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Understanding the Effect of N2200 on Performance of J71: ITIC Bulk Heterojunction in Ternary Non-fullerene Solar Cells

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Keywords: none-fullerene, interface, charge recombination, efficiency, ternary organic solar cells

Abstract

None-fullerene solar cells with ternary architecture have attracted much attention because it is an effective approach for boosting the device power conversion efficiency. Here, the crystalline polymer N2200 as the third component is integrated into J71:ITIC bulk heterojunction. A series of characterizations indicate that N2200 could increase photo-harvesting, balanced hole and electron mobilities, enhanced exciton dissociation, and suppressed charge recombination, which result in the comprehensive improvement of open circuit voltage, short circuit current and fill factor in the device. Moreover, after introduction of N2200, the morphology of the ternary active layer is optimized, and the film crystallinity is improved. This work demonstrates that adding a small quantity of high crystallization acceptor into non-fullerene donor: acceptor mixture is a promising strategy toward developing high-performance organic solar cells.

Toc Figure

Introduction

The overuse of fossil fuels has brought a series of social risks, such as greenhouse effect, acid rain and haze. The development of clean and renewable energy resources is considered as an effective approach to solve the energy problems, such as wind, nuclear, geothermal and solar power.^{1,2} In particular, organic solar cells (OSCs) have drawn a great deal of attention with the potential of light-weight, flexibility, high throughput, abundant raw materials, simplicity of fabrication process and low production cost.³⁻⁹ Much effort has been invested in strategies of materials engineering, device architecture design, and manufacturing technology, the power conversion efficiency (PCE) of the state-of-the-art single-junction OSC has reached over 15%.¹⁰⁻¹³ However, the further improvement of performance of single-junction OSCs are limited by the low photon harvesting and high energy loss due to the narrow absorption window and strong Coulomb interaction with the opposite charge of organic materials. Tandem OSCs that combined with two or more single cells are one efficient method to solve the problem,¹⁴ but the fussy and unsatisfactory fabricating progress with many layers is one big bottleneck.¹⁵⁻¹⁷ The ternary OSCs that integrate third component acceptor or donor into a binary photovoltaic layer, show the advantages compared to single junction and tandem OSCs, with the great potential for obtaining the high efficiency with bright application prospects.¹⁸⁻²⁰ The third component in the active layer provides the additional absorber with a complementary absorption spectrum that resulting in much increased short-circuit current, and offers the matched energy level as well as

ameliorates the blend morphology that thereby facilitating charge transport with less charge recombination loss.²¹⁻²³

In bulk heterojunction (BHJ) devices, donor and acceptor are fully mixed in the whole active layer, the ubiquitous nanoscale network greatly increases the interface area of the heterojunction and improves the dissociation efficiency of excitons. Charge transfer at interface depends on transudation between donor or accept domain. If the domain size is too large, the separation efficiency of excitons will be low. If the domain size is too small, the transfer of charge also will be affected, and thus the recombination rate of free charge will increase. An appropriate domain size and a bicontinuous interpenetrating network morphology are required to satisfy effective exciton separation and charge transport in device.²⁴⁻²⁸ In ternary OSCs, the blend comprises three components, and their molecular interactions could cause more complex interface and morphology than the binary blend.²⁹⁻³² Considering that the proportion of the third component is very few, it is hard to create its own charge transport route, the separation of excitons and charge transport still depend on dominating system. In addition, the poor compatibility between different organic semiconductor materials results that the third component often suffers defect states in the active layer. Therefore, the introduction of the third component not only needs to create the matched level gradient and expand the absorption spectra,³³⁻³⁷ but also need to achieve the interfacial contact and ideal morphology that promote exciton dissociation and charge transport.³⁸⁻⁴⁰

In this work, we introduce the highly crystalline polymer poly((N,N'-bis (2-octyldodecyl)-1,4,5,8-naphthalenedicarboximide-2,6-diyl)-alt-5,5'-(2,2'-bithiophene)) (N2200) as the guest acceptor into a host binary blend based on a wide-band gap donor polymer poly[2,6 - (4,8 - bis (5 - (tripropylsilyl)thiophen - 2 - yl)benzo[1,2 - b:4,5 - b']dithiophene - alt - 4,7 - Bis(5 - thiophen - 2 - yl) - 2 - (2 - hexyldecyl) - 5,6 - difluoro - 2H - benzo[d] - [1,2,3]triazole] (J71) and the non-fullerene small molecule acceptor (4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithieno[3,2-b]thiophene - 2,7 - diyl) bis(2 - (3 - oxo - 2,3 - dihydroinden - 1 - ylidene)malononitrile) (ITIC). The previous work has demonstrated that the N2200 features the broad light absorption, high electron mobility, and high electron affinity. The addition of N2200 creates the cascade-type energy level alignments at the ternary junction, which benefits the excitation dissociation and charge transfer. A series of characterizations indicate that N2200 balances hole and electron mobilities, suppresses charge bimolecular recombination and trap-assisted recombination, as well as improves blend morphology, resulting in the comprehensive improvement of open circuit voltage, short circuit current and fill factor in the device. As expected, the combined benefits increase the PCE from 10.09% for J71:ITIC binary device to 11.18% for the optimized ternary device containing 10% N2200.

Results and discussion

The chemical structure of J71, ITIC and N2200 are shown in Figure 1a. Figure 1b shows the normalized UV-vis absorption spectra of the corresponding pristine films.

The maximum absorption peaks of J71 and ITIC are located at 550 and 710 nm, respectively. The third component N2200 has two clear absorption peaks at 398 and 710 nm, which are well complementary with that of J71 and ITIC for harvesting more photon. Ultraviolet photoelectron spectroscopy (UPS) is applied to estimate the energy levels of the donor and acceptors in Figure 1c. The ionization potential (IP) is derived from the secondary electron cut-off (the left panel) and the frontier edge of the occupied density of the states (the right panel). The electron affinity (EA) are obtained from the IP subtracting the optical absorption gap. From the energy level diagram illustrated in Figure 1d, the IP values of J71, ITIC and N2200 are -5.2, -5.6 and -5.7 eV, respectively, and the EA values for -3.23, -4.03 and -4.26 eV, respectively. It could be seen clearly that the energy levels of ITIC properly located in between the corresponding levels of J71 and N2200, offering the cascading energy levels and the large energy offsets at the J71/ITIC and J71/N2200 interfaces. It means that the electrons could effectively transfer from J71 to ITIC or N2200 and the opposite holes could effectively be blocked in the ternary active layer.

Figure 2a displays the UV-vis absorption spectra of the J71:N2200:ITIC blend films with various N2200 contents. With the increase of the N2200, the absorption intensity before 600 nm is enhanced, while the absorption from 600 to 800 nm is decreased. When the content of the N2200 is smaller than 30%, the decrease from 600 to 800 nm is insignificant compared to the absorption of the binary J71:ITIC. We fabricate the ternary and the binary reference OSCs with the inverted device structure

of ITO/ZnO/J71:N2200:ITIC/MoO₃/Ag. Figure 2b exhibits the current density-voltage (*J-V*) characteristics of the optimized devices under simulated AM 1.5 G illumination at 100 mW/cm², and the related photovoltaic parameters are summarized in Table 1. The binary device based on J71: ITIC yields a PCE of 10.09% with a V_{oc} of 0.925 eV, a J_{sc} of 16.96 mA/cm² and a FF of 64%. With increasing the content of N2200 up to 10%, all device parameters significantly enhance, and the PCE of the ternary OSC is 11.18%, accompanied with a V_{oc} of 0.942 V, a J_{sc} of 17.58 mA/cm² and a FF of 68%. Further addition of N2200 (20%), the V_{oc} , J_{sc} , and FF decrease to 0.932, 17.33 and 64%, but the PCE of 10.31 % remain higher than that of the binary J71: ITIC device. The results demonstrate that a small amount of N2200 as the third component has the excellent compatibility to the J71: ITIC system. When the content of N2200 is beyond 30%, the PCE of the ternary OSC continuously decreases. The J71: N2200 device has a very low PCE of 1.32% due to large phase separation and surface roughness, which will be discussed in Figure 4. The PCE evolution of the ternary OSCs versus the ratio of N2200 is plotted in Figure 2c, where the PCE reaches the maximum value at the ratio of 1:0.1:0.9. The external quantum efficiency (EQE) spectra of the devices confirm current enhancement in the nearly entire absorption range from 400 to 700 nm when the content of N2200 is less than 30%. By integrating the EQE spectra, the calculated J_{CAL} for the binary and ternary devices are listed in Table S1 of the supporting information, which are in line with the values obtained by the *J-V* measurements with a difference smaller than 5%.

To understand the effect of N2200 on charge transport properties, the charge mobility in the ternary films with different ratios of N2200 contents are investigated using the space charge limited current (SCLC) method, see Figure 3a-3b, Figure S1 and Table S2 of the supporting information. Both electron (μ_e) and hole (μ_h) mobility decrease with increasing N2200 content. For J71:N2200:ITIC (1: 0.1: 0.9) blend, the ratio of electron and hole mobility μ_e/μ_h is estimated to be 1.09. The charge mobility becomes more balanced, accounting for the enhanced FF in the device as observed in Figure 2b. Furthermore, the dependence of J_{sc} and V_{oc} on light intensity (P_{light}) are shown in Figure 3c and 3d, respectively. The relationship between J_{sc} and P_{light} can be expressed by $J_{sc} \propto P_{light}^\alpha$, where α is close to 1 when bimolecular recombination is negligible. The extracted α values for the J71: ITIC, J71:N2200: ITIC (1:0.1:0.9) and J71:N2200 are 0.93, 0.97 and 0.96, respectively, indicating the bimolecular recombination is highly suppressed in the optimized ternary OSC. The dominant recombination can be distinguished from the V_{oc} as a function of P_{light} . The trap-assisted recombination in the primary process has the slope of $2KT/e$ (where K is the Boltzmann constant, and T is temperature), while the bimolecular dominant recombination has a slope of KT/e . As present in Figure 3d, the optimized ternary device exhibit as a slope of $1.54 KT/e$, while the binary devices have slopes of 1.62 for J71: ITIC and 1.93 for J71:N2200, respectively. The results reveal that the introduction of 10% N2200 in J71: ITIC system could significantly reduce charge bimolecular recombination and trap-assisted recombination, which are benefiting charge transport and leading to the increased V_{oc} and FF. We measure the impedance spectroscopy in dark condition. As

shown in Figure S2, the resistance of the ternary device with 10% N2200 is smaller than that of the binary devices, well supporting that the optimized ternary device has the better charge transport properties.⁴¹⁻⁴²

To characterize the charge generation and dissociation dynamic process, we measure the steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) of the pristine, binary and ternary blend films. As shown in Figure 3e, the pristine J71 and ITIC exhibit strong PL emission peaks at 700 nm and 770 nm, respectively, and the pristine N2200 has a very weak PL emission peak at 850 nm. The PL quenching of the J71: ITIC blend is clearly observed, indicating that the efficient exciton dissociation occurs at J71/ITIC interface. Upon introducing N2200 into J71:ITIC blend, the PL emission is further quenched, which confirms that the third component N2200 promotes exciton dissociation. Additionally, there is strong PL quenching in ITIC: N2200 blend, suggesting the partial charge transfer at ITIC/N2200 interface. The result agrees with their energy levels in Figure 1d. Figure 3f displays the TRPL spectra of the corresponding films. The PL lifetimes can be obtained by fitting the decay curves with a biexponential decay function consisting two components: a fast decay and a slow decay.⁴³ The fitted average lifetime values for J71, J71:ITIC and J71:ITIC:N2200 blends are obtained as 0.42, 0.26 and 0.17 ns, respectively. The lifetime of the ternary J71: ITIC: N2200 is much faster than that of the pristine J71 and binary J71: ITIC. The emission lifetime of ITIC: N2200 is 0.23 ns, which is faster than that of pure N2200 (0.25 ns) and ITIC (0.28 ns), furthering verifying charge transfer at

ITIC/N2200 interface. Therefore, we could conclude that adding N2200 in the ternary system enhance dissociation of excitons.

The performances of ternary OSCs are closely correlated to the location of the third component in the ternary active layer, affecting the electron and hole transport. Previous reports have verified that surface energy play an important role in the segregation tendency of each material employed in blends,^{44,45} and the surface energy of each component can be estimated from the contact angle. We measure the contact angle of J71, ITIC and N2200 using water and ethylene glycol in Figure S3, and the information of the liquid contact angle and surface energies are summarized in Table S3. The surface energies of J71, ITIC and N2200 are 28.57, 26.12 and 24.58 mN m⁻¹, respectively, which means that the third component is likely segregate to the top film/air side. The accurate location of N2200 can be further predicted by the parameter wetting coefficient (ω) based on interfacial surface energy, which is calculated according to Young's equation⁴⁶ and Neumann's equation.⁴⁷ If $\omega > 1$, the third component will be tend to located in the domains of J71, if $\omega < -1$, the third component will be tend to embedded in the domains of ITIC. If $-1 < \omega < 1$, the third component will be tend to distributed at the interface between J71 and ITIC.⁴⁸ The ω value of the N2200 in the blend of J71 and ITIC is estimated to be -2.27, which indicates that the N2200 thereby locates in the domains of ITIC.

Figure 4 shows the tapping-mode atom force microscopy to provide the topography information of the ternary blends with different N2200 contents. The root mean square (RMS) roughness values gradually increase from 1.45 to 8.08 nm along with increasing N2200 content. The increased phase separation and surface roughness accord with the decrease of charge mobility as discussed in Figure 3a. For the ternary blend film with 10% N2200, the value of the RMS is as low as 1.56 nm, and the uniform fibrillar structure is well formed, which are found beneficial to exciton dissociation and charge transport. Moreover, grazing-incidence wide-angle X-ray scattering (GIWAXS) measurement is performed to reveal the molecular packing and crystallinity in the ternary blends. The 2D diffraction patterns and the corresponding line-cuts are presented in Figure 5. The arclike scattering appears in the 2D diagrams and indicates that the binary and ternary systems both show the preferential face-on orientation, which is conducive to vertical charge transport in OSC devices. As seen from Figure 5h, however, we can see that as increasing the concentration of N2200, out-of-plane π - π stacking (010) peak has been shift from 1.75 to 1.64 $\text{\AA}^{-1}$, indicating that the charge transfer has been changed and this may have an important impact on the performance of the device. As illustrated from the in-plane line, with increasing N2200, a typical diffuse reflection for N2200 at 0.25 $\text{\AA}^{-1}$ was clearly observed and the peak at 0.31 $\text{\AA}^{-1}$ was almost disappear, meaning that N2200 formed its own domain as a new electron-transport network and the original charge transfer path was cut off. Fitted curves of the 1D GIWAXS profiles in the in-plane directions are given in the Supporting Information (Figure S4) and the related data was displayed in Table S4. For ternary mixtures, as the

increase of N2200, the peak intensity, FWHM and the area decrease at $0.31 \text{ \AA}^{-1}$. At the same time, the peak intensity at $0.25 \text{ \AA}^{-1}$ is gradually increasing, the FWHM is still decreasing and the area also increasing, indicating that the crystallization performance of the film is better, which is consistent with the results of AFM. In other words, the addition of N2200 can improve the crystallization of J71:ITIC thin films. These results indicate that the addition of a small amount of N2200 can improve the PCE of the ternary OSCs while improving the crystallinity of the film. If the amount of N2200 is excessively increased, although the crystallinity of the film becomes well and it can form its own charge transport channel, but it is not conducive to the PCE performance of the system. Thus, integration a small amount of non-fullerene acceptors in a ternary mixture can further boost the PCE and is a promising strategy toward developing high-performance ternary OSCs.

Conclusions

In conclusion, we have fully understood the effect of the crystalline polymer N2200 as the third component on the performance of J71:ITIC bulk heterojunction in ternary non-fullerene solar cells. The ternary components expand the light absorption spectral range, and their cascade-type energy level alignments at the junction benefit the excitation dissociation and charge transfer. It is revealed that the introduction of 10% N2200 into J71:ITIC could significantly reduce charge bimolecular recombination and trap-assisted recombination, which contributes to the enhancement of V_{oc} and J_{sc} in the device. The hole and electron mobilities become more balanced, accounting for the

enhanced FF. AFM and GIWAXS characterizations indicates that the morphology of the ternary active layer is optimized, and the film crystallinity is improved. We thus demonstrate that adding a small quantity of high crystallization acceptor into non-fullerene donor: acceptor mixture could boost the PCE of the device, and it is a promising strategy toward developing high-performance ternary OSCs.

Experimental section

Materials: The polymer donor J71 and acceptor N2200 were purchased from Derthon Optoelectronic Materials Co., Ltd. The non-fullerene acceptor ITIC was obtained from 1-Material. The materials were used as received without further purification.

Photovoltaic Device fabrication and characterization: The device structure is ITO/ZnO/J71:ITIC:N2200/MoO₃/Ag. The ITO-glass substrates were sequentially washed by deionized water, acetone, absolute ethyl alcohol and isopropyl alcohol. Before film deposition, the ITO-glass substrates were UVO-cleaned in a UV-ozone chamber for 15 min. The ZnO precursor solution was spin-coated at 4000 rpm for 40 s on ITO. The solutions of photoactive layer were prepared using chloroform as a solvent at a concentration of 10 mg/mL (donor: accept = 1:1 by weight). The binary and ternary active layers were spin-coated at 2000 rpm for 1 min on the top of ZnO layer in a N₂-filled glove box. Finally, the MoO₃ (8 nm) and Ag (100 nm) electrode were thermally evaporated with a shadow mask at the pressure of 2×10^{-6} Torr. The current density-voltage (J-V) characteristics of the device cells were performed using a programmable

Keithley 2612 source measurement unit under simulated solar light (Oriel model 91160, 100 mW/cm², AM 1.5G). The external quantum efficiency (EQE) spectra were determined using a photo-modulation spectroscopic setup (Newport monochromator). The illumination intensity was calibrated by a standard Si photodiode detector with known spectral response. Alternating current impedance spectroscopy was carried out by precise impedance analyzer (Leithley 2400 Series SourceMeters).

Film Characterizations:

The UPS spectra were performed using HeI 21.22 eV as exciting source with energy resolution of 50 meV. The spectra were calibrated by referencing to the Fermi level of the Ar⁺ ion sputter-clean Au substrate. The absorption spectra were measured with Perkin Elmer Lambda 750 UV-vis spectrometer. The surface morphological images were acquired with atomic force microscope (Veeco MultiMode V) in the tapping-mode. Steady-state PL spectra were recorded using Horiba Jobin-Yvon FL-3. TRPL measurement were performed by a Time-Correlated Single Photon Counting (TCSPC) system containing a stand-alone TCSPC module (PicoHarp 300, PicoQuant), a picosecond pulsed diode laser (SC-PRO 7, YSL), and a single photon counting photomultiplier (PDM Series, MPD). Contact angle was measured on a spin-coated film by CAM 200 optical contact angle meter. Grazing incidence wide angle X-ray scattering (GIWAXS) characterizations were performed at the Advanced Light Source on beamline 7.3.3, Lawrence Berkeley National Lab (LBNL).

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Figure 1. (a) Chemical structures of J71, ITIC and N2200. (b) Normalized UV-visible absorption spectra. (c) UPS spectra. (d) Energy level diagrams.

Figure 2. (a) UV-visible absorption spectra of J71:N2200:ITIC films with different contents of N2200. (b) J - V characteristics of the optimized binary and ternary OSCs. (c) PCE for the ternary OSCs as a function of N2200 content. (d) EQE spectra with the calculated current density.

Figure 3. (a) Electron and hole mobility of the ternary films with different N2200 contents. (b) Ratios of electron versus hole mobility. (c) Dependence of J_{sc} on light intensity for the optimized J71:ITIC, J71:N2200:ITIC (1:0.1:0.9) and J71: N2200 devices. (d) Dependence of V_{oc} on light intensity. (e) PL spectra of the pristine, binary and ternary films. (f) TRPL spectra.

Figure 4. (a-g) Tapping-mode AFM height images and (h-n) phase images ($5 \times 5 \mu\text{m}$) of J71:N2200:ITIC films with different N2200 contents.

Figure 5. (a-g) 2D GIWAXS patterns and (h) scattering profiles of out-of-plane (solid line) and in-plane (dotted line) for blend films with different N2200 contents.

Table 1. Photovoltaic parameters of the ternary devices with different N2200 contents

N2200 (wt%)	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)
0	16.96	0.925	64	10.09
10	17.58	0.942	68	11.18
20	17.33	0.932	64	10.31
30	16.19	0.928	61	9.11
50	12.93	0.927	55	6.56
80	7.32	0.925	45	3.06
100	2.56	0.920	56	1.32