Supplementary Information

Efficient Small Molecule Organic Semiconductor containing Bis-dimethylfluorenyl Amino Benzo[*b*]thiophene for High Open Circuit Voltage in High Efficiency Solution Processed Organic Solar Cell

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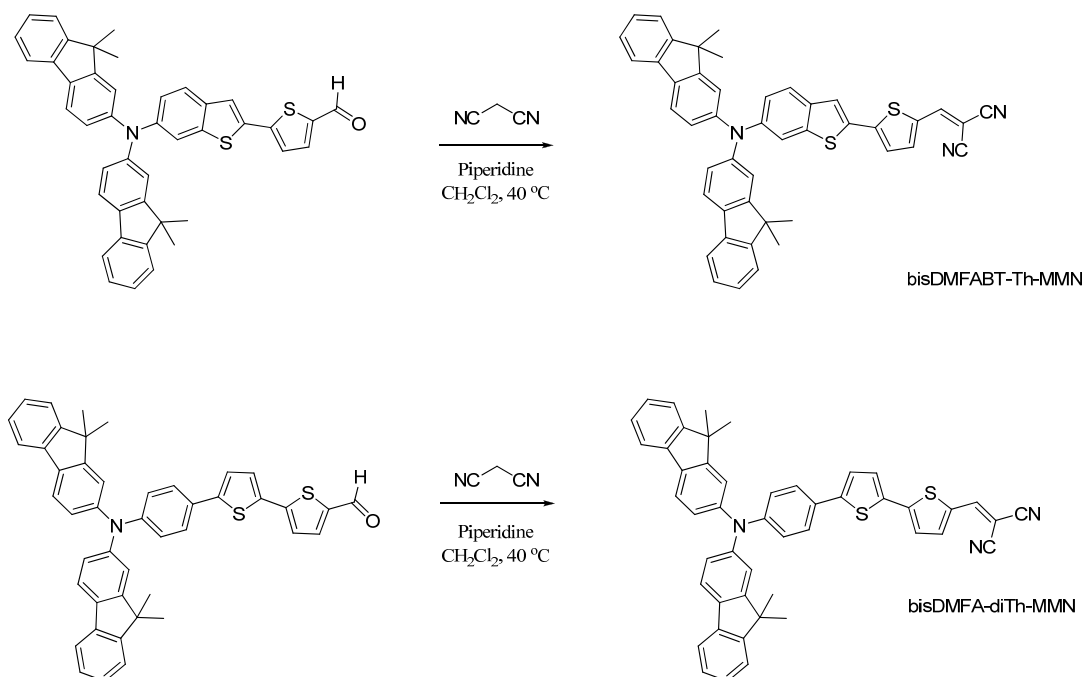
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S1. Schematic Diagram for the Synthesis of the **bisDMFA-diTh-MMN** and **bisDMFABT-Th-MMN**.

The synthetic procedures of **bisDMFABT-Th-MMN** and **bisDMFA-diTh-MMN** are shown. **BisDMFA-diTh-MMN,** 2-((5'-(4-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)phenyl)-2,2'-bithiophen-5-yl)methylene)malononitrile[1-3] and 5-(6-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)benzo[*b*]thiophen-2-yl)thiophene-2-carbaldehyde[4] were prepared according to the procedure reported previously. **BisDMFABT-Th-MMN** was synthesized by Knoevenagel condensation reaction using 5-(6-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)benzo[*b*]thiophen-2-yl)thiophene-2-carbaldehyde[4] and electron withdrawing group such as malononitrile.

S2. Synthesis and Characterization of Materials.

General Information

5-(6-(bis(9,9-dimethyl-9H-fluoren-2-yl)amino)benzo[b]thiophen-2-yl)thiophene-2-carbaldehyde was synthesized according to the procedure in the literature. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Mercury 300 spectrometer, a Varian/Oxford As-500 (500 MHz) spectrophotometer. Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants in Hertz.

2-((5-(6-(bis(9,9-dimethyl-9H-fluoren-2-yl)amino)benzo[b]thiophen-2-yl)thiophen-2-yl)methylene)malononitrile

Malononitrile (8.5 mg, 0.13 mmol) and piperidine (3~5 drops) were added to a solution of 5-(6-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)benzo[*b*]thiophen-2-yl)thiophene-2-carbaldehyde[4] (84 mg, 0.13 mmol) in CH_2Cl_2 (20 ml) at room temperature. The reaction mixture was heated under reflux for 24 hours. Concentration and purification of the residue by flash column chromatography (Hexane:Ethyl Acetate=4:1) gave 2-((5-(6-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)benzo[*b*]thiophen-2-yl)thiophen-2-yl)methylene)malononitrile (65 mg, 72 %). m/s: 691.0703 R_f 0.5 (Hexane:Ethyl Acetate=4:1). ^{1}H NMR (300 MHz, CDCl_3): δ 7.76 (s, 1H), 7.75 (d, 1H J = 6.9 Hz), 7.67-7.62 (m, 8H), 7.56-7.54 (m, 2H), 7.41-7.24 (m, 8H), 7.13 (dd, 2H, J = 8.1, 2.1 Hz), 1.42 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3): δ 155.3, 153.6, 150.1, 149.7, 147.1, 146.9, 142.0, 140.2, 138.8, 135.1, 134.9, 132.9, 127.2, 126.8, 125.3, 124.9, 123.8, 123.6, 122.6, 120.9, 119.6, 119.2, 114.4, 113.6, 47.0, 27.2.

S3. Electrochemical characterization of the **bisDMFA-diTh-MMN** and **bisDMFABT-Th-MMN** in 0.1 M TBAHFP in dichloromethane solution, scan speed 100 mV/s, potentials vs. Fc/Fc$^+$.
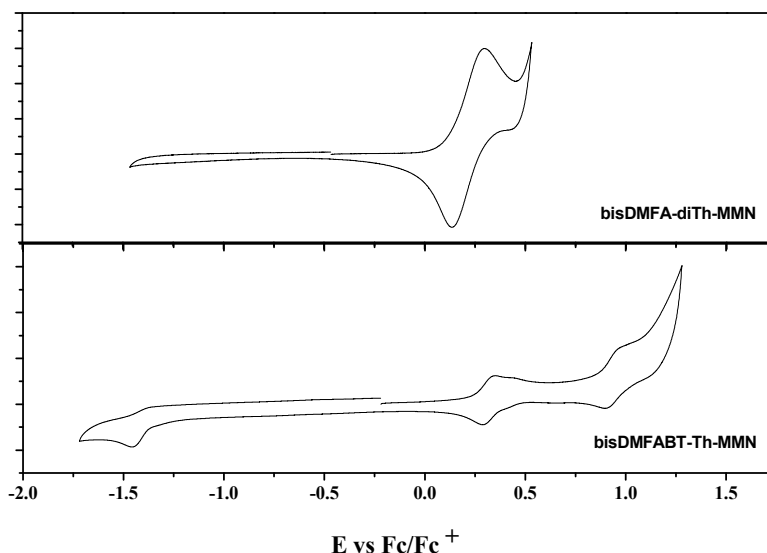
Electrochemical Measurements. Cyclic voltammetry was carried out with a BAS 100B (Bioanalytical System, Inc.). A three electrode system was used and consisted of non-aqueous Reference Electrode (0.1 M Ag/Ag$^+$ acetonitrile solution; MF-2062, Bioanalytical System, Inc.), platinum working electrode (MF-2013, Bioanalytical System, Inc.), and a platinum wire (diam. 1.0 mm, 99.9 % trace metals basis, Sigma-Aldrich) as counter electrode. Redox potential of dyes was measured in CH$_2$Cl$_2$ with 0.1 M (n-C$_4$H$_9$)$_4$N-PF$_6$ with a scan rate between 100mVs^{-1}(vs. Fc/Fc$^+$).

S4. Hole Mobility of **bisDMFA-diTh-MMN)**:C$_{71}$-PCBM and **bisDMFABT-Th-MMN)**:C$_{71}$-PCBM Films Evaluated Using the Mott-Gurney Law ($\varepsilon = 3\varepsilon_0$).

Film	μ_h (cm^2/(V s))	Thickness(nm)
bisDMFA-diTh-MMN : C$_{71}$-PCBM	2.26×10^{-5}	70
bisDMFABT-Th-MMN : C$_{71}$-PCBM	3.59×10^{-5}	70

To investigate the space-charge effects, we extracted the hole mobility from the space-charge-limited current (SCLC)[5] *J-V* characteristics obtained in the dark for hole-only devices. **Figure 2b** shows the dark-current characteristics of ITO/PEDOT:PSS/**Donor**:C$_{71}$-PCBM/Au devices as a function of the bias corrected by the built-in voltage determined from the difference in work function between Au and the HOMO level of **bisDMFA-diTh-MMN** and **bisDMFABT-Th-MMN**. We can expect that Ohm's law will be observed at low voltages as an effect of thermal free carriers. For the presence of carrier traps in the active layer, there is a trap-filled-limit (TFL) region between the ohmic and the trap-free SCLC regions. The SCLC behavior in the trap-free region can be characterized using the Mott-Gurney's square law where ε is the static dielectric constant of the medium and μ is carrier mobility.

$$J = (9/8)\varepsilon\mu(V^2/L^3)$$

S5. Isodensity surface plots of (a) of **bisDMFA-diTh-MMN** and (b) **bisDMFABT-Th-MMN**.

(a)   (b)
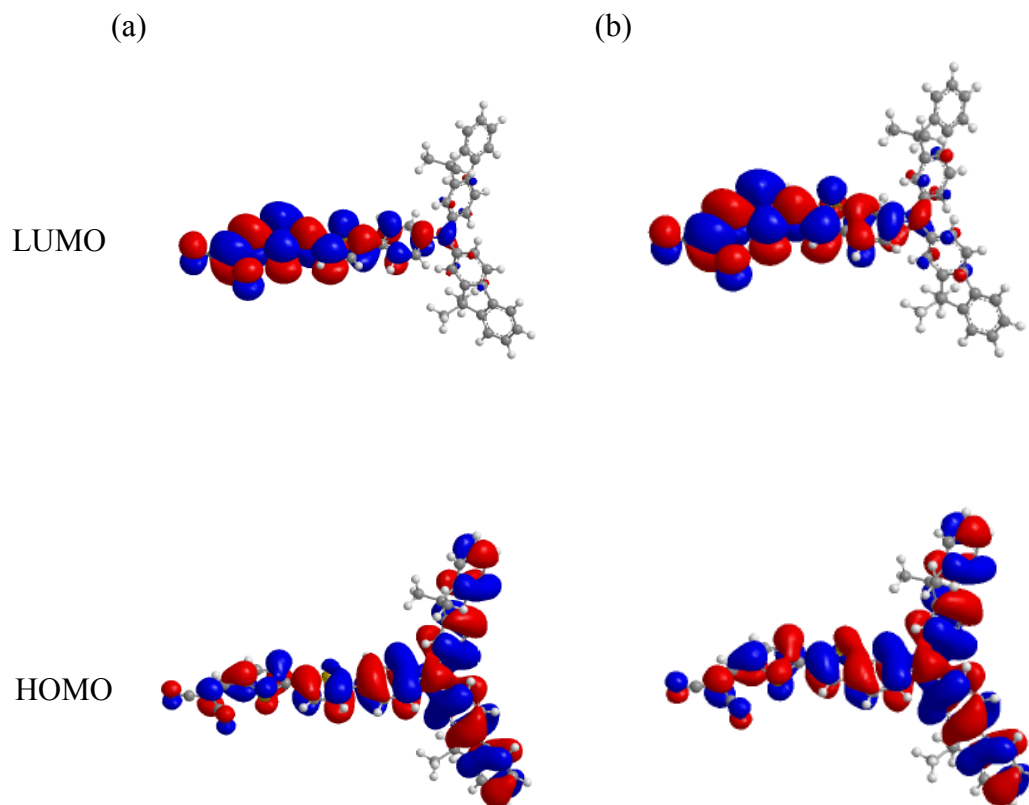
LUMO

HOMO

Density Functional Theory (DFT). Optimized structures calculated by TD-DFT using the B3LYP functional and the 6-31G* basis set. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies were determined using minimized singlet geometries to approximate the ground state.

S6. Tapping mode AFM surface topography of films cast from of (a) **bisDMFA-diTh-MMN** /C_{71}-PCBM (1:2), (b) **bisDMFABT-Th-MMN** /C_{71}-PCBM(1:3) BHJ composite.

a)
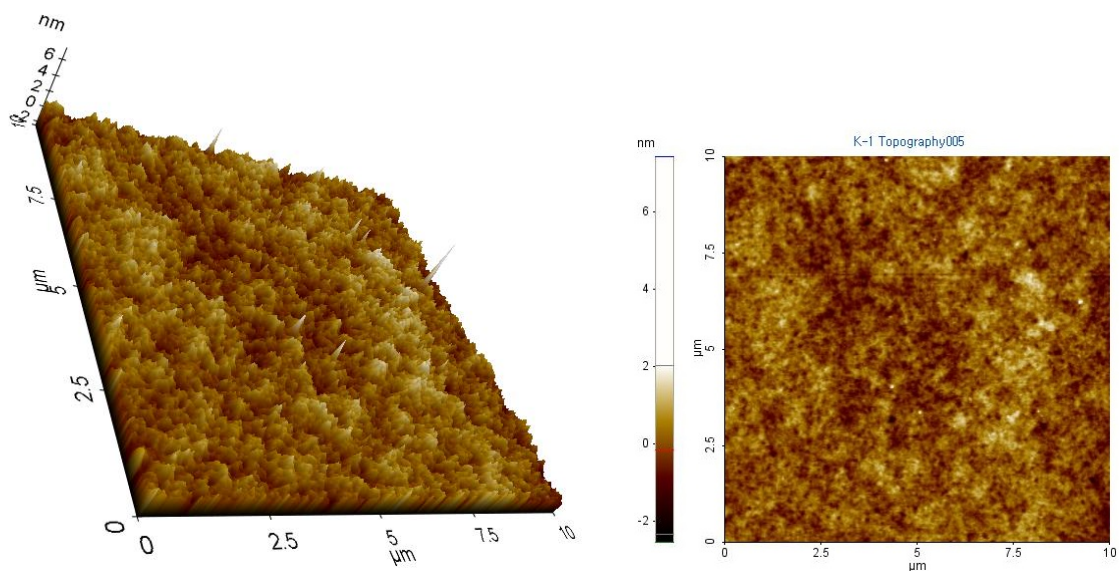
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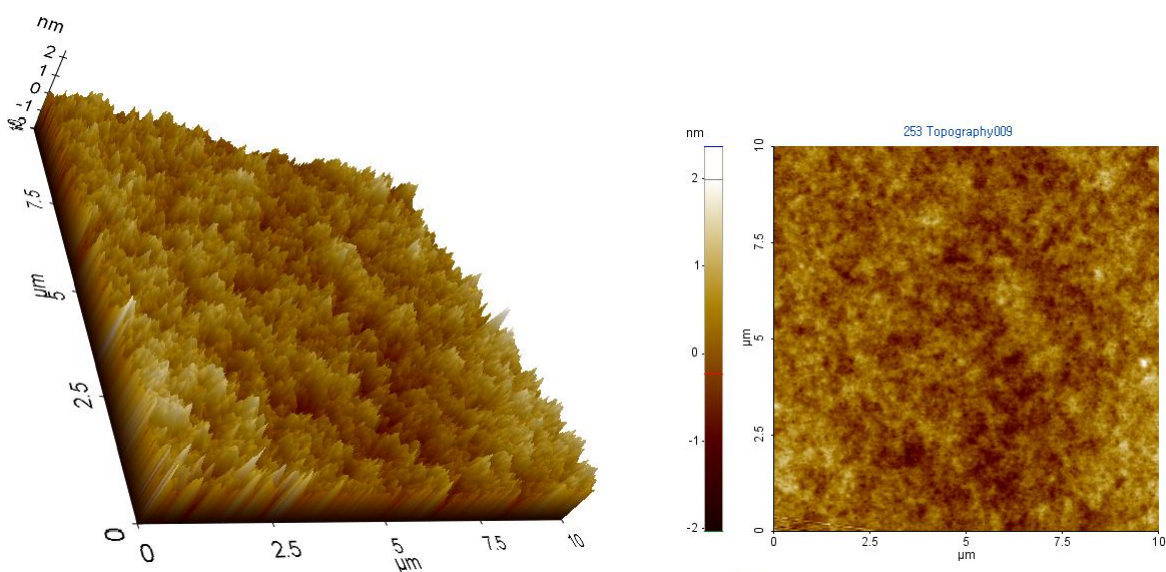
S7. Cell Fabrication and Measurement Method.

Cell fabrication Method

The BHJ films were prepared under optimized conditions according to the following procedure reported previously: The 55 indium tin oxide (ITO)-coated glass substrate was first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried overnight in an oven. PEDOT : PSS (Heraeus, AI 4083) in aqueous solution was spin-cast to form a film with thickness of approximately 40 nm. The substrate was dried for 10 min at 140 ºC in air, then transferred into a glove-box to spin-cast the photoactive layer. The **bisDMFA-diTh-MMN**:C_{71}-PCBM blend (weight ratio, 1:2) and **bisDMFABT-Th-MMN**:C_{71}-PCBM blend (weight ratio, 1:3) solutions were prepared in chlorobenzene at a concentration of 30 mg/mL. The **bisDMFA-diTh-MMN (or bisDMFABT-Th-MMN)**:C_{71}-PCBM blend solutions were then spin-cast on top of the PEDOT layer. After that, the TiO_x solution was spin-cast on top of the **bisDMFA-diTh-MMN (or bisDMFABT-Th-MMN)**:C_{71}-PCBM BHJ layer. The substrate was dried for 10 min at 80 ºC in air. Then, the device was pumped down to lower than 10^{-7} torr and a ~100 nm thick Al electrode was deposited on top.

Measurement. Solar cells efficiencies were characterized under simulated 100 mW/cm^2 AM 1.5G irradiation from a Xe arc lamp with an AM 1.5 global filter. Simulator irradiance was characterized using a calibrated spectrometer and illumination intensity was set using an NREL certified silicon diode with an integrated KG1 optical filter: spectral mismatch factors were calculated for each device in this report to be less than 5%. Short circuit currents were also found to be with 5% of values calculated using the integrated external quantum efficiency (EQE) spectra and the solar spectrum. The EQE was measured by underfilling the device area using a reflective microscope objective to focus the light output from a 75 watt Xe lamp, monochromator, and optical chopper; photocurrent was measured using a lock-in amplifier and the absolute photon flux was determined by a calibrated silicon photodiode.

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