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A_1-A-A_1 type small molecules terminated with naphthalimide building blocks for efficient non-fullerene organic solar cells

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ABSTRACT

Novel non-fullerene acceptors with an A_1-A-A_1 framework were designed and synthesized, in which benzothiadiazole and diketopyrrolopyrrole building blocks were employed as the A unit and naphthalimide units were incorporated as the A_1 units. Both acceptor systems exhibited a broadened absorption spectra from 300 nm to 700 nm in contrast to that of fullerene derivatives. Meanwhile, high-lying LUMO energy levels were also observed for both developed acceptors. To investigate photovoltaic properties of the acceptors, bulk-heterojunction organic solar cells were fabricated using an established electron donating polymer as the donor material. As anticipated, efficient non-fullerene OSCs with high V_{oc} values up to 1.01–1.12 V were achieved when the new molecules were employed as electron acceptors, leading to the PCE values of 1.23% and 1.64% in their solar cells. Our results here demonstrate that the A_1-A-A_1 type small molecule containing naphthalimide building blocks in molecular backbone could be the promising electron acceptor in organic solar cells.

1. Introduction

Bulk-heterojunction (BHJ) organic solar cells (OSCs) [1], in which the active layers are composed of electron-donors and electron-acceptors, have attracted much attention in the past few decades for their merits of low cost, light weight, and flexibility [2–4]. Currently, owing to the tremendous efforts on electron-donors, such as D-A type polymers [5,6] or small molecules [7,8], impressive progress in BHJ-OSCs with the power conversion efficiency (PCE) up to 10% has been acquired [9,10]. For instance, by employing the low band-gap polymer PffBT4T with a D-A framework as donor materials (Fig. S1, Supporting Information), OSCs processed from hydrocarbon solvents exhibited a high PCE value up to 11.7% [11]. Meanwhile, impressive PCE value of 10.10% for D-A type small molecule DRCN5T (Fig. S1, Supporting Information) was also reported by Chen et al. [12]. However, it is worth noting that the electron-acceptors for these above mentioned solar cells are usually determined as the fullerene derivatives of [6,6]-phenyl-(C_{61} or C_{71})-butyric acid methyl ester ($PC_{61}BM$ and $PC_{71}BM$) for their high electron affinity and good electron transporting ability [13,14]. It should be also mentioned that although high photovoltaic performance could be achieved when $PC_{61}BM$ or $PC_{71}BM$ was employed as the electron-acceptors in solar cells, their drawbacks are visible: 1) The price for fullerene based materials is high and these materials are also difficult to synthesize and purify, which could limit their large scale application; 2) The optical properties of fullerene derivatives, such as absorption coefficient and absorption band, is inferior in contrast to that of D-A type molecules, finally leading to the poor harvesting properties of active layers and then decrease the short circuit current (J_{sc}) values in solar cells; 3) Fullerene based materials usually displayed low-lying lowest unoccupied molecular orbital (LUMO) energy levels, which could result the inferior open-circuit voltage (V_{oc}) values owing to that the V_{oc} values in OSCs is proportional to the gap between the highest occupied molecular orbital (HOMO) energy levels of electron donors and the LUMO energy levels of electron acceptors. Therefore, developing novel non-fullerene acceptors is an important topic to further enhance the photovoltaic performance of solar cells, which is also very meaningful for the widely application of organic solar cells.

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Based on the above mentioned consideration, various of non-fullerene acceptors have been designed recently [15–18] and PCE values up to 9% has been also achieved [19–21]. Among these, the imide derivatives are paid increasing attention for their good n-type properties [21–26]. For instance, perylene diimides (PDIs) with superior optical and electric properties was first reported as the acceptors by Zhan et al. [27] and an impressive PCE value up to 3.45% was observed in their corresponding solar cells [28]. Furthermore, to overcome the strong aggregation of PDI derivatives and form the appropriate phase separations without large crystalline domains, Zhan and Yan et al. developed the 3D structured PDI acceptors to afford the high performance solar cells by introducing triphenylamine (TPA) units [29] and tetraphenylethylene (TPE) building blocks [30] as the core. However, similar to the fullerene derivatives, PDI derivatives usually exhibited the low-lying LUMO levels, which could not only induce the large energy loss, but also could result the much decreased V_{oc} values, finally leading to an inferior photovoltaic performance in solar cells. Therefore, non-fullerene acceptors with high-lying LUMO levels are urgently needed. As demonstrated, naphthalimide (NI) based molecules usually have a high-lying LUMO level [31,32]. Meanwhile, weakened inter-molecular interactions and good solubility could be also achieved for NI-based small molecules by employing the alky side chains at the N-position in molecular terminal to obtain the proper phase separations in active layers. Therefore, NI units can be utilized to construct the non-fullerene acceptors in solar cells. Bo et al. constructed highly efficient organic solar cells with a V_{oc} value up to 1.07 V utilizing NI-based planar small molecules as electron acceptors [33]. Also, efficient non-fullerene solar cells with a PCE value of 4.9% is reported by Park et al. by using the NI based DCS–NI as electron acceptors [34]. These results further demonstrated that NI-based small molecules could be the promising non-fullerene acceptors in organic solar cells.

In this paper, to enhance the electron affinity and also further explore the potential of NI-based acceptors, benzothiadiazole (BT) [35] and diketopyrrolopyrrole (DPP) [36] building blocks (A) with good electron withdrawing properties were incorporated between two NI units (A_1) in backbone to afford the A_1-A-A_1 type small molecules (NI-BT and NI-DPP). As observed, both NI-BT and NI-DPP displayed broadened absorption spectra in contrast to that of fullerene derivatives, which is also complemental to the absorption spectra of an established electron donating polymer (PTB7-Th, Fig. 4). Meanwhile, the high-lying LUMO energy levels were also observed for both NI-BT and NI-DPP, indicating the high V_{oc} values could be expected in their corresponding solar cells. To investigate the photovoltaic performance of NI-BT and NI-DPP, BHJ-OSCs were fabricated using the polymer PTB7-Th as electron donor. As displayed, when the developed NI-BT and NI-DPP were employed as the non-fullerene acceptors, efficient OSCs with high V_{oc} values up to 1.01–1.12 V were achieved, finally leading to the PCE values of 1.23% and 1.64%, respectively. Our results here indicated that the A_1-A-A_1 type small molecules containing NI building blocks in the molecular backbone are promising electron acceptors in organic solar cells.

2. Experimental section

2.1. Materials

All reagents and chemicals were purchased from commercial sources (Aldrich, Acros and TCI) and used without further purification unless stated otherwise. Compound 6-bromo-2-octyl-benzo[*de*]isoquinoline-1,3-dione (1), 4,7-bis-(5- trimethylstannanyl-thiophen-2-yl)-benzo [1,2,5]thiadiazole (2) and 2,5-bis-(2-ethylhexyl)-3,6-bis-(5-trimethylstannanyl-thiophen-2-yl)-2,5-

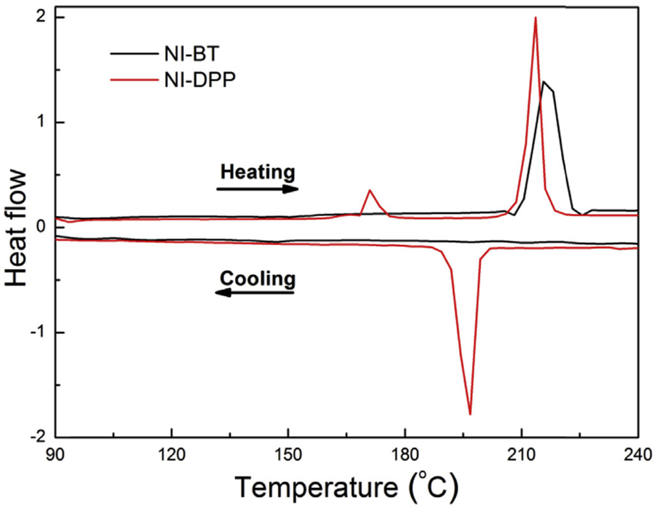
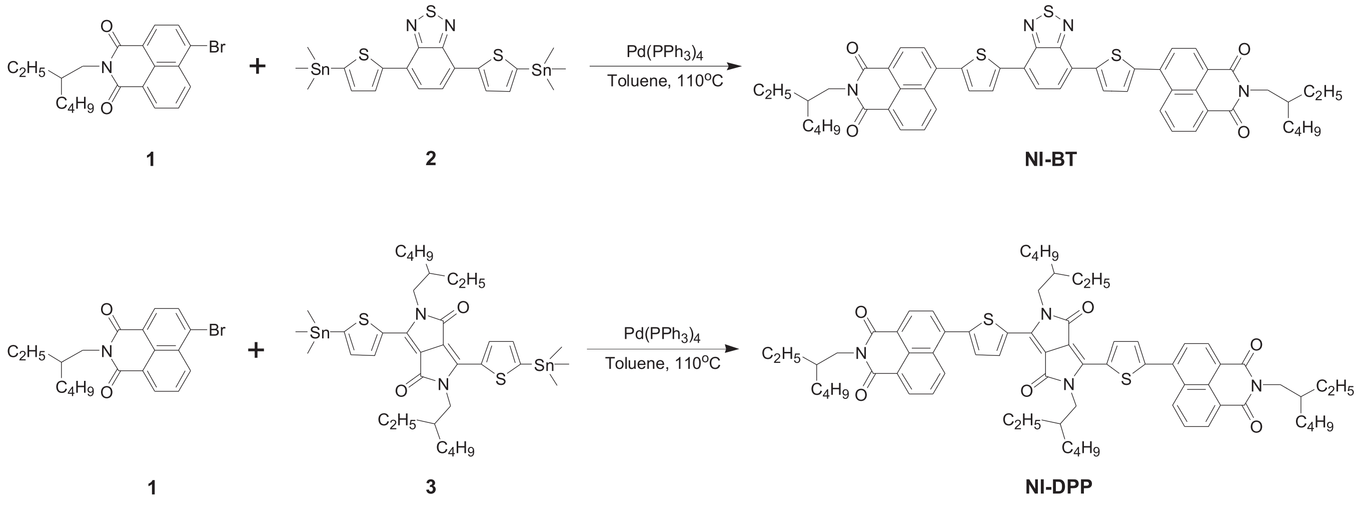


Fig. 1. DSC curves of NI-BT and NI-DPP at a heating and cooling rate of 10 °C/min under an inert atmosphere.



Scheme 1. Synthetic route and molecular structures of NI-BT and NI-DPP.