

Supporting Information

Synthesis and Characterization of Phenothiazine-Isoindigo Copolymers for Photovoltaic Applications

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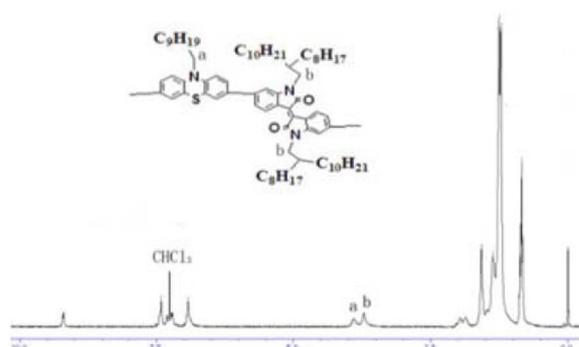
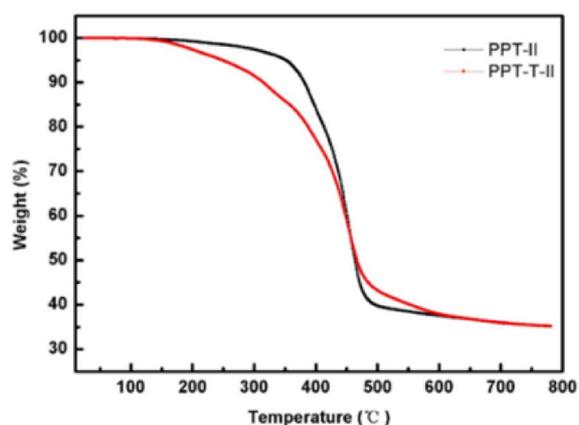
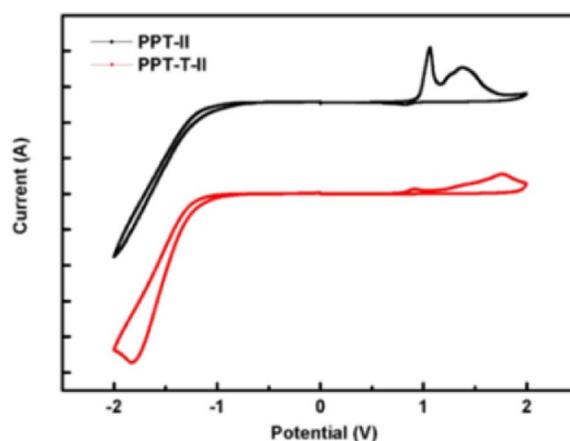
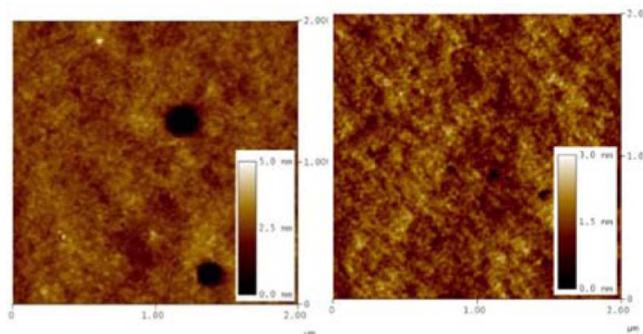
Figure S1. Proton NMR spectrum of PPT-II (CDCl₃).

Figure S2. TGA traces of PPT-II and PPT-T-II.

Measurements. Proton NMR spectra were recorded using a Varian Gemini-300 (400 MHz) spectrometer, with trimethylsilane as reference. The molecular weights of polymers were determined *via* gel permeation chromatography (GPC) with a Viscotec GPC system, using chloroform as eluent. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 2920 at a heating rate of 10 °C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed with a TA Instruments TGA 2950 at a heating rate of 10 °C/min in a nitrogen atmosphere. UV-visible absorption spectra were recorded on a Varian Cary 1

Figure S3. Cyclic voltammograms of PPT-II and PPT-T-II films deposited on ITO glass in an acetonitrile solution of 0.10 M *n*-Bu₄NPF₆ at a scan rate of 50 mV/s.Figure S4. AFM images of PPT-II/PC₇₁BM films: 1:1 (left) and 1:4 (right).

spectrophotometer. Cyclic voltammetry (CV) was performed with a VersaSTAT3 (METEK) for a polymer film deposited on ITO-coated glass, in an acetonitrile solution of 0.1 M *n*-Bu₄NPF₆, at a scan rate of 50 mV/s in an argon atmosphere, using Pt wire and Ag/AgCl as counter and reference electrode, respectively. Thin film X-ray diffraction (XRD) patterns were recorded using an on a PANalytical X-pert diffractometer operating at 30 kV and 20 mA with a Cu K α radiation ($\lambda = 1.5406$ nm) at a step size of 0.03°. The

experimental data were obtained in a scanning interval of 20 between 1 and 90°. The film samples were fabricated by drop-casting on a silicon wafer and dried under vacuum. Atomic force microscopy (AFM) was performed with a MultiMode + BioScope (Digital Instruments) in tapping mode.

6,6'-Dibromo-*N,N'*-(2-octyldodecanyl)-isoindigo (1). 10-Decyl-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazinone and 6,6'-dibromoisoinidigo were prepared *via* the reported procedures.^{1,2}

A solution of 6,6'-dibromoisoinidigo (420 mg, 1.0 mmol) and potassium carbonate (830 mg, 9.52 mmol) in *N,N*-dimethyl formamide (DMF) (20 mL), 1-bromo-2-octyldodecane (0.8 g, 2.2 mmol) was added dropwise under a nitrogen flow. The mixture was stirred for 20 h at 100 °C, cooled to room temperature, transferred to a separatory funnel, extracted with dichloromethane, and then washed with water. The combined organic layer was dried with anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified *via* silica gel chromatography (hexane/dichloromethane = 8/1) to yield compound 1 (420 mg, 43%) ¹H NMR (400 MHz, CDCl₃) δ 0.84 (m, 12H), 1.43-1.20 (m, 64H), 1.93-1.85 (m, 2H), 3.64 (d, 4H), 6.90 (d, 2H), 7.16 (d, 2H), 9.09 (d, 2H). Calc'd: C, 68.6; H, 9.0; N, 2.9. Found: C, 70.3; H, 9.2; N, 2.8.

6,6'-Dithiophen-2-yl-*N,N'*-(2-octyldodecanyl)-isoindigo (2). A solution of compound 1 (420 mg, 0.428 mmol) and 2-(tributylstannyl)thiophene (632 mg, 1.69 mmol) in anhydrous THF was bubbled with nitrogen, followed by the addition of tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃) (31 mg) and tri(*o*-tolyl)phosphine (P(*o*-tol)₃) (21 mg). The resultant mixture was stirred under nitrogen overnight at 85 °C, and then poured into water. The extracted dichloromethane solution was washed with water and dried over anhydrous magnesium sulfate. After removing the solvent under reduced pressure, the residue was purified *via* silica gel chromatography (hexane/dichloromethane = 8/1) to obtain compound 2 (353 mg, 84%) ¹H NMR (400 MHz, CDCl₃) δ 0.87-0.84 (m, 12H), 1.47-1.17 (m, 64H), 1.92 (b, 2H), 3.69 (d, 4H), 6.97 (s, 2H), 7.12 (m, 2H), 7.36-7.29 (m, 4H), 7.42 (d, 2H), 9.15 (d, 2H). Calc'd: C, 77.8; H, 9.6; N, 2.8; S, 6.5. Found: C, 79.3; H, 9.7; N, 2.7; S, 6.0.

6,6'-Bis(5-Bromothiophen-2-yl)-*N,N'*-(2-octyldodecanyl)-isoindigo (3). *N*-bromosuccinimide (133.72 mg, 0.751

mmol) was added to a solution of compound 2 (353 mg, 0.358 mmol) in anhydrous THF in several portions for 4 h (one portion every hour), and the resulting solution was further stirred for 24 h, then poured into a separatory funnel, washed with water, and extracted with chloroform. The resulting chloroform solution was dried over magnesium sulfate, and the residue was purified *via* silica chromatography (hexane/dichloromethane = 4/1) to yield compound 3 as a black solid (290 mg, 71%) ¹H NMR (400 MHz, CDCl₃) δ 0.87-0.83 (m, 12H), 1.35-1.23 (m, 64H), 1.90 (b, 2H), 3.66 (d, 4H), 6.84 (m, 2H), 7.06 (d, 2H), 7.19-7.13 (m, 4H), 9.16 (d, 2H). Calc'd: C, 67.1; H, 8.1; N, 2.5; S, 5.6. Found: C, 68.8; H, 8.2; N, 2.4; S, 5.3.

PPT-II. 10-Decyl-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazinone (219 mg, 0.37 mmol), compound 1 (230 mg, 0.37 mmol), tricyclohexyl phosphine (10.4 mg, 0.037 mmol) and tetrakis(triphenylphosphine)-palladium(0) (Pd(PPh₃)₄) (21.38 mg, 0.019 mmol) were dissolved in degassed toluene (7 mL). When the temperature of the resulting mixture increased slightly to 40 °C, one portion of tetraethylammonium hydroxide (1.2 mL, 20 wt % in water) was injected. The mixture was stirred under an argon flow at 85 °C for 3 days. Bromobenzene was added, followed by the addition of phenylboronic acid for end-capping. After 2 h, the reaction mixture was poured into a cold mixture of methanol and concentrated HCl (10/1, v/v). The reaction mixture was then filtered and purified *via* Soxhlet extraction using methanol, acetone, hexane, and finally, chloroform. The chloroform fraction was concentrated and poured into excess methanol to yield PPT-II as a dark purple solid (180 mg).

PPT-T-II. The same synthetic procedure as that described above for PPT-II was employed for the synthesis of PPT-T-II from 10-decyl-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazinone (140 mg, 0.263 mmol) and compound 3 (270 mg, 0.236 mmol). The purified PPT-T-II was a green powder (60 mg).

References

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