Electronic Supplementary Information

Formation of "pseudosuitane"-type complex between triptycene-derived bis(crown ether) host and 1,1'-(anthracene-9,10-diyl)bis(*N*-benzylmethanaminium): a new method for the synthesis of linear polyrotaxanes

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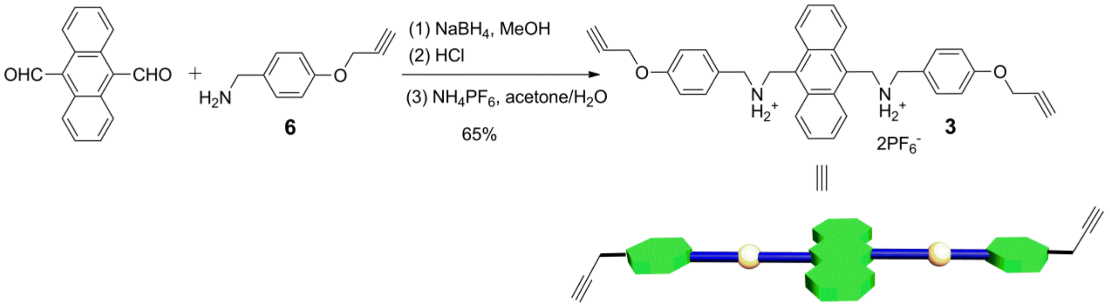
Contents

1. Experimental

General. Melting points, taken on an electrothermal melting point apparatus, are uncorrected. ^1H NMR, ^{13}C NMR spectra were recorded on a Bruker DMX300 NMR spectrometer. High Resolution Mass spectra was determined by Bruker Daltonics. Inc, APEX II. FT-ICRMS. The M_n and polydispersity index of polyrotaxane **5** were determined by gel permeation chromatography (GPC) (Waters Co.) using polystyrene (PS) as standard and dimethylformamide (DMF) as eluent.



Scheme 1. Synthesis of guest **3**

Synthesis of guest 3. A mixture of anthracene-9,10-dicarboxaldehyde (500 mg, 2.13 mmol) and **6** (688 mg, 4.27 mmol) in methanol (50 mL) was stirred at room temperature for 3 h. Then, to the reaction mixture at ice-bath was added $NaBH_4$ (484 mg, 12.81 mmol) in small portions. The reaction mixture was stirred at room temperature overnight, and then quenched by a small amount of water. To the mixture solution was added dichloromethane (50 mL), the organic layer was separated and dried over anhydrous magnesium sulfate. After the solvent was removed, the residue was purified by column chromatography (silica gel, DCM:MeOH = 100:0 ~ 70:1) to give the free amine compound. To a solution of the free amine in methanol (20 mL) was added HCl (0.5 mL) at room tempetature. After stirring for 2 h under nitrogen atmosphere, the solvent was removed under vacuum. The residue was dissolved in acetone, and then added saturated NH_4PF_6 liquid until formation of homogeneous solution. The mixture was concentrated under reduced pressure to form a yellow solid, which was isolated, washed with H_2O, and dried in vacuo to afford **3** (1.13 g, 65%). Mp: 193-194 ºC. ^{1}H NMR (300 MHz, acetone-d_6, 295 K): δ 8.43 (dd, J_1 = 10.0 Hz, J_2 = 3.2 Hz, 4H), 7.66-7.57 (m, 8H), 7.11-7.08 (d, J = 8.6 Hz, 4H), 5.31 (s, 4H), 4.85-4.84 (d, J = 2.3 Hz, 4H), 4.58 (s, 4H), 3.13-3.12 (t, J = 2.3 Hz, 2H). ^{13}C NMR (75 MHz, acetonitrile-d_3, 295 K): δ 157.8, 131.1, 130.0, 127.1, 126.6, 125.9, 124.2, 117.0, 114.9, 78.3, 75.7, 55.3, 51.8, 43.2, 29.6. HRMS cald. for $[M\text{-}PF_6]^+$: 671.2257. Found: 671.2255.

2. Fluorescent spectra of host 1 and guest 2

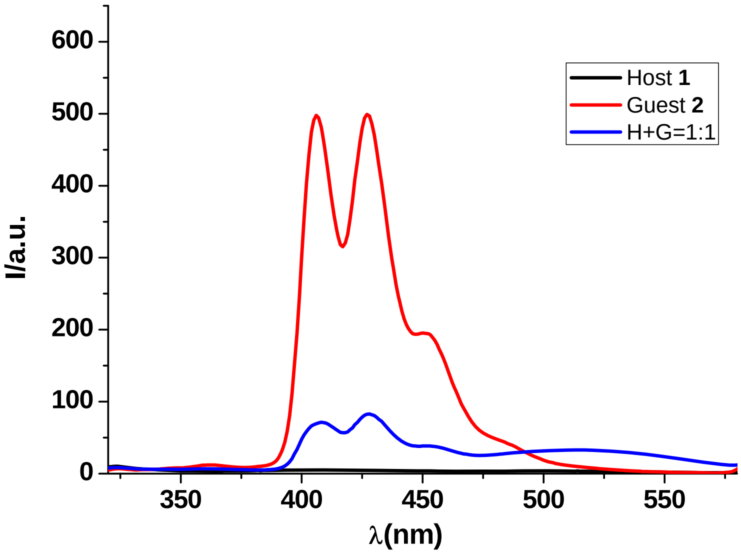


Fig. S1 Fluorescence emission spectra of **1**, **2** and **1·2** in $CHCl_3/CH_3CN$ (1:1, v/v) at 295 K. λ_{ex} = 294 nm. $[\mathbf{2}]_0 = 4.0 \times 10^{-5}$ M.

3. Fluorescence titrations of host 1 and guest 2

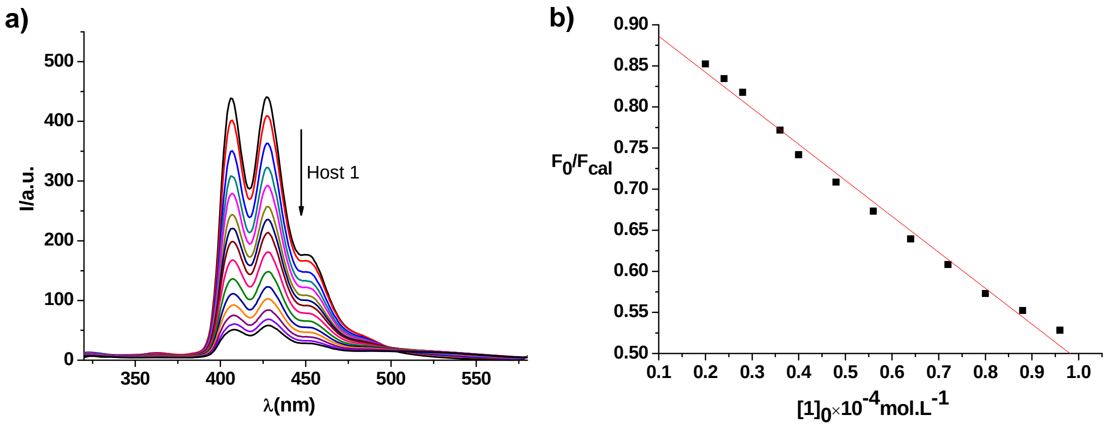


Fig. S2 (a) Emission spectra (λ_{ex}=294 nm) of **2** (4.0×10^{-5} M) in the presence of host **1** in $CHCl_3$/CH_3CN (1:1, v/v) at 295 K. The concentration of host **1** for curves from top to bottom are 0, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.8, 5.6, 6.4, 7.2, 8.0, 8.8, 9.6 ($\times 10^{-5}$ M). (b) The variation of fluorescence intensity F_0/F_{cal} of **2** versus the increase of the concentration of host **1**.

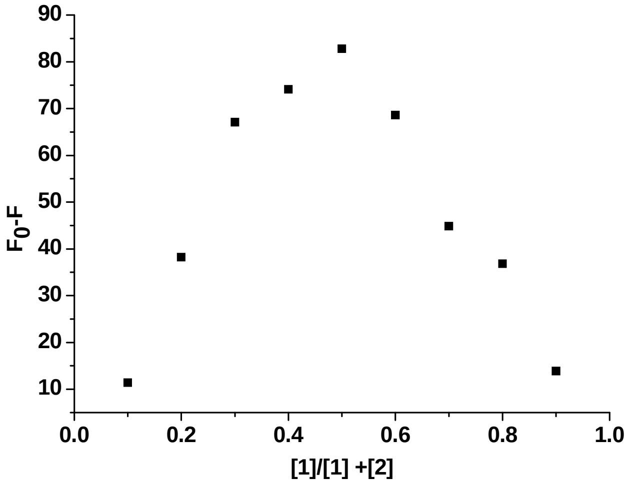


Fig. S3 Job plot for complex **1·2** in $CHCl_3$/CH_3CN (1:1, v/v) ([**1**]$_0$+[**2**]$_0$=8.0×10^{-5} M).

To eliminate the competitive absorption of host **1** at both the excitation and emission wavelengths, the fluorescence intensity F_{exp} of guest **2** was calibrated to F_{cal} according to a literature method.

$$F_{cal} = F_{exp} \frac{1-\exp(-\varepsilon_1 C_1 l)}{\varepsilon_1 C_1 l} \cdot \frac{(\varepsilon_1 C_1 l + \varepsilon_2 C_2 l)}{1-\exp(-\varepsilon_1 C_1 l - \varepsilon_2 C_2 l)} \cdot \frac{\varepsilon_3 C_3 l}{1-\exp(-\varepsilon_3 C_3 l)}$$

F_{cal}: calibrated fluorescence intensity

F_{exp}: experiment fluorescence intensity

$\varepsilon_1 C_1 l$: absorbance value of guest at excitation wavelength

$\varepsilon_2 C_2 l$: absorbance value of host at excitation wavelength

$\varepsilon_3 C_3 l$: absorbance value of guest at emission wavelength

4. Fluorescence spectra of host 1 and guest 3

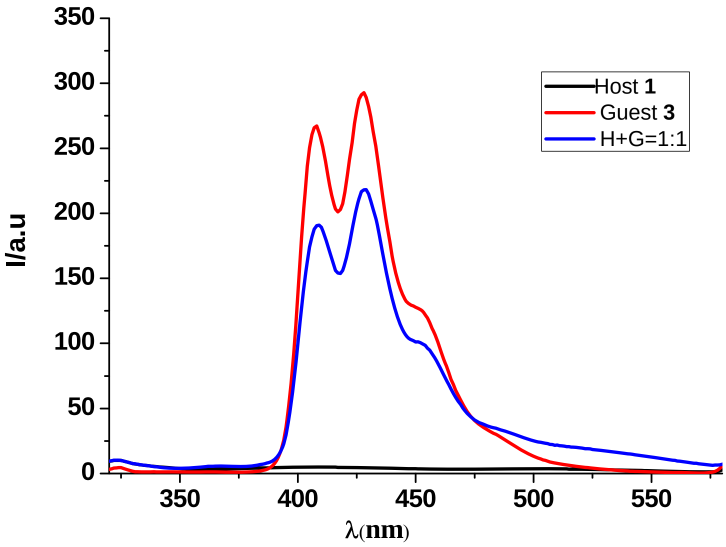
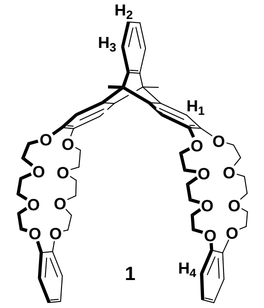
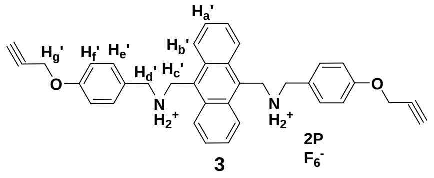


Fig. S4 Fluorescence emission spectra of **1**, **3** and **1·3** in $CHCl_3/CH_3CN$ (1:1, v/v) at 295 K. λ_{ex} = 294 nm. $[\mathbf{3}]_0 = 4.0 \times 10^{-5}$ M.

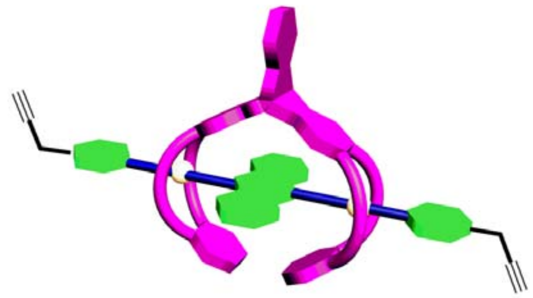
5. Complexation between host 1 and guest 3



1



3



1·3

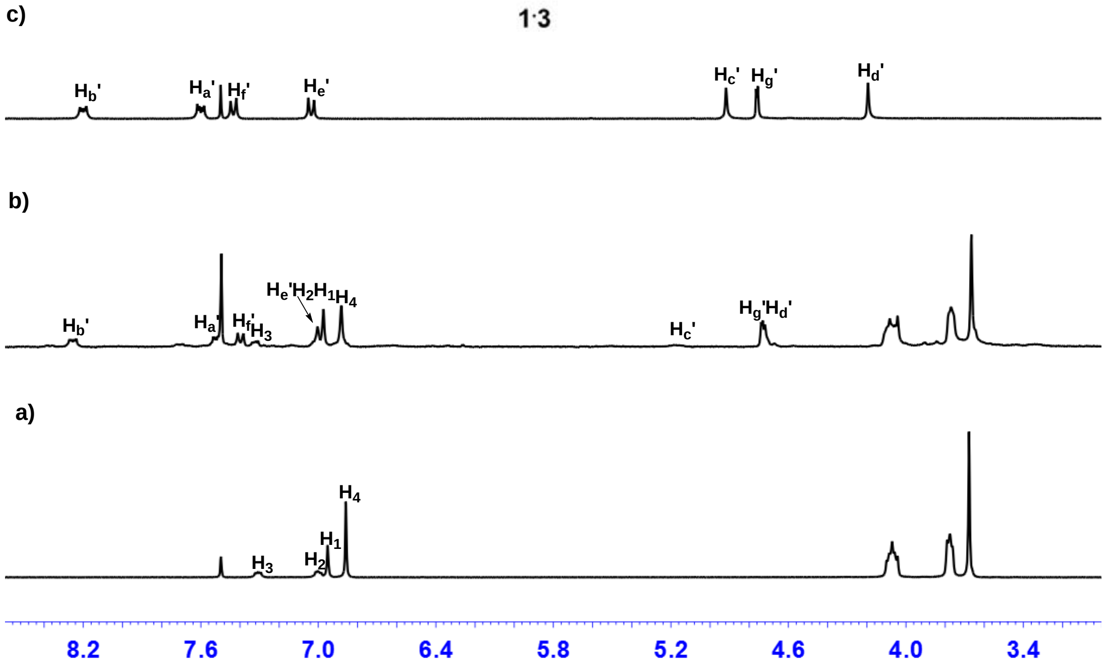
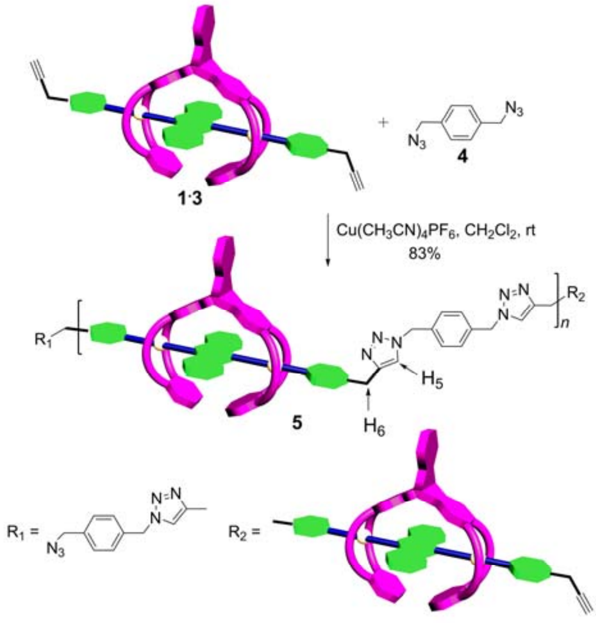


Fig. S5 Partial ^{1}H NMR spectra (300 MHz, CD_3CN:$CDCl_3$ = 1:1, v/v, 295 K) of (a) free host **1**, (b) **1** and 1.0 equiv of **3**, and (c) free guest **3**. $[\mathbf{1}]_0$ = 1.0 mM.

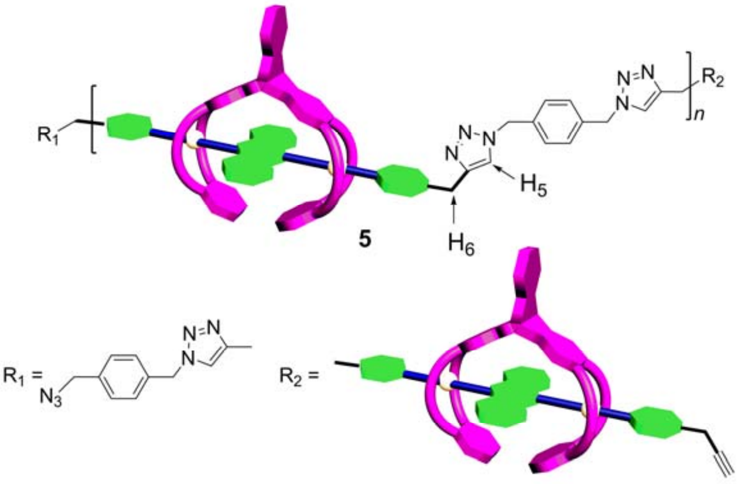
6. Synthesis of polyrotaxane 5



Scheme 2. Synthesis of polyrotaxane **5**.

The mixture of host **1** (50 mg, 4.89×10^{-2} mmol), **3** (39.9 mg, 4.89×10^{-2} mmol) was stirred in dry CH_2Cl_2 (50 mL) at room temperature overnight under nitrogen atmosphere. After one equivalent of diazide **4** (9.2 mg, 4.89×10^{-2} mmol) and catalytic amount of $Cu(CH_3CN)_4PF_6$ were added to the above solution, the mixture was stirred for another 24h at room temperature under nitrogen atmosphere. During the reaction process, the precipitation was formed. After the reaction finished, the precipitation was filtered, washed with CH_2Cl_2, CH_3OH, H_2O, and Et_2O, respectively, and then dried in vacuo to give polyrotaxane **5** (82.3 mg, 83%) as pale green powder. FT-IR: $\nu_{\equiv C\text{-}H}$ = 3502 cm^{-1}, ν_{N3} = 2101 cm^{-1}, $\nu_{trizole}$ = 1057 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6, 295 K): δ = 8.27 (br s, 4H), 7.80 (br s, 4H), 7.53-6.60 (br m, 25H), 5.55 (br s, 4H), 5.09 (br s, 4H), 4.17-3.34 (br m, 52H). GPC data : M_n = 11.9 KDa, PDI = 1.27.

7. ^{1}H NMR spectrum of polyrotaxane 5



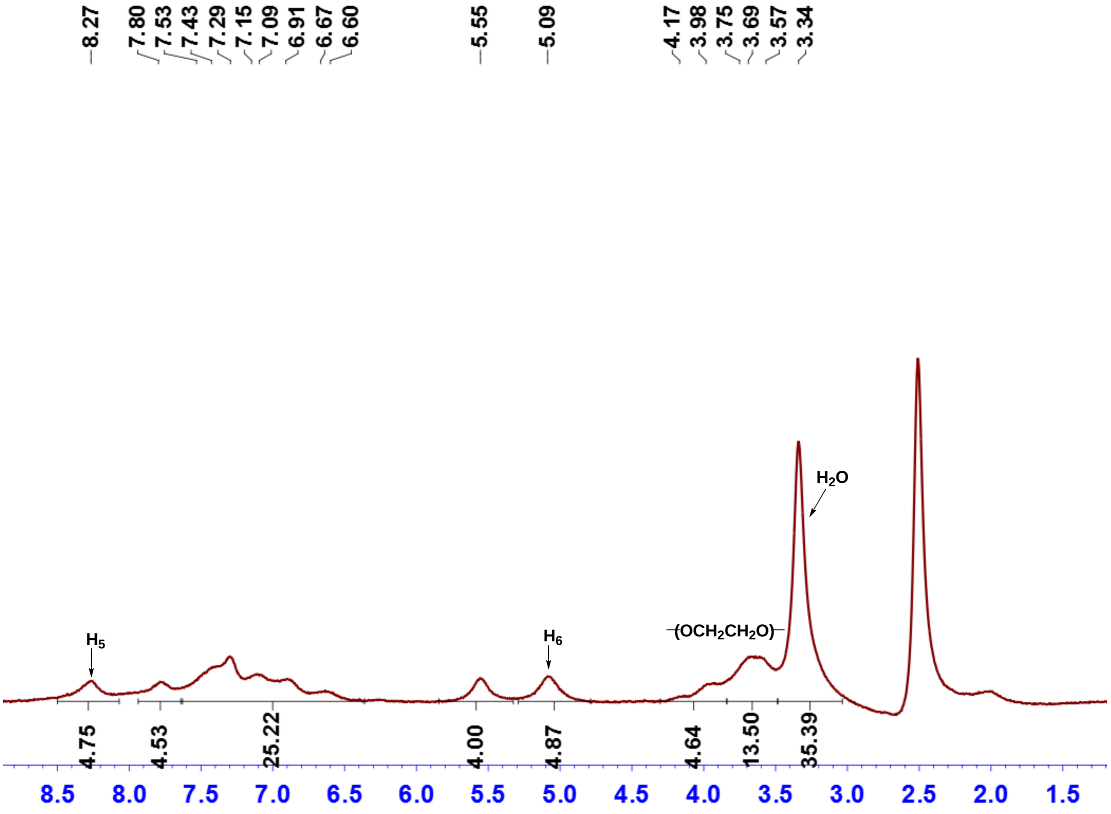


Fig. S6 ^{1}H NMR spectrum (300 MHz, DMSO-d_6, 295 K) of polyrotaxane **5**.

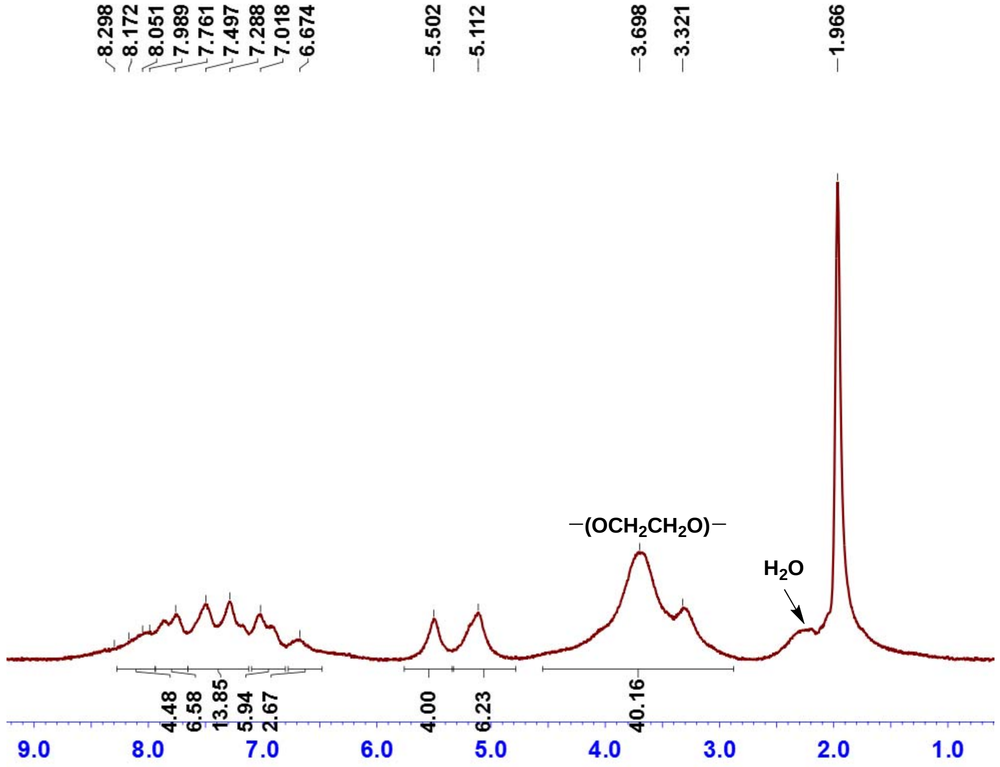


Fig. S7 ^{1}H NMR spectrum (300 MHz, acetonitrile-d_3, 295 K) of polyrotaxane **5**.

8. FT-IR spectrum of polyrotaxane 5

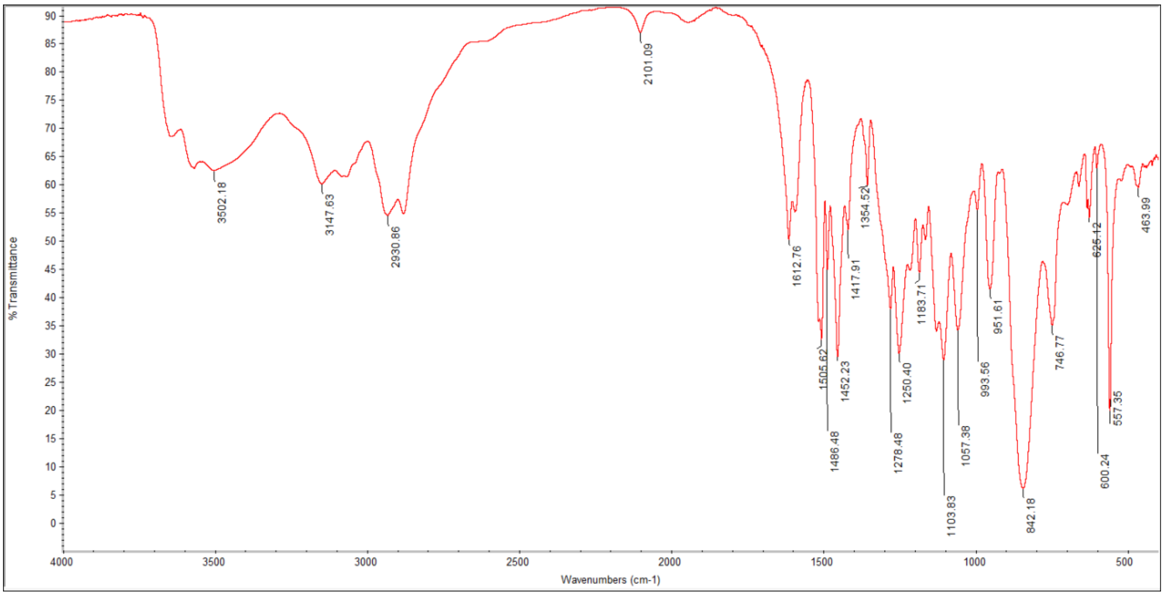
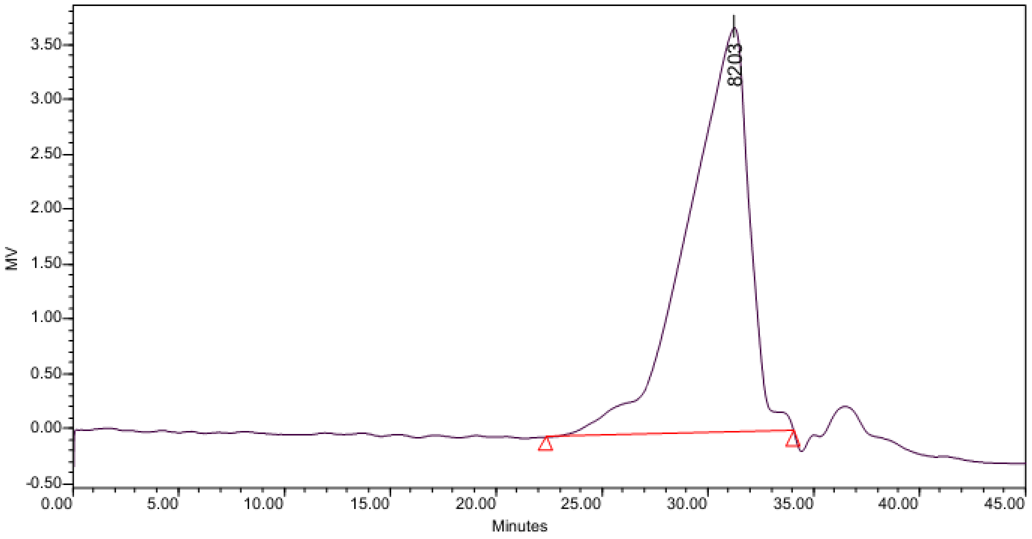


Fig. S8 FT-IR spectrum of polyrotaxane **5**.

9. GPC spectrum of polyrotaxane 5



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		31.236	31.236	31.236	11857	15109	8203	18397	22999	1.217575	1.522195

Fig. S9 GPC spectrum of polyrotanxe **5**.

10. ^{1}H NMR and ^{13}C NMR spectra of new compounds

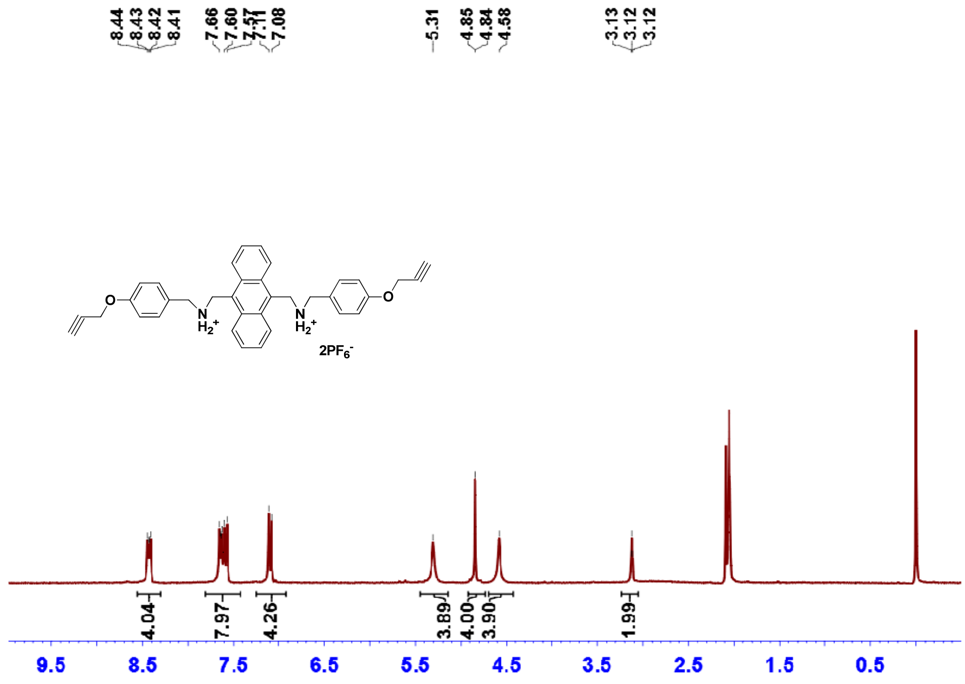


Fig. **S10** ^{1}H NMR spectrum (300 MHz, acetone-d_6, 295 K) of compound **3**.

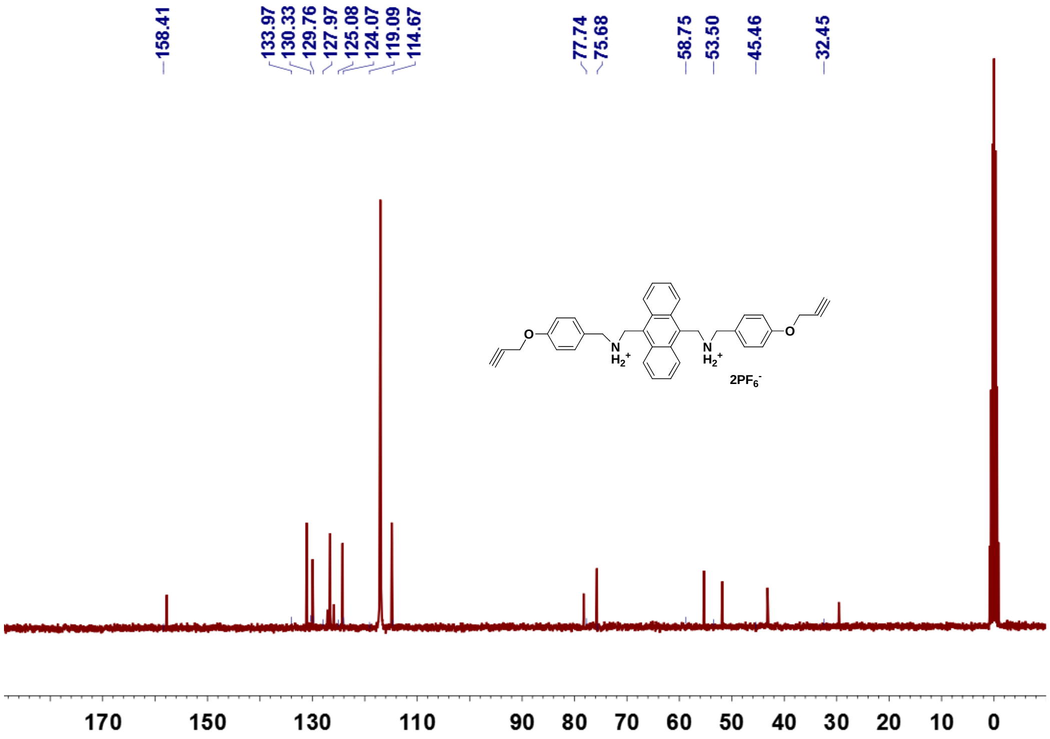


Fig. S11 ^{13}C NMR spectrum (75 MHz, acetonitrile-d_3, 295 K) of compound **3**.

11. DSC curve of polyrotaxane 5

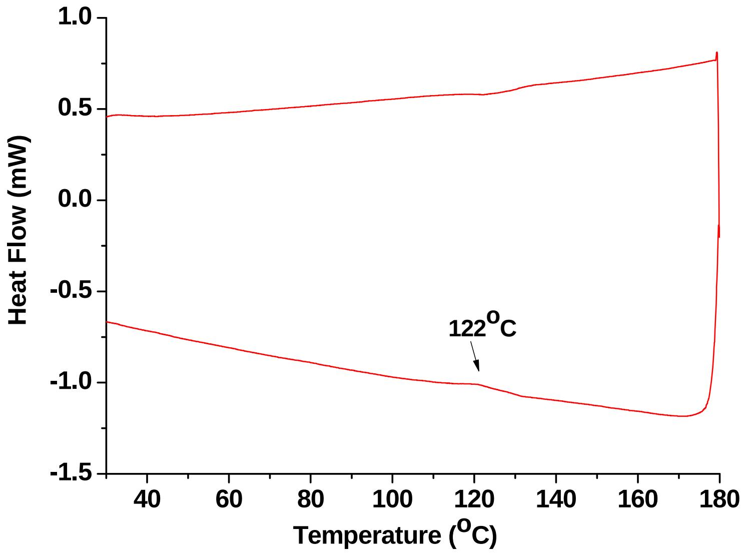
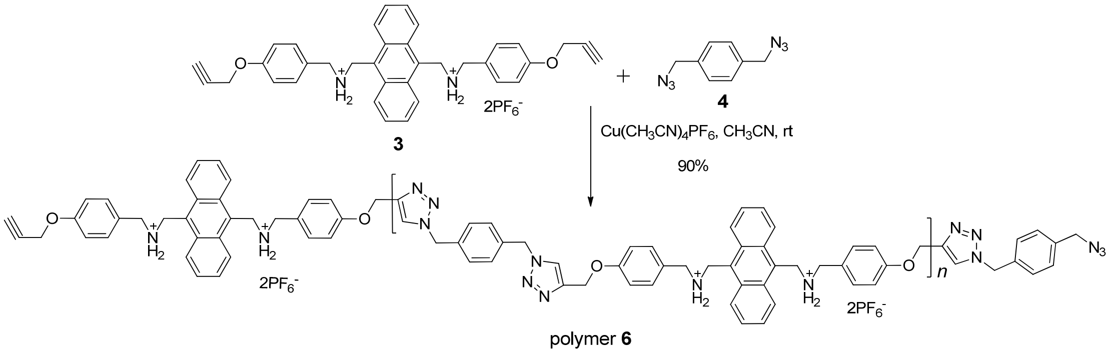


Fig. S12 DSC curve of polyrotanxe **5**.

12. Synthesis of polymer 6



The mixture of **3** (69.4 mg, 8.5×10^{-2} mmol), **4** (16.0 mg, 8.5×10^{-2} mmol) and catalytic amount of $Cu(CH_3CN)_4PF_6$ was stirred in dry CH_3CN (50 mL) at room temperature overnight under nitrogen atmosphere. During the reaction process, the precipitation was formed. After the reaction finished, the precipitation was filtered, washed with CH_2Cl_2, CH_3OH, H_2O, and Et_2O, respectively, and then dried in vacuo to give polymer **6** (76.9 mg, 90%) as yellow powder. ^{1}H NMR (300 MHz, DMSO-d_6, 295 K): δ = 8.32-8.29 (br d, 9H), 7.60-7.32 (br m, 27H), 7.09 (br s, 6H), 5.63-5.59 (br d, 6H), 5.17 (br s, 6H), 4.42 (br s, 4H). GPC data : M_n = 12.5 KDa, PDI = 1.20.

13. ^{1}H NMR and GPC spectrum of polymer 6

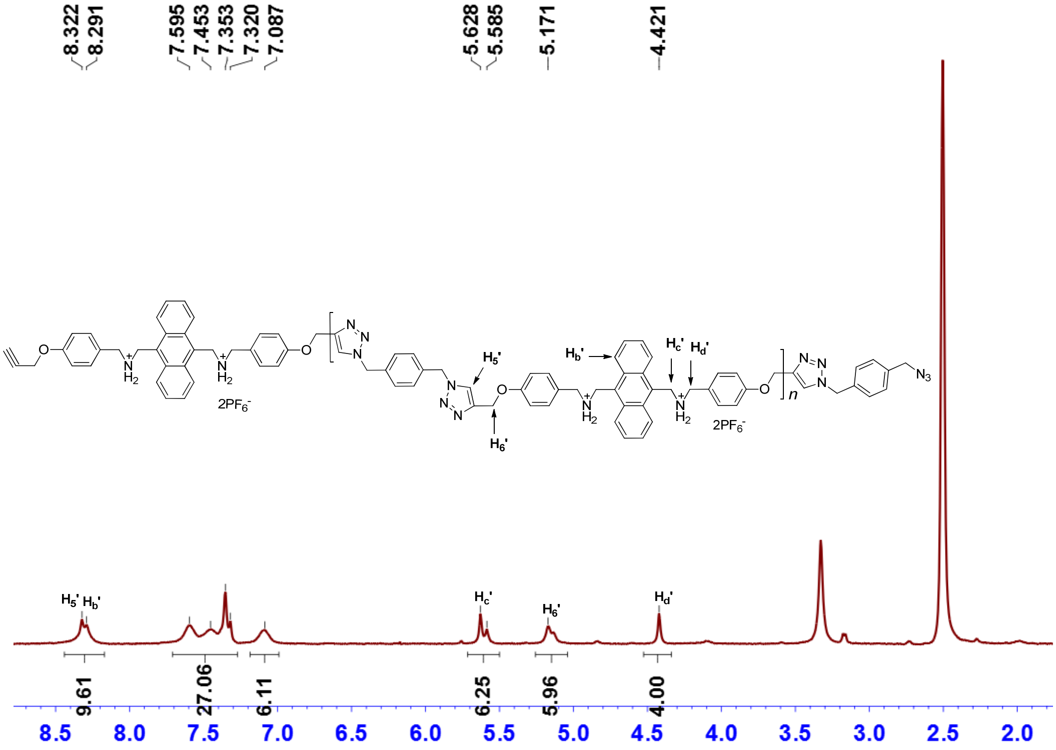


Fig. S13 ^{1}H NMR spectrum (300 MHz, DMSO-d_6, 295 K) of polymer **6**.

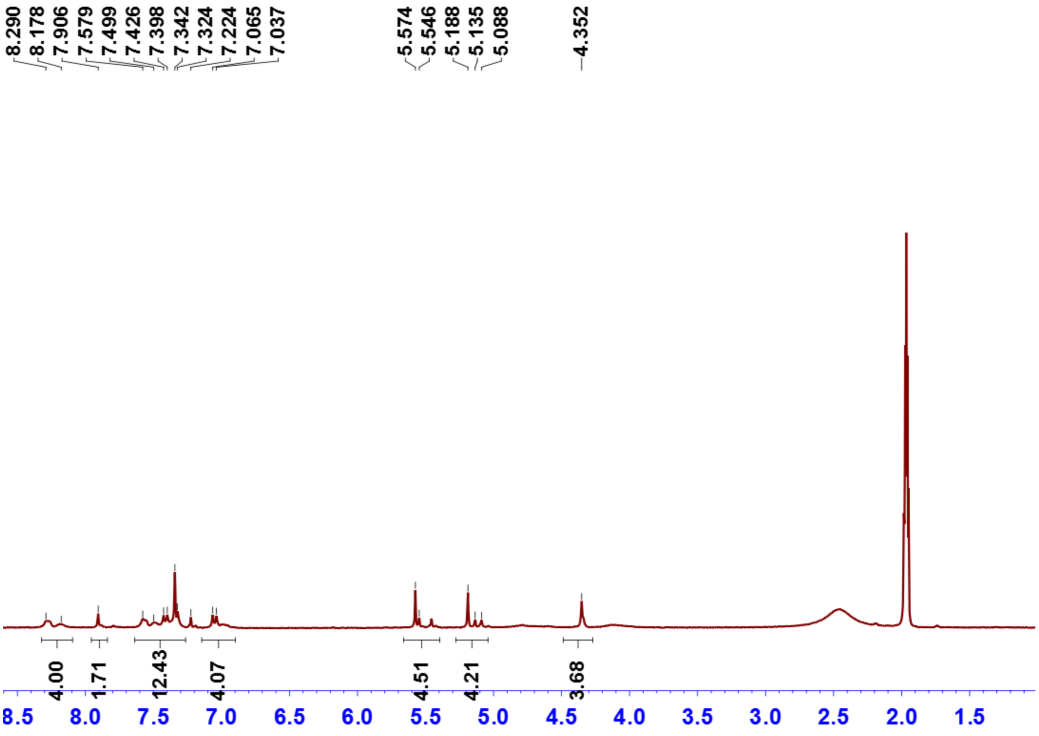
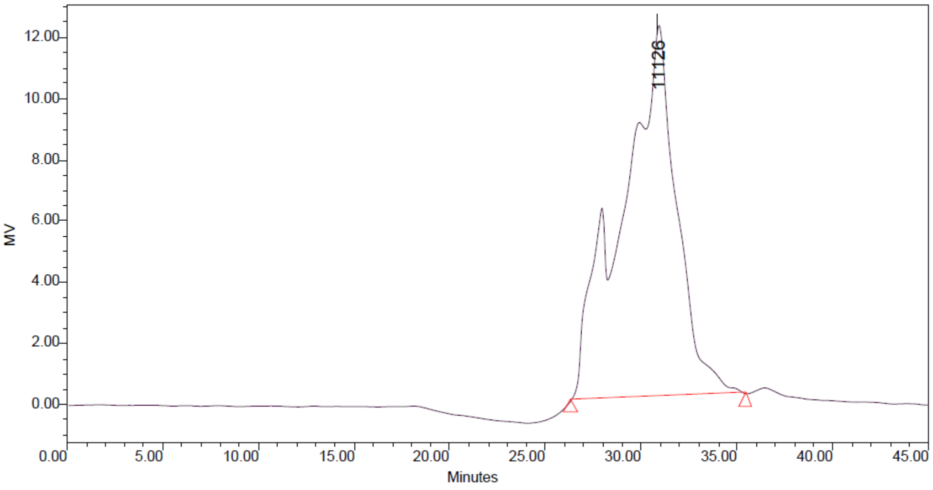


Fig. S14 ^{1}H NMR spectrum (300 MHz, acetonitrile-d_3, 295 K) of polymer **6**.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		30.873	30.873	30.873	12520	15053	11126	16709	17706	1.110008	1.176258

Fig. S15 GPC spectrum of polymer **6**.