Self-Assembly

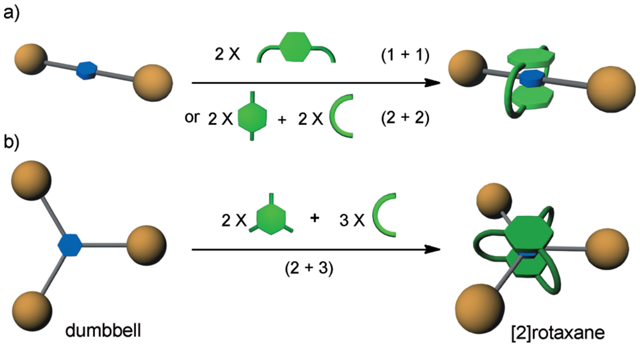
DOI: 10.1002/anie.201207048

Facile Route to an All-Organic, Triply Threaded, Interlocked Structure by Templated Dynamic Clipping**

*Andrew Pun, David A. Hanifi, Gavin Kiel, Evan O'Brien, and Yi Liu**

Dedicated to Professor Sir Fraser Stoddart on the occasion of his 70th birthday

[2]Rotaxanes are a class of mechanically interlocked molecules which are generally depicted by an "axle-in-wheel" model, in which a dumbbell-shaped linear component is threaded through a macrocyclic component (Scheme 1a).[1] Functionalization of the rotaxanes on the linear dumbbell or the macrocycle units provides access to a range of molecular,[2] supramolecular,[3] and polymeric materials[4] with unique architectures and functions, which have found many applications in nanomechanical devices,[5] molecular memories,[6] and reconfigurable nanovalves.[7] Substituting the two-terminal linear geometry with a three-terminal one, such as a triply threaded [2]rotaxane involving a macrobicyclic cage and a trifurcated component (Scheme 1b), produces a new kind of interlocked structure with higher symmetry which can be valuable for building extended arrays or networks at higher dimensions. High-symmetry interlocked structures, such as triply or quadruply interlocked homo[2]catenanes have been constructed using metal–ligand coordination.[8] Meanwhile, little has been done towards a facile and highly efficient synthesis of triply threaded rotaxanes, primarily because of the lack of a C_3-symmetric host/guest system with complementary geometry. Existing macro-bicycles, such as cyclophane-based cryptands,[9] are viable C_3-symmetric hosts and have been an active component in the synthesis of linear [2]rotaxanes and [2]catenanes.[10] The guests involved are, however, by-and-large linear bipyridinium-based electron acceptors. To obtain three-terminal interlocked structures, trifurcated guests having complementary shape and strong binding affinity to these macro-bicycles are necessary.



Scheme 1. Illustrations of a) two-terminal and b) three-terminal [2]rotaxanes synthesized by dynamic clipping.

Among the common synthetic strategies for two-terminal [2]rotaxanes, clipping of a macrocycle around a dumbbell-shaped template is one of the most convenient methods[11] as it minimizes the need for a preformed macrocyclic component, which often demands lengthy synthesis and tedious workup. Furthermore, the clipping reaction can be accomplished with higher yields and product specificity when combined with molecular-recognition-based, noncovalent templating, and reversible dynamic covalent chemistry.[12] Indeed the versatile imine chemistry has been employed for the assembly of novel structures, such as molecular cages,[13] borromean rings,[14] suitanes,[15] catenanes,[16] and rotaxanes.[17] The assembly of triply threaded [2]rotaxanes can be conceived using a similar strategy of clipping a cagelike macro-bicycle around a trifurcated guest. Herein, a series of C_3-symmetric trications were synthesized and tested for their ability to template the formation of symmetry-matching macro-bicycles. Triply threaded structures have been obtained based on one of the tricationic species which templates the (2+3) clipping reaction between simple aldehyde and amine precursors through sixfold imine bond formation. The C_3-symmetric, interlocked structure of the product has been unambiguously characterized by ^{1}H NMR spectroscopy and X-ray structural analysis.

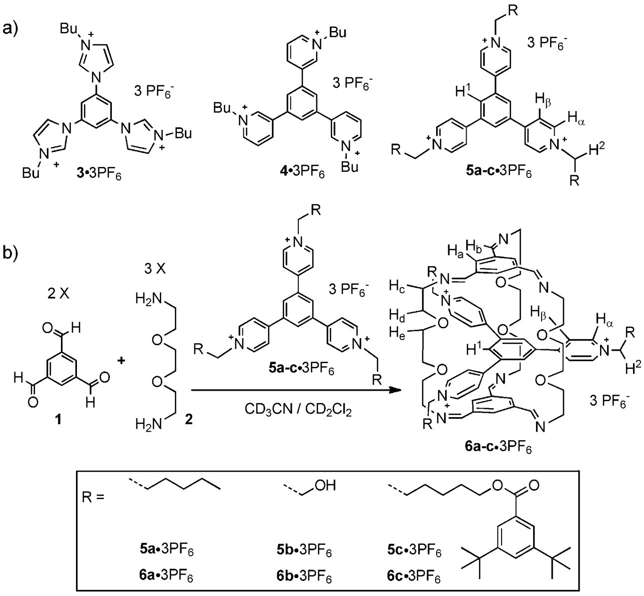
Scheme 2a lists the structures of the three types of tricationic salts, including the trisimidazolium $\mathbf{3}\cdot 3\,\mathrm{PF}_6$, the isostructural tris(*m*-pyridinium) $\mathbf{4}\cdot 3\,\mathrm{PF}_6$, and the tris(*p*-pyridinium) $\mathbf{5a\text{-}c}\cdot 3\,\mathrm{PF}_6$.[18] The clipping reactions were carried out by adding a CD_3CN solution of one trication into a mixture of 1,3,5-benzenetrialdehyde (**1**) and 2,2′-(ethylenedioxy)diethylamine (**2**) in a molar ratio of 1:2:3. ^{1}H NMR spectroscopy indicated that the reaction involving either $\mathbf{3}\cdot 3\,\mathrm{PF}_6$ or $\mathbf{4}\cdot 3\,\mathrm{PF}_6$ gave rise to a new species that corresponded to the triply threaded pseudo[2]rotaxane (see Figures S1 and S2 in the Supporting Information). However the yields were only around 40 % for $\mathbf{3}\cdot 3\,\mathrm{PF}_6$ and 29 % for $\mathbf{4}\cdot 3\,\mathrm{PF}_6$ even when two

---

[*] A. Pun, D. A. Hanifi, G. Kiel, E. O'Brien, Dr. Y. Liu
The Molecular Foundry, Lawrence Berkeley National Laboratory
One Cyclotron Road, MS 67R6110 (USA)
E-mail: yliu@lbl.gov
Homepage: http://foundry.lbl.gov/liugroup/index.html
A. Pun, G. Kiel
Department of Chemistry, University of California, Berkeley
Berkeley, CA 94720 (USA)

[**] This work was performed at the Molecular Foundry, Lawrence Berkeley National Laboratory, supported by the Office of Science, Office of Basic Energy Sciences, Scientific User Facilities Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201207048.



Scheme 2. a) Structures of the three types of trications used for templating. b) The clipping reaction for the formation of triply interlocked molecules **6a–c**·3 PF$_6$.

equivalents of the trications were used. Remarkably, the clipping efficiency was significantly improved when the N-hexyl-substituted salt **5a**·3 PF$_6$ was employed as the template. Figure 1 shows the progressive ^{1}H NMR spectroscopic changes of the clipping reaction (Scheme 2b) involving a CD$_3$CN/CD$_2$Cl$_2$ (1.6 mL, v/v 1:0.6) solution of the trisaldehyde **1**, diamine **2**, and **5a**·3 PF$_6$ in a 2:3:1 ratio. A new set of resonances corresponding to the formation of desired C_3-symmetric pseudorotaxane was observed within 10 minutes (Figure 1a), together with resonances from small but discernible amounts of unreacted precursors. Significant quantities of the unbound guest **5a**$^{3+}$ and free cage were also present in the solution. As the reaction progressed (Figure 1b–d), both the aldehyde and diamine precursors were consumed, and was commensurate with an increased amount of the interlocked species and decreased amount of the unbound guest **5a**$^{3+}$ and the free cage. No further spectroscopic changes were observed after 2 hours, thus resulting in a ratio of 1:0.41:0.22 for **6a**$^{3+}$/**5a**$^{3+}$/**fc** (Figure 1d). A binding constant of $4.2\times10^3\,\mathrm{M}^{-1}$ can be obtained from single-point calculations. Upon addition of 1.1 more equivalent of **5a**$^{3+}$ into the reaction mixture, the equilibrium was further shifted towards nearly complete consumption of the free cage (Figure 1e). Further analysis of the ^{1}H NMR spectrum of the interlocked species **6a**·3 PF$_6$ indicated that the H^1 and H$_\beta$ resonances, together with the H$_a$ and H$_b$ resonances showed significant upfield shifts in comparison to these of unbound **5a**·3 PF$_6$ and the free cage, thus consistent with a mutual shielding effect between the aromatic units. On the contrary, the H$_\alpha$ and H^2 resonances of **6a**·3 PF$_6$ shifted downfield relative to those of unbound **5a**·3 PF$_6$, thus indicating a deshielding environment imposed by the surrounding polyimine aromatic core. All of these observations are consistent with the triply threaded structure of **6a**·3 PF$_6$ having a staggered stacking geometry, in which the pyridinium units stick out through the cavities of the polyetheric macrocycles and partially overlap with the trisimine aromatic cores. The integrity of **6a**·3 PF$_6$ was further confirmed by high-resolution electrospray ionization mass spectrometry (ESI-MS). Intense molecular ions at *m*/*z* 684.8797 and 408.2649 were observed in the ESI-MS of **6a**·3 PF$_6$, thus corresponding to the loss of two and three PF$_6^-$ anions and consistent with the theoretical predictions. In comparison, the mixture of **1** and **2** in the absence of a guest only resulted in a nonspecific mixture.[17b]

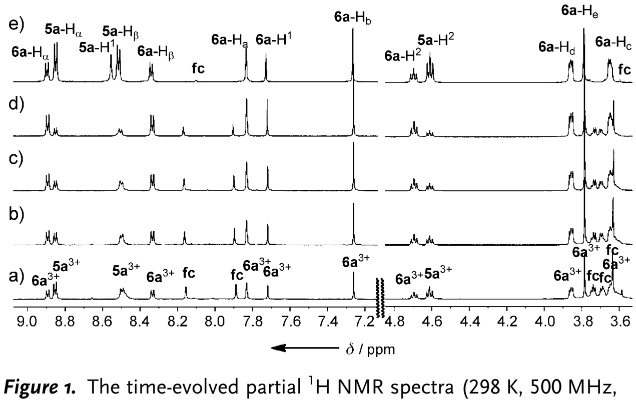


Figure 1. The time-evolved partial ^{1}H NMR spectra (298 K, 500 MHz, CD$_2$Cl$_2$/CD$_3$CN 3:5) of a mixture of **1**, **2**, and **5a**$^{3+}$ in 2:3:1 ratio. a) 10 min, b) 20 min, c) 30 min, d) 2 h, and e) after the addition of 1.1 more equivalent of **5a**·3 PF$_6$. **fc** = free cage molecule.

The coexistence of the triply threaded species, the free cage and the free trispyridinium guest in solution suggests that these compounds are under slow equilibrium. The host–guest complexation could occur through a threading process or the cleavage and reformation of the C=N bonds in the cases of **6a**,**b**·3 PF$_6$. Since threading can be interrupted by steric end groups, it is interesting to see whether the trispyridinium **5c**·3 PF$_6$ having bulky 3,5-di-*tert*-butyl benzoic ester end groups (Scheme 2) would disturb the equilibrium and the corresponding clipping efficiency. The clipping reaction involving **5c**·3 PF$_6$, **1**, and **2** in a 1:2:3 ratio resulted in a similar mixture as that obtained with the nonstoppered **5a**·3 PF$_6$, where the triply threaded [2]rotaxane **6c**·3 PF$_6$ coexisted with free **5c**·3 PF$_6$ and the free cage (see Figure S3a in the Supporting Information). Upon the addition of one more equivalent of **5c**·3 PF$_6$, the free cage decreased to less than 5 %, commensurate with the increasing fraction of the [2]rotaxane **6c**·3 PF$_6$. Since threading can be excluded on account of the bulky end groups, the decrease of free cage fraction and the concomitant formation of [2]rotaxane must follow the pathway of C=N bond cleavage and reformation.

The formation of the triply threaded species was verified by single-crystal X-ray structural analysis.[19] Suitable single crystals in the form of long colorless needles were obtained by diffusing diethyl ether vapor into the reaction mixture containing the N-ethanol derivative **5b**·3 PF$_6$. As expected, the guest is sandwiched within the cavity of the macrobicyclic cage, with the pyridinium arms threading through the three orifices (Figure 2). The six imine groups in the cage are coplanar with the conjugating benzene, thus forming two extended aromatic ring systems that lie nearly parallel with

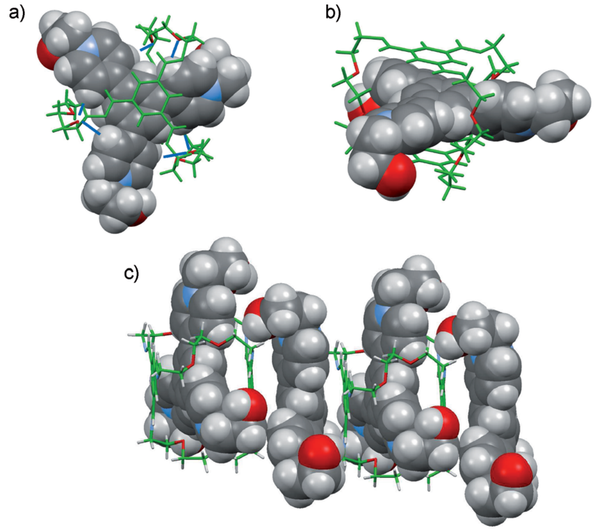


Figure 2. a) Top and b) side view of X-ray structure of **6b**·3 PF_6. c) Elongated π stacking in the 1:2 host–guest complex in the solid state. The cage and the guest pyridimium units are represented in stick and space-filled models, respectively. Solvent molecules and anions are omitted for clarity. The blue dashed lines in (a) indicate [C–H···O] interactions. See the Supporting Information for detailed bond angles and distances of such interactions.

respect to the central benzene ring in the pyridinium unit. The centroid-to-plane distances are 3.50 and 3.55 Å, respectively. The protons on pyridinium units are partially shielded by the trisiminobenzene aromatic cores, which is consistent with their chemical environment derived from solution ^{1}H NMR spectra. Notably, all three pyridinium units of the guest are twisted out of the plane of the central benzene ring. The twisting conforms with the desirable geometric arrangement for multiple [C–H···O] interactions between the oxygen atoms of the oligo(ethylene glycol) units in the cage and the H_β atoms of the three pyridinium units in the guest. In contrast, the more acidic H_α protons are too distant from the oxygen atoms to have meaningful [C–H···O] interactions. Additional [C–H···N] interactions are also indicated by the short contacts between the pyridinium H_β protons and the nitrogen atoms of one of the imine groups on each cap of the cage, which contribute cooperatively to stabilizing the host–guest complex. These structural features also help explain the different templating efficiency among **3**·3 PF_6, **4**·3 PF_6, and **5**·3 PF_6, of which **5**·3 PF_6 has the least steric hindrance in a geometry that maximizes [C–H···O] interactions with the surrounding cage molecule.

Interestingly, an uncomplexed **5b**$^{3+}$ cocrystalizes alongside the triply threaded complex to give extended π-stacking columns with a host/guest ratio of 1:2 (Figure 2c). Compared to the encapsulated **5b**$^{3+}$, the core of the exterior **5b**$^{3+}$ is also nonplanar and twisted; however its centroid is slightly offset from the π-stacking axis. Such a complex in the solid state adds to the collection of rare examples of 1:2 macrocylic host–guest systems[20] and has great potential for further covalent linkage towards catenated structures.

In conclusion, we have presented a convenient one-pot (2+3) clipping method for the assembly of C_3-symmetric interlocked rotaxanes through sixfold imine bond formation using a trispyridinium-based π template. As revealed by solid-state structures, the triply interlocked structure is stabilized by π–π interactions and multiple [C–H···O] and [C–H···N] interactions. Based on this π-template protocol, novel [2]rotaxanes can be prepared by a one-pot reaction using stoppered trispyridinium. Such triply interlocked molecules serve as a complementary entry to the well-received "axle-and-wheel"-type two-terminal [2]rotaxanes. These structures have great potential as useful synthons for further assembly or crosslinking to give higher-order assemblies or polymeric materials. It should be noted that this is a higher symmetry host–guest system built from all organic components, that is, without contributions from the widely used metal–ligand coordination,[21] thus setting a unique path to the design and assembly of mechanically interlocked systems from simple starting materials.

Received: August 31, 2012
Revised: October 22, 2012

Keywords: host-guest systems · rotaxanes · self-assembly · supramolecular chemistry · template synthesis

---

[1] a) H. W. Gibson, M. C. Bheda, P. T. Engen, *Prog. Polym. Sci.* **1994**, *19*, 843–945; b) D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725–2828; c) C. Dietrich-Buchecker, M. C. Jimenez-Molero, V. Sartor, J. P. Sauvage, *Pure Appl. Chem.* **2003**, *75*, 1383–1393; d) C. A. Schalley, T. Weilandt, J. Bruggemann, F. Vogtle, *Top. Curr. Chem.* **2004**, *248*, 141–200; e) F. Arico, J. D. Badjic, S. J. Cantrill, A. H. Flood, K. C. F. Leung, Y. Liu, J. F. Stoddart, *Top. Curr. Chem.* **2005**, *249*, 203–259; f) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem.* **2007**, *119*, 72–196; *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191; g) J. J. Gassensmith, J. M. Baumes, B. D. Smith, *Chem. Commun.* **2009**, 6329–6338.

[2] a) S. A. Vignon, T. Jarrosson, T. Iijima, H. R. Tseng, J. K. M. Sanders, J. F. Stoddart, *J. Am. Chem. Soc.* **2004**, *126*, 9884–9885; b) J. Berná, D. A. Leigh, M. Lubomska, S. M. Mendoza, E. M. Perez, P. Rudolf, G. Teobaldi, F. Zerbetto, *Nat. Mater.* **2005**, *4*, 704–710; c) V. Serreli, C.-F. Lee, E. R. Kay, D. A. Leigh, *Nature* **2007**, *445*, 523–527; d) E. Coronado, P. Gavina, S. Tatay, *Chem. Soc. Rev.* **2009**, *38*, 1674–1689; e) F. Durola, J. Lux, J.-P. Sauvage, *Chem. Eur. J.* **2009**, *15*, 4124–4134; f) S. Silvi, M. Venturi, A. Credi, *J. Mater. Chem.* **2009**, *19*, 2279–2294.

[3] a) K. Kim, *Chem. Soc. Rev.* **2002**, *31*, 96–107; b) V. Sindelar, S. Silvi, A. E. Kaifer, *Chem. Commun.* **2006**, 2185–2187; c) H. Zhang, Q. Wang, M. Liu, X. Ma, H. Tian, *Org. Lett.* **2009**, *11*, 3234–3237; d) Z. Niu, F. Huang, H. W. Gibson, *J. Am. Chem. Soc.* **2011**, *133*, 2836–2839; e) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma, F. Huang, *Angew. Chem.* **2011**, *123*, 1433–1437; *Angew. Chem. Int. Ed.* **2011**, *50*, 1397–1401; f) S. Dong, X. Yan, B. Zheng, J. Chen, X. Ding, Y. Yu, D. Xu, M. Zhang, F. Huang, *Chem. Eur. J.* **2012**, *18*, 4195–4199; g) B. Zheng, F. Wang, S. Dong, F. Huang, *Chem. Soc. Rev.* **2012**, *41*, 1621–1636.

[4] a) P. N. Taylor, M. J. O'Connell, L. A. McNeill, M. J. Hall, R. T. Aplin, H. L. Anderson, *Angew. Chem.* **2000**, *112*, 3598–3602; *Angew. Chem. Int. Ed.* **2000**, *39*, 3456–3460; b) H. W. Gibson, Z. Ge, F. Huang, J. W. Jones, H. Lefebvre, M. J. Vergne, D. M. Hercules, *Macromolecules* **2005**, *38*, 2626–2637; c) G. Wenz, B.-H. Han, A. Müller, *Chem. Rev.* **2006**, *106*, 782–817; d) Y. Jiang, J. Wu, L. He, C. Tu, X. Zhu, Q. Chen, Y. Yao, D. Yan, *Chem. Commun.* **2008**, 6351–6353; e) Q. Li, W. Zhang, O. S. Miljanic,

C.-H. Sue, Y.-L. Zhao, L. Liu, C. B. Knobler, J. F. Stoddart, O. M. Yaghi, *Science* **2009**, *325*, 855 – 859; f) C. Travelet, P. Hebraud, C. Perry, C. Brochon, G. Hadziioannou, A. Lapp, G. Schlatter, *Macromolecules* **2010**, *43*, 1915 – 1921; g) Y. Kohsaka, K. Nakazono, Y. Koyama, S. Asai, T. Takata, *Angew. Chem.* **2011**, *123*, 4974 – 4977; *Angew. Chem. Int. Ed.* **2011**, *50*, 4872 – 4875; h) N. Momčilović, P. G. Clark, A. J. Boydston, R. H. Grubbs, *J. Am. Chem. Soc.* **2011**, *133*, 19087 – 19089; i) A. Coskun, M. Hmadeh, G. Barin, F. Gandara, Q. Li, E. Choi, N. L. Strutt, D. B. Cordes, A. M. Z. Slawin, J. F. Stoddart, J.-P. Sauvage, O. M. Yaghi, *Angew. Chem.* **2012**, *124*, 2202 – 2205; *Angew. Chem. Int. Ed.* **2012**, *51*, 2160 – 2163.

[5] a) Y. Liu, A. H. Flood, P. A. Bonvallett, S. A. Vignon, B. H. Northrop, H. R. Tseng, J. O. Jeppesen, T. J. Huang, B. Brough, M. Baller, S. Magonov, S. D. Solares, W. A. Goddard, C. M. Ho, J. F. Stoddart, *J. Am. Chem. Soc.* **2005**, *127*, 9745 – 9759; b) B. K. Juluri, A. S. Kumar, Y. Liu, T. Ye, Y.-W. Yang, A. H. Flood, L. Fang, J. F. Stoddart, P. S. Weiss, T. J. Huang, *Acs Nano* **2009**, *3*, 291 – 300; c) J. J. Davis, G. A. Orlowski, H. Rahman, P. D. Beer, *Chem. Commun.* **2010**, *46*, 54 – 63.

[6] a) A. R. Pease, J. O. Jeppesen, J. F. Stoddart, Y. Luo, C. P. Collier, J. R. Heath, *Acc. Chem. Res.* **2001**, *34*, 433 – 444; b) A. H. Flood, J. F. Stoddart, D. W. Steuerman, J. R. Heath, *Science* **2004**, *306*, 2055 – 2056; c) J. W. Choi, A. H. Flood, D. W. Steuerman, S. Nygaard, A. B. Braunschweig, N. N. P. Moonen, B. W. Laursen, Y. Luo, E. Deionno, A. J. Peters, J. O. Jeppesen, K. Xu, J. F. Stoddart, J. R. Heath, *Chem. Eur. J.* **2006**, *12*, 261 – 279; d) J. E. Green, J. W. Choi, A. Boukai, Y. Bunimovich, E. Johnston-Halperin, E. Deionno, Y. Luo, B. A. Sheriff, K. Xu, Y. S. Shin, H.-R. Tseng, J. F. Stoddart, J. R. Heath, *Nature* **2007**, *445*, 414 – 417.

[7] a) T. D. Nguyen, H.-R. Tseng, P. C. Celestre, A. H. Flood, Y. Liu, J. F. Stoddart, J. I. Zink, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 10029 – 10034; b) T. D. Nguyen, Y. Liu, S. Saha, K. C. F. Leung, J. F. Stoddart, J. I. Zink, *J. Am. Chem. Soc.* **2007**, *129*, 626 – 634; c) H. Meng, M. Xue, T. Xia, Y.-L. Zhao, F. Tamanoi, J. F. Stoddart, J. I. Zink, A. E. Nel, *J. Am. Chem. Soc.* **2010**, *132*, 12690 – 12697.

[8] a) M. Fujita, N. Fujita, K. Ogura, K. Yamaguchill, *Nature* **1999**, *400*, 52 – 55; b) M. Fukuda, R. Sekiya, R. Kuroda, *Angew. Chem.* **2008**, *120*, 718 – 722; *Angew. Chem. Int. Ed.* **2008**, *47*, 706 – 710; c) A. Westcott, J. Fisher, L. P. Harding, P. Rizkallah, M. J. Hardie, *J. Am. Chem. Soc.* **2008**, *130*, 2950 – 2951; d) J. J. Henkelis, T. K. Ronson, L. P. Harding, M. J. Hardie, *Chem. Commun.* **2011**, *47*, 6560 – 6562.

[9] a) J. M. Lehn, *Science* **1985**, *227*, 849 – 856; b) H. An, J. S. Bradshaw, R. M. Izatt, *Chem. Rev.* **1992**, *92*, 543 – 572.

[10] a) F. Huang, F. R. Fronczek, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, *125*, 9272 – 9273; b) F. Huang, J. W. Jones, C. Slebodnick, H. W. Gibson, *J. Am. Chem. Soc.* **2003**, *125*, 14458 – 14464; c) C.-F. Lin, Y.-H. Liu, C.-C. Lai, S.-M. Peng, S.-H. Chiu, *Chem. Eur. J.* **2006**, *12*, 4594 – 4599; d) Z. Niu, C. Slebodnick, K. Bonrad, F. Huang, H. W. Gibson, *Org. Lett.* **2011**, *13*, 2872 – 2875.

[11] a) P. L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vicent, D. J. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 193 – 218; b) J. Berná, G. Bottari, D. A. Leigh, E. M. Perez, *Pure Appl. Chem.* **2007**, *79*, 39 – 54.

[12] a) S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem.* **2002**, *114*, 938 – 993; *Angew. Chem. Int. Ed.* **2002**, *41*, 898 – 952; b) P. T. Corbett, J. Leclaire, L. Vial, K. R. West, J.-L. Wietor, J. K. M. Sanders, S. Otto, *Chem. Rev.* **2006**, *106*, 3652 – 3711; c) B. H. Northrop, F. Arico, N. Tangchiavang, J. D. Badjic, J. F. Stoddart, *Org. Lett.* **2006**, *8*, 3899 – 3902; d) M. E. Belowich, J. F. Stoddart, *Chem. Soc. Rev.* **2012**, *41*, 2003 – 2024.

[13] a) O. Francesconi, A. Ienco, G. Moneti, C. Nativi, S. Roelens, *Angew. Chem.* **2006**, *118*, 6845 – 6848; *Angew. Chem. Int. Ed.* **2006**, *45*, 6693 – 6696; b) X. Liu, Y. Liu, G. Li, R. Warmuth, *Angew. Chem.* **2006**, *118*, 915 – 918; *Angew. Chem. Int. Ed.* **2006**, *45*, 901 – 904; c) J. Luo, T. Lei, X. Xu, F.-M. Li, Y. Ma, K. Wu, J. Pei, *Chem. Eur. J.* **2008**, *14*, 3860 – 3865; d) D. Xu, R. Warmuth, *J. Am. Chem. Soc.* **2008**, *130*, 7520 – 7521; e) T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacsa, A. M. Z. Slawin, A. Steiner, A. I. Cooper, *Nat. Mater.* **2009**, *8*, 973 – 978; f) X.-N. Xu, L. Wang, G.-T. Wang, J.-B. Lin, G.-Y. Li, X.-K. Jiang, Z.-T. Li, *Chem. Eur. J.* **2009**, *15*, 5763 – 5774; g) R. A. Bilbeisi, J. K. Clegg, N. Elgrishi, X. D. Hatten, M. Devillard, B. Breiner, P. Mal, J. R. Nitschke, *J. Am. Chem. Soc.* **2012**, *134*, 5110 – 5119; h) A. Granzhan, C. M. Schouwey, T. Riis-Johannessen, R. Scopelliti, K. Severin, *J. Am. Chem. Soc.* **2011**, *133*, 7106 – 7115; i) Y. Jin, B. A. Voss, A. Jin, H. Long, R. D. Noble, W. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 6650 – 6658; j) J. Sun, J. L. Bennett, T. J. Emge, R. Warmuth, *J. Am. Chem. Soc.* **2011**, *133*, 3268 – 3271.

[14] a) K. S. Chichak, S. J. Cantrill, A. R. Pease, S. H. Chiu, G. W. V. Cave, J. L. Atwood, J. F. Stoddart, *Science* **2004**, *304*, 1308 – 1312; b) C. D. Meyer, R. S. Forgan, K. S. Chichak, A. J. Peters, N. Tangchaivang, G. W. V. Cave, S. I. Khan, S. J. Cantrill, J. F. Stoddart, *Chem. Eur. J.* **2010**, *16*, 12570 – 12581.

[15] A. R. Williams, B. H. Northrop, T. Chang, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **2006**, *118*, 6817 – 6821; *Angew. Chem. Int. Ed.* **2006**, *45*, 6665 – 6669.

[16] a) T. Hasell, X. F. Wu, J. T. A. Jones, J. Bacsa, A. Steiner, T. Mitra, A. Trewin, D. J. Adams, A. I. Cooper, *Nat. Chem.* **2010**, *2*, 750 – 755; b) G. Koshkakaryan, D. Cao, L. M. Klivansky, S. J. Teat, J. L. Tran, Y. Liu, *Org. Lett.* **2010**, *12*, 1528 – 1531.

[17] a) P. T. Glink, A. I. Oliva, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **2001**, *113*, 1922 – 1927; *Angew. Chem. Int. Ed.* **2001**, *40*, 1870 – 1875; b) L. M. Klivansky, G. Koshkakaryan, D. Cao, Y. Liu, *Angew. Chem.* **2009**, *121*, 4249 – 4253; *Angew. Chem. Int. Ed.* **2009**, *48*, 4185 – 4189; c) J. Yin, S. Dasgupta, J. Wu, *Org. Lett.* **2010**, *12*, 1712 – 1715; d) M. E. Belowich, C. Valente, R. A. Smaldone, D. C. Friedman, J. Thiel, L. Cronin, J. F. Stoddart, *J. Am. Chem. Soc.* **2012**, *134*, 5243 – 5261.

[18] See the Supporting Information for the synthetic details of the trications.

[19] See the Supporting Information for crystallographic data and crystal growing conditions. CCDC 906913 ($\mathbf{6b}\cdot 3\,\mathrm{PF}_6$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[20] a) J.-Y. Ortholand, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, D. J. Williams, *Angew. Chem.* **1989**, *101*, 1402 – 1404; *Angew. Chem. Int. Ed. Engl.* **1989**, 28, 1394 – 1395; b) M. Asakawa, W. Dehaen, G. L'abbe, S. Menzer, J. Nouwen, F. M. Raymo, J. F. Stoddart, D. J. Williams, *J. Org. Chem.* **1996**, *61*, 9591 – 9595; c) G. Koshkakaryan, L. M. Klivansky, D. Cao, M. Snauko, S. J. Teat, J. O. Struppe, Y. Liu, *J. Am. Chem. Soc.* **2009**, *131*, 2078 – 2079.

[21] a) K. Kumazawa, K. Biradha, T. Kusukawa, T. Okano, M. Fujita, *Angew. Chem.* **2003**, *115*, 4039 – 4043; *Angew. Chem. Int. Ed.* **2003**, *42*, 3909 – 3913; b) M. Yoshizawa, J. Nakagawa, K. Kurnazawa, M. Nagao, M. Kawano, T. Ozeki, M. Fujita, *Angew. Chem.* **2005**, *117*, 1844 – 1847; *Angew. Chem. Int. Ed.* **2005**, *44*, 1810 – 1813; c) Y. Yamauchi, M. Yoshizawa, M. Fujita, *J. Am. Chem. Soc.* **2008**, *130*, 5832 – 5833.