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A low bandgap carbazole based small molecule for organic solar cells

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ABSTRACT

A new A–D–A small molecule, named **DTB3TCz**, with a weak electron donating unit (carbazole) as the core and a strong electron withdrawing unit (thiobarbituric acid) as the terminal acceptor, was designed and synthesized for organic solar cells. The new molecule shows deep highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, and narrow optical band gap of 1.61 eV. The device based on **DTB3TCz**:$PC_{71}BM$ blend film without any post treatment shows a high open circuit voltage (V_{oc}) of 1.04 V and the optimized device shows a high short-circuit current density (J_{sc}) of 11.80 mA cm^{-2} and a power conversion efficiency of 5.26%.

1. Introduction

Solution processed organic photovoltaics (OPVs) are considered as a promising alternative to silicon-based photovoltaic because of their unique advantages of low cost, light-weight, and potential to fabricate flexible large-area devices [1–4]. Polymer-based OPVs have drawn a great amount of attention [5–10], and the power conversion efficiencies (PCEs) of over 10% for a single junction and over 11% for tandem junction organic solar cells have been achieved [11–18]. Meanwhile, small-molecule-based OPVs are emerging as a competitive alternative to their polymeric counterparts due to several important advantages of small molecules, such as high purity, well defined structure and molecular weight, and thus no batch-to-batch variations [19–22]. Recently, PCEs of ~10% have been achieved for small molecule based OPVs [23–26]. To further improve the PCE and achieve commercialization of OPVs, innovation of photoactive materials, especially for donor materials, is still an important and necessary approach for both polymer based OPVs and small molecule based OPVs.

PCE is determined by the three parameters including open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), and fill factor (FF). Among these three parameters, V_{oc} and J_{sc} are highly depended on the energy level of donor materials. V_{oc} is tightly correlated with the energy level difference between the highest occupied molecular orbital (HOMO) of the donor material and the lowest unoccupied molecular orbital (LUMO) of the acceptor material for OPV devices [27–29]. Thus, high V_{oc} could be achieved through lowering the HOMO energy levels of the donor. For J_{sc}, light absorption of the donor materials is the most fundamental factor, which can be improved by lowering the band gap of the donors to extend the absorption to longer wavelengths. The band gap is determined by the difference of the HOMO energy level and the LUMO energy level of the donor material. Therefore, the donor molecule should have both deep LUMO and HOMO energy levels, in order to obtain high V_{oc} and J_{sc} simultaneously, thus high performance photovoltaic devices.

As one type of D–A structure small molecules, A–D–A molecules exhibit outstanding photovoltaic performance [30–36]. A–D–A small molecules generally consist of an electron-donating segment (D) as the core unit, two electron-accepting segments (A) as the terminal groups, and oligothiophenes as the π-conjugated bridges to link the central donor unit and the terminal acceptor units. For A–D–A small molecules, the HOMO energy levels are mainly decided by the central donor segments, and the LUMO energy levels are more related to the terminal acceptor segments [37,38]. Therefore, for OPVs based on A–D–A small donor molecules, high V_{oc} and J_{sc} could be achieved by the strategy of incorporating central donor units with weak electron donating ability and terminal acceptor units with strong electron withdrawing ability

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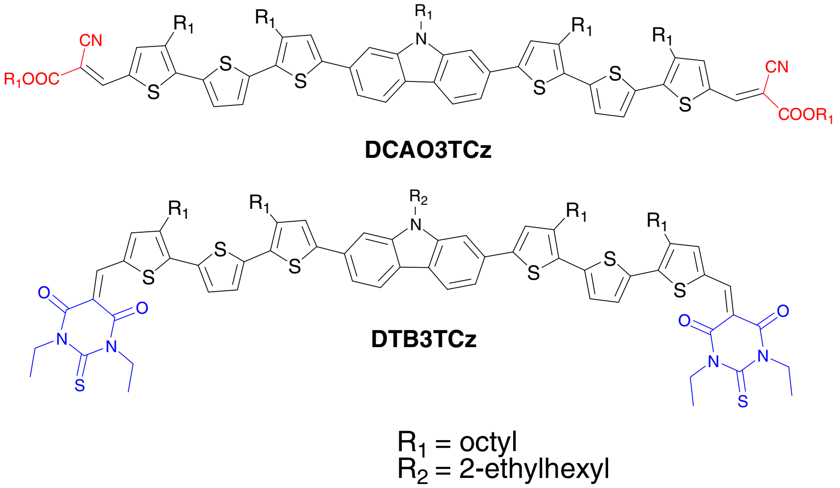


Fig. 1. Chemical structures of DCAO3TCz and **DTB3TCz**.

into the molecules to lower their HOMO and LUMO energy levels simultaneously. Carbazole, with weak electron donating ability, is one of the most important aromatic units for designing high-performance polymers/molecules for photovoltaic cells [39–45]. Recently, we have reported a A–D–A small molecule named **DCAO3TCz** with 2,7-carbazole as the core and alkyl cyanoacetate as the terminal (Fig. 1) [38]. The device based on **DCAO3TCz** showed high V_{oc} over 0.9 V due to the deep HOMO level (−5.14 eV), but relatively low J_{sc} with value of ~6 mA cm^{-2}, mainly attributed to the relatively large band gap (~1.90 eV).

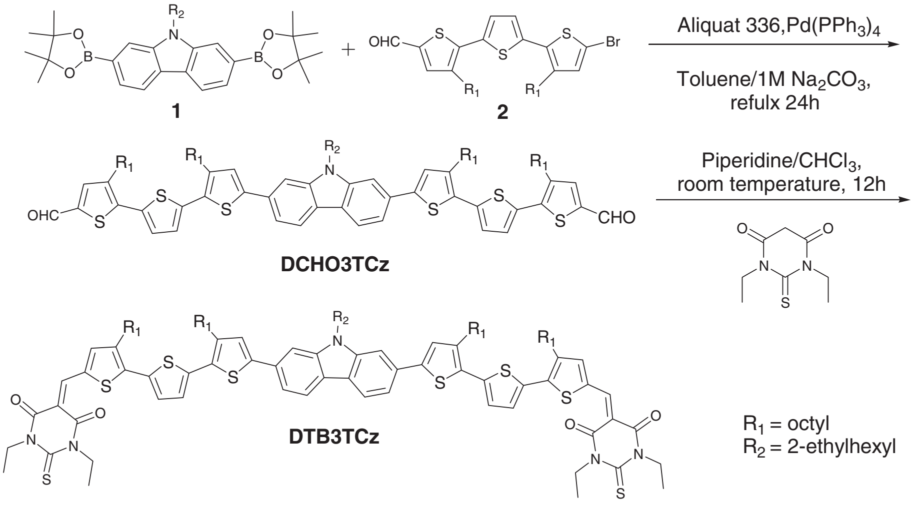
Herein, based on our previous works, we designed and synthesized a new small molecule, named **DTB3TCz** (Fig. 1), consisting of the weak electron-donating carbazole as the central donor unit and strong electron-withdrawing thiobarbituric acid as the terminal acceptor. Thiobarbituric acid, as a high electron affinity unit, has been applied in OPV small molecules reported by several groups [46–48]. Through the replacement of alkyl cyanoacetate with thiobarbituric acid, **DTB3TCz** achieves reduced LUMO energy level and a much lower optical band gap of 1.61 eV. Besides, owing to its weak electron-donating ability of cabazole unit, the new molecule maintains deep HOMO energy level of −5.16 eV. The photovoltaic device based on **DTB3TCz**:PC$_{71}$BM blend film without any post treatment yielded a high V_{oc} of 1.04 V. The optimized device showed a PCE of 5.26% with a much improved J_{sc} of 11.80 mA cm^{-2}, compared with the device based on **DCAO3TCz**. To our knowledge, it is the highest PCE for the carbazole based small molecule organic solar cells so far. These results suggest that designing A–D–A small molecules with the strategy of weak electron-donating units as central donors and strong electron-withdrawing units as terminal acceptors could be an efficient approach to obtain high V_{oc} and J_{sc} simultaneously.

2. Experiment

2.1. Materials and synthesis

All reactions and manipulations were carried under an argon atmosphere using standard Schlenk techniques. All starting materials were purchased from commercial suppliers and used without further purification. Compounds **1** and **2** were synthesized according to the literatures [23,41]. Synthesis of **DTB3TCz** is outline in Scheme 1.

Compound 3 (DTB3TCz). A solution of compounds **1** (0.90 g, 1.69 mmol) and **2** (2.2 g, 3.80 mmol) in toluene (45 mL) and



Scheme 1. Synthesis routes of **DTB3TCz**.