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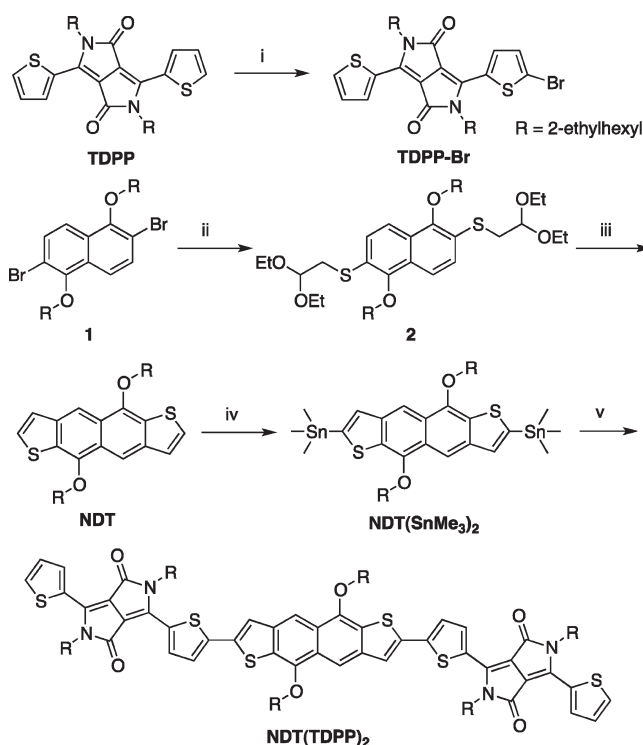
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Supporting Information

ABSTRACT: We report the synthesis, characterization, and first implementation of a naphtho[2,3-*b*:6,7-*b'*]dithiophene (NDT)-based donor molecule in highly efficient organic photovoltaics (OPVs). When NDT(TDPP)₂ (TDPP = thiophene-capped diketopyrrolopyrrole) is combined with the electron acceptor PC₆₁BM, a power conversion efficiency (PCE) of 4.06 ± 0.06% is achieved—a record for a PC₆₁BM-based small-molecule OPV. The substantial PCE is attributed to the broad, high oscillator strength visible absorption, the ordered molecular packing, and an exceptional hole mobility of NDT(TDPP)₂.

Solution-processed organic photovoltaics (OPVs) have the potential to be cost-effective, renewable energy sources due to their amenability to high-throughput roll-to-roll processing, earth-abundant constituents, and architectural tunability over multiple length scales.¹ However, a major challenge for OPVs to attain widespread implementation is to advance the power conversion efficiencies (PCEs) from recently achieved and impressive values near 7%² to ≥10%.³ Bulk-heterojunction (BHJ) solution-processed OPVs typically consist of an active layer having a phase-separated blend of an electron donor polymer and an electron acceptor fullerene placed between a tin-doped indium oxide (ITO) anode and an Al cathode. Strategies to enhance BHJ OPV performance include anode and cathode modifications with interfacial layers that block minority charge carriers while extracting majority charge carriers,⁴ and/or developing new low band gap polymeric donors having broad optical cross sections and high carrier mobility.⁵ The most efficient donor materials reported to date are copolymers incorporating the well-studied benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) moiety.^{2b–e}

Emerging and promising alternatives to polymeric OPV electron donors are small-molecule donors, offering the attraction of more straightforward synthesis and purification, less batch-to-batch variation in properties, and intrinsic monodispersity.⁶ Nevertheless, compared to polymeric donors, solution-processable molecular donors have not been extensively investigated and the resulting devices have yielded lower PCEs. Conventional

Scheme 1. Synthetic Route to NDT(TDPP)₂^a

^a (i) NBS, CHCl₃, 0 °C then RT, 53%. (ii) *n*-BuLi, Bis(2,2-diethoxyethyl) disulfide, THF, −78 °C then RT, 72%. (iii) BF₃·OEt₂, CH₂Cl₂, reflux, 14%. (iv) *n*-BuLi, (CH₃)₃SnCl, THF, −78 °C then RT, 84%. (v) TDPP-Br, Pd(PPh₃)₄, toluene/DMF, 120 °C, 80%.

small-molecule BHJs utilizing the acceptor [6,6]phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) have reached efficiencies up to 4.3–4.4%,⁷ and 5.2%⁸ after several processing steps. However, to date, small-molecule BHJ solar cells utilizing the more affordable acceptor [6,6]phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) have yielded PCEs no higher than 3.7%.⁹ These observations raise the intriguing

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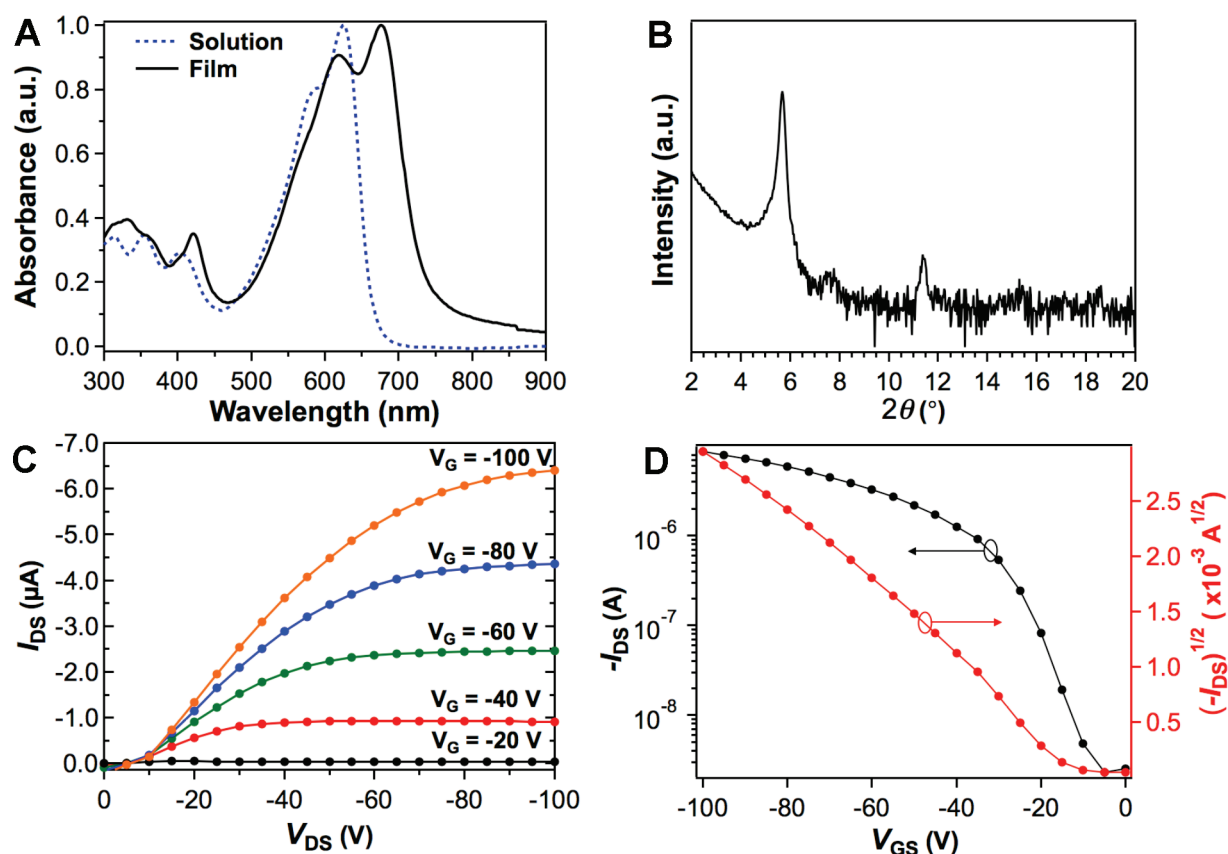


Figure 1. (A) Optical absorption spectra of NDT(TDPP)₂ in chloroform solution and as a film. (B) Log scale $\theta-2\theta$ X-ray diffraction pattern of a drop cast NDT(TDPP)₂ film (from 10 mg mL⁻¹ in chloroform) on a Si/SiO₂/HMDS substrate, annealed at 110 °C. (C) Typical output and (D) transfer plot ($V_{DS} = -100$ V) from a drop cast NDT(TDPP)₂ OFET annealed at 110 °C.

question of what new, photon-efficient OPV donor molecules might inform us about structure–response relationships.

We report here on the synthesis, characterization, and implementation in OPVs of a novel donor molecule based on the 5,10-bis(2-ethylhexyloxy)naphtho[2,3-*b*:6,7-*b'*]dithiophene (NDT) moiety. The extended π -conjugation system of NDT is expected to afford strong intermolecular orbital overlap and electron-donating properties by utilizing a favorable “push–pull” architecture. This could thereby enhance charge separation, transport, and energy level tunability. A vapor-deposited NDT variant has achieved significant organic field effect transistor (OFET) hole mobility (μ_h),¹⁰ suggesting attractive OPV properties. However, to achieve the solubility and thin film uniformity required in solution processed small-molecule OPVs, the NDT core was functionalized with 2-ethylhexyloxy groups in the 5,10 skeletal positions (Scheme 1). Furthermore, to optimize efficacy as an OPV donor component, the present synthetic strategy doubly terminates electron-rich NDT with thiophene-capped diketopyrrolopyrrole (TDPP) units to yield NDT(TDPP)₂ (Scheme 1). Electron-deficient and strongly absorbing diketopyrrolopyrrole (DPP) fragments have previously been utilized to lower the band gap in copolymer¹¹ and molecular OPV donor systems,^{7b,12} as well as in high mobility *n*-type and *p*-type OFET copolymers.¹³ Note that the branched 2-ethylhexyl substituents on TDPP further enhance solubility.

NDT(TDPP)₂ was synthesized by Stille cross-coupling of NDT(SnMe₃)₂ with TDPP-Br in 80% yield and was characterized by conventional methods (Scheme 1; see Supporting

Information (SI) for details). NDT(TDPP)₂ optical spectra in chloroform (Figure 1A) reveal $\lambda_{max} = 624$ nm with a very high molar absorption coefficient of 1.1×10^5 L·mol⁻¹·cm⁻¹. A spun cast film from CHCl₃ (10 mg mL⁻¹) exhibits a red-shifted λ_{max} of 676 nm, suggesting molecular aggregation and coplanarity in the solid state. The absorption onset for the spun cast film is 720 nm, corresponding to an optical band gap of ~ 1.72 eV. Cyclic voltammetry (CV) was used to estimate the HOMO energy (Figure S1). The onset of oxidation at 0.60 V, vs ferrocene/ferrocenium, yields a HOMO energy of -5.40 eV, and from the optical band gap and measured HOMO, the LUMO energy is estimated to be -3.68 eV. The high molar absorption, low band gap, and low-lying HOMO and LUMO of NDT(TDPP)₂ provide the necessary characteristics for large open circuit voltages (V_{OC}) and short circuit current densities (J_{SC}) in BHJ blends with the standard electron acceptor PC₆₁BM.

Note that highly ordered donor molecules are expected to afford high hole mobilities,¹⁴ a necessary condition for significant OPV photocurrents. Figure 1B shows wide-angle X-ray diffraction (WAXRD) data using standard $\theta-2\theta$ techniques for a drop cast NDT(TDPP)₂ film on a hexamethyldisilazane (HMDS)-treated Si/SiO₂ substrate. The reflections at $2\theta = 5.69^\circ$ and 11.39° correspond to *d*-spacings of 15.53 and 7.77 Å and indicate long-range order, possibly with edge-on molecular orientation.¹⁵ Crystallinity is retained in the BHJ NDT(TDPP)₂:PC₆₁BM (w:w) blend films; however the loss of the second-order reflection and the presence of peak broadening, as well as a decrease in *d*-spacing (Figure S2), suggests that PC₆₁BM is interrupting the

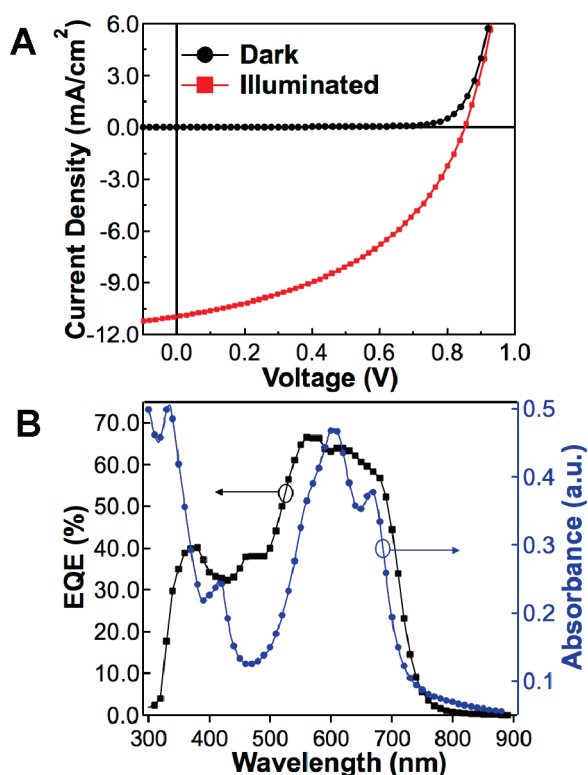


Figure 2. (A) Illuminated and dark J – V response; (B) EQE and absorption spectra of a 1.5:1.0 $\text{NDT}(\text{TDPP})_2$: PC_{61}BM active layer OPV device utilizing the architecture: ITO/PEDOT:PSS/ $\text{NDT}(\text{TDPP})_2$: PC_{61}BM /LiF/Al. Illuminated J – V recorded with an AM1.5G ($100 \text{ mW} \cdot \text{cm}^{-2}$) solar simulator.

$\text{NDT}(\text{TDPP})_2$ network and forming the essential BHJ hole and electron transporting domains. The output and transfer plots of a top-contact OFET from a drop cast $\text{NDT}(\text{TDPP})_2$ film on Si/SiO₂/HDMS (Figure 1C and 1D, respectively) indicate p -type behavior with $\mu_{\text{h}} = 7.18 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, among the highest mobilities reported for a solution-processed small-molecule OPV electron donor.^{6a} OFETs of $\text{NDT}(\text{TDPP})_2$: PC_{61}BM (w:w) blends exhibit only slightly lower μ_{h} values (e.g., $3.28 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for an optimized donor:acceptor blend—see below; Table S1), further suggesting the formation of BHJ domains by the presence of PC_{61}BM within the $\text{NDT}(\text{TDPP})_2$ network.

These promising optical, WAXRD, and OFET results motivated exploration of the photovoltaic properties of $\text{NDT}(\text{TDPP})_2$ -based devices utilizing the conventional architecture ITO/PEDOT:PSS/ $\text{NDT}(\text{TDPP})_2$: PC_{61}BM /LiF/Al. The solar cell device performance was optimized by varying both the active layer $\text{NDT}(\text{TDPP})_2$: PC_{61}BM (w:w) blend compositions (spun at 4000 rpm from 20 mg mL^{-1} CHCl_3 solutions) and annealing temperatures. The SI summarizes the results of this screening process and presents representative AFM images of the resulting morphologies. Figure 2A shows a typical current density vs voltage (J – V) response in the dark and under AM1.5G simulated light of an optimized 1.5:1.0 (w:w) $\text{NDT}(\text{TDPP})_2$: PC_{61}BM active layer blend annealed at 110°C for 10 min. The optimized device structure yields a $V_{\text{OC}} = 0.84 \pm 0.01 \text{ V}$, $J_{\text{SC}} = 11.27 \pm 0.21 \text{ mA} \cdot \text{cm}^{-2}$, fill factor (FF) = 0.42 ± 0.02 , and PCE = $4.06 \pm 0.06\%$, averaged over four devices. The high V_{OC} is consistent with the large $\text{NDT}(\text{TDPP})_2$ HOMO (-5.4 eV)– PC_{61}BM LUMO (-4.0 eV) offset.^{3a} J_{SC} is among the highest of

all solution-processed small molecule donors reported to date. The external quantum efficiency (EQE) spectrum (Figure 2B) for the optimized device has a peak EQE of 68% at 550 nm and a broad EQE response from 360 to 720 nm, consistent with the optical absorption profile (Figure 2B). Integration under the entire EQE spectrum yields $J_{\text{SC}} = 11.11 \text{ mA} \cdot \text{cm}^{-2}$, within a standard deviation of the measured J_{SC} . The high photocurrent and EQE can be attributed to the broad, high oscillator strength optical absorption, the microstructural order and exceptionally high μ_{h} of $\text{NDT}(\text{TDPP})_2$ and BHJ blend films, and the formation of well-connected BHJ domains. The FF of 0.42 ± 0.02 is a typical value for solution processed small-molecule solar cells^{6a} and represents a potential area for further device optimization. The PCE of $4.06 \pm 0.06\%$ for the 1.5:1.0 $\text{NDT}(\text{TDPP})_2$: PC_{61}BM device is the highest reported PCE for a PC_{61}BM -based small-molecule device and among the highest for any solution-processed small molecule OPV.

We conclude that 5,10-bis(2-ethylhexyloxy)naphtho[2,3-*b*:6,7-*b'*]dithiophene (NDT) substituted symmetrically by strongly absorbing and electron-deficient units (TDPP) is a useful building block for high performing organic solar cells. The high power conversion efficiency and hole mobility observed with this system suggest that further improvements of organic photovoltaic cells are possible through molecular designs that optimize electronic structure and molecular packing.

■ ASSOCIATED CONTENT

Supporting Information. Materials and methods, synthesis, characterization, and CV of $\text{NDT}(\text{TDPP})_2$, OFET and OPV device preparation, OFET and WAXRD results of blend material, OPV optimization screening, and AFM images of the blends. Complete ref 13a. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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