



# Fluorinated benzothiadiazole-based small molecules for photovoltaic applications



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## ABSTRACT

A series of medium band gap conjugated small molecules with a typical D- $\pi$ -A- $\pi$ -D structure, in which triphenylamine, thiophene, and benzothiadiazole are used as an electron-donor, a bridge, and an electron-acceptor, respectively, have been synthesized. To investigate the effects of strong electron-withdrawing fluorine atoms on various properties, one and two fluorine substituents are introduced to the central benzothiadiazole unit of N-(4-(5-(7-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)phenyl)-N-phenylbenzenamine (TPA-TBT) to give TPA-TBT-1F and TPA-TBT-2F, respectively. Owing to the significant contributions of fluorine atoms, these small molecules exhibit clearly distinctive optical and electrochemical properties. Inverted-type organic photovoltaic cells (OPVs) with a configuration of ITO/ZnO/small molecules: PC<sub>71</sub>BM/MoO<sub>3</sub>/Al were fabricated and the fabricated cells showed maximum power conversion efficiencies of 0.84, 1.15 and 1.70% for TPA-TBT, TPA-TBT-1F and TPA-TBT-2F, respectively. The superior photovoltaic performance of TPA-TBT-2F is attributed to the relatively deep energy level of highest occupied molecular orbital (HOMO) and to more balanced electron- and hole-mobility within photoconversion layer. Therefore, this study can provide insights into the tuning the properties of benzothiadiazole-based small molecules by introducing fluorine substituents.

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## 1. Introduction

Owing to their well-defined mono-disperse chemical structures as well as simple solution-based processability, organic conjugated small molecules with a donor-acceptor (D-A) structure have attracted a great deal of interest for various applications such as light-emitting diodes [1], photovoltaic cells [2,3] and field-effect transistors [4]. The band gap of conjugated D-A small molecules can be significantly reduced because of intramolecular charge transfer (ICT) between the donor and acceptor moieties along a  $\pi$ -conjugated backbone. Electron-donating groups such as triphenylamine (TPA), carbazole and fluorine, as well as electron-accepting moieties including benzothiadiazole, quinoxaline and diketopyrrolopyrrole have been widely used to prepare conjugated small molecules with low band gap [5,6]. Triphenylamine is regarded as a promising building block because it possesses excellent electron-donating properties as well as good resistance

against undesirable aggregation [7]. Likewise, benzothiadiazole (BT) has been widely selected due to its strong electron accepting capability as well as facile control of the energy levels of D-A conjugated BT-based materials [8,9]. Therefore, the combination of a triphenylamine-based electron-donor and a benzothiadiazole-based electron-acceptor is regarded as a powerful tool for the preparation of low band gap semiconductors with superior performances [10–13].

A recent development in organic photovoltaic cells (OPVs) is the introduction of electron-withdrawing fluorine atoms within the conjugated backbone, which significantly improve the overall performances of OPVs [14–18]. Fluorine atoms lower both the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels of conjugated materials while inducing promising inter- or intra-molecular interactions through existing F–F and H–F bonding [19–23]. In addition, the small size of fluorine substituents can efficiently suppress undesirable steric effects. Consequently, the high power conversion efficiency (PCE) of 8.0% was obtained from the fluorinated quinoxaline-based conjugated polymer [24] and the multiple fluorine-substituted BT-based small molecules exhibited noticeable enhancement in PCE up to 8.1% [25].

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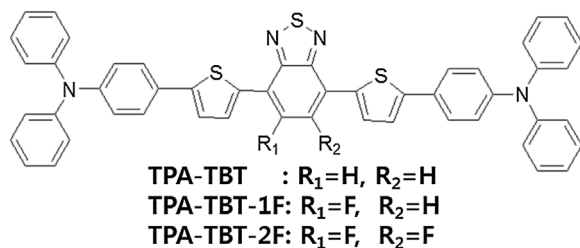


Fig. 1. Chemical structures of TPA-TBT, TPA-TBT-1F and TPA-TBT-2F.

To further investigate the impact of fluorine atoms on various characteristics of conjugated small molecules, we prepared a series of small molecules a typical D- $\pi$ -A- $\pi$ -D configuration by connecting TPA and BT moieties through thiophene bridges. In particular, benzothiadiazoles containing zero, one and two fluorine atoms at the 5,6-positions of the BT central core were incorporated into the target small molecules of TPA-TBT, TPA-TBT-1F and TPA-TBT-2F, respectively (Fig. 1). This simple but distinctive strategy allows us to understand the effects of fluorine atoms in conjugated structures by carefully investigating the optical and electrochemical properties together with photovoltaic performances of three small molecules.

## 2. Experimental section

### 2.1. Materials and instruments

Benzothiadiazole derivatives of 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (TBT), 4,7-bis(5-bromothiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (TBT-1F) and 4,7-bis(5-bromothiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (TBT-2F) were synthesized according to the reported procedures [26,27]. 4-(Diphenylamino)phenylboronic acid was purchased from Aldrich. All other chemicals and solvents were obtained from Aldrich Chemical Co., Inc. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded on a JEOL JNM ECP-400 spectrometer. Melting point of the compounds were measured using a OPTIMelt automatic melting point system (Stanford Research System). Differential scanning calorimetry (DSC) was performed by Mettler Toledo DSC STAR system. UV-vis spectra were recorded using a JASCO V-530 UV-vis spectrophotometer. Matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) spectroscopy was conducted using Bruker Ultraflex spectrometer. Cyclic voltammetry (CV) measurements were carried out using a VersaSTAT3 potentiostat (Princeton Applied Research) in tetrabutylammonium hexafluorophosphate (0.1 M, Bu<sub>4</sub>NPF<sub>6</sub>) as the electrolyte in acetonitrile. For CV measurements, a glassy carbon electrode coated with a thin layer of small molecules and a platinum wire were used as the working and counter electrode, respectively. A silver wire was used as a pseudo-reference electrode with a ferrocene/ferrocenium external standard. The thickness of films was measured by an Alpha-Step IQ surface profiler (KLA-Tencor Co.) and the atomic force microscopy (AFM) topography images were taken using a Bruker (NanoScope V) operated in the tapping mode.

### 2.2. Fabrication and analysis of photovoltaic devices

[6,6]-Phenyl C<sub>71</sub> butyric acid methyl ester (PC<sub>71</sub>BM, Cat No. nano-cPCBM-SF) was purchased from nano-C, Inc. For the fabrication of inverted type OPVs with a structure of ITO/ZnO/active layer (donor:PC<sub>71</sub>BM)/MoO<sub>3</sub>/Ag, a 25 nm-thick of ZnO film on ITO was deposited by using the sol-gel process. The sol-gel solution was prepared with zinc acetate dehydrate (0.164 g), and

ethanolamine (0.05 mL) dissolved in methoxyethanol (1 mL). The mixture was stirred for 30 min at 60 °C prior to carrying out the film deposition. The thin film of ZnO precursor was cured at 200 °C for 10 min to partly crystallize the ZnO film. The active layer was spin-cast from the blend solution of donor and PC<sub>71</sub>BM (prepared by dissolving 6 mg of donor and 12 mg of PC<sub>71</sub>BM in 1 mL of chloroform at 600 rpm for 60 s). Prior to spin coating, the active solution was filtered through a 0.2  $\mu$ m membrane filter. The typical thickness of an active layer was 80 nm. On the top of the active layer, a 20 nm-thick MoO<sub>3</sub> layer and 100 nm-thick Ag layer were thermally evaporated successively through a shadow mask with a device area of 0.13 cm<sup>2</sup> at 2  $\times$  10<sup>-6</sup> Torr. The J-V measurements under the 1.0 sun (100 mW/cm<sup>2</sup>) condition from a 150 W Xe lamp with AM 1.5 G filter were performed using a KEITHLEY Model 2400 source-measure unit. A calibrated Si reference cell with a KG5 filter certified by National Institute of Advanced Industrial Science and Technology was used to confirm the 1.0 sun condition.

### 2.3. Syntheses

**General procedure for the syntheses of TPA-TBT, TPA-TBT-1F and TPA-TBT-2F by the Suzuki-coupling reaction:** Dibrominated benzothiadiazole compounds (TBT, TBT-1F and TBT-2F) (0.3 mmol) and 4-(diphenylamino)phenylboronic acid (0.6 mmol) were dissolved in dry toluene (7 mL) under nitrogen. Tetrakis (triphenylphosphine) palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>) (0.015 mmol) and degassed potassium carbonate aqueous solution (2 M, 3 mL) were added. After purging with nitrogen for 15 min, the mixture was heated and stirred at 90 °C for 48 h under nitrogen. After cooling to room temperature, the mixture was poured into water and extracted with chloroform. The organic layers were separated, dried over magnesium sulfate, and filtered. Solvents were removed under reduced pressure and the crude residue was further purified by column chromatography (chloroform/hexane 1:1, v/v).

#### 2.3.1. N-(4-(5-(7-(5-(4-(Diphenylamino)phenyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)phenyl)-N-phenylbenzenamine (TPA-TBT)

4,7-Bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (TBT) was used as a reactant, Yield: 62% (purple solid). m.p.: 235 oC. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.09 (d, 2H), 7.84 (s, 2H), 7.55 (d, 4H), 7.31–7.24 (m, 10H), 7.13–7.02 (m, 16H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 152.6, 147.6, 147.4, 145.5, 137.8, 129.3, 129.2, 128.7, 128.0, 126.6, 125.6, 125.2, 124.8, 124.6, 123.5, 123.2. MALDI-TOF, m/z: Calcd, 786.195; found, 786.277 [M<sup>+</sup>].

#### 2.3.2. N-(4-(5-(7-(5-(4-(Diphenylamino)phenyl)thiophen-2-yl)-6-fluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)phenyl)-N-phenylbenzenamine (TPA-TBT-1F)

4,7-Bis(5-bromothiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (TBT-1F), was used as a reactant, yield: 58% (purple solid). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.22 (d, 1H), 8.10 (d, 1H), 7.74 (d, 1H), 7.55 (d, 2H), 7.29–7.24 (m, 12H), 7.14–7.02 (m, 16H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 162.3, 160.7, 156.1, 152.4, 150.5, 150.3, 150.1, 150.0, 149.4, 149.1, 139.0, 134.0, 132.3, 132.0, 130.7, 130.3, 129.4, 129.3, 128.0, 127.4, 127.3, 126.1, 126.0, 125.9, 125.3, 118.9, 118.7, 113.7, 113.6. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = -108.24. MALDI-TOF, m/z: Calcd, 804.185; found, 804.237 [M<sup>+</sup>].

#### 2.3.3. N-(4-(5-(7-(5-(4-(Diphenylamino)phenyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)phenyl)-N-phenylbenzenamine (TPA-TBT-2F)

4,7-Bis(5-bromothiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (TBT-2F) was used as a reactant, yield: 49% (purple solid). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 8.24 (s, 2H), 7.56 (d,

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