

Supporting Information

A Wide Bandgap Conjugated Polymer Based on a Vertically-Connected Benzodithiophene Unit Enabling Efficient Non-Fullerene Polymer Solar Cells

Yuhang Liu,^{a†} Shangshang Chen,^{a†} Guangye Zhang^{a†}, Philip C.Y. Chow,^a and He Yan.^{a,b}

^a Department of Chemistry and Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration & Reconstruction, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

† These authors contributed equally.

I. Experimental section.

1. Materials and Methods.

Materials. All reagents and chemicals were purchased from commercial sources and used without further purification unless stated otherwise. Tetrahydrofuran (THF) was freshly distilled before use from sodium using benzophenone as indicator. Anhydrous chlorobenzene were purchased from Sigma-Aldrich, and used as received. benzo[1,2-b:4,5-b']dithiophene-4,8-dione was purchased from Sunatech. ITIC-Th were synthesized according to literature procedure.

Characterizations of new compounds. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400 MHz NMR spectrometer. Chemical shifts are reported in parts per million (ppm, δ). ^1H NMR and ^{13}C NMR spectra were referenced to tetramethylsilane (0 ppm) or solvent residual peak (7.26 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR) as internal standard.

Electrochemical characterizations. The electrochemical cyclic voltammetry (CV) was performed in a 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile (ACN) solution with a scan speed at 0.1 V s⁻¹. A Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. A ferrocene/ferrocenium redox couple was used as an external standard. The results of CV characterization show that the increase of bandgap of PvBDTffBT comes from the raised LUMO level and instead of the down-shift of the HOMO level. Generally, a more electron-deficient unit should down-shift the HOMO level of the polymers, but it is important to note that the repeating unit of the PvBDTffBT polymer contains 36 π electrons along the polymer backbone, while the repeating unit of the PBDTffBT polymer contains 32 π electrons. (The π electrons on the alkyl thienyl side chain of PBDTffBT or on the fused thiophene units of PvBDTffBT are excluded, because these π electrons are not located on the polymers' conjugated backbone.) This means that the PvBDTffBT polymer contains one electron-deficient ffBT unit per 36 π electrons, while the PBDTffBT polymer contains one ffBT unit per 32 π electrons. Therefore, the effective density of ffBT units on the polymer backbone is lower for the PvBDTffBT polymer. As reported for quarterthiophene and terthiophene based ffBT polymers, when the effective density of ffBT units are lower (for the quarterthiophene polymers), the HOMO and LUMO levels of the polymer will be up-shifted. (*J. Am. Chem. Soc.*, **2015**, *137* (44), pp 14149–14157) For PBDTffBT and PvBDTffBT, although the vBDT unit should down-shift the HOMO level, the lower effective density of ffBT units in PvBDTffBT has an effect to up-shift the HOMO. The overall result of these two counter-acting effects is the slight up-shifted HOMO of PvBDTffBT.

UV-Vis absorption spectra were acquired on a Gary 50 UV-Vis Spectrometer. All film samples were spincoated on ITO/ZnO substrates, and a blank ITO/ZnO substrate is used as baseline for the film of the UV experiments.

AFM analysis. AFM measurements were performed by using a Scanning Probe Microscope-Dimension 3100 in tapping mode. All film samples were spincoated on ITO/ZnO substrates.

Hole-only device. The hole mobilities were measured using the space charge limited current method (SCLC) method, employing a device architecture of glass/ITO/V₂O₅/PvBDTffBT or PBDTffBT/V₂O₅/Al by taking current-voltage curves and fitting the results to a space charge limited form, where the SCLC is described by:

$$J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$$

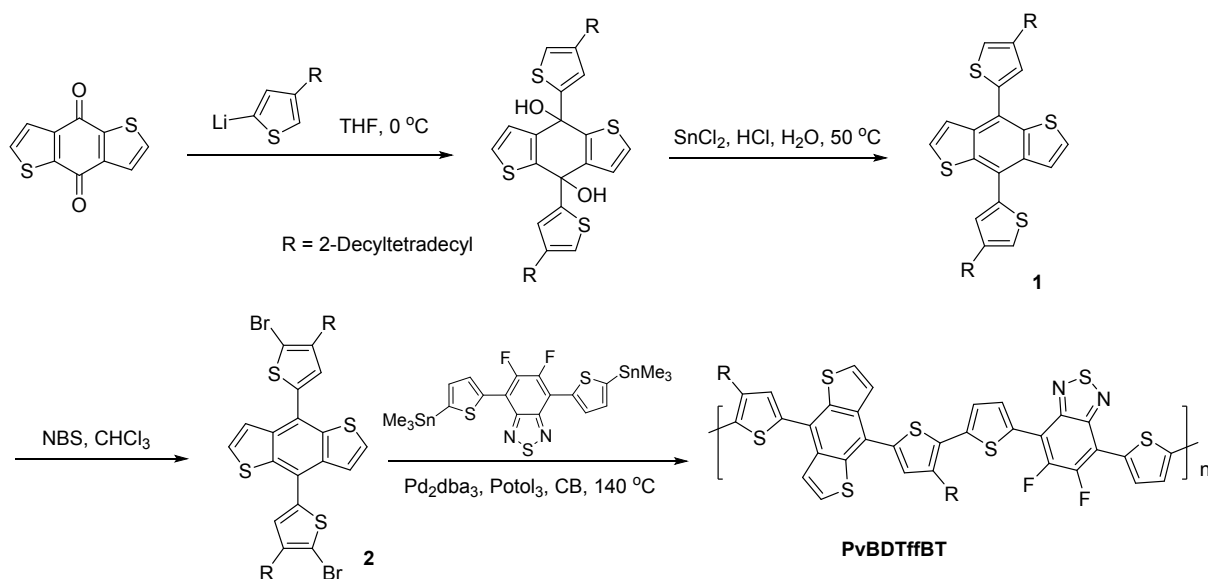
Where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, μ is the electron mobility, V is the voltage drop across the device and L is the thickness of the film.

Solar cell fabrication and testing. Diethylzinc (15% wt in toluene) and vanadium (V) oxide (V_2O_5) were purchased from Sigma-Aldrich and used as received without further treatment. Pre-patterned ITO-coated glass substrates were cleaned by sequential sonication in soap deionized water, deionized water, acetone, and isopropanol for 30 min of each step. After UV/ozone treatment for 60 min, a ZnO electron-transporting layer (~23 nm) was prepared by spin-coating a ZnO precursor solution (diethyl zinc, diluted with tetrahydrofuran) at 5000 rpm. Active layer solutions (D:A ratio 1:1.5 w/w) were prepared in DCB (polymer concentration: 10 mg mL⁻¹. To completely dissolve the polymer, the active layer solution should be stirred on a hotplate at 100 °C for at least 1 hour. Before spin-coating, both the polymer solution and ITO substrates were preheated on a hotplate at ~100 °C. Active layers were spin-coated from the warm polymer solutions onto the preheated substrates in a N₂ glovebox at 1200-1500 rpm. The blend films were then annealed at 90 °C for 5 min, before being transferred to the vacuum chamber of a thermal evaporator inside the same glovebox. At a vacuum level of ~1.5×10⁻⁴ Pa, a thin layer (7 nm) of V₂O₅ was deposited as the anode interlayer, followed by the deposition of 100 nm of Al as the top electrode. The optimized active layer thickness for PvBDTffBT:ITIC-Th and PBDTffBT:ITIC-Th were 94 nm and 90 nm, respectively. All devices were encapsulated using epoxy inside the glovebox.

Characterizations: Device *J-V* characteristics were measured under AM 1.5G (100 mW cm⁻²) using a Newport solar simulator. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity. *J-V* characteristics were recorded using a Keithley 2400 source meter unit. Typical cells have devices area of 5.9 mm², defined by a metal mask with an aperture aligned with the device area. EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source. These test protocols are exactly the same as that we used in previously certified OPVs. All thicknesses of the layers involved were determined by variable angle spectroscopic ellipsometry (J. A. Woollam Co. α -SE) in the transparent wavelength range of the films.

Synthesis

Synthetic method of the monomer of PvBDTffBT



4,8-bis(4-(2-decyltetradecyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (1). To a solution of 3-(2-decyltetradecyl)thiophene (4.2 g, 10 mmol) in THF (40 mL) was added butyllithium solution (5 mL, 2.0 M in hexane) dropwise at 0 °C. The solution was then allowed to stir at 0 °C for 1 h before benzo[1,2-b:4,5-b']dithiophene-4,8-dione (550 mg, 2.5 mmol) was added in one portion. The resulting yellow solution was allowed to stir at 50 °C for 2 h before SnCl₂ 2H₂O (11 g, 50 mmol) in 10% HCl solution (40 mL) was added and the solution was allowed to stir for additional 2 h. Hexane was added to the mixture and was followed by washing with water for three times and dried over sodium sulphate. The resulting yellow oil was purified by flash chromatography to get pure product as yellowish oil. (1.8 g, 70 %)

¹H NMR: 7.65 (d, J = 5.6 Hz, 2H), 7.42 (d, J = 5.6 Hz, 2H), 7.29 (s, 2H), 7.08 (s, 2H), 2.62 (d, J = 5.5 Hz, 4H), 1.80 – 1.69 (br, 2H), 1.48 – 1.21(m, 80H), 0.92 (t, J = 6.4 Hz, 12H).

¹³C NMR: (100 MHz, CDCl₃) δ 142.30, 139.10, 136.52, 129.98, 127.55, 124.15, 123.31, 121.88, 53.41, 39.10, 35.04, 33.52, 31.94, 30.08, 29.73, 29.68, 29.38, 26.77, 22.71, 14.13.

4,8-bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (2). To a solution of **2** (1g, 0.93 mmol) was added NBS (375.9 mg, 2.1 mmol) in one portion at 0 °C and the reaction was allowed to stir overnight. After finished, the solvent was removed under reduced pressure, and the residue yellow oil was purified by flash chromatography to get pure product as yellowish oil. (960 mg, 87%).

¹H NMR: 7.59 (d, J = 5.6 Hz, 2H), 7.47 (d, J = 5.6 Hz, 2H), 7.13 (s, 2H), 2.61 (d, J = 5.5 Hz, 4H), 1.80 – 1.69 (br, 2H), 1.48 – 1.21(m, 80H), 0.89 (t, J = 6.4 Hz, 12H).

¹³C NMR: (100 MHz, CDCl₃) δ 141.03, 138.44, 135.86, 129.14, 127.36, 122.82, 122.36, 110.01, 37.96, 33.69, 32.91, 31.31, 29.43, 29.09, 29.05, 29.02, 26.02, 22.07, 13.50.

General procedure for preparing the polymers by stille crosscoupling.

To a mixture of dibromo monomer (0.1 mmol), ditin monomer (0.1 mmol), Pd₂(dba)₃ (0.5 mg, 0.00055 mmol) and P(o-tol)₃ (1 mg, 0.0033 mmol) were added 300 μL chlorobenzene in a glove box protected with N₂. The reaction mixture was then sealed and heated at 140 °C overnight. The mixture was cooled to *r.t.* and 20 mL toluene was added before precipitated from methanol. The solid was collected by filtration, and loaded into an extraction thimble and consequentially washed with hexane, ethyl acetate,

dichloromethane, chloroform and chlorobenzene. The polymer PvBDTffBT was collected from chlorobenzene and PBDTffBT from chloroform. The resulting solution was then concentrated by evaporation, precipitated into methanol. The solid was collected by filtration and dried in vacuo to get the polymer as final product. PvBDTffBT, dark red solid, (84.4 mg, 62%), PBDTffBT, dark green solid, (48.2 mg, 35%).