Supporting Informaiton

Synthesis and Photovoltiaic Properties of 2D-Conjugated Copolymer Based on Benzodithiophene with Alkylthio-selenophene Side Chains

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I Measurements.

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker arx-400 spectrometer. UV-vis absorption spectra were acquired on a Cary 60 UV-visible spectrophotometer by Agilent Technologies. The thermo-gravimetric analyses (TGA) was carried out on a TA Instruments, Inc., discovery instrument under purified nitrogen gas flow with a 10 °C min^{-1} heating rate. GPC measurement was performed on Agilent Technologies, PL-GPC 220 High Temperature Chromatograph using 1,2,4-trichlorobenzene as the eluent at 160 ^{o}C. The electrochemical cyclic voltammetry was conducted on a Zahner Ennium Electrochemical Workstation with glassy carbon disk, Pt wire, and Ag/Ag^{+} electrodes as working electrode, counter electrode, and reference electrode respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution at a scan rate of 50 mV/s. Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 S-Twin instrument at 200 kV accelerating voltage. Atomic force microscope (AFM) was performed using a Veeco Dimension 3100 instrument.

II Fabrication and characterization of PSCs.

Polymer solar cells (PSCs) with the structure of ITO/PEDOT: PSS/**PBDTSe-S-TT**: $PC_{71}BM$/Mg/Al were fabricated under the conditions as follows: patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10-15 ohm/square was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After oxygen

plasma cleaning for 10 min, a 30 nm thick poly(3, 4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-cast onto the ITO substrate and then dried by baking in an oven at 150 ^{o}C for 15 min. The active layer was then deposited on top of the PEDOT: PSS layer by spin-coating from a 10 mg/ml chlorobenzene solution of **PBDTSe-S-TT** and $PC_{71}BM$. The thickness of the active layer was controlled by changing the spin speed during the spin-coating process and measured on an Ambios Tech. XP-2 profilometer. Finally, 20 nm Mg and 80 nm Al layer were successively deposited in vacuum onto the active layer at a pressure of ca. 4×10^{-4} Pa. The overlapping area between the cathode and anode defined a pixel size of 4 mm^2. Except for the deposition of the PEDOT: PSS layers, all the fabrication processes were carried out inside a dry box containing less than 5 ppm oxygen and moisture.

The current density-voltage (*J-V*) characteristics of the PSCs were measured with a Keithley 236 Source Measure unit, under the illumination of AM 1.5G, 100 mW/cm^2 using a xenon-lamp- based solar simulator (SAN-EI ELECTRIC CO., LTD.). The external quantum efficiency (EQE) was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology CO., Ltd.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

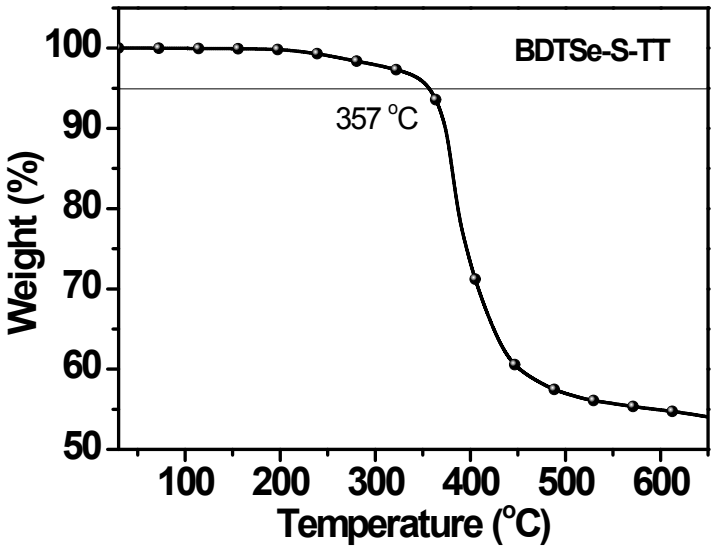

Figure S1. TGA plot of **PBDTSe-S-TT** with a heating rate of 10 °C/min under nitrogen atmosphere.

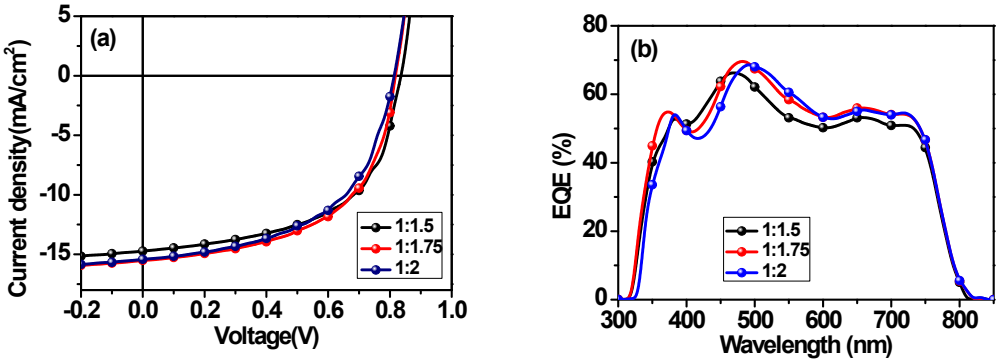

Figure S2 (a) *J*–*V* characteristics and (b) EQE curves of devices based on **PBDTSe-S-TT**: $PC_{71}BM$ blend film with different D/A weight ratio.

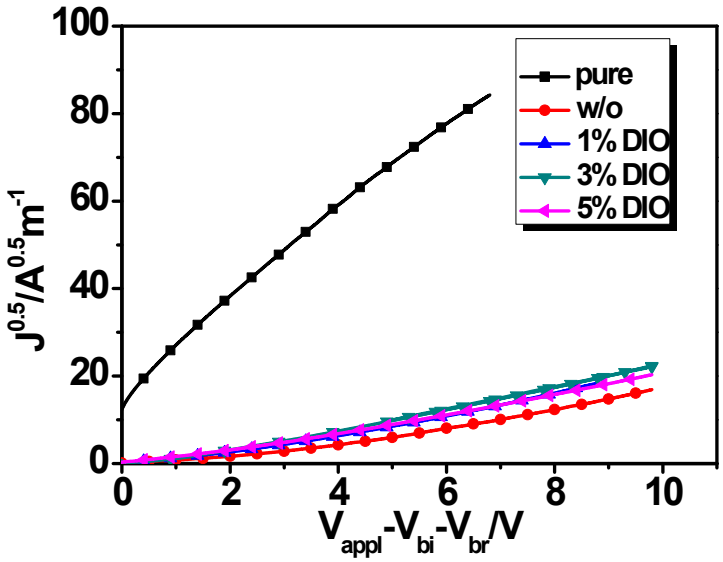

Figure S3. Plot of $J^{1/2}$ *vs*. (V_{appl}-V_{bi}-V_{br}) of the polymer for the measurement of hole mobility by the SCLC method with the device structure of ITO/PEDOT:PSS/ **PBDTSe-S-TT** or blend film/MoO_3/Al.