Supporting Information for:

Sequence- and Chain Length-Specific Complementary Double Helix Formation

Hiroshi Ito,[†] Yoshio Furusho,*[,†,‡] Toshihide Hasegawa,[†] and Eiji Yashima*[,†,‡]

[†] Yashima Super-structured Helix Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST), Japan. [‡] Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan.

E-mail: furusho@apchem.nagoya-u.ac.jp (Y.F.); yashima@apchem.nagoya-u.ac.jp (E.Y.).

Experimental Section

Materials. All starting materials and dehydrated solvents were purchased from Aldrich, Wako Pure Chemical Industries (Osaka, Japan), and Tokyo Chemical Industry (Tokyo, Japan) unless otherwise noted. $CDCl_3$ (99.8 atom %D) and THF-d_8 (99.95 atom %D) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Silica gel (SiO_2) and aminopropyl-modified silica gel (NH_2-SiO_2) for the flash chromatography were purchased from Merck and Fuji Silysia Chemical Ltd. (Kasugai, Japan), respectively. Bio-Beads SX-3 for the SEC was purchased from Bio-Rad Laboratories. Compounds **A**–H,[1] H-**A**-H,[2] **AA**,[1] **C**-H,[3] and H-**C**-H[3] were prepared according to the previously reported methods.

Instruments. The melting points were measured using a Yanaco MP-500D melting point apparatus (Kyoto, Japan) and were uncorrected. The NMR spectra were obtained using a Varian UNITY INOVA 500AS spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C. Chemical shifts are reported in parts per million (δ) downfield from tetramethysilane (TMS) as the internal standard in $CDCl_3$ and from the residual proton peaks in THF-d_8 as the internal standard in THF-d_8. The ESI-MS were recorded on a JEOL JMS-T100CS spectrometer (Akishima, Japan). The elemental analyses were performed by the laboratory of elemental analyses in the Department of Agriculture, Nagoya University. The IR spectra were recorded using a JASCO Fourier Transform IR-680 spectrophotometer (Hachioji, Japan). The absorption and CD spectra were measured in a 1.0- or 10-mm quartz cell on a JASCO V-570 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively. The temperature was controlled by a JASCO PTC-423L apparatus. The optical rotations were taken using a JASCO P-1030 polarimeter in $CDCl_3$ in a 2-cm quartz cell equipped with a temperature controller (EYELA NCB-2100). The HPLC measurements for the sequence-specific double helix formation were

performed with a JASCO PU-2080 liquid chromatograph (Hachioji, Japan) equipped with a UV-visible (328 nm; JASCO UV-2070) detector and a TSKgel Silica-60 column (Tosoh, Tokyo, Japan, ϕ0.46 × 25 cm) using hexane/$CHCl_3$ as the eluent at a flow rate of 1.0 mL/min. The SEC analyses for the chain length-specific double helix formation were performed using an LC-928R liquid chromatograph (Japan Analytical Industry, Tokyo) equipped with two SEC columns (JALGEL-1H (1 × 60 cm) and JALGEL-2H (1 × 60 cm)) in series and a UV-visible detector (254 nm, JAI UV-310). $CHCl_3$ was used as the eluent at a flow rate of 3.8 mL/min. All the reactions were monitored by TLC.

Synthetic Procedures.

AC. CuI (1.9 mg, 10 μmol) was added to a solution of **A**-H^1 (60 mg, 0.10 mmol), **C**-H^3 (50 mg, 0.10 mmol), and $(Ph_3P)_2PdCl_2$ (7.9 mg, 11 μmol) in $CHCl_3$-Et_3N (10/1 (v/v), 2.2 mL). After the mixture was stirred at room temperature for 21 h, the solvent was evaporated to dryness. The residue was purified by column chromatography (SiO_2, $CHCl_3$/MeOH = 100/0 to 100/20 (v/v)), SEC (Bio-Beads S-X3, $CHCl_3$), and column chromatography (NH_2-SiO_2, $CHCl_3$/hexane = 1/2 to 1/0 (v/v)) to afford **AC** (38 mg, 34% yield) as a white solid. $[\alpha]_D^{20}$ –714 (c = 0.1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as (**AC**)$_2$) δ 13.39 (d, J = 9.0 Hz, 1H, NH), 13.36 (d, J = 8.9 Hz, 1H, NH), 7.73 (d, J = 8.5 Hz, 2H, ArH), 7.70 (t, J = 7.8 Hz, 1H, ArH), 7.66 (d, J = 8.4 Hz, 2H, ArH), 7.62 (d, J = 8.5 Hz, 2H, ArH), 7.61 (d, J = 8.4 Hz, 2H, ArH), 7.48–7.35 (m, 8H, ArH), 7.23 (t, J = 7.4 Hz, 1H, ArH), 7.19–7.12 (m, 3H, ArH), 7.07 (t, J = 7.7 Hz, 2H, ArH), 6.77–6.69 (m, 4H, ArH), 6.60 (d, J = 8.3 Hz, 2H, ArH), 6.55 (d, J = 8.2 Hz, ArH, 2H), 3.84–3.72 (m, 2H, CH_3CHN), 2.39 (t, J = 7.2 Hz, 2H, octynyl), 1.64–1.56 (m, 2H, octynyl), 1.48–1.40 (m, 2H, octynyl), 1.36–1.26 (m, 4H, octynyl), 0.90 (t, J = 7.0 Hz, 3H, octynyl), 0.70 (d, J = 6.8 Hz, 3H, CH_3CHN), 0.59 (d, J = 6.8 Hz, 3H, CH_3CHN), 0.31 (s, 9H, $SiCH_3$), 0.27 (s, 9H, $SiCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ 176.59, 162.05, 142.81, 142.50, 142.34, 141.70, 141.38,

141.14, 140.50, 138.45, 138.02, 137.15, 136.81, 132.65, 132.09, 132.02, 131.61, 131.58, 131.50, 131.34, 130.47, 130.21, 130.07, 129.83, 129.15, 129.11, 129.09, 129.06, 128.97, 128.93, 128.92, 128.64, 128.52, 105.78, 104.08, 96.37, 94.57, 90.28, 82.52, 80.40, 80.14, 76.32, 74.64, 55.52, 55.49, 31.35, 28.71, 28.63, 22.71, 22.53, 22.52, 19.47, 14.05, 0.23, –0.01; IR (KBr, cm^{-1}): 3415 (ν_{N-H}, ν_{O-H}), 2156 ($\nu_{C\equiv C}$), 1656 ($\nu_{C=O}$, $\nu_{C=N}$); HRMS(ESI): m/*z* calcd for $[M(C_{76}H_{72}N_2O_2Si_2)+H]^+$, 1101.5211; found 1101.5168; Anal. Calcd for $C_{76}H_{72}N_2O_2Si_2$: C, 82.86; H, 6.59; N, 2.54. Found: C, 82.61; H, 6.50; N, 2.47.

AA-H. To a stirred solution of **AA**[1] (1.29 g, 1.08 mmol) in THF (50 mL) was added dropwise a solution of TBAF in THF (0.015 M, 1.3 mL, 0.0195 mmol) at ambient temperature over a period of 2.5 h. After 1M HCl (4 mL) was added, the reaction mixture was evaporated to dryness. The residue was dissolved in $CHCl_3$ (50 mL), and the resultant solution was washed with brine (25 mL), dried over Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by column chromatography (NH-SiO_2, hexane/EtOAc = 20/1 to 0/1 (v/v)) to afford **AA-H** as a white solid in 25% yield. This was used in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$ 25 °C, as **AA-H**·$(CH_3CO_2H)_2$) δ 12.75 (br s, 4H, NH), 7.81–7.75 (m, 2H, ArH), 7.55–7.50 (m, 4H, ArH), 7.33–7.20 (m, 20H, ArH), 7.06–6.99 (m, 8H, ArH), 6.72–6.63 (m, 8H, ArH), 3.96–3.88 (m, 4H, CHN), 3.12 (s, 1H, C≡CH), 2.10 (s, 6H, CH_3CO), 0.75–0.67 (m, 12H, C*H*$_3$CHN), 0.25 (s, 9H, $SiCH_3$).

CC. CuI (21 mg, 0.112 mmol) was added to a solution of **C-H**[3] (1.13 g, 2.25 mmol) and $(Ph_3P)_2PdCl_2$ (79 mg, 0.112 mmol) in Et_3N 3.0 mL) and THF (30 mL). After the mixture was stirred at ambient temperature for 3 h, the solvent was evaporated to dryness. The residue was dissolved in EtOAc (200 mL), and the resultant solution was washed with 1 M HCl (2 × 100 mL), dried over $MgSO_4$, filtered,

and evaporated to dryness. The residue was purified by column chromatography (SiO_2, hexane/EtOAc = 1/0 to 3/2 (v/v)) to afford **CC** in 84% yield as a white solid. M.p. = 138–140 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) δ 7.61–7.52 (m, 8H, ArH), 7.38–7.24 (m, 12H, ArH), 2.40 (t, J = 7.1 Hz, 4H, $CH_2C{\equiv}C$), 1.64–1.54 (m, 4H, CH_2), 1.48–1.39 (m, 4H, CH_2), 1.36–1.25 (m, 8H, CH_2), 0.89 (t, J = 7.0 Hz, 6H, octynyl), 0.29 (s, 18H, $SiCH_3$). Anal. Calcd for $C_{68}H_{66}O_4Si_2$: C, 81.39; H, 6.63. Found: C, 81.30; H, 6.48.

CC-H. To a stirred solution of **CC** (946 mg, 0.942 mmol) in THF (40 mL) was added dropwise a solution of TBAF in THF (0.16 M, 5.31 mL, 0.85 mmol) at ambient temperature over a period of 5.5 h. After 1M HCl (8 mL) was added, the reaction mixture was evaporated to dryness. The residue was dissolved in $CHCl_3$ (50 mL), and the resultant solution was washed with brine (25 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was purified by flash column chromatography (SiO_2, hexane/EtOAc = 1/0 to 6/4 (v/v)) to afford **CC-H** as an off-white solid in 20% yield. This was used in the next step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.64–7.52 (m, 8H, ArH), 7.40–7.24 (m, 12H, ArH), 3.22 (s, 1H, C≡CH), 2.40 (t, J = 7.1 Hz, 4H, $CH_2C{\equiv}C$), 1.63–1.55 (m, 4H, CH_2), 1.48–1.39 (m, 4H, CH_2), 1.36–1.24 (m, 8H, CH_2), 0.89 (t, J = 7.0 Hz, 6H, octynyl), 0.29 (s, 9H, $SiCH_3$).

AAA. CuI (0.57 mg, 3.0 μmol) was added to a solution of **AA**-H (34 mg, 30 μmol), **A**-H[1] (54 mg, 90 μmol), and $(Ph_3P)_2PdCl_2$ (2.1 mg, 3 μmol) in $CHCl_3$-Et_3N (10/1 (v/v), 13 mL). After the mixture was stirred at room temperature for 2 h, the solvent was evaporated to dryness. The residue was purified by column chromatography (NH_2-SiO_2, hexane/EtOAc = 20/1 to 4/1 (v/v)) and SEC (Bio-Beads S-X3, $CHCl_3$) to afford **AAA** (27 mg, 52% yield) as a white solid. $[\alpha]_D^{20}$ –228 (c = 0.1 in $CHCl_3$); ^{1}H NMR

(500 MHz, $CDCl_3$, 25 °C, as **AAA**·$(CH_3CO_2H)_3$) δ 13.48 (br s, 6H, NH), 7.80–7.72 (m, 3H, ArH), 7.55-–7.48 (m, 6H, ArH), 7.31–7.20 (m, 30H, ArH), 7.09–7.03 (m, 12H, ArH), 6.73–6.69 (m, 8H, ArH), 6.69–6.65 (m, 4H, ArH), 3.94–3.87 (m, 6H, CH_3CHN), 2.12 (s, 9H, CH_3CO_2), 0.76–0.69 (m, 18H, CH_3CHN), 0.26 (s, 18H, $SiCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as **AAA**·$(CH_3CO_2H)_3$) δ 178.82, 162.42, 162.37, 142.81, 142.72, 142.70, 141.64, 141.40, 141.31, 138.88, 138.80, 137.96, 132.80, 132.22, 131.91, 131.83, 130.71, 130.66, 130.46, 129.04, 129.00, 128.66, 128.41, 127.97, 127.94, 127.93, 126.56, 126.54, 123.33, 122.58, 122.56, 121.86, 121.80, 104.16, 96.05, 81.39, 81.35, 75.31, 75.28, 55.46, 55.43, 55.41, 24.01, 23.99, 22.23, –0.12; IR (KBr, cm^{-1}): 3428 (ν_{N-H}), 2156 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=N}$); ESI-MS: *m*/*z* calcd for $[M(C_{123}H_{108}N_6Si_2)+2H]^{2+}$, 863.42; found 863.28, calcd for $[M+H]^+$, 1725.83; found 1725.83; HRMS(ESI): m/*z* calcd for $[M+H]^+$, 1725.8252; found 1725.8251; Anal. Calcd for $C_{123}H_{108}N_6Si_2$: C, 85.57; H, 6.31; N, 4.87. Found: C, 85.50; H, 6.18; N, 4.69.

AAC. CuI (0.95 mg, 5.0 μmol) was added to a solution of **AA**-H (56 mg, 50 μmol), **C**-H[3] (37 mg, 74 μmol), and $(Ph_3P)_2PdCl_2$ (3.9 mg, 5.6 μmol) in $CHCl_3$-Et_3N (20/1 (v/v), 4 mL). After the mixture was stirred at room temperature for 11 h, the solvent was evaporated to dryness. The residue was purified by SEC (Bio-Beads S-X3, THF), column chromatography (SiO_2, $CHCl_3$/MeOH = 100/0 to 100/5 (v/v)), and SEC (Bio-Beads S-X3, $CHCl_3$) to afford **AAC** (31 mg, 38% yield) as a white solid. $[\alpha]_D^{20}$ –433 (*c* = 0.1 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, 25 °C, as **AAC**·CH_3COOH) δ 13.32 (d, *J* = 8.2 Hz, 2H, NH), 12.90 (br s, 2H, NH), 7.79–7.70 (m, 4H, ArH), 7.67 (d, *J* = 8.2 Hz, 2H, ArH), 7.62 (d, *J* = 8.3 Hz, 2H, ArH), 7.58 (d, *J* = 8.2 Hz, 2H, ArH), 7.53–7.50 (m, 2H, ArH), 7.49–7.36 (m, 8H, ArH), 7.34–7.14 (m, 14H, ArH), 7.08 (t, *J* = 7.8 Hz, 2H, ArH), 7.02 (t, *J* = 6.7 Hz, 4H, ArH), 6.79 (d, *J* = 7.4 Hz, 2H, ArH), 6.73 (d, *J* = 6.8 Hz, 2H, ArH), 6.69–6.64 (m, 4H, ArH), 6.61 (d, *J* = 8.2 Hz, 2H, ArH), 6.58 (d, *J* = 8.0 Hz, 2H, ArH), 3.95–3.87 (m, 2H, CH_3CHN), 3.84–3.76 (m, 2H, CH_3CHN), 2.39 (t, *J* = 7.1 Hz,

2H, octynyl), 2.10 (s, 3H, CH_3COO), 1.64–1.56 (m, 2H, octynyl), 1.48–1.40 (m, 2H, octynyl), 1.36–1.24 (m, 4H, octynyl), 0.89 (t, J = 6.9 Hz, 3H, octynyl), 0.74–0.68 (m, 9H, CH_3CHN), 0.62 (d, J = 6.8 Hz, 3H, CH_3CHN), 0.36 (s, 9H, $SiCH_3$), 0.25 (s, 9H, $SiCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as **AAC**·CH_3COOH) δ 176.87, 176.72, 162.46, 161.99, 142.70, 142.68, 142.51, 142.41, 142.30, 141.73, 141.67, 141.61, 141.29, 141.24, 141.09, 140.47, 138.86, 138.78, 138.37, 137.92, 137.17, 136.75, 132.78, 132.66, 132.23, 132.01, 131.88, 131.34, 130.69, 130.47, 130.29, 129.15, 129.05, 129.02, 128.98, 128.89, 128.75, 128.64, 128.40, 127.96, 126.53, 126.38, 126.33, 123.36, 122.66, 122.58, 122.50, 122.36, 121.95, 121.91, 121.80, 120.13, 105.48, 104.13, 96.09, 96.08, 94.74, 90.31, 82.56, 81.39, 81.26, 80.41, 80.12, 76.46, 75.74, 74.62, 55.56, 55.47, 31.35, 29.69, 28.72, 28.64, 22.63, 22.53, 22.44, 22.15, 22.11, 19.47, 14.05, 0.16, –0.12; IR (KBr, cm^{-1}): 3433 (ν_{N-H}, ν_{O-H}), 2156 ($\nu_{C\equiv C}$), 1638 ($\nu_{C=N}$); ESI-MS: m/z calcd for $[M(C_{115}H_{102}N_4O_2Si_2)+2H]^{2+}$, 814.38; found 814.39, calcd for $[M+H]^+$, 1627.76; found 1627.76; HRMS(ESI): m/z calcd for $[M+H]^+$, 1627.7620; found 1627.7610; Anal. Calcd for $C_{115}H_{102}N_4O_2Si_2$: C, 84.83; H, 6.31; N, 3.44. Found: C, 84.75; H, 6.19; N, 3.31.

ACA. CuI (4.8 mg, 25 μmol) was added to a solution of **A**-H^1 (180 mg, 0.30 mmol), H-**C**-H^3 (43 mg, 0.10 mmol), and $(Ph_3P)_2PdCl_2$ (18 mg, 25 μmol) in $CHCl_3$-Et_3N (10/1 (v/v), 11 mL). After the mixture was stirred at room temperature for 4 h, the solvent was evaporated to dryness. The residue was then dissolved in $CHCl_3$ (20 mL) and the solution was washed with 1 M HCl aq. (10 mL), water (10 mL), and brine (10 mL), successively, and dried over anhydrous Na_2SO_4. The residue was purified by SEC (Bio-Beads S-X3, THF), column chromatography (NH-SiO_2, $CHCl_3$/MeOH = 100/0 to 100/6 (v/v)), and SEC (Bio-Beads S-X3, $CHCl_3$) to afford **ACA** (33 mg, 20% yield) as a white solid. $[\alpha]_D^{20}$ –468 (c = 0.1 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, as **ACA**·$(CF_3COOH)_2$) δ 11.81–10.86 (br, 4H, NH), 7.81 (t, J = 7.5 Hz, 2H, ArH), 7.58–7.51 (m, 8H, ArH), 7.43–7.37 (m, 6H, ArH), 7.25–7.22 (m,

20H, ArH), 7.00–6.94 (m, 8H, ArH), 6.66 (d, *J* = 8.3 Hz, 4H, ArH), 6.63 (d, *J* = 7.4 Hz, 4H, ArH), 4.00–3.89 (m, 4H, CH_3CHN), 2.41 (t, *J* = 7.0 Hz, 2H, octynyl), 1.64–1.54 (m, 2H, octynyl), 1.48–1.41 (m, 2H, octynyl), 1.36–1.24 (m, 4H, octynyl), 0.90 (t, *J* = 6.8 Hz, 3H, octynyl), 0.71 (d, *J* = 6.7 Hz, 12H, CH_3CHN), 0.26 (s, 18H, $SiCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, as **ACA**·$(CF_3COOH)_2$) δ 170.71, 163.02, 161.53,161.23, 141.73, 141.48, 141.39, 141.37, 140.71, 139.80, 138.24, 137.43, 132.87, 132.59, 132.36, 132.06, 130.89, 130.64, 129.29, 129.27, 128.62, 128.53, 128.49, 128.28, 126.38, 126.35, 123.77, 122.44, 119.26, 116.97, 114.67, 103.77, 96.52, 93.28, 82.16, 80.61, 79.33, 75.91, 74.51, 55.79, 31.32, 29.69, 28.60, 28.52, 22.52, 21.88, 21.85, 19.44, 14.05, –0.16; IR (KBr, cm^{-1}): 3435 (ν_{N-H}, ν_{O-H}), 2157 ($\nu_{C\equiv C}$), 1645 ($\nu_{C=O}$, $\nu_{C=N}$); ESI-MS: *m*/*z* calcd for $[M(C_{115}H_{102}N_4O_2Si_2)+2H]^{2+}$, 814.38; found 814.35, calcd for $[M+H]^+$, 1627.76; found 1627.77; HRMS(ESI): m/*z* calcd for $[M+H]^+$, 1627.7620; found 1627.7657; Anal. Calcd for $C_{115}H_{102}N_4O_2Si_2$: C, 84.83; H, 6.31; N, 3.44. Found: C, 84.70; H, 6.15; N, 3.25.

CAC. CuI (1.5 mg, 8.0 μmol) was added to a solution of **C**-H^3 (101 mg, 0.20 mmol), H-**A**-H^2 (21 mg, 40 μmol), and $(Ph_3P)_2PdCl_2$ (5.6 mg, 8.0 μmol) in THF-Et_3N (10/1 (v/v), 26 mL). After the mixture was stirred at room temperature for 16 h, the solvent was evaporated to dryness. The residue was then dissolved in $CHCl_3$ (20 mL) and the solution was washed with 1 M HCl aq. (10 mL), water (10 mL), and brine (10 mL), successively, and dried over anhydrous Na_2SO_4. The residue was purified by column chromatography (SiO_2, hexane/THF = 20/3 to 1/1 (v/v)) and SEC (Bio-Beads S-X3, $CHCl_3$) to afford **CAC** (10 mg, 17% yield) as a white solid. $[\alpha]_D^{20}$ –358 (*c* = 0.1 in $CHCl_3$); ^1H NMR (500 MHz, THF-d_8, 25 °C) δ 14.15–14.02 (m, 2H, NH), 7.79 (t, *J* = 7.7 Hz, 1H, ArH), 7.72 (d, *J* = 8.0 Hz, 2H, ArH), 7.66 (t, *J* = 7.7 Hz, 4H, ArH), 7.62–7.34 (m, 20H, ArH), 7.24–7.13 (m, 4H, ArH), 7.07 (t, *J* = 7.3 Hz, 2H, ArH), 6.87 (d, *J* = 7.3 Hz, 2H, ArH), 6.79 (d, *J* = 6.4 Hz, 2H, ArH), 6.74 (d, *J* = 7.8 Hz, 2H,

ArH), 6.71 (d, J = 7.8 Hz, 2H, ArH), 3.87 (m, 2H, CH_3CHN), 2.42 (m, 4H, octynyl), 1.64–1.56 (m, 4H, octynyl), 1.53–1.44 (m, 4H, octynyl), 1.40–1.27 (m, 8H, octynyl), 0.95–0.87 (m, 6H, octynyl), 0.69 (d, J = 6.3 Hz, 3H, CH_3CHN), 0.60 (d, J = 6.3 Hz, 3H, CH_3CHN), 0.37 (s, 9H, $SiCH_3$), 0.24 (s, 9H, $SiCH_3$); ^{13}C NMR (125 MHz, THF-d_8, 25 °C) δ 176.95, 170.06, 163.17, 144.51, 144.35, 144.21, 143.49, 142.64, 142.52, 142.32, 142.22, 141.60, 140.63, 140.49, 140.29, 140.17, 138.45, 138.07, 134.22, 133.72, 133.59, 133,29, 133.01, 132.78, 132.61, 132.23, 131.52, 130.24, 130.20, 130.10, 130.02, 129.98, 129.80, 129.64, 127.55, 127.47, 126.15, 123.88, 123.68, 123.20, 123.14, 122.91, 122.78, 122.01, 121.20, 106.83, 106.10, 95.28, 95.13, 92.84, 90.63, 83.35, 83.00, 81.99, 81.40, 81.34, 80.60, 77.18, 76.64, 75.63, 75.60, 56.47, 32.55, 32.52, 30.82, 29.97, 29.79, 29.75, 29.71, 23.62, 23.44, 23.20, 20.14, 20.07, 14.58, 0.56, 0.18; IR (KBr, cm^{-1}): 3421 (ν_{N-H}, ν_{O-H}), 2157 ($\nu_{C\equiv C}$), 1727 ($\nu_{C=O}$), 1652 ($\nu_{C=N}$); HRMS(ESI): m/z calcd for $[M(C_{107}H_{96}N_2O_4Si_2)+H]^+$, 1529.6987; found 1529.7002; Anal. Calcd for $C_{107}H_{96}N_2O_4Si_2$: C, 83.99; H, 6.32; N, 1.83. Found: C, 83.91; H, 6.33; N, 1.64.

CCA. CuI (0.50 mg, 2.7 μmol) was added to a solution of **CC**-H (25 mg, 27 μmol), **A**-H[1] (48 mg, 80 μmol), and $(Ph_3P)_2PdCl_2$ (1.9 mg, 2.7 μmol) in THF-Et_3N (10/1 (v/v), 11 mL). After the mixture was stirred at room temperature for 20 h, the solvent was evaporated to dryness. The residue was then dissolved in $CHCl_3$ (30 mL) and the solution was washed with 1 M HCl aq. (10 mL), water (10 mL), and brine (10 mL), successively, and dried over anhydrous Na_2SO_4. The residue was purified by column chromatography (NH_2-SiO_2, $CHCl_3$/AcOH = 100/0 to 100/2 (v/v)). The eluent was washed with saturated $NaHCO_3$ aq. (30 mL × 2), water (30 mL), 1 M HCl aq. (30 mL), water (30 mL), and brine (30 mL), successively, and dried over anhydrous Na_2SO_4. The residue was further purified by column chromatography (SiO_2, hexane/THF = 20/1 to 1/1 (v/v)) and SEC (Bio-Beads S-X3, $CHCl_3$) to afford **CCA** (9.4 mg, 25% yield) as a white solid. $[\alpha]_D^{20}$ –534 (c = 0.1 in $CHCl_3$); ^{1}H NMR (500 MHz,

$CDCl_3$, 25 °C) δ 13.41–13.28 (m, 2H, NH), 7.77–7.55 (m, 13H, ArH), 7.48–7.25 (m, 15H, ArH), 7.18–7.13 (m, 3H, ArH), 7.09 (t, *J* = 7.7 Hz, 2H, ArH), 6.77 (d, *J* = 7.5 Hz, 2H, ArH), 6.74–6.68 (m, 2H, ArH), 6.62 (d, *J* = 8.2 Hz, 2H, ArH), 6.55 (d, *J* = 8.2 Hz, 2H, ArH), 3.83–3.72 (m, 2H, CH_3CHN), 2.43–2.37 (m, 4H, octynyl), 1.64–1.55 (m, 4H, octynyl), 1.49–1.40 (m, 4H, octynyl), 1.36–1.27 (m, 8H, octynyl), 0.93–0.86 (m, 6H, octynyl), 0.69 (d, *J* = 6.7 Hz, 3H, CH_3CHN), 0.59 (d, *J* = 6.7 Hz, 3H, CH_3CHN), 0.31 (s, 9H, $SiCH_3$) , 0.27 (s, 9H, $SiCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ 176.61, 162.09, 142.72, 142.42, 142.38, 141.69, 141.37, 141.16, 140.51, 138.56, 138.03, 137.19, 136.83, 132.79, 132.68, 132.60, 132.10, 132.04, 131.76, 131.64, 131.35, 129.11, 129.00, 128.95, 128.67, 128.54, 128.40, 126.33, 126.29, 123.55, 122.79, 122.54, 122.11, 121.91, 121,84, 121.54, 120.34, 105.78, 104.10, 96.38, 94.59, 90.29, 82.09, 81.75, 80.80, 80.78, 80.74, 80.44, 79.34, 76.25, 76.03, 75.56, 75.05, 55.58, 55.54, 55.47, 31.37, 31.32, 29.69, 28.73, 28.65, 28.60, 28.53, 22.79, 22.55, 22.52, 19.49, 19.42, 14.06, 14.04, 0.24, 0.00; IR (KBr, cm^{-1}): 3424 (ν_{N-H}, ν_{O-H}), 2157 ($\nu_{C\equiv C}$), 1719 ($\nu_{C=O}$), 1649 ($\nu_{C=N}$); HRMS(ESI): m/*z* calcd for $[M(C_{107}H_{96}N_2O_4Si_2)+H]^+$, 1529.6987; found 1529.6925; Anal. Calcd for $C_{107}H_{96}N_2O_4Si_2$: C, 83.99; H, 6.32; N, 1.83. Found: C, 83.87; H, 6.20; N, 1.82.

CCC. CuI (0.57 mg, 3.0 μmol) was added to a solution of **CC**-H (28 mg, 30 μmol), **C**-H[3] (45 mg, 90 μmol), and $(Ph_3P)_2PdCl_2$ (2.1 mg, 3.0 μmol) in THF-Et_3N (10/1 (v/v), 11 mL). After the mixture was stirred at room temperature for 14 h, the solvent was evaporated to dryness. The residue was then dissolved in $CHCl_3$ (30 mL) and the solution was washed with 1 M HCl aq. (10 mL), water (10 mL), and brine (10 mL), successively, and dried over anhydrous Na_2SO_4. The residue was purified by column chromatography (SiO_2, hexane/THF = 10/1 to 8/3 (v/v)) and SEC (Bio-Beads S-X3, $CHCl_3$) to afford **CCC** (18 mg, 42% yield) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 7.65–7.53 (m, 12H, ArH), 7.39–7.35 (m, 6H, ArH), 7.35–7.30 (m, 8H, ArH), 7.28–7.24 (m, 4H, ArH), 2.40 (t, *J* = 7.1

Hz, 6H, octynyl), 1.63–1.55 (m, 6H, octynyl), 1.42–1.40 (m, 6H, octynyl), 1.35–1.27 (m, 12H, octynyl), 0.92–0.86 (m, 9H, octynyl), 0.30 (s, 18H, $SiCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ 176.38, 140.22, 140.10, 139.62, 139.41, 139.25, 139.19, 132.73, 132.70, 131.97, 131.82, 131.60, 128.39, 128.26, 126.02, 125.84, 127.96, 121.76, 121.66, 104.87, 96.13, 95.65, 93.22, 93.05, 81.40, 81.34, 79.42, 79.33, 75.85, 75.78, 31.34, 28.61, 28.55, 22.54, 19.44, 14.06, 0.05; IR (KBr, cm^{-1}): 3138 (ν_{O-H}), 2157 ($\nu_{C\equiv C}$), 1700 ($\nu_{C=O}$); HRMS(ESI): m/*z* calcd for $[M(C_{99}H_{90}O_6Si_2)-H]^-$, 1429.6198; found 1429.6144; Anal. Calcd for $C_{99}H_{90}O_6Si_2$: C, 83.04; H, 6.34. Found: C, 82.95; H, 6.36.

AAAA. CuI (2.25 mg, 0.012 mmol) was added to a solution of **AA-H** (266 mg, 0.24 mmol) and $(Ph_3P)_2PdCl_2$ (8.3 mg, 0.012 mmol) in Et_3N (0.5 mL) and THF (5.0 mL). After the mixture was stirred at ambient temperature for 3 h, the solvent was evaporated to dryness. The residue was then purified by column chromatography (NH-SiO_2, hexane/EtOAc = 6/1 (v/v)) to afford **AAAA** (154 mg, 58% yield) as a white solid. M.p. = 179–181 °C. ^1H NMR (500 MHz, $CDCl_3$, 25 ºC, as **AAAA**·$(CH_3CO_2H)_4$) δ 12.67 (br s, 8H, NH), 7.83–7.75 (m, 4H, ArH), 7.57–7.51 (m, 8H, ArH), 7.35–7.21 (m, 40H, ArH), 7.07–6.99 (m, 16H, ArH), 6.74–6.63 (m, 16H, ArH), 2.10 (s, 12H, CH_3CO_2), 0.78–0.67 (m, 24H, C*H*$_3$CHN), 0.26 (s, 18H, $SiCH_3$). HRMS(ESI): m/*z* calcd for $[M+2H]^{2+}$, 1126.5364; found 1123.5369.

CCCC. CuI (3.05 mg, 0.016 mmol) was added to a solution of **CC-H** (298 mg, 0.320 mmol) and $(Ph_3P)_2PdCl_2$ (11.2 mg, 0.016 mmol) in Et_3N (0.35 mL) and THF (3.5 mL). After being stirred at ambient temperature for 3 h, the mixture was partitioned between $CHCl_3$ (100 mL) and 1 M HCl (50 mL), and the organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporate to dryness. The residue was purified by column chromatography (SiO_2, hexane/THF = 2/1 (v/v)) and recycling preparative SEC ($CHCl_3$) to afford **CCCC** (208 mg, 70% yield) as a white solid. M.p. > 300 °C; ^1H

NMR (500 MHz, $CDCl_3$, 1.5 mM, 25 ºC) δ 7.67–7.54 (m, 16H, ArH), 7.42–7.22 (m, 24H, ArH), 2.40 (t, J = 7.1 Hz, 8H, $CH_2C{\equiv}C$), 1.67–1.52 (m, 8H, CH_2), 1.49–1.38 (m, 8H, CH_2), 1.36–1.25 (m, 16H, CH_2), 0.95–0.83 (m, 12H, octynyl), 0.30 (s, 18H, $SiCH_3$). HRMS(ESI): m/z calcd for $[M]^-$, 1858.8052; found 1858.7951.

AA·CC. AA[1] (10.23 mg, 8.527 μmol) and **CC** (8.55 mg, 8.527 μmol) were dissolved in $CDCl_3$ (4.0 mL), and the solution was stirred at ambient temperature. The solution was evaporated to dryness to afford **AA·CC** (18.78 mg, quant.) as a white solid. Mp: 270 °C (decomp.). ^{1}H NMR ($CDCl_3$, 2.1 mM, 25 °C) δ 13.39 (d, J = 9.1 Hz, 2H, NH), 13.34 (d, J = 8.9 Hz, 2H, NH), 7.76–7.58 (m, 18H, ArH), 7.48–7.28 (m, 18H, ArH), 7.18–7.08 (m, 10H, ArH), 6.79 (d, J = 7.4 Hz, 4H, ArH), 6.73–6.67 (m, 4H, ArH), 6.61 (d, J = 8.4 Hz, 4H, ArH), 6.55 (d, J = 8.3 Hz, 4H, ArH), 3.82–3.71 (m, 4H, CHN), 2.40 (t, J = 7.2 Hz, 4H, $CH_2C{\equiv}C$), 1.65–1.52 (m, 4H, CH_2), 1.49–1.40 (m, 4H, CH_2), 1.38–1.28 (m, 8H, CH_2), 0.95–0.86 (m, 6H, CH_3), 0.67 (d, J = 6.8 Hz, 6H, NCHCH_3), 0.59 (d, J = 6.7 Hz, 6H, NCHCH_3), 0.31 (s, 18H, TMS), 0.27 (s, 18H, $SiCH_3$). Anal. Calcd for $C_{152}H_{144}N_4O_4Si_4$: C, 82.86; H, 6.59; N, 2.54. Found: C, 82.68; H, 6.67; N, 2.45.

AAA·CCC. **AAA** (3.5 mg, 2.0 μmol) and **CCC** (2.9 mg, 2.0 μmol) were dissolved in $CHCl_3$ (5 mL). After the mixture was allowed to stand at room temperature for 2 h, the solvent was evapolated. The crude product was purified by recycling preparative SEC with $CHCl_3$ as the eluent to afford **AAA·CCC** (5.3 mg, 84% yield) as a white solid. $[\alpha]_D^{20}$ –689 (c = 0.05 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 13.41 (d, J = 9.1 Hz, 2H, NH), 13.36 (d, J = 9.0 Hz, 2H, NH), 13.32 (d, J = 8.7 Hz, 2H, NH), 7.79–7.69 (m, 11H, ArH), 7.69–7.64 (m, 12H, ArH), 7.61 (d, J = 8.3 Hz, 4H, ArH), 7.50–7.24 (m, 28H, ArH), 7.18–7.08 (m, 14H, ArH), 6.84 (d, J = 7.5 Hz, 4H, ArH), 6.79 (d, J = 7.5 Hz, 4H, ArH),

6.72–6.67 (m, 4H, ArH), 6.65–6.59 (m, 8H, ArH), 6.55 (d, J = 8.2 Hz, 4H, ArH), 3.83–3.72 (m, 6H, CH_3CHN), 2.40 (t, J = 7.1 Hz, 6H, octynyl), 1.66–1.54 (m, 6H, octynyl), 1.48–1.41 (m, 6H, octynyl), 1.37–1.28 (m, 12H, octynyl), 0.93–0.87 (m, 9H, octynyl), 0.70–0.63 (m, 12H, CH_3CHN), 0.59 (d, J = 6.7 Hz, 6H, CH_3CHN), 0.31 (s, 18H, $SiCH_3$), 0.27 (s, 18H, $SiCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ 176.55, 162.10, 142.62, 142.40, 142.37, 142.22, 141.70, 141.65, 141.35, 141.32, 141.18, 141.10, 140.58, 140.50, 140.45, 138.70, 138.63, 138.58, 138.05, 137.19, 136.85, 136.82, 132.11, 132.00, 131.96, 131.88, 131.66, 131.53, 131.34, 129.20, 129.12, 129.09, 128.99, 128.95, 128.70, 128.54, 126.39, 126.34, 126.27, 123.54, 122.82, 122.73, 122.59, 122.55, 122.48, 122.00, 121.92, 121.84, 120.57, 120.51, 105.77, 104.11, 102.35, 96.36, 94.61, 90.33, 90.25, 81.48, 81.44, 81.18, 81.15, 80.46, 80.41, 75.97, 75.93, 75.19, 55.57, 55.50, 55.44, 31.37, 28.73, 28.65, 22.82, 22.60, 22.55, 22.49, 19.49, 14.06, 0.23, 0.00; IR (KBr, cm^{-1}): 3430 (ν_{N-H}, ν_{O-H}), 2156 ($\nu_{C\equiv C}$), 1655 ($\nu_{C=O}$, $\nu_{C=N}$); CSI-MS: m/z calcd for $[M(C_{222}H_{198}N_6O_6Si_4)+2H]^{2+}$, 1578.72; found 1578.90; Anal. Calcd for $C_{222}H_{198}N_6O_6Si_4$: C, 84.42; H, 6.32; N, 2.66. Found: C, 84.32; H, 6.33; N, 2.72.

AAC·CCA. **AAC** (3.3 mg, 2.0 μmol) and **CCA** (3.1 mg, 2.0 μmol) were dissolved in $CHCl_3$ (5 mL). After the mixture was allowed to stand at room temperature for 14 h, the solvent was evapolated. The crude product was purified by recycling preparative SEC with $CHCl_3$ as the eluent to afford **AAC·CCA** (4.4 mg, 70% yield) as a white solid. $[\alpha]_D^{20}$ –693 (c = 0.05 in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 13.48–13.28 (m, 6H, NH), 7.79–7.57 (m, 27H, ArH), 7.53–7.21 (m, 28H, ArH), 7.19–7.04 (m, 14H, ArH), 6.86 (d, J = 7.6 Hz, 2H, ArH), 6.82–6.67 (m, 10H, ArH), 6.65–6.58 (m, 8H, ArH), 6.55 (d, J = 7.8 Hz, 4H, ArH), 3.87–3.71 (m, 6H, CH_3CHN), 2.44–2.35 (m, 6H, octynyl), 1.69–1.40 (m, 12H, octynyl), 1.37–1.28 (m, 12H, octynyl), 0.93–0.86 (m, 9H, octynyl), 0.75–0.56 (m, 18H, CH_3CHN), 0.31 (s, 18H, $SiCH_3$), 0.27 (s, 9H, $SiCH_3$), 0.27 (s, 9H, $SiCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ

176.61, 176.55, 162.05, 143.17, 142.85, 142.61, 142.51, 142.41, 142.35, 142.15, 141.69, 141.40, 141.34, 141.16, 140.52, 140.45, 138.71, 138.63, 138.56, 138.47, 138.42, 138.03, 137.17, 136.86, 136.83, 136.79, 132.76, 132.66, 132.10, 132.04, 131.95, 131.88, 131.68, 131.60, 131.51, 131.34, 130.22, 129.20, 129.13, 129.09, 128.99, 128.93, 128.69, 128.53, 126.41, 126.34, 123.54, 122.81, 122.78, 122.69, 122.61, 122.55, 122.49, 122.38, 122.29, 122.00, 121.91, 121.84, 120.52, 120.19, 120.16, 105.79, 104.09, 96.34, 90.38, 90.30, 82.56, 81.48, 80.44, 80.41, 80.37, 80.17, 80.15, 75.96, 75.94, 75.24, 74.72, 74.67, 55.56, 55.45, 31.36, 28.72, 28.65, 22.54, 19.49, 14.06, 0.23, 0.00; IR (KBr, cm^{-1}): 3432 (ν_{N-H}, ν_{O-H}), 2156 ($\nu_{C\equiv C}$), 1655 ($\nu_{C=O}$, $\nu_{C=N}$); CSI-MS: *m*/*z* calcd for $[M(C_{222}H_{198}N_6O_6Si_4)+2H]^{2+}$, 1578.73; found 1578.90; Anal. Calcd for $C_{222}H_{198}N_6O_6Si_4$: C, 84.42; H, 6.32; N, 2.66. Found: C, 84.33; H, 6.05; N, 2.81.

ACA·CAC. **ACA** (3.3 mg, 2.0 μmol) and **CAC** (3.1 mg, 2.0 μmol) were dissolved in $CHCl_3$ (5 mL). After the mixture was allowed to stand at room temperature for 14 h, the solvent was evapolated. The crude product was purified by recycling preparative SEC with $CHCl_3$ as the eluent to afford **ACA·CAC** (4.2 mg, 66% yield) as a white solid. $[\alpha]_D^{20}$ –697 (*c* = 0.05 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ 13.48 (d, *J* = 9.0 Hz, 2H, NH), 13.39 (d, *J* = 8.9 Hz, 2H, NH), 13.36 (d, *J* = 9.0 Hz, 2H, NH), 7.76–7.58 (m, 27H, ArH), 7.48–7.35 (m, 25H, ArH), 7.27–7.21 (m, 3H, ArH), 7.19–7.13 (m, 6H, ArH), 7.11–7.04 (m, 8H, ArH), 6.82 (d, *J* = 7.6 Hz, 4H, ArH), 6.77–6.69 (m, 8H, ArH), 6.64–6.58 (m, 8H, ArH), 6.55 (d, *J* = 8.2 Hz, 4H, ArH), 3.85–3.72 (m, 6H, CH_3CHN), 2.43–2.35 (m, 6H, octynyl), 1.68–1.50 (m, 6H, octynyl), 1.48–1.38 (m, 6H, octynyl), 1.38–1.20 (m, 12H, octynyl), 0.93–0.85 (m, 9H, octynyl), 0.74–0.66 (m, 12H, CH_3CHN), 0.59 (d, *J* = 6.8 Hz, 6H, CH_3CHN), 0.31 (s, 18H, $SiCH_3$), 0.27 (s, 18H, $SiCH_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ 176.68, 176.60, 162.06, 162.00, 142.84, 142.63, 142.53, 142.35, 141.71, 141.40, 141.17, 140.52, 138.45, 138.41, 138.03, 137.16, 136.81,

136.74, 129.21, 129.14, 129.08, 128.99, 128.92, 128.90, 128.60, 128.53, 126.43, 126.35, 126.30, 123.54, 122.78, 122.69, 122.65, 122.55, 122.40, 122.31, 121.82, 120.15, 120.13, 105.79, 104.09, 96.39, 94.58, 90.44, 90.30, 82.58, 80.41, 80.14, 76.43, 74.69, 74.62, 55.53, 31.36, 29.69, 28..72, 28.64, 22.74, 22.54, 19.48, 14.05, 0.23, –0.01; IR (KBr, cm^{-1}): 3432 (ν_{N-H}, ν_{O-H}), 2156 ($\nu_{C\equiv C}$), 1655 ($\nu_{C=N}$, $\nu_{C=N}$); Anal. Calcd for $C_{222}H_{198}N_6O_6Si_4$: C, 84.42; H, 6.32; N, 2.66. Found: C, 84.24; H, 6.10; N, 2.79.

AAAA·CCCC. AAAA (5.00 mg, 2.21 μmol) and **CCCC** (4.13 mg, 2.21 μmol) were dissolved in $CDCl_3$ (10 mL), and the solution was stirred at ambient temperature. The solution was evaporated to dryness to afford **AAAA·CCCC** (9.13 mg, quant.) as a white solid. Mp: > 300 °C. ^{1}H NMR ($CDCl_3$, 1.0 mM, 25 °C) δ 13.51–13.25 (m, 8H, NH), 7.80–7.57 (m, 36H, ArH), 7.53–7.28 (m, 36H, ArH), 7.19–7.06 (m, 20H, ArH), 6.90–6.52 (m, 32H, ArH), 3.86–3.71 (m, 8H, CHN), 2.40 (t, J = 7.2 Hz, 8H, $CH_2C\equiv C$), 1.68–1.51 (m, 8H, $C\equiv CCH_2$), 1.50–1.41 (m, 8H, CH_2), 1.39–1.20 (m, 16H, CH_2), 0.98–0.81 (m, 12H, CH_3), 0.68–0.55 (m, 24H, NCHCH_3), 0.31 (s, 18H, $SiCH_3$), 0.27 (s, 18H, TMS). Anal. Calcd for $C_{292}H_{252}N_8O_8Si_4$: C, 85.26; H, 6.17; N, 2.72. Found: C, 85.27; H, 6.02; N, 2.83.

Supporting Reference

1. Tanaka, Y.; Katagiri, H.; Furusho, Y.; Yashima, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 3867–3870.
2. Ikeda, M.; Tanaka, Y.; Hasegawa, T.; Furusho, Y.; Yashima, E. *J. Am. Chem. Soc.* **2006**, *128*, 6806–6807.
3. Maeda, T.; Furusho, Y.; Sakurai, S.-i.; Kumaki, J.; Okoshi, K.; Yashima, E. *J. Am. Chem. Soc.* **2008**, *130*, 7938–7945.

1. Double Helix Formation of Dimers

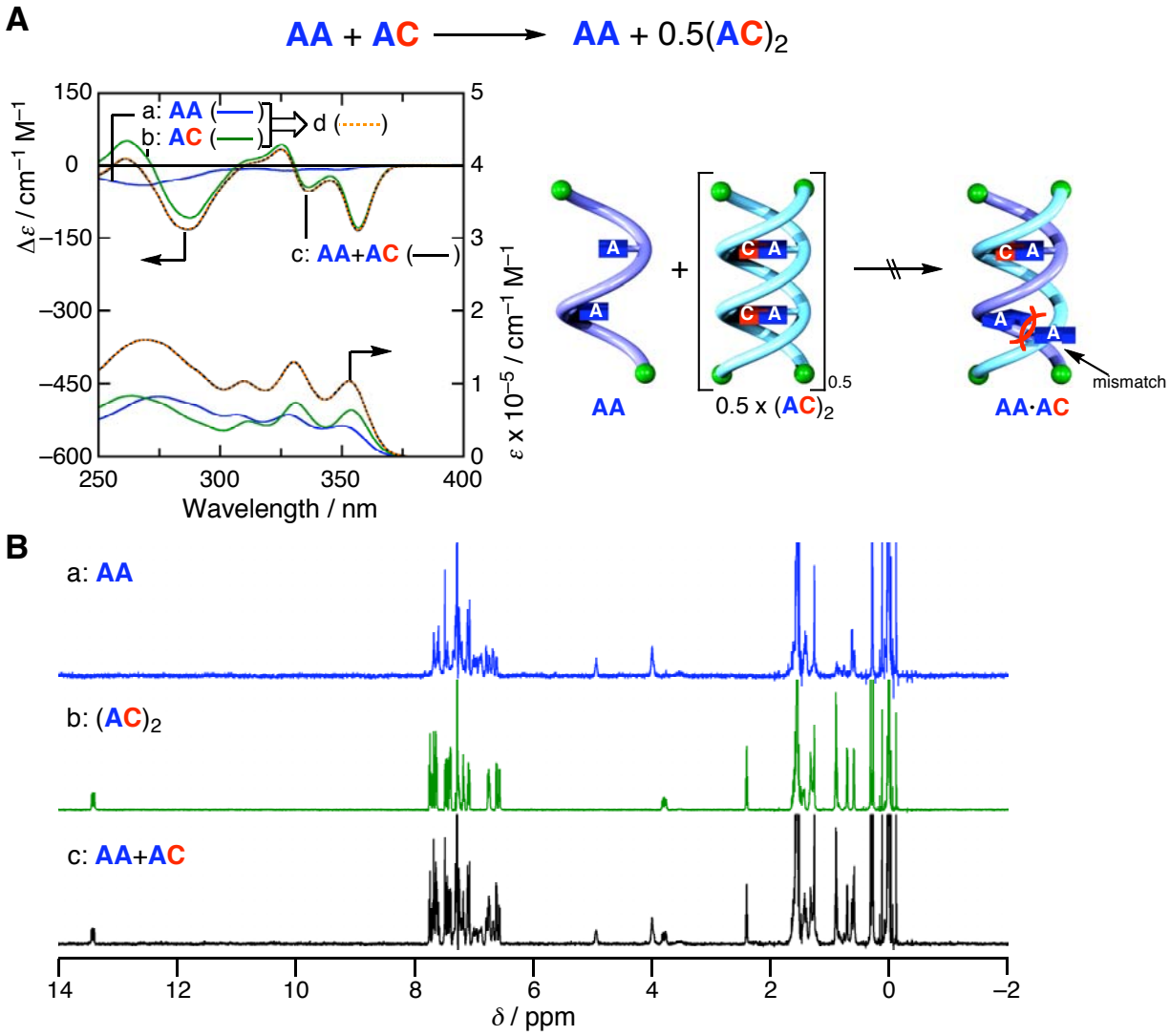
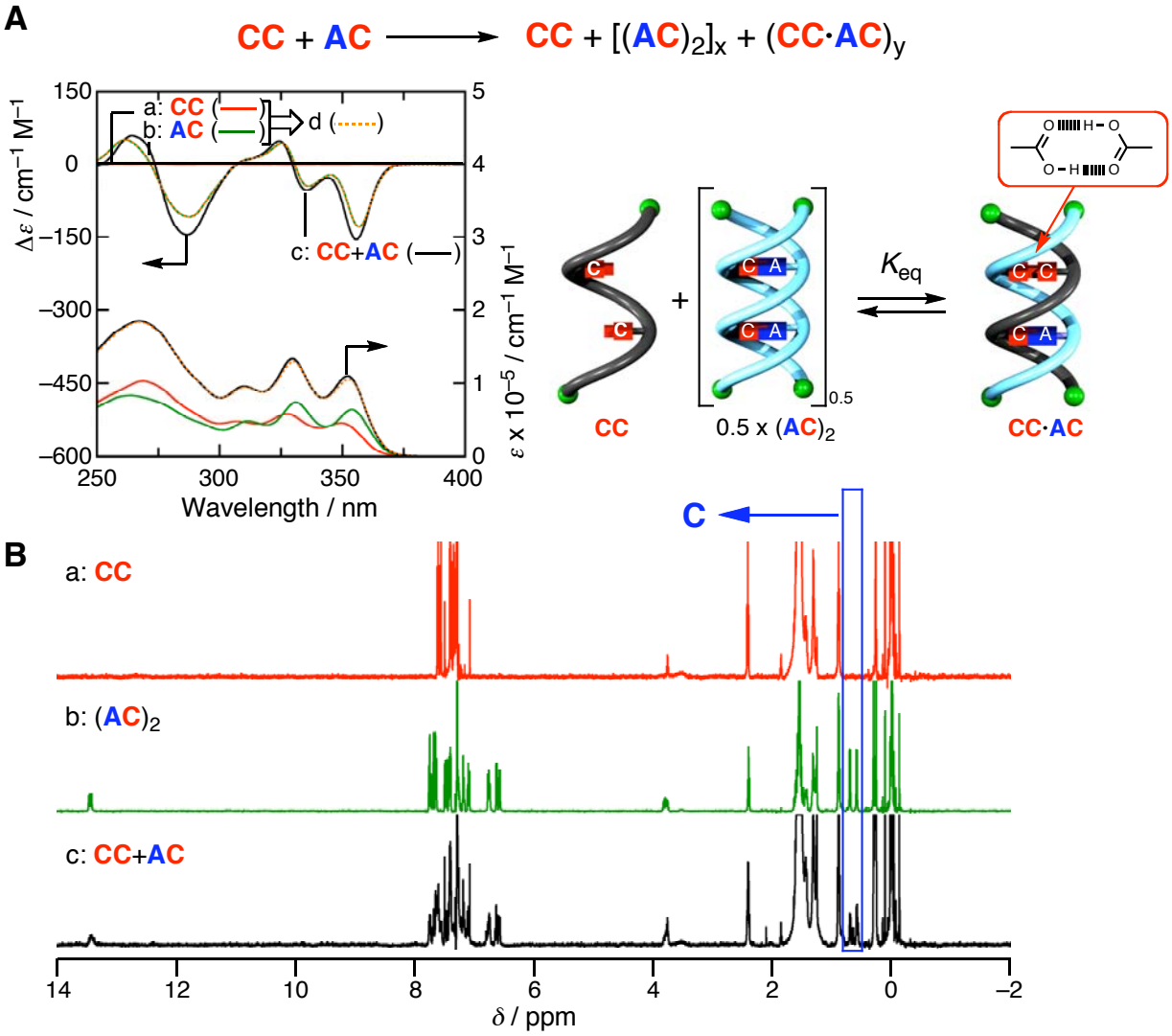


Figure S1. (A) CD and absorption spectra of **AA** (a, blue), **AC** (b, green), and an equimolar mixture of **AA** and **AC** (c, black) in $CDCl_3$ (0.10 mM, 25 °C, cell length: 0.1 cm), and the sum spectrum of a and b (d, dashed orange), (B) ^{1}H NMR spectra of **AA** (a, blue), $(\mathbf{AC})_2$ (b, green), and an equimolar mixture of **AA** and **AC** (c, black) in $CDCl_3$ (0.10 mM, 25 °C).


A
CC + AC
CC + [(AC)2]x + (CC·AC)y
a: CC
b: AC
d
c: CC+AC
Δε / cm−1 M−1
ε x 10−5 / cm−1 M−1
Wavelength / nm
Keq
CC
0.5 x (AC)2
CC·AC
B
C
a: CC
b: (AC)2
c: CC+AC
δ / ppm

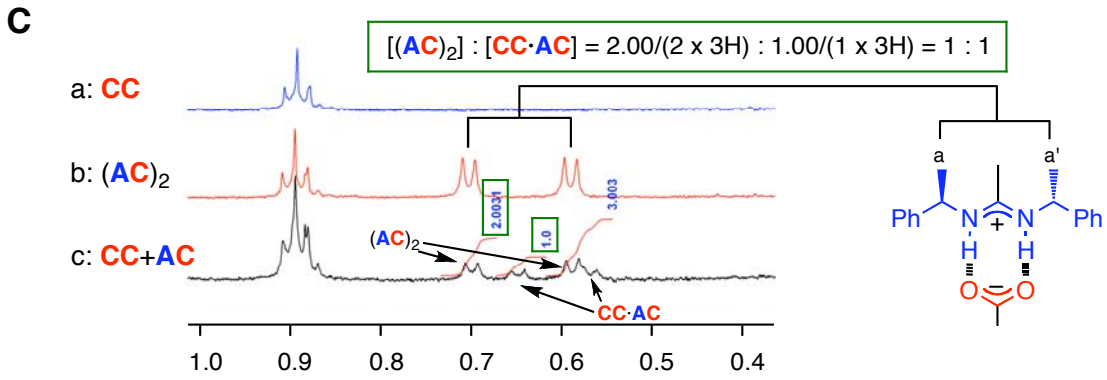


Figure S2. (A) CD and absorption spectra of **CC** (a, red), **AC** (b, green), and an equimolar mixture of **CC** and **AC** (c, black) in $CDCl_3$ (0.10 mM, 25 °C, cell length: 0.1 cm), and the sum spectrum of a and b (d, dashed orange),. (B, C) ^1H NMR spectra of **CC** (a, red), $(\mathbf{AC})_2$ (b, green), and an equimolar mixture of **CC** and **AC** (c, black) in $CDCl_3$ (0.10 mM, 25 °C).

2. Sequence-Specific Sorting of Dimers through Double Helix Formation

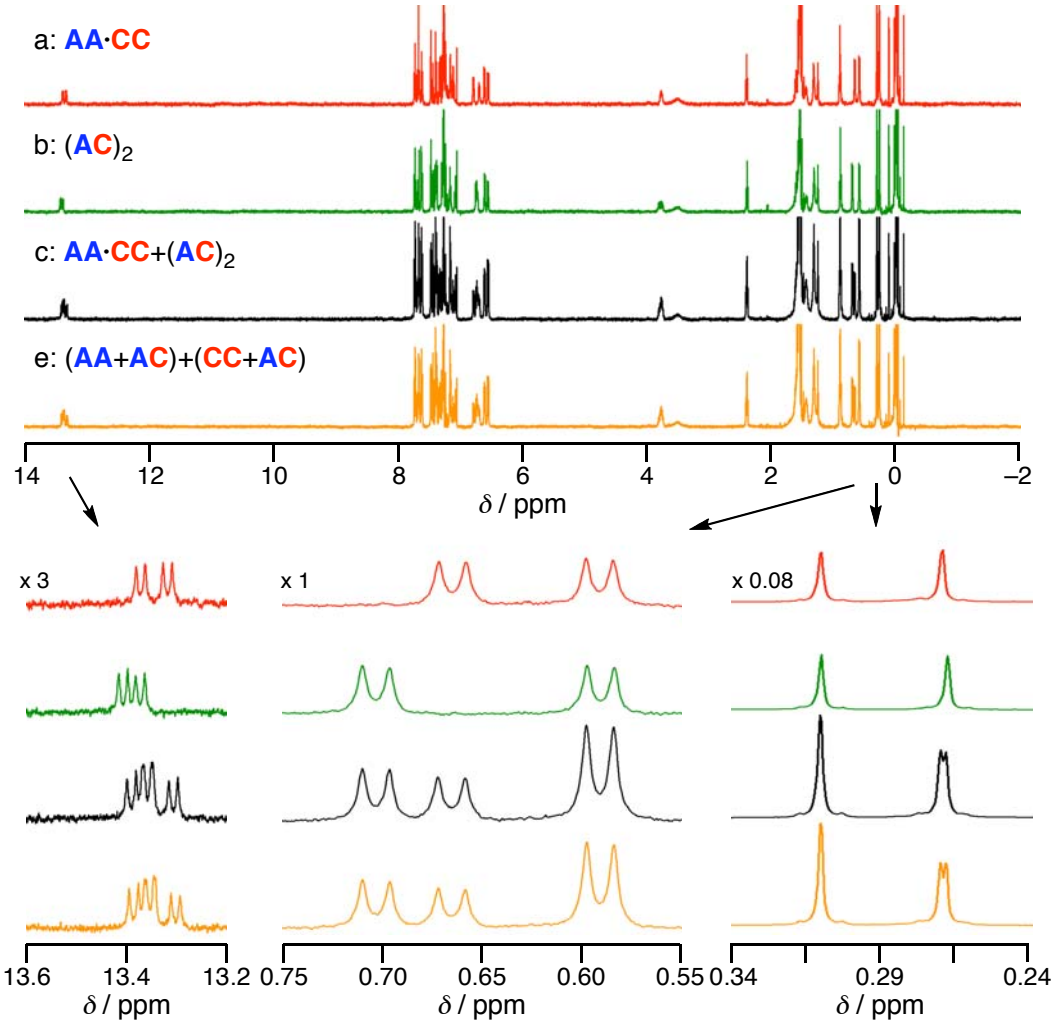


Figure S3. ^{1}H NMR spectra of **AA·CC** (a, red, 0.10 mM), (**AC**)$_2$ (b, green, 0.10 mM), the mixture of **AA·CC** and (**AC**)$_2$ (c, black, 50 μM), and the mixture of (**AA**+**AC**) and (**CC**+**AC**) (e, orange) in $CDCl_3$ at 25 °C.

3. Double Helix Formation of Trimers

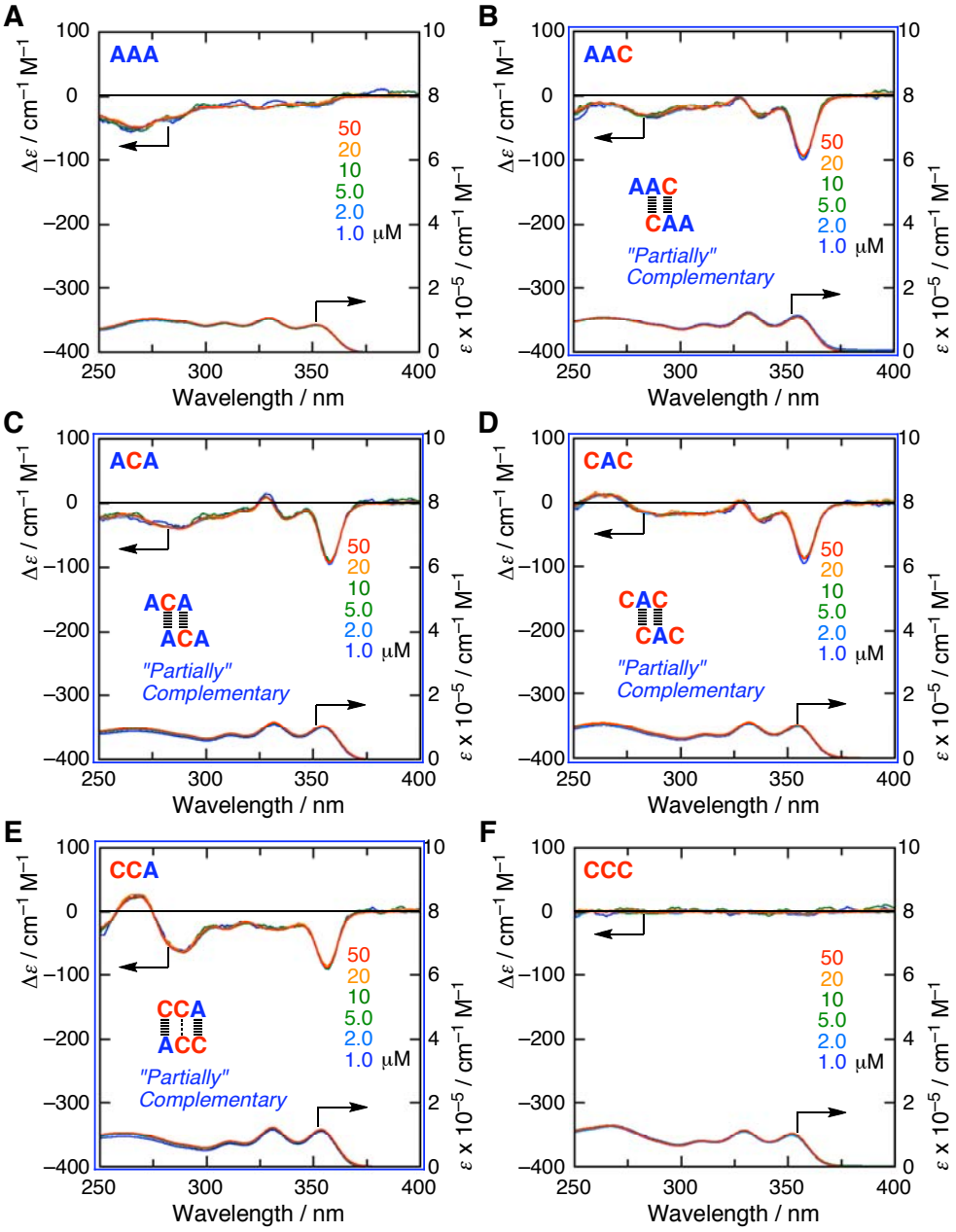


Figure S4. Concentration dependent changes in CD and absorption spectra of **AAA** (A), **AAC** (B), **ACA** (C), **CAC** (D), **CCA** (E), and **CCC** (F) in $CDCl_3$ at 25 °C measured in 0.1-cm (50 μM, 20 μM, 10 μM) and 1.0-cm (5.0 μM, 2.0 μM, 1.0 μM) quartz cells.

4. Sequence-Specific Sorting of Trimers through Double Helix Formation

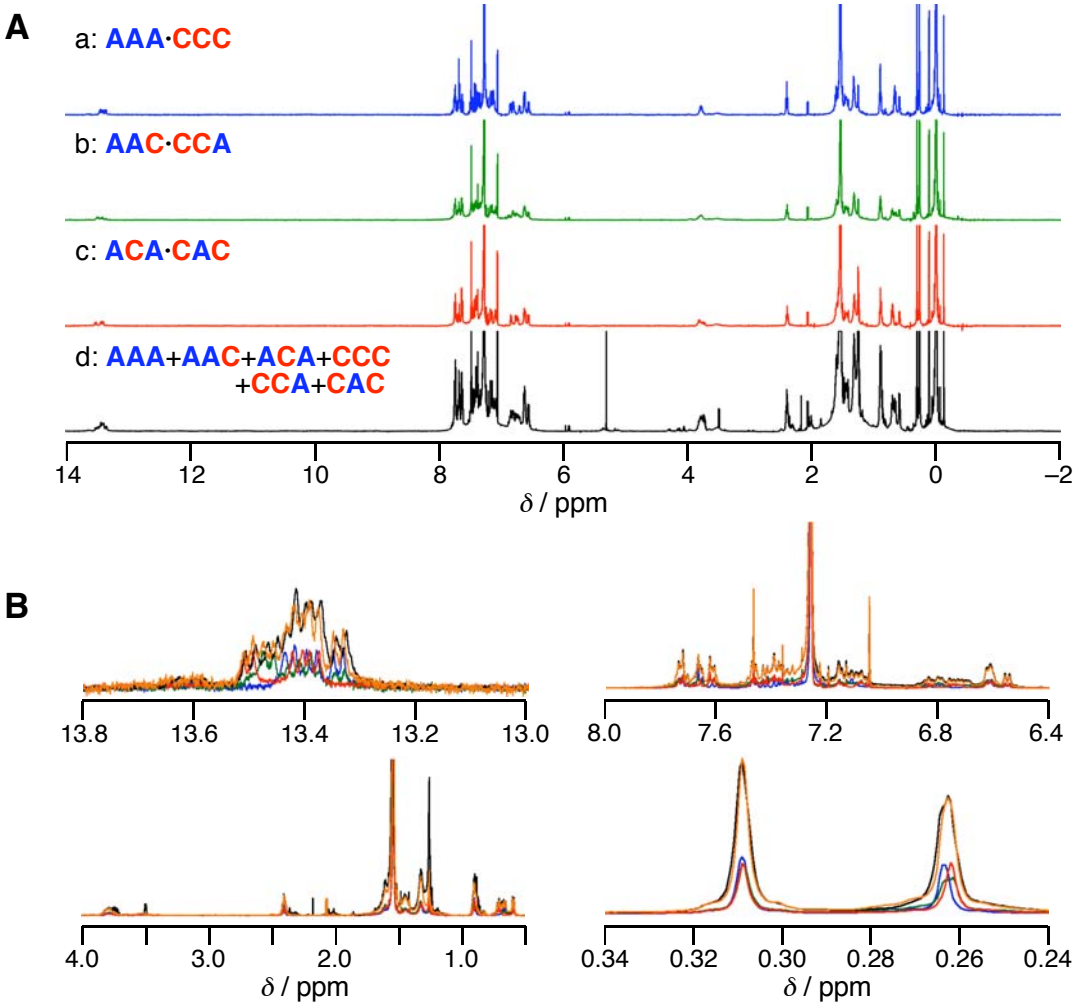


Figure S5. (A) ^{1}H NMR spectra of **AAA·CCC** (a, blue), **AAC·CCA** (b, green), **ACA·CAC** (c, red), and an equimolar mixture of **AAA**, **AAC**, **ACA**, **CCC**, **CCA**, and **CAC** (d, the sample had been allowed to stand for 36 h, black) in $CDCl_3$ (17 μM, 25 °C). (B) Partial ^{1}H NMR spectra of a (blue), b (green), c (red), and d (black), and that simulated for an equimolar mixture of separately prepared **AAA·CCC**, **AAC·CCA**, and **ACA·CAC** (orange).

5. Sequence-Specific Binding of Trimers.

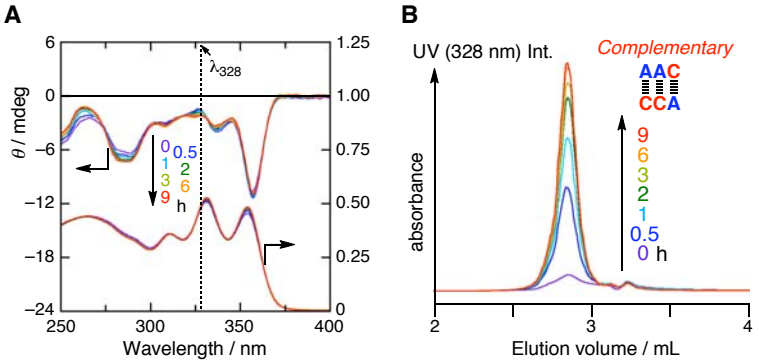


Figure S6. (A) Time dependent CD and absorption spectral changes of an equimolar mixture of **AAA**, **AAC**, **ACA**, and **CCA** (**CCA** was added 12 h after **AAA**, **AAC**, and **ACA** were mixed in $CHCl_3$) 0–9 h after mixing in $CHCl_3$ (10 μM) measured in a 1.0-mm quartz cell at 25 °C. (B) Changes in the HPLC chromatograms of an equimolar mixture of **AAA**, **AAC**, **ACA**, and **CCA** 0–9 h after mixing in $CHCl_3$ at 25 °C (column: TSKgel Silica-60 (Tosoh, ϕ 0.46 x 25 cm); eluent: $CHCl_3$/hexane (1/1, v/v), 1.0 mL/min).

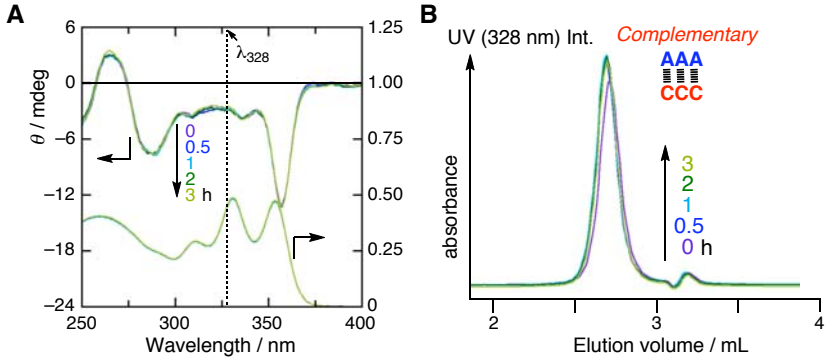


Figure S7. (A) Time dependent CD and absorption spectral changes of an equimolar mixture of **AAA**, **CAC**, **CCA**, and **CCC** (**CCC** was added 12 h after **AAA**, **CAC**, and **CCA** were mixed in $CHCl_3$) 0–3 h after mixing in $CHCl_3$ (10 μM) measured in a 1.0-mm quartz cell at 25 °C. (B) Changes in the HPLC chromatograms of an equimolar mixture of **AAA**, **CAC**, **CCA**, and **CCC** 0–3 h after mixing in $CHCl_3$ at 25 °C (column: TSKgel Silica-60 (Tosoh, ϕ 0.46 x 25 cm); eluent: $CHCl_3$/hexane (1/1, v/v), 1.0 mL/min).

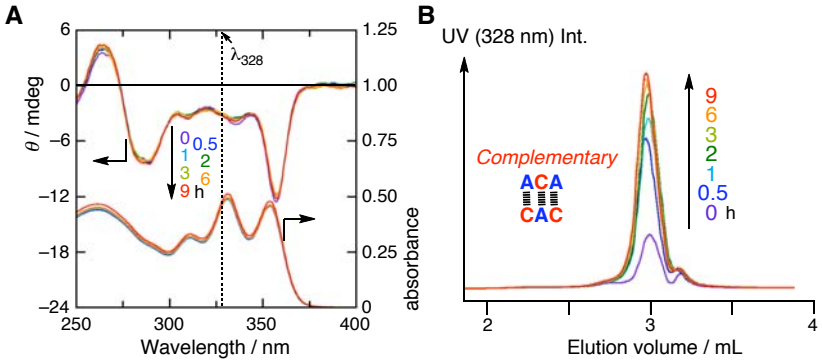


Figure S8. (A) Time dependent CD and absorption spectral changes of an equimolar mixture of **ACA**, **CAC**, **CCA**, and **CCC** (**ACA** was added 12 h after **CAC**, **CCA**, and **CCC** were mixed in $CHCl_3$) 0–9 h after mixing in $CHCl_3$ (10 μM) measured in a 1.0-mm quartz cell at 25 °C. (B) Changes in the HPLC chromatograms of an equimolar mixture **ACA**, **CAC**, **CCA**, and **CCC** 0–9 h after mixing in $CHCl_3$ at 25 °C (column: TSKgel Silica-60 (Tosoh, ϕ 0.46 x 25 cm); eluent: $CHCl_3$/hexane = 1/1 (v/v), 1.0 mL/min).

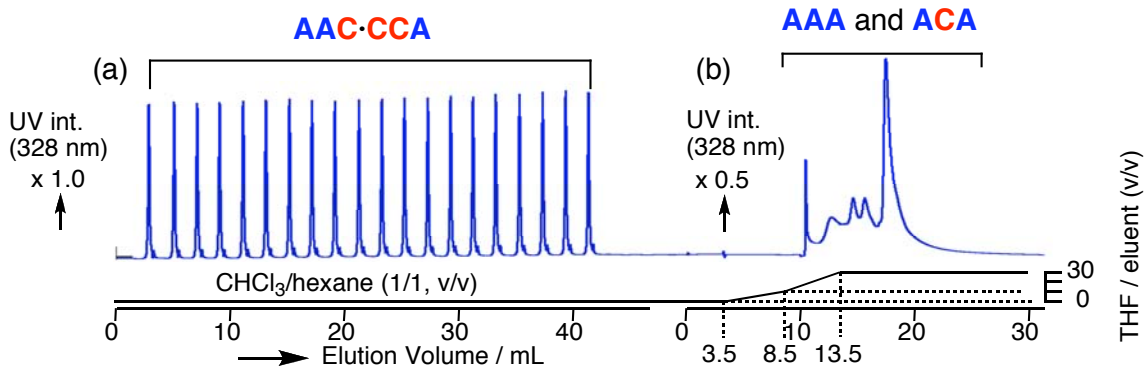


Figure S9. UV (328 nm) detected HPLC chromatogram for the isolation of **AAC·CCA** from an equimolar mixture of **AAA**, **AAC**, **ACA**, and **CCA**. (a) The sample was injected 20 times at regular intervals of 2 min, and the fractions containing **AAC·CCA** were collected with the eluent of $CHCl_3$/hexane (1/1, v/v). (b) The other components adsorbed on the stationary phase of the column were eluted after changing the eluent to that containing 30 vol% of THF.

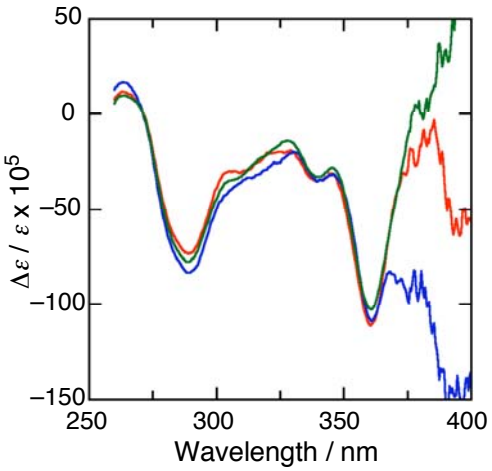


Figure S10. CD spectra ($\Delta\varepsilon/\varepsilon$) of **AAC·CCA** ($5.0 \times 10^{-5}$ M in $CHCl_3$, green), **AAC·CCA** isolated by HPLC from the mixture of **AAA**, **AAC**, **ACA**, and **CCA** in $CHCl_3$ (red), and from the mixture of **AAC** and **CCA** in $CHCl_3$ (blue).

6. Chain Length-Specific Double Helix Formation.

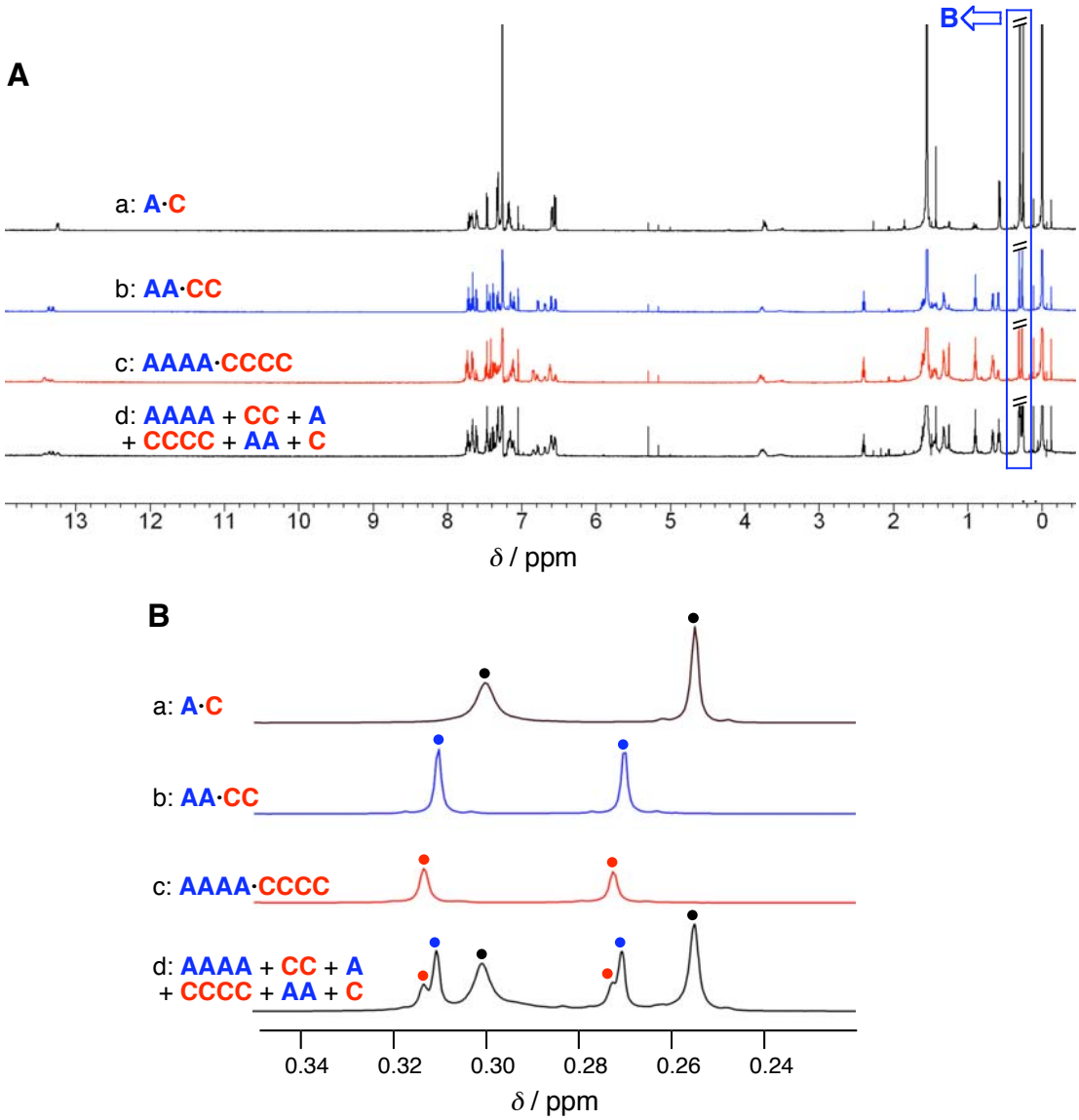


Figure S11. (A) ^{1}H NMR spectra of **A·C** (0.1 mM) (a), **AA·CC** (0.05 mM) (b), **AAAA·CCCC** (0.025 mM) (c), and a mixture of **AAAA** (12.5 μM), **CC** (25 μM), **A** (50 μM), **CCCC** (12.5 μM), **AA** (25 μM), and **C** (50 μM) (d, after mixing in this order) in $CDCl_3$ at 25 °C. (B) Partial ^{1}H NMR spectra of the terminal trimethylsilyl region of (a), (b), (c), and (d).