Supplementary Information

Benzothiadiazole End Capped Donor-Acceptor Based Small Molecule for Organic Electronics

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Experimental

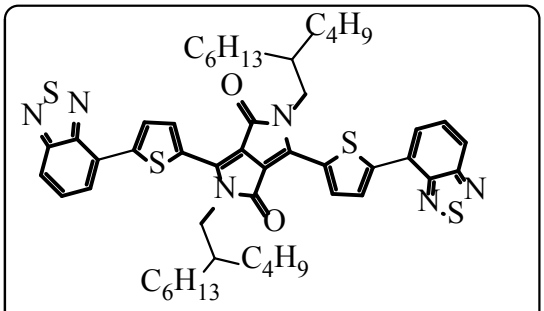
General

All the solvents, catalysts and reagents were purchased from Sigma-Aldrich, Strem, Acros and used without further purification. Most of the reactions were conducted using Schlenk techniques in an argon or nitrogen atmosphere with anhydrous solvents. Compounds 1, 2 and 3 were synthesized according to earlier reported procedures.

Characterization

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy measurements were conducted on a Bruker DPX 300 MHz or 400 MHz spectrometer using solvent $CDCl_3$. The chemical shifts were recorded in ppm using TMS as an internal standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Autoflex TOF/TOF

instrument using dithranol as the matrix. Elemental analysis was conducted on a CHNSO Elemental Analyzer for quantitative measurements using FLASH EA-112 series by Themro Electron Corporation. Ultraviolet-visible (UV-Vis) spectra were recorded on a Shimadzu model 2501-PC. Photoelectron spectroscopy in air (PESA) measurement was done on the thin film of **BO-DPP-BTZ** small molecule spin coated on glass using Riken Photoelectron Spectrometer (Model AC-2). Thermal gravimetric analysis (TGA) was carried out using a TA Instrument TGA Q500 instrument (heating rate of 10°C min^{-1}). Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC Q100 instrument (scanning rate of 10°C min^{-1}). Cyclic voltammetry experiments were performed using an Autolab potentiostat (model PGSTAT30) by Echochimie. Measurements were recorded in dichloromethane solutions of **BO-DPP-BTZ** under argon at room temperature with a conventional three-electrode arrangement consisting of a platinum wire working electrode, a gold counter electrode, and an Ag/AgCl in 3M KCl reference electrode, respectively. HOMO values were calculated from the corresponding oxidation onsets which were converted to SCE (saturated calomel electrode), based on an -4.4 eV SCE energy level relative to vacuum using IP = - ($E_{ox\text{-}onset}$ + 4.4) eV. Likewise, LUMO levels were obtained from the reduction onsets via EA = - ($E_{red\text{-}onset}$ + 4.4) eV.



BO-DPP-BTZ

Synthesis of 3,6-bis(5-(benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2,5-bis(2 butyloctyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (BO-DPP-BTZ):

To a 50 mL Schlenk flask, 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-butyloctyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.500 g, 0.629 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c][1,2,5]thiadiazole (0.702 g, 2.68 mmol) were dissolved in toluene (18 mL). 2M K_2CO_3 (10 mL) was added in the above reaction mixture. The solution was purged

with argon for 30 min, and then tetrakis (triphenylphosphine)palladium (50 mg, 0.037 mmol) was added. The reaction was stirred at 80°C for 3 d. The resulting mixture was poured into water and washed with chloroform. Organic phase was removed via separatory funnel, dried by magnesium sulfate ($MgSO_4$) and finally removed on rotary evaporator. The crude compound was purified by column chromatography using Hexane: Chloroform solvent mixture gave pure compound (55 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09-9.08 (d, 2H), 8.19-8.18 (d, 2H), 8.01-7.99 (d, 4H), 7.69-7.65 (t, 2H), 4.18-4.16 (t,4H), 2.05 (s, 2H) 1.39-1.22 (m, 32H), 0.88-0.81 (t, 12H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.21, 155.85, 152.36, 144.63, 140.50, 136.60, 131.60, 129.96, 128.57, 126.93, 126.33, 121.68, 46.88, 38.52, 32.24, 31.77, 31.48, 30.20, 28.98, 26.75, 23.57, 23.04, 14.49.

Elemental Analysis Calculated for $C_{50}H_{60}N_6O_2S_4$ (theoretical): C 66.33, H 6.68, N 9.28, S 14.17 %; Elemental Analysis Obtained for (experimental): C 66.36, H 6.66, S 13.46 %. MS (MALDI-TOF, m/z): found 904.07; calcd. for $C_{50}H_{60}N_6O_2S_4$= 905.31

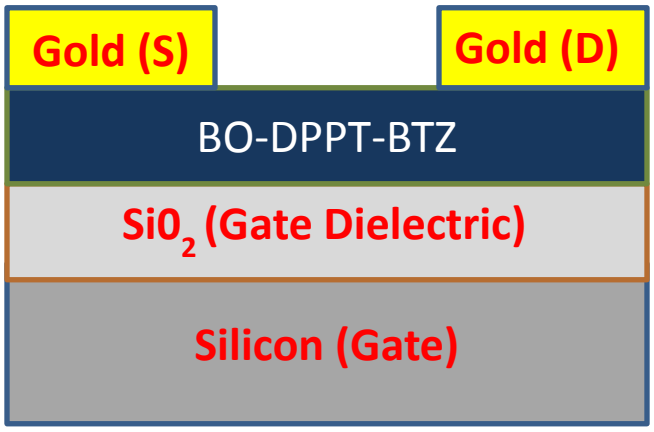
λmax (UV-vis-Near IR): 598 nm (in chloroform); 722 nm (thin film). Absorption cutoff from thin film= 800 nm.

OTFT Fabrication and Characterization

Top contact/bottom gate OFET devices were fabricated using n^+-Si/SiO_2 substrates where n^+-Si and SiO_2 work as gate electrode and gate dielectric, respectively. Substrates were cleaned using ultrasonication in acetone, methanol and de-ionized water consequently. The cleaned substrates were dried under a nitrogen flow and heated at 100 °C for 5 min. The substrates were then treated in UV-ozone for 20 min. Then, the substrate was kept in a desiccator with a few drops of octyltrichlorosilane (OTS). The desiccator was evacuated for 3 min and placed in an oven at 110 °C for 3 hr. The substrate was removed from the desiccator, thoroughly rinsed with isopropanol, and dried under a nitrogen flow. For all sets of OFETs, thin film of **BO-DPP-BTZ** was spin coated on OTS treated Si/SiO_2 substrates from chloroform solution. Patterned gold layers of thickness ~ 100 nm were deposited for use as source (S) and drain (D) electrodes through a shadow mask. For typical OFET devices reported here, the source-drain channel length (L) and channel width (W) were 100 μm and 1mm, respectively. The device characteristics of the

OFETs were measured at room temperature under nitrogen with a Keithley 4200 parameter analyzer. The field effect mobility (μ) was calculated from the saturation regime of transfer characteristics. The saturation mobility $\mu_{sat.}$ is calculated from the slope of $\sqrt{|I_{DS}|}$ vs. V_G that is obtained from the output characteristics in the saturation region:

$$\mu_{sat.} = \left(\frac{\sqrt{|I_{DS}|}}{V_G} \right)^2_{V_{DS}} \frac{2L}{WC_i}$$

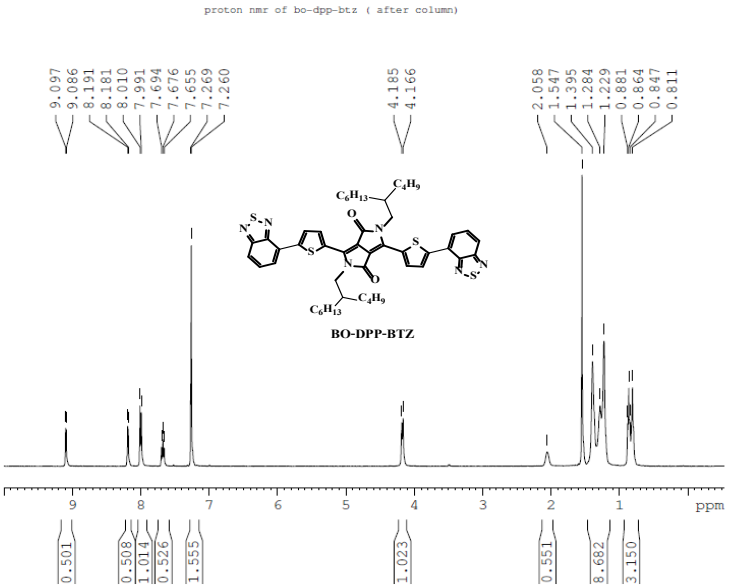


Computational Set Up:

Structures and spectra: Gaussian 09, medium = chloroform, basis = 6-31g(d,p),

Functional = for optimization / frequency, orbital plots: B3LYP for TDDFT: B3LYP, CAM-B3LYP.

(a)



(b)

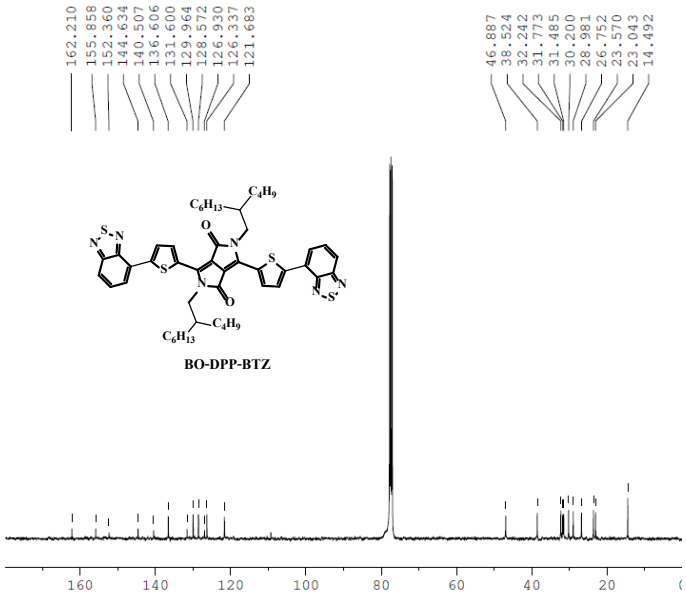
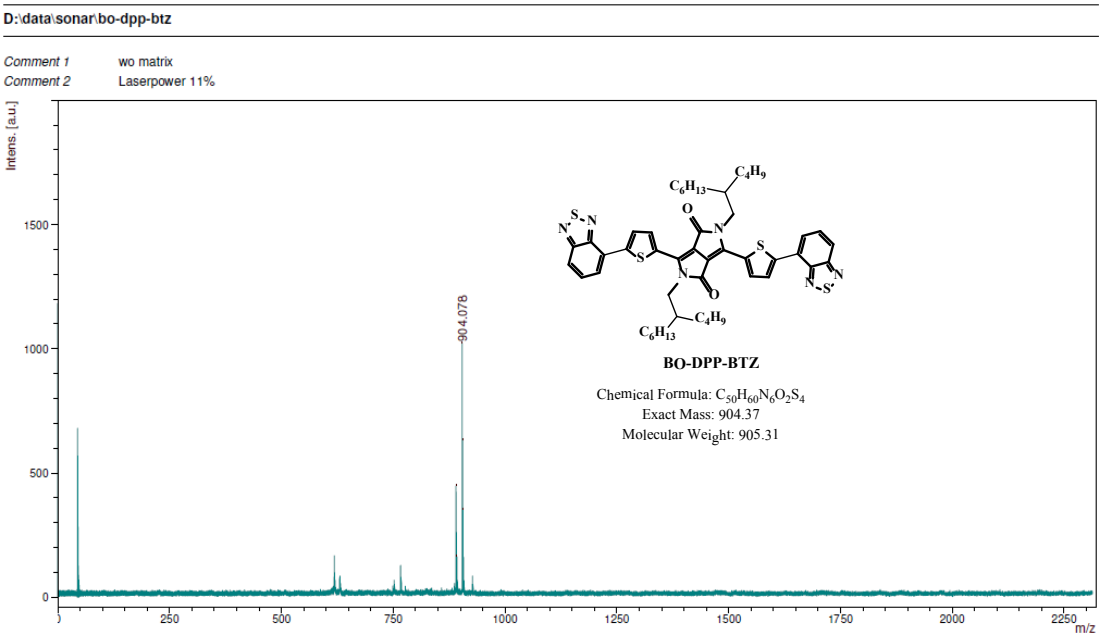


Figure S1. (a) ^{1}H NMR and (b) ^{13}C spectra of 3,6-bis(5-(benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2,5-bis(2 butyloctyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**BO-DPP-BTZ**).

(a)



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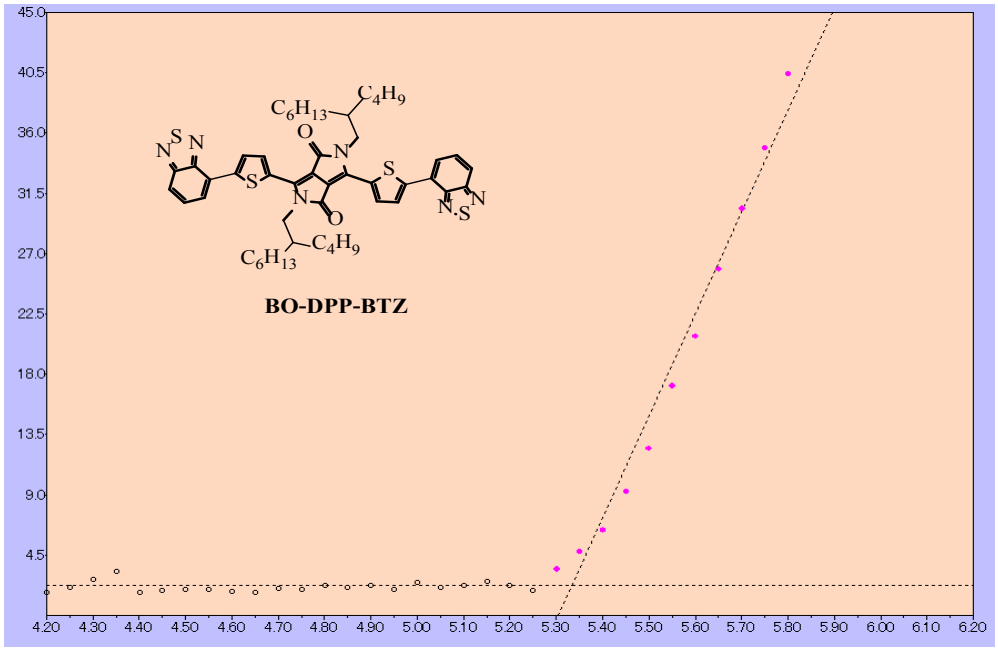
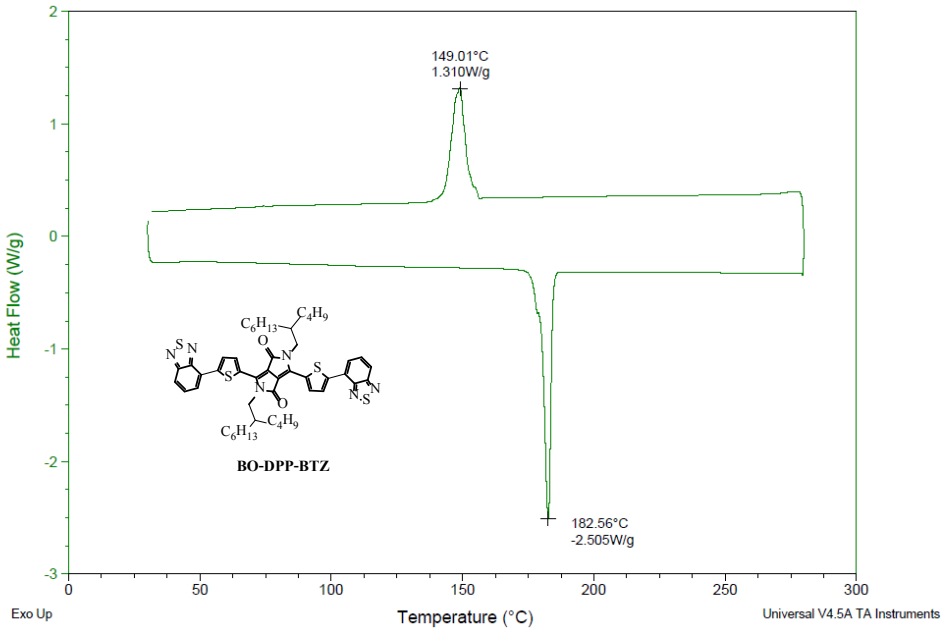


Figure S2. Matrix assisted laser deposition-time of flight (MALDI-TOF) and PESA graph of 3,6-bis(5-(benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2,5-bis(2 butyloctyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**BO-DPP-BTZ**).

(a)



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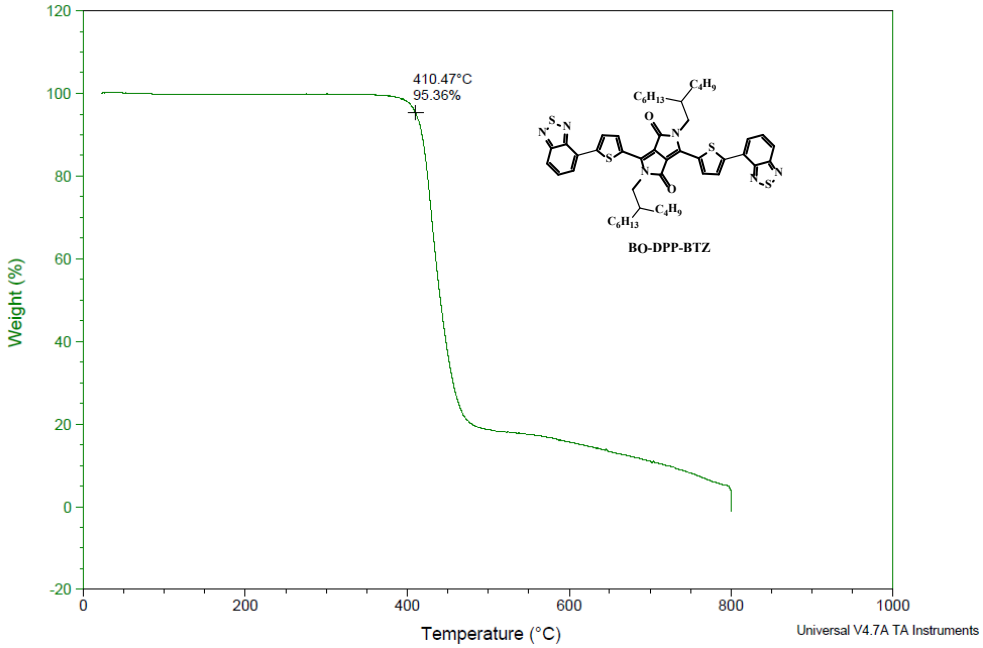
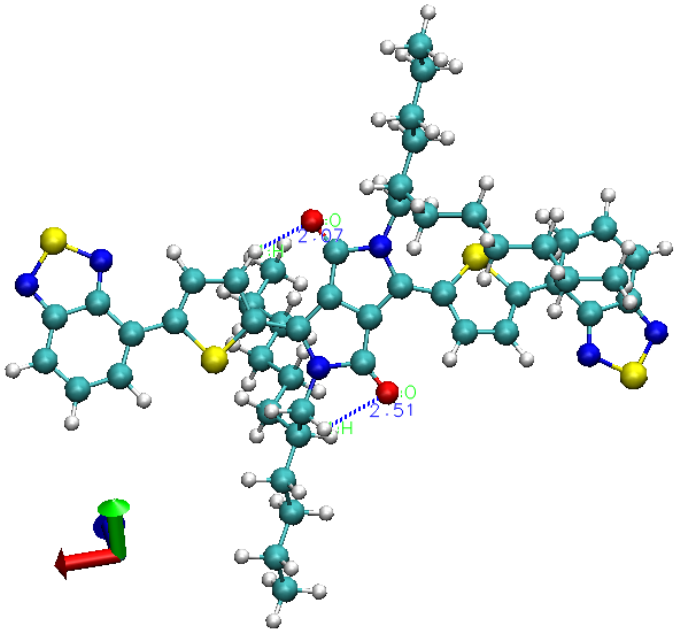


Figure S3. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of 3,6-bis(5-(benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2,5-bis(2 butyloctyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**BO-DPP-BTZ**).

(a)



(b)

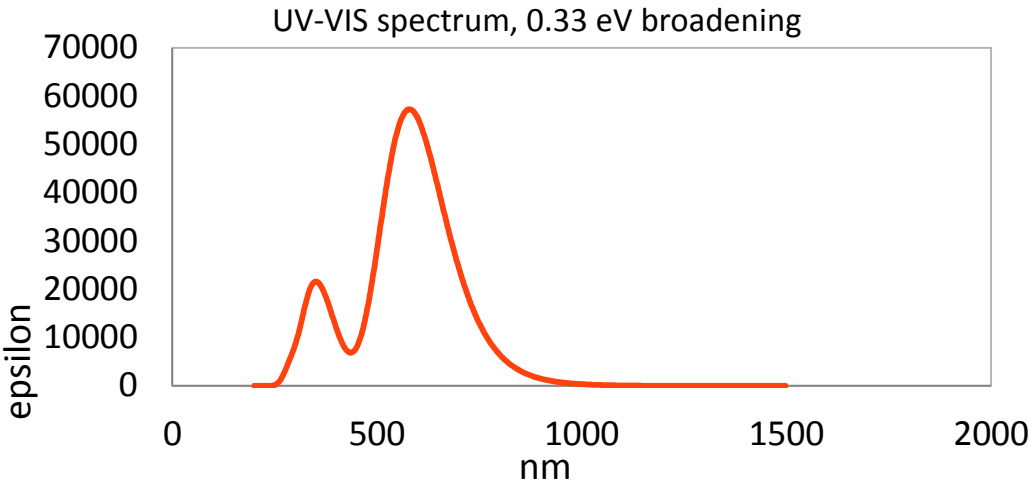


Figure S4. (a) The optimized geometry and (b) theoretical UV-vis absorption (in chloroform) of 3,6-bis(5-(benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-2,5-bis(2 butyloctyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**BO-DPP-BTZ**).

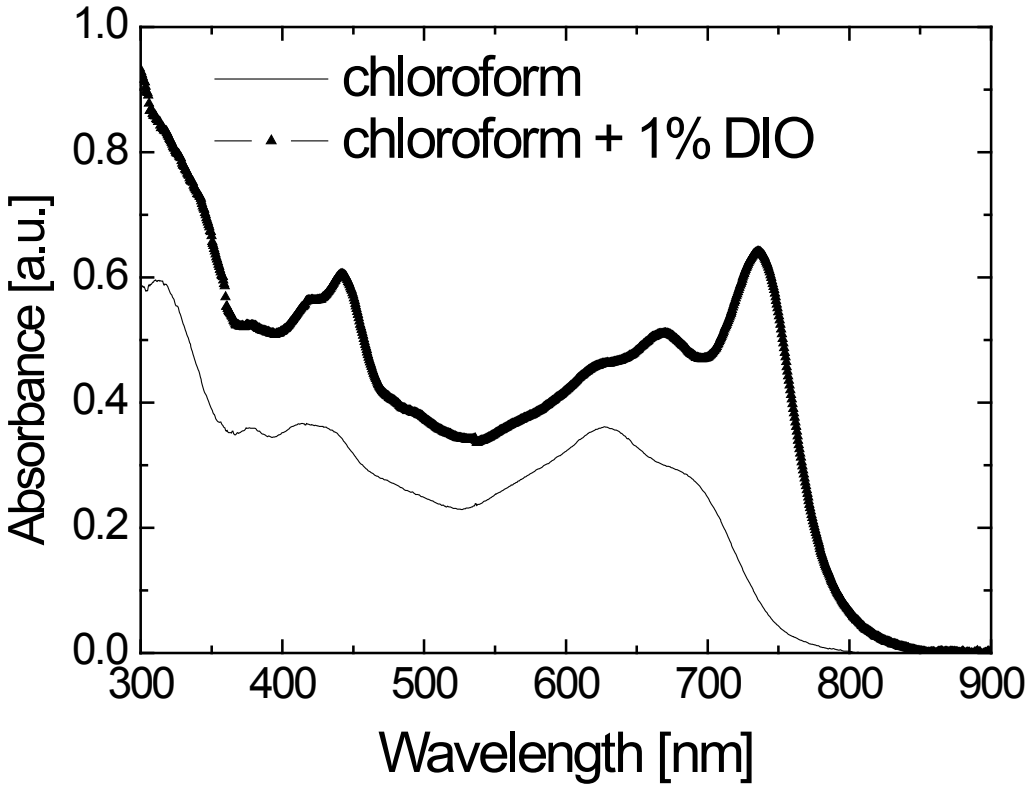


Figure S5. UV-vis absorption spectra of **BO-DPP-BTZ** and [70]PCBM blended thin films processed from pure chloroform and chloroform:DIO mixture.

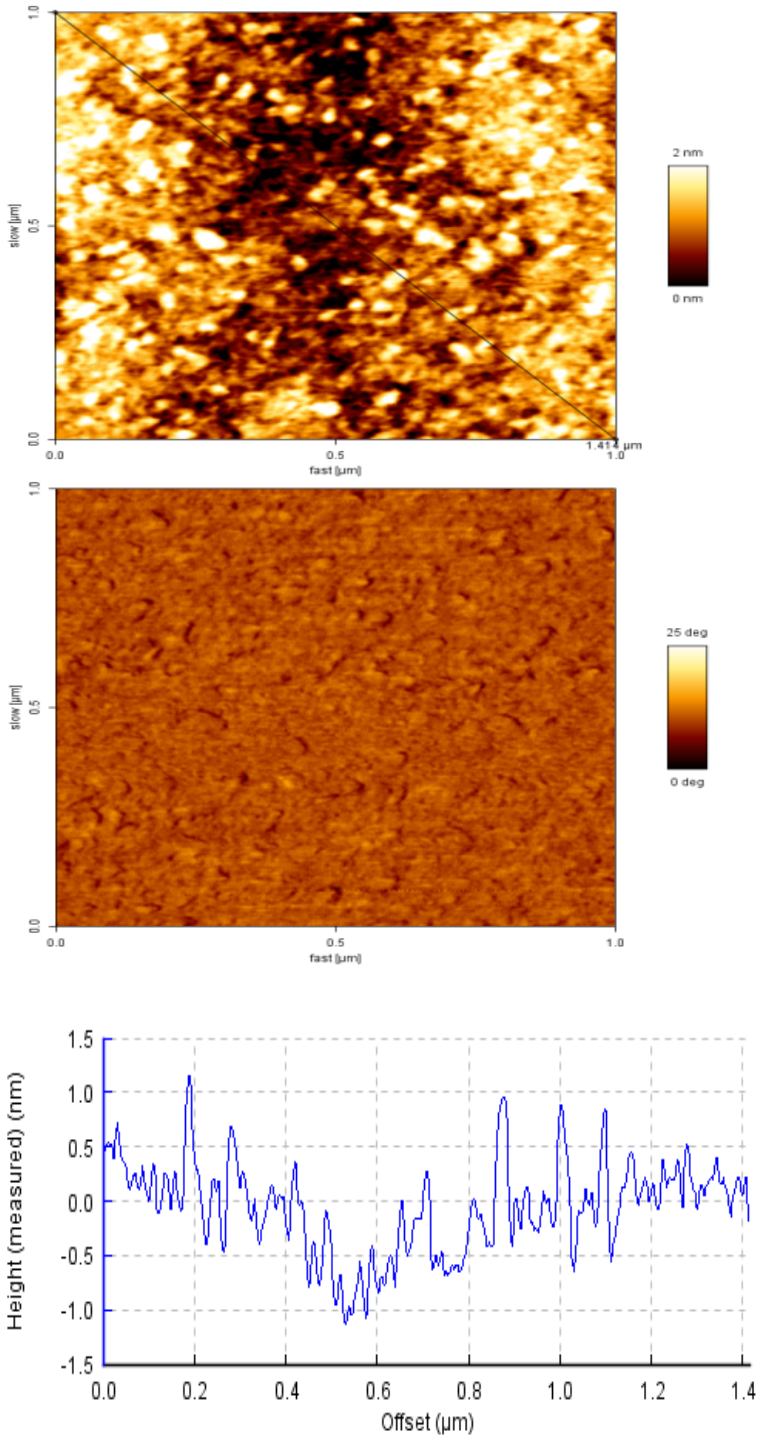


Figure S6. AFM images (height, phase, and line profile) of the **BO-DPP-BTZ**:[70]PCBM BHJ film spin coated from chloroform. The surface is smooth and rather featureless, the donor and acceptor are thought to be well mixed.

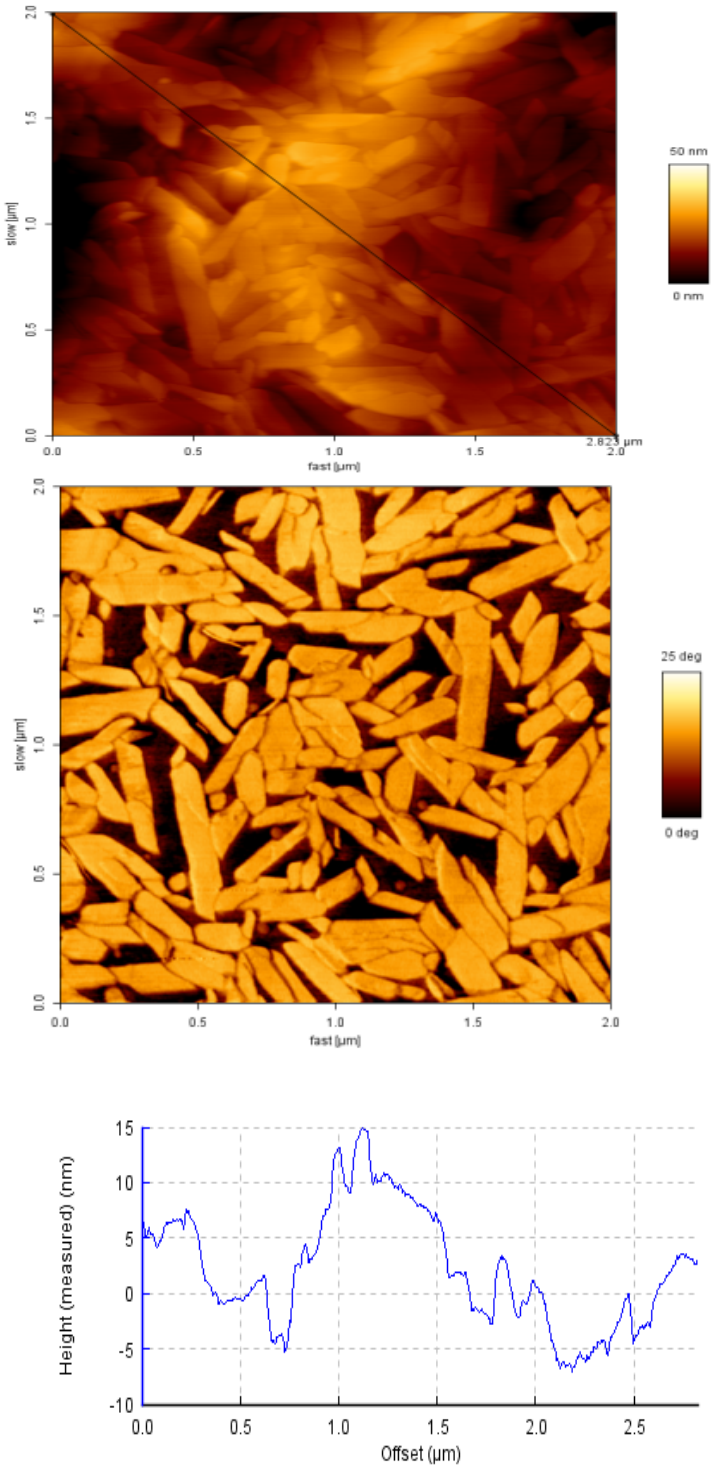


Figure S7. AFM images (height, phase, and line profile) of the **BO-DPP-BTZ**:[70]PCBM BHJ film spin coated from chloroform:DIO. The surface is rough and crystalline features are evident. The addition of DIO is understood to allow the **BO-DPP-BTZ** to crystallize, in agreement with the strong optical absorption in the longer wavelength part of the spectrum (S5 and Fig 2a).