RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSCAdvances

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

COMMUNICATION

Chemical-responsive complexation between a pillar[10]arene with mono(ethylene oxide) substituents and a 2,7-diazapyrenium salt †

Xiaodong Chi and Min Xue*

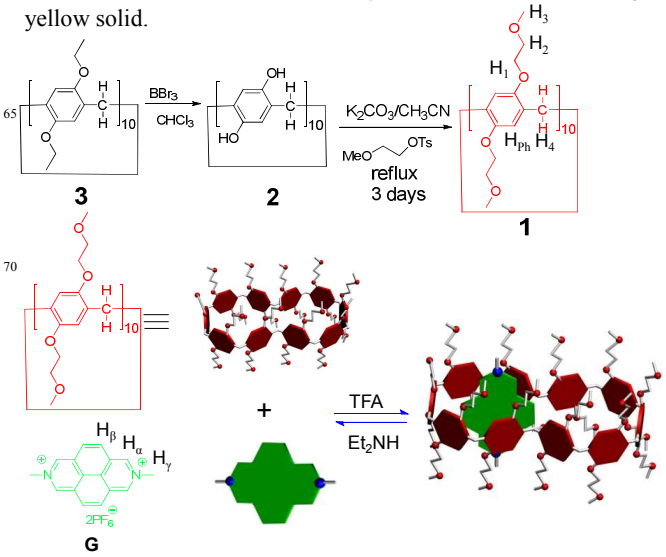
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/c0xx00000x

A pillar[10]arene with mono(ethylene oxide) substituents was synthesized and its chemical-responsive complexation with a 2,7-diazapyrenium salt was investigated.

Of the great majority of stimuli (mechanical force,[1] electrochemical,[2] photo[3] and heat[4]) which can push the development of molecular machines,[5] supramolecular polymers,[6] or other supramolecular systems,[7] chemical stimulus has gained particular attention because of its accessibility and instant action. Therefore, plenty of chemical-responsive host–guest systems based on macrocyclic compounds (such as crown ethers,[8] cyclodextrins,[9] calixarenes[10] and cucurbiturils[11]) have been constructed and intensively studied. Pillar[*n*]arenes, as a new class of supramolecular hosts, have attracted more attention since their first synthesis in 2008.[12] Thanks to their excellent host–guest binding properties with different guests, supramolecular polymers,[12d,13] functional vesicles,[14] and other interesting supramolecular systems[15] have been studied to explore the application in different areas with fascinating properties. However, limited by the cavity size, most investigations on host–guest chemistry and self-assembly of pillar[*n*]arenes have been based on pillar[5]arenes and pillar[6]arenes. These studies were restricted to a certain extent, therefore, the preparation of advanced pillar[*n*]arenes ($n \geqslant 7$) with excellent host–guest binding properties plays a significant role in the evolution of pillar[*n*]arenes.[16]

On the other hand, 2,7-diazapyrenium (DAP) derivatives, which combine the features of pyrene, viologens, and nucleic acid intercalators, have been proved to be attractive building blocks in supramolecular chemistry.[3b,17] With the excellent π-electron-deficient and luminescence properties, DAP derivatives have been incorporated in a variety of supramolecular systems and widely used as fluorescence probes for the detection of ions[18] and neurotransmitters,[19] both of which are important substances in life processes. However, up to now, inclusion complexes and self-assembled structures from DAP derivatives and pillar[*n*]arenes have never been reported, possibly because of the smaller cavity sizes of pillar[5,6]arenes to allow the DAP derivatives to thread into the cavity. Therefore, the design and investigation of new recognition motifs based on pillararenes and DAP derivatives will undoubtedly promote not only the development of pillararene supramolecular chemistry but also research on DAP-based host–guest chemistry. Herein, we report the synthesis of a novel pillar[10]arene with mono(ethylene oxide) substituents **1** and its application in host–guest chemistry with dimethyldiazapyrenium (DMDAP, **G**) dication. Furthermore, the disassembly and assembly of the inclusion complex between pillar[10]arene **1** and DMDAP can be reversibly controlled by the sequential addition of Et_2NH and TFA, respectively.

Compound **G** was synthesized according to a previously reported procedure.[17a] Pillar[10]arene **1** was synthesized by introducing mono(ethylene oxide) groups on both rims of the macrocycle (Scheme S1). *per*-Hydroxylated pillar[10]arene **2** was obtained by dealkylation of **3**.[20] After stirring a mixture of *per*-hydroxylated pillar[10]arene **2** and excess 2-methoxyethyl *p*-toluenesulfonate at reflux for 3 days, **1** was obtained as a light yellow solid.

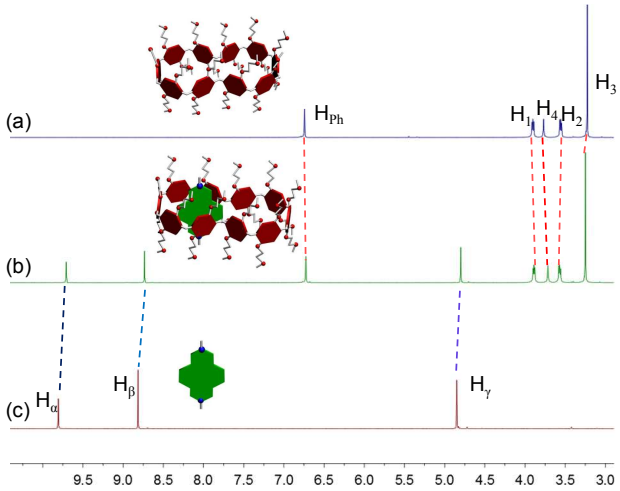


Scheme 1 Synthetic route to pillar[10]arene derivatives **1** and the chemical structure of dimethyldiazapyrenium dication **G** and cartoon representation of chemical-responsive complexation between **1** and **G**.

Due to the existence of twenty mono(ethylene oxide) groups on both rims, pillar[10]arene **1** is expected to be an excellent host for π-electron-deficient guest molecules.[15h,15i] When equimolar **G**

was added to an acetonitrile solution of 1.00 mM pillar[10]arene **1**, the color of the solution turned to yellow immediately, suggesting the charge transfer between the electron-rich aromatic rings of the pillar[10]arene host and the π-electron-deficient rings of the DMDAP guest, giving a direct evidence for host–guest complexation (Scheme 1).

The complexation between **G** and **1** was firstly studied by ^{1}H NMR spectroscopy. The proton NMR spectrum of an equivmolar acetonitrile-d_3 solution of 1.00 mM host **1** and guest **G** is shown in Fig. 1 (spectrum b); only one set of peaks is found, indicating fast-exchange complexation on the proton NMR time scale. Peaks corresponding to H_2 and H_3 of host **1** shifted downfield by 0.01 ppm and 0.03 ppm, respectively, while H_1, H_{ph} and H_4 of host **1** and H_α, H_β and H_γ of guest **G** shifted upfield by 0.02 ppm, 0.04 ppm, 0.11 ppm, 0.10 ppm and 0.04 ppm, respectively (Fig. 1). All these chemical shift changes indicated that the complexation of **1** with **G** took place in solution.



Further evidence for the complexation between host **1** and guest **G** was obtained from UV-vis absorption spectroscopy. When **1** and **G** were mixed at a 1:1 molar ratio, the spectrum exhibited a broad absorption above 450 nm, which corresponded to the characteristic absorption of the charge-transfer complex between electron-rich **1** and electron-deficient **G** (Fig. S7, ESI†).

Fig. 1 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 293 K) of: (a) **1** (1.00 mM); (b) **1** (1.00 mM) and **G** (1.00 mM); (c) **G** (1.00 mM).

2D NOESY is a useful tool to study the relative positions of the components in host–guest inclusion complexes. The 2D NOESY spectrum (Fig. S9) of a mixture of **1** and **2** with a 1:1 molar ratio shows correlations A–F between the signals of the protons of **G** and those of protons of **1**. A, B and C represent the correlations between the signal of protons H_α of **G** and those of protons H_3, H_2 and H_1 on the mono(ethylene oxide) groups of **1**. D, E and F represent the correlations between the signal of protons H_β of **G** and those of protons H_3, H_2 and H_1 on the mono(ethylene oxide) groups of **1**. All of these correlations supported that DMDAP **G** threaded into the cavity of **1** to form an inclusion complex.

The stoichiometry of the complex between pillar[10]arene **1** and DMDAP **G** was determined to be 1:1 in solution by a mole ratio plot based on the fluorescence titration experiments (Fig. S5, ESI†). Additionally, Electrospray ionization mass spectrometry (ESI-MS) also confirmed this stoichiometry. A relevant peak was found for **1**⊃**G**: m/z = 1521.5, corresponding to $[\mathbf{1}\supset\mathbf{G} - 2PF_6]^{2+}$ (Fig. S8, ESI†). The association constant (K_a) was determined in acetonitrile by using a fluorescence titration method to be 2.5 (± 0.2) × 10^3 M^{-1}.

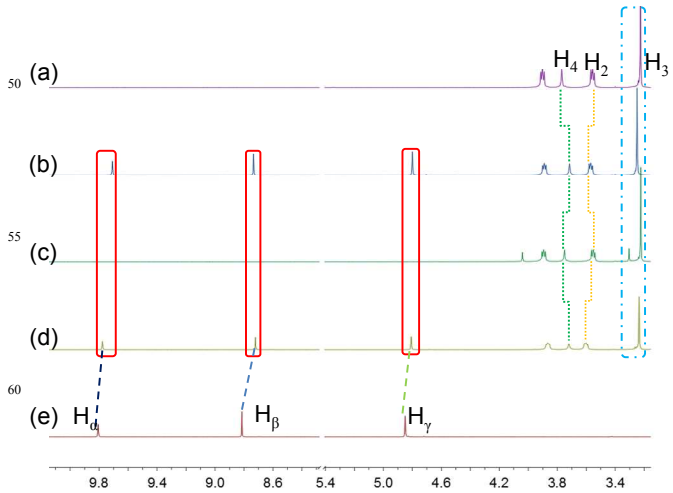


Fig. 2 Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 293 K) of: (a) 1.00 mM **1**; (b) 1.00 mM **1** and **G**; (c) after addition of 10.0 equiv. of DEA to (b); (d) after addition of 10.0 equiv. of TFA to (c); (e) 1.00 mM **G**.

What is more interesting is that the assembly and disassembly of the inclusion complex between pillar[10]arene **1** and DMDAP **G** can be reversibly controlled by the sequential addition of diethylamine (DEA) and trifluoroacetic acid (TFA). When 10.0 equiv. of DEA was added into a yellow acetonitrile solution of 1.00 mM **1** and **G**, it became dark green (Fig. S10, ESI†), because the more stable adduct between **G** and DEA was formed while the complex **1**⊃**G** was dissociated.[17c] Subsequently, the complex **1**⊃**G** could form again when enough TFA was added to neutralize DEA. At the same time, the dark green solution gradually reverted to yellow (Fig. S10, ESI†). This reversible process was confirmed by proton NMR experiments (Fig. 2). When DEA (10.0 equiv.) was added to a solution of **1** (1.00 mM) and **G** (1.00 mM) in acetonitrile-d_3, the intensity of the aromatic signals of **G** disappeared substantially and the protons of **1** almost returned to their uncomplexed values (Fig. 2c). However, after addition of TFA (10.0 equiv.) to this solution, the complexation between **1** and **G** was recovered; most chemical shift changes corresponding to the protons of **1** and **G** were observed again (Fig. 3d). This chemical-controlled reversible complexation process provides a convenient switch to fabricate novel responsive supramolecular materials.

In summary, we reported the synthesis of a novel pillar[10]arene with mono(ethylene oxide) substituents and investigation of its host–guest complexation with DMDAP. Moreover, we demonstrated that the assembly and disassembly of the inclusion complex between pillar[10]arene **1** and DMDAP **G** can be reversibly controlled by the sequential addition of diethylamine and trifluoroacetic acid. This chemical-responsive host–guest binding property is a novel feature about the host–guest chemistry of

pillar[10]arenes. Furthermore, these derived supramolecular systems will have easily detected fluorescence output, making it convenient to monitor their chemical-controlled operation. Moreover, owing to the robust interactions between DAP derivatives and nucleic acids or nucleotides, this new chemical-responsive host–guest recognition motif would have potential applications in the biological field.

We acknowledge the National Natural Science Foundation of China (31002701) and the China Postdoctoral Science Foundation (2013M541767).

Notes and references

Center for Chemistry of High-Performance and Novel Materials, Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China., Fax: +86-571-8795-3189; Tel: +86-571-8795-3189; E-mail: xuemin@zju.edu.cn

† Electronic Supplementary Information (ESI) available: [Synthetic procedures, characterizations.]. See DOI: 10.1039/c0xx00000x.

1 W. Chen and J. Du, *Sci. Rep.*, 2013, **3**, 2162−2171.

2 (*a*) V. Bermudez, N. Capron, T. Gase, F. G. Gatti, F. Kajzar, D. A. Leigh, F. Zerbetto and S. Zhang, *Nature*, 2000, **406**, 608–611; (*b*) X. Ma, R. Sun, W. Li and H. Tian, *Polym. Chem.*, 2011, **2**, 1068−1070; (*c*) A. Feng, Q. Yan, H. L. Peng and J. Yuan, *Chem. Commun.*, 2014, DOI: 10.1039/C4CC00463A.

3 (*a*) X. Ma and H. Tian, *Chem. Soc. Rev*. 2010, **39**, 70–80; (*b*) M. Liu, X. Yan, M. Hu, X. Chen, M. Zhang, B. Zheng, X. Hu, S. Shao and F. Huang, *Org. Lett.*, 2010, **12**, 2588–2561; (*b*) J.-F. Xu, Y.-Z. Chen, D. Wu, L.-Z. Wu, C.-H. Tung and Q. –Z. Yang, *Angew. Chem., Int. Ed.*, 2013, **52**, 9738–9742; (*c*) D. Xia, G. Yu, J. Li and F. Huang, *Chem. Commun.*, 2014, DOI: 10.1039/C3CC49686D.

4 Z. Ge, J. Hu, F. Huang and S. Liu, *Angew. Chem., Int. Ed.*, 2009, **48**, 1798–1802.

5 J. D. Badjić, V. Balzani, A. Credi, S. Silvi and J. F. Stoddart, *Science*, 2004, **303**, 1845–1849.

6 (*a*) F. Huang, F. R. Fronczek and H. W. Gibson, *J. Am. Chem. Soc.*, 2003, **125**, 9272–9273; (*b*) F. Huang and H. W. Gibson, *J. Am. Chem. Soc.*, 2004, **126**, 14738–14739; (*c*) F. Huang, D. S. Nagvekar, C. Slebodnick and H. W. Gibson, *J. Am. Chem. Soc*., 2005, **127**, 484–485; (*d*) F. Wang, C. Han, C. He, Q. Zhou, J. Zhang, C. Wang, N. Li and F. Huang, *J. Am. Chem. Soc.*, 2008, **130**, 11254-11255; (*e*) F. Wang, J. Zhang, X. Ding, S. Dong, M. Liu, B. Zheng, S. Li, K. Zhu, L. Wu, Y. Yu, H. W. Gibson and F. Huang, *Angew. Chem., Int. Ed.*, 2010, **49**, 1090–1094; (*f*) S. Li, J. Chen, B. Zheng, S. Dong, Z. Ma, H. W. Gibson and F. Huang, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 4067-4073; (*g*) Z. Niu, F. Huang and H. W. Gibson, *J. Am. Chem. Soc.*, 2011, **133**, 2836–2839; (*h*) X. Yan, D. Xu, X. Chi, J. Chen, S. Dong, X. Ding, Y. Yu and F. Huang, *Adv. Mater.*, 2012, **24**, 362–369; (*i*) X. Yan, F. Wang, B. Zheng and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 6042–6065; (*j*) D.-S. Guo and Y. Liu, *Chem. Soc. Rev.*, 2012, **41**, 5907–5921; (*k*) Y. Liu, Z. Wang and X. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 5922–5932; (*l*) E. A. Appel, J. Barrio, X.-J. Loh and O. A. Scherman, *Chem. Soc. Rev*., 2012, **41**, 6195–6214; (*m*) V. N. Vukotic and S. J. Loeb, *Chem. Soc. Rev.*, 2012, **41**, 5896–5906; (*n*) S. –L. Li, T. Xiao, C. Lin and L. Wang, *Chem. Soc. Rev.*, 2012, **41**, 5950–5968; (*o*) X. Chi, X. Yan, J. Chen, M. Zhang, B. Hu, Y. Yu and F. Huang, *Polym. Chem*., 2013, **4**, 2767–2772.

7 B. Jiang, L.-J. Chen, L. Xu, S.-Y. Liu and H.-B. Yang, *Chem. Commun.*, 2013, **49**, 6977-6979.

8 (*a*) C. Zhang, S. Li, J. Zhang, K. Zhu, N. Li and F. Huang, *Org. Lett.*, 2007, **9**, 5553-5556; (*b*) W. Jiang, A. Schäfer, P. C. Mohr and C. A. Schalley, *J. Am. Chem. Soc.*, 2010, **132**, 2309–2320; (*c*) S. Dong, Y. Luo, X. Yan, B. Zheng, X. Ding, Y. Yu, Z. Ma, Q. Zhao and F. Huang, *Angew. Chem., Int. Ed.*, 2011, **50**, 1905–1909; (*d*) X. Yan, M. Zhang, P. Wei, B. Zheng, X. Chi, X. Ji and F. Huang, *Chem. Commun.*, 2011, **47**, 9840–9842; (*e*) L. Chen, Y. Tian, Y. Ding, Y. Tian and Wang, F. *Macromolecules* 2012, **45**, 8412–8419; (*f*) S. Dong, B. Zheng, D. Xu, X. Yan, M. Zhang and F. Huang, *Adv. Mater.*, 2012, **24**, 3191-3195; (*g*) M. Zhang, D. Xu, X. Yan, J. Chen, S. Dong, B. Zheng and F. Huang, *Angew. Chem., Int. Ed.*, 2012, **51**, 7011-7015; (*h*) K. Zhu, V. N. Vukotic and S. J. Loeb, *Angew. Chem., Int. Ed.*, 2012, **51**, 2168–2172.

9 H. Chen, X. Liu, Y. Dou, B. He, L. Liu, Z. Wei, J. Li, C. Wang, C. Mao, J. Zhang and G. Wang, *Biomaterials*, 2013, **34**, 4159–4172.

10 M. Lee, S.-J. Lee and L.-H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 12724−12725.

11 S. Angelos, N. M. Khashab, Y.-W. Yang, A. Trabolsi, H. A. Khatib, J. F. Stoddart and J. I. Zink, *J. Am. Chem. Soc.*, 2009, **131**, 12912–12914.

12 (*a*) Z. Zhang, B. Xia, C. Han, Y. Yu and F. Huang, *Org. Lett.,* 2010, **12**, 3285–3287; (*b*) C. Han, F. Ma, Z. Zhang, B. Xia, Y. Yu and F. Huang, *Org. Lett.,* 2010, **12**, 4360–4363; (*c*) C. Li, L. Zhao, J. Li, X. Ding, S. Chen, Q. Zhang, Y. Yu and X. Jia, *Chem. Commun.*, 2010, **46**, 9016–9018; (*d*) N. L. Strutt, R. S. Forgan, J. M. Spruell, Y. Y. Botros and J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 5668–5671; (*e*) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma and F. Huang, *Angew. Chem., Int. Ed.*, 2011, **50**, 1397–1401; (*f*) X.-Y. Hu, P. Zhang, X. Wu, W. Xia, T. Xiao, J. Jiang, C. Lin and L. Wang, *Polym. Chem.*, 2012, **3**, 3060–3063; (*g*) Y. Guan, M. Ni, X. Hu, T. Xiao, S. Xiong, C. Lin and L. Wang, *Chem. Commun.*, 2012, **48**, 8529–8531; (*h*) Z. Zhang, C. Han, G. Yu and F. Huang, *Chem. Sci.*, 2012, **3**, 3026–3031; (*i*) G. Yu, X. Zhou, Z. Zhang, C. Han, Z. Mao, C. Gao and F. Huang, *J. Am. Chem. Soc.*, 2012, **134**, 19489–19497; (*j*) Shu, S. Chen, J. Li, Z. Chen, L. Weng, X. Jia and C. Li, *Chem. Commun.*, 2012, **48**, 2967–2969; (*k*) C. Li, J. Ma, L. Zhao, Y. Zhang, Y. Yu, X. Shu, J. Li and X. Jia, *Chem. Commun.*, 2013, **49**, 1924–1926; (*l*) Y. Fang, L. Wei, J. Liao, L. Chen, Y. Yang, N. Liu, L. He, S. Zou, W. Feng and L. Yuan, RSC Adv., 2013, 3, 12376-12383; (*m*) Z.-Y. Li, Y. Zhang, C.-W. Zhang, L.-J. Chen, C. Wang, H. Tan, Y. Yu, X. Li and H.-B. Yang, *J. Am. Chem. Soc.*, 2014, DOI: 10.1021/ja413047r; (*n*) R. Manoni, P. Neviani, P. Franchi, E. Mezzina and M. Lucarini, *Eur. J. Org. Chem.*, 2014, **1**,147-151.

13 (*a*) T. Ogoshi, H. Kayama, D. Yamafiji, T. Aoki and T.-a. Yamagishi, *Chem. Sci.*, 2012, **3**, 3221–3226; (*b*) N. L. Strutt, H. Zhang, M. A. Giesener, J. Lei and J. F. Stoddart, *Chem. Commun.*, 2012, **48**, 1647–1649; (*c*) B. Xia, B. Zheng, C. Han, S. Dong, M. Zhang, B. Hu, Y. Yu and F. Huang, *Polym. Chem.*, 2013, **4**, 2019–2024; (d) J.-F. Xu, Y.-Z. Chen, L.-Z. Wu, C.-H. Tung and Q.-Z. Yang, *Org. Lett.,* 2013, **15**, 6148–6151.

14 (*a*) H. Zhang, X. Ma, J. Guo, K. T. Nguyen, Q. Zhang, X.–J. Wang, H. Yan, L. Zhu and Y. Zhao, *RSC Adv.*, 2013, **3**, 368–371; (*b*) Q. Duan, C. Yu, L. Yan, X. Hu, T. Xiao, C. Lin, Y. Pan and L. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 10542–1054; (*c*) H. Zhang and Y. Zhao, *Chem. Eur. J.*, 2013, **19**, 16862–16879.

15 (*a*) T. Ogoshi, Y. Nishida, T.–a. Yamagishi and Y. Nakamoto, *Macromolecules*, 2010, **43**, 3145–3147; (*b*) X.-B. Hu, L. Chen, W. Si, Y. Yu and J.-L. Hou, *Chem. Commun.*, 2010, **46**, 9016–9018; (*c*) L. Liu, D. Cao, Y. Jin, H. Tao, Y. Kou and H. Meier, *Org. Biomol. Chem.*, 2011, **9**, 7007–7010; (*d*) X. Shu, J. Li, X. Wang, W. Chen, X. Jia and C. Li, *Org. Biomol. Chem.*, 2012, **10**, 3393–3397; (*e*) I. Nierengarten, S. Guerra, M. Holler, J.-F. Nierengarten and R. Deschenaux, *Chem. Commun.*, 2012, **48**, 8072–8074; (*f*) X.-B. Hu, Z. Chen, G. Tang, J.-L. Hou and Z.-T. Li, *J. Am. Chem. Soc.,* 2012, **134**, 8384–8387; (g) H. Li, D.-X. Chen, Y.-L. Sun, Y. Zheng, L.-L. Tan, Paul S. Weiss and Y.-W. Yang, *J. Am. Chem. Soc.*, 2013, **135**, 1570–1576; (*h*) X. Chi, M. Xue, Y. Yao and F. Huang, *Org. Lett.*, 2013, **15**, 4722–4725; (*i*) X. Chi, M. Xue, Y. Ma, X. Yan and F. Huang, *Chem. Commun.*, 2013, **49**, 8175–8177.

16 (*a*) Y. Chen, H. Q. Tao, Y. H. Kou, H. Meier, J. L. Fu and D. R. Cao, *Chin. Chem. Lett.*, 2012, **23**, 509–511; (*b*) X.-B. Hu, Z. Chen, L. Chen, L. Zhang, J.-L. Hou and Z.-T. Li, *Chem. Commun.*, 2012, **48**, 10999–11001; (*c*) Z. Li, J. Yang, G. Yu, J. He, Z. Abliz and F. Huang, *Chem. Commun.*, 2014, **50**, 2841–2843.

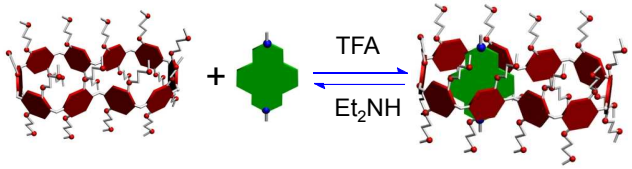
17 (*a*) A. J. Blacker, J. Jazwinski and J. M. Lehn, *Helv. Chim. Acta*., 1987, **70**, 1–11; (b) M. A. Cejas and F. M. Raymo, *Langmuir*, 2005, **21**, 5795–5802; (*c*) X. Yan, X. Wu, P. Wei, M. Zhang and F. Huang, *Chem. Commun.*, 2012, **48**, 8201–8203; (d) J.-F. Xu, Y.-Z. Chen, L. -Z. Wu, C.-H. Tung and Q.-Z. Yang, *Org. Lett.,* 2014, **16**, 684–687.

18 C.-F. Lin, Y.-H. Liu, C.-C. Lai, S.-M. Peng, S.-H. Chiu, *Chem. Eur. J.*, 2006, **12**, 4594–4599.

19 V. Sindelar, M. A. Cejas, F. M. Raymo, W. Chen, S. E. Parker, A. E. Kaifer, *Chem. Eur. J.*, 2005, **11**, 7054–7059.

20 J. Yang, X. Chi, Z. Li, G. Yu, J. He, Z. Abliz, N. Li and F. Huang, *Org. Chem. Front.*, 2014,**1**, 630–633.

Colour Graphic:



Text:

A novel pillar[10]arene with twenty mono(ethylene oxide) substitutents was synthesized and its chemical-responsive binding to a 2,7-diazapyrenium salt was studied.