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Conformational Interconversions in [2]Catenanes Containing a Wide Rigid Bis(*p*-benzyl)methyl Spacer

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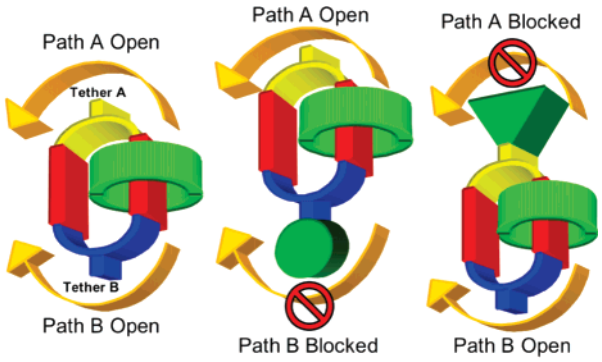
Received April 26, 2007



The conformational interconversions of four [2]catenanes (**1**−**4**) containing a dibenzo-34-crown-10 ether (BPP34C10) interlocked with rings containing two 4,4′-dipyridiniums tethered by 1,3-bis(ethyloxy)-phenyl and bis(*p*-benzyl)methyl spacers have been studied by VT ^{1}H NMR spectroscopy. Symmetrically placed blocking groups on thickened tethers enabled either pathway for circumrotation of the BPP34C10 between isoenergetic sites to be blocked. On the basis of chemical shifts of the BPP34C10, its internal *p*-hydroquinone forms $\pi-\pi$-stacking interactions with only one 4,4′-dipyridinium ring at a time. The activation barrier for migration along either open tether was approximately 11.5 kcal/mol. This study demonstrates an ability to select the pathway for conformational interconversions in these [2]catenanes containing the rigid bis(*p*-benzyl)methyl tether and the lowering the barrier for interconversion through destabilization of the ground state structures.

Introduction

Noncovalent interactions such as $\pi-\pi$-stacking, van der Waal interactions, and hydrogen bonding are often crucial factors in determining the molecular properties of compounds having biological and materials relevance.[1] The ability not only to understand but also to control these interactions is especially important in the preparation of mechanical−chemical molecular machines and switches.[2] Of particular interest is to alter the activation barrier for interconversions in nanoscaled devices by either changing the transition state energy relative to a ground state energy or changing the ground state energy relative to a transition state energy. We have previously demonstrated the ability through alterations in the required transition state energy to select paths for the conformational interconversion of bistable [2]catenanes containing a 1,3-bis(ethyloxyl)phenyl spacer and a 1,3- or 1,4-xylyl spacer connecting two 4,4′-dipyridinium groups and an interlocked BPP34C10 ring (Figure 1).[3] Such electron rich−electron poor [2]catenanes form bistable com-

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10.1021/jo070809v CCC: $37.00
Published on Web 07/14/2007

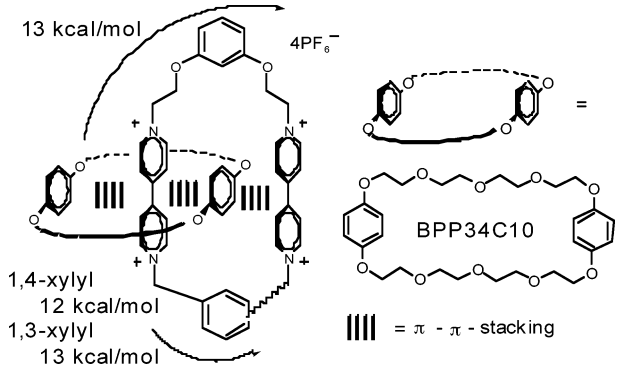


FIGURE 1. BPP34C10 rotation in previous [2]catenanes **3a**.

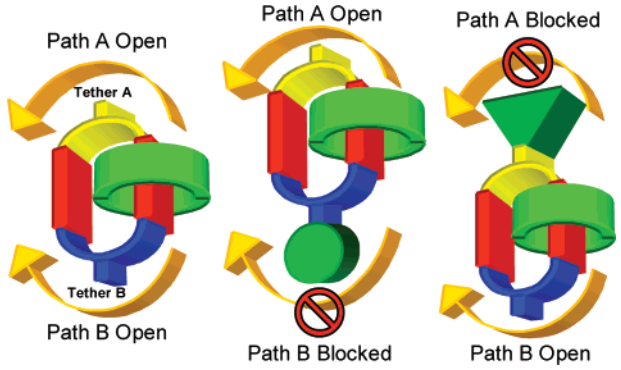
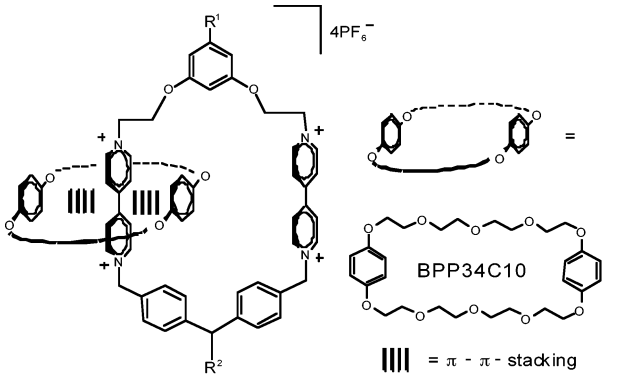


FIGURE 2. Cartoon representation of [2]catenanes.

plexes where the *p*-phenoxy rings of the crown ether prefer to π-stack over either of the dipyridinium groups.[4] Passage of the BPP34C10 over the thin 1,4-xylyl spacer was established to be approximately 1 kcal/mol more favorable than that over the 1,3-xylyl spacer, while passage over the 1,3-bis(ethyloxy)phenyl spacer was energetically similar to passage over the 1,3-xylyl spacer.[3a] Since these xylyl groups functioned as fairly narrow spacers with respect to the separation of the two dipyridinium groups, they allowed the internal *p*-phenoxy ring of the crown ether to π-stack simultaneously with both 4,4′-dipyridinium moieties. We anticipated that changing to the wider, rigid bis-(*p*-benzyl)methane spacer would disrupt one of these $\pi-\pi$-stacking interactions and perhaps have energetic consequences for the circumrotation of the BPP34C10 ring through changes in the ground state energies. We report herein our ability to prepare these wider [2]catenanes, evidence for invoking $\pi-\pi$-stacking interactions with only a single dipyridinium group at a time, and a determination of the lowered energy barriers for the circumrotation of the BPP34C10 ring between the stable $\pi-\pi$-stacked forms.

Results and Discussion

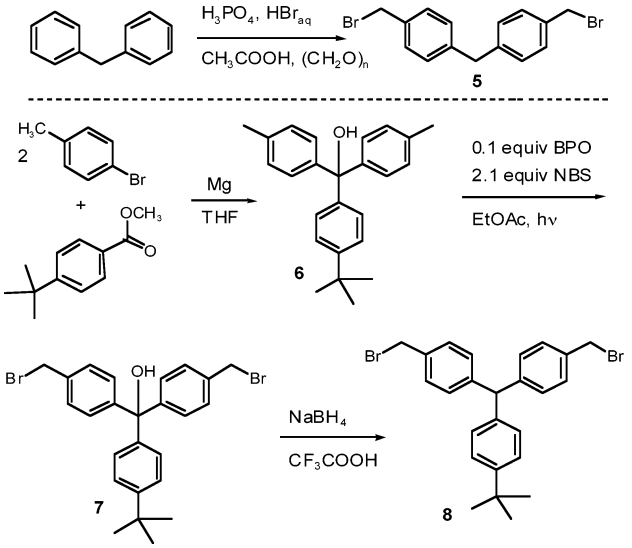
To determine the energy barrier for a selected translation along Path A in Figure 2, we attached a blocking group to tether B to allow only circumrotation of the crown ether along thin Pathway A. With Path A blocked, interconversion would occur



1 R^1 = H , R^2 = H
2 R^1 = H , R^2 = 4-*tert*-butylphenyl
3 R^1 = bis(4-methylphenyl)methyl , R^2 = H
4 R^1 = bis(4-methylphenyl)methyl , R^2 = 4-*tert*-butylphenyl

FIGURE 3. [2]Catenanes in this study.

SCHEME 1. Synthesis of Rigid Tethers



only along the thin Pathway B. With neither blocking group present, passage along both tethers would be allowed. Extending our earlier work[3a] and the work of Stoddart,[5] we have prepared [2]catenanes **1**−**4** having either the resorcinol-based tether blocked or not blocked and the bis(*p*-benzyl)methane-based tether blocked or not blocked (Figure 3).

The preparations of the two bis(4-bromomethylphenyl)-methane bridging groups were accomplished through modifications of literature procedures and are shown in Scheme 1. Diphenylmethane was conveniently bromomethylated by using aqueous rather than gaseous HBr and paraformaldehyde to give bis(4-bromomethylphenyl)methane (**5**),[6] which was purified through a trituration procedure. Triarylmethanol **6** was prepared through a Grignard reaction in which *p*-bromotoluene was added to a mixture of magnesium turnings and methyl 4-*tert*-butylbenzoate. Radical bromination of the two benzylic methyl groups by NBS in ethyl acetate gave bis(bromomethyl) adduct

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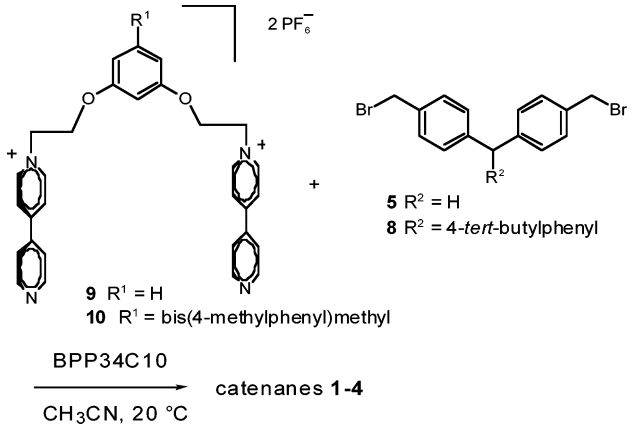
SCHEME 2. [2]Catenane Synthesis



7, which was reduced by sodium borohydride in trifluoroacetic acid to give tethering group **8**.[7] The resorcinol-tethered bis(mono-pyridinium) salt **9** and 5-[bis(4-methylphenyl)methyl]-resorcinol derivative **10** were prepared as previously reported.[3a]

Catenanes **1**−**4** were formed through three-component reactions between 1 equiv of bis(pyridiniums) **9** or **10**, 1.3 equiv of bis(4-bromomethylphenyl)methane (**5**) or triaryl dibromide **8**, and 1.6 equiv of BPP34C10 in acetonitrile at room temperature under 1 atm of nitrogen for 4 days (Scheme 2). After solvent removal, the catenanes were isolated by preparative TLC on silica, initially at 50 °C with 1:1 methanol−ethyl acetate, to promote dethreading of any pseudorotaxanes and rapid elution of the crown ether to the top of the plate. A second elution at room temperature with 7:2:1 methanol−2 M aqueous ammonium chloride−nitromethane[8] moved the catenanes to about 0.3−0.4 R_f and left uncoordinated pyridinium salts near the origin of the plate. The silica gel with the catenanes was removed and extracted with the 7:2:1 solvent system. The filtrate was concentrated and aqueous NH_4PF_6 was added to precipitate the catenanes as orange to red solids in 18% to 24% yield. We found that the yields of the [2]catenanes were significantly improved by using very high purity BPP34C10. We have found that the most convenient and reliable preparation of this crown ether was a modification of a one-pot cyclization from hydroquinone and the ditosylate of tetraethylene glycol.[9] As described in the Experimental Section, suitable purity of the BPP34C10 was obtained by a series of extractions and column purifications.

Two rotational temperature-dependent isomerizations of related [2]catenanes have been established by Stoddart.[4] Typically, the rotation of a BPP34C10 about a single dipyridinium group has an energy barrier of approximately 16 kcal/mol determined by using established NMR techniques.[10] In such cases, the internal hydroquinone ring exhibited a very high field ^{1}H NMR resonance near 3.8 ppm due to $\pi-\pi$-stacking with both dipyridinium moieties as depicted in Figure 1.[3a] The external hydroquinone ring could only interact with a single dipyridinium unit and can be found around 6.1 ppm. Typically both sets of signals are observed at room temperature for [2]catanenes of BPP34C10 and dipyridium-based rings; they generally coalesce above 50 °C to give a single averaged signal near 5 ppm. The energy barrier for the translocation or circumrotation of the crown ether from near one dipyridinium group to the other typically requires several kilocalories per mole less energy.[4]

TABLE 1. Summary of Data and Calculation of Activation Energy

catenane	coalescence temp (K)	freq difference (Hz)	energy of activation (kcal/mol)
1	228	79	10.8
2	238	79	11.4
3	248	166	11.5
4	>335	84	>15

Given these prior findings, catenanes **1**−**4** exhibited quite unusual ^{1}H NMR spectra at room temperature in that only one set of signals for the hydrogen atoms on the hydroquinone rings were observed at about 6.1 ppm. These signals remained unchanged in the temperature range −40 to +60 °C. Below −40 °C the observed decoalescence of the BPP34C10 signals was most likely due the freezing out of a known rocking motion of the crown ether rather than its translocation.[4] We ascribe these findings to the presence of similar chemical shift environments for the two hydroquinone rings—inside and outside the catenated dipyridinium ring both have only a single $\pi-\pi$-stacking interaction with one dipyridinium group as they would in a rotaxane complex.[4a] We conclude that the second dipyridinium ring cannot interact with the internal hydroquinone due to the spacing enforced by the wide, rigid bis(*p*-benzyl)methyl tether (see depiction in Figure 3). Previous analogous catenations involving the wide 4,4′-bis(methylene)-1,1-biphenyl tether between 4,4′-dipyridinium groups led only to the formation of [3]catenanes where two BPP34C10 rings were interlocked onto either side of a single tetracationic ring.[11] In our preparation of catenanes **1**−**4**, only [2]catenanes were observed despite evidence for $\pi-\pi$-stacking with only one dipyridinium group at a time.

The energy barriers for the translocation of the crown ether in [2]catenanes **1**−**4** were determined by analyzing the desymmetrization of the dipyridinium rings in VT ^{1}H NMR spectroscopy. At room temperature a single set of averaged signals was observed for the protons at the 2 and 2′ dipyridyl positions for catenanes **1**−**3**. Below −40 °C, the 1:1 set of dipyridyl signals indicated that both exchange processes were in the slow exchange region. For catenane **4** containing blocking groups on both thick tethers, the slow exchange spectrum was observed up to 60 °C. The coalescence temperature and frequency difference of exchanging sets of signals were used to calculate the activation barrier for the translocation of the crown ether between the bistable states.[10] The data are summarized in Table 1.

Catenane **1** having thin unsubstituted resorcinol and bis(*p*-benzyl)methyl linkers gave an activation barrier of 10.8 kcal/mol. When both the resorcinol and bis(*p*-benzyl)methyl tethers were thickened in catenane **4**, both pathways were blocked. Since no line broadening was observed in the ^{1}H NMR spectra up to 60 °C the activation barrier for passing over either of

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these blocking groups should be higher than the 15 kcal/mol calculated from the observed chemical shift difference and 335 K as a minimum temperature of coalescence. When only the resorcinol-based tether was blocked in **3**, passage over the thin bis(*p*-benzyl)methyl required 11.5 kcal/mol, and a similar 11.4 kcal/mol barrier was measured for passage over the thin 1,3-bis(ethyloxy)benzene tether in **2**.

We note that the energy barriers for passage along either the rigid thin bis(*p*-benzyl)methane and the flexible thin 1,3-bis-(ethyloxy)phenyl tethers are nearly identical (11.4−11.5 kcal/mol). In catenane **1** where both paths are available, the lowered activation barrier of 10.8 kcal/mol nicely reflects the entropic contribution of two accessible paths. Interestingly, circumrotation of the crown ether along the same thin resorcinol tether in **2** is about 1.5 kcal/mol lower in activation energy than in our previous 1,3-bis(ethyloxy)phenyl-tethered catenanes shown in Figure 1.[3a] This lowering of the barrier is unlikely to be due to a lowering of the unfavorable energetic interactions in the transition state structures since the interactions in the transition state structure as the crown ether passes along these same tethers should be about the same in the two catenanes. Given our NMR spectroscopic evidence for the presence of just a single $\pi-\pi$-stacking interaction in catenanes **1**−**4** and the typical double $\pi-\pi$-stacking interactions seen in previous [2]catenanes, it seems most likely that the activation barrier differences are due to ground state destabilization in **1**−**4**.

Conclusion

In summary, through the appropriate incorporation of blocking groups on one or both of the tethers it was possible to block one or both of the two pathways for circumrotation in bistable catenanes **1**−**4**. The wide rigid bis(*p*-benzyl)methyl tether allows $\pi-\pi$-stacking interactions with only one dipyridinium moiety at a time. This destabilization of the ground state led to lowered energy barriers for passage along a thin 1,3-bis(ethyloxyl)-benzene tether of 11.5 kcal/mol. Passage of BPP34C10 over a thin but wider bis(*p*-benzyl)methane tether was 11.4 kcal/mol. This study demonstrates an ability to alter the activation barriers through ground state destabilization and to choose different pathways for circumrotation in these noncovalently linked compounds.

Experimental Section

BPP34C10 Synthesis.[9] Tetraethylene glycol bis(toluene-*p*-sulfonate)[12] (50.2 g, 0.134 mol) was added to 2-propanol (450 mL) containing *p*-hydroxyquinone (14.7 g, 0.134 mol) and sodium hydroxide (9.1 g, 0.228 mol) predissolved in water (10 mL). The mixture was refluxed for approximately 24 h under nitrogen. The reaction mixture was cooled to room temperature, then filtered via vacuum filtration, and the insoluble solids were washed with 2-propanol. The liquid filtrate was collected and concentrated under reduced pressure (6.1 g of crude product).

BPP34C10 Purification. Crude bis(*p*-phenylene)-34-crown-10 (BPP34C10) (21.6 g, brown solid) was dissolved in hot ethyl acetate (500 mL) and the insoluble solids were removed via vacuum filtration. The liquid filtrate was collected, concentrated under reduced pressure, and purified via flash column chromatography (neutral Al_2O_3; ethyl acetate) to give a viscous yellow oil (2.8 g) that solidified at room temperature to give a waxy yellow semisolid. The yellow semisolid was dissolved in hot ethyl acetate (10 mL) and triturated with petroleum ether (approximately 200 mL) to give an off-white solid. The off-white solid was collected via vacuum filtration, washed with diethyl ether, and allowed to air-dry to give an off-white powder (1.2 g). A portion of the off-white powder (300 mg) was purified via column chromatography [$SiO_2-CH_2Cl_2-Et_2O$ (3:7), v/v] as previously reported[13] to give pure BPP34C10 (150 mg). The ^{1}H NMR spectrum of the purified product was consistent with literature data.[9,13] The melting point of the purified product was 93−94 °C, which was also consistent with literature data.[9]

Compound 6.[7] Magnesium turnings (2.2 g, 0.091 mol) were added to a three-necked flask. The ports of the three-neck flask were affixed with a reflux condenser, addition funnel, and rubber septa. The flask was purged with nitrogen and dry THF (50 mL) was added to the flask under nitrogen via a syringe. Approximately 6−10 drops of 1,2-dibromoethane were added to the reaction flask under nitrogen via a syringe to activate the magnesium. The magnesium/THF mixture was heated to approximately 50 °C via an oil bath. THF (50 mL) and 4-bromotoluene (8 mL, 0.065 mol) were sequentially added to the addition funnel under nitrogen. Methyl-4-tertbutylbenzoate (5.0 mL, 0.026 mol) was added to the reaction flask under nitrogen via a syringe. The 4-bromotoluene/THF mixture was added to the mixture dropwise and the reaction mixture was refluxed at 70−80 °C for 20−24 h. The reaction mixture was cooled to room temperature and poured into a solution of ice (100 mL) and concentrated H_2SO_4 (3.3 mL) followed by the addition of NH_4Cl (3.3 g) to the aqueous mixture. The aqueous mixture was extracted with diethyl ether (3 × 100 mL). The combined organic fractions were washed with 5 wt % $NaHCO_3$ (3 × 100 mL) and water (3 × 100 mL), dried ($MgSO_4$), and concentrated under reduced pressure (9.0 g, quantitative crude yield). The crude product was purified via column chromatography [SiO_2−petroleum ether−CH_2Cl_2 (2:1), v/v] to give pure compound **6** (3.4 g, 38% yield). The ^{1}H NMR spectrum of the purified product was consistent with the chemical structure and that reported in the literature.[5]

Compound 7.[14a−c] NBS (1.8 g, 0.01 mol) and benzoyl peroxide (0.1 g, 0.0005 mol) were added to a 50 mL sealed round-bottomed flask and purged with nitrogen for 30 min. Compound **6** (1.7 g, 0.005 mol) and ethyl acetate (17 mL) were added to a separate 50 mL sealed round-bottomed flask and purged with nitrogen for 10 min. The solution of compound **6** and ethyl acetate was transferred via syringe to the sealed flask containing NBS and benzoyl peroxide at room temperature under nitrogen. The reaction mixture was refluxed via a heat lamp (250 W) for 24 h under a nitrogen atmosphere, cooled to room temperature, and extracted with ethyl acetate (40 mL). The organic fraction was washed with aqueous saturated $NaHCO_3$ (3 × 25 mL) and H_2O (3 × 25 mL), dried ($MgSO_4$), and concentrated under reduced pressure (1.8 g, 73% crude yield). The ^{1}H NMR spectrum of crude compound **7** was consistent with the chemical structure and that reported in the literature. A small amount of the over-brominated product was also observed in the ^{1}H NMR spectrum.

Compound 8.[15] A mixture of compound **7** (2.4 g, 4.8 mmol) and trifluoroacetic acid (72 mL) was cooled to 0 °C in an ice bath under nitrogen. $NaBH_4$ (1.8 g, 47.8 mmol) was slowly added to the reaction mixture under nitrogen and the reaction mixture was stirred for 5 min at 0 °C. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in water (50 mL) followed by the addition of $NaHCO_3$ (50 mL). The aqueous

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mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic fractions were dried (Na_2SO_4) and concentrated under reduced pressure (1.5 g, 65% crude yield). The ^{1}H NMR spectrum of crude compound **8** was consistent with the chemical structure and that reported in the literature.

Bis(4-bromomethylphenyl)methane.[6] A mixture of diphenylmethane (42 g, 0.25 mol), paraformaldehyde (32.5 g, 1.08 mol), phosphoric acid (61.5 mL), 48% aqueous hydrobromic acid (82.5 mL), and glacial acetic acid (102 mL) was stirred under nitrogen at 100 °C for 24 h. The reaction mixture was cooled to 0 °C in an ice bath and the aqueous phase was separated from the organic layer. Reagent grade acetone (0 °C) was added to the organic phase and the mixture was placed in the laboratory refrigerator at 4 °C. The off-white solid product was collected via vacuum filtration (0.5442 g). The yellow liquid filtrate was concentrated under reduced pressure, then triturated with methanol (0 °C), and more off-white solid was isolated via vacuum filtration to yield additional product (1.1254 g). The overall combined product yield was 2%. The ^{1}H NMR spectrum of compound **5** was consistent with the chemical structure.

Purification of Catenanes. After being stirred for 3 to 4 days the catenane solutions were purified and isolated according to the following method. The dark red solid was dissolved in approximately 10 mL of CH_3OH/EtOAc/CH_3COCH_3 (1:1:1) and loaded onto a 2 mm preparative TLC plate. After drying, the plate was eluted twice with CH_3OH/EtOAc (1:1) at 35 °C (R_f 0.1) and finally with CH_3OH/2 M NH_4Cl/CH_3NO_2 (7:2:1) at room temperature (R_f 0.3−0.4). The product was washed from the silica gel with the final eluant and NH_4PF_6 (0.300 g) was added to the red solution. Solvents CH_3OH and CH_3NO_2 were removed via rotary evaporator leaving a red solid suspended in water. This red product was filtered, washed with distilled water, and allowed to dry.

Catenane 1. 1,3-Di(2-(4,4′-dipyridinium)ethoxy)benzene dihexafluorophosphate (**9**) (0.123 g, 0.16 mmol), bis(4-bromomethylphenyl)methane (**5**) (0.068 g, 0.192 mmol), and BPP34C10 (0.223 g, 0.416 mmol) were combined and dissolved in CH_3CN (20 mL). The reaction vessel was sealed with a septum. This red solution was stirred 4 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified and after removal of solvent in vacuo, 0.063 g (22%) of red solid was obtained. ^{1}H NMR (C_3D_6O, 300 MHz at 20 °C): δ (ppm) 9.25 (m, J = 6.1, 6.5 Hz, 8H), 8.29 (d, J = 6.4 Hz, 4H), 8.23 (d, J = 6.3 Hz, 4H), 7.58 (d, J = 7.8 Hz, 4H), 7.48 (d, J = 8.0 Hz, 4H), 7.24 (t, J = 8.4, 1H), 6.87 (t, J = 2.1 Hz, 1H), 6.67 (dd, J = 8.4, 2.1 Hz, 2H), 6.07 (s, 8H), 6.02 (s, 4H), 5.36 (t, J = 4.1 Hz, 4H), 4.76 (t, J = 4.1 Hz, 4H), 4.07 (s, 2H), 3.76∼3.35 (m, 32H). ^{13}C NMR (C_3D_6O, 100 MHz): δ (ppm) 145.9, 130.5, 129.9, 129.5, 126.3, 125.9, 11.8, 106.6, 103.5, 70.3, 69.9, 69.4, 67.2, 65.8, 63.9, 60.9, 40.8. MS (ESI): m/z 450.5 ($M^{4+}PF_6^-$), 748.3 (M^{4+} $2PF_6^-$) (M^{4+} = $C_{73}H_{82}N_4O_{12}^{4+}$ requires 1206.59).

Catenane 2. 1,3-Di(2-(4,4′-dipyridinium)ethoxy)benzene dihexafluorophosphate (**9**) (0.092 g, 0.120 mmol), 1,1′-[[4-(1,1-dimethylethyl)phenyl]methylene]bis[4-(bromomethyl)benzene] (**8**) (0.076 g, 0.156 mmol), and BPP34C10 (0.103 g, 0.192 mmol) were combined and dissolved in CH_3CN (20 mL). The reaction vessel was sealed with a septum. This red solution was stirred 4 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified and after removal of solvent in vacuo, 0.055 g (24%) of red solid was obtained. ^{1}H NMR (C_3D_6O, 300 MHz at 20 °C): δ (ppm) 9.31 (d, J = 5.9 Hz, 8H), 8.37 (d, J = 6.7 Hz, 4H), 8.31 (d, J = 6.7 Hz, 4H), 7.66 (d, J = 8.2 Hz, 4H), 7.44 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.0 Hz, 4H), 7.28 (t, J = 8.5 Hz, 1H), 7.17 (d, J = 8.2 Hz, 2H), 6.94 (t, J = 2.3 Hz, 1H), 6.72 (dd, J = 8.5, 2.3 Hz, 2H), 6.13 (s, 12H), 5.77 (s, 1H), 5.44 (t, J = 3.8 Hz, 4H), 4.76 (t, J = 4.1 Hz, 4H), 3.85−3.47 (m, 32H), 1.32 (s, 9H). ^{13}C NMR (C_3D_6O, 100 MHz): δ (ppm) 145.7, 130.3, 130.2, 129.1, 128.7, 126.3, 125.7, 125.2, 114.7, 106.4, 103.4, 70.4, 70.0, 69.6, 67.4, 65.8, 64.0, 60.8, 55.35, 30.6. MS (ESI): m/z 494.9 ($M^{4+}PF_6^-$), 814.3 ($M^{4+}2PF_6^-$) (M^{4+} = $C_{83}H_{94}N_4O_{12}^{4+}$ requires 1338.68).

Catenane 3. 1,3-Bis-(2-(4,4′-dipyridinium)ethoxy)-5-di-*p*-tolylmethylbenzene dihexafluorophosphate (**10**) (0.158 g, 0.164 mmol), bis(4-bromomethylphenyl)methane (**5**) (0.075 g, 0.213 mmol), and BPP34C10 (0.141 g, 0.263mmol) were combined and dissolved in CH_3CN (20 mL). The reaction vessel was sealed with a septum. This red solution was stirred 4 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified and after removal of solvent in vacuo, 0.058 g (18%) of red solid was obtained. ^{1}H NMR (C_3D_6O, 300 MHz at 20 °C): δ (ppm) 9.36 (d, J = 7.0 Hz, 4H), 9.23 (d, J = 6.7 Hz, 4H), 8.34 (m, J = 6.5, 5.3 Hz, 8H), 7.61 (d, J = 8.5 Hz, 4H), 7.52 (d, J = 8.2 Hz, 4H), 7.10 (d, J = 8.5 Hz, 4H), 7.01 (d, J = 8.2 Hz, 4H), 6.80 (t, J = 2.1 Hz, 1H), 6.47 (d, J = 2.1 Hz, 2H), 6.10 (s, 12H), 5.51 (s, 1H), 5.37 (t, J = 4.1 Hz, 4H), 4.61 (t, J = 4.1 Hz, 4H), 4.12 (s, 2H), 3.76−3.39 (m, 32H), 2.30 (s, 6H). ^{13}C NMR (C_3D_6O, 100 MHz): δ (ppm) 146.2, 146.0, 129.5, 129.2, 128.9, 128.8, 125.9, 114.6, 107.6, 101.3, 70.3, 69.9, 69.5, 67.1, 65.8, 64.1, 61.0, 55.9, 40.9, 27.5. MS (ESI): m/z 515.2 ($M^{4+}PF_6^-$), 845.8($M^{4+}2PF_6^-$) (M^{4+} = $C_{88}H_{96}N_4O_{12}^{4+}$ requires 1400.70).

Catenane 4. 1,3-Bis(2-(4,4′-dipyridinium)ethoxy)-5-di-*p*-tolylmethylbenzene dihexafluorophosphate (**10**) (0.140 g, 0.146 mmol), 1,1′-[[4-(1,1-dimethylethyl)phenyl]methylene]bis[4-(bromomethyl)benzene] (**8**) (0.092 g, 0.190 mmol), and BPP34C10 (0.125 g, 0.233mmol) were combined and dissolved in CH_3CN (20 mL). The reaction vessel was sealed with a septum. This red solution was stirred 4 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified and after removal of solvent in vacuo, 0.057 g (19%) of red solid was obtained. ^{1}H NMR (C_3D_6O, 300 MHz at 20 °C): δ (ppm) 9.38 (m, J = 6.7, 5.6 Hz, 4H), 9.32 (d, J = 7.0 Hz, 2H), 9.07 (d, J = 6.7 Hz, 2H), 8.49 (m, J = 6.8, 6.5 Hz, 4H), 8.21 (dd, J = 6.7, 2.1 Hz, 4H), 7.66 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 7.9 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 7.9 Hz, 4H), 7.03 (d, J = 8.2 Hz, 4H), 6.79 (t, J = 2.1 Hz, 1H), 6.48 (dd, J = 10.9, 2.1 Hz, 2H), 6.14−6.10 (m, 12H), 5.77 (s, 1H), 5.52 (s, 1H), 5.36 (m, 4H), 4.62 (m, 4H), 3.79−3.41 (m, 32H), 2.31 (s, 6H), 1.35 (s, 9H). ^{13}C NMR (C_3D_6O, 100 MHz): δ (ppm) 146.3, 146.2, 145.6, 130.4, 130.0, 129.3, 129.0, 128.9, 128.7, 126.7, 125.3, 125.0, 114.7, 108.3, 106.6, 101.2, 70.3, 70.0, 69.5, 67.3, 67.2, 68.9, 64.3, 63.8, 61.5, 60.4, 55.9, 55.4, 30.7.20.0. MS (ESI): m/z 911.9($M^{4+}2PF_6^-$) (M^{4+} = $C_{98}H_{108}N_4O_{12}^{4+}$ requires 1532.79).

Acknowledgment. The support for R.L.H. as a DAAD guest professor at TU-Berlin and the University of Oklahoma Research Council is appreciated. J.L.M. acknowledges the DOEd for a GAANN Fellowship.

Supporting Information Available: NMR spectra for compounds **1**−**8** and VT ^{1}H NMR spectra of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO070809V