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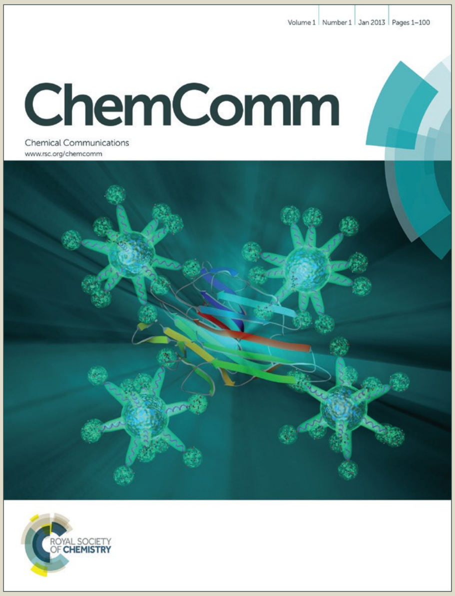

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A pillar[6]arene-based [2]pseudorotaxane in solution and in the solid state and its photo-responsive self-assembly behavior in solution†

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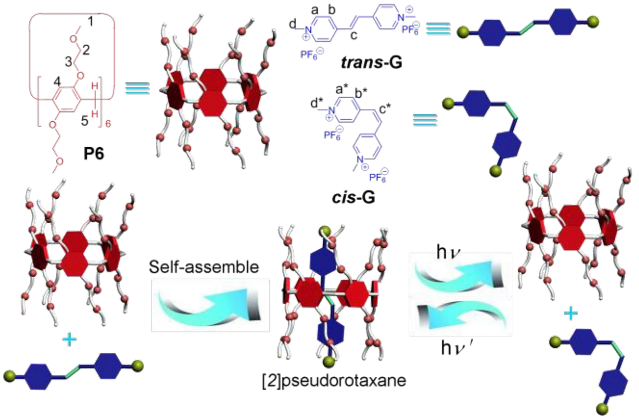
A pillar[6]arene-based [2]pseudorotaxane was constructed in solution and studied in the solid state and its photo-responsive self-assembly behavior in solution was investigated.

Supramolecular chemistry has developed rapidly by taking aim at mimicking nature in which complex and highly-ordered self-assembled structures are ubiquitous and going beyond that to facilitate the construction of supramolecular structures with new topologies and significant functions.[1] Threaded structures[2] have played an important role in topology and the fabrication of advanced supramolecular systems, such as functional supramolecular polymers,[3] artificial molecular machines,[4] and so on. As basic threaded structures, pseudorotaxanes, in which ring components are threaded onto axles, have been a topic of great interest, since they are fundamental building blocks for the preparation of advanced supramolecular species with intriguing properties.[5] Various host–guest recognition motifs have been applied for the preparation of threaded structures.[6] Macrocycles are always fascinating and attractive building blocks to construct threaded structures, owing to their interesting topology structures and excellent host–guest properties in supramolecular chemistry.[7] Pillar[*n*]arenes, a new class of host macrocycles introduced by the Nakamoto group,[8a,b] have become one of the most popular topics recently.[8] Due to their rigid and pillar structures, electron-donating cavities, and easy functionalization, pillararenes have shown interesting host–guest binding properties with plenty of guest molecules, thereby providing a useful platform for the construction of various interesting supramolecular systems, such as threaded structures, supramolecular polymers, artificial transmembrane channels, detectors, green catalysis, and functional assemblies.[9] Until now, the studies of pillar[*n*]arenes have been mainly centered on pillar[5]arenes and pillar[6]arenes. The host−guest chemistry of pillar[5]arenes has been widely explored while that of pillar[6]arenes has not been invesigated widely.[8h,9b] Since pillar[6]arenes have larger cavities than pillar[5]arenes, their host−guest chemistry should be different from that of pillar[5]arenes. The investigation of the host−guest chemistry of pillar[6]arenes should be able to greatly promote the development of pillararene supramolecular chemistry.

Moreover, control of the complexation behavior and the relative positional changes that occur within host–guest systems are of great importance for the construction of advanced functional supramolecular structures.[10] Photo-responsive threaded structures are important buiding bolcks to construct advanced functional supramolecular systems.[11] Our group has reported photo-responsive host–guest systems based on pillararenes and azobenzene-containing guests.[11a,d,h] From these studies, it has been known that UV light could not destroy the complexation between the azobenzene-containing guests and those pillararene hosts. Vinylogous viologens, as π-extended viologens, not only are electron-poor π-systems, but also can undergo photoinduced *cis*–*trans* isomerization accompanied by large molecular property changes,[12] which make them proper guests for pillararenes with photo-responsive binding property. Herein, we constructed a [2]pseudorotaxane based on a 1,4-bis(methoxyethoxy)-substituted pillar[6]arene **P6** and a vinylogous viologen dication ***trans*-G**. The [2]pseudorotaxane showed photo-responsive self-assembly behavior in acetonitrile (Scheme 1). More importantly, there was no complexation between ***cis*-G** and **P6**, indicating that UV light at a certain wavelength could destroy the complexation between ***trans*-G** and **P6**. Therefore, a novel pillararene-based photo-responsive host–guest recoginition motif was constructed.



Scheme 1. Chemical structures of compounds **P6**, ***trans*-G** and ***cis*-G** and cartoon representation of reversible formation of the pillar[6]arene-based [2]pseudorotaxane upon photo irradiation.

First, a mole ratio plot (Fig. S1, ESI†) based on UV-vis absorbance data demonstrated that **P6**⊃***trans*-G** was of 1:1 stoichiometry in acetonitrile. The association constant (K_a) of

P6⊃*trans*-G in acetonitrile was determined to be (3.55 ± 0.24) × 10^2 M^{-1} by probing the charge-transfer band of the complex using a UV-vis spectroscopy titration method (Fig. S2, ESI†). In addition, electrospray ionization mass spectrometry (ESIMS) confirmed the complexation stoichiometry between **P6** and ***trans*-G**: *m*/*z* 821.4 for [**P6⊃*trans*-G** – $2PF_6]^{2+}$ and 1787.1 for [**P6⊃*trans*-G** – $PF_6]^+$ (Fig. S3, ESI†).

Furthermore, ^{1}H NMR spectroscopy was used to study the host–guest complex **P6⊃*trans*-G** (Fig. 1). Significant chemical shift changes of the signals for the protons on ***trans*-G** and **P6** occurred upon mixing them together (Fig. 1b). The peaks related to H_a, H_b, H_c, and H_d on ***trans*-G** shifted upfield ($\Delta\delta = -0.44$, -0.61, -0.88, and -0.23 ppm, respectively). The extensive changes of chemical shifts of ***trans*-G** result from the formation of a threaded structure **P6⊃*trans*-G**, in which the guest protons are located within the cavity of **P6** and shielded by the electron-rich cyclic structure. Moreover, these peaks became broad owing to complexation dynamics.[9a] In addition, protons H_1 and H_2 on **P6** also exhibited slight chemical shift changes ($\Delta\delta$ = 0.048 and 0.034 ppm, respectively). These phenomena provided convincing proof for the formation of a [2]pseudorotaxane between **P6** and ***trans*-G**.

A 2D NOESY NMR experiment was employed to study the relative positions of the components in **P6⊃*trans*-G** (Fig. 2). NOE correlation signals were observed between proton H_a of **G** and protons H_1, H_2, H_3, and H_4 of **P6** (Fig. 2, A, B, C, and D), between proton H_b of **G** and protons H_2, H_3, H_4, and H_5 of **P6** (Fig. 2, E, G, H, and F), and between proton H_d of **G** and proton H_1 of **P6** (Fig. 2, I), indicating that ***trans*-G** threaded into the cavity of **P6**. These confirmed the above-mentioned ^{1}H NMR results.

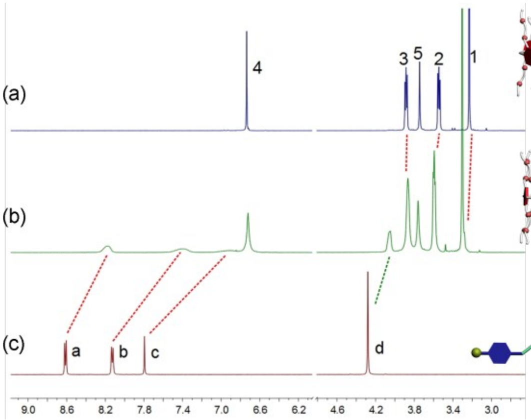


Fig. 1 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, room temperature): (a) **P6** (5.00 mM); (b) 5.00 mM ***trans*-G** + 5.00 mM **P6**; (c) ***trans*-G** (5.00 mM).

Single crystals of the complex **P6⊃*trans*-G** with 1:1 stoichiometry suitable for X-ray diffraction analysis were grown by slow diffusion of isopropyl ether into an acetonitrile solution of **P6** and ***trans*-G**. As shown in the crystal structure of **P6⊃*trans*-G**, guest ***trans*-G** threads through the cavity of host **P6** to form an inclusion complex in the solid state, stabilized by hydrogen bonding interactions and C–H•••π interactions (Fig. 3). The inclusion of ***trans*-G** in the cavity of **P6** in the solid state is consistent with the ^{1}H NMR chemical shift changes of the protons on **P6** and ***trans*-G** in solution. Five hydrogen bonds (A, B, C, D, and E) are formed between five pyridinium hydrogen atoms of guest ***trans*-G** and five oxygen atoms on mono(ethylene oxide) substituents of pillar[6]arene **P6**, indicating that guest ***trans*-G** is threaded unsymmetrically into the cavity of host **P6**. The C–H•••π distances, 2.81 and 2.58 Å, were shorter than 3.05 Å, and the C–H•••π angles, 165 ° and 146 ° were larger than 90 °, indicating the existence of the C–H•••π interactions (F and G in Fig. 3).[8d,f]

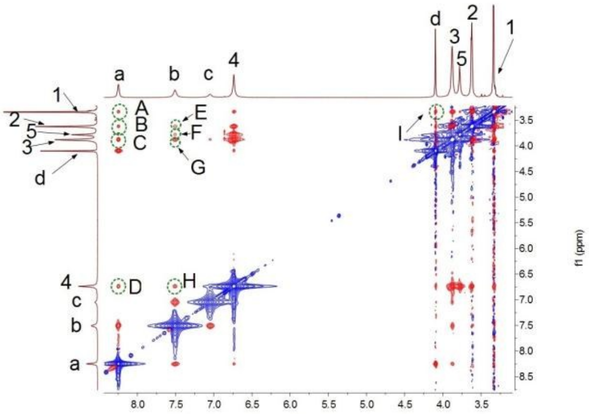


Fig. 2 Partial 2D NOESY spectra (400 MHz, CD_3CN, room temperature) of **P6⊃*trans*-G** (12.5 mM).

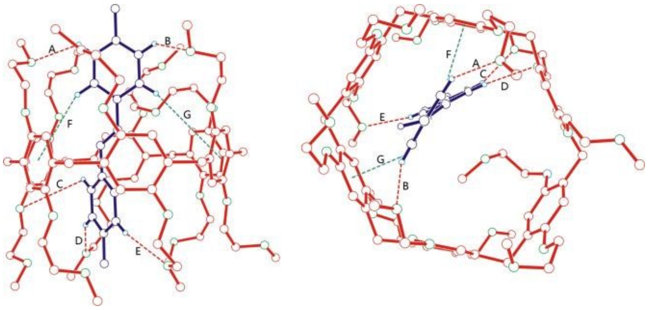


Fig. 3 Ball-stick views of the crystal structure of **P6⊃*trans*-G**. Host **P6** is red, guest ***trans*-G** is blue, hydrogen atoms are sky blue, oxygen atoms are green, and nitrogen atoms are black. PF_6^- counterions, solvent molecules and hydrogens except the ones involved in hydrogen bonding were omitted for clarity. Red dashed lines indicate hydrogen bonds (A, B, C, D, and E) and green dashed lines indicate C–H•••π interactions (F and G). Hydrogen bond parameters are as follows: H–O distance (Å), C–O distance (Å), C–H•••O angles (deg): A, 2.50, 3.35, 148; B, 2.44, 3.33, 156; C, 2.51, 3.18, 128. C–H•••π interactions parameters: C–H•••π distance (Å), C–H•••π angle (deg): F, 2.81, 165; G, 2.58, 146.

Moreover, the formation of the [2]pseudorotaxane based on the recognition of **P6** by guest ***trans*-G** is responsive to UV light due to the photoinduced *trans*–*cis* isomerization of ***trans*-G**. First, the photo-responsive ability of ***trans*-G** was investigated *via* ^{1}H NMR spectroscopy and UV-vis absorption spectroscopy. As shown in Fig. S4, the signals for protons H_a, H_b, H_c, and H_d of ***trans*-G** gradually weakened accompanied by the enhancement of the protons H_{a*}, H_{b*}, H_{c*}, and H_{d*} of ***cis*-G** with irradiation by UV light at 365 nm (Fig. S4, spectra a–d, ESI†), indicating the photoisomerization from the *trans* state to the *cis* state and reaching a photostationary state, which corresponds to a *trans*–*cis* conversion of 65%. Meanwhile, converse results were observed upon irradiation with UV light at 265 nm (Fig S4, spectra d–g, ESI†). The photoinduced *trans*–*cis* isomerization behavior of ***trans*-G** was further investigated by UV-vis absorption spectroscopy. The absorption spectrum of ***trans*-G** exhibited one absorption band at 317 nm, corresponding to the *trans* state absorption of vinylogous viologen derivatives.[13] Upon irradiation with UV light at 365 nm for 2.5 h, the absorption band of ***trans*-G** at 317 nm decreased dramatically, accompanied by enhancement of the band around 235 nm, indicating the photoisomerization from the *trans* state to *cis* state. One isosbestic point was observed at around 270 nm (Fig. S5a, ESI†).[13] Furthermore, upon irradiation with UV light at 265 nm for 6.0 h, converse results were observed (Fig. S5b, ESI†).

Then the photo-responsive self-assembly behavior of the [2]pseudorotaxane based on **P6** and ***trans*-G** was further studied (Fig. 4). After irradiating a solution of **P6⊃*trans*-G** with UV light at 365 nm for 2.5 h, the peaks related to H_a, H_b, H_c, and H_d on ***trans*-G** became weaker and showed slight chemical shift changes and the signals for protons H_{a*}, H_{b*}, H_{c*}, and H_{d*} on free ***cis*-G** were clearly observed (Fig. 4d), suggesting that the host–guest interactions between **P6** and ***trans*-G** were destroyed and there was no complexation between **P6** and ***cis*-G**. The reason is that the size of ***cis*-G** is larger than the cavity of **P6**.[11a] Therefore, upon irradiation with the UV light at 365 nm, the conformation of some ***trans*-G** molecules changed to the *cis* state, and these ***cis*-G** molecules could not thread the cavity of **P6** anymore. Upon further irradiation with the UV light at 265 nm for 6 h, ***cis*-G** went back to ***trans*-G**, and the proton signals related to the mixed solution of **P6** and **G** went back to the original state (Fig. 4f), suggesting that the photo-controllable self-assembly of the [2]pseudorotaxane was achieved.

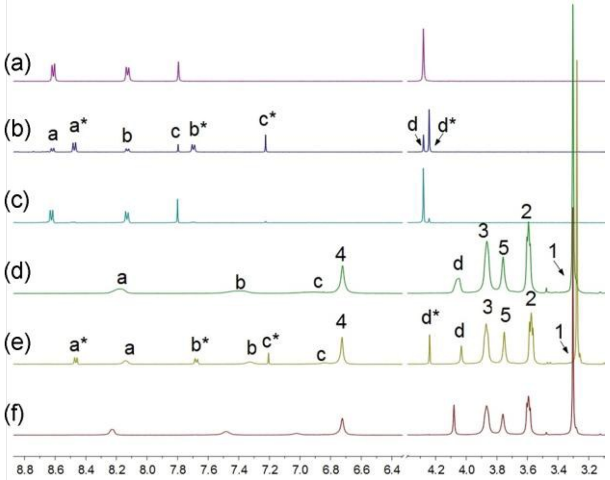


Fig. 4 Partial ^{1}H NMR spectra (400 MHz, CD$_3$CN, room temperature): (a) ***trans*-G** (5.00 mM); (b) ***trans*-G** (5.00 mM) after irradiation with UV light at 365 nm for 2.5 h; (c) ***trans*-G** (5.00 mM) after further irradiation with UV light at 265 nm for 6 h; (d) **P6⊃*trans*-G** (5.00 mM); (e) **P6⊃*trans*-G** (5.00 mM) after irradiation with UV light at 365 nm for 2.5 h; (f) **P6⊃*trans*-G** (5.00 mM) after further irradiation with UV light at 265 nm for 6 h.

In conclusion, we designed and synthesized a [2]pseudorotaxane based on the recognition of a 1,4-bis(methoxyethoxy)-substituted pillar[6]arene **P6** by a vinylogous viologen dications ***trans*-G** in solution and in the solid state. Furthermore it showed reversibly photo-responsive self-assembly ability in acetontrile. This photo-responsive self-assembly can be potentially used to fabricate nanostructures which can be applied in various fields such as functional supramolecular polymers, detection, and nanoreactors.

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† Electronic Supplementary Information (ESI) available: UV-vis spectra, electrospray ionization mass spectrometry, ^{1}H NMR spectra, X-ray crystal data and other materials. See DOI: 10.1039/c0xx00000x.

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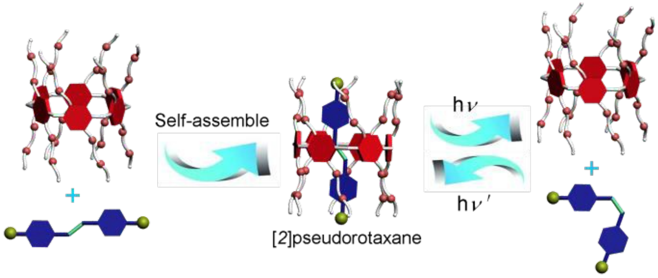
ToC Graphic:



Text:

A pillar[6]arene-based [2]pseudorotaxane was obtained in solution and studied in the solid state and its photo-responsive self-assembly behavior in solution was investigated.