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Supporting Information

69451 Weinheim, Germany

Increasing the Size of an Aromatic Helical Foldamer Cavity by Strand Intercalation**

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Supporting Information.

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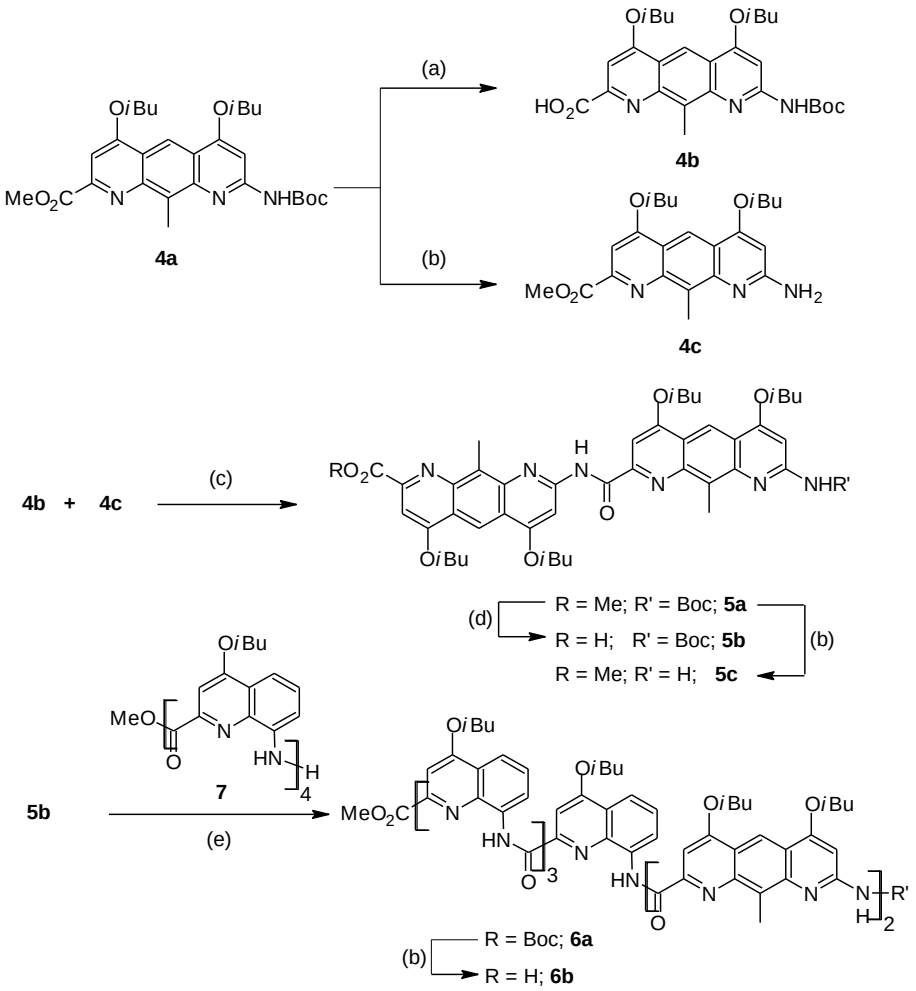
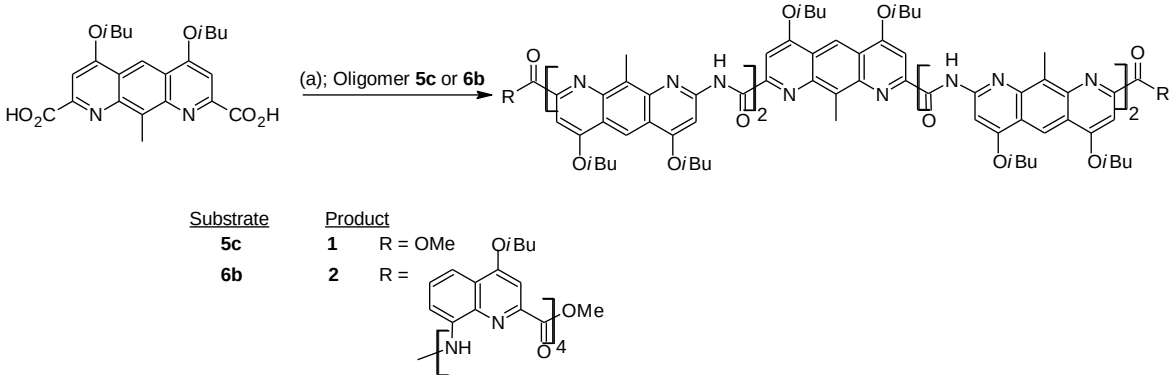
1) Synthetic Schemes



Scheme S1: Synthesis of **4a** – **6b**: (a) 3 equiv. NaOH, Dioxane, H_2O; (b) trifluoroacetic acid, CH_2Cl_2; (c) 3 equiv. PyBOP, 3 equiv. dipea, $CHCl_3$, 40 °C; (d) 4 equiv. NaOH, dimethylformamide, H_2O; (e) 1 equiv. tetramer amine **7**, 2 equiv. PPh_3, 2 equiv. trichloroacetonitrile, 3 equiv. diisopropylethylamine, $CHCl_3$



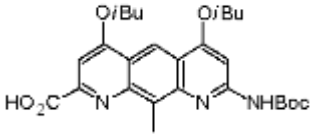
Scheme S2: Synthesis of pentamer **1** and tridecamer **2**: (a) 6 equiv. PyBOP, 6 equiv. dipea, $CHCl_3$, 40 °C;

2) Experimental Details

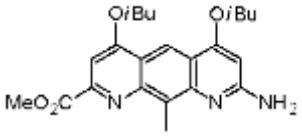
General Procedures. Unless otherwise stated all solvents and reagents were used without further purification. When required, dry solvents and bases were obtained directly prior to use by either distillation from CaH_2 ($CHCl_3$, triethylamine, and diisopropylethyl amine) or dried over alumina (THF, Toluene, and DCM). All solvent mixtures for chromatography are reported as (v/v). The syntheses of monomer **4a**, diacid **4d**, and tetramer quinoline amine **7** have been previously reported.[S1-3] NMR spectra were recorded on Bruker Avance II 300 and Bruker AVANCE 400 spectrometers. ^1H and ^{13}C NMR chemical shifts are reported in ppm and are calibrated against residual ^1H and ^{13}C solvent signals of $CDCl_3$ or D_5-Pyridine. Coupling constants are reported in hertz. The following notation is used for the ^1H NMR spectral splitting patterns: singlet (s), broad singlet (bs), doublet (d), triplet (t), multiplet (m). High resolution electrospray ionization orbitrap (ESI-orbitrap) mass spectra were measured in the positive ion mode. Gel permeation chromatography was performed on an LC-9130G NEXT (Japan Analytical Industry Co., Ltd.) setup equipped with two preparative columns (Inner diameter of 20mm and length of 600mm): a JAIGEL 2.5H and a JAIGEL 3H. Column temperatures were regulated at 37 °C in an oven. Chloroform (HPLC grade, ethanol stabilized) was used for the separations.

S1) *T. Qi, T. Deschrijver, I. Huc, Nature Protocols* ***2013***, 8, *693*
S2) J. Garric, J.-M. Le´ger and I. Huc, *Chem.–Eur. J.* **2007**, 13, 8454.
S3) M. L. Singleton, N. Castellucci, S. Massip, B. Kauffmann,Y. Ferrand, I. Huc, *J. Org. Chem.* **2014**, *79*, 2115.

Synthetic Procedures

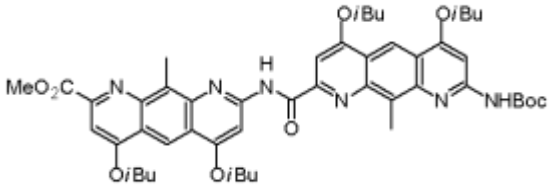


1,8-diaza-4,5-diisobutoxy-7-[(*tert*-butoxycarbonyl)amino]-9-methyl-2-anthracene carboxylic acid, (Monomer 4b). In a 50 mL round bottom flask, monomer **4a** (2 g, 3.91 mmol) was slurried in 15 mL of dioxane. Sodium hydroxide (0.470 g, 1.17 mmol, 3 equiv.) in 2 mL of H_2O was added dropwise. The reaction was stirred overnight at room temperature, after which time it was poured into 100 mL of 5% citric acid solution and then extracted into $CHCl_3$. The product was washed with water and brine and then dried over Na_2SO_4. After filtration, solvent was removed by rotary evaporation and the yellow solid was dried on the vacuum line to give **4c** as a bright yellow solid. (1.9 g, 98%). ^1H NMR ($CDCl_3$, 300 MHz): δ 9.05 (s, 1H), 7.72 (s, 1H), 7.58 (s, 1H), 7.54 (s, 1H), 4.17 (d, J_{HH} = 6.4 Hz, 2H), 4.12 (d, J_{HH} = 6.4 Hz, 2H), 3.13 (s, 3H), 2.36 (m, 2H), 1.58 (s, 9H), 1.19 (d, J_{HH} = 6.8 Hz, 12H). Limited solubility of Monomer 4b prevented characterization by ^{13}C NMR. HRMS (ESI-Orbitrap) m/z calcd for $C_{27}H_{36}N_3O_6$ $[M+H]^+$ 498.2599, found 498.2610.

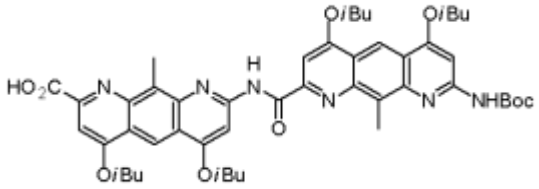


Methyl 1,8-diaza-4,5-diisobutoxy-7-[(amino]-9-methyl-2-anthracene carboxylic acid, (Monomer 4c). In a 50 mL round bottom flask, monomer **4a** (2.0 g, 3.91 mmol) was dissolved in 25 ml of 1:1 CH_2Cl_2:TFA.

The reaction was stirred for 3 hours at room temperature and then solvent was removed on the rotary evaporator. The crude yellow oil was partitioned between $CHCl_3$ and saturated $NaHCO_3$ solution. The organic layer was washed with water and brine and then dried over Na_2SO_4. After removal of solvent, the product was dried overnight on the vacuum line to give **4c** as a yellow solid. (1.4 g, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.90 (s, 1H), 7.39 (s, 1H), 6.07 (s, 1H), 4.99 (bs, 2H), 4.09 (d, J_{HH} = 6.4 Hz, 2H), 4.07 (s, 3H), 3.96 (d, J_{HH} = 6.4 Hz, 2H), 3.21 (s, 3H), 2.31 (m, 2H), 1.18 (d, J_{HH} = 6.8 Hz, 6H), 1.17 (d, J_{HH} = 6.8 Hz, 6H). Limited solubility of Monomer 4c prevented characterization by ^{13}C NMR. HRMS (ESI) m/z calcd for $C_{23}H_{30}N_3O_4$ $[M+H]^+$ 412.2231, found 412.2246.

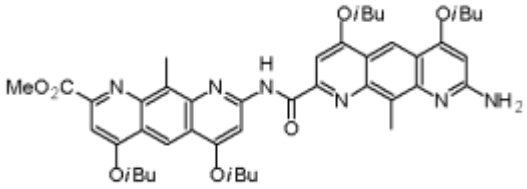


Dimer 5a. In a 50 mL round bottom flash, under a argon atmosphere, monomer **5b** (1.45 g, 2.92 mmol), monomer **4c** (1.2 g, 2.92 mmol, 1 equiv.), and PyBOP (4.56 g, 8.76 mmol, 3 equiv.) were dissolved in 20 mL of dry $CHCl_3$. Triethylamine (1.39 mL, 11.1 mmol, 3.8 equiv.) was added and the reaction was stirred at 45 °C overnight. Solvent was removed on the rotary evaporator and the product with recrystallized from DCM/MeOH to give **5a** as a yellow solid. (2.21 g, 85 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 11.10 (s, 1H), 9.01 (s, 1H), 9.00 (s, 1H), 8.17 (s, 1H), 7.67 (s, 1H), 7.63 (s, 1H), 7.42 (s, 1H), 4.17 (d, J_{HH} = 6.4 Hz, 2H), 4.15 (d, J_{HH} = 6.4 Hz, 2H), 4.11 (d, J_{HH} = 6.4 Hz, 4H), 4.10 (s, 3H), 3.40 (s, 3H), 3.31 (s, 3H), 2.37 (m, 2H), 1.60 (s, 9H), 1.23-1.19 (m, 24H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.8, 164.1, 163.6, 163.4, 152.8, 152.6, 151.9, 150.3, 149.1, 146.1, 145.2, 145.0, 134.6, 132.8, 120.1, 119.8. 119.1, 118.9, 113.5, 113.1, 97.7, 95.1, 93.1, 91.8, 81.4, 75.1, 74.8, 53.1, 28.5, 19.4, 19.4, 12.7, 12.5. HRMS (ESI) m/z calcd for $C_{50}H_{63}N_6O_9$ $[M+H]^+$ 891.4656, found 891.4663.

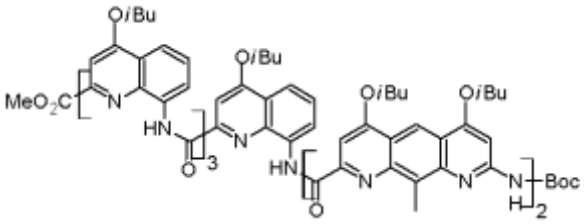


Dimer 5b. In a 25 mL round-bottomed flask **5a** (0.526 g, 0.59 mmol) was slurried in 15 mL of DMF. Sodium hydroxide (0.095 g, 2.36 mmol, 4 equiv.) in 1 mL of H_2O was added and the reaction was stirred overnight. The reaction was quenched with 1 mL of 5% citric acid solution and solvent was removed on the vacuum line. The crude yellow solid was slurried in 100 mL of 5% citric acid solution and extracted into $CHCl_3$. The organic layer was washed with water and brine and then dried over Na_2SO_4. After filtration, solvent was removed on a rotary evaporator and the yellow solid dried under vacuum to give **5b** as a yellow solid. (0.48 g, 93 %). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 11.03 (s, 1H), 8.94 (s, 1H), 8.93 (s, 1H), 8.16 (s, 1H), 7.63 (s, 1H), 7.58 (s, 1H), 7.53 (s, 1H), 7.44 (s, 1H), 4.16 (d, J_{HH} = 6.4 Hz, 2H), 4.12-4.09 (m, 6H), 3.26 (s, 3H), 3.24 (s, 3H), 2.35 (m, 2H), 1.60 (s, 9H), 1.24-1.19 (m, 24H). Limited solubility of Dimer

2b prevented characterization by ^{13}C NMR. HRMS (ESI) m/z calcd for $C_{49}H_{61}N_6O_9$ $[M+H]^+$ 877.4435, found 877.4531.

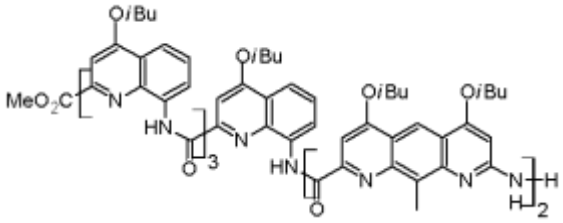


Dimer 5c. In a 50 mL round-bottomed flask **5a** (0.5 g, 0.56 mmol) was dissolved in 10 mL of 1:1 DCM:TFA. The reaction was stirred for 4 hours at room temperature. Solvent was removed on the rotary evaporator and the resulting yellow oil was partitioned between a saturated $NaHCO_3$ solution and $CHCl_3$. The organic layer was washed with water and brine and then dried over Na_2SO_4. After filtration, solvent was removed on the rotary evaporator and the resulting solid was dried on the vacuum line to give **5c** as a yellow solid. (0.44 g, 99%). ^1H NMR ($CDCl_3$, 300 MHz): δ 11.21 (s, 1H), 9.08 (s, 1H), 8.95 (s, 1H), 8.24 (s, 1H), 7.64 (s, 1H), 7.46 (s, 1H), 6.09 (s, 1H), 4.89 (s, 2H), 4.19 (d, J_{HH} = 6.4 Hz, 2H), 4.16 (d, J_{HH} = 6.4 Hz, 2H), 4.13 (d, J_{HH} = 6.4 Hz, 2H), 4.10 (s, 3H), 3.99 (s, 3H), 3.97 (s, 3H), 2.36 (m, 2H), 1.23-1.18 (m, 24H). Limited solubility of Dimer 2b prevented characterization by ^{13}C NMR. HRMS (ESI) m/z calcd for $C_{45}H_{55}N_6O_7$ $[M+H]^+$ 791.4127, found 791.4134.

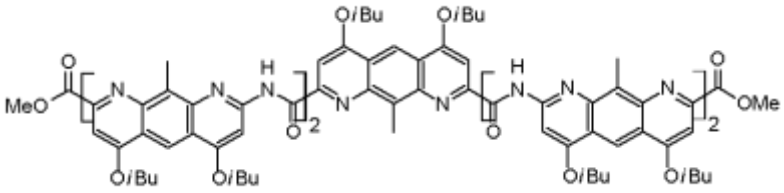


Hexamer, 6a . In a dry 25 mL round-bottomed flask dimer **5b** (0.1 g, 0.11 mmol), quinoline tetramer amine **7** (0.114 g, 0.11 mmol, 1 equiv.), and triphenylphosphine (0.060 g., 0.23 mmol, 2 equiv.) were slurried in 5 mL of dry $CHCl_3$. Dry dipea (0.060 mL, 0.34 mmol, 3 equiv.) and trichloroacetonitrile (0.023 mL, 0.23 mmol, 2 equiv.) were added and the reaction was stirred at room temperature overnight. Solvent was removed on the rotary evaporator and the crude product was purified by silica gel chromatography with 30% EtOAc in cyclohexane. After drying under vacuum, hexamer **6a** was obtained as a bright yellow solid. (0.15 g, 71%) ^1H NMR ($CDCl_3$, 300 MHz): δ 12.02 (s, 1H), 11.93 (s, 1H), 11.83 (s, 1H), 11.80 (s, 1H), 10.76 (s, 1H), 9.09 (s, 1H), 9.07 (s, 1H), 8.58 (dd, J_{HH} = 7.5, 0.8 Hz, 1H), 8.53 (dd, J_{HH} = 7.9, 0.8 Hz, 1H), 8.23 (dd, J_{HH} = 8.1, 0.8 Hz, 1H), 8.19 (dd, J_{HH} = 8.0, 0.8 Hz, 1H), 8.12 (s, 1H), 8.09 (dd, J_{HH} = 8.1, 1.1 Hz, 1H), 8.01 (d, J_{HH} = 8.3 Hz, 2H), 7.74 (s, 1H), 7.72-7.61 (m, 6H), 7.35 (t, J_{HH} = 7.9 Hz, 1H), 7.30 (t, J_{HH} = 8.3 Hz, 1H), 7.29 (s, 1H), 2.60 - 2.05 (m, 8H), 1.54 (s, 9H), 1.36-1.22 (m, 32H). ^{13}C NMR ($CDCl_3$, 75 MHz): *δ*163.8, 163.7, 163.5, 163.4, 163.1, 162.9, 162.7, 162.2, 161.9, 161.7, 161.2, 160.9, 152.9, 152.6, 151.1, 150.3, 150.2, 149.9, 148.9, 148.6, 145.4, 144.8, 144.6, 144.1, 144.0, 139.1, 138.2, 138.0, 134.1, 133.7, 133.6, 133.5, 132.6, 127.4, 126.9, 126.8, 126.5, 121.9, 121.7, 119.6, 119.1, 118.7, 118.5, 117.1, 116.9, 116.6, 116.3, 116.0, 115.8, 115.7, 115.6, 113.1, 112.7, 100.2, 99.3, 97.7, 96.4, 96.1, 94.9, 91.7,

81.3, 75.2, 75.1, 75.0, 74.8, 74.7, 51.9, 28.5, 28.4, 28.3, 28.1, 27.7, 19.6, 19.5, 19.4, 19.4, 19.3, 19.2, 19.1, 18.9, 12.4, 11.5. HRMS (ESI) m/z calcd for $C_{106}H_{120}N_{14}O_{17}$ $[M+H]^+$ 1860.8956, found 1860.8988.

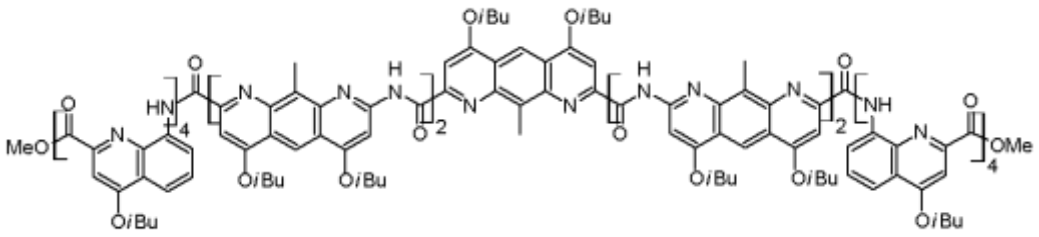


Hexamer 6b, In a 25 mL round-bottomed flask, **6a** (0.15 g, 0.08 mmol) was dissolved in 5 mL of 8:2 DCM/TFA and the reaction was stirred for 4 hours. Solvent was then removed by rotary evaporation and the crude yellow residue was partitioned between a saturated $NaHCO_3$ solution and $CHCl_3$. The organic layer was washed with 100 mL of saturated $NaHCO_3$ solution, water and then brine before being dried over Na_2SO_4. Solvent was removed by rotary evaporation and the solid was dried on the vacuum line to give **6b** as a yellow solid (0.133 g, 94%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 12.02 (s, 1H), 11.92 (s, 1H), 11.85 (s, 1H), 11.83 (s, 1H), 10.79 (s, 1H), 9.10 (s, 1H), 8.98 (s 1H), 8.58 (d, J_{HH} = 7.5 Hz, 1H), 8.54 (d, J_{HH} = 7.4 Hz, 1H), 8.24 (d, J_{HH} = 7.6 Hz, 1H), 8.20 (d, J_{HH} = 7.9 Hz, 1H), 8.18 (s, 1H), 8.10 (d, J_{HH} = 7.9 Hz, 1H), 8.04-8.01 (m, 2H), 7.71-7.66 (m, 3H), 7.48 (s, 1H) 7.39-7.28 (m, 4H), 6.84 (s, 1H), 6.50 (s, 1H), 6.35 (s, 1H), 6.14 (s, 1H), 5.00 (bs, 2H), 4.45 (d, J_{HH} = 7.7 Hz, 1H), 4.42 (d, J_{HH} = 7.0 Hz, 1H), 4.26 – 4.11 (m, 6H), 4.02 (d, J_{HH} = 6.4 Hz, 2H), 3.95 (d, J_{HH} = 6.4 Hz, 2H), 3.71 (m, 2H), 3.51 (m, 1H), 3.26 (s, 3H), 3.16 (m, 1H), 3.11 (s, 3H), 2.61-2.07 (m, 8H), 2.01 (s, 3H), 1.35-1.01 (m, 48H). HRMS (ESI) m/z calcd for $C_{101}H_{111}N_{14}O_{15}$ $[M+H]^+$ 1760.8431, found 1760.8457.



Pentamer 1. In a dry 25 mL round-bottomed flask, diacid **4d** (0.107 g, 0.25 mmol), **5c** (0.397 g. 0.50 mmol, 2 equiv.), and PyBOP (0.784 g, 1.51 mmol, 6 equiv.) were dissolved in 30 mL of dry $CHCl_3$. Dry dipea (0.263 mL, 1.50 mmol, 6 equiv.) was added and the reaction was stirred at 40 °C for 24 hours. Solvent was removed by rotary evaporation and the solid was redissolved in DCM and washed with a saturated $NaHCO_3$ solution. The organic phase was dried over Na_2SO_4. After removal of solvent the crude product was purified by gel permeation chromatography to give **1** as a yellow solid. (0.140 g, 47%). X-ray quality crystals were obtained by layering a solution of **1** in $CHCl_3$ with hexane. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.90 (s, 4H), 10.75 (s, 4H), 8.44 (s, 4H), 8.43 (s, 4H), 7.79 (s, 2H), 7.58 (s, 4H), 7.51 (s, 4H), 7.39 (s, 4H), 6.87 (s, 4H), 4.36 (dd, J_{HH} = 8.2, 6.45 Hz, 4H), 4.28-4.20 (m, 12H), 4.17 (s, 6H), 4.05-3.76 (m, 24H), 3.92 (s, 12H), 3.19 (s, 12H), 2.87 (s, 12H), 2.45 (m, 12H), 2.29 (m, 8H), 1.37 – 1.26 (m, 40H), 1.21 – 1.17 (m, 20H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.7, 163.7, 163.1, 162.6, 162.5, 162.3, 162.3, 151.1, 150.6, 149.7, 149.5, 148.2, 145.0, 144.9, 144.4, 144.2, 137.5, 134.6, 134.5, 120.0, 119.2, 118.5, 118.4, 112.1, 111.6, 97.4, 97.3, 94.9, 94.4, 92.6, 92.4, 74.8, 74.7, 74.5, 74.5, 74.4, 52.3, 52.1, 28.7, 28.5,

28.4, 19.6, 19.5, 19.4, 19.3, 19.3, 19.3, 19.2, 12.9, 12.4. HRMS (ESI) m/z calcd for double helix: $(C_{113}H_{131}N_{14}O_{18})_2H_3$ $[M+3H]^{3+}$ 1315.6589, found 1315.6699.



Tridecamer, 2 In a dry 10 mL round-bottomed flask, **6b** (0.133 g, 0.076 mmol), diacid **4d** (0.016 g, 0.038 mmol, 0.5 equiv.) and PyBOP (0.177 g., 0.34 mmol, 4.5 equiv.) were dissolved in 7 mL of dry $CHCl_3$. Dry dipea (0.059 mL, 0.34 mmol, 4.5 equiv.) was added and the reaction was stirred at 40 °C overnight. After removal of solvent, the crude product was purified by silica gel chromatography using 30% EtOAc/cyclohexane to elute the product. After removal of solvent and drying under vacuum, **2** was obtained as a yellow solid. (0.085 g, 56 %). Crystals of X-ray quality were obtained by layering a solution of **2** in $CHCl_3$ with hexane. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 11.88 (s, 2H), 11.55 (s, 2H), 11.41 (s, 2H), 11.22 (s, 2H), 10.78 (s, 2H), 10.21 (s, 2H), 9.36 (s, 1H), 8.53 (s, 2H), 8.22 (d, J_{HH}=6.4 Hz, 2H), 8.15 (d, J_{HH}=6.8 Hz, 2H), 8.08 (d, J_{HH}=7.2 Hz, 2H), 8.02 (s, 2H), 7.99 (s, 2H), 7.97 (d, J_{HH}=7.2 Hz, 2H), 7.88 (s, 2H), 7.86 (d, J_{HH}=7.2 Hz, 2H), 7.68 (t, J_{HH}=7.5 Hz, 4H), 7.53 (t, J_{HH}=7.9 Hz, 2H), 7.36 (t, J_{HH}=7.9 Hz, 2H), 7.19 (t, J_{HH}=7.9 Hz, 2H), 7.16 (s, 2H), 7.08-7.05 (m, 4H), 6.92-6.87 (m, 2H), 6.57 (s, 2H), 6.54 (s, 2H), 6.19 (s, 2H), 5.86 (s, 2H), 4.42-4.22 (m, 16H), 3.96-3.83 (m 15H), 3.68 (t, J_{HH}=7.6 Hz, 2H), 3.38 (d, J_{HH}=6.4 Hz, 4H), 3.09 (t, J_{HH}=7.9 Hz, 2H), 2.86 (s, 6H), 2.84 (s, 6H), 2.63-2.29 (m, 18H), 1.98 (s, 6H), 1.45-1.22 (m, 84H), 0.79 (d, J_{HH}=6.4Hz, 12H), 0.66 (dd, J_{HH}=6.4, 3.2, 12Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.0, 163.9, 163.7, 163.6, 163.5, 163.2, 162.9, 162.5, 162.1, 161.9, 161.8, 161.6, 161.3, 161.0, 160.7, 151.0, 150.8, 150.6, 150.0, 150.0, 148.6, 148.4, 145.4, 145.1, 144.2, 144.1, 143.7, 143.5, 139.0, 138.7, 138.3, 138.0, 136.8, 134.5, 134.0, 133.7, 133.6, 133.5, 127.3, 126.9, 126.8, 126.1, 122.1, 121.8, 121.6, 121.5, 119.3, 118.8, 117.8, 117.2, 116.8, 116.5, 116.2, 115.7, 115.6, 115.5, 115.1, 114.2, 112.4, 111.9, 100.1, 99.0, 97.7, 96.1, 96.0, 95.8, 94.6, 91.7, 90.5, 75.7, 75.2, 75.1, 74.7, 74.3, 52.0, 31.1, 28.8, 28.6, 28.5, 27.9, 27.6, 20.1, 19.8, 19.7, 19.6, 19.6, 19.5, 19.4, 19.2, 19.2, 19.1, 18.9, 12.8, 12.0, 10.8. HRMS (ESI) m/z calcd for $(C_{225}H_{244}N_{30}O_{34})H_2$ $[M+2H]^{2+}$ 1955.9221, found 1955.9349.

2) Solution Studies

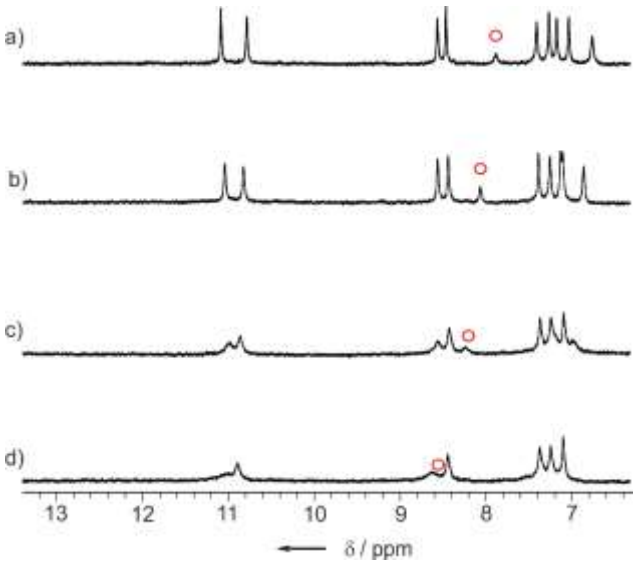


Figure S1. Part of the variable temperature ^{1}H NMR spectra of **1** (0.5 mM) in CD_2Cl_4 at: a) 25 °C; b) 50 °C; c) 75 °C and d) 100 °C. Open red circles (o) indicate the 10 position of the central anthracene unit which integrate for half of the other signals. Upon heating this signal is shifted at lower field.

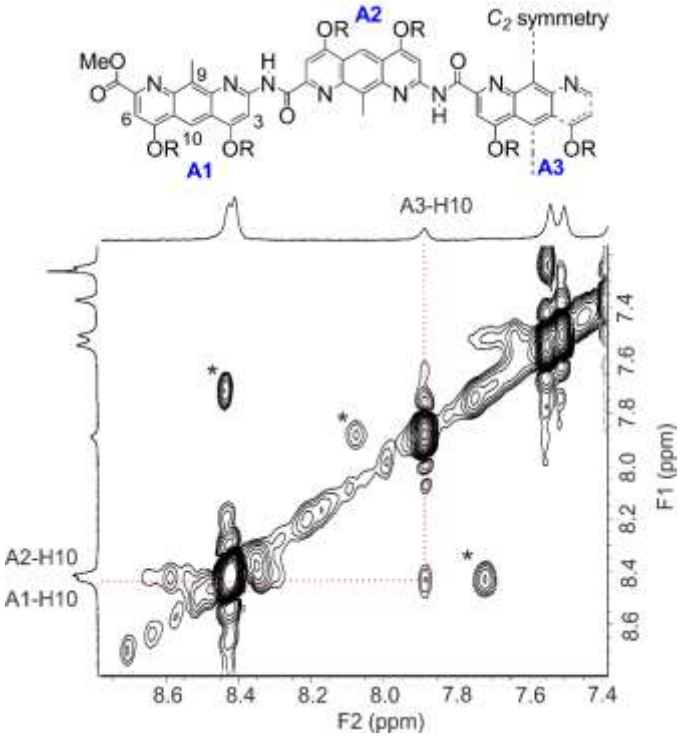


Figure S2. ^{1}H-^{1}H NOESY spectrum of **1** (3mM) in $CDCl_3$ showing NOE transfer between the 10 position protons of the monomer units in **1**. Labels on the spectrum correspond to those shown on the schematic representation of the symmetric portion of **1** shown above. Exchange peaks for **1** with a possible triple helical structure are indicated with a *.

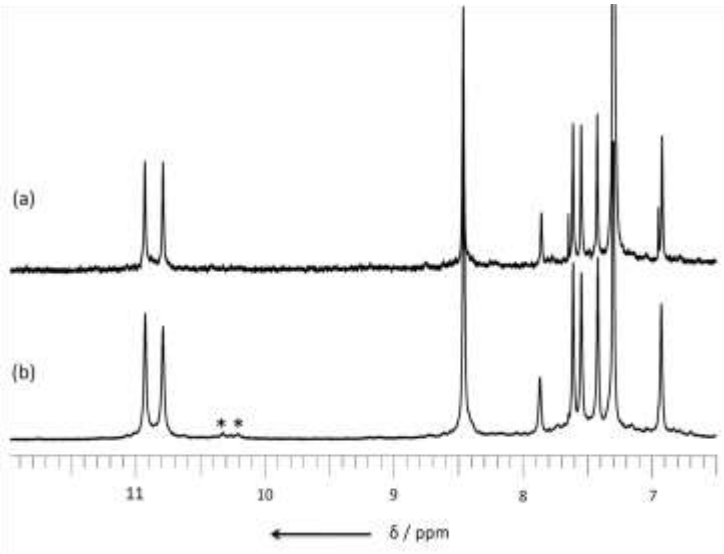


Figure S3. Part of the ^{1}H NMR spectra of **1** in $CDCl_3$ (298K) at concentrations of: a) 0.5 mM and b) 5 mM. Amide signals assigned to possible triple helical structure are indicated with *.

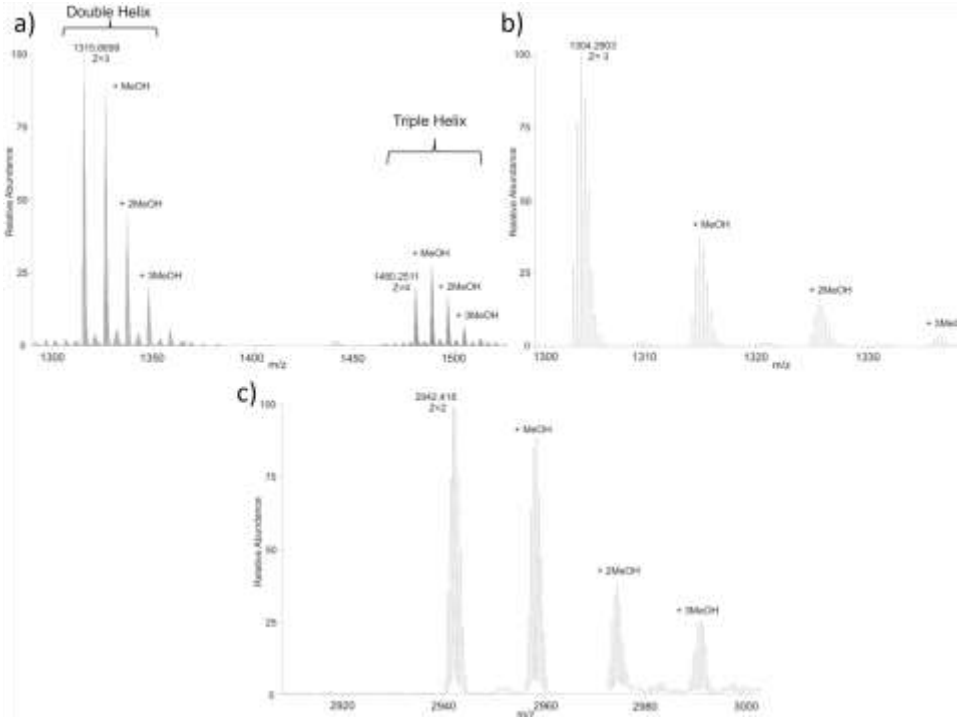


Figure S4. Electrospray Ionization (Orbitrap) mass spectra of: a) **1**; b) **2**; and c) **2⊂1**.

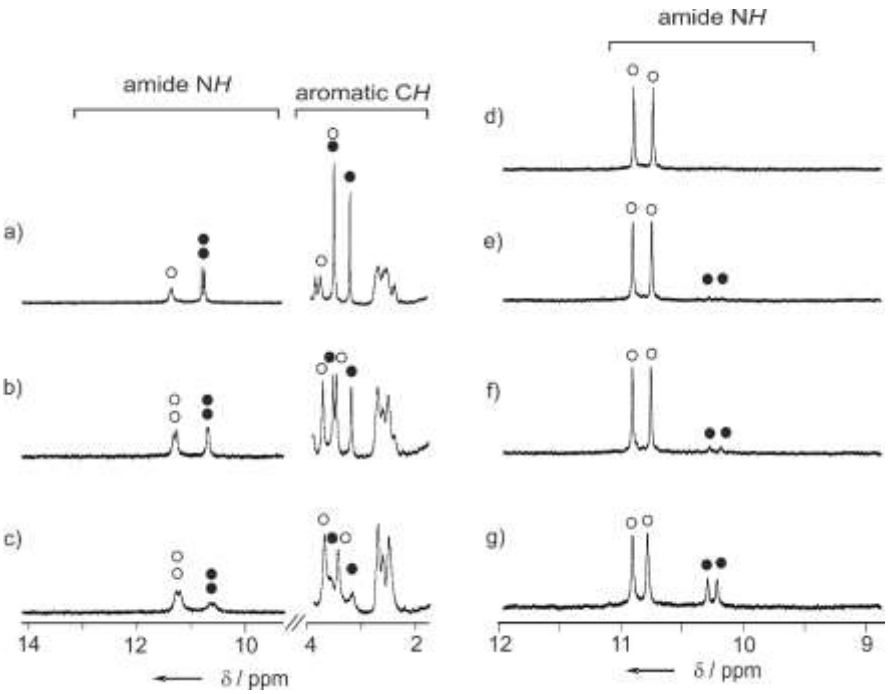


Figure S5. Part of the variable temperature ^{1}H NMR spectra (400 MHz) of **1** (1 mM) in [D5]-pyridine at: a) 30 °C, b) 50 °C, and c) 70 °C. Excerpts of the ^{1}H NMR (400 MHz) titration at 298 K of **1** (0.5 mM) in $CDCl_3$/[D_6]-pyridine mixtures in the following vol/vol ratios: d) 100:0; e) 90:10; f) 80:20; g) 60:40. Open circles (o) indicate a duplex wheras closed circles (•) indicate a triple helical structure.

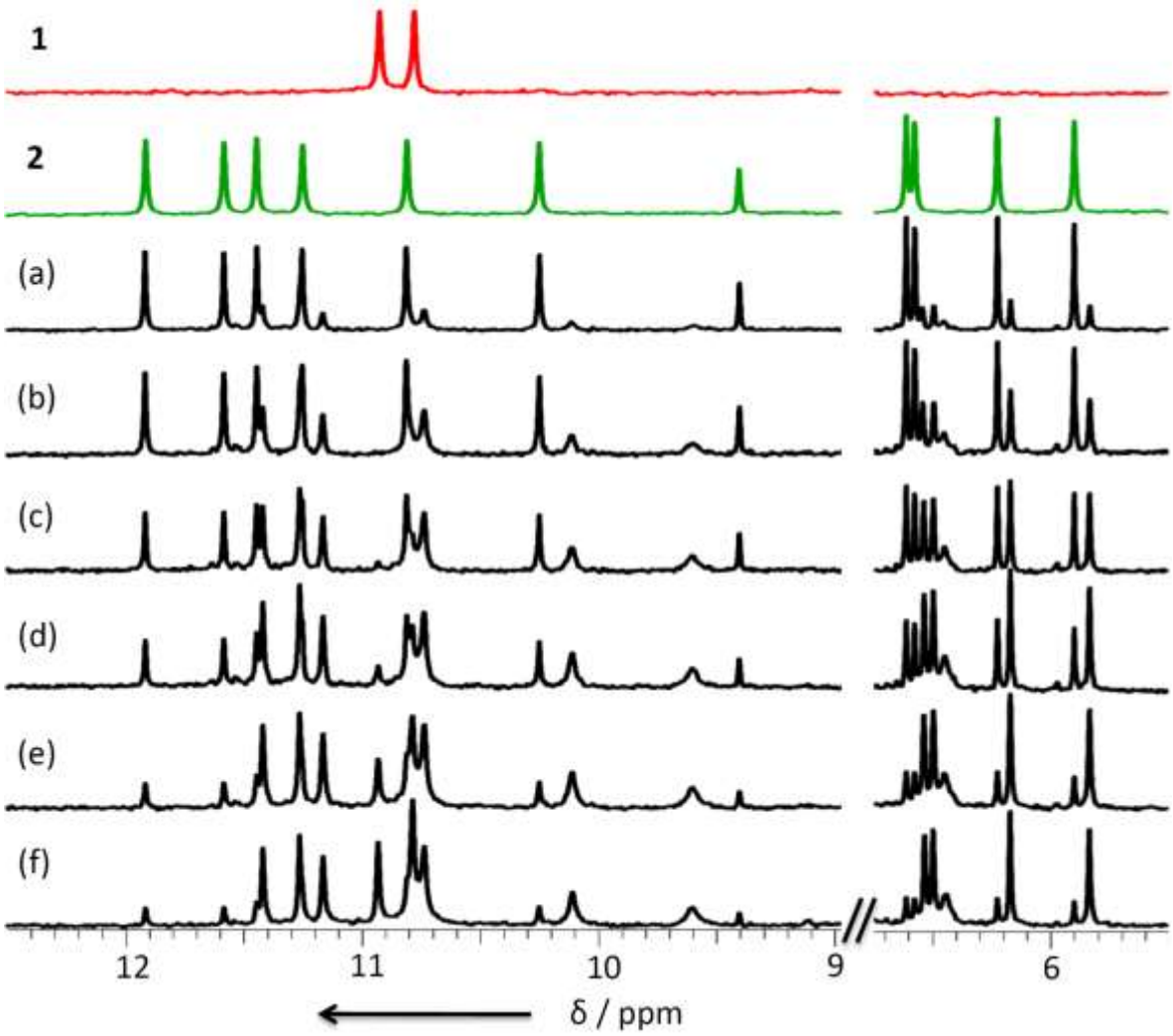


Figure S6. Part of the ^{1}H NMR 300 MHz spectra at 298K of **2** (1mM) in $CDCl_3$ with: a) 0.25 equiv.; b) 0.5 equiv.; c) 0.75 equiv.; d) 1 equiv.; e) 1.5 equiv. and f) 2.0 equiv. of **1.**

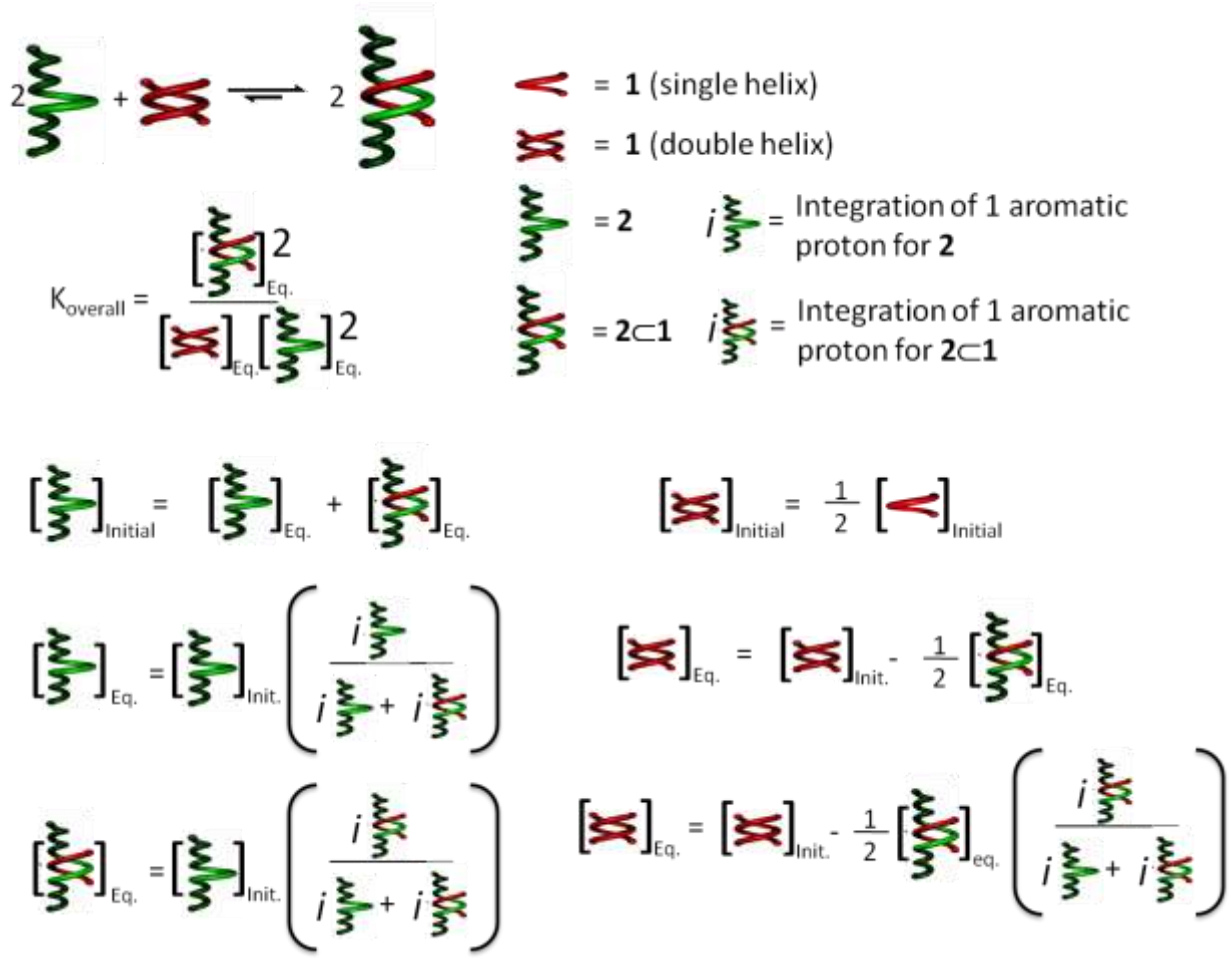


Figure S7. Calculation of the overall association constant *($K_{overall}$)* between $(\mathbf{1})_2$ and two molecules of **2** and the derived association constant between one molecule of **1** and **2**. (Continued on next page)

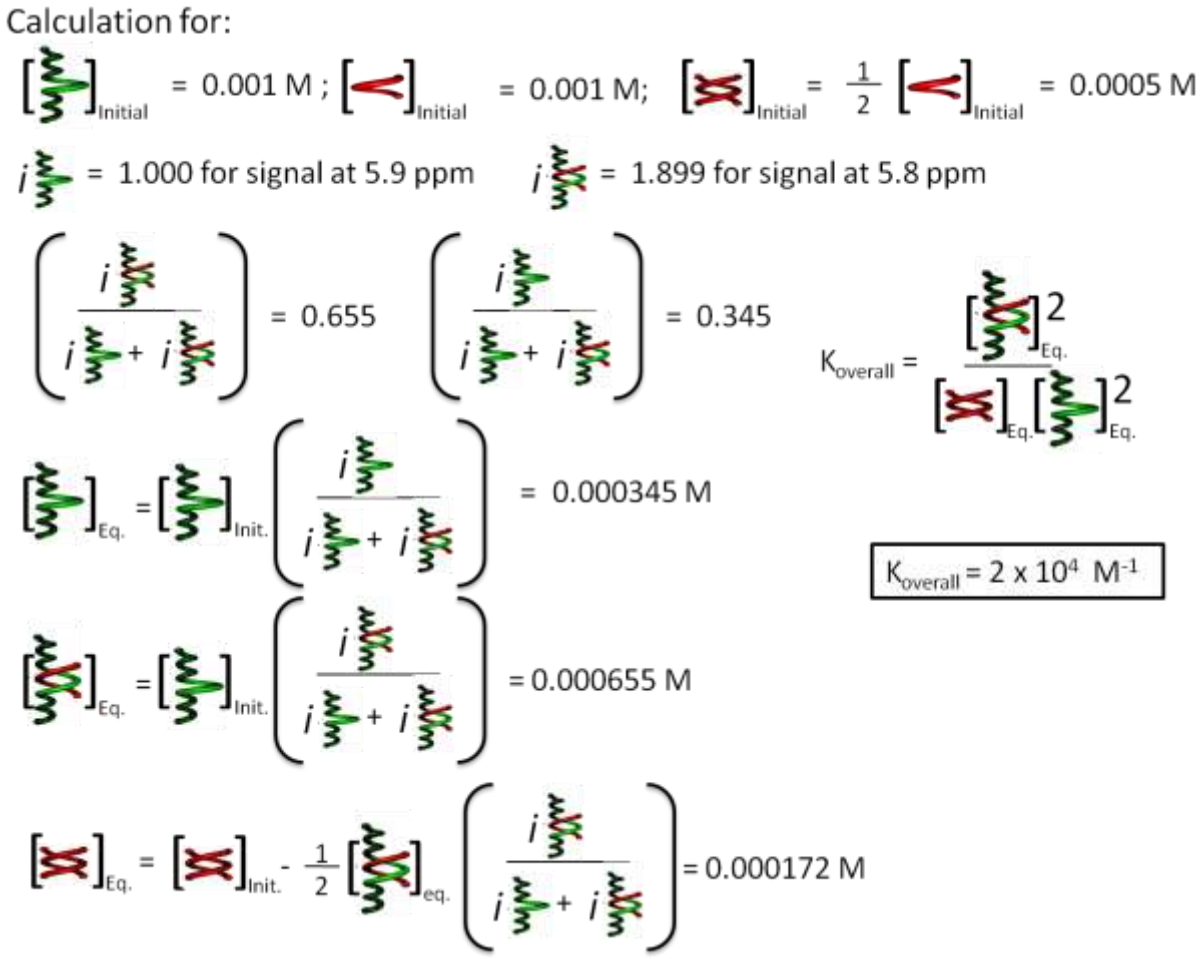


Figure S7 (continued). Calculation of the overall association constant *($K_{overall}$)* between $(\mathbf{1})_2$ and two molecules of **2** and the derived association constant between one molecule of **1** and **2**. (Continued on next page)

To obtain the association constant (K_a) between one molecule of **1** and one molecule of **2** the following formula was used. The formation of the cross-hybrid complex must proceed through two steps. First there is the dissociation of $(\mathbf{1})_2$ into two molecules of **1**. These then react with two molecules of **2** to form two molecules of the cross hybrid product. This means that $K_{overall}$ is the product of the dissociation constant of $(\mathbf{1})_2$ $(K_{dim})^{-1}$ and the square of the association constant between **1** and **2**, $(K_a)^2$. Thus K_a is equal to the square root of $(K_{overall}K_{dim})$.

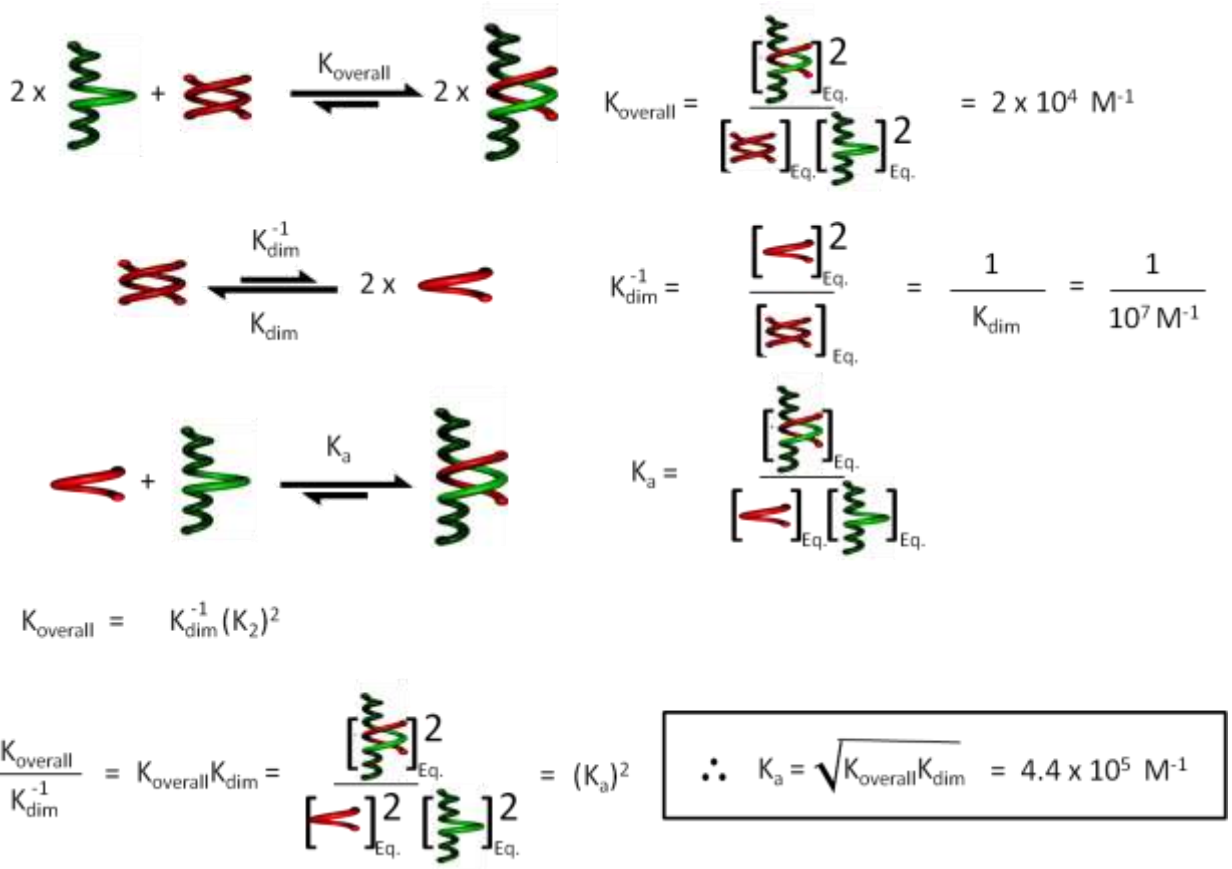


Figure S7 (continued). Calculation of the overall association constant *($K_{overall}$)* between $(\mathbf{1})_2$ and two molecules of **2** and the derived association constant between one molecule of **1** and **2**.

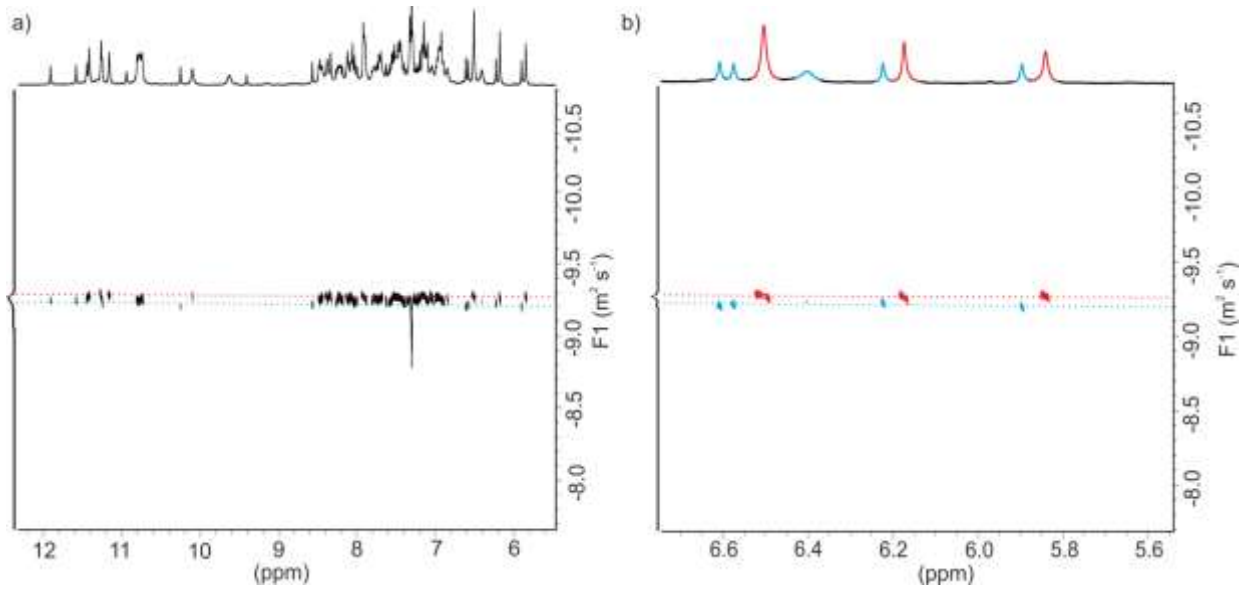


Figure S8. DOSY spectrum of a 1:1 mixture of oligomers **1** (3mM) and **2** (3mM) in $CDCl_3$ at 298K showing: a) the full aromatic and amide region and b) an expansion of the region between 5.6 and 6.7 ppm. In b) **2** and **2⊂1** resonances are shown in red and blue, respectively.

3) X-ray crystallographic data

Methods:

Data collections were performed at the IECB X-ray facility on a high flux microfocus Rigaku FRX rotating anode at the copper k_α wavelength equipped with a Dectris Pilatus 200K hybrid detector at 100K. The crystals were mounted on cryo-loops after quick soaking on Paratone—N oil from Hampton research and flash-frozen. The data were processed with the CrystalClear suite version 2.1b25. All three crystal structures were solved using the charge flipping algorithm implemented in the SUPERFLIP software[S4] and were refined using SHELXL 2013 version.[S5] The crystal structure of compound 2 could only be determined and refined in a monoclinic $P2_1/c$ space group although the beta angle is close to 90°. Full-matrix least-squares refinement were performed on F^2 for all unique reflections, minimizing $w(Fo^2- Fc^2)^2$, with anisotropic displacement parameters for non-hydrogen atoms. Hydrogen atoms were positioned in idealized positions and refined with a riding model, with Uiso constrained to 1.2 Ueq value of the parent atom (1.5 Ueq when CH_3). The positions and isotropic displacement parameters of the remaining hydrogen atoms were refined freely. SIMU and DELU commands were used to restrain some isobutoxy side chains as rigid groups and restrain their displacement parameters. AFIX 66 and AFIX116 commands were used to restrain some quinoline and anthracen rings to be idealized hexagons with C-C and C-N bonds equal to 1.39 Å. The BYPASS/SQUEEZE[S6] procedure was used to take into account the electron density in the potential solvent area for all three crystal structures, which resulted in an electrons count of 342 within a volume of 1792.2 $Å^3$ for compound 1, 1705 within a volume of 6054.8 $Å^3$ for compound 2

and 576 within a volume of 4141.2 $Å^3$ for the cross hybrid complex. Data statistics are reported in the table1 and in the cif files.

S4) L. Palatinus, G. Chapuis, *J. Appl. Cryst.*, **2007**, 40, 786-790
S5) G. M. Sheldrick, *Acta Cryst. A*, **2008** , A64, 112-122.
S6) A. L. Spek, *J. Appl. Cryst*, **2003**, 36, 7-13.

Table S2: X-ray crystallographic parameters for Oligomers 1, 2, their cross-hybrid 2⊂1,

Compound	Oligomer 1	Oligomer 2	Hybrid 2⊂1
Solvent/precipitant	CHCl3/Hexane	CHCl3/Hexane	CHCl3/DMSO
Formula	$C_{238}H_{280}Cl_{18}N_{28}O_{36}$	$C_{225}H_{241}N_{30}O_{34}$	$C_{348}H_{398}Cl_6N_{44}O_{59}S_4$
Aspect	Yellow	Yellow	Yellow
Crystal System	triclinic	monoclinic	triclinic
Space Group	P-1	$P2_1/c$	P-1
Z	2	4	2
Unit Cell Parameters			
a, Å	21.534(9)	30.145(17)	22.00(4)
b, Å	25.964(9)	22.295(12)	26.90(5)
c, Å	28.6078(10)	37.17(2)	36.30(7)
α, °	64.98(5)	90	84.90(3)
β, °	70.17(5)	90.03(12)	84.60(3)
γ, °	70.52(10)	90	70.60(3)
Temperature, K	100	100	100
Volume, Å3	13291	24981	20135
FW, g.mol-1	4747.02	3909.46	6482.10
ρ, g.cm-3	1.186	1.039	1.069
λ, E	2.252	0.552	1.136
θ min	1.926	2.311	2.450
θ max	47.240	44.69	51.076
Radiation	Copper	Copper	Copper
Reflections Measured	102983	124653	123987
Reflections Unique ([*Fo* > 2σ*Fo*)])	23900	19631	41860
Parameters/restraints	2786/12	2321/138	3863/85
GOF	1.172	1.532	1.022
R1 (I>2σ(I))	0.1820	0.1815	0.1464
wR2 (all data)	0.4158	0.4595	R1 (I>2σ(I))
CCDC#	1016817	1016810	1016811

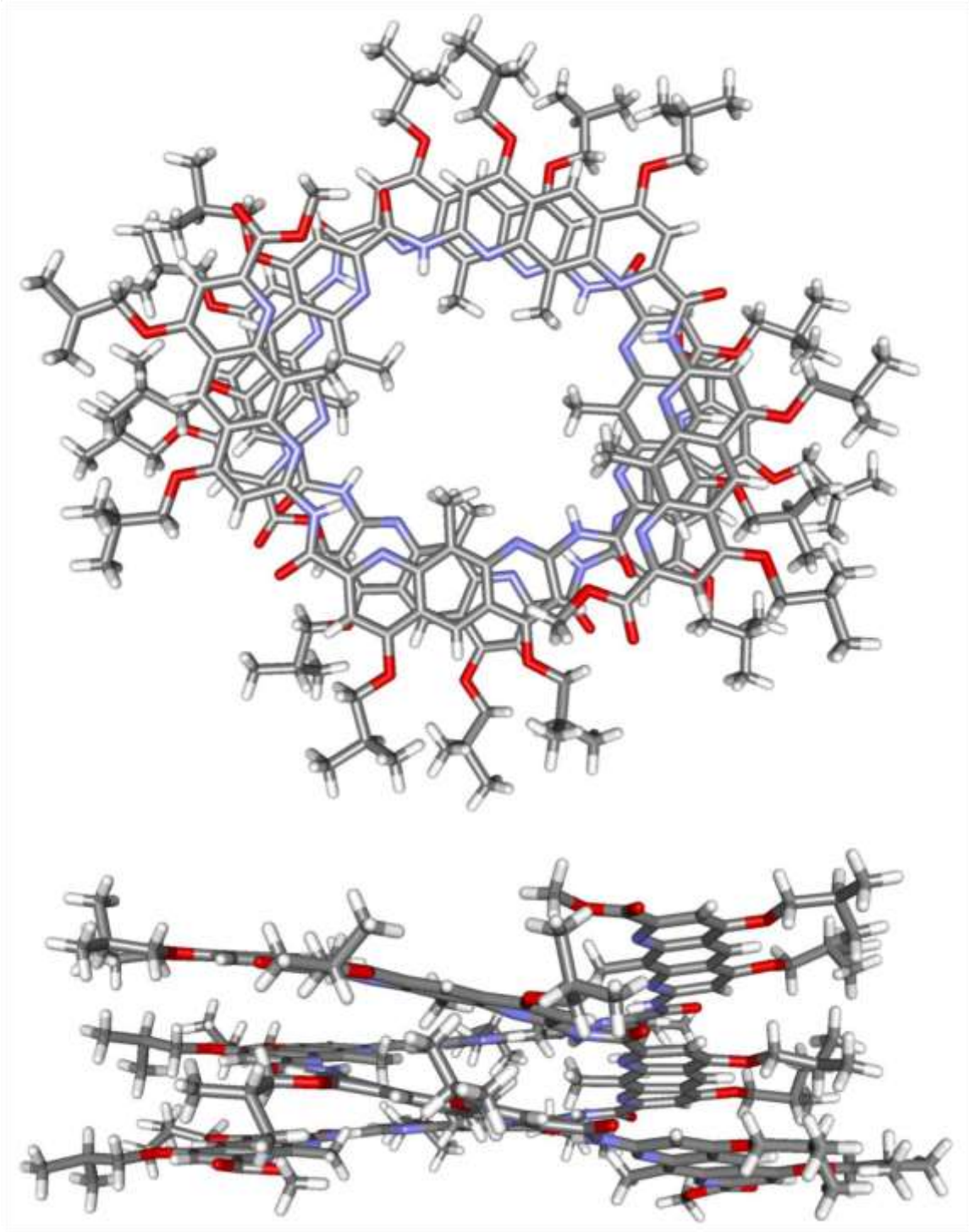


Figure S9: X-ray crystal structure of $(\mathbf{1})_2$ as viewed along the helical axis (top) and perpendicular to the helical axis (bottom).

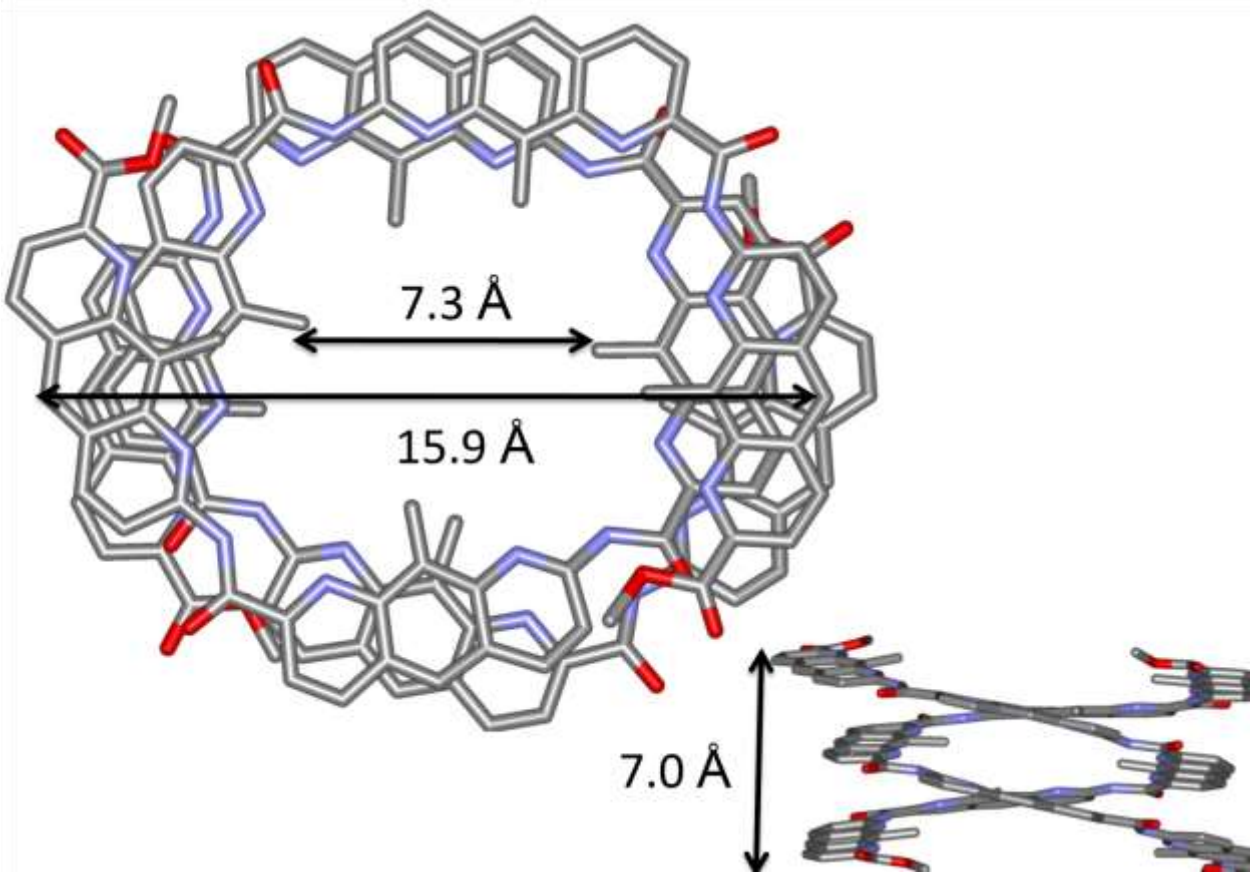


Figure S10: X-ray crystal structure of the aromatic portion of $(\mathbf{1})_2$ showing interior and exterior distances as view along the helical axis (top) and perpendicular to the helical axis (bottom right). Isobutoxy side chains, protons, and included solvent molecules have been removed for clarity.

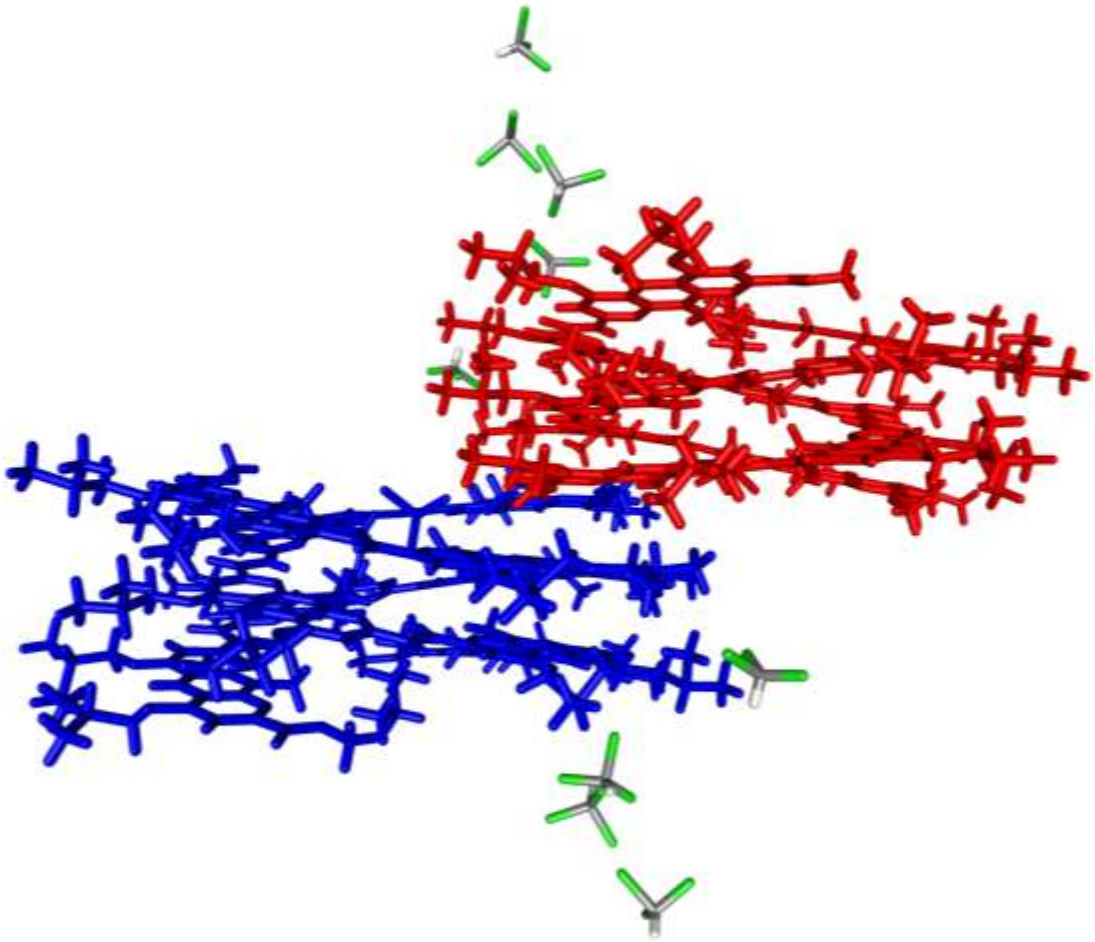


Figure S11: View of the unit cell of $(1)_2$ showing two molecules of $(1)_2$ and included solvent molecules.

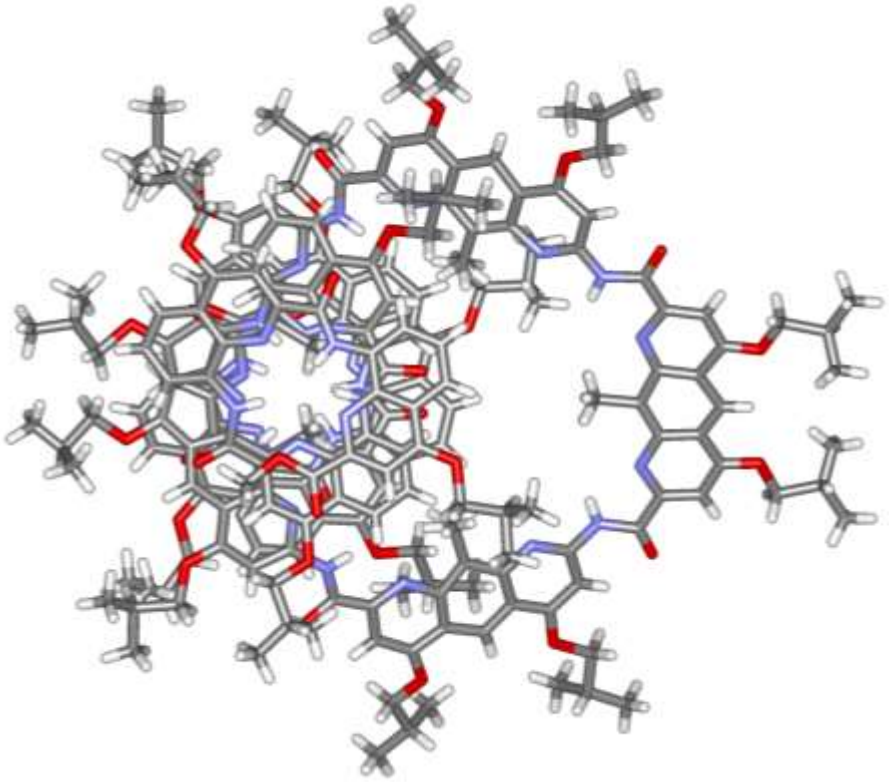


Figure S12: X-ray crystal structure of oligomer **2** as viewed along the helical axis

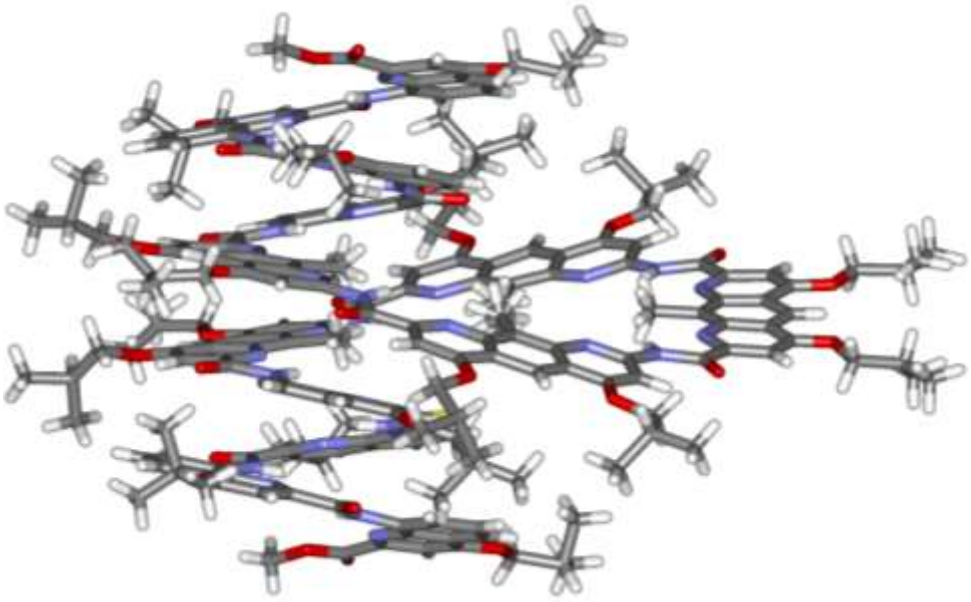


Figure S13: X-ray crystal structure of oligomer **2** as viewed perpendicular to the helical axis

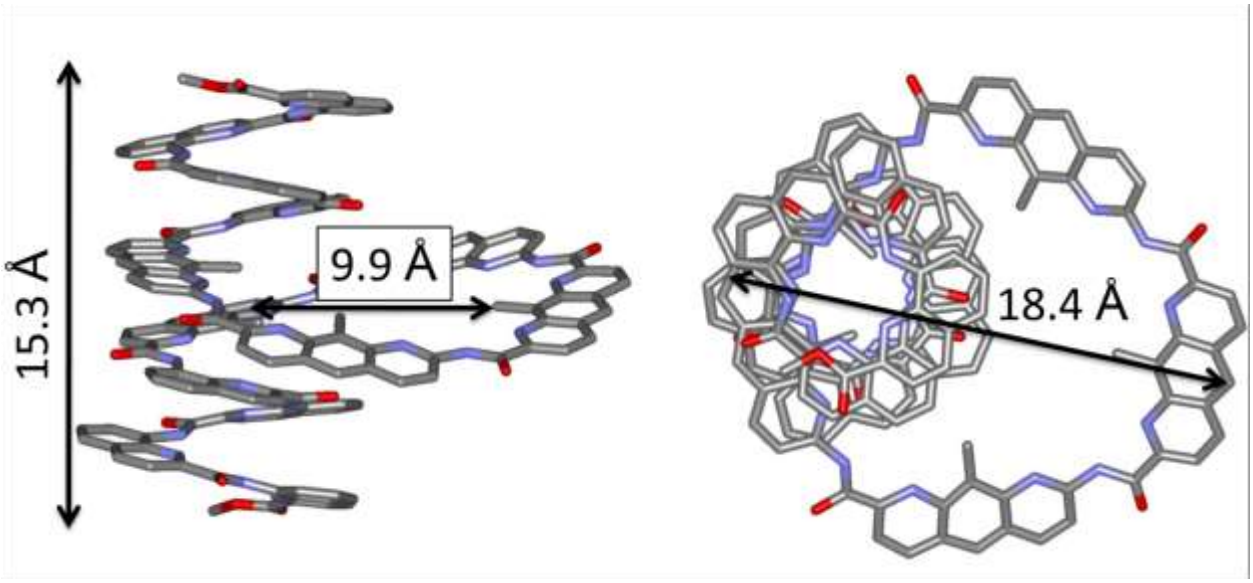


Figure S14: X-ray crystal structure of the aromatic portion of **2** showing interior and exterior distances as view perpendicular to the helical axis (left) and along the helical axis (right). Isobutoxy side chains, protons, and included solvent molecules have been removed for clarity.

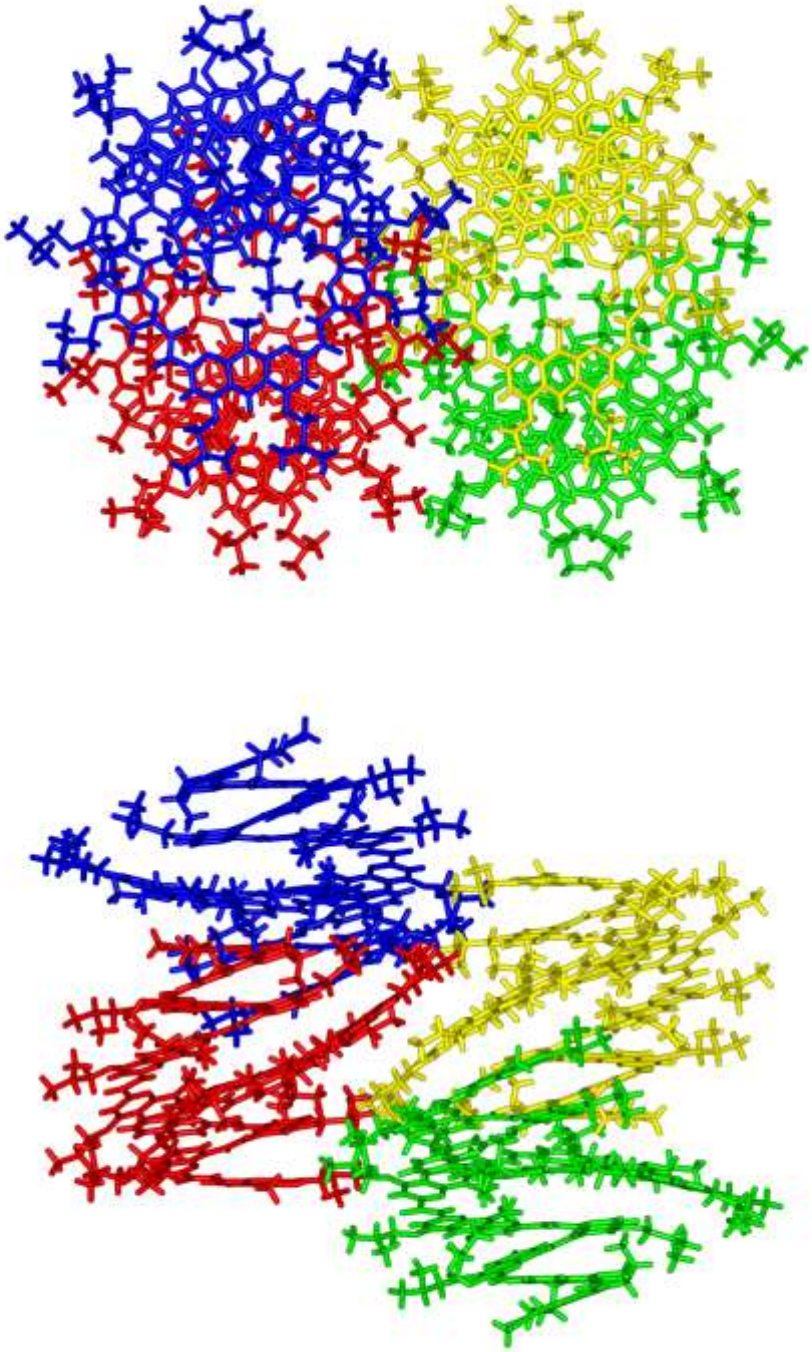
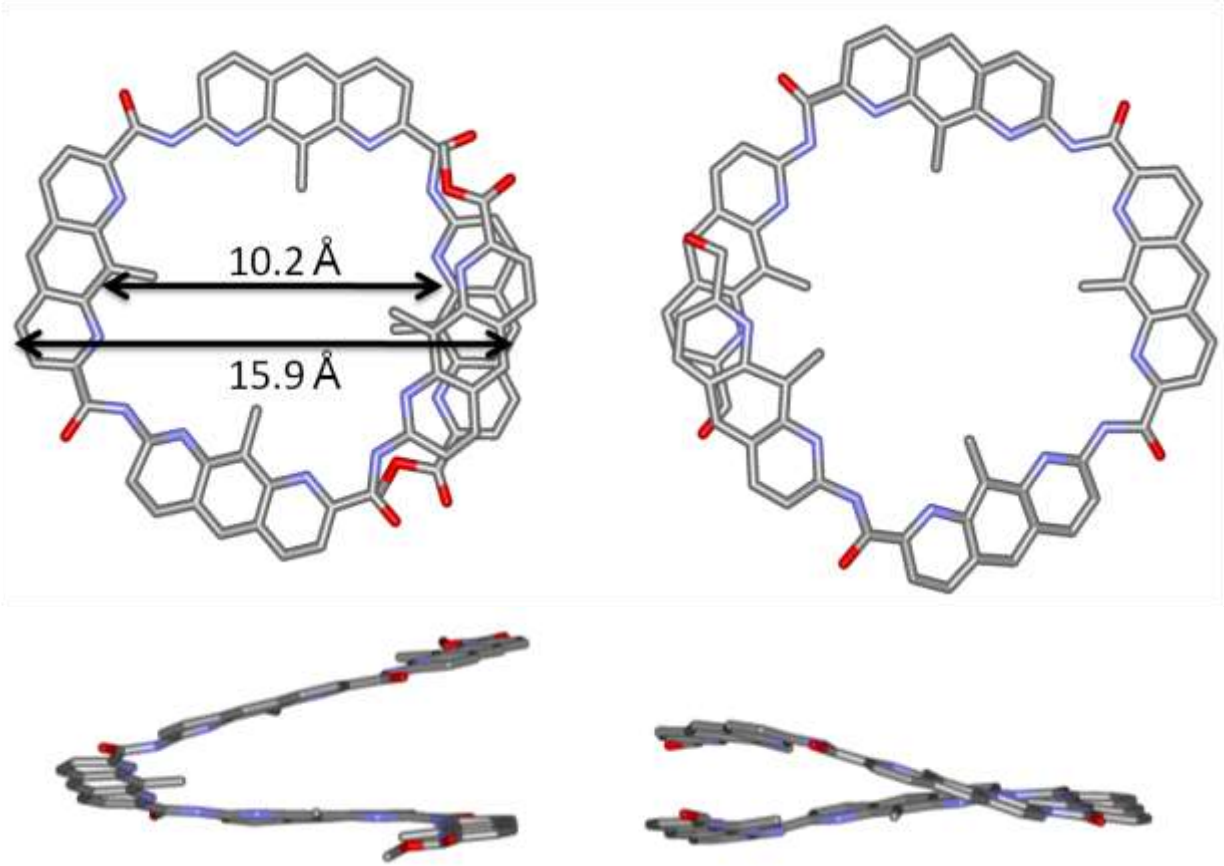


Figure S15: Two views of the unit cell of **2**. The four different molecules of **2** are shown in different colors.



The circumference ($C=2\pi r$) for one turn (four units) in $(1)_2$ is between 32 – 50 Å. Given an increase in helical pitch of 3.5 Å, this corresponds to a total change of 4.0 - 6.3 ° by $\Theta = \sin^{-1}$ (pitch/circumference) in the twist angle or an average change across approximately four units of only 1 – 1.6 ° per unit.

Figure S16: Comparison of the central A5 unit in a single strand of $(\mathbf{1})_2$ (left) and **2** (right) as viewed along the helical axis (top) and perpendicular to the helical axis (bottom). The method for calculating average change in twist angle for $\mathbf{(1)_2}$ is described.

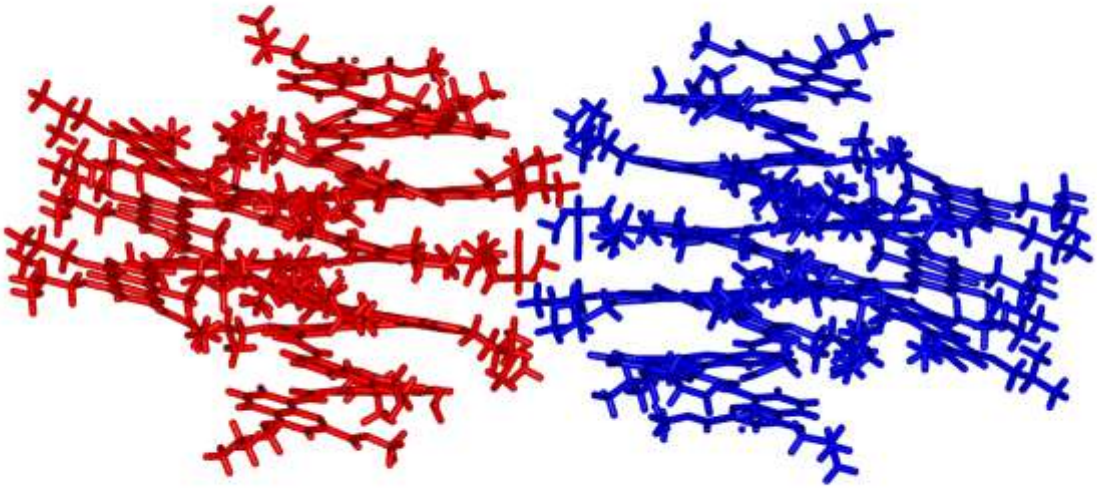


Figure S17: View of the unit cell of **2⊂1** showing two molecules of **2⊂1** and included solvent molecules, the two molecules are shown in different colors.

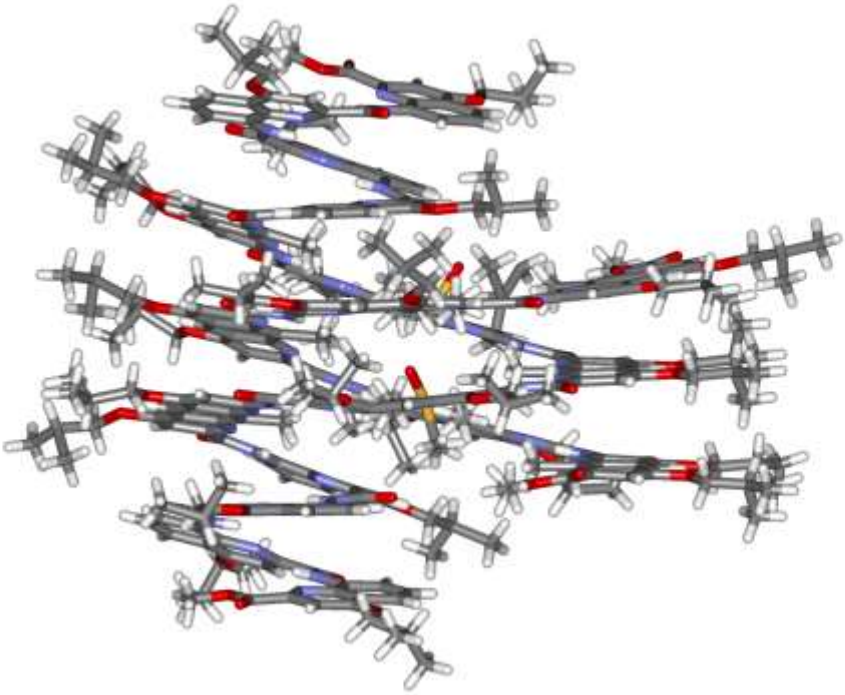


Figure S18: X-ray crystal structure of oligomer **2⊂1** as viewed perpendicular to the helical axis

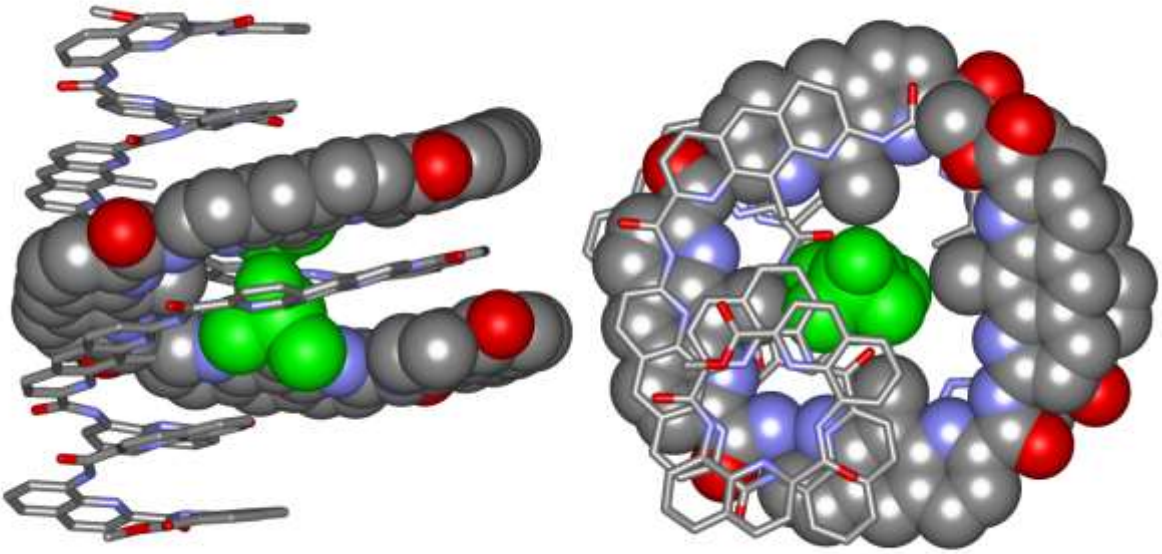


Figure S19: X-ray structure of **2⊂1** as viewed perpendicular to the helical axis (left) and along the helical axis. (right) The A_5 unit and included DMSO molecules shown as CPK representations with the DMSO molcecules colored green. Protons, additional solvent molecules, and isobutoxy side chains have been removed for clarity.

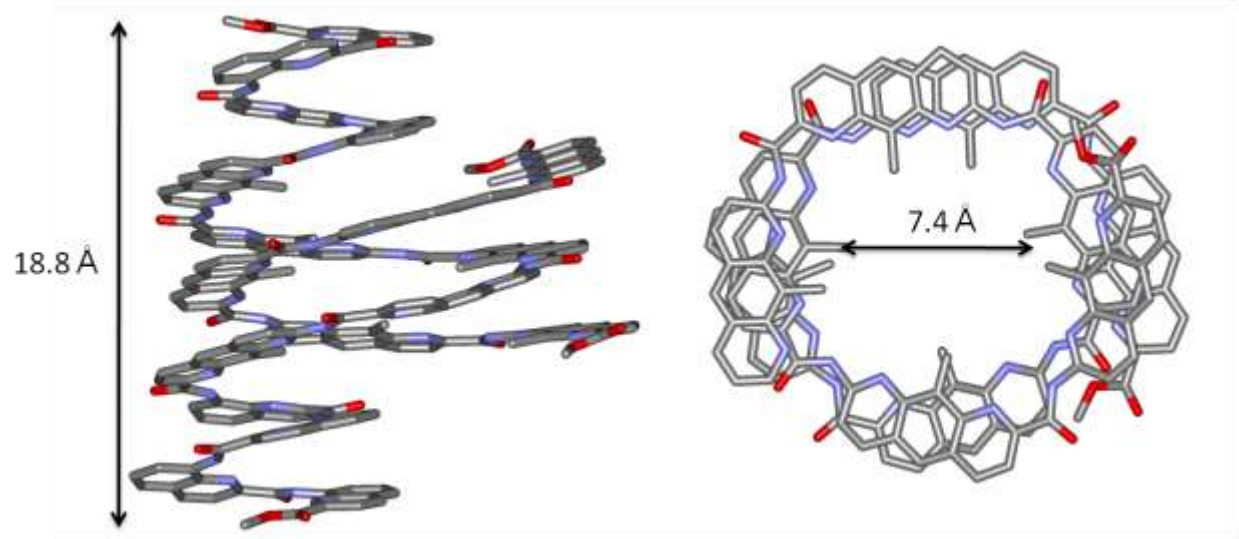
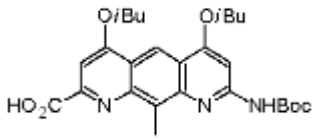
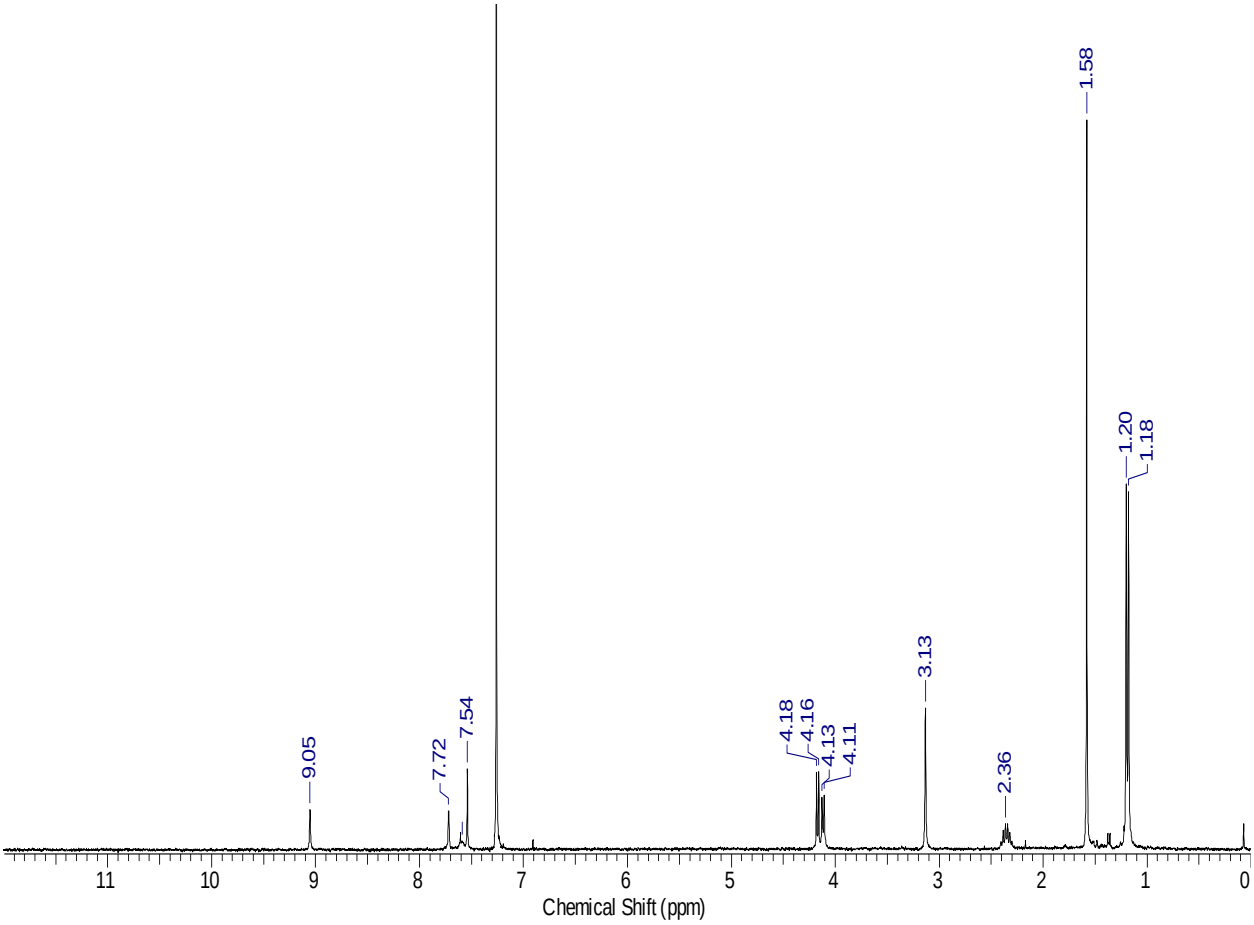


Figure S20: X-ray crystal structure of **2⊂1** showing interior and exterior distances as view perpendicular to the helical axis (left) and along the helical axis (right). Isobutoxy side chains, protons, and included solvent molecules have been removed for clarity. For the view along the helical axis the quinoline tetramer segments have been removed to more clearly show the interior cavity.

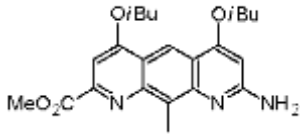
5) ^{1}H NMR spectra of 1-6 and their derivatives

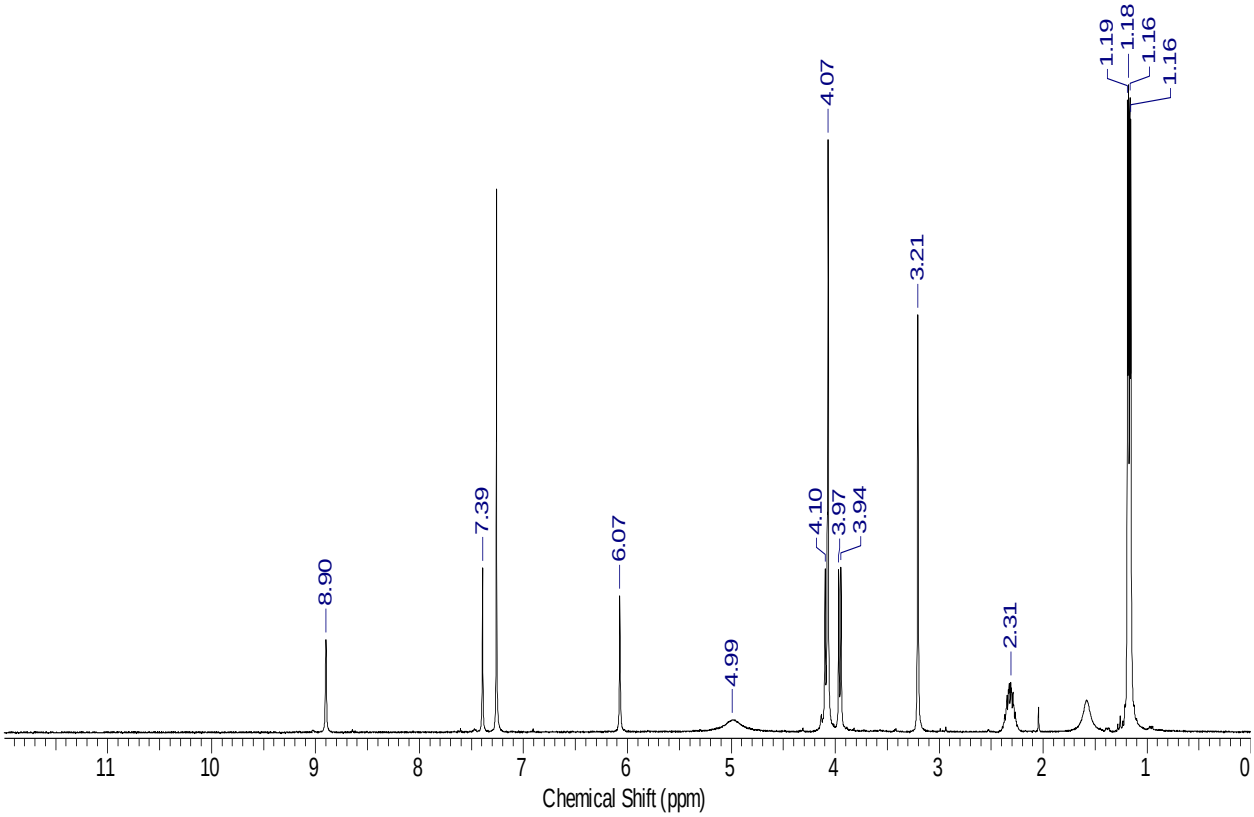
1,8-diaza-4,5-diisobutoxy-7-[(*tert*-butoxycarbonyl)amino]-9-methyl-2-anthracene carboxylic acid, (Monomer **3b**).



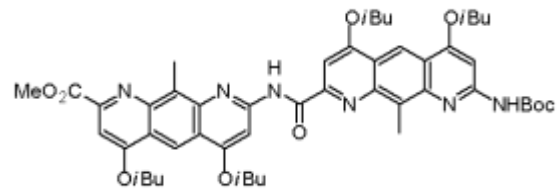


Methyl 1,8-diaza-4,5-diisobutoxy-7-[(amino]-9-methyl-2-anthracene carboxylic acid, (Monomer **3c**).





Dimer, **4a**.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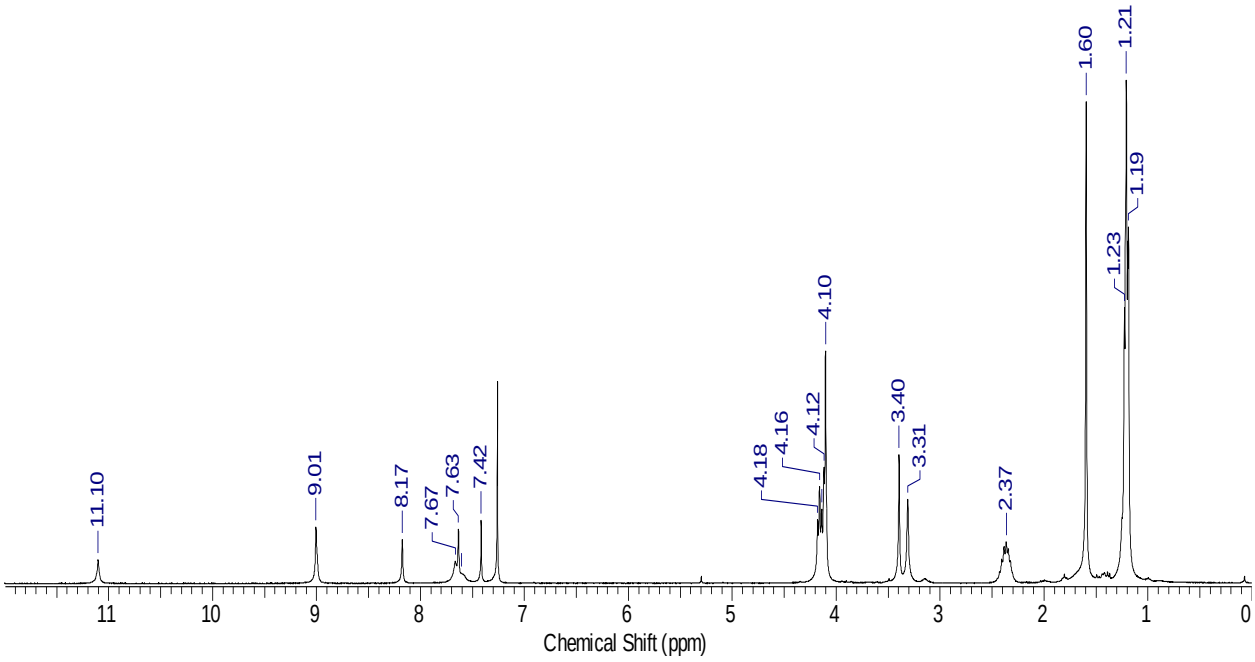
N
H
N
O
N
N
NHBoc
OiBu
OiBu
OiBu
OiBu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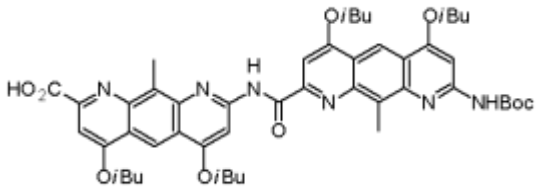
9.01
8.17
7.67
7.63
7.42
4.18
4.16
4.12
4.10
3.40
3.31
2.37
1.60
1.23
1.21
1.19
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

Dimer **4b**.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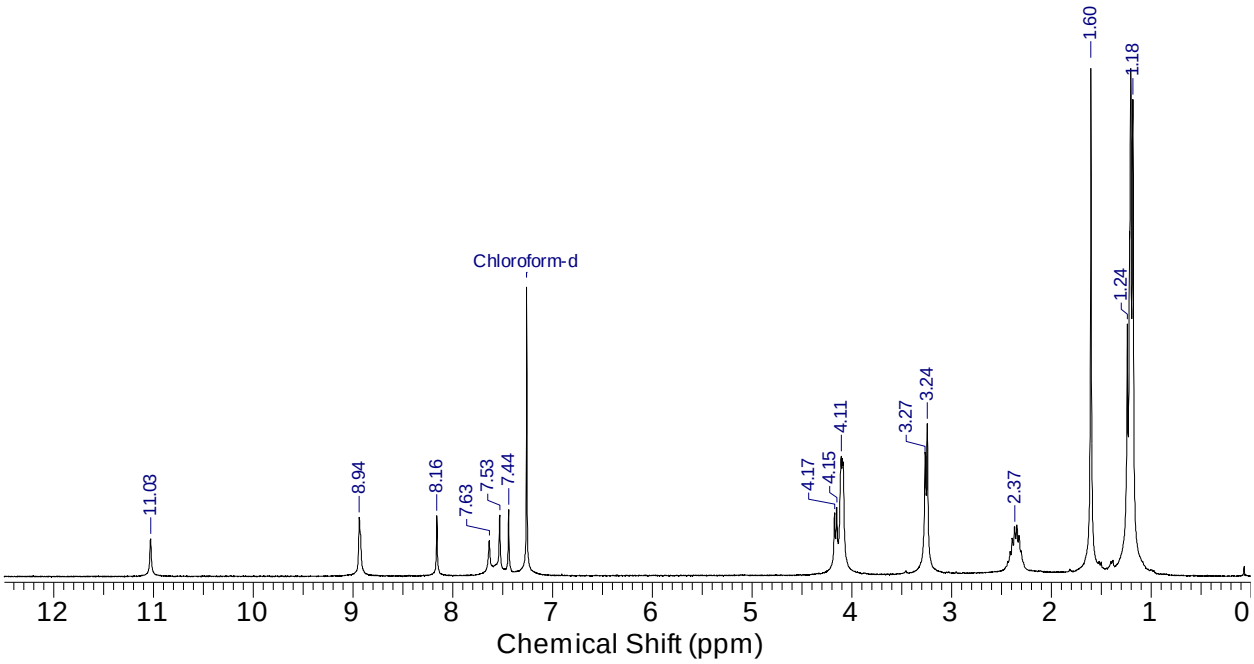
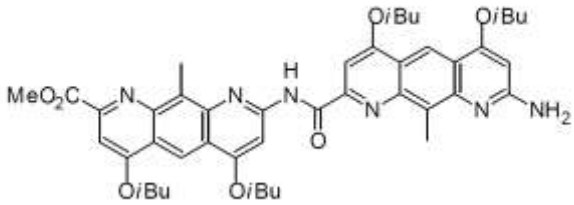
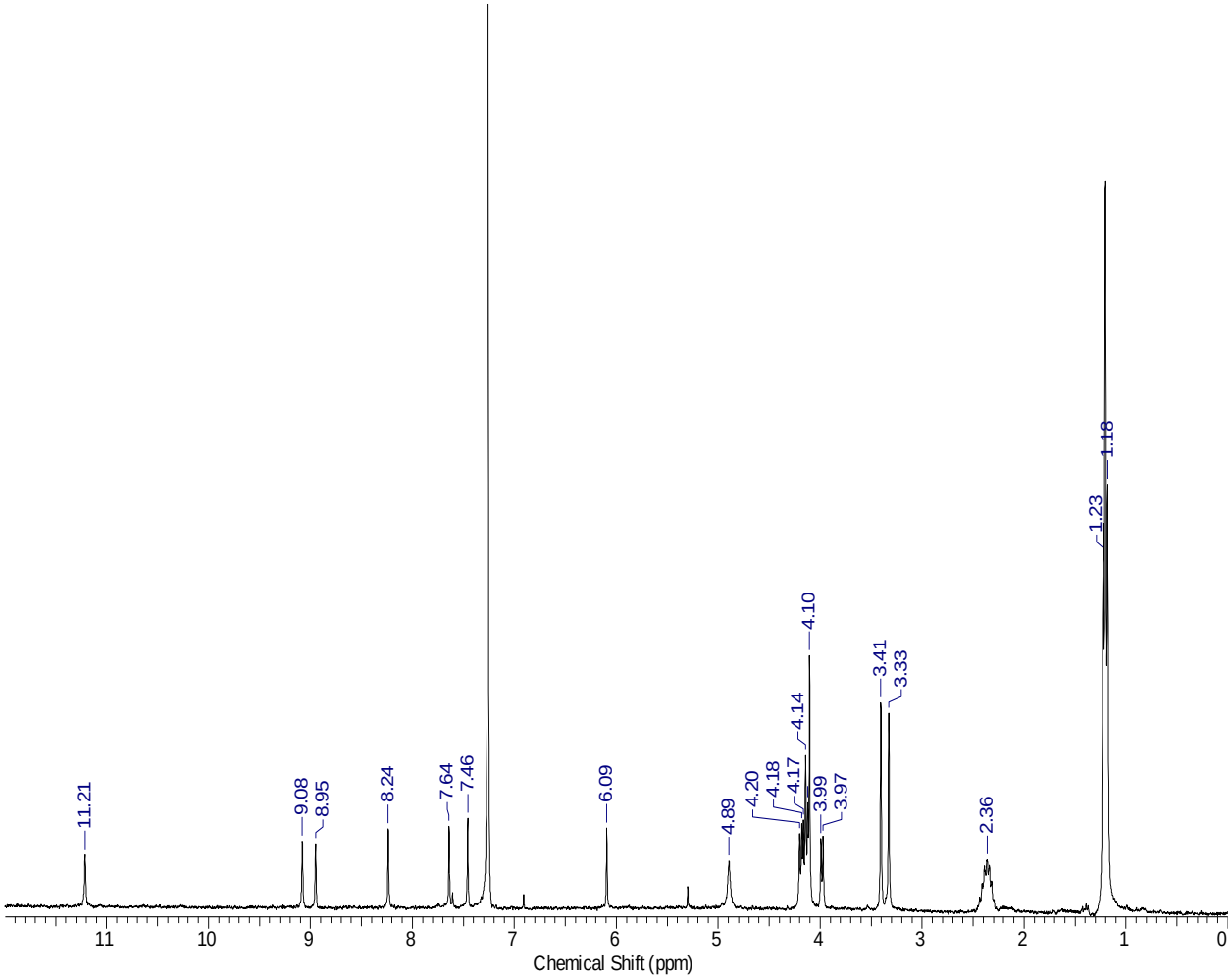
N
N
H
N
O
N
N
NHBoc
OiBu
OiBu
OiBu
OiBu


11.03
8.94
8.16
7.63
7.53
7.44
Chloroform-d
4.17
4.15
4.11
3.27
3.24
2.37
1.60
1.24
1.18
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

Dimer **4c**.


OiBu
OiBu
MeO2C
N
N
H
N
O
N
N
NH2
OiBu
OiBu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8.24
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6.09
4.89
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4.17
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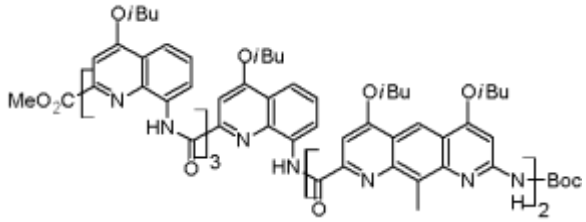
3.99
3.97
3.41
3.33
2.36
1.23
1.18
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

Hexamer, **5a**.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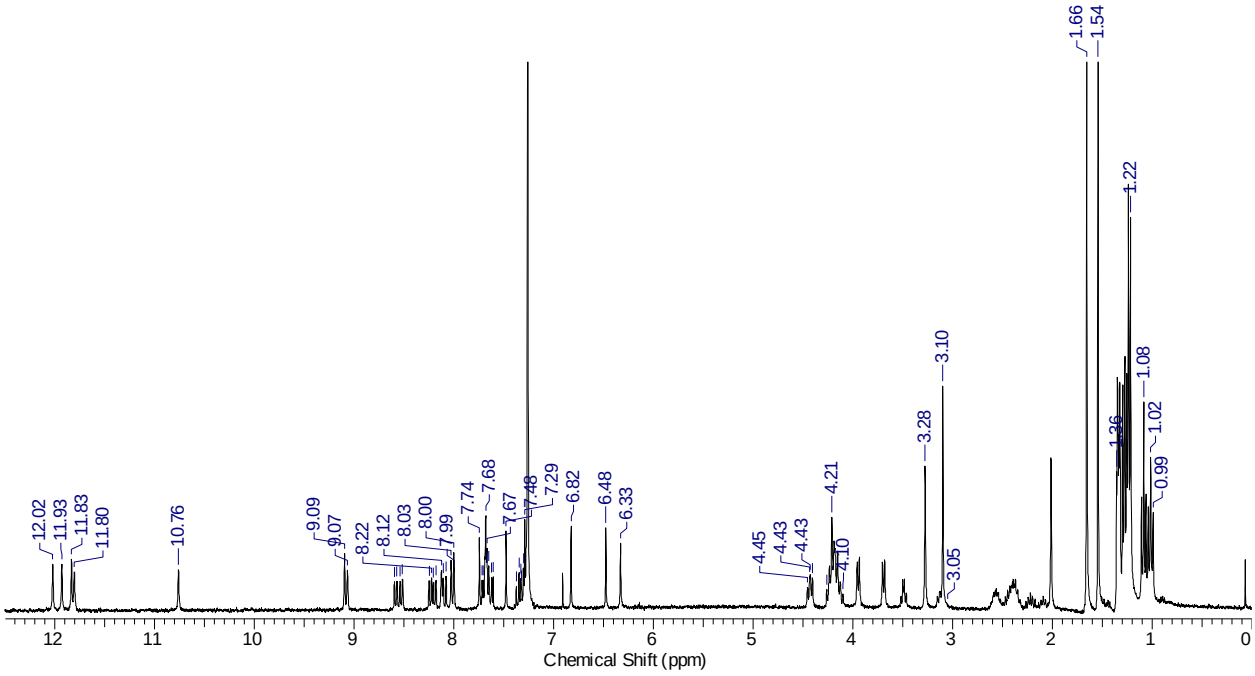
HN
O
3
OiBu
N
HN
OiBu
N
OiBu
N
N
Boc
H
2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8.22
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8.03
8.00
7.99
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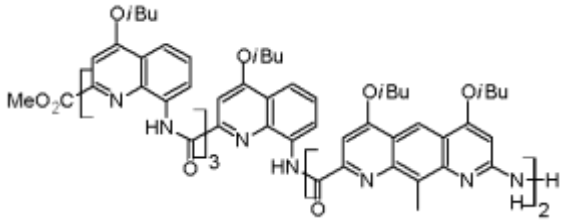
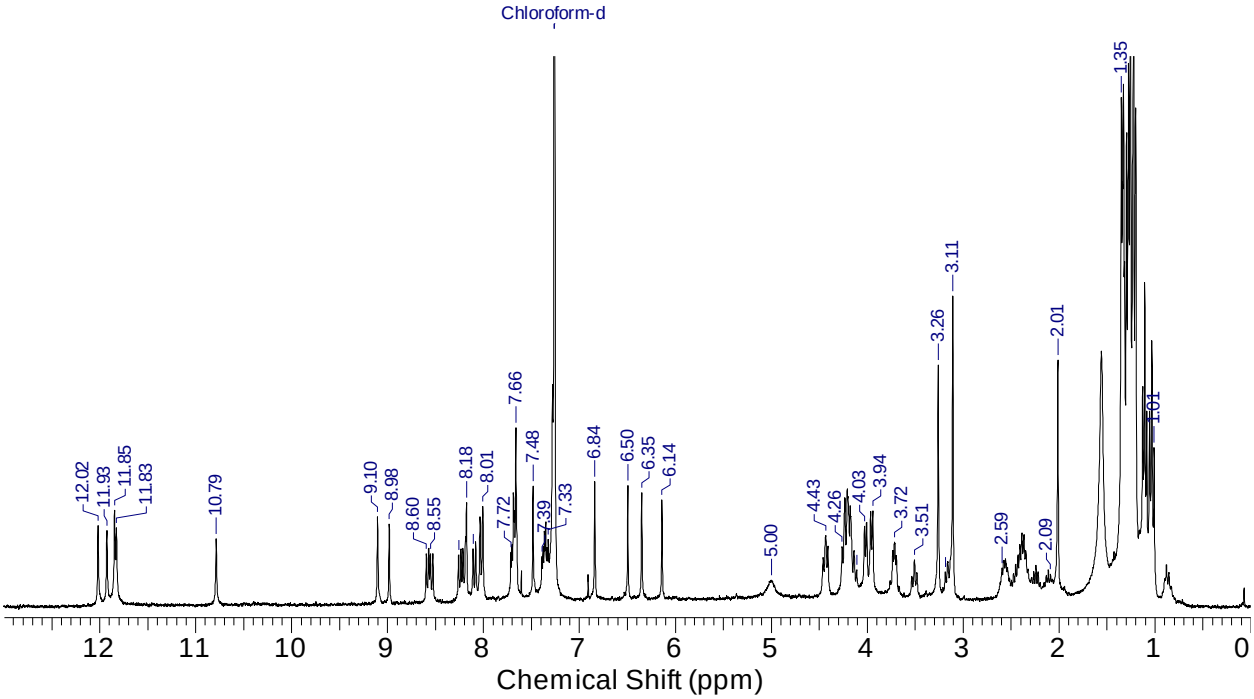
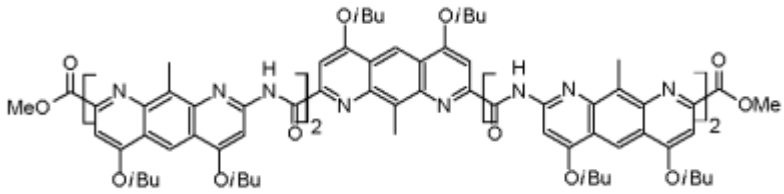
7.68
7.67
7.48
7.29
6.82
6.48
6.33
4.45
4.43
4.43
4.21
4.10
3.28
3.10
3.05
1.66
1.54
1.22
1.26
1.08
1.02
0.99
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

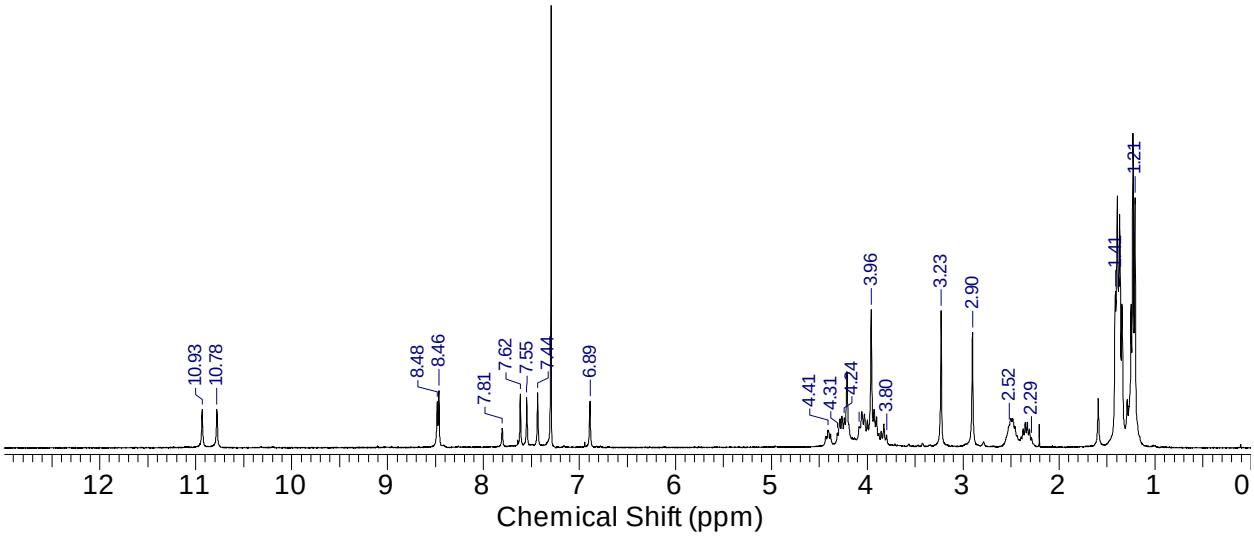
Hexamer **5b**


O*i*Bu
MeO2C
N
HN
O
3
N
HN
O
N
N
N
H
H2


Chloroform-d
12.02
11.93
11.85
11.83
10.79
9.10
8.98
8.60
8.55
8.18
8.01
7.72
7.66
7.48
7.39
7.33
6.84
6.50
6.35
6.14
5.00
4.43
4.26
4.03
3.94
3.72
3.51
3.26
3.11
2.59
2.09
2.01
1.61
1.35
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

Pentamer **1**


MeO
OMe
O/Bu
O/Bu
O/Bu
O/Bu
O/Bu
O/Bu
H
N
O
2


10.93
10.78
8.48
8.46
7.81
7.62
7.55
7.44
6.89
4.41
4.31
4.24
3.96
3.80
3.23
2.90
2.52
2.29
1.41
1.21
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

Tridecamer, **2**