Construction of Type III-C Rotaxane-Branched Dendrimers and Their Anion-Induced Dimension Modulation Feature

Xu-Qing Wang[†], Wei-Jian Li[†], Wei Wang[†*], Jin Wen[§], Ying Zhang[‡], Hongwei Tan[‡], Hai-Bo Yang[†*]

[†]Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, Chang-Kung Chuang Institute, East China Normal University, 3663 N. Zhongshan Road, Shanghai 200062, P. R. China

§ Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 16610 Prague 6, Czech Republic

[‡] Department of Chemistry, Beijing Normal University, Beijing, 100050, P.R. China

[*]To whom correspondence should be addressed:

E-mail: weiwang@stu.ecnu.edu.cn (W. Wang); hbyang@chem.ecnu.edu.cn (H.-B. Yang)

Table of Contents (62 Pages)

Section A. Materials and general methods

All reagents were commercially available and used as supplied without further purification, compounds **S_1**, **S_2**, **S_3** and **S_4** were prepared according to the published procedures.[S1-S3] Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA).

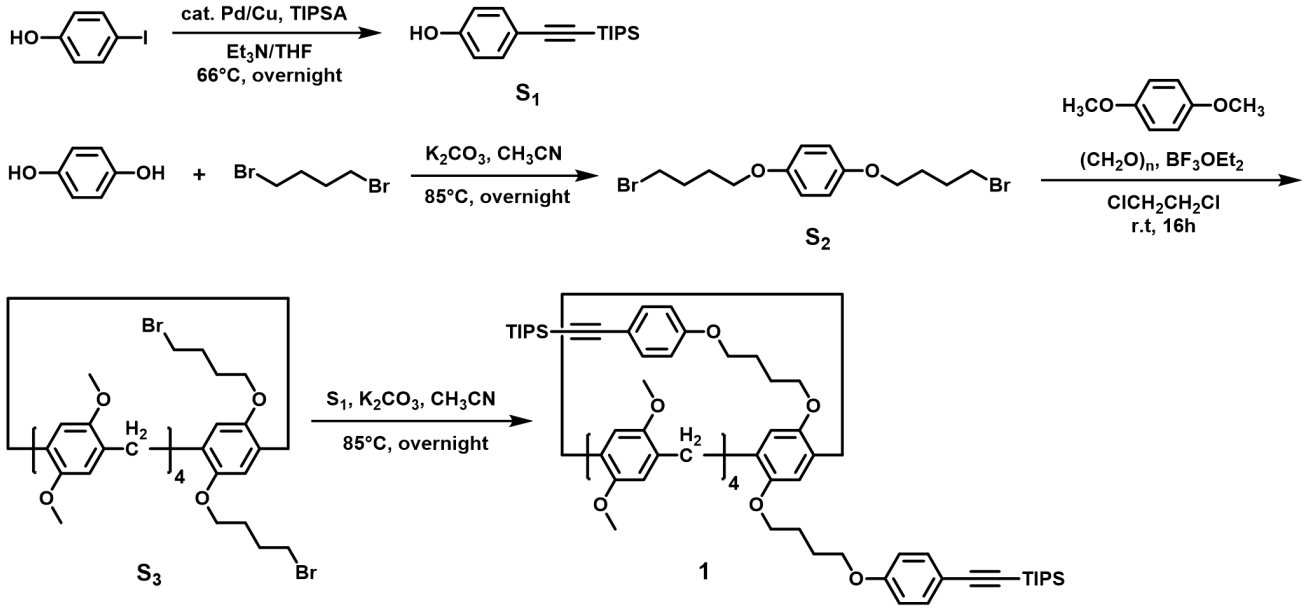
All solvents were dried according to standard procedures and all of them were degassed under N_2 for 30 minutes before use. All air-sensitive reactions were carried out under inert N_2 atmosphere. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Bruker 300 MHz Spectrometer (^{1}H: 300 MHz; ^{31}P: 122 MHz), Bruker 400 MHz Spectrometer (^{1}H: 400 MHz; ^{13}C: 101 MHz, ^{31}P: 162 MHz) and Bruker 500 MHz Spectrometer (^{1}H: 500 MHz; ^{13}C: 126 MHz, ^{31}P: 202 MHz) at 298 K. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P {^{1}H} NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). 2D NMR spectra (^{1}H-^{1}H COSY, ROESY and DOSY) were recorded on Bruker 500 MHz Spectrometer (^{1}H: 500 MHz) at 298 K. The MALDI MS experiments were carried out on a Bruker UltrafleXtreme MALDI TOF/TOF Mass Spectrometer (Bruker Daltonics, Billerica, MA), equipped with smartbeam-II laser. All spectra were measured in positive reflectron or linear mode. All the AFM images were obtained on a Dimension FastScan (Bruker), using ScanAsyst mode under ambient condition.

General procedure of preparing TEM samples: the solution of Type III-C rotaxane-branched dendrimers **G1-G4** in THF (c = 10^{-5} M) were prepared, the TEM samples were deposited on copper grids, followed by a slow evaporation in air at room temperature. TEM measurements were performed under a Tecnai G2 20 TWIN device.

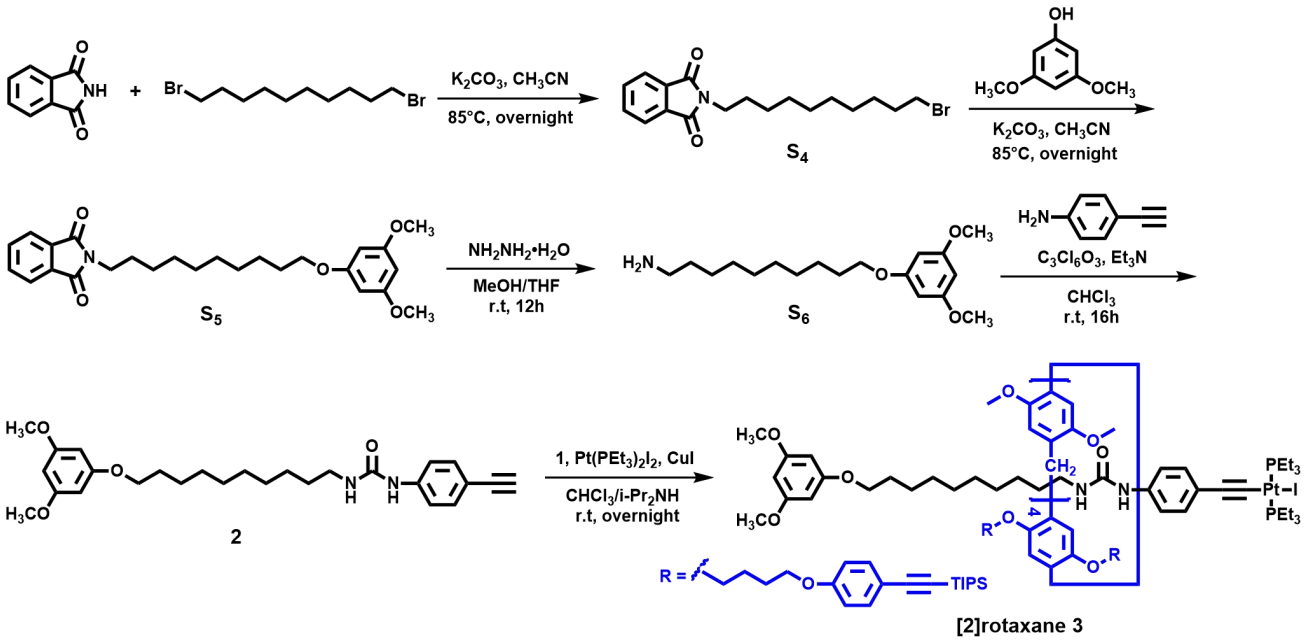
General procedure of preparing AFM samples: the solution of Type III-C rotaxane-branched dendrimers **G1-G4** in THF (c = 10^{-7} M) were prepared, the samples were prepared by drop casting method using mica sheet as substrate. The measurement was under ambient condition using ScanAsyst mode.

Section B. Synthesis and characterization of switchable building block [2]rotaxane.

Scheme S1: The synthesis route of macrocycle **1**.



Scheme S2: The synthesis route of [2]rotaxane **3**.



Synthesis of 1: Mixing compound **S3** (2 g, 2.05 mmol) and **S1** (1.4 g, 5.11 mmol) in acetonitrile (predried by Na_2SO_4, 100 mL), then K_2CO_3 (2.26 g, 16.36 mmol) was added into the reaction flask. The resultant suspension was refluxed at 85 °C overnight. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated in vacuum. The resultant residue was

purified by column chromatography (SiO_2; PE/DCM) to yield a white solid **1** (1.37g, 49.3%). Mp: 76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.43 (d, J = 12.0 Hz, 4H), 6.77-6.82 (m, 14H), 3.62-4.02 (m, 42H), 1.95- 1.98 (m, 8H), 1.14 (s, 42H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.00, 150.83, 150.81, 150.76, 150.69, 149.92, 133.44, 128.30, 128.25, 128.22, 128.09, 115.69, 114.94, 114.24, 114.19, 114.05, 113.91, 107.14, 88.60, 67.86, 67.50, 55.78, 55.75, 29.71, 29.63, 26.33, 26.12, 18.66, 11.34. MS (ESI-TOF): Calculated for [**1**+H]$^+$: 1379.75; Found: 1380.13.

Synthesis of S_5: Mixing compound **S_4** (9.96 g, 27.28 mmol) and commercial 3, 5-dimethoxyphenol (4.21 g, 27.28 mmol) in acetonitrile (pre-dried by Na_2SO_4, 200 mL), then K_2CO_3 (15.07 g, 109.12 mmol) was added into the reaction flask. The resultant suspension was refluxed at 85 °C overnight. After cooling to room temperature, the reaction mixture was filtered and the filtrate was concentrated in vacuum. The resultant residue was purified by column chromatography (SiO_2; PE/DCM) to yield a white solid **S_5** (8.46 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.85 (m, 2H), 7.69-7.72 (m, 2H), 6.07 (s, 3H), 3.88-3.92 (t, J = 6.0 Hz, 2H), 3.76 (s, 6H), 3.65-3.70 (t, J = 7.5 Hz, 2H), 1.67-1.79 (m, 4H), 1.29-1.42 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.41, 161.45, 161.03, 133.77, 132.17, 123.10, 93.37, 92.83, 68.01, 55.28, 55.26, 38.02, 29.40, 29.35, 29.28, 29.18, 29.10, 28.54, 26.80, 25.98. HRMS (EI-TOF): Calculated for [**S_5**]$^+$: 439.2359; Found: 439.2353.

Synthesis of 2: A $CHCl_3$ (20 mL) solution of triphosgene (425 mg, 1.43 mmol) was added into a Schlenk flask, the Schlenk flask was evacuated and back-filled with N_2 three times. Then a $CHCl_3$ (20 mL) solution of 4-ethynylbenzenamine (508 mg, 4.34 mmol) and triethylamine (2.4 mL) were added into the reaction flask and stirred at 0 °C. After 4 h, adding the $CHCl_3$ (20 mL) solution of **S_6** (1.34 g, 4.34 mmol) into the reaction flask, then the reaction mixture was allowed to warm to room temperature and stirred for 18 h. The solution was concentrated and the residue purified through chromatography (SiO_2; PE/acetone) to afford compound 2 as a pale-yellow solid (1.72 g, 87%). Mp: 111 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.03 (s, 1H), 7.49-7.51 (d, J = 6.0 Hz, 2H), 7.33-7.35 (d, J = 6.0 Hz, 2H), 6.07 (s, 3H), 5.83 (t, 1H), 3.92-3.95 (t, 2H), 3.74 (s, 6H), 3.49 (s, 1H), 3.17-3.22 (m, 2H), 1.72-1.75 (m, 2H), 1.29-1.52 (m, 14H). ^{13}C NMR (126 MHz, acetone-d_6): δ 162.68, 162.17, 155.78, 142.58, 133.41, 118.47, 115.52, 94.14, 93.60, 84.68, 77.52, 68.58, 55.60, 40.50, 31.08, 27.68, 26.87. HRMS (EI-TOF): Calculated for [**2**]$^+$: 452.2675; Found: 452.2679.

Synthesis of [2]rotaxane 3: A Schlenk flask was charged with macrocycle component **1** (1.5 g, 1.09 mmol), thread component **2** (98 mg, 0.22 mmol) and $Pt(PEt_3)_2I_2$ (596 mg, 0.87 mmol). The Schlenk flask was then evacuated and back-filled with N_2 three times. Next, the mixture solvent of degassed $CHCl_3$ and i-Pr_2NH (v/v, 6/3 mL) was added via syringe. The resultant solution was stirred for two

hours under -10 °C. Then a catalytic amount of CuI was added to the mixture under an inert atmosphere. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solution was concentrated and the residue was purified by column chromatography (SiO_2; PE/DCM). A white solid **3** (400 mg, 77%) was obtained. Mp: 86 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.21-7.41 (m, 9H), 6.81-7.00 (m, 14H), 6.09 (s, 3H), 3.71-4.07 (m, 50H), 2.81 (t, 1H), 2.18-2.28 (m, 12H), 1.96-2.07 (m, 8H), 1.61-1.68 (m, 4H), 1.14-1.23 (m, 60H), 0.89-1.08 (m, 6H), 0.59 (m, 2H), -0.18 (m, 2H), -1.70 (m, 2H), -1.97 (m, 2H). ^{31}P NMR (122 MHz, CD_2Cl_2): δ 8.91. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 162.11, 161.55, 159.76, 159.65, 154.36, 151.32, 151.12, 150.76, 150.70, 150.28, 150.21, 138.54, 133.81, 133.77, 131.42, 129.54, 129.20, 129.09, 129.03, 128.80, 128.74, 122.56, 119.33, 116.01, 115.89, 115.43, 114.82, 114.76, 113.66, 113.54, 107.65, 107.58, 100.17, 93.81, 92.90, 89.04, 88.94, 68.74, 68.51, 68.32, 68.21, 57.30, 56.85, 56.75, 55.70, 40.10, 31.45, 30.84, 30.48, 30.27, 29.86, 29.54, 27.13, 27.04, 26.86, 26.75, 26.53, 25.31, 18.90, 17.28, 17.11, 16.93, 11.83, 8.53. HRMS (MALDI-TOF-MS): Calculated for [**3**+H]$^+$: 2389.0668; Found: 2389.0732.

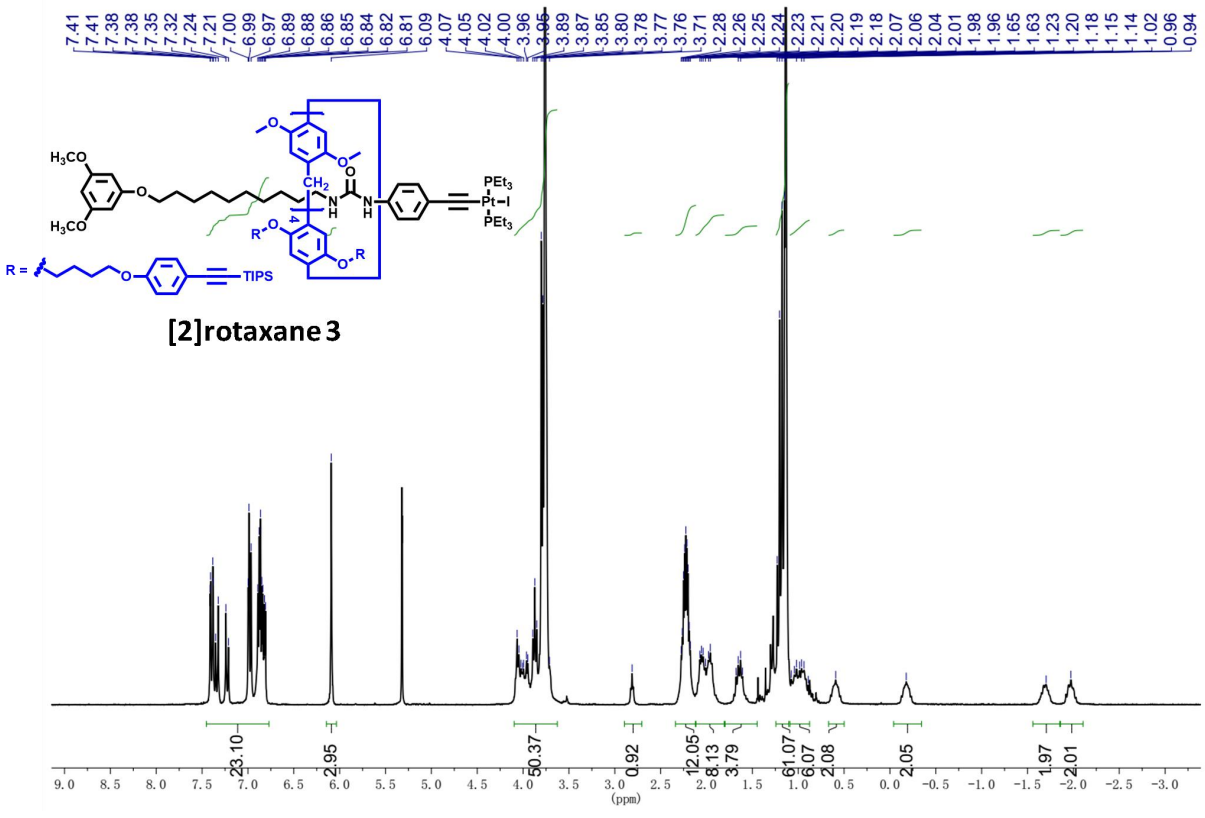


Fig. S1 ^{1}H NMR spectrum (CD_2Cl_2, 298 K, 300 MHz) of [2]rotaxane **3**.

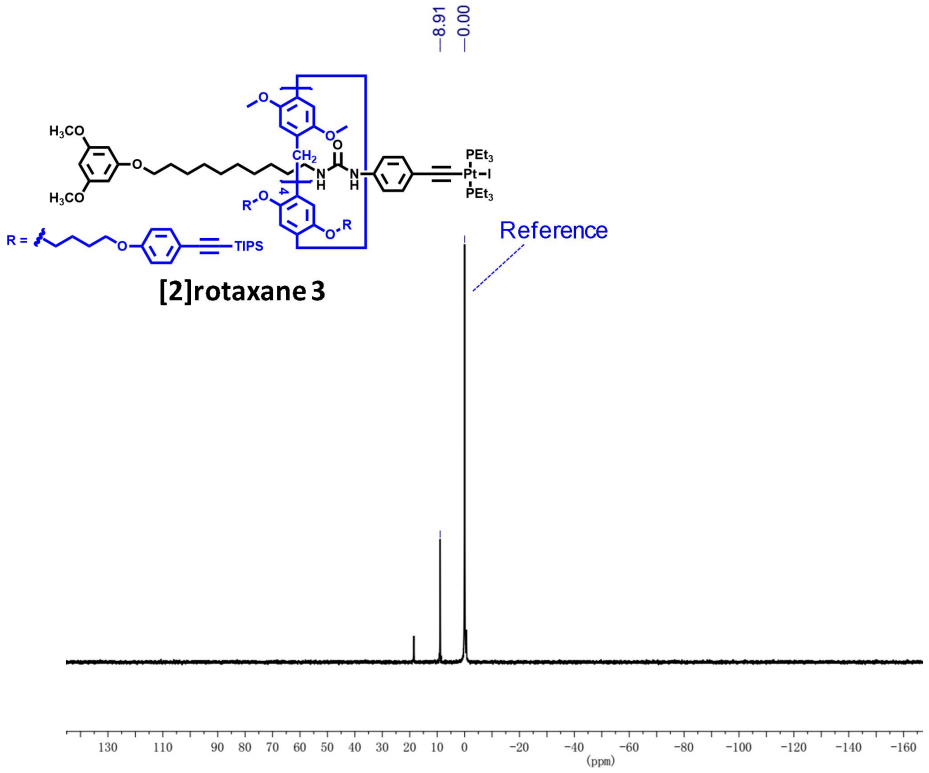


Fig. S2 ^{31}P NMR spectrum (CD_2Cl_2, 298 K, 122 MHz) of [2]rotaxane **3**.

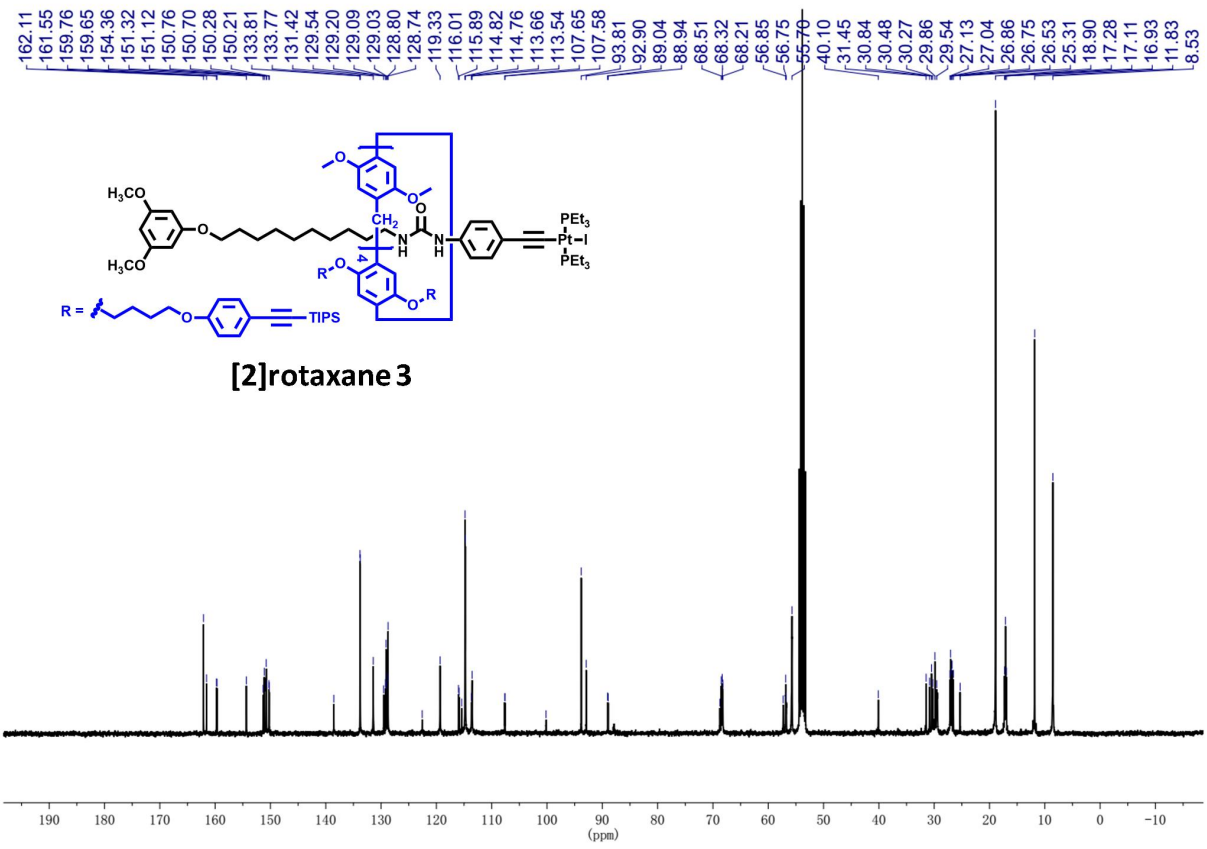
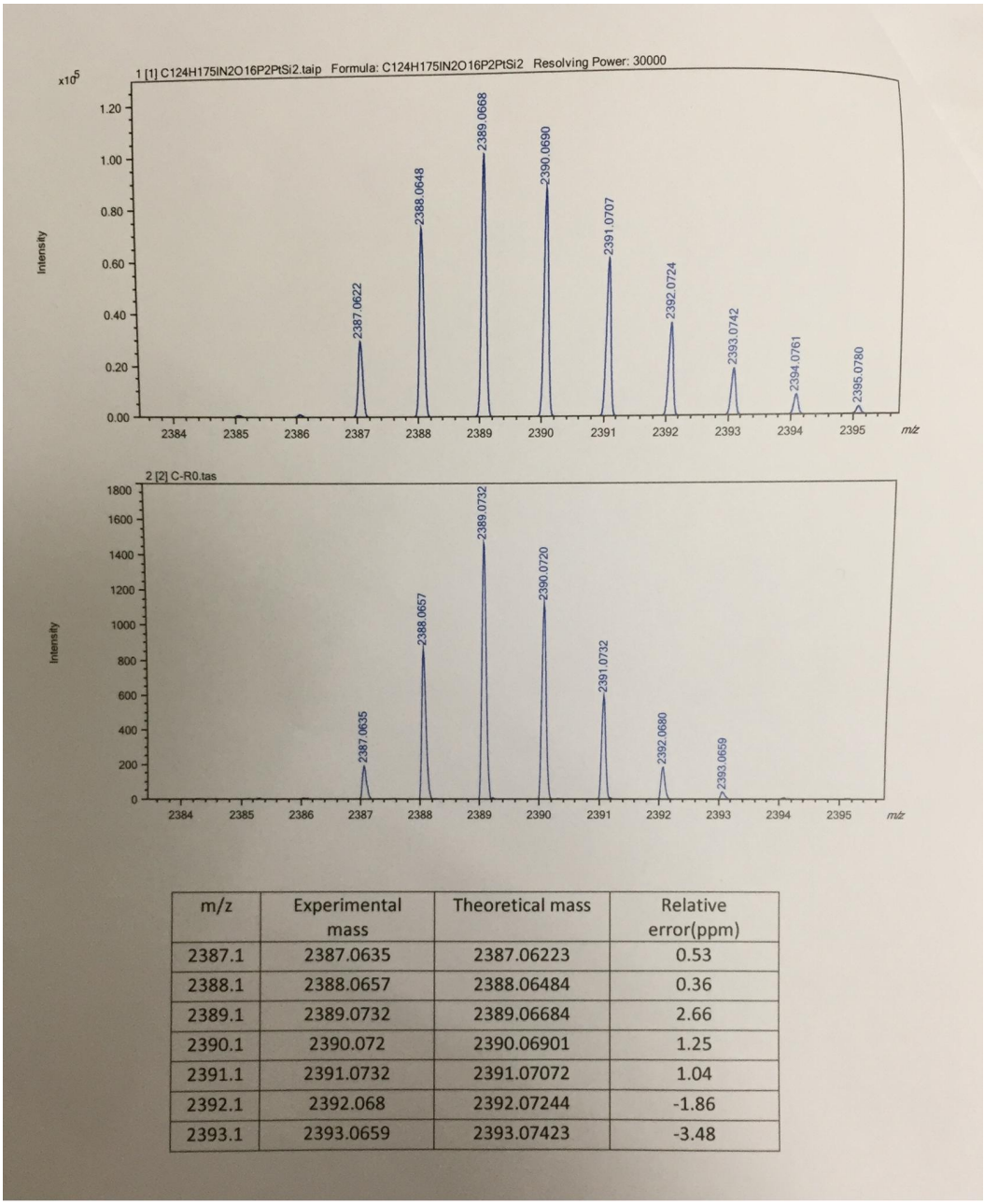


Fig. S3 ^{13}C NMR spectrum (CD_2Cl_2, 298 K, 101 MHz) of [2]rotaxane **3**.



m/z	Experimental mass	Theoretical mass	Relative error(ppm)
2387.1	2387.0635	2387.06223	0.53
2388.1	2388.0657	2388.06484	0.36
2389.1	2389.0732	2389.06684	2.66
2390.1	2390.072	2390.06901	1.25
2391.1	2391.0732	2391.07072	1.04
2392.1	2392.068	2392.07244	-1.86
2393.1	2393.0659	2393.07423	-3.48

Fig. S4 HRMS (MALDI-TOF-MS) spectrum of [2]rotaxane **3**.

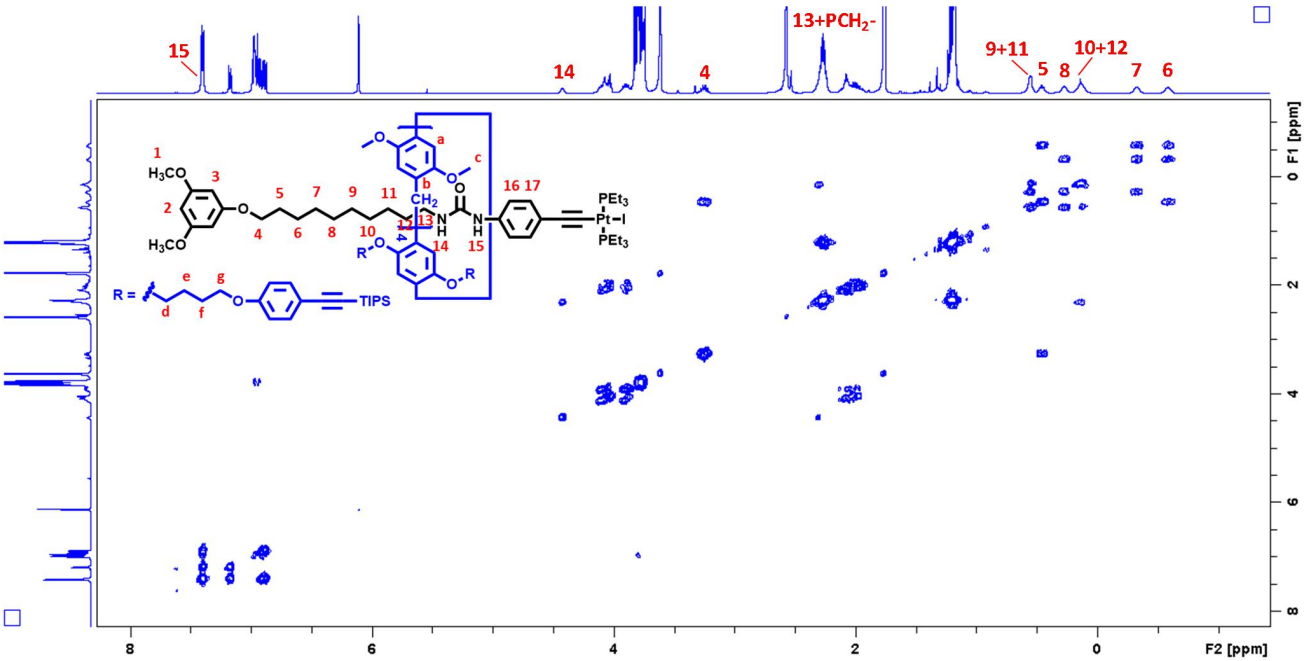


Fig. S5 2D ^{1}H-^{1}H COSY spectrum (THF-d_8, 298 K, 500 MHz) of [2]rotaxane **3**.

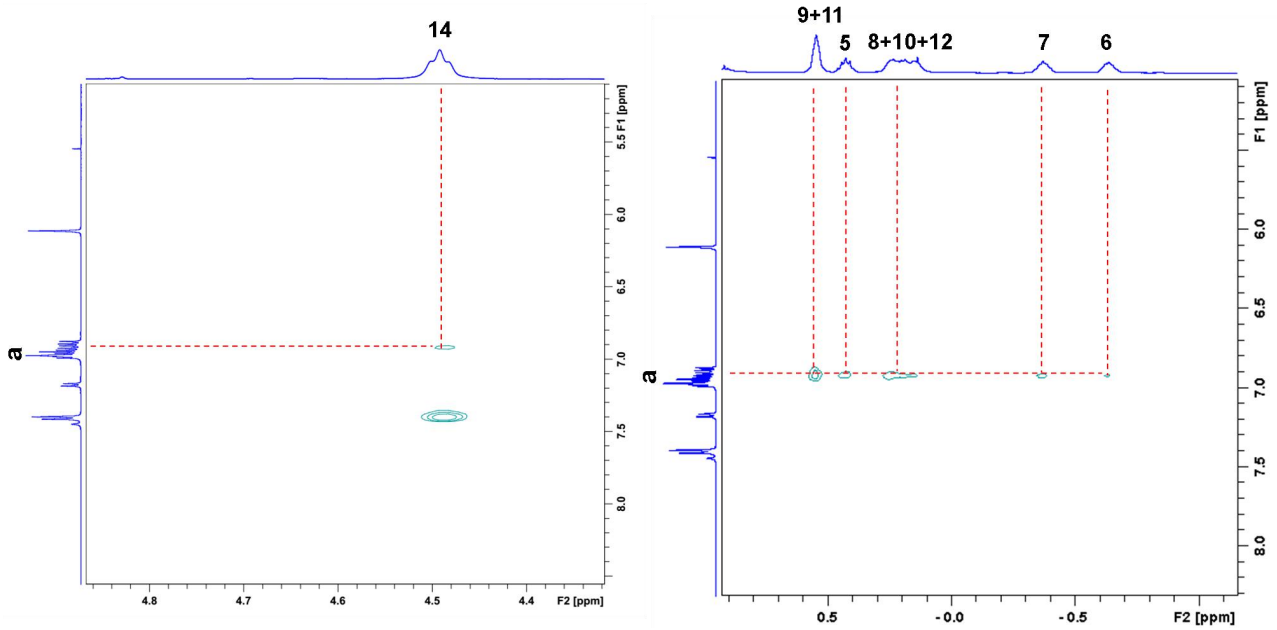


Fig. S6 2D ^{1}H-^{1}H ROESY spectrum (THF-d_8, 298 K, 500 MHz) of [2]rotaxane **3**.

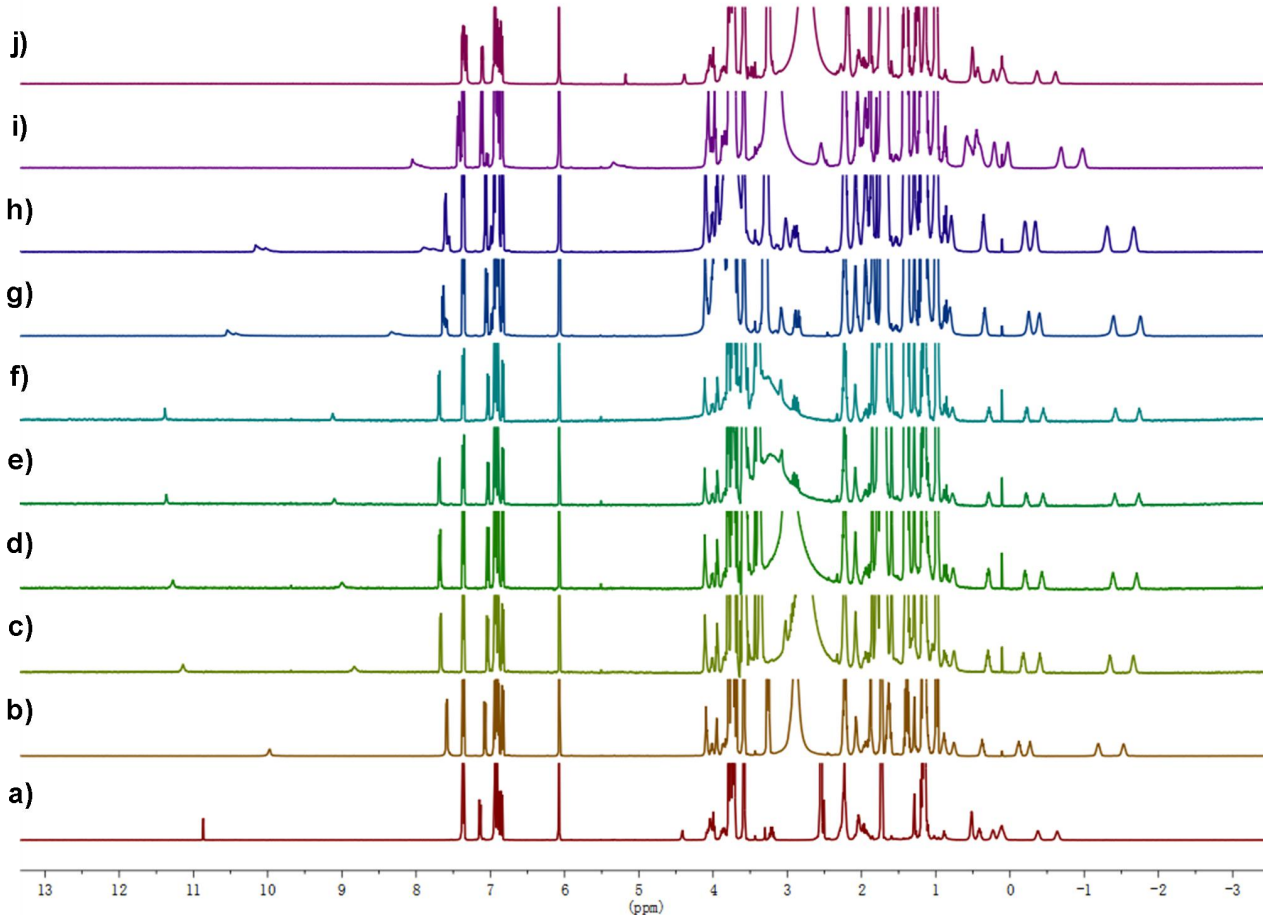


Fig. S7 Stacked ^{1}H NMR spectra (THF-d_8, 298 K, 500 MHz) of anion-induced switching behavior of [2]rotaxane **3**. a) **3**; the mixture of **3** and TBAA, for each rotaxane unit: b) TBAA (1 equiv); c) TBAA (2 equiv); d) TBAA (3 equiv); e) TBAA (4 equiv); f) TBAA (5 equiv); and the mixture obtained after adding $NaPF_6$ to the solution in f), for each rotaxane unit: g) $NaPF_6$ (5 equiv); h) $NaPF_6$ (6 equiv); i) $NaPF_6$ (8 equiv); j) $NaPF_6$ (10 equiv).

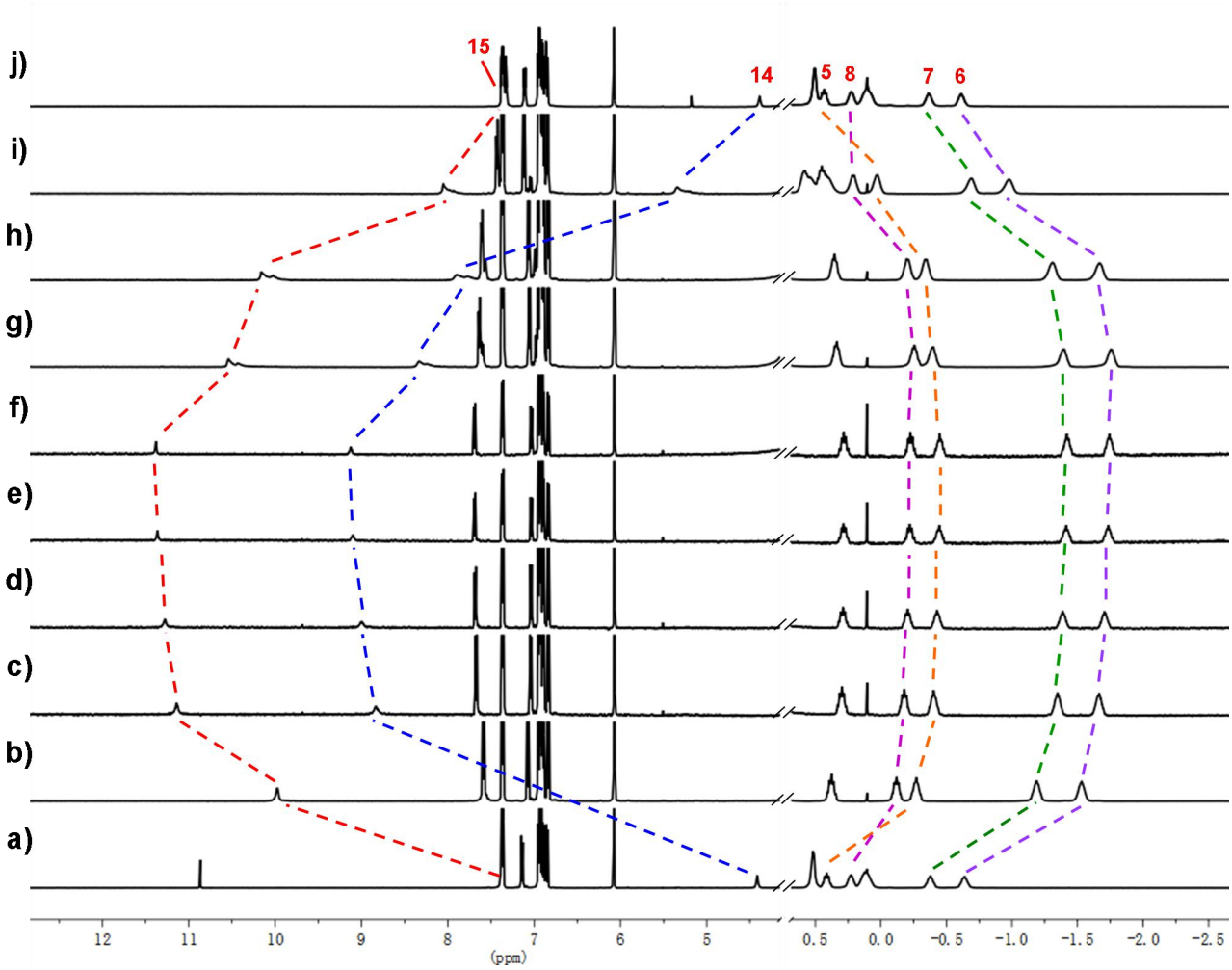


Fig. S8 Partial ^{1}H NMR spectra (THF-d_8, 298 K, 500 MHz) of anion-induced switching behavior of [2]rotaxane **3**. a) **3**; the mixture of **3** and TBAA, for each rotaxane unit: b) TBAA (1 equiv); c) TBAA (2 equiv); d) TBAA (3 equiv); e) TBAA (4 equiv); f) TBAA (5 equiv); and the mixture obtained after adding $NaPF_6$ to the solution in f), for each rotaxane unit: g) $NaPF_6$ (5 equiv); h) $NaPF_6$ (6 equiv); i) $NaPF_6$ (8 equiv); j) $NaPF_6$ (10 equiv).

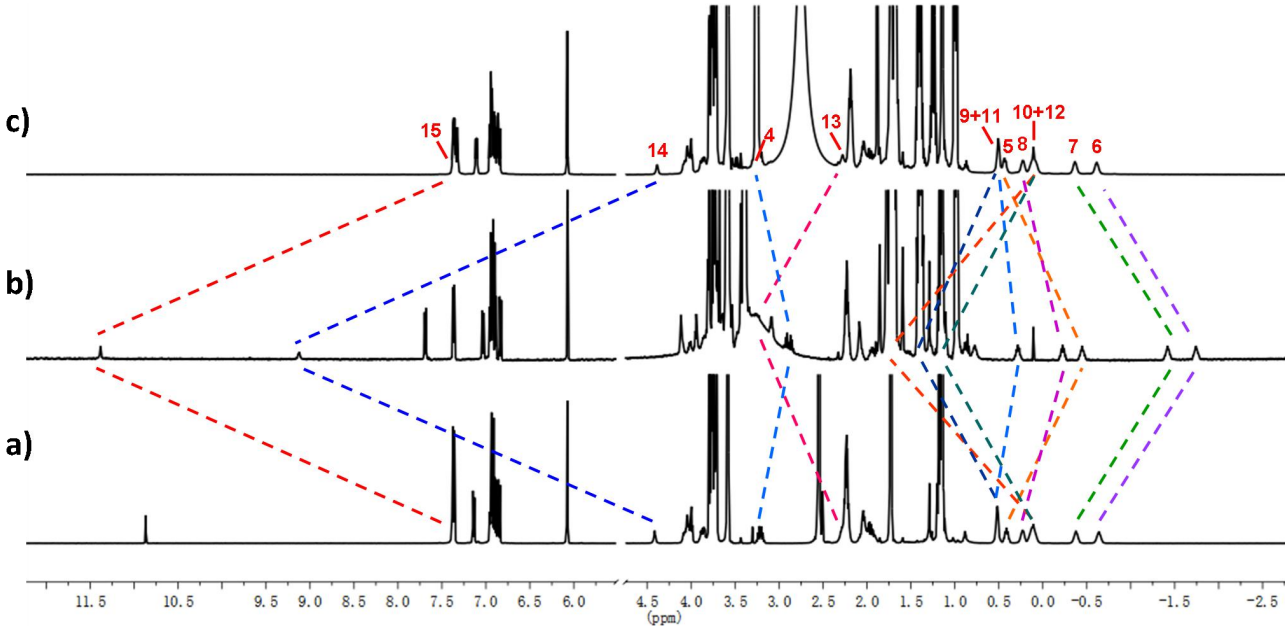


Fig. S9 ^{1}H NMR spectra (THF-d_8, 298 K, 500 MHz) of anion-induced switching behavior of [2]rotaxane **3**. a) [2]rotaxane **3**; b) **3** with the addition of TBAA (5 eq.); c) the mixture after adding $NaPF_6$ (10 eq.) into the solution in b).

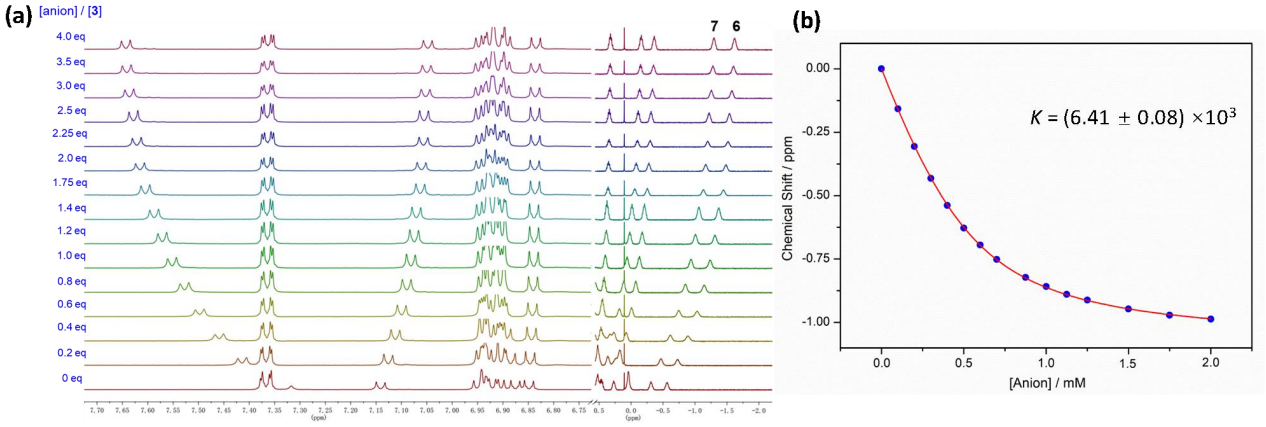


Fig. S10 (a) The expanded region of the ^{1}H NMR spectra (THF-d_8, 298 K, 500 MHz) of [2]rotaxane **3** (Host) with the addition of acetate anion (Guest); (b) The 1H NMR titration isotherm of [2]rotaxane **3** with the addition of acetate anion (TBAA) recorded at 500 MHz in THF-d_8 at 298 K.

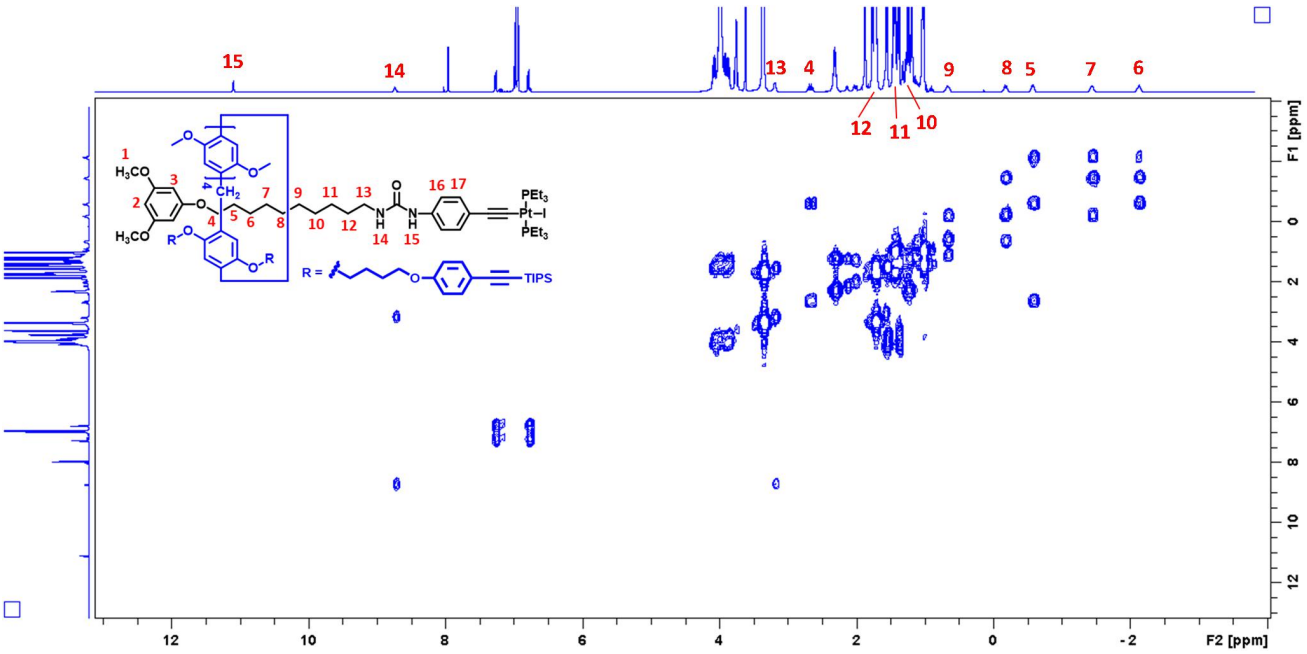


Fig. S11 2D ^{1}H-^{1}H COSY spectrum (THF-d_8, 298 K, 500 MHz) of [2]rotaxane **3** with the addition of TBAA (5 eq.).

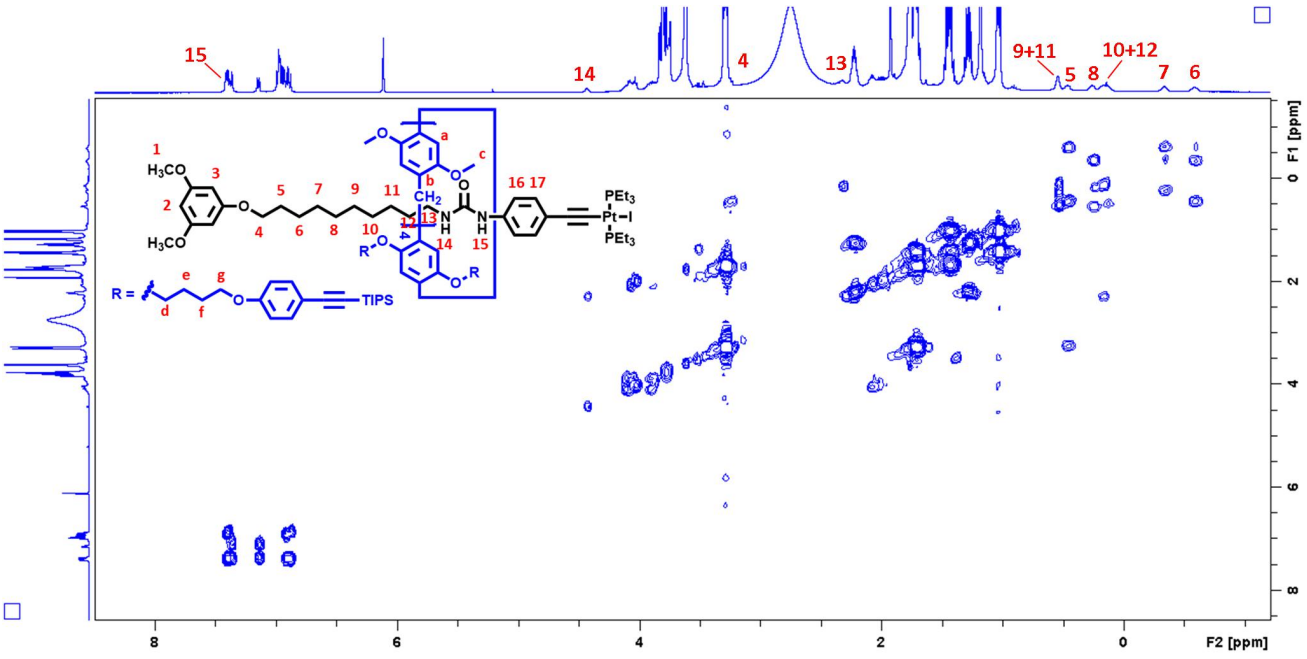


Fig. S12 2D ^{1}H-^{1}H COSY spectrum (THF-d_8, 298 K, 500 MHz) of the mixture after adding $NaPF_6$ (10 eq.) into the solution of [2]rotaxane **3** and TBAA.

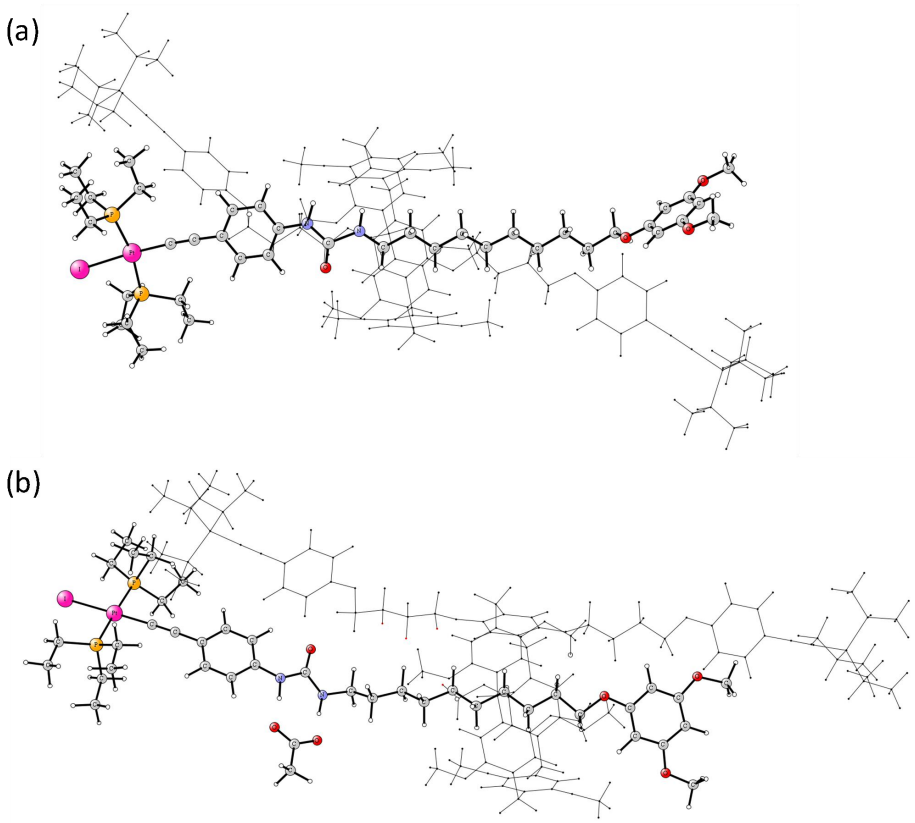
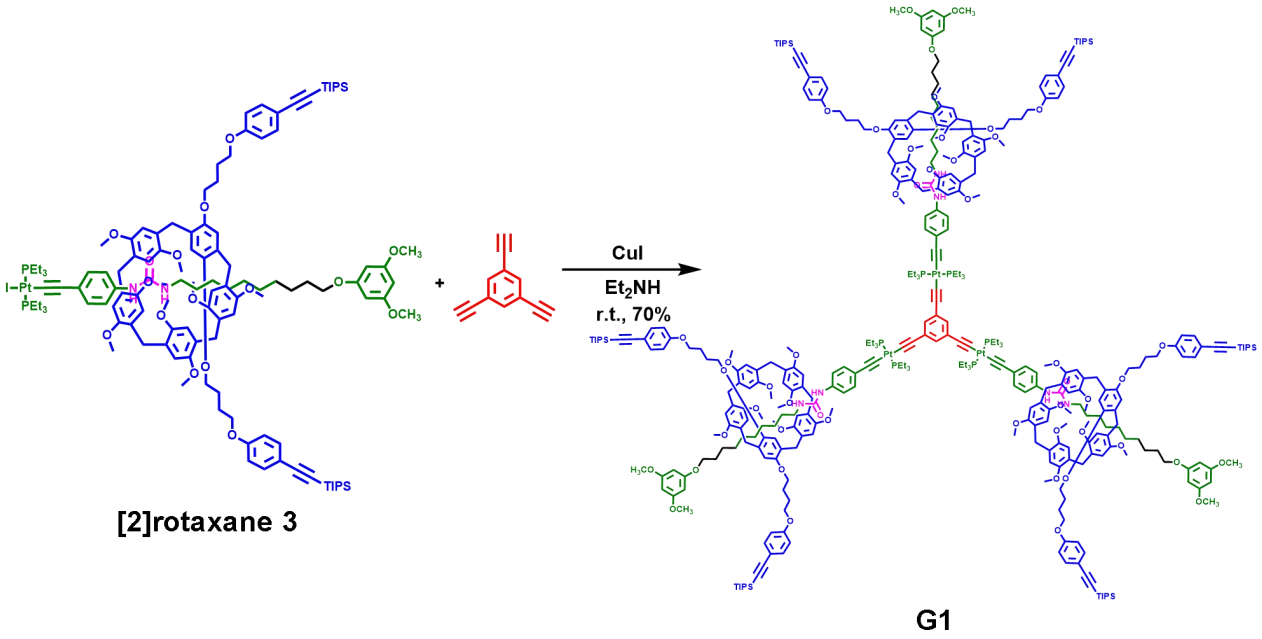


Fig. S13 Theoretically calculated structures of (a) [2]rotaxane **3**; (b) anion-induced switching motion of macrocycle component in [2]rotaxane **3**.

Section C. Synthesis and characterization of Type III-C rotaxane-branched dendrimers.

1. Synthesis of the first-generation Type III-C rotaxane-branched dendrimer G1.

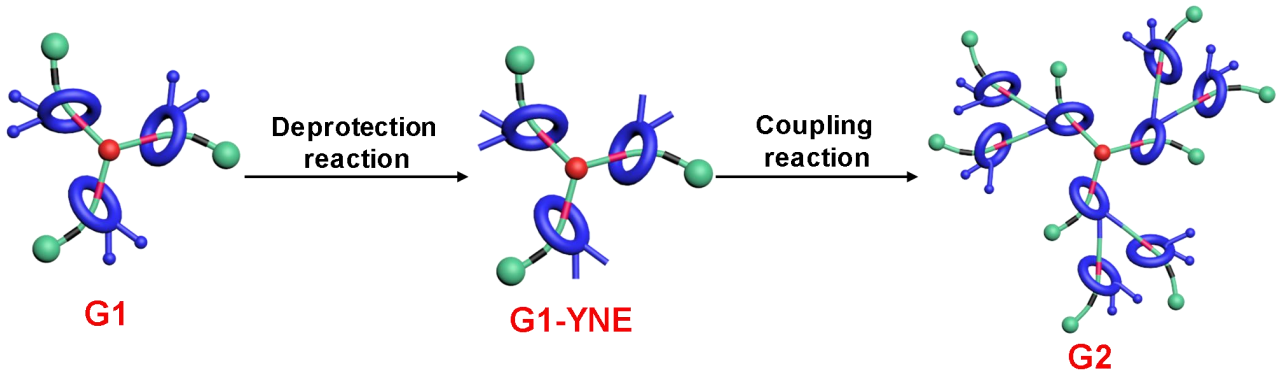
Scheme S3: Synthesis route of Type III-C rotaxane-branched dendrimer **G1**.



Synthesis of the first-generation Type III-C rotaxane-branched dendrimer G1: A mixture of 1, 3, 5-triethynylbenzene (3.8 mg, 0.025 mmol) and [2]rotaxane **3** (200 mg, 0.084 mmol) were added in a Schlenk flask, the Schlenk flask was then evacuated and back-filled with N_2 three times. Next, degassed diethylamine (10 mL) and a catalytic amount of CuI was added under an inert atmosphere. The reaction was stirred overnight at room temperature. The solvent was evaporated and the residue was purified by column chromatography (SiO_2; PE/DCM) and preparative gel permeation chromatography (GPC) to yield a yellow solid **G1** (124 mg, 70%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.23-7.43 (m, 27H), 6.84-7.01 (m, 45H), 6.10-6.11 (m, 9H), 3.78-4.07 (m, 150H), 2.91 (t, 3H), 2.20-2.23 (m, 36H), 1.97-2.08 (m, 24H), 1.58-1.65 (m, 6H), 1.23-1.31 (m, 54H), 1.00-1.15 (m, 150H), 0.60 (m, 6H), -0.14 (m, 6H), -1.61 (m, 6H), -1.87 (m, 6H). ^{31}P NMR (122 MHz, CD_2Cl_2): δ 11.64. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 162.12, 161.57, 159.79, 159.66, 154.51, 151.31, 151.12, 150.79, 150.30, 150.22, 138.12, 133.82, 133.79, 131.59, 129.51, 129.17, 129.07, 128.75, 119.37, 116.01, 115.87, 115.40, 114.85, 114.77, 113.55, 107.72, 107.61, 93.83, 92.88, 89.04, 88.90, 68.75, 68.52, 68.33, 68.22, 57.25, 56.81, 55.70, 55.67, 40.14, 31.44, 30.85, 30.45, 30.30, 30.14, 29.84, 29.51, 27.15, 27.06, 26.87, 26.66, 26.55, 25.40, 18.93, 17.07, 16.89, 16.72, 11.85, 8.63. MALDI-TOF-MS: Calculated for [**G1** + Na]$^+$: *m/z* = 6,953.5 and [**G1** + H + Na]$^{2+}$: *m/z* = 3,477.2; Found: *m/z* = 6952.7 and *m/z* = 3476.5.

2. Synthesis of the second-generation Type III-C rotaxane-branched dendrimer G2.

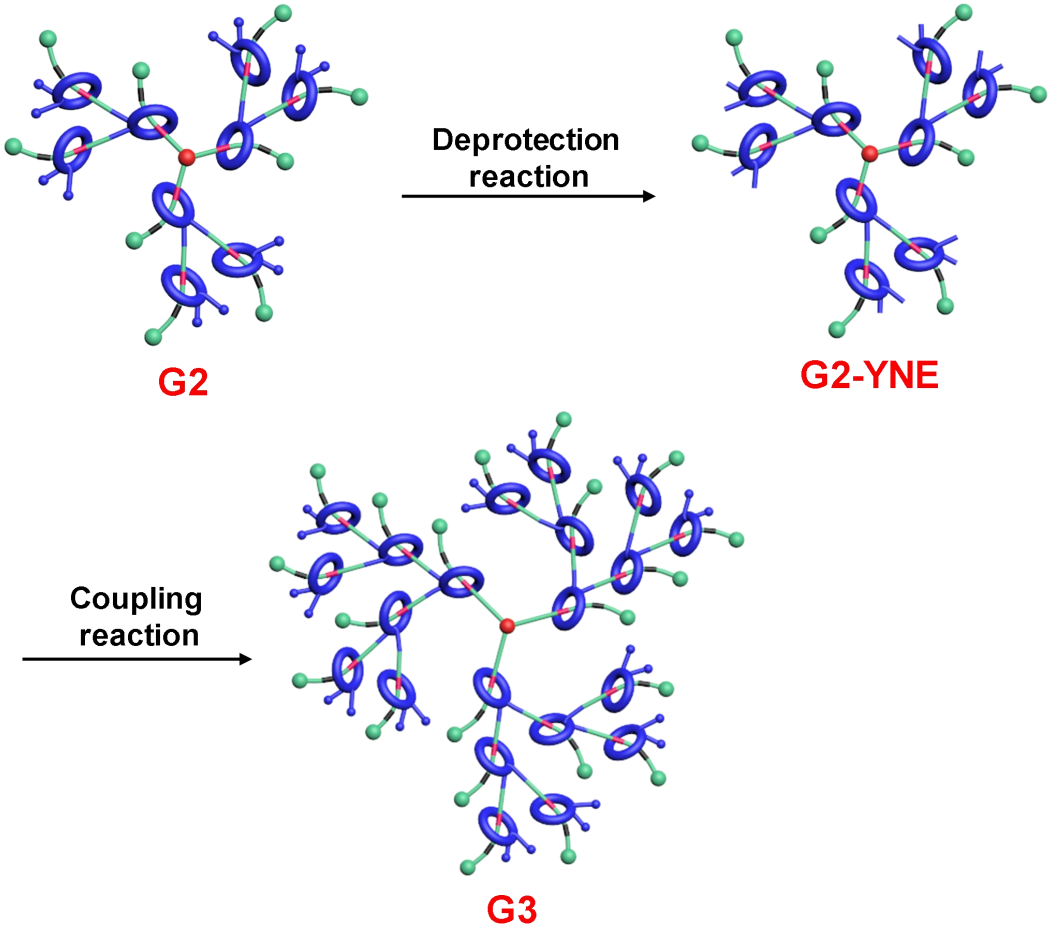
Scheme S4: Synthesis route of Type III-C rotaxane-branched dendrimer **G2**.



Synthesis of Type III-C rotaxane-branched dendrimer G2: A reaction flask was charged with a THF solution of **G1** (100 mg, 0.0144 mmol) and then a solution of $Bu_4NF{\cdot}3H_2O$ (54 mg, 0.173 mmol) in THF was added dropwise into the reaction flask. The reaction mixture was stirred at room temperature for 2h, the obtained residue was washed by water, then dried with Na_2SO_4 and concentrated. The residue was further purified by column chromatography (SiO_2; DCM) and preparative gel permeation chromatography (GPC) to afford a pale-yellow solid **G1-YNE**. Then the obtained **G1-YNE** (60mg, 0.01 mmol) and [2]rotaxane **3** (160 mg, 0.066 mmol) were added in a Schlenk flask, the Schlenk flask was then evacuated and back-filled with N_2 three times. Next, degassed diethylamine (10 mL) and a catalytic amount of CuI were added under an inert atmosphere. The reaction was stirred overnight at room temperature. The solvent was evaporated and the residue was purified by column chromatography (SiO_2; DCM/EA) and preparative gel permeation chromatography (GPC) to yield a pale-yellow solid **G2** (140 mg, 52%). Mp: 110 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 6.78-7.41 (m, 210H), 6.09-6.12 (m, 27H), 3.77-4.07 (m, 450H), 2.84-2.97 (m, 9H), 1.95-2.23 (m, 180H), 1.62-1.64 (m, 18H), 1.14-1.29 (m, 450H), 1.00-1.01 (m, 36H), 0.59 (m, 18H), -0.16 (m, 18H), -1.91-(-1.51) (m, 36H). ^{31}P NMR (122 MHz, CD_2Cl_2): δ 11.68. ^{13}C NMR (126 MHz, CD_2Cl_2): δ 162.06, 161.55, 161.51, 159.74, 159.61, 157.30, 157.23, 154.48, 154.40, 151.25, 151.05, 151.02, 150.73, 150.71, 150.66, 150.23, 150.15, 138.05, 133.79, 133.75, 132.21, 131.54, 129.47, 129.12, 129.02, 128.96, 128.74, 128.69, 123.13, 119.30, 115.94, 115.80, 114.79, 114.71, 114.59, 114.50, 113.57, 113.45, 107.65, 107.54, 93.73, 92.82, 89.00, 88.85, 68.68, 68.51, 68.47, 68.27, 68.16, 68.09, 57.25, 57.22, 56.81, 56.77, 56.69, 55.76, 55.67, 40.07, 31.43, 30.82, 30.45, 30.41, 30.26, 29.82, 29.78, 29.50, 29.39, 27.09, 27.00, 26.94, 26.82, 26.70, 26.66, 26.62, 26.49, 25.30, 18.88, 18.86, 16.95, 16.81, 16.67, 11.79, 11.78, 8.60, 8.58, 1.18. MALDI-TOF-MS: Calculated for [**G2** + Na]$^+$: *m/z* = 19,592.7 and [**G2** + 2Na]$^{2+}$: *m/z* = 9,807.9; Found: *m/z* = 19,592.5 and *m/z* = 9,809.0.

3. Synthesis of the third-generation Type III-C rotaxane-branched dendrimer G3.

Scheme S5: Synthesis route of Type III-C rotaxane-branched dendrimer **G3**.

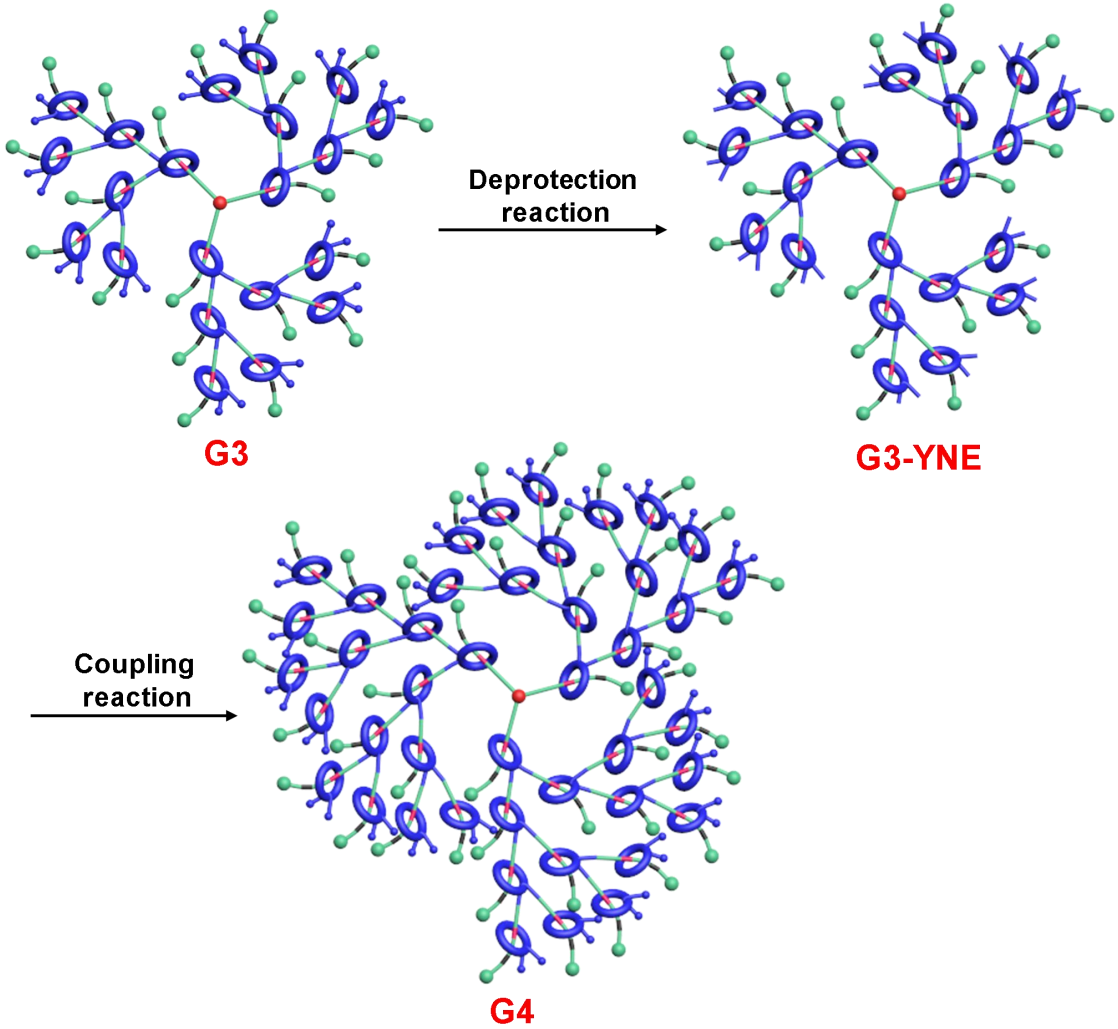


Synthesis of Type III-C rotaxane-branched dendrimer G3: A reaction flask was charged with a THF solution of **G2** (107 mg, 0.0055 mmol) and then a THF solution of $Bu_4NF{\cdot}3H_2O$ (41 mg, 0.13 mmol) was added dropwise into the reaction flask, the reaction mixture was stirred at room temperature for 2h. The obtained residue was washed by water, then dried with Na_2SO_4 and concentrated. The residue was further purified by column chromatography (SiO_2; DCM) and preparative gel permeation chromatography (GPC) to afford a pale-yellow solid **G2-YNE**. Then the obtained **G2-YNE** (65mg, 0.0037 mmol) and [2]rotaxane **3** (115 mg, 0.048 mmol) were added in a Schlenk flask, the Schlenk flask was then evacuated and back-filled with N_2 three times. Next, the mixture solvent of degassed Et_2NH and CH_2Cl_2 (v/v, 5/5 mL) was added via syringe. Subsequently, a catalytic amount of CuI was added under an inert atmosphere. The reaction was stirred overnight at room temperature. The solvent was evaporated and the residue was purified by column chromatography (SiO_2; DCM/EA) and preparative gel permeation chromatography (GPC) to yield a yellow solid **G3** (102 mg, 42%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 6.77-7.40 (m, 486H), 6.08-6.10 (m, 63H), 3.75-4.06 (m, 1050H), 2.83-2.97 (m, 21H), 2.16-2.20 (m, 252H), 1.95-2.05 (m, 168H),

1.00-1.27 (m, 1092H), 0.58 (m, 42H), -0.17 (m, 42H), -1.93-(-1.52) (m, 84H). ^{31}P NMR (122 MHz, CD_2Cl_2): δ 11.86. ^{13}C NMR (126 MHz, CD_2Cl_2): δ 162.04, 161.54, 161.50, 159.72, 159.60, 157.39, 154.50, 154.39, 151.23, 151.03, 150.71, 150.20, 150.13, 138.18, 133.77, 133.73, 132.21, 131.54, 130.23, 129.44, 129.09, 129.00, 128.67, 122.89, 119.26, 115.92, 115.78, 115.32, 114.77, 114.69, 114.59, 114.50, 113.57, 113.44, 107.63, 107.52, 93.72, 92.79, 88.98, 88.84, 68.66, 68.50, 68.46, 68.26, 68.15, 57.21, 56.78, 56.74, 56.67, 55.75, 55.65, 40.06, 32.32, 31.69, 31.40, 30.81, 30.42, 30.34, 30.25, 30.18, 30.09, 29.91, 29.78, 29.72, 29.48, 29.37, 27.56, 27.07, 26.98, 26.80, 26.63, 26.48, 25.31, 23.09, 18.86, 16.95, 16.81, 16.67, 14.29, 11.77, 8.57, 1.16.

4. Synthesis of the fourth-generation Type III-C rotaxane-branched dendrimer G4.

Scheme S6: Synthesis route of Type III-C rotaxane-branched dendrimer **G4**.



Synthesis of Type III-C rotaxane-branched dendrimer G4: A reaction flask was charged with a THF solution of **G3** (33 mg, 0.74 μmol) and then a THF solution of $Bu_4NF{\cdot}3H_2O$ (11 mg, 0.0355 mmol) was added dropwise into the reaction flask, the reaction mixture was stirred at room

temperature for 2h. The obtained residue was washed by water, then dried with Na_2SO_4 and concentrated. The residue was further purified by column chromatography (SiO_2; DCM/EA) and preparative gel permeation chromatography (GPC) to afford a pale-yellow solid **G3-YNE**. Then the obtained **G3-YNE** (15 mg, 0.37 μmol) and [2]rotaxane **3** (25 mg, 0.0105 mmol) were added in a Schlenk flask, the Schlenk flask was then evacuated and back-filled with N_2 three times. Next, the mixture solvent of degassed Et_2NH and CH_2Cl_2 (v/v, 3/3 mL) was added via syringe. Subsequently, a catalytic amount of CuI was added under an inert atmosphere. The reaction was stirred overnight at room temperature. The solvent was evaporated and the residue was purified by column chromatography (SiO_2; DCM/EA) and preparative gel permeation chromatography (GPC) to yield a pale-yellow solid **G4** (20 mg, 29%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.82-7.40 (m, 1038H), 6.06-6.08 (m, 135H), 3.75-4.06 (m, 2250H), 3.02 (m, 90H), 2.82 (m, 45H), 1.94-2.19 (m, 900H), 0.97-1.35 (m, 2178H), 0.58 (m, 90H), -0.18 (m, 90H), -1.67 (m, 90H), -1.94 (m, 90H). ^{31}P NMR (122 MHz, CD_2Cl_2): δ 11.66. ^{13}C NMR (126 MHz, CD_2Cl_2): δ 162.05, 161.54, 161.50, 159.72, 159.61, 151.26, 151.04, 150.72, 150.21, 150.15, 133.78, 133.74, 132.26, 131.58, 129.48, 129.12, 129.02, 128.68, 119.29, 115.93, 115.79, 114.78, 114.70, 114.63, 114.53, 113.48, 107.63, 107.52, 93.74, 93.72, 92.82, 89.00, 88.86, 68.69, 68.51, 68.46, 68.27, 68.16, 57.26, 56.78, 56.71, 55.76, 55.66, 40.06, 31.43, 30.81, 30.45, 30.24, 30.09, 29.81, 29.37, 27.08, 26.98, 26.81, 26.70, 26.48, 23.10, 18.87, 18.84, 16.98, 16.84, 16.71, 14.29, 11.78, 11.77, 8.59, 1.17.

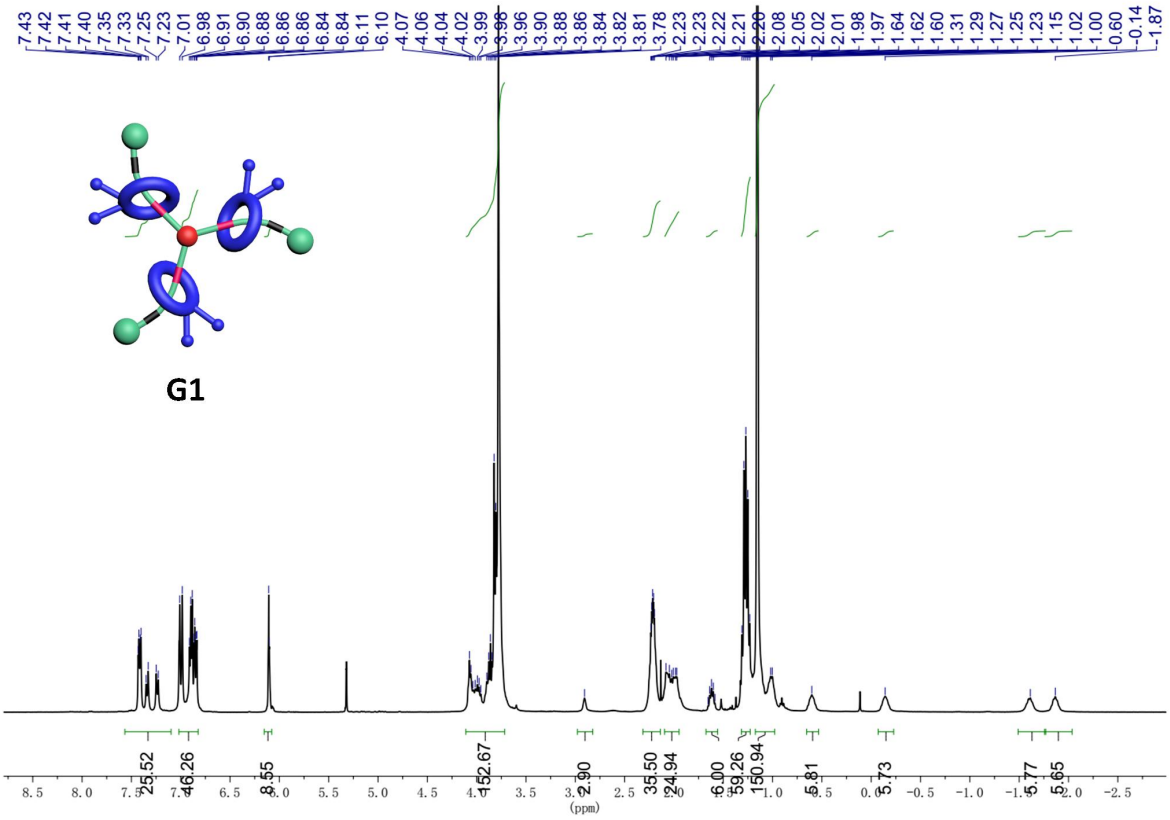


Fig. S14 ^{1}H NMR spectrum (THF-d_8, 298 K, 400 MHz) of **G1**.

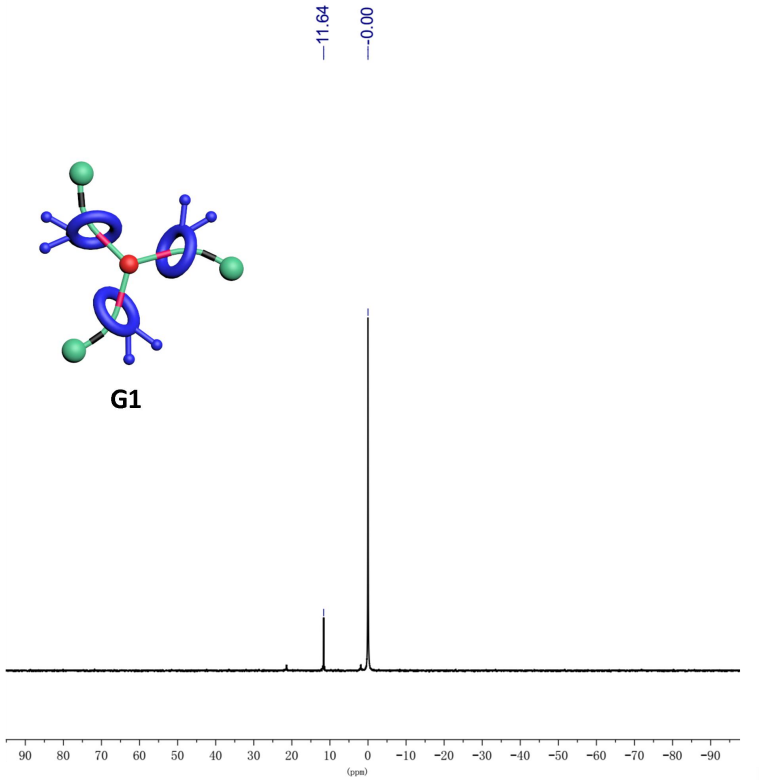


Fig. S15 ^{31}P NMR spectrum (THF-d_8, 298 K, 122 MHz) of **G1**.

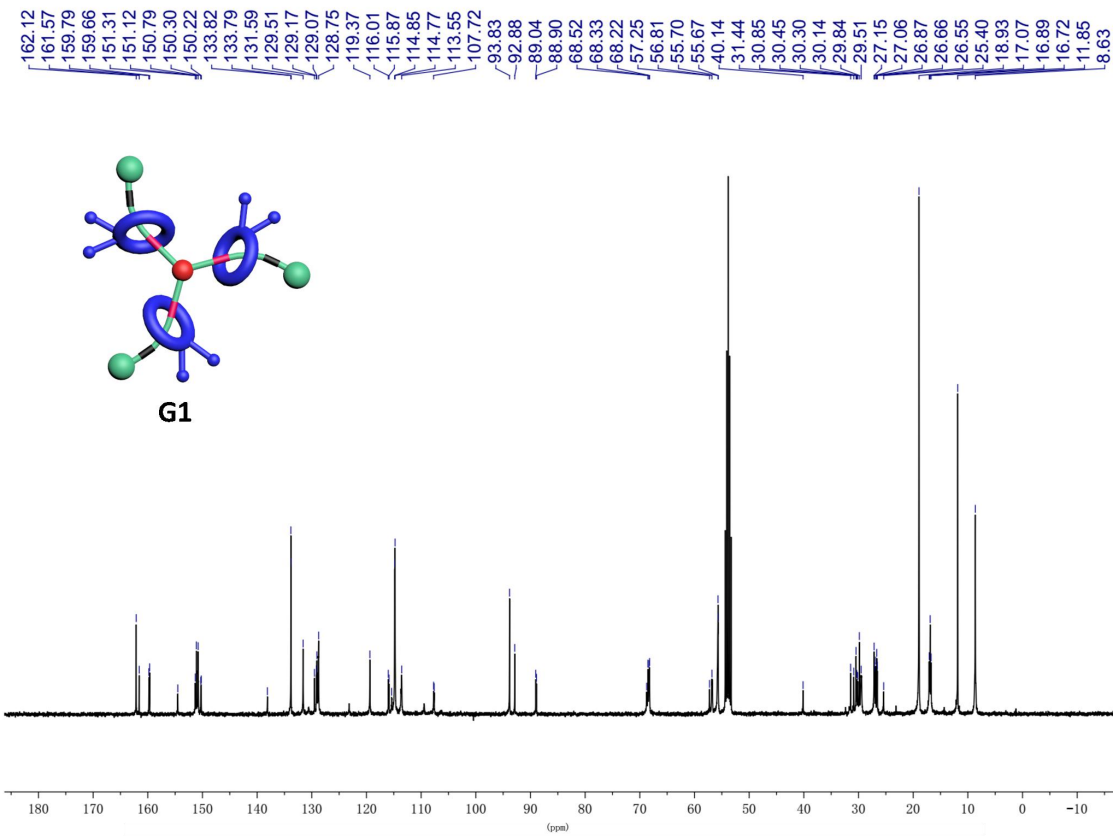


Fig. S16 ^{13}C NMR spectrum (CD_2Cl_2, 298 K, 101 MHz) of **G1**.

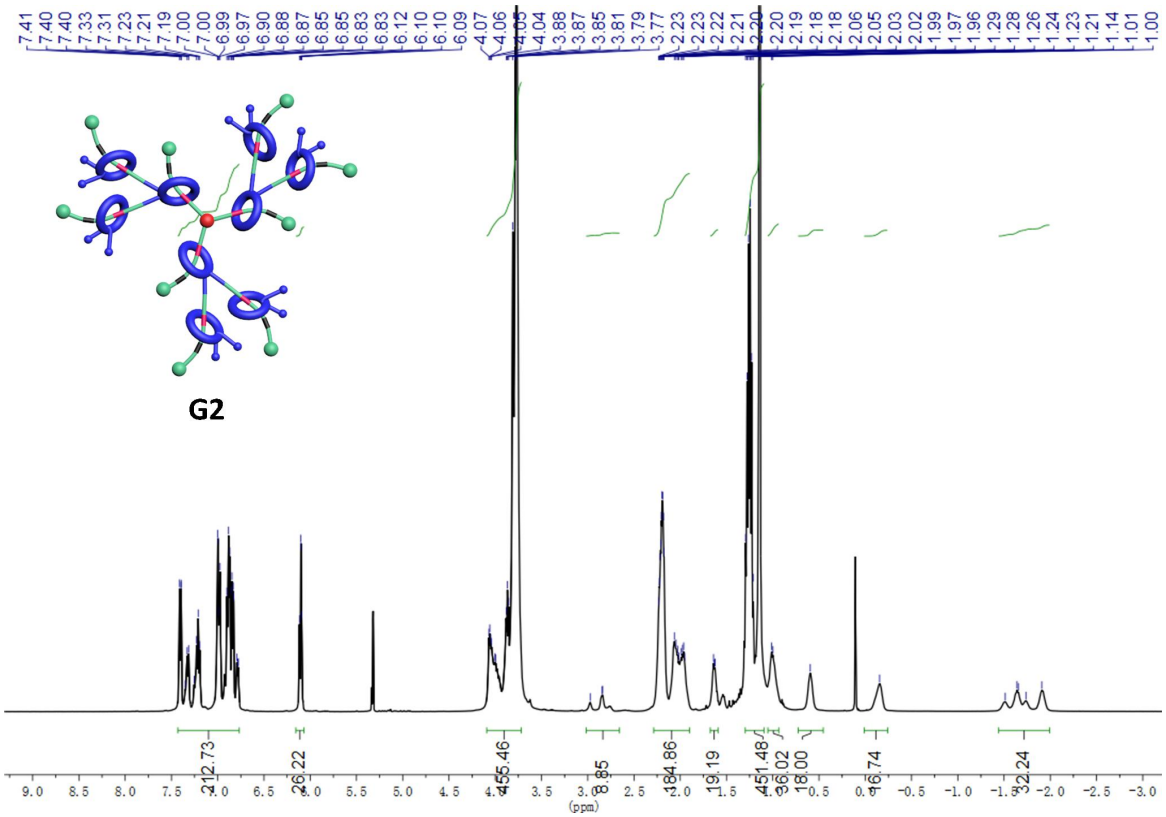


Fig. S17 ^{1}H NMR spectrum (CD_2Cl_2, 298 K, 500 MHz) of **G2**.

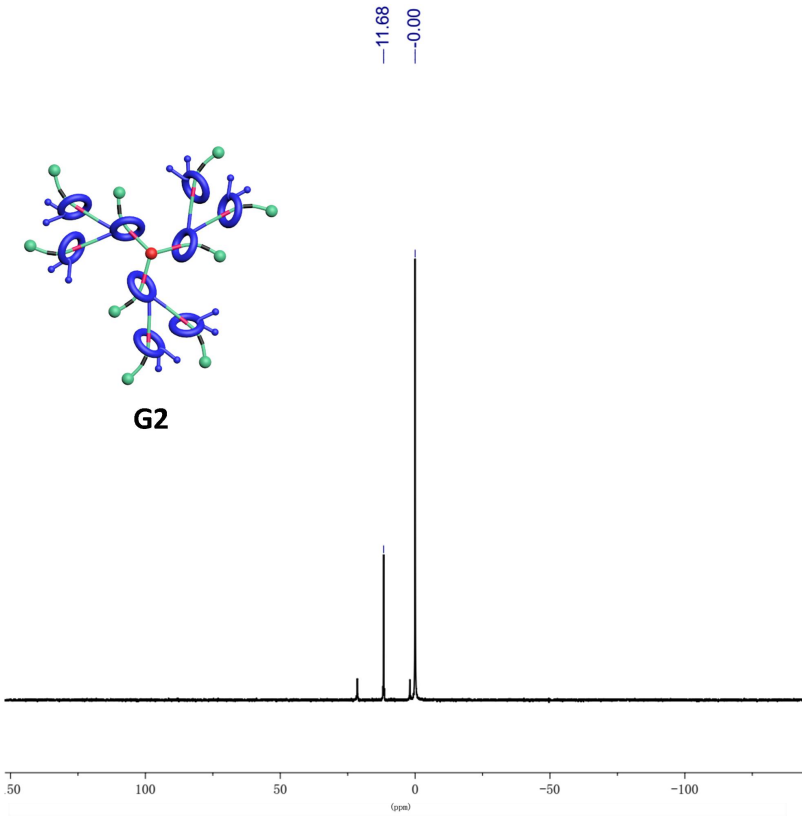


Fig. S18 ^{31}P NMR spectrum (CD_2Cl_2, 298 K, 122 MHz) of **G2**.

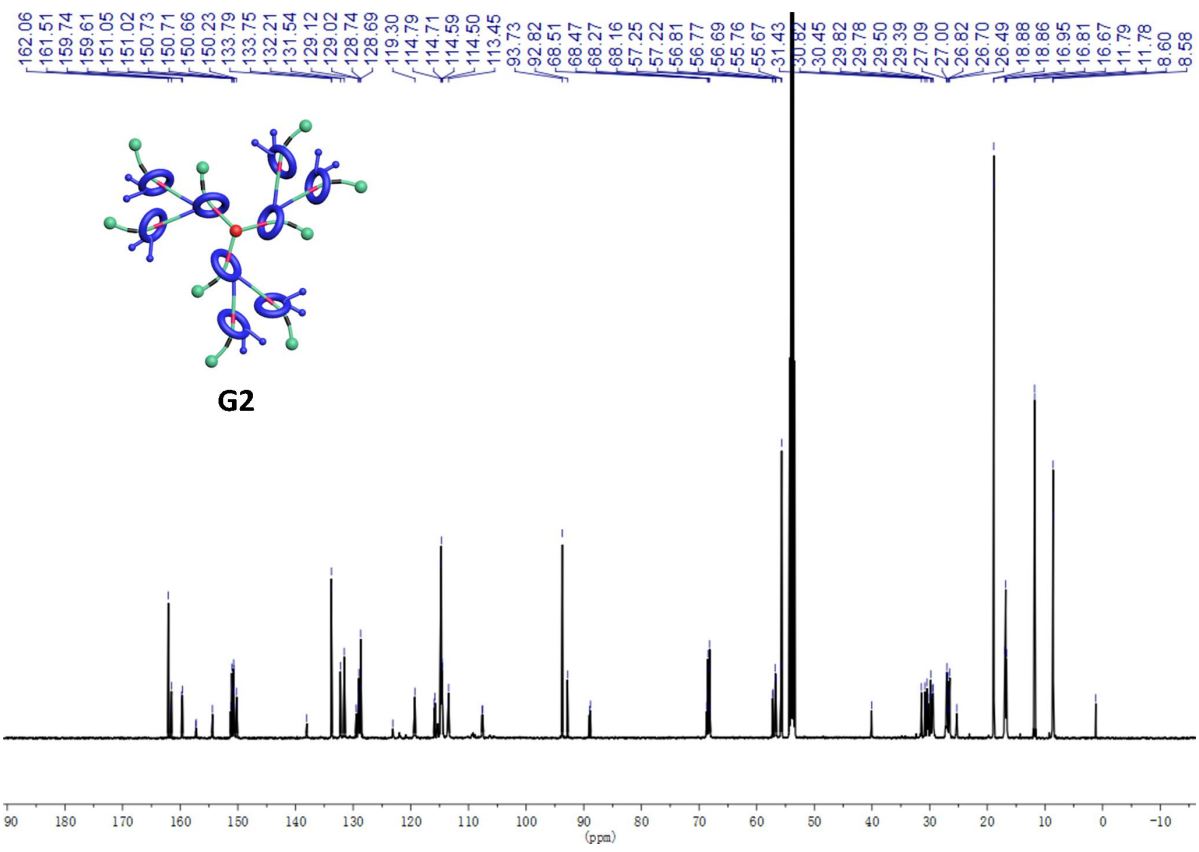


Fig. S19 ^{13}C NMR spectrum (CD_2Cl_2, 298 K, 126 MHz) of **G2**.

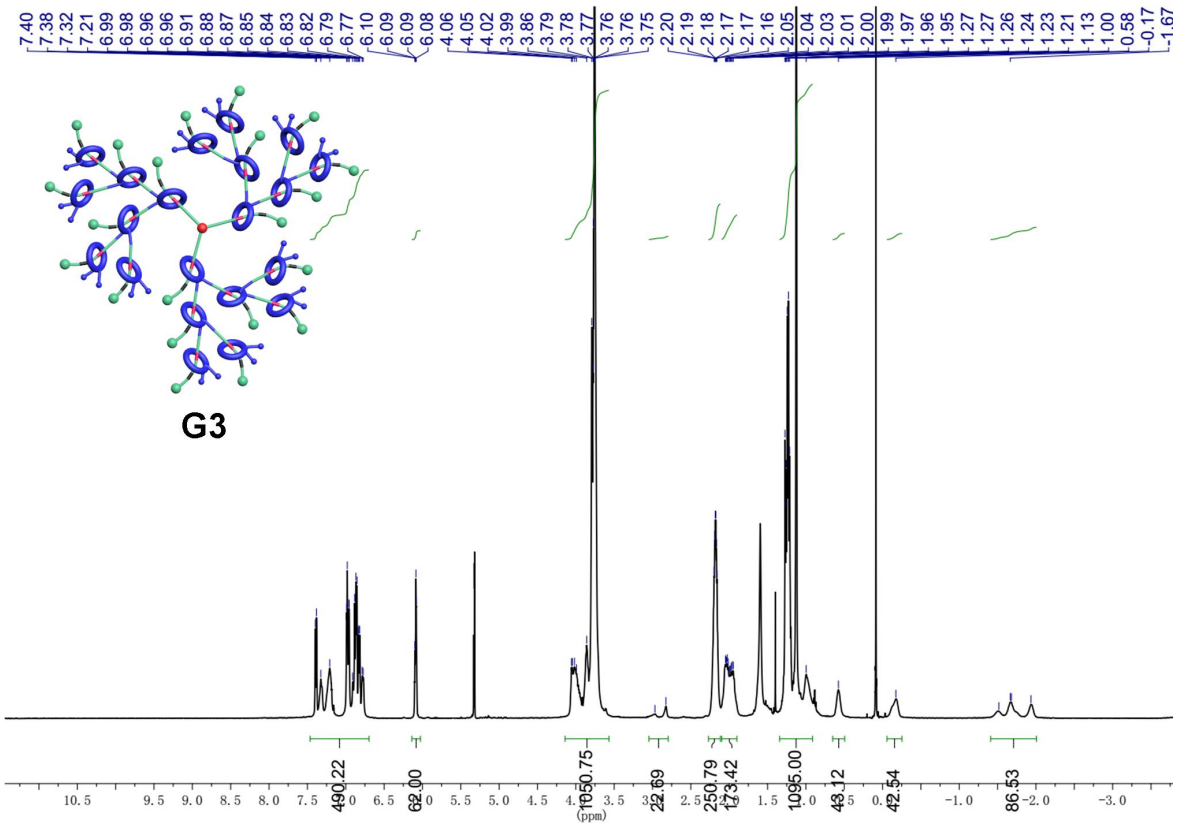


Fig. S20 ^{1}H NMR spectrum (CD_2Cl_2, 298 K, 500 MHz) of **G3**.

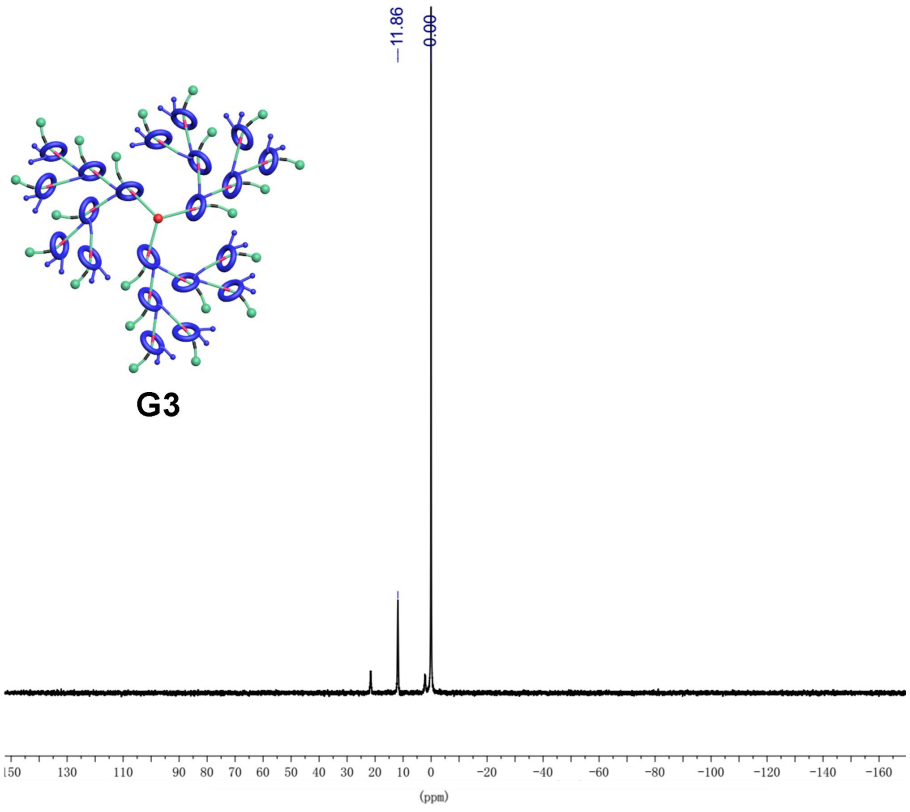


Fig. S21 ^{31}P NMR spectrum (CD_2Cl_2, 298 K, 122 MHz) of **G3**.

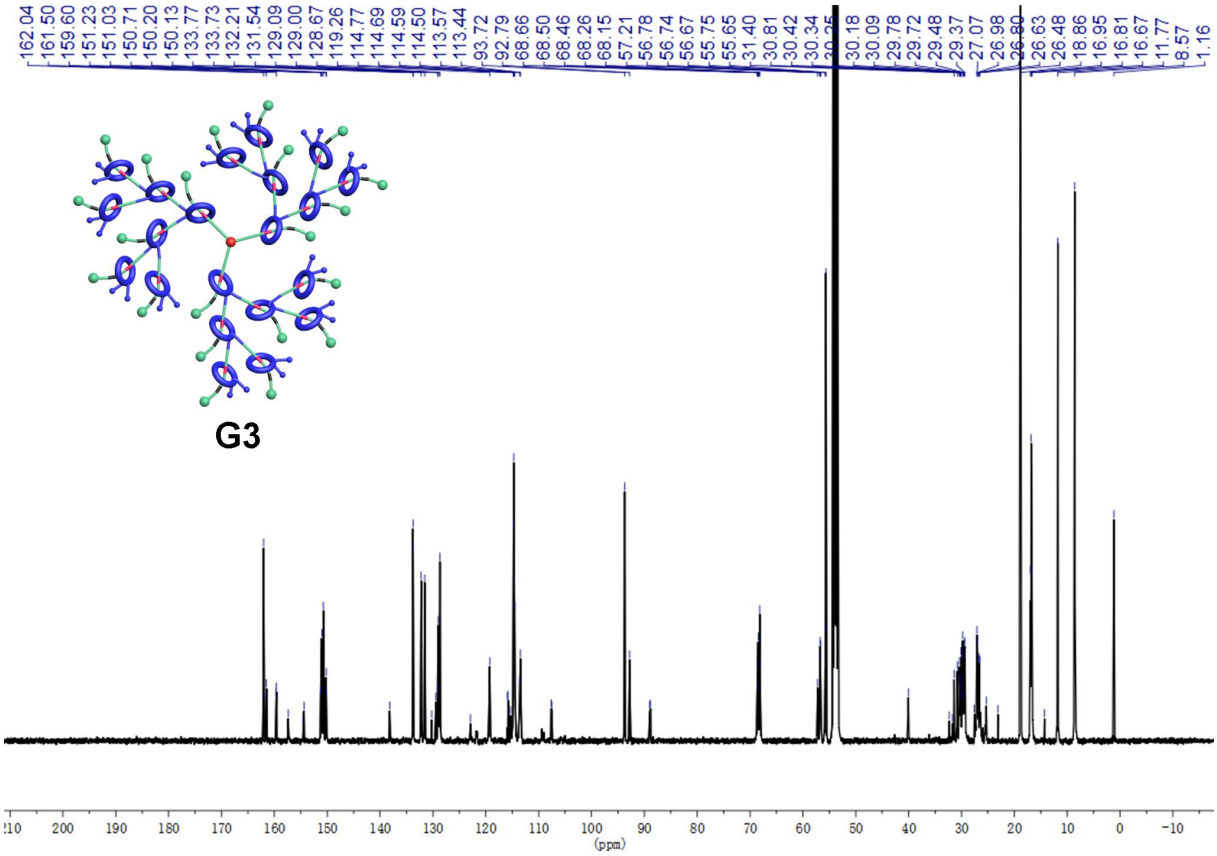


Fig. S22 ^{13}C NMR spectrum (CD_2Cl_2, 298 K, 126 MHz) of **G3**.

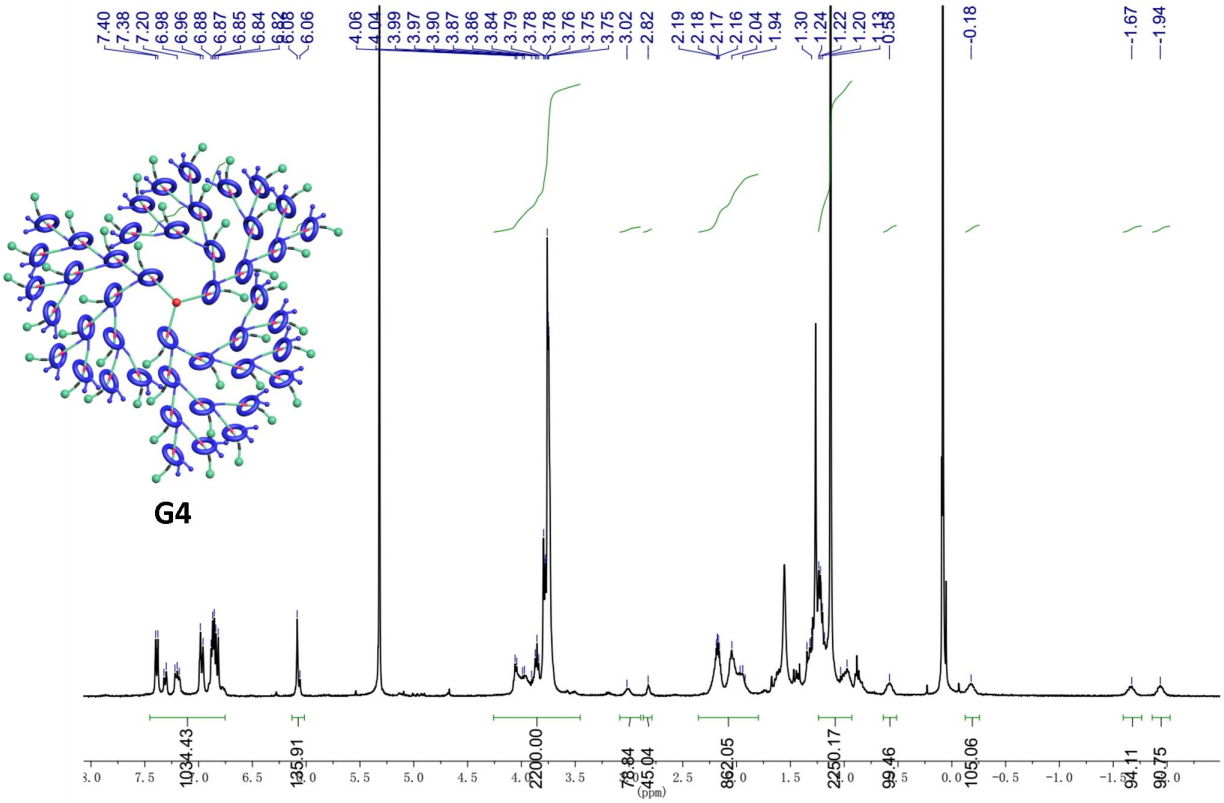


Fig. S23 ^{1}H NMR spectrum (CD_2Cl_2, 298 K, 400 MHz) of **G4**.

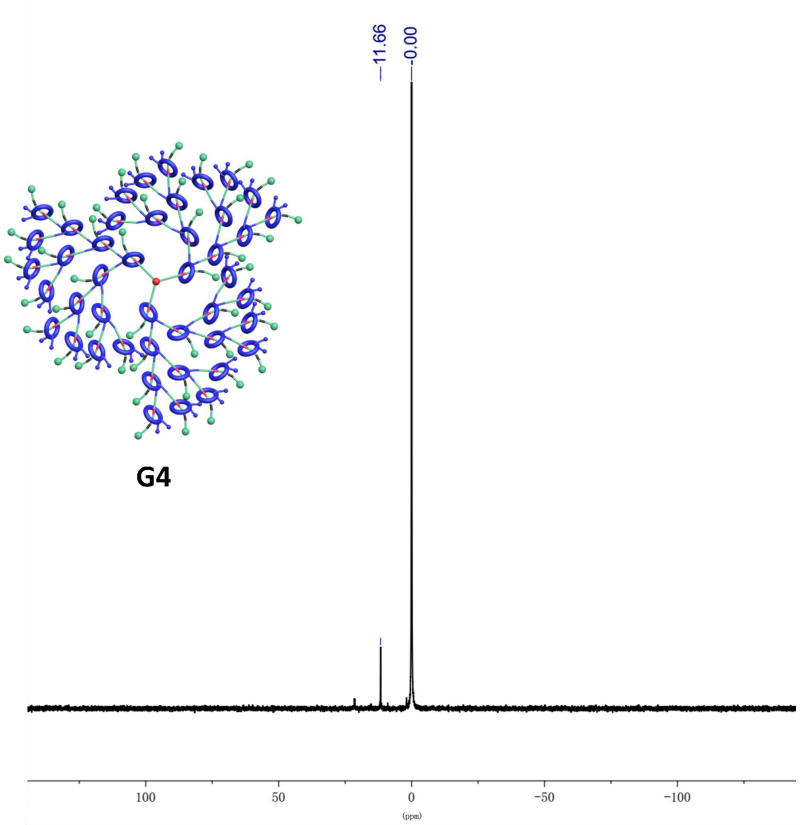


Fig. S24 ^{31}P NMR spectrum (CD_2Cl_2, 298 K, 122 MHz) of **G4**.

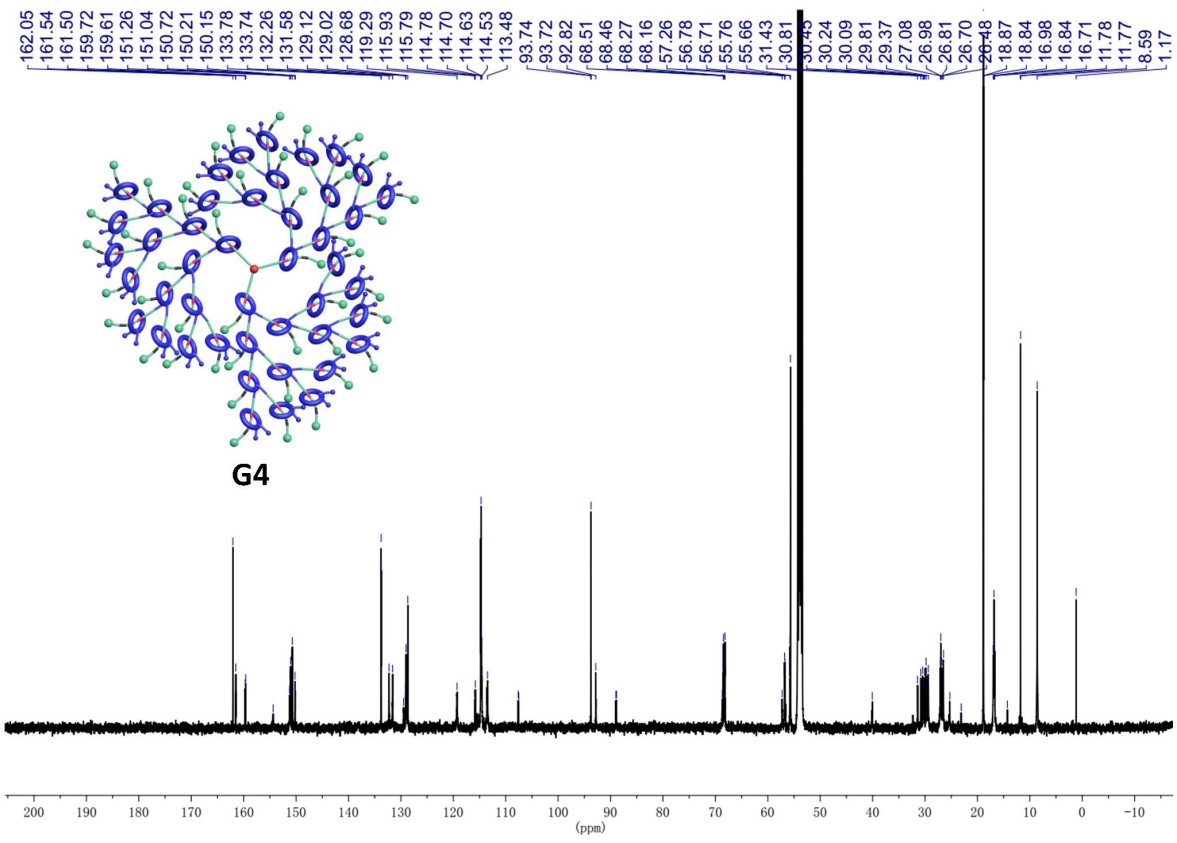


Fig. S25 ^{13}C NMR spectrum (CD_2Cl_2, 298 K, 126 MHz) of **G4**.

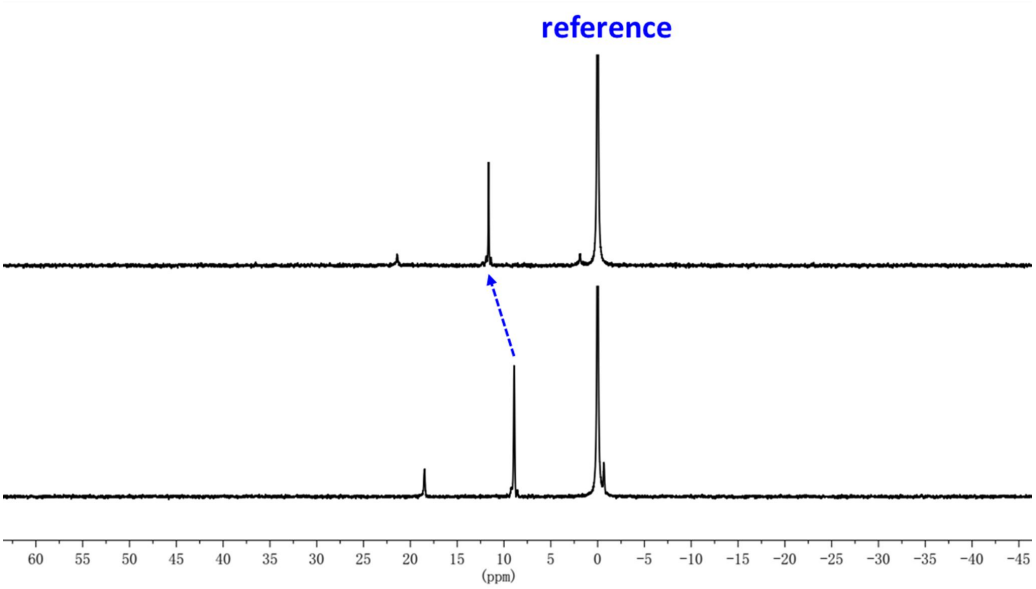


Fig. S26 ^{31}P NMR spectra (CD_2Cl_2, 298 K, 122 MHz) of Type III-C rotaxane-branched dendrimer **G1** (*top*) and [2]rotaxane **3** (*bottom*).

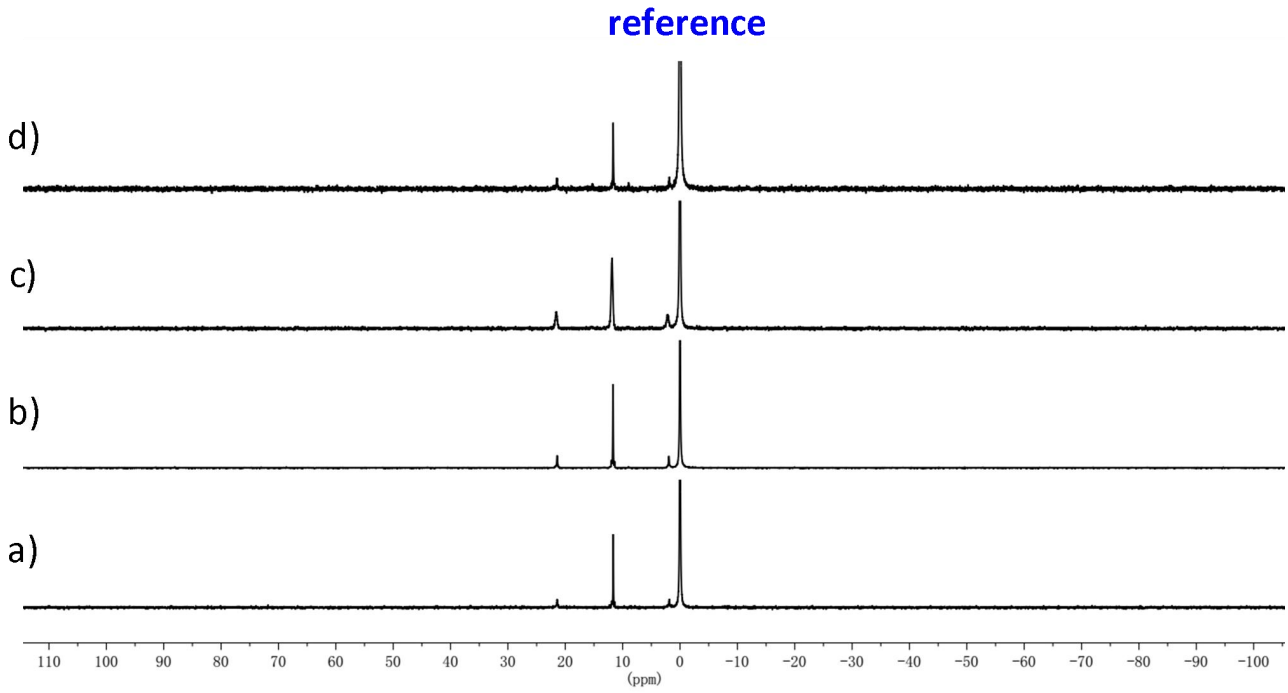


Fig. S27 Stacked ^{31}P NMR spectra (CD_2Cl_2, 298 K, 122 MHz) of Type III-C rotaxane-branched dendrimers: a) **G1**; b) **G2**; c) **G3**; d) **G4**.

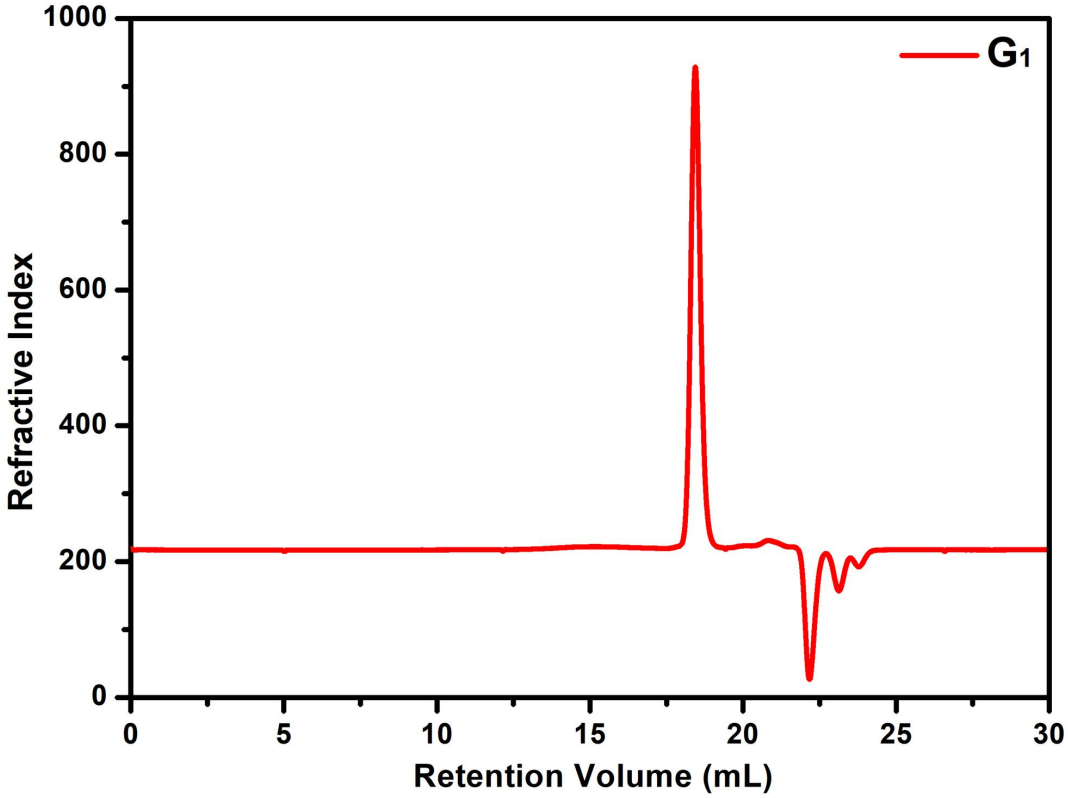


Fig. S28 GPC spectrum of Type III-C rotaxane-branched dendrimer **G1**.

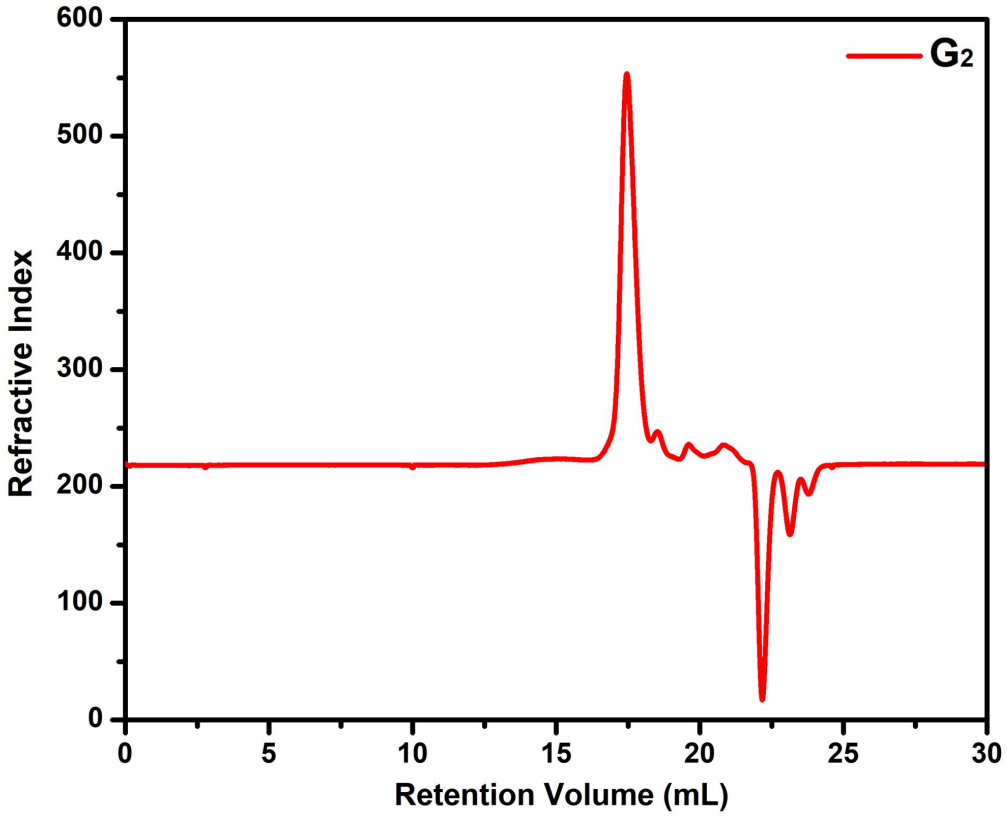


Fig. S29 GPC spectrum of Type III-C rotaxane-branched dendrimer **G2**.

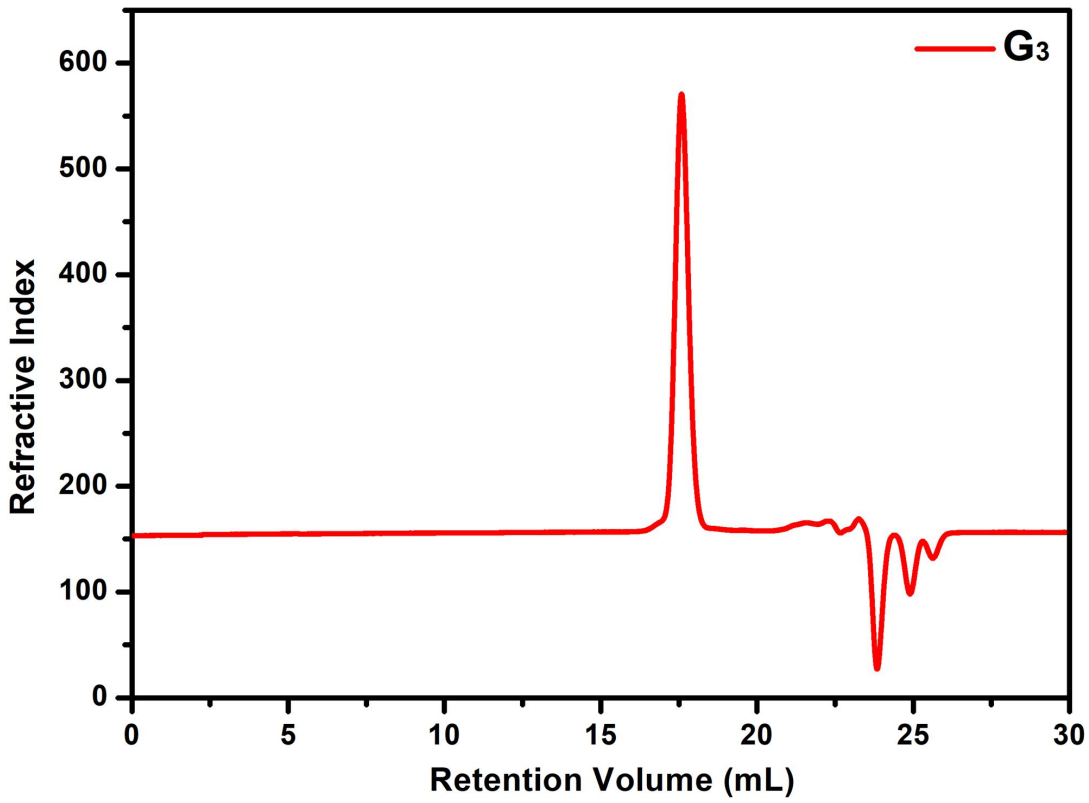
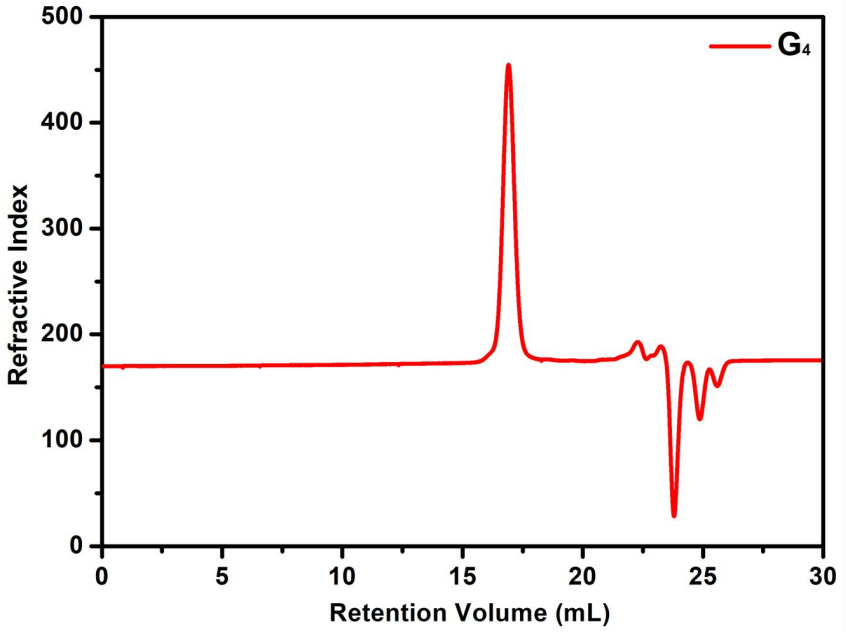


Fig. S30 GPC spectrum of Type III-C rotaxane-branched dendrimer **G3**.



Peak RV - (ml)	16.907
Mn - (Daltons)	105,800
Mw - (Daltons)	110,195
Mz - (Daltons)	115,384
Mp - (Daltons)	107,589
Mw / Mn	1.042
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.1942
Rh(w) - (nm)	6.770
Rg(w) - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	-1.004
Mark-Houwink logK	4.368
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	169.28
UV Area - (mvml)	0.00
RALS Area - (mvml)	46.25
LALS Area - (mvml)	25.22
IVDP Area - (mvml)	24.01

Fig. S31 GPC spectrum of Type III-C rotaxane-branched dendrimer **G4**.

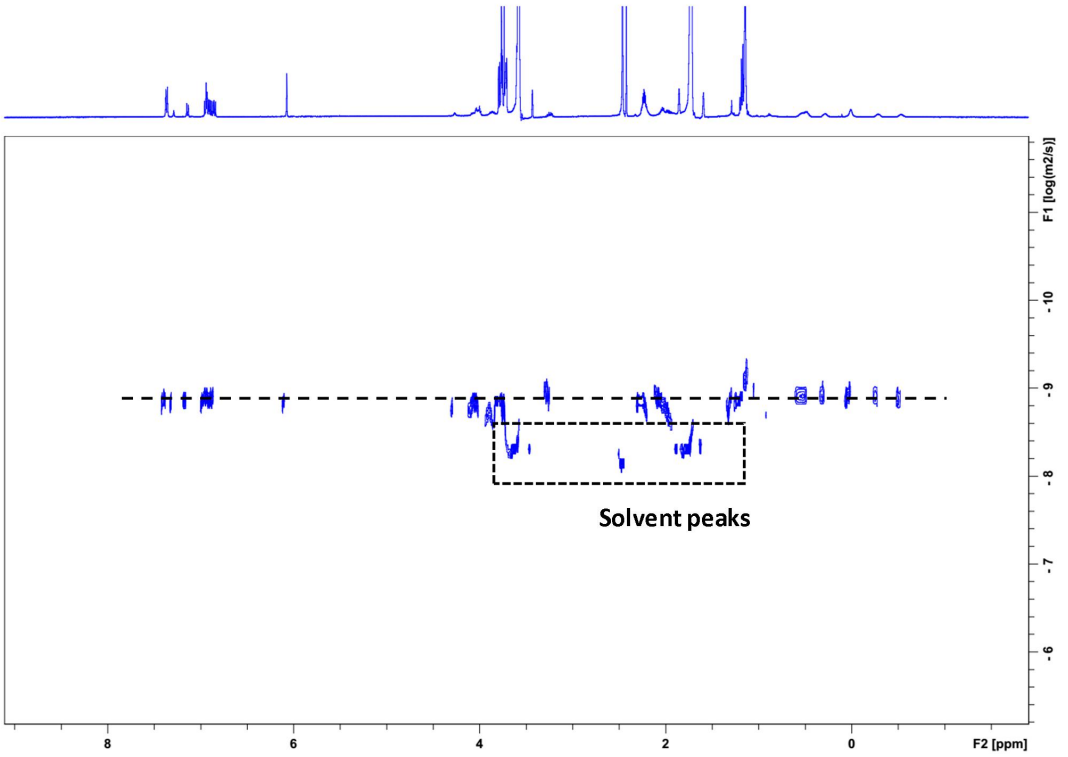


Fig. S32 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of [2]rotaxane **3**. The diffusion coefficient D is (14.13± 0.14) × 10^{-10} m^2s^{-1}.

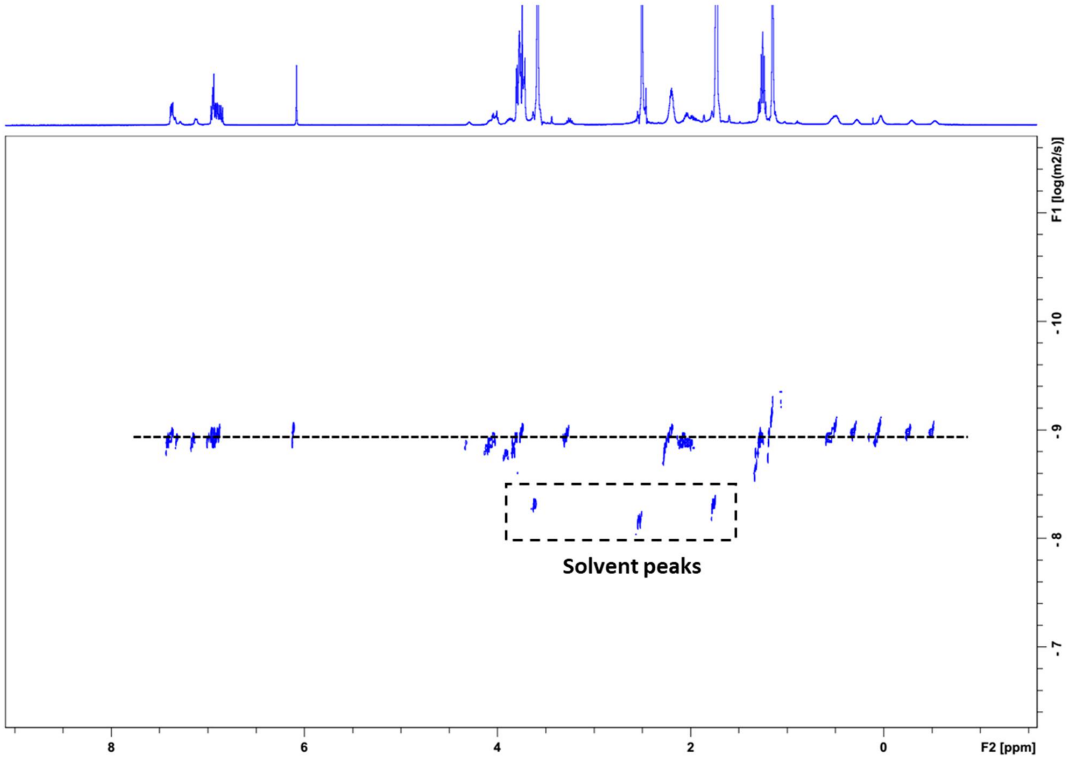


Fig. S33 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of **G1**.The diffusion coefficient D is (10.96±0.24)× 10^{-10} m^2s^{-1}.

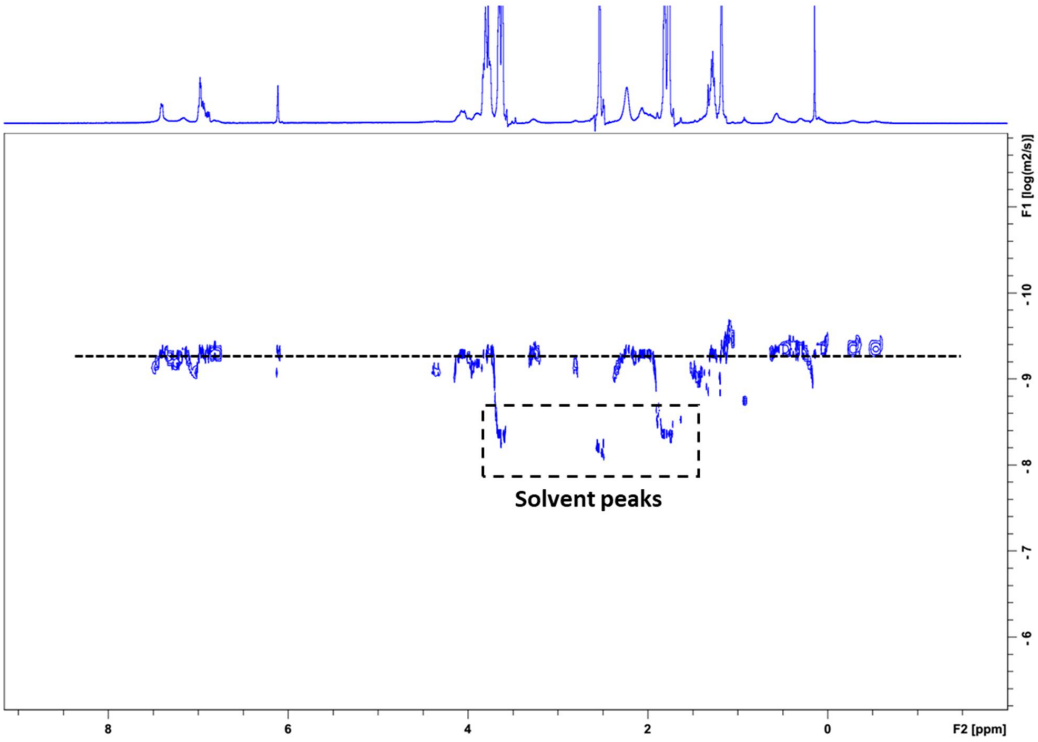


Fig. S34 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of **G2**. The diffusion coefficient D is $(5.13\pm0.12) \times 10^{-10}$ m^2s^{-1}.

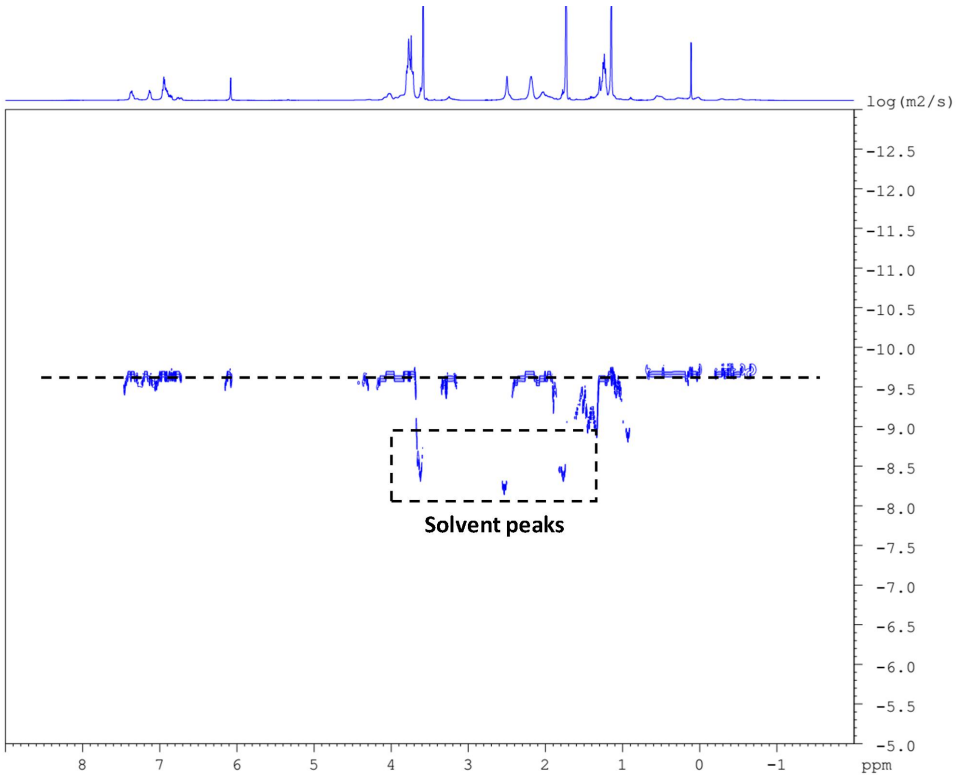


Fig. S35 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of **G3**. The diffusion coefficient D is $(2.75\pm0.16) \times 10^{-10}$ m^2s^{-1}.

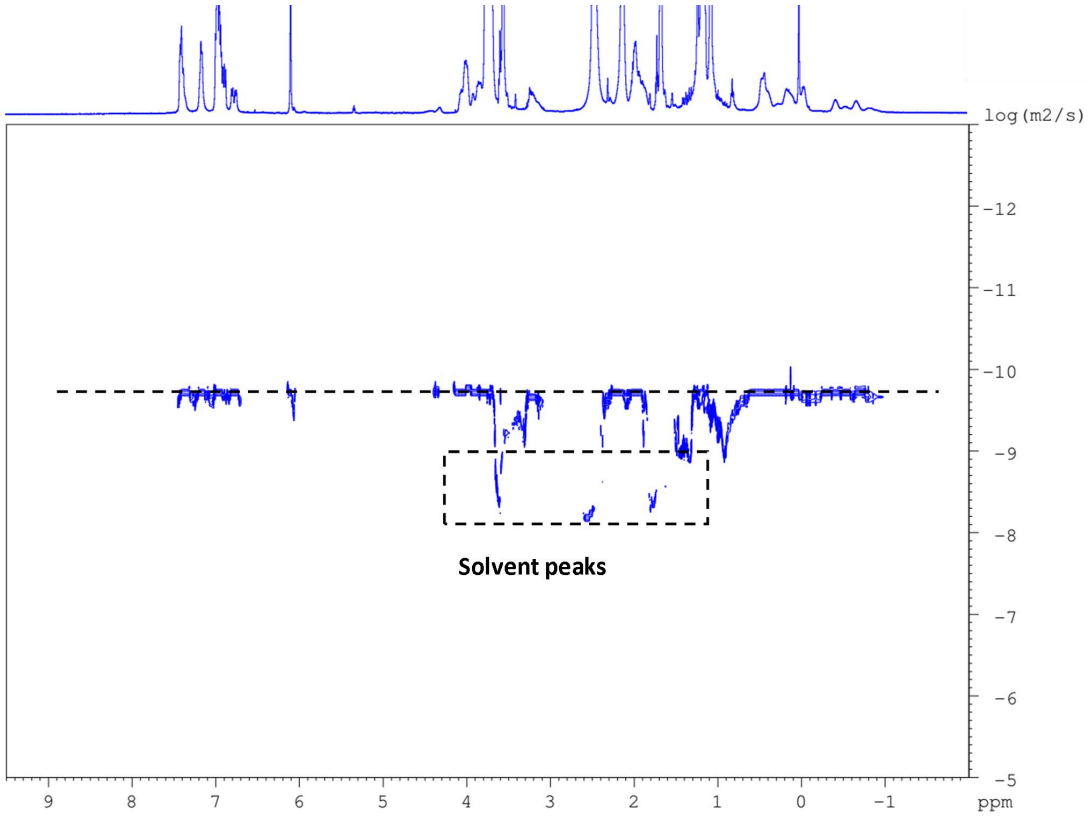


Fig. S36 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of **G4**. The diffusion coefficient D is (1.66±0.15) × 10^{-10} m^2s^{-1}.

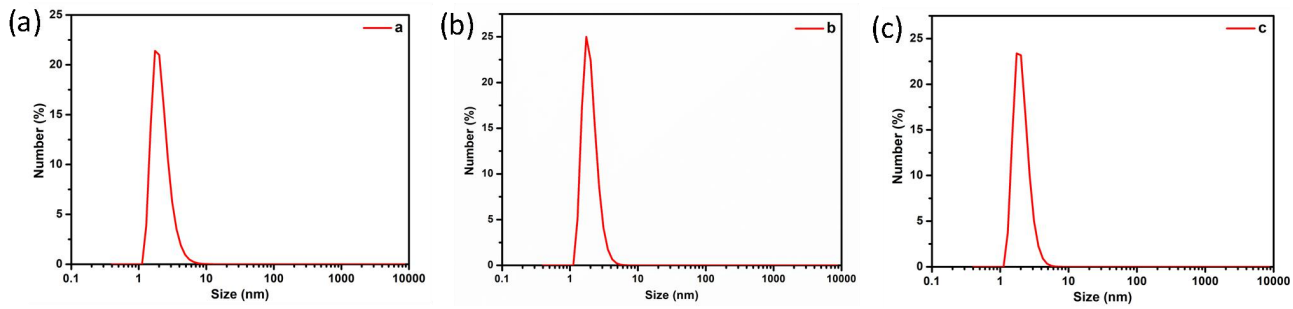


Fig. S37 DLS spectra of Type III-C rotaxane-branched dendrimer **G1**: (a) 2.21 nm; (b) 2.02 nm; (c) 2.09 nm. The average hydrodynamic size was 2.11 ± 0.10 nm.

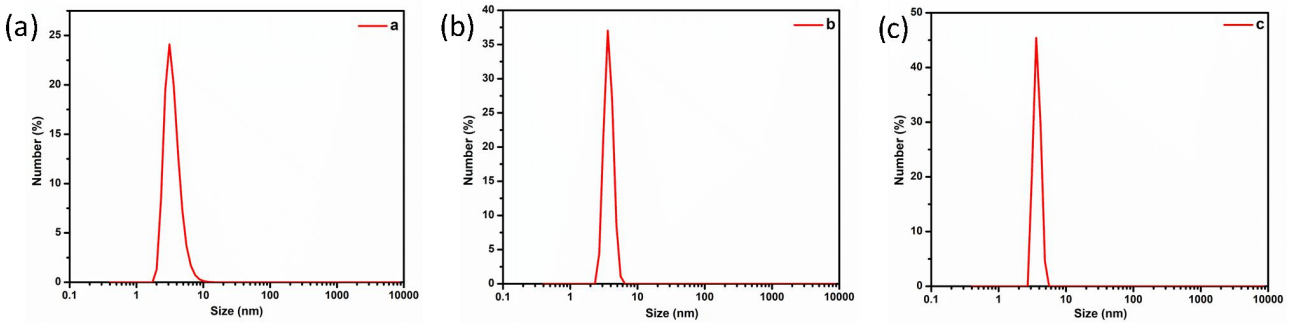


Fig. S38 DLS spectra of Type III-C rotaxane-branched dendrimer **G2**: (a) 3.53 nm; (b) 3.75 nm; (c) 3.74 nm. The average hydrodynamic size was 3.67 ± 0.14 nm.

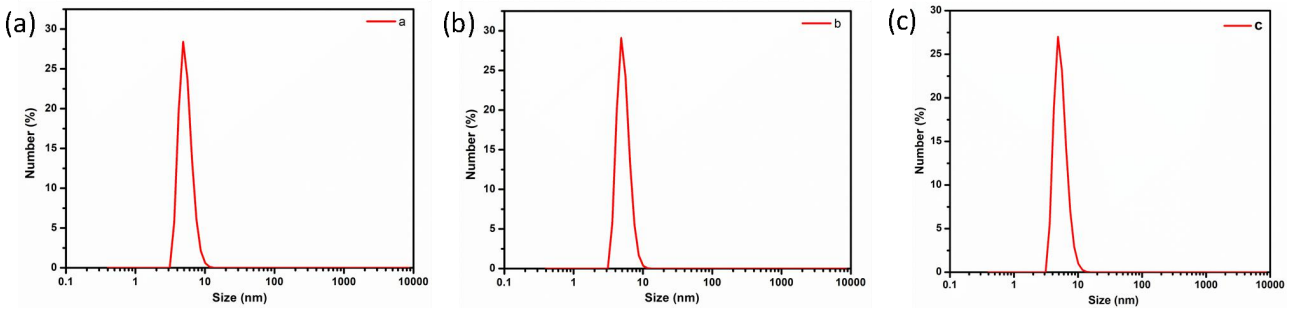


Fig. S39 DLS spectra of Type III-C rotaxane-branched dendrimer **G3**: (a) 5.34 nm; (b) 5.29 nm; (c) 5.44 nm. The average hydrodynamic size was 5.36 ± 0.08 nm.

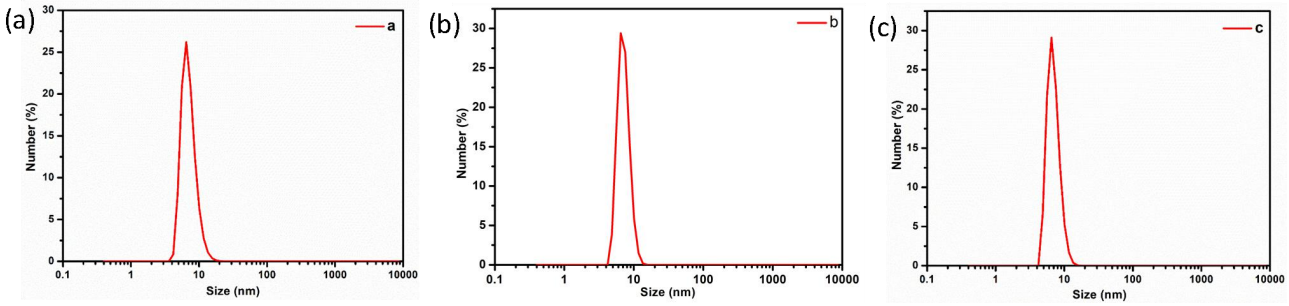


Fig. S40 DLS spectra of Type III-C rotaxane-branched dendrimer **G4**: For (a) 7.15 nm; (b) 7.20 nm; (c) 7.02 nm. The average hydrodynamic size was 7.12 ± 0.10 nm.

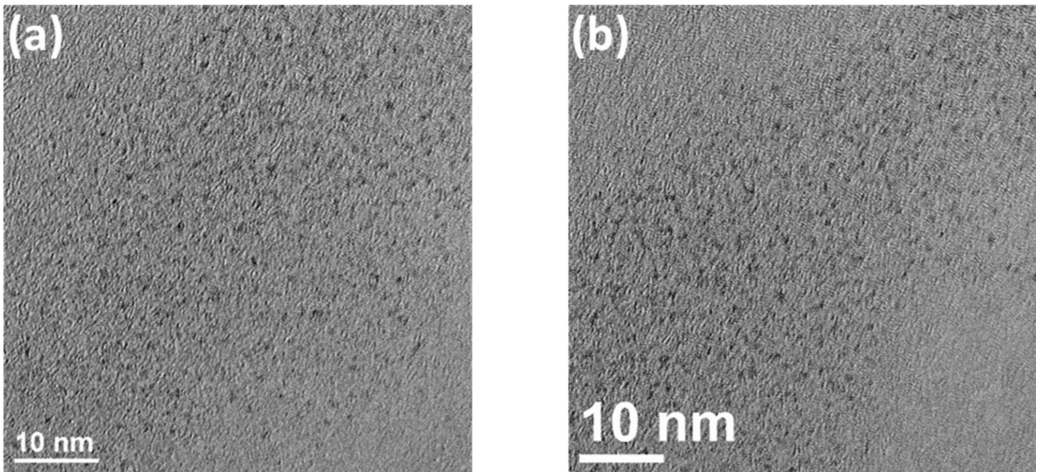


Fig. S41 TEM images of Type III-C rotaxane-branched dendrimer **G1**. The size range is 1.70 ± 0.20 nm.

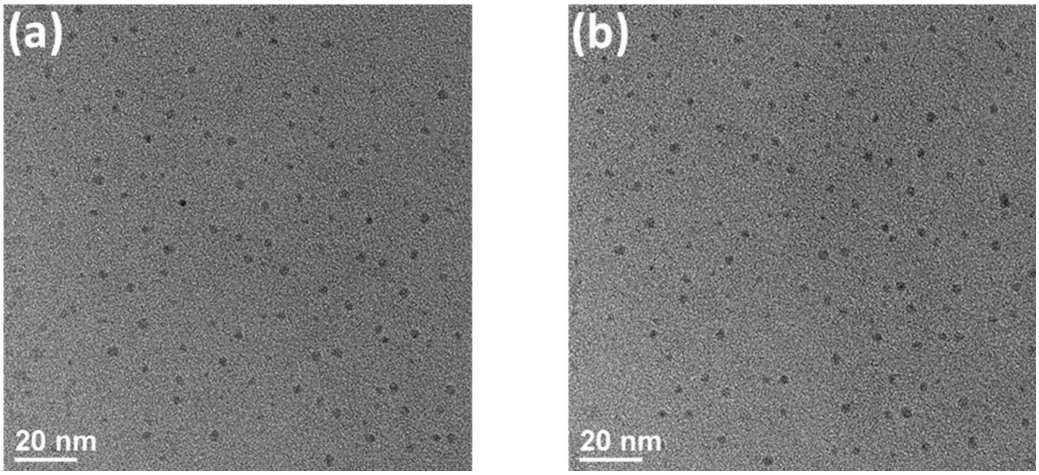


Fig. S42 TEM images of Type III-C rotaxane-branched dendrimer **G2**. The size range is 2.65 ± 0.22 nm.

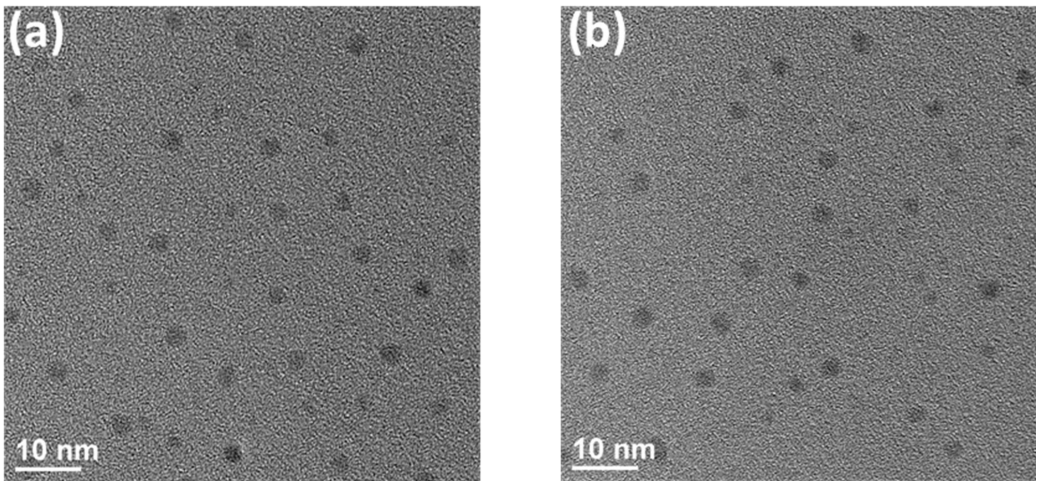


Fig. S43 TEM images of Type III-C rotaxane-branched dendrimer **G3**. The size range is 3.60 ± 0.30 nm.

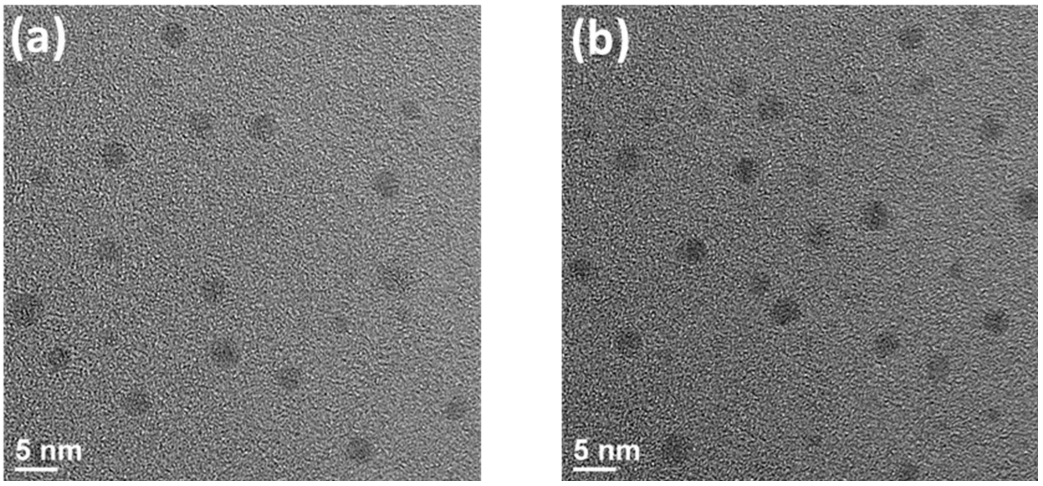
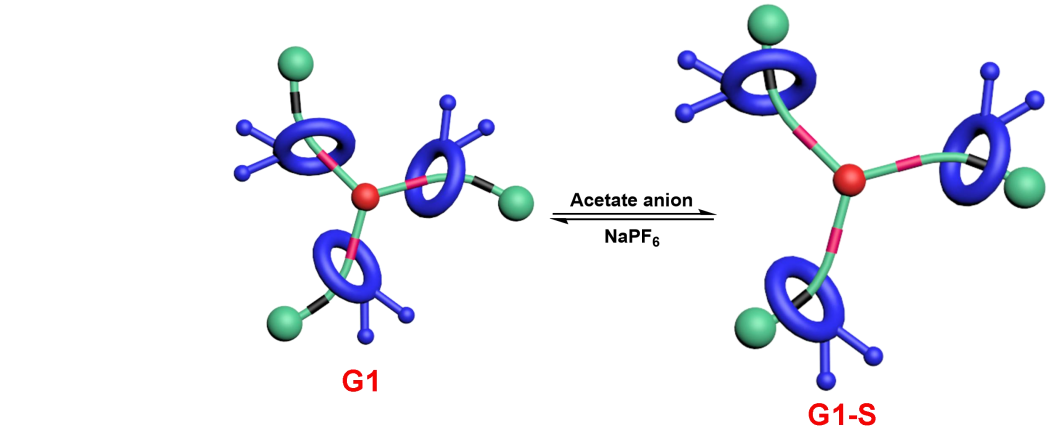


Fig. S44 TEM images of Type III-C rotaxane-branched dendrimer **G4**. The size range is 4.65 ± 0.30 nm.

Section D. Anion-induced dimension modulation of Type III-C rotaxane-branched dendrimers.

Scheme S7 Cartoon representation of anion-induced switching motion of Type III-C rotaxane-branched dendrimer **G1**.



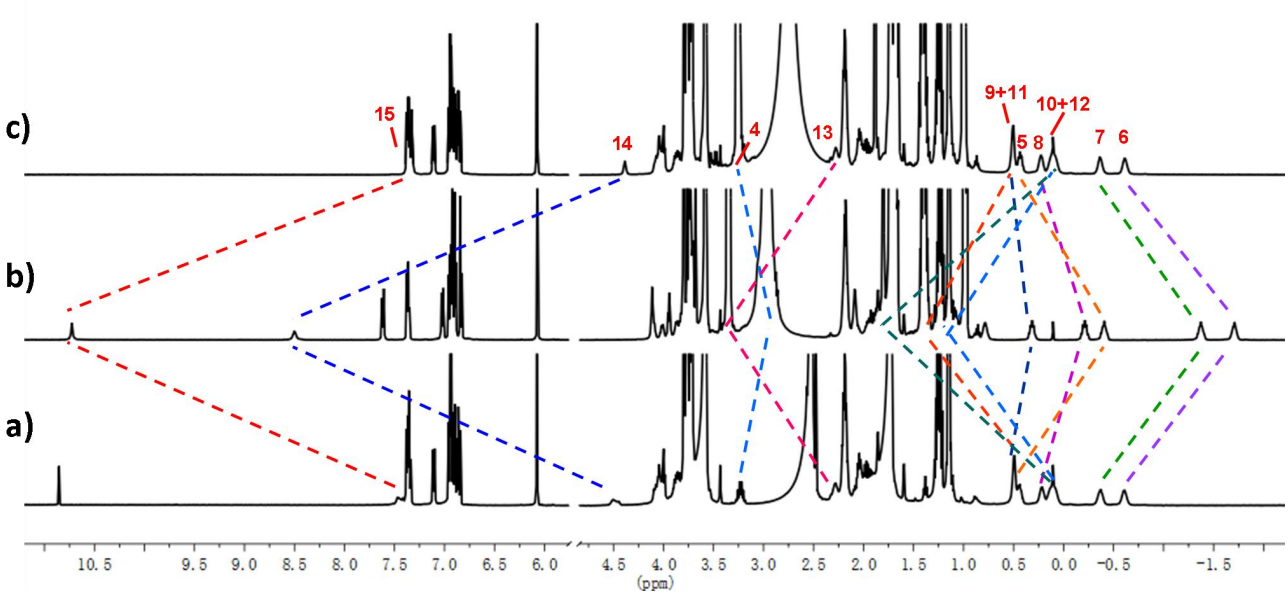
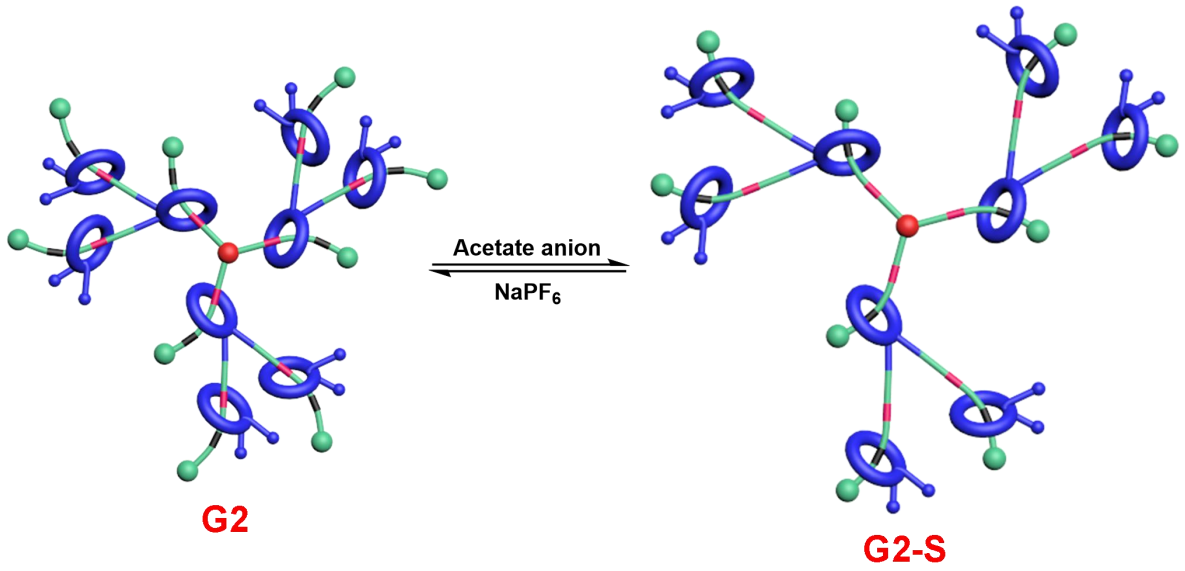


Fig. S45 ^{1}H NMR spectra (THF-d_8, 298 K, 500 MHz) of anion-induced switching behavior of Type III-C rotaxane-branched dendrimer **G1**. a) **G1**; b) **G1** with the addition of TBAA (5 eq. for each urea unit); c) the mixture after adding $NaPF_6$ (10 eq. for each urea unit) into the solution in b).

Scheme S8 Cartoon representation of anion-induced switching motion of Type III-C rotaxane-branched dendrimer **G2**.



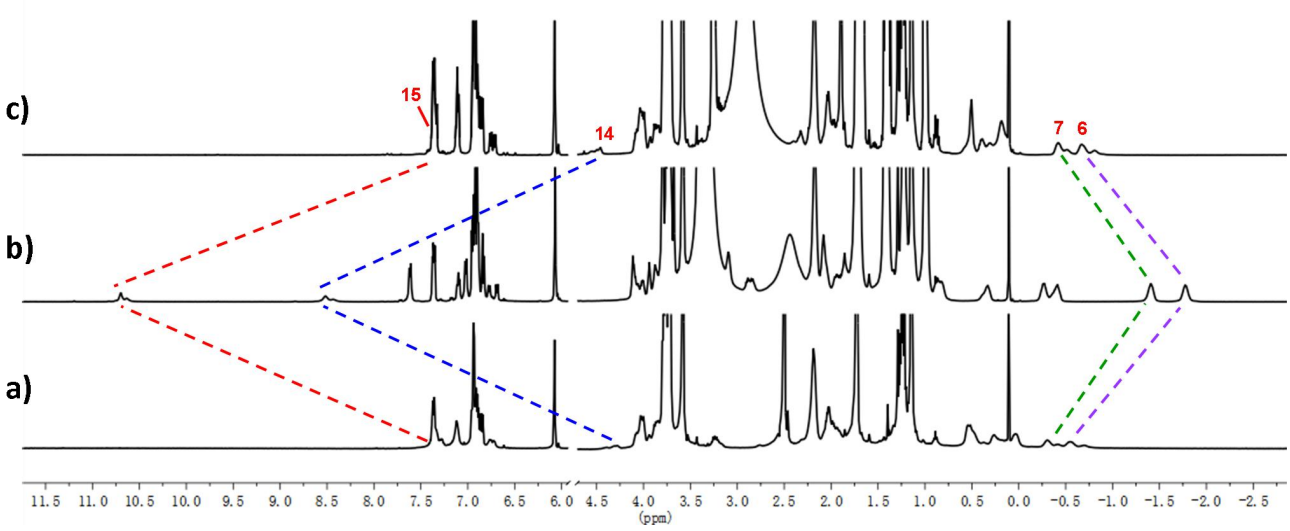
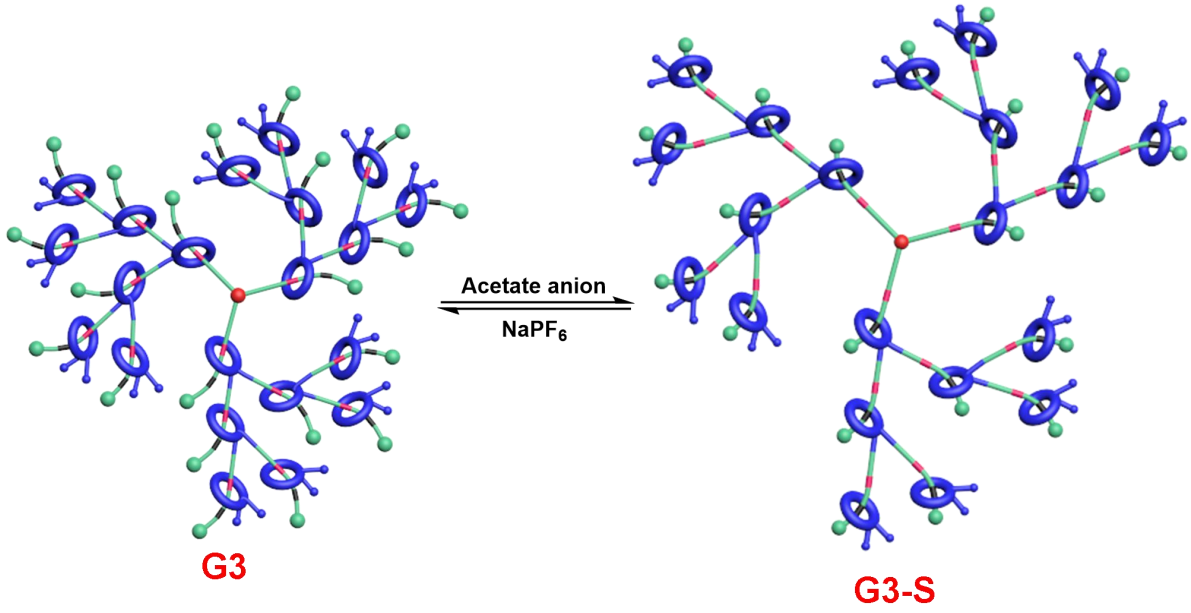


Fig. S46 ^{1}H NMR spectra (THF-d_8, 298 K, 500 MHz) of anion-induced switching behavior of Type III-C rotaxane-branched dendrimer **G2**. a) **G2**; b) **G2** with the addition of TBAA (5 eq. for each urea unit); c) the mixture after adding $NaPF_6$ (10 eq. for each urea unit) into the solution in b).

Scheme S9 Cartoon representation of anion-induced switching motion of Type III-C rotaxane-branched dendrimer **G3**.



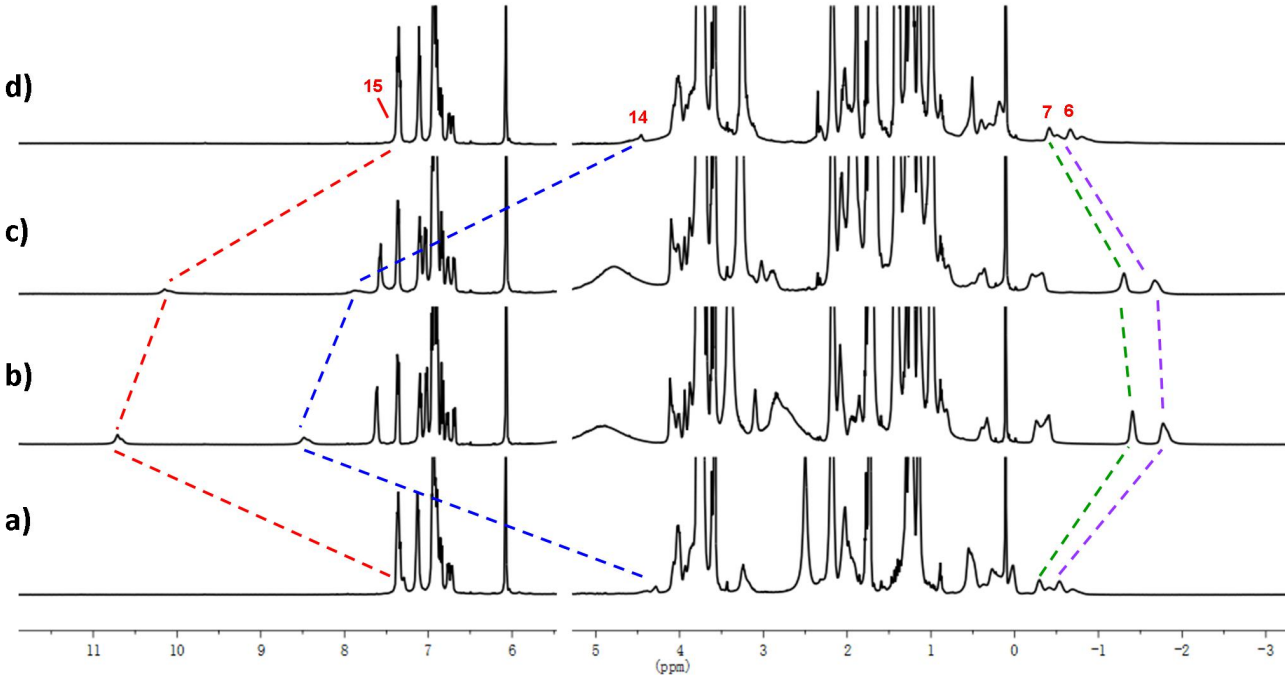
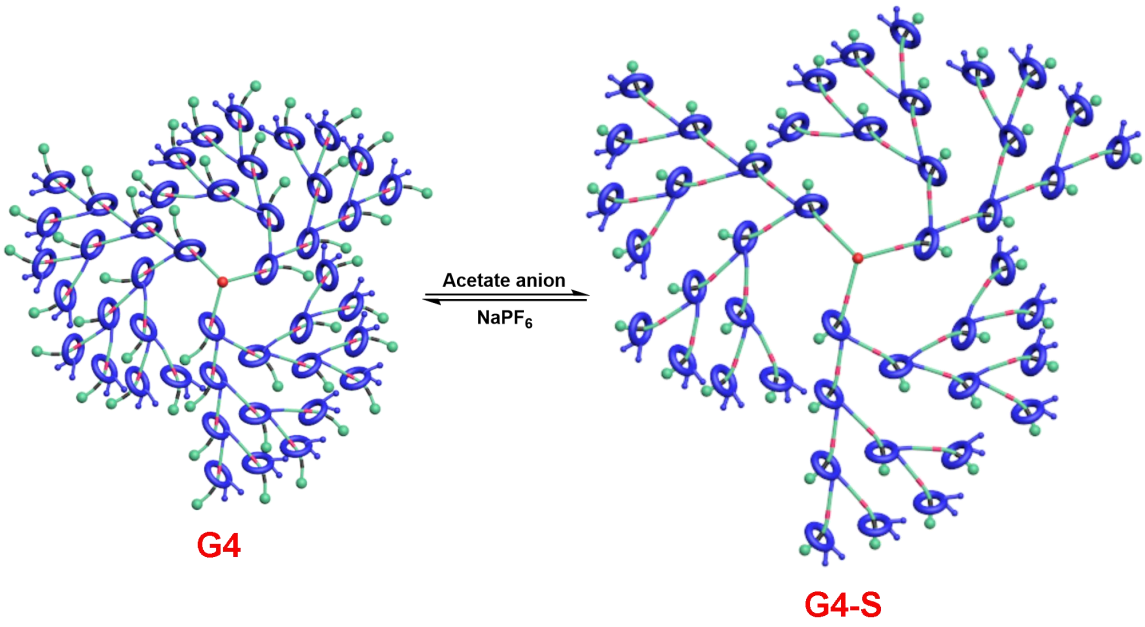


Fig. S47 ^{1}H NMR spectra (THF-d_8, 298 K, 500 MHz) of anion-induced switching behavior of Type III-C rotaxane-branched dendrimer **G3**. a) **G3**; b) **G3** with the addition of TBAA (5 eq. for each urea unit); the mixture after adding $NaPF_6$ into the solution in b): for c) $NaPF_6$ (10 eq. for each urea unit); d) $NaPF_6$ (12 eq. for each urea unit).

Scheme S10 Cartoon representation of anion-induced switching motion of Type III-C rotaxane-branched dendrimer **G4**.



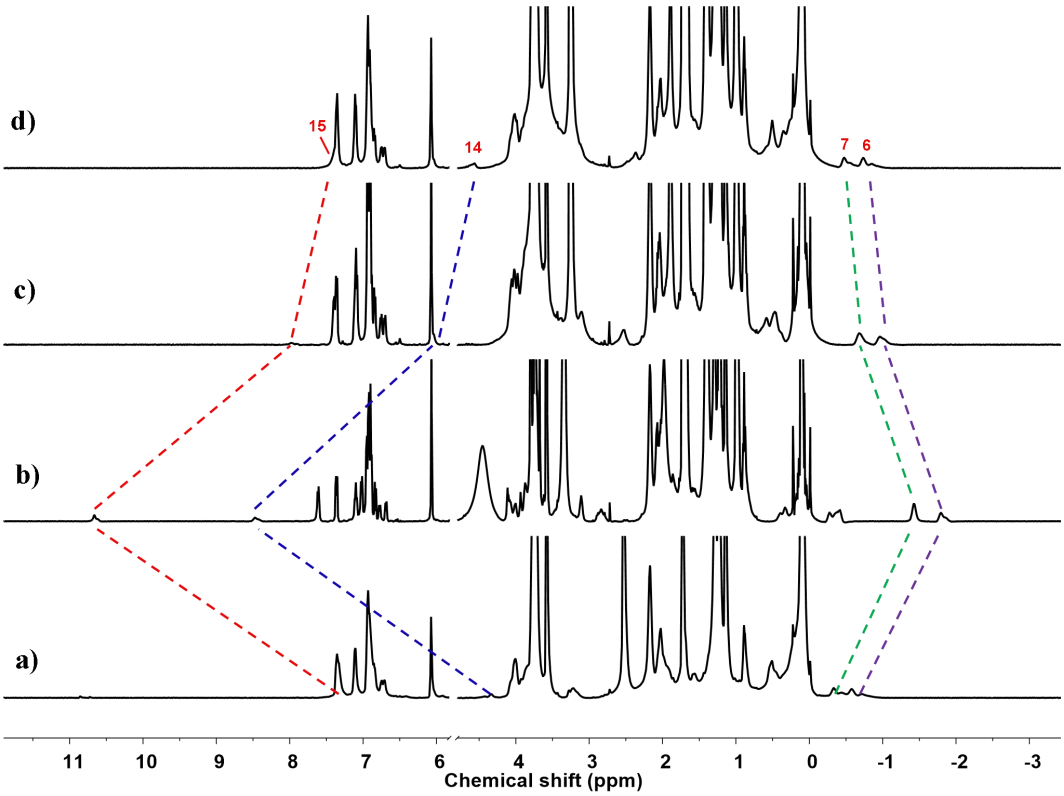


Fig. S48 ^{1}H NMR spectra (THF-d_8, 298 K, 500 MHz) of anion-induced switching behavior of Type III-C rotaxane-branched dendrimer **G4**. a) **G4**; b) **G4** with the addition of TBAA (5 eq. for each urea unit); the mixture after adding $NaPF_6$ into the solution in b): for c) $NaPF_6$ (12 eq. for each urea unit); d) $NaPF_6$ (14 eq. for each urea unit).

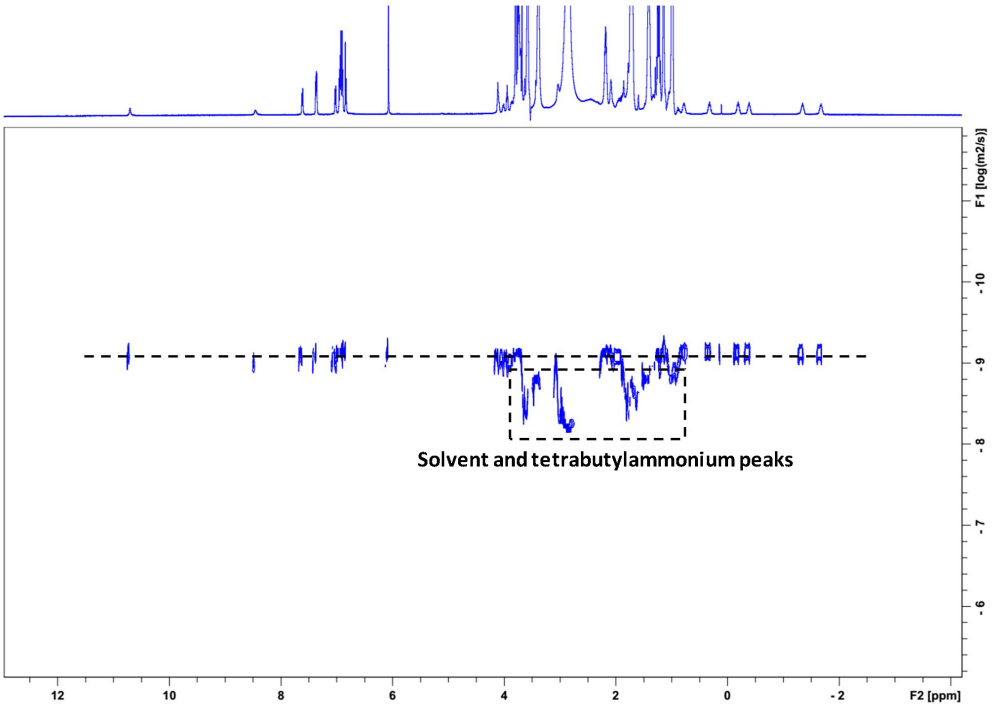


Fig. S49 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of Type III-C rotaxane-branched dendrimer **G1** with the addition of TBAA (5 eq. for each urea unit). The diffusion coefficient *D* is (8.91± 0.20) × 10^{-10} m^2s^{-1}.

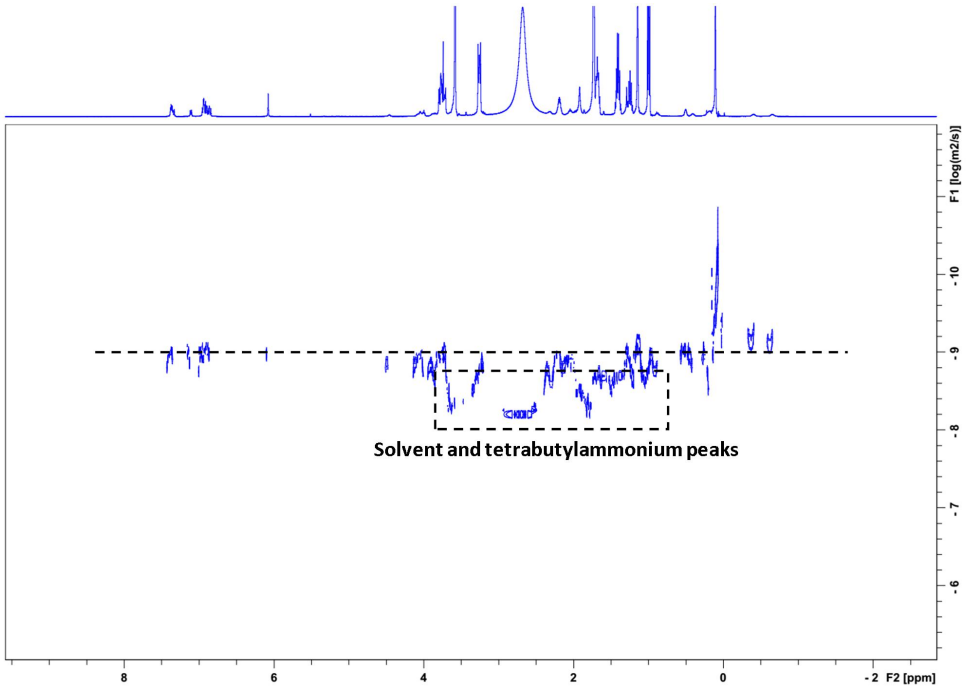


Fig. S50 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of the mixture after adding $NaPF_6$ into the solution of Type III-C rotaxane-branched dendrimer **G1** and TBAA.The diffusion coefficient *D* is (10.23± 0.25) × 10^{-10} m^2s^{-1}.

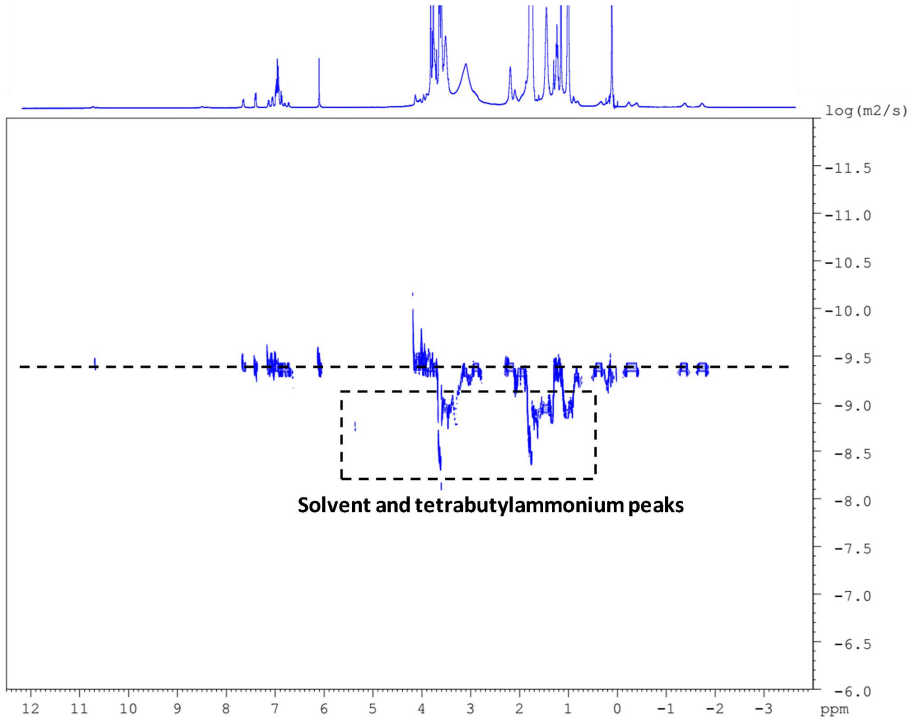


Fig. S51 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of Type III-C rotaxane-branched dendrimer **G2** with the addition of TBAA (5 eq. for each urea unit). The diffusion coefficient *D* is (3.98± 0.10) × 10^{-10} m^2s^{-1}.

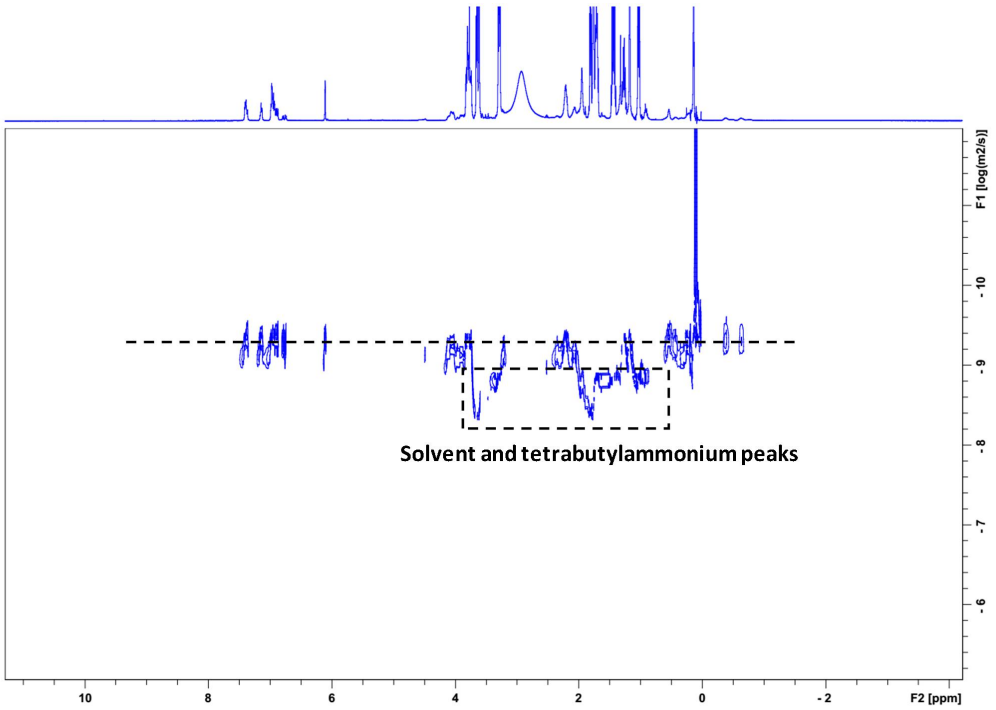


Fig. S52 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of the mixture after adding $NaPF_6$ into the solution of Type III-C rotaxane-branched dendrimer **G2** and TBAA.The diffusion coefficient *D* is (4.90± 0.20) × 10^{-10} m^2s^{-1}.

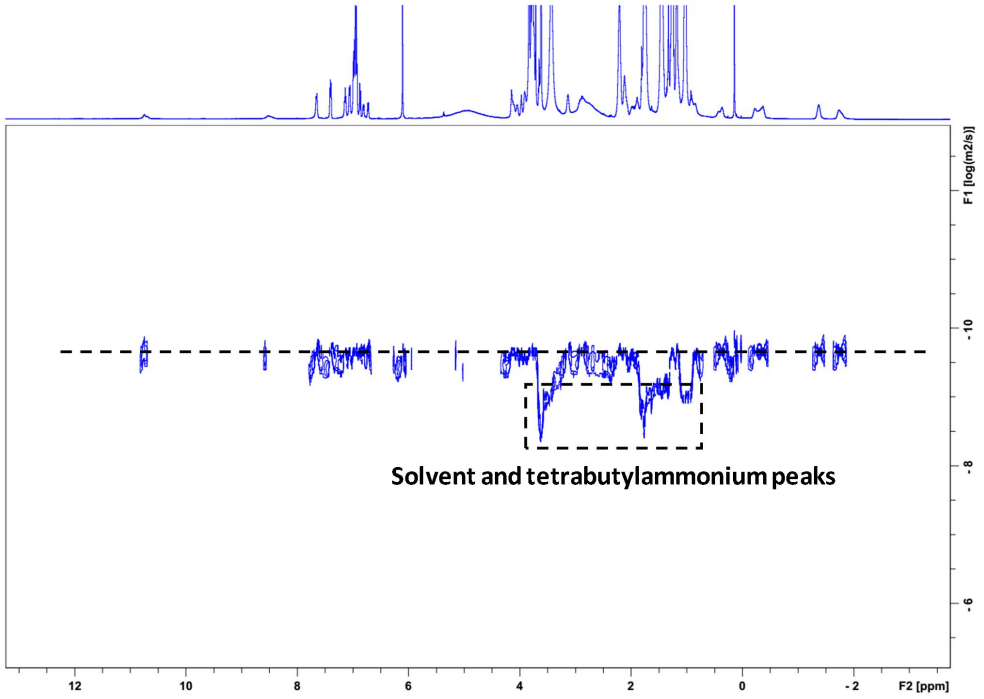


Fig. S53 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of Type III-C rotaxane-branched dendrimer **G3** with the addition of TBAA (5 eq. for each urea unit). The diffusion coefficient D is $(2.04\pm 0.15) \times 10^{-10}$ m^2s^{-1}.

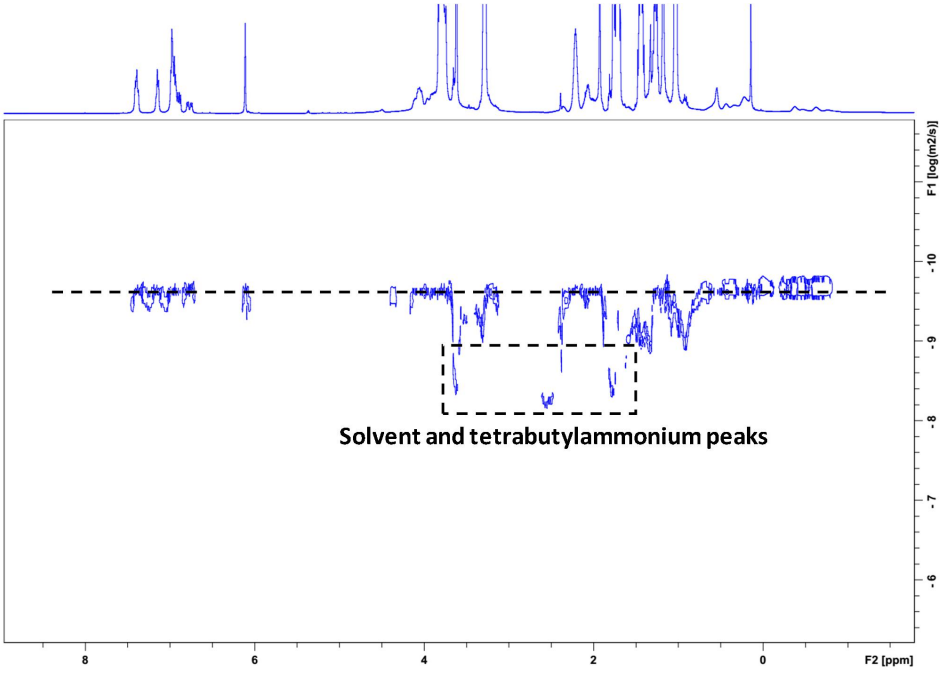


Fig. S54 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of the mixture after adding $NaPF_6$ into the solution of Type III-C rotaxane-branched dendrimer **G3** and TBAA. The diffusion coefficient D is $(2.51\pm 0.15) \times 10^{-10}$ m^2s^{-1}.

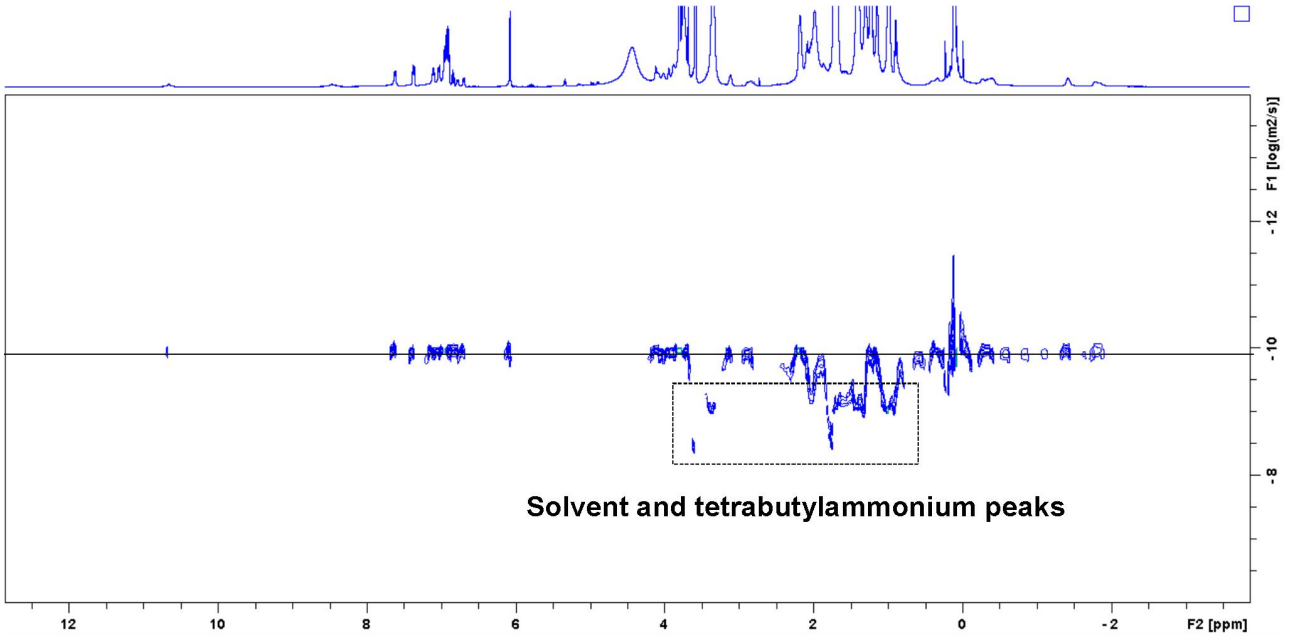


Fig. S55 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of Type III-C rotaxane-branched dendrimer **G4** with the addition of TBAA (5 eq. for each urea unit). The diffusion coefficient D is (1.20± 0.08) × 10^{-10} m^2s^{-1}.

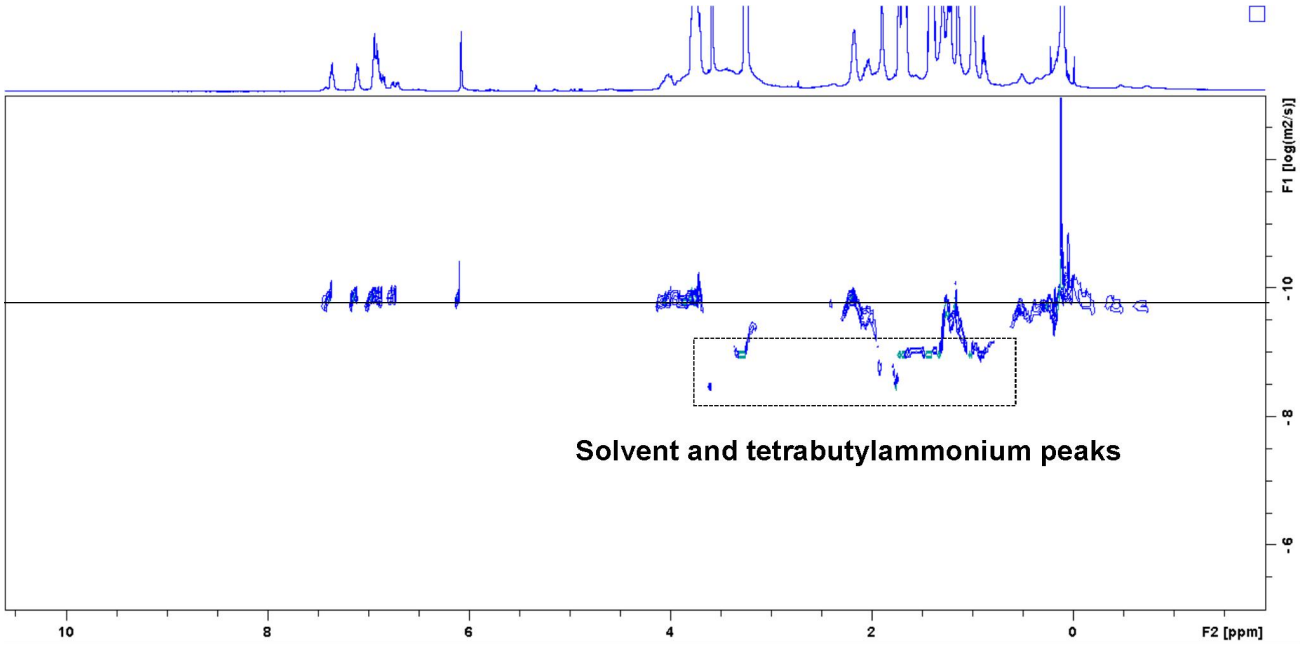


Fig. S56 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of the mixture after adding $NaPF_6$ into the solution of Type III-C rotaxane-branched dendrimer **G4** and TBAA. The diffusion coefficient D is (1.58± 0.10) × 10^{-10} m^2s^{-1}.

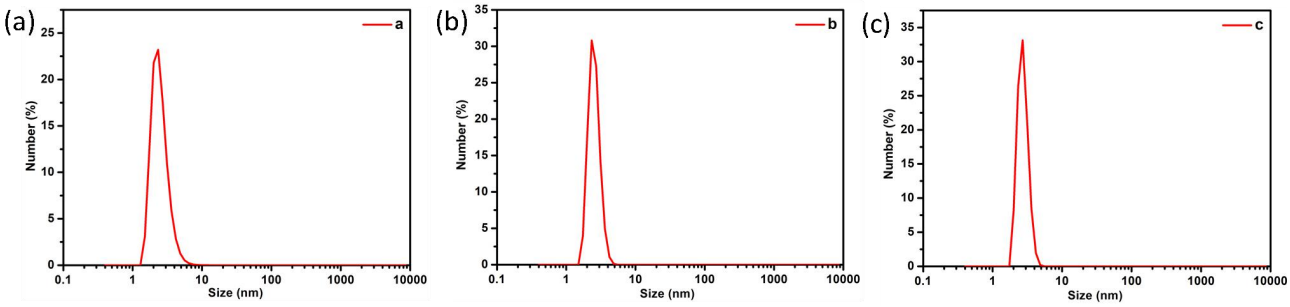


Fig. S57 DLS spectra of Type III-C rotaxane-branched dendrimer **G1** with the addition of TBAA (5 eq. for each urea unit): (a) 2.51 nm; (b) 2.55 nm; (c) 2.75 nm. The average hydrodynamic size was 2.60 ± 0.15 nm.

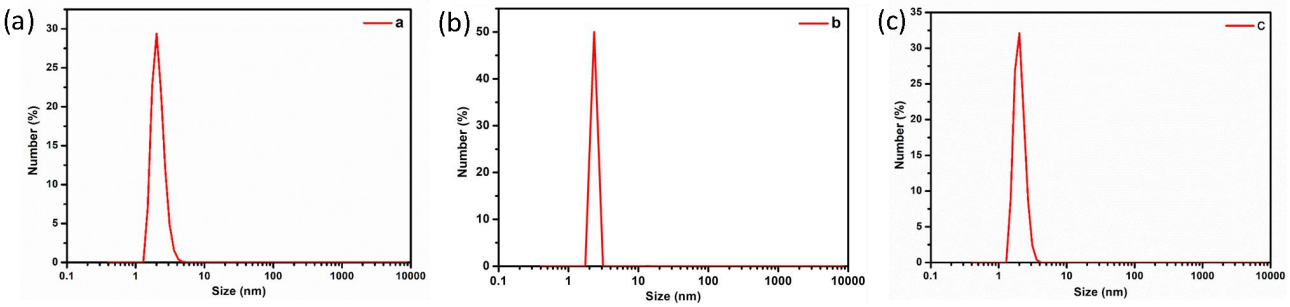


Fig. S58 DLS spectra of the mixture after adding $NaPF_6$ into the solution of Type III-C rotaxane-branched dendrimer **G1** and TBAA: (a) 2.16 nm; (b) 2.34 nm; (c) 2.05 nm. The average hydrodynamic size was 2.18 ± 0.16 nm.

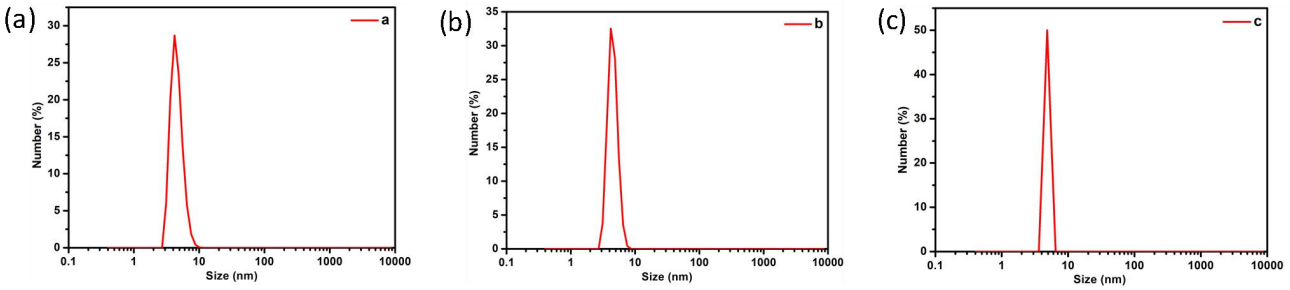


Fig. S59 DLS spectra of Type III-C rotaxane-branched dendrimer **G2** with the addition of TBAA (5 eq. for each urea unit): (a) 4.57 nm; (b) 4.88 nm; (c) 4.51 nm. The average hydrodynamic size was 4.65 ± 0.23 nm.

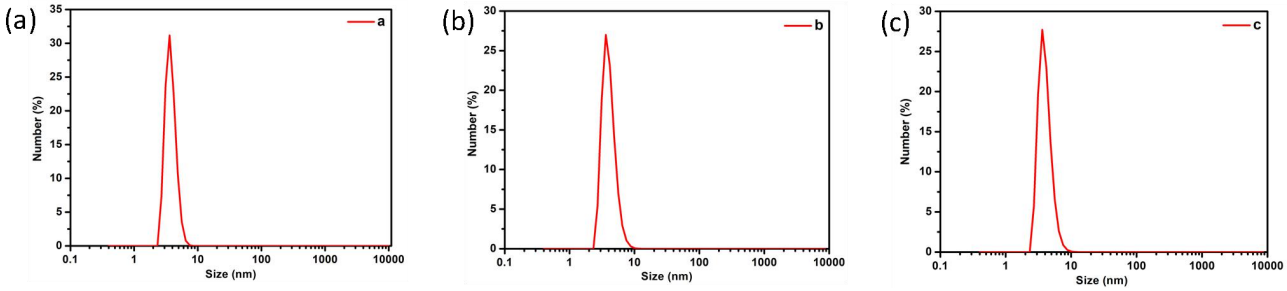


Fig. S60 DLS spectra of the mixture after adding $NaPF_6$ into the solution of Type III-C rotaxane-branched dendrimer **G2** and TBAA: (a) 3.79 nm; (b) 4.07 nm; (c) 4.02 nm. The average hydrodynamic size was 3.97 ± 0.18 nm.

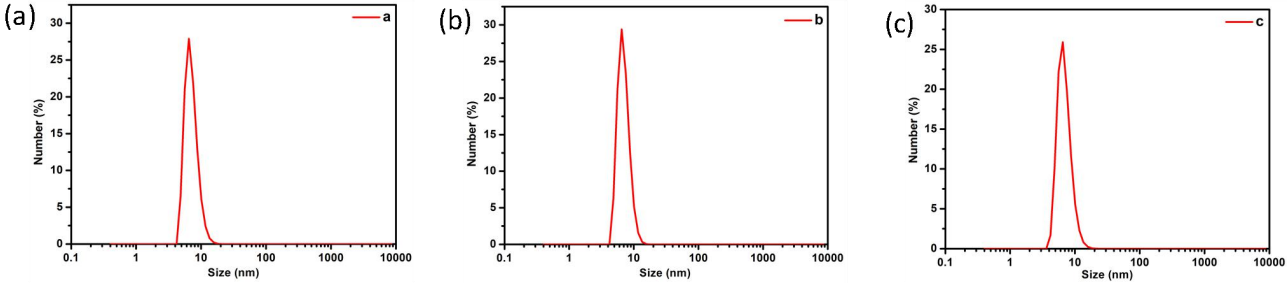


Fig. S61 DLS spectra of Type III-C rotaxane-branched dendrimer **G3** with the addition of TBAA (5 eq. for each urea unit): (a) 7.14 nm; (b) 7.02 nm; (c) 6.96 nm. The average hydrodynamic size was 7.04 ± 0.10 nm.

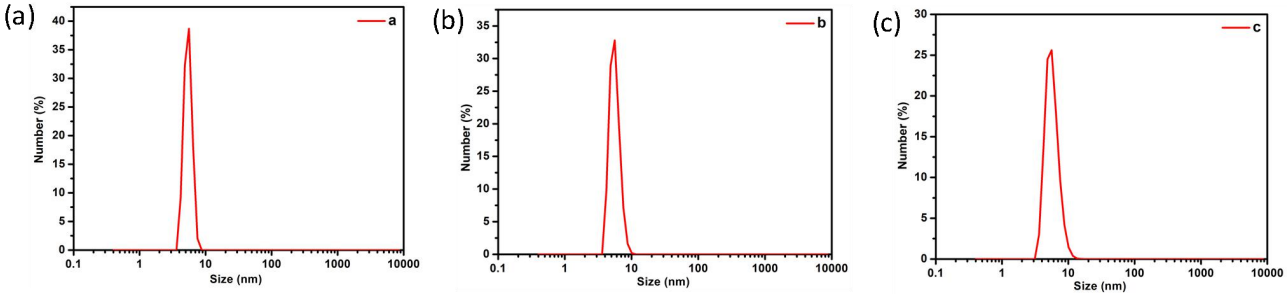


Fig. S62 DLS spectra of the mixture after adding $NaPF_6$ into the solution of Type III-C rotaxane-branched dendrimer **G3** and TBAA: (a) 5.43nm; (b) 5.62 nm; (c) 5.74 nm. The average hydrodynamic size was 5.60 ± 0.17 nm.

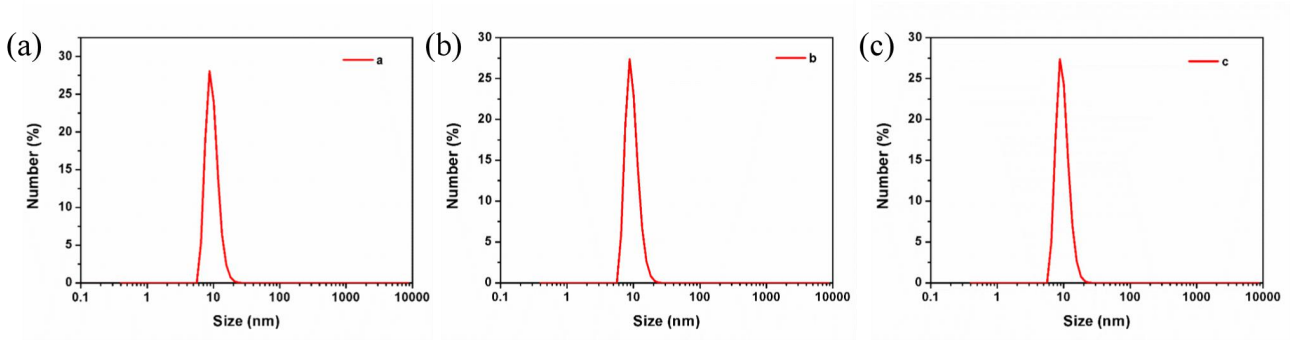


Fig. S63 DLS spectra of Type III-C rotaxane-branched dendrimer **G4** with the addition of TBAA (5 eq. for each urea unit): (a) 9.69 nm; (b) 9.70 nm; (c) 9.79 nm. The average hydrodynamic size was 9.73 ± 0.05 nm.

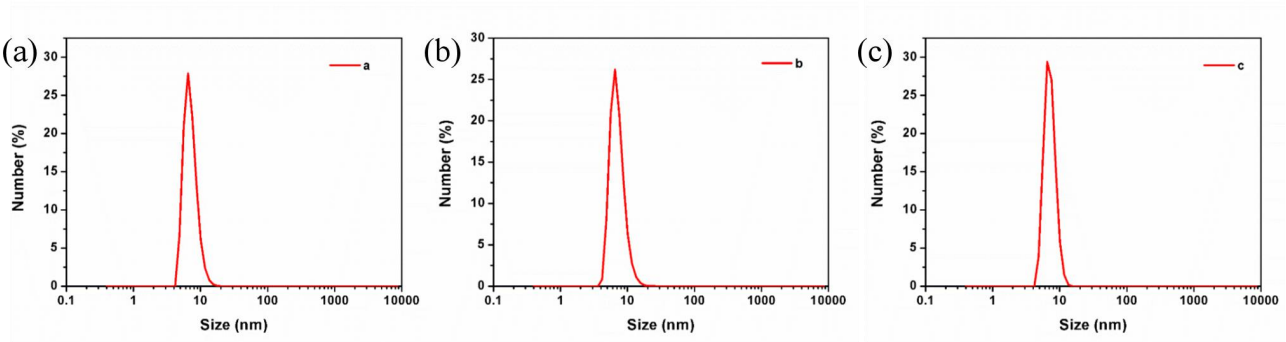


Fig. S64 DLS spectra of the mixture after adding $NaPF_6$ into the solution of Type III-C rotaxane-branched dendrimer **G4** and TBAA: (a) 7.15 nm; (b) 7.15 nm; (c) 7.20 nm. The average hydrodynamic size was 7.17 ± 0.03 nm.

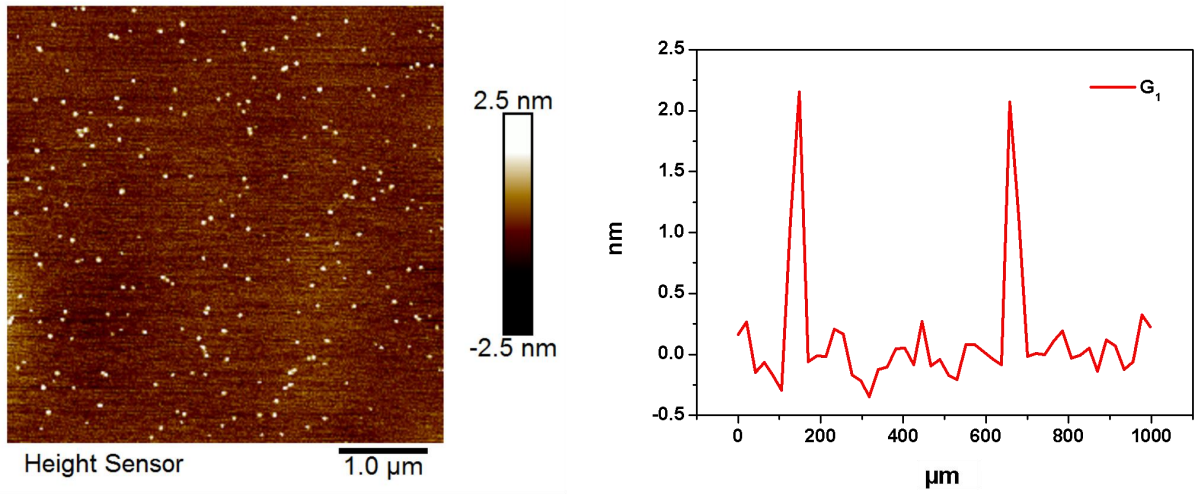


Fig. S65 AFM image of Type III-C rotaxane-branched dendrimer **G1** with the addition of TBAA (5 eq. for each urea unit) (*left*) and the height range is 2.11 ± 0.23 nm (*right*).

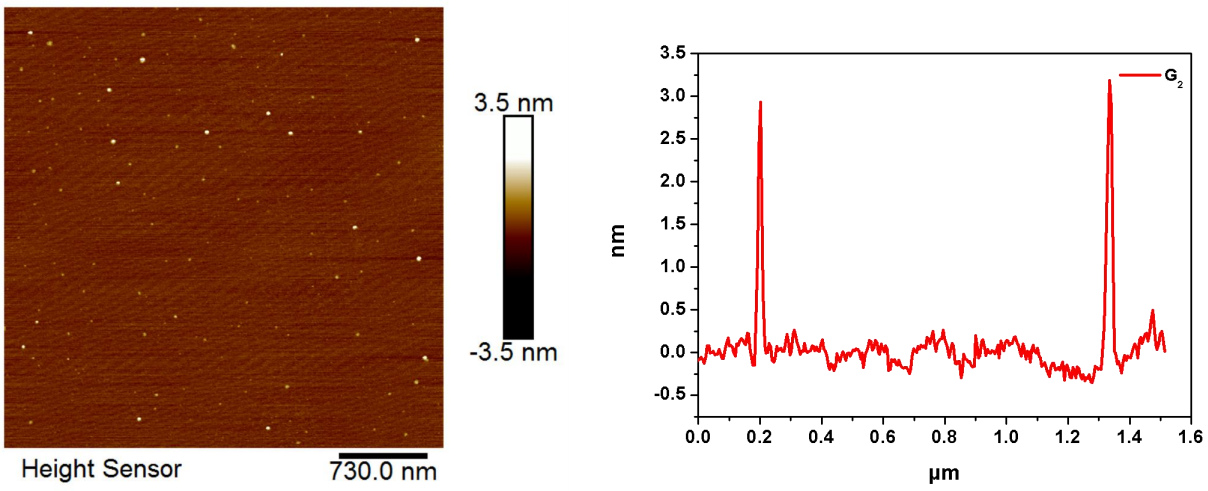


Fig. S66 AFM image of Type III-C rotaxane-branched dendrimer **G2** with the addition of TBAA (5 eq. for each urea unit) (*left*) and the height range is 3.05 ± 0.19 nm (*right*).

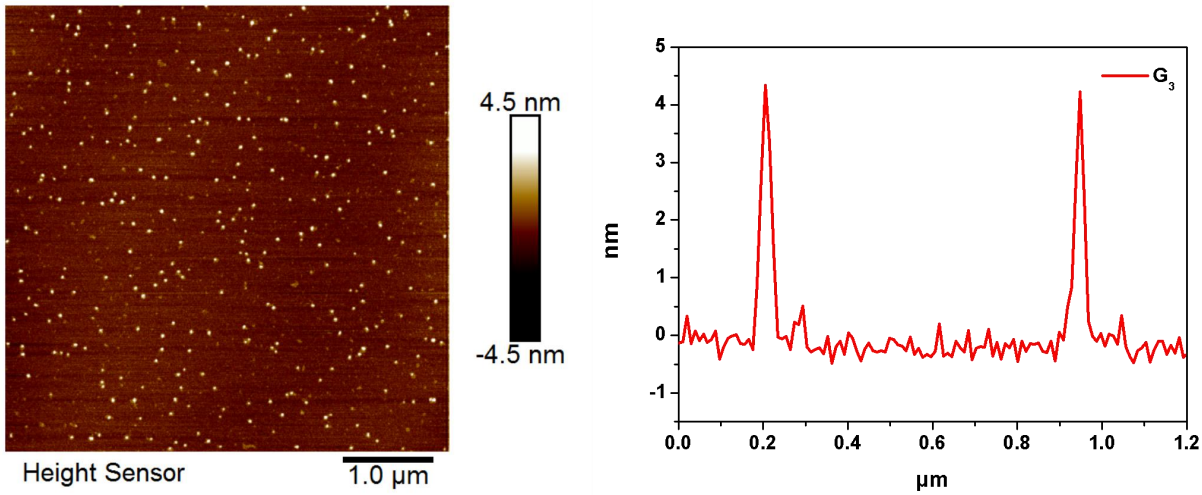


Fig. S67 AFM image of Type III-C rotaxane-branched dendrimer **G3** with the addition of TBAA (5 eq. for each urea unit) (*left*) and the height range is 4.29 ± 0.16 nm (*right*).

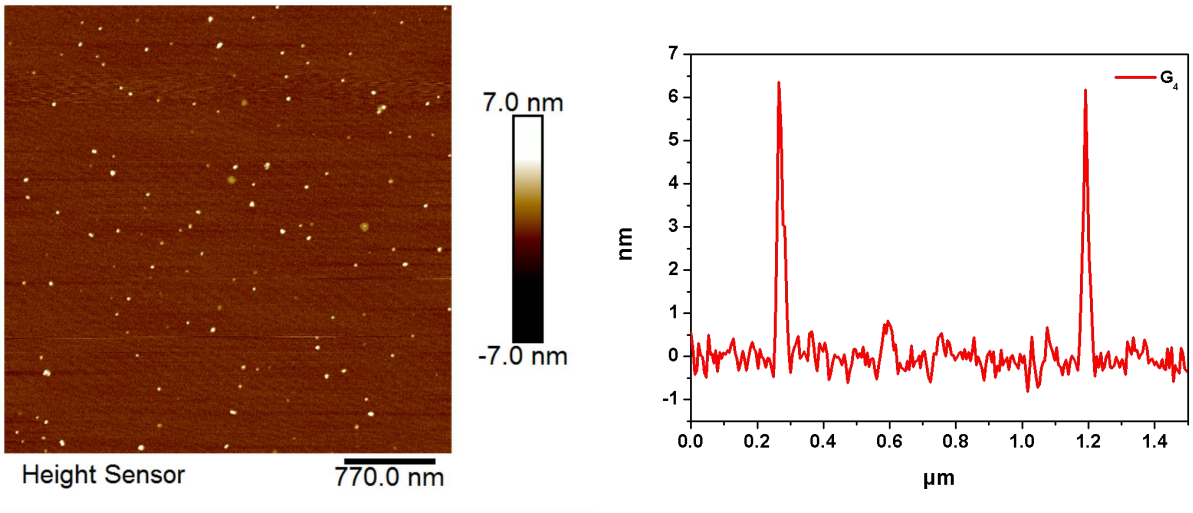


Fig. S68 AFM image of Type III-C rotaxane-branched dendrimer **G4** with the addition of TBAA (5 eq. for each urea unit) (*left*) and the height range is 6.47 ± 0.28 nm (*right*).

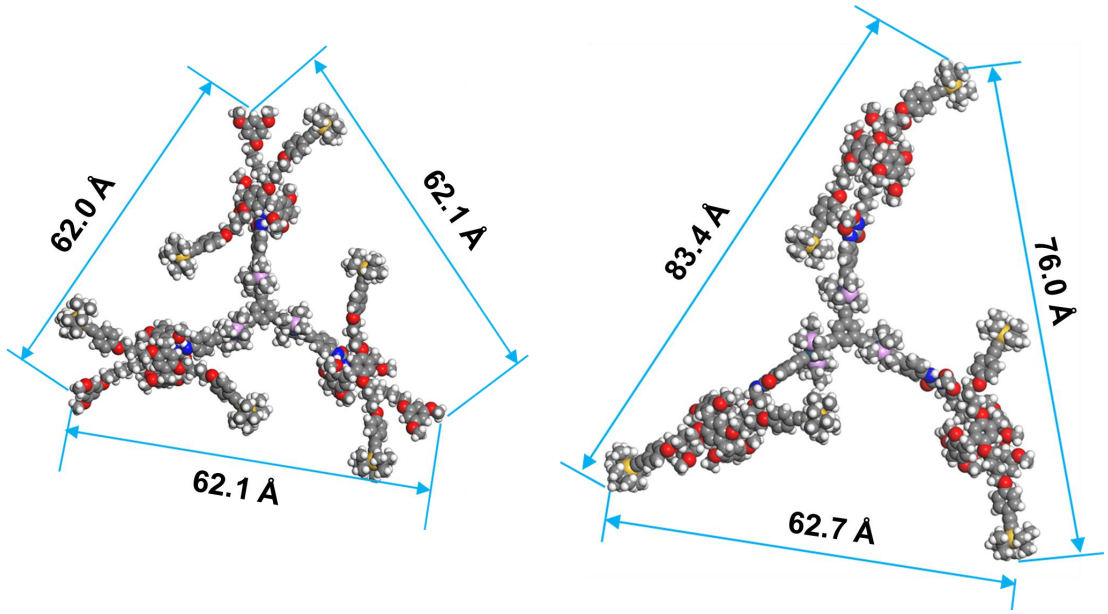


Fig. S69 Optimized structures of the Type III-C rotaxane-branched dendrimer **G1** before *(left)* and after *(right)* the addition of TBAA as stimulus. According to the simulations, the swelling ratio of **G1** is 17% after the addition of TBAA.

Table S1. Surface Areas of **G2** and **G2-S** Calculated by Different Probe Radii.

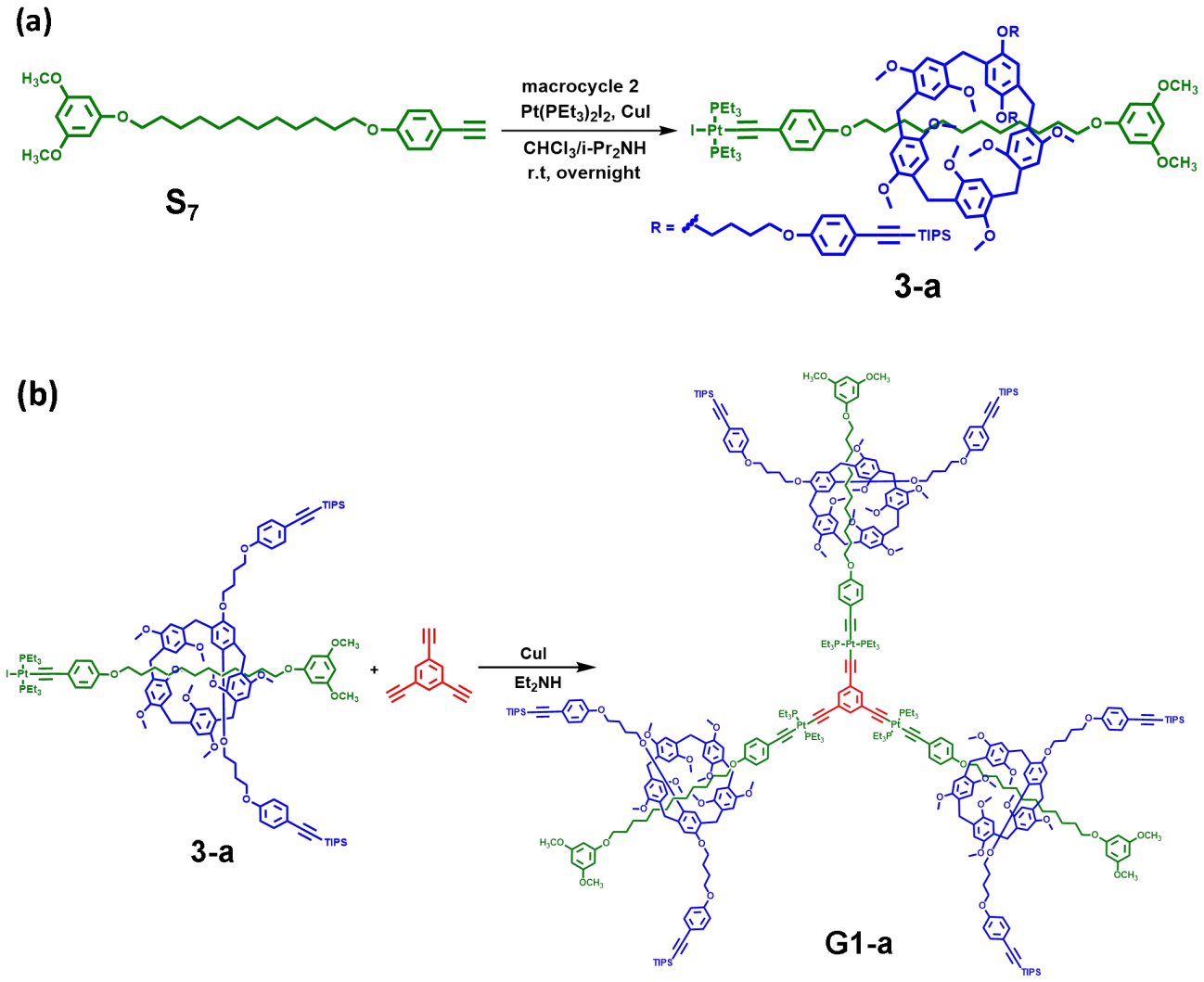
Probe radius / Å	**40**	**50**	**60**	**70**	**80**
S_{G2}/Å^2	14180.5	14501.8	14789.8	15044.2	15257.8
$S_{G2\text{-}S}$/Å^2	22740.9	23481.8	24100.3	24563.4	25002.2
$(S_{G2\text{-}S}/S_{G2})^{-1/2}$	1.27	1.27	1.28	1.28	1.28

Table S2. Volumes of **G2** and **G2-S** Calculated by Different Probe Radii.

Probe radius / Å	**40**	**50**	**60**	**70**	**80**
V_{G2}/Å^3	72296.9	77602.0	82017.9	85604.3	88588.1
$V_{G2\text{-}S}$/Å^3	101103.5	115600.0	128814.9	138435.8	147402.1
$(V_{G2\text{-}S}/V_{G2})^{-1/2}$	1.18	1.22	1.25	1.27	1.29

Section E. Synthesis of the model rotaxane-branched dendrimer G1-a.

Scheme S11: The synthesis route of (a) model [2]rotaxane **3-a** without urea moiety in the axle component and (b) model first-generation rotaxane-branched dendrimer **G1-a** from corresponding building block [2]rotaxane **3-a**.



Synthesis of [2]rotaxane 3-a: A Schlenk flask was charged with $\mathbf{S_7}$ (100 mg, 0.23 mmol), macrocycle component **1** (1.57 g, 1.14 mmol) and $Pt(PEt_3)_2I_2$ (630 mg, 0.92 mmol). The Schlenk flask was then evacuated and back-filled with N_2 three times. Next, the mixture solvent of degassed $CHCl_3$ and i-Pr_2NH (v/v, 6/3 mL) was added via syringe. The resultant solution was stirred for one hour under -10 °C. Then CuI (4 mg) was added to the mixture under an inert atmosphere and the mixture was allowed to warm to room temperature and stirred overnight. The solution was concentrated and the residue was purified by column chromatography (SiO_2; PE/DCM). A pale yellow solid **3-a** (360 mg, 66%) was obtained. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.38-7.40 (m, 4H), 7.21-7.22 (m, 2H), 6.75-6.90 (m, 16H), 6.06 (s, 3H), 3.70-4.01 (m, 48H), 3.38-3.42 (m, 2H),

3.18-3.23 (m, 2H), 2.20-2.24 (m, 12H), 1.90-2.01 (m, 8H), 1.13-1.20 (m, 60H), 0.77-0.80 (m, 2H), 0.66 (m, 4H), 0.44-0.48 (m, 4H), 0.33 (m, 2H), 0.06 (m, 2H), -0.07 (m, 2H), -0.25 (m, 2H), -0.50 (m, 2H). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 8.86. ^{13}C NMR (126 MHz, CD_2Cl_2): δ 171.29, 162.04, 161.65, 159.66, 157.93, 150.80, 150.78, 150.76, 150.75, 150.72, 150.70, 150.23, 150.16, 133.79, 133.78, 132.01, 128.80, 128.71, 128.53, 128.51, 128.46, 128.39, 120.89, 115.93, 115.89, 114.74, 114.72, 114.53, 114.43, 113.81, 113.77, 113.60, 113.52, 113.46, 107.60, 107.57, 99.91, 93.87, 92.27, 88.98, 88.95, 87.13, 87.02, 68.68, 68.67, 68.30, 68.21, 68.19, 64.58, 31.11, 30.68, 30.64, 29.73, 29.62, 29.42, 29.36, 29.23, 27.08, 27.06, 26.74, 25.07, 24.67, 21.15, 19.56, 18.89, 17.19, 17.05, 16.91, 14.97, 13.93, 11.80, 8.52, 8.26. MALDI-TOF-MS: Calculated for [**3-a** + H]$^+$: *m/z* = 2375.07; Found: *m/z* = 2375.1.

Synthesis of the first-generation model rotaxane-branched dendrimer G1-a: A mixture of model compound [2]rotaxane **3-a** (110 mg, 0.046 mmol) and 1, 3, 5-triethynylbenzene (2.1 mg, 0.014 mmol) were added in a Schlenk flask, the Schlenk flask was then evacuated and back-filled with N_2 three times. Next, degassed diethylamine (8.0 mL) and a catalytic amount of CuI were added under an inert atmosphere. The reaction was stirred overnight at room temperature. The solvent was evaporated and the residue was purified by column chromatography (SiO_2; PE/DCM) and preparative gel permeation chromatography (GPC) to yield a pale-yellow solid **G1-a** (40 mg, 42%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.38-7.41 (m, 12H), 7.19-7.21 (m, 6H), 6.80-6.94 (m, 45H), 6.74-6.75 (m, 6H), 6.06 (s, 9H), 3.70-4.02 (m, 144H), 3.38-3.43 (m, 6H), 3.19-3.24 (m, 6H), 2.15-2.21 (m, 36H), 1.91-2.02 (m, 24H), 1.13-1.27 (m, 180H), 0.78-0.81 (m, 6H), 0.65-0.68 (m, 12H), 0.44-0.47 (m, 12H), 0.31 (m, 6H), 0.05-0.06 (m, 6H), -0.06 (m, 6H), -0.26 (m, 6H), -0.50 (m, 6H). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 11.66. ^{13}C NMR (126 MHz, CD_2Cl_2): δ 171.32, 171.22, 162.03, 161.64, 159.67, 159.65, 150.78, 150.75, 150.71, 150.19, 150.16, 133.78, 133.77, 132.18, 128.77, 128.70, 128.51, 128.48, 128.44, 128.38, 115.89, 115.88, 114.75, 114.70, 114.53, 114.41, 113.80, 113.74, 113.57, 113.51, 107.57, 93.85, 92.27, 88.95, 80.43, 68.67, 68.26, 68.20, 68.16, 64.58, 60.64, 55.91, 55.85, 55.79, 55.68, 55.65, 55.62, 42.31, 31.10, 31.09, 30.66, 30.63, 29.73, 29.61, 29.41, 29.34, 29.24, 27.46, 27.04, 26.71, 25.41, 25.09, 24.65, 21.18, 21.14, 19.53, 18.87, 18.85, 16.96, 16.82, 16.68, 14.41, 13.89, 12.01, 11.78, 11.56, 8.59. MALDI-TOF-MS: Calculated for [**G1-a** + H]$^+$: *m/z* = 6895.1; Found: *m/z* = 6898.7.

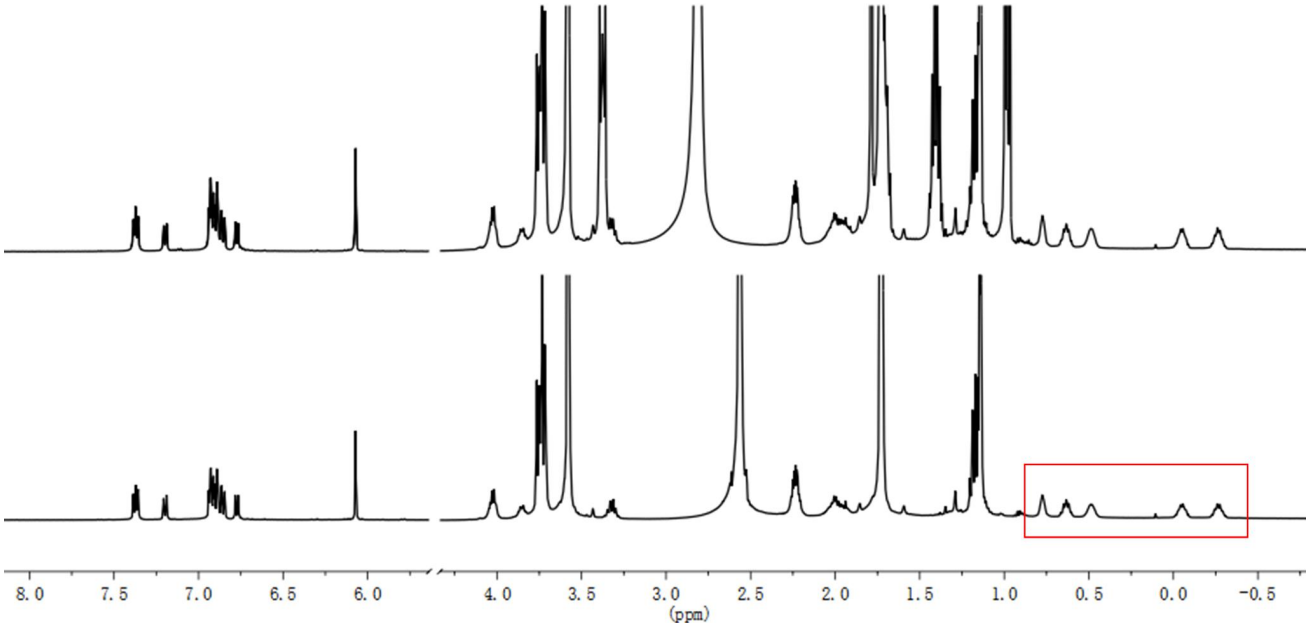


Fig. S70 ^{1}H NMR spectra (THF-d_8, 298 K, 500 MHz) of the model compound [2]rotaxane **3-a** *(bottom)*; model complex **3-a** with the addition of TBAA (5 eq.) *(top)*.

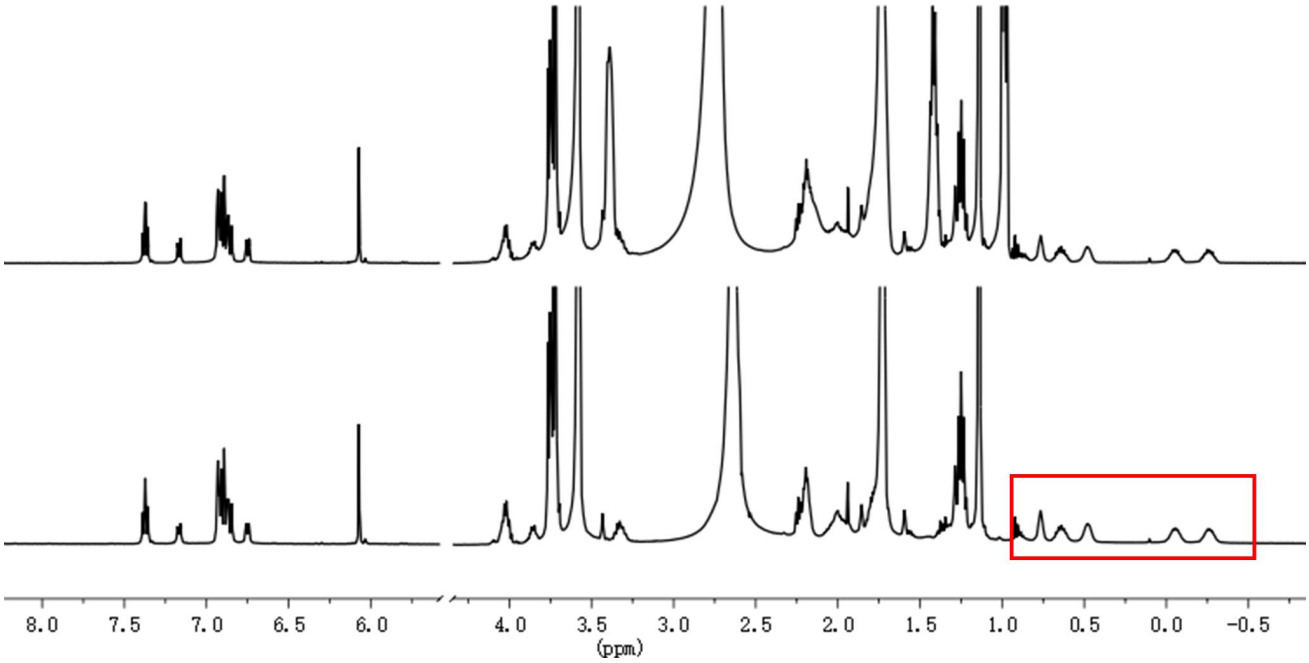


Fig. S71 ^{1}H NMR spectra (THF-d_8, 298 K, 500 MHz) of the model dendrimer **G1-a** *(bottom)*; model complex **G1-a** with the addition of TBAA (15 eq.) *(top)*.

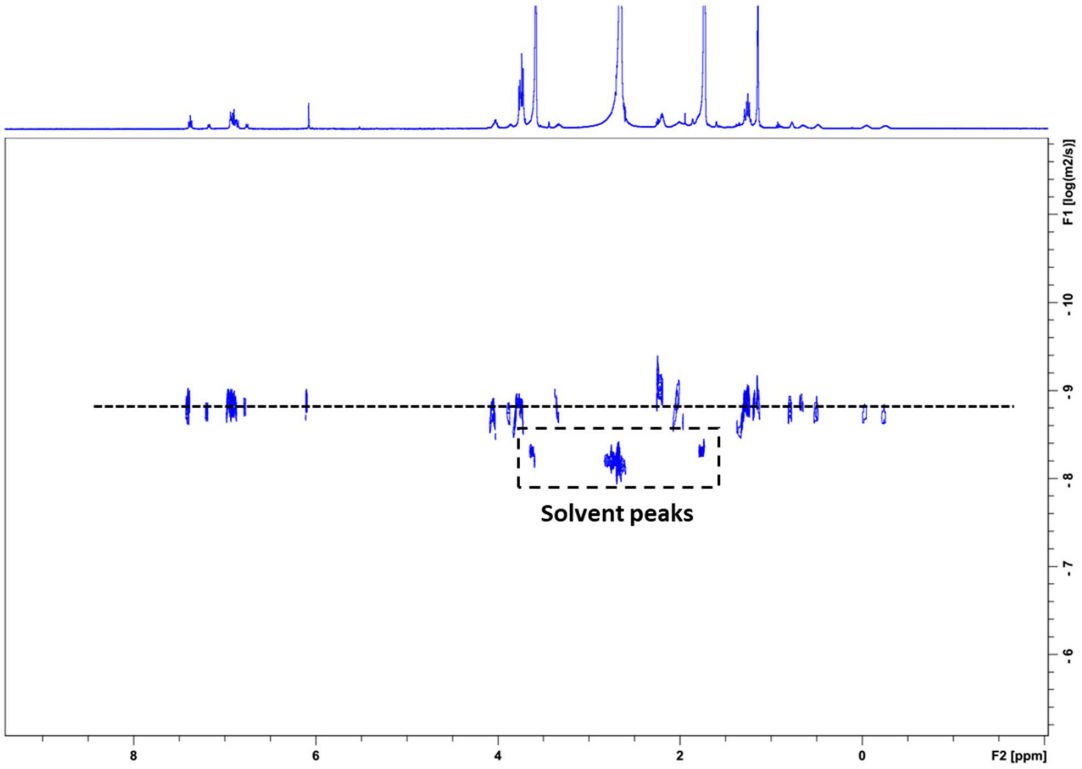


Fig. S72 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of the model rotaxane-branched dendrimer **G1-a**. The diffusion coefficient D is (1.55±0.14) × 10^{-9} m^2 s^{-1}.

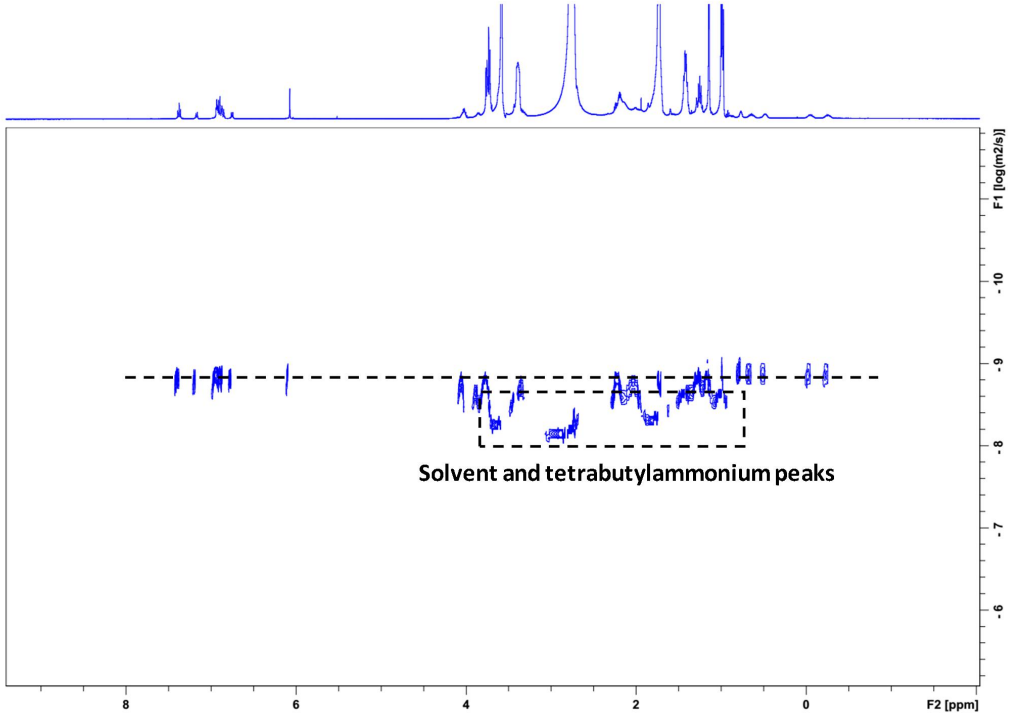


Fig. S73 2-D DOSY spectrum (THF-d_8, 298 K, 500 MHz) of the model rotaxane-branched dendrimer **G1-a** with the addition of TBAA (5 eq. for each urea unit).The diffusion coefficient D is (1.48±0.12) × 10^{-9} m^2 s^{-1}.

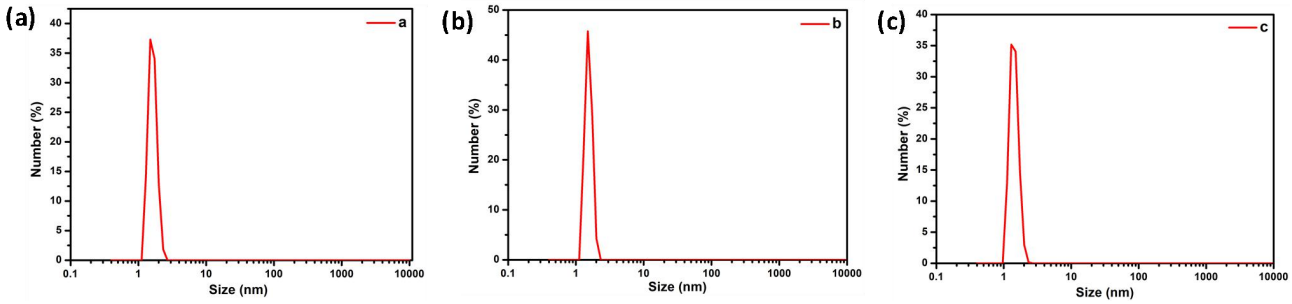


Fig. S74 DLS spectra of model rotaxane-branched dendrimer **G1-a**: (a) 1.63 nm; (b) 1.55 nm; (c) 1.43 nm. The average hydrodynamic size was 1.54 ± 0.11 nm.

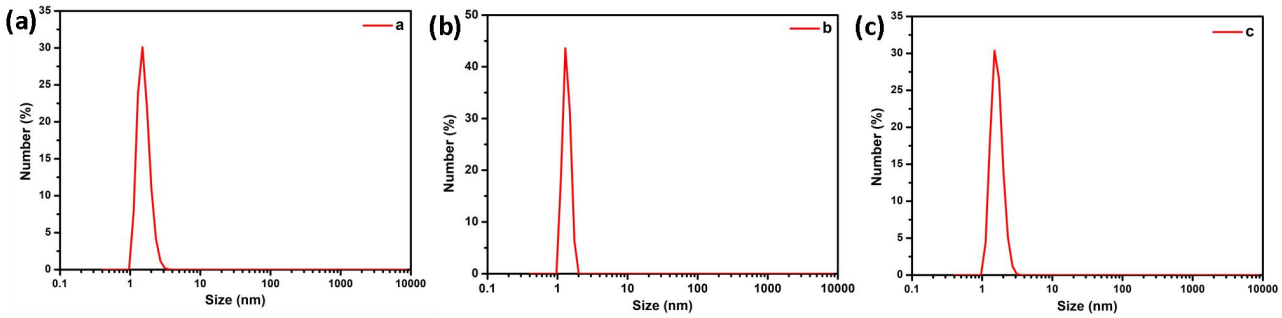


Fig. S75 DLS spectra of model rotaxane-branched dendrimer **G1-a** with the addition of TBAA (15 eq.): (a) 1.58 nm; (b) 1.35 nm; (c) 1.64 nm. The average hydrodynamic size was 1.52 ± 0.17 nm.

Section F. Supplementary data

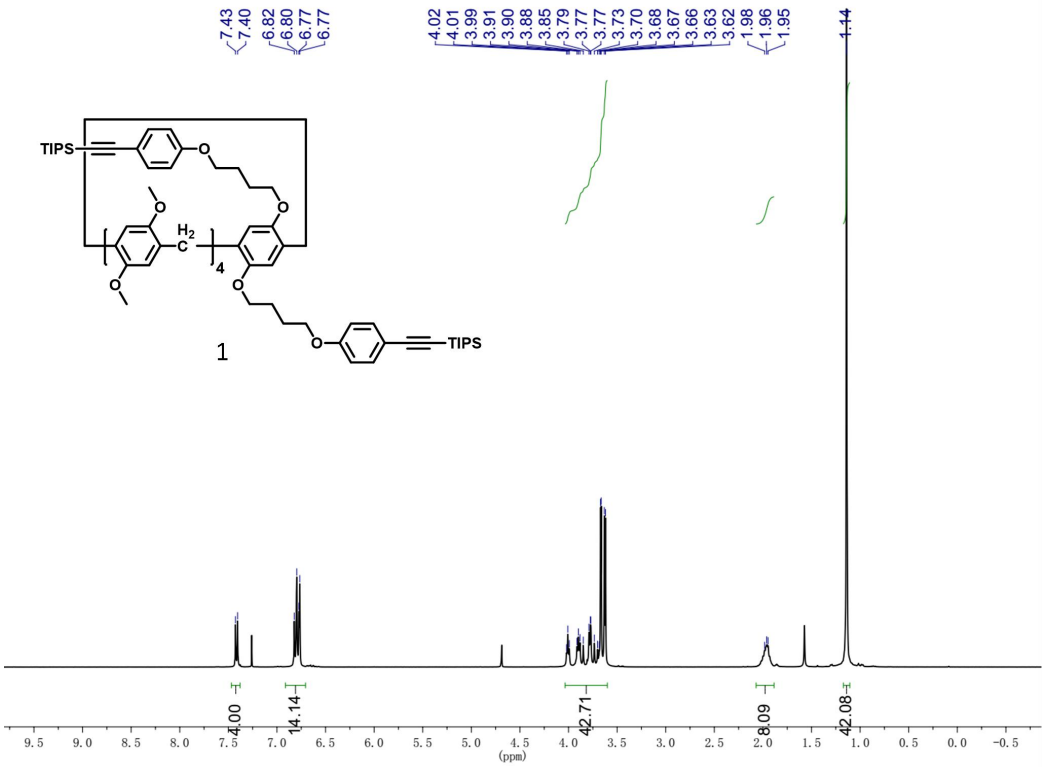


Fig. S76 ^{1}H NMR spectrum ($CDCl_3$, 298 K, 400 MHz) of macrocycle **1**.

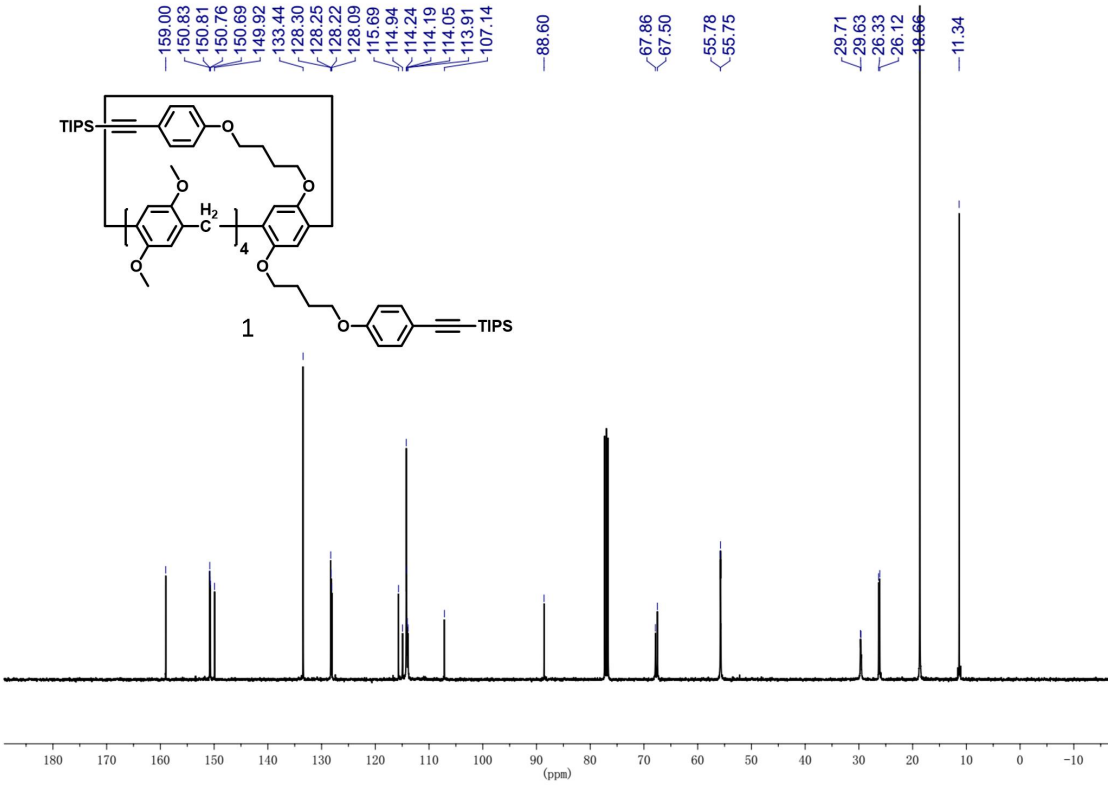


Fig. S77 ^{13}C NMR spectrum ($CDCl_3$, 298 K, 101 MHz) of macrocycle **1**.

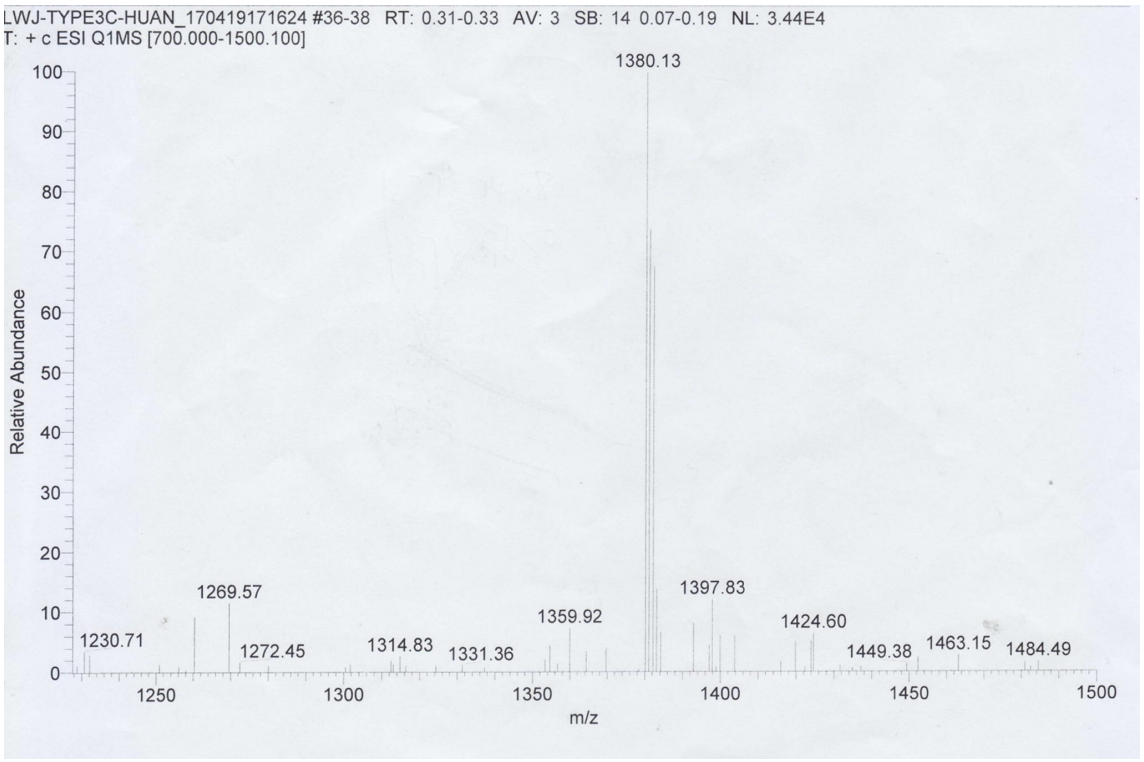


Fig. S78 ESI-MS spectrum of macrocycle **1**.

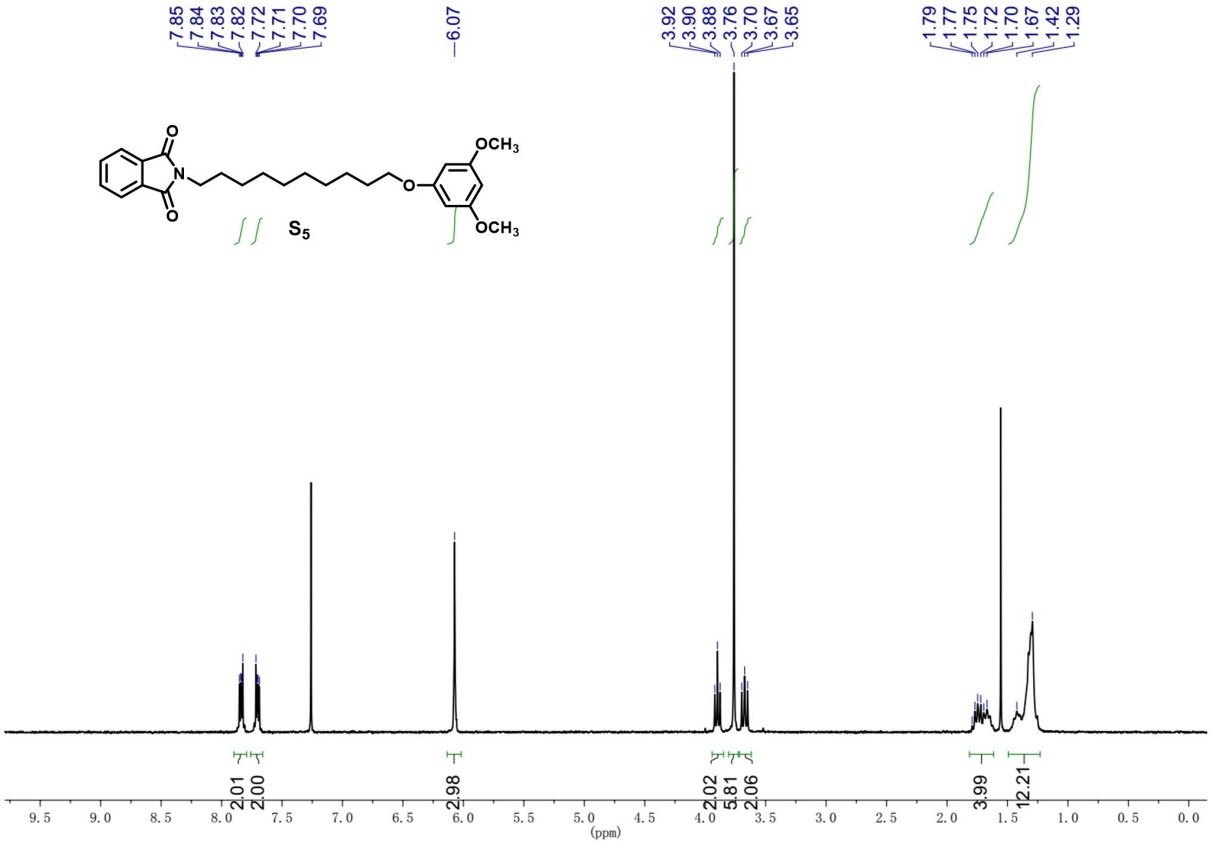


Fig. S79 ^{1}H NMR spectrum ($CDCl_3$, 298 K, 300 MHz) of $\mathbf{S_5}$.

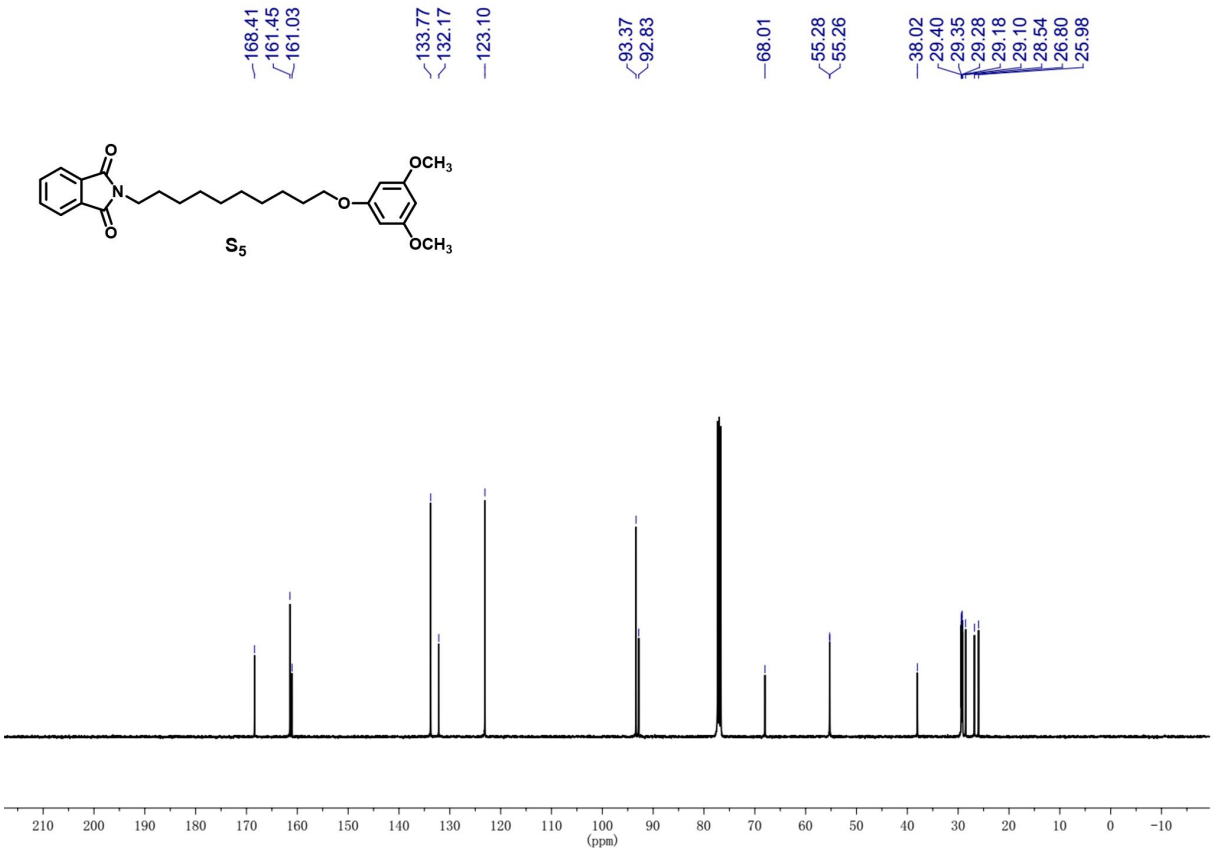


Fig. S80 ^{13}C NMR spectrum ($CDCl_3$, 298 K, 101 MHz) of **S_5**.

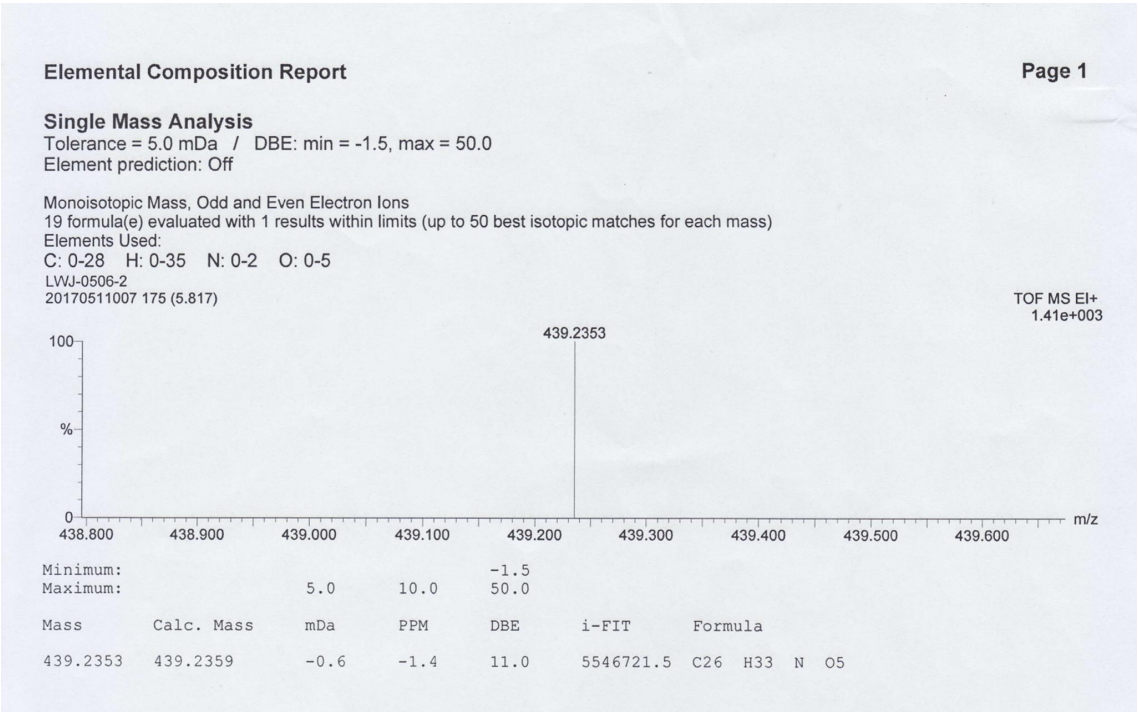


Fig. S81 HRMS (EI-TOF) spectrum of **S_5**.

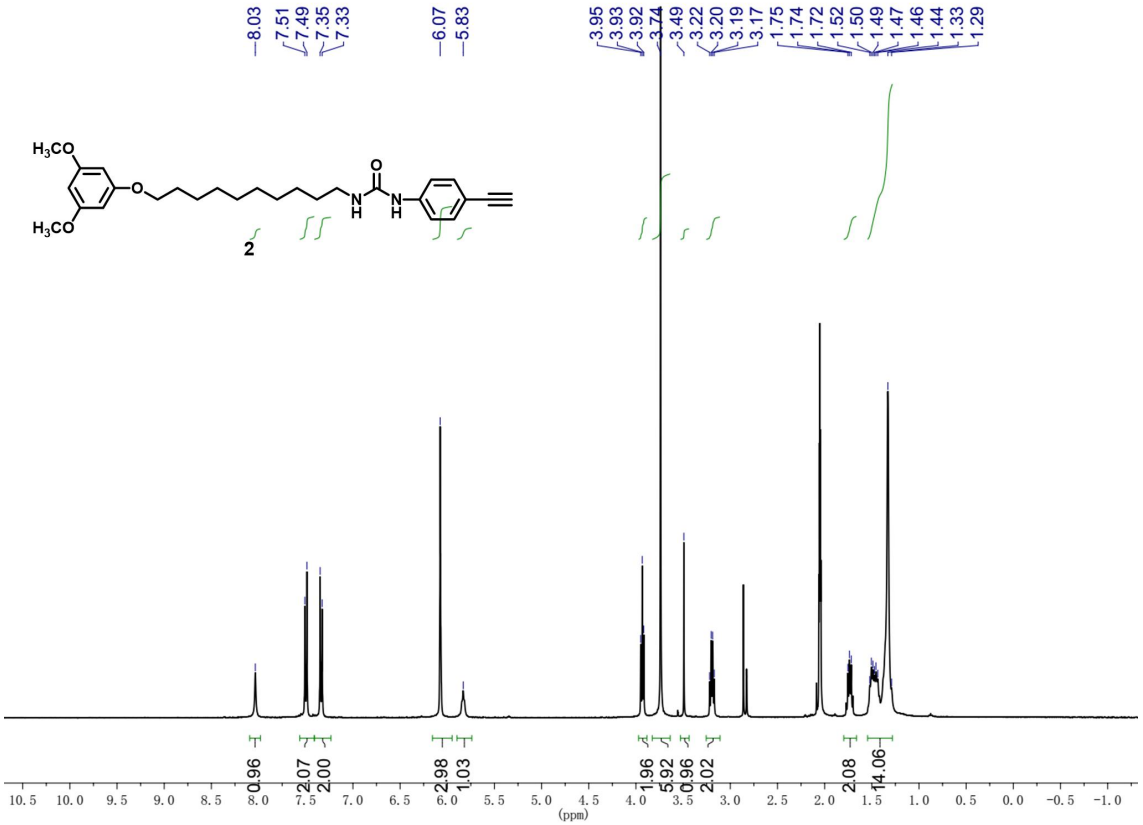


Fig. S82 ^{1}H NMR spectrum (acetone-d_6, 298 K, 400 MHz) of thread component **2**.

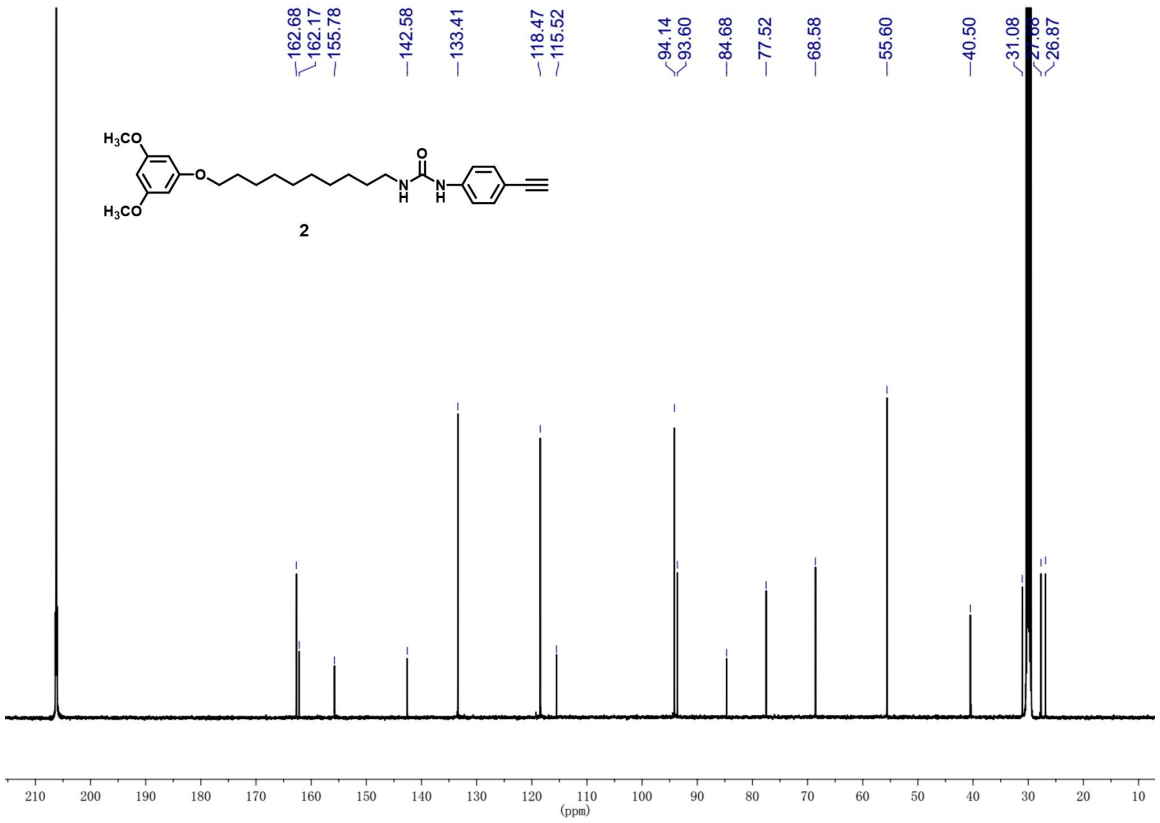


Fig. S83 ^{13}C NMR spectrum (acetone-d_6, 298 K, 126 MHz) of thread component **2**.

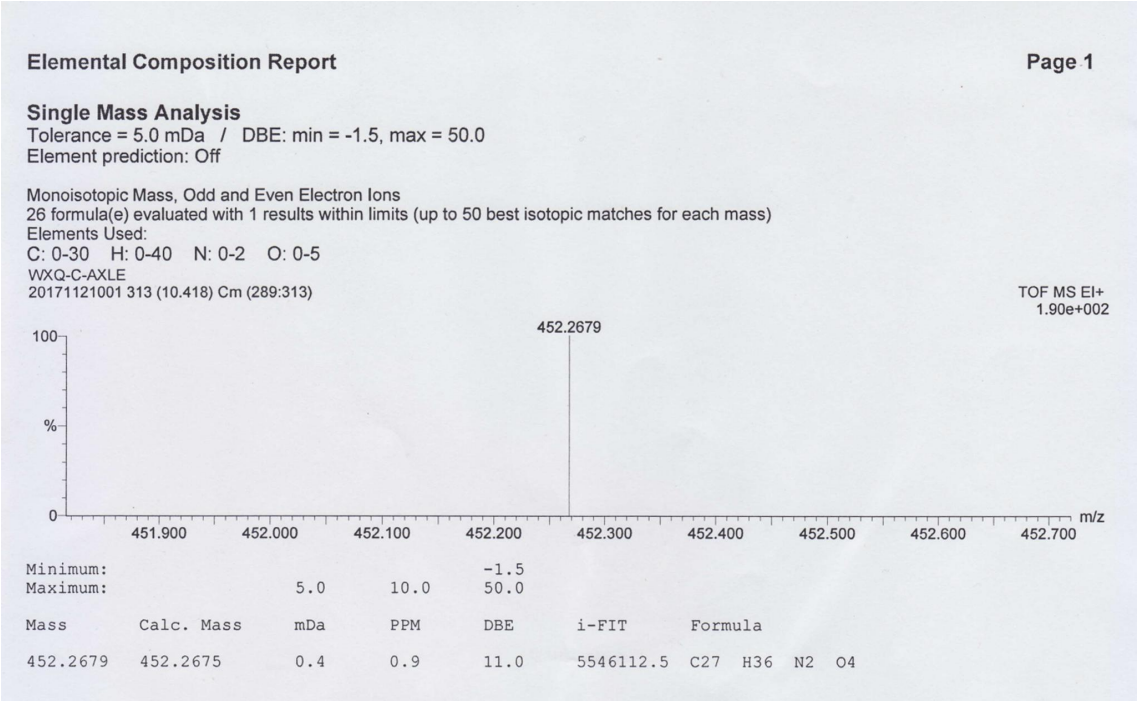


Fig. S84 HRMS (EI-TOF) spectrum of thread component **2**.

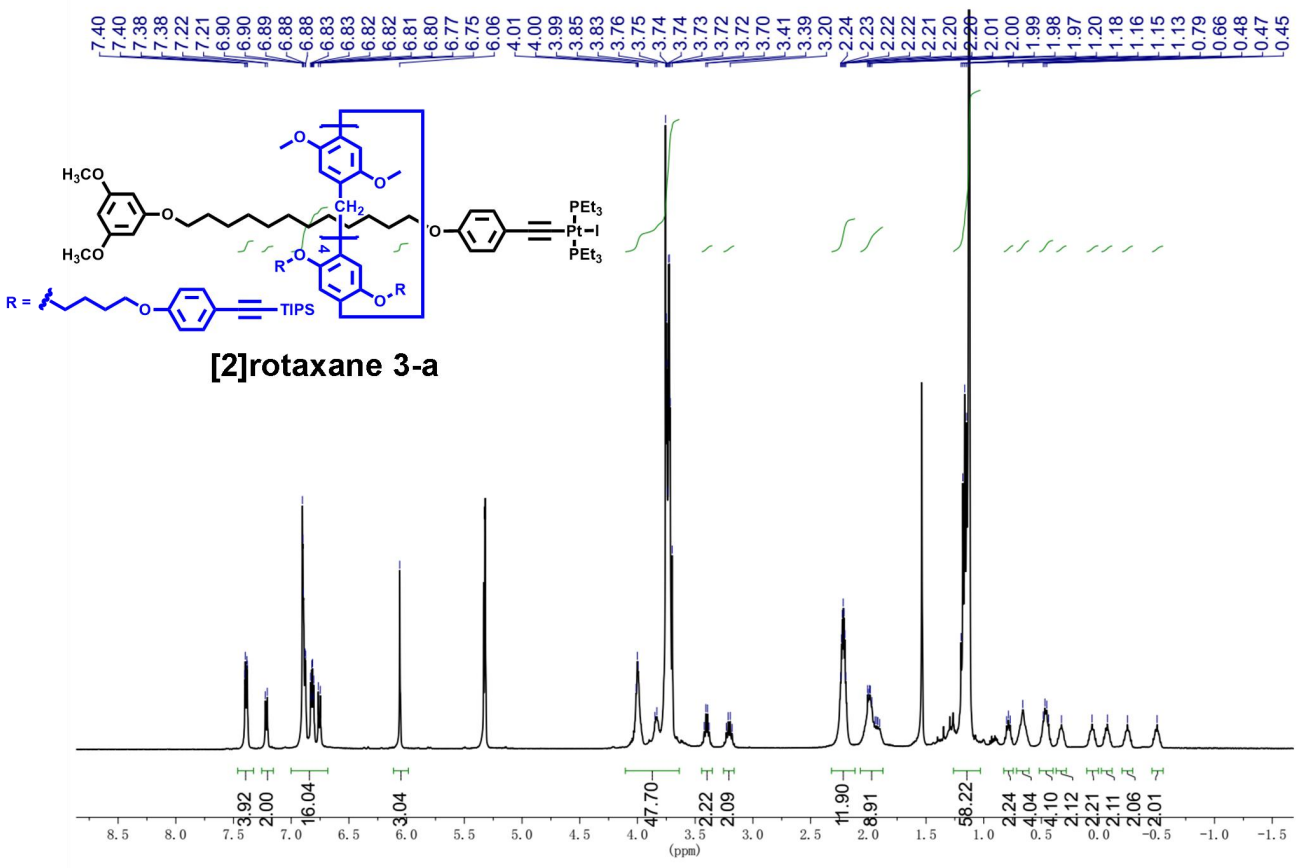


Fig. S85 ^{1}H NMR spectrum (CD_2Cl_2, 298 K, 500 MHz) of model [2]rotaxane **3-a**.

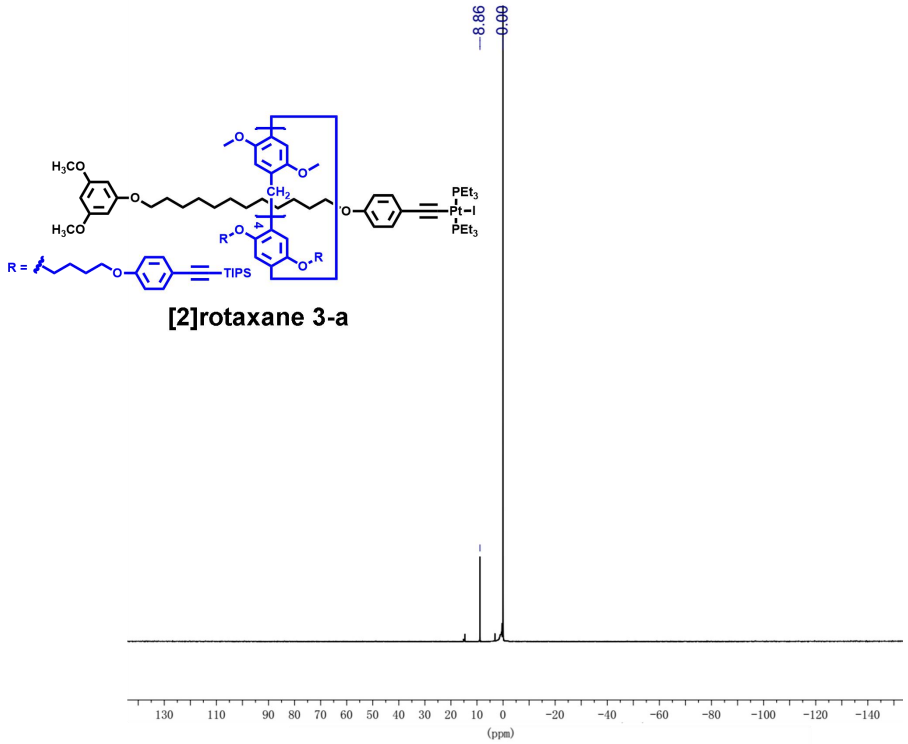


Fig. S86 ^{31}P NMR spectrum (CD_2Cl_2, 298 K, 202 MHz) of model [2]rotaxane **3-a**.

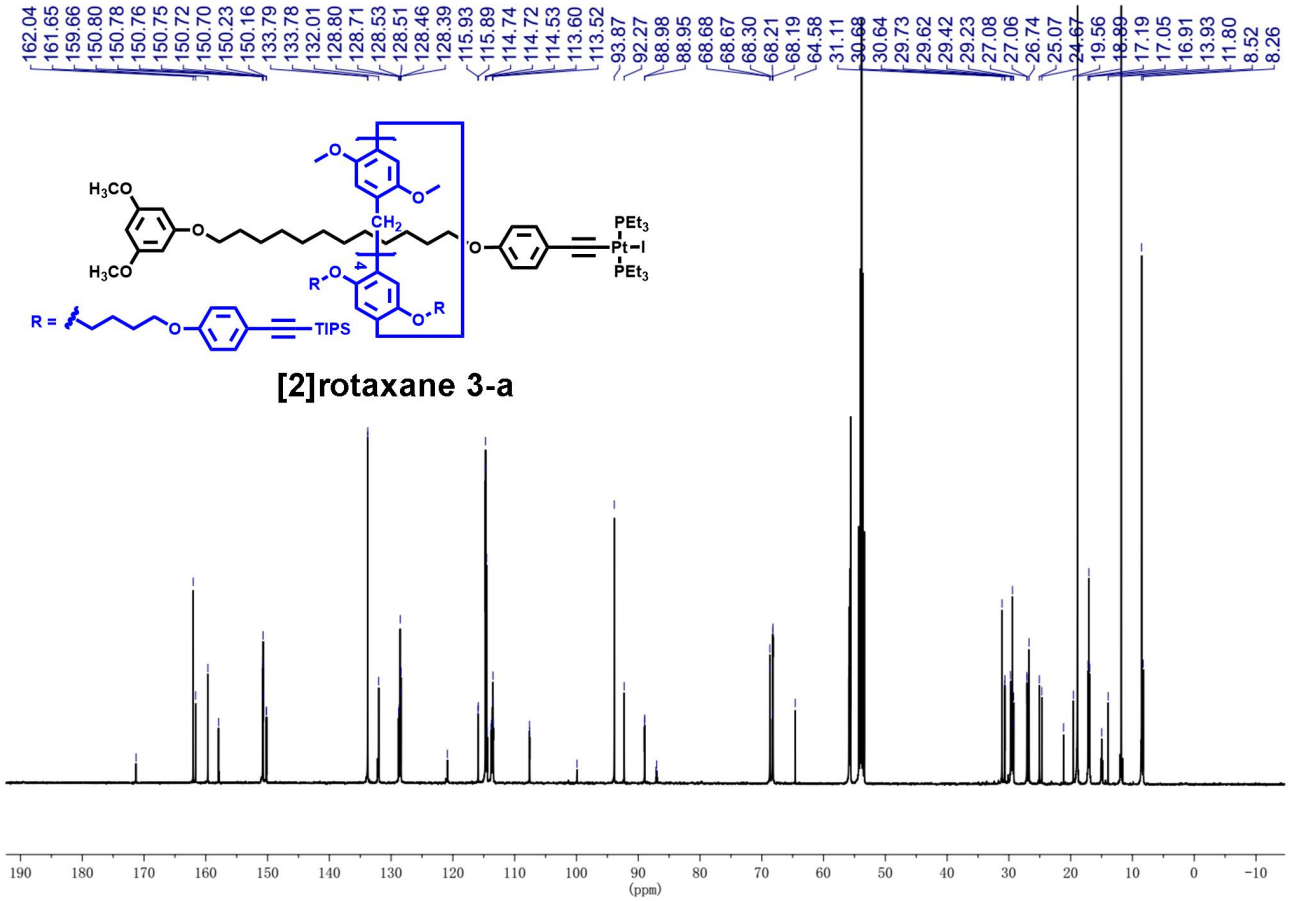


Fig. S87 ^{13}C NMR spectrum (CD_2Cl_2, 298 K, 126 MHz) of model [2]rotaxane **3-a**.

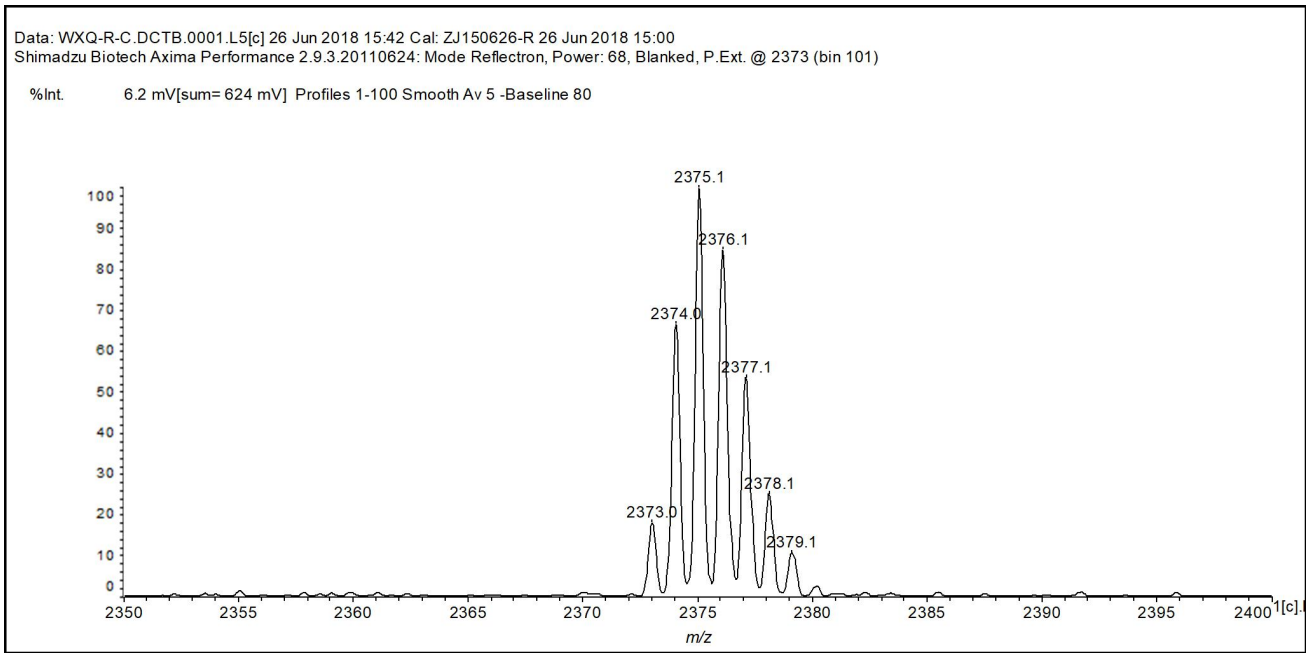


Fig. S88 MALDI-TOF-MS spectrum of model [2]rotaxane **3-a**.

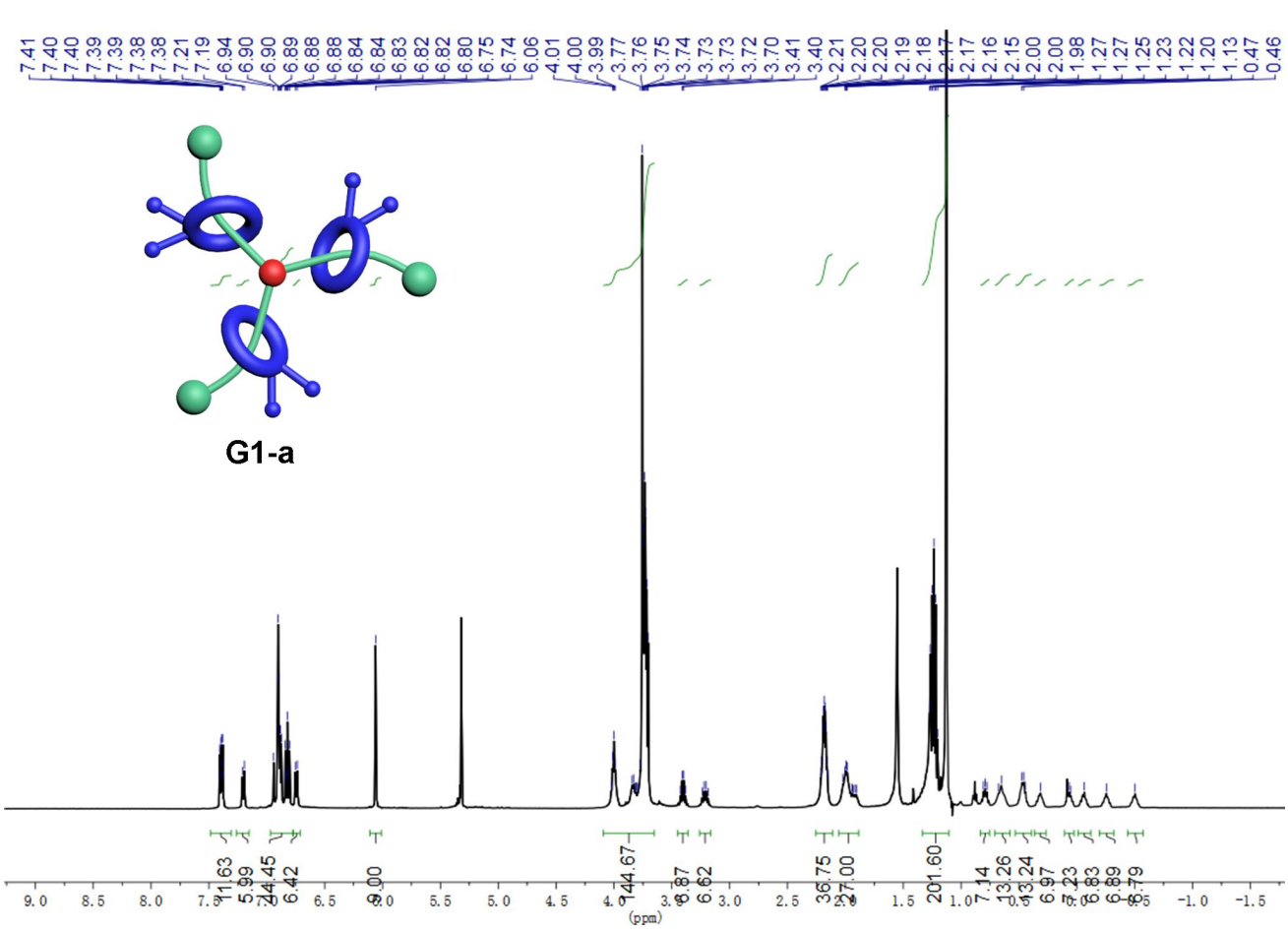


Fig. S89 ^{1}H NMR spectrum (CD_2Cl_2, 298 K, 500 MHz) of model rotaxane-branched dendrimer **G1-a**.

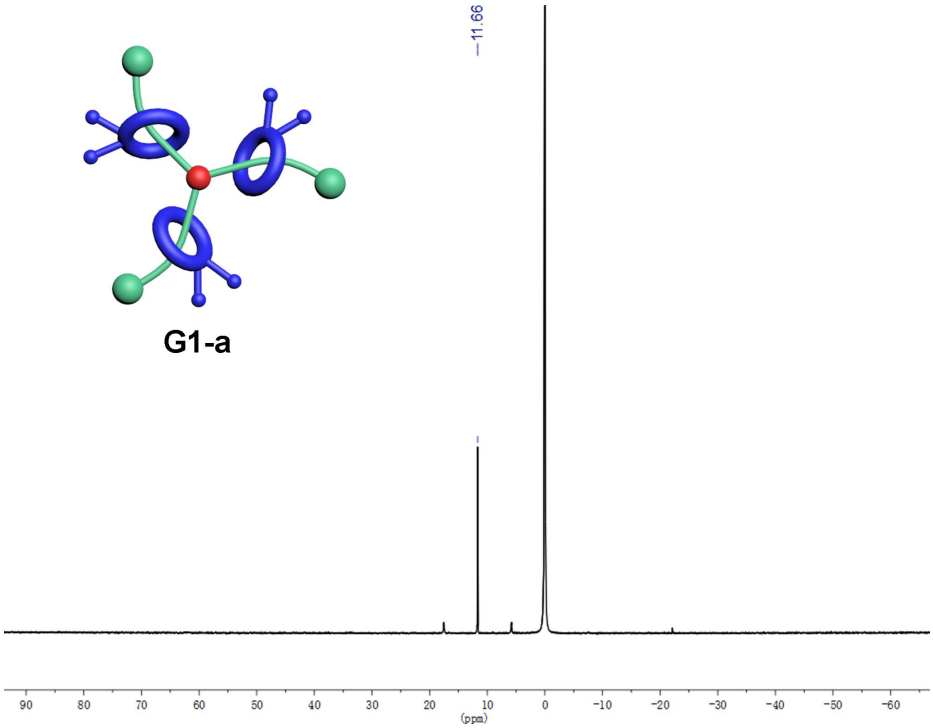


Fig. S90 ^{31}P NMR spectrum (CD_2Cl_2, 298 K, 202 MHz) of model rotaxane-branched dendrimer **G1-a**.

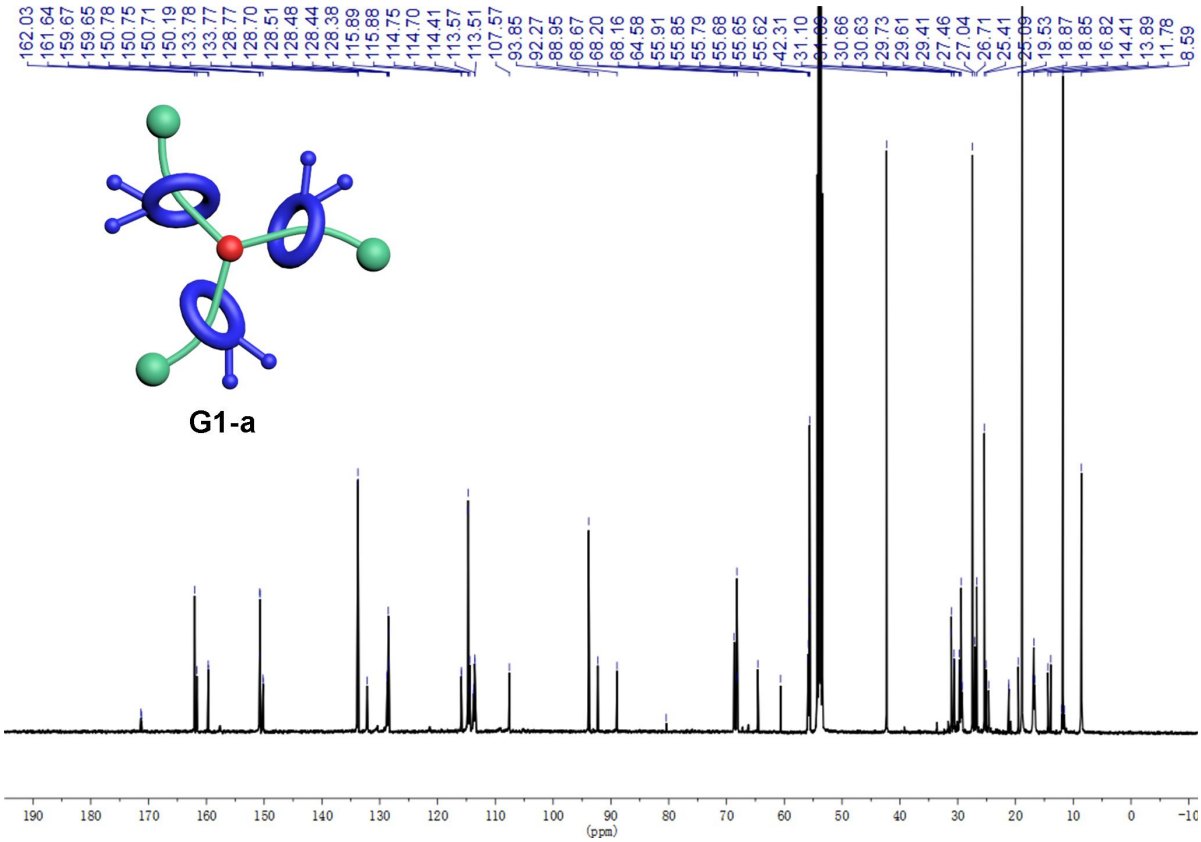


Fig. S91 ^{13}C NMR spectrum (CD_2Cl_2, 298 K, 126 MHz) of model rotaxane-branched dendrimer **G1-a**.

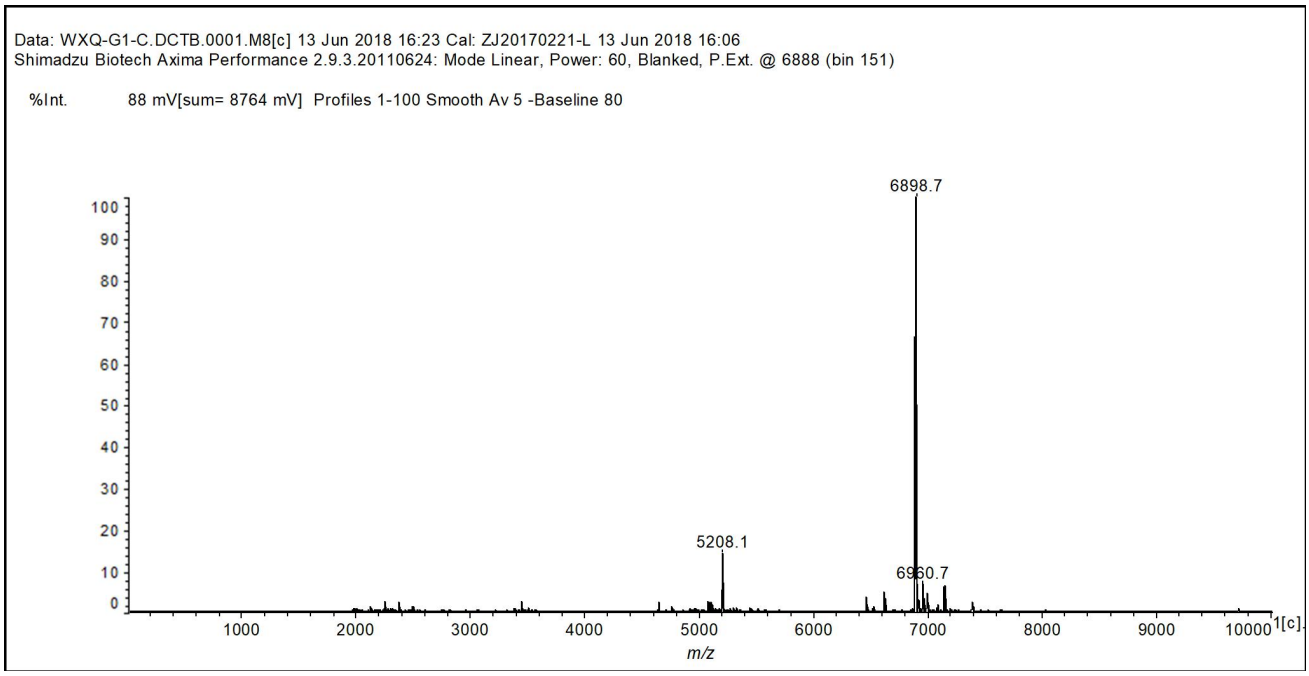


Fig. S92 MALDI-TOF-MS spectrum of model rotaxane-branched dendrimer **G1-a**.

Section G. References

1. R. Reuter, H. A. Wegner, *Chem. Commun.*, **2013**, *49*, 146-148.
2. Q. Lin, Y.-Q. Fan, P.-P. Mao, L. Liu, J. Liu, Y.-M. Zhang, H. Yao, T.-B. Wei, *Chem. Eur. J.*, **2018**, *24*, 777 –783.
3. X. F. Kong, Z. Q. He, Y. N. Zhang, L. P. Mu, C. J. Liang, B. Chen, X. P. Jing, A. N. Cammidge, *Org. Lett.*, **2011**, *13*, 764–767.