Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic supplementary information for

Efficient fullerene-free organic solar cells based on fused-ring oligomer molecules

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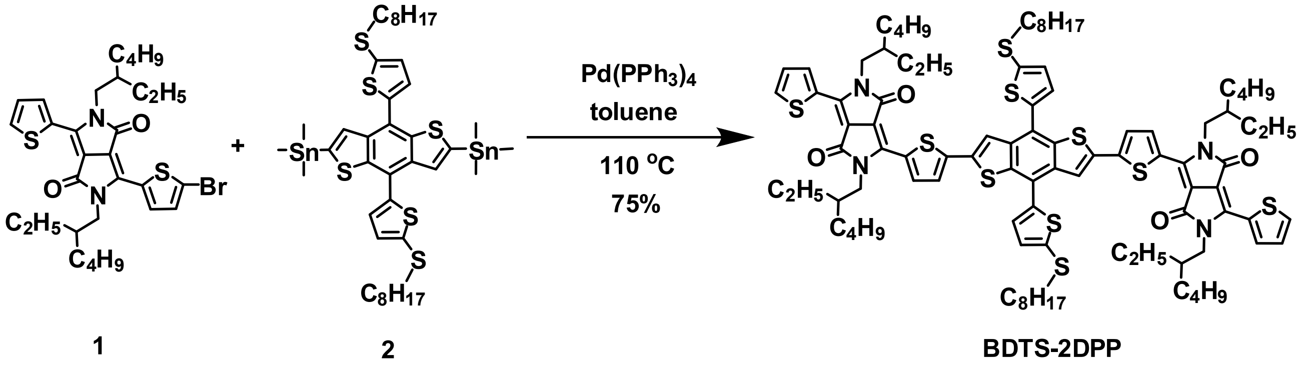
Experimental details

Materials and measurements: Unless stated otherwise, solvents and chemicals were obtained commercially and were used without further purification. Toluene was distilled from sodium benzophenone under nitrogen prior to use. BDT-2DPP[1] and IEIC[2] were synthesized according to the literature procedures. The ZnO precursor solution was prepared by dissolving 0.14 g of zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 99.9%, Aldrich, U.S.A.) and 0.5 g of ethanolamine ($NH_2CH_2CH_2OH$, 99.5%, Aldrich, U.S.A.) in 5 ml of 2-methoxyethanol ($CH_3OCH_2CH_2OH$, 99.8%, J&K Scientific, Canada). The NMR spectra were measured on a Bruker AVANCE 300 or 400 MHz spectrometer. Mass spectra were measured on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer using MALDI mode. Elemental analyses were carried out using a FLASH EA1112 elemental analyzer. Solution (dichloromethane) and thin-film (on quartz substrate) UV-vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen in a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) in CH_3CN using a computer-controlled CHI660C electrochemical workstation, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and Ag/AgCl as a reference electrode. Potentials were referenced to the ferrocenium/ferrocene ($FeCp_2^{+/0}$) couple by using ferrocene as an internal standard. X-ray diffraction

(XRD) of thin film was performed in the reflection mode at 40 kV and 200 mA with Cu-Ka radiation using a 2 kW Rigaku D/max-2500 X-ray diffractometer. The nanoscale morphology of blended films was observed using a Veeco Nanoscopy V atomic force microscope (AFM) in tapping mode.

Mobility measurements: Hole- or electron-only diodes were fabricated using the architectures: ITO/PEDOT: PSS/BDT-2DPP, BDTS-2DPP, BDT-2DPP: IEIC or BDTS-2DPP: IEIC/Au for holes and Al/BDT-2DPP: IEIC or BDTS-2DPP: IEIC/Al for electrons. Mobilities were extracted by fitting the current density–voltage curves using space charge limited current (SCLC).[3] The *J*–*V* curves of the devices were plotted as $J^{0.5}$ versus V using Eq. $J = 9\varepsilon_0\varepsilon_r\mu_h(\mu_e)V^2/8d^3$ for holes and electrons, where J is current density, d is film thickness of active layer (*ca.* 130 nm), μ_h is hole mobility, μ_e is electron mobility, ε_r is relative dielectric constant of the transport medium, and ε_0 is permittivity of free space (8.85×10^{-12} F m^{-1}). $V = V_{appl} - V_{bi}$, V_{appl} is the applied voltage, V_{bi} is the offset voltage (for hole-only diodes, V_{bi} is 0.2 V; for electron-only diodes, V_{bi} is 0 V)

Molecular modeling. Computational details are presented as follows: DFT calculations were performed with the Gaussian 09 program[4] using the B3LYP functional.[5, 6] All-electron double-ξ valence basis sets with polarization functions 6-31G* were used for all atoms.[7] Geometry optimizations were performed with full relaxation of all atoms in gas phase without solvent effects. Vibrational frequency calculations were performed to check that the stable structures had no imaginary frequency.



Scheme S1. Synthetic route to BDTS-2DPP.

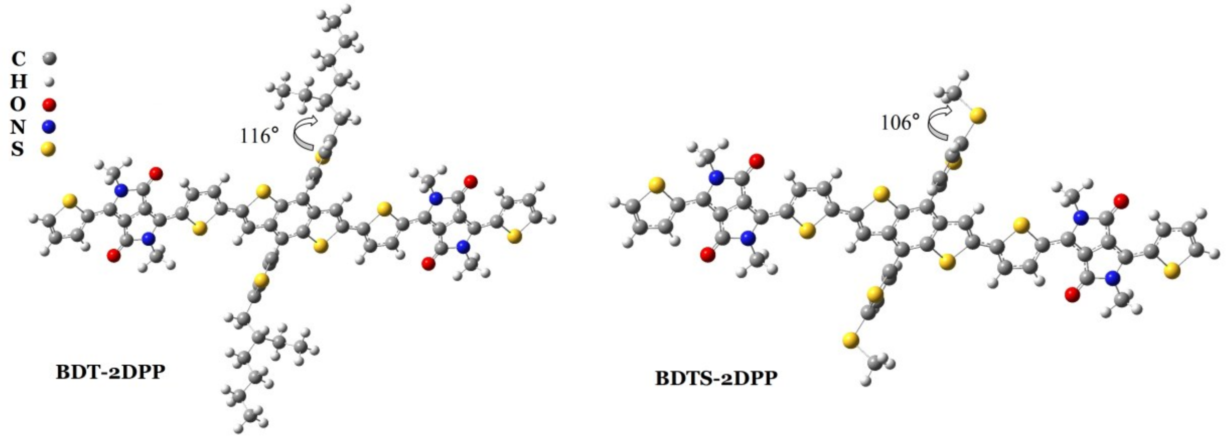


Fig. S1. The optimal conformation of BDT-2DPP and BDTS-2DPP, where alkyls are simplified to methyl except for the 2-ethylhexyl on thiophene of BDT-2DPP.

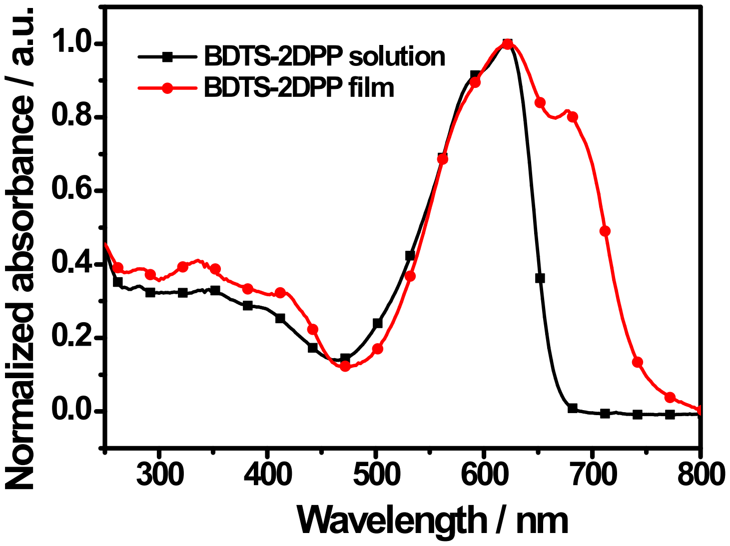


Fig. S2. UV-vis absorption spectra of BDTS-2DPP in dichloromethane solution and in thin film.

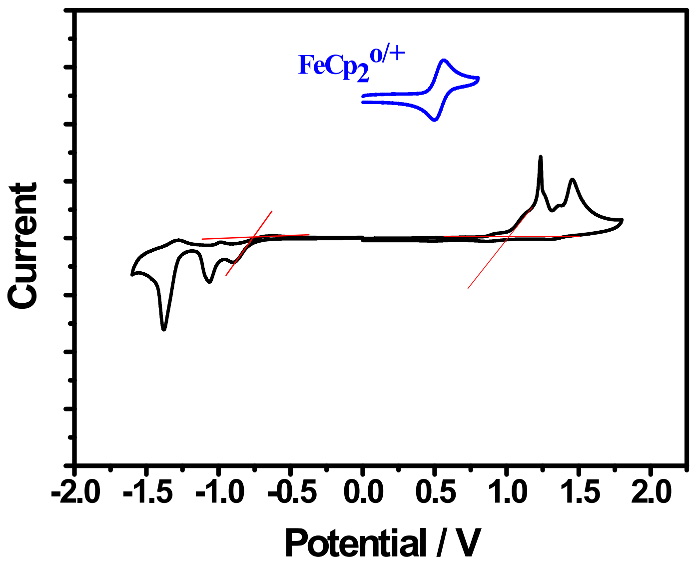


Fig. S3. Cyclic voltammogram for BDTS-2DPP film in CH_3CN / 0.1 M $[^nBu_4N]^+[PF_6]^-$ at 100 mV s^{-1}. The horizontal scale refers to an Ag/AgCl electrode.

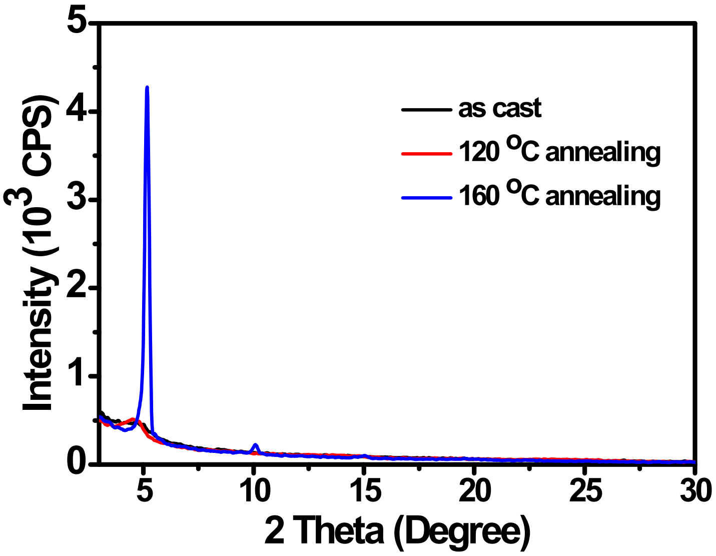


Fig. S4. XRD pattern of BDTS-2DPP film on Si substrate.

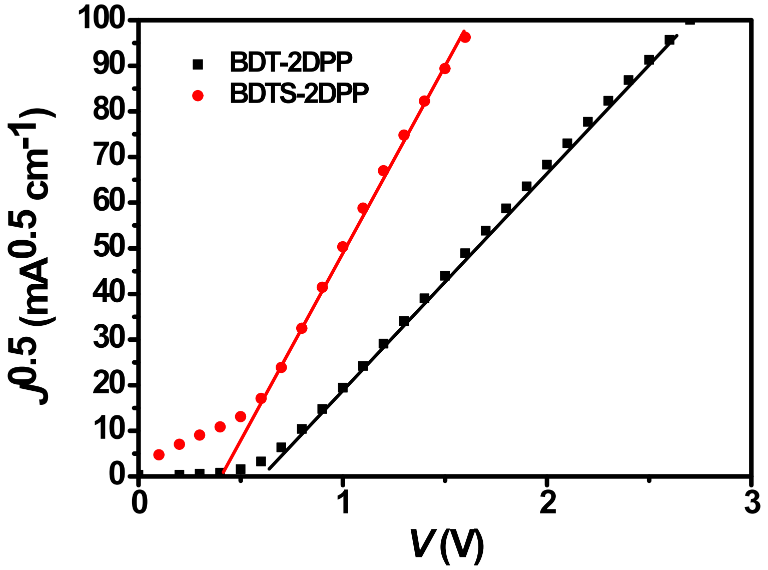


Fig. S5. $J^{0.5}$–V plots for the BDT-2DPP or BDTS-2DPP-based hole-only devices.

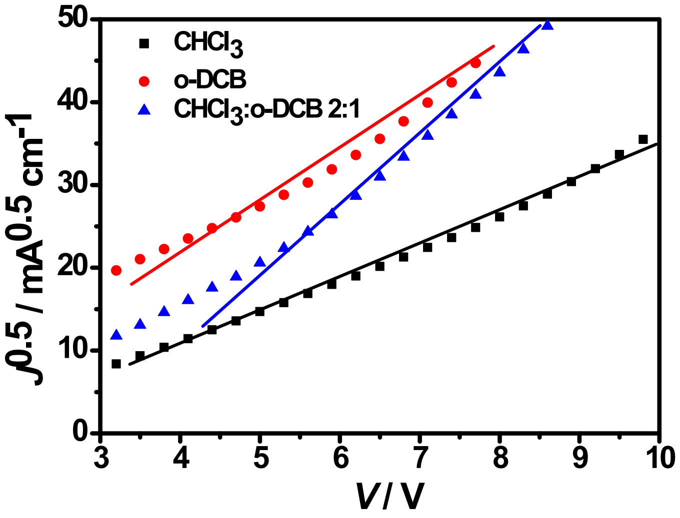


Fig. S6. $J^{0.5}$–V plots for the BDT-2DPP: IEIC (1:1, w/w)-based hole-only devices.

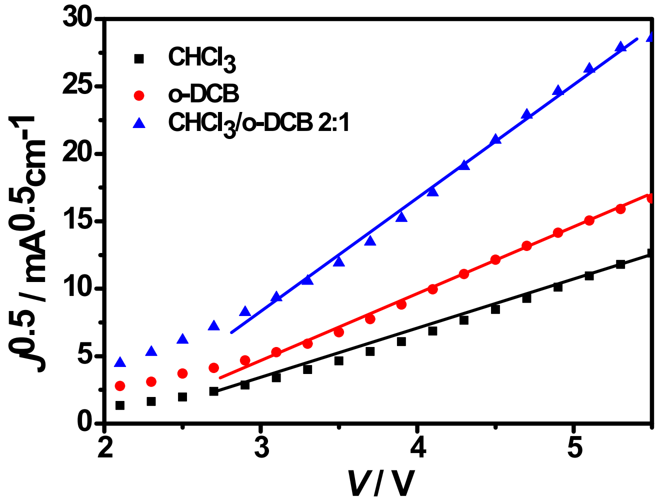


Fig. S7. $J^{0.5}$–V plots for the BDT-2DPP: IEIC (1:1, w/w)-based electron-only devices.

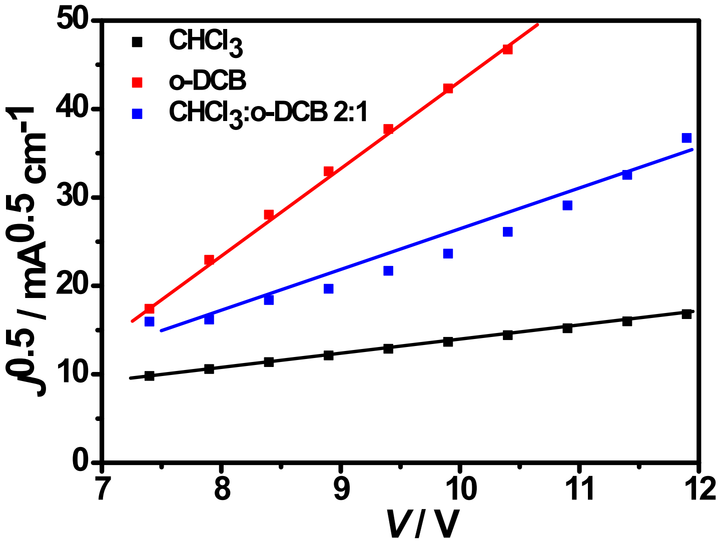


Fig. S8. $J^{0.5}$–V plot for the BDTS-2DPP: IEIC (1:1, w/w)-based hole-only devices.

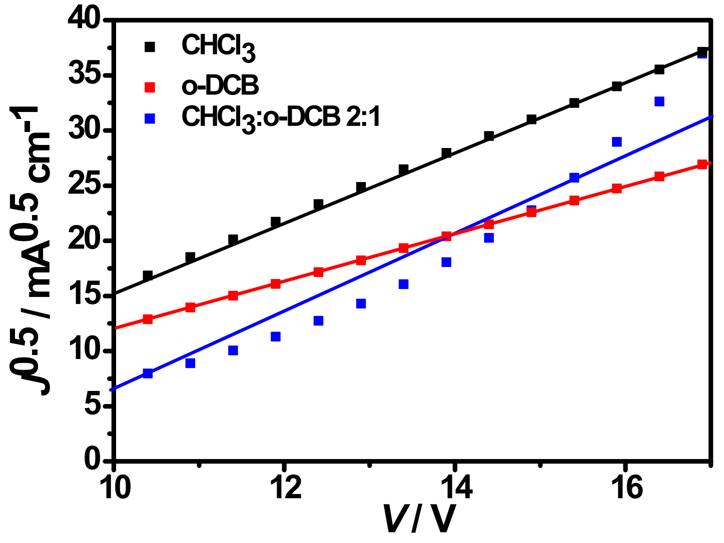


Fig. S9. $J^{0.5}$–V plot for the BDTS-2DPP: IEIC (1:1, w/w)-based electron-only devices.

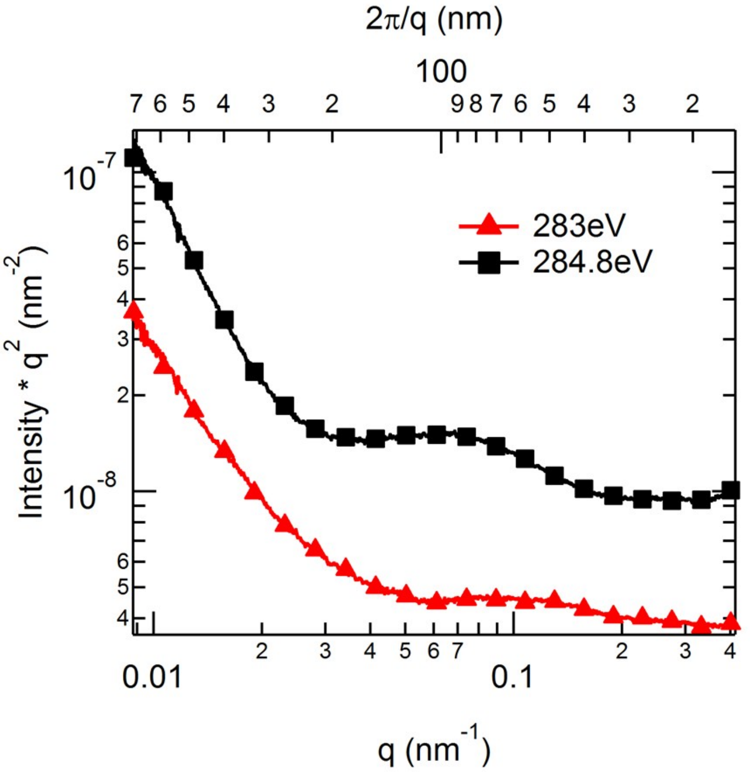


Fig. S10. R-SoXS profiles of blend film processed with *o*-DCB obtained at 283 eV and 284.8 eV. Since the contrast is lower before the absorption edge, there is no clear peak observed at 283 eV.

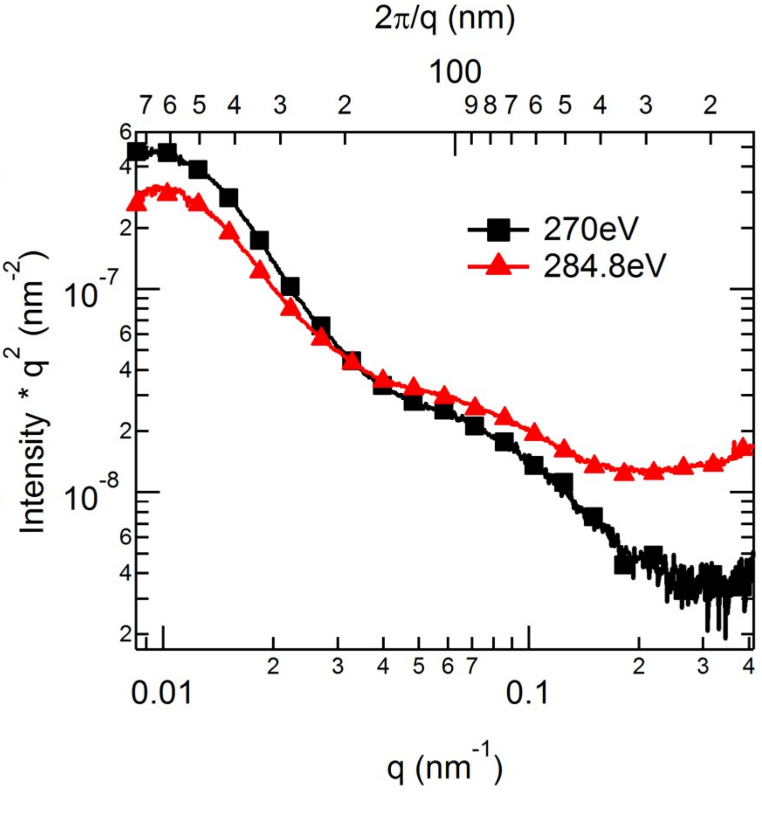


Fig. S11. R-SoXS profiles of blend film processed with *o*-DCB/$CHCl_3$ obtained at 270 eV and 284.8 eV, demonstrating that the peak at q ≈ 0.01 nm^{-1} is surface roughness.

References

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