



# Wide-bandgap polymers containing fluorinated phenylene units for polymer solar cells with high open-circuit voltage

Jingkun Ren<sup>a</sup>, Zhanfeng Li<sup>a,\*</sup>, Jinbo Chen<sup>a</sup>, Qinjun Sun<sup>a</sup>, Hua Wang<sup>b</sup>, Yuying Hao<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Advanced Transducers and Intelligent Control System, Ministry of Education and Shanxi Province, College of Physics and Optoelectronics, Taiyuan University of Technology, Taiyuan 030024, China

<sup>b</sup> Key Laboratory of Interface Science and Engineering in Advanced Materials, Taiyuan University of Technology, Taiyuan 030024, China

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## ABSTRACT

In this work, two wide-bandgap polymers PBDTBT-1FB and PBDTBT-2FB were designed and synthesized with fluorobenzene (1FB) and difluorobenzene (2FB), respectively, which were inserted between the benzodithiophene (BDT) and benzothiadiazole units (BT) in polymer backbone. Functionalization of the phenylene unit with fluorine atom has a significantly effect on the energy levels and charge transportation properties of the polymers. Both PBDTBT-1FB and PBDTBT-2FB exhibited wide-bandgaps of  $\sim 1.98$  eV with deeper-lying HOMO levels. PBDTBT-2FB containing 2FB showed better hole transportation abilities than PBDTBT-1FB due to its good film quality. As a result, polymer PBDTBT-1FB containing 1FB has reached power conversion efficiency (PCE) of 2.16%, with open circuit voltage ( $V_{oc}$ ) of 0.95 V in optimized devices. The photovoltaic performance of PBDTBT-2FB was improved by increasing its  $V_{oc}$  up to 1.0 V, resulting in a PCE of 3.34%. The wide-bandgap polymers containing fluorinated phenylene units result in the simultaneous promotion of  $V_{oc}$ .

## 1. Introduction

In the past decades, polymer solar cells (PSCs) have attracted considerable attention due to their light weight, solution processing, low cost and the capability to fabricate large-area devices. To promote the performance of PSCs, great efforts have been made to improve the novel materials in the active layer, and have also made to vary the parameters of the PSC device to maximize the open-circuit voltage ( $V_{oc}$ ), short-circuit current ( $J_{sc}$ ), and fill factor (FF) under a given incident light power density [1–3]. In the polymer-fullerene solar cells,  $V_{oc}$  is closely correlated to the offset between the highest occupied molecular orbital (HOMO) of the polymer donor and the lowest unoccupied molecular orbital (LUMO) of the fullerene [4]. Unlike low-bandgap polymers, wide-bandgap polymers have been overlooked for PSCs since they only absorb photons in a restricted range [5]. However, the development of efficient wide-bandgap polymers are importance for PSCs, because they have specific advantages of achieving high  $V_{oc}$  of devices due to lower-lying HOMO levels [6–9]. In addition, wide-bandgap polymers with excellent photovoltaic properties can be used for efficient tandem or ternary PSCs [10–12].

In the recent years, electron donor-acceptor (D-A) wide-bandgap polymers have received increasing attention. Among the various electron donor groups used in photovoltaic wide-bandgap polymers, the

benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) is one of the most promising units because of its desirable electron-rich nature and adjustable energy levels in resulting polymers by copolymerizing with suitable A units [13–16]. These BDT-based wide-bandgap polymers usually absorb photons in the UV–vis region, showing lowered HOMO levels, enable to get larger  $V_{oc}$  and obtain higher PCEs in the devices [17,18]. On the other hand, benzothiadiazole (BT) derivatives as electron acceptor moieties have attracted much attention recently as they have shown promising performance characteristics in PSCs [19]. For instance, Duan and co-workers developed a novel wide-bandgap polymer BDT-FBT-2Fu based on BDT and BT units with a wide-bandgap of 1.78 eV, and the PSC based on BDT-FBT-2Fu exhibited a high  $V_{oc}$  of 0.86 V, resulting in a PCE of 4.4% [20]. Hou et al. designed and synthesized a polymer PBDTP-DTBT based on BDTP and BT units, which exhibited a bandgap of 1.70 eV and a deeper HOMO energy level. Consequently, the PSCs based on PBDTP-DTBT afforded a PCE of 5.09% with a  $V_{oc}$  of 0.92 V [21]. Song et al. report a novel D-A conjugated polymer PFBDT-DTffBT by copolymerizing fluorine side-chained BDT unit with fluorinated BT. The PFBDT-DTffBT-based PSCs showed a high  $V_{oc}$  of 0.96 V and a PCE of 7.33% [22].

Moreover, due to the high electro negativity of fluorine, the fluorinated polymers are observed to have deeper-lying HOMO and LUMO energy level without significant changes in bandgap, which can

\* Corresponding authors.

E-mail addresses: [lizhanfeng@tyut.edu.cn](mailto:lizhanfeng@tyut.edu.cn) (Z. Li), [haoyuying@tyut.edu.cn](mailto:haoyuying@tyut.edu.cn) (Y. Hao).

enhance  $V_{oc}$  without deterioration of  $J_{sc}$  [23,24]. In addition, fluorination can influence the charge carrier mobility and fibril structure of conjugated polymers, contributing to both enhancement of  $J_{sc}$  and FF [25]. Functionalization of the phenylene units with fluorine atoms have a market effect on the optical band gaps and electronic properties of resulting polymers [26]. As far as we know, to date, fluorinated phenylene units have been used to tune the energy levels and increase the charge mobilities of some cases of D-A conjugated polymers [27,28].

Compared to the typical D-A polymer, the widely used multi-component polymerization can adjust the absorption properties and molecular orbital energy levels at the time [29]. Embedding the third component into the D-A polymer, in which three units regularly alternate along the backbone chain, are promising candidates for designing new conjugated polymers targeted at high-efficiency PSCs [30,31]. Inspired by the aforementioned priorities, fluorobenzene (1FB) and difluorobenzene (2FB) units were introduced as a second D unit to construct two wide-bandgap regular polymers, PBDBTBT-1FB and PBDBTBT-2FB, respectively, which containing benzothiadiazole (BT) derivative as A unit and benzodithiophene (BDT) derivative as D unit. Different fluoridated phenylene units were modifiable to regulate the energy levels and charge transportation properties of the polymer. Both PBDBTBT-1FB and PBDBTBT-2FB exhibited wide-bandgap of  $\sim 1.98$  eV with deeper-lying HOMO and LUMO energy levels. 2FB unit in PBDBTBT-2FB increases its hole transportation abilities due to its good film quality, and thus significantly enhances the photovoltaic performance. As a result, the PBDBTBT-2FB based polymer solar cells showed a PCE of 3.34%, with a high  $V_{oc}$  of 1.0 V, a  $J_{sc}$  of  $6.31 \text{ mA cm}^{-2}$ , and an FF of 53%. PBDBTBT-1FB showed a relatively lower efficiency of 2.16%, with a  $V_{oc}$  of 0.95 V, mainly due to its poor film quality. Obviously, wide-bandgap polymers containing fluoridated phenylene units result in the simultaneous promotion of  $V_{oc}$ .

## 2. Experimental

### 2.1. Materials

4,8-Bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl bis(trimethylstannane) (M1) was purchased from Gr-chem. 2,4-Dibromo-1-fluorobenzene (1FB) and 1,4-Dibromo-2,5-difluorobenzene (2FB) were purchased from Energy-chemical. 4,7-Bis(4-hexyl-5-(trimethylstannyl)thiophen-2-yl) benzo[*c*][1,2,5]thiadiazole was purchased from Derthon. [6,6]-Phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) was purchased from Hyper chemical. The dry toluene was prepared by refluxing with the alloy of sodium. Other reagents were used as received without further purification, unless stated otherwise. The polymers were prepared by the Stille coupling reaction, and the precipitations were filtered into a Soxhlet extractor.

### 2.2. Synthesis of monomers and polymers

2,6-Bis(4-bromo-2-fluorophenyl)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (M2) and 2,6-bis(4-bromo-2,5-difluorophenyl)-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*] dithiophene (M3) were prepared according to the procedures in the literature [32,33]. Two polymers PBDBTBT-1FB and PBDBTBT-2FB were synthesized via Stille polymerization reaction [34].

#### 2.2.1. Synthesis of compound M2 and M3

M1 (0.5 g, 0.65 mmol), 1FB (0.79 g, 3.10 mmol) or 2FB (0.88 g, 3.25 mmol), and tetrakis(triphenylphosphine)palladium ( $\text{Pd}(\text{PPh}_3)_4$ ) (22.5 mg, 19.5  $\mu\text{mol}$ ) were dissolved in toluene ( $\sim 100$  mL). The reaction mixture was stirred at  $80^\circ\text{C}$  for  $\sim 6$  h under nitrogen. After cooled to room temperature, the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  and washed by water, after drying with anhydrous  $\text{MgSO}_4$ , the organic layer was concentrated. The crude product was purified by silica-gel column chromatography (hexane:  $\text{CH}_2\text{Cl}_2 = 4:1$  (v/v)).

The product M2 was collected as yellow powder (yield 55%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.889$  (s, 2H), 7.491–7.467 (m, 4H), 4.226–4.212 (d, 4H), 1.870–1.810 (m, 2H), 1.747–1.532 (m, 8H), 1.418 (m, 8H), 1.062–1.025 (m, 6H), 0.969–0.934 (t, 6H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 160.530, 158.167, 144.509, 141.075, 135.580, 133.903, 132.664, 130.182, 129.504, 127.901, 122.988, 120.180, 116.949, 144.152, 108.610, 76.058, 40.704, 30.502, 29.280, 23.885, 23.224, 14.119, 11.400$ . HRMS (MALDI-TOF):[M–H]  $m/z$  calcd for  $\text{C}_{38}\text{H}_{42}\text{Br}_2\text{F}_2\text{O}_2\text{S}_2$ :790.096228, found: 790.095555.

The product M3 was collected as light-yellow powder (yield 50%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.579$  (s, 2H), 7.549–7.499 (m, 8H), 4.147–4.134 (d, 4H), 1.812–1.782 (m, 2H), 1.595–1.458 (m, 8H), 1.352 (m, 8H), 0.995–0.958 (t, 6H), 0.902–0.867 (t, 6H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 156.733, 154.496, 144.625, 134.940, 133.855, 132.784, 131.808, 129.962, 128.544, 125.935, 122.437, 121.067, 120.271, 115.568, 108.416, 76.031, 40.690, 30.433, 29.291, 23.919, 23.152, 14.320, 11.374$ . HRMS (MALDI-TOF):[M–H]  $m/z$  calcd for  $\text{C}_{38}\text{H}_{40}\text{Br}_2\text{F}_4\text{O}_2\text{S}_2$ :826.076962, found: 826.076711.

#### 2.2.2. Synthesis of PBDBTBT-1FB

Under an argon protection, M2 (0.2 g, 0.25 mmol), tBT (0.201 g, 0.25 mmol), tris(dibenzylideneacetone)dipalladium ( $\text{Pd}_2(\text{dba})_3$ ) (11.5 mg, 12.0  $\mu\text{mol}$ ), triphenylphosphine ( $\text{PPh}_3$ ) (14.2 mg, 48.2  $\mu\text{mol}$ ), toluene (10 mL), and DMF (2 mL) were added in a 100 mL round-bottom flask. The reaction mixture was stirred to reflux gradually for 60 h under nitrogen. After mixture cooled to room temperature, the resulted solid was precipitated by addition of methanol (200 mL). Then it was collected by filtration and purified by Soxhlet extraction with methanol, hexane and acetone, respectively. The residue was finally extracted with  $\text{CHCl}_3$  and precipitated again by MeOH. Finally, the polymer was collected by filtration, dried under vacuum at  $60^\circ\text{C}$  overnight and afforded PBDBTBT-1FB as a dark red solid (280 mg, yield 78%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.65$  (br, 4H), 5.03–4.88 (br, 4H), 2.50–1.78 (br, 5H), 1.55–0.78 (br, 88H). The molecular weights were decided by GPC as:  $M_n = 17.1$  kDa,  $M_w = 19.5$  kDa, PDI = 1.33.

#### 2.2.3. Synthesis of PBDBTBT-2FB

Using a procedure similar to that described above for previous, a mixture of M3 (0.2 g, 0.24 mmol), tBT (0.19 g, 0.24 mmol),  $\text{Pd}_2(\text{dba})_3$  (11.8 mg, 12.5  $\mu\text{mol}$ ) and  $\text{PPh}_3$  (19.0 mg, 62.5  $\mu\text{mol}$ ) in dry toluene (10 mL) and DMF (2 mL) was polymerized to give PBDBTBT-2FB as a dark red solid (350 mg, yield 72%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.65$ –7.35 (br, 4H), 5.0–4.6 (br, 4H), 2.20–1.75 (br, 5H), 1.45–0.90 (br, 88H). The molecular weights were decided by GPC as:  $M_n = 16.1$  kDa,  $M_w = 17.7$  kDa, PDI = 1.27.

### 2.3. Characterization

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker Advance IIIITM (400 MHz) spectrometer in  $\text{CDCl}_3$  and ambient conditions with the chemical shift against tetramethylsilane (TMS). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were performed using a MS Bruker Daltonik Reflex III and Bruker solarix spectrometer. Molecular weights and distributions of the polymer were measured by gel permeation chromatography (GPC) method on Waters 1515 with polystyrenes as reference standard and THF as an eluent at  $40^\circ\text{C}$ . Thermal gravimetric analysis (TGA) was carried on a STA 409 PC instrument at a heating rate of  $10^\circ\text{C min}^{-1}$  under nitrogen. Absorption spectra were recorded on a Hitachi U-3900 UV–vis Spectrophotometer at room temperature. The electrochemical data was obtained from a CHI 660E electrochemical workstation in a three electrode system using 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) in acetonitrile as the electrolyte at a scan rate of  $100 \text{ mV s}^{-1}$  at room temperature. A glassy carbon working-electrode coated with the polymer film, platinum wire, and platinum electrode were used as working electrode, counter electrode, and

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