Electronic Supplementary Material (ESI) for Polymer Chemistry.

Mechanically Linked Poly[2]rotaxanes Constructed from the Benzo-21-Crown-7/Secondary Ammonium Salt Recognition Motif

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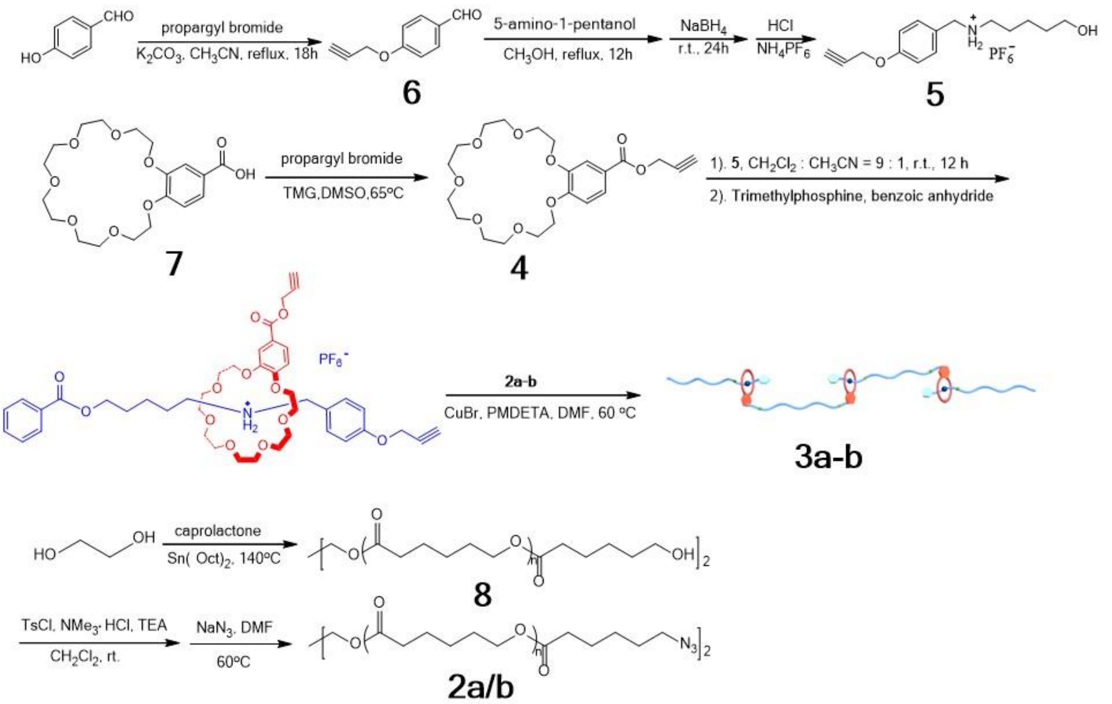
Supporting Information

1. *Materials and Methods*

Ethylene glycol (EG), ε-caprolactone (CL, 99%, Acros), triethylamine (TEA), dichloromethane (CH_2Cl_2), acetone, dimethylsulfoxide (DMSO) and acetonitrile (MeCN) were dried over CaH_2 and distilled just prior to use. K_2CO_3, trimethylamine hydrochloride and benzo-21-crown-7 were dried over P_4O_{10} in a vacuum oven just prior to use. Tetrahydrofuran (THF) and toluene were dried by refluxing over sodium/benzophenone and distilled. 4-Hydroxybenzaldehyde (99%), tetramethylguanidine (99%) and 5-amino-1-pentanol (99%) were purchased from Energy Chemical and used as received. N,N,N′,N″,N″-Pentamethyldiethylenetriamine (PMDETA, Aldrich), copper(I) bromide (CuBr, 98%, Aldrich), sodium azide (NaN_3, Aldrich), propargyl bromide (80% in toluene stabilized with MgO, Alfar Aesar), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, 95%, Sigma), sodium borohydride (99%, Aldrich), ammonium hexafluorophosphate (NH_4PF_6, Aldrich), and all other reagents were used as received.

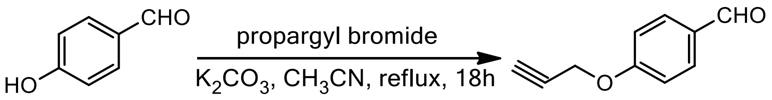
^1H NMR spectra were collected on a Varian Unity INOVA-300 spectrometer with TMS as the internal standard. Electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Breman, Germany) equipped with an ESI interface and ion trap analyzer. Molecular weights and molecular weight distributions were determined by GPC/MALS using an SSI pump connected to a Wyatt DAWNHELEOS II light scattering instrument and Wyatt S18 Optilab T-rEX with THF as the eluent at a flow rate of 1.0 mL/min. Viscosity measurements were carried out with Ubbelohde semi-micro dilution viscometer (Shanghai Liangjing Glass Instrument Factory, 0.47 mm inner diameter) at 25 ℃ in chloroform. The thermal transitions were determined with DSC by using a Perkin–Elmer Pyris DSC under a nitrogen atmosphere with heating and cooling rates of 10 K min^{-1}. Optical photographs were taken with an Olympus BX-51 optical microscopy, for which the measured samples were melted at 100 ℃ for 5 min and promptly quenched to around 40 ℃.

2. *Synthetic routes to the targeted poly[2]rotaxanes*



Scheme S1. Synthetic route to poly[2]rotaxanes **3a-b**.

2.1. Synthesis of compound ***6***



A solution of 4-hydroxy benzaldehyde (2.00 g, 16.4 mmol) and propargyl bromide (3.30 g, 28.0 mmol) in MeCN (100 mL) was refluxed with K_2CO_3 (4.00 g, 29.0 mmol) overnight. The mixture was cooled to room temperature and filtrated. The filtration was evaporated. The crude product was purified by flash column chromatography (SiO_2, petroleum ether/CH_2Cl_2, 10:1 *v*/*v* as the eluent) to give **6** (1.99 g, 77 %) as a white solid. The ^{1}H NMR spectrum of compound **1** is shown in Fig. S1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91(s, 1H), 7.87 (d, *J*= 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 4.79 (d, *J* = 2.4 Hz, 2H), 2.57 (d, *J* = 2.4 Hz, 2H).

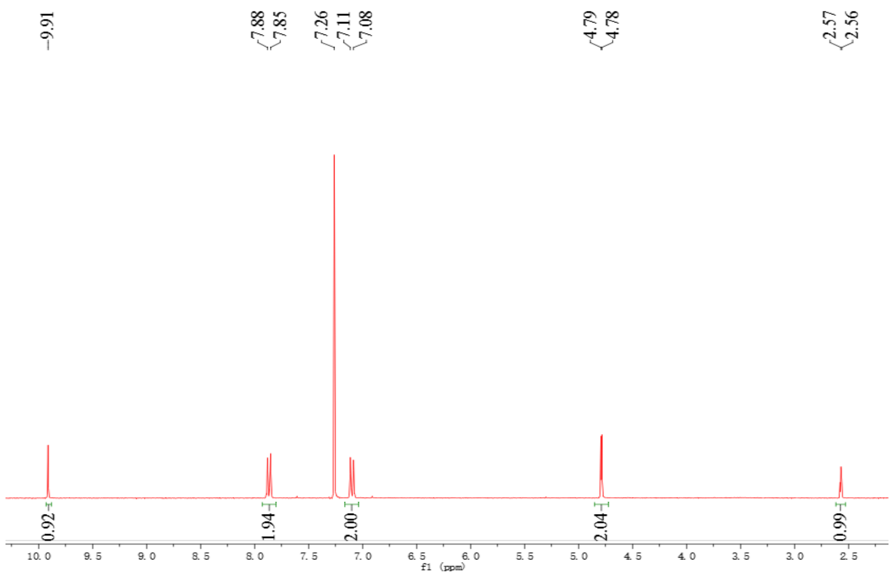
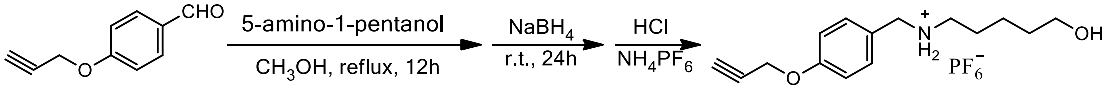


Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, r.t.) of compound **6**.

2.2. *Synthesis of compound* ***5***



A solution of 5-amino-1-pentanol (0.117 g, 1.14 mmol) and compound **6** (0.182 g, 1.14 mmol) was refluxed overnight in MeOH (5 mL). After the reaction mixture was cooled to r.t., $NaBH_4$ (0.100g, 2.63 mmol) was added portion-wise to the stirring solution over a period of 0.5 h. The mixture was stirred at r.t. for another 24 h, after which 5.00 M HCl was added to neutralize excess $NaBH_4$. The mixture was filtered and MeOH was removed. The residue was extracted with ethyl acetate and the extract was concentrated to get a yellow oil. Then the oil was added to a hydrochloric acid solution, and a white precipitate formed. The mixture was filtered and the residue was dissolved in water. After that a saturated aqueous NH_4PF_6 was added to produce a white precipitate, which was collected by suction filtration and recrystallized from deionized water to afford compound **5** (0.170 g, 38 %) as a white solid. The ^{1}H NMR spectrum of compound **5** is shown in Fig. S2. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.42 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 8.5 Hz, 2H), 4.77 (d, J= 2.3 Hz, 2H), 4.11 (d, J = 15.2 Hz, 2H), 3.58 (t, J = 6.1 Hz, 2H), 3.09 – 2.97 (m, 2H), 2.96 (t, J = 2.3 Hz, 1H), 1.80 – 1.65 (m, 2H), 1.57 (dd, J = 13.2, 6.8 Hz, 2H), 1.47 (d, J = 7.0 Hz, 2H).

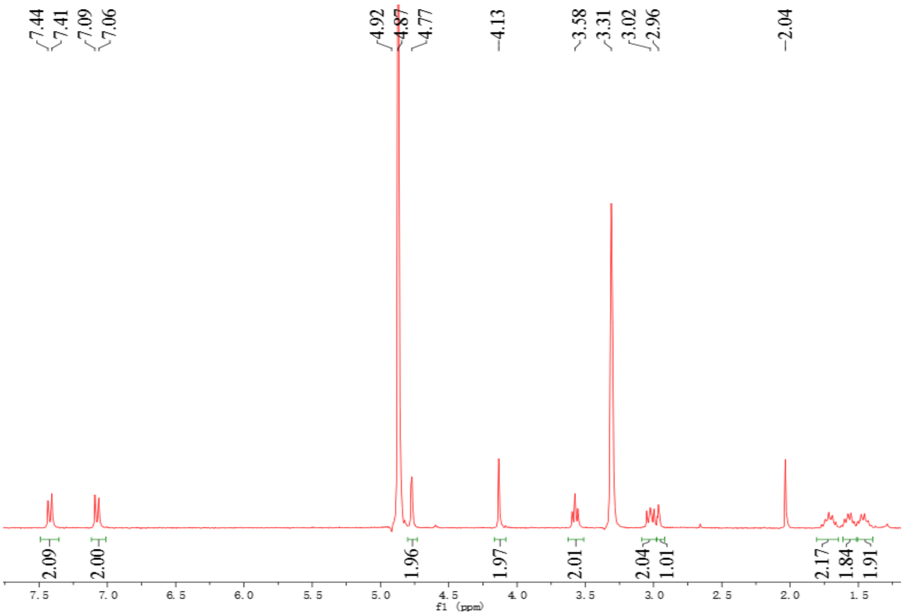
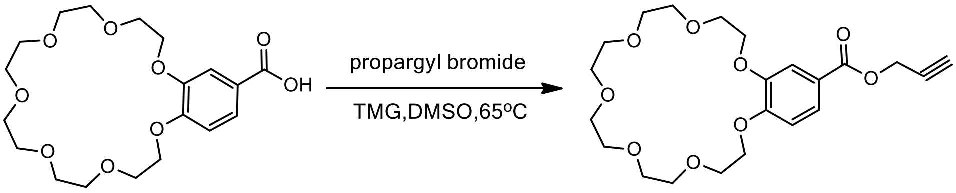


Figure S2. ^{1}H NMR spectrum (300 MHz, DMSO-d_6, r.t.) of compound **5**.

2.3. Synthesis of compound ***4***



A solution of compound **7** (1.00 g, 2.36 mmol), propargyl bromide (0.400 g, 3.39 ml) in DMSO (25 mL) was stirred with tetramethylguanidine (0.500 g, 4.35 mmol) at 65 ℃ for 18 h. After cooled to r.t., the mixture was diluted with CH$_2$Cl$_2$ (100 mL) and washed with H$_2$O (100 ml × 5). The organic phase was dried over MgSO$_4$, and evaporated. The crude product was purified by flash column chromatography (SiO$_2$, CH$_2$Cl$_2$/MeOH, 20:1 *v*/*v* as the eluent) to give **4** (0.420 g, 40 %) as a white solid. The ^{1}H NMR spectrum of compound **4** is shown in Fig. S3. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.69 (dd, J = 8.4, 1.9 Hz, 1H), 7.55 (d, J = 1.9 Hz, 1H), 6.87 (d, J = 8.5 Hz, 1H), 4.88 (d, J = 2.4 Hz, 2H), 4.24 – 4.16 (m, 4H), 3.93 (dd, J = 8.8, 3.7 Hz, 4H), 3.80 (d, J = 2.4 Hz, 4H), 3.74 (d, J = 5.0 Hz, 4H), 3.66 (d, J = 5.0 Hz, 8H), 2.50 (t, J = 2.4 Hz, 1H).

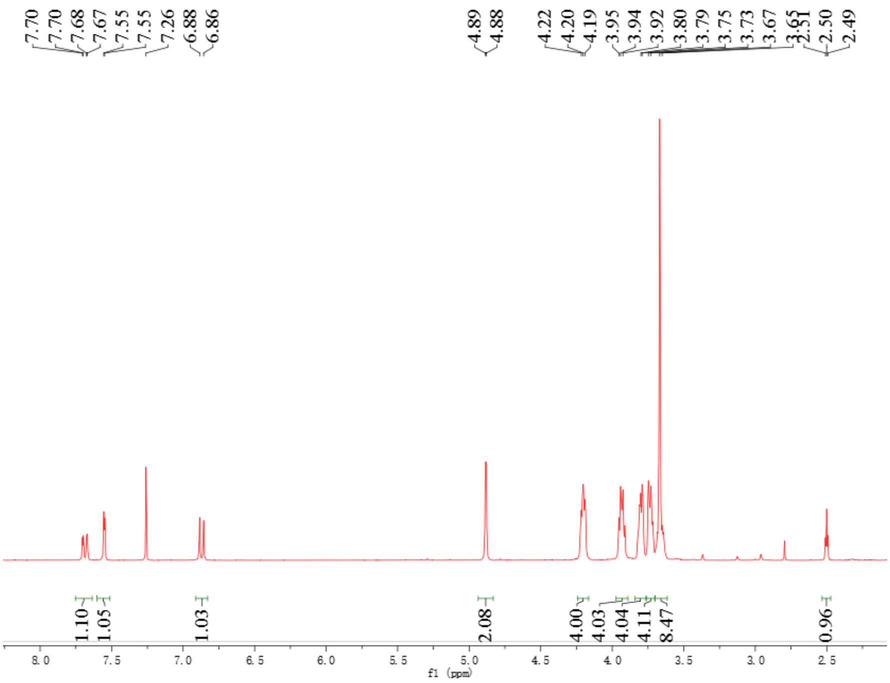
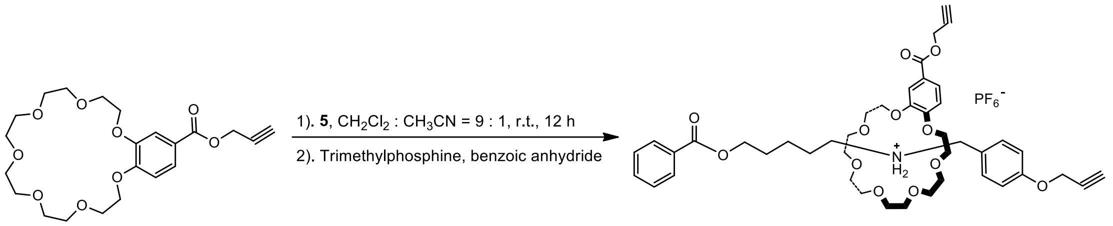


Figure S3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, r.t.) of compound **4**.

2.4. Synthesis of rotaxane ***1***



A solution of compound **4** (0.660 g, 1.48 mmol) and compound **5** (0.580 g, 1.48 mmol) in CH_2Cl_2 (27 mL) and CH_3CN (3 mL) was stirred at r.t. for 12 h. Then benzoic anhydride (1.34 g, 5.93 mmol) and Me_3P (catalytic amount) were added and stirred at r.t. for 24 h. The solution was evaporated. The crude product was purified by flash column chromatography (SiO_2, CH_2Cl_2/CH_3COCH_3, 10:1 *v*/*v* as the eluent) to give **1** (0.620 g, 48 %) as a white solid. The ^{1}H NMR spectrum of compound **1** is shown in Fig. S4. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, J = 7.2 Hz, 2H), 7.70 (d, J = 8.6 Hz, 1H), 7.60 – 7.38 (m, 6H), 7.19 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 3H), 4.88 (d, J = 2.4 Hz, 2H), 4.67 (d, J = 2.4 Hz, 2H), 4.33 (t, J = 6.3 Hz, 4H), 4.23 (d, J = 6.5 Hz, 4H), 3.95 (s, 2H), 3.86–3.31 (m, 20H), 2.52 (s, 2H), 1.77 (s, 2H), 1.62 (s, 2H), 1.51 (s, 2H). The ^{13}C NMR spectrum of compound **1** is shown in Fig. S5. ^{13}C NMR (300 MHz,

$CDCl_3$) δ 166.56, 165.19, 158.15, 151.18, 146.62, 133.69, 133.13, 131.45, 130.15, 129.48, 128.46, 125.17, 124.61, 122.55, 115.24, 112.65, 111.60, 78.07, 77.76, 75.88, 75.09,71.55, 71.07, 70.75, 70.56, 69.61, 69.07, 68.57, 64.16, 55.85, 52.46, 50.46, 46.90, 30.94, 28.22, 26.18, 23.60. ESI–MS: *m*/*z*: $[M + H]^+$ = 790.3787.

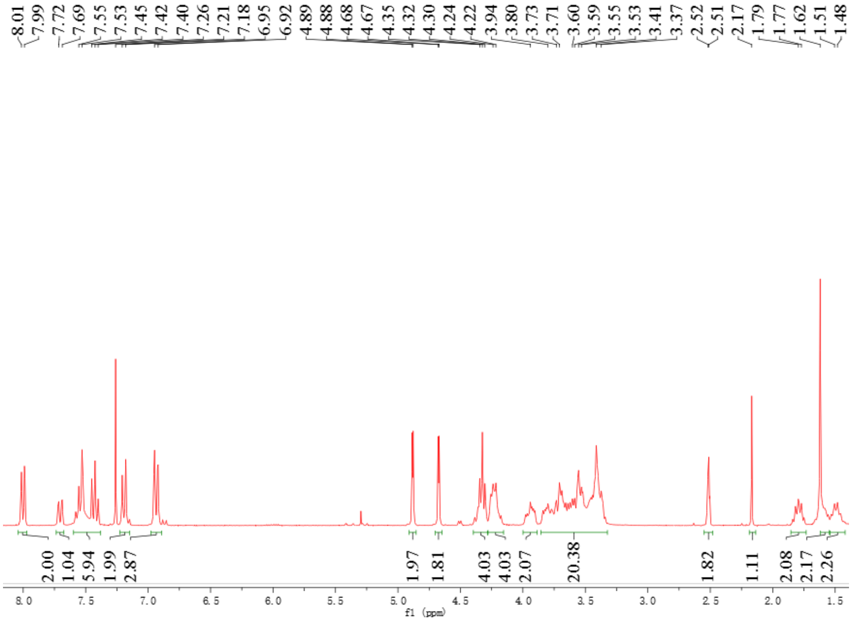


Figure S4. ^1H NMR spectrum (300 MHz, $CDCl_3$, r.t.) of rotaxane **1**.

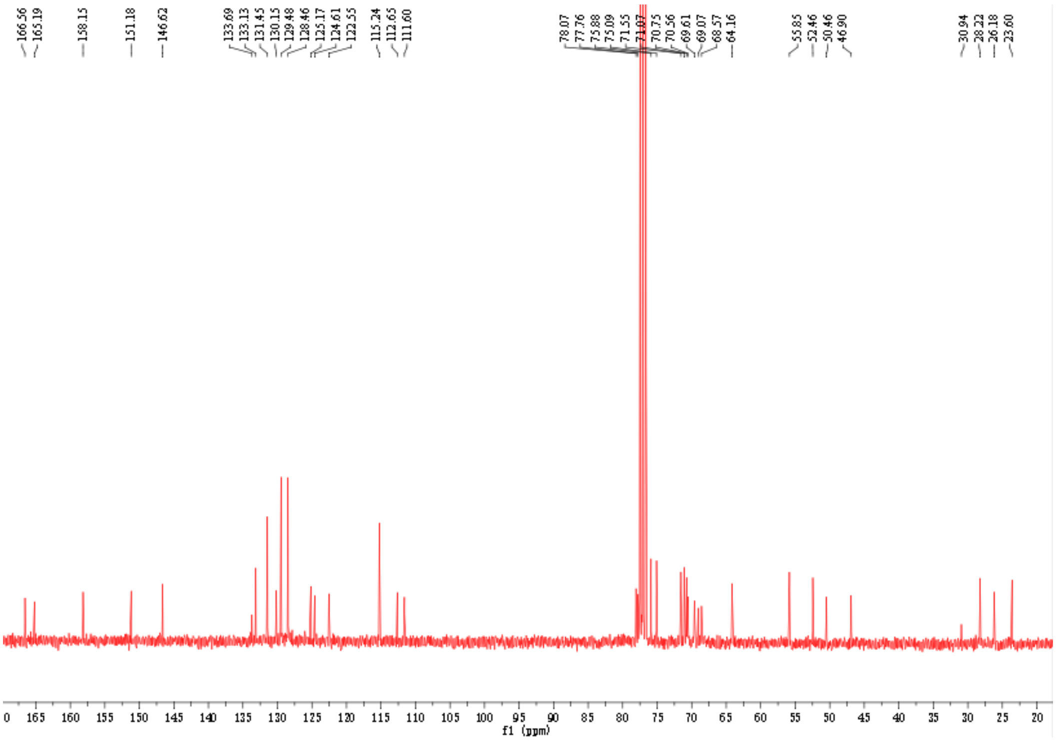


Figure S5. ^{13}C NMR spectrum (300 MHz, $CDCl_3$, r.t.) of rotaxane **1**.

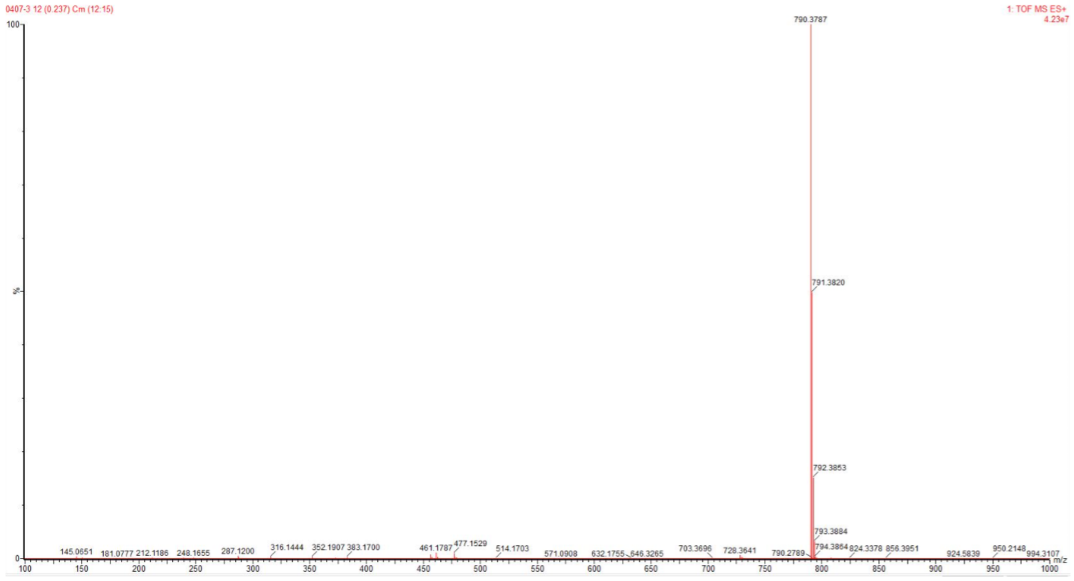
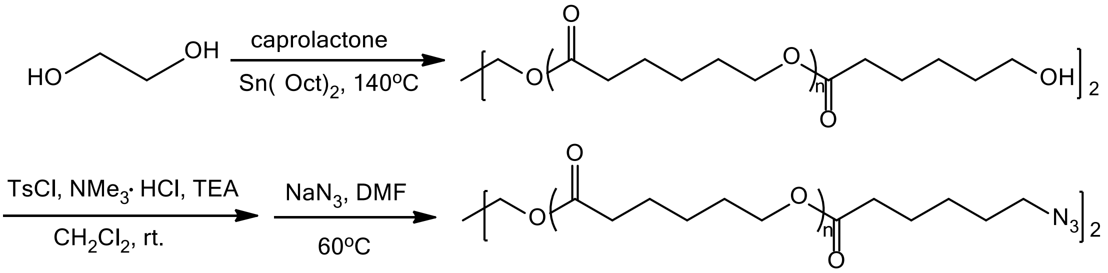


Figure S6. Electrospray ionization mass spectrum of rotaxane **1**.

*2.5. Synthesis of PCLs **2a-b***



To a previously flamed Schlenk tube equipped with a magnetic stirring bar, ethylene glycol (800 mg, 1.29 mmol), Sn(Oct)$_2$ in toluene (0.100 mol/L, 0.250 mL), CL (6.60 g, 58 mmol), and dry toluene (12 mL) were added. After removing ~5 mL toluene under reduced pressure, the tube was carefully degassed by three freeze-pump-thaw cycles, sealed under vacuum, and placed in an oil bath thermostat at 140 ℃. After 24 h, the reaction mixture was dissolved in THF, precipitated into an excess of diethyl ether. After filtration, the sediments were dissolved in THF and precipitated into an excess of diethyl ether, the above dissolution-precipitation cycle was repeated for three times. After drying in a vacuum oven overnight at room temperature, PCL-OH (prepared for **2b**, and PCL-OH for **2a** was purchased from Aldrich) was obtained as a white solid (5.10 g, yield: 77 %).

To a previously flamed 100 mL one-neck round-bottom flask, PCL-OH (2.00 g, 0.3 mmol), triethylamine (0.160 g, 1.6 mmol), trimethylamine hydrochloride (0.020 g, 0.21

mmol), and dry CH_2Cl_2 (50 mL) were added. After cooling to 0 ℃, tosylchloride (0.300 g, 1.6 mmol) in 20 mL dry CH_2Cl_2 was added dropwise over 1 h at 0 ℃. The reaction mixture was kept stirring overnight at room temperature. After removing insoluble salts by suction filtration, the solvents were removed on a rotary evaporator. The residues were dissolved in THF and passed through a neutral alumina column to remove residual salts. After concentration and repeated precipitation into an excess of diethyl ether, PCL-OTs was obtained as a white solid (1.10 g, yield: 55 %).

The azidation of PCL-OTs afforded PCL-N_3, and a typical procedure was as follows. To a 100 mL round-bottom flask, PCL-OTs (0.500 g), DMF (15 mL), and NaN_3 (0.040 g, 0.6 mmol) were added. The reaction mixture was allowed to stir at 60 ℃ for 24 h. After removing most of the solvents at reduced pressure, the remaining portion was diluted with THF, and then precipitated into an excess of *n*-hexane. The sediments were re-dissolved in THF and passed through a neutral alumina column to remove residual sodium salts, and then precipitated into an excess of diethyl ether. The obtained product PCL-N_3 (**2b**), was dried in a vacuum oven, yielding a white solid (0.400 g, yield: 80 %; M_n =8.9 kDa, M_w/M_n =1.28). **2a** was prepared as the same procedure as **2b**, which was obtained as a white solid (0.200 g, yield 80 %, M_n =1.2 kDa, M_w/M_n =1.33).

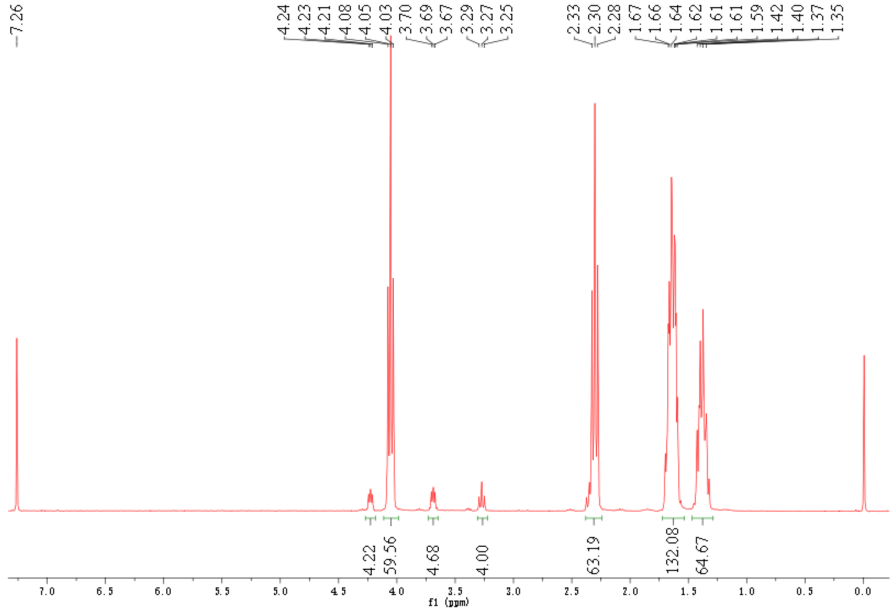


Figure S7. ^1H NMR spectrum (300 MHz, $CDCl_3$, r.t.) of PCL **2a**.

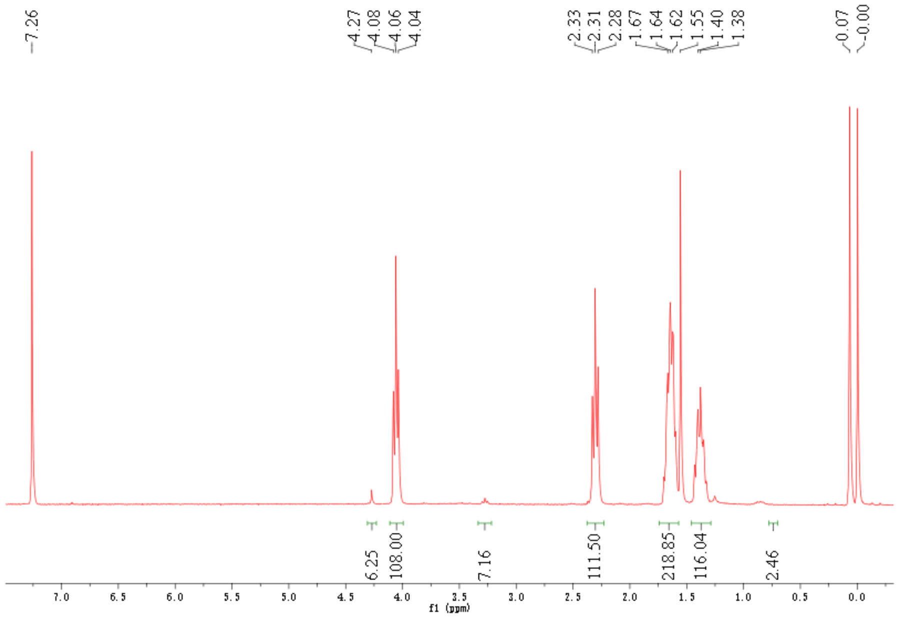
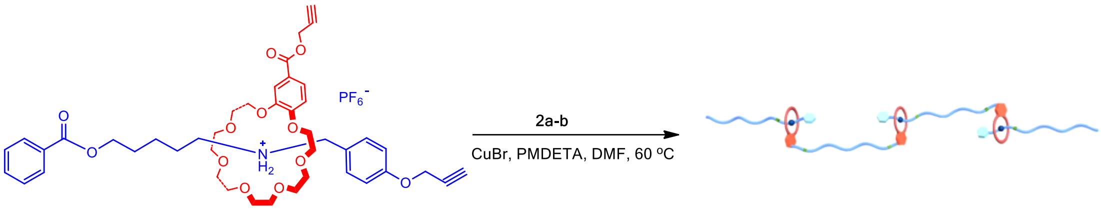


Figure S8. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, r.t.) of PCL **2b**.

*2.6. Synthesis of poly[2]rotaxanes **3a-b***



To a previously flamed Schlenk tube equipped with a magnetic stirring bar, [2]rotaxane **5** (0.050 g, 0.05 mmol), PCL-N_3 **2a** (0.060 g, 0.05 mmol), PMDETA (9 mg, 0.05 mmol) and dried DMF(3 mL), were added. And the tube was carefully degassed by two freeze-pump-thaw cycles, sealed under vacuum, then CuBr (7.50 mg, 0.05 mmol) was added, followed by another freeze-pump-thaw cycles. After that the tube was placed in an oil bath thermostat at 100 ℃. After 12 h, the reaction mixture was dissolved in THF, filtered by neutral alumina, and precipitated into an excess of diethyl ether. After filtration, the sediments were dissolved in THF and precipitated into an excess of diethyl ether, the above dissolution-precipitation cycle was repeated for three times. After drying in a vacuum oven overnight at room temperature, poly[2]rotaxane **3a** was obtained as a gray solid (80 mg, yield: 72 %, M_n =16.5 kDa, M_w/M_n =1.29). **3b** was prepared as the same procedure as **3a**, which was obtained as a white solid (100 mg, yield 80 %, M_n =27.6 kDa, M_w/M_n =1.24).

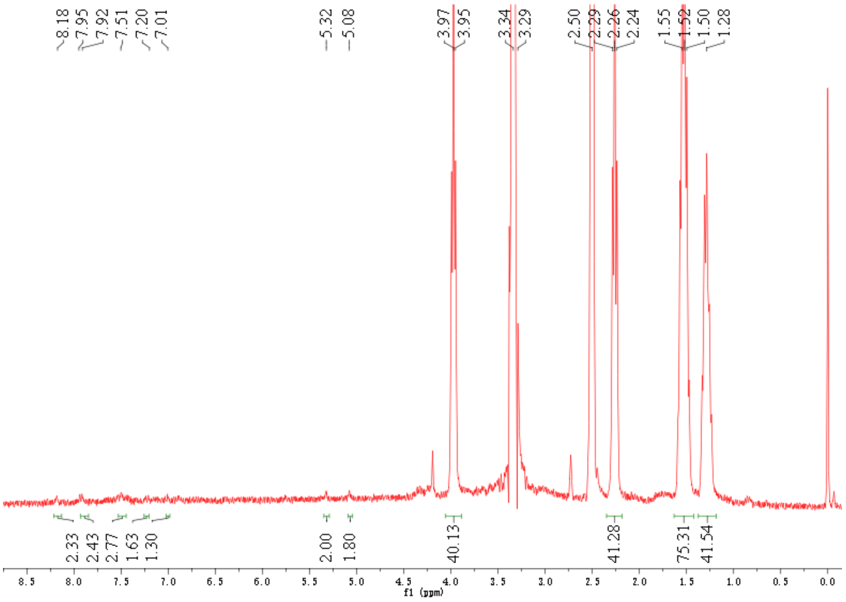


Figure S9. ^{1}H NMR spectrum (300 MHz, DMSO-d_6, r.t.) of poly[2]rotaxane **3a**.

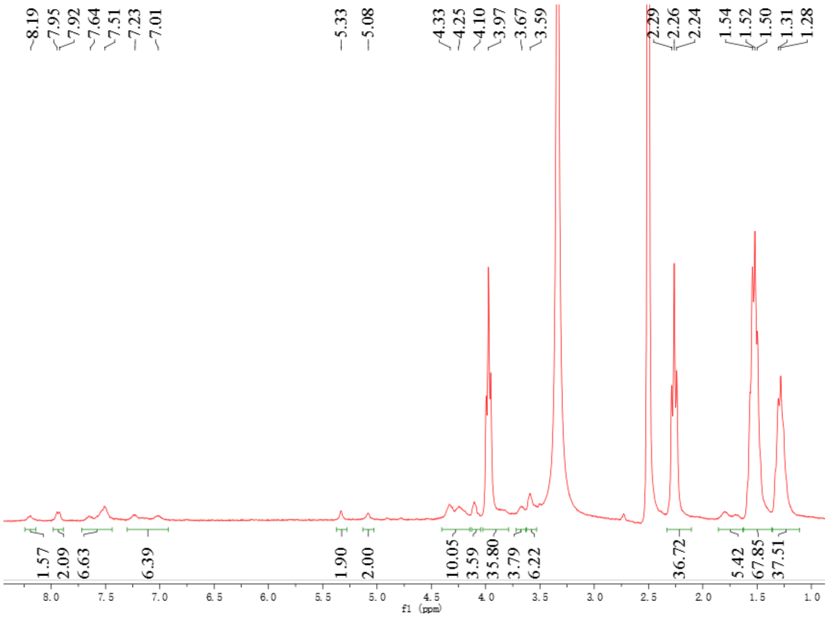


Figure S10. ^{1}H NMR spectrum (300 MHz, DMSO-d_6, r.t.) of poly[2]rotaxane **3b**.

3. *FT-IR spectra of rotaxane **1** and poly[2]rotaxanes **3a–b***

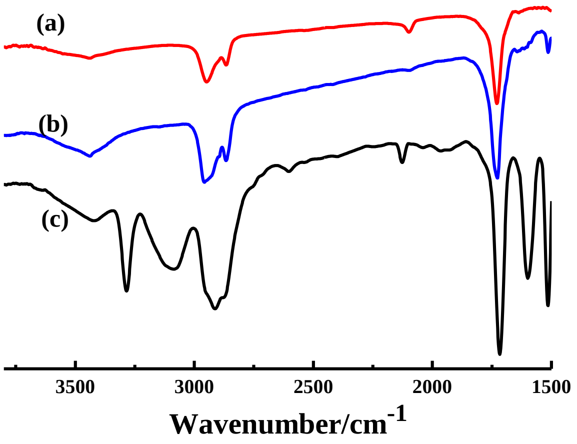


Figure S11. FT-IR spectra of (a) PCL **2b**, (b) poly[2]rotaxane **3b**, and (c) rotaxane **1**.

4. *GPC traces of PCLs **2a–b** and poly[2]rotaxanes **3a–b***

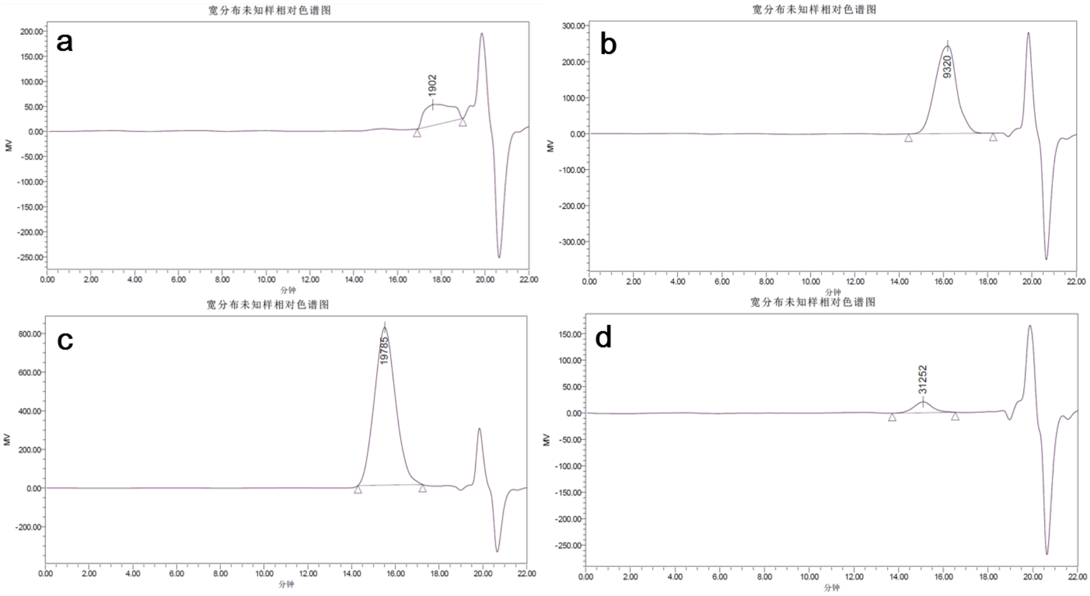


Figure S12. Gel permeation chromatography trace of (a) PCL **2a**, (b) PCL **2b**, (c) poly[2]rotaxane **3a**, (d) poly[2]rotaxane **3b**.

Table S1. GPC data of poly[2]rotaxane **3a–b** and the precursors PCL **2a–b**

Polymers	M_n/Da	M_w/Da	*MP*	M_z/Da	M_z+1/Da	M_n/M_w	M_z/M_w	M_z+1/M_w
2a	1197	1598	1902	2022	2372	1.335812	1.264879	1.483876
2b	8898	11426	9320	14460	17960	1.284151	1.265560	1.571819
3a	16523	21376	19785	26723	32292	1.293746	1.250116	1.510632
3b	27623	34381	31252	42043	50787	1.244667	1.222854	1.477162

5. *DSC traces of PCLs **2a–b** and poly[2]rotaxanes **3a–b***

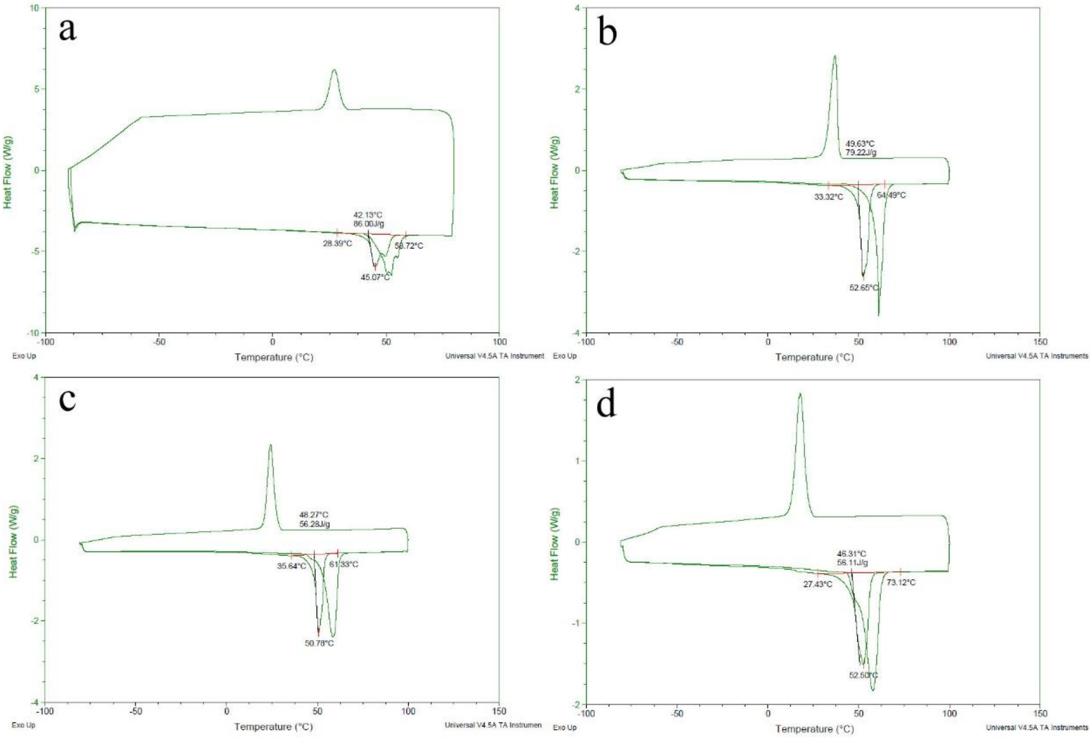


Figure S13. Differential scanning calorimetry trace of (a) PCL **2a**, (b) PCL **2b**, (c) poly[2]rotaxane **3a**, (d) poly[2]rotaxane **3b**.

6. *POM photos of PCLs **2a–b** and poly[2]rotaxanes **3a–b***

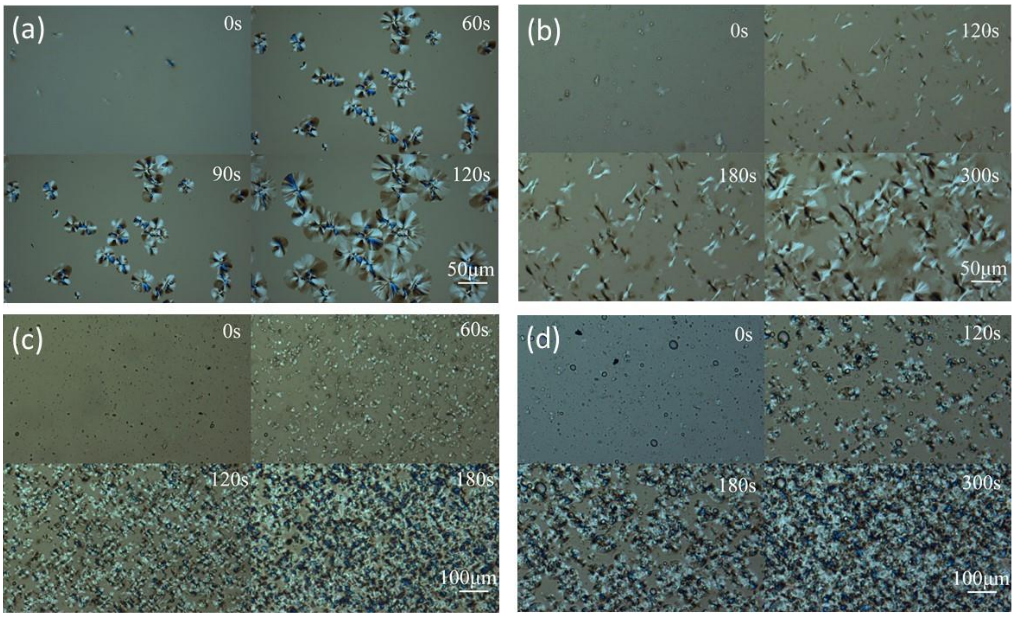


Figure S14. Real-time polarized optical microscopy photos: (a) PCL **2a** recorded from 0 s to 120 s at 27 ℃, (b) PCL **2b** recorded from 0 s to 300 s, at 45 ℃, (c) poly[2]rotaxane **3a** recorded from 0 s to 180 s at 45ºC, (d) poly[2]rotaxane **3b** recorded from 0 s to 300 s at 40 ℃. The samples were melted at 100 ℃ for 5 min and quenched to text temperature, respectively.

7. *Specific viscosities of PCL* ***2b*** *and poly[2]rotaxane* ***3b***

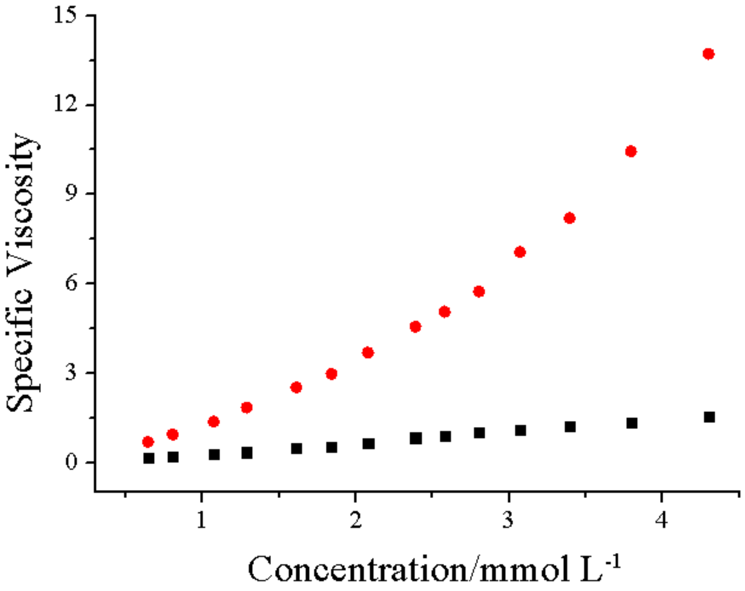


Figure S15. Specific viscosities (chloroform, 25 ℃) for PCL **2b** (■) and poly[2]rotaxane **3b** (●).