JOC Article
pubs.acs.org/joc

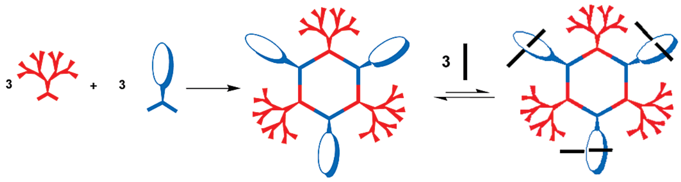
Self-Assembly of Dendritic Tris(crown ether) Hexagons and Their Complexation with Dibenzylammonium Cations

Xing-Dong Xu,[†] Hai-Bo Yang,*[,†] Yao-Rong Zheng,[‡] Koushik Ghosh,[‡]
Matthew M. Lyndon,[§] David C. Muddiman,[§] and Peter J. Stang[‡]

[†]*Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai, China, 200062,* [‡]*Department of Chemistry, University of Utah, 315 South 1400 East, Room 2020, Salt Lake City, Utah 84112, United States, and* [§]*W. M. Keck FT-ICR Mass Spectrometry Laboratory and Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695, United States*

hbyang@chem.ecnu.edu.cn

Received August 20, 2010



The construction of a new series of dendritic tris(crown ether) hexagons via coordination-driven self-assembly is described. Combining 120° crown ether-containing diplatinum(II) acceptors with 120° dendritic dipyridyl donors in a 1:1 ratio allows for the formation of a new family of dendritic triple crown ether derivatives with a hexagonal cavity in quantitative yields. The number and the position of these pendant groups can be precisely controlled on the hexagonal metallacycle. The structures of all dendritic multiple crown ether hexgaons are confirmed by multinuclear NMR (^{1}H and ^{31}P), ESI-MS and ESI-TOF-MS, and elemental analysis. The complexation of these dendritic trivalent receptors with dibenzylammonium cations was investigated by ^{1}H NMR titration experiments. The thermodynamic binding constants between the receptors and guests were established by using the nonlinear least-squares fit method based on ^{1}H NMR titration experiments. It was found that the association constants of each assembly decrease correspondingly upon the increase of the generation of the dendrons from [G0] to [G3], which might be caused by the steric effect of the dendrons on host−guest complexation.

Introduction

With the aim of obtaining a further insight into biological processes in nature, a great deal of effort has been made to investigate artificial functional supramolecular systems.[1] Compared to the conventional stepwise formation of covalent bonds, the self-assembly process driven by noncovalent interactions, such as hydrogen bonding, electrostatic forces, donor−acceptor, van der Waals forces, and coordination bonding etc., offers considerable synthetic advantages including significantly fewer steps, fast and facile formation of the final products, and inherent defect-free assembly. More importantly, the application of noncovalent interactions allows for the selective and spontaneous formation of nanoscopically controlled multicomponent structures with designed functionality.[2] The power and versatility of this bioderived motive has been illustrated by numerous examples of the application of noncovalent interactions in the

---

(1) (a) Vögtle, F. *Supramolecular Chemistry*; John Wiley and Sons: New York, 1991. (b) Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests*; Royal Society of Chemistry: Cambridge, U.K., 1994. (c) Lehn, J.-M. *Supramolecular Chemistry*; VCH Publishers: New York, 1995. (d) Atwood, J. L.; Davies, J. E. D. D.; MacNicol, D.; Vögtle, F., Eds. *Comprehensive Supramolecular Chemistry*; Pergamon Press: New York, 1996. (e) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley and Sons: New York, 2000.

(2) (a) Lehn, J.-M. *Angew. Chem., Int. Ed.* **1990**, *29*, 1304–1319. (b) Philip, D.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **1996**, *35*, 1155–1196. (c) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418–2421. (d) Lehn, J.-M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4763–4768. (e) Hori, A.; Yamashita, K.-I.; Fujita, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 5016–5019. (f) Lehn, J.-M. *Science* **2002**, *295*, 2400–2403. (g) Lehn, J.-M. *Rep. Prog. Phys.* **2004**, *67*, 249–265. (h) Lehn, J.-M. *Chem. Soc. Rev.* **2007**, *36*, 151–160.

DOI: 10.1021/jo101648p

synthesis of large supramolecular assemblies in the past few decades.[3] However, the design and construction of high-order supramolecular architectures still remains a considerable challenge for supramolecular chemists.

Since Pederson's milestone work[4a] in 1967, crown ethers and their structural analogues[4] have attracted considerable attention because of their wide applications in host−guest chemistry and the construction of structurally interesting molecular architectures.[5,6] During the last two decades, considerable research interest has been devoted to the design of multiple crown ether derivatives, which can be used in multicomponent host−guest recognition or in the construction of higher order complexes.[7] For example, Stoddart and coworkers prepared two analogous multivalent crown ether derivatives and investigated their complexation with mono- and divalent dialkylammonium ligands.[7i] Moreover, Gibson et al. has reported the construction of a supramolecular triarm star polymer from a homotritopic tris(crown ether) host and a monotopic paraquat-terminated polystyrene guest.[7j] Chen's group has provided a facile way to prepare a novel [4]pseudocatenane from a triptycene tris(crown ether) compound.[7k] However, the covalent synthetic protocols for the synthesis of multiple crown ether derivatives often suffer from time-consuming procedures and unsatisfactory yields resulted from steric congestions. Moreover, previous approaches to the construction of single molecule, nonpolymeric multiple crown ether units have been limited to either attachment of crown ethers to a helical peptide scaffold or dendritic construction of multiple crown ether units.[7a−h] Thus it is necessary to explore a highly efficient approach for the formation of such sophisticated compounds.

In the past decade, coordination-driven self-assembly has evolved as a well-established approach to construct discrete supramolecular polygons and polyhedra.[8] Employing such methodology, a variety of nanoscopic ensembles of predetermined shape, sizes, and symmetry have been prepared in high efficiency.[9] Very recently, we have developed a new approach to prepare functionalized supramolecular assemblies with

---

(3) (a) Lehn, J.-M. *Angew. Chem.* **1988**, *100*, 91–116. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89−112. (b) Cram, D. J. *Angew. Chem.* **1988**, *100*, 1041–1052. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1009 −1020. (c) Pedersen, C. J. *Angew. Chem.* **1988**, *100*, 1053–1059. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1021−1027. (d) Ikkala, O.; Brinke, G. *Science* **2002**, *295*, 2407. (e) Fiedler, D.; Bergman, R. G.; Raymond, K. N. *Angew. Chem., Int. Ed.* **2006**, *45*, 745. (f) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *Science* **2007**, *316*, 85. (g) Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251–254. (h) Nishioka, Y.; Yamaguchi, T.; Yoshizawa, M.; Fujita, M. *J. Am. Chem. Soc.* **2007**, *129*, 7000–7001. (i) Leung, D. H.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 2746–2747. (j) Qin, L.; Banholzer, M. J.; Xu, X.; Huang, L.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 14870–14870. (k) Masar, M. S., III; Gianneschi, N. C.; Oliveri, C. G.; Stern, C. L.; Nguyen, S. T.; Mirkin, C. A. *J. Am. Chem. Soc.* **2007**, *129*, 10149–10158. (l) Gianneschi, N. C.; Bertin, P. A.; Nguyen, S. T.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 10508–10509.

(4) (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017–7036. (b) Bradshaw, J. S.; Izatt, R. M. *Acc. Chem. Res.* **1997**, *30*, 338–345. (c) Gokel, G. W.; Leevy, W. M.; Weber, M. E. *Chem. Rev.* **2004**, *104*, 2723–2750. (d) Jarosz, S.; Listkowski, A. *Curr. Org. Chem.* **2006**, *10*, 643–662. (e) Steed, J. W. *Coord. Chem. Rev.* **2001**, *215*, 171–221. (f) Ritch, J. S.; Chivers, T. *Angew. Chem. Intl. Ed.* **2007**, *46*, 4610–4613. (g) Tsukube, H. *Coord. Chem. Rev.* **1996**, *148*, 1–17. (h) Sasaki, S.; Shionoya, M.; Koga, K. *J. Am. Chem. Soc.* **1985**, *107*, 3371–3372. (i) Voyer, N. *J. Am. Chem. Soc.* **1991**, *113*, 1818–1821. (j) Voyer, N.; Roby, J.; Deschenes, D.; Bernier, J. *Supramol. Chem.* **1995**, *5*, 61–69. (k) Huang, Z. B.; Chang, S. H. *Synlett* **2005**, *14*, 2257–2259. (l) Tanaka, M.; Higuchi, Y.; Adachi, N.; Shibutani, Y.; Ahmed, S. A.; Kado, S.; Nakamura, M.; Kimura, K. *Tetrahedron* **2005**, *61*, 8159–8166. (m) Dykes, G. M.; Smith, D. K. *Tetrahedron* **2003**, *59*, 3999–4009. (n) Sathiyendiran, M.; Liao, R.-T.; Thanasekaran, P.; Luo, T.-T.; Venkataramanan, N. S.; Lee, G.-H.; Peng, S.-M.; Lu, K.-L. *Inorg. Chem.* **2006**, *45*, 10052–10054. (o) Li, C.; Law, G.-L.; Wong, W.-T. *Org. Lett.* **2004**, *6*, 4841–4844.

(5) (a) Schill, G., Ed. *Catenanes, Rotaxanes, and Knots*; Academic Press: New York, 1971. (b) Dietrich-Buchecker, C. O.; Sauvage, J. P., Eds. *Molecular Catenanes, Rotaxanes and Knots*; Wiley-VCH: New York, 1999. (c) Sauvage, J. P. *Acc. Chem. Res.* **1990**, *23*, 319–327. (d) Hoss, R.; Vögtle, F. *Angew. Chem., Int. Ed.* **1994**, *33*, 375–384. (e) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725–2828. (f) Jäger, R.; Vögtle, F. *Angew. Chem., Int. Ed.* **1997**, *36*, 930–944. (g) Nepogodiev, S. A.; Stoddart, J. F. *Chem. Rev.* **1998**, *98*, 1959–1976. (h) Sauvage, J. P. *Acc. Chem. Res.* **1998**, *31*, 611–619. (i) Raymo, F. M.; Stoddart, J. F. *Chem. Rev.* **1999**, *99*, 1643–1664. (j) Tian, H.; Wang, Q.-C. *Chem. Soc. Rev.* **2006**, *35*, 361–374. (k) Wenz, G.; Han, B.-H.; Mueller, A. *Chem. Rev.* **2006**, *106*, 782–817. (l) Loethen, S.; Kim, J.-M.; Thompson, D. H. *Polym. Rev.* **2007**, *47*, 383–418. (m) Raymo, F. M.; Stoddart, J. F. *Chem. Rev.* **1999**, *99*, 1643–1663. (n) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348–3391. (o) Collin, J.-P.; Dietrich-Buchecker, C.; Gaviòa, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, *34*, 477–487. (p) Schalley, C. A.; Beizai, K.; Vögtle, F. *Acc. Chem. Res.* **2001**, *34*, 465–476. (q) Badjić, J. D.; Balzani, V.; Credi, A.; Silvi, S.; Stoddart, J. F. *Science* **2004**, *303*, 1845–1849.

(6) (a) Liu, Y.; Yu, L.; Chen, Y.; Zhao, Y.-L.; Yang, H. *J. Am. Chem. Soc.* **2007**, *129*, 10656–10657. (b) Park, C.; Oh, K.; Lee, S. C.; Kim, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 1455–1457. (c) Hoffart, D. J.; Loeb, S. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 901–904. (d) Huang, F.; Nagvekar, D. S.; Slebodnick, C.; Gibson, H. W. *J. Am. Chem. Soc.* **2005**, *127*, 484–485. (e) Nostro, P. L; Lopes, J. R.; Cardelli, C. *Langmuir* **2001**, *17*, 4610–4615. (f) Yamaguchi, N.; Nagvekar, D. S.; Gibson, H. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 2361–2364. (g) Gibson, H. W.; Yamaguchi, N.; Jones, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 3522–3533. (h) Cate, A. T.; Kooijman, H.; Spek, A. L.; Sijbesma, R. P.; Meijer, E. W. *J. Am. Chem. Soc.* **2004**, *126*, 3801–3808. (i) Yelamaggad, C. V.; Achalkumar, A. S.; Rao, D. S. S.; Prasad, S. K. *J. Am. Chem. Soc.* **2004**, *126*, 6506–6507. (j) Kim, H. J.; Zin, W. C.; Lee, M. *J. Am. Chem. Soc.* **2004**, *126*, 7009–7014.

(7) (a) Sasaki, S.; Shionoya, M.; Koga, K. *J. Am. Chem. Soc.* **1985**, *107*, 3371–3372. (b) Voyer, N. *J. Am. Chem. Soc.* **1991**, *113*, 1818–1821. (c) Voyer, N.; Roby, J.; Deschenes, D.; Bernier, J. *Supramol. Chem.* **1995**, *5*, 61–69. (d) Huang, Z. B.; Chang, S. H. *Synlett* **2005**, *14*, 2257–2259. (e) Tanaka, M.; Higuchi, Y.; Adachi, N.; Shibutani, Y.; Ahmed, S. A.; Kado, S.; Nakamura, M.; Kimura, K. *Tetrahedron* **2005**, *61*, 8159–8166. (f) Dykes, G. M.; Smith, D. K. *Tetrahedron* **2003**, *59*, 3999–4009. (g) Sathiyendiran, M.; Liao, R.-T.; Thanasekaran, P.; Luo, T.-T.; Venkataramanan, N. S.; Lee, G.-H.; Peng, S.-M.; Lu, K.-L. *Inorg. Chem.* **2006**, *45*, 10052–10054. (h) Li, C.; Law, G.-L.; Wong, W.-T. *Org. Lett.* **2004**, *6*, 4841–4844. (i) Fulton, D. A.; Cantrill, S. J.; Stoddart, J. F. *J. Org. Chem.* **2002**, *67*, 7968–7981. (j) Huang, F.; Nagvekar, D. S.; Slebodnick, C.; Gibson, H. W. *J. Am. Chem. Soc.* **2005**, *127*, 484–485. (k) Zhu, X.-Z.; Chen, C.-F. *J. Am. Chem. Soc.* **2005**, *127*, 13158–13159.

(8) (a) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502–518. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853–908. (c) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022–2043. (d) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972–983. (e) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509–518. (f) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975–982. (g) Gianneschi, N. C.; Masar, M. S., III; Mirkin, C. A. *Acc. Chem. Res.* **2005**, *38*, 825–837. (h) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759–771. (i) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369–378. (j) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 349–358. (k) Steel, P. J. *Acc. Chem. Res.* **2005**, *38*, 243–250. (l) Zangrando, E.; Casanova, M.; Alessio, E. *Chem. Rev.* **2008**, *108*, 4979–5013. (m) Oliveri, C. G.; Ulmann, P. A.; Wiester, M. J.; Mirkin, C. A. *Acc. Chem. Res.* **2008**, *41*, 1618–1629. (n) Lee, S. J.; Hupp, J. T. *Coord. Chem. Rev.* **2006**, *250*, 1710–1723. (o) Goshe, A. J.; Steele, I. M.; Ceccarelli, C.; Rheingold, A. L.; Bosnich, B. *Proc. Natl. Acad. Sci.* **2002**, *99*, 4823–4829.

(9) (a) Fujita, M.; Oguro, D.; Miyazawa, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469–471. (b) Olenyuk, B.; Levin, M. D.; Whiteford, J. A.; Shield, J. E.; Stang, P. J. *J. Am. Chem. Soc.* **1999**, *121*, 10434–10435. (c) Olenyuk, B.; Whiteford, J. A.; Fechtenkotter, A.; Stang, P. J. *Nature* **1999**, *398*, 796–799. (d) Takeda, N.; Umemoto, K.; Yamaguchi, K.; Fujita, M. *Nature* **1999**, *398*, 794–796. (e) Fujita, M.; Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* **1999**, *400*, 52–55. (f) Lee, S. J.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 4554–4555. (g) Kuehl, C. J.; Kryschenko, Y. K.; Radhakrishnan, U.; Seidel, S. R.; Huang, S. D.; Stang, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4932–4936. (h) Huang, X.-C.; Zhang, J.-P.; Chen, X.-M. *J. Am. Chem. Soc.* **2004**, *126*, 13218–13219. (i) Davis, A. V.; Raymond, K. N. *J. Am. Chem. Soc.* **2005**, *127*, 7912–7919. (j) Hiraoka, S.; Sakata, Y.; Shionoya, M. *J. Am. Chem. Soc.* **2008**, *130*, 10058–10059. (k) Hiraoka, S.; Harano, K.; Shiro, M.; Ozawa, Y.; Yasuda, N.; Toriumi, K.; Shionoya, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 6488–6491. (l) Merlau, M. L.; Mejia, M. D. P.; Nguyen, S. T.; Hupp, J. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4239–4242. (m) Sun, S.-S.; Stern, C. L.; Nguyen, S. T.; Hupp, J. T. *J. Am. Chem. Soc.* **2004**, *126*, 6314–6326. (n) Murase, T.; Sato, S.; Fujita, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1083–1085. (o) Kawano, M.; Kawamichi, T.; Haneda, T.; Kojima, T.; Fujita, M. *J. Am. Chem. Soc.* **2007**, *129*, 15418–15419. (p) Ghosh, S.; Mukherjee, P. S. *J. Org. Chem.* **2006**, *71*, 8412–8416. (q) Leininger, S.; Schmitz, M.; Stang, P. J. *Org. Lett.* **1999**, *1*, 1921–1923.

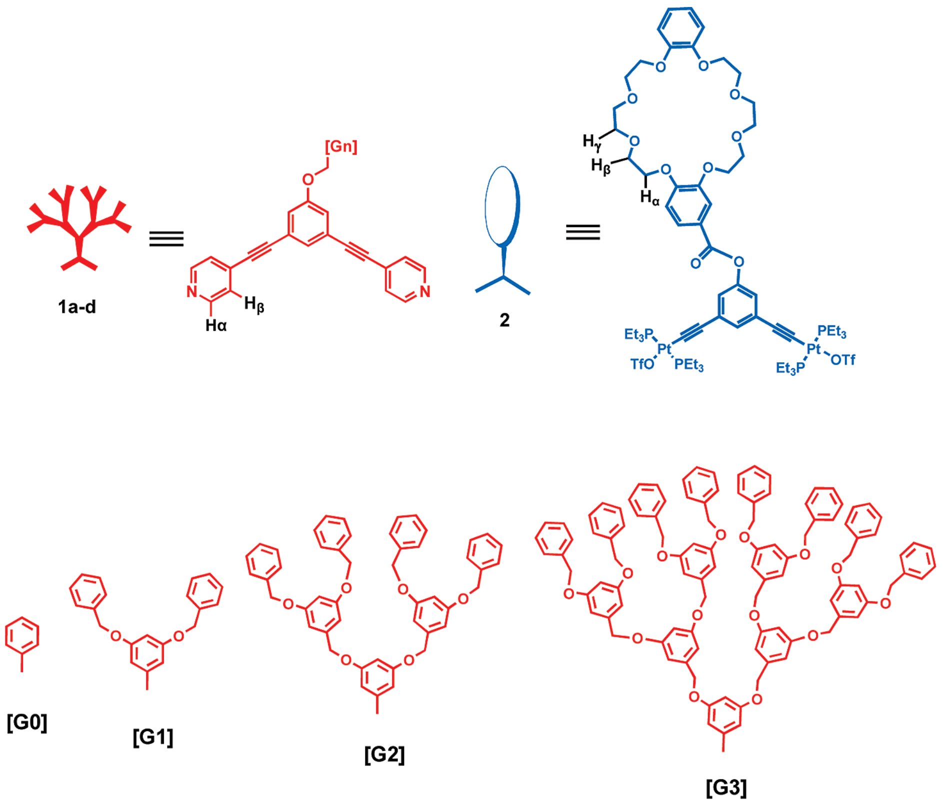


FIGURE 1. Schematic and molecular structure of 120° dendritic donor subunits **1a–d** and 120° crown ether-containing acceptor **2**.

well-defined shape, size, and symmetry through an *exofunctionlization* strategy.[10] This strategy allows for precise control over the shape and size of the final construction as well as the distribution and total number of incorporated functional moieties. For example, we have demonstrated that the introduction of a functional group, such as crown ether,[11] ferrocene,[12] and Fréchet-type dendrons,[13] at the vertex of 120° building blocks enables the preparation of two-dimensional (2-D) novel, functionalized cavity-cored assemblies. Moreover, stable multifunctional cuboctahedral complexes have been constructed via a similar strategy.[14] Encouraged by the power and versatility of this methodology, we envisioned that the construction of dendritic multiple crown ether derivatives with well-designed and controlled cavity would be realized via coordination-driven self-assembly. This new family of dendritic multiple crown ether derivatives are of interest because of their potential application in the construction of mechanically interlocked dendrimers, which have become one of the most attractive topics within modern supramolecular chemistry.[15,16]

Upon combination of dibenzo[24]crown-8 (**DB24C8**)-containing 120° di-Pt(II) acceptor building blocks[11b] **2** with 120° dendritic dipyridyl donors[13a] (substituted with Fréchet-type dendrons) **1a–d** (Figure 1), a new family of dendritic tris(crown ether) hexagons was formed via coordination-driven self-assembly in one step. Subsequently their complexation with dibenzylammonium cations ($R_2NH_2^+$) was investigated via ^{1}H NMR titration experiments. We found

---

[10] Northrop, B. H.; Yang, H.-B.; Stang, P. J. *Chem. Commun.* **2008**, 5896–5908.

[11] (a) Yang, H.-B.; Ghosh, K.; Northrop, B. H.; Zheng, Y.-R.; Lyndon, M. M.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 14187–1489. (b) Ghosh, K.; Yang, H.-B.; Northrop, B. H.; Lyndon, M. M.; Zheng, Y.-R.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 5320–5334.

[12] (a) Yang, H.-B.; Ghosh, K.; Zhao, Y.; Northrop, B. H.; Lyndon, M. M.; Muddiman, D. C.; White, H. S.; Stang, P. J. *J. Am. Chem. Soc.* **2008**, *130*, 839–841. (b) Ghosh, K.; Zhao, Y.; Yang, H.-B.; Northrop, B. H.; White, H. S.; Stang, P. J. *J. Org. Chem.* **2008**, *73*, 8553–8557.

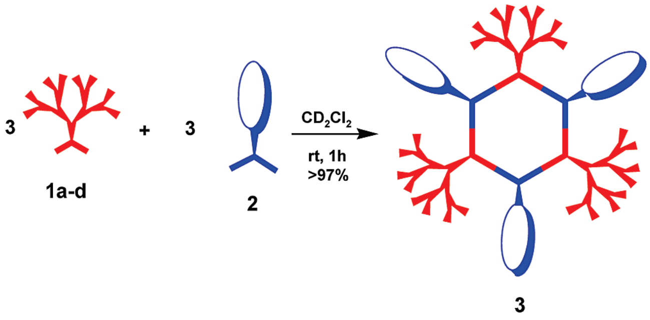
[13] (a) Yang, H.-B.; Das, N.; Huang, F.; Hawkridge, A. M.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 10014–1005. (b) Yang, H.-B.; Hawkridge, A. M.; Huang, S. D.; Das, N.; Bunge, S. D.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 2120–2129. (c) Yang, H.-B.; Northrop, B. H.; Zheng, Y.-R.; Ghosh, K.; Lyndon, M. M.; Muddiman, D. C.; Stang, P. J. *J. Org. Chem.* **2009**, *74*, 3524–3527. (d) Yang, H.-B.; Northrop, B. H.; Zheng, Y.-R.; Ghosh, K.; Stang, P. J. *J. Org. Chem.* **2009**, *74*, 7067–7074.

[14] Ghosh, K.; Hu, J.; White, H. S.; Stang, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 6695–6697.

[15] Supramolecular dendrimers are comprised of noncovalently bonded subunits: (a) Zimmerman, S. C.; Zeng, F.; Reichert, D. E. C.; Kolotuchin, S. V. *Science* **1996**, *271*, 1095–1098. (b) Emrick, T.; Fréchet, J. M. J. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 15–23. (c) Percec, V.; Cho, W.-D.; Ungar, G. *J. Am. Chem. Soc.* **2000**, *122*, 10273–10281. (d) Lee, J. W.; Ko, Y. H.; Park, S.-H.; Yamaguchi, K.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 746–749. (e) Zeng, F.; Zimmerman, S. C.; Kolotuchin, S. V.; Reichert, D. E.; Ma, C. Y. *Tetrahedron* **2002**, *58*, 825–843. (f) Percec, V.; Cho, W.-D.; Mosier, P. E.; Ungar, G.; Yeardley, J. P. *J. Am. Chem. Soc.* **1998**, *120*, 11061–11070. (g) Uppuluri, S.; Swanson, D. R.; Piehler, L. T.; Li, J.; Hagnauer, G. L.; Tomalia, D. A. *Adv. Mater.* **2000**, *12*, 796–800. (h) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *Chem.—Eur. J.* **2002**, *8*, 2011–2025. (i) Zong, Q.-S.; Zhang, C.; Chen, C.-F. *Org. Lett.* **2006**, *8*, 1859–1862. (j) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689–1746. (k) Newkome, G. R.; Moorefield, F.; Vögtle, F.; Baker, G. R.; Johnson, A. L.; Behara, R. K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1176–1178. (l) Constable, E. C. *Chem. Commun.* **1997**, 1073–1080.

[16] (a) Gibson, H. W.; Yamaguchi, N.; Hamilton, L.; Jones, J. W. *J. Am. Chem. Soc.* **2002**, *124*, 4653–4665. (b) Leung, K. C.-F.; Aricó, F.; Cantrill, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 5808–5810. (c) Elizarov, A. M.; Chang, T.; Chiu, S.-H.; Stoddard, J. F. *Org. Lett.* **2002**, *4*, 3565–3568. (d) Leung, K. C.-F.; Mendes, P. M.; Magonov, S. N.; Northrop, B. H.; Kim, S.; Patel, K.; Flood, A. H.; Tseng, H.-R.; Stoddard, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 10707–10715. (e) Elizarov, A. M.; Chiu, S.-H.; Glink, P. T.; Stoddart, J. F. *Org. Lett.* **2002**, *4*, 679–682.

SCHEME 1. Graphical Representation of the Synthesis of Dendritic Tris-DB24C8 Hexagons 3a−d via [3 + 3] Coordination-Driven Self-Assembly



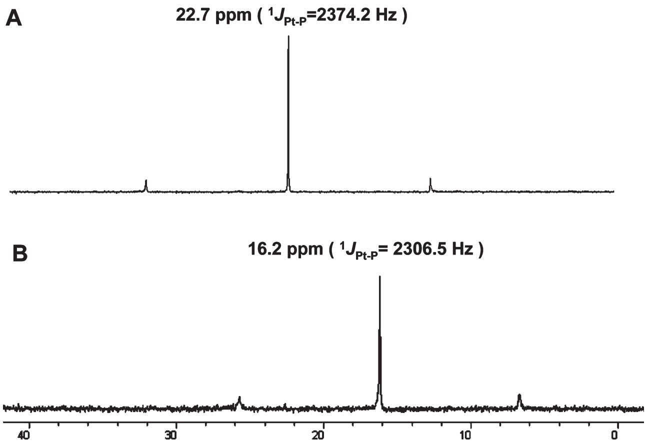


FIGURE 2. ^{31}P{^{1}H} NMR spectra (300 MHz, CD_2Cl_2, 298 K) of **DB24C8**-containing 120° di-Pt(II) acceptor **2** (A) and [G3] dendritic tris-**DB24C8** hexagon **3d** (B).

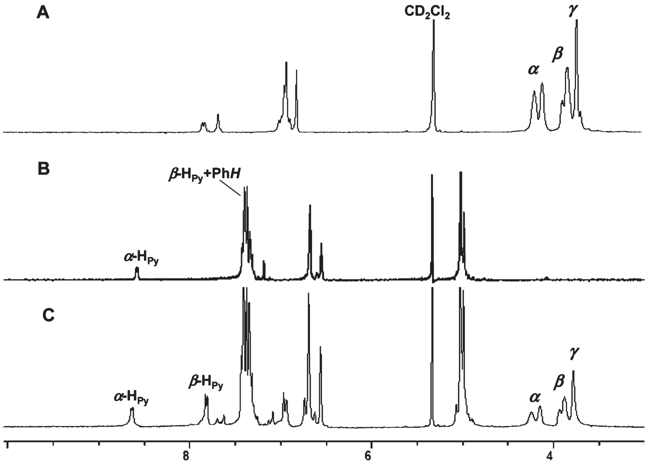


FIGURE 3. ^{1}H NMR spectra (300 MHz, CD_2Cl_2, 298 K) of **DB24C8**-containing 120° di-Pt(II) acceptor **2** (A), [G3] dendritic dipyridyl donor **1a** (B), and [G3] dendritic tris-**DB24C8** hexagon **3d** (C).

that each dendritic multiple crown ether hexagon was able to complex dibenzylammonium ions without disrupting the underlying metallacyclic hexagon, which demonstrates the utility and scope of the orthogonal self-assembly technique. In addition this strategy may provide a possibility to the preparation of novel dendritic multiple crown ether derivatives with desired functionality arising from their unique interior cavities and multifunctional exteriors.

Results and Discussion

Self-Assembly of Dendritic Tris-DB24C8 Hexagons. According to the "directional bonding" model and the "symmetry interaction" model, the shape of an individual 2-D polygon is usually determined by the value of the turning angle within its angular components.[8b] For instance, discrete hexagonal species of type $A^2_3X^2_3$ can be self-assembled from a combination of two complementary ditopic building blocks, A^2 and X^2, each incorporating 120° angles between the active coordination sites, allowing for the generation of hexagonal structures.[9q] Additionally, we have demonstrated that the introduction of functional groups, such as crown ether, ferrocene, and Fréchet-type dendrons, at the vertex of the 120° building blocks does not hinder their self-assembly.[10−13] Thus the formation of dendritic multiple crown ether derivatives bearing a hexagonal cavity could be realized by combining three 120° dendritic pyridyl donor building blocks and three 120° crown ether-containing di-Pt(II) acceptors.

Upon mixing the [G0]−[G3] 120° donors **1a−d** with an equimolar amount of the 120° crown ether-containing di-Pt(II) acceptor in dichloromethane-d_2, the [3 + 3] dendritic tris-**DB24C8** hexagons **3a−d** were obtained in excellent yields (>97%), respectively (Scheme 1). The self-assembly of hexagonal dendritic tris-**DB24C8** derivatives was monitored by multinuclear NMR (^{1}H and ^{31}P) spectroscopy. Analysis of the multinuclear NMR of **3a−d** presented very similar characteristics, which indicated the formation of discrete, highly symmetric species. The ^{31}P{^{1}H} NMR spectra of [G0]−[G3] assemblies displayed a sharp singlet shifted upfield from the starting crown ether-containing di-Pt(II) acceptor **2** by approximately 5.5 ppm. This change, as well as the decrease in coupling of the flanking ^{195}Pt satellites (ca, $\Delta J = -68$ Hz), is consistent with back-donation from the platinum atoms. Likewise, the ^{1}H NMR exhibited simple and sharp resonances, indicative of the generation of the desired symmetric hexagonal ensembles. For example, in the ^{1}H NMR spectrum of each assembly, the hydrogen atoms of the pyridine rings exhibited shifts downfield (for α proton, $\Delta\delta = 0.02-0.025$ ppm, for β proton, $\Delta\delta = 0.42-0.48$ ppm) due to the loss of electron density that occurs upon coordination of the pyridine-N atom with the Pt(II) metal center. The sharp NMR signals in both ^{31}P and ^{1}H NMR along with the solubility of these assemblies ruled out the formation of oligomers. The ^{1}H and ^{31}P{^{1}H} NMR spetra of [G3] assembly **3d** are shown in Figures 2 and 3 as representative examples.

Mass spectrometric studies of all four hexagons were performed with use of ESI-MS and ESI-TOF-MS techniques, which allows the assemblies to remain intact during the ionization process while obtaining the high resolution required for isotopic distribution. All results of mass studies of assemblies **3a−d** provided further support for the formation of the [3 + 3] dendritic tris-**DB24C8** hexagons. In the ESI-MS spectra of [G0]−[G1] hexagonal assemblies **3a**,**b** (Figure 4A, B), for example, peaks attributable to the loss of triflate counterions, $[M - 4OTf]^{4+}$ (*m*/*z* 1472.0 for **3a**, *m*/*z* 1631.2 for **3b**) and $[M - 5OTf]^{5+}$ (*m*/*z* 1147.9 for **3a**, *m*/*z* 1275.2 for **3b**), where M represents the intact assembly, were observed and their isotopic resolution are in excellent agreement with the

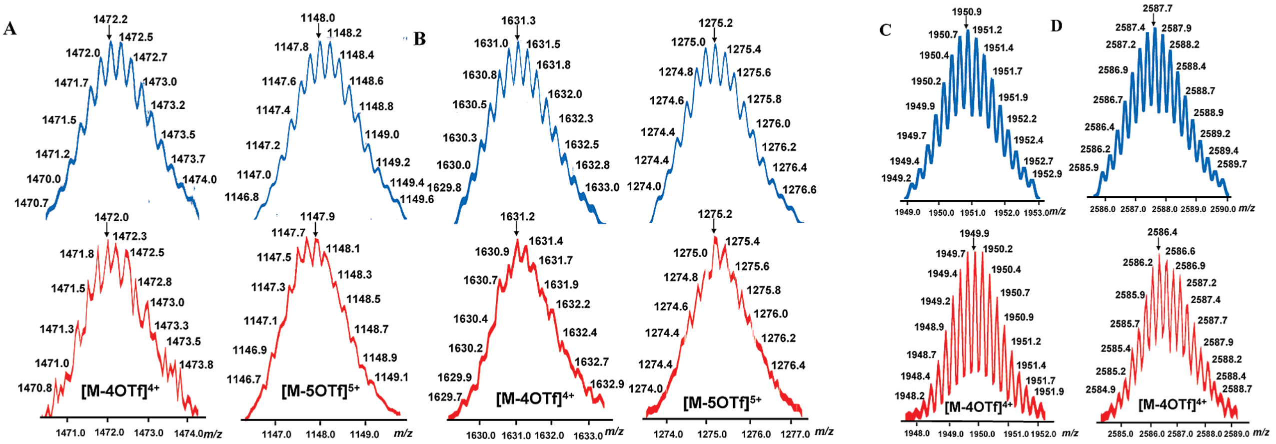


FIGURE 4. Calculated (top) and experimental (bottom) ESI-MS (A for **3a**, B for **3b**) and ESI-TOF-MS spectra (C for **3c**, D for **3d**) of dendritic tris-**DB24C8** hexagons **3a**−**d**.

theoretical distribution. Similarly, the ESI-TOF-MS spectra of [G2]−[G3] hexagonal assemblies **3c**,**d** (Figure 4C,D) exhibited one charged state at *m*/*z* 1949.9 for **3c** and *m*/*z* 2586.4 for **3d**, corresponding to $[M - 4OTf]^{4+}$, respectively. These peaks were isotopically resolved, and they agree very well with their theoretical distribution.

Unfortunately, all attempts to grow X-ray quality single crystals of the dendritic hexagonal tris-**DB24C8** derivatives have so far proven unsuccessful. Therefore, molecular force-field simulations were used to gain further insight into the structural characteristics of the newly designed assembly. In the case of [G3] dendritic tris-**DB24C8** hexagon **3d**, a 1.0 ns molecular dynamics simulation (MMFF force field) was used to equilibrate the supramolecule, followed by energy minimization of the resulting structures to full convergence. An internal diameter of 3.0 nm was observed in the simulated molecular model of **3d** (Figure 5). Interestingly, simulations reveal that the underlying hexagonal structure—"scaffold"—retain its planar and rigid structure even when derivatized with pendent dendron and crown ether units, while the flexible nature of the pendent crown ether moieties and the less flexible nature of the Fréchet-type dendrons can be observed from modeling study.

Investigation of the Complexation of Dendritic Tris(crown ether) Hexagons with Dibenzylammonium Cations. With these newly designed dendritic tris-**DB24C8** hexagons in hand, an investigation of their complexation with dibenzylammonium cations was carried out. For many years crown ethers have been recognized as exceptionally versatile hosts for a wide variety of cationic guests, particularly for substituted ammonium ions. It has been well-known that the appropriately sized crown ether macrocycles bind $R_2NH_2^+$ ions in solution, in the solid state, and in the gas phase in a threaded rather than face to face manner.[17] The formation of a pseudorotaxane complex from the complementary host, e.g. **DB24C8**, and guest components in a 1:1 molar ratio is mostly driven by strong $[N-H\cdots O]$ hydrogen bonds between the acidic NH_2^+ protons and the oxygen atoms of the **DB24C8** ring. Additional $[C-H\cdots O]$ hydrogen bonding and $\pi-\pi$ stacking interactions, as well as electrostatic forces, further contribute to the stability of the resultant pseudorotaxanes. By employing the orthogonal, noninteracting nature of metal−ligand and hydrogen-bonding noncovalent interactions in solution, we have demonstrated that the tris[2]pseudorotaxane hexagons could be prepared by three different methods.[11a] Herein we significantly focused on the investigation of the complexation of these dendritic tris(crown ether) hexagons with dibenzylammonium ions in a stepwise manner (Scheme 2).

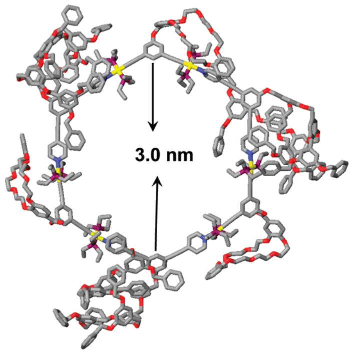


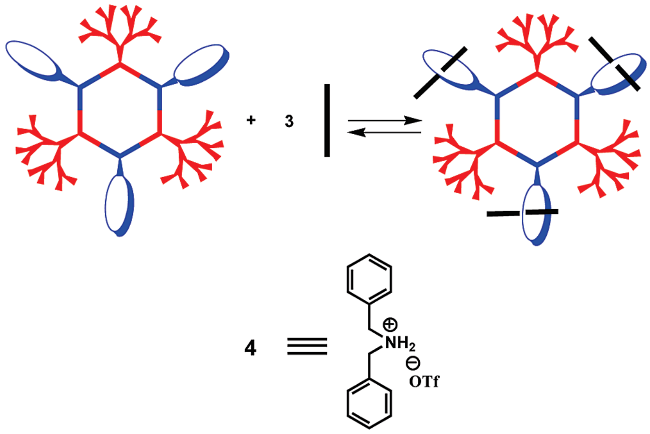
FIGURE 5. Computational simulation (MMFF force field) of [G3] dendritic tris-**DB24C8** hexagon **3d** (hydrogen atoms have been removed for clarity).

The complexation of hexagonal dendritic tris-**DB24C8** derivatives **3a**−**d** with dibenzylammonium triflate salt **4** was characterized by multinuclear NMR (^1H and ^{31}P). Within 10 min of adding 3 equiv of **4** to a solution of dendritic tris-**DB24C8** hexagons **3a**−**d** (2.25 mM) in dichloromethane, a pale yellow solution was obtained, respectively. Compared to the starting hosts **3a**−**d**, no significant change was observed in the $^{31}P\{^1H\}$ NMR spectrum of each complex, indicating that

---

[17] (a) Yamaguchi, N.; Hamilton, L. M.; Gibson, H. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 3275–3279. (b) Ishow, E.; Credi, A.; Balzani, V.; Spadola, F.; Mandolini, L. *Chem.—Eur. J.* **1999**, *5*, 984–989. (c) Bryant, W. S.; Guzei, I. A.; Rheingold, A. L.; Gibson, H. W. *Org. Lett.* **1999**, *1*, 47–50. (d) Meillon, J. C.; Voyer, N.; Biron, E.; Sanschagrin, F.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 143–145. (e) Ashton, P. R.; Campbell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; Williams, D. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 1869–1871. (f) Aricó, F.; Badjić, J. D.; Cantrill, S. J.; Flood, A. H.; Leung, K. C.-F.; Liu, Y.; Stoddart, J. F. *Top. Curr. Chem.* **2005**, *279*, 203–2509. (g) Ashton, P. R.; Campbell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; Williams, D. J. *Angew. Chem., Int. Ed.* **1995**, *34*, 1865–1869. (h) Metcalfe, J. C.; Stoddart, J. F.; Jones, G. *J. Am. Chem. Soc.* **1977**, *99*, 8317–8319. (i) Krane, J.; Aune, O. *Acta Chem. Scand., Ser. B* **1980**, *34*, 397. (j) Metcalfe, J. C.; Stoddart, J. F.; Jones, G.; Atkinson, A.; Kerr, I. S.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 540–543. (k) Abed-Ali, S. S.; Brisdon, B. J.; England, R. *J. Chem. Soc., Chem. Commun.* **1987**, 1565–1566.

SCHEME 2. Graphical Representation of Complexation of Dendritic Triple Crown Ether Hexagons 3a–d with Dibenzylammonium Ions 4



the threading process of dibenzylammonium ions does not substantially change the chemical environment of the phosphorus atoms present in the hexagons. However, the ^{1}H NMR spectra exhibited characteristic shifts related to the complexation of dibenzylammonium ion **4** by **DB24C8** (Figure 6). For example, a 0.45 ppm downfield shift of the signal for the benzylic methylene protons adjacent to the NH_2^+ center was observed in each spectrum, and protons H_α, H_β, and H_γ of **DB24C8** exhibited upfield shifts of 0.03, 0.08, and 0.25 ppm, respectively. It is worth noting that the equilibrium ratio of complexed to uncomplexed species was observed to be somewhat less than 1:1, indicating a slight excess of uncomplexed species. This observation is analogous to previous assemblies[11b] composed of di-Pt(II) crown ether acceptors **2** and further supports the conclusion that covalent attachment of the crown ether derivatives to di-Pt(II) acceptors lowers the binding abilities of the typically electron-rich macrocycles. Further characterization with two-dimensional spectroscopic techniques (^{1}H–^{1}H COSY and NOESY) is in agreement with the complexation of the dendritic tris(crwon ether) hexagons with dibenzylammonium cations. For example, through-space interactions between the α-H proton of the complexed crown ether and the benzylic methylene protons were observed in the NOESY spectrum of each complex (see the Supporting Information).

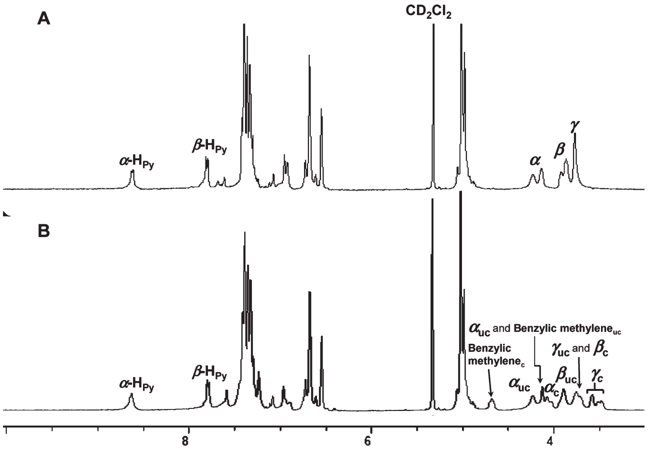


FIGURE 6. ^{1}H NMR spectra (500 MHz, CD_2Cl_2, 298 K) of [G3] dendritic tris-**DB24C8** hexagon **3d** (A) and the complex of [G3] dendritic tris-**DB24C8** hexagon **3d** with dibenzylammonium ions **4** in a 1:3 ratio (B).

TABLE 1. Thermodynamic Binding Constants (CD_2Cl_2, 298 K) of [G0]–[G3] Dendritic Tris(crown ether) Hexagons 3a–d with Dibenzylammonium Ions

Host	$K_{a.1}$ (M^{-1})	$K_{a.2}$ (M^{-1})	$K_{a.3}$ (M^{-1})
3a	$(2.2 \pm 0.4) \times 10^4$	$(1.3 \pm 0.1) \times 10^3$	$(4.3 \pm 0.5) \times 10^2$
3b	$(9.3 \pm 0.9) \times 10^3$	$(2.5 \pm 0.2) \times 10^3$	$(2.6 \pm 0.2) \times 10^2$
3c	$(6.4 \pm 0.4) \times 10^3$	$(8.1 \pm 0.2) \times 10^2$	$(1.6 \pm 0.2) \times 10^2$
3d	$(2.9 \pm 0.2) \times 10^3$	$(5.4 \pm 0.8) \times 10^2$	$(5.2 \pm 0.9) \times 10^1$

The further study of the complexation between dendritic tris(crown ether) hexagons and guests was established by using the nonlinear least-squares fit method[18] based on ^{1}H NMR titration experiments (see the Supporting Information). Titration experiments were carried out by the addition of a concentrated CD_2Cl_2 solution of the ammonium triflate salt **4** to solutions of hexagonal dendritic tris-**DB24C8** hosts **3a–d** in CD_2Cl_2, respectively.[19] To account for dilution effects, these ammonium triflate salt solutions also contained hosts at its initial concentration. The association constants were calculated by the Hyperquad2003 program[20] using changes in chemical shift of γ-proton resonance of crown ether in the ^{1}H NMR spectra. The ^{1}H NMR titration isotherms of host **3a–d** with the addition of guest **4** were shown in Figure S13–S16 in the Supporting Information.

It was found that the equilibriums between the host and the complexes were slow, while the transformation between the complexes was characterized by a rapid equilibrium, at least on the NMR time scale. Fitting the data to a 1:3 binding mode for hosts **3a–d** gave rise to the host–guest association constants summarized in Table 1. These values suggest that [G0] tris(crown ether) hexagon **3a** has a similar ability to bind dibenzylammonium guest(s) as does **DB24C8** in nonpolar solvents such as dichloromethane. In addition, it was found that the association constants of each assembly decreased correspondingly upon the increase of the generation of the dendrons from [G0] to [G3]. For example, compared to the [G0] host **3a**, $K_{a.1}$ decreased approximately 1 order of magnitude in the case of [G3] hexagonal tris-**DB24C8** host **3d**. From the ratios of binding constants it is clear that the crown ether sites act more or less independent of each other and the progress of complexation is not influenced by any sort of cooperative effects.[16a] Rather, the decrease in the efficiency of the threading process may be attributed to the entropic cost of forming higher order pseudorotaxanes or, potentially, the result of steric effects imposed by the dendron units on the approaching dibenzylammonium cations to the crown ether unit.

---

[18] Bourson, J.; Pouget, J.; Valeur, B. *J. Phys. Chem.* **1993**, *97*, 4552–4557.

[19] It is well-known that the binding of dibenzylammonium cations by crown ethers is concentration dependent, that is, association constants can differ depending on the concentrations at which they are measured: Chang, T.; Heiss, A. M.; Cantrill, S. J.; Fyfe, M. C. T.; Pease, A. R.; Rowan, S. J.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Org. Lett.* **2000**, *2*, 2947–2950. In this study, the concentration of dendritic trivalent hosts **3a–d** was kept in the range of 6.4×10^{-4} to 6.6×10^{-4} M because the supramolecular polygons constructed via coordination-driven self-assembly are usually stable under low concentration.

[20] Hyperquad2003 software, Protonic Software, http://www.hyperquad.co.uk.

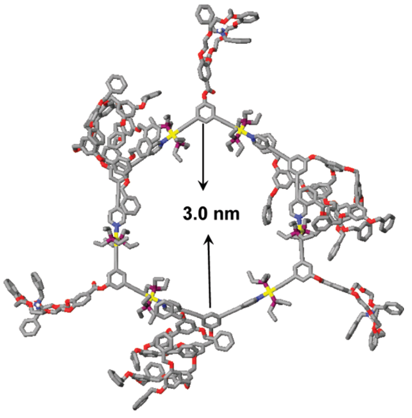


FIGURE 7. Computational simulation (MMFF force field) of hexagonal [G3] dendritic tris[2]pseudorotaxane (hydrogen atoms have been removed for clarity).

Molecular force field simulations were used to gain further insight into the structural characteristics of a cavity-cored dendritic tris[2]pseudorotaxane. The computational model of [G3] tris[2]pseudorotaxane is shown in Figure 7. The molecular simulations reveal that the addition of dibenzylammonium cations to **DB24C8** hosts does not disrupt the underlying polygonal scaffolds as ammonium salts are complexed by their pendant **DB24C8** macrocycles, further illustrating the orthogonality of the noncovalent interactions involved in self-assembly. In all cases, the underlying rigid nature of the 2-D polygonal cavity is retained while the flexibility of each crown ether is reduced as a result of host−guest complexation.

Conclusion

By employing the *exofunctionlization* strategy,[10] we have prepared a new family of dendritic tris(crown ether) derivatives with hexagonal cavity in high yields via coordination-driven self-assembly, which avoids the time-consuming procedures and lower yields often encountered in covalent synthetic protocols. The synthesis is straightforward and the yield is quantitative, thus eliminating the need of purification. The resulting structures incorporate a discrete hexagonal cavity as their main scaffold and the pendant dendrons and crown ether subunits at alternate vertexes. It is noted that the number and the position of these pendant groups can be precisely controlled on the hexagonal metallacycle. Further investigation of the complexation of dendritic tris(crown ether) hexagons and dibenzylammonium cations has also been carried out by utilizing the orthogonal, noninteracting nature of coordination-driven self-assembly of the underlying polygons and the hydrogen-bonding/electrostatic/$\pi-\pi$ stacking promoted self-assembly of crown ether−dialkyl ammonium pseudorotaxanes. The NMR titration studies revealed that [G0] tris(crown ether) host has a similar ability to bind dibenzylammonium guest(s) as does **DB24C8** in nonpolar solvent. Moreover, the association constants of [G0]−[G3] tris(crown ether) hexagons decreased with the increase of the dendron generation, which reflects the steric effect of the dendrons on host−guest complexation. Extending this idea to additional two-dimensional structure and even three-dimensional architectures is currently under investigation.

Experimental Section

Deuterated solvents and all other reagents were purchased and used without further purification. NMR spectra were recorded on a 300 or 500 MHz spectrometer. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P NMR resonances are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system or on an ESI-TOF mass spectrometer. The solvent for ESI-TOF mass spectra is dichloromethane.

The molecular structures of multiple crown ether derivative as well as tris[2]pseudorotaxane were each constructed with the MMFF force field.[21] A 1.0 ns molecular dynamics simulation (0.05 fs time step) at a simulation temperature of 300 K was used to equilibrate each structure. Following each molecular dynamics simulation a full energy minimization was used to obtain the final optimized structures.

General Procedure for the Preparation of [G0]−[G3] Hexagonal Dendritic Tris-DB24C8 Derivatives. To a 0.5 mL CD_2Cl_2 solution of 120° crown ether containing di-Pt(II) acceptor **2** (7.99 mg, 0.0045 mmol) was added a 0.5 mL dichloromethane-d_2 solution of the appropriate [G0]−[G3] dendritic donor precursors **1a−d** drop by drop with continuous stirring (10 min), respectively. The reaction mixture was stirred for 30 min at room temperature. The solution was evaporated to dryness, and the products of [G0]−[G3] hexagonal dendritic tris-**DB24C8** derivatives **3a−d** were collected.

3a: Yield: 9.53 mg (pale yellow solid), 98%. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.62 (d, ^3J = 6.0 Hz, 12H; H_α-Py), 7.81 (d, J = 6.3 Hz, 12H; H_β-Py), 7.65 (s, 3H; Ar*H*), 7.59 (s, 6H; Ar*H*), 7.37−7.48 (m, 18H; Ph*H* and Ar*H*), 7.33 (s, 6H; Ph*H*), 7.06 (s, 3H; Ph*H*), 6.90−6.94 (m, 18H; Ph*H*), 5.06 (s, 6H; OCH_2), 4.21 (br, 12H; α-CH_2), 4.13 (br, 12H; α-CH_2), 3.86−3.91 (m, 24H; β-CH_2), 3.78 (br, 24H; γ-CH_2), 1.79−1.83 (m, 72H; PCH_2CH$_3$), 1.13−1.26 (m, 108H, PCH$_2$CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz): δ 16.3 (s, $^1J_{Pt-P}$ =2307.7 Hz). Anal. Calcd for $C_{264}H_{336}F_{18}N_6O_{51}P_{12}Pt_6S_6$: C, 48.89; H, 5.22; N, 1.30. Found: C, 48.63; H, 5.33; N, 1.19.

3b: yield 10.58 mg (pale yellow solid), 99%; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 8.63 (d, ^3J = 6.0 Hz, 12H; H_α-Py), 7.81 (d, J = 6.3 Hz, 12H; H_β-Py), 7.66 (s, 3H; Ar*H*), 7.59 (s, 6H; Ar*H*), 7.31−7.45 (m, 39H; Ph*H* and Ar*H*), 7.07 (s, 3H; Ph*H*), 6.91−6.94 (m, 18H; Ph*H*), 6.71 (d, ^3J = 1.8 Hz, 6H; Ph*H*), 6.59 (s, 3H; Ph*H*), 5.11 (s, 6H; OCH_2), 5.06 (s, 12H; OCH_2), 4.23 (br, 12H; α-CH_2), 4.14 (br, 12H; α-CH_2), 3.87−3.93 (m, 24H; β-CH_2), 3.77 (br, 24H; γ-CH_2), 1.79−1.83 (m, 72H; PCH_2CH$_3$), 1.13−1.26 (m, 108H, PCH$_2$CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz) δ 16.3 (s, $^1J_{Pt-P}$ = 2308.3 Hz). Anal. Calcd for $C_{306}H_{372}F_{18}N_6O_{57}P_{12}Pt_6S_6$: C, 51.60; H, 5.26; N, 1.18. Found: C, 51.29; H, 5.33; N, 1.12.

3c: yield 12.22 mg (pale yellow solid), 97%; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 8.62 (d, ^3J = 5.7 Hz, 12H; H_α-Py), 7.81 (d, J = 6.3 Hz, 12H; H_β-Py), 7.67 (s, 3H; Ar*H*), 7.59 (s, 6H; Ar*H*), 7.31−7.43 (m, 69H; Ph*H* and Ar*H*), 7.07 (s, 3H; Ar*H*), 6.91−6.94 (m, 18H; Ar*H*), 6.69 (d, ^3J = 2.1 Hz, 18H; Ar*H*), 6.56 (s, 9H; Ar*H*), 5.10 (s, 6H; OCH_2), 5.04 (s, 24H; OCH_2), 5.01 (s, 12H; OCH_2), 4.23 (br, 12H; α-CH_2), 4.14 (br, 12H; α-CH_2), 3.87−3.92 (m, 24H; β-CH_2), 3.77 (br, 24H; γ-CH_2), 1.80−1.82 (m, 72H; PCH_2CH$_3$), 1.12−1.23 (m, 108H, PCH$_2$CH_3); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.4 MHz) δ 16.3 (s, $^1J_{Pt-P}$ = 2309.5 Hz). Anal. Calcd for $C_{390}H_{444}F_{18}N_6O_{69}P_{12}Pt_6S_6$: C, 55.79; H, 5.33; N, 1.00. Found: C, 55.46; H, 5.47; N, 0.98.

3d: yield 15.92 mg (pale yellow glassy solid), 97%; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 8.61 (d, ^3J = 5.7 Hz, 12H; H_α-Py), 7.79(d, J = 6.3 Hz, 12H; H_β-Py), 7.67 (s, 3H; Ar*H*), 7.60 (s, 6H; Ar*H*),

---

(21) (a) Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440–467. (b) Halgren, T. A. *J. Comput. Chem.* **1996**, *17*, 490–519.

7.29−7.41 (m, 129H; Ph*H* and Ar*H*), 7.06 (s, 3H; Ph*H*), 6.91−6.94 (m, 18H; Ph*H*), 6.60−6.71 (m, 45H; Ar*H*), 6.54 (s, 18H; Ar*H*), 5.05 (s, 6H; OCH_2), 5.01 (s, 60H; OCH_2), 4.98 (s, 24H; OCH_2), 4.23 (br, 12H; α-CH_2), 4.14 (br, 12H; α-CH_2), 3.87−3.93 (m, 24H; β-CH_2), 3.78 (br, 24H; γ-CH_2), 1.78−1.81 (m, 72H; PCH_2CH_3), 1.11−1.21 (m, 108H, PCH$_2$CH_3); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 121.4 MHz) δ 16.2 (s, $^1J_{Pt-P}$ = 2306.5 Hz). Anal. Calcd for $C_{558}H_{588}F_{18}N_6O_{93}P_{12}Pt_6S_6\cdot CH_2Cl_2$: C, 60.88; H, 5.39; N, 0.76. Found: C, 60.55; H, 5.48; N, 0.72.

Acknowledgment. H.-B.Y. thanks the NSFC (20902027), Shanghai Pujiang Program (09PJ1404100), Shanghai Shuguang Program (09SG25), Innovation Program of SMEC (10ZZ32), and “the Fundamental Research Funds for the Central Universities” for financial support. P.J.S. thanks the NIH (GM-057052) for financial support. We thank Prof. Mei-Xiang Wang and Dr. Han-Yuan Gong for their help with the calculation of thermodynamic binding constants.

Supporting Information Available: ^{1}H NMR spectra, ^{31}P NMR spectra, and two-dimensional spectra (^{1}H−^{1}H COSY and NOESY) of **3a**−**d**, and experimental data for ^{1}H NMR titration experiments. This material is available free of charge via the Internet at http://pubs.acs.org.