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Self-Assembling Calix[4]arene [2]Catenanes. Preorganization, Conformation, Selectivity, and Efficiency

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A novel class of preorganized U-shape calix[4]arene clefts, dicationic salts **3a**,**c**,**e·2Cl**, **3b·2PF$_6$**, and **3f·2Br**, consisting of one cone calix[4]arene and two bipyridine residues being linked by an aliphatic chain, have been designed and synthesized as precursors for self-assembly of calix[4]-arene [2]catenanes by utilizing π-stacking interactions between the hydroquinone and bipyridinium units. Conformationally flexible **6·2PF$_6$** and cone **10·2Cl**, whose conformation is fixed by two propyloxy groups on the lower rim, were also prepared in order to explore the effects of conformation and hydrogen bonding of the calix[4]arene moiety on self-assembly. For all reactions, bis-*p*-phenylene-34-crown ether-10 (**11**) was employed as the donor component. Alternate cone [2]catenane **13·4Cl** is obtained in 8% yield from reaction of ethylene-incorporating **3a·2Cl** and 1,4-bis-(bromomethyl)benzene (**12a**). Three cone and one conformationally flexible [2]catenanes were obtained in moderate to good yields from reactions of propylene-incorporating **3b·PF$_6$** and **3c·2Cl** with **12a**, 1,3-bis(bromomethyl)benzene (**12b**) or 4,4′-(bromomethyl)biphenyl (**12c**). Both cone and partial cone [2]catenanes were generated in moderate yields from butylene-incorporating **3c·2Cl** with four *tert*-butyl groups on the calix[4]arene moiety and with **12a**. In contrast, only cone [2]-catenane was obtained from similar *tert*-butyl-free cleft **3d·2Cl**. Cone and conformationally flexible [2]catenanes were obtained in moderate yields, respectively, from the reactions of **3d·2Cl** and **3e·2Cl** with **12c**. No catenanes were isolated from reaction of phenylene-incorporating **3f·2Br** or **6·2Cl**, whereas reaction of **10·2Cl** afforded cone [2]catenane in low yield. It was demonstrated that hydrogen bonding, which may be destroyed after catenation, within the calix[4]arene moiety is crucial for efficient self-assembly of the [2]catenanes. The dynamic ^{1}H NMR and absorption spectra and luminescent properties of the [2]catenanes were investigated, which reveal that incorporation of calix[4]arene into the tetracationic cyclophane reduces π-stacking interactions between the donor and acceptor units and catenation has substantial influence on conformational distributions of the calix[4]arene moiety. The results demonstrate the versatility of calix[4]arene derivatives as building blocks in the construction of supramolecular structures.

Introduction

The self-assembly of mechanically interlocked structures[1] such as catenanes and rotaxanes has attracted considerable attention in the field of supramolecular chemistry[2] due not only to their unusual structures but also to their potential applications in new materials and nanoscale molecular devices. Several different noncovalent interactions have been developed for templating the formation of catenanes:[1] (1) π-stacking of electronically complementary aromatic donors and acceptors, (2) chelation of metal cations, (3) hydrogen-bonding interactions between amides, and (4) hydrophobic interactions between cyclodextrins and linear amphiphilic compounds. The first approach, pioneered by Stoddart's group,[3] based on the intermolecular interactions of electron-rich aromatic ethers with electron-poor bipyridinium cations, has been utilized by them and by other groups to construct catenanes of more complicated structures or exhibiting specific properties by changing the donor and/or acceptor components.[4] However, most catenanes generated by this

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(1) (a) Schill, G. *Catenanes, Rotaxanes and Knots*; Academic: New York, 1973. (b) Sauvage, J.-P. *Acc. Chem. Res.* **1990**, *23*, 319. (c) Gibson, H; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, *19*, 843. (d) Amabilino, D. B.; Stoddart, J. F. *Chem Rev.* **1995**, *95*, 2725. (e) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154. (f) Vögtle, F.; Dünnwald, T.; Schmidt, T. *Acc. Chem. Res.* **1996**, *29*, 451. (g) Leigh, D. A.; Murphy, A.; Smart, J. P.; Deleuze, M. S.; Zerbetto, F. *J. Am. Chem. Soc.* **1998**, *120*, 6458. (h) Hunter, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 5303.

(2) (a) Lehn, J.-M. *Supramolecular Chemistry*: *Concepts and Perspectives*; VCH: Weinheim, 1995. (b) *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. V., MacNicol, D. D., Vögtle, F., Eds.; Pergamon: Oxford, U.K., 1996; 11 volumes. (c) Fyfe, M. C. T.; Stoddart, J. *Acc. Chem. Res.* **1997**, *30*, 393.

(3) Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandofi, M. T.; Goodmow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Redington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 193.

(4) (a) Amabilino, D. B.; Anelli, P.-L.; D. B.; Ashton, P. R.; Brown, G. R.; Córdova, E; Godínez, L. A.; Hayes, W.; Kaifer, A. E.; Philp, D; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 11142. (b) Amabilino, D. B.; Dietrich-Buchecker, C. O.; Livoreil, A.; Pérez-García, L.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1996**, *118*, 3905. (c) Barllardini, R.; Balzani, V.; Credi, A.; Brown, C. L.; Gillard, R. E.; Montalti, M.; Philp, D.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, B. J.; Williams, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 12503. (d) Ballardini, R.; Balzani, V.; Gandolfi, M. T.; Gillard, R. E.; Stoddart, J. F.; Tabellini, E. *Chem. Eur. J.* **1998**, *4*, 449. (e) Vögtle, F.; Müller, W. M.; Müller, U.; Bauer, M.; Rissanen, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1295. (f) Gunter, M. J.; Johnston, M. R. *J. Chem. Soc., Chem. Commun.* **1994**, 829. (g) Gunter, M. J.; Hockless, D. C. R.; Johnston, M. R.; Skelton, B. W.;

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approach comprise rigid tetracationic cyclophanes, in which the bipyridinium residues are linked with xylyl or 4,4′-biphenylene.[5] It has been reported that replacing the aromatic linker with a flexible aliphatic spacer will reduce remarkably the efficiency of the π-stacking, due to reduced level of preorganization of the host toward its potential guests.[6] Given that many biological receptors are rather flexible[7] and nonrigid cyclophanes often exhibit an "induced fit" recognition feature,[8] it is necessary to investigate systematically self-assembly processes of catenanes with flexible acceptor cyclophanes. Such investigations should provide new insight into the nature of this important intermolecular interactions. New precursors therefore need be developed in order to improve the efficiency of self-assembly. A possible approach to this end is to employ as precursors preorganized molecular clefts[9] in which the bipyridine residues are linked by a U-shaped spacer.

Calix[4]arenes are a class of phenol−formaldehyde cyclic oligomers which can be functionalized in various ways at the phenolic hydroxyl groups or the *para* positions of the phenolic rings.[10] These approaches can be used separately or in combination; therefore calix[4]-arenes are ideal starting materials for synthesis of various types of receptors for ions and neutral molecules.[10,11] Recently, calix[4]arenes have been used as building blocks for construction of large supramolecular systems with defined structures or functions.[12,13] For example, Rebek has reported that capsules and polymeric capsules could be assembled from calix[4]arene tetraurea

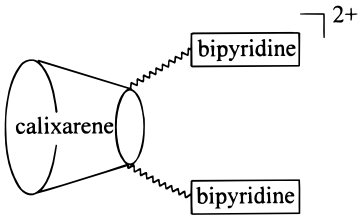


Figure 1. Design scheme for calix[4]arene precursors.

derivatives,[13a−c] whereas Reinhoudt found that bis-(melamine)calix[4]arenes could spontaneously form well-defined box-like assemblies with 5,5-diethylbarburic acid.[13d,e] In all of these systems, the cone conformation of the calix[4]arenes is fixed by substitution at the four phenolic oxygen atoms with bulky substituents. In this paper,[14] we wish to describe (1) the preparation of a novel class of calix[4]arene-derived clefts, (2) the self-assembly and characterization of a new type of calix[4]arene [2]-catenanes, (3) the effect of catenation on the conformational change of the calix[4]arene moiety, and (4) the dynamic NMR spectroscopic properties of the [2]catenanes.

Results and Discussion

Design Considerations. Several classes of molecular clefts or tweezers, in which two functional groups are covalently linked by a single spacer unit, have been developed as receptors. These preorganized molecules can complex or recognize organic molecules of appropriate size and length much more efficiently than the related flexible podands.[15] The overall aspect of such molecules is their U-shape. Since self-assembly of catenanes needs efficient π-stacking between electronically complementary aromatic ethers and bipyridiniums, it is anticipated that incorporating two bipyridine units into a U-shaped precursor might promote the formation of the corresponding catenanes, if the precursor is designed to make an appropriate spatial separation between the two bipyridine units. Although the above-mentioned U-shaped backbones, in principle, could be utilized to self-assemble the corresponding catenanes, we chose cone calix[4]arene derivatives to generate our cleft precursors (Figure 1).[16] The use of cone calix[4]arenes for building molecular

White, A. H. *J. Am. Chem. Soc.* **1994**, *116*, 4810. (h) Li, Z.-T.; Stein, P. C.; Becher, J.; Jensen, D.; Mörk, P.; Svenstrup, N. *Chem. Eur. J.* **1996**, *2*, 624. (i) Li, Z.-T.; Becher, J. *Chem. Commun.* **1996**, 639. (j) Li, Z.-T.; Becher, J. *Synlett* **1997**, 557.

(5) For examples of other aromatic linkers, see: (a) Hamilton, D. G.; Feeder, N.; Prodi, L.; Teat, S. J.; Clegg, W.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1998**, *120*, 1096. (b) Benniston, A. C.; Mackie, P. R.; Harriman, A. *Tetrahedron Lett.* **1997**, *38*, 3577. (c) Asakawa, M.; Ashton, P. R.; Boyd, S. E.; Brown, C. L.; Menzer, S.; Pasini, D.; Stoddart, J. F.; Tolley, M. S.; White, A. J. P.; Williams, D. J.; Wyatt, P. G. *Chem. Eur. J.* **1997**, *3*, 463. (d) Ashton P. R.; Boyd, S. E.; Menzer, S.; Pasini, D.; Raymo, F. M.; Spencer, N.; Stoddart, J. F.; White, A. J. P.; Williams, D. J.; Wyatt, P. G. *Chem. Eur. J.* **1998**, *4*, 299. (e) Gillard, R. E.; Raymo, F. M.; Stoddart, J. F. *Chem. Eur. J.* **1997**, *3*, 1933.

(6) (a) Ashton, P. T.; Iriepa, I.; Reddington, M. V.; Spencer, N.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Tetrahedron Lett.* **1994**, *35*, 4835. (b) Ashton, P. R.; Boyd, S. E.; Claessens, C. G.; Gillard, R. E.; Stoddart, J. F.; Tolley, M. S.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1997**, *3*, 788.

(7) (a) Dugas, H. *Bioorganic Chemistry: A Chemical Approach to Enzyme Action*; Springer-Verlag: New York, 1989. (b) Suckling, C. J. *Enzyme Chemistry: Impact and Implicitions*, 2nd ed.; Chapman and Hall: London, New York, 1990. (c) Krogsgard-Larson, P. A. *A Textbook of Drug Design and Development*; Harwood Academic: Switzerland, 1991; pp 419−428.

(8) (a) Diederich F. *Cyclophanes*; Royal Society of Chemistry: Cambridge, 1990. (b) Vögtle, F. *Cyclophan Chemie*; Teubner-Stuttgart, 1990. (c) Gavin, J. A.; Deng, N.; Alcalà, M.; Mallouk, T. E. *Chem. Mater.* **1998**, *10*, 1937. (d) Garcia, M. E.; Gavin, J. A.; Deng, N.; Andrievsky, A. A.; Mallouk, T. E. *Tetrahedron Lett.* **1996**, *37*, 8313. (e) Anderson, S.; Aplin, R. T.; Claridge, T. D. W.; Goodson, T., III; Maciel, A. C.; Rumbles, G.; Ryan, J. F.; Anderson, H. L. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2383. (f) Marti, T.; Peterson, B. R.; Fürer, A.; Mordasini-Denti, T.; Zarske, J. Jaun, B.; Diederich, F.; Gramlich, V. *Helv. Chim. Acta* **1998**, *81*, 109. (g) Wallimann, P.; Mattei, S.; Seiler, P.; Diederich, F. *Helv. Chim. Acta* **1997**, *80*, 2368. (h) Zhu, S. S.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 12568.

(9) (a) Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 245. (b) Zimmerman, S. C. *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1993; Vol. 165, p 71.

(10) (a) Gutsche, C. D. *Calixarenes*; RSC: Cambridge, 1989. (b) Gutsche, C. D. *Aldrichimica Acta* **1995**, *28*, 3. (c) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713.

(11) Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713.

(12) (a) Conn, M. M.; Rebek, J., Jr. *Chem. Rev.* **1997**, *97*, 1647. (b) Rebek, J., Jr. *Chem. Soc. Rev.* **1996**, 255.

(13) (a) Castellano, R. K.; Rudkevich, D. M.; Rebek, J., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 7132. (b) Shimizu, K. D.; Rebek, J., Jr. *Proc.Natl. Acad. Sci. U.S.A.* **1995**, *92*, 12403. (c) Hamann, B. C.; Shimizu, K. D.; Rebek, J., Jr. *Angew. Chem, Int. Ed. Engl.* **1996**, *35*, 1326. (d) Timmerman, P.; Vreekamp, R. H.; Hulst, R.; Verboom, W.; Reinhoudt, D. N.; Rissanen, K.; Udachin, K. A.; Ripmeester, J. *Chem. Eur. J.* **1997**, *3*, 1823. (e) Calama, M. C.; Hulst, R.; Fokkens, R.; Nibbering, N. M. M.; Timmerman, P.; Reinhoudt, D. N. *Chem. Commun.* **1998**, 1021. (f) Vreekamp, P. H.; Verboom, W.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 363.

(14) Li, Z.-T.; Ji, G.-Z.; Yuan, S.-D.; Ding, H.; Du, A.-L.; Wei, M. *Tetrahedron Lett.* **1998**, *39*, 6517.

(15) (a) Conn, M. M.; Deslongchamps, G.; de Mendoza, J.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 3548. (b) Jeong, K. S.; Tjivikua, T.; Wolfe, J. Rebek, J., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 201. (c) Zimmerman, S. C.; VanZyl, C. M.; Hamilton, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 1373. (d) Li, C.; Medina, J. C.; Maguire, G. E. M.; Abel, E.; Atwood, J. L.; Gokel, G. W. *J. Am. Chem. Soc.* **1997**, *119*, 1609. (e) Chen, C.-W.; Whitlock, H. W. *J. Am. Chem. Soc.* **1978**, *100*, 4921.

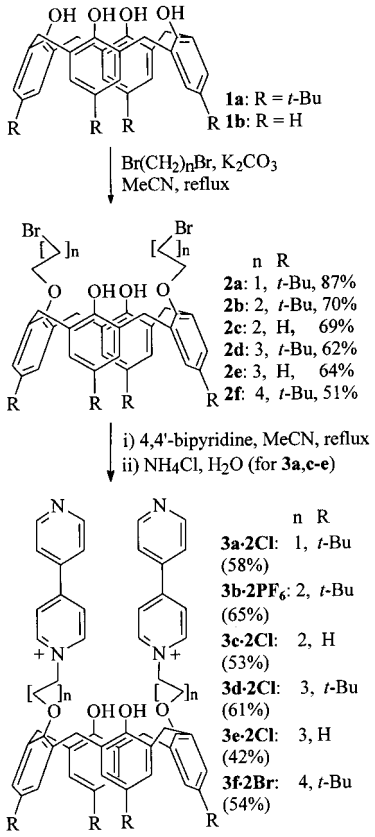
(16) (a) Ulrich, G.; Ziessel, R.; Manet, I.; Guardigli, M.; Sabbatini, N.; Fraternali, F.; Wipff, G. *Chem. Eur. J.* **1997**, *3*, 1815. (b) Beer, P. D.; Martin, J. P.; Drew, M. G. B. *Tetrahedron* **1992**, *48*, 9917. (c) Grigg, R.; Holmes, J. M.; Jones, S. K.; Amilaprasadh Norbert, W. D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 185. (d) Beer, P. D.; Chen, Z.; Goulden, A. J.; Grieve, A.; Hesek, D.; Szemskj, F.; Wear, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1269. (e) Regnouf de Vains, J.-B.; Lamartine, R. *Tetrahedron Lett.* **1996**, *37*, 6311.

clefts has several advantages. First, the cone calix[4]arene moiety can efficiently provide the resulting molecule with the desired U-shape, in which the two bipyridine units can be positioned in parallel planes. Thus, the stacking interactions between them and the electronically rich hydroquinone units of the crown ether component can, in principle, be augmented. Second, the cone conformation of calix[4]arene can be fixed conveniently either by simple 1,3-disubstitution or further tetrasubstitutation of the hydroxyl groups at the lower rim with appropriate substrates by using standard calix[4]arene synthetic chemistry. Third, by changing the aliphatic chains linking the calix[4]arene and bipyridine units, a variety of precursors with different spatial separations between the bipyridine units can be constructed. An additional consideration is that calix[4]arenes readily undergo chemical modifications and all conformational isomers can be selectively prepared according to reported procedures. Therefore, a systematic investigation of the effects of various factors, such as hydrogen bonding, spatial hindrance, flexibility, and conformational change, on the self-assembly of catenanes might be made possible.

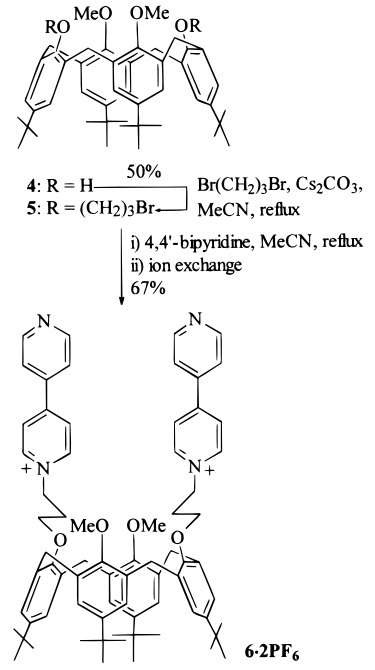
Synthesis of Calix[4]arene Precursors. To investigate the structure−efficiency relationship of self-assembly of calix[4]arene catenanes, we synthesized eight bis(pyridine)calix[4]arene precursors, i.e., **3a·2Cl**, **3b·2PF$_6$**, **3c−e·2Cl**, **3f·2Br**, **6·2PF$_6$**, and **10·2Cl**. The first six compounds are all in cone conformations due to the presence of intramolecular hydrogen bondings between the hydroxyl and oxy groups of the calix[4]arene moiety. **6·2PF$_6$** is conformationally flexible as a result of rapid interconversion of the methoxyl-substituted benzenes, while the cone conformation of **10·2Cl** is fixed because of the propyl groups preventing internal rotations of the calix[4]arene macrocycle.[17] For all of these compounds, the calix[4]arene and bipyridine units are linked with polymethylene chains. Molecular modeling indicated that the bipyridine units of these compounds could reach a separation of 7 Å, which is optimal for effective stacking interactions,[3] by adjusting the relative position of the benzenes of the calix[4]arene moiety.

The syntheses are relatively straightforward, requiring only two-step procedures starting from readily available materials. Thus, alkylation of *p-tert*-butylcalix[4]arene (**1a**) or calix[4]arene (**1b**) with an excess of the respective α,ω-dibromides was carried out in MeCN in the presence of potassium carbonate as a base. Dibromides **2a−f** were obtained in yields ranging from 51 to 87% (Scheme 1). Subsequent reactions of **2a−f** with an excess of 4,4′-bipyridine were also carried out in MeCN at reflux. The corresponding dicationic compounds **3a−f** were isolated as the chloride, hexafluorophosphate, or bromide salts, respectively, in yields ranging from 42 to 65% after column chromatography.[18] Two methods were used to synthesize conformationally flexible **5** (Scheme 2). Reaction of dimethoxycalix[4]arene (**4**) with an excess of 1,3-dibromopropane in THF in the presence of sodium hydride as a base yielded dibromide **5** in 42% yield.

Scheme 1



Scheme 2

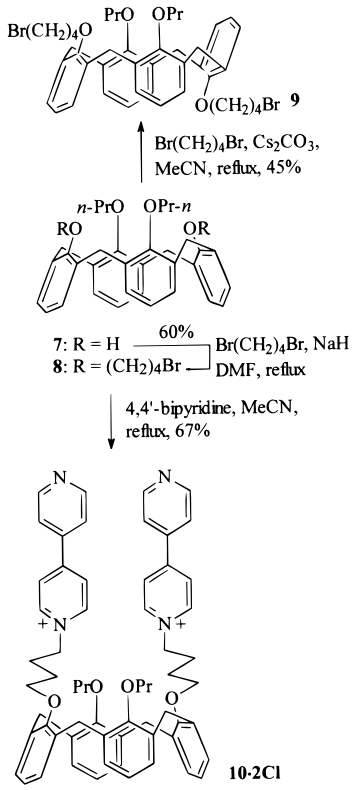


Alternatively, using cesium carbonate as the base and MeCN as solvent, **5** could be obtained in 50% yield after workup. Compound **6·2PF$_6$** was prepared in 67% yield after column chromatography and counterion exchange by treating **5** with an excess of bipyridine in refluxing acetonitrile. The synthetic route for **10·2Cl** is shown in Scheme 3. First, the cone conformer **8** was selectively obtained in a yield of 60% from the reaction of compound **7** with an excess of 1,4-dibromobutane using sodium

(17) The propyl group is the smallest alkyl which can suppress the ring inversion, see: Iwamoto, K.; Araki, K.; Shinkai, S. *J. Org. Chem.* **1991**, *56*, 4955.

(18) The dichlorides and the catenanes in the form of tetrachlorides described in this paper have poor water solubility and could be separated from ammonium chloride, after chromatography, by simply washing thoroughly with water. Therefore, it is not necessary to convert them to the corresponding phosphates as usually.

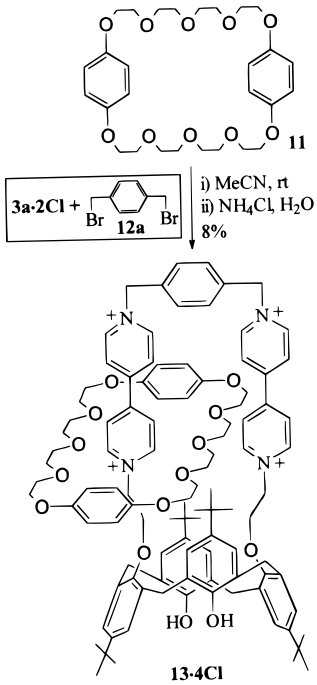
Scheme 3



hydride as a base.[19] Treatment of **8** with an excess of bipyridine in refluxing MeCN afforded **10·2Cl** in 67% yield. Unexpectedly, the attempt to synthesize the 1,3-alternate conformer of **10·2Cl** by the reaction of **7** with an excess of 1,4-dibromobutane in MeCN using cesium carbonate as the base, which is the standard reaction condition for preparing this conformation of calix[4]-arenes,[20] mainly resulted in the formation of partial cone compound **9** in 45% yield, together with a small amount of **8** (12%). None of the 1,3-alternate product was isolated, and consequently no related dicationic compound of 1,3-alternate conformation was prepared. The cone conformation of compounds **2a**−**f**, **3a·2Cl**, **3b·2PF$_6$**, **3c**−**e·2Cl**, **3f·2Br**, and **10·2Cl** were easily inferred from their ^{1}H NMR spectra, in which $ArCH_2Ar$ protons exhibit the typical AX system of a fixed cone conformation.[21] The partial cone conformation of **9** was determined on the basis of its ^{1}H and ^{13}C NMR spectra.[21]

[2]Catenanes by Self-Assembly. Catenations were performed under the reaction conditions reported by Stoddart.[3] Thus, when a solution of *p*-bis(bromomethyl)-benzene (**12a**), **3a·2Cl**, and an excess of bis(*p*-phenylene)-34-crown-10 (**11**) in MeCN was stirred at room temperature for 14 days, [2]catenane **13·4Cl** in a fixed 1,3-alternate conformation was obtained in 8% yield after column chromatography (Scheme 4). Although **3a·2Cl** is fixed in the cone conformation, no cone [2]catenane was

Scheme 4



isolated from this reaction. Self-assembly of calix[4]arene catenanes was achieved most efficiently from **3b·2PF$_6$** and **3c·2Cl**, in which the calix[4]arene and bipyridine units are linked with propylene chains. Thus, reaction of **3b·2PF$_6$** and **12a** in the presence of an excess of **11** in MeCN resulted in the formation of cone [2]catenane **14a·4PF$_6$** in 43% yield after 10 days. No catenanes of other conformations were obtained. When the same reaction was carried out in DMF, **14a·4PF$_6$** could be obtained in higher yield (51%). An analogous reaction, employing *m*-bis(bromomethyl)benzene (**12b**) as a linker to build the cyclophane, led to cone [2]catenane **14b·4Cl** in 33% yield (Scheme 5). Replacing **12a** with the "extended" spacer 4,4′-bis(bromomethyl)biphenyl (**12c**), under similar reaction conditions, resulted in the formation of conformationally flexible [2]catenane **14c·4Cl** in 22% yield after 14 days. No [3]catenanes in which two crown ether rings are threaded simultaneously through the tetracationic cyclophane were isolated from the reaction.[22] Starting from compound **3c·2Cl**, cone [2]catenane **15·4Cl** could be obtained in 49% yield after 10 days (Scheme 6). When DMF was used as the solvent, the same reaction afforded **15·4Cl** in 53% yield. As in the reaction yielding **14a·4PF$_6$**, no catenanes of other conformations were isolated from this reaction. It was reported that [3]catenanes could be generated in very low yields from the aliphatic nucleophilic reaction of less rigid dicationic salts with 1,4-bis(bromoethoxy)benzene in the presence of several appropriate crown ethers.[6b] Therefore, another possible route, i.e., utilizing the reaction of **16·2PF$_6$** and **2c** to build the tetracationic cyclophane of **15·4Cl**, was also investigated. Stirring a solution of **16·2PF$_6$**, **2c**, and an excess **11** in MeCN at room temperature for 5 weeks did not result in the formation of any **15·4Cl**, as detected by TLC. However, when the temperature was increased

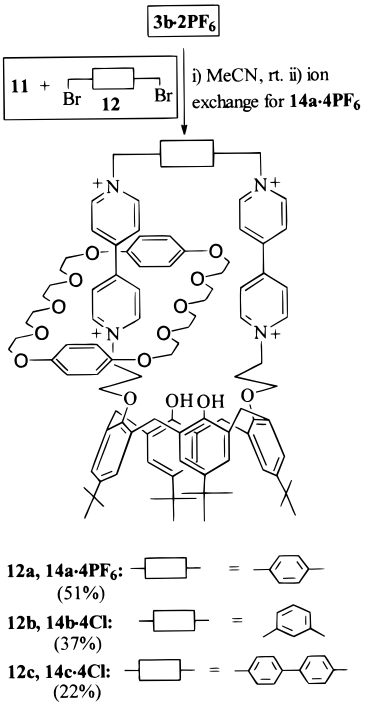
(19) Groenen, L. C.; Ruel, B. H.; Casnati, A.; Timmerman, P.; Verboom, W.; Harkema, S.; Pochini, A.; Ungaro, R.; Reinhoudt, D. N. *Tetrahedron Lett.* **1991**, *32*, 2675.

(20) (a) Verboom, W.; Datta, S.; Asfari, Z.; Harkema, S.; Reinhoudt, D. N. *J. Org. Chem.* **1992**, *57*, 5394. (b) Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M.-J.; Egberink, R. J. M.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 2767. (c) Ikeda, A.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 3102. (d) Ikeda, A.; Tsudera, T.; Shinkai, S. *J. Org. Chem.* **1997**, *62*, 3568.

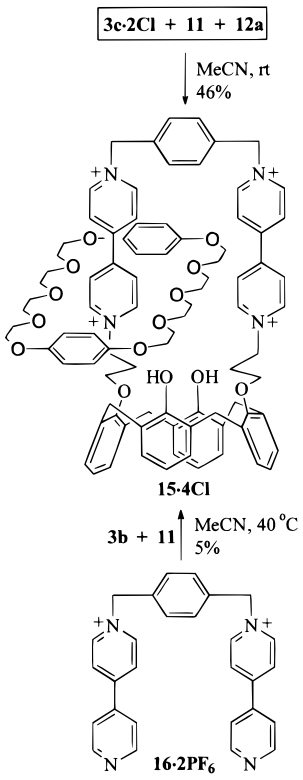
(21) Molins, M. A.; Nieto, P. M.; Sanchez, C.; Prodos, P.; de Mendoza, J.; Pons, M. O. *J. Org. Chem.* **1992**, *57*, 6924.

(22) Amabilino, D. B.; Ashton, P. R.; Brown, C. L.; Córdova, E; Gonínez, L. A.; Goodnow, T. T.; Kaifer, A. E.; Newton, S. P.; Pietraszkiewicz, M.; Philp, D; Raymo, F. M.; Reder, A. S.; Rutland, M. T.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 1271.

Scheme 5

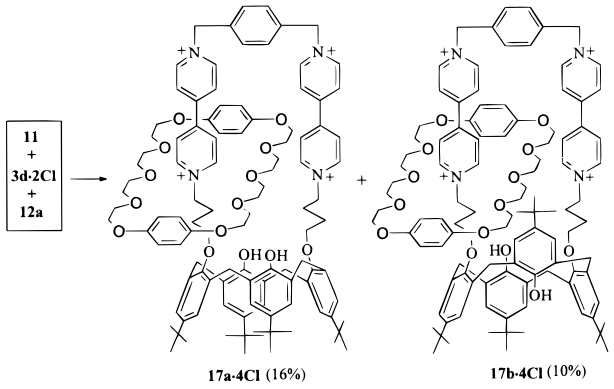


Scheme 6

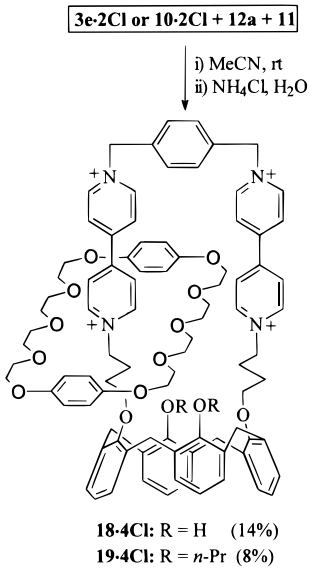


to 40 °C, the reaction yielded **15·4Cl** albeit in a low yield of 5% after 21 days (Scheme 6). The low yield might be rationalized in terms of the large flexibility of **2c**. Under the same reaction conditions as described above for self-assembling [2]catenane **15·4Cl**, the reaction of conformationally flexible dicationic salt **6·2PF$_6$** with **12a** in the presence of an excess of **11** did not result in the formation of expected [2]catenanes but gave only insoluble solid residue.

Scheme 7

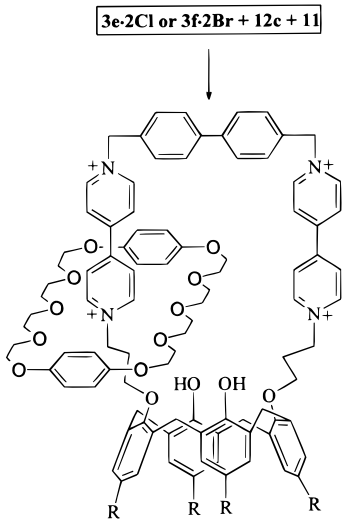


Scheme 8



Dicationic salts **3d·2Cl** or **3e·2Cl** incorporating longer tetramethylene chains could also be used as precursors to build calix[4]arene catenanes, although the yields of catenanes were reduced considerably. Thus, when **3d·2Cl** was reacted with **12a** in MeCN in the presence of an excess of crown ether **11** at room temperature for 10 days, [2]catenane **17·4Cl** was generated in 26% yield as a mixture of cone **17a·4Cl** and partial cone **17b·4Cl**. Both **17a·4Cl** and **17b·4Cl** are stable at room temperature and do not interconvert, but they could not be separated (Scheme 7). In contrast, an analogous reaction starting from the debutylated dicationic salt **3e·2Cl** afforded cone [2]catenane **18·4Cl** in 22% yield selectively (Scheme 8), but no partial cone [2]catenane was isolated. Although **10·2Cl** is also in the cone conformation, its reaction with **12a** in MeCN in the presence of an excess of **11** at room temperature for 21 days afforded cone [2]catenane **19·4Cl** but only in a low yield of 8%. When **3d·2Cl** was treated with dibromide **12c** in the presence of **11** in MeCN at room temperature for 14 days, cone [2]catenane **20·4Cl** was obtained in 18% yield (Scheme 9). However, the reaction of **3e·2Cl**, **12c**, and **11** under similar conditions resulted in the formation of [2]catenane **21·4Cl** (12%) as a mixture of conformationally stable isomers which could not be separated (Scheme 9). No catenanes were isolated from the reactions of **3f·2Br** incorporating two pentamethylene chains with dibromides **12a** **12b**, and **12c** in the presence of **11**. Only insoluble solid

Scheme 9



20·4Cl: R = H (20%)
21·4Cl: R = *t*-Bu (12%)

residues were obtained. It is noteworthy that no corresponding tetracationic cyclophanes were isolated and attempts to use templating threadlike molecules incorporating hydroquinone rings to prepare these cyclophanes only resulted in the formation of insoluble linear residues.[23]

The results which are reported herein reveal that self-assembly of the calix[4]arene [2]catenanes was influenced and controlled by various factors including hydrogen bonding, the presence or absence of upper rim *tert*-butyl groups and conformational flexibility of the calix[4]arene moiety, the length of the aliphatic chains linking the bipyridine and calix[4]arene units, and the nature of the aromatic spacers. Possibly because the ethylene chains linking the calixarene and bipyridine units are not able to provide enough spatial separation between the two bipyridiniums, catenation of **3a·2Cl**, i.e., the crown ether component being locked within the calix[4]arene tetracationic cyclophane, destroys the hydrogen bonding within the hydroxyl and alkoxy oxygen groups of the cyclophane. Consequently, the calix[4]arene moiety of **13·4Cl** exists in a 1,3-alternate conformation, which renders the tetracationic cyclophane a larger cavity. The low yield of [2]catenane **13·4Cl** also reveals that the π-stacking between the hydroquinone and bipyridinium units was rather inefficient after the first substitution occurred to form the tricationic intermediate. The fact that the reaction of conformationally flexible **6·2PF$_6$** did not yield catenanes indicates that the cone conformation of the calix[4]arene moiety is indispensable. This observation is not surprising, since it can be envisioned that the two bipyridine cations in **6·2PF$_6$** may prefer to stay away from each other as a result of electrostatic repulsion. This repulsion might be canceled out by the hydrogen bonding within the calix[4]arene moiety of other dicationic precursors. The lower yield of [2]catenane **19·4Cl**, relative to that of **18·4Cl**, is rationalized by considering the following factors. First, the hydrogen bonding between the hydroxyl groups of the calix[4]arene moiety and the oxygen groups of the crown ether component may promote the formation of **18·4Cl**, a factor which can be confirmed by ^{1}H NMR NOE (vide infra). Second, the tetramethylene chains of **10·2Cl** are more flexible than those of **3e·2Cl** due to lack of hydrogen bondings at the lower rim of its calix[4]arene moiety. Third, the two propyl groups in **10·2Cl** may have some spatial interaction with the crown ether ring, which could reduce the efficiency of π-stacking. The fact that [2]catenanes **14a·4PF$_6$**, **14b·4Cl**, and **15·4Cl** are all in the cone conformation implies that the spatial separation between the bipyridinium units are optimal and, hence, there is no large strain within the tetracationic cyclophane. The *tert*-butyl groups on the calix[4]arenes do not have significant influences on the self-assembling efficiency but remarkably affect the conformational distribution of the corresponding [2]catenanes, probably due to the spatial interactions within them and between them and the crown ether component when the calix[4]arene moiety assumes a partial cone or 1,3-alternate conformation. The results also reveal that propylene-incorporating **3b·2PF$_6$** and **3c·2Cl** as molecular clefts are the most efficient. It is expected that incorporating longer aliphatic chains will increase their flexibility and weaken and even cancel the effect of the corresponding dicationic salts as molecular clefts. Therefore, the effects of butylene-incorporating **3d·4Cl** and **3e·4Cl** as clefts are reduced considerably, whereas **3e·4Cl** does not yield any catenanes.

(Dynamic) ^{1}H NMR Spectroscopy. The structures of the calix[4]arene [2]catenanes were characterized by ^{1}H NMR and, wherever possible, ^{13}C NMR spectra. The 1,3-alternate conformation of **13·4Cl** was inferred from the ^{1}H NMR spectrum, which exhibits an AM system (δ 3.88, 3.81 ppm) for the bridging methylene protons of the calix[4]arene moiety, and ^{13}C NMR spectrum, which shows the characteristic signal (δ 38.3 ppm) for *anti*-oriented nuclei in the calix[4]arene.[21,24] The cone conformations of [2]catenanes **14a·4PF$_6$** **14b·4Cl**, **15·4Cl**, **18·4Cl**, **19·4Cl**, and **20·4Cl** were easily determined by their ^{1}H NMR spectra, which all show the characteristic AM system of ArCH$_2$Ar protons of the cone calix[4]arene moiety. The ^{1}H NMR spectrum of [2]catenane **14c·4Cl** is composed of broad peaks in all regions, indicating that it is a mixture of conformational isomers which are in rapid equilibrium. The ^{1}H NMR spectrum of **17·4Cl** reveals that it is a mixture of two conformational isomers, cone **17a·4Cl** and partial cone **17b·4Cl**, with a ratio of ca. 3:2 (based on the integral intensities). The two isomers are kinetically stable or at least interconvert to each other slowly in solution at room temperature, since the ^{1}H NMR spectrum exhibits two sets of sharp signals. Assignments were made on the basis of the chemical shifts and integrated strengths of the calix[4]arene protons in a combination of 2D-COSY and NOESY spectra.[21] The^{1}H NMR spectrum of **21·4Cl** is composed of overlapped sharp signals and therefore cannot give useful information.

The resonances of the [2]catenanes were assigned using a combination of 2D-COSY 45 and 2D-NOESY 45 spectroscopy. NOE interactions were observed both within the tetracationic cyclophane and between the tetracation and the crown ether protons, confirming the inclusion of the hydroquinone ring within the tetracationic cyclophane. The interaction between the hydroxyl and the

(23) Capobianchi, S.; Doddi, S.; Ercolani, G.; Keyes, J. W. Mencarelli, *J. Org. Chem*. **1997**, *62*, 7015.

(24) Ghidini, E.; Ugozzoli, F.; Ungaro, R.; Harkema, S.; El-Fadi, A. A.; Reinhoudt, D. N. *J. Am. Soc. Chem*. **1990**, *112*, 6979.

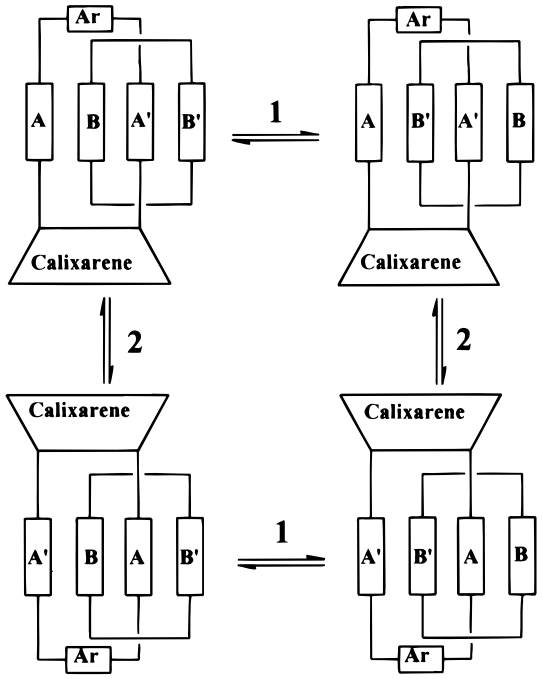


Figure 2. Dynamic processes with the calix[4]arene [2]-catenanes.

ethylene protons of the crown ether was also exhibited, implying that hydrogen bonds may form between the hydroxy protons and the oxygens of the crown ether. Such an interaction is not observed when using CD_3OD as the solvent, as a result of the stronger solvation.

The solution-state properties of the calix[4]arene [2]-catenanes have also been investigated by means of variable-temperature ^{1}H NMR spectroscopy. The kinetic and thermodynamic data associated with the dynamic processes (Figure 2) taking place in the [2]catenanes are listed in Table 1.[25] The kinetic and thermodynamic parameters for passage of the crown ether component through the cavity of the tetracationic cyclophane component (Process 1, Figure 2) reveal that the activation barrier to this process is decreased markedly upon introduction of calix[4]arene into the skeleton of the tetracationic cyclophane of the "parent" [2]catenane **22·4PF$_6$** (Figure 3). This result implies that the strength of the donor−acceptor interactions within these calix[4]-arene [2]catenanes is reduced, which is attributable to the less rigid calix[4]arene tetracationic cyclophane, relative to the "parent" cyclophane in **22·4PF$_6$**. The second process (Figure 2), i.e., swinging of the tetracationic cyclophane around the "inside" hydroquinone ring of the crown ether component (the circumrotation of the tetracationic cyclophane through the cavity of the crown ether ring is restricted obviously by the bulky calix[4]-arene moiety), which leads to exchange of bipyridinium subunits B and B′ between positions inside and alongside the crown ether ring, was also observed for [2]catenanes **14a·4PF$_6$**, **14b·4Cl**, **15·4Cl**, **17a·4Cl**, and **17b·4Cl**. No coalescence temperature for this process was observed for [2]catenanes **13·4Cl**, **18·4Cl**, **19·4Cl**, and **20·4Cl** due to signal overlap or broadening. Although the α-protons of the pyridines attached to the aliphatic chains of **14a·4PF$_6$**, **14b·4Cl**, and **17b·4Cl** were also overlapped or broadened, the coalescence temperature of the corresponding α-proton resonances were observed for [2]-catenanes **15·4Cl** and **17a·4Cl**.

Significant changes were also observed in the ^{1}H NMR spectra of these calix[4]arene [2]catenanes above room temperature. Over the temperature range between room temperature and 100 °C, changes in chemical shifts were exhibited, but no signals of any new conformational isomers emerged. At higher temperature, conformational isomerization of the calix[4]arene moiety in some of these [2]catenanes might occur (Figure 4). For example, upon warming a solution of **15·4Cl** (in DMSO-d_6) up to about 100 °C, a new set of signals began to emerge, which could be attributed to those of the partial cone conformer, according to the typical signals for the aromatic protons of the calix[4]arene moiety. The signals of the 1,3-alternate conformer emerged at 110 °C. Percentages of partial cone and 1,3-alternate conformers increased with the temperature, and the equilibrium constants for the interconversion between the three isomers were calculated directly from the integral intensities of the bipyridinium α-protons. **15·4Cl** decomposed gradually at 130 °C. On lowering the temperature, the signal intensities of the 1,3-alternate and partial cone conformers decreased gradually, indicating that these two isomers were converted to the more stable one. As was found in [2]-catenane **15·4Cl**, conversion of **14a·4PF$_6$**, **14b·4Cl**, and **18·4Cl** to other conformers and interconversion of **17a·4Cl** and **17b·4Cl** were also observed starting at different temperatures. No such conformational isomerization took place in **13·4Cl** and **20·4Cl** even when their solutions in DMSO-d_6 were heated to the temperature at which they decomposed. Since no broadening of the resonances in the ^{1}H NMR spectra was observed, the conformational interconversions of the calix[4]arene moieties in these [2]-catenanes were slow on the ^{1}H NMR time scale after the equilibria were achieved. The K_{eq} values and the related free energies ($\Delta G°$) are listed in Table 2, and the derived enthalpies and entropies are reported in Table 3. The results show that the equilibrium position between the conformational isomers is mainly entropically driven over the temperature range studied. Due to their instability at higher temperature, no corresponding enthalpy and entropy values were obtained for other [2]catenanes. The ^{1}H NMR spectrum of **14c·4Cl** did not become sharp either below (to −50 °C) or above (to 130 °C) room temperature, indicating that the conversions of the isomers to each other are rapid on the ^{1}H NMR time scale. Within the above temperature range, no useful information was given by the ^{1}H NMR spectra of **21·4Cl**. It is noteworthy that no conformational isomerization was observed for the conformationally fixed calix[4]arene ionic precursors, probably because there is no obvious steric strain within the calix[4]arene moiety. Unfortunately, no comparisons could be made with the free calix-[4]arene tetracationic cyclophanes because of their unavailability.

Absorption Spectra and Luminescence Properties. The calix[4]arene [2]catenanes contain several chromophoric units, i.e., aromatic rings of the calix[4]-arene moiety, bipyridinium units, and macrocyclic aromatic ethers. A summary of their absorption data is

(25) The coalescence method (Sandstroom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; Chapter 6) uses the expression $K_c = \pi(\Delta\nu)/2^{1/2}$ to approximate the rotation rate at the coalescence temperature T_c, where $\Delta\nu$ is the limiting chemical shift difference (Hz) between coalescing signals in the absence of exchange. Free energy of activation ΔG_c was then determined with the Eyring equation.

Table 1. Kinetic and Thermodynamic Parameters for the Proposed Processes 1 and 2 of Figure 2 Obtained from the Temperature-Dependent 400 MHz ^{1}H NMR Spectra Recorded on Some Calix[4]arene [2]Catenanes by the Coalescence Method

catenane	probe protons	$\Delta\nu$ (Hz)[a]	k_c (s^{-1})	T_c (K)	$\Delta G^{\ddagger}$ (kcal mol^{-1})	process[b]	solvent
13·4Cl	OC_6H_4O	935	2080	230	10.1	1	CD_3OD/CD_3CN
14a·4PF$_6$	OC_6H_4O	1120	2405	228	10.0	1	CD_3OD
	α-CH[c]	40	90	232	11.7	2	CD_3OD
14b·4Cl	OC_6H_4O	900	1995	235	10.4	1	CD_3OD
	α-CH[c]	45	100	238	11.9	2	CD_3OD
15·4Cl	OC_6H_4O	970	2150	243	10.7	1	CD_3OD
	α-CH[c]	60	130	233	11.5	2	CD_3OD
	α-CH[d]	70	160	250	12.3	2	C_3OD
	$^+NCH_2$[e]	25	55	248	12.7	2	CD_3OD
17a·4Cl	OC_6H_4O	925	2050	238	10.5	1	CD_3OD
	α-CH[c]	90	195	248	12.1	2	CD_3OD
	α-CH[d]	40	85	233	11.8	2	CD_3OD
17b·4Cl	OC_6H_4O	925	2050	238	10.5	1	CD_3OD
	α-CH[c]	50	105	228	11.4	2	CD_3OD
18·4Cl	OC_6H_4O	960	2130	230	10.1	1	CD_3OD
19·4Cl	OC_6H_4O	720	1600	228	10.2	1	CD_3OD/CD_3CN
20·4Cl	OC_6H_4O	840	1060	235	10.4	1	CD_3OD
22·4PF$_6$[f]	OC_6H_4O	678	1505	354	15.6	1	CD_3CN
22·4PF$_6$[f]	α-CH	74	165	250	12.0	2	CD_3OCD_3

[a] The errors are 10%. [b] Shown in Figure 2. [c] Protons relate to the pyridine attached to the xylyl spacer. [d] Protons relate to the pyridine attached to the aliphatic chains. [e] Protons relate to the methylene groups of the xylyl spacer. [f] Data cited from ref 3 for comparison.

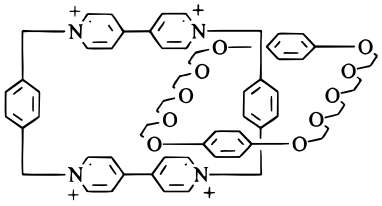


Figure 3. The structure of the "parent" [2]catenane **22·4PF$_6$**.

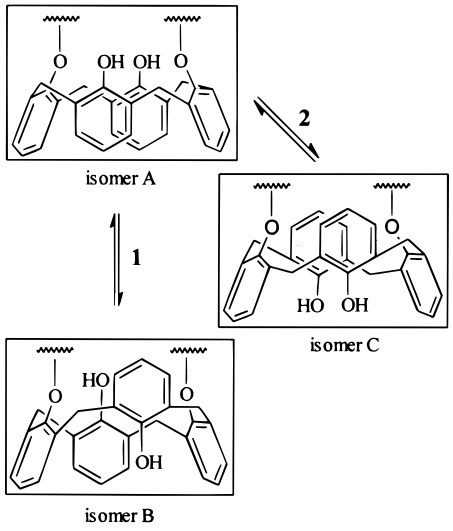


Figure 4. Conformational isomerization of calix[4]arene [2]-catenanes.

Table 2. Equilibrium Constants K_{eq}[a] and Related Free Energies $\Delta G°$ at Given Temperatures Associated with the Equilibrium between the Isomers A and B or C of Some Calix[4]arene [2]Catenanes

catenane	T (K)	K_{eq}	$\Delta G°$ (kcal mol^{-1})	process[b]
14a·4PF$_6$	383	0.20 ± 0.04	1.22 ± 0.13	1
	388	0.28 ± 0.06	0.99 ± 0.14	1
	393	0.41 ± 0.05	0.70 ± 0.09	1
	403	0.90 ± 0.10	0.08 ± 0.05	1
14b·4Cl	373	0.22 ± 0.03	1.12 ± 0.09	1
	383	0.33 ± 0.03	0.84 ± 0.06	1
	388	0.39 ± 0.03	0.72 ± 0.06	1
	393	0.51 ± 0.04	0.53 ± 0.06	1
	403	0.75 ± 0.05	0.23 ± 0.05	1
	403	0.15 ± 0.02	1.52 ± 0.10	2
15·4Cl	373	0.15 ± 0.03	1.41 ± 0.15	1
	383	0.27 ± 0.04	0.99 ± 0.10	1
	388	0.39 ± 0.04	0.73 ± 0.10	1
	393	0.52 ± 0.05	0.46 ± 0.05	1
	398	0.70 ± 0.06	0.28 ± 0.04	1
	403	0.92 ± 0.10	0.07 ± 0.02	1
	383	0.18 ± 0.04	1.31 ± 0.14	2
	388	0.23 ± 0.05	1.13 ± 0.14	2
	393	0.36 ± 0.05	0.80 ± 0.10	2
	398	0.50 ± 0.06	0.55 ± 0.08	2
	403	0.67 ± 0.08	0.32 ± 0.08	2
17·4Cl	403	0.89 ± 0.05	1.30 ± 0.20	1
18·4Cl	403	0.45 ± 0.05	0.64 ± 0.08	1

[a] Defined by the equations K_{eq} = [isomer B/[isomer A] for process 1 and K_{eq} = [isomer C]/[isomer A] for process 2. [b] Shown in Figure 4.

Table 3. Enthalpies and Entropies Associated with the Isomerizations of Some Calix[4]arene [2]Ccatenanes, Obtained from the Temperature Dependence of K_{eq} in Table 2

catenane	$\Delta H°$ (kcal mol^{-1})	$\Delta S°$ (cal mol^{-1} K^{-1})	process[a]
14a·4PF$_6$	23.4 ± 0.5	52 ± 5	1
14b·4Cl	12.1 ± 0.2	28 ± 3	1
15·4Cl	18.1 ± 0.5	43 ± 4	1
15·4Cl	20.1 ± 0.5	46 ± 5	2

[a] Shown in Figure 4.

presented in Table 4. The intense absorption bands with maxima at ca. 266 nm arise from the bipyridine residues. Although the much less intense bands for the dibromides **2a**−**f**, **5**, **8**, and **9** with maxima at ca. 305 nm, attributable to the phenol and aromatic ethers of the calix[4]arene moiety, can be observed, the bands for the calix[4]arene moieties of the catenanes are all buried in the intense bands of the bipyridine residues. In the visible region, the characteristic charge-transfer absorption bands, arising from donor−acceptor interactions between the bipyridinium and hydroquinone units, are also observed. It is seen that the molar extinction coefficients at the charge-transfer absorption maxima are smaller relative to those of the "parent" [2]catenane **22·4PF$_6$** (λ_{max} 478 nm, ϵ 700 M^{-1} cm^{-1}),[3] indicating that the donor−acceptor

Table 4. Charge-Transfer Absorptions of Calix[4]arene [2]Catenanes, Recorded in Methanol at Room Temperature

catenane	λ_{max} (nm)	ϵ ($M^{-1}\,cm^{-1}$)	catenane	λ_{max} (nm)	ϵ ($M^{-1}\,cm^{-1}$)
13·4Cl	457	430	**14a·4PF$_6$**	451	490
14b·4Cl	455	480	**14c·4PF$_6$**	463	400
15·4Cl	452	520	**17·4Cl**	455	450
18·4Cl	457	420	**19·4Cl**	462	410
20·4Cl	452	380	**21·4Cl**	449	390
22·4PF$_6$[a]	478	700			

interactions within the calix[4]arene [2]catenanes are weaker. This is in accordance with the results of the ^{1}H NMR investigations. Although excitation at the maxima of the absorption bands of **2a**−**f** (the aromatic ethers and the phenols) results in emission bands with maxima at ca. 310 and 335 nm, respectively, and excitation at the maximum of the absorption band of **5**, **8**, and **9** (the aromatic ethers) affords emission bands with maxima at ca. 310 nm, no emission is observed for the [2]catenanes, implying that the low energy levels arising from the charge-transfer interactions within the catenanes quench the luminescence exhibited by both the crown ether component and the aromatic subunits of the calix[4]arene moiety.

Summary

The research described in this paper has shown that the 1,3-disubstituted cone calix[4]arene dicationic salts can function efficiently as molecular clefts to promote the formation of the corresponding catenanes. The hydrogen bonding within the calix[4]arene moiety is crucial in providing the bipyridine residues with appropriate spatial separations. Propylene-incorporating calix[4]arene dicationic salts are the most efficient clefts. The efficiency of the calix[4]arene derivatives as clefts decreases rapidly with the increase of the length of the aliphatic chains, as a result of increased flexibility of the chains. The calix[4]arene precursor, whose cone conformation is fixed by introduction of large substituents at the lower rim, affords a [2]catenane only in low yield, whereas the conformationally flexible precursor did not give any catenanes. Conformational distributions of the calix[4]arene moiety may be changed substantially after catenation. 1,3-Alternate, cone, partial cone, or conformationally flexible [2]catenanes can be obtained by changing the aliphatic chains and the aromatic spacers or by introducing *tert*-butyl groups on the calix[4]arene moiety. Incorporation of the calix[4]arene moiety into the tetracationic cyclophane reduces the activation barrier to the dynamic processes within the [2]catenanes, as a result of reduced rigidity of the tetracationic cyclophane. Considering that calix[4]arenes can readily undergo various chemical reactions both at the lower and upper rims, we believe that, by further modifying the precursors or the calix[2]arene catenanes in appropriate ways, new supramolecular systems with specific properties or functions may be developed in the future.

Experimental Section[26]

Methods and Materials. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 63 MHz, respectively. Variable-temperature ^{1}H NMR spectra were recorded at 400 MHz. For mass spectra recorded in the FAB mode, 3-nitrobenzyl alcohol was used as a matrix. Elemental analysis was carried out at the SIOC analytical center, and the ionic samples were further recrystallized from water/methanol after workup. 25,26,27,28-Tetrahydroxy-*p*-*tert*-butylcalix[4]arene (**1a**),[27a] tetrahydroxycalix[4]arene (**1b**),[27b] 25,27-dimethoxy-*p*-*tert*-butyl-calix[4]arene (**4**),[28a] 25,27-diproxycalix[4]arene (**7**),[28b] bis(*p*-phenylene)-34-crown-10 **11**,[3] 1,1′-(*p*-phenylenedimethylene)bis(4,4′-bipyridinium) di(hexafluorophosphate) (**18**)[3], and 1,1′-bis(bromomethyl)-4,4′-biphenyl (**12c**)[29] were prepared as described in the literature. Solvents were purified according to standard procedures and reagents used as received. The presence of the solvents in the samples is determined by ^{1}H NMR spectra.

25,27-Bis(3-bromopropoxy)-26,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene (2b). To a suspension of *p*-*tert*-butylcalix[4]arene (**1a**) (6.46 g, 10.0 mmol) in MeCN (250 mL) were added 1,3-dibromopropane (20.2 g, 0.10 mmol) and K_2CO_3 (3.45 g, 25.0 mmol). The reaction mixture was refluxed for 48 h. The solvent and unreacted dibromide were then removed in vacuo, and the residue was quenched with 5% HCl (100 mL) and $CHCl_3$ (200 mL). The organic phase was separated, washed with water, and dried. The solvent was then distilled off, and the oily residue was subjected to column chromatography (CH_2Cl_2−petroleum ether (60−90 °C) 2:3) to give white, pure compound **2b** (4.10 g, 70%): mp 288−290 °C; ^{1}H NMR ($CDCl_3$) δ 7.70 (s, 2H, OH), 7.15, 6.88 (s, 4H each, ArH), 4.27 (d, J = 13.0 Hz, 4H, $ArCH_2Ar$), 4.12 (t, J = 7.8 Hz, 4H, $OCH_2CH_2CH_2$), 4.01 (t, J = 8.0 Hz, 4H, $BrCH_2CH_2CH_2$), 3.35 (d, J = 13.0 Hz, 4H, $ArCH_2Ar$), 2.53 (m, 4H, $BrCH_2CH_2CH_2$), 1.27 (s, 18H, CH_3), 1.02 (s, 18H, CH_3); ^{13}C NMR ($CDCl_3$) δ 150.7, 149.3, 147.4, 141.8, 132.8, 127.7, 125.5 (d), 77.1 (t), 73.5, 34.0 (d), 33.6, 31.0, 31.8, 31.1, 30.3; MS (FAB), *m*/*z* 890 (M^+). Anal. Calcd for $C_{50}H_{66}Br_2O_4\cdot0.25CH_2Cl_2$: C, 66.19; H, 7.37. Found: C, 66.30; H, 7.37.

25,27-Bis(2-bromoethoxy)-26,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene (2a). A suspension of **1a** (3.23 g, 5.00 mmol), K_2CO_3 (1.52 g, 11.0 mmol), and 1,2-dibromoethane (37.6 g, 0.20 mmol) in MeCN (100 mL) was refluxed for 4 days. The reaction mixture was then quenched as reported for **2b**. Pure **2a** (3.75 g) was obtained as white solid by crystallization from $CHCl_3$−petroleum ether (60−90 °C) (2:1) in 87% yield; mp 278−280 °C; ^{1}H NMR ($CDCl_3$) δ 7.06 (s, 4H, ArH), 7.04 (s, 2H, OH), 6.81 (s, 4H, ArH), 4.40−4.25 (m, 8H, OCH_2CH_2, $ArCH_2Ar$), 3.86 (t, 4H, J = 7.8 Hz, $BrCH_2CH_2$), 3.34 (d, J = 13.1 Hz, 4H, $ArCH_2Ar$), 1.29 (s, 18H, CH_3), 0.97 (s, 18H, CH_3); ^{13}C NMR ($CDCl_3$) δ 150.6, 149.4, 147.3, 141.8, 132.4, 127.8, 125.5 (d), 77.3 (t), 75.5, 34.0, 32.3, 31.8, 31.1, 29.4; MS (EI), *m*/*z* 862 (M^+). Anal. Calcd for $C_{48}H_{62}Br_2O_4\cdot0.2CH_2Cl_2$: C, 65.94; H, 7.18. Found: C, 66.05; H, 7.16.

25,27-Bis(3-bromopropoxy)-26,28-dihydroxycalix[4]arene (2c). This compound (2.30 g, 69%) was prepared from **1b** (2.12 g, 5.00 mmol) and 1,3-dibromopropane (20.2 g, 0.10 mol) as a white solid, employing the same procedure as that described for compound **2a**: mp 220−222 °C; ^{1}H NMR ($CDCl_3$) δ 8.05 (s, 2H, OH), 7.10, 6.94 (d, J = 6.2 Hz, J = 6.5 Hz, 4H each, ArH *meta*), 6.77, 6.70 (4, J = 6.2 Hz, J = 6.4 Hz, 2H each, ArH *para*), 4.32 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 4.16 (t, J = 8.0 Hz, 4H, $OCH_2CH_2CH_2$), 4.06 (t, J = 7.2 Hz, 4H, $BrCH_2CH_2CH_2$), 3.44 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 2.58 (m, 4H, $BrCH_2CH_2CH_2$); ^{13}C NMR ($CDCl_3$) δ 133.9, 133.2, 129.4, 129.1, 129.0,128.3 (d), 127.9, 125.7, 122.6, 119.3, 119.1, 73.6, 68.0, 38.1, 33.5, 32.7, 31.6, 31.4, 30.9, 30.3, 30.0; MS (EI), *m*/*z* 666 (M^+). Anal. Calcd for $C_{34}H_{34}Br_2O_4$: C, 61.27; H, 5.15. Found: C, 60.96; H, 5.16.

25,27-Bis(4-bromobutoxy)-26,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene (2d). This compound (2.84 g,

(26) For reasons of clarity, the name calix[4]arene was used instead of the official CA name: pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecane.

(27) (a) Gutsche, C. D. *Org. Synth*. **1989**, *68*, 234. (b) Gutsche, C. D.; Lin, L.-G. *Tetrahedron* **1986**, *42*, 1633.

(28) (a) Dijkstra, P. J.; Brunink, J. A. J.; Bugge, K.-E.; Reinhoudt, D. N.; Harkema, S.; Ungaro, R.; Ugozzoli, F.; Ghidini, E. *J. Am. Chem. Soc*. **1989**, *111*, 7567. (b) Casnati, A.; Comelli, E.; Fabbi, M.; Bocchi, V.; Mori, G.; Ugozzoli, F.; Manotti Lanfredi, A. M.; Pochini, A.; Ungaro, R. *Recl. Trav. Chim. Pay-Bas* **1993**, *112*, 384.

(29) Helms, A.; Heiler, D.; McLendon, G.; *J. Am. Chem. Soc*. **1992**, *114*, 6227.

62%) was prepared from **1a** (3.23 g, 5.00 mmol) and 1,4-dibromobutane (21.6 g, 0.10 mol) as a white solid, employing the same procedure as that described for compound **2a**: mp 204−6 °C; ^{1}H NMR ($CDCl_3$) δ 7.47 (s, 2H, OH), 7.06 (s, 4H), 6.81 (s, 4H), 4.23 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 4.00 (t, J = 8.2 Hz, 4H, $OCH_2CH_2CH_2$), 3.64 (t, J = 8.1 Hz, 4H, $BrCH_2CH_2CH_2$), 3.32 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 2.33 (m, 4H, $OCH_2CH_2CH_2$), 2.15 (m, 4H, $BrCH_2CH_2CH_2$), 1.29 (s, 18H, CH_3), 0.97 (s, 18H, CH_3); ^{13}C NMR ($CDCl_3$) δ 151.6, 149.8, 147.4, 141.0, 133.4, 128.8, 125.5 (d), 77.5, 74.1, 34.0, 32.3, 31.8, 31.1, 29.4, 24.6, 20.1; MS (EI), m/z 918 (M^+). Anal. Calcd for $C_{52}H_{70}Br_2O_4$: C, 67.95; H, 7.69. Found: C, 68.03; H, 7.82.

25,27-Bis(4-bromobutoxy)-26,28-dihydroxycalix[4]-arene (2e). This compound (2.22 g, 64%) was prepared from **1b** (2.12 g, 5.00 mmol) and 1,4-dibromobutane (21.6 g, 0.10 mol) as a white solid, employing the same procedure as that described for compound **2a**: mp 134−36 °C; ^{1}H NMR ($CDCl_3$) δ 8.02 (s, 2H, OH), 7.15, 6.91(d, J = 3.7, 4.0 Hz, 4H each, ArH *meta*), 6.86−6.71 (m, 4H, ArH *para*), 4.32 (d, J = 13.0 Hz, 4H, $ArCH_2Ar$), 4.07 (t, J = 8.3 Hz, 4H, OCH_2CH_2), 3.82 (t, J = 7.6 Hz, 4H, $BrCH_2CH_2$), 3.45 (d, J = 13.4 Hz, 4H, $ArCH_2Ar$), 2.39 (m, 4H, OCH_2CH_2), 2.25 (m, 4H, $BrCH_2CH_2$); ^{13}C NMR ($CDCl_3$) δ 153.3, 151.8, 133.1, 129.0, 128.6, 128.0, 125.5, 119.2, 75.7, 33.6, 31.4, 29.5, 28.8; MS (EI), m/z 695 ($M^+ + H$). Anal. Calcd for $C_{36}H_{38}Br_2O_4$: C, 62.25; H, 5.53. Found: C, 62.26; H, 5.73.

25,27-Bis(5-bromopentoxy)-26,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene (2f). This compound (2.41 g, 51%) was prepared from **1a** (3.23 g, 5.00 mmol) and 1,5-dibromopentane (23.0 g, 0.10 mol) as a white solid, employing the same procedure for compound **2a**: mp 164−168 °C; ^{1}H NMR ($CDCl_3$) δ 7.50 (s, 2H, OH), 7.05 (s, 4H), 6.81 (s, 4H), 4.26 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 3.98 (t, J = 7.6 Hz, 4H, $OCH_2CH_2CH_2$), 3.50(t, J = 8.0 Hz, 4H, $BrCH_2CH_2CH_2$), 3.31-(d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 2.05 (m, 4H,$OCH_2CH_2CH_2$), 1.85 (m, 4H, $BrCH_2CH_2CH_2$), 1.29 (s, 18H, CH_3), 1.21 (m, 4H, $BrCH_2CH_2CH_2CH_2$), 0.97 (s, 18H, CH_3); ^{13}C NMR ($CDCl_3$) δ 150.8, 149.9, 146.9, 141.5, 132.7, 127.9, 125.7 (d), 125.4 (d), 77.3, 76.1, 34.0, 33.9, 32.7, 32.0, 31.6, 31.3, 29.3, 24.8; MS (FAB), m/z 945 ($M^+ + 1$). Anal. Calcd for $C_{54}H_{74}Br_2O_4$: C, 67.29; H, 7.77. Found: C, 67.31; H, 7.99. HPLC showed that there is a small amount of conformational isomers (ca. 5%) in **2e**.

25,27-Bis[3-(4,4′-bipyridine-1′-yl)propoxy]-26,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene Dihexafluorophosphate (3b·2PF$_6$). A solution of 4,4′-bipyridine (4.00 g, 25.3 mmol) and **2b** (1.78 g, 2.00 mmol) in MeCN (100 mL) was heated under reflux for 2 days. The solvent was removed in vacuo and the solid residue washed with $CHCl_3$ to afford crude material which was subjected to flash chromatography (MeOH−2 N NH_4Cl−$MeNO_2$ 7:2:1). After the product-containing fractions were stripped of solvent in vacuo, the resulting solid was washed with ice water. The crude product was dissolved in hot water (60 °C, 10 mL). The product recrystallyzed from the liquor upon addition of a saturated NH_4PF_6 and was isolated by filtration (1.72 g, 65%): mp 196 °C (dec); ^{1}H NMR (CD_3OD) δ 9.66 (d, J = 6.5 Hz, 4H), 8.81 (dd, J = 6.5 Hz, J = 5.8 Hz, 4H), 8.69 (d, J = 5.7 Hz, 4H), 7.34 (s, 2H, OH), 7.24, 7.16 (s s, 4H each), 5.42 (t, J = 6.9 Hz, 4H, $NCH_2CH_2CH_2$), 4.29 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 4.26 (t, J = 7.2 Hz, 4H, $OCH_2CH_2CH_2$), 3.50 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 3.07 (m, 4H, $BrCH_2CH_2CH_2$), 1.27 (s, 18H, CH_3), 1.08 (s, 18H, CH_3); ^{13}C NMR (CD_3OD) δ173.5, 154.3, 151.1, 149.4, 149.2, 148.8, 145.3, 143.4, 141.2, 133.9, 129.1, 126.2 (d), 125.5, 121.9, 72.2, 58.2, 34.1, 33.7, 30.9, 30.5, 21.0 (m); MS (ES), m/z 1187 [M − PF_6]$^+$, 521 [M − 2PF_6]$^{2+}$. Anal. Calcd for $C_{70}H_{82}F_{12}N_4O_4P_2$: C, 63.04; H, 6.21; N, 4.20. Found: C, 62.76; H, 6.48; N, 4.15.

25,27-Bis[3-(4,4′-bipyridine-1′-yl)ethoxy]-26,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene Dichloride (3a·2Cl). A solution of **2a** (1.29 g, 1.50 mmol) and 4,4′-bipyridine (2.37 g, 15.0 mmol) in MeCN (200 mL) was refluxed for 3 days. The solvent was removed in vacuo and the reaction mixture purified by column chromatography (MeOH−2 N NH_4Cl−$MeNO_2$ 7:2:1). Product-containing fractions were stripped of the solvent in vacuo, and the residue was washed completely with ice water, affording the crude product which was recrystallized from MeOH−MeCN to give **3a·2Cl** (0.94 g) in 58% yield as a pale solid: mp 187 °C (dec); ^{1}H NMR (CD_3OD) δ 9.67 (d, J = 6.8 Hz, 4H), 8.85 (d, J = 6.4 Hz, 4H), 8.81 (d, J = 6.8 Hz, 4H), 7.94 (d, J = 6.5 Hz, 4H), 7.28 (s, 2H, OH), 7.10, 6.93 (s, 4H each, ArH), 5.50 (t, J = 7.8 Hz, 4H, $NCH_2CH_2CH_2$), 4.57 (t, J = 8.2 Hz, 4H, $OCH_2CH_2CH_2$), 3.86 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 3.30 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 1.16 (s, 18H, CH_3), 0.98 (s, 18H, CH_3); ^{13}C NMR (CD_3OD) δ 152.8, 150.9, 149.6, 149.1, 147.0, 146.3, 141.5, 140.8, 132.0, 127.3, 126.2 (d), 125.5, 125.2, 121.9, 74.2, 60.0, 33.7, 33.5, 31.4, 30.6; MS (ES), m/z 2137 [2 M − Cl]$^+$, 1593 [3 M − 2Cl]$^{2+}$, 1050 [M − Cl]$^+$, 508 [M − 2Cl]$^{2+}$. Anal. Calcd for $C_{68}H_{78}Cl_2N_4O_4$: C, 75.17; H, 7.25; N, 5.16. Found: C, 74.88; H, 7.22; N, 4.75.

25,27-Bis[3-(4,4′-bipyridine-1′-yl)propoxy]-26,28-dihydroxycalix[4]arene dichloride (3c·2Cl). This compound (0.71 g, 53%) was prepared from **2c** (1.00 g, 1.50 mmol) and 4,4′-bipyridine (2.37 g, 15.0 mmol) as a pale solid, employing the same procedure as for **3a·2Cl**: mp 178 °C (dec); ^{1}H NMR (CD_3OD) δ 9.68 (d, J = 6.6 Hz, 4H), 8.78 (dd, J = 6.6 Hz, J = 6.4 Hz, 8H), 8.73 (d, J = 6.4 Hz, 4H), 7.98 (dd, J = 6.8 Hz, J = 6.5 Hz, 4H), 7.34 (s, 2H, OH), 7.15, 6.99 (tt, J = 6.8 Hz, J = 6.5 Hz, 2H each, ArH), 5.41 (t, J = 7.8 Hz, 4H, $NCH_2CH_2CH_2$), 4.31 (t, J = 8.1 Hz, 4H, $OCH_2CH_2CH_2$), 4.30 (d, J = 13.1 Hz, 4H, $ArCH_2Ar$), 3.47 (d, J = 13.1 Hz, 4H, $ArCH_2Ar$), 3.08 (m, 4H, $OCH_2CH_2CH_2$); ^{13}C NMR (CD_3OD) δ 154.7, 153.2, 152.5, 151.2, 146.2, 142.8, 133.9, 133.6, 129.0, 128.7, 126.9, 125.9, 123.0, 120.4, 73.2, 59.4, 32.1, 31.7; MS (ES), m/z 1744 [2 M − Cl]$^+$, 854 [M − Cl]$^+$, 817 [M − 2Cl]$^{2+}$, 409 [M − 2Cl]$^{2+}$. Anal. Calcd for $C_{54}H_{50}Cl_2N_4O_4$: C, 72.87; H, 5.67; N, 6.30. Found: C, 72.46; H, 5.76; N, 6.59.

25,27-Bis[3-(4,4′-bipyridine-1′-yl)butoxy]-26,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene Dichloride (3d·2Cl). This compound (1.04 g, 61%) was prepared from **2d** (1.38 g, 1.50 mmol) and 4,4′-bipyridine (2.37 g, 15.0 mmol) as a white solid, employing the same procedure as that described for **3a·2Cl**: mp 186 °C (dec); ^{1}H NMR (CD_3OD) δ 9.48 (d, J = 6.7 Hz, 4H), 9.01 (d, J = 6.4 Hz, 4H), 8.75 (d, J = 6.7 Hz, 4H), 8.16 (d, J = 6.4 Hz, 4H), 7.32, 7.19 (s, 4H each, ArH), 5.18 (t, J = 6.8 Hz, 4H, NCH_2CH_2), 4.39 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 4.31 (t, J = 7.8 Hz, 4H, $OCH_2CH_2CH_2$), 3.58 (d, J = 12.8 Hz, 4H, $ArCH_2Ar$), 2.73 (m, 4H, $OCH_2CH_2CH_2$), 2.33 (m, 4H, $OCH_2CH_2CH_2$), 1.43 (s, 18H, CH_3), 1.22 (s, 18H, CH_3); ^{13}C NMR (CD_3OD) δ 154.6, 151.2, 150.4, 150.3, 148.5, 146.2, 143.2, 142.9, 133.6, 128.9, 126.7, 126.4, 125.7, 123.0, 76.1, 61.8, 34.4, 34.2, 31.9, 31.5, 31.0, 28.5, 27.1; MS (ES), m/z 2248 [2 M − Cl]$^+$, 1677 [3 M − 2Cl]$^{2+}$, 1105 [M − Cl]$^+$, 535 [M − 2Cl]$^{2+}$. Anal. Calcd for $C_{72}H_{86}Cl_2N_4O_4$: C, 75.69; H, 7.60; N, 4.90. Found: C, 75.60; H, 7.47; N, 5.01.

25,27-Bis[3-(4,4′-bipyridine-1′-yl)butoxy]-26,28-dihydroxycalix[4]arene Dichloride (3e·2Cl). This compound (0.58 g, 42%) was prepared from **2e** (1.04 g, 1.50 mmol) and 4,4′-bipyridine (2.37 g, 15.0 mmol) as a white solid, employing the same procedure as that described for compound **3a·2Cl**.: mp 174 °C (dec); ^{1}H NMR (D_2O) δ 8.99 (d, 4H), 8.70 (d, 4H), 8.26 (d, 4H), 7.60 (d, 4H), 6.73 (d, 4H, ArH, *meta*), 6.46 (d, 4H, ArH *meta*), 6.10−6.01 (m, 4H, *para*), 4.80 (t, 4H, NCH_2CH_2), 3.90 (t, 4H, OCH_2CH_2), 3.80 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 3.06 (d, J = 12.6 Hz, 4H, $ArCH_2Ar$), 2.17, 1.96 (m, 4H each, NCH_2CH_2, OCH_2CH_2); ^{13}C NMR (CD_2O) δ 156.2, 155.0, 152.8, 152.4, 147.5, 144.4, 135.1, 131.6, 130.7, 128.7, 128.5, 125.0, 122.6, 78.1, 63.6 (t), 51.6, 33.2, 29.9; MS (FAB), m/z 883 [M − Cl]$^+$. Anal. Calcd for $C_{56}H_{54}Cl_2N_4O_4$: C, 73.26; H, 5.94; N, 6.10. Found: C, 72.98; H, 5.76; N, 6.26.

25,27-Bis[3-(4,4′-bipyridine-1′-yl)pentoxy]-26,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene Dichloride (3f·2Br). A solution of **2f** (1.89 g, 2.00 mmol) in MeCN (100 mL) was added dropwise to a refluxing solution of 4,4′-bipyridine (3.16 g, 20.0 mmol) in MeCN (100 mL) over a period of 6 h. The solution was refluxed for another 24 h and the solvent removed in vacuo. The solid material was subject to column chromatography (MeOH), affording a solid. The crude product was recrystallized from methanol−acetone, giving pure **3f·2Br** (1.35 g) in 54% yield as a pale solid: mp 182 °C (dec); ^{1}H NMR (CD_3OD) δ 9.51 (br, 2H), 9.34 (d, J = 6.8 Hz, 2H), 9.04 (d, J = 6.5 Hz, 2H), 8.97 (br, 2H), 8.73 (d, J = 6.8

Hz, 2H), 8.64 (br, 2H), 8.19 (d, J = 6.5 Hz, 2H), 8.01 (d, J = 6.6 Hz, 2H), 7.19, 7.10 (s, 4H each, ArH), 4.93 (t, J = 7.8 Hz, 4H, $NCH_2CH_2CH_2$), 4.19 (t, J = 7.9 Hz, 4H, $OCH_2CH_2CH_2$), 4.11 (d, J = 12.5 Hz, 4H, $ArCH_2Ar$), 3.35 (d, J = 12.5 Hz, 4H, $ArCH_2Ar$), 2.30 (m, 2H), 1.90 (m, 6H), 1.49 (m, 4H, $CH_2CH_2CH_2O$), 1.33 (s, 18H, CH_3), 1.24 (s, 18H, CH_3); ^{13}C NMR (CD_3OD) δ 155.7, 154.6, 153.2, 152.9, 151.9, 150.3, 148.7, 147.4, 146.5, 143.2, 142.8, 133.4, 133.0, 128.9, 128.4, 127.8, 126.7, 126.3, 125.9, 123.4, 76.2, 62.0, 34.5, 34.4, 31.8, 31.6, 31.2, 28.6, 24.3, 24.0; MS (ES), m/z 1179 $[M - Br]^+$, 535 $[M - 2Br]^{2+}$. Anal. Calcd for $C_{74}H_{90}Br_2N_4O_4$: C, 70.82; H, 7.22; N, 4.45. Found: C, 70.64; H, 6.98; N, 4.61.

25,27-Bis(bromopropoxy)-26,28-dimethoxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene (5). Method A. A suspension of 60% of NaH (0.50 g, 12.5 mmol) and **4** (3.38 g, 5.00 mmol) was stirred for 1 h at room temperature in THF (100 mL). 1,3-Dibromopropane (10.1 g, 50.0 mmol) was added and the mixture stirred at 75 °C for 2 days. After cooling, n HCl solution (2N, 10 mL) was added and the solvent removed in vacuo. The residue was taken up in $CHCl_3$ (300 mL), and the organic phase washed with water and brine, and dried. After $CHCl_3$ was evaporated, the residue was subjected to column chromatography (silica gel, CH_2Cl_2−petroleum ether (60−90 °C) 1:1), yielding **5** (1.93 g, 42%) as a white solid mixture of conformational isomers: mp >190 °C; ^{1}H NMR ($CDCl_3$) δ 7.34−5.25 (m, 8H, ArH), 4.45−3.04 (m, 16H), 2.47−2.32 (m, 4H, $CH_2CH_2CH_2$), 1.42−0.97 (m, 36H, CH_3); MS (EI), m/z 918 (M^+). Anal. Calcd for $C_{52}H_{70}Br_2N_4O_4Br_2$: C, 67.95; H, 7.69. Found: C, 67.93; H, 7.72.

Method B. A solution of **4** (1.70 g, 2.50 mmol), Cs_2CO_3 (3.42 g, 10.5 mmol), and 1,4-dibromobutane (5.40 g, 25.0 mmol) in MeCN (50 mL) was refluxed for 5 days. The solvent was removed in vacuo and the residue taken up in CH_2Cl_2 (100 mL). After workup as in Method A, 1.14 g (50%) of **5** was obtained. This compound showed spectroscopic data identical to those of the compound obtained with Method A.

25,27-Dimethoxy-26,28-bis[3-(4,4′-bipyridine-1′-yl)propoxy]-5,11,17,23-tetra(*tert*-butyl)calix[4]arene Di(hexafluorophosphate) (6·2PF$_6$). A solution of **5** (1.38 g, 1.50 mmol) in MeCN (100 mL) was added to a solution of 4,4′-bipyridine (2.37 g, 15.0 mmol) in MeCN (100 mL) under reflux. The solution was then refluxed for 24 h. The solvent was removed and the resulting residue subjected to column chromatography (MeOH−2 N NH_4Cl−$MeNO_2$ 7:2:1). The product-containing fractions were combined and the solvents removed in vacuo. The crude product was taken with MeOH and then the solvent evaporated. The residue was dissolved in warm water and a saturated aqueous NH_4PF_6 solution added to afford a solid. After filtration, the product was recrystallyzed from MeOH−MeCN to afford compound **6·2PF$_6$** (1.65 g) as a white solid in 67% yield: mp 162 °C (dec); ^{1}H NMR (CD_3OD) δ 8.88 (br, 4H), 8.21 (br, 4H), 8.00 (br, 4H), 7.59 (br, 4H), 7.18−6.87 (m, 8H, ArH), 4.95 (m, 4H, NCH_2CH_2), 4.30−3.42 (m, 20H), 2.56 (m, 4H, $CH_2CH_2CH_2$), 1.32−1.09 (m, 36H, CH_3); MS (ES), m/z 532 $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{72}H_{86}F_{12}N_4O_4P_2 \cdot H_2O$: C, 62.68; H, 6.44; N, 4.06. Found: C, 62.76; H, 6.72; N, 4.15.

25,27-Bis(bromobutoxy)-26,28-dipropoxycalix[4]arene (Cone) (8). A mixture of compound **7** (2.55 g, 5.02 mmol) and 60% of sodium hydride (0.60 g, 15.1 mmol) in 100 mL of dry DMF was stirred at room temperature for 0.5 h. Subsequently 1,4-dibromobutane (20.0 g, 0.10 mol) was added. The reaction mixture was heated with stirring at 80 °C for 24 h. DMF was evaporated in vacuo, and the residue was taken up in $CHCl_3$ (200 mL) and washed with 1 N HCl (50 mL × 2) and brine (50 mL), and dried ($MgSO_4$). After filtration the solvent was evaporated, and the residue was subject to column chromatography (petroleum ether (60−90 °C)−$CHCl_3$, 2:3), yielding a pure white solid (2.34 g, 60%): mp 100−102 °C; ^{1}H NMR ($CDCl_3$) δ 6.62 (m, 12H), 4.32 (d, J = 14.7 Hz, 4H, $ArCH_2$-Ar), 3.89 (m, 8H, OCH_2), 3.48 (t, J = 7.5 Hz, 4H, $BrCH_2$), 3.16 (d, J = 14.7 Hz, 4H, $ArCH_2Ar$), 2.18−1.82 (m, 12H), 1.12 (t, J = 6.8 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 156.3 (d), 135.0, 128.2, 122.1 (d), 73.8, 33.4, 32.5, 31.0, 29.7, 23.4, 10.4; MS (EI), m/z 778 (M^+). Anal. Calcd for $C_{42}H_{50}Br_2O_4$: C, 64.77; H, 6.48. Found: C, 65.10; H, 6.44.

25,27-Bis(bromobutoxy)-26,28-dipropoxycalix[4]arene (Partial Cone) (9). Compound **7** (3.20 g, 6.30 mmol) was dissolved in MeCN (150 mL), and an excess of Cs_2CO_3 (13.7 g, 42.0 mmol) and 1,4-dibromobutane (27.2 g, 0.13 mol) was added. The reaction mixture was stirred under reflux for 4 days. Then MeCN was removed in vacuo and the oily residue taken up in 200 mL of $CHCl_3$. The organic phase was washed with 5% HCl (50 mL), water (50 mL × 2), and brine (50 mL) and dried ($MgSO_4$). After the solvent and unreacted 1,4-dibromobutane were distilled off in vacuo, the residue was subjected to column chromatography (petroleum ether (60−90 °C)−CH_2Cl_2 1:3) to give compounds **8** (0.58 g, 12%) and **9** (2.20 g, 45%). The first product afforded spectroscopic data identical to those of the compound obtained in the former reaction. Compound **9**: mp 110−112 °C; ^{1}H NMR ($CDCl_3$) δ 7.24 (d, J = 5.8 Hz, 2H), 7.09 (d, J = 5.7 Hz, 2H), 6.93−6.87 (m, 4H), 6.46 (t, J = 5.8 Hz, 2H), 6.30 (d, J = 5.3 Hz, 2H), 4.05 (d, J = 13.3 Hz, 2H, $ArCH_2Ar$), 3.78 (t, J = 6.4 Hz, 2H), 3.74 (t, J = 6.5 Hz, 2H), 3.69 (d, J = 13.1 Hz, 2H, $ArCH_2Ar$), 3.62 (d, J = 13.1 Hz, 2H, $ArCH_2Ar$), 3.56 (t, J = 6.5 Hz, 2H), 3.51 (t, J = 6.5 Hz, 2H), 3.44 (t, J = 6.4 Hz, 2H), 3.38 (t, 2H), 3.06 (d, J = 13.3 Hz, 2H, $ArCH_2Ar$), 2.08 (m, 4H), 1.87 (m, 4H), 1.72 (m, 2H), 1.52(m, 2H), 1.17 (m, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 157.5, 156.8, 155.6, 156.9, 134.0, 133.4, 132.0, 130.6, 129.3, 129.1, 128.6 (d), 122.6, 122.1, 121.6, 76.3, 72.9, 71.9, 36.1, 33.8, 33.6, 30.6, 30.0, 29.8, 29.6, 28.1, 23.9, 11.0; MS (EI), m/z 778 (M^+). Anal. Calcd for $C_{42}H_{50}Br_2O_4$: C, 64.77; H, 6.48. Found: C, 64.72; H, 6.48.

25,27-Bis[3-(4,4′-bipyridine-1′-yl)butoxy]-26,28-dipropoxycalix[4]arene Dichloride (10·2Cl). A solution of compound **8** (1.56 g, 2.00 mmol) in MeCN (120 mL) was added over a period of 5 h to a solution of 4,4′-bipyridine (3.16 g, 20.0 mmol) in MeCN (80 mL) under reflux. The solution was stirred under reflux for 36 h, and the solvent was removed. The resulting residue was subject to column chromatography (MeOH−2 N NH_4Cl−$MeNO_2$ 7:2:1). The fractions containing the product were combined and the solvents evaporated in vacuo to give a residue, which was washed completely with ice water. The crude product was then recrystallyzed from MeOH to afford pure compound **10·2Cl** as a white solid in 67% yield: mp 140 °C (dec); ^{1}H NMR (CD_3OD) δ 9.36 (d, J = 6.8 Hz, 4H), 9.04 (d, J = 6.6 Hz, 4H), 8.75 (d, J = 6.8 Hz, 4H), 8.21 (d, J = 6.7 Hz, 4H), 6.91 (d, J = 5.8 Hz, 4H, ArH *meta*), 6.81 (t, J = 5.7 Hz, 2H, ArH *para*), 6.68 (m, 6H), 4.99 (t, J = 7.8 Hz, 4H, $NCH_2CH_2CH_2$), 4.61 (d, J = 13.3 Hz, 4H, $ArCH_2$-Ar), 4.17, 4.06 (tt, J = 7.8, 7.7 Hz, 4H each, OCH_2CH_2), 3.33 (d, J = 13.3 Hz, 4H, $ArCH_2Ar$), 2.44, 2.25, (mm, 4H each, $CH_2CH_2CH_2$), 2.10 (m, 4H, $CH_2CH_2CH_3$), 1.14 (t, J = 6.9 Hz, 6H, CH_3); ^{13}C NMR (CD_3OD) δ 158.3, 157.3, 155.4, 152.2, 146.9, 143.8, 136.8, 136.1, 129.9, 129.7, 127.5 (d), 123.9, 123.6, 123.4, 78.1, 75.1 (*t*), 62.8, 32.3, 29.7, 28.2, 24.8, 11.3; MS (ES), m/z 965 $[M - Cl]^+$, 466 $[M - 2Cl]^{2+}$. Anal. Calcd for $C_{62}H_{66}Cl_2N_4O_4$: C, 68.24; H, 6.05; N, 5.14. Found: C, 67.70; H, 5.76; N, 5.46.

[25,27-Dihydroxy-5,11,17,23-tetra(*tert*-butyl)-26,28-{3-[*p*-xylylbis[4-(4,4′-bipyridine-1′-yl)]ethoxy]}calix[4]arene (1,3-Alternate) Tetrachloride]−[1,4,7,10,17,20,23,26,28,32-Decaoxa[13.13]paracyclophane] [2]Catenane (13·4Cl). 11 (0.32 g, 0.60 mmol), **3a·2Cl** (0.11 g, 0.10 mmol), and 1,4-bis(bromomethyl)benzene (**12a**) (0.03 g, 0.12 mmol) were dissolved in MeCN (35 mL). The solution was stirred at 25 °C for 14 days. The solvent was removed, and the remaining residue was washed with CH_2Cl_2. The residue was purified using column chromatography (MeOH−2 N NH_4Cl−$MeNO_2$ 7:2:1). The product fractions were combined and taken to dryness. The residue was washed well with ice water and then recrystallyzed from MeOH−Me_2CO to give pure **13·4Cl** (0.015 g, 8%) as an orange solid: mp 162 °C (dec); ^{1}H NMR (CD_3OD) δ 9.85 (d, J = 6.9 Hz, 4H), 9.46 (d, J = 6.3 Hz, 4H), 9.05 (d, J = 6.8 Hz, 4H), 8.63 (d, J = 6.4 Hz, 4H), 7.88 (s, 4H, $CH_2C_6H_4$-CH_2), 7.67 (s, 4H, ArH), 7.20 (s, 4H, ArH), 6.87 (s, 4H, $NCH_2C_6H_4$), 6.15 (t, J = 7.8 Hz, 4H, NCH_2CH_2), 5.71 (br, 8H, OC_6H_4O), 4.73 (t, J = 8.8 Hz, 4H, OCH_2CH_2N), 3.88 (d, J = 13.0 Hz, 4H, $ArCH_2Ar$), 3.81 (d, J = 13.0 Hz, 4H, $ArCH_2Ar$), 3.72−3.58 (m, 32H, OCH_2CH_2O), 1.41 (s, 18H, CH_3), 1.02 (s,

18H, CH_3); ^{13}C NMR (CD_3OD) δ 154.2, 152.3, 149.3, 146.8, 145.2, 134.2, 133.6, 130.9, 130.4, 127.5, 126.3, 125.9, 118.4, 115.0, 114.7, 73.6, 70.8, 70.4, 70.0, 67.8, 58.6, 38.3 (t), 21.8, 20.4, 11.2, 8.6; MS (ES), *m*/*z* 1765 $[M - Cl]^+$, 1162 $[2\ M - 3Cl]^{3+}$, 862 $[M - 2Cl]^{2+}$. Anal. Calcd for $C_{104}H_{126}Cl_4N_4O_{14}$: C, 69.46; H, 7.08; N, 3.12. Found: C, 69.20; H, 7.01; N, 3.18.

[25,27-Dihydroxy-5,11,17,23-tetra(*tert*-butyl)-26,28-{3-[*p*-xylylbis[4-(4,4′-bipyridine-1′-yl)]propoxy]}calix[4]arene (Cone) Tetra(hexafluorophosphate)]−1,4,7,10,17,20,23,26,28,32-Decaoxa[13.13]paracyclophane] [2]Catenane (14a·4PF$_6$). Method A. A solution of **11** (0.27 mg, 0.50 mmol), **3b·2PF$_6$** (0.13 mg, 0.10 mmol), and **12a** (0.03 mg, 0.12 mmol) in MeCN (30 mL) was stirred at 25 °C for 10 days. The solution was concentrated, and the residue was triturated with CH_2Cl_2 (100 mL). The solid material was then subjected to column chromatography (silica gel, MeOH−2 N NH_4Cl−$MeNO_2$ 7:2:1). The fractions containing the product were combined, and the solvent was evaporated. The residue was washed with ice water and then dissolved in warm water. The catenane precipitated out of solution upon addition of a saturated aqueous NH_4PF_6 solution. The solid was filtered and recrystallized from methanol−acetone; pure **14a·4PF$_6$** (0.10 g) was obtained in 43% yield as an orange solid: mp 208 °C (dec); ^1H NMR (CD_3CN) δ 9.02 (d, J = 6.5 Hz, 4H), 8.85 (d, J = 6.3 Hz, 4H), 7.93 (s, 4H, $CH_2C_6H_4CH_2$), 7.84 (d, J = 6.5 Hz, 4H), 7.82 (d, J = 6.3 Hz, 4H), 7.59 (s, 2H, OH), 7.32 (s, 4H, ArH), 7.23 (s, 4H, ArH), 5.87 (s, 4H, $NCH_2C_6H_4$), 5.60 (br, 8H, OC_6H_4O), 4.66 (t, J = 7.8 Hz, 4H, $OCH_2CH_2CH_2$), 4.36 (d, J = 13.5 Hz, 4H, $ArCH_2Ar$), 4.10 (t, J = 7.5 Hz, 4H, OCH_2CH_2O), 3.86 (m, 16H), 3.78 (m, 8H), 3.56 (d, J = 13.5 Hz, 4H, $ArCH_2$-Ar), 3.47 (m, 4H), 2.75 (m, 4H, $CH_2CH_2CH_2$), 1.33 (s, 18H, CH_3), 1.19 (s, 18H, CH_3); ^{13}C NMR (CD_3CN) δ 173.4, 151.7, 149.9, 149.6, 148.4, 145.7, 133.1, 130.9, 127.5, 126.1, 125.6, 117.6, 115.4, 114.5, 73.5, 70.5, 70.5, 70.2, 69.6, 67.5, 58.2, 34.0, 33.7, 30.9, 30.4, 21.5 (q), and 20.3 (q); MS (ES), *m*/*z* 1972 $[M - 2PF_6]^+$, 1826 $[M - 3PF_6]^+$, 1365 $[2\ M - 3PF_6]^{3+}$, 987 $[M - 2PF_6]^{2+}$, 610 $[M - 3PF_6]^{4+}$, 536 [ether]$^+$. Anal. Calcd for $C_{106}H_{130}F_{24}N_4O_{14}P_4$: C, 56.22; H, 5.80; N, 2.47. Found: C, 56.06; H, 5.74; N, 2.37.

Method B. 11 (0.14 g, 0.25 mmol), **3b·2PF$_6$** (0.067 g, 0.050 mmol), and **12a** (0.016 g, 0.060 mmol) were dissolved in DMF (10 mL). The solution was stirred at room temperature for 10 days. Ether (50 mL) was added, and the solid residue was triturated with CH_2Cl_2 (100 mL). After workup, pure **14a·4PF$_6$** (57 mg) was obtained in 51% yield as an orange solid. This compound afforded spectroscopic data identical to those of the compound obtained using Method A.

[25,27-Dihydroxy-5,11,17,23-tetra(*tert*-butyl)-26,28-{3-[*m*-xylylbis[4-(4,4′-bipyridine-1′-yl)]propoxy]}calix[4]arene (Cone) Tetrachloride]−[1,4,7,10,17,20,23,26,28,32-Decaoxa[13.13]paracyclophane] [2]Catenane (14b·4Cl). This catenane (67 mg, 37%) was prepared from **3b·2PF$_6$** (0.13 g, 0.1 mmol), dibromide **12b** (0.03 g, 0.12 mmol), and crown ether **11** (0.14 g, 0.25 mmol) as an orange solid, employing the same procedure as that described for **13·4Cl**: mp 178 °C (dec); ^1H NMR (CD_3OD) δ 9.37 (d, J = 6.8 Hz, 4H), 9.29 (d, J = 6.3 Hz, 4H), 8.41 (d, J = 6.7 Hz, 4H), 8.34 (d, J = 6.3 Hz, 4H), 8.16 (s, 4H), 8.10 (s, 4H), 7.40 (s, 4H), 6.26 (s, 4H, NCH_2-Ar), 6.04 (br, 8H, OC_6H_4O), 5.02 (t, J = 8.2 Hz, 4H, NCH_2-CH_2CH_2), 4.53 (d, J = 13.1 Hz, 4H, $ArCH_2Ar$), 4.28 (t, J = 8.3 Hz, 4H, $OCH_2CH_2CH_2$), 3.99 (m, 24H, OCH_2CH_2O), 3.76 (m, 8H, OCH_2CH_2O), 3.64 (d, J = 13.1 Hz, 4H, $ArCH_2Ar$), 2.97 (m, 4H, $NCH_2CH_2CH_2$), 1.54, 1.11 (s, 18H each, CH_3); ^{13}C NMR (CD_3OD) δ 153.5, 151.6, 151.1, 149.0, 147.4, 147.1, 143.8, 136.3, 134.9, 133.6, 132.5 (d), 132.2, 129.6, 127.6, 127.4, 126.8, 116.6, 74.4, 72.2, 72.0, 71.5, 69.3, 65.6, 60.0, 35.2, 35.1, 33.1, 32.5, 32.4, 31.8; MS (ES), *m*/*z* 1787 $[M - Cl]^+$, 876 $[M - 2Cl]^{2+}$, 536 [ether]$^+$. Anal. Calcd for $C_{106}H_{130}Cl_4N_4O_{14}$: C, 69.71; H, 7.19; N, 3.07. Found: C, 69.52; H, 7.07; N, 2.98.

[25,27-Dihydroxy-5,11,17,23-tetra(*tert*-butyl)-26,28-{3-[4,4′-biphenylenedimethylene]bis[4-(4,4′-bipyridine-1′-yl)]propoxy]}calix[4]arene Tetrachloride]−[1,4,7,10,17,20,23,26,28,32-Decaoxa[13.13]paracyclophane] [2]Catenane (14c·4Cl). This catenane (42 mg, 22%) was obtained from **3b·2PF$_6$** (0.13 g, 0.10 mmol), **12c** (0.04 g, 0.12 mmol), and crown ether **11** (0.14 g, 0.25 mmol), employing the same procedure as that described for **13·4Cl**: mp 178 °C (dec); ^1H NMR (CD_3OD) δ 9.21−7.10 (m, 34H), 6.22−5.51 (m, 12 H), 4.53−2.56 (m, 52 H), 1.49−1.05 (m, 36 H); MS (ES), *m*/*z* 1826 $[M - 2Cl]^+$, 1233 $[2\ M - 3Cl]^{3+}$, 916 $[M - 2Cl]^{2+}$, and 597 $[M - 3Cl]^{3+}$. Anal. Calcd for $C_{112}H_{134}Cl_4N_4O_{14}$: C, 70.71; H, 7.11; N, 2.95. Found: C, 70.49; H, 7.06; N, 3.20.

25,27-Dihydroxy-26,28-{3-[*p*-xylylbis[4-(4,4′-bipyridine-1′-yl)]propoxy]}calix[4]arene (Cone) Tetrachloride]−[1,4,7,10,17,20,23,26,28,32-Decaoxa[13.13]paracyclophane] [2]Catenane (15·4Cl). Method A. This catenane (73 mg, 46%) was prepared from compound **3c·2Cl** (0.09 g, 0.10 mmol), **12a** (0.03 g, 0.12 mmol), and **11** (0.14 g, 0.25 mmol), employing the same procedure as that described for **13·4Cl**: mp 162 °C (dec); ^1H NMR (CD_3OD) δ 9.52 (d, J = 6.5 Hz, 4H), 9.33 (d, J = 5.8 Hz, 4H), 8.40 (d, J = 6.5 Hz, 4H), 8.30 (d, J = 5.8 Hz, 4H), 8.24 (s, 4H, $CH_2C_6H_4CH_2$), 8.20 (s, 2H, OH), 7.38 (4H, ArH *meta*), 6.98−6.94 (m, 10H), 6.88 (t, J = 5.4 Hz, 2H, ArH *para*), 6.16 (s, 4H, NCH_2Ar), 5.85 (br, 8H, OC_6H_4O), 5.02 (t, J = 7.8 Hz, 4H, $NCH_2CH_2CH_2$), 4.56 (d, J = 13.4 Hz, 4H, $ArCH_2Ar$), 4.30 (t, J = 7.5 Hz, 4H, $OCH_2CH_2CH_2$), 3.96, 3.74 (m, 16H each, OCH_2CH_2O), 3.67 (d, J = 13.4 Hz, 4H, $ArCH_2$-Ar), 2.99 (m, 4H, $CH_2CH_2CH_2$); ^{13}C NMR (CD_3OD) δ 153.4, 152.7, 152.5, 148.1, 147.6, 146.4, 145.8, 137.3, 133.3, 131.5, 129.5 (d), 128.8, 126.8, 126.4, 125.8, 120.2, 117.7, 115.2, 73.8, 70.9 (t), 68.3, 65.1, 58.8, 49.3, 31.9, 31.2, 21.2 (m); MS (ES), *m*/*z* 1565 $[M - Cl]^+$, 1166 $[3\ M - 4Cl]^{4+}$, 1032 $[2\ M - 3Cl]^{3+}$, 764 $[M - 2Cl]^{2+}$, 746 $[M - 3Cl]^{3+}$, 536 [ether]$^+$, 365 $[M - 4Cl]^{4+}$. Anal. Calcd for $C_{90}H_{98}Cl_4N_4O_{14}$: C, 67.48; H, 6.18; N, 3.50. Found: C, 67.51; H, 5.76; N, 3.24.

Method B. A solution of **3c** (0.07 g, 0.10 mmol), **16·2PF$_6$** (0.11 g, 0.12 mmol), and **11** (0.15 g, 0.3 0 mmol) in MeCN (15 mL) was stirred at 40 °C for 21 days. The solvent was evaporated and the residue washed with CH_2Cl_2 (50 mL). The resulting precipitate was subjected to column chromatography (MeOH−2 N NH_4Cl−$MeNO_2$ 7:2:1), affording pure **15·4Cl** (8 mg) in 5% yield as an orange solid with identical physical properties to those for a sample obtained by Method A.

[25,27-Dipropoxy-5,11,17,23-tetra(*tert*-butyl)-26,28-{3-[*p*-xylylbis[4-(4,4′-bipyridine-1′-yl)]butoxy]}calix[4]arene (Cone) Tetrachloride]−[1,4,7,10,17,20,23,26,28,32-Decaoxa[13.13]paracyclophane] [2]Catenane (17a·4Cl) and [25,27-Dihydroxy-5,11,17,23-tetra(*tert*-butyl)-26,28-{3-[*p*-xylylbis[4-(4,4′-bipyridine-1′-yl)]butoxy]}calix[4]arene (Partial Cone) Tetrachloride]−[1,4,7,10,17,20,23,26,28,32-Decaoxa[13.13]paracyclophane] [2]Catenane (17b·4Cl). A solution of compound **11** (0.32 g, 0.60 mmol), **3d·2Cl** (0.29 g, 0.20 mmol), and 1,4-bis(bromomethyl)benzene (0.06 g, 0.24 mmol) in MeCN (50 mL) was stirred at 25 °C for 10 days. The solvent was evaporated in vacuo, and the remaining residue was washed with CH_2Cl_2 (100 mL). The remaining residue was purified using column chromatography (MeOH−2 N NH_4Cl−$MeNO_2$ 7:2:1). The product fractions were taken to dryness. The residue was washed with ice water. The crude product was recrystallyzed from MeOH−MeCN to give a mixture of **17a·4Cl** and **17b·4Cl** as an orange solid (96 mg, 26%, 3:2 based on the ^1H NMR spectrum): mp 153 °C (dec); ^1H NMR (CD_3OD) δ 9.66 (d, J = 6.5 Hz, **B**: 4H), 9.54 (d, J = 6.6 Hz, **B**: 4H), 9.50 (d, J = 6.2 Hz, **A**: 4H), 9.30 (d, J = 5.9 Hz, **A**: 4H), 8.91 (d, J = 6.3 Hz, **B**: 4H), 8.88 (d, J = 6.4 Hz, **B**: 4H), 8.38 (d, J = 6.0 Hz, **A**: 4H), 8.36 (d, J = 6.2 Hz, **A**: 4H), 8.17 (s, **A**: 3/5* 4H, **B**: 2/5* 4H, $CH_2C_6H_4CH_2$), 7.82 (d, J = 8.3 Hz, **B**: 2H), 7.75 (d, J = 8.3 Hz, **B**: 2H), 7.39 (s, Ar, **A**: 4H), 7.32 (s, ArH, **B**: 2H), 7.18 (s, ArH, **A**, **B** each: 2H), 6.19 (s, $NCH_2C_6H_4$, **B**: 4H), 6.17 (s, $NCH_2C_6H_4$, A: 4H), 5.86 (br, OC_6H_4O, **A**, **B** each: 8H), 5.28 (t, J = 7.8 Hz, NCH_2CH_2, **A**: 4H), 5.09 (t, J = 7.9 Hz, NCH_2CH_2, **B**: 4H), 4.47 (d, J = 12.8 Hz, $ArCH_2Ar$, **A**: 4H), 4.41 (m, $OCH_2CH_2CH_2$, **A**: 4H; $ArCH_2Ar$, **B**: 2H), 4.31 (t, J = 7.0 Hz, OCH_2CH_2O, **B**: 4H), 4.04−3.79 (m, OCH_2CH_2O, **B**: 32H; OCH_2CH_2O, $ArCH_2Ar$, **A**: 36H), 3,66 (d, J = 12.8 Hz, $ArCH_2Ar$, **A**: 4H), 3.59 (d, J = 14.5 Hz, $ArCH_2Ar$, **B**: 2H), 2.75 (m, $NCH_2CH_2CH_2O$, **B**: 4H), 2.62 (m, $NCH_2CH_2CH_2$, **A**: 4H), 2.36 (m, $OCH_2CH_2CH_2$, **B**: 4H), 2.25 (m, $OCH_2CH_2CH_2$, **A**: 4H), 1.49 (s, CH_3, **A**: 18H), 1.43 (s, CH_3, **B**: 18H), 1.20 (s, CH_3, **A**: 18H; CH_3, **B**: 9H); ^{13}C

NMR (CD_3OD) δ 153.4, 150.9, 149.2, 147.2, 146.8, 144.1, 138.1, 134.5, 134.5, 132.4, 131.3, 131.1, 130.0, 129.8, 128.9, 128.8, 127.7, 127.4, 127.3, 127.2, 126.7, 126.6, 116.1, 76.7, 72.1, 71.9, 71.5, 69.2, 62.6, 46.3, 35.3, 35.1, 32.8, 32.7, 32.4, 31.9, 30.0, and 27.5; MS (ES), *m/z* 1817 $[M - Cl]^+$, 1200 $[2M - 3Cl]^{3+}$, 891 $[M - 2Cl]^{2+}$. Anal. Calcd for $C_{108}H_{134}Cl_4N_4O_{14}$: C, 69.95; H, 7.30; N, 3.02. Found: C, 69.86; H, 7.42; N, 3.15.

[25,27-Dihydroxy-26,28-{3-[*p*-xylylbis[4-(4,4′-bipyridine-1′-yl)]butoxy]}calix[4]arene (Cone) Tetrachloride]−[1,4,7,10,17,20,23,26,28,32-Decaoxa[13.13]paracyclophane] [2]-Catenane (18·4Cl). This [2]catenane (23 mg, 14%) was prepared from **3e·2Cl** (0.09 g, 0.10 mmol), **12a** (0.03 g, 0.12 mmol), and **11** (0.16 g, 0.30 mmol), employing the same procedure as that described for **17·4Cl**: mp 175 °C (dec); ^{1}H NMR (CD_3CN) δ 9.30 (d, J = 6.2 Hz, 4H), 8.99 (d, J = 6.1 Hz, 4H), 8.15 (d, J = 6.1 Hz, 8H), 7.99 (s, 4H, $CH_2C_6H_4$), 7.24 (d, J = 5.3 Hz, 4H, ArH *meta*), 7.09 (d, J = 5.1 Hz, 4H, ArH *meta*), 6.91−6.72 (m, 4H, ArH *para*), 5.96 (s, 4H, CH_2Py), 5.59 (br, 8H, OC_6H_4O), 4.81 (t, J = 8.1 Hz, 4H, $NCH_2CH_2CH_2$), 4.23 (m, 8H, $ArCH_2Ar$, $OCH_2CH_2CH_2$), 3.81 (m, 8H, OCH_2CH_2O), 3.75 (m, 28H, OCH_2CH_2O), 3.65 (m, 16H, OCH_2CH_2O), 3.20 (d, J = 13.2 Hz, 4H, $ArCH_2Ar$), 2.42 (m, 4H, $NCH_2CH_2CH_2$), 2.09 (m, 4H, $OCH_2CH_2CH_2$); ^{13}C NMR (CD_3CN) δ 156.9, 154.8, 151.5, 150.0, 149.7, 146.5, 146.2, 144.0, 143.7, 136.1, 136.0, 134.2, 130.1, 129.5, 128.0, 127.9, 127.5, 127.0, 125.3, 124.3, 122.9, 121.0, 119.5, 113.6, 112.7, 78.6, 73.6, 70.9, 6 8.8, 68.5, 67.8, 67.0, 66.1, 63.9, 60.9, 33.4, 30.7, 27.7, 26.0, 22.3, 22.0; MS (ES), *m/z* 1590 $[M - Cl]^+$, 778 $[M - 2Cl]^{2+}$, 536 $[ether]^+$, 370 $[M - 4Cl]^{4+}$. Anal. Calcd for $C_{92}H_{102}Cl_4N_4O_{14}$: C, 67.80; H, 6.32; N, 3.44. Found: C, 67.61; H, 6.09; N, 3.40.

[25,27-Diproxy-5,11,17,23-tetra(*tert*-butyl)-26,28-{3-[*p*-xylylbis[4-(4,4′-bipyridine-1′-yl)]butoxy]}calix[4]arene (Cone) Tetrachloride]−[1,4,7,10,17,20,23,26,28,32-Decaoxa-[13.13]paracyclophane] [2]Catenane (19·4Cl). This [2]-catenane (27 mg, 8%) was prepared from **10·2Cl** (0.20 g, 0.20 mmol), **12a** (0.06 g, 0.24 mmol), and **11** (0.42 g, 0.80 mmol), employing the same procedure as that described for **17a·4Cl**: mp 168 °C (dec); ^{1}H NMR (CD_3CN) δ 9.36 (d, J = 6.2 Hz, 4H), 8.89 (d, J = 6.1 Hz, 4H), 8.20 (d, J = 6.2 Hz, 4H), 8.17 (d, J = 6.1 Hz, 4H), 8.01 (s, 4H, $CH_2C_6H_4$), 7.12 (d, J = 4.8 Hz, 4H, ArH *meta*), 6.95 (t, J = 4.7 Hz, 2H, ArH *para*), 6.79 (d, J = 4.8 Hz, 4H, ArH *meta*), 6.47 (t, J = 4.8 Hz, 2H, ArH *para*), 5.97 (s, 4H, $PyCH_2Ar$), 5.59 (br, 8H, OC_6H_4O), 4.57 (m, 4H, $NCH_2CH_2CH_2O$), 4.03 (d, J = 13.3 Hz, 4H, $ArCH_2Ar$), 4.01 (m, 4H, $OCH_2CH_2CH_2$), 3.84−3.57 (m, 32H, OCH_2CH_2O), 3.30 (d, J = 13.3 Hz, 4H, $ArCH_2Ar$), 2.17 (m, 8H, $NCH_2CH_2CH_2$, $OCH_2CH_2CH_2$), 1.95 (m, 4H, $OCH_2CH_2CH_3$), 1.06 (t, J = 7.9 Hz, 6H, CH_3); ^{13}C NMR (CD_3CN) δ 156.5, 155.2, 151.1, 150.7, 150.6, 146.5, 146.0, 144.8, 144.7, 136.3, 136.2, 133.3, 130.4, 128.5, 128.3, 128.0, 127.9, 127.8, 127.3, 125.8, 125.3, 122.1, 121.7, 121.5, 114.9, 114.0, 76.6, 72.7, 70.0, 69.8, 69.5, 69.0, 67.6, 67.1, 63.9, 60.6, 30.4, 30.2, 27.9, 26.1, 22.9, 22.8, 9.0; MS (ES), *m/z* 1675 $[M - Cl]^+$, 820 $[M - 2Cl]^{2+}$, 536 $[ether]^+$, 392 $[M - 4Cl]^{4+}$. Anal. Calcd for $C_{98}H_{114}Cl_4N_4O_{14}$: C, 68.67; H, 6.72; N, 3.27. Found: C, 68.41; H, 6.70; N, 3.09.

[25,27-{3-[1,1 -[4,4′-Biphenylenedimethylene]bis[4-(4,4′-bipyridine-1′-yl)]butoxy]}[26,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene (Cone) Tetrachloride]−[1,4,7,10,17,20,23,26,28,32-Decaoxa[13.13]paracyclophane][2]Catenane (20·4Cl). This [2]catenane (40 mg, 20%) was prepared from **3d·2Cl** (0.11 g, 0.10 mmol), **12c** (0.04 g, 0.12 mmol), and **11** (0.16 g, 0.30 mmol), employing the same procedure as that described for **18·4Cl**: mp 150 °C (dec); ^{1}H NMR (CD_3OD) δ 9.66 (d, J = 6.1 Hz, 4H), 9.56 (d, J = 6.0 Hz, 4H), 8.92 (d, J = 6.1 Hz, 4H), 8.89 (d, J = 6.1 Hz, 4H), 7.96 (d, J = 5.8 Hz, 4H), 7.88 (d, J = 5.8 Hz, 4H), 7.32 (s, 4H, ArH), 7.18 (s, 4H, ArH), 6.22 (s, 4H, $NCH_2C_6H_4$), 6.02 (br, 8H, OC_6H_4O), 5.27 (t, 4H, NCH_2CH_2), 4.43 (d, J = 12.7 Hz, 4H, $ArCH_2Ar$), 4.31 (t, J = 7.9 Hz, 4H, $OCH_2CH_2CH_2$), 4.02−3.62 (m, 32H, OCH_2CH_2O), 3.45 (d, J = 12.7 Hz, 4H, $ArCH_2Ar$), 2.74 (m, 4H, NCH_2CH_2), 2.36 (m, 4H, $OCH_2CH_2CH_2$), 1.42 (s, 18H, CH_3), 1.22 (s, 18H, CH_3); ^{13}C NMR (CD_3CN) δ 157.1, 155.8, 151.9, 150.1, 149.7, 146.3, 146.0, 144.6, 143.8, 138.1, 136.0, 134.2, 130.5, 129.4, 129.0, 127.4, 127.0, 126.5, 124.9, 122.9, 121.2, 119.8, 113.7, 112.1, 78.5, 73.0, 70.3, 68.8, 68.2, 67.7, 67.1, 66.6, 63.3, 60.9, 33.6, 30.5, 27.8, 27.0, 22.7; MS (ES), *m/z* 928 $[M - 2Cl]^{2+}$, 912 $[M - 3Cl]^{2+}$, 608 $[M - 3Cl]^{3+}$, 595 $[M - 4Cl]^{4+}$, 536 $[ether]^+$. Anal. Calcd for $C_{114}H_{138}Cl_4N_4O_{14}$: C, 70.93; H, 7.22; N, 2.90. Found: C, 70.78; H, 7.08; N, 3.01.

25,27-{3-[1,1-[4,4′-Biphenylenedimethylene]bis[4-(4,4′-bipyridine-1′-yl)]butoxy]}-26,28-dihydroxycalix[4]-arene (Mixture of Conformational Iomers) Tetrachloride]−[1,4,7,10,17,20,23,26,28,32-Decaoxa[13.13]paracyclocyclophane] [2]Catenane (21·4Cl). This [2]catenane (41 mg, 12%) was prepared from **3e·2Cl** (0.18 g, 0.20 mmol), **12c** (0.08 g, 0.24 mmol), and **11** (0.42 g, 0.80 mmol) as mixture of conformational isomers, employing the same procedure as that described for **18·4Cl**: mp 142 °C (dec); ^{1}H NMR (CD_3OD−CD_3CN) δ 9.41−9.18 (m, 4H), 8.64−8.45 (m, 4H), 7.84−7.42 (m, 8H), 7.21−7.02 (m, 8H), 6.84 (m, 2H), 6.65 (m, 2H), 6.40 (br, 8H, OC_6H_4O), 5.98 (m, $ArCH_2Py$, 4H), 5.01 (m, 4H, NCH_2CH_2), 4.62−3.32 (m, 40H, $ArCH_2Ar$, OCH_2CH_2O), 2.51 (m, 4H, NCH_2CH_2), 2.17 (m, 4H, $OCH_2CH_2CH_2$); MS (ES), *m/z* 1667 $[M - Cl]^+$, 816 $[M - 2Cl]^{2+}$, 798 $[M - 3Cl]^{2+}$, 536 $[ether]^+$. Anal. Calcd for $C_{98}H_{106}Cl_4N_4O_{14}$: C, 69.00; H, 6.28.; N, 3.29. Found: C, 68.70; H, 6.40; N, 3.41.

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