Supporting Information

Supramolecularly Templated Catenane Initiator and a Controlled Ring Expansion Strategy

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Contents

Experimental Section

Materials

All reagents were used as received from Aldrich Chemical Company unless otherwise specified. ε-Caprolactone (CL, 99%, Alfa Aesar) was distilled from CaH_2 under reduced pressure. Tri(ethylene glycol) was purchased from Alfa Aesar and used directly. Benzoylated cellulose tubing (MWCO 2000) were purchased from Sigma and used directly.

Characterization

^1H NMR spectra were recorded on a General Electric QE-400 spectrometer. UV-vis spectra were recorded on an Agilent 8453 spectrometer. Fluorescence spectra were obtained using a Perkin-Elmer LS45 luminescence spectrometer. GPC was carried out on a Viscotek 270 instrument with a triple detector array (RALS, IV, RI, or UV) equipped with 2 GMHHR-M and 1 GMHHR-L mixed bed Visco Gel columns (eluent: THF; flow rate: 1 mL min^{-1}). M_n was obtained by Universal Calibration with linear polystyrene as the standard. The intrinsic viscosity analyses were performed using the Viscotek viscometer described above and the results were analyzed using Omni SEC software. FTIR measurements were done using a Digilab FTS 7000 step scan spectrometer. The thermal properties of the polymers was investigated by differential scanning calorimetry (DSC) using a heating rate of 15 ℃/min. DSC data was analyzed using TA Instruments Universal Analysis software. Atomic Force

Microscopy (AFM) imaging was conducted under ambient conditions with PicoSPM II (Picoplus, Molecular Imaging – Agilent Technologies) with a scan rate of 1.0 line/s. Tapping mode tips (TAP300, Silicon AFM Probes, Ted Pella, Inc.) were used on cantilevers with a resonance frequency in the range of 290-410 kHz. All AFM topographic images were processed using Gwyddion 2.19 software. Voyager DE-STR MALDI-TOF mass spectrometer (Applied Biosystems) was operated in the positive ion linear mode with acceleration voltage ranging from 20kv to 30kv, extraction delay time ranging from 300 nsec to 400 nsec, used 2,5-dihydroxybenzoic acid as matrix.

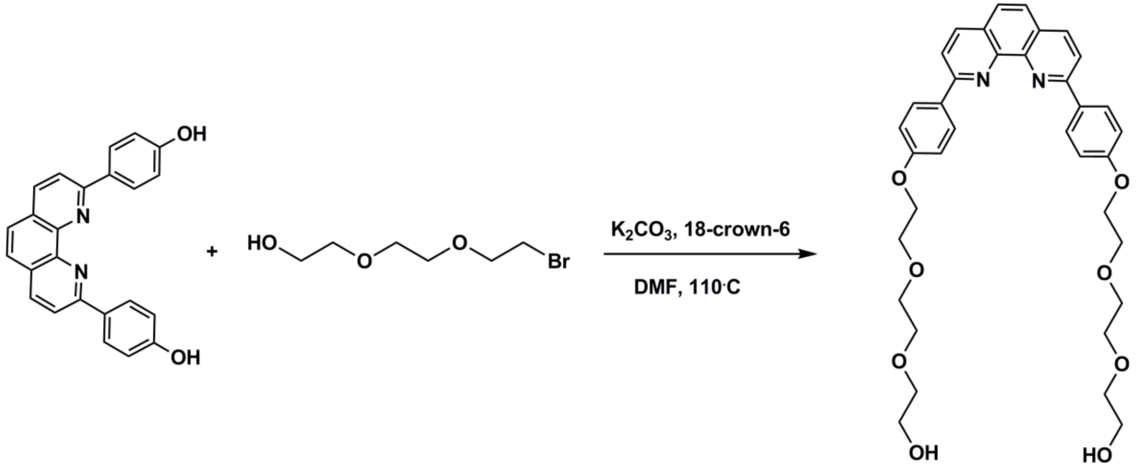
Synthesis

1. Synthesis of 2-(2’-(2’’-bromoethoxy)ethoxy)ethanol[1]

To a solution of tri(ethylene glycol) (4.08 g, 27.1 mmol) in dichloromethane (50 mL) at 0 ^{o}C was added carbon tetrabromide (3.00 g, 9.05 mmol) and triphenylphosphine (2.61 g, 9.95 mmol). The reaction mixture was stirred at room temperature for 2 hours, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (hexane/ethyl acetate=1/2) to give 1.61 g (83 %) of desired product as yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm: 3.35 (t, *J*=6.3 Hz, 2H), 3.44 (t, *J*=4.6Hz, 2H), 3.53 (m, 4H), 3.58 (t, *J*=4.6Hz, 2H), 3.68 (t, *J*=6.0Hz, 2H); ^{13}C NMR (500 MHz, $CDCl_3$), δ ppm: 30.1 (CH_2Br), 61.5 (CH_2OH), 70.1, 70.3, 71.1, 72.3; *m*/*z* (+FAB): found 214.9 ($M+H^+$, calculated: 214.1 for $C_6H_{13}O_3Br$ (81Br)), 213.4 ($M+H^+$, calculated: 212.1 for $C_6H_{13}O_3Br$ (79Br)).

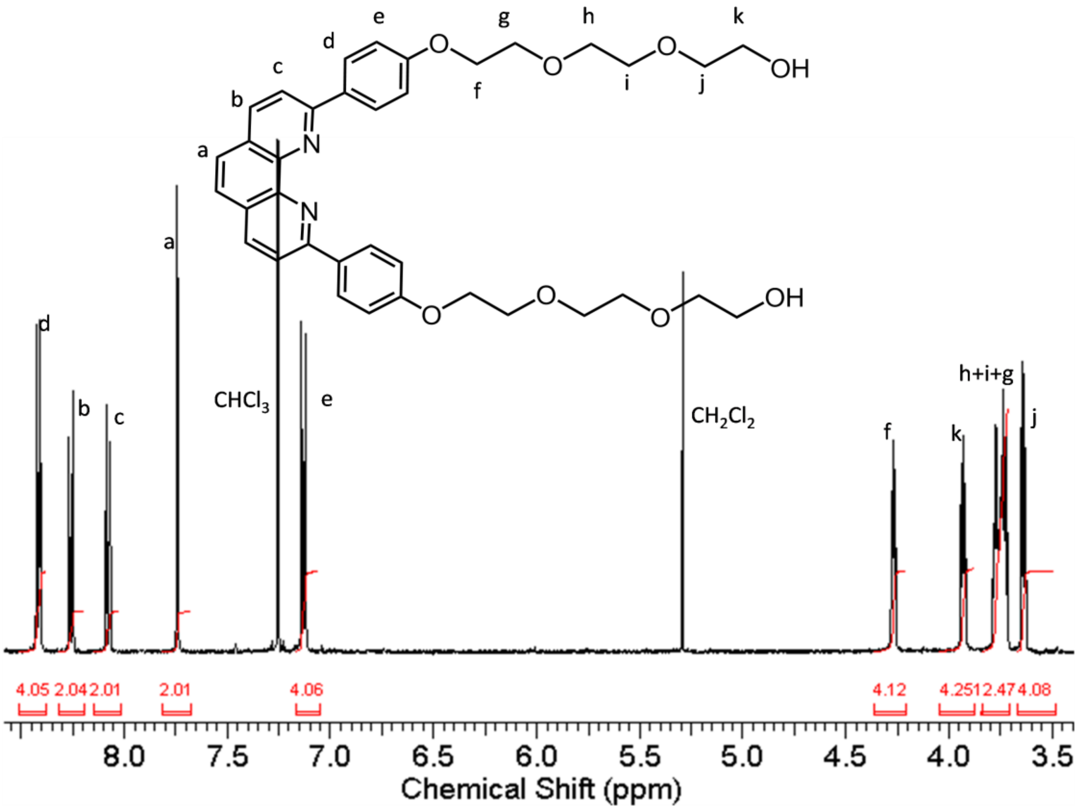
2. Synthesis and characterization of 2, 9-di(*p*-hydroxyphenyl)-1, l0-phenanthroline has been previously reported by our group.[2]

3. Synthesis of 2,9-bis(*p*-{2-[2’-hydroxyethoxy(ethoxy(ethoxy))]}phenyl)-1,10-phenanthroline



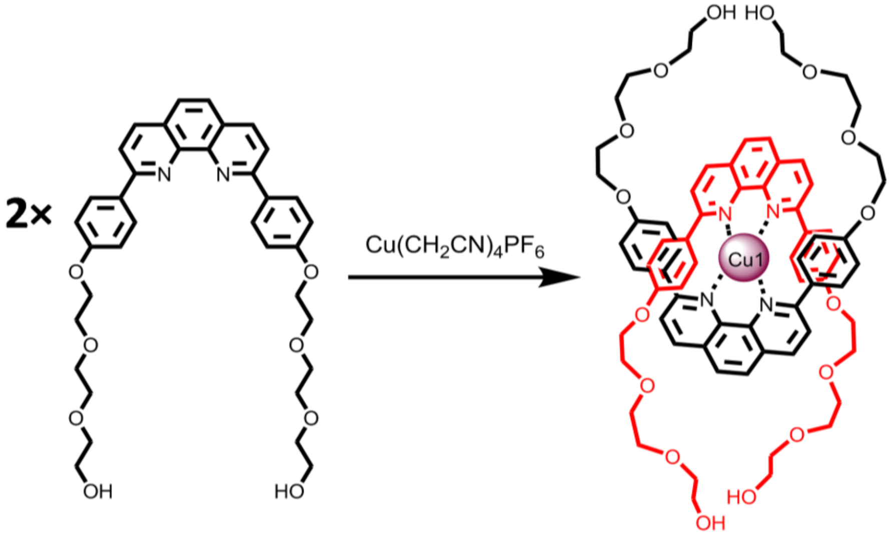
SI Scheme 1. Synthesis of compound **1**

A mixture of 2, 9-di(*p*-hydroxyphenyl)-1,l0-phenanthroline (2.0 g, 5.5 mmol), 2-(2’-(2’’-bromoethoxy)ethoxy)ethanol (1.5 g, 12 mmol), K_2CO_3 (6.9 g, 50 mmol) and 18-crown-6 (0.10g, 0.38mmol) in 100 mL of DMF was prepared and placed in an oil bath at a temperature of 110 °C under nitrogen for 12 h. After cooling down, K_2CO_3 was filtered out and then the filtrate was vacuum distilled to remove the solvent. The obtained crude product was re-dissolved in 60 mL of dichloromethane and the solution was washed with water (20 mL×4). Further purification was achieved by column chromatography using 5% MeOH/DCM to obtain the desired product as yellow solid with 83% yield. ^{1}H NMR ($CDCl_3$), δ ppm: 8.42 (d, *J*=8.8Hz, 4H), 8.26 (d, *J*=8.5Hz, 2H), 8.08 (d, *J*=8.5Hz, 2H), 7.74 (s, 2H), 7.13 (d, *J*=8.8Hz, 4H), 4.27 (t, *J*=4.9Hz, 4H), 3.94 (t, *J*=4.8Hz, 4H), 3.79-3.69 (m, 12H), 3.63 (t, *J*=4.6Hz, 4H); ^{13}C NMR (500MHz, $CDCl_3$), δ ppm: 159.2, 156.4, 146.0, 136.9, 132.7, 129.0, 127.6, 125.6, 119.2, 114.8, 72.7, 69.7, 69.5, 67.6, 66.0, 61.6; *m*/*z* (+FAB) found 629.3 $[M+H^+]$, calculated: 628.7 for $C_{36}H_{40}N_2O_8$.



SI Figure 1. ^{1}H NMR spectrum of compound **1.**

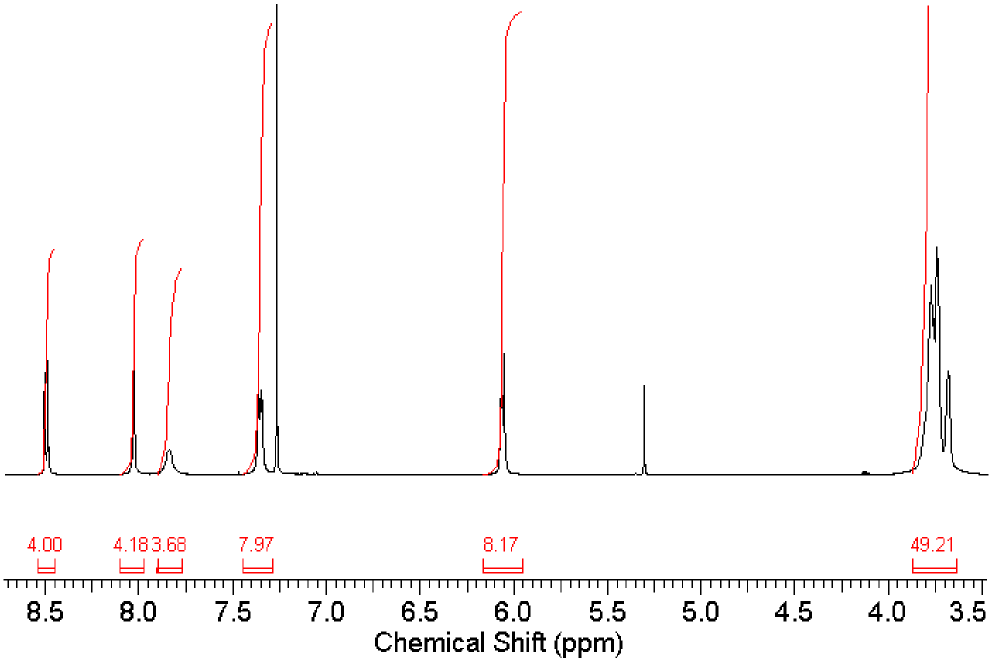
4. Preparation of complex (compoud **2**)



1 **2**

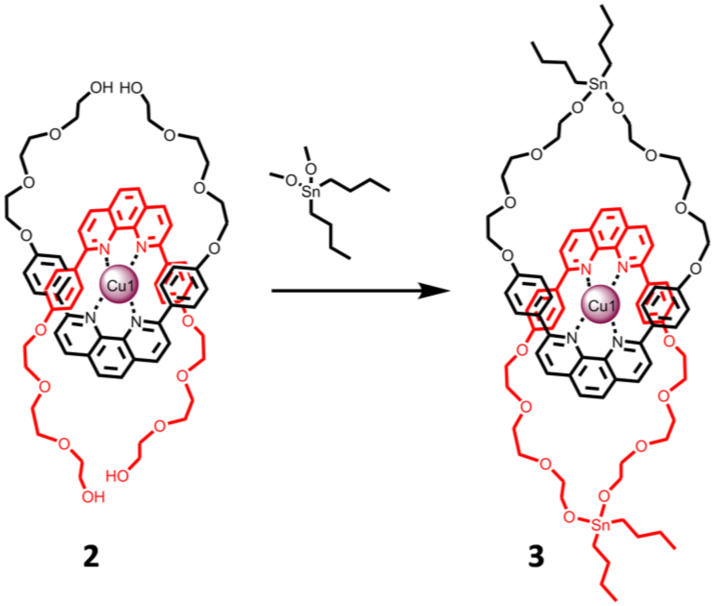
SI Scheme 2. Preparation of complex (compound **2**)

Compound **1** (0.063g, 0.10 mmol) and $Cu(CH_3CN)_4PF_6$ (0.023g, 0.12 mmol) were dissolved in 25 mL of dichloromethane (DCM) and 25 mL of acetonitrile (CH_3CN), respectively. After both of the solutions were bubbled with N_2 for 15 mins, the CH_3CN solution of $Cu(CH_3CN)_4BF_6$ was slowly transferred to the DCM solution of compound **1** with a cannula to obtain a reddish solution. The solvent was removed to obtain the product as reddish solid with 97% yield. ^{1}H NMR ($CDCl_3$, 500MHz), δ ppm: 8.49 (d, *J*=8.6Hz, 4H), 8.02 (s, 4H), 7.83 (s, 4H), 7.34 (d, *J*=8.0Hz, 8H), 6.06 (d, *J*=8.6Hz, 8H), 3.79-3.66 (m, 48H); ^{13}C NMR (500MHz, $CDCl_3$), δ ppm: 159.3, 153.3, 142.5, 137.4, 129.2, 128.0, 126.4, 119.6, 113.2, 111.7, 72.6, 70.8, 70.4, 69.5, 67.3, 61.8; *m/z* (+FAB) found 1319.75 [M^+], calculated: 1320.9 for $C_{72}H_{80}N_4O_{16}Cu$.



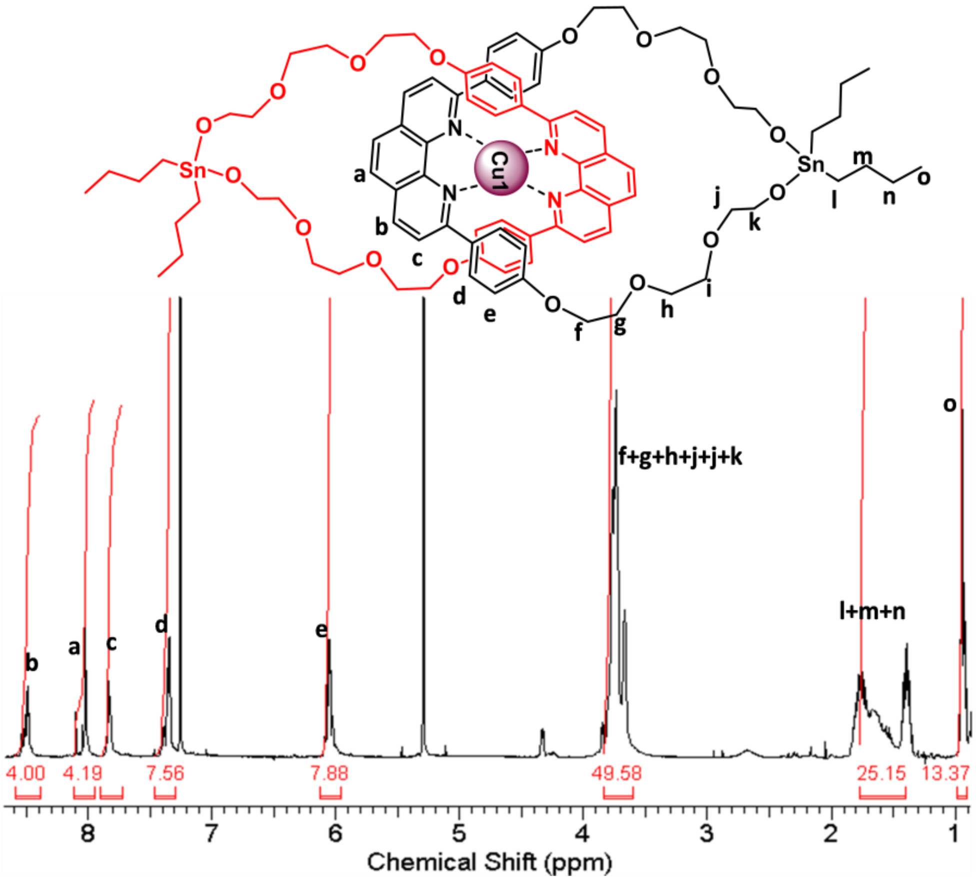
SI Figure 2. ^{1}H NMR spectrum of complex (compound **2**)

5. Preparation of compound **3** (catenane initiator)



SI Scheme 3. Preparation of catane initiator (compound **3**)

Compound **2** obtained above (0.086g, 0.050 mmol) was dissolved in 500 mL of chloroform and placed in a round-bottom flask. To this, dibutyldimethoxytin (0.031g, 0.11 mmol) was added. The reaction mixture was refluxed overnight under the N_2. The solvent and leftover dibutyldimethoxytin was removed by vacuum to obtain the product as reddish solid with 95% yield. ^{1}H NMR ($CDCl_3$, 500MHz), δ ppm: 8.49 (d, *J*=8.6Hz, 4H), 8.02 (s, 4H), 7.83 (s, 4H), 7.34 (d, *J*=8.0Hz, 8H), 6.06 (d, *J*=8.6Hz, 8H), 3.79-3.66 (m, 48H), 1.85-1.33(m, 24H), 0.96-0.87(m, 12H); ^{13}C NMR ($CDCl_3$), δ ppm: 159.3, 153.3, 137.5, 137.4, 129.2, 128.0, 126.4, 119.6, 113.2, 111.7, 72.6, 70.8, 70.4, 69.5, 67.3, 61.8, 29.8, 27.4, 26.7, 13.7. UV-vis spectrum: λ_{max}=281nm, 330nm, 455nm and 595 nm.

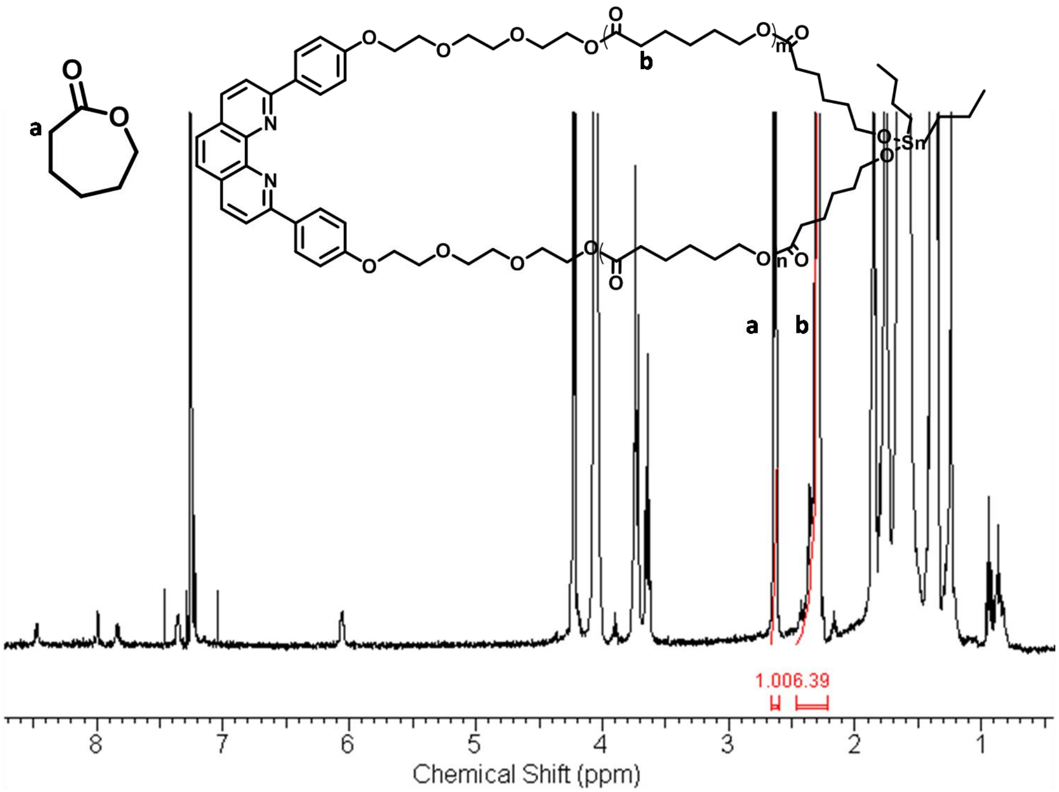


SI Figure 3. ^{1}H NMR spectrum of catenane initiator (compound **3**)

6. Polymerization of caprolactone with catenane initiator

Catenane initiators (0.043g, 0.025 mmol) and caprolactone monomers (0.228g, 2.00 mmol) were combined in a round bottom flask. The mixture was degassed by three freeze-pump-thaw cycles, backfilled with N_2 and then subjected to polymerization in oil bath at 80 °C under nitrogen atmosphere for 18h. The ^{1}H NMR spectrum for the obtained polymer before purification is shown in SI Figure 4.

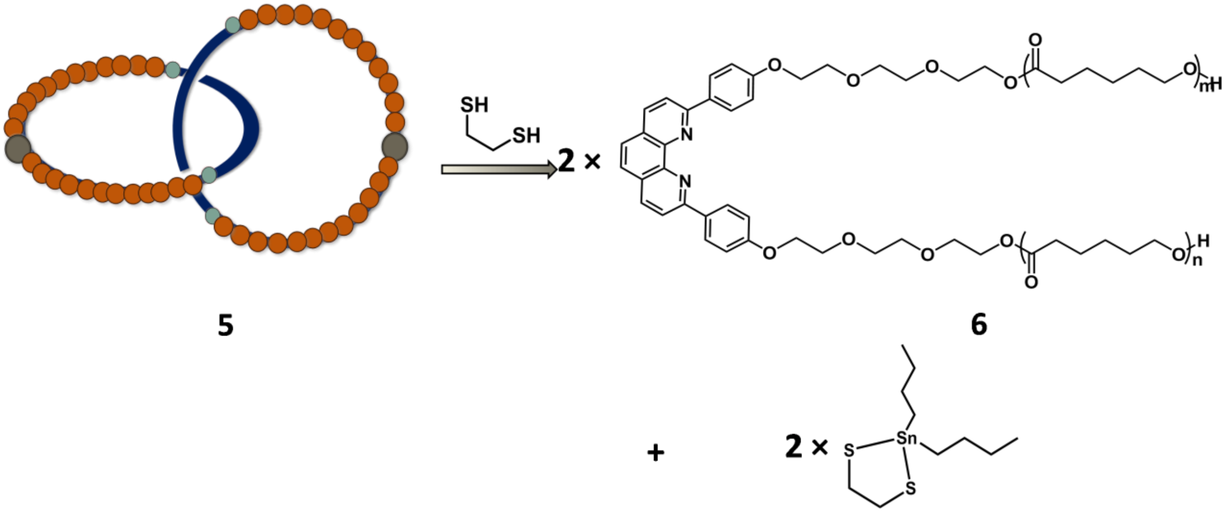
From the ^{1}H NMR spectrum of the polymer product before purification as shown in SI Figure 4, the monomer conversion was calculated to be 86%.



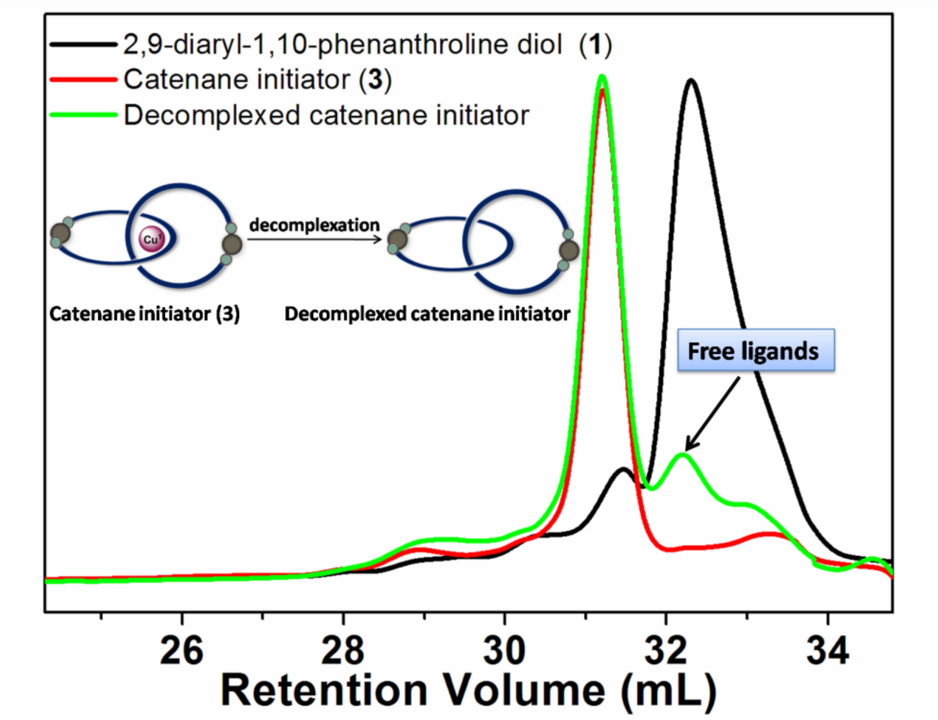
SI Figure 4. The catenated polymer before purification

7. Decomplexation of the catenated polymer was performed according to a similar procedure previously reported by our group.[2]

Supplementary Figures and Schemes:

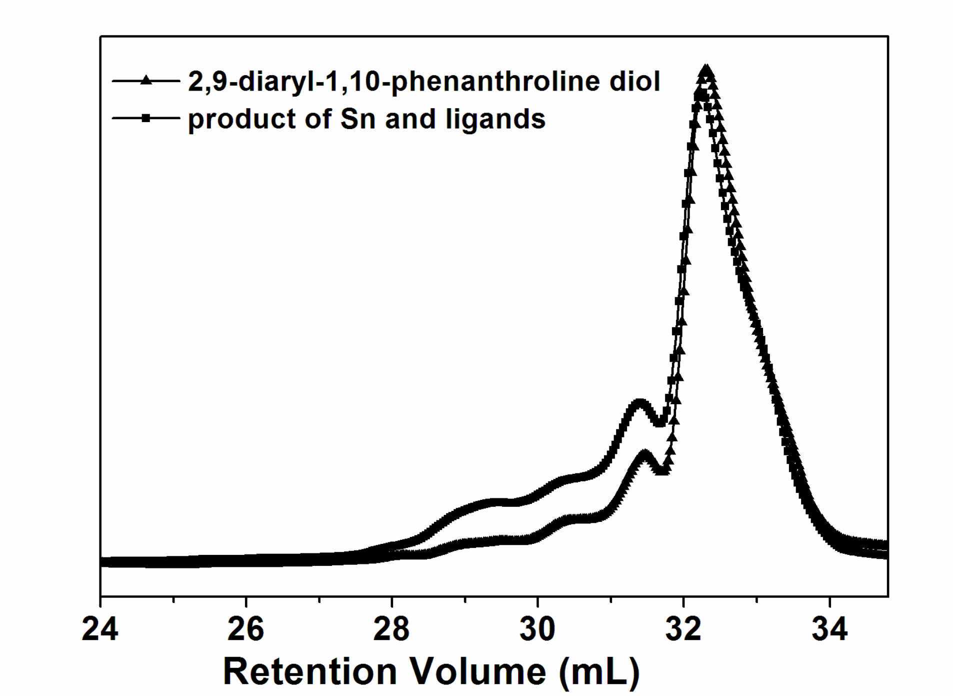


SI Scheme 4. Reaction of catenated polymers with dimercaptoethane (DME)

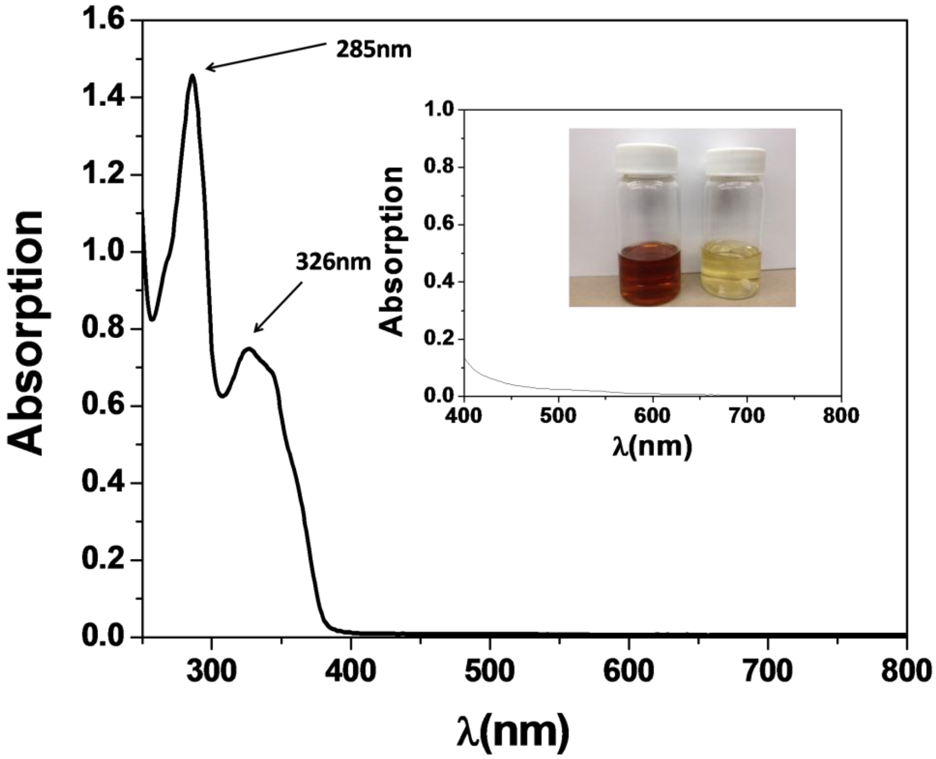


SI Figure 5. GPC curves for 2,9-diaryl-1,10-phenanthroline diol (**1**), catenane initiator (**3**), and decomplexed catenane initiator

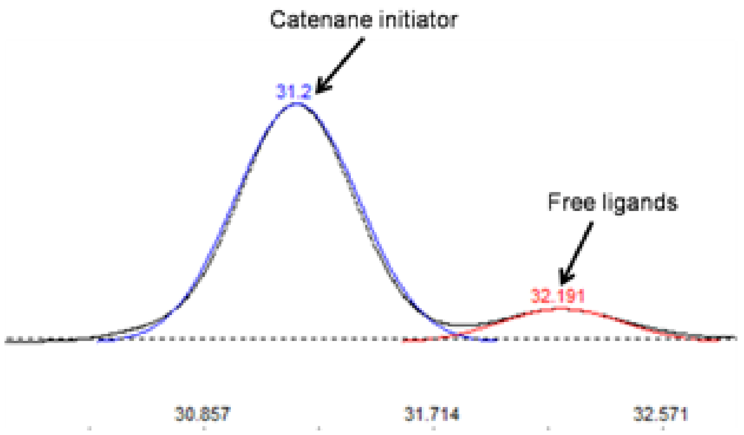
SI Figure 6. UV-Vis spectrum of 2,9-diaryl-1,10-phenanthroline diol (black line) and complex of ligands (red line)



SI Figure 7. GPC curves of 2,9-diaryl-1,10-phenanthroline diol (**1**) , and reaction product of 2,9-diaryl-1,10-phenanthroline diol and dibutyldimethoxytin

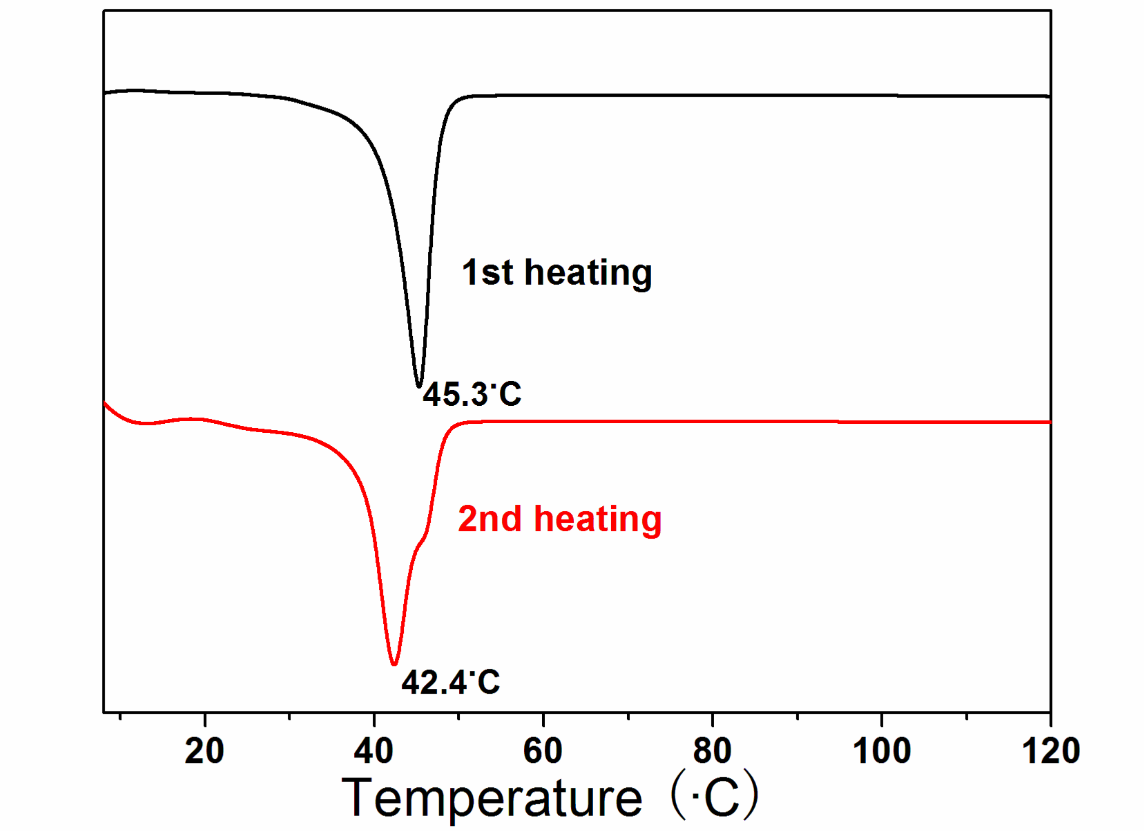


SI Figure 8. UV-Vis spectrum of copper free catenane initiators, inset is the color change before and after decomplexation



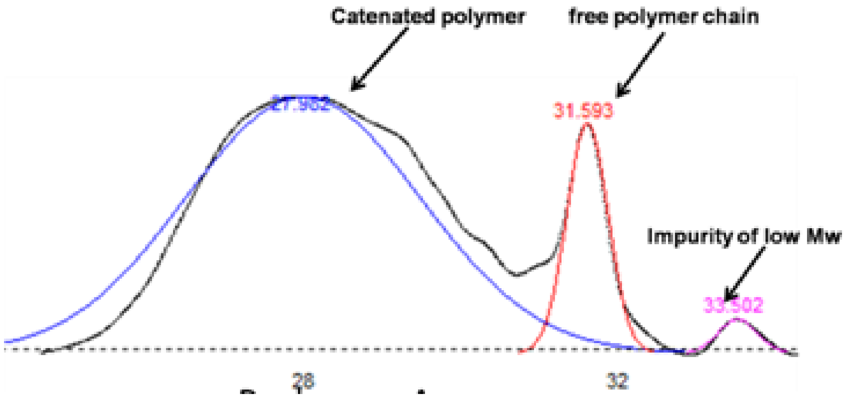
Peak	Area	% Abundance
1	7.798	87.657
2	1.098	12.343

SI Figure 9. Comparative areas for the decomplexed initiators—catenane initiators and free ligands



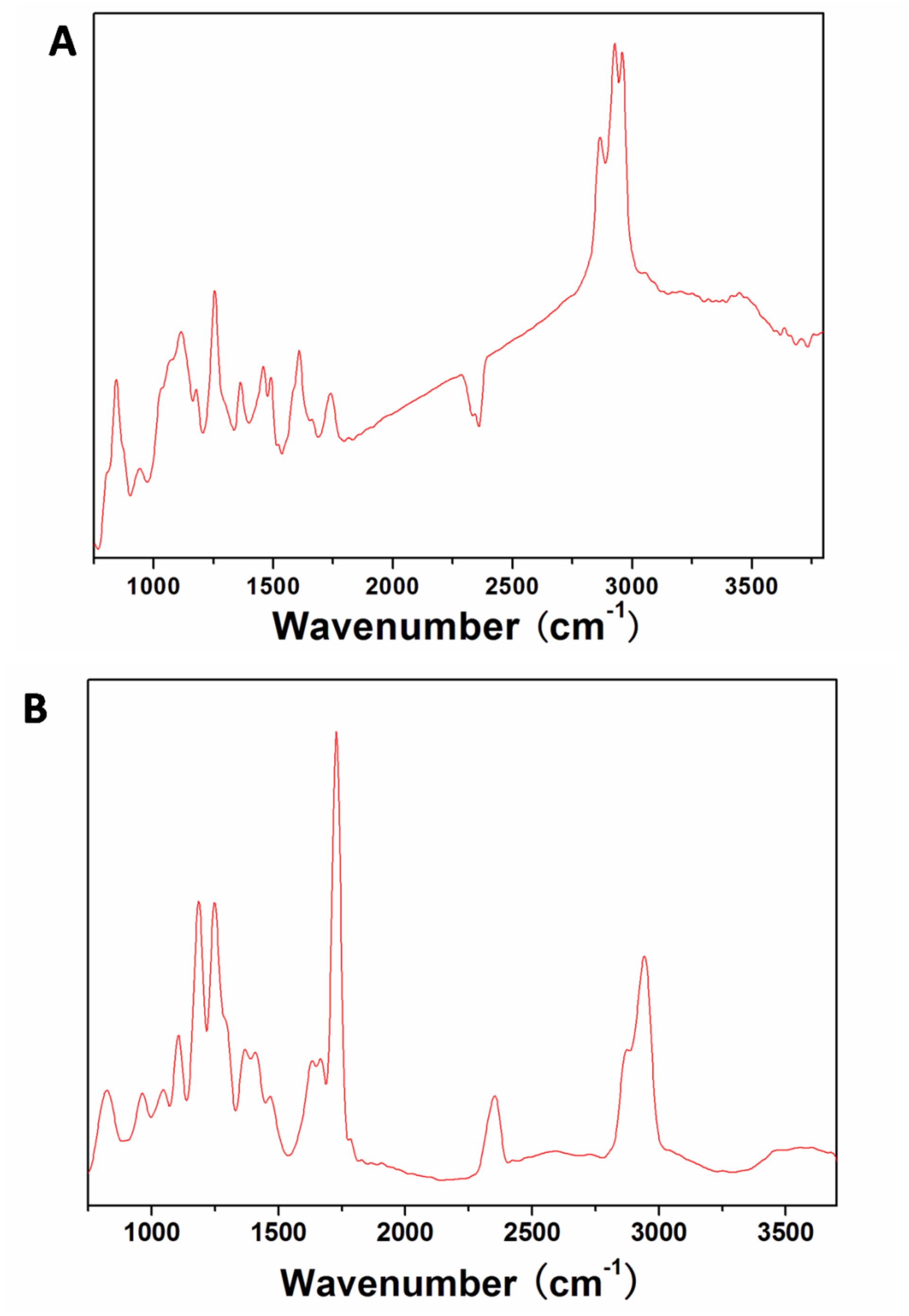
SI Figure 10. DSC curves of catenated polymers with complexation—1st heating (black line), 2nd heating (red line)

DSC measurements showed apparent melting temperature peak (T_m) at 45.3 °C and 42.4 °C for the first and second heating cycle, respectively, which are typical values for poly(ε-caprolactone).[3]



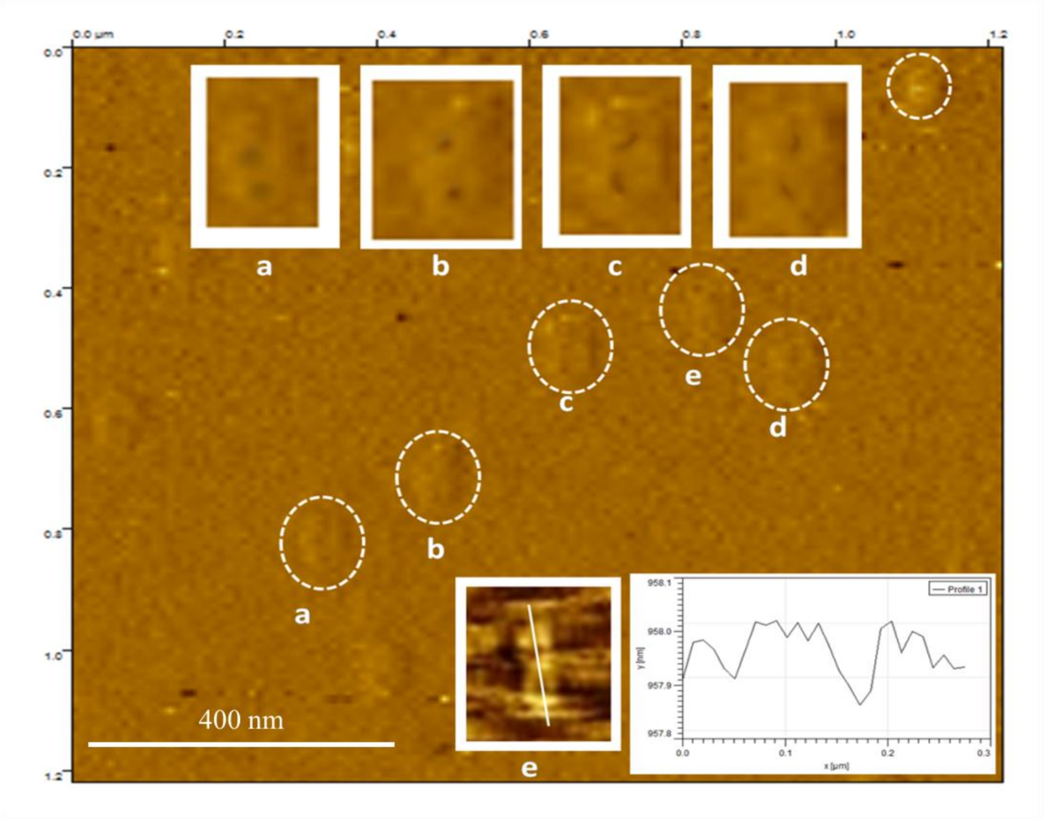
Peak	Area	% Abundance
1	21.008	84.754
2	3.316	13.378
3	0.463	1.868

SI Figure 11. Comparative areas for the decomplexed polymers—catenated polymers, free polymer chain and some low molecular weight impurities (18-crown-6, it was added during the decomplexation of catenated polymer)

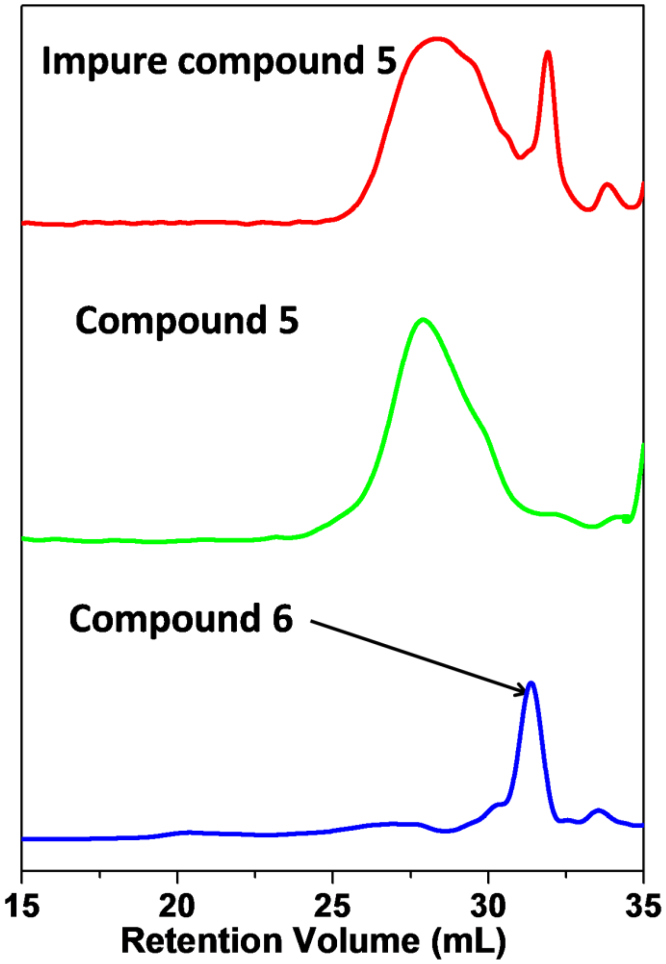


SI Figure 12. IR spectrum of catenane initiator (**A**) and catenated polymer (**B**)

The IR spectrum of the obtained catenated polymers showed strong and broad peaks at 1730 cm^{-1} and 1163 cm^{-1}, which corresponded to the typical stretching vibrations of C=O and C-O bonds, respectively.



SI Figure 13. AFM image of catenated polymers containing the phenanthroline copper (I) complex



SI Figure 14. GPC curves of (A) decomplexation product of catenated polymer, (B) pure catenated polymer, (C) catenated polymer treated by the 1,2-dimercaptoethane (DME).[4]

Linear polymer analogue was synthesized with dibutyldimethoxytin as initiator, caprolactone as monomers. (The polymerization condition was exactly the same as shown for the synthesis of catenated polymer described above.)

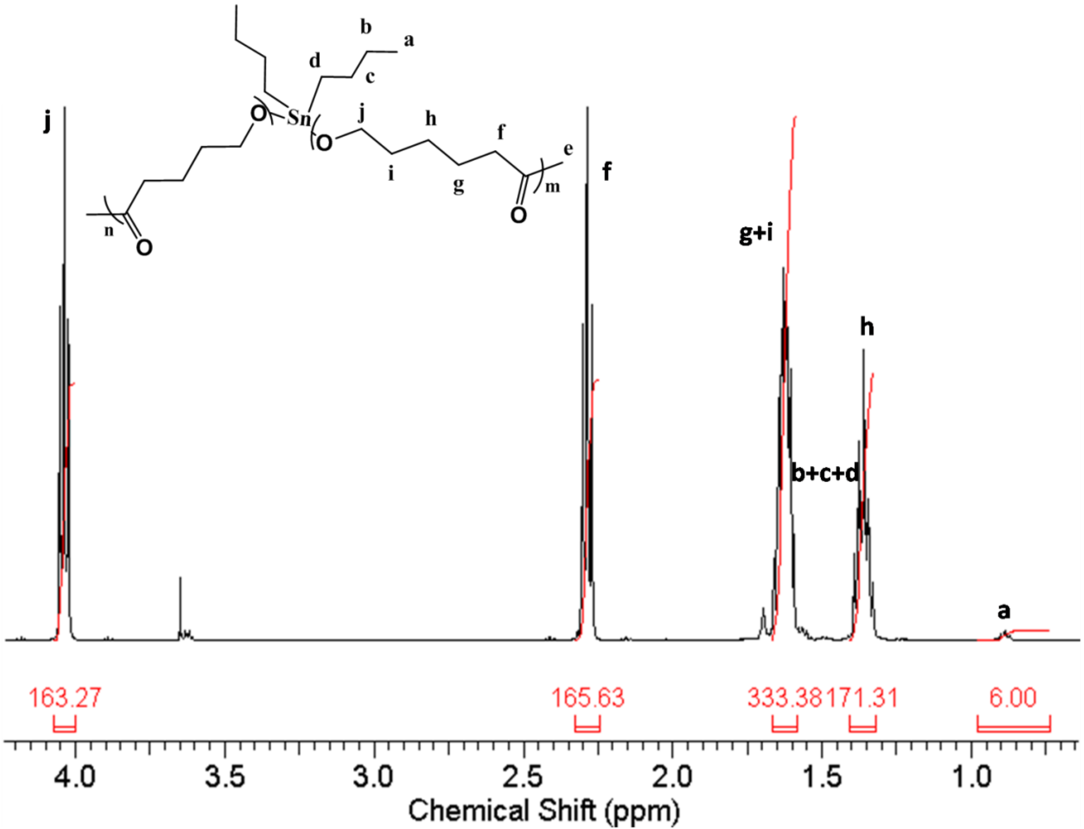


Figure 15. ^{1}H NMR spectrum of linear polymer analogue.

Relative calculation from ^{1}H NMR:

The absolute M_n of linear analogous was calculated from the comparative integration of j and a.

m+n=163.27/2=81.6.

So absolute M_n=285+81.6×114=9.6 kDa

The absolute M_n of catenated polymer is 9.3 kDa, with 3% difference.

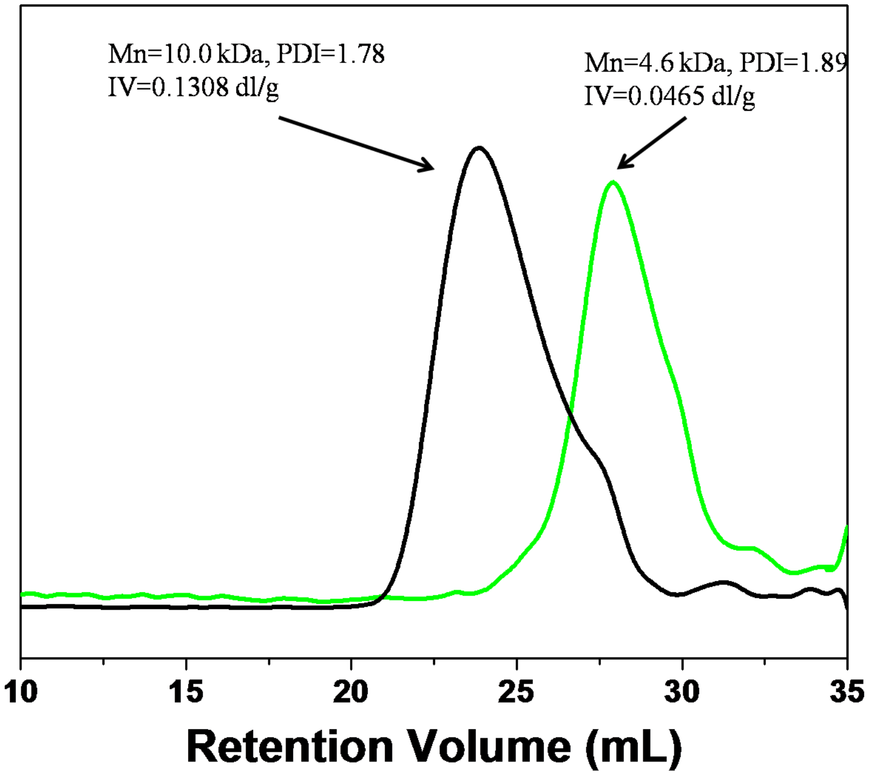


Figure 16. Comparative GPC curves of catenated polymer (green line) and linear analogue (black line)

References:

(1) (a) J. Lee, E. J. Jeong, J. Kim, *Chem. Commun*. 2011, **47**, 358–360; (b) C. A. Hurley, J. B. Wong, J. Ho, M. Writer, S. A. Irvine, M. J. Lawrence, S. L. Hart, A. B. Tabor, H. C. Hailes, *Org. Biomol. Chem.* 2008, **6**, 2554-2559.

(2) A. Bunha, M. C. Tria, R. Advincula, *Chem. Commun.* 2011, **47**, 9173–9175.

(3) (a) M. E. Córdova, A. T. Lorenzo, A. J. Müller, J. N. Hoskins, S. M. Grayson, *Macromolecules* 2011, **44**, 1742–1746; (b) H. R. Kricheldorf, S. R. Lee, *Macromolecules* 1995, **28**, 6718-6725.

(4) The treatment of the catenated polymer with dimercaptoethane is simiar with the previous report by Kricheldorf.[3b] Firstly, according to the reference, we added 1.3 equivalent of 1,2-dimercaptoethane to the DCM solution of catenated polymer and the mixture was stirred in room temperature for 24h. But unfortunately, under this condition the conversion is incomplete (around 80%), perhaps due to the low concentration of the reaction (around 1mg/mL) or the oxidation of DME. Lastly, 5 equivalents of 1,2-dimercaptoethane was added to the solution, and the mixture was stirred for 24 h under the protection of nitrogen. This allowed for nearly 100% conversion.