Supporting information for

A novel benzodipyrrolidone-based low band gap polymer for organic solar cells

Materials and synthesis

Extra dry *o*-DCB and toluene were obtained from Sigma-Aldrich and used as received. Compound **1** and **2** were prepared according to literature procedure.

Polymerization of PBDPDP-DTP

A mixture of 2,6-di(trimethyltin)-*N*-(1-pentylhexyl)dithieno[3,2-*b*:2',3'-*d*]-pyrrole (**1**, 93.3 mg, 0.142 mol), 3,7-bis(4-bromophenyl)-1,5-bis(2-ethylhexyl)pyrrolo[2,3-*f*]indole-2,6(1*H*,5*H*)-dione (100 mg, 0.139 mol), tris(dibenzylideneacetone)dipalladium (Pd₂dba₃, 2.60 mg, 2.80 x 10⁻³ mmol), and tri-*o*-tolylphosphine (P(*o*-Tol)₃, 6.80 mg, 2.22 x 10⁻² mmol) was degassed with N₂, and then toluene (14 mL) was added. The mixture was further purged with N₂ for 20 min and heated to 120 °C for 48 h. After being cooled to room temperature, the solution was precipitated into methanol. The crude polymer was collected by filtration and then extracted on a Soxhlet's extractor with acetone, hexane and chloroform in succession. The final polymer was obtained by precipitating the chloroform solution in methanol as a dark brown sheet with a yield of 72% (90.0 mg). GPC: M_n 29000; PDI 3.65. ¹H NMR (600 MHz, CDCl₃, δ , ppm): 7.42-7.83 (m, 8 H), 7.17-7.26 (m, 2 H), 6.27 (s, 2H), 4.28 (s, br, 1 H), 3.58-3.63 (m, 4 H), 1.80-2.16 (m, br, 6 H), 1.16-1.50 (m, br, 28 H), 0.84-0.99 (m, br, 18 H). Anal. Calcd for C₅₇H₇₁N₃O₂S₂ (%): C, 76.55; H, 8.00; N, 4.70. Found (%): C, 76.41; H, 8.11; N, 4.76.

Measurements

¹H NMR spectra were recorded on a Bruker Avance III 600 spectrometer. High temperature gel permeation chromatography (HT-GPC) measurements were conducted on PL-GPC220

equipment at 150 °C with 1,2,4-trichlorobenzene as eluent and polystyrene as standards. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 449C Jupiter simultaneous thermal analyzer at a heating rate of 10 °C min⁻¹ under Argon flow. UV-vis absorption was recorded on a Varian 50 Bio UV-vis spectrophotometer. Elemental analysis was performed on a PerkinElmer 2400 system. Cyclic voltammetry (CV) was performed on a CHI660B electrochemical analyzer (CH Instruments) using a three-electrode cell set up with 0.1 M TATBF₄ in acetonitrile as electrolyte at a scan rate of 200 mV·s⁻¹. A glassy carbon working electrode with a diameter of 1 mm, a platinum-counter electrode, and Ag/Ag⁺ phedo reference electrode had been applied. The potential was calibrated against the ferrocene/ferrocenium redox couple (Fc/Fc⁺, 4.8 eV below the vacuum level). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were estimated by the equations: HOMO = - (4.80 + E_{ext}^{onset}), and LUMO = - (4.80 + E_{ext}^{onset}). Tapping-mode AFM images was obtained with a Veeco Multimode V instrument.

Solar Cells Fabrication and Characterization

PSCs were fabricated with a structure of ITO/PEDOT:PSS/**PBDPDP-DTP**:PCBM/LiF (0.6 nm)/Al (100 nm). Firstly, patterned ITO glass substrates were cleaned by sequential ultrasonic treatment in detergent-water, acetone, deionized water and isopropyl alcohol, the organic residue was further wiped off in UV-ozone for 20 min. Secondly, a thin film of PEDOT:PSS (~40 nm) was spin-coated on the substrates and dried at 150 °C for 20 min. Then the active layer with a thickness of 90-110 nm was prepared by spin-coating the chloroform or chlorobenzene solution containing 1.5% (v/v) DIO of **PBDPDP-DTP** and PCBM on the substrate. Finally Al and LiF anode was deposited at a vacuum level of 1.0×10^{-6} mbar through a shadow mask (active area 7.25 mm²). The current density-voltage characteristics of the PSCs were measured by using a

Keithley 2400 (I-V) digital source meter under a simulated AM 1.5 G solar irradiation at 100 mW cm⁻² (Newport, Class AAA solar simulator, 94023A-U). The light intensity is calibrated by a certified Oriel Reference Cell (91150V). The external quantum efficiency (EQE) was performed using a certified IPCE equipment (Zolix Instruments Inc, SolarCellScan 100).

Hole-only and Electron-only Devices

Hole-only and electron-only devices were fabricated to measure the hole and electron mobility of the blend films using the space charge limited current (SCLC) method. The device structure is ITO/PEDOT:PSS/Polymer:PCBM (1:2)/MoO₃/Al and ITO/Al/Polymer:PCBM (1:2)/LiF/Al. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation $J = 9/8 \varepsilon_0 \varepsilon_r \mu_{h,e} (V^2)/(d^3)$, where J is the current, $\mu_{h,e}$ is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi}$.



Figure S1. TGA plots of PBDPDP-DTP.



Figure S2. Cyclic voltammograms of **PBDPDP-DTP** films with TATBF₄ (0.1 M in acetonitrile) as the electrolyte at a scan rate of 200 mV \cdot s⁻¹.



Figure S3. $J^{1/2}$ vs. V characteristics of blend films hole-only (a) and electron-only (b) devices.



Figure S4. AFM height images of **PBDPDP-DTP**:PCBM (1:2) blend films: cast from chloroform solution (left), cast from chlorobenzene solution (right).

Table S1. Charge transport properties of Polymer:PCBM blend films measured by the SCLC method ($cm^2V^{-1}s^{-1}$).

	Chloroform	CB
Hole-mobility	$1.0 imes 10^{-6}$	$2.0 imes 10^{-5}$
Electron-mobility	3.50×10^{-4}	2.50×10^{-4}