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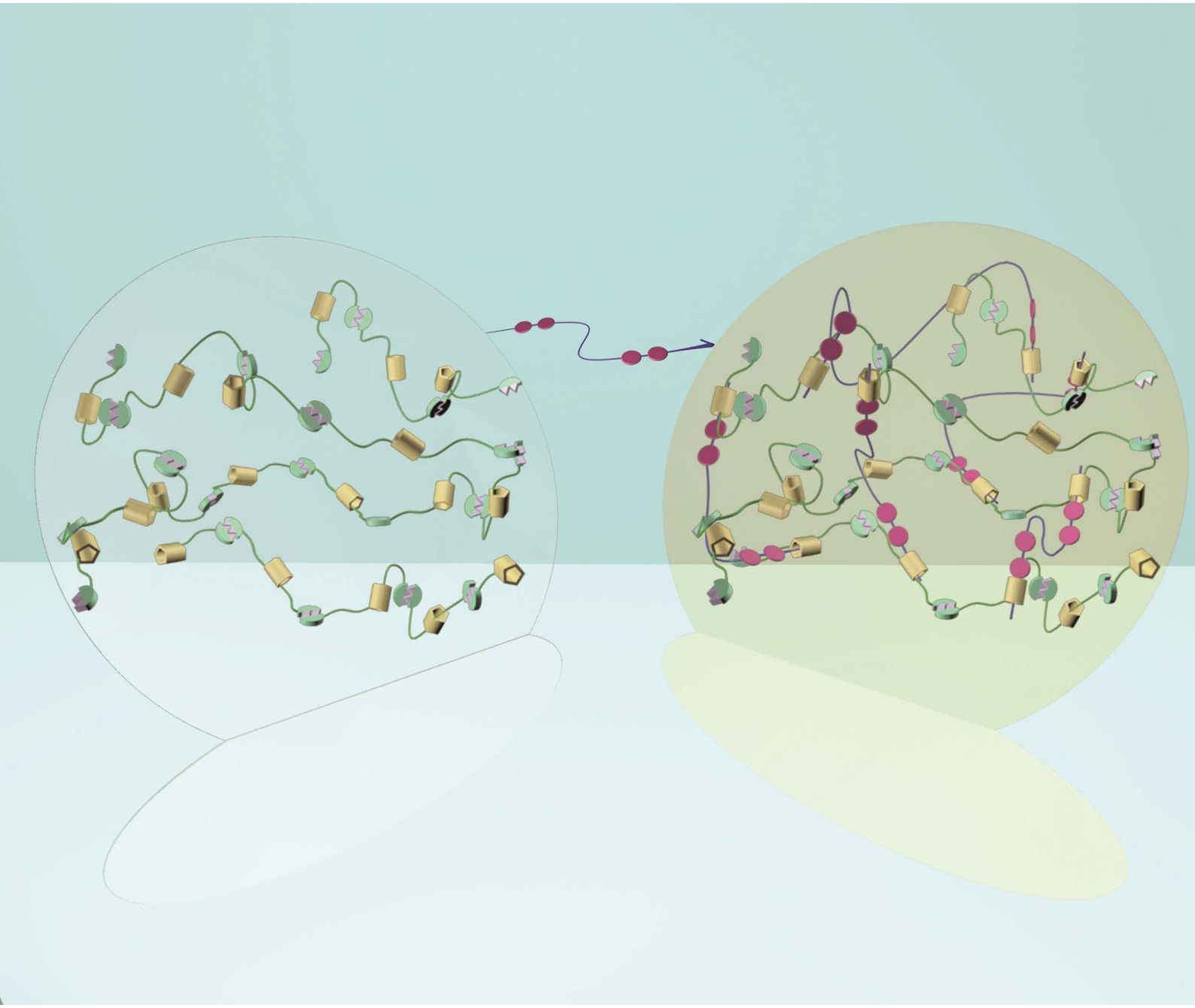

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Pillar[5]arene-based supramolecular polypseudorotaxane polymer networks constructed by orthogonal self-assembly†

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A novel pillar[5]arene-based supramolecular polypseudorotaxane network constructed by orthogonal self-assembly has been successfully fabricated. The obtained supramolecular polypseudorotaxane polymer was formed by a combination of two different non-covalent interactions, quadruple hydrogen bonding and pillararene-based host–guest interactions. Furthermore, a translucent film could be generated from the combination of this supramolecular polymer with PEG-2000 as the polymer matrix. The present study will provide a convenient and efficient way for the creation of pillararene-based advanced supramolecular materials.

Supramolecular polymers, in which monomeric units are self-assembled by reversible and highly directional non-covalent interactions, have attracted increasing attention and have become a fascinating topic in the last two decades.[1] The thermodynamically reversible nature of non-covalent interactions has provided a promising approach towards novel and smart design of advanced supramolecular architectures, such as self-healing materials and drug delivery systems.[2] The combination of different non-covalent interactions is a convenient and efficient way for the creation of advanced or smart supramolecular architectures. Recently, novel supramolecular polymers constructed by multiple orthogonal non-covalent interactions have gained more and more attention,[3,4] in which supramolecular polypseudorotaxane/polyrotaxane networks are particularly the most fascinating class of cross-linked polymers due to their unique structural features and specific properties. Although the reversible and stimuli-responsive properties of non-covalent interactions allow the development of novel supramolecular polymers that combine excellent adaptive features and good processability, the synthesis of supramolecular polypseudorotaxane/polyrotaxane networks assisted by non-covalent interactions as the polymeric backbones is relatively less common.[4d,f,5] Therefore, the exploration of an effective method for the construction of novel supramolecular polypseudorotaxane networks which could possess some unique and adaptive properties still remains a challenge.

Pillar[5]arene derivatives, a new class of macrocyclic hosts, have attracted considerable attention due to their unique structures and extensive applications in host–guest chemistry[6] and self-assembly systems,[7] and very compelling work for the construction of various supramolecular polymers has also been accomplished.[7c,8] For example, Huang and co-workers reported the first example of a pillar[5]arene-based supramolecular polypseudorotaxane driven by C–H$\cdots\pi$ interactions.[8b] Later, Ogoshi and co-workers developed a novel supramolecular polymer with alternating pillar[5]arene and pillar[6]arene units from a highly selective multiple host–guest complexation system.[8d] Recently, our group has reported a novel linear supramolecular polymer constructed from mono-ureidopyrimidinone modified pillar[5]arenes and bisparaquat derivatives based on orthogonal non-covalent binding interactions.[8c] Although there is considerable interest in the creation of pillararene-based interlocked molecules and linear supramolecular polymers, to the best of our knowledge, supramolecular polypseudorotaxane networks constructed by pillararene-based polymers as the polymeric backbones based on the orthogonal supramolecular interactions have not been reported yet. According to our previous work on pillar[5]arene-based supramolecular polypseudorotaxanes and dynamic polyrotaxanes interlocked by the quadruple hydrogen bonding ureidopyrimidinone (**UPy**) motif,[9] we envisioned that since the bifunctionalized **UPy** pillar[5]arenes could self-assemble into large linear supramolecular polymers at high concentrations,[10] which could be utilized as the polymeric backbones for the construction of networks, and an appropriate bisparaquat derivative could be utilized as the axle threading into the cavity of the pillararene unit in such a linear polymer, a polypseudorotaxane

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† Electronic supplementary information (ESI) available: Experimental procedures and characterization data for all the compounds; results of various ^{1}H NMR, NOESY, fluorescent titrations and DLS experiments. See DOI: 10.1039/c3py00575e

network might be possibly achieved in the concentrated solution. Herein, we report a novel pillararene-based supramolecular polypseudorotaxane network constructed by cross-linking the quadruple hydrogen bonded linear pillar[5]arene-based supramolecular polymer backbones *via* the threading of bis-paraquat molecules into pillar[5]arene units of the resulting linear polymer backbones based on orthogonal self-assembly, including quadruple hydrogen bonding and host–guest interactions which were believed to play vital roles in the construction of such supramolecular polypseudorotaxane networks (Fig. 1).

Using the strategy "non-covalent polymeric backbone formation followed by cross-linking *via* bisparaquat units", we initially synthesized the monomer bifunctional **UPy** pillar[5]-arene (**H1**)[9b] as shown in Fig. 1, and then ^{1}H NMR titration experiments were performed to investigate the formation of the linear supramolecular polymer by monomer **H1** in high concentration as well as the [3]pseudorotaxane complex formed between two molecules of **H1** and one bisparaquat derivative (**D1**)[4f] in low concentration. It was found that for the individual monomer **H1** in relatively high concentrations, the **UPy** N–H signals showed a large downfield shift together with a little lower intensity (between 10.0 and 13.0 ppm), which gave direct evidence for the **UPy** unit dimerization in the examined solvent indicating the linear polymer formation (ESI†, Fig. S5). Subsequently, the ability of two molecules of monomer **H1** with one molecule of **D1** to form a [3]pseudorotaxane complex in low concentration was assessed by ^{1}H NMR titration experiments by adding increasing amounts of **H1** into a 5.0 mM solution of **D1** in a $CDCl_3$–CD_3CN (1.5/1, v/v) solution (Fig. 2). In the spectrum of individual **D1**, it exhibited only one set of peaks due to the similar chemical environments of H_a and H_a'. However, when

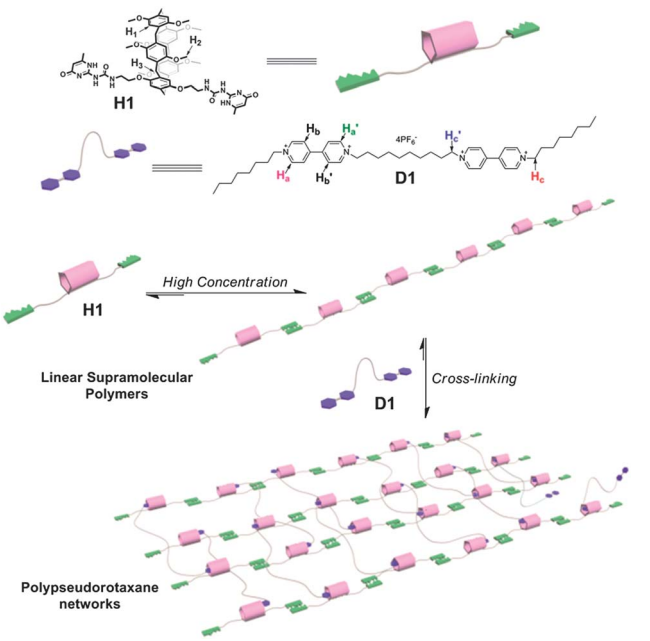

Fig. 1 Graphical representation of the construction of a polypseudorotaxane network from the monomer **H1** and cross-linker **D1**.

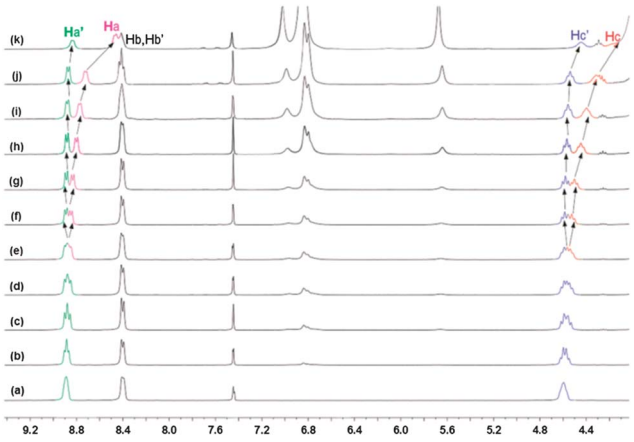

Fig. 2 Partial ^{1}H NMR titration spectra (300 MHz, 298 K) of 5.0 mM **D1** with various equivalents of **H1** in $CDCl_3$–CD_3CN (1.5/1, v/v) solutions: (a) 0.0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, (f) 1.0, (g) 2.0, (h) 4.0, (i) 6.0, (j) 10.0, and (k) 30.0.

more than 1.0 equiv. of **H1** was added, H_a and H_a' started to split into two different sets of 1 : 1 peaks. With the increasing amount of **H1**, the proton signals corresponding to H_a showed a much larger upfield shift than H_a'. Similar signal changes were also observed for H_c and H_c'. The addition of 30.0 equiv. of **H1** resulted in an upfield shift of 0.44 ppm for H_a and 0.38 ppm for H_c protons of the guest **D1**, while the protons belonging to H_a' and H_c' on **D1** shifted upfield very slightly (0.05 ppm for H_a', 0.12 ppm for H_c'). The above results are attributed to the different chemical environments of methylene groups (H_c and H_c') and pyridinium rings (H_a and H_a') at the outer and inner sides of the viologen moieties, strongly suggesting that the methylene moieties and pyridinium rings at both outer ends of the bisparaquat guest partially threaded into the cavity of pillar-[5]arene host; therefore, the [3]pseudorotaxane complex as a building unit of the supramolecular network was formed from **H1** and **D1**. Moreover, the complexation between pillar[5]arene and paraquat units shows a fast-exchanging process on the proton NMR time scale, and the percentage of the complexed species of pillararene–paraquat moieties increased as the concentration of **H1** increased.

The assignment and correlation of the protons of the [3] pseudorotaxane complex obtained above were further confirmed by the 2D NOESY NMR spectroscopy of **H1** and 0.50 equiv. **D1** mixtures in low concentration (Fig. 3). NOE peaks between protons H_1 and H_a, H_a', H_2/H_3 and H_a, H_a', and H_2/H_3 and H_c were observed, indicating that the paraquat moieties partially threaded into the cavity of the pillar[5]arene host. What is more, an optimized inclusion structure based on the model compounds of DMpillar[5]arene (**H2**) and a paraquat guest (dihexyl viologen salt, **D2**) which is an analogue of **D1**, was obtained using the density functional theory (DFT) calculation (see the ESI†, Fig. S17). The optimized geometry also indicated that the paraquat moieties of the guest molecule **D2** were partially located in the electron-rich cavity of pillar[5]arene **H2**. In addition, electrospray ionization mass spectrometry (ESI-MS) is a very convenient technique for determining the stoichiometry of the charged host–guest complexes. In equimolar

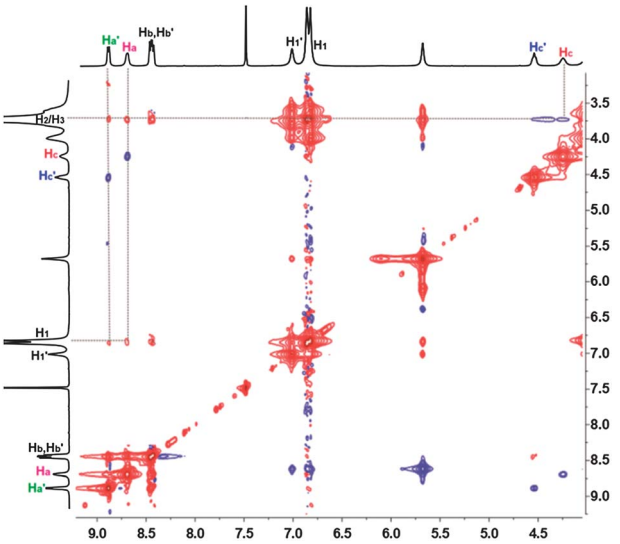

Fig. 3 Partial 2D NOESY spectra of **H1** with **D1** in a $CDCl_3$–CD_3CN (1.5/1, v/v) solution with a mixing time of 600 ms (400 MHz, 298 K, the concentrations of **H1** and **D1** are 30.0 and 15.0 mM, respectively).

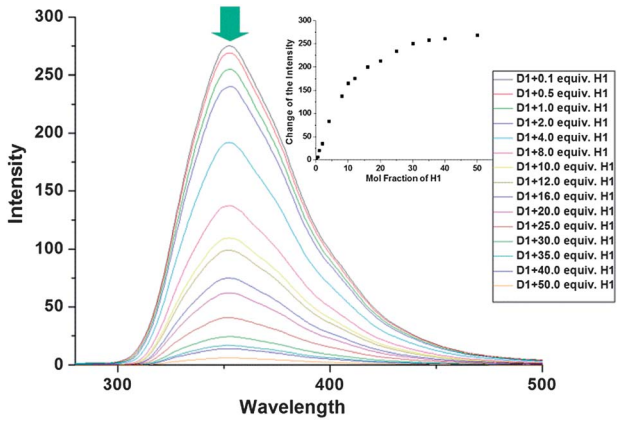

Fig. 4 Fluorescent titration of **D1** (1×10^{-5} M) in a $CHCl_3$–CH_3CN (1.5/1, v/v) solution with various equivalents of **H1** (Inset: titration profile of the absorption changes upon addition of **H1**. Changes in the fluorescence intensities at 353 nm from **D1** upon addition of **H1** were plotted).

solutions of **H1** and **D1** in low concentration, peaks for both 1 : 1 $\{[\mathbf{H1} + \mathbf{D1} - 4PF_6]^{4+}$ (*m*/z: 447.45), $[\mathbf{H1} + \mathbf{D1} - 3PF_6]^{3+}$ (*m*/z: 644.95), $[\mathbf{H1} + \mathbf{D1} - 2PF_6]^{2+}$ (*m*/z: 1039.90)$\}$ and 2 : 1 $\{[2\mathbf{H1} + \mathbf{D1} - 4PF_6]^{4+}$ (*m*/z: 725.20), $[2\mathbf{H1} + \mathbf{D1} - 3PF_6]^{3+}$ (*m*/z: 1015.25), $[2\mathbf{H1} + \mathbf{D1} - 2PF_6]^{2+}$ (*m*/z: 1595.50)$\}$ host–guest complexes were found (see the ESI†, Fig. S1). On the basis of the above evidence as well as the ^{1}H NMR experiment results, the formation of the [3] pseudorotaxane complex from **H1** and **D1** in low concentration was confirmed, which would reasonably support the speculation that the supramolecular polypseudorotaxane network could be possibly formed at relatively high concentrations through the cross-linking of the quadruple hydrogen bonded linear pillar[5]arene-based supramolecular polymers as polymer backbones and the bisparaquat molecules as cross-linkers as shown in Fig. 1.

Furthermore, fluorescent titration experiments showed that the emission peak of **D1** could be gradually quenched to 2.3% of its initial value upon addition of 50 equiv. of **H1** (Fig. 4), which might be due to the inhibition of the electron transfer from **D1** to **H1** in their complex by a steric shielding effect.[11] In order to investigate the binding affinity of the pillararene–paraquat recognition motif and avoid the disturbance of the **UPy** moiety, the model compounds **H2** and **D3** (dioctyl viologen salt), analogues of **H1** and **D1**, respectively, were applied for the fluorescent titration experiments, where the association constant (K_a) of the pillararene–paraquat recognition for **H2** and **D3** was calculated to be $(3.13 \pm 0.09) \times 10^3$ M^{-1} ($CHCl_3$–CH_3CN = 1.5/1, v/v) according to the reported method, which was approximated as the K_a value between **H1** and **D1**. The reason we chose this mixed solvent system is based on the different solubilities of the pillararene host and paraquat guest (see the ESI†, Fig. S12).

The formation of the supramolecular polypseudorotaxane network was then investigated by the ^{1}H NMR spectroscopy of **D1** with **H1** in a 1 : 2 molar ratio at various concentrations in the range of 0.5–80 mM (Fig. 5). As expected, under the examined conditions the **UPy** N–H signals showed downfield shifts (between 10.0 and 13.0 ppm, Fig. S6†), giving direct evidence for the dimerization of **UPy** units which is the main driving force for the supramolecular polymer backbone formation. Moreover, it was also found that as the concentration of **H1** and **D1** increased, the bisparaquat protons H_a and H_c showed upfield shifts and broadening effects, indicating that the paraquat moieties threaded into the cavity of the pillararene host, as well as the formation of a supramolecular polymer. The association ratios between the pillararene moieties and the paraquat groups were also calculated at different concentrations (see the ESI†, Table S1), which proved that the percentage of complexed viologen moieties increased with the increasing concentration of **H1** and **D1**, suggesting that the [3]pseudorotaxane unit was cross-linked from low to high concentration and resulted in the formation of the polypseudorotaxane network in a concentrated solution. In particular, the broadening of the main peaks in

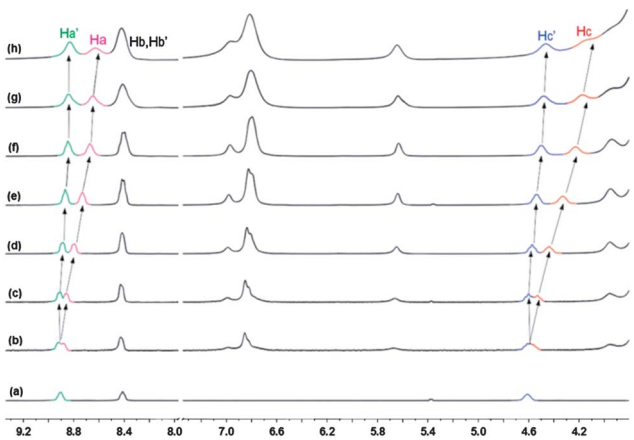

Fig. 5 Partial ^{1}H NMR spectra (300 MHz, 298 K, $CDCl_3$–CD_3CN = 1.5/1, v/v) of **D1** with **H1** in 1 : 2 ratio at various **D1** concentrations (mM): (a) 0.5, (b) 1.0, (c) 2.5, (d) 7.5, (e) 15.0, (f) 25.0, (g) 50.0, and (h) 80.0.

^{1}H NMR spectra in high concentrations also gave evidence for the high-molecular-weight polymer formation.

The formation of the supramolecular polypseudorotaxane network was sequentially examined by viscometry, which is a very convenient method to test the polymerization characteristics of macromolecules. As presented in Fig. 6a, the aggregates assembled from individual **H1** were first investigated, and they presented a viscosity transition and showed a change in slope at about 19 mM. In the low concentration region, the curve slope was 1.13, indicating the predominance of cyclic oligomers in diluted solutions. When the concentration increased over the critical polymerization concentration (CPC, 19 mM), an obvious increase of the slope (1.89) was observed, indicating a transition from small sized cyclic oligomers to the linear supramolecular polymers with increasing size of assembly.

Furthermore, in order to investigate the cross-linking of the hydrogen bonded linear supramolecular polymers with the bisparaquat molecules to form the target supramolecular network, reduced viscosity (V_R) experiments of **H1** and **D1** (varied from 0.1 to 0.5 equiv.) mixtures at different concentrations were performed. It was found that the reduced viscosity increased gradually with the increasing amount of **D1** in the same concentration of the **H1** solution, especially at high concentrations (Fig. 6b). This might be mainly due to the increased cross-linking ratio of the linear supramolecular polymer backbones with bisparaquat units, leading to the increased percentage of the complexed pillararene and paraquat units at higher concentrations. Moreover, the reduced viscosity of **H1** with the addition of 0.5 equiv. **D1** varied nearly exponentially upon increasing the monomer concentration, indicating the formation of the polypseudorotaxane network.

Two-dimensional diffusion-ordered ^{1}H NMR spectroscopy (DOSY) is a convenient and reliable method to investigate the size of the aggregates in solution.[4f,7c,12] Thus diffusion coefficients D of individual **H1** and mixtures of **H1** with 0.5 equiv. **D1** at different concentrations were measured. As shown in Fig. 7a, the average measured diffusion constant of individual **H1** decreased 5-fold from 5.0 mM to 120.0 mM, indicating the formation of high-molecular-weight polymeric aggregates at relatively high concentrations. With the addition of bisparaquat **D1** into the solution of **H1**, the paraquat moieties can thread into the cavity of the pillararene units of **H1** to form the pseudorotaxanes. The average measured diffusion constants are much smaller than those of the individual **H1** at the same concentrations from 5.0 mM to 120.0 mM, suggesting the increase of the average size of the aggregates due to the cross-linking of the linear polymeric structures and bisparaquat molecules to form the polypseudorotaxane network.

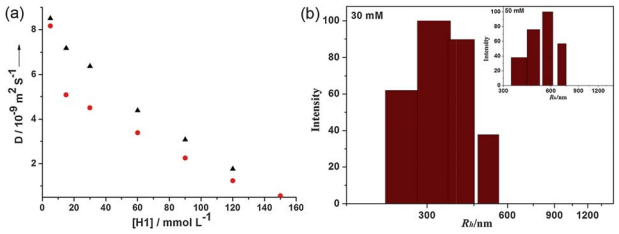

Fig. 7 (a) Concentration dependence of diffusion coefficient D (400 MHz, $CDCl_3$–CD_3CN (1.5/1, v/v), 298 K) of individual **H1** (▲), and mixtures of **H1** with 0.50 equiv. **D1** (●) (when the systems had different assemblies, we chose the larger one). (b) Distribution of the hydrodynamic diameter of **H1** with 0.50 equiv. **D1** in a $CHCl_3$–CH_3CN solution (1.5/1, v/v) at 298 K (30 mM, *inset*: 50 mM).

We also conducted dynamic light scattering (DLS) measurements of the mixtures of **H1** and 0.5 equiv. **D1** in a $CHCl_3$–CH_3CN solution to investigate the size of the supramolecular aggregates (Fig. 7b). The aggregate of **H1** and **D1** showed the average hydrodynamic radius (R_h) values of 322 nm and 574 nm at concentrations of 30 mM and 50 mM in solution, respectively, indicating the formation of large size supramolecular aggregates in both cases and the formation of bigger aggregates at high concentration than at low concentration. Furthermore, transmission electron microscopy (TEM) was also used to provide further insight into the size and shape of the aggregates.[13] Representative TEM images of the supramolecular aggregates formed in a $CHCl_3$–CH_3CN solution are shown in Fig. 8 (for details, see the ESI†, Fig. S15). In most cases, the supramolecular aggregates were observed as dark gray spherical aggregates, which might have originated from further assembly of the supramolecular network in solution. And the mean size of the aggregates was more than 300 nm in diameter, which is in agreement with the DLS results (Fig. 7b). Therefore, the above results further indicated the formation of large size supramolecular aggregates.

Conventional polymers usually possess excellent mechanical properties and superior processability, while supramolecular polymers can exhibit dynamic, self-healing and even adaptive features due to the non-covalent interactions; therefore the

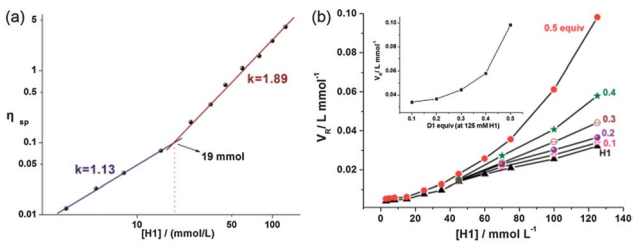

Fig. 6 (a) Specific viscosity of **H1** in a $CHCl_3$–CH_3CN solution (1.5/1, v/v) at 298 K. (b) Reduced viscosity V_R of individual **H1** (▲) and mixtures of **H1** with 0.1–0.5 equiv. of **D1** *versus* the **H1** concentration in $CHCl_3$–CH_3CN (1.5/1, v/v) solutions at 298 K; the *inset* shows the reduced viscosity changes with the addition of 0.1–0.5 equiv. **D1** to the **H1** (125 mM) solution.

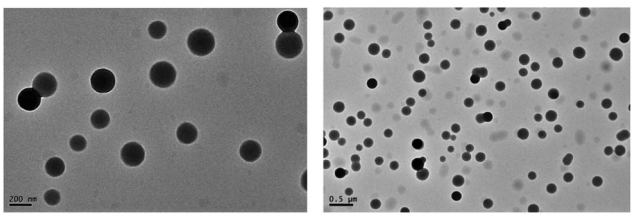

Fig. 8 TEM micrograph of the supramolecular aggregates (samples were prepared by placing one drop of the $CHCl_3$–CH_3CN solution of the mixtures of **H1** with 0.50 equiv. **D1** onto a carbon-coated copper grid).

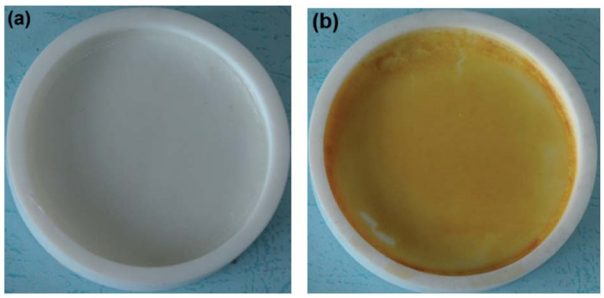

Fig. 9 Film formation experiments (samples were prepared by placing **PEG-2000** (10 equiv.) with the $CHCl_3$ solution of **H1** (1 equiv.) (a), and the $CHCl_3$–CH_3CN solution of the mixtures of **H1** (1 equiv.) and **D1** (0.5 equiv.) (b) into a Teflon mould, respectively).

combination of these two types of polymers may provide a novel platform for studying supramolecular polymers or achieving innovative materials by combining their advantages. Along this line, blending the supramolecular polymer with a conventional polymer might be the most straightforward and easily achieved way. Firstly, the polycarbonate (PC, $M_W = 19\,000$) was chosen for investigation, which showed good solubility in chloroform and exhibited a nice film-forming character. It was dissolved with the linear supramolecular polymers formed from **H1**, and then transferred into a Teflon mould, but unfortunately after completely evaporating the solvent, macrophase-separated results were always obtained with **H1** segregated. Further investigation of the film formation was carried out using the supramolecular polypseudorotaxane polymer networks formed from **H1** and **D1** with conventional poly(ethylene glycol) (**PEG-2000**) as the polymer matrix, and in particular, neither of them could individually form a film. The representative film images of the complex are shown in Fig. 9 (for details, see the ESI†, Fig. S16). For **PEG-2000**, it could not form a film individually, but was usually obtained as a waxy solid due to its strong crystallizability. However, in the presence of the supramolecular polymers obtained above (**H1** or **H1** with **D1**), translucent films could be obtained in white (**H1** with **PEG-2000**) or yellow color (**H1** and **D1** with **PEG-2000**), in which the color change also confirmed the formation of a host–guest inclusion complex due to charge transfer interactions between **H1** and **D1**. But unfortunately, the film was so fragile that it was difficult to further investigate its mechanical properties. Some other kinds of conventional polymers will be examined, and especially the preparation of well-designed chemically modified polymers is underway for further exploring the complexation of conventional and supramolecular polymers.

Conclusions

In summary, we have fabricated a novel pillar[5]arene-based supramolecular polypseudorotaxane network constructed by the cross-linking of linear quadruple hydrogen bonded supramolecular polymer backbones with the bisparaquat molecules threading into the cavity of the pillar[5]arene units in solution, and such supramolecular networks could further assemble to much bigger spherical aggregates. This obtained supramolecular polymer was fully investigated by the combination of various techniques, such as variable-concentration ^{1}H NMR, NOESY, DOSY, fluorescent titrations, dynamic laser light scattering (DLS), viscosity, and TEM measurement. In such a novel supramolecular polypseudorotaxane network, the **UPy** motifs particularly play quite important roles in the formation of the reversible and tunable supramolecular polymer backbones, which would potentially bring unique, applicable properties to these polypseudorotaxane structures. Furthermore, a translucent film could be created using the supramolecular polymers with **PEG-2000** as the polymer matrix, particularly, either of which could not form a film individually. The construction of more intriguing pillararene-based supramolecular architectures based on quadruple hydrogen bonding interactions and other host–guest interactions as well as their combination with conventional polymers for their application in materials science is in progress in our lab.

Acknowledgements

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