Electronic Supplementary Information

Stereospecific control of the helical orientation of indolocarbazole–pyridine hybrid foldamers by rational modification of terminal chiral appendages

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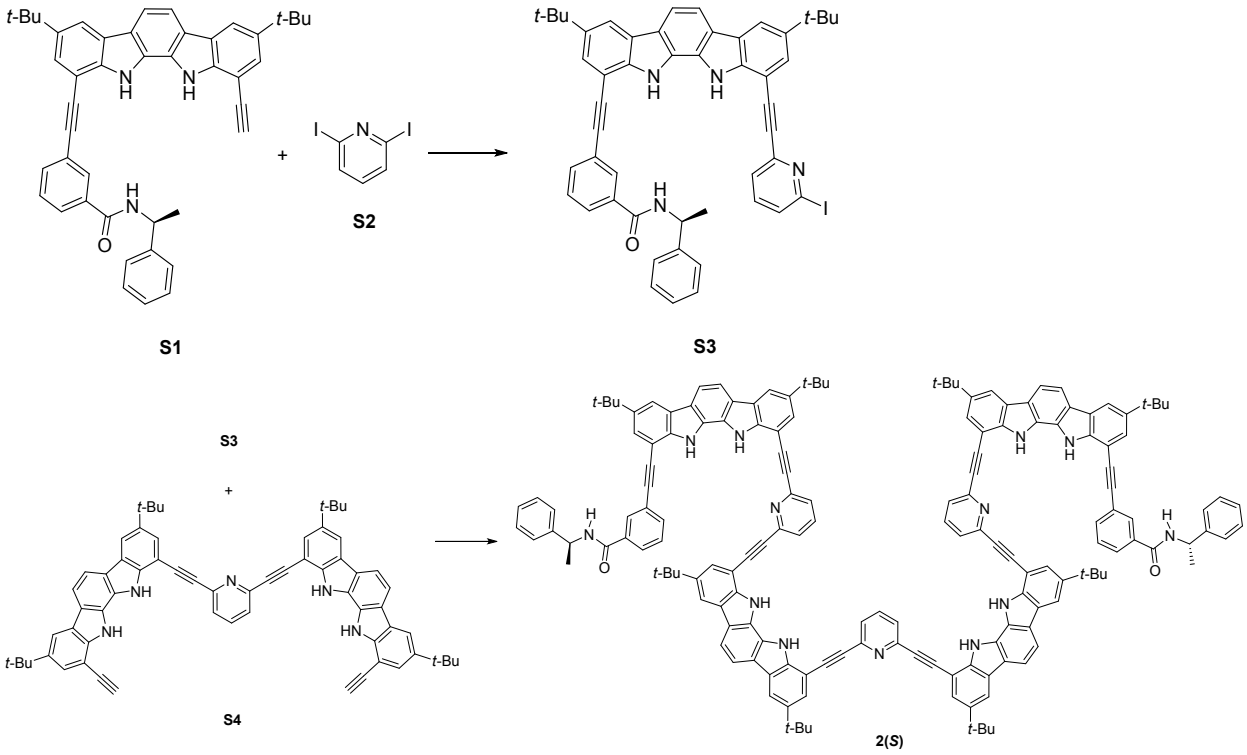
Contents

1. Syntheses and characterization of new compounds

1.1 General: All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. Dichloromethane (CH_2Cl_2) was purified by drying over calcium hydride (CaH_2), followed by distillation. Hexane, ethyl acetate (EtOAc), and acetone were distilled. Water-saturated deuterated solvents were prepared by sonication of a mixture of solvent containing a few drops of distilled water for 10 min. After 1 h standing, organic layer was carefully separated out for use. Thin layer chromatography (TLC) was performed on Merck (silica gel 60, F-254, 0.25 mm). Silica gel 60 (230-400 mesh, Merck) was used for column chromatography. Melting points were determined with a Barnstead Electrothermal (IA9100) apparatus. 1D and 2D NMR spectra were measured by using Bruker DRX 400, Avance II instruments. Chemical shifts were reported using residual protonated solvent peaks (for ^{1}H NMR spectra, acetone-d_6 2.05 ppm; $CDCl_3$ 7.26 ppm; CD_2Cl_2 5.32 ppm; $(CD_2Cl)_2$ 3.72 ppm; DMSO-d_6 2.50 ppm and for ^{13}C NMR spectra, acetone-d_6 206.26 ppm; $CDCl_3$ 77.16 ppm; CD_2Cl_2 53.84 ppm; DMSO-d_6 39.52 ppm). FT-IR spectra were measured by using a Vertex70 FT-IR spectrometer. Gas chromatographic analysis was performed on Agilent 7890A instrument with FID detector and an Agilent HP-5 capillary column. MALDI-TOF mass spectrometric measurements were performed on a Bruker (LRF20). The ESI-HRMS spectrometric measurements were obtained from *the Organic Chemistry Research Center* at Sogang University.

1.2 Synthesis of compound **2**(*S*)



S3: The synthesis of **S1**[S1] and **S2**[S2] were described previously. A Schlenk flask containing **S1** (0.24 g, 0.38 mmol), CuI (1.4 mg, 0.008 mmol), $Pd(PPh_3)_2Cl_2$ (5.3 mg, 0.008 mmol) and **S2** (0.37 g, 1.14 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed tetrahydrofuran (THF) (2 mL) and triethylamine (Et_3N) (2 mL) were added in order under nitrogen. The solution was stirred at 55 °C for 2 h and cooled to room temperature. The mixture was filtered through Celite with CH_2Cl_2 and concentrated. The residue was dissolved in CH_2Cl_2, washed with brine and $NaHCO_3$, dried over anhydrous Na_2SO and concentrated. The residue was purified by flash column chromatography (silica gel, hexane/diethyl ether = 1:2) to give **S3** as a yellow solid (0.28 g,

[S1] J.-m. Suk, V. R. Naidu, X. Liu, M. S. Lah and K.-S. Jeong, *J. Am. Chem. Soc.*, 2011, **133**, 13938–13941.

[S2] (a) W. Baker, R. F. Curtis and M. G. Edwards, *J. Chem. Soc.*, 1951, 83–87. (b) B. X. Colasson, C. Dietrich-Buchecker and J.-P. Sauvage, *Synlett*, 2002, 0271–0272. (c) G. R. Newkome and J. M. Roper, *J. Organomet. Chem.*, 1980, **186**, 147–153. (d) G. D. Harzmann, M. Neuburger and M. Mayor, *Eur. J. Inorg. Chem.*, 2013, 3334–3347.

88%); mp > 196 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 10.57 (s, 1H), 10.54 (s, 1H), 8.41 (d, J = 1.6 Hz, 1H), 8.36 (d, J = 1.6 Hz, 1H), 8.26–8.23 (m, *2*H), 8.08 (s, 2H), 8.00 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 8.0Hz, 1H), 7.84 (d, J = 7.6Hz, 1H), 7.80 (d, J = 7.6Hz, 1H), 7.78 (d, J = 1.7Hz, 1H), 7.72 (d, J = 1.7Hz, 1H), 7.62 (t, J = 7.8Hz, 1H), 7.58 (t, J = 7.8Hz, 1H), 7.49 (d, J = 7.7Hz, 2H), 7.33 (t, J = 7.4Hz, 2H), 7.23 (t, J = 7.4Hz, 1H), 5.38 (quint, J = 7.4Hz, 1H), 1.61 (d, J = 7.0Hz, 3H), 1.51 (s, 18H); ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ 166.0, 145.7, 145.1, 143.7, 143.6, 139.5, 139.4, 136.5, 135.4, 135.0, 131.4, 129.8, 129.3, 128.4, 128.0, 127.8, 127.4, 127.2, 127.1, 126.7, 125.6, 125.3, 124.5, 122.8, 122.5, 119.6, 118.7, 118.3, 113.5, 113.4, 105.9, 104.6, 93.3, 92.4, 88.5, 87.8, 50.2, 35.5, 35.5, 32.4, 32.3, 22.7; MALDI-TOF *m/z* calcd for $C_{50}H_{44}IN_4O$ $[M+H]^+$ 843, found 843; IR (thin film) υ 3339 (NH), 2204 (C≡C), 1638 (C=O) cm^{-1}.

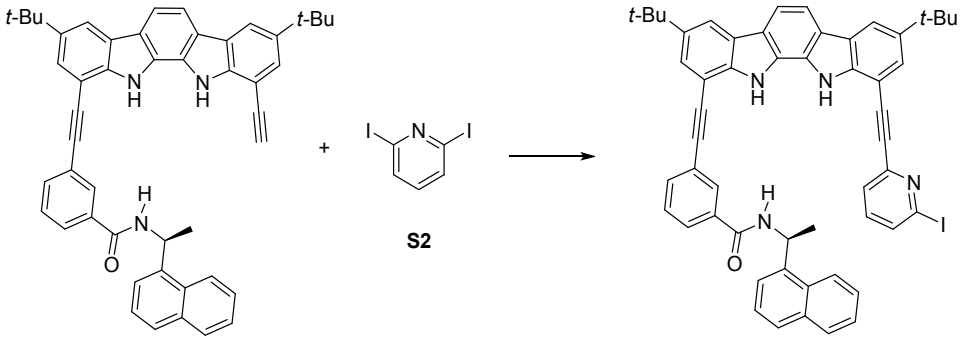
2(*S*)**:** The synthesis of **S4** was described previously.[S3] A Shlenk flask containing **S3** (0.15 g, 0.16 mmol), **S4** (0.27 g, 0.32 mmol), CuI (1.5 mg, 0.008 mmol) and $Pd(PPh_3)_2Cl_2$ (5.6 mg, 0.008 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (2 mL) and Et_3N (2 mL) were added in order under nitrogen. The solution was stirred at 55 °C for 2 h and cooled to room temperature. The mixture was filtered through Celite with EtOAc and concentrated. The residue was dissolved in EtOAc, washed with brine and $NaHCO_3$, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 4:1) to give **2**(*S*) as a yellow solid (119 mg, 32%); mp > 178 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 10.70 (s, 2H), 10.65 (s, 2H), 10.46 (s, 2H), 10.22 (s, 2H), 8.26 (d, J = 1.6 Hz, 2H), 8.24 (d, J = 1.5 Hz, 2H), 8.13(s, 2H), 8.05 (s, 2H), 7.99 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.80 (s, 2H), 7.53 (d, J = 1.6 Hz, 2H), 7.49 (d, J = 1.6 Hz, 2H), 7.47 (d, J = 4.1 Hz, 2H), 7.36 (d, J = 7.4 Hz, 2H), 7.25–7.13 (m, 12H), 7.06 (d, J = 7.5 Hz, 2H), 6.96 (d, J = 6.4 Hz, 2H), 6.78 (t, J = 7.8 Hz, 1H), 6.69 (t, J = 8.0 Hz, 2H), 6.67 (d, J = 7.7 Hz, 2H), 6.39 (d, J = 7.8 Hz, 2H),

[S3] H.-G. Jeon, J. Y. Jung, P. Kang, M.-G. Choi and K.-S. Jeong, *J. Am. Chem. Soc.*, 2016, **138**, 92–95.

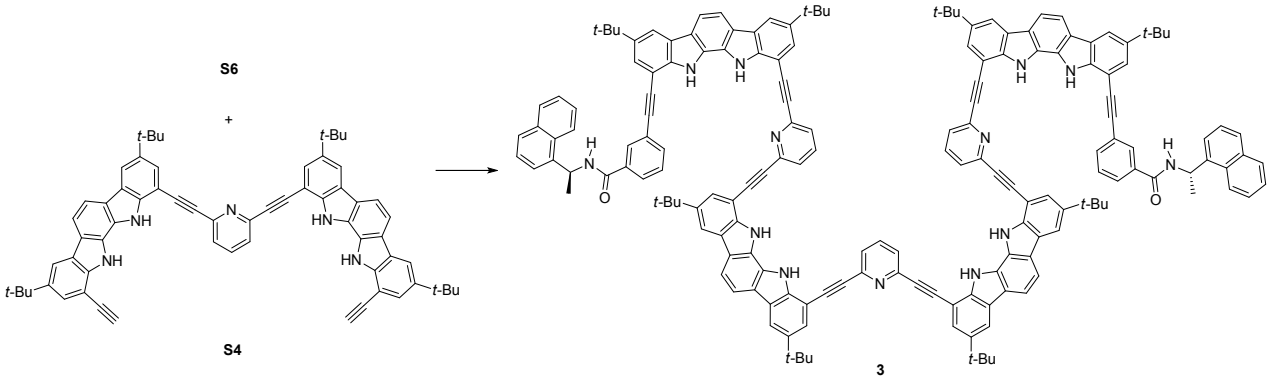
5.21 (quint, J = 7.3 Hz, 2H), 1.49 (s, 18H), 1.48 (s, 18H), 1.47 (s, 18H), 1.46 (s, 18H); ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ 165.6, 145.5, 142.9, 142.6, 142.5, 142.4, 142.0, 142.0, 141.8, 140.4, 140.2, 138.9, 138.9, 136.9, 135.3, 134.8, 133.9, 130.2, 129.0, 128.2, 127.5, 127.3, 127.2, 127.1, 127.1, 127.0, 126.9, 126.2, 126.0, 125.9, 125.2, 125.1, 125.0, 124.9, 124.8, 124.4, 123.9, 123.4, 122.3, 122.3, 122.1, 122.1, 118.7, 117.7, 112.8, 112.8, 112.8, 112.6, 105.8, 104.8, 104.7, 104.1, 93.1, 92.7, 92.6, 88.5, 88.2, 87.6, 87.0, 49.9, 35.3, 35.2, 35.2, 32.7, 32.6, 32.4, 22.3; MALDI-TOF *m/z* calcd for $C_{165}H_{142}N_{13}O_2$ $[M+H]^+$ 2338, found 2338; ESI-HRMS *m/z* calcd for $C_{164}H_{143}N_{13}O_2$ $[M+H]^+$ 2338.1443, found 2338.1428; IR (thin film) υ 3443 (NH), 2206 (C≡C), 1656 (C=O) cm^{-1}.

Foldamer **2**(*R*) was prepared by the same procedures described for the preparation of **2**(*S*) using (*R*)-1-phenylethanamine instead of (*S*)-1-phenylethanamine. The physical and spectroscopic properties of **2**(*R*) are identical to those of **2**(*S*) except the CD as described in Text and shown later in the ESI, section 3.

1.3 Synthesis of compound **3**



S5 **S2** **S6**

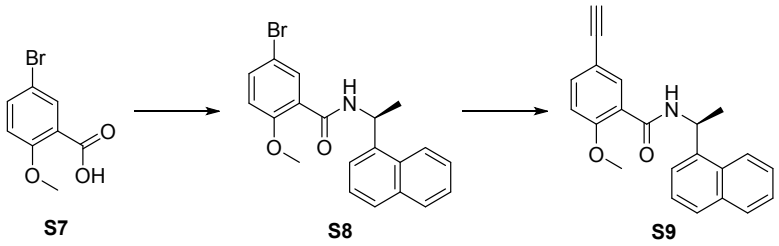


S6: The synthesis of **S5** was described previously.[S1] A Schlenk flask containing **S5** (0.26 g, 0.38 mmol), **S2** (0.37 g, 1.14 mmol), CuI (1.4 mg, 0.008 mmol) and $Pd(PPh_3)_2Cl_2$ (5.3 mg, 0.008 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (4 mL) and Et_3N (4 mL) were added in order under nitrogen. The solution was stirred at 55 °C for 2 h and cooled to room temperature. The mixture was filtered through Celite and concentrated. The residue was dissolved in CH_2Cl_2, washed with $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 1:3 (v/v)) to give **S6** as an yellow solid (0.21 mg, 62%); mp > 219 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 10.52 (s, 1H), 10.50 (s, 1H), 8.38 (d, J = 1.4 Hz, 1H), 8.34–8.33 (m, *2*H), 8.27 (d, J = 8.6 Hz, 1H), 8.25 (s, 1H), 8.05 (s, 2H), 8.00 (d, J = 7.9 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.81–7.70 (m, 6H), 7.67 (d, J = 7.8 Hz, 1H), 7.55–7.45 (m, 5H), 6.19 (quint, J = 7.2 Hz, 1H), 1.76 (d, J = 6.9 Hz, 3H), 1.50 (s, 18H); ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ 166.0, 145.1, 143.7, 143.6, 140.8, 139.5, 139.4, 139.3, 136.4, 135.3, 135.0, 132.1, 131.5, 129.8, 128.6, 128.4, 128.0, 127.4, 127.2, 127.2, 126.7, 126.6, 126.4, 125.6, 125.4, 124.5, 124.3, 123.6, 122.8, 122.5, 119.5, 118.7, 118.3, 113.5, 113.4, 105.9, 104.6, 93.3, 92.4, 88.5, 87.9, 46.4, 35.5, 35.5, 32.4, 32.4, 21.9; MALDI-TOF *m/z* calcd for $C_{54}H_{45}IN_4O$ $[M]^+$ 892, found 892; IR (thin film) υ 3347 (NH), 2204 (C≡C), 1639 (C=O).

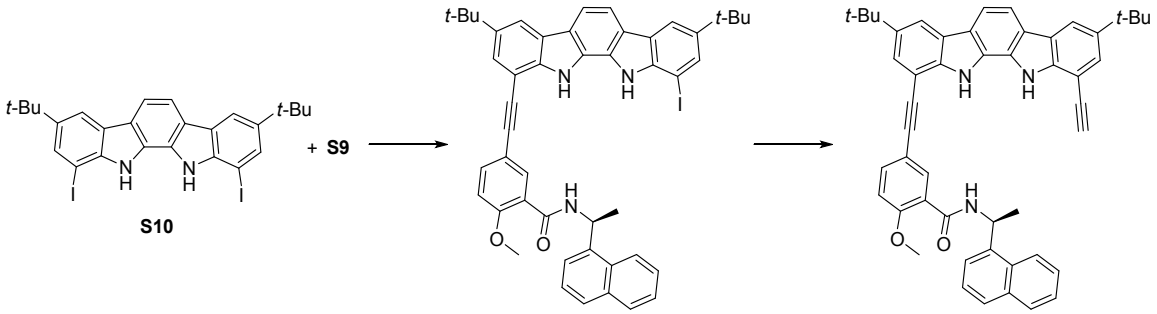
3: A Schlenk flask containing **S6** (157 mg, 0.176 mmol), **S2** (80 mg, 0.088 mmol), CuI (1.3 mg, 0.007 mmol) and $Pd(PPh_3)_2Cl_2$ (4.9 mg, 0.007 mmol) was evacuated under vacuum

and back-filled with nitrogen. Anhydrous, degassed THF (2 mL) and Et_3N (2 mL) were added in order under nitrogen. The solution was stirred at 55 °C for 2.5 h and cooled to room temperature. The mixture was filtered through Celite with CH_2Cl_2 and concentrated. The residue was diluted in CH_2Cl_2, washed with brine and $NaHCO_3$, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, hexane/diethyl ether = 2:1) to give **3** as a yellow solid (133 mg, 62%); mp > 232 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, ppm) δ 10.68 (s, 2H), 10.63 (s, 2H), 10.44 (s, 2H), 10.20 (s, 2H), 8.25 (d, J = 1.6 Hz, 2H), 8.23 (d, J = 1.6 Hz, 2H), 8.16–8.14 (m, 2H), 8.11 (d, J = 1.3 Hz, 2H), 8.05 (d, J = 1.5 Hz, 2H), 8.01 (d, J = 8.1 Hz, 2H), 7.98 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.3 Hz, 2H), 7.84–7.77 (m, 8H), 7.73 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 7.1 Hz, 2H), 7.52 (d, J = 1.7 Hz, 2H), 7.47 (d, J = 1.7 Hz, 2H), 7.45–7.36 (m, 8H), 7.21 (d, J = 1.3 Hz, 2H), 7.17 (t, J = 7.7 Hz, 2H), 7.17 (s, 2H), 7.04 (d, J = 7.4 Hz, 2H), 6.95 (d, J = 7.7 Hz, 1H), 6.73 (t, J = 7.4 Hz, 1H), 6.68–6.63 (m, 4H), 6.33 (d, J = 7.5 Hz, 2H), 6.01 (quint, J = 7.4 Hz, 2H), 1.59 (d, J = 6.9 Hz, 6H), 1.49 (s, 18H), 1.48 (s, 18H), 1.47 (s, 18H), 1.45 (s, 18H); ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ 165.6, 143.0, 142.8, 142.6, 142.5, 142.1, 142.1, 142.0, 141.0, 140.4, 140.3, 139.0, 139.0, 136.8, 135.4, 134.8, 134.6, 133.9, 131.9, 130.6, 129.5, 128.3, 128.3, 127.3, 127.3, 127.2, 127.1, 127.1, 126.9, 126.3, 126.1, 126.0, 125.3, 125.1, 124.9, 124.9, 124.6, 124.1, 123.5, 123.4, 122.4, 122.3, 122.2, 122.1, 118.7, 117.8, 112.9, 112.9, 112.8, 112.6, 105.9, 104.9, 104.8, 104.2, 93.2, 92.9, 92.8, 88.6, 88.2, 87.6, 87.1, 45.9, 35.3, 35.3, 35.2, 32.7, 32.6, 32.5, 21.6; MALDI-TOF *m/z* calcd for $C_{173}H_{145}N_{13}O_2$ $[M]^+$ 2437, found 2437; ESI-HRMS *m/z* calcd for $C_{173}H_{145}N_{13}NaO_2$ $[M+Na]^+$ 2460.1575, found 2460.1575; IR (thin film) υ 3449 (NH), 2206 (C≡C), 1655 (C=O).

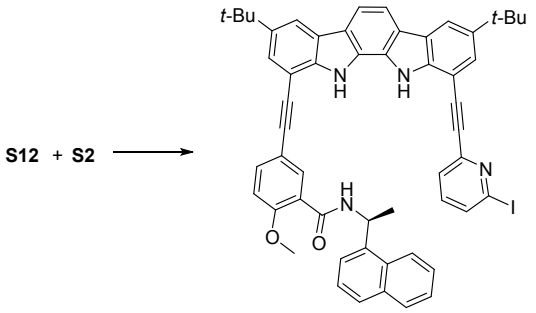
1.4 Synthesis of compound **4**(*S*)



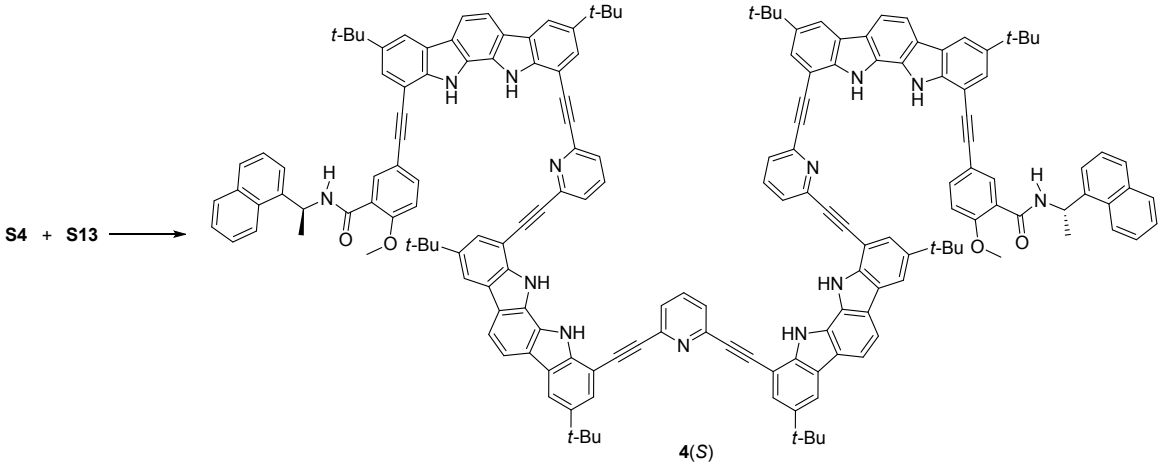
S7 **S8** **S9**



S10 **S11** **S12**



S13



4(*S*)

S8: To a solution of **S7** [S4] (1.00 g, 4.33 mmol) in CH_2Cl_2 (22 mL), was carefully added oxalyl chloride (0.74 mL, 8.7 mmol) and a catalytic amount of DMF at 0 °C under Ar. The solution was stirred at room temperature for 2.5 h, and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (22 mL) and placed at 0 °C. Diisopropylethylamine (1.13 mL) and (*S*)-1-(naphthalen-1-yl)ethanamine (0.74 g, 4.33 mmol) were slowly added, and the resulting solution was stirred for 0.5 h at room temperature. After concentration, the residue was taken up in CH_2Cl_2, washed with water and concentrated. The residue was purified by flash column chromatography (CH_2Cl_2) to give **S8** as a white solid (1.64 g, 99%); mp = 148 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm) 8.35 (d, *J* = 2.6 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 8.20 (d, *J* = 4.7 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.59–7.45 (m, 4H), 7.42 (dd, *J* = 8.8 Hz and 2.6 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 1H), 6.12 (quint, *J* = 7.1 Hz, 1H), 3.71 (s, 3H), 1.77 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, ppm) δ 162.8, 156.4, 138.8, 135.1, 134.7, 133.9, 130.9, 128.8, 128.1, 126.3, 125.7, 125.3, 123.4, 123.2, 122.5, 113.7, 113.3, 56.2, 45.6, 21.4; MALDI-TOF *m/z* calcd for $C_{20}H_{18}BrNO_2$ $[M]^+$ 383, found 383; IR (thin film) υ 3396 (NH), 1650 (C=O), 1242 (C-O) cm^{-1}.

S9: A Schlenk flask containing **S8** (1.00 g, 2.60 mmol), CuI (5.0 mg, 0.026 mmol) and $Pd(PPh_3)_2Cl_2$ (18.3 mg, 0.026 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (6.0 mL), Et_3N (7.0 mL) and trimethylsilyl acetylene (1.11 mL, 7.81 mmol) were added in order and the solution was stirred at 80 °C for 21 h. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The solution was washed with $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was dissolved in dissolved in THF (6 mL) and tetrabutylammonium fluoride (TBAF) (7.81 mL, 1.0 M solution in THF) was added into the solution. The solution was stirred for 10 min at room temperature and concentrated. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 2:1 (v/v)) to give **S9** as an ivory solid (0.43 mg, 50%); mp >148 °C (dec); ^{1}H NMR (400 MHz,

[S4] A. S. Hussey and I. J. Wilk, *J. Am. Chem. Soc.*, 1950, **72**, 830–832.

acetone-d_6, 298 K, ppm) 8.35 (d, J = 6.4 Hz, 1H), 8.28 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 2.3 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 7.1 Hz, 1H), 7.61–7.48 (m, 4H), 7.16 (d, J = 8.6 Hz, 1H), 6.10 (quint, J = 7.2 Hz, 1H), 3.97 (s, 3H), 3.57 (s, 1H), 1.71 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6, 298 K, ppm) δ 163.8, 158.7, 140.9, 136.7, 135.9, 135.0, 131.8, 129.7, 128.5, 127.0, 126.5, 126.4, 124.3, 123.8, 123.5, 115.7, 113.2, 83.4, 78.4, 56.8, 46.2, 22.1; MALDI-TOF *m/z* calcd for $C_{22}H_{19}NNaO_2$ $[M+Na]^+$ 352, found 352; IR (thin film) υ 3397 (NH), 3290 (C(sp^3)-H), 2105 (C≡C), 1650 (C=O), 1252 (C-O) cm^{-1}.

S11: A Schlenk flask containing **S10** (0.60 g, 0.97 mmol), **S9** (0.32 g, 0.97 mmol), CuI (2.0 mg, 0.0097 mmol) and $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.0097 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (5.0 mL) and Et_3N (5.0 mL) were added in order and the solution was stirred at 55 °C for 2 h. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The solution was washed with $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1:1 (v/v)) to give **S11** as a white solid (0.33 mg, 42%); mp >230 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, 298 K, ppm) 10.75 (s, 1H), 9.89 (s, 1H), 8.49 (d, J = 7.7 Hz, 1H), 8.30 (d, J = 1.8 Hz, 1H), 8.29 (d, J = 2.3 Hz, 1H), 8.27–8.24 (m, 2H), 8.03 (d, J = 8.3 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.89 (dd, J = 7.5 Hz and 1.9, 1H), 7.85 (d, J = 1.6 Hz, 1H), 7.80–7.76 (m, 2H), 7.71 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 1.8 Hz, 1H), 7.54–7.46 (m, 3H), 7.27 (d, J = 8.6 Hz, 1H), 6.17 (quint, J = 7.2 Hz, 1H), 4.04 (s, 3H), 1.74 (d, J = 6.9 Hz, 3H), 1.49 (s, 9H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, acetone-d_6, 298 K, ppm) δ 164.3, 158.5, 145.3, 143.3, 140.6, 140.3, 139.2, 136.4, 135.6, 134.8, 132.0, 131.6, 129.5, 128.4, 126.9, 126.8, 126.6, 126.3, 126.3, 126.2, 125.4, 125.0, 124.0, 123.6, 123.4, 122.8, 122.4, 118.0, 117.2, 116.7, 113.4, 113.3, 113.2, 106.1, 93.0, 86.4, 76.3, 56.8, 46.4, 35.3, 35.2, 32.2, 32.2, 22.2; MALDI-TOF *m/z* calcd for $C_{48}H_{45}IN_3O_2$ $[M+H]^+$ 822, found 822; IR (thin film) υ 3386 (NH), 2207 (C≡C), 1639 (C=O), 1251 (C-O) cm^{-1}.

S12: A Schlenk flask containing **S11** (0.29 g, 0.35 mmol), CuI (1.3 mg, 0.007 mmol) and $Pd(PPh_3)_2Cl_2$ (5.0 mg, 0.007 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (3.0 mL), Et_3N (4.0 mL) and trimethylsilyl acetylene (0.15 mL, 1.1 mmol) were added in order and the solution was stirred at 55 °C for 2.5 h. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The solution was washed with $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was dissolved in dissolved in THF (6 mL) and TBAF (1.0 mL, 1.0 M solution in THF) was added into the solution. The solution was stirred for 10 min at room temperature and concentrated. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 2:1 (v/v)) to give **S12** as an yellow solid (0.18 mg, 71%); mp >185 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, 298 K, ppm) 10.70 (s, 1H), 10.25 (s, 1H), 8.47 (d, J = 7.7 Hz, 1H), 8.32–8.27 (m, 4H), 8.02 (s, 2H), 7.92 (dd, J = 8.6 Hz and 1.4 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.76 (dd, J = 8.6 Hz and 2.3 Hz, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 1.8 Hz, 1H), 7.63 (d, J = 1.8 Hz, 1H), 7.58–7.48 (m, 3H), 7.25 (d, J = 8.6 Hz, 1H), 6.17 (quint, J = 7.1 Hz, 1H), 4.02 (s, 3H), 4.00 (s, 1H), 1.75 (d, J = 6.9 Hz, 3H), 1.49 (s, 9H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, acetone-d_6, 298 K, ppm) δ 164.2, 158.7, 143.5, 143.4, 140.9, 139.7, 139.3, 136.5, 135.6, 135.1, 131.9, 129.8, 128.7, 127.1, 127.1, 127.1, 126.7, 126.6, 126.5, 125.3, 125.3, 124.3, 123.9, 123.6, 122.6, 122.5, 118.5, 118.2, 116.9, 113.5, 113.3, 113.2, 106.3, 105.2, 93.1, 86.6, 83.2, 83.2, 81.7, 57.0, 46.4, 35.4, 35.4, 32.4, 32.4, 22.3; MALDI-TOF *m/z* calcd for $C_{50}H_{45}N_3O_2$ $[M]^+$ 719, found 719; IR (thin film) υ 3386 (NH), 3301 (C(sp^3)-H), 2205 (C≡C), 1639 (C=O), 1259 (C-O) cm^{-1}.

S13: A Schlenk flask containing **S12** (0.136 g, 0.189 mmol), **S2** (0.188 g, 0.189 mmol), CuI (3.6 mg, 0.019 mmol) and $Pd(PPh_3)_2Cl_2$ (13.3 mg, 0.019 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (1.8 mL) and Et_3N (2.0 mL) were added in order and the solution was stirred at 55 °C for 2 h. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The solution was washed with $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel,

EtOAc/hexane = 2:1 (v/v)) to give **S13** as a white solid (0.117 mg, 67%); mp >220 °C (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K, ppm) 10.74 (s, 1H), 10.56 (s, 1H), 8.47 (d, *J* = 2.1 Hz, 1H), 8.36 (d, *J* = 6.9 Hz, 1H), 8.20 (d, *J* = 1.5 Hz, 1H), 8.15 (d, *J* = 1.6 Hz, 1H), 7.89 (s, 2H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.62–7.59 (m, 2H), 7.53 (dd, *J* = 8.6 Hz and 2.0 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 7.0 Hz, 1H), 7.33–7.23 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.7 Hz, 1H), 6.77 (d, *J* = 8.6 Hz, 1H), 5.89 (quint, *J* = 6.8 Hz, 1H), 3.87 (s, 3H), 1.56 (d, *J* = 6.8 Hz, 3H), 1.50 (s, 9H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K, ppm) *δ* 164.9, 157.5, 144.4, 142.6, 139.3, 139.1, 138.8, 137.4, 136.3, 136.2, 133.9, 133.7, 130.4, 128.5, 127.9, 126.6, 126.5, 126.5, 126.0, 126.0, 125.8, 125.6, 125.5, 124.6, 124.3, 122.4, 122.0, 121.6, 121.4, 121.2, 118.7, 117.5, 117.5, 117.2, 112.2, 112.2, 111.6, 105.3, 103.7, 91.7, 91.5, 89.1, 86.4, 56.7, 47.2, 35.1, 35.0, 32.2, 32.2, 22.5; MALDI-TOF *m/z* calcd for $C_{55}H_{48}N_4O_2$ $[M+H]^+$ 923, found 923; IR (thin film) υ 3386 (NH), 2205 (C≡C), 1638 (C=O), 1253 (C-O) cm^{-1}.

4(*S*)**:** A Schlenk flask containing **S4** (0.045 g, 0.050 mmol), **S13** (0.092 g, 0.100 mmol), CuI (1.0 mg, 0.005 mmol) and $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (1.0 mL) and Et_3N (1.0 mL) were added in order and the solution was stirred at 55 °C for 2 h. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The solution was washed with $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, EtOAc/hexane = 1:3 (v/v)) to give **4**(*S*) as a yellow solid (0.083 mg, 67%); mp >240 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, 298 K, ppm) 10.76 (s, 2H), 10.62 (s, 2H), 10.51 (s, 2H), 9.94 (s, 2H), 8.10 (d, *J* = 1.3 Hz, 2H), 8.05 (s, 4H), 7.99 (d, *J* = 1.4 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.80–7.67 (m, 12H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 1.7 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.39–7.19 (m, 12H), 7.03 (d, *J* = 1.4 Hz, 2H), 6.93 (d, *J* = 1.5 Hz, 2H), 6.57 (d, *J* = 7.6 Hz, 2H), 6.47 (d, *J* = 7.6 Hz, 2H), 6.39 (dd, *J* = 8.4 Hz and 2.0 Hz, 2H), 5.67 (d, *J* = 8.4 Hz, 2H), 5.64 (s, 2H), 5.48 (t, *J* = 7.6 Hz, 4H), 4.62 (d, *J* = 7.6 Hz, 2H), 3.24 (s, 6H), 1.68 (s, 18H), 1.51 (s, 18H), 1.51 (s, 18H), 1.38 (s, 18H), 1.28 (d, *J* = 6.1 Hz,

6H); ^{13}C NMR (100 MHz, acetone-d_6, 298 K, ppm) δ 163.8, 156.8, 142.5, 142.4, 142.3, 142.1, 141.9, 141.8, 141.5, 140.9, 140.5, 140.3, 139.4, 138.7, 136.7, 135.2, 134.8, 134.2, 133.4, 131.5, 129.5, 128.1, 127.6, 127.4, 127.0, 126.9, 126.8, 126.7, 126.4, 126.2, 126.2, 125.5, 125.4, 125.1, 125.1, 124.9, 124.9, 124.5, 124.4, 123.9, 122.8, 122.7, 122.4, 122.3, 121.7, 121.7, 120.8, 118.5, 118.4, 118.4, 116.8, 115.6, 112.9, 112.4, 112.2, 111.9, 110.9, 107.2, 106.1, 105.3, 104.0, 93.3, 92.7, 92.5, 92.2, 89.2, 88.3, 87.6, 85.5, 55.9, 46.1, 35.5, 35.3, 35.3, 35.1, 33.0, 32.6, 32.5, 32.5, 22.3; MALDI-TOF *m/z* calcd for $C_{175}H_{150}N_{13}O_4$ $[M+H]^+$ 2498, found 2498; ESI-HRMS *m/z* calcd for $C_{175}H_{150}N_{13}O_4$ $[M+H]^+$ 2498.1967, found 2498.1966; IR (thin film) υ 3394 (NH), 2205 (C≡C), 1648 (C=O), 1252 (C-O) cm^{-1}.

Foldamer **4**(*R*) was prepared by the same procedures described for the preparation of **4**(*S*) using (*R*)-1-phenylethanamine instead of (*S*)-1-phenylethanamine. The physical and spectroscopic properties of **4**(*R*) are identical to those of **4**(*S*) except the CD as described in Text and shown later in the ESI, section 3.

2. ^{1}H NMR studies

2.1 Partial ^{1}H NMR spectra of **2–4**

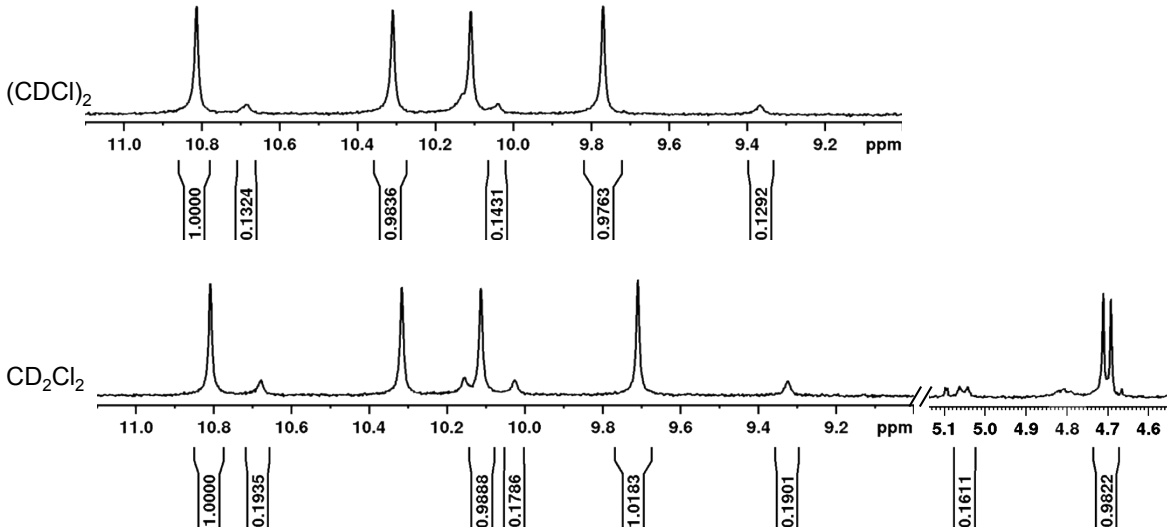


Fig. S1 Partial ^{1}H NMR spectra of **2**(*S*) (2.0 mM, 298 K) with the integration values in water-saturated $(CD_2Cl)_2$ and CD_2Cl_2.

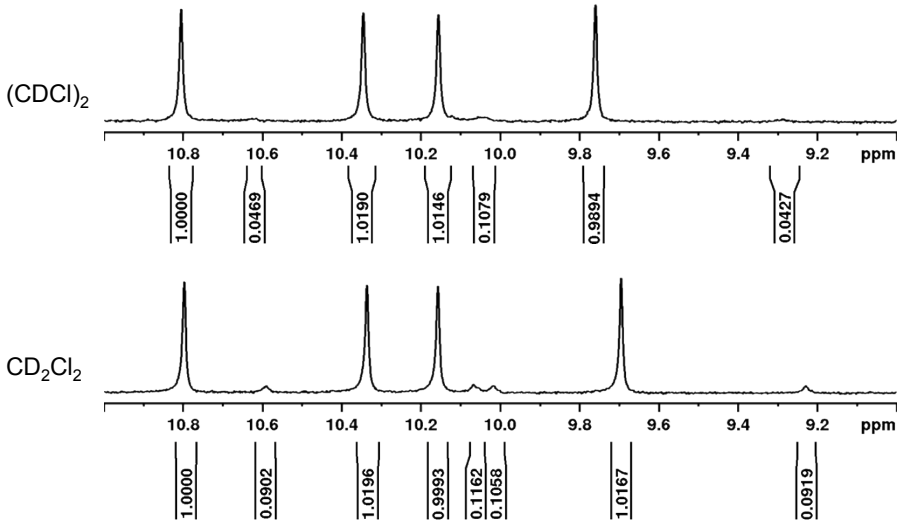


Fig. S2 Partial ^{1}H NMR spectra of **3** (2.0 mM, 298 K) with the integration values in water-saturated $(CD_2Cl)_2$ and CD_2Cl_2.

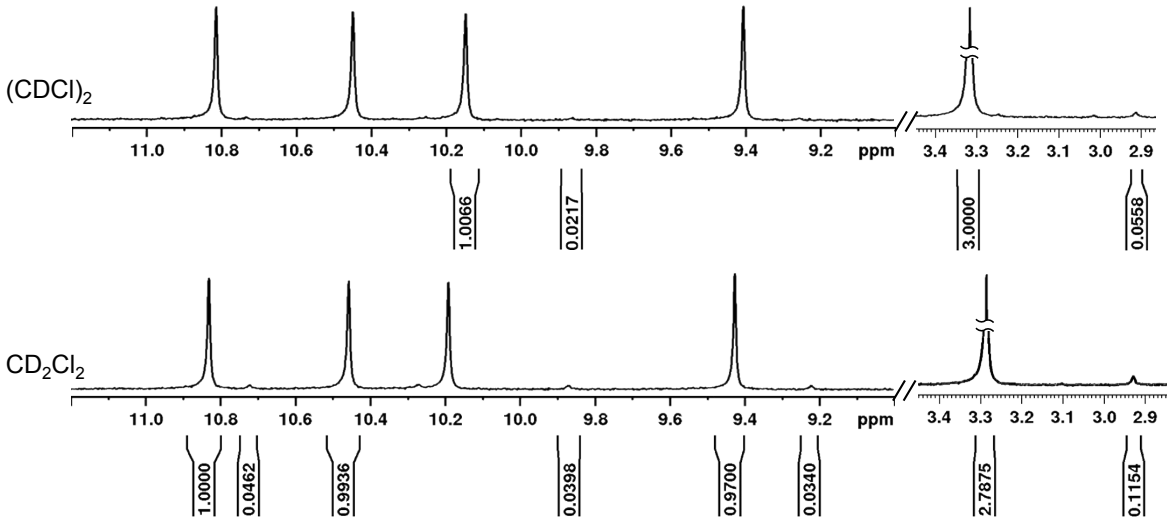


Fig. S3 Partial ^{1}H NMR spectra of **4**(*S*) (2.0 mM, 298 K) with the integration values in water-saturated $(CD_2Cl)_2$ and CD_2Cl_2.

2.2 ^{1}H NMR signals of the terminal amide NH of **2**–**4**

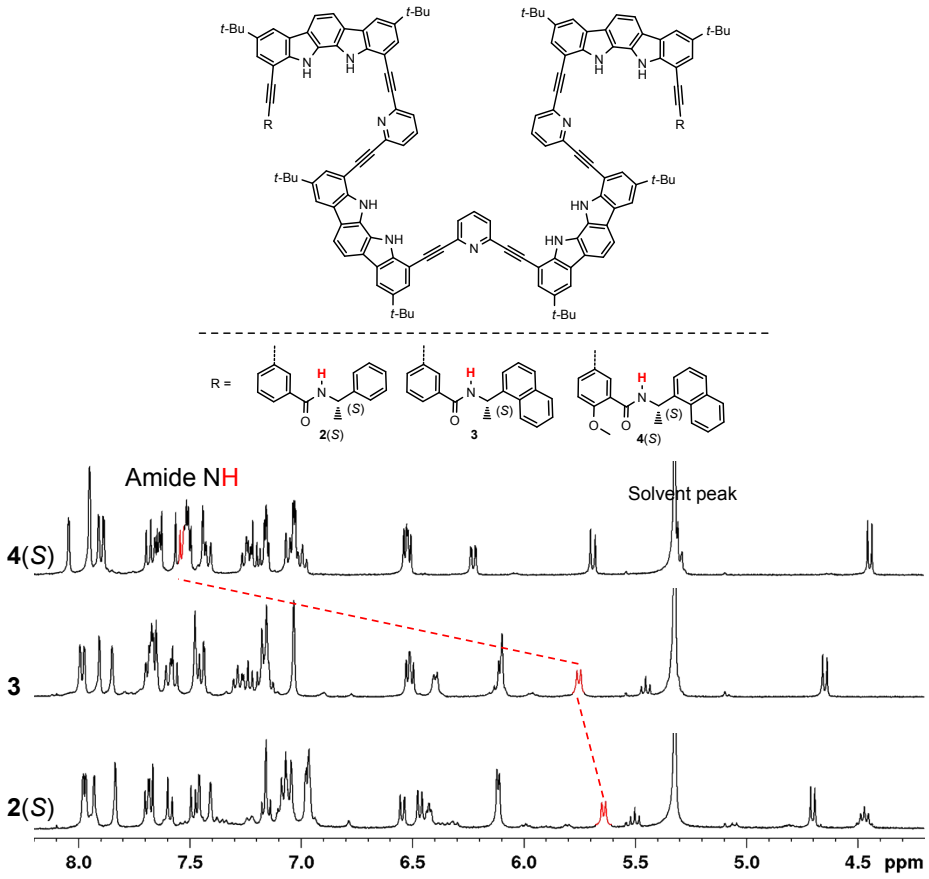


Fig. S4 Partial ^{1}H NMR spectra of **2**–**4** (1.0 mM, 298 K) in water-saturated CD_2Cl_2. The chemical shifts for the terminal amide NH's of **2**–**4** are 5.64, 5.75 and 7.54 ppm, respectively.

3. Circular dichroism (CD) studies

The CD spectra were taken under the following conditions (scanning rate: 500 nm min^{-1}, band width: 1.0 nm, response time: 1.0 sec, accumulations: 2 scan).

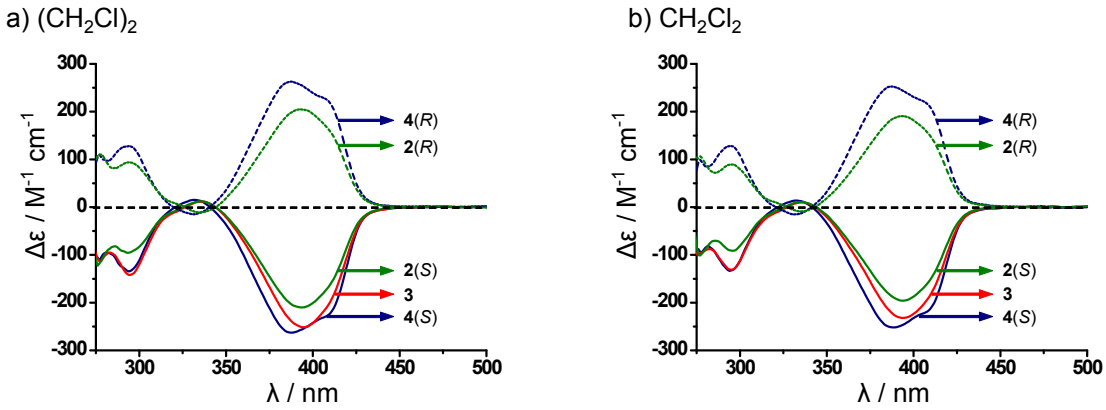


Fig. S5 CD spectra of **2**(*S*), **2**(*R*), **3**, **4**(*S*) and **4**(*R*) (1.0×10^{-5} M, 25 °C) in a) $(CH_2Cl)_2$, b) CH_2Cl_2.

4. Modeling studies[S5]

An energy-minimized structure of **2**(*S*) was obtained through Monte Carlo conformational search using MacroModel 9.1 program with MMFFs force field in gas phase. Two amide oxygen at both ends form hydrogen bond with internal water molecules symmetrically.

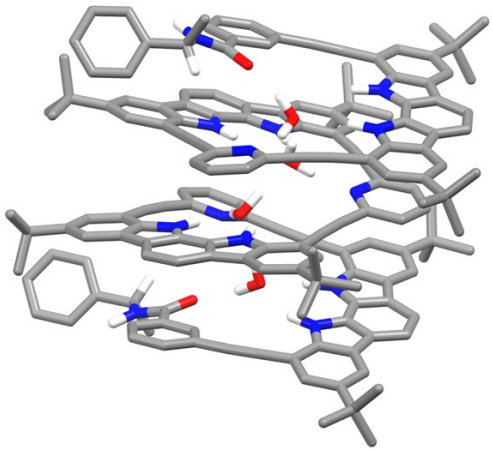


Fig. S6 An energy-minimized and symmetrical helix of **2**(*S*).

[S5] (*a*) F. Mohamadi, N. G. J. Richards, W. C. Guida, R. Liskamp, M. Lipton, C. Caufield, G. Chang, T. Hendrickson and W. C. Still, *J. Comp. Chem.*, 1990, **11**, 440; (*b*) G. A. Kaminski, R. A. Friesner, J. Tirado-Rives and W. J. Jorgensen, *J. Phys. Chem. B*, 2001, *105*, 6474; (*c*) *MacroModel, version 9.1*, Schrödinger, LLC, New York, NY, 2005.

On the basis of the crystal structure of **2**(*S*), an energy-minimized *M*-helix was obtained through additional minimization process using MacroModel 9.1 program with MMFFs force field in $CHCl_3$. The corresponding putative *P*-helix was obtained by inverting the helical orientation and maintaining the carbonyl oxygen to hydrogen bond with a water molecule. In the energy-minimized structure of the *P*-helix, hydrogen atom at the chiral center is directed towards the helix plane, but the phenyl group aligns with an adjacent indolocarbazole plane. The calculated energy difference between the *M*- and *P*-helix was found to be 25.5kJ/mol.

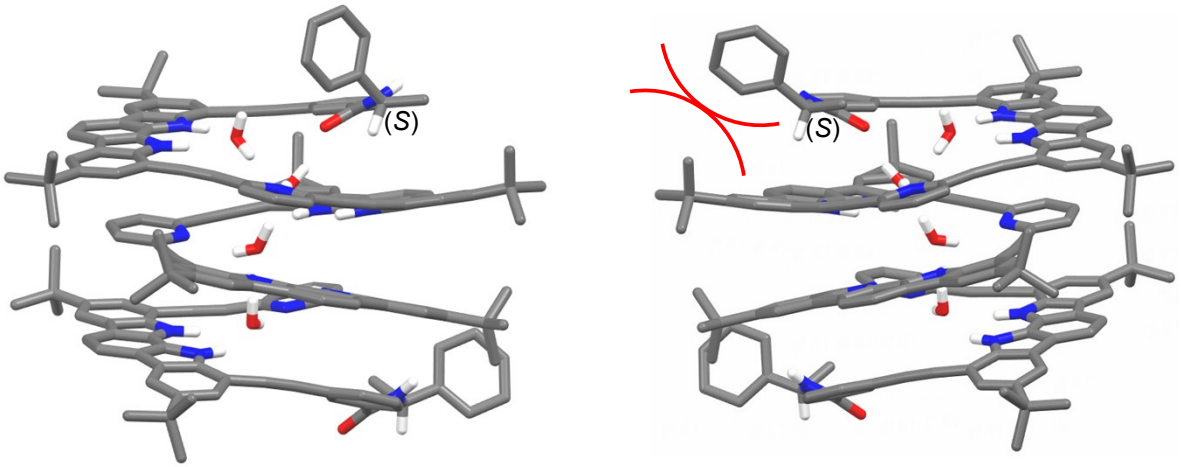


Fig. S7 Energy-minimized structures of *M*- (left) and *P*-helices (right) of **2**(*S*).

5. X-ray crystallographic analyses

5.1 Crystal growing

Foldamers **2**(*S*) and **2**(*R*): A racemic mixture of **2**(*S*) and **2**(*R*) was dissolved in toluene, hexane and a few drops of CH_2Cl_2. Hexane was slowly vapor-diffused to the solution for few days at room temperature to yield single crystals suitable for X-ray diffraction.

Foldamers **4**(*S*) and **4**(*R*): A racemic mixture of **4**(*S*) and **4**(*R*) was dissolved in $(CH_2Cl)_2$, hexane and a few drops of CH_2Cl_2. Hexane was slowly vapor-diffused to the solution for few days at room temperature to yield single crystals suitable for X-ray diffraction.

5.2 Data collection

The diffraction data from a yellow crystals of **2**(*S*) and **2**(*R*) (0.17 × 0.121 × 0.086 mm^3) mounted on a MiTeGen MicroMount© were collected at 100 K on a ADSC Quantum 210 CCD diffractometer with synchrotron radiation (0.63000 Å) at Supramolecular Crystallography 2D, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The ADSC Q210 ADX program[S6] was used for data collection (detector distance is 63 mm, omega scan; $\Delta\omega = 1^{\circ}$, exposure time is 3 sec/frame for each crystal and HKL3000sm (Ver. 703r)[S7] was used for cell refinement, reduction and absorption correction. The crystal structures were solved by the direct method with SHELX-XT (Ver. 2014/5)[S8] and refined by full-matrix least-squares calculations with the SHELX-XL (Ver. 2016/4)[S9] program package.

The diffraction data from a yellow crystals of **4**(*S*) and **4**(*R*) (0.34 × 0.19 × 0.12 mm^3) mounted on a MiTeGen MicroMount© were collected at 100 K on a Bruker D8 Venture

[S6] A. J. Arvai and C. Nielsen, *ADSC Quantum-210 ADX Program, Area Detector System Corporation*, Poway, CA, USA, 1983.
[S7] Z. Otwinowski and W. Minor, *Methods in Enzymology*, ed. C. W. Carter Jr. and R. M. Sweet, Academic Press, New York, 1997, Vol. 276, part A, pp. 307–326.
[S8] G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3–8.
[S9] G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3–8.

diffractometer with MoK_α (λ = 0.71073 Å) radiation. The initial cell constants were obtained from two series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program.[S10] The final cell constants were calculated from a set of 15996 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.81 Å. A total of 272525 data were harvested by collecting 6 sets of frames with 0.5º scans in ω and φ with an exposure time 20 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.

5.3 Structure solution and refinement

2⊃$4H_2O$: The systematic absences in the diffraction data were uniquely consistent for the monoclinic space group $P2_1/n$ that yielded chemically reasonable and computationally stable results of refinement [S9,11].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Terminal phenyl group bonded to the chiral center observed as disordered and modeled two different orientations using RIGU, SADI, ISOR and FLAT restraints.

[S10] Bruker-AXS. (2007-2013) APEX2 (Ver. 2013.2-0), SADABS (2012-1), and SAINT+ (Ver. 8.30C) Software Reference Manuals. Bruker-AXS, Madison, Wisconsin, USA.

[S11] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339–341.

The final least-squares refinement of 3443 parameters against 103706 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0809 and 0.2637, respectively. The final difference Fourier map was featureless.

4⊃$4H_2O$: The systematic absences in the diffraction data were uniquely consistent for the space group P-1 that yielded chemically reasonable and computationally stable results of refinement.

The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The final least-squares refinement of 1805 parameters against 33145 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0618 and 0.1867, respectively. The final difference Fourier map was featureless.

5.4 Summary

2⊃$4H_2O$: Crystal Data for $C_{165}H_{149}N_{13}O_6$ (M =2409.96 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 25.792(5) Å, b = 30.143(6) Å, c = 39.026(8) Å, β = 96.73(3)°, V = 30132(11) $Å^3$, Z = 8, T = 100 K, μ(synchrotron) = 0.051 mm^{-1}, *Dcalc* = 1.062 g/cm^3, 201941 reflections measured (2.878° ≤ 2Θ ≤ 56°), 103706 u nique (R_{int} = 0.0794, R_{sigma} = 0.1309) which were used in all calculations. The final R_1 was 0.0809 (I > 2σ(I)) and wR_2 was 0.2637 (all data).

Table S1. Crystal data and structure refinement for **2**(*S*) and **2**(*R*).

Identification code	racemic_heptamer
Empirical formula	$C_{165}H_{149}N_{13}O_6$

Formula weight	2409.96
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	25.792(5)
b/Å	30.143(6)
c/Å	39.026(8)
α/°	90
β/°	96.73(3)
γ/°	90
Volume/Å^3	30132(11)
Z	8
ρ_{calc}g/cm^3	1.062
μ/mm^{-1}	0.051
F(000)	10224.0
Crystal size/mm^3	0.17 × 0.121 × 0.086
Radiation	synchrotron (λ = 0.630)
2Θ range for data collection/°	2.878 to 56
Index ranges	$-38 \leq h \leq 38$, $-44 \leq k \leq 44$, $-58 \leq l \leq 58$
Reflections collected	201941
Independent reflections	103706 [R_{int} = 0.0794, R_{sigma} = 0.1309]
Data/restraints/parameters	103706/166/3443
Goodness-of-fit on F^2	0.915
Final R indexes [I>=2σ (I)]	R_1 = 0.0809, wR_2 = 0.2175
Final R indexes [all data]	R_1 = 0.1836, wR_2 = 0.2637
Largest diff. peak/hole / e Å-3	0.79/-0.44

Table S2. Hydrogen-bonding distances (Å) in the crystal structure of **2**(*S*)⊃4H_2O

Donor···Acceptor	Distance
N(187)···O(365)	3.278
N(190)···O(365)	2.921
O(365)···N(266)	2.908
O(365)···O(366)	2.810
N(207)···O(366)	3.318
N(210)···O(366)	2.996
O(366)···N(272)	2.773
O(366)···O(367)	2.697
O(367)···N(278)	2.775
O(367)···O(323)	2.624
N(230)···O(367)	3.027
O(368)···O(367)	2.925
N(247)···O(368)	2.817
N(250)···O(368)	2.974

Table S3. Hydrogen-bonding distances (Å) in the crystal structure of **2**(*R*)⊃4H_2O

Donor···Acceptor	Distance
N(3)···O(181)	3.058
N(6)···O(181)	2.958
O(181)···N(82)	2.957
O(181)···O(182)	2.928
N(26)···O(182)	3.093
O(182)···N(88)	2.873
O(182)···O(183)	2.797
N(46)···O(183)	3.010
O(183)···N(94)	2.796

O(183)···O(139)	2.635
O(184)···O(183)	2.947
N(63)···O(184)	2.831
N(66)···O(184)	2.979

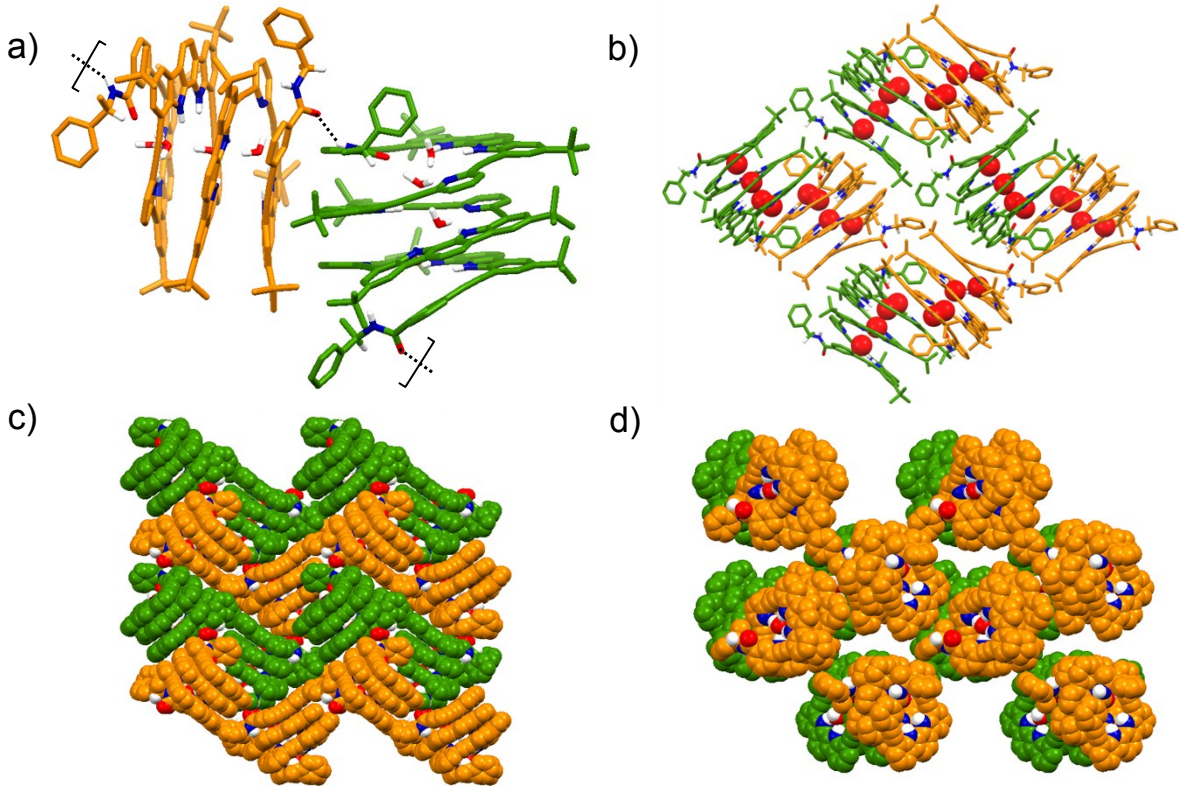


Fig. S8 a) The asymmetric unit of the crystal structures of **2**(*S*)⊃4H_2O and **2**(*R*)⊃4H_2O. Intermolecular hydrogen bonding networks between two opposite helices are shown. b) capped stick representation of **2**(*S*)⊃4H_2O and **2**(*R*)⊃4H_2O. Space-filling representations of **2**(*S*)⊃4H_2O and **2**(*R*)⊃4H_2O; c) top and d) side views. Helices are shown in green (*P*-helix) and orange (*M*-helix). CH hydrogens except one in the chiral center are all omitted in a), b), c) and d) and *t*-butyl groups are omitted in c) and d) for clarity.

4⊃$4H_2O$: Crystal Data for $C_{175}H_{157}N_{13}O_8$ (M =2570.13 g/mol): triclinic, space group P-1 (no. 2), a = 18.4463(12) Å, b = 18.6186(12) Å, c = 27.4771(17) Å, α = 76.253(3)°, β = 73.468(3)°, γ = 68.847(3)°, V = 8340.5(9) Å^3, Z = 2, T = 100 K, μ(MoKα) = 0.063 mm^{-1}, *Dcalc* = 1.023 g/cm^3, 272525 reflections measured (4.128° ≤ 2Θ ≤ 52.392°), 33145 unique (R_{int} = 0.0885, R_{sigma} = 0.0483) which were used in all calculations. The final R_1 was 0.0618 (I > 2σ(I)) and wR_2 was 0.1867 (all data).

Table S4. Crystal data and structure refinement for **4**(*S*) and **4**(*R*).

Identification code	methoxy_naphthyl_heptamer
Empirical formula	$C_{175}H_{157}N_{13}O_8$
Formula weight	2570.13
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	18.4463(12)
b/Å	18.6186(12)
c/Å	27.4771(17)
α/°	76.253(3)
β/°	73.468(3)
γ/°	68.847(3)
Volume/Å^3	8340.5(9)
Z	2
ρcalcg/cm^3	1.023
μ/mm^{-1}	0.063
F(000)	2724.0
Crystal size/mm^3	0.34 × 0.19 × 0.12
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	4.128 to 52.392
Index ranges	$-22 \leq h \leq 22$, $-23 \leq k \leq 23$, $-33 \leq l \leq 34$
Reflections collected	272525
Independent reflections	33145 [Rint = 0.0885, Rsigma = 0.0483]
Data/restraints/parameters	33145/0/1805
Goodness-of-fit on F2	1.199
Final R indexes [I>=2σ (I)]	R1 = 0.0618, wR2 = 0.1711
Final R indexes [all data]	R1 = 0.0949, wR2 = 0.1867

Table S5. Hydrogen-bonding distances (Å) in the crystal structure of **4**(*S*)⊃4H_2O

Donor···Acceptor	Distance
N(125)···O(119)	2.698
O(193)···O(124)	2.739
N(6)···O(193)	3.016
N(82)···O(193)	2.879
O(194)···O(193)	2.729
N(26)···O(194)	2.899
O(194)···N(88)	2.807
O(195)···O(194)	2.805
O(195)···N(94)	2.890
N(43)···O(195)	3.164
N(46)···O(195)	2.895
O(196)···O(195)	2.846
O(196)···O(147)	2.743
N(63)···O(196)	2.759
N(66)···O(196)	3.133
N(148)···O(142)	2.676

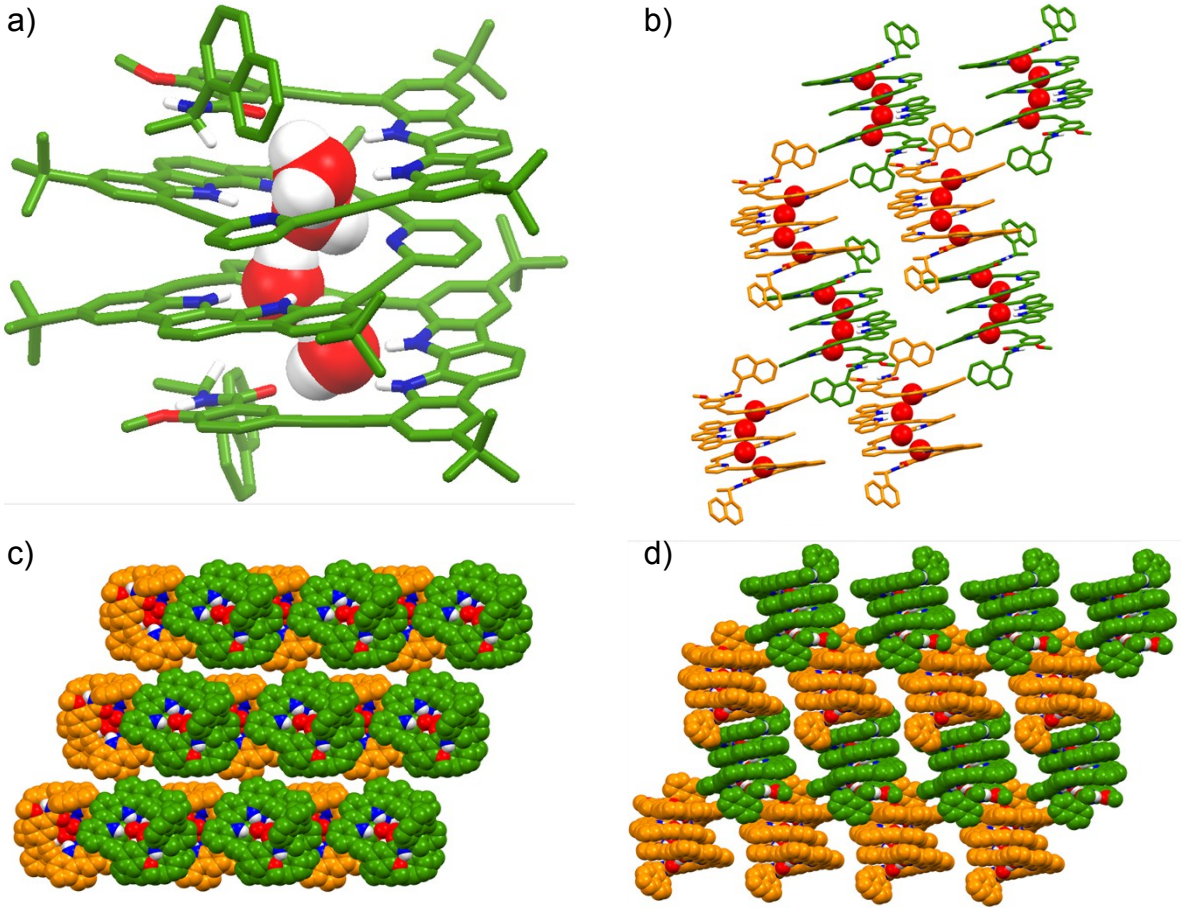


Fig. S9 a) Crystal structure of **4**(*R*)⊃4H_2O. b) capped stick representation of **4**(*S*)⊃4H_2O and **4**(*R*)⊃4H_2O. Space-filling representations of **4**(*S*)⊃4H_2O and **4**(*R*)⊃4H_2O; c) top and d) side views. Helices are shown in green (*P*-helix) and orange (*M*-helix). CH hydrogens except one in the chiral center are all omitted in a), b), c) and d) and *t*-butyl groups are omitted in b), c) and d) for clarity.

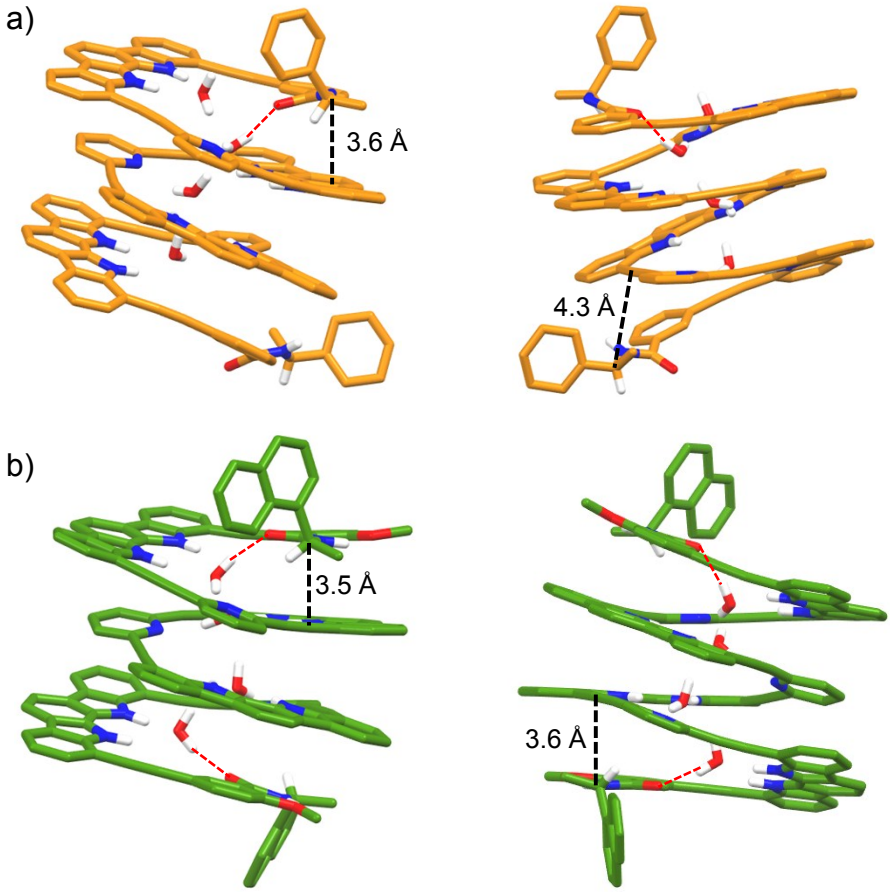


Fig. S10 Distances between the chiral centers and adjacent indolocarbazole planes in the crystal structures of a) **2**(*S*) and b) **4**(*S*). CH hydrogens except one in the chiral center and *t*-butyl groups are omitted for clarity.