Electronic Supplementary Information

Acceptor-Acceptor Type Isoindigo-Based Copolymers for High-Performance *n*-Channel Field-Effect Transistors

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Table of Contents

Experimental Section

Materials and Instruments: 6-Bromooxindole was purchased from CAPOT chemical company, 6-bromoisatin was purchased from TCI and other chemicals and solvent were purchased either from Aldrich or Acros and used without further purification. 6,6'-Dibromoisoindigo, 6,6'-(*N,N'*-2-octyldodecyl)-dibromoisoindigo (**M1**), were synthesized according to the literature.[1, 2] ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VNRS 600 MHz (Varian USA) spectrophotometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard and MALDI MS spectra were obtained from Ultraflex III (Bruker, Germany). UV-VIS-NIR spectra were taken on UV-1800 (SHIMADZU) spectrometer. Number-average (M_n) and weight average (M_w) molecular weights, and polydispersity index (PDI) of the polymer products were determined by gel permeation chromatography (GPC) with Perkin-Elmer Series 200 using a series of mono disperse polystyrene as standards in THF (HPLC grade) at 313 K. Preparative GPC (pre-GPC) was performed on FUTECS HPLC System NS-4000 with Shodex GPC K-2004 column using a chloroform (HPLC grade) at 298 K. Cyclic voltammetry (CV) measurements were performed on AMETEK VersaSTAT 3 with a three-electrode cell in a nitrogen bubbled 0.1 M tetra-*n*-butylammonium hexafluorophosphate (n-Bu_4NPF_6) solution in acetonitrile at a scan rate of 50 mV/s at room temperature. A used as the Ag/Ag^+ (0.1 M of $AgNO_3$ in acetonitrile) reference electrode, platinum counter electrode and polymer coated platinum working electrode respectively. The Ag/Ag^+ reference electrode was calibrated using a ferrocene/ferrocenium redox couple as an external standard, whose oxidation potential is set at –4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation: $\mathrm{HOMO} = -(E_{ox}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$ eV. The LUMO levels of polymers were obtained from the equation: $\mathrm{LUMO} = -(E_{red}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$ eV. Tapping-mode atomic force microscopy (AFM) measurements were performed using an Agilent 5500 scanning probe microscope (SPM) running with a Nanoscope V controller. The Rigaku high power X-ray diffractometer was used (D/MAZX 2500V/PC) to observe out-of-plane molecular packing in polymer films. X-ray diffraction (XRD) patterns were recorded under an X-ray power of 40 kV and a scan rate of 1 ^{o}/min.

Synthesis of 6,6'-(*N,N'*-2-octyldodecyl)-Pinacoldiboronisoindigo (3): 6,6'-(*N,N'*-2-octyldodecyl)-dibromoisoindigo (2 g, 2.04 mmol), bis(pinacolato)diboron (2.07 g, 8.16 mmol), potassium acetate (1.2 g, 12.24 mmol), and PdCl$_2$(dppf) (90 mg, 0.12 mmol) in anhydrous 1,4-dioxane (20 mL) were stirred at 80 °C for 2 d. The reaction was quenched by water and extracted with methylene chloride. The separated organic layer was washed with water and brine, then dried over MgSO$_4$ and removed under reduced pressure. The crude product was purified by column chromatography (silica gel, hexane to 50% methylene chloride in hexane) to afford 1.7 g (78%) of **3** as red-brown solid. ^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm) 9.14 (d, 2H, *J*= 7.8 Hz), 7.48 (d, 2H, *J*= 7.8 Hz), 7.15 (s, 2H), 3.69 (d, 4H, *J*= 6.2 Hz), 1.95 (m, 2H), 1.40-1.26 (m, 88H), 0.87-0.84 (t, 12H, *J*= 6.6 Hz). ^{13}C NMR (150 MHz, CDCl$_3$) δ (ppm) 168.24, 144.61, 134.46, 129.01, 128.86, 124.38, 113.64, 84.18, 44.60, 36.26, 32.07, 32.05, 31.73, 30.16, 29.79, 29.78, 29.74, 29.50, 29.46, 26.57, 25.02, 22.83, 22.82, 14.27. Elemental Analysis: C, 75.96; H, 10.50; N, 2.61; O, 8.93 Found: C, 75.97; H, 10.52; N, 2.61; O, 8.85. MALDI-TOF-MS *m/z*: $[M]^{+\bullet}$ = 1076.24; calcd, 1075.25.

PIIG-BT: In a Schlenk flask, 6,6'-(*N,N'*-2-octyldodecyl)-dibromoisoindigo (**2**) (200 mg, 0.204 mmol) and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (79 mg, 0.204 mmol) was dissolved in toluene (7 mL), to this a solution of K$_3$PO$_4$ (217 mg, 1.02 mmol), tri-*o*-tolylphosphine (3.7 mg, 12.2 μmol) and deionized water (1.5 ml) was added. The mixture was vigorously stirred at room temperature under argon. After 30 min, Pd$_2$(dba)$_3$ (2.8 mg, 3.06 μmol) was added to the reaction mixture and stirred at 90 ^{o}C for 3 days (end capped with phenylboronic acid and bromobenzene). After then, the solution was precipitated in a mixture of methanol and ammonia (4:1 v/v, 250 mL). This was filtered off through paper filter under the vacuum, washed on Soxhlet apparatus with methanol (1d), acetone (1d) and hexane (1d) to remove low molecular weight. Finally, Soxhlet extracted chloroform fraction re-precipitated into methanol and filtered off through 0.45 μm Teflon filter. 170 mg (87%) of the polymer was recovered as a dark-green powder ($M_n = 2.50 \times 10^4$ g/mol, PDI=1.32). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 9.42-9.23 (br, 2H), 7.95-6.28 (br, 8H), 3.96-3.67 (br, 4H), 2.04-1.26 (br, 64H) 0.95-0.85 (br, 12H). Elemental Analysis: C, 77.77; H, 9.68; N, 5.85; O, 3.34; S, 3.35 Found: C, 77.03; H, 9.62; N, 5.74; O, 3.32; S, 3.26.

PIIG-TPD: In a Schlenk flask, 6,6'-(*N,N'*-2-octyldodecyl)-pinacoldiboronisoindigo (**3**) (219 mg, 0.204 mmol) and 1,3-dibromo-5-hexyl-thieno[3,4-c]pyrrole-4,6-dione (81 mg, 0.204 mmol) was dissolved in toluene (7 mL), to this a solution of K_3PO_4 (217 mg, 1.02 mmol), tri-*o*-tolylphosphine (3.7 mg, 12.2 μmol) and deionized water (1.5 ml) was added. The mixture was vigorously stirred at room temperature under argon. After 30 min, $Pd_2(dba)_3$ (2.8 mg, 3.06 μmol) was added to the reaction mixture and stirred at 90 ^{o}C for 3 days (end capped with phenylboronic acid and bromobenzene). After then, the solution was precipitated in a mixture of methanol and ammonia (4:1 v/v, 250 mL). This was filtered off through paper filter under the vacuum, washed on Soxhlet apparatus with methanol (1d), acetone (1d) and hexane (1d) to remove low molecular weight. Finally, Soxhlet extracted chloroform fraction re-precipitated into methanol and filtered off through 0.45 μm Teflon filter. 134 mg (61%) of the polymer was recovered as a black powder ($M_n = 5.71 \times 10^4$ g/mol, PDI=3.30). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 9.27-9.02 (br, 2H), 8.57-8.10 (br, 2H), 7.36-6.65 (br, 2H), 4.14-3.32 (br, 6H) 2.44-0.99 (br, 79H), 0.86-0.70 (br, 15H). Elemental Analysis: C, 77.37; H, 9.92; N, 3.87; O, 5.89; S, 2.95 Found: C, 77.12; H, 9.83; N, 3.74; O, 5.94; S, 2.81.

OFET Fabrication and Measurement: Bottom-gate top-contact OFET devices based on the isoindigo (IIG) copolymers were fabricated on a highly *n*-doped Si substrate with thermally grown 300-nm-thick SiO_2 layer (C_i = 10 $nFcm^{-2}$), where the highly *n*-doped Si and SiO_2 layer were used as the gate electrode and dielectric, respectively. The surface of SiO_2/Si wafer was modified with *n*-octadecyltrimethoxysilane (OTS), as reported previously.[3-5] After cleaning the SiO_2/Si wafers with piranha solution (a 7:3 mixture of H_2SO_4 and H_2O_2), OTS solution (3 mM in trichloroethylene) was spin-coated on the SiO_2/Si substrate at 3000 rpm for 30 s. The OTS-coated wafers were exposed to ammonia vapor in a desiccator for 12 h. Then, the wafers were rinsed with toluene, acetone, and isopropyl alcohol. The contact angle (DI water) on the hydrophobic OTS-modified wafer was typically ~110°.

The IIG-based copolymers (**PIIG-BT** and **PIIG-TPD**) were dissolved in anhydrous chloroform (~3 mg mL^{-1}) and the polymer films were prepared on the OTS-modified SiO_2/Si substrates by drop-casting method. Then, the polymer films were annealed on a hot plate at 150 °C for 30 min under N_2 atmosphere. Gold electrodes (40 nm) were thermally evaporated through a shadow mask with a channel length (L) of 50 μm and width (W) of 1000 μm. The current−voltage characteristics were measured in a N_2-filled glovebox by using a Keithley 4200 semiconductor parametric analyzer. The field-effect mobility was calculated in the saturation regime using the following equation:

$$I_{DS} = \tfrac{1}{2}(W/L)\mu C_i(V_G - V_T)^2$$

where I_{DS} is the drain current, W and L are the semiconductor channel width and length, respectively, μ is the mobility, C_i is the capacitance per unit area of the gate dielectric, and V_G and V_T are the gate voltage and threshold voltage, respectively.

Table S1. Peak assignments for the out-of-plane XRD patterns obtained from IIG-based copolymer thin films

Condition	(00*n*)	**PIIG-BT**		**PIIG-TPD**	
		2θ [°]	*d*-spacing [Å]	2θ [°]	*d*-spacing [Å]
As-cast	(001)	3.86	22.87	3.60	24.52
	(002)	7.64	-	-	-
After annealing at 150 ^{o}C	(001)	3.78	23.36	-	-
	(002)	7.48	-	-	-
	(003)	11.18	-	-	-

Table S2. Detailed electrical parameters of OFET devices for **PIIG-BT** and **PIIG-TPD** films

Condition		μ_{max} [cm^2 V^{-1} s^{-1}]	μ_{avg} [cm^2 V^{-1} s^{-1}]	$I_{\mathrm{on}}/I_{\mathrm{off,\ avg}}$	$V_{\mathrm{T,\ avg}}$[c] [V]
PIIG-BT	As-cast	0.005	0.003 (±0.0009)[a]	1.0×10^{7} ($\pm7.2\times10^{6}$)	48.3 (±3.1)
	150 °C	0.22	0.09 (±0.06)	1.3×10^{7} ($\pm2.3\times10^{7}$)	41.5 (±7.1)
PIIG-TPD	As-cast	0.004	0.003 (±0.01)	2.4×10^{6} ($\pm7.5\times10^{5}$)	10.1 (±3.5)
	150 °C	0.01	0.008 (±0.003)	4.1×10^{6} ($\pm4.4\times10^{6}$)	8.3 (±6.4)
PIIG-TPD[b]	150 °C	0.001	6.0×10^{-4} ($\pm2.0\times10^{-4}$)	6.5×10^{6} ($\pm7.5\times10^{5}$)	27.1 (±5.8)

[a] The standard deviation. [b] The fractionated **PIIG-TPD** (M_{n} = 32.0 kDa, PDI = 1.5).

[c] The relatively higher V_{T} of **PIIG-BT** might originate from the larger injection barrier (due to the higher LUMO level) for electrons with respect to gold electrodes.

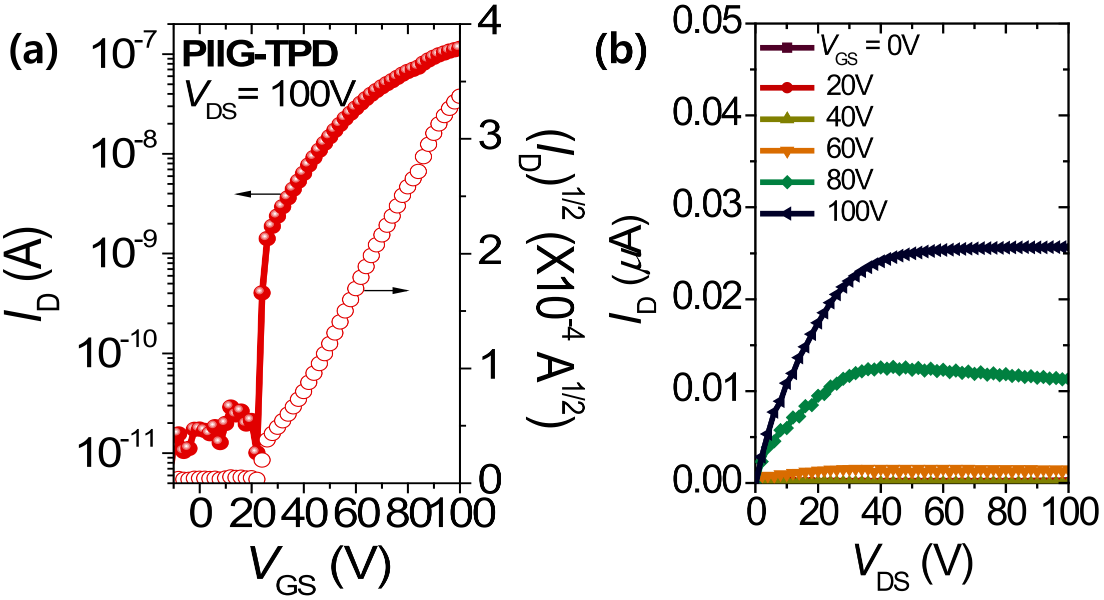

Fig. S1 OFET performance of the fractionated **PIIG-TPD** (M_n = 32.0 kDa, PDI = 1.5) thin films after annealing at 150 °C. (a) Transfer curve at V_{DS} = +100V and (b) output characteristics.

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