Supporting Information for

Synthesis of 5H-dithieno[3,2-b:2',3'-d]pyran as an Electron-rich Building Block for Donor-Acceptor Type Low-bandgap Polymers

Letian Dou^{1,2}, Chun-Chao Chen¹, Ken Yoshimura^{3*}, Kenichiro Ohya³, Wei-Hsuan Chang^{1,2}, Jing Gao¹, Yongsheng Liu¹, Eric Richard¹ and Yang Yang^{1,2*}

¹⁾ Department of Materials Science and Engineering, ²⁾ California NanoSystems Institute, University of California, Los Angeles, California 90095, USA. ³⁾ Tsukuba Material Development Laboratory, Sumitomo Chemical Co., Ltd.

1. Materials Characterization

Instrumentation. ^1H and ^{13}C NMR spectra were measured on a Bruker ARX-400 spectrometer. Absorption spectra were taken on a Varian Cary 50 ultraviolet-visible spectrometer. Gel permeation chromatographic analysis (GPC) was performed on a Varian Star Chromatography Workstation (column: MIXED-C from Polymer Laboratories) connected with one UV-Vis detector from Varian (ProStar 340). All GPC analyses were performed on polymer/chloroform solution at the flow rate of 1 ml/min at 40 °C and calibrated with polystyrene. TGA measurement was performed on a Perkin-Elmer TGA-7 under nitrogen protection. X-ray fluorescence (XRF) was carried out using Rigaku supermini X-ray Fluorescence spectrometer (wavelength dispersive X-ray fluorescence mode, X-ray tube: 50 kV, 200 W Pd-anode). Around 100 mg polymer powder was used for each testing. The electrochemical cyclic voltammetry (CV) was conducted with Pt disk, Pt plate, and Ag/AgCl electrode as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The polymer films for electrochemical measurements were coated from a polymer chloroform solution, ca. 5 mg/mL. For calibration, the redox potential of ferrocene/ferrocenium (Fc/Fc^+) was measured under the same conditions, and it is located at 0.39 V vs. the Ag/AgCl electrode. It is assumed that the redox potential of Fc/Fc^+ has an absolute energy level of -4.80 eV to vacuum. The energy levels of the highest (HOMO) and lowest unoccupied molecular orbital (LUMO) were then calculated according to the following equations

$$E_{\text{HOMO}} = -(\phi_{\text{ox}} + 4.39) \text{ (eV)}$$

$$E_{\text{LUMO}} = -(\phi_{\text{re}} + 4.39) \text{ (eV)}$$

Where φ_{ox} is the onset oxidation potential vs Ag/AgCl and φ_{re} is the onset reduction potential vs Ag/AgCl.

Computational Calculation

The geometry of all compounds was subjected to density functional theory (DFT) optimizations by Gaussian 03 software package. Hybrid three-parameter B3LYP functional combined with 6-31G(d) basis set was used. The highest occupied molecular orbital (HOMO) as well as lowest unoccupied molecular orbital (LUMO) energy levels were analyzed using minimized singlet geometries to approximate the ground state.

2. Device Fabrication and Measurement

Bulk hetero-junction solar cell device. PDTP-DFBT was co-dissolved with PC₇₁BM in 1,2-dichlorobenzene (DCB) with a weight ratio of 1:2 with a concentration of 8 mg/mL. ITO-coated glass substrates (15Ω/cm²) were cleaned stepwise in detergent, water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried in an oven for 5 h. A thin layer (~30 nm) of PEDOT:PSS (Baytron P VP A1 4083) was spin-coated onto the ITO surface which was pretreated by ultraviolet ozone for 15 min. Low-conductivity PEDOT:PSS was chosen to minimize measurement error from device area due to lateral conductivity of PEDOT:PSS. After being baked at 120 °C for ~ 20 min, the substrates were transferred into a nitrogen-filled glove box (<0.1 ppm O₂ and H₂O). A polymer/PC₇₁BM composite layer (ca.100 nm thick) was then spin-cast from the blend solutions at 2500 rpm on the ITO/PEDOT:PSS substrate without further special treatments. Then the film was transferred into a thermal evaporator that is located in the same glovebox. A Ca layer

(20 nm) and an Al layer (100 nm) were deposited in sequence under a vacuum of 2×10^{-6} torr. The effective area of the device was measured to be 0.10 cm^2 .

Current-voltage measurement. The fabricated device was encapsulated in a nitrogen-filled glovebox by UV cured epoxy and a cover glass. The current density-voltage (J-V) curves were measured using a Keithley 2400 source-measurement unit. The photocurrent was measured under AM 1.5 G illumination at 100 mW/cm^2 under a Newport Thermal Oriel 91192 1000W solar simulator. The light intensity was determined by a Si photodiode as a reference cell, followed by the calculation of spectral mismatch factor and then short circuit current (J_{SC}) correction. External quantum efficiencies (EQEs) were measured using a lock-in amplifier (SR830, Stanford Research Systems) with current preamplifier (SR570, Stanford Research Systems) under short-circuit conditions. The devices were illuminated by monochromatic light from a xenon lamp passing through a monochromator (SpectraPro-2150i, Acton Research Corporation) with a typical intensity of $10 \mu\text{W}$. The photocurrent signal is then amplified by an SR570 and detected with an SR830. A calibrated monosilicon diode with known spectral response is used as a reference.

Hole mobility. Hole mobility was measured using the space charge limited current model (SCLC), using a diode configuration of ITO/PEDOT:PSS/polymer:PC₇₁BM/Au and taking current-voltage measurements in the range of 0-10 V and fitting the results to a space charge limited form, where the SCLC is described by

$$J = (8/9)\epsilon_r\epsilon_0\mu_e(V^2/L^3)$$

Where ϵ_0 is the permittivity of free space, ϵ_r is the dielectric constant of the polymer, μ is the hole mobility, V is the voltage drop across the device ($V = V_{\text{appl}} - V_r - V_{bi}$, where V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact

resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the difference in work function of the two electrodes), L is the polymer thickness. The dielectric constant ϵ_r is assumed to be 3, which is a typical value for conjugated polymers. The thickness of the polymer films is measured by using a Dektak profilometer.

Transmission electron microscopy measurements. Transmission electron microscopy was conducted with a JEOL 2010F electron microscope.

Figure S2. ^1H NMR spectrum of compound M1 at 298 K.

Figure S3. ^1H NMR spectrum of PDTP-DFBT at 298 K.

Figure S4. TGA plots of PDTP-DFBT with a heating rate of 5 °C/min under nitrogen.

Figure S5. Comparison of the curvature and molecular geometry of three repeating units of BDT, CPDT, and DTP based co-polymers at minimized energy.

Figure S6. Calculated HOMO/LUMO levels by DFT for BDT, CPDT and DTP units.

Figure S7. Current density-voltage characteristics of PDTP-DFBT/PC₇₁BM single junction solar cells at different blend ratios under AM1.5G illumination (100 mW/cm²).

Figure S8. Current density-voltage characteristics of low molecular weight PCPDT-DFBT(DMO)/PC₇₁BM single junction solar cells under AM1.5G illumination (100 mW/cm^2).

Figure S9. TEM image of PCPDT-DFBT-DMO:PC₇₁BM (w/w=1:2) blend film casted from CB with 3% DIO.