

## Supporting Information For:

# A Supramolecular Approach to Polymer-Shape Transformation via Calixarene-Fullerene Complexation

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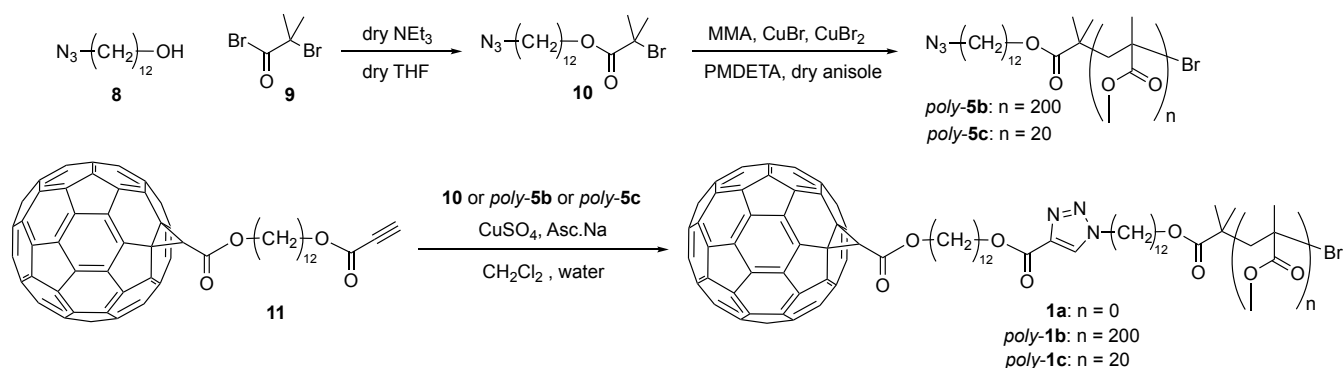
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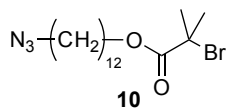
## General

All reagents and solvents were commercial reagent grade and were used without further purification unless otherwise noted. Dry anisole and dry triethylamine (NEt<sub>3</sub>) were obtained by distillation over CaH<sub>2</sub>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian mercury-300 spectrometer, and chemical shifts were reported on the delta scale in ppm relative to residual chloroform ( $\delta$  = 7.26 and 77.0 for <sup>1</sup>H and <sup>13</sup>C, respectively). UV/vis absorption spectra were recorded on a JASCO V-560 spectrometer. DOSY experiments were carried out on JEOL JNM-ECA500 spectrometer. Fluorescence spectra were recorded on a JASCO FP-6500 spectrometer. High resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL hybrid FTMS by electron spray ionization (ESI) methods. Melting points (M.p.) were measured with a Yanagimoto micro melting point apparatus. Infrared (IR) spectra were recorded on a JASCO FT/IR-4600 spectrometer with ZeSe ATR accessory. Solution viscosity were recorded on Anton Paar Microviscometer Lovis 2000ME. Dynamic light scattering (DLS) measurements were carried out using a Zetasizer Nano ZS (Malvern Instruments) setup equip with He-Ne laser (633 nm, 40 mW power), and the scattering angle was 173° in 10 × 10 mm glass cuvette. Differential scanning calorimetry (DSC) curves were recorded on SEIKO INSTRUMENTS Inc. EXSTAR6000 DSC6200 under a nitrogen atmosphere at the heating rate of 15 °C / min. The specimens were sealed in an aluminum pan. Preparative separations were performed by silica gel gravity column chromatography (Silica Gel 60 N (spherical, neutral)). Recycling preparative GPC-HPLC separations were carried out on JAI LC-908s using preparative JAIGEL-2H, 2H, 1H columns in series. Size exclusion chromatogram was recorded on Shimadzu LC-20AC with CTO-20AC accessory and TOSOH UV-8011 detector using preparative Shodex GPC-K-804, K-803, K-802.5 columns in series. The number-average molecular weights (*M<sub>n</sub>*) of the poly methyl methacrylates (PMMAs) were determined by the size exclusion chromatography (SEC) based on polystyrene standards in chloroform. Previously synthesized **2**<sup>[1]</sup> and **3**<sup>[1]</sup> were used for this work. **4**<sup>[2]</sup>, **8**<sup>[3]</sup>, **11**<sup>[4]</sup>, **12**<sup>[5]</sup>, and **13**<sup>[6]</sup> were synthesized according to reported methods.

## Synthesis



**Scheme S1.** Synthesis of **1a**, **poly-1b**, and **poly-1c**. THF = tetrahydrofuran, MMA = methyl methacrylate, PMDETA = *N,N,N',N'',N'''*-pentamethyldiethylenetriamine, Asc.Na = sodium ascorbate.

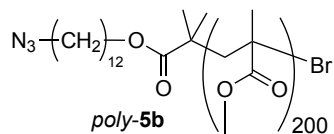


Synthesis of 2-bromo-2-methyl-propionic acid 12-azido-dodecyl ester (**10**):

To a solution of **8** (5.16 g, 22.7 mmol) and dry NEt<sub>3</sub> (3.50 mL, 25.0 mmol) in dry THF (65 mL) was added **9** (3.09 mL, 25.0 mmol, *TOKYO CHEMICAL INDUSTRY CO., LTD., JAPAN*, 98 %) dropwise with stirring at 0 °C under an argon atmosphere. After being stirred for 1 h at 0 °C, the reaction mixture allowed to warm gradually to room temperature. The reaction mixture was further stirred for 12 h at room temperature under an argon atmosphere. The resulting mixture was extracted with ethylacetate. The organic layer was washed with saturated aqueous NaHCO<sub>3</sub>, saturated aqueous NaCl, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (0-10 % ethylacetate in *n*-hexane, eluent) gave desired product **10** as colorless oil (7.85 g, 92 %).

Compound data for **10**:

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 4.16 (*t*, *J* = 6.8 Hz, 2H), 3.25 (*t*, *J* = 6.8 Hz, 2H), 1.93 (*s*, 6H), 1.61–1.73 (*m*, 2H), 1.51–1.64 (*m*, 2H), 1.23–1.45 (*m*, 16H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 171.7, 66.1, 56.0, 51.5, 30.8, 29.4, 29.1, 28.8, 28.3, 26.7, 25.8 ppm; FTIR-ATR (neat): ν 2927, 2855, 2094, 1735, 1464, 1386, 1370, 1349, 1275, 1163, 1108, 1012, 982, 923 cm<sup>-1</sup>; HRMS (ESI<sup>+</sup>) calcd for C<sub>40</sub>H<sub>44</sub>N<sub>2</sub>O<sub>10</sub>Na *m/z* 398.14136 [M+Na]<sup>+</sup>, found *m/z* 398.14212.

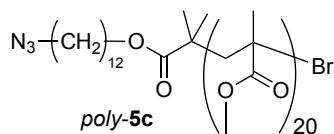


Synthesis of 2-[PMMA]<sub>200</sub>-2-methyl-propionic acid 12-azido-dodecyl ester *poly-5b*:

**10** (177 mg, 0.469 mmol), dry anisole (10 mL), and methyl methacrylate (MMA) (10.0 mL, 93.9 mmol, *Nacalai Tesque, Inc., JAPAN*, ≥99%) were placed in Schlenk-flask. After three cycles of freeze-pump-thaw, CuBr (23.5 mg, 0.164 mmol), CuBr<sub>2</sub> (15.7 mg, 0.0704 mmol), and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA) (48.9 μL, 0.235 mmol) were added in sequence to the resulting solution under a nitrogen atmosphere. After being stirred for 6 h in the dark at 65 °C, the resulting mixture was further stirred for 1 h at room temperature under an open-air atmosphere. The resulting mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, passed through aluminum oxide 90 (CH<sub>2</sub>Cl<sub>2</sub>, eluent), and then concentrated *in vacuo*. The crude product was purified by reprecipitation from CH<sub>2</sub>Cl<sub>2</sub> solution with methanol to afford desired product *poly-5b* as a white solid (3.59 g, 38 %).

Compound data for *poly-5b*:

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.77 (m, 2H), 3.60 (m, 3H × n), 3.26 (m, 2H), 1.73–2.04 (m, 6H + 2H × n), 1.06–1.47 (m, 20H), 0.76–1.09 (m, 2H × n) ppm; *M*<sub>n,SEC</sub> = 20069 g mol<sup>-1</sup>, PDI = 1.10.

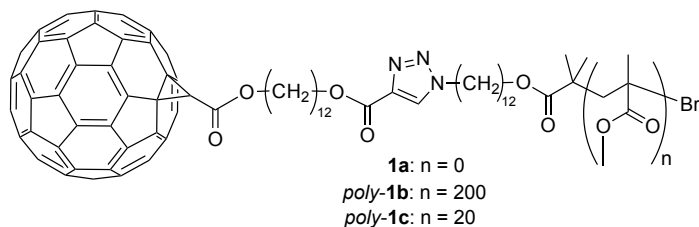


Synthesis of 2-[PMMA]<sub>20</sub>-2-methyl-propionic acid 12-azido-dodecyl ester *poly-5c*:

**10** (180 mg, 0.477 mmol), dry anisole (10 mL), and MMA (1.02 mL, 9.58 mmol, *Nacalai Tesque, Inc., JAPAN*, ≥99%) were placed in Schlenk-flask. After three cycles of freeze-pump-thaw, CuBr (23.9 mg, 0.167 mmol), CuBr<sub>2</sub> (16.0 mg, 0.0716 mmol), and PMDETA (49.8 μL, 0.239 mmol) were added in sequence to the resulting solution under a nitrogen atmosphere. After being stirred for 6 h in the dark at 65 °C, the resulting mixture was further stirred for 1 h at room temperature under an open-air atmosphere. The resulting mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, passed through aluminum oxide 90 (CH<sub>2</sub>Cl<sub>2</sub>, eluent), and then concentrated *in vacuo*. The crude product was purified by reprecipitation from CH<sub>2</sub>Cl<sub>2</sub> solution with methanol to yield desired product *poly-5c* as a white solid (698 mg, 56 %).

Compound data for *poly-5c*:

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.76 (m, 2H), 3.59 (m, 3H × n), 3.26 (m, 2H), 1.74–2.08 (m, 6H + 2H × n), 0.96–1.40 (m, 20H), 0.74–1.00 (m, 2H × n) ppm; *M*<sub>n,SEC</sub> = 2620 g mol<sup>-1</sup>, PDI = 1.23.



#### Synthesis of model fullerene **1a**:

To a solution of **11** (26.5 mg, 26.1  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (5.6 mL) and water (1.9 mL) were added **10** (9.85 mg, 26.1  $\mu\text{mol}$ ), sodium ascorbate (Asc.Na) (5.17 mg, 26.1  $\mu\text{mol}$ ), and  $\text{CuSO}_4$  (4.17 mg, 26.1  $\mu\text{mol}$ ). After being stirred for 48 h at room temperature under an argon atmosphere, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. The crude product was purified by GPC to give desired product **1a** as a brown solid (6.80 mg, 19 %).

**poly-1b** (a brown solid, 29% yield) and **poly-1c** (a brown solid, 31% yield) were synthesized by the same procedure as that used for the synthesis of **1a** using **poly-5b** (1.15g, 57.3  $\mu\text{mol}$ ) and **poly-5c** (158mg, 60.2  $\mu\text{mol}$ ) as coupling reagents, respectively.

#### Compound data for **1a**:

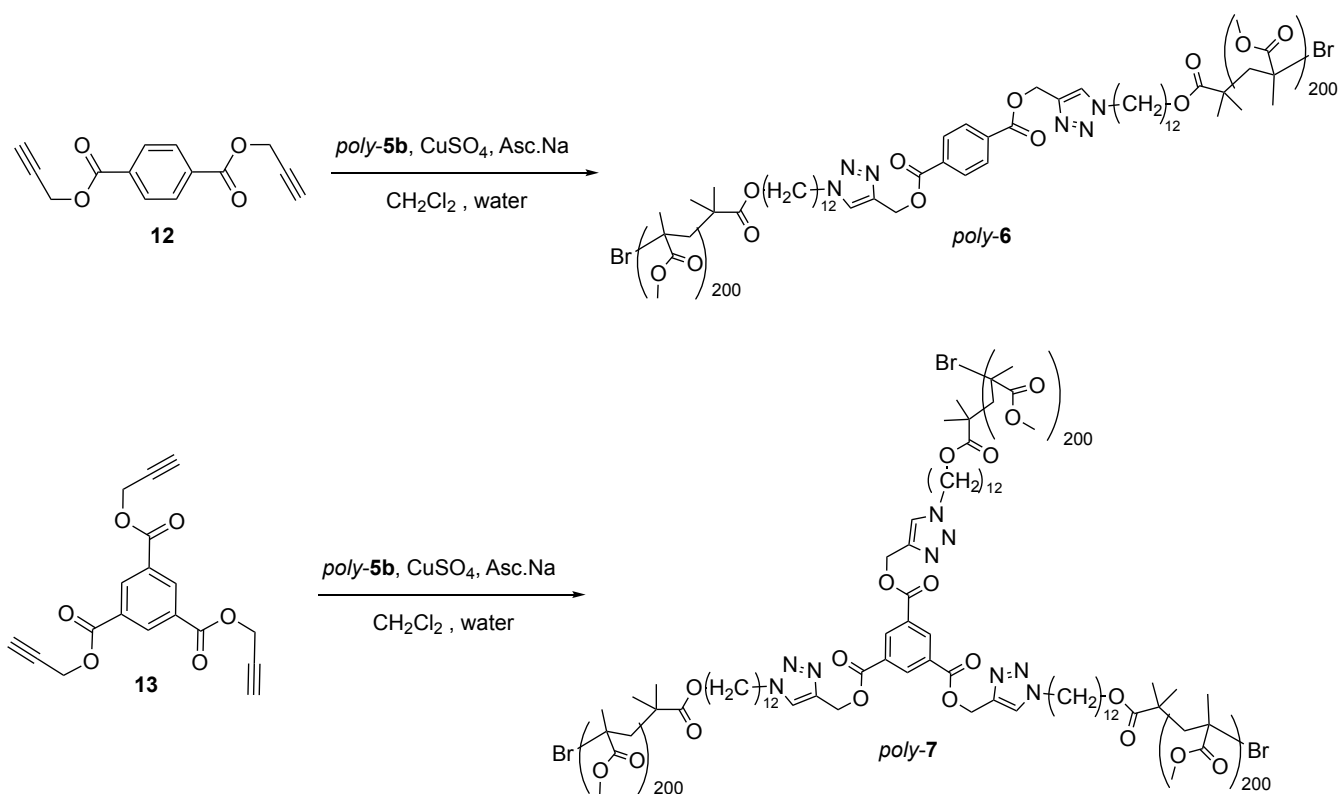
M.p. 130–132  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (s, 1H), 4.80 (s, 1H), 4.32–4.50 (m, 6H), 4.16 (t,  $J = 6.5$  Hz, 2H), 1.16–1.94 (m, 46H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.7, 166.5, 148.3, 145.8, 145.6, 145.2, 145.2, 145.2, 145.1, 144.7, 144.6, 144.4, 143.9, 143.7, 143.2, 143.1, 143.0, 142.9, 142.8, 142.4, 142.2, 142.1, 141.1, 140.9, 140.5, 136.3, 70.6, 66.6, 66.1, 65.5, 56.0, 39.1, 30.8, 30.1, 29.5, 29.5, 29.4, 29.3, 29.3, 29.1, 28.9, 28.7, 28.3, 26.4, 26.1, 25.9, 25.7 ppm; FTIR-ATR (neat):  $\nu$  2919, 2847, 1727, 1537, 1458, 1428, 1269, 1185, 1155, 1106, 1036, 950  $\text{cm}^{-1}$ ; HRMS (ESI $^+$ ) calcd for  $\text{C}_{93}\text{H}_{57}\text{N}_3\text{O}_6\text{Br}$   $m/z$  1390.34253  $[\text{M}+\text{Na}]^+$ , found  $m/z$  1390.34429.

#### Compound data for fullerene terminated [PMMA] $_{200}$ **poly-1b**:

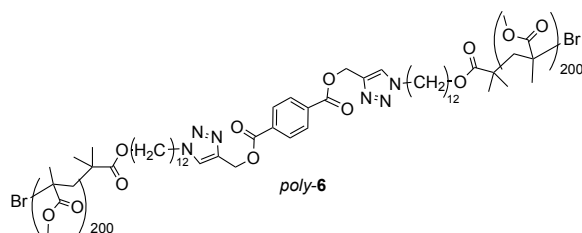
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (s, 2H), 4.30–4.41 (m, 6H), 3.99 (m, 2H), 3.57 (m,  $3\text{H} \times n$ ), 1.64–2.07 (m,  $6\text{H} + 2\text{H} \times n$ ), 1.15–1.48 (m, 20H), 0.72–1.11 (m,  $2\text{H} \times n$ ) ppm;  $M_{n,\text{SEC}} = 20612 \text{ g mol}^{-1}$ , PDI = 1.07.

#### Compound data for fullerene terminated [PMMA] $_{20}$ **poly-1c**:

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06 (s, 2H), 4.80 (s, 2H), 4.30–4.50 (m, 6H), 3.99 (m, 2H), 3.54–3.75 (m,  $3\text{H} \times n$ ), 1.67–2.06 (m,  $6\text{H} + 2\text{H} \times n$ ), 1.19–1.48 (m, 20H), 0.72–1.16 (m,  $2\text{H} \times n$ ) ppm;  $M_{n,\text{SEC}} = 3734 \text{ g mol}^{-1}$ , PDI = 1.30



**Scheme S2.** Synthesis of *poly-6* and *poly-7*.

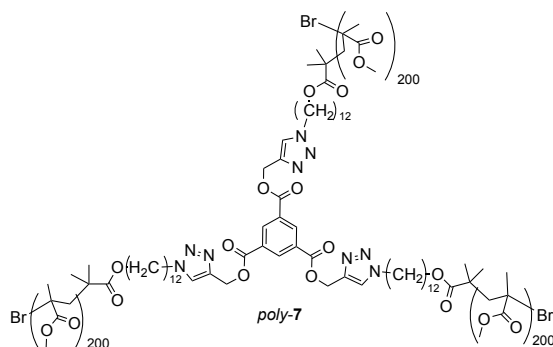


#### Synthesis of model long PMMA *poly-6*:

**12** (4.07 mg, 16.8  $\mu\text{mol}$ ) was added to the solution of *poly-5b* (885 mg, 44.1  $\mu\text{mol}$ ) in CH<sub>2</sub>Cl<sub>2</sub>. To the resulting mixture was added a solution of Asc.Na (8.32 mg, 42.0  $\mu\text{mol}$ ) and CuSO<sub>4</sub> (6.70 mg, 42.0  $\mu\text{mol}$ ) in water (1.0 mL). After being stirred for 48 h at room temperature under an argon atmosphere, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. The crude product was passed through GPC to remove unreacted starting materials to afford desired product *poly-7* as a white solid (99.6 mg, 11 %).

#### Compound data for *poly-6*:

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.67–3.85 (m, 8H), 3.60 (m, 6H  $\times$  n), 1.76–2.07 (m, 12H + 4H  $\times$  n), 1.10–1.48 (m, 40H), 0.73–1.08 (m, 4H  $\times$  n) ppm;  $M_{n,\text{SEC}}$  = 52362 g mol<sup>-1</sup>, PDI = 1.08.



Synthesis of model star PMMA *poly-7*:

**13** (3.7 mg, 11  $\mu\text{mol}$ ) was added to the solution of *poly-5b* (970 mg, 48  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$ . To the resulting mixture was added a solution of Asc.Na (9.1 mg, 46  $\mu\text{mol}$ ) and  $\text{CuSO}_4$  (7.4 mg, 46  $\mu\text{mol}$ ) in water (4.5 mL). After being stirred for 48 h at room temperature under an argon atmosphere, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with water, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. The crude product was passed through GPC to remove unreacted starting materials to yield desired product *poly-7* as a white solid (99 mg, 14 %).

Compound data for *poly-7*:

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.70–3.86 (m, 12H), 3.59 (m,  $9\text{H} \times n$ ), 1.76–2.09 (m,  $18\text{H} + 6\text{H} \times n$ ), 1.08–1.51 (m, 60H), 0.76–1.07 (m,  $6\text{H} \times n$ ) ppm;  $M_{n,\text{SEC}} = 63182 \text{ g mol}^{-1}$ , PDI = 1.10.

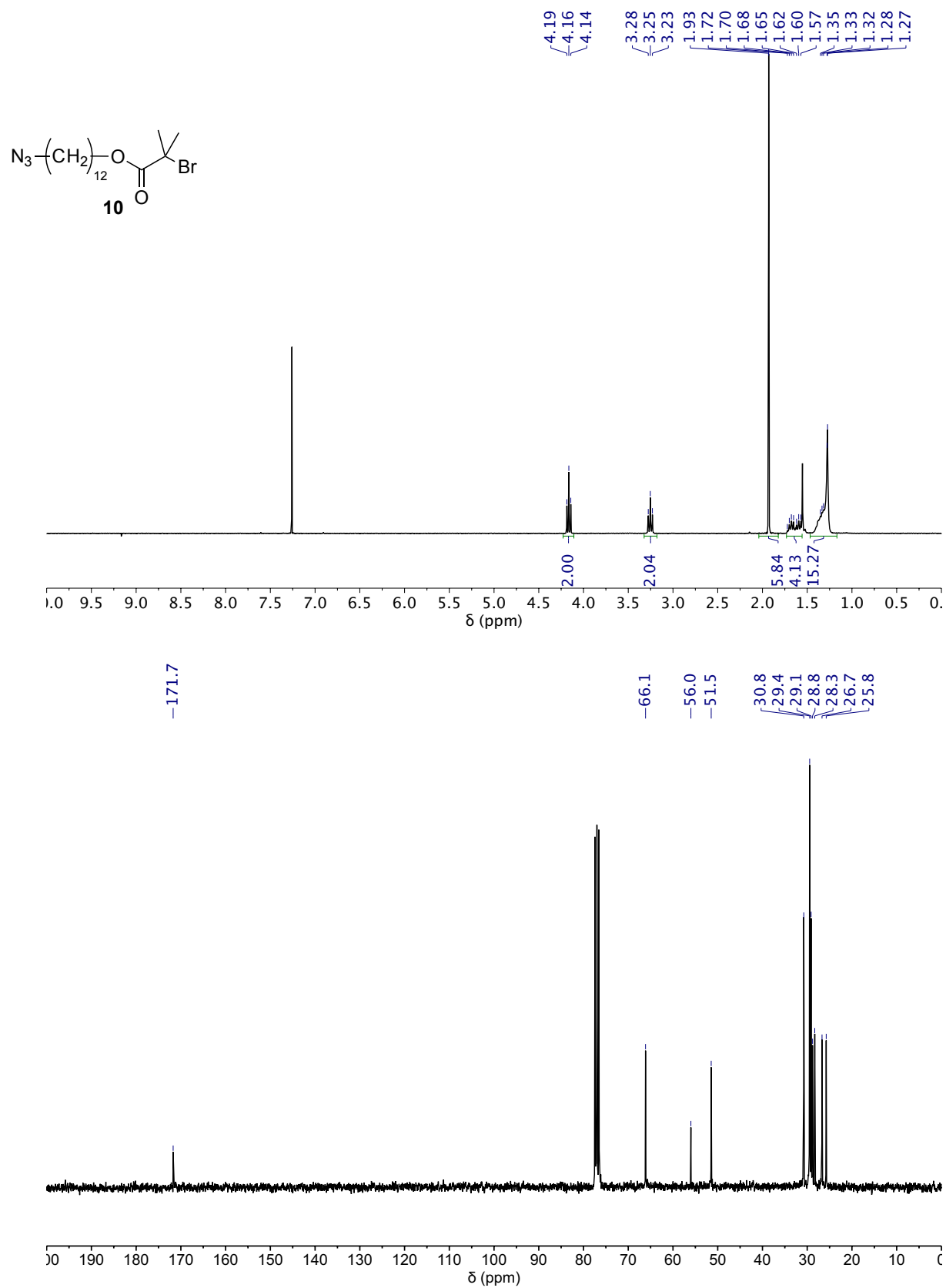
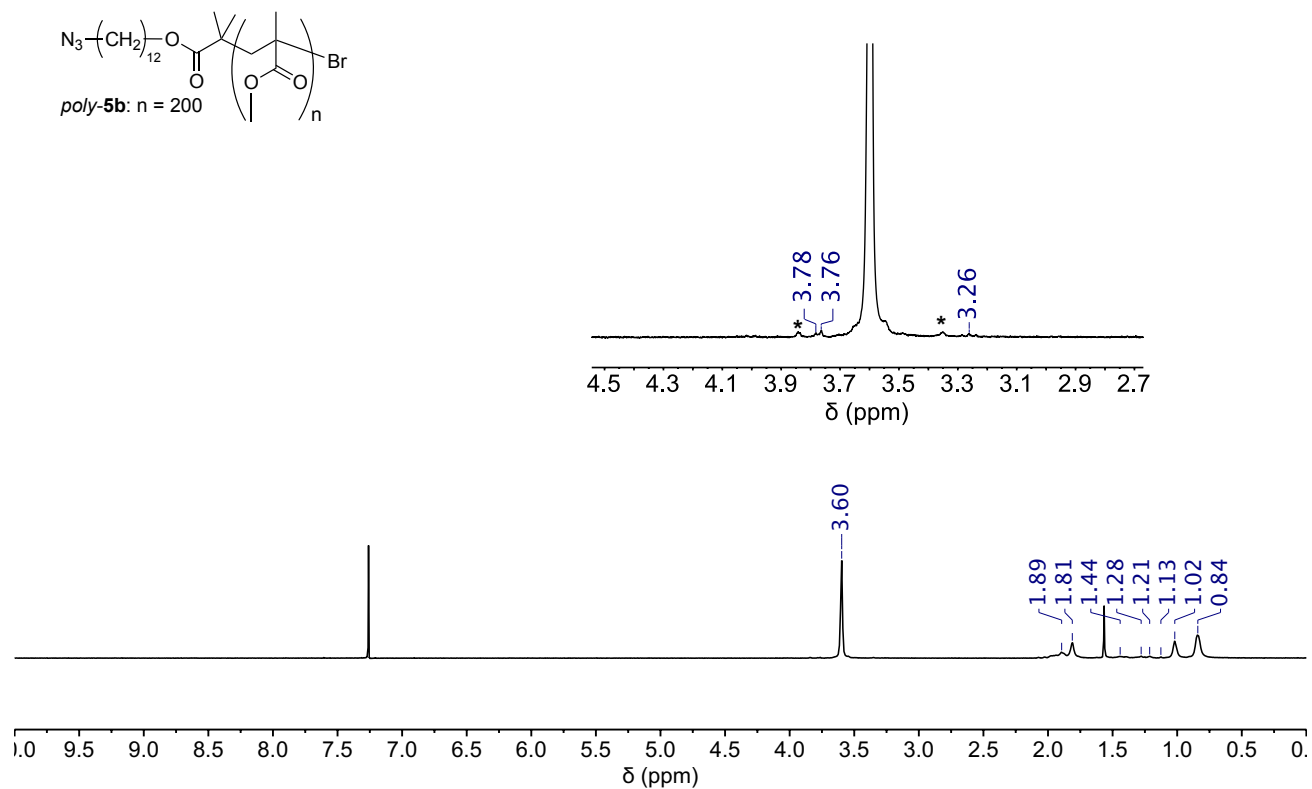
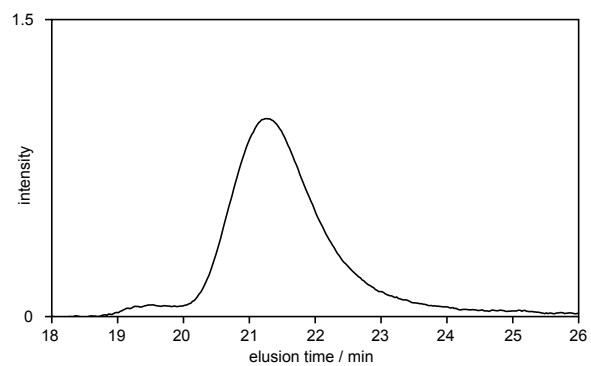


Figure S1. <sup>1</sup>H and <sup>13</sup>C NMR spectra of **10**.

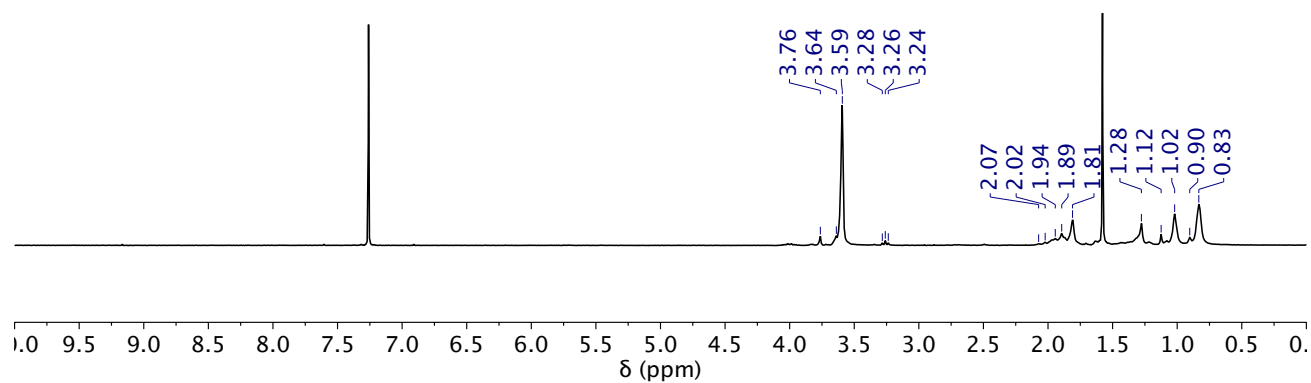
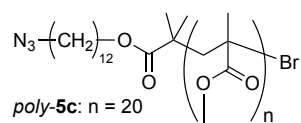




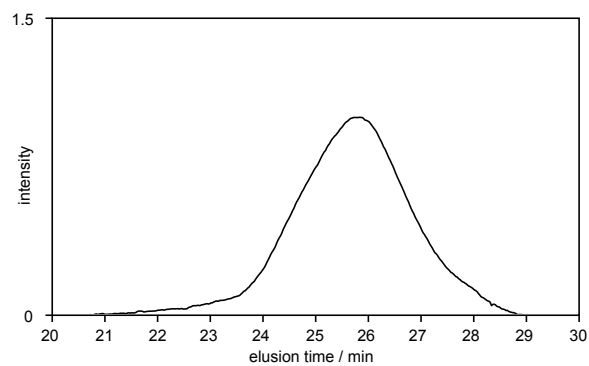
**Figure S2.**  $^1\text{H}$  NMR spectrum of *poly-5b*. The \* denotes spinning side band.



**Figure S3.** Size-exclusion chromatogram of *poly-5b* (eluent: chloroform).



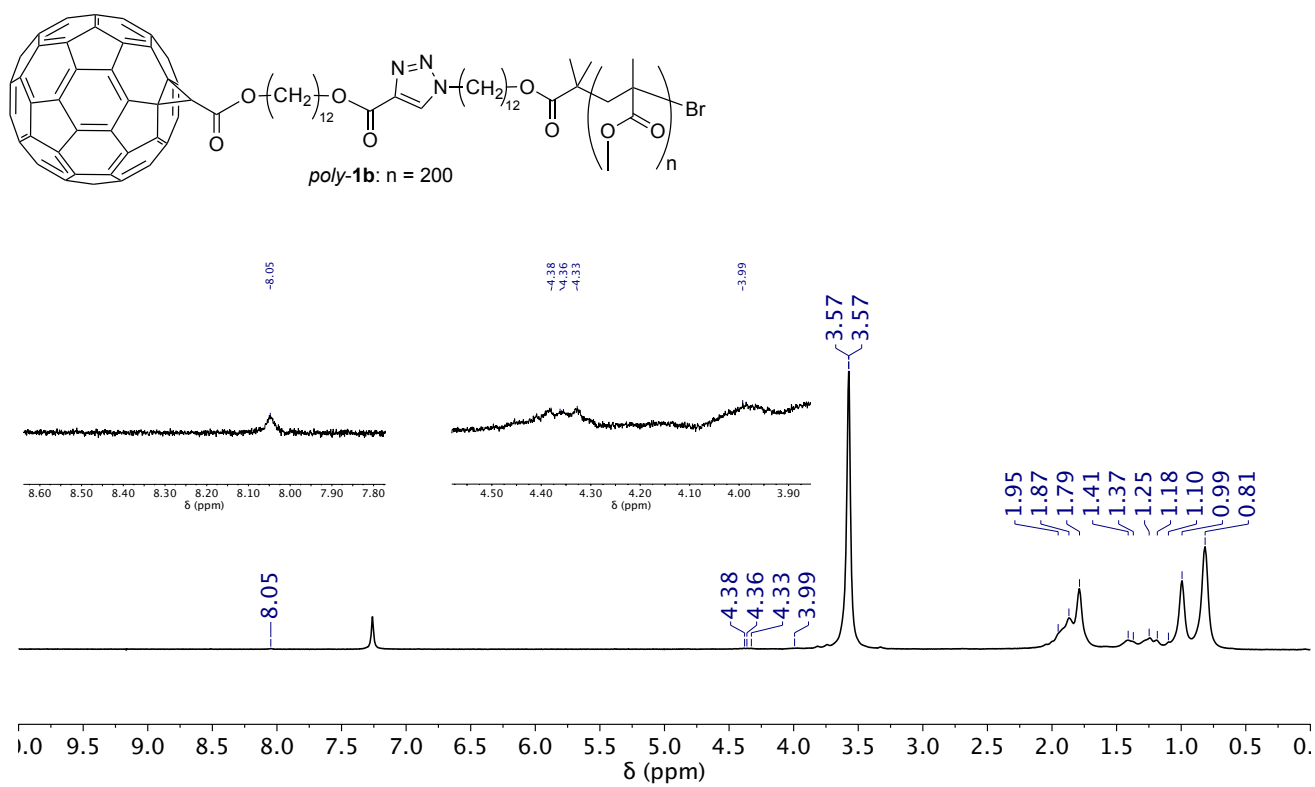
**Figure S4.**  $^1\text{H}$  NMR spectrum of *poly-5c*.



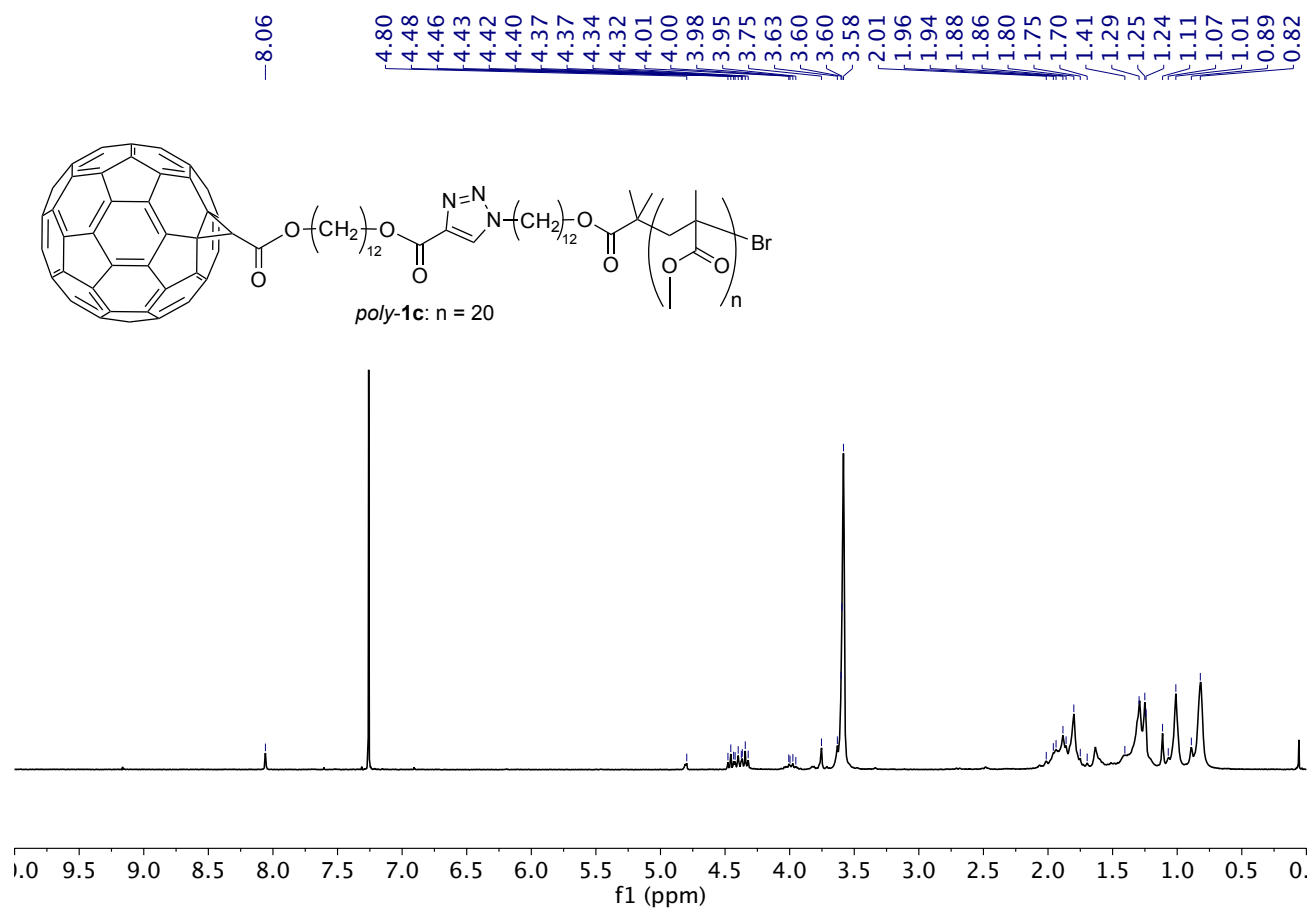
**Figure S5.** Size-exclusion chromatogram of *poly-5c* (eluent: chloroform).



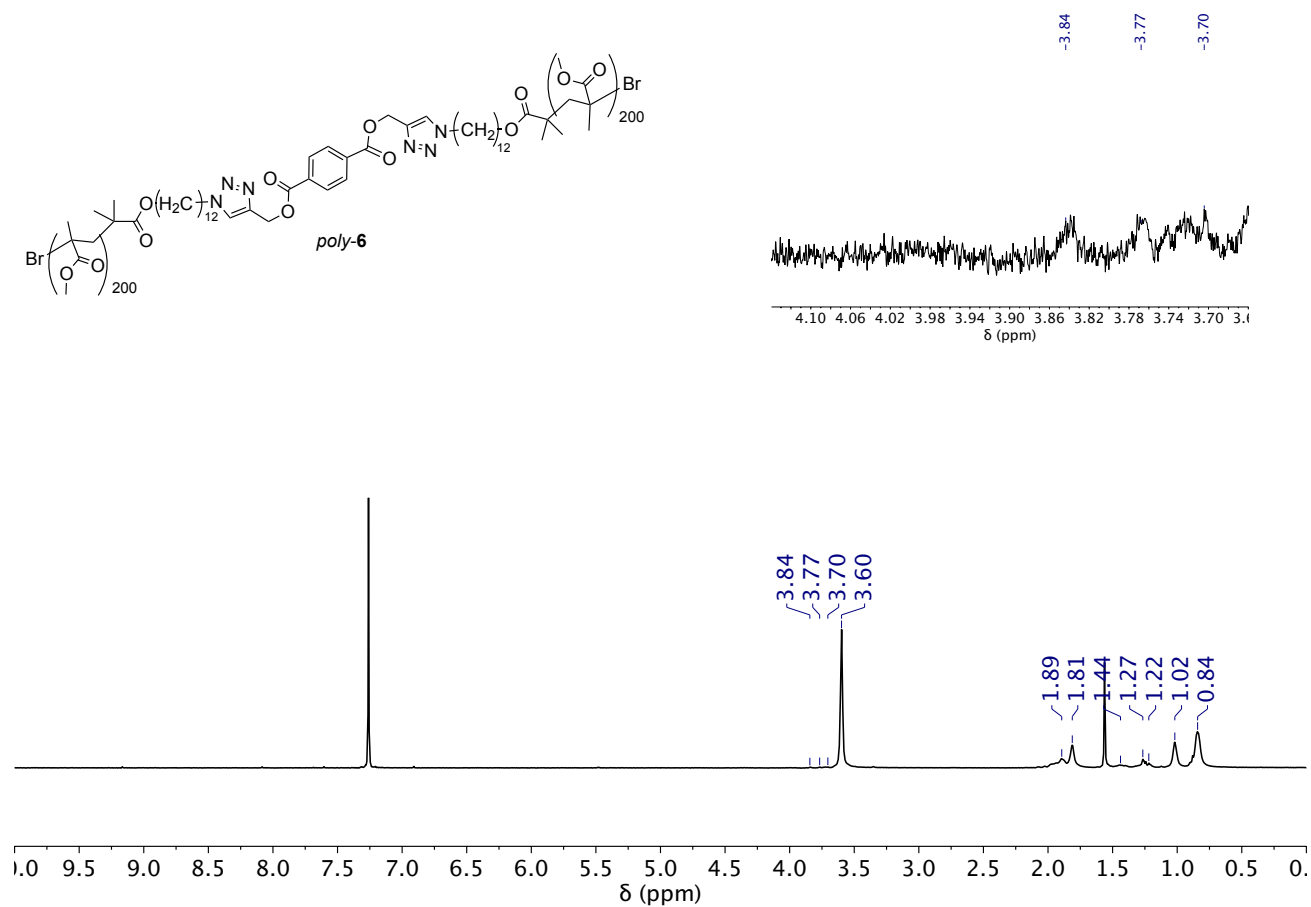
Figure S6. <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1a**.



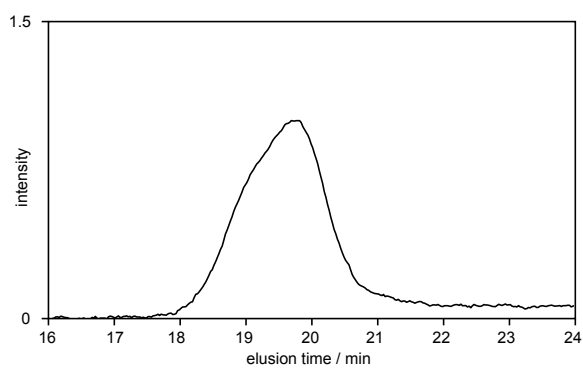
**Figure S7.**  $^1\text{H}$  NMR spectrum of poly-1b.



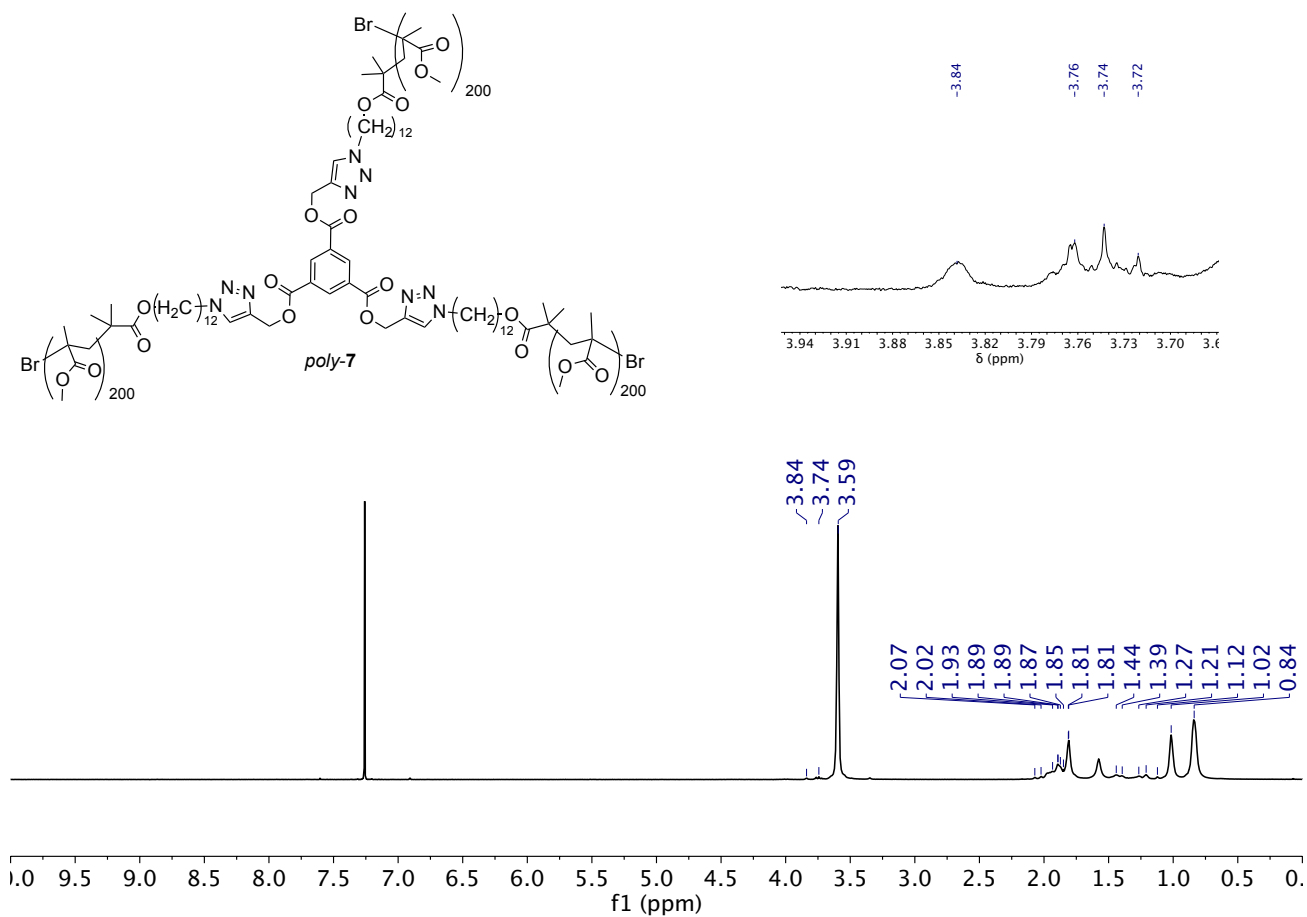
**Figure S8.** <sup>1</sup>H NMR spectrum of *poly-1c*.



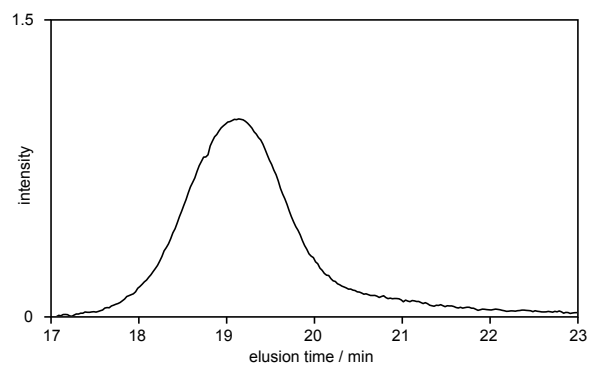
**Figure S9.**  $^1\text{H}$  NMR spectrum of *poly-6*.



**Figure S10.** Size-exclusion chromatogram of *poly-6* (eluent: chloroform).



**Figure S11.**  $^1\text{H}$  NMR spectrum of *poly-7*.



**Figure S12.** Size-exclusion chromatogram of *poly-7* (eluent: chloroform).

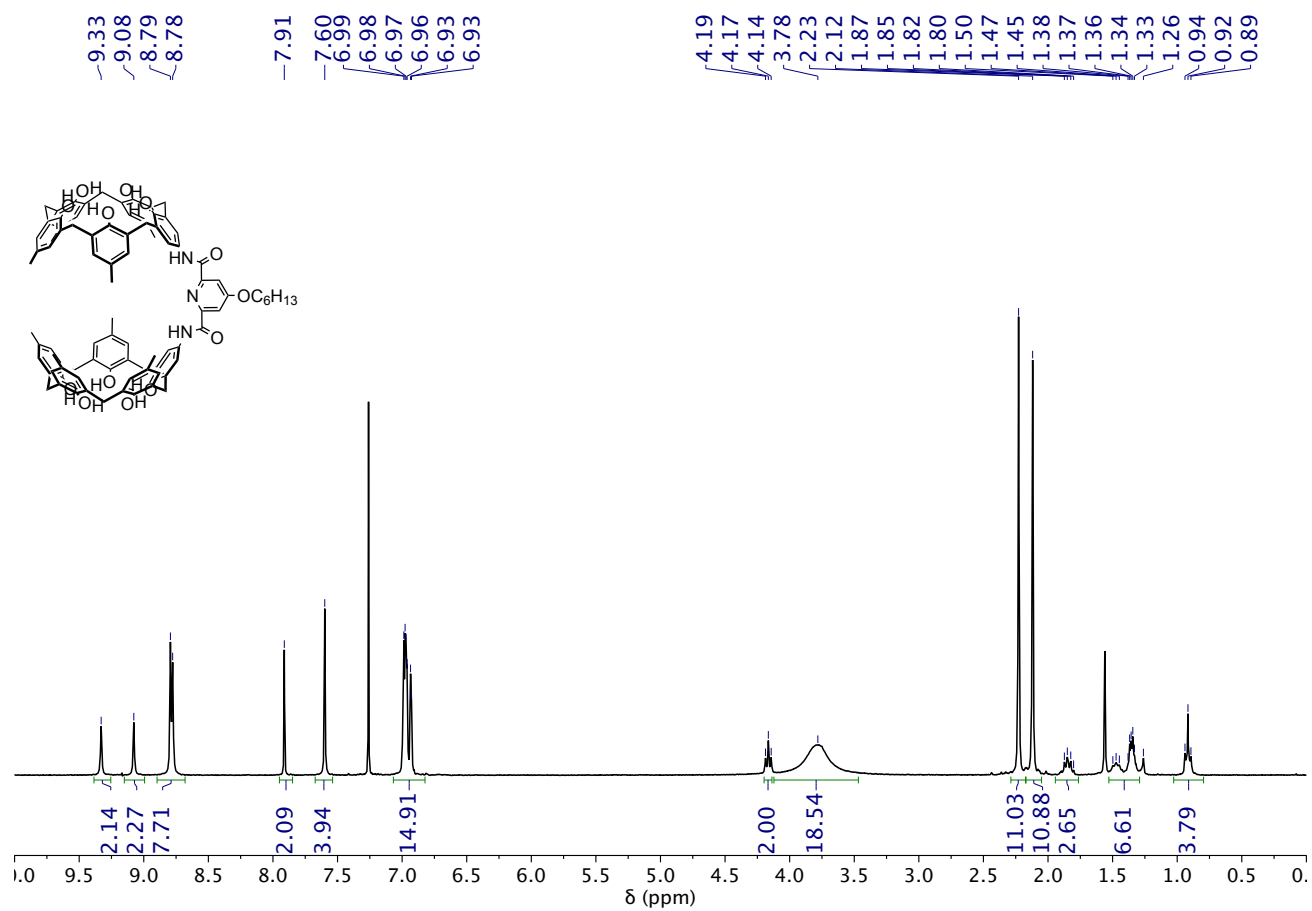
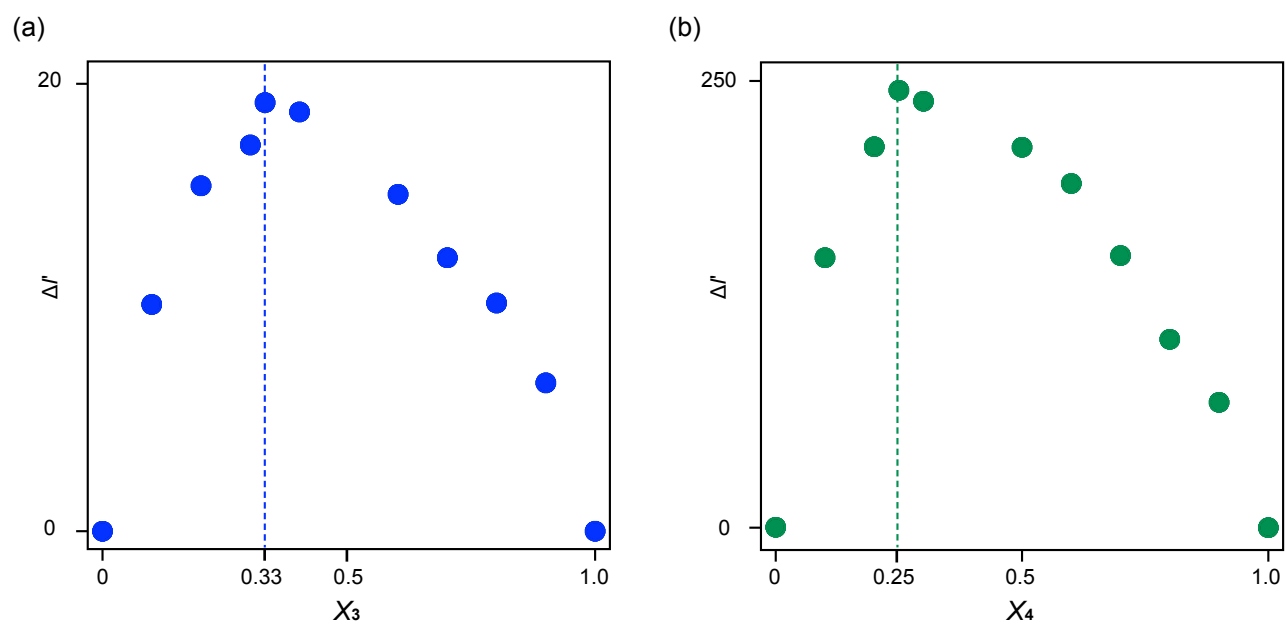
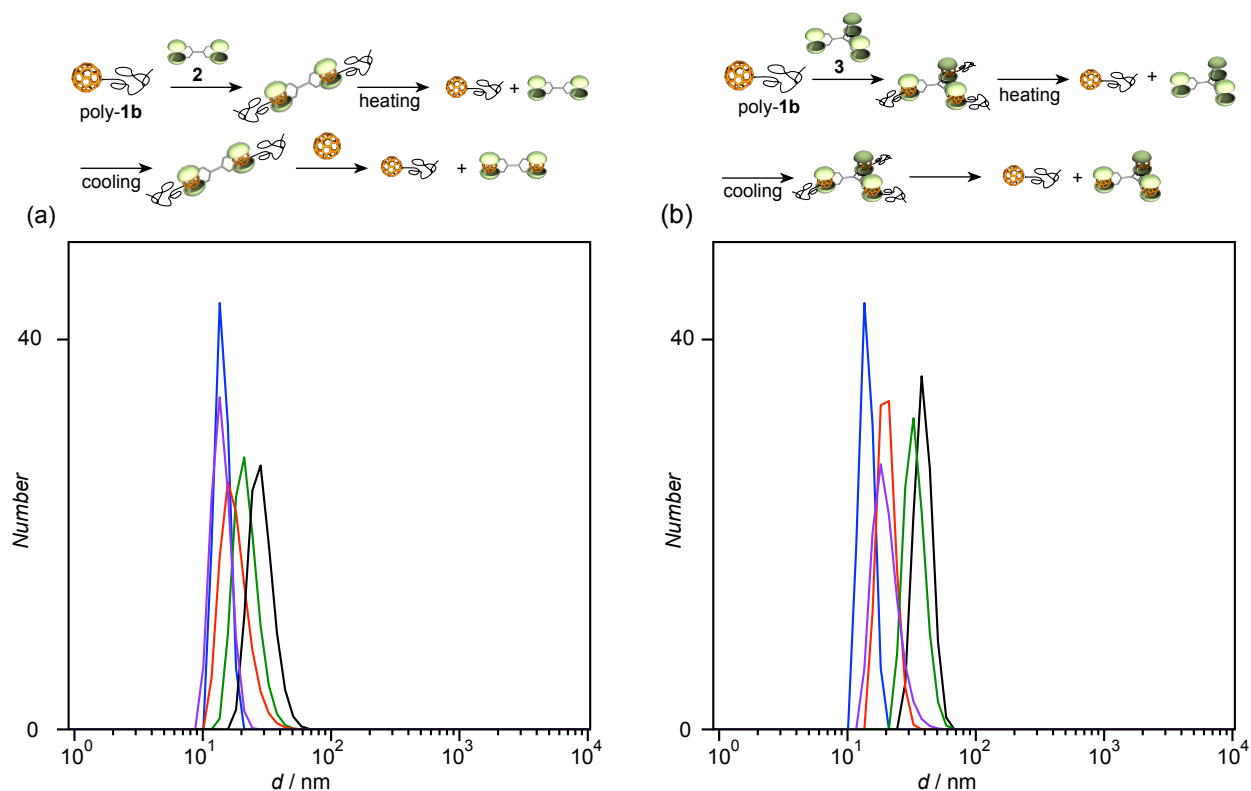


Figure S13. <sup>1</sup>H NMR spectrum of 4.

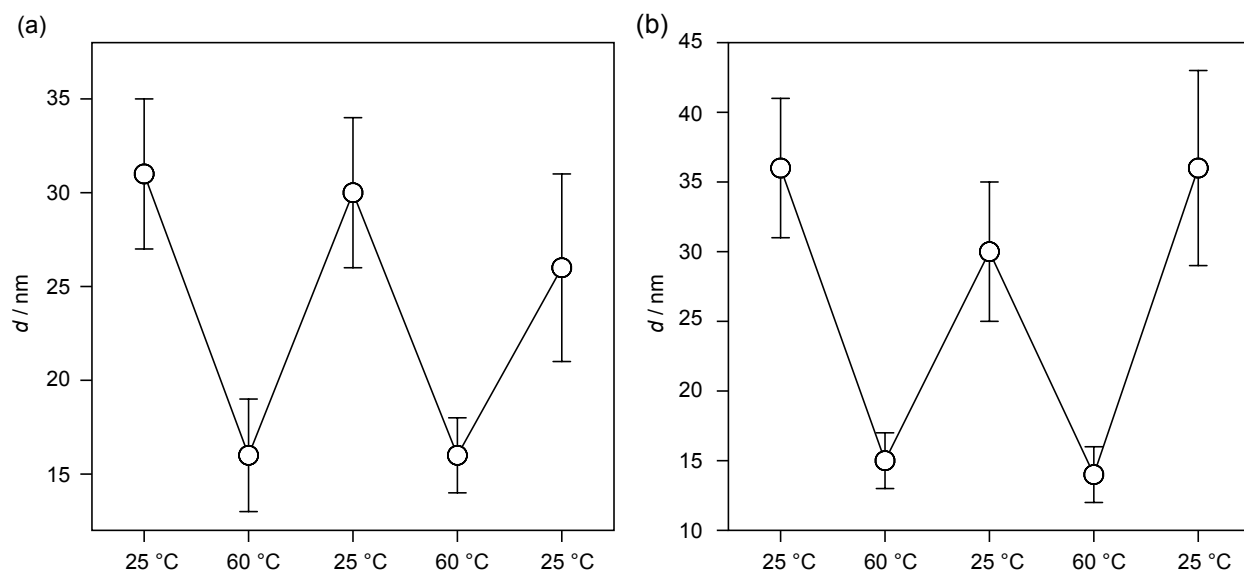




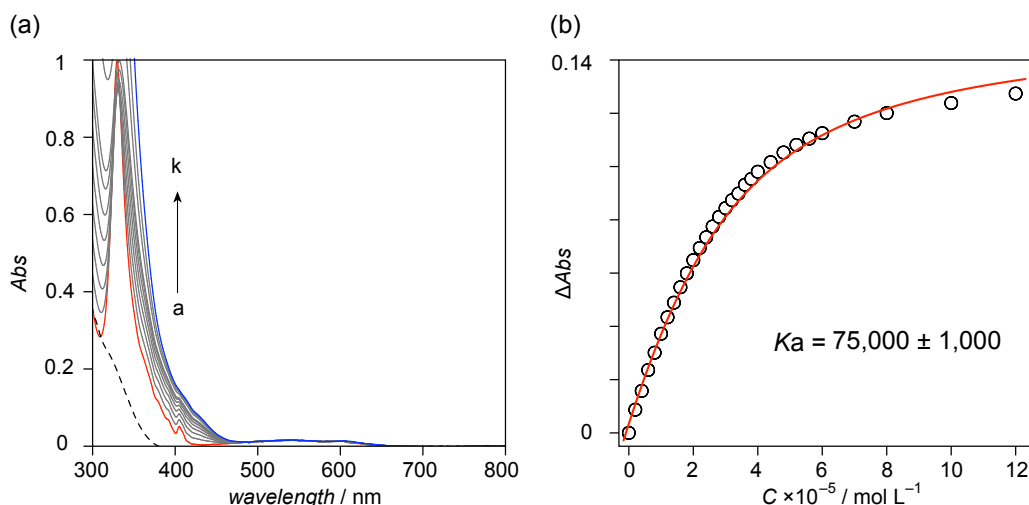
**Figure S14.** Job plots for (a) **1a** and **2**, and (b) **1a** and **3**.  $X$  represents the mole fraction of **2,3**.  $\Delta I'$  indicates  $|I_{\text{obs}} - I_0 \cdot X|$ , where  $I_{\text{obs}}$  and  $I_0$  denote observed fluorescence intensity and fluorescence intensity of **2,3**, respectively.



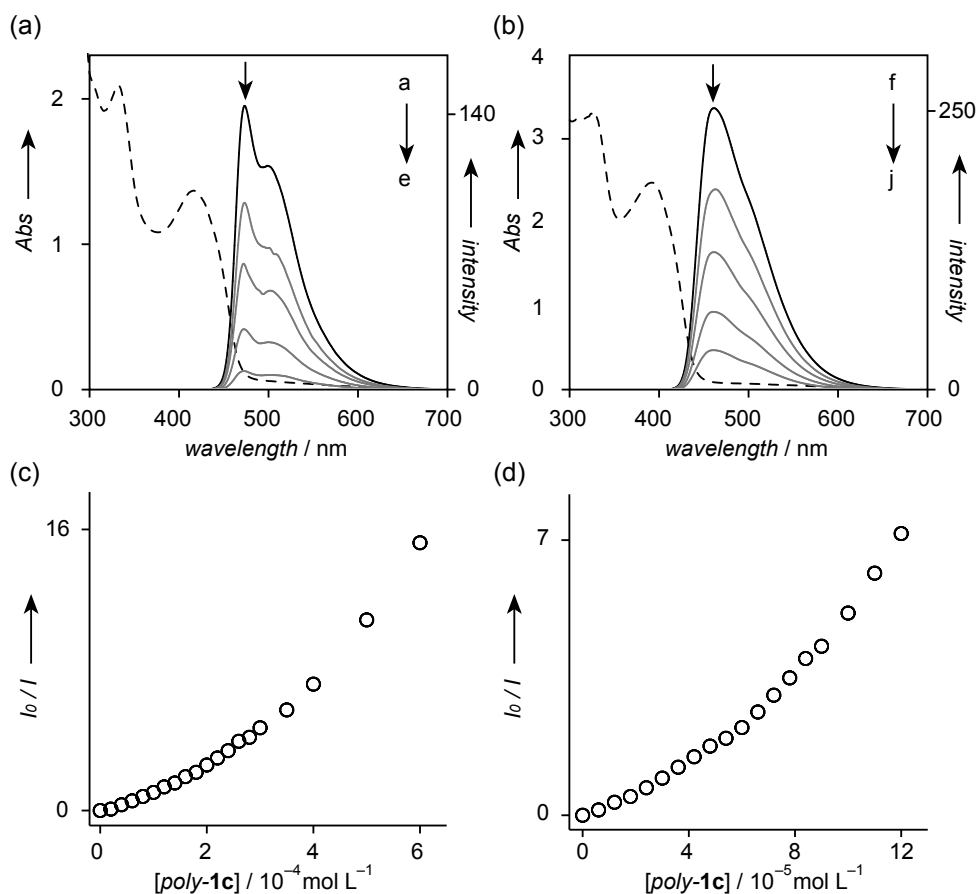
**Figure S15.** Schematic illustrations and the corresponding hydrodynamic diameter ( $d$ ) changes of (a) linear-to-linear and (b) linear-to-star transformations between polymer shapes. The graphs show that the sequential changes of the hydrodynamic diameter ( $d$ ) of (blue) poly-**1b** ( $1.0 \times 10^{-5}$  mol L $^{-1}$ ) at 25 °C in toluene: in the presence of (black) **2** (0.5 equiv.) or **3** (0.33 equiv.); (red) equilibrating at 60 °C, (green) re-equilibrating at 25 °C, and (purple) addition of pristine [60]fullerene molecule (5 equiv.), as inferred from DLS experiments. The expanded graphs are shown in Fig. 6.



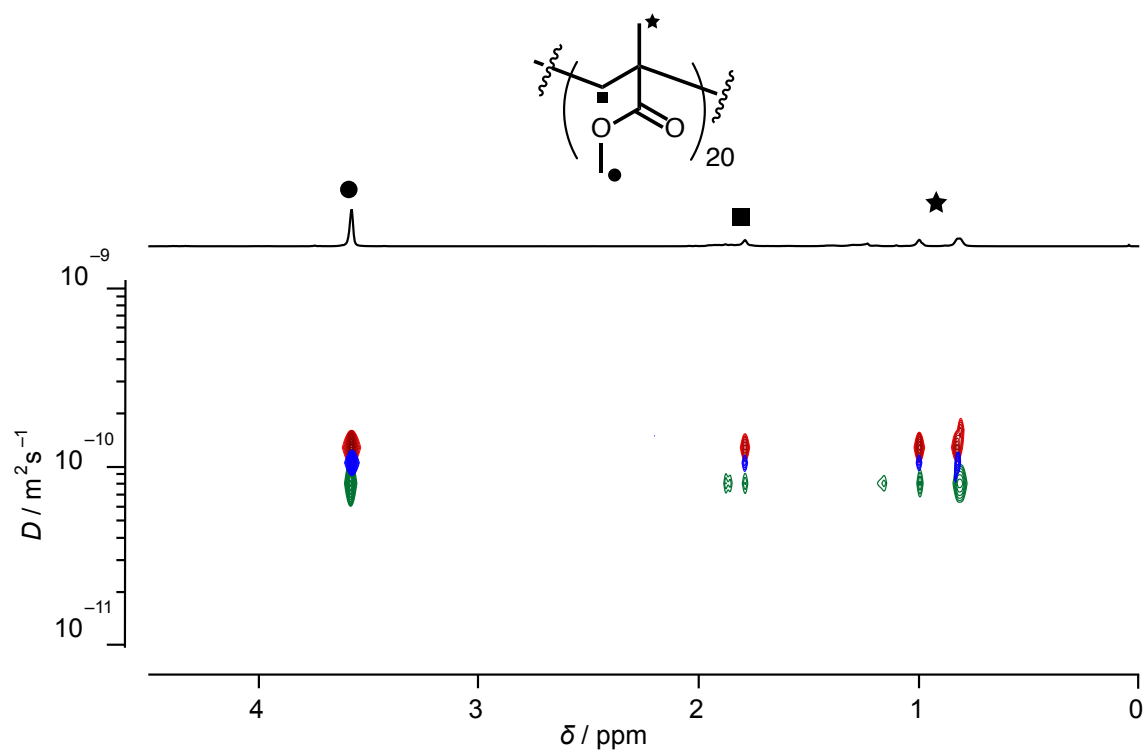
**Figure S16.** Reversible changes in hydrodynamic diameter ( $d$ ) with heating and cooling the solutions of (a) a mixture of poly-**1b** ( $1.0 \times 10^{-5}$  mol L $^{-1}$ ) and **2** ( $0.5 \times 10^{-5}$  mol L $^{-1}$ ), and (b) a mixture of poly-**1b** ( $1.0 \times 10^{-5}$  mol L $^{-1}$ ) and **3** ( $0.33 \times 10^{-5}$  mol L $^{-1}$ ).



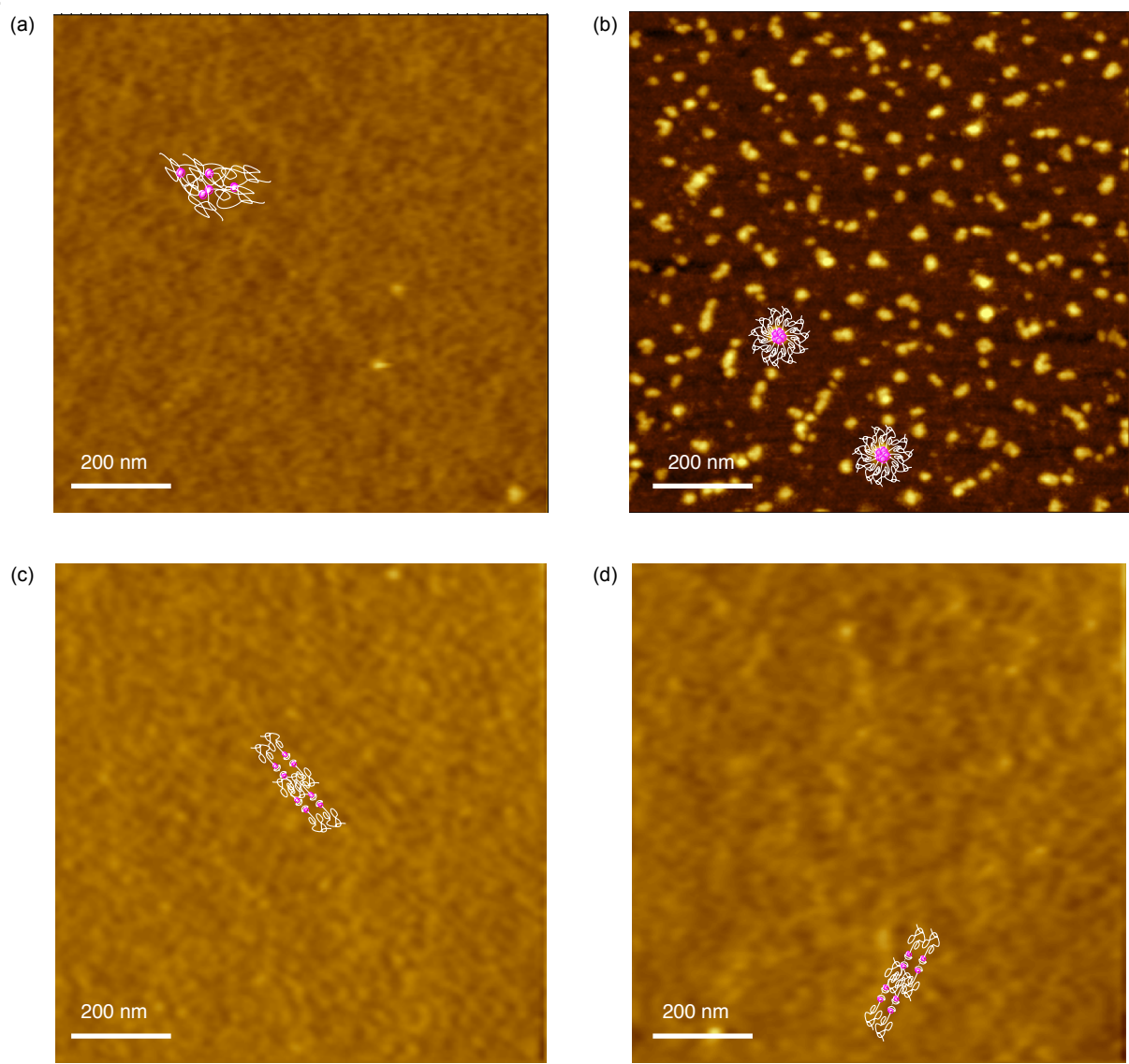
**Figure S17.** (a) Changes in the UV/vis absorption spectrum of [60]fullerene ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ) upon the addition of **4** at  $25^\circ\text{C}$  in chloroform. The concentrations of **4** are a-k: 0.0, 0.6, 1.2, 1.8, 2.4, 3.0, 3.6, 4.0, 6.0, 8.0,  $12 \times 10^{-5} \text{ mol L}^{-1}$ . The red line, blue line, and broken line indicate the first point and the last point of the titration, and absorption spectrum of **4** ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ), respectively. (b) Plot of *Abs* (400 nm) against [**4**] and the fitting curve obtained by a 1:1 fitting model.



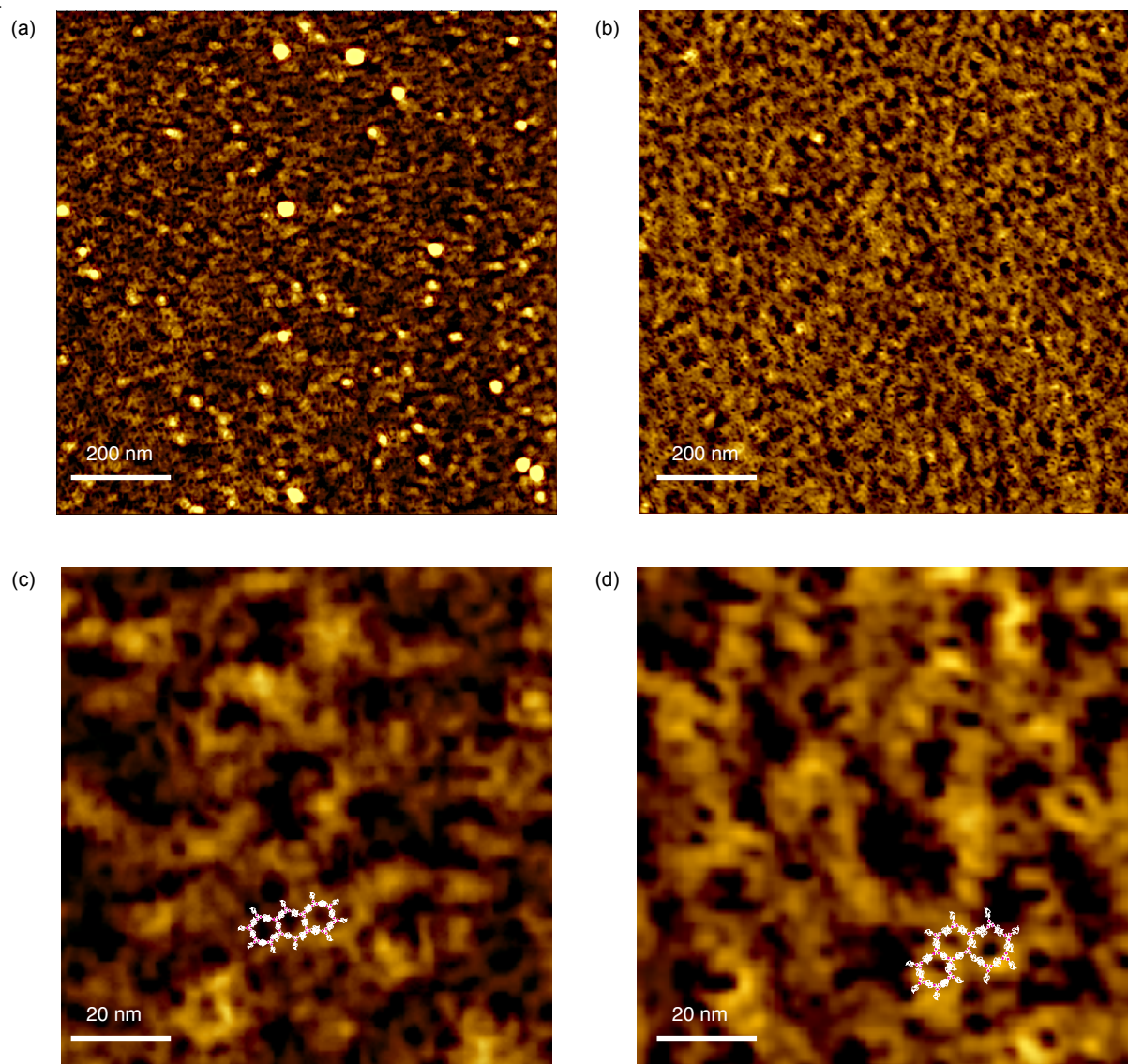
**Figure S18.** Changes in the fluorescence spectra of (a) **2** ( $1.0 \times 10^{-4} \text{ mol L}^{-1}$ ,  $\lambda_{\text{ex}} = 420 \text{ nm}$ ) and (b) **3** ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ,  $\lambda_{\text{ex}} = 400 \text{ nm}$ ) upon the addition of poly-**1c** (a-e: 0.0, 0.6, 1.2, 2.6,  $6 \times 10^{-4} \text{ mol L}^{-1}$ , f-j: 0.0, 1.8, 3.6, 7.2,  $12 \times 10^{-5} \text{ mol L}^{-1}$ ) at  $25^\circ\text{C}$  in chloroform. The red line, blue line, and broken line indicate the first point of the titration, the last point of the titration, and absorption spectrum of **2** or **3** ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ), respectively. Stern-Volmer plots for (c) **2** and (d) **3** in the presence of poly-**1c**. Concentrations of poly-**1c** were calculated based on its  $M_n$ .



**Figure S19.** Diffusion coefficients ( $D$ s) of poly-**1c**, as inferred from 2D DOSY measurement in chloroform- $d$ . The red line, blue line, and green line denote the spectra obtained from pure poly-**1c** solution, a 2:1 mixture of poly-**1c** and **2** and a 3:1 mixture of poly-**1c** and **3**, respectively.



**Figure S20.** Schematic representation of plausible structures formed from (a) poly-**1b**, (b) poly-**1c**, (c) a 2:1 mixture of poly-**1b** and **2**, and (d) a 2:1 mixture of poly-**1c** and **2**.



**Figure S21.** AFM images of cast films of (a) a 3:1 mixture of poly-**1b** and **3**, and (b) a 3:1 mixture of poly-**1c** and **3** on mica. Schematic representation of plausible structures formed by (c) a 3:1 mixture of poly-**1b** and **3**, and (d) a 3:1 mixture of poly-**1c** and **3**.

## References

- [1] T. Hirao, M. Tosaka, S. Yamago, T. Haino, *Chem. –Eur. J.*, **2014**, *20*, 16138-16146.
- [2] T. Haino, Y. Matsumoto, Y. Fukazawa, *J. Am. Chem. Soc.*, **2005**, *127*, 8936-8937.
- [3] A. Pinto, J. H. Ciesla, A. Palucci, B. P. Sutliff, C. T. Nomura, *ACS Macro Lett.*, **2016**, *5*, 215-219.
- [4] H. Yan, S. Chen, M. Lu, X. Zhu, Y. Li, D. Wu, Y. Tu, X. Zhu, *Mater. Horiz.*, **2014**, *1*, 247-250.
- [5] S. H. Sonawane, M. Anniyappan, J. Athar, S. Banerjee, A. K. Sikder, *RSC Adv.*, **2016**, *6*, 8495-8502.
- [6] G. Chen, J. Kumar, A. Gregory, M. H. Stenzel, *Chem. Commun.*, **2009**, 6291-6293.