

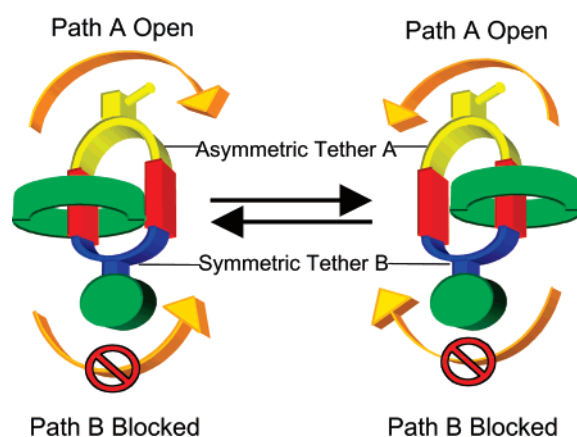
## Translational Isomerizations in [2]Catenanes with Unsymmetrically Substituted Resorcinol-Based Tethers

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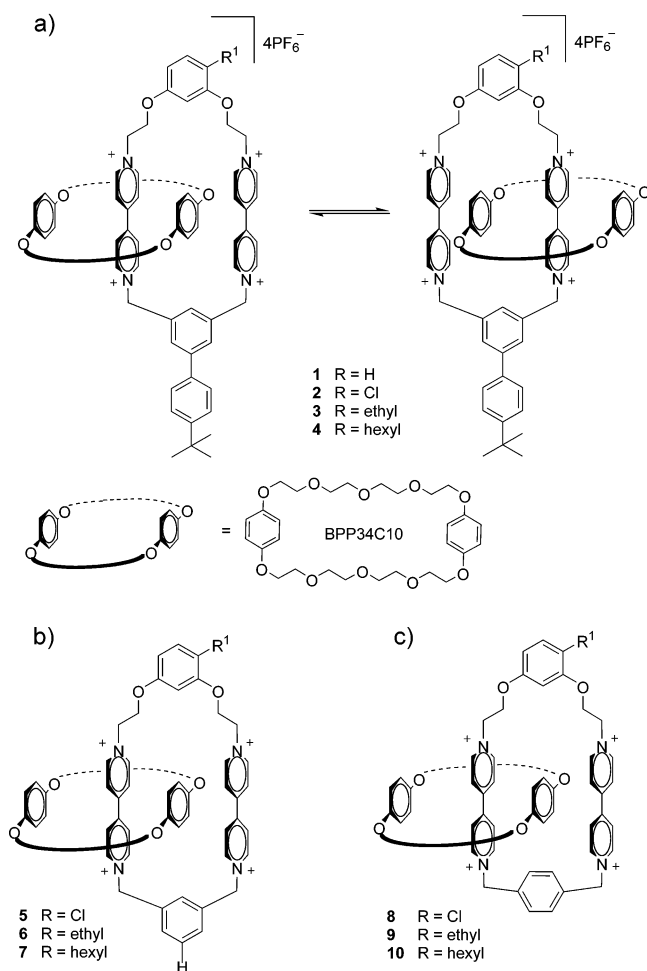


The translational isomerizations of nine [2]catenanes (**2–10**) containing an electron-rich dibenzo-34-crown-10 ether (BPP34C10) interlocked with rings containing an unsymmetric 4-substituted (chloro, ethyl, or hexyl) resorcinol-based tether linking two electron-deficient dipyridyl groups have been studied by variable temperature (VT)  $^1\text{H}$  NMR spectroscopy. The second symmetric tether between the dipyridyl groups was a large 5-(4-*tert*-butylphenyl)-1,3-xylyl (catenanes **2–4**), a narrower 1,3-xylyl (catenanes **5–7**), or a narrow 1,4-xylyl (catenanes **8–10**) group. The presence of the unsymmetrically placed substituent on the resorcinol tether substantially affected the binding energy of the BPP34C10 ring when  $\pi$ -stacked over either of the dipyridyl groups; the equilibrium constant between the bistable states was found to range from 1.5 to 3.5. The origin of these energy differences is postulated to stem from an unsymmetric twisting of the resorcinol tether to minimize interaction between the 4-substituent and the ethoxy group at the 3-position. The activation barriers for passage over the 4-substituted resorcinol-based tether were 12.5, 13, and 15 kcal/mol for the chloro, ethyl, and hexyl substituents, respectively.

### Introduction

Bistable [2]catenanes comprising an electron-rich BPP34C10 ring mechanically interlocked with electron-deficient tethered bis(dipyridinium) rings have developed as important platforms to study noncovalent interactions, molecular motion, and molecular switching.<sup>1–3</sup> Stoddart has established an ability to favor one binding isomer in [2]catenanes containing different  $\pi$ -electron-rich rings that have different degrees of affinity for  $\pi$ -electron-deficient 4,4'-dipyridyls.<sup>4</sup> We were particularly interested in understanding how changes in the tethering groups control the rate, path, and extent of translational equilibria in such [2]catenanes.<sup>5,6</sup> Information regarding the relative binding

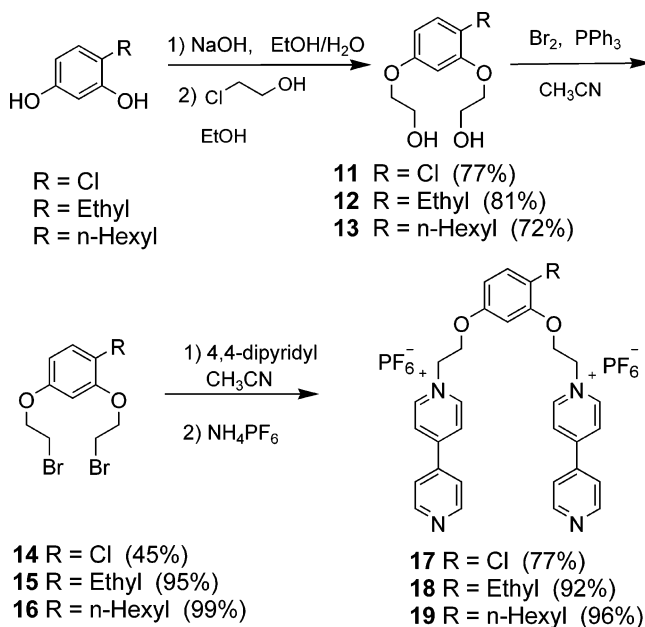
affinity at the bistable sites and the energy barrier as one ring passes along a nonbinding tether between the binding sites on a second ring can provide valuable insights into nonbonding interactions as well as path selection in reactions or interconversions.<sup>5</sup> For isomerizations in bistable catenanes, direct interactions between the tethering groups and the binding site could cause perturbations in the binding ability of one isomer, causing one isomer to become more or less stable than the other isomer. We would like to isolate and minimize the effect of changes in the structure of the tether on binding affinities and thus be able to focus on the effects of changing the nature of the tether on the passage of the second ring along this tether. In previous work, we established the barrier for migration of a



**FIGURE 1.** Resorcinol-based [2]catenanes.

BPP34C10 ring over the resorcinol-based tether in [2]catenane **1** at 13 kcal/mol (Figure 1).<sup>5</sup> In this current report, we examine the effect of remote, unsymmetrically located substituents on the 4-position of a resorcinol ring on the activation barrier and equilibrium constant for the migration of the BPP34C10 ring from one dipyrindyl station to the other along the resorcinol tether in [2]catenanes **2–4** where the substituted xylyl-based tether blocks passage of the crown ether (Figure 1). Comparisons are made with [2]catenanes **5–10** in which translational intercon-

### SCHEME 1



versions can take place along either the resorcinol-based tether or the narrower 1,3-xylyl (catenanes **5–7**) or 1,4-xylyl (catenanes **8–10**) tethers.

### Results and Discussion

In an attempt to isolate 4-resorcinol substituents from the BPP34C10 group while docked at either of the dipyrindium groups, we included synthetically accessible ethyl spacers between the resorcinol ring and the dipyrindium groups. The preparation of the 4-substituted resorcinol derivatives of 1,3-bis(2-(4,4'-dipyridinium)ethoxy)benzene dihexafluorophosphates **17–19** is summarized in Scheme 1.<sup>5,7</sup> All three resorcinol analogues, 4-chlorobenzene-1,3-diol, 4-ethylbenzene-1,3-diol, and 4-*n*-hexylbenzene-1,3-diol, were commercially available and used without further purification. Deprotonation with sodium hydroxide in ethanol/water followed by substitution using 2-chloroethanol converted these starting materials to 1,3-bis(2-hydroxyethoxy)-4-chlorobenzene (**11**), bis(2-hydroxyethoxy)-4-ethylbenzene (**12**), and bis(2-hydroxyethoxy)-4-*n*-hexylbenzene (**13**) in 72–81% yields. In each case, the <sup>1</sup>H NMR spectra of diols **11–13** exhibited different chemical shifts for the methylene hydrogen atoms on the hydroxyethyl arms proximal and distal to the 4-substituent on resorcinol. Bromination of the

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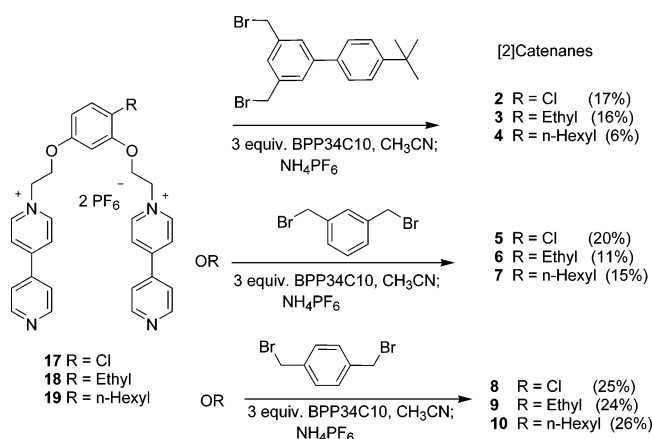
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## SCHEME 2



hydroxy groups was effectively performed using an in situ generated  $\text{Ph}_3\text{PBr}^+\text{Br}^-$  reagent to form bis(2-bromoethoxy) derivatives **14–16** in 45–99% yield.<sup>5</sup> Treatment of these dibromides with 4 equiv of 4,4'-dipyridyl followed by exchange of the bromide to hexafluorophosphate salt provided bis(dipyridyls) **17–19** in 77–96% yield. The twofold excess of 4,4'-dipyridyl seemed sufficient to favor quaternization of only one nitrogen in each 4,4'-dipyridyl group, perhaps owing to the decreased nucleophilicity of the second nitrogen in the initially formed monocationic 4,4'-dipyridiniums.

In each case, the  $^1\text{H}$  NMR spectra of dipyridyls **17–19** exhibited five or six signals for the 4,4'-dipyridinium hydrogen atoms. Nonequivalence due to the influence of the 4-resorcinol substituent was most often observed for the hydrogens  $\beta$  to the cationic nitrogen atom. Also in each compound the ethanolic  $-\text{CH}_2\text{N}^+$  signals were differentiated by  $\Delta\delta$  0.04–0.05 ppm, while the  $-\text{CH}_2\text{O}-$  signals were co-incident. Mass spectral data of the dipyridyl salts **17–19** provided readily identifiable  $[\text{MPF}_6]^+$  and  $[\text{M}]^{2+}$  signals.

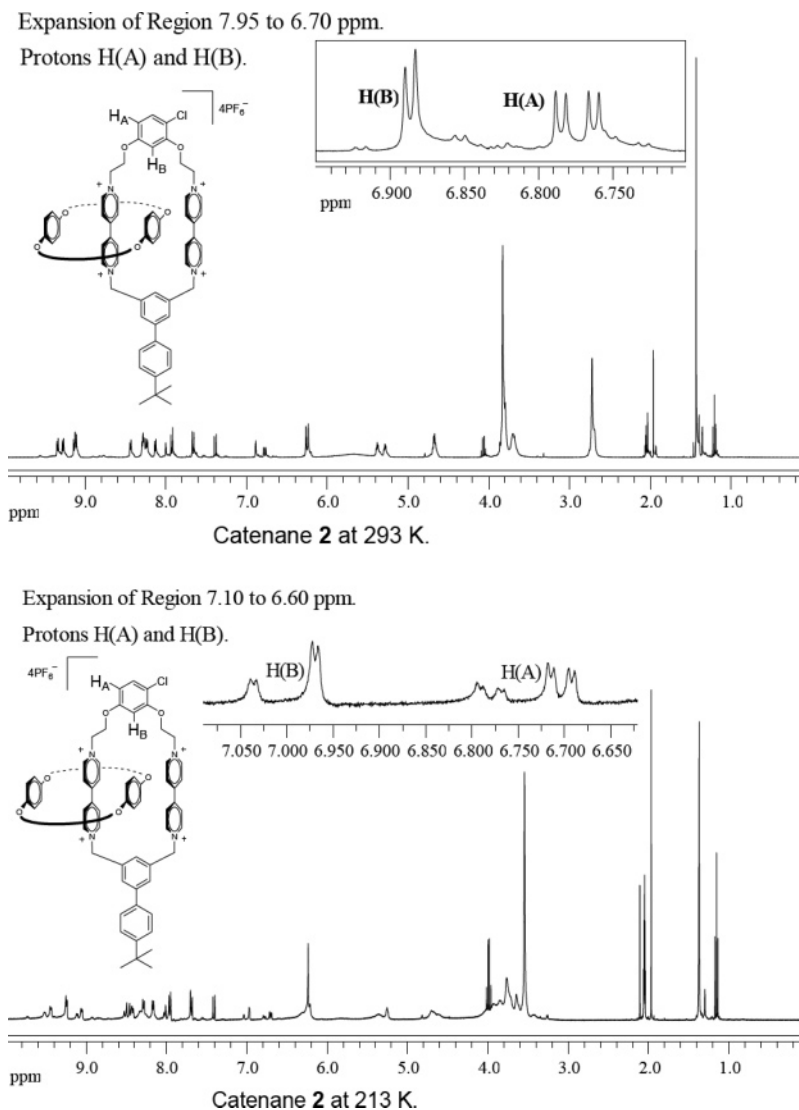
The synthesis of [2]catenanes **2–10** was accomplished according to established three-component procedures.<sup>4</sup> After dissolution of 1 equiv of dipyridyl-substituted resorcinol derivatives **17–19** and 3 equiv of BPP34C10 in acetonitrile, 1.2 equiv of the  $\alpha,\alpha'$ -dibromoxylene tethers—4-*tert*-butylphenyl-substituted **20**,<sup>5,8</sup> 1,3-di(bromomethyl)benzene, or 1,4-di(bromomethyl)benzene—was added as illustrated in Scheme 2. Within 20 min, evidence for formation of red  $\pi$ -stacked complexes appeared. These reaction mixtures were stirred at room temperature for 3–4 days under a nitrogen atmosphere to enable complete consumption of the starting material. By the end of the reaction time, the solutions had turned a deep red color and a yellow precipitate had separated out. After removing the solvent by rotary evaporation, these crude catenane products were purified by preparative  $\text{SiO}_2$  thin layer chromatography. It was noted that, while the commonly used solvent mixture (7:2:1  $\text{CH}_3\text{OH}/2\text{ M NH}_4\text{Cl}/\text{CH}_3\text{NO}_2$ ) did elute the tetracationic [2]catenane, presumably a pseudorotaxane impurity coeluted. By initially eluting the plate with a 1:1 methanol/ethyl acetate mixture at 50 °C, the pseudorotaxanes could dethread and the relatively less polar BPP34C10 could move to the top of the plate.<sup>5</sup> Thus prevented from rethreading to re-form pseudorotaxanes where the cationic dipyridinium groups are shielded by the crown ether, the noncatenated material remained near the baseline when a

second elution of the plate with the 7:2:1 solvent mixture moved the desired [2]catenane to the center of the plate. The product was washed from the silica gel using the 7:2:1 solvent mixture,  $\text{NH}_4\text{PF}_6$  was added, and the nonaqueous solvents were removed by rotary evaporation. The resulting solid was separated by filtration, washed with water, dried, and examined by NMR spectroscopy. If the purity of the sample was not at the desired level, the preparative TLC purification was repeated. No differences were noted when the hexafluorophosphate salts were chromatographed.

Evidence for the formation of the targeted [2]catenanes was provided by mass spectroscopy. For each of the catenanes **2–10**, diagnostic signals were seen for the  $(\text{M}2\text{PF}_6)^{2+}$ ,  $(\text{MPF}_6)^{2+}$ ,  $(\text{MPF}_6)^{3+}$ ,  $(\text{M})^{3+}$ , and  $(\text{M})^{4+}$  ions (M being the tetracationic [2]catenane without counteranions). In all cases, the bistable [2]catenanes **2–10** were translationally mobile at ambient temperatures, generally exhibiting fast exchange in their  $^1\text{H}$  NMR spectra at or above room temperature. Evidence for the alkylation of the dipyridyl groups was seen in the disappearance of signals arising from the bromomethyl groups and the appearance of signals near 6.1 ppm for the xylyl methylenes attached to a cationic pyridinium nitrogen atom. The ratio of signals arising from the methylene hydrogens in BPP34C10 (3.6–3.9 ppm) with dipyridyl signals (9–9.5 ppm) was evidence for the formation of [2]catenanes. At this temperature, the signals for the aromatic hydrogens in BPP34C10 were not observed due to intermediate exchange. For most of the new [2]catenanes, two of the four sets of hydrogen atoms  $\alpha$  to the pyridinium nitrogen atom were clearly separated while the other two sets were co-incident or nearly overlapping (9–9.5 ppm). The signals for the four sets of hydrogen atoms  $\beta$  to the pyridinium nitrogen atoms were typically all separated (8–8.5 ppm). The signals for the two xylyl methylene groups—proximal and distal—to the 4-resorcinol substituent were also separated in each of the catenanes (ca. 6.1 ppm). Thus, the effect of the 4-substituent on the resorcinol ring was felt over a remarkably long distance for the shielding effects to be due to any direct shielding changes. Rather, these chemical shift differences point toward a difference in the populations of BPP34C10 binding to the two dipyridyl groups. If one dipyridyl is preferentially  $\pi$ -stacked with BPP34C10, differences in the shifts of hydrogen atoms mentioned above could be rationalized. The variable temperature (VT) NMR results discussed below support this explanation.

Low-temperature  $^1\text{H}$  NMR spectra were acquired for the catenanes **2–10**. In each case, the spectra clearly indicated the presence of two isomers, but rather than the anticipated 1:1 ratios, the ratios of these isomers were 1.5:1 to 3.5:1. Evidently the remote 4-substituent on the resorcinol ring still strongly influenced the binding affinity of the BPP34C10 ring to the two dipyridinium groups. Illustrative high- and low-temperature NMR spectra are shown in Figure 2 for 4-chlororesorcinol-derived catenane **2**. Complete VT NMR spectra for catenanes **2–10** are included in the Supporting Information. An indication as to a possible origin for the long-range effect of the 4-substituent on the binding affinities can be seen by examining the chemical shift of the hydrogen atom at the 2-position of resorcinol. In catenane **1**, where the substituent on the 4-position was a hydrogen atom, this catenane was symmetric, and at low-temperature, H-2 remained one signal as expected for an atom on an axis of symmetry. Surprisingly, H-2 [H(B) in Figure 2 for catenane **2**] split into two signals at low temperature in each of the catenanes **2–10**. While we anticipated that the chemical

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**FIGURE 2.**  $^1\text{H}$  NMR spectra of catenane **2** at 293 and 213 K.

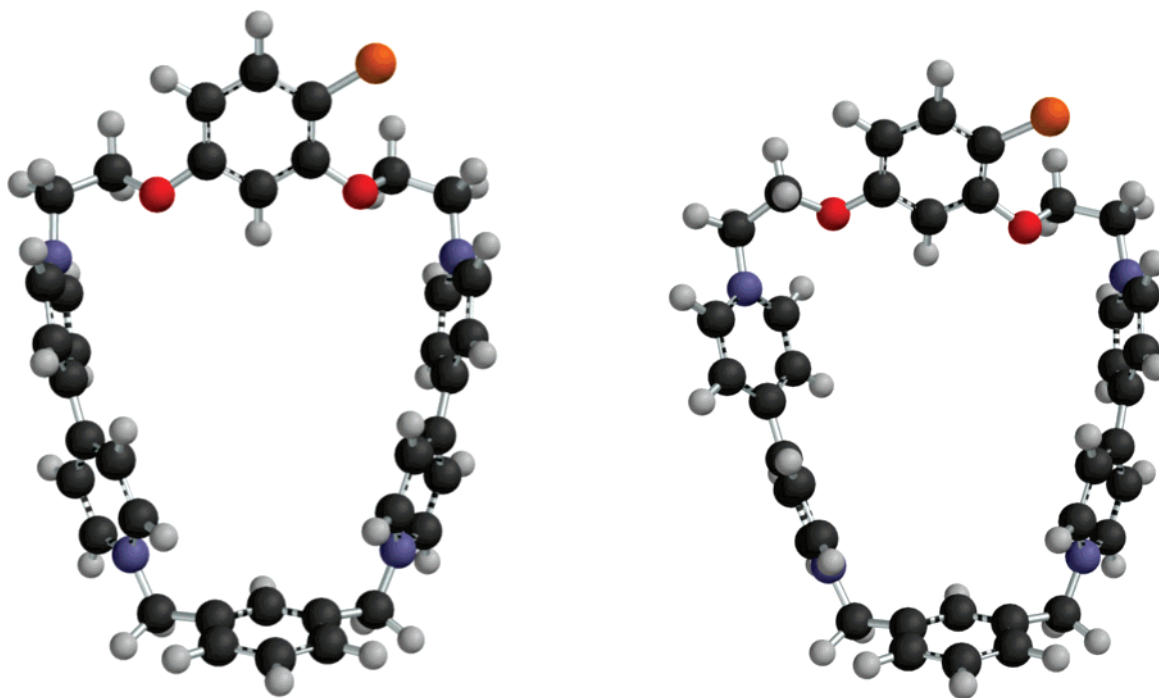
shift environment for H-2 should be similar with the BPP34C10 ring docked at either dipyriddy group, these spectra indicated that H-2 is not in a pseudo-symmetrical environment. Some qualitative insight into the origins of the chemical shift differences could be obtained by looking at AM1 energy-minimized structures for the macrocycle in **2**. The conformation depicted in Figure 3a with the expected symmetrical placement of H-2 was found to be a local energy minimum. A lower-energy minimum has the twisted structure shown in Figure 3b in which H-2 is angled toward one of the dipyriddy groups. In this nonsymmetrical placement, it is understandable that the chemical shift of H-2 with the BPP34C10 docked to the two different dipyriddy groups could give different chemical shifts at slow exchange. The twisting apparent in this conformation minimizes interactions between the 4-substituent and the ethoxy tether.

From the VT NMR spectra, we could extract the energy parameters for the translational interconversions in catenanes **2–10**, and these are summarized in Table 1. We had previously established that in catenane **1** migration over the resorcinol tether required 13 kcal/mol, and migration over the 5-(4-*tert*-butylphenyl)-1,3-xylyl tether required in excess of 18 kcal/mol. Thus, in catenanes **2**, **5**, and **8**, migration should only take place over

the lower barrier presented by the substituted resorcinol tether (12.5–15 kcal/mol). In the catenanes with unsubstituted 1,3- or 1,4-xylyl tethers, migration would be energetically similar over the resorcinol or xylyl tethers (11–12.5 kcal/mol). The 4-hexyl substituent appeared to provide a higher barrier for interconversion than either the smaller and conformationally less mobile 4-chloro or 4-ethyl substituents.

Given our design objectives to isolate the 4-resorcinol substituent from interacting directly with BPP34C10 in low-energy  $\pi$ - $\pi$ -stacked isomeric forms, we were surprised by the 1.5:1 up to 3.5:1 ratios of bistable catenane states at low temperature. Despite significant 2D NMR correlation efforts, we do not know which conformation is favored at equilibrium—whether the BPP34C10 is preferentially over the dipyriddy groups proximal or distal to the 4-resorcinol substituent. The ratios were insensitive to changes in the NMR solvent from chloroform to either acetone or acetonitrile. We do note that the signal for H-2 on the resorcinol tether shifted the minor component further downfield in each of the catenanes **2–10**. If this relative shift is a consistent indicator, then the preferred isomeric forms would be the same in each case. The energy differences in these translational isomers range from 0.2 to 0.6 kcal/mol. The origin of the energetic inequality in the two  $\pi$ - $\pi$ -





**FIGURE 3.** Energy-minimized structures: (a) energy minimum with symmetric structure (991.6 kcal/mol by AM1); (b) energy minimum with twisted structure (990.4 kcal/mol by AM1).

**TABLE 1.** Energy Parameters for Conformational Interconversions in 2–10

catenane	resorcinol tether	xylyl tether	$K_{eq}$	$\Delta G^{\ddagger}_{HardReturn}$ (kcal/mol)
2	4-chloro	<i>tert</i> -butylphenyl-1,3-xylyl	2.5:1	12.5
3		1,3-xylyl	3:1	12
4		1,4-xylyl	2:1	11
5	4-ethyl	<i>tert</i> -butylphenyl-1,3-xylyl	2.5:1	13
6		1,3-xylyl	2.5:1	12.5
7		1,4-xylyl	1.5:1	11
8	4-hexyl	<i>tert</i> -butylphenyl-1,3-xylyl	3.5:1	15
9		1,3-xylyl	2.5:1	12.5
10		1,4-xylyl	1.5:1	11

stacked translational isomers may stem from the low-energy twisted conformation of the dipyrindyl macrocycle depicted in Figure 3b. This twisting of the resorcinol ring may either render one set of dipyrindyls less able to  $\pi$ -stack the BPP34C10 or allow some direct interactions between the 4-resorcinol substituent and the BPP34C10 ring. Attempts to help rationalize a 0.2–0.6 kcal/mol energy difference in these large  $\pi$ – $\pi$ -stacked translational isomers by semiempirical calculations were not conclusive. Although the origin for the energy difference between the translational isomers stems from the 4-substituent on the resorcinol ring, the mechanism for transferring this perturbation to binding energies in a  $\pi$ – $\pi$ -stacked tetracationic salt is yet to be established.

## Conclusion

[2]Catenanes 2–10 were prepared containing one ring with a 4-substituted resorcinol tether linking two dipyrindyl groups and a second BPP34C10 interlocked ring. The remote 4-substituent was intended to cause differences in the activation barriers for interconverting two  $\pi$ – $\pi$ -stacked translational isomers but not in the ground state equilibrium constants. Perhaps due to twisting induced to minimize interactions

between the 4-resorcinol substituent and the 3-ethoxy tether, the ground-state isomer energy differences ranged from 1.5:1 to 3.5:1 in catenanes 2–10. A better understanding of this interesting gearing effect will likely be possible only through additional studies on related structures. The larger 4-hexyl substituent did also provide a higher barrier for interconverting the conformations than did the 4-chloro or 4-ethyl substituents.

## Experimental Details

**1,3-Bis(2-hydroxyethoxy)-4-chlorobenzene (11).** Sodium hydroxide (8.30 g, 207.54 mmol) was dissolved in a solution of ethanol (150 mL) and water (20 mL). To this solution was added 4-chlorobenzene-1,3-diol (10.00 g, 69.18 mmol) previously dissolved in ethanol (25 mL), creating a dark red solution that was allowed to stir for 10 min. 2-Chloroethanol (16.71 g, 207.54 mmol) was added to the stirring solution after which the entirety was refluxed 3 days. Precipitate formed in the reaction vessel, and the solution became ruby red in color. After cooling to room temperature, the solvent was removed in vacuo, leaving a red solid that was dissolved in EtOAc (100 mL) and washed with water (100 mL). The water was extracted twice more with EtOAc (30 mL). After combining, the organic fractions were washed with brine (50 mL) and dried over  $MgSO_4$ . Flash chromatography using diethyl ether provided 12.72 g (79% yield) of pure material:  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.24 (d,  $J$  = 8.7 Hz, 1H), 6.71 (d,  $J$  = 2.7 Hz, 1H), 6.53 (dd,  $J$  = 8.7, 2.7 Hz, 1H), 4.14 (s, 2H), 4.06 (s, 2H), 4.00–3.96 (m, 2H), 3.90 (m,  $J$  = 4.7, 2.8 Hz, 2H), 3.85 (m,  $J$  = 4.7, 2.8 Hz, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  161.1, 157.1, 131.8, 115.6, 108.5, 103.4, 72.6, 72.0, 62.24, 62.17; MS (EI)  $m/z$  255.7 ( $MNa^+$ ), 232.0 ( $M^+$ ) ( $C_{10}H_{13}ClO_4$  requires 232.7).

**1,3-Bis(2-hydroxyethoxy)-4-ethylbenzene (12).** Sodium hydroxide (4.34 g, 108.6 mmol) was dissolved in a solution of ethanol (30 mL) and water (5 mL). To this solution was added 4-ethylbenzene-1,3-diol (5.00 g, 36.19 mmol) previously dissolved in ethanol (15 mL), creating a dark red solution that was allowed to stir for 10 min. 2-Chloroethanol (8.74 g, 108.6 mmol) was added to the stirring solution after which the entirety was refluxed 3 days.

Precipitate formed in the reaction vessel, and the solution became ruby red in color. After cooling to room temperature, the solvent was removed in vacuo, leaving a red solid that was dissolved in EtOAc (50 mL) and washed with water (100 mL). The water was extracted twice more with EtOAc (30 mL). After combining, the organic fractions were washed with brine (50 mL) and dried over MgSO<sub>4</sub>. Flash chromatography using diethyl ether provided 6.6 g (81% yield) of pure material: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.00 (d, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.44 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.07–4.00 (m, 6H), 3.93–3.82 (m, 4H), 2.56 (q, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.5, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 160.3, 159.3, 130.8, 126.5, 106.9, 101.5, 71.5, 71.4, 62.40, 62.37, 24.2, 16.0; MS (EI) *m/z* 226.2 (M<sup>+</sup>), 211.2, 183.2, 149.1, 139.1, 123.1; (EI) *m/z* 249.1 (MNa<sup>+</sup>) (C<sub>12</sub>H<sub>18</sub>O<sub>4</sub> requires 226.3).

**1,3-Bis(2-hydroxyethoxy)-4-*n*-hexylbenzene (13).** Sodium hydroxide (4.73 g, 118 mmol) was dissolved in a solution of ethanol (50 mL) and water (15 mL). To this solution was added 4-*n*-hexylbenzene-1,3-diol (7.66 g, 39 mmol) previously dissolved in ethanol (15 mL), creating a dark red solution that was allowed to stir for 10 min. 2-Chloroethanol (9.52 g, 7.93 mL, 118 mmol) was added to the stirring solution after which the entirety was refluxed 4 days. Precipitate formed in the reaction vessel, and the solution became ruby red in color. After cooling to room temperature, the solvent was removed in vacuo, leaving a red solid that was dissolved in EtOAc (50 mL) and washed with water (100 mL). The water was extracted twice more with EtOAc (30 mL). After combining, the organic fractions were washed with brine (50 mL) and dried over MgSO<sub>4</sub>. Flash chromatography using diethyl ether provided 10.0 g (72% yield) of pure material: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.02 (d, *J* = 8.3 Hz, 1H), 6.48–6.42 (m, 2H), 4.04 (m, *J* = 8.3 Hz, 4H), 3.94 (m, *J* = 8.3 Hz, 4H), 2.54 (m, 2H), 2.31 (br s, 2H), 1.58–1.47 (m, 2H), 1.35–1.25 (m, 7H), 0.88 (m, 3H); <sup>13</sup>C NMR (C<sub>3</sub>D<sub>6</sub>O, 75 MHz) δ 160.3, 159.4, 131.6, 125.1, 106.9, 101.5, 71.5, 71.4, 62.4, 62.4, 33.5, 31.9, 31.1, 24.3, 15.4; MS (EI) *m/z* 282.1 (M<sup>+</sup>), 211.1, 149.1, 121.2 (C<sub>16</sub>H<sub>26</sub>O<sub>4</sub> requires 282.4).

**1,3-Bis(2-bromoethoxy)-4-chlorobenzene (14).** PPh<sub>3</sub> (41.64 g, 158.7 mmol) was added to CH<sub>3</sub>CN (200 mL) and cooled to –10 °C. Br<sub>2</sub> (25.36 g, 158.7 mmol) dissolved in CH<sub>3</sub>CN (30 mL) was slowly added to the stirring PPh<sub>3</sub> mixture so as not to exceed 0 °C. The mixture was allowed to warm to room temperature after the addition was complete. 1,3-Bis(2-hydroxyethoxy)-4-chlorobenzene (11) (15.77 g, 69.00 mmol) dissolved in CH<sub>3</sub>CN (30 mL) was added to the mixture and allowed to stir for 2 h. Solvent was removed in vacuo, and the crude product was purified via column chromatography using CH<sub>2</sub>Cl<sub>2</sub> to elute. The product was obtained in 45% yield (25.6 g), and analysis by NMR showed it to be pure: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.26 (d, *J* = 8.7 Hz, 1H), 6.54 (d, *J* = 2.7 Hz, 1H), 6.47 (dd, *J* = 8.7, 2.7 Hz, 1H), 4.31 (t, *J* = 6.5 Hz, 2H), 4.26 (t, *J* = 6.1 Hz, 2H), 3.66 (dd, *J* = 6.5 Hz, 2H), 3.64 (dd, *J* = 6.5 Hz, 2H); MS (EI) *m/z* 384.9 (MNa<sup>+</sup>), 357.9 (M<sup>+</sup>), 277.1 (M<sup>+</sup> – Br) (C<sub>10</sub>H<sub>11</sub>Br<sub>2</sub>ClO<sub>2</sub> requires 358.5).

**1,3-Bis(2-bromoethoxy)-4-ethylbenzene (15).** PPh<sub>3</sub> (21.84 g, 83.24 mmol) was added to CH<sub>3</sub>CN (100 mL) and cooled to –10 °C. Br<sub>2</sub> (13.30 g, 83.24 mmol) dissolved in CH<sub>3</sub>CN (20 mL) was slowly added to the stirring PPh<sub>3</sub> mixture so as not to exceed 0 °C. The mixture was allowed to warm to room temperature after the addition was complete. 1,3-Bis(2-hydroxyethoxy)-4-ethylbenzene (12) (8.04 g, 36.14 mmol) dissolved in CH<sub>3</sub>CN (20 mL) was added to the mixture and allowed to stir for 5 h. Solvent was removed in vacuo, and the crude product was purified via column chromatography using CH<sub>2</sub>Cl<sub>2</sub> to elute. The product was obtained in 95% yield (12.1 g), and analysis by NMR showed it to be pure: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.06 (d, *J* = 8.5 Hz, 1H), 6.45 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.42 (s, 1H), 4.27 (m, *J* = 6.1 Hz, 4H), 3.67 (m, *J* = 6.1 Hz, 2H), 3.62 (m, *J* = 6.1 Hz, 2H), 2.61 (q, *J* = 7.5 Hz, 2H), 1.18 (t, *J* = 7.5 Hz, 3H); MS (EI) *m/z* 352.0 (M<sup>+</sup>) (C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>Br<sub>2</sub> requires 352.1).

**1,3-Bis(2-bromoethoxy)-4-*n*-hexylbenzene (16).** PPh<sub>3</sub> (12.63 g, 48.1 mmol) was added to CH<sub>3</sub>CN (100 mL) and cooled to

–10 °C. Br<sub>2</sub> (7.69 g, 5.5 mmol) dissolved in CH<sub>3</sub>CN (10 mL) was slowly added to the stirring PPh<sub>3</sub> mixture so as not to exceed 0 °C. The mixture was allowed to warm to room temperature after the addition was complete. 1,3-Bis(2-hydroxyethoxy)-4-*n*-hexylbenzene (13) (5.24 g, 48.1 mmol) dissolved in CH<sub>3</sub>CN (10 mL) was added to the mixture and allowed to stir overnight. Solvent was removed in vacuo, and the crude product was purified via column chromatography using CH<sub>2</sub>Cl<sub>2</sub> to elute. The product was obtained in 99% yield (7.9 g), and analysis by NMR showed it to be pure: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.04 (d, *J* = 6.1 Hz, 1H), 6.46–6.41 (m, 2H), 4.26 (m, *J* = 6.1 Hz, 4H), 3.66 (m, *J* = 6.1 Hz, 2H), 3.63 (m, *J* = 6.2 Hz, 2H), 2.56 (m, 2H), 1.62–1.50 (m, 2H), 1.37–1.29 (m, 6H), 0.93–0.86 (m, 3H); MS (EI) *m/z* 407.9 (M<sup>+</sup>), 346.0 (C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>Br<sub>2</sub> requires 408.2).

**1,3-Bis(2-(4,4'-dipyridinium)ethoxy)-4-chlorobenzene dihexafluorophosphate (17).** 1,3-Bis(2-bromoethoxy)-4-chlorobenzene (14) (3.99 g, 11.20 mmol) and 4,4-dipyridyl (7.00 g, 44.82 mmol) were added to 40 mL of CH<sub>3</sub>CN. This solution was stirred at 70 °C for 2 days during which a yellow solid precipitated onto the sides of the flask. After cooling to room temperature, the solvent was decanted with residual solvent being removed in vacuo, leaving a dark yellow solid. Water was added, and upon heating, the solid dissolved, producing a yellow solution. Addition of NH<sub>4</sub>PF<sub>6</sub> (6 g, 33.6 mmol) produced a yellow oil which was isolated and washed with CHCl<sub>3</sub> (3 × 20 mL) to remove impurities, leaving the same yellow oil which was then dissolved in CH<sub>3</sub>CN and dried with MgSO<sub>4</sub>. Removal of the solvent in vacuo left 6.9 g (77%) of yellow solid: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 9.35 (m, *J* = 6.0 Hz, 4H), 8.89 (m, 4H), 8.74 (m, *J* = 6.0 Hz, 2H), 8.69 (m, *J* = 6.4 Hz, 2H), 8.05–7.97 (m, 4H), 7.28 (d, *J* = 8.8 Hz, 1H), 6.84 (d, *J* = 2.7 Hz, 1H), 6.65 (dd, *J* = 8.8, 2.7 Hz, 1H), 5.37 (m, *J* = 4.9 Hz, 2H), 5.33 (m, *J* = 4.9 Hz, 2H), 4.73 (m, *J* = 4.9 Hz, 4H); MS (ESI) *m/z* 655.1 (MPF<sub>6</sub><sup>+</sup>), 255.1 (M<sup>2+</sup>) (C<sub>30</sub>H<sub>27</sub>ClO<sub>2</sub>N<sub>4</sub><sup>2+</sup> requires 511.0).

**1,3-Bis(2-(4,4'-dipyridinium)ethoxy)-4-ethylbenzene dihexafluorophosphate (18).** 1,3-Bis(2-bromoethoxy)-4-ethylbenzene (15) (8.7 g, 25.0 mmol) and 4,4-dipyridyl (15.62 g, 100 mmol) were added to 100 mL of CH<sub>3</sub>CN. This solution was stirred at 70 °C for 2 days during which time a yellow brown solid was deposited on the sides of the flask. After cooling to room temperature, the solvent was decanted and the solid washed with additional CH<sub>3</sub>CN (2 × 30 mL). Residual solvent was then removed in vacuo, leaving a brown solid. Water was added, and upon heating, the solid dissolved, producing a yellow solution. Addition of NH<sub>4</sub>PF<sub>6</sub> (12.0 g, 0.75 mmol) produced a yellow oil which was isolated and washed with CHCl<sub>3</sub> (3 × 30 mL) to extract impurities, leaving a yellow oil which was then dissolved in CH<sub>3</sub>CN and dried with MgSO<sub>4</sub>. Removal of the solvent in vacuo left 18.3 g of yellow solid for a yield of 92%: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 9.39 (m, *J* = 6.6 Hz, 2H), 9.35 (m, *J* = 6.6 Hz, 2H), 8.89 (m, *J* = 6.2, 2.7 Hz, 4H), 8.76 (m, *J* = 7.0 Hz, 2H), 8.70 (m, *J* = 6.9 Hz, 2H), 8.03 (m, 4H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 6.53 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.37 (m, 2H), 5.32 (m, 2H), 4.67 (m, 4H), 2.45 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H); MS (ESI) *m/z* 649.2 (MPF<sub>6</sub><sup>+</sup>), 252.1 (M<sup>2+</sup>) (C<sub>32</sub>H<sub>32</sub>O<sub>2</sub>N<sub>4</sub><sup>2+</sup> requires 504.6).

**1,3-Bis(2-(4,4'-dipyridinium)ethoxy)-4-*n*-hexylbenzene dihexafluorophosphate (19).** 1,3-Bis(2-bromoethoxy)-4-*n*-hexylbenzene (16) (1.00 g, 2.45 mmol) and 4,4-dipyridyl (1.66 g, 10.64 mmol) were added to 15 mL of CH<sub>3</sub>CN. This solution was stirred at 70 °C for 2 days during which a dark yellow solid was produced. After cooling to room temperature, the solvent was decanted with residual solvent being removed in vacuo, leaving a brown solid. Water was added, and upon heating, the solid dissolved, producing a brown solution. Addition of NH<sub>4</sub>PF<sub>6</sub> (11 g) produced a brown oil which was isolated and washed with CHCl<sub>3</sub> (3 × 20 mL) to remove impurities, leaving a yellow oil which was then dissolved in CH<sub>3</sub>CN and dried with MgSO<sub>4</sub>. Removal of the solvent in vacuo left 1.66 g (96%) of yellow solid: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 9.47 (m, *J* = 7.1 Hz, 2H), 9.40 (m, *J* = 7.1 Hz, 2H), 8.87 (m, 4H), 8.74 (m, *J* = 7.1 Hz, 4H), 8.01 (m, *J* = 6.1 Hz, 4H), 7.00 (d, *J* =

8.3 Hz, 1H), 6.73 (d,  $J = 2.4$  Hz, 1H), 6.51 (dd,  $J = 8.3, 2.4$  Hz, 1H), 5.38 (m, 2H), 5.33 (m, 2H), 4.71 (m,  $J = 5.0$  Hz, 4H), 2.41 (m, 2H), 1.33–1.23 (m, 2H), 1.21–1.09 (m, 6H), 0.73 (m, 3H); MS (ESI)  $m/z$  705.3 (MPF<sub>6</sub><sup>+</sup>), 280.1 (M<sup>2+</sup>) (C<sub>36</sub>H<sub>40</sub>O<sub>2</sub>N<sub>4</sub><sup>2+</sup> requires 560.7).

**Purification of Catenanes.** After stirring for 3–4 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<sub>3</sub>OH/EtOAc/CH<sub>3</sub>COCH<sub>3</sub> (1:1:1) and loaded onto a 2 mm PLC plate. After drying, the plate was eluted twice with CH<sub>3</sub>OH/EtOAc (1:1) at 35 °C and finally with CH<sub>3</sub>OH/2 M NH<sub>4</sub>Cl/CH<sub>3</sub>NO<sub>2</sub> (7:2:1) at room temperature. The product was washed from the silica gel using the final eluant, and NH<sub>4</sub>PF<sub>6</sub> (0.300 g) was added to the red solution. Solvents CH<sub>3</sub>OH and CH<sub>3</sub>NO<sub>2</sub> 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. Impurities detected after the first separation were removed by an additional purification using a 0.5 mm PLC plate and identical procedures.

**Catenane 2.** 1,3-Bis(2-(4,4'-dipyridinium)ethoxy)-4-chlorobenzene dihexafluorophosphate (**17**) (0.128 g, 0.16 mmol) and BPP34C10 (0.223 g, 0.416 mmol) were combined and dissolved in CH<sub>3</sub>CN (15 mL). This solution was allowed to stir for 10 min at which point 5-bis(bromomethyl)-4'-(1,1'-dimethylethyl)-1,1'-biphenyl (0.0765 g, 0.192 mmol) was added and the reaction vessel sealed with a septa. This red solution stirred 4 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified, and after drying, 51 mg (17%) of pure product was recovered: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  9.34 (m,  $J = 7.0$  Hz, 2H), 9.27 (m,  $J = 7.0$  Hz, 2H), 9.13 (d,  $J = 7.1$  Hz, 1H), 9.11 (d,  $J = 7.1$  Hz, 1H), 8.44 (m,  $J = 4.1, 1.6$  Hz, 2H), 8.29 (d,  $J = 4.8$  Hz, 1H), 8.27 (d,  $J = 4.8$  Hz, 1H), 8.23 (m,  $J = 7.0$  Hz, 2H), 8.13 (m,  $J = 7.0$  Hz, 2H), 8.00 (t,  $J = 1.4$  Hz, 1H), 7.93 (m,  $J = 8.6$  Hz, 2H), 7.66 (m,  $J = 8.6$  Hz, 2H), 7.39 (d,  $J = 8.9$  Hz, 1H), 6.89 (d,  $J = 2.7$  Hz, 1H), 6.77 (dd,  $J = 8.9, 2.7$  Hz, 1H), 6.26 (s, 2H), 6.24 (s, 2H), 5.66 (br s, 8H), 5.38 (m, 2H), 5.29 (m, 2H), 4.68 (m,  $J = 9.5, 5.0$  Hz, 4H), 3.88–3.62 (m, 32H), 1.43 (s, 9H); MS (ESI) 786.3 (M<sub>2</sub>PF<sub>6</sub><sup>2+</sup>), 476.2 (MPF<sub>6</sub><sup>3+</sup>), 427.6 (M<sup>3+</sup>), 320.7 (M<sup>4+</sup>) (C<sub>76</sub>H<sub>75</sub>ClN<sub>4</sub>O<sub>12</sub><sup>4+</sup> requires 1283.97).

**Catenane 3.** 1,3-Bis(2-(4,4'-dipyridinium)ethoxy)-4-ethylbenzene dihexafluorophosphate (**18**) (0.123 g, 0.16 mmol) and BPP34C10 (0.223 g, 0.416 mmol) were combined and dissolved in CH<sub>3</sub>CN (15 mL). This solution was allowed to stir for 10 min at which point 5-bis(bromomethyl)-4'-(1,1'-dimethylethyl)-1,1'-biphenyl (0.0765 g, 0.192 mmol) was added and the reaction vessel sealed with a septa. This red solution stirred 4 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified, and after drying, 48 mg (16%) of pure product was recovered: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  9.34 (m,  $J = 6.6$  Hz, 2H), 9.27 (m,  $J = 6.6$  Hz, 2H), 9.15 (m,  $J = 7.0$  Hz, 2H), 9.10 (m,  $J = 7.0$  Hz, 2H), 8.44 (m,  $J = 6.6$  Hz, 2H), 8.26 (m,  $J = 6.6, 7.0$  Hz, 6H), 8.11 (m,  $J = 7.0$  Hz, 2H), 8.00 (t,  $J = 1.5$  Hz, 1H), 7.93 (m,  $J = 8.5$  Hz, 2H), 7.66 (m,  $J = 8.5$  Hz, 2H), 7.16 (d,  $J = 8.4$  Hz, 1H), 6.76 (d,  $J = 2.4$  Hz, 1H), 6.66 (dd,  $J = 8.4, 2.4$  Hz, 1H), 6.27 (s, 2H), 6.23 (s, 2H), 6.03–5.46 (m, 8H), 5.36 (m, 2H), 5.27 (m, 2H), 4.63 (m, 2H), 4.58 (m, 2H), 3.87–3.64 (m, 32H), 2.68 (q,  $J = 7.5$  Hz, 2H), 1.43 (s, 9H), 1.20 (t,  $J = 7.5$  Hz, 3H); MS (ESI)  $m/z$  1718.6 (M<sub>3</sub>PF<sub>6</sub><sup>3+</sup>), 783.3 (M<sub>2</sub>PF<sub>6</sub><sup>2+</sup>), 473.9 (MPF<sub>6</sub><sup>3+</sup>), 427.6 (M<sup>3+</sup>), 319.4 (M<sup>4+</sup>) (C<sub>78</sub>H<sub>92</sub>N<sub>4</sub>O<sub>12</sub><sup>4+</sup> requires 1277.58).

**Catenane 4.** 1,3-Bis(2-(4,4'-dipyridinium)ethoxy)-4-*n*-hexylbenzene dihexafluorophosphate (**19**) (0.123 g, 0.16 mmol) and BPP34C10 (0.223 g, 0.416 mmol) were combined and dissolved in CH<sub>3</sub>CN (15 mL). This solution was allowed to stir for 10 min at which point  $\alpha, \alpha'$ -dibromo-*p*-xylene (0.051 g, 0.192 mmol) was added and the reaction vessel sealed with a septa. This red solution stirred 4 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified, and after drying, 17 mg (6%) of pure product was recovered: <sup>1</sup>H NMR (CDCl<sub>3</sub>,

400 MHz)  $\delta$  9.34 (m,  $J = 6.7$  Hz, 2H), 9.28 (m,  $J = 6.7$  Hz, 2H), 9.14 (m,  $J = 6.6$  Hz, 2H), 9.07 (m, 2H), 8.44 (m,  $J = 3.8$  Hz, 2H), 8.36–8.06 (m, 2H), 8.01 (m, 1H), 7.94 (d,  $J = 8.5$  Hz, 2H), 7.66 (d,  $J = 8.5$  Hz, 2H), 7.15 (d,  $J = 8.5$  Hz, 1H), 6.77 (d,  $J = 2.0$  Hz, 1H), 6.65 (dd,  $J = 8.4, 2.0$  Hz, 1H), 6.26 (s, 2H), 6.23 (s, 2H), 5.74 (br s, 8H), 5.34 (m, 2H), 5.26 (m, 2H), 4.64–4.55 (m, 4H), 3.88–3.63 (m, 32H), 2.68–2.65 (m, 2H), 1.62 (m, 2H), 1.43 (s, 9H), 1.40–1.33 (m, 7H), 0.91 (m,  $J = 6.9$  Hz, 3H); MS (ESI) 666.4 (M<sup>2+</sup>), 492.9 (MPF<sub>6</sub><sup>3+</sup>), 333.2 (M<sup>4+</sup>) (C<sub>82</sub>H<sub>100</sub>N<sub>4</sub>O<sub>12</sub><sup>4+</sup> requires 1333.69).

**Catenane 5.** 1,3-Bis(2-(4,4'-dipyridinium)ethoxy)-4-chlorobenzene dihexafluorophosphate (**17**) (0.128 g, 0.16 mmol) and BPP34C10 (0.172 g, 0.320 mmol) were combined and dissolved in CH<sub>3</sub>CN (15 mL). This solution was allowed to stir for 10 min at which point  $\alpha, \alpha'$ -dibromo-*m*-xylene (0.051 g, 0.192 mmol) was added and the reaction vessel sealed with a septa. This red solution stirred 4 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified, and after drying, 55 mg (20%) of pure product was recovered: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  9.25 (m,  $J = 7.0$  Hz, 2H), 9.17 (m,  $J = 7.0, 4.05$  Hz, 4H), 9.11 (m,  $J = 6.7$  Hz, 2H), 8.31 (m,  $J = 6.6$  Hz, 2H), 8.27 (m,  $J = 6.5$  Hz, 2H), 8.23 (m,  $J = 6.7$  Hz, 2H), 8.15 (m,  $J = 7.7, 6.9$  Hz, 4H), 8.06 (t,  $J = 1.6$  Hz, 1H), 7.90 (t,  $J = 7.8$  Hz, 1H), 7.39 (d,  $J = 8.9$  Hz, 1H), 6.90 (d,  $J = 2.7$  Hz, 1H), 6.76 (dd,  $J = 8.9, 2.7$  Hz, 1H), 6.20 (s, 2H), 6.17 (s, 2H), 5.39 (s, 2H), 5.29 (s, 2H), 5.03 (br s, 8H), 4.68 (t,  $J = 3.8$  Hz, 4H), 3.91–3.51 (m, 32H); MS (ESI) 648.3 (M<sub>1</sub>PF<sub>6</sub><sup>2+</sup>), 432.2 (MPF<sub>6</sub><sup>3+</sup>), 383.5 (M<sup>3+</sup>), 288.2 (M<sup>4+</sup>) (C<sub>66</sub>H<sub>75</sub>ClN<sub>4</sub>O<sub>12</sub><sup>4+</sup> requires 1151.77).

**Catenane 6.** 1,3-Bis(2-(4,4'-dipyridinium)ethoxy)-4-ethylbenzene dihexafluorophosphate (**18**) (0.123 g, 0.16 mmol) and BPP34C10 (0.172 g, 0.320 mmol) were combined and dissolved in CH<sub>3</sub>CN (15 mL). This solution was allowed to stir for 10 min at which point  $\alpha, \alpha'$ -dibromo-*m*-xylene (0.051 g, 0.192 mmol) was added and the reaction vessel sealed with a septa. This red solution stirred 4 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified, and after drying, 29 mg (11%) of pure product was recovered: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  9.25 (m,  $J = 7.0$  Hz, 2H), 9.15 (m,  $J = 7.0$  Hz, 4H), 9.09 (m,  $J = 7.0$  Hz, 2H), 8.28 (m,  $J = 7.0$  Hz, 2H), 8.27–8.22 (m, 4H), 8.16 (dd,  $J = 7.7, 1.2$  Hz, 2H), 8.11 (m,  $J = 7.0$  Hz, 2H), 8.06 (t,  $J = 1.2$  Hz, 1H), 7.89 (t,  $J = 7.7$  Hz, 1H), 7.16 (d,  $J = 8.4$  Hz, 1H), 6.76 (d,  $J = 2.4$  Hz, 1H), 6.65 (dd,  $J = 8.4, 2.4$  Hz, 1H), 6.19 (s, 2H), 6.16 (s, 2H), 5.72 (br s, 8H), 5.36 (m,  $J = 4.9$  Hz, 2H), 5.27 (m,  $J = 4.8$  Hz, 2H), 4.64 (m,  $J = 4.9$  Hz, 2H), 4.59 (m,  $J = 4.8$  Hz, 2H), 3.89–3.63 (m, 32H), 2.68 (q,  $J = 7.7$  Hz, 2H), 1.20 (t,  $J = 7.7$  Hz, 3H); MS (ESI) 717.3 (M<sub>2</sub>PF<sub>6</sub><sup>2+</sup>), 430.2 (MPF<sub>6</sub><sup>3+</sup>), 286.3 (M<sup>4+</sup>) (C<sub>68</sub>H<sub>80</sub>N<sub>4</sub>O<sub>12</sub><sup>4+</sup> requires 1145.38).

**Catenane 7.** 1,3-Bis(2-(4,4'-dipyridinium)ethoxy)-4-*n*-hexylbenzene dihexafluorophosphate (**19**) (0.123 g, 0.16 mmol) and BPP34C10 (0.223 g, 0.416 mmol) were combined and dissolved in CH<sub>3</sub>CN (15 mL). This solution was allowed to stir for 10 min at which point  $\alpha, \alpha'$ -dibromo-*m*-xylene (0.051 g, 0.192 mmol) was added and the reaction vessel sealed with a septa. This red solution stirred 4 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified, and after drying, 43 mg (15%) of pure product was recovered: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  9.26 (m,  $J = 6.9$  Hz, 2H), 9.17 (m,  $J = 6.9$  Hz, 4H), 9.09 (m,  $J = 6.9$  Hz, 2H), 8.31–8.23 (m, 6H), 8.19–8.11 (m, 4H), 8.07–8.05 (m, 1H), 7.90 (t,  $J = 7.7$  Hz, 1H), 7.16 (d,  $J = 8.4$  Hz, 1H), 6.78 (d,  $J = 2.4$  Hz, 1H), 6.66 (dd,  $J = 8.4, 2.4$  Hz, 1H), 6.20 (s, 2H), 6.17 (s, 2H), 5.77 (br s, 8H), 5.36 (s, 2H), 5.28 (s, 2H), 4.61 (m,  $J = 4.9$  Hz, 4H), 3.90–3.62 (m, 32H), 2.08 (m,  $J = 3.1$  Hz, 2H), 1.68–1.56 (m, 2H), 1.43–1.29 (m, 6H), 0.91 (t,  $J = 6.9$  Hz, 3H); MS (ESI) 745.3 (M<sub>2</sub>PF<sub>6</sub><sup>2+</sup>), 672.8 (MPF<sub>6</sub><sup>3+</sup>), 600.5 (M<sup>2+</sup>), 448.6 (MPF<sub>6</sub><sup>3+</sup>), 400.2 (M<sup>3+</sup>), 300.2 (M<sup>4+</sup>) (C<sub>72</sub>H<sub>88</sub>N<sub>4</sub>O<sub>12</sub><sup>4+</sup> requires 1201.49).

**Catenane 8.** 1,3-Bis(2-(4,4'-dipyridinium)ethoxy)-4-chlorobenzene dihexafluorophosphate (**17**) (0.128 g, 0.16 mmol) and BPP34C10 (0.223 g, 0.416 mmol) were combined and dissolved



in CH<sub>3</sub>CN (15 mL). This solution was allowed to stir for 10 min at which point  $\alpha,\alpha'$ -dibromo-*p*-xylene (0.051 g, 0.192 mmol) was added and the reaction vessel sealed with a septa. This red solution stirred 4 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified, and after drying, 70 mg (25%) of pure product was recovered: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  9.37 (m, *J* = 7.1 Hz, 2H), 9.31 (m, *J* = 7.1 Hz, 2H), 9.15 (m, *J* = 7.1, 1.3 Hz, 4H), 8.25 (m, *J* = 7.1 Hz, 2H), 8.13 (m, *J* = 7.1 Hz, 2H), 8.08 (m, *J* = 7.0, 3.4 Hz, 4H), 8.06 (m, *J* = 2.5 Hz, 4H), 7.37 (d, *J* = 8.8 Hz, 1H), 6.82 (d, *J* = 2.7 Hz, 1H), 6.75 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.10 (s, 2H), 6.07 (s, 2H), 5.64–5.39 (m, 8H), 5.35 (m, 2H), 5.25 (m, 2H), 4.69 (m, 2H), 4.64 (m, 2H), 3.91–3.82 (m, 20H), 3.80–3.76 (m, 6H), 3.66–3.62 (m, 6H); MS (ESI) 1586.5 (M3PF<sub>6</sub><sup>+</sup>), 720.3 (M2PF<sub>6</sub><sup>2+</sup>), 432.2 (MPF<sub>6</sub><sup>3+</sup>), 287.9 (M<sup>4+</sup>) (C<sub>66</sub>H<sub>75</sub>ClN<sub>4</sub>O<sub>12</sub><sup>4+</sup> requires 1151.77).

**Catenane 9.** 1,3-Bis(2-(4,4'-dipyridinium)ethoxy)-4-ethylbenzene dihexafluorophosphate (**18**) (0.123 g, 0.16 mmol) and BPP34C10 (0.223 g, 0.416 mmol) were combined and dissolved in CH<sub>3</sub>CN (15 mL). This solution was allowed to stir for 10 min at which point  $\alpha,\alpha'$ -dibromo-*p*-xylene (0.051 g, 0.192 mmol) was added and the reaction vessel sealed with a septa. This red solution stirred 3 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified, and after drying, 67 mg (24%) of pure product was recovered: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  9.40 (m, *J* = 7.0 Hz, 2H), 9.34 (m, *J* = 7.0 Hz, 2H), 9.20 (m, *J* = 7.0 Hz, 2H), 9.15 (m, *J* = 7.0 Hz, 2H), 8.29 (m, *J* = 7.0 Hz, 2H), 8.15 (m, *J* = 7.0 Hz, 4H), 8.11–8.04 (m, 6H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 6.63 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.11 (s, 2H), 6.08 (s, 2H), 5.35 (m, 2H), 5.26 (m, 2H), 4.64 (m, 2H), 4.58 (m, 2H), 3.95–3.48 (m, 32H), 2.63 (dd, *J* = 7.5 Hz, 2H), 1.16 (t, *J* = 7.5 Hz, 3H); MS (ESI) 572.3 (M<sup>2+</sup>), 381.5 (M<sup>3+</sup>), 286.1 (M<sup>4+</sup>) (C<sub>68</sub>H<sub>80</sub>N<sub>4</sub>O<sub>12</sub><sup>4+</sup> requires 1145.38).

**Catenane 10.** 1,3-Bis(2-(4,4'-dipyridinium)ethoxy)-4-*n*-hexylbenzene dihexafluorophosphate (**19**) (0.123 g, 0.16 mmol) and BPP34C10 (0.223 g, 0.416 mmol) were combined and dissolved in CH<sub>3</sub>CN (15 mL). This solution was allowed to stir for 10 min at which point  $\alpha,\alpha'$ -dibromo-*p*-xylene (0.051 g, 0.192 mmol) was added and the reaction vessel sealed with a septa. This red solution stirred 4 days under ambient conditions after which time the solvent was removed in vacuo. The catenane was purified, and after drying, 75 mg (26%) of pure product was recovered: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  9.44 (m, *J* = 7.0 Hz, 2H), 9.40 (m, *J* = 7.0 Hz, 2H), 9.25 (m, *J* = 7.0 Hz, 2H), 9.20 (m, *J* = 7.0 Hz, 2H), 8.34 (m, *J* = 7.0 Hz, 2H), 8.20 (m, *J* = 7.0 Hz, 4H), 8.15 (m, *J* = 7.0 Hz, 2H), 8.12 (m, 2H), 8.08 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 6.68 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.16 (s, 2H), 6.14 (s, 2H), 5.40 (m, 2H), 5.32 (m, 2H), 4.68 (m, 2H), 4.63 (m, 2H), 4.02–3.54 (m, 40H), 2.68 (t, *J* = 7.4 Hz, 2H), 1.63 (m, 2H), 1.37 (m, 6H), 0.93 (m, *J* = 6.7 Hz, 3H); MS (ESI) 1636.4 (M3PF<sub>6</sub><sup>+</sup>), 745.3 (M2PF<sub>6</sub><sup>2+</sup>), 448.8 (MPF<sub>6</sub><sup>3+</sup>), 300.4 (M<sup>4+</sup>) (C<sub>72</sub>H<sub>88</sub>N<sub>4</sub>O<sub>12</sub><sup>4+</sup> requires 1201.49).

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**Supporting Information Available:** NMR spectra for compounds **2–19**. VT <sup>1</sup>H NMR spectra of compounds **2–10**. Details of energy minimized structure computations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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