Electronic Supporting Information for
Electron deficient conjugated polymers based on benzotriazole

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Experimental Procedures

Materials. All reactions were performed using anhydrous solvent under an inert atmosphere unless stated otherwise. Syntheses of benzotriazole monomers **1** and **2** have been reported previously.[1] Synthesis of 4,8-dibromo-benzo[1,2-*c*;4,5-*c'*]bis[1,2,5]thiadiazole **6** was previously outlined by Tam and co-workers[2] and was followed without further modification. The syntheses of monomers **4** and **5** are described in the following section. All other chemicals were commercially available. All solvents were dried over molecular sieves type 4A (2.5-5.0 mm) and kept in their containers plugged with rubber septum. Toluene, xylene, and distilled water were degassed with N_2 gas thoroughly prior to use for polymerization. Thin-layer chromatography (TLC) was carried out on Merck Kieselgel 60 silica gel on glass (0.25 mm thick) and viewed using 365 nm UV lamp. Column chromatography was performed using silica with 230-400 mesh.

Characterisation. ^{1}H and ^{13}C NMR spectroscopies 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. Gel permeation chromatography (GPC) data were obtained using a Viscotek GPC Max VE2001 solvent/sample module equiped with a Viscotek VE3580 refractive index detector. Toluene was used as the eluent with a 200 μl sample volume injection. Samples were passed through three 30 cm, PL gel (5 μm) mixed C columns and one 30 cm, PL gel (3 μm) mixed E column at 0.6 mL/min. Molecular mass distributions were calculated relative to narrow polystyrene reference standards.
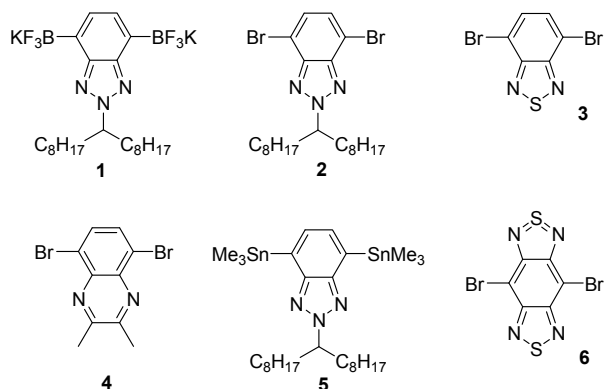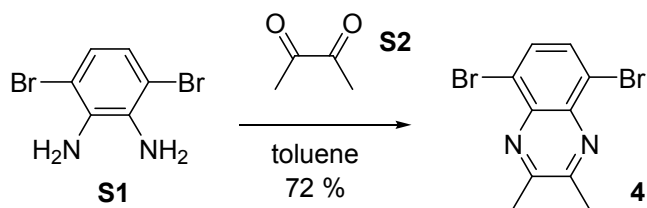

Figure S1. List of monomers used in polymer synthesis.

Monomer syntheses

5, 8-Dibromo-2,3-dimethylquinoxaline (4): The diamine **S1**[3] (3.00 g, 11.28 mmol), butane-2,3-dione **S2** (11.02 mL, 11.62 mmol), and ethanol (100 mL) were charged into a 250 mL round-bottom flask fitted with a Soxhlet extractor packed with molecular sieves (type 4A 2.5-5.0 mm). The reaction was heated to reflux temperature and stirred for 13 hours. After cooling the reaction, the solvent was removed under reduced pressure. Water (100 mL) was added and the resulting mixture was extracted with $CHCl_3$ (50 mL x 3). The combined organic portions were passed through a silica pad then dried over Na_2SO_4. The solvent was removed under reduced pressure. The resulting solid was recyrstallized in ethanol to form yellow crystals (2.57 g, 72 % yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.82 (s, 1H, Ar-**H**), 2.82 (s, 6H, -C**H**$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 155.42, 139.54, 132.26, 122.93, 23.07. HRMS (ESI+) calculated for $C_{10}H_8Br_2N_2$ 316.91065, found 316.91077.
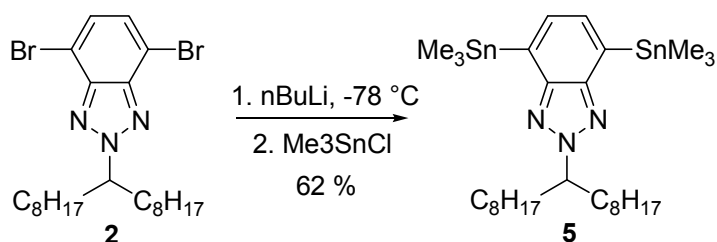
2-(Heptadecan-9-yl)-4,7-bis(trimethylstannyl)-2H-benzo[d][1,2,3]triazole (5): To a magnetically-stirred solution of benzotriazole monomer **2** (2.00 g, 3.88 mmol) in anhydrous THF (30 mL) was added nBuLi (2.5 M solution in hexanes, 3.41 mL) dropwise with a syringe at -78 ºC under N_2 atmosphere. The resulting solution was stirred for 10 minutes at -78 ºC. Trimethylstannyl chloride (1.0 M in THF, 8.54 mL) was then added dropwise into the solution. After stirring the reaction for 30 minutes at -78 ºC, the reaction was allowed to warm to ambient temperature and

stirred for another 2 hours. The reaction was quenched with water (50 mL) and Et_2O (100 mL). The organic solution was extracted, washed with brine (50 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting viscous liquid was recrystallised with isopropyl alcohol in the freezer to obtain white crystals (1.31 g, 49% yield). m.p. 52 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41 (s, 1H, Ar-**H**), 4.76 (dd, $J = 9.4, 4.5$ Hz, 1H, -**CH**-), 2.21 – 2.07 (m, 2H, -**CH$_2$**-), 1.87 (dd, $J = 14.1, 9.3$ Hz, 2H, -**CH$_2$**-), 1.56 (t, $J = 0.6$ Hz, 8H, -**CH$_2$**-), 1.36 – 1.11 (m, 22H, -**CH$_2$**-), 1.05 (t, 6H, -**CH$_2$CH$_3$**). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 147.81, 133.03, 132.31, 67.29, 35.57, 31.83, 30.92, 29.39, 29.21, 25.89, 22.62, 14.08. Elemental analysis calculated for $C_{29}H_{55}N_3Sn_2$: C, 50.98%; H, 8.11%; N, 6.15%; Sn, 34.75%, found: C, 50.83%; H, 8.38%; N, 6.28%. FTIR (neat, cm^{-1}): 2955, 2919, 2852, 1548, 1468, 1389, 1336, 1264, 1219, 1185, 1120, 958, 873, 838, 721, 654. HRMS (ESI+) calculated for $C_{29}H_{55}N_3Sn_2$ 684.25178, found 684.25055.

Optical Measurements

Solution spectra of all the polymers were performed using EMSURE® ACS, ISO, Reag. Ph Eur grade chloroform as solvent. Glass slides (Menzel-Glaser, cut into 1 cm x 1 cm dimension) were cleaned with detergent (Extran, Merck), distilled water, and then sonicated for 20 minutes in isopropyl alcohol. All polymers (ca. 1 mg/mL *o*-dichlorobenzene) and blends (1:1 by weight, *o*-dichlorobenzene as solvent) were spin-casted onto the glass substrates at 1000 rpm for 30 s. Absorption spectra were recorded using a Cary 50 UV-Vis spectrophotometer. Emission spectra were obtained using a Varian Cary Eclipse Fluorescence Spectrophotometer.
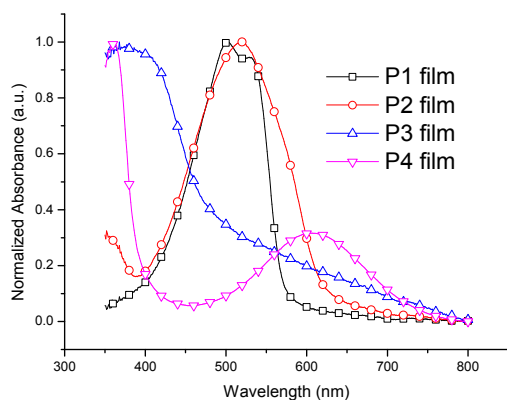

Figure S2. Thin film absorption spectra of **P1** to **P4**.

Fluorescence quantum yields were calculated using equation **1**, where Φ is the fluorescence quantum yield of the sample, A is the fraction of light absorbed, I is the integrated intensity, and n is the refractive index. The subscript R refers to the reference fluorophore (9,10-diphenylanthracene), $\Phi = 0.90$ in cyclohexane used for **P3**, and disodium fluorescein, $\Phi = 0.97$ in ethanol used for **P1** and **P2**. Polymer solutions were made up in spectroscopic grade chloroform.

$$\Phi = \Phi_R \frac{I}{I_R}\left(\frac{A_R}{A}\right)\left(\frac{n^2}{n_R^2}\right) \qquad \textbf{(Equation 1)}$$

Time-correlated single photon counting

Time-resolved photoluminescence experiments were performed using the time-correlated single photon counting (TCSPC) technique. The excitation source is a mode-locked and cavity dumped titanium/sapphire laser (Coherent Mira 900F/PulseSwitch) with a pulse width of 100 fs and pulse repetition rate of 5 MHz. Second harmonic generation in non-linear crystals generated the excitation wavelengths used for sample excitation. The fluorescence from the sample was focused onto the slit of a 1/4 m monochromator (CVI Digikrom CM110) and detected by a microchannel plate photomultiplier tube (Eldy, St. Petersburg, Russia, model EM1-132). The instrument has an instrument response function and spectral resolution of 100 ps and 2 nm, respectively. Fluorescence lifetimes were determined by analysis of the collected fluorescence decay profiles using iterative reconvolution procedures. Further details can be found elsewhere.[4]

Polybenzotriazole P1

Exponential Components Analysis (Reconvolution)

Fitting range	634; 1300 channels					
χ^2	1.003					
Shift	-0.006 ± 0.07 ns					
Decay background	7.649 ± 0.869					
IRF background	0					

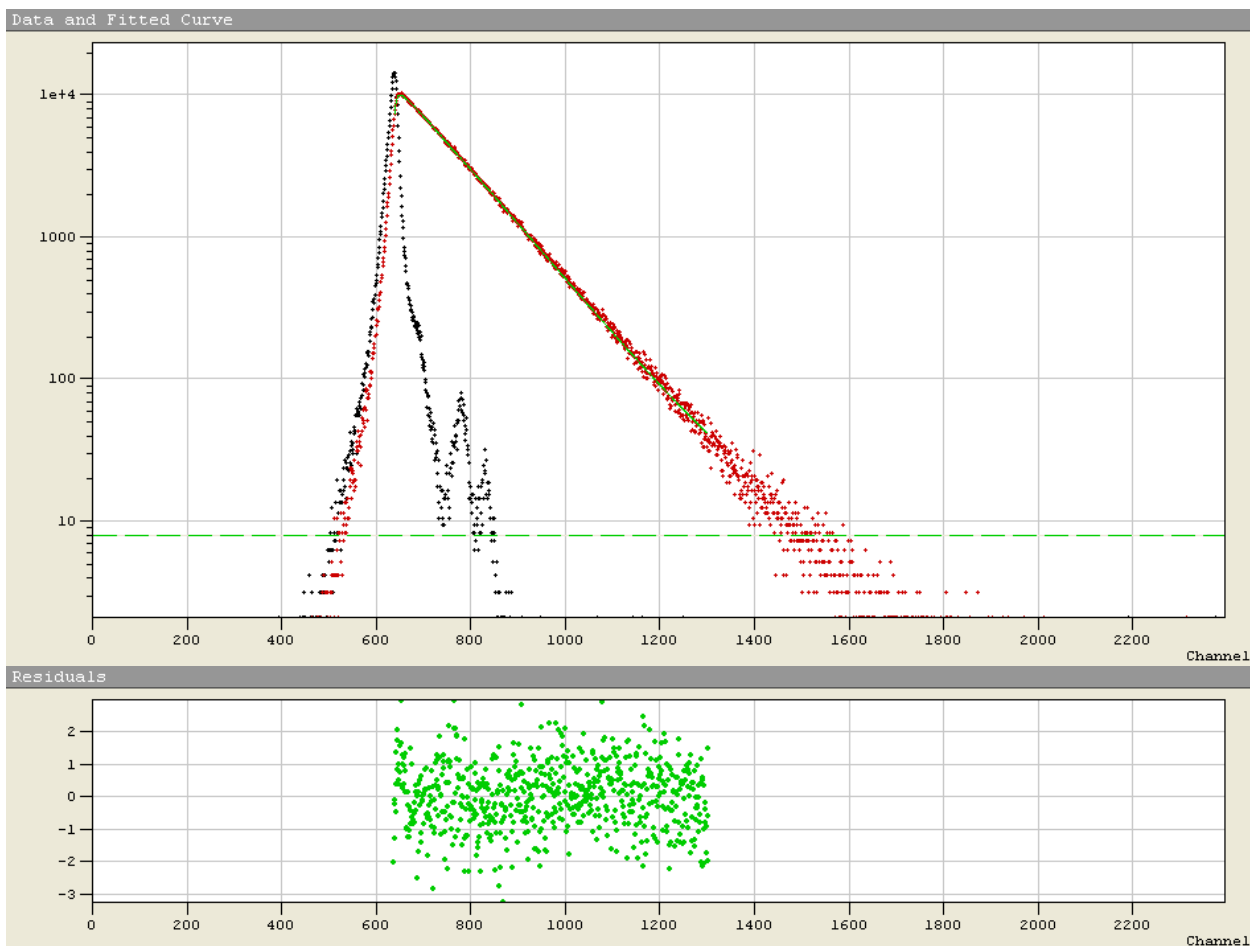|	B_i	ΔB_i	f_i (%)	Δf_i (%)	τ_i (ns)	$\Delta \tau_i$ (ns)
1	0.0407	5.5 x 10^{-5}	100	0.30	0.902	0.001

Figure S3. Data and fitted curve (top) and residual plot (bottom)

Poly(benzotriazole-*alt*-benzothiadiazole) P2

Exponential Components Analysis (Reconvolution)

Fitting range	634; 1300 channels
χ^2	1.086
Shift	-0.0009 ± 0.077 ns
Decay background	20.13 ± 2.525
IRF background	0

	B_i	**ΔB_i**	**f_i (%)**	**Δf_i (%)**	**τ_i (ns)**	**$\Delta \tau_i$ (ns)**
1	0.0383	4.9 x 10^{-5}	100	0.24	1.273	0.001

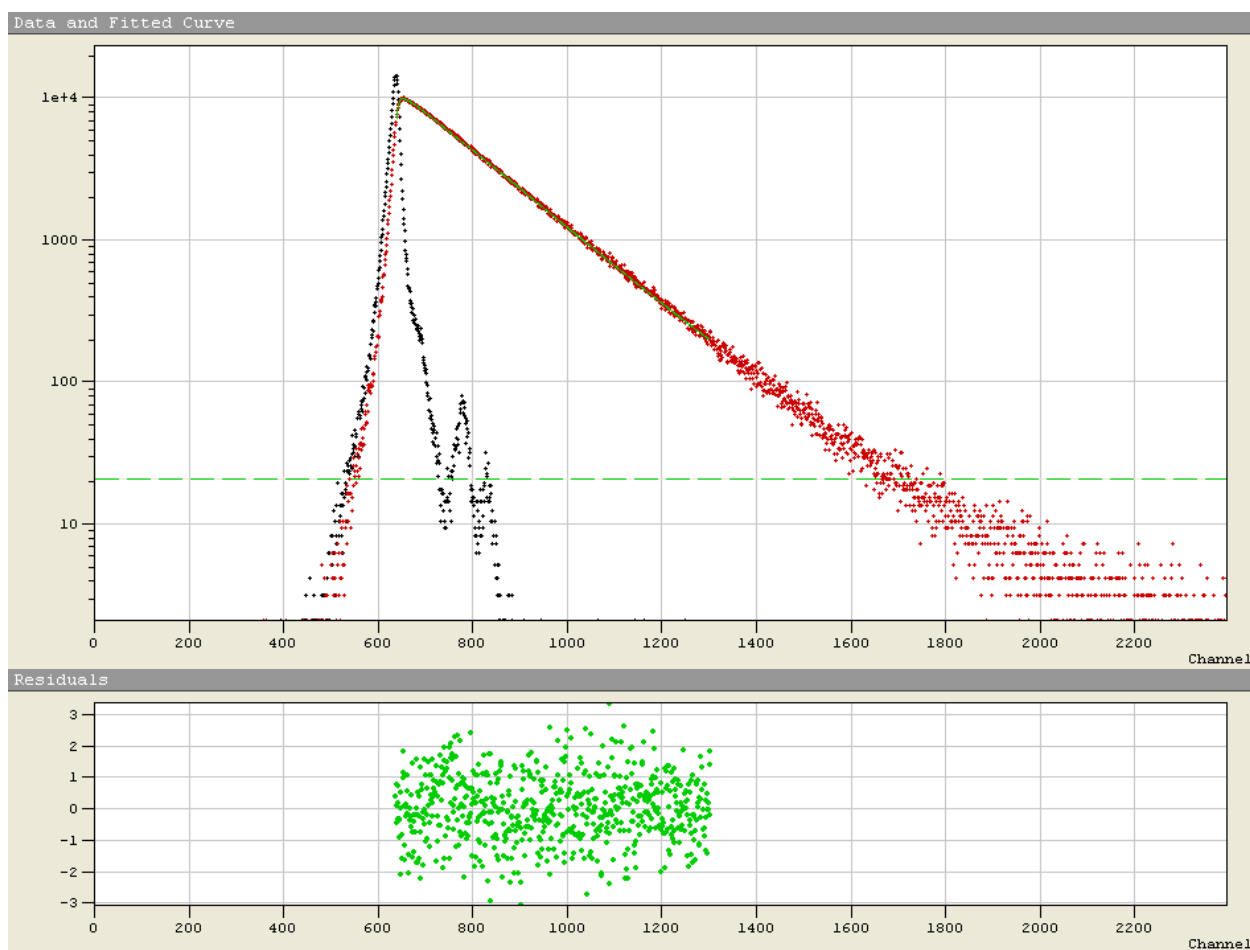
Figure S4. Data and fitted curve (top) and residual plot (bottom)

Poly(benzotriazole-*alt*-quinoxaline) P3

Exponential Components Analysis (Reconvolution)

Fitting range	634; 1300 channels
χ^2	1.101
Shift	0.07 ± 0.054 ns
Decay background	10.000
IRF background	0

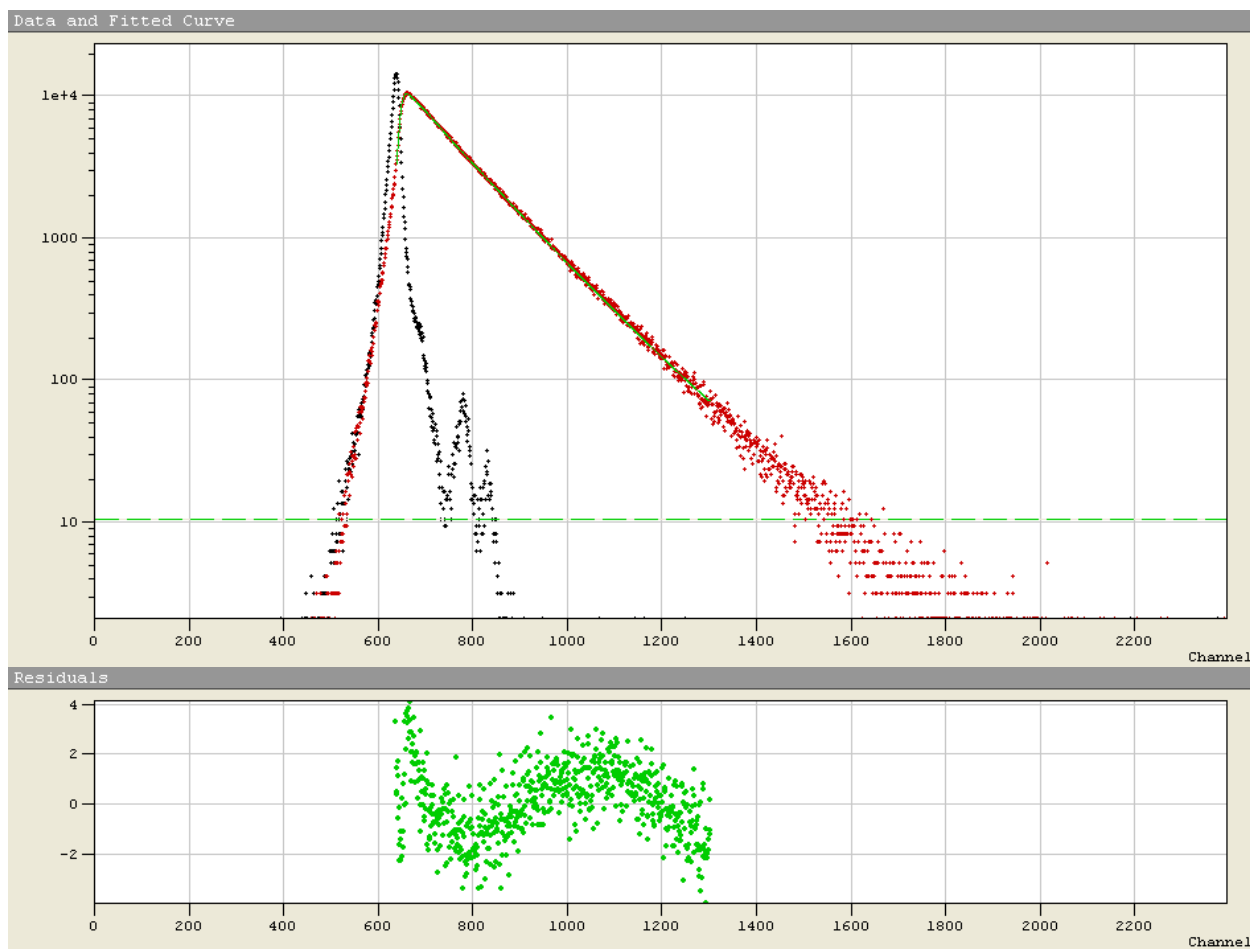|	**B_i**	**ΔB_i**	**f_i (%)**	**Δf_i (%)**	**τ_i (ns)**	**$\Delta \tau_i$ (ns)**
1	0.0108	8.0×10^{-4}	14.59	3.75	0.524	0.095
2	0.0319	9.0×10^{-4}	85.41	2.95	1.035	0.007

Figure S5. Data and fitted curve (top) and residual plot (bottom)
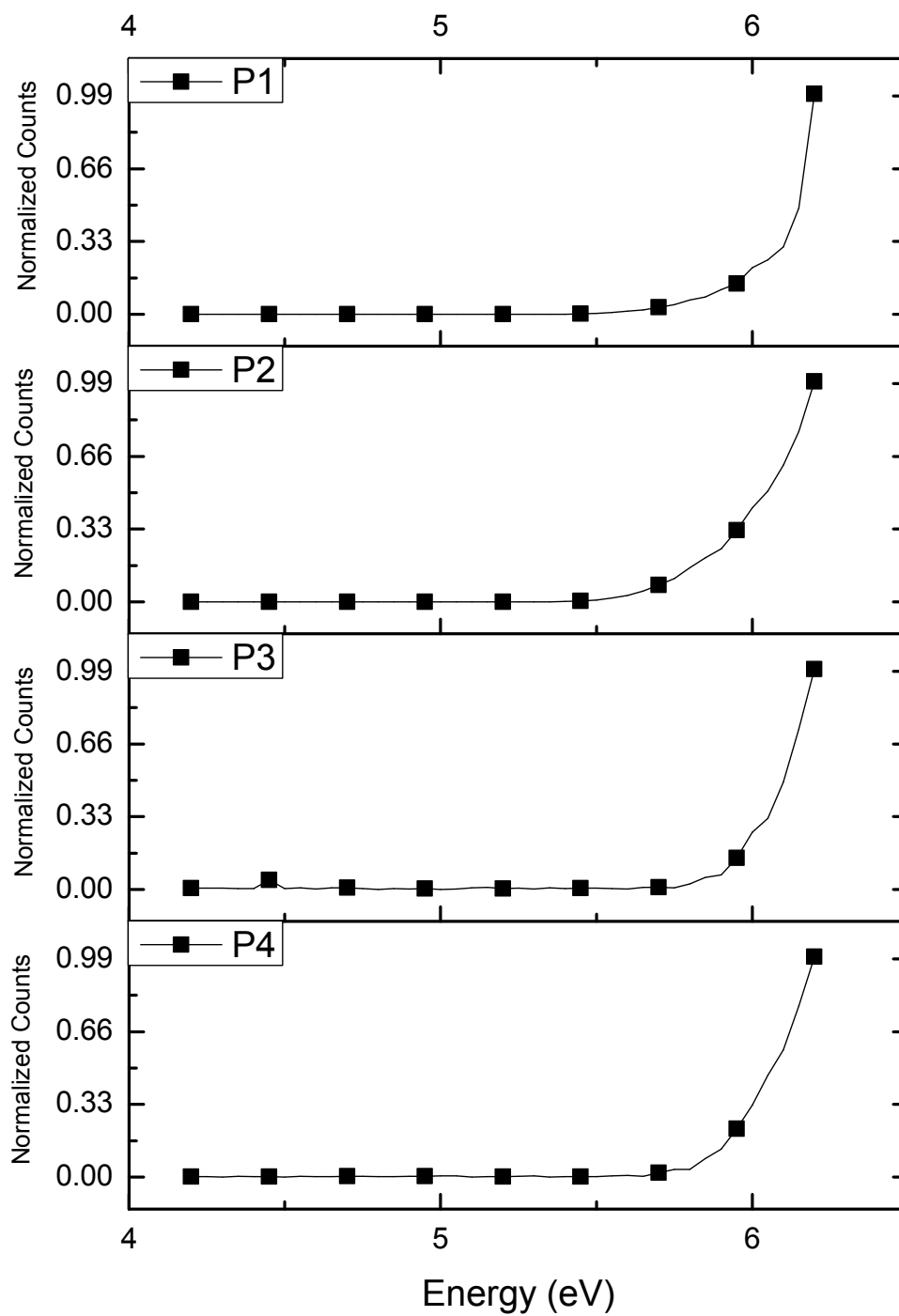
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Photoelectron Spectroscopy in Air (PESA)

Figure S6. Energy of electron affinity of polymers as measured by photoelectron spectroscopy in air.

Device fabrication and characterization

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 (30 nm) of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Baytron AI 4083 from HC Starck) was spin-coated on a ultrasonically cleaned ITO substrates, followed by baking on a hot plate at 140 °C for 10 min. An active layer of the device was deposited by spin coating a chlorobenzene solution containing 10 mg of P3HT and 10 mg of P2 or P4 and 3% of 1,8-diiodooctane (DIO). The thickness of the active layer was measured as 75 nm. A thin layer of ZnO nanopaticle was deposited on the active layer by spin-coating (3000 rpm) to form 25nm of ZnO layer.[5] The films were then transferred to a metal evaporation chamber and aluminum (100 nm) were deposited through a shadow mask (active area was 0.1 cm^2) 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/m^2 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.

For PLED device fabrication, 1% polymer (**P1/P2/P3**) in chlorobenzene was spin-casted on a layer of PEDOT:PSS deposited on ITO-coated glass. The cathode was formed by spin coating from ZnO nanoparticle solution, followed by thermal deposition of Al. The current density-voltage measurements of the PLED devices were measured with a Keithley 2400 source measurement unit. Electroluminescence spectra were collected using a NEWPORT OSM 400 -UV/Vis optical spectrometer.
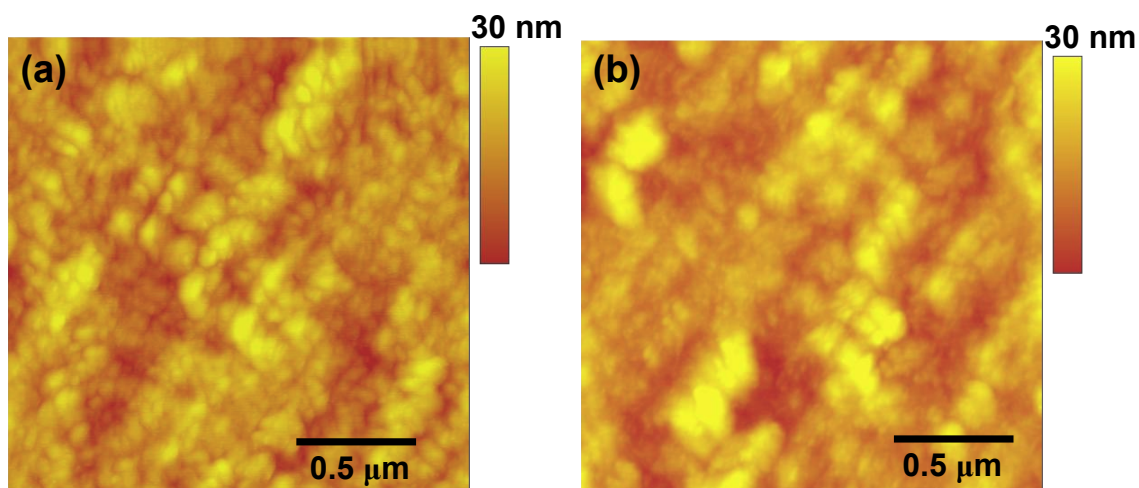
Figure S7. Tapping mode AFM height images of the active layer (a) P3HT:**P2** and (b) P3HT:**P4**.

References

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