

# [2]Pseudorotaxanes Based on the Recognition of Cryptands to Vinylogous Viologens

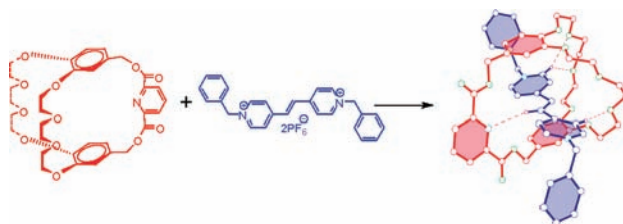
Xuzhou Yan, Peifa Wei, Mingming Zhang, Xiaodong Chi, Jiyong Liu, and Feihe Huang\*

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

fhuang@zju.edu.cn

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## ABSTRACT



Host–guest complexation between two crown ether-based cryptands and two vinylogous viologens has been studied. Formation of [2]-pseudorotaxanes from a dibenzo-24-crown-8-based cryptand and these vinylogous viologens can be reversibly controlled by adding and removing potassium cation in acetone. Furthermore, the complexation between a bis(*m*-phenylene)-32-crown-10-based cryptand and a vinylogous viologen exhibits a high association constant,  $1.18 \times 10^6 \text{ M}^{-1}$  in acetone, and leads to the formation of a supramolecular poly[2]-pseudorotaxane in the solid state.

Threaded structures,<sup>1</sup> such as pseudorotaxanes, rotaxanes and catenanes, have attracted much attention not only because of their topological importance,<sup>2</sup> but also due to their application in the fabrication of artificial molecular machines,<sup>3</sup> functional supramolecular polymers,<sup>4</sup> and so on. As the fundamental building blocks for the preparation of advanced mechanically interlocked supramolecular assemblies with intriguing properties,

pseudorotaxanes, self-assembly structures in which ring components are threaded onto axles, have been widely studied.<sup>5</sup> However, the currently available host–guest recognition motifs which are good for the preparation of threaded structures are still limited.<sup>6,7a,7d</sup> This has impeded the development of research on threaded structures. Therefore, it is of importance to find new host–guest

(1) (a) Badjić, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845–1849. (b) Loeb, S. J. *Chem. Soc. Rev.* **2007**, *36*, 226–235. (c) Serreli, V.; Lee, C. F.; Kay, E. R.; Leigh, D. A. *Nature* **2007**, *445*, 523–527. (d) Zhang, C.; Li, S.; Zhang, J.; Zhu, K.; Li, N.; Huang, F. *Org. Lett.* **2007**, *9*, 5553–5556. (e) Frey, J.; Tock, C.; Collin, J.-P.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **2008**, *130*, 4592–4593.

(2) (a) Collin, J.-P.; Dietrich-Buchecker, C.; Gaviña, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, *34*, 477–487. (b) Wang, L.; Vysotsky, M. O.; Bogdan, A.; Bolte, M.; Böhmer, V. *Science* **2004**, *304*, 1312–1314. (c) Zhu, X.-Z.; Chen, C.-F. *J. Am. Chem. Soc.* **2005**, *127*, 13158–13159. (d) Forgan, R. S.; Sauvage, J.-P.; Stoddart, J. F. *Chem. Rev.* **2011**, *111*, 5434–5464.

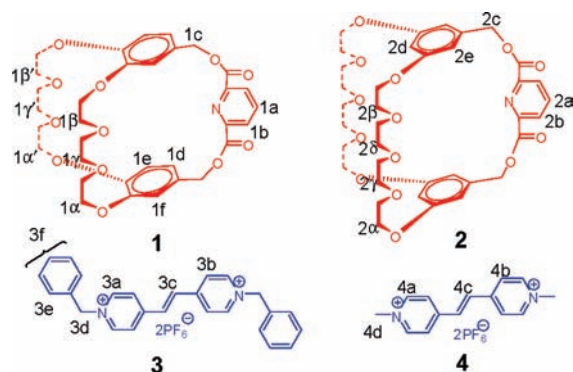
(3) (a) Loeb, S. J. *Chem. Commun.* **2005**, 1511–1518. (b) Wang, W.; Kaifer, A. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 7042–7046. (c) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72–191. (d) Zheng, H.; Zhou, W.; Lv, J.; Yin, X.; Li, Y.; Liu, H.; Li, Y. *Chem.—Eur. J.* **2009**, *15*, 13253–13262. (e) Ma, X.; Tian, H. *Chem. Soc. Rev.* **2010**, *39*, 70–80. (f) Fang, L.; Wang, C.; Fahrenbach, A. C.; Trabolsi, A.; Botros, Y. Y.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1805–1809.

(4) (a) Yamaguchi, N.; Gibson, H. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 143–147. (b) Greef, T. F. A.; Smulders, M. M. J.; Schenning, A. P. H. J.; Sijbesma, R. P.; Meijer, E. W. *Chem. Rev.* **2009**, *109*, 5687–5754. (c) Wang, F.; Zhang, J.; Ding, X.; Dong, S.; Liu, M.; Zheng, B.; Li, S.; Wu, L.; Yu, Y.; Gibson, H. W.; Huang, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 1090–1094. (d) Niu, Z.; Huang, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2011**, *133*, 133–136. (e) Yan, X.; Zhou, M.; Chen, J.; Chi, X.; Dong, S.; Zhang, M.; Ding, X.; Yu, Y.; Shao, S.; Huang, F. *Chem. Commun.* **2011**, *47*, 7086–7088.

(5) (a) Harada, A. *Acc. Chem. Res.* **2001**, *34*, 456–464. (b) Hernandez, J. V.; Kay, E. R.; Leigh, D. A. *Science* **2004**, *306*, 1532–1537. (c) Zhu, K.; Li, S.; Wang, F.; Huang, F. *J. Org. Chem.* **2009**, *74*, 1322–1328. (d) Niu, Z.; Slebodnick, C.; Gibson, H. W. *Org. Lett.* **2011**, *13*, 4616–4619. (e) Zhang, M.; Zheng, B.; Huang, F. *Chem. Commun.* **2011**, *47*, 10103–10105.

(6) (a) Pease, A. R.; Jeppesen, J. O.; Stoddart, J. F.; Luo, Y.; Collier, C. P.; Heath, J. R. *Acc. Chem. Res.* **2001**, *34*, 433–444. (b) Niu, Z.; Gibson, H. W. *Chem. Rev.* **2009**, *109*, 6024–6046. (c) Rieth, S.; Hermann, K.; Wang, B.-Y.; Badjić, J. D. *Chem. Soc. Rev.* **2011**, *40*, 1609–1622. (d) Wang, M.-X. *Acc. Chem. Res.* **2011**, DOI: 10.1021/ar200108c.

recognition motifs, especially the ones which can respond to external stimuli. Cryptands, which have gained a wide range of interests during the past decade in virtue of a significant contribution made by Gibson, Huang, and co-workers, are exceptional hosts for organic salts because of the introduction of additional binding sites and the pre-organization of the host structures during the association process.<sup>4d,7</sup> Paraquat derivatives (*N,N'*-dialkyl-4,4'-bipyridinium salts) are commonly used guests in supramolecular chemistry.<sup>1a,4d,7,8</sup> A series of mechanically interlocked structures and supramolecular polymers have been prepared with high efficiency based on the cryptand/paraquat recognition motif.<sup>4a,7,8</sup> However, as  $\pi$ -extended viologens, vinylogous viologens, which were designed and synthesized to modify and expand the properties and functions of paraquat derivatives (for example, intriguing fluorescent property and photocontrolled isomerization), have been rarely employed as building blocks to construct threaded structures.<sup>9</sup> Therefore, the design and investigation of new recognition motifs based on cryptands and vinylogous viologens will undoubtedly promote not only the development of cryptand host–guest chemistry but also the research on threaded structures. Herein, we report the preparation of [2]pseudorotaxanes based on the recognition of cryptands to vinylogous viologens. It is demonstrated here that the formation of [2]pseudorotaxanes from a dibenzo-24-crown-8 (DB24C8)-based cryptand and vinylogous viologens can be reversibly controlled by addition of  $\text{KPF}_6$  and then dibenzo-18-crown-6 (DB18C6). Moreover, a [2]pseudorotaxane obtained from self-assembly of a bis(*m*-phenylene)-32-crown-10 (BMP32C10)-based cryptand and a vinylogous viologen guest can form a supramolecular poly[2]pseudorotaxane structure in the solid state.



**Figure 1.** Chemical structures of *cis*-dibenzo-24-crown-8-based cryptand **1**, bis(*m*-phenylene)-32-crown-10-based cryptand **2**, and vinylogous viologens **3** and **4**.

(7) (a) Zhu, K.; Wu, L.; Yan, X.; Zheng, B.; Zhang, M.; Huang, F. *Chem.—Eur. J.* **2010**, *16*, 6088–6098. (b) Liu, M.; Yan, X.; Hu, M.; Chen, X.; Zhang, M.; Zheng, B.; Hu, X.; Shao, S.; Huang, F. *Org. Lett.* **2010**, *12*, 2558–2561. (c) Zhang, M.; Zhu, K.; Huang, F. *Chem. Commun.* **2010**, 46, 8131–8141. (d) Niu, Z.; Slebodnick, C.; Bonrad, K.; Huang, F.; Gibson, H. W. *Org. Lett.* **2011**, *13*, 2872–2875. For a correction to this paper, see: (e) *Org. Lett.* **2011**, *13*, 5411.

Equimolar acetone solutions of cryptands **1** and **2** with vinylogous viologens **3** and **4** are yellow because of charge transfer between the electron-rich aromatic rings of the cryptand host and the electron-poor pyridinium rings of the vinylogous viologen guest, a direct evidence for complexation (Figure 1). Job plots<sup>10</sup> (Figure S1, Supporting Information) based on UV–vis spectroscopy absorbance data in acetone demonstrated that all these host–guest complexes were of 1:1 stoichiometry in solution. This was further confirmed by electrospray ionization mass spectrometry. All equimolar mixtures of **1** and **3**, **1** and **4**, **2** and **3**, and **2** and **4** have strong mass fragments of  $[\text{H}\text{D}\text{G} - \text{PF}_6]^+$ :  $m/z$  1148.6 (100%) for  $[\mathbf{1}\text{D}\mathbf{3} - \text{PF}_6]^+$ ,  $m/z$  996.5 (100%) for  $[\mathbf{1}\text{D}\mathbf{4} - \text{PF}_6]^+$ ,  $m/z$  1236.7 (100%) for  $[\mathbf{2}\text{D}\mathbf{3} - \text{PF}_6]^+$ , and  $m/z$  1084.7 (100%) for  $[\mathbf{2}\text{D}\mathbf{4} - \text{PF}_6]^+$ , respectively (Figures S6–S9, Supporting Information). No peaks with other complexation stoichiometries were found.

The association constants ( $K_a$ ) of **1D3**, **1D4**, **2D3**, and **2D4** were determined in acetone by probing the charge-transfer bands of the complexes by UV–vis spectroscopy and employing a titration method (Figures S2–S5, Supporting Information). Treatment of the collected absorbance data with a nonlinear curve-fitting program afforded the corresponding  $K_a$  values:  $3.33 \times 10^4 \text{ M}^{-1}$  for **1D3**,  $5.12 \times 10^5 \text{ M}^{-1}$  for **1D4**,  $5.74 \times 10^5 \text{ M}^{-1}$  for **2D3**, and  $1.18 \times 10^6 \text{ M}^{-1}$  for **2D4**. It is worth noting that these values are comparable to the corresponding cryptand/paraquat host–guest systems ( $10^4$ – $10^6 \text{ M}^{-1}$ )<sup>11</sup> and much higher than the recently reported crown ether/vinylogous viologen complexes ( $10^2 \text{ M}^{-1}$ ),<sup>9c</sup> indicating that the new cryptand/vinylogous viologen recognition motif presented here can be used in the efficient fabrication of complicated threaded structures.

Equimolar (2.00 mM) acetone-*d*<sub>6</sub> solutions of cryptands **1** and **2** with vinylogous viologens **3** and **4** were all examined by proton NMR spectrometry (Figures 2 and S10, Supporting Information). After complexation between **2** and **3**, peaks corresponding to  $\text{H}_{3a}$ ,  $\text{H}_{3b}$ ,  $\text{H}_{3c}$ ,  $\text{H}_{3d}$ , and  $\text{H}_{3e}$  of guest **3** and  $\text{H}_{2c}$ ,  $\text{H}_{2d}$ , and  $\text{H}_{2e}$  of host **2** shifted upfield, while  $\text{H}_{2a}$  and  $\text{H}_{2b}$  of host **2** moved downfield (spectra c–e in Figure 2). Similar chemical shift changes were also observed for the cases of **1D4** and **2D4** (Figure S10, Supporting Information). After **3** was mixed with **2**,

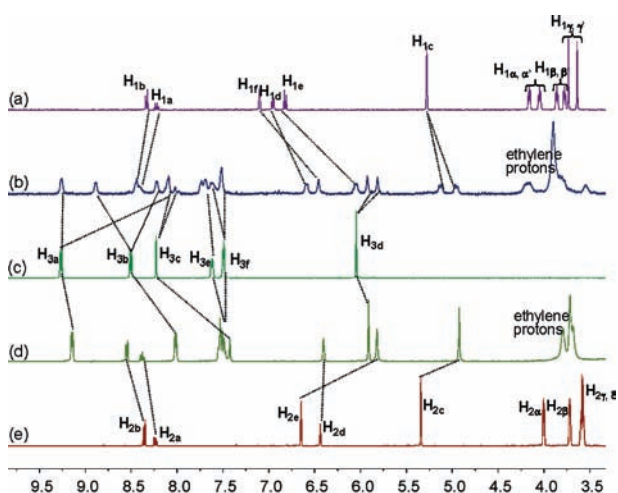
(8) (a) Klivansky, L. M.; Koshkaryana, G.; Cao, D.; Liu, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 4185–4189. (b) Liu, M.; Li, S.; Zhang, M.; Zhou, Q.; Wang, F.; Hu, M.; Fronczek, F. R.; Li, N.; Huang, F. *Org. Biomol. Chem.* **2009**, *7*, 1288–1291. (c) Li, S.; Liu, M.; Zheng, B.; Zhu, K.; Wang, F.; Li, N.; Zhao, X.-L.; Huang, F. *Org. Lett.* **2009**, *11*, 3350–3353. (d) Liu, M.; Li, S.; Hu, M.; Wang, F.; Huang, F. *Org. Lett.* **2010**, *12*, 760–763.

(9) (a) Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Memzer, S.; Pérez-García, L.; Prodi, L.; Stoddart, J. F.; Venturi, M. A.; White, J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11171–11197. (b) Kim, K.; Kim, D.; Lee, J. W.; Ko, Y. H.; Kim, K. *Chem. Commun.* **2004**, 848–849. (c) Yan, X.; Zhang, M.; Wei, P.; Zheng, B.; Chi, X.; Ji, X.; Huang, F. *Chem. Commun.* **2011**, 47, 9840–9842.

(10) Job, P. *Ann. Chim.* **1928**, *9*, 113–203.

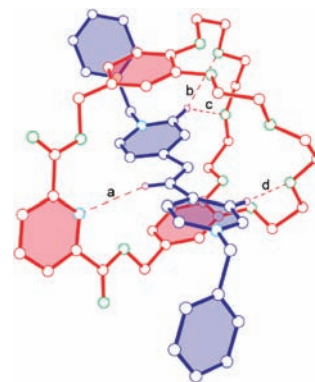
(11) (a) Huang, F.; Switek, K. A.; Zakharov, L. N.; Fronczek, F. R.; Slebodnick, C.; Lam, M.; Golen, J. A.; Bryant, W. S.; Mason, P. E.; Rheingold, A. L.; Ashraf-Khorassani, M.; Gibson, H. W. *J. Org. Chem.* **2005**, *70*, 3231–3241. (b) Zhang, J.; Huang, F.; Li, N.; Wang, H.; Gibson, H. W.; Gantzel, P.; Rheingold, A. L. *J. Org. Chem.* **2007**, *72*, 8935–8938.

the peaks corresponding to its protons did not split, while each of these peaks split into two peaks after it was mixed with **1**. This difference is possibly a result of the combination of the following three factors. First, cryptand **1** has a lower symmetry than cryptand **2**. Second, the threading of guest **3** into the cryptand cavity is asymmetrical as shown by the crystal structure of **1**⊃**3** (Figure 3). Third, the two terminal phenyl rings of **3** become different after the asymmetrical threading of **3** into **1** and the resulted two different terminal phenyl rings have different shielding effects on the protons of **3**.



**Figure 2.** Partial  $^1\text{H}$  NMR spectra (400 MHz, acetone- $d_6$ , 293 K) of (a) 2.00 mM **1**; (b) 2.00 mM **1** + 2.00 mM **3**; (c) 2.00 mM **3**; (d) 2.00 mM **2** + 2.00 mM **3**; (e) 2.00 mM **2**.

In order to further investigate the host–guest complexation between these cryptands and vinylogous viologens, single crystals of **1**⊃**3** suitable for X-ray analysis were grown by vapor diffusion. The crystal structure of the complex between **1** and **3** demonstrates that host **1** and guest **3** form a [2]pseudorotaxane-type threaded structure in the solid state, which is stabilized by hydrogen bonding and face-to-face  $\pi$ -stacking interactions (Figure 3). Four hydrogen bonds (**a**, **b**, **c**, **d**) are formed between three hydrogen atoms of guest **3** and the oxygen and nitrogen atoms on cryptand **1**. Not only two pyridinium hydrogen atoms but also a bridge ethylene hydrogen atom is involved in these hydrogen bonding interactions. The crystals of **1**⊃**3** have a yellow color due to charge-transfer between the electron-rich aromatic rings of **1** and the electron-poor pyridinium rings of **3**. What is more interesting is that guest **3** is threaded asymmetrically into the cavity of host **1**; only one of the two pyridinium rings of **3** is involved in face-to-face  $\pi$ -stacking interactions with the two phenylene rings of **1**. The dihedral angle between the two pyridinium rings of **3** is  $25^\circ$  (Figure 3). This twist presumably results from the maximization of hydrogen bonding interactions between **1** and **3**.

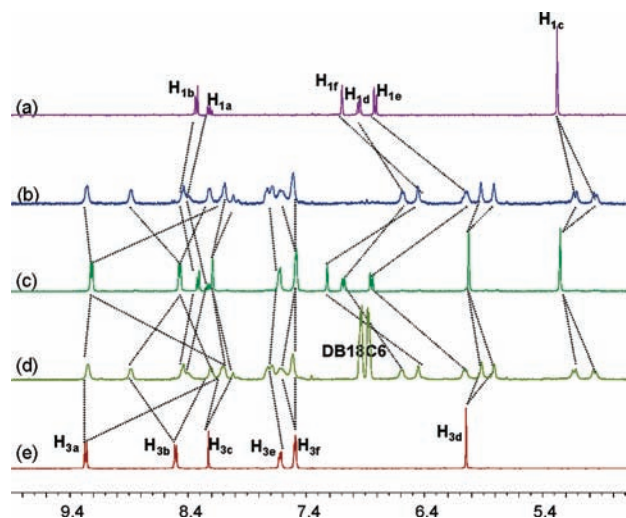


**Figure 3.** Ball-stick views of the X-ray crystal structure of **1**⊃**3**. Host **1** is red, guest **3** is blue, hydrogens are purple, oxygens are green, and nitrogens are sky blue.  $\text{PF}_6^-$  counterions, a solvent molecule and hydrogens except the ones involved in hydrogen bonding between **1** and **3** were omitted for clarity. Hydrogen bond parameters are as follows:  $\text{H}\cdots\text{O}$  (N) distance (Å),  $\text{C}\cdots\text{O}$  (N) distance (Å),  $\text{C}-\text{H}\cdots\text{O}$  (N) angle (deg): a, 2.64, 3.53, 161; b, 2.65, 3.48, 149; c, 2.38, 3.16, 142; d, 2.60, 3.53, 175. The centroid–centroid distance (Å) and dihedral angle (deg) between the two pyridinium rings of **3**: 6.57, 25.

Moreover, the formation of the [2]pseudorotaxanes based on cryptand **1** and vinylogous viologens **3** and **4** can be controlled by adding and removing potassium cation. When  $\text{KPF}_6$  is added, cryptand **1** can form a more stable complex with  $\text{K}^+$ , which can cause the complex between **1** and **3** to disassemble. Subsequently, the complex **1**⊃**3** can form again when enough DB18C6 is added to trap the added  $\text{K}^+$ . This reversible process was confirmed by proton NMR experiments (Figure 4). When  $\text{KPF}_6$  (2.00 equiv) was added to **1** and **3** (each 2.00 mM) in acetone- $d_6$  (0.5 mL), the chemical shifts corresponding to the protons of guest **3** returned to almost their uncomplexed values (Figure 4, c and e). Correspondingly, the color of the solution changed from yellow to colorless, indicating the total dissociation of the **1**⊃**3** complex. However, after addition of DB18C6 (2.00 equiv) to this solution, the complexation between **1** and **3** was recovered; large chemical shift changes and splits of the peaks corresponding to the protons on **3** were observed again (Figure 4, d and e) and accordingly the yellow color of the solution recovered, representing the reformation of the **1**⊃**3** complex.<sup>12</sup> It is noteworthy that the  $K_a$  values of **1**⊃**3** and **1**⊃**4** are  $3.33 \times 10^4$  and  $5.74 \times 10^5 \text{ M}^{-1}$ , respectively. Therefore, we can infer that the realization of the reversible switch of the **1**⊃**4** complex is much more difficult than that of the **1**⊃**3** complex. This was confirmed by proton NMR experiments (Figure S12, Supporting Information). No doubt, this cation-responsive binding of

(12) The chemical shift changes of the protons on the host or guest after complexation could not be fully recovered. Two possible reasons are as follows: (i) the ionic strength of the solution increased, and (ii) different counterions are introduced, influencing ion pairing. These factors could change the chemical shifts and/or decrease the complexation percentage.

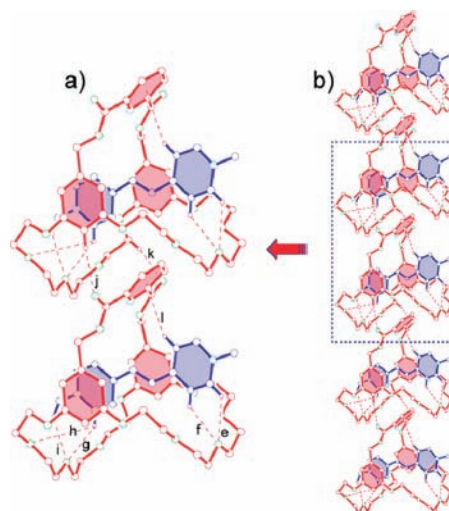
DB24C8 based cryptand **1** to vinyllogous viologens can be used in the construction of controllable molecular shuttles and machines.



**Figure 4.** Partial  $^1\text{H}$  NMR spectra (400 MHz, acetone- $d_6$ , 293 K) of (a) 2.00 mM **1**; (b) 2.00 mM **1** + 2.00 mM **3**; (c) after addition 1.50 mg of  $\text{KPF}_6$  (2.00 equiv) to b; (d) after addition 2.88 mg of **DB18C6** (2.00 equiv) to c; (e) 2.00 mM **3**.

X-ray analysis of a single crystal of the **2**⊃**4** complex showed that **2**⊃**4** forms a supramolecular poly[2]pseudorotaxane structure in the solid state (Figure 5b). The complex is stabilized by hydrogen bonding, face-to-face  $\pi$ -stacking, and aromatic edge-to-face  $\pi$ -stacking interactions. The crystal structure shows that five hydrogen bonds (**e**, **f**, **g**, **h**, and **i**) are formed between the hydrogen atoms on the same side of **4** and oxygen atoms on the cryptand **2**. Two  $\alpha$ -pyridinium hydrogens, one  $\beta$ -pyridinium hydrogen, and one *N*-methyl hydrogen are involved in these hydrogen-bonding interactions. The pyridine nitrogen atom of the cryptand host is not involved in hydrogen-bonding interactions between the host and guest here, in sharp contrast with the case of **1**⊃**3**. However, an aromatic edge-to-face interaction (Figure 5a, **l**) between a pyridinium ring of **4** and the pyridine moiety of cryptand **2** is found in the solid state. Interestingly, two ester carbonyl oxygen atoms of cryptand **2** form two hydrogen bonds (Figure 5a, **j** and **k**) with one aromatic hydrogen and one *O*-methylene hydrogen of the cryptand in the adjacent [2]pseudorotaxane and [2]pseudorotaxanes are arranged linearly to afford a poly[2]pseudorotaxane packing structure in the solid state (Figure 5b).

In summary, we studied the host–guest complexation between two crown ether-based cryptands and two vinyllogous viologens. By self-assembly of DB24C8-based cryptand **1** with vinyllogous viologen **3**, a [2]pseudorotaxane with guest **3** threading into the cryptand cavity asymmetrically formed, which can be switched off and on in a controllable manner by adding  $\text{KPF}_6$  and then **DB18C6**,



**Figure 5.** (a) Ball-stick views of the X-ray crystal structure of **2**⊃**4**. Host **2** is red, guest **4** is blue, hydrogens are purple, oxygens are green, and nitrogens are sky blue.  $\text{PF}_6^-$  counterions, solvent molecules and hydrogens except the ones involved in hydrogen bonding between **2** and **4** were omitted for clarity. Hydrogen bond parameters are as follows: H...O distance (Å), C...O distance (Å) C–H...O angle (deg): e, 2.73, 3.30, 121; f, 2.52, 3.20, 131; g, 2.56, 3.34, 142; h, 2.65, 3.41, 140; i, 2.61, 3.43, 143; j, 2.59, 3.50, 166; k, 2.47, 3.45, 164. The edge-to-face  $\pi$ -stacking interaction **l** is defined by an H...pyridine centroid distance (Å) of 3.00 and a C...centroid distance (Å) of 3.87. (b) Supramolecular poly[2]pseudorotaxane packing structure of **2**⊃**4** in the solid state.

providing a new cation-responsive host–guest pair for constructing stimuli-responsive molecular shuttles and machines. Further studies showed that the reversible switch of the **1**⊃**4** complex is more difficult than that of the **1**⊃**3** complex due to an increase in association constant. Moreover, the complexation between **BMP32C10**-based cryptand **2** and guest **4** exhibits a rather high association constant ( $1.18 \times 10^6 \text{ M}^{-1}$  in acetone) and leads to the formation of a supramolecular poly[2]pseudorotaxane structure in the solid state. Our current efforts are focused on extending this new cryptand/vinyllogous viologen recognition motif to fabricate functional molecular machines and supramolecular polymers.

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**Supporting Information Available.** Job plots, mass spectra, 2D COSY spectrum of **1**⊃**3**, crystal data for **1**⊃**3** and **2**⊃**4**, and other materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.