High-Performance Non-Fullerene Acceptor Derived from Diathiafulvalene Wings for Solution-Processed Organic Photovoltaics

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1. INTRODUCTION

Organic photovoltaics (OPV) offer several technological advantages over their inorganic counterparts such as low production cost and the possibility of fabricating lightweight and flexible devices via simple solution deposition techniques. Conjugated polymer-based organic solar cells (OSCs) achieved power conversion efficiencies (PCEs) over 10%, a benchmark widely considered to be the threshold for commercialization.

Design and development of conjugated polymer donors for OPV application has been an attractive research field during the past few decades. The interest is shifted toward the development of solution-processable high performance small molecule donor and acceptors for OPV application in past few years because the small organic molecules have certain advantages compared to conjugated polymers in making organic solar cells as they have definite molecular weight, higher degree of purity, and absence of batch-to-batch variation during production.

High PCEs of 9–10% have been achieved in the case of solution-processed, small-molecule donor-based organic solar cells. However, in the case of acceptors, most of the research groups are mainly modifying fullerene and its derivative, [6,6]-Phenyl-C_{61}/71-butyric acid methyl ester (PCBM), although PCBM and other fullerene derivatives have limited absorption, wide band gaps, high synthetic costs, are difficult to purify, and exhibit limited open circuit voltage ($V_{oc}$) in the case of OSCs made with those compounds. To overcome the aforesaid drawbacks, researchers recently started working on the development of nonfullerene acceptors (NFAs), which offers defined molecular structures, tunable absorbance and energy gaps, adjustable frontier molecular orbital energy levels, facile synthesis, low-cost production, and easy purifications.

Some high-performance NFAs have been recently developed for OPV applications, and the BHJ organic solar cells fabricated with these molecules show high PCEs exceeding 11%. The most common structural template involves small molecules containing electron-deficient units, viz., perylene diimides, diketopyrrolopyrrole, benzo[c][1,2,5]thiadiazolo, and dicyanovinyl. Although a significant advancement in this field occurred only in the last few years, the first ever bilayer OSC invented by Tang in 1986 was made from an NFA, namely, 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI), and small-molecule donor copper phthalocyanine (CuPc) yielding a PCE of 1%.

In the following years, photovoltaic performance of few other NFAs,
e.g., 3-pentyl-substituted PDI\textsuperscript{11,32} and DPP-thiophene-2-carbonitrile terminated alkylated fluorene (F8-DPPTCN),\textsuperscript{33} was reported. Ding et al. synthesized a series of NFAs from fluoranthened-fused imide (FF1), and the OPV devices constructed incorporating those molecules with donor poly-(3-hexylthiophene-2,5-diyli) (P3HT) showed PCEs in the range of 2.11–2.9\%\textsuperscript{30} Asymmetric electron acceptors based on fluorene, benzo[b]thiadiazole (BT), dicyanovinyl (DCV), and DCV-substituted quinacridone were also developed by some research groups.\textsuperscript{28,35} Winzenberg et al. designed and synthesized an NFA-containing molecule with end-cap of indane-1,3-dione and achieved PCE up to 2.43\% when blended with P3HT.\textsuperscript{30} An NFA labeled as IDT-2BR bearing a benzo[b]thiadiazole rhodanine terminated indacenodithiophenophiene unit was synthesized by Wu et al., and a PCE of 5.12\% was reported from a P3HT:IDT-2BR-based solar cell.\textsuperscript{37} A perylene bisimide (PBI) dimer-based acceptor SiPBI-S, developed by Sun et al., yielded a PCE of 7.16\% comprising a wide band gap polymer PDBT-T1 as the electron donor.\textsuperscript{38} A high PCE of 9.6\% was reported from a solar cell constructed with an efficient fused-ring NFA named ITIC-Th based on an indacenodithieno[3,2-b]-thiophene core and thienyl side chains.\textsuperscript{4,39} In this work, we have synthesized a small-molecule NFA BAF-2HDT (Figure 1) with a broad absorption range and a high ε value having fluorene (a weak electron donating unit) as the core with arms of HDT-terminated benzo[b]thiadiazole (BT) (electron-withdrawing parts). Organic solar cells based on calamitic-type NFAs having an electron-rich moiety such as fluorene as a central core show better performance in comparison to those acceptors having an electron-deficient central unit like benzo[b]thiadiazole. This may be in part because typical electron-deficient units like benzo[b]thiadiazole have no position available for alkyl chains, and therefore, solubilizing groups must be located on the periphery of the molecule, making the lowest unoccupied molecular orbital (LUMO) energy level less sterically accessible for electron transfer.\textsuperscript{4,39,40} A fluorene core with two aliphatic side chains at the 9-position and the deep-lying highest occupied molecular orbital (HOMO) energy level are advantageous for improving the solubility of the molecule and facilitating charge transport in the case of devices. The π-conjugation of fluorene was extended by incorporating benzo[b]thiadiazole at the 2,7-positions of the alkylated fluorene. Benzo[b]thiadiazole, which is a fused heteroaromatic molecule, has strong electron-withdrawing properties; thus, it increases the electron-deficient character toward the outside of the molecule. The introduction of benzo[b]thiadiazole lowers the LUMO energy level of fluorene as well, which may result in high Voc in solar cells. Fluorene-2,1,3-benzothiadiazole has strong light absorption, high charge carrier mobility, and good thermodynamic stability because of its coplanar molecular structure with strong σ–π and σ–σ interactions similar to tetrathiafulvalenes (TTFs) and diathiafulvalenes (DTFs).\textsuperscript{41} Introduction of hexadithiafulvalene (HDT) to fluorene-2,1,3-benzothiadiazole extends the π-electron conjugation in the molecular backbone, which is expected to promote the charge-transport mechanism and provide a broader absorption in the UV-vis region.

The photovoltaic performance of BAF-2HDT has been investigated in an inverted structure BHJ solar cell blending with a low band gap conjugated polymer poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-alt-(3,3′-di(2-octyldodecyl)2,2′′;5′′;2′′′;5′′′′-quaterthiophen-5,5′′-diyl)] (PfBT4T-2OD), commonly known as PCE11 (Figure 1). A systematic study on structural, optical, and electrochemical properties of the BAF-2HDT molecule and the photovoltaic performance of PfBT4T-2OD:BAF-2HDT-based BHJ solar cells is reported here.

2. EXPERIMENTAL SECTION

2.1. Synthesis and Characterization of BAF-2HDT. The synthetic route of BAF-2HDT is illustrated in the Supporting Information. Reaction of 9,9-didecylfluorene-2,7-diboronic acid pinacol ester with electron-withdrawing bromo-2,1,3-benzothiadiazole-4-carboxaldehyde by a Suzuki coupling reaction catalyzed by [Pd(PPh3)4]\textsuperscript{a} afforded the aryl dialdehyde intermediate (BAF-2CHO). The HDT group introduced through a Horner–Wittig reaction provided BAF-2HDT with a dark pink color. The introduction of HDT in BAF-2CHO induced a color change of the acceptors toward a more visible region (red shift). This molecule shows good solubility in common organic solvents such as chloroform, THF, and dichloromethane at room temperature. The structure and purity of BAF-2HDT have been characterized and confirmed by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, and MALDI-TOF MS measurements. The results are available in the Supporting Information.

2.2. OPV Device Fabrication. Patterned indium tin oxide (ITO) coated glass substrates were used as the transparent bottom electrode, i.e., the cathode. The substrates were first thoroughly cleaned with detergent and then ultrasonicated with deionized (DI) water, acetonitrile and 2-propanol consecutively for 15 min each and subsequently dried under a flow of anhydrous nitrogen. After ultraviolet/ozone treatment for 15 min, a seed layer of zinc oxide (ZnO), which was previously synthesized by the method reported elsewhere, was spin-coated on precleaned ITO substrates at 5000 rpm for 30 s to obtain a film thickness of approximately 40 nm. PfBT4T-2OD (1-materials), o-dichlorobenzene (o-DCB), diiodoacene (DIO), and chlorobenzene (CB) (Aldrich), molybdnum oxide (MoO\textsubscript{3}) (Alfa Aesar, 99.9995\%), and silver (Alfa Aesar, 99.99\%) were used. At first, PfBT4T-2OD (10 mg) and BAF-2HDT (13–17 mg) were initially dissolved in 1 mL of mixed solvent o-DCB/CB/DIO (1:1:0.03). The solution was allowed to stir for 6 h at 80 °C. Thereafter, ZnO-coated ITO substrates were preheated on a hot plate at 110 °C. A photoactive blend was spun-coated at 800 rpm for 20 s to give rise to a film thickness of ~290 nm. The active layer was either (i) thermally annealed at 80 °C for 15 min or (ii) placed in the anechoic chamber of the glovebox under vacuum at room temperature for 2 h. Finally,
20 nm MoO₃ and 100 nm silver (Ag) were evaporated using the shadow mask by thermal evaporation to form the anode. All cells were encapsulated using epoxy inside the N₂-filled glovebox.

2.3. Device Characterization. The current density–voltage (J–V) characteristics of the devices were measured by a Keithley 2420 semiconductor device parameter analyzer. The light J–V curves were recorded under standard 1 sun illumination of 100 mW·cm⁻² light intensity of a xenon arc lamp based solar simulator (SCIENCETECH SS 150 Solar Simulator) using AM 1.5G filter. The light intensity of the solar simulator was calibrated with a standard monocrystalline silicon reference cell. The external quantum efficiency (EQE) of the solar cells was measured with a standard lock-in amplifier after the device area was illuminated with monochromator light from a tungsten lamp. All the measurements were performed under ambient conditions.

3. RESULTS AND DISCUSSION

3.1. UV–vis Absorption Spectra. The UV–vis absorption spectrum of BAF-2HDT in chloroform ([CHCl₃]) solution with concentration 0.01 mg·mL⁻¹ is shown in Figure 2a along with that of PC₇₁BM. The BAF-2HDT shows absorption in the wavelength range of 300–600 nm with a maximum absorption peak at 509 nm. The ε value at this wavelength was calculated to be 9.32 × 10⁷ M⁻¹·cm⁻¹, whereas the ε value for PC₇₁BM is 2.8 × 10⁴ M⁻¹·cm⁻¹. The molecule also has two very closely lying peaks at 324 and 345 nm. In comparison with fullerene-based acceptors that absorb more near UV, the HOMO value for PC₇₁BM is 9.32 eV, whereas the LUMO level was calculated by the tangent of the absorption spectrum. The values of the HOMO and LUMO energy levels for BAF-2HDT are 3.58 eV, respectively. These values are well synchronized with most of the low-band gap polymers used as the donor for OPV device fabrication.

3.2. Electrochemical Behavior. The electrochemical behavior of the BAF-2HDT acceptor was studied by cyclic voltammetry (CV) in dichloromethane (DCM) solution (Figure 3). BAF-2HDT was dissolved in DCM containing 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte at a concentration of 10⁻³ M. Ag/AgCl (calomel) was used as a reference electrode, while ferrocene was used as a standard compound. The value of the HOMO energy level of BAF-2HDT was estimated from the onset of oxidation, and its LUMO level was calculated by the corresponding HOMO level and optical band gap (Eₒ–Eₘ), which was measured from the tangent of the absorption spectrum. The values of the HOMO and LUMO energy levels of BAF-2HDT are found to be −5.69 and −3.58 eV, respectively. These values are well synchronized with most of the low-band gap polymers used as the donor for OPV device fabrication.

3.3. Photovoltaic Performance. The BHJ solar cells were fabricated in inverted architecture with the device configuration of the ITO/ZnO/active layer/MoO₃/Ag using PbFT4T-2OD as an electron donor and BAF-2HDT as the acceptor (see the Experimental Section). The device structure and corresponding energy band diagram are schematically illustrated in parts a and b, respectively, of Figure 4. The devices were tested under 100 mW·cm⁻² air mass 1.5 global (AM 1.5 G) solar illumination. The devices were fabricated with different PbFT4T-2OD:BAF-2HDT weight ratios and additive concentrations. The optimized D/A ratio was found to be 1:1.5 w/w, whereas the 3% (v/v) content of DIO in the active layer blend solution gave rise to best photovoltaic performance of the device (Table S1). The active layer was either (i) thermally annealed at 80 °C for 15 min (conventional fast solvent evaporation) or (ii) placed in...
an antechamber of the glovebox under vacuum at room temperature for 2 h to facilitate slow solvent evaporation.

Figure 5a shows the current–density vs voltage (J–V) characteristics of P̄BFBT4T-2OD:BAF-2HDT (1:1.5 w/w) based BHJ solar cells made from “thermally annealed” and “vacuum-dried” photoactive layers, and the photovoltaic parameters have been summarized in Table 1. The “thermally annealed” devices have an average PCE of 5.31% and a maximum PCE of 5.51% with an open circuit voltage (Voc) of 0.76 V, short-circuit current density (Jsc) of 13.69 mA·cm⁻², and fill factor (FF) of 0.53. The PCE was significantly improved for the devices where the active layer was dried in vacuo with an average PCE of 7.04% and a maximum PCE of 7.13%, Jsc of 14.64 mA·cm⁻², Voc of 0.77 V, and FF of 0.64. As can be seen from Table 1, a significant enhancement of ~30% in PCE is obtained by slow solvent evaporation, thereby facilitating the gradual self-organization of the P̄BFBT4T-2OD:BAF-2HDT blend. The FF is enhanced by 21% with vacuum drying treatment (Table 1), which suggests that the slow drying of the film could be a critical factor for improving FF in the case of NFA-based BHJ solar cells. A decrease in the value of series resistance (Rs) from 16.1 to 4.5 Ω·cm² and an increase in the shunt resistance (Rsh) from 0.4 to 0.5 kΩ·cm² in the “vacuum-dried” devices as compared to “thermally annealed” samples indicates better charge transport in BHJ film. The statistical histogram of PCEs obtained from each category of devices is illustrated in Figure 5b, and the corresponding photovoltaic parameters have been tabulated in Table S2. The OPV devices also have been made from “as cast” films without any further postfilm formation treatment from the same run (under similar experimental conditions), and the corresponding characteristic J–V curve is presented in Figure S1. The “as cast” device shows a PCE of 3.7% with lower Jsc and FF of 10.7 mA·cm⁻² and 0.45, respectively. Solar cells cast from annealed active layer without any additive show comparatively better photovoltaic performance than the “as cast” samples. The best performing solar cell from this set of devices shows a PCE of 4.5% with Jsc of 11.89

Figure 4. (a) Schematic of P̄BFBT4T-2OD:BAF-2HDT BHJ in inverted device configuration: ITO/ZnO/P̄BFBT4T-2OD:BAF-2HDT/MoO3/Ag. Cross-sectional view shows the different constituent layers along with their thicknesses. (b) Energy band diagram of the device. All energy values are negative with respect to vacuum level.

Figure 5. (a) Characteristic current density versus voltage (J–V) curves of inverted structure solar cells with device configuration of ITO/ZnO/P̄BFBT4T-2OD:BAF-2HDT/MoO3/Ag fabricated from “vacuum-dried” and “thermally annealed” photo-active layers, (b) Statistical histogram of PCEs of the respective polymer solar cells (50 devices for each case), (c) the EQE curves of both categories of solar cells, (d) dependence of Voc on incident light intensity (I) as observed during J–V characterization of the devices.
mA·cm⁻² and FF of 0.49 (Figure S1 and Table S3). However, no significant change was found in the value of $V_{oc}$.

### 3.4. Spectral Response

The “thermally annealed” PFbBT4T-2OD:BAF-2HDT BHJ solar cell exhibited a maximum external quantum efficiency (EQE) of 54% at 696 nm as shown in Figure S5c. The EQE value approaches 64% at 696 nm for the “vacuum-dried” device. The $J_{sc}$ calculated from the EQE spectrum from 300 to 800 nm is 14.5 mA·cm⁻², in good agreement (ca. 1% error) with $J_{sc}$ of 14.64 mA·cm⁻² obtained from the light $J−V$ curve. Interestingly, a consistent EQE value of 60% was observed in the wavelength range between 300 and 450 nm due to a large absorption of BAF-2HDT.

### 3.5. Charge Recombination Study

The charge recombination mechanism in our devices has been studied by recording the value of $V_{oc}$ at different incident light intensities during $J−V$ measurements. Figure S5d shows the dependence of $V_{oc}$ on the incident light intensity ($I$) in a semilogarithmic plot, the slope of which defines the degree of trap-assisted Shockley–Read–Hall (SRH) recombination in the BHJ solar cell. In the case of strong trap-assisted recombination, it was observed that the slope of $V_{oc}$ vs. $\ln (I)$ linear fit is close to $2kT/q$, where $k$ is Boltzmann’s constant, $T$ is absolute temperature, and $q$ is elementary charge. In our case, the OSC fabricated from “thermally annealed” PFbBT4T-2OD:BAF-2HDT blend film shows a slope of 1.68$kT/q$ that indicates strong SRH recombination. On the other hand, a “vacuum-dried” PFbBT4T-2OD:BAF-2HDT solar cell obtains a smaller slope of 1.27$kT/q$ only. These findings are consistent with the decreased value of $R_s$ and an increased value of $R_h$ in the “vacuum-dried” devices as compared to “thermally annealed” samples (Table 1) as obtained from analysis of light $J−V$ characteristics. The lower value of $KT/q$ is an indication of improved film morphology and favorable phase segregation of the blend layer (also confirmed by grazing incidence X-ray diffraction spectroscopy, Figure S2 in SI), which facilitates charge transport and an improved metal-organic interface, which aids charge collection.

### 3.6. Charge Carrier Mobility

The bulk electron and hole mobility of the PFbBT4T-2OD:BAF-2HDT blend system were measured by Mott–Gurney’s space-charge-limited current (SCLC) method. The structures of electron-only and hole-only devices for SCLC measurements were ITO/ZnO/active layer/Al and ITO/PEDOT:PSS/active layer/Au, respectively. The measured $J−V$ curves and Mott–Gurney equation fitting of the data are shown in Figure 6 for the two processing conditions: thermally (80 °C) annealed and vacuum-dried BHJ films. The hole mobility ($\mu_h$) of the donor polymer (PFbBT4T-2OD) in the “thermally annealed” blends is found to be $2.1 \times 10^{-4}$ cm²·V⁻¹·s⁻¹, which is marginally increased after vacuum drying to $2.7 \times 10^{-4}$ cm²·V⁻¹·s⁻¹. However, the electron mobility increases significantly from $1.4 \times 10^{-4}$ cm²·V⁻¹·s⁻¹ in the “thermally annealed” blends to $3.5 \times 10^{-4}$ cm²·V⁻¹·s⁻¹ in the case of “vacuum-dried” blends, which possibly contributed to the improvement in the FF from 53% to 64%. It is important to note that the observed hole and electron mobilities are significantly balanced in both “thermally annealed” ($\mu_e/\mu_h = 0.7$) and “vacuum-dried” blend devices ($\mu_e/\mu_h = 1.3$).

### 3.7. Photoluminescence Spectra

Photoluminescence (PL) measurements were carried out on the blend in o-DCB/CB/DIO (1:1:0.03) mixed solvent with increasing concentration of BAF-2HDT in order to scrutinize the charge separation and photoinduced electron transfer from the donor to the NFA molecule. Figure 7 shows the PL spectra for the PFbBT4T-2OD:BAF-2HDT blend solution with different donor–acceptor weight ratios starting from 1:0 (pristine PFbBT4T-2OD) to 1:1.75. As can be noticed, a PL maximum of the pristine PFbBT4T-2OD at around 738 nm when excited at 530 nm corresponds to the radiative decay of excitons to the ground state. However, a consistent and significant decrease in the PL peak intensity was observed for the PFbBT4T-2OD:BAF-2HDT blend solution with a gradual increase in the acceptor content. This quenching of PL peak can be attributed to the exciton dissociation due to a very efficient intramolecular charge transfer from PFbBT4T-2OD to BAF-2HDT. The PL emission of blend solution was quenched with a quenching
Stern weight ratio in the blend solution varying from 1:0 to 1:1.75. Inset: cosolvent with increasing concentrations of BAF-2HDT × 1.8

The Stern quenching results indicate a highly efficient charge transfer from donor to the donor and acceptor individually (Figure S3). Thus, the PL behavior was also observed in the solid state by exciting both morphology was investigated by atomic force microscopy the photovoltaic performance of OPVs. The mesoscale surface charge-carrier transport inside the active layer and determining photoactive layer plays a crucial role in the improvement the rougher surface with a root-mean-square (RMS) roughness of 1.4 nm, which resulted in an enhancement in the PCE after vacuum drying of the samples. The internal morphology of the PbBT4T-2OD:BAF-2HDT blend film without vacuum-drying treatment shows a rougher surface with a root-mean-square (RMS) roughness of 2.9 nm with large pin holes, whereas in the case of “vacuum-dried” films the pin holes are reduced and it shows a smooth surface with RMS roughness of 1.4 nm, which resulted in an enhancement in the PCE after vacuum drying of the samples. The internal morphology of the PbBT4T-2OD:BAF-2HDT blend film was further examined by transmission electron microscopy (TEM), and the image is displayed in Figure 8c.d. However, the TEM images did not show any noticeable difference in the nanostructure level. The high uniformity indicates good compatibility and miscibility of BAF-2HDT with the donor molecule PbBT4T-2OD.

4. CONCLUSION

We have designed and developed a solution-processable, small-molecule non-fullerene acceptor BAF-2HDT containing fluorene as a central block unit, and HDT as the end-capping group led to a broad band absorption from 300 to 580 nm with maximum absorbance at 509 nm and high ε value as compared PC_{71}BM. The BAF-2HDT has a very good electron-accepting nature with a K_{sv} value of 1.8 × 10^5 M\(^{-1}\) as confirmed by PL quenching experiments. It is shown that the vacuum-drying technique gives better morphology as compared to conventional annealing technique, and a BHJ solar cell with PbBT4T-2OD as the donor and BAF-2HDT as the acceptor gave a maximum PCE of 7.13%. Thus, the molecule fluorene-2,1,3-benzothiadiazole with HDT as the end-capping groups, having strong light absorption, high charge carrier mobility, and good thermodynamic stability because of its coplanar molecular structure with strong π–π and σ–π interactions, could be an excellent electron-acceptor candidate as a substitute of fullerene derivatives in low-cost solution-processable organic photovoltaics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b07778.

Experimental details of UV-visible absorption spectroscopy, electrochemical characterization, photovoltaic results of the OSCs with variation in donor-to-acceptor weight ratio, device performance of reference solar cells, grazing incidence X-ray diffraction spectroscopy of differently treated films, photoluminescence in solid state, experimental details on synthesis of fullerene acceptors, and structural characterization by \(^1\)H NMR, \(^13\)C NMR, ESI-MS, and MALDI-TOF (PDF)
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REFERENCES


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