

Electronic Supporting Information for

Benzotriazole-based donor-acceptor conjugated polymers with broadened absorption in the visible

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General experimental details

All reactions were performed using anhydrous solvent under an inert atmosphere unless stated otherwise. Gel permeation chromatography (GPC) data was obtained using a Viscotek GPC Max VE2001 solvent/sample module equipped with a Viscotek VE3580 refractive index detector. Toluene was used as the eluent with a 200 μ l sample volume injection. Samples were passed through three 30 cm, PL gel (5 μ m) mixed C columns and one 30 cm, PL gel (3 μ m) mixed E column at 0.6 mL/min. Molecular mass distributions were calculated relative to narrow polystyrene reference standards. ^1H and ^{13}C NMR spectroscopy were carried out using either the Varian Inova-400 (400 MHz) or the Varian Inova-500 (500 MHz). IR spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer while UV-vis spectra were recorded using a Cary 50 UV-vis spectrometer. Photoluminescence was measured with a Varian Cary Eclipse fluorimeter. Elemental analyses were obtained commercially through Chemical & Analytical Services Pty. Ltd. (Australia) an Exeter Analytical CE-440 elemental analyzer. Thermal gravimetric analysis (TGA) experiments were carried out with a Mettler Toledo TGA/SDTA851e and differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Sapphire DSC. Electrochemical measurements were recorded on a Solartron 1287A Potentiostat/Galvanostat.

Thermal gravimetric analysis (TGA)

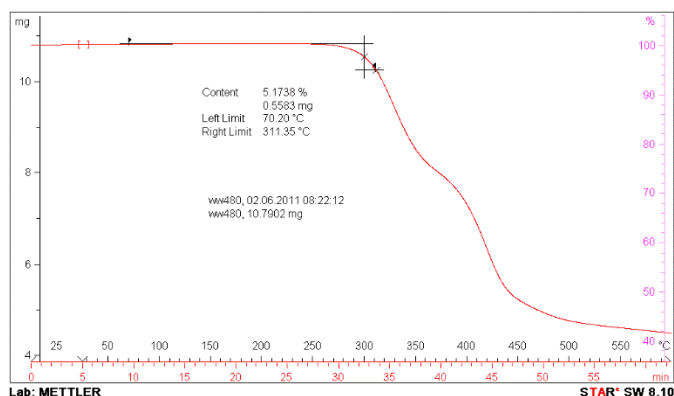


Figure S1. TGA analysis of polymer **P1** with decomposition temperature (5% weight loss) recorded at 310 °C.

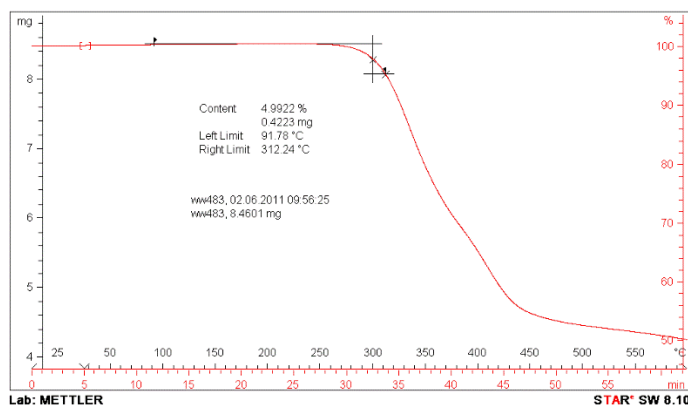


Figure S2. TGA analysis of polymer **P2** with decomposition temperature (5% weight loss) recorded at 312 °C.

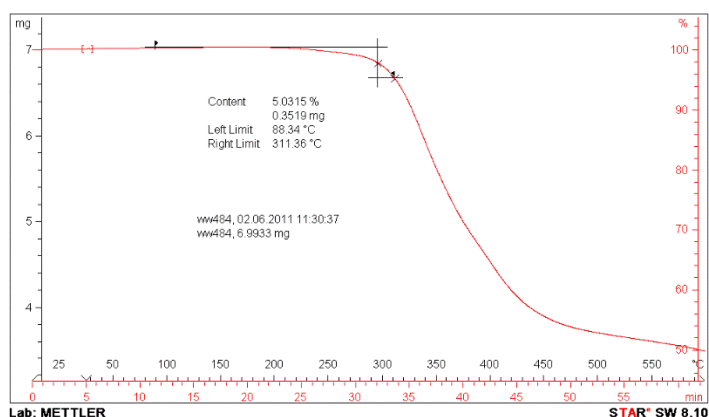


Figure S3. TGA analysis of polymer **P3** with decomposition temperature (5% weight loss) recorded at 311 °C.

Differential scanning calorimetry (DSC)

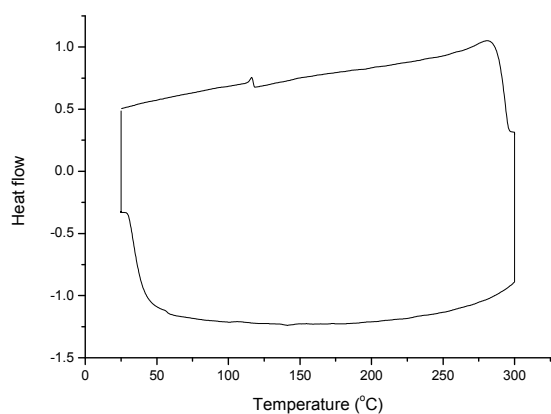


Figure S4. DSC analysis plot of polymer **P1** with a melting process detected at 120 °C.

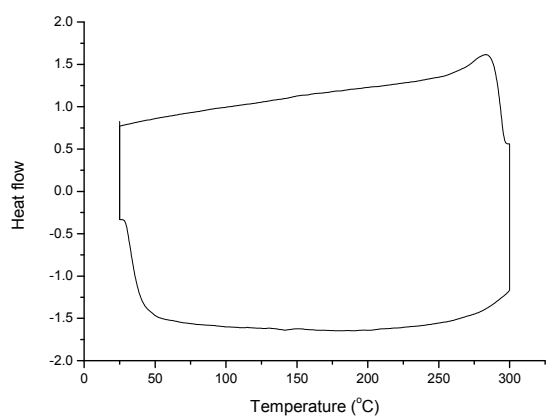


Figure S5. DSC analysis plot of polymer **P2**.

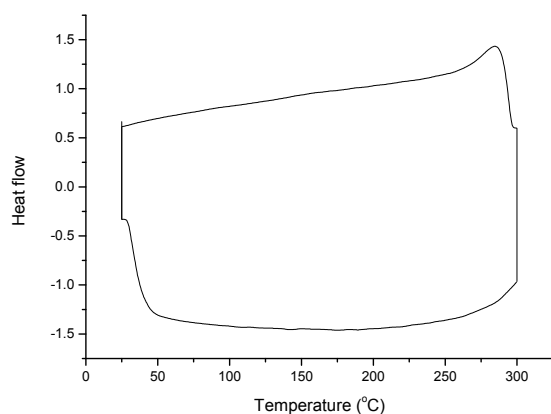


Figure S6. DSC analysis plot of polymer **P3**.

Photoluminescence (PL) spectrum

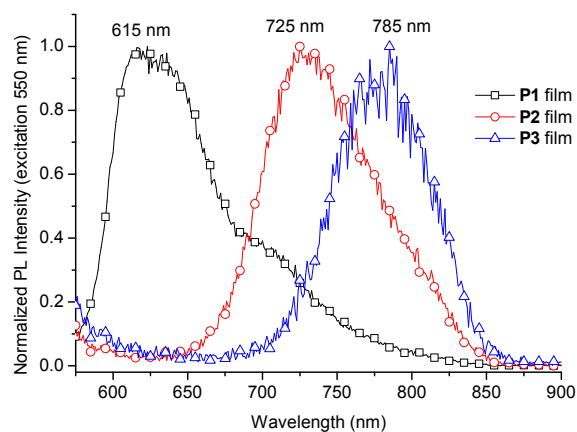


Figure S7. PL spectrum of polymers as thin films with excitation wavelength of 550 nm. Note: No emission was detected for blend films of polymer and PC₇₁BM (1:1).

Two-dimensional wide angle X-ray scattering (2DWAXS)

2D-WAXS measurements were performed using a home-build setup consisting of the Siemens Kristalloflex X-ray source (copper anode X-ray tube, operated at 35 kV/20 mA), Osmic confocal MaxFlux optics, two collimating pinholes (1.0 and 0.5 mm – Owis, Germany) and an antiscattering pinhole (0.7 mm – Owis, Germany). The patterns were recorded on a MAR345 image plate detector (Marresearch, Germany). The samples were prepared by filament extrusion (30 °C) using a custom-built mini-extruder. Before the measurement, the samples were annealed at 150 °C for 1hr.

Grazing incidence wide angle X-ray scattering (GIWAXS)

GIWAXS measurements were performed using a custom setup consisting of rotating anode X-ray source (Rigaku Micromax). By orienting the substrate surface at or just below the critical angle for total reflection with respect to the incoming X-ray beam ($\sim 0.2^\circ$), scattering from the deposited film was maximized with respect to scattering from the substrate. The GIWAXS data were acquired using a camera comprising an evacuated sample chamber with an X-ray photosensitive image plate. A rotating Cu-anode operating at 42 kV and 20 mA (Cu $K\alpha$, $\lambda = 1.5418 \text{ \AA}$) was used as X-ray source, focused, and monochromatized by a 1D multilayer. Diffraction patterns were recorded on a MAR345 image plate detector. The polymer-fullerene blend films were prepared by spin coating from chlorobenzene solution on to glass/ITO substrate giving thin films of approximately 100 nm thick.

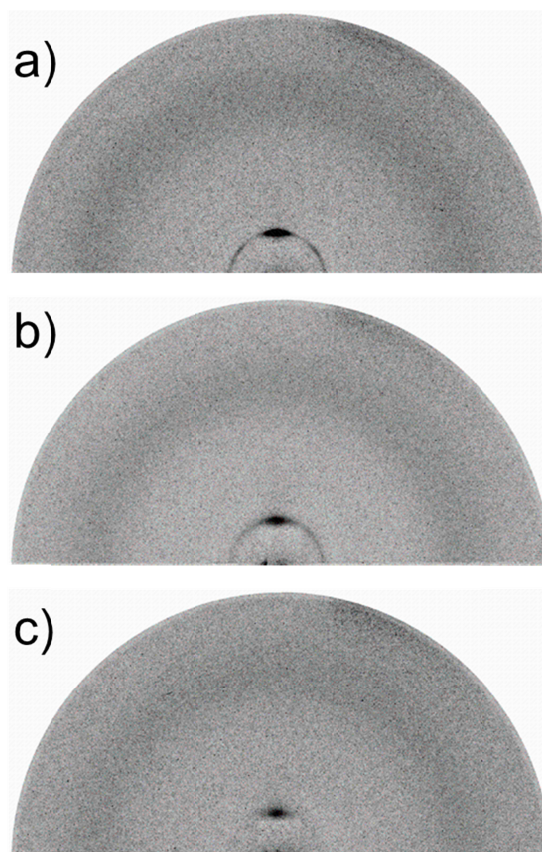


Figure S8. GIWAXS of polymer:PC₆₁BM (1:1) thin films for a) **P1**, b) **P2** and c) **P3**.

Device fabrication and characterization

Organic field-effect transistors (OFET)

For all devices fabricated and studied, highly doped silicon was used as the gate electrode, while a 200 nm thick SiO₂ oxide film was used as the dielectric. Bottom contact (channel lengths $L = 5\text{-}100\ \mu\text{m}$ and widths $W = 0.35\text{ to }7.0\ \text{mm}$, $W/L = 70$) FETs were prepared by spin coating (1200 rpm), 25 mg/mL in chlorobenzene solution on top of the SiO₂ dielectric modified with self-assembled monolayers (SAMs) of HMDS (by vapor deposition, resulting in contact angles of $93.2 \pm 1.3^\circ$). All the samples were annealed at 150°C for 20 min. The electrical characterization by using a Keithley SCS 4200 was performed inside a nitrogen filled glovebox (oxygen and humidity < 0.1 ppm, pressure $\sim 1120\ \text{Pa}$) at room temperature ($\sim 25^\circ\text{C}$).

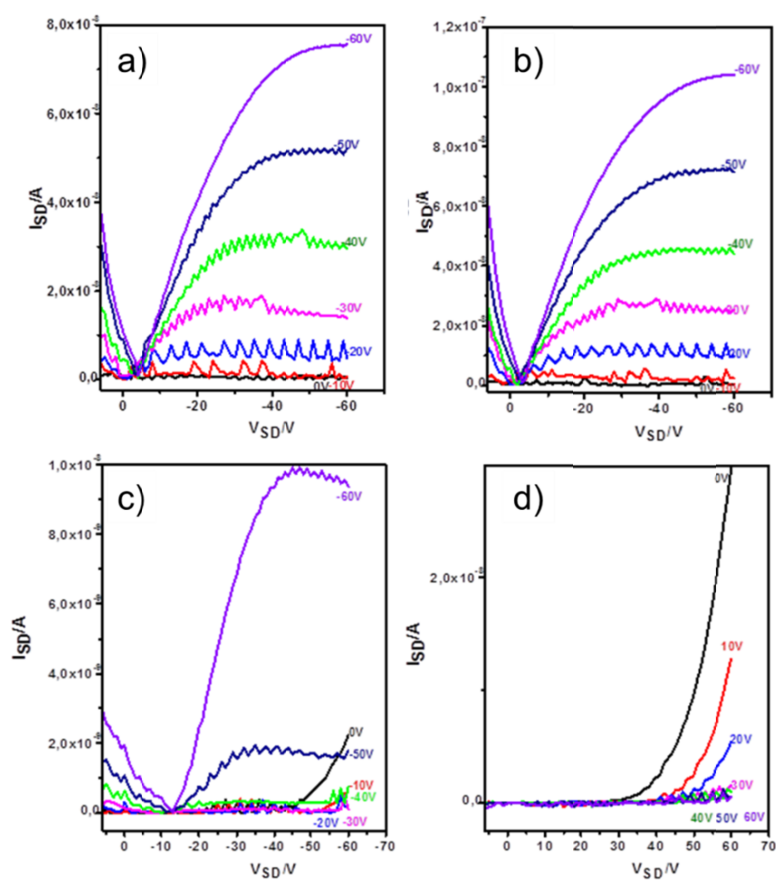


Figure S9. Output curves recorded for a) P1, b) P2 and c,d) P3.

Polymer solar cells

Polymer solar cells were processed on pre-patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω per square. First, a thin layer of ZnO nanoparticle (NP) was deposited on cleaned ITO substrate by spin-coating (3000 rpm) to form 30 nm of ZnO layer, followed by backing on a hot plate at 140 °C for 5 min. Zinc oxide nanoparticles (ZnO NP) were synthesized as reported by a sol-gel method using precursors of zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and tetramethyl-ammonium hydroxide (TMAH, $(\text{CH}_3)_4\text{NOH}$). [G. Sarasqueta, K. R. Choudhury, J. Subbiah, F. So. *Adv. Funct. Mater.*, **2011**, *21*, 167–171.] In a typical process, ZnO nano-particles are synthesized by drop-wise addition of 0.4 M TMAH dissolved in ethanol to 0.1 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ dissolved in dimethyl sulfoxide (DMSO). The resulting ZnO nano-particles are washed and dispersed in ethanol at a concentration of 25 mg/mL. An active layer of the device was deposited by spin coating a ortho-dichlorobenzene solution containing 8 mg of polymer and 16 mg of PC₇₁BM along with 3% of 1,8-diiodooctane (DIO). The thickness of the active layer was measured as 90 nm. The films were then transferred to a metal evaporation chamber and MoO₃ (10 nm) and silver (100 nm) were thermally deposited through a shadow mask (active area was 0.1 cm²) at approximately 1 x10⁻⁶ torr. Film thickness was determined by Veeco Dektak 150+Surface Profiler. The current density-voltage measurements of the devices were carried out using a 1 kW Oriel solar simulator with an AM 1.5G filter as the light source in conjunction with a Keithley 2400 source measurement unit. Solar measurements were carried out under 1000 W/m² AM 1.5G illumination conditions. For accurate measurement, the light intensity was calibrated using a reference silicon solar cell (PVmeasurements Inc.) certified by the National Renewable Energy Laboratory. Device fabrication and characterizations were performed in an ambient environment without any encapsulation. Tapping-mode AFM (NanoScope II, Dimension, Digital Instrument Inc.) was carried out with commercially available tapping mode tips.

Space charge limited current (SCLC) charge transport studies

The space charge limited current (SCLC) in the polymers (**P1 - P3**) were studied using hole-only devices to find the charge-transport properties. The hole-only devices, consisting of active layer sandwiched between a PEDOT:PSS coated ITO electrode and Au counter-electrode as the electron-blocking contact, were fabricated as shown in Figure S10. From the current density as a function of voltage data, the hole mobility in the space-charge limited current (SCLC) region can be estimated using the Mott-Gurney equation, $J=9(\epsilon_r\epsilon_0\mu)/8 \times (V^2/d^3)$, where J is the current density, $V = V_{\text{appl}} - V_{\text{bi}} - V_r$, V_{appl} is the applied potential, V_{bi} is the built-in potential resulting from workfunction difference between two electrodes, V_r is the voltage drop due to the device resistance, ϵ_r is the dielectric constant of the polymer, ϵ_0 is the permittivity of vacuum, μ is the hole mobility, d is the sample thickness.

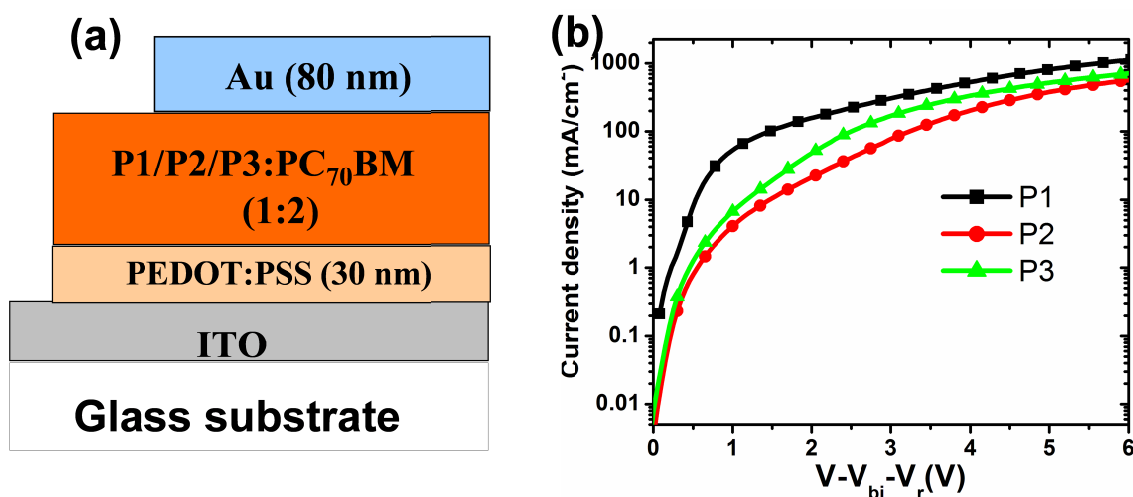


Figure S10. (a) Schematic diagram of hole-only device and (b) Current density-voltage curves for the hole only devices based on **P1/P2/P3:PC₇₀BM** blends.