New thiophene substituted isoindigo based copolymer for high performing ambipolar transistors

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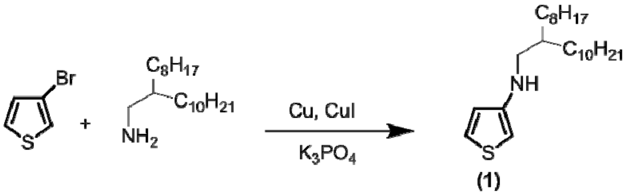
Experimental Section

All chemicals were purchased from commercial suppliers unless otherwise specified. ^{1}H NMR and ^{13}C NMR spectra were recorded on BRUKER 400 spectrometer in $CDCl_3$ or DMSO-d_6 solution at 298 K. Number-average (Mn) and weight-average (Mw) were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. Electrospray mass spectrometry was performed with a Thermo Electron Corporation DSQII mass spectrometer. UV-vis spectra were recorded on a UV-1601 Shimadzu Uv-vis spectrometer. Column chromatography was carried out on silica gel (for flash chromatography, VWR). Cyclic voltammograms (CV) were obtained using a cylindrical platinum working electrode and a platinum mesh counter electrode in acetonitrile at a potential scan rate of 0.1 $V \cdot s^{-1}$. Ag/Ag$^+$ was used as reference electrode and calibrated against ferrocene. All the measurements were carried out in an argon-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) in anhydrous acetonitrile. X-ray diffraction (XRD) measurements were carried out with a PANALYTICAL X'PERT-PRO MRD diffractometer equipped with a nickel-filtered Cu Kα_1 beam and a X' CELERATOR detector, using a current of 40 mA and an accelerating voltage of 40 kV.

FETs Measurements

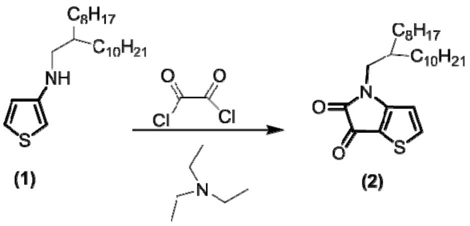
Polymer IGT-BT FETs were characterized by using the top-gate/bottom-contact (TGBC) configuration. Specifically, the gold source and drain bottom electrodes (with Cr as the adhesion layer) were patterned by photolithography on clean low-sodium glass substrates. A layer of IGT-BT was then deposited on top by spin coating a polymer solution in anhydrous 1,2-dichlorobenzene (10 mg/mL) at a speed of 1500 rpm for 60 s. For as-spun FETs, solvent drying was performed at 80 °C for more than two hours. For annealed FETs, after solvent drying samples were further placed on a hotplate (preheated to the annealing temperature) for 30 minutes before cooling down to room temperature. Subsequently, a PMMA solution (45 mg/mL in *n*-butyl acetate) was then spin-coated onto the semiconducting polymer resulting in a dielectric layer of ~500 nm thick. Gate electrodes comprising a layer of gold (20-nm-thick) were then evaporated through a shadow mask onto the dielectric layer by thermal evaporation. Starting from the step of making the semiconductor polymer solution to the final step of FET measurements, all procedures/measurements were carried out inside a dry nitrogen glove box. Mobility values quoted in the text are averaged over typically 5-10 individual devices prepared under the same conditions.

Synthesis of N-(2-octyldodecyl)thiophen-3-amine (1):



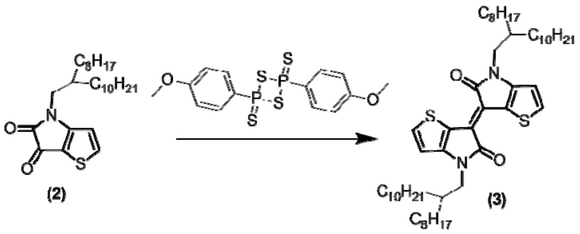
3-bromothiophene (2.87 ml, 30.7 mmol), 2-octyldodecan-1-amine (13.69 g, 46.0 mmol), copper (0.097 g, 1.533 mmol), copper(I) iodide (0.292 g, 1.533 mmol) and Potassium phosphate tribasic (13.02 g, 61.3 mmol) were stirred in 50 mL of dimethyl aminoethanol at 80 ^{0}C for 48 h. The mixture is filtered and solvent removed by vacuum. The crude product was then purified by chromatography over silica gel (2.5% EtOAc/hexanes).Yield of N-(2-octyldodecyl)thiophen-3-amine (1) was about 35%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm: 7.18 (dd, 1H), 6.65 (dd, 1H), 5.95 (m, 1H), 3.61 (s, 1H), 3.01 (d, 2H), 1.63 (m, 1H), 1.30-1.35 (bm, 32H), 0.92 (m, 6H) ^{13}C NMR ($CDCl_3$): δ/ppm: 149.14, 124.99, 119.95, 94.79, 49.90, 37.84, 32.23, 31.94, 30.09, 29.67, 29.37, 26.82, 22.71, 14.14. TOF MS ES+(*m/e*): 380.33 (M^+, 100%).

Synthesis of 4-(2-octyldodecyl)-4*H*-thieno[3,2-*b*]pyrrole-5,6-dione (2):



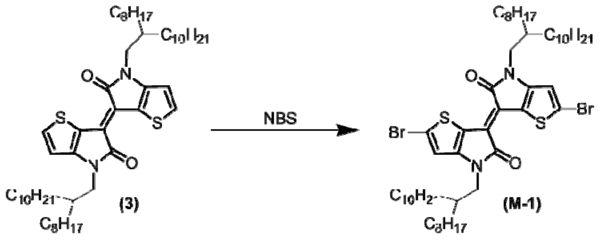
N-(2-octyldodecyl)thiophen-3-amine (3 g, 7.90 mmol) in 10 mL of DCM was added dropwise to oxalyl dichloride (0.9 ml, 10.64 mmol) in 20 mL of DCM at 0 ^{0}C. After 30 minutes, triethylamine (5 ml, 35.9 mmol) in 5 mL of DCM was added dropwise and stirred overnight at room temperature. Solvents were removed under vacuum and crude product was purified by chromatography on silica gel in hexane : ethyl acetate mixture. 4-(2-octyldodecyl)-4*H*-thieno[3,2-*b*]pyrrole-5,6-dione (2) was obtained as red oil in 40 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm: 8.00 (d, 1H), 6.78 (d, 1H), 3.61 (d, 2H), 1.79 (m, 1H), 1.26-1.33 (bm, 32H), 0.89 (m, 6H) ^{13}C NMR ($CDCl_3$): δ/ppm: 172.99, 165.54, 161.76, 143.75, 113.13, 111.07, 46.48, 37.00, 31.91, 31.86, 31.40, 29.91, 29.61, 29.56, 29.51, 29.33, 26.37, 22.68, 14.12. TOF MS ES+(*m/e*): 434.31 (M^+, 100%).

Synthesis of (*E*)-4,4'-bis(2-octyldodecyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (3):



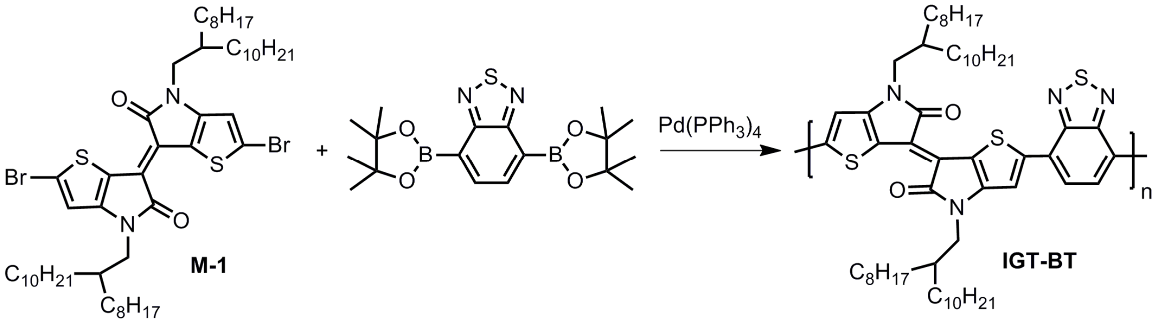
A solution of 4-(2-octyldodecyl)-4*H*-thieno[3,2-b]pyrrole-5,6-dione (1.17 g, 2.70 mmol) and Lawesson's Reagent (0.546 g, 1.349 mmol) in 15 mL *o*-xylene were stirred at 60 ^{0}C for 2h. Progress of reaction was monitored by TLC and change in colour (from red to violet blue). The reaction mixture was then cooled down to room temperature. After removal of solvent, the crude product was purified by chromatography on silica gel in hexane : DCM mixture.Yield 35 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm: δ/ppm: 7.55 (d, 2H), 6.81 (d, 2H), 3.71 (d, 4H), 1.91 (m, 2H), 1.25-1.34 (bm, 64H), 0.89 (m, 12H) ^{13}C NMR ($CDCl_3$): δ/ppm: 171.33, 151.57, 134.22, 121.08, 114.25, 111.36, 46.16, 31.88, 31.48, 29.95, 29.63, 29.57, 29.52, 29.35, 29.28, 26.42, 22.67, 14.12. TOF MS ES+(*m/e*): 834.61 (M^+, 100%).

Synthesis of (*E*)-2,2'-dibromo-4,4'-bis(2-octyldodecyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (M-1):



To an ice cold solution of (*E*)-4,4'-bis(2-octyldodecyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (0.410 g, 0.491 mmol) in 15 mL THF, NBS (0.188 g, 1.055 mmol) in THF(1 mL) was added drop wise over 30 minutes. The reaction progress was monitored by TLC. After completion, reaction was quenched by addition of water (10 mL), dichloromethane (50 mL) was added and organic layer separated. The organic layer was washed with water (2 x 10 mL), brine (10 mL) and dried over $MgSO_4$. After removal of solvent, the crude product was purified by chromatography on silica gel using hexane and DCM as eluent. After removal of solvent, the crude product was purified by chromatography on silica gel in hexane : DCM mixture. Obtained blue solid was further purified by washing with methanol. Yield 70 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm: 6.84 (s, 2H), 3.66 (d, 4H), 1.86 (m, 2H), 1.27-1.35 (bm, 64H), 0.89 (m, 12H) ^{13}C NMR ($CDCl_3$): δ/ppm: 170.43, 150.21, 123.15, 119.73, 114.98, 114.72, 46.18, 37.19, 31.88, 31.39, 29.95, 29.64, 29.57, 29.52, 29.35, 29.30, 28.35, 22.68, 14.12. TOF LD+(*m/e*): 993 (M^+, 100%).

Synthesis of polymer P-1:



Degassed toluene (1.5 ml), aqueous sodium carbonate (0.3 ml, , 1M) and 2 drops of Aliquat 336 were added to (*E*)-2,2'-dibromo-4,4'-bis(2-octyldodecyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (0.050 g, 0.050 mmol) **(M-1)**, 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (0.020 g, 0.050 mmol) and Pd(PPh3)4 (1.164 mg, 1.007 µmol). The solution was thoroughly degassed under Argon, and then the Argon inlet was removed and the reaction heated for 72 h at 120 °C (oil bath temperature). After cooling to RT, the polymer was precipitated into methanol (100 mL), and filtered through a Soxhlet thimble. The polymer was extracted (Soxhlet) with methanol, acetone, hexane and, chloroform. The chloroform solution was concentrated and precipitated into methanol, and the precipitates were filtered and dried under vacuum to get **IGT-BT**, as a black solid. Obtained polymer was dried under high vacuum for 24h. Yield (0.035 g, 70%). GPC (chlorobenzene, 80 ^oC): Mn = 40000 g/mol, Mw = 90000 g/mol; λ_{max} (film) = 1035 nm.

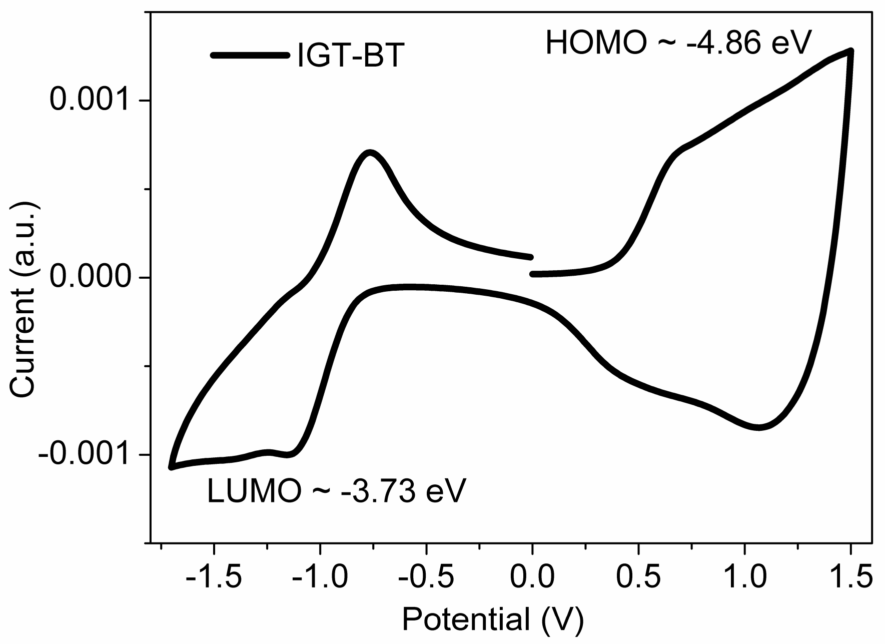


Figure S1. Cyclic voltammogram of **IGT-BT** in CH_3CN/0.1 M $[nBu_4N]^+[PF_6]$ at 0.1V s^{-1}.

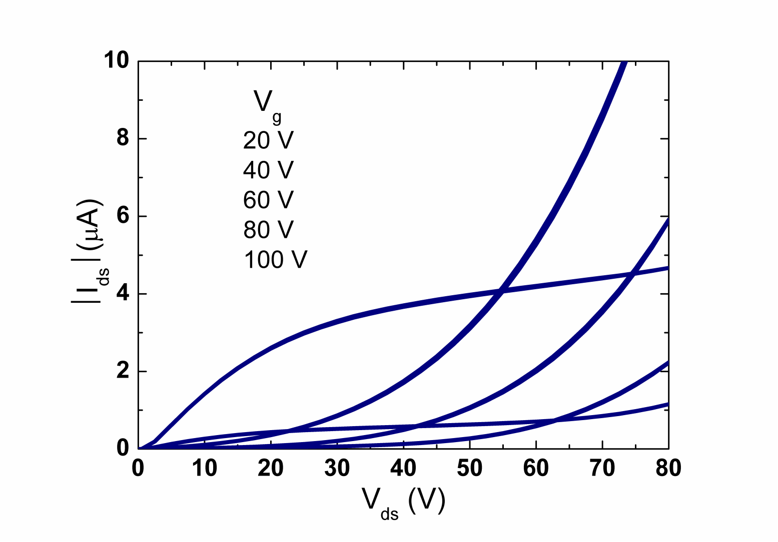


Figure S2. Output characteristics at positive source-drain bias of an ambipolar transistor, *L* = 20 μm, *W* = 1000 μm, based on **IGT-BT** annealed at 300 °C.