Cracking perylene diimide backbone for fullerene-free polymer solar cells

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ABSTRACT

Through cracking perylene diimide by inserting a single bond, small π-conjugation unit thiophene and large π-conjugation unit indaceno[1,2-b:5,6-b′]dithiophene, three molecules were synthesized and used as electron acceptors for solution-processed polymer solar cells. These three compounds showed excellent thermal stability with decomposition temperatures over 370 °C. As the size of inserted conjugation units increased, the extinction coefficient increased from 2.9×10^4 to $6.5 \times 10^4 \, M^{-1} \, cm^{-1}$, the absorption wavelength maximum in thin film red shifted from 360 to 488 nm, the optical band gap decreased from 2.98 to 2.25 eV, the highest occupied molecular orbital energy level was upshifted from -6.18 to -5.67 eV, the lowest unoccupied molecular orbital energy level was downshifted from -3.59 to -3.68 eV, power conversion efficiencies of solar cells based on blends of poly(3-hexylthiophene) donor and these acceptors increased from 0.28% to 2.36%.

1. Introduction

Solution-processed bulk heterojunction (BHJ) [1] polymer solar cells (PSCs) are cost-effective alternative approach for utilizing solar energy due to their attractive advantages, such as light weight, low cost and flexibility [2—6]. During the past three years, power conversion efficiencies (PCEs) of PSCs based on blends of polymer donors and fullerene acceptors have exceeded over 10% [7—13]. Novel acceptors were explored in recent years, but still lagged behind donor materials [14—19]. Fullerenes and their derivatives are still dominant electron acceptors in PSCs because they possess favorable physical and chemical properties, such as high electron affinity and mobility, isotropic electron transport and the capability to form favorable nanoscale networks with electron donors [20—22]. However, fullerenes have some shortcomings, such as weak absorption in the visible region, limited electronic level tuning and morphology instability [23—25]. To overcome these existing problems, non-fullerene acceptors with strong and broad absorption spectra and appropriate energy levels were explored. Although novel non-fullerene acceptors with high efficiency over 6% have been designed [26—31], most of the fullerene-free PSCs have exhibited PCEs below 4% [32—39].

Perylene diimide (PDI) has been studied for over one century and its derivatives are used as n-type semiconductors for organic electronics [40—45]. Due to their good light-harvesting property, strong electron-accepting ability and high electron mobility, many promising solution-processed small molecule or polymer non-fullerene acceptors based on PDI have been developed [46—50]. However, high planarity of PDI backbones and strong intermolecular interaction lead to micrometer scale crystallization of PDIs in blends, which is disastrous to the performance of PDI-based PSCs [51—53]. To restrict their inherent crystallinity, PDI cores were modified by side chains substituted on their imide nitrogen atoms or on bay-region positions [54,55]. A series of PDI dimers [56—61] and star-shaped PDIs were also explored [62—66]. A few studies developed novel non-fullerene acceptors through cracking PDI backbones and inserting conjugation units [67—69].
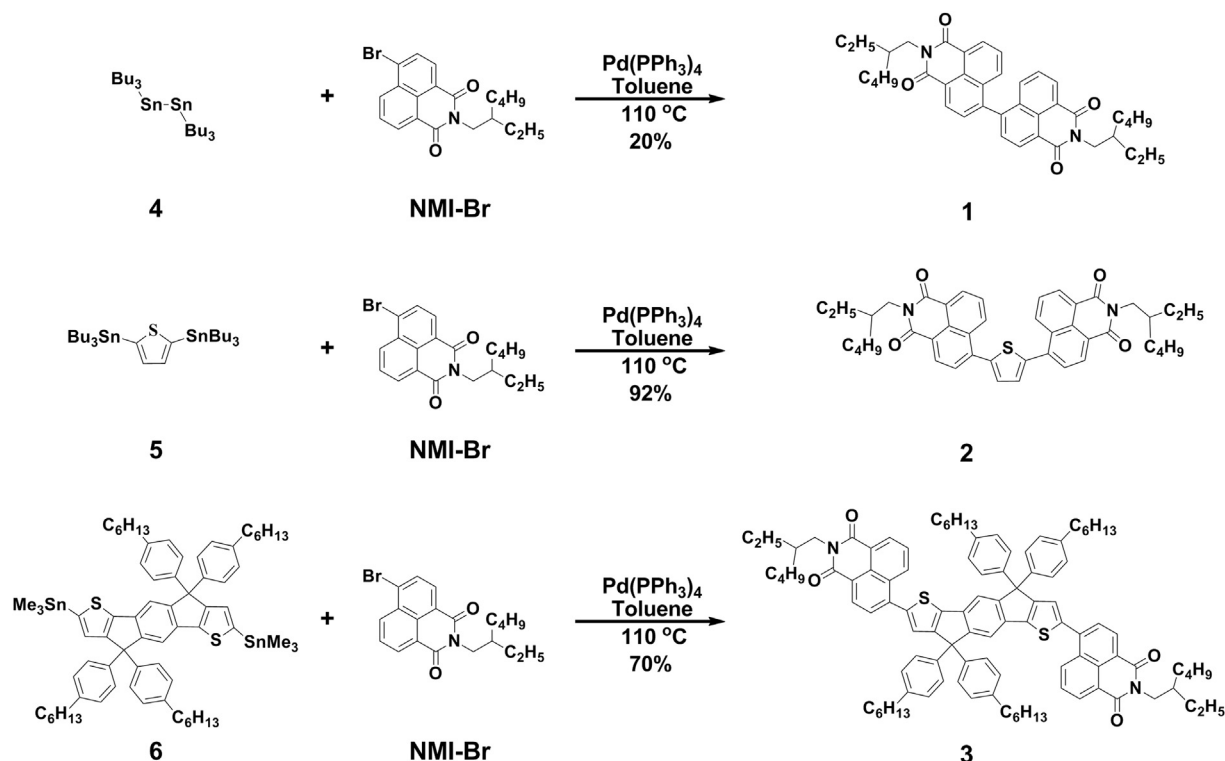
In this work, we synthesized three non-fullerene acceptors (**1—3**) by cracking PDI backbone and inserting a single bond, small

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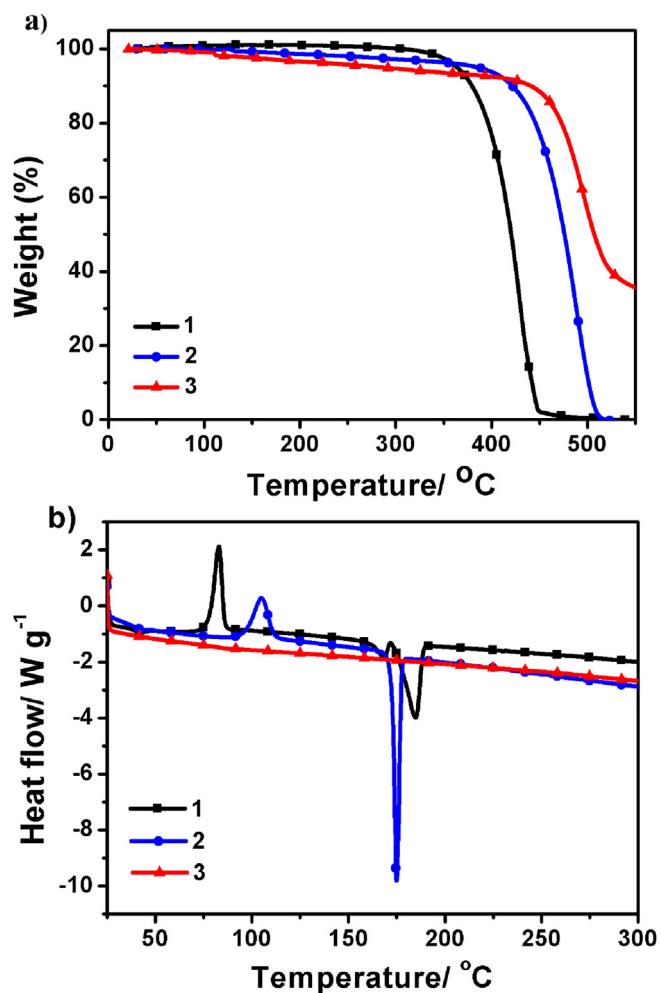
Scheme 1. Synthetic routes to compounds **1**–**3**.

Fig. 1. (a) TGA and (b) DSC curves of compounds **1**–**3**.

π-conjugation unit thiophene and large π-conjugation group indaceno[1,2-*b*:5,6-*b*′]dithiophene (IDT) (Scheme 1). We used compounds **1**–**3** as electron acceptors and blended with the widely used polymer donor poly(3-hexylthiophene) (P3HT) to fabricate polymer solar cells. We investigated the effects of inserted bridges on absorption, energy level, charge transport, morphology and photovoltaic properties of these molecules.

2. Experimental section

2.1. Molecular modeling

Computational details were presented as follows: Density functional theory calculations were performed with the Gaussian 09 program [70], using the B3LYP functional [71,72]. All-electron double-ξ valence basis sets with polarization functions 6-31G* were used for all atoms [73]. Geometry optimizations were performed with full relaxation of all atoms in gas phase without solvent effects. Vibration frequency calculation was performed to check that the stable structures had no imaginary frequency. Charge distribution of the molecules was calculated by Mulliken population analysis.

2.2. Measurements and characterization

The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AVANCE 300 or 400 MHz spectrometer. Mass spectra were measured on a GCT-MS micromass spectrometer using the electron impact (EI) mode or on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer in MALDI mode. Elemental analyses were carried out using a FLASH EA1112 elemental analyzer. Solution (chloroform) and thin film (on quartz substrate) UV–vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen with a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) in CH$_3$CN using a computer-controlled CHI660C