Electronic Supplementary Material (ESI) for ChemComm.
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SUPPORTING INFORMATION

Polymeric Catenanes by "Click" Chemistry and Atom Transfer Radical Coupling

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Experimental

Materials

All chemicals were purchased from Aldrich Chemical Company and were used directly without further purification unless otherwise indicated. All solvents were degassed with nitrogen gas before use.

Instrumentation

^{1}H NMR spectra were recorded on a JEOL ECS 500 spectrometer (500MHz). GPC was carried out on a Viscotek 270 instrument with a triple detector array (RALS, IV, RI) equipped with 2 GMHHR-M and 1 GMHHR-L mixed bed ViscoGel columns (eluent: THF; flow rate: 1 mL min^{-1}). UV-vis measurements were taken on an Agilent technologies 8453 spectrometer. The FTIR spectra were obtained on a Digilab FTS 7000 equipped with a HgCdTe detector from 4000 to 600 (cm^{-1}) wavenumbers. All atomic force microscopy (AFM) images were recorded in air under ambient conditions on PicoScan 2500 (Agilent Technologies formerly Molecular Imaging, Corp.) equipped with a 10 × 10 μm scanner. The AFM tip used was a silicon-nitride AFM probe from Ted Pella Inc.

Synthesis of 2,9-bis(4-(2-azidoethoxy)phenyl))-1,10-phenanthroline 1 (Ligand-N_3)

The solution of 2,9-bis(4-(hydroxy)phenyl))-1,10-phenanthroline[1] (0.21 g, 0.50 mmol) and 2-azidoethyl 4-methylbenzenesulfonate[2] (0.22 g, 0.75 mmol) in DMF (15 mL) was added to K_2CO_3 (0.21 g, 1.5 mmol) and the suspension was heated to 80 °C for 18 h. After cooling to room temperature, the reaction mixture was poured into mixture of ethyl acetate: water (50 mL). The aqueous layer was extracted with ethyl acetate (3 × 50 mL), and the combined organic fractions were washed with brine (50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting crude oil was then purified by precipitating from hexane to yield **1** as a pale yellow solid (0.2 g, yield 74%). ^{1}H NMR ($CDCl_3$): 8.43 (m, 4H, H_o), 8.25 (d, 2H, $H_{4,7}$), 8.08 (d, 2H, $H_{3,8}$), 7.74 (s, 2H, $H_{5,6}$), 7.14 (m, 4H, H_m), 4.26 (t, 4H, $-CH_2-N_3$), 3.66 (t, 4H, $-PhOCH_2$).

Synthesis of Ligand-N_3 Cu(I) complex 2

By the double-ended needle transfer technique, 3 mg (0.60 mmol) of $Cu(CH_3CN)_4PF_6$ in 3 mL degassed CH_3CN was transferred under nitrogen at room temperature to a stirred degassed solution of **1** (10 mg, 3.0 mmol) in 3 mL DCM. The mixture turned dark red instantaneously, indicating the formation of **2**. After the solution was stirred for 1 h under nitrogen at room temperature, the solvents were evaporated to dryness to obtain dark red solid of crude **2** in quantitative yield (12 mg, 1.5 mmol). Complex **2** was used without further purification.

Synthesis of alkyne-PS 3

A mixture of styrene (16.0 mL, 139.2 mmol), anisole (1.60 mL) and PMDETA (600 µL, 2.89 mmol) was deoxygenated in a dry Schlenk flask by performing four freeze–pump–thaw cycles. The contents were frozen again and Cu(I)Br (207.5 mg, 1.44 mmol) was added. The freeze–pump–thaw cycle was repeated two more times, after which the mixture was allowed to melt. The Schlenk flask was immersed in an oil bath at a preset temperature of 90 ^oC. Prop-2-ynyl 2-bromo-2-methylpropanoate9 (800 mg, 2.89 mmol) initiator was added using a N_2 purged syringe. The polymerization was stopped after 2 h. The mixture was then diluted with THF and passed through a neutral alumina column to remove the catalyst. The polymer was precipitated in methanol. The ^{1}H NMR spectrum of purified alkyne-PS (**3**) was shown in Figure S3.

Synthesis of PS Cu(I)-complex 4 *via* click coupling reaction

Ligand-N_3 Cu(I) complex **2** (10 mg, 0.12 mmol), alkyne functionalized PS **3** (75.0 mg, 0.9 mmol), PMDETA (3.24 mg, 0.9 mmol) and 3 mL DMF were added to a Schlenk flask. The solution was purged with nitrogen and degassed by performing four freeze–pump–thaw cycles and then Cu(I)Br (1.49 mg, 0.9 mmol) was added. The resulting homogeneous reddish brown solution was stirred at room temperature for 24 h. After passing the solution through alumina, the PS Cu(I)-complex **4** was precipitated from methanol. The excess alkyne-PS was removed by graduated precipitation method. Generally, the polymer mixture was dissolved in toluene and methanol was added dropwise. The PS Cu(I)-complex (**4**) tend to precipitate out before the alkyne-PS due to the much higher molecular weight. GPC analysis of the collected precipitate was performed time by time, and only the precipitates without alkyne-PS was utilized for the next step.

Synthesis of PS catenane 5 via ATRC

ATRC was performed as per literature procedure[3]: A 500 mL Schlenk flask containing a 100 mL THF solution of Cu(I)Br (574 mg, 4.0 mmol) and nanosized copper (254 mg, 4.0 mmol) was sealed with a rubber septum, evacuated with four freeze-pump-thaw cycles, backfilled with N_2, and sealed from the Schlenk line. The flask was then placed in an oil bath and stirred at 75 ^{o}C. After allowing the metal solution to reach the temperature of the bath, Me_6TREN (1.07 mL, 4.0 mmol) was introduced *via* a nitrogen flushed syringe. A syringe pump held a 50 mL syringe containing an 18 mL THF solution of PS Cu(I) complex **4** (10 mg), which had separately been subjected to three freeze-pump-thaw cycles and backfilled with N_2. The solution of PS Cu(I) complex **4** was slowly dripped through a needle piercing the rubber septum into the stirring THF solution of the metal ligand, over approximately 24 h (approximate rate = 0.75 mL/h). After the contents of the syringe had been added to the reaction mixture, the reaction mixture was stirred for an additional 1 h. The resulting polymer catenane **5** was passed through an alumina column and precipitated into cold methanol.

Synthesis of PS catenane 6

Demetallation of PS catenane **5** was performed as following procedure. KCN (100 mg, 1.53 mmol) dissolved in water (2 mL) was added to PS catenane **5** (3.5 mg, 0.88 μmol) in 6 mL mixture of THF: methanol (3:1) and stirred for 24 h at room temperature. After stirring, the solvent was evaporated under vacuum, and the resulting polymer was extracted twice by DCM: water mixture. The DCM layer containing the polymers were mixed together and dried over anhydrous Na_2SO_4 which upon evaporation under vacuum, yields PS catenane **6.**

Supplementary Figures:

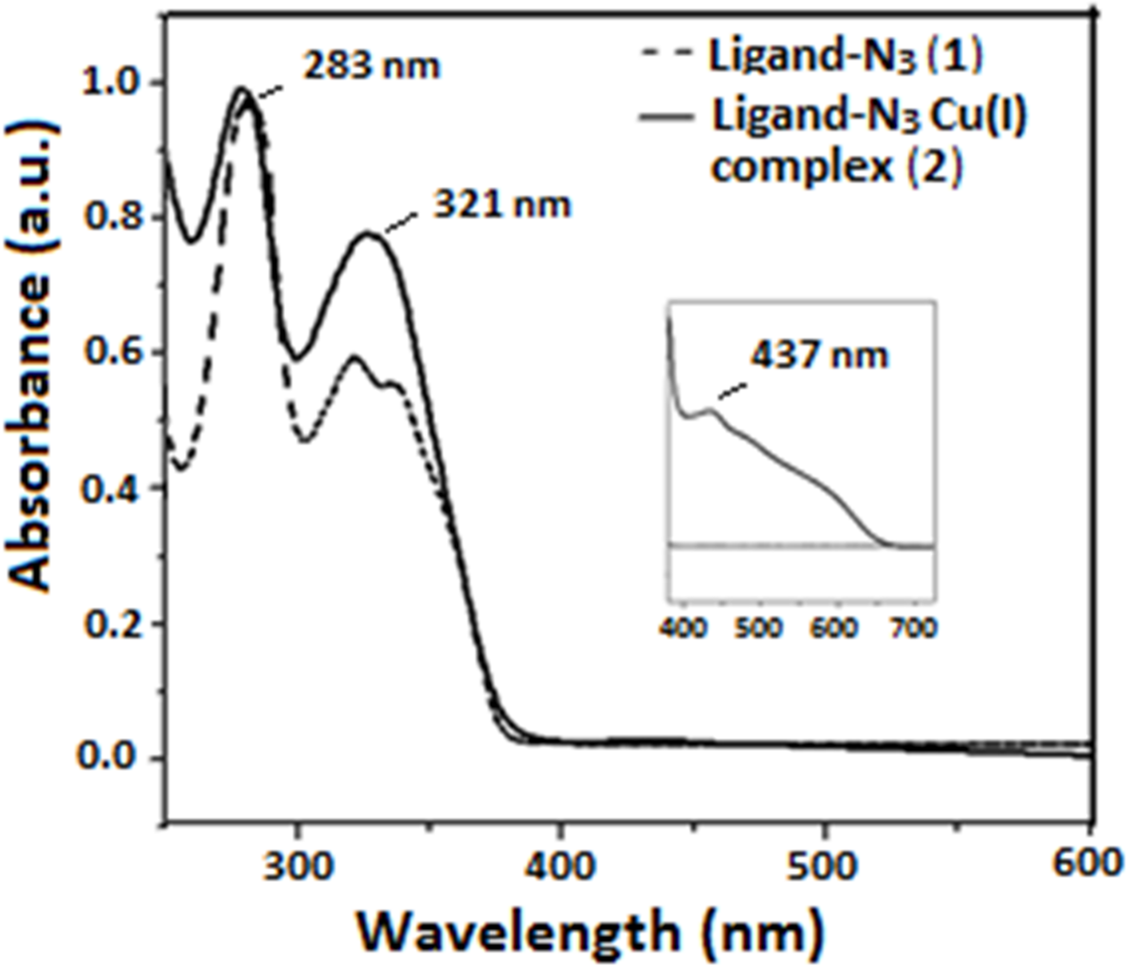


Figure S1. UV-Vis spectra of (a) Ligand-N_3 (**1**) and Ligand-N_3 Cu(I) complex (**2**) (inset: visible region of the Ligand-N_3 Cu(I) -complex (**2**) spectrum)

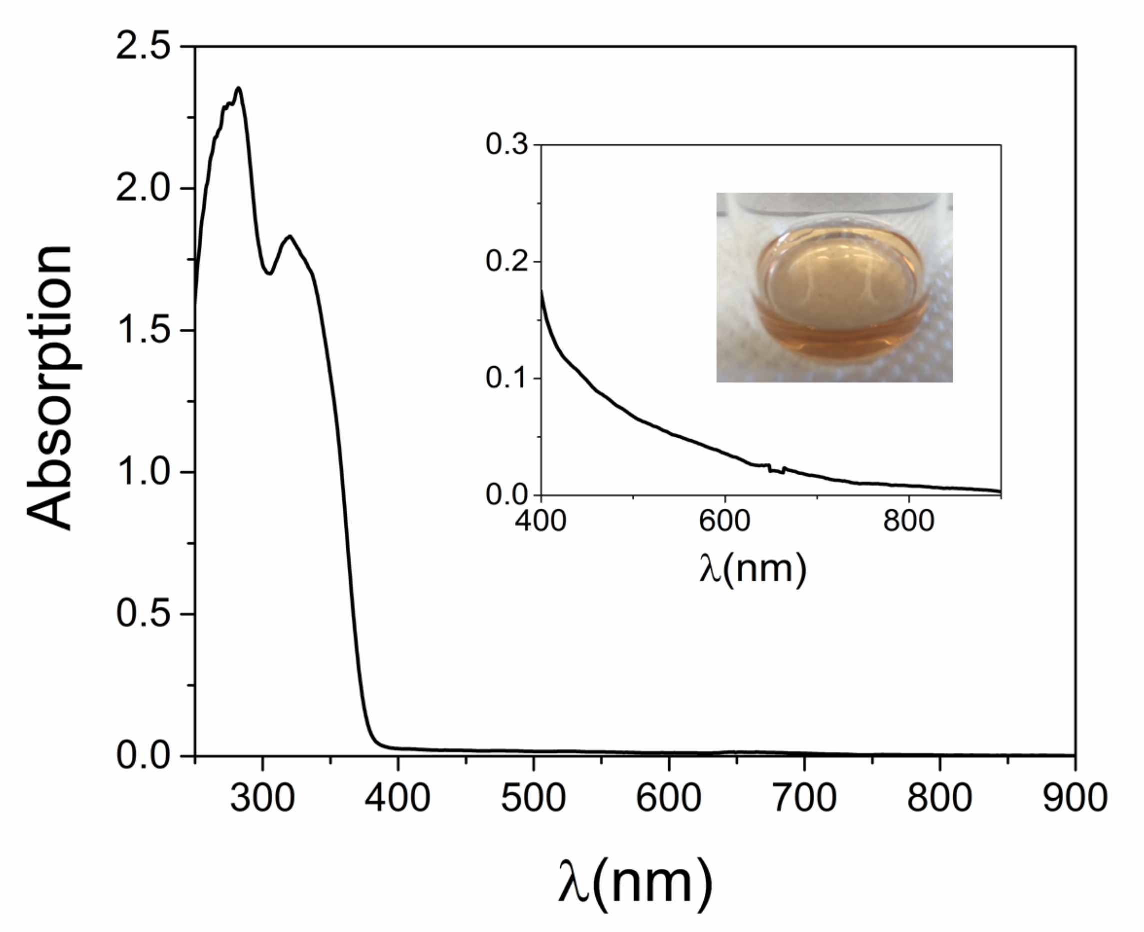


Figure S2. UV-Vis spectrum of PS-Cu(I) complex (**4**) (inset: the spectrum in the visible region with higher concentration of complex **4** and the photograph of the THF solution of complex **4**)

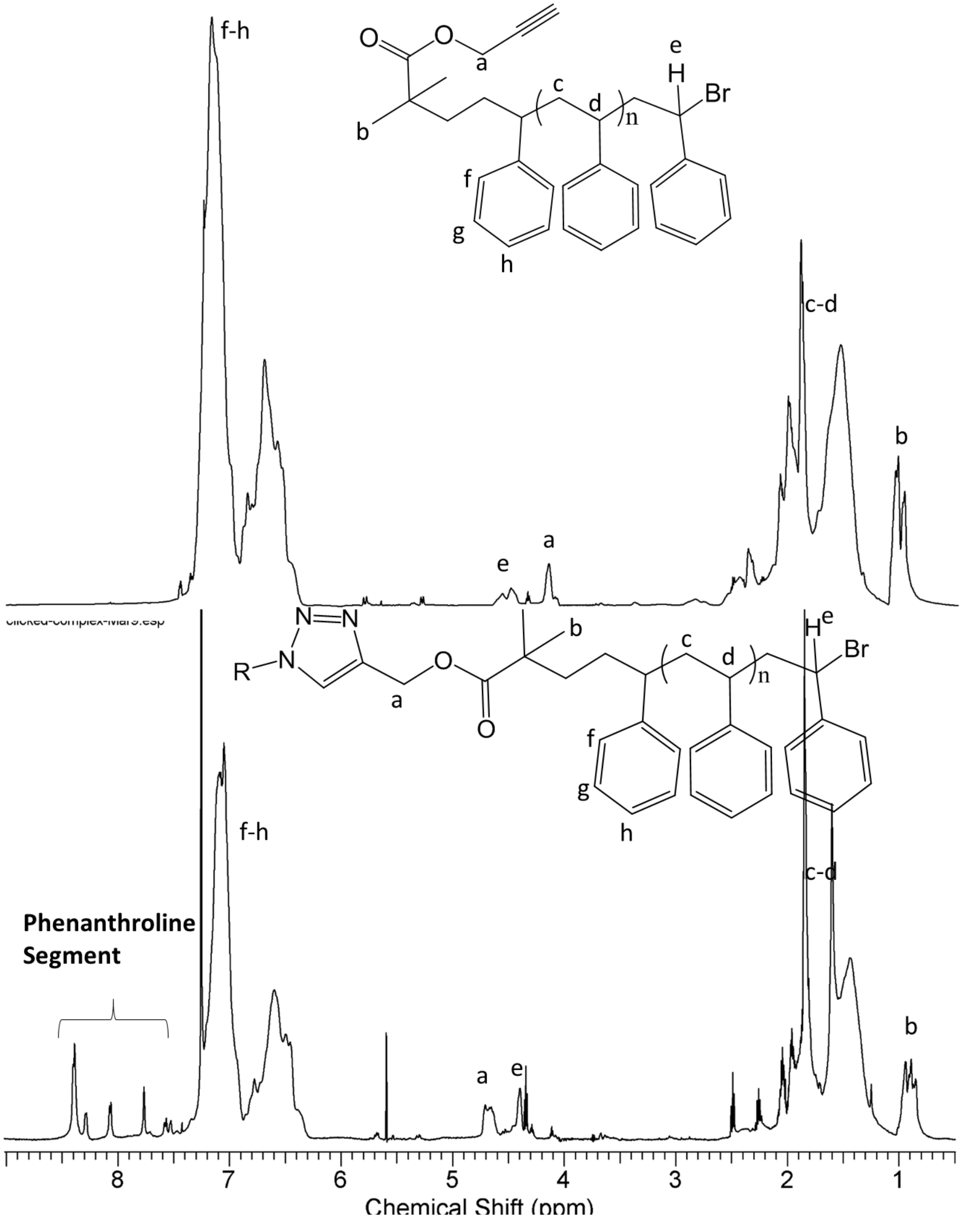


Figure S3. ^{1}H NMR spectrum of a) PS-alkyne **3** (top) and b) PS Cu(I)-complex **4** (bottom)

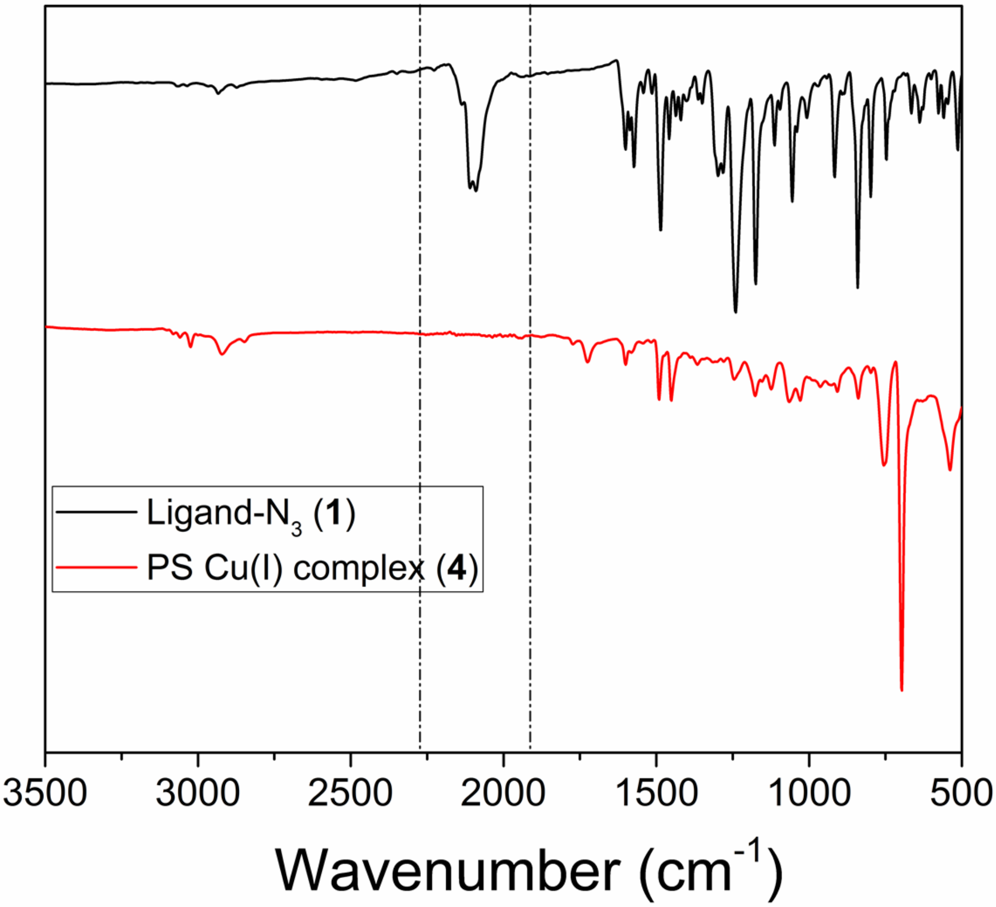
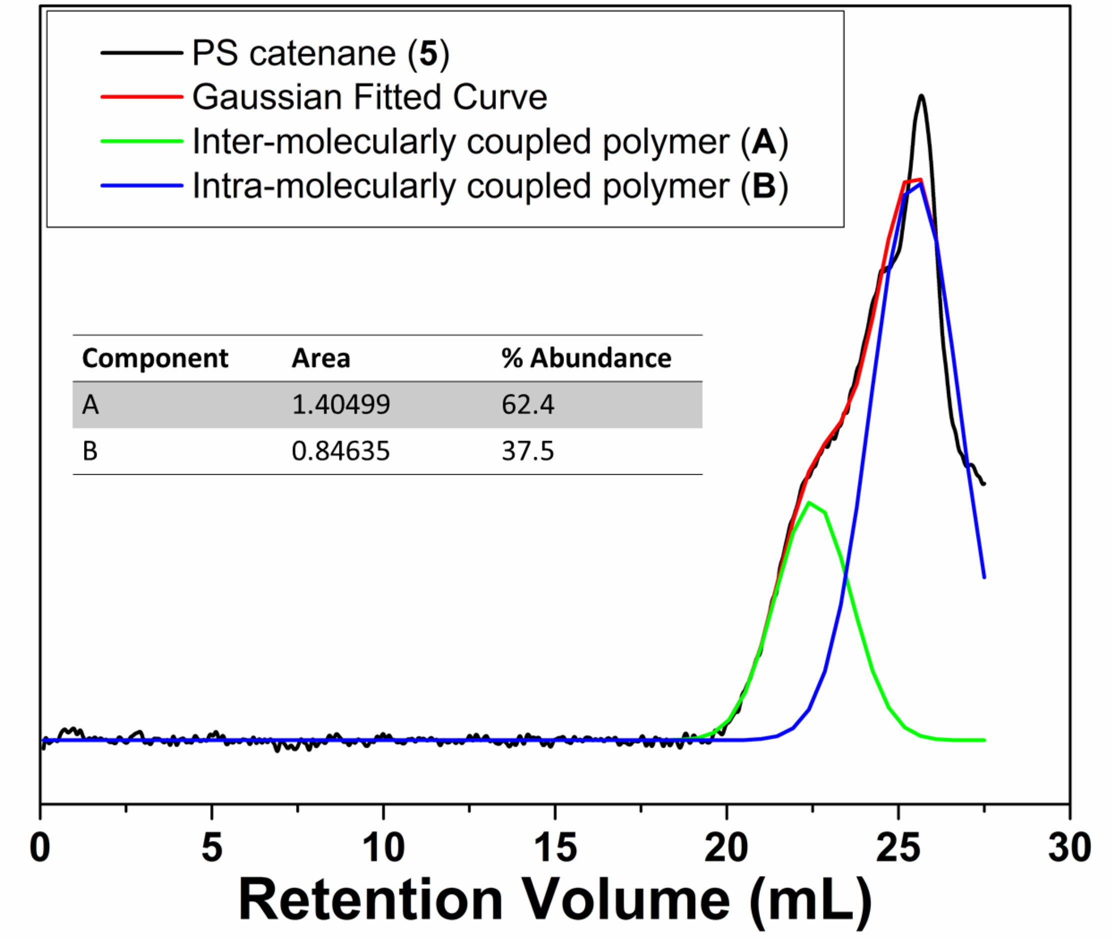
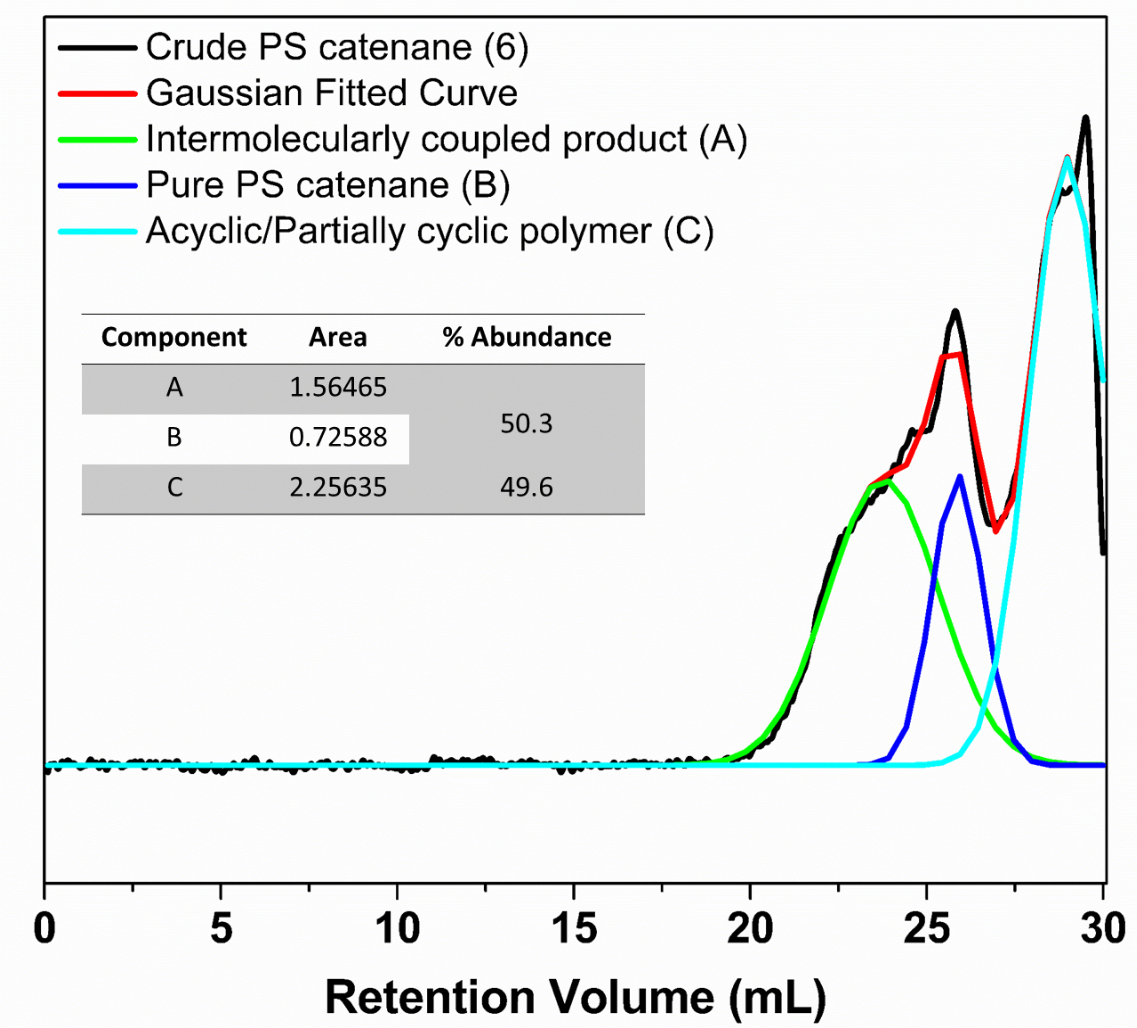


Figure S4. Comparative FT-IR spectrum of a) Ligand-N_3 **1** and b) PS-Cu(I) complex **4**



Component	Area	% Abundance
A	1.40499	62.4
B	0.84635	37.5

Figure S5. GPC traces of PS catenane **5** (ATRC product)



Component	Area	% Abundance
A	1.56465	50.3
B	0.72588	
C	2.25635	49.6

Figure S6. GPC traces of crude PS catenane **6**

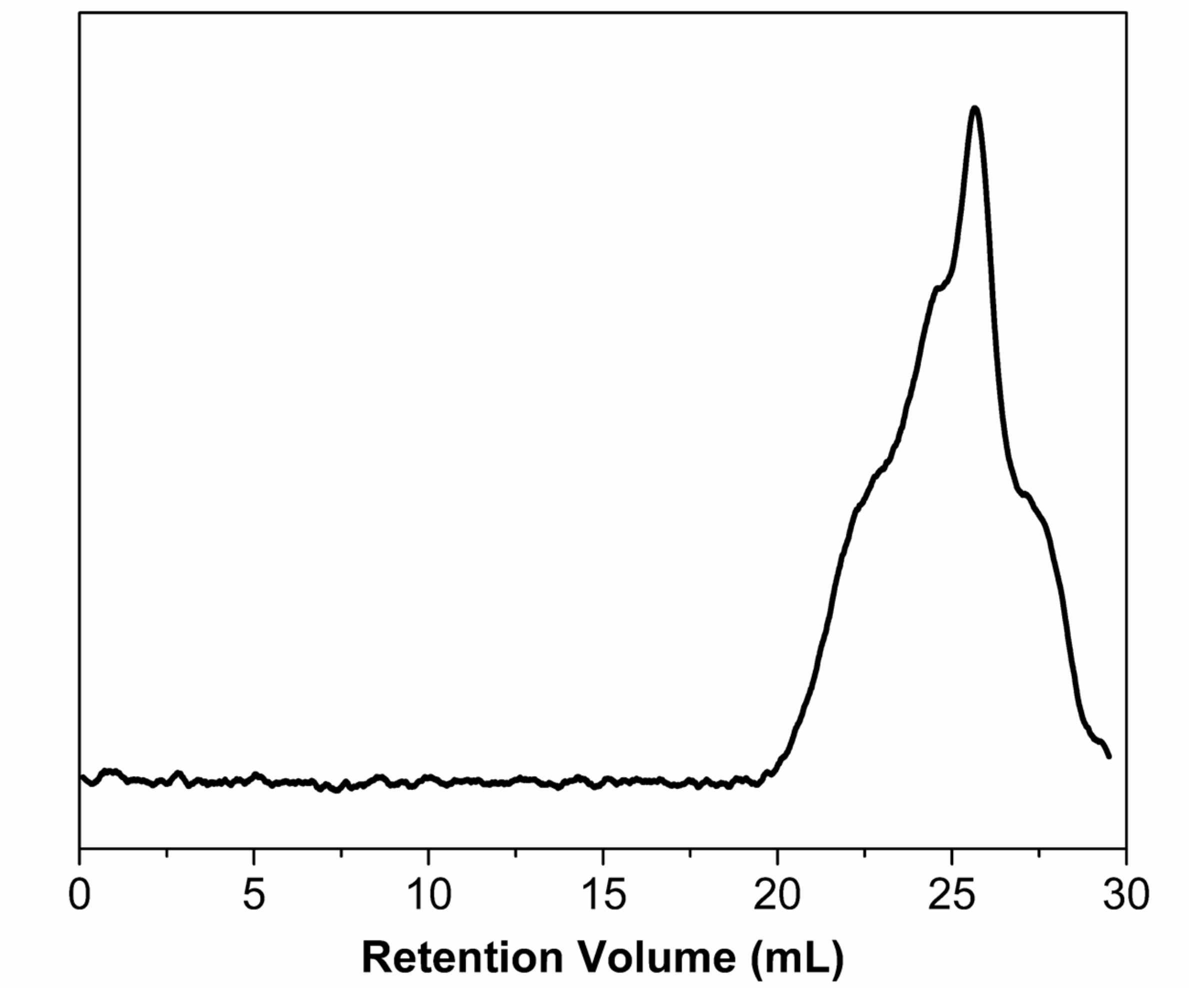


Figure S7. GPC traces of purified PS catenane **6**

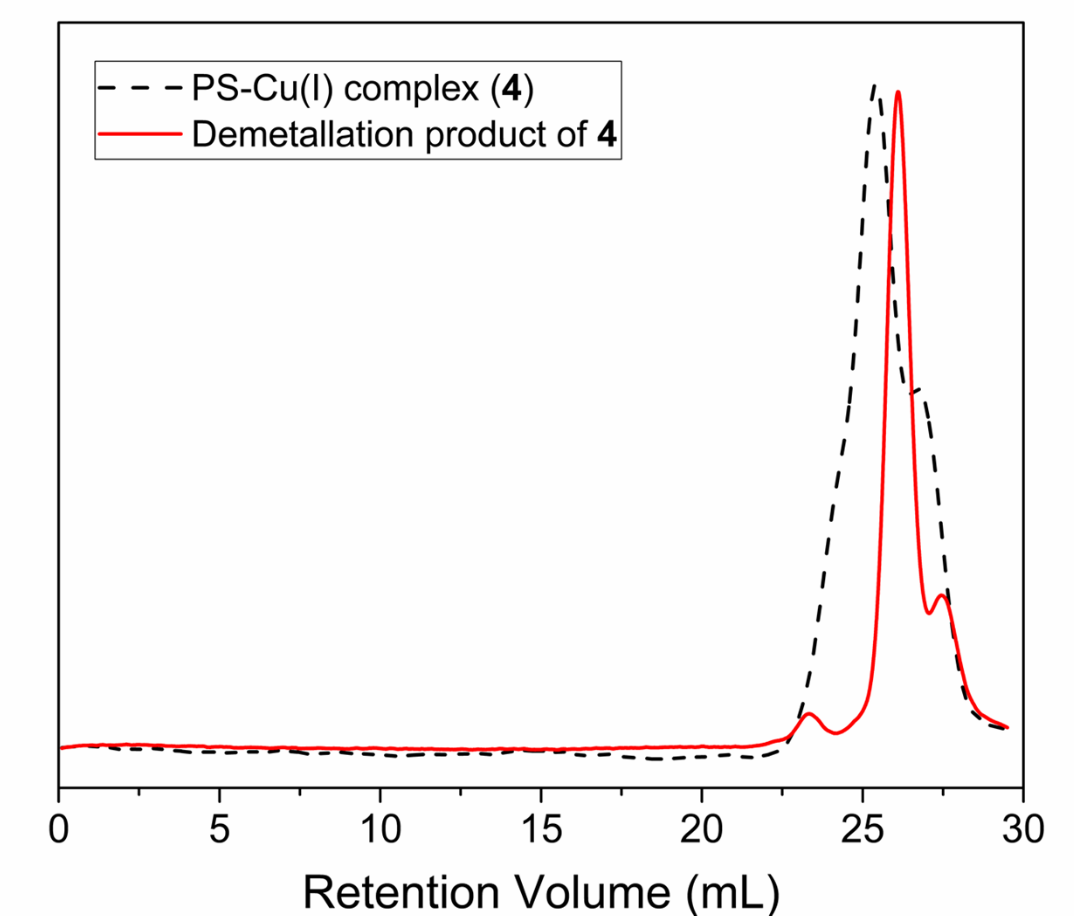


Figure S8. GPC traces of demetallation study of PS-Cu(I) complex **4**

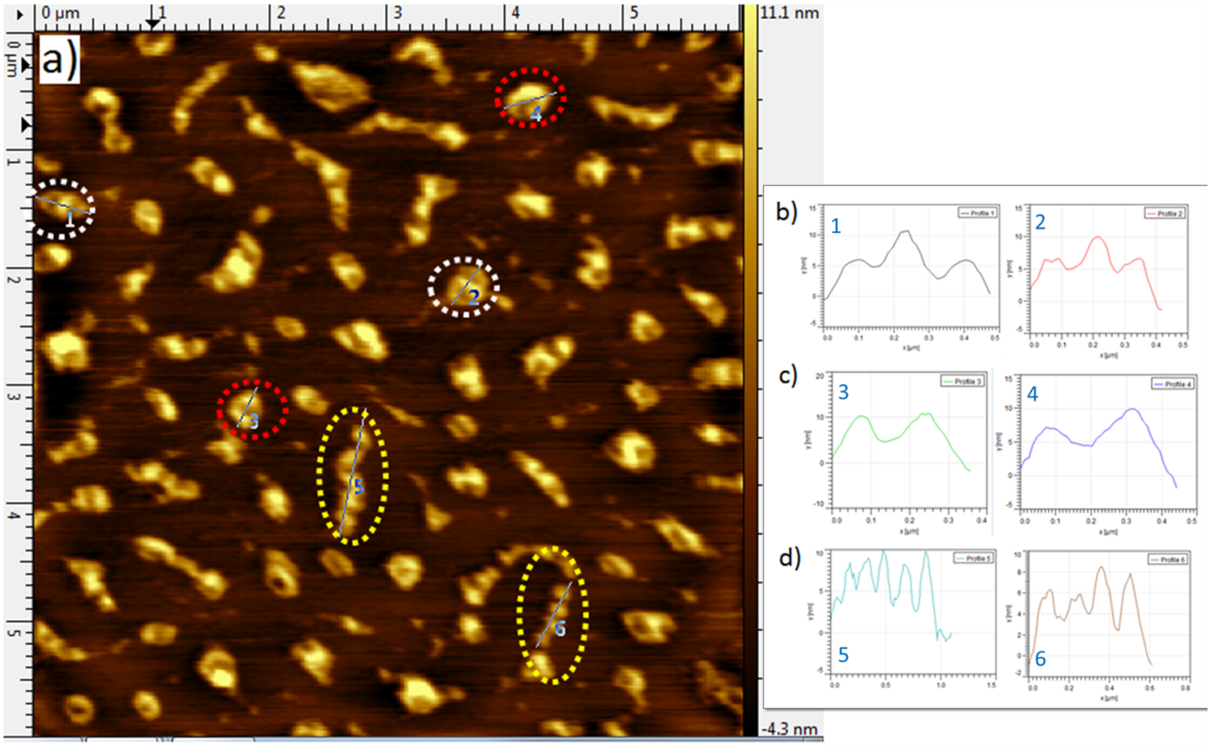


Figure S9. (a) AFM topography image of PS catenanes (**6**) on a 6×6 µm scale on mica, line profile of the representative samples of (b) PS-[2]catenanes, (c) cyclic isomer of PS, and (d) PS-[n]catenanes (n≥3).

References:

[1] C. Dietrich-Bucheker and J. P. Sauvage, *Tetrahedron,* 1990, **46**, 502.

[2] J. Zhan, X. Zhu, F. Fang, F. Miao, D. Tian, H. Li, *Tetrahedron,* 2012, **68**, 5579–5582.

[3] G. Shi, X. Tang, C. Pan, *J. Polym. Sci. Polym. Chem.*, 2008, **46**, 2390.