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Synthesis of [2]Catenanes by Template-Directed Clipping Approach

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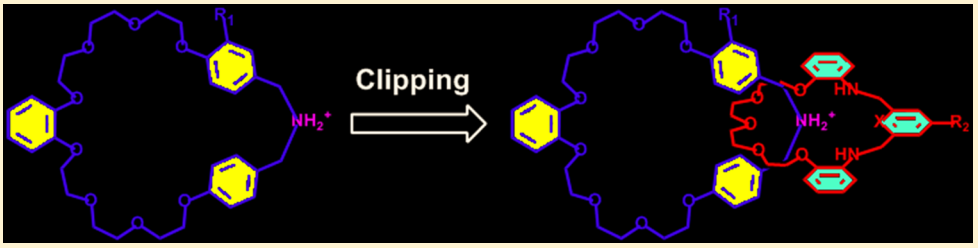
Supporting Information



ABSTRACT: A series of [2]catenanes were efficiently synthesized in high yields by a template-directed clipping approach with the formation of one macrocycle around another macrocycle containing a dialkylammonium recognition site. Their structures were identified by the NMR spectra and ESI mass spectrometry, and their geometries were investigated by the theoretical calculation.

In the field of molecular devices and machines, studies on the mechanically interlocked molecular architectures such as rotaxanes, catenanes and knots have become the focus of research.[1] The efficient synthesis of mechanically interlocked molecules is crucial for their successful applications. Catenanes, topologically unique structures possessing two or more mechanically interlocked rings, have been known for nearly half a century.[2] In recent years, the rapid development of catenanes has promoted the understanding of design strategies and self-assembling structures of synthetic supramolecular systems. Current synthetic approaches mainly rely on supramolecular preorganization of the macrocyclic precursors utilizing noncovalent interactions such as hydrogen bonding, metal coordination, hydrophobic forces, electronic effects and $\pi-\pi$ stacking.[3] This "template-directed" approach can efficiently promote formation of the desired catenanes upon the final ring-closing reaction. For instance, Stoddart and Saha utilized the $\pi-\pi$ stacking and donor−acceptor interactions to develop numerous functional catenanes.[4] Metal template based on the coordination was also used to synthesize mechanically interlocked catenanes.[5,6] Beer et al. utilized anions as hydrogen-bond acceptor and developed an efficient synthetic method of catenanes.[7] Recently, Leigh et al. reported the synthetic strategy of [2]catenanes by the active metal templated click chemistry.[8] Olefine metathesis reaction as the classical cyclization was usually used for the synthesis of catenane molecules after the formation of pseudorotaxanes by threading.[9]

The dynamic clipping protocol for the synthesis of rotaxanes has been widely reported, which took advantage of noncovalent bonding interactions to control the formation of ring by templation.[10] Recently, Liu reported a π-templated dynamic clipping reaction to construct [2]catenanes from dialdehyde, diamine and bipyridyl tetracationic cyclophane.[11] The template-directed clipping reaction based on 2,6-pyridinedicarboxaldehyde and tetra(ethylene glycol) bis(2-aminophenyl)ether can efficiently form dynamic macrocycles around the dialkylammonium recognition sites.[10,12] However, few reports investigated the clipping efficiency of the macrocyclic alkylammonium sites. It was worth mentioning that the clipping reaction based on 2,6-pyridinedicarboxaldehyde and tetra(ethylene glycol) bis(2-aminophenyl)ether could form catenanes having different geometry due to the configuration of N-heterocrown ether component, which promoted us to explore the application of clipping reaction in the synthesis of catenanes and steric configuration of catenanes. Herein, we designed and synthesized two macrocycles having alkylammonium site, which were used to successfully prepare a series of [2]catenanes in high yields by template-directed clipping reactions, as shown in Scheme 1.

The stepwise synthesis of macrocyclic alkylammonium salts **1a**,**b** was shown in Scheme 2. The 4-(aminomethyl)phenol (**5**) as starting material was treated with 4-hydroxybenzaldehyde (**4a**) and 4-hydroxy-3-methoxybenzaldehyde (**4b**) to afford the corresponding dynamic imine **6a** and **6b** in the presence of anhydrous magnesium sulfate, respectively, which were then reduced by $NaBH_4$ in the solution of THF and MeOH to give the kinetically stable amine **7a** and **7b**, respectively, in 63−85% yields for two steps. The cyclization was performed by the condensation of the amines **7a**,**b** with the pseudo crown ether **8** in the condition of Cs_2CO_3, in which the Cs^+ was also served as the template of cyclization simultaneity. Compound **8** was

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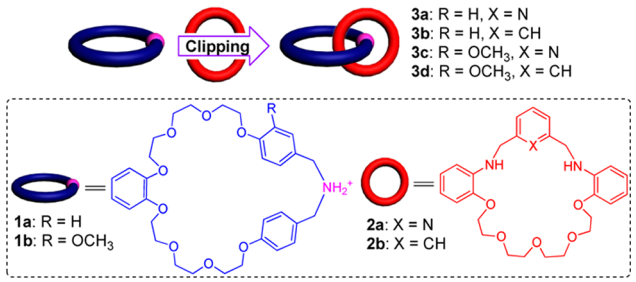
Scheme 1. Schematic Representation of the Template-Directed Clipping Approach for the Synthesis of [2]Catenanes



synthesized according to the previous literature.[13] In view of convenient purification, the NH of free amines was protected by the Boc_2O before purification. Subsequently, the Boc-protected macrocyclic alkylamines **9a** and **9b** were obtained in 23−26% yields for two steps. Their Boc protective groups were removed with excess trifluoroacetic acid (TFA) in dry dichloromethane, and the as-formed amines were simultaneously protonated. Subsequent counterion exchange with saturated NH_4PF_6 afforded the macrocyclic alkylammonium salts **1a** and **1b** in 91−93% yields. The key intermediates were well characterized by the standard spectroscopic techniques such as NMR spectroscopy, mass spectrometry and elemental analysis. Additionally, for comparison, *N*-heterocrown ethers **2a** and **2b** as one of the components of catenanes were also synthesized in 43−75% yields by the condensation of 2,6-pyridinedicarboxaldehyde (**10a**), 1,3-benzenedialdehyde (**10b**) and tetra(ethylene glycol) bis(2-aminophenyl)ether (**11**), respectively, and reduction with BH_3·THF under the effect of dibenzylammonium **12**,[12c] which was outlined in Scheme 2. The chemical structures of all new compounds were well-confirmed by standard spectroscopic characterizations such as ^1H NMR, ^{13}C NMR, elemental analyses and mass spectrometry (see the Supporting Information).

The clipping reaction was first investigated for the symmetrical macrocyclic alkylammonium salt **1a** by mixing together equimolar amounts of **10a** and **11** in CD_3CN, and a light yellow solution was observed because of the formation of Schiff bases. Subsequently, the clipping process was followed by ^1H NMR spectroscopy. A complicated mixture containing imine oligomer was observed after one day by NMR. Simultaneously, a broad singlet at 9.71 ppm for ammonium NH_2^+ protons was observed, which was well in agreement with the chemical shift of ammonium reported in the previous literature.[12] The results suggested the existence of a dynamic [2]catenane. Then, the mixture was treated with BH_3·THF to reduce the dynamic imine bond into the kinetically stable C−NH bonds, and then the [2]catenane **3a** was separated by column chromatography in 63% yield. In the ^1H NMR spectra (Figure 1), the resonance

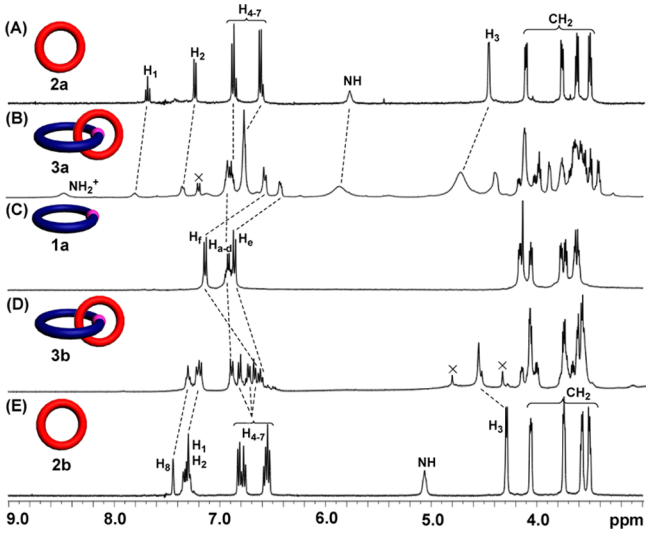
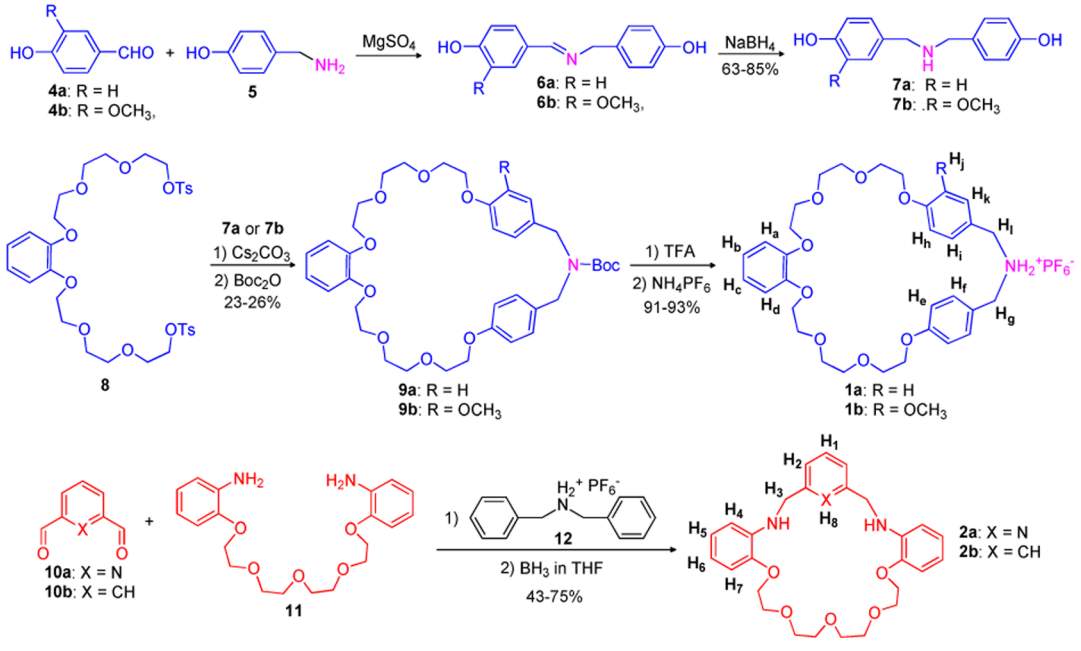


Figure 1. Partial ^1H NMR spectra (400 MHz, CD_3CN, 298 K) of **2a** (A), **3a** (B), **1a** (C), **3b** (D), and **2b** (E).

Scheme 2



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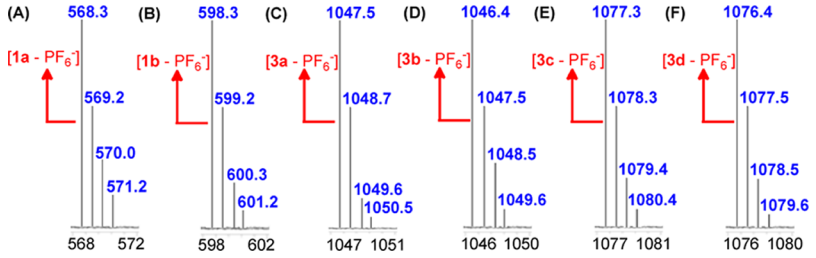

Figure 2. ESI mass spectra of compounds **1a** (A), **1b** (B), **3a** (C), **3b** (D), **3c** (E), and **3d** (F).

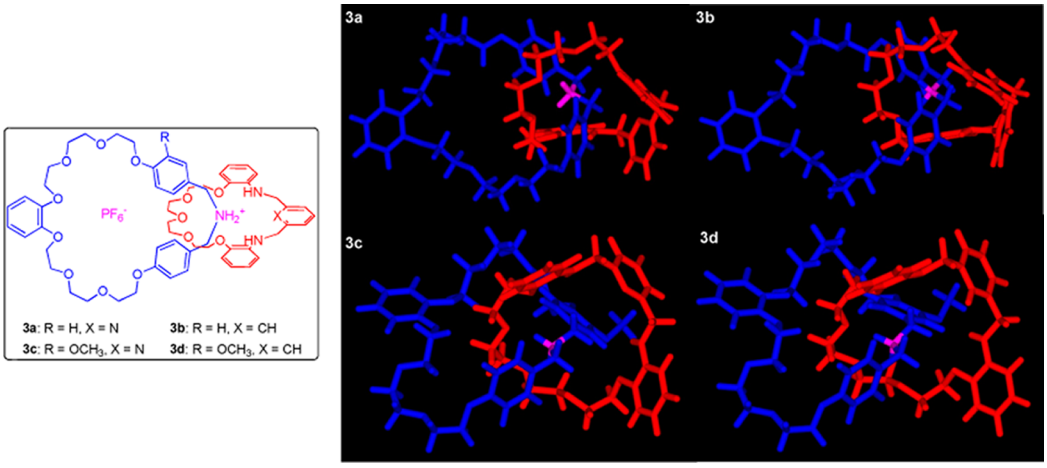

Figure 3. The energy-minimized structures of [2]catenanes **3a**–**d** based on density functional theory (DFT) calculations at the B3LYP/6-31G* level by using Gaussian 09 programs.

of ammonium NH_2^+ proton in the kinetically stable [2]-catenane **3a** showed an obvious upfield shift (singlet at 8.46 ppm) compared with the dynamic [2]catenane, as shown in Figure 1B. Furthermore, the resonance of the protons on the adjacent benzene rings (H_e and H_f) showed obvious upfield shifts according to the ^{1}H NMR spectra of macrocycle **1a** in Figure 1C. The results indicated the heterocrown ether encircled onto the template-site of macrocyclic ammonium salt. Therefore, we demonstrated that the template-directed clipping reaction was applied for efficient synthesis of [2]catenanes. Further proof was performed by the electrospray ionization mass spectrometry (ESI-MS) in acetonitrile. As can be seen from Figure 2C, the peak at m/z 1047.5 can be assigned to the $[M - PF_6^-]^+$ species, in which M was the [2]catenane **3a**.

Stoddart et al. found that the 1,3-benzenedialdehyde (**10b**) could also replace the 2,6-pyridinedicarboxaldehyde (**10a**) to perform the clipping reaction.[12b] Then we investigated the clipping reaction of 1,3-benzenedialdehyde (**10b**) and tetra-(ethylene glycol) bis(2-aminophenyl)ether (**11**) with macrocyclic ammonium salt **1a** in CH_3CN. After stirring for 2 weeks and reducing with BH_3·THF, the pure [2]catenane **3b** was successfully obtained by column chromatography in 51% yield. In the ^{1}H NMR spectrum, the resonance of the protons on the adjacent benzene rings (H_e and H_f) showed obvious upfield shifts compared with the macrocyclic ammonium salt **1a**, which indicated that the heterocrown ether encircled onto the macrocyclic ammonium salt. Furthermore, in comparison to [2]catenane **3a**, a downfield shift (H_e and H_f) was observed in the ^{1}H NMR spectrum of **3b**, possibly due to the weaker deficient-electron of the benzene ring in **2b** than pyridine ring in **2a**. In addition, the ESI-MS in Figure 2(D) (peak at m/z 1046.4) further confirmed the existence of [2]catenane **3b**. Subsequently, we investigated the performance of unsymmetric macrocyclic ammonium **1b** with the methoxy group in the clipping reaction. The clipping reaction was performed in CH_3CN. The results exhibited that the macrocyclic ammonium **1b** can also work well in the clipping reactions based on 2,6-pyridinedicarboxaldehyde (**10a**), 1,3-benzenedialdehyde (**10b**) with tetra(ethylene glycol) bis(2-aminophenyl)ether (**11**), respectively. And the pure [2]catenanes **3c** and **3d** were obtained after column chromatography in high yields. Similarly, the resonance of the protons on the adjacent benzene rings (H_e, H_f, H_h, H_i and H_k) of [2]catenanes **3c** and **3d** showed obvious upfield shifts compared with the ^{1}H NMR spectra of unsymmetrical macrocyclic alkylammonium salt **1b**, which were well in agreement with the [2]catenanes **3a** and **3b** (see Supporting Information: Figure S1). Moreover, the formation of catenanes was further confirmed by ESI mass spectrometry in Figure 2. These results indicated that the introduction of substituted group on the macrocyclic ammonium displayed little effect.

Despite that the template-directed clipping reaction has been confirmed to be efficient for the construction of [2]catenane according to the above experiment, the steric configuration of [2]catenane was not defined. In this respect, the steric configuration of [2]catenane **3** included two possible types: (1) the pyridine or benzene unit (which contained H_1 and H_2 hydrogen atoms) of **2** was wrapped by the ammonium-based crown ether **1** and located within the center of **1**, and (2) the pyridine or benzene unit was situated at the periphery of **1**. For this case, we investigated their ^{1}H–^{1}H ROESY spectra (see Supporting Information: Figure S2–S6); however, no evident relevant signals of protons were observed between the pyridine

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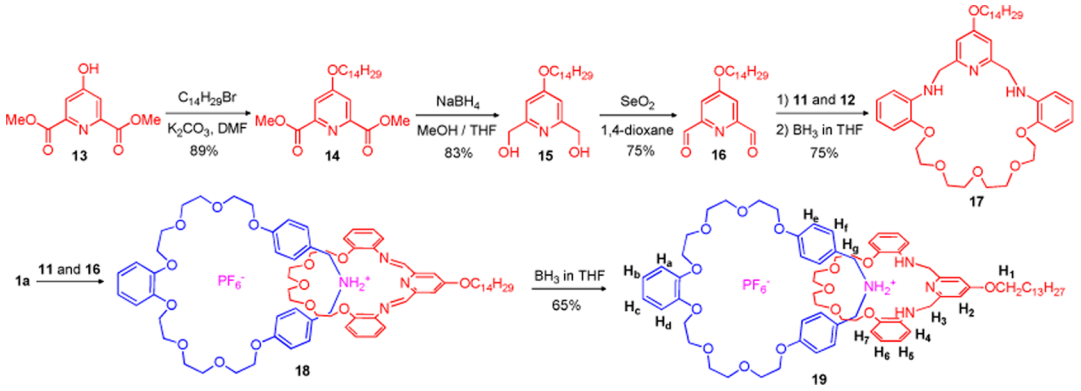
Scheme 3



or benzene units (H_1, H_2 and H_8) and macrocyclic ammonium salt **1**. As a result, it was possible that the pyridine or benzene (which contained H_1 and H_2 hydrogen atoms) unit was situated at the periphery of **1**. To clarify that, we sought for theoretical calculations. On the basis of the density functional theory (DFT), calculation at B3LYP/6-31G* level was performed by using Gaussian 09 programs. By comparison, we found that these configurations possessed the minimized energy when the pyridine or benzene unit was situated at the periphery of **1**, as shown in Figure 3 (see Supporting Information: Table S1).

On the basis of the above theoretical calculations, if the bigger substituted group was introduced to the 4-site of 2,6-pyridinedicarboxaldehyde (**10a**) such as compound **16**, it would also replace **10** to perform the clipping reaction. In order to prove this hypothesis, we first needed to prepare compound **16**. According to Scheme 3, compound **13** was used as starting materials to prepare compound **14** in an 89% yield, which was reduced with $NaBH_4$ to give diol **15** in an 83% yield. The oxidation based on diol **15** afforded the 4-site alkoxyl-substituted 2,6-pyridinedicarboxaldehyde **16**, which was cyclized with **11** in the presence of template **12** to get N-heterocrown ether **17** in a high yield. Subsequently, the clipping reaction based on **11**, **16** with **1a** was investigated. As recorded by ^{1}H NMR spectra in Figure 4, an obvious imine signal at 8.28 ppm and a broad resonance signal for ammonium NH_2^+ at 9.74 ppm were observed, and the chemical shift of ammonium was similar to previous reports.[12] The results suggested the formation of dynamic [2]catenane **18** and further confirmed

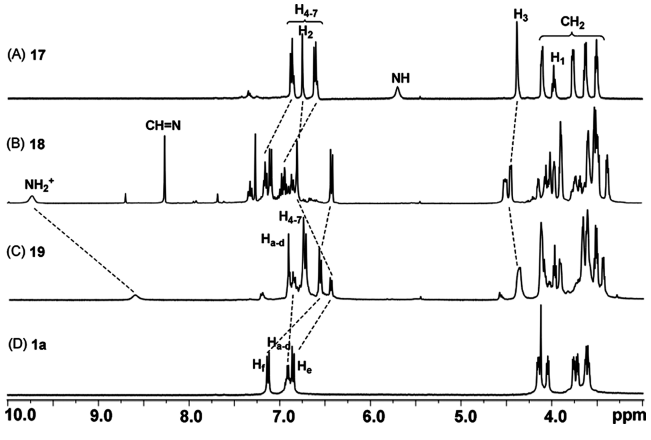


Figure 4. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of **2a** (A), **3c** (B), **1b** (C), **3d** (D), and **2b** (E).

the pyridine or benzene unit was situated at the periphery of macrocycles. Subsequently, the mixture was treated with BH_3·THF to give the kinetically stable [2]catenane **19** in 65% yield. It is worth mentioning that the ammonium of [2]catenane **19** revealed very evident downfield shift compared with the dynamic [2]catenane. Simultaneously, some similar changes of ^{1}H NMR spectra were also found in Figure 4 as same as **3a** and **3c**. Additionally, we also utilized Gaussian 09 programs to optimize and obtain the energy-minimized structure via density functional theory (DFT) calculations at the B3LYP/6-31G* level, as shown in Figure 5.

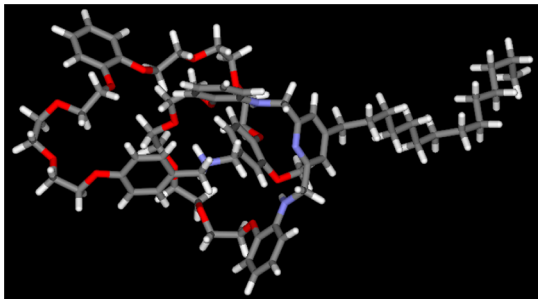


Figure 5. The energy-minimized structure of [2]catenane **19** based on density functional theory (DFT) calculation at the B3LYP/6-31G* level by using Gaussian 09 programs.

In conclusion, five [2]catenanes were efficiently synthesized in high yields by a template-directed clipping approach. This research further confirmed that the template-directed clipping reaction could be also utilized as an efficient approach to synthesize catenanes. Such approach could also be used for the synthesis of more complicated catenanes and molecular necklaces.

EXPERIMENTAL SECTION

General Methods. All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. THF was distilled under nitrogen from sodium–benzophenone. EtOH and MeOH were distilled under drying pipe from magnesium–iodine. DMF was dried with magnesum sulfate and then distilled under a vacuum. ^{1}H and ^{13}C NMR spectra were collected with either a 400 or 600 MHz spectrometer. Mass spectra were measured in the ESI mode. Elemental analyses were performed by investigation of C, H, and N.

Synthesis of Compound 6b ((*E*)-4-(((4-Hydroxybenzyl)-imino)methyl)-2-methoxyphenol). To a solution of 4-hydroxy-3-methoxybenzaldehyde **4b** (0.61 g, 4.0 mmol) in anhydrous EtOH (80

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mL) was added 4-(aminomethyl)phenol **5** (0.49 g, 4.0 mmol) with anhydrous magnesium sulfate acting as drying agent under a argon atmosphere. The mixture was refluxed for 24 h. The formed precipitate was collected, and the crude product was washed with EtOH to give a yellow solid **6b**. Yield: 0.92 g, 89%. mp 205−207 °C. Compound **6b**: ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm = 3.78 (s, 3H, OCH_3), 4.58 (s, 2H, CH_2), 6.75 (d, J = 7.6 Hz, 2H, Ar), 6.84 (d, J = 7.6 Hz, 1H, Ar), 7.12 (t, J = 13.2 Hz, 3H, Ar), 7.36 (s, 1H, Ar), 8.27 (s, 1H, CH═N); ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm = 56.2 (s, OCH_3), 63.6 (s, CH_2), 109.9, 115.2, 123.0, 127.8, 129.3, 130.1, 148.0, 149.6, 156.3, 160.7 (s, Ar and CH═N). Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.23; H, 5.80; N, 5.32.

Synthesis of Compound 7a (4,4′-(Azanediylbis(methylene))-diphenol). To a solution of 4-hydroxybenzaldehyde **4a** (0.49 g, 4.0 mmol) in anhydrous EtOH (80 mL) was added 4-(aminomethyl)-phenol **5** (0.49 g, 4.0 mmol) with anhydrous magnesium sulfate acting as drying agent under a argon atmosphere. The mixture was refluxed for 24 h. The solvent was removed under a vacuum, and the residue was dissolved in THF (60 mL) and MeOH (60 mL), and then $NaBH_4$ (0.61 g, 16.0 mmol) was added slowly in 10 portions. After stirring overnight, the reaction was quenched with the saturated ammonium chloride (aq). The solvents were removed under a vacuum, and the residue was extracted by absolute ethyl ether and then dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure and purification on a silica gel column using petroleum ether/ethyl acetate (1:9) as the eluent obtained the target compound **7a** as a brown solid. Yield: 0.58 g, 63%. mp 141−142 °C. Compound **7a**: ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm = 3.52 (s, 4H, CH_2), 6.70 (d, J = 8.0 Hz, 4H, Ar), 7.11 (d, J = 8.0 Hz, 4H, Ar), 9.27 (s, 2H, OH); ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm = 51.7 (s, CH_2), 114.9, 129.1, 131.0, 156.0 (s, Ar); EI MS m/z = 229.1 $[M]^+$; calculated exact mass = 229.1. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.22; H, 6.72; N, 6.03.

Synthesis of Compound 7b (4-(((4-Hydroxybenzyl)amino)-methyl)-2-methoxyphenol). The Schiff base **6b** (1.00 g, 4.0 mmol) was dissolved in THF (60 mL) and MeOH (60 mL), and then $NaBH_4$ (0.61 g, 16.0 mmol) was added slowly in 10 portions. After stirring overnight, the reaction was quenched with the saturated ammonium chloride (aq). The solvents were removed under a vacuum, and the residue was extracted by absolute ethyl ether and then dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure and purification on a silica gel column using petroleum ether/ethyl acetate (1:9) as the eluent obtained the target compound as a brown solid Yield: 0.88 g, 85%. mp 146−147 °C. Compound **7b**: ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm = 3.56 (s, 4H, CH_2), 3.75 (s, 3H, OCH_3), 6.72 (d, J = 8.0 Hz, 4H, Ar), 6.92 (s, 1H, Ar), 7.13 (d, J = 8.4 Hz, 2H, Ar); ^{13}C NMR (100 MHz, DMSO-d_6) δ ppm = 51.6 (s, CH_2), 51.9 (s, CH_2), 55.5 (s, OCH_3), 112.2, 115.0, 115.1, 120.5, 129.3, 130.7, 131.4. 145.2, 147.5, 156.1 (s, Ar); EI MS m/z = 259.1 $[M]^+$; calculated exact mass = 259.1. Anal. Calcd for: $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.25; H, 6.76; N, 5.48.

Synthesis of Compound 9a. A mixture of **8** (0.34 g, 0.5 mmol) and **7a** (0.12 g, 0.5 mmol) in dry DMF (150 mL) was added dropwise over a period of 12 h to a stirred suspension of Cs_2CO_3 (0.65 g, 2.0 mmol) at 80 °C under a dry N_2 atmosphere. After the addition was completed, the mixture was stirred at 80 °C for a further 3 d. The resulting mixture was allowed to cool to room temperature and filtered. After that, the solvents were removed under a vacuum, and the residue was extracted by ethyl ether and then dried over anhydrous sodium sulfate. Solvent was removed under reduced pressure and dried. The unpurified product was dissolved in dry chloroform (20 mL), and then Boc_2O (0.30 g, 1.4 mmol) and triethylamine (0.24 mL) were added. The mixture was stirred at room temperature for 24 h. Removal of solvent under reduced pressure and purification on a silica gel column using petroleum ether/ethyl acetate (1:1) as the eluent obtained the Boc-protected macrocycle **9a** as a light yellow liquid. Yield: 0.09 g, 26%. Compound **9a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 1.47 (s, 9H, Boc), 3.70−3.76 (m, 8H, CH_2), 3.80 (t, J = 4.0 Hz, 4H, CH_2), 3.87 (t, J = 4.0 Hz, 4H, CH_2), 4.05 (t, J = 4.0 Hz, 4H, CH_2), 4.15 (t, J = 4.0 Hz, 4H, CH_2), 4.32 (s, 2H, CH_2), 4.41 (s, 2H, CH_2), 6.66 (t, J = 8.0 Hz, 4H, Ar), 6.77 (d, J = 8.0 Hz, 2H, Ar), 6.87−6.95 (m, 6H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 28.3, 51.1, 67.4, 68.8, 69.6, 69.75, 70.8, 79.7, 114.3, 114.7, 121.5, 128.8, 129.7, 130.5, 130.8, 148.8, 155.8, 157.4; EI MS m/z = 667.4 $[M]^+$; calculated exact mass = 667.3. Anal. Calcd for $C_{37}H_{49}NO_{10}$: C, 66.55; H, 7.40; N, 2.10. Found: C, 66.43; H, 7.25; N, 2.24.

Synthesis of Compound 9b. Compound **9b** was prepared by an analogous method similar to that used for to **9a** and was obtained as a light yellow liquid. Yield: 0.08 g, 23%. Compound **9b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm = 1.47 (s, 9H, Boc), 3.64−3.75 (m, 12H, OCH_3 and CH_2), 3.81 (d, J = 4.4 Hz, 4H, CH_2), 3.87 (t, J = 4.8 Hz, 4H, CH_2), 4.06 (t, J = 4.4 Hz, 2H, CH_2), 4.13−4.41 (m, 9H, CH_2), 6.40−6.99 (m, 11H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm = 28.3, 51.0, 51.4, 55.5, 60.2, 67. 5, 68.8, 69.6, 69.7, 69.7, 70.7, 77.2, 79.7, 111.1, 112.0, 113.7, 114.3, 114.6, 120.0, 120.8, 121.4, 128.9, 129.8, 130.7, 131.5, 131.9, 147.0, 148.8, 149.3, 155.6, 157.6 (d); ESI MS m/z = 720.2 $[M + Na^+]$, 736.1 $[M + K^+]$; calculated exact mass = 697.3. Anal. Calcd for $C_{38}H_{51}NO_{11}$: C, 65.41; H, 7.37; N, 2.01. Found: C, 65.26; H, 7.46; N, 2.09.

Synthesis of Compound 1a. To a solution of the Boc-protected amine **9a** (0.13 g, 0.19 mmol) in dry DCM (10 mL), TFA (0.06 mL, 0.95 mmol) was added at room temperature. After stirring for 2 h under nitrogen atmosphere, the solvent was removed under a vacuum. The residue was dissolved in MeOH (1.0 mL), and then saturated NH_4PF_6 (2.0 mL, aq) was added to yield a brown precipitate. After filtering, washing with H_2O and drying under a vacuum, the title compound was obtained as the light yellow gum. Yield: 0.12 g, 91%. Compound **1a**: ^{1}H NMR (400 MHz, CD_3CN) δ ppm = 3.60−3.65 (m, 8H, CH_2), 3.72−3.74 (m, 4H, CH_2), 3.76−3.78 (m, 4H, CH_2), 4.05−4.07 (m, 4H, CH_2), 4.13 (s, 4H, CH_2), 4.15−4.17 (m, 4H, CH_2), 6.86 (d, J = 8.8 Hz, 4H, Ar), 6.89−6.95 (m, 4H, Ar), 7.14 (d, J = 8.8 Hz, 4H, Ar); ^{13}C NMR (150 MHz, CD_3CN) δ ppm = 51.9, 69.1, 69.4, 70.6, 70.6, 71.4, 71.7, 115.4, 116.5, 118.7, 122.9, 124.1, 132.8, 149.6, 160.9; ESI MS m/z = 568.3 $[M - PF_6^-]$; calculated exact mass = 713.3. Anal. Calcd for $C_{32}H_{42}F_6NO_8P$: C, 53.86; H, 5.93; N, 1.96. Found: C, 53.93; H, 6.03; N, 1.81.

Synthesis of Compound 1b. Compound **1b** was prepared by an analogous method similar to that used for to **1a** and was obtained as a light yellow liquid. Yield: 0.13 g, 93%. Compound **1b**: ^{1}H NMR (600 MHz, CD_3CN) δ ppm = 3.57−3.61 (m, 8H, CH_2), 3.69 (t, J = 3.6 Hz, 4H, CH_2), 3.73−3.75 (m, 8H, CH_2), 4.01−4.03 (m, 4H, CH_2), 4.10 (d, J = 7.8 Hz, 4H, CH_2), 4.15 (s, 3H, OCH_3), 6.78−6.93 (m, 9H, Ar), 7.18 (d, J = 8.4 Hz, 2H, Ar); ^{13}C NMR (150 MHz, CD_3CN) δ ppm = 50.0, 55.0, 67.8, 68.1, 69.0, 69.9, 70.0, 105.1, 114.0, 114.8, 116.2, 121.0, 122.4, 131.2, 148.2, 148.8, 149.2, 159.4; ESI MS m/z = 598.3 $[M - PF_6^-]$; calculated exact mass = 743.3. Anal. Calcd for $C_{33}H_{44}F_6NO_9P$: C, 53.30; H, 5.96; N, 1.88. Found: C, 53.19; H, 6.08; N, 1.92.

Synthesis of Compound 2b. A solution of isophthalaldehyde **10b** (0.13 g, 1.0 mmol), 2,2′-((((oxybis(ethane-2,1-diyl))bis(oxy))-bis(ethane-2,1-diyl))bis(oxy))dianiline **11** (0.38 g, 1.0 mmol), and dibenzylammonium hexafluorophosphate **12** (0.34 g, 1.0 mmol) in acetonitrile (50 mL) was stirred at room temperature overnight. BH_3·THF (1.0 M in THF, 5 mL, 5.0 mmol) was added to the mixture, which was left stirring at rt for 4 h. The excess of solvent was removed under a vacuum, and the residue was partitioned between 2 M aqueous NaOH solution and $CHCl_3$. The residue was extracted with DCM, and the organic layer was washed with water, dried over anhydrous sodium sulfate, and then purified by column chromatography (silica gel, CH_2Cl_2) to give compounds **2b** as the light yellow gum. Yield: 0.21 g, 43%. Compound **2b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 − 3.46 (m, 4H), 3.62−3.55 (m, 4H), 3.75 (d, J = 4.2 Hz, 4H), 4.11−4.03 (m, 4H), 4.29 (d, J = 5.2 Hz, 4H), 5.07 (s, 2H), 6.56 (dd, J = 15.0, 7.7 Hz, 4H), 6.86−6.74 (m, 4H), 7.33 (dd, J = 11.9, 6.6 Hz, 3H), 7.45 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.9, 70.0, 70.2, 70.9, 71.0, 110.8, 113.6, 116.9, 122. 7, 126.4, 127.3, 129.1, 139.9, 141.4, 146.5; ESI MS m/z = 478.9 $[M]^+$; calculated exact mass = 478.2. Anal. Calcd for: $C_{28}H_{34}N_2O_5$: C, 70.27; H, 7.16; N, 5.85. Found: C, 70.46; H, 7.32; N, 5.67.

Synthesis of Compounds 3a−d. A mixture of macrocyclic dialkylammonium **1a,b** (71.3 mg or 74.3 mg, 0.1 mmol),

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tetraethyleneglycol bis(2-aminophenyl) ether **11** (37.6 mg, 0.1 mmol) and dicarboxaldehyde **10a,b** (13.5 mg or 13.4 mg, 0.1 mmol) was stirred for 10 d in dry CH_3CN (10 mL) under nitrogen atmosphere at room temperature. Then, BH_3·THF solution (0.8 mL) was added, and the mixture was further stirred overnight. The solvents were removed under a vacuum, and the residue was purified by column chromatography (silica gel, DCM/MeCN/MeOH = 100:0:0–75:25:1) to give the [2]catenane.

Compound 3a. The white solid. Yield: 75.1 mg, 63%; mp >300 °C; ^{1}H NMR (400 MHz, CD_3CN) δ ppm = 3.41–3.43 (m, 3H, CH_2), 3.48–3.51 (m, 3H, CH_2), 3.53–3.70 (m, 17H, CH_2), 3.74–3.77 (m, 5H, CH_2), 3.87–3.89 (m, 3H, CH_2), 3.97–4.03 (m, 5H, CH_2), 4.11–3.18 (m, 8H, CH_2), 4.37–4.40 (m, 4H, CH_2), 6.41–6.43 (m, 2H, Ar), 6.57 (d, J = 8.0 Hz, 3H, Ar), 6.75–6.77 (m, 8H, Ar), 6.86–6.94 (m, 7H, Ar), 7.18–7.20 (m, 1H, Ar), 7.34 (d, J = 8.0 Hz, 1H, Ar), 7.79 (t, J = 8.0 Hz, 1H, Ar), 8.47 (s, 2H, NH_2^+); the ^{13}C NMR spectrum was not collected because of the poor solubility of **3a**; ESI MS m/z = 1047.5 [M − PF_6^-]; calculated exact mass = 1192.5. Anal. Calcd for $C_{59}H_{75}F_6N_4O_{13}P$: C, 59.39; H, 6.34; N, 4.70. Found: C, 59.51; H, 6.28; N, 4.63.

Compound 3b. The white solid. Yield: 60.8 mg, 51%; mp >300 °C; ^{1}H NMR (400 MHz, CD_3CN) δ ppm = 3.57–3.65 (m, 15H, CH_2), 3.67–3.70 (m, 3H, CH_2), 3.72–3.81 (m, 9H, CH_2), 4.01–4.06 (m, 3H, CH_2), 4.07–4.12 (m, 7H, CH_2), 4.16–4.18 (m, 2H, CH_2), 4.30–4.35 (m, 2H, CH_2), 4.55 (d, J = 12.0 Hz, 5H, CH_2), 4.79–4.82 (m, 2H, CH_2), 6.48–6.91 (m, 17H, Ar), 7.18–7.33 (m, 7H, Ar); the ^{13}C NMR spectrum was not collected because of the poor solubility of **3b**; ESI MS m/z = 1046.4 [M − PF_6^-]; calculated exact mass = 1191.5. Anal. Calcd for $C_{60}H_{76}F_6N_3O_{13}P$: C, 60.45; H, 6.43; N, 3.52. Found: C, 60.53; H, 6.29; N, 3.63.

Compound 3c. The white solid. Yield: 88.0 mg, 72%; mp >300 °C; ^{1}H NMR (400 MHz, CD_3CN) δ ppm = 3.23 (s, 1H, CH_2), 3.40–3.79 (m, 24H, CH_2), 3.84–3.97 (m, 4H, CH_2), 4.04–4.15 (m, 8H, CH_2), 4.40–4.47 (m, 4H, CH_2), 4.75 (s, 8H, CH_2), 5.03 (s, 2H, CH_2), 6.35 (s, 1H, Ar), 6.41 (d, J = 4.0 Hz, 1H, Ar), 6.52–6.93 (m, 17H, Ar), 7.19–7.23 (m, 2H, Ar), 7.38 (d, J = 4.0 Hz, 1H, Ar), 7.81 (t, J = 4.0 Hz, 1H, Ar), 8.40 (s, 2H, NH_2^+); the ^{13}C NMR spectrum was not collected because of the poor solubility of **3c**; ESI MS m/z = 1077.3 [M − PF_6^-]; calculated exact mass = 1222.5. Anal. Calcd for $C_{60}H_{77}F_6N_4O_{14}P$: C, 58.91; H, 6.34; N, 4.58. Found: C, 59.02; H, 6.18; N, 4.52.

Compound 3d. The white solid. Yield: 81.8 mg, 67%; mp >300 °C; ^{1}H NMR (400 MHz, CD_3CN) δ ppm = 3.51–3.67 (m, 16H, CH_2), 3.70–3.82 (m, 12H, CH_2), 4.04–4.13 (m, 11H, CH_2), 4.15–4.18 (m, 2H, CH_2), 4.30 (s, 2H, CH_2), 4.36 (s, 2H, CH_2), 4.58 (s, 4H, CH_2), 4.80–4.91 (m, 2H, CH_2), 6.51–6.93 (m, 15H, Ar), 7.19–7.47 (m, 9H, Ar); the ^{13}C NMR spectrum was not collected because of the poor solubility of **3d**; ESI MS m/z = 1076.4 [M−PF_6^-]; calculated exact mass = 1221.5. Anal. Calcd for $C_{61}H_{78}F_6N_3O_{14}P$: C, 59.94; H, 6.43; N, 3.44. Found: C, 59.88; H, 6.36; N, 3.56.

Synthesis of Compound 14 (Dimethyl 4-(Tetradecyloxy)-pyridine-2,6-dicarboxylate). A mixture of compound dimethyl 4-hydroxypyridine-2,6-dicarboxylate **13** (2.10 g, 10 mmol), 1-bromotetradecane (2.80 g, 10 mmol), K_2CO_3 (2.80 g, 20 mmol) in dry DMF (100 mL) was heated to 50 °C under argon atmosphere for 24 h. The solvent was removed under a vacuum, and the residue was extracted with ethyl ether. The organic layer was washed with water and dried over anhydrous sodium sulfate, and the excess of solvent was then removed under a vacuum. The residue was purified by recrystallization in methanol to give compound **14** as the yellow solid. Yield: 3.62 g, 89%; mp 78–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.4 Hz, 3H, CH_3), 1.26 (br, 20H, CH_2), 1.35–1.47 (m, 2H, CH_2), 1.77–1.86 (m, 2H, CH_2), 3.55 (s, 6H, COOMe), 4.13 (t, J = 6.4 Hz, 2H, OCH_2), 7.81 (s, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 23.0, 23.2, 25.8, 28.7, 29.2, 29.3, 29.5, 29.6, 30.0, 31.9, 41.9, 53.2, 65.2, 69.1, 114.5, 149.6, 165.2, 167.1; EI MS m/z = 407.4 [M]$^+$; calculated exact mass =407.3. Anal. Calcd for: $C_{23}H_{37}NO_5$: C, 67.78; H, 9.15; N, 3.44. Found: C, 67.64; H, 9.46; N, 3.23.

Synthesis of Compound 15 ((4-(Tetradecyloxy)pyridine-2,6-diyl)dimethanol). Compound **14** (1.80 g, 5.2 mmol) was dissolved in a mixture of solvents of MeOH (50 mL) and THF (50 mL), and powder of $NaBH_4$ (0.70 g) was then added in portions. The mixture was stirred at room temperature for 24 h, and the excess of solvent was removed under a vacuum. The residue was extracted with ethyl ether, and the organic layer was washed with water. The organic layer was washed with water and dried over anhydrous sodium sulfate. The residue was purified by recrystallization in DCM/hexane to give compound **15** as the white solid. Yield: 1.52 g, 83%; mp 90–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.4 Hz, 3H, CH_3), 1.26 (br, 20H, CH_2), 1.35–1.47 (m, 2H, CH_2), 1.75–1.80 (m, 2H, CH_2), 4.01 (t, J = 6.4 Hz, 2H, OMe), 4.69 (s, 4H, CH_2), 6.69 (s, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.9, 28.8, 29.3, 29.3, 29.5, 29.6, 29.6, 31.9, 64.4, 68.2, 105.6, 160.3, 166.6; EI MS m/z = 351.5 [M]$^+$; calculated exact mass = 351.3. Anal. Calcd for: $C_{21}H_{37}NO_3$: C, 71.75; H, 10.61; N, 3.98. Found: C, 71.64; H, 10.78; N, 3.77.

Synthesis of Compound 16 (4-(Tetradecyloxy)pyridine-2,6-dicarbaldehyde). A mixture of **15** (0.79 g, 2.3 mmol) and SeO_2 (0.50 g, 4.6 mmol) in dioxane (10 mL) was heated to 90 °C under argon atmosphere for 16 h. After cooling, the mixture was filtered and washed with more dioxane. The excess of solvent in the filtrate was removed under a vacuum, and the residue was purified by column chromatography (silica gel, CH_2Cl_2) to give compound **16** as the light brown solid. mp 61–62 °C. Yield: 0.59 g, 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.4 Hz, 3H, CH_3), 1.26 (br, 20H, CH_2), 1.45–1.47 (m, 2H, CH_2), 1.81–1.86 (m, 2H, CH_2), 4.14 (t, J = 6.4 Hz, 2H, OCH_2), 7.63 (s, 2H, Ar), 10.12 (s, 2H, CHO); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.8, 28.6, 29.2, 29.3, 29.5, 29.5, 29.6, 31.9, 69.3, 111.5, 154.7, 167.1, 192.4; EI MS m/z = 347.4 [M]$^+$; calculated exact mass = 347.2. Anal. Calcd for: $C_{21}H_{33}NO_3$: C, 72.58; H, 9.57; N, 4.03. Found: C, 72.64; H, 9.45; N, 3.89.

Synthesis of Compound 17. A solution of **16** (0.35 g, 1.0 mmol), **11** (0.38 g, 1.0 mmol), and dibenzylammonium hexafluorophosphate **12** (0.34 g, 1.0 mmol) in acetonitrile (50 mL) was stirred at room temperature overnight. BH_3·THF (1.0 M in THF, 5 mL, 5.0 mmol) was added to the mixture, which was left stirring at rt for 4 h. The excess of solvent was removed under a vacuum, and the residue was partitioned between 2 M aqueous NaOH solution and $CHCl_3$. The residue was extracted with DCM, and the organic layer was washed with water, dried over anhydrous sodium sulfate, and then purified by column chromatography (silica gel, CH_2Cl_2) to give compound **17** as the light yellow gum. Yield: 0.52 g, 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.4 Hz, 3H, CH_3), 1.26 (br, 20H, CH_2), 1.38 (br, 2H, CH_2), 1.69–1.73 (m, 2H, CH_2), 3.56 (t, J = 4.4 Hz, 4H, CH_2), 3.74 (t, J = 4.4 Hz, 4H, CH_2), 3.84 (s, 4H, CH_2), 3.92 (t, J = 6.4 Hz, 2H, CH_2), 4.15 (s, 4H, CH_2), 4.43 (s, 4H, CH_2), 5.73 (s, 2H), 6.60–6.66 (m, 4H, Ar), 6.74 (s, 2H, Ar), 6.85 (d, J = 7.6 Hz, 2H, Ar), 6.91 (t, J = 7.6 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.9, 28.9, 29.3, 29.3, 29.5, 29.6, 29.6, 31.9, 49.3, 68.0, 70.0, 70.3, 70.7, 70.8, 106.3, 110.6, 114.3, 116.4, 122.9, 140.0, 146.1, 160.0, 166.5; ESI MS m/z = 691.0 [M]$^+$; calculated exact mass = 691.5. Anal. Calcd for: $C_{41}H_{61}N_3O_6$: C, 71.17; H, 8.89; N, 6.07. Found: C, 71.34; H, 9.01; N, 5.89.

Synthesis of Compound 19. Catenane **19** was prepared by an analogous method similar to that of **3** and was obtained as light yellow gum. Yield: 91.3 mg, 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (d, J = 6.7 Hz, 3H), 1.28 (br, 20H), 1.39 (br, 2H), 1.73 (dd, J = 13.7, 6.6 Hz, 2H), 3.44 (dd, J = 11.5, 6.6 Hz, 5H), 3.51 (dd, J = 10.3, 5.3 Hz, 9H), 3.71–3.57 (m, 12H), 3.92 (t, J = 8.2 Hz, 5H), 3.97 (t, J = 5.4 Hz, 2H), 4.10 (dd, J = 15.5, 5.3 Hz, 11H), 4.36 (d, J = 4.2 Hz, 6H), 6.49–6.41 (m, 2H), 6.57 (d, J = 8.5 Hz, 4H), 6.76 (t, J = 13.9 Hz, 8H), 6.89–6.82 (m, 4H), 6.96–6.90 (m, 4H), 8.62 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ ppm = 14.0, 23.0, 26.2, 29.3, 29.7, 29.9, 30.0, 32.3, 50.4, 52.1, 65.2, 68.1, 68.4, 69.0, 69.8, 70.1, 70.9, 71.5, 71.9, 108.9, 110.9, 113.1, 114.8, 115.3, 116.0, 120.1, 122.0, 124.9, 131.3, 138.0, 147.4, 149.2, 159.9, 161.0, 167.2; ESI MS m/z = 1259.6 [M − PF_6^-]; calculated exact mass = 1404.7. Anal. Calcd for $C_{73}H_{103}F_6N_4O_{14}P$: C, 62.38; H, 7.39; N, 3.99. Found: C, 62.59; H, 7.60; N, 3.66.

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■ ASSOCIATED CONTENT

Supporting Information

Details on the synthesis, characterization, NMR, MS spectra of intermediates and [2]catenanes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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