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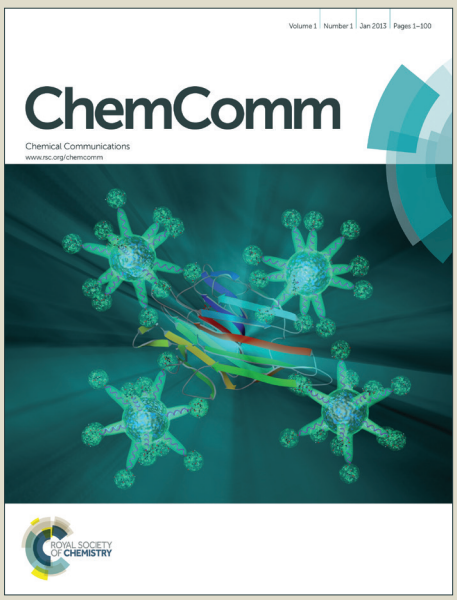

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Pilllar[5]arene and Crown Ether Fused Bicyclic Host, Synthesis, Guest Discrimination and Simultaneous Binding of Two Guests with Different Shape, Size and Electronic Constitution

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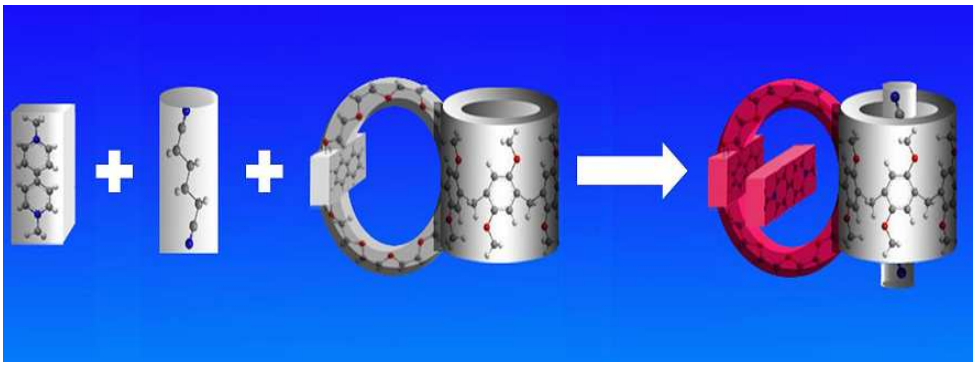

Pillar[5]arene- and crown ether-based bicyclic host molecule binds two guest species selectively by its two independent cyclic host subunits

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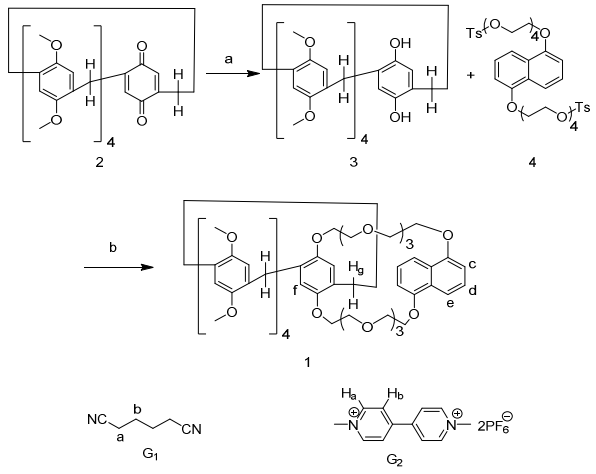
A bicyclic host molecule 1 consisting of a pillar[5]arene and a 1,5-dioxynaphthalene-based crown ether unit has been synthesized, and the two cyclic subunits in 1 were found to recognize two different guest molecules (1,4-dicyanobutane and paraquat) selectively or taking up the two guest molecules simultaneously.

The fabrication of elegant supramolecular systems through host-guest interactions is one of the research focuses in supramolecular chemistry.[1] Synthetic macrocycles, such as crown ethers,[2] cyclodextrins,[3] calixarenes,[4] cucurbiturils,[5] and cyclophanenes,[6] are commonly used host components in the construction of such supramolecular systems. In these systems, each of these macrocyclic receptors possesses specific modes of noncovalent interactions (ion-dipole, hydrogen bonding, charge-transfer, π-π stacking and van der Waals force) toward guests of suitable shape, size and electronic constitution. Pillararenes,[7] added to the list of macrocyclic hosts in 2008, have drawn considerable attention from supramolecular chemists. The two open ended tubular cavities, as well as the regularly positioned alkoxy functionalities in the tubular ends, have afforded pillararenes outstanding ability in molecular recognitions and in the construction of supramolecular systems. Examples include selective binding of different guests,[8] formation of supramolecular polymers,[9] synthesis of mechanically interlocked molecules,[10] construction of artificial transmembrane channels,[11] and stimuli-responding materials.[12]

By utilizing selective guest binding ability of different macrocyclic host molecules, a number of complex supramolecular architectures, such as heterorotaxanes[13] and twin-axial heterorotaxane,[14] have been assembled via multiple host-guest interactions. Macrocyclic receptors bearing multiple binding sites for recognition of different neutral guests and ion pairs have also been reported.[15] However, most of the current studied macrocyclic host molecules are capable of binding only guests of similar shape, size, and electronic constitution. The integration of two macrocyclic host moieties of different shape, size and mode of noncovalent binding toward substrate into one single host molecule, which could potentially be used to: 1) recognize one kind of guest species discriminatively over others by a specific macrocyclic domain of the host molecule, 2) bind two guest molecules of different shape, size and electronic constitution simultaneously, 3) assemble elegant topological novel structures, remains less exploited,[16] which may be due to the difficulty of integrating structures which are different in molecular geometry, rigidity and mode of host-guest interaction into one host molecule in an appropriate arrangement. The tubular shaped pillararenes and flexible crown ethers are two different kinds of macrocyclic host molecules and recognize guest species *via* different modes of supramolecular interactions. We envisioned that the easy functionalization of pillararenes and crown ethers would provide an opportunity to integrate them into a single host molecule with two independent guest binding pockets with different functionalized surfaces. In such a bicyclic host molecule, the pillararene and crown ether host units recognize guest molecules of different shapes, sizes and electronic constitutions selectively *via* different modes of supramolecular interactions, taking up two different guest species simultaneously. Previously, Huang and coworkers used pillar[5]arene and crown ether to construct a dynamic [1]catenane with pH-responsiveness.[17] Ogoshi and coworkers synthesized a pillar[5]arene-based planar chiral pseudo[1]catenane involving two macrocyclic units which showed chiral inversion upon addition of achiral guest and solvents.[18] Herein, we report our results on the synthesis of a novel bicyclic host molecule **1** by integration of a pillar[5]arene subunit and a crown ether subunit into a single molecule and the use of **1** in host-guest interactions. In the molecular structure of **1**, one 1,4-hydroquinone unit of the pillar[5]arene scaffold acts as a functional surface of the crown ether ring (Scheme 1). The pillar[5]arene binding pocket of **1** was found to form a host-guest complex with 1,4-dicyanobutane $\mathbf{G_1}$, similar to the results of pillar[5]arene obtained by Li and coworkers,[19] while crown ether cavity in **1** was found to selectively interact with paraquat (MV^{2+}) $\mathbf{G_2}$, a commonly used guest molecule for crown ethers,[20] which previously was also reported to interact with the π-electron rich cavity of pillar[5]arenes,[9c-d,12,21] but not the case in **1**. Additionally, the simultaneous complexation of the two different guest species ($\mathbf{G_1}$ and $\mathbf{G_2}$) by the bicyclic host **1** was achieved both in solution and in the solid state.

The synthetic route for the host structure **1** is shown in Scheme 1. Benzoquinone-derived pillar[5]arene **2** and the corresponding dihydroxylated pillar[5]arene **3** were obtained by following Ogoshi's procedures.[22] The bicyclic host **1** was obtained by the reaction of dihydroxylated pillar[5]arene **3** with bistosylated 1,5-dioxynaphthalene-based ethylene glycol **4** in a reasonable yield. The

structure of **1** was characterized by ^{1}H, ^{13}C NMR and MS spectroscopies (ESI†).



Scheme 1 Synthesis of the Bicyclic Host **1**. $\mathbf{G_1}$ and $\mathbf{G_2}$ are Guest Species.

Due to the size effect of the naphthalene unit, the naphthalene-based ethylene glycol chain in **1** cannot be self-included into the pillar[5]arene tubular cavity to form a pseudo[1]catenane *via* rotation of the 1,4-hydroquinone units, as the one reported by Ogoshi.[18] Thus, the two topologically different macrocyclic host units (pillar[5]arene and crown ether) in **1** can act as two independent binding pockets to interact selectively with guest molecules which are different in shape, size and electronic constitution.

The host-guest interaction between **1** and 1,4-dicyanobutane $\mathbf{G_1}$ was examined in $CDCl_3$. As shown in Fig. 1, upon mixing **1** and $\mathbf{G_1}$ in 1:1 and 1:2 molar ratios in $CDCl_3$, large upfield shifts ($\Delta\delta$ = -2.77 and -3.30 ppm for H_a and H_b, respectively) in ^{1}H NMR of $\mathbf{G_1}$ caused by the strong shielding effect of the tubular cyclophane were observed, indicating the formation of a threaded host-guest complex $G_1 \subset 1$. The broadening of the $\mathbf{G_1}$ methylene proton peaks revealed the slow guest exchange on the NMR timescale. A 1:1 stoichiometry between the host and the guest in the complex was confirmed by integration of all the proton peaks.

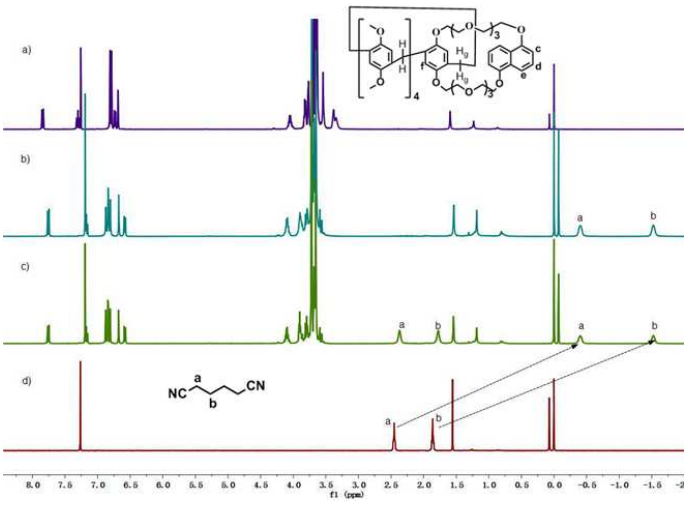


Fig. 1 ^{1}H NMR spectra (400 MHz, $CDCl_3$): a) free **1** (1.0 mM); b) **1** (1.0 mM) + $\mathbf{G_1}$ (1.0 mM); c) **1** (1.0 mM) + $\mathbf{G_1}$ (2.0 mM); d) free $\mathbf{G_1}$ (2.0 mM)

The 2D NOESY data (Fig. S3) showed that the NOE correlations between the entrapped $\mathbf{G_1}$ methylene signals (H_a and H_b) and the pillar[5]arene aromatic protons of **1**, which supported assignment of the threaded structure of the complex. No NOE correlations between the $\mathbf{G_1}$ methylene signals (H_a and H_b) and the protons of crown ether in **1** were observed, indicating no host-guest interaction exists between the crown ether of **1** and $\mathbf{G_1}$. Since no free guest was observed in the 1:1 mixture of **1** and $\mathbf{G_1}$, suggesting very strong binding affinities between the tubular pillar[5]arene cavity of **1** and $\mathbf{G_1}$ in $CDCl_3$. It is thus hard to calculate the binding constant for **G1** in $CDCl_3$. The association constant (K_a) between **1** and $\mathbf{G_1}$ ($\mathbf{G_1} \subset \mathbf{1}$) in $(CD_3)_2CO$ was determined to be (6.1 ± 0.2) x 10^3 M^{-1} (ESI†).

Due to the limited solubility of paraquat ($MV^{2+}\cdot 2PF_6$) $\mathbf{G_2}$ in $CDCl_3$, the host-guest interaction between **1** and $\mathbf{G_2}$ was thus examined in acetone-d_6. Mixing the colorless acetone solutions of **1** and $\mathbf{G_2}$ resulted in a clear red solution immediately, indicating the formation of a charge-transfer complex. The complexation behavior was further explored by ^{1}H NMR spectroscopy in acetone-d_6. Addition of 1.0 equiv of **G2** to a solution of **1** in acetone-d_6 caused the signals of α- and β-pyridinium protons of $\mathbf{G_2}$ to shift upfield by 0.37 and 0.69 ppm, respectively (Fig. 2), indicating the complexation between **1** and $\mathbf{G_2}$ in acetone-d_6. Upon complexation between **1** and $\mathbf{G_2}$, upfield shifts were observed for the signals of the naphthalene protons (H_c, H_d and H_e), protons (H_f) of the hydroquinone unit of the crown ether, and the protons (H_g) of pillar[5]arene bridging methylene groups

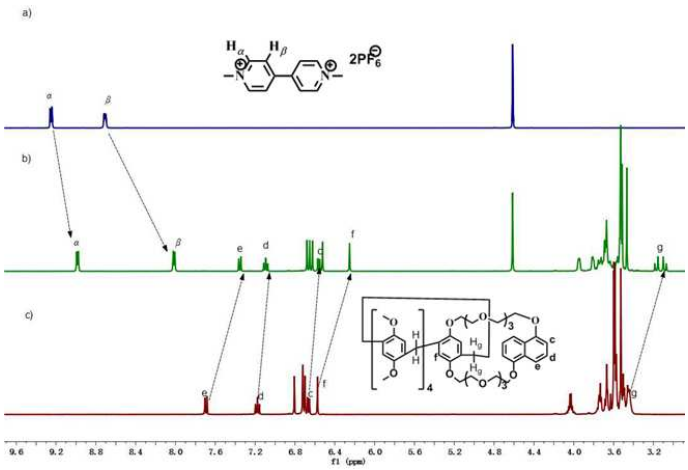


Fig. 2. Partial ^{1}H NMR spectra (400 MHz, acetone-d_6): a) free $\mathbf{G_2}$ (1.0 mM); b) **1** (1.0 mM) + $\mathbf{G_2}$ (1.0 mM); c) free **1** (1.0 mM).

connected to the crown ether hydroquinone unit which possibly resulted from face-to-face π-stacking and charge transfer interactions between the two electron-rich aromatic rings of the crown ether host in **1** and the electron-poor $\mathbf{G_2}$ guest. The splitting of the protons H_g indicated the changes of the magnetic environments of the two methylene protons caused by the rotational restriction of the hydroquinone unit upon formation of a threaded complex $\mathbf{1} \supset \mathbf{G_2}$. 2D ^{1}H NMR NOESY spectrum (Fig. S7) clearly showed the correlations of the signals of α-pyridinium protons (H_a) and N-methyl protons of $\mathbf{G_2}$ with those of the oligo-ethylene glycol protons of **1**, and the correlation between the signals of β-pyridinium protons (H_b) of $\mathbf{G_2}$ and those of the naphthalene protons (H_c, H_d and H_e), as well as those of the crown ether hydroquinone unit of **1**. This result provided strong evidence for the formation of a threaded complex $\mathbf{1} \supset \mathbf{G_2}$. MS (ESI) spectrum of an equimolar mixture of **1** and $\mathbf{G_2}$ exhibited a peak at m/z = 692.35 (Fig. S8), assigned to $[\mathbf{1} \supset \mathbf{G_2} - 2PF_6]^{2+}$, indicating the formation of a complex between **1** and $\mathbf{G_2}$ in a 1:1 stoichiometry. The above data are consistent with the ^{1}H NMR spectrum of a mole

ratio plot of the naphthalene proton H_e in host **1** (Fig. S9a), as well as the mole ratio plot of the *β*-pyridinium protons of $\mathbf{G_2}$ (Fig. S9b). The association constant (K_a) of $\mathbf{1}\supset\mathbf{G_2}$ in acetone-d_6 was determined to be (2.6 ± 0.6) x 10^4 M^{-1} with a ^{1}H NMR titration method (Fig. S11 and Fig. S12).

The simultaneous binding of two guest molecules ($\mathbf{G_1}$ and $\mathbf{G_2}$) by the bicyclic host **1** was examined in acetone-d_6. A clear red solution was immediately formed from mixing equimolar colorless acetone solutions of **1**, $\mathbf{G_1}$ and $\mathbf{G_2}$, indicating the formation of a charge-transfer complex between **1** and $\mathbf{G_2}$. The complexation behavior between host **1** and guests $\mathbf{G_1}$ and $\mathbf{G_2}$ was further studied with ^{1}H NMR spectroscopy in acetone-d_6. ^{1}H NMR spectra of host **1**, guests $\mathbf{G_1}$ and $\mathbf{G_2}$, and an equimolar mixture of **1**, $\mathbf{G_1}$ and $\mathbf{G_2}$ are shown in Fig, 3; large upfield shifts for H_a and H_b ($\Delta\delta$ = -2.68 and -3.29 ppm, respectively, similar to the ^{1}H NMR spectrum of **1** + $\mathbf{G_1}$) of $\mathbf{G_1}$ in the mixture **1**, $\mathbf{G_1}$, and $\mathbf{G_2}$ are consistent with formation of threaded host-guest complex $\mathbf{1}\supset\mathbf{G_1}$ The little change indicated the presence of $\mathbf{G_2}$ did not affect the binding strength between **1** and $\mathbf{G_1}$. The upfield shifts of signals of the α- and β-pyridinium protons of $\mathbf{G_2}$ and those of the naphthalene protons (H_c, H_d and H_e), together with the upfield shift and splitting of signal the protons (H_g) of pillar[5]arene bridging methylene groups connected to the crown ether hydroquinone unit, lead to a conclusion that $\mathbf{G_2}$ complexes with the crown ether unit of supramolecular complex $\mathbf{1}\supset\mathbf{G_1}$. These NMR data provided strong evidence of the formation of a 1:1:1 inclusion host-guest complex between the bicyclic host **1** and guests $\mathbf{G_1}$ and $\mathbf{G_2}$. In this complex, guests $\mathbf{G_1}$ and $\mathbf{G_2}$ thread the pillar[5]arene and crown ether cavities of **1**, respectively. The supramolecular host-guest complex can be expressed as $\mathbf{G_1}\subset\mathbf{1}\supset\mathbf{G_2}$.

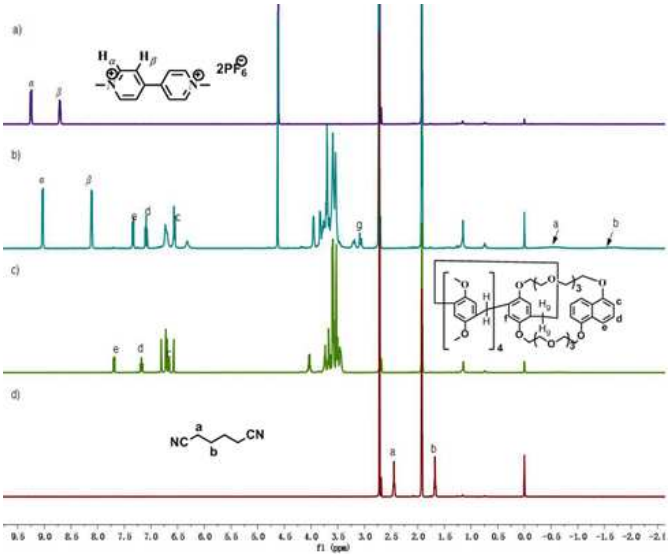


Fig. 3 ^{1}H NMR spectra (400 MHz, acetone-d_6): a) free $\mathbf{G_2}$ (1.0 mM); b) **1** (1.0 mM) + $\mathbf{G_1}$ (1.0 mM) + **G2** (1.0 mM); c) free **1** (1.0 mM); d) free $\mathbf{G_1}$ (1.0 mM).

Further unambiguous evidence of the formation of a 1:1:1 supramolecular complex between the bicyclic host molecule **1** and guests $\mathbf{G_1}$ and $\mathbf{G_2}$ comes from single crystal X-ray diffraction analysis. Deep red single crystals of $\mathbf{G_1}\subset\mathbf{1}\supset\mathbf{G_2}$ complex suitable for X-ray diffraction analysis were obtained by slow diffusion of methanol into an acetone solution of **1**, $\mathbf{G_1}$ and $\mathbf{G_2}$. The crystal structure of $\mathbf{G_1}\subset\mathbf{1}\supset\mathbf{G_2}$ shows that $\mathbf{G_1}$ threads the tubular pillar[5]arene cavity of the bicyclic host of **1**, and $\mathbf{G_2}$ is hosted by the 1,5-dioxynaphthalene-based crown ether motif of **1**, forming an inclusion complex of one host binding two guests which are different in shape, size and electronic constitution in the solid state, as shown in Fig. 4. The host-guest complex was stabilized by multiple supramolecular interactions which include: hydrogen bonding and C-H…π interactions between **1** and $\mathbf{G_1}$,[19] hydrogen bonding, π…π stacking and charge-transfer interactions between **1** and $\mathbf{G_2}$. The solid state structure of the complex is consistent with the structure in the solution as was determined by ^{1}H NMR spectroscopy.

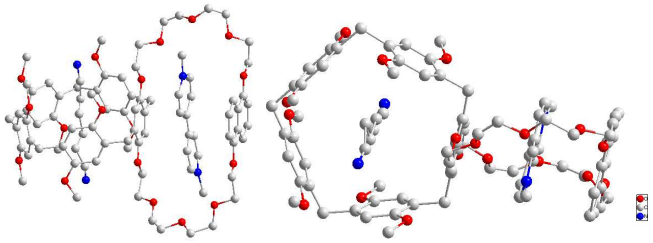


Fig. 4 Single crystal structure of $\mathbf{G_1}\subset\mathbf{1}\supset\mathbf{G_2}$. Hydrogen atoms and PF_6^- counterions are omitted for clarity.

Conclusions

In summary, we have successfully constructed a novel pillar[5]arene- and crown ether-based bicyclic host molecule 1. The selective recognition of $\mathbf{G_1}$ and $\mathbf{G_2}$ by the pillar[5]arene and crown ether motifs, respectively, of **1** is driven by favorable supramolecular interactions between the macrocyclic host motifs and the guests which match the host motifs in shape, size and electronic constitution. The present work could be particularly useful in promoting the development of macrocyclic host molecules possessing multiple binding pockets which are different in shape, cavity size and flexibility. Such systems hold the potential in many applications, such as the construction of complex supramolecular systems, the development of sensors for detection of multiple substrates, and the development of drug delivery systems for the delivery of multiple therapeutic agents in a single formulation.

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Notes and references

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†Electronic supplementary information (ESI) available: Full experimental details and characterization data including copies of ^{1}H NMR and ^{13}C NMR spectra for host **1**, 2D NOESY NMR spectra of **G1⊂1** and **G2⊂1**, ESI-MS of **G2⊂1**, Job plots, determination of the association constants, X-ray crystallographic data of **G1⊂1⊃G2** (CIF).

1 (a) J.-M. Lehn, *Chem. Soc. Rev.*, 2007, **36**, 151-160; (b) A. Coskun, M. Banaszak, R. D. Astumian, J. F. Stoddart and B. A. Grzybowski, *Chem.*

Soc. Rev., 2012, **41**, 19-30; (c) B. Zheng, F. Wang, S. Dong and F. Huang, *Chem. Soc. Rev.,* 2012, **41**, 1621-1636.
2 (a) C. J. Pedersen, *J. Am. Chem. Soc.,*1967, **89**, 7017-7036; (b) C. J. Pedersen, *Angew. Chem., Int. Ed. Engl.,* 1988, **27**, 1021-1027.
3 (a) A. Harada, *Acc. Chem. Res.,* 2001, **34**, 456-464; (b) L. Zhu, D. Zhang, D. Qu, Q. Wang, X. Ma, H. Tian, *Chem. Commun.* 2010, **46**, 2587-2589; (c)K.-R. Wang, D.-S. Guo, B.-P. Jiang, Y. Liu, *Chem. Commun.* 2012, **48**, 3644-3646.
4 (a) C. D. Gutsche, *Calixarenes Revisited*, Royal Society of Chemistry, Cambridge, 2000; (b) C. D. Gutsche, *Calixarenes, An Introduction;* 2nd ed.; Royal Society of Chemistry: Cambridge, 2008.
5 (a) K. Kim, *Chem. Soc. Rev.,* 2002, **31**, 96-107; (b)A. E. Kaifer, W. Li, S. Silvi and V. Sindelar, *Chem. Commun*., 2012, **48**, 6693-6695.
6 (a) F. Diederich, *Cyclophanes*, The Royal Society of Chemistry, Cambridge, 1991; (b) B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.,* 1988, **27**, 1547-1550; (c) J. C. Barnes, M. Juríček, N. L. Strutt, M. Frasconi, S. Sampath, M. A. Giesener, P. L. McGrier, C. J. Bruns, C. L. Stern, A. A. Sarjeant and J. F. Stoddart, *J. Am. Chem. Soc*., 2013, **135**, 183-192; (d) H.-Y. Gong, B. M. Rambo, E. Karnas, V. M. Lynch and J. L. Sessler, *Nat. Chem*. 2010, **2**, 406−409.
7 (a) T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.,* 2008, **130**, 5022-5023; (b) M. Xue, Y. Yang, X. Chi, Z. Zhang and F. Huang, *Acc. Chem. Res.,* 2012, **45**, 1294-1308; (c) P. J. Cragg and K. Sharma, *Chem. Soc. Rev*. 2012, 41, 597-607; (d) T. Ogoshi and T. Yamagishi, *Eur. J. Org. Chem.,* 2013*,* 2961-2975.
8 (a) C. Li, Q. Xu, J. Li, F. Yao and X. Jia, *Org. Biomol. Chem.,* 2010, **8**, 1568-1576; (b) C. Li, L. Zhao, J. Li, X. Ding, S. Chen, Q. Zhang, Y. Yu and X. Jia, *Chem. Commun.,* 2010, **46**, 9016-9018; (c) C. Li, X. Shu, J. Li, S. Chen, K. Han, M. Xu, B. Y. Y Hu and, X. Jia, *J. Org. Chem.,* 2011, **76**, 8458-8465; (d) H. Zhang, N. L. Strutt , R. S. Stoll, H. Li, Z. Zhu and J. F. Stoddart, *Chem. Commun.,* 2011, **47**, 11420-11422; (e) T. Ogoshi, K. Demachi, K. Kitajima and T. Yamagishi, *Chem. Commun.,* 2011, **47**, 7164-7166; (f) Y. Ma, X. Chi, X. Yan, J. Liu, Y. Yao, W. Chen, F. Huang and J.-L. Hou, *Org. Lett.* 2012, **14**, 1532-1535; (g) W. Xia, X.-Y. Hu , Y. Chen, C. Lin and L. Wang, *Chem. Commun.,* 2013, **49**, 5085-5087; (h) J. Fan, H. Deng, J. Li, X. Jia and C. Li, *Chem. Commun.,* 2013, **49**, 6343-6345.
9 (a) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma and F. Huang, *Angew. Chem., Int. Ed.,* 2011, **50**, 1397-1401; (b) T. Ogoshi, H. Kayama, D. Yamafuji, T. Aoki and T. Yamagishi, *Chem. Sci.,* 2012, **3**, 3221-3226; (c) T. Ogoshi, Y. Nishida, T. Yamagishi and Y. Nakamoto, *Macromolecules* 2010, **43**, 3145-3147; (d) T. Ogoshi, Y. Nishida, T. Yamagishi and Y. Nakamoto, *Macromolecules* 2010, **43**, 7068-7072.
10 (a) N. L. Strutt, R. S. Forgan, J. M. Spruell, Y. Y. Botros and J. F. Stoddart, *J. Am. Chem. Soc.,* 2011, **133**, 5668-5671; (b) Z. Zhang, C. Han, G. Yu and F. Huang, *Chem. Sci.,* 2012, **3**, 3026-3031; (c) T. Ogoshi, D. Yamafuji, T. Aoki and T. Yamagishi, *Chem. Commun.,* 2012, **48**, 6842–6844; (d) T. Ogoshi, D. Yamafuji, T. Aoki, K. Kitajima, T. Yamagishi, Y. Hayashi and S. Kawauchi, *Chem. Eur. J.,* 2012, **18**, 7493-7500; (e) T. Ogoshi, T. Aoki, R. Shiga, R. Iizuka, S. Ueda, K. Demachi, D. Yamafuji, H. Kayama and T. Yamagishi, *J. Am. Chem. Soc.,* 2012, **134,** 20322-20325; (f) S. Dong, C. Han, B. Zheng, M. Zhang and F. Huang, *Tetrahedron Lett.,* 2012, **53**, 3668-3671; (g) T. Ogoshi, D. Yamafuji, T. Yamagishia and A. M. Brouwer, *Chem. Commun.,* 2013, **49**, 5468–5470; (h) K. Ke, N. L. Strutt, H. Li, X. Hou, K. J. Hartlieb, P. R. McGonigal, Z. Ma, J. Iehl, C. L. Stern, C. Cheng, Z. Zhu, N. A.Vermeulen, T. J. Meade, Y. Y. Botros and J. F. Stddart, *J. Am. Chem. Soc.,* 2013, **135**, 17019-17030.
11 (a) W. Si, L. Chen, X.-B. Hu, G. Tang, Z. Chen, J.-L. Hou and Z.-T. Li, *Angew. Chem., Int. Ed.,* 2011, **50**, 12564-12568; (b) X.-B. Hu, Z. Chen, G. Tang, J.-L. Hou and Z.-T. Li, *J. Am. Chem. Soc.,* 2012, **134**, 8384-8387; (c) L. Chen, W. Si, L. Zhang, G. Tang, Z.-T. Li and J.-L. Hou, *J. Am. Chem. Soc.,* 2013, **135**, 2152-2155.
12 (a) G. Yu, M. Xue, Z. Zhang, J. Li, C. Han and F. Huang, *J. Am. Chem. Soc.,* 2012, **134**, 13248-13251; (b) H. Li, D.-X. Chen, Y.-L. Sun, Y. B. Zheng, L.-L. Tan, P. S. Weiss and Y.-W.Yang, *J. Am. Chem. Soc.,* 2013, **135**, 1570-1576.
13 (a) P. R. Ashton, P. T. Glink, M.-V. Martinez-Diaz, J. F. Stoddart, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed. Engl.,* 1996**, 35**, 1930-1933; (b) W. Jiang, H. D. F. Winkler and C. A. Schalley, *J. Am. Chem. Soc.,* 2008, **130**, 13852-13853; (c) P.-N. Chen, C.-C. Lai and S.-H. Chiu, *Org. Lett.,* 2011, **13**, 4660-4663; (d) E. Masson, X. Lu, X. Ling and D. L. Patchell, *Org. Lett.,* 2009, **11**, 3798-3801; (e) H.Takahashi, Y. Takashima, H. Yamaguchi and A. Harada, *J. Org. Chem.,* 2006**, 71**, 4878-4883; (f) X. Zhao, X.-K. iang, M. Shi, Y.-H. Yu, W. Xia and Z.-T. Li, *J. Org. Chem.,* 2001, **66**, 7035-7043; (g) M. V. Rekharsky, H. Yamamura, M Kawai, I. Osaka, R. Arakawa, A. Sato, Y. H. Ko, N. Selvapalam, K. Kim and Y. Inoue, *Org. Lett.,* 2006, **8**, 815-818; (h) C. Ke, R. A. Smaldone, T. Kikuchi, H. Li, A. P. Davis and J. F. Stoddart, *Angew. Chem., Int. Ed.,* 2013, **52**, 381-387; (i) W. Jiang and C. A. Challey, *Proc. Natl. Acad. Sci. U.S.A*. 2009, **106**, 10425-10429.
14 Z. J. Zhang, H. Y. Zhang, H. Wang and Y. Liu, *Angew. Chem., Int. Ed.,* 2011, **50**, 10834-10383.
15 (a) H, Sato, K. Tashiro, H. Shinmori, A. Osuka and T. Aida Chem. Commun., 2005, 2324-2326; (b) S. K. Kim and J. L. Sessler, Chem. Soc. Rev., 2010, 39, 3784-3809; (c) A. J. McConnell and P. D. Beer, Angew. Chem., Int. Ed., 2012, 51, 5052-5061.
16 (a) H. Sato, K. Tashiro, H. Shinmori, A. Osuka, Y. Murata, K. Komatsu and T. Aida, *J. Am. Chem. Soc*., 2005**, 127,** 13086-13087; (b) M. Juríček, J. C. Barnes, E. J. Dale, W.-G. Liu, N. L. Strutt, C. J. Bruns, N. A. Vermeulen, K. C. Ghooray, A. A. Sarjeant, C. L. Stern, Y. Y. Botros, W. A. Goddard, III and J. F. Stoddart, *J. Am. Chem. Soc*., 2013**, 135,** 12736-12746.
17 X. Yan, P. Wei, Z. Li, B. Zheng, S.Dong, F. Huang and Q. Zhou, *Chem. Commun.,* 2013, **49**, 2512-2514.
18 T. Ogoshi, T. Akutstu, D. Yamafuji, T. Aoki and T. Yamagishi, *Angew. Chem., Int. Ed.,* 2013, **52**, 8111-8115.
19 X. Shu, S. Chen, J. Li, Z. Chen, L. Weng, X. Jia and C. Li, *Chem. Commun.,* 2012, **48**, 2967-2969.
20 (a) B. L. Allwood, H. Shahriari-Zavareh, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.,* 1987, 1058-1061; (b) B. L. Allwood, N. Spencer, H. Shahriari-Zavareh, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.,* 1987, 1064-1066; (c) F. Huang, H. W. Gibson, W. S. Bryant, D. S. Nagveker and F. R. Fronczek, *J. Am. Chem. Soc.,* 2003, **125,** 9367-9371; (d) H. W. Gibson and D. S. Nagvekar, *Can. J. Chem.,* 1997, **75**, 1375-1384; (e) Q.-S. Zong and C.-F. Chen, *Org. Lett.,* 2006**, 8,** 211-214; (f) F. Wang, B. Zheng, K. Zhu, Q. Zhou, C. Zhai, S. Li, N. Li and F. Huang, *Chem. Commun.,* 2009, 4375-4377.
21 (a) Y. Guan, M. Ni, X. Hu, T. Xiao, S. Xiong, C. Lin and L.Wang, *Chem. Commun.,* 2012, **48**, 8529-8531; (b) N. L. Strutt, H. Zhang, M. A. Giesener, J. Leia and J. F. Stoddart, *Chem. Commun.,* 2012, **48**, 1647-1649; (c) X. Chi, M. Xue,Y. Yao and F. Huang, *Org. Lett.,* 2013, **15**, 4722-4725.
22 T. Ogoshi, D. Yamafuji, D. Kotera, T. Aoki, S. Fujinami and T. Yamagishi, *J. Org. Chem.* 2012, **77**, 11146-11152.

