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Pillar[5]arene-based supramolecular polypseudorotaxanes constructed from quadruple hydrogen bonding†

Xiao-Yu Hu, Pingyuan Zhang, Xuan Wu, Wei Xia, Tangxin Xiao, Juli Jiang, Chen Lin and Leyong Wang*

Novel linear supramolecular polypseudorotaxanes constructed from bifunctional ureidopyrimidinone (UPy) pillar[5]arene as the wheel and alkyl diamine as the axle were successfully prepared. This supramolecular polymer was stabilized by the combination of two different non-covalent interactions: quadruple hydrogen bonding and pillararene-based host–guest interactions.

Polypseudorotaxanes, the supramolecular precursors of poly-rotaxanes, have attracted considerable interest in the fields of supramolecular chemistry and materials chemistry in the past decade, not only for their topological importance but also due to their potential applications in the preparation of molecular devices and machines.[1] For the construction of polypseudorotaxanes/poly-rotaxanes, cyclodextrins[2] and crown ethers[3] were initially utilized as the macrocyclic components (the 'wheels'). Harada *et al.* first reported the construction of polypseudorotaxanes by cyclodextrins (the 'wheels') and linear polymers (the 'axles') such as poly(ethylene glycol) and poly(propylene glycol).[2a–c] In 2009, Huang and co-workers demonstrated crown ether-based polypseudorotaxanes with supramolecular polymers as backbones *via* two self-sorting host–guest recognition motifs.[4] The ongoing search for new macrocyclic hosts and linear guest molecules to form templated-pseudorotaxane could increase the options available for the development of novel rotaxanes, catenanes, switches, and machines.[5] Thus, many new types of macrocycles such as cucurbiturils,[6] calixarenes,[7] and cyclophanes[8] have been investigated. Pillar[5]arene, first reported by Ogoshi *et al.* in 2008[9] can be regarded as an analogue of the calixarenes and cyclo-dextrins. It can also form very stable host–guest complexes and has shown very interesting properties in host–guest chemistry.[10] Recently, a successful example has shown that DMpillar[5]arene could form [2] pseudorotaxanes with 1,8-diaminooctane, and the superstructure of such 1 : 1 host–guest based complexes was supported by the template-directed synthesis of a related [2]rotaxane.[11] The pillararenes with their specific structural characteristics and π-rich cavities are suitable wheels for the construction of various pseudorotaxanes with linear electron accepting molecules as axles based on such non-

covalent interactions. For example, Ogoshi and co-workers successfully synthesized a novel polypseudorotaxane and polyrotaxane constructed from pillar[5]arene as the cyclic rings and viologen derivatives as the polymeric chain based on efficient electron transfer.[12] Huang reported the first example of using the host–guest chemistry (C–H···π interactions) of pillararenes in the preparation of supramolecular polymers.[13] More recently, Stoddart has demonstrated that pillar[5]arene carrying a viologen side-chain exhibited self-complexing and self-assembling behavior and could form concentration-dependent supramolecular daisy chain oligomers and polymers.[14]

The combination of different non-covalent interactions is a convenient and efficient way for the creation of complicated supramolecular architectures.[15] The highly directional quadruple hydrogen bonding ureidopyrimidinone (**UPy**) motif disclosed by Meijer and co-workers represented one of the most widely used units in supramolecular polymer construction due to its strong association constant ($K_{ass} > 10^7$ M^{-1} in chloroform) and synthetic accessibility.[16] We recently have constructed supramolecular polypseudorotaxane networks by cross-linking quadruple hydrogen bonded linear supramolecular polymer backbones *via* bisparaquat molecules.[17] More recently, we also have reported the formation of dynamic [2] catenane by the selective cyclization of a supramolecular polymer based on the quadruple hydrogen bonding **UPy** motif.[18] Therefore, we envisioned that if we could incorporate two **UPy** groups into two sides of pillar[5]arenes to obtain a bifunctional **UPy** pillar[5]arene, then the resulting pillar[5]arenes could self-assemble into large linear supramolecular polymers at high concentrations. In addition, if an appropriate guest molecule such as 1,4-butanediamine (**G**) as an axis could be threaded into the cavity of pillararene, a poly-pseudorotaxane may be obtained in the concentrated solution. Herein, we report for the first time a novel type of linear poly-pseudorotaxane constructed by efficient quadruple hydrogen bonding interactions with the assistance of pillararene-based host–guest complexation (Fig. 1). This study will provide a novel and simple way to fabricate supramolecular polymeric materials and it can also enrich the application of the host–guest chemistry of pillararenes.

Initially, we designed and synthesized a bifunctional **UPy** pillar[5] arene (**H1**) (Scheme S1, ESI†), and then the formation of the linear polymer was investigated by ^{1}H NMR experiments in chloroform at concentrations in the range of 2.0–150 mM (Fig S1, ESI†). It was found that the **UPy** N–H signals showed large downfield shifts
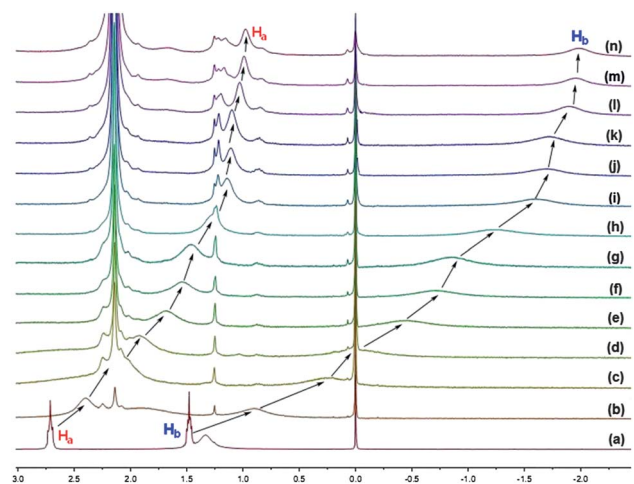
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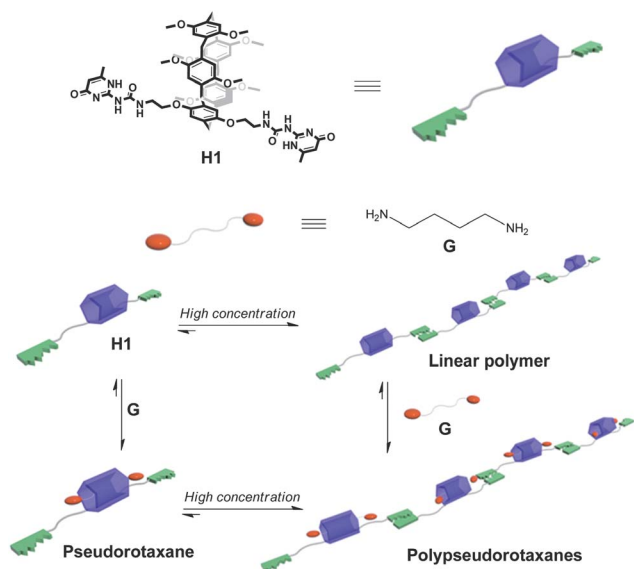
Fig. 1 Graphical representation of the construction of poly-pseudorotaxane polymers from **H1** and **G**.

Fig. 3 2D NOESY analysis of **H1** with **G** in CDCl$_3$ (400 MHz, 298 K).

(between 10 and 13.5 ppm), which gave direct evidence for the dimerization of the **UPy** units. Moreover, such signals also showed lower intensity and became broad, indicating linear polymer formation at relatively high concentrations. Subsequently, the ability of **H1** to form a pseudorotaxane complex with **G** was assessed by ^{1}H NMR titration experiments of **H1** into a 10.0 mM solution of **G** in chloroform (Fig. 2). With increasing concentration of **H1**, the proton signals corresponding to H$_a$ and H$_b$ of **G** shifted upfield clearly. The addition of 1.0 equiv. of **H1** resulted in an upfield shift of 1.03 ppm for the H$_a$ protons of **G**, while the protons belonging to H$_b$ on **G** shifted upfield even more (1.93 ppm). Moreover, after the addition of more than 5 equiv. of **H1**, the chemical shifts of protons H$_a$ and H$_b$ remained almost unchanged, indicating that the wheel is fully threaded by the axle and the formation of a pseudorotaxane complex

between the pillar[5]arene host and the 1,4-butanediamine guest in chloroform is achieved.

The assignment and correlation of the protons were further confirmed by the 2D NOESY NMR spectrum of the solution of **H1**–**G** (Fig. 3). Strong correlations were observed between the diamine protons (H$_a$ and H$_b$) and the aromatic protons (H$_1$), as well as the bridging methylene protons (H$_2$) of the pillar[5]arene host, indicating that the diamine guest was deeply threaded into the cavity of the pillararene unit.

The ESI mass experiment is a very convenient technique for determining the stoichiometry of the charged host–guest complex. In our case, the ESI mass spectrum of an equimolar mixture of **H1** and **G** showed one intense peak for the 1 : 1 host–guest complex ([**H1**–**G** + H]$^+$, m/z 1199.60) (Fig. S3, ESI†). What's more, Job plots based on the proton NMR data also demonstrated that the complex formed of **H1** with **G** was of 1 : 1 complexation stoichiometry (Fig. S4, ESI†), which was in accordance with the mentioned results

Fig. 2 Partial ^{1}H NMR spectra (CDCl$_3$, 298 K, 300 MHz) of **G** at a concentration of 10 mM with different concentrations (mM) of **H1**: (a) 0.0, (b) 3.0, (c) 6.0, (d) 7.5, (e) 10.0, (f) 13.0, (g) 15.0, (h) 20.0, (i) 25.0, (j) 30.0, (k) 35.0, (l) 50.0, (m) 70.0 and (n) 80.0.
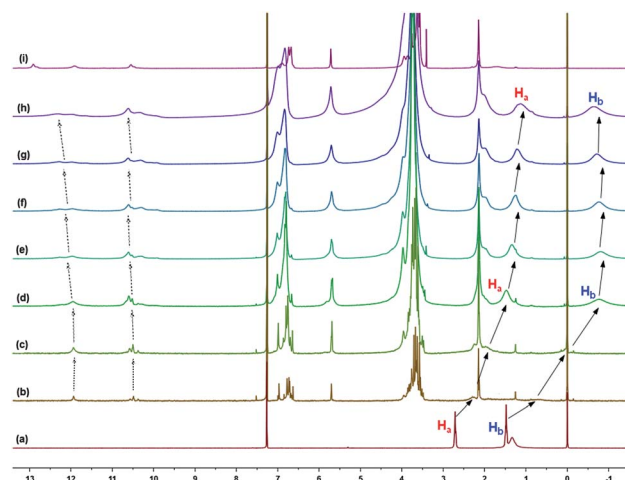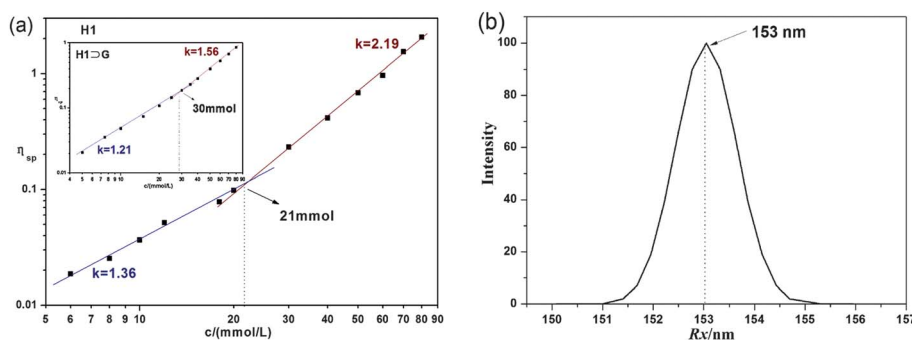

Fig. 4 ^{1}H NMR spectra (300 MHz, CDCl$_3$, 298 K) of (a) only **G**; equimolar mixtures of **H1** and **G** at different **H1** concentrations: (b) 1, (c) 2.5, (d) 10, (e) 20, (f) 50, (g) 100, (h) 200 mM, and (i) only **H1**.

Fig. 5 (a) Specific viscosity of chloroform solutions of **H1**, and the equimolar mixtures of **H1** and **G** (inset) *versus* **H1** concentration (298 K). (b) Distribution of the hydrodynamic diameter of a 40 mM equimolar mixture solution of **H1** and **G** in chloroform at 298 K.

of ESI-MS above. Combined with the ^{1}H NMR and 2D NOESY experiments, we can unambiguously confirm the formation of the [2]pseudorotaxane-type complex, as shown in Fig. 1. By a non-linear curve-fitting method, the association constant (K_a) between the guest (**G**) and host (**H1**) could be calculated, which was $(2.74 \pm 0.05) \times 10^2$ M^{-1} in chloroform (Fig. S5, ESI†). This K_a value is of the same order of magnitude as that of the previously reported complex constructed by a simple DMpillar[5]arene and a diamine guest.[11]

The formation of the linear polymers was then investigated by ^{1}H NMR spectra of an equimolar mixture of **H1** and **G** (CDCl$_3$, 300 MHz, 298 K) at concentrations in the range of 1–200 mM (Fig. 4). As expected, the **UPy** N–H signals showed a large downfield shift together with a lower intensity (between 10.5 and 13.0 ppm), giving direct evidence for the dimerization of the **UPy** units. Moreover, it was also found that as the concentration of the mixture of **H1** and **G** increased, the signals of the diamine protons H$_a$ and H$_b$ showed significant upfield changes, suggesting the host–guest interactions of pillararene and diamine in the solution and the concentration dependent percentage of the association ratio of pillar[5]arene and diamine unit. In addition, all of the proton signals became broad at high concentrations, strongly indicating the formation of high-molecular-weight polymers.

Viscometry is a convenient method to test the polymerization properties of polymer molecules. Therefore, we measured the specific viscosities of **H1** and equimolar mixture solutions of **H1** and **G** in chloroform, using a Cannon Ubbelohde semi-microdilution viscometer. As presented in Fig. 5, the linear supramolecular polymer assembled from **H1** exhibited a viscosity transition with a dramatic change in the slope at 21 mM, indicating a progression from the presence of small oligomers (slope = 1.36) in solution to supramolecular polymers with longer chains (slope = 2.19). The slope value in this case is similar to that obtained from the **UPy**-based self-assembling systems reported by Meijer *et al.*[16d,f] What's more, with respect to the equimolar mixture solutions of **H1** and **G**, the curve slope is 1.21 in the low concentration region; when the concentration was increased to above 30 mM, a curve slope of 1.56 was observed, indicating a transition from the small oligomer to bigger sized linear supramolecular polymers. This slope value is lower than that of the reported **UPy**-based self-assembling systems above, which implies that there might be some degree of disruption of the polymers due to the breakdown of quadruple hydrogen bonding **UPy** in solution by the diamine guest (alkali molecule). Based on the K_{dim} value of the **UPy** groups of 5.7×10^7 M^{-1},[16h] the average degree of

polymerization (DP) at 80 mM of **H1** as well as in the presence of the diamine guest (**G**) was estimated to be 3150 and 2670, respectively (ESI†).

Dynamic light scattering (DLS) measurements can be applied to estimate the size of the supramolecular oligomers in solution. Thus, we also conducted DLS measurements of an equimolar mixture of **H1** and **G** in chloroform to investigate the size of the aggregates (Fig. 5b). The aggregate of **H1** and **G** at a concentration of 40 mM in solution shows an average hydrodynamic radius (R_h) value of 153 nm, indicating the formation of large sized supramolecular polymers.

Conclusions

In summary, we have reported the formation of a new linear supramolecular polypseudorotaxane constructed from difunctionalized **UPy** pillar[5]arene as the wheel and alkyl diamine as the axle. This supramolecular polymer was stabilized by a combination of two different kinds of non-covalent interactions, namely quadruple hydrogen bonding and pillararene based host–guest interactions, and it was fully confirmed by the combination of various techniques, such as ^{1}H NMR, 2D NOESY NMR, ESI-MS, DLS, viscosity measurements, and SEM. The experimental results demonstrate that the formation of large supramolecular polymers is dependent on the concentration of the monomers. Moreover, the present study affords the first example of a linear supramolecular polypseudorotaxane driven by efficient quadruple hydrogen bonding interactions, with the assistance of pillararene based host–guest complexation, and it also enriches the applications of the host–guest chemistry of pillararenes. Considering the easy availability of the difunctionalized **UPy** pillar[5]arene monomers and the reversibility and tunability of pillararene based supramolecular polymers, the present study will provide a novel and simple way to fabricate supramolecular polymeric materials. The construction of more complicated cross-linked polypseudorotaxane networks by these two kinds of non-covalent interactions is ongoing.

Acknowledgements

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