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Synthesis and photovoltaic properties of new small molecules with rhodanine derivative as the end-capped blocks

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ABSTRACT

Two new acceptor–donor–acceptor (A–D–A) type small molecules DCAO3TIDT and DCNR3TIDT, with 4,4,9,9-tetrakis(4-(dodecyloxy)phenyl)-4,9-dihydro-s-indaceno-[1,2-b:5,6-b']dithiophene (IDT) as the core group and 2-ethylhexyl cyanoacetate (CAO) and 2-(1,1-dicyanomethylene)-3-octyl rhodanine (CNR) as different end-capped blocks, have been designed and synthesized. Both of them have been employed as donor for solution-processed bulk hetero-junction (BHJ) organic solar cells (OSCs). The two compounds showed deep highest occupied molecular orbital (HOMO) energy levels (\sim –5.30 eV) and strong absorption. The DCAO3TIDT and DCNR3TIDT with PC₇₁BM as acceptor based BHJ solar cell devices showed short circuit current density (J_{sc}) of 6.93 mA/cm² and 8.59 mA/cm², power conversion efficiency (PCE) of 3.34% and 4.27%, respectively, and with almost same open-circuit voltage (\sim 0.93 V), under the illumination of AM 1.5 G, 100 mW/cm². The high J_{sc} for DCNR3TIDT could result from its wider and red-shifted absorption than that of DCAO3TIDT, which was probably induced by the end-capped block rhodanine derivative. The results demonstrate that the end group would be taken into full account when designing new solution-processed small molecules, which is an important factor to determine their photovoltaic properties.

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1. Introduction

In recent years, bulk hetero-junction (BHJ) organic solar cells (OSCs) have made significant progress due to the attractive advantages, such as light weight, potential to low cost, and flexible [1]. Power conversion efficiency (PCE) which is higher than 9% has been reached recently [2–14]. Currently, BHJ OSCs are based on two types of

donor materials, conjugated polymers and small molecules [15,16]. Compared to their conjugated polymer counterparts, small molecules offer potential advantages in terms of defined molecular structure, uniform molecular weight, easy purification, and no batch to batch variations [17–21]. Thus, solution-processed small molecules BHJ OSCs have stimulated more and more attention, and the PCE of the devices based on small molecules as the donors and fullerene derivatives as the acceptors has been up to 8% [22]. The immense progress of OSCs is mainly ascribed to the versatile chemical structures of donor–acceptor (D–A) type, which allows the molecular orbital to be easily tuned so as to emerge intra-molecular charge transfer (ICT), and

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the ICT exhibits absorption band at longer wavelength direction [23,24]. Until now, a lot of efficient D building blocks have been reported, such as benzodithiophene (BDT), fluorene, dithienosilole (DTS), and indacenodithiophene (IDT). However, compared with the research of the D units, the A moieties have attracted relatively lower attention [25].

2-(1,1-Dicyanomethylene)-3-octyl rhodanine (CNR) is a new strong electron acceptor, which is rhodanine's derivative. Rhodanine is a common dye, and its derivatives have been used as acceptor moiety in a variety of push-pull organic compounds for non-linear optics, electrically conducting materials, molecular rectification, dyes, solvatochromism [26–28], and more recently, they have been used in the BHJ OSCs [22,29,30]. For improving the light absorption of the compound, malononitrile unit has been introduced into the rhodanine structure. Here CNR can bring wide absorption because both of the malononitrile and rhodanine units can guarantee strong electron accepting ability. On the other hand, 2-ethylhexyl cyanoacetate (CAO) has been proved that it is an efficient electron acceptor group, where cyano moiety and 2-ethylhexyl chain can simultaneously induce ICT band and improve solubility [31]. Thus, CAO has been chosen to compare with CNR. Among various electron donor groups, 4,4,9,9-tetrakis(4-(dodecyloxy)phenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']-dithiophene (IDT) has drawn much attention because of their good photovoltaic performance [32]. The IDT can enhance inter-chain interaction of the molecules and lead to higher carrier mobility [32–36]. Herein, two acceptor-donor-acceptor (A–D–A) type molecules DCAO3TIDT and DCNR3TIDT (Scheme 1) with IDT as the core D unit, CAO and CNR as the A unit, and trithiophene as the linker have been designed and synthesized. To reduce the steric effect,

there is no any side chain in the trithiophene unit [37,38]. As expected, the ability of electron withdrawing of CNR is stronger than CAO, and DCNR3TIDT shows a broad absorption than that of DCAO3TIDT, which could improve the short circuit current density (J_{sc}) and result in higher PCE for DCNR3TIDT-based OSC.

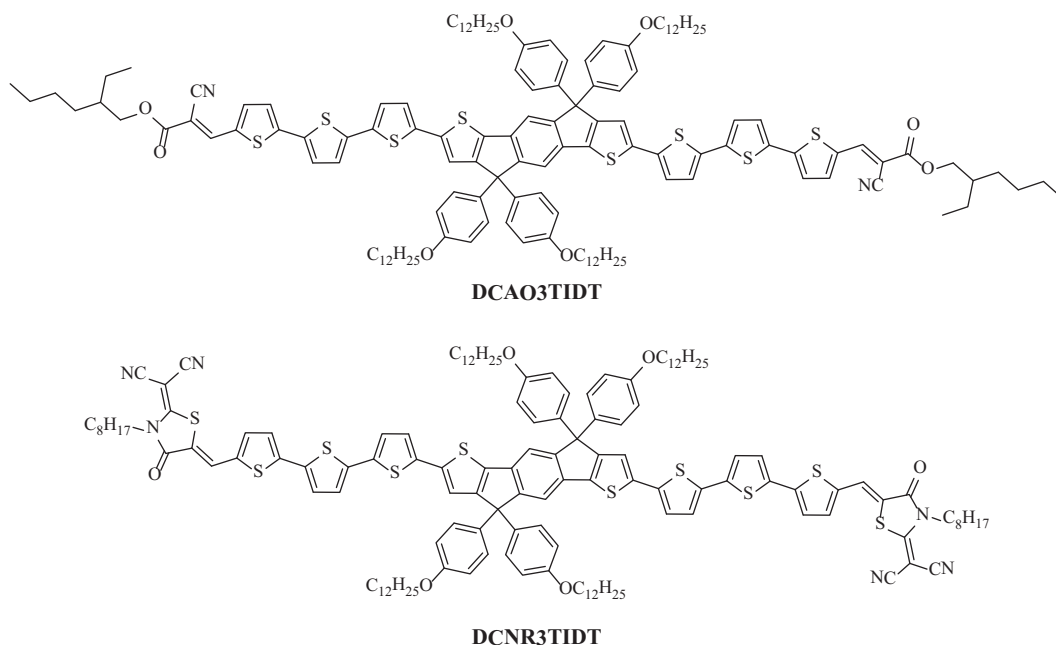
2. Experimental

2.1. Materials

5''-Bromo-[2,2':5',2''-terthiophene]-5-carbaldehyde, (4, 4,9,9-tetrakis(4-(dodecyloxy)phenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(trimethylstannane) and 2-(1,1-dicyanomethylene)-3-octyl rhodanine were prepared according to the literature [22,35,36,39]. Solvents were dried by standard procedure and distilled before use. All of the other chemicals were purchased from Aladdin and used without further purification.

2.2. Measurements and instrumentation

NMR spectra were carried out on a Bruker Advance III 600 spectrometer using tetramethylsilane as an internal standard. High resolution mass spectra were recorded on a Bruker Maxis UHR TOF spectrometer under APCI mode. The thermogravimetric analysis (TGA) was carried out on a SDT Q600 Simultaneous DSC–TGA Instrument under purified nitrogen gas flow with a 10 °C/min heating rate. UV–vis absorption spectra were carried out on a Hitachi U-4100 spectrophotometer. Cyclic voltammetry was measured on a CHI660D electrochemical workstation. Surface roughness and morphology of thin film were characterized by atomic force microscopy (AFM) on an Agilent 5400.



Scheme 1. The chemical structures of DCAO3TIDT and DCNR3TIDT.

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