Supporting Information

Indolo[3,2-b]carbazole-based Thin-film Transistors with High Mobility and Stability

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Experimental Section

1. Measurements

^{1}H NMR spectra were recorded in $CDCl_3$ on a 300 MHz Bruker Spectrospin 300 spectrometer with tetramethylsilane as an 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. AFM experiments were performed with a NT-MDT Solver P47 scanning probe microscope operated in the tapping mode under ambient conditions. 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. Materials Synthesis

All reagents were used as received from Sigma-Aldrich. 5,11-Dihydridoindolo[3,2-b]carbazole, **2**, was synthesized by double Fischer indolization starting from phenylhydrazine and 1,4-cyclohexanedione according to the literature.[11]

5,11-Dioctylindolo[3,2-b]carbazole 1a. A freshly prepared 50% aq. NaOH solution (4 mL) was added to a well-stirred mixture of 5,11-dihydridoindolo[3,2-b]carbazole, **2** (0.513 g, 2 mmol), benzyltriethylammonium chloride (0.09 g, 0.4 mmol), 1-bromooctane (1.55 g, 8 mmol), and DMSO (20 mL) in a 100-mL flask under an argon atmosphere. The mixture was stirred at room temperature for 2.5 h and then heated to 65 °C and maintained at this temperature for 4 h. Subsequently the reaction mixture was cooled down to room temperature and poured into 200 mL methanol with stirring. The precipitated yellow solid was filtered off and washed with water, and 3 times each with *N,N*-dimethylformamide, methanol, and acetone. The yellow solid was purified by column chromatography on silica gel using hexane as eluent. Recrystallization from hexane yielded 0.867 g (90.1 %) of 5,11-dioctylindolo[3,2-b]carbazole, **1a**, which was subject to train sublimation to obtain electrically pure material for OTFT fabrication. DSC showed two endotherms at 84 °C and 101 °C on heating. ^{1}H NMR ($CDCl_3$): δ 8.21 (d, J = 7.6 Hz, 2H), 8.01 (s, 2H), 7.47 (dd, J_1 = 7.0 Hz, J_2 = 0.9 Hz, 2H), 7.41 (d, J = 7.6 Hz, 2H), 7.21 (dd, J_1 = 7.0 Hz, J_2 = 0.9 Hz, 2H), 4.40 (t, J = 7.3 Hz, 4H), 1.95 (pent, J = 7.3 Hz, 4H), 1.25 – 1.50 (m, 20H), 0.86 (m, 6H); IR (NaCl): 3050, 2952, 2921, 2852, 1510, 1469, 1482, 1326, 737 cm^{-1}.

5,11-Bis(4-octylphenyl)indolo[3,2-b]carbazole 1b. The reagent, 1-iodo-4-octylbenzene which was used in the condensation reaction was obtained as follows. A mixture of 1-phenyloctane (14.87 g, 78.13 mmol), iodine (7.93 g, 31.25 mmol), H_5IO_6 (3.56 g, 15.63 mmol), acetic acid (40 mL), deionized water (7 mL), and 98% sulfuric acid (2.59 g) in a 100 mL flask was heated at 80 °C for about 3 h until the purple iodine color disappeared. The reaction mixture was extracted with dichloromethane, neutralized with saturated aq. $NaHCO_3$, and washed three times with water. The organic layer was separated, dried over $MgSO_4$, filtered, and the solvent was removed using a rotary evaporator. After column chromatography on silica gel using hexane, 22.53 g of a colorless viscous liquid was obtained; ^{1}H NMR indicated that the crude product was a mixture of 1-iodo-4-octylbenzene (69%), 1-iodo-2-octylbenzene (24%), and unreacted 1-phenyloctane (7%). This crude product was used in subsequent preparation of 5,11-bis(4-octylphenyl)indolo[3,2-b]carbazole, **1b**, without complications. ^{1}H NMR data for 1-iodo-4-octylbenzene ($CDCl_3$): δ 7.54 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 8.2 Hz, 2H), 2.53 (t, J = 7.7 Hz, 2H), 1.55 (m, 2H), 1.20 – 1.40 (m, 10H), 0.88(t, J = 6.9 Hz, 3H).

A mixture of 5,11-dihydridoindolo[3,2-b]carbazole, **2** (3.00 g, 11.7 mmol), 18-crown-6 (0.62 g, 2.34 mmol), K_2CO_3 (12.94 g, 93.6 mmol), 1-iodo-4-octylbenzene (16.09 g, 35.1 mmol, 69% of purity) as prepared above, copper (2.97 g, 46.8 mmol), and 1,2-dichlorobenzene (50 mL) was charged into an argon-filled 200 mL flask fitted with a condenser. The mixture was heated under reflux in an argon atmosphere for 24 h. Subsequently, the reaction mixture was cooled down to room temperature, diluted with tetrahydrofuran, and filtered. A viscous liquid, obtained after removal of solvent using a rotary evaporator, was added to 400 mL of methanol with vigorous stirring. The precipitated yellow solid was filtered, washed several times with water and methanol, dissolved in 400 mL of hexane by heating, and filtered to remove the insoluble impurities. The filtrate was concentrated to about 50 mL and allowed to cool down to room temperature, and then chilled at 0 °C overnight. The crystallized yellow product was filtered, washed with a small amount of hexane, and dried to yield 5.32 g of 5,11-bis(4-octylphenyl)indolo[3,2-b]carbazole, **1b**, which was subject to train sublimation to obtain electrically pure compound for OTFT fabrication. DSC showed a melting point at 131 °C on first heating. ^{1}H NMR ($CDCl_3$): δ 8.12 (d, J = 7.6 Hz, 2H), 8.05 (s, 2H), 7.58 (d, J = 8.3 Hz, 4H), 7.47 (d, J = 8.3 Hz, 4H), 7.39 – 7.40 (m, 4H), 7.19 – 7.21 (m, 2H), 2.78 (t, J = 7.8 Hz, 4H), 1.78 (pent, J = 7.4 Hz, 4H), 1.30 – 1.50 (m, 20H), 0.92 (m, 6H); IR (NaCl): 3047, 2956, 2923, 2852, 1517, 1451, 1324, 1236, 842, 731 cm^{-1}.

5,11-Bis(4-methylphenyl)indolo[3,2-b]carbazole 1c. A mixture of 5,11-dihydridoindolo[3,2-b]carbazole, **2** (2.56 g, 10 mmol), 18-crown-6 (0.52 g, 2.0 mmol), K_2CO_3 (11.06 g, 80 mmol), 4-

iodotoluene (6.54 g, 30 mmol), copper (2.54 g, 40 mmol), and 1,2-dichlorobenzene (40 mL) was charged into an argon-filled 200 mL flask fitted with a condenser. The mixture was heated under reflux in an argon atmosphere for 24 h. Subsequently, the reaction mixture was cooled down to room temperature, diluted with toluene, and filtered. The solid was stirred in 50 mL of DMF and 50 mL of 2N HCl was added drop-wise and the mixture was stirred for 30 min. The yellow suspension was decanted and filtered to give a yellow solid. The solid was then stirred in a mixture of DMSO (200 mL) and 20% NaOH (50 mL) for 30 min and then filtered. The solid was washed with deionized water, methanol, and dried to yield 1.65 g of 5,11-bis(4-methylphenyl)indolo[3,2-b]carbazole, which was subject to train sublimation to obtain electrically pure compound for OTFT fabrication. DSC showed two endotherms at 305 °C and 322 °C on first heating. ^{1}H NMR ($CDCl_3$): δ 8.11 (d, *J* = 7.8 Hz, 2H), 8.04 (s, 2H), 7.57 (d, *J* = 8.3 Hz, 4H), 7.48 (d, *J* = 8.3 Hz, 4H), 7.39 (d, *J* = 3.7 Hz, 4H), 7.21 (m, 2H), 2.54 (s, 6H); IR (NaCl): 3034, 2916, 1606, 1515, 1451, 1323, 1235, 1191, 819, 741 cm^{-1}.

3. Device Fabrication and Evaluation

Experimental bottom-gate OTFT devices were built on an n-doped silicon wafer as the gate electrode with a 100-nm thermal silicon oxide (SiO_2) as the dielectric layer. The SiO_2 surface was first modified with a self-assembled monolayer (SAM) of octyltrichlorosilane (OTS-8) by immersing a clean wafer substrate in 0.1 M OTS-8 solution in toluene at 60 °C for 20 min. The OTS-8 SAM was used to direct and facilitate molecular self-organization during semiconductor deposition. A 100-nm thick semiconductor layer of **1** was deposited on the OTS-8-treated substrate by vacuum evaporation at a rate of 2 Å/s. Since **1** has very good solubility in common organic solvents, a solution-processed semiconductor layer of **1** was also prepared by spin coating its 1.0 wt% solution in chlorobenzene on the substrate at a spin rate of 1000 rpm for 30 s, followed by drying in a vacuum oven for 1 hour. Subsequently, gold source-drain electrode pairs were deposited on the semiconductor layer through a shadow mask, thus creating a series of OTFTs with various channel lengths (L) and widths (W). Patterned transistors with channel length of 90 or 190 μm and channel width of 1 or 5 mm were used for

I-V measurements. The devices were then stored in ambient conditions under amber light to study their stability characteristics.

The mobility in the linear and saturated regimes was extracted from the following equations:

Linear regime ($V_D << V_G$): $I_D = V_D C_i \mu (V_G-V_T) W/L$

Saturated regime ($V_D > V_G$): $I_D = C_i \mu (W/2L) (V_G-V_T)^2$

where I_D is the drain current, C_i is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are respectively the gate voltage and threshold voltage. V_T of the device was determined from the relationship between the square root of I_D at the saturated regime and V_G of the device by extrapolating the measured data to $I_D = 0$.