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Supplementary Information for

A Columnar Liquid-Crystalline Shape-Persistent Macrocyclic Having a Nanosegregated Structure

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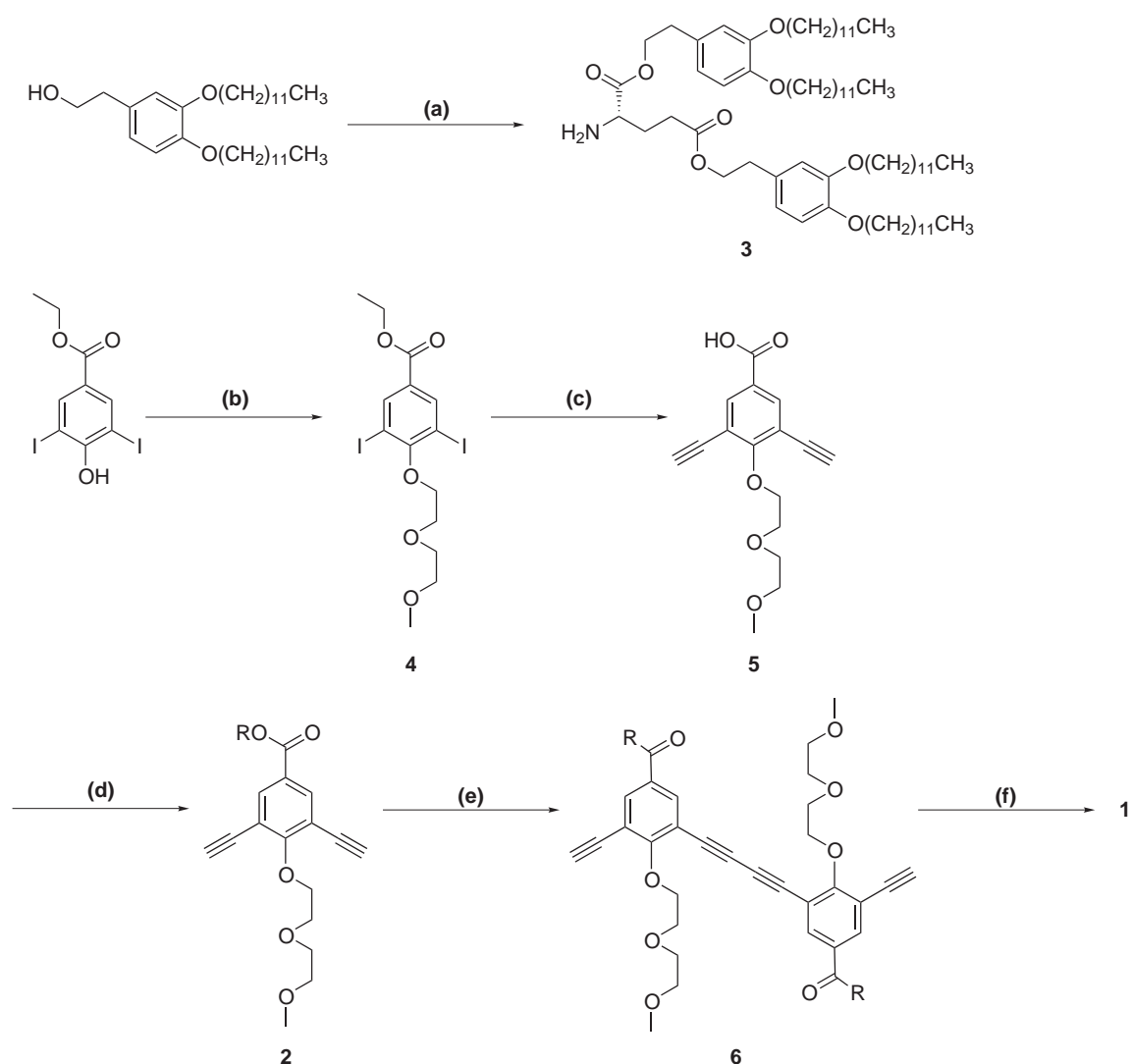


Figure S1. Synthesis of macrocyclic compound **1**. (a)(i) N-carbobenzoxy-L-glutamic acid, EDC, DMAP, CH_2Cl_2 , r.t., (ii) Pd/C, EtOAc, EtOH, 50 °C; (b) 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate, K_2CO_3 , DMF, 80 °C; (c)(i) ethynyltrimethylsilane, $\text{Pd}(\text{PPh}_3)_4$, CuI, triethylamine, r.t., (ii) TBAF, THF, H_2O , r.t., (iii) NaOH, EtOH, 80 °C; (d) **3**, EDC, DMAP, CH_2Cl_2 , r.t.; (e) $\text{CuCl}(\text{OH})\cdot\text{TMEDA}$, CHCl_3 , r.t.; (f) $\text{Cu}(\text{OAc})_2$, benzene, pyridine, r.t.

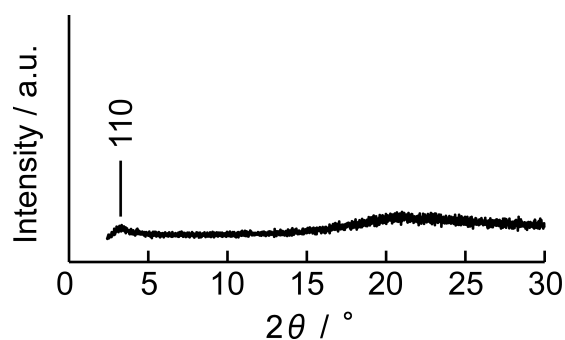


Figure S2. Wide angle X-ray diffraction pattern of **1** at 25 °C.

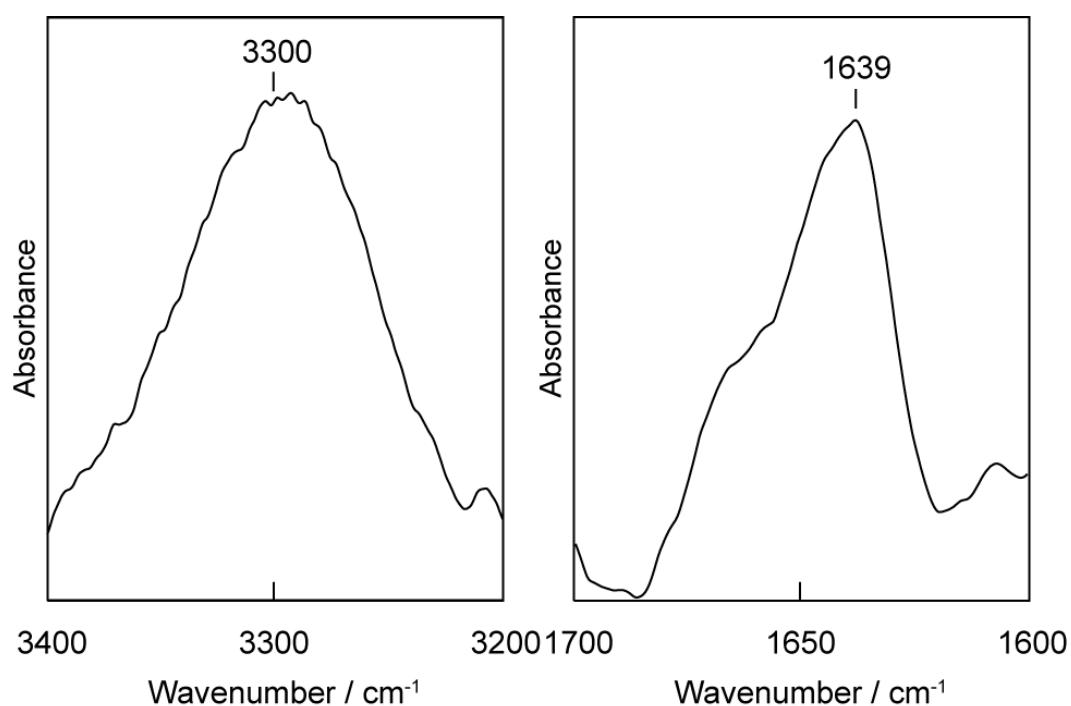


Figure S3. IR spectrum of **1** in the bulk state at 25 °C.

Experimental Section

General procedures: Recycling preparative gel permeation chromatography (GPC) was conducted with a Japan Analytical Industry LC-908 chromatograph. ^1H and ^{13}C NMR spectra were obtained using a JEOL JNM-LA400 at 400 and 100 MHz in CDCl_3 , respectively. Chemical shifts of ^1H and ^{13}C NMR signals were quoted to internal standard Me_4Si and expressed by chemical shifts in ppm (δ), multiplicity, coupling constant (Hz), and relative intensity. IR measurements were conducted using a JASCO FT/IR-660 Plus on KBr plates. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF)

mass spectra were performed on an Applied Biosystems Voyager-DE STR spectrometer. Elemental analyses were carried out using a Perkin-Elmer CHNS/O 2400 apparatus and a Yanaco MT-6 CHN autocoder. Differential scanning calorimetry (DSC) measurements (scanning rate of $10^{\circ}\text{C min}^{-1}$) were conducted using a NETZSCH DSC 204 Phoenix differential scanning calorimeter. An Olympus BH-2 optical polarizing microscope equipped with a Mettler FP82 HT hot-stage was used to verify thermal transitions and characterize anisotropic textures. Wide-Angle X-ray diffraction (WAXD) patterns were obtained using a Rigaku RINT-2500 diffractometer with $\text{CuK}\alpha$ radiation. Two-dimensional small-angle X-ray scattering (2D SAXS) patterns of the aligned materials were also recorded using an image plate detector (R-AXIS DS3C).

Materials. All chemical reagents and solvents were obtained from commercial sources and used without purification. All reactions were carried out under argon atmosphere in anhydrous solvents.

(S)-2-Aminopentanedioic acid bis-[2-(3,4-didodecyloxyphenyl)ethyl]ester **3**

The synthesis of compound **3** was conducted according to the same procedure given in the literature.¹ $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3391, 2953, 2926, 2850, 1727, 1589, 1519, 1470, 1428, 1389, 1329, 1266, 1231, 1182, 1141, 1068, 1021, 996, 956, 916, 864 and 814; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 6.81–6.70 (m, 6H), 4.31–4.23 (m, 4H), 3.98–3.94 (m, 8H), 3.42 (m, 1H), 2.89–2.83 (m, 4H), 2.43 (t, $J = 7.2\text{Hz}$, 2H), 2.03 (m, 1H), 1.84–1.75 (m, 9H), 1.46–1.26 (m, 72H) and 0.88 (t, $J = 6.8\text{Hz}$, 12H); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 175.4, 173.0, 149.14, 149.10, 147.90, 147.85, 130.3, 129.9, 121.0, 114.7, 114.6, 114.0, 69.34, 69.26, 65.6, 65.2, 53.7, 34.6, 31.9, 30.5, 29.67, 29.63, 29.61, 29.49, 29.43, 29.41, 29.34, 29.31, 26.0, 22.7 and 14.1; m/z (MALDI) 1092.1 (M^+ , $\text{C}_{69}\text{H}_{121}\text{NO}_8$ requires 1092.7).

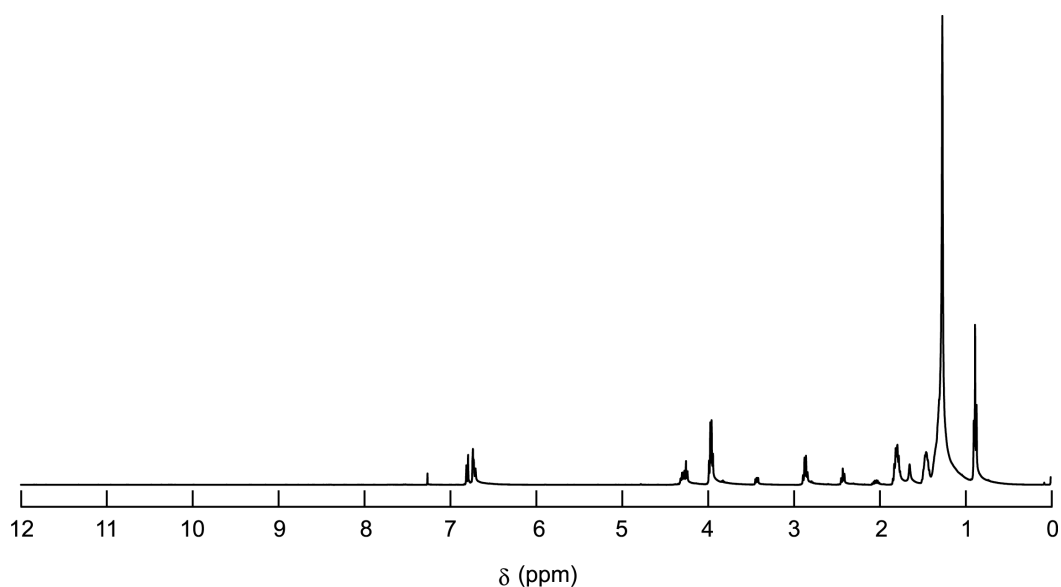


Figure S4. ^1H NMR spectrum of **3**.

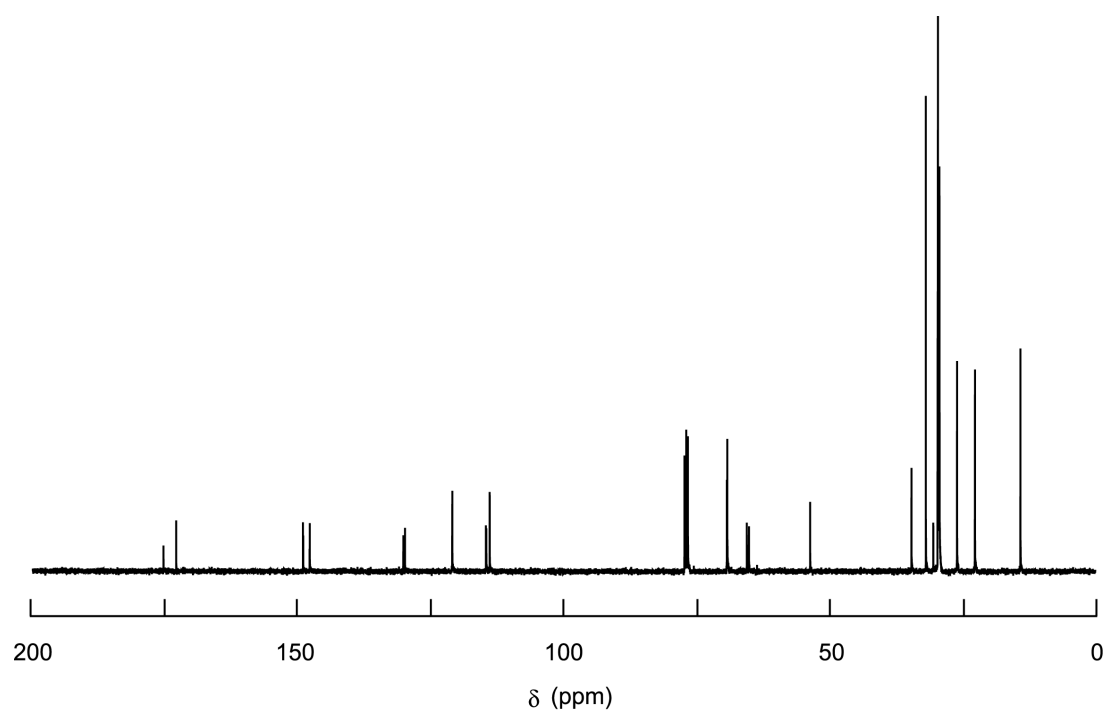


Figure S5. ^{13}C NMR spectrum of **3**.

3,5-Diiodo-4-[2-(2-methoxyethoxy)ethoxy]benzoic acid ethyl ester 4

A DMF suspension of 3,5-diiodobenzoic acid ethyl ester (10.0 g, 23.9 mmol), toluene-4-sulfonic acid 2-(2-methoxyethoxy)ethyl ester (8.52 g, 31.1 mmol) and K_2CO_3 (10.0 g, 71.4 mmol) was vigorously stirred for 3 h at 60 °C. The reaction mixture was poured into a saturated NH_4Cl aqueous solution and extracted from EtOAc three times. The combined organic extracts were washed with brine. The resulting organic phase was dried over anhydrous $MgSO_4$, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel (eluent: Hexane/EtOAc = 3/1) to give 4 (12.0 g, 97 %) as a white solid; $\nu_{max}(KBr)/cm^{-1}$ 3063, 2980, 2950, 2875, 2808, 1793, 1715, 1671, 1655, 1638, 1628, 1577, 1560, 1541, 1509, 1489, 1475, 1459, 1440, 1423, 1389, 1371, 1325, 1278, 1244, 1198, 1138, 1118, 1086, 1057, 1026, 1011, 901, 868, 846 and 819; $\delta_H(400\text{ MHz}; CDCl_3; Me_4Si)$ 8.43 (s, 2H), 4.36 (q, $J = 7.2\text{ Hz}$, 2H), 4.22 (t, $J = 5.2\text{ Hz}$, 2H), 4.01 (t, $J = 5.2\text{ Hz}$, 2H), 3.80 (t, $J = 4.8\text{ Hz}$, 2H), 3.61 (t, $J = 4.8\text{ Hz}$, 2H), 3.41 (s, 3H) and 1.38 (t, $J = 7.2\text{ Hz}$, 3H); $\delta_C(100\text{ MHz}; CDCl_3; Me_4Si)$ 163.1, 161.2, 141.0, 129.3, 90.2, 72.2, 71.8, 70.6, 69.8, 61.4, 59.0 and 14.1; m/z (MALDI) 542.7 ($M+Na^+$, $C_{14}H_{18}I_2O_5$ requires 519.9).

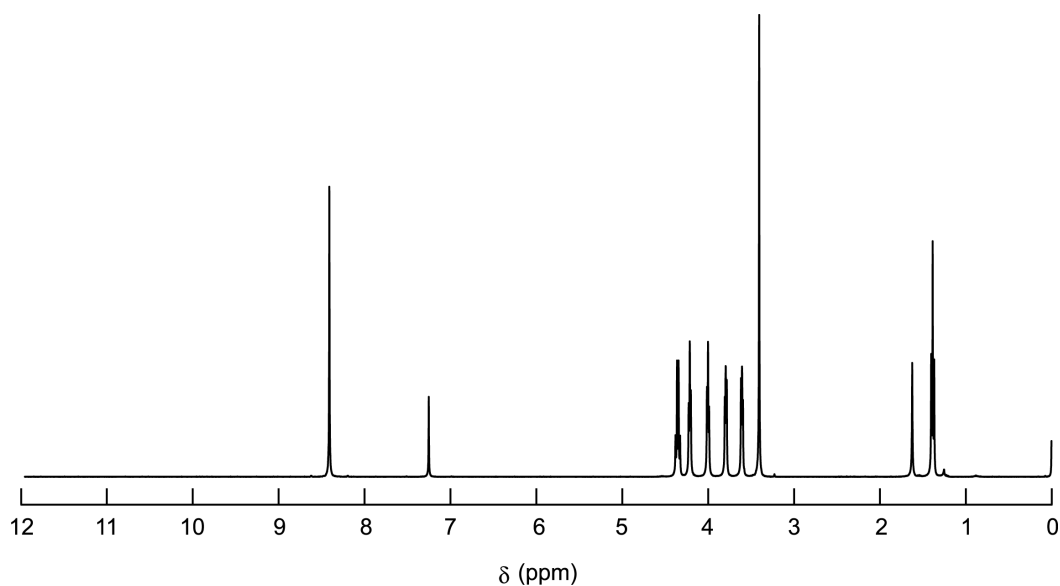


Figure S6. 1H NMR spectrum of 4.

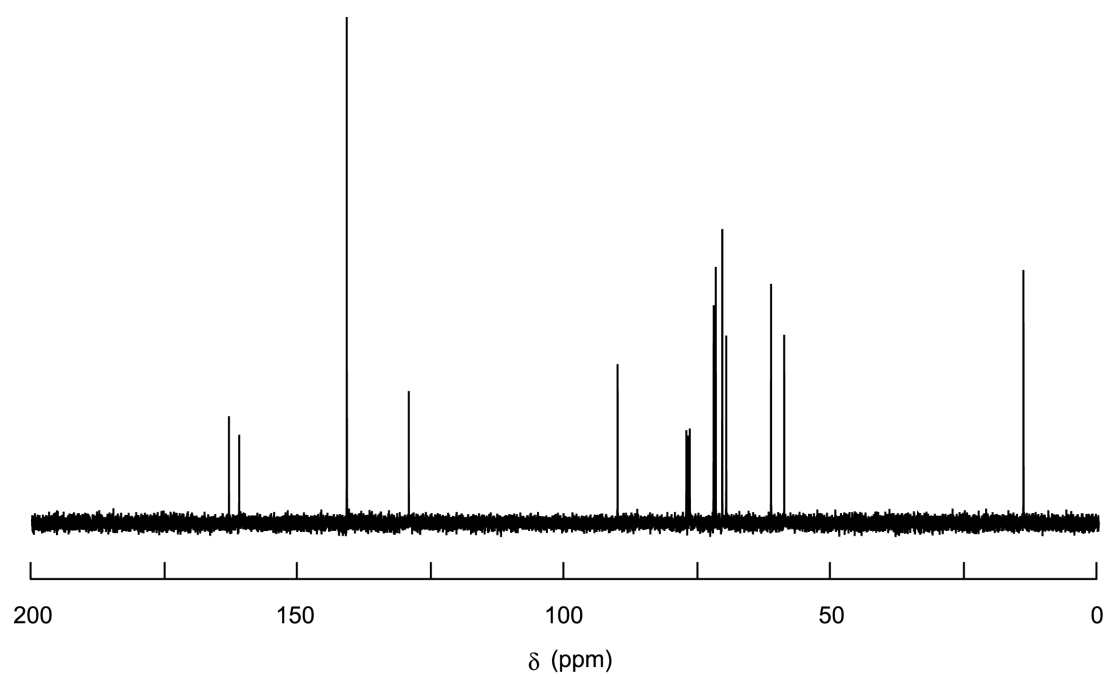


Figure S7. ^{13}C NMR spectrum of **4**.

3,5-Diethynyl-4-[2-(2-methoxyethoxy)ethoxy]benzoic acid **5**

A solution of **4** (4.00 g, 7.68 mmol), trimethylsilylacetylene (3.00 g, 30.7 mmol), CuI (60 mg, 314 μmol), Pd(PPh₃)₄ (88 mg, 68.0 μmol) in freshly distilled triethylamine was stirred for 24 h at 25 °C. A saturated NH₄Cl aqueous solution was added to the resulting mixture, and the products were extracted with EtOAc. The combined organic extracts were washed with brine. The resulting organic phase was dried over anhydrous MgSO₄, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel (eluent: Hexane/EtOAc = 5/1). The solution of the product and NaOH (0.4 g, 10.0 mmol) in ethanol was stirred under the refluxed condition for 3 h and cooled to room temperature. The reaction mixture was neutralized with 5 % HCl, and the products were extracted with EtOAc. The combined organic extracts were washed with brine. The resulting organic phase was dried over anhydrous MgSO₄, filtered, and evaporated. The residue was purified by recrystallization from hexane to give **5** (1.85 g, 84 %) as a pale yellow solid; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3447, 3294, 3224, 3086, 2932, 2877, 2600, 2526, 2102, 1727, 1692, 1588, 1458, 1419, 1392, 1359, 1307, 1227, 1113, 1075, 1034, 947, 914, 889, 856, 835, 772, 751, 699, 626, 587, 561, 542, 457 and 420; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 8.17 (s, 2H), 4.58 (t, $J = 4.8\text{Hz}$, 2H), 3.89 (t, $J = 4.8\text{Hz}$, 2H), 3.73 (t, $J = 4.8\text{Hz}$, 2H), 3.55 (t, $J = 4.8\text{Hz}$, 2H), 3.38 (s, 3H) and 3.34 (s, 2H); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 169.4, 165.9, 136.5, 124.4, 116.3, 83.0, 78.4, 73.4, 71.8, 70.5, 70.4 and 58.9; m/z (MALDI) 311.1 ($\text{M}+\text{Na}^+$, C₁₆H₁₆O₅ requires 288.3).

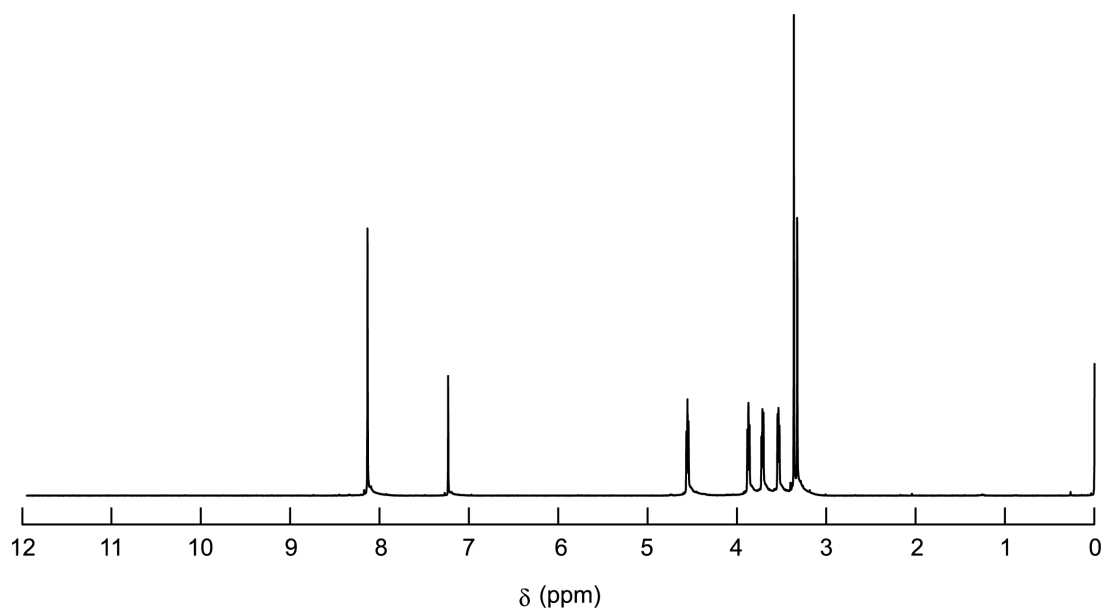


Figure S8. ¹H NMR spectrum of **5**.

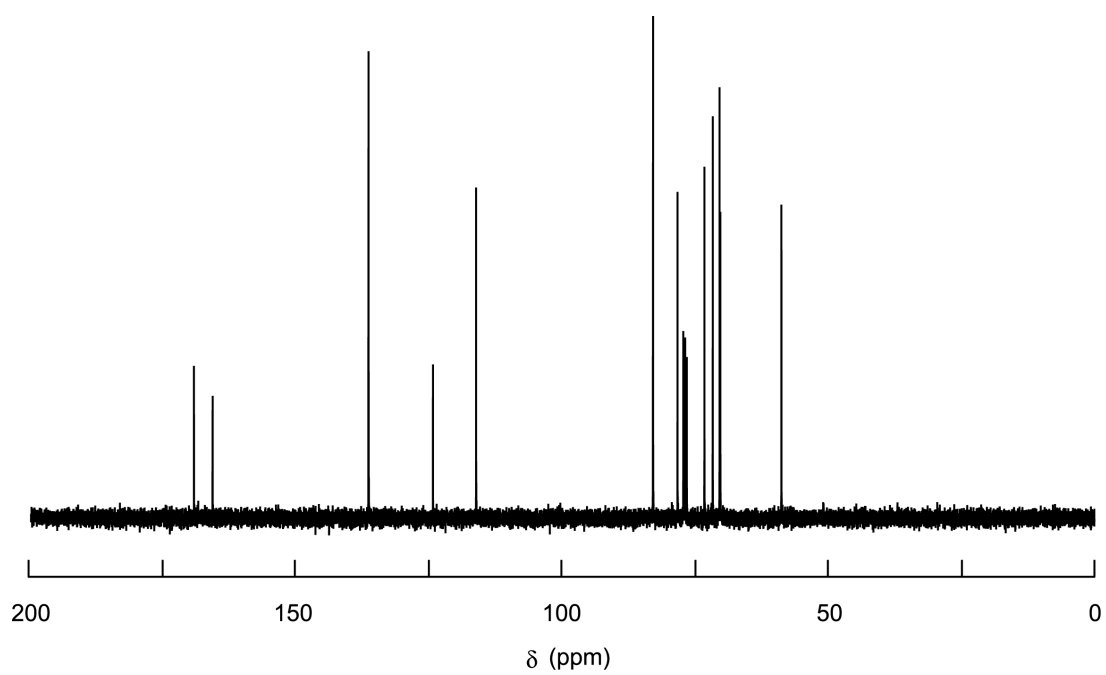


Figure S9. ^{13}C NMR spectrum of **5**.

(S)-2-{3,5-Diethynyl-4-[2-(2-methoxyethoxy)ethoxy]benzoylamino} pentanedioic acid bis-[2-(3,4-didodecyloxyphenyl)ethyl]ester **2**

A Solution of **3** (2.41 g, 2.21 mmol), **5** (0.70 g, 2.43 mmol), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) (0.64 g, 3.31 mmol), and 4-dimethylaminopyridine (DMAP) (0.11 g, 0.88 mmol) in dry CH₂Cl₂ (30 mL) was stirred for 24 h at room temperature. The reaction mixture was poured into a saturated NH₄Cl aqueous solution and the products were extracted with EtOAc. The solvent was evaporated. The resulting organic phase was dried over MgSO₄, filtered, and evaporated. The residue was purified by flash column chromatography on silica gel (eluent: Hexane/EtOAc = 5/1) to give **2** (1.43 g, 67 %) as a pale yellow solid (Found: C, 74.76; H, 10.16; N, 1.05. C₈₅H₁₃₅NO₁₂ requires C, 74.90; H, 9.98; N, 1.03 %); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3279, 2928, 2850, 1735, 1632, 1589, 1541, 1518, 1468, 1429, 1390, 1344, 1265, 1168, 1141, 1104, 1072, 1031, 1002, 851, 800 and 719; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 7.89 (s, 2H), 6.99 (d, $J = 7.2\text{Hz}$, 1H), 6.85–6.65 (m, 6H), 4.91–4.65 (m, 1H), 4.50 (t, $J = 4.8\text{Hz}$, 2H), 4.35 (t, $J = 7.2\text{Hz}$, 2H), 4.24 (t, $J = 7.2\text{Hz}$, 2H), 4.02–3.90 (m, 8H), 3.87 (t, $J = 4.8\text{Hz}$, 2H), 3.72 (t, $J = 4.4\text{Hz}$, 2H), 3.55 (t, $J = 4.4\text{Hz}$, 2H), 3.38 (s, 3H), 3.32 (s, 2H), 2.89 (t, $J = 7.2\text{Hz}$, 2H), 2.83 (t, $J = 7.2\text{Hz}$, 2H), 2.54–2.31 (m, 2H), 2.30–2.18 (m, 1H), 2.14–1.99 (m, 1H), 1.90–1.72 (m, 8H), 1.59–1.09 (m, 72H) and 0.88 (t, $J = 6.8\text{Hz}$, 12H); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 173.2, 171.7, 164.9, 164.6, 149.2, 149.1, 148.0, 147.9, 133.5, 130.0, 129.7, 128.7, 121.1, 116.6, 114.8, 114.6, 114.0, 83.0, 78.6, 73.5, 71.6, 70.7, 70.4, 69.4, 69.3, 66.3, 65.6, 59.1, 52.5, 34.5, 31.9, 30.3, 29.7, 29.6, 29.4, 29.4, 26.9, 26.0, 22.7 and 14.1; m/z (MALDI) 1402.4 (M+K⁺, C₈₅H₁₃₅NO₁₂ requires 1363.0).

Dimer 6

A solution of **2** (355 mg, 260 μmol), $\text{CuCl}(\text{OH}) \cdot \text{TMEDA}$ (6.0 mg, 13 μmol) in dry CH_2Cl_2 (5 mL) was stirred for 90 min at room temperature. The reaction mixture was poured into a saturated NH_4Cl aqueous solution and the products were extracted with CH_2Cl_2 . The solvent was evaporated. The residue was purified by flash column chromatography on silica gel (eluent: Hexane/EtOAc = 5/2) followed by GPC to give **6** (56 mg, 16 %) as a yellow solid; $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3286, 2927, 2853, 1734, 1634, 1589, 1542, 1518, 1468, 1390, 1265, 1235, 1170, 1141, 1072, 1026, 897, 548, 799 and 722; $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 7.95 (d, $J = 1.6\text{Hz}$, 2H), 7.90 (d, $J = 1.6\text{Hz}$, 2H), 7.00 (d, $J = 7.2\text{Hz}$, 2H), 6.84–6.62 (m, 12H), 4.80–4.69 (m, 2H), 4.55 (t, $J = 4.8\text{Hz}$, 4H), 4.35 (t, $J = 7.2\text{Hz}$, 4H), 4.25 (t, $J = 7.2\text{Hz}$, 4H), 4.00–3.83 (m, 16H), 3.89 (t, $J = 4.8\text{Hz}$, 4H), 3.74 (t, $J = 4.4\text{Hz}$, 4H), 3.56 (t, $J = 4.4\text{Hz}$, 4H), 3.35 (s, 6H), 3.34 (s, 2H), 2.89 (t, $J = 7.2\text{Hz}$, 4H), 2.84 (t, $J = 7.2\text{Hz}$, 4H), 2.53–2.31 (m, 4H), 2.31–2.18 (m, 2H), 2.13–1.99 (m, 2H), 1.89–1.69 (m, 16H), 1.59–1.09 (m, 144H) and 0.88 (t, $J = 6.8\text{Hz}$, 24H); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 173.1, 171.7, 165.3, 164.7, 149.2, 149.1, 148.0, 147.9, 134.0, 133.9, 130.0, 129.6, 128.8, 121.1, 116.4, 116.0, 114.8, 114.6, 114.0, 83.4, 78.7, 78.5, 77.9, 73.8, 71.9, 70.8, 70.5, 69.3, 66.4, 65.6, 59.0, 52.4, 34.5, 31.9, 30.3, 29.7, 29.6, 29.5, 29.3, 27.0, 26.1, 22.7 and 14.1; m/z (MALDI) 2747.0($\text{M}+\text{Na}^+$, $\text{C}_{170}\text{H}_{268}\text{N}_2\text{O}_{24}$ requires 2723.9).

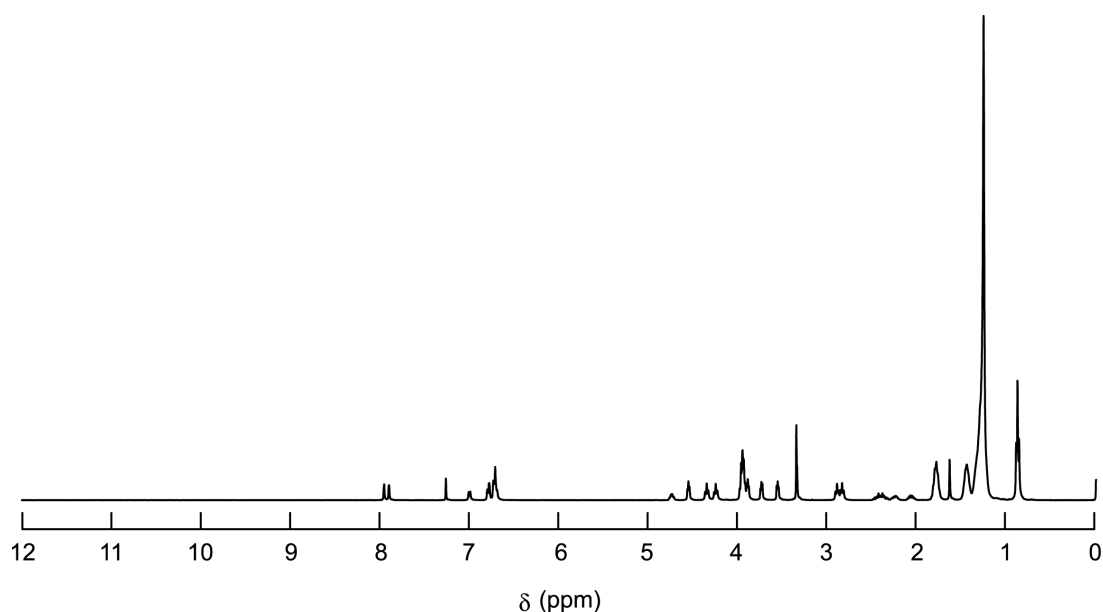


Figure S10. ^1H NMR spectrum of **6**.

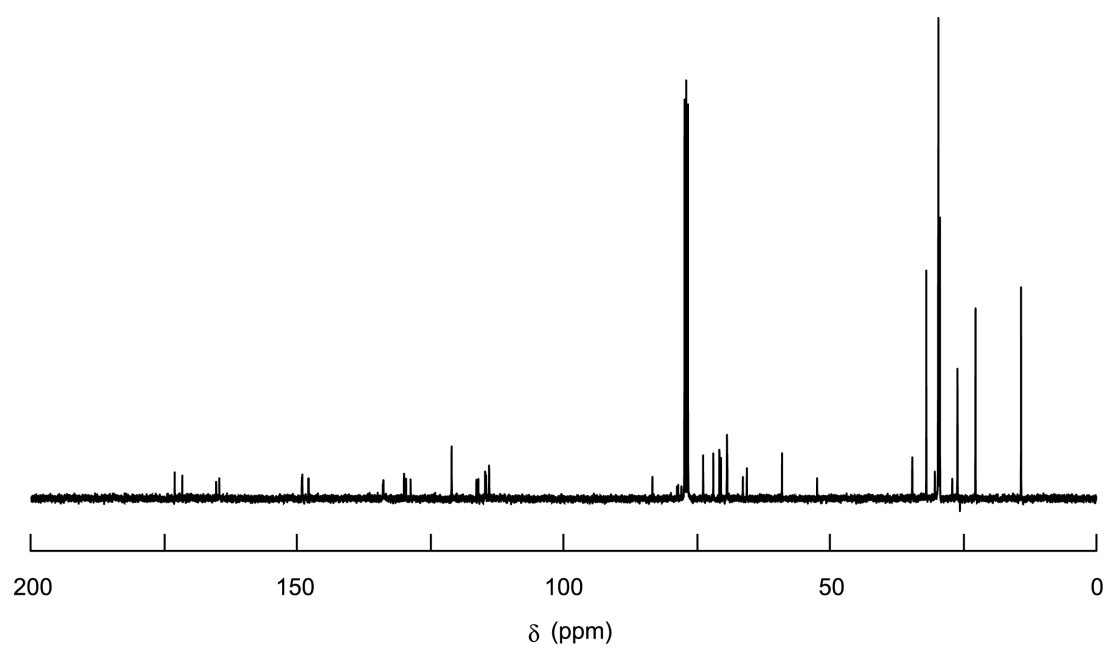


Figure S11. ^{13}C NMR spectrum of **6**.

Macrocycle 1

A solution of **6** (30.0 mg, 11.0 μmol) in 25 mL of pyridine/benzene (3/2, v/v) was added to a solution of $\text{Cu}(\text{OAc})_2$ (40.0 mg, 220 μmol) in 25 mL of the same solvent, which had been deaerated for 15 min, during a 5 h period at room temperature. The mixture was stirred for 19 h and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: CH_2Cl_2) followed by GPC to give **1** (8.9 mg, 29 %) as a yellow solid (Found: C, 74.76; H, 9.93, N, 1.00. $\text{C}_{510}\text{H}_{798}\text{N}_6\text{O}_{72}$ requires C, 75.01; H, 9.85; N, 1.03%); δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 7.94 (s, 12H), 6.99 (d, $J = 7.2\text{Hz}$, 6H), 6.85–6.60 (m, 36H), 4.80–4.68 (m, 6H), 4.58 (t, $J = 4.8\text{Hz}$, 12H), 4.35 (t, $J = 7.2\text{Hz}$, 12H), 4.26 (t, $J = 7.2\text{Hz}$, 12H), 4.02–3.80 (m, 48H), 3.90 (t, $J = 4.8\text{Hz}$, 12H), 3.71 (t, $J = 4.4\text{Hz}$, 12H), 3.52 (t, $J = 4.4\text{Hz}$, 12H), 3.30 (s, 18H), 2.89 (t, $J = 7.2\text{Hz}$, 12H), 2.85 (t, $J = 7.2\text{Hz}$, 12H), 2.52–2.31 (m, 12H), 2.31–2.15 (m, 6H), 2.15–1.99 (m, 6H), 1.87–1.68 (m, 48H), 1.51–1.10 (m, 432H) and 0.87 (t, $J = 6.8\text{Hz}$, 72H); δ_{C} (100 MHz; CDCl_3 ; Me_4Si) 173.0, 171.7, 167.0, 164.6, 149.2, 149.1, 148.0, 147.9, 133.6, 130.1, 129.6, 129.0, 121.1, 116.2, 114.8, 114.6, 114.1, 79.1, 77.2, 74.3, 71.9, 70.9, 70.7, 69.4, 69.3, 66.5, 65.6, 59.0, 52.4, 34.6, 31.9, 30.3, 29.7, 29.7, 29.5, 29.4, 27.2, 26.1, 22.7 and 14.1; ν_{max} (KBr)/ cm^{-1} 3295, 2921, 2853, 1736, 1639, 1590, 1541, 1516, 1468, 1429, 1390, 1263, 1167, 1140, 1107, 1072, 1026, 903, 848, 804, 767 and 722; m/z (MALDI) 8205.7 ($\text{M}+\text{K}^+$, $\text{C}_{510}\text{H}_{798}\text{N}_6\text{O}_{72}$ requires 8165.8).

References

1. K. Kanie, M. Nishii, T. Yasuda, T. Taki, S. Ujiie and T. Kato, *J. Mater. Chem.*, 2001, **11**, 2875-2886.