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Construction of Rotacatenanes Using Rotaxane and Catenane Frameworks

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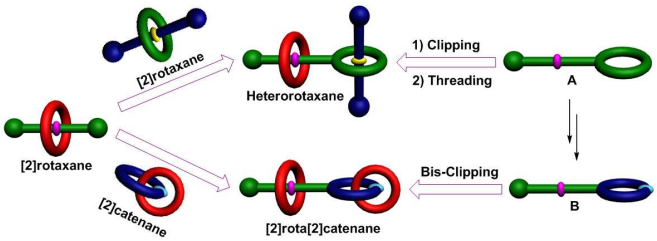
The construction of novel mechanically interlocked structures has become a fashion due to the requirements of topology and their potential application in molecular machines and devices. Rotaxane and catenane as two basic topological frameworks can be used to construct the fused structures. In the current investigation, a class of novel ammonium backbones was synthesized. The ammonium group incorporated in the linear part of molecules can be used for templating rotaxane formation while the macrocyclic part of the molecules can be used for templating catenane formation. Accordingly, they were subjected to perform the dynamic covalent chemistry, resulting a series of [n]rota[n]catenane structures (n = 2, 3, 4). In this process, the N-hetero crown ethers were installed on ammonium template sites of linear and macrocyclic components all at once by the template-directed clipping reaction. The results showed that the novel building blocks could assemble with high efficiencies. Finally, this investigation provides a foundation for future studies aimed at constructing the complicated integration or polymer with multi topological units.

Introduction

The mechanical bonds widely existing in numerous molecules such as rotaxanes, catenanes, knots and links, have evoked considerable interest in exploring intriguing architectures and topologies, molecular switches and devices, nanotechnology, biological functional machines, drug delivery and materials science based on mechanically interlocked structures.[1] As a result, the design and construction of mechanically interlocked molecules (MIMs) with novel configuration became one of the most popular research projects in supramolecular chemistry and self-assembly. Accompany with the great development of MIMs, rotaxanes and catenanes, as the most common MIMs, have showed the trends from single and simple structures to complicated and polymeric structures over the past decades.[1] For examples, rotaxanes can be used to construct main-chain or side-chain polyrotaxanes, dendrimers and poly[c2]daisy chains.[1r, 2] While catenanes can be applied in the construction of main-chain, side-chain, bridged, or pendant polycatenanes and dendrimers.[2a, 2g, 3] Additionally, the integrated architectures such as hetero[n]rotaxanes with different macrocyclic components or different dumbbell-shaped components are gaining increasing attention.[4] Recently, we reported one type of novel dual functional building blocks (**A**) containing both a crown ether and an ammonium cation group. They were employed to construct the novel topological hetero[n]rotaxanes (In Scheme 1) in which the ammonium unit served as a template for incorporating an encircling macrocyclic ring by using template-directed clipping reaction while the crown ether component was then subjected to a threading-followed-by-stoppering sequence to install a second encircling crown ether ring as part of the new heterorotaxane.[5] Similar work was also reported by Leung.[6] The above integration was constructed only by fusing one type of mechanically interlocked framework.



Scheme 1. Schematic Representation of the Route for Heterorotaxane and Rotacatenane Integration.

In contrast, the other integration involved in different mechanically interlocked frameworks. As early in 1999, Stoddart's group reported one type of novel integration by fusing rotaxane moiety and catenane moiety which was named as rotacatenane.[7] Recently, they found this structure had multistate switchable properties.[8] In 2012, the same group reported a flexible donor-acceptor [3]catenane that, through a particular disposition of its three rings in water, could act as a host for a chainlike guest, resulting in the formation of a 1:1 complex with a hitherto unknown topology that was termed a [2]pseudorota[3]catenane.[9] Satio's group also reported a series of [2]rota[2]catenanes were synthesized by the catalytic reaction using a macrocyclic phenanthroline-CuI complex followed by the installation of another ring under the template effect recently.[10] In view of the structural character described above and foundation on the novel building blocks of heterorotaxane integration, herein we have designed a series of novel ammonium

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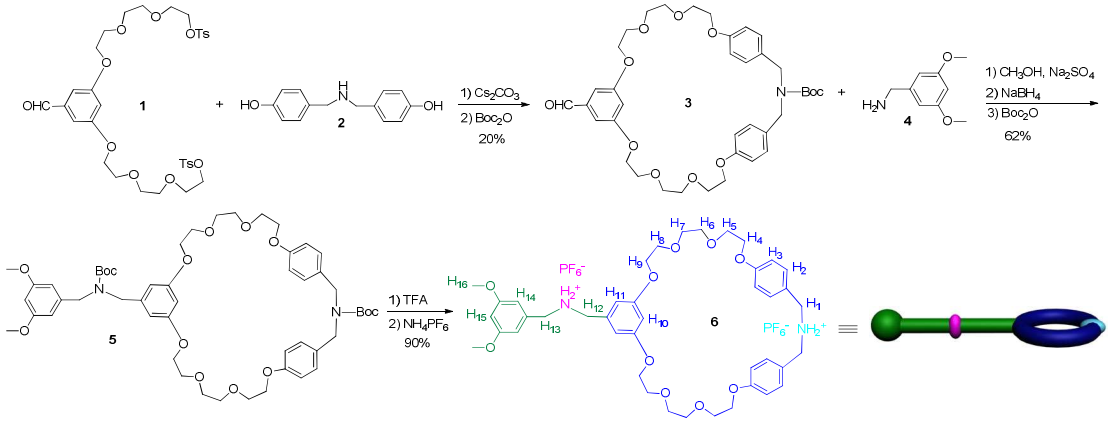
blocks (**B**) which were composed of ammonium on the linear component of backbone and another ammonium on the macrocyclic component of backbone (In Scheme 1). The ammonium on the linear component of backbone was designed to have the ability with construction of rotaxane while another ammonium on the macrocyclic component of backbone played the role of construction of catenane. The results indicated that these new building blocks could highly efficiently assemble [n]rota[n]catenanes via the template-directed clipping reaction all at once.

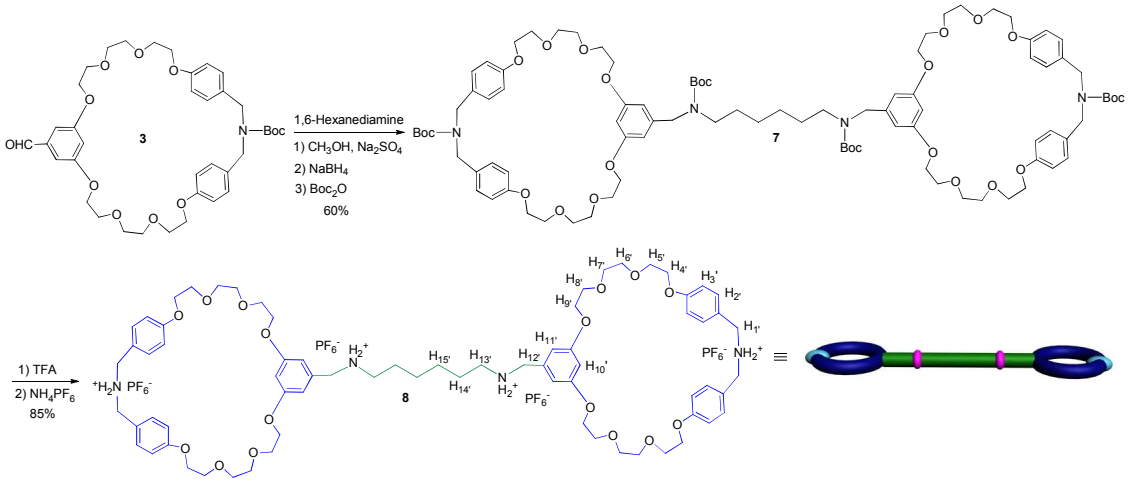
Results and discussion

Design of Ammonium Blocks and Rotacatenanes. As described above, we have developed a series of heterorotaxanes possessing novel topological structure by employing a host-guest dual-functional building block (**A**) as shown in Scheme 1. Furthermore, numerous researches have confirmed that the template-directed clipping reaction can efficiently self-assemble rotaxanes.[11] Accordingly, if another ammonium was introduced to the macrocyclic component to afford bisammnoium (**B**) involving in a ammonium on the linear component of backbone and the second ammonium on the macrocyclic component of backbone such as in Scheme 1, the new building block would be capable of constructing the integration (rotacatenane) of rotaxane and catenane. Additionally, we have confirmed that the macrocyclic ammoniums could efficiently self-assemble catenane by use of the template-directed clipping reaction in our previous work.[5a] According to this envisage, the bisammonium (**B**) can be employed to perform the bis-clipping reaction, constructing the integration of rotacatenane in one pot through the congenerous self-assembly of two different ammonium templates.

Synthesis of Ammoniums Frameworks. The first bis-ammonium **6** was synthesized utilizing the route shown in Scheme 2. The cyclization of diphenol **2** [5a] with the pseudo crown ether **1** [5b] in the presence of Cs_2CO_3 produced the aldehyde-substituted macrocyclic alkylamine. To facilitate purification, the NH of free amines was protected by the Boc_2O before purification. Subsequently, the Boc-protected macrocyclic amine **3** was obtained in 20% yields for two steps. In the presence of anhydrous sodium sulfate, the **3** as starting material was treated with 3,5-dimethoxybenzylamine **4** to afford the corresponding dynamic imine, which was then reduced by $NaBH_4$ in the solution of THF and MeOH to give the kinetically stable amine. Similarly, the NH of free amines was protected by the Boc_2O. Subsequently, the Boc-protected macrocyclic compound **5** was obtained in 62% yields for three steps. And then the Boc groups were removed with excess trifluoroacetic acid (TFA) in dry dichloromethane. Protonation of the as-formed amine and subsequent counterion exchange with saturated NH_4PF_6 aqueous solution afforded the target ammonium **6** in 90% yields for two steps.



Scheme 2. Synthesis of bis-ammonium **6**.



Scheme 3. Synthesis of tetra-ammonium **8**.

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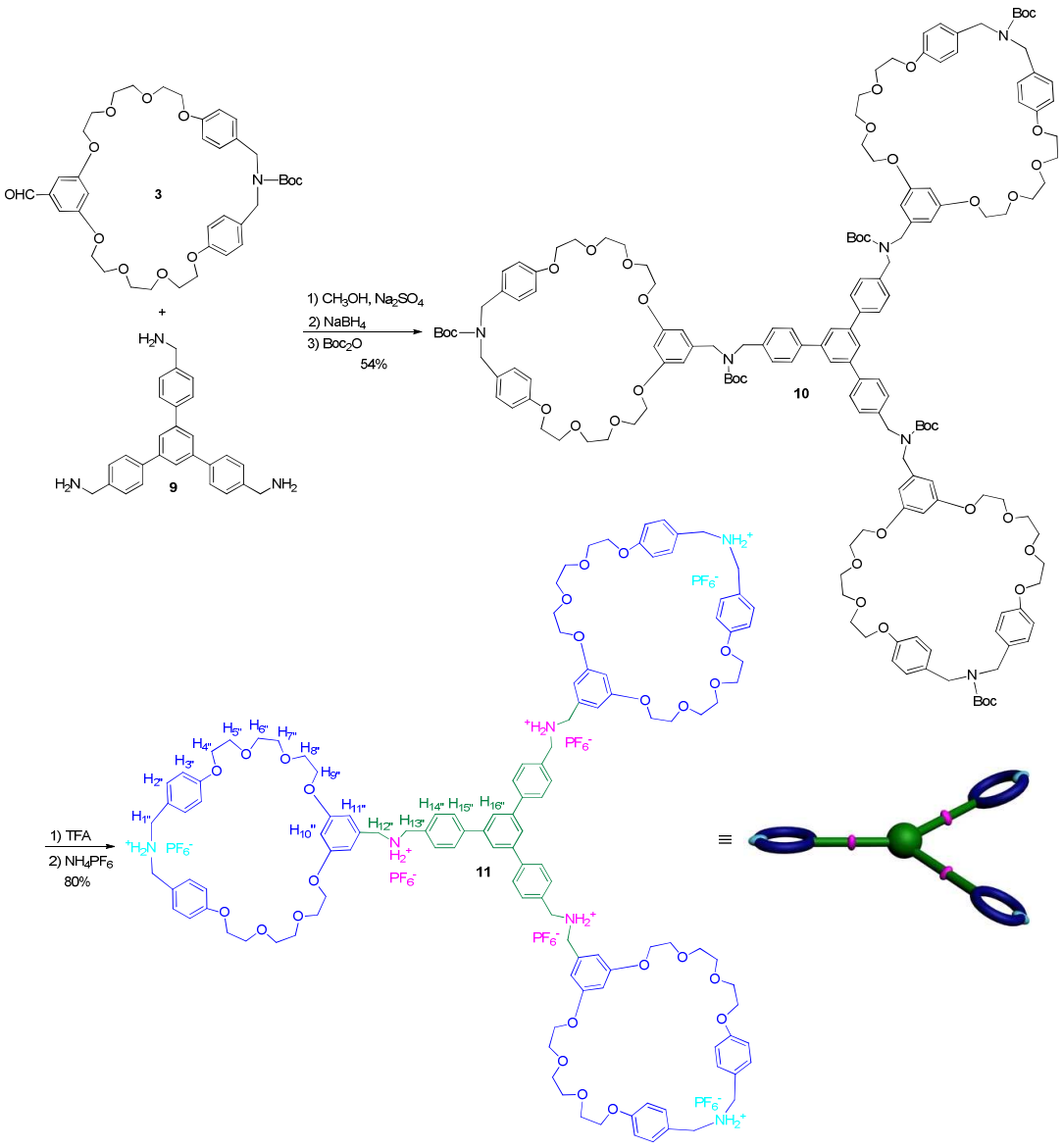

Scheme 4. Synthesis of hexa-ammonium **11**.

A similar synthetic strategy was employed to prepare the tetra-ammonium **8**, which contained two ammoniums on the linear component of backbone and two ammoniums on the macrocyclic component of backbone (Scheme 3), respectively. Reductive amination of **3** with 1,6-hexanediamine gave the precursor of the Boc-protected amino crown ether **7** in 60% yield, produced for the purpose of convenient purification. Boc-deprotection with trifluoroacetic acid (TFA) in dry dichloromethane followed by counterion exchange with saturated aqueous NH_4PF_6 generated the target tetra-ammonium **8**. The successful construction of building blocks **6** and **8** inspired us to further explore the synthesis of triangular hexa-ammonium **11**. Accordingly, the star-shaped triamine **9** [12] was selected as starting material to treat with **3**, affording the triangular compound **10**. Subsequent deprotection and counterion exchange gave the hexa-ammonium **11** in yield of 80%. All of the new building blocks were well characterized by standard spectroscopic techniques such as NMR spectroscopy, mass spectrometry and elemental analysis (see the Supporting Information).

Rotacatenanes Assembly. The poly-ammonium salts **6**, **8** and **11** including dialkylammonium recognition sites on the linear component and dialkylammonium sites on the macrocyclic component were treated with **12a** or **12b** and **13** in CH_3CN, respectively. And then a light yellow solution was observed on account of the formation of dynamic imine, which was well in agreement with experimental phenomena reported in previous literatures.[5, 13] Then, the mixture was treated with BH_3·THF to reduce the dynamic imine bonds to the kinetically stable C−NH bonds, and the pure forms of [2]rota[2]catenane **14** (Scheme 5), [3]rota[3]catenane **16** (Scheme 6) and [4]rota[4]catenane **17** (Scheme 7) were obtained by column chromatography. The process of self-assembly was monitored by ^{1}H NMR spectroscopy. Additionally, considering the fact that one component of substances needed to aid spectroscopic analysis of self-assembling processes, the *N*-hetero crown ethers **15a** and **15b** as the important components of rotacatenanes were synthesized in 43-75% yields according our previous reports.[5, 13c]

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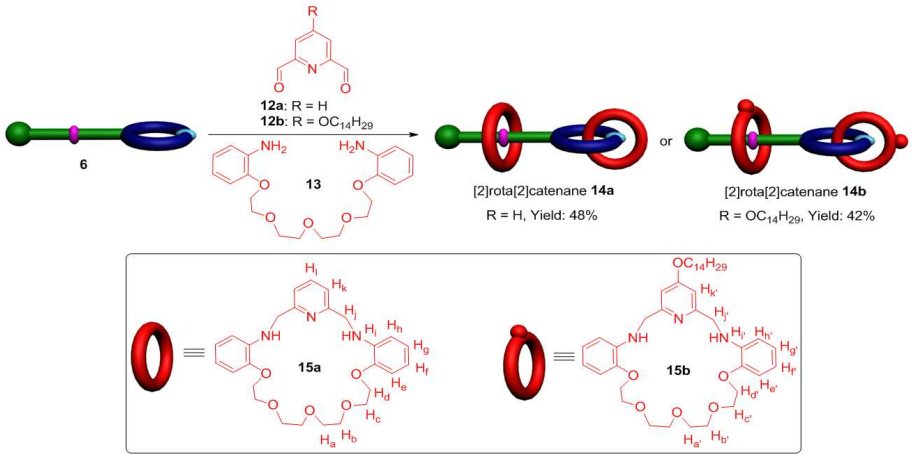
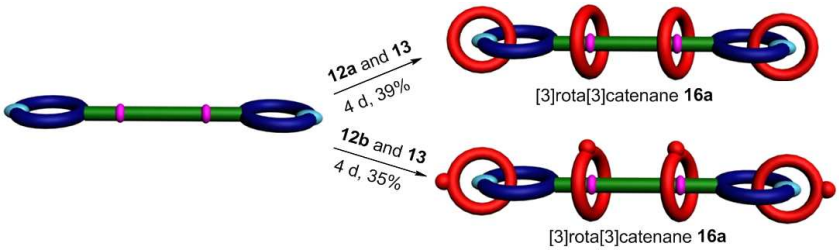


Scheme 5. Synthesis of [2]rota[2]catenanes **14a-b.**



Scheme 6. Synthesis of [3]rota[3]catenanes **16a-b.**

In the ^{1}H NMR spectra, there were all obviously two sets of the characteristic resonance signals of ammonium NH_2^+ protons as broad peaks in the kinetically stable [2]rota[2]catenane **14a** (Figure 1B) and **14b** (Figure 1D). For the **14a**, as shown in Figure 1B, the resonance signals of the two sides methylene protons (H_1, H_{12} and H_{13}) adjacent to the ammonium residue displayed obvious downfield shift in comparison to the ammonium **6** in Figure 1C. While the corresponding benzene ring protons (H_2 and H_3, H_{10} and H_{11}, H_{14} and H_{15}) showed significant upfield shifts as a result of shielding effects associated with the encircling N-hetero crown ethers. For example, protons H_2 at 7.30 ppm and H_3 at 6.97 ppm shifted to 6.75 and 6.51 ppm, respectively, implying the formation of a [2]catenane structure. Furthermore, these changes were in agreement with our previous report.[5a] Likewise, the resonance of protons (H_{10} and H_{11}, H_{14} and H_{15}) on the benzene rings adjacent to the other ammonium residue also displayed upfield shifts in comparison to those in the ammonium **6** (Figure 1C), suggesting that this moiety was encircled by a crown ether component. These shifts were in agreement with those noted in our previous works.[5a, 13] Another changes of resonance signals on the pyridine components could be observed in Figure 1. According to the ^{1}H NMR spectra in Figure 1A, the protons (H_l and H_k) were split two sets of peaks, respectively, owing to the different chemical environment where N-hetero crown ether components were in. These results indicated the bis-ammonium **6** efficiently assembled the [2]rota[2]catenane **14a** in one pet. Similar research was also performed well in the construction of [2]rota[2]catenane **14b**, as presented in Figure 1. Further proof was performed by the matrix assisted laser desorption ionization (MALDI) mass spectrometry in acetonitrile, the peaks at *m/z* 1705.8 and 2130.4 can be assigned to the $[M - PF_6^- - HPF_6]^+$ species, in which M were the **14a** and **14b** (See Supporting Information).

Evidence for the formation of **16a** and **16b** in this process came from analysis of its ^{1}H NMR spectra. As shown in Figure 2A and 2C, there were also obviously two sets of the characteristic signals of ammonium NH_2^+ protons as broad peaks in the kinetically stable [3]rota[3]catenane **16a** and **16b**. Some obvious downfield shifts of the resonance for the methylene protons ($H_{1'}$ and $H_{12'}$) were observed while protons ($H_{2'}$, $H_{3'}$, $H_{10'}$ and $H_{11'}$) on the adjacent benzene rings showed significant upfield shifts compared with the tetra-ammonium salt **8** (In Figure 2B), suggesting the N-hetero crown ethers **15a** and **15b** encircled onto the linear ammonium sites and macrocyclic ammonium sites of template **8**. As well as [2]rota[2]catenane **14a**, two sets of split peaks on the pyridine ring (H_l and H_k) were also observed. The results further demonstrated that the template-directed clipping reaction efficiently applied in synthesis of [n]rota[n]catenane integration. Additional proof was performed by the MALDI mass spectrometry in acetonitrile. As can be seen from the supporting Information, the peaks at *m/z* 3192.4 and 4041.2 can be assigned to the $[M - PF_6^- - 3HPF_6]^+$ species, in which M were the [3]rota[3]catenane **16a** and **16b**.

The final effort focused on the investigation of star-shaped structure. Similarly, two sets of the characteristic signals of ammonium NH_2^+ protons as broad peaks were found in the ^{1}H NMR spectra of kinetically stable [4]rota[4]catenane **17a** and **17b**, as shown in Figure 3A and 3C. Compared with the spectrum of the hexa-ammonium salt **11** (Figure 3B), the methylene protons ($H_{1''}$, $H_{12''}$ and $H_{13''}$) displayed downfield shifts while the resonance of the protons on the adjacent benzene rings ($H_{2''}$, $H_{3''}$, $H_{10''}$, $H_{11''}$, $H_{14''}$, $H_{15''}$, and $H_{16''}$) showed

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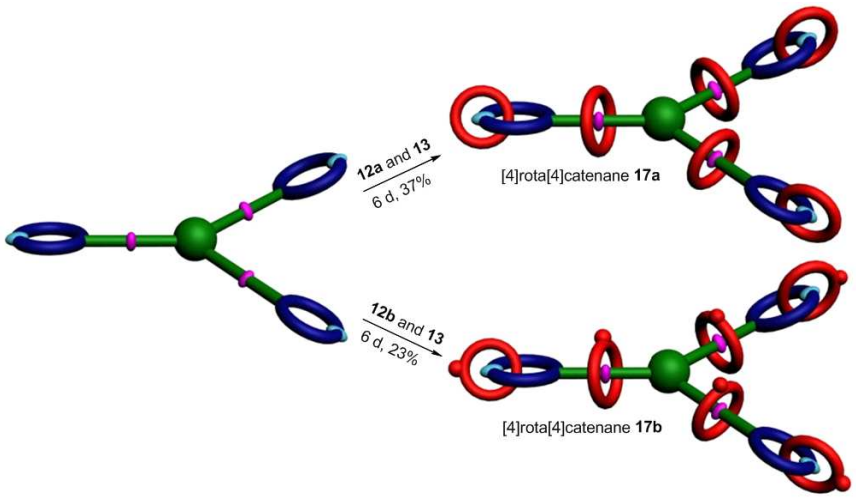

Scheme 7. Synthesis of [4]rota[4]catenanes **17a-b.**

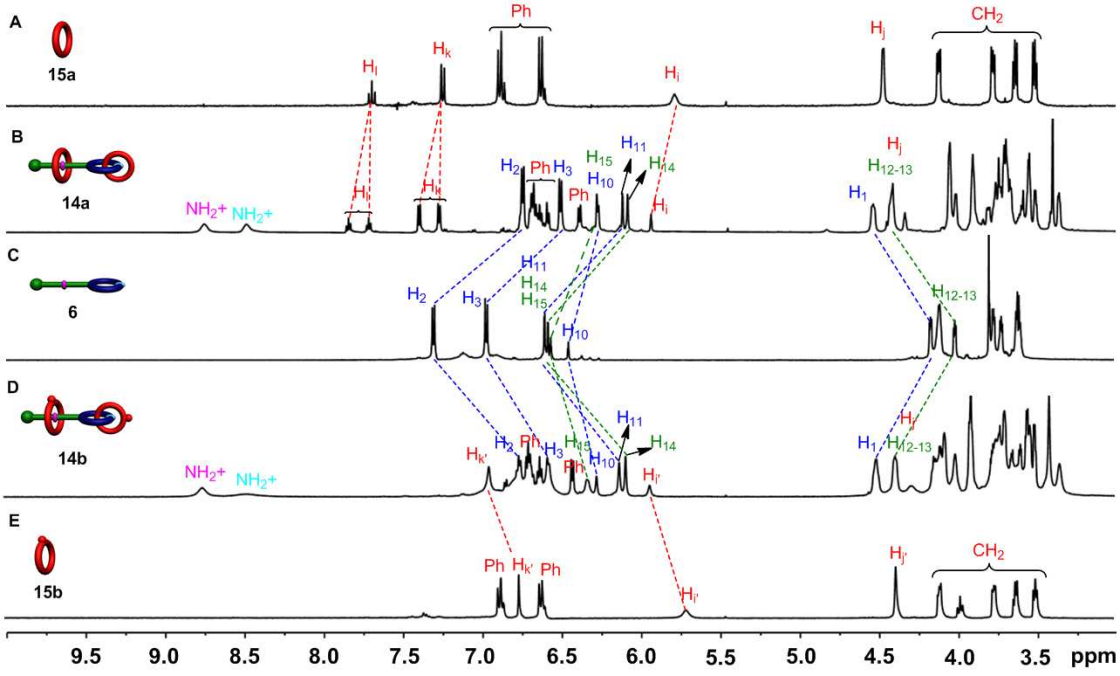

Figure 1. Partial ^{1}H NMR spectra (600 MHz, CD_3CN, 298 K) of **15a** (A), [2]rota[2]catenane **14a** (B), **6** (C), [2]rota[2]catenane **14b** (D), and **15b** (E)

upfield shifts, owing to the shielding effect of the encircling. Therefore, these data supported the finding that the N-hetero crown ethers **15a** and **15b** encircled onto the linear ammonium sites and macrocyclic ammonium sites of template **11**, affording [4]rota[4]catenane **17a** and **17b**. Similarly, additional evidence supporting this conclusion came from analysis of the MALDI Mass spectrometry (supporting information), which contained a peak at *m/z* 5007.6 and 6280.6 that corresponded to the $[M - PF_6^- - 5HPF_6]^+$ species of [4]rota[4]catenane **17a** and **17b**, respectively.

Conclusions

In conclusion, we developed three novel polyfunctional building blocks possessing the different ammonium sites, and The ammonium group incorporated in the linear part of the molecules **6**, **8**, **11** can be used for templating rotaxane formation while the macrocyclic part of the molecules **6**, **8**, **11** can be used for templating catenane formation. Therefore, these new frameworks were employed to assemble a series of [n]rota[n]catenanes (n = 2, 3, 4) with high efficiencies, and in which, the N-hetero crown ether components were installed on ammonium template sites of linear and macrocyclic components all at once. The successful construction of [n]rota[n]catenanes provides a foundation for future studies aimed at constructing the complicated integration or supramolecular polymer by use of multi mechanically interlocked frameworks.

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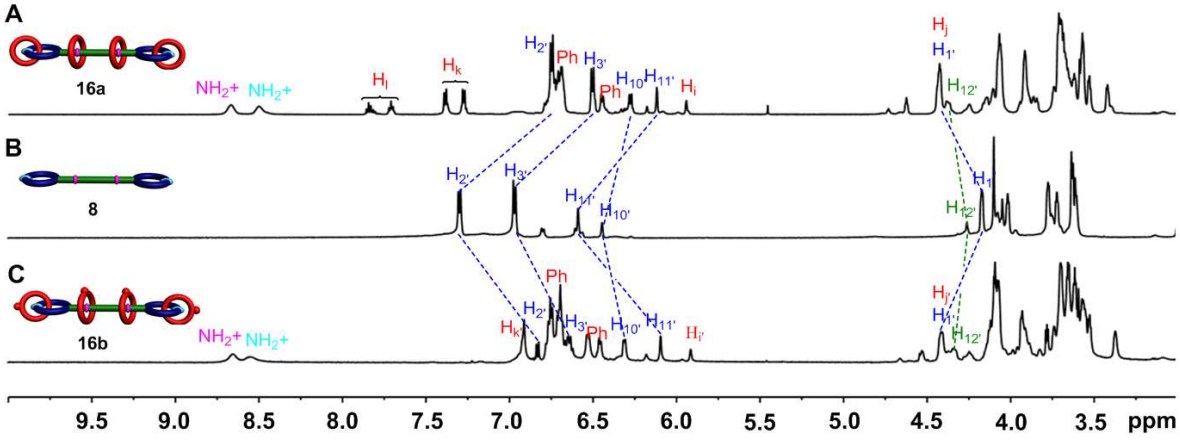

Figure 2. Partial ^{1}H NMR spectra (600 MHz, CD_3CN, 298 K) of [3]Rota[3]catenane **16a** (A), **8** (B) and [3]Rota[3]catenane**16b**(C)

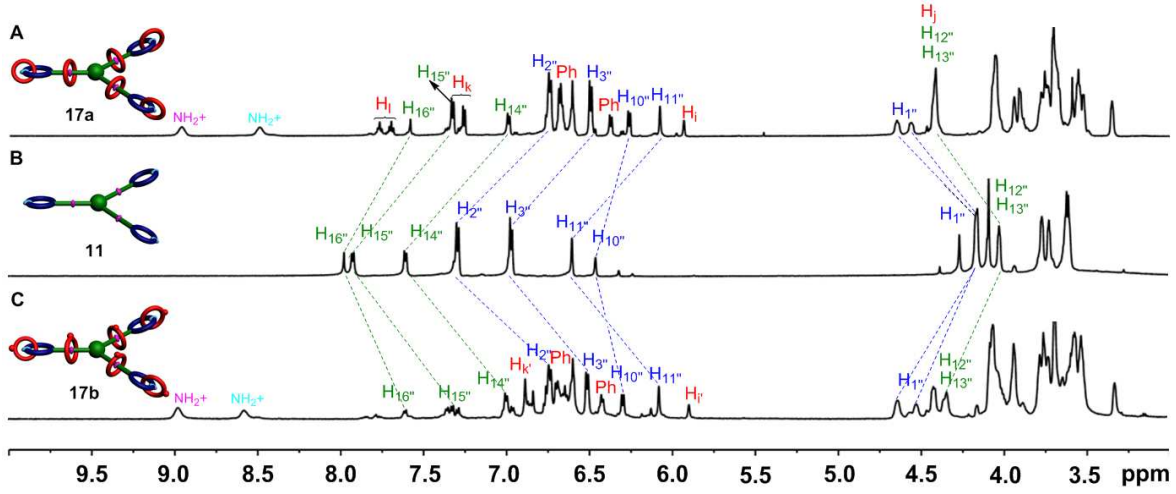

Figure 3. Partial ^{1}H NMR spectra (600 MHz, CD_3CN, 298 K) of [4]Rota[4]catenane **17a** (A), **11** (B), and [4]Rota[4]catenane **17b** (C).

Experimental

Materials and 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 3.A mixture of **1** (0.71 g, 1.0 mmol) and 4,4'-(azanediylbis(methylene))diphenol **2** (0.23 g, 1.0 mmol) in dry DMF (400 mL) was added dropwise over a period of 24 h to a stirred suspension of Cs_2CO_3 (1.30 g, 4.0 mmol) in DMF (200 mL) at 80℃ under an argon atmosphere. And then the mixture was stirred at 80℃ for a further 48 h. The resulting mixture was allowed to cool to room temperature, and filtered. After that, the solvent was removed under vacuum, and the residue was extracted by ethyl acetate, and then dried over anhydrous sodium sulfate. After removing the solvent, the residue was dissolved in dry chloroform (20 mL), and then Boc_2O (0.44 g, 2 mmol) and triethylamine (0.43 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 DCM/ethyl acetate (5:1) as the eluent obtained the Boc-protected macrocycle **3** as a light yellow liquid. Yield: 0.14 g, 20%. Compound **3**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.00 (s, 4H), 6.88 (s, 2H), 6.80 (s, 4H), 6.76 (s, 1H), 4.32 (s, 2H), 4.23 (s, 2H), 4.13 (s, 8H), 3.85 (s, 8H), 3.74 (s, 8H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 160.3, 157.8, 156.0, 138.2, 129.7, 128.8, 114.6, 108.2, 107.8, 79.7, 69.8, 69.5, 67.8, 67.5, 28.4. ESI-MS m/z = 718.5 [M + Na^+], 734.5 [M + K^+]; calculated exact mass = 695.3. Anal. Calcd for: $C_{38}H_{49}NO_{11}$: C, 65.65; H, 7.01; N, 2.10. Found: C, 65.59; H, 7.10; N, 2.01.

Synthesis of 5: To a solution of **3** (0.50 g, 0.72 mmol) in anhydrous MeOH (80 mL) was added 3,5-dimethoxybenzylamine **4** (0.18 g, 1.08 mmol) with anhydrous sodium sulfate acting as drying agent under argon atmosphere. The mixture was refluxed for 24 h. After removing the solvent, and the residue was dissolved in THF (30 mL) and MeOH (30 mL), and then $NaBH_4$ (0.15 g, 4.0 mmol) was added slowly in 10 portions. After stirring overnight, the reaction was quenched with the saturated ammonium chloride (aq). The solvent was

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removed under a vacuum, and the residue was extracted by absolute ethyl ether and then dried over anhydrous sodium sulfate. After removing the solvent, the residue was dissolved in dry chloroform (60 mL), and then Boc_2O (0.31 g, 1.44 mmol) and triethylamine (0.31 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 DCM/ethyl acetate (3:1) as the eluent obtained the Boc-protected amine **5** as a yellow liquid. Yield: 0.42 g, 62%. Compound **5**: ^{1}H NMR (600 MHz, $CDCl_3$) δ7.02 (s, 2H), 6.88 (s, 2H), 6.81 (s, 4H), 6.41 (s, 2H), 6.39-6.30 (m, 4H), 4.33 (s, 4H), 4.24 (s, 4H), 4.13 (s, 4H), 4.05 (s, 4H), 3.85 (s, 8H), 3.76 (s, 6H), 3.74 (s, 8H), 1.47 (d, J = 18 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 160.0, 157.9, 156.0, 140.5, 130.2, 130.0, 129.7, 128.9, 114.6, 106.6, 105.9, 105.7, 105.1, 100.1, 99.1, 80.0, 79.8, 70.9, 69.8, 69.7, 67.4, 67.3, 55.2, 49.4, 49.0, 28.4. ESI-MS m/z = 969.8 [M + Na^+], 985.8 [M + K^+]; calculated exact mass = 946.5. Anal. Calcd for $C_{52}H_{70}N_2O_{14}$: C, 65.87; H, 7.38; N, 2.89. Found: C, 65.94; H, 7.45; N, 2.96.

Synthesis of **6:** To a solution of the Boc-protected amine **5** (0.19 g, 0.2 mmol) in dry DCM (10 mL), TFA (0.25 mL, 4.0 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: 0.19 g, 90%. Compound **6**: ^{1}H NMR (600 MHz, CD_3CN) δ 7.29 (d, J = 6 Hz, 4H), 7.11 (s, 4H, NH_2^+), 6.96 (d, J = 6 Hz, 4H), 6.60 (d, J = 6 Hz, 2H), 6.57 (d, J = 6 Hz, 2H), 6.56 (t, J = 6 Hz, 1H), 6.44 (t, J = 6 Hz, 1H), 4.17-4.15 (m, 4H), 4.11 (s, 8H), 4.03-3.99 (m, 4H), 3.78 (s, 6H), 3.78 -3.76 (m, 4H, CH_2), 3.72 (t, J = 6 Hz, 4H, CH_2), 3.61 (m, 8H, CH_2); ^{13}C NMR (100 MHz, CD_3CN) δ 161.8, 160.8, 160.3, 133.0, 132.3, 123.0, 115.6, 108.9, 108.4, 101.6, 71.0, 69.8, 69.7, 68.2, 55.8, 51.8, 50.8; ESI-MS m/z = 747.5 [M-PF^-_6-HPF_6]; calculated exact mass = 1038.3; Anal. Calcd for $C_{42}H_{56}F_{12}N_2O_{10}P_2$: C, 48.63; H, 5.52; N, 2.62. Found: C, 48.56; H, 5.43; N, 2.70.

Synthesis of [2]Rota[2]catenanes 14a and 14b: A mixture of **6** (100 mg, 0.10 mmol), tetraethyleneglycol bis(2-aminophenyl) ether **13** (75 mg, 0.20 mmol) and dicarboxaldehyde **12a** (26 mg, 0.20 mmol) or **12b** (70 mg, 0.20 mmol) was stirred for 2 d in dry CH_3CN (10 mL) under nitrogen atmosphere at room temperature. Then, BH_3·THF solution (1.6 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/MeOH = 100:0−80:1) to give [2]rota[2]catenanes **14a** and **14b**. [2]Rota[2]catenane **14a**: White solid, Yield: 95 mg, 48%. ^{1}H NMR (600 MHz, CD_3CN) δ 8.74 (s, 2H), 8.48 (s, 2H), 7.84 (t, J = 6.0 Hz, 1H), 7.71 (t, J = 6.0 Hz, 1H), 7.39 (d, J = 6.0 Hz, 2H), 7.27 (d, J = 6.0 Hz, 2H), 6.74 (d, J = 12.0 Hz, 4H), 6.66-6.70 (m, 8H), 6.63 (d, J = 12.0 Hz, 4H), 6.58 (d, J = 12.0 Hz, 2H), 6.50 (d, J = 6.0 Hz, 4H), 6.39 (d, J = 6.0 Hz, 2H), 6.27 (s, 1H), 6.26 (s, 1H), 6.11 (s, 2H), 6.08 (s, 2H), 4.54 (s, 4H), 4.41 (s, 8H), 4.05 (s, 8H), 4.01 (d, J = 6.0 Hz, 4H), 3.91 (s, 8H), 3.76 (s, 4H), 3.75 (s, 8H), 3.70 (d, J = 6.0 Hz, 8H), 3.67 (d, J = 6.0 Hz, 4H), 3.59 (d, J = 6.0 Hz, 4H), 3.55 (d, J = 6.0 Hz, 8H), 3.51 (d, J = 6.0 Hz, 4H), 3.41 (s, 6H). ^{13}C NMR (100 MHz, CD_3CN) δ 161.3, 160.3, 159.4, 159.2, 158.8, 146.9, 138.6, 138.3, 137.3, 137.2, 134.7, 134.3, 130.8, 124.4, 122.6, 122.2, 121.6, 121.5, 120.0, 119.7, 117.5, 115.2, 112.7, 112.6, 110.4, 110.4, 107.2, 107.1, 102.6, 101.2, 71.6, 71.4, 71.3, 70.7, 70.6, 69.5, 69.4, 68.1, 67.7, 55.2, 52.9, 51.9. MALDI-MS m/z = 1705.8 [M-PF^-_6-HPF_6]; calculated exact mass = 1996.8; Anal. Calcd for $C_{96}H_{122}F_{12}N_8O_{20}P_2$: C, 57.78; H, 6.09; N, 5.55. Found: C, 57.71; H, 6.15; N, 5.61. [2]Rota[2]catenane **14b**: White solid, Yield: 100 mg, 42%. ^{1}H NMR (600 MHz, CD_3CN) δ 8.75 (s, 2H), 8.48 (s, 2H), 6.94 (s, 4H), 6.77 – 6.74 (m, 4H), 6.71-6.66 (m, 8H), 6.62 (t, J = 6.0 Hz, 4H), 6.58 (s, 2H), 6.42 (d, J = 6.0 Hz, 4H), 6.33 (s, 2H), 6.32 (s, 1H), 6.27 (s, 1H), 6.12 (s, 2H), 6.08 (s, 2H), 4.50 (s, 4H), 4.39 (s, 4H), 4.10 – 4.06 (m, 8H), 4.01 (s, 4H), 3.91 (t, J = 6.0 Hz, 8H), 3.73 (s, 8H), 3.70 (s, 8H), 3.61 – 3.59 (m, 4H), 3.56 – 3.53 (m, 8H), 3.51 (d, J = 4.8 Hz, 4H), 3.42 (s, 6H), 1.28 (s, 48H), 0.89 (m, 10H). ^{13}C NMR (100 MHz, CD_3CN) δ 161.8, 160.9, 160.1, 147.4, 137.7, 131.5, 125.0, 122.2, 115.8, 107.8, 101.7, 72.0, 71.3, 70.0, 68.7, 68.2, 55.8, 53.5, 52.6, 50.5, 32.5, 30.2, 29.9, 23.2, 14.2. MALDI-MS m/z = 2130.4 [M-PF^-_6-HPF_6]; calculated exact mass = 2421.2; Anal. Calcd for $C_{124}H_{178}F_{12}N_8O_{22}P_2$: C, 61.40; H, 7.37; N, 4.55. Found: C, 61.47; H, 7.41; N, 4.63.

Synthesis of 7: To a solution of **3** (0.50 g, 0.72 mmol) in anhydrous MeOH (80 mL) was added 1,6-hexanediamine (42 mg, 0.36 mmol) with anhydrous sodium sulfate acting as drying agent under argon atmosphere. The mixture was refluxed for 24 h. After removing the solvent, and the residue was dissolved in THF (40 mL) and MeOH (20 mL), and then $NaBH_4$ (0.15 g, 4.0 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. After removing the solvent, the residue was dissolved in dry chloroform (60 mL), and then Boc_2O (0.31 g, 1.44 mmol) and triethylamine (0.31 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 DCM/ethyl acetate (2:1) as the eluent obtained the Boc-protected amine **7**. Yield: 0.36 g, 60%. Compound **7**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (s, 4H, Ar), 6.88 (s, 4H, Ar), 6.80 (s, 8H), 6.39 (s, 4H), 6.35 (s, 2H), 4.33 (s, 8H), 4.24 (s, 4H), 4.13 (s, 8H), 4.05 (s, 8H), 3.83 (d, J = 12.0 Hz, 16H), 3.72 (s, 16H), 3.14 (s, 2H), 3.05 (s, 2H), 1.44 (d, J = 24.0 Hz, 36H), 1.26 (d, J = 6.0 Hz, 4H), 1.21 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 157.8, 155.9, 141.0, 130.2, 130.0, 129.8, 128.9, 114.5, 106.2, 105.6, 100.0, 79.8, 79.4, 70.8, 69.7, 67.4, 67.2, 60.3, 49.4, 46.2, 28.4, 27.9, 27.7, 26.6, 14.1; MALDI-MS m/z = 1697.8 [M + Na^+], 1713.8 [M + K^+]; calculated exact mass = 1674.9; Anal. Calcd for $C_{92}H_{130}N_4O_{24}$: C, 65.86; H, 7.90; N, 3.27. Found: C, 65.93; H, 7.82; N, 3.34.

Synthesis of 8: To a solution of the Boc-protected amine **7** (100 mg, 0.06 mmol) in dry DCM (10 mL), TFA (0.16 mL, 2.40 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 **7** was obtained as the light yellow gum. Yield: 90 mg, 85%. Compound **7**: ^{1}H NMR (600 MHz, CD_3CN) ^{1}H NMR (600 MHz, cd_3cn) δ 7.29 (d, J = 6.0 Hz, 8H), 6.96 (d, J = 6.0 Hz, 8H), 6.58 (s, 4H), 6.44 (s, 2H), 4.26 (s, 4H), 4.17 (s, 8H), 4.10 (s, 8H), 4.04-3.99 (m, 8H), 3.77 (s, 8H), 3.75-3.70 (m, 8H), 3.63 (d, J = 6.0 Hz, 8H), 3.60 (d, J = 6.0 Hz, 8H), 2.98 (m, 4H), 1.42 (s, 4H), 1.28 (s, 4H); ^{13}C NMR (100 MHz, CD_3CN) δ 160.8, 160.3, 133.5, 132.3, 123.1, 115.5, 108.7, 102.3, 70.9, 69.8, 68.2, 51.8, 50.5, 48.0, 28.1,

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25.7; MALDI-MS m/z = 1275.7, [M -PF^-_6-3HPF_6]; calculated exact mass = 1858.6; Anal. Calcd for $C_{72}H_{102}F_{24}N_4O_{16}P_4$: C, 46.59; H, 5.47; N, 3.10. Found: C, 46.51; H, 5.53; N, 3.01.

Synthesis of [3]Rota[3]catenanes 16a and 16b: A mixture of Compound **8** (93 mg, 0.05 mmol), tetraethyleneglycol bis(2-aminophenyl) ether **13** (75 mg, 0.20 mmol) and dicarboxaldehyde **12a** (26 mg, 0.20 mmol) or **12b** (70 mg, 0.20 mmol) was stirred for 4 d in dry CH_3CN (10 mL) under nitrogen atmosphere at room temperature. Then, BH_3·THF solution (1.6 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/MeOH = 100:0−60:1) to give the [3]rota[3]catenanes **16a** and **16b**. [3]Rota[3]catenane **16a**: White solid, Yield: 66 mg, 39%. ^{1}H NMR (600 MHz, CD_3CN) δ 8.67 (s, 4H), 8.50 (s, 4H), 7.84 (t, *J* = 9.0 Hz, 2H), 7.71 (t, *J* = 6.0 Hz, 2H), 7.38 (d, *J* = 6.0 Hz, 4H), 7.27 (d, *J* = 6.0 Hz, 4H), 6.75 (m, 20H), 6.72 – 6.65 (m, 16H), 6.50 (d, *J* = 6.0 Hz, 8H), 6.45 (d, *J* = 6.0 Hz, 4H), 6.28 (d, *J* = 6.0 Hz, 2H), 6.12 (s, 4H), 4.43 (s, 8H), 4.38 (s, 4H), 4.07 (d, *J* = 6.0 Hz, 16H), 3.92 (s, 16H), 3.74 (s, 8H), 3.69 (m, 48H), 3.62 (t, *J* = 3.9 Hz, 8H), 3.59-3.55 (m, 16H), 3.55-3.48 (m, 8H), 3.42 (s, 8H), 2.94 (s, 4H), 1.42 (s, 4H), 1.29 (s, 4H); ^{13}C NMR (100 MHz, CD_3CN) δ 160.9, 160.0, 159.4, 159.3, 147.9, 147.5, 139.3, 138.9, 137.9, 137.8, 131.4, 125.0, 122.9, 122.7, 122.2, 122.1, 120.5, 115.8, 115.4, 113.7, 113.3, 111.0, 107.6, 102.8, 72.2, 71.8, 71.3, 71.1, 70.0, 68.5, 68.3, 52.5, 50.8, 50.6, 49.2; MALDI-MS m/z = 3192.4, [M -PF^-_6-3HPF_6]; calculated exact mass = 3375.6. Anal. Calcd for $C_{180}H_{234}F_{24}N_{16}O_{36}P_4$: C, 57.32; H, 6.18; N, 5.85. Found: C, 57.23; H, 6.24; N, 5.93.; [3]Rota[3]catenane **16b**: Light yellow solid, Yield: 81 mg, 35%. ^{1}H NMR (600 MHz, CD_3CN) δ 8.65 (s, 4H), 8.55 (s, 4H), 6.91 (s, 8H), 6.79-6.72 (m, 16H), 6.69 (m, 20H), 6.52 (d, *J* = 6.0 Hz, 8H), 6.45 (d, *J* = 6.0 Hz, 4H), 6.31 (d, *J* = 6.0 Hz, 2H), 6.09 (s, 4H), 4.41 (d, *J* = 6.0 Hz, 8H), 4.34 (s, 4H), 4.11 (s, 8H), 4.11-4.08 (m, 16H), 4.07 (s, 16H), 3.91 (m, 16H), 3.73 (s, 8H), 3.70 (s, 16H), 3.66-3.64 (m, 16H), 3.63-3.60 (m, 16H), 3.58-3.54 (m, 16H), 3.52 (t, *J* = 3.9 Hz, 8H), 2.96 (s, 4H), 1.83-1.74 (m, 8H), 1.48 (m, 4H), 1.42(s, 12H), 1.28 (s, 80H), 0.89 (t, *J* = 6.0 Hz, 12H); ^{13}C NMR (100 MHz, CD_3CN) δ 167.7, 161.1, 160.9, 160.0, 147.8, 147.5, 138.0, 131.5, 125.1, 122.1, 120.5, 115.8, 114.2, 111.0, 109.2, 72.1, 71.9, 71.3, 71.2, 71.0, 70.3, 70.1, 70.0, 69.5, 68.6, 68.5, 68.3, 52.5, 51.0, 32.5, 30.2, 29.9, 28.5, 26.9, 26.5, 26.4, 23.2; MALDI-MS m/z = 4041.2, [M -PF^-_6-3HPF_6]; calculated exact mass = 4624.4. Anal. Calcd for : $C_{236}H_{346}F_{24}N_{16}O_{40}P_4$: C, 61.33; H, 7.62; N, 4.75. Found: C, 61.26; H, 7.54; N, 4.84.

Synthesis of 10: To a solution of **3** (0.50 g, 0.72 mmol) in anhydrous MeOH(80 mL) was added **9** (0.094 g, 0.24 mmol) with anhydrous sodium sulfate acting as drying agent under argon atmosphere. The mixture was refluxed for 48 h. After removing the solvent, and the residue was dissolved in THF (40 mL) and MeOH (20 mL), and then $NaBH_4$ (0.15 g, 4.0 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. After removing the solvent, the residue was dissolved in dry chloroform (60 mL), and then Boc_2O (0.31 g, 1.44 mmol) and triethylamine (0.31 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 DCM/ethyl acetate (1:1) as the eluent obtained the Boc-protected amine **10**. Yield: 0.35 g, 54%. Compound **10**: ^{1}H NMR (600 MHz, $CDCl_3$) ^{1}H NMR δ 7.77 (s, 3H), 7.67 (s, 6H), 7.35 (d, *J* = 6.0 Hz, 3H), 7.30 (d, *J* = 6.0 Hz, 3H), 7.03 (d, *J* = 6.0 Hz, 6H), 6.89 (d, *J* = 6.0 Hz, 6H), 6.81 (s, 12H), 6.43 (s, 6H), 6.38 (s, 3H), 4.38 (d, *J* = 4.8 Hz, 6H), 4.34 (s, 6H), 4.30 (s, 6H), 4.24 (s, 6H), 4.17-4.11 (m, 12H), 4.06 (s, 12H), 3.84 (m, 24H), 3.74 (d, *J* = 3.0 Hz, 24H), 1.48 (m, 54H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 157.8, 155.9, 141.9, 140.3, 139.9, 137.3, 130.1, 129.7, 128.9, 128.4, 127.9, 127.4, 124.8, 114.6, 106.6, 106.0, 100.3, 80.1, 79.8, 77.3, 77.0, 76.7, 70.8, 69.8, 69.6, 67.5, 67.4, 49.4, 48.9, 29.6, 29.3, 28.4. MALDI-MS m/z = 2754.2 [M + Na^+], 2770.2 [M + K^+]; calculated exact mass = 2731.4.; Anal. Calcd for $C_{156}H_{198}N_6O_{36}$: C, 68.62; H, 7.23; N, 3.14. Found: C, 68.55; H, 7.30; N, 3.07.

Synthesis of 11: To a solution of the Boc-protected amine **10** (0.16 g, 0.06 mmol) in dry DCM (10 mL), TFA (0.23 ml, 3.60 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: 0.14 g, 80%. Compound **10**: ^{1}H NMR (600 MHz, CD_3CN) δ 7.97 (s, 3H), 7.92 (d, *J* = 12.0 Hz, 6H), 7.60 (d, *J* = 6.0 Hz, 6H), 7.29 (d, *J* = 12.0 Hz, 12H), 6.97 (d, *J* = 6.0 Hz, 12H), 6.60 (s, 6H), 6.46 (s, 3H), 4.16 (d, *J* = 6.0 Hz, 24H), 4.09 (s, 12H), 4.03 (s, 12H), 3.77 (s, 12H), 3.73 (s, 12H), 3.62 (d, *J* = 6.0 Hz, 24H). ^{13}C NMR (100 MHz, CD_3CN) δ 160.8, 160.3, 141.8, 133.8, 132.0, 131.3, 131.1, 128.3, 125.6, 123.1, 117.8, 115.7, 108.7, 102.6, 70.8, 69.7, 68.2, 51.9, 51.5, 50.6; MALDI-MS m/z = 2132.1, [M-PF^-_6-5HPF_6]; calculated exact mass = 3006.9. Anal. Calcd for: $C_{126}H_{156}F_{36}N_6O_{24}P_6$: C, 50.21; H, 5.15; N, 2.86. Found: C, 50.30; H, 5.23; N, 2.79.

Synthesis of [4]Rota[4]catenanes 17a and 17b: A mixture of **11** (100 mg, 0.033 mmol), tetraethyleneglycol bis(2-aminophenyl) ether **13** (75 mg, 0.20 mmol) and dicarboxaldehyde **12a** (26 mg, 0.20 mmol) or **12b** (70 mg, 0.20 mmol) was stirred for 6 d in dry CH_3CN (10 mL) under nitrogen atmosphere at room temperature. Then, BH_3·THF solution (1.6 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/MeOH = 100:0−40:1) to give the [4]rota[4]catenanes **17a** and **17b**. [4]Rota[4]catenane **17a**: White solid, Yield: 72 mg, 37%. ^{1}H NMR (600 MHz, CD_3CN) δ 8.96 (s, 6H), 8.49 (s, 6H), 7.77 (t, *J* = 7.2 Hz, 3H), 7.70 (t, *J* = 7.8 Hz, 3H), 7.59 (s, 3H), 7.33 (d, *J* = 7.2 Hz, 6H), 7.27 (d, *J* = 7.2 Hz, 6H), 7.00 (d, *J* = 7.8 Hz, 6H), 6.77 (s, 6H), 6.75 (d, *J* = 8.4 Hz, 12H), 6.68 (t, *J* = 6.6 Hz, 24H), 6.61 (s, 20H), 6.50 (d, *J* = 8.4 Hz, 12H), 6.38 (d, *J* = 7.8 Hz, 8H), 6.27 (d, *J* = 7.8 Hz, 3H), 6.08 (s, 6H), 4.65 (s, 6H), 4.57 (s, 6H), 4.42 (s, 24H), 4.06 (d, *J* = 3.2 Hz, 48H), 3.93 (m, 24H), 3.76 (m, 24H), 3.71 (s, 24H), 3.60 (s, 12H), 3.56 (s, 24H), 3.53 (s, 12H); The ^{13}C NMR spectrum was not collected due to the poor solubility of [4]rota[4]catenane **17a**; MALDI-MS m/z = 5007.6, [M-PF^-_6-5HPF_6]; calculated exact mass = 5882.4. Anal. Calcd for: $C_{288}H_{354}F_{36}N_{24}O_{54}P_6$: C, 58.70; H, 6.13; N, 5.66. Found: C, 58.77; H, 6.06; N, 5.71. [4]Rota[4]catenane **17b**: White solid, Yield: 54 mg, 23%. ^{1}H NMR (600 MHz, CD_3CN) δ 8.97 (s, 6H), 8.57 (s, 6H), 7.60 (d, *J* = 7.8 Hz, 3H), 7.42-7.18 (m, 12H), 6.99 (d, *J* = 7.8 Hz, 6H), 6.88 (s, 6H), 6.74 (m, 12H), 6.72-6.60 (m, 24H), 6.59 (s, 20H), 6.50 (d, *J* = 7.8 Hz, 12H), 6.44-6.38 (m, 8H), 6.29 (d, *J* = 7.8 Hz, 3H), 6.07 (s, 6H), 4.63 (s, 6H), 4.52 (s, 6H), 4.42 (s, 12H),

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4.34 (s, 12H), 4.13-3.97 (m, 48H), 3.93 (s, 24H), 3.85-3.69 (m, 48H), 3.69 (s, 24H), 3.58 (d, J = 9.9 Hz, 24H), 3.53 (s, 24H), 1.74 (d, J = 8.7 Hz, 12H), 1.40 (d, J = 6.2 Hz, 12H), 1.26 (s, 120H), 0.86 (s, 18H); The ^{13}C NMR spectrum was not collected due to the poor solubility of [4]rota[4]catenane **17b**; MALDI-MS m/z = 6280.6, [M-PF_6^--5HPF_6]; calculated exact mass = 7155.6. Anal. Calcd for : $C_{372}H_{522}F_{36}N_{24}O_{60}P_6$: C, 62.49; H, 7.27; N, 4.60. Found: C, 62.40; H, 7.35; N, 4.69.

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Notes and references

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†Electronic Supplementary Information (ESI) available: The ^{1}H NMR, ^{13}C NMR and MS spectra of all the new intermediates and [n]rota[n]catenanes. See DOI: 10.1039/b000000x/

1. For selected reviews, see (a) Pease, A. R.; Jeppesen, J. O.; Stoddart, J. F.; Luo, Y.; Collier, C. P.; Heath, J. R. *Acc. Chem. Res.* **2001**, *34*, 433; (b) Balzani, V.; Credi, A.; Venturi, M. *Chem.—Eur. J.* **2002**, *8*, 5524; (c) Lukin, O.; Godt, A.; Vögtle, F. *Chem.—Eur. J.* **2004**, *10*, 1878; (d) Saha, S.; Stoddart, J. F. *Chem. Soc. Rev.* **2007**, *36*, 77; (e) Saha, S.; Leung, K. C.-F.; Nguyen, T. D.; Stoddart, J. F.; Zink, J. I. *Adv. Funct. Mater.* **2007**, *17*, 685; (f) Willner, I.; Basnar, B.; Willner, B. *Adv. Funct. Mater.* **2007**, *17*, 702; (g) Fenlon, E. E. *Eur. J. Org. Chem.* **2008**, 5023; (h) Faiz, J. A.; Heitz, V.; Sauvage, J.-P. *Chem. Soc. Rev.* **2009**, *38*, 422; (i) Amabilino, D. B.; Pérez-García, L. *Chem. Soc. Rev.* **2009**, *38*, 1562; (j) Davis, J. J.; Orlowski, G. A.; Rahmana, H.; Beer, P. D. *Chem. Commun.* **2010**, *46*, 54; (k) Chen, Y.; Liu, Y. *Chem. Soc. Rev.* **2010**, *39*, 495; (l) Beves, J. E.; Blight, B. A.; Campbell, C. J.; Leigh, D. A.; McBurney, R. T. *Angew. Chem., Int. Ed.* **2011**, *50*, 9260; (m) Silvi, S.; Venturia, M.; Credi, A. *Chem. Commun.* **2011**, *47*, 2483; (n) Qu, D. H.; Tian, H. *Chem. Sci.* **2011**, *2*, 1011; (o) Feringa, B. *Nat. Chem.* **2011**, 3, 915; (p) Yang, Y.-W. *Med. Chem. Commun.* **2011**, *2*, 1033; (q) Coskun, A.; Banaszak, M.; Astumian, R. D.; Stoddart, J. F.; Grzybowski, B. A. *Chem. Soc. Rev.* **2012**, *41*, 19; (r) Vukotic, V. N.; Loeb, S. J. *Chem. Soc. Rev.* **2012**, *41*, 5896; (s) Fahrenbach, A. C.;Warren, S. C.; Incorvati, J. T.; Avestro, A. J.; Barnes, J. C.; Stoddart, J. F.; Grzybowski, B. A. *Adv. Mater.* **2013**, *25*, 331; (t) Chambron, J. C.; Sauvage, J.-P. *New J. Chem.* **2013**, *37*, 49.

2. (a) Gibson H. W.; Bheda M. C.; Engen P. T. *Prog. Polym. Sci.*, **1994**, *19*, 843; (b) Fyfe, M. C. T.; Stoddart, J. F. *Coord. Chem. Rev.*, **1999**, *183*, 139; (c) Raymo, F. M.; Stoddart, J. F. *Chem. Rev.* **1999,** *99,* 1643; (d) Wenz, G.; Han, B. H.; Müller, A. *Chem. Rev.* **2006,** 106, 782. (e) Harada, A.; Hashidzume, A.; Yamaguchi, H.; Takashima, Y. *Chem. Rev.* **2009,** *109,* 5974; (f) Harada, A.; Takashima, Y.; Yamaguchi, H. *Chem. Soc. Rev.*, **2009**, *38*, 875; (g) Gibson, H. W.; Farcas, A.; Jones, J. W.; Ge, Z.; Huang, F; Vergne, M.; Hercules, D. M. *J. Polym. Sci., Part A: Polym. Chem.*, **2009**, *47*, 3518; (h) Fang, L.; Olson, M. A.; Benítez, D.; Tkatchouk, E.; Goddard III, W. A.; Stoddart, J. F. *Chem. Soc. Rev.*, **2010**, *39*, 17; (i) Chen, G.; Jiang, M. *Chem. Soc. Rev.,* **2011**, *40*, 2254; (j)Yang, J.; Ma, J. F.; Batten, S. R. *Chem. Commun.,* **2012**, *48*, 7899; (k) Zheng, B.; Wang, F.; Dong, S.; Huang, F. *Chem. Soc. Rev.,* **2012**, *41*, 1621; (l) Avestro, A. J.; Belowich, M. E.; Stoddart, J. F. *Chem. Soc. Rev.,* **2012**, *41*, 5881; (m) Li, S. L.; Xiao, T.; Lin, C.; Wang, L. *Chem. Soc. Rev.,* **2012**, *41*, 5950; (n) Yan, X.; Wang, F.; Zheng, B.; Huang, F. *Chem. Soc. Rev.,* **2012**, *41*, 6042; (o) Yan, X.; Zheng, B; Huang, F. *Polym. Chem.*, **2013**, *4*, 2395.

3. (a) Godt, A. *Eur. J. Org. Chem.* **2004**, 1639.;(b) Niu, Z.; Gibson, H. W., *Chem. Rev.* **2009,** *109,* 6024.

4. (a) Ashton, P. R.; Glink, P. T.; Martínez-Díaz, M.-V.; Stoddart, J. F.; White, A. J. P.;Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1930; (b) Kiehne, U.; Lützen, A. *Org. Lett*. **2007**, *9*, 5553; (c) Jiang, W.; Winkler, H. D. F.; Schalley, C. A. *J. Am. Chem. Soc.* **2008**, *130*, 13852; (d) Chen, P. N.; Lai, C. C.; Chiu, S. H. *Org. Lett.* **2011**, *13*, 4660; (e) Zhang, Z. J.; Zhang, H. Y.; Wang, H.; Liu, Y. *Angew. Chem., Int. Ed.* **2011**, *50*, 10834.

5. (a) Li, Z.; Liu, W.; Wu, J.; Liu, S. H.; Yin, J. *J. Org. Chem*. **2012**, *77*, 7129; (b) Li, Z.; Liu, G.; Xue, W.; Wu, D.; Yang, Y. W.; Wu, J.; Yoon, J,; Liu, S. H.; Yin, J. *J. Org. Chem*. **2013**, *78*, 11560.

6. Ho, W. K.-W.; Lee, S.-F.; Wong, C.-H.; Zhu, X.-M.; Kwan, C.-S.; Chak, C.-P.; Mendes, P. M.; Cheng, C. H. K.; Leung, K. C.-F. *Chem. Commun.,* **2013**, *49*, 10781.

7. Amabilino, D. B.; Ashton, P. R.; Bravo, J. A.; Raymo, F. M.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Eur. J. Org. Chem.* **1999**, 1295.

8. Barin, G.; Coskun, A.; Friedman, D. C.; Olson, M. A.; Colvin, M. T.; Carmielli, R.; Dey, S. K.; Bozdemir, O. A.; Wasielewski, M. R.; Stoddart, J. F. *Chem.—Eur. J.* **2011**, *17*, 213.

9. Forgan, R. S.; Gassensmith, J. J.; Cordes, D. B.; Boyle, M. M.; Hartlieb, K. J.; Friedman, D. C.; Slawin, A. M. Z.; Stoddart, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 17007.

10. Ryuto Hayashi, R.; Wakatsuki, K.; Yamasaki, R.; Mutoh, Y.; Kasama, T.; Saito, S. *Chem. Commun.*, **2014**, *50*, 204.

11. Belowich, M. E.; Valente, C.; Stoddart, J. F. *Angew. Chem. Int. Ed.* **2010**, *49*, 7208.

12. (a) Vivekanand, P. A.; Balakrishnan, T. *Appl. Catal., A: General*. **2009**, *364*, 27; (b) Zhao, S.; Kang, L.; Ge, H.; Yang, F.; Wang, C.; Li, C.; Wang, Q.; Zhao, M. *Synth. Commun*. **2012**, *42*, 3569; (c) Zhou, W.; Xu, J.; Zhang, L.; Jiao, N. *Org. Lett*. **2010**, *12*, 2888; (d) Bosch, I.; Costa, A. M.; Martín, M.; Urpí, F.; Vilarrasa, J. *Org. Lett*. **2000**, *2*, 397.

13. (a) Yin, J.; Dasgupta, S.; Wu, J. *Org. Lett*. **2010**, *12*, 1712; (b) Yin, J.; Chi, C.; Wu, J. *Org. Biomol. Chem.* **2010**, *8*, 2594; (b) Liu, G.; Li, Z.; Wu, D.; Xue, W.; Li, T.; Liu, S. H.; Yin J. *J. Org. Chem*. **2014**, *79*, 643.