Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

for

Modular Construction of Macrocycle-based Topological Polymers *via* High-Efficient Thiol Chemistry

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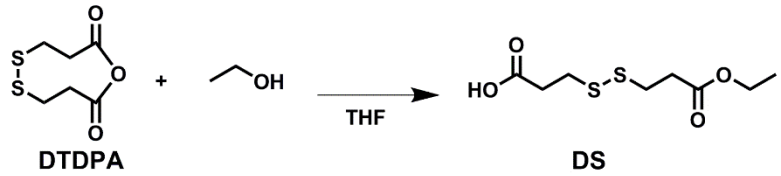
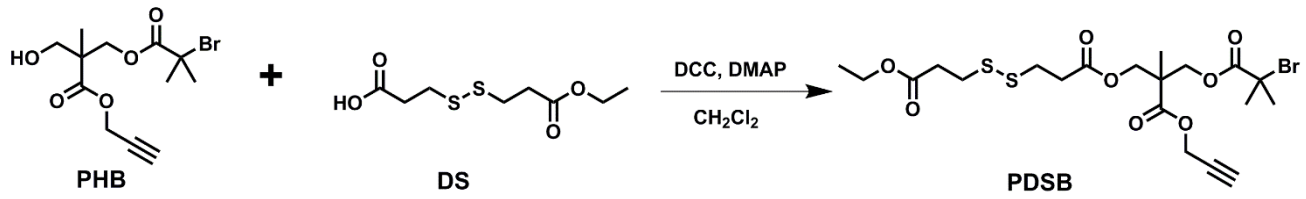
Experimental Section



Scheme S1. Synthesis of Compound **DS**.

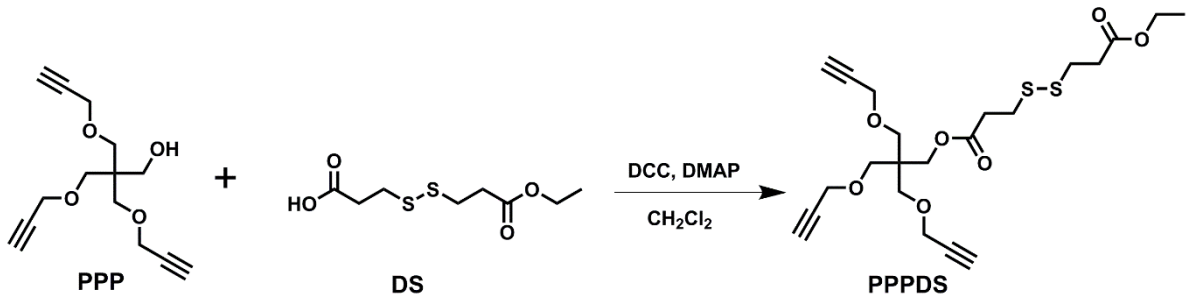
3-((3-ethoxy-3-oxopropyl)disulfanyl)propanoic acid (DS). 3, 3'-Dithiodipropionic acid anhydride (DTDPA, 3.50 g, 18.21 mmol) which was synthesized according to the literature[1], ethyl alcohol absolute (2.5 mL, 42.93 mmol) were dissolved in 10 mL anhydrous THF under magnetic stirring to fully dissolve the solid. The reaction mixture was slowly warmed to reflux overnight, then, the mixture was cooled to ambient temperature, and after removal of solvent, the residue was purified by flash column chromatography on silica gel with hexane/EA (v/v = 3:1) as eluent to obtian pure DS as a colorless oil. Yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 4.20 (q, 2H, -C<u>H</u>$_2$CH$_3$), 2.96-2.91 (m, 4H, -CH$_2$C<u>H</u>$_2$S$_2$C<u>H</u>$_2$CH$_2$-), 2.83-2.71 (m, 4H, -C<u>H</u>$_2$CH$_2$S$_2$CH$_2$C<u>H</u>$_2$-), 1.30 (t, 3H, -CH$_2$C<u>H</u>$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 177.47, 171.85, 60.89, 34.13, 33.86, 33.13, 32.68, 14.16.



Scheme S2. Synthesis of Compound **PDSB**.

PDSB. Propargyl-3-[(2-bromo-2-methylpropanoyl)oxy]-2-(hydroxymethyl)-2-methylpropanoate (PHB, 5.00 g, 15.57 mmol) which was synthesized according to the literature[2], DMAP (0.95 g, 7.78 mmol) and **DS** (4.45 g, 18.68 mmol) mixing with anhydrous CH_2Cl_2 (50 mL) were added into a 100 mL round-bottomed flask equipped with a magnetic stirrer. Then DCC (3.85 g, 18.68 mmol) was dissolved in CH_2Cl_2 (10 mL)

and added dropwise to the above mixture, which was stirred overnight at room temperature and the precipitate byproduct was filtere, the filtrate was washed with brine and water, the combined organic phase was dried with anhydrous Na_2SO_4, after the solvent was removed by rotary evaporation, the crude product was chromatographed on a silica gel column. Eluting with a mixed solvent of hexane/EA (v/v = 5:1) afforded the pure compound **PDSB** as a colorless oil. Yiled: 87%. ^{1}H NMR (300 MHz, DMSO-d_6, ppm, δ): 4.76 (d, 2H, HC≡CC$\underline{H}_2$O-), 4.27 (dd, 4H, -C$\underline{H}_2$OCOCH$_2$CH$_2$S$_2$-+-C$\underline{H}_2$OCOC(CH$_3$)$_2$Br), 4.11 (q, 2H, -OCOC$\underline{H}_2$CH$_3$), 3.60 (t, 1H, $\underline{H}$C≡C-), 2.93 (m, 4H, -CH$_2$C$\underline{H}_2$S$_2$C$\underline{H}_2$CH$_2$-), 2.75 (m, 4H, -C$\underline{H}_2$CH$_2$S$_2$CH$_2$C$\underline{H}_2$-), 1.87 (s, 6H, - OCOC(C$\underline{H}_3$)$_2$Br), 1.25 (s, 3H, -CC$\underline{H}_3$), 1.21 (t, 3H, -OCOCH$_2$C$\underline{H}_3$). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 171.65, 171.53, 170.94, 170.89, 75.43, 66.31, 65.34, 60.73, 55.34, 52.71, 46.50, 34.09, 33.82, 33.15, 32.83, 30.60, 17.70, 14.20. (**Figure S1**)



Scheme S3. Synthesis of Compound **PPPDS**.

PPPDS. Tripropargylpentaerythritol (PPP, 1.00 g, 4.00 mmol) which was synthesized according to the literature[3], DMAP (0.24 g, 2.00 mmol) and **DS** (1.14 g, 4.79 mmol) mixing with anhydrous CH_2Cl_2 (20 mL) were added into a 50 mL round-bottomed flask equipped with a magnetic stirrer. Then DCC (0.93 g, 4.79 mmol) was dissolved in CH_2Cl_2 (5 mL) and added dropwise to the above mixture, which was stirred overnight at room temperature and the precipitate byproduct was filtere, the filtrate was washed with brine and water, the combined organic phase was dried with anhydrous Na_2SO_4, after the solvent was removed by rotary evaporation, the crude product was chromatographed on a silica gel column. Eluting with a mixed solvent of hexane/EA (v/v = 5:1) afforded the pure compound **PPPDS** as a colorless oil. Yiled: 80%. ^{1}H

NMR (300 MHz, $CDCl_3$, ppm, δ): 4.19-4.11 (m, 10H, $(HC{\equiv}CC\underline{H_2}OCH_2)_3CC\underline{H_2}OCO$-), 3.52 (s, 6H, $HC{\equiv}CCH_2OC\underline{H_2}$-), 1.29 (t, 3H, $-CH_2C\underline{H_3}$), 2.77 (q, 4H, $-C\underline{H_2}CH_2S_2CH_2C\underline{H_2}$-), 2.43 (t, 3H, HC≡C-), 1.29 (t, 3H, $-CH_2C\underline{H_3}$). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ):171.60, 171.21, 79.76, 74.43, 68.62, 63.72, 60.77, 58.66, 43.97, 34.13, 34.11, 33.16, 33.04, 14.20. (**Figure S7**)

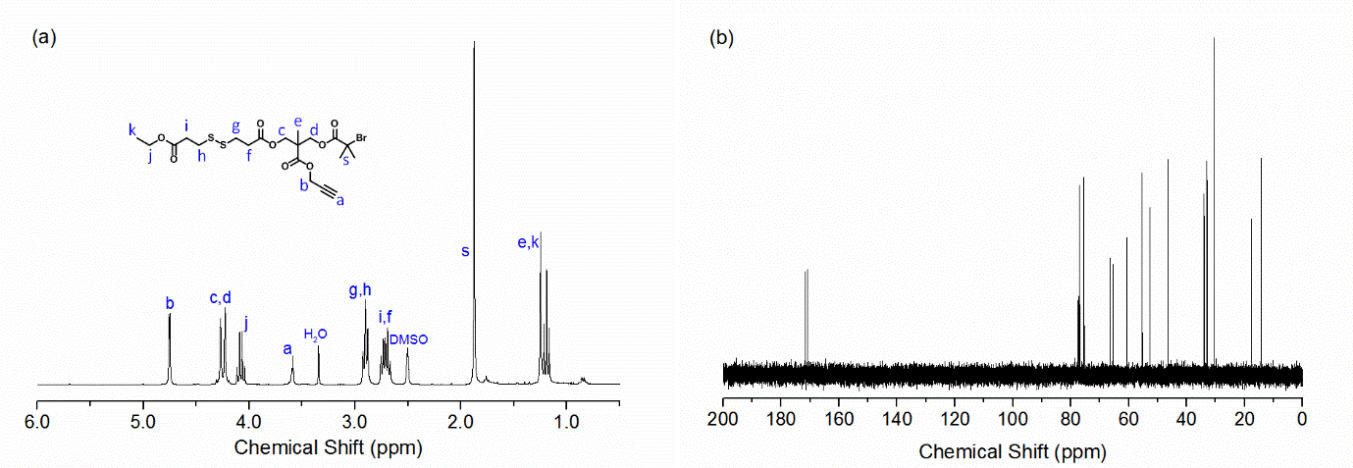


Figure S1. ^1H NMR (a) and ^{13}C NMR (b) spectra of Compound **PDSB**.

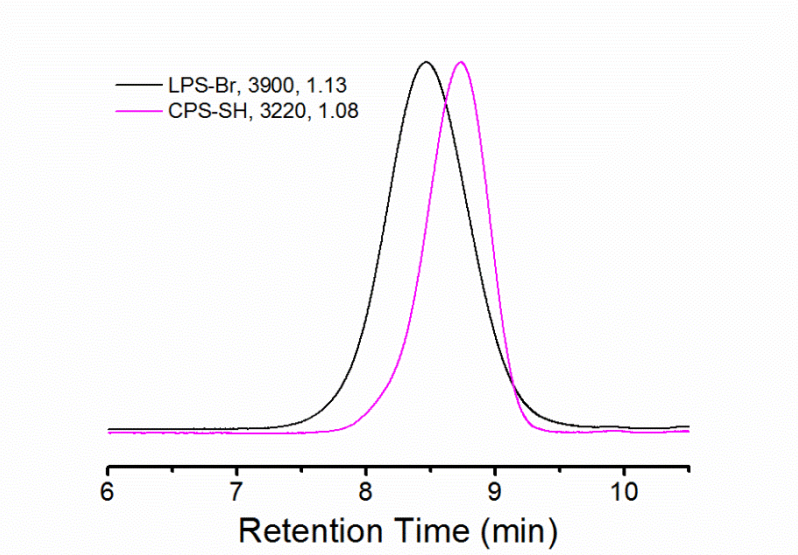


Figure S2. SEC RI traces of LPS-Br (M_p = 4290), CPS-SH (M_p = 3190). THF was used as the eluent, and PS standards were used for the calibration. All SEC traces were normalized to height.

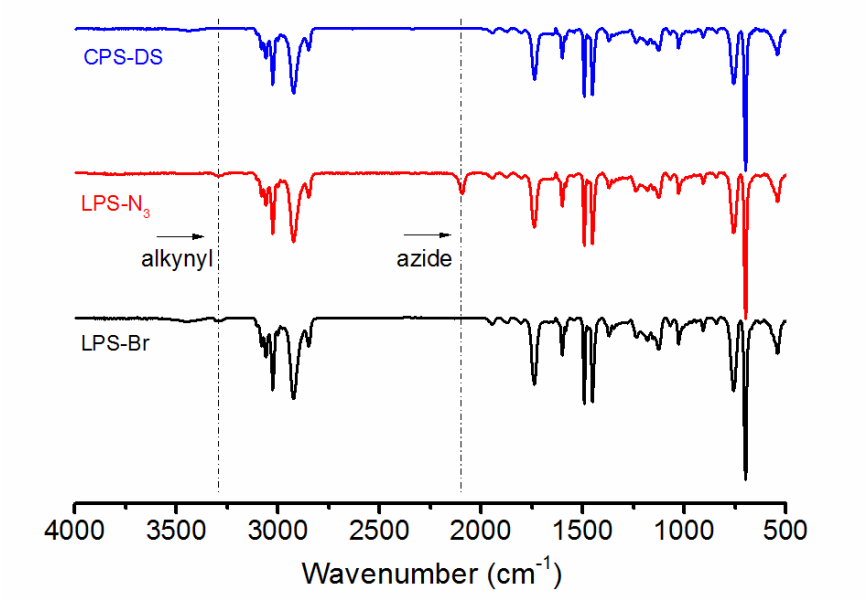


Figure S3. FT-IR spectra of LPS-Br (black curve), LPS-N_3 (red curve), CPS-DS (blue curve).

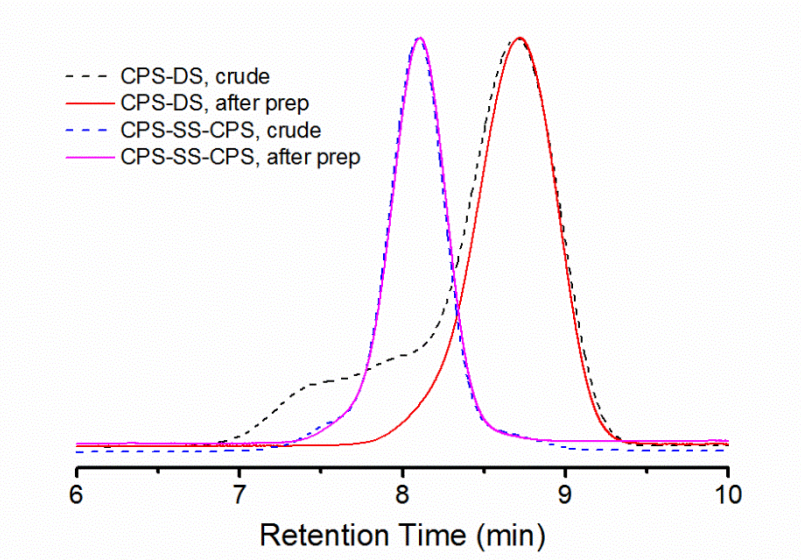


Figure S4. SEC RI traces of CPS-DS (crude, black dotted curve; purified by preparative SEC, red solid curve, yield: 75%), CPS-SS-CPS (crude, blue dotted curve; purified by preparative SEC, pink solid curve, yield: 95%). SEC analysis was based on the polystyrene calibration curve. All SEC traces were normalized to height.

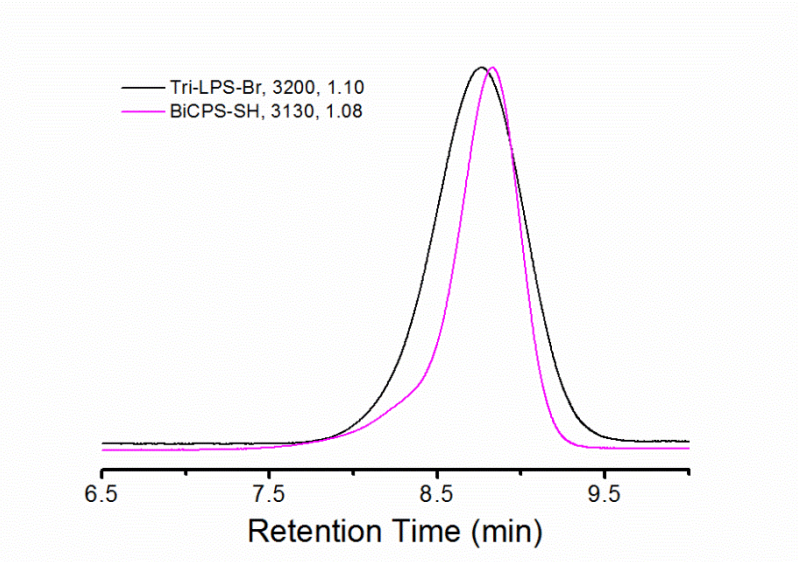


Figure S5. SEC RI traces of Tri-LPS-Br (M_p = 3310), BiCPS-SH (M_p = 2980). THF was used as the eluent, and PS standards were used for the calibration. All SEC traces were normalized to height.

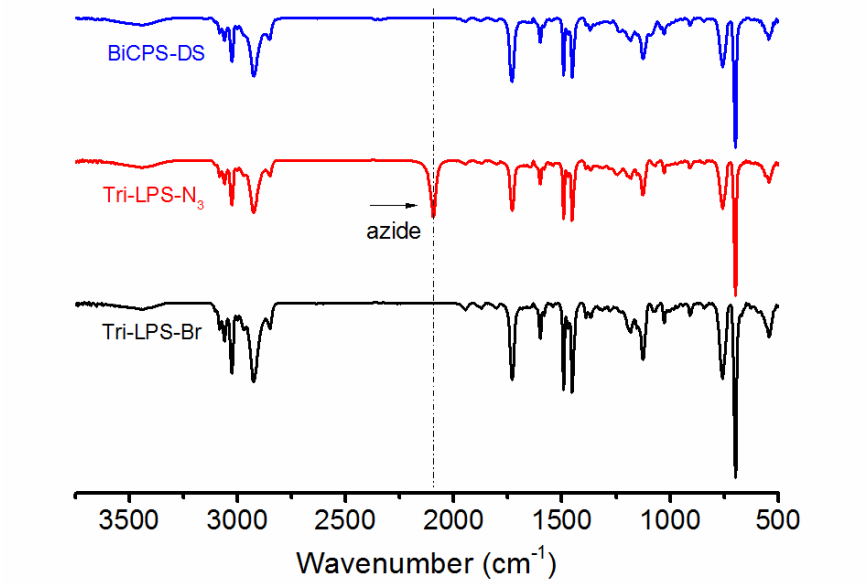


Figure S6. FT-IR spectra of Tri-LPS-Br (black curve), Tri-LPS-N_3 (red curve), BiCPS-DS (blue curve).

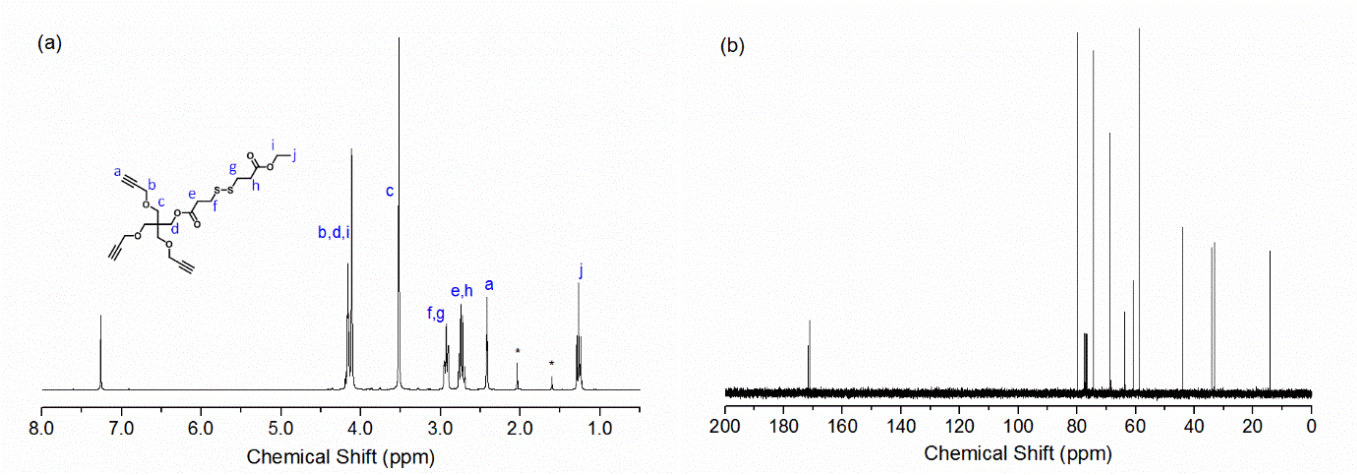


Figure S7. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of Compound **PPPDS**.

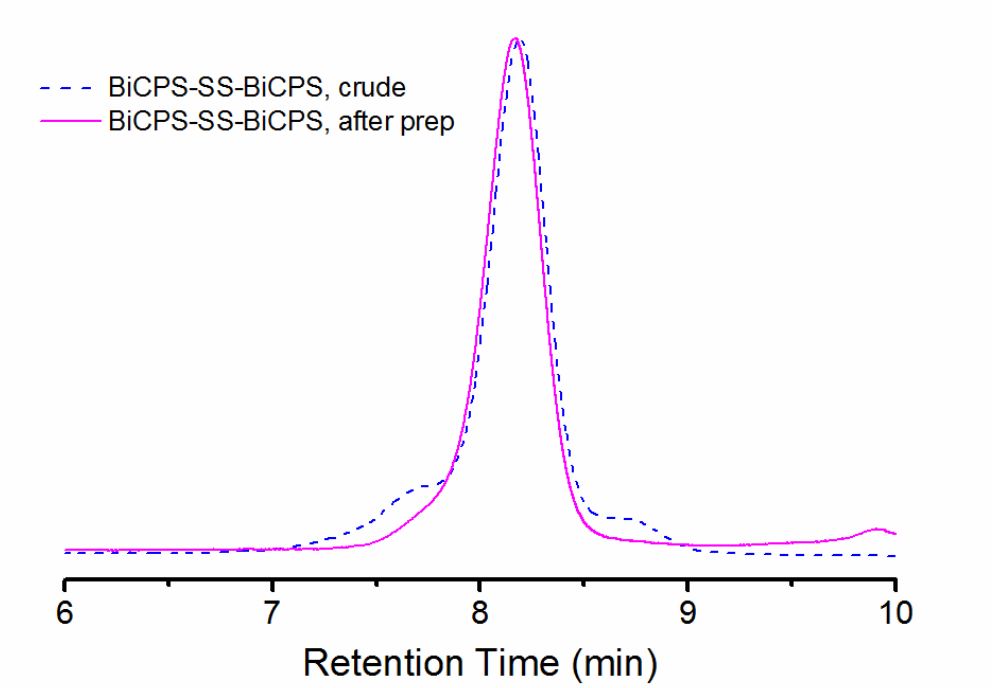


Figure S8. SEC RI traces of BiCPS-SS-BiCPS (crude, blue dotted curve; purified by preparative SEC, pink solid curve, yield: 90%). SEC analysis was based on the polystyrene calibration curve. All SEC traces were normalized to height.

Reference

1 M. Cao, H. Jin, W. Ye, P. Liu, L. Wang and H. Jiang, *J. Appl. Polym. Sci.*, 2012, **123**, 3137.

2 E. Gungor, H. Durmaz, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 4459.

3 J. Zhu, X. Zhu, E. Kang and K. Neoh, *Polymer*, 2007, **48**, 6992.