Supporting Information for

Mesogens Induced Self-Assembly for Hybrid Bulk Heterojunction Solar Cells based on a Liquid Crystal D-A Copolymer and ZnO Nanocrystals

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Experimental Part

Materials: $Pd(PPh_3)_4$, Aliquat 336, 4,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole (**monomer 2**), LiF (99.99%), Al (99.998%) and other materials are purchased from Alfa, or Aldrich and used without further purification. Toluene and tetrahydrofuran (THF) was dried over sodium. Indium-tin oxide (ITO) glass was purchased from Delta Technologies Limited, whereas PEDOT:PSS (Baytron PAl4083) was obtained from Bayer Inc. The **monomer 1** was prepared according to the procedure in our previously reported literature.

Polymerization: The polymerization reaction and manipulations were carried out under nitrogen using Schlenk techniques in a vacuum line system or in an inert-atmosphere glovebox (Vacuum Atmospheres), except for the purification of the polymer, which was done in an open atmosphere.

P3HbpT-BTD: Monomer 1 (156 mg, 0.3 mmol) and Pinacol ester-substituted BTD (monomer 2) (116.5 mg, 0.3 mmol), K_2CO_3 (3 ml, 2 M) and 1 drop of aliquat 336 were dissolved in 5 ml toluene and 1ml water in a 50 ml Schlenk flask. The solution was purged with Argon for 30 minutes, then tetrakis(triphenylphosphine) palladium ($Pd(PPh_3)_4$) was added. The reaction was stirred at 110 ºC for 3 days. Then a toluene

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solution of phenyl boronate ester was added followed by the addition of bromobenzene and stirred overnight. The resulting mixture was poured into a mixture of methanol and concentrated hydrochloric acid (2:1) and stirred overnight. The precipitated dark solid was redissolved in THF and added dropwise to methanol (200 ml). The resulting solid was filtered off and subjected to Soxhlet extraction for 2 days in acetone. The residue was then redissolved in THF and precipitated again from methanol, filtered, washed with methanol, and dried [1]. (123 mg, 87% yield)

Synthesis of ZnO Nanoparticles: The synthesis of ZnO nanoparticles was accomplished using minor modification of the procedure previously described in the literature [2, 3]. The synthesis is carried out under N_2 atmosphere. At first, 1.23 g of $Zn(Ac)_2 \cdot 2H_2O$ was dissolved in 55 mL of methanol at room temperature. Then, 25 mL of a methanol solution containing 0.48 g of KOH is added dropwise over a 20 min time interval at 60 ^{o}C with magnetic stirring. After the KOH solution is added, the solution is stirred at 60 ^{o}C for 2 h. The product appears as a white precipitate. After collecting by centrifugation, this white precipitate is washed three times with methanol until it transforms to a gel-like precipitate. Each washing process includes dispersion into methanol by sonication and subsequent centrifugation. Finally, the gel-like precipitate is redispersed in chlorobenzene and 10 vol % of propanol is added for stabilization.

P3HbpT-BTD/ZnO blend (1:3 wt %). Blend of **P3HbpT-BTD** and **ZnO** NPs were prepared starting by dissolving **P3HbpT-BTD** in chlorobenzene. The exact amount of the ZnO nanoparticle stock solution needed to reach the desired amounts of ZnO in the blends was determined from the ZnO concentration in the sol. This ZnO concentration was determined from the solid residue after solvent evaporation. The ZnO solution was used within three days after synthesis, because this led to the best cells with the highest reproducibility. On average a ZnO concentration of 60 mg/ml had been obtained. In a typical procedure, **P3HbpT-BTD** (5 mg) was dissolved in chlorobenzene (0.5 mL), 250 μL of a chlorobenzene was added, followed by 250 μL of the ZnO solution. Finally, 1 ml chlorobenzene solution of **P3HbpT-BTD/ZnO** blend was obtained.

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 (δ=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 ^{o}C through a Styragel column set, Styragel HT3 and HT4 (19 mm$\times$300 mm, 10^3+10^4 Å) to separate molecular weight (MW) ranging from 10^2 to 10^6. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA 7 for thermogravimetry at a heating rate of 10 ^{o}C/min under nitrogen with a sample size of 8–10 mg. Differential scanning calorimetry (DSC) was used to determine phase-transition temperatures on a Perkin-Elmer DSC 7 differential scanning calorimeter with a constant heating/cooling rate of 20 ^{o}C/min. Texture observations by polarizing optical microscopy (POM) were made with a Nikon E600POL polarizing optical microscope equipped with an Instec HS 400 heating and cooling stage. The X-ray diffraction (XRD) study of the samples was carried out on a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target (λ =1.54 Å) and at a scanning rate of 1^{o}/min. The fluorescence lifetime was determined with an Edinburgh Instrument FLS920 fluorescence spectrophotometer using a H_2 gas lamp as the light source. TEM images were recorded using a JEOL-2100F transmission electron microscope and an internal charge-coupled device (CCD) camera. The surface morphology observations of active layer films were made by Atomic force microscopic (AFM) images which were measured on a nanoscope III A (Digital Instruments) scanning probe microscope using the tapping mode. Cyclic voltammograms (CV) were performed in a three-electrode cell using platinum electrodes at a scan rate of 50 mV/s and a Ag/Ag+ (0.1 M of $AgNO_3$ in acetonitrile) reference electrode in an anhydrous and nitrogen-saturated solution of 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in acetonitrile. The HOMO energy level of polymers was determined from the oxidation onset of the second scan from CV data. 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 [4-6].

$$E_{HOMO} = -\,(E_{onset}^{ox} + 4.71)\ (\mathrm{eV}) \qquad (1)$$

$$E_{LUMO} = -(E_{onset}^{red} + 4.71)\ (\mathrm{eV}) \qquad (2)$$

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

Annealing of films was conducted by heating in the setting temperature for 1 h, followed by cooling to room temperature at a cooling speed of 1 deg/min. All the thermal treatments were performed under ambient atmosphere.

Device Fabrication and Characterization

The hybrid solar cells were fabricated with the active layer consisting of the copolymer **P3HbpT-BTD/ZnO NPs** in 1:3 (wt/wt). The 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 Al4083) was then spun-cast onto clean ITO substrates at 4000 rpm for 60 s and then baked at 120 ^{o}C. The copolymer were dissolved in chlorobenzene to make 20 mg·mL^{-1} solutions, followed by blending with ZnO nanoparticles (60 mg/ml dispersed in chlorobenzene) in 75 wt %. The active layers were obtained by spin-coating the blend solutions at 1200 rpm for 60 s and the thickness of films were ~ 90 nm. Subsequently, LiF (0.8 nm) and Al (100 nm) electrodes were deposited via thermal evaporation in vacuum (<10^{-6} Torr) in thickness of approximately. The thicknesses of all the films were measured by a Dektak profiler. Annealing of some devices was conducted by heating at different temperatures for 60 min, followed by cooling to room temperature at a cooling speed of 1 deg/min. 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 Sun 2000). 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.

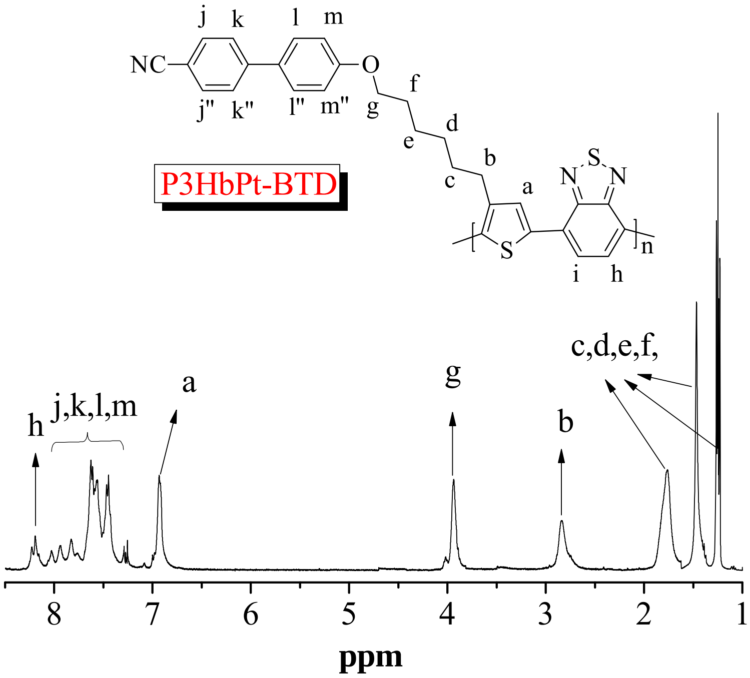

Figure S1. ^{1}H NMR spectrum of **P3HbpT-BTD.**

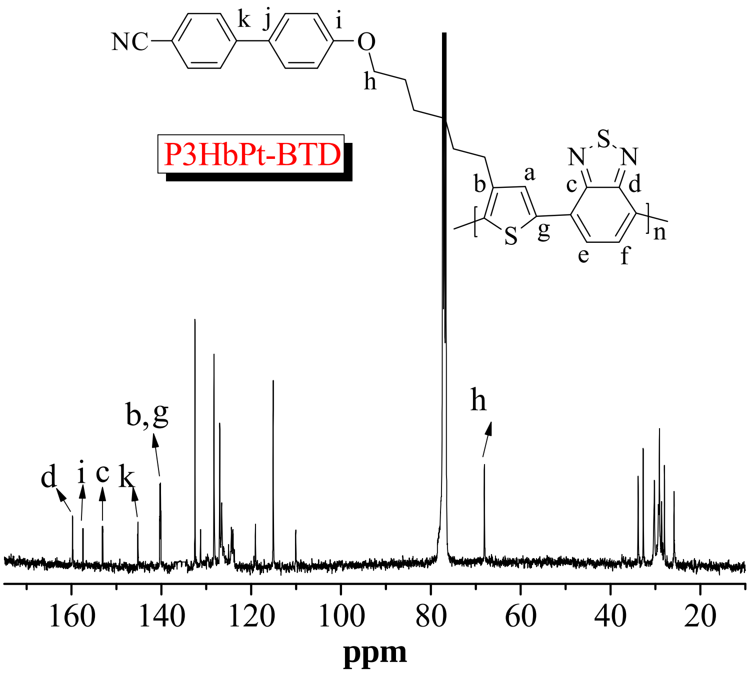

Figure S2. ^{13}C NMR spectrum of **P3HbpT-BTD.**

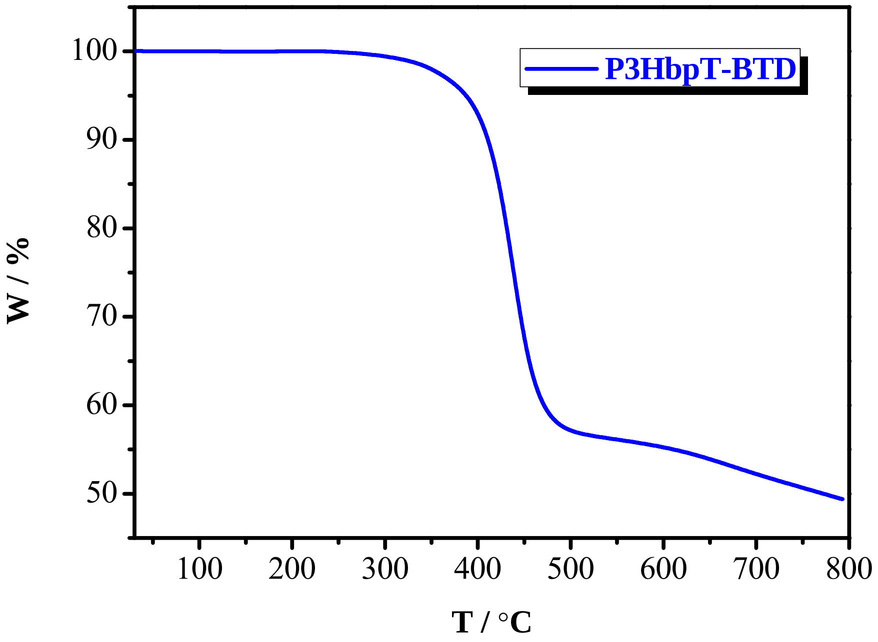

Figure S3. TG thermograms of the **P3HbpT-BTD** under nitrogen at a heating rate of 20 ^{o}C/min.

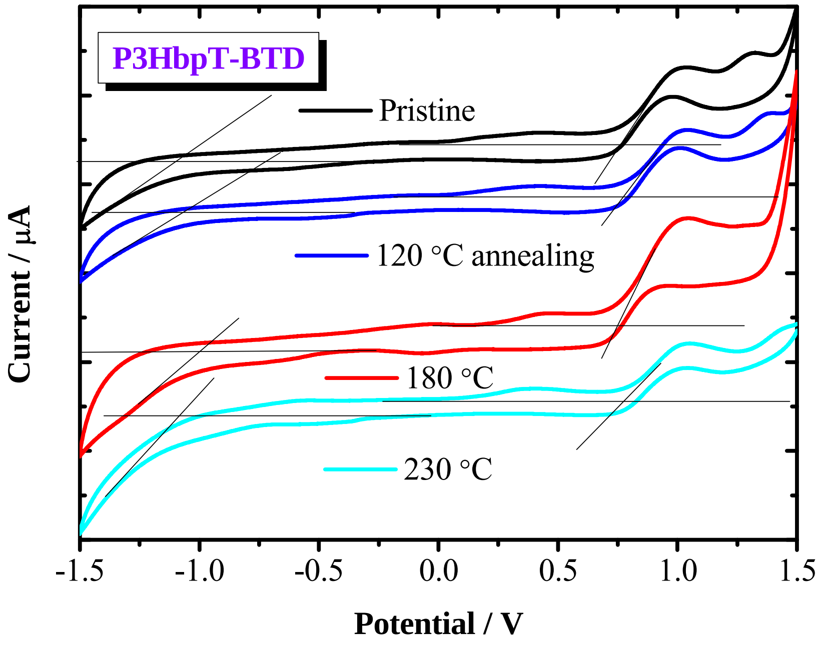

Figure S4. Cyclic voltammetry (CV) of the **PFcbpDTBT** thin films annealed at 120 °C, 180 °C and 230 °C for 60 min followed by cooling to room temperature (cooling speed: 1 deg/min). Measured in a 0.1 M solution of Bu_4NPF_6 in CH_3CN with a Pt electrode and a $Ag/AgNO_3$ reference electrode.

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