Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information For:

Polymerization of a Biscalix[5]arene Derivative

Takehiro Hirao,[‡, †] Kazushi Fukuta,[§, †] and Takeharu Haino[‡, *]

[‡]Department of Chemistry, Graduate School of Advanced Science and Engineering, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8526, Japan.

[§]Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, 739-8526, Japan.

*Email: haino@hiroshima-u.ac.jp

[†]These authors contributed equally.

Contents

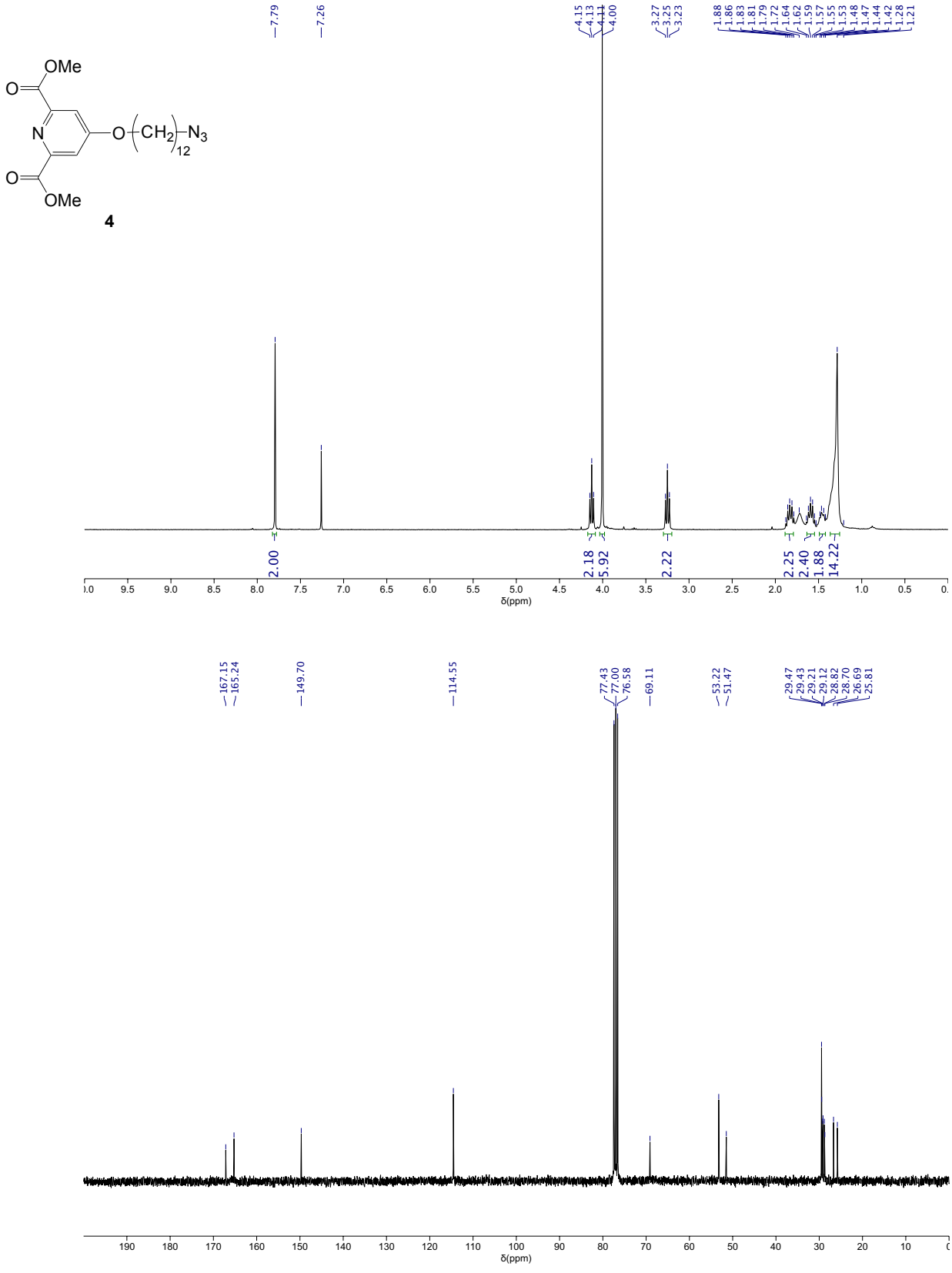


Figure S1. ^{1}H and ^{13}C NMR spectra of **4** in chloroform-*d*.

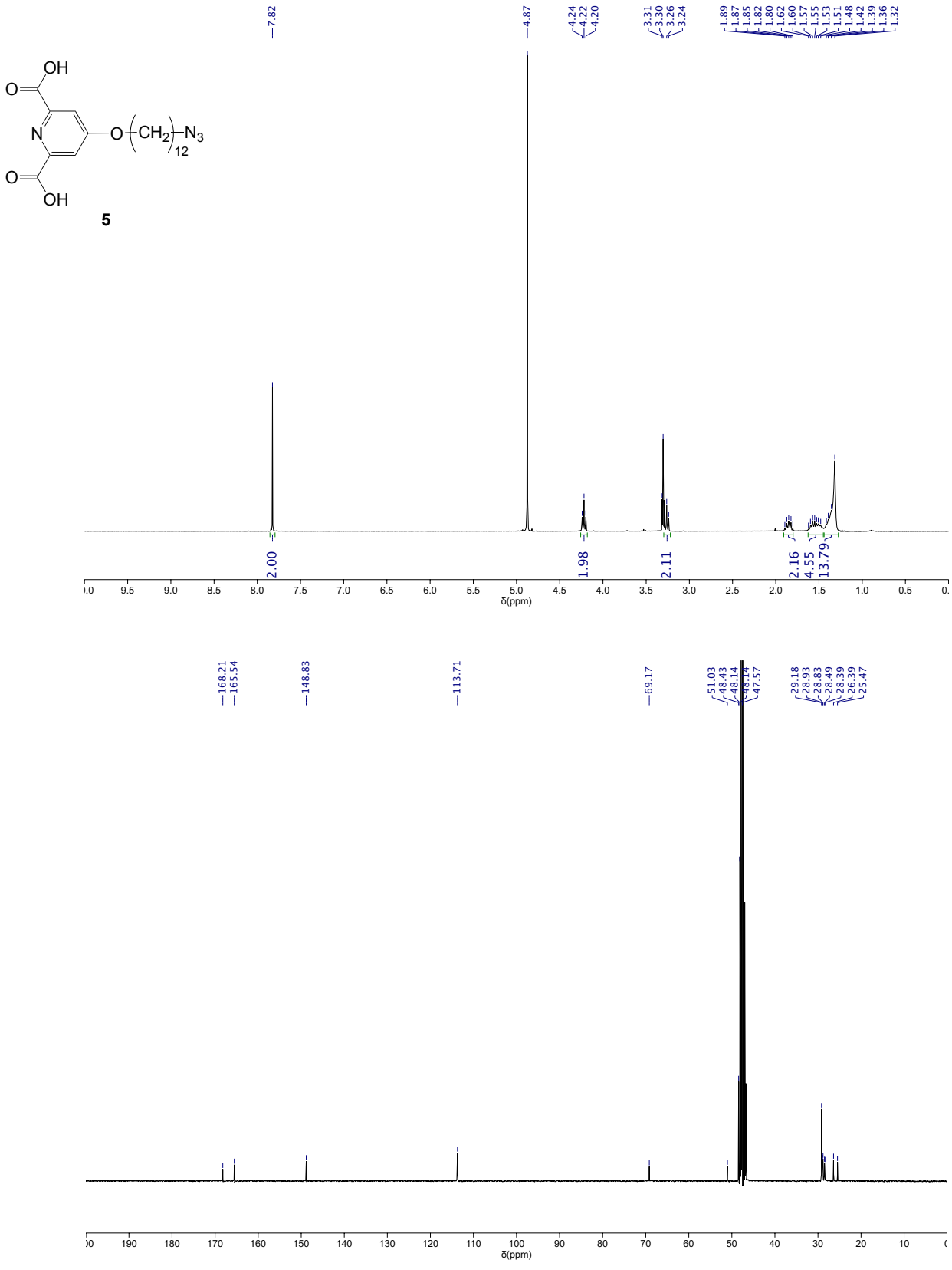


Figure S2. ^{1}H and ^{13}C NMR spectra of **5** in methanol-d_4.

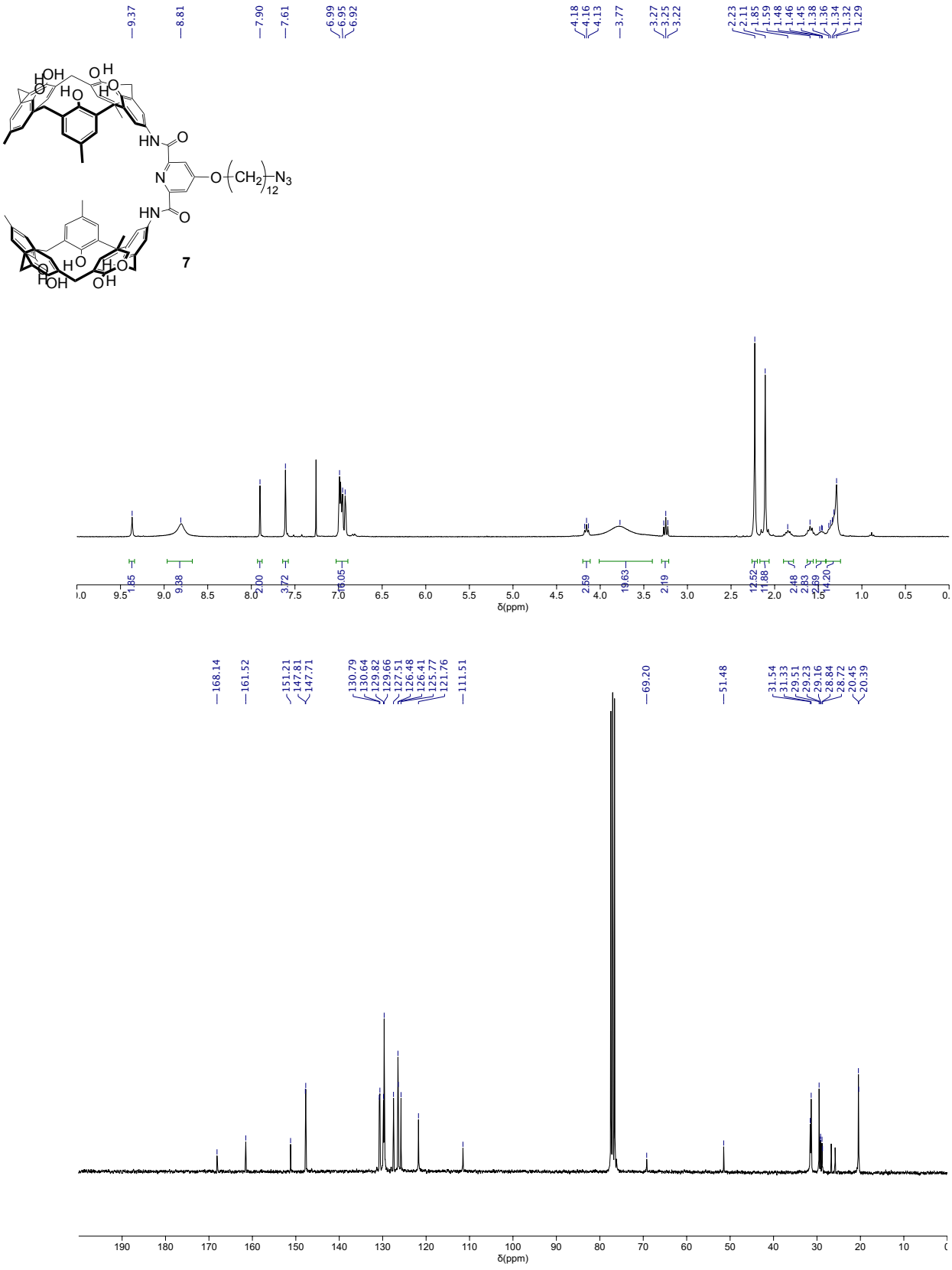


Figure S3. ^{1}H and ^{13}C NMR spectra of **7** in chloroform-*d*.

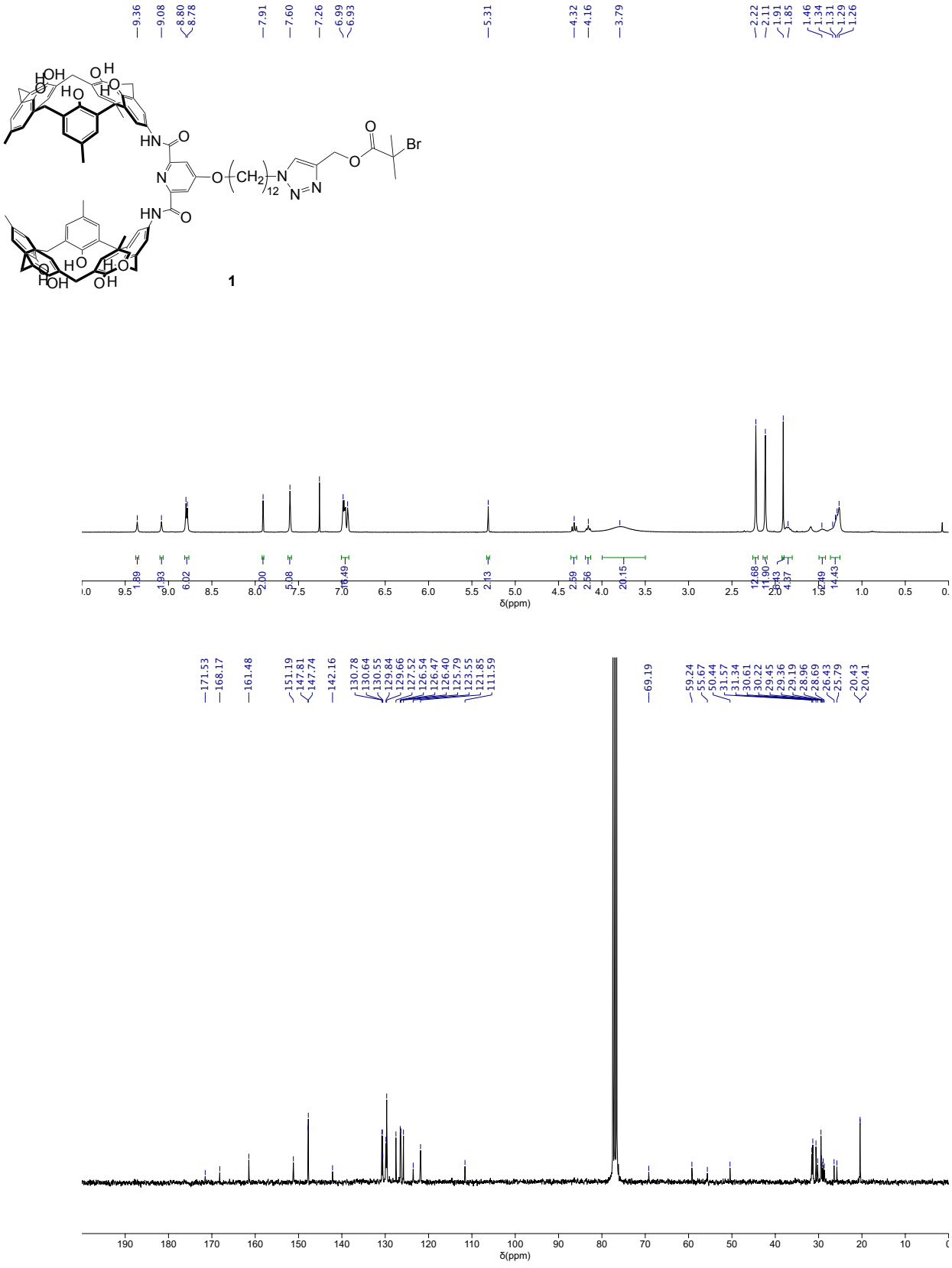


Figure S4. ^{1}H and ^{13}C NMR spectra of **1** in chloroform-*d*.

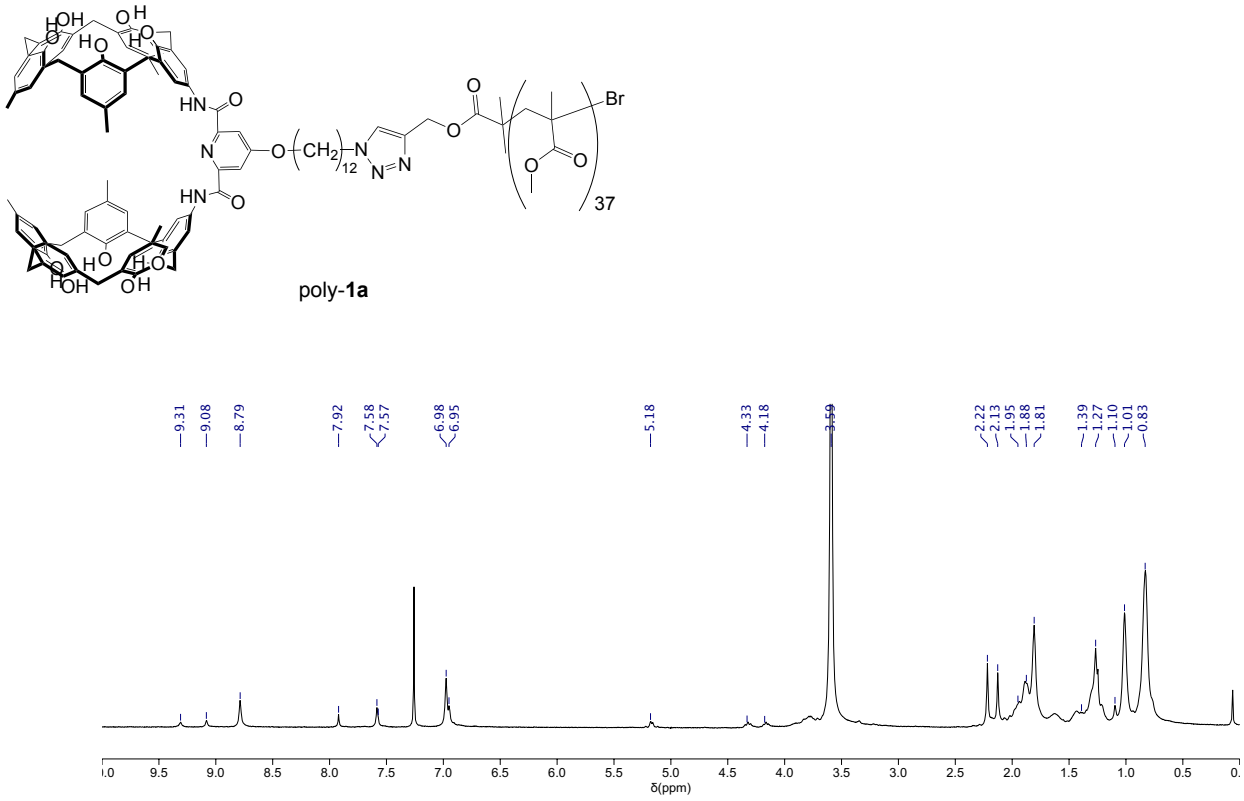


Figure S5. ^{1}H NMR spectrum of poly-**1a** in chloroform-*d*.

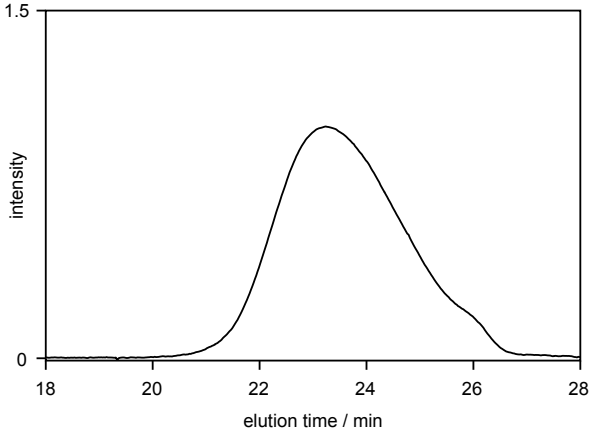


Figure S6. Size-exclusion chromatogram of poly-**1a** (eluent: chloroform).

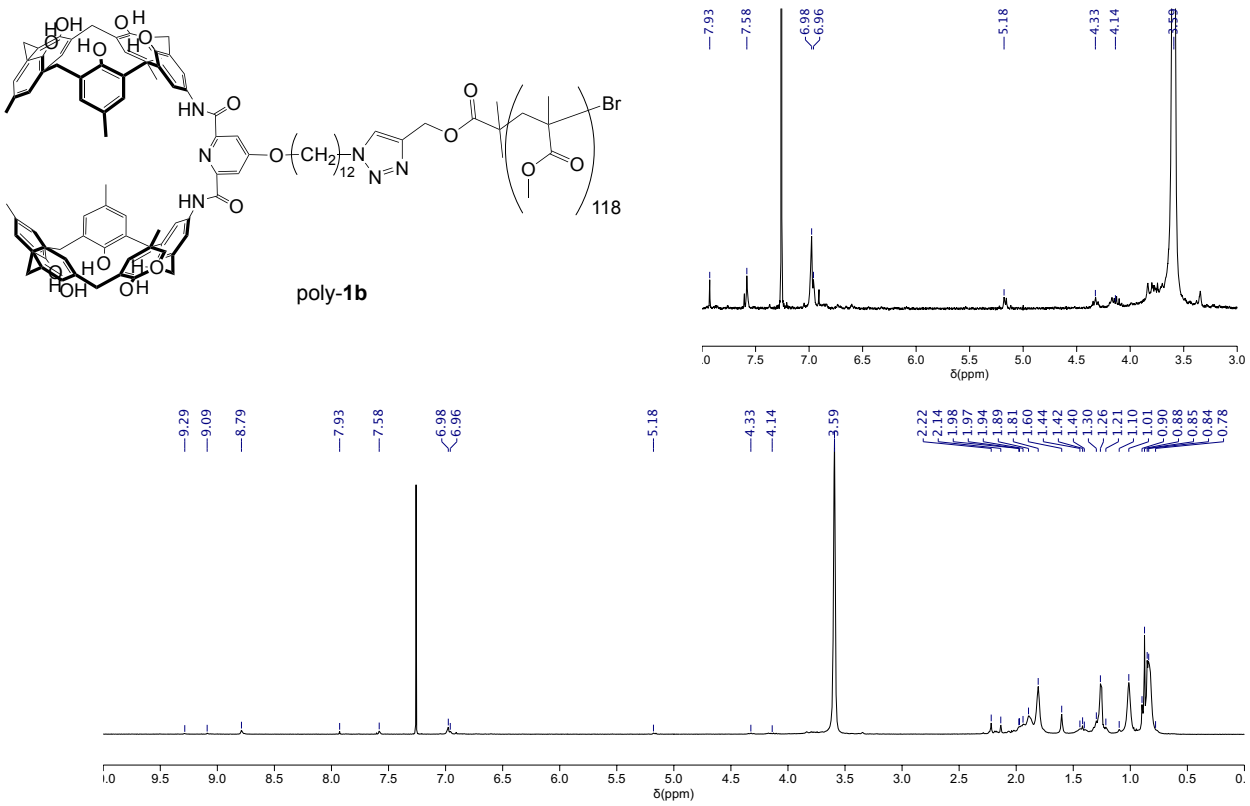


Figure S7. ^{1}H NMR spectrum of poly-**1b** in chloroform-*d*.

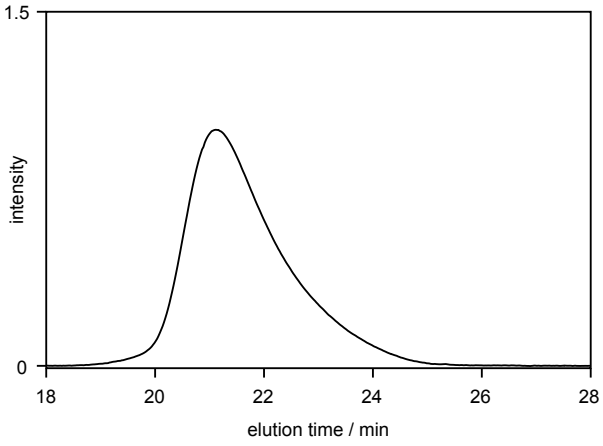


Figure S8. Size-exclusion chromatogram of poly-**1b** (eluent: chloroform).

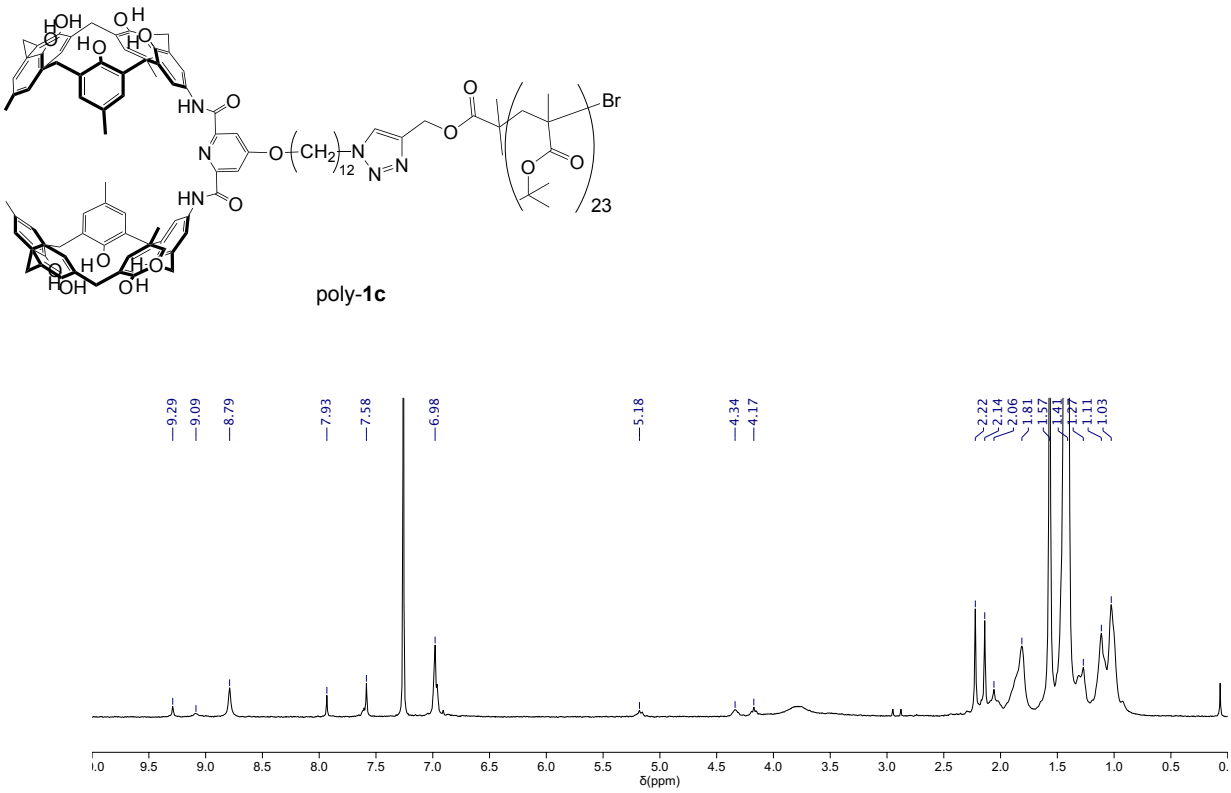


Figure S9. ^{1}H NMR spectrum of poly-**1c** in chloroform-*d*.

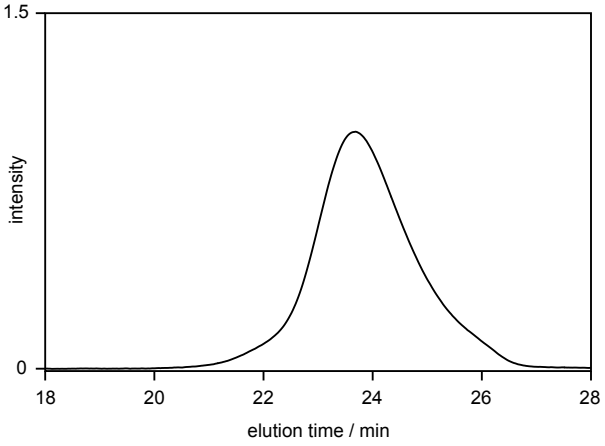


Figure S10. Size-exclusion chromatogram of poly-**1c** (eluent: chloroform).

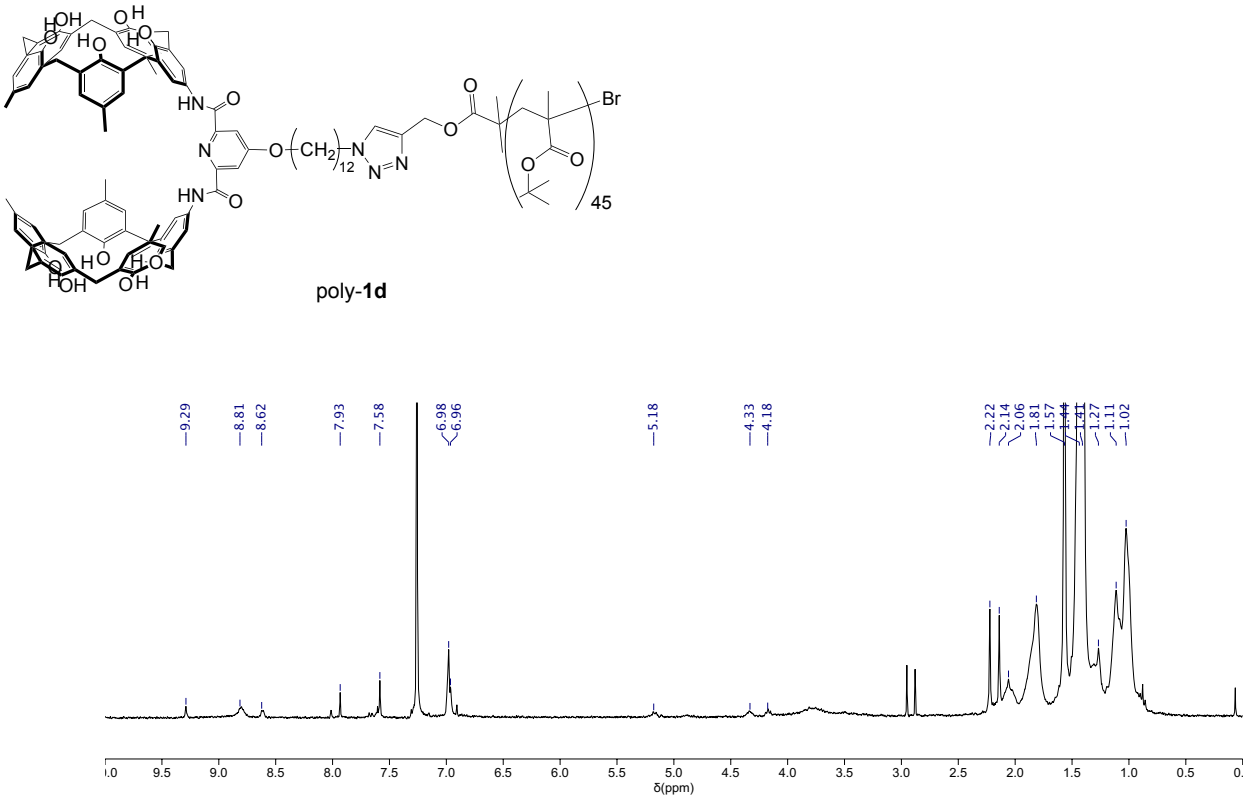


Figure S11. ^{1}H NMR spectrum of poly-**1d** in chloroform-*d*.

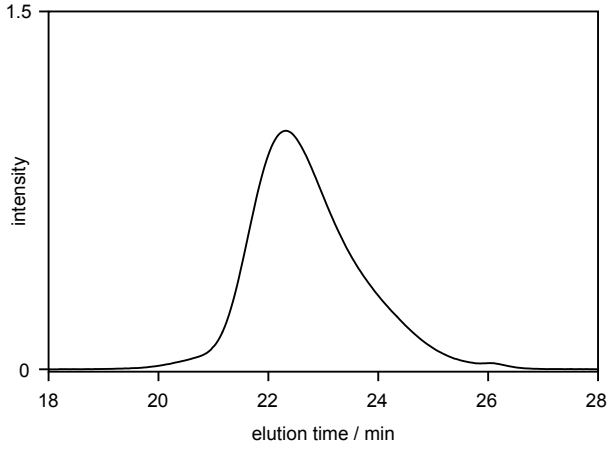


Figure S12. Size-exclusion chromatogram of poly-**1d** (eluent: chloroform).

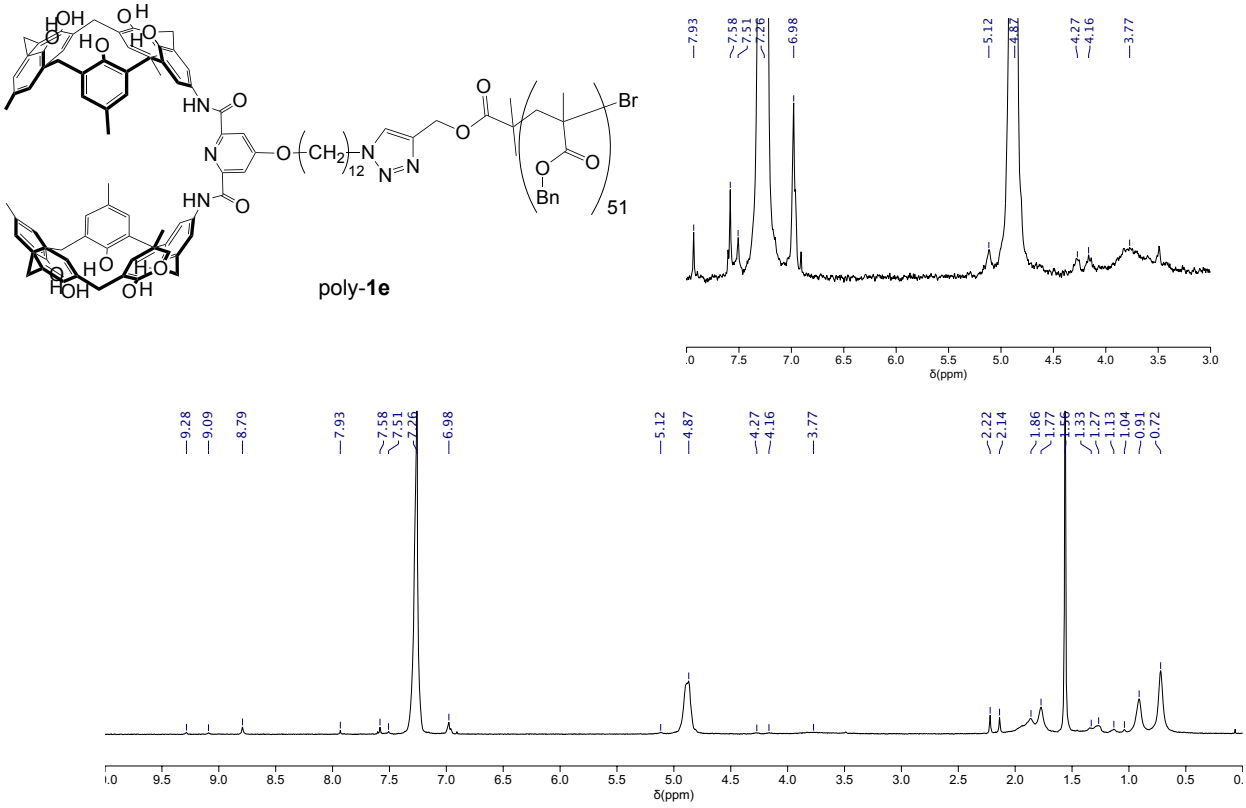


Figure S13. ^{1}H NMR spectrum of poly-**1e** in chloroform-*d*.

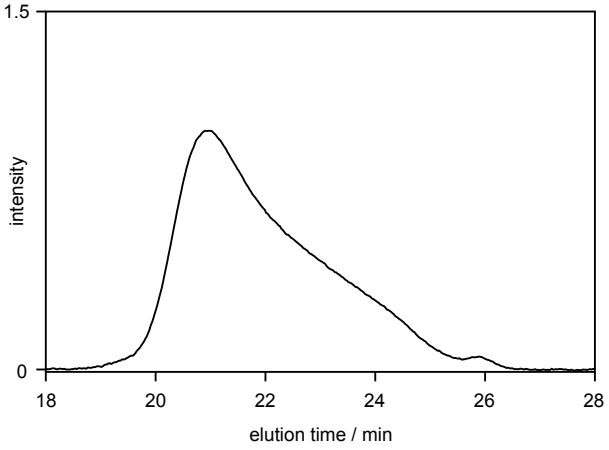


Figure S14. Size-exclusion chromatogram of poly-**1e** (eluent: chloroform).

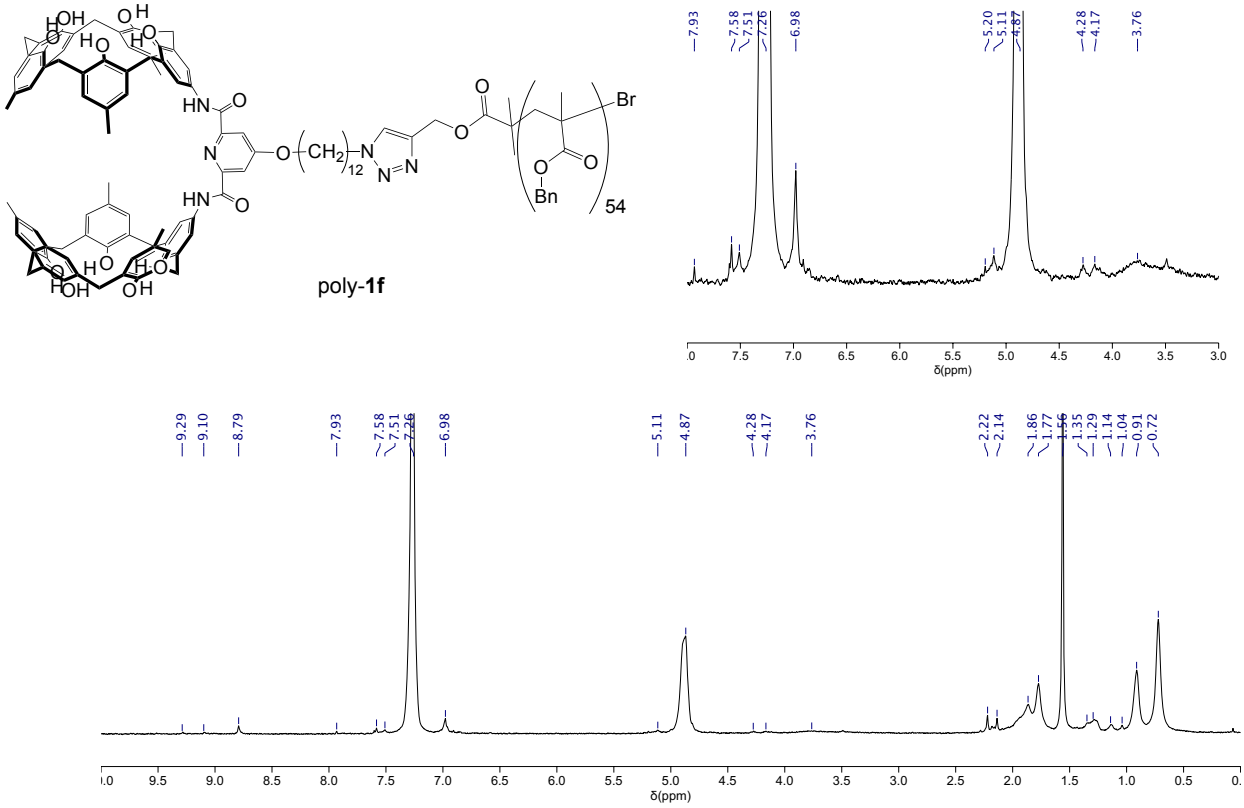


Figure S15. ^{1}H NMR spectrum of poly-**1f** in chloroform-*d*.

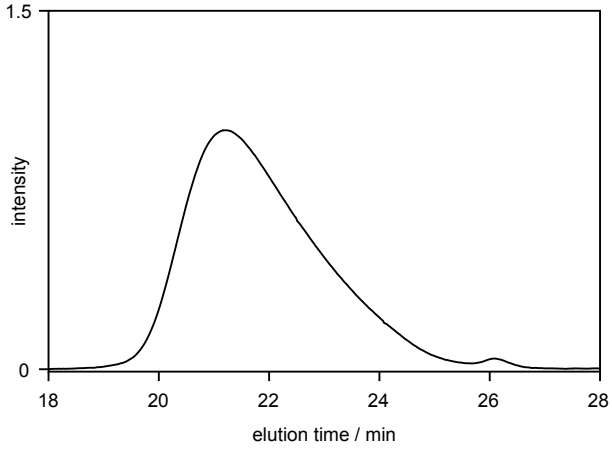


Figure S16. Size-exclusion chromatogram of poly-**1f** (eluent: chloroform).

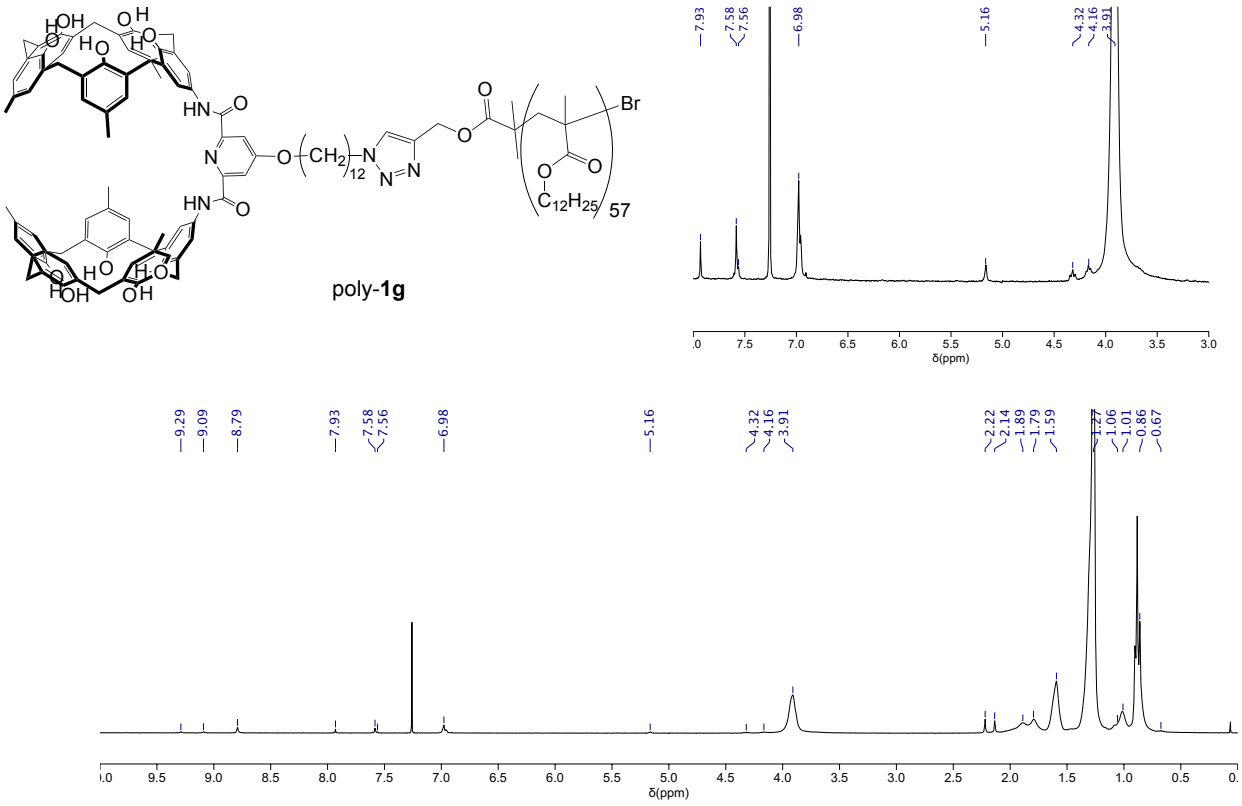


Figure S17. ^{1}H NMR spectrum of poly-**1g** in chloroform-*d*.

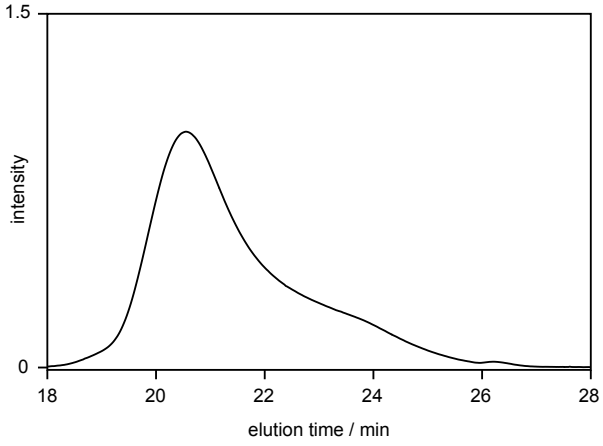


Figure S18. Size-exclusion chromatogram of poly-**1g** (eluent: chloroform).

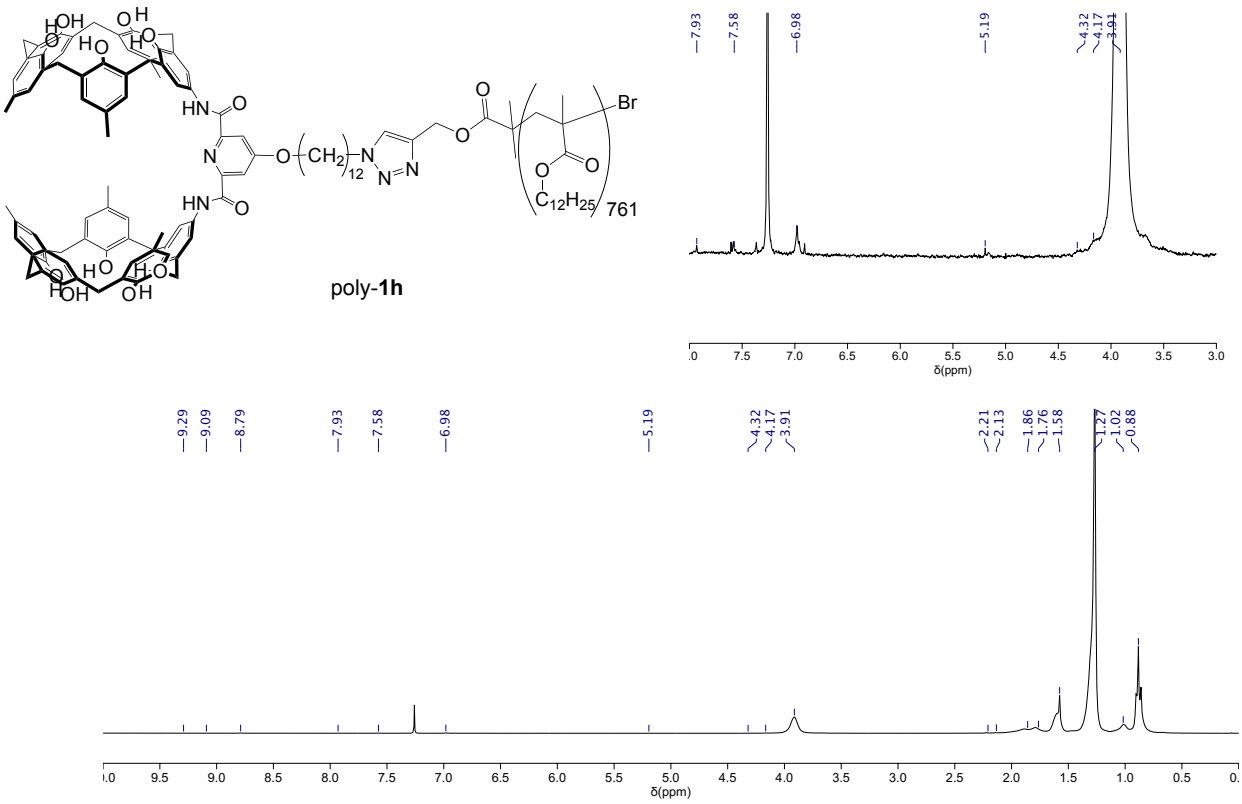


Figure S19. ^{1}H NMR spectrum of poly-**1h** in chloroform-*d*.

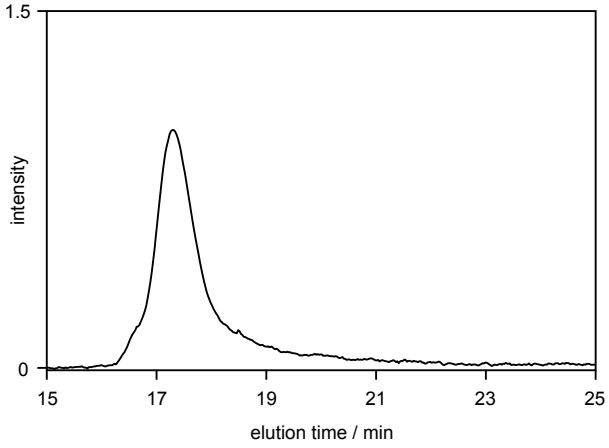
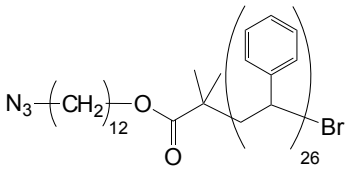


Figure S20. Size-exclusion chromatogram of poly-**1h** (eluent: chloroform).



poly-**9**

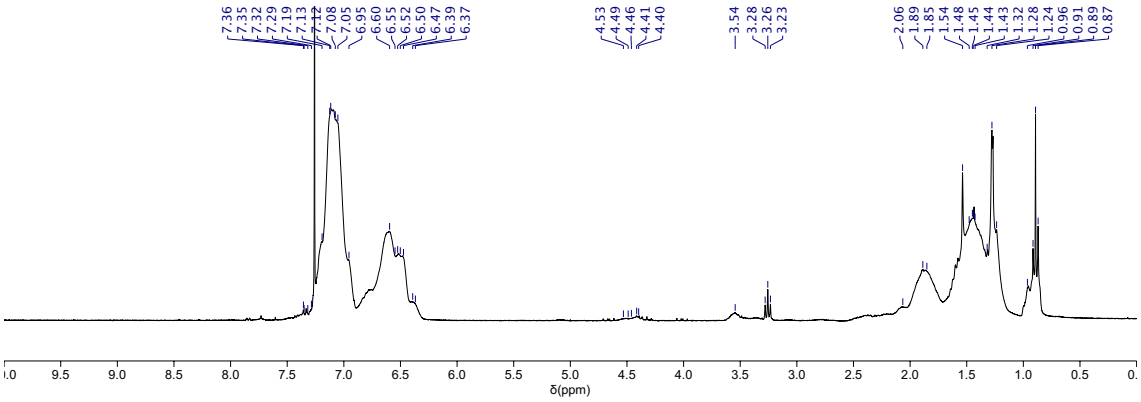


Figure S21. ^{1}H NMR spectrum of poly-**9** in chloroform-*d*.

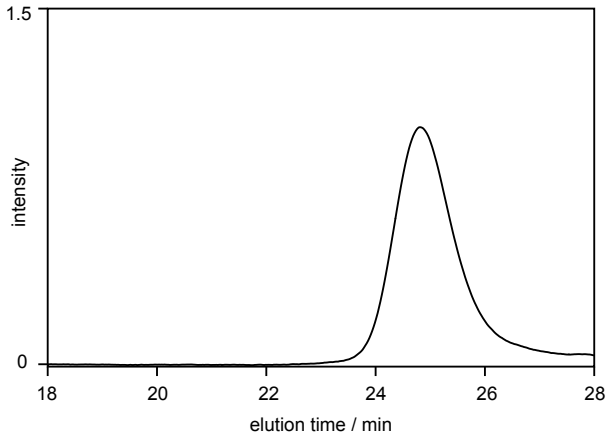


Figure S22. Size-exclusion chromatogram of poly-**9** (eluent: chloroform).

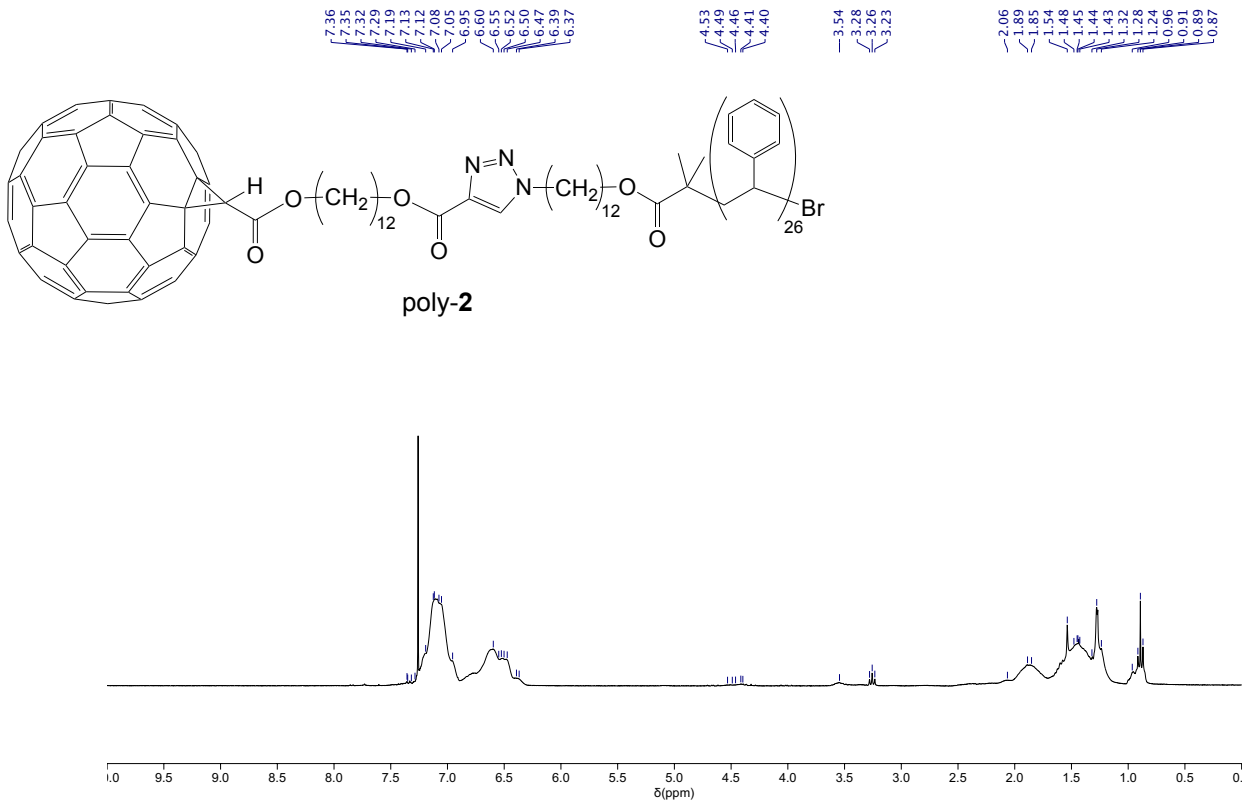


Figure S23. ^{1}H NMR spectrum of poly-**2** in chloroform-*d*.

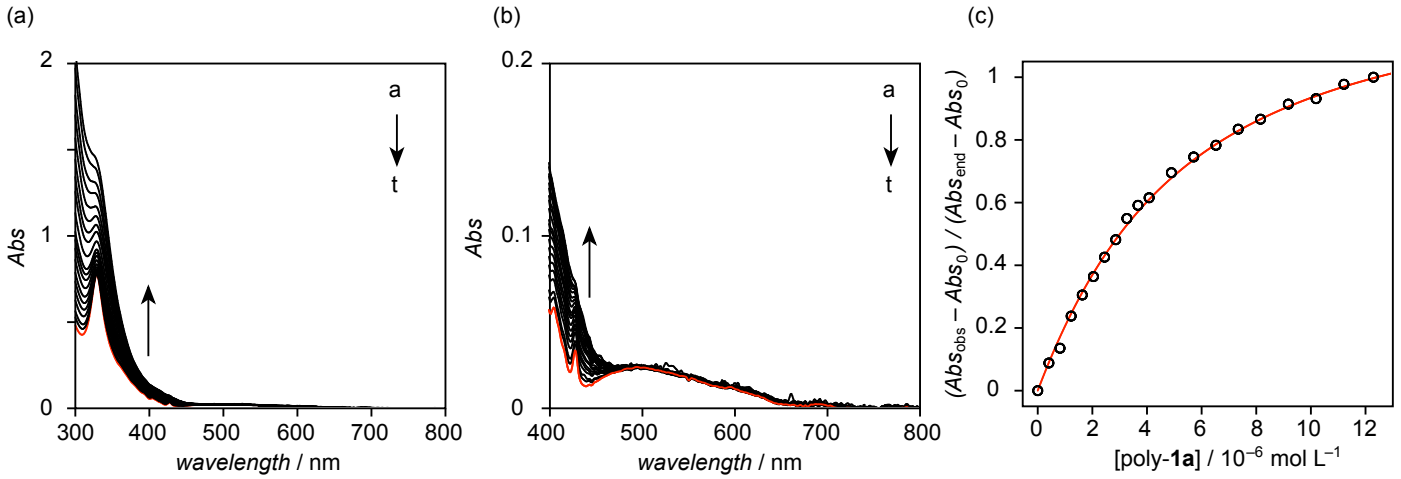


Figure S24. (a) UV/vis absorption spectra of **2** (2.0×10^{-5} mol L^{-1}) and (b) its expanded view upon addition of poly-**1a** at 25 °C in chloroform. The concentrations of poly-**1a** are a–t: 0.0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.8, 5.6, 6.4, 7.2, 8.0, 9.0, 10, 11, 12×10^{-5} mol L^{-1} estimated from its M_n. The red line indicates the absorption spectrum of **2** (2.0×10^{-5} mol L^{-1}). (c) Plot of normalized Δ*Abs* (400 nm) against [poly-**1a**] and the fitting curve obtained by a 1:1 fitting model, where Abs_{obs}, Abs_0, and Abs_{end} denote observed *Abs* at each concentration, *Abs* of poly-**1a**, and *Abs* of poly-**1a** in the presence of **2** (12×10^{-5} mol L^{-1}), respectively.

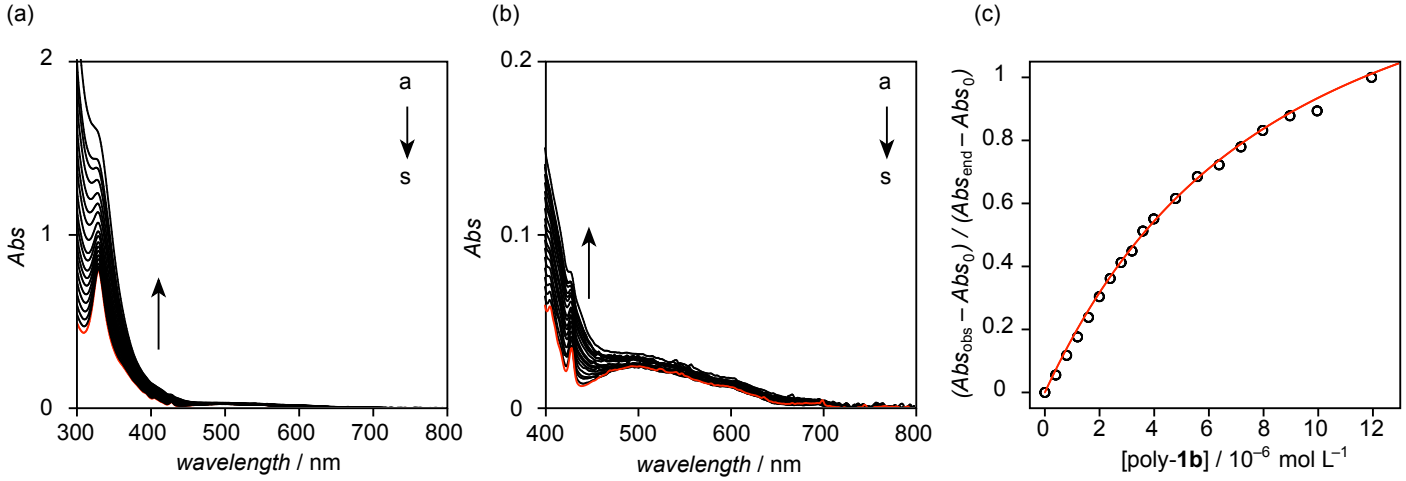


Figure S25. (a) UV/vis absorption spectra of **2** (2.0×10^{-5} mol L^{-1}) and (b) its expanded view upon addition of poly-**1b** at 25 °C in chloroform. The concentrations of poly-**1b** are a–s: 0.0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.8, 5.6, 6.4, 7.2, 8.0, 9.0, 10, 12×10^{-5} mol L^{-1} estimated from its M_n. The red line indicates the absorption spectrum of **2** (2.0×10^{-5} mol L^{-1}). (c) Plot of normalized Δ*Abs* (400 nm) against [poly-**1b**] and the fitting curve obtained by a 1:1 fitting model, where Abs_{obs}, Abs_0, and Abs_{end} denote observed *Abs* at each concentration, *Abs* of poly-**1b**, and *Abs* of poly-**1b** in the presence of **2** (12×10^{-5} mol L^{-1}), respectively.

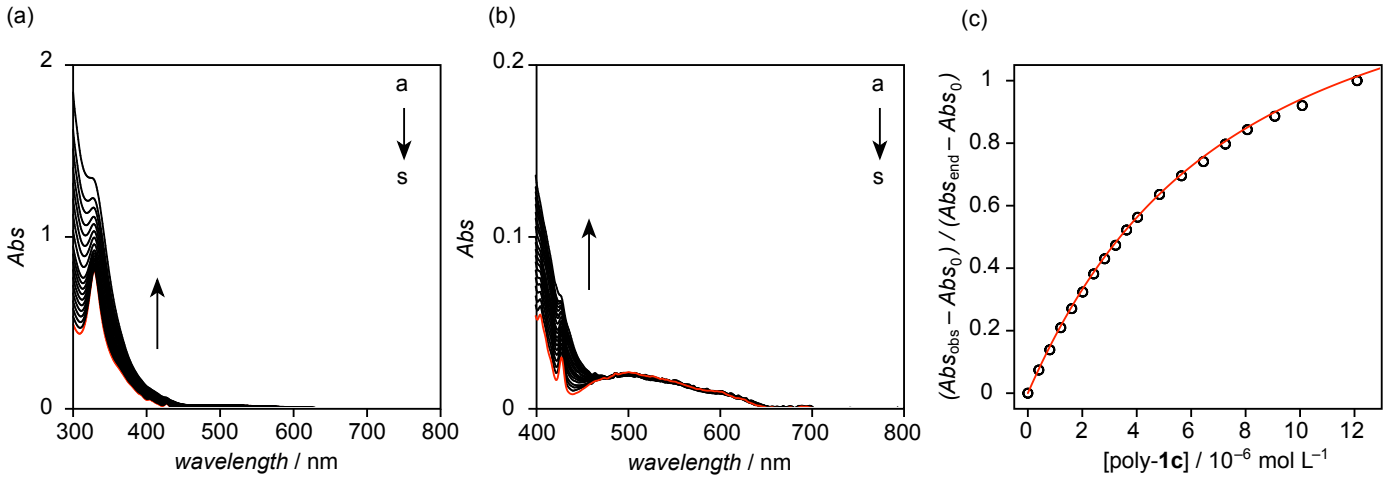


Figure S26. (a) UV/vis absorption spectra of **2** (2.0×10^{-5} mol L^{-1}) and (b) its expanded view upon addition of poly-**1c** at 25 °C in chloroform. The concentrations of poly-**1c** are a–s: 0.0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.8, 5.6, 6.4, 7.2, 8.0, 9.0, 10, 12×10^{-5} mol L^{-1} estimated from its M_n. The red line indicates the absorption spectrum of **2** (2.0×10^{-5} mol L^{-1}). (c) Plot of normalized Δ*Abs* (400 nm) against [poly-**1c**] and the fitting curve obtained by a 1:1 fitting model, where Abs_{obs}, Abs_0, and Abs_{end} denote observed *Abs* at each concentration, *Abs* of poly-**1c**, and *Abs* of poly-**1c** in the presence of **2** (12×10^{-5} mol L^{-1}), respectively.

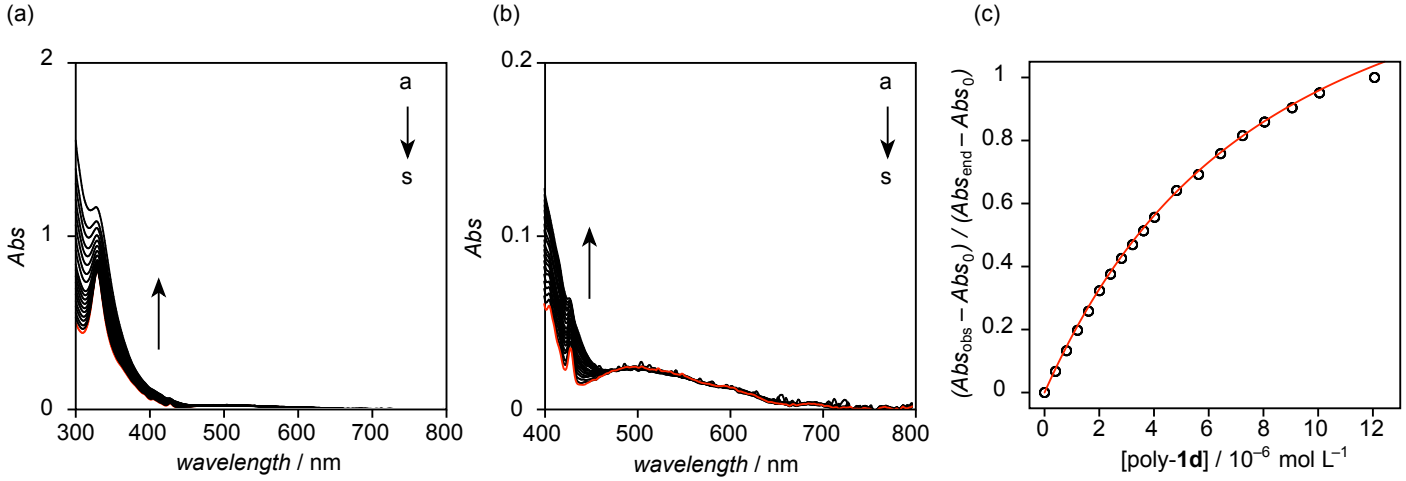


Figure S27. (a) UV/vis absorption spectra of **2** (2.0×10^{-5} mol L^{-1}) and (b) its expanded view upon addition of poly-**1d** at 25 °C in chloroform. The concentrations of poly-**1d** are a–s: 0.0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.8, 5.6, 6.4, 7.2, 8.0, 9.0, 10, 12×10^{-5} mol L^{-1} estimated from its M_n. The red line indicates the absorption spectrum of **2** (2.0×10^{-5} mol L^{-1}). (c) Plot of normalized Δ*Abs* (400 nm) against [poly-**1d**] and the fitting curve obtained by a 1:1 fitting model, where Abs_{obs}, Abs_0, and Abs_{end} denote observed *Abs* at each concentration, *Abs* of poly-**1d**, and *Abs* of poly-**1d** in the presence of **2** (12×10^{-5} mol L^{-1}), respectively.

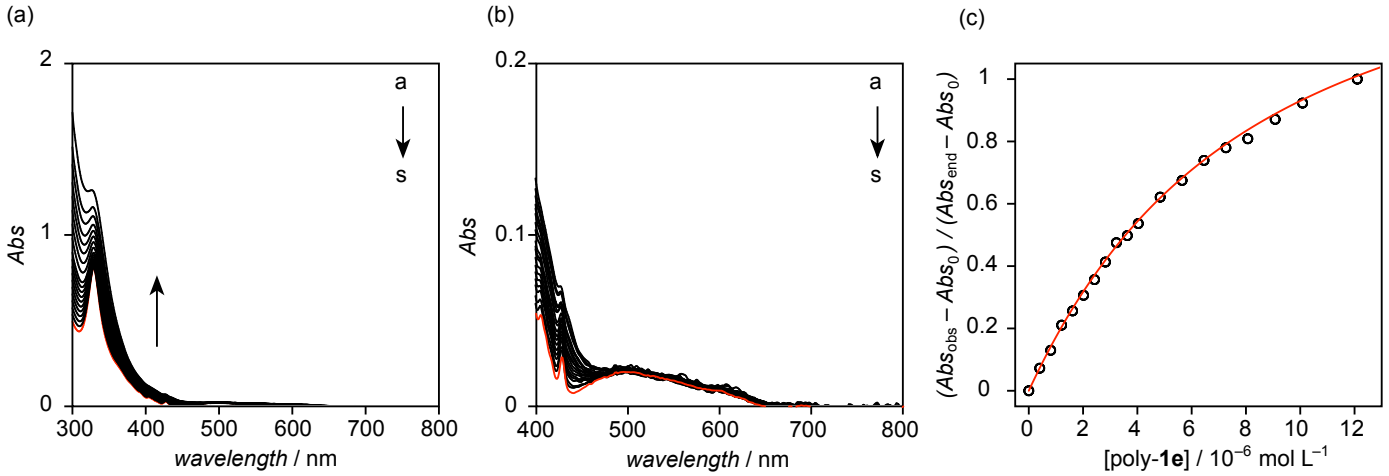


Figure S28. (a) UV/vis absorption spectra of **2** (2.0×10^{-5} mol L^{-1}) and (b) its expanded view upon addition of poly-**1e** at 25 °C in chloroform. The concentrations of poly-**1e** are a–s: 0.0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.8, 5.6, 6.4, 7.2, 8.0, 9.0, 10, 11, 12×10^{-5} mol L^{-1} estimated from its M_n. The red line indicates the absorption spectrum of **2** (2.0×10^{-5} mol L^{-1}). (c) Plot of normalized ΔAbs (400 nm) against [poly-**1e**] and the fitting curve obtained by a 1:1 fitting model, where Abs_{obs}, Abs_0, and Abs_{end} denote observed *Abs* at each concentration, *Abs* of poly-**1e**, and *Abs* of poly-**1e** in the presence of **2** (12×10^{-5} mol L^{-1}), respectively.

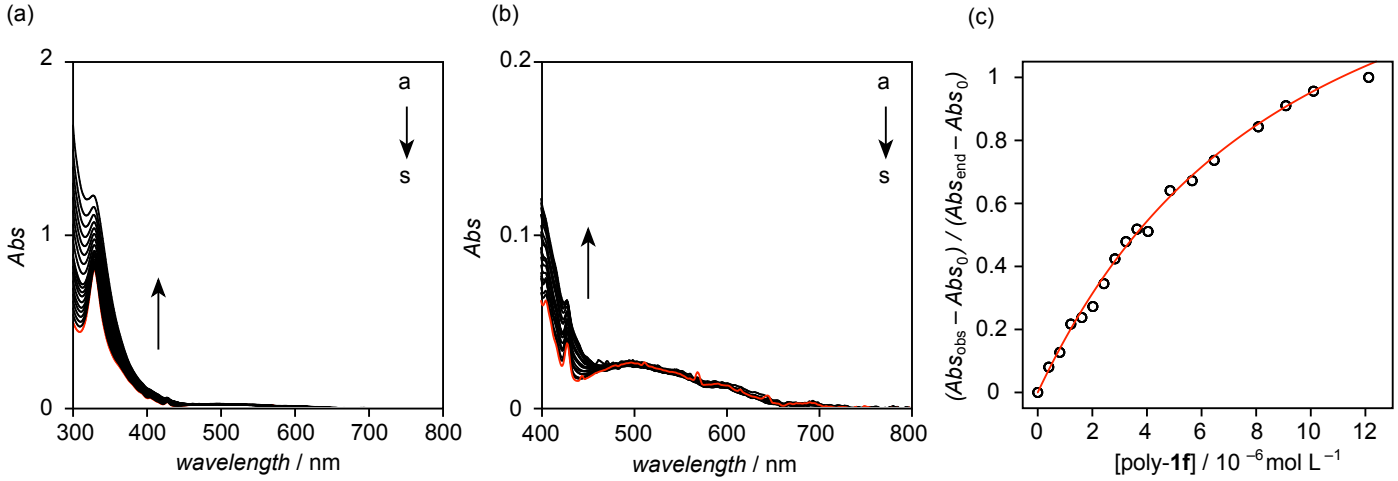


Figure S29. (a) UV/vis absorption spectra of **2** (2.0×10^{-5} mol L^{-1}) and (b) its expanded view upon addition of poly-**1f** at 25 °C in chloroform. The concentrations of poly-**1f** are a–s: 0.0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.8, 5.6, 6.4, 7.2, 8.0, 9.0, 10, 12×10^{-5} mol L^{-1} estimated from its M_n. The red line indicates the absorption spectrum of **2** (2.0×10^{-5} mol L^{-1}). (c) Plot of normalized ΔAbs (400 nm) against [poly-**1f**] and the fitting curve obtained by a 1:1 fitting model, where Abs_{obs}, Abs_0, and Abs_{end} denote observed *Abs* at each concentration, *Abs* of poly-**1f**, and *Abs* of poly-**1f** in the presence of **2** (12×10^{-5} mol L^{-1}), respectively.

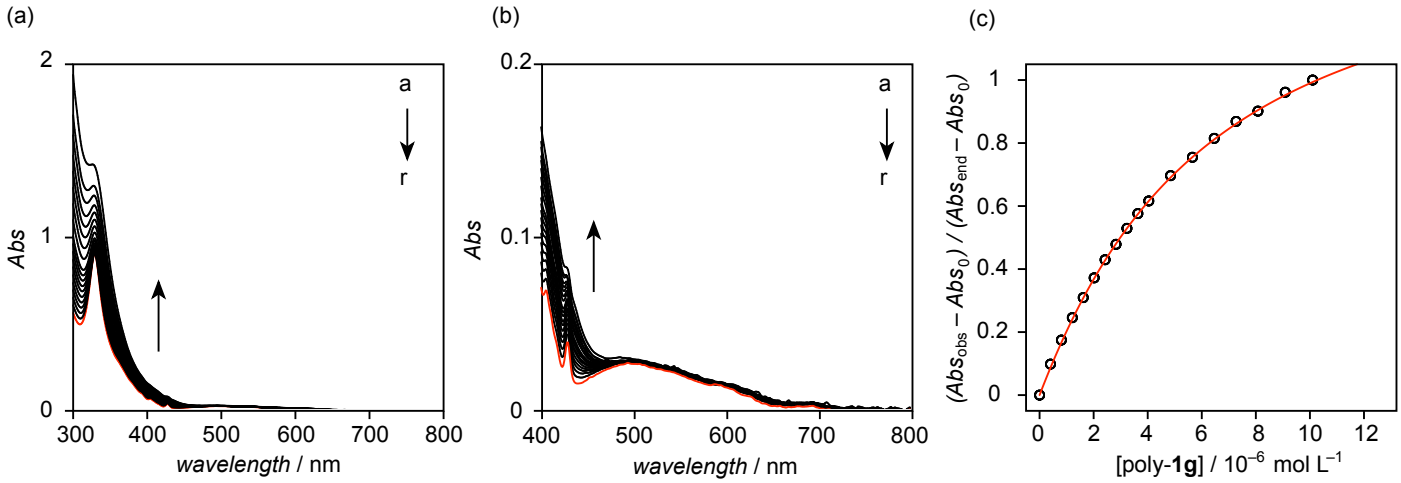


Figure S30. (a) UV/vis absorption spectra of **2** (2.0×10^{-5} mol L^{-1}) and (b) its expanded view upon addition of poly-**1g** at 25 °C in chloroform. The concentrations of poly-**1g** are a–r: 0.0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.8, 5.6, 6.4, 7.2, 8.0, 9.0, 10×10^{-5} mol L^{-1} estimated from its M_n. The red line indicates the absorption spectrum of **2** (2.0×10^{-5} mol L^{-1}). (c) Plot of normalized ΔAbs (400 nm) against [poly-**1g**] and the fitting curve obtained by a 1:1 fitting model, where Abs_{obs}, Abs_0, and Abs_{end} denote observed *Abs* at each concentration, *Abs* of poly-**1g**, and *Abs* of poly-**1g** in the presence of **2** (10×10^{-5} mol L^{-1}), respectively.

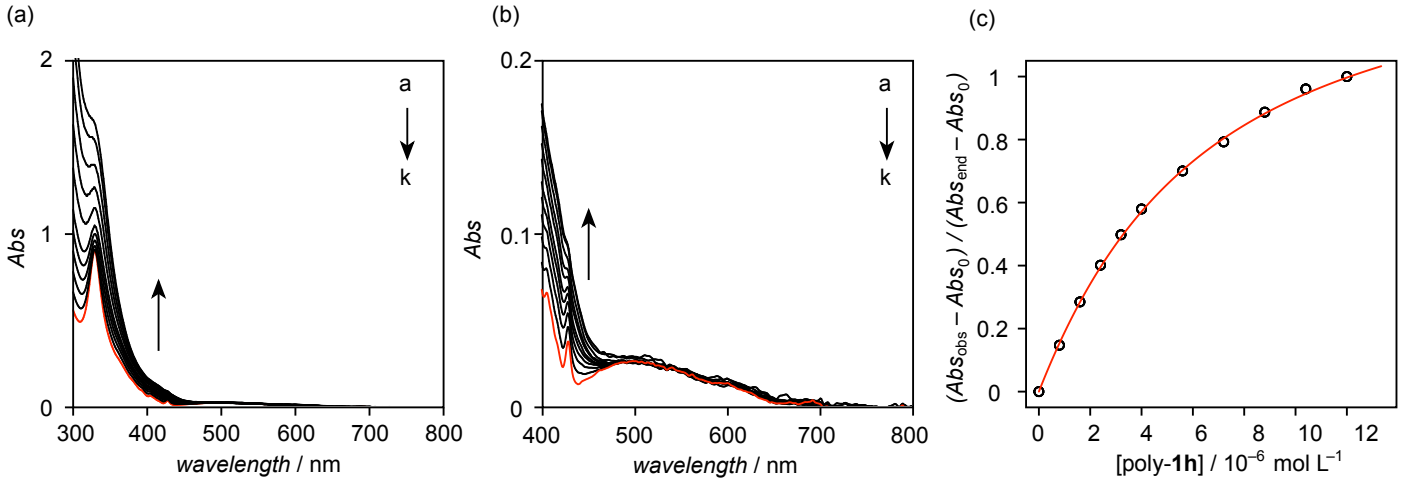


Figure S31. (a) UV/vis absorption spectra of **2** (2.0×10^{-5} mol L^{-1}) and (b) its expanded view upon addition of poly-**1h** at 25 °C in chloroform. The concentrations of poly-**1h** are a–k: 0.0, 0.8, 1.6, 2.4, 3.2, 4.0, 5.6, 7.2, 8.8, 10, 12×10^{-5} mol L^{-1} estimated from its M_n. The red line indicates the absorption spectrum of **2** (2.0×10^{-5} mol L^{-1}). (c) Plot of normalized ΔAbs (400 nm) against [poly-**1h**] and the fitting curve obtained by a 1:1 fitting model, where Abs_{obs}, Abs_0, and Abs_{end} denote observed *Abs* at each concentration, *Abs* of poly-**1h**, and *Abs* of poly-**1h** in the presence of **2** (12×10^{-5} mol L^{-1}), respectively.

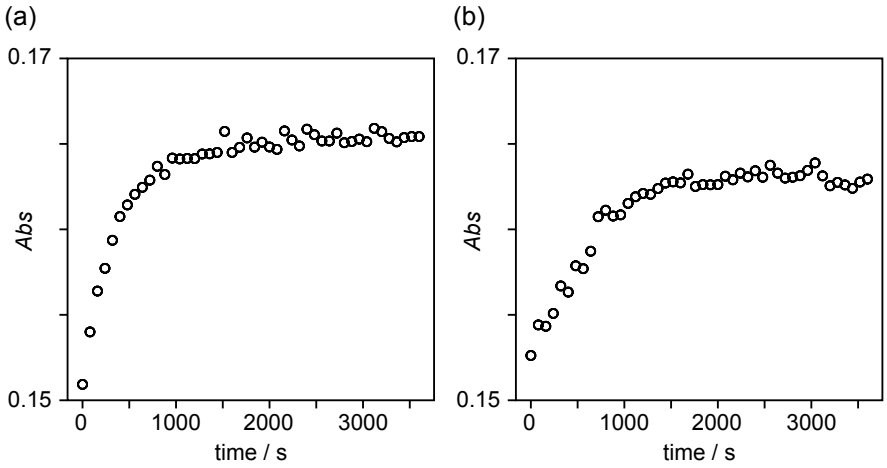


Figure S32. Time-dependent changes in the absorbance value at 427 nm seen in (a) an equimolar mixture of **1** and **2**, and (b) an equimolar mixture of poly-**1b** and **2**. The initial concentration of **1**, **2** and poly-**1b** is 2.0×10^{-5} mol L^{-1}.

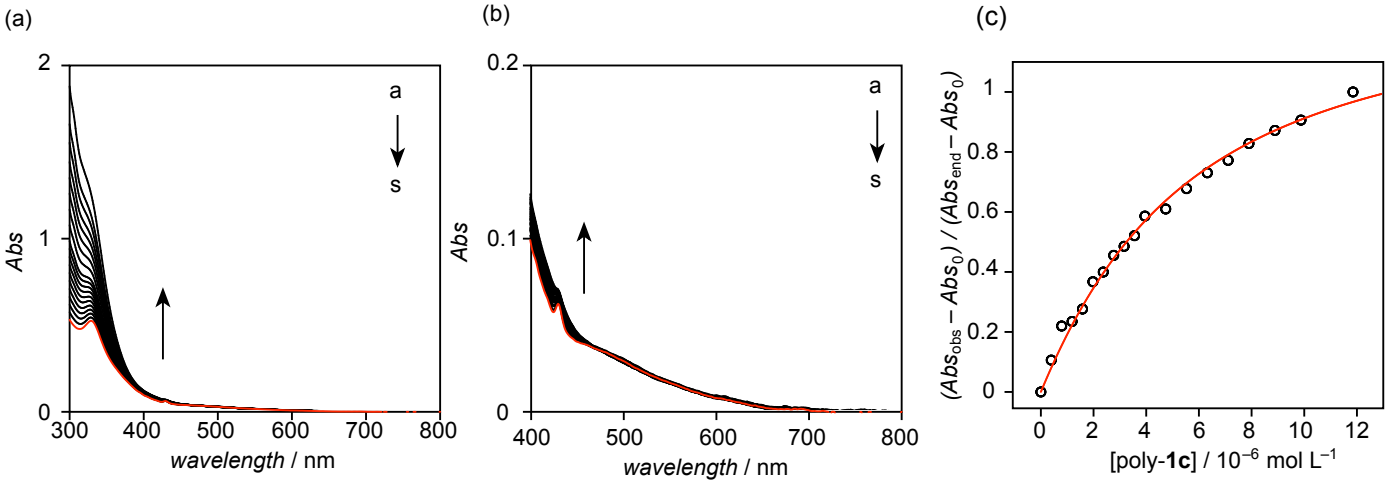


Figure S33. (a) UV/vis absorption spectra of poly-**2** (2.0×10^{-5} mol L^{-1}) and (b) its expanded view upon addition of poly-**1c** at 25 °C in toluene. The concentrations of poly-**1c** are a–s: 0.0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.5, 4.0, 4.7, 5.5, 6.4, 7.1, 8.0, 8.9, 10, 12 × 10^{-5} mol L^{-1} estimated from its M_n. The red line indicates the absorption spectrum of poly-**2** (2.0×10^{-5} mol L^{-1}). (c) Plot of normalized ΔAbs (400 nm) against [poly-**1c**] and the fitting curve obtained by a 1:1 fitting model, where Abs_{obs}, Abs_0, and Abs_{end} denote observed *Abs* at each concentration, *Abs* of poly-**1c**, and *Abs* of poly-**1c** in the presence of poly-**2** (12×10^{-5} mol L^{-1}), respectively.