ORGANIC
LETTERS

2013
Vol. 15, No. 18
4722–4725

Redox-Responsive Complexation between a Pillar[5]arene with Mono(ethylene oxide) Substituents and Paraquat

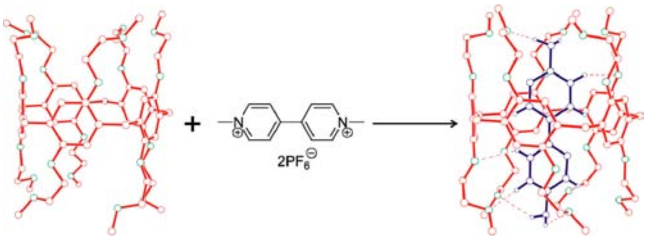
Xiaodong Chi, Min Xue, Yong Yao, and Feihe Huang*

Center for Chemistry of High-Performance and Novel Materials, Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310027, PR China

fhuang@zju.edu.cn

Received July 19, 2013

ABSTRACT



Host−guest complexation between a pillar[5]arene with mono(ethylene oxide) substituents and paraquat was studied. We demonstrated that this pillar[5]arene can form a 1:1 complex with paraquat in solution and in the solid state. The formation of this complex was confirmed by proton NMR spectroscopy, electrospray ionization mass spectrometry, and single crystal X-ray analysis. Furthermore, this complexation can be reversibly controlled through the sequential addition and removal of Zn powder. The host substituent effect on the complexation ability was also addressed.

Stimuli-responsive host−guest complexation has played an important role in the development of supramolecular chemistry and been widely applied in the fabrication of various functional supramolecular systems,[1−4] including molecular switches,[1] molecular machines,[2] and supramolecular polymers.[3] Therefore, the discovery of novel host−guest complexes with responsiveness to external stimuli will certainly accelerate the development of supramolecular chemistry.[5] Paraquat, an important herbicide that has rich electrochemical properties,[6] has been commonly used as the guest component in the preparation of redox-responsive

---

(1) (a) Huang, F.; Switek, K. A.; Gibson, H. W. *Chem. Commun.* **2005**, 3655–3657. (b) Gibson, H. W.; Wang, H.; Slebodnick, C.; Merola, J.; Kassel, W. S.; Rheingold, A. L. *J. Org. Chem.* **2007**, *72*, 3381–3393. (c) Zhang, M.; Zheng, B.; Huang, F. *Chem. Commun.* **2011**, *47*, 10103–10105. (d) Zhang, H.; Zhou, B.; Li, H.; Qu, D.-H.; Tian, H. *J. Org. Chem.* **2013**, *78*, 2091–2098.

(2) (a) Badjić, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845–1849. (b) Liu, Y.; Klivansky, L. M.; Khan, S. I.; Zhang, X. *Org. Lett.* **2007**, *9*, 2577–2580.

(3) (a) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071–4097. (b) Huang, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2004**, *126*, 14738–14739. (c) Huang, F.; Nagvekar, D. S.; Slebodnick, C.; Gibson, H. W. *J. Am. Chem. Soc.* **2005**, *127*, 484–485. (d) 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. (e) Dong, S.; Luo, Y.; Yan, X.; Zheng, B.; Ding, X.; Yu, Y.; Ma, Z.; Zhao, Q.; Huang, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1905–1909. (f) Yan, X.; Xu, D.; Chi, X.; Chen, J.; Dong, S.; Ding, X.; Yu, Y.; Huang, F. *Adv. Mater.* **2012**, *24*, 362–369. (g) Chi, X.; Yan, X.; Chen, J.; Zhang, M.; Hu, B.; Yu, Y.; Huang, F. *Polym. Chem.* **2013**, *4*, 2767–2772.

(4) (a) Klivansky, L. M.; Koshkakaryan, G.; Cao, D.; Liu, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 4185–4189. (b) Davidson, G. J. E.; Sharma, S.; Loeb, S. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 4938–4942. (c) Liu, Y.; Liu, K.; Wang, Z.; Zhang, X. *Chem.—Eur. J.* **2011**, *17*, 9930–9935. (d) Niu, Z.; Huang, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2011**, *133*, 2836–2839. (e) Zhang, M.; Xu, D.; Yan, X.; Chen, J.; Dong, S.; Zheng, B.; Huang, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 7011–7015. (f) Yan, X.; Wang, F.; Zheng, B.; Huang, F. *Chem. Soc. Rev.* **2012**, *41*, 6042–6065. (g) Vukotic, V. N.; Harris, K. J.; Zhu, K.; Schurko, R. W.; Loeb, S. J. *Nat. Chem.* **2012**, *4*, 456–460.

(5) (a) Jiang, W.; Winkler, H. D. F.; Schalley, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 13852–13853. (b) Koshkakaryan, G.; Klivansky, L. M.; Cao, D.; Snauko, M.; Teat, S. J.; Struppe, J. O.; Liu, Y. *J. Am. Chem. Soc.* **2009**, *131*, 2078–2079. (c) Guo, D.-S.; Chen, S.; Qian, H.; Zhang, H.-Q.; Liu, Y. *Chem. Commun.* **2010**, *46*, 2620–2622. (d) Yan, X.; Wei, P.; Zhang, M.; Chi, X.; Liu, J.; Huang, F. *Org. Lett.* **2011**, *13*, 6370–6373. (e) Chen, L.; Tian, Y.; Ding, Y.; Tian, Y.; Wang, F. *Macromolecules* **2012**, *45*, 8412–8419. (f) Tian, Y.; Chen, L.; Tian, X.-Y.; Wang, X.; Wang, F. *Polym. Chem.* **2013**, *4*, 453–457.

(6) Aramendia, M. A.; Borau, V.; Lafont, F.; Marinas, A.; Marinas, J. M.; Moreno, J. M.; Porras, J. M.; Urbano, F. J. *Food Chem.* **2006**, *97*, 181–188.

(7) Zhao, J.-M.; Zong, Q.-S.; Han, T.; Xiang, J.-F.; Chen, C.-F. *J. Org. Chem.* **2008**, *73*, 6800–6806.

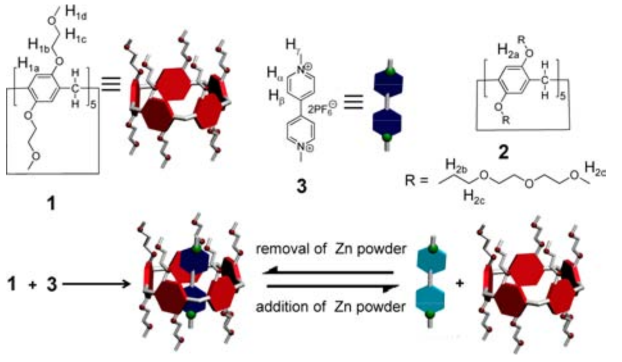
10.1021/ol402048n

supramolecular systems with many kinds of hosts, including crown ethers,[3b,c,7] cyclodextrins,[8] calixarenes,[9] and cucurbiturils.[8a,10]

Pillararenes,[11] a new class of supramolecular host, have become one of the most popular topics in supramolecular chemistry since their first synthesis in 2008.[12] A lot of host–guest complexes have been fabricated on the basis of their recognition to various guests based on their rigid symmetrical pillar structures.[13] The complexation of paraquat dereratives with *per*-hydroxylated pillar[5]arene has been investigated.[11a,c,13b] However, how the host interacts with the guest is still not clear in these host–guest complexes since no host–guest complex crystal structure for such complexation has been reported. Furthermore, although a redox-responsive pillar[6]arene-based inclusion complex with a ferrocenium guest was reported recently,[13e] the redox-responsive property of the pillar[5]arene/paraquat recognition motif has not been explored.

Herein, we investigated the complexation of paraquat **3** with [*n*]ethylene glycol-functionalized ($n = 1, 3$) pillar[5]arenes **1** and **2** (Scheme 1). The crystal structure of the complex between **1** and **3** was reported. It provided the convincing evidence for the formation of a 1:1 pillar[5]arene/paraquat inclusion complex. In order to explore the host substituent effect on the host–guest complexation, the short mono(ethylene oxide) chains and the long tri(ethylene oxide) chains were both introduced to the pillar[5]arene host. Furthermore, the reversible redox-controlled pillar[5]arene/paraquat complexation was realized by addition and removal of Zn powder.

Scheme 1. Chemical Structures of Pillar[5]arene Derivatives **1**–**2** and Paraquat **3** and Cartoon Representation of Redox-Responsive Complexation between Pillar[5]arene **1** and Paraquat **3**



Pillar[5]arenes **1** and **2** were synthesized according to a previously reported procedure.[11q] The chemical structure of **1** was confirmed by single crystal X-ray analysis. Similar to 1,4-dimethoxypillar[5]arene,[11a] the pillar shape is also kept in the crystal structure of pillar[5]arene **1** (Figure 1).

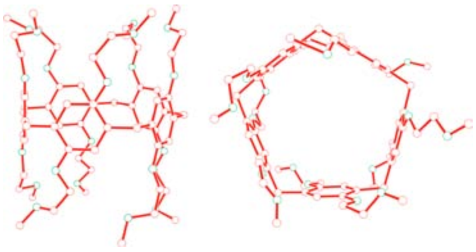


Figure 1. Ball-stick views of the crystal structure of **1**. Hydrogen atoms are omitted for clarity.

When an acetonitrile solution of pillar[5]arene **1** or **2** was mixed with equimolar paraquat **3**, the colorless solution changed to yellow. This is due to the charge transfer between the electron-rich aromatic rings of the pillar[5]arene host and the electron-poor pyridinium rings of the paraquat guest (Scheme 1). The recognition possibilities of **1** and **2** to paraquat **3** were investigated by ^{1}H NMR. The proton NMR spectra of equimolar acetonitrile-d_3

---

(8) (a) Liu, Y.; Li, X.-Y.; Zhang, H.-Y.; Li, C.-J.; Ding, F. *J. Org. Chem.* **2007**, *72*, 3640–3645. (b) Harada, A. *Acc. Chem. Res.* **2001**, *34*, 456–464.

(9) Guo, D.-S.; Wang, L.-H.; Liu, Y. *J. Org. Chem.* **2007**, *72*, 7775–7778.

(10) Liu, Y.; Yu, Y.; Gao, J.; Wang, Z.; Zhang, X. *Angew. Chem., Int. Ed.* **2010**, *49*, 6576–6579.

(11) (a) Ogoshi, T.; Kanai, S.; Fujinami, S.; Yamagishi, T.; Nakamoto, Y. *J. Am. Chem. Soc.* **2008**, *130*, 5022–5023. (b) Cao, D.; Kou, Y.; Liang, J.; Chen, Z.; Wang, L.; Meier, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 9721–9723. (c) Li, C.; Xu, Q.; Li, J.; Yao, F.; Jia, X. *Org. Biomol. Chem.* **2010**, *8*, 1568–1576. (d) Zhang, Z.; Luo, Y.; Xia, B.; Han, C.; Yu, Y.; Chen, X.; Huang, F. *Chem. Commun.* **2011**, *47*, 2417–2419. (e) Si, W.; Chen, L.; Hu, X.-B.; Tang, G.; Chen, Z.; Hou, J.-L.; Li, Z.-T. *Angew. Chem., Int. Ed.* **2011**, *50*, 12564–12568. (f) Li, C.; Chen, S.; Li, J.; Han, K.; Xu, M.; Hu, B.; Yu, Y.; Jia, X. *Chem. Commun.* **2011**, *47*, 11294–11296. (g) Xia, B.; He, J.; Abliz, Z.; Yu, Y.; Huang, F. *Tetrahedron Lett.* **2011**, *52*, 4433–4436. (h) Zhang, Z.; Yu, G.; Han, C.; Liu, J.; Ding, X.; Yu, Y.; Huang, F. *Org. Lett.* **2011**, *13*, 4818–4821. (i) Ma, Y.; Chi, X.; Yan, X.; Liu, J.; Yao, Y.; Chen, W.; Huang, F.; Hou, J.-L. *Org. Lett.* **2012**, *14*, 1532–1535. (j) Holler, M.; Allenbach, N.; Sonet, J.; Nierengarten, J.-F. *Chem. Commun.* **2012**, *48*, 2576–2578. (k) Li, C.; Han, K.; Li, J.; Zhang, H.; Ma, J.; Shu, X.; Chen, Z.; Weng, L.; Jia, X. *Org. Lett.* **2012**, *14*, 42–45. (l) Xue, M.; Yang, Y.; Chi, X.; Zhang, Z.; Huang, F. *Acc. Chem. Res.* **2012**, *45*, 1294–1308. (m) Hu, X.-B.; Chen, Z.; Tang, G.; Hou, J.-L.; Li, Z.-T. *J. Am. Chem. Soc.* **2012**, *134*, 8384–8387. (n) Duan, Q.; Xia, W.; Hu, X.; Ni, M.; Jiang, J.; Lin, C.; Pan, Y.; Wang, L. *Chem. Commun.* **2012**, *48*, 8532–8534. (o) Hu, X.-Y.; Wu, X.; Duan, Q.; Xiao, T.; Lin, C.; Wang, L. *Org. Lett.* **2012**, *14*, 4826–4829. (p) Yao, Y.; Xue, M.; Chen, J.; Zhang, M.; Huang, F. *J. Am. Chem. Soc.* **2012**, *134*, 15712–15715. (q) Ogoshi, T.; Shiga, R.; Yamagishi, T. *J. Am. Chem. Soc.* **2012**, *134*, 4577–4580.

(12) (a) Zhang, Z.; Xia, B.; Han, C.; Yu, Y.; Huang, F. *Org. Lett.* **2010**, *12*, 3285–3287. (b) Han, C.; Ma, F.; Zhang, Z.; Xia, B.; Yu, Y.; Huang, F. *Org. Lett.* **2010**, *12*, 4360–4363. (c) Strutt, N. L.; Forgan, R. S.; Spruell, J. M.; Botros, Y. Y.; Stoddart, J. F. *J. Am. Chem. Soc.* **2011**, *133*, 5668–5671. (d) Zhang, Z.; Luo, Y.; Chen, J.; Dong, S.; Yu, Y.; Ma, Z.; Huang, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1397–1401. (e) Hu, X.-Y.; Zhang, P.; Wu, X.; Xia, W.; Xiao, T.; Jiang, J.; Lin, C.; Wang, L. *Polym. Chem.* **2012**, *3*, 3060–3063. (f) Guan, Y.; Ni, M.; Hu, X.; Xiao, T.; Xiong, S.; Lin, C.; Wang, L. *Chem. Commun.* **2012**, *48*, 8529–8531. (g) Zhang, Z.; Han, C.; Yu, G.; Huang, F. *Chem. Sci.* **2012**, *3*, 3026–3031. (h) Yu, G.; Zhou, X.; Zhang, Z.; Han, C.; Mao, Z.; Gao, C.; Huang, F. *J. Am. Chem. Soc.* **2012**, *134*, 19489–19497. (i) Li, H.; Chen, D.-X.; Sun, Y.-L.; Zheng, Y.; Tan, L.-L.; Weiss, P. S.; Yang, Y.-W. *J. Am. Chem. Soc.* **2013**, *135*, 1570–1576. (j) Sonawane, M.; Jacobs, J.; Thomas, J.; Meervelt, L. V.; Dehaen, W. *Chem. Commun.* **2013**, *49*, 6310–6312.

(13) (a) Hu, X.-B.; Chen, L.; Si, W.; Yu, Y.; Hou, J.-L. *Chem. Commun.* **2010**, *46*, 9016–9018. (b) Ogoshi, T.; Yamafuji, D.; Aoki, T.; Yamagishi, T. *J. Org. Chem.* **2011**, *76*, 9497–9503. (c) Shu, X.; Chen, S.; Li, J.; Chen, Z.; Weng, L.; Jia, X.; Li, C. *Chem. Commun.* **2012**, *48*, 2967–2969. (d) Fan, J.; Deng, H.; Li, J.; Jia, X.; Li, C. *Chem. Commun.* **2013**, *49*, 6343–6345. (e) Xia, W.; Hu, X.; Chen, Y.; Lin, C.; Wang, L. *Chem. Commun.* **2013**, *49*, 5085–5087. (f) Li, C.; Ma, J.; Zhao, L.; Zhang, Y.; Yu, Y.; Shu, X.; Li, J.; Jia, X. *Chem. Commun.* **2013**, *49*, 1924–1926.

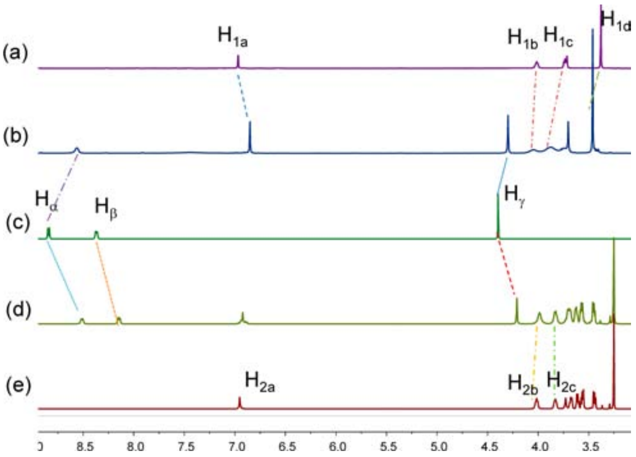


Figure 2. Partial ^1H NMR spectra (400 MHz, CD_3CN, 293 K): (a) 1.00 mM **1**; (b) 2.00 mM **1** + 2.00 mM **3**; (c) 2.00 mM **3**; (d) 2.00 mM **2** + 2.00 mM **3**; (e) 1.00 mM **2**.

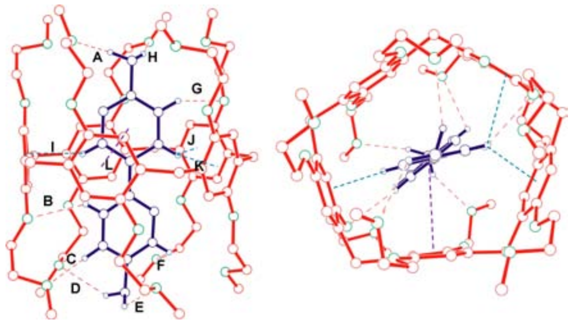


Figure 3. Ball-stick views of the crystal structure of **1**$\supset$**3**. Host **1** is red, guest **3** is blue, hydrogen atoms are sky blue, oxygen atoms are green, and nitrogen atoms are black. PF_6^- counterions, solvent molecules and hydrogens except the ones involved in hydrogen bonding were omitted for clarity. Red dashed lines indicate hydrogen bonds (**A**, **B**, **C**, **D**, **E**, **F**, **G**, and **H**) and blue dashed lines indicate C—H$\cdots\pi$ interactions (**I**, **J**, and **K**). Hydrogen bond parameters are as follows: C$\cdots$O distance (Å), H$\cdots$O distance (Å), C—H$\cdots$O angles (deg): **A**, 3.12, 2.40, 129.7; **B**, 3,35, 2.57, 139.8; **C**, 3.29, 2.41, 154.4; **D**, 3.32, 2.54, 136.7; **E**, 3.23, 2.64, 119.2; **F**, 3.17, 2.71, 111.1; **G**, 3.24, 2.50, 134.9; **H**, 3.36, 2.44, 156.9. C—H$\cdots\pi$ interactions parameters: C—H$\cdots\pi$ distance (Å), C—H$\cdots\pi$ angle (deg): **I**, 2.39, 155.7; **J**, 2.50, 129.30; **K**, 3.01, 111.1. Face-to-face π-stacking parameters: centroid−centroid distance (Å): **L**, 4.00; ring plane−ring plane inclination (deg): 8.75.

solutions of hosts **1** and **2** with guest **3** are shown in Figure 2; only one set of peaks was found for the solution of **1** or **2** with **3**, indicating fast-exchange complexation on the proton NMR time scale. After the complexation of **1** and **3**, peaks corresponding to H_{1a} of host **1** and H_α and H_γ of guest **3** shifted upfield, while the ethyleneoxy protons of host **1** moved downfield (Figure 2a−c). Similar chemical shift changes were also observed for the complexation between **2** and **3** (Figure 2c−e). What are more interesting are the significant differences among these two sets of NMR spectra. First, two peaks corresponding to pyridinium protons H_α and H_β of guest **3** shifted upfield upon the complexation of **2** with **3** (Figure 2c−e), while for the complexation between **1** and **3**, one signal of **3** (H_α) moved upfield and the other (H_β) disappeared. It may result from the different shielding effects by the short mono(ethylene oxide) chains of **1** and the long tri(ethylene oxide) chains of **2**. Second, one peak corresponding to methoxy protons (H_{1d}) of **1** shifted downfield, while for the complexation between **2** and **3**, one signal of **2** (H_{2d}) had no chemical shift change, indicating that **3** was located in the center of the electron-rich cavity of pillar[5]arene **1**. The 2D NOESY spectrum (Figure S6, Supporting Information) of an acetonitrile solution of equimolar **1** and **3** showed the correlation between the signal of protons H_γ of guest **3** and that of protons H_{1a} of host **1**, which also indicated that paraquat resides in the cavity of **1**. The similar correlations were also found for the complexation between **2** and **3** (Figure S7, Supporting Information).

Further investigation of the complexations of pillar[5]arenes **1** and **2** with paraquat **3** was carried out by isothermal titration calorimetry (ITC), which is a powerful tool for studying the host−guest complexes because it not only gives the complexation association constants (K_a) but also yields their thermodynamic parameters (enthalpy and entropy changes). A 1:1 stoichiometry was established for the complexations between pillar[5]arenes **1** and **2** with paraquat **3** by ITC experiments (Figures S1 and S2, Supporting Information). The association constants (K_a) were determined in acetonitrile to be $(3.35 \pm 0.22) \times 10^4$ M^{-1} for **1**$\supset$**3**, and $(1.79 \pm 0.38) \times 10^3$ M^{-1} for **2**$\supset$**3** (Figures S1 and S2, Supporting Information). The big difference in K_a for these two complexes demonstrated that the substituent groups on hosts have a big effect on the host−guest complexation in solution. The shorter the [*n*]ethylene glycol chain substituents, the higher the association constant. The long [*n*]ethylene glycol chains might hinder the paraquat guest to thread into the cavity of the pillar[5]arene host, leading to the low association constant. Additionally, electrospray ionization mass spectrometry of equimolar mixtures of **1** and **2** with **3** exhibited a peak at m/z = 1519.9, corresponding to $[$**1**$\supset$**3** $- PF_6]^+$, and a peak at m/z = 1349.1, corresponding to $[$**2**$\supset$**3** $- 2PF_6]^{2+}$ (Figures S3 and S4, Supporting Information), which also revealed a 1:1 stoichiometry for the complexations between pillar[5]arenes **1** and **2** and paraquat **3**.

To further study how the host interacts with the guest, a crystal of **1**$\supset$**3** was obtained by slow diffusion of isopropyl ether into an equimolar acetonitrile solution of **1** and **3**. The crystal of **1**$\supset$**3** has a yellow color due to the charge-transfer between the electron-rich aromatic rings of **1** and the electron-poor pyridinium rings of **3**. The crystal structure of **1**$\supset$**3** shows that paraquat threads through the cavity of host **1** to form a 1:1 inclusion complex in the solid state, which is stabilized by C—H$\cdots$O bonding interactions, C—H$\cdots\pi$ interactions and face-to-face π-stacking interactions (Figure 3). The inclusion of guest **3** into the cavity of host **1** in the solid state is in accordance with the above-mentioned significant upfield chemical-shift changes of

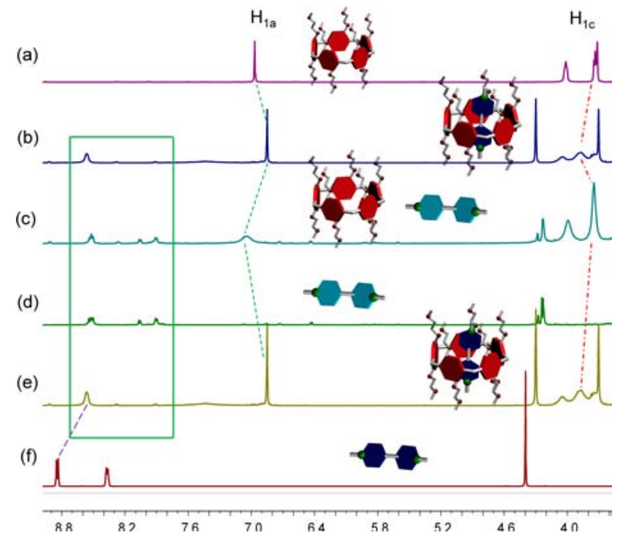


Figure 4. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 293 K): (a) 1.00 mM **1**; (b) 1.00 mM **1** and **3**; (c) after addition of 10.0 equiv of Zn powder to (b); (d) after addition of Zn powder to 1.00 mM **3**; (e) after removal of excess Zn powder from (d) and exposed to air for two hours; (f) 1.00 mM **3**.

protons H_α and the disappearance of protons of H_β in solution. Eight C—H···O hydrogen bonds (**A**–**H**) are formed between eight hydrogen atoms of guest **3** and eight oxygen atoms on mono(ethylene oxide) substituents of pillar[5]arene **1**. The mono(ethylene oxide) substituents play a crucial role in the formation of **1**⊃**3** because pillar[5]arene **1** can engulf the central part of paraquat. Not only four pyridinium hydrogen atoms but also four *N*-methyl hydrogen atoms are involved in these hydrogen bonding interactions. The C—H···π-plane distances of three hydrogen atoms of guest **3** (**I**, **J**, **K**) are 2.39, 2.50, and 3.01 Å, respectively, shorter than 3.05 Å, implying the existence of C—H···π interactions.[12a]

After the confirmation of the interactional mode and the stoichiometry for the complexation between **1** and **3**, redox-responsiveness was studied for this complexation. Previously Zn powder was used to bring about the reduction of paraquat to its radical cationic form.[14] When 10.0 equiv of Zn powder was added into a yellow acetonitrile solution of 1.00 mM **1** and **3**, it became green. Subsequently, the solution color gradually reverted to yellow again after excess Zn powder was removed by filtration and the solution was exposed to air for two hours, suggesting the formation of the complex **1**⊃**3** again (Figure S5, Supporting Information). This reversible process was confirmed by proton NMR experiments (Figure 4). When Zn powder (10.0 equiv) was added to a solution of 1.00 mM **1** and **3** in acetonitrile-d_3, the chemical shift of the phenyl protons of **1** returned to almost their uncomplexed value, indicating that the complexation between **1** and **3** was quenched (Figure 4, spectrum c). However, after removal of excess Zn powder and exposure of this solution to air for two hours, the complexation between **1** and **3** was recovered; chemical shift changes corresponding to the protons on **1** and **3** were observed again (Figure 4, spectrum e). Therefore, the complexation between **1** and **3** can be reversibly controlled by the addition or removal of Zn powder (Scheme 1). This redox-controlled reversible complexation process provides a convenient switch to fabricate novel responsive supramolecular materials.

In summary, we investigated the complexation between two [*n*]ethylene glycol-functionalized pillar[5]arenes and paraquat. It was found that these pillar[5]arenes can form 1:1 complexes with paraquat both in solution and in the solid state. The crystal structure of **1**⊃**3** gave convincing evidence for the formation of a [2]pseudorotaxane. The long [*n*]ethylene glycol chain substituents led to the low association constant. More importantly, we demonstrated that this host–guest complexation could be switched off by adding Zn powder. This redox-responsive host–guest binding property is a novel feature of the host–guest chemistry of pillar[5]arenes. It is therefore believed that these redox-responsive host–guest complexes can be further utilized as the fundamental building blocks to fabricate novel functional supramolecular materials.

Acknowledgment. This work was supported by National Basic Research Program (2013CB834502), the National Natural Science Foundation of China (91027006 and 21125417), and the Fundamental Research Funds for the Central Universities (2012QNA3013).

Supporting Information Available. Determination of stoichiometries, ESI-MS, ITC data, X-ray crystallographic files (CIF) for **1** and **1**⊃**3**, and other materials. This material is available free of charge via the Internet at http://pubs.acs.org.

---

[14] (a) Endo, T.; Ageishi, K.; Okawara, M. *J. Org. Chem.* **1986**, *59*, 4309–4310. (b) Fahrenbach, A. C.; Barnes, J. C.; Lanfranchi, D. A.; Li, H.; Coskun, A.; Gassensmith, J. J.; Liu, Z.; Benítez, D.; Trabolsi, A.; Goddard, W. A., III; Elhabiri, M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 3061–3072.

The authors declare no competing financial interest.