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D1-A-D2-A-D1-type constitutional π-conjugated small molecular isomers bearing benzodithiophene, benzothiadiazole, and thiophene

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ABSTRACT

Two constitutional π-conjugated small molecular isomers **M7a** and **M7b** were prepared by regioselective Stille reactions. **M7a** and **M7b** have the same D1-A-D2-A-D1 structure configuration, where D1, A, and D2 are hexylthiophene, fluorobenzothiadiazole (FBT), and benzodithiophene (BDT), correspondingly. Nevertheless, they differ in the mode of fluoro substitution. Namely, F-substituents are located proximal and distal to the BDT central unit for **M7a** and **M7b**, respectively. **M7a** and **M7b** showed significant dissimilarities in their thermal, optical, electrochemical characteristics. Particularly, with the same device construction and under the identical test conditions, the organic solar cells based on **M7a** and **M7b** exhibited different photovoltaic performance. This study investigated the relationship between the substitution mode of fluorine atoms and the molecular properties, which will provide guidelines for future structural design regarding fine tuning of molecular properties and selection of regioisomeric π-conjugated small molecules.

1. Introduction

Optical and electrochemical properties are not only primarily determined by the backbone of π-conjugated polymers and oligomers, but also related to substituents, especially electron donating and withdrawing groups. To obtain narrow energy gap π-conjugated compounds, a usual way is the alternative incorporation of donor (D) and acceptor (A) segments to generate main polymer/oligomer frameworks, such as D-A-D or A-D-A [1–3]. In the last two decades, π-conjugated polymers and small molecules containing such D-A moieties have been intensively developed due to their outstanding performance in the application of organic photovoltaics [4–7] and organic field-effect transistors [8–10]. For example, solar cells having the D-A-D π-conjugated polymer PBDB-TSF bearing benzodithiophene and 1,3-di(thiophen-2-yl)benzo[1,2-c:4,5-c']dithiophene-4,8-dione reached a power conversion efficiency (PCE) of 13.1% [11], and the devices with A-D-A π-conjugated small molecule BTID-2F containing benzodithiophene, thienothiophene, and indenedione exhibited a highest PCE of 11.08% [12]. Moreover, the energy levels of target molecules can be further tailored via substitution on D and A units with electron donating or withdrawing groups [13]. Among all these polymers and small molecules, F-substituents are most common in fine tuning molecular features such as orbital energies, self-assembly, and consequently PCE [14–18]. In the case of BTID-0F, BTID-1F, and BTID-2F, increasing the number of F-substituents improved the PCE of photovoltaic device from 8.21% (BTID-0F) to 10.37% (BTID-1F) and 11.08% (BTID-2F), respectively [12]. It appears, however, that the effect of precisely positioning of fluorine substituents has not gained enough attention yet. There are only a few publications present the importance of F-substituents induced regioregular conjugated polymers and small molecular regioisomers [19–23]. It has been noted that all these research are rely upon the regioreactivity of the two Br-substituents in 4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole [20,21]. Especially, Woo et al. recently reported Dis-FBT and Prox-FBT (Fig. 1), which exhibited difference in their photophysical, packing, and optoelectronic properties [24]. With a larger optical bandgap and higher phase transfer temperatures, Dis-FBT revealed better photovoltaic performance.

Herein, we synthesized **M7a** and **M7b** with similar structure configuration as Dis-FBT and Prox-FBT, but using rigid benzodithiophene (BDT) instead of flexible 1,4-dithiophenylbenzene of Dis- and Prox-FBT. Additionally, we found that **M7a** structurally corresponding to Prox-FBT, however, showed higher PCE in solar cells. **M7a** and **M7b** have identical backbone structures based on the D1-A-D2-A-D1 design, where D1 is 2-hexylthiophene, A is fluorobenzothiadiazole (FBT), and D2 is BDT (Fig. 1) [25,26]. In **M7a** (same as Prox-FBT) the two fluorine substituents point towards the central donor moiety, whereas in **M7b**

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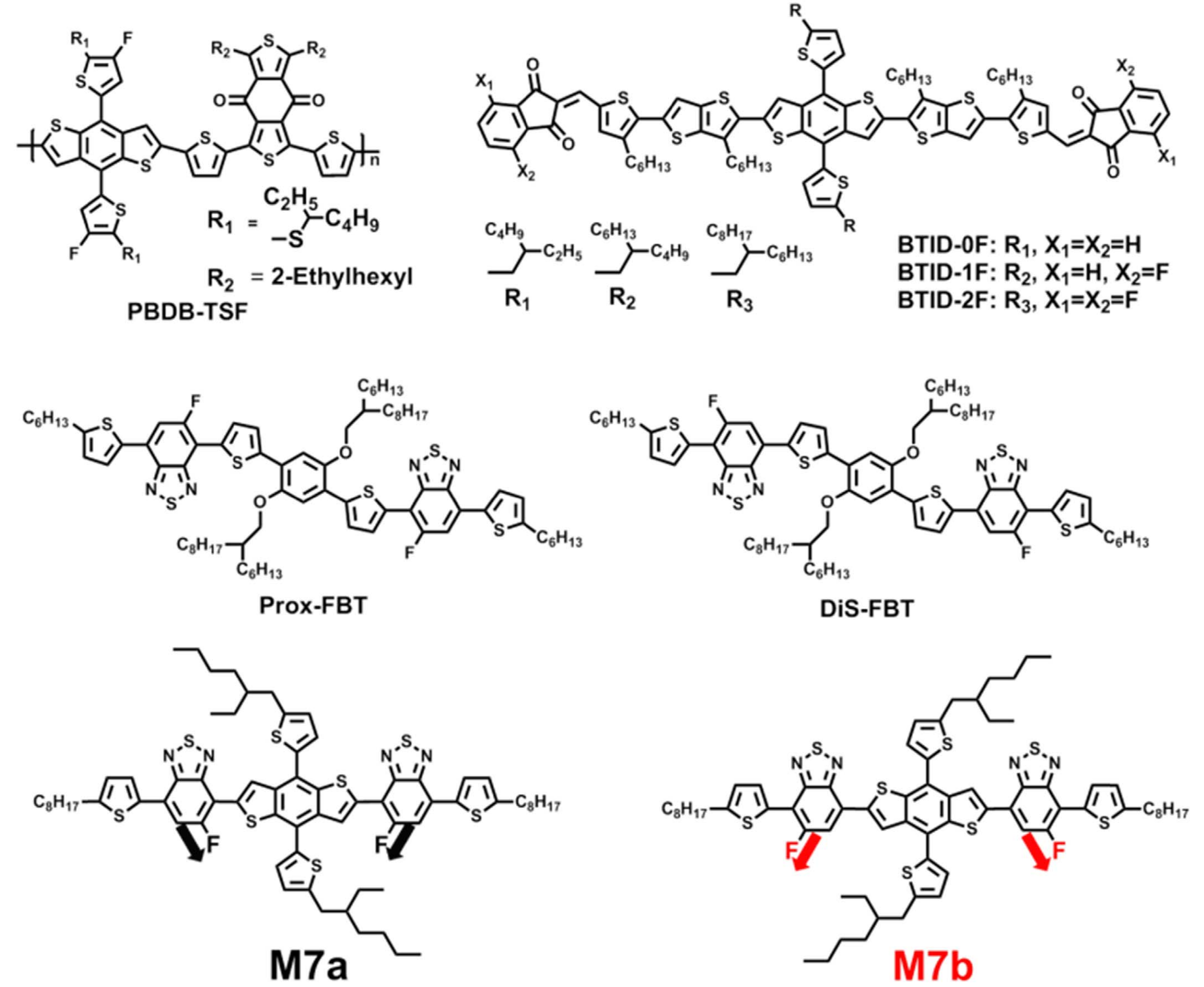

Fig. 1. The molecule structures of PBDB-TSF, BTID and Prox/Dis-FBT and **M7a**/**M7b**.

(same as Dis-FBT) they are directed to the molecular terminals.

2. Materials and methods

All reactions were carried out under argon atmosphere with the use of standard Schlenk techniques. Starting materials were purchased from Alfa-Aesar and Sigma-Aldrich and used without further purifications. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker DRX 250 or Bruker DRX 500. Matrix-assisted laser desorption/ionization time of flight mass spectra (MALDI-TOF-MS) were recorded on a Bruker Reflex II-TOF Spectrometer using a 337 nm nitrogen laser with TCNQ as matrix. Ultraviolet-visible absorption spectra (UV-vis) were recorded on a Perkin-Elmer Lambda 9 spectrophotometer at room temperature. Cyclic voltammetry (CV) measurements were carried out on a computer-controlled GSTAT12 in a three-electrode cell with dichloromethane solution of tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6, 0.1 M) by a scan rate of 50 mV/s at room temperature. (Counter electrode: a Pt wire; Reference electrode: a silver wire; Work electrode: a glassy carbon). Differential scanning calorimetry (DSC) was carried out with a Mettler DSC 30 with a heating rate of 10 K/min from 50 °C to 250 °C. Thermogravimetric analysis (TGA) was carried out on a Mettler 500 thermogravimetric analyzer.

2.1. Synthesis of the isomers

To synthesize **M7a** and **M7b**, three starting materials: 4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole (**1**), 2,6-ditrimethyltin-4,8-bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-b:4,5-b']dithiophene (**2**) and 2-tributyltin-5-octylthiophene (**3**) were prepared according to methods reported in the literature [21,27,28]. Using **1**, **2** and **3** through two Stille-couplings with different sequences (Scheme 1), products **M7a** and **M7b** were obtained, respectively. The key starting material **1** is an asymmetric structure, exhibiting different reactivity of the two non-identical Br-substituents due to the influence of the electron-withdrawing F-atom. Intermediate **4** was synthesized by the Stille-reaction between 2 eq. of **1** and 1 eq. of **2**. In the synthesis of **5**, the Stille-coupling between **1** and **3** in a ratio of 1:1 were carried out at a low reaction temperature (80 °C) to ensure high selectivity of the Br at the 7-position of FBT. The target product **M7a** was obtained through a standard Stille-reaction between **5** and **2** in a molar ratio of 2:1. Similarly, **M7b** could be furnished via Stille-coupling between **4** and **3** with a molar ratio of 1:2. Both **M7a** and **M7b** showed good solubility in dichloromethane. The pure products were collected by precipitation from methanol and drying in a vacuum oven at 70 °C for 12 h.