Research Article

Nano Research
2019, 12(9): 2400–2405

ISSN 1998-0124 CN 11-5974/O4
https://doi.org/10.1007/s12274-019-2362-3

The impact of fluorination on both donor polymer and non-fullerene acceptor: The more fluorine, the merrier

Nicole Bauer[1], Qianqian Zhang[1], Jeromy James Rech[1], Shuixing Dai[2], Zhengxing Peng[3], Harald Ade[3], Jiayu Wang[2], Xiaowei Zhan[2], and Wei You[1] (✉)

[1] *Department of Chemistry, University of North Carolina at Chapel Hill, North Carolina 27599, USA*
[2] *Department of Materials Science and Engineering, College of Engineering, Key Laboratory of Polymer Chemistry and Physics of Ministry Education, Peking University, Beijing 100871, China*
[3] *Department of Physics and ORaCEL, North Carolina State University, Raleigh, North Carolina 27695, USA*

Received: 29 December 2018 / **Revised:** 24 February 2019 / **Accepted:** 25 February 2019

ABSTRACT

Fluorination of the donor polymer or non-fullerene acceptor (NFA) in an organic photovoltaic device is an effective method to improve device efficiency. Although there have been many studies on donor polymer fluorination, blends containing both a fluorinated donor and fluorinated NFA have rarely been reported. In this study, we use two donor polymers (4'-FT-HTAZ and 4'-FT-FTAZ) and two NFAs (ITIC-Th and ITIC-Th1) with different amounts of fluorine (from 2F to 6F) to investigate how the degree of fluorination in a blend impacts device performance. We find that fluorinating the NFA leads to a higher short-circuit current density (J_{sc}) and fill factor (FF), however, the open-circuit voltage (V_{oc}) is decreased due to a depressed lowest unoccupied molecular orbital (LUMO) level. Adding additional fluorine to the donor polymer does not have a large effect on the J_{sc} or FF, but it does lead to an improved V_{oc}. By fluorinating the NFA and having more fluorine on the donor polymer, we obtain both a high J_{sc} and V_{oc} simultaneously, leading to a power conversion efficiency over 10% in the case of 4'-FT-FTAZ:ITIC-Th1, which has the most amount of fluorine (6F).

KEYWORDS

organic solar cells, non-fullerene acceptors, fluorination, bulk heterojunction

1 Introduction

Fluorination of the donor polymer is an effective, well-studied method to improve the power conversion efficiency (PCE) of organic photovoltaics (OPVs) [1–4]. By adding fluorine substituents to the donor polymer, both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels are pulled down simultaneously, increasing the open-circuit voltage (V_{oc}) without decreasing the band gap and the short-circuit current (J_{sc}) [5–8]. Additionally, the small size of the fluorine atom allows for the tuning of these properties without introducing a large amount of steric hindrance to the polymer, largely maintaining the backbone planarity (and the band gap). In fact, fluorine substituents, when properly positioned, can even enhance the backbone planarity via fluorine induced non-covalent interactions [9].

This fluorine impact continues to be studied today, in both fullerene acceptors and non-fullerene acceptors based OPV systems [10–19]. For example, Zhang et al. investigated the impact of fluorinating the thiophene linker groups in a copolymer containing benzodithiophene (BnDT) and benzotriazole (TAZ) [9]. They found that fluorinating the thiophene linkers between the BnDT and TAZ moieties can lead to a similar OPV device performance to that of fluorinating only the TAZ unit, when the polymers are paired with PCBM, and fluorinating both the thiophene and TAZ unit simultaneously can further improve device performance. In a non-fullerene acceptor based system with the small molecule acceptor IDIC, Yang et al. compared wide band gap donor copolymers of quinoxaline and phenylene with varying amounts of fluorination on the phenylene unit [20]. They found that by adding up to two fluorine atoms to the phenlyene unit, the V_{oc} and J_{sc} are increased relative to having zero or one fluorine, leading to an improvement in the PCE.

Recently, non-fullerene acceptors (NFAs) have become increasingly common as a replacement for traditional fullerene derivatives, and there have been a few reports of fluorinated acceptors which outperform their non-fluorinated counterparts in OPV devices, similar to the donor polymers discussed previously [21–27]. For example, Zhao et al. synthesized the fluorinated acceptor ITIC-Th1, which has an indacenodithieno[3,2-*b*]thiophene (IDTT) core and fluorinated 1,1-dicyanomethylene-3-indanone (INCN) end groups [28]. The ITIC-Th1-based device exhibits a PCE of 12.1%, much higher than the 8.8% obtained by the non-fluorinated ITIC-Th-based one. Additionally, some of the highest performing devices currently reported utilize both a fluorinated donor polymer and a fluorinated NFA [29, 30]. This demonstrates that acceptor fluorination is also a promising technique to further improve the performance of OPVs.

Although NFA fluorination has been shown to increase device efficiency, there have not been many studies into the underlying causes for this improvement. Additionally, it is not yet well understood how fluorinating both the donor and NFA simultaneously impacts device performance. For future acceptor design, it is important to understand these structure-property relationships and how fluorination impacts device performance. In this study, we aim to gain a deeper understanding of why NFA fluorination leads to an improvement

---

Address correspondence to wyou@unc.edu

in device efficiency, and whether the underlying causes for this improvement are similar to those observed with donor polymer fluorination. Additionally, we will investigate how the degree of fluorination in a bulk heterojunction (BHJ) blend impacts the device performance, and whether or not the efficiency continues to increase as fluorine is added to both the donor and acceptor.

To accomplish this, we fabricated BHJ devices with varying amounts of fluorine by using two donor polymers with either two (4'-FT-HTAZ) or four (4'-FT-FTAZ) fluorine atoms per repeat unit and two NFAs with either zero (ITIC-Th) or two (ITIC-Th1) fluorine atoms per molecule (Scheme 1). We found that for each polymer, fluorination of the NFA leads to an increase in the J_{sc} and fill factor (FF), but a decrease in the V_{oc}. For each NFA, increasing the amount of fluorine on the donor polymer increases the V_{oc} while maintaining the J_{sc} and FF. The device containing the most fluorine achieved the highest PCE of over 10%, due to obtaining both a high J_{sc} and V_{oc} simultaneously.

2 Experimental

2.1 Synthesis

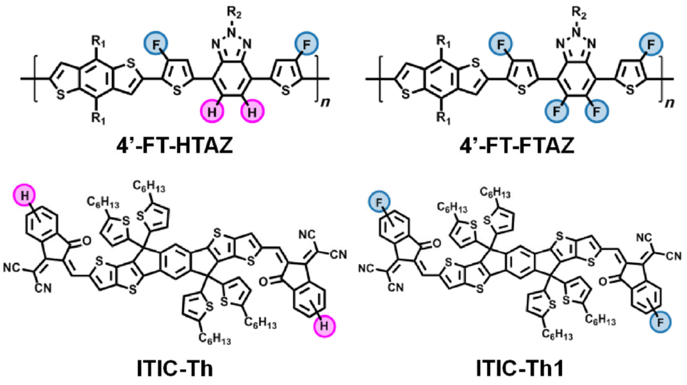
4'-FT-HTAZ, 4'-FT-FTAZ [9], ITIC-Th, and ITIC-Th1 [28] were synthesized according to literature procedure.

2.2 UV–visible spectroscopy

UV–visible absorption spectra were obtained with a Shimadzu UV-2600 spectrophotometer. Neat films were fabricated by spincasting a 15 mg/mL solution of polymer or NFA in toluene on glass. Blend films were spun cast from a 6 mg/mL polymer (D:A=1:1) solution in toluene.

2.3 Device fabrication and testing

Solar cells were fabricated on glass substrates with patterned indium doped tin oxide (ITO). ITO substrates were sonicated for fifteen minutes each in deionized water, acetone, and isopropyl alcohol, followed by UV–ozone treatment for fifteen minutes. The ZnO precursor solution was prepared by dissolving 1 g zinc acetate dihydrate and 0.28 g ethanolamine in 10 mL of 2-methoxyethanol. The solution was stirred overnight, then spun cast onto the cleaned ITO slides at 4,000 rpm for 30 s and baked for 30 min at 150 °C in air. The substrates were then transferred to a nitrogen filled glovebox for active layer deposition. Active layer solutions (D:A = 1:1, 6 mg/mL polymer) were prepared for all four blends in toluene and stirred overnight, then spun cast onto the ZnO to yield ~ 100 nm films. The devices were finished by evaporation of 10 nm of MoO_3 and 70 nm of aluminum to give a device area of 0.13 cm^2, then tested under AM 1.5G irradiation with an intensity of 100 mW/cm^2 (Oriel 91160, 300 W) calibrated with an NREL certified standard silicon solar cell. Current density versus voltage (J–V) curves were recorded with a Keithley 2400 digital source meter. EQE were detected under monochromatic illumination (OrielCornerstone 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 (Model No.: Newport 71580).



Scheme 1 Chemical structures of 4'-FT-HTAZ, 4'-FT-FTAZ, ITIC-Th, and ITIC-Th1.

2.4 SCLC measurements

Electron and hole mobilities were measured via the space-charge limited current (SCLC) method. Electron-only devices were fabricated with the configuration ITO/ZnO/D:A/Ca/Al, and hole-only devices were also prepared with the configuration ITO/PEDOT:PSS/D:A/ MoO_3/Al. The dark current densities were measured with an applied voltage from 0 to 6 V using a Keithley 2400 digital source meter. The applied voltage was corrected from the voltage drop due to series and contact resistance. The Mott-Gurneys law was utilized to extract mobility values:

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu_h\frac{V^2}{L^3}$$

where ε_r is the dielectric constant of the polymer, ε_0 is the permittivity of free space, μ_h is the hole mobility, V is the voltage drop across the device, and L is the thickness of the active layer.

2.5 Morphology

GIWAXS, RSoXS and NEXAFS reference spectra measurements were respectively performed at the beamline 7.3.3 [31] and beamline 11.0.1.2 [32], beamline 5.3.2.2 [33], Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, following the previously established protocols. GIWAXS data were acquired just above the critical angle (0.13°) of the films with a hard X-ray energy of 10 keV, and Silver Behenate (AgB) was used for geometry calibration. RSoXS was performed in a transmission geometry with linearly polarized photons under high vacuum (1×10^{-7} Torr) and a cooled (–45 °C) CCD (Princeton PI-MTE, 2,048 pixels × 2,048 pixels) was used to capture the soft X-ray scattering 2D maps and PS300 was used for geometry calibration. The raw 2D X-ray data was processed with a modified version of NIKA into 1D scattering profiles $I(q)$ [34].

3 Results and discussion

3.1 Optical and electrochemical properties

We first investigated the optical and electronic properties of the donor polymers and NFAs used in this study. The absorbance spectra of the neat materials in thin film were measured by UV–Vis spectroscopy, and the results are displayed in Fig. 1(a). The donor polymers (4'-FT-HTAZ and 4'-FT-FTAZ) have similar absorption spectra, which are complementary to the absorption of both ITIC-Th and ITIC-Th1. Combined together, any donor/acceptor pair in this study has sufficient spectral coverage from 400 to 800 nm, which is beneficial for current generation in a photovoltaic device. Additionally, ITIC-Th1 displays a red-shift relative to ITIC-Th, which could lead to higher J_{sc} in a device. The HOMO levels of the donors and acceptors were measured by cyclic voltammetry, and the LUMO levels were calculated from the HOMO levels and absorption onsets from UV–Vis (Fig. 1(b)). As shown in Fig. 1(b), the energy levels of both donor polymers are well-matched with those of the two acceptors, a prerequisite to forming efficient BHJ solar cells.

3.2 Photovoltaic performance

We then studied the photovoltaic properties of these materials by fabricating BHJ solar cells with an inverted architecture of ITO/ZnO/ Donor:Acceptor/MoO_3/Al. A summary of the results is displayed in Table 1, with representative J–V curves for each blend shown in Fig. 2(a). For each donor polymer, fluorinating the acceptor (i.e.,