

## Fluoro-benzoselenadiazole-based low band gap polymers for high efficiency organic solar cells†

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Low band gap polymers are of great interest for future applications in solar cells. By using monofluoro-2,1,3-benzoselenadiazole (FBSe) as the electron acceptor and benzodithiophene (BDT) or indacenodithiophene (IDT) as the electron donor, two novel FBSe-based polymers, PBDT-T-FBSe and PIDT-T-FBSe, were synthesized via a microwave-assisted palladium-catalyzed Stille polymerization. Both of the polymers exhibited broad absorption and lower highest occupied molecular orbital (HOMO) energy levels, which contribute to the high short current density ( $J_{sc}$ ) and open circuit voltage ( $V_{oc}$ ). Higher power conversion efficiencies of 5.00% for PBDT-T-FBSe and 4.65% for PIDT-T-FBSe were achieved in a bulk heterojunction (BHJ) photovoltaic device with a configuration of ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM/bis-C<sub>60</sub>/Ag under the illumination of AM1.5G at 100 mA cm<sup>-2</sup>. These results demonstrate the importance of FBSe as an electron-deficient unit in the design of donor-acceptor photovoltaic polymers.

As an economically viable source of renewable energy, encouraging progress has been made over the last three years in the field of organic photovoltaics (OPVs) using p-type conjugated polymers, which exhibit great industrial potential due to their cost-effective manufacturing, light weight and mechanical flexibility.<sup>1-4</sup> Power conversion efficiencies (PCEs) of over 8% have now been reported in single junction polymer solar cells (PSCs).<sup>5</sup> Among the developed versatile semiconducting polymers, low band gap materials have gained broader interest for implementation in PSCs in the last few years due to their enhanced visible and near-infrared absorption and a better

match with the solar spectrum, which maximizes light harvesting, thereby minimizing photon energy loss.<sup>6-10</sup>

A straightforward strategy to reduce the polymer band gap is to incorporate both the electron-rich and electron-deficient moieties into the conjugated polymer backbone, in which the hybridization of the energy levels of the electron donor (D) and acceptor (A) moieties results in D-A systems with unusually low HOMO-LUMO separation. It is well known that thiophene and its derivatives are broadly used as electron-rich building blocks in conjugated polymers. A simple method to further tune the optical and electronic properties of thiophene-based polymers is the replacement of the sulfur (S) atom in thiophene with a selenium (Se) atom, which is expected to have several advantages over sulfur-containing polymers. In comparison to thiophene, the reduced aromaticity of selenophene increases the ground state quinoid resonance character of the resultant polymers, leading to improved planarity, an increased effective conjugation length, and also a decreased band gap.<sup>11,12</sup> In addition, the Se-containing unit is more polarizable than its S analogue, which often results in an improvement of the charge mobility of the polymers because of interchain Se...Se interactions.<sup>13</sup> So far, some promising Se-containing photovoltaic materials have been reported in the literature. For example, in a benzodithiophene-diketopyrrolopyrrole D-A copolymer, replacing thiophene as a  $\pi$ -bridge with selenophene resulted in an 11% enhancement of the PCE in devices, from 6.5% in the thiophene-based polymer to 7.2% in the selenophene analogue.<sup>14</sup> The promising results from a new electron-rich building block, selenolo[3,2-*b*]thiophene, have also been reported, with improved device efficiencies from 5.6% to 6.8%.<sup>15</sup> However, not all of the Se-containing electron-deficient unit-based polymers exhibit good photovoltaic performance. For instance, in the benzothiadiazole (BT) and dialkoxybenzodithiophene-based copolymer, replacing the BT unit with benzoselenadiazole (BSe) enhanced the light absorption across the solar spectrum, but did not improve the device performance.<sup>16</sup> Similar results were also reported by Wu *et al.*, who replaced S with Se in 4,7-dithien-2-yl-2,1,3-benzothiadiazole-based polymers, leading to a disappointing result in which the

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maximum PCE reached only 2.5% compared to the S analogue (7.1%).<sup>17</sup> Therefore, the design and preparation of novel high-efficiency Se-based polymers, which can be used to fabricate PSCs with reduced energy loss and increased photocurrent density, is still a great challenge.

Owing to the electron-withdrawing character of fluorine (F), conjugated polymers with backbones functionalized with F groups usually exhibit lower HOMO energy levels and larger open-circuit voltages ( $V_{oc}$ ) of the corresponding device.<sup>18–21</sup> By adding fluorine substituents in the polymer system, a reduced bimolecular recombination will occur and lead to an improved short-circuit current density ( $J_{sc}$ ) and fill factor (FF).<sup>22,23</sup> In this contribution, we first designed and developed a new Se-containing electron-deficient building block, monofluoro-2,1,3-benzoselenadiazole (FBSe), and then synthesized two novel FBSe-based polymers, PBDT-T-FBSe and PIDT-T-FBSe, *via* a microwave-assisted palladium-catalyzed Stille polymerization which has been demonstrated to produce polymers with high molecular weights<sup>24</sup> (Scheme 1). Compared to the similar benzoselenadiazole-based conjugated polymers with limited  $V_{oc}$  and  $J_{sc}$  values,<sup>13,16</sup> both of these two new PSCs shows higher  $V_{oc}$  and  $J_{sc}$  values, which could be attributed to the relatively lower HOMO energy levels and the decreased bimolecular recombination caused by introducing an F atom into the polymer backbone. As a result, the power conversion efficiencies obtained in this work are 5.00% for PBDT-T-FBSe, and 4.65% for PIDT-T-FBSe.

These new low band gap polymers exhibited very good solubility in common organic solvents, such as chloroform (CF), chlorobenzene (CB) and *o*-dichlorobenzene (*o*-DCB), making them useful for solution-processable devices. The number-average molecular weights of PBDT-T-FBSe and PIDT-T-FBSe were 27.6 kDa and 32.2 kDa respectively, with polydispersity indexes (PDI) of 2.14 and 2.37. As shown in Fig. 1 and Table 1, both of these polymers show two characteristic peaks. The

longer wavelength band is due to intramolecular charge transfer (ICT) between the BDT/IDT and FBSe units, and the other band at shorter wavelengths is attributed to localized  $\pi-\pi^*$

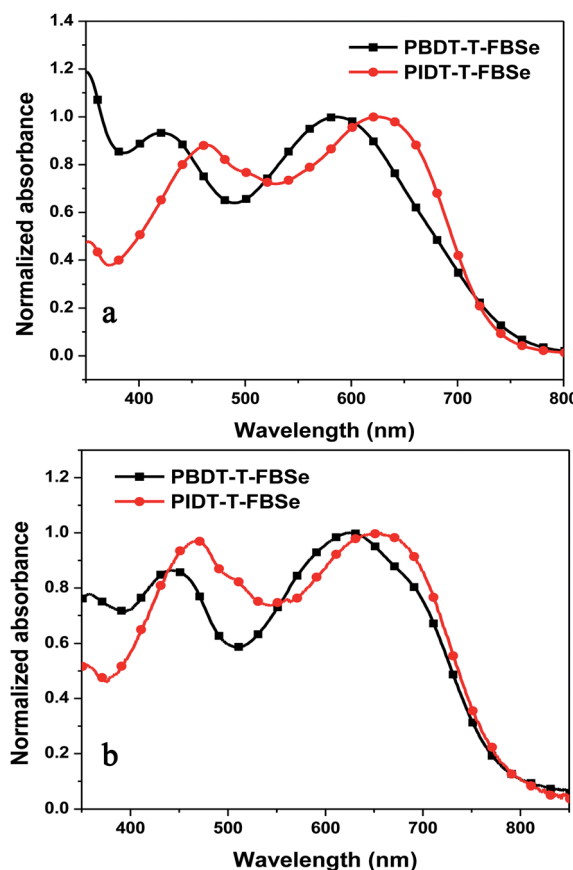
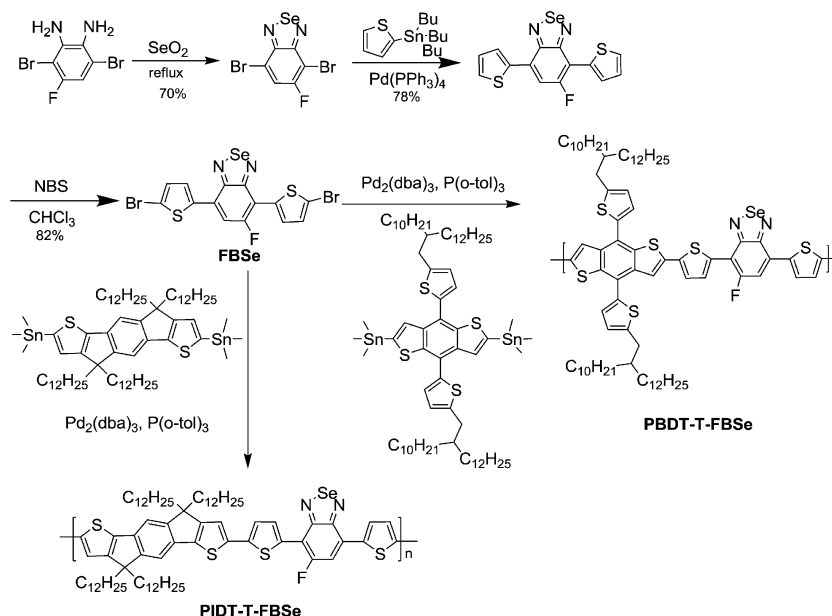


Fig. 1 The UV/Vis absorption spectra of the samples in (a) CB solution and (b) as a thin film.



Scheme 1 Synthesis of FBSe, PBDT-T-FBSe and PIDT-T-FBSe.

Table 1 Optical and electrochemical properties of the polymers

Polymer	UV-Vis absorption					Cyclic voltammetry	
	Solution		Film				
	$\lambda_{\text{max}}$ (nm)	$\lambda_{\text{onset}}$ (nm)	$\lambda_{\text{max}}$ (nm)	$\lambda_{\text{onset}}$ (nm)	Band gap	HOMO (eV)	LUMO (eV)
PBDT-T-FBSe	586.2	748.5	633.7	774.3	1.60	−5.19	−3.12
PIDT-T-FBSe	634.7	729.3	654.9	784.3	1.58	−5.21	−3.30

transitions. For PBDT-T-FBSe, an absorption peak at 586 nm was observed in the CB solution while its maximum peak in the film was red-shifted to 634 nm, which correlates with its solid-state packing. A new peak at 692 nm in the thin film indicates a more ordered structure in the solid state due to stronger inter-chain packing. Notably, PIDT-T-FBSe also showed red-shifted absorption maxima in the thin film compared to those in CB solution, which can be ascribed to the strong aggregation of the polymer backbone. Both polymers possess narrow optical band gaps, 1.60 for PBDT-T-FBSe and 1.58 eV for PIDT-T-FBSe, according to the absorption edges of these films.

The frontier orbital energy levels of the polymers were measured using cyclic voltammetry (CV) on the polymer films. As shown in Fig. 2, the potentials were measured against Ag/Ag<sup>+</sup> as the reference electrode, with a platinum counter electrode in a 0.1 M electrolyte containing tetrabutyl-ammonium hexafluorophosphate in acetonitrile with a scan rate of 100 mV s<sup>−1</sup>. The HOMO and LUMO energy levels were estimated from the onsets of the oxidation and reduction waves,<sup>25</sup> and the results are summarized in Table 1. The corresponding HOMO and LUMO energy levels for PBDT-T-FBSe and PIDT-T-FBSe are (−5.19, −3.21) and (−5.21, −3.30) eV, respectively. Owing to the incorporated weak donor moiety, both polymers feature reasonably low-lying HOMO levels, which are promising for achieving a high  $V_{\text{oc}}$  in their photovoltaic devices.

As the active material for polymer solar cells, the charge carrier mobility is one of the most important factors dictating the device performance as it is directly related to exciton dissociation, charge transport and recombination.<sup>26–28</sup> PBDT-T-FBSe and PIDT-T-FBSe-based field-effect transistors (FETs), with

a bottom-gate and top-contact device configuration, were fabricated onto an n-doped silicon wafer. The calculated saturation hole mobility for PBDT-T-FBSe is  $1.1 \times 10^{-4}$  cm<sup>2</sup> V<sup>−1</sup> s<sup>−1</sup> with an on-off ratio of  $1.7 \times 10^2$ , while PIDT-T-FBSe shows a hole mobility of  $3.0 \times 10^{-3}$  cm<sup>2</sup> V<sup>−1</sup> s<sup>−1</sup> and an on-off ratio of  $4 \times 10^4$ . The threshold voltages for the polymers are −24 and −20 V, respectively. (Fig. 3) These results suggest that PIDT-T-FBSe will greatly facilitate the charge transport to the electrodes in the bulk-heterojunction solar cells.

The photovoltaic properties of both polymers were investigated initially with a bulk heterojunction (BHJ) device configuration of ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM/bis-C<sub>60</sub>/Ag under the illumination of AM1.5G at 100 mA cm<sup>−2</sup>.<sup>29</sup> Typical  $J$ - $V$  curves of the devices are shown in Fig. 4a and the performance of the devices is summarized in Table 2. Due to the better overlap with the solar emission spectrum and the reduced HOMO energy levels of the polymers, PBDT-T-FBSe and PIDT-T-FBSe are expected to show promising device performance. Indeed, the PBDT-T-FBSe device shows a good PCE of 5.00% with a  $V_{\text{oc}}$  of 0.78 V, a  $J_{\text{sc}}$  of 11.80 mA cm<sup>−2</sup> and a FF of 0.54, while PIDT-T-FBSe exhibits a relatively lower PCE of 4.65% with a  $V_{\text{oc}}$  of 0.83 V, a  $J_{\text{sc}}$  of 10.57 mA cm<sup>−2</sup> and a FF of 0.53. Remarkably, large differences in  $V_{\text{oc}}$  are observed due to the differences in the HOMO levels of the polymers. It is well known that the  $V_{\text{oc}}$  of a PSC is proportional to the difference between the HOMO level of the polymer and the LUMO level of PC<sub>71</sub>BM. Hence, the reduced HOMO level of the donor polymer results in a higher  $V_{\text{oc}}$ . To verify the improved  $J_{\text{sc}}$ , the external quantum efficiencies (EQEs) of the polymer/PC<sub>71</sub>BM devices were measured, and are shown in Fig. 4b. The  $J_{\text{sc}}$  values calculated from the EQE curves under the standard AM1.5G conditions match well with those obtained from the  $J$ - $V$  measurements. It should be noted that the PBDT-T-FBSe blend with PC<sub>71</sub>BM exhibited significant contributions to the photocurrent at much longer wavelengths than the PIDT-T-FBSe-based devices, although for both conjugated polymers the UV/Vis absorption at longer wavelengths is comparable. This increase in the EQE for the PBDT-T-FBSe-based device can be explained by two factors. Firstly, the cyclic voltammetry measurements showed that the LUMO level of PBDT-T-FBSe moved up by 0.18 eV. Considering the LUMO offset between the polymers and PC<sub>71</sub>BM, it has been argued that the efficiency of charge separation is largely dependent on this extra energy.<sup>30,31</sup> As a result, PBDT-T-FBSe with a large LUMO offset will obtain much more of a driving force to separate the excitons, which leads directly to the enhanced EQE. More efficient exciton dissociation in PBDT-T-FBSe/PC<sub>71</sub>BM

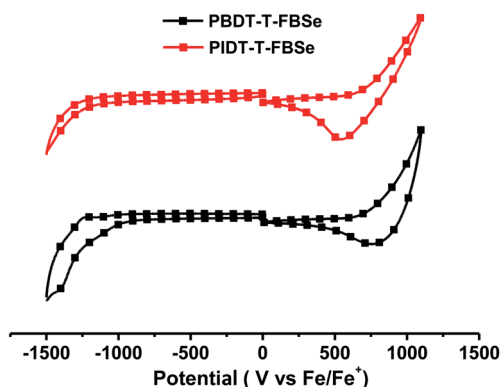


Fig. 2 CV curves of the sample films.

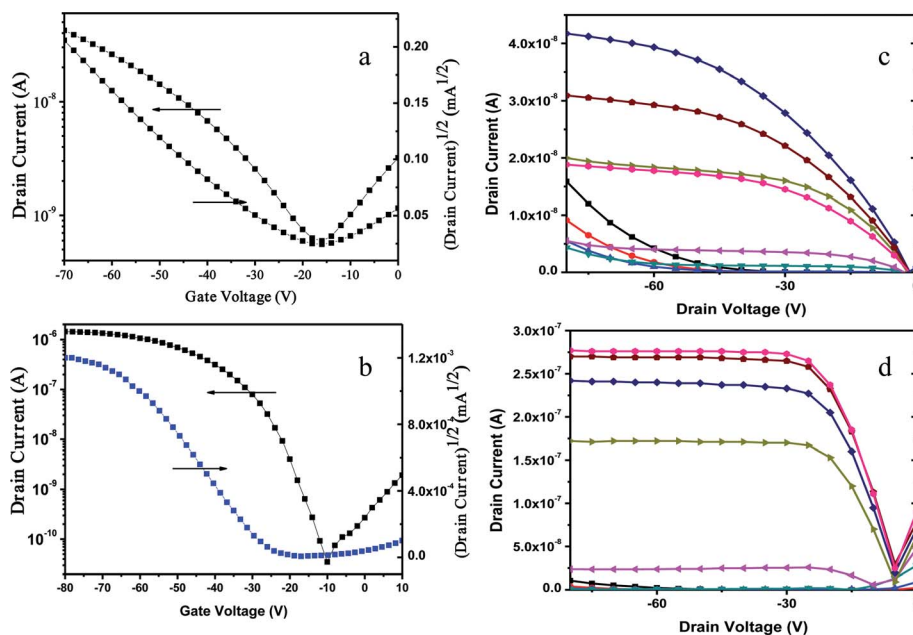


Fig. 3 Output (a and b) and transfer (c and d) characteristics of PBTD-T-FBSe (a and c) and PIDT-T-FBSe (b and d).

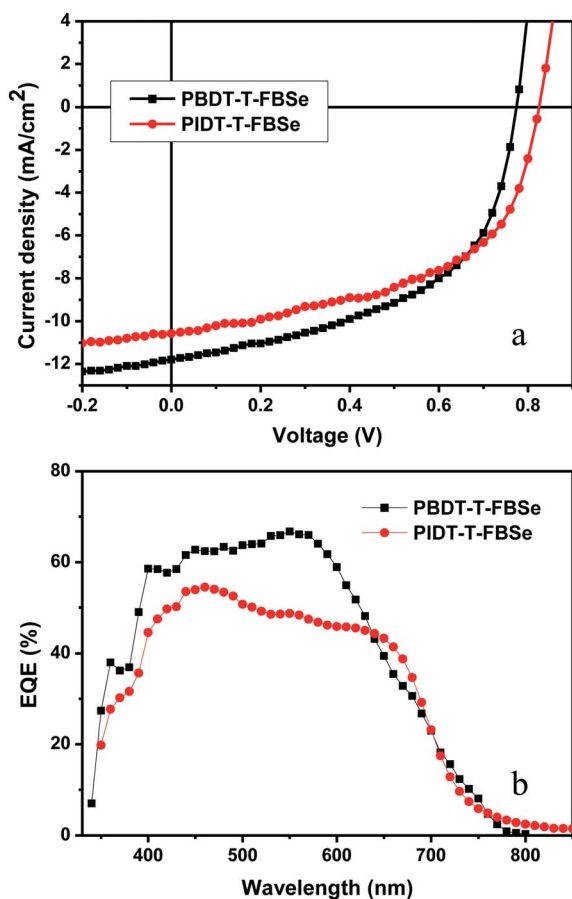


Fig. 4 Current–voltage characteristics (a) and EQE (b) of the photovoltaic devices based on PBTD-T-FBSe and PIDT-T-FBSe, with the blending ratio as 1 : 2.5 under illumination with  $100 \text{ mW cm}^{-2}$  (AM1.5G).

Table 2 Photovoltaic properties of the PSCs based on the polymers as the donor and PC<sub>71</sub>BM as the acceptor under the illumination with AM1.5G,  $100 \text{ mW cm}^{-2}$

Polymer	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF	PCE (%)
PBTD-T-FBSe	0.78	11.80	0.54	5.00
PIDT-T-FBSe	0.83	10.57	0.53	4.65

than in PIDT-T-FBSe/PC<sub>71</sub>BM is another factor which should be taken into account. Tapping-mode atomic force microscopy (AFM) confirmed that there are large domains on the surface of the film based on PIDT-T-FBSe:PC<sub>71</sub>BM (see Fig. S1†). This increases exciton recombination as the phase domains are substantially larger than the exciton diffusion length, making excitons less likely to reach the donor–acceptor interface, inhibiting the formation of free charge carriers, and thus resulting in the lower EQE and  $J_{sc}$ .

In summary, we developed a new Se-containing electron-deficient building block, FBSe. By using a microwave-assisted palladium-catalyzed Stille polymerization, two novel FBSe-based low band gap polymers, PBTD-T-FBSe and PIDT-T-FBSe, were successfully synthesized. Higher power conversion efficiencies of 5.00% for PBTD-T-FBSe and 4.65% for PIDT-T-FBSe were achieved in the BHJ photovoltaic cells. These results provide new insight for the development of new generation low band gap materials.

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