Supporting Information

Oligoindole-Based Foldamers with a Helical Conformation Induced by Chloride

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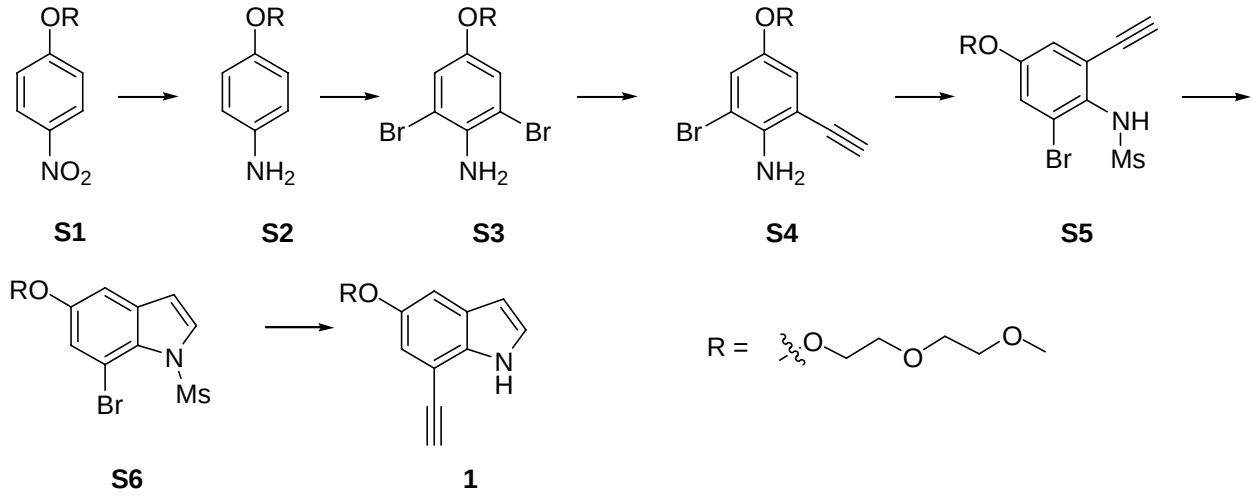
Contents

1. Synthesis

1.1 Synthesis of Monoindole **1**



S1 **S2** **S3** **S4** **S5**

S6 **1**

4-(2-(2-Methoxyethoxy)ethoxyl)aniline (**S2**)**: S1** was prepared from *p*-nitrophenol as follows: *p*-Nitrophenol (10 g, 75 mmol) and diethylene glycol monomethyl ether monotosylate (18 g, 71 mmol) was dissolved in DMF (140 mL), and K_2CO_3 (4.9 g, 35 mmol) was added. The solution was stirred at 65–70 ^oC for 19 h. The solvent was removed and the residue was dissolved in EtOAc (250 mL), and washed with 1N NaOH aqueous solution (200 mL × 2) and brine (100 mL × 2). The organic layer was dried over anhydrous Na_2SO_4 and was concentrated to give **S1** (16 g, 94 %): mp 80-81 ^oC; ^1H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, J = 8.5 Hz, 2H), 6.97 (d, J = 8.5 Hz, 2H), 4.23 (m, 2H), 3.89 (m, 2H), 3.71 (m, 2H), 3.57 (m, 2H), 3.38 (s, 3H; OCH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ 164.2, 142.0, 126.2, 114.9, 72.3, 71.2, 69.7, 68.5, 59.4; IR (KBr) 1608 (C=C), 1514 (N=O) cm^{-1}.

S1 (14 g, 58 mmol) was dissolved in EtOAc (160 mL) and Pd/C (1.4 g, 10 wt %) was suspended, which was stirred at room temperature for 10 h under hydrogen atmosphere (H_2 balloon). The solution was filtered through celite and concentrated to give **S2** as a reddish oil (12 g, 96 %): ^1H NMR (500 MHz, DMSO-d_6) δ 6.68 (d, J = 8.5 Hz, 2H), 6.55 (d, J = 8.5 Hz, 2H), 4.56 (s, 2H; NH_2), 3.94 (m, 2H), 3.68 (m, 2H), 3.58 (m, 2H), 3.47 (m, 2H), 3.26 (s, 3H; OCH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 150.0, 142.5, 115.4, 115.1, 71.4, 69.8, 69.3, 67.7, 58.1; IR (thin film) 3430(NH_2) cm^{-1}.

2,6-Dibromo-4-(2-(2-methoxyethoxy)ethoxyl)aniline (**S3**): To a solution of **S2** (13 g, 63 mmol) in 60

mL CH_2Cl_2/MeOH(1:1) was added dropwise a solution of Br_2 (8 mL, 156 mmol) in 60 mL CH_2Cl_2/MeOH(1:1) under N_2 at 0 ^oC. After stirred at room temperature for 30 h, the solution was concentrated. The residue was taken up in CH_2Cl_2 (200 mL), and washed sequentially with 1N NaOH aqueous solution (200 mL × 2), saturated $Na_2S_2O_3.5H_2O$ (100 mL × 2), and brine (100 mL × 2). The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, EtOAc/hexanes = 1:3) to give **S3** as a brownish oil (15 g, 66%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.05 (s, 2H), 4.20 (s, 2H; NH_2), 4.04 (m, 2H), 3.80 (m, 2H), 3.69 (m, 2H), 3.57 (m, 2H), 3.39 (s, 3H; OCH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 136.8, 119.5, 109.3, 72.3, 71.1, 70.0, 69.1, 59.4; IR (thin film) 3458(NH_2) cm^{-1}. Anal. Calcd for $C_{11}H_{15}Br_2NO_3$: C, 35.80; H, 4.10; N, 3.80. Found: C, 36.30; H, 4.15; N, 3.72.

2-Bromo-6-ethynyl-4-(2-(2-methoxyethoxy)ethoxyl)aniline (**S4**):[1] **S3** (15 g, 40.6 mmol), CuI (0.19 g, 0.025 equiv) and $Pd(PPh_3)_2Cl_2$ (0.57 g, 0.025 equiv) were placed in a Schlenk flask. The flask was degassed under high vacuum and back-filled with nitrogen, which process was repeated three times. Degassed tetrahydrofuran (THF, 50 mL), triethylamine (Et_3N, 150 mL) and trimethylsilyl(TMS)-ethyne (5.7 mL, 40.6 mmol) were added, and the resulting solution was stirred under nitrogen at 80–82 ^oC for 14 h. After cooled to ambient temperature, the reaction mixture was filtered through celite and concentrated. The residue was dissolved in $CHCl_3$ (150 mL), and washed with saturated $NaHCO_3$ solution (100 mL × 2) and brine (100 mL × 1). The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, EtOAc/hexanes = 1:3) to give a TMS-protected precursor as a yellowish oil (7.8 g, 50 %): ^1H NMR (500 MHz, DMSO-d_6) δ 7.13 (d, J = 2.0 Hz, 1H), 6.86 (d, J = 2.0 Hz, 1H), 4.85 (s, 2H; NH_2), 3.99 (m, 2H), 3.65 (m, 2H), 3.56 (m, 2H), 3.45 (m, 2H), 3.24 (s, 3H; OCH_3), 0.25 (s, 9H; $Si(CH_3)_3$); ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.4, 141.2, 121.4, 117.0, 108.0, 107.7, 101.4, 100.3, 71.3, 70.0, 68.9, 68.3, 58.1, 0.25; IR (thin film)

[1] (a) Sonogashira, K. In Metal-Catalyzed Cross-Coupling Reactions; Diederch, F.; Stang, P. J. Eds.; Wiley: Weinheim (Germany), 1997; Chapter 5, pp 203-229. (b) Zhang, J.; Pesak, D. J.; Ludwick, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4227. (c) Erdelyi, M.; Gogoll, A. *J. Org. Chem.* **2001**, *66*, 4165.

3470(NH_2), 2146(C≡ C) cm^{-1}. Anal. Calcd for $C_{16}H_{24}BrNO_3Si$: C, 49.74; H, 6.26; N, 3.63. Found: C, 50.12; H, 6.31; N, 4.17.

The TMS group (7.2 g, 18.6 mmol) was removed by stirring the precursor in MeOH (70 mL) containing K_2CO_3 (0.51 g, 3.72 mmol) at room temperature for 5 min to give **S4** as a yellow liquid (5.7 g, 97 %): ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.16 (d, J = 2.0 Hz, 1H), 6.92 (d, J = 2.0 Hz, 1H), 4.92 (s, 2H; NH_2), 4.52 (s, 1H; C≡CH), 4.02 (m, 2H), 3.69 (m, 2H), 3.58 (m, 2H), 3.47 (m, 2H); 3.26 (s, 3H; OCH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.3, 141.3, 120.9, 117.7, 107.9, 107.2, 86.3, 80.0, 71.2, 69.6, 68.9, 68.2, 58.0; IR (thin film) 3463(NH_2), 3284(C(sp)-H), 2097(C≡ C) cm^{-1}. Anal. Calcd for $C_{13}H_{16}BrNO_3$: C, 49.70; H, 5.13; N, 4.46. Found: C, 49.89; H, 5.09; N, 4.23.

Compound **S5**: **S4** (5.7 g, 18 mmol), DMAP (0.44 g, 3.6 mmol) and pyridine (4.4 mL) were dissolved in dry CH_2Cl_2 (80 mL) and MsCl (2.1 mL, 27 mmol) was added at 0 ^{o}C (ice-water bath). The solution was stirred under argon for 20 h and concentrated. The residue was directly subjected to column chromatography (silica gel, EtOAc/hexanes = 1:1) to give **S5** as a white solid (3.8 g, 54 %): mp 115–116 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.32 (s, 1H; NH), 7.37 (s, 1H), 7.14 (s, 1H), 4.48 (s, 1H; C≡CH), 4.17 (m, 2H), 3.73 (m, 2H), 3.59 (m, 2H), 3.49 (m, 2H), 3.26 (s, 3H; mesyl-CH_3), 3.14 (s, 3H; OCH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.1, 130.3, 127.0, 126.0, 120.8, 118.9, 86.5, 81.4, 71.9, 70.3, 69.3, 68.8, 58.7, 44.4; IR (KBr) 3419(NH) cm^{-1}. Anal. Calcd for $C_{14}H_{18}BrNO_5S$: C, 42.87; H, 4.63; N, 3.57. Found: C, 42.93; H, 4.58; N, 3.59.

Compound **S6**: A solution of **S5** (3.5 g, 8.9 mmol) and $Cu(OAc)_2$ (0.16 g, 0.89 mmol) in dry 1,2-dichloromethane (60 mL) was refluxed at 90–93 ^{o}C under nitrogen for 1 h.[2] The solution was concentrated and the residue was purified by column chromatography (silica gel, EtOAc/hexanes = 1:1) to give **S6** as an oily liquid (3.2 g, 91 %): ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.66 (d, J = 3.0 Hz, 1H), 7.25 (s, 1H), 7.22 (s, 1H), 6.74 (d, J = 3.0 Hz, 1H), 4.13 (m, 2H), 3.82 (s, 3H; mesyl-CH_3), 3.74 (m, 2H), 3.58 (m, 2H), 3.46 (m, 2H), 3.24 (s, 3H; OCH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.0, 135.1, 130.8,

[2] Hiroya, K.; Itoh, S.; Sakamoto, T. *J. Org. Chem*. **2004**, *69*, 1126.

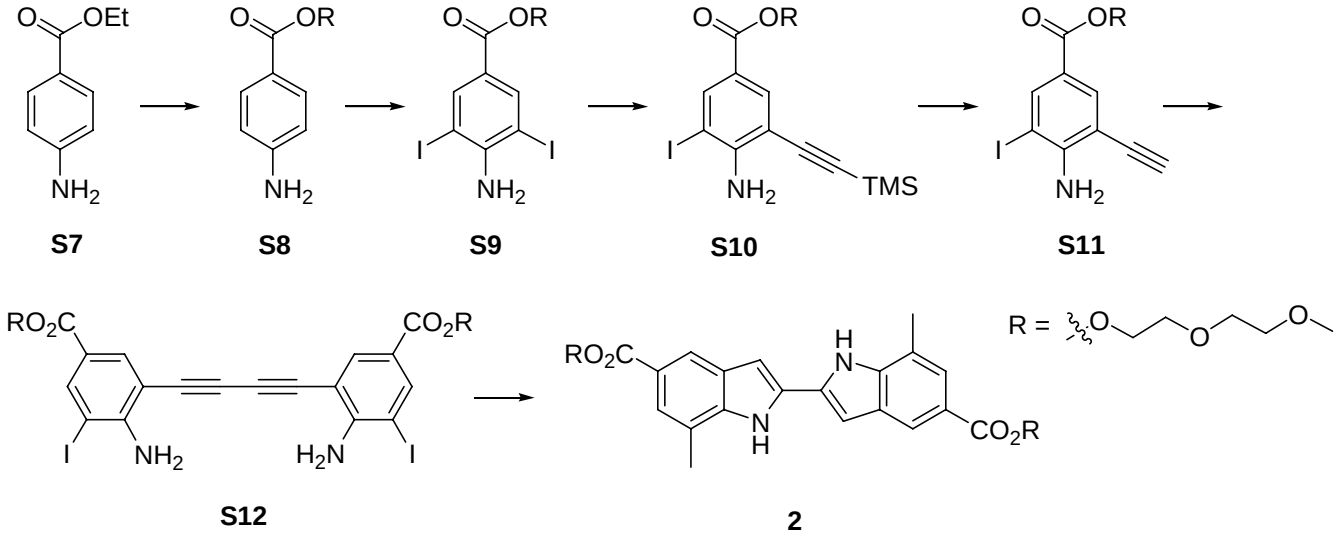
127.5, 118.8, 107.0, 105.0, 104.9, 71.3, 69.8, 68.9, 68.0, 58.1, 44.3; IR (thin film) 1364(S=O), 1174(S=O) cm^{-1}. Anal. Calcd for $C_{14}H_{18}BrNO_5S$: C, 42.87; H, 4.63; N, 3.57. Found: C, 42.93; H, 4.64; N, 3.41.

Monoindole **1**: **S6** (3.0 g, 7.65 mmol), PPh_3 (0.20 g, 0.77 mmol), CuI (29 mg, 0.15 mmol) and $Pd(dba)_2$ (88 mg, 0.15 mmol) were placed in a Schlenk flask. The flask was degassed under high vacuum and back-filled with nitrogen, which process was repeated three times. Degassed THF (10 mL), Et_3N (50 mL) and TMS-ethyne (3.2 mL, 23 mmol) were added, and the resulting solution was stirred under nitrogen at 80–82 ^oC for 13 h. After cooled to ambient temperature, the reaction mixture was filtered through celite and concentrated. The residue was dissolved in EtOAc (45 mL), and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, EtOAc/hexanes = 1:2) to give a precursor (3.0 g, 94 %), which contains both TMS and Ms groups: ^1H NMR (500 MHz, DMSO-d_6) δ 7.65 (d, J = 3.5 Hz, 1H), 7.34 (s, 1H), 7.08 (s, 1H), 6.74 (d, J = 3.5 Hz, 1H), 4.16 (m, 2H), 3.78 (m, 3H; Ms-CH_3), 3.77 (m, 2H), 3.62 (m, 2H), 3.49(m, 2H), 3.27 (s, 3H; OCH_3), 0.26 (s, 9H; TMS); ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.2, 133.4, 129.4, 127.2, 118.9, 108.2, 107.7, 106.4, 102.0, 99.6, 71.3, 69.8, 69.0, 68.0, 58.1, 43.9, 0.24; IR (thin film) 2156(C≡C), 1366(S=O) cm^{-1}; Anal. Calcd for $C_{19}H_{27}NO_5SSi$: C, 55.72; H, 6.64; N, 3.42; found: C, 55.91; H, 6.49; N, 3.34.

The precursor (2.70 g, 6.59 mmol) was dissolved in THF (50 mL) and TBAF (1M solution in THF, 13.2 mL, 13.2 mmol) was added. The resulting solution was stirred at room temperature for 13 h, while both TMS and Ms groups were removed. The product was purified by column chromatography (silica gel, EtOAc/hexanes = 2:1) to give **1** as an oily liquid (1.54 g, 90 %): ^1H NMR (500 MHz, DMSO-d_6) δ 11.11 (s, 1H; NH), 7.30 (s, 1H), 7.16 (s, 1H), 6.87 (d, J = 1.5 Hz, 1H), 6.39 (s, 1H), 4.42(s, 1H; C≡CH), 4.09 (m, 2H), 3.74 (m, 2H), 3.60 (m, 2H), 3.47 (m, 2H), 3.25 (s, 3H, OCH_3); ^{13}C NMR (126 MHz, DMSO) δ 151.9, 132.1, 128.4, 126.9, 114.7, 105.6, 105.3, 101.7, 84.2, 80.3, 71.3, 69.7, 69.1, 68.0, 58.1; IR (thin film) 3422(NH), 3280(C(sp)-H), 2106(C≡C) cm^{-1}. Anal. Calcd for $C_{15}H_{17}NO_3$: C,

69.48; H, 6.61; N, 5.40. Found: C, 69.62; H, 6.64; N, 5.22.

1.2 Synthesis of Biindole **2**



Compound **S8**: Ethyl *p*-aminobenzoate (**S7**) was prepared from *p*-aminobenzoic acid following a literature procedure.[3] To a flask containing **S7** (25 g, 0.15 mol) and dry diethyleneglycol monomethyl ether (62 mL, 3.5 equiv), finely ground K_2CO_3 (2.1 g, 0.1 equiv) was added. After stirred under nitrogen at 75-80 °C for 7 h, excess diethyleneglycol monomethyl ether was removed using Kugelrohr apparatus (80-85 °C, 10 mmHg) over 1.5 h.[4] The residue was taken up in CH_2Cl_2 (200 mL), and K_2CO_3 was removed by filtration. The organic solution was washed with brine, and dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by a short column chromatography (silica gel. EtOAc/hexanes =1:1) to give **S8** as an oily liquid (33 g, 90%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 MHz, 2H), 6.61(d, J = 8.0 MHz, 2H), 4.42 (m, 2H), 4.15 (s, 2H; NH_2), 3.80 (m, 2H), 3.68 (m, 2H), 3.56 (m, 2H), 3.37 (s, 3H; OCH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 151.1, 131.8, 119.6, 113.8, 72.0, 70.6, 69.5, 63.6, 59.1; IR (thin film) 3456(NH_2), 1694(C=O) cm^{-1}.

[3] Zafar, A.; Melendez, R.; Geib, S. J.; Hamilton, A. D. *Tetrahedron* **2002**, *58*, 683.
[4] Gin, M. S.; Yokozawa, T.; Prince, R. B.; Moore, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 2643.

Compound **S9**: To a solution of **S8** (27 g, 11 mmol) in EtOH (1.4 L, HPLC grade) was added I_2 (60 g, 0.24 mol, 2.2 equiv) and Ag_2SO_4 (74 g, 0.24 mol, 2.2 equiv).[5] After stirring for 1 h at room temperature, the reaction solution was filtered and the filter cake was thoroughly washed with EtOAc. The organic solution was concentrated and the residue was re-dissolved in CH_2Cl_2 (500 mL). The solution was washed with 5% NaOH aqueous solution, dried over anhydrous $MgSO_4$ and concentrated. The crude product was re-crystallized from EtOH (450 mL) to give **S9** a white floppy solid (52 g, 95 %): mp: 82-83 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 2H), 5.06 (s, 2H), 4.40 (m, 2H), 3.78 (m, 2H), 3.65 (m, 2H), 3.54 (m, 2H), 3.37 (s, 3H; OCH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 149.8, 141.1, 122.4, 79.4, 72.8, 70.6, 69.3, 64.1, 59.2; IR (KBr) 3428(NH_2), 1705(C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{15}I_2NO_4$: C, 29.35; H, 3.08; N, 2.85. Found: C, 29.46; H, 2.95; N, 3.10.

Compound **S10**: A Schlenk flask containing **S9** (18 g, 37 mmol), $Pd(PPh_3)_2Cl_2$ (0.52 g, 0.02 equiv), and CuI (0.18 g, 0.025 equiv) was evacuated under vacuum and back-filled with nitrogen three times. Degassed THF (50 mL), Et_3N (300 mL), and trimethylsiliyethyne (5.2 mL, 1.0 equiv) were sequentially added, and the solution was stirred at 58-60 °C for 18 h. The mixture was filtered through Celite and the organic solution was concentrated. The residue was dissolved in CH_2Cl_2 and the organic solution was washed with saturated $NaHCO_3$ solution and brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, EtOAc/hexanes = 1:3) to give **S10** as an oily liquid (8.5 g, 50%): ^1H NMR (500 MHz, DMSO-d_6) δ 7.13 (s, 1H), 6.86 (s, 1H), 5.06 (s, 2H; NH_2), 4.40 (m, 2H), 3.78 (m, 2H), 3.65 (m, 2H), 3.54 (m, 2H), 3.37 (s, 3H; OCH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.7, 152.5, 140.7, 133.4, 118.6, 105.2, 100.8, 100.3, 81.2, 71.2, 69.6, 68.3, 63.6, 58.1, 0.25; IR (thin film) 3472(NH_2), 2149(C≡ C), 1711(C=O) cm^{-1}. Anal. Calcd for $C_{17}H_{24}INO_4Si$: C, 44.26; H, 5.24; N, 3.04. Found: C, 44.13; H, 5.27; N, 2.97.

Compound **S11**: Acetic acid (1.0 M in THF, 1.1.equiv) was added to a solution of **S10** (7.7 g, 17 mmol) in THF (40 mL). The solution was cooled down to 0 °C (ice-water bath) and then tetrabutylammonium

[5] Lindsay, D. M.; Dohle, W.; Jensen, A. E.; Kopp, F.; Knochel, P. *Org. Lett.* **2002**, *4*, 1819.

fluoride (TBAF, 1M in THF, 1.05 equiv) was slowly added over 10 minutes. The reaction solution was stirred at room temperature for 1 h and concentrated. The crude product was purified by column chromatography (silica gel, EtOAc/hexanes = 2:1) to give **S11** (6.4g, 98 %) as a white solid: ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.16 (s, 1H), 6.92 (s, 1H), 5.06 (s, 2H, NH_2), 4.40 (m, 2H), 3.78 (m, 2H), 3.65 (m, 2H), 3.54 (m, 2H), 3.37 (s, 3H; OCH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.8, 153.0, 140.7, 133.7, 118.6, 104.7, 87.0, 81.4, 79.2, 71.3, 69.6, 68.3, 63.8, 58.1; IR (thin film) 3429 (NH_2), 3241(C(sp)-H), 2101(C≡ C), 1706(C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{16}INO_4$: C, 43.21; H, 4.14; N, 3.60. Found: C, 43.43; H, 4.15; N, 3.52.

Compound **S12**: **S11** (6.0 g, 15 mmol) was dissolved in pyridine (60 mL) and $Cu(OAc)_2{\cdot}H_2O$ (3.4 g, 17 mmol) was added.[6] After stirring at room temperature for 15.5 h, the mixture was filtered through Celite and the filtrate was concentrated. The residue was dissolved in CH_2Cl_2, and the solution was washed with water and brine and dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography to (silica gel, EtOAc/CH_2Cl_2 = 1:1) give **S12** as a yellow solid (4.5 g, 75 %): mp 113-114 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.18 (s, 1H), 7.88 (s, 1H), 6.42 (s, 2H, NH_2), 4.40 (m, 2H), 3.78 (m, 2H), 3.65 (m, 2H), 3.54 (m, 2H), 3.37 (s, 3H; OCH_3); ^{13}C NMR (126 MHz, DMSO) δ 163.6, 153.8, 141.5, 134.4, 118.6, 103.1, 82.0, 79.2, 71.2, 70.0, 68.3, 64.0, 58.1; IR (KBr) 3470(NH_2), 2128(C≡ C), 1704(C=O) cm^{-1}. Anal. Calcd for $C_{28}H_{30}I_2N_2O_8$: C, 43.32; H, 3.89; N, 3.61. Found: C, 43.29; H, 3.92; N, 3.50.

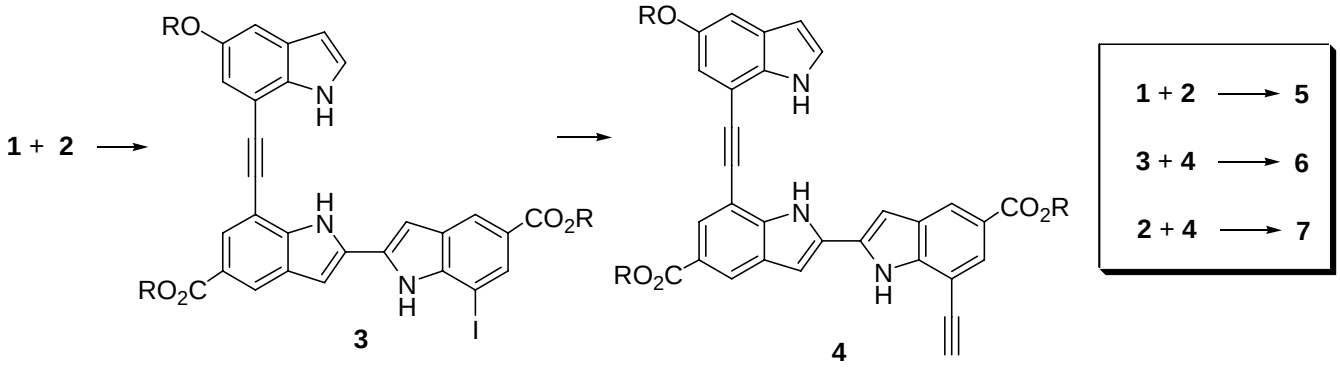
Biindole **2**: A solution containing **S12** (4.0 g, 5.2 mmol) and CuI (2.0 g, 10 mmol, 2.1 equiv) in DMF (50 mL) was heated at reflux for 8.5 h.[7] The reaction mixture was cooled down to ambient temperature, filtered through celite, and concentrated. The residue was dissolved in $CHCl_3$ and was washed by water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, $CHCl_3$/acetone = 5:1) to give **2** as a white solid (3.2 g, 80 %): mp 161-162 ^{o}C; ^{1}H NMR (500

[6] Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem*., *Int. Ed.* **2004**, *69*, 1126.

[7] (a) Terry M. C.; Juro. O.; Franz. S.; *J. Org. Chem*. **1977**, *42*, 2130. (b) Ezquerra, J.; Pedregal, C.; Lamas, C.; Barluenga, J.; Perez, M.; Garcia-Martin, M. A.; Gonzalez, J. M. *J. Org. Chem*. **1996**, *61*, 5804. (c) Gribble, G. W. *J. Chem. Soc., Perkin*

MHz, DMSO-d_6) δ 11.66 (s, 2H; NH), 8.24 (s, 2H), 8.10 (s, 2H), 7.48 (s, 2H), 4.39 (m, 4H), 3.77 (m, 4H), 3.61 (m, 4H), 3.47 (m, 4H), 3.26 (s, 6H; OCH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.2, 141.3, 132.3, 132.0, 128.0, 123.2, 122.4, 104.0, 76.2, 71.2, 70.0, 68.4, 64.0, 58.1; IR (KBr) 3437(NH), 1711(C=O) cm^{-1}. Anal. Calcd for $C_{28}H_{32}I_2N_2O_8$: C, 43.21; H, 4.14; N, 3.60. Found: C, 43.34; H, 3.79; N, 3.76.

1.3 Synthesis of Oligoindoles



Trimer **3** and tetramer **5**: Biindole **2** (2.60 g, 3.35 mmol), CuI (16 mg, 0.025 equiv) and $PdCl_2(Ph_3P)_2$ (47 mg, 0.02 equiv) were placed in a Schlenk flask. The flask was degassed under high vacuum and back-filled with nitrogen, which process was repeated three times. Degassed THF (40 mL) and Et_3N (90 mL) were added, and then a THF solution (10 mL) of monoindole **1** (0.87 g, 3.35 mmol, 1.0 equiv) was added under a cannula. The solution was stirred under nitrogen at 52-54 ^{o}C for 15 h, and then cooled down to ambient temperature. The mixture was filtered through celite and the filtrate was concentrated. The residue was dissolved in CH_2Cl_2 (70 mL), and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography (silica gel, EtOAc/hexanes = 4:1) to give **3** (1.37 g, 45 %) and **4** (0.52 g, 15 %):

Trimer **3**: mp 122-123 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.06 (s, 1H; NH), 11.75 (s, 1H; NH), 11.43 (s, 1H; NH), 8.34 (s, 1H), 8.31 (s, 1H), 8.16 (s, 1H), 8.13 (s, 1H), 7.52 (s, 2H), 7.46 (s, 1H),

Trans. 1, **2000**, 1045.

7.26 (s, 2H), 6.48 (s, 1H), 4.47 (m, 4H), 4.18 (s, 2H), 3.81 (m, 6H), 3.65 (m, 6H), 3.50 (s, 9H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.0, 165.3, 152.1, 141.5, 139.2, 132.8, 132.5, 131.8, 131.6, 128.5, 128.3, 128.0, 126.8, 123.2, 122.5, 121.8, 114.8, 106.3, 105.8, 103.6, 103.3, 101.8, 90.4, 88.5, 76.2, 71.3, 69.7, 69.2, 68.4, 68.1, 63.9, 58.1; IR (KBr) 3430(NH), 1709(C=O) cm^{-1}. Anal. Calcd for $C_{43}H_{46}IN_3O_{11}$: C, 56.89; H, 5.11; N, 4.63. Found: C, 56.85; H, 4.74; N, 4.59.

Tetramer **5**: Mp 86-87 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.09 (s, 1H; NH), 11.39 (s, 1H, NH), 8.38 (s, 2H), 8.19 (s, 2H), 7.49 (s, 2H), 7.40 (s, 2H), 7.28 (s, 2H), 7.23(s, 2H), 6.47(s, 2H), 4.45 (m, 4H), 4.14 (m, 4H), 3.80 (m, 4H), 3.76 (m, 4H), 3.75 (m, 4H), 3.74 (m, 4H), 3.61 (m, 8H), 3.26 (s, 12H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.0, 152.1, 139.3, 132.8, 131.5, 128.4, 127.1, 126.7, 123.2, 121.8, 114.9, 106.3, 105.9, 105.7, 103.2, 101.8, 90.4, 88.5, 71.3, 69.7, 69.1, 68.5, 68.0, 63.9, 58.1; IR (KBr) 3430(NH), 1709(C=O) cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{58}H_{62}N_4O_{14}$ 1038.4263, found 1038.4283. Anal. Calcd for $C_{58}H_{62}N_4O_{14}$: C, 67.04; H, 6.01; N, 5.39. Found: C, 66.75; H, 5.99; N, 5.23.

Compound **4**: Trimer **3** (0.60 g, 0.66 mmol), Ph_3P (35 mg, 0.2 equiv), CuI (5 mg, 0.04 equiv) and $Pd(dba)_2$ (15 mg, 0.04 equiv) were placed in a Schlenk flask. The flask was degassed under high vacuum and back-filled with nitrogen, which process was repeated three times. Degassed THF (15 mL), triethylamine Et_3N (20 mL) and trimethylsilyl(TMS)-ethyne (0.50 mL, 3.3 mmol, 5 equiv) were added. The solution was stirred under nitrogen at 52-54 ^{o}C for 12 h, and then cooled down to ambient temperature. The mixture was filtered through celite and the filtrate was concentrated. The residue was dissolved in CH_2Cl_2 (150 mL), and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography (silica gel, EtOAc/hexanes = 1:3) to give a TMS-protected precursor (0.44 g, 75 %): mp 101-102 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.08 (s, 1H; NH), 11.98 (s, 1H; NH), 11.44 (s, 1H, NH), 8.37 (s, 1H), 8.35 (s, 2H), 8.23 (s, 1H), 7.87 (s, 1H), 7.47 (s, 3H), 7.27 (s, 1H), 6.49 (s, 1H), 4.45 (s, 4H), 4.15 (s, 2H), 3.81 (m, 6H), 3.63 (m, 6H), 3.48 (s, 6H), 3.27 (s, 6H), 3.26 (s, 3H) ; ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.0, 165.8, 152.2, 139.2, 132.9, 132.6, 131.6, 128.2, 127.4, 127.0, 126.7, 123.6,

123.2, 121.8, 121.7, 114.7, 106.2, 105.9, 105.7, 105.5, 103.3, 103.1, 101.8, 100.9, 99.3, 90.5, 88.6, 71.3, 69.6, 69.2, 68.5, 67.9, 63.9, 58.1, 0.25 ; IR(KBr) 3437(NH), 2152(C≡C), 1712(C=O) cm^{-1}. Anal. Calcd for $C_{48}H_{55}N_3O_{11}Si$: C, 65.66; H, 6.31; N, 4.79. Found: C, 65.30; H, 6.34; N, 4.57.

As described above for the preparation of **S11** from **S10,** the TMS group (0. 30 g, 0.34 mmol) was carefully removed with acetic acid (1.0 equiv) and TBAF (1.0 equiv) in THF (10 mL) to give **4** as a white solid (0.25 g, 92%): mp 103-104 ^oC; ^1H NMR (500 MHz, DMSO-d_6) δ 12.17 (s, 1H; NH), 12.00 (s, 1H), 11.41 (s, 1H), 8.34 (s, 2H), 8.16 (s, 1H), 7.87 (s, 1H), 7.51 (s, 1H), 7.45 (s, 2H), 7.27 (s.1H), 7.25 (s, 1H), 6.49 (s, 1H), 4.66 (s, 1H, C≡CH), 4.45 (m, 4H), 4.16 (m, 2H), 3.78 (m, 6H), 3.63 (m, 6H), 3.50 (m, 6H), 3.27 (s, 9H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.7, 166.4, 152.7, 140.4, 139.9, 133.5, 133.3, 132.2, 129.1, 128.9, 127.6, 127.5, 124.1, 123.8, 122.4, 122.3, 115.4, 106.9, 106.6, 106.5, 105.8, 103.7, 103.5, 102.5, 91.1, 89.1, 86.2, 80.2, 71.9, 70.3, 69.8, 69.1, 68.7, 64.6, 58.7; IR (KBr) 3433(NH), 3293(C(sp)-H), 2209(C≡C), 1711(C=O) cm^{-1}. Anal. Calcd for $C_{45}H_{47}N_3O_{11}$: C, 67.07; H, 5.88; N, 5.21. Found: C, 66.83; H, 5.97; N, 5.19.

Hexamer **6**: **3** (0.10 g, 0.11 mmol), CuI (1.4 mg, 0.06 equiv) and $PdCl_2(Ph_3P)_2$ (5.0 mg, 0.06 equiv) were placed in a Schlenk flask. The flask was degassed under high vacuum and back-filled with nitrogen, which process was repeated three times. Degassed THF (2.5 mL) and Et_3N (1.5 mL) were added, and then a THF solution (1 mL) of **4** (89 mg, 0.11 mmol, 1 equiv) was added under a cannula. The solution was stirred under nitrogen at 52-54 ^oC for 15 h, and then cooled down to ambient temperature. The mixture was filtered through celite and the filtrate was concentrated. The residue was dissolved in CH_2Cl_2 (20 mL), and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography (slica gel, EtOAc/hexanes = 4:1 then acetone/$CHCl_3$ = 1:2) to give slightly impure **6**. This was washed with distilled water and then solidified in CH_3CN to give **6** in a pure form as an off-white solid (0.12 g, 70 %): mp 146-148 ^oC; ^1H NMR (500 MHz, DMSO-d_6) δ 12.30 (s, 2H; NH), 12.13 (s, 2H; NH), 11.37 (s, 2H; NH), 8.43 (s, 2H), 8.34 (s, 2H), 8.25 (s, 2H), 8.19 (s, 2H), 7.54 (s, 4H), 7.37(s,

2H), 7.23 (s, 4H), 6.44 (s, 2H), 4.44 (s, 9H), 4.10 (s, 3H), 3.79 (s, 12H), 3.64 (s, 12H), 3.59 (s, 12H), 3.24 (s, 12H), 3.22 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.43, 152.49, 139.90, 139.77, 133.34, 131.99, 128.81, 127.65, 127.07, 123.98, 123.60, 122.24, 115.23, 106.74, 106.43, 106.10, 103.66, 103.52, 102.21, 90.88, 89.98, 88.99, 71.73, 70.12, 69.59, 68.91, 68.39, 64.37, 58.49,; IR (KBr) 3433(NH), 1708(C=O) cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{88}H_{92}N_6O_{22}$ 1584.6257, found 1584.6265. Anal. Calcd for $C_{88}H_{92}N_6O_{22}$: C, 66.65; H, 5.85; N, 5.30. Found: C, 66.36; H, 5.84; N, 5.31.

Octamer **7**: **7** was prepared by following the procedure for the preparation of **6**. The product was first purified by column chromatography (silica gel, methanol/EtOAc = 1:8), and the resulting product was washed with distilled water and then solidified in acetonitrile to give **7** in a pure form as off-white solid (0.19 g, 70 %): mp 194-195 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.35 (s, 2H; NH), 12.23 (s, 2H; NH), 12.03 (s, 2H; NH), 11.35 (s, 2H; NH), 8.39 (s, 2H), 8.35 (s, 2H), 8.31 (s, 2H), 8.27 (s, 2H), 8.16 (s, 4H), 7.57 (s, 2H), 7.50 (s, 2H), 7.47 (s, 2H), 7.38 (s, 2H), 7.22 (s, 2H), 7.20 (s, 2H), 6.44 (s, 2H), 4.43 (s, 12H), 4.10 (s, 4H), 3.79 (s, 16H), 3.60 (s, 16H), 3.46 (s, 16H), 3.25 (s, 18H), 3.16 (s, 6H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 166.0, 152.0, 139.4, 132.9, 131.5, 128.4, 127.3, 126.6, 123.4, 123.1, 121.7, 114.8, 106.1, 105.6, 103.0, 101.8, 90.3, 89.5, 88.6, 71.2, 69.7, 69.1, 68.4, 67.9, 63.8, 58.0; IR (KBr) 3435(NH), 1711(C=O) cm^{-1}; MALDI-TOF (MH^+) calcd for $C_{118}H_{122}N_8O_{30}$ 2130.83, found 2131.28. Anal. Calcd for $C_{118}H_{122}N_8O_{30}$: C, 66.47; H, 5.77; N, 5.26. Found: C, 66.37; H, 5.78; N, 5.26.

2. Computer Modeling Structures

Energy-minimized structures of tetramer **5** and complexes **5**+**Cl**$^-$, **6**+**Cl**$^-$, and **7**+**Cl**$^-$ were generated using MacroModel[8] 7.1 program on a Silicon Graphics Indigo^2 IMPACT workstation. The structures was found with AMBER* force field[9] in the gas phase via 1000 (**5** and **5**+**Cl**$^-$) and 3000 separated search steps (**6**+**Cl**$^-$ and **7**+**Cl**$^-$) in Monte Carlo conformational search.[10] For convenient calculation, the side chains of oligoindoles were replaced with hydrogens.

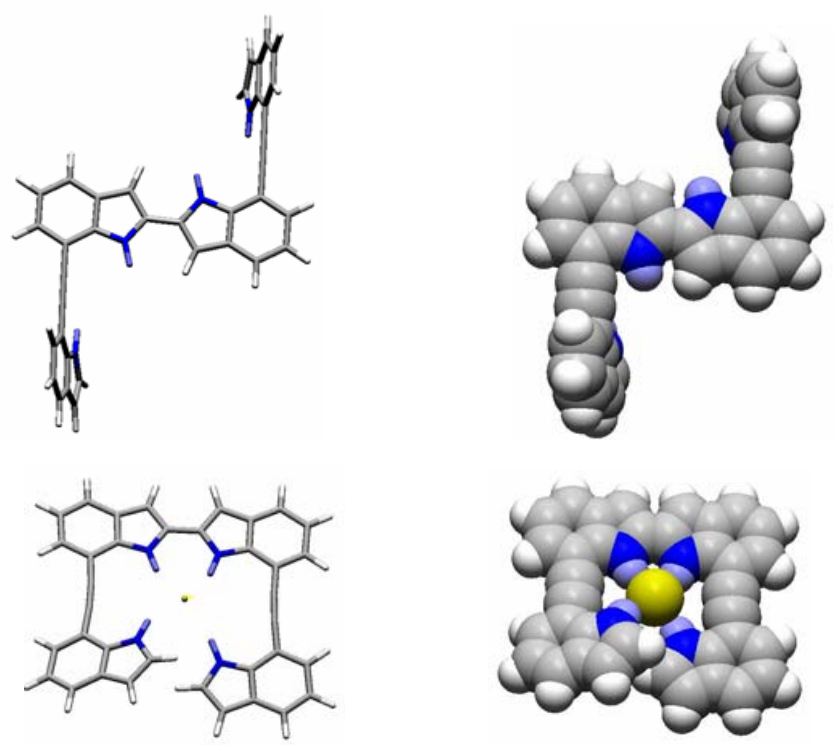


Figure S1. Polytube (left) and CPK (right) representations of energy-minimized structures for tetramer **5** (top) and complex **5**+**Cl**$^-$ (bottom)

[8] Mohamedi, F.; Richards, N. G. T.; Liskamp, W. C. H.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comp. Chem*. **1990**, *11*, 440.
[9] Ferguson, D. M.; Kollman, P. A. *J. Comp. Chem*. **1991**, *12*, 620.
[10] Saunders, M.; Houk, K. N.; Wu, Y. D.; Still, W. C.; Lipton, M.; Chang. G.; Guida, W. C. *J. Am. Chem. Soc.* **1990**, *112*, 1419.

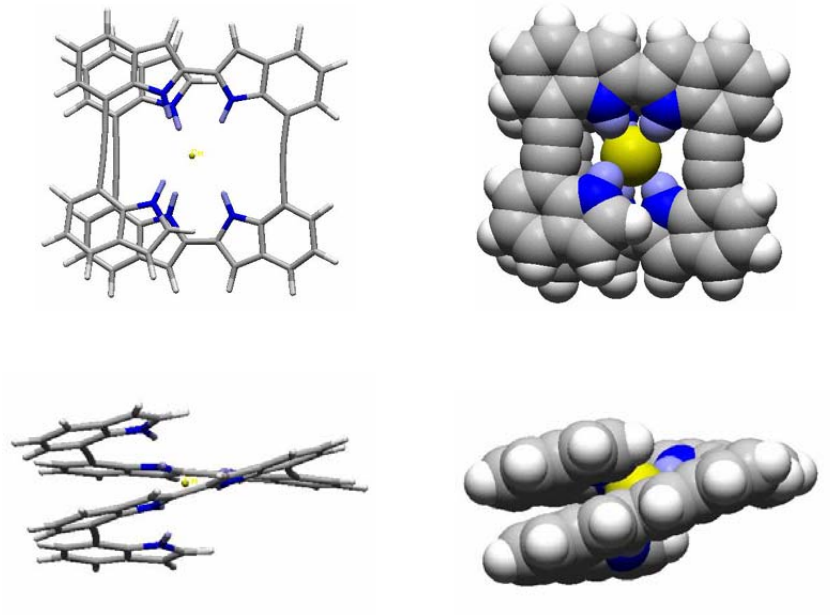


Figure S2. Top and side views of energy-minimized structures for complex **6**+**Cl**$^-$ (bottom)

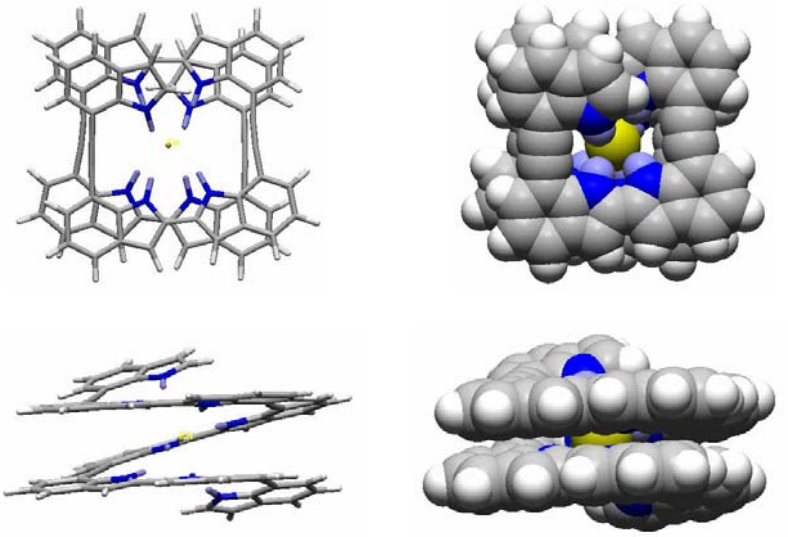


Figure S3. Top and side views of energy-minimized structures for tetramer **7**+**Cl**$^-$ (bottom)

3. ^{1}H NMR Experiments with Hexamer **6** and Complex **6 + Cl**$^-$

3-1. ^{1}H NMR Spectral Changes of **6** Induced by Cl^-

Two separate stock solutions of hexamer **6** (0.5×10^{-3} M in CD_3CN) and TBA^+Cl^- (10×10^{-3} M in CD_3CN) were separately prepared at 25 ^{o}C. A small portion of the Cl^- solution was added to a NMR tube containing a 600 μL of hexamer **6**, and each spectrum was recorded as shown below. From this

experiment, we could able to assign some of ^{1}H NMR signals of free hexamer **6**, which was not well resolved relative to that of complex **6**+**Cl**$^{-}$.

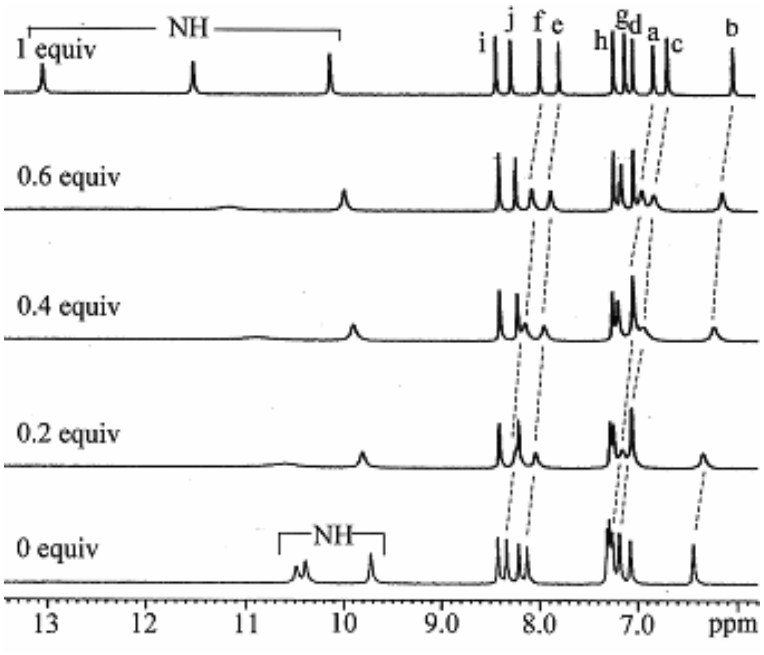
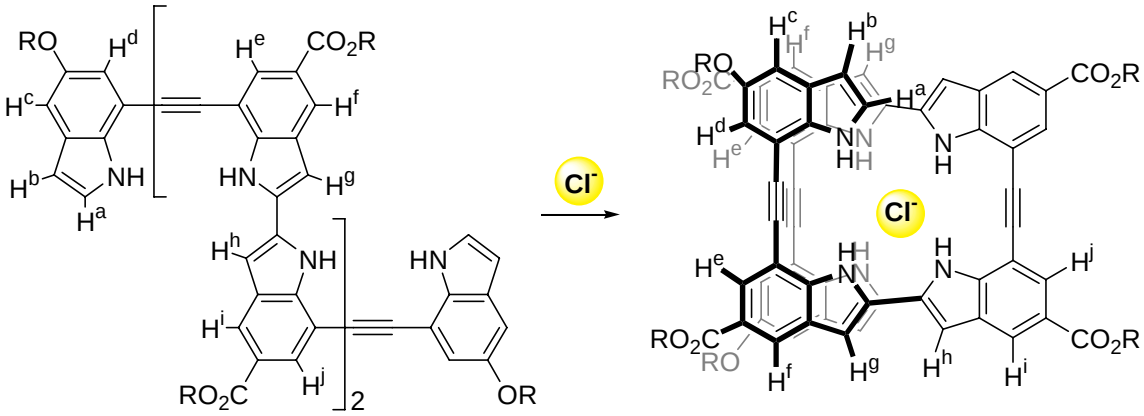


Figure S4. Partial ^{1}H NMR spectral changes (500 MHz in CD_3CN at 25 ^{o}C) of hexamer **6** upon addition of chloride.

3-2. 2D TOCSY, NOESY and ROESY Spectra of Complex **6** + **Cl**$^{-}$



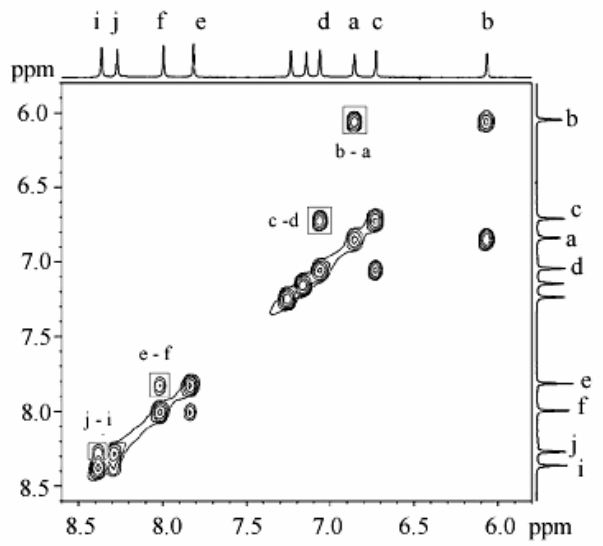


Figure S5. TOCSY spectrum of **6** + **Cl**$^-$ (500 MHz, 25 ^{o}C, 50 mM in CD_3CN, mixing time = 80 ms)

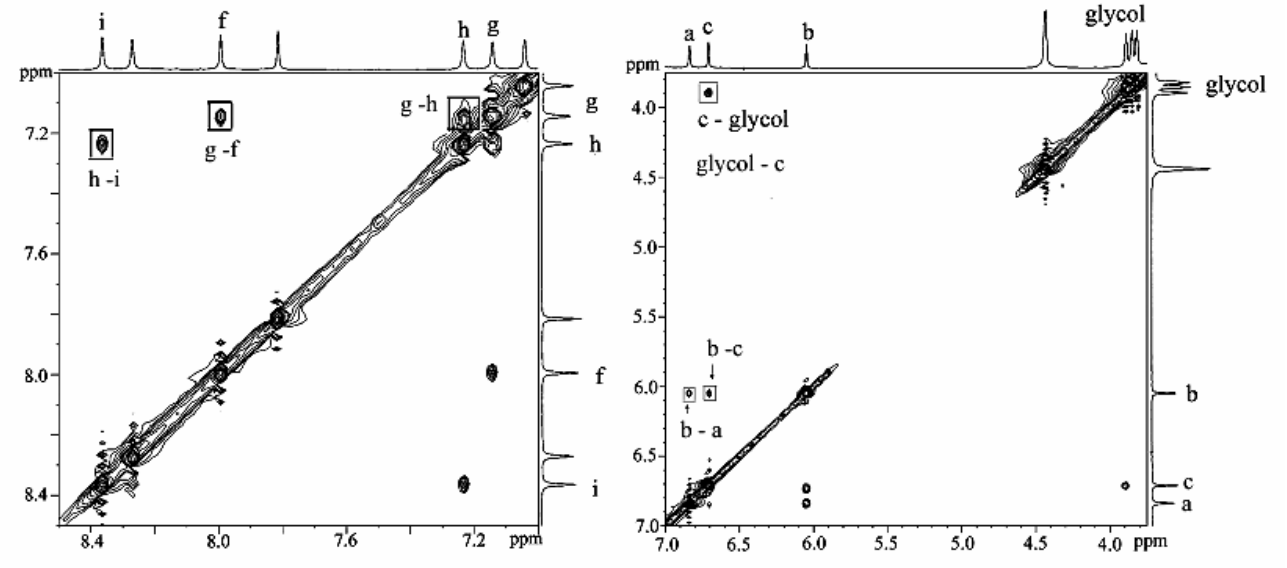


Figure S6. NOESY spectra of **6** + **Cl**$^-$ (500 MHz, 25 ^{o}C, 10 mM in CD_3CN, mixing time = 600 ms, relaxation delay = 2 s)

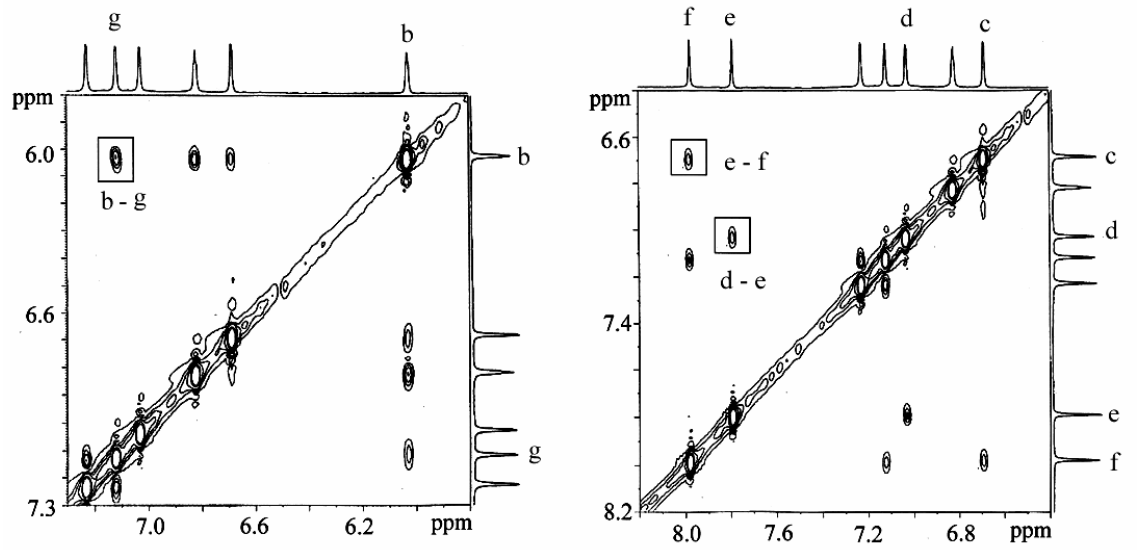


Figure S7. ROESY spectra of **6** + Cl^- (500 MHz, 25 ^oC, 10 mM in CD_3CN, mixing time = 400 ms, relaxation delay = 2 s)

4. UV/visible Titration Experiments

Titrations: The titration experiments were conducted using UV-visible spectroscopy and were all duplicated at 22 ± 1 ^oC, and CH_3CN (spectroscopic grade) was used as purchased. A CH_3CN (50.0 mL) solution of an oligoindole, **5** (2.00×10^{-5} M), **6** (1.00×10^{-5} M) or **7** (1.00×10^{-5} M), was first prepared. Using this solution as a solvent, a stock solution of TBA^+Cl^- was prepared. A 2.00 mL of an oligoindole solution was transferred to a UV cell (3 mL), and an initial spectrum was taken. Small portions of the chloride solution (5 μL initially, then 10-50 μL, and finally 100 μL) were added to the oligoindole solution, and the spectrum was recorded after each addition and 13-14 data points were obtained. Upon addition of an anion, the UV-visible spectra were gradually changed, showing mutiple isosbestic points at wavelengths (**5**: 241, 271, 292, 321 and 348 nm, **6**: 263, 313 and 382 nm, **7**: 269, 313 and 387 nm). The association constants (K_a) were determined by nonlinear curve fitting of the titration curves,[11] plotting the absorbance changes at two or three different wavelengths against equivalents of chloride added. All of the titration curves were well fitted to the expression of a 1: 1 binding isotherm as shown

[11] (a) Long, J. R.; Drago, R. S. *J. Chem. Edu*. **1982**, *59*, 1037. (b) Connors, K. A. *Binding Constants*; John Wiley & Sons: New York, 1987.

below.

$$H + G \rightleftharpoons HG \qquad K_a = \frac{[HG]}{[H][G]}$$

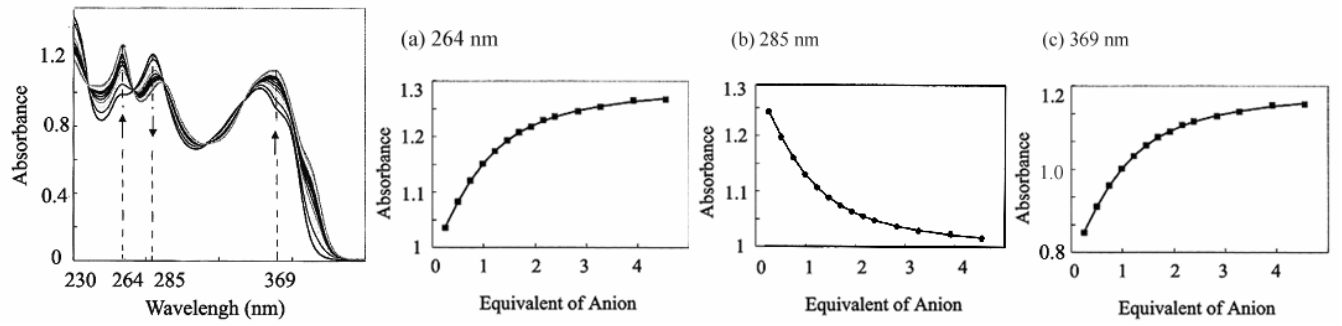
$$A = A_{free} + \frac{\Delta A_{\max}}{2[H]_0}\left[K_a^{-1} + [H]_0 + [G]_0 - \sqrt{(K_a^{-1} + [H]_0 + [G]_0)^2 - 4[H]_0[G]_0}\right]$$

$$\chi^2 = \sum(\Delta A_{calcd} - \Delta A_{obsd})^2$$

Here, A is the UV-visible absorbance observed at each titration point, A_{free} is the absorbance of free host, $[H]_0$ and $[G]_0$ is the initial concentrations of host and guest, respectively, and $\Delta A_{\max}$ is the difference in UV-VIS absorbance between the complex and free host. Minimizing the sum of the squared deviations χ^2 affords the association constant (K_a) along with $\Delta A_{\max}$.

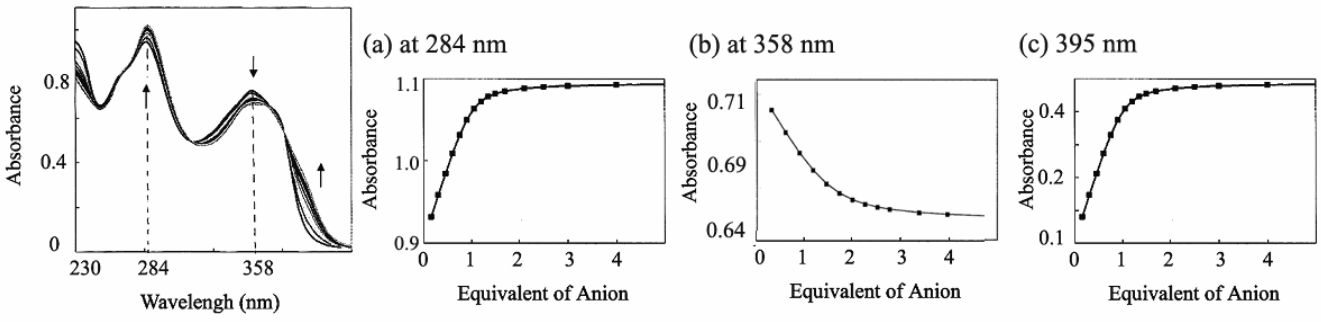
4-1. UV/visible spectra and titration curves at 22 ± 1 °C.

(i) Tetramer **5** in CH_3CN



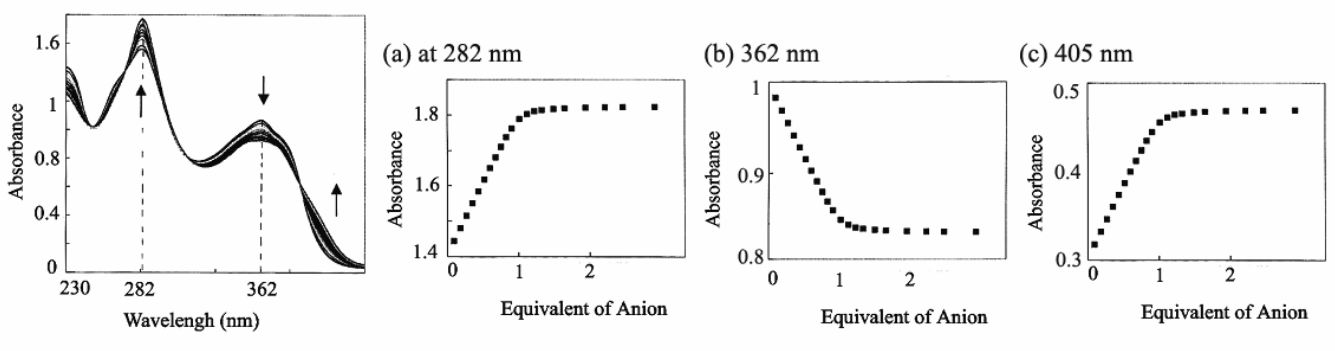
The solid lines in the titration curves were generated by fitting with K_a = 1.20 ×10^5 M^{-1} (264 nm), = 1.30 ×10^5 M^{-1} (285 nm), and 1.21×10^5 M^{-1} (369 nm), respectively.

(ii) Hexamer **6** in CH_3CN

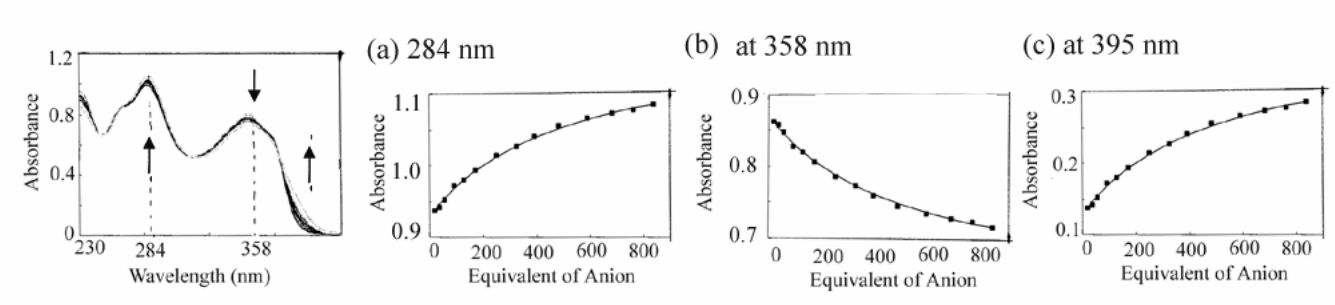


The solid lines in the titration curves were generated by fitting with K_a = 1.31 ×10^6 M^{-1} (284 nm), 1.24 ×10^6 M^{-1} (258 nm), and 1.22 ×10^6 M^{-1} (395 nm), respectively.

(iii) Octamer **7** in CH_3CN

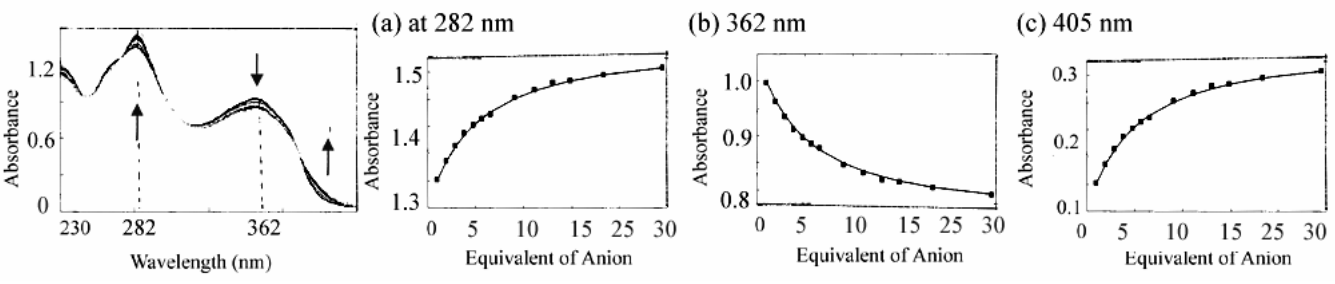


(iv) Hexamer **6** in 10% H_2O/CH_3CN



The solid lines in the titration curves were generated by fitting with K_a = 200 M^{-1} (284 nm), 230 M^{-1} (358 nm), and 214 M^{-1} (395 nm), respectively.

(v) Octamer **7** in 10% H_2O/CH_3CN



The solid lines in the titration curves were generated by fitting with K_a = 2.32 ×10^4 M^{-1} (282

nm), 2.51 $\times 10^4$ M^{-1} (362 nm), and 2.27 $\times 10^4$ M^{-1} (405 nm), respectively.

4-2. Job's plots

Stock solutions of an oligoindole (3.0×10^{-5}, 2.0×10^{-5}, and 1.0×10^{-5} M for **5**, **6** and **7,** respectively) and of tetrabutylammonium chloride (the concentration is exactly same as that of the corresponding oligoindoles) were separately prepared in volumetric flasks. To an UV/visible cell, a total 1.00 mL solution of an oligoindole and Cl^- was added in the following ratios (oligoindole/Cl^-): 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9, 0:10, and each spectrum was recorded. Job's plots were constructed by plotting $[HG]\cdot\alpha$ against mol fraction of the oligoindoles (see below).

$$A = A_H + A_{HG} \quad \cdots\cdots \quad (1)$$

Here, A is the observed UV absorbance of the each solution, and A_H and A_{HG} correspond to the UV absorbance of the free oligoindole and its complex, respectively. According to Beer-Lambert's law and by introducing $\gamma = \frac{\varepsilon_{HG}}{\varepsilon_H}$, the equation (1) becomes, $\frac{A}{b\varepsilon_H} = [H]_0 + [HG](\gamma - 1) \cdots\cdots (2)$

The equation (2) can be rewritten into the equation (3) by replacing $\gamma - 1 = \alpha$

$[HG]\alpha = \frac{A}{b\varepsilon_H} - [H]_0 \quad \cdots\cdots \quad (3)$, where $\alpha = \frac{\varepsilon_{HG}}{\varepsilon_H} - 1 = \frac{\Delta\varepsilon_{HG}}{\varepsilon_H}$