Electronic Supplementary Information

Development of low bandgap polymers for red and near infrared fullerene-free organic photodetectors

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Experimental details

Materials

3-3-dibromo-2,2-bithiophene, (\pm) -2,2'-Bis(diphentylphosphino)-1,1'-binaphthalene, tris(dibenzylideneacetone)dipalladium(0), trimethyltin chloride and all the solvents were purchased from Sigma-Aldrich. Tri(o-tolyl)phosphine was provided by Alfa Aesar. 2-ethylhexyl-1-amine was provided by TCI, 2-ethylhexyl-4,6-dibromo-3fluoroth-ieno[3,4-b] thiophene-2-carboxylate (TT) from Suna Tech Inc. All the chemicals were used as received, without further purification.

Characterization of materials

The ¹H nuclear magnetic resonance spectra were recorded at 25 °C with a Bruker Ascend TM-400 spectrometer. The absorption spectra were measured by a Shimadzu UV-2550 UV–visible spectrophotometer. The cyclic voltammetry measurments were conducted at a scan rate of 30 mV/s by using a BASi 100B/W electrochemical analyzer with a three-electrode cell and a 0.1 N Bu₄NBF₄ solution in acetonitrile as the electrolyte; the working electrode was coated with the polymer films by dipping into their solutions in chloroform. All the measurements were calibrated against an internal standard of ferrocene (Fc), whose ionization potential is -4.8 eV for the Fc/Fc⁺ redox system. The gel permeation chromatography analysis was conducted with a Waters Breeze 2 system at room temperature by using chloroform as the eluent.

Device Characterization

The absorption spectrum of active layer was measured by SCINCO Mega-800 UV/VIS spectrometer. The atomic force microscopy (AFM, SII SPA400) in tapping mode was used to

obtain the morphology and RMS roughness of active layer. The cross-sectional images of the devices were obtained by field emission scanning electron microscopy (FE-SEM) (JEOL JSM-7410F, JEOL Ltd.). The current density-voltage (J-V) characteristics were measured using a Keithley 2602B source meter under 680 nm red LED (Thorlabs, M680L4). The light intensity was calibrated by using a standard photodiode power sensor (Thorlabs, S120C). The EQE spectrum was obtained by passing a 400 W xenon lamplight through a mono-chromator using a filter of appropriate wavelength (Newport, QUANTX-300). The chopping frequency (i.e., 100 Hz) was measured from 350 to 1200 nm.



Fig. S1. ¹H NMR of *4-(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (2)*



Fig. S2. ¹H NMR of (4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6diyl)bis(trimethylstannane) (4)



Fig. S3. Gel permeation chromatogram of Poly[(4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)-alt-(2-ethylhexyl-3-fluorothieno[3,4-b]thiophene-2-carboxylate 4,6-diyl)] (PDTPTT)



Fig. S4. Gel permeation chromatogram of Poly[(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl)-alt-(2-ethylhexyl-3-fluorothieno[3,4-b]thiophene-2-carboxylate 4,6-diyl)] (PCPDTTT)



Fig. S5. ¹H nuclear magnetic resonance spectrum of PDTPTT



Fig. S6. ¹H nuclear magnetic resonance spectrum of PCPDTTT



Fig. S7. Topographic AFM images of blended (a) PDTPTT:IDIC and (b) PCPDTTT:IDIC films.



Fig. S8. Cross-sectional SEM images of blended (a) PDTPTT:IDIC and (b) PCPDTTT:IDIC films.



Fig. S9. *J-V* characteristics of the PCPDTTT:IDIC devices on (a) bare ZnO layer and (b) 0.1 wt% PEIE treated ZnO layer as a function of flux under 680 nm red LED illumination.

| Polymer film | Contact angle (θ) | |
|--------------|--------------------------|-------|
| | Isopropanol | Water |
| PCPDTTT | 8.4 | 91.8 |
| PDTPTT | 3.4 | 93.5 |
| IDIC | 8.2 | 83.4 |

Table S1. Wetting angle measurement on pristine PDTPTT, PCPDTTT and IDIC films by

 water or isopropyl alcohol

Table S2. Calculated interfacial energy (γ_{SL}) between PCPDTTT, PDTPTT, IDIC and chloroform.

| Interfacial Energy | $\gamma_{ij} (mJ/m^2)$ |
|----------------------------------|------------------------|
| PDTPTT ↔ IDIC | 1.91 |
| PCPDTTT ↔ IDIC | 1.25 |
| $PCPDTTT \leftrightarrow CHCl_3$ | 1.394 |
| $PDTPTT \leftrightarrow CHCl_3$ | 0.862 |
| $IDIC \leftrightarrow CHCl_3$ | 5.128 |