Supplementary Material

Experimental

^{1}H NMR spectra were acquired using either a Bruker AMX-400 400 MHz NMR or a Bruker WP100SY 100 MHz spectrometer. ^{13}C NMR spectra were acquired using a Bruker AMX-400 100 MHz spectrometer. Electron impact (70 eV) and chemical ionization (isobutane) mass spectra were obtained using a Hewlett Packard 5985 mass spectrometer. MALDI-TOF mass spectra were obtained on 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 the matrix. IR spectra were obtained using a Thermo Nicolet Nexus 670 FT-IR E.S.P. spectrometer. Melting points were determined with a Fisher-Johns apparatus and uncorrected. Liquid Secondary Ion Mass Spectrometry (HRMS(LSIMS)) were obtained on a Kratos Concept H double focusing mass spectrometer was using *m*-nitro benzyl alcohol as a matrix and polyethylene glycol as a calibrant. Polarized optical microscopy was carried out using an Olympus BX50 microscope with crossed polarizers using a Linkam LTS350 heating stage. Differential scanning calorimetry was carried out on a PerkinElmer DSC7. X-Ray studies were carried out on a Rigaku R-Axis Rapid diffractometer equipped with a temperature controller. All elemental analyses were carried out at Simon Fraser University my Mr. Miki Yang.

2,3-Didecyloxynapthalene (2). 2,3-Dihydroxynaphthalene (2.00 g, 12.5 mmol), 1-bromodecane (11.2 g, 50.8 mmol), and 75 mL of N,N-dimethylformamide were combined and purged under N_2 for 1 hour. K_2CO_3 (17.6 g, 127 mmol) was added and the sample was stirred for 44 hours at 125 °C under nitrogen. The sample was poured over ice (600 g). The sample was then collected by vacuum filtration, washed thoroughly with water, and dried. The product was purified by column chromatography using silica gel and hexanes, 32:1 hexanes:EtOAc, and 16:1 hexanes:ethyl acetate as eluents. The product was obtained as a white solid (5.11 g, 11.6 mmol, 93 %). mp 57-58 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.674 (dd, J = 6.0, 3.3 Hz, 2H), 7.324 (dd, J 6.2, 3.2 Hz, 2H), 7.134 (s, 2H), 4.120 (t, J = 6.6 Hz, 4H), 1.919 (m, 4H), 1.303-1.582 (m, 28H), 0.906 (t, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.45, 129.24, 126.20, 123.90, 107.83, 68.83, 31.94, 29.66, 29.61, 29.46, 29.38, 29.12, 26.10, 22.71, 14.13; MS (MALDI-TOF, 2,5-dihydroxybenzoic acid): m/z 464 ($M^{\bullet+}$+Na), 440 ($M^{\bullet+}$). Anal. Calcd for $C_{30}H_{48}O_2$: C, 81.76; H, 10.98. Found: C, 81.40; H, 11.12.

1,4-Dibromo-2,3-didecyloxynapthalene (3). Bromine (1.20 mL, 23.3 mmol) was added to 2,3-didecyloxynapthalene (2.00 g, 4.53 mmol) and 250 mL of acetic acid. The sample was stirred at RT for 18 hours. The sample was poured into ice (1 kg) and collected by filtration. The product was obtained as a white solid (2.65 g, 4.43 mmol, 98 %). mp 46-47 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.236 (dd, J = 6.4, 3.3 Hz, 2H), 7.543 (dd, J = 6.3, 3.2 Hz, 2H), 4.121 (t, J = 6.7 Hz, 4H), 1.889 (m, 4H), 1.288-1.577 (m, 28H), 0.894 (t, J = 6.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.06, 130.12, 127.23, 126.91, 116.38, 74.43, 31.91, 30.29, 29.65, 29.61, 29.51, 29.35, 26.10, 22.69, 14.12; MS (MALDI-TOF, 2,5-dihydroxybenzoic acid): m/z 598 ($M^{\bullet+}$). Anal. Calcd for $C_{30}H_{46}O_2Br_2$: C, 60.20; H, 7.75. Found: C, 60.07; H, 7.72.

2,3-Didecyloxy-1,4-dimethylnapthalene (4). 1,4-Dibromo-2,3-didecyloxynapthalene (1.00 g, 1.67 mmol) in dry Et_2O (20 mL) was added to a solution of 1.6 M *n*-butyl lithium in hexanes (3.2 mL, 5.12 mmol) in dry Et_2O (20 mL) at –78 °C in a dry ice bath. The sample was stirred at –78 °C for 1 hour. Methyl iodide (0.9 mL, 14.4 mmol) was added, and the sample was allowed to warm slowly to RT and then stirred for 42 hours. The sample was diluted with $CHCl_3$ (100 mL), washed once with H_2O (50 mL), dried over $MgSO_4$, and the solvent evaporated. The sample was purified using a short plug of silica gel and hexanes as an eluent to give a clear, colorless oil (0.729 g, 1.55 mmol, 93 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.922 (dd, J = 6.4, 3.3 Hz, 2H), 7.440 (dd, J = 6.4, 3.3 Hz, 2H), 3.977 (t, J = 6.8 Hz, 4H), 2.578 (s, 6H), 1.830 (m, 4H), 1.286-1.551 (m, 28H), 0.892 (t, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.51, 130.66, 124.47, 124.32, 123.96, 73.84, 31.89, 30.46, 29.64, 29.58, 29.32, 26.23, 22.66, 14.07, 11.31; MS (CI, isobutane): m/z (%) 467 (6), 468 (22), 469 ($M^{\bullet+}$+1, 100), 470 (32), 471 (1). Anal. Calcd for $C_{32}H_{52}O_2$: C, 81.99; H, 11.18. Found: C, 81.93; H, 11.22.

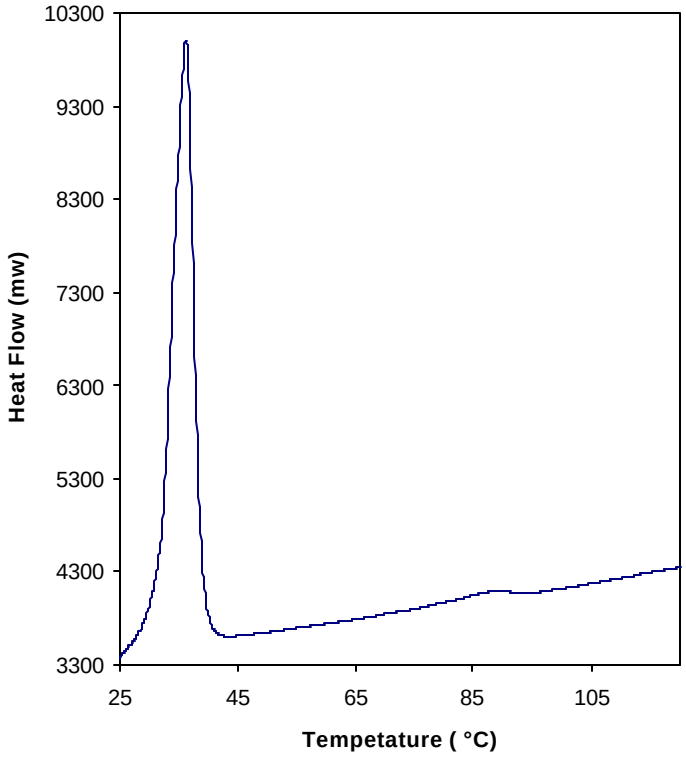
6,7-Dibromo-2,3-didecyloxy-1,4-dimethylnapthalene (5). Bromine (1.6 mL, 31.0 mmol) was added to a solution of 2,3-didecyloxy-1,4-dimethylnapthalene(1.44 g, 3.08 mmol) in CH_2Cl_2 (100 mL), and the solution was stirred at RT for two hours. The sample was washed with 10 % NaOH (2 × 100 mL), dried over $MgSO_4$, and the solvent evaporated. The resulting oil was redissolved in dimethylsulfoxide (25 mL) and purged under N_2 for 40 minutes. $NaBH_4$ (0.0603 g, 1.59 mmol) was added, and the solution was stirred at 49 °C for 64 hours. The sample was placed in an ice bath and then 10 % HCl (50 mL) was added dropwise. The mixture was extracted with $CHCl_3$ (3 × 50 mL). The combined $CHCl_3$ extracts were washed with H_2O (4 × 100 mL), dried over $MgSO_4$, and the solvent evaporated to give a yellow oil. The product was purified by column chromatography using a short plug of silica gel and hexanes as the eluent. The product was obtained as a white solid (1.45 g, 2.31 mmol, 75 %). mp 28-30 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.153 (s, 2H), 3.958 (t, J = 6.7 Hz, 4H), 2.503 (s, 6H), 1.890 (m, 4H), 1.280-1.551 (m, 28H), 0.887 (t, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.61, 130.80, 128.01, 123.48, 120.67, 73.87, 31.88, 30.40, 29.63, 29.58, 29.55, 28.32,

26.18, 22.57, 14.08, 11.84; MS (MALDI-TOF, 2,5-dihydroxybenzoic acid): m/z 627 ($M^{\bullet+}$). Anal. Calcd for $C_{32}H_{50}O_2Br_2$: C, 61.34; H, 8.04. Found: C, 61.45; H, 8.24.

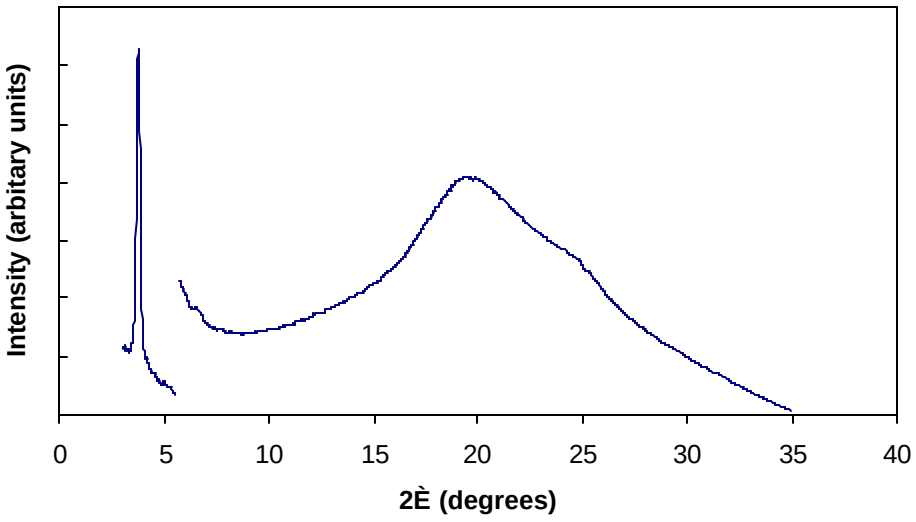
2,3-Didecyloxy-6,7-bis(3',4'-dimethoxyphenyl)-1,4-dimethylnaphthalene (6). 6,7-Dibromo-2,3-didecyloxy-1,4-dimethylnapthalene (0.4754 g, 0.76 mmol), 3,4-dimethoxyphenylboronic acid (0.415 g, 2.28 mmol), tetrakis(triphenylphosphine)palladium(0) (0.0044 g, 3.8 μmol), 2 M Na_2CO_3 in deoxygenated H_2O (14 mL), and deoxygenated 1,2-dimethoxyethane (8 mL) were combined and stirred under nitrogen for 41 hours at 70 °C. The sample was cooled to RT, diluted with H_2O (50 mL), and extracted with $CHCl_3$ (3×50 mL). The combined extracts were dried over $MgSO_4$, and the solvent evaporated. The sample was purified by column chromatography using silica gel and CH_2Cl_2 as an eluent, followed by two successive recrystallizations from ethanol to give the product as the white solid (0.224 g, 0.30 mmol, 40 %). mp 106-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.940 (s, 2H), 6.900 (dd, J = 8.2, 2.0 Hz, 2H), 6.829 (d, J = 8.3 Hz, 2H), 6.666 (d, J = 2.0 Hz, 2H), 4.001 (t, J = 6.7 Hz, 4H), 3.884 (s, 6H), 3.614 (s, 6H), 2.608 (s, 6H), 1.840 (m, 4H), 1.285-1.596 (m, 28H), 0.890 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.54, 149.27, 148.71, 129.05, 126.85, 123.88, 123.75, 120.35, 117.49, 105.10, 104.57, 74.01, 56.03, 56.01, 31.92, 30.54, 29.71, 29.63, 28.38, 26.30, 22.69, 14.11, 11.51; MS (MALDI-TOF, 2,5-dihydroxybenzoic acid): m/z 742 ($M^{\bullet+}$); Anal. Calcd for $C_{48}H_{68}O_6$: C, 77.80; H, 9.25. Found: C, 77.93; H, 9.36.

11,12-Didecyloxy-2,3,6,7-tetramethoxy-10,13-dimethylbenzo[b]triphenylene (1a). $FeCl_3$ (0.295 g, 1.82 mmol) was added to a solution of 2,3-didecyloxy-6,7-bis(3',4'-dimethoxyphenyl)-1,4-dimethylnaphthalene (0.2243 g, 0.30 mmol) in CH_2Cl_2 (50 mL). The sample was stirred at RT for 5 hours. Methanol (25 mL) and then 10 % HCl (50 mL) were added. The sample was extracted three times with $CHCl_3$ (3×50 mL). The combined $CHCl_3$ extracts were washed with 10 % HCl (100 mL), dried over $MgSO_4$, and the solvent evaporated. The sample was purified by column chromatography using silica gel and CH_2Cl_2 as the eluent, followed by two successive recrystallizations from ethanol to give a yellow solid (0.0997 g, 0.13 mmol, 44 %). mp 144-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.822 (s, 2H), 8.006 (s, 2H), 7.632 (s, 2H), 4.134 (s, 6H), 4.092 (s, 6H), 4.059 (t, J = 6.7 Hz, 4H), 2.764 (s, 6H), 1.888 (m, 4H), 1.251-1.593 (m, 28H), 0.895 (t, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.54, 149.27, 148.71, 129.25, 126.35, 123.88, 123.75, 123.35, 117.49, 105.10, 104.57, 74.01, 56.03, 56.01, 31.92, 30.54, 29.70, 29.63, 29.38, 26.30, 22.69, 14.11, 11.51; MS (MALDI-TOF, 2,5-dihydroxybenzoic acid): m/z 740 ($M^{\bullet+}$). Anal. Calcd for $C_{48}H_{66}O_6$: C, 78.01; H, 9.00. Found: C, 77.69; H, 9.05 (V_2O_5 accelerant added).

2,3,6,7,11,12-Hexadecyloxy-10,13-dimethylbenzo[b]triphenylene (1b). Boron tribromide (0.20 mL, 2.12 mmol) was added to a solution of 11,12-didecyloxy-2,3,6,7-tetramethoxy-10,13-dimethylbenzo[b]triphenylene (0.1630 g, 0.22 mmol) in dry CH_2Cl_2 (12 mL) at –78 °C in a dry ice/acetone bath. The sample was allowed to warm slowly to RT and stirred for 18 hours. Ice (12 g) was added and then the sample was collected by vacuum filtration. The crude solid was combined with 1-bromodecane (0.657 g, 2.97 mmol) and N,N-dimethylformamide (12 mL) and purged under N_2 for 50 minutes. K_2CO_3 (1.96 g, 14.2 mmol) was then added and the sample was heated at 109 °C for 5 days. The sample was poured into ice (400 g) and then collected by vacuum filtration. The sample was purified by column chromatography using silica gel and 2:1 hexanes:CH_2Cl_2 as the eluent to give yellow solid (0.116 g, 0.09 mmol, 42 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.918 (s, 2H), 8.164 (s, 2H), 7.805 (s, 2H), 4.285 (t, J = 6.4 Hz, 4H), 4.242 (t, J = 6.4 Hz, 4H), 4.040 (t, J = 6.8 Hz, 4H), 2.785 (s, 6H), 1.251-1.983 (m, 96H), 0.864-0.905 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.70, 149.51, 149.04, 129.31, 126.60, 124.41, 124.11, 123.38, 117.62, 108.33, 107.73, 73.99, 69.78, 69.73, 31.91, 30.52, 29.69, 29.61, 29.53, 29.48, 29.36, 26.29, 26.20, 22.68, 14.09, 11.55; MS (MALDI-TOF, 2,5-dihydroxybenzoic acid): m/z 1244 ($M^{\bullet+}$). MS (LSIMS): Calcd for $C_{84}H_{138}O_6$ m/z 1243.0493($M^{\bullet+}$). Found m/z 1243.0458($M^{\bullet+}$). Anal. Calcd for $C_{84}H_{138}O_6$: C, 81.10; H, 11.18. Found: C, 80.69; H, 11.47 (V_2O_5 accelerant added).



Supplementary Figure 1: DSC curve of the first heating run for compound **1b**.



Supplementary Figure 2: X-Ray diffraction pattern obtained for compound **1b** at 50 °C; composite of wide angle- and low-angle studies shown.