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Energy level modulation of ITIC derivatives: Effects on the photodegradation of conventional and inverted organic solar cells

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Abstract

Next-generation organic photovoltaic technology is currently geared towards non-fullerene organic solar cells. Among the non-fullerene small molecule acceptors, ITIC derivatives play a central role with power conversion efficiency above 15% in single junction cells. However, knowledge about the stability of these new types of devices is lagging behind, creating an efficiency-lifetime gap for commercial viability. Here, we study the photostability of three ITIC derivatives, namely ITIC together with IT-M and IT-F, representative of methylated and halogenated ITIC, the usual modification to this small molecule acceptor. While the best performing solar cell yields a PCE of 8.6%, we find that the photostability of the devices greatly depends on the structure of the acceptor and the configuration of the devices. The methylation of ITIC into IT-M improves V_{oc} but does not greatly affect the photostability of the devices. While fluorination generally decreases the efficiency of the cells, the stability of the fluorinated ITIC-based cells appears to depend on the device structure. Thus, the change from ITIC to IT-F may not in all cases necessarily be beneficial to the advancement of the technology. Subtle changes in molecular

structure coupled with imbalance charge mobilities is at the origin of the observed differences in degradation.

1. Introduction

A few months ago, organic solar cells made another great stride in power conversion efficiency (PCE), reaching a record 17.3% [1] surpassing for the first time the bar of 15%. This is ascribed to advancement in all aspects of the technology ranging from processing techniques [2] to the device structure [3] and through especially the synthesis of novel materials [4,5]. Materials are at the very centre of this progress and have received even greater attention over the past decade. In the bulk heterojunction (BHJ) configuration, the active layer plays a crucial role and embodies a mixture of a donor (D) and acceptor (A) materials. In recent years the acceptor materials have received a boost with the synthesis of myriad novel small molecules or polymers, in what is termed non-fullerene acceptors (NFAs).[6,7] This is an attempt to find an alternative to the fullerene derivative acceptors (i.e [70]PCBM especially) which are deemed expensive through their synthesis route with time-consuming purification [4] and not as stable as the NFAs [8–13]. The fullerene derivatives also have limited absorption in the visible and near-infrared ranges and have put a limit on the obtainable open circuit voltage (V_{oc}) due to losses.

The advent of non-fullerene small molecule acceptors with high absorption in the visible range renewed the growing interest in organic solar cells (OSCs). OSCs have finally broken the 10% barrier and are rapidly approaching the PCE of 15% in binary single junction configuration. [3,14] Of all these new non-fullerene acceptors (NFAs), the workhorse NFA is ITIC. [5,15,16] This is the material that nearly broke the 1V barrier of the V_{oc} and thus, showed improved PCE. Until the advent of the NFAs, the massive use of fullerene derivatives can be attributed to the attractive features exhibited such as D:A charge transfer within picoseconds, very efficient exciton dissociation [17], favorable morphology with small domain sizes with high mobility that fits well the BHJ structure and obviously the lack of efficient alternative acceptors. In an attempt to improve further the PCE, series of ITIC derivatives have been developed,

namely, IT-M, IT-F, IT-DM, IT-Th and IT-Cl. [12,14,15,18] The new series brought the PCE of 11.5% [16] for ITIC based OSC to about 14.2% [14] for IT-Cl based single junction BHJ OSCs. The addition of electron-rich group like methyl to the end groups of ITIC, to make IT-M, increases the LUMO level and thus achieve a higher V_{oc} than ITIC if matched with the same donor. Similarly, adding strong electron-withdrawing halogen atoms like fluorine (F) or chlorine (Cl) lowers the LUMO levels, redshifts absorption edges toward the near-infrared region and enhance intermolecular charge transport because of a better π - π stacking, thus improving the current J_{sc} . With appropriate donors these acceptors pushed the barrier of the PCEs of OSCs achieved so far to 14.6% for single junction BHJ OSCs [3] to 17.3% for multijunction OSCs [1].

Figure 1: Chemical structures of PBDB-T donor polymer and ITIC derivative acceptors used in this work with their energy level diagram showing differences in HOMO-LUMO levels of IT-M and IT-F compared to ITIC.

The attention has been much focused on the PCE and the effect of these subtle changes in these novel materials on the photo-stability of their solar cells has only been recently studied in inverted structure.[19]

In their study Du et al.[19] found that photodegradation is strongly dependent on the end-group of the NFAs. Thus, fluorination of the end-group slows down photodegradation, while the addition of methyl groups accelerates photodegradation. Here we do not only present a systematic study of the photodegradation of the OSCs with this class of NFAs but also, we study under the same conditions, using the same donor polymer, the effects that the addition of the methyl (CH_3) groups or the F atoms onto the ITIC have on the photostability of their respective OSCs. In this paper, we consider as shown in Figure 1 three NFAs, namely, ITIC, IT-M, and IT-F. They differ only in the substituted atom/group of atoms (R) on the outer benzene ring of each of the A components in the A-D-A structure of the ITIC molecule. We mix each of them with PBDB-T, the workhorse polymer, to make conventional and inverted solar cells. In general, we find that fluorination of ITIC into IT-F does not help in improving the PCE compared to ITIC and IT-M when mixed with PBDB-T. It is equally not photostable, recording the fastest PCE decay among the three acceptors based conventional OSCs. However, in an inverted structure, IT-F based solar cells show potential for better photostability than the rest over time. IT-M based OSCs, on the other hand, appear to perform as or slightly better than ITIC based OSCs in terms of photostability, irrespective of the structure of the solar cells. We employ techniques such as *J-V* characteristics, UV-vis absorption spectroscopy, atomic force microscopy (AFM), 2D grazing incidence wide-angle X-ray scattering (2D GIWAXS), charge transport and light intensity dependence measurements to explain and understand the reason behind these photodegradation behaviours. We find that subtle changes in molecular stacking as revealed by GIWAXS coupled with imbalance charge mobilities as revealed by the charge transport measurements is at the origin of the observed differences in degradation.

2. Experimental Section

2.1. Materials & Solutions preparation

All materials used are both commercially and locally supplied. Prof. Hou's group supplied a set of PBDB-T, ITIC, IT-M, and IT-F while PBDB-T and another set of ITIC, IT-M, and IT-F are purchased from Solarmer Energy Inc. and Brilliant Matters respectively. The synthetic route of PBDB-T, ITIC, IT-M, and IT-F has been previously reported. [15,18,20] All the solvents and anhydrous zinc acetate ($\text{Zn}(\text{OAc})_2$) were obtained from Sigma-Aldrich and used without further purification.

PBDB-T:ITIC derivatives blend solutions with a ratio of 1:1 are made by dissolving the materials in anhydrous chlorobenzene (CB) without additive in a concentration of 20 mg.mL^{-1} . The solutions are stirred at 40°C overnight in a glovebox. Zinc oxide (ZnO) solution is prepared as earlier reported. [21]

2.2. Device preparation

Pre-patterned ITO glass substrates are carefully and successively cleaned in soap, ultraclean water, acetone, and isopropanol while sonicating them for 10 minutes, then spin-dried. Additional drying steps are carried out in an oven at 140°C for 10 minutes and in UV-ozone steriliser for 20 minutes. For conventional OSCs, bare ITO is used or (pH-neutral) PEDOT:PSS solution (Heraeus Clevis P VP AI4083, H. C. Stark) is spin-coated on the ITO substrate in ambient and annealed at 140°C for 10 minutes to form a $\sim 50 \text{ nm}$ layer atop ITO. For inverted devices, a $\sim 30 \text{ nm}$ ZnO layer is instead spin-coated, then annealed at 170°C for 30 minutes in air. The substrates are transferred into a glovebox under inert conditions for spin-coating of the active layer at 1500 rpm for 5 seconds to obtain a thickness of 100 nm. Finally, the top electrodes are thermally evaporated under vacuum at $<1 \times 10^{-7} \text{ mbar}$: LiF (1 nm) and Al (100 nm) for conventional devices, or MoO_3 (10 nm) and Al or Ag (100 nm) for inverted devices. For the current-voltage measurements, the cells are kept at room temperature by active cooling under continuous illumination at open circuit condition for two hours. For single carrier devices, similar steps are followed with the only differences are in the device structures. For hole-only devices Cr (1 nm)/Au (20 nm)/PEDOT:PSS/polymer:ITIC derivatives/Pd (15 nm)/Au (80 nm) and the electron-only devices Al (20 nm)/polymer:ITIC derivatives/LiF (1 nm)/Al (100 nm).

2.3. Characterisations

2.3.1. UV-visible absorption & Morphology

UV-visible absorption profiles and atomic force microscopy (AFM) measurements are obtained as previously reported. [21,22]

2.3.2. 2D Grazing incidence wide-angle X-ray scattering (GIWAXS)

GIWAXS measurements were performed using the MINA instrument, an X-ray scattering instrument built on a Cu rotating anode source ($\lambda=1.5413 \text{ \AA}$). 2D patterns were collected using a Vantec500 detector (1024x1024 pixel array with a pixel size 136 x 136 microns) located 122 mm away from the sample. The thin films were placed in reflection geometry at certain incident angles α_i with respect to the direct beam using a Huber goniometer. GIWAXS patterns were acquired using incident angles of 0.2° (close to the incident angle of the materials). An exposure time of 1h per pattern is used. The direct beam centre position on the detector and the sample-to-detector distance were calibrated using the diffraction rings from standard silver behenate and Al_2O_3 powders. The GIWAXS patterns are presented as a function of the in-plane modulus of scattering vector q_y and the near out-of-plane scattering vector q_z , defined as:

$$q_y = \frac{2\pi}{\lambda} [\sin(2\theta_f) \cos(\alpha_f)] \text{ and } q_z = \frac{2\pi}{\lambda} [\sin(\alpha_f) + \sin(\alpha_i)] \quad (1)$$

3. Results & Discussion

Bulk heterojunction organic solar cells are fabricated with either PBDB-T:ITIC or PBDB-T:ITIC-M or PBDB-T:IT-F blends as the active layer in conventional and inverted structures. We measure the current density-voltage (J - V) parameters of the fresh devices and also investigate the photo-induced degradation behaviour in all three solar cells in both configurations. We eliminate any other competing effects such as oxygen/moisture and elevated (or difference in) temperature that may exacerbate the degradation behaviour.[23] For the degradation measurements, the cells are kept at room temperature by active

cooling under continuous illumination at open circuit condition for two hours. With the devices kept in an inert atmosphere with H_2O and O_2 levels kept below 0.1 ppm, the parameters are measured every 5 mins. Figure 1 shows the structures of the materials used together with their energy levels. The energy level alignments depicted in Figure 1 can help to predict some optical and photovoltaic properties with the PBDB-T:ITIC as a reference system. The addition of the methyl group on the outer benzene rings of ITIC to form IT-M increases the LUMO and HOMO levels by 0.04 and 0.03 eV respectively, leading to a slightly higher optical band gap of 1.60 eV as against 1.59 eV for ITIC. Consequently, the optical absorption of IT-M should be blue shifted (see Figure s1a), which could lead to a shift and an increase in intensity at higher energies in the region of overlap with the PBDB-T absorption spectrum (see Figure s1a,b). Additionally, a higher V_{oc} should be obtained as a result of enhanced energy offset between the LUMO of the acceptor and the HOMO of the donor. In contrast, the LUMO and HOMO levels are respectively 0.12 and 0.05 eV lower for the fluorinated ITIC (IT-F) than for ITIC, resulting in an optical band gap of 1.52 eV. A red-shifted absorption should be observed which could result in higher values of J_{sc} . However, this improvement could be counterbalanced by lower V_{oc} arising from a lower LUMO energy level. Additionally, LUMO levels alignment between the donor and acceptors provides enough energy for an efficient charge dissociation, all of them higher than the estimated 0.3 eV [24]: 0.45 eV for IT-M, 0.49 eV for ITIC and 0.61 eV for IT-F. Finally, the HOMO levels alignment between the donor and acceptors also provides enough energy for an efficient charge transfer: 0.25 eV for IT-M, 0.28 eV for ITIC and 0.33 eV for IT-F. Figure s2 displays the J - V curves and the device counts for the two device structures while Table 1 highlights the J - V parameters of the best-performing devices. The recorded PCEs are close to the literature values for the inverted devices. [16,19,25–27] Little to no significant differences in J_{sc} values for the three blend solar cells are observed, especially for the inverted devices ($\sim 14.5 \text{ mA}\cdot\text{cm}^{-2}$), which testifies to almost equal photon harvesting as shown in Figure s2c and a negligible effect of the shifted absorptions of IT-M and IT-F, earlier highlighted and shown in Figure s1a,b. However, V_{oc} values confirm the trend predicted from the energy level alignments shown in Figure 1. Compared to the 880 mV (0.831 mV for the inverted device) of the ITIC blend, IT-M blend has an

enhanced V_{oc} close to 900mV, while IT-F based devices exhibit V_{oc} values much lower, around 700mV. This pronounced energy loss in IT-F blends is worsened by a reduced fill factor (FF), which testifies to a less effective charge extraction and/or stronger recombination mechanisms than in the other blends. Consequently, IT-F blend solar cells record lower PCEs. Moving from conventional to inverted structure improves the performances of the ITIC and IT-M blend solar cells significantly, mainly because of the better J_{sc} and FF, despite modest losses (tens of mV) in open-circuit voltage. The reduction in V_{oc} compared to the conventional devices may be due to the inherent structural defects in the ZnO layer. [28] Overall, the efficiencies are slightly lower than previously reported [16,25–27] due to differences in device fabrication processes and conditions, however, the initial efficiencies do not much affect the general outcome of the study on device stability.

Table 1: Photovoltaic parameters of the best performing conventional and inverted solar cells.

Devices	Structure	Calc. J_{sc} (mA.cm ⁻²)	J_{sc} (mA.cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
PBDB-T:ITIC	Conventional	13.3	13.4	0.880	63.9	7.5
	<i>Inverted</i>		<i>14.5</i>	<i>0.831</i>	<i>71.1</i>	<i>8.6</i>
PBDB-T:IT-M	Conventional	13.6	12.9	0.917	60.2	7.8
	<i>Inverted</i>		<i>14.4</i>	<i>0.890</i>	<i>65.0</i>	<i>8.2</i>
PBDB-T:IT-F	Conventional	14.6	14.3	0.718	60.2	6.2
	<i>Inverted</i>		<i>14.5</i>	<i>0.684</i>	<i>57.5</i>	<i>5.7</i>

All devices are processed under the same conditions unless mentioned otherwise. Figure 2 reveals the average photo-induced degradation behaviour of the conventional organic solar cells (six devices for each blend). A burn-in behaviour is observed in Figure 2a in the first 10-20 minutes of the illumination in all cells. This observed behaviour is caused by the continuous illumination of the devices, as devices kept under dark have far longer stability/lifetime with T_{80s} above 11 days (a minimum T_{80} of 264 hours) for inverted cells as shown in Figure s3. Similar trends are also observed for conventional cells. Additionally, we observed that the degradation is caused by the near UV region of the lamp's spectrum.[29] However, if one removes the UV part of the spectrum by the use of a UV-filter (cutting off wavelength up to 425 nm), the cells remain mostly photostable. A more pronounced burn-in effect is recorded for the IT-F

blends, lasting for 20 mins, than the ITIC and IT-M blends lasting only for 10 mins. The fast-initial degradation process is followed by a prolonged linear regime which extends over the 2 hours. The PBDB-T:IT-M blends show the most photostable behaviour of the three with an average PCE loss of 12%, followed by the PBDB-T:ITIC blends' 15% and finally 22% PCE loss for the PBDB-T:IT-F blends. While the J_{sc} remains practically constant for all three cells, the main contributory factors to the degradation trend observed in the device efficiency are substantially due the losses in FF, between 10-18% decrease, and minor changes in V_{oc} (~ 6% decrease). Since these parameters are related to the physical properties of the active layer materials and the devices, their evolution brings to light the degradation pathway within the devices. The minimal but similar decreasing trend in J_{sc} in all three devices means very little to no changes in both i) optical absorptions as shown in Figure s1c and ii) charge extraction at short circuit upon exposure. Whereas unaltered or change in V_{oc} is an indication that the energy levels of both the HOMO and the LUMO of the materials are unmodified or are experiencing some changes over the period of the experiment. Figure 2d appears to reveal that the HOMO-LUMO levels of the IT-F blend have undergone pronounced change as compared to the other blends. However, these changes are not as significant as the changes in the FF.

Figure 2: Time evolution of the average J - V parameters (6 devices each with the standard error of the mean) of the three conventional solar cells: PCE (a), FF (b), J_{sc} (c), and V_{oc} (d).

The FF is related to the competition between the free charges extraction rate, k_{ext} , and the recombination rate, k_{rec} , as follows: [30]

$$FF \sim \frac{k_{ext}}{k_{rec}} = \frac{\mu_e \mu_h V_{int}^2}{\gamma G L^4} \quad (2)$$

where V_{int} is the internal voltage proportional to the V_{oc} , γ is the recombination coefficient, G the generation rate of free charges and L is the active layer thickness.

While J_{sc} and V_{oc} values are largely stable, the fill factor continues to fall during the illumination, narrowing the underlying degradation process to either recombination strength and/or variations in charge carrier mobilities. Morphological changes could explain an increase in recombination rate with isolated

domains or dead-end point or growth in domain sizes above the exciton diffusion length. However, in Figure s4 no significant modifications of blend morphology are observed for the three blends before and after two hours of light exposure. The exposed films (Figure s4 bottom row) exhibit the same fibril-like domains as the fresh ones (Figure s4 top row), with only small variations in the roughness as seen in Figure s4 bottom row. Moreover, J_{sc} and V_{oc} light intensity dependence measurements in Figure 3 reveal no to little change in slope before and after exposure for all three solar cells. In the case of J_{sc} , α values for fresh and exposed devices in Figure 3(a,b,c) remain unaffected and close to unity (0.95, 0.96 and 0.94 respectively for ITIC, IT-M, and IT-F based blends), suggesting weak but similar bimolecular recombination behaviour [25] in all three solar cells (fresh and exposed). For the V_{oc} plots, the slopes $nk_B T/q$ with n the ideality factor, do not significantly change. However, it is important to note that in Figure 3(d,e,f), while n slightly increases for PBDB-T:IT-F from 1.12 to 1.16; it slightly decreases for PBDB-T:ITIC solar cell from 1.27 to 1.22 and for PBDB-T:IT-M solar cell from 1.29 to 1.24. These two observations confirm that an increase in trap-assisted recombination strength cannot explain the observed degradation, at least for PBDB-T:ITIC and PBDB-T:IT-M solar cells. However, the high initial number of traps in these two devices could be playing a role in their degradation.

Figure 3: J_{sc} (a,b,c) and V_{oc} (d,e,f) light intensity dependence measurements for fresh (0h) and exposed (2h) devices of PBDB-T:ITIC (a,d), PBDB-T:IT-M (b,e) and PBDB-T:IT-F (c,f).

To get an insight into the variations in charge carrier mobilities, single carrier devices, both electrons only (EO) and holes only (HO) devices, are fabricated for all three NFAs and the blends and their electron and hole mobilities are extracted through the space charge limited current (SCLC) method by fitting their measured J - V curves (see Figure s5) before and after illumination to the Murgatroyd equation: [31]

$$J_{SCLC} = \frac{9}{8} \epsilon_o \epsilon_r \mu \frac{V^2}{L^3} \exp \left[0.891 \gamma(T) \sqrt{\frac{V}{L}} \right] \quad (3)$$

where μ is the mobility of the studied charge carrier, L is the thickness of the active layer and $\gamma(T)$ a field-dependent coefficient. The NFAs show similar electron current strength in their fresh state and mobilities as demonstrated by their J - V curves in Figure s5 a-c. After exposure, only IT-M shows a slight improvement in electron current while the other remain unchanged and equal to their fresh state electron currents. PBDB-T:IT-F single-carrier devices exhibit a good hole mobility (as seen in the current in figure

s5i) of one order of magnitude higher than its electron mobility and those of PBDB-T:ITIC and PBDB-T:IT-M (J - V curves in Figure s5d-h), which leads to a great imbalance in charge transports, with $\mu_h/\mu_e = 16 \gg 1$. Similar effects but lower ratios are observed for PBDB-T:IT-M and PBDB-T:ITIC blends with both having $\mu_h/\mu_e = 3 > 1$. Unbalanced mobilities induce different extraction rates at the electrodes and the build-up of space charge within the devices. The accumulation of charges obstructs the flow of currents, raises the charge carrier densities and thus explains the reason for the observed faster degradation for the IT-F blends. The imbalance in mobility of the IT-F blend is more upset during the photodegradation process, due to a faster decrease in the electron mobility (-69%) compared to the hole mobility (-43%), resulting in even higher ratio compared to the rest of the blends as shown in Table 2. IT-M shows a reduction in the ratio from 3.0 to 2.0 and thus, indicating a more balanced charge transport compared to the other blends with 6.0 and ~ 29.0 respectively for PBDB-T:ITIC and PBDB-T:IT-F devices.

Table 2: Mobility values for fresh and exposed blend devices

Devices	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	PBDB-T:ITIC	PBDB-T:IT-M	PBDB-T:IT-F
Fresh	μ_e	5.1×10^{-5}	1.2×10^{-5}	5.5×10^{-5}
	μ_h	15×10^{-5}	3.6×10^{-5}	8.8×10^{-4}
	μ_h/μ_e^*	3.0	3.0	16.0
Exposed	μ_e	2.8×10^{-5}	1.0×10^{-5}	1.7×10^{-5}
	μ_h	17×10^{-5}	2.0×10^{-5}	5.0×10^{-4}
	μ_h/μ_e^*	6.0	2.0	~ 29.0

* unitless quantity

The imbalance in charge transport clearly explains the trends observed in the photo-induced degradation of the three devices. However, the cause of this imbalance over time remains unclear. To clarify this point, we performed GIWAXS analysis to gather information about any possible photo-induced changes in structural orientation, crystallinity and the π - π stacking of the different blend films, namely PBDB-T:ITIC, PBDB-T:IT-M, and PBDB-T:IT-F. All the measured blends show a clear (100) peak located at about 2.9 nm^{-1} together with some more or less defined extra peaks at higher angles, related to the crystalline molecular packing. [32] The GIWAXS of the fresh and degraded blend films are shown in Figure s6 and s7. It is clear from Figure s7(c,f) that the IT-F blend shows no significant change in

structure as compared to ITIC blend in Figure s7(a,d) which shows a clear decrease of the in-plane intensity in the region around $10\text{-}20\text{ nm}^{-1}$ and of the near out-of-plane intensity around 2 nm^{-1} . However, there is a slight change in orientation in IT-F blends upon illumination. The intensity along q_z increases while it decreases along q_y . Thus, a change in orientation of the IT-F blends towards edge-on. The overall crystallinity of ITIC blends seems to go down upon light-induced degradation. In particular, the disappearance of the (010) in-plane peak located at 17.1 nm^{-1} and indicative for the π - π stacking of the edge-on fraction suggests a significant, negative influence of photo-illumination onto the crystalline structure of the PBDB-T:ITIC blend. [33] Compared to ITIC blend films, IT-M blend films also reveal some structural change between the fresh and exposed films as seen in Figure s7(b,e). Though we can pin the observed degradation behaviour on the difference in the chemical structure of the ITIC derivatives through these subtle changes, can this imbalance in charge transport observed in the IT-F blend devices be induced/exacerbated by the interfacial layers employed in device fabrication?

Figure 4: Time evolution of the average J - V parameters (4 devices each with the error in the mean) of the three inverted solar cells: PCE (a), FF (b), J_{sc} (c), and V_{oc} (d).

If that is the case, the work function of electrodes or the acidity of PEDOT:PSS can be the reason. [22] The work function of Al/Ag electrode varies upon direct illumination in conventional structures, so there is a possibility of series resistances, leakage currents, at the electrode interfaces. Thus, we can use stable inorganic interfacial layers, namely, ZnO as the electron transporting layer (ETL) and MoOx as the hole transporting layer (HTL) in the inverted structure. [34,35] This allows to prevent the acidic reaction of PEDOT:PSS with the ITO electrode and/or the active layer. [34–38] We make inverted solar cells of the three blends. The results show an improvement in device photostability as known for this type of device structure as revealed in Figure 4 and also a dramatic change in photodegradation behaviour of the IT-F blends which apparently becomes as photostable as the other blends in all J - V parameters. Thus, the observed degradation is no more dominated by one J - V parameter. Even more surprising, the FF effect disappears, indicating that the degradation trend caused by the imbalance in charge transport may be due to the used interfacial layers. An added value can be the matching of energy levels in the inverted configuration, explaining the stabilisation behaviour observed in IT-F. Very recently, while writing this manuscript, it was found by Du *et al.* that PBDB-T:IT-F inverted solar cells show prominent photostability with a filtered white LED light source (UV part removed) under an extended time of exposure. [19] With longer time, PBDB-T:ITIC would become the most photostable of three cells as evident after one-hour illumination and the degradation behaviour then becomes more and more dominated by losses in J_{sc} and FF as shown in Ref. [19].

Figure 5: Time evolution of the J - V parameters of conventional PBDB-T:IT-F solar cells with PEDOT:PSS, pH-neutral PEDOT:PSS and bare ITO: PCE (a), FF (b), J_{sc} (c), and V_{oc} (d).

To be sure that this behaviour of IT-F blends is due to (or the acidity of) PEDOT:PSS and not due to the device structure itself, we finally make conventional PBDB-T:IT-F solar cells as before with PEDOT:PSS or pH-neutral PEDOT:PSS as the HTL or with bare ITO. Figure 5 shows the time evolution plots of the J - V parameters under continuous 1 sun illumination. The devices with bare ITO and pH-neutral PEDOT:PSS generally perform even worse than the device with PEDOT:PSS with huge losses in J_{sc} and V_{oc} which is not the case for the PEDOT:PSS device. Thus, this device structure dependence stability behaviour of the PBDB-T:IT-F blend devices has nothing to do with PEDOT:PSS or its acidity. The reason for this behaviour remains unclear and beyond the scope of this current work. Further investigation may be needed to comprehend this singularity in behaviour fully.

4. Conclusions

The current study was designed to investigate and determine the effect of the HOMO-LUMO energy modulation of ITIC, through subtle changes such as methylation and fluorination of the ITIC acceptor, on the efficiency and photostability of their organic conventional and inverted solar cells. Methylation of ITIC into IT-M improves the efficiency, mainly V_{oc} , but makes no significant difference to the performance of the organic solar cells in terms of stability. While IT-M seems to improve a bit the photostability of the devices in the conventional structure, it makes no difference under the inverted structure. Both ITIC and IT-M, therefore perform almost equally in efficiency and stability. However, fluorination of ITIC into IT-F decreases the efficiency of the cells irrespective of the device structure. It has a conflicting effect in terms of photostability depending on the device structure. While being unstable compared to ITIC in conventional structure devices, it is as stable as ITIC and IT-M in inverted structure devices. Thus, the subtle changes in the ITIC to synthesise its derivatives play a role in the degradation of their non-fullerene solar cells. Subtle structural changes as revealed by GIWAXS is possibly at the origin of the observed degradation in the cells. Finally, an imbalance in charge mobilities upon light exposure is the cause of the differences observed in the degradation behaviour of the three cells, especially in the case of the conventional solar cells.

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Supporting Information

The Supporting Information is available free of charge on the website or can be freely obtained from N.Y.D. and includes Absorption of pristine and blend films, *J-V* parameters of the studied solar cells, Solar cells lifetime in the dark, AFM images of blend films, charge transport in the devices, and GIWAXS image and peak intensity plots.

Notes

The authors declare no competing interests.

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Energy level modulation of ITIC derivatives: Effects on the photodegradation of conventional and inverted organic solar cells

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Highlights

- The effect of the energy modulation of ITIC derivatives on polymer solar cell performance
- The fluorination of ITIC small molecule acceptor into IT-F reduces the V_{oc} of the solar cells
- The addition of methyl groups onto ITIC to form IT-M increases the V_{oc} of the solar cells
- IT-M has no significant effect on the photostability
- The photostability of IT-F-based cell depends on the device structure