Communication

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

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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 ($E_{\text{opt}} \sim 2.1$ 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 PC₇₁BM. 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/cm²) 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.¹⁻³ While conventional (single-cell) BHJ devices composed of poly(3-hexylthiophene) (P3HT) and PC₇₁BM 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,⁶⁻⁸ PTB7,⁹ and several other analogs,¹⁰⁻¹⁴ 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.² In particular, F-substituted benzothiadiazole,¹⁵⁻¹⁷ thieno[3,4-*b*]thiophene,¹⁸⁻²⁰ benzo[1,2-*b*:4,5-*b'*]dithiophene,²¹⁻²² quinoxaline,²³⁻²⁴ isindigo,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, 29} ii) more favorable orientation of the polymer aggregates relative to the device substrate,¹⁶ iii) improved molecular arrangement and orbital overlap at the donor/acceptor interface,¹⁷ iv) dipole-driven charge separation,¹⁹ and v) lower-lying HOMO levels that contribute to larger open-circuit voltages (V_{OC}) in BHJ devices.¹⁸ 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%).³⁰⁻³¹ However, we note that only a few polymer systems combine a band-gap wider than that of P3HT ($E_{\text{opt}} \sim 1.9$ eV), a low-lying

HOMO amenable to larger open-circuit voltages (V_{OC}), and comparably high PCEs in BHJ devices.³²⁻³³

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 ($E_{\text{opt}} \sim 2.1$ eV), and show that the fluorinated analog poly(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-3,4-difluorothiophene), namely PBDT[2F]T (Chart 1), outperforms both P3HT ($E_{\text{opt}} \sim 1.9$ eV) and its non-fluorinated counterpart PBDT[2H]T (described in earlier work³⁴⁻³⁵) in BHJ solar cells with PC₇₁BM.

Chart 1. Structures of P3HT, and the Wide Band-Gap PBDT[2X]T Polymers (with X = H or F).

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 PC₇₁BM. 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,⁸ yielding batches of comparable MW (cf. SI, Table Si).

Figure 1. (a) Potential energy surfaces resulting from the rotation of the [2X]T motifs (X = H or F) with respect to BDT; 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 analogs, 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, electronic, 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*/0° and *syn*/180° 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, suggesting 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

Figure 2. (a) Superimposed, normalized UV-Vis optical absorption 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_{opt} , squares) estimated from the onset of the UV-Vis absorption spectra (films), DFT-calculated HOMO energy levels ($|HOMO|$, absolute value, stars) and HOMO→LUMO gaps (HL_{gap} , pentagons) for the polymers.

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 polymers. 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_{opt}) of 2.1 eV, estimated from the onset of their thin-film absorption ($E_{opt}(P_3HT) = 1.9$ eV). However, as shown in Fig. 2b, the IP of PBDT[2F]T (5.29 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_{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 PBDT[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 tetramers 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 reproduce the electronic and optical properties of analogous polymers appropriately.⁴⁰ The DFT-estimated HOMO energy for the tetramer of PBDT[2F]T (-5.05 eV) is predicted to be 0.17 eV deeper than that of PBDT[2H]T (-4.88 eV) – relative values in line with the significant IP offset of 0.26 eV inferred earlier from the PESA measurements (Fig. 2b). In parallel, the comparable LUMO offset of 0.2 eV calculated for the tetramers makes the predicted HOMO-LUMO gap consistent with the near-identical E_{opt} values of 2.1 eV estimated from the thin-film absorption of PBDT[2H]T and PBDT[2F]T (see Fig. 2b).

Table 1. PV Performance of P₃HT and the PBDT[2X]T Derivatives in Standard BHJ Devices with PC₇₁BM.^{a,d}

Polymer	An. ^{b/} Add. ^c	J_{sc} [mA/ cm ²]	V_{oc} [V]	FF [%]	Avg. PCE [%]	Max. PCE [%]
P ₃ HT ^e	Y/N	10.0	0.60	64	3.8	4.0
[2H]T	N/N	4.3	0.79	66	2.1	2.2
[2H]T	Y/N	4.6	0.79	64	2.2	2.3
[2H]T	N/5%	5.7	0.79	60	2.3	2.7
[2H]T ^e	Y/5%	6.3	0.80	58	2.8	2.9
[2F]T	N/N	8.6	0.90	69	5.2	5.4
[2F]T	Y/N	8.4	0.90	69	5.2	5.3
[2F]T ^e	N/5%	10.7	0.90	72	6.8	7.0
[2F]T	Y/5%	9.9	0.91	74	6.3	6.7

^aDevices with optimized PBDT[2X]T:PC₇₁BM ratio of 1:1.5 (wt/wt) solution-cast from chlorobenzene (CB), and P₃HT:PC₇₁BM ratio of 1:1 (wt/wt) cast from dichlorobenzene (DCB); average values across 10 devices (device area: 0.1 cm²).

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

Thin-film BHJ solar cells with the standard device architecture ITO/PEDOT:PSS/Polymer:PC₇₁BM/Ca/Al (device area: 0.1 cm²) were fabricated and tested under AM_{1.5}G solar illumination (100 mW/cm²). The cells with optimized PBDT[2X]T:PC₇₁BM blend ratios (1:1.5, wt/wt) were cast from chlorobenzene (CB) (cf. details in SI, film thicknesses in the range 70–90 nm); the control P₃HT:PC₇₁BM (1:1, wt/wt) devices were cast from dichlorobenzene (DCB) according to established optimized protocols.⁴¹ As shown in Table 1 (device statistics provided in the SI, Fig. S4), “as-cast” BHJ devices made from PBDT[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 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), 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.^{42–44} In parallel, “as-cast” BHJ solar cells made from PBDT[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 PBDT[2F]T (Fig. 2b), improved FFs (69%), and a two-fold increase in J_{sc} (8.4 mA/cm²) compared to PBDT[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 PBDT[2F]T-based solar cells (5% CN, no thermal annealing) and the control P₃HT-based devices 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.⁴ The comparable J_{sc} values achieved in PBDT[2F]T- and P₃HT-based BHJ solar cells (Fig. 3a) are consistent with the external

Figure 3. (a) Characteristic J - V curves of optimized BHJ solar cells fabricated from PBDT[2H]T (cast from CB, 5% CN v/v, thermally annealed), PBDT[2F]T (cast from CB, 5% CN v/v, no thermal annealing), and P₃HT (cast from DCB, no additive, thermally annealed); AM_{1.5}G solar illumination. **(b)** EQE spectra of the devices fabricated from PBDT[2X]T and P₃HT under optimized conditions. Integrated EQEs are in agreement (± 0.5 mA/cm²; $\pm 2.5\%$) with the J_{sc} values reported in Table 1.

quantum efficiency (EQE) spectra (Fig. 3b); with PBDT[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 PBDT[2F]T and P₃HT (Fig. 2a). In contrast, the EQE response of optimized PBDT[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; $\pm 2.5\%$) with the J_{sc} values reported in Table 1. The BHJ morphologies of optimized PBDT[2H]T- and PBDT[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.^{42–43, 45–46} Here, the BHJ morphologies of the optimized PBDT[2X]T 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 PBDT[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 work⁴⁷) and SCL carrier transport measurements across the BHJs. In Figure S8, the photocurrent (J_{photo}) is plotted as a function of the effective applied voltage (V_{eff}). Here, reverse the bias sweeps applied to optimized PBDT[2X]T-based BHJ devices show that J_{photo} levels off rapidly at V_{eff} values as low as ca. 0.5 V in the PBDT[2F]T device, whereas J_{photo} in the PBDT[2H]T device does not saturate in the 6 V voltage window swept. In paral-

lel, PBDT[2F]T devices achieve significantly higher J_{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.⁴⁸ 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: $3.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ vs. $1.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 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 wide band-gap polymer donors for BHJ solar cells with PC₇₁BM 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 ($E_{\text{opt}} \sim 2.1 \text{ eV}$) is amenable to larger device V_{OC} values (0.9 V). Combined with high J_{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 PC₇₁BM; here, PBDT[2F]T:PC₇₁BM-based cells rival P3HT:ICBA devices (up to ca. 6.5% PCE). In parallel, we have shown that PBDT[2F]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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