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Electronic supplementary information (ESI)

Helical aromatic foldamers with tubular cavities capable of accommodating multiple halide ions

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Contents

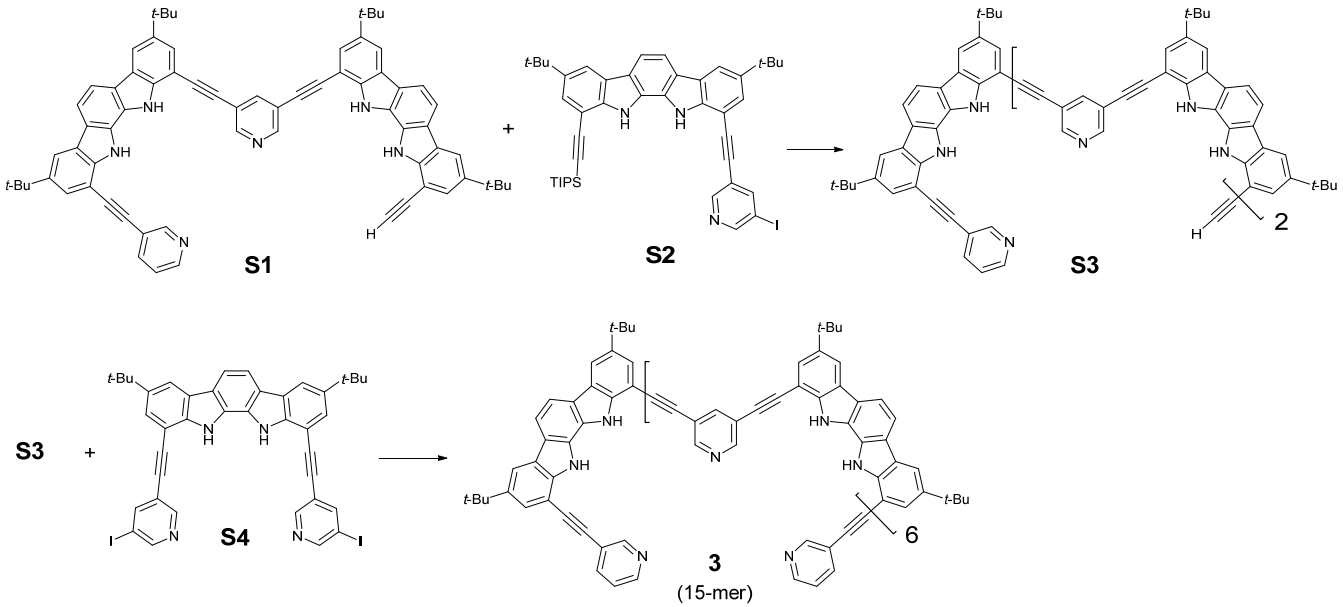
1. Syntheses and characterisation of new compounds
2. ^{1}H NMR spectral analyses
    2.1 Partial ^{1}H NMR spectra of oligomers **4**–**6** in organic solvents
    2.2 Partial ^{1}H NMR spectra of oligomers **4**–**6** and monomeric references **7**–**9** in CD_3NO_2
    2.3 1D-, 2D-^{1}H NMR spectral analyses of oligomers **4**–**6**
    2.4 ^{1}H NMR titration experiments
3. X-ray crystallographic analyses
4. ^{1}H and ^{13}C NMR spectra of new compounds
5. ESI mass spectra of oligomer **4**
6. References

General methods: 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. *n*-Hexane, ethyl acetate (EtOAc), and acetone were distilled. 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 Electro thermal (IA9100) apparatus. 1D and 2D NMR spectra were measured by using Bruker Avance II DRX 400 and Avance III HD 300 instruments. Chemical shifts were reported using residual protonated solvent peaks (for ^{1}H NMR spectra, acetone-d_6 2.05 ppm; CD_3NO_2 4.33 ppm; CD_3CN 1.94 ppm; CD_3OH 3.31 ppm; DMF-d_7 2.75, 2.92 and 8.03 ppm; DMSO-d_6 2.50 ppm; and for ^{13}C NMR spectra, acetone-d_6 206.3 ppm; DMF-d_7 29.8, 34.9, 163.2 ppm; DMSO-d_6 39.5 ppm). MALDI-TOF mass spectrometric measurements were performed on a Bruker (Autoflex Max). ESI-MS measurements were obtained in positive ion mode using an Agilent 6410 instrument. High-resolution mass spectrometry (ESI-HRMS) measurements were obtained in positive ion mode using a TripleTOF 5600 plus instrument (Sciex) at the *Center for Research Facilities of Chungnam National University*.

1. Syntheses and characterisation of new compounds

The synthesis of **1** (7-mer), **2** (11-mer), **9**, **S1**, **S2**, **S4**,[1] **S5**[2] and **S6**[3] were prepared following the procedures described in the literature.

1.1 Synthesis of **3**

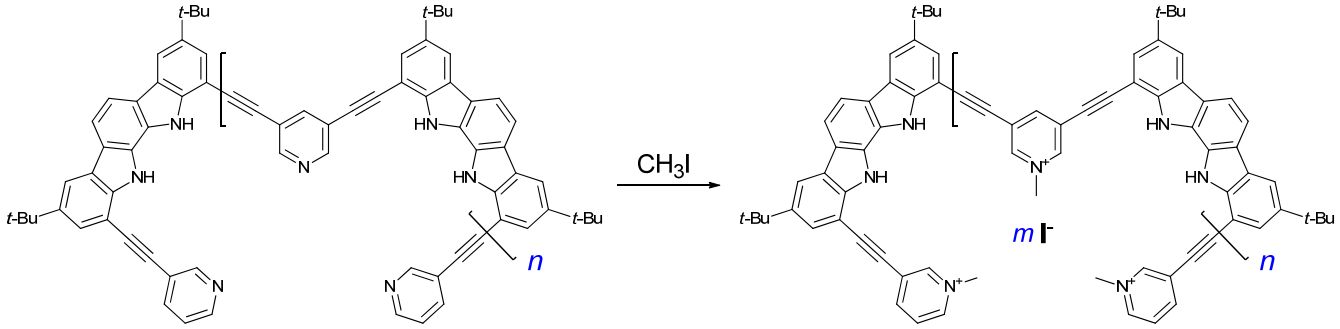


S3: A Schlenk flask containing **S1**[1] (261 mg, 0.265 mmol), **S2**[1] (232 mg, 0.299 mmol), CuI (1.5 mg, 0.008 mmol) and $Pd(PPh_3)_2Cl_2$ (5.5 mg, 0.008 mmol) was evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed tetrahydrofuran (THF) (5.0 mL) and triethylamine (Et_3N) (4.0 mL) were sequentially added and the solution was stirred at 55 °C for 3 h. The

mixture was filtered through Celite and concentrated, and the residue was dissolved in EtOAc. The organic solution was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was dissolved in tetrahydrofuran (THF) (9 mL), and tetrabutylammonium fluoride (TBAF) (0.7 mL, 1.0 M solution in THF) was added. The mixture was stirred for 1.5 h at room temperature. The mixture was concentrated, and the residue was dissolved in EtOAc. The organic solution was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (SiO_2, MeOH:EtOAc=1:25) to give compound **S3** (288 mg, 73%) as a yellow solid; mp > 240 °C (dec); ^{1}H NMR (400 MHz, acetone-d_6, 25 °C, ppm) δ 10.57 (s, 1H, NH), 10.51 (s, 2H, NH), 10.43 (s, 1H, NH), 10.36 (s, 1H, NH), 10.19 (s, 1H, NH), 8.89 (d, J = 1.9 Hz, 1H), 8.87 (d, J = 1.7 Hz, 1H), 8.78 (d, J = 1.2 Hz, 1H), 8.74 (d, J = 1.9 Hz, 1H), 8.70 (d, J = 1.6 Hz, 1H), 8.43 (d, J = 1.5 Hz, 1H), 8.42 (d, J = 1.5 Hz, 1H), 8.38 (d, J = 1.6 Hz, 1H), 8.36 (d, J = 1.8 Hz, 1H), 8.34 (d, J = 1.7 Hz, 1H), 8.31 (dd, J = 4.7 Hz and 1.2 Hz, 1H), 8.29 (d, J = 1.7 Hz, 1H), 8.27 (s, 1H), 8.23 (t, J = 1.9 Hz, 1H), 8.12 (s, 2H), 8.05 (s, 2H), 8.03 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.91 (dt, J = 7.9 Hz and 1.6 Hz, 1H), 7.77 (d, J = 1.6 Hz, 1H), 7.75 (s, 1H), 7.74 (s, 2H), 7.69 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 1.8 Hz, 1H), 7.19 (dd, J = 7.9 Hz and 4.7 Hz, 1H), 3.97 (s, 1H), 1.52 (s, 9H, *t*-Bu), 1.50 (s, 9H, *t*-Bu), 1.49 (s, 9H, *t*-Bu), 1.49 (s, 9H, *t*-Bu), 1.48 (s, 9H, *t*-Bu), 1.45 (s, 9H, *t*-Bu); ^{13}C NMR (100 MHz, acetone-d_6, 25 °C, ppm) δ 152.8, 151.8, 151.7, 151.7, 149.7, 143.7, 143.6, 143.5, 143.4, 140.9, 140.9, 127.1, 127.0, 126.9, 126.8, 125.5, 125.2, 124.2, 122.7, 122.6, 121.2, 121.1, 119.3, 119.2, 118.9, 118.6, 113.6, 113.5, 113.4, 105.5, 105.2, 105.2, 91.5, 91.4, 90.3, 89.9, 83.2, 81.6, 35.5, 35.4, 32.4, 32.3; MALDI-TOF m/z: $[M]^+$ Calcd for $C_{105}H_{89}N_9$ 1475.7; Found 1475.9.

3: A Schlenk flask containing **S3** (167 mg, 0.113 mmol), **S4**[1] (44 mg, 0.054 mmol), CuI (0.4 mg, 0.002 mmol) and $Pd(PPh_3)_2Cl_2$ (1 mg, 0.001 mmol) were evacuated under vacuum and back-filled with nitrogen. Anhydrous, degassed triethylamine (Et_3N) (1 mL) and *N*,*N*-dimethylformamide (DMF) (4 mL) were added 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 EtOAc. The organic solution was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (SiO_2, EtOAc) to give compound **3** (170 mg, 89%) as a yellow solid; mp > 270 °C (dec); ^{1}H NMR (400 MHz, DMF-d_7, 25 °C, ppm) δ 11.16 (s, 3H, NH), 11.13 (s, 3H, NH), 11.06 (s, 1H, NH), 8.87 (s, 1H), 8.82 (s, 1H), 8.77 (s, 1H), 8.74 (s, 2H), 8.71 (s, 2H), 8.49 (d, J = 1.4 Hz, 1H), 8.45–8.40 (m, 7H), 8.23 (s, 2H), 8.18 (s, 1H), 8.16 (s, 1H), 8.15 (s, 1H), 8.13 (s, 2H), 8.11 (s, 2H), 8.11 (s, 1H), 8.00 (dt, J = 7.9 Hz and 1.7 Hz, 1H), 7.78 (d, J = 1.8 Hz, 1H), 7.77 (d, J = 1.7 Hz, 2H), 7.75–7.70 (m, 4H), 7.33 (dd, J = 7.9 Hz and 5.0 Hz, 1H), 1.52 (s, 9H, *t*-Bu), 1.48 (s, 45H, *t*-Bu), 1.47 (s, 9H, *t*-Bu); ^{13}C NMR (100 MHz, DMF-d_7, 25 °C, ppm) δ 152.5, 151.5, 151.3, 149.5, 143.0, 143.0, 140.4, 140.3, 140.2, 138.9, 138.8, 126.9, 126.9, 126.4, 126.3, 125.1, 124.9, 124.1, 121.9, 121.8, 120.6, 119.0, 118.7, 113.1, 104.9, 104.6, 104.6, 91.0, 90.2, 89.9, 89.4, 32.1; MALDI-TOF m/z: $[M+H]^+$ Calcd for $C_{250}H_{209}N_{22}$ 3518.7; Found 3518.7.

1.2 Synthesis of **4–6**



1 (7-mer) : *n* = 2
2 (11-mer) : *n* = 4
3 (15-mer) : *n* = 6

4 (7-mer) : *n* = 2, *m* = 4
5 (11-mer) : *n* = 4, *m* = 6
6 (15-mer) : *n* = 6, *m* = 8

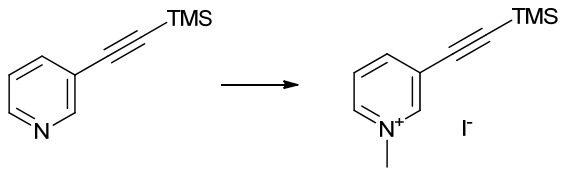
4: Compound **1**[1] (30 mg, 0.019 mmol) was dissolved in anhydrous CH_2Cl_2 (2.0 mL). Iodomethane (CH_3I) (120 μL, 1.93 mmol, 100 equiv) was added, and the reaction mixture was stirred in the dark at room temperature for 24 h. The solvent was then evaporated, and the resulting solid was washed with diethyl ether and dried under vacuum, yielding a red solid (40 mg, 98%); mp > 280 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ 11.16 (s, 1H, NH), 11.13 (s, 1H, NH), 10.89 (s, 1H, NH), 10.17 (s, 1H), 8.67 (s, 1H), 8.53 (s, 1H), 8.46 (s, 1H), 8.28 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 8.08 (s, 1H), 8.00 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.85 (d, *J* = 5.3 Hz, 1H), 7.70 (s, 1H), 7.55 (s, 1H), 7.15 (s, 1H), 6.99 (s, 1H), 6.97 (dd, *J* = 8.3 Hz and 7.9 Hz, 1H), 4.03 (s, 3H, Me), 3.52 (s, 3H, Me), 1.66 (s, 9H, *t*-Bu), 1.51 (s, 9H, *t*-Bu), 1.45 (s, 9H, *t*-Bu); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, ppm) δ 147.8, 144.9, 143.9, 142.9, 142.7, 142.2, 142.0, 141.7, 138.7, 138.1, 137.8, 126.1, 125.8, 125.5, 125.0, 124.8, 124.3, 124.0, 123.6, 123.4, 121.6, 121.6, 121.3, 121.2, 120.4, 119.5, 119.2, 119.0, 113.2, 112.3, 103.7, 102.9, 102.8, 95.2, 94.5, 93.6, 86.3, 86.2, 84.9, 47.8, 46.3, 34.8, 34.6, 34.5, 32.0, 31.9, 31.8; HRMS (ESI) m/z: $[M-2I]^{2+}$ Calcd for $C_{114}H_{104}N_{10}I_2$ 933.3262; Found 933.3233.

5: Compound **2**[1] (21 mg, 0.008mmol) was dissolved in anhydrous CH_2Cl_2 (0.8 mL). Iodomethane (CH_3I) (51 μL, 0.81 mmol, 100 equiv) was added, and the reaction mixture was stirred in the dark at room temperature for 24 h. The solvent was then evaporated, and the resulting solid was washed with diethyl ether and dried under vacuum, yielding a red solid (27 mg, 98%); mp > 280 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ 11.39 (s, 1H, NH), 10.86 (s, 1H, NH), 10.77 (s, 1H, NH), 10.68 (s, 1H, NH), 10.40 (s, 1H, NH), 9.92 (s, 1H), 9.69 (s, 1H), 8.63 (s, 1H), 8.59 (s, 1H), 8.38 (s, 1H), 8.36 (s, 1H), 8.27 (s, 1H), 8.26 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.91 (s, 1H), 7.73 (s, 1H), 7.69 (s, 1H), 7.68 (s, 1H), 7.66 (s, 1H), 7.48 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.14 (s, 1H), 7.10 (s, 1H), 6.85 (d, *J* = 8.0 Hz and 6.5 Hz, 1H), 6.61 (s, 1H), 6.57 (s, 1H), 6.26 (s, 1H), 6.14 (s, 1H), 3.93 (s, 3H, Me), 3.78 (s, 3H, Me), 3.05 (s, 3H, Me), 1.70 (s, 9H, *t*-Bu), 1.57 (s, 9H, *t*-Bu), 1.43 (s, 9H, *t*-Bu), 1.39 (s, 9H, *t*-Bu), 1.39 (s, 9H, *t*-Bu); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, ppm) δ 146.9, 144.4, 143.6, 142.7, 142.3, 142.0, 141.7, 141.5, 140.6, 140.0, 139.3, 138.8, 138.0, 137.7, 137.2, 126.1, 125.7, 125.3, 125.2, 124.9, 124.7, 124.5, 123.7, 123.5, 123.3, 123.2, 122.9, 121.6, 121.4, 120.9, 120.6, 120.4, 119.9, 119.8, 119.7, 119.4, 118.8, 118.6, 112.9, 112.5, 112.2,

111.8, 110.7, 104.3, 103.7, 102.8, 102.7, 102.1, 95.2, 94.3, 94.1, 94.0, 93.2, 86.3, 85.9, 84.8, 84.5, 84.3, 54.4, 54.4, 47.6, 47.4, 45.6, 34.8, 34.7, 34.5, 34.5, 34.4, 32.2, 32.0, 31.9, 31.7; HRMS (ESI) m/z: $[M-3I]^{3+}$ Calcd for $C_{186}H_{168}N_{16}I_3$ 1002.0252; Found 1002.0219.

6: Compound **3** (16 mg, 0.005 mmol) was dissolved in anhydrous CH_2Cl_2 (1.0 mL). Iodomethane (CH_3I) (30 μL, 0.46 mmol, 100 equiv) was added, and the reaction mixture was stirred in the dark at room temperature for 24 h. The solvent was then evaporated, and the resulting solid was washed with diethyl ether and dried under vacuum, yielding a red solid (21 mg, 97%); mp > 280 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ 10.90 (s, 1H, NH), 10.87 (s, 1H, NH), 10.74 (s, 1H, NH), 10.57 (s, 1H, NH), 10.53 (s, 1H, NH), 10.17 (s, 1H, NH), 10.16 (s, 1H, NH), 9.69 (s, 1H), 9.40 (s, 1H), 9.28 (s, 1H), 8.57 (s, 1H), 8.44 (s, 1H), 8.43 (s, 1H), 8.33 (s, 1H), 8.31 (s, 1H), 8.21 (s, 1H), 8.08 (s, 2H), 7.99 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.93 (s, 1H), 7.80 (s, 1H), 7.63 (s, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.44 (s, 2H), 7.39 (s, 1H), 7.30 (d, J = 6.9 Hz, 1H), 7.10 (s, 1H), 7.04–6.92 (m, 4H), 6.81 (s, 1H), 6.63 (s, 1H), 6.56 (s, 1H), 6.45 (s, 1H), 5.88 (s, 3H), 5.73 (s, 1H), 3.78 (s, 3H, Me), 3.75 (s, 3H, Me), 3.59 (s, 3H, Me), 2.89 (s, 3H, Me), 1.63 (s, 9H, *t*-Bu), 1.61 (s, 9H, *t*-Bu), 1.50 (s, 9H, *t*-Bu), 1.38 (s, 9H, *t*-Bu), 1.35 (s, 9H, *t*-Bu), 1.32 (s, 9H, *t*-Bu), 1.30 (s, 9H, *t*-Bu); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, ppm) δ 146.8, 146.4, 145.8, 144.2, 143.5, 142.3, 142.0, 141.4, 141.3, 140.1, 139.7, 139.6, 139.5, 139.4, 139.0, 138.9, 138.6, 137.7, 137.6, 137.1, 125.6, 125.5, 125.1, 124.8, 124.7, 124.5, 124.4, 123.6, 123.5, 123.3, 123.1, 122.8, 122.3, 121.6, 121.2, 121.0, 120.8, 120.5, 120.3, 119.7, 119.5, 119.1, 118.8, 118.6, 118.3, 112.9, 112.4, 112.1, 111.8, 110.3, 109.7, 104.4, 104.2, 103.4, 102.6, 102.3, 101.8, 101.7, 95.2, 94.3, 93.9, 93.7, 92.9, 86.2, 85.7, 84.6, 84.4, 84.2, 47.3, 47.1, 45.3, 34.7, 34.5, 34.4, 34.4, 34.2, 32.1, 31.9, 31.9, 31.8, 31.6; HRMS (ESI) m/z: $[M-4I]^{4+}$ Calcd for $C_{258}H_{232}N_{22}I_4$ 1036.3746; Found 1036.3694.

1.3 Synthesis of **7**



S5 **7**

7: Compound **S5**[2] (52 mg, 0.297 mmol) was dissolved in anhydrous CH_2Cl_2 (0.3 mL), and iodomethane (CH_3I) (185 μL, 2.97 mmol) was added. The mixture was stirred in the dark for 24 h at room temperature. The solvent was then evaporated, and the resulting solid was washed with diethyl ether and dried under vacuum, yielding a beige solid (84 mg, 89%); mp > 207 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ 9.28 (s, 1H), 8.98 (d, J = 6.1 Hz, 1H), 8.63 (d, J = 8.2 Hz, 1H), 8.12 (dd, J = 8.2 Hz and 6.1 Hz, 1H), 4.31 (s, 3H, Me), 0.29 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, ppm) δ 148.3, 146.6, 145.2, 127.6, 122.1, 102.9, 97.6, 48.1, −0.6; ESI-MS *m/z*: $[M-I]^+$ Calcd for $C_{11}H_{16}NSi$ 190.1; Found 190.1.

1.4 Synthesis of **8**

S6 **8**

8: Compound **S6**[3] (53 mg, 0.195 mmol) was dissolved in anhydrous CH_2Cl_2 (0.2 mL), and iodomethane (CH_3I) (122 μL, 1.95 mmol) was added. The mixture was stirred in the dark for 24 h at room temperature. The solvent was then evaporated, and the resulting solid was washed with diethyl ether and dried under vacuum, yielding a yellow solid (73 mg, 90%); mp > 215 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ 9.26 (s, 2H), 8.76 (s, 1H), 4.25 (s, 3H, Me), 0.28 (s, 18H, $Si(CH_3)_3$); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C, ppm) δ 148.3, 147.6, 122.2, 103.9, 96.9, 48.1, −0.7; ESI-MS *m/z*: $[M-I]^+$ Calcd for $C_{16}H_{24}NSi_2$ 286.1; Found 286.1.

2. ^{1}H NMR spectral analyses

2.1 Partial ^{1}H NMR spectra of oligomers **4**–**6** in organic solvents

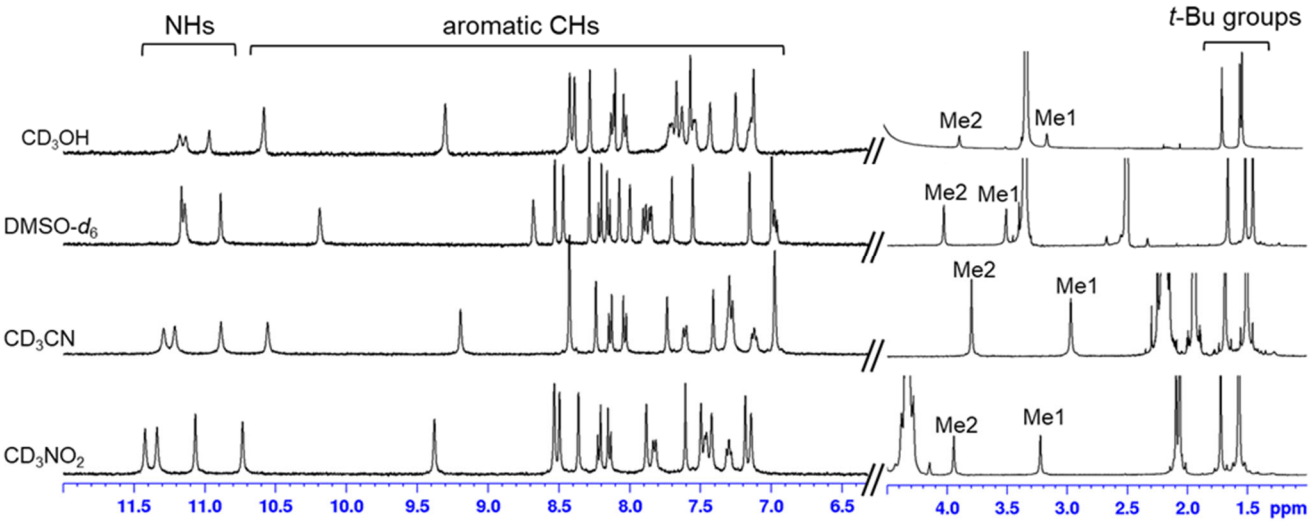


Fig. S1 Partial ^{1}H NMR spectra (400 MHz, 25 °C) of oligomer **4** (1.0 mM) in organic solvents. The concentration of oligomer **4** in CD_3OH is approximately 0.5 mM due to low solubility.

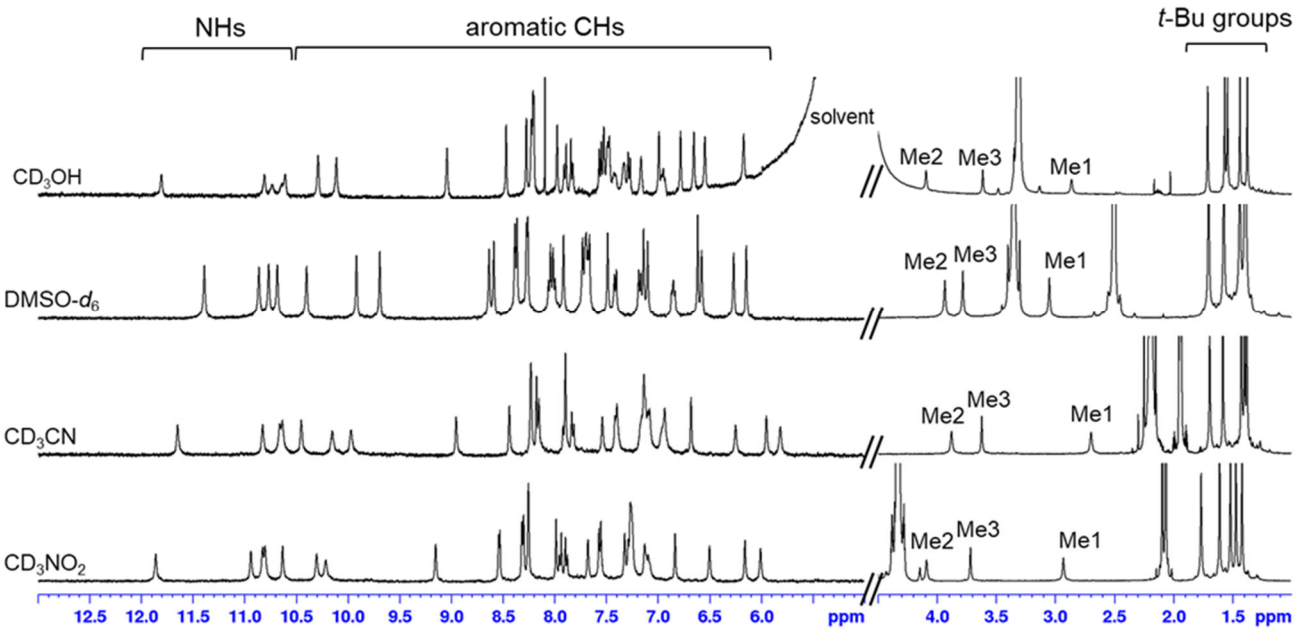


Fig. S2 Partial ^{1}H NMR spectra (400 MHz, 25 °C) of oligomer **5** (1.0 mM) in organic solvents. The concentration of oligomer **5** in CD_3OH is approximately 0.3 mM due to low solubility.

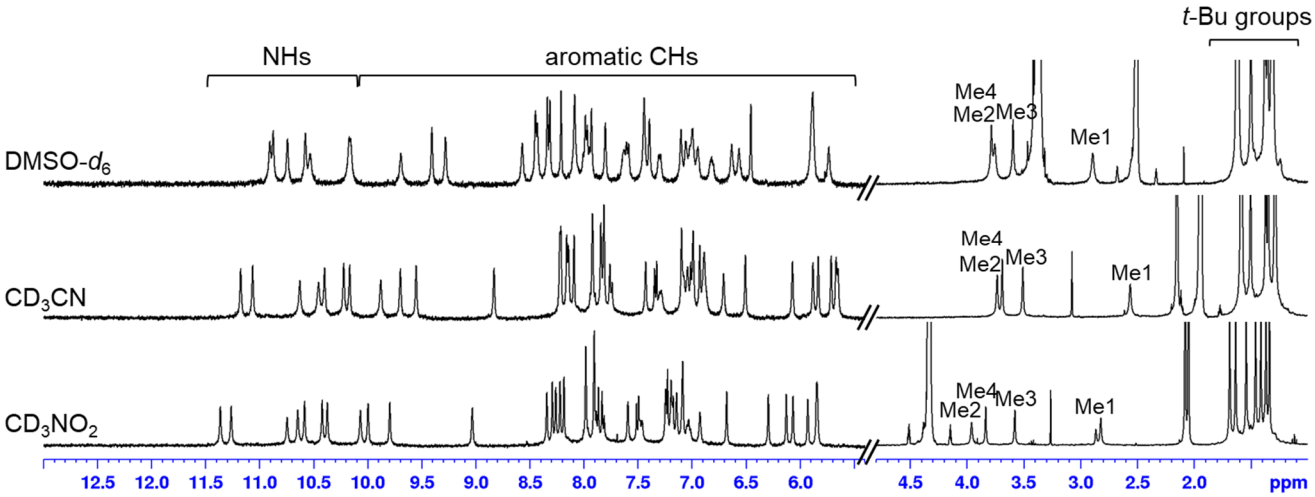


Fig. S3 Partial ^{1}H NMR spectra (400 MHz, 25 °C) of oligomer **6** (1.0 mM) in organic solvents.

2.2 Partial ^{1}H NMR spectra of oligomers **4**–**6** and monomeric references **7**–**9** in CD_3NO_2

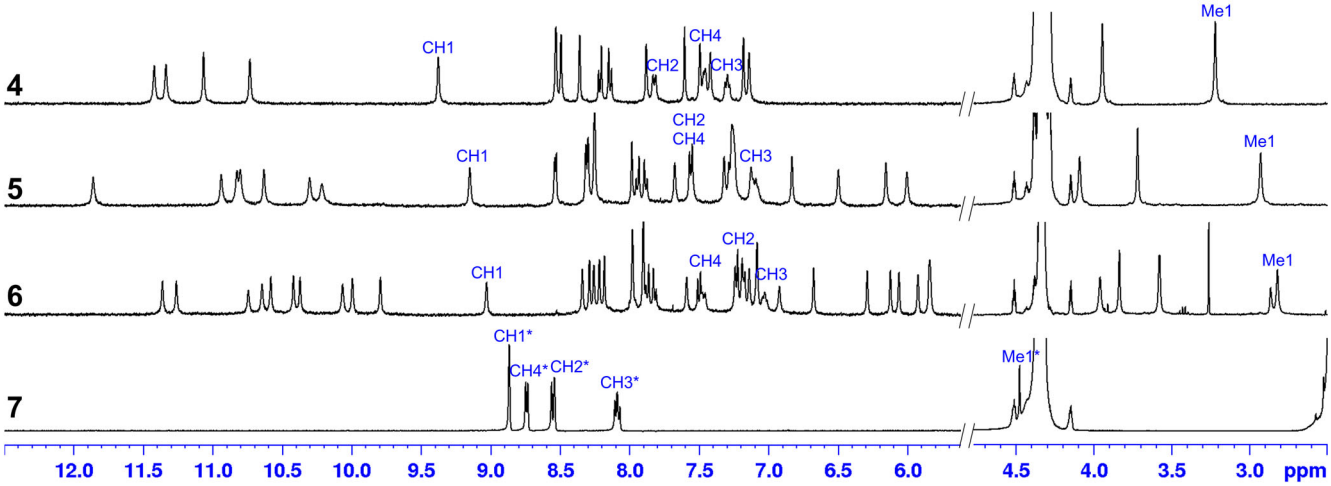


Fig. S4 Partial ^{1}H NMR spectra (400 MHz, 25 °C, 1.0 mM) of oligomers **4**–**6** and monomer **7** in CD_3NO_2.

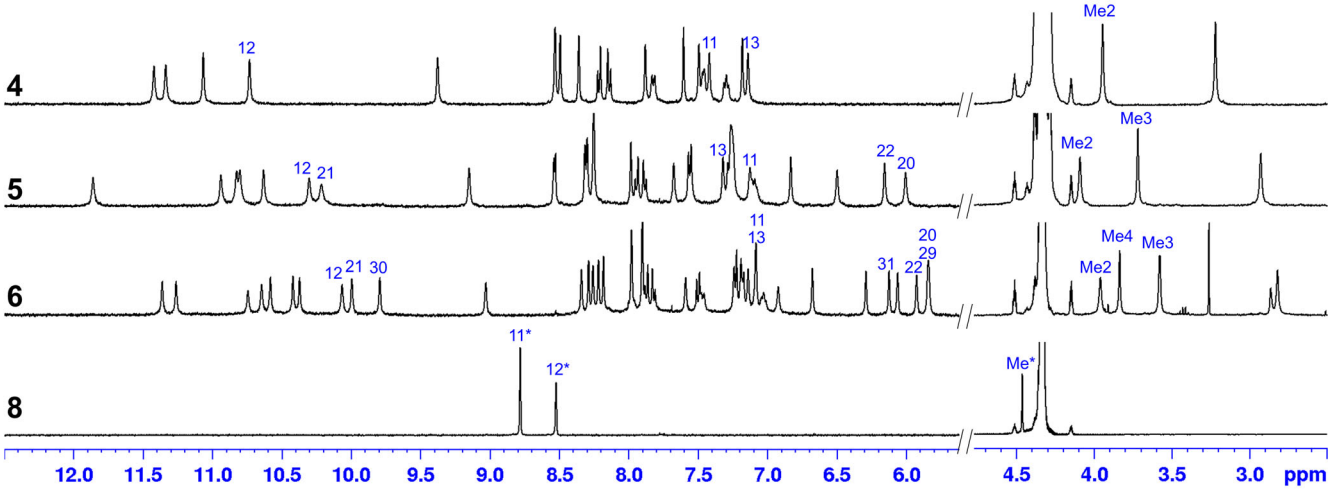


Fig. S5 Partial ^{1}H NMR spectra (400 MHz, 25 °C, 1.0 mM) of oligomers **4**–**6** and monomer **8** in CD_3NO_2.

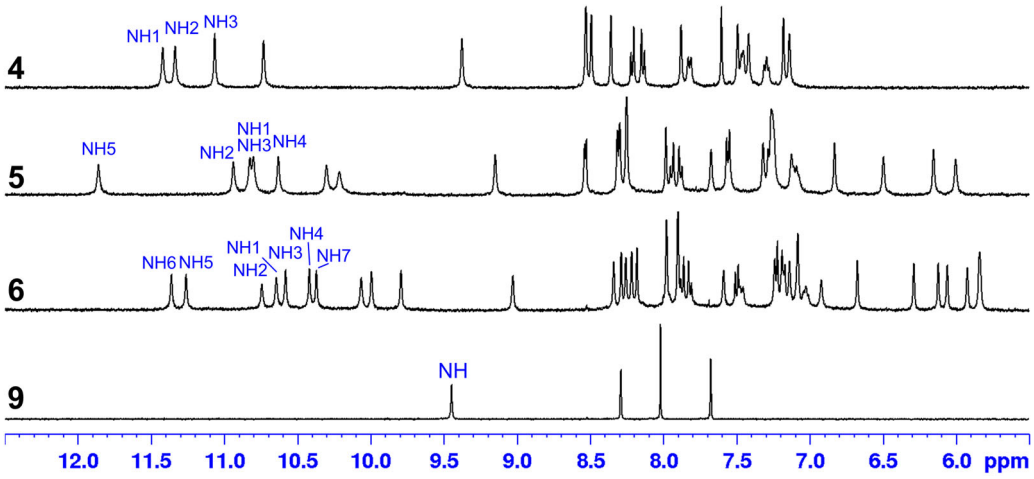


Fig. S6 Partial ^{1}H NMR spectra (400 MHz, 25 °C, 1.0 mM) of oligomers **4**–**6** and monomer **9** in CD_3NO_2.

2.3 1D-, 2D-^{1}H NMR spectral analyses of oligomers **4**–**6**

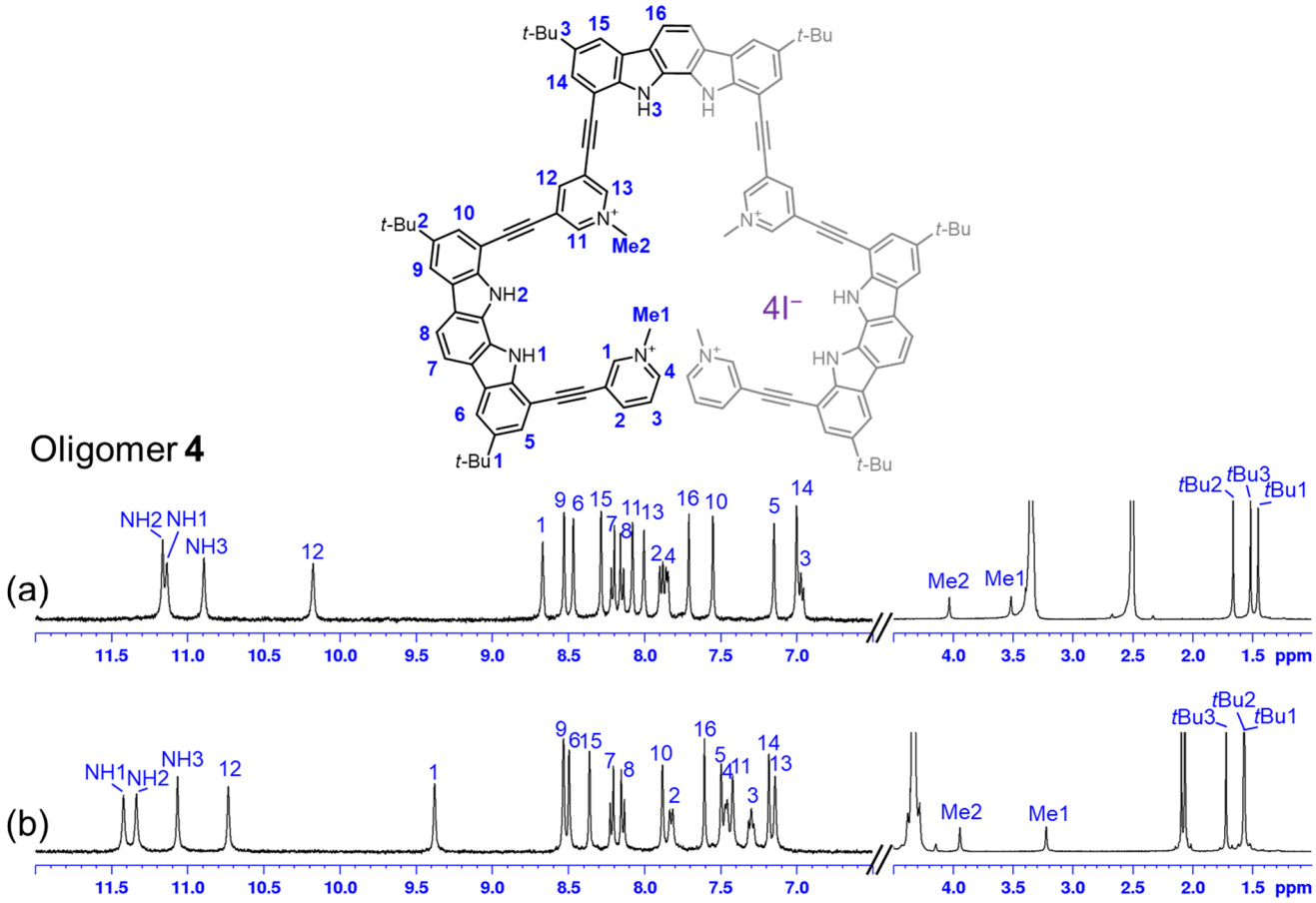


Fig. S7 Partial ^{1}H NMR spectra (400 MHz, 25 °C) of **4** (1.0 mM) in (a) DMSO-d_6 and (b) CD_3NO_2.

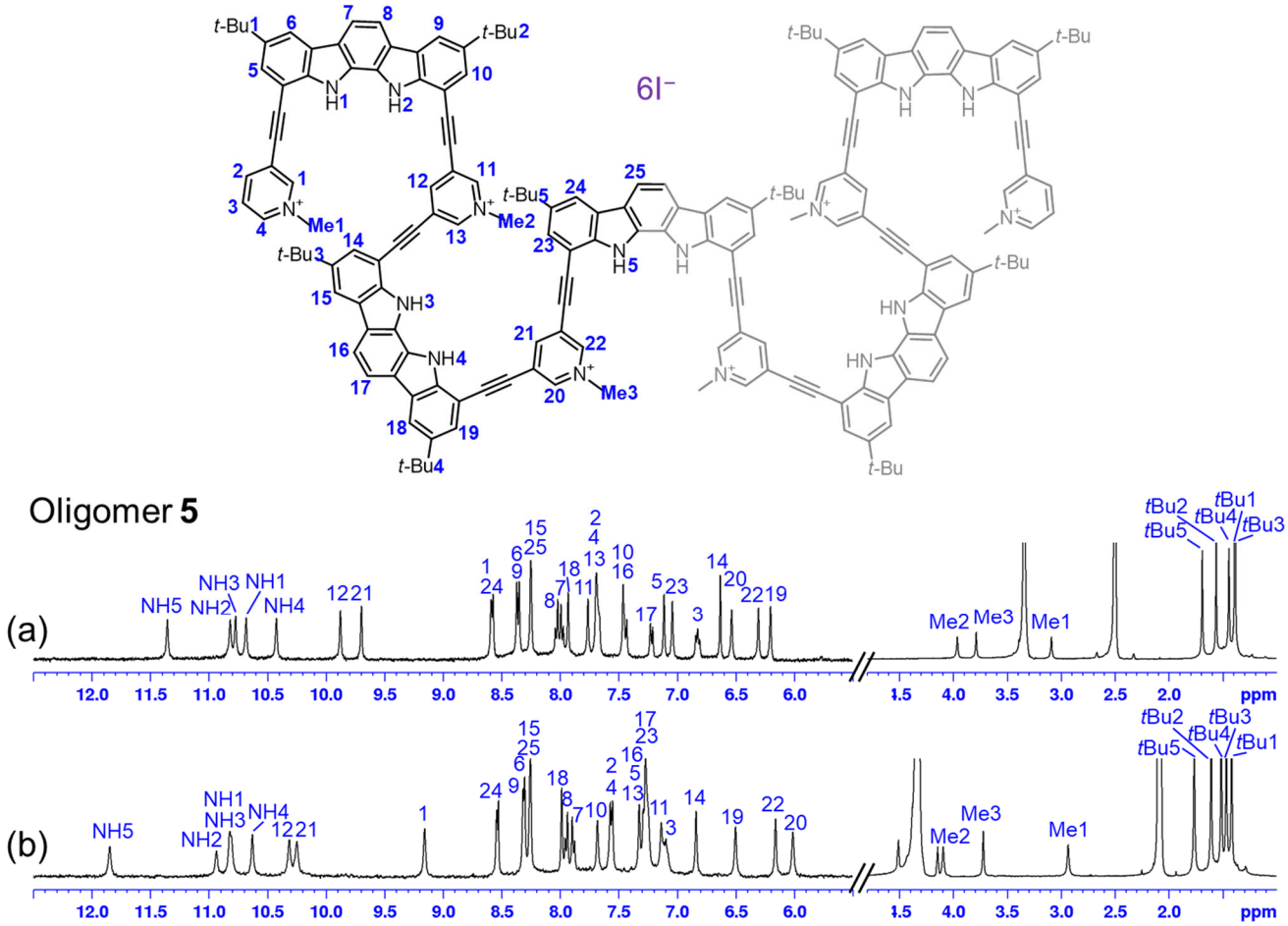


Fig. S8 Partial ^{1}H NMR spectra (400 MHz, 25 °C) of **5** (1.0 mM) in (a) DMSO-d_6 and (b) CD_3NO_2.

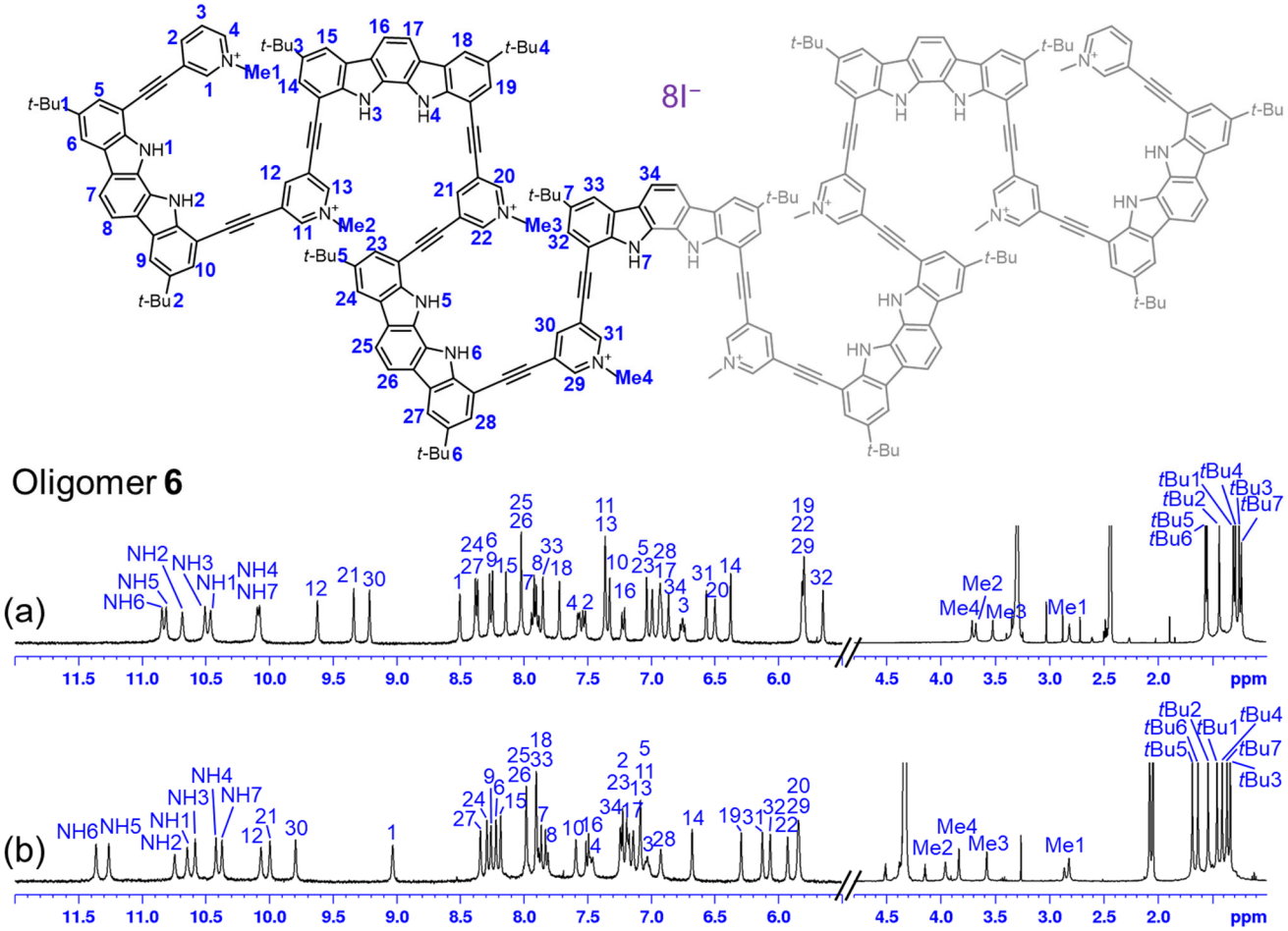


Fig. S9 Partial ^{1}H NMR spectra (400 MHz, 25 °C) of **6** (1.0 mM) in (a) DMSO-d_6 and (b) CD_3NO_2.

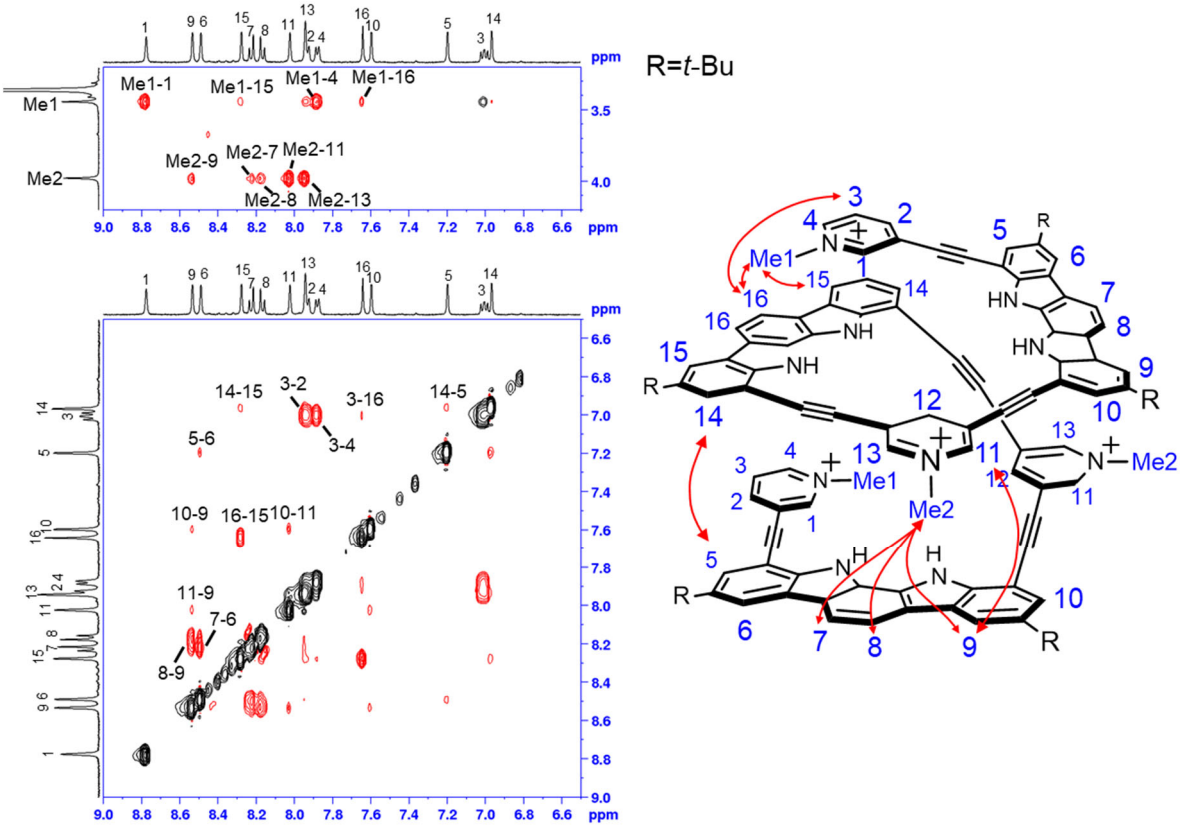


Fig. S10 Partial ROESY spectra (DMSO-d_6, 25°C, mixing time: 400 ms) of oligomer **4**.

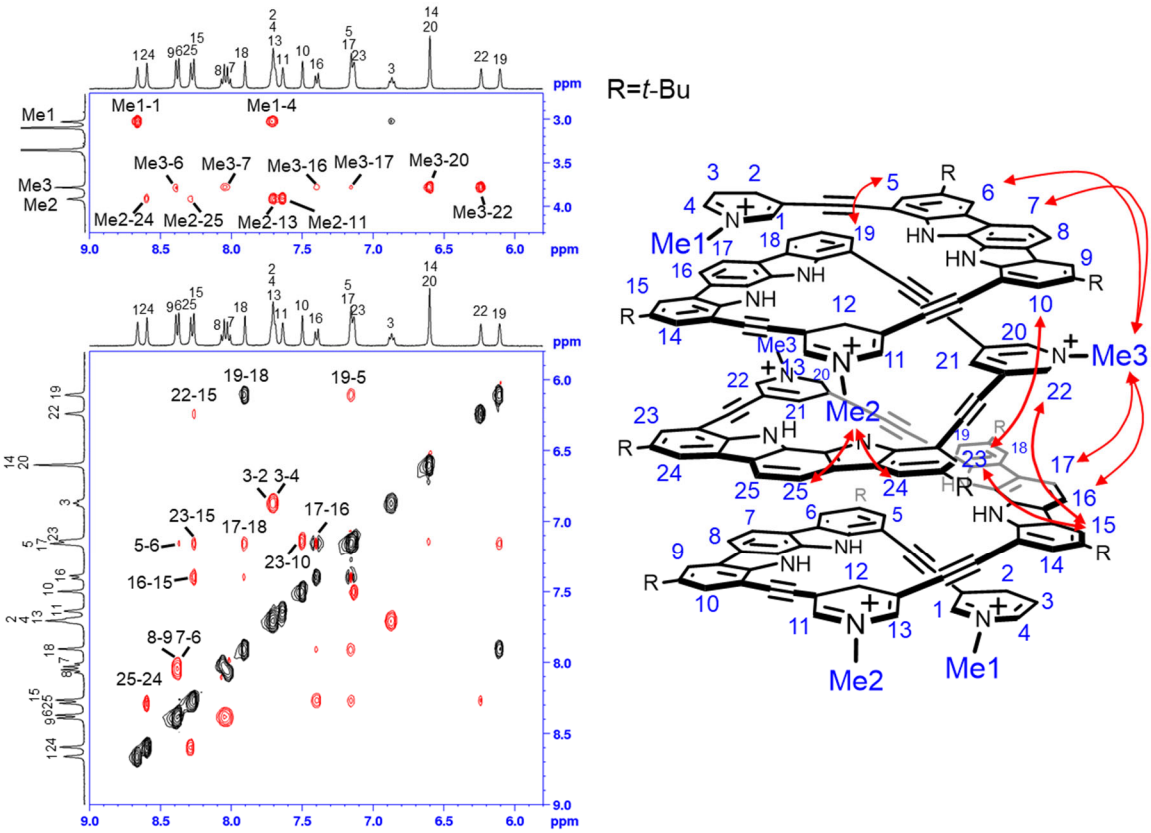


Fig. S11 Partial ROESY spectra (DMSO-d_6, 25°C, mixing time: 400 ms) of oligomer **5**.

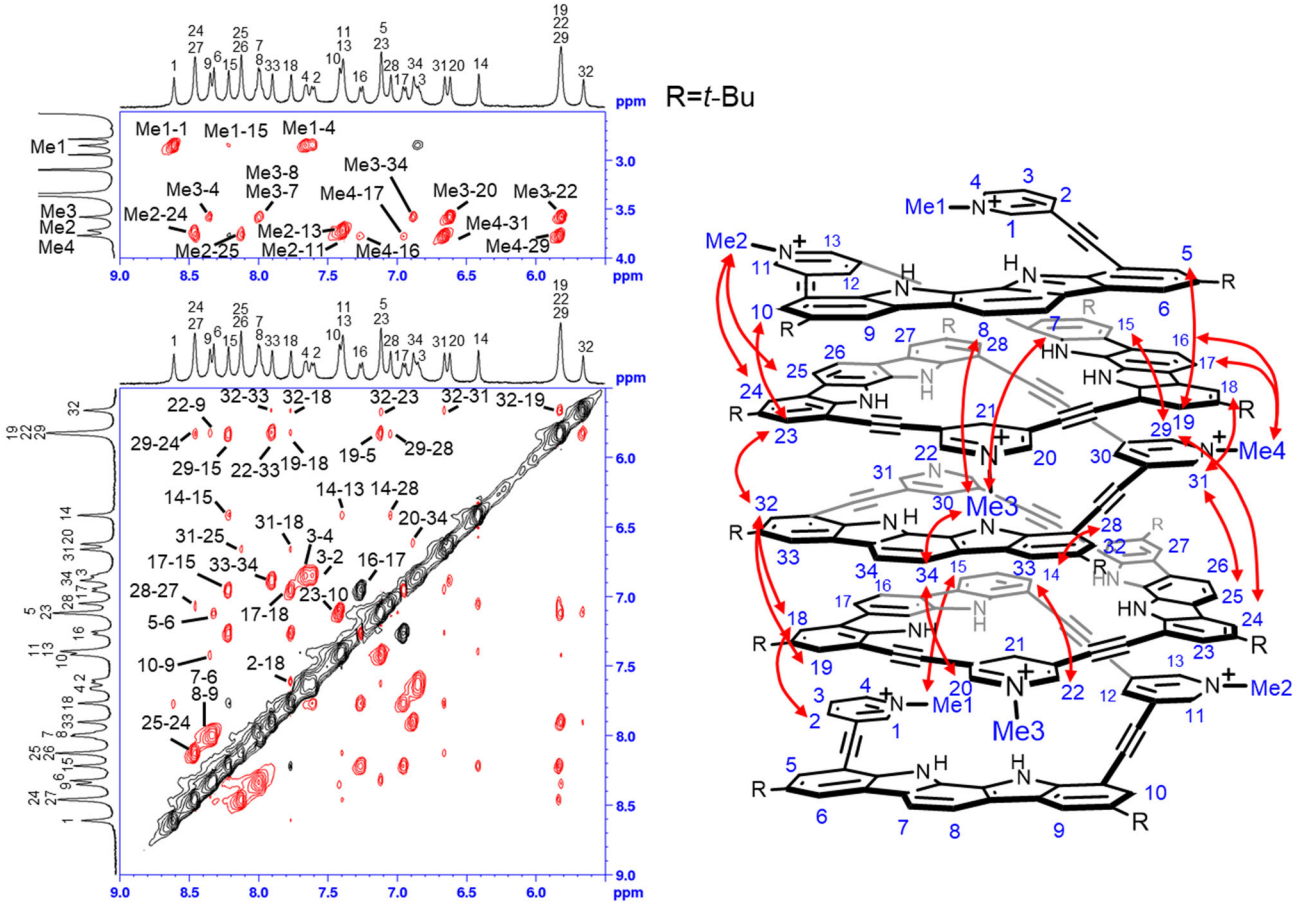


Fig. S12 Partial ROESY spectra (DMSO-d_6, 25°C, mixing time: 400 ms) of oligomer **6**.

2.4 ^{1}H NMR titration experiments

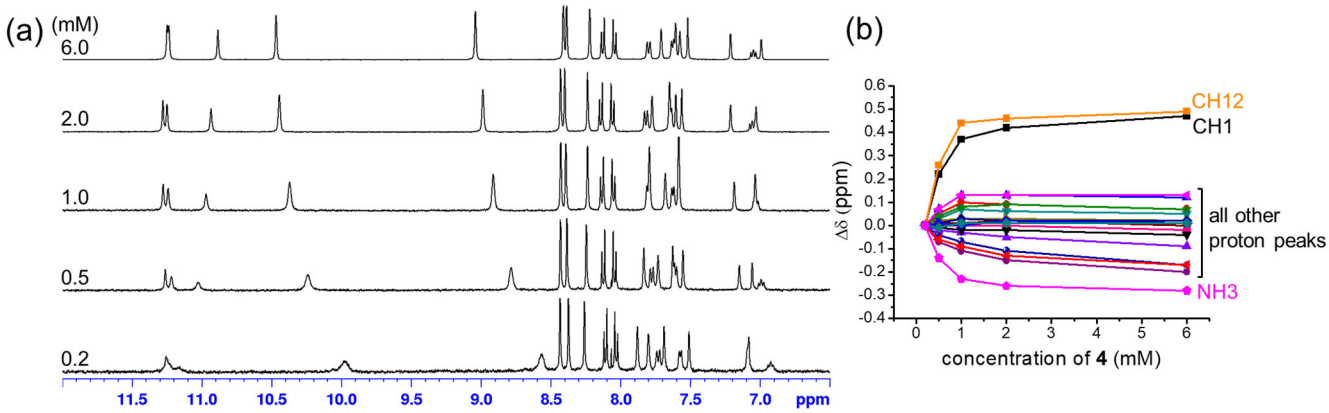


Fig. S13 (a) Concentration-dependent ^{1}H NMR spectra (400 MHz, 25 °C) of oligomer **4** (6.0 mM, 2.0 mM, 1.0 mM, 0.5 mM, 0.2 mM) in 1:1 (v:v) CD_3OH:DMSO-d_6. (b) Plots of chemical shift changes against concentrations.

Sample preparation: A stock solution of oligomer **4** (1.00×10^{-3} M) was prepared in 1:1 (v:v) CD_3OH/DMSO-d_6. Using this solution, a stock solution (3.00×10^{-2} M, 1.0 mL) of tetrabutylammonium salts (TBACl or TBABr) was prepared. An aliquot (400 μL) of the oligomer

4 solution was transferred to an NMR tube, and an initial spectrum was recorded at 25 °C. Small portions of the TBACl (or TBABr) solution were added, and the spectrum was recorded after each addition.

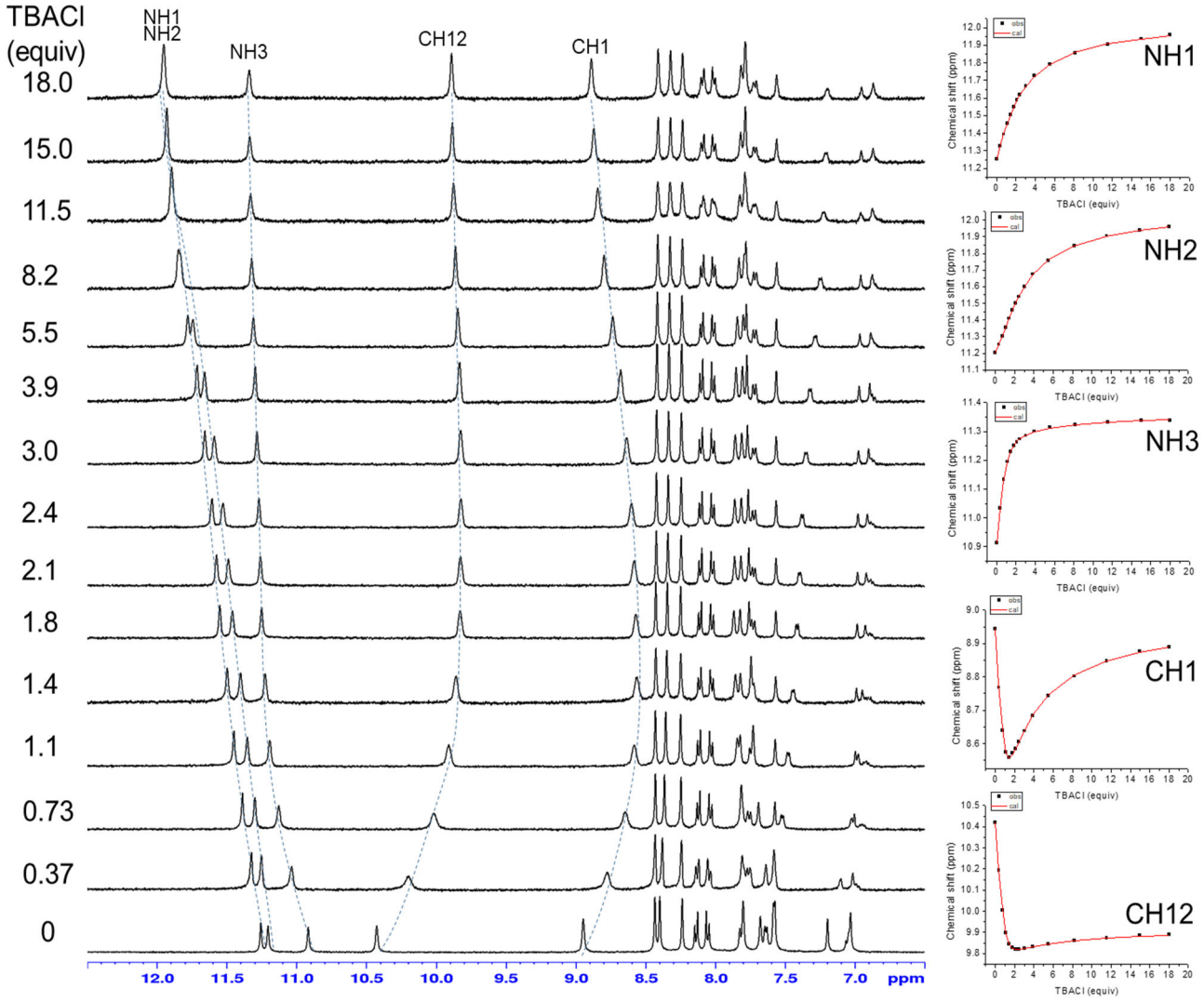


Fig. S14 Partial ^{1}H NMR spectral changes (400 MHz, in 1:1 (v/v) CD_3OH:DMSO-d_6 at 25 °C) of oligomer **4** (1.0 mM) upon the addition of TBACl. Global fitting of the titration curves with a 1:2 binding mode was performed using a HypNMR2008 program,[4] based on the chemical shifts of NH1, NH2, NH3, CH1, and CH12. The experimental data (dots) and theoretically fitting (lines) curves are shown right.

Table S1. Equilibrium constants (K_1 and K_2) between oligomer **4** and TBACl in 1:1 (v/v) CD_3OH:DMSO-d_6 at 25 °C

(M^{-1})	K_1	K_2
Titration 1	15500	345
Titration 2	13000	321
Average (±s.d)	14300 (±1200)	333 (±12)

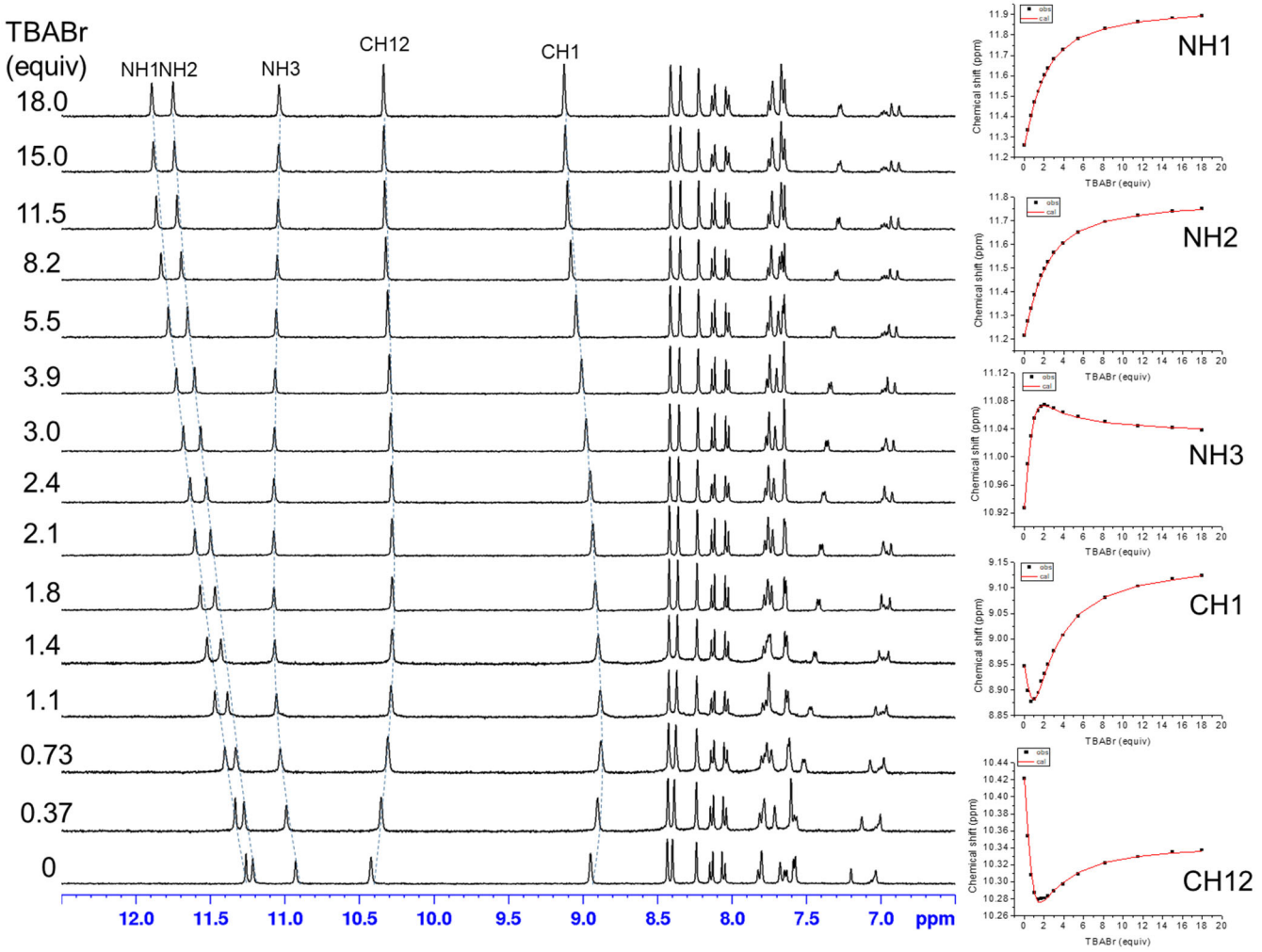


Fig. S15 Partial ^{1}H NMR spectral changes (400 MHz, in 1:1 (v/v) CD_3OH:DMSO-d_6 at 25 °C) of oligomer **4** (1.0 mM) upon the addition of TBABr. Global fitting of the titration curves with a 1:2 binding mode was performed using a HypNMR2008 program,[4] based on the chemical shifts of NH1, NH2, NH3, CH1, and CH12. The experimental data (dots) and theoretically fitting (lines) curves are shown right.

Table S2. Equilibrium constants (K_1 and K_2) between oligomer **4** and TBABr in 1:1 (v/v) CD_3OH:DMSO-d_6

(M^{-1})	K_1	K_2
Titration 1	13600	520
Titration 2	16300	505
Average (±s.d)	14900 (±1400)	512 (±8)

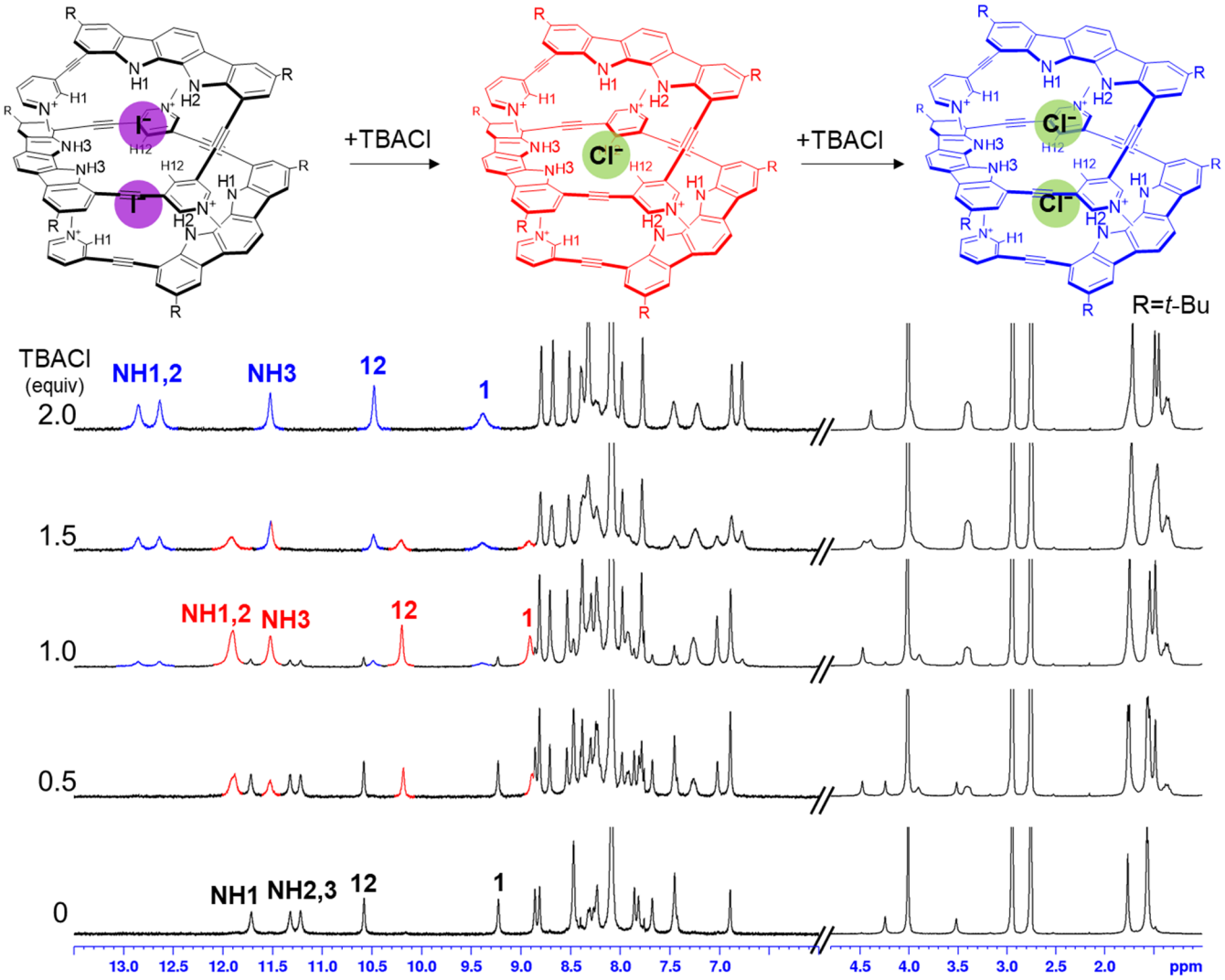


Fig. S16 Partial ^{1}H NMR spectra for oligomer **4** (2.0 mM) upon the addition of TBACl in DMF-d_7 at −50 °C. The red and blue peaks correspond to 1:1 and 1:2 complexes, respectively.

3. X-ray crystallographic analyses

3.1 Crystal growing

Oligomer **4**: Oligomer **4** was dissolved in acetonitrile in a test tube. Benzene was slowly vapor-diffused into the solution for a few days at room temperature, yielding single crystals suitable for X-ray diffraction.

Oligomer **5**: Oligomer **5** was dissolved in 10% (v/v) DMSO/MeOH solution in a test tube. Diethyl ether was slowly vapor-diffused into the solution for a few days at room temperature, yielding single crystals suitable for X-ray diffraction.

Oligomer **6**: Oligomer **6** was dissolved in 1:1:1 (v/v/v) acetone/$CHCl_3$/*N*,*N*-dimethylacetamide solution in a test tube. Benzene was slowly vapor-diffused into the solution for a few days at room temperature, yielding single crystals suitable for X-ray diffraction.

3.2 Data collection

Crystals were coated with *Parabar oil*, and their diffraction data were measured using synchrotron radiation on a Rayonix MX225HS detector with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. Data collection was conducted using the PAL BL2D-SMDC program,[5] and cell refinement, reduction, and absorption correction were performed with HKL3000sm (Ver. 716.7).[6]

Oligomer **4**: λ = 0.800000 Å, detector distance is 66 mm, omega scan; $\Delta\omega$ = 3º, exposure time is 1.6 sec per frame.

Oligomer **5**: λ = 0.800000 Å, detector distance is 66 mm, omega scan; $\Delta\omega$ = 3º, exposure time is 0.3 sec per frame.

Oligomer **6**: λ = 0.800000 Å, detector distance is 66 mm, omega scan; $\Delta\omega$ = 3º, exposure time is 1.0 sec per frame.

3.3 Structure solution and refinement

The crystal structures were solved by the intrinsic phasing method using SHELXT[7] and the direct method using SHELXD[8] and refined by full-matrix least-squares calculations with the SHELX-XL[9] in the Olex2[10] program package. The structure solutions of crystals were obtained 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 idealised positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients.

Oligomer **4**: Indolocarbazole and *N*-methylpyridinium units were observed as disordered and modeled using AFIX constraint, DFIX, SIMU, SADI, DELU, ISOR restraints. Two *t*-butyl groups and one benzene (solvent) were refined with isotropic displacement parameters. The final least-squares refinement of 0.0746 parameters against 0.1324 data resulted in residuals R (based on F2 for ≥ 2σ) and wR (based on F2 for all data) of 0.2965 and 0.1859, respectively. The final difference Fourier map was featureless.

Oligomer **5**: Indolocarbazole and *N*-methylpyridinium units were observed as disordered and modeled using AFIX constraint, DFIX, SIMU, SADI, DELU, ISOR restraints. 25 *t*-butyl groups and 3 water molecules were refined with isotropic displacement parameters. The final least-squares refinement of 0.0990 parameters against 0.2367 data resulted in residuals R (based on F2 for ≥ 2σ) and wR (based on F2 for all data) of 0.3423 and 0.3213, respectively. The final difference Fourier map was featureless.

Oligomer **6**: Indolocarbazole and *N*-methylpyridinium units were observed as disordered and modeled using AFIX constraint, DFIX, SIMU, SADI, DELU, ISOR restraints. One methyl and 12 *t*-butyl groups were refined with isotropic displacement parameters. The final least-squares refinement of 0.1313 parameters against 0.3387 data resulted in residuals R (based on F2 for I ≥ 2σ) and wR (based on F2 for all data) of 0.3776 and 0.4544, respectively. The final difference Fourier map was featureless.

For oligomers **4**, **5**, and **6**, A-level and B-level alerts were detected by the IUCr's checkCIF routine. These alerts are attributed to weak crystal diffraction, highly disordered side chains (*t*-butyl groups) and solvent molecules, data incompleteness, and moderate resolution due to the challenges of refining large crystal structures.

3.4 Summary

Oligomer **4** for $C_{115.5}H_{99.5}I_4N_{10}$ (*M* =2135.15 g/mol): triclinic, space group *P*-1 (no. 2), *a* = 22.459(5) Å, *b* = 30.925(6) Å, *c* = 33.796(7) Å, *α* = 100.82(3)°, *β* = 101.36(3)°, *γ* = 91.89(3)°, *V* = 22544(8) Å^3, *Z* = 8, *T* = 100 K, μ(synchrotron) = 1.588 mm^{-1}, *Dcalc* = 1.258 g/cm^3, 123015 reflections measured (2.652° ≤ 2Θ ≤ 54°), 63118 unique (R_{int} = 0.2973, R_{sigma} = 0.5971) which were used in all calculations. The final R_1 was 0.0746 (I > 2σ(I)) and wR_2 was 0.1859 (all data).

Oligomer **5** for $C_{186}H_{111.75}I_6N_{16}O_{0.75}$ (*M* =3344.06 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 38.554(8) Å, *b* = 51.490(10) Å, *c* = 43.138(9) Å, *β* = 93.47(3)°, *V* = 85478(30) Å^3, *Z* = 16, *T* = 100 K, μ(synchrotron) = 1.261 mm^{-1}, *Dcalc* = 1.039 g/cm^3, 643669 reflections measured (2.142° ≤ 2Θ ≤ 67.344°), 187809 unique (R_{int} = 0.4856, R_{sigma} = 0.6712) which were used in all calculations. The final R_1 was 0.0990 (I > 2σ(I)) and wR_2 was 0.3213 (all data).

Oligomer **6** for $C_{258}H_{123}I_8N_{22}O$ (*M* =4561.98 g/mol): triclinic, space group *P*-1 (no. 2), *a* = 25.200(5) Å, *b* = 25.207(5) Å, *c* = 29.256(6) Å, *α* = 104.05(3)°, *β* = 103.30(3)°, *γ* = 116.80(3)°, *V* = 14802(7) Å^3, *Z* = 2, *T* = 100 K, μ(synchrotron) = 1.215 mm^{-1}, *Dcalc* = 1.024 g/cm^3, 88769 reflections measured (2.222° ≤ 2Θ ≤ 56°), 45583 unique (R_{int} = 0.2634, R_{sigma} = 0.5391) which were used in all calculations. The final R_1 was 0.1292 (I > 2σ(I)) and wR_2 was 0.4456 (all data).

Table S3. Crystal data and structure refinement for oligomer **4**

Identification code	Oligomer **4**
Empirical formula	$C_{115.5}H_{99.5}I_4N_{10}$
Formula weight	2135.15
Temperature/K	100
Crystal system	triclinic
Space group	*P*-1
a/Å	22.459(5)
b/Å	30.925(6)
c/Å	33.796(7)
α/°	100.82(3)
β/°	101.36(3)
γ/°	91.89(3)
Volume/Å^3	22544(8)
Z	8
ρ_{calc}g/cm^3	1.258
μ/mm^{-1}	1.588
F(000)	8596.0
Crystal size/mm^3	0.100 × 0.020 × 0.015
Radiation (Å)	synchrotron (λ = 0.800000)
2Θ range for data collection/°	2.652 to 54
Index ranges	-25 ≤ h ≤ 25, -35 ≤ k ≤ 35, -35 ≤ l ≤ 34
Reflections collected	123015
Independent reflections	63118 [R_{int} = 0.2973, R_{sigma} = 0.5971]
Data/restraints/parameters	63118/3120/4155
Goodness-of-fit on F^2	0.690
Final R indexes [I>=2σ (I)]	R_1 = 0.0746, wR_2 = 0.1324
Final R indexes [all data]	R_1 = 0.2965, wR_2 = 0.1859
Largest diff. peak/hole / e Å^{-3}	1.72/-0.98
CCDC number	2389562

Table S4. Crystal data and structure refinement for oligomer **5**

Identification code	Oligomer **5**
Empirical formula	$C_{186}H_{111.75}I_6N_{16}O_{0.75}$
Formula weight	3344.06
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	38.554(8)
b/Å	51.490(10)
c/Å	43.138(9)
α/°	90
β/°	93.47(3)
γ/°	90
Volume/Å^3	85478(30)
Z	16
ρ_{calc}g/cm^3	1.039
μ/mm^{-1}	1.261
F(000)	26620.0
Crystal size/mm^3	0.05 × 0.04 × 0.03
Radiation	synchrotron (λ = 0.800000)
2Θ range for data collection/°	2.142 to 67.344
Index ranges	-48 ≤ h ≤ 48, -60 ≤ k ≤ 60, -53 ≤ l ≤ 54
Reflections collected	643669
Independent reflections	187809 [R_{int} = 0.4856, R_{sigma} = 0.6712]
Data/restraints/parameters	187809/4530/6254
Goodness-of-fit on F^2	0.693
Final R indexes [I>=2σ (I)]	R_1 = 0.0990, wR_2 = 0.2367
Final R indexes [all data]	R_1 = 0.3423, wR_2 = 0.3213
Largest diff. peak/hole / e Å^{-3}	1.21/-1.31
CCDC number	2389563

Table S5. Crystal data and structure refinement for oligomer **6**

Identification code	Oligomer **6**
Empirical formula	$C_{258}H_{123}I_8N_{22}O$
Formula weight	4561.98
Temperature/K	100
Crystal system	triclinic
Space group	*P*-1
a/Å	25.200(5)
b/Å	25.207(5)
c/Å	29.256(6)
α/°	104.05(3)
β/°	103.30(3)
γ/°	116.80(3)
Volume/Å^3	14802(7)
Z	2
ρ_{calc}g/cm^3	1.024
μ/mm^{-1}	1.215
F(000)	4514.0
Crystal size/mm^3	0.15 × 0.02 × 0.02
Radiation	synchrotron (λ = 0.800000)
2Θ range for data collection/°	2.222 to 56
Index ranges	-29 ≤ h ≤ 29, -29 ≤ k ≤ 29, -34 ≤ l ≤ 34
Reflections collected	88769
Independent reflections	45583 [R_{int} = 0.2634, R_{sigma} = 0.5391]
Data/restraints/parameters	45583/1838/2030
Goodness-of-fit on F^2	0.694
Final R indexes [I>=2σ (I)]	R_1 = 0.1292, wR_2 = 0.3323
Final R indexes [all data]	R_1 = 0.3728, wR_2 = 0.4456
Largest diff. peak/hole / e Å^{-3}	0.63/-0.82
CCDC number	2389564

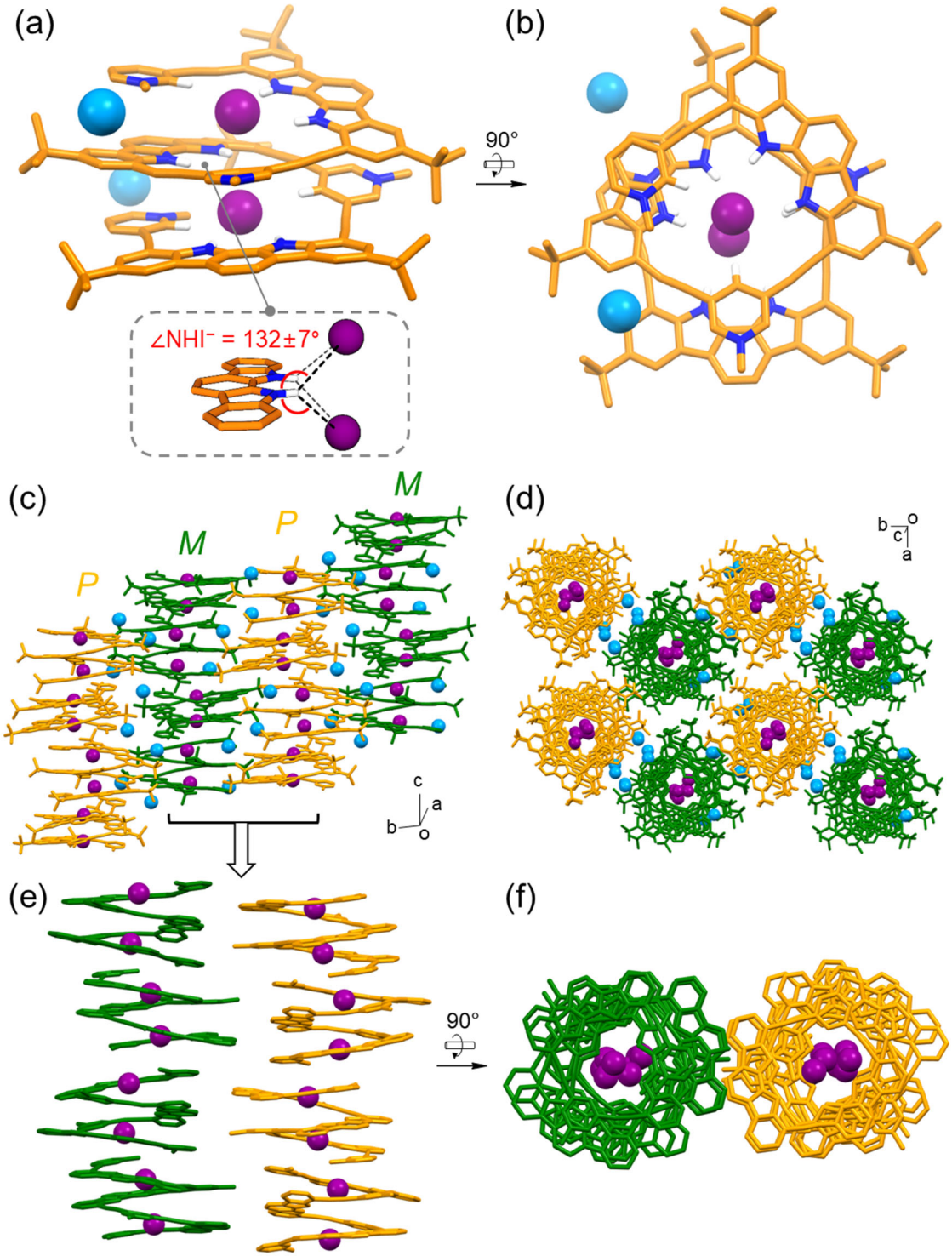


Fig. S17 (a, b) Two different views of X-ray crystal structure of oligomer **4**. Among four iodides, the two iodides within the cavity are shown as purple, and the two external iodides are shown as light blue. (c–f) Crystal packing views of oligomer **4**. In (c,d), all iodides within the cavity are shown as purple, and all external iodides are shown as light blue. In (e,f), *t*-butyl groups, all hydrogen atoms, and all external iodides are omitted for clarity.

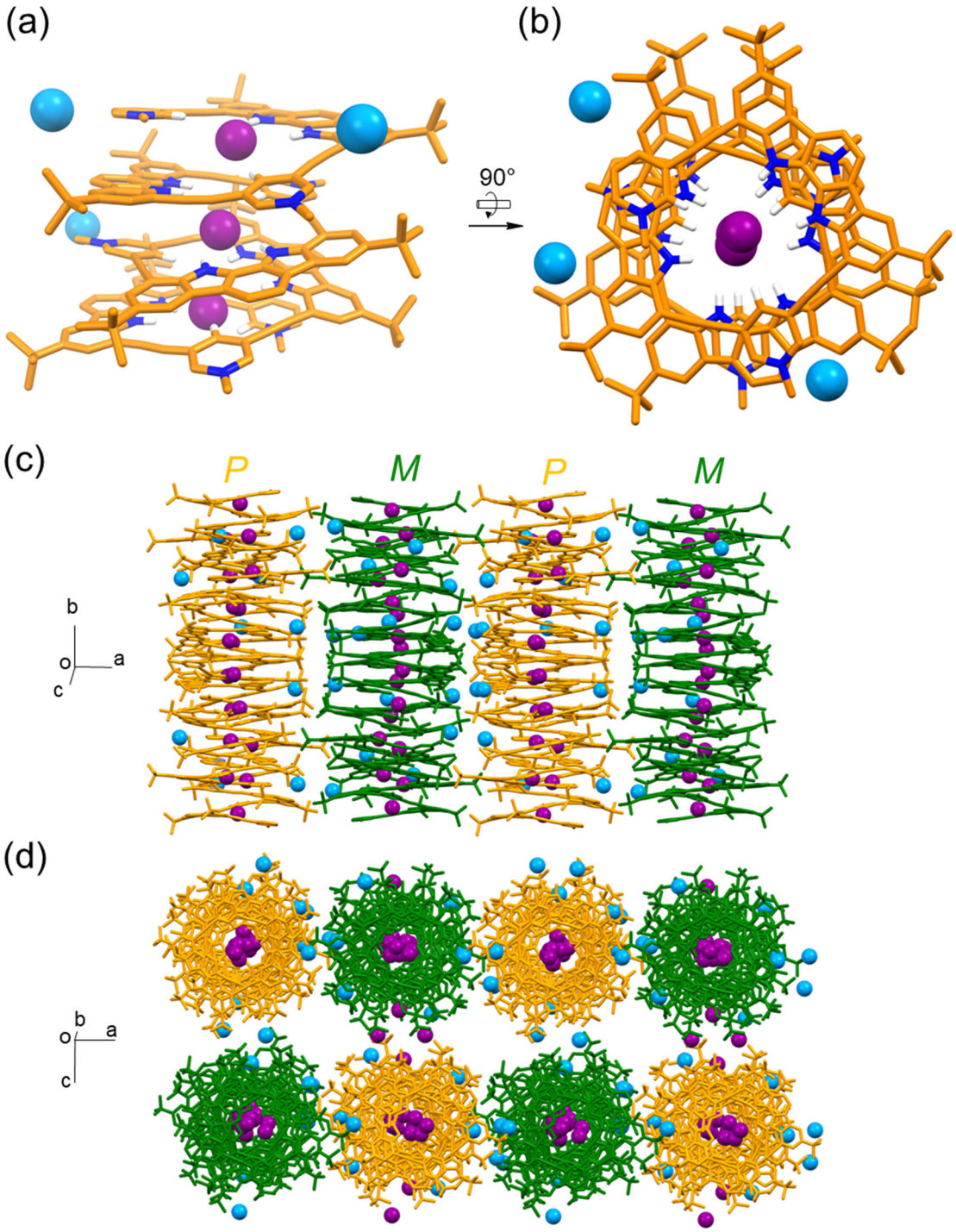


Fig. S18 (a, b) Two different views of X-ray crystal structure of oligomer **5**. Among six iodides, the three iodides within the cavity are shown as purple, and the three external iodides are shown as light blue. (c, d) Crystal packing views of oligomer **5**. All iodides within the cavity are shown as purple, and all external iodides are shown as light blue.

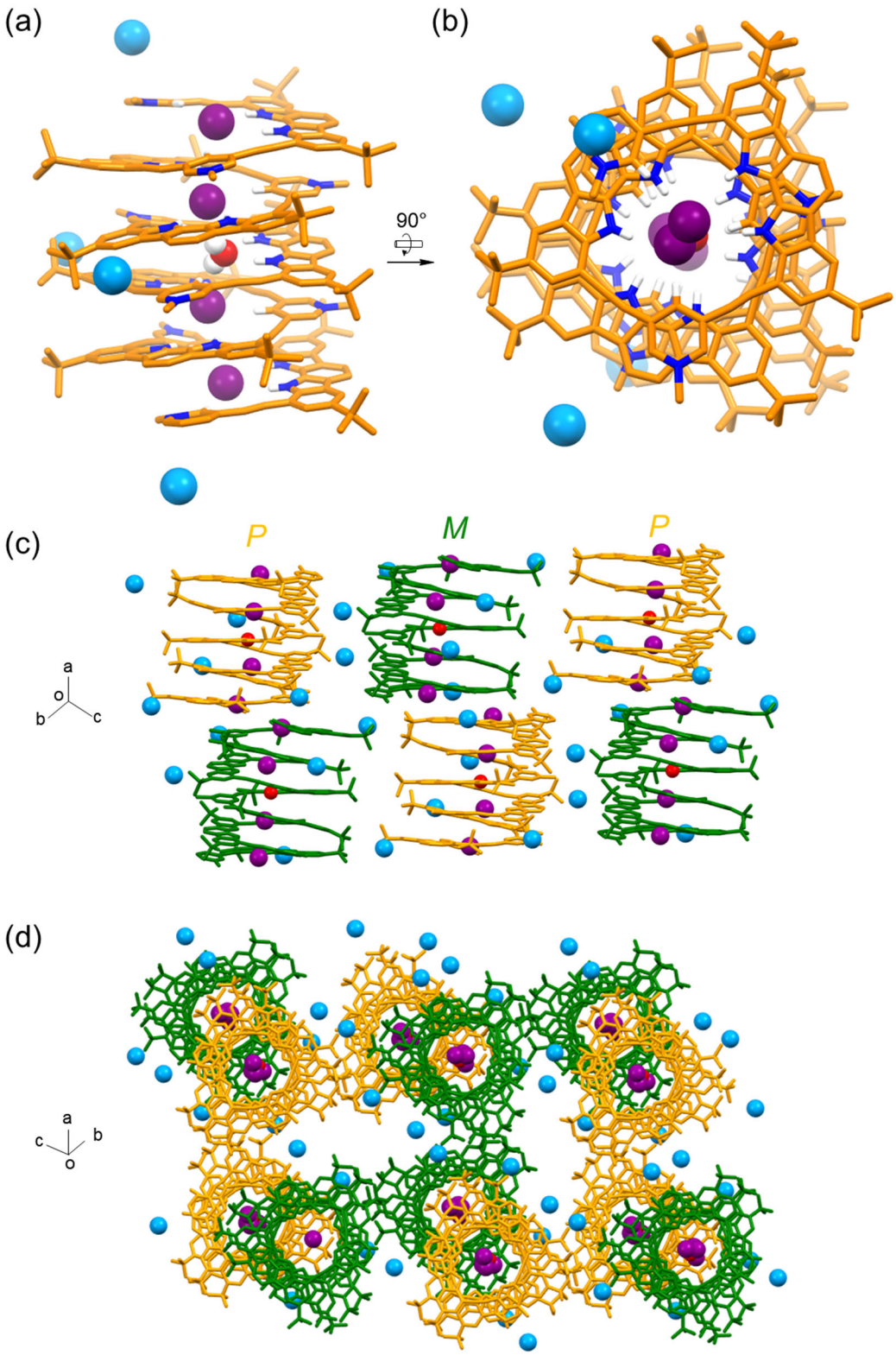


Fig. S19 (a, b) Two different views of X-ray crystal structure of oligomer **6**. Among eight iodides, the four iodides within the cavity are shown as purple, and the four external iodides are shown as light blue. (c, d) Crystal packing views of oligomer **6**. All iodides within the cavity are shown as purple, and all external iodides are shown as light blue.

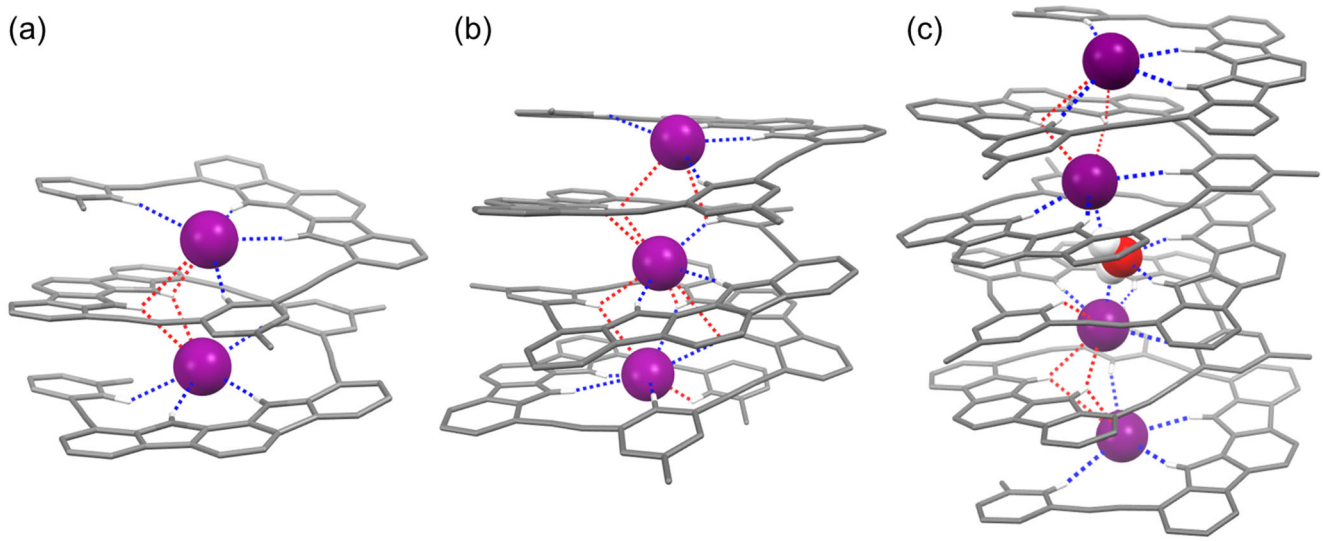


Fig. S20 X-ray crystal structures of oligomers (a) **4**, (b) **5**, and (c) **6**. Hydrogen bonds are shown as dashed lines; red dashed lines represent weak interactions due to poor D-H···I⁻ directionality (<140°). *t*-Butyl groups, and all CH protons except hydrogen-bonded CH protons are omitted for clarity.

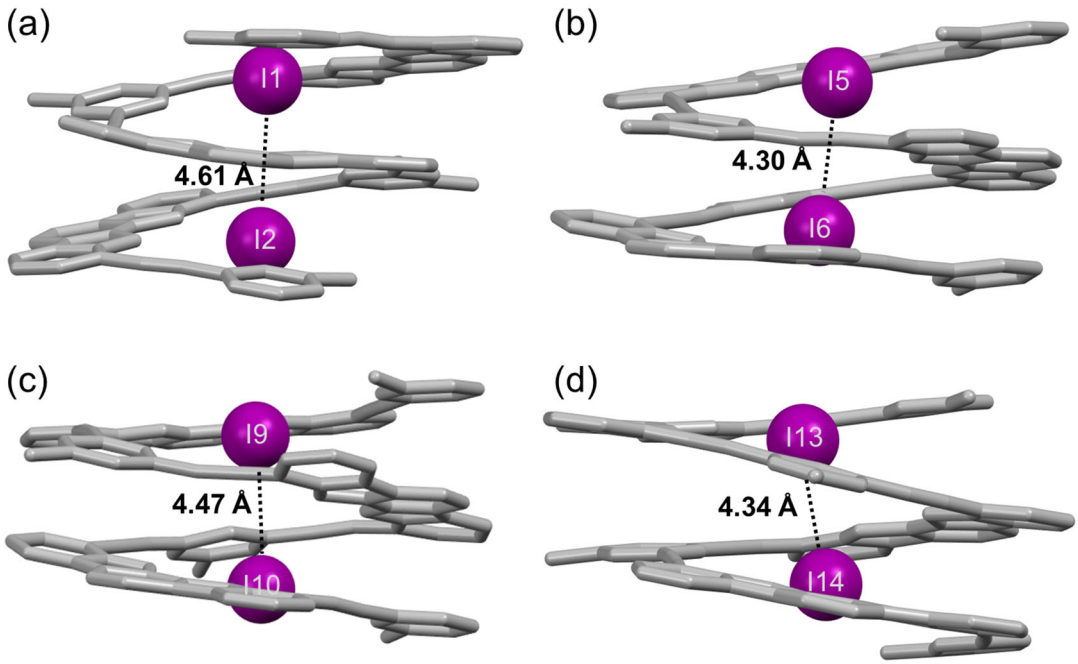


Fig. S21 Distances between iodide ions in the cavity in the X-ray crystal structure of oligomer **4**. The asymmetric unit contains four oligomers (Z' = 4).

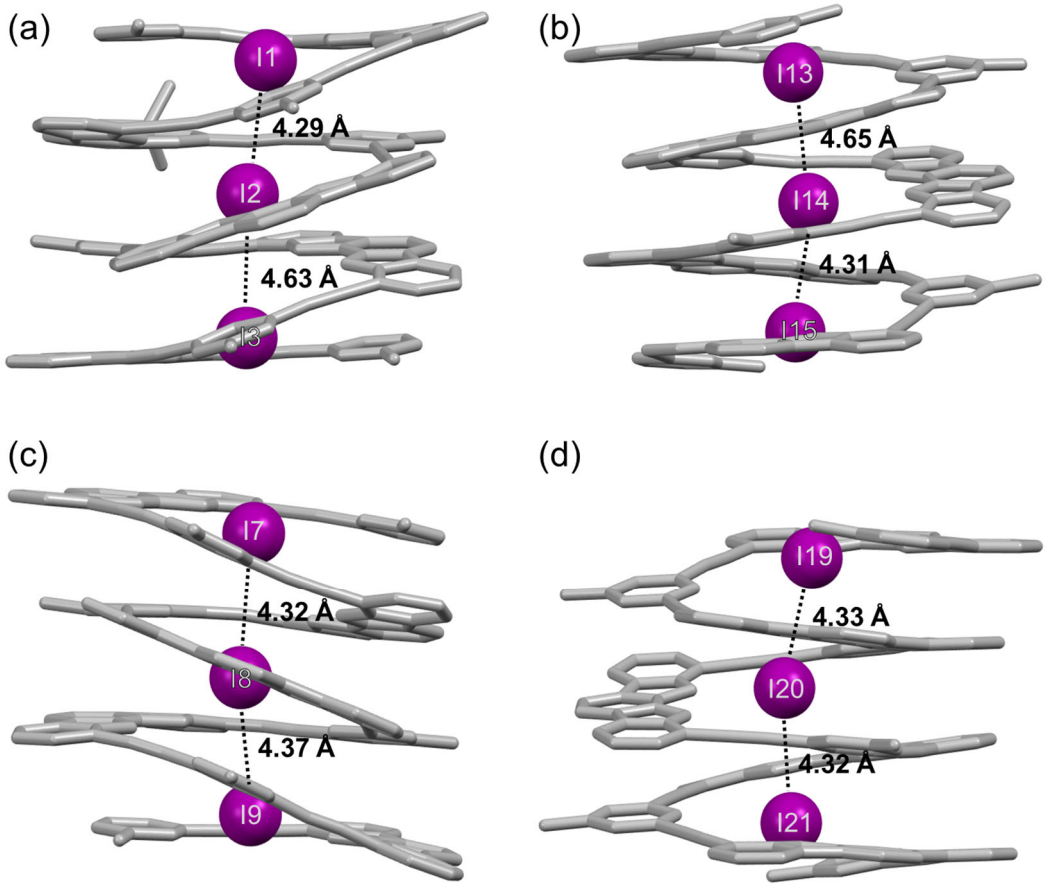


Fig. S22 Distances between iodide ions in the cavity in the X-ray crystal structure of oligomer **5**. The asymmetric unit contains four oligomers (Z' = 4).

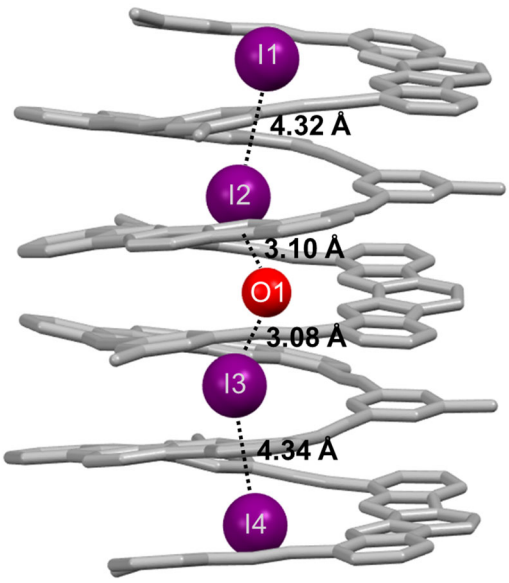


Fig. S23 Distances between iodide ions and a water molecule in the cavity in the X-ray crystal structure of oligomer **6**.

4. ^{1}H and ^{13}C NMR spectra of new compounds

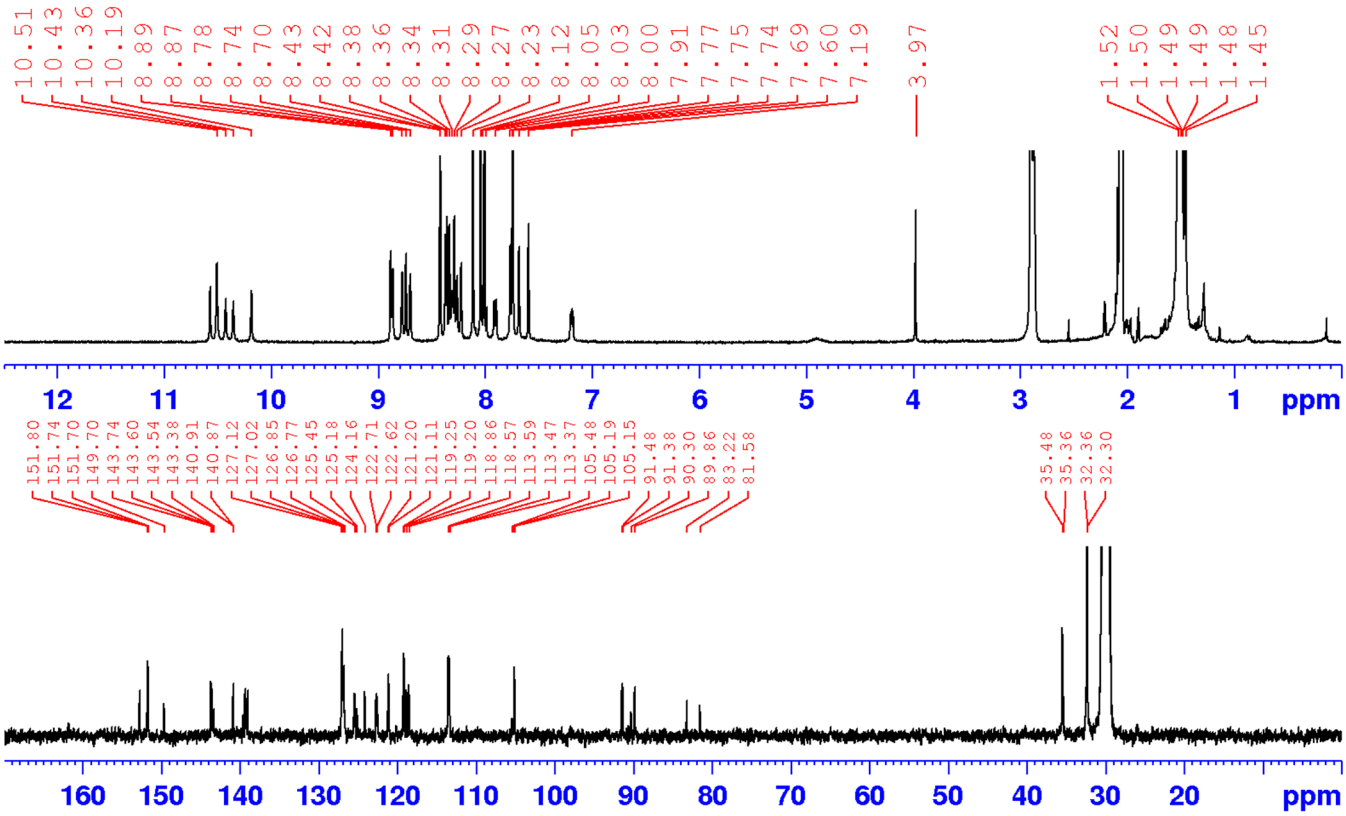


Fig. S24 ^{1}H and ^{13}C spectra of compound **S3** (acetone-d_6, 25 °C)

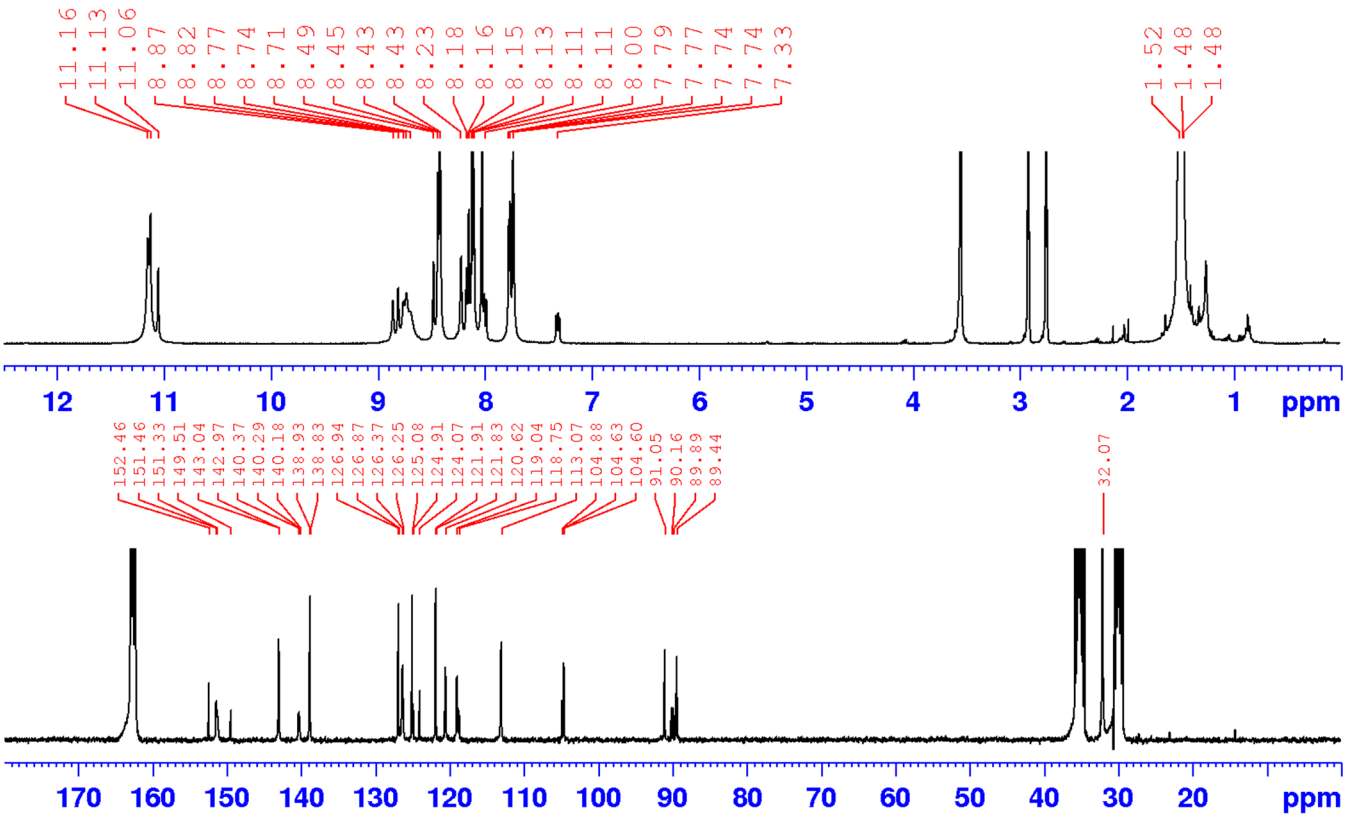


Fig. S25 ^{1}H and ^{13}C spectra of compound **3** (DMF-d_7, 25 °C)

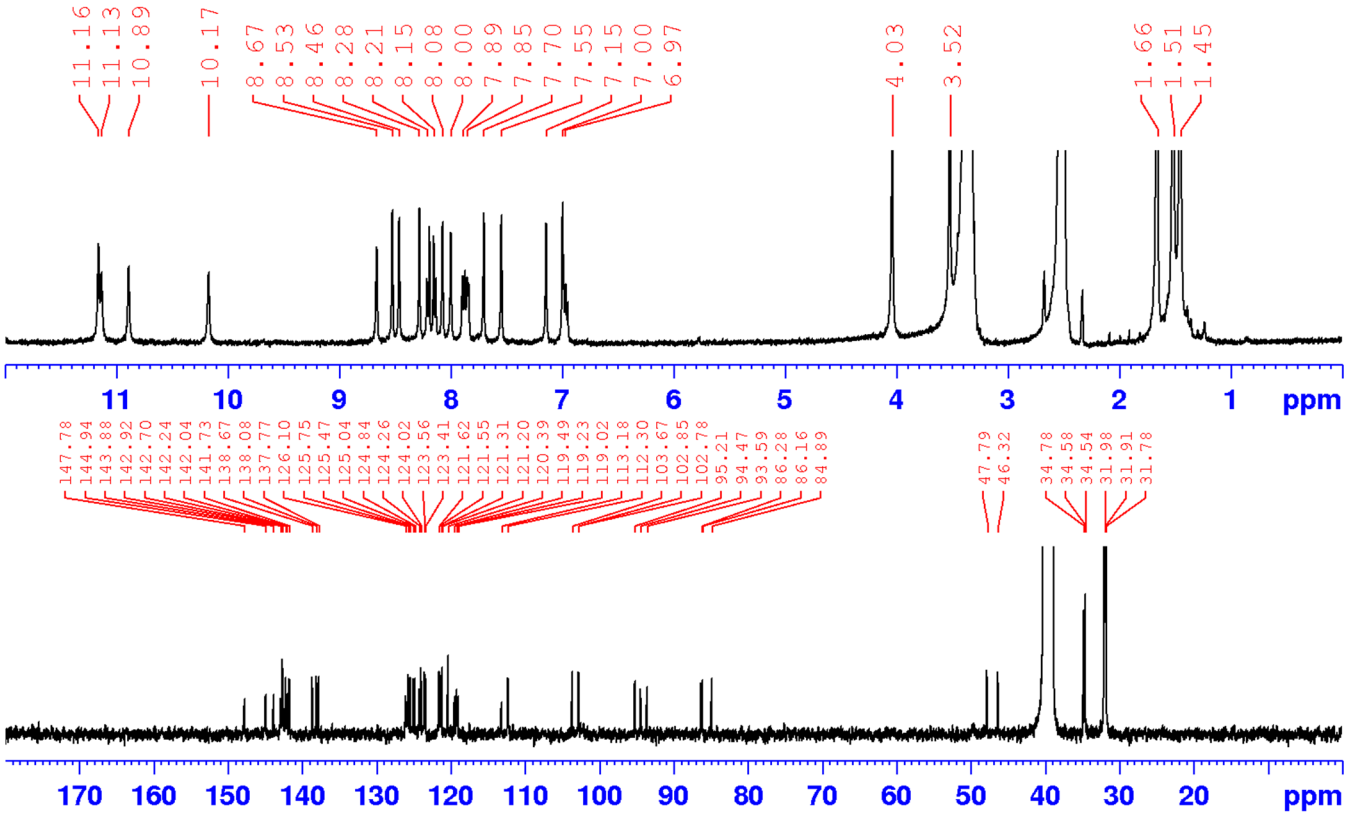


Fig. S26 ^{1}H and ^{13}C spectra of compound **4** (DMSO-d_6, 25 °C)

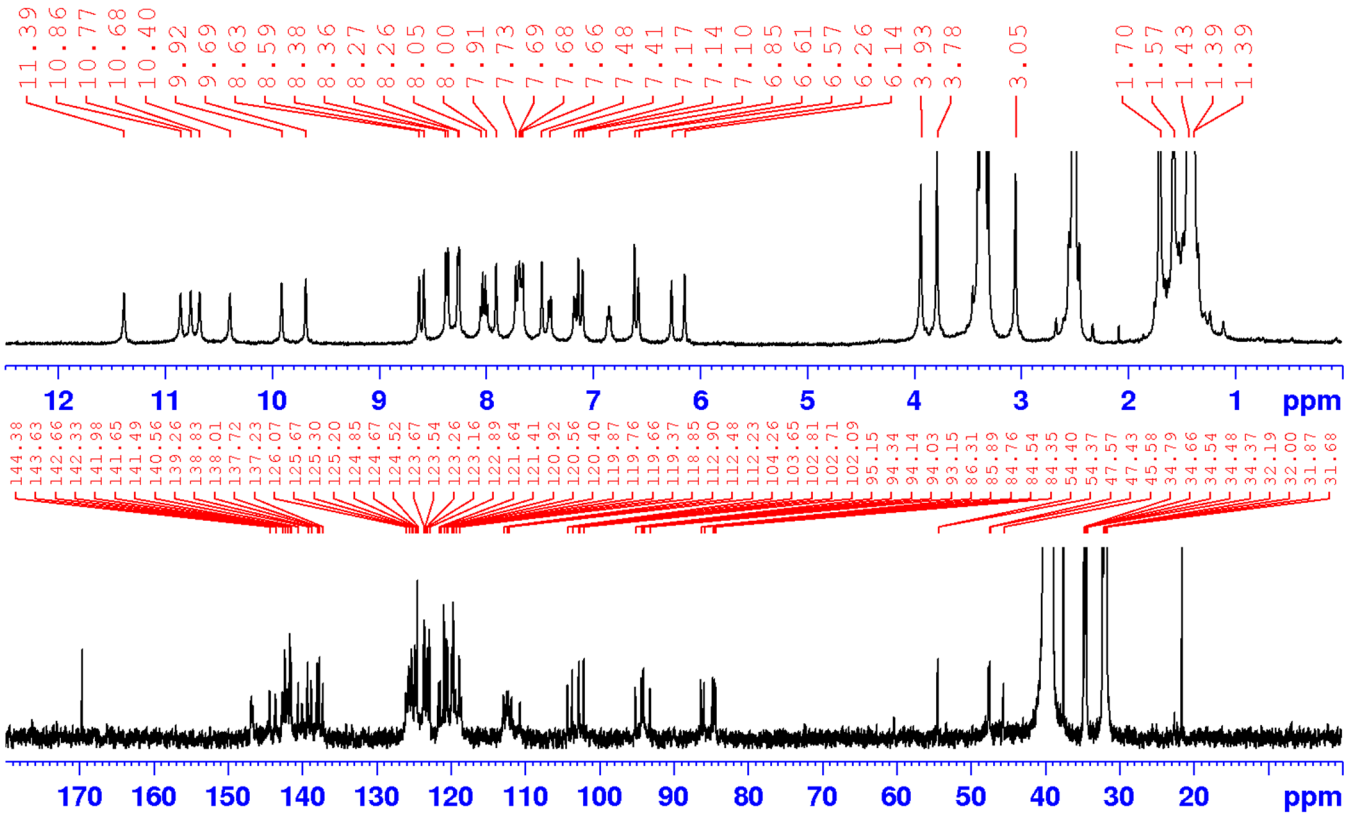


Fig. S27 ^{1}H and ^{13}C spectra of compound **5** (DMSO-d_6, 25 °C)

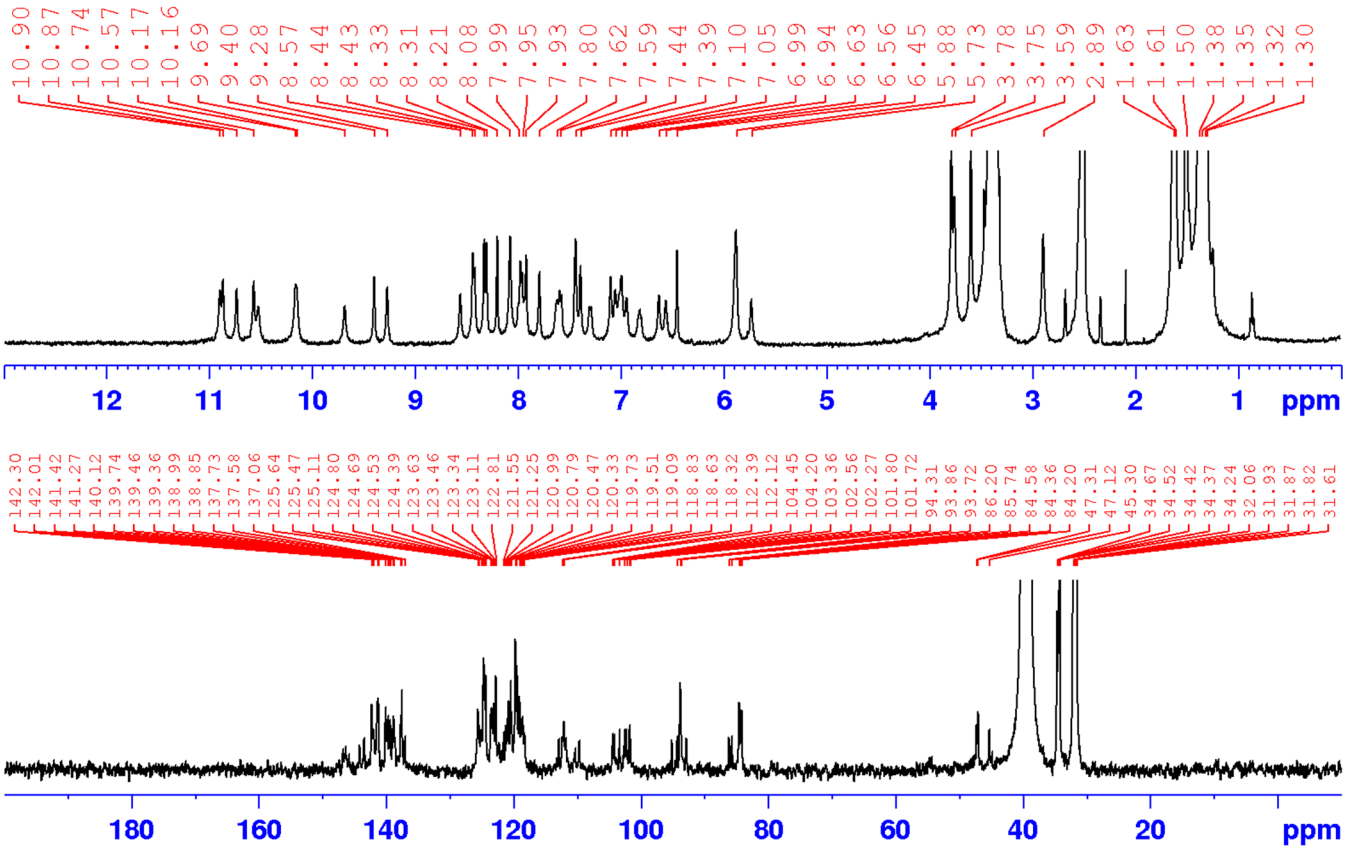


Fig. S28 ^{1}H and ^{13}C spectra of compound **6** (DMSO-d_6, 25 °C)

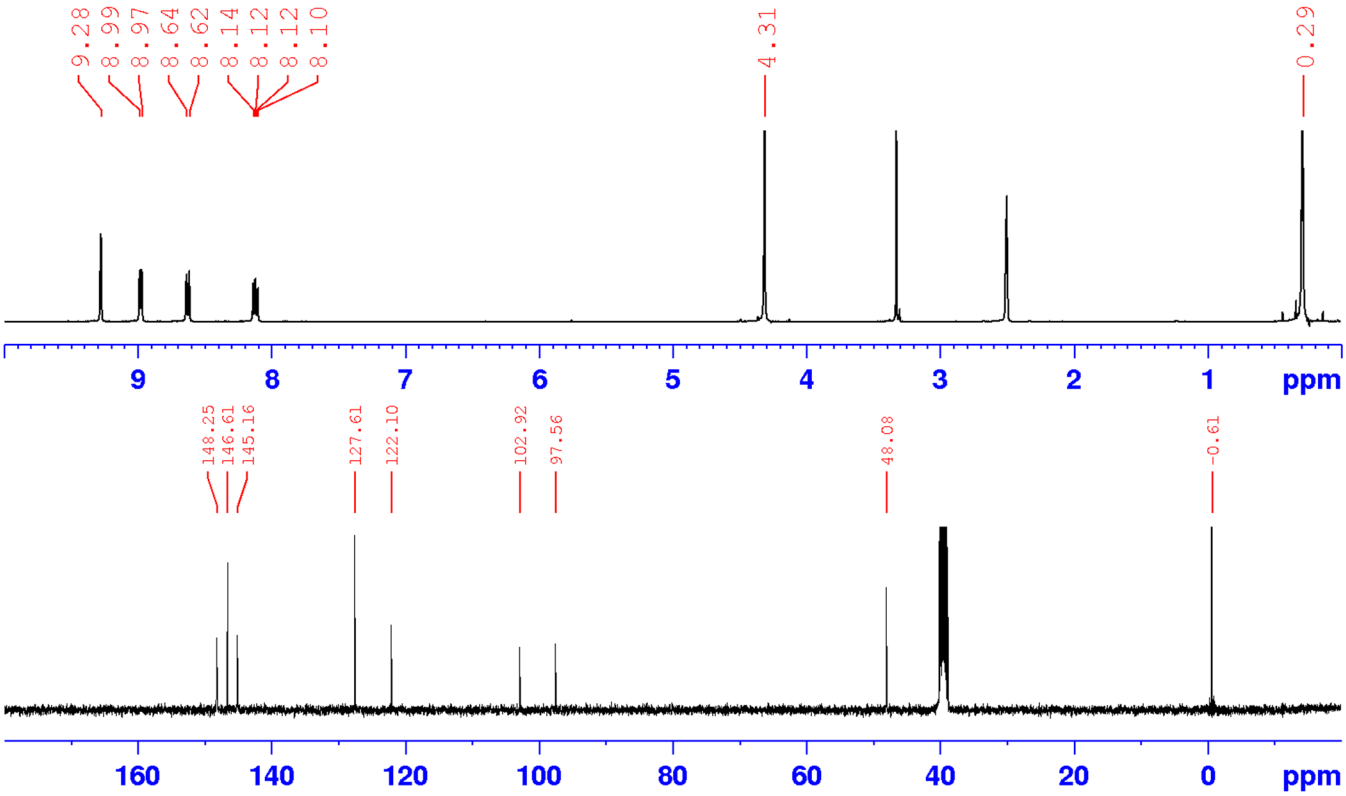


Fig. S29 ^{1}H and ^{13}C spectra of compound **7** (DMSO-d_6, 25 °C)

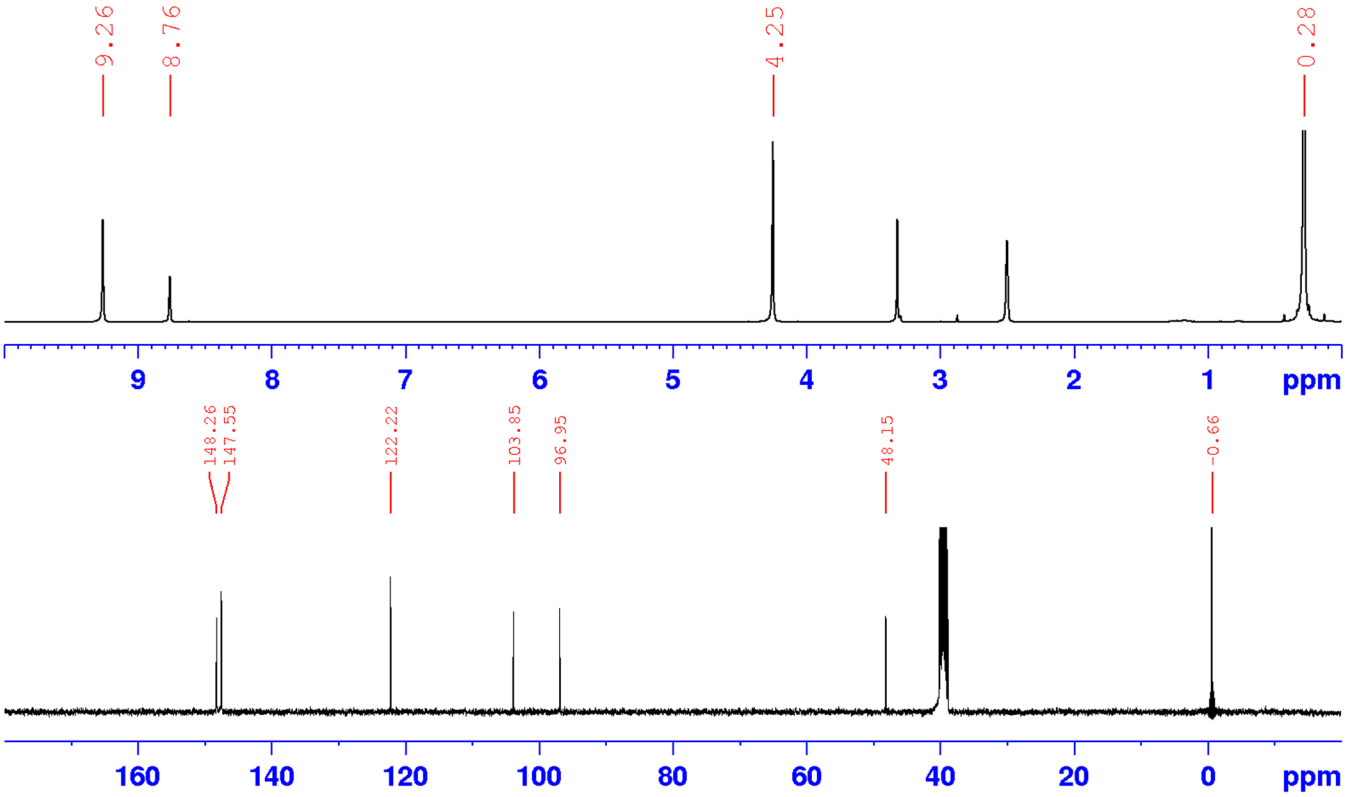


Fig. S30 ^{1}H and ^{13}C spectra of compound **8** (DMSO-d_6, 25 °C)

5. ESI mass spectra of oligomer 4

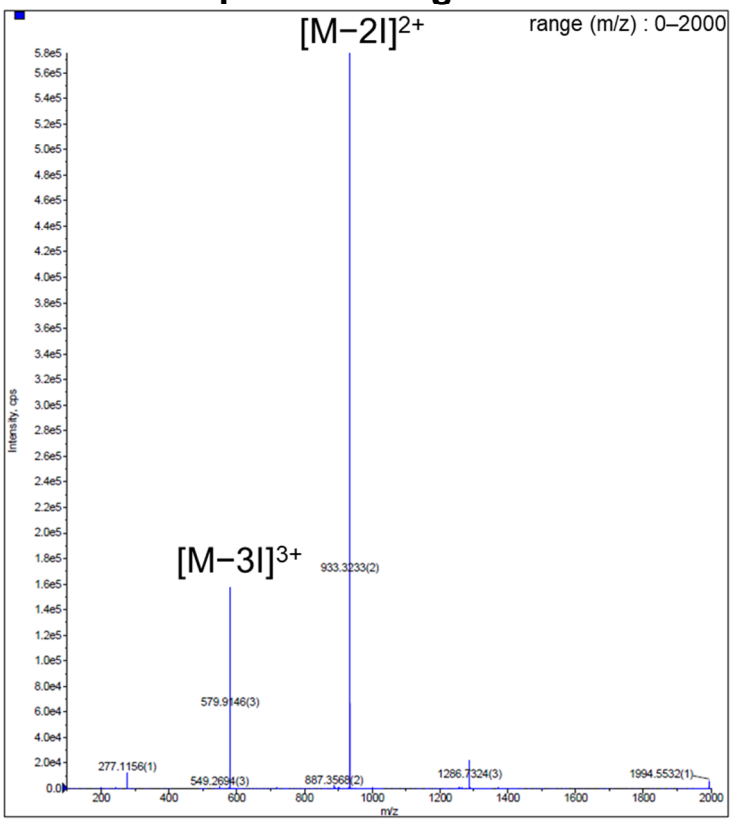


Fig. S31 ESI-HRMS spectra of oligomer **4**.

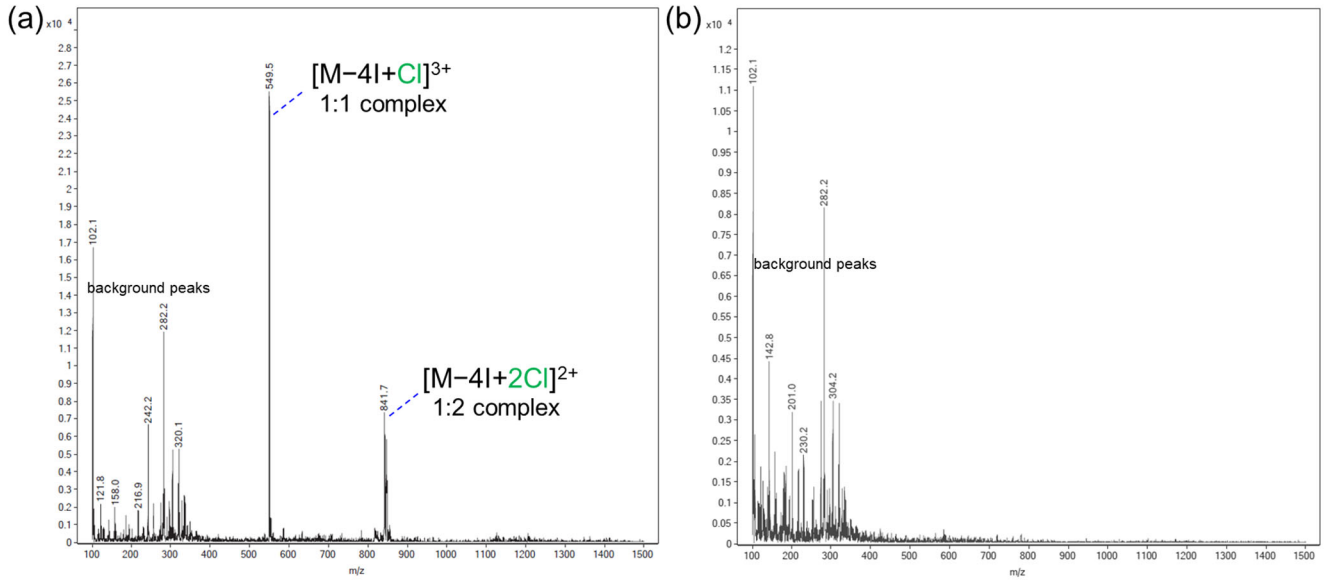


Fig. S32. (a) ESI-MS spectrum for a mixture of oligomer **4** (7-mer) and TBACl (2 equiv), and (b) a background spectrum without any sample.

6. References

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