Electronic Supplementary Material (ESI) for ChemComm.

Reversible formation of a poly[3]rotaxane based on photo dimerization of an anthracene-capped [3]rotaxane

Peifa Wei, Xuzhou Yan, and Feihe Huang*

State Key Laboratory of Chemical Engineering, Department of Chemistry, Zhejiang University, Hangzhou, 310027 (P. R. China)

Email: fhuang@zju.edu.cn.

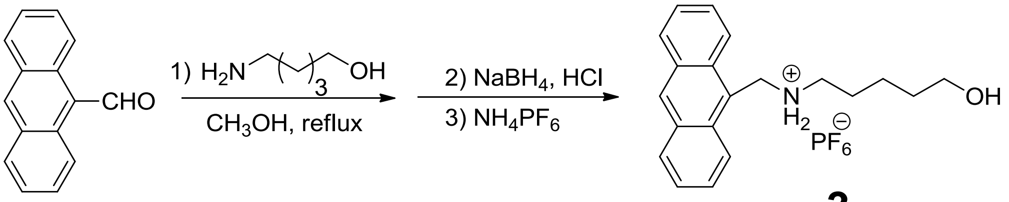
Electronic Supplementary Information (23 pages)

1. Materials and methods

Compound **2**[S1] and **5**[S2] were synthesized according to literature procedures. All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer with the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals. The two-dimensional diffusion-ordered (2D DOSY) NMR spectra, NOESY NMR spectra (2D NOESY), and H-H correlation NMR spectra (2D COSY) were recorded on a Bruker DRX500 spectrometer. Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system or a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH, Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. UV-Vis spectroscopy was performed on a Shimadzu UV-2550 instrument at room temperature. The photo reactions were carried out by using a xenon lamp (500 W) with a filter. The melting point was collected on a SHPSIC WRS-2 automatic melting point apparatus. Molecular weight distributions were measured on a conventional gel permeation chromatography (GPC) system equipped with a Waters 1525 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR1, HR2 and HR4, 7.8 mm × 300 mm). GPC measurements were carried out at 35 °C using a THF solution as the eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. Thermogravimetric analysis (TGA) of the polymer was recorded on a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 20 °C/min from 35 to 600 °C. The thermal property of the sample was characterized using a differential scanning calorimeter (TAQ 2000, USA) under a nitrogen atmosphere. The sample was first heated from 50 °C to 150 °C, followed by cooling to 50 °C, and finally reheated to 150 °C to obtain the glass transition temperature of the polymer. All the process was at the same rate, 10 °C min^{-1}.

*2. Synthesis of **3**, **4**, and [3]rotaxane **1***

Scheme S1. Synthesis of **3**



3

A solution of 5-aminopentan-1-ol (5.16 g, 50.0 mmol) and anthracene-9-carbaldehyde (10.8 mL, 50.0 mmol) was heated under reflux overnight in MeOH (300 mL). After the reaction mixture was cooled to ambient temperature, $NaBH_4$ (3.80 g, 100 mmol) was added portionwise to the stirring solution over a period of 0.5 h. Stirring was maintained under ambient conditions for further 24 h. Then 5 M HCl was added to neutralize excess $NaBH_4$. The mixture was filtered and MeOH was removed with a rotaevaporator. The residue was extracted with ethyl acetate and the extract was concentrated to get yellow oil. After the oil was added to a hydrochloric acid solution and stirred for a moment, a white precipitate formed. The mixture was filtered and the solid was dissolved in water to get a saturated solution. The solution was added to a saturated aqueous NH_4PF_6 solution to produce a precipitate, which was collected by suction filtration and recrystallized from deionized water to afford **3** (13.0 g, 59%) as a white solid, mp 170.1−171.2 ℃. The ^{1}H NMR spectrum of **3** is shown in Figure S1. ^{1}H NMR (400 MHz, CD_3CN, 293 K) δ (ppm): 8.68 (s, 1H), 8.40–8.42 (d, 2H, J = 8 Hz), 8.07–8.10 (d, 2H, J = 12 Hz), 7.57–7.61 (t, 2H, J = 16 Hz), 7.49–7.52 (t, 2H, J = 12.0 Hz), 5.55 (s, 2H), 3.65–3.69 (t, 2H, J = 16 Hz), 3.41–3.44 (m, 2H), 1.86–1.91 (m, 2H), and 1.43–1.45 (m, 4H). The ^{13}C NMR spectrum of **2** is shown in Figure S2. ^{13}C NMR (100 MHz, CD_3CN, 293 K) δ (ppm): 32.74, 26.76, 32.74, 45.06, 50.45, 61.99, 122.77, 124.37, 126.51, 128.49, 130.38, 131.57, 131.91, and 132.34. LRESIMS is shown in Figure S3: m/z 294.1 (100%) for $[M - PF_6]^+$. HREIMS: m/z calcd for $[M - HPF_6 - H_2O]$ $C_{20}H_{20}N$ 275.1677, found 275.1674, error 1.1 ppm.

.

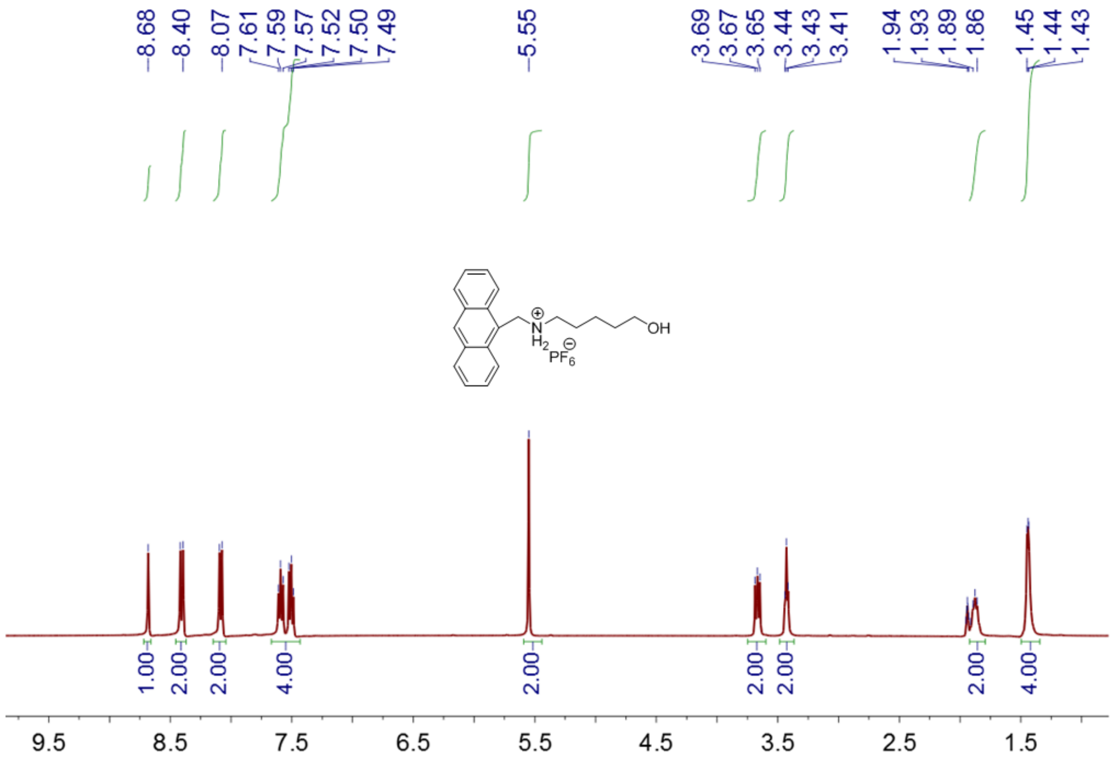


Figure S1. ^{1}H NMR spectrum (400 MHz, CD_3CN, 293 K) of **3**.

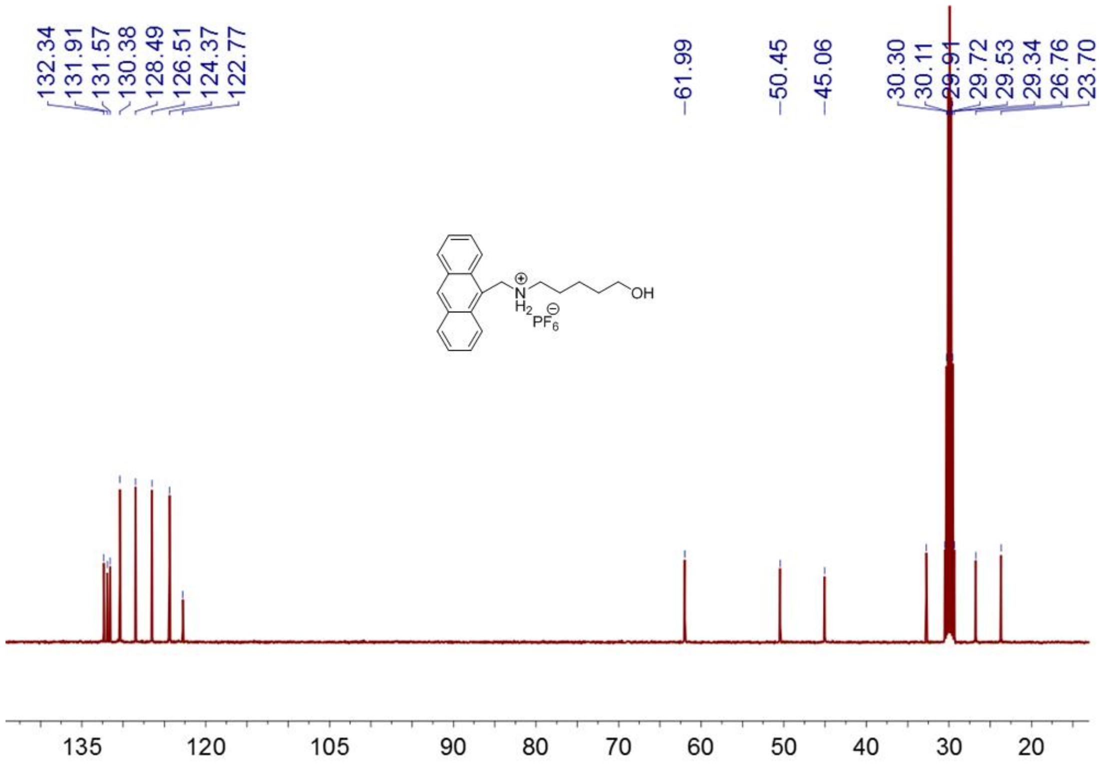
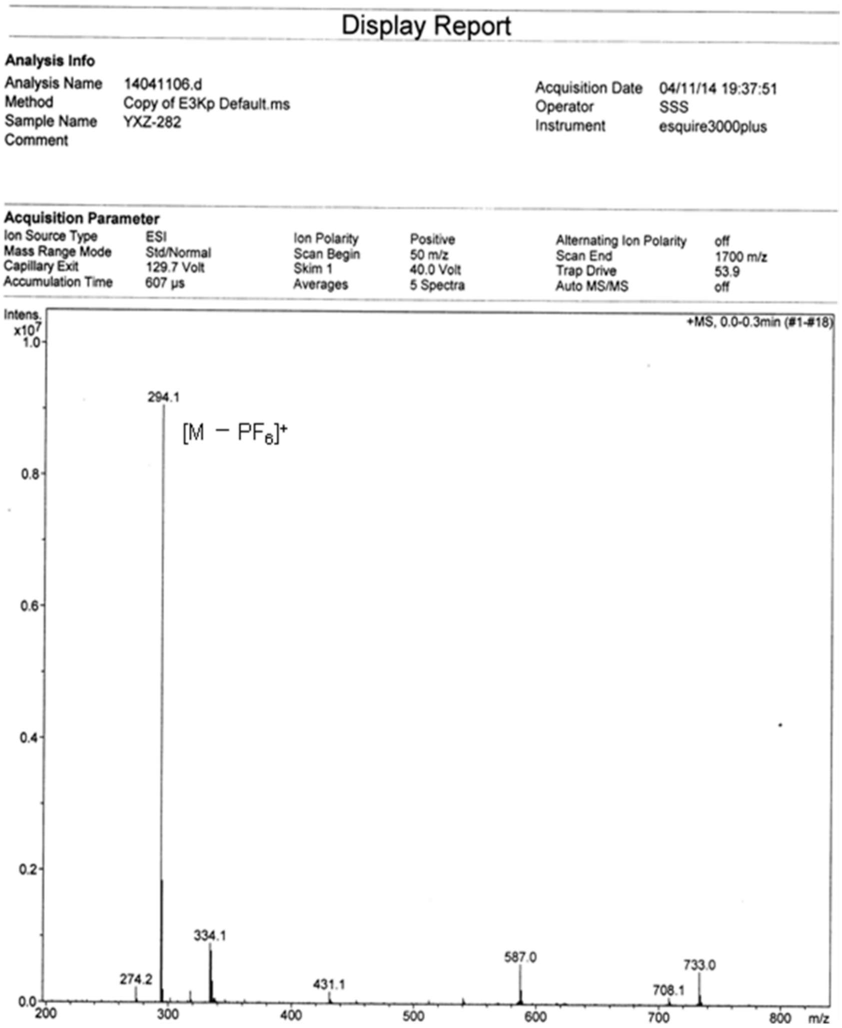


Figure S2. ^{13}C NMR spectrum (100 MHz, CD_3CN, 293 K) of **3**.



Display Report

Analysis Info

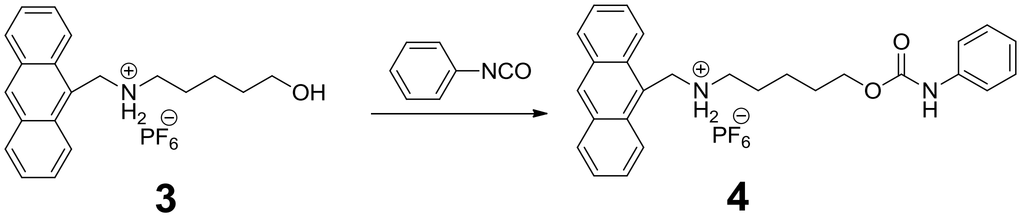
Analysis Name	14041106.d	Acquisition Date	04/11/14 19:37:51
Method	Copy of E3Kp Default.ms	Operator	SSS
Sample Name	YXZ-282	Instrument	esquire3000plus
Comment			

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Std/Normal	Scan Begin	50 m/z	Scan End	1700 m/z
Capillary Exit	129.7 Volt	Skim 1	40.0 Volt	Trap Drive	53.9
Accumulation Time	607 µs	Averages	5 Spectra	Auto MS/MS	off

Figure S3. LRESI mass spectrum of **3**.

Scheme S2. Synthesis of **4**



A solution of **3** (0.680 g, 1.55 mmol), catalytic amount of dibutyltin dilaurate (DBTDL, 80.0 mg) and phenyl isocyanate (0.420 g, 3.53 mmol) in dichloromethane (50 mL) was stirred at room temperature for two days. Upon removal of DCM, a pale yellow oil was obtained, which was purified by flash column chromatography (methanol/dichloromethane, 1:100 *v/v*) to afford **4** as a white solid (0.658 g, 76%), mp 46.4−47.5 °C. The ^{1}H NMR spectrum of **4** is shown in Figure S4. ^{1}H NMR (400 MHz, CD$_3$CN, 293 K) δ (ppm): 8.69 (s, 1H), 8.32–8.33 (d, 2H, J = 4 Hz), 8.13–8.15 (d, 2H, J = 8 Hz), 7.67–7.70 (m, 2H), 7.57–7.60 (t, 2H, J = 12 Hz), 5.13 (s, 2H), 4.09–4.11 (t, 2H, J = 8 Hz), 3.18–3.21 (t, 2H, J = 12 Hz), 1.64–1.74 (m, 4H), and 1.41–1.46 (m, 4H). The ^{13}C NMR spectrum of **4** is shown in Figure S5. ^{13}C NMR (100 MHz, CD$_3$CN, 293 K) δ (ppm): 22.23, 25.41, 27.74, 43.85, 48.67, 63.82, 118.20, 122.54, 122.59, 123.18, 125.25, 127.05, 128.54, 129.08, 129.87, 130.40, 131.01, 138.54, and 153.51. LRESIMS is shown in Figure S6: *m*/*z* 413.1 (100%) for $[M - PF_6]^+$. HRESIMS: *m*/*z* calcd for $[M - PF_6]^+$ $C_{27}H_{29}N_2O_2$ 413.2229, found 728.2211, error −4.4 ppm.

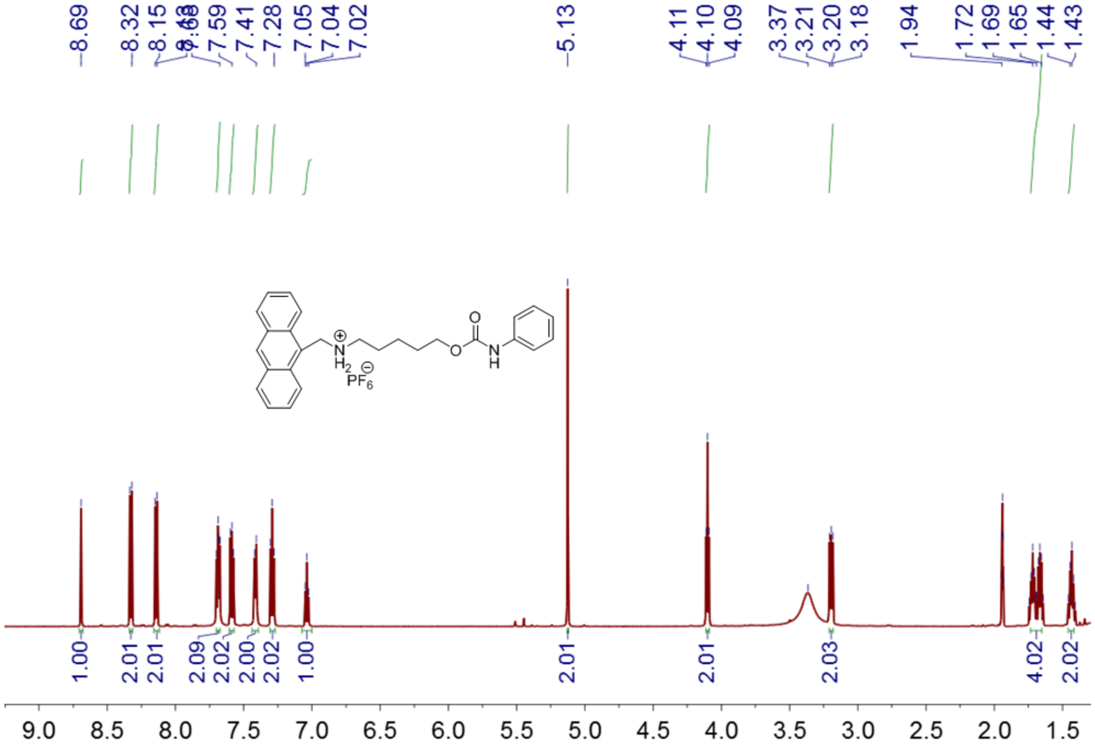


Figure S4. ^{1}H NMR spectrum (400 MHz, CD$_3$CN, 293 K) of **4**.

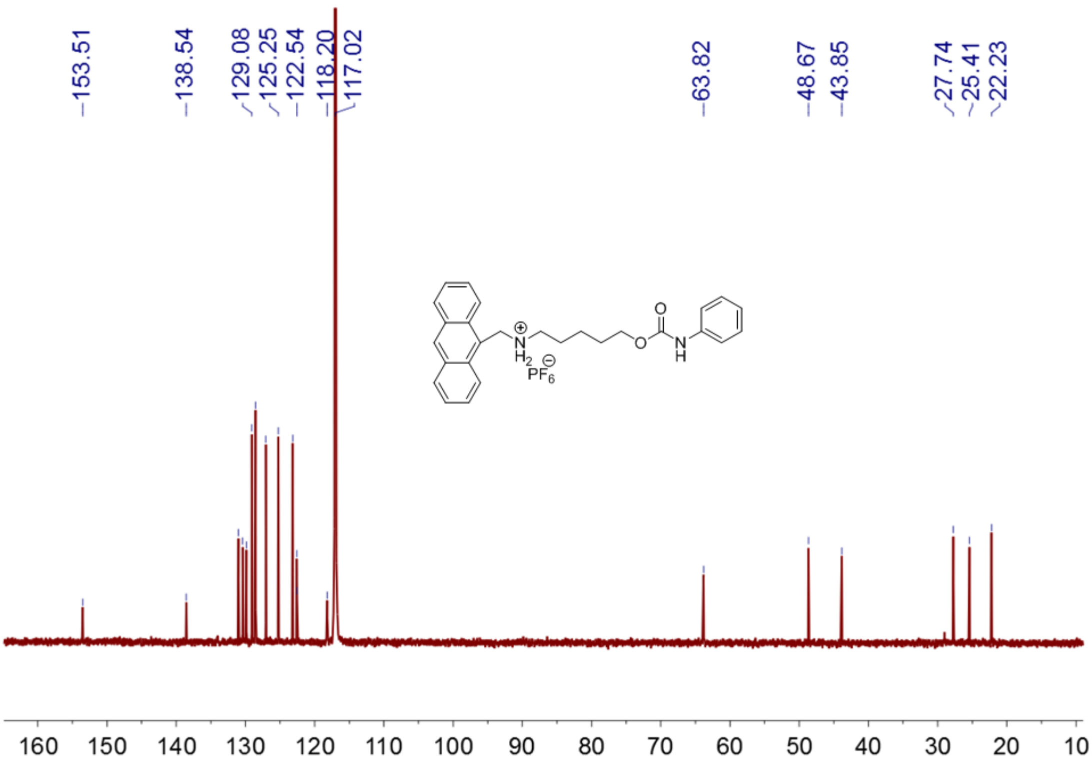
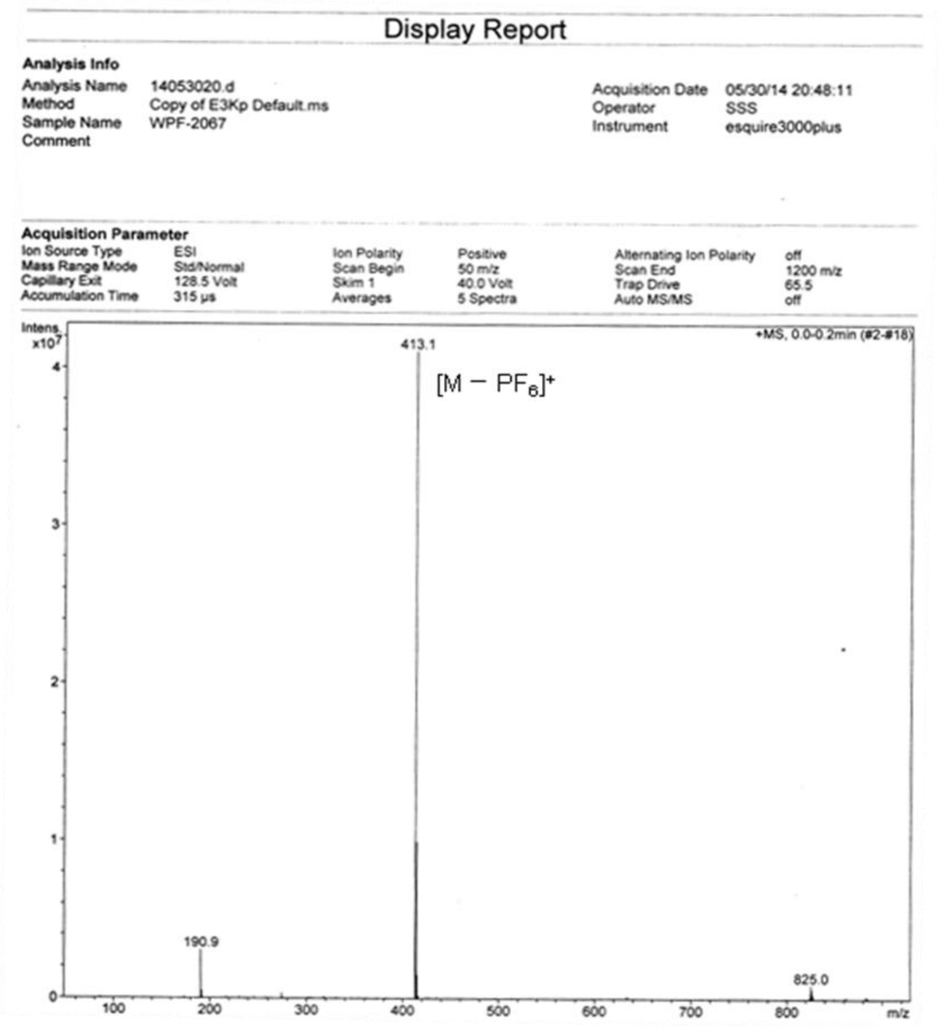


Figure S5. ^{13}C NMR spectrum (100 MHz, CD_3CN, 293 K) of **4**.



Display Report

Analysis Info

Analysis Name 14053020.d
Method Copy of E3Kp Default.ms
Sample Name WPF-2067
Comment

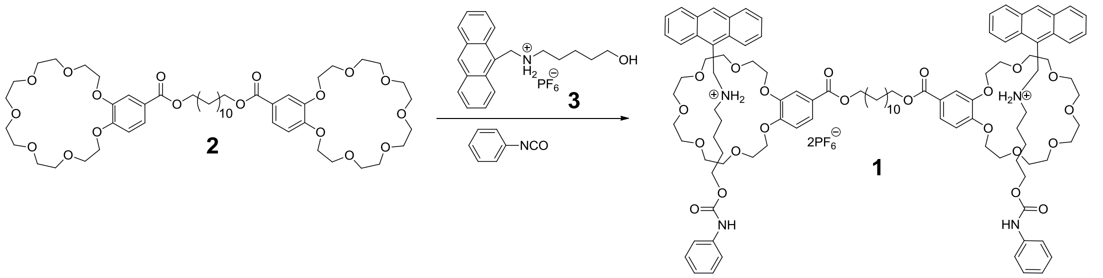
Acquisition Date 05/30/14 20:48:11
Operator SSS
Instrument esquire3000plus

Acquisition Parameter

Ion Source Type ESI
Mass Range Mode Std/Normal
Capillary Exit 128.5 Volt
Accumulation Time 315 µs
Ion Polarity Positive
Scan Begin 50 m/z
Skim 1 40.0 Volt
Averages 5 Spectra
Alternating Ion Polarity off
Scan End 1200 m/z
Trap Drive 65.5
Auto MS/MS off

Figure S6. LRESI mass spectrum of **4**.

Scheme S3. Synthesis of **1**



A solution of **2** (0.674 g, 0.700 mmol) and **3** (0.680 g, 1.55 mmol) in dichloromethane (80 mL) was stirred at reflux for 12 h. Upon cooling to room temperature, catalytic amount of dibutyltin dilaurate (DBTDL, 88.0 mg) and phenyl isocyanate (0.417 g, 3.50 mmol) were added to the solution which was stirred at room temperature for two days. Upon removal of DCM, a pale yellow oil was obtained, which was purified by flash column chromatography (methanol/dichloromethane, 1:100 *v/v*) to afford **1** as a white solid (0.80 g, 55%), mp 104.2–105.1 ℃. The ^{1}H NMR spectrum of **1** is shown in Figure S7. ^{1}H NMR (400 MHz, CD_3CN, 293 K) δ (ppm): 8.50–8.53 (d, 2H, J = 12 Hz), 8.41–8.44 (t, 4H, J = 12 Hz), 8.00–8.03 (t, 4H, J = 12 Hz), 7.71 (s, 2H), 7.59–7.64 (m, 4H), 7.48–7.53 (m, 8H), 7.41–7.44 (m, 4H), 7.27–7.30 (m, 4H), 7.01–7.04 (t, 2H, J = 12 Hz), 6.86–6.88 (d, 2H, J = 8 Hz), 5.16–5.20 (m, 16H), 4.31–4.39 (m, 4H), 4.13–4.22 (m, 12H), 4.01–4.05 (m, 4H), 3.92–3.93 (m, 4H), 3.69–3.82 (m, 12H), 3.58–3.62 (m, 4H), 3.39–3.43 (m, 4H), 3.26–3.31 (m, 4H), 3.05–3.09 (m, 4H), 2.88–2.91 (m, 4H), 2.57–2.65 (m, 4H), 1.70–1.77 (m, 8H), 1.51–1.64 (m, 8H), 1.25–1.31 (m, 4H), and 1.12–1.14 (m, 8H). The ^{13}C NMR spectrum of **1** is shown in Figure S8. ^{13}C NMR (100 MHz, CD_3CN, 293 K) δ (ppm): 14.33, 22.90, 24.88, 25.29, 27.95, 28.06, 28.44, 28.53, 28.58, 28.70, 28.82, 42.52, 47.65, 68.31, 68.71, 69.10, 69.34, 69.43, 69.79, 70.03, 70.45, 70.75, 111.28, 111.98, 117.02, 118.04, 122.54, 122.82, 124.96, 126.69, 128.55, 128.77, 129.48, 130.66, 138.56, 146.25, 150.36, 153.44, and 165.18. LRESIMS is shown in Figure S9: *m*/*z* 896.8 (100%) for $[M - 2PF_6]^{2+}$. HRESIMS: *m*/*z* calcd for $[M - 2PF_6]^{2+}$ $C_{104}H_{136}N_4O_{22}$ 896.4827, found 896.4818, error 1.0 ppm.

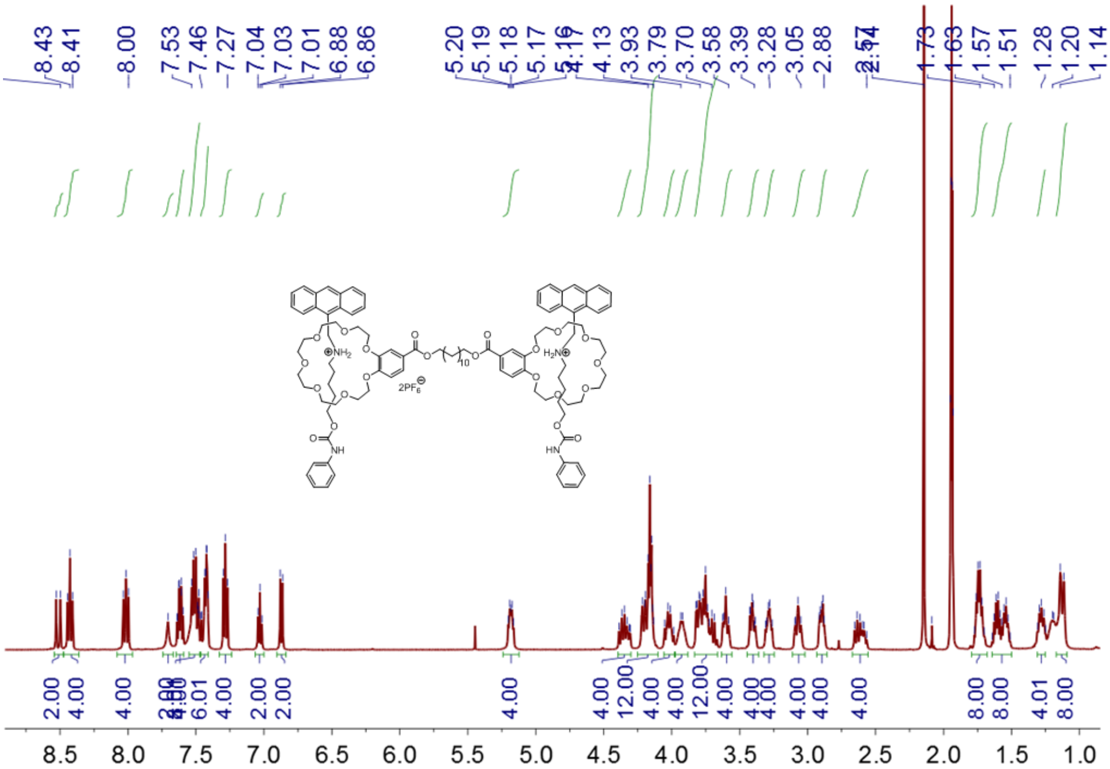


Figure S7. ^{1}H NMR spectrum (400 MHz, CD_3CN, 293 K) of **1**.

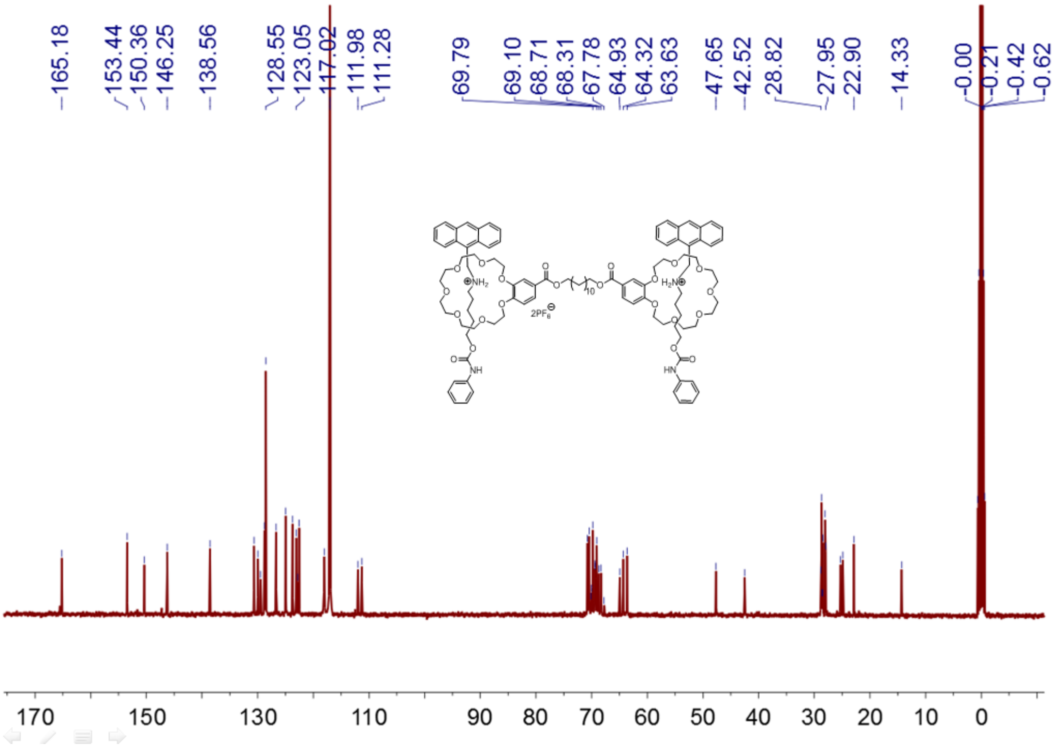


Figure S8. ^{13}C NMR spectrum (100 MHz, CD_3CN, 293 K) of **1**.

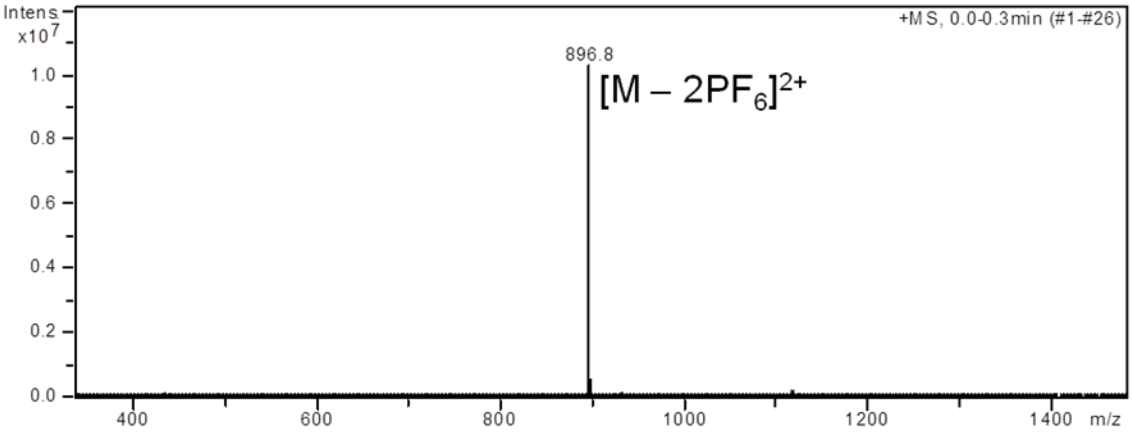


Figure S9. LRESI mass spectrum of **1**.

3. Partial ^{1}H NMR spectra of ***1****,* ***2****, and* ***4*** *in DMSO-d_6*

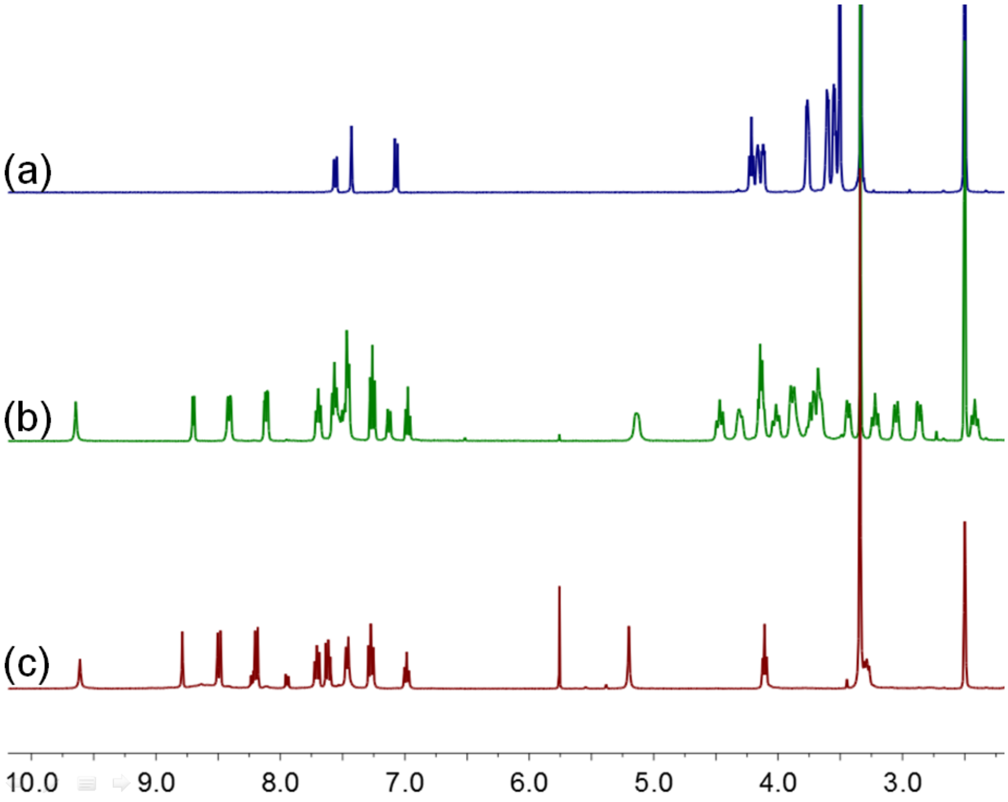


Figure S10. Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6, 293 K): (a) **2**; (b) **1**; c) **4**. c = 2.00 mM.

4. COSY NMR spectra of ***1***

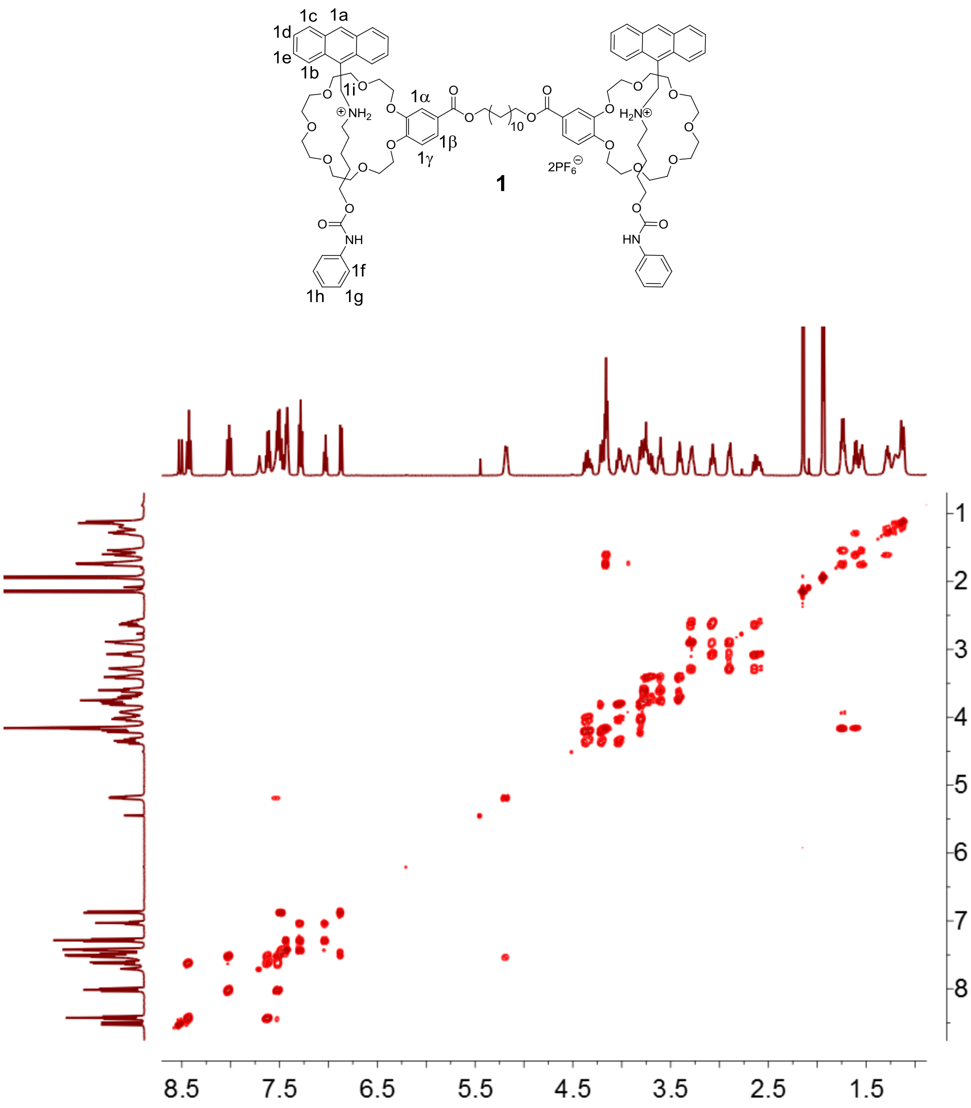


Figure S11. Full COSY NMR spectrum (500 MHz, CD_3CN, 293 K) of **1**.

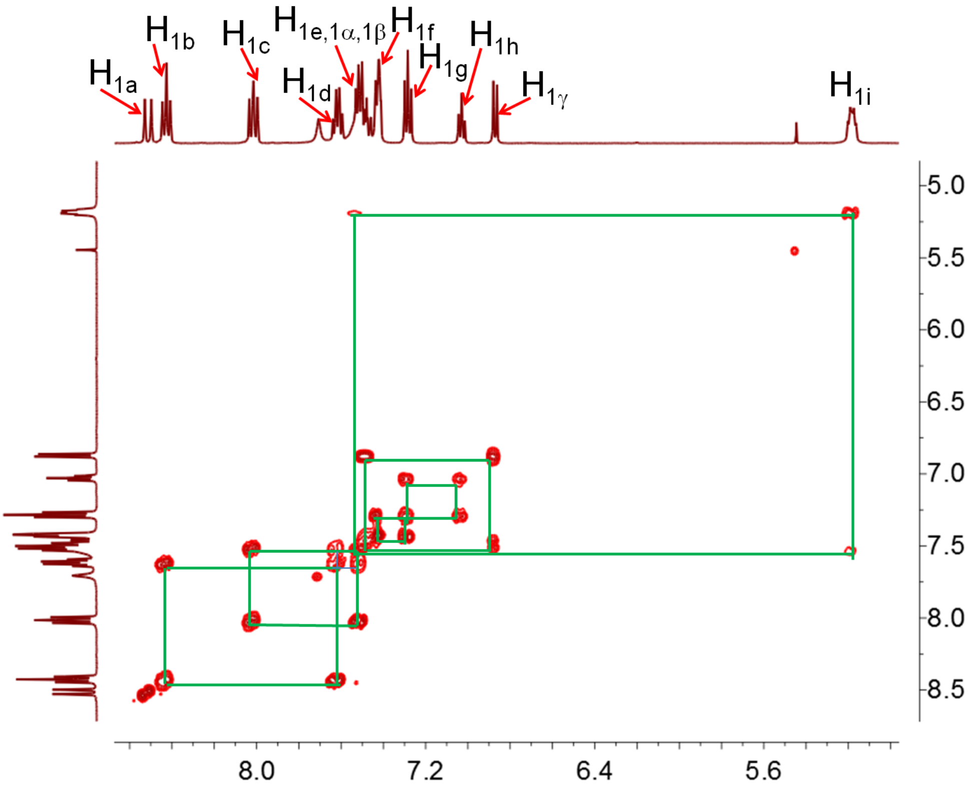


Figure S12. Partial COSY NMR spectrum (500 MHz, CD_3CN, 293 K) of **1**.

5. *Partial NOESY NMR spectrum of **1***

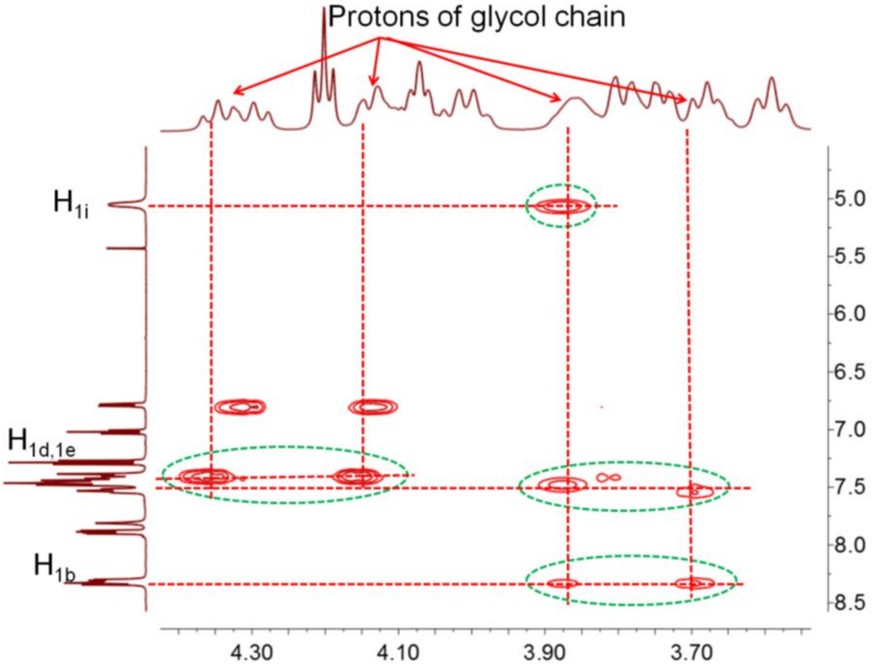


Figure S13. Partial NOESY NMR spectrum (500 MHz, CD_3CN, 293 K) of **1**.

6. ^{1}H NMR spectra of ***1*** *upon UV irradiation and heating treatments*

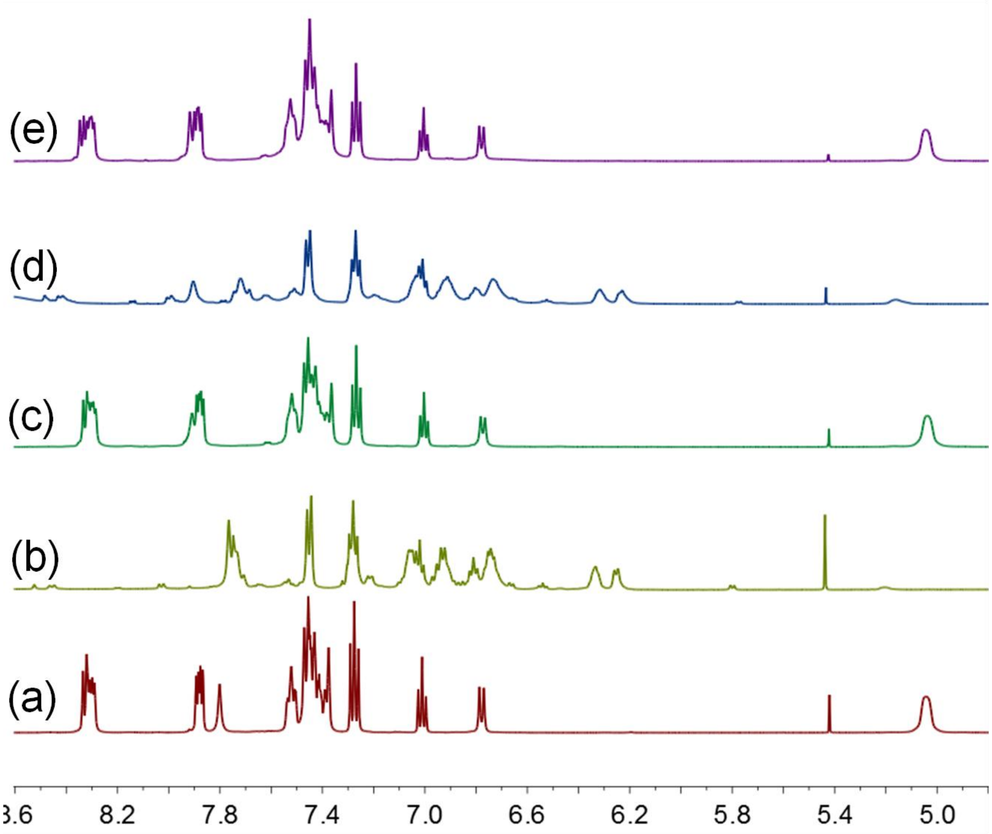


Figure S14. Partial ^{1}H NMR spectra (500 MHz, CD_3CN, 293 K): (a) **1**; (b) irradiation of (a) for 12 h ($\lambda > 360$ nm); (c) heating (b) for 24 h; (d) irradiation of (c) for 12 h ($\lambda > 360$ nm); (e) heating (d) for 24 h.

7. *DOSY NMR spectra of **1** upon UV irradiation and heating treatments*

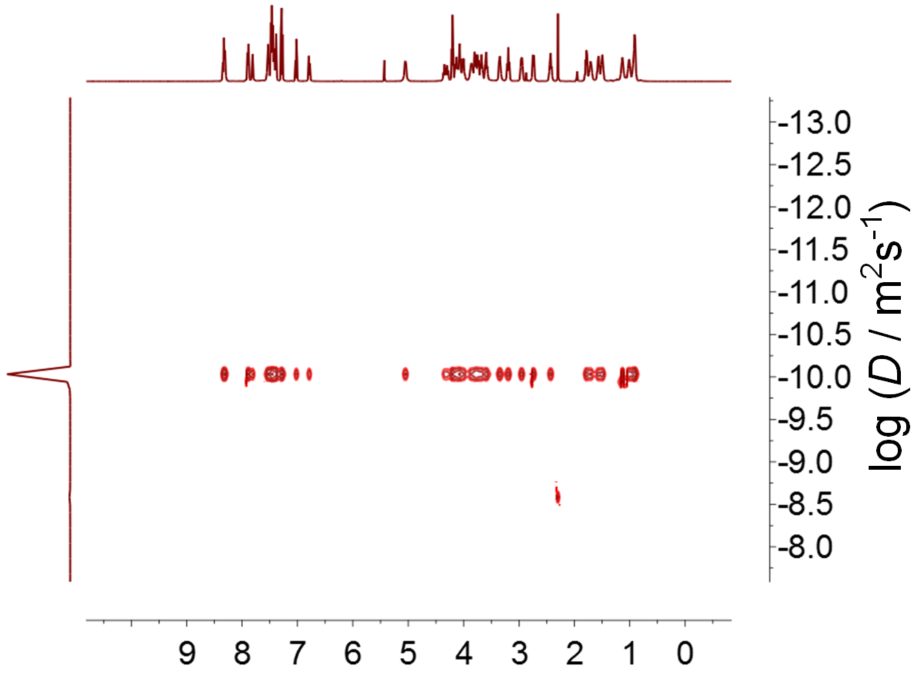


Figure S15. Full DOSY NMR spectrum (500 MHz, CD_3CN, 293 K) of **1** prior to irradiation.

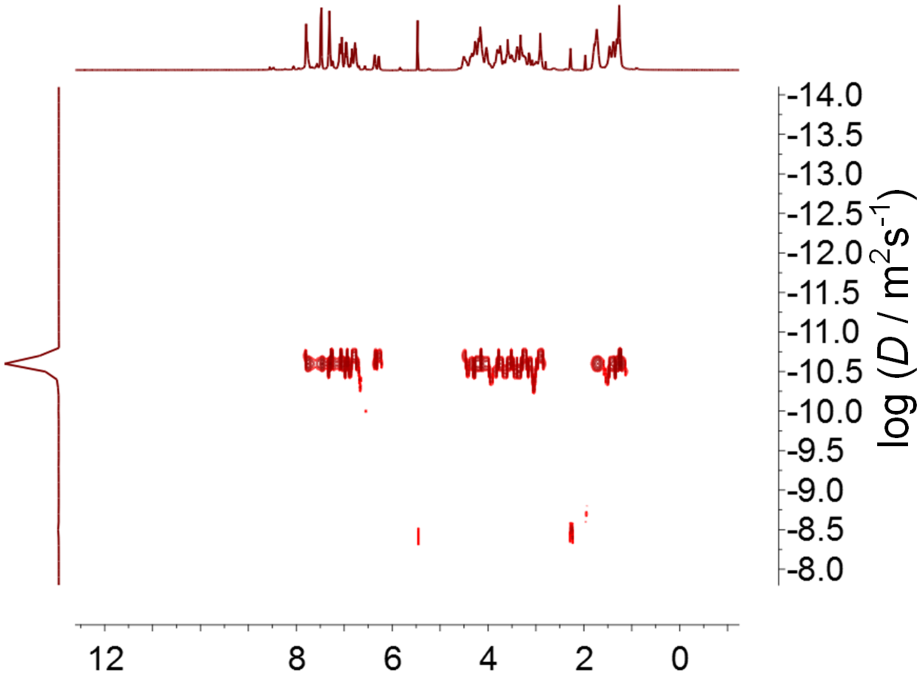


Figure S16. Full DOSY NMR spectrum (500 MHz, CD_3CN, 293 K) of **1** after irradiation for 12 h ($\lambda > 360$ nm).

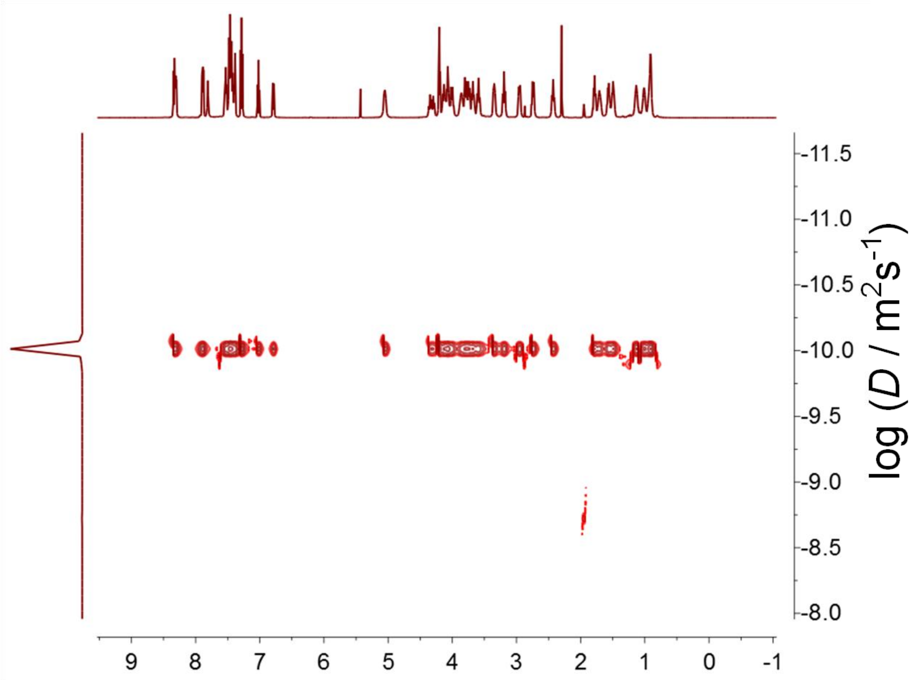


Figure S17. Full DOSY NMR spectrum (500 MHz, CD_3CN, 293 K) of **1** after irradiation for 12 h ($\lambda > 360$ nm) followed by heating for 24h.

8. *Degree of polymerization calculated by ^1H NMR and GPC*

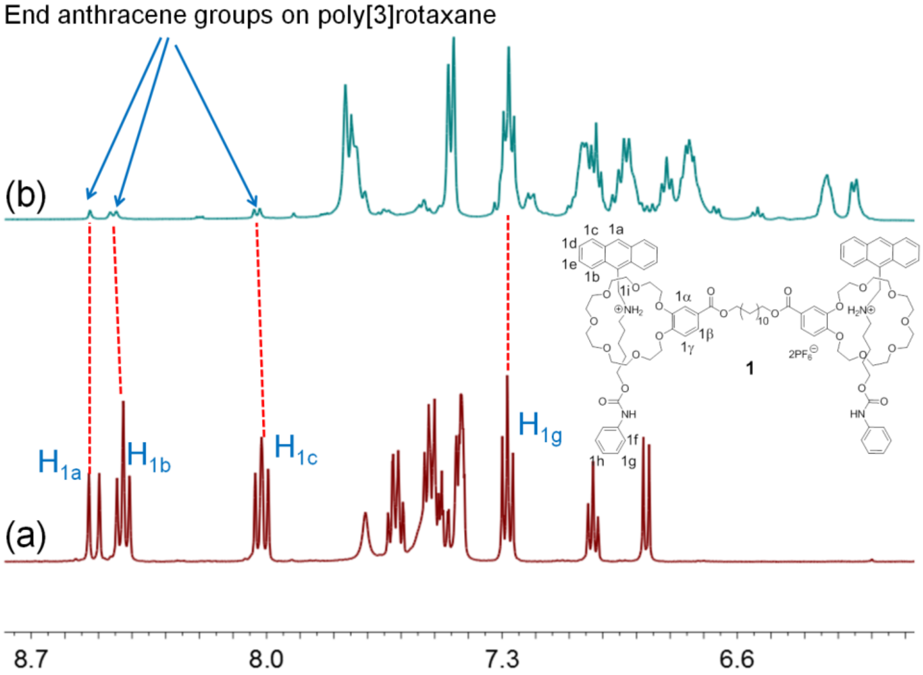


Figure S18. Partial ^1H NMR spectra (500 MHz, CD_3CN, 293 K) of [3]rotaxane (a) prior to and (b) after irradiation for 12 hours.

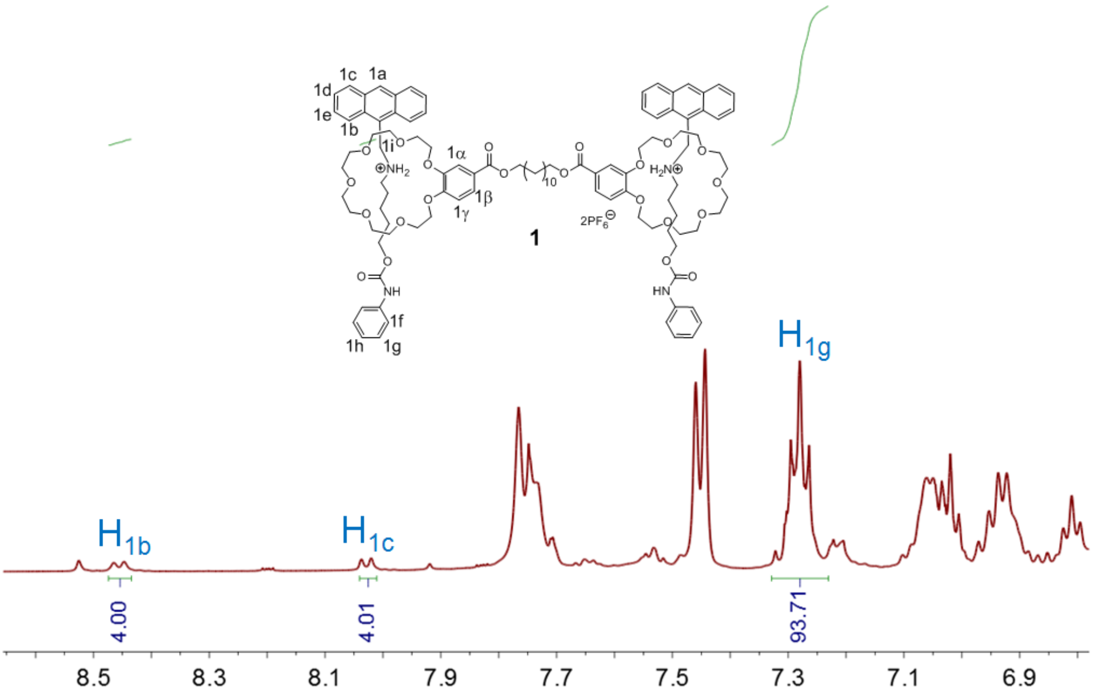


Figure S19. Partial ^{1}H NMR spectrum (500 MHz, CD_3CN, 293 K) of poly[3]rotaxane.

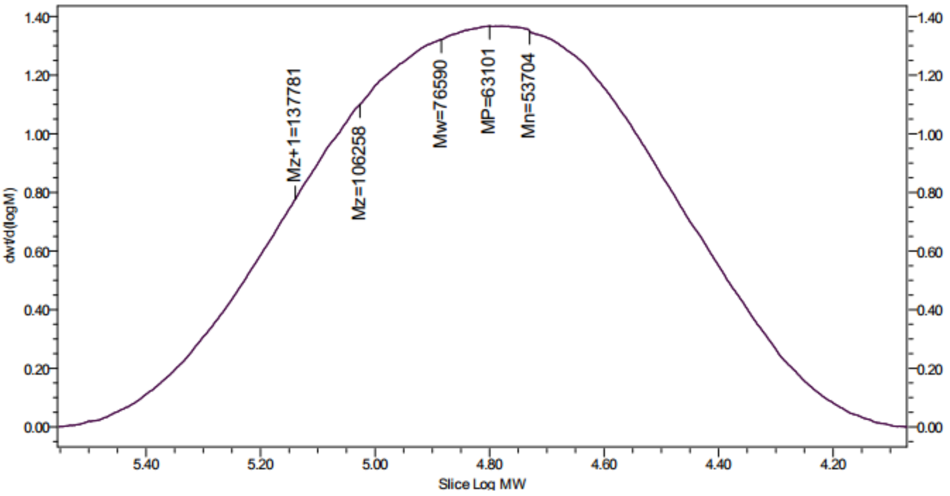


Figure S20. GPC analysis of the poly[3]rotaxane using conventional calculations, with polystyrenes as the standards and THF as the solvent. M_n and polydispersity of the poly[3]rotaxane were 54 kDa and 1.4, respectively.

M_n	M_w	M_p	M_z	M_{z+1}	PDI
53704	76590	63101	106258	137781	1.426151

9. *TGA and DSC of poly[3]rotaxane*

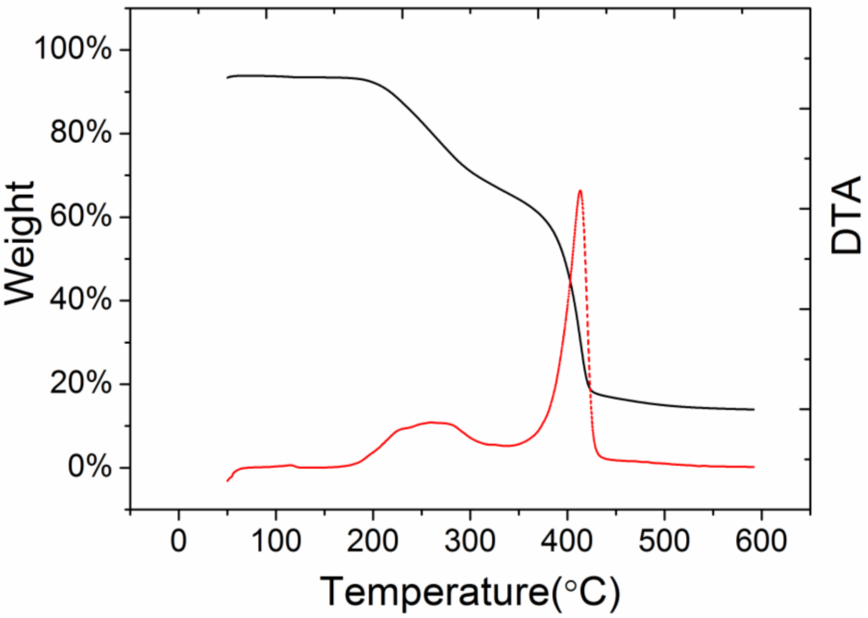


Figure S21. Thermogravimetric analysis scan (TGA) of the poly[3]rotaxane at a heating rate of 20 °C/min from 35 °C to 600 °C.

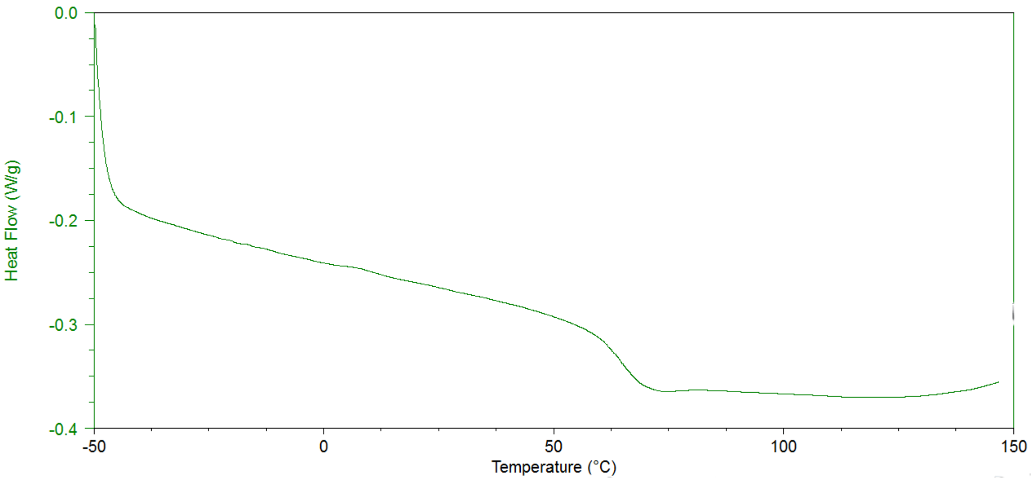
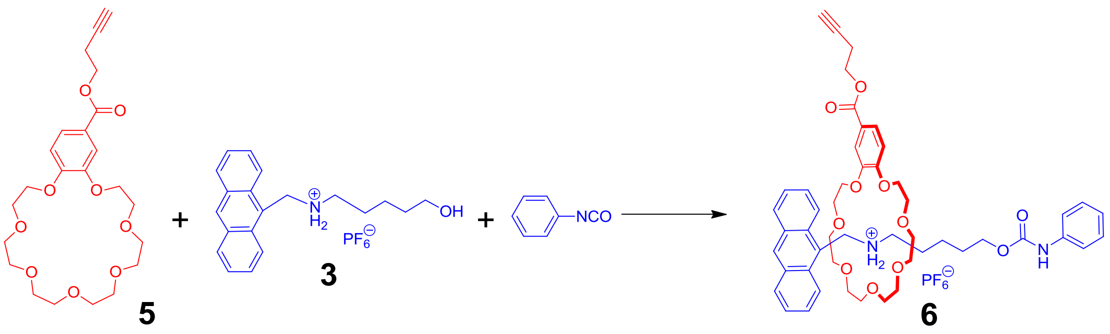


Figure S22. DSC of the poly[3]rotaxane (second heating).

*10. Synthesis of [2]rotaxane **6** and ^{1}H NMR of photoreaction of [2]rotaxane **6***

Scheme S4. Synthesis of **6**



A solution of **5** (0.500 g, 1.10 mmol), **3** (0.439 g, 1.00 mmol), catalytic amount of dibutyltin dilaurate (DBTDL, 0.060 mL), and phenyl isocyanate (0.240 g, 2.00 mmol) in dichloromethane (20.0 mL) was stirred at reflux for 12 h. Upon removal of DCM, a pale yellow oil was obtained, which was purified by flash column chromatography (methanol/dichloromethane, 1:100 *v/v*) to afford **6** as a yellow solid (0.56 g, 55%), mp 85.6–86.4 °C. The ^{1}H NMR spectrum of **6** is shown in Figure S23. ^{1}H NMR (400 MHz, CD_3CN, 293 K) δ (ppm): 8.54 (s, 1H), 8.45–8.47 (d, 2H, J = 8 Hz), 8.03–8.05 (d, 2H, J = 8 Hz), 7.72 (s, 1H), 7.63–7.66 (m, 2H), 7.52–7.56 (m, 4H), 7.44–7.48 (m, 3H), 7.28–7.32 (m, 2H), 7.03–7.06 (m, 1H), 6.93–6.95 (d, 2H, J = 8 Hz), 5.21–5.24 (m, 2H), 4.34–4.42 (m, 2H), 4.29–4.32 (m, 2H), 4.23–4.26 (m, 2H), 4.16–4.19 (m, 2H), 4.03–4.05 (m, 2H), 3.96–3.97 (m, 2H), 3.71–3.84 (m, 6H), 3.61–3.65 (m, 2H), 3.41–3.45 (m, 2H), 3.29–3.33 (m, 2H), 3.08–3.12 (m, 2H), 2.91–2.95 (m, 2H), 2.60–2.70 (m, 4H), 2.23–2.24 (t, 1H, J = 4 Hz), 1.72–1.79 (m, 4H), and 1.55–1.59 (m, 2H). The ^{13}C NMR spectrum of **6** is shown in Figure S24. ^{13}C NMR (100 MHz, CD_3CN, 293 K) δ (ppm): 18.17, 22.88, 24.94, 28.05, 42.72, 47.76, 62.13, 63.62, 68.41, 68.78, 69.27, 69.32, 69.37, 69.76, 69.93, 70.49, 70.51, 70.79, 70.80, 80.21, 111.58, 112.23, 122.59, 122.70, 123.12, 123.26, 123.88, 125.05, 126.78, 128.57, 128.87, 129.61, 130.10, 130.82, 138.56, 146.36, 150.60, 153.46, and 165.05. LRESIMS is shown in Figure S25: *m*/*z* 865.6 for $[M - PF_6]^+$, *m*/*z* 897.7 for $[M - PF_6 + CH_3OH]^+$, *m*/*z* 915.4 for $[M - PF_6 + CH_3OH + H_2O]^+$.

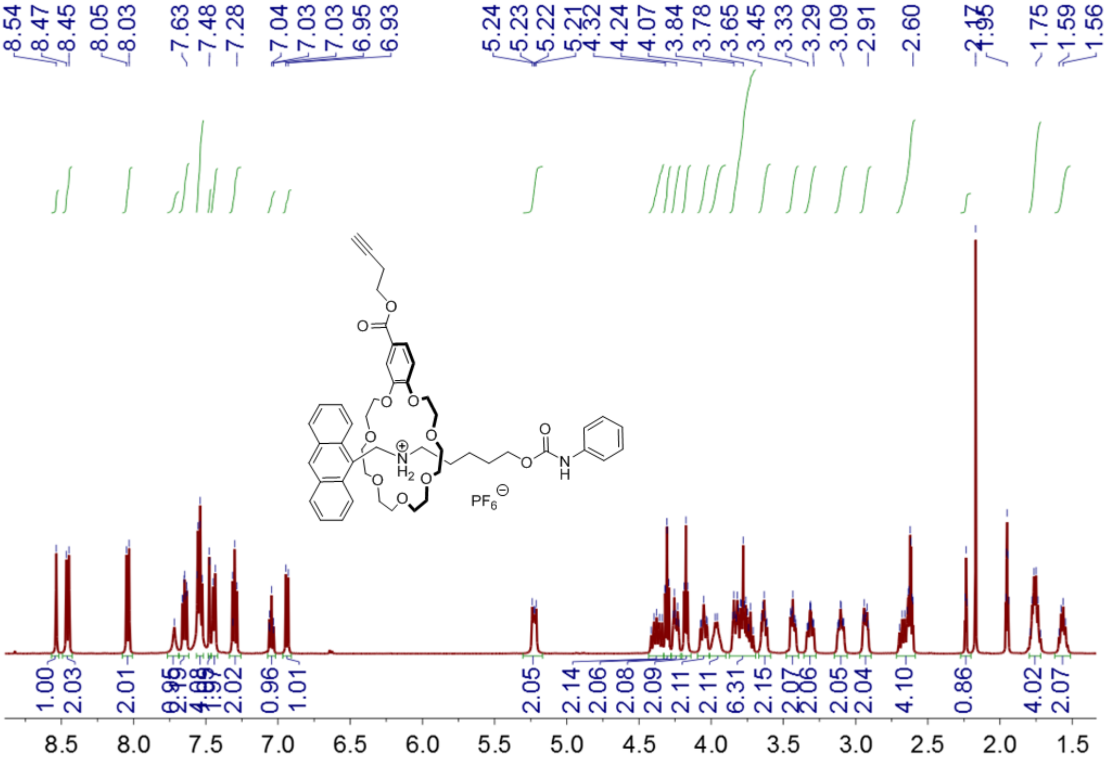


Figure S23. ^{1}H NMR spectrum (400 MHz, CD_3CN, 293 K) of **6**.

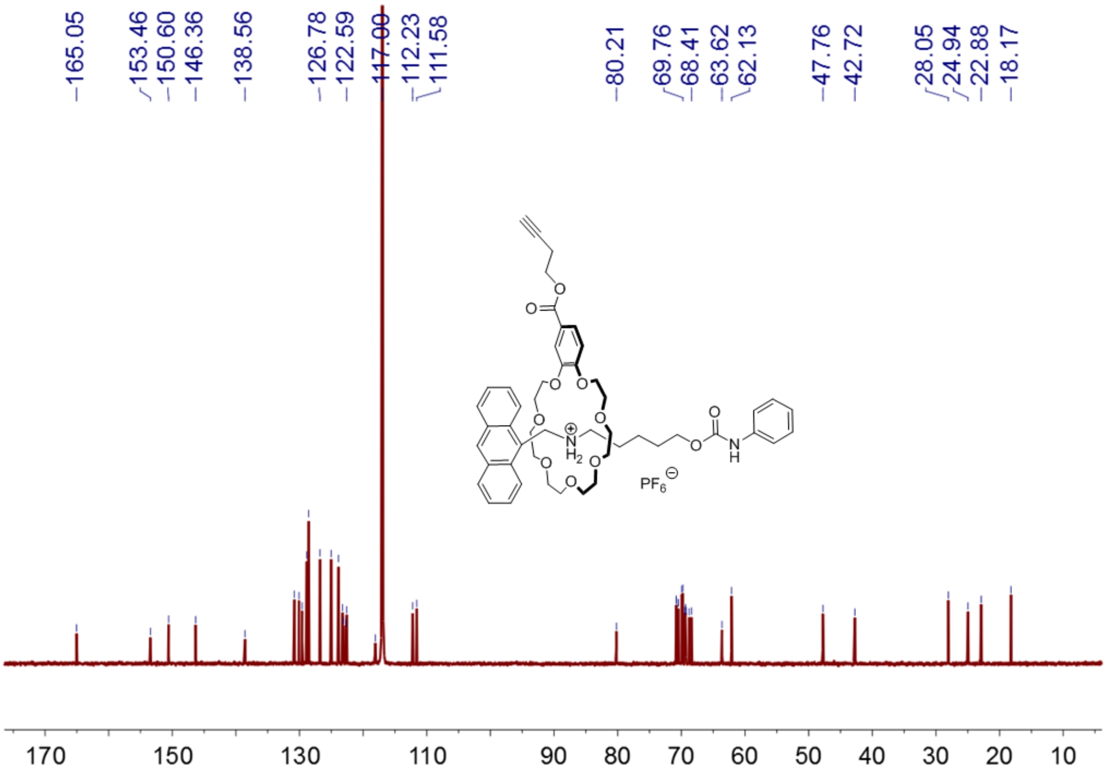


Figure S24. ^{13}C NMR spectrum (100 MHz, CD_3CN, 293 K) of **6**.

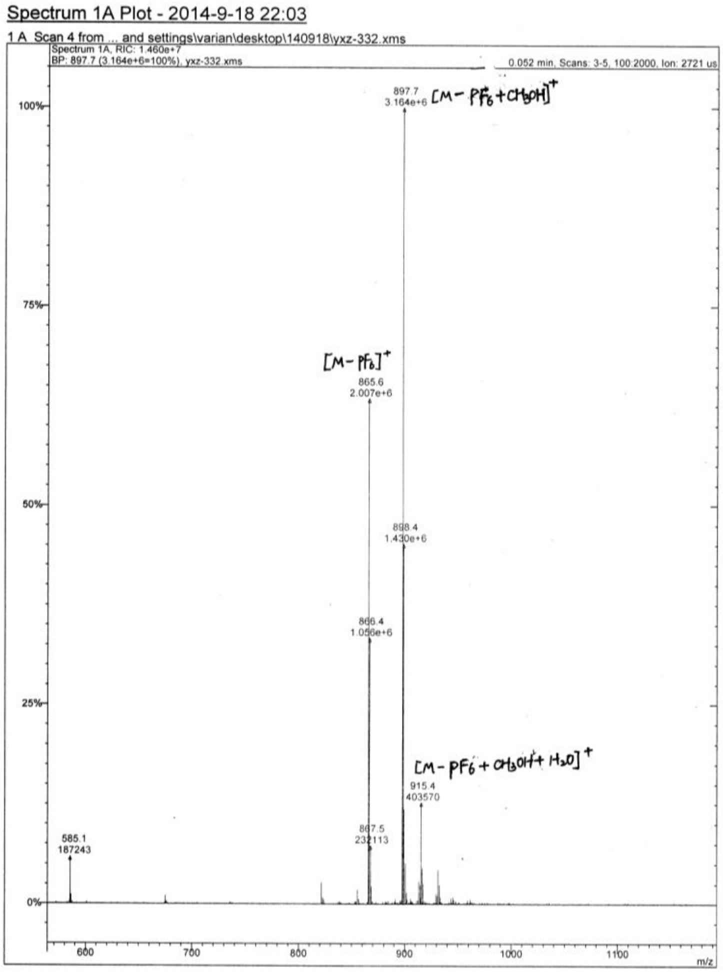
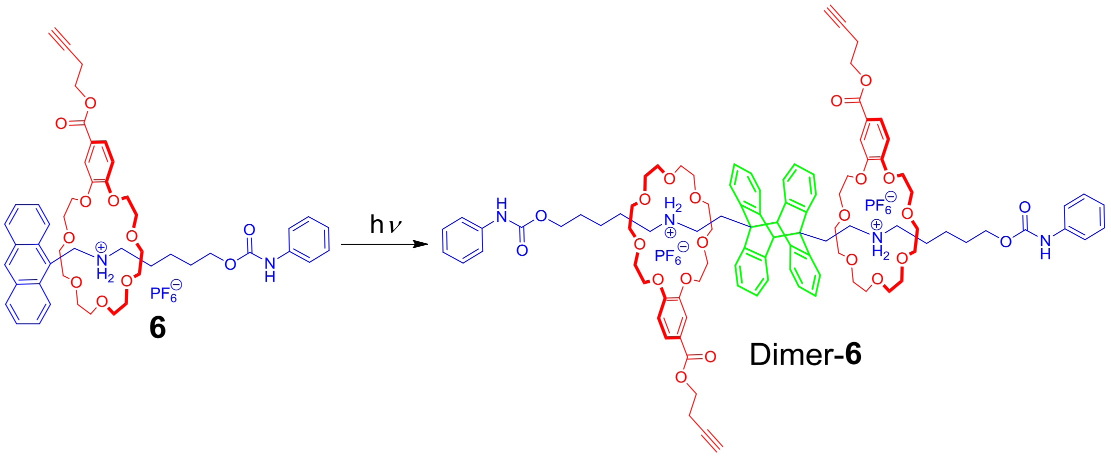


Figure S25. LRESI mass spectrum of **6**.

Scheme S5. Formation of Dimer-**6** upon photo irradiation ($\lambda > 360$ nm)



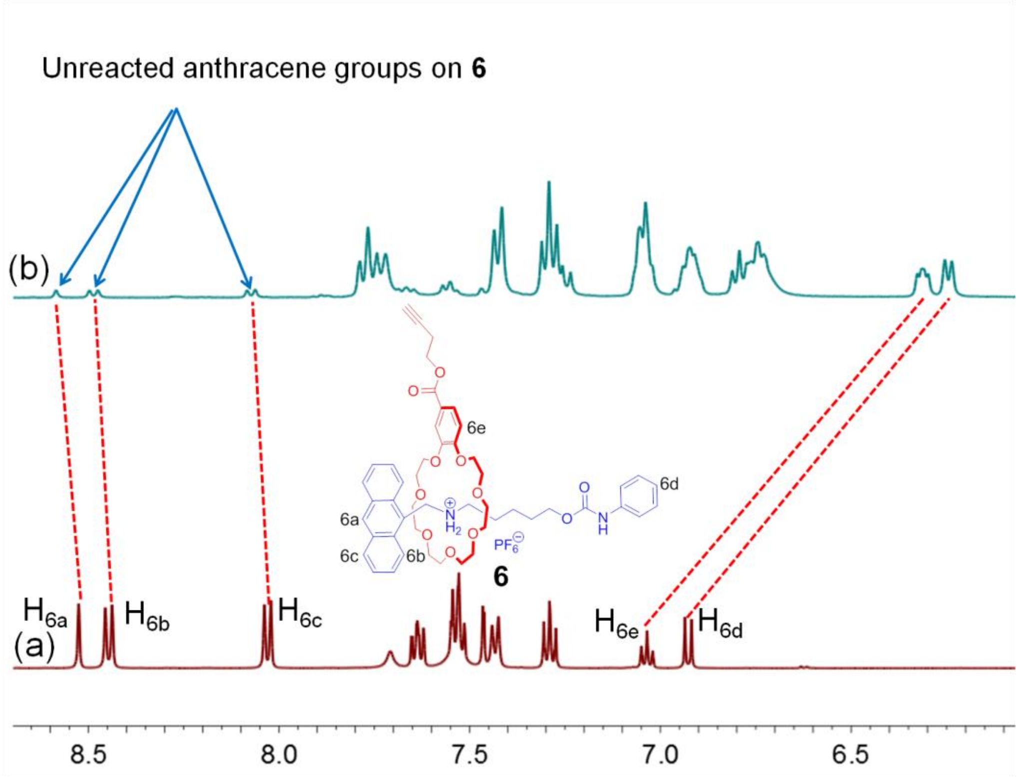


Figure S26. Partial ^{1}H NMR spectra (500 MHz, CD_3CN, 293 K) of [2]rotaxane **6** (a) prior to and (b) after irradiation for 12 hours.

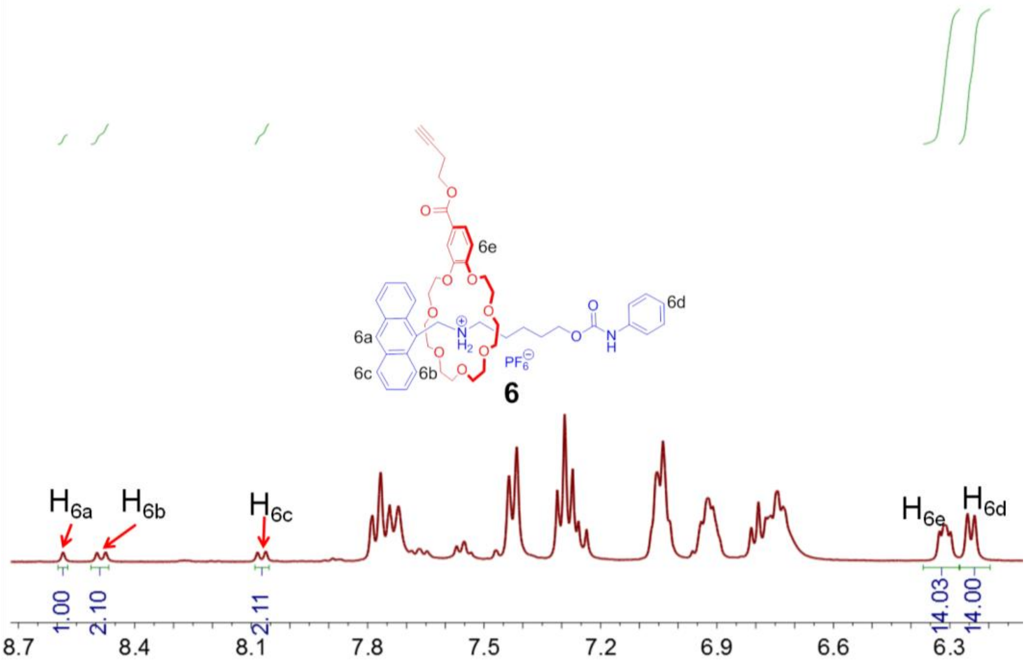


Figure S27. Partial ^{1}H NMR spectrum (500 MHz, CD_3CN, 293 K) of [2]rotaxane **6**.

The residual ^{1}H NMR signal of $H_{6a\text{–}c}$ on anthracene was assignable to the unreacted anthracene groups of the [2]rotaxane. Therefore, by comparing the integration of H_{6d}

or H_{6e} in the benzyl group of the “axle” component with that of H_{6a}, the yield of dimerization was determined to be 93%. These NMR data illustrates that the regioselectivity of the photodimerization takes place in the *anti* fashion which favores the extension of the polymer chain.

11. Reversible fluorescence spectra of ***1*** *upon UV irradiation*

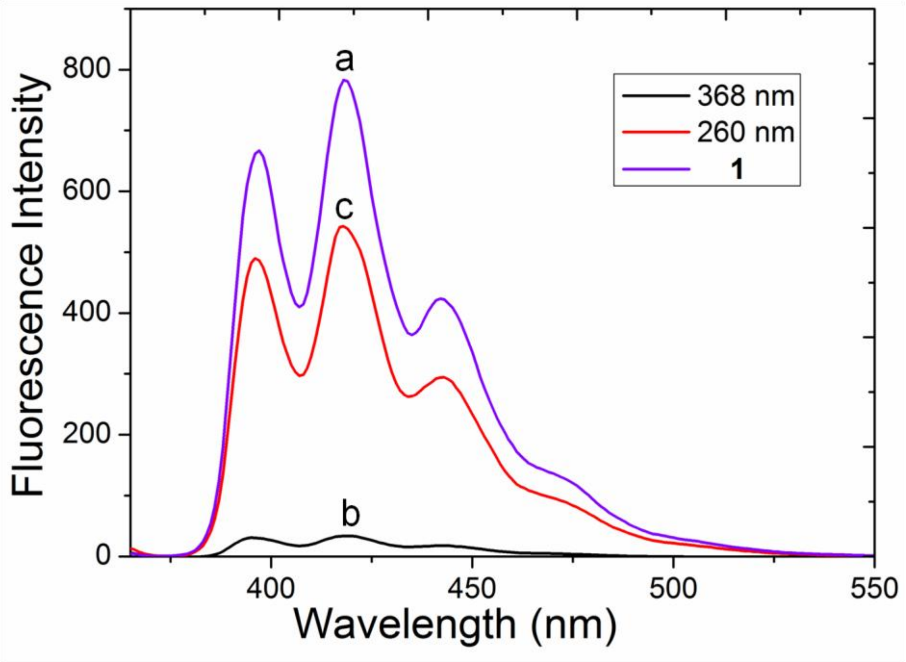


Figure S28. Fluorescence spectra: (a) [3]rotaxane **1** (20.0 μM); (b) irradiation of (a) for 6 h at λ = 368 nm; (c) irradiation of (b) for 6 h at λ = 260 nm.

References:

S1. X. Yan, D. Xu, J. Chen, M. Zhang, B. Hu, Y. Yu and F. Huang, *Polym. Chem.*, 2013, **4**, 3312–3322.

S2. X. Yan, D. Xu, X. Chi, J. Chen, S. Dong, X. Ding, Y. Yu and F Huang, *Adv. Mater.*, 2012, **24**, 362–369.