Supporting Information for: “Structural factors controlling the self-assembly of columnar liquid crystals”

E. Johan Foster, R. Bradley Jones, Christine Lavigneur and Vance E. Williams*

Experimental

All solvents employed were reagent grade. 1,2-Phenylenediamine, 4,5-dichloro-1,2-phenylenediamine, 1,2-dichloro-1,2-phenylenediamine, 1,2-ethylenediamine, 2,3-diaminonaphthalene, 4,5-dimethyl-1,2-phenylenediamine, 4-fluoro-2-nitroaniline, 4-amino-3-nitrobenzonitrile, and 4-methoxy-2-nitroaniline were purchased from Aldrich and used without further purification. 1,2-Dimethoxy-4,5-dinitrobenzene, compounds 1^2 and 3d^3 were prepared according to previously published methods. 4-Fluoro-1,2-phenylenediamine, 4-cyano-1,2-phenylenediamine and 4-methoxy-1,2-phenylenediamine were prepared from the appropriate 2-nitroaniline derivatives, as described below.

400 MHz $^1$H and 100 MHz $^{13}$C NMR spectra were obtained using Bruker AMX-400 400 MHz spectrometer. Infrared spectroscopy was carried out on a Thermo Nicolet Nexus 670 FT-IR E.S.P. spectrometer and performed in KBr pellets. Mass spectrometry was carried out using a Perseptive Voyager-DE STR (MALDI-TOF) from PE Applied Biosystems with a nitrogen laser (337 nm) to desorb the ions from the source using 2,5-dihydroxybenzoic acid as a matrix. Phase transition temperatures and enthalpies were
investigated using differential scanning calorimetry on a Perkins Elmer DSC 7, heating and cooling at a rate of 10 °C min⁻¹. Texture analysis was carried out using optical polarizing microscopy on an Olympus BX50 microscope with crossed polarizers using a Linkam LTS350 heating stage. X-ray scattering experiments were conducted using a Rigaku R-Axis Rapid diffractometer equipped with a temperature controller. Microanalyses (C, H, N) were performed at Simon Fraser University by Mr. Mikki Yang on a EA1110 CHN CE Instrument using WO₃ as an accelerant.

**Synthesis**

*4-Fluoro-1,2-phenylenediamine.* 4-Fluoro-2-nitroaniline (0.100 g, 0.641 mmol) was dissolved in 10 mL ethanol and 0.050 g 10% palladium on activated carbon was added. Hydrazine hydrate (0.16 ml, 3.2 mmol) was added dropwise and the mixture was then refluxed for 3 hours. The resulting solution was filtered hot through a plug of silica. This plug was washed with 50 mL ethanol, and the solvent evaporated under reduced pressure. The resulting solid was used immediately without further purification.

*4-Cyano-1,2-phenylenediamine* was synthesized from 4-amino-3-nitrobenzonitrile according to the method described above. The resulting solid was used immediately without further purification.

*4-Methoxy-1,2-phenylenediamine* was synthesized from 4-methoxy-2-nitroaniline according to the method described above. The resulting solid was used immediately without further purification.
4,5-Dimethoxy-1,2-phenylenediamine was synthesized from 1,2-dimethoxy-4,5-dinitrobenzene according to the method described above. This compound is extremely unstable and was used immediately without further purification.

**General synthesis of compounds 2, 3a-c, 3e-k, 4**

A solution of 2,3,6,7-tetrakis(hexyloxy)-phenanthrene-9,10-dione (80 mg, 0.132 mmol) and the appropriate 1,2-diamine (0.52 mmol) were heated in 15 mL refluxing acetic acid for 12 hours. Upon cooling, 150 mL water was added and the mixture extracted three times with 25 mL CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extracts were combined, washed with water, dried (MgSO$_4$), filtered, and evaporated under reduced pressure. The resulting solid was eluted through a short plug of silica with dichloromethane, and then purified by column chromatography (silica gel, 1:1 CH$_2$Cl$_2$:hexanes gradient to 100% CH$_2$Cl$_2$ as eluent). The product was recrystallized from a mixture of CH$_2$Cl$_2$ and methanol to afford the dibenzo[a,c]phenazine derivative.

6,7,10,11-Tetrakis-hexyloxy-dibenzo[f,h]quinoxaline (2) was synthesized by the condensation of compound 1 and 1,2-ethylene diamine to afford a yellow solid (72%).

$^1$H NMR (CDCl$_3$) δ 0.91-0.95 (m, 12H), 1.35-1.60 (m, 24H), 1.93-1.98 (m, 8H), 4.24-4.28 (m, 8H), 7.73 (s, 2H), 8.55 (s, 2H), 8.77 (s, 2H); $^{13}$C NMR (CDCl$_3$) δ 14.0, 22.6, 25.7, 29.2, 29.3, 31.6, 68.9, 69.5, 105.8, 107.2, 123.5, 125.7, 140.4, 141.9, 149.4, 151.1; MALDI-TOF MS (IAA) m/z 727 (M+); Elemental analysis: Calculated for C$_{40}$H$_{58}$N$_2$O$_4$: C, 76.15; H, 9.27; N, 4.44. Found: C, 76.49; H, 9.35; N, 4.24%. 
2,3,6,7-tetrakis-hexyloxy-dibenzo[\(a,c\)]phenazine (3a). Compound 1 and 1,2-phenylenediamine were condensed according to method described above to afford 3a as a yellow solid (73%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.92-0.97 (m, 12H), 1.37-1.65 (m, 24H), 1.94-2.02 (m, 8H), 4.26-4.39 (m, 8H), 7.75 (s, 2H), 7.81 (dd, \(J_{12} = J_{34} = 3\)Hz, \(J_{13} = J_{24} = 7\)Hz, 2H), 8.32 (d, \(J_{12} = J_{34} = 3\)Hz, \(J_{23} = 7\)Hz, 2H), \(8.81\) (s, 2H); \(^1^3\)C NMR (CDCl\(_3\)) \(\delta\) 14.0, 14.0, 22.6, 22.6, 25.7, 25.8, 29.2, 29.2, 31.6, 69.2, 69.6, 106.3, 108.8, 126.7, 128.7, 128.7, 128.7, 129.2, 129.3, 149.5, 152.0; MALDI-TOF MS (IAA) m/z 682 (M+1); Elemental analysis: Calculated for C\(_{44}\)H\(_{60}\)N\(_2\)O\(_4\): C, 77.61; H, 8.88; N, 4.11. Found: C, 77.56; H, 8.87; N, 3.93%.

11-Fluoro-2,3,6,7-tetrakis-hexyloxy-dibenzo[\(a,c\)]phenazine (3b) 4-Fluoro-1,2-phenylenediamine was condensed with compound 1 to yield a yellow solid (89%). \(^1\)H (CDCl\(_3\)) \(\delta\) 0.92-0.95 (m, 12H), 1.24-1.55 (m, 24H), 1.95-1.99 (m, 8H), 4.26-4.36 (m, 8H), 7.58-7.63 (dd, \(J_{12} = J_{34} = 2\)Hz, \(J_{13} = J_{24} = 9\)Hz, 1H), 7.73 (s, 2H), 7.99-8.02 (d, \(J = 9\)Hz, 1H), 8.37 (d, \(J = 2\)Hz, 1H), 8.75 (s, 2H); \(^1^3\)C NMR (CDCl\(_3\)) \(\delta\)14.0, 22.6, 25.7, 25.8, 29.2, 29.2, 31.6, 69.1, 69.2, 69.5, 106.2, 106.3, 108.6, 108.8, 111.8, 120.1, 122.7, 123.0, 126.5, 127.0, 130.8, 130.9, 149.5, 152.0, 152.2; MALDI-TOF MS (IAA) m/z 698 (M+) Elemental analysis: Calculated for C\(_{44}\)H\(_{59}\)FN\(_2\)O\(_4\): C, 75.61; H, 8.51; N, 4.01. Found: C, 75.39; H, 8.60; N, 4.30%.

11-Chloro-2,3,6,7-tetrakis-hexyloxy-dibenzo[\(a,c\)]phenazine (3c) was synthesized by the condensation of compound 1 and 4-chloro-1,2-phenylenediamine, yielding a yellow solid (86%). \(^1\)H (CDCl\(_3\)) \(\delta\) 0.92-0.97 (m, 12H), 1.40-1.61 (m, 24H), 1.95-1.99 (m, 8H),
2,3,6,7-Tetrakis-hexyloxy-dibenzo[a,c]phenazine-11-carbonitrile (3e) 4-Amino-3-nitrobenzonitrile was reduced as described above and the resulting diamine condensed with compound 1 to afford an orange solid (89%). $^1$H NMR (CDCl$_3$) $\delta$ 0.93-0.96 (m, 12H), 1.41-1.60 (m, 24H), 1.94-2.01 (m, 8H), 4.24-4.32 (m, 8H), 7.63-7.65 (dd, J$_{12}$=J$_{34}$= 2Hz, J$_{13}$=J$_{24}$= 7Hz, 1H), 7.75 (s, 2H), 8.10 (d, J = 2Hz, 1H), 8.20-8.21 (d, J = 7Hz, 1H), 8.80 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$14.0, 22.6, 25.8, 25.8, 29.2, 29.2, 31.6, 69.1, 69.4, 105.8, 106.0, 108.5, 108.8, 111.6, 118.7, 122.8, 126.8, 127.3, 128.8, 130.5, 135.2, 140.0, 142.4, 143.2, 143.6, 149.3, 149.4, 152.3, 152.6; IR (KBr) $\nu_{max}$/cm$^{-1}$: 2949, 2926, 2849, 2228, 1607, 1513, 1500, 1443, 1386, 1265, 1178, 1074, 1047, 923, 873, 826; MALDI-TOF MS (IAA) m/z 714 (M+); Elemental analysis: Calculated for C$_{44}$H$_{59}$ClN$_2$O$_4$: C, 73.97; H, 8.31; N, 3.92. Found: C, 73.82; H, 8.42; N, 3.94%.

2,3,6,7-Tetrakis-hexyloxy-dibenzo[a,c]phenazine-11-nitro (3f) was synthesized by the condensation of 1 and 4-nitro-1,2-phenylenediamine to yield a red solid (91%). $^1$H NMR (CDCl$_3$) $\delta$ 0.94-0.98 (m, 12H), 1.43-1.61 (m, 24H), 1.92-1.98 (m, 8H), 4.18-4.29 (m, 8H), 7.70 (s, 2H), 8.40 (d, J = 9Hz 1H), 8.52-8.55 (dd, J$_{12}$ = J$_{34}$ = 2Hz, J$_{13}$=J$_{24}$ = 9Hz, 1H), 8.75 (s, 2H), 9.23 (d, J = 2Hz 1H); $^{13}$C NMR (CDCl$_3$) $\delta$14.0, 22.6, 25.8, 25.8, 29.2,
2,3,6,7-Tetrakis-hexyloxy-11-methyl-dibenzo[\textit{a,}c]phenazine (3g) was synthesized by the condensation of compound 1 and 3,4-diaminotoluene, yielding a yellow solid (78%). 1H NMR (CDCl$_3$) $\delta$ 0.92-0.95 (m, 12H), 1.24-1.64 (m, 24H), 1.93-2.01 (m, 8H), 2.66 (s, 3H), 4.25 4.36 (m, 8H), 7.63 (dd, $J_{12}$ = $J_{34}$ = 2Hz, $J_{13}$=$J_{24}$ = 7Hz, 1H), 7.71 (s, 2H), 8.11 (s, 2H), 8.21 (d, $J$ = 7Hz, 1H), 8.78 (d, $J$ = 2Hz, 1H); 13C NMR (CDCl$_3$) $\delta$14.0, 22.0, 22.6, 25.8, 29.2, 29.3, 31.6, 69.1, 69.6, 106.3, 108.5, 126.2, 128.5, 131.6, 149.3, 149.4, 151.5; MALDI-TOF MS (IAA) m/z 695 (M+1); Elemental analysis: Calculated for C$_{45}$H$_{62}$N$_2$O$_4$: C, 77.77; H, 8.99; N, 4.03. Found: C, 77.45; H, 8.99; N, 3.90%.

2,3,6,7-Tetrakis-hexyloxy-11-methoxy-dibenzo[\textit{a,}c]phenazine (3h) 4-Methoxy-2-nitroaniline was reduced as above and the resulting diamine condensed with compound 1, yielding a yellow solid (84%). 1H NMR (CDCl$_3$) $\delta$ 0.92-0.95 (m, 12H), 1.37-1.59 (m, 24H), 1.93-2.01 (m, 8H), 4.06 (s, 3H), 4.25 4.37 (m, 8H), 7.46 (dd, $J_{12}$ = $J_{34}$ = 2Hz, $J_{23}$ = 6Hz, 1H), 7.59 (s, 2H), 8.18 (d, $J$ = 6Hz, 1H), 8.75 (s, 2H), 8.79 (d, $J$ = 2Hz, 1H); 13C NMR (CDCl$_3$) $\delta$14.0, 22.6, 25.7, 29.2, 29.6, 31.6, 55.8, 69.1, 69.2, 69.5, 69.6, 106.2, 106.5, 108.2, 108.7, 123.4, 125.7, 130.1, 149.4, 149.5, 151.3; MALDI-TOF MS (IAA)
m/z 711 (M+1). Elemental analysis: Calculated for C_{45}H_{62}N_{2}O_{5}: C, 76.02; H, 8.79; N, 3.94. Found: C, 75.91; H, 9.15; N, 3.67%.

11,12-Dichloro-2,3,6,7-tetrakis-hexyloxy-dibenzo[a,c]phenazine (3i) was synthesized by the condensation of compound 1 and 4,5-dichlorobenzene-1,2-phenylenediamine, yielding a yellow solid (89%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.92-0.96 (m, 12H), 1.40-1.60 (m, 24H), 1.94-2.00 (m, 8H), 4.25-4.32 (m, 8H), 7.68 (s, 2H), 8.42 (s, 2H), 8.68 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 14.0, 22.6, 22.6, 25.7, 29.2, 29.2, 31.6, 69.1, 69.5, 106.1, 108.6, 126.8, 129.4, 133.1, 139.9, 149.4, 152.2; MALDI-TOF MS (IAA) m/z 748 (M+); Elemental analysis: Calculated for C\(_{44}\)H\(_{58}\)Cl\(_2\)N\(_2\)O\(_4\): C, 70.48; H, 7.80; N, 3.74. Found: C, 70.70; H, 7.92; N, 3.59%.

2,3,6,7-Tetrakis-hexyloxy-11,12-dimethyl-dibenzo[a,c]phenazine (3j) Synthesized by the condensation of compound 1 and 4,5-dimethyl-1,2-phenylenediamine, yielding a yellow solid (78%). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.92-0.96 (m, 12H), 1.36-1.60 (m, 24H), 1.92-1.99 (m, 8H), 2.57 (s, 6H), 4.25 4.36 (m, 8H), 7.72 (s, 2H), 8.10 (s, 2H), 8.79 (s, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 14.0, 14.0, 20.5, 22.6, 25.8, 25.8, 29.2, 29.3, 31.6, 69.2, 69.6, 106.4, 108.6, 126.4, 127.4, 140.3, 149.5, 151.7; MALDI TOF MS (IAA) m/z 708 (M+); Elemental analysis: Calculated for C\(_{46}\)H\(_{64}\)N\(_2\)O\(_4\): C, 77.92; H, 9.10; N, 3.95. Found: C, 77.76; H, 9.08; N, 4.15%.

2,3,6,7-Tetrakis-hexyloxy-11,12-dimethoxy-dibenzo[a,c]phenazine (3k) 1,2-Dimethoxy-4,5-dinitrobenzene was reduced as above and the resulting diamine
condensed with compound 1, yielding a orange solid (85%). $^1$H NMR (CDCl$_3$) $\delta$ 0.92-0.96 (m, 12H), 1.36-1.60 (m, 24H), 1.92-2.01 (m, 8H), 4.13 (s, 6H), 4.24-4.35 (m, 8H), 7.53 (s, 2H), 7.70 (s, 2H), 8.71 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$14.0, 22.6, 25.7, 29.2, 29.2, 31.6, 69.2, 69.6, 106.3, 108.8, 126.7, 128.7, 129.2, 149.5, 152.0; MALDI-TOF MS (IAA) m/z 741 (M+1); Elemental analysis: Calculated for C$_{46}$H$_{64}$N$_2$O$_6$: C, 74.56; H, 8.71; N, 3.78. Found: C, 74.85; H, 8.96; N, 3.45%.

2,3,6,7-Tetrakis-hexyloxy-9,16-diaza-dibenzo[a,c]napthacene (4) Synthesized by the condensation of compound 1 and 2,3-diaminonaphthalene, yielding a yellow solid (74%). $^1$H NMR (CDCl$_3$) $\delta$ 0.93-0.98 (m, 12H), 1.39-1.64 (m, 24H), 1.94-2.00 (m, 8H), 4.22-4.35 (m, 8H), 7.53-7.58 (m, 2H), 7.67 (s, 2H), 8.15-8.17 (m, 2H), 8.81 (s, 2H), 8.90 (s, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 14.0, 22.6, 22.6, 25.7, 25.8, 29.2, 31.6, 69.1, 69.5, 106.4, 109.0, 123.5, 126.0, 126.7, 128.3, 133.5, 137.8, 138.2, 143.0, 149.3, 152.0. MALDI-TOF MS (IAA) m/z 730 (M+); Elemental analysis: Calculated for C$_{48}$H$_{62}$N$_2$O$_4$: C, 78.86; H, 8.55; N, 3.83. Found: C, 78.51; H, 8.35; N, 3.70%.
**X-Ray Diffraction Data**

**Figure S1.** I(Q) curve for compound 3c at 170° C.

**Figure S2.** I(Q) curve for compound 3e at 150° C.
Figure S3. I(Q) curve for compound 3f at 150° C.

Figure S4. I(Q) curve for compound 3i at 170° C.
Figure S5. I(Q) curve for compound 4 at 130° C.

References