

## Supplementary Information

# Correlations of nanoscale film morphologies and topological confinement of three-arm cage block copolymers

Brian J. Ree,<sup>a</sup> Yusuke Satoh,<sup>b</sup> Takuya Isono,<sup>a</sup> and Toshifumi Satoh<sup>a,\*</sup>

<sup>a</sup>Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

<sup>b</sup>Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-8628, Japan

### Synthesis

In this study, *Cage-A*, -B, and -C were synthesized in accordance to the previous reported method.<sup>1</sup>

**Materials.**  $\alpha$ -(1-(6-azidohexyloxy)-2,2-bis((6-azidohexyloxy)methyl)-3-propoxy)- $\alpha'$ -(1,1,1-tris(hydroxymethyl)-2-ethoxy)-*p*-xylene ((N<sub>3</sub>)<sub>3</sub>-(OH)<sub>3</sub>),<sup>1</sup> (decyl glycidyl ether (DGE, **M1**),<sup>2</sup> 2-(2-(2-methoxyethoxy)ethoxy)ethyl glycidyl ether (TEGGE, **M2**),<sup>3</sup> and propargyl-functionalized Wang resin (PSt-C≡CH)<sup>4</sup> were synthesized according to reported methods, purified by distillation under vacuum over calcium hydride, and stored under an argon atmosphere. Propargyl bromide, 60% NaH, *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA), and 10% palladium on carbon (Pd/C; wetted with ca. 55% water) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI), and used as received. *t*-Bu-P<sub>4</sub> (in *n*-hexane as 1.0 mol L<sup>-1</sup> solution), and copper (I) bromide (CuBr), aluminum oxide (alumina) were purchased from the Sigma-Aldrich, and used as received. Dry dimethylformamide (DMF; >99.5%; water content, <0.005%), dry toluene (>99.5%; water

content, <0.001%), and dry tetrahydrofuran (THF; >99.5%; water content, <0.001%) were purchased from Kanto Chemical Co., Inc., and used as received.

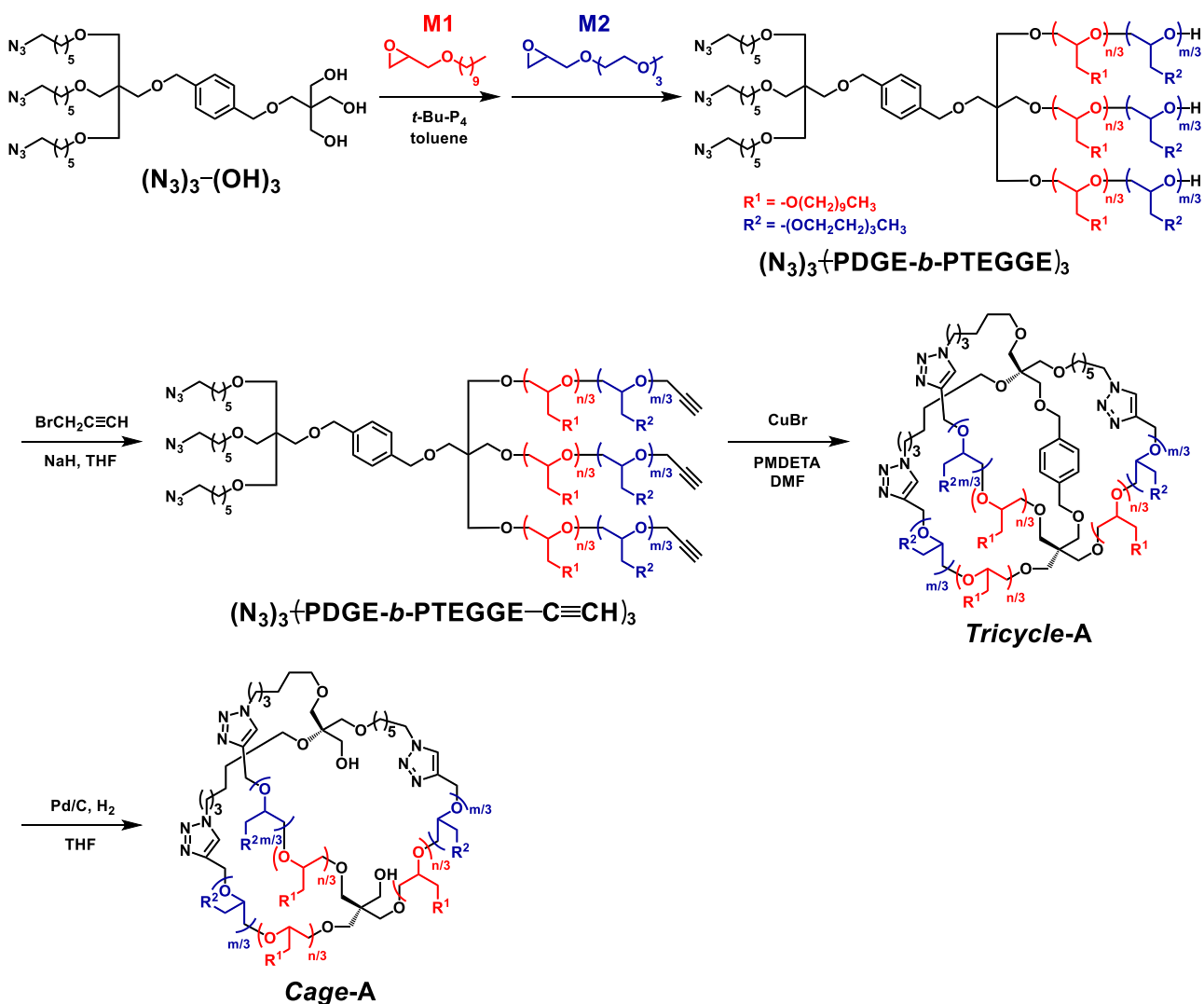
**Instruments.** All polymerization procedures were carried out inside a MBRAUN UNIlab Plus stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere ( $\text{H}_2\text{O}$ ,  $\text{O}_2$  < 0.1 ppm) (MBRAUN Inc., Stratham, NH 03885, USA). The moisture and oxygen levels inside the glovebox were monitored by a moisture sensor (MB-MO-SE 1, MBRAUN Inc.) and an oxygen sensor (MB-OX-SE 1, MBRAUN Inc.), respectively. Dry toluene (> 99.5%; water content, < 0.001%, Kanto Chemical Co., Inc.) used in the polymerization was purified by passing through a solvent purification system (MB SPS Compact, MBRAUN Inc.) consisting of a column of activated alumina and a column with activated copper catalyst.

Size exclusion chromatography (SEC) was performed at 40 °C in THF with the flow rate of 1.0 mL min<sup>-1</sup> through a JASCO high-performance liquid chromatography (HPLC) system (PU-2080 Plus Intelligent HPCL pump, CO-2065 Plus column oven, RI-2031 Plus differential refractive index detector, and DG-2080-54 degasser) (JASCO, Inc., Easton, MD 21601, USA) equipped with two Shodex KF-804L columns (linear, 8 mm × 300 mm) (Showa Denko K. K., Tokyo, Japan). The calculated number-average molecular weight ( $M_{n,SEC}$ ) and dispersity values ( $\bar{D}$ ) of the block copolymers were calibrated with polystyrene (PSt) standards.

Preparative SEC was performed in  $\text{CHCl}_3$  with a flow rate of 3.5 mL min<sup>-1</sup> at 23 °C through a JAI LC-9201 equipped with a JAI JAIGEL-2H column (20 mm × 600 mm; exclusion limit, 5 × 10<sup>3</sup>), a JAI JAIGEL-3H column (20 mm × 600 mm; exclusion limit, 7 × 10<sup>4</sup>) and a JAI RI-50s refractive index detector (Japan Analytical Industry Co. Ltd., Tokyo, Japan).

The <sup>1</sup>H (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were measured using a JEOL ECS400 instrument (JEOL Ltd., Tokyo, Japan).

The Fourier transform infrared spectroscopy (FT-IR) analysis was carried out using a Perkin-Elmer Frontier MIR spectrometer equipped with a Single Reflection Diamond Universal Attenuated Total Reflection (ATR) accessory (PerkinElmer, Inc., Waltham, MA 02454 USA).



**Scheme S1.** The synthesis of *Cage-A*.

**Synthesis of  $(N_3)_3-(PDGE-b-PTEGGE)_3$ .** DGE (774  $\mu\text{L}$ , 3.27 mmol) was added to a stirred solution of  $(N_3)_3-(OH)_3$  (49.0 mg, 65.3  $\mu\text{mol}$ ) and *t*-Bu-P<sub>4</sub> (65.3  $\mu\text{L}$  of a 1.0 mol L<sup>-1</sup> stock solution in *n*-hexane, 65.3  $\mu\text{mol}$ ) in toluene (467  $\mu\text{L}$ ), and the mixture was stirred at room temperature for 20 h. TEGGE (674  $\mu\text{L}$ , 3.27 mmol) and toluene (1.29 mL) were added to the mixture, and the mixture was stirred at room temperature for 20 h. An excess of benzoic acid was then added to the mixture to terminate the polymerization, and the polymer was then purified by passing through a pad of alumina and washed with THF to give  $(N_3)_3-(PDGE-b-PTEGGE)_3$  as a colorless waxy solid (1.38 g). Yield: 94.0%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.25 (aromatic), 4.43 (–PhCH<sub>2</sub>–), 3.86–3.28 (–(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>–, –CCH<sub>2</sub>OCH<sub>2</sub>Ph–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–, –CH<sub>2</sub>CH(CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>)O–), 3.24 (N<sub>3</sub>CH<sub>2</sub>–), 1.79–1.17 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O–, –

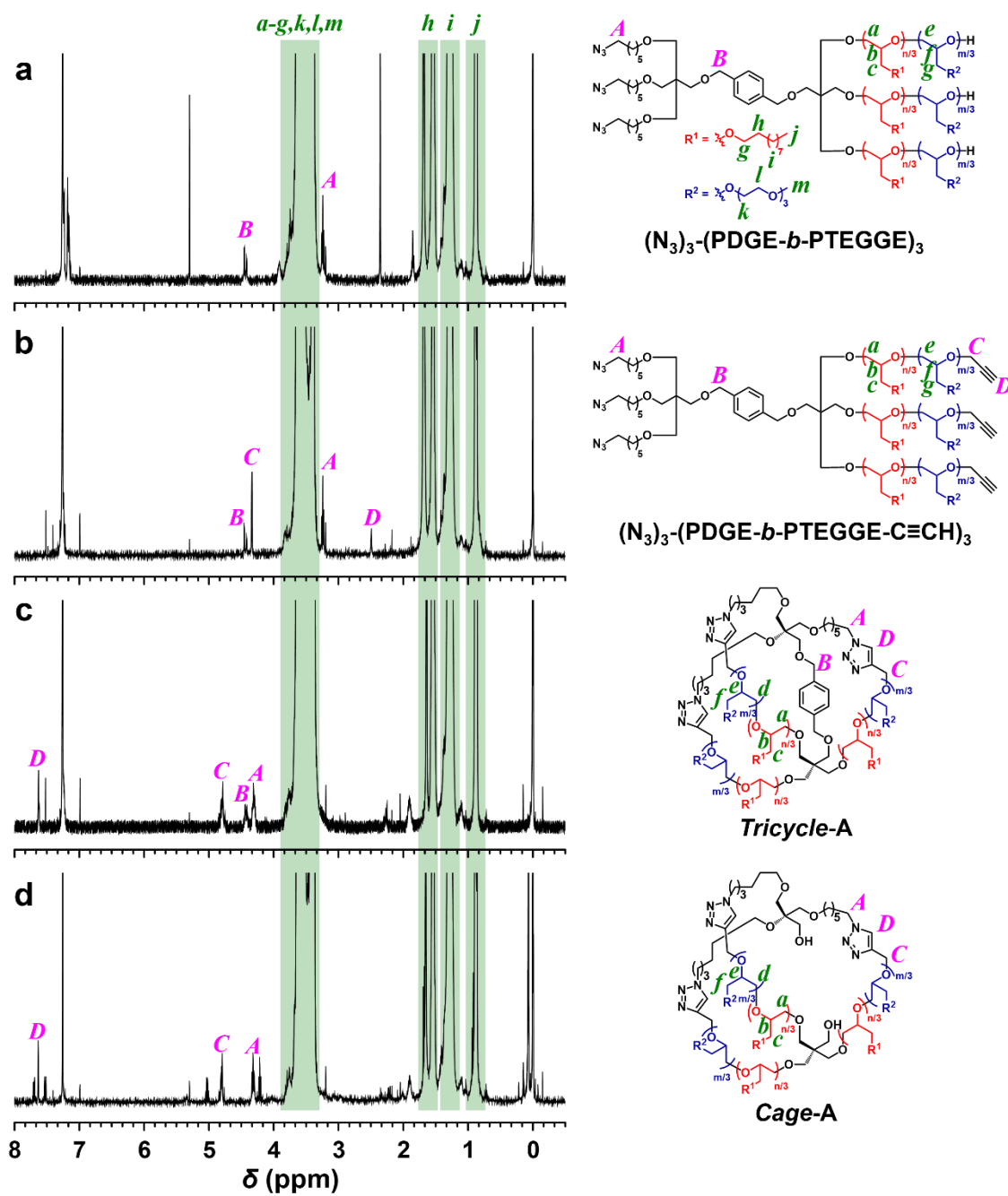
OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)O–), 0.95–0.78 (–OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–).  $M_{n,NMR} = 22,500 \text{ g mol}^{-1}$ ;  $M_{n,SEC} = 17,100 \text{ g mol}^{-1}$ ;  $\mathcal{D} = 1.03$ .

**Synthesis of (N<sub>3</sub>)<sub>3</sub>-(PDGE-*b*-PTEGGE-C≡CH)<sub>3</sub>.** To a stirred solution of (N<sub>3</sub>)<sub>3</sub>-(PDGE-*b*-PTEGGE)<sub>3</sub> (1.38 g, 60.9 μmol) in THF (5 ml) was added NaH (24.4 mg, 609 μmol; 60% in mineral oil), and the solution was stirred at 40 °C for 30 min. After cooling to room temperature, propargyl bromide (45.7 μL, 609 μmol) was then added to the solution, and the whole mixture was stirred at room temperature for 48 h. The polymer was purified by passing through a pad of alumina to give (N<sub>3</sub>)<sub>3</sub>-(PDGE-*b*-PTEGGE-C≡CH)<sub>3</sub> as a pale yellow waxy solid (946 mg). Yield: 68.6%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.25 (aromatic), 4.43 (–PhCH<sub>2</sub>–), 4.34 (HC≡CCH<sub>2</sub>O–), 3.87–3.28 (–(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>–, –CCH<sub>2</sub>OCH<sub>2</sub>Ph–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–, –CH<sub>2</sub>CH(CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>)O–), 3.24 (N<sub>3</sub>CH<sub>2</sub>–), 2.50 (HC≡C–), 1.80–1.17 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)O–), 0.99–0.75 (–OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–).  $M_{n,NMR} = 22,900 \text{ g mol}^{-1}$ ;  $M_{n,SEC} = 17,800 \text{ g mol}^{-1}$ ;  $\mathcal{D} = 1.03$ .

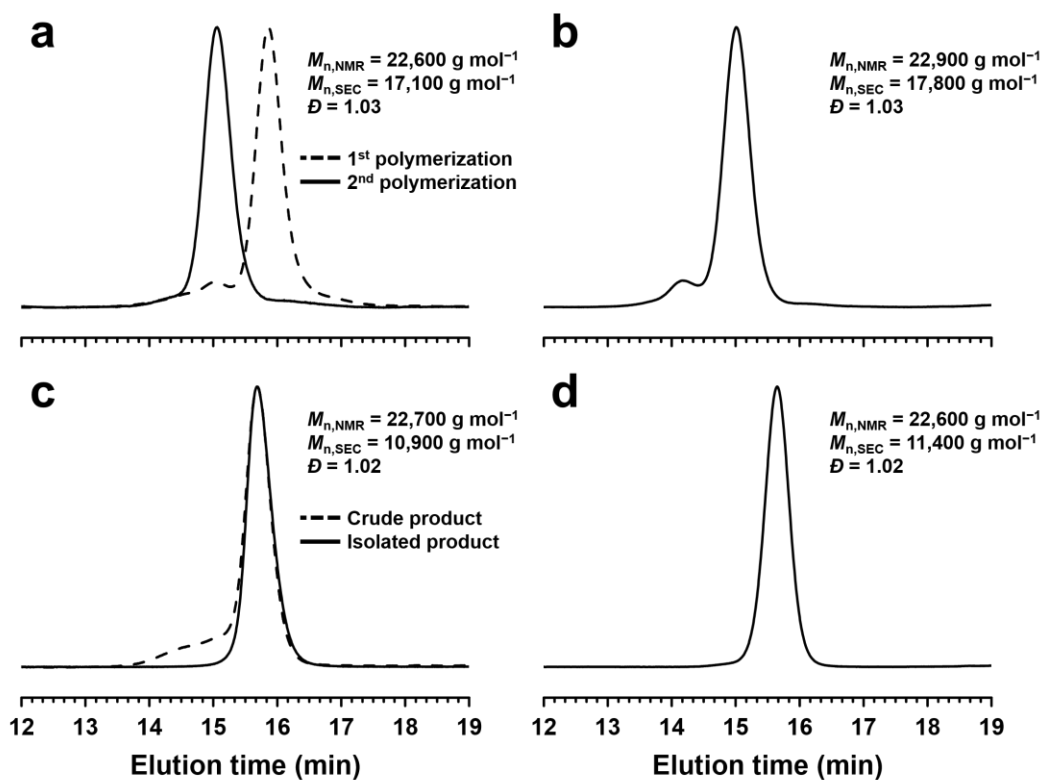
**Synthesis of *Tricycle-A*.** A solution of (N<sub>3</sub>)<sub>3</sub>-(PDGE-*b*-PTEGGE-C≡CH)<sub>3</sub> (900 mg, 39.5 μmol) in degassed DMF (20 mL) was added to a solution of CuBr (567 mg, 3.95 mmol) and PMDETA (1.65 mL, 7.90 mmol) in degassed DMF (260 mL) using a syringe pump at the rate of 0.6 mL h<sup>–1</sup> at 95 °C under a N<sub>2</sub> atmosphere. After completing the addition, PSt–C≡CH (270 mg), CuBr (113 mg, 790 μmol), and PMDETA (330 μL, 1.58 mmol) were added to the reaction mixture. After stirring at 95 °C for 24h, the solvent of the mixture was removed by evaporation, and the residue was purified by passing through a pad of alumina followed by preparative SEC to give *Tricycle-A* as a light brown waxy solid (592 mg). Yield: 65.8%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.63 (triazole methine), 7.25 (aromatic), 4.79 (–OCH<sub>2</sub>–triazole ring–), 4.42 (–PhCH<sub>2</sub>–), 4.31 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>O–), 3.84–3.25 (–(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>–, –CCH<sub>2</sub>OCH<sub>2</sub>Ph–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–, –CH<sub>2</sub>CH(CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>)O–), 1.72–1.17 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)O–), 0.95–0.79 (–OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–).  $M_{n,NMR} = 22,700 \text{ g mol}^{-1}$ ;  $M_{n,SEC} = 10,900 \text{ g mol}^{-1}$ ;  $\mathcal{D} = 1.02$ .

**Synthesis of *Cage-A*.** Pd/C (480 mg) was added to a stirred solution of *Tricycle-A* (200 mg, 8.81 mmol) in dry THF (5 mL) under a H<sub>2</sub> atmosphere using a balloon. After stirring at 25 °C for 3 weeks, the Pd/C was removed using Celite filter, and then the solvent of the mixture was removed by

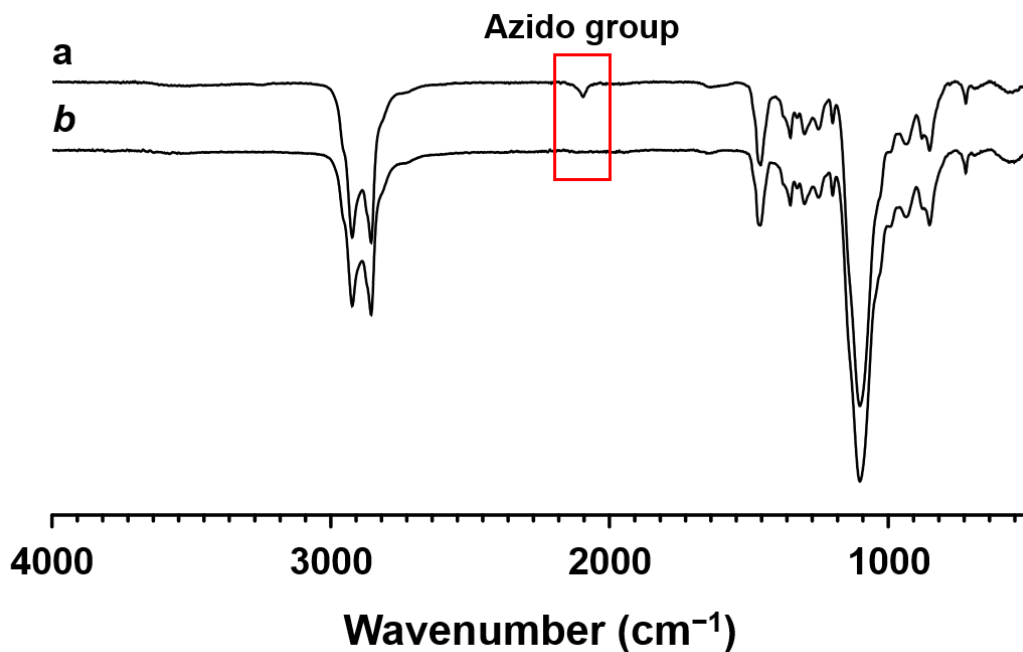
evaporation. The residue was dissolved in AcOEt, and then the solution was washed with NaCN aqueous solution and brine. The combined organic layer was dried over anhydrous MgSO<sub>4</sub>, and then concentrated to give **Cage-A** as a colorless waxy solid (97.6 mg). Yield: 43.3%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.63 (triazole methine), 7.25 (aromatic), 4.80 (–OCH<sub>2</sub>–triazole ring–), 4.32 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>O–), 3.84–3.23 (–(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>–, –CCH<sub>2</sub>OCH<sub>2</sub>Ph–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–, –CH<sub>2</sub>CH(CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>)O–), 1.79–1.15 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)O–), 0.99–0.75 (–OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–). *M*<sub>n,NMR</sub> = 22,600 g mol<sup>–1</sup>; *M*<sub>n,SEC</sub> = 11,900 g mol<sup>–1</sup>; *D* = 1.02.



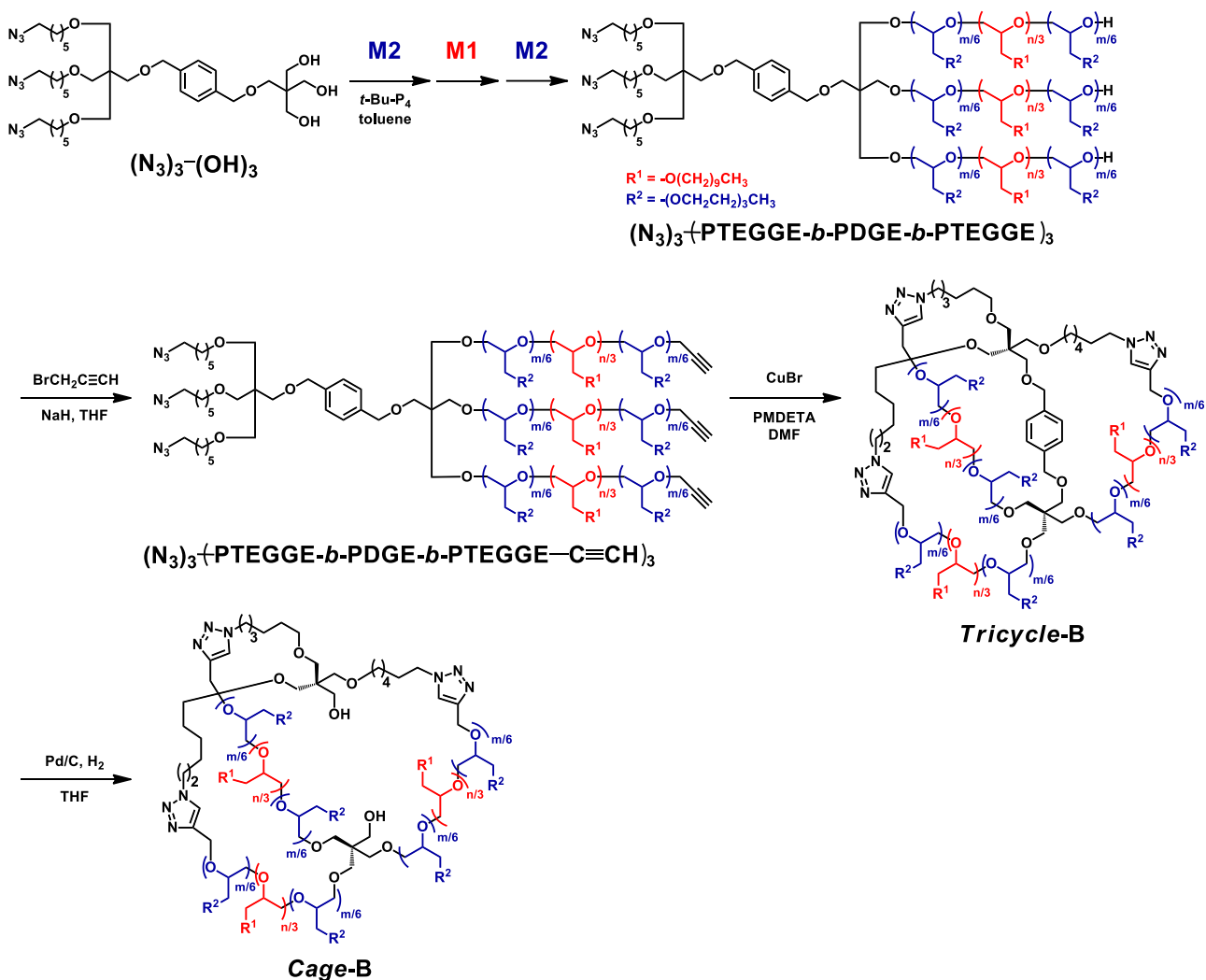
**Figure S1.**  $^1\text{H}$  NMR spectra of: (a)  $(\text{N}_3)_3\text{-(PDGE-}b\text{-PTEGGE)}_3$ , (b)  $(\text{N}_3)_3\text{-(PDGE-}b\text{-PTEGGE-C}\equiv\text{CH)}_3$ , (c) *Tricycle-A*, and (d) *Cage-A*.



**Figure S2.** SEC traces of: (a)  $(N_3)_3$ -(PDGE-*b*-PTEGGE) $_3$ , (b)  $(N_3)_3$ -(PDGE-*b*-PTEGGE-C $\equiv$ CH) $_3$ , (c) *Tricycle-A*, and (d) *Cage-A*. In (c), the crude product (dashed line) was purified using preparative SEC.



**Figure S3.** FT-IR spectra of: (a)  $(N_3)_3$ -(PDGE-*b*-PTEGGE-C $\equiv$ CH) $_3$ , and (b) *Tricycle-A*.



**Scheme S2.** The synthesis of *Cage-B*.

**Synthesis of (N<sub>3</sub>)<sub>3</sub>-(PTEGGE-*b*-PDGE-*b*-PTEGGE)<sub>3</sub>.** TEGGE (299  $\mu\text{L}$ , 1.45 mmol) was added to a stirred solution of (N<sub>3</sub>)<sub>3</sub>-(OH)<sub>3</sub> (43.4 mg, 57.9  $\mu\text{mol}$ ) and *t*-Bu-P<sub>4</sub> (57.9  $\mu\text{L}$  of a 1.0 mol L<sup>-1</sup> stock solution in *n*-hexane, 57.9  $\mu\text{mol}$ ) in toluene (208  $\mu\text{L}$ ), and the mixture was stirred at room temperature for 20 h. Afterwards, DGE (686  $\mu\text{L}$ , 2.90 mmol) and toluene (1.05 mL) were added to the mixture, and the mixture was stirred at room temperature for 20 h. TEGGE (299  $\mu\text{L}$ , 1.45 mmol) was then added to the mixture, and the mixture was stirred at room temperature for 20 h. An excess of benzoic acid was then added to the mixture to terminate the polymerization, and the polymer was then purified by passing through a pad of alumina and washed with THF to give (N<sub>3</sub>)<sub>3</sub>-(PTEGGE-*b*-PDGE-*b*-PTEGGE)<sub>3</sub> as a colorless waxy solid (1.12 g). Yield: 88.6%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.25 (aromatic), 4.44 (-PhCH<sub>2</sub>-), 3.85–3.28 (-(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>-, -CCH<sub>2</sub>OCH<sub>2</sub>Ph-, -OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O-, -CH<sub>2</sub>CH(CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>)O-), 3.24 (N<sub>3</sub>CH<sub>2</sub>-), 1.73–



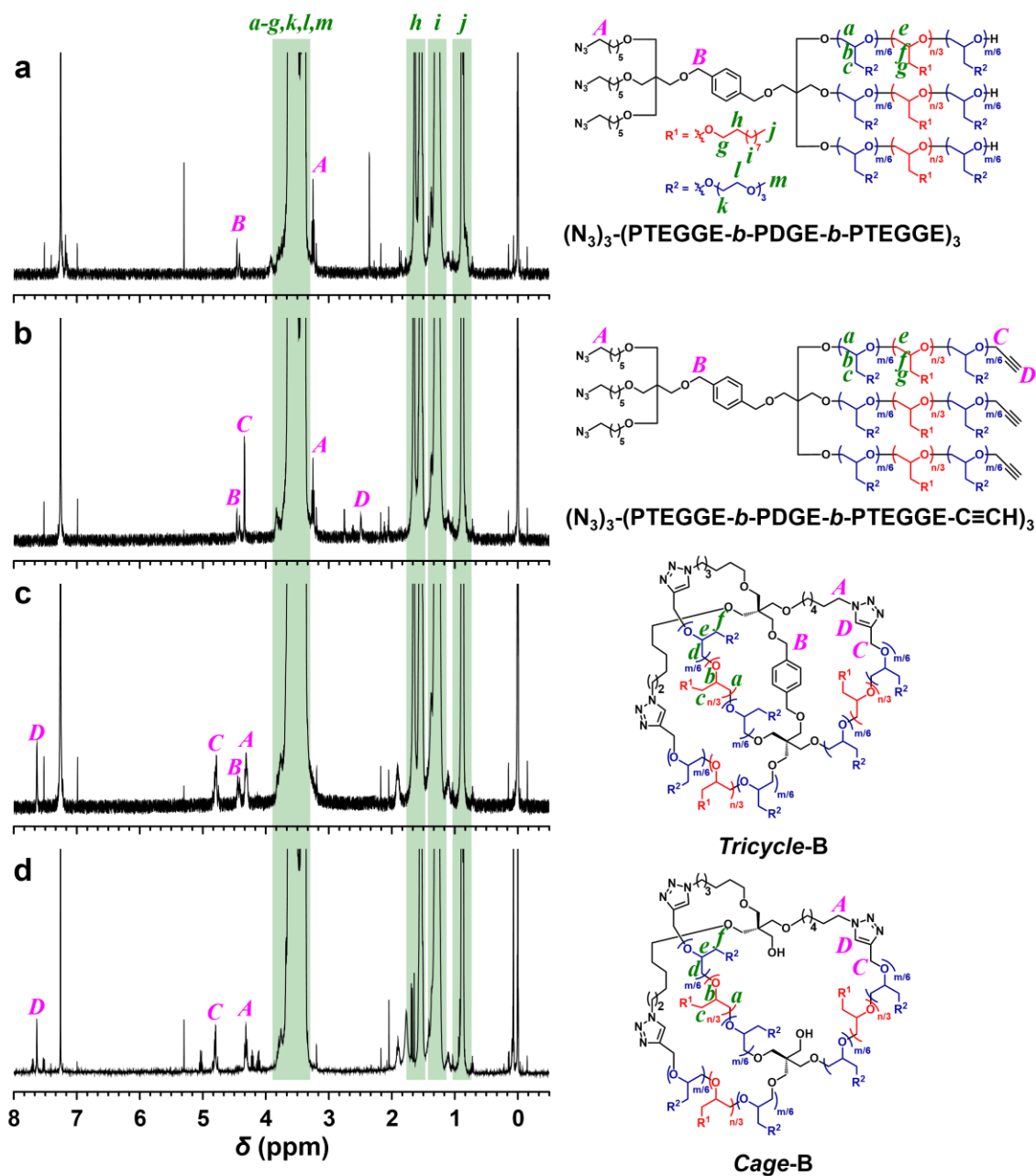
1.15 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)O–), 0.97–0.75 (–OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–).  $M_{n,NMR} = 22,600 \text{ g mol}^{-1}$ ;  $M_{n,SEC} = 16,100 \text{ g mol}^{-1}$ ;  $D = 1.03$ .

**Synthesis of (N<sub>3</sub>)<sub>3</sub>-(PTEGGE-*b*-PDGE-*b*-PTEGGE-C≡CH)<sub>3</sub>.** To a stirred solution of (N<sub>3</sub>)<sub>3</sub>-(PTEGGE-*b*-PDGE-*b*-PTEGGE)<sub>3</sub> (1.11 g, 49.1 μmol) in THF (5 ml) was added NaH (29.5 mg, 737 μmol; 60% in mineral oil), and the solution was stirred at 40 °C for 30 min. After cooling to room temperature, propargyl bromide (55.3 μL, 737 μmol) was then added to the solution, and the whole mixture was stirred at room temperature for 48 h. The polymer was purified by passing through a pad of alumina to give (N<sub>3</sub>)<sub>3</sub>-(PTEGGE-*b*-PDGE-*b*-PTEGGE-C≡CH)<sub>3</sub> as a pale yellow waxy solid (1.10 g). Yield: 99.1%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.25 (aromatic), 4.44 (–PhCH<sub>2</sub>–), 4.34 (HC≡CCH<sub>2</sub>O–), 3.87–3.29 (–(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>–, –CCH<sub>2</sub>OCH<sub>2</sub>Ph–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–, –CH<sub>2</sub>CH(CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>)O–), 3.24 (N<sub>3</sub>CH<sub>2</sub>–), 2.49 (HC≡C–), 1.77–1.16 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)O–), 0.99–0.74 (–OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–).  $M_{n,NMR} = 22,800 \text{ g mol}^{-1}$ ;  $M_{n,SEC} = 15,500 \text{ g mol}^{-1}$ ;  $D = 1.03$ .

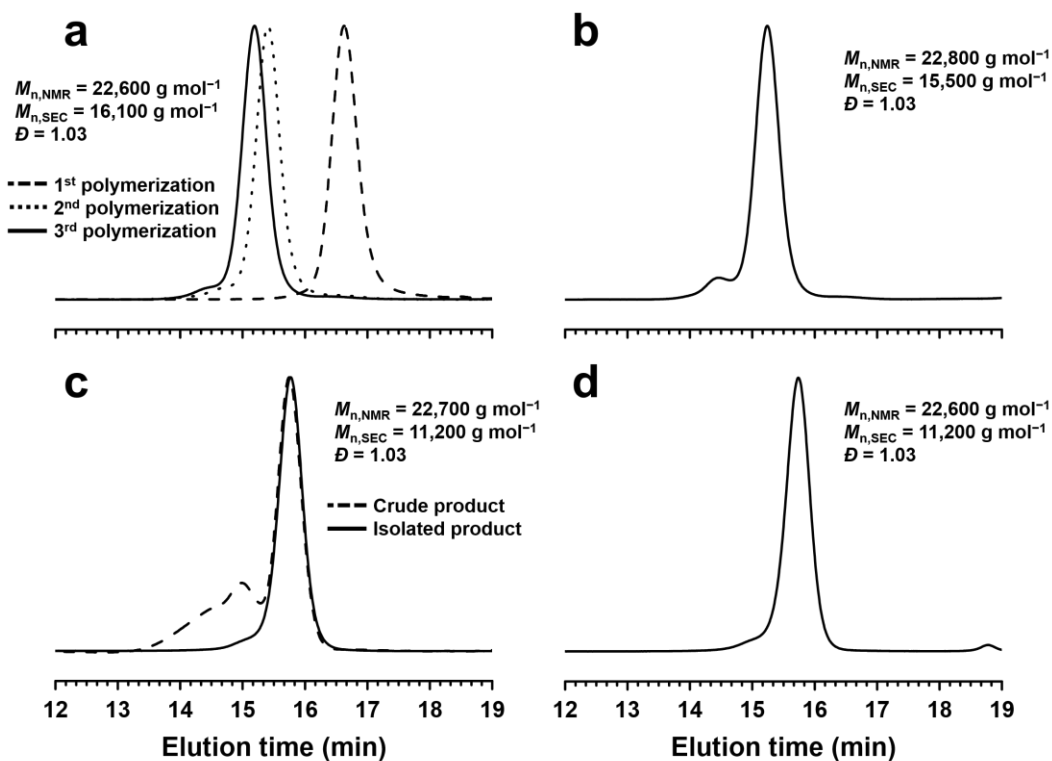
**Synthesis of *Tricycle-B*.** A solution of (N<sub>3</sub>)<sub>3</sub>-(PTEGGE-*b*-PDGE-*b*-PTEGGE-C≡CH)<sub>3</sub> (1.08 g, 47.6 μmol) in degassed DMF (24 mL) was added to a solution of CuBr (683 mg, 4.76 mmol) and PMDETA (1.99 mL, 9.52 mmol) in degassed DMF (317 mL) using a syringe pump at the rate of 0.6 mL h<sup>-1</sup> at 95 °C under a N<sub>2</sub> atmosphere. After completing the addition, PSt–C≡CH (320 mg), CuBr (137 mg, 952 μmol), and PMDETA (397 μL, 1.90 mmol) were added to the reaction mixture. After stirring at 95 °C for 24h, the solvent of the mixture was removed by evaporation, and the residue was purified by passing through a pad of alumina followed by preparative SEC to give *Tricycle-B* as a light brown waxy solid (337 mg). Yield: 31.2%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.63 (triazole methine), 7.25 (aromatic), 4.80 (–OCH<sub>2</sub>–triazole ring–), 4.43 (–PhCH<sub>2</sub>–), 4.31 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>O–), 3.84–3.23 (–(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>–, –CCH<sub>2</sub>OCH<sub>2</sub>Ph–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–, –CH<sub>2</sub>CH(CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>)O–), 1.79–1.17 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)O–), 0.98–0.76 (–OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–).  $M_{n,NMR} = 22,700 \text{ g mol}^{-1}$ ;  $M_{n,SEC} = 11,200 \text{ g mol}^{-1}$ ;  $D = 1.03$ .

**Synthesis of *Cage-B*.** Pd/C (450 mg) was added to a stirred solution of *Tricycle-B* (150 mg, 6.61 mmol) in dry THF (5 mL) under a H<sub>2</sub> atmosphere using a balloon. After stirring at 25 °C for 3 weeks,

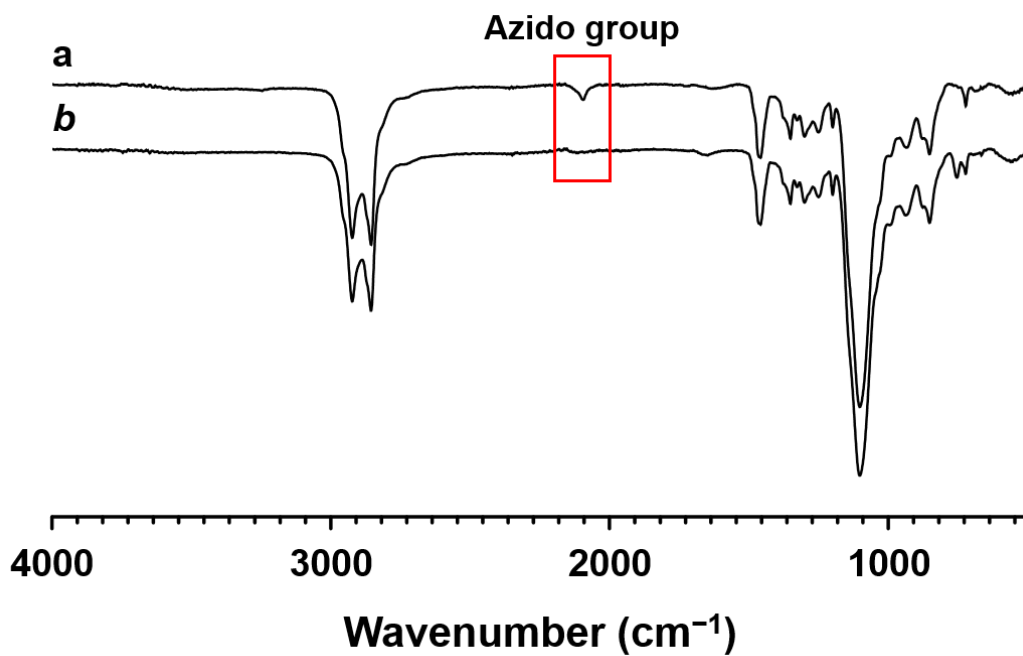
the Pd/C was removed using Celite filter, and then the solvent of the mixture was removed by evaporation. The residue was dissolved in AcOEt, and then the solution was washed with NaCN aqueous solution and brine. The combined organic layer was dried over anhydrous MgSO<sub>4</sub>, and then concentrated to give **Cage-B** as a colorless waxy solid (113 mg). Yield: 75.3%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.63 (triazole methine), 7.25 (aromatic), 4.80 (–OCH<sub>2</sub>–triazole ring–), 4.30 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>O–), 3.84–3.24 (–(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>–, –CCH<sub>2</sub>OCH<sub>2</sub>Ph–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–, –CH<sub>2</sub>CH(CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>)O–), 1.63–1.16 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)O–), 0.99–0.79 (–OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–). *M*<sub>n,NMR</sub> = 22,600 g mol<sup>–1</sup>; *M*<sub>n,SEC</sub> = 11,200 g mol<sup>–1</sup>; *D* = 1.03.



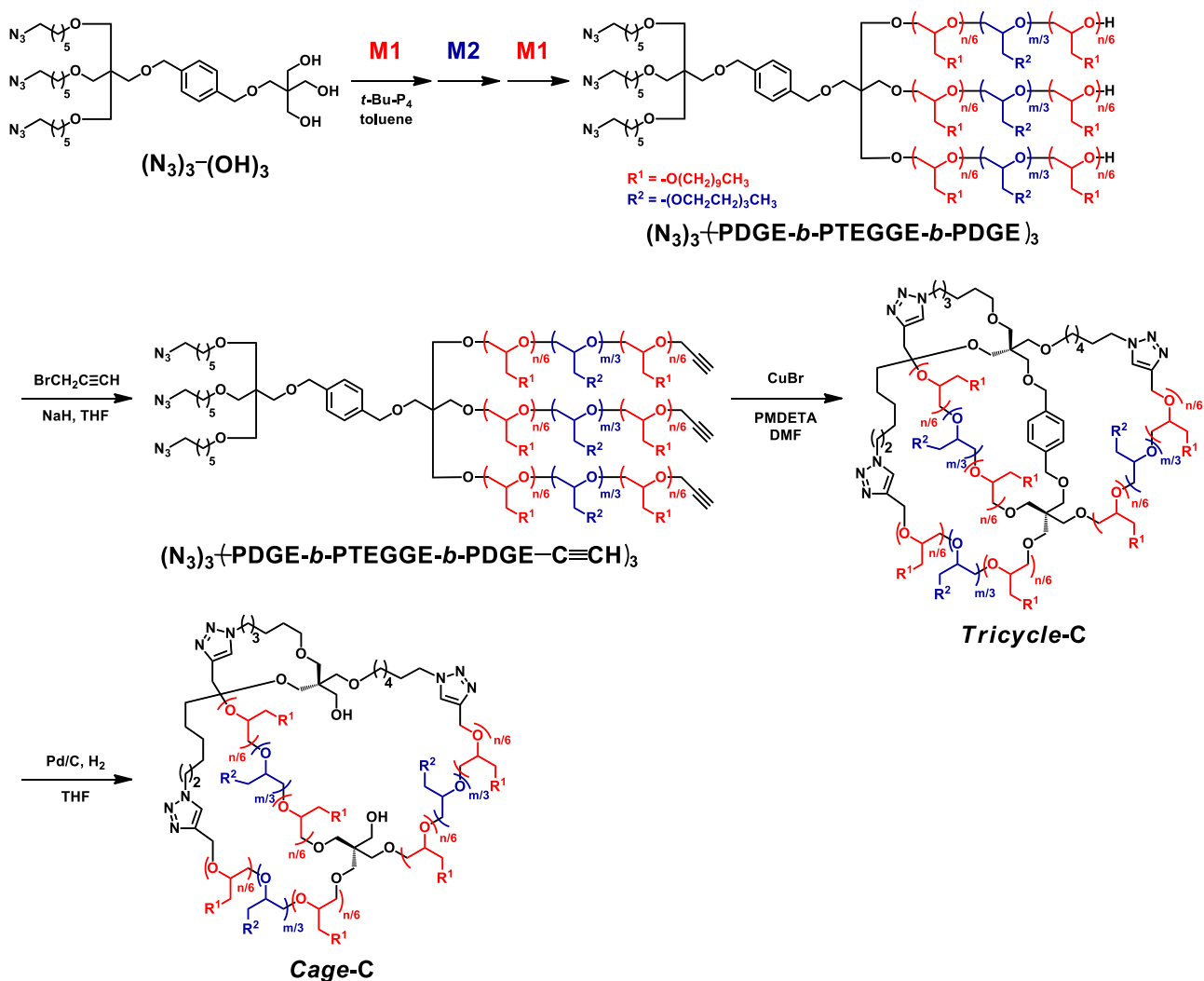
**Figure S4.** <sup>1</sup>H NMR spectra of: (a) (N<sub>3</sub>)<sub>3</sub>-(PTEGGE-*b*-PDGE-*b*-PTEGGE)<sub>3</sub>, (b) (N<sub>3</sub>)<sub>3</sub>-(PTEGGE-*b*-PDGE-*b*-PTEGGE-C≡CH)<sub>3</sub>, (c) *Tricycle-B*, and (d) *Cage-B*.



**Figure S5.** SEC traces of: (a)  $(N_3)_3$ -(PTEGGE-*b*-PDGE-*b*-PTEGGE)<sub>3</sub>, (b)  $(N_3)_3$ -(PTEGGE-*b*-PDGE-*b*-PTEGGE-C≡CH)<sub>3</sub>, (c) *Tricycle-B*, and (d) *Cage-B*. In (c), the crude product (dashed line) was purified using preparative SEC.



**Figure S6.** FT-IR spectra of: (a)  $(N_3)_3$ -(PTEGGE-*b*-PDGE-*b*-PTEGGE-C≡CH)<sub>3</sub>, and (b) *Tricycle-B*.



Scheme S3. The synthesis of *Cage-C*.

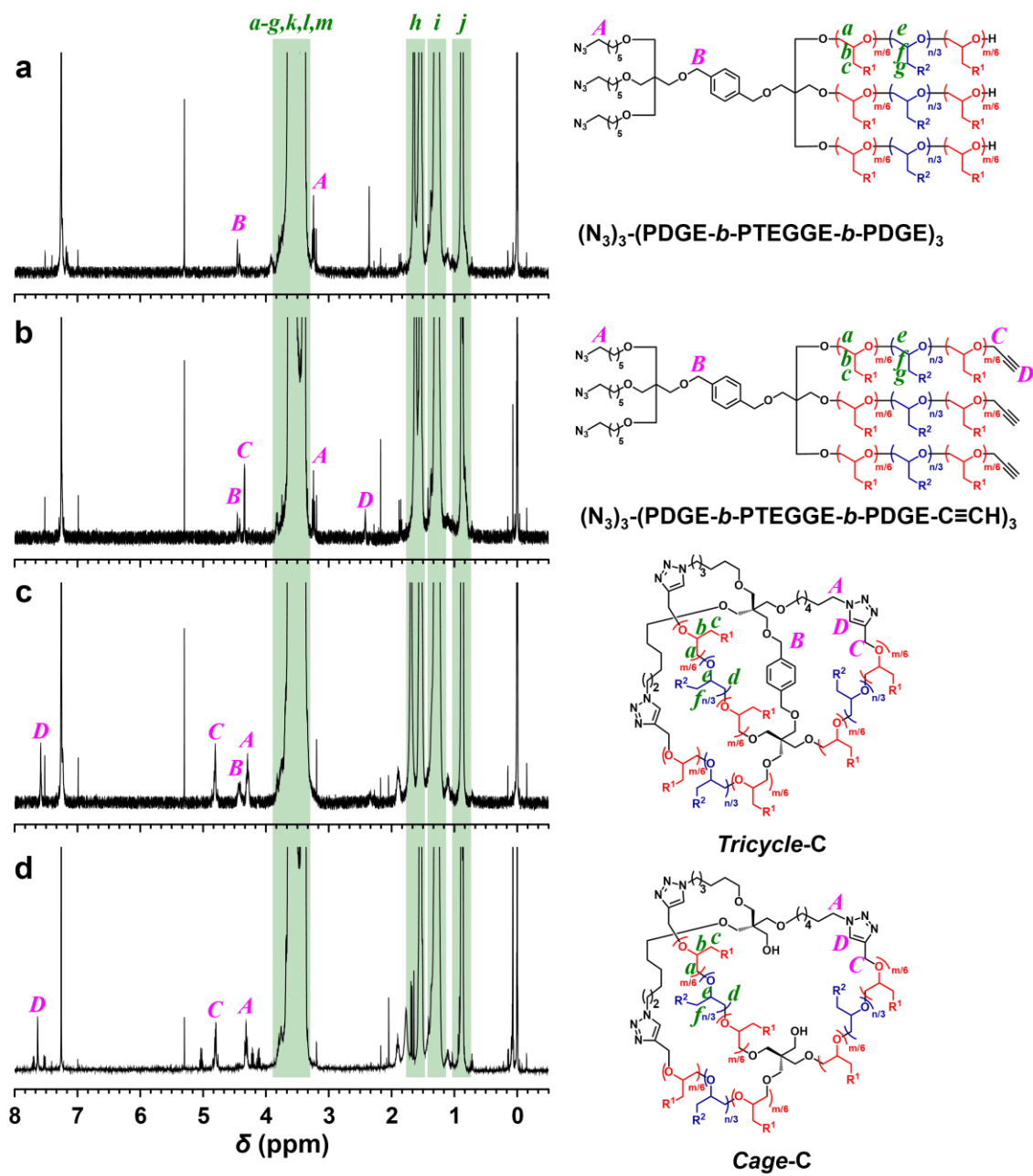
**Synthesis of  $(N_3)_3-(PDGE-b-PTEGGE-b-PDGE)_3$ .** DGE (320  $\mu$ L, 1.35 mmol) was added to a stirred solution of  $(N_3)_3-(OH)_3$  (40.6 mg, 54.1  $\mu$ mol) and *t*-Bu-P<sub>4</sub> (54.1  $\mu$ L of a 1.0 mol L<sup>-1</sup> stock solution in *n*-hexane, 54.1  $\mu$ mol) in toluene (166  $\mu$ L), and the mixture was stirred at room temperature for 20 h. Afterwards, TEGGE (559  $\mu$ L, 2.71 mmol) and toluene (1.07 mL) were added to the mixture, and the mixture was stirred at room temperature for 20 h. DGE (320  $\mu$ L, 1.35 mmol) was then added to the mixture, and the mixture was stirred at room temperature for 20 h. An excess of benzoic acid was then added to the mixture to terminate the polymerization, and the polymer was then purified by passing through a pad of alumina and washed with THF to give  $(N_3)_3-(PDGE-b-PTEGGE-b-PDGE)_3$  as a colorless waxy solid (1.06 g). Yield: 89.8. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.25 (aromatic), 4.44 (–PhCH<sub>2</sub>–), 3.84–3.28 (–(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>–, –CCH<sub>2</sub>OCH<sub>2</sub>Ph–,

$-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2(\text{CH}_2)_8\text{CH}_3)\text{O}-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3)\text{O}-$ , 3.25 ( $\text{N}_3\text{CH}_2-$ ), 1.74–1.15 ( $-\text{triazole ring}-\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{O}-$ ,  $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3)\text{O}-$ ), 0.97–0.75 ( $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2(\text{CH}_2)_8\text{CH}_3)\text{O}-$ ).  $M_{n,\text{NMR}} = 22,700 \text{ g mol}^{-1}$ ;  $M_{n,\text{SEC}} = 17,500 \text{ g mol}^{-1}$ ;  $\mathcal{D} = 1.03$ .

**Synthesis of  $(\text{N}_3)_3$ -(PDGE-*b*-PTEGGE-*b*-PDGE-C $\equiv$ CH) $_3$ .** To a stirred solution of  $(\text{N}_3)_3$ -(PDGE-*b*-PTEGGE-*b*-PDGE) $_3$  (1.05 g, 46.3  $\mu\text{mol}$ ) in THF (5 ml) was added NaH (27.8 mg, 695  $\mu\text{mol}$ ; 60% in mineral oil), and the solution was stirred at 40 °C for 30 min. After cooling to room temperature, propargyl bromide (52.1  $\mu\text{L}$ , 695  $\mu\text{mol}$ ) was then added to the solution, and the whole mixture was stirred at room temperature for 48 h. The polymer was purified by passing through a pad of alumina to give  $(\text{N}_3)_3$ -(PDGE-*b*-PTEGGE-*b*-PDGE-C $\equiv$ CH) $_3$  as a pale yellow waxy solid (1.04 mg). Yield: 99.0%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.25 (aromatic), 4.44 ( $-\text{PhCH}_2-$ ), 4.33 ( $\text{HC}\equiv\text{CCH}_2\text{O}-$ ), 3.80–3.27 ( $-(\text{CH}_2)_5\text{CH}_2\text{OCH}_2-$ ,  $-\text{CCH}_2\text{OCH}_2\text{Ph}-$ ,  $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2(\text{CH}_2)_8\text{CH}_3)\text{O}-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3)\text{O}-$ ), 3.24 ( $\text{N}_3\text{CH}_2-$ ), 2.42 ( $\text{HC}\equiv\text{C}-$ ), 1.79–1.13 ( $-\text{triazole ring}-\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{O}-$ ,  $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3)\text{O}-$ ), 0.98–0.76 ( $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2(\text{CH}_2)_8\text{CH}_3)\text{O}-$ ).  $M_{n,\text{NMR}} = 22,700 \text{ g mol}^{-1}$ ;  $M_{n,\text{SEC}} = 16,800 \text{ g mol}^{-1}$ ;  $\mathcal{D} = 1.04$ .

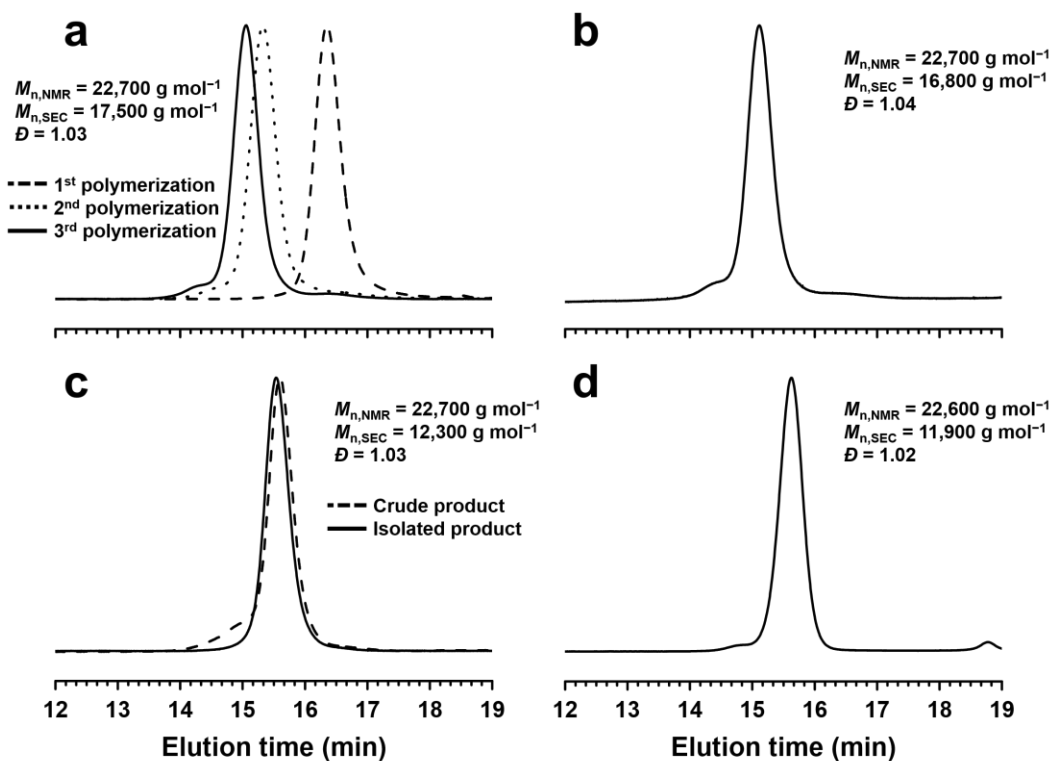
**Synthesis of *Tricycle-C*.** A solution of  $(\text{N}_3)_3$ -(PDGE-*b*-PTEGGE-*b*-PDGE-C $\equiv$ CH) $_3$  (1.04 g, 45.9  $\mu\text{mol}$ ) in degassed DMF (23 mL) was added to a solution of CuBr (658 mg, 4.59 mmol) and PMDETA (1.92 mL, 9.18 mmol) in degassed DMF (306 mL) using a syringe pump at the rate of 0.6 mL h $^{-1}$  at 95 °C under a  $\text{N}_2$  atmosphere. After completing the addition, PSt-C $\equiv$ CH (310 mg), CuBr (132 mg, 918  $\mu\text{mol}$ ), and PMDETA (384  $\mu\text{L}$ , 1.84 mmol) were added to the reaction mixture. After stirring at 95 °C for 24h, the solvent of the mixture was removed by evaporation, and the residue was purified by passing through a pad of alumina followed by preparative SEC to give *Tricycle-C* as a light brown waxy solid (719 mg). Yield: 69.1%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.58 (triazole methine), 7.25 (aromatic), 4.81 ( $-\text{OCH}_2$ -triazole ring-), 4.42 ( $-\text{PhCH}_2-$ ), 4.29 ( $-\text{triazole ring}-\text{CH}_2(\text{CH}_2)_5\text{O}-$ ), 3.84–3.22 ( $-(\text{CH}_2)_5\text{CH}_2\text{OCH}_2-$ ,  $-\text{CCH}_2\text{OCH}_2\text{Ph}-$ ,  $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2(\text{CH}_2)_8\text{CH}_3)\text{O}-$ ,  $-\text{CH}_2\text{CH}(\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3)\text{O}-$ ), 1.83–1.16 ( $-\text{triazole ring}-\text{CH}_2(\text{CH}_2)_4\text{CH}_2\text{O}-$ ,  $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_3)\text{O}-$ ), 0.99–0.75 ( $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2(\text{CH}_2)_8\text{CH}_3)\text{O}-$ ).  $M_{n,\text{NMR}} = 22,700 \text{ g mol}^{-1}$ ;  $M_{n,\text{SEC}} = 12,300 \text{ g mol}^{-1}$ ;  $\mathcal{D} = 1.03$ .

**Synthesis of Cage-C.** Pd/C (480 mg) was added to a stirred solution of *Tricycle-C* (200 mg, 8.81 mmol) in dry THF (5 mL) under a H<sub>2</sub> atmosphere using balloon. After stirring at 25 °C for 3 weeks, the Pd/C was removed using Celite filter, and then the solvent of the mixture was removed by evaporation. The residue was dissolved in AcOEt, and then the solution was washed with NaCN aqueous solution and brine. The combined organic layer was dried over anhydrous MgSO<sub>4</sub>, and then concentrated to give *Cage-C* as a colorless waxy solid (97.6 mg). Yield: 43.3%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.60 (triazole methine), 7.25 (aromatic), 4.81 (–OCH<sub>2</sub>–triazole ring–), 4.30 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>O–), 3.84–3.21 (–(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>–, –CCH<sub>2</sub>OCH<sub>2</sub>Ph–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–, –CH<sub>2</sub>CH(CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>)O–), 1.79–1.16 (–triazole ring–CH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O–, –OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>)O–), 0.99–0.77 (–OCH<sub>2</sub>CH(CH<sub>2</sub>OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>)O–). *M*<sub>n,NMR</sub> = 22,600 g mol<sup>–1</sup>; *M*<sub>n,SEC</sub> = 11,900 g mol<sup>–1</sup>; *D* = 1.02.

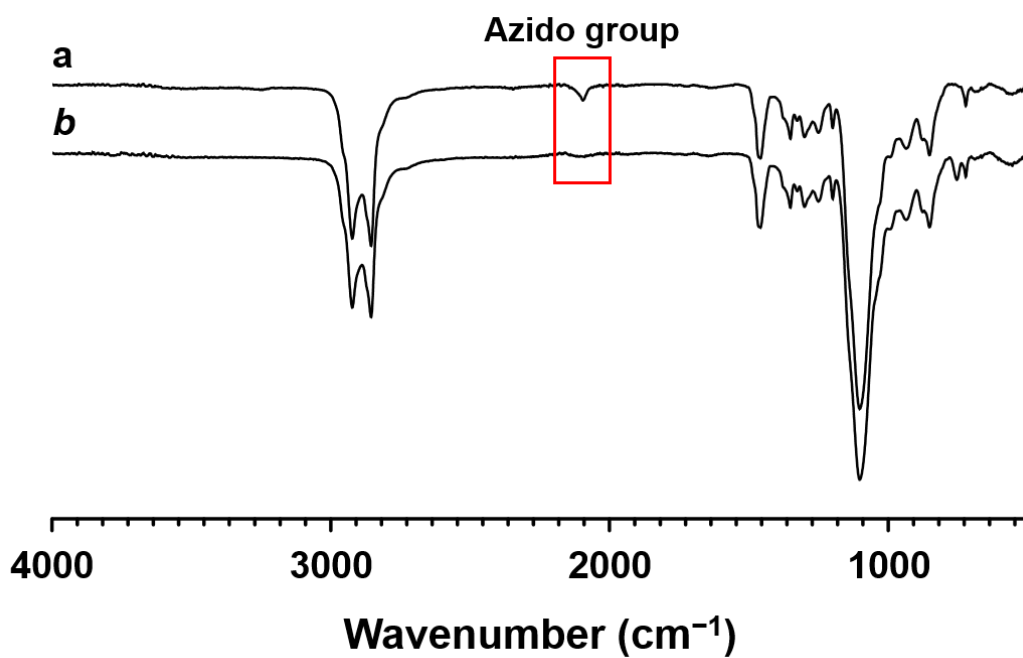


**Figure S7.** <sup>1</sup>H NMR spectra of: (a) (N<sub>3</sub>)<sub>3</sub>-(PDGE-*b*-PTEGGE-*b*-PDGE)<sub>3</sub>, (b) (N<sub>3</sub>)<sub>3</sub>-(PDGE-*b*-PTEGGE-*b*-PDGE-C≡CH)<sub>3</sub>, (c) *Tricycle-C*, and (d) *Cage-C*.





**Figure S8.** SEC traces of: (a)  $(N_3)_3$ -(PDGE-*b*-PTEGGE-*b*-PDGE)<sub>3</sub>, (b)  $(N_3)_3$ -(PDGE-*b*-PTEGGE-*b*-PDGE-C≡CH)<sub>3</sub>, (c) *Tricycle-C*, and (d) *Cage-C*. In (c), the crude product (dashed line) was purified using preparative SEC.



**Figure S9.** FT-IR spectra of: (a)  $(N_3)_3$ -(PDGE-*b*-PTEGGE-*b*-PDGE-C≡CH)<sub>3</sub>, and (b) *Tricycle-C*.

## Grazing Incidence X-Ray Scattering (GIXS) Data Analysis

The intensity of GIXS ( $I_{\text{GIXS}}$ ) from structures in a thin film can be expressed by the scattering formula derived recently:<sup>5-8</sup>

$$I_{\text{GIXS}}(\alpha_f, 2\theta_f) \cong \frac{1}{16\pi^2} \cdot \frac{1 - e^{-2\text{Im}(q_z)t}}{2\text{Im}(q_z)} \cdot \left[ \begin{array}{l} |T_i T_f|^2 I_1(q_{\parallel}, \text{Re}(q_{1,z})) + \\ |T_i R_f|^2 I_1(q_{\parallel}, \text{Re}(q_{2,z})) + \\ |T_f R_i|^2 I_1(q_{\parallel}, \text{Re}(q_{3,z})) + \\ |R_i R_f|^2 I_1(q_{\parallel}, \text{Re}(q_{4,z})) \end{array} \right] \quad (1)$$

where  $\alpha_f$  and  $2\theta_f$  are the out-of-plane and in-plane exit angle of the out-going X-ray beam respectively,  $\text{Im}(q_z) = |\text{Im}(k_{z,f})| + |\text{Im}(k_{z,i})|$ ,  $\text{Re}(x)$  is the real part of  $x$ ,  $t$  is the film thickness,  $R_i$  and  $T_i$  are the reflected and transmitted amplitudes of the incoming X-ray beam respectively, and  $R_f$  and  $T_f$  are the reflected and transmitted amplitudes of the outgoing X-ray beam respectively. In addition,  $q_{\parallel} = \sqrt{q_x^2 + q_y^2}$ ,  $q_{1,z} = k_{z,f} - k_{z,i}$ ,  $q_{2,z} = -k_{z,f} - k_{z,i}$ ,  $q_{3,z} = k_{z,f} + k_{z,i}$ , and  $q_{4,z} = -k_{z,f} + k_{z,i}$ ; here,  $k_{z,i}$  is the  $z$ -component of the wave vector of the incoming X-ray beam, which is given by  $k_{z,i} = k_o \sqrt{n_R^2 - \cos^2 \alpha_i}$ , and  $k_{z,f}$  is the  $z$ -component of the wave vector of the outgoing X-ray beam, which is given by  $k_{z,f} = k_o \sqrt{n_R^2 - \cos^2 \alpha_f}$ , where  $k_o = 2\pi/\lambda$ ,  $\lambda$  is the wavelength of the X-ray beam,  $n_R$  is the refractive index of the film given by  $n_R = 1 - \delta + i\zeta$  with dispersion  $\delta$  and absorption  $\zeta$ , and  $\alpha_i$  is the out-of-plane grazing incident angle of the incoming X-ray beam.  $q_x$ ,  $q_y$ , and  $q_z$  are the components of the scattering vector  $\mathbf{q}$ .  $I_1$  is the scattering intensity of the structure in the film, which can be calculated kinematically.

In eq 1,  $I_1$  is the scattered intensity from morphological structures in a film and, thus, can be expressed by the following equation:<sup>5-10</sup>

$$I_1(\mathbf{q}) = P(\mathbf{q}) \cdot S(\mathbf{q}) \quad (2)$$

where  $P(\mathbf{q})$  is the form factor that describes the shape, size, and orientation of scatterers in the thin film, and  $S(\mathbf{q})$  is the structure factor which provides information on the relative positions of the group

of scatterers, such as the crystal lattice parameters, orientation, dimension, and symmetry in an ordered structure and the interdistance of domains.

In the case of two phase elliptical hexagonal cylinder structure, the form factor  $P(\mathbf{q})$  of a cylindrical scatterer with a length  $L_c$  and cross-section semi axes  $r_{cz}$  and  $r_{cy}$  can be expressed as the following equation:<sup>10-12</sup>

$$P(\mathbf{q}) = \left\{ 2\pi r_{cz} r_{cy} L_c \cdot \frac{J_1 \left[ (q_z^2 r_{cz}^2 + q_y^2 r_{cy}^2)^{1/2} \right]}{(q_z^2 r_{cz}^2 + q_y^2 r_{cy}^2)^{1/2}} \cdot \frac{\sin(q_x L_c / 2)}{q_x L_c / 2} \right\}^2 \quad (3)$$

Finally, the expression for the two phase (core-shell) cylinder can be summarized as the following:

$$P(\mathbf{q}) = P_{\text{core}}(\mathbf{q})(\rho_{\text{core}} - \rho_{\text{shell}}) + P_{\text{shell}}(\mathbf{q})(\rho_{\text{shell}} - \rho_{\text{matrix}}). \quad (4)$$

For the lamellar structure consisted of three layers, the form factor  $P(\mathbf{q})$  can be expressed by the following equation:

$$P(\mathbf{q}) = \left[ \begin{aligned} & 4L_x L_y H_{\text{inner}} (\rho_{\text{inner}} - \rho_{\text{outer}}) \cdot \frac{\sin(q_x L_x)}{q_x L_x} \cdot \frac{\sin(q_y L_y)}{q_y L_y} \cdot \frac{\sin(q_z H_{\text{inner}})}{q_z H_{\text{inner}}} \\ & 4L_x L_y H_{\text{outer}} (\rho_{\text{outer}} - \rho_{\text{matrix}}) \cdot \frac{\sin(q_x L_x)}{q_x L_x} \cdot \frac{\sin(q_y L_y)}{q_y L_y} \cdot \frac{\sin(q_z H_{\text{outer}})}{q_z H_{\text{outer}}} \end{aligned} \right]^2 \quad (5)$$

where  $L_x$  and  $L_y$  are the length and width of lamellar structure respectively,  $H_{\text{inner}}$  and  $H_{\text{outer}}$  are the inner and outer layer heights respectively, and  $\rho_{\text{inner}}$  and  $\rho_{\text{outer}}$  are the relative electron densities of the inner and outer layers respectively.  $\rho_{\text{matrix}}$  is the relative electron density of the matrix layer. For the lamellar structure,  $H_{\text{inner}}$  can be assigned to the layer thickness  $l_1$  of phase-1 having a relatively electron density  $\rho_{\text{inner}}$ . The layer thickness  $l_2$  of phase-2 (namely, interfacial layer thickness  $l_i$ ) having a relatively electron density  $\rho_{\text{outer}}$  ( $= \rho_i$ ) can be estimated from  $H_{\text{inner}}$  and  $H_{\text{outer}}$ :  $l_2 = l_i = (H_{\text{outer}} - H_{\text{inner}})/2$ . The third layer thickness  $l_3$  having the relatively electron density  $\rho_{\text{matrix}}$  can be obtained from

the long period  $D_L$  of lamellar structure that is extracted from the structure factor  $S(\mathbf{q})$ :  $l_3 = (D_L - l_1 - 2l_2)$ .

For the form factors, all structural parameters can be further assumed to follow a Gaussian distribution  $G(A)$ :

$$G(A) = \frac{1}{\sqrt{2\pi}\sigma_A} \exp\left[-\frac{(A - \bar{A})^2}{2\sigma_A^2}\right] \quad (6)$$

where  $A$  can be one of the parameters,  $\bar{A}$  is the mean value, and  $\sigma_A$  is the standard deviation of  $A$  from  $\bar{A}$ .

For a paracrystalline lattice consisting of the three layers described above, the structure factor  $S(\mathbf{q})$  (the so-called interference function or lattice factor) can be determined from the Fourier transform of a complete set of lattice points.<sup>5-9,13,14</sup> In a paracrystal with distortion of the second kind, the positions of the lattice points can only be described with a positional distribution function (i.e.,  $g$ -factor). In the simple case where the autocorrelation function of the crystal lattice is given by the convolution product of the distributions of the lattice points along three axes, and the distribution function is a Gaussian,  $S(\mathbf{q})$  can be expressed by the following equation:<sup>13</sup>

$$S(\mathbf{q}) = \prod_{k=1}^3 Z_k(\mathbf{q}) \quad (7)$$

$$Z_k(\mathbf{q}) = 1 + \frac{F_k(\mathbf{q})}{1 - F_k(\mathbf{q})} + \frac{F_k^*(\mathbf{q})}{1 - F_k^*(\mathbf{q})} \quad (8)$$

$$F_k(\mathbf{q}) = |F_k(\mathbf{q})| e^{-i\mathbf{q}\cdot\mathbf{a}_k} \quad (9)$$

$$|F_k(\mathbf{q})| = \exp\left[-\frac{1}{2}(q_1^2 g_1^2 + q_2^2 g_2^2 + q_3^2 g_3^2)\right]. \quad (10)$$

Here  $g_1$ ,  $g_2$ , and  $g_3$  ( $= g$ ) are the components of the  $g$ -factor defined as

$$g_1 = \Delta \mathbf{a}_1 / \mathbf{a}_1 \quad (11)$$

$$g_2 = \Delta \mathbf{a}_2 / \mathbf{a}_2 \quad (12)$$

$$g_3 = \Delta \mathbf{a}_3 / \mathbf{a}_3 \quad (13)$$

where  $\mathbf{a}_k$  is the component of the fundamental vector  $\mathbf{a}$  of the domain structure and  $\Delta \mathbf{a}_k$  is the displacement of the vector  $\mathbf{a}_k$ . And  $q_1$ ,  $q_2$ , and  $q_3$  are the components of the scattering vector  $\mathbf{q}$ .

For two phase elliptical hexagonal cylinder structure, the components of  $\mathbf{q}$  in eq 10 are defined by

$$q_1 = \mathbf{a}_1 \cdot q_y + \mathbf{a}_1 \cdot q_z = \left| L_y \times q_y + 0 \times q_z \right| \quad (14a)$$

$$q_2 = \mathbf{a}_2 \cdot q_y + \mathbf{a}_2 \cdot q_z = \left| \left( -\frac{1}{2} \cdot L_y \right) \times q_y + L_z \times q_z \right| \quad (14b)$$

$$q_3 = \mathbf{a}_3 \cdot q_y + \mathbf{a}_3 \cdot q_z = \left| \left( -\frac{1}{2} \cdot L_y \right) \times q_y + (-1 \cdot L_z) \times q_z \right| \quad (14c)$$

where  $L_y$  and  $L_z$  are the lattice dimension parameters (i.e.,  $d$ -spacing values) along the  $q_y$ - and  $q_z$ -direction respectively.

For the lamellar structure composed of three layers, the components of  $\mathbf{q}$  in eq 10 are defined by

$$q_1 = \mathbf{a}_1 \cdot q_x = \left| d_x \times q_x \right| \quad (15a)$$

$$q_2 = \mathbf{a}_2 \cdot q_y = \left| d_y \times q_y \right| \quad (15a)$$

$$q_3 = \mathbf{a}_3 \cdot q_z = \left| D_L \times q_z \right| \quad (15a)$$

where  $d_x$  and  $d_y$  are the lattice dimension parameters (i.e.,  $d$ -spacing values) along the  $q_x$ - and  $q_y$ -direction respectively, and  $D_L$  is the long period along the  $q_z$ -direction.

Moreover, for a structure with a given orientation in a film, its fundamental vectors can be rotated and transformed by a rotation matrix. When the structure of the film is randomly oriented in the plane of the film but uniaxially oriented out of plane, the peak position vector  $\mathbf{q}_c$  of a certain reciprocal lattice point  $\mathbf{c}^*$  in the sample reciprocal lattice is given by

$$\begin{aligned}\mathbf{q}_c &= \mathbf{R} \cdot \mathbf{c}^* \\ \mathbf{q}_c &\equiv (q_{c,x}, q_{c,y}, q_{c,z})\end{aligned}\quad (16)$$

where  $\mathbf{R}$  is a  $3 \times 3$  matrix to decide the preferred orientation of the structure in the film, and  $q_{c,x}$ ,  $q_{c,y}$ , and  $q_{c,z}$  are the  $x$ ,  $y$ ,  $z$  components of the peak position vector  $\mathbf{q}_c$ , respectively. Using eq 16, every peak position can be obtained. Because of cylindrical symmetry, the Debye-Scherrer ring composed of the in-plane randomly oriented  $\mathbf{c}^*$  cuts an Ewald sphere at two positions in its top hemisphere:  $q_{\parallel} = q_{c,\parallel} \equiv \pm \sqrt{q_{c,x}^2 + q_{c,y}^2}$  with  $q_z = q_{c,z}$ . Thus diffraction patterns with cylindrical symmetry are easily calculated in the  $\mathbf{q}$ -space. It is then convenient to determine the preferred orientation of known structures and further to analyze anisotropic X-ray scattering patterns. However, since  $\mathbf{q}$ -space is distorted in GIXS by refraction and reflection effects, the relation between the detector plane expressed as the Cartesian coordinate defined by two perpendicular axes (i.e., by  $2\theta_f$  and  $\alpha_f$ ) and the reciprocal lattice points is needed. The two wave vectors  $k_{z,i}$  and  $k_{z,f}$  are corrected for refraction as  $k_{z,i} = k_o \sqrt{n_R^2 - \cos^2 \alpha_i}$  and  $k_{z,f} = k_o \sqrt{n_R^2 - \cos^2 \alpha_f}$  respectively. Therefore, the two sets of diffractions that result from the incoming and outgoing X-ray beams, and denoted by  $q_1$  and  $q_3$  respectively, are given at the exit angles by the following expression:

$$\alpha_f = \arccos \left( \sqrt{n_R^2 - \left( \frac{q_{c,z}}{k_o} \pm \sqrt{n_R^2 - \cos^2 \alpha_i} \right)^2} \right) \quad (17)$$

where  $q_{c,z}/k_o > \sqrt{n_R^2 - \cos^2 \alpha_i}$ . In eq 17, the positive sign denotes diffractions produced by the outgoing X-ray beam, and the negative sign denotes diffractions produced by the incoming X-ray beam. The in-plane incidence angle  $2\theta_i$  is usually zero, so the in-plane exit angle  $2\theta_f$  can be expressed as follow:

$$2\theta_f = \arccos \left[ \frac{\cos^2 \alpha_i + \cos^2 \alpha_f - \left( \frac{q_{c,\parallel}}{k_o} \right)^2}{2 \cos \alpha_i \cos \alpha_f} \right]. \quad (18)$$

Therefore, diffraction spots detected on the detector plane in GIXS measurements can be directly compared to those derived using eqs 16-18 from an appropriate model and thus analyzed in terms of the model.

To obtain information on the orientation of the paracrystal lattice of the phase separated micro domain structures from GIXS data, the distribution of the orientation vector  $\mathbf{n}$  is given by a function  $D(\varphi)$ , where  $\varphi$  is the polar angle between the  $\mathbf{n}$  vector and the out-of-plane of the film; for example,  $\varphi$  is zero when the  $\mathbf{n}$  vector in the film is oriented normal to the film plane. To calculate the 2D GIXS patterns,  $D(\varphi)$  should be represented by a numerical function. In relation to the distribution of the lattice orientation,  $D(\varphi)$  can generally be considered as a Gaussian distribution:

$$D(\varphi) = \frac{1}{\sqrt{2\pi}\sigma_\varphi} \exp \left[ -\frac{(\varphi - \bar{\varphi})^2}{2\sigma_\varphi^2} \right] \quad (19)$$

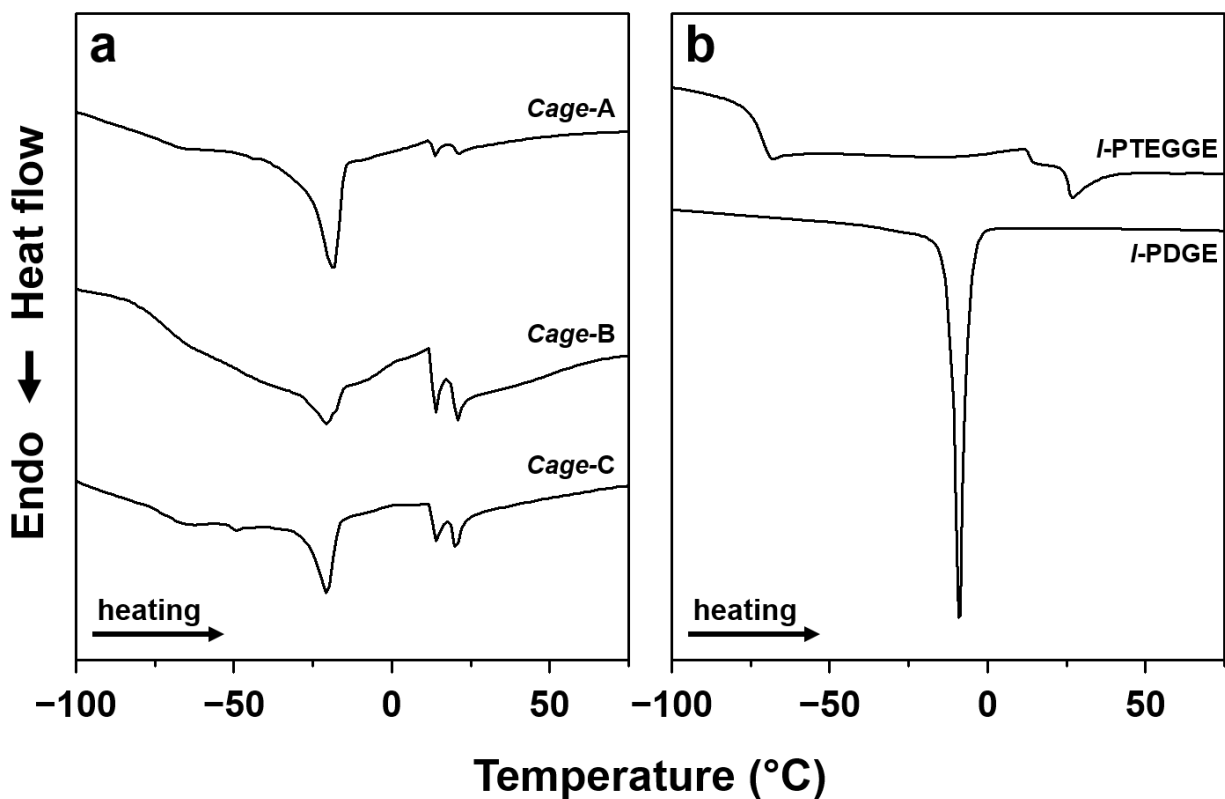
where  $\bar{\varphi}$  and  $\sigma_\varphi$  are the mean angle and standard deviation of  $\varphi$  from  $\bar{\varphi}$ , respectively. The observed scattering intensity  $I_{\text{GIXS},\varphi}(\mathbf{q})$  is obtained by integrating  $I_{\text{GIXS}}(\mathbf{q})$  over possible orientations of the lattice:

$$I_{\text{GIXS},\varphi}(\mathbf{q}) = \int_{-\pi}^{\pi} I_{\text{GIXS}}(\mathbf{q}) D(\varphi) d\varphi \quad (20)$$

The second order orientation factor  $O_s$  can be defined as the following equation:<sup>13-15</sup>

$$O_s = \int D(\varphi) \frac{(3\cos^2 \varphi - 1)}{2} d\varphi \quad (21)$$

When  $D(\varphi)$  is strongly peaked around  $\varphi = 0^\circ$  (i.e. vertical alignment),  $\cos\varphi = 1$  and  $O_s = 1$ . On the other hand, when  $\varphi = 90^\circ$ ,  $\cos\varphi = 0$  and  $O_s = -0.5$ . If the orientation is entirely random,  $\langle \cos^2\varphi \rangle = 1/3$  and  $O_s = 0$ . Thus,  $O_s$  is a measure of the orientation of nanostructures.



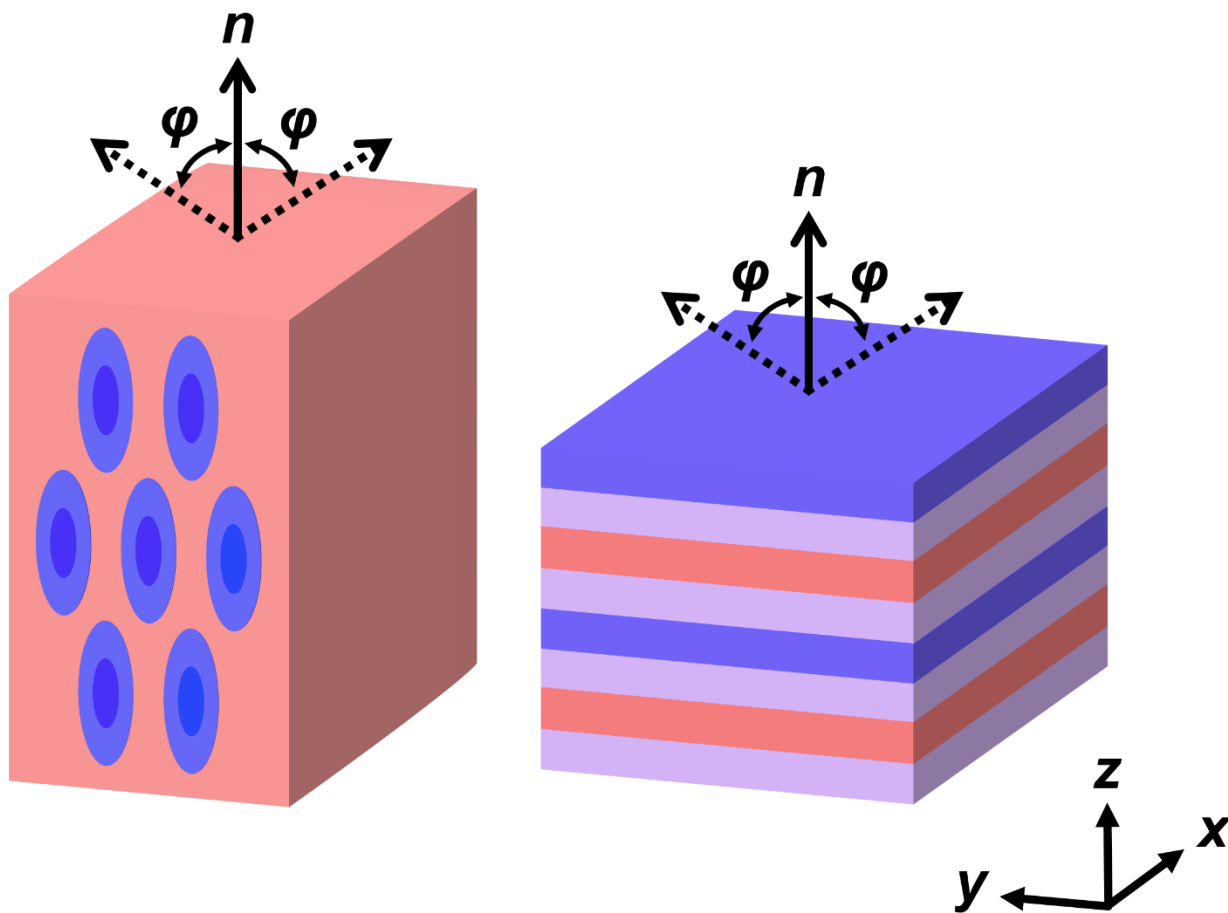
**Fig. S10** DSC thermograms measured with a rate of  $10.0\text{ }^\circ\text{C min}^{-1}$  in a nitrogen atmosphere: (a) *Cage-A*, *Cage-B*, and *Cage-C*; (b) PTEGGE and PDGE homopolymers.



**Table S1.** Thermal properties of BCPs in various molecular topologies

Polymer	$T_{g,\text{midpoint}}^a$ (°C)	$T_m^b$ (°C)
<i>Cage-A</i>	-72.3	-18.4, 13.7, 21.0
<i>Cage-B</i>	-73.7	-20.2, 14.0, 20.8
<i>Cage-C</i>	-70.8	-20.1, 14.0, 20.4
PDGE	- <sup>c</sup>	-9.0
PTEGGE	-72.2	26.9

<sup>a</sup>Midpoint temperature of glass transition at a heating rate of 10 °C min<sup>-1</sup> in differential scanning calorimetry (DSC) in a nitrogen atmosphere. <sup>b</sup>Melting temperature. <sup>c</sup>Glass transition temperature was not discernable.



**Fig. S11** Schematic representation of orientation vector and polar angle for cylindrical and lamellar structure. Polar angle  $\varphi$  is the angle between the orientation vector  $n$  set normal to the {001} planes of horizontal hexagonal cylinders and lamellae, and the out-of-plane direction of the film.

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