



Naphthalene diimide-based small molecule acceptors for fullerene-free organic solar cells



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ABSTRACT

Non-fullerene acceptors have attracted great attention as an alternative to fullerene derivatives to overcome their disadvantages such as limited molecular design due to fullerene moiety, electronic tuning via structural modification, and weak absorption in the visible range. In this work, we design a new class of naphthalenediimide (NDI)-based small molecule acceptors by introducing an NDI central core unit and A-D-A-D-A-type moiety. The NDI-TR is a promising material as an electron acceptor for OSCs because of many advantages including high electron affinity and electron mobility, and well-matched energy levels with polymer donors. The device based on NDI-TR had the highest fill factor (0.69) and power conversion efficiency (3.07%) among fullerene-free organic solar cells with NDI small molecule acceptors. This high device efficiency may be attributed to improved charge transport and minimized bimolecular recombination due to the smooth surface roughness and pronounced face-on orientation of polymer backbones in the bulk heterojunction film.

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The power conversion efficiency (PCE) of organic solar cells (OSCs) has gradually improved due to intensive developments in new organic semiconductors, and interfacial and morphology engineering. Efficiencies of up to 11% may now be achieved (Peet et al., 2007; Liu et al., 2014, 2015; Liao et al., 2014; Zhang et al., 2015). These improvements have mainly resulted from the development of novel donor polymers (Deng et al., 2014; Chen et al., 2014; Li et al., 2012). In bulk heterojunction (BHJ) systems, fullerene derivatives including [6,6]-phenyl-C₆₀-butyric acid methyl ester (PC₆₀BM) have typically been used as electron acceptors because of their strong electron affinity. However, PC₆₀BM has some disadvantages such as limited molecular design due to fullerene moiety, electronic tuning via structural modification, and weak absorption in the visible range (Zang et al., 2014; He et al., 2010; Nielsen et al., 2015).

To solve these problems, researchers have worked hard to design and synthesize non-fullerene acceptors. Two kinds of non-fullerene acceptors are now available: conjugated polymers and small molecules (Anthony, 2011; Shu et al., 2011; Sonar et al.,

2011; Kozma and Catellani, 2013; Chochos et al., 2013). Although polymer-type acceptors have achieved higher PCEs than small molecules, small molecules have advantages such as strong batch-to-batch dependence and complex purification process (Small et al., 2012; He et al., 2012; Duan et al., 2016).

Among small molecule acceptors, naphthalene diimide (NDI)- and perylene diimide (PDI)-based small molecules have been widely studied for use in fullerene-free OSCs (Zang et al., 2014; Zhong et al., 2014; Lu et al., 2014). Despite the high PCE of devices based on PDI small molecules, macromolecular phase separation reduces electron mobility due to its high planarity and strong intermolecular interaction between PDI molecules (Liu et al., 2015). Efficiencies as high as 7.16% have been achieved in PDI-based small molecules (Sun et al., 2015). NDI small molecules (NDI-SM) have many advantages including simple synthetic routes, strong absorption in the visible range, excellent solubility in organic solvents, and good electron mobility (Mao et al., 2014; Ren et al., 2012, 2011; Ahmed et al., 2011). Liu et al. synthesized a dimer of NDI as an electron acceptor and reported a PCE of 2.42% by employing a PTB7:NDI BHJ system for fullerene-free OSCs (Liu et al., 2015). Recently, NDI-SM with a 2-(4-nitrophenyl)-acetonitrile terminal accepting group has been designed and blended with poly(3-hexylthiophene), achieving a PCE of 2.24%

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(Srivani et al., 2016). However, the highest device efficiency was lower than 3% for devices based on NDI-SM acceptors, implying that there is considerable room for further efficiency improvements in devices using NDI-SM acceptors.

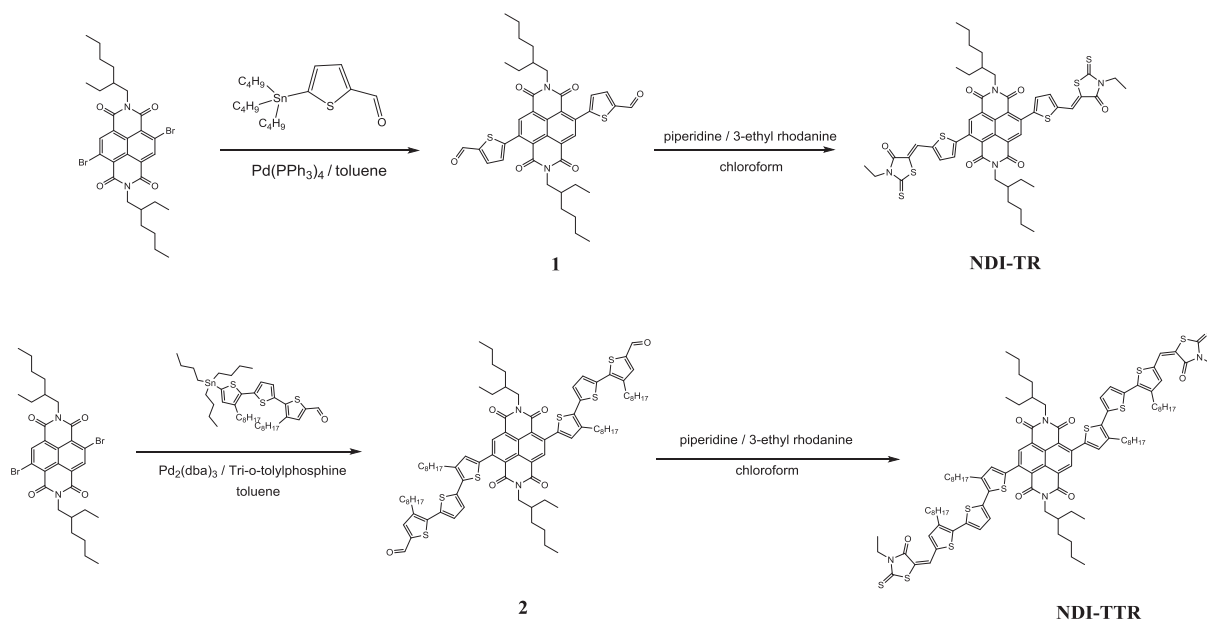
In this work, we designed a new class of acceptor-donor-acceptor-donor-acceptor (A-D-A-D-A)-type SM acceptor with NDI as the central core unit. To compare donor abilities, we synthesized two kinds of NDI-SM acceptors with different donor abilities, 9-bis((Z)-(3-ethyl-4-oxo-2-thioxothiazolidin-5-ylidene)methyl)thiophen-2-yl)-2,7-bis(2-ethylhexyl)benzo[lmn][3,8]phena-nthrolin-1,3,6,8 (2H,7H)-tetraone (NDI-TR) with thiophene as a donor unit and 4,9-bis(5''-(E)-(3-ethyl-4-oxo-2-thioxothiazolidin-5-ylidene)methyl)-3,3''-dioctyl-[2,2':5',2''-terthiophen]-5-yl)-2,7-bis(2-ethylhexyl)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (NDI-TTR) with terthiophene as a donor unit. We expected that the new class NDI-SM acceptors would be efficient because they have high electron affinity and stability, high electron mobility, and an appropriate LUMO energy level, which is similar to that of fullerene derivatives for efficient energy off-set between the LUMO levels of the donor and acceptor. The devices with a NDI-TR acceptor exhibited a high fill factor (FF) of 0.69 and a PCE of 3.07%. To the best of our knowledge, these FF and PCE values are the highest found to date for fullerene-free OSCs based on NDI-SM.

The new class of (A-D-A-D-A) type SM acceptors, NDI-TR and NDI-TTR, were synthesized by Stille coupling reaction and Knoevenagel condensation (Scheme 1). The structure of NDI-TR and NDI-TTR were characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and Mass spectroscopies. The detailed synthetic methods and characterization data are described in the Supporting Information (Figs. S1–S4). Both compounds had good solubility in common organic solvents such as chloroform, dichlorobenzene, which is prerequisite for solution process.

Thermogravimetric analysis (TGA) showed that both of NDI-TR and NDI-TTR have good thermal stability with a 5% weight loss (Td) around 380 °C and 404 °C, respectively (Fig. S5). Differential scanning calorimetry (DSC) thermogram exhibits an endothermic peak at 273 °C and 232 °C for NDI-TR and NDI-TTR, and exothermic peak at 227 °C and 205 °C for NDI-TR and NDI-TTR, respectively. From the results, it is suggested that both compounds indicate the crystalline structure. NDI-TR with thiophene donor has higher thermal

transition temperature than NDI-TTR with dialkyl terthiophene donor because of its rigidity (Fig. S5). In order to estimate the energy of frontier orbitals and 3-dimensional structure of NDI-TR and NDI-TTR, Density Functional Theory (DFT) calculations were carried out using b3LYP 6-311G** for full geometry optimization. Methyl groups were replaced for long alkyl groups to limit computation. The 3D structures and the HOMO and LUMO surface plots of the ground state optimized structures were displayed in Fig. 1. The NDI-TR with thiophene between NDI and rodarine terminal group has more distorted structure than NDI-TTR with expanded terthiophenes. The HOMO is located on terminal thiophene and rodarine for both compound. The LUMO is located on the central NDI and thiophene for NDI-TTR while that is located along the entire molecule of the backbone for NDI-TR. The calculated HOMO and LUMO energies are -6.20 eV and -4.03 eV for NDI-TR, and -5.70 eV and -3.80 eV for NDI-TTR, respectively. It is suggested that NDI-TR is strong electron acceptor and can have stable electron mobility. Cyclic voltammetry (CV) was carried out to investigate the HOMO and LUMO energy levels. The HOMO and LUMO energy levels, calculated from the oxidation onset and reduction onset, are -5.81 and -3.95 eV for NDI-TR, and -5.60 and -3.95 eV for NDI-TTR, respectively (Fig. S6 and Table S1). The electrochemical data are similar tendency with calculated data. Fig. 1a depicted the UV-vis absorption spectra of thin films of NDI-TR and NDI-TTR. NDI-TR had absorption maxima at 416 nm and 539 nm while NDI-TTR showed absorption maxima at 482 nm and 630 nm, respectively, in the solution (Fig. S7). It may suggest that the increasing of donor unit induces the strong intermolecular charge transfer as well as planarity of backbone. The film spectra were broaden and red-shifted by 10–20 nm for NDI-TR and 30–60 nm for NDI-TTR relative to their corresponding solution spectra. So, the NDI-TR had absorption in the range of 300–700 nm, whereas NDI-TTR had broad absorption from UV to NIR region (300–900 nm). Those absorption capabilities can complement insufficient light absorption of donor polymer in visible-NIR wavelength region.

We fabricated fullerene-free OSCs using a simple and conventional device configuration of ITO/PEDOT:PSS/PTB7-Th:NDI-SM/Al (Fig. 1b). We chose PTB7-Th as the electron donor; this is a high-performance donor polymer in polymer solar cells. From the CV



Scheme 1. Synthesis of NDI-TR and NDI-TTR.

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