



Novel D(A-Ar)₂ type small molecules with oligothiophene, diketopyrrolopyrrole and benzo[4,5]thieno [2,3-*b*]indole units: investigation on relationship between structure and property for organic solar cells

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ABSTRACT

Two novel D(A-Ar)₂ type small molecules (SMs) of 3T(DPP-BTI)₂ and 4T(DPP-BTI)₂ were synthesized and characterized, which contain diketopyrrolopyrrole (DPP) arms, 6-dodecyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (BTI) terminals, and oligomerthiophene donor unit (3T=trithiophene, 4T=tetrathiophene). The relationship between structure and property was investigated. Compared with their corresponding parent A-D-A type SMs, both D(A-Ar)₂ type SMs exhibited a significantly increasing circuit current density (*J*_{sc}) by 1.39~1.59 times and hole mobility (μ_h) by one order of magnitude, as well as a comparable power conversion efficiency (PCE) in their OPV and hole-only devices. The better photovoltaic properties with PCE of 3.02% and *J*_{sc} of 10.41 mA cm⁻² were obtained in the 3T(DPP-BTI)₂ based OPV cells. It indicates that appending the BTI terminal unit into A-D-A-type SMs is beneficial to increasing the *J*_{sc} and μ_h values of its resulting D(A-Ar)₂ type SMs in their corresponding devices.

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1. Introduction

Solution-processing organic photovoltaic (OPV) cells have recently received a great deal of interest due to their advantages of low-cost, light weight, flexible substrates.^{1,2} The photovoltaic properties have been improved through precisely tuning molecular structure of organic semiconductors, controlling nanostructures of the active layers, and optimizing device structures.^{3,4} Using a blend of *p*-type polymers and *n*-type soluble fullerene derivatives as the active layer, the polymer-based OPV cells with bulk hetero-junction (BHJ) structure demonstrated high power conversion efficiency (PCE) over 10%.^{5–7} Like *p*-type polymeric materials, small molecules (SMs) have also made considerable progress with comparable photovoltaic performances in SMs-based OPV cells.^{8–10} The major challenge in these OPV cells is the enhancement of PCE and short-circuit current density (*J*_{sc}).

As diketopyrrolopyrrole (DPP) has strong light absorption, thermal and photo-chemical stability, good charge transporting property, high co-planarity and large-scale synthesis,^{11–15} it was often coupled with a variety of electron-rich groups to form low band-gap polymers and SMs.^{16–22} The improved photovoltaic performances were obtained in the DPP-based polymers and SMs. For example, a kind of donor (D)-acceptor (A) type polymers with DPP unit showed a dramatic PCE value of 9.4% in polymers-based OPV cells.²³ The DPPEZnP-TEH SMs containing porphyrin and DPP units exhibited a PCE of 8.08% in SMs-based OPV cells.²⁴ In our previous work, some linear and star SMs were developed with D(A-Ar)₂ framework using DPP arms as acceptor units and phenanthrene as aryl (Ar) hydrocarbon terminals, as well as triphenylamine, carbazole and fluorene as central donor unit.^{25–27} It was found that their photovoltaic properties were significantly improved by appending larger planar phenanthrene groups into molecular terminals and tuning the central cores for the D(A-Ar)₂-type SMs.

Oligothiophenes are common electron-donating groups, they were used as donor cores to build A-D-A-type SMs with the DPP unit.²⁸ However, these A-D-A-type SMs with DPP unit exhibited

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inferior photovoltaic properties in OPV cells. Therefore, it is urgent to develop a strategy to improve photovoltaic property for the DPP-based SMs with the A-D-A framework. Considering that appending large planar aryl in D-A-type SMs is favorable to enhance molecular interaction and charge transport by directed molecular self-assembly, in this context, a hetero-aryl unit of 6-dodecyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (BTI), is primarily employed as terminal unit to construct the D(A-Ar)₂ type SMs on the base of A-D-A type SMs. The designed and synthesized SMs are 3T(DPP-BTI)₂ and 4T(DPP-BTI)₂, which contain two planar BTI terminals, two DPP arms and a different donor core of oligothiophenes (3T=trithiophene, 4T=tetrathiophene). Their molecular structures are shown in Fig. 1. The influence of the BTI terminal and different oligothiophene cores on photovoltaic performance has been investigated for two SMs in OPV cells. As expected, compared to their counterparts of 3TDPP₂ and 4TDPP₂ without BTI terminals, both 3T(DPP-BTI)₂ and 4T(DPP-BTI)₂ exhibited a significantly increasing circuit current density (*J*_{sc}) by 1.39~1.59 times and hole mobility (*μ*_h) by one order of magnitude, as well as a comparable power conversion efficiency (PCE) in their OPV and hole-only devices, respectively.²⁸ Better photovoltaic properties with a maximum PCE of 3.02% and *J*_{sc} of 10.41 mAcm⁻² were obtained in the solution-processed 3T(DPP-BTI)₂-based OPV devices utilizing PC₇₁BM as acceptor. This work indicates that appending the large planar BTI unit into A-D-A-type SMs is an efficient approach to improve *J*_{sc} and hole mobility for its resulting SMs.

2. Results and discussion

2.1. Measurements and materials

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400 spectrometer using tetramethylsilane as a reference in deuterated chloroform solution at 298 K. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex III MALDI-TOF. Thermogravimetric analysis (TGA) was conducted under a dry nitrogen gas flow at a heating rate of 10 °C min⁻¹ on a Perkin–Elmer TGA 7. UV–vis absorption spectra were recorded on a HP-8453 UV visible system. Cyclic voltammetry was carried out on a CHI660A electrochemical work station in a three-electrode cell dipped in a 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution under nitrogen protection at a scan rate of 100 mV s⁻¹ at room temperature. In this three-electrode cell, a platinum rod, platinum wire and saturated Ag/AgCl electrode were used as a working electrode, counter

electrode and reference electrode, respectively. All solvents were carefully dried and distilled prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were performed under nitrogen atmosphere and monitored by thin-layer chromatography.

As shown in Scheme 1, 5-bromo-1-dodecyl-1*H*-indole (**2**) was synthesized by an alkylation of 5-bromo-1*H*-indole (**1**) with 1-bromododecane. 9-Bromo-6-dodecyl-6*H*-benzo[4,5]thieno[2,3-*b*]indole (BTI-Br) was prepared according to the literature method.²⁹ The reaction of BTI-Br and bis(pinacolato)diboron gave benzo[4,5]thieno[2,3-*b*]indole borate (BTI-B) with a yield of 89.9%. Compound DPP-BTI was synthesized by Suzuki coupling reaction of compound BTI-B and bromo-pyrrolo[3,4-*c*]pyrrole-1,4-(2*H*,5*H*)-dione (DPP-Br) using Pd(PPh₃)₄ as a catalyst. Compound DPP-BTI-Br was prepared by a bromination of compound DPP-BTI in *N*-bromosuccinimide (NBS). 3T(DPP-BTI)₂ and 4T(DPP-BTI)₂ were synthesized by Stilling coupling reaction between DPP-BTI-Br and 2,5-bis(trimethylstannyl)thiophene or 5,5'-bis(trimethylstannyl)-2,2'-bithiophene with a yield of 67.0% and 62.1%, respectively. The detailed synthesis and characterization of 3T(DPP-BTI)₂ and 4T(DPP-BTI)₂ were given in the experimental section. They were fully characterized with ¹H NMR, and MALDI-TOF mass spectra.

2.2. Thermal property

Thermogravimetric analyses (TGA) curves of 3T(DPP-BTI)₂ and 4T(DPP-BTI)₂ are depicted in Fig. 2 under N₂ atmosphere and their corresponding data are summarized in Table 1. High thermal stability with decomposition temperature (*T*_d) values of 396 and 401 °C are observed for 3T(DPP-BTI)₂ and 4T(DPP-BTI)₂ at a 5% weight loss under N₂ protection, respectively.

2.3. Optical properties

The UV–vis absorption spectra of 3T(DPP-BTI)₂ and 4T(DPP-BTI)₂ in CH₂Cl₂ solution and in neat film are presented in Fig. 3. The corresponding absorption data are listed in Table 1. In solution, both SMs exhibit similar UV absorption profile with two typical absorption bands, in which the moderate high-lying band about 420 nm is assigned to the π–π* transitions of their conjugated backbones and another intense low-lying band about 650 nm originates from the intramolecular charge transfer (ICT) transitions. In the neat films, both SMs show obviously red-shifted and quite wide absorption profiles from 500~800 nm. Furthermore, another shoulder is observed at 720 nm for

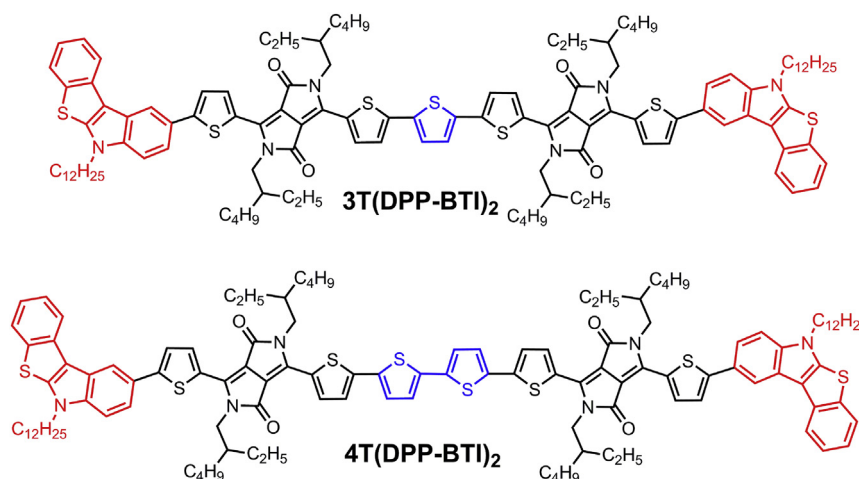


Fig. 1. Molecular structures of 3T(DPP-BTI)₂ and 4T(DPP-BTI)₂.

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