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Supplementary Information

Thiazolyl substituted benzodithiophene copolymers: synthesis, properties and photovoltaic applications

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General

Unless noted, all materials were reagent grade and used as received without further purification. Chromatographic separations were performed using standard column methods with silica gel (Merck 9385 Kieselgel 60). Thin layer chromatography was performed on Merck Kieselgel 60 silica gel on glass (0.25 mm thick). IR spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer and UV-vis spectra were recorded using a Cary 50 UV-Vis spectrometer. Photoluminescence was measured with a Varian Cary Eclipse fluorimeter. Melting points were determined on a Büchi 510 melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were carried out on a 400 MHz spectrometer. All NMR data was referenced to the chloroform signal and peak multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublets of doublets, m = multiplet, br = broad). All high resolution mass spectrometry experiments were conducted with use of a commercially available hybrid linear ion trap and Fourier-transform ion cyclotron resonance mass spectrometer, equipped with ESI. Cyclic voltammetry (CV) experiments were performed at a sweep rate of 100 mV/s. CVs were carried out in a three-electrode cell consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/Ag$^+$ reference electrode. The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6). The solutions were deoxygenated by sparging with argon prior to each scan and blanketed with argon during the scans. The platinum disc working electrode was polished with 0.05 mm alumina and washed well with deionized water and dry CH_3CN prior to each scan.

Fabrication of the BHJ 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 (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 an ODCB solution containing 10 mg of polymer and 20 mg of $PC_{71}BM$. A thin layer of ZnO nanopaticle was deposited on the active layer by spin-coating (3000 rpm) to form 25nm of ZnO layer.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 1×10^{-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 (PV measurements Inc.) certified by the National Renewable Energy Laboratory. Device fabrication and characterizations were performed in an ambient environment without any encapsulation.

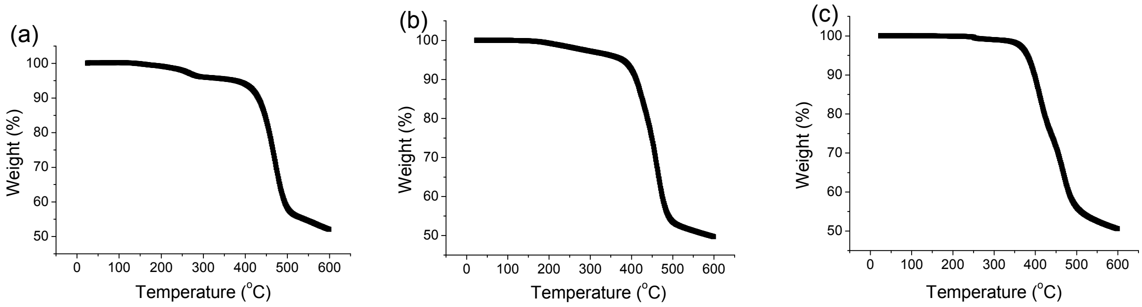


Fig. S1 TGA traces of polymer **P1** (a), **P2** (b) and **P3** (c). TGA experiments were carried out with a Mettler Toledo TGA/SDTA851e. Heating rate, 10 °C/min, under nitrogen.

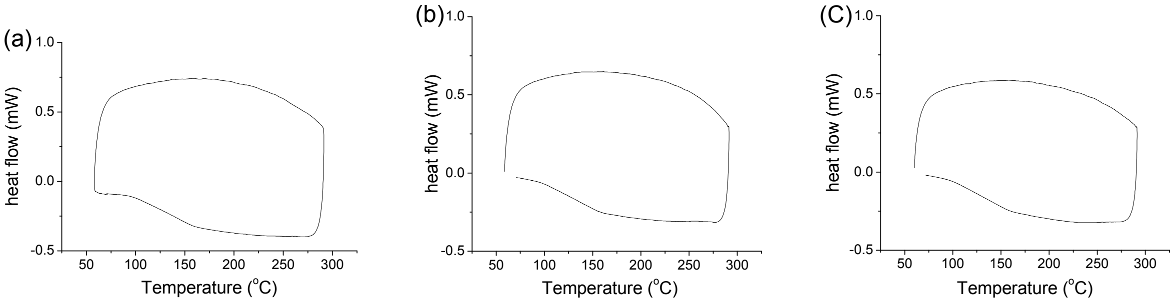


Fig. S2 DSC traces of polymer **P1** (a), **P2** (b) and **P3** (c). DSC experiments were performed on a Perkin-Elmer Sapphire DSC. The second heating and cooling traces were recorded. Heating rate, 20 °C/min.

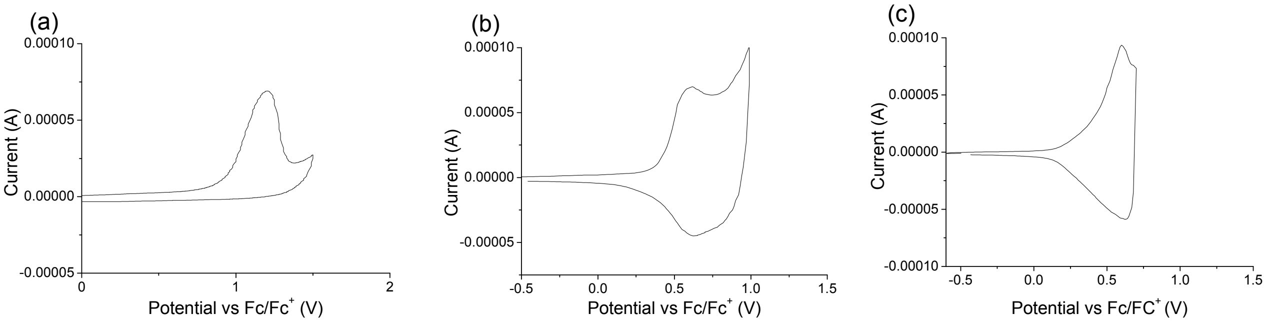
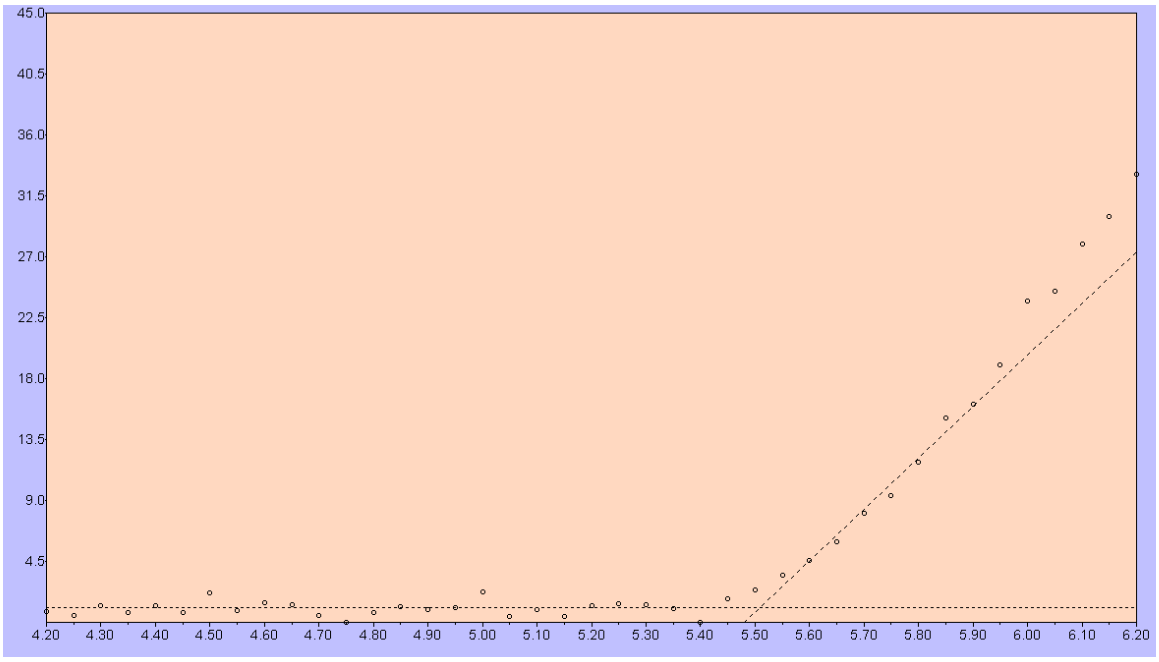
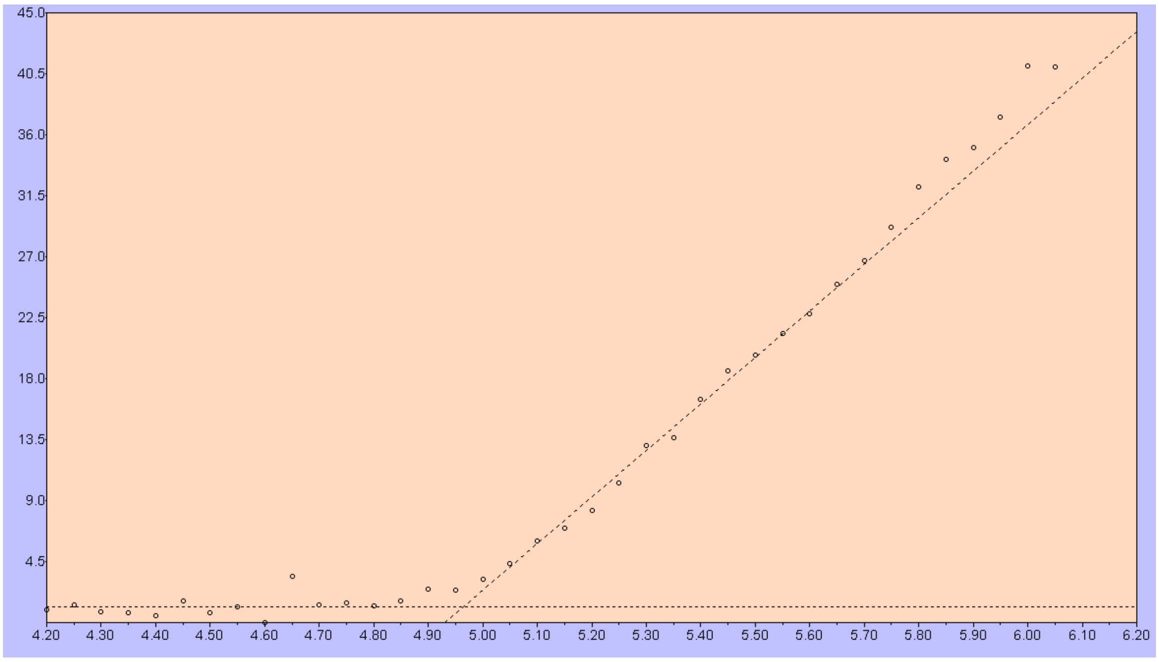


Fig. S3 Cyclic voltammograms of polymer **P1** (a), **P2** (b) and **P3** (c). Cyclic voltammetry (CV) experiments were performed at a sweep rate of 100 mV/s and were carried out in a three-electrode cell consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/Ag$^+$ reference electrode. The supporting electrolyte was 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6).



(a)



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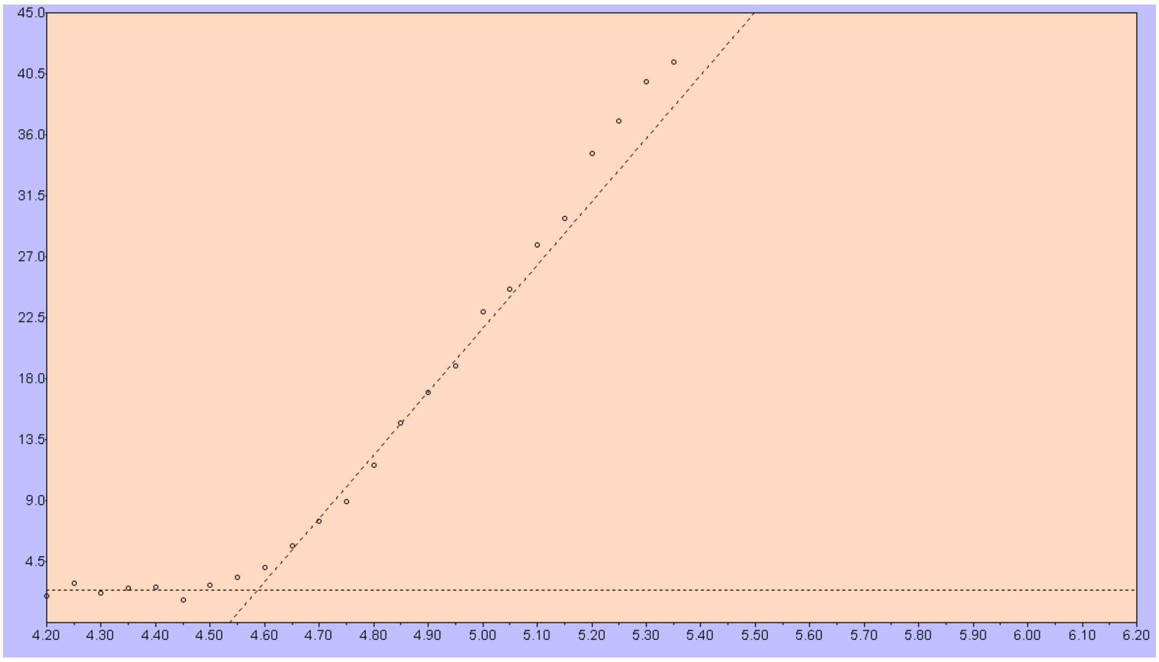
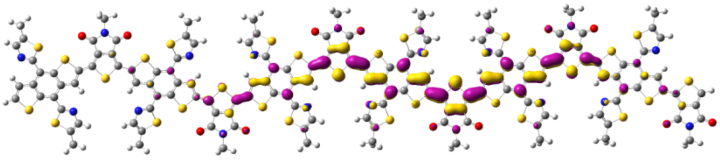
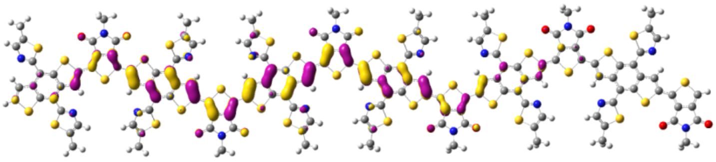


(c)

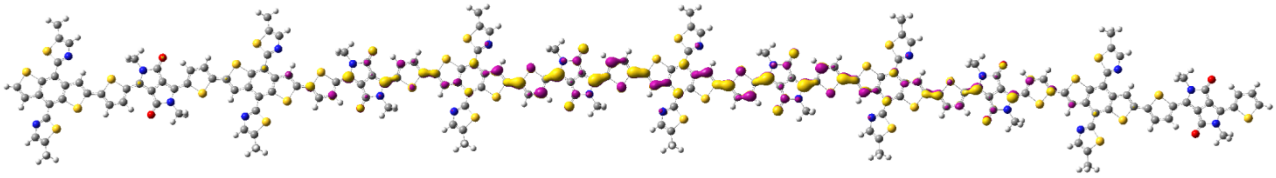
Fig. S4 Photoelectron spectroscopy of polymer **P1**(a), **P2** (b) and **P3**(c). Samples were analysed by PhotoElectron Spectroscopy in Air (PESA) using a Riken Keiki AC-2 spectrometer. Analyses were carried out with a light intensity of 5nW and data are plotted using a power number of 0.5.



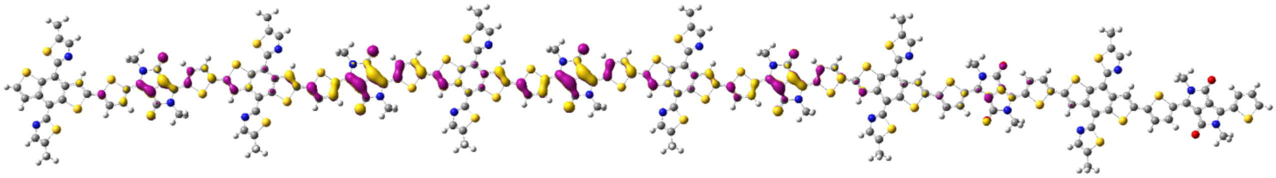
P1-sexamer-LUMO



P1-sexamer-HOMO



P2-sexamer-LUMO



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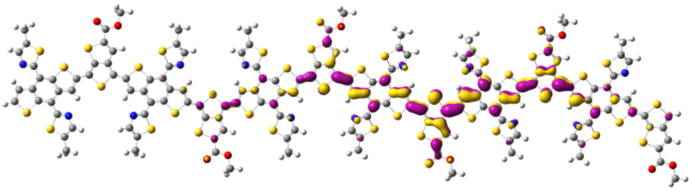
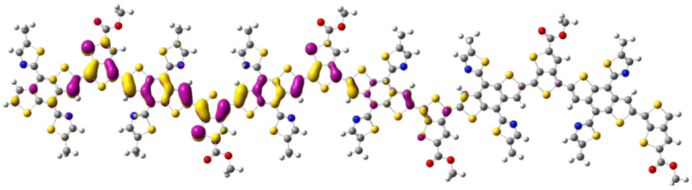


P3-sexamer-LUMO



P3-sexamer-LUMO

Fig. S5 The molecular frontier orbitals of the polymers **P1**-**P3** calculated by DFT at the B3LYP/6-31G level using Gaussian 09.

Table S1 Calculated ground and excited state dipole moments of **P1**, **P2** and **P3** monomers with DFT/TDDFT B3LYP/6-31G level using Gaussian 09.

Dipole (monomer)	μ_x	μ_y	μ_z	Total	$\Delta\mu_{ge}$
P1- μ_g	2.6800	-0.0057	-0.2027	2.6876	0.3529
P1- μ_e	2.9853	0.1254	-0.0839	2.9891	
P2- μ_g	0.9138	0.0786	-0.0750	0.9202	2.2670
P2- μ_e	-1.2487	0.0561	0.6051	1.3887	
P3- μ_g	1.2620	-2.4058	0.1548	2.7211	2.4284
P3- μ_e	-1.1075	-2.4483	-0.3751	2.7132	

$\Delta\mu_{ge}$ is calculated by $\Delta\mu ge = [(\mu_{gx} - \mu_{ex})^2 + (\mu_{gy} - \mu_{ey})^2 + (\mu_{gz} - \mu_{ez})^2]^{1/2}$.

Table S2 Photovoltaic performance of polymers **P1-P3**

Sample	Voc (V)	Jsc (mA/cm2)	FF(%)	PCE (%)
P1:PC$_{71}$BM 800rpm	0.75	-0.60	26	0.12
P1:PC$_{71}$BM 800rpm, annealing	0.66	-0.42	23	0.06
P1:PC$_{71}$BM 1200rpm	0.82	-1.05	32	0.27
P1:PC$_{71}$BM 1200rpm, annealing	0.74	-0.83	28	0.17
P2:PC$_{71}$BM 800rpm, annealing	0.46	-9.30	34	1.46
P2:PC$_{71}$BM 1200rpm, annealing	0.44	-7.60	49	1.63
P3:PC$_{71}$BM 800rpm	0.46	-11.98	34	1.86
P3:PC$_{71}$BM 800rpm, annealing	0.48	-9.01	50	2.16
P3:PC$_{71}$BM 1500rpm	0.47	-7.06	26	0.88
P3:PC$_{71}$BM 1500rpm, annealing	0.48	-5.34	48	1.24
P3:PC$_{71}$BM 2000rpm	0.48	-9.03	46	1.98
P3:PC$_{71}$BM 2000rpm, annealing	0.48	-6.05	51	1.48
P3:PC$_{71}$BM 3000rpm	0.44	-4.53	49	0.98
P3:PC$_{71}$BM 3000rpm, annealing	0.44	-3.47	47	0.72
P3:PC$_{71}$BM 3vol% DIO 800rpm	0.45	-8.22	29	1.07
P3:PC$_{71}$BM 3vol% DIO 800rpm, annealing	0.43	-7.80	28	0.95

The polymer PC$_{71}$BM was 1:2, thermal annealing was conducted at 70 ^{o}C, all the data are averaged from 6 devices.

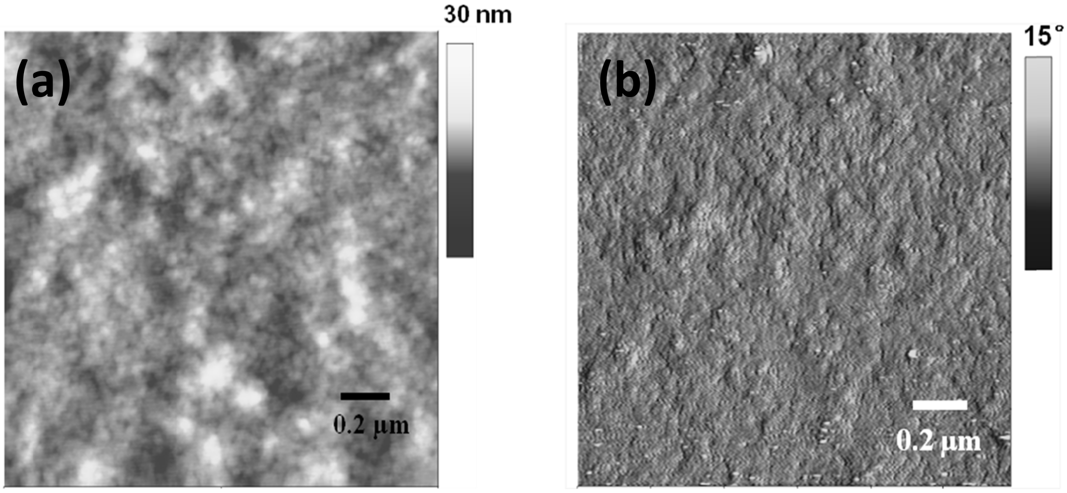


Fig. S6 AFM images of films spin coated from**P2**:PCBM on ZnO surface. (a) height image; (b) phase image.

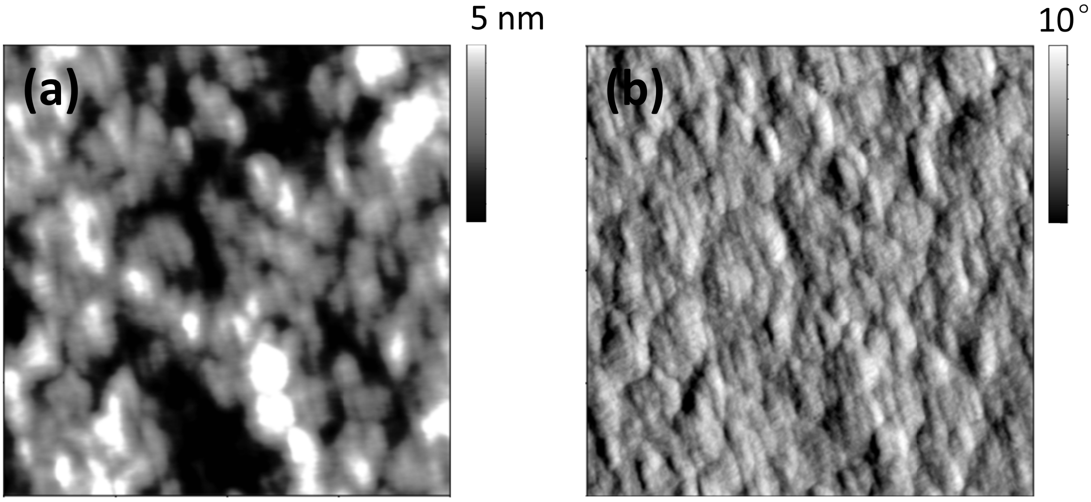


Fig. S7 AFM images of films spin coated from **P3**:PCBM with 1% DIO as additive. (a) height image; (b) phase image. Images are 2 × 2 μm.

SCLC measurement

The space charge limited current (SCLC) in the polymers (P1, P2, 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 Fig. S8. 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 (εμ)/8 x (V2/d3), where ε is the dielectric constant, μ is the charge-carrier mobility, d is the sample thickness.

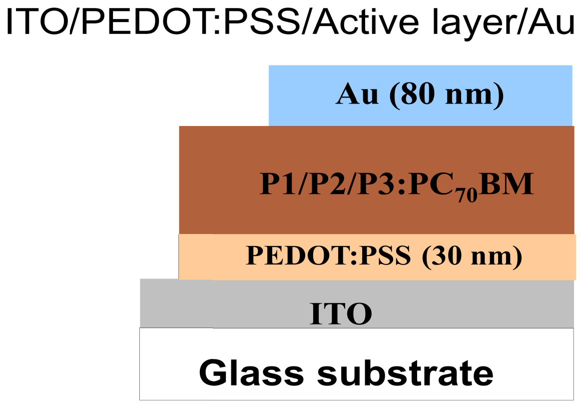


Fig. S8 Configuration of the hole only device.

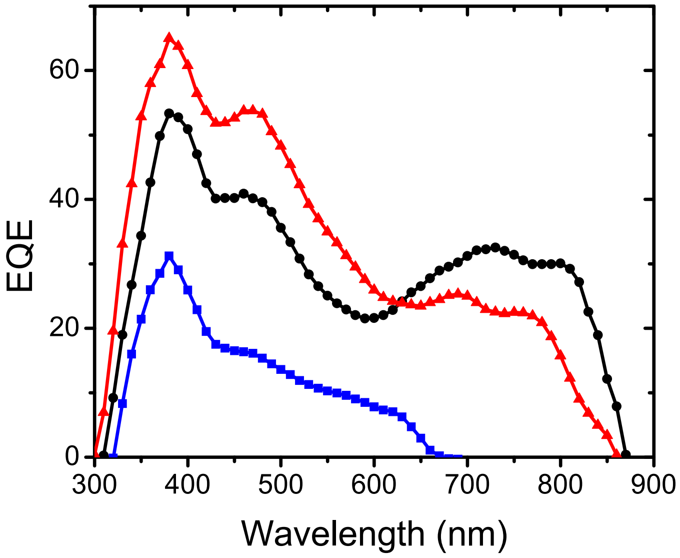
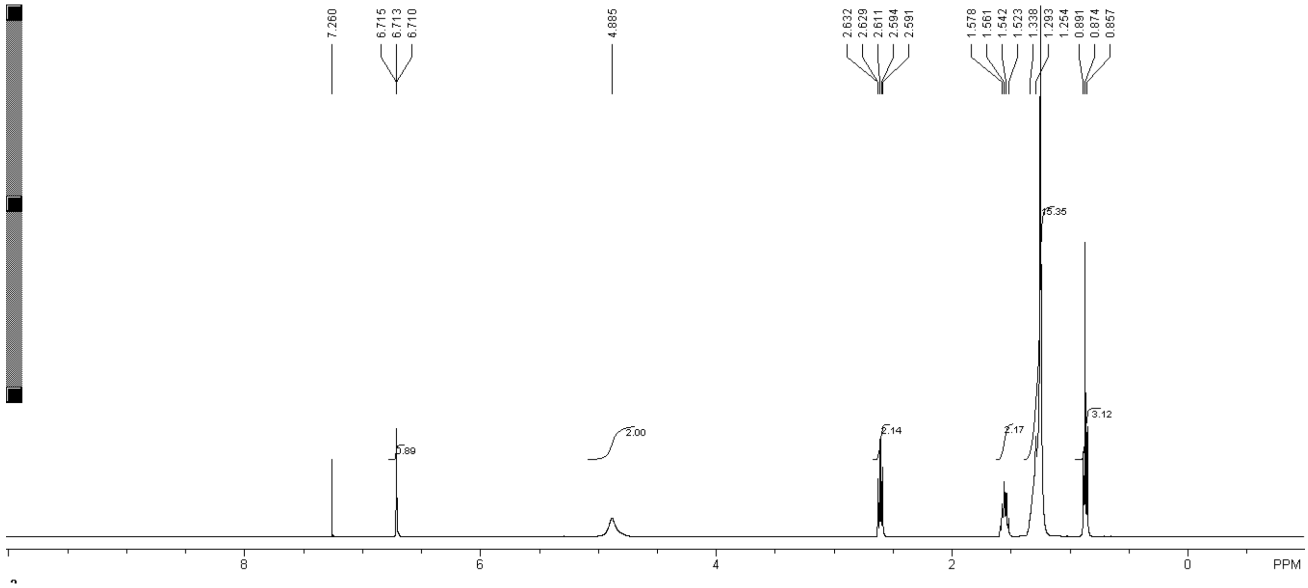
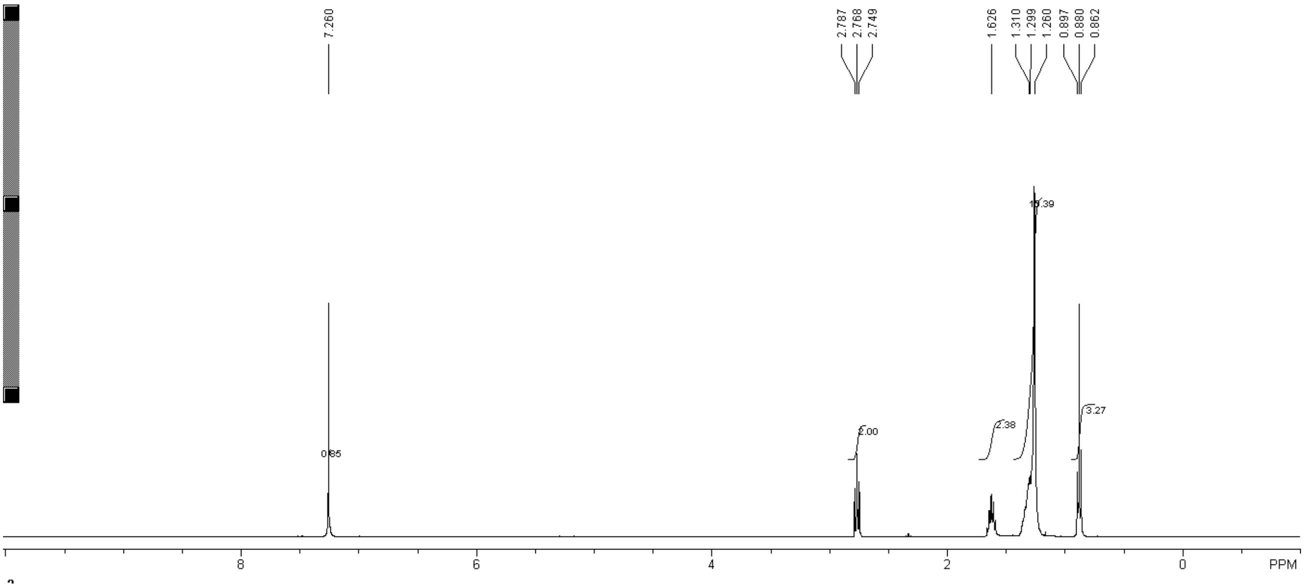


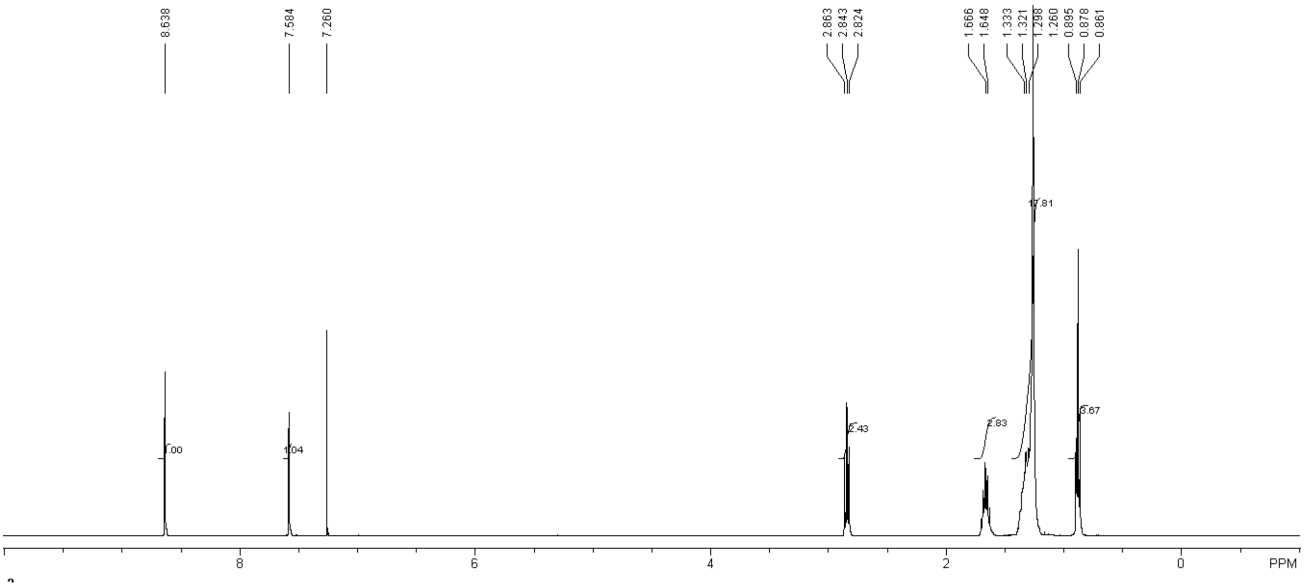
Fig. S9 EQE curves of P1 (blue), P2 (black) and P3 (red) based solar cells.



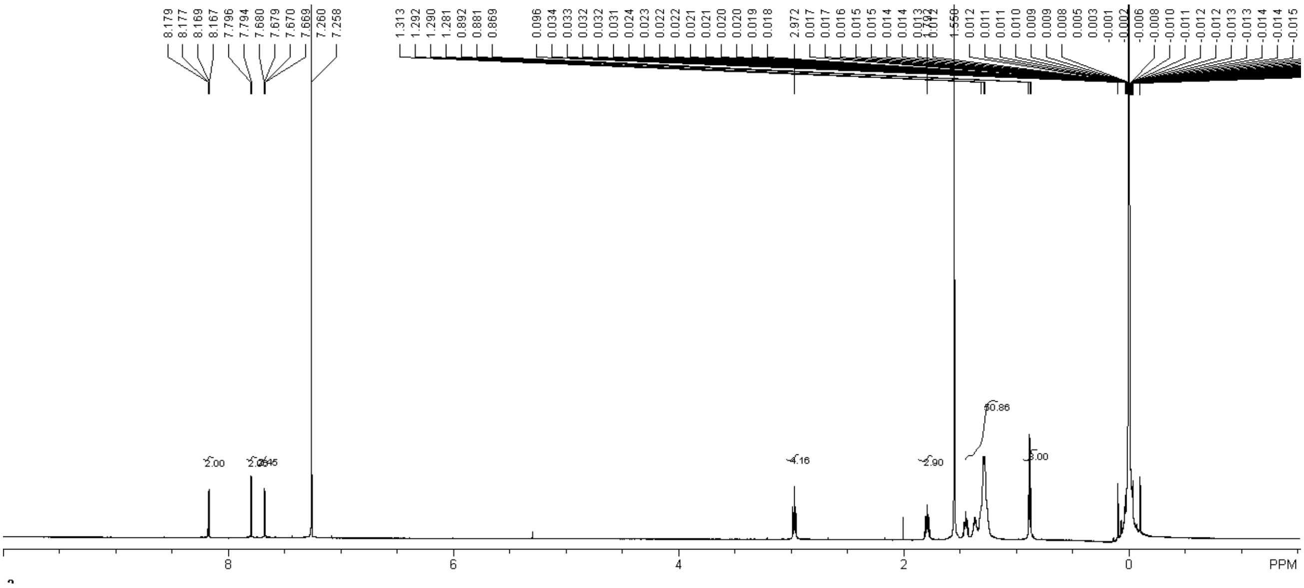
^{1}H NMR of compound 1.



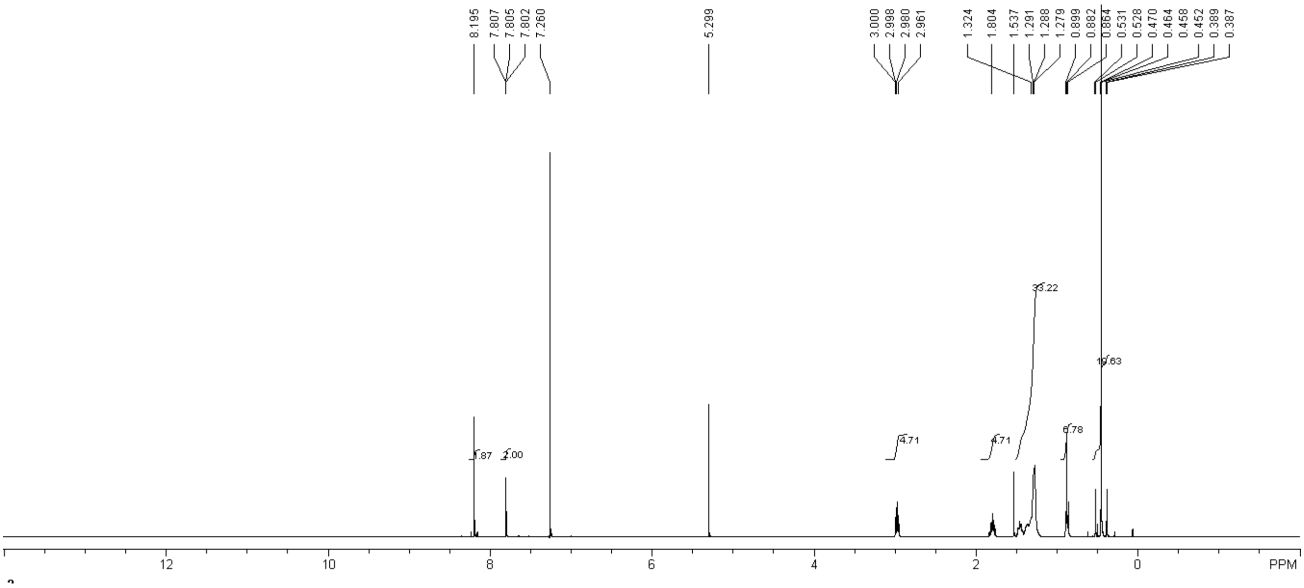
^{1}H NMR of compound 2.



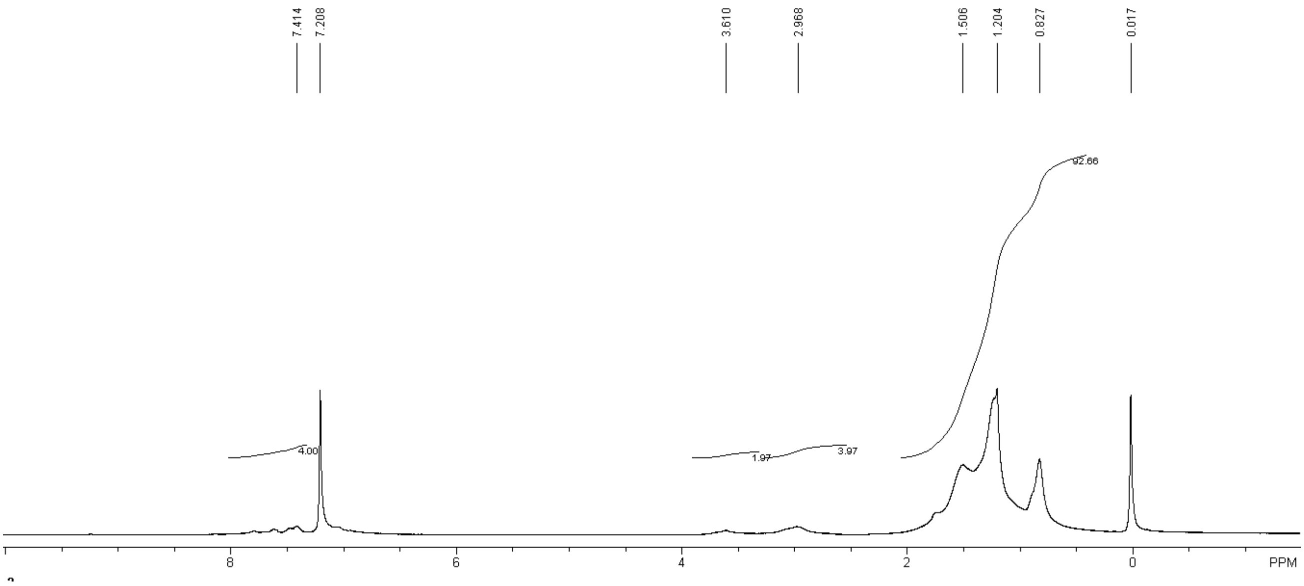
^{1}H NMR of compound 3.



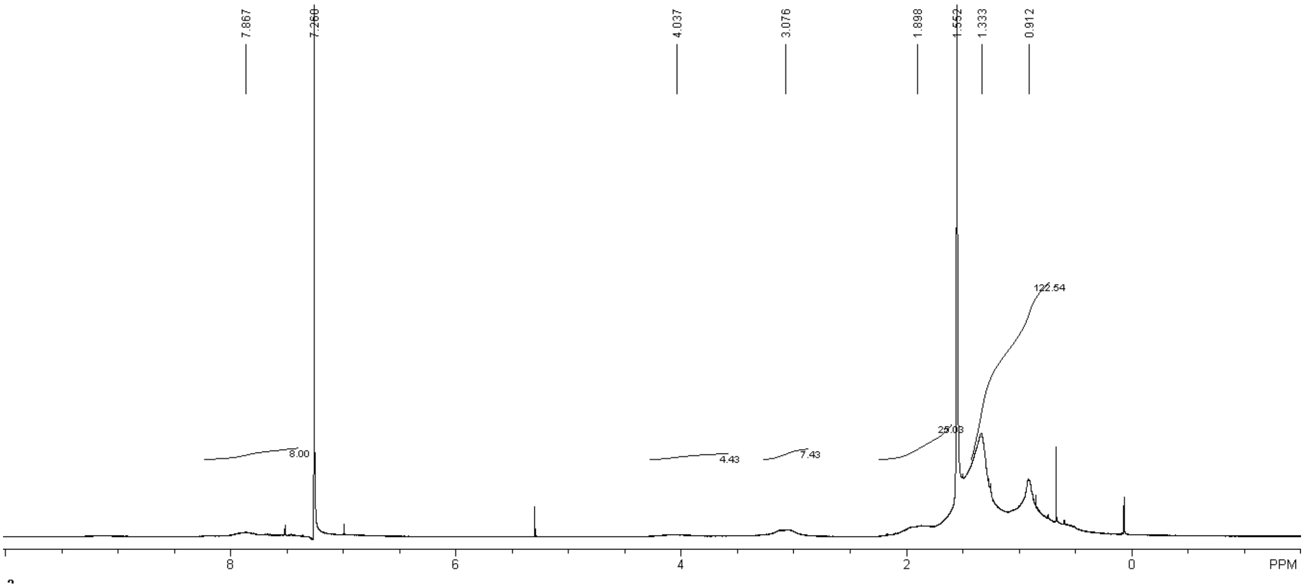
^{1}H NMR of compound 4.



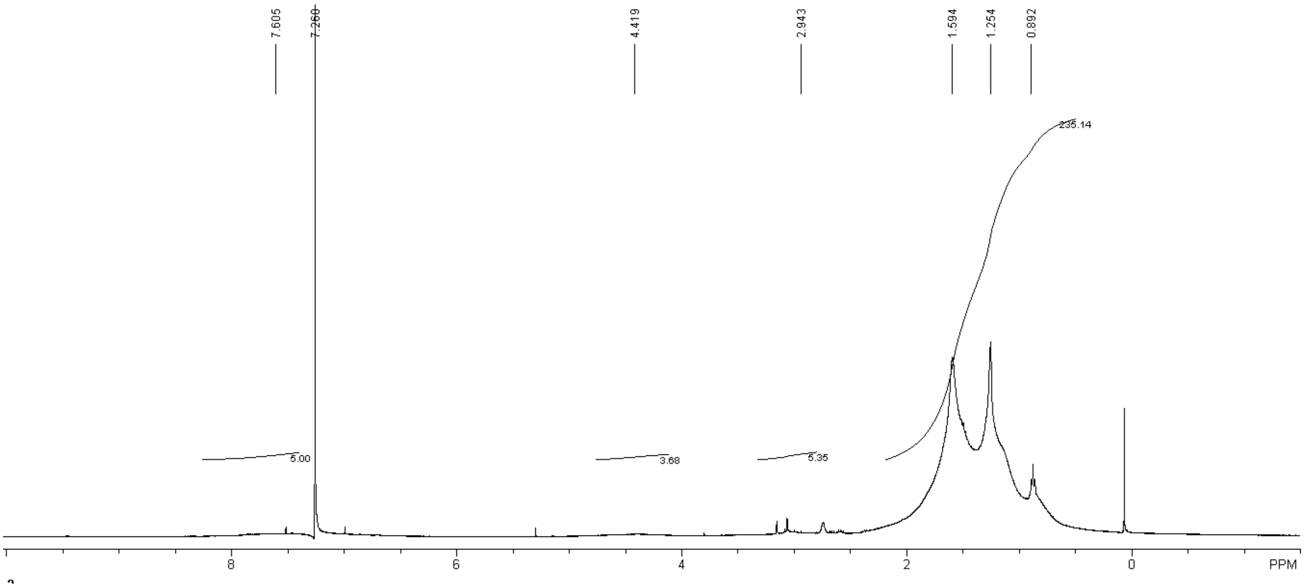
^{1}H NMR of compound 5.



^{1}H NMR of polymer P1.



^{1}H NMR of polymer P2.



^{1}H NMR of polymer P3.