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<th>Item Type</th>
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<tr>
<td>Authors</td>
<td>Wolf, Jannic Sebastian; Cruciani, Federico; El Labban, Abdulrahman; Beaujuge, Pierre</td>
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<tr>
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Communication

Wide Band-Gap 3,4-Difluorothiophene-Based Polymer with 7% Solar Cell Efficiency: an Alternative to P3HT

Jannic Wolf, Federico Cruciani, Abdulrahman El Labban, and Pierre M. Beaujuge

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Wide Band-Gap 3,4-Difluorothiophene-Based Polymer with 7% Solar Cell Efficiency: an Alternative to P3HT

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Supporting Information Placeholder

ABSTRACT: We report on a wide band-gap polymer donor composed of benzo[1,2-b:4,5-b']dithiophene (BDT) and 3,4-difluorothiophene ([2F]T) units (E_{opt} ∼2.1 eV), and show that the fluorinated analog PBDT[2F]T performs significantly better than its non-fluorinated counterpart PBDT[2H]T in BHJ solar cells with PC_{71}BM. While control P3HT- and PBDT[2H]T-based devices yield PCEs of ca. 4% and 3% (Max.) respectively, PBDT[2F]T-based devices reach PCEs of ca. 7%, combining a large V_{OC} of ca. 0.9 V and short-circuit current values (ca. 10.7 mA/cm^2) comparable to those of the best P3HT-based control devices.

In bulk-heterojunction (BHJ) solar cells of π-conjugated polymer donors and fullerene acceptors, such as phenyl-C61-butyric acid methyl ester or its C71 analog (PCBM), some important design rules govern the efficiency of the polymer donor.1,2 While conventional (single-cell) BHJ devices composed of poly(3-hexylthiophene) (P3HT) and PC_{71}BM or the indene-C60 bisadduct ICBA can yield power conversion efficiencies (PCE) of ca. 4%4 and 6.5%,5 respectively, lower band-gap systems that absorb visible light at longer wavelengths (550-800 nm), such as PBDTTPD,6,7 PTB7,8 and several other analogs,9-14 have been shown to reach PCEs > 8%. Among those, several low band-gap systems substituted with fluorine (-F) atoms have been described as especially promising compared to their non-fluorinated counterparts.15 In particular, F-substituted benzo-thiadiazole,15,16 thieno[3,4-b]-thiophene,17-19 benzo[1,2-b:4,5-b']dithiophene,19 quinoxaline,20-22 benzotriazole,23-24 isoindigo,25-26 and more recently thiophene27-28 motifs, have frequently been included in the backbone of low band-gap polymer donors. It is worth noting, however, that the underlying reasons that may justify the importance of F-substituted motifs in polymer donors remain a matter of some debate. A wide range of possible determining factors have been suggested, spanning i) improved polymer backbone planarity, resulting in higher carrier mobilities,24,25 ii) more favorable orientation of the polymer aggregates relative to the device substrate,26 iii) improved molecular arrangement and orbital overlap at the donor/acceptor interface,27 iv) dipole-driven charge separation,28 and v) lower-lying HOMO levels that contribute to larger open-circuit voltages (V_{OC}) in BHJ devices.28 While low band-gap polymer donors are especially promising in single-cell BHJ devices with PCBM, and are commonly used in efficient tandem and triple-junction solar cells, wide-band-gap analogs that can outperform P3HT in the high-band-gap cell of multi-junction devices are required in order to continue improving upon currently reported PCEs (ca. 11.6%).29-31 However, we note that only a few polymer systems combine a band-gap wider than that of P3HT (E_{opt} ∼1.9 eV), a low-lying HOMO amenable to larger open-circuit voltages (V_{OC}), and comparably high PCEs in BHJ devices.26-33

In this contribution, we report on a wide band-gap polymer donor composed of benzo[1,2-b:4,5-b']dithiophene (BDT) and 3,4-difluorothiophene ([2F]T) motifs (E_{opt} ∼2.1 eV), and show that the fluorinated analog poly(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-3,4-difluoro- thiophene), namely PBDT[2F]T (Chart 1), outperforms both P3HT (E_{opt} ∼1.9 eV) and its non-fluorinated counterpart PBDT[2H]T (described in earlier work34-35) in BHJ solar cells with PC_{71}BM.


Importantly, we point to the relevance of the [2F]T motifs – unit practically unexplored to date – in the design of efficient polymer donors used as alternatives to P3HT, and emphasize the stark differences in device characteristics between PBDT[2F]T and PBDT[2H]T in the BHJs with PC_{71}BM. Our device analyses suggest notably improved charge separation and extraction in PBDT[2F]T-based BHJ solar cells.

The PBDT[2X]T polymers (with X = H or F) were synthesized via a microwave-assisted approach (150 °C in chlorobenzene (CB), for 1 h, ca. 190 W) in order to control polymer growth and molecular weight (MW), while minimizing reaction times. Both analogs were prepared following the same Pd-mediated cross-coupling polymerization conditions (cf. details in Supporting Information (SI)); being found soluble, the polymers were purified using established methods, yielding batches of comparable MW (cf. SI, Table S1).
both PBDT\[2X\]T polymers are expected to be rather coplanar
relative energies determined by DFT modeling at the
B3LYP/6-31G(d,p) level. (b) Representations of the BDT[2F]T
tetramer HOMO and LUMO as obtained at the B3LYP/6-
31G(d,p) level of theory (see BDT[2H]T tetramer in SI; Fig.
S1). Both frontier orbitals are well delocalized along the π-
conjugated backbone.

It is worth noting that the 2-ethylhexyl (2EH)-substituted
BDT motifs provided sufficient solubility in both PBDT[2X]T
analogues and that PBDT[2H]T serves as a model polymer in
this study (along with P3HT). Prior to examining the effect of
swapping –H for –F in [2X]T motifs on the ionization, elec-
tronic, and optical properties of the PBDT[2X]T polymers, it
is important to understand how –F substitutions influence
backbone geometry. Figure 1a shows the potential energy
surfaces (PES) for twisting the [2X]T unit relative to the BDT
motif; density functional theory (DFT) calculations at the
B3LYP/6-31G(d,p) level (cf. details in SI).\(^{36-38}\) The PES plot
pertaining to PBDT[2F]T reaches two minima, corresponding
to the fully planar anti/\(^{1}\) and syn/\(^{1\circ}\)\(^{2}\) conformations. The
anti conformation is predicted to be only slightly more stable
by 0.31 kcal mol\(^{-1}\) (ca. 0.5 kT) at room temperature, suggest-
ing that backbone planarization in PBDT[2F]T is achieved via
statistical syn and anti conformations. On the other hand,
the PES plot of PBDT[2H]T shows a shallow minimum at ca.
10° and a higher-energy local minimum at 150°, with an energy
difference of 0.92 kcal mol\(^{-1}\) (ca. 1.5 kT) between the two
conformations, indicating that ca. 25 [2H]T motifs out of 100
adopt the syn conformation at thermodynamic equilibrium
(cf. SI). From these results, it is worth noting that the
PBDT[2F]T backbone is expected to be slightly more planar
than that of PBDT[2H]T – result consistent with the higher
binding energies induced by nontraditional intramolecular
hydrogen-bonding interactions.\(^{39}\) Overall, the significant
energetic barrier of 2.5-3.5 kcal mol\(^{-1}\) on going from anti to
syn conformations parallels the idea that the backbones of
both PBDT[2X]T polymers are expected to be rather coplanar
(i.e. disfavoring "out-of-plane" conformations).

The thin-film UV-Vis optical absorption spectra of P3HT
and the PBDT[2X]T polymers (with X = H or F) are

superimposed in Figure 2a (normalized spectra); Figure S2
accounts for the relative thin-film absorbance (ca. 40 nm)
and solution absorption coefficients of the PBDT[2X]T poly-
mers. Figure 2b provides the ionization potentials (IP) of the
polymers measured by photoelectron spectroscopy in air
(PESA). As seen from Figure 2a, the range of absorption of
both PBDT[2H]T and PBDT[2F]T falls within that of P3HT
(400-650 nm), with a slight apparent hypsochromic shift of the
absorption onset (by ca. 50 nm compared to P3HT). The
two derivatives have near-identical optical gaps (\(E_{\text{opt}}\)) of \(2.1\)
eV, estimated from the onset of their thin-film absorption
(\(E_{\text{opt}}\)\(\text{P3HT} = 1.9\) eV). However, as shown in Figure 2b, the IP of
PBDT[2F]T/T (2.92 eV) is significantly larger than that of its
non-fluorinated counterpart PBDT[2H]T (5.03 eV), and also
markedly larger than that of P3HT (4.65 eV). Considering that
the two PBDT[2X]T analogs have the same \(E_{\text{opt}}\) values, it
can be inferred that the [2F]T motifs suppresses both the
HOMO and LUMO of PBDT[2F]T comparably. In parallel,
comparing the solution and thin-film absorption data of
PBDT[2H]T and PBDT[2F]T (see Fig. S2), the slight intensity
variations of the higher-wavelength absorption peak point to
the presence of π-aggregates in both solutions and films.
The temperature-dependent UV-Vis spectroscopy data, shown in
Figure S3, confirms the propensity of the two polymers to form
π-aggregates albeit aggregation in PBDT[2H]T can be
more efficiently mitigated at elevated temperatures. Overall,
the tendency of the BDT[2X]T analogs to form π-
aggregates, and the weak bathochromic shifts observed on
moving from solution to film, are in agreement with the high
degree of backbone coplanarity predicted by DFT (Fig. 1a)
and suggest pronounced polymer ordering in solution. The
DFT-computed frontier orbitals of the BDT[2X]T tetrators
shown in Figures 1b and S1 are well delocalized along the π-
conjugated backbones, correlating with predicted backbone
planarity. Note that tetramers have been shown to re-

Figure 2. (a) Superimposed, normalized UV-Vis optical abs-
sorption spectra of P3HT and the wide band-gap PBDT[2X]T
systems (with X = H or F) (neat films). (b) PESA-estimated
ionization potentials (IP, triangles), optical band-gaps (\(E_{\text{opt}}\),
rectangles) estimated from the onset of the UV-Vis absorption
spectra (films), DFT-calculated HOMO energy levels
(\(\text{HOMO}\), absolute value, stars) and HOMO-LUMO gaps
(\(\Delta\text{HOMO-LUMO}\), pentagons) for the polymers.
Derivatives in Standard BHJ Devices with PCBM.

<table>
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<tr>
<th>Polymer</th>
<th>An.</th>
<th>Add.</th>
<th>(J_{SC}) [mA/cm²]</th>
<th>(V_{OC}) [V]</th>
<th>FF [%]</th>
<th>Avg. PCE [%]</th>
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<tr>
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<td>60</td>
<td>2.3</td>
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<td>58</td>
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<td>0.90</td>
<td>69</td>
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<td>9.9</td>
<td>0.91</td>
<td>74</td>
<td>6.3</td>
<td>6.7</td>
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"Devices with optimized PBTD[2X]T:PCBM ratio of 1:3.5 (wt/wt) solution-cast from chlorobenzene (CB), and P3HT:PCBM ratio of 1:1 (wt/wt) cast from dichlorobenzene (DCB); average values across 10 devices (device area: 0.1 cm²)."  

Thermal annealing: 100 °C for 10 min. Devices prepared from blends containing 5% (v/v) of the processing additive 1-chloronaphthalene (CN). Additional device statistics, including standard deviations, are provided in the SI (Fig. S4).  

Optimized device conditions.

Thin-film BHJ solar cells with the standard device architecture ITO/PEDOT:PSS/Polymer:PCBM/Ca/Al (device area: 0.1 cm²) were fabricated and tested under AM1.5G solar illumination (100 mW/cm²). The cells were tested using as-cast blends containing 5% (v/v) of the processing additive 1-chloronaphthalene (CN), and thermally annealed at 100 °C for 10 min (cf. details in SI). Devices prepared from chlorobenzene (CB) (cf. details in SI, film thicknesses in the range 70-90 nm); the control P3HT:PCBM (1:1, wt/wt) devices were cast from dichlorobenzene (DCB), according to established optimized protocols. As shown in Table 1 (device statistics provided in the SI, Fig. S4), "as-cast" BHJ devices made from PBTD[2H]T achieved modest average PCEs of 2.1%, mainly limited by low \(J_{SC}\) (4.3 mA/cm²) and average FF (66%) values. Optimized devices made from PBTD[2H]T achieved 5% (v/v) of the processing additive 1-chloronaphthalene (CN), and then thermally annealed at 100 °C for 10 min (cf. details in SI), showed improved \(J_{SC}\) (6.3 mA/cm²), and reached PCEs of 2.9% (Max.). Small-molecule additives, such as CN and 1,8-diiodooctane (DIO), are now commonly used in the optimization of polymer-PCBM BHJ blend morphologies. In parallel, "as-cast" BHJ solar cells made from PBTD[2F]T achieved significantly higher PCEs of 5.2% (Avg.), combining a large \(V_{OC}\) of 0.9 V in agreement with the large PESA-estimated IP of PBTD[2F]T (Fig. 2b), improved FFs (69%), and a two-fold increase in \(J_{SC}\) (8.4 mA/cm²) compared to PBTD[2H]T-based "as-cast" devices. Here, devices made with CN (5%, v/v) achieved PCEs of up to ca. 7% (Max.), correlated to a net increase in \(J_{SC}\) (8.4 to 10.7 mA/cm²) and FF (72%). Importantly, optimized PBTD[2F]T-based solar cells (5% CN, no thermal annealing) and the control PBTD[2H]T-based solar cells reached comparable \(J_{SC}\) values (see Fig. 3a) in the range 10-11 mA/cm², albeit with lower \(V_{OC}\) (0.6 V; due to the high-lying HOMO of P3HT) and FF (64%) values in P3HT-based devices, and in turn, lower PCEs of ca. 3.8% (Avg.; Max. 4.0%) consistent with those of prior reports. The comparable \(J_{SC}\) values achieved in PBTD[2F]T- and PBTD[2H]T-based BHJ solar cells (Fig. 3a) are consistent with the external quantum efficiency (EQE) spectra (Fig. 3b); with PBTD[2F]T-based devices showing EQE values higher by 7-15% in the range 350-575 nm, while the EQE response of P3HT-based devices is limited to ca. 60% in the same range, yet extends to longer wavelengths (up to ca. 625 nm). This observation is consistent with the distinct absorption onsets of PBTD[2F]T and P3HT (Fig. 2a). In contrast, the EQE response of optimized PBTD[2H]T-based solar cells remains under 47% in the range 350-575 nm, in agreement with the modest \(J_{SC}\) of 6.3 mA/cm² estimated from the J-V plot (Fig. 3a). Integrated EQEs are in agreement (± 0.5 mA/cm²; ± 2.5%) with the \(J_{SC}\) values reported in Table 1. The BHJ morphologies of optimized PBTD[2H]T- and PBTD[2F]T-based devices were inspected by bright-field electron transmission microscopy (TEM; cf. details in SI), and the TEM images shown in Figure S6a-h emphasize the effect of CN additives and thermal annealing on the development of the BHJ morphologies. Significant differences in phase separation patterns are known to impact polymer-PCBM BHJ solar cell performance. Here, the BHJ morphologies of the optimized PBTD[2X]T-based devices are comparably well mixed, and no net difference in phase separation patterns can be observed at the scale of those analyses. These observations are in agreement with the high photoluminescence (PL) quenching efficiency of the PBTD[2X]T analogs in the presence of PCBM (Fig. S7) with ca. 98% PL quenching observed in both cases – indicating that morphological aspects are not limiting the diffusion of photogenerated excitons to the interfaces between polymer- and PCBM-rich domains.

In BHJ thin films for which finely-mixed morphologies are apparent via direct TEM imaging, the presence of poorly connected small-sized domains and aggregate trap states are difficult to discern, yet those can effectively lower the EQE/IQE in actual BHJ solar cells. The presence of these morphological features can be inferred from reverse bias analyses (method detailed in earlier work) and SCL carrier transport measurements across the BHJs. In Figure S8, the photocurrent (\(I_{ph}\)) is plotted as a function of the effective applied voltage (\(V_{app}\)). Here, reverse the bias sweeps applied to optimized PBTD[2X]T-based BHJ devices show that \(I_{ph}\) levels off rapidly at \(V_{ftr}\) values as low as ca. 0.5 V in the PBTD[2F]T device, whereas \(I_{ph}\) in the PBTD[2H]T device does not saturate in the 6 V voltage window swept. In parallel,
lel, PBDT[2F]T devices achieve significantly higher $J_{\text{photo}}$ values at all biases (inclusive of the operating voltage range of the devices) – results suggesting that charges can be more efficiently separated and extracted in PBDT[2F]T-based BHJs, and that optimized PBDT[2H]T-based BHJs remain hindered by morphological effects. While more detailed spectroscopic and morphological analyses are beyond the scope of this concise report, future work should shed light on the morphology-correlated charge dynamics in those systems. Last, and while on the same order of magnitude, it should also be noted that the hole mobilities of the PBDT[2F]T-based BHJs estimated from the space charge limited current (SCLC) model are approximately twice as high as those of the PBDT[2H]T counterparts: $3.1 \times 10^{-4}$ cm$^2$/Vs vs. $1.5 \times 10^{-4}$ cm$^2$/Vs, respectively (see SI, Fig. S9).

In summary, our study shows that 3,4-difluorothiophene ([2F]T) motifs are attractive building blocks in the design of efficient band-gap polymer donors for BHJ solar cells with PC$_{61}$BM as the fullerene acceptor. While P3HT is commonly used in the high-band-gap cell of tandem- and triple-junction solar cells, the deeper HOMO of PBDT[2F]T ($E_{\text{opt}} \sim 2.1$ eV) is amenable to larger device $V_{\text{oc}}$ values (0.9 V). Combined with high $J_{\text{sc}}$ (ca. 10.7 mA/cm$^2$) and FFs (72%), PBDT[2F]T outperforms P3HT, achieving up to ca. 7% PCE in standard BHJ solar cells with PC$_{61}$BM; here, PBDT[2F]T:PC$_{61}$BM-based cells rival P3HT:ICBA devices (up to ca. 6.5% PCE). In parallel, we have shown that PBDT[2H]T performs significantly better than its non-fluorinated counterpart PBDT[2H]T (PCE ca. 3%). Max.), and that charges may be more efficiently separated and extracted in PBDT[2F]T-based BHJs. Efficient wide band-gap polymer donors used as alternatives to P3HT are expected to help improve upon current tandem and triple-junction solar cell efficiencies.

ASSOCIATED CONTENT

Supporting Information
Experimental methods, characterization, and additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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