Electronic Supplementary Information

Modulation of helix stability of indolocarbazole–pyridine hybrid foldamers

Jee Seon Kim, Hae-Geun Jeon and Kyu-Sung Jeong*

**Department of Chemistry, Yonsei University, Seoul, 120-749, Korea*

Fax: +82-2-364-7050

Tel: +82-2123-2643

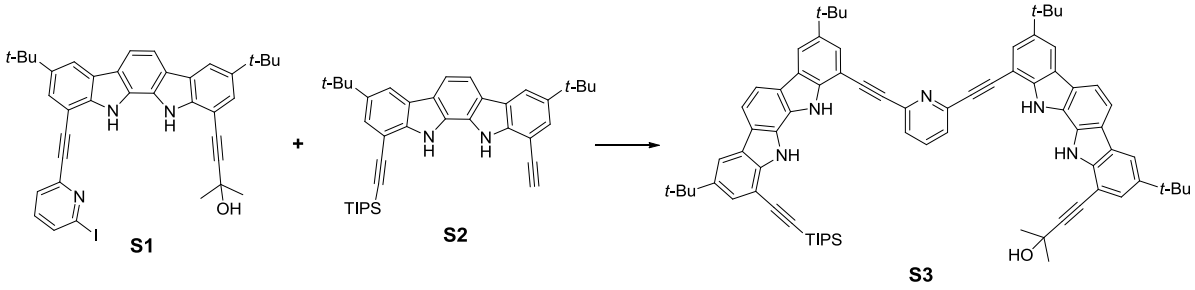
E-mail: ksjeong@yonsei.ac.kr

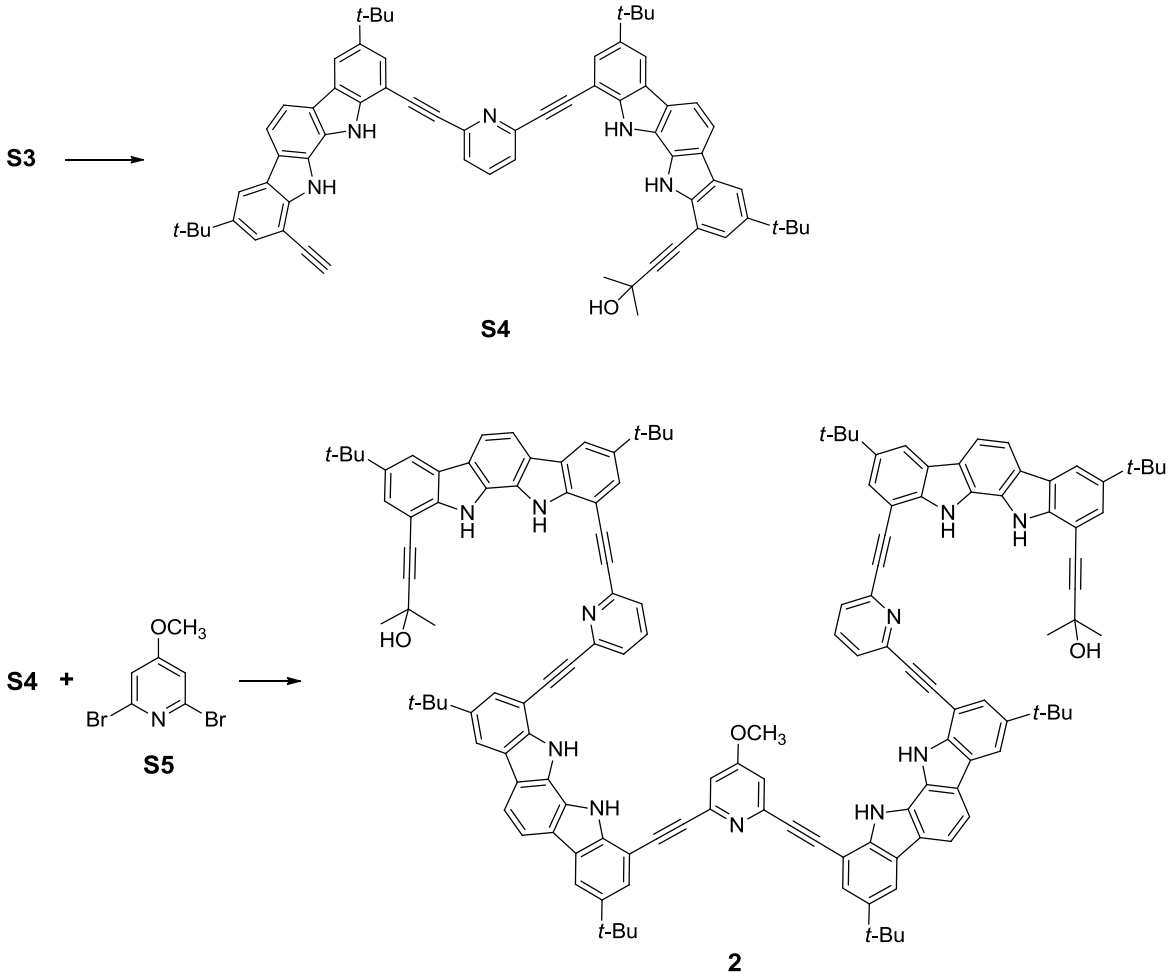
Contents

1. Syntheses and spectroscopic properties 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 CD_2Cl_2, toluene-d_6 and chlorobenzene-d_5 were prepared by sonication of a mixture of solvent containing a few drops of distilled water for 30 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; CD_2Cl_2 5.32 ppm; chlorobenzene-d_5 7.14 ppm, DMSO-d_6 2.50 ppm; toluene-d_8 7.09 ppm and for ^{13}C NMR spectra, acetone-d_6 206.26 ppm; CD_2Cl_2 53.84 ppm). FT-IR spectra were measured by using a Vertex70 FT-IR spectrometer. 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**





S3: The synthesis of **S1** and **S2** was described previously.[S1] A Schlenk flask containing compound **S1** (90 mg, 0.16 mmol), **S2** (107 mg, 1.0 eq), CuI (3.0 mg, 0.1 eq) and $Pd(PPh_3)_2Cl_2$ (11.0 mg, 0.1 eq) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed tetrahydrofuran (THF) (1.0 mL) and trimethylamine (Et_3N) (1.0 mL) were added in order and the solution was stirred at 55 ℃ for 4 h. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The organic solution was washed with brine and saturated $NaHCO_3$ solution, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 3:1 (v/v)) to give **S3** as a yellow solid (129 mg, 73%); Mp > 274 ℃ (dec); ^{1}H NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 10.59 (s, 1H, NH), 10.52 (s, 1H, NH),

[S1] H.-G. Jeon, J. Y. Jung, P. Kang, M.-G. Choi and K.-S. Jeong, *J. Am. Chem. Soc*., 2016, **138**, 92.

10.24 (s, 2H, NH), 8.44 (d, *J* = 1.5 Hz, 1H), 8.43 (d, *J* = 1.5 Hz, 1H), 8.34 (d, *J* = 1.7 Hz, 1H), 8.28 (d, *J* = 1.7 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.83 (t, *J* = 1.7 Hz, 1H), 7.64 (d, *J* = 1.8 Hz, 1H), 7.53 (d, *J* = 1.8 Hz, 1H), 4.50 (s, 1H), 1.54 (s, 18H, *t*-Bu), 1.54 (s, 6H), 1.47 (s, 18H, *t*-Bu), 1.06 (s, 3H), 1.05 (s, 18H); ^{13}C NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 144.8, 143.6, 143.5, 143.4, 143.3, 139.5, 139.4, 139.0, 138.9, 138.1, 127.9, 127.7, 127.1, 127.0, 126.9, 126.9, 126.7, 125.6, 125.6, 125.5, 125.4, 125.4, 125.0, 125.0, 122.7, 122.7, 122.6, 122.4, 119.4, 119.2, 118.5, 117.6, 113.4, 113.2, 106.4, 106.3, 105.2, 104.7, 104.7, 94.8, 93.2, 92.8, 78.5, 65.4, 65.3, 35.4, 35.4, 35.2, 35.2, 32.3, 32.2, 32.2, 32.1, 19.0, 12.0; MALDI-TOF *m/z* calcd for $C_{77}H_{83}N_5OSi$ $[M+H]^+$ 1122, found 1122; IR (NaCl) υ 3564 (OH), 3396 (NH), 2198 (C≡C), 1252 (Si-CH_3), 1157 (C-O) cm^{-1}.

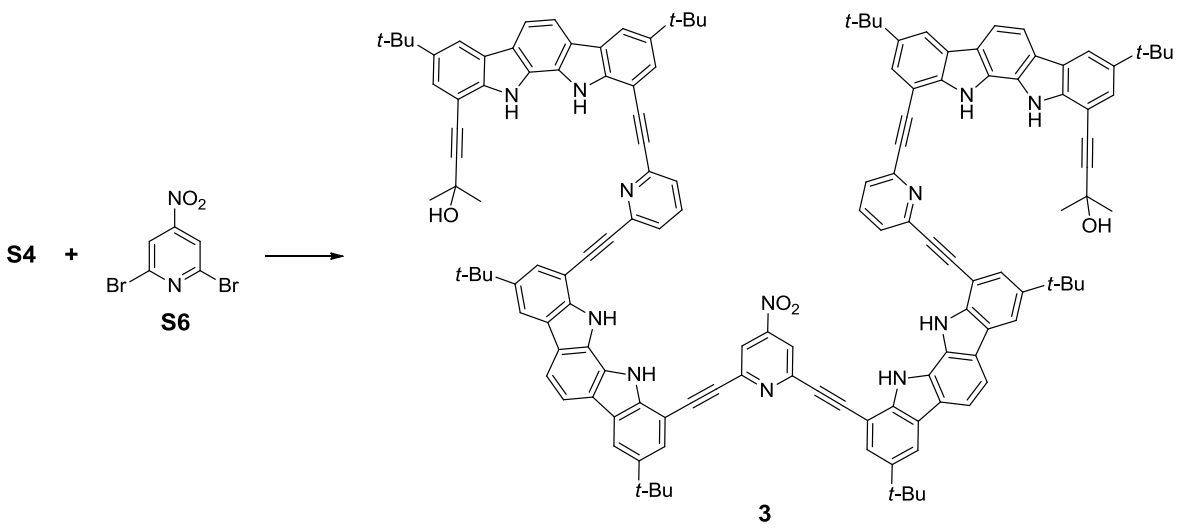
S4: **S3** (150 mg, 0.13 mmol) was dissolved in THF (1.34 mL). To the solution tetrabutylammonium fluoride (TBAF) (0.29 mL, 1.0 M solution in THF, 2.2 eq) was added at 0 ℃, and the solution was stirred for 45 min at room temperature. After concentration, the residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 3:1 (v/v)) to give **S4** as a yellow solid (128 mg, 98%); Mp >224 ℃ (dec); ^{1}H NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 10.79 (s, 1H, NH), 10.66 (s, 1H, NH), 10.31 (s, 1H, NH), 10.27 (s, 1H, NH), 4.53 (s, 1H, OH), 3.96 (s, 1H), 1.54 (s, 6H), 1.53 (s, 18H), 1.46 (s, 18); ^{13}C NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 145.2, 145.1, 143.9, 143.7, 140.0, 139.8, 139.5, 138.6, 128.1, 127.5, 127.4, 127.4, 127.3, 126.9, 125.9, 125.8, 125.5, 125.3, 123.1, 122.9, 122.8, 122.7, 119.7, 119.7, 118.8, 118.0, 113.7, 113.6, 113.5, 106.7, 105.5, 105.1, 93.4, 88.0, 87.9, 83.4, 81.8, 78.8, 65.8, 35.8, 35.6, 33.0, 32.7, 32.6, 32.6, 32.6, 32.5, 23.7, 14.7; MALDI-TOF *m/z* calcd for $C_{68}H_{63}N_5O$ 966, found 966; IR (NaCl) υ 3564 (OH), 3406 (NH), 3309 (C(sp)-H), 2206 (C≡C), 1160 (C-O) cm^{-1}.

2: **S5** was prepared according to literature procedures.[S2] A Schlenk flask containing **S4** (120 mg, 0.124 mmol, 2.5 eq), **S5** (13.3 mg, 1.0 eq), CuI (1.0 mg, 0.1 eq) and $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.1 eq) was evacuated under vacuum and back-filled with nitrogen. Anhydrous,

[S2] U. Neumann, F. Vögtle, *Chem. Ber*., 1989, **122**, 589.

degassed THF (0.5 mL) and Et_3N (0.5 mL) were added in order and the solution was stirred at room temperature for 4 h 20 min. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The organic solution was washed with brine and saturated $NaHCO_3$ solution, 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 **2** as a yellow solid (66 mg, 65%); Mp >268 ℃ (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K, ppm) δ 10.53 (s, 2H, NH), 10.36 (s, 2H, NH), 9.95 (s, 2H, NH), 9.59 (s, 2H, NH), 8.10 (s, 2H), 7.97 (s, 2H), 7.92 (s, 2H), 7.90 (s, 2H), 7.88 (d, *J*= 8.2 Hz, 2H), 7.76 (d, *J*= 8.1 Hz, 2H), 7.69 (d, *J*= 8.2 Hz, 2H), 7.59 (d, *J*= 8.1 Hz, 2H), 7.34 (s, 2H), 7.07 (t, *J*= 7.7 Hz, 2H), 7.03 (s, 2H), 6.94 (s, 2H), 6.87 (s, 2H), 6.50 (d, *J* = 7.6 Hz, 2H), 6.39 (d, *J* = 7.6 Hz, 2H), 4.84 (s, 2H), 3.44 (s, 3H), 1.50 (s, 18H, *t*-Bu), 1.48 (s, 18H, *t*-Bu), 1.44 (s, 18H, *t*-Bu), 1.39 (s, 18H, *t*-Bu), 0.82 (s, 2H, OH), 0.81 (s, 6H, Me), 0.54 (s, 6H, Me); ^{13}C NMR (400 MHz, CD_2Cl_2, 298 K, ppm) δ 142.5, 142.2, 142.1, 142.1, 141.8, 141.5, 140.2, 140.0, 139.7, 138.8, 138.8, 136.3, 126.7, 126.4, 126.3, 126.2, 125.2, 124.9, 124.7, 124.6, 124.5, 124.5, 124.2, 123.9, 123.7, 122.0, 121.8, 121.6, 121.1, 118.6, 118.1, 118.0, 116.6, 112.8, 112.7, 112.5, 112.2, 111.5, 111.4, 110.0, 109.9, 104.9, 104.6, 104.2, 104.1, 103.8, 97.3, 92.2, 92.0, 91.9, 87.1, 86.7, 78.1, 65.1, 35.0, 34.9, 34.9, 32.5, 32.3, 32.2, 32.2, 30.9, 30.1; MALDI-TOF *m/z* calcd for $C_{142}H_{129}N_{11}O_3$ 2037, found 2038; ESI-HRMS *m/z* calcd for $C_{142}H_{130}N_{11}O_3$ $[M+H]^+$ 2038.0392, found $[M+H]^+$ 2038.0372; IR (NaCl) υ 3543 (OH), 3444 (NH), 2205 (C≡C), 1158 (C–O) cm^{-1}.

1.3 Synthesis of compound **3**

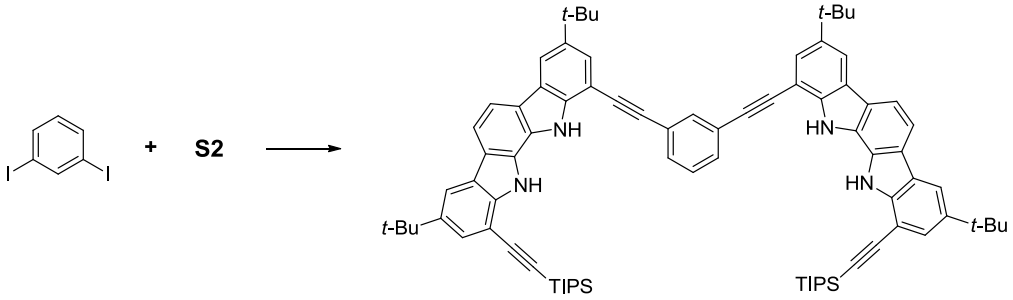


3: S6 was prepared according to literature procedures.[S3] A Schlenk flask containing **S4** (49 mg, 0.05 mmol, 2.5 eq), **S6** (5.7 mg, 1.0 eq), CuI (1.2 mg, 0.3 eq) and $Pd(PPh_3)_2Cl_2$ (4.3 mg, 0.3 eq) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (0.5 mL) and Et_3N (0.5 mL) were added in order and the solution was stirred at room temperature for 2 h. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The organic solution was washed with brine and saturated $NaHCO_3$ solution, 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 **3** as an orange solid (23 mg, 56%); Mp >272 ℃ (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K, ppm) δ 10.54 (s, 2H, NH), 10.38 (s, 2H, NH), 9.95 (s, 2H, NH), 9.52 (s, 2H, NH), 8.18 (s, 2H), 8.02 (s, 2H), 8.00 (d, *J*= 8.2 Hz, 2H), 7.97 (s, 2H), 7.82 (s, 2H), 7.78 (d, *J*= 8.2 Hz, 2H), 7.62 (d, *J*= 8.2 Hz, 2H), 7.41 (s, 2H), 7.32 (d, *J*= 8.1 Hz, 2H), 7.13 (t, *J*= 7.7 Hz, 2H), 7.04 (s, 2H), 6.97 (s, 2H), 6.88 (s, 2H), 6.46 (d, *J*= 7.6 Hz, 2H), 6.38 (d, *J*= 7.6 Hz, 2H), 5.67 (s, 2H), 1.56 (s, 18H, *t*-Bu), 1.53 (s, 18H, *t*-Bu), 1.41 (s, 18H, *t*-Bu), 1.38 (s, 18H, *t*-Bu), 0.94 (s, 2H, OH), 0.82 (s, 6H, Me), 0.45 (s, 6H, Me); ^{13}C NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 144.8, 143.6, 143.4, 143.4, 143.3, 143.1, 143.0, 141.2, 140.7, 139.2, 138.4, 137.4, 128.7, 127.7, 127.6, 127.4, 127.2, 126.8, 126.2, 125.8, 125.4, 125.3, 125.0, 123.2,

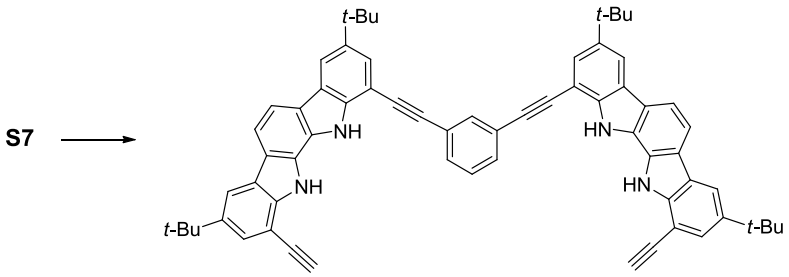
[S3] (a) J. C. Rodriguez-Ubis, R. Sedano, G. Barroso, O. Juanes and E. Brunet, *Helv. Chim. Acta*, 1997, **80**, 86; (b) M. Nettekoven and C. Jenny, *Org. Proces Res. Dev.*, 2003, **7**, 38.

122.9, 122.6, 122.5, 120.5, 119.5, 119.1, 117.9, 116.6, 113.9, 113.7, 113.4, 113.0, 106.7, 105.1, 104.9, 104.4, 99.4, 93.5, 93.1, 93.1, 91.6, 91.2, 88.8, 87.8, 78.6, 65.5, 65.4, 35.8, 35.7, 33.0, 32.8, 32.7, 32.0, 23.8; MALDI-TOF *m/z* calcd for $C_{141}H_{126}N_{12}O_4$ 2052, found 2053; ESI-HRMS *m/z* calcd for $C_{141}H_{127}N_{12}O_4$ $[M+H]^+$ 2053.0137, found $[M+H]^+$ 2053.0125; IR (NaCl) υ 3542 (OH), 3444 (NH), 2207 (C≡C), 1160 (C–O), 1396, 1364 (N=O) cm^{-1}.

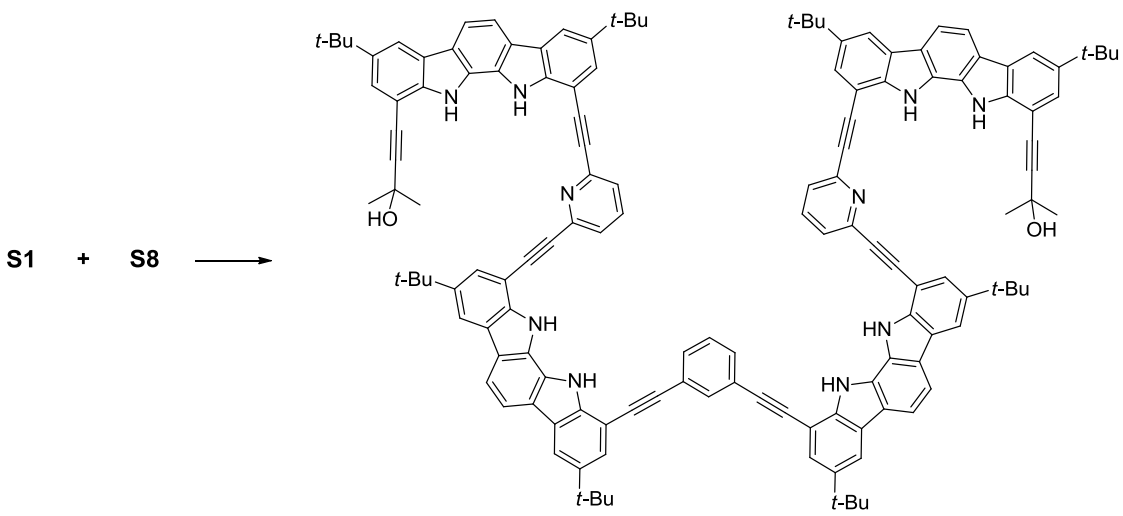
1.4 Synthesis of compound **4**



S7



S8



S7: A Schlenk flask containing 1,3-diiodobenzene (0.17 g, 0.51 mmol), **S2** (0.60 g, 1.05 mmol), CuI (1.0 mg, 0.0053 mmol) and $Pd(PPh_3)_2Cl_2$ (4.0 mg, 0.0057 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (5.0 mL), Et_3N (5.0 mL) were sequentially added, and the solution was stirred at 55 ℃ for 4 h. The mixture was filtered through Celite and concentrated. The residue was dissolved in CH_2Cl_2, washed with water and brine, and dried over anhydrous Na_2SO_4. After concentration under reduced pressure, the residue was purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1:5 (v/v)) to give **S7** as a brown solid (0.43 g, 67%); Mp: 304–305 ℃; ^{1}H NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 10.38 (s, 2H, NH), 10.13 (s, 2H, NH), 8.37 (d, J = 1.4 Hz, 2H), 8.32 (d, J = 1.4 Hz, 2H), 8.09 (s, 1H), 8.07 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.4 Hz, 2H), 7.85 (dd, J= 7.7 Hz and 1.4 Hz, 2H), 7.76 (d, J = 1.6 Hz, 2H), 7.65 (t, J = 7.7 Hz, 1H), 7.62 (d, J = 1.7 Hz, 2H), 1.53 (s, 9H, *t*-Bu), 1.46 (s, 9H, *t*-Bu), 1.06 (s, 3H), 1.05 (s, 18H); ^{13}C NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 143.6, 143.5, 139.6, 139.3, 135.1, 132.7, 130.2, 127.6, 127.1, 126.5, 125.5, 125.4, 125.1, 122.8, 122.8, 118.7, 118.6, 113.5, 113.4, 106.5, 105.9, 105.2, 95.0, 93.2, 88.3, 35.5, 35.4, 32.4, 32.3, 19.1, 12.1; MALDI-TOF *m/z* calcd for $C_{84}H_{98}N_4Si_2$ 1219, found 1218; IR (NaCl) υ 3406 (NH), 2206 (C≡C) cm^{-1}.

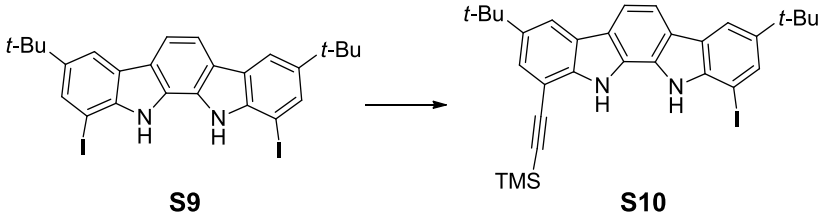
S8: S7 (80 mg, 0.07 mmol) was dissolved in THF (0.66 mL). To the solution TBAF (0.28

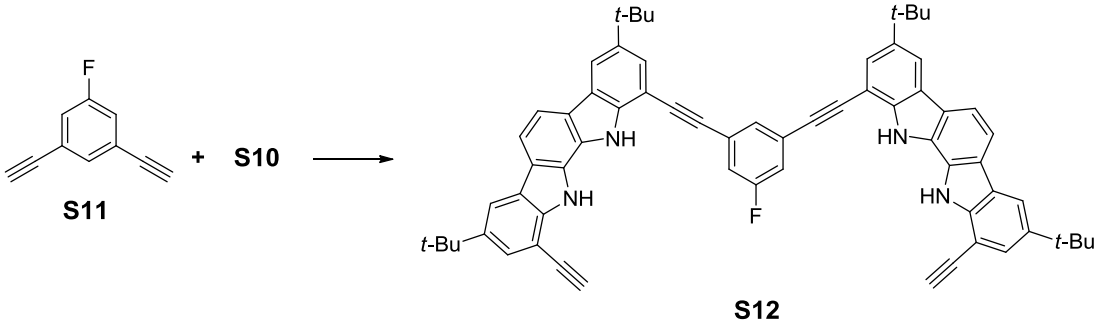
mL, 1.0 M solution in THF, 4.4 eq) was added at 0 ℃, and stirred for 2 h at room temperature. After concentration, the residue was purified by flash column chromatography (silica gel, hexane/EtOAc = (v/v) 6:1) to give **S8** as an ivory solid (55 mg, 93%); Mp > 212 ℃ (dec); ^{1}H NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 10.66 (s, 2H, NH), 10.26 (s, 2H, NH), 8.38 (d, *J* = 1.5 Hz, 2H), 8.33 (d, *J* = 1.5 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.98 (s, 1H), 7.78 (dd, *J*= 7.4 Hz and 1.5 Hz, 2H), 7.78 (d, *J* = 1.8 Hz, 2H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 1.8 Hz, 2H), 3.99 (s, 2H), 1.52 (s, 9H, *t*-Bu), 1.46 (s, 9H, *t*-Bu); ^{13}C NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 143.5, 143.4, 139.6, 139.3, 135.1, 132.5, 130.2, 127.1, 127.1, 127.0, 126.8, 125.3, 125.2, 125.0, 122.6, 122.6, 118.7, 118.5, 113.3, 113.3, 105.7, 105.2, 92.9, 88.3, 83.2, 81.2, 35.4, 35.3, 32.3, 32.3; MALDI-TOF *m/z* calcd for $C_{66}H_{58}N_4$ 906, found 906; IR (NaCl) υ 3406 (NH), 3309 (C(sp)-H), 2206 (C≡C) cm^{-1}.

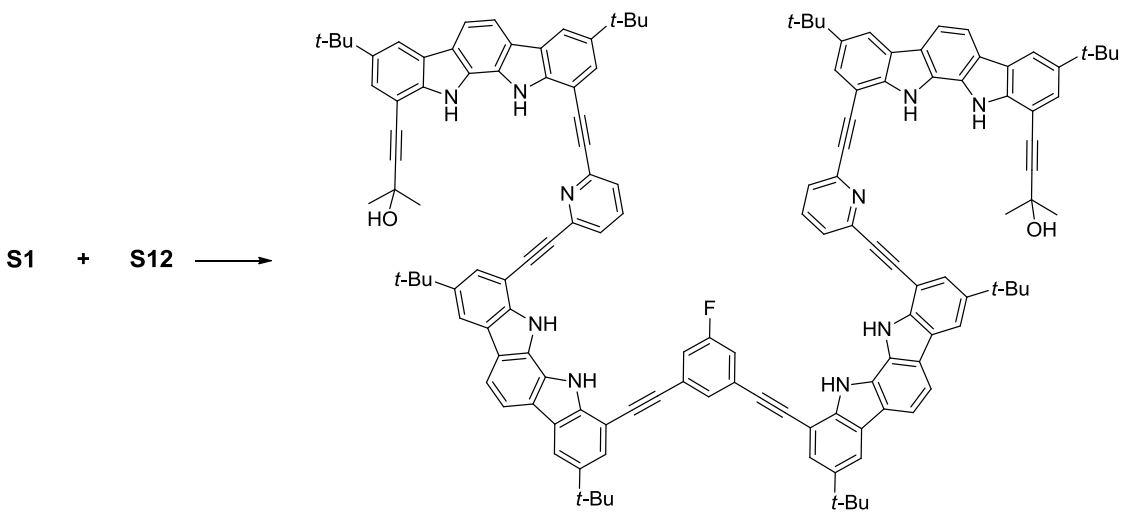
4: A Schlenk flask containing **S8** (54 mg, 0.06 mmol), **S1** (81 mg, 2.0 eq), CuI (1.1 mg, 0.1 eq) and $Pd(PPh_3)_2Cl_2$ (4.2 mg, 0.1 eq) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (0.6 mL) and Et_3N (0.6 mL) were added in order and the solution was stirred at 55 ℃ for 4 h. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The organic solution was washed with brine and saturated $NaHCO_3$ solution, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 3:1 (v/v) and EtOAc/pentane = 1:4 (v/v)) to give **4** as a yellow solid (64 mg, 53%); Mp >260 ℃ (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K, ppm) δ 11.48 (s, 2H, NH), 9.62 (s, 2H, NH), 9.32 (s, 4H, NH), 8.30 (s, 2H), 8.01 (s, 2H), 7.98 (d, *J*= 8.0 Hz, 2H), 7.94 (s, 2H), 7.85 (d, *J*= 8.0 Hz, 2H), 7.77 (s, 2H), 7.74 (d, *J*= 8.0 Hz, 2H), 7.61 (d, *J*= 8.0 Hz, 2H), 7.43 (s, 1H), 7.26 (s, 2H), 7.25 (s, 2H), 7.07 (s, 4H), 6.64 (t, *J*= 7.7 Hz, 2H), 6.13 (d, *J* = 7.7 Hz, 2H), 6.07 (d, *J* = 7.7 Hz, 2H), 5.76 (t, *J*= 7.0 Hz, 1H), 5.42 (d, *J* = 7.6 Hz, 2H), 1.55 (s, 18H, *t*-Bu), 1.48 (s, 18H, *t*-Bu), 1.41 (s, 18H, *t*-Bu), 1.39 (s, 18H, *t*-Bu), 0.80 (s, 12H, Me), 0.77 (s, 2H, OH); ^{13}C NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 144.6, 144.5, 143.7, 143.5, 143.4, 139.5, 139.4, 139.2, 139.1, 137.7, 132.3, 129.8, 127.5, 127.5, 127.2, 127.2, 127.1, 127.1,

126.9, 126.8, 126.8, 125.6, 125.3, 125.1, 125.1, 124.7, 122.8, 122.8, 122.6, 122.4, 119.3, 119.3, 118.6, 117.7, 113.5, 113.4, 113.4, 113.3, 113.3, 106.4, 105.8, 104.9, 104.8, 99.9, 93.1, 93.1, 93.0, 92.9, 88.2, 87.5, 87.4, 78.6, 65.5, 35.5, 35.5, 35.4, 35.3, 32.4, 32.3, 32.2; MALDI-TOF *m/z* calcd for $C_{142}H_{128}N_{10}O_2$ 2006, found 2007; ESI-HRMS *m/z* calcd for $C_{142}H_{128}N_{10}NaO_2$ $[M+Na]^+$ 2029.0153, found $[M+Na]^+$ 2029.0144; IR (NaCl) υ 3406 (NH), 2205 (C≡C), 1160 (C–O) cm^{-1}.

1.5 Synthesis of compound **5**







5

S10: The synthesis of **S9** was described previously.[S4] A Schlenk flask containing **S9** (1.00 g, 1.61 mmol, 1.0 eq), CuI (26 mg, 0.085 eq) and $Pd(PPh_3)_2Cl_2$ (29 mg, 0.026 eq) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (28 mL), Et_3N (18 mL) and distilled trimethylsilane acetylene (TMS-acetylene) (0.32 mL, 1.4 eq) were sequentially added in order and the solution was stirred at 55 ℃ for 13 h. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The organic solution was washed with water, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1:2 (v/v)) to give **S10** as a dark green solid (290 mg, 30%); Mp 197–198 ℃; ^{1}H NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 10.48 (s, 1H, NH), 9.85 (s, 1H, NH), 8.32 (d, *J*= 1.7 Hz, 1H), 8.28 (d, *J*= 1.4 Hz, 1H), 8.03 (d, *J*= 8.3 Hz, 1H), 7.99 (d, *J*= 8.4 Hz, 1H), 7.87 (d, *J*= 1.6 Hz, 1H), 7.63 (d, *J*= 1.8 Hz, 1H), 1.47 (s, 9H, *t*-Bu), 1.46 (s, 9H, *t*-Bu), 0.34 (s, 9H); ^{13}C NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 145.7, 143.5, 140.5, 139.3, 132.4, 127.5, 127.1, 126.7, 125.6, 125.4, 123.2, 122.7, 118.6, 117.4, 113.6, 113.6, 106.2, 103.3, 98.6, 76.5, 35.4, 35.4, 32.4, 32.4, 0.4; MALDI-TOF *m/z* calcd for $C_{32}H_{35}IN_2Si$ 590, found 590; IR (NaCl) υ 3390 (NH), 2128 (C≡C), 1250 (Si-CH_3) cm^{-1}.

[S4] (a) K.-J. Chang, D. Moon, M. S. Lah and K.-S. Jeong, *Angew. Chem. Int. Ed.*, 2005, **44**, 7926; (b) N.-K. Kim, K.-J. Chang, D. Moon, M. S. Lah and K.-S. Jeong, *Chem. Commun.*, 2007, 3401.

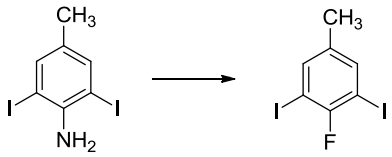
S12: S11 was prepared according to literature procedures.[S5] A Schlenk flask containing **S11** (17 mg, 0.118 mmol, 1.0 eq), **S10** (144 mg, 2.1 eq), CuI (2 mg, 0.09 eq) and $Pd(PPh_3)_2Cl_2$ (6 mg, 0.07 eq) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (1.0 mL) and Et_3N (1.5 mL) were added in order and the solution was stirred at 55 ℃ for 3.5 h. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The organic solution was washed with water, dried over anhydrous Na_2SO_4 and concentrated. The crude mixture dissolved in THF (16 mL). To the solution TBAF (0.73 mL, 1.0 M solution in THF, 6.2 eq) was added, and stirred for 5 min at room temperature. After concentration, the residue was purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1:1 (v/v)) to give **S12** as an ivory solid (68 mg, 60%); Mp >235 ℃ (dec); ^{1}H NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 10.66 (s, 2H, NH), 10.24 (s, 2H, NH), 8.39 (d, *J*= 1.2 Hz, 2H), 8.32 (d, *J*= 1.2 Hz, 2H), 8.06 (d, *J*= 8.4 Hz, 2H), 8.04 (d, *J*= 8.4 Hz, 2H), 7.82 (s, 1H), 7.79 (d, *J*= 1.6 Hz, 2H), 7.63 (d, *J*= 1.5 Hz, 2H), 7.57 (d, *J*= 8.5 Hz, 2H), 3.97 (s, 2H), 1.51 (s, 18H, *t*-Bu), 1.50 (s, 18H, *t*-Bu); ^{13}C NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 143.7, 143.5, 139.8, 139.5, 131.6, 127.2, 127.1, 127.1, 127.0, 125.6, 125.3, 122.8, 122.6, 119.4, 119.2, 119.1, 118.6, 113.5, 113.4, 105.3, 105.3, 91.9, 89.6, 83.2, 81.7, 55.1, 35.4, 35.4, 32.5, 32.4; MALDI-TOF *m/z* calcd for $C_{66}H_{57}FN_4$ 924, found 925; IR (NaCl) υ 3418 (NH), 3311 (C(sp)–H), 2208 (C≡C) cm^{-1}.

5: A Schlenk flask containing **S1** (86 mg, 0.127 mmol, 2.0 eq), **S12** (59 mg, 1.0 eq), CuI (1 mg, 0.08 eq) and $Pd(PPh_3)_2Cl_2$ (4 mg, 0.09 eq) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (1.0 mL) and Et_3N (1.6 mL) were added in order and the solution was stirred at 55 ℃ for 2.5 h. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The organic solution was washed with water, dried over anhydrous Na_2SO_4 and concentrated. The residue was

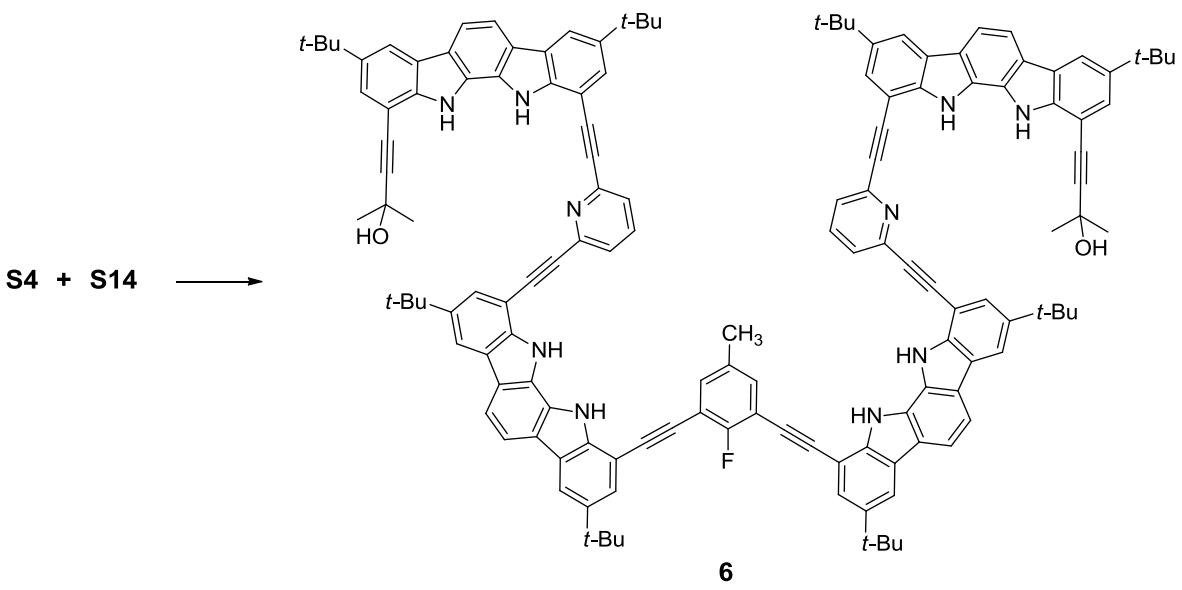
[S5] J. Dash, R. Nath Das, N. Hegde, G. D. Pantoş, P. S. Shirude and S. Balasubramanian, *Chem. Eur. J.*, 2012, **18**, 554.

purified by flash column chromatography (silica gel, EtOAc/hexane = 1:4 (v/v)) to give **5** as a yellow solid (80 mg, 62%); Mp >261 ℃ (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K, ppm) δ 11.49 (s, 2H, NH), 9.59 (s, 2H, NH), 9.29 (s, 2H, NH), 9.26 (s, 2H, NH), 8.32 (d, *J*= 1.6 Hz, 2H), 8.05 (d, *J*= 1.6 Hz, 2H), 8.02 (s, 1H), 8.00 (s, 2H), 7.96 (d, *J*= 1.6 Hz, 2H), 7.87 (d, *J*= 8.2 Hz, 2H), 7.64 (d, *J*= 8.2 Hz, 2H), 7.25 (d, *J*= 1.6 Hz, 2H), 7.21 (d, *J*= 1.8 Hz, 2H), 7.16 (s, 1H), 7.03 (d, *J*= 1.7 Hz, 2H), 6.98 (d, *J*= 1.3 Hz, 2H), 6.63 (t, *J*= 7.7 Hz, 2H), 6.10 (dd, *J*= 7.7 Hz and 0.8 Hz, 2H), 6.01 (dd, *J*= 7.7 Hz and 0.8 Hz, 2H), 4.95 (d, *J*= 9.3 Hz, 2H), 1.55 (s, 18H, *t*-Bu), 1.47 (s, 18H, *t*-Bu), 1.41 (s, 18H, *t*-Bu), 1.40 (s, 18H, *t*-Bu), 0.79 (s, 12H, Me), 0.63 (s, 2H, OH); ^{13}C NMR (400 MHz, CD_2Cl_2, 298 K, ppm) δ 143.2, 142.9, 142.6, 142.3, 141.9, 141.6, 141.0, 139.0, 138.7, 138.4, 138.1, 136.0, 129.2, 129.0, 128.8, 128.3, 128.1, 127.9, 126.7, 126.5, 126.3, 125.8, 125.6, 125.4, 125.2, 124.9, 124.5, 124.3, 123.9, 122.0, 121.9, 121.9, 121.9, 118.9, 118.3, 117.1, 116.9, 115.6, 112.9, 112.5, 111.8, 106.1, 104.7, 104.7, 103.9, 96.6, 92.8, 92.8, 92.5, 91.4, 89.2, 87.9, 86.5, 78.6, 65.6, 35.3, 35.1, 35.0, 34.9, 32.5, 32.5, 32.3, 32.3, 30.6; MALDI-TOF *m/z* calcd for $C_{142}H_{127}FN_{10}O_2$ 2025, found 2024; ESI-HRMS *m/z* calcd for $C_{142}H_{128}FN_{10}O_2$ $[M+H]^+$ 2025.0239, found $[M+H]^+$ 2025.0237; IR (NaCl) υ 3443 (NH), 2205 (C≡C), 1161 (C–O) cm^{-1}.

1.6 Synthesis of compound **6**



S13 **S14**



6

S14: S13 was prepared according to literature procedures.[S6] To a solution of 48% HBF_4 (2.9 mL) at 0 ℃ was added dropwise $NaNO_2$ (377 mg). A solution of **S13** (280 mg) and THF (0.7 mL) was then added and the resultant yellow suspension stirred at 0 ℃ for 30 min. The yellow solid was filtered and washed with cold water. The solid was dried in vacuum and 305 mg of the diazonium salt was gained. The solid was then heated to 120 ℃ under nitrogen for 1.5 h. The yellow solid changed into dark brown liquid. The residue was dissolved in CH_2Cl_2 and washed with water, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1:2 (v/v)) to give **S14** as a yellow solid (168 mg, 60%); Mp 59–60 ℃; ^{1}H NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 7.685 (d, J = 4.0 Hz, 2H), 2.3 (s, 3H); ^{13}C NMR (400 MHz, acetone-d_6, 298 K, ppm) δ 141.1, 140.7, 139.1, 80.7, 19.7; GC-MS *m/z* calcd for $C_7H_5FI_2$ 362, found 362; IR (NaCl) υ 2921, 1509, 1380, 1247, 1037, 851, 757, 710, 691, 552.

6: A Schlenk flask containing **S4** (81 mg, 0.084 mmol, 2.5 eq), **S14** (12.1 mg, 1.0 eq), CuI

[S6] (a) S. B. Junne, A. Y. Vibhute, Y. B. Vibhute and V. M. Gurav, *Int. J. ChemTech Res.*, 2009, **1**, 1005; (b) Korner Contrach-ATTI Lines, 1913, **22**, 824.

(0.6 mg, 0.1 eq) and $Pd(PPh_3)_2Cl_2$ (2.3 mg, 0.1 eq) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed THF (0.3 mL) and Et_3N (0.3 mL) were added in order and the solution was stirred at room temperature for 6 h. The mixture was filtered through Celite and concentrated, and the residue was dissolved in CH_2Cl_2. The organic solution was washed with brine and saturated $NaHCO_3$ solution, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (silica gel, EtOAc/pentane = 1:5 (v/v)) to give **6** as a yellow solid (52 mg, 77%); Mp >284 ℃ (dec); ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K, ppm) δ 9.90 (s, 2H, NH), 9.59 (s, 2H, NH), 9.14 (s, 2H, NH), 8.32 (s, 2H, NH), 8.08 (s, 2H), 8.01 (d, *J*= 8.0 Hz, 2H), 7.97 (s, 2H), 7.90 (d, *J*= 8.0 Hz, 2H), 7.79 (d, *J*= 8.0 Hz, 2H), 7.70 (s, 2H), 7.57 (d, *J*= 8.0 Hz, 2H), 7.33 (s, 1H), 7.20 (s, 2H), 7.05 (s, 2H), 6.95 (s, 4H), 6.68 (t, *J*= 7.9 Hz, 2H), 6.13 (d, *J* = 8.2 Hz, 2H), 6.11 (d, *J* = 8.0 Hz, 2H), 5.08 (d, *J* = 6.7 Hz, 2H), 1.76 (s, 3H), 1.58 (s, 18H, *t*-Bu), 1.44 (s, 18H, *t*-Bu), 1.41 (s, 18H, *t*-Bu), 1.38 (s, 18H, *t*-Bu), 0.78 (s, 12H, Me), 0.60 (s, 2H, OH); ^{13}C NMR (400 MHz, CD_2Cl_2, 298 K, ppm) δ 143.1, 142.3, 142.2, 141.7, 140.1 138.8, 138.8, 136.1, 131.5, 131.5, 127.3, 127.3, 126.9, 126.5, 126.4, 126.2, 125.7, 125.7, 125.4, 125.1, 125.1, 124.8, 124.5, 124.3, 124.2, 123.9, 123.7, 122.2, 122.2, 122.1, 118.8, 117.9, 117.2, 116.7, 112.8, 112.6, 112.6, 111.8, 111.4, 105.7, 105.0, 104.9, 104.5, 104.4, 99.9, 97.4, 91.9, 91.3, 88.7, 86.9, 78.5, 65.5, 65.2, 64.7, 35.3, 35.1, 35.0, 34.9, 34.9, 32.5, 32.5, 32.4, 32.3, 30.8; MALDI-TOF *m/z* calcd for $C_{143}H_{130}FN_{10}O_2$ $[M+H]^+$ 2039, found 2039; ESI-HRMS *m/z* calcd for $C_{143}H_{129}FN_{10}NaO_2$ $[M+Na]^+$ 2061.0215, found $[M+Na]^+$ 2061.0204; IR (NaCl) υ 2240 (C≡C), 1161 (C–O) cm^{-1}.

2. ^{1}H NMR studies

2.1 Solvent-dependent ^{1}H NMR spectra

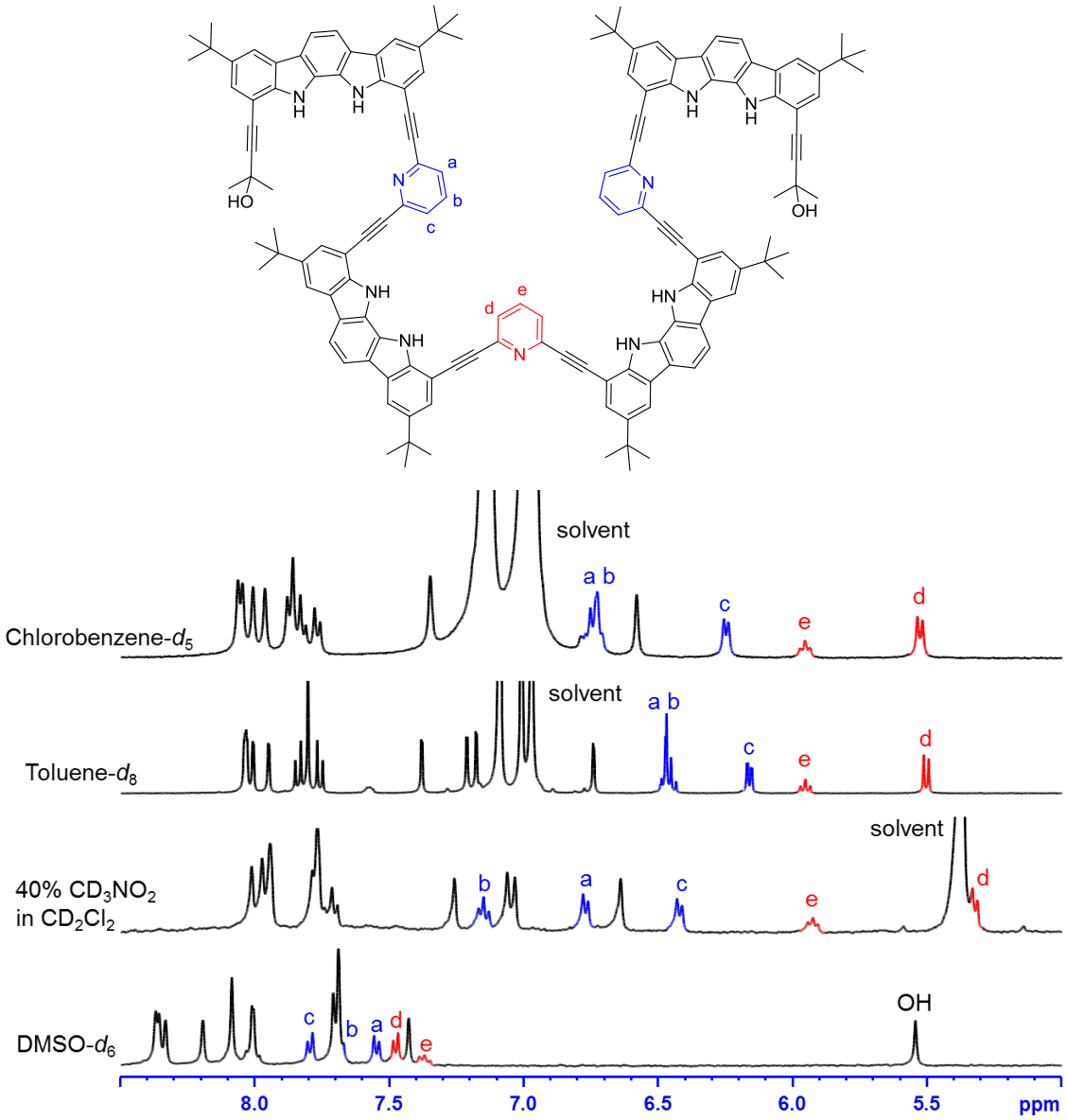


Fig S1. Partial ^{1}H NMR spectra (25 ℃) of **1**[S1] (1.0~4.0 mM) in DMSO-d_6, water-saturated CD_2Cl_2, CD_3NO_2/water-saturated CD_2Cl_2 (4:6, v/v), water-saturated toluene-d_8 and water-saturated chlorobenzene-d_5. The red- and blue-colored peaks correspond to the CH signals of central pyridine and two outer pyridines, respectively.

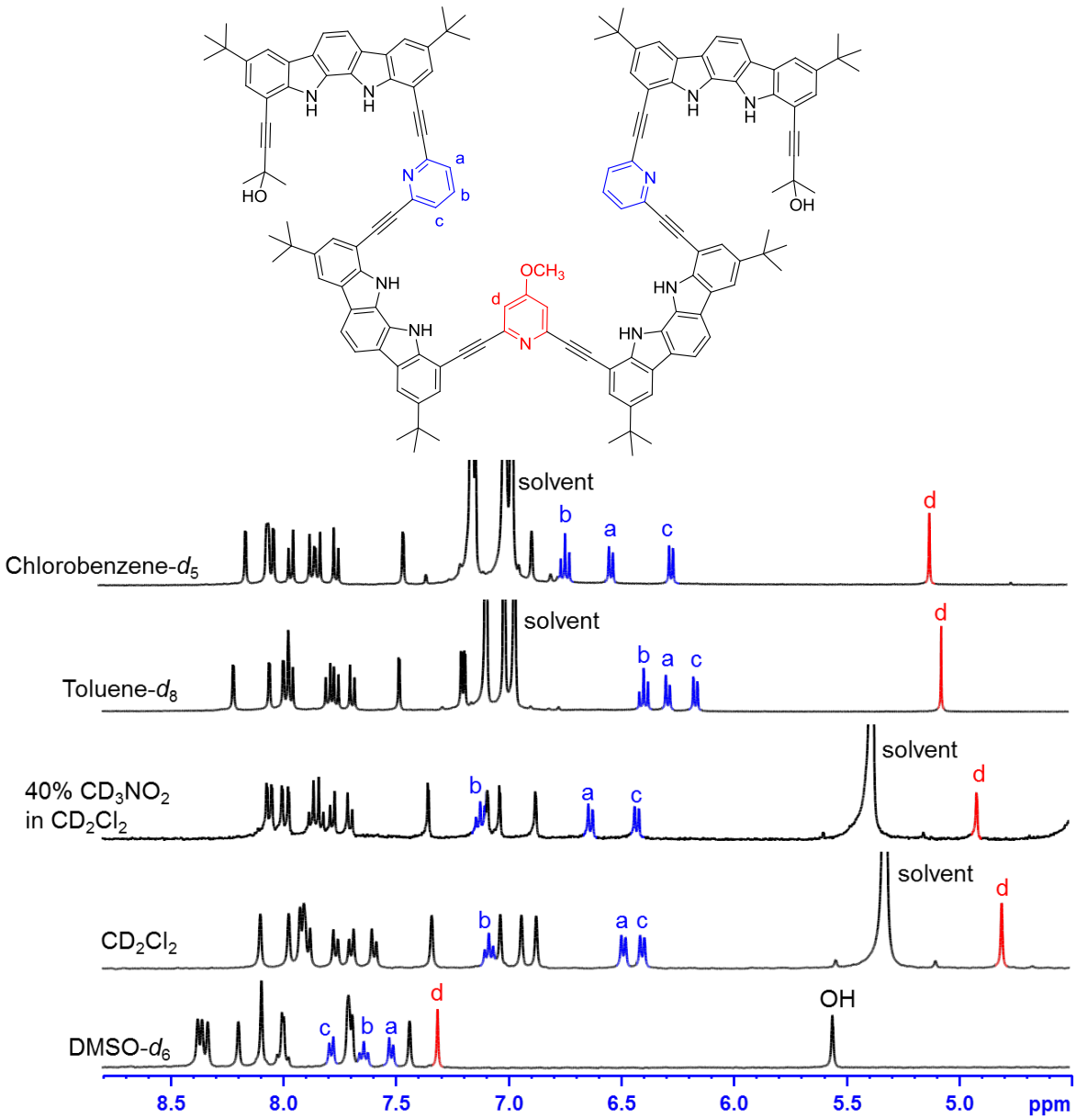


Fig S2. Partial ^{1}H NMR spectra (25 ℃) of **2** (1.0~4.0 mM) in DMSO-d_6, water-saturated CD_2Cl_2, CD_3NO_2/water-saturated CD_2Cl_2 (4:6, v/v), water-saturated toluene-d_8 and water-saturated chlorobenzene-d_5. The red- and blue-colored peaks correspond to the CH signals of central pyridine and two outer pyridines, respectively.

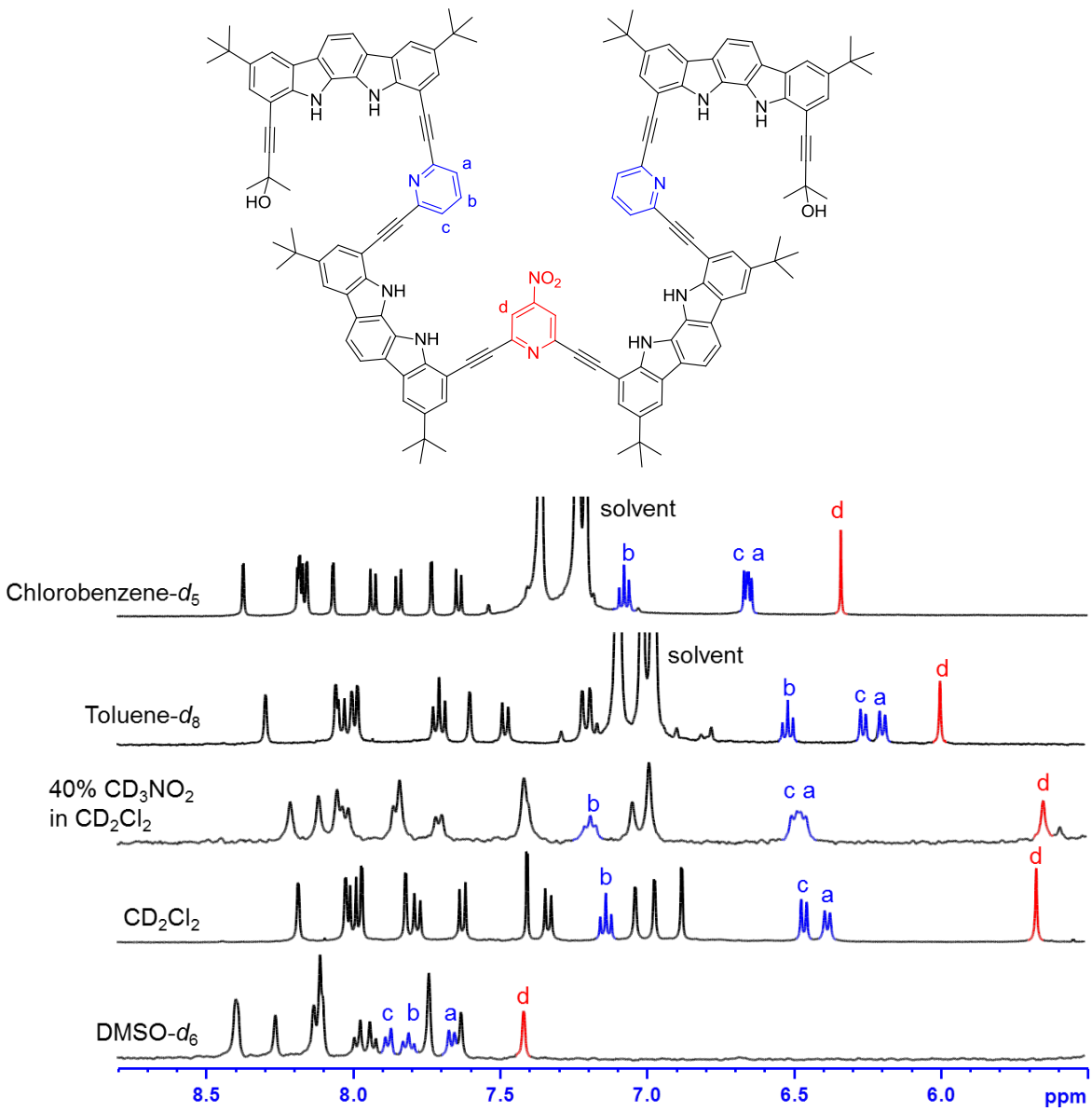


Fig S3. Partial ^{1}H NMR spectra (25 °C) of **3** (1.0~4.0 mM) in DMSO-d_6, water-saturated CD_2Cl_2, CD_3NO_2/water-saturated CD_2Cl_2 (4:6, v/v), water-saturated toluene-d_8 and water-saturated chlorobenzene-d_5. The red- and blue-colored peaks correspond to the CH signals of central pyridine and two outer pyridines, respectively.

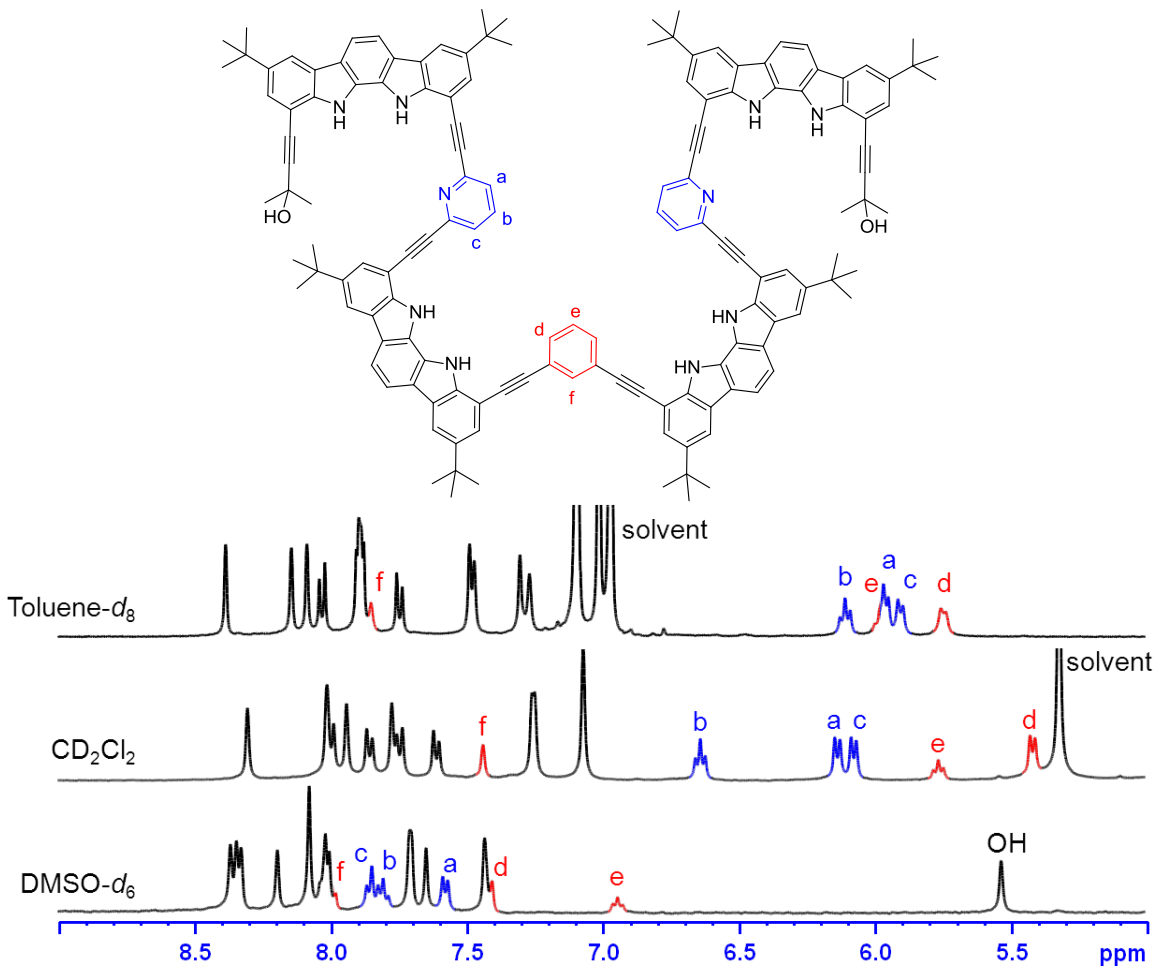


Fig S4. Partial ^{1}H NMR spectra (25 ℃) of **4** (1.0~4.0 mM) in DMSO-d_6, water-saturated CD_2Cl_2 and water-saturated toluene-d_8. The red- and blue-colored peaks correspond to the CH signals of central benzene and two outer pyridines, respectively.

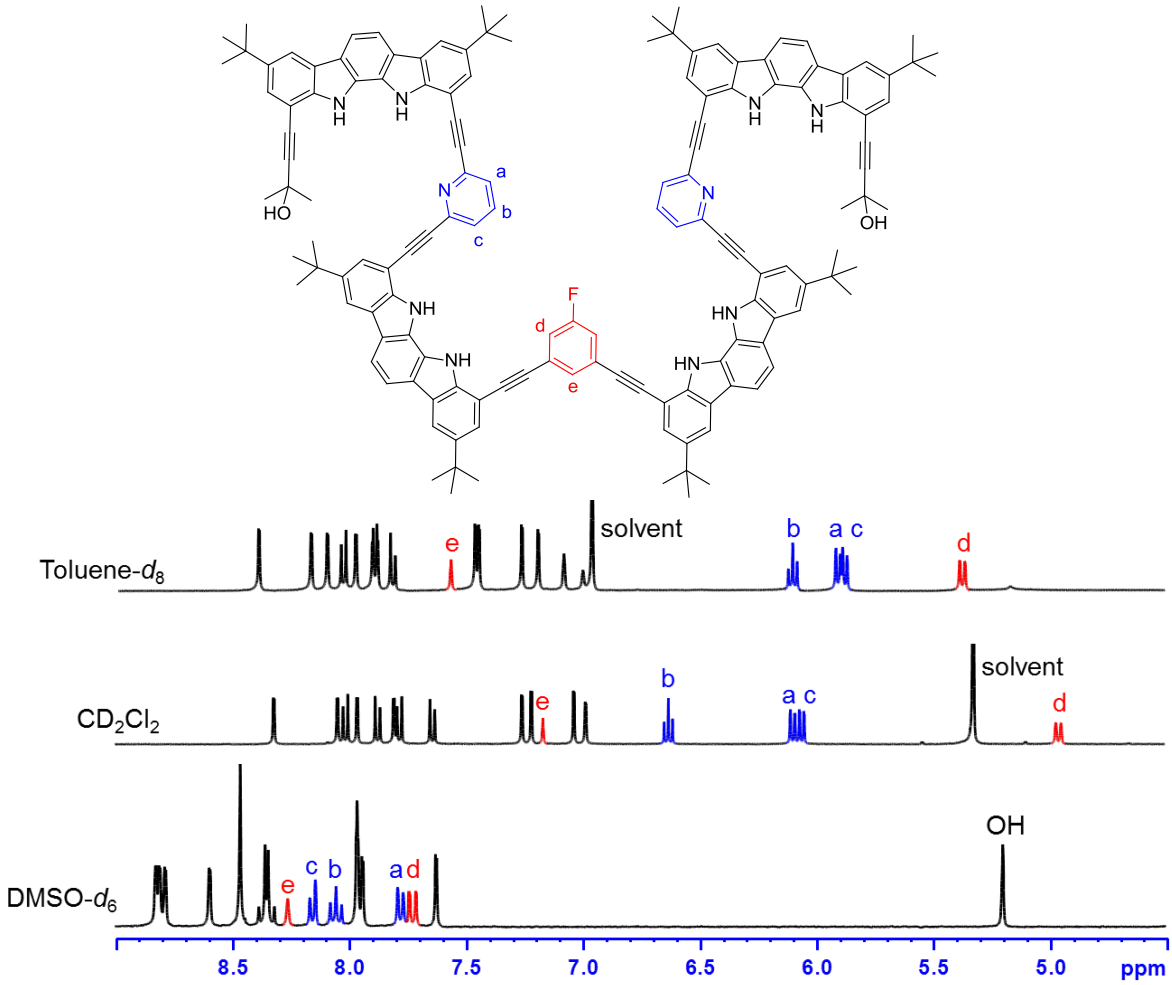


Fig S5. Partial ^{1}H NMR spectra (25 ℃) of **5** (1.0~4.0 mM) in DMSO-d_6, water-saturated CD_2Cl_2 and water-saturated toluene-d_8. The red- and blue-colored peaks correspond to the CH signals of central benzene and two outer pyridines, respectively.

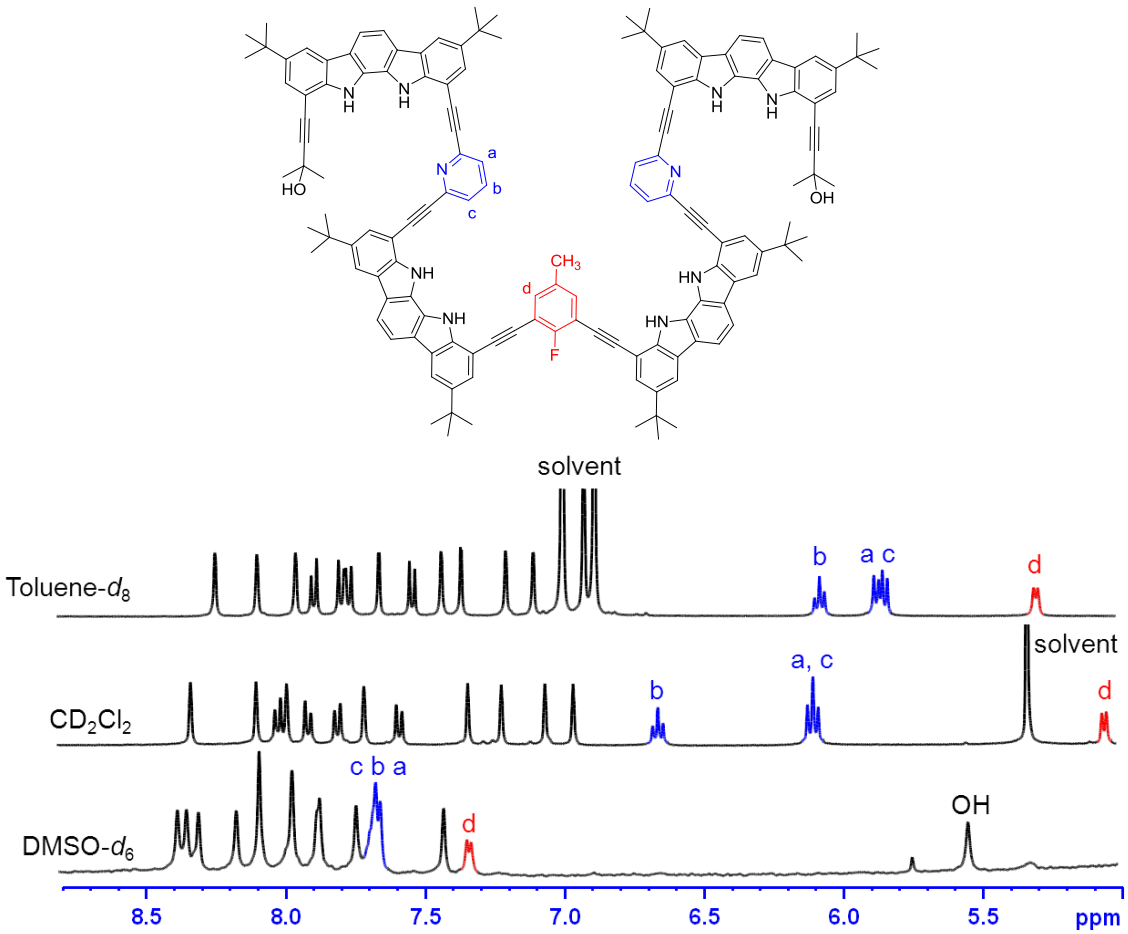


Fig S6. Partial ^{1}H NMR spectra (25 ℃) of **6** (1.0~4.0 mM) in DMSO-d_6, water-saturated CD_2Cl_2 and water-saturated toluene-d_8. The red- and blue-colored peaks correspond to the CH signals of central benzene and two outer pyridines, respectively.

Table S1. ^{1}H NMR chemical shifts (ppm) of **1**–**6** (1.0~4.0 mM) in DMSO-d_6, water-saturated CD_2Cl_2, CD_3NO_2/water-saturated CD_2Cl_2 (4:6, v/v), water-saturated toluene-d_8 and water-saturated chlorobenzene-d_5 at 298 K.

		δ (DMSO-d_6)	δ (CD_2Cl_2)	δ (CD_3NO_2/CD_2Cl_2 4:6)	δ (toluene-d_8)	δ (chlorobenzene-d_5)
1	a	7.55 (d, J = 7.7 Hz)	6.66 (d, J = 7.7 Hz)	6.77 (d, J = 7.5 Hz)	6.49 (d, J = 7.7 Hz)	6.72 (d, J = 7.5 Hz)
	b	7.69 (t, J = 7.7 Hz)	7.07 (t, J = 7.7 Hz)	7.15 (t, J = 7.4 Hz)	6.52 (t, J = 7.8 Hz)	6.74 (t, J = 7.8 Hz)
	c	7.79 (d, J = 7.6 Hz)	6.38 (d, J = 7.2 Hz)	6.42 (d, J = 7.5 Hz)	6.21 (dd, J = 6.7 Hz and 2.0 Hz)	6.25 (d, J = 6.6 Hz)

	d	7.48 (d, *J* = 7.7 Hz)	5.27 (d, *J* = 7.7 Hz)	5.32 (d, *J* = 7.7 Hz)	5.55 (d, *J* = 7.6 Hz)	5.53 (d, *J* = 7.6 Hz)
	e	7.38 (t, *J* = 7.6 Hz)	5.93 (t, *J* = 7.7 Hz)	5.93 (t, *J* = 7.7 Hz)	6.00 (t, *J* = 7.6 Hz)	5.96 (t, *J* = 8.2 Hz)
2	a	7.51 (d, *J* = 7.6 Hz)	6.50 (d, *J* = 7.6 Hz)	6.63 (d, *J* = 7.5 Hz)	6.31 (d, *J* = 7.0 Hz)	6.53 (d, *J* = 7.6 Hz)
	b	7.63 (t, *J* = 7.8 Hz)	7.07 (t, *J* = 7.7 Hz)	7.12 (t, *J* = 7.8 Hz)	6.41 (t, *J* = 7.6 Hz)	6.73 (t, *J* = 7.7 Hz)
	c	7.78 (d, *J* = 7.7 Hz)	6.39 (d, *J* = 7.6 Hz)	6.42 (d, *J* = 7.3 Hz)	6.15 (d, *J* = 7.6 Hz)	6.26 (d, *J* = 7.6 Hz)
	d	7.31 (s)	4.84 (s)	4.91(s)	5.11 (s)	5.11 (s)
3	a	7.66 (d, *J* = 7.7 Hz)	6.38 (d, *J* = 7.6 Hz)	6.47 (d, *J* = 7.4 Hz)	6.19 (d, *J* = 7.6 Hz)	6.32 (d, *J* = 7.6 Hz)
	b	7.80 (t, *J* = 7.7 Hz)	7.13 (t, *J* = 7.7 Hz)	7.19 (t, *J* = 8.2 Hz)	6.51 (t, *J* = 7.8 Hz)	6.81 (t, *J* = 7.6 Hz)
	c	7.87 (d, *J* = 7.8 Hz)	6.46 (d, *J* = 7.6 Hz)	6.50 (d, *J* = 7.9 Hz)	6.26 (d, *J* = 7.6 Hz)	6.33 (d, *J* = 7.6 Hz)
	d	7.41 (s)	5.67 (s)	5.65 (s)	5.99 (s)	5.99 (s)
4	a	7.57 (d, *J* = 7.4 Hz)	6.13 (d, *J* = 7.7 Hz)	—[a]	5.96 (d, *J* = 7.3 Hz)	—[a]
	b	7.80 (t, *J* = 7.8 Hz)	6.64 (t, *J* = 7.7 Hz)	—[a]	6.10 (t, *J* = 7.6 Hz)	—[a]
	c	7.85 (d, *J* = 7.5 Hz)	6.07 (d, *J* = 7.7 Hz)	—[a]	5.90 (d, *J* = 7.0 Hz)	—[a]
	d	7.41 (d, *J* = 7.5 Hz)	5.42 (d, *J* = 7.6 Hz)	—[a]	5.75 (d, *J* = 7.2 Hz)	—[a]
	e	6.94 (t, *J* = 7.4 Hz)	5.76 (t, *J* = 7.0 Hz)	—[a]	5.96 (t, *J* = 7.2 Hz)	—[a]
	f	7.98 (s)	7.43 (s)	—[a]	7.85 (s)	—[a]
5	a	7.55 (d, *J* = 7.6 Hz)	6.10 (dd, *J* = 7.7 Hz and 0.8 Hz)	—[a]	5.91 (d, *J* = 7.6 Hz)	—[a]
	b	7.76 (t, *J* = 7.7 Hz)	6.63 (t, *J* = 7.7 Hz)	—[a]	6.11 (t, *J* = 7.7 Hz)	—[a]
	c	7.84 (d, *J* = 7.6 Hz)	6.01 (dd, *J* = 7.7 Hz and 0.8 Hz)	—[a]	5.88 (d, *J* = 7.6 Hz)	—[a]
	d	7.51 (dd, *J* = 9.2 Hz and 1.1 Hz)	4.95 (d, *J* = 9.3 Hz)	—[a]	5.37 (d, *J* = 9.2 Hz)	—[a]
	e	7.92 (s)	7.16 (s)	—[a]	7.57 (s)	—[a]
6	a	7.68 (d, *J* = 7.4 Hz)	6.13 (d, *J* = 8.2 Hz)	—[a]	5.91 (d, *J* = 7.6 Hz)	—[a]
	b	7.67 (t, *J* = 7.8 Hz)	6.68 (t, *J* = 7.9 Hz)	—[a]	6.12 (t, *J* = 7.7 Hz)	—[a]
	c	7.65 (d, *J* = 7.5 Hz)	6.11 (d, *J* = 8.0 Hz)	—[a]	5.87 (d, *J* = 7.7 Hz)	—[a]
	d	7.33 (d, *J* = 6.6 Hz)	5.08 (d, *J* = 6.7 Hz)	—[a]	5.31 (d, *J* = 6.4 Hz)	—[a]

[a] not measured.

Table S2. The chemical shift differences (ppm) of **1**–**6** (1.0~4.0 mM) in water-saturated CD_2Cl_2, CD_3NO_2/water-saturated CD_2Cl_2 (4:6, v/v), water-saturated toluene-d_8, water-saturated chlorobenzene-d_5 and DMSO-d_6 at 298 K.

		δ (DMSO-d_6) − δ (CD_2Cl_2)	δ (DMSO-d_6) − δ (CD_3NO_2/CD_2Cl_2 4:6)	δ (DMSO-d_6) − δ (toluene-d_8)	δ (DMSO-d_6) − δ (chlorobenzene-d_5)
1	a	0.89	0.78	1.06	0.83
	b	0.62	0.54	1.17	0.95
	c	1.41	1.37	1.58	1.54
	d	2.21	2.16	1.93	1.95
	e	1.45	1.45	1.38	1.42
2	a	1.01	0.88	1.2	0.98
	b	0.56	0.51	1.22	0.9
	c	1.39	1.36	1.63	1.52
	d	2.47	2.4	2.2	2.2
3	a	1.28	1.19	1.47	1.34
	b	0.67	0.61	1.29	0.99
	c	1.41	1.37	1.61	1.54
	d	1.74	1.76	1.42	1.42
4	a	1.44	—[a]	1.61	—[a]
	b	1.16	—[a]	1.7	—[a]
	c	1.78	—[a]	1.95	—[a]
	d	2.15	—[a]	1.82	—[a]
	e	1.18	—[a]	0.98	—[a]
	f	0.55	—[a]	0.13	—[a]
5	a	1.45	—[a]	1.64	—[a]
	b	1.13	—[a]	1.65	—[a]
	c	1.83	—[a]	1.96	—[a]
	d	2.56	—[a]	2.14	—[a]
	e	0.76	—[a]	0.35	—[a]
6	a	1.55	—[a]	1.77	—[a]
	b	1.12	—[a]	1.68	—[a]
	c	1.74	—[a]	1.98	—[a]
	d	2.25	—[a]	2.02	—[a]

[a] not measured.

2.2 Temperature-dependent ^{1}H NMR spectra

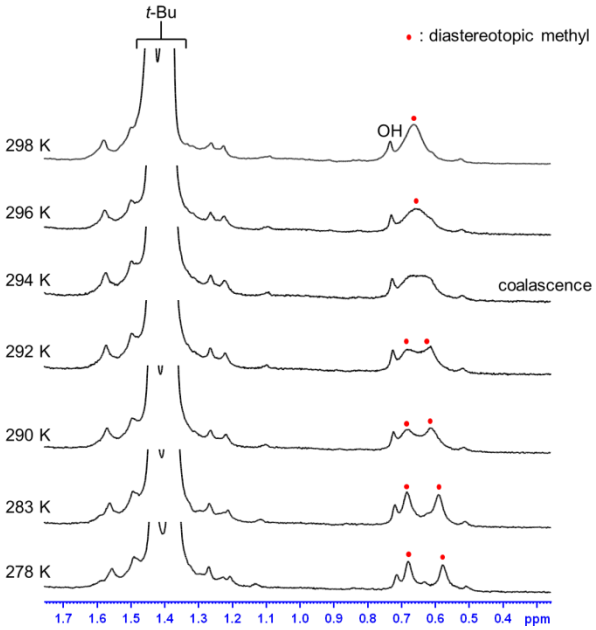


Fig S7. Temperature-dependent ^{1}H NMR spectra of **1** (1.0 mM) in CD_3NO_2/water-saturated CD_2Cl_2 (4:6, v/v).

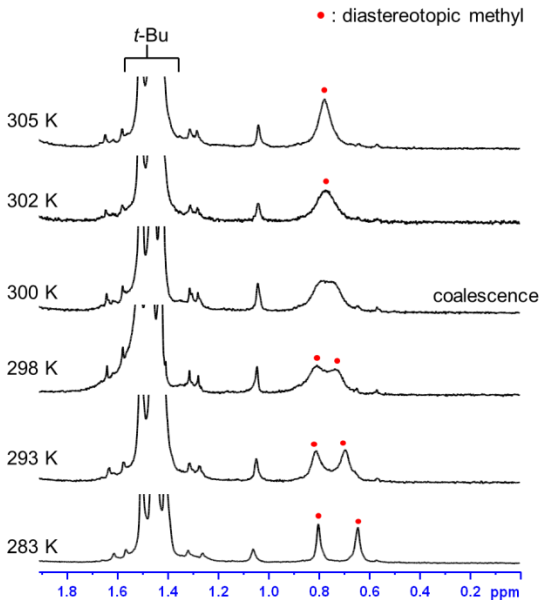


Fig S8. Temperature-dependent ^{1}H NMR spectra of **2** (1.0 mM) in CD_3NO_2/water-saturated CD_2Cl_2 (4:6, v/v).

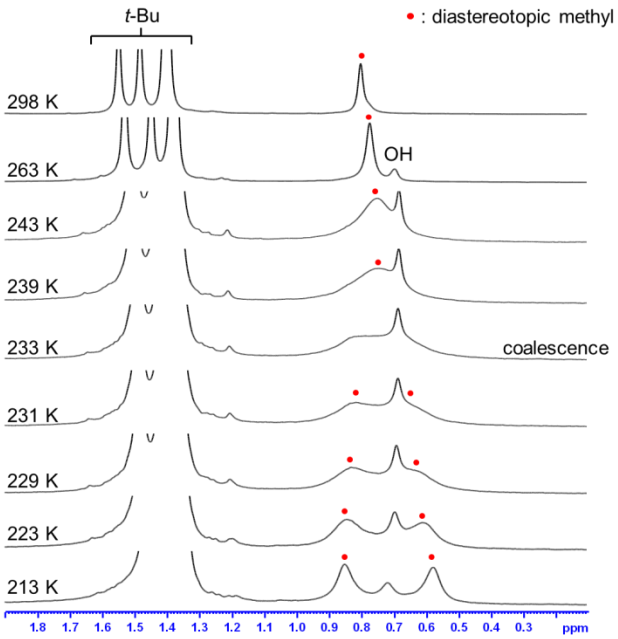


Fig S9. Temperature-dependent ^{1}H NMR spectra of **4** (4.0 mM) in water-saturated CD_2Cl_2.

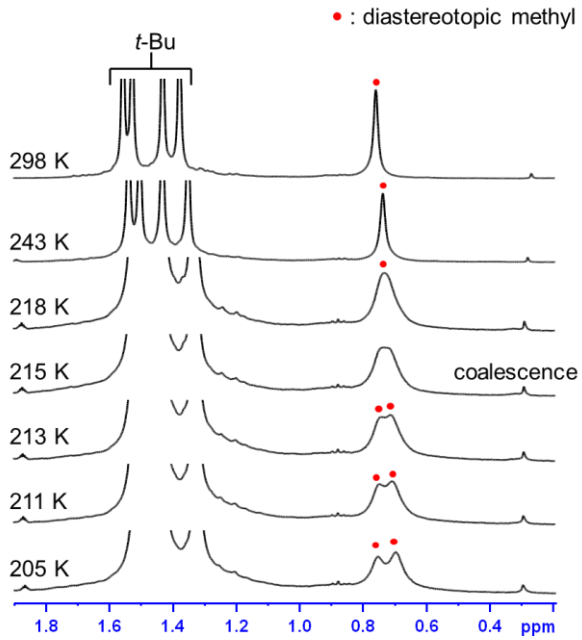


Fig S10. Temperature-dependent ^{1}H NMR spectra of **4** (4.0 mM) in water-saturated toluene-d_8.

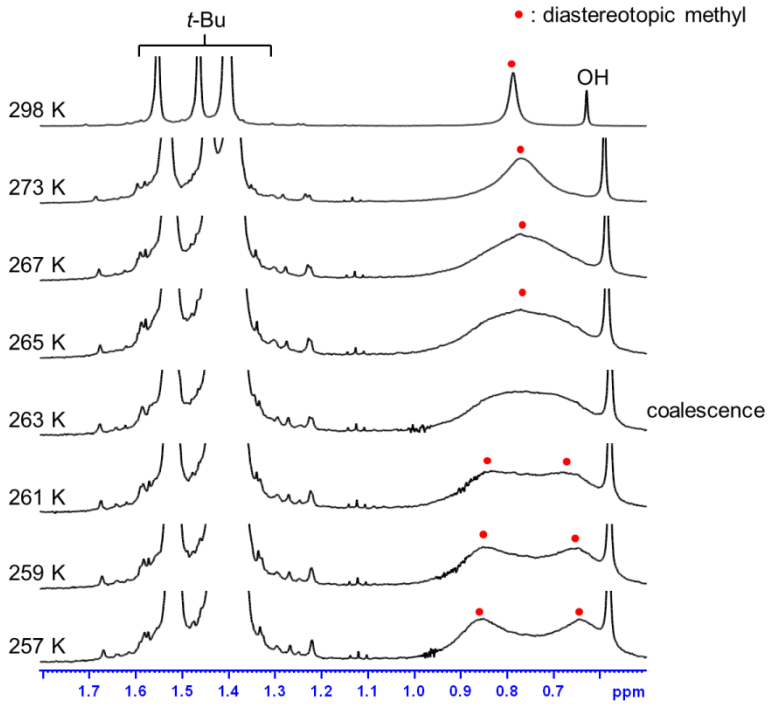


Fig S11. Temperature-dependent ^{1}H NMR spectra of **5** (4.0 mM) in water-saturated CD_2Cl_2.

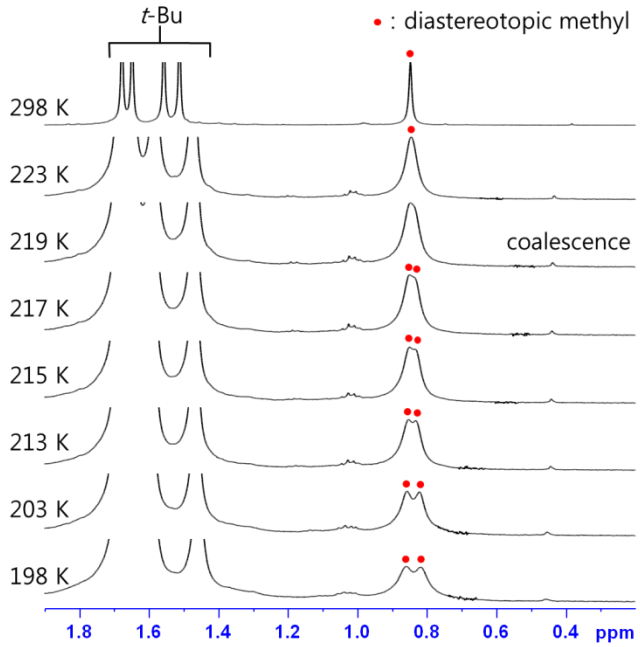


Fig S12. Temperature-dependent ^{1}H NMR spectra of **5** (4.0 mM) in water-saturated toluene-d_8.

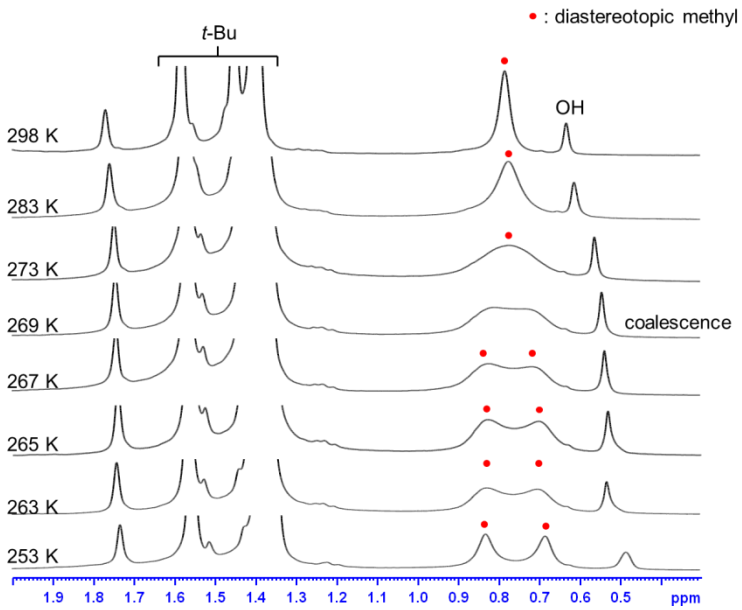


Fig S13. Temperature-dependent ^{1}H NMR spectra of **6** (4.0 mM) in water-saturated CD_2Cl_2.

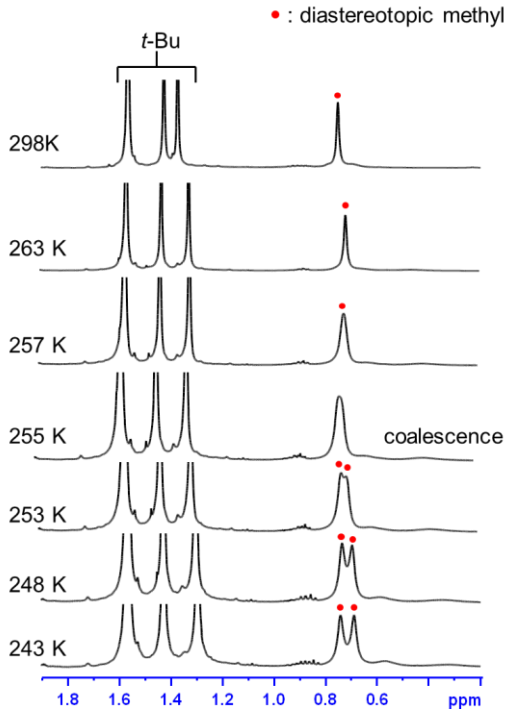


Fig S14. Temperature-dependent ^{1}H NMR spectra of **6** (4.0 mM) in water-saturated toluene-d_8.

The exchange rate constant (k) at the coalescence temperature[S7] was calculated employing the equations (1), (2), (6), and (7) shown below where ν_A and ν_B were the peak frequencies (Hz) of each exchangeable component.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \quad (1)$$

$$k = k_1 + k_{-1} \quad (2)$$

$$k = \frac{\pi \Delta \nu}{\sqrt{2}} \quad (6)$$

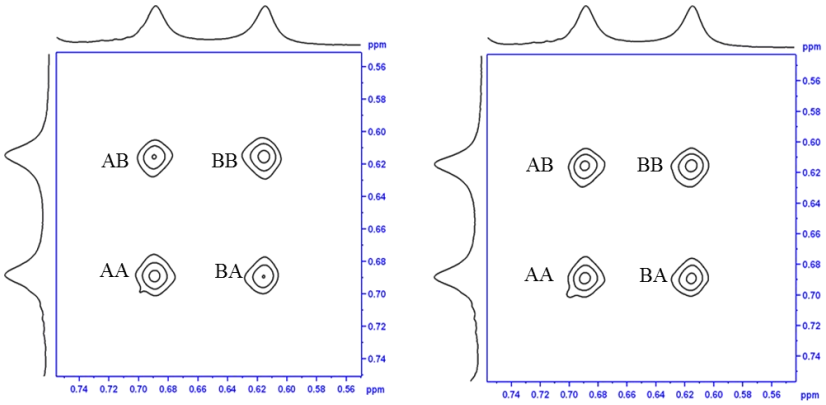
$$\Delta \nu = \nu_A - \nu_B \quad (7)$$

2.3 2D-EXSY NMR spectra

2D-EXSY NMR studies[S8] : Each of compounds **1**, **2** and **3** (4.0 mM) was prepared in a NMR tube and the solution was degassed using the freeze-pump-thaw method under nitrogen. The EXSY spectra of **1**, **2** and **3** were recorded with the phase sensitive NOESY pulse sequence supplied with the Bruker software. TPPI was used to obtain quadrature detection in F1. Each of the 128 F1 increments was the accumulation of 2–16 scans.

[S7] H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, VCH, Weinheim, 1991, pp. 269-273.

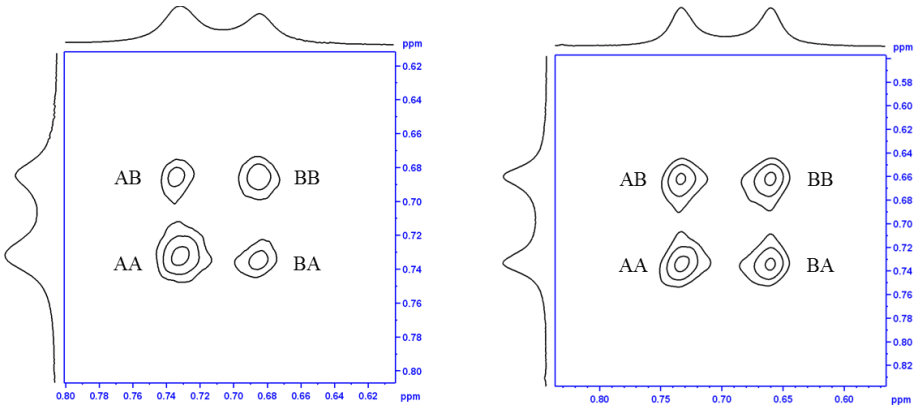
[S8] (a) C. L. Perrin and T. J. Dwyer, *Chem. Rev.*, 1990, **90**, 935; (b) S.-Y. Chang, J. S. Choi and K.-S. Jeong, *Chem. Eur. J.*, 2001, **7**, 2687; (c) Q. Gan, Y. Ferrand, D. Bao, B. Kauffman, A. Grélard, H. Jiang and I. Huc, *Science*, 2011, **331**, 1172; (d) Y. Ferrand, N. Chandramouli, A. M. Kendhale, C. Aube. B. Kauffmann, A. Grélard, M. Laguerre, D. Dubreuil and I. Huc, *J. Am. Chem. Soc.*, 2012, **134**, 11282.



τ_m = 0.1 s
k = 19.0 s^{-1}
$\Delta G^{\ddagger}$ = 15.7kcal/mol

τ_m = 0.2 s
k = 18.4 s^{-1}
$\Delta G^{\ddagger}$ = 15.8kcal/mol

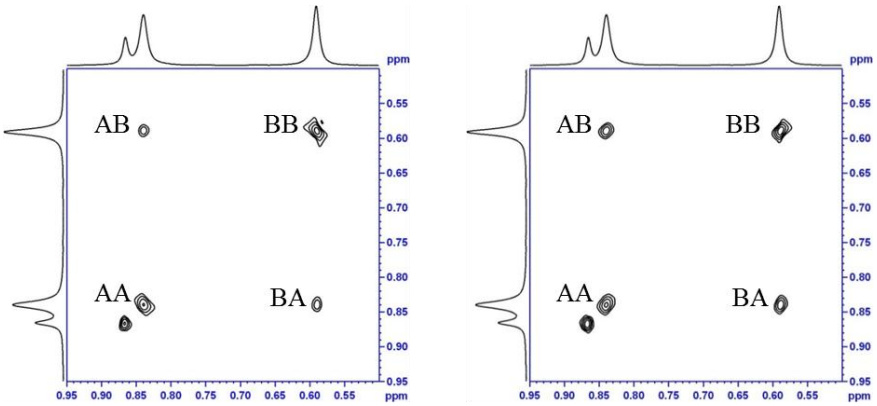
Fig S15. EXSY spectra (water-saturated toluene-d_8, 25 ℃) of **1** (4.0 mM). The exchange rate constant (k) and free energy barrier ($\Delta G^{\ddagger}$) were determined with two different mixing times (τ_m).



τ_m = 0.1 s
k = 9.8 s^{-1}
$\Delta G^{\ddagger}$ = 16.1 kcal/mol

τ_m = 0.2 s
k = 13.9 s^{-1}
$\Delta G^{\ddagger}$ = 15.9 kcal/mol

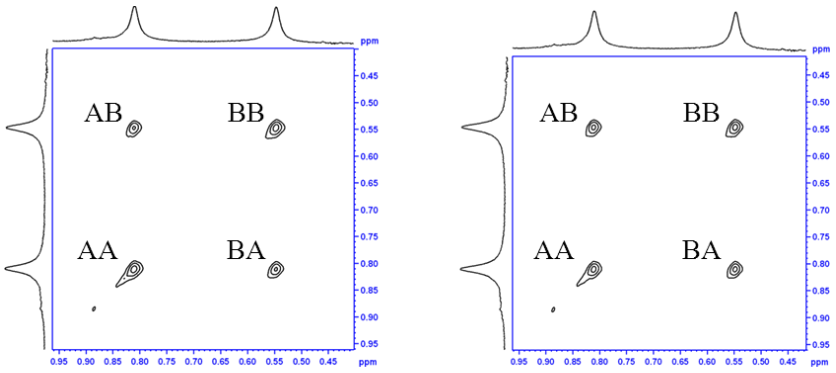
Fig S16. EXSY spectra (water-saturated chlorobenzene-d_5, 25 ℃) of **1** (4.0 mM). The exchange rate constant (k) and free energy barrier ($\Delta G^{\ddagger}$) were determined with two different mixing times (τ_m).



τ_m = 0.1 s
k = 5.1 s^{-1}
$\Delta G^{\ddagger}$ = 16.5 kcal/mol

τ_m = 0.2 s
k = 1.7 s^{-1}
$\Delta G^{\ddagger}$ = 16.3 kcal/mol

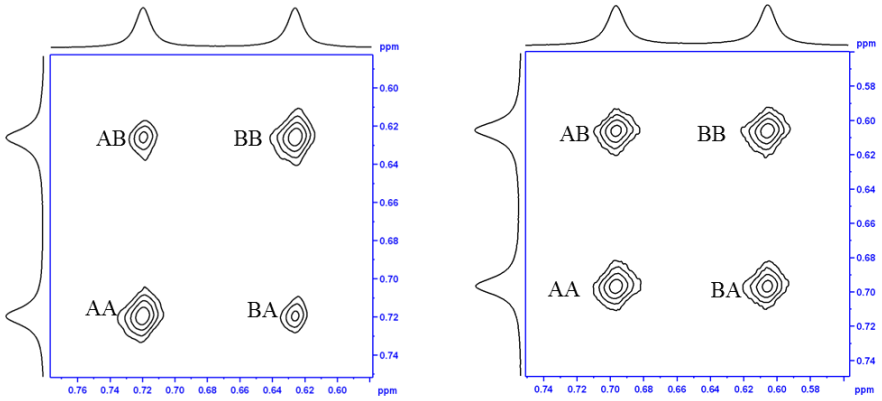
Fig S17. EXSY spectra (water-saturated CD_2Cl_2, 25 ℃) of **2** (4.0 mM). The exchange rate constant (k) and free energy barrier ($\Delta G^{\ddagger}$) were determined with two different mixing times (τ_m).



τ_m = 0.1 s
k = 13.9 s^{-1}
$\Delta G^{\ddagger}$ = 16.2 kcal/mol

τ_m = 0.2 s
k = 11.9 s^{-1}
$\Delta G^{\ddagger}$ = 16.3 kcal/mol

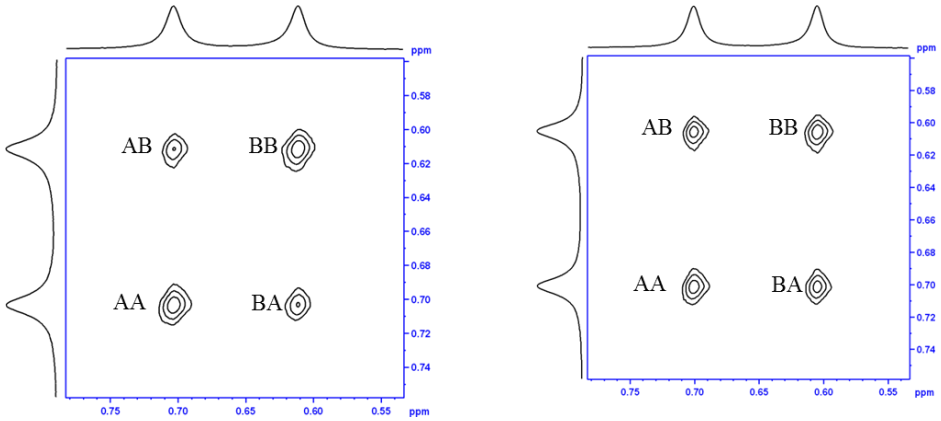
Fig S18. EXSY spectra (water-saturated CD_2Cl_2, 30 ℃) of **2** (4.0 mM). The exchange rate constant (k) and free energy barrier ($\Delta G^{\ddagger}$) were determined with two different mixing times (τ_m).



τ_m =0.1 s
k =6.0 s^{-1}
$\Delta G^{\ddagger}$ =16.4 kcal/mol

τ_m =0.2 s
k =11.9 s^{-1}
$\Delta G^{\ddagger}$ =16.0 kcal/mol

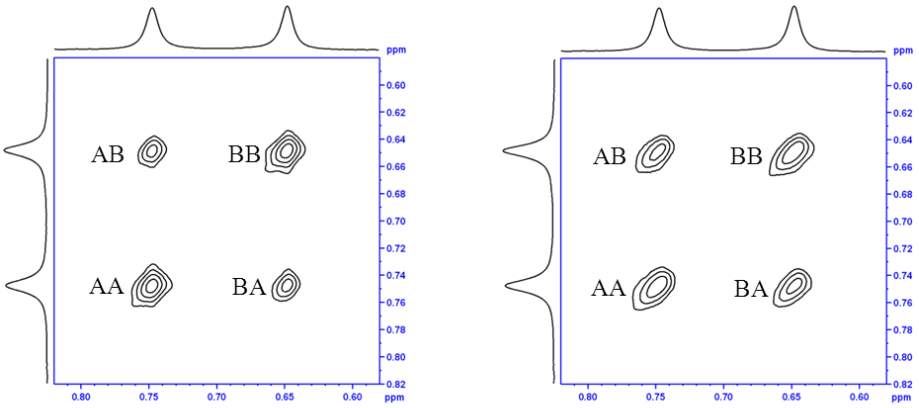
Fig S19. EXSY spectra (water-saturated toluene-d_8, 25 ℃) of **2** (4.0 mM). The exchange rate constant (k) and free energy barrier ($\Delta G^{\ddagger}$) were determined with two different mixing times (τ_m).



τ_m = 0.1 s
k=10.9 s^{-1}
$\Delta G^{\ddagger}$ = 16.3 kcal/mol

τ_m = 0.2 s
k=11 s^{-1}
$\Delta G^{\ddagger}$ = 16.3 kcal/mol

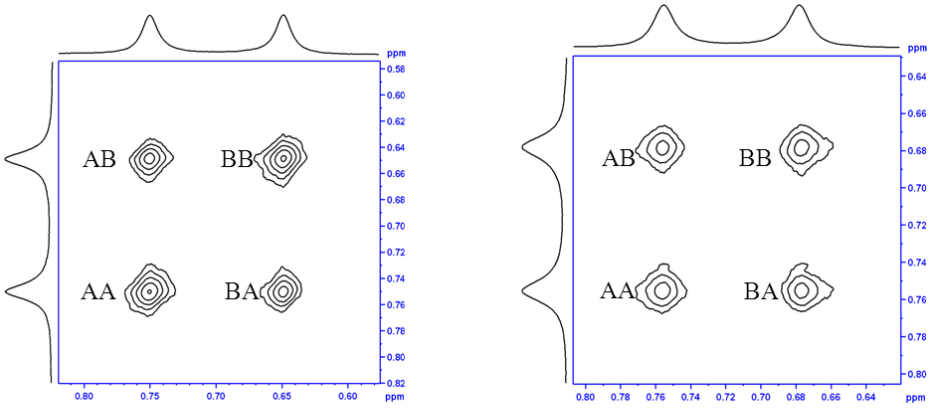
Fig S20. EXSY spectra (water-saturated toluene-d_8, 30 ℃) of **2** (4.0 mM). The exchange rate constant (k) and free energy barrier ($\Delta G^{\ddagger}$) were determined with two different mixing times (τ_m).



τ_m = 0.1 s
k = 7.7 s^{-1}
$\Delta G^{\ddagger}$ =16.2 kcal/mol

τ_m = 0.2 s
k = 8.4 s^{-1}
$\Delta G^{\ddagger}$ =16.2 kcal/mol

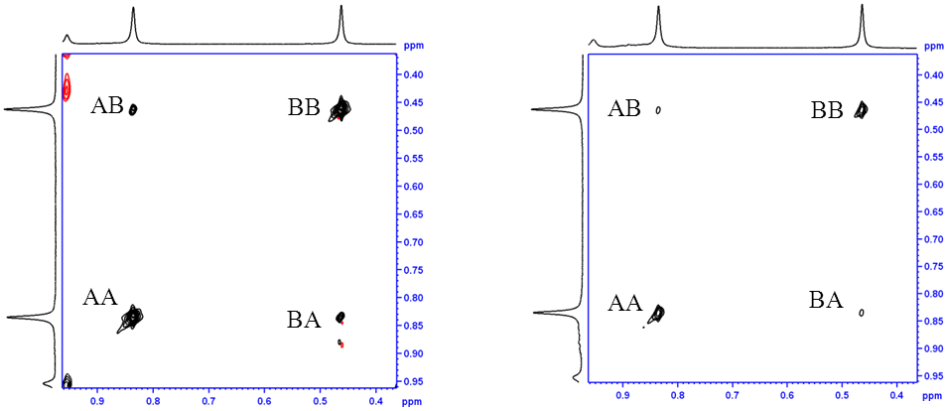
Fig S21. EXSY spectra (water-saturated chlorobenzene-d_5, 25 ℃) of **2** (4.0 mM). The exchange rate constant (k) and free energy barrier ($\Delta G^{\ddagger}$) were determined with two different mixing times (τ_m).



τ_m =0.1 s
k =14.0 s^{-1}
$\Delta G^{\ddagger}$ =16.2 kcal/mol

τ_m =0.2 s
k =14.1 s^{-1}
$\Delta G^{\ddagger}$ =16.2 kcal/mol

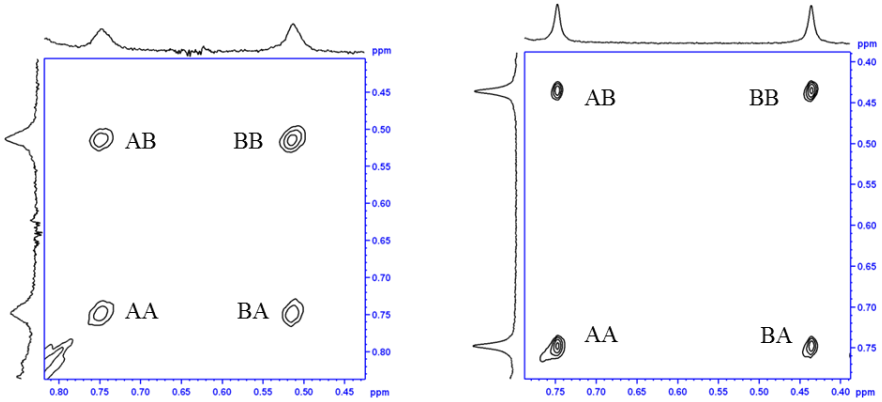
Fig S22. EXSY spectra (water-saturated chlorobenzene-d_5, 30 ℃) of **2** (4.0 mM). The exchange rate constant (k) and free energy barrier ($\Delta G^{\ddagger}$) were determined with two different mixing times (τ_m).



τ_m = 0.2 s
k = 0.64 s^{-1}
$\Delta G^{\ddagger}$ = 18.3 kcal/mol

τ_m = 0.4 s
k = 0.31 s^{-1}
$\Delta G^{\ddagger}$ = 18.8 kcal/mol

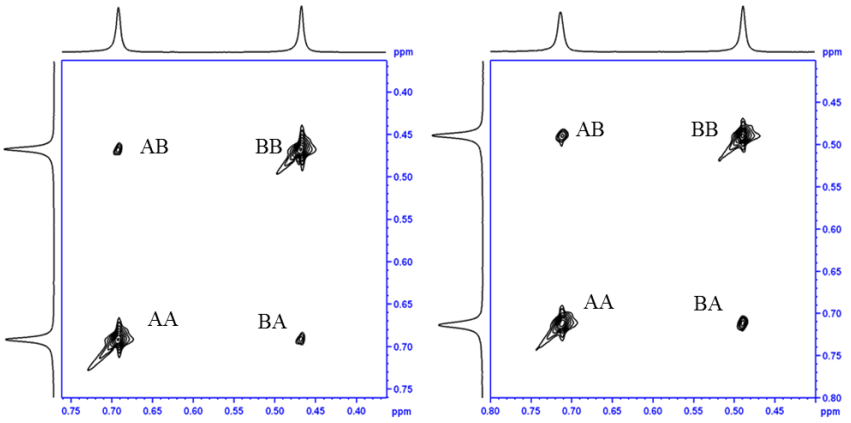
Fig S23. EXSY spectra (water-saturated CD_2Cl_2, 35 ℃) of **3** (4.0 mM). The exchange rate constant (k) and free energy barrier ($\Delta G^{\ddagger}$) were determined with two different mixing times (τ_m).



τ_m = 0.2 s
k = 10.0 s^{-1}
$\Delta G^{\ddagger}$ = 16.6 kcal/mol

τ_m = 0.4 s
k = 4.8 s^{-1}
$\Delta G^{\ddagger}$ = 17.1 kcal/mol

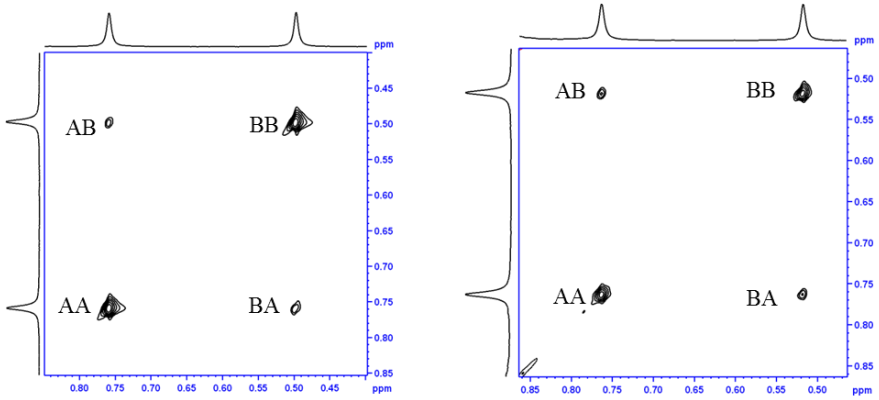
Fig S24. EXSY spectra (40% CD_3NO_2 in water-saturated CD_2Cl_2, 35 ℃) of **3** (4.0 mM). The exchange rate constant (k) and free energy barrier ($\Delta G^{\ddagger}$) were determined with two different mixing times (τ_m).



τ_m = 0.2 s
k = 0.37 s^{-1}
$\Delta G^{\ddagger}$ = 18.6 kcal/mol

τ_m = 0.4 s
k = 0.43 s^{-1}
$\Delta G^{\ddagger}$ = 18.6 kcal/mol

Fig S25. EXSY spectra (water-saturated toluene-d_8, 35 ℃) of **3** (4.0 mM). The exchange rate constant (k) and free energy barrier ($\Delta G^{\ddagger}$) were determined with two different mixing times (τ_m).



τ_m = 0.2 s
k = 0.58 s^{-1}
$\Delta G^{\ddagger}$ = 18.4 kcal/mol

τ_m = 0.4 s
k = 0.73 s^{-1}
$\Delta G^{\ddagger}$ = 18.2 kcal/mol

Fig S26. EXSY spectra (water-saturated chlorobenzene-d_5, 35 ℃) of **3** (4.0 mM). The exchange rate constant (k) and free energy barrier ($\Delta G^{\ddagger}$) were determined with two different mixing times (τ_m).

Exchange rate constants (k) and free energy barriers ($\Delta G^{\ddagger}$) were calculated employing equations (1)–(5) shown below, where I_{AB} and I_{BA} were cross peak volumes, and I_{AA} and I_{BB} were diagonal peak volumes.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \quad (1)$$

$$k = k_1 + k_{-1} \quad (2)$$

$$k = \frac{1}{\tau_m} \times \ln\frac{r+1}{r-1} \quad (3)$$

$$r = \frac{I_{AA}+I_{BB}}{I_{AB}+I_{BA}} \quad (4)$$

$$\Delta G^{\ddagger} = -RT\ln\frac{kh}{k_B T} \quad (5)$$

($R = 1.9872$ cal·K^{-1}·mol^{-1}, $k_B = 3.2995 \times 10^{-24}$ cal·K^{-1}, $h = 1.5836 \times 10^{-34}$ cal·s)

2.4 Activation free energies ($\Delta G^{\ddagger}$)

Table S3. Activation free energies (kcal/mol)[a] for inter-conversion of *P* and *M* helices in four different media[b]

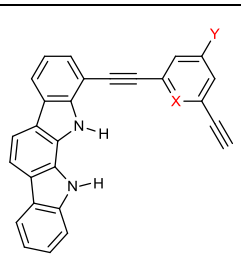
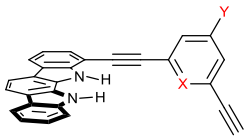
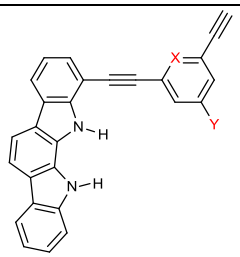
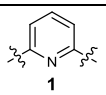
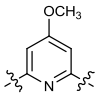
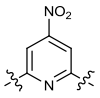
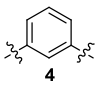
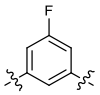
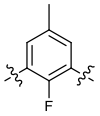
		CD_2Cl_2		40% CD_3NO_2 in CD_2Cl_2[c]		Toluene-d_8		Chlorobenzene-d_5	
	Method	T (℃)	$\Delta G^{\ddagger}$	T (℃)	$\Delta G^{\ddagger}$	T (℃)	$\Delta G^{\ddagger}$	T (℃)	$\Delta G^{\ddagger}$
1	EXSY	25	15.6 ± 0.2	—[d]	—[d]	25	15.8 ± 0.1	25	16.0 ± 0.1
	Coalescence	—[d]	—[d]	21	14.7	—[d]	—[d]	—[d]	—[d]
2	EXSY	25	16.4 ± 0.1	—[d]	—[d]	25	16.2 ± 0.2	25	16.2 ± 0.1
	EXSY	30	16.2 ± 0.1	—[d]	—[d]	30	16.3 ± 0.1	30	16.2 ± 0.1
	Coalescence	—[d]	—[d]	27	14.6	—[d]	—[d]	—[d]	—[d]
3	EXSY	35	18.5 ± 0.2	35	17.0 ± 0.3	35	18.6 ± 0.1	35	18.3 ± 0.1
4	Coalescence	−40	11.0	—[d]	—[d]	−58	10.8	—[d]	—[d]
5	Coalescence	−10	12.4	—[d]	—[d]	−54	11.1	—[d]	—[d]
6	Coalescence	−4	13.1	—[d]	—[d]	−18	12.9	—[d]	—[d]

[a] 2D-EXSY experiments were all at least duplicated using different mixing times (100 and 200 ms). [b] Water-saturated deuterated solvents were used. [c] Prepared by mixing 40% (v/v) CD_3NO_2 in water-saturated CD_2Cl_2. [d] Not determined.

3. Computer modeling

Energy-minimized structures were generated using MacroModeling 9.1[S9] program with MMFFs force field[S10] in the chloroform solvent. Higher energy structures were generated by dihedral driving calculation.

Table S4. Relative conformational energies (kJ/mol) of indolocarbazole-arylethynes

Conformation / Aryl ring	 **A** (syn-coplanar)	 **B** (perpendicular)	 **C** (anti-coplanar)
 **1**	0 (most stable)	+ 4.3	+ 7.1
 **2**	0 (most stable)	+ 4.3	+ 6.4
 **3**	0 (most stable)	+ 4.7	+ 6.8
 **4**	+ 1.5	0 (most stable)	+ 1.8
 **5**	+ 1.4	0 (most stable)	+ 1.5
 **6**	0 (most stable)	+ 3.2	+ 5.0

[S9] (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. Comput. Chem.*, 1990, **11**, 440; (b) MacroModel, version 9.1, Schrödinger, LLC, New York, NY, 2005.

[S10] T. A. Halgren, *J. Comput. Chem.*, 1996, **17**, 490.