Supporting Information

Random copolymer based on dithienothiophene and diketopyrrolopyrrole units for high performance organic solar cell

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Instrumentation and characterization:

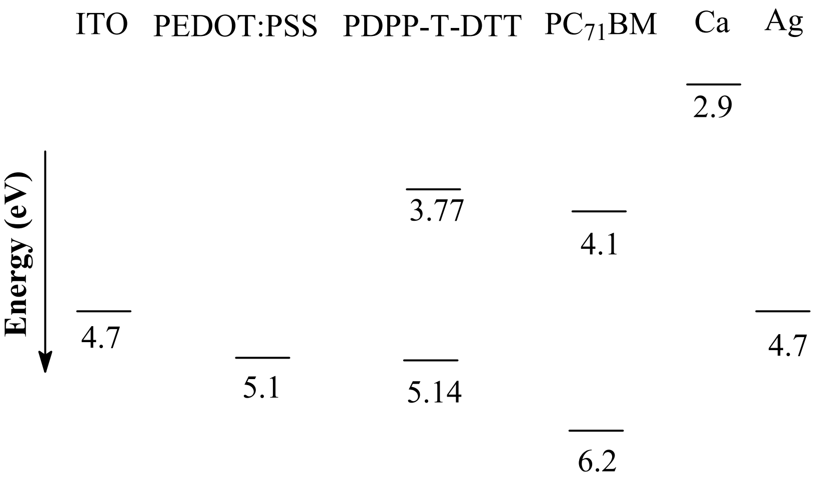
^{1}H NMR data were acquired on a Bruker DPX 400 MHz spectrometer. Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC Q100 instrument (scanning rate of 10 ^{o}C min^{-1}). Thermogravimetric analysis (TGA) was carried out using a TGA Q500 instrument (heating rate of 10 ^{o}C min^{-1}). Molecular weight determinations were carried out in hot chlorobenzene solution on a Shimadzu Prominence CBM-20A series HPLC using Agilent PLGel 5 micrometer Mixed-C column (79911 GP-MXC) with polystyrene calibration standards. Cyclic voltammetry experiments were performed using an Autolab potentiostat (model PGSTAT30) by Echochimie. A glassy carbon disk was used as working electrode, a platinum wire as counter electrode and a silver wire as reference electrode. Ferrocene was used for potential calibration. UV-Vis-NIR spectra were recorded on a Shimadzu model 2501-PC.

OTFT devices Fabrication:

Top-contact, bottom-gate TFT test devices were prepared in ambient conditions (humidity level ~55~ 60%) without taking any special precautions to exclude air, moisture and ambient light. A heavily n-doped silicon wafer with a 200-nm thermal silicon dioxide (SiO_2) was used as the substrate/gate electrode, with the SiO_2 layer serving as the gate dielectric. The SiO_2/Si substrate was first immersed in acetone and ultrasonicated for 10 minutes, withdrawn and blow dried with nitrogen gas. It was then immersed again in a piranha solution (60ml of H_2SO4 : 30ml of H_2O_2) for 8 minutes, followed by rinsing with deionized water, and then re-immersed in a solution of octyltrichlorosilane (OTS-8) in toluene at 60 °C for 20 minutes. It was then rinsed with toluene and then blow dried with nitrogen gas. The semiconductor layer was deposited on top of the OTS-8-modified SiO_2 surface by spin coating a solution of PDPP-T-DTT in chlorobenzene (~0.4 weight %) at 1000 rpm for 60 seconds and vacuum dried for 30 min to give a thin film semiconductor layer. Subsequently, gold source/drain electrode pairs were deposited by thermal evaporation through a metal shadow mask to create a series of TFTs with channel length (L) of 120 μm and width (W) of 4 mm. Silicon oxide at the backside of the silicon wafer of the TFT device was removed with sandpaper to provide a conductive gate contact.

Organic Photovoltaic Device Fabrication:

For the BHJ solar cells, polymer was dissolved in 1,2-dichlorobenzene (DCB) solution at a concentration of 8-10 mg mL^{-1}. Blends of polymer with $PC_{71}BM$ were prepared in the mass ratio from 1:2 to 1:4 in DCB. The patterned ITO glass substrates were first sonicated in a detergent bath for half an hour, followed by rinsing with de-ionized water for 20 min. This was succeeded by sonicating in an acetone and iso-propanol bath for 15 min and 20 min respectively. The cleaning step was concluded by drying the substrates in an oven at 80 ^{o}C for at least an hour. The substrates were subjected to UV-ozone treatment for 10 min before a 40 nm thick PEDOT:PSS was spin-coated onto the ITO surface. The polymer/PCBM solution was then spin-coated onto the PEDOT:PSS layer and left standing to dry for 2 hours. Film thickness of the active layer was about 120 nm. A 10 nm thick calcium layer, followed by 100 nm of silver, were deposited onto the blend layer via thermal evaporation to form the cathode. The active area of the device is 9 mm^2. Current density-Voltage (J-V) measurements were carried out in an inert environment (MBraun glovebox, N_2 atmosphere) under 1 Sun (AM1.5G) conditions using a solar simulator (SAN-EI Electric XES-301S 300W Xe Lamp JIS Class AAA).



Synthetic procedure for PDPP-T-DTT:

The monomers were weighed and added to a reaction vial equipped with a magnetic stirrer. The vial was then transferred to a glovebox where tris(dibenzylideneacetone)dipalladium(0) (2 mol%), tri(o-tolyl)phosphine (8 mol%) and anhydrous chlorobenzene (20 mL) were added. The vial was then stirred at 120 °C for 36 hours using an oil bath. The reaction mixture was poured into 200 mL of methanol and 10 mL of concentrated hydrochloric acid and stirred overnight to remove the stannylated end-groups. The polymers were subjected to Soxhlet extraction with ethanol, hexanes and chloroform for 24 h each to remove the small molecules and oligomers. Then the polymer was Soxhlet extracted with chlorobenzene, precipitated into methanol and filtered to obtain the final product

(65% yield). ^{1}H NMR (1,1,2,2-tetrachloroethane-d4, 400 MHz, 120 ºC) δ 8.85 (s, 2H), 7.42-7.26 (m, 10H), 4.11 (s, 4H), 3.06 (s, 8H), 2.08-1.94 (m, 12H), 1.56-1.26 (m, 64H), 0.97-0.95 (m, 24H). Anal. calcd. for $C_{126}H_{186}N_2O_2S_{11}$: C, 71.60; H, 8.87; N, 1.33. Found C, 71.95; H, 8.89; N, 1.37.

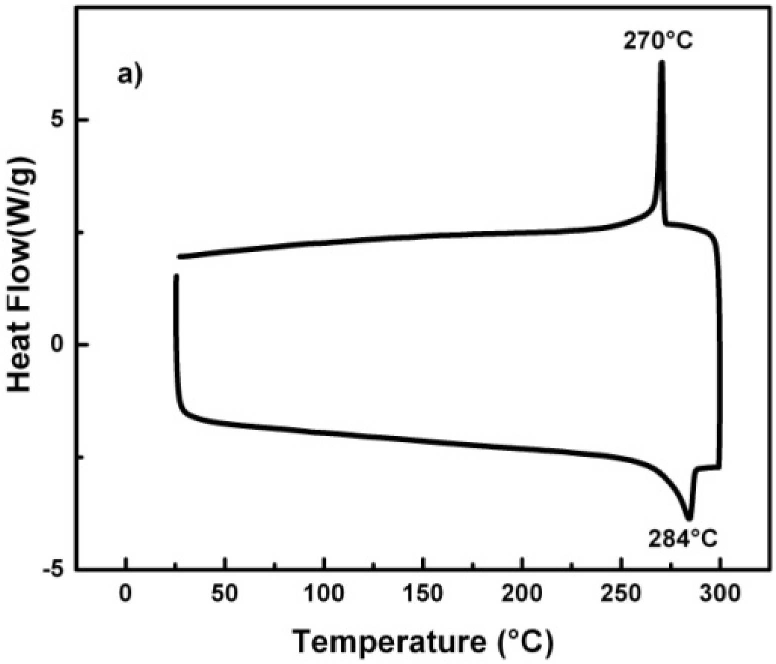


Figure S1. DSC scans of PDPP-T-DTT. The sample was heated from room temperature to 300 ^{o}C and back to room temperature at a ramp rate of 10 °C min^{-1}.

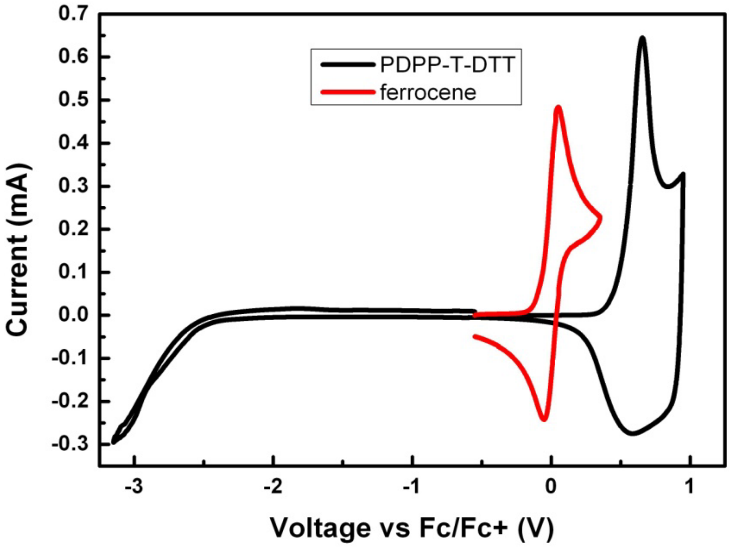


Figure S2. Cyclic voltammetry spectra of PDPP-T-DTT: oxidative state (black line) and reductive state (red line), ferrocene curve for calibration (blue line).