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A [2]Rota[2]catenane, Constructed from a Pillar[5]arene-Crown Ether Fused Double-Cavity Macrocycle: Synthesis and Structural Characterization

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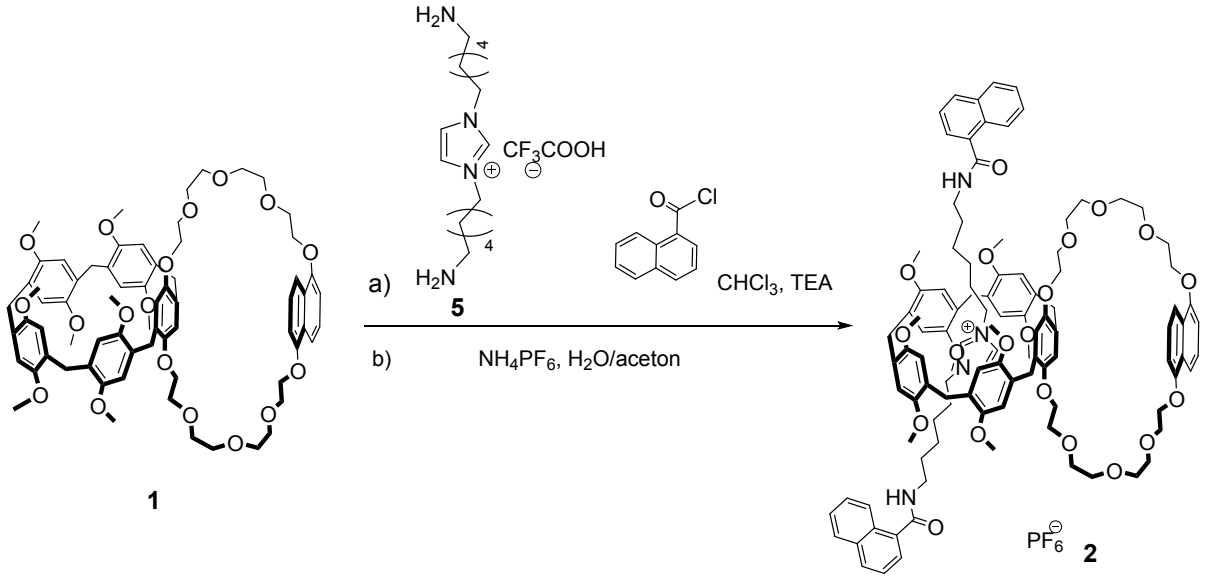
General Methods: Unless otherwise noted, all commercial reagents and solvents were used without purification. Separation by flash column chromatography was performed on Merck silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded at a 400 MHz spectrometer with TMS as the reference. Mass spectra (ESI analysis) were recorded on an Esquire 6000 spectrometer (LC/MS). Single crystal X-ray diffraction data were collected on a SMART APEX 2 X-ray diffractometer equipped with a normal focus Mo-target X-ray tube (λ = 0.71073 Å) and data reduction included absorption corrections by the multi-scan method. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXS-97. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added at their geometrically ideal positions and refined isotropically.

Synthesis of 2：



Compound **1** was prepared as previously reported.[S1]

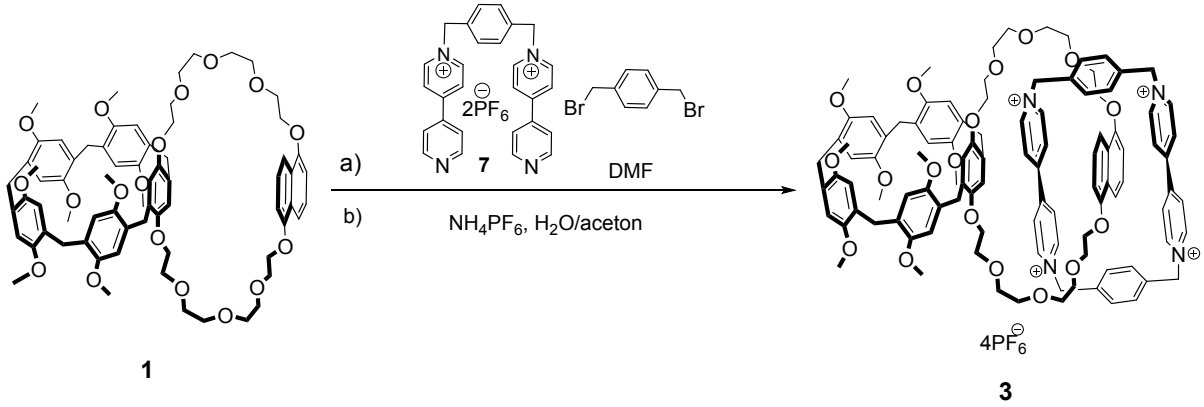
1,3-Bis(6-aminohexyl)-1H-imidazol-3-ium trifluoroacetate 5 To a solution of *tert*-butyl(6-bromohexyl)carbamate (1.11 g，4.00 mmol) and imidazole (108.9 mg，1.60 mmol) and in CH_3CN (20 mL) was added K_2CO_3 (552.8 mg，4.00 mmol), and the reaction mixture was stirred at 70 ºC for 24 h, concentrated under reduced pressure. The resulting residue was purified by chromatography with a mixed solvent of CH_2Cl_2/MeOH (200:1, v/v) to give 1,3-

bis(5-((tert-butoxycarbonyl)amino)pentyl)-1*H*-imidazol-3-ium as a yellow liquid which was then dissolved in $CHCl_3$ (20.0 mL), followed by the addition of CF_3COOH (2.0 mL). The mixture was stirred at 40 ºC for 18 h, and concentrated under reduced pressure to result in a residue which was purified chromatography with a mixed solvent of CH_2Cl_2/MeOH/triethylamine (TEA) (100:20:1, v/v/v) to afford **5** as a colorless liquid (308.2 mg, 50%). ^{1}H NMR (400 MHz, CD_3OD, ppm) δ 9.11 (s, 1H), 7.69 (d, *J*= 1.6 Hz, 2H),, 4.25 (t, *J*= 7.4 Hz, 4H), 3.01-2.89 (m, 4H), 2.02-1.86 (m, 4H), 1.80 -1.62 (m, 4H), 1.57-0.53 (m, 8H) ppm; ^{13}C NMR (101 MHz, CD_3OD, ppm) δ 163.49, 163.14, 162.80, 162.46, 137.21, 123.80, 122.60, 119.69, 116.77, 113.86, 50.67, 40.51, 30.84, 28.26, 26.76, 26.70 ppm; MS (ESI): *m/z* calcd [M-CF_3COO^-] $C_{15}H_{31}N_4^+$: 267.3; Found: 267.3.

[2]Rotaxane (2): After a solution of host **1** (30.00 mg, 0.025 mmol), **5** (9.50 mg, 0.025 mmol) and TEA (101.2 mg, 0.10 mmol) in $CHCl_3$ (30 mL) was stirred at 5 ºC for 30 min, 1-naphthoyl chloride (20.0 mg, 0.10 mmol) was added The resulting reaction mixture was stirred for 1 h, and concentrated under reduced pressure to afford a residue which was purified by chromatography with a mixed solvent of CH_2Cl_2/MeOH (50:1, v/v). The resultant product was dissolved in a mixed solvent of acetone and H_2O (2/:1, v/v, 3.0 mL), followed by addition of NH_4PF_6 (30.0 mg, 0.18 mmol). The mixture was stirred for 5 h, then poured into H_2O (10 mL), and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were washed with brine (4 mL), dried over Na_2SO_4, and concentrated to afford **2** as a yellow solid (14.0 mg, 30%). ^{1}H NMR (600 MHz, CD_3CN) δ 8.32 (d, *J* = 8.3 Hz, 2H), 8.03 (d, *J* = 8.2 Hz, 2H), 8.01 – 7.96 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.67 (m, 2H), 7.66 – 7.55 (m, 6H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.10 (s, 1H), 7.08 (m, 2H), 6.95 (s, 2H), 6.94 (s, 2H), 6.88 (s, 2H), 6.85 (s, 2H), 6.81 (d, *J* = 7.6 Hz, 2H), 6.58 (s, 2H), 6.54 (s, 2H), 4.15 (m, 4H), 3.88 (m, 4H), 3.84 – 3.79 (m, 2H), 3.79 – 3.76 (m, 4H), 3.76 – 3.71 (m, 22H), 3.71 – 3.68 (m, 4H), 3.68 – 3.63 (m, 6H), 3.63 – 3.56 (m, 18H), 3.54 (m, 2H), 3.42 (m, 4H), 2.33 (m, 4H), 1.57 – 1.45 (m, 4H), 1.05 – 0.81 (m, 4H), 0.57 – 0.41 (m, 4H), 0.27 – 0.10 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.72, 154.28, 150.73, 150.65, 150.11, 134.80, 133.74, 132.82, 130.38, 130.32, 130.01, 129.38, 129.30, 129.25, 129.18, 128.35, 126.88, 126.61, 126.29, 125.49, 125.12, 125.03, 124.88, 122.20, 116.25, 114.73, 114.62, 114.55, 114.48, 105.43, 70.97, 70.81, 70.70, 70.37,

70.10, 69.66, 69.34, 67.80, 56.86, 56.81, 56.70, 56.62, 48.44, 39.76, 29.70, 29.57, 29.27, 28.96, 28.52, 25.73, 25.62. MS (ESI): *m/z* calcd [M-PF_6^-+H^+] $C_{106}H_{126}N_4O_{20}^{2+}$: 887.4; Found: 887.8.

Synthesis of 3



1 **3**

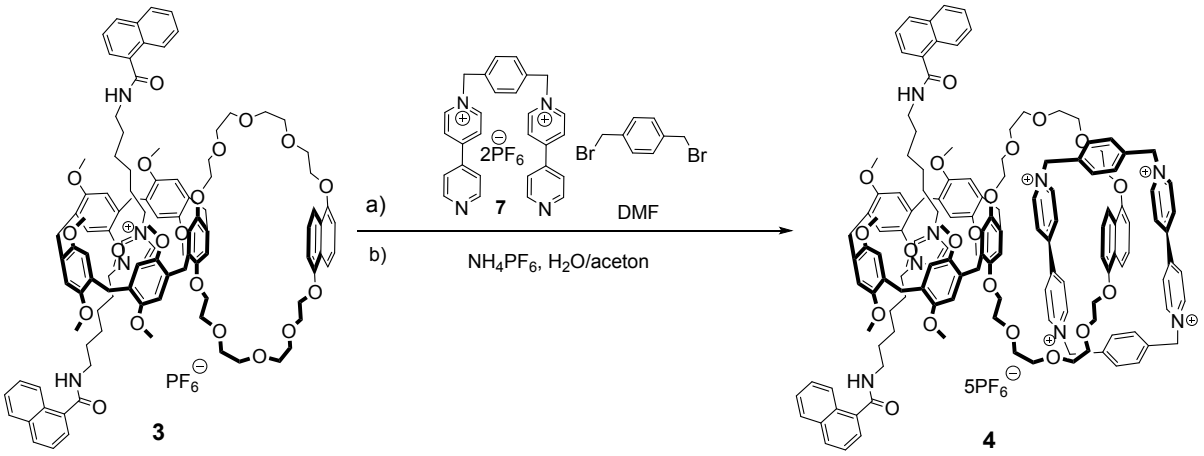
Compound **1** and **7** were prepared as previously reported.[S2]

[2]Catenane (3): A solution of host **1** (30.0 mg 0.025 mmol), **7** (9.5 mg, 0.025 mmol) and 1,4-di(bromomethyl)benzene (7mg, 0.025 mmol) in DMF (10 mL) was stirred at room temperature for 3 days, and concentrated under reduced pressure to result in a residue which was washed with $CHCl_3$ (10 mL) and then H_2O (10 mL). The resulting solid product was dissolved a mixed solvent of acetone and H_2O (2/:1, v/v, 3.0 mL), followed by addition of NH_4PF_6 (30.0 mg, 0.18 mmol). The mixture was stirred at room temperature for 5 h, and concentrated under reduced pressure to result in a red solid crude product which was recrystallized to afford pure product **3** (40.0 mg, 70%). ^{1}H NMR (400 MHz, CD_3CN) δ 9.03 (s, 1H), 8.88 (d, *J* = 5.1 Hz, 2H), 8.64 (d, *J* = 6.3 Hz, 2H), 8.56 (d, *J* = 6.3 Hz, 2H), 8.11 (m, 4H), 7.98 (m, 4H), 7.39-6.98 (m, 8H), 6.84 (m, 6H), 6.61 (s, 2H), 6.22 (d, 2H), 6.05 (s, 2H), 6.02-5.86 (m, 4H), 5.86-5.61 (m, 6H), 4.18 (m, 12H), 3.90 (m, 12H), 3.77-3.58 (m, 34H), 3.48-3.28 (m, 4H), 3.16 (m, 4H), 2.43 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, CD_3CN) δ 152.13, 151.08, 151.06, 150.99, 150.92, 149.14, 145.60, 145.25, 145.10, 144.59, 137.70, 137.66, 132.64, 132.29, 132.20, 132.01, 129.66, 129.56, 129.34, 128.80, 128.57, 126.51,

125.65, 125.49, 125.36, 124.85, 114.60, 114.05, 114.00, 113.94, 113.62, 109.27, 104.97, 72.30, 71.73, 71.55, 70.87, 70.84, 70.78, 69.17, 68.37, 66.05, 66.01, 56.30, 56.25, 56.21, 56.08, 29.77, 29.60, 29.52. MS (ESI): *m/z* calcd [M-4PF_6^-] $C_{105}H_{114}N4O_{18}^{4+}$: 429.7; Found: 429.4.

Crystallographic Data of 3: [$C_{105}H_{113}N_4O_{18}F_{27}P_{4.5}$]; *Mr* = 2371.36; T = 173 (2) K; triclinic; space group $P\bar{1}$; *a* = 14.1777(6); *b* = 20.5414(9); *c* = 24.6430(10) Å; α = 71.1160(10); β = 78.710(2); γ = 76.663(2); *V* = 6549.9(5) Å^3; Z = 2; ρ_{calcd} = 1.202 g/cm^3; crystal size = 0.42 x 0.18 x 0.15 mm; μ = 0.158 mm^{-1}; reflections collected 76514; unique reflections 22945; data/restraints/parameters 22945/0/1429; *GOF* on F^2 0.982; R_{int} for independent data 0.0698; final R_1 = 0.1070, wR_2 = 0.2908; R indices (all data) R_1 = 0.1707, wR_2 = 0.3280; largest diff. peak and hole: 0.826 and -0.772 eÅ^{-3}.

Synthesis of 4



[3]Rotacatenane (4): A solution of **2** (57.0 mg 0.03 mmol), **G3** (11.0 mg, 0.03 mmol) and 1,4-di(bromomethyl)benzene **6** (8.0 mg, 0.03 mmol) in DMF (30 mL) was stirred at room temperature for 20 days, and concentrated under reduced pressure to result in a residue which was washed with $CHCl_3$ (10 mL) and then H_2O (10 mL), The resulting solid product was dissolved a mixed solvent of acetone and H_2O (2/:1, v/v, 3.0 mL), followed by addition of

NH_4PF_6 (30.0 mg, 0.18 mmol). The mixture was stirred at room temperature for 20 h, and concentrated under reduced pressure to result in a crude which was recrystallized to afford pure product **4** (23.0 mg, 25%). ^{1}H NMR (400 MHz, CD_3CN) δ 9.07 (d, *J* = 5.9 Hz, 2H), 8.82 (d, *J* = 6.5 Hz, 2H), 8.54 (m, 4H), 8.36-8.23 (m, 2H), 8.13-7.98 (m, 8H), 7.85 (m, 4H), 7.69-7.57 (m, 8H), 7.23 (d, *J* = 4.8 Hz, 2H), 7.19 (s, 1H), 7.15 (d, *J* = 4.9 Hz, 2H), 7.06 (m, 4H), 6.98 (t, *J* = 5.5 Hz, 2H), 6.91-6.79 (m, 6H), 6.63 (s, 2H), 6.52 (d, *J* = 1.4 Hz, 2H), 6.13 (d, *J* = 7.9 Hz, 2H), 6.09 (s, 2H), 5.91-5.80 (m, 4H), 5.80 – 5.60 (m, 6H), 4.22 (m, 6H), 4.12 – 4.03 (m, 4H), 4.00 (m, 2H), 3.89 (m, 4H), 3.80 (m, 4H), 3.79-3.74 (m, 4H), 3.74-3.73 (m, 2H), 3.72-3.63 (m, 32H), 3.60-3.56 (m, 2H), 3.38 (d, *J* = 12.3 Hz, 2H), 3.28 (m, 4H), 3.17 (d, *J* = 12.2 Hz, 2H), 2.80 (m, 2H), 2.35 (d, *J* = 8.2 Hz, 2H), 2.33-2.28 (m, 4H), 1.37-1.28 (m, 4H), 0.73 (m, 4H), 0.32 (m, 4H), 0.12 (m, 4H). ^{13}C NMR (101 MHz, CD_3CN) δ 170.09, 152.09, 151.77, 151.61, 151.50, 151.41, 149.48, 145.65, 145.60, 145.47, 145.20, 144.58, 137.61, 137.50, 136.06, 134.71, 133.97, 132.60, 132.25, 132.10, 131.94, 131.18, 131.07, 130.26, 130.21, 129.46, 129.22, 128.98, 127.88, 127.48, 126.58, 126.33, 126.11, 126.01, 125.63, 125.57, 125.24, 124.83, 122.41, 116.04, 115.78, 115.55, 114.62, 114.58, 109.19, 104.94, 72.18, 71.61, 71.07, 70.86, 70.67, 70.55, 70.50, 69.22, 68.56, 66.01, 57.67, 57.43, 57.40, 57.07, 49.50, 40.52, 30.67, 29.61, 29.52, 29.40, 29.04, 26.76, 26.67. MS (ESI): *m/z* calcd [M-$5PF_6^-$] $C_{142}H_{157}N_8O_{20}^{5+}$: 458.8; Found: 458.8.

Crystallographic Data of 4: [$C_{166}H_{205}N_8O_{26}F_{30}P_5$]; *Mr* = 3453.22; T = 173(2) K; T = 173(2) K; triclinic; space group $P\bar{1}$; *a* = 20.5486(17); *b* = 21.3959(19); *c* = 24.984(2) Å; *α* = 65.6220(10); *β* = 74.3130(10); *γ* = 66.014(2); *V* = 9071.2(13) Å^3; Z = 2; ρ_{calcd} = 1.264 g/cm^3; crystal size = 0.300 x 0.250 x 0.100 mm; *μ* = 0.146 mm^{-1}; reflections collected 63342; unique reflections 38333; data/restraints/parameters 38333/91/2071; *GOF* on F^2 1.027; R_{int} for independent data 0.0356; final R_1 = 0.1115, wR_2 = 0.3021; R indices (all data) R_1 = 0.1918, wR_2 = 0.3579; largest diff. peak and hole: 0.776 and -0.530 eÅ^{-3}.

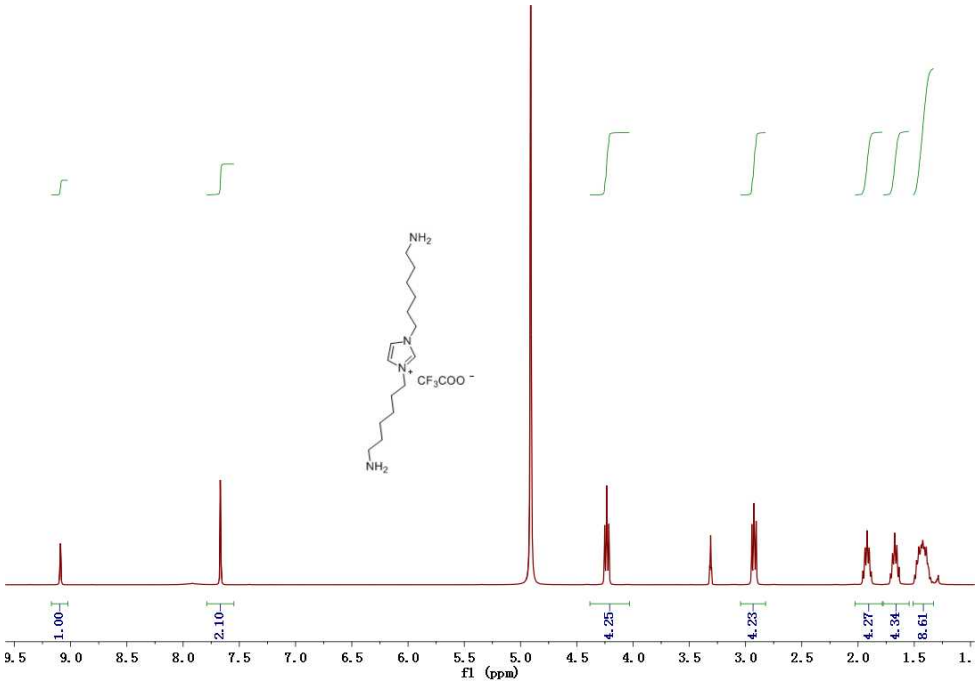


Fig. S1 ^{1}H NMR spectrum of **5** in CD_3CN

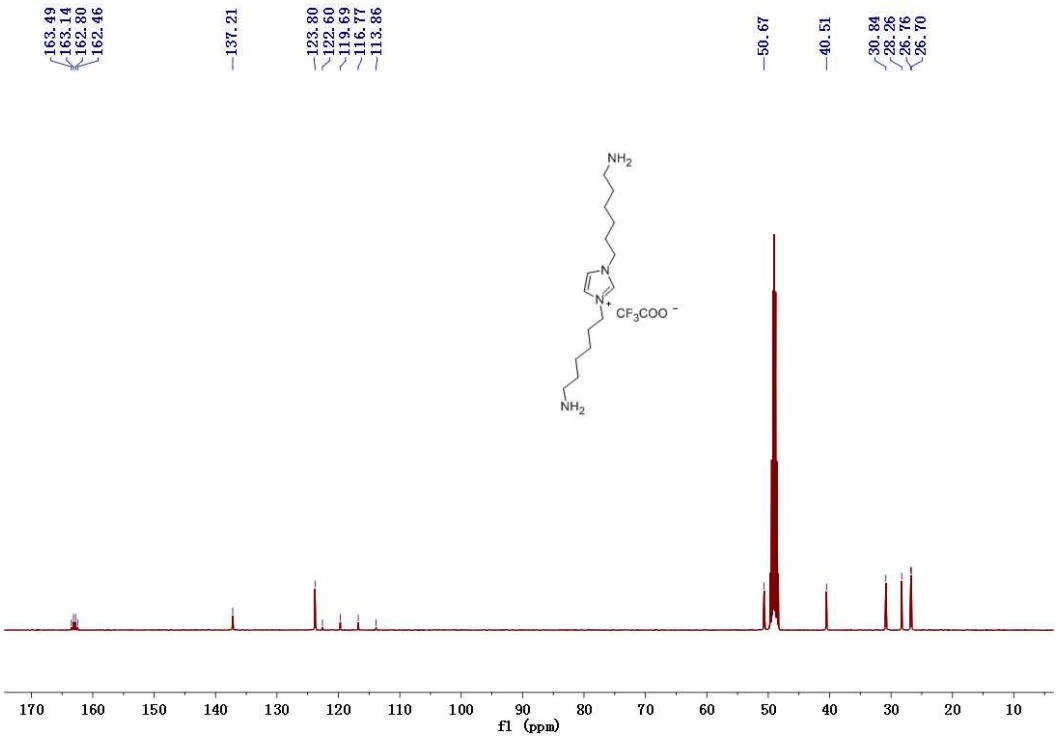


Fig. S2 ^{13}C NMR spectrum of **5** in CD_3OD

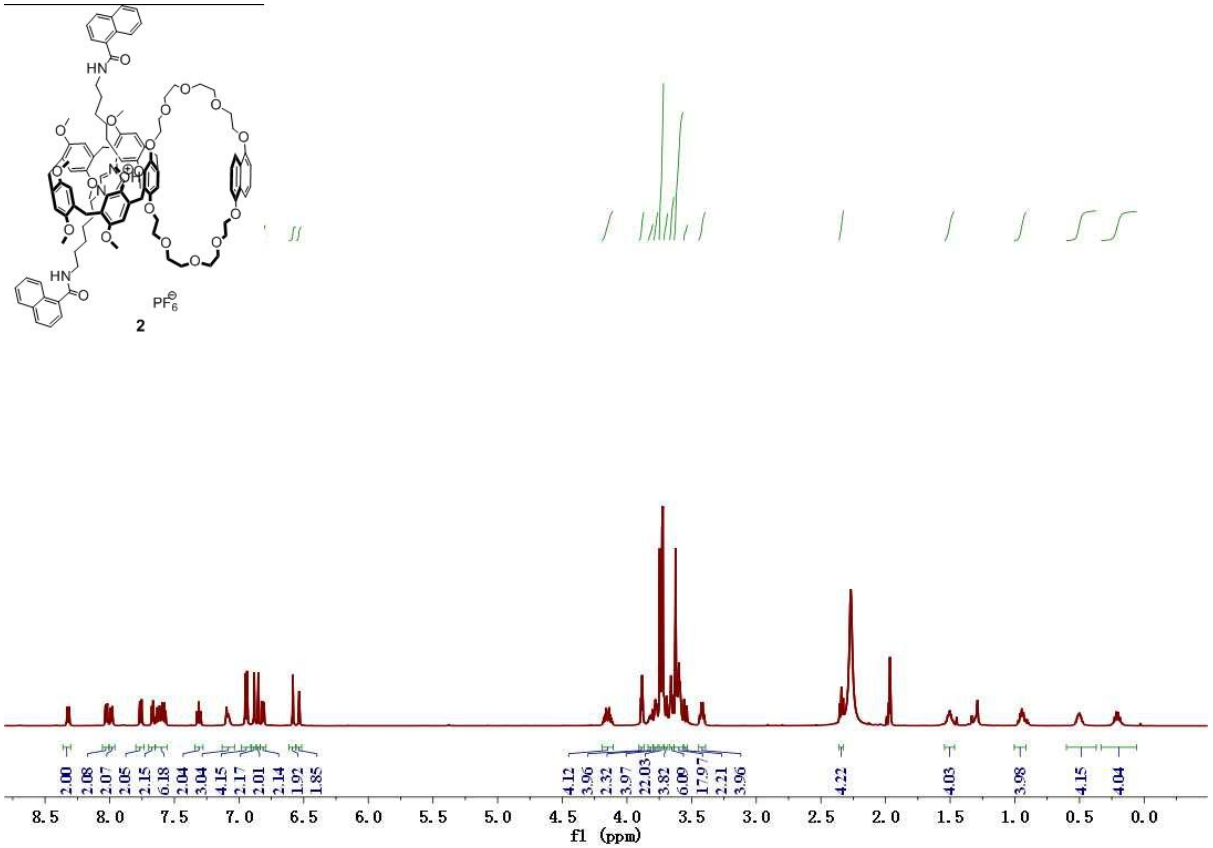


Fig. S3 ^{1}H NMR spectrum of [2]rotaxane **2** in CD_3CN

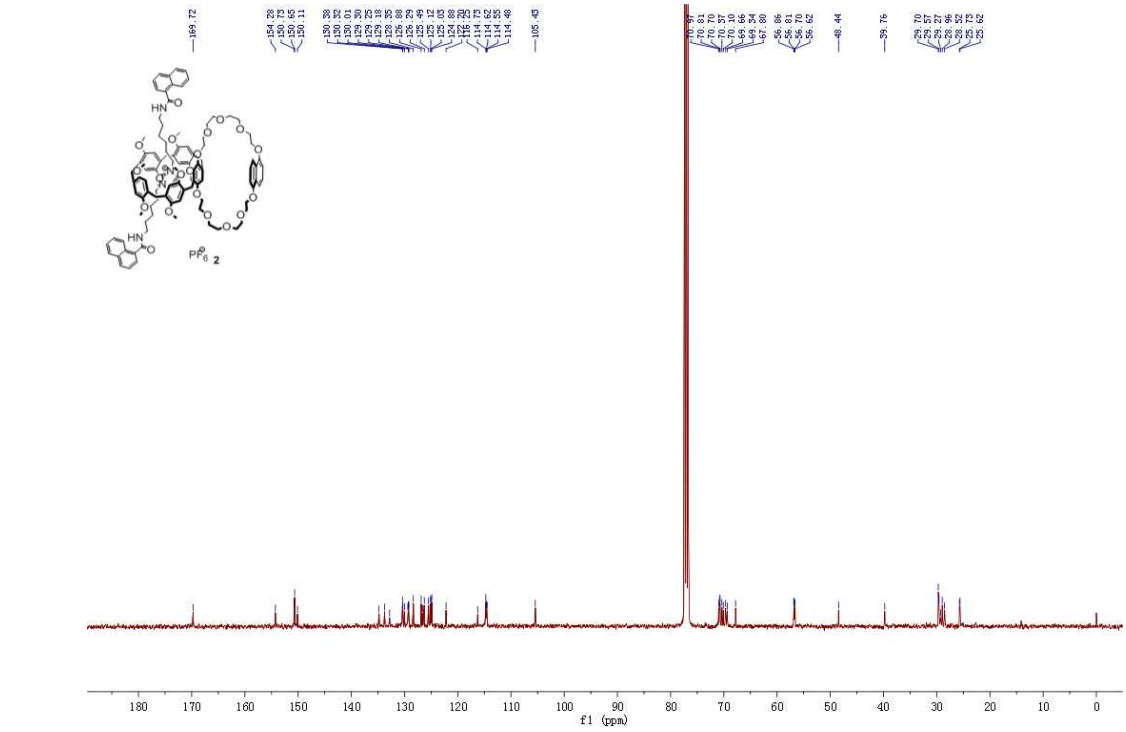


Fig. S4 ^{13}C NMR spectrum of [2]rotaxane **2** in $CDCl_3$

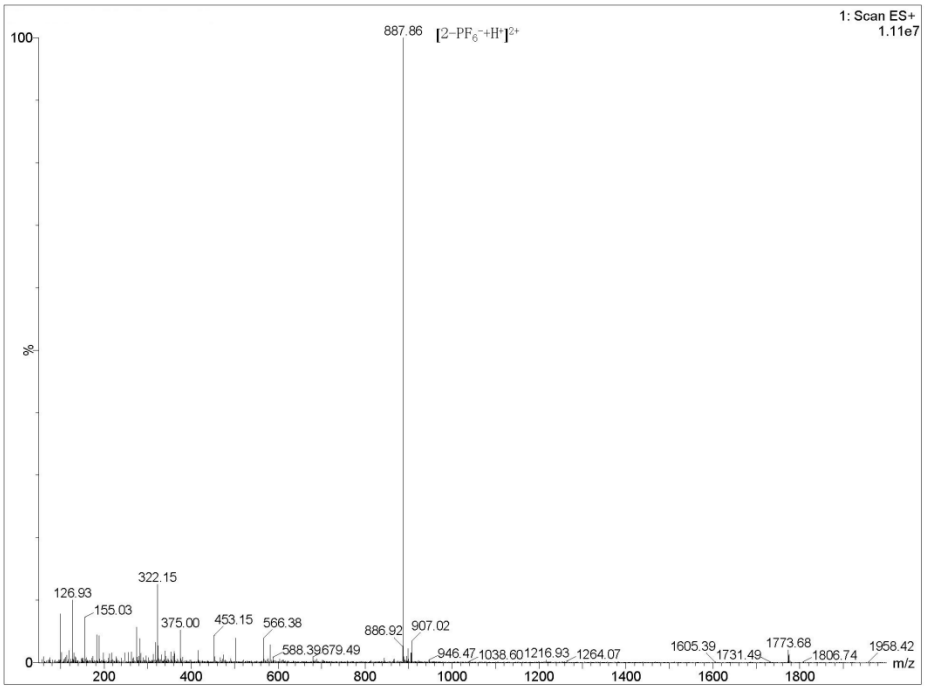


Fig. S5 Mass spectrum of [2]rotaxane **2**

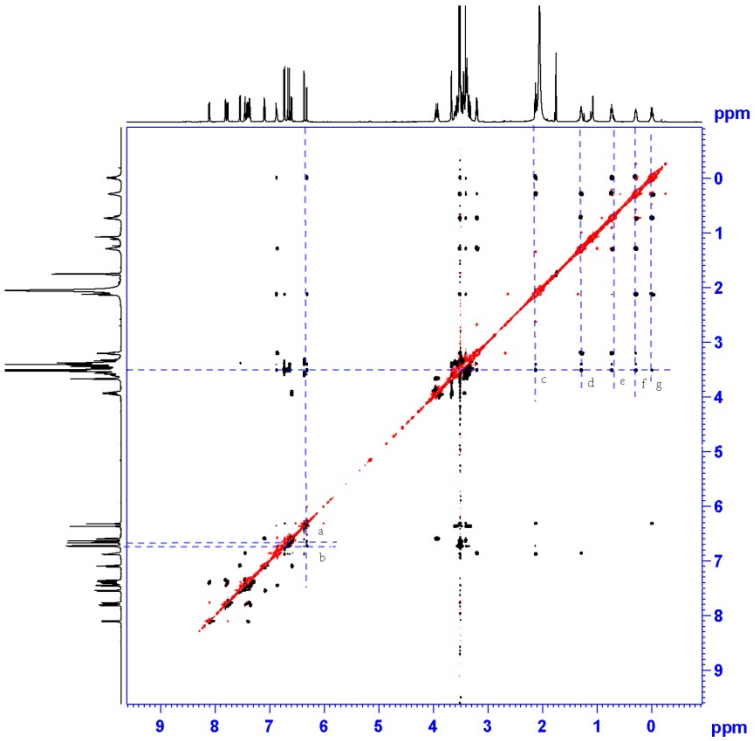


Fig. S 6 ^{1}H-^{1}H ROSY NMR Spectroscopy of [2]rotaxane **2** in CD_3CN

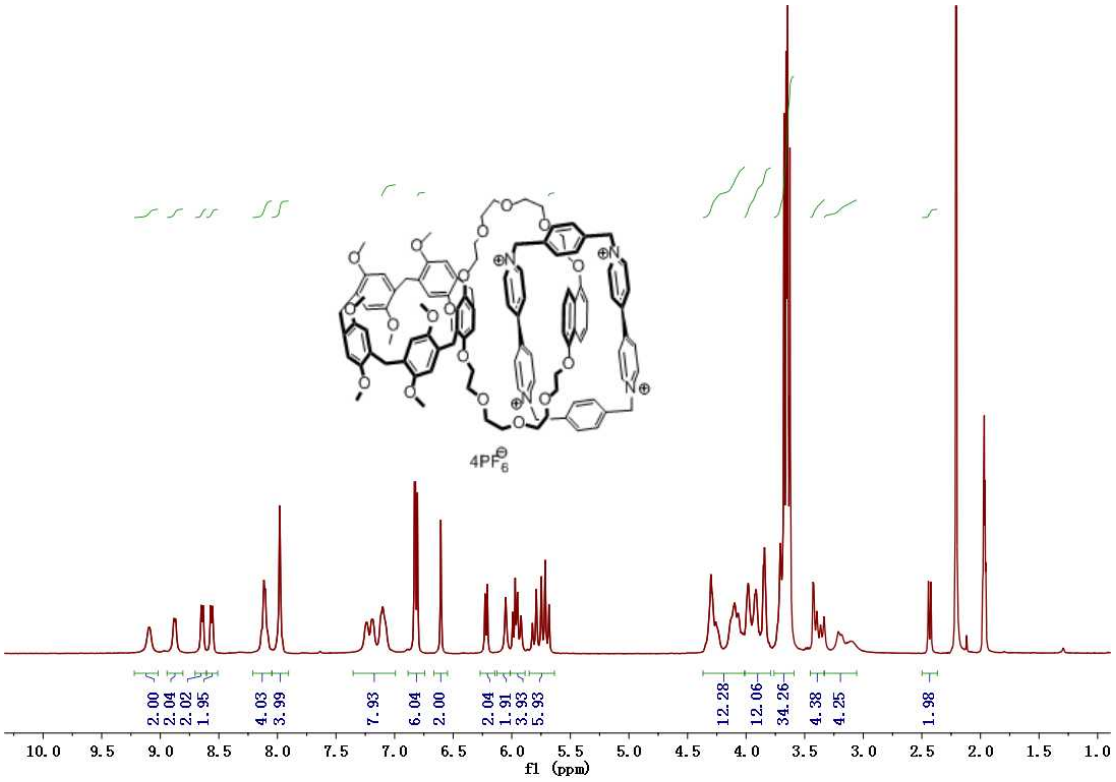


Fig. S7 ^{1}H NMR spectrum of [2]catenane **3** in CD_3CN

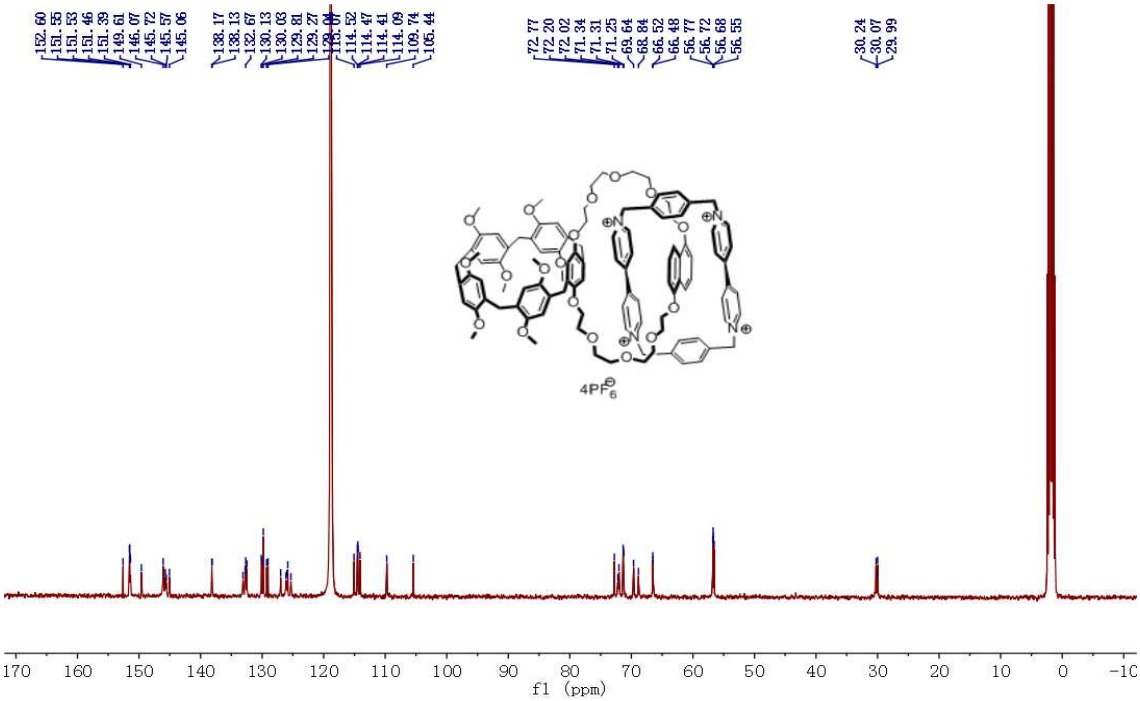


Fig. S8 ^{13}C NMR spectrum of [2]catenane **3** in CD_3CN

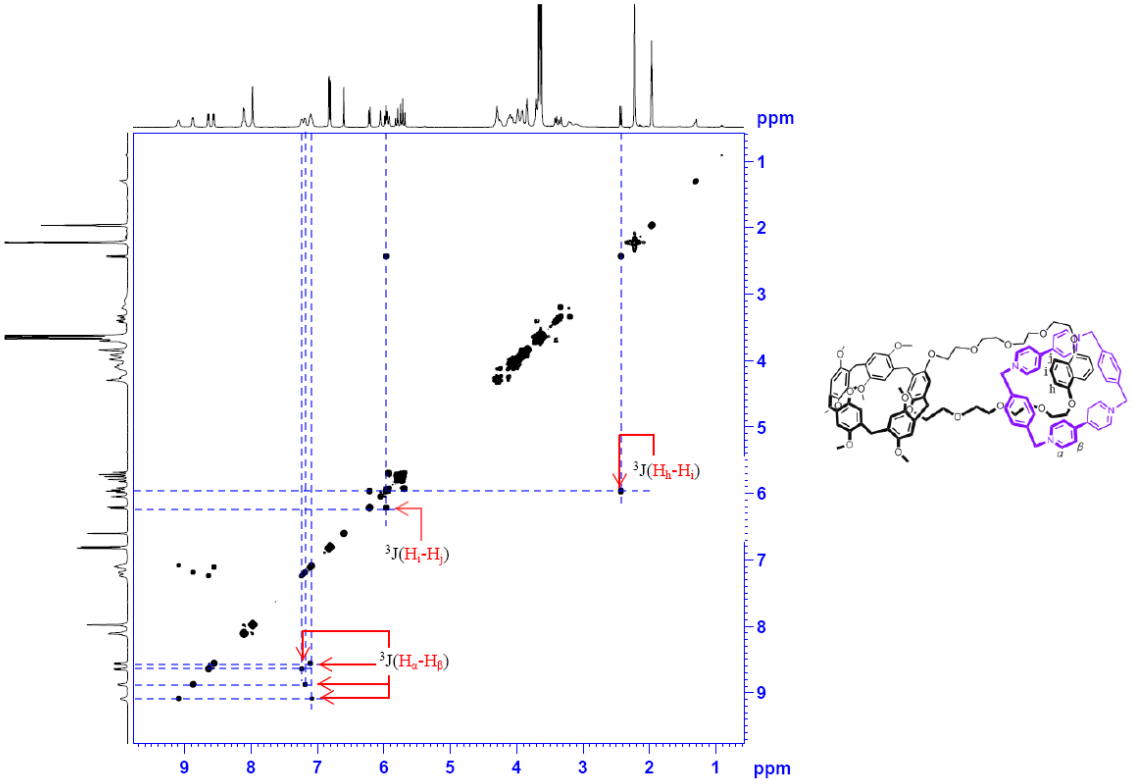


Fig. S9 ^{1}H-^{1}H COSY NMR Spectrum of [2]catenane **3** in CD_3CN

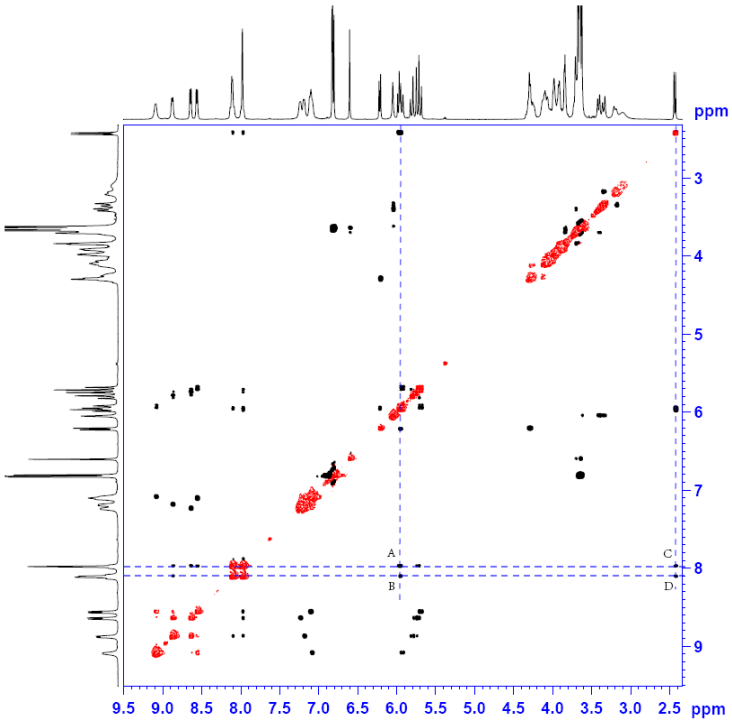


Fig. S10 ^{1}H-^{1}H NOESY NMR Spectrum of [2]catenane **3** in CD_3CN

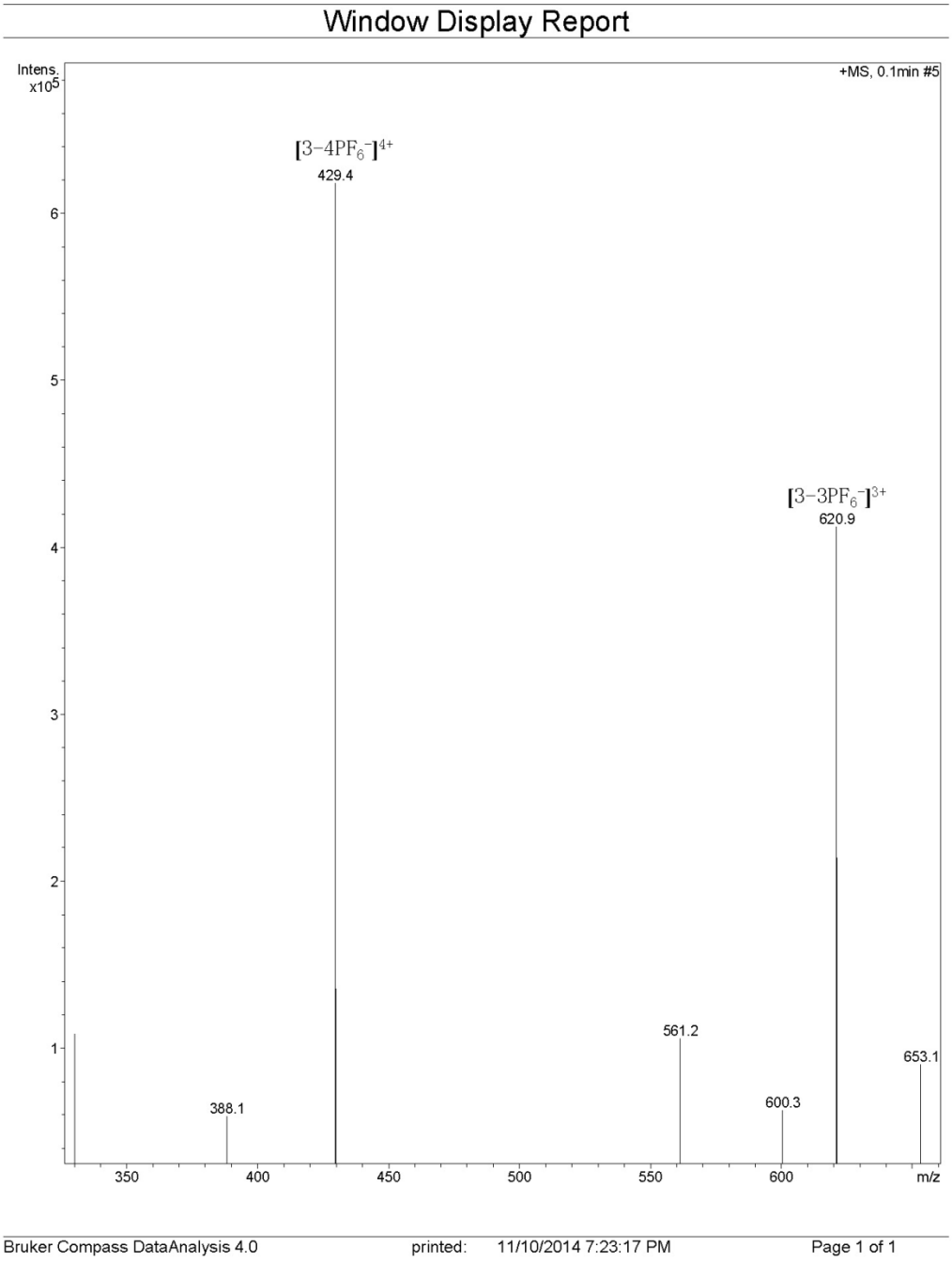


Fig. S11 Mass spectrum of [2]catenane **3**

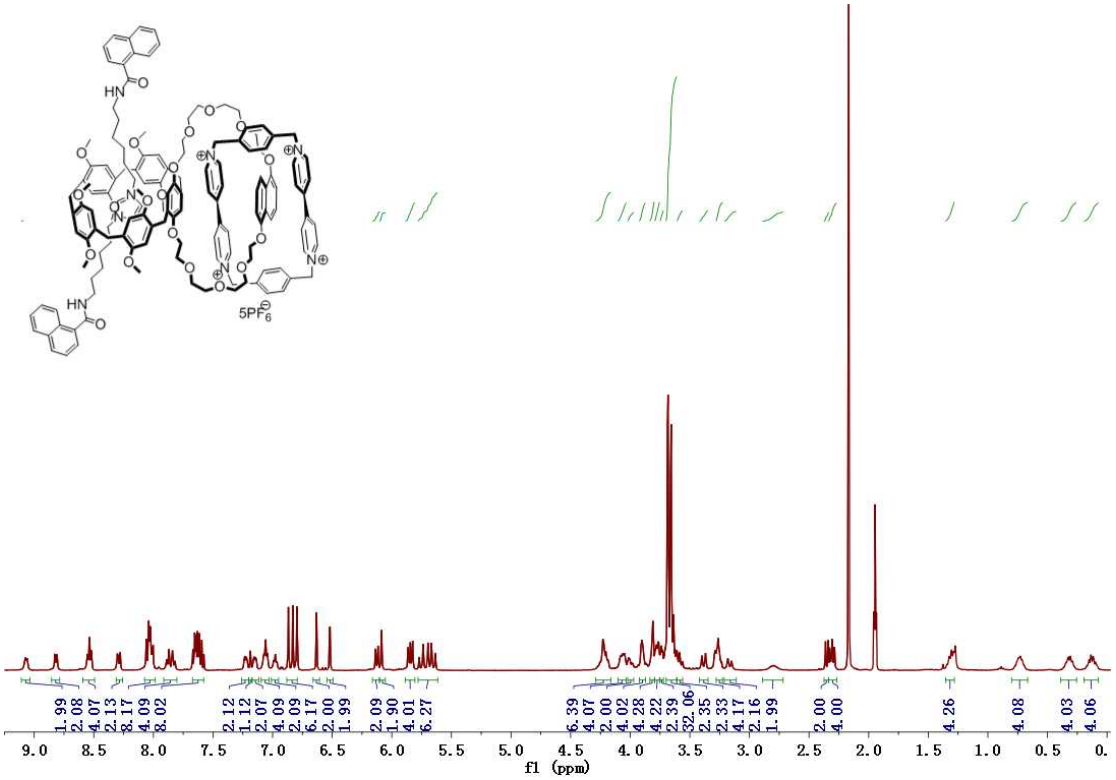


Fig. S12 ^{1}H NMR spectrum of [3]rotacatenane **4** in CD_3CN

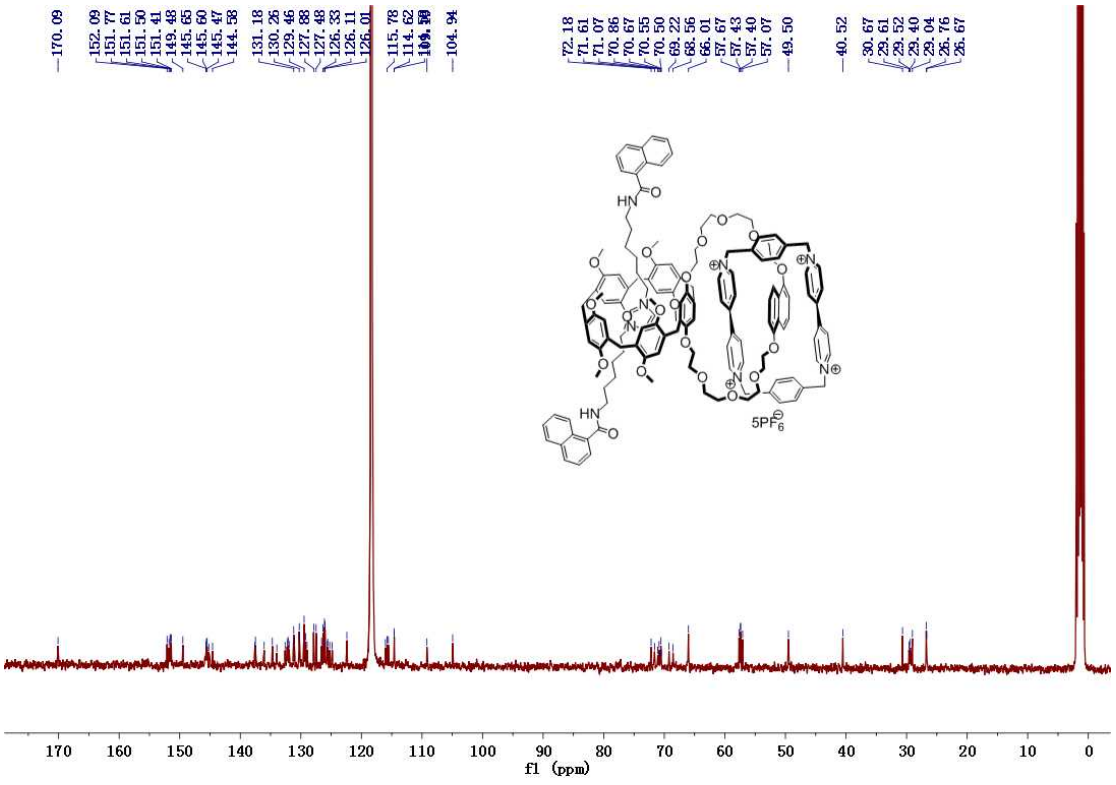


Fig. S13 ^{13}C NMR spectrum of [3]rotacatenane **4** in CD_3CN

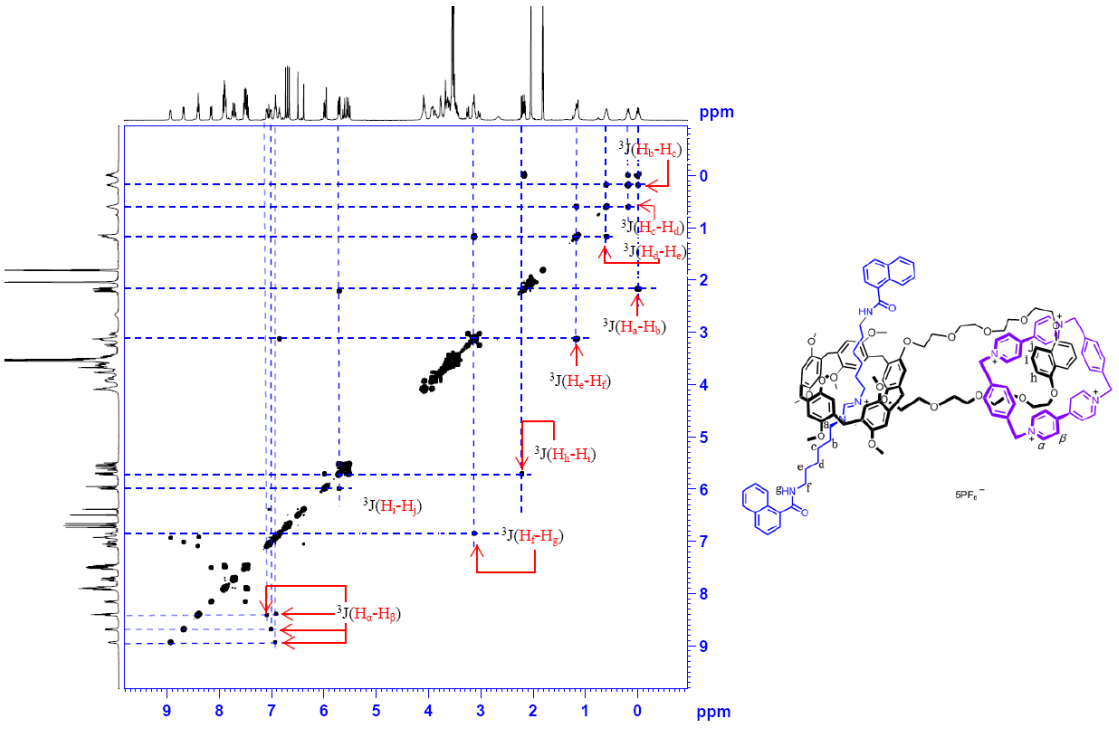


Fig. S14 ^{1}H-^{1}H COSY NMR Spectrum of [3]rotacatenane **4** in CD_3CN

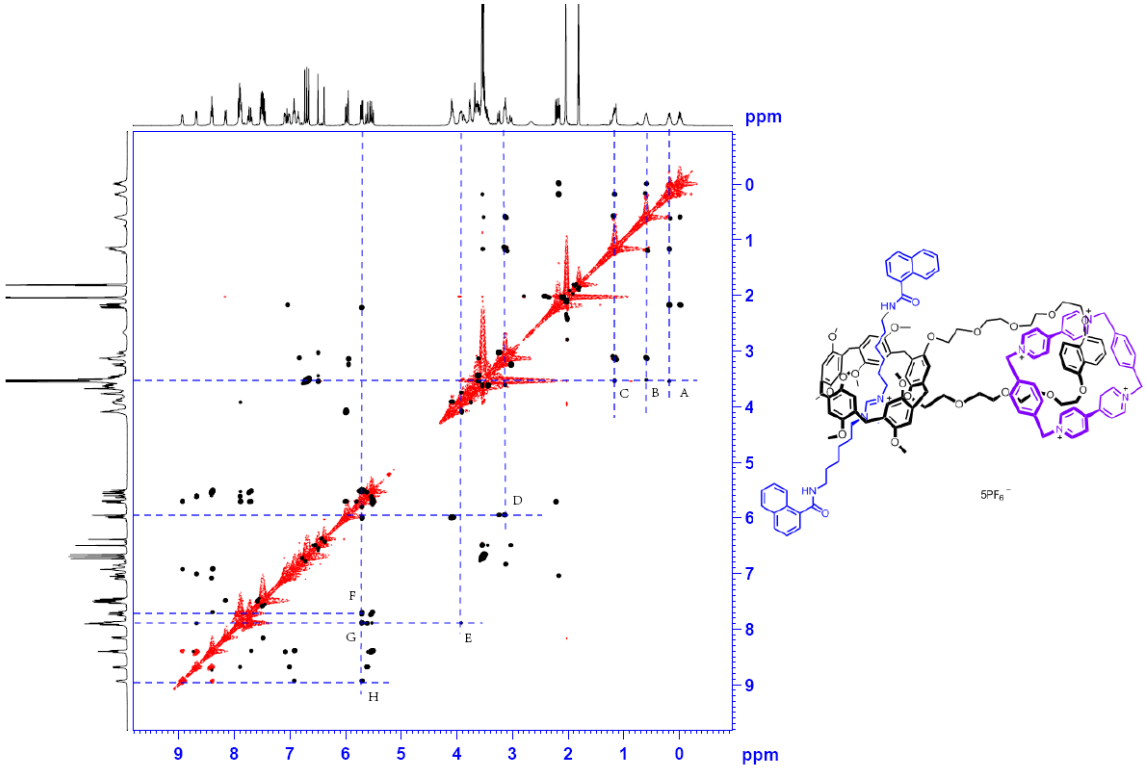


Fig. S15 ^{1}H-^{1}H ROSY NMR Spectroscopy of [3]rotacatenane **4** in CD_3CN

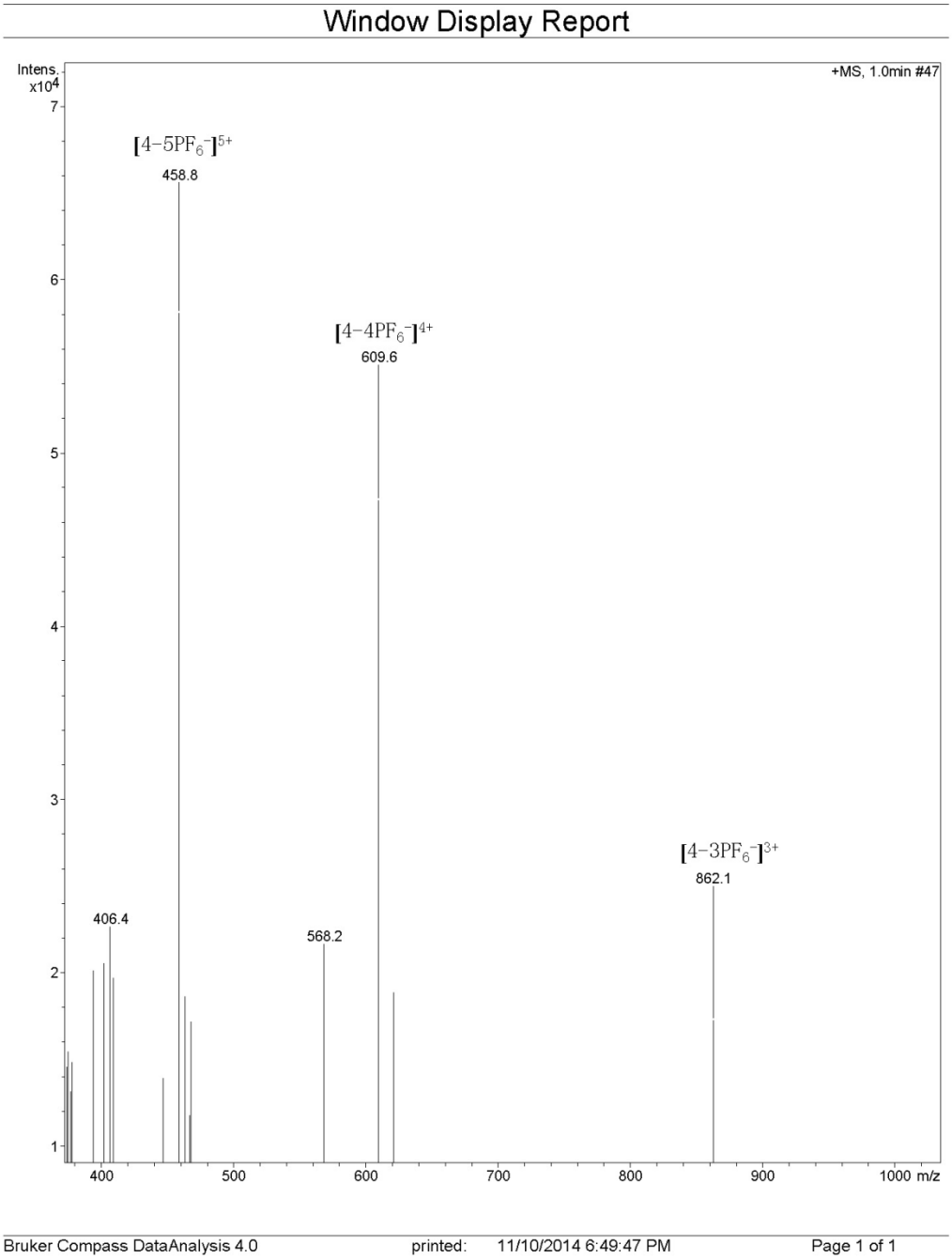


Fig. S16 Mass spectrum of [3]rotacatenane **4**

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S1 a) Hu, W.-B.; Yang, H.-M.; Hu, W.-J.; Ma, M.-L.; Zhao, X.-Li.; Mi, X.-Q.; Liu, Y. A.; Li, J.-S.; Jiang, B.; Wen, K. *Chem. Commun.* **2014**, *50*, 10460. b) Ogoshi, T.; Yamafuji, D.; Kotera, D.; Aoki, T.; Fujinami, S.; Yamagishi, T. *J. Org. Chem.* **2012**, *77*, 11146.

S2 a) Liu, H.; Li, X.-Y.; Zhao, X.-L.; Liu, Y. A.; Li, J.-S.; Jiang, B.; Wen, K. *Org. Lett*. **2014**, *16*, 5894. b) Tang, B.; Yang, H.-M.; Hu, W.-J.; Ma, M.-L.; Liu, Y. A.; Li, J.-S.; Jiang, B.; Wen, K. *Eur. J. Org. Chem.* **2014**, 6925.