Supporting Information

Supramolecular network Derived by Rotaxane Tethering Three Ureido Pyrimidinone Groups

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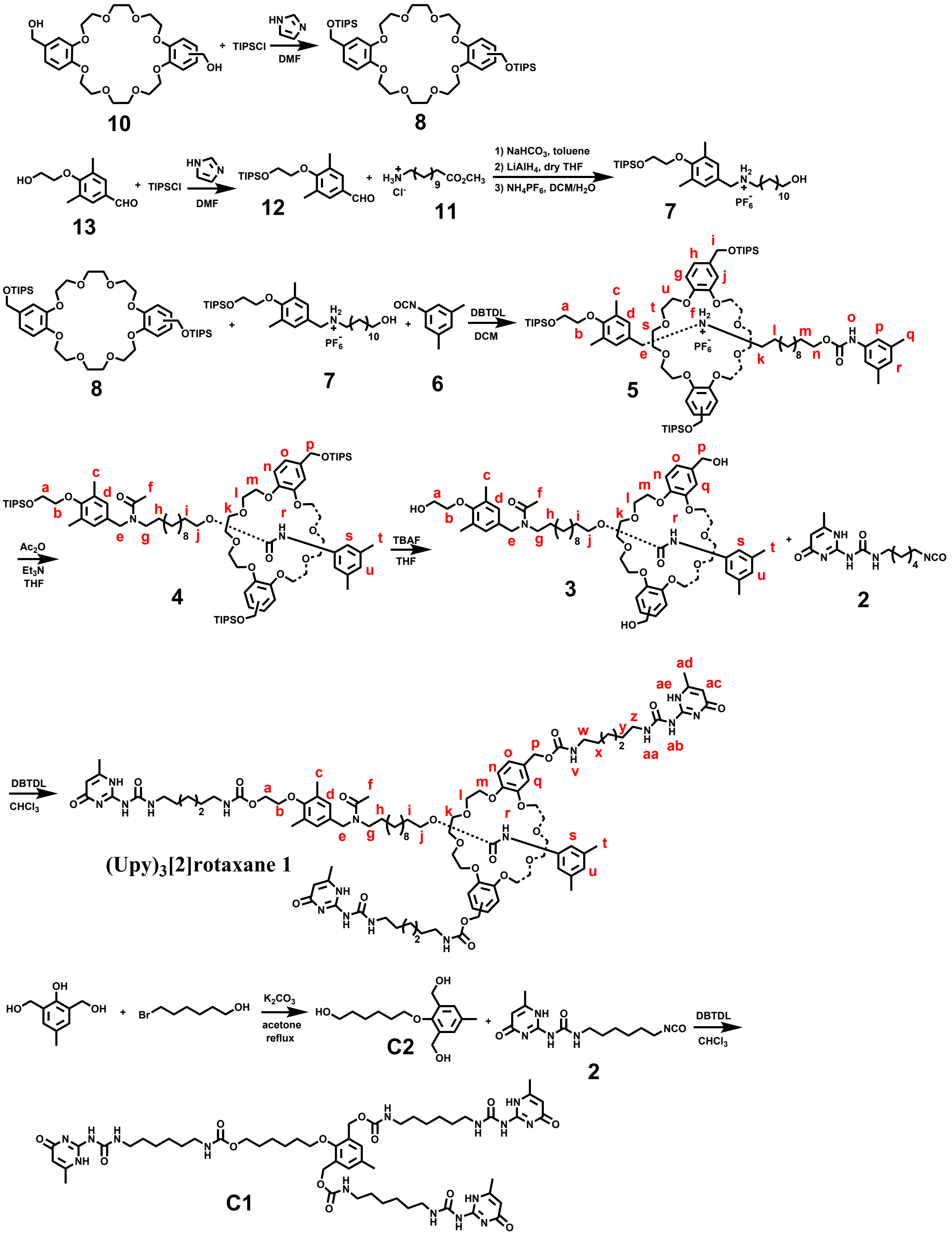
1. General Information

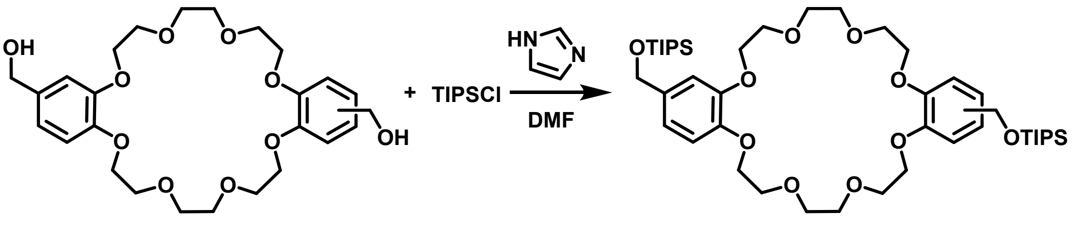
Chemicals were purchased from TCI and used as received unless otherwise stated. Solvents were reagent grade pure, which were dried and distilled prior to use according to standard procedures. All reactions were carried out under an atmosphere of dry nitrogen unless otherwise stated. NMR spectra (^{1}H NMR, ^{13}C NMR, ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY) were measured on a Brüker AVANCEⅢHD500 spectrometer. The electronic spray ionization (ESI) mass spectra were obtained on a Bruker Daltonica micrOTOF Ⅱ at the Center for Advanced Material Analysis, Tokyo Institute of Technology on request. Melting point was obtained by WRS-1B of Shanghai Jinke Industrial Co. Ltd. Thermogravimetric analysis was measured under N_2 using a SHIMADAUEZ DTG-60 in the range of 25-585 ℃. Differential scanning calorimetry (DSC) was performed under N_2 using a SHIMADAUEZ DSC-60 at a heating/cooling rate of 10 ℃/min in the range of 0-185 ℃. Data from the second heating cycle and the reverse heat flow curve are reported unless indicated otherwise (T_g = glass transition temperature). Powder x-ray diffraction was performed using a Philips (PANalytical) X'Pert-MPD-OES at the Center for Advanced Material Analyses, Tokyo Institute of Technology on request. Dynamic mechanical analysis (DMA) were performed using TA instruments AR 2000ex in tension mode. The frequency of oscillation was 1 Hz and amplitude 20 μm. The sample was heated from 0 ℃ to 117.5 ℃ at a heating rate of 2.5 ℃/min. Rheology was measured using TA instruments AR 2000ex in frequency mode. Tensile tests were carried out at 25 ℃ using a SHIMADZUEZ graph equipped with a 50 N load cell at elongation rate of 50 mm/min. Samples were prepared using a pinching blade (No. 7, KOBUNSHI KEIKI CO., LTD) conformed to ISO 37-4 specimens (dumbbell shape, 12 mm × 2 mm).

2. Synthesis



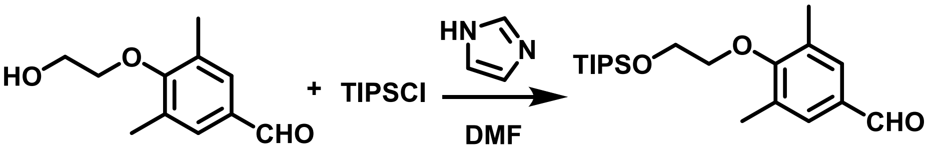
Scheme S1. The synthetic routes to control compound **C1** and **(Upy)$_3$[2]rotaxane 1**

Compound **2**[S1], compound **10**[S2], compound **11**[S3] and compound **13**[S4] were synthesized according to the previously reported literatures.



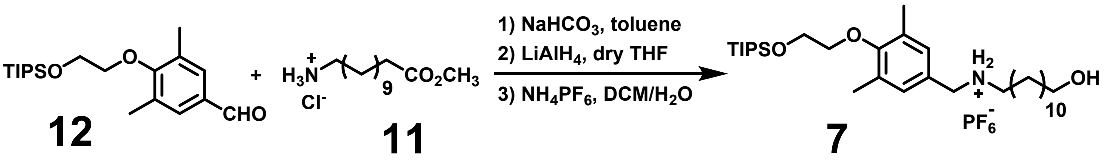
10 **8**

Compound **8**: Compound **10** (5.52 g, 0.011 mol) and lmidazole (3.90 g, 0.057 mol) were dissolved in DMF (30 mL) and TIPSCl (8.58 g, 0.044 mol) was added to the mixture and stirred at room temperature for 5 hours. Then, 100 mL saturated brine were added and the mixture was extracted by EA (3 × 80 mL). The organic layers were collected and dried over Na_2SO_4 and concentrated under reduced pressure. After removal of the solvent, the crude product was purified by chromatography on a silica gel column (CH_2Cl_2/methanol = 200/1) to yield the compound **8** (8.14 g, 91.3 %) as a white solid. M.p.: 94.4-96.8 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (s, 2H), 6.82 (s, 4H), 4.74 (s, 4H), 4.14 (dd, J = 9, 6 Hz, 8H), 3.91 (dd, J = 5, 5.0 Hz, 8H), 3.83 (d, J = 2 Hz, 8H), 1.18 – 1.13 (m, 6H), 1.08 (d, J = 7 Hz, 36H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 147.6, 135.1, 118.3, 114.0, 111.8, 111.7, 71.3, 71.2, 70.0, 69.9, 69.6, 69.3, 69.2, 64.7, 18.1, 12.1. HRMS (ESI) (*m/z*): $[M + Na]^+$ calcd for $C_{44}H_{76}O_{10}Si_2Na$: 843.4875, found: 843.4869.

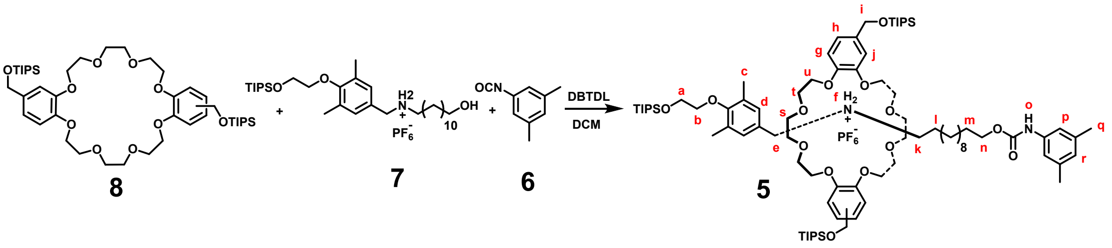


13 **12**

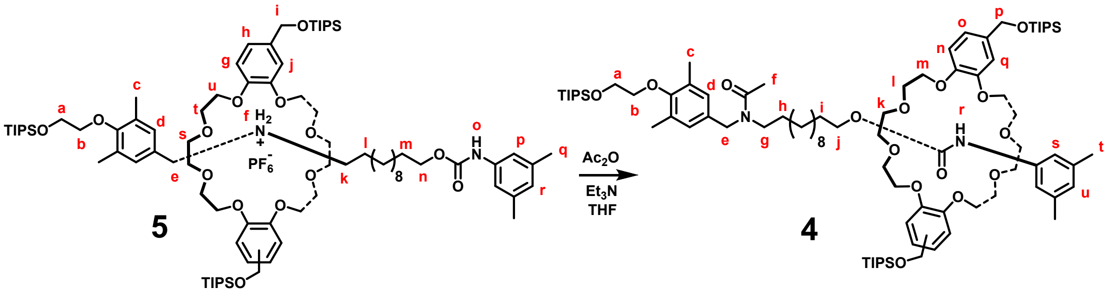
Compound **12**: Compound **13** (9.08 g, 0.047 mol) and Imidazole (8.20 g, 0.120 mol) were dissolved in DMF (30 mL) and TIPSCl (18.07 g, 0.093 mol) was added to the mixture and stirred at room temperature for 5 hours. Then, 100 mL saturated brine were added and the mixture was extracted by EA (3 × 100 mL). The organic layers were collected and dried over Na_2SO_4 and concentrated under reduced pressure. After removal of the solvent, the crude product was purified by chromatography on a silica gel column (hexane/EA = 10/1) to yield the compound **12** (14.60 g, 89.2 %) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.51 (s, 2H), 4.03 (t, J = 5 Hz, 2H), 3.91 (t, J = 5 Hz, 2H), 2.33 (s, 6H), 1.12 (m, 3H), 1.09 – 1.04 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.6, 161.4, 132.2, 132.1, 130.7, 73.8, 62.9, 18.0, 16.3, 11.9. HRMS (ESI) (*m/z*): $[M + Na]^+$ calcd for $C_{20}H_{34}O_3SiNa$: 373.2175, found: 373.2161.



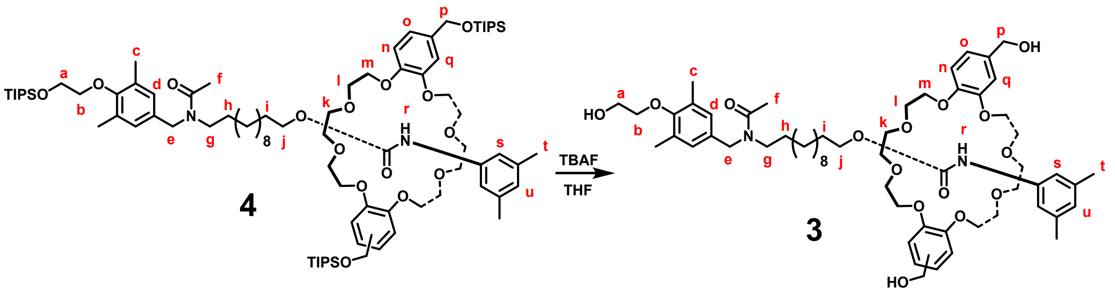
Compound **7**: Compound **12** (17.02 g, 0.049 mol) and compound **11** (15.69 g, 0.059 mol) were dissolved toluene (100 mL) and $NaHCO_3$ (8.59 g, 0.102 mol) was added to the mixture. Then, the mixture was heated and stirred under reflux in an argon atmosphere for 24 hours. After cooling, toluene was evaporated under reduced pressure. The crude product was dissolved in dry THF (200 mL) and $LiAlH_4$ (7.39 g, 0.195 mol) was slowly added in portions to the mixture under ice bath. Then 8.0 mL water and 8.0 mL 15 % aqueous sodium hydroxide were added slowly to the mixture to quench the reaction. The mixture was filtered and the solid was washed by THF (100 mL). The collected organic phase was washed with water (3 × 100 mL). The organic layers were combined and dried over Na_2SO_4 and finally concentrated under reduced pressure. The crude product was dissolved in DCM (100 mL), and washed with saturated NH_4PF_6 aqueous solution (3 × 100 mL). The organic layers were collected and dried over Na_2SO_4 and concentrated under reduced pressure. After removal of the solvent, the crude product was purified by chromatography on a silica gel column (hexane/EA = 1/3) to yield the compound **7** (15.29 g, 46.2 %) as a white solid. M.p.: 114.4-116.7 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 2H), 4.12 (s, 2H), 4.02 (t, J = 5 Hz, 2H), 3.86 (t, J = 5 Hz, 2H), 3.59 (t, J = 7 Hz, 2H), 2.93 (t, J = 8 Hz, 2H), 2.29 (s, 6H), 1.67 (m, 2H), 1.54 – 1.48 (m, 2H), 1.27 (m, 16H), 1.17 – 1.10 (m, 3H), 1.08 (d, J = 6 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.4, 132.7, 130.47, 124.27, 73.7, 63.1, 62.9, 51.9, 47.2, 32.5, 29.2, 29.2, 29.2, 29.1, 29.0, 28.7, 26.0, 25.8, 25.5, 18.0, 16.2, 12.2, 12.0, 11.7. HRMS (ESI) (m/z): $[M - PF_6]^+$ calcd for $C_{32}H_{62}NO_3Si$: 536.4493, found: 536.4485.



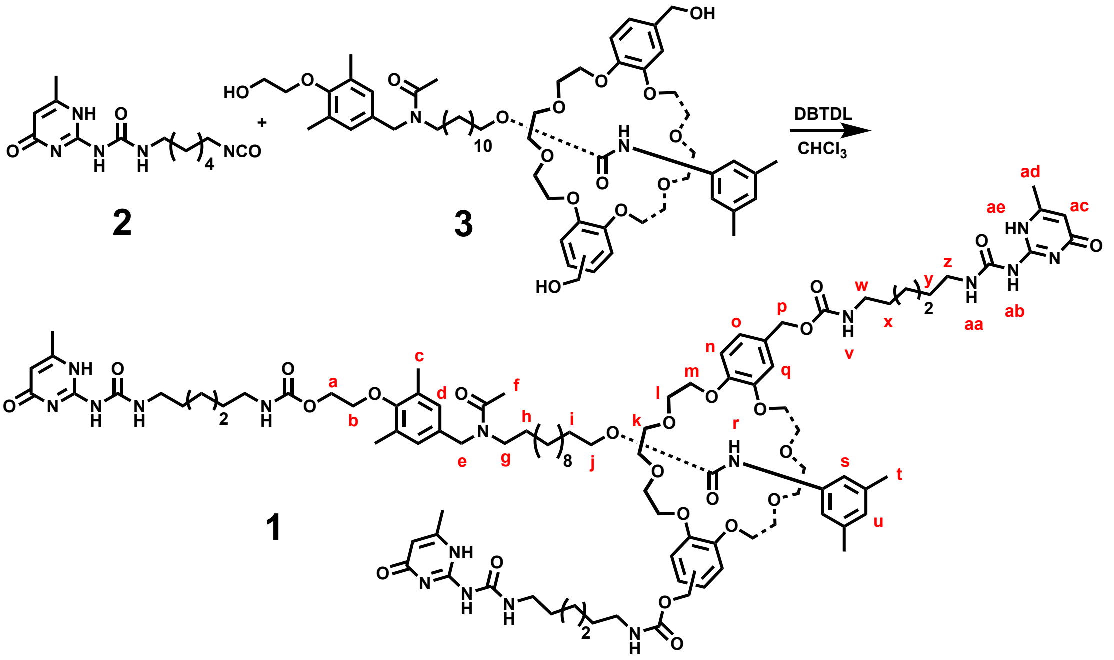
Compound **5**: Compound **8** (2.4713 g, 3.0 mmol) and compound **7** (2.0519 g, 3.0 mmol) were dissolved in DCM (15.0 mL) and stirred at room temperature for 1 hour. Then, compound **6** (1.50 mL, 10.7 mmol) and DBTDL (18.0 μL, 0.03 mmol) were added to the mixture and stirred under Ar atmosphere at room temperature for 15 hours. The organic phase was washed by deionized water (3 × 20 mL). The organic layers were collected and dried over Na_2SO_4 and concentrated under reduced pressure. After removal of the solvent, the crude product was purified by chromatography on a silica gel column (hexane/EA = 1/1) to yield the compound **5** (1.813 g, 36.5 %) as a white solid. M.p.: 120.1-121.3 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.08 (s, 2H), 7.01 (s, 4H), 6.93 (s, 2H), 6.86 (d, J = 8 Hz, 2H), 6.81 (d, J = 8 Hz, 2H), 6.69 (s, 1H), 6.52 (s, 1H), 4.74 (s, 4H), 4.48 – 4.43 (m, 2H), 4.25 – 4.17 (m, 4H), 4.16 – 4.05 (m, 6H), 4.01 (t, J = 5 Hz, 2H), 3.84 – 3.76 (m, 10H), 3.62 (dd, J = 11, 6 Hz, 4H), 3.41 (m, 6H), 3.07 (s, 2H), 2.28 (s, 6H), 2.16 (s, 6H), 1.65 (m, 4H), 1.41 – 1.34 (m, 4H), 1.32 – 1.24 (m, 4H), 1.19 – 1.12 (m, 13H), 1.08 (t, *J* = 7 Hz, 54H), 0.98 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 156.5, 147.4, 146.3, 138.7, 137.8, 135.5, 131.5, 130.2, 127.7, 125.1, 118.6, 112.5, 110.3, 73.8, 70.73, 70.71, 70.3, 70.2, 68.5, 68.3, 65.3, 64.4, 62.9, 51.9, 48.9, 29.57, 29.56, 29.5, 29.4, 29.3, 29.0, 26.6, 26.4, 25.9, 21.4, 18.1, 18.0, 16.2, 12.0, 12.0, 11.8. HRMS (ESI) (*m/z*): $[M - PF_6]^+$ calcd for $C_{85}H_{147}N_2O_{14}Si_3$: 1505.0188, found: 1505.0172



Compound **4**: Compound **5** (4.4521g, 2.70 mmol) was dissolved in dry THF (30.0 mL), Ac_2O (3.40 mL, 36.0 mmol) and Et_3N (4.20 mL, 30.2 mmol) were added to the mixture and stirred under Ar atmosphere at room temperature 40 hours. Then, 40 mL CH_3Cl was added, and the mixture was washed by saturated brine (3 × 50 mL). The organic layers were collected and dried over Na_2SO_4 and concentrated under reduced pressure. After removal of the solvent, the crude product was purified by chromatography on a silica gel column (hexane/EA = 2/1) to yield the compound **4** (2.9014 g, 69.5 %) as a white solid. M.p.: 117.3-119.9 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.41 (d, *J* = 14 Hz, 1H), 7.18 (s, 2H), 6.91 (s, 2H), 6.85 (s, 1H), 6.80 (m, 5H), 6.50 (s, 1H), 4.75 (s, 4H), 4.46 (s, 1H), 4.39 (s, 1H), 4.32 (s, 2H), 4.16 (s, 4H), 4.08 (s, 4H), 4.03 (d, *J* = 5 Hz, 2H), 3.83 (d, *J* = 5 Hz, 11H), 3.52 (dd, *J* = 23, 10 Hz, 8H), 3.32 (t, *J* = 8 Hz, 1H), 3.15 (t, *J* = 8 Hz, 1H), 2.27 (dd, *J* = 11, 6 Hz, 7.5H), 2.16 (s, 2H), 2.09 (d, *J* = 4 Hz, 7.5H), 1.68 (d, *J* = 6 Hz, 4H), 1.52 (d, *J* = 5 Hz, 2H), 1.43 (dd, *J* = 14, 7 Hz, 2H), 1.24 (s, 4H), 1.20 – 1.11 (m, 13H), 1.08 (d, *J* = 7 Hz, 54H), 0.98 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 170.9, 170.4, 155.2, 155.0, 148.3, 147.3, 138.0, 132.8, 131.6, 131.1, 128.3, 126.4, 117.6, 115.9, 111.5, 109.9, 73.7, 73.5, 69.7, 68.1, 67.9, 64.8, 62.9, 51.3, 47.7, 47.4, 46.0, 29.68, 29.65, 29.58, 29.49, 29.45, 29.0, 28.3, 27.6, 27.1, 26.9, 25.7, 21.9, 21.5, 21.3, 18.1, 18.0, 16.3, 16.2, 12.1, 12.0, 11.8. HRMS (ESI) (*m/z*): $[M + Na]^+$ calcd for $C_{87}H_{148}N_2O_{15}Si_3Na$: 1569.0113, found: 1569.0119.

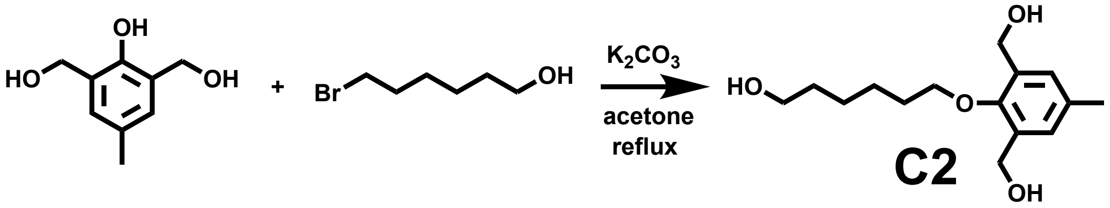


Compound **3**: Compound **4** (2.9014 g, 1.88 mmol) was dissolved in 1.0 M TBAF solution (solvent: THF, 12.0 ML) and stirred under Ar atmosphere at room temperature 15 hours. Then, 25 mL DCM were added to the mixture. And the mixture was washed by saturated brine (3 × 30 mL). The organic layers were collected and dried over Na_2SO_4 and concentrated under reduced pressure. After removal of the solvent, the crude product was purified by chromatography on a silica gel column (DCM/CH_3OH = 30/1) to yield the compound **3** (1.5118 g, 74.8 %) as a white solid. M.p.: 121.4-122.9 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 7 Hz, 2H), 6.89 – 6.83 (m, 5H), 6.79 (dd, *J* = 8, 4 Hz, 3H), 6.51 (d, *J* = 5 Hz, 1H), 4.59 (t, *J* = 5 Hz, 4H), 4.45 (d, *J* = 5 Hz, 1H), 4.40 (s, 1H), 4.32 (d, *J* = 6 Hz, 2H), 4.18 (d, *J* = 9 Hz, 4H), 4.10 (dt, *J* = 14, 4 Hz, 4H), 3.97 – 3.84 (m, 8H), 3.84 – 3.78 (m, 4H), 3.60 – 3.44 (m, 8H), 3.35 – 3.30 (m, 1H), 3.18 – 3.14 (m, 1H), 2.29 – 2.24 (m, 6H), 2.14 (d, *J* = 5 Hz, 1.5H), 2.11 (s, 7.5H), 2.06 (t, *J* = 6 Hz, 1H), 1.89 (d, *J* = 6 Hz, 1H), 1.52 (dd, *J* = 14, 7 Hz, 2H), 1.47 – 1.37 (m, 2H), 1.24 – 1.00 (m, 14H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 170.6, 154.7, 154.5, 148.6, 148.0, 139.7, 138.0, 133.5, 133.3, 132.3, 131.4, 130.7, 128.5, 126.6, 123.4, 119.2, 115.8, 111.7, 111.1, 73.1, 69.8, 68.2, 65.3, 64.8, 62.3, 51.3, 47.9, 47.4, 45.9, 29.6, 29.5, 29.4, 29.0, 28.3, 27.4, 26.9, 26.8, 25.8, 21.9, 21.5, 21.3, 16.4. HRMS (ESI) (*m/z*): $[M + Na]^+$ calcd for $C_{60}H_{88}N_2O_{15}Na$: 1099.6082, found: 1099.6073.

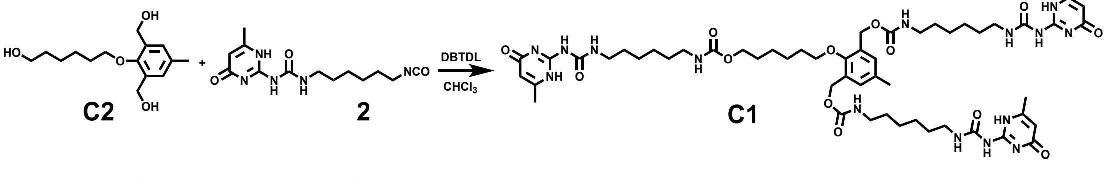


Compound **1**: Compound **2** (0.2124 g, 0.72 mmol) and compound **3** (0.1681 g, 0.16 mmol) were dissolved in dry $CHCl_3$ (5.0 mL) and DBTDL (9.0 μL, 0.016 mmol) was added to the mixture. Then, the mixture was stirred under reflux in an argon atmosphere for 24 hours. After cooling, 25 mL DCM was added to the mixture. And the mixture was washed by saturated brine (3 × 30 mL). The organic layers were collected and dried over Na_2SO_4 and concentrated under reduced pressure. After removal of the solvent, the crude product was purified by chromatography on a silica gel column (DCM/CH_3OH = 15/1) to yield the compound **1** (0.1583 g, 41.0 %) as a white solid. M.p.: 134.6-136.9 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.11 (s, 3H), 11.84

(s, 3H), 10.14 (s, 3H), 8.29 (s, 1H), 7.13 (s, 2H), 6.90 – 6.80 (m, 5H), 6.80 – 6.73 (m, 3H), 6.49 (s, 1H), 5.91 – 5.78 (m, 3H), 4.99 (s, 4H), 4.44 (s, 1H), 4.37 (s, 2H), 4.31 (s, 1H), 4.16 (s, 4H), 4.07 (s, 4H), 3.89 (d, *J* = 10 Hz, 6H), 3.79 (d, *J* = 10 Hz, 4H), 3.53 (s, 5H), 3.47 (s, 3H), 3.34 – 3.05 (m, 16H), 2.26 – 2.13 (m, 16.5H), 2.08 (s, 7.5H), 1.59 (s, 6H), 1.51 (s, 10H), 1.36 (s, 14H), 1.24 (d, *J* = 14 Hz, 4H), 1.15 (d, *J* = 19 Hz, 4H), 1.05 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 170.5, 156.6, 154.7, 148.4, 138.0, 133.2, 131.4, 130.8, 129.0, 128.4, 126.5, 123.3, 120.9, 115.8, 106.7, 70.6, 70.4, 69.6, 66.6, 64.8, 63.9, 47.8, 47.4, 40.8, 39.6, 31.0, 29.6, 29.5, 29.3, 28.9, 26.9, 26.1, 25.7, 21.9, 21.5, 21.3, 18.9, 16.3, 16.2. HRMS (ESI) (*m/z*): $[M + Na]^+$ calcd for $C_{99}H_{145}N_{17}O_{24}Na$: 1980.0574, found: 1980.0584, $1/2[M + 2Na]^{2+}$ calcd for $C_{60}H_{88}N_2O_{15}Na_2$: 1001.5233, found: 1001.5279.



Compound **C2**: 2,6-Bis(hydroxymethyl)-p-cresol (1.231 g, 7.3 mmol), 6-bromohexanol (2.720 g, 15.0 mmol) and K_2CO_3 (3.040 g, 0.022 mmol) were dissolved in acetone (30.0 mL). Then, the mixture was stirred under reflux in an argon atmosphere for 24 hours. After cooling, the mixture was washed by saturated brine (3 × 60 mL). The organic layers were collected and dried over $MgSO_4$ and concentrated under reduced pressure. After removal of the solvent, the crude product was purified by chromatography on a silica gel column (hexane/EA = 1/5) to yield the compound **C1** (1.365 g, 69.5 %) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (s, 2H), 4.64 (d, *J* = 6 Hz, 4H), 3.84 (t, *J* = 6 Hz, 2H), 3.63 (dd, *J* = 11, 6 Hz, 2H), 2.70 (t, *J* = 6 Hz, 2H), 2.29 (s, 3H), 2.12 (t, *J* = 5 Hz, 1H), 1.83 – 1.74 (m, 2H), 1.61 – 1.55 (m, 2H), 1.50 (dd, *J* = 15, 8 Hz, 2H), 1.47 – 1.41 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 134.1, 133.7, 129.5, 74.8, 62.6, 60.9, 32.5, 30.2, 25.6, 25.4, 20.8. HRMS (ESI) (*m/z*): $[M + Na]^+$ calcd for $C_{15}H_{24}O_4Na$: 291.1567, found: 291.1569.



Compound **C1**: Compound **C2** (0.6782 g, 2.53 mmol) and compound **2** (2.2362 g, 7.61 mmol) were dissolved in dry $CHCl_3$ (25.0 mL) and DBTDL (0.25 mL, 0.38 mmol) was added to the mixture. Then, the mixture was stirred under reflux in an argon atmosphere for 24 hours. After cooling, 25 mL DCM was added to the mixture. And the mixture was washed by saturated brines (3 × 50 mL). The organic layers were collected and dried over Na_2SO_4 and concentrated under reduced pressure. After removal of the solvent, the crude product was purified by chromatography on a silica gel column (DCM/CH_3OH = 10/1) to yield the compound **C1** (0.9836 g, 33.9 %) as a white solid. M.p.: 123.3-125.7 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 13.10 (s, 3H), 11.83 (s, 3H), 10.14 (s, 3H), 7.13 (s, 2H), 5.80 (s, 3H), 5.09 (s, 4H), 4.02 (s, 2H), 3.78 (s, 2H), 3.25 – 3.10 (m, 12H), 2.30 – 2.12 (m, 12H), 1.72 (s, 4H), 1.57 (s, 10H), 1.50 (s, 10H), 1.36 (s, 8H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 173.2, 156.5, 154.7, 148.3, 133.7, 131.9, 130.5, 106.7, 64. 6, 62.7, 61.5, 40.7, 39.6, 29.9, 29.7, 29.3, 26.3, 25.8, 25.6, 20.8, 20.4, 18.9. HRMS (ESI) (*m/z*): [M + Na]$^+$ calcd for $C_{54}H_{81}N_{15}O_{13}Na$: 1170.6036, found: 1170.6050.

The corresponding original spectra of the above compounds are displayed as Figures S1-S31 in the following section

3. Characterization

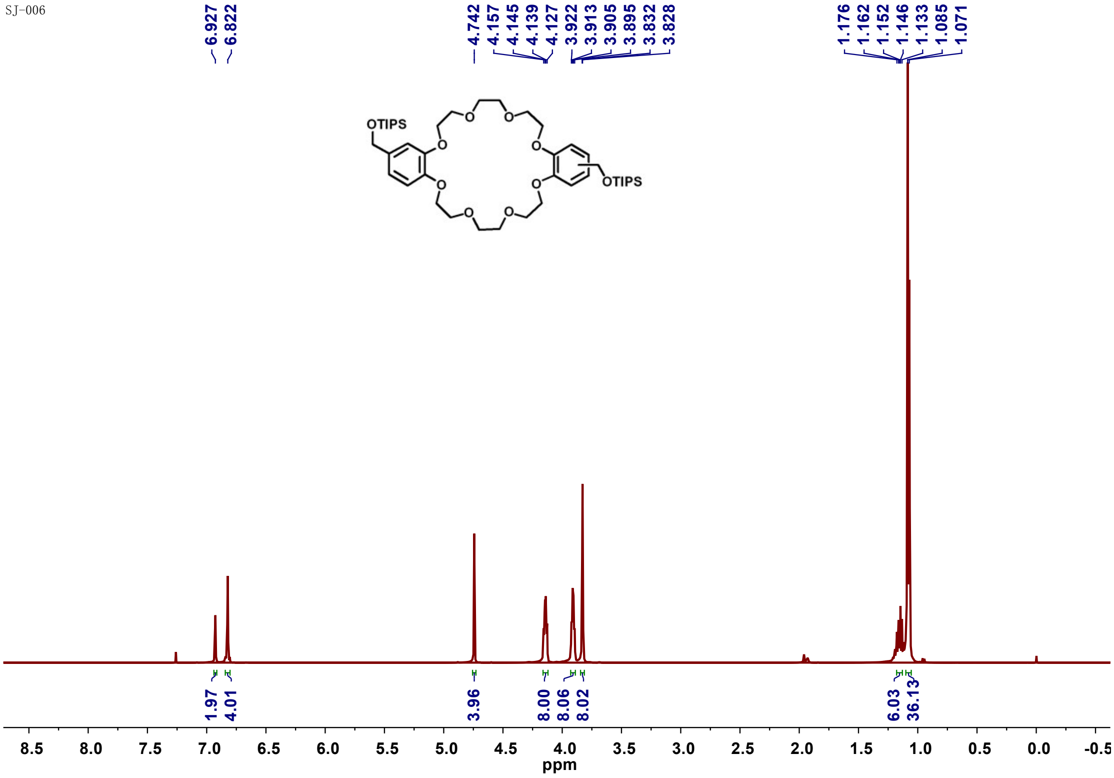


Figure S1. ^{1}H NMR spectrum of compound **8** (500 MHz, 298 K, CDCl$_3$)

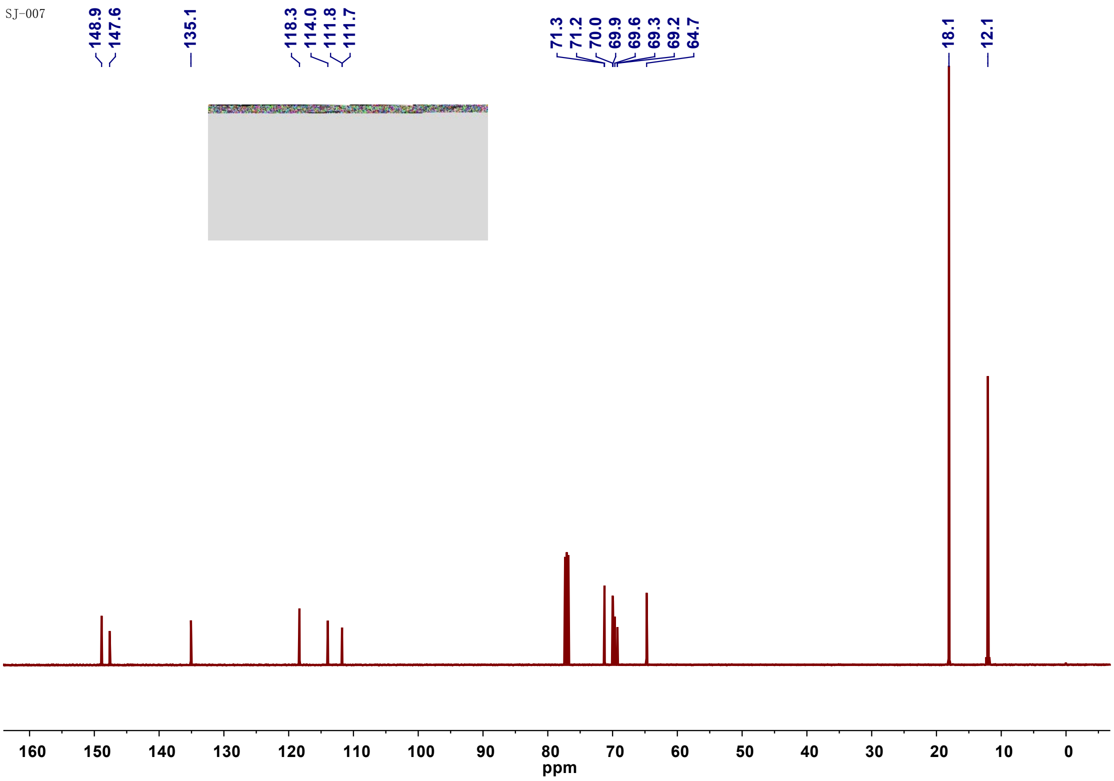
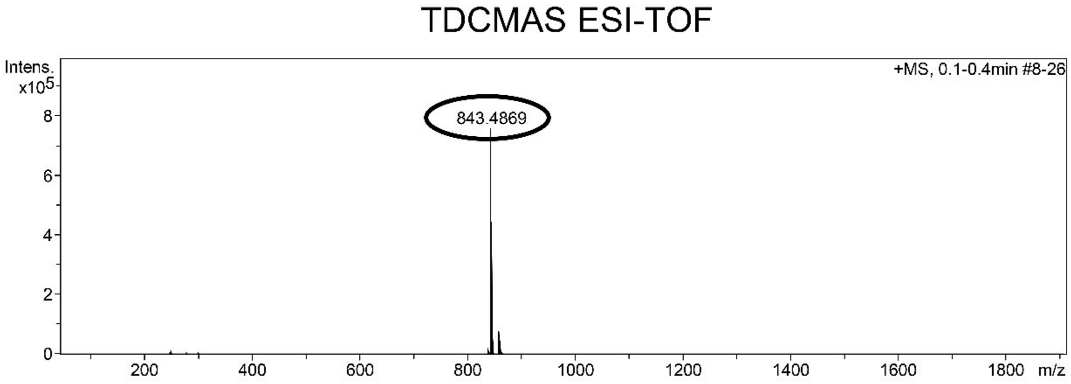


Figure S2. ^{13}C NMR spectrum of compound **8** (125 MHz, 298 K, $CDCl_3$)



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Meas. m/z  #  Ion Formula          Score       m/z  err [mDa]  err [ppm]  mSigma   rdb  eP    Conf  N-Rule  Adduct
843.486877 1  C44H76NaO10Si2      100.00  843.486922        0.0        0.1     5.2   8.5  even          ok  M+Na
           2  C45H72N4NaO6Si2      41.92  843.488260        1.4        1.6    14.5  13.5  even          ok  M+Na
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Figure S3. ESI-mass spectrum of compound **8** ([M + Na]$^+$: 843.4869).

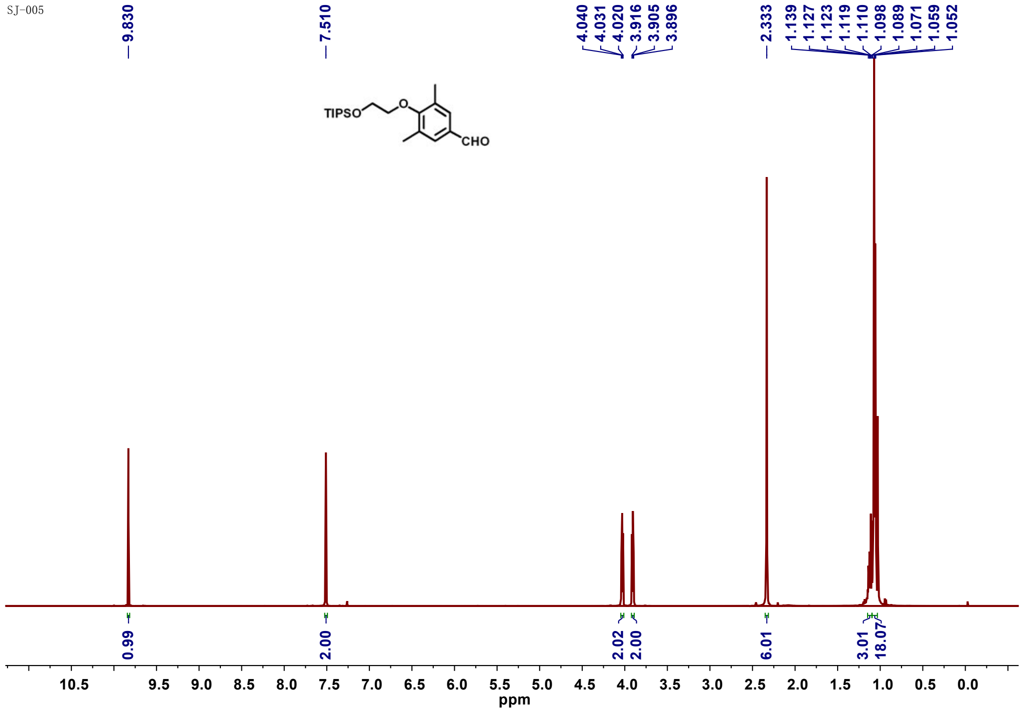


Figure S4. ^{1}H NMR spectrum of compound **12** (500 MHz, 298 K, $CDCl_3$)

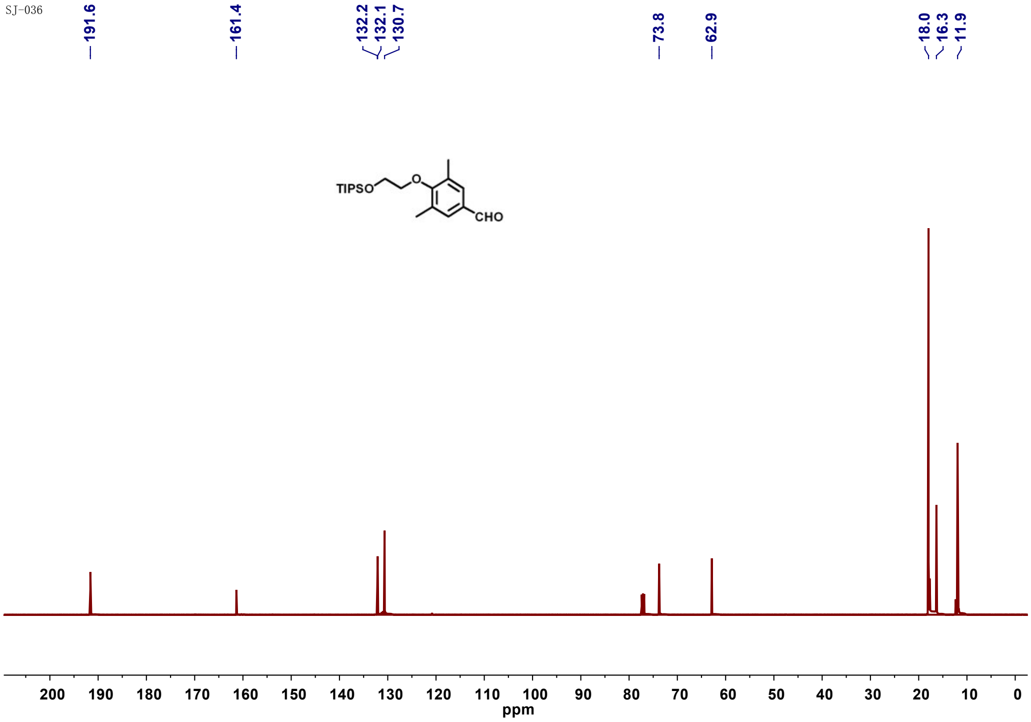
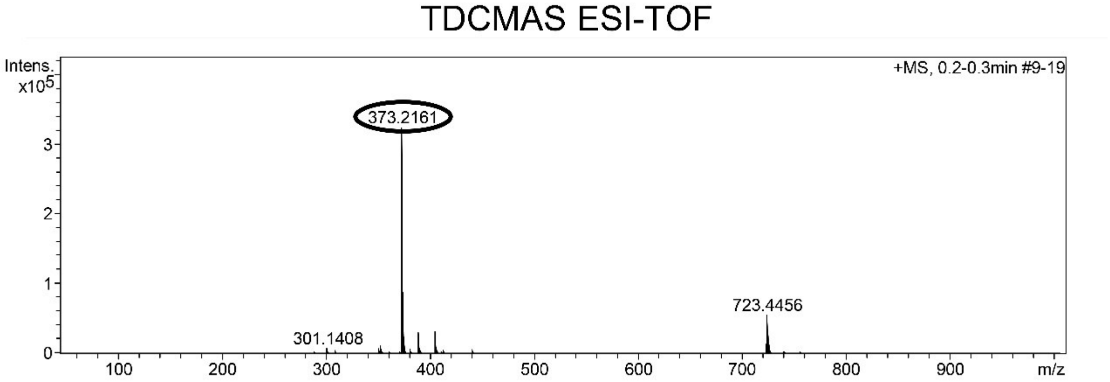


Figure S5. ^{13}C NMR spectrum of compound **12** (125 MHz, 298 K, $CDCl_3$)



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	eP	Conf	N-Rule	Adduct
373.216088	1	C20H34NaO3Si	100.00	373.216942	0.9	2.3	1.7	4.5	even		ok	M+Na

Figure S6. ESI-mass spectrum of compound **12** ($[M + Na]^+$: 373.2161).

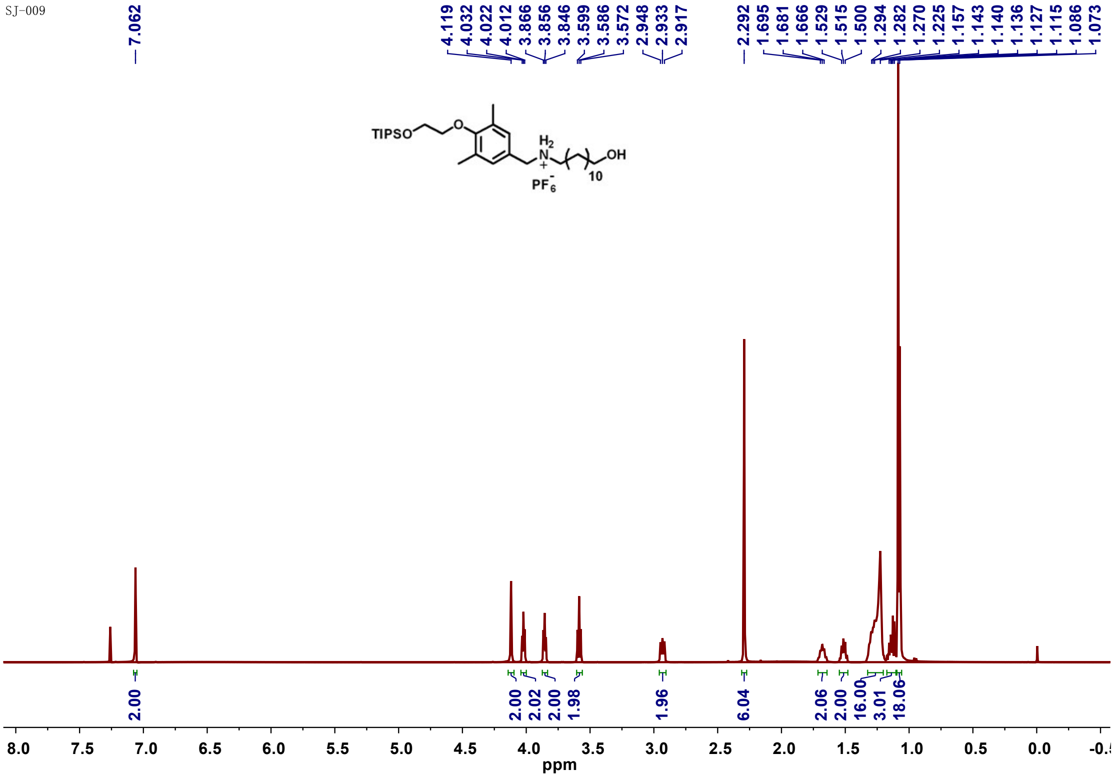


Figure S7. ^1H NMR spectrum of compound **7** (500 MHz, 298 K, $CDCl_3$)

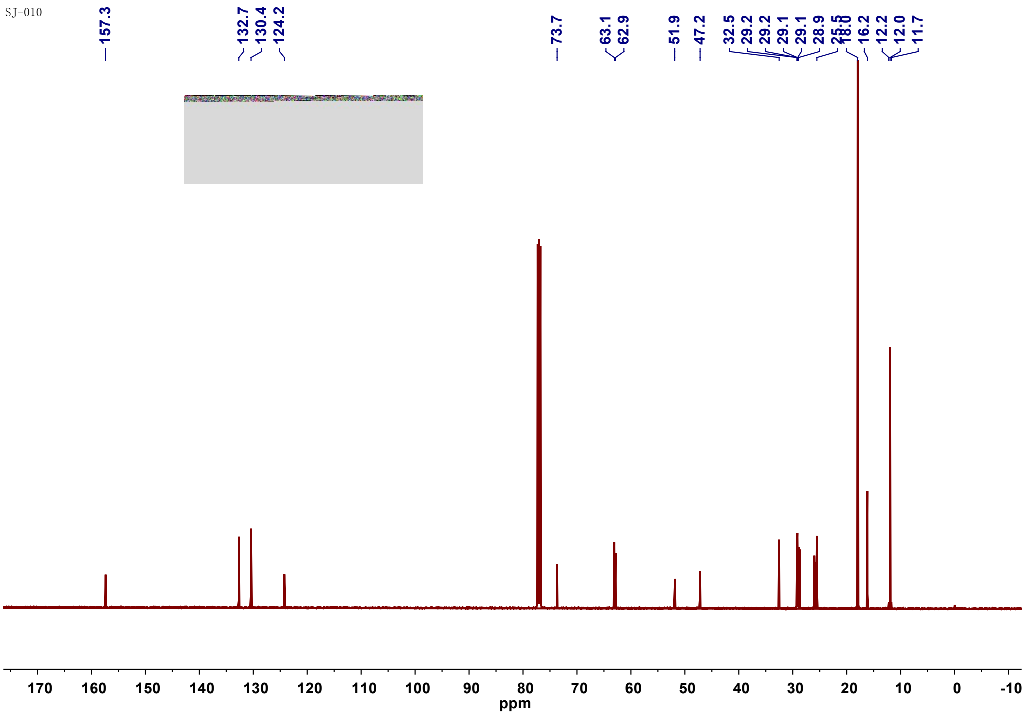
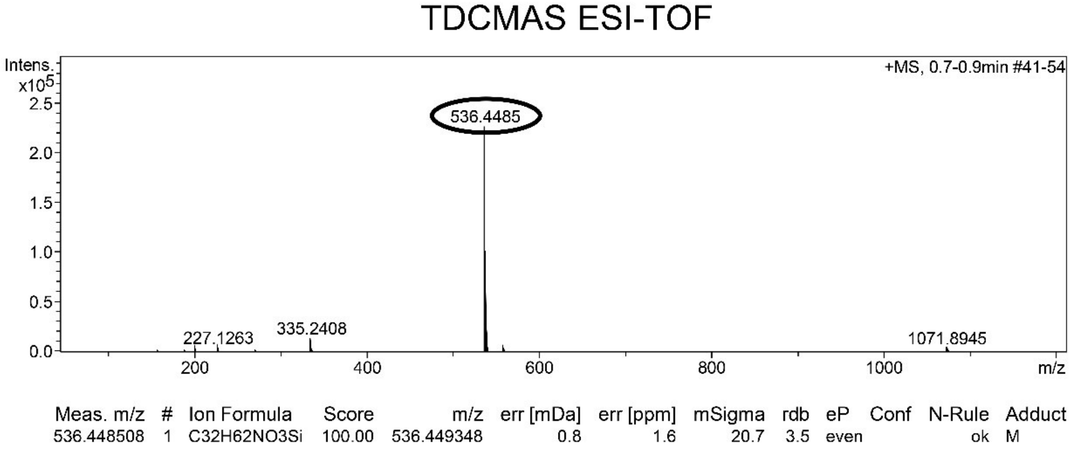


Figure S8. ^{13}C NMR spectrum of compound **7** (125 MHz, 298 K, CDCl$_3$)



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	eP	Conf	N-Rule	Adduct
536.448508	1	C32H62NO3Si	100.00	536.449348	0.8	1.6	20.7	3.5	even		ok	M

Figure S9. ESI-mass spectrum of compound **7** ([M – PF$_6$]$^+$: 536.4485).

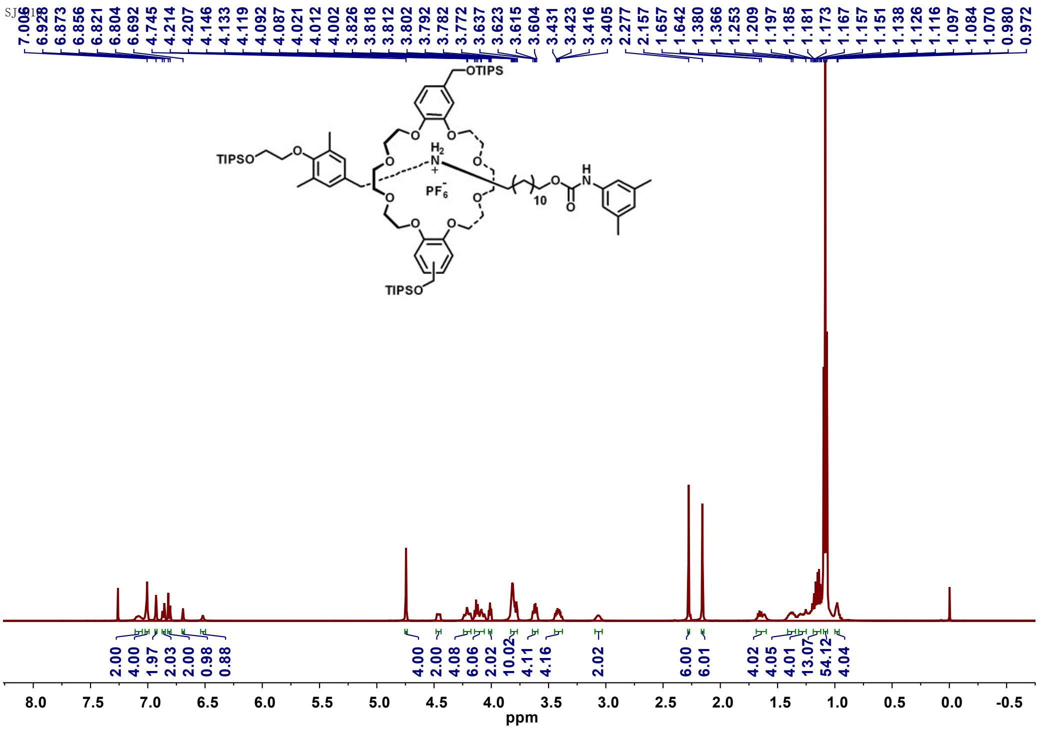


Figure S10. ^{1}H NMR spectrum of compound **5** (500 MHz, 298 K, $CDCl_3$)

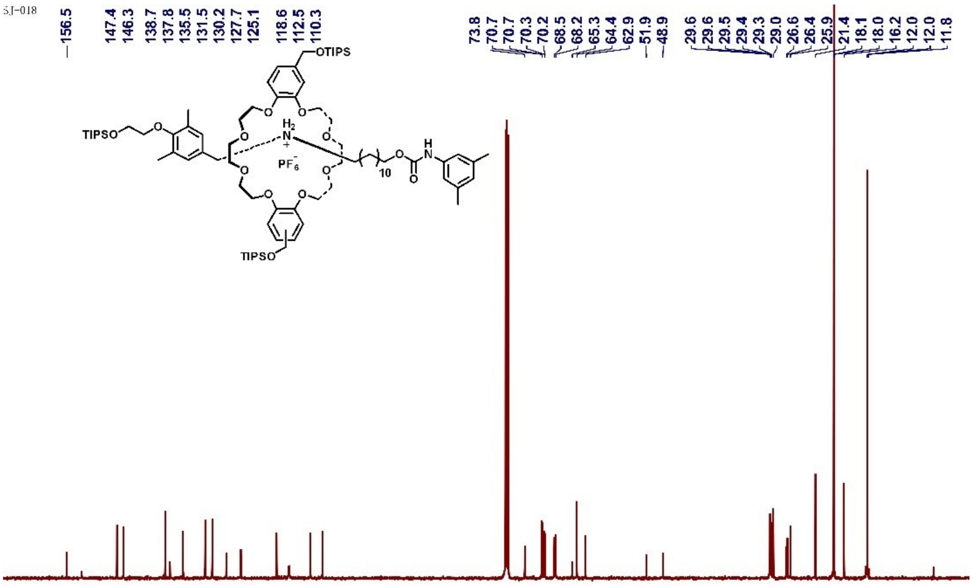


Figure S11. ^{13}C NMR spectrum of compound **5** (125 MHz, 298 K, $CDCl_3$)

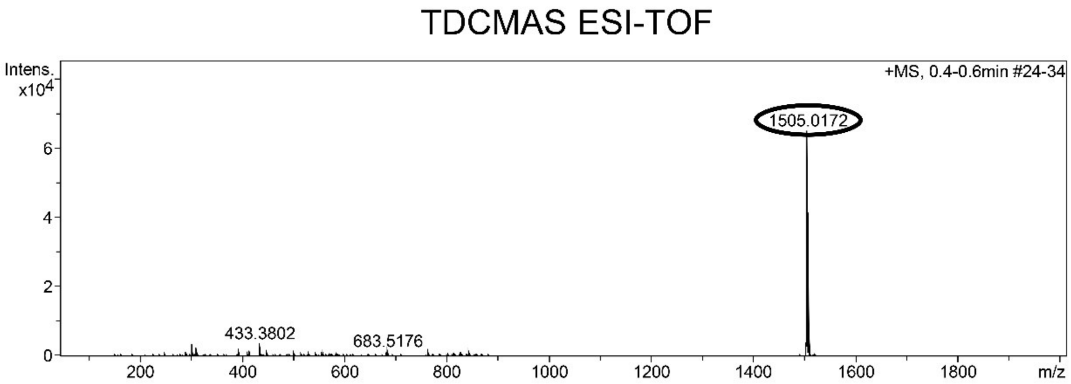


Figure S12. ESI-mass spectrum of compound **5** ($[M - PF_6]^+$: 1505.0172).

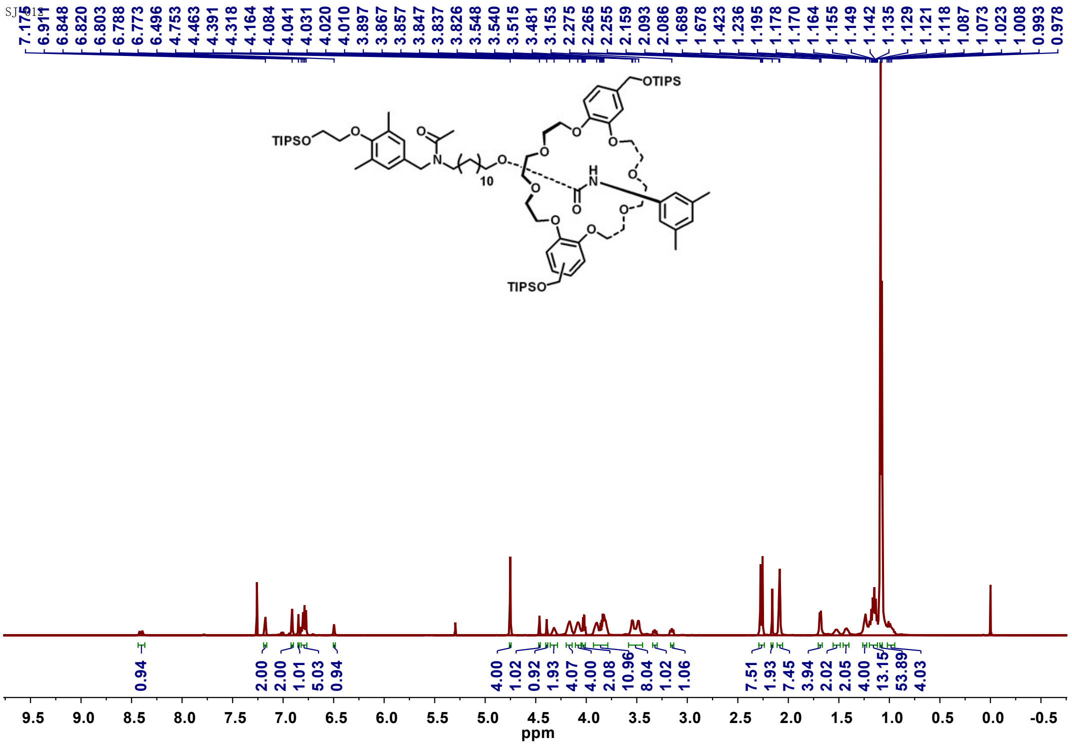


Figure S13. ^{1}H NMR spectrum of compound **4** (500 MHz, 298 K, $CDCl_3$)

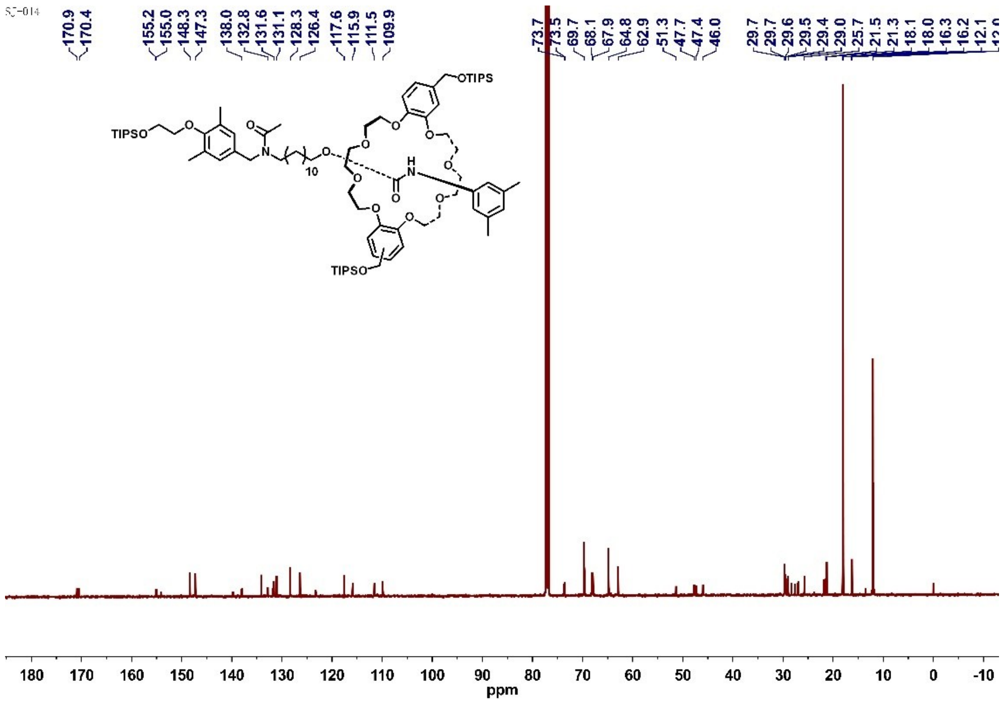
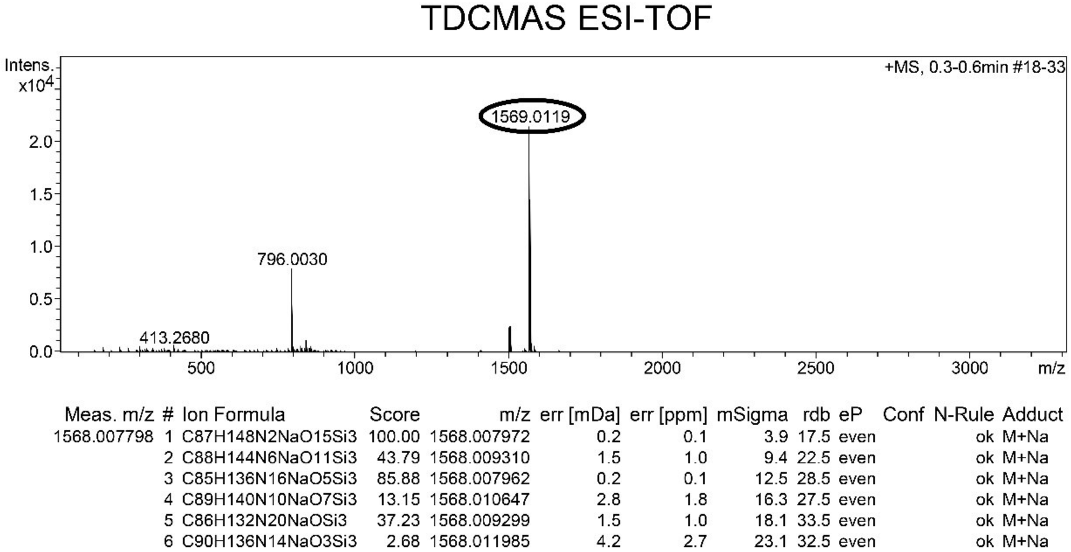


Figure S14. ^{13}C NMR spectrum of compound **4** (125 MHz, 298 K, CDCl$_3$)



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	eP	Conf	N-Rule	Adduct
1568.007798	1	C87H148N2NaO15Si3	100.00	1568.007972	0.2	0.1	3.9	17.5	even		ok	M+Na
	2	C88H144N6NaO11Si3	43.79	1568.009310	1.5	1.0	9.4	22.5	even		ok	M+Na
	3	C85H136N16NaO5Si3	85.88	1568.007962	0.2	0.1	12.5	28.5	even		ok	M+Na
	4	C89H140N10NaO7Si3	13.15	1568.010647	2.8	1.8	16.3	27.5	even		ok	M+Na
	5	C86H132N20NaOSi3	37.23	1568.009299	1.5	1.0	18.1	33.5	even		ok	M+Na
	6	C90H136N14NaO3Si3	2.68	1568.011985	4.2	2.7	23.1	32.5	even		ok	M+Na

Figure S15. ESI-mass spectrum of compound **4** ([M + Na]$^+$: 1569.0119).

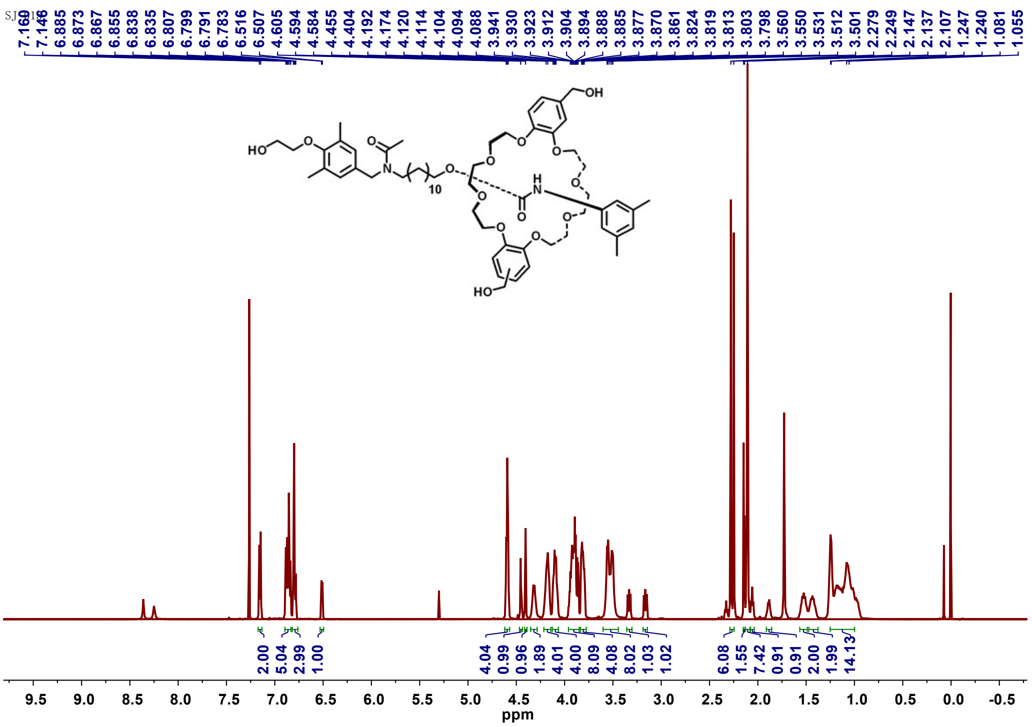


Figure S16. ^{1}H NMR spectrum of compound **3** (500 MHz, 298 K, CDCl$_3$)

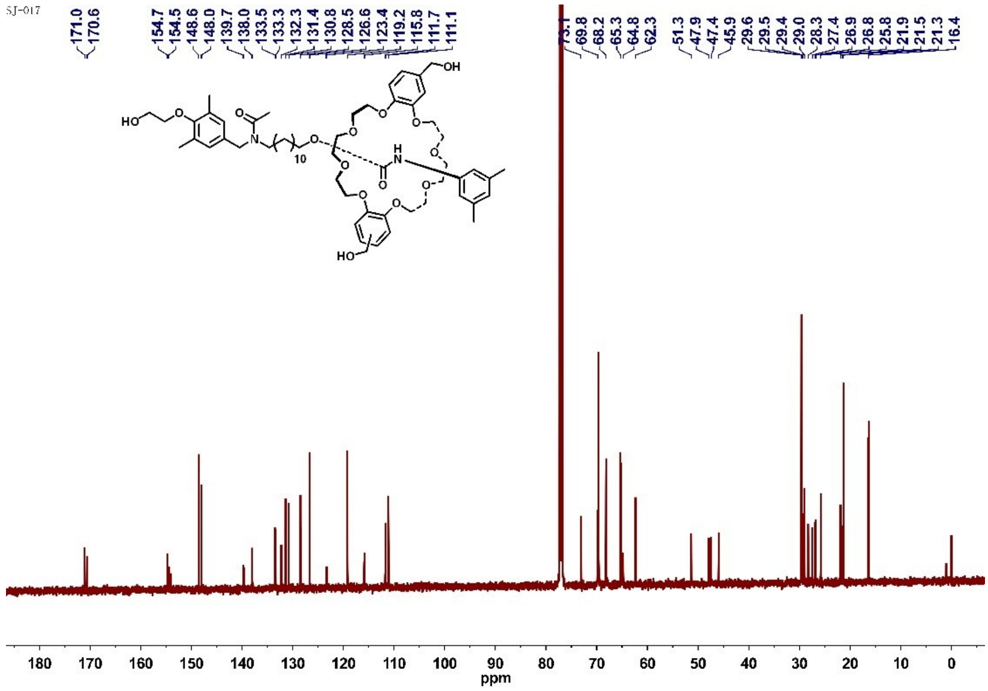
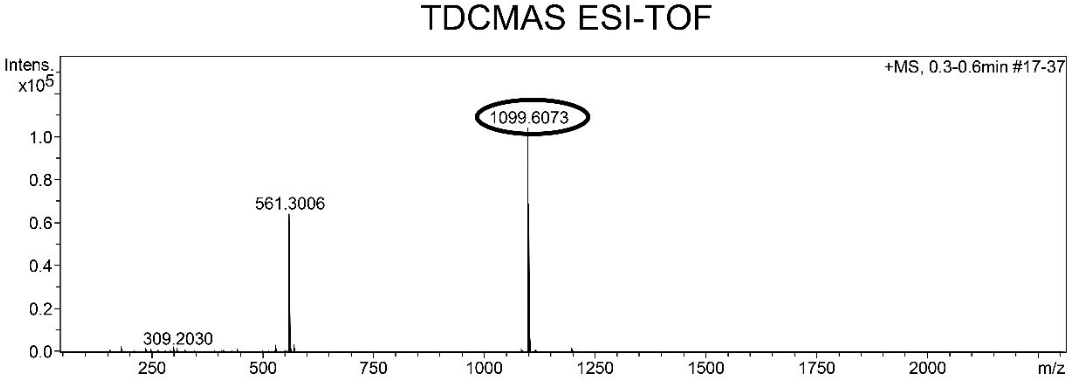


Figure S17. ^{13}C NMR spectrum of compound **3** (125 MHz, 298 K, CDCl$_3$)



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	eP	Conf	N-Rule	Adduct
1099.607286	1	C60H88N2NaO15	100.00	1099.607691	0.4	0.4	4.9	17.5	even		ok	M+Na
	2	C57H80N12NaO9	70.88	1099.606343	-0.9	-0.9	8.7	23.5	even		ok	M+Na
	3	C56H84N8NaO13	27.09	1099.605005	-2.3	-2.1	11.0	18.5	even		ok	M+Na
	4	C54H72N22NaO3	25.09	1099.604995	-2.3	-2.1	14.6	29.5	even		ok	M+Na
	5	C61H84N6NaO11	37.38	1099.609028	1.7	1.6	15.7	22.5	even		ok	M+Na
	6	C58H76N16NaO5	80.90	1099.607680	0.4	0.4	16.4	28.5	even		ok	M+Na
	7	C59H72N20NaO	29.68	1099.609018	1.7	1.6	26.6	33.5	even		ok	M+Na
	8	C62H80N10NaO7	9.47	1099.610366	3.1	2.8	26.7	27.5	even		ok	M+Na
	9	C69H76N10NaO2	4.10	1099.604492	-2.8	-2.5	64.7	36.5	even		ok	M+Na

Figure S18. ESI-mass spectrum of compound **3** ($[M + Na]^+$: 1099.6073).

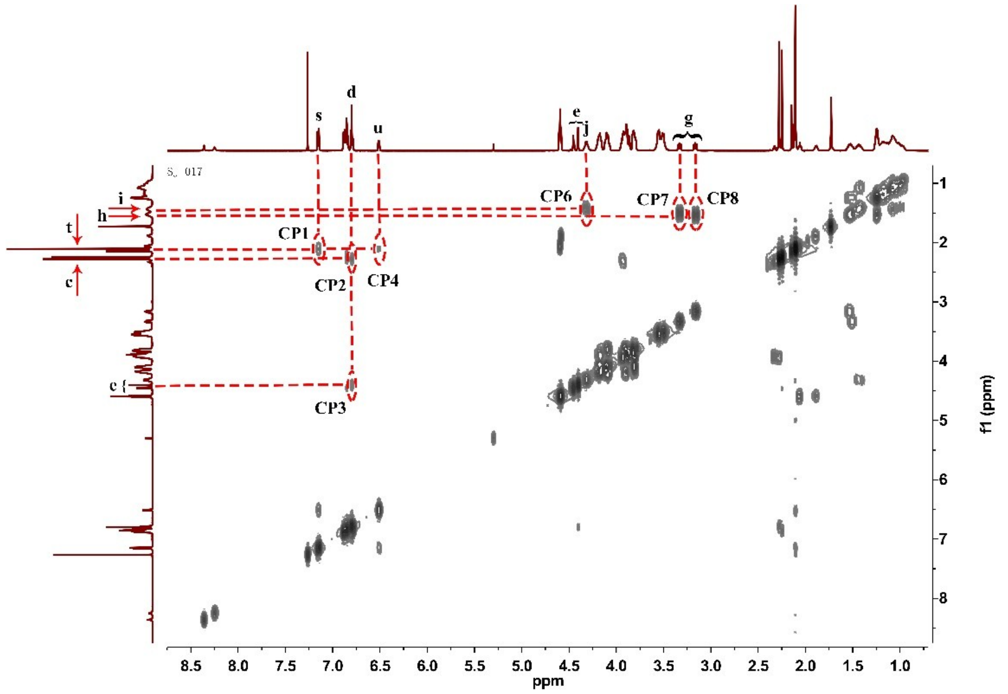


Figure S19. ^1H-^1H COSY spectrum of compound **3** (500 MHz, 298 K, $CDCl_3$)

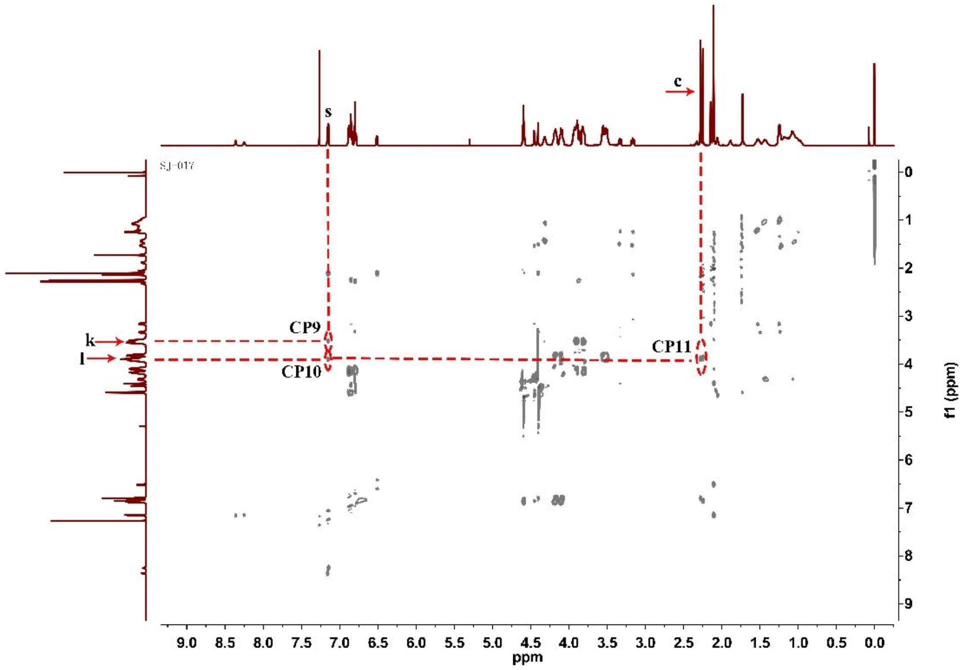


Figure S20. ^{1}H-^{1}H ROESY spectrum of compound **3** (500 MHz, 298 K, CDCl$_3$)

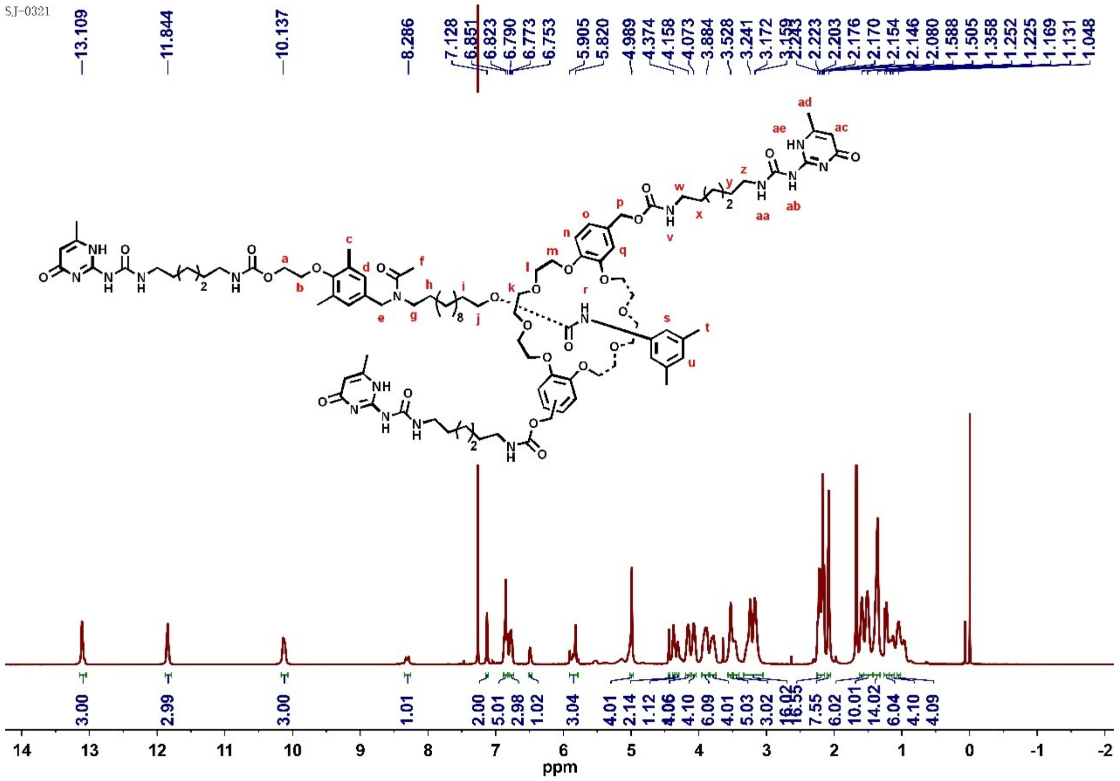


Figure S21. ^{1}H NMR spectrum of **(Upy)$_3$[2]rotaxane 1** (500 MHz, 298 K, CDCl$_3$)

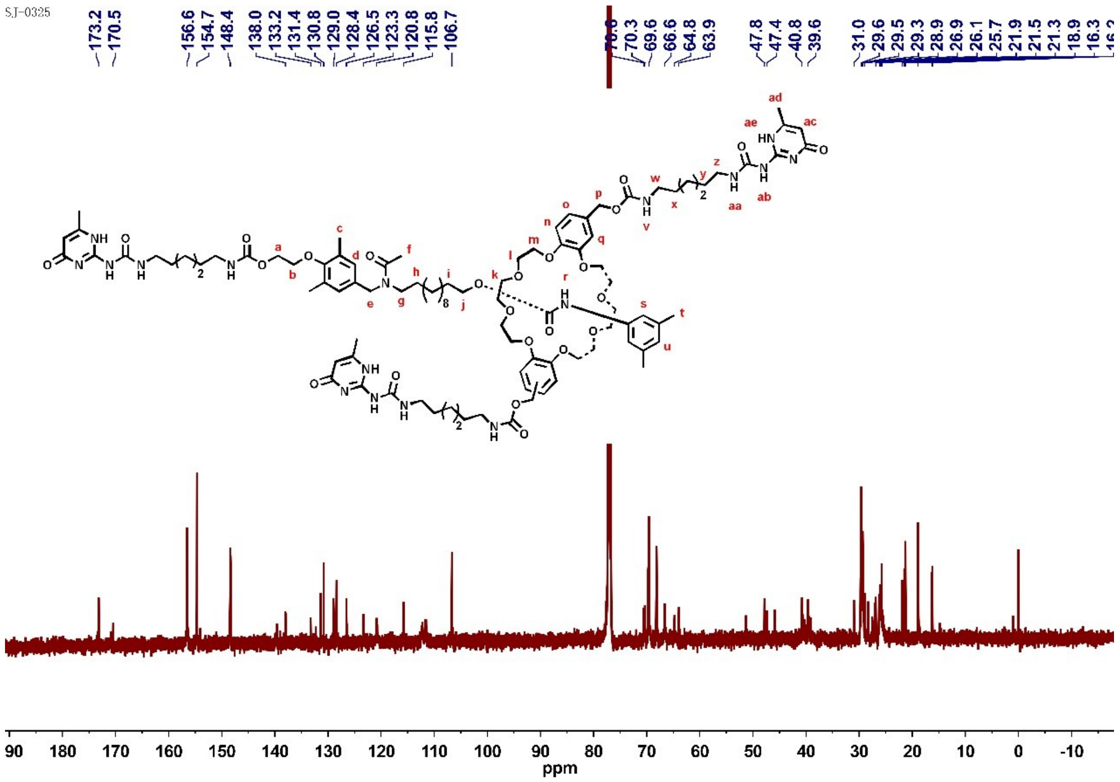
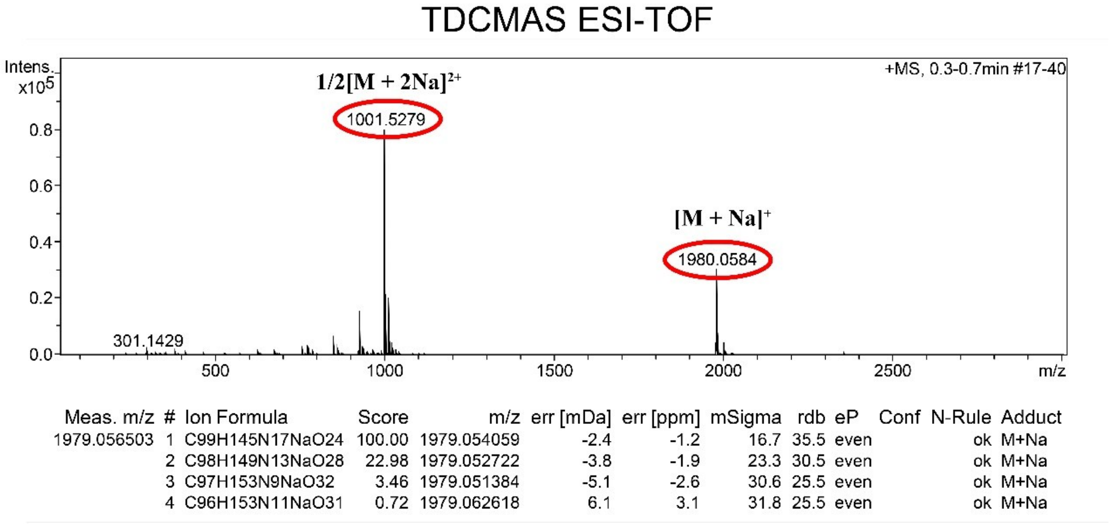


Figure S22. ^{13}C NMR spectrum of **(Upy)$_3$[2]rotaxane 1** (125 MHz, 298 K, $CDCl_3$)



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	eP	Conf	N-Rule	Adduct
1979.056503	1	C99H145N17NaO24	100.00	1979.054059	-2.4	-1.2	16.7	35.5	even		ok	M+Na
	2	C98H149N13NaO28	22.98	1979.052722	-3.8	-1.9	23.3	30.5	even		ok	M+Na
	3	C97H153N9NaO32	3.46	1979.051384	-5.1	-2.6	30.6	25.5	even		ok	M+Na
	4	C96H153N11NaO31	0.72	1979.062618	6.1	3.1	31.8	25.5	even		ok	M+Na

Figure S23. ESI-mass spectrum of **(Upy)$_3$[2]rotaxane 1** ($[M + Na]^+$: 1980.0584, $[M + 2Na]^{2+}$: 1001.5279)

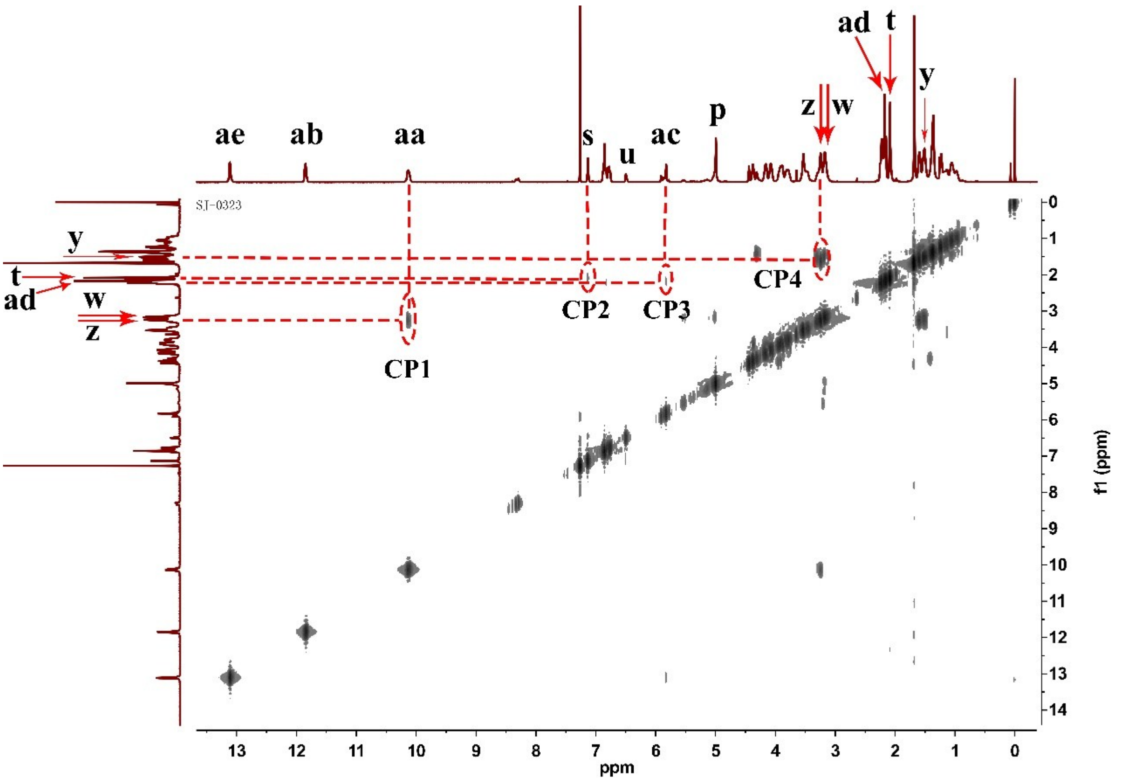


Figure S24. ^{1}H-^{1}H COSY spectrum of **(Upy)$_3$[2]rotaxane 1** (500 MHz, 298 K, CDCl$_3$)

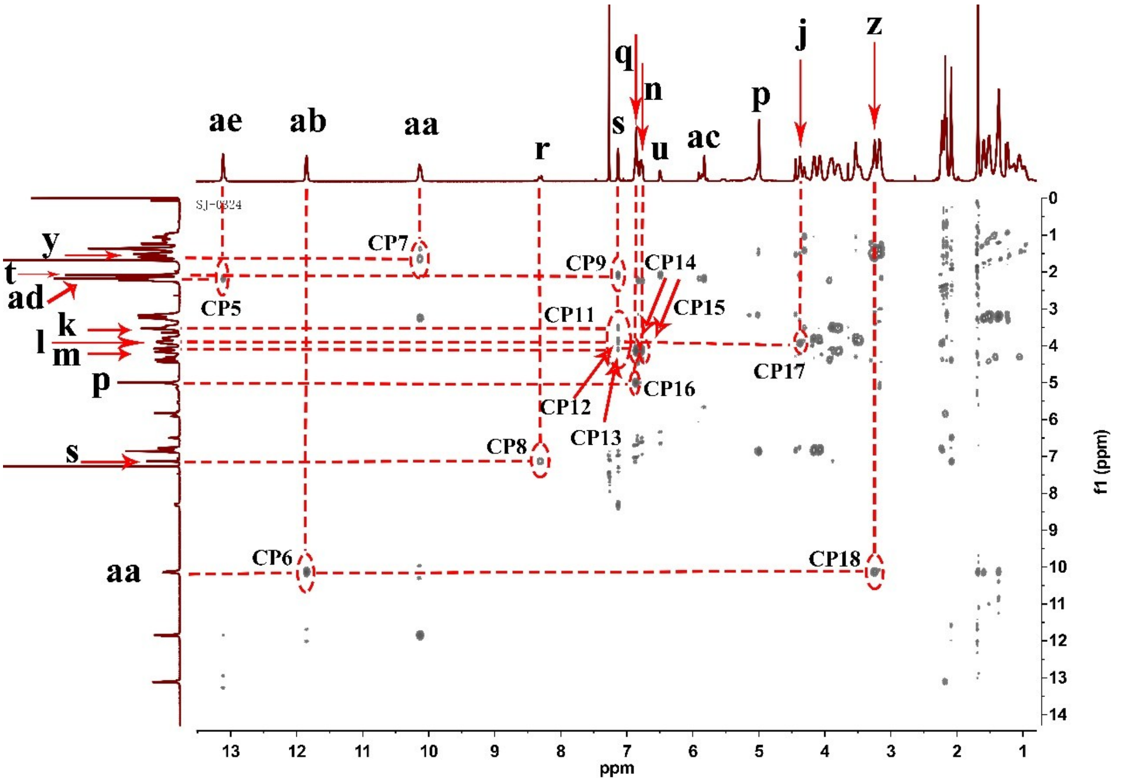


Figure S25. ^{1}H-^{1}H ROESY spectrum of **(Upy)$_3$[2]rotaxane 1** (500 MHz, 298 K, CDCl$_3$)

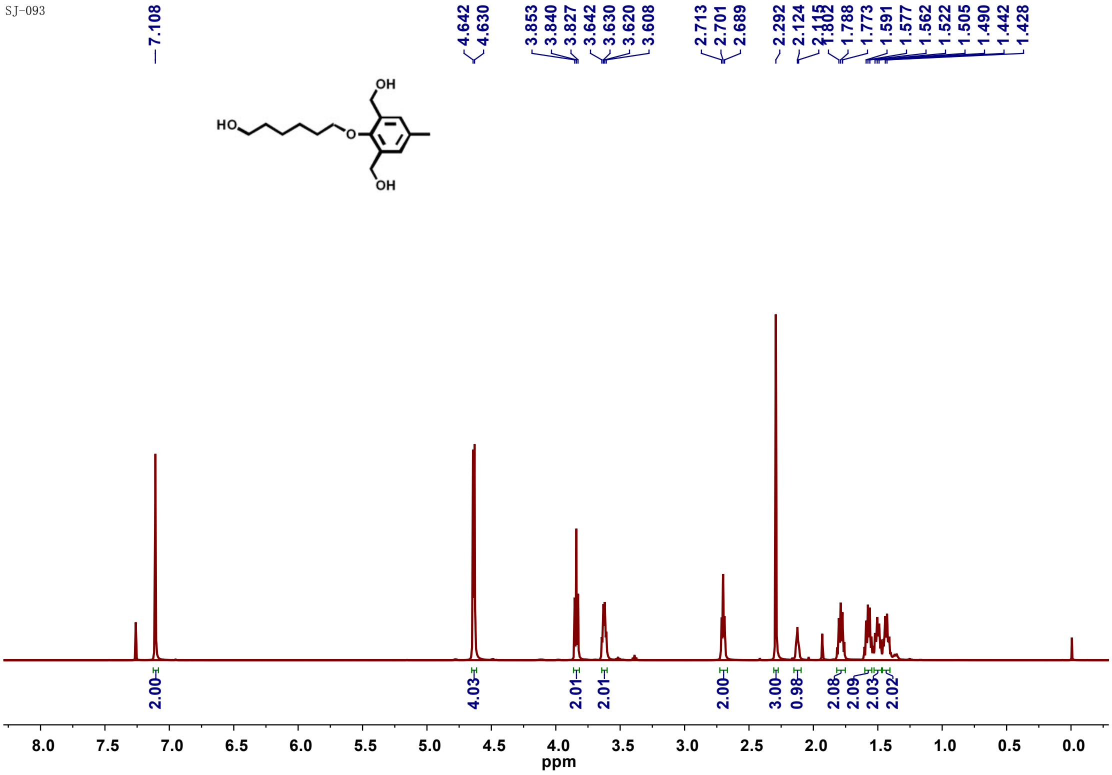


Figure S26. ^{1}H NMR spectrum of compound **C2** (500 MHz, 298 K, $CDCl_3$)

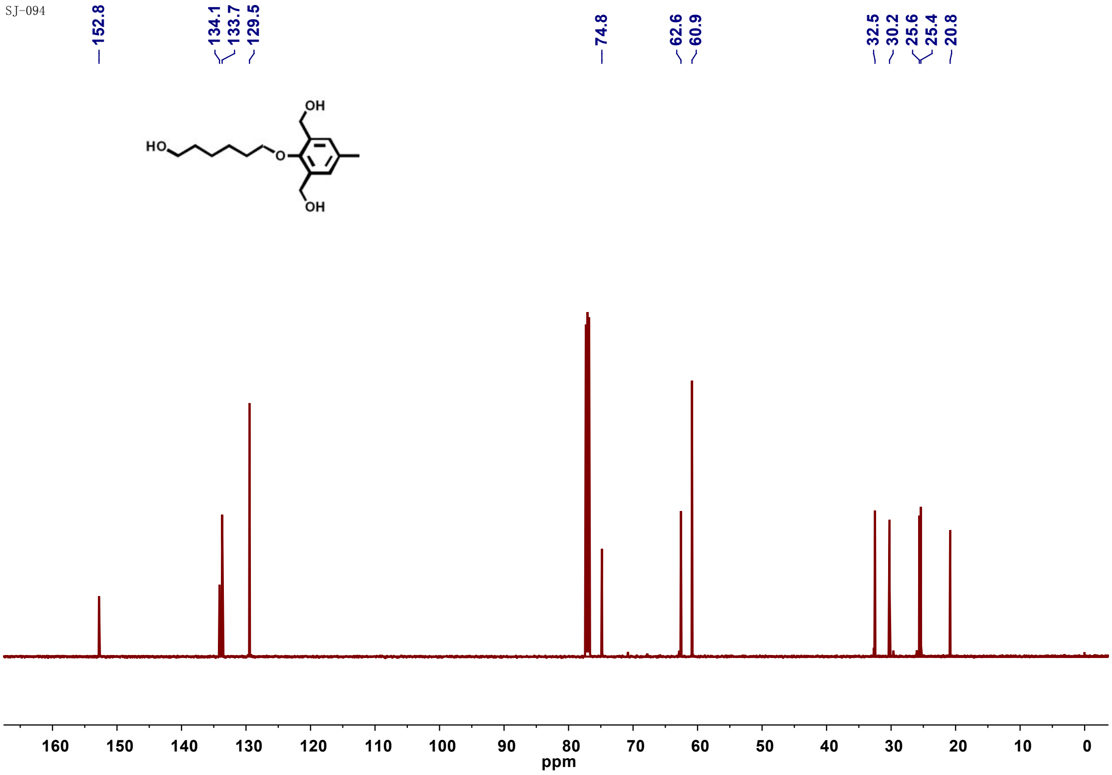
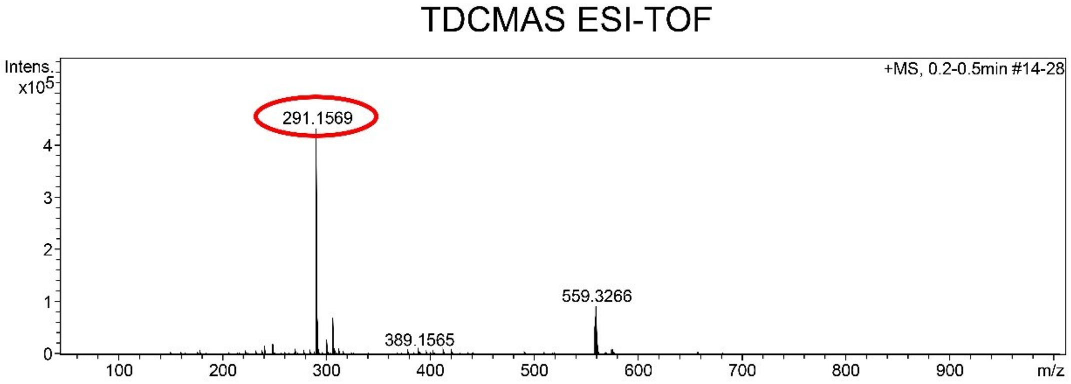


Figure S27. ^{13}C NMR spectrum of compound **C2** (125 MHz, 298 K, $CDCl_3$)



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	eP	Conf	N-Rule	Adduct
291.156854	1	C15H24NaO4	100.00	291.156680	-0.2	-0.6	2.2	3.5	even		ok	M+Na

Figure S28. ESI-mass spectrum of compound **C2** ($[M + Na]^+$: 291.1569)

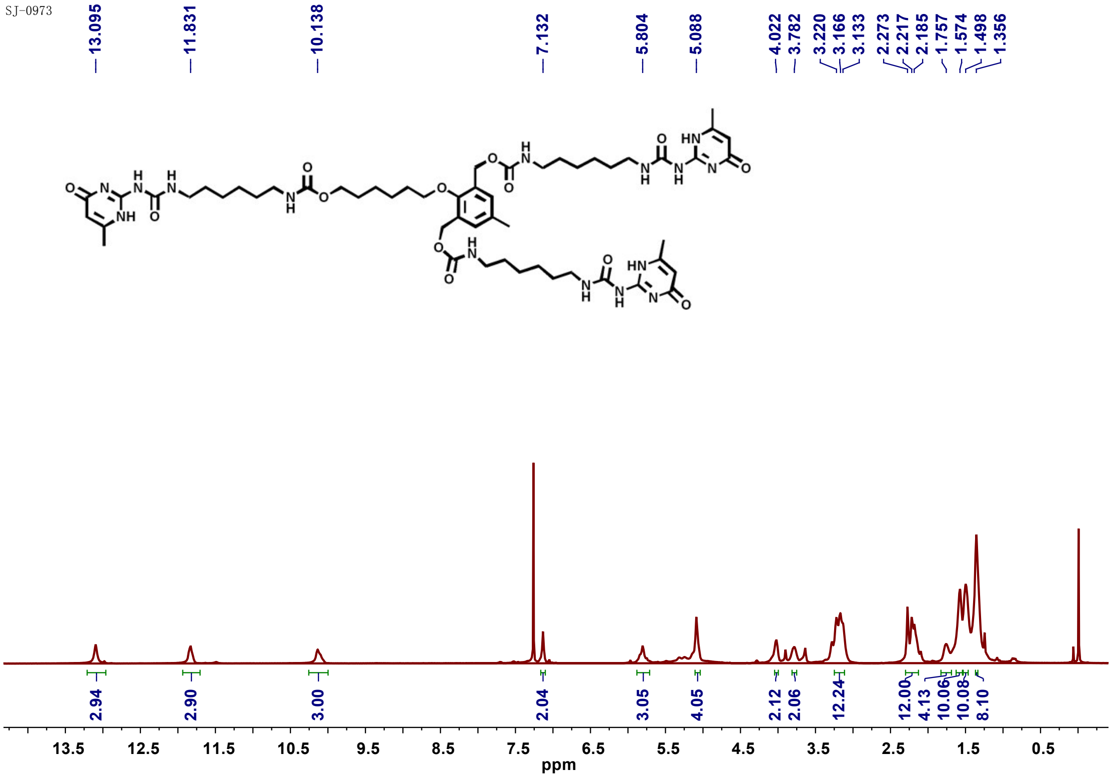


Figure S29. ^{1}H NMR spectrum of compound **C1** (500 MHz, 298 K, $CDCl_3$)

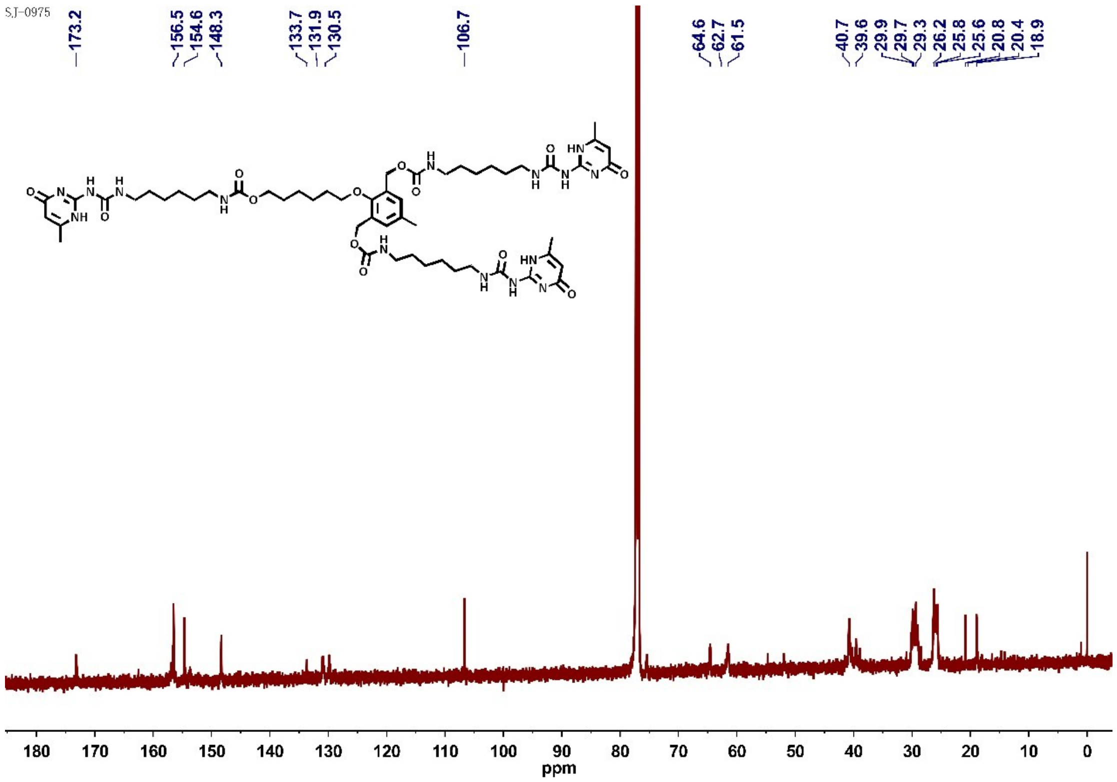
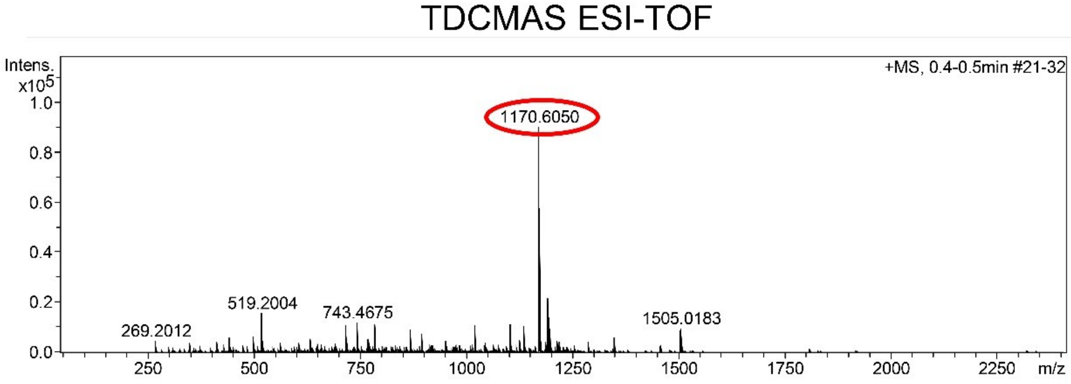


Figure S30. ^{13}C NMR spectrum of compound **C1** (125 MHz, 298 K, $CDCl_3$)



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	eP	Conf	N-Rule	Adduct
1170.604980	1	C56H93NNaO23	44.36	1170.603059	-1.9	-1.6	5.9	10.5	even		ok	M+Na
	2	C54H81N15NaO13	43.99	1170.603048	-1.9	-1.6	5.9	21.5	even		ok	M+Na
	3	C57H89N5NaO19	100.00	1170.604396	-0.6	-0.5	6.7	15.5	even		ok	M+Na
	4	C53H85N11NaO17	13.21	1170.601711	-3.3	-2.8	6.9	16.5	even		ok	M+Na
	5	C51H73N25NaO7	12.28	1170.601700	-3.3	-2.8	10.3	27.5	even		ok	M+Na
	6	C55H77N19NaO9	83.15	1170.604386	-0.6	-0.5	16.2	26.5	even		ok	M+Na
	7	C52H69N29NaO3	34.95	1170.603038	-1.9	-1.7	17.6	32.5	even		ok	M+Na
	8	C56H73N23NaO5	60.73	1170.605723	0.7	0.6	27.0	31.5	even		ok	M+Na
	9	C57H69N27NaO	19.33	1170.607061	2.1	1.8	38.1	36.5	even		ok	M+Na

Figure S31. ESI-mass spectrum of compound **C1** ($[M + Na]^+$: 1170.6050)

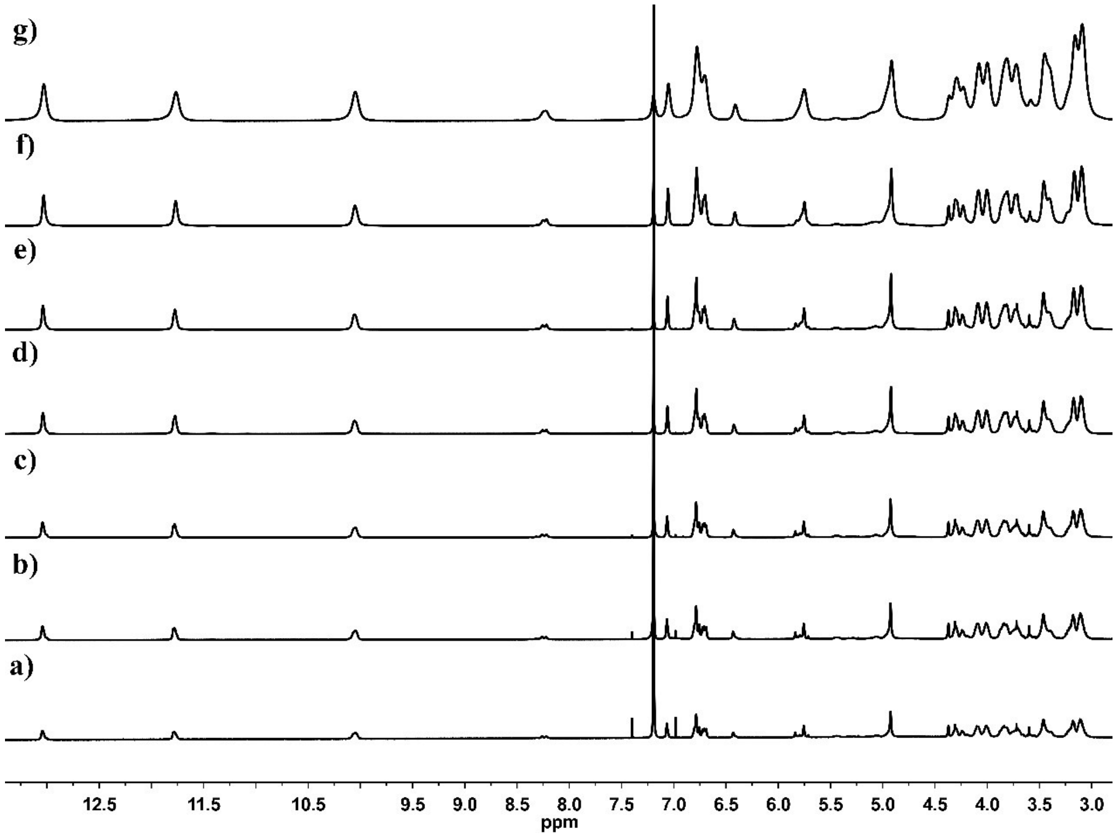


Figure S32. Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 298K) of **(Upy)$_3$[2]rotaxane 1** at different concentrations: (a) 0.2 mM, (b) 0.6 mM, (c) 1.0 mM, (d) 5.0 mM, (e) 10.0 mM, (f) 20.0 mM, (g) 30.0 mM

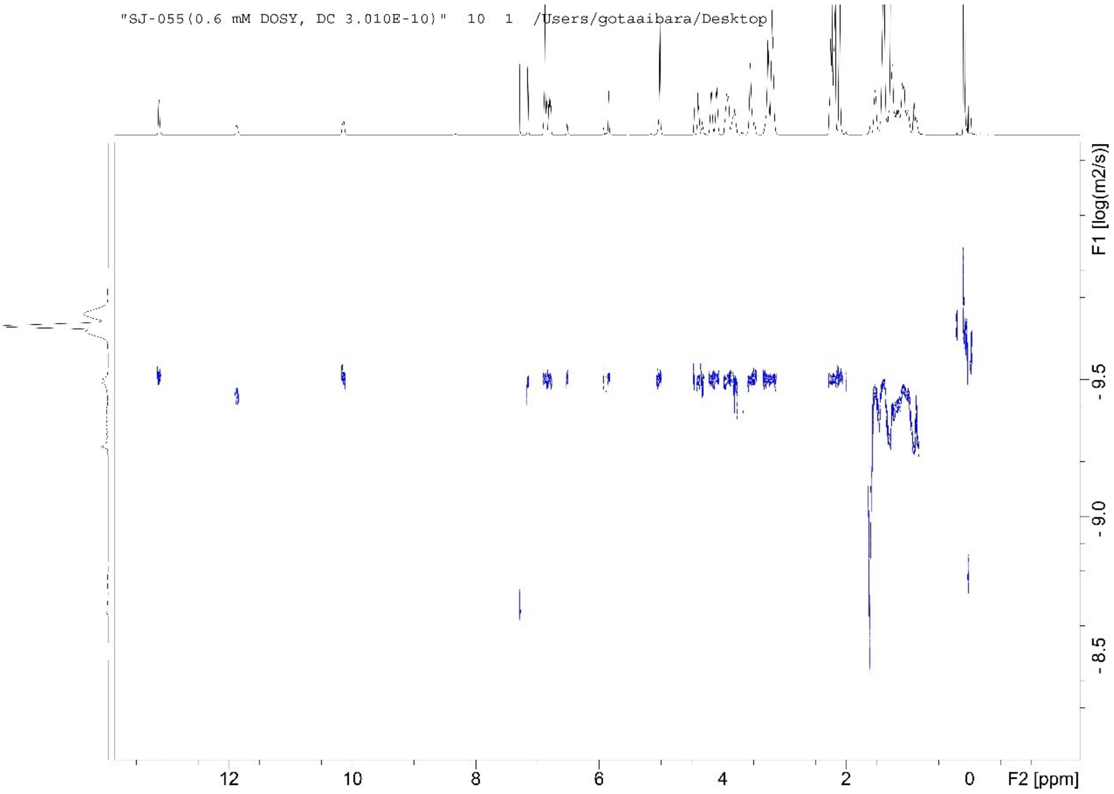


Figure S33. Partial DOSY spectrum of **(Upy)$_3$[2]rotaxane 1** (c = 0.6 mM, 500 MHz, 298 K, $CDCl_3$)

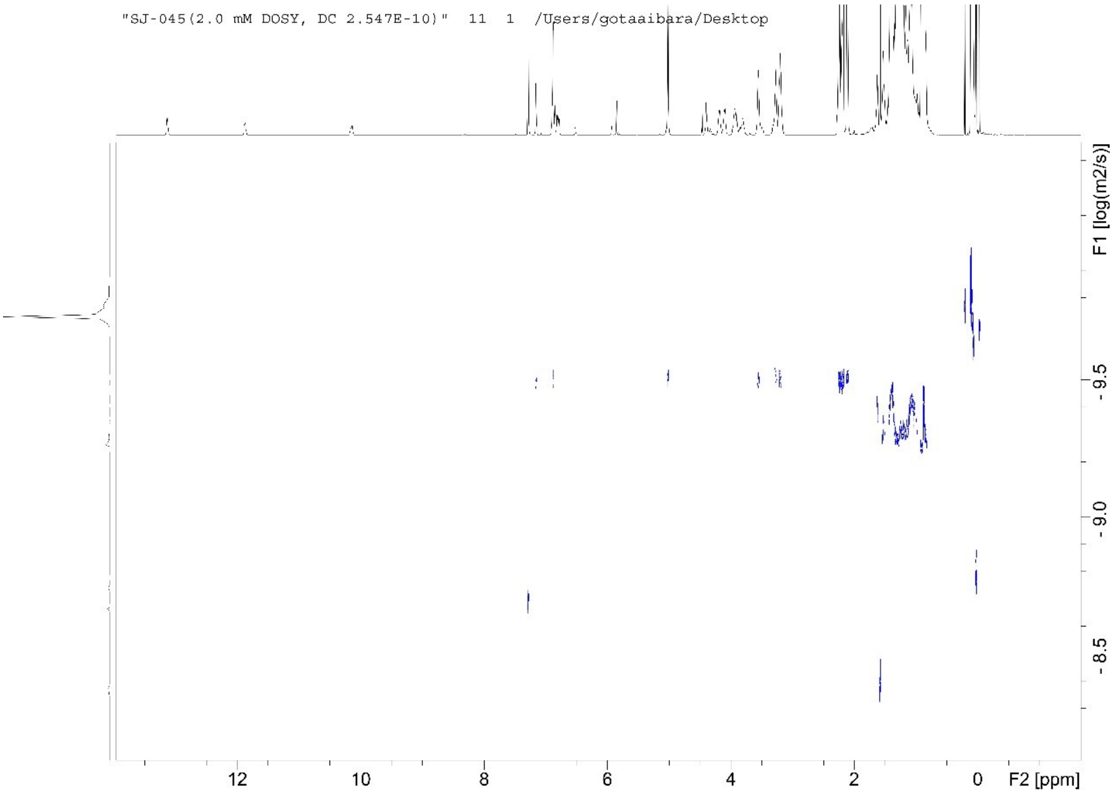


Figure S34. Partial DOSY spectrum of **(Upy)$_3$[2]rotaxane 1** (c = 2.0 mM, 500 MHz, 298 K, CDCl$_3$)

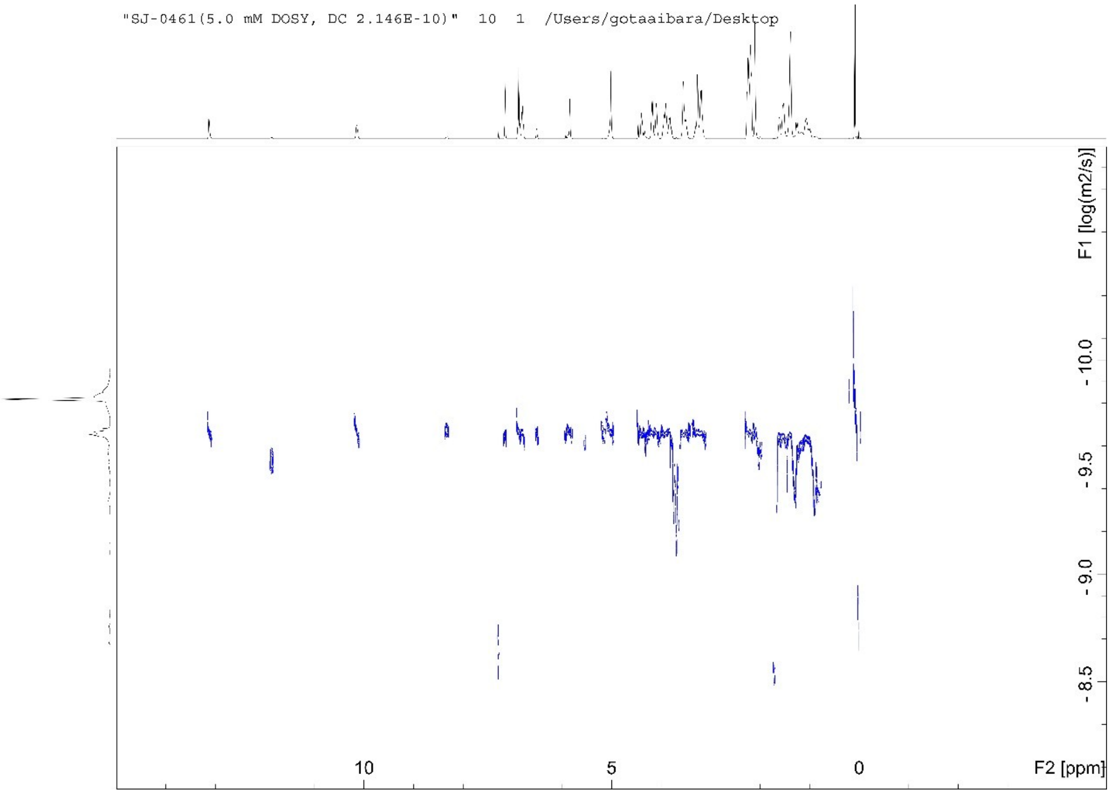


Figure S35. Partial DOSY spectrum of **(Upy)$_3$[2]rotaxane 1** (c = 5.0 mM, 500 MHz, 298 K, CDCl$_3$)

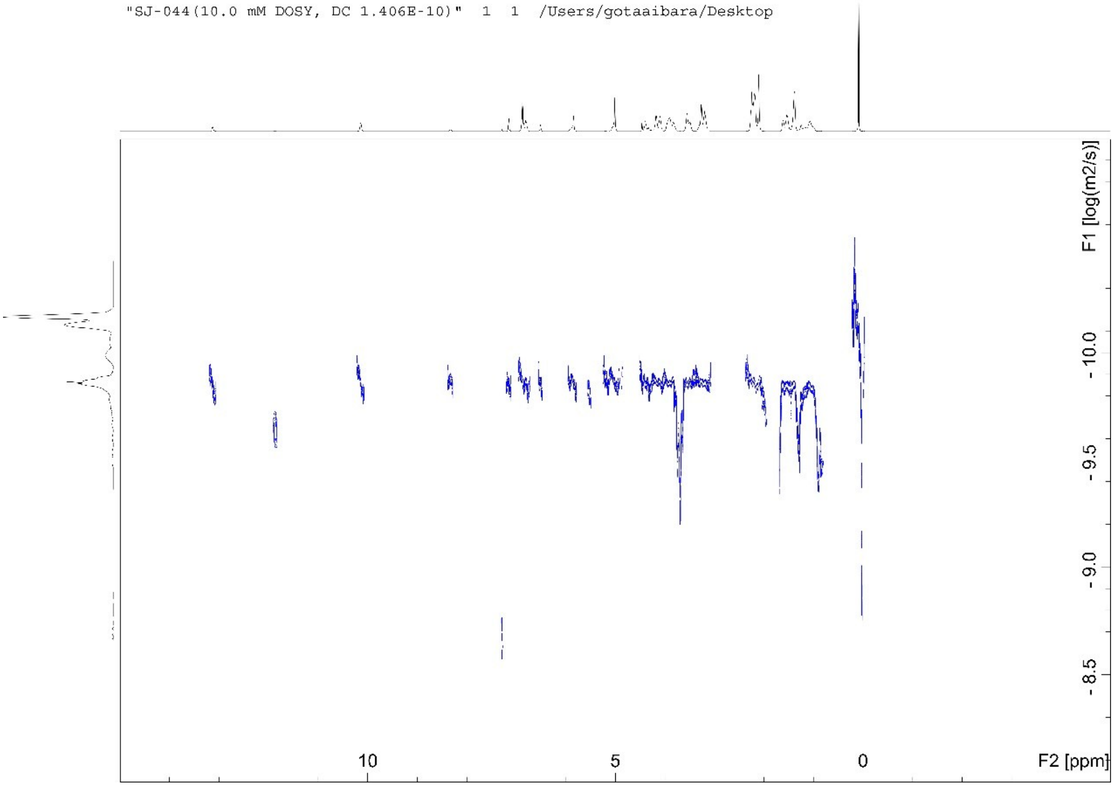


Figure S36. Partial DOSY spectrum of **(Upy)$_3$[2]rotaxane 1** (c = 10.0 mM, 500 MHz, 298 K, CDCl$_3$)

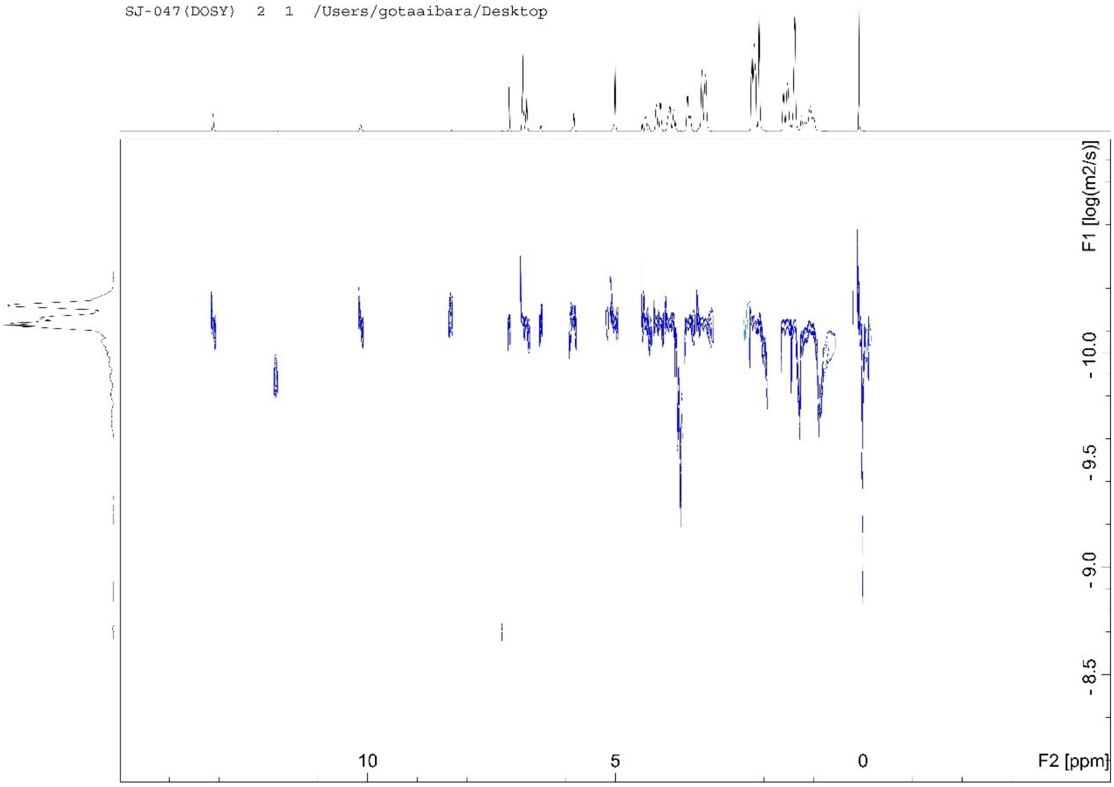


Figure S37. Partial DOSY spectrum of **(Upy)$_3$[2]rotaxane 1** (c = 20.0 mM, 500 MHz, 298 K, CDCl$_3$)

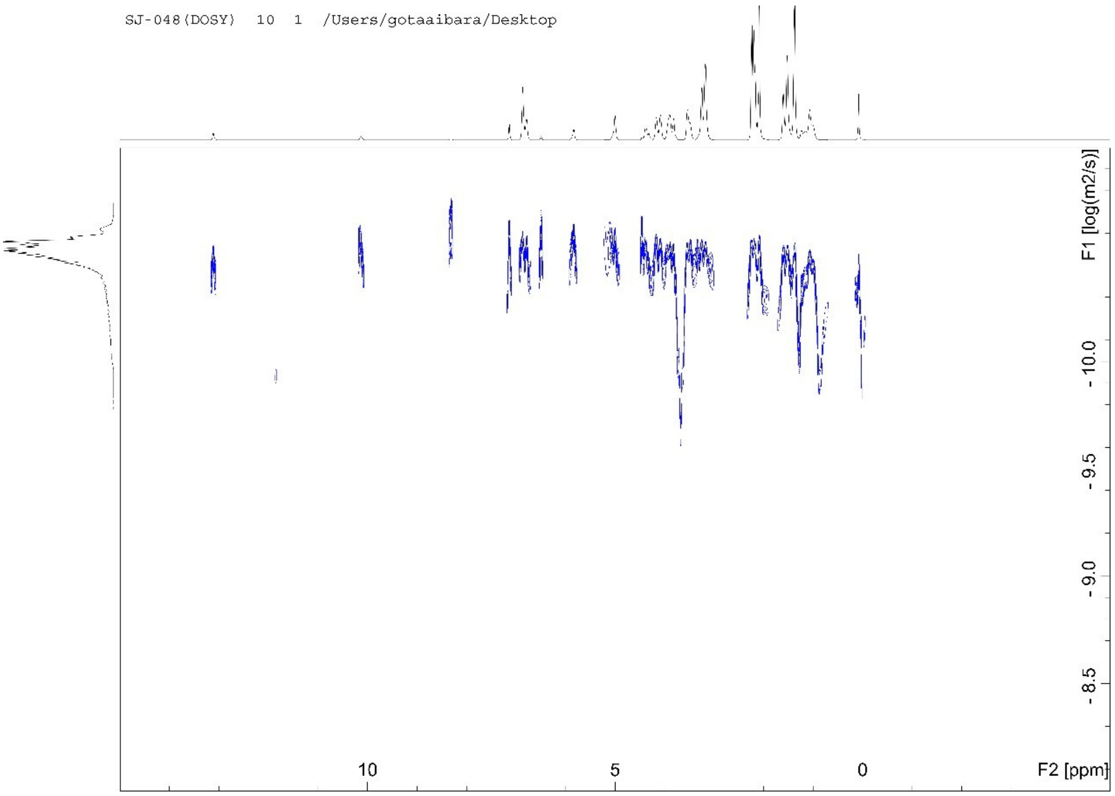


Figure S38. Partial DOSY spectrum of **(Upy)$_3$[2]rotaxane 1** (c = 30.0 mM, 500 MHz, 298 K, CDCl$_3$)

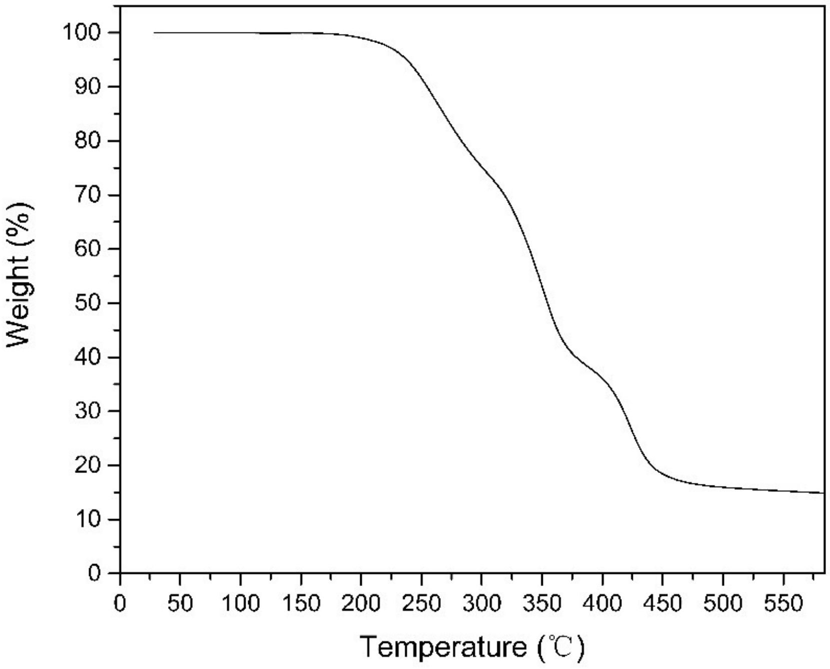


Figure S39. Thermal analysis of (Upy)$_3$[2]rotaxane 1. Thermogravimetric analysis (TGA) curve of **(Upy)$_3$[2]rotaxane 1** from 25 to 585 ℃. The experiment was performed at a heating rate of 10 ℃/min under N_2 atmosphere.

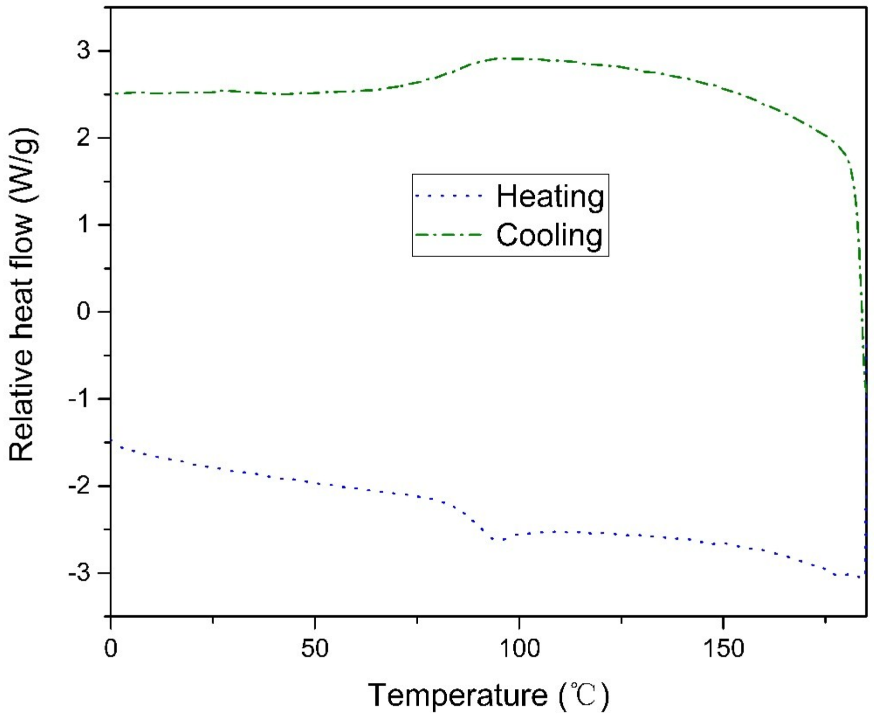


Figure S40. Thermal analysis of (Upy)$_3$[2]rotaxane 1. Differential scanning calorimetry (DSC) curve of **(Upy)$_3$[2]rotaxane 1** from 0 to 185 °C. The experiment was performed at heating and cooling rate of 10 °C/min under N$_2$ atmosphere.

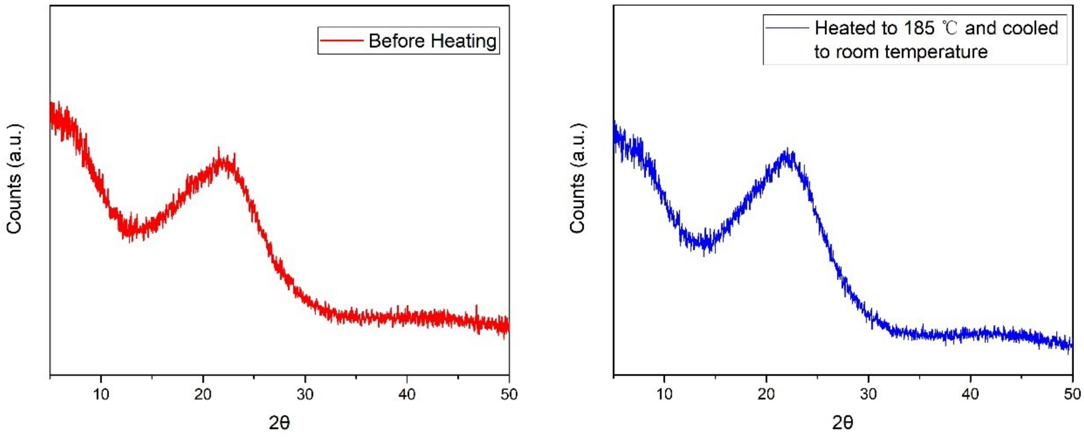


Figure S41. Powder x-ray diffraction of (Upy)$_3$[2]rotaxane 1. Shown are the diffractograms of left: before heated. Right: after heated to 185 °C and cooled to room temperature.

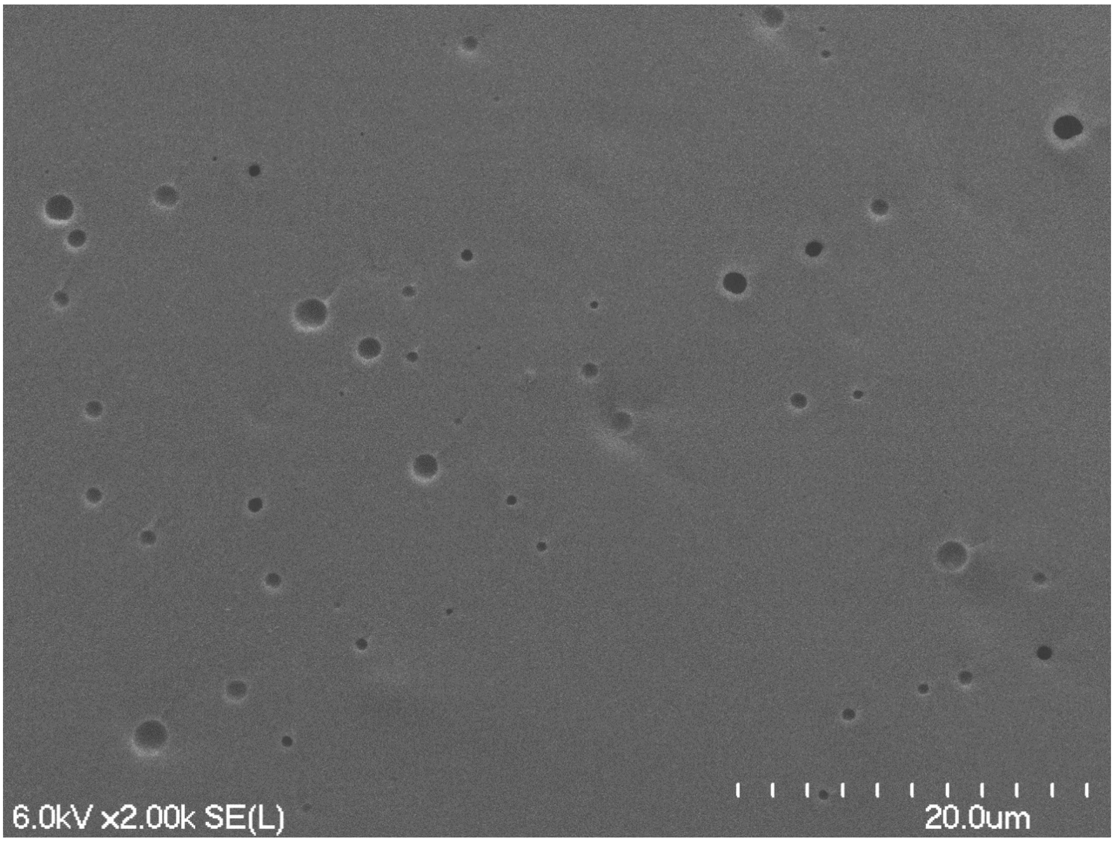


Figure S42. SEM image of rotaxane-cross -linked film.

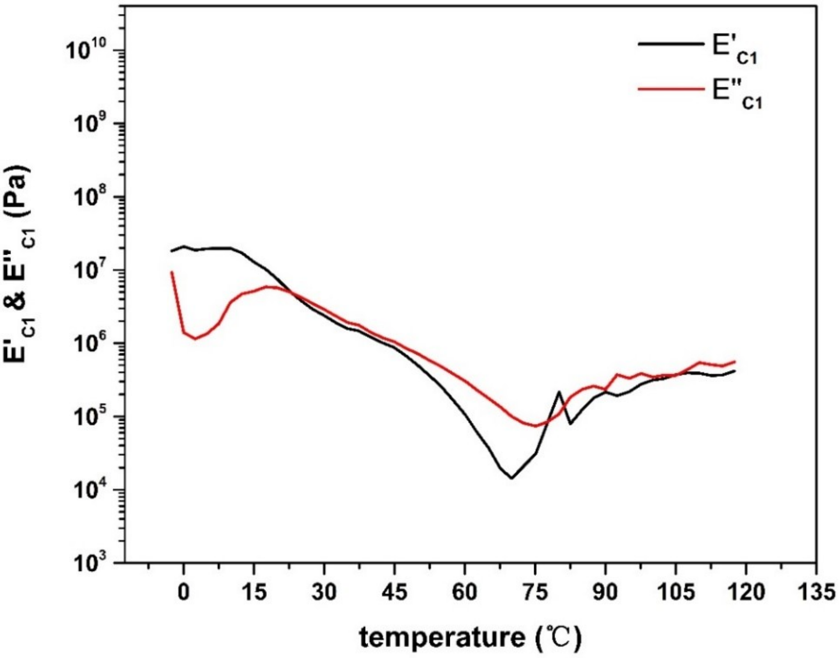


Figure S43. Dynamic mechanical analysis (DMA, 2.5 ℃/min) trace of non-rotaxane-cross-linked film; shown are storage moduli (E'_{C1}) and loss moduli (E''_{C1})

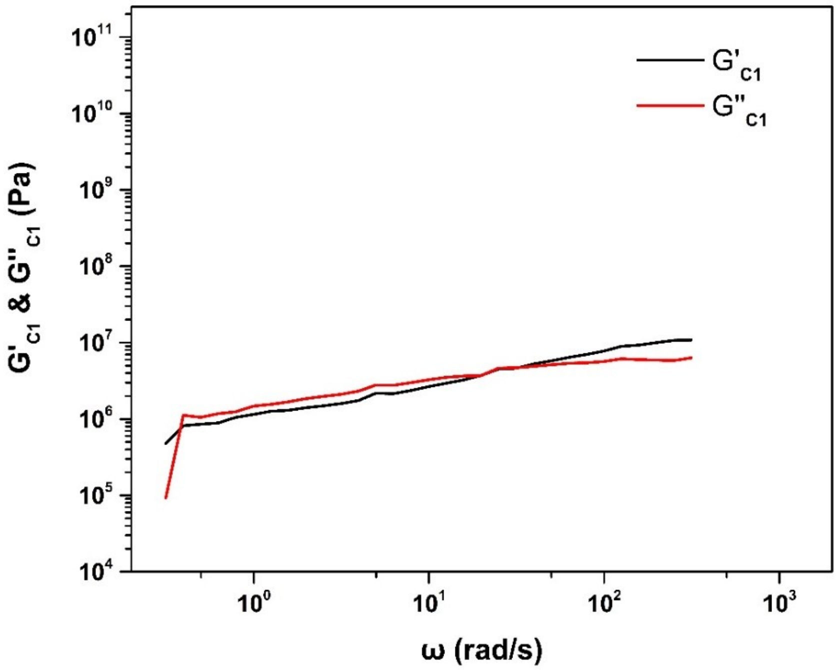


Figure S44. Storage moduli (G'_{C1}) and loss moduli (G''_{C1}) of non-rotaxane-cross-linked film versus frequency (ω) at 298 K.

References:

(S1) B. Qin, S. Zhang, Z. Huang, J. F. Xu, X. Zhang, *Macromolecules* 2018, **51,** 1620-1625.
(S2) Y. Kohsaka, G. I. Konishi, T. Takata, *Polymer Journal,* 2007, **39,** 861-873.
(S3) J. Sawada, D. Aoki, T. Takata, *Macromol. Symp.,* 2017, **372,** 115-119.
(S4) D. Aoki, S. Uchida, T. Takata, *Angew. Chem. Int. Ed.* 2015, **54,** 6770-6774