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Solution-Processed, Molecular Photovoltaics that Exploit Hole Transfer from Non-Fullerene, n-Type Materials

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Organic photovoltaics (OPVs) continue to attract research attention for their potential to be flexible, lightweight, and efficient devices for power generation.^[1,2] Recent work in materials design has primarily focused on the development of p-type polymers that pair with n-type phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and PC₇₁BM in bulk heterojunction (BHJ) devices. These polymer:PCBM solar cells have achieved power conversion efficiencies (PCEs) beyond 8% in single junction devices;^[3–6] however their reproducibility is hindered by the inherent polydispersity of polymer samples and batch-to-batch variations in active layer components.^[7] Moreover, fullerene derivatives such as PCBM are costly to synthesize, difficult to purify, and show little potential for engineering optoelectronic properties.^[8,9]

Fullerene derivatives are the archetypal n-type materials in OPVs because they possess chemical properties that promote unmatched efficiencies for exciton dissociation^[10] and electron transport.^[11] Electron affinities of fullerene derivatives, however, are difficult to tune and can limit device open-circuit voltages $(V_{\rm OC})^{[9,12]}$ Additionally, derivatives like PC₆₁BM often exhibit low extinction coefficients in the visible spectrum^[8,13] and have a tendency to form large crystallites upon annealing in BHJ blends.^[14,15] These characteristics impair device short-circuit current density ($J_{\rm SC}$) since poor light absorption limits exciton generation, and phase segregation restricts exciton diffusion.^[16] Although no materials have surpassed fullerene derivatives in terms of electronic performance, there is clear potential for improvement in the design of new n-type materials.

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In pursuit of materials with enhanced purity and reproducibility, solution-processable small molecules have been explored as both p- and n-type OPV active layer components.^[17,18] Small molecules rather than polymers are uniquely suited for this purpose because they can be definitively purified and characterized as monodisperse compounds.^[19,20] Recently, p-type molecules have shown remarkable performance improvements and achieved PCEs up to 8% when paired with PCBM in BHJ devices.^[21-23] Non-fullerene n-type molecules, on the other hand, have not shown PCEs above 4%.^[24-30] Despite their lower Isc values, these devices reveal two distinct design advantages that non-fullerene small molecules have over materials like PCBM. First, the materials have a tunable bandgap that can be engineered to exhibit a stronger absorption across a broader spectrum, thereby contributing to increased exciton formation. Second, the electron affinities of the materials can be lowered (i.e. higher LUMO energy level) to provide greater V_{OC} values in devices. If these two design principles can be exploited without compromising the efficiency of charge splitting, it may be possible to design a n-type material that performs better in solar cells than PCBM.

Herein, we demonstrate that n-type molecules, when combined with a p-type small molecule, provide solution-processed BHJ solar cells with efficiencies as high as 2.4%. Compared to PCBM, our materials exhibit broader-spectrum light absorption and higher extinction coefficients that enable exciton formation via n-type photoexcitation. Moreover, their low electron affinities afford high device open-circuit voltages (>0.85 V). Analysis of our highest performing solar cell with external quantum efficiency (EQE) and photoluminescence (PL) quenching shows that the active layer blend favors charge splitting via hole transfer from excitons generated on the n-type material. With an open circuit voltage above 1.0 V and a fill factor of 0.60, our optimized OPVs are among the highest performing solution-processed, non-fullerene, all-molecular devices in the literature.^[31]

The n-type small molecules in this report are designed around a symmetric donor (D)–acceptor (A) motif of A–D–A– D–A, with solubilizing chains appended to the terminal acceptor moieties (**Scheme 1**). Benzothiadiazole (BT) and isothianaphthene-nitrile (ITNCN) were chosen as the π -conjugated cores in order to impart significant electron affinity to the molecules. BT is a common acceptor monomer that is found in many high performing materials,^[27,32–35] and ITNCN is a promising subunit that we recently used to synthesize a n-type polymer.^[36] Adjacent to thiophene (T) linker units, phthalimide (PI) and thienoimide (TI) were chosen as the terminal acceptor units for their electron deficiency and solubilizing ability. In particular,





Scheme 1. Syntheses and structures of the three n-type molecule classes in this study: BT(TPI)₂ (upper left), ITNCN(TPI)₂ (upper right), and BT(TTI)₂ (lower left). The structure of p-type DPP-Py is shown in the lower right.

TI was an attractive moiety because of its isomeric relationship to thienopyrroledione (TPD), which has been incorporated into several high-performing OPV polymers.^[4,37–39] Since the extent of side-chain branching is known to affect OPV device performance,^[37,40] linear *n*-dodecyl (*n*12) and branched 2-ethylhexyl (EH) alkyl groups were appended to the small molecules to provide a range of material processability.

Each molecule was synthesized through a convergent approach that began with the terminal moieties and culminated in a Suzuki-Miyaura cross-coupling to the electron-deficient core (Scheme 1). The PI (2) and TI (11) end groups were chosen as the synthetic starting points since their side chains can impart solubility to subsequent intermediates, unlike the BT (6) and ITNCN (7) cores. Functionalization of the TPI fragment (3) with either a bromide (4) or boronate ester (5) enabled cross-coupling with 6 or 7 to provide $BT(TPI)_2$ or $ITNCN(TPI)_2$, respectively. The TTI fragment (12) was brominated (13) and cross-coupled with BT (6) to furnish $BT(TTI)_2$.

In order to analyze the conformation of our molecules, we performed density functional theory (DFT) calculations with a hybrid B3LYP correlation functional and a 6-31G(d) basis set. Calculations show that the BT core is nearly coplanar (ca. 1°) with its flanking thiophene units, while the ITNCN core is twisted 30.3° due to the increased steric interactions of a fused six- versus five-membered ring (Figure S1, S2, Supporting Information). The terminal phthalimide moieties found in BT(TPI)₂ and ITNCN(TPI)₂ also induce significant twisting in the conjugated backbone with torsion angles >20°. Torsion at the terminal moiety is minimized with thienoimide as is demonstrated by BT(TTI)₂, which displays a twist of 12.0°. In agreement with our design, BT(TTI)₂ exhibits the highest backbone coplanarity since it contains the least sterically-hindered conjugated subunits. This molecular planarity is anticipated to promote strong π - π interactions and tight solid-state packing, and benefit the electronic performance of the material in thin-film devices.

UV-vis spectroscopy of the n-type molecules shows that quinoidal character and backbone coplanarity have strong effects on thin-film (Figure 1a) and solution (Figure S3, Supporting Information) absorption spectra. With an alternating phenyl-thiophenyl backbone structure, the BT(TPI)₂ molecules have the most blue-shifted absorption onsets (ca. 620 nm) and the largest optical bandgaps (2.00-2.02 eV). Replacement of PI for TI leads to BT(TTI)₂ molecules with slightly lower bandgaps (1.89–1.92 eV), which may arise from increased backbone coplanarity, increased effective conjugation length, and stronger π - π interactions. The ITNCN(TPI)2 molecules have the most redshifted absorption onsets (ca. 710 nm) and narrow bandgaps (1.75 eV), primarily because the isothianaphthene core imparts significant quinoidal character.^[36] Since all of the molecules exhibit broader absorption spectra and higher extinction coefficients than PC71BM, these non-fullerene, n-type materials have the potential to play a much larger role in generating excitons within the active layer via light absorption (Table 1).

Electrochemical properties of the n-type materials, as measured by cyclic voltammetry (CV), reveal that the molecular highest and lowest occupied molecular orbital (HOMO and LUMO) energy levels are primarily influenced by the central acceptor subunits, where ITNCN-based materials exhibit narrower bandgaps than BT-based materials (Table 1). The competing aromatic and quinoidal resonance forms of isothianaphthene lead to destabilized HOMO and stabilized LUMO energy levels in ITNCN-based materials, which results in smaller bandgaps.^[41] For identical molecular backbones, sidechain variation does not significantly affect the electrochemical energy levels. Interestingly, despite their structural differences, the TPI and TTI end groups hardly affect the molecular HOMO and LUMO energy levels (variations within 0.1 eV). Yet despite the electrochemical similarities between BT(TTI)2 and BT(TPI)₂, the materials are anticipated to perform differently in solar cells based on their variation in structure and molecular planarity.



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Figure 1. a) Thin-film absorption spectra of the n-type molecules cast from chloroform. b) Characteristic *J*–*V* plots for DPP-Py:n-type BHJ devices fabricated under optimized conditions.

Table 1. Small molecule optoelectronic and device properties.

was evaluated in all-molecular BHJ devices with the following architecture: ITO/PEDOT:PSS/DPP-Py:non-fullerene n-type/ Ca/Al (Figure 1b). We chose DPP-Py as the p-type molecule because it has an absorption spectrum (onset ca. 720 nm, 1.72 eV bandgap) that is complementary with our n-type molecules and would effectively broaden the active layer absorption profile. Additionally, we have shown that this diketopyrrolopyrrolebased molecule can achieve relatively high PCEs in BHJ blends with PC71BM, due to its strong self-assembling properties via π -stacking of pyrene moieties.^[43] Under AM 1.5 G illumination at 100 mW cm⁻², devices fabricated with $BT(TPI-n12)_2$ and BT(TPI-EH)₂ obtained V_{OC} values above 1.0 V but were plagued with low short-circuit current densities and PCEs (0.8% and 0.2%, respectively). Comparatively, devices containing ITNCN(TPI)₂ provided higher I_{SC} and PCE values (up to 1.4%), despite a drop in V_{OC} (ca. 0.9 V). Given the twisted structure of ITNCN(TPI)₂, it is unlikely that the performance enhancements are the result of improved solid-state order. Rather, the broader absorption profiles and higher extinction coefficients of ITNCN(TPI)₂ versus BT(TPI)₂ probably enable the active layers to absorb more light and generate more excitons. Devices fabricated from BT(TTI-n12)₂ and BT(TTI-EH)₂, which exhibit the highest extinction coefficients, provided the highest shortcircuit currents and PCEs (2.3% and 1.6%, respectively). These performance trends suggest that the overall light absorption of the active layers is strongly dependent on the presence and properties of our n-type molecules. With a maximum PCE of 2.4%, our OPVs based on DPP-Py:BT(TTI-n12)2 are among the highest performing solution-processed, non-fullerene, allmolecular devices.

In order to correlate OPV performance with nanostructural order and morphology, DPP-Py:n-type blend films were analyzed by grazing-incidence X-ray diffraction (GIXD) and atomic force microscopy (AFM). X-ray diffraction patterns show that side chains greatly affect intermolecular packing, where EH-substituted molecules display less order than those substituted with *n*12 side chains (**Figure 2**a). Blend films containing BT(TTI-*n*12)₂ display the most distinct dif-

Non-Fullerene n-Type Molecule	Optoelectronic Properties				Device Properties ^{d)}			
	HOMO ^{a)} [eV]	LUMO ^{a)} [eV]	E _g ^{b)} [eV]	α ^{c)} [× 10 ⁴ cm ⁻¹]	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF	PCE ^{e)} [%]
BT(TPI-n12) ₂	5.93	3.47	2.02	5.81	1.01	-1.44	0.54	0.76 ± 0.04 (0.85)
BT(TPI-EH) ₂	5.86	3.55	2.00	8.68	1.07	-0.46	0.41	0.19 ± 0.02 (0.23)
ITNCN(TPI-n12)2 ^{f)}	5.81	3.96	1.75	8.45	0.92	-1.77	0.47	0.72 ± 0.06 (0.82)
ITNCN(TPI-EH)2 ^{f)}	5.85	3.89	1.75	10.1	0.89	-3.13	0.46	1.28 ± 0.09 (1.44)
BT(TTI-n12) ₂	5.99	3.53	1.89	18.5	1.05	-3.72	0.60	2.33 ± 0.05 (2.40)
BT(TTI-EH) ₂	5.96	3.61	1.92	11.0	0.95	-3.37	0.49	1.55 ± 0.08 (1.71)

^{a)}Measured by cyclic voltammetry, potential onsets vs. Fc/Fc⁺ at -5.13 eV;^{[42] b})Determined by absorption onset of thin films; ^{c)}Measured at λ_{max} of thin films. PC₇₁BM was measured to have an extinction coefficient of 3.26 × 10⁴ cm⁻¹; ^d)Films composed of DPP-Py:n-type were spun from chloroform solutions in a 1:2 blend ratio and annealed at 130 °C, unless otherwise noted; ^{e)}Mean average values are determined from at least 8 devices, the data in parentheses are maximum values; ^{f)}Films were spun from chloroform solutions in a 1:1 blend ratio of DPP-Py:n-type.





Figure 2. Characterization of active layer blend films through: a) two-dimensional grazing incidence X-ray diffraction (GIXD) and b) atomic force microscopy (AFM, height images).

fraction peaks, which suggests that these small molecules generate the most well-oriented domains in films. Nanostructural order is especially crucial to non-fullerene materials since they lack the three-dimensional structure of PCBM, which enables isotropic charge delocalization and enhanced transport properties. The crystallinity of BT(TTI-n12)2 films may result from close packing via strong π - π interactions of a highly coplanar conjugated backbone. Achieving these orbital interactions is essential for films of conjugated materials since molecular ordering facilitates bulk charge transport via carrier hopping.^[44] It is likely that the presence of these well-ordered domains, formed from the assembly of planar molecules, play a key role in enabling DPP-Py:BT(TTI-n12)₂ devices to achieve the highest JSC values in the series, up to 3.72 mA cm⁻². AFM height images of the blend films reveal that active layers containing BT(TTI)₂ exhibit the finest intermixing of p- and n-type components, based on their low root



mean square (RMS) roughness (Figure 2b). Overall, these data provide strong evidence that the superior fill factors, short-circuit current densities and PCEs of $BT(TTI)_2$ blend devices are a result of favorably smooth films that consist of nanoscale, ordered domains.

Since one of the goals of designing a nonfullerene, n-type molecule is to participate in light absorption, we sought to investigate whether our materials were involved in exciton formation. In a BHI device where blend components exhibit complementary absorptions, external quantum efficiency (EQE) analysis can reveal how each component contributes to the generation of free charge carriers. In agreement with the poor I_{SC} values of BT(TPI)₂ devices, BT(TPI)₂ blend films also demonstrated low EQE spectra and quantum efficiencies below 15% (Figure S6, Supporting Information). In contrast, BT(TTI)₂ devices that displayed the highest Isc values demonstrated EQEs of 15-25% in the spectral region that corresponds to the absorption profile of BT(TTI)₂ molecules (400-550 nm, Figure 3a). This overlap between EQE and absorption spectra suggests that excitation of the n-type, rather than p-type, material generates free charge carriers more efficiently. This result may be attributed to the higher extinction coefficient of BT(TTI-n12)2 versus DPP-Py $(1.9 \times 10^5 \text{ cm}^{-1} \text{ vs } 6.3 \times 10^4 \text{ cm}^{-1})$, but it may also be indicative that charge splitting is more favorable from an n-type-localized exciton. Although photocurrent originating from the excitation of n-type material is often not considered in organic solar cells, it has been observed in a few polymer-fullerene blend systems.^[45,46] In such cases, free holes and electrons are generated by the dissociation of n-type-localized excitons through a

hole transfer mechanism.

In general, bound excitons dissociate into free charge carriers through two possible mechanisms: electron or hole transfer. Since OPV materials are often designed to generate excitons through p-type excitation, electron transfer from the LUMO_{p-type} to the LUMO_{n-type} is the major pathway for producing free holes and electrons.^[47] If the n-type material is capable of absorbing light and forming an exciton, then charge carriers can also be generated by hole transfer from the HOMO_{n-type} to the HOMO_{p-type}.^[48] With either mechanism, a stronger driving force for electron or hole transfer is anticipated from greater LUMO_{p-type} – LUMO_{n-type} (ΔE_{LUMO}) or HOMO_{p-type} – HOMO_{n-type} (ΔE_{HOMO}) energy offsets, respectively.^[49,50] Based on our previous report of DPP-Py, the CV-determined HOMO energy level of our p-type molecule is calculated to be –5.53 eV (relative to Fc/Fc⁺ = –5.13 eV), which is offset from the HOMO of BT(TTI-*n*12)₂ by 0.46 eV (ΔE_{HOMO}).^[43]



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Figure 3. a) External quantum efficiency (EQE) plot of the active layer blend overlaid with the absorption spectra of DPP-Py and BT(TTI-n12)₂. b,c) Plots of active layer photoluminescence (PL) emission upon excitation at 470 nm (b) or 625 nm (c).

 $(E_{\rm HOMO} + E_{\rm g}^{\rm optical})$ energy levels of DPP-Py and BT(TTI-n12)₂ are estimated at -3.81 and -4.10 eV, respectively. By direct comparison of $\Delta E_{\rm HOMO}$ (0.46 eV) versus $\Delta E_{\rm LUMO}$ (0.29 eV) in electrochemical potentials, this active layer blend would be expected to favor hole transfer as the mechanism for charge splitting from a bound electron–hole pair.

In order to evaluate the efficacy of hole and electron transfer pathways in our devices, we measured the COMMUNICATION



Figure 4. Possible mechanisms for exciton dissociation in DPP-Py:BT(TTI-*n*12)₂ blends to generate free carriers. a) Electron transfer from DPP-Py-localized excitons is dependent on material LUMO level offsets. b) Hole transfer from BT(TTI)₂-localized excitons is dependent on material HOMO level offsets. Orbital energy levels are based on cyclic voltammetry and absorption spectroscopy measurements.

photoluminescence (PL) quenching of DPP-Py:BT(TTI-n12)₂ films at different blend ratios (Figure 3b,c). Excitation of either $BT(TTI-n12)_2$ or DPP-Py was achieved with relative selectivity by exploiting their complementary absorption spectra and irradiating blend films at 470 or 625 nm, respectively. Pristine films of BT(TTI-n12)₂ show a strong emission near 750 nm, while DPP-Py emits near 920 nm. From overlaid plots of PL emission it is apparent that the BT(TTI-n12)2 excited state energy transfers efficiently to DPP-Py, even at blend ratios as low as 1:10 (Figure 3b). Conversely, the PL of excited DPP-Py only shows significant quenching when $BT(TTI-n12)_2$ is present in films at ratios equal to or greater than 1:1 (Figure 3c). Since PL from $BT(TTI-n12)_2$ is more effectively quenched by DPP-Py and not vice-versa, in combination with the EQE measurement, it suggests that hole transfer is more efficient than electron transfer in these material blends (Figure 4). These data provide evidence that DPP-Py:BT(TTI-n12)₂ blend OPVs are greatly reliant on the formation of n-type localized excitons and subsequent dissociation into free charge carriers. Not only do these n-type molecular materials promote charge splitting and electron transport, like PCBM, they also contribute significantly to exciton generation within the active layers.

In conclusion, we report the synthesis and performance of six non-fullerene, n-type molecules in all-molecular, organic solar cells. Through a combination of DFT calculations, absorption spectroscopy and cyclic voltammetry, we have correlated the optoelectronic properties of each material with their degrees of molecular planarity and quinoidicity. As the most planar molecule in the series, $BT(TTI-n12)_2$ exhibits a V_{OC} above 1.0 V, a FF of 0.60, and a device efficiency as high as 2.4% in BHJ blends with DPP-Py. Film analyses by GIXD and AFM reveal nanoscale morphologies, where finely intermixed, ordered domains promote efficient exciton diffusion and dissociation. EQE and PL quenching studies demonstrate that n-type photoexcitation is more efficient at generating free charge carriers in our system, since hole transfer has a greater thermodynamic driving force than electron transfer. The high performance of these all-molecular devices and their explicit demonstration of photocurrent generation via hole transfer highlight the potential for light absorbing, non-fullerene materials to serve as viable components for BHJ OPVs.



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Supporting Information

Supporting Information is available from Wiley Online Library or from the author. The synthetic procedure for the small-molecule synthesis, device fabrication details, DFT calculations, solution and blend UV-vis spectra, GIXD, and EQE spectra are available.

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