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Investigation on the Effect of Non-Fullerene Acceptor and Conjugated Polymer Donor on Organic Semiconductor Solar Cell

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Abstract – The progress of bulk-heterojunction (BHJ) polymer solar cells (PSCs) is closely related to the innovation of photoactive materials (donor and acceptor materials), interface engineering, and device optimization. Especially, the development of the photoactive materials dominates the research filed in the past decades. Photoactive materials are basically classified as p-type organic semiconductor donor (D) and an n-type organic semiconductor acceptor (A). In the past two decades, fullerene derivatives are the dominant acceptors for high efficiency PSCs. Nevertheless, the limited absorption and challenging structural tunability of fullerenes hinder further improve the efficiency of PSCs. Encouragingly, the recent progresses of fused-ring based A-D-A type nonfullerene acceptors exhibit great potential in enhancing the photovoltaic performance of devices, driving the power conversion efficiency to over 13%. Such kind of nonfullerene acceptors is usually based on indacenodithiophene (IDT) or its extending backbone core and end-caped with strong electron-withdrawing group. Owing to the strong push-pulling effects, the acceptors possess strong absorption in the visible-NIR region and low-lying HOMO (highest occupied molecular orbital) level, which can realize both high open-circuit voltage and short-circuit current density of the devices. Moreover, the photo-electronic and aggregative properties of the acceptors can be flexibly manipulated via structural design. Many strategies have been successfully employed to tune the energy levels, absorption features, and aggregation properties of the fused-ring based acceptors. In this review, we will summarize the recent progress in developing highly efficient fused-ring based nonfullerene acceptors. We will mainly focus our discussion on the correlating factors of molecular structures to their absorption, molecular energy levels, and photovoltaic performance. It is envisioned that an analysis of the relationship between molecular structures and photovoltaic properties would contribute to a better understanding of this kind of acceptors for high-efficiency PSCs.

Keywords: Solar, Cell, Acceptor

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INTRODUCTION

Especially, the development of PSCs is always accompanied by photoactive material innovations. As the key component, photoactive materials are basically classified as a p-type organic semiconductor donor (D) and an n-type organic semiconductor acceptor (A). Due to the unique advantages of strong electron-accepting and high electron-transport capabilities, fullerene derivatives were predominately used as the acceptor in PSCs in the past two decades, driving the power conversion efficiency (PCE) of PSCs to 11–12%.

Nevertheless, fullerenes based acceptors show critical shortcomings of weak absorption and limited structural modification, hindering further improve photovoltaic performance of devices. To overcome these obstacles of fullerenes based acceptors, many efforts have been devoted to developing new kind of nonfullerene acceptor materials.

Very recently, A-D-A conjugated fused-ring molecules based on indacenodithiophene (IDT) or DTIDT unit were reported as excellent nonfullerene acceptors for high performance PSCs, leading the PCE of device to over 13%.

Unlike fullerene derivatives, fused-ring based nonfullerene acceptor materials offer many molecular design strategies to tune their optoelectronic properties and thus photovoltaic performance. In this review, we will provide some representative cases of molecular manipulation on IDT and DTIDT based nonfullerene acceptors to fine-tune the physicochemical and photovoltaic

properties. We hope that this review article would contribute to a better understanding of the design strategies of high performance fused-ring based acceptors for efficient nonfullerene PSCs.

IDT unit which features phenylene ring fused to thiophene was firstly reported by Wong in 2006. Such fused rings structure is beneficial to forming effective interchain π-π overlap and enhance the rigidity of the molecular backbone as well as the degree of conjugation. Zhan et al. innovatively used IDT as central core to develop an A-D-A (A = acceptor, D = donor) type acceptor material (NA1) with 2-(3-oxo-2,3-dihydroinden-1-ylidene)-malononitrile as terminal acceptor unit.

NA1 showed promising energy levels and absorption spectrum as acceptor material for PSCs. By using NA1 as acceptor and PDBT-T1 as donor to fabricate PSC device, a high PCE of 7.39% was obtained, with V_{oc} = 0.92 V, J_{sc} = 13.39 mA cm^{-2}, and FF = 0.60. Molecular optimization based on NA1 greatly affects the photovoltaic performance. In the following, we will discuss the molecular design strategies including extension of conjugated backbone, substituted side chains, and end-capped group were conducted on NA1.

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The V_{oc} of PSCs device is tightly correlated with the energy level difference between the HOMO of the donor and the LUMO of the acceptor. Therefore, high LUMO level of acceptor material is essential for achieving high V_{oc} value. In D-A conjugated molecular system, the donor unit mainly determines the HOMO level. In other words, the optical bandgap (E_g) of D-A based molecules can be tuned by incorporating donor unit as conjugated extension while maintaining the similar LUMO level. For example, Zhan et al. employed one and two IDT units as conjugated extension block to develop two molecules NA2 and NA3.

Due to the longer conjugated backbone, the absorption profiles of NA2 and NA3 are effectively red-shifted compared to NA1, and NA3 possesses the lowest E_g of 1.53 eV. On the other hand, NA2 and NA3 showed up-shifted HOMO levels while similar LUMO levels. Due to the weaker molecular π-π stacking compared to NA1, the NA2 based device exhibited a low PCE of 2.58%, while no photovoltaic response was observed from the NA3 based device. In comparison with NA1, NA4 with thiophene units as π-bridge for conjugated extension showed slightly red-shifted absorption spectrum (E_g = 1.55 eV), up-shifted HOMO level of −5.42 eV, and similar LUMO level of −3.85 eV.

The device based on PBDTTT-C-T:NA4 exhibited a PCE of 3.93%, with a V_{oc} of 0.90 V, J_{sc} of 8.33 mA cm^{-2}, and FF of 0.523. Presumably owing to the conjugated twists, the E_g was increased to 1.57 eV when attaching 2-ethylhexyl chains in thiophene π-bridge of NA1.

By using IEIC as acceptor and PTB7-Th as donor to fabricate device, a promising PCE of 6.31% was obtained, with V_{oc} = 0.97 V, J_{sc} = 13.55 mA cm^{-2}, and FF = 0.48. To reduce the E_g of IEIC, Hou et al. replaced the 2-ethylhexyl chains of IEIC with alkoxy chains to develop a new acceptor IEICO .

Attributing to the strong electron-donating ability of alkoxy chains, IEICO exhibited a lower E_g of 1.34 eV than IEIC. Relative to IEIC, the density functional theory calculation result suggests that the introduction of alkoxy chains effectively up-shifted the HOMO level (~0.19 eV) while maintaining the similar LUMO level (0.01 eV lower than IEIC). The PSCs using IEICO as acceptor yielded a high PCE of 8.4%, with a V_{oc} of 0.82 V and a J_{sc} of 17.7 mA cm^{-2}, while the control device with IEIC as acceptor exhibited a much lower PCE of 4.9%.

In comparison with IEIC-based PSCs, the higher J_{sc} value of IEICO-based device should be resulted from the much broader photo-response spectrum with higher external quantum efficiency. Bo et al. used bis(alkoxy)-substituted or dialkyl-substituted benzene ring as π bridge for conjugated extension to develop two molecules NA5 and NA6.

Benefiting from the non-covalent S···O interaction locks, NA6 exhibited better planarity and broader absorption spectrum than NA5, with a lower E_g of 1.63 eV. In addition, NA6 with locked conformation exhibited a higher quantum yield, which can effectively suppress the non-radiative energy loss and afford higher V_{oc} for devices. The device based on NA6 realized a promising PCE of 9.60%, with V_{oc} = 1.01 V, J_{sc} = 17.52 mA cm^{-2}, and FF = 0.54, while the NA5 based device showed a much lower PCE of 2.3%.

Since the LUMO distribution is mainly located at the acceptor unit in D-A conjugated molecular system, using acceptor unit as building block can simultaneously manipulate the LUMO level and E_g of the molecules. Zhan et al. develop a nonfullerene acceptor NA7 using benzothiadiazole as π-bridge. NA7 shows flat backbone configuration which is beneficial for charge transport, and a large dihedral angle between the hexylphenyl group and backbone plane which can prevent the over self-aggregation when blending with P3HT. Due to the relatively high LUMO level of NA7, the device based on P3HT:NA7 exhibited a high V_{oc} of 0.84 V, with a high PCE of 5.12%.

Relative to NA7 (E_g = 1.68 eV), NA8 exhibited a similar E_g of 1.67 eV, while NA9 showed a slightly larger E_g of 1.71 eV. The orientations of the fluorine

atoms show little influence in the HOMO and LUMO levels but affect the calculated conformational diversity and the electrostatic potential of the molecules.

DISCUSSION

The device based on PTzBI:NA8 exhibited a PCE of 7.44%, higher than that of PTzBI:NA9 based device (PCE = 5.28%). The photovoltaic performance of NA9 based device is poorer than that of NA8 based device, which should be resulted from the less optimal BHJ morphology. Zhou et al. replaced the benzothiadiazole units of NA7 by benzotriazole units to develop NA10.

Due to the weaker electron-accepting ability of benzotriazole than benzothiadiazole, NA10 showed a higher LUMO level than NA7. Therefore, the J61:NA10 based device achieved an encouraging V_{oc} of 1.24 V, with a PCE of 3.02%.

In short, the extension of conjugated backbone with donor or acceptor units will generally broaden absorption spectra and reduce E_g of the resulting molecules, and the introduction of donor units as π-bridge is more effective to reduce the E_g than acceptor units. On the other hand, the LUMO levels will be up-shifted when using donor units as π-bridge, while the incorporation of acceptor units will lead to higher LUMO levels.

The conjugated side chains substituents on the IDT unit will increase steric hindrance, reduce intermolecular interactions, and prevent over self-aggregation and large phase separation in blend film. Herein, the physicochemical and photovoltaic properties of IDT based acceptors can easily tune via side chains engineering in IDT unit. Zhan et al. developed an acceptor with non-conjugated alkyl chains in IDT unit.

NA11 exhibited a nearly flat molecular backbone configuration, with a lower E_g, higher HOMO level, and higher electron mobility than NA7.

The device based on PTB7-Th:NA11 yielded a higher PCE of 8.7% than that of PTB7-Th:NA7 based device. Furthermore, the NA11 based device exhibited better thermal stability and photo stability in comparison with NA7 based device. McCulloch et al. reported two alkyl chains substituted IDT based nonfullerene acceptors NA12 and NA 13.

NA12 with linear alkyl chains showed a stronger crystallinity and a narrower E_g relative to NA13 with branched chains, resulting in higher J_{sc} and PCE values. In addition, the oxidative stability of these devices is superior to the benchmark P3HT:$PC_{60}BM$ device.

Unexpectedly, IDTO showed slightly blue-shifted absorption range relative to IDTC. Nevertheless, the introduction of alkoxy groups effectively improved the intermolecular interactions and up-shifted the LUMO level of IDTO. The device based on PBDB-T:IDTC exhibited a PCE of 9.35%, with a V_{oc} of 0.917 V, while the PBDB-T:IDTO based device showed a higher PCE of 10.02% and a higher V_{oc} of 0.943 V.

Hou et al. introduced fluorine atoms onto the end group of IEICO (IEICO-4F) to enhance the intramolecular charge transfer effect. IEICO-4F showed lower *E*g of 1.24 eV and higher LUMO level of −4.19 eV than IEICO. Using IEICO-4F as acceptor, PBDTTT-EFT or J52 as donor, high J_{sc} values over 20 mA cm^{-2} were both recorded in the corresponding devices.

CONCLUSION

Due to the enhanced intermolecular interactions and molecular ordering, IDTN shows a better molecular planarity and higher electron mobility than NA1. Therefore, an outstanding PCE of 12.2% was achieved from the PBDB-TF:IDTN based device, which is significantly higher than that of the NA1 based device (PCE = 7.4%). Zhan et al. used 2-(benzo[c][1,2,5]- thiadiazol-4-ylmethylene)-malononitrile as end-capped groups to develop a new acceptor NA14.

Relative to NA7, the stronger electron-withdrawing ability of end-capped units of NA14 leads to a lower E_g of 1.60 eV, lower LUMO of −3.8 eV, and lower HOMO of −5.6 eV. The PBDTTT-C-T:NA14 based device afforded a relatively high PCE of 4.26%. Zhou et al. systematically engineered the end-capped units of three nonfullerene acceptors to carefully tune the driving force for high V_{oc} and J_{sc} values.

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