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Solar Cells

Development of Fluorinated Benzothiadiazole as a Structural Unit for a Polymer Solar Cell of 7 % Efficiency**

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Fluorinated organic molecules exhibit a series of unique features such as great thermal and oxidative stability,[1] elevated resistance to degradation,[2] enhanced hydrophobicity, high lipophobicity of perfluorinated substances,[3] and inverted charge density distribution in fluorinated aromatic compounds.[4] These special features are related to the unique properties of the fluorine atom:[5] a) fluorine is the most electronegative element, with a Pauling electronegativity of 4.0, which is much larger than that of hydrogen (2.2); b) fluorine is the smallest electron-withdrawing group (van der Waals radius, $r = 1.35$ Å, only slightly larger than hydrogen, $r = 1.2$ Å). Furthermore, these fluorine atoms often have a great influence on inter- and intramolecular interactions through C-F···H, F···S, and C-F···π_F interactions.[2,6] As a result, fluorinated conjugated materials have been explored for their applications in organic field-effect transistors (OFET)[7] and organic light-emitting diodes (OLED).[4,8] However, there are only a few examples of applying fluorinated compounds in organic photovoltaics,[9] especially as *p*-type semiconductors in bulk heterojunction (BHJ) polymer solar cells.

Since the fluorine atom is a strong electron-withdrawing substituent, the introduction of F into the conjugated backbone would lower both the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels of the conjugated polymers, as demonstrated by Heeger and Brédas in a theoretical study of poly(phenylene vinylene) having various substituents.[10] Experimentally, Yu et al. confirmed the electronic effect of the fluorine substituent in their study of a series of benzodithiophene thieno[3,4-*b*]thiophene copolymers.[9b] After one fluorine atom was substituted onto the thieno[3,4-*b*]thiophene unit, the copolymer exhibited decreased LUMO and HOMO energy levels, but with a similar band gap, as compared with those of the nonfluorinated analogue. A larger open-circuit voltage (V_{oc}) was observed from the BHJ device based on the F-substituted polymer, and this difference is largely because of the lower HOMO energy level. Moreover, the short-circuit current (J_{sc}) and the fill factor (*FF*) were noticeably increased by judicious selection of solvent and additives,[11] possibly because of an optimized film morphology facilitated by these F atoms. A similar enhancement on the morphology by employing F atoms was observed by Kim et al. in their study of poly(3-hexylthiophene) (P3HT) having various end-groups.[9a] The CF_3 end-group-modified P3HT showed significant improvement in both the J_{sc} and *FF* values for its BHJ devices, thus leading to a 40 % increase in the efficiency (η). The much improved morphology of the polymer/$PC_{61}BM$ blend was attributed to the decreased surface energy of the fluorine-containing polymer. However, there has been no precedent study on the photovoltaic properties of F-containing low-band-gap polymers constructed using the donor–acceptor strategy,[12] which is a common approach to create new polymers for BHJ polymer solar cells.[13]

Herein we report the first successful application of fluorine to a donor–acceptor conjugated polymer that has exceptional performance in BHJ solar cells (Scheme 1). For the acceptor we chose the ubiquitous 2,1,3-benzothiadiazole (BT).[14] By replacing the remaining two hydrogen atoms on the BT unit with two fluorine atoms, we envisioned that the electron density on the benzene ring would be decreased, and that both the LUMO and HOMO energy levels of the resulting polymer would decrease.[15] Furthermore, substituting hydrogen atoms with fluorine atoms, which are of similar size, would not impose additional steric hindrance between adjacent monomers. Finally, the two alkylated thienyl units flanking the fluorinated BT unit can provide the necessary solubility of the resulting polymer with negligible twisting between the conjugated units, as shown by us previously.[16] The structure of the newly conceived 5,6-difluoro-4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTffBT) is shown in Scheme 1.

As for the donor, benzo[1,2-*b*:4,5-*b*′]dithiophene (BnDT) was chosen for the following reasons: a) as a weak donor, it would maintain a low HOMO energy level of the resulting polymer,[17] as demonstrated in other weak donor–strong

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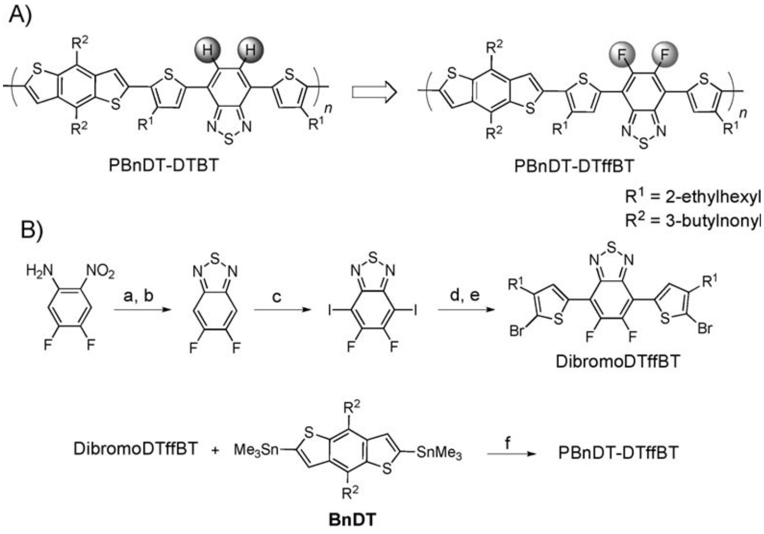

Scheme 1. A) Structures of PBnDT-DTBT and PBnDT-DTffBT. B) Synthetic route to the PBnDT-DTffBT polymer. a) Pd/C, H_2, methanol/HAc, 3 days; b) $SOCl_2$, Et_3N, chloroform, 5 h; c) I_2, fuming H_2SO_4, 60 °C, 24 h; d) (2-ethylhexylthiophen-2-yl) trimethylstannane, $[Pd(PPh_3)_4]$, toluene, reflux, 2 days; e) NBS, THF, 8 h; f) $[Pd_2(dba)_3]$, $P(o\text{-tolyl})_3$, *o*-xylene, microwave, 150 °C, 20 min. dba = dibenzylideneacetone, NBS = *N*-bromosuccinimide.

acceptor polymers;[15,16b,18] b) its structural symmetry and the rigid fused aromatic system could enhance the electron delocalization and interchain interaction to improve the charge mobility.[19] PBnDT-DTffBT was therefore envisioned (Scheme 1). Our preliminary investigation of BHJ devices derived from PBnDT-DTffBT demonstrate a significant improvement on efficiency, that is, approximately a 45 % increase compared with that of the nonfluorinated analogue PBnDT-DTBT (Scheme 1). To the best of our knowledge, PBnDT-DTffBT is among the top high-performing polymers with total efficiencies exceeding 7 %.[11,20] This efficiency indicates a great potential for incorporating the DTffBT unit and fluorine atoms into polymers in creating high performance materials for BHJ solar cells.

The syntheses of the DTffBT unit and PBnDT-DTffBT are shown in Scheme 1. A microwave-assisted Stille coupling[14c] was used to prepare both PBnDT-DTBT and PBnDT-DTffBT in high yields. To eliminate any complications of the chain effect on photovoltaic properties, identical side chains were employed for both polymers.[16b,c] Therefore these two polymers only differ by two F atoms, enabling us to accurately investigate the impact of F substituents on the physical properties of PBnDT-DTffBT and related BHJ solar cells. Although we tried to achieve good solubility by anchoring 2-ethylhexyl and 3-butylnonyl side chains on DTffBT and BnDT, respectively,[16a] both polymers exhibited limited solubility in common organic solvents at room temperature. This low solubility is due to the fact that low-molecular-weight fractions were discarded during Soxhlet extraction and the chlorobenzene fractions were collected, thus leading to noticeably high molecular weights for both polymers (Table 1). The similarity in molecular weights also eliminates any possible impact upon the photovoltaic properties of either of the polymers that is caused by significantly different molecular weights.

UV/Vis absorption spectra of PBnDT-DTffBT under various conditions are shown in Figure 1. The absorption maximum of PBnDT-DTffBT in a chlorobenzene (CB) solution is red-shifted by approximately 80 nm when the temperature drops from 100 °C to room temperature, at which point aggregation of the polymers occurs. In addition, PBnDT-DTffBT exhibits an additional absorption shoulder in its thin film, implying additional polymer-chain stacking in the solid state.[14c] A band gap of 1.7 eV for PBnDT-DTffBT was calculated from the onset of the film absorption, and was similar to that of PBnDT-DTBT.[21] The HOMO and LUMO energy levels of PBnDT-DTffBT were estimated from its cyclic voltammogram,[21] and both were lower in energy than those of PBnDT-DTBT (Table 1).

Computational studies using density functional theory (DFT) calculations were additionally performed to evaluate the influence of these fluorine atoms on the electronic and optical properties of PBnDT-DTffBT (Table 1). Both the LUMO and

Table 1: Polymerization results and energy levels of PBnDT-DTBT and PBnDT-DTffBT.

Polymer	Yield	Mn [kg mol⁻¹][a]/ PDI	Measured by CV		Simulated	
			HOMO [eV][b]	LUMO [eV][b]	HOMO [eV][c]	LUMO [eV][c]
PBnDT-DTBT	77 %	41.2/1.7	−5.40	−3.13	−5.20	−2.92
PBnDT-DTffBT	89 %	33.8/2.6	−5.54	−3.33	−5.30	−2.97

[a] Number average molecular weight (Mn). Determined by GPC analysis in 1,2,4-trichlorobenzene (TCB) at 135 °C using polystyrene standards. [b] HOMO and LUMO energy levels were calculated from the cyclic voltammogram. [c] HOMO and LUMO energy levels simulated by DFT theory calculations.

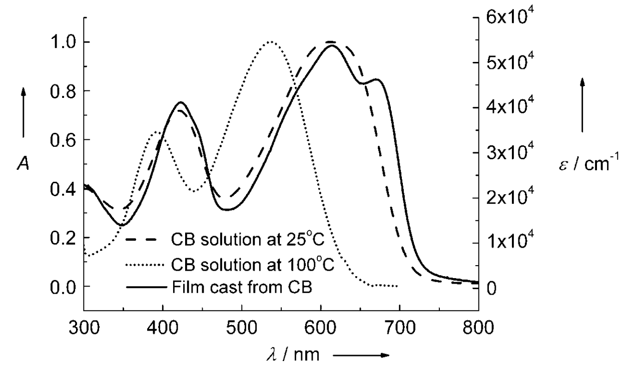

Figure 1. Absorption spectra of PBnDT-DTffBT in chlorobenzene at room temperature (dashed line), 100 °C (dotted line), and as a thin film (solid line).

HOMO energy levels were slightly lower in PBnDT-DTffBT than those in PBnDT-DTBT. PBnDT-DTffBT was predicted to have both a similar band gap and UV/Vis absorption spectrum as PBnDT-DTBT.[21] The simulated data from the DFT calculations was in agreement with the experimental results estimated from the cyclic voltammograms. Our results corroborate the previous discovery of the utility of F atoms in lowering both the HOMO and LUMO energy levels of related conjugated polymers.[2,3] With a similar band gap but a lower HOMO level, PBnDT-DTffBT-based BHJ devices would offer a similar J_{sc} value, but a larger V_{oc} value than that of the nonfluorinated analogue (PBnDT-DTBT).

Table 2: Photovoltaic properties of BHJ solar cells derived from PBnDT-DTBT and PBnDT-DTffBT and processed with a polymer/$PC_{61}BM$ 1:1 (w/w) blend in 1,2-dichlorobenzene.

Polymers	Thickness [nm]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE_{max} ($PCE_{average}$) [%]
PBnDT-DTBT	175	10.03	0.87	57.3	5.0 (4.7)
PBnDT-DTffBT	190	12.91	0.91	61.2	7.2 (6.9)

Typical BHJ solar cells consisting of these polymers as the electron donors and $PC_{61}BM$ as the electron acceptor were fabricated and then tested under simulated AM1.5G illumination (100 mW cm^{-2}; Table 2). The best-performing PBnDT-DTffBT/$PC_{61}BM$ BHJ solar cells were fabricated by spin-coating a polymer/$PC_{61}BM$ (1:1 w/w) blend in dichlorobenzene onto a PEDOT/PSS coated indium-doped tin oxide (ITO) substrate, thus generating a thick active layer of 190 nm. The devices were then completed by adding the top electrode of Ca (40 nm)/Al (70 nm). The active area of each cell is 0.12 cm^2, and a typical current density–voltage (*J–V*) curve is shown in Figure 2a. With a low-energy HOMO level of −5.54 eV, the PBnDT-DTffBT-based device exhibits a V_{oc} of 0.91 V, that is, 0.04 V larger than that of the PBnDT-DTBT-based device. Despite the similarity in the band gap of these two polymers, we achieved a larger J_{sc} value for PBnDT-DTBT devices relative to PBnDT-DTffBT devices. Incident photon to current efficiencies (IPCE) of BHJ devices were then acquired to verify the measured J_{sc} values (Figure 2b). A significant photon-to-current response was obtained in nearly the entire visible range for the PBnDT-DTffBT-based device, thus suggesting a highly efficient photoconversion process.[11,18] In contrast, the IPCE of the PBnDT-DTBT device is noticeably smaller. The calculated J_{sc} values from IPCE are in agreement with the photocurrent obtained by the *J–V* measurements (within 2% error). This high IPCE response for the PBnDT-DTffBT device, together with a high fill factor of 61.2%, suggests a balanced charge transport and an improved active-layer morphology for the PBnDT-DTffBT device, and is likely due to of the introduction of the F atoms. It is worth mentioning that the active-layer thickness of the PBnDT-DTffBT device almost doubles the typically observed 100 nm in most low-band-gap polymer solar cells[11,16b,18,22] and is close to that of P3HT-based devices after annealing,[23] thus indicating the formation of a near optimal morphology of PBnDT-DTffBT devices without annealing or additives. The PBnDT-DTffBT blend with $PC_{61}BM$ has a higher absorption coefficient than that of the PBnDT-DTBT blend. Therefore at a similar thickness, PBnDT-DTffBT films can absorb more photons, which likely accounts for the higher J_{sc} value observed in PBnDT-DTffBT devices relative to that in PBnDT-DTBT devices. We are additionally investigating how these F atoms affect the morphology of PBnDT-DTffBT BHJ devices, and whether the newly emerged DTffBT can also be used in conjunction with other weak donors to offer highly efficient polymers for BHJ solar cells.

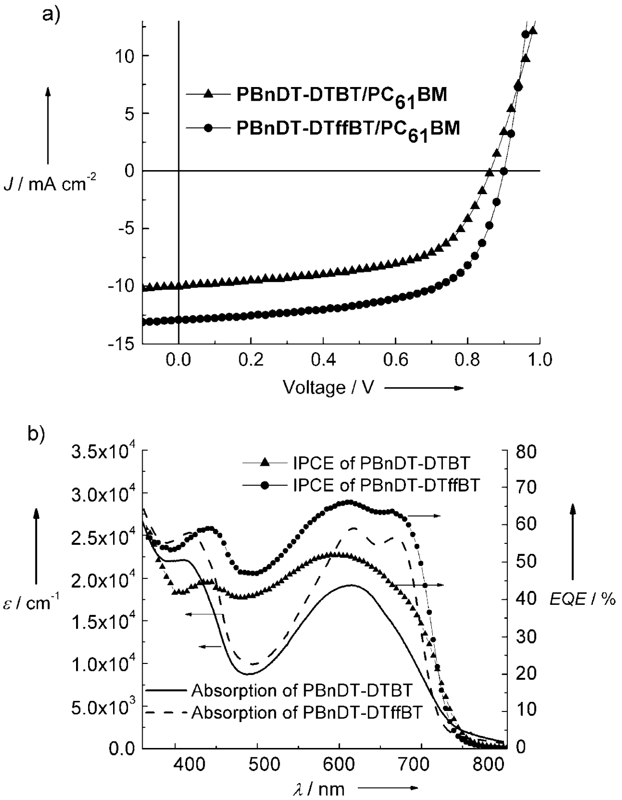

Figure 2. a) Characteristic *J–V* curves for the BHJ solar cells derived from PBnDT-DTffBT (circle) and PBnDT-DTBT (triangle) under 1 Sun condition (100 mW cm^{-2}). b) IPCE and absorption spectra for the BHJ devices derived from PBnDT-DTffBT and PBnDT-DTBT.

In summary, a new structural unit—DTffBT—was successfully synthesized and applied in constructing a new low-band-gap polymer—PBnDT-DTffBT—having both a decreased HOMO and LUMO energy level. With a noticeably high V_{oc} of 0.91 V, a fairly high J_{sc} of 12.9 mA cm^{-2}, and an enhanced *FF* of 0.61, the overall efficiency of the PBnDT-DTffBT BHJ device achieved 7.2% in initial trials. This efficiency is among the highest obtained for polymer/$PC_{61}BM$ BHJ solar cells cells,[11,18] and shows a great potential for the DTffBT unit and the incorporation of fluorine atoms in creating high performance materials for BHJ solar cells.

Experimental Section

Reagents and Instrumentation. All reagents and chemicals were purchased from commercial sources (Aldrich, Acros, and Matrix

Scientific) and used without further purification unless stated otherwise. Microwave assisted polymerizations were conducted in a CEM Discover Benchmate microwave reactor. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC 220 instrument (at the University of Chicago) using TCB as the eluent (stabilized with 125 ppm BHT) at 135 °C. The obtained molecular weight is relative to the polystyrene standard. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) measurements were recorded either with a Bruker Avance 300 MHz AMX or Bruker 400 MHz DRX spectrometer. UV-visible absorption spectra were obtained by a Shimadzu UV-2401PC spectrophotometer. The film thicknesses were recorded by a profilometer (Alpha-Step 200, Tencor Instruments). Cyclic voltammetry measurements were carried out using a Bioanalytical Systems (BAS) Epsilon potentiostat.

Polymer solar cell fabrication and testing. Glass substrates coated with patterned indium-doped tin oxide (ITO) were purchased from Thin Film Devices, Inc. The 150 nm sputtered ITO pattern had a resistivity of 15 Ω/□. Prior to use, the substrates were subjected to cleaning with ultrasonication in acetone, deionized water, and 2-propanol successively for 20 min each. The substrates were dried under a stream of nitrogen and subjected to the treatment of UV-Ozone for 30 min. A filtered dispersion of PEDOT:PSS in water (Baytron PH500) was then spun cast onto clean ITO substrates and then baked at 140 °C for 15 min. A blend of polymer and PCBM was dissolved in chlorinated solvent with heating at 110 °C for 8 h. All the solutions were then spun cast onto PEDOT:PSS layer and dried at room temperature in the glovebox under a nitrogen atmosphere for 12 h. Then a 40 nm film of calcium and a 70 nm aluminum film were thermally deposited at a pressure of ca. 1×10^{-6} mbar. There are eight devices per substrate, each with an active area of 0.12 cm^2. Device characterization was carried out under AM 1.5G irradiation with the intensity of 100 mW cm^{-2} (Oriel 91160, 300 W) calibrated by a NREL certified standard silicon cell. Current density versus potential (J-V) curves were recorded with a Keithley 2400 digital source meter. EQE were detected under monochromatic illumination (Oriel Cornerstone 260 $^1/_4$ m monochromator equipped with Oriel 70613NS QTH lamp) and the calibration of the incident light was performed with a monocrystalline silicon diode. All fabrication steps after adding the PEDOT:PSS layer onto ITO substrate, and characterizations were performed in gloveboxes under nitrogen.

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