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Electronic Supplementary Information

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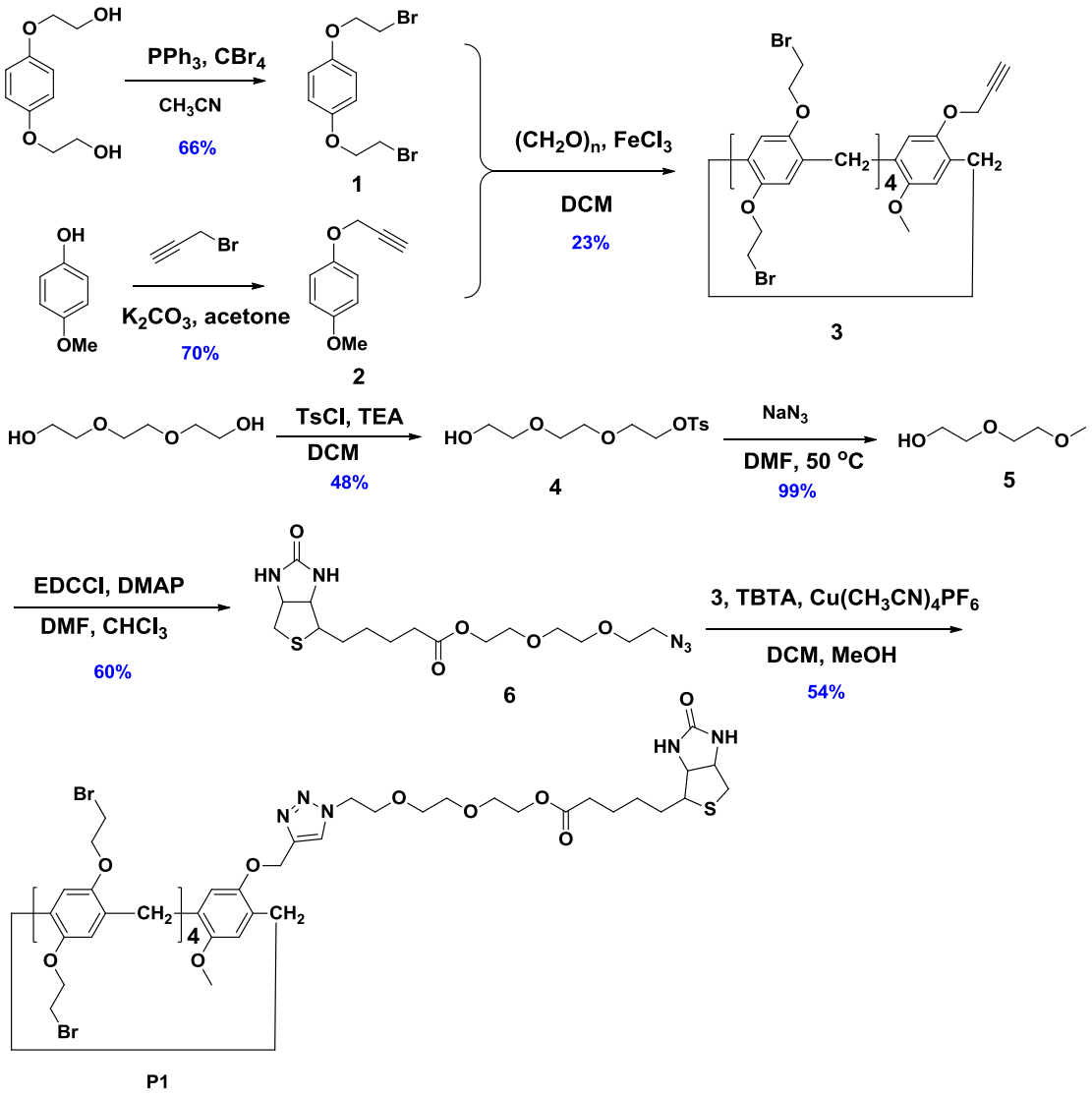
Table of Contents

1. General information

All reactions were performed in air atmosphere unless otherwise stated. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. Column chromatography was performed with silica gel (200-300 mesh) produced by Qingdao Marine Chemical Factory, Qingdao (China). All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer (or Bruker DPX400 MHz spectrometer) with internal standard tetramethylsilane (TMS) and solvent signals as internal references at room temperature, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan Mat TSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion. Melting points (M.p.) were determined using a Focus X-4 apparatus (made in China) and were not corrected.

2. Experimental procedure



Scheme S1. The synthesis route of **P1**.

1,4-Bis(2-bromoethoxy)benzene **1**[S1]: A solution of 1,4-bis(2-hydroxyethoxy)benzene (3.99 g, 20 mmol) and triphenylphosphine (13.9 g, 60 mmol) in dry acetonitrile (150 mL) was cooled to 0 °C with an ice bath. Under vigorous stirring, carbon tetrabromide (19.9 g, 60 mmol) was slowly added. The mixture was stirred at 25 °C for 4 h. Then cold water (100 mL) was added to the reaction mixture to give white precipitation. The precipitate was collected, washed with methanol/water (3:2, *v*/*v*, 3 × 100 mL), recrystallized from methanol, and dried under vacuum to afford compound **1** as white crystals (4.1 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 6.86 (s, 4H, Ar*H*), 4.24 (t, *J* = 6.3 Hz, 4H, OCH_2), 3.61 (t, *J* = 6.3 Hz, 4H, BrCH_2).

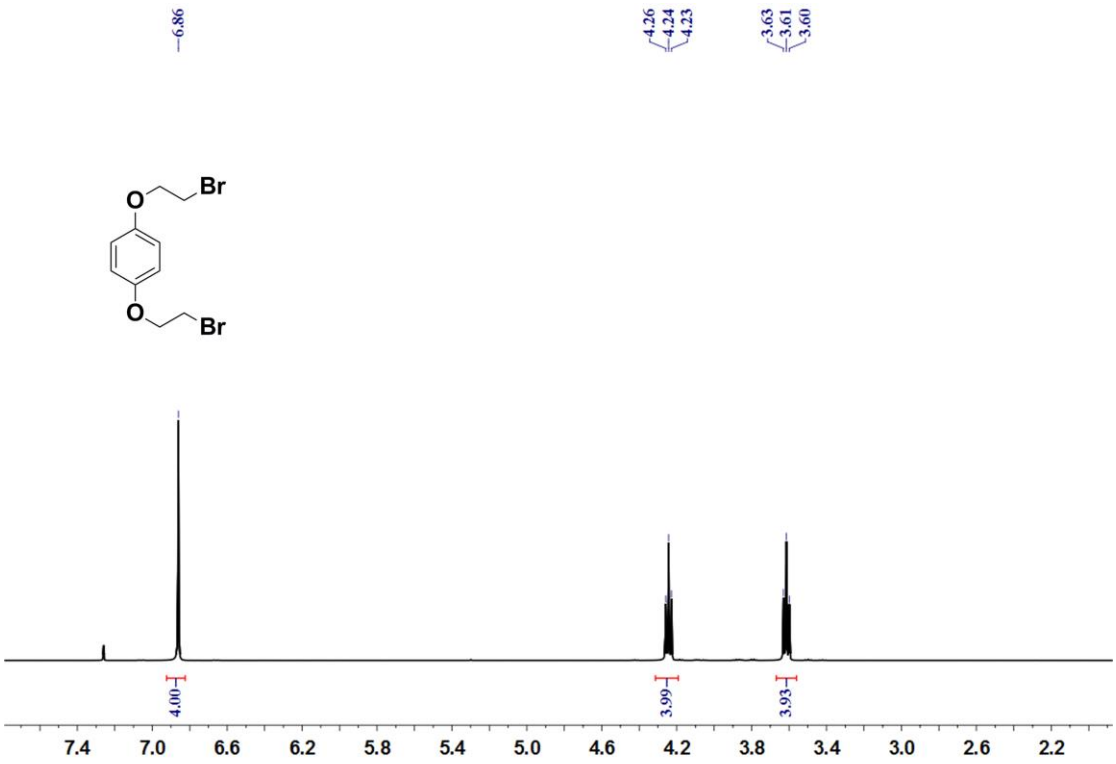


Fig. S1 ^{1}H NMR spectrum of **1** (400 MHz, $CDCl_3$, 298 K).

1-Methoxy-4-(prop-2-yn-1-yloxy)benzene **2**[S2]: K_2CO_3 (4.11 g, 30 mmol) and 3-bromoprop-1-yne (3.56 g, 30 mmol) were added to a solution of 4-methoxyphenol (1.24 g, 10 mmol) in acetone (100 mL). The resulting mixture was stirred at reflux temperature overnight and the reaction was stopped by filtration and evaporation under vacuum. And the crude product was purified by column chromatography over silica (dichloromethane/*n*-hexane = 1/1, *v/v*) to give the target product **2** as a yellow oil (2.25 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 6.93 (d, J = 9.2 Hz, 2H, Ar*H*), 6.84 (d, J = 9.2 Hz, 2H, Ar*H*), 4.63 (d, J = 2.4 Hz, 2H, OCH_2), 3.76 (s, 3H, OCH_3), 2.50 (t, J = 2.4 Hz, 1H, C≡C*H*).

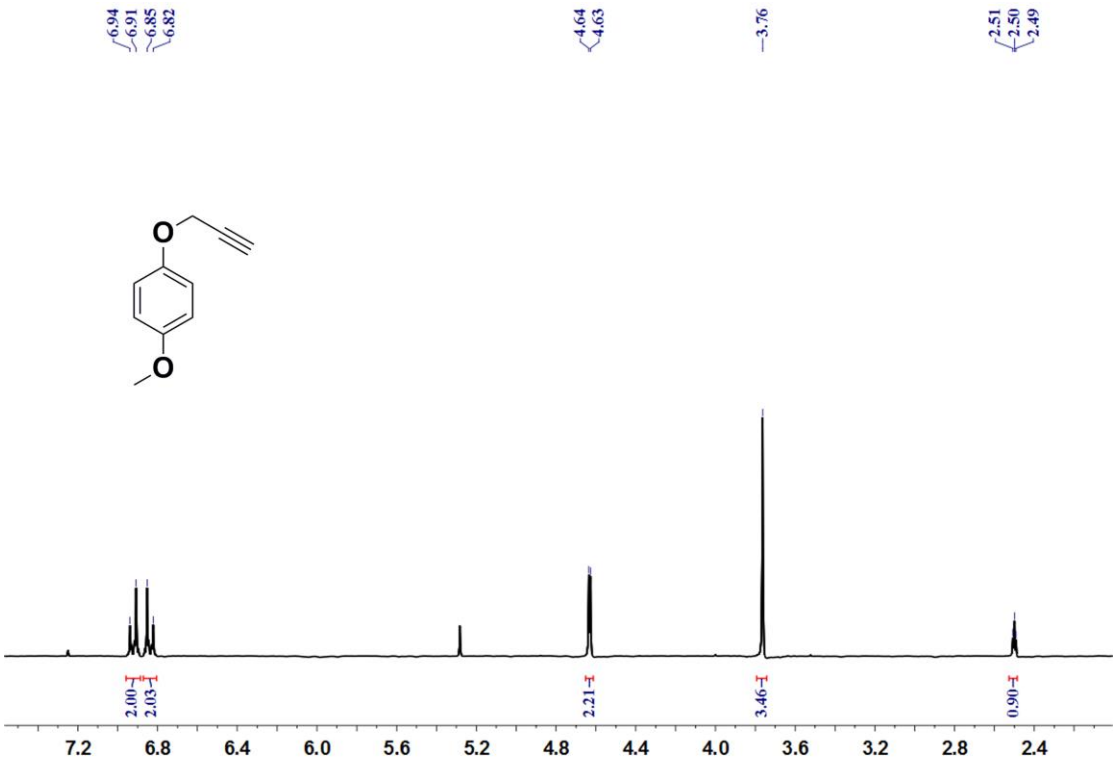


Fig. S2 ^{1}H NMR spectrum of **2** (300 MHz, $CDCl_3$, 298 K).

Pillar[5]arene **3**: Paraformaldehyde (1.08 g, 36 mmol) was added to a solution of **1** (3.84 g, 12 mmol) and **2** (0.12 g, 0.75 mmol) in dry CH_2Cl_2 (500 mL) under nitrogen atmosphere. Then, $FeCl_3$ (0.31 g, 1.92 mmol) was added to the solution and the mixture was stirred at 25 ^{o}C for 3 h. HCl solution (1 N, 100 mL) was then poured into the reaction mixture and the organic phase was collected and then washed with aqueous $NaHCO_3$ (2 × 200 mL) and brine (150 mL). The organic layer was dried over Na_2SO_4, concentrated under vacuum, and subjected to silica gel chromatography (dichloromethane/n-hexane = 1:1, *v/v*) to give compound **3** (0.25 g, 23%) as a white solid. M.p. 112−113 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 6.96−6.65 (m, 10H, Ar*H*), 4.53 (d, J = 2.3 Hz, 2H, OCH_2CCH), 4.28−4.08 (m, 16H, OCH_2), 3.90−3.76 (m, 13H, ArCH_2, OCH_3), 3.69−3.54 (m, 16H, BrCH_2), 2.08 (t, J = 2.3 Hz, 1H, C≡C*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ (ppm): 151.2, 149.7, 149.6, 148.7, 129.4, 129.2, 129.0, 128. 9, 128.7, 128.2, 116.1, 115.9, 115.8, 115.6, 115.5, 115.3, 114.1, 79.4, 74.9, 56.6, 56.1, 53.2, 30.7, 30.6, 30.5, 30.2, 29.7, 29.4, 29.2, 28.9. HR-ESI-MS: *m/z* Calcd. for $C_{55}H_{58}Br_8NaO_{10}^+$ $[M+Na]^+$ 1540.7308, found 1540.7323.

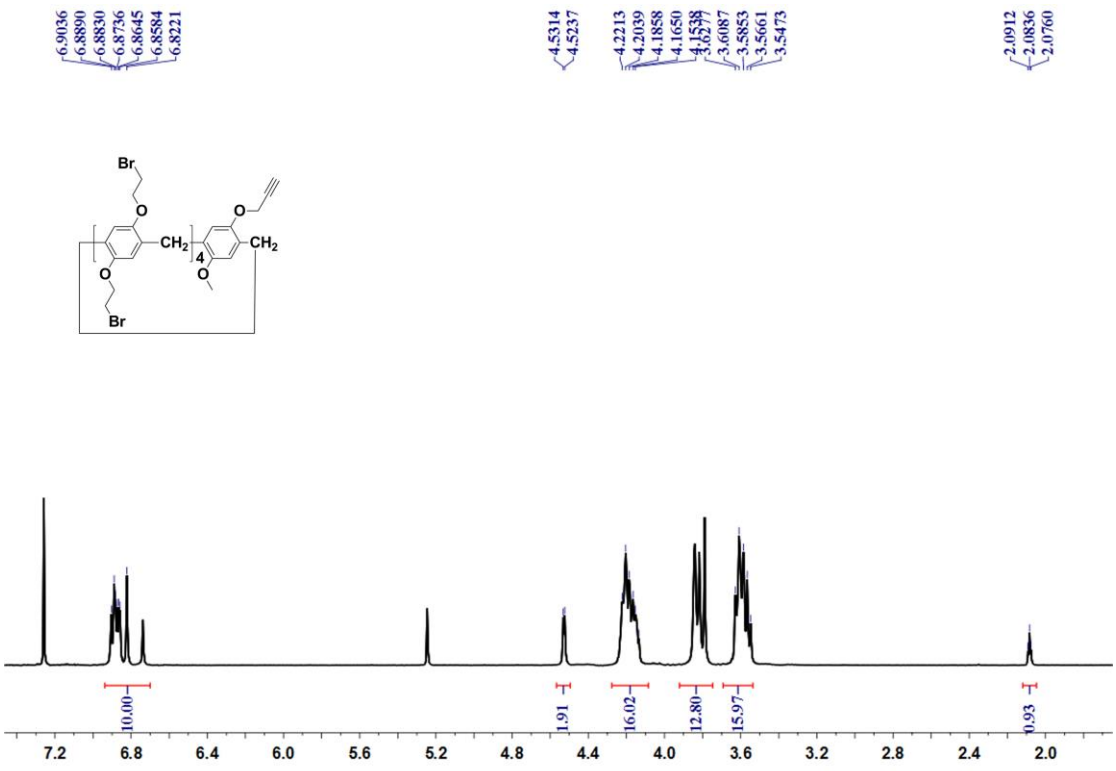


Fig. S3 ^{1}H NMR spectrum of **3** (300 MHz, $CDCl_3$, 298 K).

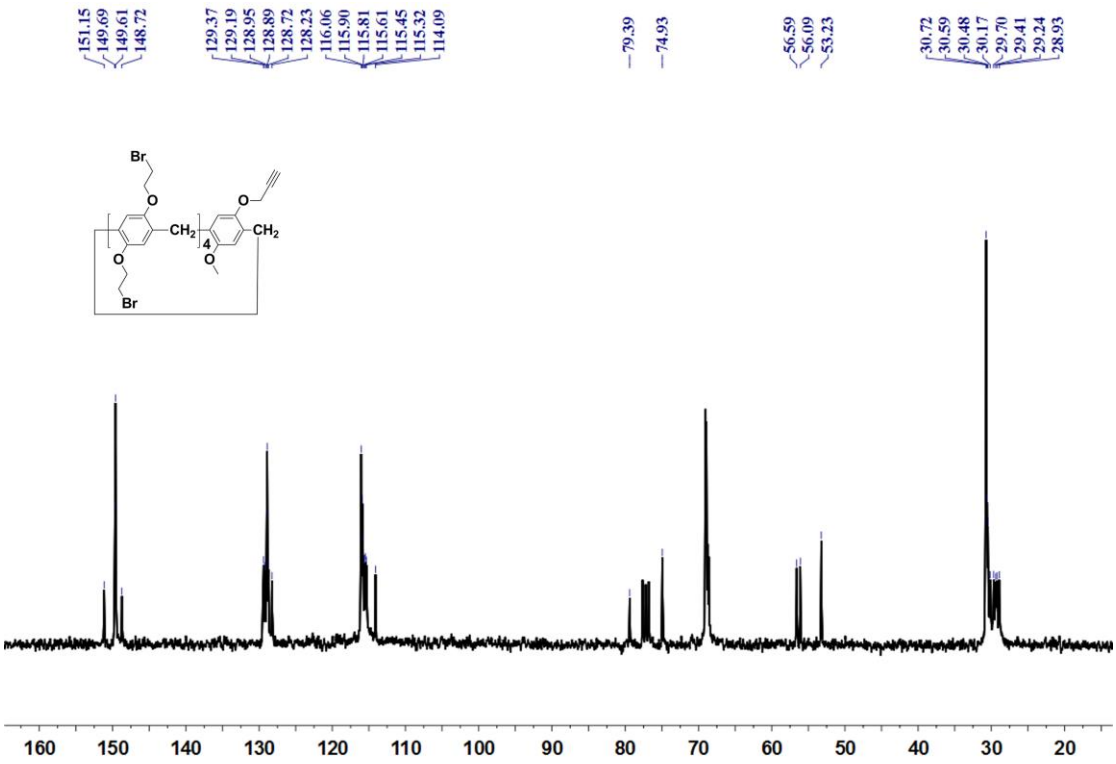


Fig. S4 ^{13}C NMR spectrum of **3** (75 MHz, $CDCl_3$, 298 K).

2-(2-(2-Hydroxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate **4**[S3]: Diethyleneglycol (4.50 g, 30 mmol) and triethylamine (TEA) (8.0 mL) were dissolved in dichloromethane (60 mL). Then,

tosyl-chloride (5.70 g, 30 mmol) was added in one portion. The resulting mixture was stirred for 1 h at 25 °C. After washing with $KHSO_4$ (1 M, 40 mL) and $NaHCO_3$ (5%, 40 mL) and drying over Na_2SO_4, the crude product was obtained by evaporation and subsequently purification by column chromatography over silica (dichloromethane/MeOH = 100:1, *v/v*) to obtain the target product **4** as a colorless oil (4.2 g, 48%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 7.78 (d, J = 7.7 Hz, 2H, Ar*H*), 7.33 (d, J = 7.7 Hz, 2H, Ar*H*), 4.20−4.09 (t, J = 4.8 Hz, 2H, OHCH_2), 3.74−3.64 (m, 4H, TsOCH_2, OCH_2), 3.62−3.49 (m, 6H, OCH_2), 2.43 (s, 3H, CH_3).

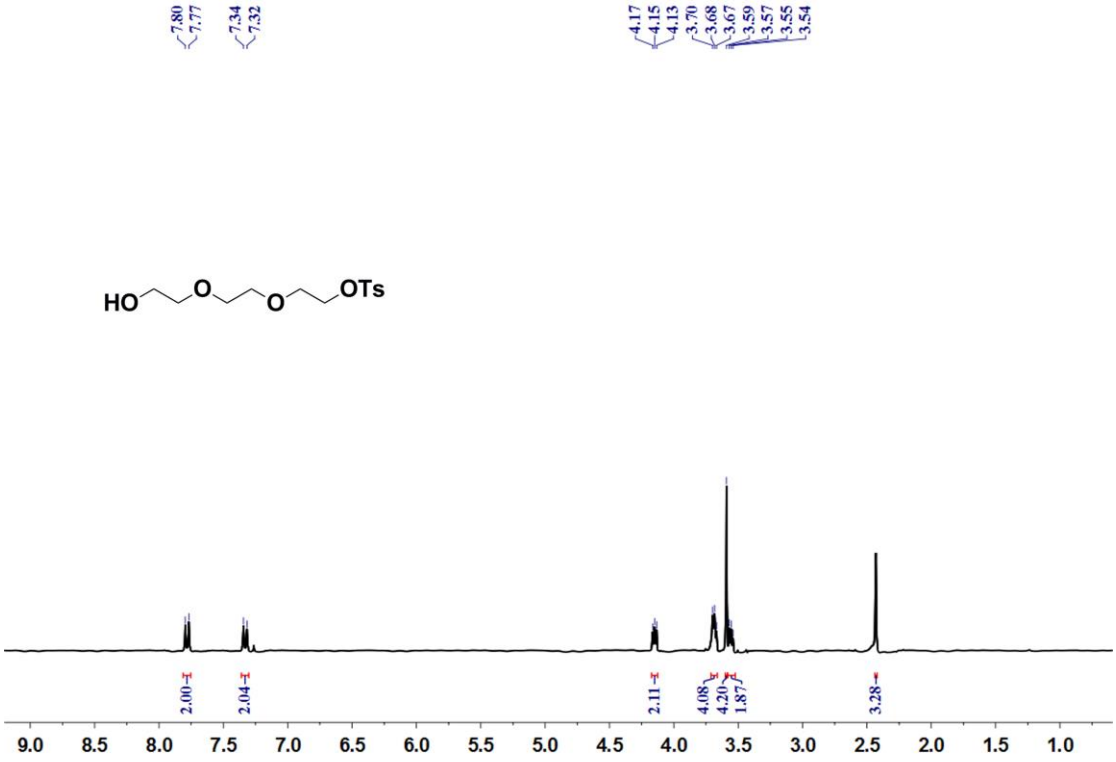


Fig. S5 ^{1}H NMR spectrum of **4** (300 MHz, $CDCl_3$, 298 K).

Azo tri(ethylene glycol) **5**[S4]: To a solution of compound **4** (7.00 g, 23 mmol) in dimethyl formide (85 mL), NaN_3 (2.5 g, 38.5 mmol) was added. The reaction suspension was heated to 50 °C in an oil bath and stirred for 17 h. Then, water (50 mL) was added and the reaction mixture was cooled to room temperature. The product was then extracted using dichloromethane (3 × 80 mL), which was then washed with water (3 × 55 mL) and dried over anhydrous Na_2SO_4. After removing the solvent, the target product **5** was obtained as a light yellow oil (4.0 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 3.75 (t, J = 3.9 Hz, 2H, OHCH_2), 3.71−3.65 (m, 6H, OCH_2), 3.64−3.60 (m, 2H, OCH_2), 3.41 (t, J = 5.0 Hz, 2H, N_3CH_2).

Fig. S6. ^{1}H NMR spectrum of **5** (300 MHz, $CDCl_3$, 298 K).

Biotin-PEG-N_3 ester **6**[S4]: In a 50 mL round bottom flask, D (+)-Biotin (0.12 g, 0.5 mmol) was added under argon in DMF (2 mL) and the suspension was heated to 80 ^{o}C until the biotin was dissolved. Then, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCCl) (0.11 g, 0.6 mmol), 4-dimethylaminopyridine (DMAP) (0.012 g, 0.01 mmol), and compound **4** (0.10 g, 0.6 mmol) in dry $CHCl_3$ (10 mL) were added, and the mixture was stirred at 60 ^{o}C for 24 h. Subsequently, the solvents were evaporated under reduced pressure and the residue was resuspended with saturated aqueous $NaHCO_3$ and extracted with $CHCl_3$ (2 × 5 mL). The organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (dichloromethane/methanol = 50:1, *v*/*v*), and compound **6** was obtained as a colorless oil (0.12 g, 60%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ (ppm): 5.66 (s, 1H, N*H*), 4.58−4.43 (m, 1H, NHC*H*), 4.38−4.28 (m, 1H, NHC*H*), 4.24 (dd, *J* = 5.2, 2.7 Hz, 2H, OCH_2), 3.75−3.62 (m, 8H, OCH_2), 3.40 (t, *J* = 5.0 Hz, 2H, N_3CH_2), 3.16 (dd, *J* = 11.3, 6.9 Hz, 1H, SC*H*), 2.92 (dd, *J* = 12.8, 4.7 Hz, 1H, SC*H*), 2.75 (d, *J* = 12.8 Hz, 1H, SC*H*), 2.38 (t, *J* = 7.4 Hz, 2H, COCH_2), 1.80−1.58 (m, 4H, CH_2), 1.53−1.38 (m, 2H, CH_2).

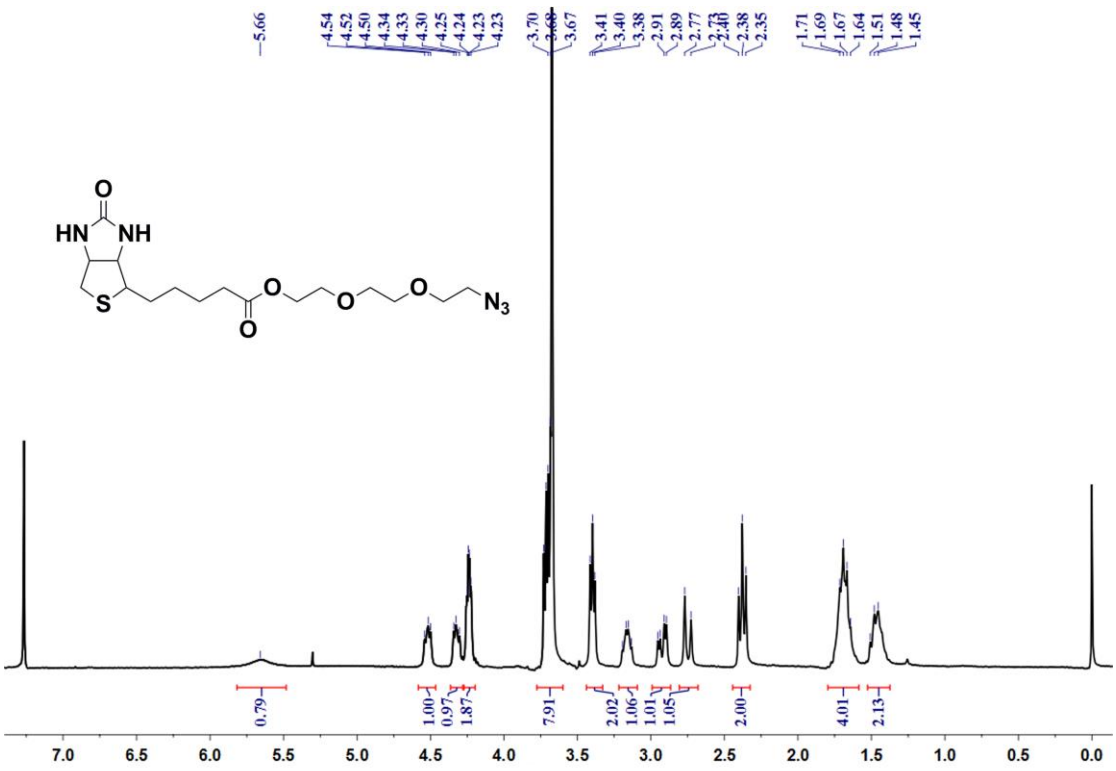


Fig. S7 ^{1}H NMR spectrum of **6** (300 MHz, $CDCl_3$, 298 K).

Biotin-PEG-P5 **P1**: Tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amine (TBTA) (0.005 g, 0.01 mmol) and $[Cu(CH_3CN)_4]PF_6$ (0.004 g, 0.01 mmol) were added to a solution of **6** (0.06 g, 0.15 mmol) and **3** (0.15 g, 0.1 mmol) in chloroform (300 mL) under argon atmosphere, and the mixture was stirred at 25 ^{o}C for 12 h. The resulting solution was concentrated in vacuo. The crude product was purified by column chromatography (dichloromethane/methanol = 50:1, *v*/*v*) to afford the target molecule **P1** as a while solid (0.110 g, 54%). M.p. 150−152 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ (ppm): 8.21 (s, 1H, C=C*H*), 7.16−6.75 (m, 10H, Ar*H*), 6.41 (s, 1H, N*H*), 6.36 (s, 1H, N*H*), 5.06 (s, 2H, NCH_2), 4.58 (s, 2H, OCH_2), 4.41−3.39 (m, 57H, CH_2, CH_3 and C*H*), 3.07 (s, 1H, SC*H*), 2.82 (dd, *J* = 12.4, 5.1 Hz, 1H, SC*H*), 2.57 (d, *J* = 12.4 Hz, 1H, SC*H*), 2.27 (s, 2H, COCH_2), 1.69−1.25 (m, 6H, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K) δ (ppm): 173.3, 163.2, 150.6, 149.5, 149.4, 149.3, 149.1, 142.5, 129.2, 129.0, 128.7, 128.5, 128.1, 125.0, 115.9, 115.6, 115.6, 115.3, 115.0, 70.1, 69.2, 69.0, 68.6, 63.5, 62.3, 61.5, 59.7, 55.8, 49.9, 33.7, 32.7, 29.2, 28.8, 28.4, 24.9. HR-ESI-MS: *m/z* Calcd. for $C_{71}H_{85}Br_8N_5NaO_{15}S^+$ $[M+Na]^+$ 1941.9041, found 1941.9035.

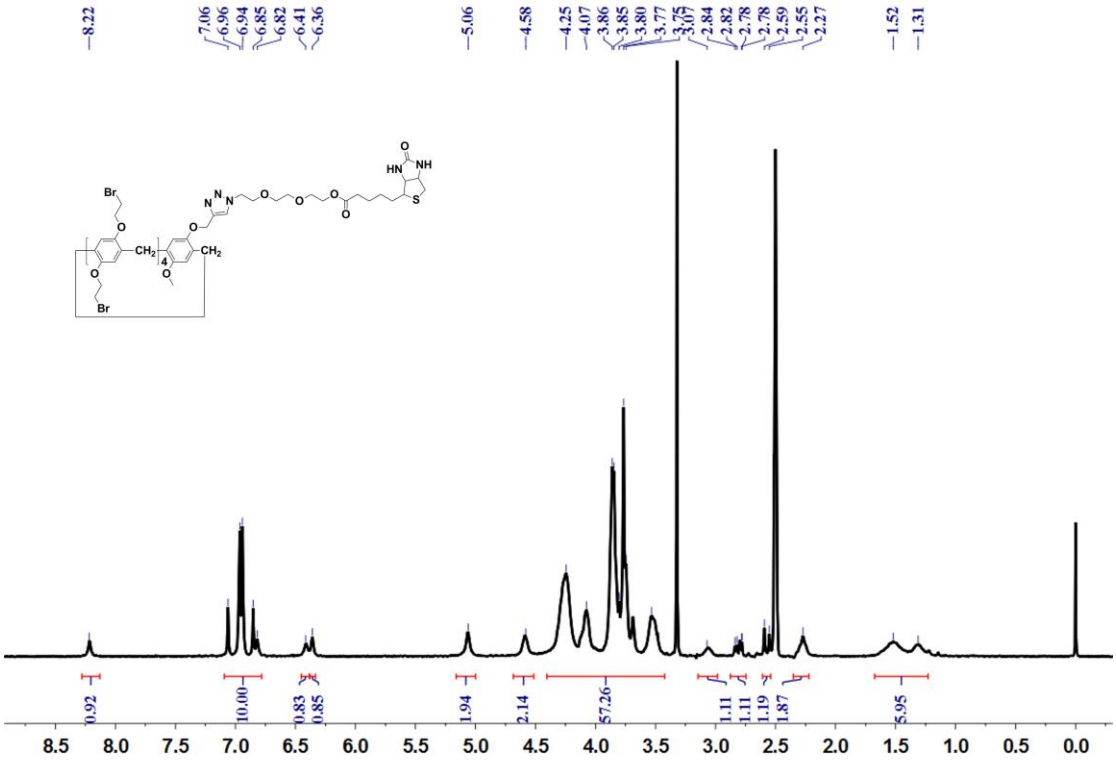


Fig. S8 ^{1}H NMR spectrum of **P1** (300 MHz, DMSO-d_6, 298 K).

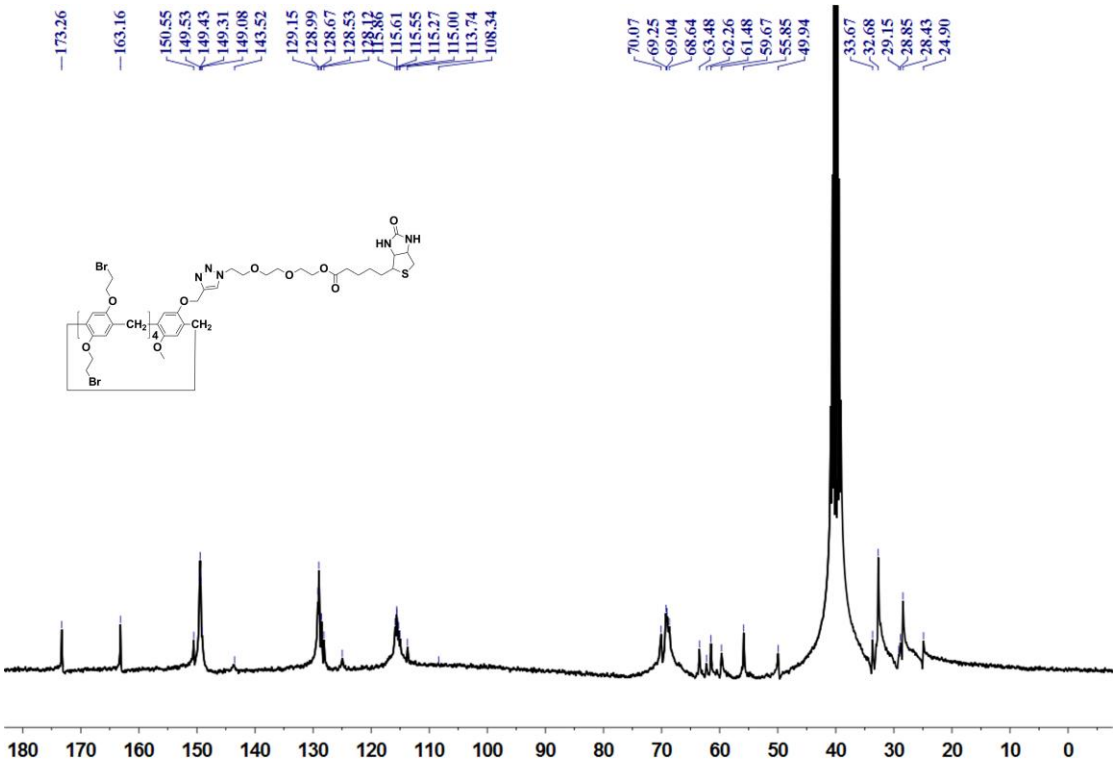
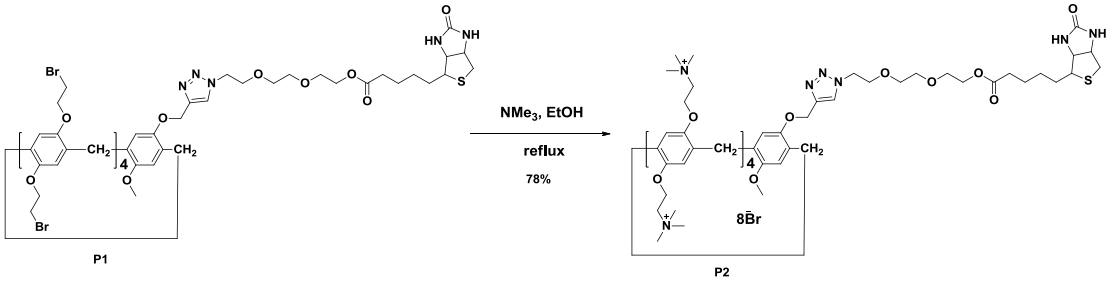


Fig. S9 ^{13}C NMR spectrum of **P1** (75 MHz, DMSO-d_6, 298 K).



Scheme 2. The synthesis rout of **P2**

Compound **P1** (0.071 g, 0.035 mmol) was dissolved in ethanol (15.0 mL), and trimethylamine (33.0% in ethanol, 4.5 mL, 16.7 mmol) were added to the above solution. The mixture was refluxed for 12 h. After removing the solvent, methanol (0.5 mL) was added to redissolve the solid. Then, the solution was added dropwise into Et_2O (100 mL) to generate a white precipitate, after filtration the target product **P1** was obtain as a white solid (0.060 g, 78%). M.p. 252−254 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6, 298 K) δ (ppm): 8.32 (s, 1H, C=C*H*), 7.17−6.64 (m, 10H, Ar*H*), 5.20−4.98 (m, 2H, OCH_2), 4.74−3.44 (m, 61H, CH_2, CH_3 and C*H*), 3.34−3.02 (m, 73H, CH_3 and SC*H*), 2.84−2.72 (m, 1H, SC*H*), 2.61−2.52 (m, 1H, SC*H*), 1.68−1.78 (m, 6H, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K) δ (ppm): 73.4, 163.2, 150.7, 149.6, 149.3, 149.1, 143.7, 129.2, 128.8, 128.6, 127.9, 125.4, 116.5, 116.1, 115.9, 115.44, 115.40, 70.0, 69.2, 68.8, 65.0, 63.5, 63.1, 61.5, 59.7, 56.9, 56.4, 55.9, 54.5, 53.6, 52.7, 50.0, 33.7, 29.2, 29.0, 28.5, 25.0. HR-ESI-MS: *m/z* Calcd. For $C_{95}H_{157}Br_6N_{13}O_{15}S^{2+}$ $[M-2Br]^{2+}$ 1116.3352, found 1116.3352; $C_{95}H_{157}Br_5N_{13}O_{15}S^{3+}$ $[M-3Br]^{3+}$ 717.2512, found 717.2518; $C_{95}H_{157}Br_4N_{13}O_{15}S^{4+}$ $[M-4Br]^{4+}$ 518.2087, found 518.2093; $C_{95}H_{157}Br_3N_{13}O_{15}S^{5+}$ $[M-5Br]^{5+}$ 398.3836, found 398.3840.

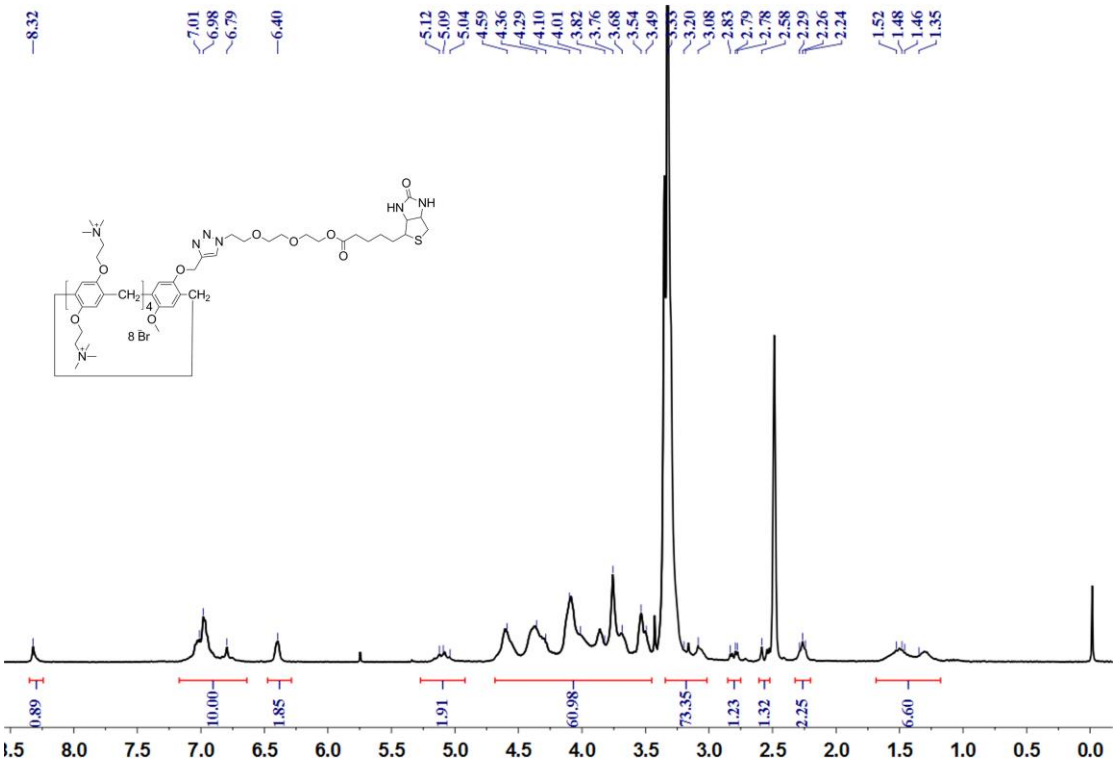


Fig. S10 ^{1}H NMR spectrum of **P2** (300 MHz, DMSO-d_6, 298 K).

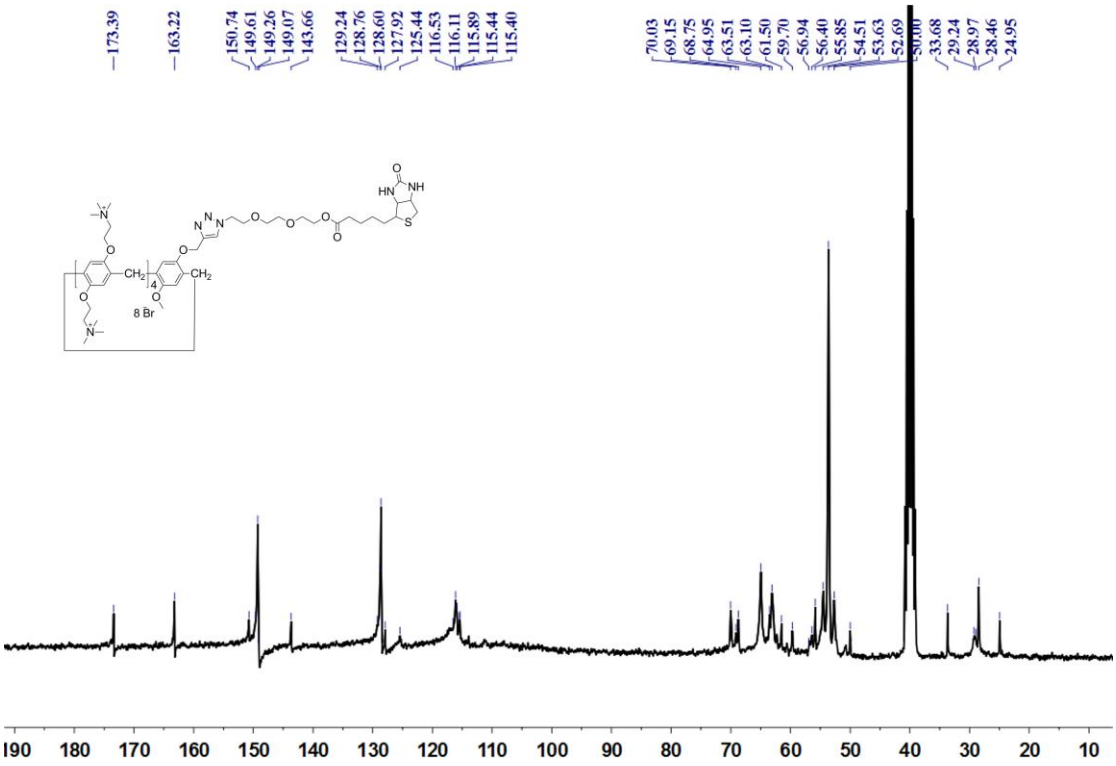


Fig. S11 ^{13}C NMR spectrum of **P2** (75 MHz, DMSO-d_6, 298 K).

3. Host-guest study between compounds 3 and 6

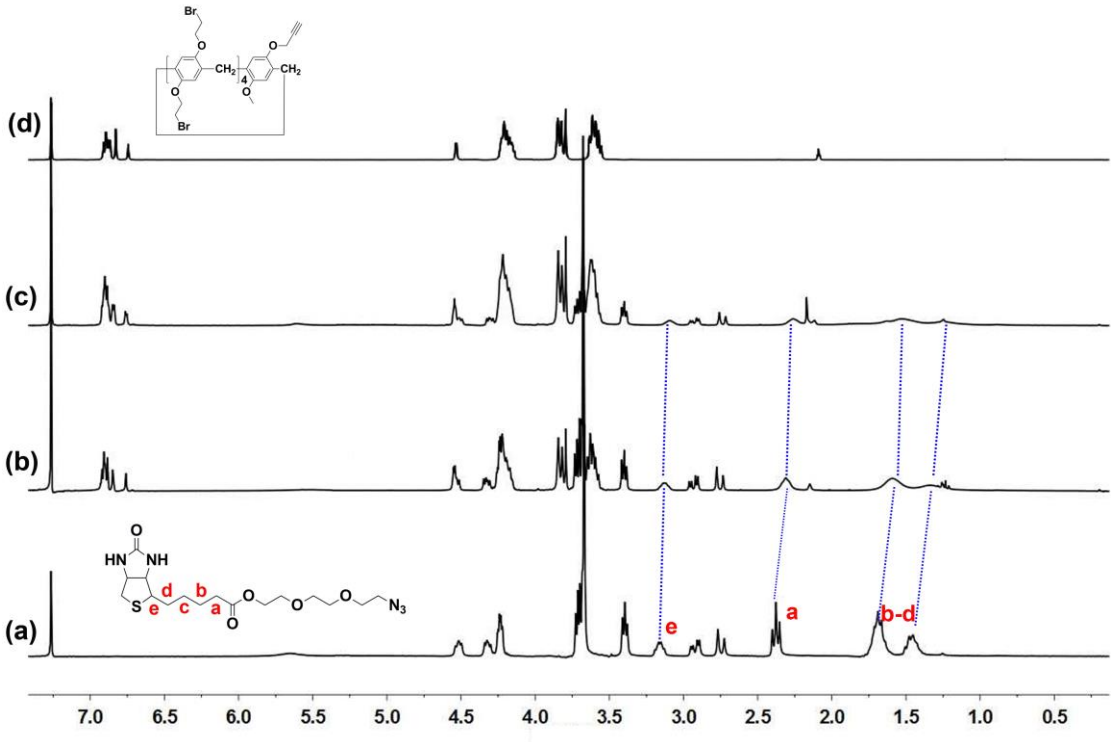


Fig. S12 ^{1}H NMR spectra (300 MHz, $CDCl_3$, 298 K) of (a) **6** (10 mM), (b) **6** (10 mM) + **3** (5 mM), (c) **6** (10 mM) + **3** (10 mM), and (d) **3** (10 mM).

4. DOSY experiments of pseudo[1]rotaxane P1'

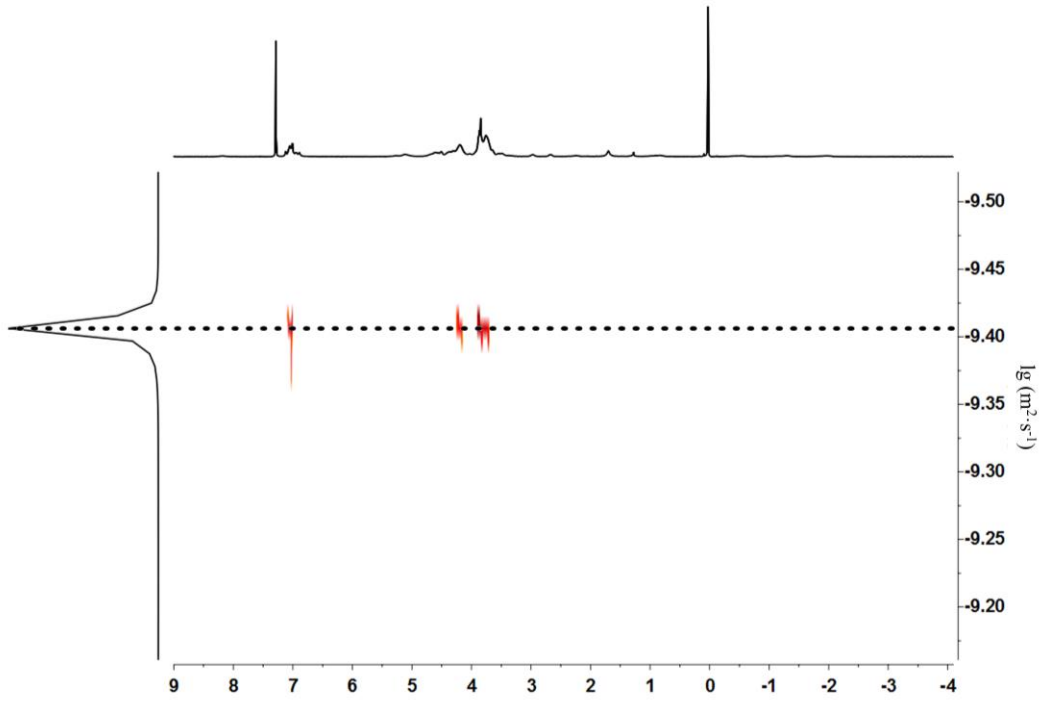


Fig. S13 DOSY spectrum (400 MHz, $CDCl_3$, 291 K) of the pseudo[1]rotaxane **P1'** at a concentration of 10 mM. Notice that only one set of signals of **P1'** could be observed from the DOSY spectrum (D = 3.92 $\times 10^{-10}$ m^2 s^{-1}).

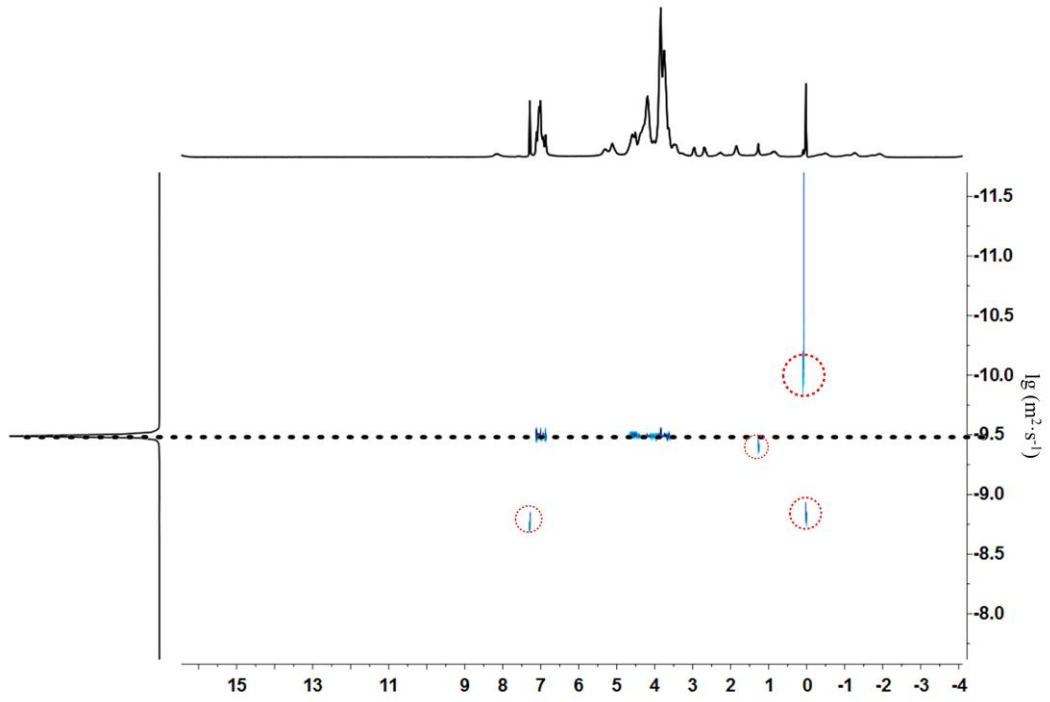


Fig. S14 DOSY spectrum (400 MHz, $CDCl_3$, 291 K) of the pseudo[1]rotaxane **P1'** at a concentration of 45 mM. Notice that only one set of signals of **P1'** could be observed from the DOSY spectrum (D = 3.20 $\times 10^{-10}$ m^2 s^{-1}). (The red cycles indicate the solvent residue).

Considering the fact that the viscosity of the solution increased with the rising of solution concentration, the diffusion coefficient of **P1'** did not change much as the concentration increased from 10 mM to 45 mM, which was in agreement with the results of variable concentration ^{1}H NMR spectra (Fig. 2).

The hydrodynamic radius of pseudo[1]rotaxane **P1'** in $CDCl_3$ was calculated by the Stokes-Einstein relation (Equation 1).

$$r = \frac{kT}{6\pi\eta D} \qquad \text{Equation 1}$$

Where D is the diffusion coefficient (obtained from Fig. S13), k is the Boltzmann constant (1.3807×10^{-23} m^2 kg s^{-2} K^{-1}), T is the temperature in Kelvin (291 K), η is the viscosity of the solution (chloroform 5.37×10^{-4} kg m^{-1} s^{-1}), and r is the radius of the molecular sphere. The calculated results were listed in Table S1.

Table S1. The hydrodynamic radius of the pseudo[1]rotaxane **P1'** calculated from the DOSY experiments.

Sample	P1
lg D (lg m^2 s^{-1})	−9.406
D (10^{-10} m^2 s^{-1})	3.92
r (Å)	9.98

5. Theoretical calculation of the self-inclusion structure of P1'.

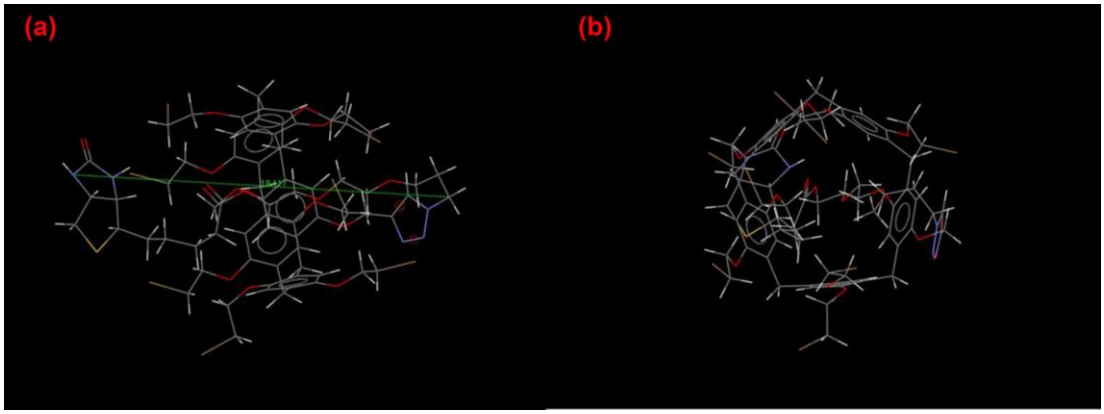


Fig. S15 Geometry optimized structure of **P1'** (Gaussian 09, PM3), (a) side view, (b) top view. From the optimized structure, the diameter of **P1'** was 18.12 Å (r = 9.06 Å).

6. Reference

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