Supplementary Materials

Experimental

Compounds were characterized by 400 MHz ^{1}H-NMR and 100 MHz ^{13}C-NMR (Brucker AMX-400 400 MHz spectrometer), FT-IR spectroscopy (Thermo Nicolet Nexus 670 FT-IR E.S.P. spectrometer, performed in KBr) and mass spectrometry (MALDI-TOF using a Perseptive Voyager-DE STR 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 or EI (70 eV) using a Hewlett Packard 5985 mass spectrometer). Melting points of intermediates were determined using a Fisher Johns Melting Point Apparatus, and are uncorrected. Phase transition temperatures and enthalpies for compounds **6a-f** were investigated using differential scanning calorimetry (Perkins Elmer DSC 7, heating and cooling rate was 5°C min^{-1}). Texture analysis was carried out using optical polarising microscopy (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. Miki Yang.
The target compounds were prepared according to Scheme II. 3,3',4,4' tetrakis-hydroxybenzil , used in the synthesis of **1d-f**, was synthesised using previously reported methods.[1]

1,2-Didecyloxy-4-iodobenzene (2d)[2] A solution of 1,2-didecyloxy-benzene (0.5 g, 1.28 mmol) and iodine (0.1692 g, 0.667 mmol) in 15 mL of glacial acetic acid, 5 mL of water, and 0.4 mL of sulphuric acid was heated to 40°C and 0.025 g iodic acid was added. The solution stirred at 40°C for 1 hour at which time a second fraction of 0.025 g iodic acid was added. After another hour, a third portion of 0.025 g iodic acid was added. The solution was then allowed to stir a further 1.5 hours at 40°C. Upon cooling the solution was added to 30 mL of water and extracted with diethyl ether three times with 25 mL each time. The combined ether extracts were washed with aqueous 50 mL Na_2CO_3, 50 mL brine, dried ($MgSO_4$) and the solvent removed under reduced pressure. The resulting product was recrystallized from ethanol to afford an off-white solid 0.2343 g, 68%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.18-7.20 (dd, 1H J = 2.0, 8.5 Hz), 7.11-7.14 (d, 1H J = 2.0 Hz), 6.54-6.73 (d, 1H J = 8.5 Hz), 3.90-4.05 (t, 4H J = 6.5 Hz), 1.20-2.00 (m, 32H), 0.80-1.03 (m, 6H). Elemental analysis (%): calc. (found) for $C_{26}H_{45}IO_2$. C, 60.46(60.58); H, 8.78(8.65). Melting Point 38-39°C

4-Iodo-1,2-dimethoxy-benzene (2a) was synthesized from 1,2-dimethoxy-benzene (4.00 g, 29.29 mmol) in the manner described above to afford **2a** as a red liquid product (5.01 g, 65%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.18-7.21 (dd, 1H J = 1.9, 8.9 Hz), 7.12-7.15 (d, 1H J = 2.0 Hz), 6.55-6.75 (d, 1H J = 8.8 Hz), 3.84 (s, 6H). EI-MS calc. (found) 264(264). [3]

1,2-Dihexyloxy-4-iodo-benzene (2b) was synthesized from 1,2-dihexyloxy-benzene (2.00 g, 7.18 mmol) in the manner described above to afford a red liquid (1.946 g, 67%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm) 7.19-7.21 (dd, 1H J = 2.1, 8.7 Hz), 7.11-7.14 (d, 1H J = 2.1 Hz), 6.54-6.71 (d, 1H J = 8.7 Hz), 3.95-4.11 (t, 4H J = 6.5 Hz), 1.20-2.01 (m, 16H), 0.83-1.05 (m, 6H). EI-MS calc. (found) 404(404). [2]

4-Iodo-1,2-dioctyloxy-benzene (2c) was synthesized from 1,2-dioctyloxy-benzene (2.00 g, 5.98 mmol) in the manner described above to afford a white solid product (1.982 g, 72%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.18-7.20 (dd, 1H J = 2.0, 8.8 Hz), 7.12-7.14 (d, 1H J = 2.0 Hz), 6.54-6.71 (d, 1H J = 8.8 Hz), 3.90-4.06 (t, 4H J = 6.5 Hz), 1.20-2.00 (m, 24H), 0.80-1.01 (m, 6H). EI-MS calc. (found) 460(460). Melting Point 36-38°C.

1,2-Didecyloxy-4-ethynyl-benzene (3) To a solution of 1,2-didecyloxy-4-iodobenzene (1.30 g, 2.52 mmol), copper (I) iodide, (0.1631 g, 0.856 mmol), and $PdCl_2(PPh_3)2$ (0.0472 g, 0.0673 mmol) in 40mL anhydrous THF was added 4.3 mL of (trimethylsilyl)acetylene (0.030 mmol) and 1 mL of diisopropylamine under N_2. The solution was heated at 60°C for 24 hours under a nitrogen atmosphere. Upon cooling the solution was passed through a short column of silica and the solvent evaporated. The resulting brown oil was subjected to column chromatography (silica gel, 10% ethyl acetate in hexanes). A solution of (3,4-Didecyloxy-phenylethynyl)-trimethylsilane (1.38 g, 2.84 mmol) and potassium carbonate (1.0213 g, 7.390 mmol) in 60 mL of a 1:1 MeOH:THF mixture was stirred for 24 hrs. The solution was passed through a column (silica gel, CH_2Cl_2), the solvent evaporated to yield a brown solid. The solid was subjected to further column chromatography (silica gel, 10% ethyl acetate in hexanes) to yield a yellow-white solid (2.098 g, 74%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.18-7.19 (d, 1H J = 2.0 Hz), 7.11-7.13 (dd, 1H J = 2.0, 8.7 Hz), 6.82-6.84 (d, 1H J = 8.6 Hz), 3.91-4.08 (t, 4H J = 6.4 Hz), 3.05 (s, 1H), 1.20-2.01 (m, 32H), 0.83-1.04 (m, 6H). Maldi-TOF. calc. (found) 414(414). [4].

3,4-Didecyloxy-3'4'-dioctyloxy-diphenylacetylene (4c) To a stirred solution of 1,2-didecyloxy-4-ethynylbenzene (0.942 g, 2.27 mmol), 4-iodo-1,2-dioctyloxybenzene (1.054 g, 2.29 mmol), copper (I) iodide, (0.131 g, 0.689 mmol), and $Pd(PPh_3)_4$ (0.045 g, 0.39 mmol) in 100 mL of anhydrous THF was added 8 mL of diisopropylamine. The solution was heated at 60°C for 19 hours. Upon cooling, the solution was passed through a short plug of silica gel and the resulting solid was subjected to column chromatography (silica gel, 10% ethyl acetate in hexanes) to yield a yellow-white solid (1.493 g, 88%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.00-7.06 (dd, 2H J = 2.0, 8.7 Hz), 6.99-7.00 (d, 2H J = 2.0 Hz), 6.81-6.83 (d, 2H J = 8.7 Hz), 3.96-3.99 (m, 8H), 1.20-1.81 (m, 56H), 0.84-0.90 (m, 12H). ^{13}C-NMR ($CDCl_3$) 145.6; 144.8; 123.9; 123.7; 116.7; 115.8; 114.4; 88.1; 88.0; 69.3; 69.3; 32.0; 31.5; 30.1; 30.0; 30.0; 29.9; 29.8; 29.7; 29.6; 29.5; 29.3; 29.2; 26.2; 25.8; 22.9; 22.8; 14.1; 14.0; 14.0; 14.0. Elemental analysis (%): calc. (found) for $C_{50}H_{82}O_4$. C, 80.37(80.24); H, 11.06(11.13). Melting Point 76-77 °C. MALDI-TOF. calc. (found) 747(770 M + Na).

3,4-Didecyloxy-3'4'-dimethoxy-diphenylacetylene (4a) was synthesized from 1,2-didecyloxy-4-ethynylbenzene (0.5002 g, 1.206 mmol) and 4-iodo-1,2-dimethoxy-benzene (0.318 g, 1.21 mmol) in the manner described above to afford **4a** a white product (0.491 g, 74%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.01-7.07 (dd, 2H J = 2.0, 8.7 Hz), 7.01 (d, 2H J = 2.1 Hz), 6.80-6.82 (d, 2H J = 8.8 Hz), 3.99-4.02 (t, 4H J = 6.8 Hz), 3.90 (s, 6H), 1.23-1.80 (m, 32H), 0.82-0.99 (m, 6H). ^{13}C-NMR ($CDCl_3$)) 147.3, 147.1, 144.1, 144.0, 124.4, 124.3, 119.7, 118.4, 115.0, 114.6, 114.5, 91.0, 72.6, 72.6, 56.3, 56.3, 32.5, 32.5, 30.6, 30.6, 30.3, 30.3, 30.3, 30.3, 30.1, 30.0, 26.6, 26.6, 24.2, 23.1, 14.1, 14.0. Elemental analysis (%): calc. (found) for $C_{36}H_{54}O_4$. C, 78.50(78.61); H, 9.88(9.92). Melting Point 88-89 °C. MALDI-TOF. calc. (found) 551(551).

3,4-Didecyloxy-3'4'-dihexyloxy-diphenylacetylene (4b) was synthesized from 1,2-didecyloxy-4-ethynylbenzene (1.121 g, 2.703 mmol) and 1,2-dihexyloxy-4-iodo-benzene (1.103 g, 2.73 mmol) in the manner described above to afford **4b** an off-white solid (1.658 g, 89%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.01-7.07 (dd, 2H J = 2.1, 8.6 Hz), 7.01 (d, 2H J = 2.0 Hz), 6.80-6.82 (d, 2H J = 8.6 Hz), 3.98-4.01 (m, 8H), 1.26-1.83 (m, 48H), 0.86-0.91 (m, 12H). ^{13}C-NMR ($CDCl_3$) ^{13}C-NMR ($CDCl_3$) 149.6; 148.8; 124.9; 116.7; 115.8; 113.4; 88.1; 69.4; 69.3; 32.1; 31.8; 30.1; 29.8; 29.8; 29.6; 29.5; 29.3; 29.2; 26.2; 25.8; 22.9; 22.8; 14.3; 14.2. Elemental analysis (%): calc. (found) for $C_{46}H_{74}O_4$. C, 79.95(80.13); H, 10.79(10.68). Melting Point 73-75°C. MALDI-TOF. calc. (found) 691(691).

3,4-Didecyloxy-3'4'-dimethoxybenzil (1a) was synthesised from 3,4-didecyloxy-3'4'-dimethoxy-diphenylacetylene (0.300 g, 0.545 mmol) and iodine (0.138 g, 0.545 mmol) in the manner described above to afford **1a** an off-white solid (0.286 g, 82%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.57-7.59 (d, 2H J = 2.0 Hz), 7.46-7.49 (dd, 1H J = 2.0, 8.4 Hz), 7.41-7.44 (dd, 1H 2.0, 8.4 Hz), 6.86-6.88 (d, 1H J= 8.3 Hz), 6.84-6.87 (d, 1H 8.3 Hz), 4.04-4.07 (t, 4H J = 6.7 Hz), 3.95 (s, 6H), 1.20-2.00 (m, 32H), 0.80-1.00 (m, 6H). ^{13}C-NMR ($CDCl_3$) 193.7, 193.6, 155.0, 154.7, 151.9, 151.6, 149.5, 128.5, 127.9, 127.6, 126.5, 114.5, 110.9, 110.3, 69.3, 69.2, 69.1, 31.9, 29.6, 29.5, 29.4, 29.3, 29.4, 29.0, 28.9, 26.0, 25.9, 25.9, 22.65, 14.1. Elemental analysis (%): calc. (found) for $C_{36}H_{54}O_6$. C, 74.19(74.29); H, 9.34(9.45). Melting Point 78-79 °C. MALDI-TOF. calc. (found) 583 (583).

3,4-Didecyloxy-3'4'-dihexyloxybenzil (1b) was synthesized from 3,4-didecyloxy-3'4'-dihexyloxy-diphenylacetylene (0.105 g, 0.152 mmol) and iodine (0.039 g, 0.152 mmol) in the manner described above to afford **1b** as an off-white solid (0.0742 g, 68%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.55-7.56 (d, 2H J = 2.0 Hz), 7.41-7.44 (dd, 2H J = 2.0, 8.8 Hz), 6.83-6.84 (d, 2H J= 8.8), 4.03-4.07 (m, 8H), 1.20-2.00 (m, 48H), 0.80-1.00 (m, 12H). ^{13}C-NMR ($CDCl_3$)) 187.7, 185.5, 182.9, 155.1, 147.6, 138.6, 138.1, 137.9, 137.5, 135.3, 114.2, 101.8, 89.4, 78.0, 75.3, 74.9, 43.7, 42.6, 38.7, 37.4, 36.6, 35.5, 33.5, 33.5, 32.1, 32.1, 32.1, 31.8, 30.4, 30.4, 30.1, 30.1, 29.9, 29.9, 29.6, 29.5, 29.4, 29.4, 29.2, 29.2, 29.1, 29.1, 29.0, 26.2, 26.2, 26.2, 26.1, 25.8, 25.7, 23.1, 14.3, 14.2, 14.1, 14.0. Elemental analysis (%): calc. (found) for $C_{46}H_{74}O_6$. C, 76.41(76.40); H, 10.32(10.42). Melting Point 84-86 °C. MALDI-TOF. calc. (found) 723(746 M + Na).

3,4-Didecyloxy-3'4'-dioctyloxybenzil (1c) A solution of 3,4-didecyloxy-3'4'-dioctyloxy-diphenylacetylene (0.950 g, 1.27 mmol) and iodine (0.352 g, 1.39 mmol) in 70 mL of DMSO was heated at 145°C for 3 hrs. Upon cooling the solution was poured into 200 mL of an aqueous 1% sodium thiosulfate pentahydrate solution. The resulting solution was collected by vacuum filtration and then purified by column chromatography (silica gel, 5:1 toluene:hexanes) to yield a beige solid (0.812 g, 82%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.56-7.57 (d, 2H J = 2.0 Hz), 7.41-7.44 (dd, 2H J = 2.0 Hz, 8.4 Hz), 6.83-6.85 (d, 2H J= 8.4 Hz), 4.03-4.07 (m, 8H), 1.20-2.00 (m, 56H), 0.80-1.00 (m, 12H). ^{13}C-NMR ($CDCl_3$) 193.8, 154.9, 149.3, 126.2, 126.1, 112.3, 111.6, 69.2, 69.1, 31.9, 31.8, 29.6, 29.5, 29.3, 29.3, 29.1, 28.9, 25.9, 25.9, 22.6, 14.1. Elemental analysis (%): calc. (found) for $C_{50}H_{82}O_6$. C, 77.07(77.41); H, 10.61(10.55). Melting Point 109-111 °C. MALDI-TOF. calc. (found) 779(779).

3,3',4,4' Tetrakis-decyloxyl-benzil (1f) [1] A stirred solution of 3,3',4,4' tetrakis-hydroxybenzil (1.633 g, 5.96 mmol) and 1-bromodecane (5.27 g, 23.8 mmol) in 300 mL DMF was stirred for 15 minutes while being purged with N_2. K_2CO_3 was added (3.29 g, 23.8 mmol) and the solution purged with N_2 for a further 15 minutes before stirring overnight at 70°C. The solution was allowed to cool, poured over 1000 mL ice, and vacuum filtered. The resulting solid was purified by column chromatography (silica gel, 10% ethyl acetate in hexanes) to yield **1f,** an off-white solid (4.593 g, 92%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.58-7.59 (d, 2H J = 2.0 Hz), 7.41-7.43 (dd, 2H J 2.0, 8.4 Hz), 6.83-6.85 (d, 2H 8.4 Hz), 4.04-4.06 (t, 8H J =6.6 Hz), 1.20-2.00 (m, 64H), 0.80-1.00 (m, 12H). ^{13}C-NMR ($CDCl_3$) 194.1, 194.1, 155.2, 149.5, 146.3, 146.2, 126.3, 124.6, 115.1, 112.4, 112.3, 111.7, 111.1, 111.0, 69.5, 69.4, 69.3, 64.1, 63.2, 51.5, 33.0, 32.1, 32.0, 31.1, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.1, 26.4, 26.2, 26.1, 26.0, 23.0, 22.9, 14.3. Melting Point 72-73 °C. MALDI-TOF. calc. (found) 835 (835).

3,3',4,4' Tetrakis-hexyloxybenzil (1d) was synthesized from 3,3',4,4' tetrakis-hydroxybenzil (2.32 g, 8.46 mmol) and 1-bromohexane (5.73 g, 34.7 mmol) in the manner described above to afford **1d,** an off-white solid (4.60 g, 89%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.55-7.57 (d, 2H J = 2.1 Hz), 7.42-7.44 (dd, 2H J = 2.0, 8.5 Hz), 6.86-6.88 (d, 2H J= 8.5 Hz), 4.04-4.06 (t, 8H J = 6.6 Hz), 1.20-2.00 (m, 32H), 0.80-1.00 (m, 12H). ^{13}C-NMR ($CDCl_3$) 194.2, 194.2, 194.0, 155.1, 155.1, 152.4, 149.4, 147.3, 126.9, 126.3, 126.2, 124.0, 115.2, 112.4, 112.3, 111.7, 111.2, 111.0, 77.5, 77.2, 77.0, 69.4, 69.3, 32.0, 31.8, 31.1, 29.5, 29.5, 29.4, 29.2, 29.1, 26.2, 26.1, 22.8, 14.3. Melting Point 78-80 °C. MALDI-TOF. calc. (found) 610 (610).

3,3',4,4' Tetrakis-octyloxybenzil (1e) was synthesized from 3,3',4,4' tetrakis-hydroxybenzil (1.51 g, 5.51 mmol) and 1-bromooctane (4.99 g, 22.6 mmol) in the manner described above to afford **1e,** an off-white solid (3.61 g, 91%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.56-7.57 (d, 2H J = 2.0 Hz), 7.41-7.43 (dd, 2H J = 2.0, 8.4 Hz), 6.86-6.88 (d, 2H J= 8.5 Hz), 4.05-4.07 (t, 8H J = 6.6 Hz), 1.20-2.00 (m, 48H), 0.80-1.00 (m, 12H). ^{13}C-NMR ($CDCl_3$) 194.2, 194.2, 194.0, 155.1, 155.1, 152.4, 149.2, 147.0, 126.9, 126.3, 126.2, 124.0, 115.2, 112.4, 112.1, 111.6, 111.0, 111.0, 69.2, 31.9, 31.8, 31.1, 29.5, 29.4, 29.2, 26.2, 26.0, 22.2, 14.3. Melting Point 85-88 °C. MALDI-TOF. calc. (found) 723 (723).

2,3-Didecyloxy-6,7-dioctyloxy-phenanthrene-9,10-dione (5c)[5] To a stirred solution of 3,4-didecyloxy-3'4'-dioctyloxybenzil (0.501 g, 0.64 mmol) and 0.27 mL of boron trifluoride etherate in 80 mL of anhydrous dichloromethane was added vanadium (V) oxytrifluoride (0.174 g, 1.41 mmol). This mixture stirred at room temperature for 30 min and then was poured over 200mL of 10% citric acid. The organic layer was separated and the aqueous layer was extracted three times with 40 mL CH_2Cl_2. The CH_2Cl_2 layers were combined, washed with water, dried ($MgSO_4$), filtered, and rotary evaporated. The resulting product was passed through a column (silica gel, CH_2Cl_2) under vacuum to yield a deep red solid (0.474 g, 95%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.56 (s, 2H), 6.65 (s, 2H), 3.95-4.35 (m, 8H), 1.20-2.00 (m, 56H), 0.80-1.00 (m, 12H). ^{13}C-NMR ($CDCl_3$) 179.7; 156.1; 148.8; 132.2; 124.6; 114.8; 106.8; 69.8; 69.5; 32.2; 30.7; 29.8; 29.6; 29.6; 29.5; 29.3; 29.2; 29.2; 26.2; 26.1; 25.7; 25.6; 22.8; 22.4; 14.3. Elemental analysis

(%): calc. (found) for $C_{50}H_{80}O_6$. C, 77.27(77.34); H, 10.38(10.17). Melting Point 68-70 °C. MALDI-TOF. calc. (found) 777 (790 M + Na).

2,3-Didecyloxy-6,7-dimethoxy-phenanthrene-9,10-dione (5a) was synthesized from 3,4-didecyloxy-3'4'-dimethoxybenzil (0.30 g, 0.52 mmol) in the manner described above to afford **5a** as a deep red solid (0.289 g, 96%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.62 (s, 2H), 7.02 (s, 2H), 3.95-4.35 (m, 4H), 3.77 (s, 6H), 1.20-2.00 (m, 32H), 0.80-1.00 (m, 6H). ^{13}C-NMR ($CDCl_3$). 173.5, 155.0, 154.4, 151.6, 149.4, 128.6, 128.5, 123.4, 123.4, 114.5, 113.4, 112.6, 110.2, 69.2, 69.2, 69.1, 56.1, 56.0, 55.9, 55.8, 31.8, 29.5, 29.5, 29.3, 29.3, 29.30, 29.0, 29.8, 25.9, 25.9, 25.8, 22.7. Elemental analysis (%): calc. (found) for $C_{36}H_{52}O_6$. C, 74.45(74.77); H, 9.02(8.87). Melting Point 114-117 °C. MALDI-TOF. calc. (found) 549 (572 = M + Na).

2,3-Didecyloxy-6,7-dihexyloxy-phenanthrene-9,10-dione (5b) was synthesized from 3,4-didecyloxy-3'4'- dihexyloxybenzil (1.06 g, 1.47 mmol) in the manner described above to afford **5b** as a deep red solid (1.025 g, 97%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.49 (s, 2H), 7.08 (s, 2H), 4.04-4.19 (m 8H), 1.20-2.00 (m, 48H), 0.80-1.00 (m 12H). ^{13}C-NMR ($CDCl_3$)179.4; 155.7; 149.6; 131.3; 124.6; 113.1; 107.3; 69.7; 69.3; 32.1; 31.7; 29.8; 29.8; 29.6; 29.5; 29.3; 29.3; 29.2; 29.2; 26.2; 26.1; 25.8; 25.8; 22.9; 22.8; 14.3; 14.2. Elemental analysis (%): calc. (found) for $C_{46}H_{72}O_6$. C, 76.62(76.31); H, 10.06(10.26). Melting Point 59-92 °C. MALDI-TOF. calc. (found) 721 (721).

2,3,6,7-Tetrakis-hexyloxyphenanthrene-9,10-dione (5d) was synthesized from 3,3',4,4' tetrakis-hexyloxybenzil (3.00 g, 4.91 mmol) in the manner described above to afford **5f** as a deep red solid (2.87 g, 96%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.49 (s, 2H), 7.07 (s, 2H), 4.16-4.19 (t 4 H J = 6.8 Hz), 4.03-4.06 (t 4H J = 6.8 Hz), 1.20-2.00 (m, 32H), 0.80-1.00 (m 12H). ^{13}C-NMR ($CDCl_3$) 179.3, 155.8, 149.5, 131.2, 124.6, 113.1, 107.2, 69.7, 69.4, 69.3, 69.0, 31.7, 31.6, 29.3, 29.2, 29.1, 25.8, 25.8, 22.8, 14.2. Melting Point 104-106 °C. MALDI-TOF. calc. (found) 608 (609 M+1).

2,3,6,7-Tetrakis-octyloxy-phenanthrene-9,10-dione (5e) was synthesized from 3,3',4,4' tetrakis-octyloxybenzil (1.03 g, 1.42 mmol) in the manner described above to afford **5e** a deep red solid (0.97 g, 94%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.48 (s, 2H), 7.07 (s, 2H), 4.16-4.19 (t 4H J = 6.4 Hz), 4.03-4.06 (t 4H J = 6.4 Hz), 1.20-2.00 (m, 48H), 0.80-1.00 (m 12H). ^{13}C-NMR ($CDCl_3$) 179.4, 155.7, 131.3, 124.6, 113.1, 107.3, 100.9, 86.0, 69.7, 69.4, 69.3, 69.0, 31.7, 31.6, 29.3, 29.2, 29.1, 25.8, 25.8, 22.8, 14.2. Melting Point 98-100 °C. MALDI-TOF. calc. (found) 721 (721).

2,3,6,7-Tetrakis-decyloxyphenanthrene-9,10-dione (5f) was synthesized from 3,3',4,4' tetrakis-decyloxybenzil (3.01 g, 3.59 mmol) in the manner described above to afford **5f** as a deep red solid (2.86 g, 95%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 7.47 (s, 2H), 7.06 (s, 2H), 4.16-4.19 (t 4H J = 6.4 Hz), 4.02-4.05 (t 4H J = 6.4 Hz), 1.20-2.00 (m, 64H), 0.80-1.00 (m 12H). ^{13}C-NMR ($CDCl_3$)) 179.4, 155.7, 149.6, 131.3, 126.3, 113.1, 107.2, 69.7, 69.4, 69.4, 69.3, 32.1, 32.0, 29.8, 29.8, 29.6, 29.6, 29.3, 29.3, 29.1, 26.2, 26.2, 26.1, 25.9, 22.9, 22.8, 22.7, 14.3, 14.2, 14.1. Melting Point 101-103 °C. MALDI-TOF. calc. (found) 833 (833).

6,7-Didecyloxy-10,11-dioctyloxy-dibenzo[f,h]quinoxaline-2,3-dicarbonitrile (6c) A solution of 2,3-didecyloxy-6,7-dioctyloxy-phenanthrene-9,10-dione (0.106 g, 0.137 mmol), diaminomaleonitrile (0.221 g 2.05 mmol) and 20mL AcOH were refluxed for 2 days. Upon cooling, 50 mL of water added and was extracted three times with 40 mL $CHCl_3$. The $CHCl_3$ layers were combined, washed with water, dried ($MgSO_4$), filtered, and rotary evaporated. The resulting brown solid was passed through a short column (silica gel, CH_2Cl_2), and then passed through a longer column (silica gel, 5:1 toluene:hexanes) to yield a yellow solid (0.063 g, 54%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 8.35 (s, 2H), 7.64 (s, 2H), 4.17-4.35 (m, 8H), 1.17-2.24 (m, 56H), 0.78-1.10 (m, 12H). ^{13}C-NMR ($CDCl_3$). 142.3, 142.3, 142.1, 142.0, 128.2, 126.4, 124.1, 122.3, 122.2, 108.7, 108.6, 72.4, 72.4, 72.3, 32.4, 32.1, 32.0, 30.6, 30.6, 30.5, 30.3, 30.3, 30.2, 30.0, 30.0, 29.9, 29.4, 26.6, 26.5, 26.5, 26.5, 23.1, 23.1, 23.0, 14.1, 14.1, 14.1. Elemental analysis (%): calc. (found) for $C_{54}H_{80}N_4O_4$. C, 76.37(76.21); H, 9.50(9.70); N, 6.60(6.21). MALDI-TOF. calc. (found) 829 (829).

6,7-Didecyloxy-10,11-dimethoxy-dibenzo[f,h]quinoxaline-2,3-dicarbonitrile (6a) was synthesized from 2,3-didecyloxy-6,7-dimethoxy-phenanthrene-9,10-dione (0.106 g, 0.137 mmol) in the manner described above to afford **6a** as a yellow solid (0.071 g, 61%). ^{1}H-NMR (CDCl3, TMS) δ(ppm), 8.39 (s, 2H), 7.62 (s, 2H), 4.15-4.35 (m, 4H), 3.76 (s 6H), 1.20-2.20 (m, 32H), 0.80-1.13 (m, 6H). ^{13}C-NMR ($CDCl_3$). 145.3, 145.3, 142.3, 142.1, 128.1, 126.3, 126.2, 125.1, 124.0, 123.1, 114.7, 114.6, 108.9, 108.6, 72.5, 56.1, 56.0, 32.1, 32.1, 30.6, 30.5, 30.2, 30.1, 30.1, 30.1, 30.0, 30.0, 26.8, 26.8, 23.1, 23.0, 14.1, 14.1. Elemental analysis (%): calc. (found) for $C_{50}H_{72}N_4O_4$. C, 73.59(73.38); H, 8.03(8.35); N, 8.58(8.51). Melting point: 264.1° C. MALDI-TOF. calc. (found) 653 (676 M + Na).

6,7-Didecyloxy-10,11-dihexyloxy-dibenzo[f,h]quinoxaline-2,3-dicarbonitrile (6b)
Was synthesised from 2,3-didecyloxy-6,7-dihexyloxy-phenanthrene-9,10-dione (0.113 g, 0.157 mmol) in the manner described above to afford **6b** a yellow solid (0.067 g, 57%). ^{1}H-NMR (CDCl3, TMS) δ(ppm), 8.46 (s, 2H), 7.63 (s, 2H), 4.15-4.35 (m, 8H), 1.20-2.21 (m, 48H), 0.80-1.13 (m, 12H). ^{13}C-NMR ($CDCl_3$). 142.6, 142.6, 142.5, 128.2, 126.4, 126.3, 124.1, 122.2, 114.4, 114.2, 108.6, 73.1, 73.0, 32.5, 32.4, 32.4, 30.6, 30.5, 30.5, 30.2, 30.1, 30.0, 30.0, 30.0, 26.6, 23.2, 23.1, 23.0, 14.1, 14.1, 14.1. Elemental analysis (%): calc. (found) for $C_{50}H_{72}N_4O_4$. C, 75.72(75.78); H, 9.15(9.08); N, 7.06(7.35). MALDI-TOF. calc. (found) 793 (793).

6,7,10,11-Tetrakis-hexyloxy-dibenzo[f,h]quinoxaline-2,3-dicarbonitrile (6d) was synthesized from 2,3,6,7-tetrakis-hexyloxyphenanthrene-9,10-dione (0.200 g, 0.329 mmol) in the manner described above to afford **6d** a yellow solid (0.128 g, 57%).^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 8.37 (s, 2H), 7.55 (s, 2H), 4.17-4.37 (m, 8H), 1.20-2.21 (m, 48H), 0.83-1.10 (m, 12H). ^{13}C-NMR ($CDCl_3$)154.1, 151.0, 141.2, 127.1, 127.1, 120.6, 114.3, 114.2, 107.6, 104.4, 76.9, 69.7, 69.4, 31.8, 31.7, 29.9, 29.3, 29.3, 29.1, 25.9, 25.8, 25.8, 22.8, 22.8, 22.7, 14.2, 14.1. Elemental analysis (%): calc. (found) for $C_{42}H_{56}N_4O_4$. C, 74.08(74.43); H, 8.29(8.53); N, 8.23(8.18). MALDI-TOF. calc. (found) 681 (681).

6,7,10,11-Tetrakis-octyloxy-dibenzo[f,h]quinoxaline-2,3-dicarbonitrile (6e) was synthesized from 2,3,6,7-tetrakis-octyloxyphenanthrene-9,10-dione (0.446 g, 0.618 mmol) in the manner described above to afford **6e** a yellow solid (0.269 g, 55%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 8.31 (s, 2H), 7.56 (s, 2H), 4.09-4.31 (m, 8H), 1.20-2.21 (m, 48H), 0.85-1.08 (m, 12H). ^{13}C-NMR ($CDCl_3$) 153.8, 150.0, 140.9, 128.1, 128.0, 120.8, 114.6, 107.8, 104.9, 76.9, 69.6, 69.4, 32.2, 32.0, 30.0, 29.9, 29.8, 29.7, 29.5, 29.4, 26.4, 26.3, 23.0, 22.9, 14.3. Elemental analysis (%): calc. (found) for $C_{50}H_{72}N_4O_4$. C, 75.72(75.47); H, 9.15(9.12); N, 7.06(7.21). MALDI-TOF. calc. (found) 793 (793).

6,7,10,11-Tetrakis-decyloxy-dibenzo[f,h]quinoxaline-2,3-dicarbonitrile (6f)[6] was synthesized from 2,3,6,7-tetrakis-decyloxyphenanthrene-9,10-dione (0.201 g, 0.240 mmol) in the manner described above to afford **6f** as a yellow solid (0.122 g, 56%). ^{1}H-NMR ($CDCl_3$, TMS) δ(ppm), 8.51 (s, 2H), 7.72 (s, 2H), 4.10-4.32 (m, 8H), 1.21-2.22 (m, 64H), 0.81-1.11 (m, 12H). ^{13}C-NMR ($CDCl_3$). 155.7, 149.6, 131.3, 124.6, 113.1, 113.1, 107.3, 32.1, 31.7, 29.8, 29.8, 29.6, 29.6, 29.5, 29.3, 29.3, 29.2, 29.2, 26.2, 26.2, 25.8, 25.8, 22.9, 22.8, 14.3, 14.2. Elemental analysis (%): calc. (found) for $C_{55}H_{88}N_4O_4$. C, 76.95(76.84); H, 9.80(10.12); N, 6.19(5.89). MALDI-TOF. calc. (found) 905 (905).

Figure S1a. Polarized optical micrograph of compound **6c** (200x) at 230° C.

Figure S1b. Polarized optical micrograph of compound **6b** (200x) at 210º C.

Figure S1c. Polarized optical micrograph of compound **6e** (200x) at 250º C.

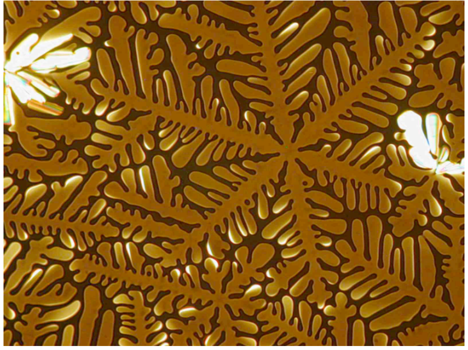
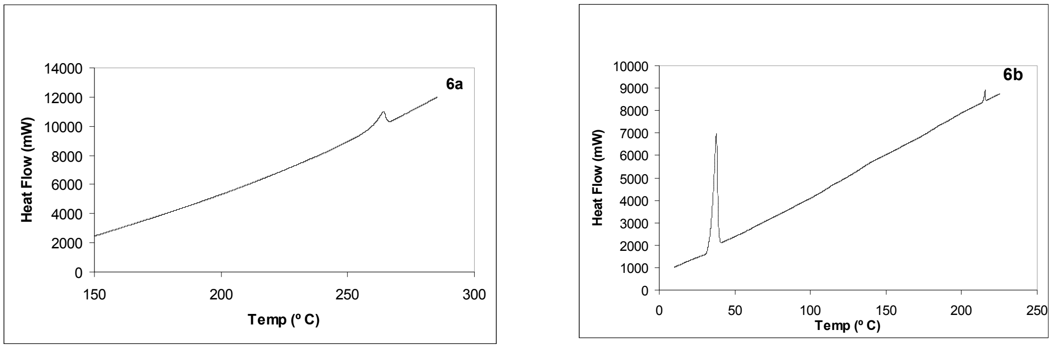
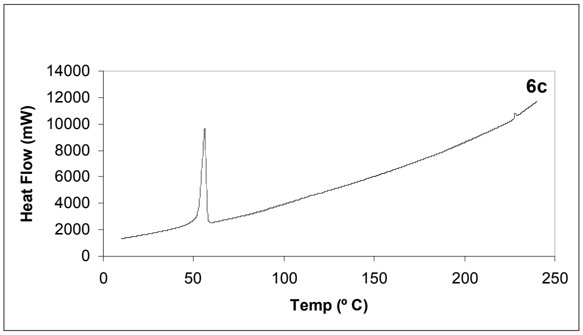
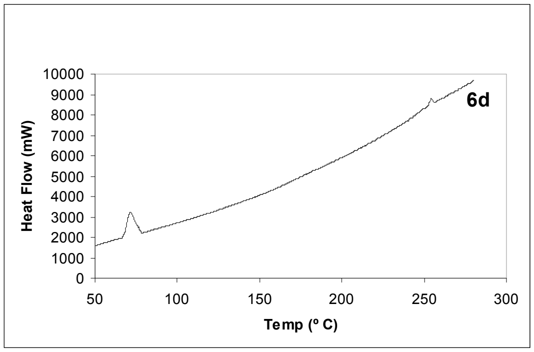
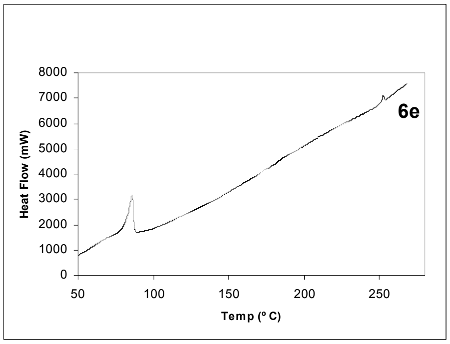


Figure S2. DSC endotherms of compounds **6a-f**. Scan rate=5º C/min. First heating scans shown.









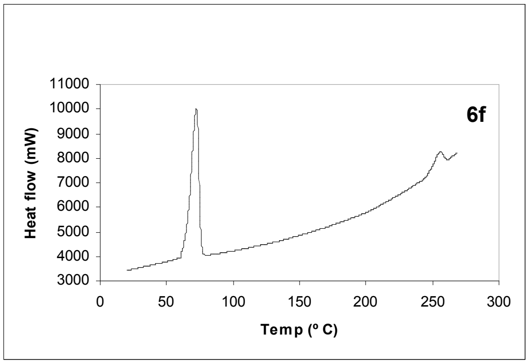
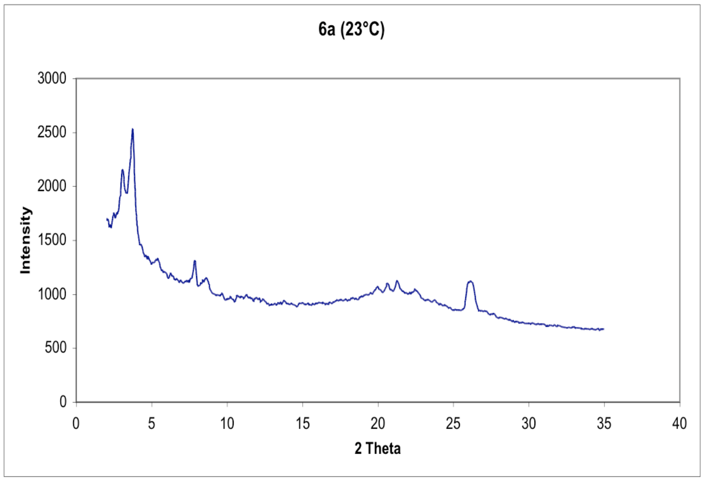
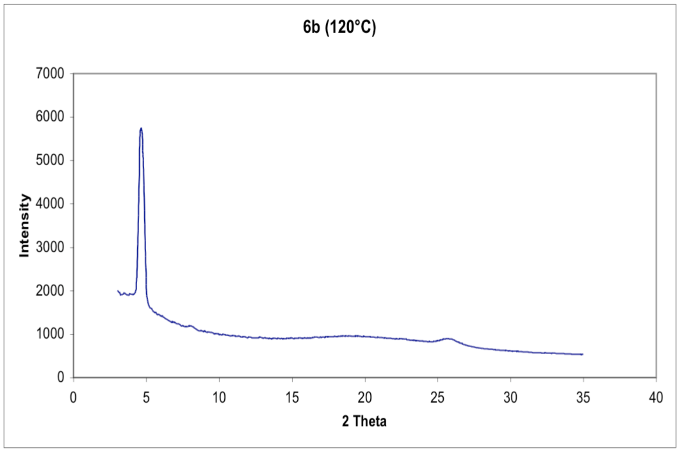


Figure S3. XRD patterns of compounds **6a**-**f**.




6b (120°C)
Intensity
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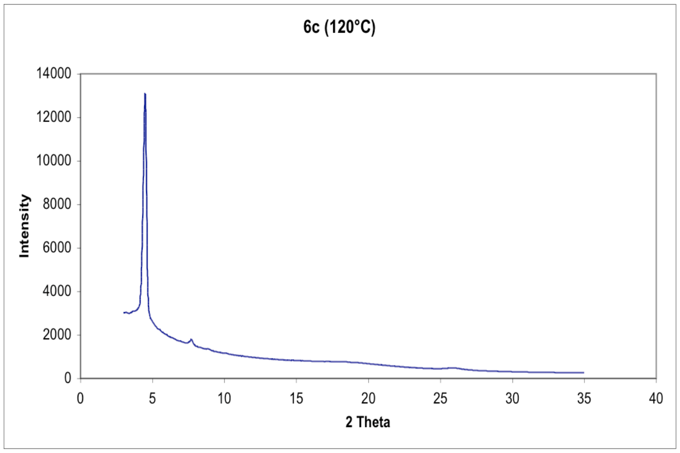
6000
5000
4000
3000
2000
1000
0
0
5
10
15
20
25
30
35
40
2 Theta


6c (120°C)
Intensity
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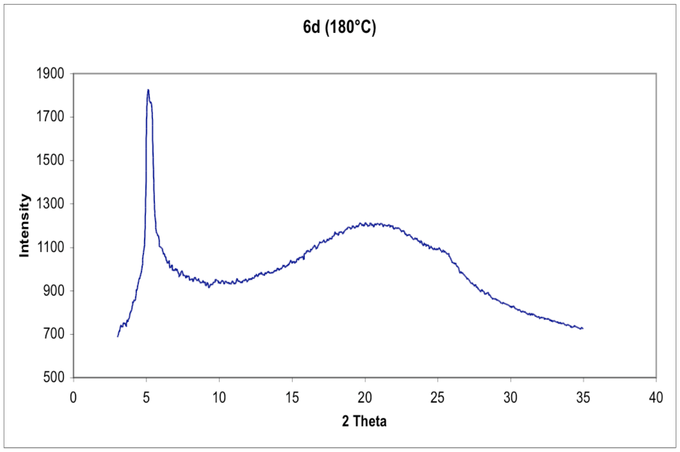
8000
6000
4000
2000
0
0
5
10
15
20
25
30
35
40
2 Theta


6d (180°C)
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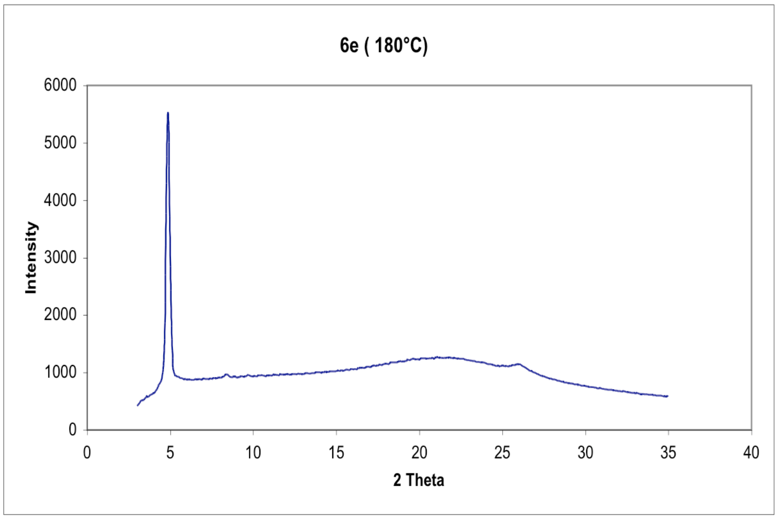
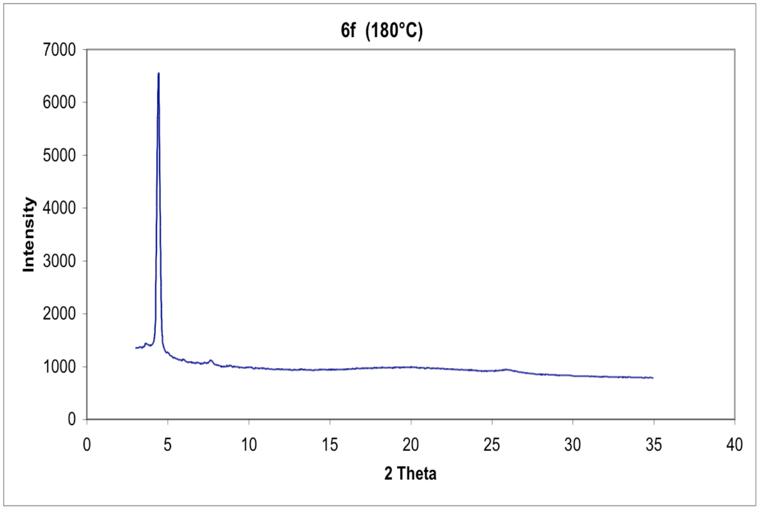
1300
1100
900
700
500
0
5
10
15
20
25
30
35
40
2 Theta





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