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Novel Peripherally Substituted Indolo[3,2-b]carbazoles for High-mobility Organic Thin-film Transistors**

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1. Measurements

^{1}H NMR spectra were recorded in $CDCl_3$ or DMSO-d6 on a 300 MHz Bruker Spectrospin 300 spectrometer with respectively tetramethylsilane or residual DMSO in DMSO-d6 as internal standard. IR spectra were obtained on a Nicolet Magna-IR 500 Series II spectrophotometer. UV-vis absorption spectra were carried out on a Varian Cary 5 UV-Vis NIR spectrophotometer. Thermal analysis was conducted on TA Instruments DSC 2910 differential scanning calorimeter (DSC) at a heating rate of 5 °C per min under nitrogen atmosphere. Cyclic voltammetric measurements were performed on a BAS 100 voltammetric system with a three-electrode cell in a solution of Bu_4NClO_4 (0.10 M) in dichloromethane at a scanning rate of 40 mV/s. X-ray diffraction was recorded at room temperature on a Rigaku MiniFlex Diffractometer using Cu Kα radiation (λ 1.5418 Å) with a θ-2θ scans configuration. OTFTs were characterized using Keithley SCS-4200 characterization system in ambient conditions.

2. Synthesis

5,11-Didodecylindolo[3,2-b]carbazole 2a. A freshly prepared 50% aq. NaOH solution (20 mL) was added to a well-stirred mixture of indolo[3,2-b]carbazole **1a** (2.56 g, 10 mmol) [as prepared according to published procedure in Robinson, B. *J. Chem. Soc.* **1963**, 3097], benzyltriethylammonium chloride (0.46 g, 2 mmol), 1-bromododecane (7.48 g, 30 mmol), and DMSO (100 mL) in a 250-mL flask under an argon atmosphere. The mixture was stirred at room temperature for 2.5 h and then at 65 °C for 4 h. After the reaction, the mixture was cooled down to room temperature and poured into 400 mL of stirring methanol. The precipitated yellow solid was filtered, washed 3 times each with water, DMF, methanol, and acetone. The yellow solid was then dissolved in hexane and passed through a silica gel column. The yellow solid obtained after removal of hexane was recrystallized from DMF and then from hexane to give 4.35 g (77.3 %) of reasonably pure **2a,** which was subject to train sublimation to obtain electrically pure material for OTFT fabrication.

DSC showed a melting point at 95 °C.

^{1}H NMR ($CDCl_3$): δ 8.20 (d, *J* = 7.7 Hz, 2H), 8.01 (s, 2H), 7.39 – 7.50 (m, 4H), 7.19 – 7.24 (m, 2H), 4.40 (t, *J* = 7.3 Hz, 4H), 1.95 (pent, *J* = 7.3 Hz, 4H), 1.25 – 1.50 (m, 36H), 0.86 (t, *J* = 6.6 Hz, 6H).

IR (NaCl): 2954, 2922, 2847, 1510, 1466, 735 cm^{-1}.

2,8-Dichloroindolo[3,2-b]carbazole 1b. To a well-stirred suspension of 4-chlorophenylhydrazine hydrochloride (24.5 g, 0.137 mol) in ethanol (200 mL) in a 500-mL flask was added a solution of sodium acetate trihydrate (56.34 g, 0.414 mol) in water (100 mL), and the resultant mixture was stirred for 15 min at room temperature. Subsequently, a solution of 1,4-cyclohexandione (7.67 g, 68.4 mmol) in ethanol (50 mL) was added, followed by addition of 50 mL of acetic acid. The reaction mixture was heated at 50 °C for 1 h before cooling down to 0 °C and maintained there for 1 h. The precipitated light yellow crude cyclohexane-1,4-dione bis[(4-chlorophenyl)hydrazone] was filtered, washed with water, air-dried, and added in small portions to a mixture of acetic acid (75 mL) and sulfuric acid (15 mL, 98%) in a 1-L flask with stirring at 10 °C over a period of 10 min, and then allowed to warm to 25 °C and stirred for 10 min. Subsequently, the mixture was heated to about 65 °C until reaction occurred, and further

stirred at 65 °C for 15 min before cooling down to and stirred at room temperature overnight. The product was filtered, washed with methanol and water, and then stirred in 200 mL of boiling methanol for 30 minutes , filtered, and dried in vacuo at 50 °C for 5 h to give 4.26 g (22.8 %) of 2,8-dichloroindolo[3,2-b]carbazole **1b** which was pure enough for subsequent preparation of 2,8-dichloro-5,11-didodecylindolo[3,2-b]carbazole **2b**.

^{1}H NMR (DMSO-*d*6): 11.34 (s, 2H), 8.33 (d, J =1.9 Hz, 2H), 8.21 (s, 2H), 7.46 (d, J = 8.6 Hz, 2H), 7.38 (dd, J_1 = 8.6 Hz, J_2 = 1.9 Hz, 2H).

***2,8-Dichloro-5,11-didodecylindolo[3,2-b]carbazole 2b*.** 50% aq. NaOH solution (4 mL) was added to a well-stirred mixture of 2,8-dichloroindolo[3,2-b]carbazole (0.65 g, 2 mmol), benzyltriethylammonium chloride (90 mg, 0.4 mmol), and 1-bromododecane (1.99 g, 8 mmol) in DMSO (20 mL) in a 100-mL flask, and the resultant mixture was stirred at room temperature for 1 h and then at 50 °C for 4 h. Subsequently, the mixture was poured into MeOH (200 mL), and the precipitated yellow solid was filtered and washed 3 times each with water, DMF, methanol, and acetone, yielding 1.16 g (88.0%) of 2,8-dichloro-5,11-didodecylindolo[3,2-b]carbazole **2b** after drying in vacuo. It was then subject to train sublimation to obtain electrically pure samples for OTFT fabrication.

DSC showed two endotherms at 128 °C and 155 °C on heating.

^{1}H NMR ($CDCl_3$): δ 8.15 (d, J = 1.9 Hz, 2H), 7.94 (s, 2H), 7.43 (dd, J_1 = 8.6 Hz, J_2 = 1.9 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 4.38 (t, J = 7.2 Hz, 4H), 1.92 (pent, J = 7.2 Hz, 4H), 1.30 – 1.50 (m, 36 H), 0.87 (t, J = 6.8 Hz, 6H).

IR (NaCl): 2947, 2920, 2846, 1513, 1464, 1440, 1316, 1127, 1068, 847, 787, 726 cm^{-1}.

***3,9-Dichloroindolo[3,2-b]carbazole 1c*.** This compound was synthesized using the same procedure as described for the preparation of 2,8-dichloroindolo[3,2-b]carbazole, starting from 3-chlorophenylhydrazine hydrochloride instead of 4-chlorophenylhydrazine hydrochloride. The crude product after double Fischer indolization was found to contain about 20% isomeric by-products. It was purified by recrystallization 3 times from DMF to yield 2.01 g (8.8 %) of light yellow product after drying in vacuo at 50 °C for 5 h and was used in the subsequent preparation of 3,9-dichloro-5,11-didodecylindolo[3,2-b]carbazole **2c**.

^{1}H NMR (DMSO-*d*6): 11.39 (s, 2H), 8.23 (d, J = 8.3 Hz, 2H), 8.16 (s, 2H), 7.48 (s, 2H), 7.14 (d, J = 8.3 Hz, 2H).

***3,9-Dichloro-5,11-didodecylindolo[3,2-b]carbazole 2c*.** This compound was synthesized in about 97 % yield using the same procedure as described for the preparation of 2,8-dichloro-5,11-didodecylindolo[3,2-b]carbazole **2b** using 3,9-dichloroindolo[3,2-b]carbazole **1c** as a starting material. Electronically pure samples of **2c** suitable for OTFT fabrication were obtained by train sublimation.

DSC showed a melting point at 161 °C.

^{1}H NMR ($CDCl_3$): 8.08 (d, J = 8.3 Hz, 2H), 7.94 (s, 2H), 7.38 (d, J = 1.5 Hz, 2H), 7.18 (dd, J_1 = 1.5 Hz, J_2 = 8.3 Hz, 2H), 4.34 (t, J = 7.2 Hz, 4H), 1.93 (pent, J = 7.2 Hz, 4H), 1.20 – 1.50 (m, 36 H), 0.87 (t, J = 6.6 Hz, 6H).

IR (NaCl): 2947, 2921, 2846, 1462, 845, 784 cm^{-1}.

***2,8-Dibromoindolo[3,2-b]carbazole 1d*.** This compound was synthesized in about 24% yield using the same procedure as described for the preparation of 2,8-dichloroindolo[3,2-b]carbazole **1b**, starting from 4-bromophenylhydrazine hydrochloride (22.4 g, 0.10 mol) and 1,4-cyclohexanedione (5.61 g, 0.05 mol).

^{1}H NMR (DMSO-*d*6): 11.34 (s, 2H), 8.46 (s, 2H), 8.21 (s, 2H), 7.50 (dd, J_1 = 8.6 Hz, J_2 = 1.5 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H).

***2,8-Dibromo-5,11-didodecylinodolo[3,2-b]carbazol 2d*.** This compound was synthesized in about 85 % yield using the same procedure as described for the preparation of 2,8-dichloro-5,11-didodecylindolo[3,2-b]carbazole **2b** using 2,8-dibromoindolo[3,2-

b]carbazole **1d** (2.07 g, 5 mmol) as the starting material. Attempted purification by train sublimation led to decomposition.

DSC showed two endotherms at 128 °C and 159 °C on heating.

^{1}H NMR ($CDCl_3$): δ 8.31 (d, J = 1.9 Hz, 2H), 7.95 (s, 2H), 7.55 (dd, J_1 = 8.7 Hz, J_2 = 1.9 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 4.36 (t, J = 7.2 Hz, 4H), 1.92 (pent, J = 7.2 Hz, 4H), 1.30 – 1.50 (m, 36 H), 0.87 (t, J = 6.7 Hz, 6H).

IR (NaCl): 2947, 2921, 2846, 1462, 846, 784, 719 cm^{-1}.

***3,9-Dibromoindolo[3,2-b]carbazole 1e*.** This compound was synthesized in 7.5% yield using the same procedure as described for the preparation of 3,9-dichloroindolo[3,2-b]carbazole **1c**, starting from 3-bromophenylhydrazine hydrochloride (25.58 g, 0.114 mol) and 1,4-cyclohexanedione (6.42 g, 0.057 mol).

^{1}H NMR (DMSO-*d*6): 11.25 (s, 2H), 8.18 (d, J = 8.2 Hz, 2H), 8.17 (s, 2H), 7.63 (s, 2H), 7.27 (d, J = 8.3 Hz, 2H).

***3,9-Dibromo-5,11-didodecylindolo[3,2-b]carbazole 2e*.** This compound was synthesized in 95 % yield using the same procedure as described for the synthesis of 2,8-dichloro-5,11-didodecylindolo[3,2-b]carbazole **2b** using 3,9-dibromoindolo[3,2-b]carbazole **1e** (1.59 g, 3.85 mmol) as a starting material. Attempted purification by train sublimation led to decomposition.

DSC showed a melting point at 170 °C.

^{1}H NMR ($CDCl_3$): 8.03 (d, J = 8.2 Hz, 2H), 7.95 (s, 2H), 7.54 (d, J = 1.4 Hz, 2H), 7.32 (dd, J_1 = 1.4 Hz, J_2 = 8.2 Hz, 2H), 4.34 (t, J = 7.2 Hz, 4H), 1.93 (pent, J = 7.2 Hz, 4H), 1.20 – 1.50 (m, 36 H), 0.87 (t, J = 6.6 Hz, 6H).

IR (NaCl): 2944, 2918, 2849, 1602, 1508, 1466, 1436, 1285, 1115, 912, 841, 808, 798 cm^{-1}.

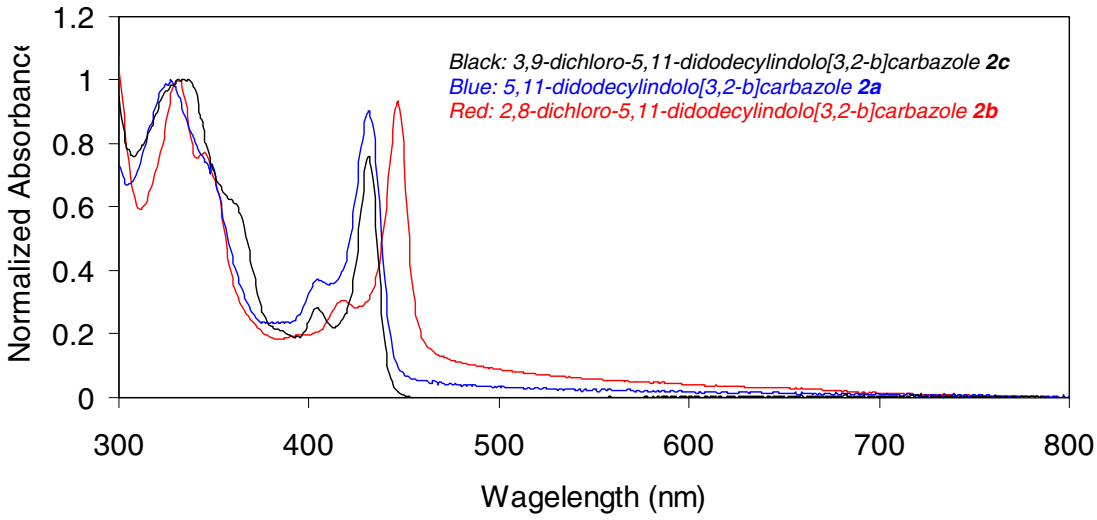

Figure 4. Thin-film UV-vis spectra of 5,11-didodecylindolo[3,2-b]carbazole **2**.

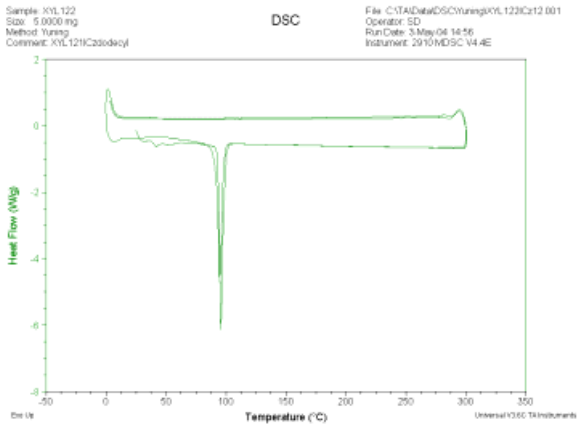

Figure 5. DSC curves (1st and 2nd scans) of 5,11-didodecylindolo[3,2-b]carbazole **2a**.

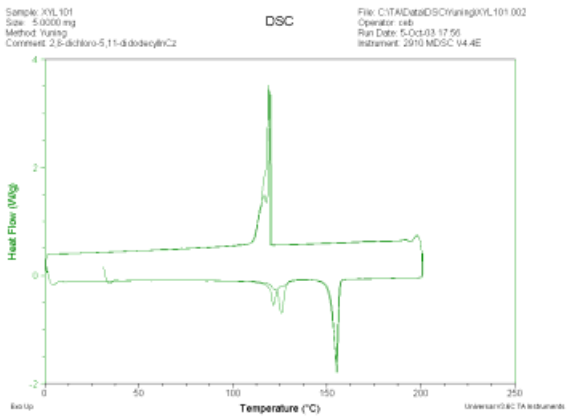

Figure 6. DSC curves (1st and 2nd scans) of 2,8-dichloro-5,11-didodecylindolo[3,2-b]carbazole **2b**.

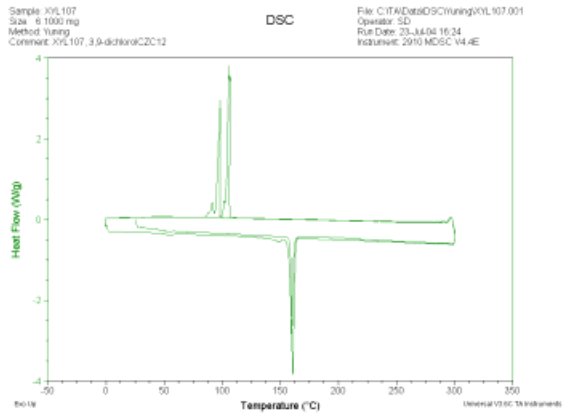

Figure 7. DSC curves (1st and 2nd scans) of 3,9-dichloro-5,11-didodecylindolo[3,2-b]carbazole **2c**.