

Influence of Water-Soluble Polythiophene as an Interfacial Layer on the P3HT/PCBM Bulk Heterojunction Organic Photovoltaics

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Experimental Part

Materials: 3-bromothiophene, Dibromohexane, n-Bromosuccinimide, CH₃MgBr, Ni(dppp)Cl₂, trimethylamine (2mol/L in THF), n-BuLi, LiF (99.99%), Al (99.998%), PC60BM (99.9%) and other materials are purchased from Alfa, or Aldrich and used without further purification. HPLC grade hexane and Tetrahydrofuran (THF) were dried over sodium. Indium-tin oxide (ITO) glass was purchased from Delta Technologies Limited, whereas PEDOT:PSS (Baytron PA14083) was obtained from Bayer Inc. 2,5-Dibromo-3-bromohexylthiophene and poly[(9,9-bis{3'-[(N,N-dimethyl)-N-ethylammonium] propyl}-2,7-fluorene)-2,7-(9,9-dioctylfluorene)-co-(4,7,-dithien-2-yl)-2,1,3-benzotiadiazole] (PFNBr-DBT15) were prepared according to the published process of McCullough et al and Cao et al. The GRIM polymerization of 3-bromohexylthiophene to produce regioregular poly(3-(6-bromohexyl)thiophene) (P3HTBr) is shown in Scheme 1.

Synthesis of HT-Poly(3-bromohexylthiophene). To a 100 mL round-bottom flask equipped for stirring was added 2,5-dibromo-3-hexylbromothiophene (2.03g, 5 mmol) and 20 mL of freshly distilled THF. CH₃MgBr (2 mL, 6 mmol) was added via syringe.

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The solution was heated to reflux and stirred for 1 h, and Ni(dppp)Cl₂ (16 mg, 0.06 mmol) was added. The mixture was stirred for 2 h, and then the reaction was quenched with methanol. The solid polymer was washed with methanol then acetone, by using a Soxhlet extractor. The polymer was dissolved by chloroform and precipitate with methanol again, and the residue was dried under vacuum to yield 0.72 g of poly-(3-bromohexylthiophene) with 59% yield.

¹H NMR (δ, CDCl₃): 6.98 (s, 1H), 3.42 (t, 2H), 2.81 (t, 2H), 1.90 (m, 2H), 1.75-1.28 (m, 8H). Anal. Calcd for C₁₀H₁₃SBr: C, 48.9; H, 5.3; Found: C, 49.1; H, 5.41. Mn=26.4 kg/mol; polydispersity = 1.82.

Synthesis of HT-Poly[3-(6'-N,N,N-trimethylammonium)-hexyl thiophene],

P3HTN. Condensed trimethylamine (5 mL) was added dropwise to a solution of the neutral polymer, Poly(3-bromohexylthiophene) (200mg) in THF (20 mL) at -78 °C. The mixture was allowed to warm to room temperature. The precipitate was redissolved by the addition of water (10 mL). After the mixture was cooled to -78 °C, extra trimethylamine (2 mL) was added and the mixture was stirred for 24h at room temperature. After removing most of the solvent, n-hexane was added to precipitate P3HTN (164mg, 66%). ¹H NMR (δ, D₂O): 7.51 (s, 1H), 3.52 (t, 2H), 2.98 (m, 2H), 1.72-1.09 (m, 8H), 1.04 (s, 9H). Anal. Calcd for C₁₃H₂₂NSBr: C, 51.3; H, 7.23; N, 4.61; Found: C, 51.1; H, 7.30; N, 4.50.

Characterizations

The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 600 NMR spectrometer with deuterated chloroform as the solvent and with

tetramethylsilane ($\delta=0$) as the internal standard. The ultraviolet–visible (UV) spectra of the samples were recorded on a PerkinElmer Lambda 750 spectrophotometer. Fluorescence measurement for photoluminescence (PL) of the polymers was carried out on a Hitachi F-7000 PC spectrofluorophotometer with a xenon lamp as the light source. The gel permeation chromatography (GPC), so-called size-exclusion chromatography (SEC) analysis, was conducted with a Breeze Waters system equipped with a Rheodyne injector, a 1515 Isocratic pump and a Waters 2414 differential refractometer using polystyrenes as the standard and tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min and 40 °C through a Styragel column set, Styragel HT3 and HT4 (19 mm×300 mm, 10^3+10^4 Å) to separate molecular weight (MW) ranging from 10^2 to 10^6 . AFM measurement was carried out using a Digital Instrumental Nanoscope 31 operated in the tapping mode. Work-function was investigated using a Kelvin probe (KP 6500 Digital Kelvin probe, McAllister Technical Services. Co., Ltd.), which can detect the contact potential difference (VCPD) and the work-function difference ($\Delta\Phi = e \times \text{VCPD}$), where e is the electron charge between the probe and the sample. Cyclic voltammograms (CV) were performed in a three-electrode cell using platinum electrodes at a scan rate of 50 mV s⁻¹ and a Ag/Ag⁺ (0.1 M of AgNO₃ in acetonitrile) reference electrode in an anhydrous and nitrogen-saturated solution of 0.1 M tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) in THF. Under these conditions, the onset oxidation potential ($E_{1/2 \text{ ox}}$) of ferrocene was 0.2 V versus Ag/Ag⁺. The HOMO energy level of polymers was determined from the oxidation onset of the second scan from CV data.

It is assumed that the redox potential of Fc/Fc^+ has an absolute energy level of -4.60 eV to vacuum. The energy of HOMO and LUMO levels were calculated according to the eqs 1 and 2; the electrochemically determined band gaps were deduced from the difference between onset potentials from oxidation and reduction of copolymers as depicted in eq 3.

$$E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{ox}} + 4.4) \text{ (eV)} \quad (1)$$

$$E_{\text{LUMO}} = -(E_{\text{onset}}^{\text{red}} + 4.4) \text{ (eV)} \quad (2)$$

$$E_{\text{gap}}^{\text{EC}} = (E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}) \text{ (eV)} \quad (3)$$

Thermal annealing: All thermal annealing processes were carried out on a calibrated and stabilized heat stage (HCS600V, INSTEC) in air for 30min. After annealing, the devices were placed on a metal plate at room temperature to cool down. Cooling was carried out under the same atmosphere as the annealing process (in air).

Device Fabrication and Characterization

The water-soluble polythiophene was used as an interfacial dipole layer in devices. The structure of the devices was ITO/PEDOT:PSS/P3HT:PCBM/P3HTN/metal cathode. Prior to use, the glass substrates were ultrasonicated for 20 min in acetone followed by deionized water and then 2-propanol. The substrates were dried under a stream of nitrogen and subjected to the treatment of UV ozone over 30 min. A filtered dispersion of PEDOT: PSS in water (Baytron A14083) was then spun-cast onto clean ITO substrates at 4000 rpm for 60 s and then baked at 140°C for 10min. A solution of P3HT (10 mg ml⁻¹) and PCBM (10 mg ml⁻¹) in 1mL of chlorobenzene was spin-coated on the PEDOT:PSS layers to obtain a thickness of 90 nm. Finally,

electrodes were deposited on top of the active layer via thermal evaporation. A 1 nm layer of LiF followed by a 100 nm layer of Al were evaporated under vacuum ($<10^{-6}$ Torr) to form the electrodes. Or a 0.2 wt% solution of P3HTN in methanol was spin coated on the P3HT:PCBM layer as an interfacial dipole layer to replace LiF. For comparison, solar cells without the P3HTN layer were also fabricated using experimental procedures identical to those used to make the cells with the P3HTN layer. The thicknesses of all the films were measured by a Dektak profiler. Current-voltage (J-V) characteristics were recorded using Keithley 2400 Source Meter in the dark and under 100 mW/cm^2 simulated AM 1.5 G irradiation (Abet Solar Simulator Sun2000). All the measurements were performed under ambient atmosphere at room temperature. EQE were detected under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon diode.

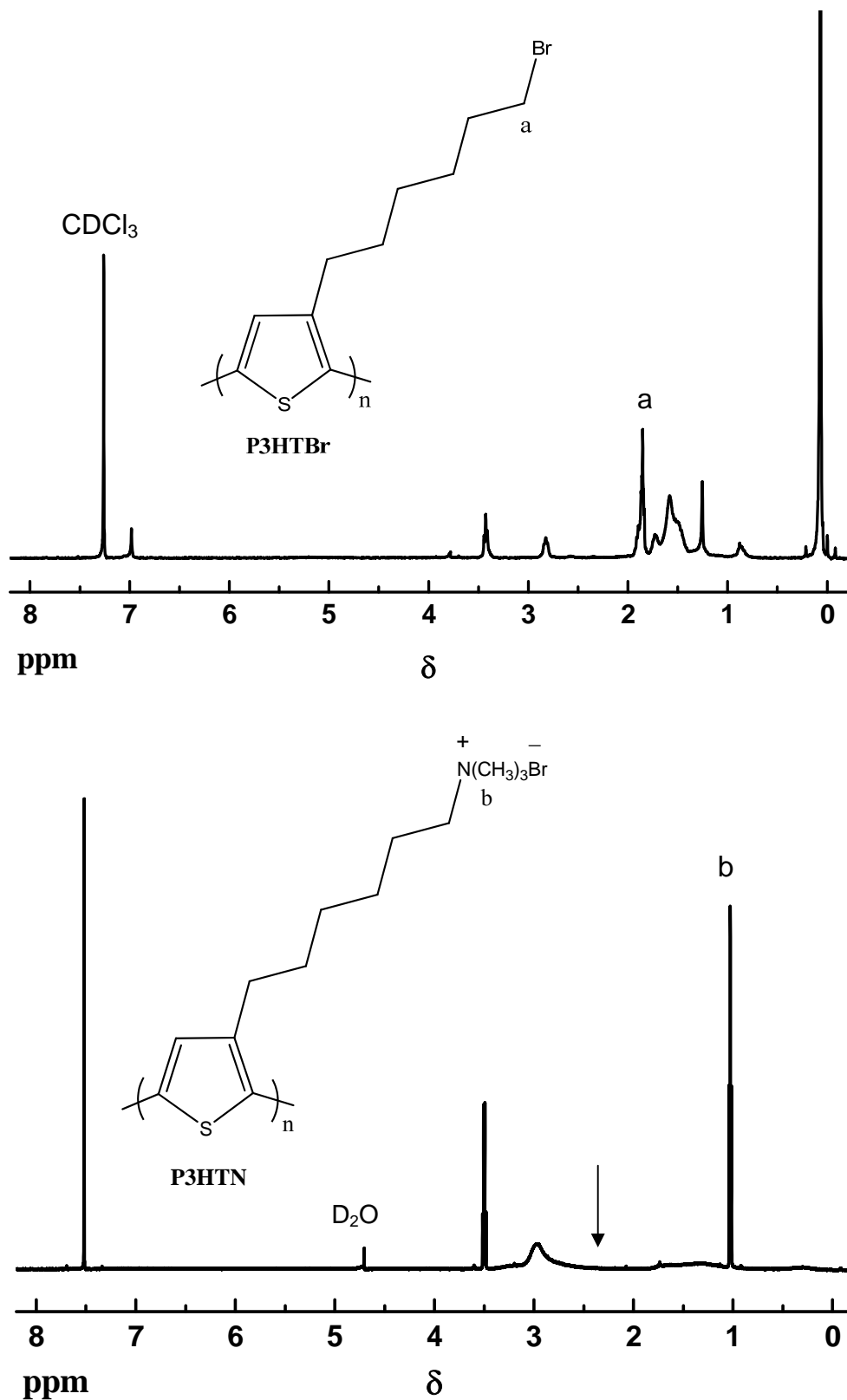


Figure S1. ^1H NMR spectra of P3HTBr (up) in chloroform-*d* and P3HTN (down) in D_2O .

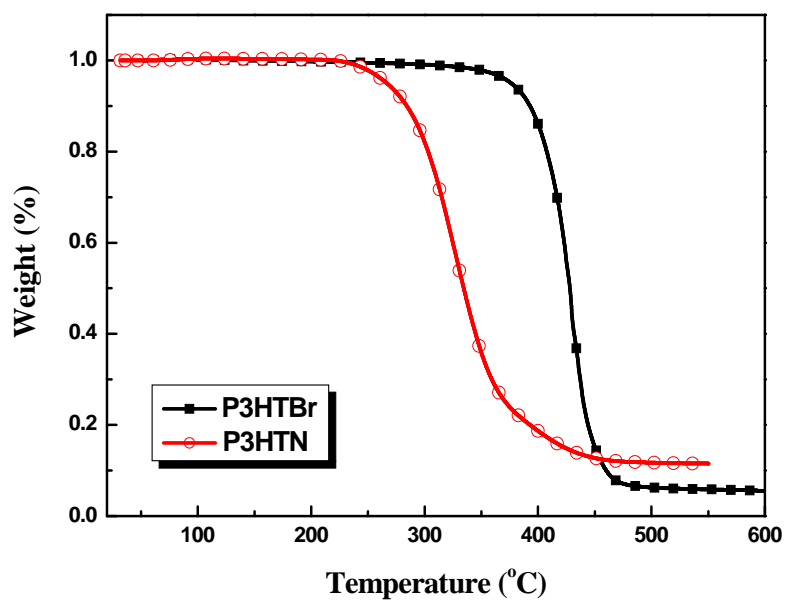


Figure S2. TG thermograms of the polymers under nitrogen at a heating rate of 10 °C/min.

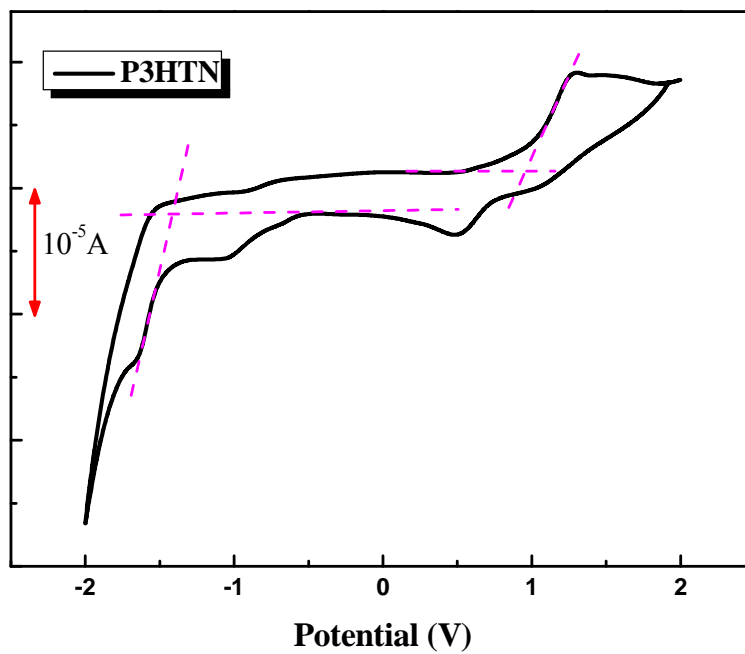


Figure S3. Cyclic voltammetry (CV) of the P3HTN thin film, measured in a 0.1 M solution of Bu₄NPF₆ in THF with a Pt electrode and a Ag/AgNO₃ reference electrode.

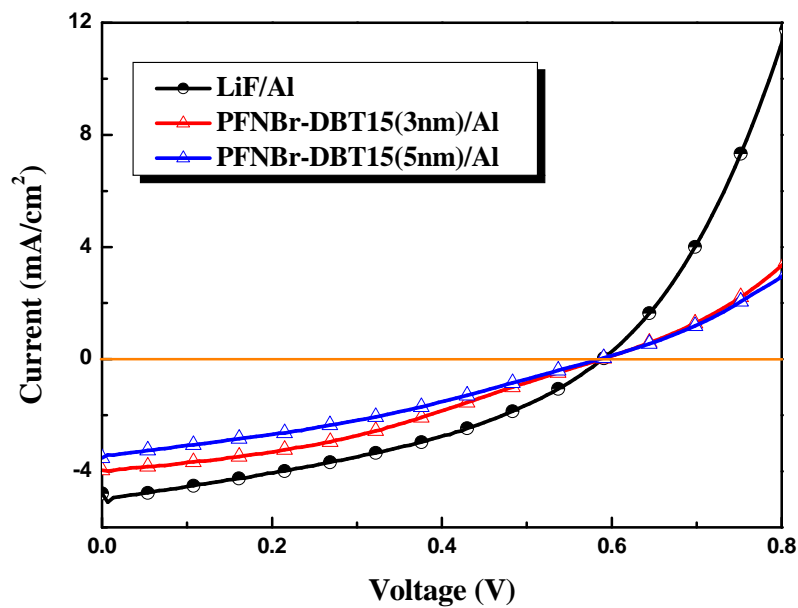


Figure S4. The current-voltage characteristics of photovoltaic cells based on devices with LiF layer (Control II: ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al) and with PFNBr-DBT15 layer (ITO/PEDOT:PSS/P3HT:PCBM/PFNBr-DBT15/Al) at different thickness without thermal treatment.

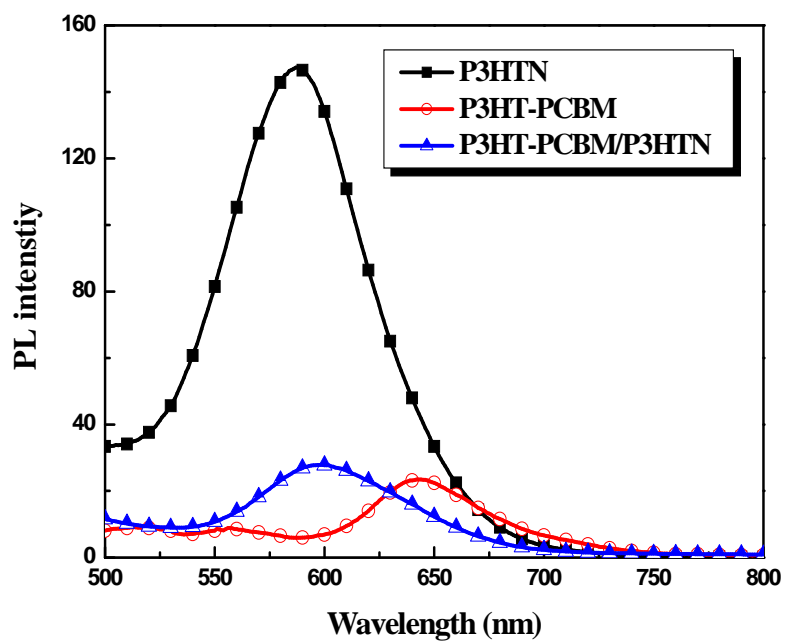


Figure S5. Fluorescence spectra of P3HTN film, P3HT:PCBM film and there bilayer films on a quartz plate. ($\lambda_{\text{ex}} = 460 \text{ nm}$)