold from 4.0 mM to 120.0 mM, indicating the formation of extended, high-molecular-weight polymeric aggregates at relatively high concentrations. With the addition of bisparaquats into the solution of **P1**, the paraquat groups can thread into the cavity of the crown

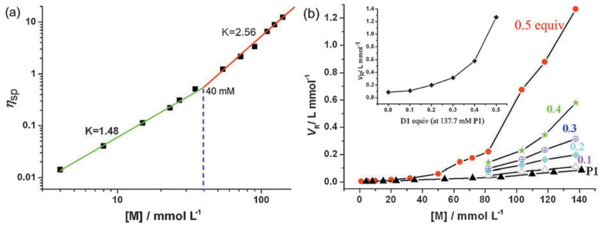

Fig. 3 (a) Specific viscosity η_{sp} of chloroform/acetonitrile (1 : 1, v/v) solutions of individual **P1** *versus* the monomer concentration at 27 °C; (b) reduced viscosity V_R of chloroform/acetonitrile (1 : 1, v/v) solutions of individual **P1** (▲) and mixtures of **P1** with 0.10–0.50 equiv. of **D1**, *versus* the **P1** concentration at 27 °C, the inset shows the reduced viscosity changes with the addition of 0–0.50 equiv. **D1** to the **P1** (137.7 mM) solution.

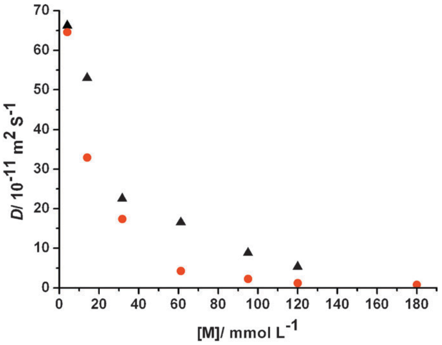

Fig. 4 Concentration dependence of diffusion coefficient D (500 MHz, 1 : 1 $CDCl_3$–CD_3CN, 298K) of individual **P1** (▲), and mixtures of **P1** with 0.50 equiv. **D1** (●) (when the systems have different assemblies, we chose the larger one).

ether units of **P1** to form the pseudorotaxanes. The diffusion constants of the mixtures are much smaller than those of the individual **P1** at the same concentrations from 4.0 mM to 120.0 mM, suggesting the increase in the average size of the aggregates due to the cross-linking of the **P1** polymeric structures to form the polypseudorotaxane networks.

In summary, we have constructed polypseudorotaxane networks with the cross-linking of linear quadruple hydrogen bonded supramolecular polymer backbones by the bisparaquat molecules in solution. This was confirmed by the combination of various techniques, such as variable-concentration ^{1}H NMR, NOESY, DOSY, UV-Vis spectra, and viscosity measurement. The reversible and tunable supramolecular polymer backbones would potentially bring unique, applicable properties to these traditional polypseudorotaxane structures. The construction of supramolecular [2]cantenane and new polypseudorotaxanes based on the ureidopyrimidione unit is now underway in our lab.

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