[2]Catenane Assembly from Calix[4]arene Crown Ethers

Zhan-Ting Li,*,† Xiu-Lian Zhang,† Xiong-Dong Lian,† Yi-Hua Yu,† Yi Xia,† Cheng-Xue Zhao,‡ Zhang Chen,† Zhi-Ping Lin,† and Huan Chen‡

Shanghai Institute of Organic Chemistry (SIOC), Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China, and School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, 800 Dongchuan Lu, 200240 Shanghai, China

ztli@pub.sioc.ac.cn

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A variety of novel calix[4]arene-incorporating crown ethers with or without intramolecular hydrogen bonding have been prepared by two efficient methods and utilized as donor rings to assemble calix[4]arene [2]catenanes based on π-stacking interaction between hydroquinone and bipyridinium units. Treatment of calix[4]arene crown ethers **4**, **10a**, or **10b**, whose cone conformation was fixed by intramolecular hydrogen bonding within the calix[4]arene moiety, with dicationic salt **15·2PF$_6$** and dibromide **16** afforded the corresponding [2]catenanes **17a·4PF$_6$**, **17b·4PF$_6$,** and **17c·4PF$_6$** in 20%, 53%, and 55% yields, respectively, whereas from the reactions of **15·2PF$_6$** and dibromide **16** in the presence of conformationally flexible **11** or **12** with a cone conformation kept by two propyl groups, [2]catenanes **18·4PF$_6$** and **19·4PF$_6$** were obtained in 12% and 6% yields. [2]Catenanes **21a·4Cl**, **21b·4Cl**, and **21c·4Cl**, incorporating calix[4]arene in both the donor and acceptor rings, were also successfully assembled from **10a** or **10b**, **16**, and dicationic salts **20a·2PF$_6$** or **20b·2PF$_6$**. The dynamic ^{1}H NMR and absorption spectra of the [2]catenanes have been investigated, which revealed a strongest donor−acceptor interaction in **17a·4PF$_6$** and that the cone [2]catenanes **17a**−**c·4PF$_6$** can isomerize to the partial cone isomer at high temperature. The difference of the dynamic properties of these catenanes was discussed. The results demonstrate that catenation is one new general method to change the conformational distributions of calix[4]arenes.

Introduction

Following crown ethers and cyclodextrins, calixarenes[1] and their derivatives are enjoying a burgeoning role in host−guest and supramolecular chemistry.[2] In particular calix[4]arenes and their derivatives provide a versatile platform of well-defined shape for construction of sophisticated and functional structures.[3,4] For example, calix[4]arene moieties have been incorporated into multiple systems,[5,6] connected to porphyrins,[7] crown ethers,[8] fullerenes,[9] and cyclodextrins.[10] We recently reported the synthesis of one new class of calix[4]arene [2]catenanes,[11] in which the calix[4]arene moiety was incorporated into the tetracationic acceptor rings, by using the donor−acceptor interaction principle[12] and found that the existence of the calix[4]arene moiety has significant effect on self-assembling efficiency and dynamic properties of the corresponding catenanes. Therefore we had decided to further explore the possibility of incorporating the calix[4]arene moiety into the donor rings, not only to investigate the scope and limitations of cali[4]xarene catenane assembly, but also to study the effect of calixarene moieties on the dynamic properties of the corresponding catenanes and the effect of catenation on calixarene conformational distribution. In the present work we

† Chinese Academy of Sciences.

‡ Shanghai Jiaotong University.

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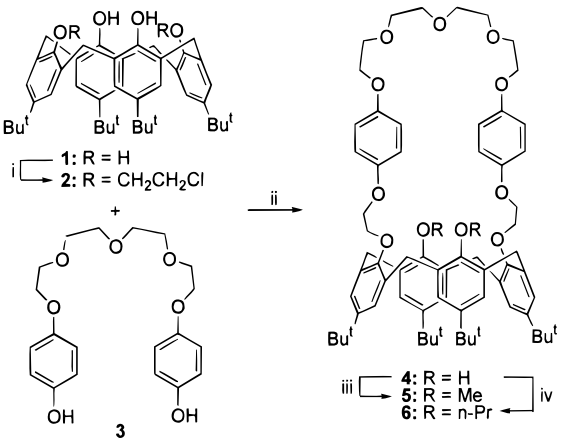
Scheme 1[a]



[a] Key: (i) $ClCH_2CH_2OTs$, K_2CO_3, MeCN, 80 °C, 65%; (ii) K_2CO_3, MeCN, 80 °C, 36%; (iii) MeI, NaH, THF, 40 °C, 95%; (iv) *n*-PrBr, K_2CO_3, THF, 65 °C, 35%.

report the assembly and spectral investigation of eight novel calix[4]arene [2]catenanes, in all of which one calix[4]arene moiety is incorporated into the donor ring.

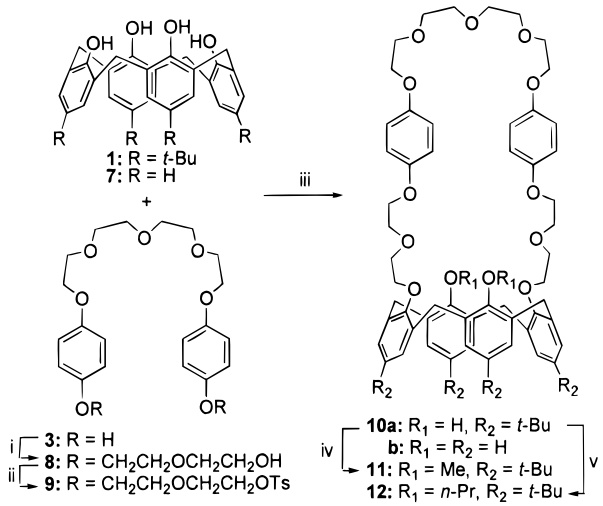
Results and Discussion

Synthesis of Calix[4]arene Crown Ethers. A variety of calix[4]arene crown ethers with different functional groups at the lower and/or upper rims of the calix[4]arene moiety have been synthesized. In all these compounds, the calix[4]arene unit is linked to two hydroquinone units through two ether chains with the same length. Two methods have been developed for preparation of calix[4]arene crown ethers with two free hydroxyl groups at the lower rim. The route that leads to compounds **4**−**6** is outlined in Scheme 1. Thus, calix[4]arene **1** was first converted to **2** with 2-chloroethyl tosylate. Compound **2** then reacted with diol **3** with potassium carbonate as a base, to afford calix[4]arene crown ether **4**. Compound **4** reacted with methyl iodide or propyl bromide in the presence of sodium hydride, giving compounds **5** or **6**, respectively.

Treatment of calix[4]arene **1** or **7** with ditosylate **9** in acetonitrile in the presence of potassium carbonate could result in the formation of calix[4]arene crown ethers **10a** or **10b**. Compound **9** could be prepared conveniently starting from **3** through intermediate **8**. Under the similar conditions as for preparing **5** and **6**, compounds **11** and **12** were also prepared from **10a** (Scheme 2). Calix[4]arene crown ether **10a** could also be prepared through another route (Scheme 3). Thus, calix[4]arene **1** first reacted with excessive (2-chloroethoxy)ethanol to afford intermediate **13**, which was then ditosylated to give calix[4]arene derivative **14**. Treatment of compound **14** with diol **3** in the presence of potassium carbonate resulted in the formation of **10a**. It is worthwhile to note that conversion of **13** to **14** was selective and the phenol hydroxyl was not tosylated during the reaction.

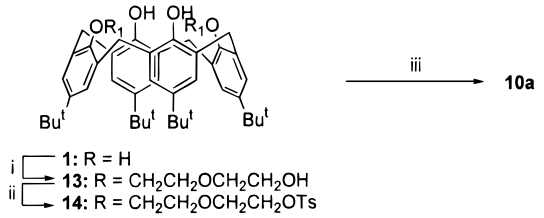
The calix[4]arene moiety of compounds **4**, **10a** and **10b** was exclusively in the cone conformation, as indicated by their ^{1}H NMR spectra, all of which exhibited the typical AB system for the $ArCH_2Ar$ protons.[13] As expected, compounds **5** and **11** were mixtures of conformational isomers at rapid equilibrium. The cone conformation of **6** and **12** were inferred from their ^{1}H NMR spectra.[14,15]

Scheme 2[a]



[a] Key: (i) $ClCH_2CH_2OCH_2CH_2OH$, K_2CO_3, MeCN, 80 °C, 74%; (ii) TsCl, pyridine, $CHCl_3$, 0 °C, 82%; (iii) K_2CO_3, MeCN, 80 °C, 34% (**10a**) and 40% (**10b**); (iv) MeI, NaH, THF, 40 °C, 98%; (v) n-PrBr, K_2CO_3, THF, 65 °C, 38%.

Scheme 3[a]



[a] Key: (i) $ClCH_2CH_2OCH_2CH_2OH$, K_2CO_3, MeCN, 80 °C, 74%; (ii) TsCl, pyridine, $CHCl_3$, 0 °C, 71%; (iii) **3**, K_2CO_3, MeCN, 80 °C, 42%.

The possibility to prepare the tetraalkylated calix[4]arene derivatives from reactions of the readily available 1,3-dimethoxyl or 1,3-dipropoxy derivatives[16] of **1** or **7** with compound **3** were also investigated, but no expected products were generated. These reactions only gave undissolved oligomers. This observation, together with the fact that **4**, **10a**, and **10b** could be prepared in acceptable yields, demonstrates that the hydrogen bonding at the lower rim of the calix[4]arene moiety is indispensable for efficient formation of the macrocyclic crown ethers, which may be attributed to the preorganized U-shaped feature of the cone calix[4]arene derivatives.

[2]Catenanes Self-Assembly. Catenations have been performed under the standard reaction conditions for the π-stacking principle.[12] Thus, dicationic salt **15**·$2PF_6$ reacted with **16** in the presence of excessive **4**, **10a** or **10b** in MeCN at room temperature for 7 days, to afford [2]catenanes **17a**−**c**·$4PF_6$ in 20%, 53%, or 55% yields after column chromatography and anionic exchange with

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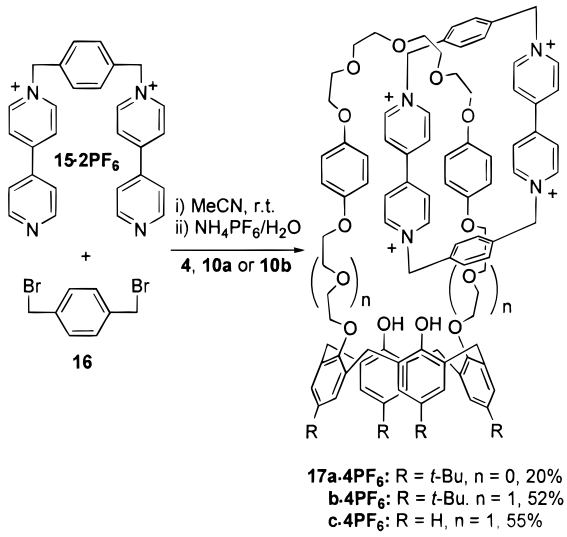
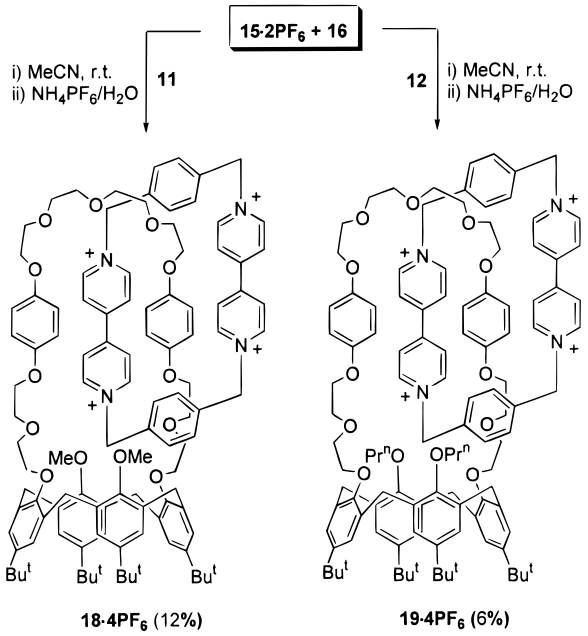
Scheme 4



ammonium hexafluorophosphate (Scheme 4). The calix[4]arene moieties in all the [2]catenanes were in the cone conformation as indicated by their ^{1}H NMR spectra. No catenanes, in which calix[4]arene was in other conformations, were obtained from the reactions. The remarkably higher yields of **17b·4PF$_6$** and **17c·4PF$_6$**, compared with **17a·4PF$_6$**, demonstrated that the spatial separation between the hydroquinone units in **10a** and **10b** were more suitable for efficient π-stacking than that in **4**. Since CPK molecular model analysis showed that, if hydrogen bonding in calix[4]arene was not considered, both **4** and **10a** and **10b** displayed very changeable spatial separations between the hydroquinones, the above observations implied that the hydrogen bonding in **4**, **10a**, and **10b** played a significant role to hold the hydroquinones to a relatively fixed distance.

Stirring a solution of **15·2PF$_6$**, **16**, and **5** or **6** in acetonitrile or *N*,*N*-dimethylformamide at room temperature for a long time (21 days) did not afford any detectable amount of catenane products, whereas treatment of **15·2PF$_6$** and **16** with excessive **11** or **12** could result in formation of [2]catenanes **18·4PF$_6$** or **19·4PF$_6$** in 12% or 6% yields, respectively (Scheme 5). These results once again demonstrated that the hydrogen bonding within the calix[4]arene moiety was crucial to efficient donor−acceptor interaction. The low assembling efficiency of **18·4PF$_6$** might be the result of rapid conformational isomerization of the calix[4]arene moiety, which was unfavorable for efficient π-stacking by producing spatial hindrance and raising the flexibility of the donor ring. The low yield of **19·4PF$_6$** from the precursor **12**, relative to that of **17b·4PF$_6$** and **17c·4PF$_6$** from **10a** and **10b**, reflected the unique function of the hydrogen bonding within the calix[4]arene unit to promote self-assembly. It was reasonable to assume that the ring of the cone **12**, formed by large alkyl groups, was more flexible than that of the cone **10a**, induced by intramolecular hydrogen bonding. The spatial hindrance from the propyl groups in **12** should be, if any, small since a CPK model investigation showed that their spatial distance to hydroquinones was long enough. As expected, the calix[4]arene in **18·4PF$_6$** was a mixture of conformational isomers at rapid equilibrium, while the cone conformation of the calix[4]arene moiety in **19·4PF$_6$** was kept unchanged.

Scheme 5

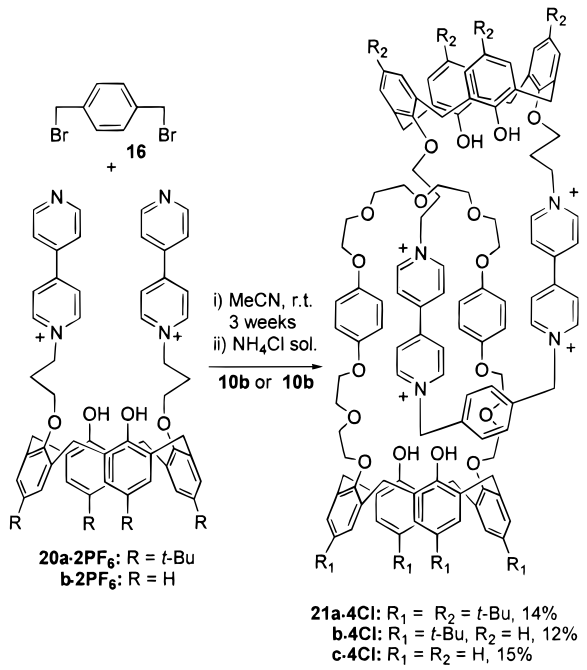


Three [2]catenanes **21a·4Cl**, **21b·4Cl**, and **21c·4Cl**, which had one calix[4]arene unit in both the donor and acceptor rings, were assembled in 14%, 12%, and 15% yields as pale yellow solids from the reactions of dicationic precursors **20a·2PF$_6$** or **20b·4PF$_6$**[11b] with **16** in the presence of excessive **10a** or **10b** albeit after a prolonged time (Scheme 6). The yields are acceptable considering that both donor and acceptor precursors are more flexible than the model reaction precursors,[12] probably reflecting the preorganization feature of U-shaped **20a·2PF$_6$** or **20b·4PF$_6$**, which had been proved to promote formation of calix[4]arene [2]catenanes.[11b] The ^{1}H NMR spectra showed that, for all these three [2]catenanes, the cone conformation of the calix[4]arene subunits in both the donor and acceptor rings were unchanged. Under the same reaction conditions, no similar catenanes were obtained from **4**.

^{1}H NMR Spectra. The solution-state properties of the calix[4]arene [2]catenanes have been investigated by dynamic ^{1}H NMR spectroscopy. The ^{1}H NMR spectra of **17a−c·4PF$_6$**, **18·4PF$_6$**, and **19·4PF$_6$** display temperature dependence between 223 and 393 K as a result of the dynamic processes shown in Figure 1. The first process involves the circumrotation of the tetracationic cyclophane through the cavity of the macrocyclic calix[4]arene polyether and the second one involves the circumrotation of the calix[4]arene polyether through the cavity of the tetracationic cyclophane. The kinetic and thermodynamic data associated with the two processes are showed in Table 1.[17] It can be found that, although all the activation barriers to both processes are reduced compared to that of the "parent" [2]catenane,[12] [2]catenane **17a·4PF$_6$** exhibits a higher activation barrier value associated to the second process, implying that the donor−acceptor interaction in this [2]catenane is stronger.

(17) The coalescence method (Sandstroom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982) 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 $\Delta G_c^{\neq}$ was calculated with the Eyring equation.

Scheme 6



The possibility of conformational change of the calix[4]arene units in these [2]catenanes at high temperature have also been explored by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **17a·4PF$_6$** in DMSO-d_6 began to exhibit signals of the partial cone conformer at above 115 °C, which could be inferred by the typical signals for the aromatic protons of the calix[4]arene moiety (Figure 2).[13−15] The ratio of the partial cone conformer with the cone conformer rose and reached to a value of ∼0.35 at 130 °C, according to their signal intensities. When the temperature decreased, the partial cone conformer isomerized to the cone one gradually. Similar isomerization was also observed for [2]catenanes **17b·4PF$_6$** and **17c·4PF$_6$** albeit emerging at the higher temperature of ∼125 °C. The ratio of the partial cone isomer with the cone one could reach ∼0.15 and 0.20 for these two compounds at the available temperature of 130 °C. No signals of the 1,3-alternate conformer were observed for all the three [2]catenanes. Between the investigated temperature range, no such isomerization was observed for free calix[4]arene crown ethers **4**, **10a**, and **10b**, therefore the conformational isomerization in **17a**−**c·4PF$_6$** must have been induced by the tetracationic cyclophane in these compounds. The lower isomerizaiton temperature displayed by **17a·4PF$_6$** shows that there exists a larger spatial interaction between its tetracationic cyclophane and calix[4]arene moiety, as a result of its smaller donor ring. Such conformational isomerization has also been found in [2]catenanes, in which one calix[4]arene was incorporated into the acceptor ring, although in those systems the 1,3-alternate conformer could also be generated.[11b] Therefore these results appear to indicate that catenation represents one new unique method to affect or control the conformation of calix[4]arene derivatives, which may find applications for future supramolecular design.

Although some distinct chemical shifts were also displayed for [2]catenanes **21a**−**c·4Cl**, no coalescence temperature could be observed between the investigated temperature range to determine the exchange rates and free energy barriers. The cone calix[4]arene moieties within both the donor and acceptor did not isomerize to other conformers at ∼120 °C when they began to decompose. These results may reflect the expanded cavity size and higher flexibility of the two components of these [2]catenanes and consequently catenation does not have substantial effect on the hydrogen bonding within both the donor and acceptor calix[4]arenes.

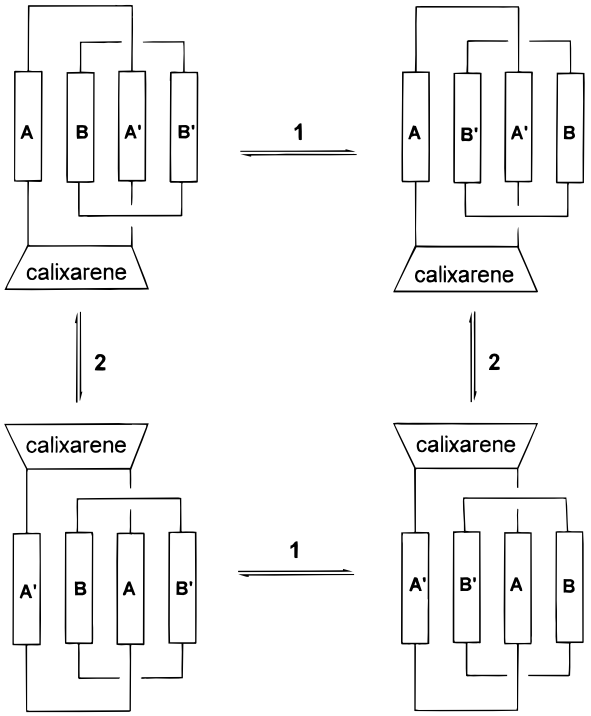


Figure 1. Dynamic processes associated with calix[4]arene [2]catenanes.

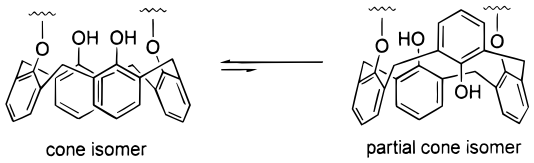


Figure 2. Conformational isomerization of **17a**−**c·4PF$_6$**.

Electronic Absorption Spectra. The charge-transfer behavior of all the calix[4]arene [2]catenanes has been investigated by UV-absorption spectroscopy. A summary of their absorption data, characteristic of the donor−acceptor interactions between the bipyridinium and hydroquinone units, is presented in Table 2. It can be observed that all the molar extinction coefficients at the charge-transfer absorption maxima are smaller than those of the "parent" [2]catenane (λ_{max} 478 nm, ϵ 700 M^{-1} cm^{-1}),[12] indicating a reduced donor−acceptor interaction within these calix[4]arene [2]catenanes. This observation is consistent with the above ^{1}H NMR investigations. However, although the assembling efficiency of **17a·4PF$_6$** is not so high as that of **17b·4PF$_6$** or **17c·4PF$_6$**, it exhibits the highest molar extinction coefficients. This may be attributed to the narrower spatial separation between the hydroquinones of its donor component and consequently more efficient donor−acceptor interaction with the dipyridinium unit. The fact that [2]catenanes **21a**−**c·4Cl** exhibit much lower values reflects that there exists very weak π-stacking interaction in these catenanes.

Table 1. Kinetic and Thermodynamic Parameters for the Dynamic Processes of Figure 1 Associated with Some Calix[4]arene [2]Catenanes

catenane	probe proton	$\Delta\nu$ (Hz)[a]	k_c[b] (s^{-1})	T_c[c] (K)	$\Delta G^{\ddagger}$[d] (kcal mol^{-1})	process[e]	solvent
17a·4PF$_6$	α-CH[f]	60	133	228	11.0	1	CD_3OD
	N^+CH_2	70	155	233	11.2	1	CD_3OD
	OC_6H_4O	725	1610	338	14.9	2	CD_3SOCD_3
17b·4PF$_6$	α-CH[f]	45	100	223	10.9	1	CD_3OD
	N^+CH_2	86	190	238	11.3	1	CD_3OD
	OC_6H_4O	1050	2332	328	14.2	2	CD_3SOCD_3
17b·4Cl	α-CH[f]	50	111	223	10.8	1	CD_3OD
	OC_6H_4O	1072	2380	333	14.3	2	CD_3OD
17c·4PF$_6$	α-CH[f]	65	144	230	11.1	1	CD_3OD
	N^+CH_2	55	122	233	11.3	1	CD_3OD
	OC_6H_4O	1120	2487	328	14.1	2	CD_3OD
18·4PF$_6$	α-CH[f]	73	162	228	10.9	1	CD_3OD
	OC_6H_4O	906	2011	326	14.2	2	CD_3OD
19·4PF$_6$	α-CH[f]	96	213	236	11.2	1	CD_3OD
	OC_6H_4O	1025	2276	325	14.1	2	CD_3OD

[a] Error ± 2 Hz. [b] Error ± 5 s^{-1}. [c] Error ± 1 K. [d] Error ± 0.2 kcal mol^{-1}. [e] Shown in Figure 1. [f] Related to the pyridine protons.

Table 2. 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})
17a·4PF$_6$	460	550	**17b·4PF$_6$**	455	420
17b·4Cl	455	415	**17c·4PF$_6$**	452	410
18·4PF$_6$	458	360	**19·4PF$_6$**	464	375
21a·4Cl	467	165	**21b·4Cl**	466	160
21c·4Cl	470	170			

Conclusions

A series of novel crown ethers incorporating calix[4]arene units have been prepared and utilized to assemble a variety of calix[4]arene [2]catenanes. The hydrogen bonding within the calix[4]arene moiety of the donor rings facilitates the formation of catenane structures and introduction of methyl groups at the calix[4]arene lower rim will greatly reduce the assembling efficiency. The calix[4]arene crown ether in which the cone conformation is kept by large alkyl groups also exhibits much less efficient templating ability. Incorporation of the calix[4]arene moiety into the donor ring generally reduces the activation barrier to the dynamic processes within the [2]catenanes, especially within [2]catenanes consisting of two calix[4]arene-incorporating rings. The conformational isomerization exhibited by [2]catenanes **17a**−**c·4PF$_6$** demonstrates that catenation represents one new principle to change or control the conformational distributions of calix[4]arene derivatives.

Experimental Section

General Methods and Materials. See ref 11b.

25,27-Bis(2-chloroethoxy)-26,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene (2). A solution of chloroethanol (16.0 g, 200 mmol) in chloroform (150 mL) was added slowly with stirring to a solution of toluene-*p*-sulfonyl chloride (38.0 g, 200 mmol) and pyridine (100 mL) in chloroform (300 mL), which was cooled to 0 °C. The solution was then warmed to room temperature and stirred for 48 h and then poured into ice−water (500 mL). The aqueous phase was extracted with chloroform (100 mL×3) and the combined organic phase washed and dried. After workup, 28.0 g of 2-chloroethyl tosylate was obtained in 60% yield. ^{1}H NMR ($CDCl_3$): δ 2.38 (s, 3 H), 4.07 (t, 2 H), 4.20 (t, 2 H), 7.22 (d, 2 H), 7.40 (d, 2 H). EIMS: *m/z* 234 (M^+). Anal. Calcd for $C_9H_{11}ClO_3S$: C, 46.06; H, 4.69. Found: C, 45.82; H, 4.81. A suspension of calix[4]arene **1** (6.48 g, 10.0 mmol) and potassium carbonate (3.04 g, 22.0 mmol) in acetonitrile (200 mL) was stirred at room temperature for 1 h and a solution of 2-chloroethyl tosylate (4.91 g, 21.0 mmol) in acetonitrile (100 mL) added. The mixture was stirred under reflux for 48 h and the solvent removed. The residue was triturated in chloroform (300 mL). After workup, the product was purified by column chromatography (chloroform/petroleum ether 1:1) to afford compound **2** (5.02 g, 65%) as a white solid: Mp: >280 °C. ^{1}H NMR ($CDCl_3$): δ 0.97 (s, 18 H, CH_3), 1.27 (s, 18 H, CH_3), 3.32 (d, 4 H, J = 12.9 Hz, $ArCH_2Ar$), 3.76 (t, 4 H), 4.05 (t, 4 H), 4.23 (d, J = 12.9 Hz, 4H, $ArCH_2Ar$), 6.80 (s, 4 H), 7.07 (s, 4H), 7.47 (s, 2 H, OH). EIMS: *m/z* 772 (M^+). Anal. Calcd for $C_{48}H_{62}Cl_2O_4$: C, 74.49; H, 8.09. Found: C, 74.03; H, 7.82.

[25,27-Dihydroxy-5,11,17,23-tetra(*tert*-butyl)-26,28-[4,4′-[bis[1,13-(1,4,7,10,13-pentaoxa)tridecylene]phenylene]-1,1′-oxy]ethoxycalix[4]arene (4). A suspension of calix[4]arene **2** (7.72 g, 10.0 mmol), **3**[12] (3.78 g, 10.0 mmol), potassium iodide (3.32 g, 20.0 mmol), and potassium carbonate (2.76 g, 20.0 mmol) in acetonitrile (200 mL) was refluxed for 4 days. The solvent was then removed in vacuo and the residue quenched with 2 N hydrochloric acid (50 mL) and chloroform (300 mL). The organic phase was washed with water and brine and dried ($MgSO_4$). The solvent was then distilled off, and the resulting residue subjected to column chromatography on silica gel (methylene chloride/ethyl acetate 5:1) to afford **4** (3.88 g, 36%) as a white solid. Mp: >260 °C. ^{1}H NMR ($CDCl_3$): δ 0.98 (s, 18 H), 1.28 (s, 18 H), 3.32 (d, 4 H, J = 13.0 Hz, $ArCH_2Ar$), 3.70 (m, 4 H), 3.82 (m, 4 H), 3.95 (m, 4 H), 4.00 (m, 4 H), 4.15 (m, 4 H), 4.36 (d, 4 H, J = 13.0 Hz, $ArCH_2Ar$), 6.65 (m, 8 H), 6.75 (s, 4 H), 7.02 (s, 4 H), 7.36 (s, 2 H). EIMS: *m/z* 1078 (M^+). Anal. Calcd for $C_{68}H_{86}O_{11}$: C, 75.65; H, 8.05. Found: C, 75.32; H, 8.14.

[25,27-Dimethoxy-5,11,17,23-tetra(*tert*-butyl)-26,28-[4,4′-[bis[1,13-(1,4,7,10,13-pentaoxa)tridecylene]phenylene]-1,1′-oxy]ethoxycalix[4]arene (5). To a solution of **4** (1.08 g, 1.00 mmol) in dried tetrahydrofuran (50 mL) was added sodium hydride (60%) (0.80 g, 20.0 mmol). The mixture was stirred at room temperature for 1 h and then methyl iodide (0.66 mL, 1.50 g) added with a syringe. The solution was warmed at 40 °C with stirring for 24 h and then quenched water carefully. After workup, the resulting residue was purified by flash chromatography on silica gel (dichloromethane/ethyl acetate 5:1), to give pure compound **5** (1.05 g) as a white solid in 95% yield. Mp: 233−236 °C. ^{1}H NMR ($CDCl_3$): δ 1.05−1.25 (m, 36 H), 3.33 (m, 4 H), 3.68−3.95 (m, 14 H), 4.15−4.36 (m, 12 H), 6.89 (m, 16 H). EIMS: *m/z* 1106 (M^+). Anal. Calcd for $C_{70}H_{90}O_{11}$: C, 75.90; H, 8.21. Found: C, 76.00; H, 8.35.

[25,27-Diproxy-5,11,17,23-tetra(*tert*-butyl)-26,28-[4,4′-[bis[1,13-(1,4,7,10,13-pentaoxa)tridecylene]phenylene]-1,1′-oxy]ethoxycalix[4]arene (Cone) (6). A solution of **4** (2.16 g, 2.00 mmol) and sodium hydride (60%, 0.80 g, 20.0 mmol) in dried tetrahydrofuran (150 mL) was stirred at room temperature for 1 h and then propyl bromide (1.22 g, 10 mmol) added. The solution was warmed to 65 °C with stirring and kept at this temperature for 48 h. After cooled to room temperature, 2 N hydrochloric acid was added dropwise to

quench the reaction. After workup and purification by flash chromatography on silica gel (dichloromethane/ethyl acetate 10:1), **6** was obtained (0.87 g, 35%) as a white solid. Mp: >270 °C. ^{1}H NMR ($CDCl_3$): δ 0.94 (s, 18 H), 1.06 (t, 6 H), 1.26 (s, 18 H), 1.89 (m, 4 H), 3.10 (d, 4 H, J = 13.0 Hz, $ArCH_2Ar$), 3.70−4.02 (m, 24 H), 4.16 (m, 4 H), 4.35 (d, 4 H), 6.60 (s, 4 H), 6.74 (d, d, 8 H), 7.16 (m, 4 H). FABMS: m/z 1162 (M^+). Anal. Calcd for $C_{74}H_{98}O_{11}$: C, 76.38; H, 8.51. Found: C, 75.96; H, 8.42.

1,11-Bis[4-[2-(2-hydroxyethoxy)ethoxy]phenoxy]-3,6,9-trioxaundecane (8). 2-(2-Chloroethoxy)ethanol (18.0 g, 145 mmol) was added to a suspension of potassium carbonate (20.0 g, 145 mmol), potassium iodide (24.1 g, 145 mmol), and **3** (16.0 g, 42.3 mmol) in acetonitrile (300 mL). The slurry was then refluxed with stirring for 7 days and, after cooling to room temperature, filtered. The solid was washed well with acetonitrile and the solvent was removed in vacuo. The residue was triturated in ethyl acetate and the solution washed with water, brine, and dried ($MgSO_4$). After the solvent was evaporated in vacuo, the residue was purified by flash chromatography on silica gel (methanol/chloroform, 1:20) to afford 17.3 g of compound **8** (74%) as a colorless solid. Mp: 68−69 °C (lit.[18] mp 66−68 °C). ^{1}H NMR ($CDCl_3$): δ 1.89 (s, 2 H), 3.72 (m, 8 H), 3.77 (m. 12 H), 3.85 (m, 8 H), 4.08 (m, 4 H), 6.84 (s, 8 H). EIMS: m/z 554 (M^+).

1,11-Bis[4-[2-(2-toluene-*p*-sulfonylethoxy)ethoxy]phenoxy]-3,6,9-trioxaundecane (9). Tosyl chloride (12.2 g, 64.2 mmol) in chloroform was added slowly with stirring to a solution of compound **8** (11.9 g, 21.5 mmol) and triethylamine (18.2 g, 160 mmol) in chloroform (300 mL), while the solution was maintained at ∼0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 48 h. The solution was washed with 2 N hydrochloric acid, water, and brine and finally dried ($MgSO_4$). The solvent was evaporated and the residue obtained purified by column chromatography (ethyl acetate/chloroform 1:3) to give compound **9** (15.1 g) in 82% yield as a colorless oil, which solidified slowly to a colorless solid. Mp: 58−60 °C. ^{1}H NMR ($CDCl_3$): δ 2.46 (s, 6 h, CH_3), 3.76 (m, 16 H), 3.87 (m, 4 H), 4.02 (t, 4 H), 4.13 (t, 4 H), 4.23 (t, 4 H), 6.86 (dd, 8 H), 7.35 (d, 4 H), 7.83 (d, 4 H). FABMS: m/z 862 (M^+). Anal. Calcd for $C_{42}H_{54}O_{15}S_2$: C, 58.44; H, 6.32. Found: C, 58.35; H, 6.30.

[25,27-Dihydroxy-5,11,17,23-tetra(*tert*-butyl)-26,28-[4,4′-[bis[1,13-(1,4,7,10,13-pentaoxa)tridecylene]phenylene]-1,1′-oxy]ethoxyethoxycalix[4]arene (10a). Method A. A suspension of **1** (6.48 g, 10.0 mmol), **9** (8.62 g, 10.0 mmol), and potassium carbonate (2.76 g, 20.0 mmol) in acetonitrile (200 mL) was refluxed for 4 days. The solvent was then removed in vacuo and the residue quenched with 2 N hydrochloric acid (50 mL) and chlorform. The organic phase was washed with water and then dried ($MgSO_4$). The solvent was then distilled off and the resulting residue subjected to column chromatography on silica gel (methylene chloride/ethyl acetate 5:1) to give **10a** (3.96 g, 34%) as a white solid. Mp: 285 °C. ^{1}H NMR ($CDCl_3$): δ 0.96 (s, 18 H), 1.30 (s, 18 H), 3.31 (d, 4 H, J = 13.5 Hz, $ArCH_2Ar$), 3.71 (m, 8 H), 3.84 (m, 4 H), 3.97 (m, 4 H), 4.06 (m, 8 H), 4.15 (m, 4 H), 4.38 (d, 4 H, J = 13.5 Hz, $ArCH_2Ar$), 6.68 (m, 8 H), 6.73 (s, 4 H), 7.06 (s, 4 H), 7.34 (s, 2 H). EIMS: m/z 1166 (M^+). Anal. Calcd for $C_{72}H_{94}O_{13}$: C, 74.06; H, 8.13. Found: C, 74.22; H, 8.19. **Method B.** A suspension of **3** (1.89 g, 5.00 mmol), **14** (5.50 g, 5.0 mmol), and potassium carbonate (1.38 g, 10.0 mmol) in acetonitrile (200 mL) was refluxed for 48 h. After workup, **10a** was obtained in 42% yield.

[25,27-Dihydroxy-26,28-[4,4′-[bis[1,13-(1,4,7,10,13-pentaoxa)tridecylene]phenylene]-1,1′-oxy]ethoxyethoxycalix-[4]arene (10b). This compound was prepared in 40% yield as a white solid from the reaction of calix[4]arene **7** and compound **9**, as described for preparing **10a** by method A. Mp: 272 °C. ^{1}H NMR ($CDCl_3$): δ 3.37 (d, 4 H, J = 13.5 Hz, $ArCH_2Ar$), 3.71 (m, 8 H), 3.84 (m, 4 H), 3.97 (m, 4 H), 4.07 (m, 12 H), 4.18 (m, 4 H), 4.42 (d, 4 H, J = 13.5 Hz, $ArCH_2Ar$), 6.64−6.84 (m, 12 H), 6.90 (d, 4 H), 7.07 (d, 4 H), 7.86 (s, 2 H). EIMS: m/z 942 (M^+). Anal. Calcd for $C_{56}H_{62}O_{13}$: C, 71.32; H, 6.64. Found: C, 70.94; H, 6.57.

[25,27-Dimethoxy-5,11,17,23-tetra(*tert*-butyl)-26,28-[4,4′-[bis[1,13-(1,4,7,10,13-pentaoxa)tridecylene]phenylene]-1,1′-oxy]ethoxyethoxycalix[4]arene (11). This compound was prepared as a white solid in 98% yield by using the procedure as described above for **5**. Mp: 292 °C. ^{1}H NMR ($CDCl_3$): δ 1.00−1.28 (m, 36 H), 3.31 (m, 4 H), 3.71 (m, 14 H), 3.86−3.95 (m, 8 H), 4.10−4.38 (m, 12 H), 6.70−7.02 (m, 16 H). EIMS: m/z 1194 (M^+). Anal. Calcd for $C_{74}H_{98}O_{13}$: C, 74.33; H, 8.28. Found: C, 74.04; H, 8.32.

[25,27-Diproxy-5,11,17,23-tetra(*tert*-butyl)-26,28-[4,4′-[bis[1,13-(1,4,7,10,13-pentaoxa)tridecylene]phenylene]-1,1′-oxy]ethoxyethoxycalix[4]arene (Cone) (12). This compound was prepared as a white solid in 38% yield by using a similar procedure as described above for **6**. Mp: 200−202 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (s, 18 H), 1.03 (t, 6 H), 1.26 (s, 18 H), 1.99 (m, 4 H), 3.13 (d, 4 H, J = 13.0 Hz, $ArCH_2Ar$), 3.72 (m, 16 H), 3.89 (m, 8 H), 4.00 (m, 8 H), 4.20 (m, 4 H), 4.35 6.65 (s, 4 H), 6.74 (d, d, 8 H), 7.02 (m, 4 H). FABMS: m/z 1250 (M^+). Anal. Calcd for $C_{78}H_{106}O_{13}$: C, 74.83; H, 8.55. Found: C, 74.60; H, 8.42.

25,27-Bis(2-hydroxyethoxy)ethoxy-26,28-dihydroxy-5,-11,17,23-tetra(*tert*-butyl)calix[4]arene (13). A suspension of calix[4]arene **1** (6.46 g, 10.0 mmol), 2-(2-chloroethoxy)-ethanol (4.96 g, 40.0 mmol), and K_2CO_3 (2.76 g, 20.0 mmol) in MeCN (300 mL) was refluxed for 6 days. After workup and purification by column chromatography on silica gel (methylene chloride/ methanol 20:1), compound **13** (6.10 g) was obtained as a white solid in 74% yield. Mp: 142−144 °C. ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 18 H, CH_3), 1.23 (s, 18 H, CH_3), 3.35 (d, 4 H, J = 12.8 Hz, $ArCH_2Ar$), 3.81 (m, 8 H), 4.14 (m, 8 H), 4.27 (b, 2 H), 4.40 (d, 4 H, J = 12.8 Hz, $ArCH_2Ar$), 7.01 (s, 4 H), 7.03 (s, 4 H), 8.90 (s, 2 H). EIMS: m/z 824 (M^+). Anal. Calcd for $C_{52}H_{72}O_8 \cdot 1.5H_2O$: C, 73.28; H, 8.89. Found: C, 72.98; H, 8.56.

25,27-Bis(2-toluene-*p*-sulfonylethoxy)ethoxy-26,28-dihydroxy-5,11,17,23-tetra(*tert*-butyl)calix[4]arene (14). Toluene-*p*-sulfonyl chloride (1.70 g, 9.00 mmol) in dichloromethane (30 mL) was added slowly to a solution of compound **13** (3.75 g, 4.55 mmol) and pyridine (3.0 mL) in chloroform (50 mL) at 0 °C with stirring. The solution was then allowed to warm to room temperature and, after stirring for 72 h, washed with 2 N of hydrochloric acid, water, and brine and finally dried ($MgSO_4$). The solvent was then removed. The oily residue was subjected to column chromatography (ethyl acetate/dichloromethane 1:10) to give **14** (3.55 g, 71%) as a colorless solid. Mp: 122−124 °C. ^{1}H NMR ($CDCl_3$) δ 0.95 (s, 18 H), 1.20 (s, 18 H), 2.38 (s, 6 H), 3.88 (m, 8 H), 4.04 (m, 4 H), 4.21 (m, 4 H), 4.26 (d, 4 H, J = 13.2 Hz, $ArCH_2Ar$), 6.78 (s, 4 H), 7.05 (s, 4 H), 7.20 (s, 2 H), 7.22 (d, 4 H), 7.74 (d, 4 H). FABMS: m/z 1132 (M^+). Anal. Calcd for $C_{66}H_{84}O_{12}S_2$: C, 70.00; H, 7.54. Found: C, 69.77; H, 7.54.

[2]Catenane 17a·4PF$_6$. To the solution of calix[4]arene crown ether **4** (1.62 g, 1.50 mmol) in acetonitrile (50 mL) was added dicationic salt **15·2PF$_6$** (210 mg, 0.33 mmol) and dibromide **16** (103 mg, 0.40 mmol). After the solution was stirred at 25 °C for 7 days, the solvent was removed in vacuo. The remaining residue was triturated in CH_2Cl_2 and filtrated. The residue was subjected to column chromatography on silica gel (MeOH−2 N NH_4Cl−$MeNO_2$ 7:2:1). The orange product fractions were combined and taken to dryness. The residue obtained was dissolved in warm water, saturated NH_4PF_6 solution was added until no more precipitate formed. The precipitate was filtrated, washed with water, and dried. It was then recrystallyzed from MeOH-Me_2CO−H_2O to give **17a·4PF$_6$** (144 mg, 20%) as an orange solid. Mp: 250 °C dec. ^{1}H NMR (CD_3OD): δ 0.92 (s, 18 H), 1.33 (s, 18 H), 3.22 (d, 4 H), 3.42 (m, 8 H), 4.10 (m, 16 H), 4.34 (d, 4 H), 4.52 (m, 4 H), 5.99 (s, 8 H), 6.24 (br 8 H), 6.73 (s, 4 H), 7.25 (s, 4 H), 7.90 (s, 8 H), 8.00 (d, 8 H), 9.22 (d, 8 H). ESMS (m/z): 2034 ($M - PF_6)^+$, 945 ($M - 2PF_6)^{2+}$, 582 ($M - 3PF_6)^{3+}$. Anal. Calcd for $C_{104}H_{118}N_4O_{11}F_{24}P_4 \cdot 2H_2O$: C, 56.36; H, 5.53; N, 2.50. Found: C, 56.04; H, 5.64; N, 2.47.

(18) 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.

[2]Catenane 17b·4PF$_6$. This orange solid was obtained in 52% from the reaction of **15·2PF$_6$** and **16** (7 days) in the presence of compound **10a** by using the procedure described above for **17a·4PF$_6$**. Mp: >268 °C dec. ^{1}H NMR (CD_3OD): δ 0.91 (s, 18 H), 1.31 (s, 18 H), 3.20 (d, 4 H), 3.35−3.52 (m, 16 H), 3.56−4.12 (m, 16 H), 4.30 (d, 4 H), 4.50 (m, 4 H), 5.95 (s, 8 H), 6.20 (br, 4 H), 6.79 (s, 4 H), 7.15(s, 4 H), 7.95 (s, 8 H), 8.01 (d, 8 H), 9.26 (d, 8 H). ESMS (*m*/*z*): 1184 $(2M - 3Cl)^{3+}$, 878 $(M - 2Cl)^{2+}$, 860 $(M - 3Cl)^{2+}$, 562 $(M - 4Cl)^{3+}$. Anal. Calcd for $C_{108}H_{126}Cl_4N_4O_{13}\cdot H_2O$: C, 70.18; H, 6.99; N, 3.03. Found: C, 70.00; H, 6.72; N, 2.87. This [2]catenane was converted to **17b·4PF$_6$** via anionic exchange with saturated aqueous NH_4PF_6 solution. Mp: >270 °C dec. ^{1}H NMR (CD_3CN): δ 0.95 (s, 18 H), 1.31 (s, 18 H), 3.22 (d, 4 H), 3.38−4.12 (m, 32 H), 4.35 (d, 4 H), 4.50 (m, 4 H), 5.90 (s, 8 H), 6.19 (br, 4 H), 6.69 (s, 4 H), 7.22 (s, 4 H), 7.95 (s, 8 H), 7.96 (d, 8 H), 9.29 (d, 8 H). ESMS: *m*/*z* 2120 $(M - PF_6)^+$, 988 $(M - 2PF_6)^{2+}$.

[2]Catenane 17c·4PF$_6$. This compound was obtained in 55% yield as an orange solid from the reaction of **15·2PF$_6$** and **16** (7 days) in the presence of compound **10b**. Mp: >280 °C dec. ^{1}H NMR (CD_3CN): δ 3.24 (d, 4 H), 3.35−4.22 (m, 32 H), 4.30 (d, 4 H), 4.55 (m, 4 H), 5.98 (s, 8 H), 6.25 (br, 4 H), 6.69 (d, 4 H), 7.15−7.28 (m, 8 H), 7.95 (s, 8 H), 7.96 (d, 8 H), 9.29 (d, 8 H). ESMS: *m*/*z* 1898 $(M - PF_6)^+$, 1752 $(M - 2PF_6)^+$, 876 $(M - 2PF_6)^{2+}$. Anal. Calcd for $C_{92}H_{94}N_4O_{13}F_{24}P_4\cdot H_2O$: C, 53.59; H, 4.70; N, 2.72. Found: C, 53.23; H, 4.76; N, 2.66.

[2]Catenane 18·4PF$_6$. This compound was prepared in 12% yield (14 days) as an orange solid from **15·2PF$_6$** and **16** in the presence of excessive **11**. Mp: >298 °C dec. ^{1}H NMR (CD_3CN): δ 1.04 (s, 18 H), 1.30 (s, 18 H), 3.40 (m. 4 H), 3.70−3.88 (m, 30 H), 4.08 (s, 8 H), 4.46 (br, 4 H), 5.68 (s, 8 H), 6.89 (s, 8 H), 7.25 (s, 2 H), 7.62 (m, 8 H), 7.74 (m, 8 H), 8.78 (d, 8 H). ESMS: *m*/*z* 2150 $(M - PF_6)^+$, 1002 $(M - 2PF_6)^{2+}$, 620 $(M - 3PF_6)^{3+}$. Anal. Calcd for $C_{110}H_{130}N_4O_{13}F_{24}P_4\cdot 2H_2O$: C, 56.64; H, 5.80; N, 2.40. Found: C, 56.32; H, 5.89; N, 2.34.

[2]Catenane 19·4PF$_6$. This compound was prepared in 6% yield (28 days) as an orange solid from **15·2PF$_6$** and **16** in the presence of excessive **12**. Mp: >258 °C dec. ^{1}H NMR (CD_3CN): δ 0.90 (s, 18 H), 1.02 (t, 6 H), 1.29 (s, 18 H), 2.04 (m, 4 H), 3.25 (d, 4 H), 3.35−4.15 (m, 36 H), 4.35 (d, 4 H), 5.90 (s, 8 H), 6.30 (br, 8 H), 6.63 (s, 4 H), 7.25 (s, 4 H), 7.68 (s, 8 H), 7.90 (d, 8 H), 9.24 (d, 8 H). ESMS: *m*/*z* 1030 $(M - 2PF_6)^{2+}$, 639 $(M - 3PF_6)^{3+}$. Anal. Calcd for $C_{114}H_{138}N_4O_{13}F_{24}P_4\cdot 3H_2O$: C, 56.89; H, 6.04; N, 2.33. Found: C, 56.62; H, 6.09; N, 2.30.

[2]Catenane 21a·4Cl: A solution of dication salt **20a·2PF$_6$** (240 mg, 0.20 mmol), **16** (63.0 mg, 0.24 mmol), and **10a** (1.74 g, 1.50 mmol) in MeCN (50 mL) was stirred at 25 °C for 21 days. After workup, **21a·4Cl** (68 mg) was obtained as a pale yellow solid in 14% yield. Mp: 249 °C dec. ^{1}H NMR (CD_3OD/CD_3CN): δ 0.94 (s, 18 H), 1.04 (s, 18 H), 1.24 (s, 18 H), 1.30 (s, 18 H), 3.00 (m, 4 H), 3.31 (d, 4 H), 3.34 (m, 4 H), 3.72−3.75 (m, 12 H), 3.92 (m, 4 H), 3.95−4.01 (m, 16 H), 4.10 (m, 4 H), 4.35 (m, 8 H), 5.85 (m, 4 H), 6.20 (s, 4 H), 6.75 (m, 8 H), 6.75 (s, 4 H), 6.82 (s, 4 H), 7.26 (s, 4 H), 7.30 (s, 4 H), 7.87 (s, 4 H), 7.90 (d, 4 H), 7.96 (d, 4 H), 9.23 (d, 4 H), 9.26 (d, 4 H). ESMS: *m*/*z* 1192 $(M - 2Cl)^{2+}$, 1175 $(M - 3Cl)^{2+}$, 783 $(M - 3Cl)^{3+}$, 578 $(M - 4Cl)^{4+}$. Anal. Calcd for $C_{150}H_{184}Cl_4N_4O_{17}\cdot 2H_2O$: C, 72.25; H, 7.62; N, 2.25. Found: C, 72.10; H, 7.68; N, 2.09.

[2]Catenane 21b·4Cl. This catenane was obtained from the reaction of **20b·2PF$_6$** and **16** in the presence of **10a** in 12% yield as a pale yellow solid. Mp: 268 °C dec. ^{1}H NMR (CD_3OD): δ 0.95 (s, 18 H), 1.24 (s, 18 H), 3.04 (m, 4 H), 3.34 (d, d, 8 H), 3.72 (m, 12 H), 3.95 (m, 4 H), 3.98 (m, 16 H), 4.11 (m, 4 H), 4.39 (m, 8 H), 5.83 (m, 4 H), 6.21 (s, 4 H), 6.78 (m, 8 H), 6.78 (m, 8 H), 6.82 (d, 4 H), 7.30 (s, 4 H), 7.32 (s, 4 H), 7.90 (s, 4 H), 7.95 (d, 4 H), 7.99 (d, 4 H), 9.20 (d, 4 H), 9.26 (d, 4 H). ESMS: *m*/*z* 1080 $(M - 2Cl)^{2+}$, 522 $(M - 4Cl)^{4+}$. Anal. Calcd for $C_{134}H_{152}Cl_4N_4O_{17}\cdot 3H_2O$: C, 70.39; H, 6.91; N, 2.49. Found: C, 70.10; H, 7.00; N, 2.19.

[2]Catenane 21c·4Cl. This catenane was obtained from the reaction of **20b·2PF$_6$** and **16** in the presence of **10b** in 15% yield as a pale yellow solid. Mp: >288 °C dec. ^{1}H NMR (CD_3OD): δ 3.06 (m, 4 H), 3.35 (d, d, 8 H), 3.70 (m, 12 H), 3.90 (m, 4 H), 3.95 (m, 16 H), 4.20 (m, 4 H), 4.38 (m, 8 H), 5.86 (m, 4 H), 6.60 (s, 4 H), 6.78 (m, 8 H), 6.80 (m, 12 H), 6.85 (d, 4 H), 7.33 (d, 4 H), 7.36 (d, 4 H), 7.92 (s, 4 H), 7.90 (d, 4 H), 7.95 (d, 4 H), 9.15 (d, 4 H), 9.23 (d, 4 H). ESMS: *m*/*z* 1970 $(M - Cl)^+$, 968 $(M - 2Cl)^{2+}$. Anal. Calcd for $C_{118}H_{120}Cl_4N_4O_{17}\cdot 2H_2O$: C, 69.34; H, 6.04; N, 2.74. Found: C, 69.10; H, 6.21; N, 2.59.

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