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# bandgap difluorobenzochalcogenadiazole-based polymers for

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## high-performance organic thin-film transistors and polymer solar cells<sup>†</sup>

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† Electronic supplementary information (ESI) available: Experimental details, graphics (Fig.

S1–S19) and tables (Table S1–S9).

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## Abstract

View Article Online DOI: 10.1039/D0NJ01006E

A bithiophene donor unit, 3-alkoxy-3'-alkyl-bithiophene (TRTOR), was copolymerized with difluorobenzochalcogenadiazole (ffBZ) containing different heteroatoms on their diazole structure to afford a series of PffBZ copolymers (where Z = X, T, Se) with narrow optical bandgaps in the range of 1.34–1.47 eV. The effects of ffBZ heteroatoms (O, S, and Se) on the optical properties, electrochemical characteristics and film morphologies of polymers as well as device performance were fully investigated. The results revealed that the highest occupied molecular orbitals (HOMOs) of polymers are gradually elevated accompanied by increased material solubility in common organic solvents as the size of heteroatoms increases. The PffBZ copolymers exhibit substantial hole mobility of 0.08-1.6 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in organic thin-film transistors (OTFTs). The PffBX, PffBT, and PffBSe-based polymers exhibit maximum power conversion efficiencies (PCEs) of 5.47%, 10.12%, and 3.65%, respectively in polymer solar cells (PSCs). For PffBZ copolymers, the alkyl chain exerts a great influence on the morphology of the polymer:PC<sub>71</sub>BM blend films and hence affect PCEs in PSCs. It was found that the performing of polymers branching on the 2<sup>nd</sup> position for alkyl chain and the 3<sup>rd</sup> position for alkoxy chain were the best among PffBT and PffBSe-based polymers, and it is different from the tetrathiophene-based benchmark polymer branching on the 2<sup>nd</sup> position of the alkyl chain. X-ray diffraction revealed that all PffBZ-based polymers has obvious a face-on dominated orientation, and that chalcogen atom and branched position on alkoxy chain have a great influence on the morphologies of neat and blend films. The above results indicated that the branching positions and chalcogen atoms should be carefully optimized to maximize performance.

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## Introduction

 $\pi$ -Conjugated polymers have attracted much attention over the past decades due to their great potentials for fabricating lightweight, flexible and large-area electronic devices such as organic thin-film transistors (OTFTs) and polymer solar cells (PSCs).<sup>1-8</sup> The design and synthesis of novel polymer semiconductors with optimized physicochemical and electronic properties play a crucial role in achieving high device performance.<sup>9-11</sup> Among existing materials, in-chain donor-acceptor (D-A) type copolymers demonstrate widely adjustable physicochemical property and optimized film morphology, and hence improves device performance in OTFTs and PSCs.<sup>12-15</sup> For organic electronic devices, modulating the frontier molecular orbital (FOM) energy levels of the polymer semiconductors including both the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are critical in promoting device performance, since they are closely related to injection/generation, transport, and collection of charge carrier.<sup>14,16-18</sup> The HOMO and LUMO energy levels of the polymer semiconductors can be effectively adjusted through the orbital hybridization among these units by copolymerizing appropriate donor and acceptor units, thus providing better performance for organic electronic devices.

The head-to-head linkage containing bithiophene units with side chains substituted by alkoxy has proved to be a promising electron donor in constructing D-A type copolymers for PSCs and OTFTs,<sup>19-22</sup> which is because that their reduced steric hindrance (because the -CH<sub>2</sub>-moiety connected to thiophene unit was replaced by a smaller oxygen atom) and extra introduced intramolecular  $S \cdots O$  interaction, featuring high coplanar molecular backbones

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and strong electron-donating abilities leads to a pronounced red-shifted absorption and a smaller bandgap of the D-A polymers to be obtained when compared to the conventional 3,3'-dialkyl-2,2'-bithiophene units (BTR)-based polymer analogues.<sup>19</sup> Previous studies also demonstrate that the side chains of 3-alkoxy-3'-alkyl-2.2'-bithiophene (TRTOR), whose the side chains between the two adjacent thiophene units are substituted by only one alkoxyl group at the 3-positions of thiophene, and offers more advantages than the analogue donor units with two alkoxyl groups at the 3-positions of thiophene (BTOR) while maintaining a coplanar molecular geometry and strong electron-donating property.<sup>19,23</sup> Especially the HOMO energy level of TRTOR-based polymers are lower than that of BTOR-based polymers, thus resulting in an increased  $V_{oc}$  and better device performance in the PSC devices.<sup>19</sup> Our previous work has proved that TRTOR-based polymer PffBT-3 (Fig. 1) shows a more pronounced red-shifted absorption spectra and a smaller bandgap than the terthiophene or tetrathiophene-based polymer analogues if it is copolymerized with benzothiadiazole.<sup>19,20,24-26</sup> When blended with PC<sub>71</sub>BM, the PffBT-3-based bulk heterojunction (BHJ) PSCs shows a remarkable power conversion efficiency (PCE) of 9.76%,<sup>20</sup> attributing to their excellent solar light absorption, ordered film morphology, and substantial charge carrier mobility. These results clearly demonstrate that TRTOR is an excellent building block for constructing high-performance polymer semiconductors.<sup>19,20</sup>

Among various acceptor units that have been reported, difluorobenzothiazole (ffBT) is widely used for constructing high-performance in-chain donor-acceptor copolymers due to its strong electron-withdrawing capability and compact geometry. The ffBT-based polymer semiconductors have shown the currently most promising PCEs in fullerene solar cells.<sup>25,27,28</sup>

A new acceptor unit difluorobenzoxadiazole (ffBX) is obtained by replacing S atom  $^{29,30}$  The electron deficiency of ffBX is more than that of ffBT because the electron negativity of O atom is higher than that of S atom. When ffBX was copolymerized with various donor units, the polymers to be obtained showed larger  $V_{oc}$  in PSCs and facile tunable charge carrier polarity in OTFTs due to the high electron deficiency of ffBX.<sup>29-32</sup> The difluorobenzoselenadiazole (ffBSe) unit is afforded if S atom in ffBT is substituted with a heavier Se atom. Several studies have shown that polymers containing ffBSe exhibit red-shifted and broadened absorption spectra compared with their ffBT-based polymer analogues, and these spectra will enhance their light harvesting capability in PSCs.<sup>33-35</sup> Based on our previous results,<sup>20</sup> the high performance of PffBT-3 devices drives us to further investigate the physicochemical properties and device performance of PffBX and PffBSe-based polymer analogues in organic semiconductors.

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**Fig. 1** Chemical structures of the PffBZ-based polymer semiconductors containing different chalcogen heteroatoms on the ffBZ moiety and different branching position of alkoxy chain on the TRTOR unit.

Herein, the TRTOR donor unit was copolymerized with a variety of ffBZ acceptor units, ffBX, ffBT, and ffBSe to afford a series of polymer semiconductors with narrow bandgaps of 1.34–1.47 eV (Fig. 1). The influences of heteroatoms on the optical properties, electrical characteristics, and device performance of the polymer semiconductors were systematically investigated. The results indicate that the backbone planarity and intermolecular aggregation gradually decrease as the chalcogen atom size increases from O to S and to Se. Among all polymers, the PffBT-based polymers exhibit better device performance than PffBX and PffBSe-based polymer analogues. In addition, the branching positions of the side chains were

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systematically changed to probe their influences on the device performance. It was found that the branching positions of side chain are critical for the aggregation of polymer chain, film morphology, and hence device performance. Polymer PffBT-3 with 2<sup>nd</sup> position branching away from backbone on the alkyl chain and 3<sup>rd</sup> position branching away from backbone on the alkoxy chain (Fig. 1) afford the highest PCE of 10.12% with a remarkable  $J_{sc}$  of 21.46 mA cm<sup>-2</sup> in PSCs (Fig. 6 and Table 3) and the highest hole mobility ( $\mu_{\rm h}$ ) of 1.58 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in OTFTs (Fig. S14) due to its high degree of backbone planarity, narrow optical bandgap and the improvement of film crystallinity. Different from the tetrathiophene-based benchmark polymer having branching positions on the 2<sup>nd</sup> position of alkyl chain,<sup>25</sup> the polymer analogues PffBT-2 with 2<sup>nd</sup> position branching from backbone on both alkyl and alkoxy chains (Fig. 1) reduce charge carrier mobility and PCE. Polymer PffBT-2 shows a lower PCE of 7.42% than PffBT-3 because film morphology is degraded. The results indicate that the branching position of side chain should be carefully optimized to maximize performance in the PffBZ-based polymer semiconductors.

## **Results and discussion**

#### Material synthesis

The ffBT monomer was purchased from commercial resource, and the monomers ffBX and ffBSe were synthesized according to the published procedures (see Supporting Information for the synthetic details).<sup>29,30,36</sup> TRTOR monomers with two branching positions on their side chains were synthesized to fine-tune the film morphology and study the correlations between materials structure, property and device performance. All TRTORs could be readily stannylated to obtain tin monomers, which were used for polymerizations

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with three ffBZ units via Pd-mediated Stille coupling-based polycondensation, reaction still and the stille online After polymerization, all polymer chains were end-caped with mono-functionalized thiophene and then subjected to Soxhlet extraction with methane, acetone, hexane to remove the small molecular weight portions, and then with dichloromethane, chloroform, chlorobenzene, and o-dichlorobenzene (o-DCB) to extract the high molecular weight polymer products. The polymers were collected and used as polymer semiconductors after they were extracted with the final solvent possessed the highest molecular weight. The decent molecular weights  $(M_n s)$  of all polymers were 11-35 kDa and their comparable polydispersity index (PDI) were 1.3-1.7 (Table 1). Among all polymers, PffBT-based copolymers show limited solubility at room temperature, but they can be readily dissolved in hot o-DCB and toluene, and the PffBSe-based polymers show better solubility, which can be dissolved in o-DCB and toluene at room temperature. However, the solubility of PffBX-based polymers is worse in hot o-DCB and toluene. In terms of polymer solubility, it seems that the solubility of polymers becomes strong as the size of the heteroatoms increases, thus proving that the inter-chain interaction occurs and has a profound impact on the device performance in OTFTs and PSCs.

Compared to the PffBT-based polymer PffBT-3, the PffBX-based polymer analogue PffBX-3 with the same side chains was also synthesized. However, the polymer PffBX-3 is quite easily aggregated even in hot *o*-DCB (~ 100 °C), which renders it poor solubility. The polymer PffBX-2 was also synthesized to improve the polymer solubility, it shows good solubility in hot *o*-DCB (~ 100 °C), thus exhibiting higher performance in OTFTs and PSCs than PffBX-3. The polymer PffBSe-3 shows good solubility in *o*-DCB at room temperature, but the temperature needs to be elevated to ~ 100 °C for polymer PffBT-3 with the same side chains to achieve comparable solubility, and only limited solubility is observed even in hot *o*-DCB (~ 100 °C) for polymer PffBX-3, which makes it difficult to fabricate device, and

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## Theoretical computation of the polymer semiconductors

In order to better understand the influences of chalcogen atoms on the optoelectrical properties of the PffBZ-based polymer semiconductors, density functional theory (DFT)-based computation was performed for the dyads of polymer repeating units by using a hybrid B3LYP/6–31G (d, p) basis set (Gaussian 09). All the branched alkyl side chains were truncated in order to facilitate the calculation. The optimized geometries of the polymer dyads are shown in Fig. 2, and the FMO spatial distributions are shown in Table S1. The calculation results revealed that all these PffBZ-based polymers show quite planar backbone with the dihedral angles between any two neighboring arenes in the range of 0.05–0.23°, which is attributed to the compact geometry of the building blocks as well as the intramolecular interaction of noncovalent S…O, F…S, and F…H.<sup>38-41</sup> It was found that the dihedral angle between neighboring arenes of ffBZ and thiophene slightly increased as the size of the chalcogen atom increased from O to S and to Se on the ffBZ unit, probably because atomic size is larger, thus increasing steric hindrance between ffBZ and thiophene.

The low-lying  $E_{LUMO}/E_{HOMO}$  (-3.00/-4.99 eV) of polymer PffBX-3 dyads is lower than that (-2.87 eV/-4.80 eV) of polymer PffBT-3 dyads if ffBT is substituted with ffBX because the electronegativity of O atom is higher than that of S atom.<sup>29</sup> Due to the high-lying  $E_{HOMO}$ , the small  $V_{oc}$  (0.66–0.67V) is the major bottleneck for the performance of PffBT-based PSCs,

while the low-lying  $E_{\text{HOMO}}$  should be beneficial to increase the  $V_{\text{oc}}$  for PffBX-based PSCS. The  $E_{\text{LUMO}}$  (-2.91 eV) of PffBSe-3 is lowered by 0.04 eV but the  $E_{\text{HOMO}}$  (-4.74 eV) is raised by 0.06 eV compare to PffBT-3, the relatively raised  $E_{\text{HOMO}}$  of PffBSe-3 versus that of PffBT-3 could be ascribed to the smaller electronegativity of Se (vs S) and the higher quinoidal character upon the substitution of S with Se,<sup>42-44</sup> therefore, the PffBSe-3 shows the smallest bandgap (Table 1). The high-lying  $E_{\text{HOMO}}$  of PffBSe-3 may result in the smallest  $V_{\text{oc}}$ in PSCs (*vide infra*) among PffBZ-based polymers. The electron densities are well delocalized on the HOMOs energy level of main polymer chain (Table S1), which should be beneficial to intramolecular transport of charge carriers.



**Fig. 2** Optimized geometries of the dyads of polymer repeat units of (a) PffBX-3, (b) PffBT-3, and (c) PffBSe-3. Calculations are carried out at the DFT//B3LYP/6-31G (d, p) level. Dihedral angles between neighboring arenes are indicated by the red dotted circles. Alkyl substituents are truncated for calculation simplicity.

## Optical and electrochemical properties of the polymers.

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The optical absorption spectra of all these PffBZ-based polymers are shown in Fig. 3a and 3b, and the relevant data are summarized in Table 1. All polymers show two distinctive absorption bands in the states of both solution and film. The high energy absorption in the range of 390-430 nm can be attributed to the  $\pi$ - $\pi$ \* transitions, and the low energy absorption in the range of 550-900 nm can be assigned to the intramolecular charge transfer (ICT) process.<sup>45,46</sup> On the basis of the polymer absorption onsets, the derived optical bandgaps  $(E_{\sigma}^{opt}s)$  are 1.46, 1.47, and 1.34 eV for PffBX-3, PffBT-3, and PffBSe-3, respectively. The changes in the branching positions of PffBZ-based polymers has minimum effect on the absorption profile of the polymer and the absorption maximum ( $\lambda_{max}$ ), indicating comparable backbone conformation, which is attributed to the greatly reduced steric hindrance by inserting the oxygen atom and effective conformation locking enabled by intramolecular interaction of noncovalent S...O.<sup>47</sup> Among all these PffBZ-based polymers, the PffBSe-3 exhibits the most red-shifted absorption with an absorption maximum ( $\lambda_{max}$ ) of 820 nm and the narrowest optical band gap  $(E_g^{opt})$  of 1.33 eV.<sup>44</sup> This trend is consistent with how the absorption of the acceptors monomers ffBZs evolves (Fig. S10). As the heteroatoms varying from O to S and to Se, PffBX-3 and PffBT-3 show similar absorption and the Se-containing polymer PffBSe-3 exhibit a substantially red-shifted absorption onset, the red-shift absorption of polymer PffBSe-3 is possibly caused by increase in quinoidal feature and decrease in aromaticity as one atom changes from S to Se atom. 33,35,44,48,49



**Fig. 3** Optical absorption spectra of PffBZ-based polymers (a) in solution  $(10^{-5} \text{ M in } o\text{-dichlorobenzene})$  and (b) in film state, spin-coated on glass from 5 mg mL<sup>-1</sup> o-dichlorobenzene solution. (c) Cyclic voltammogram of polymer films measured in 0.1 M  $(n\text{-Bu})_4\text{N}\text{\cdot}\text{PF}_6$  acetonitrile solution at a scan rate of 50 mV s<sup>-1</sup>. The ferrocene/ferrocium (Fc/Fc<sup>+</sup>) was used as the internal standard.

All PffBZ-based polymers show minimal red-shifted absorption  $\lambda_{max}s$  and  $\lambda_{onset}s$  from solution to thin film, and it indicates their aggregated forms in solution if combination with their structured absorption profiles.<sup>25,50</sup> To further investigate the aggregation of these polymers, temperature-dependent absorption spectra of their diluted *o*-DCB solutions were characterized at various temperatures from 30 °C to 100 °C (Fig. S11). Based on how their absorption evolves, the polymers are gradually disaggregated as the temperature increases, as revealed by the disappearance of absorption shoulders and greatly blue-shifted absorption  $\lambda_{max}s$  at elevated temperatures. The benzoxadiazole-based PffBX-3 shows the strongest aggregation behavior among PffBX-3, PffBT-3, and PffBSe-3, as indicated by its less red-shifted  $\lambda_{max}$  at 100 °C (Fig. S11b), while the benzoselenadiazole-based PffBSe-3 exhibits the weakest aggregation. The PffBSe-3 is almost completely disaggregated at 100 °C (as revealed by the disappearance of the absorption shoulder (Fig. S11f). As the heteroatoms vary

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 from O to S and to Se, the aggregation gradually decreases, which maybe is correlated with the slightly increased size of the chalcogen atom and the increased backbone torsion. Among all PffBZ-based polymers, the aggregation of PffBX-2, PffBT-2, and PffBSe-2 will decrease by moving the branching position closer to the polymer backbone as steric hindrance increases, because all branching positions are on the 2<sup>nd</sup> position in these three polymers.

 Table 1. Molecular weights, optical, and electrochemical properties of the PffBZ-based polymer semiconductors.

Polymer	M <sub>n</sub>	$PDI^{a}$	T <sub>d</sub>	$\lambda_{ m max}$	$\lambda_{ m max}$	$\lambda_{\mathrm{onset}}$	E <sub>HOMO</sub>	$E_{\rm LUMO}$	$E_{\rm g}^{\rm opt}$
	(kDa) <sup>a</sup>		$[\ {}^{\mathbf{C}}]^b$	(nm <sup>c</sup>	$(nm)^d$	$(nm)^d$	$(eV)^e$	(eV) <sup>f</sup>	$(eV)^g$
PffBX-2	10.8	1.31	345	777	771	850	-5.41	-3.95	1.46
PffBX-3	15.6	1.50	357	788	775	852	-5.42	-3.96	1.46
PffBT-2	23.3	1.46	354	767	765	847	-5.20	-3.74	1.46
PffBT-3	35.5	1.63	377	748	759	842	-5.20	-3.74	1.47
PffBSe-2	16.0	1.73	356	664	826	912	-5.13	-3.77	1.36
PffBSe-3	17.2	1.56	368	799	820	923	-5.14	-3.80	1.34

<sup>*a*</sup>GPC vs. polystyrene standards, 1,2,4-trichlorobenzene as the eluent measured at 150 °C. <sup>*b*</sup>Decomposition temperature defined as the temperature with 5% weight loss. <sup>*c*</sup>From solution absorption (1 × 10<sup>-5</sup> M in *o*-DCB). <sup>*d*</sup>From absorption of polymer film casted from *o*-DCB solution. <sup>*e*</sup>E<sub>HOMO</sub> =  $-(E_{ox}^{onset} + 4.80)$  eV,  $E_{ox}^{onset}$  determined electrochemically using Fc/Fc<sup>+</sup> internal standard. <sup>*f*</sup>E<sub>LUMO</sub> =  $E_{HOMO} + E_{g}^{opt}$ . <sup>*g*</sup>Derived from absorption onset of as-casted film using the equation:  $E_{g}^{opt} = 1240/\lambda_{onset}$  (eV).

## Electrochemical properties of the polymer

The electrochemical properties of PffBZ-based polymers were characterized by using cyclic voltammetry (CV) with the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an internal standard. As shown in Fig. 3c, all polymers exhibit obvious oxidation peaks, and the HOMO energy levels  $(E_{\text{HOMOS}})$  of the polymer was determined by using the equation:  $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.80)$  eV,<sup>51,52</sup> and the derived  $E_{\text{HOMOS}}$  for PffBX-3, PffBT-3, and PffBSe-3 were -5.42, -5.20, and

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-5.14 eV, respectively (Table 1). The LUMO energy levels ( $E_{LUMOS}$ ) was -3.96,  $^{OQ}3.743$ ,  $^{SO}4.73$ ,  $^{OQ}4.73$ ,

#### Thermal properties of the polymer

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out under  $N_2$  atmosphere to study the thermal properties of PffBZ-based polymers. The curves of DSC and TGA for the polymers are shown in Fig. S12 and S13, respectively, and the relevant data are compiled in Table 1. The decomposition temperatures with 5% weight loss were above 340 °C for all these PffBZ-based polymers, suggesting their good thermal stability for device fabrication and optimization. According to DSC curves (Fig. S12), the PffBT-based polymers show thermal transition at higher temperatures than the PffBX and PffBSe-based polymers, which possibly indicates the increased film crystallinity of the PffBT-based polymers. Polymer PffBT-3 exhibits the highest crystallinity as revealed by the sharpest transition peak. Therefore, the film crystallinity can be increased by moving branching points away from the polymer backbone, which should be attributed to the reduced

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steric hindrance between the adjacent bulky side chains. The charge carrier mobilities online Onterior Difference on the other of the control of the control



**Fig. 4** Transfer and output characteristics of (a, d) PffBX-2; (b, e) PffBX-3; (c, f) PffBT-2; (g, j) PffBT-3; (h, k) PffBSe-2, and (i, l) PffBSe-3-based OTFT devices fabricated under the optimal condition.

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## Organic thin-film transistor performance of the polymers

The charge transport properties of all these PffBZ-based polymer semiconductors were investigated by fabricating OTFTs with a top-gate/bottom-contact (TG/BC) device architecture, in which an amorphous fluoropolymer poly(perfuorobutenylvinyl ether) (CYTOP) was used as dielectric layer. The parameters of OTFT performance are shown in Table 2 and the representative OTFT transfer and output curves are shown in Fig. 4. During the device optimization, it was found that the PffBX-2, PffBX-3, PffBT-2, PffBT-3, PffBSe-2, and PffBSe-3 showed the optimal performance with maximum hole mobility ( $\mu_h$ ) of 0.14, 0.084, 0.55, 0.69,<sup>20</sup> 0.12, and 0.28 cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup>, respectively if o-DCB was used as the processing solvent under thermal annealing at 250 °C. Polymer PffBX-3 exhibited a lower  $\mu_{\rm h}$ and higher threshold voltage  $(V_T)$  than analogue PffBT-3, which could be attributed to the low-lying  $E_{HOMO}$  of PffBX-based polymer and a larger hole injection barrier thus generated. PffBSe-3 showed a lower  $\mu_h$  than PffBT-3, possibly because of its more twisted polymer backbone and decreased film crystallinity. Polymer PffBT-3 exhibited the highest  $\mu_h$  among all PffBZ-based polymers, which was attributed to its high crystallinity and excellent film morphology (vide infra). For the best-performing polymer PffBT-3-based OTFTs, off-center spin-coating (OCSC) method was utilized to improve polymer chain alignment,<sup>54,55</sup> and the OTFTs show a further increased  $\mu_h$  to 1.58 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (Fig. S14).

 Table 2. Device performance parameters of TG/BC OTFTs containing PffBZ-based polymers

 as the active layer under the optimal device fabrication conditions.

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-	Polymer	Tannealing	$\mu_{ m lin}$	$\mu_{ m sat}$	$V_{\mathrm{t}}$	$I_{\rm on}/I_{\rm offDOI}$	View Article Online 10.1039/D0NJ01006E
		[℃]	$[\mathrm{cm}^2 \mathrm{V}^{-1}\mathrm{s}^{-1}]^a$	$[\text{cm}^2 \text{ V}^{-1}\text{s}^{-1}]^a$	[V]		
-	PffBX-2	250	0.07 (0.05)	0.14 (0.11)	-50	10 <sup>5</sup>	
	PffBX-3	250	0.046(0.024)	0.084(0.044)	-56	$10^{4}$	
	PffBT-2	250	0.19 (0.16)	0.55 (0.37)	-27	10 <sup>6</sup>	
	PffBT-3 <sup>b</sup>	250	0.36 (0.32)	0.69 (0.53)	-19	$10^{4}$	
	PffBT-3 <sup>c</sup>	200	0.66 (0.52)	1.58 (1.15)	-20	10 <sup>3</sup>	
	PffBSe-2	250	0.069(0.057)	0.12(0.086)	-31	$10^{5}$	
	PffBSe-3	250	0.13 (0.09)	0.28 (0.21)	-28	$10^{5}$	

<sup>*a*</sup> Maximum mobility with average value from at least 5 devices shown in parentheses. <sup>*b*</sup> Data is taken from polymer P3 in the literature.<sup>20</sup> <sup>*c*</sup> Device fabricated using the off-center spin-coating method.

#### Photovoltaic characteristics of polymer solar cells.

Inverted BHJ PSCs with a device architecture of ITO/ZnO/polymer:PC71BM/MoO3/Ag were firstly fabricated to investigate the photovoltaic performance of all these PffBZ-based polymers. In order to fully optimize the PSC performance, we systematically changed the polymer:PC<sub>71</sub>BM ratios, active layer thicknesses, and processing additives of the blend films. The performance parameters under various fabrication conditions are summarized in Table 3 and S2-S4, and the current-voltage (J-V) curves are presented in Fig. 5a. During the device optimization, it was found that the PSCs with a polymer:  $PC_{71}BM$  ratio of 1:1.5 typically showed improved performance and that the PSC performance could be further improved by insertion thin of layer а poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) between the active layer and the ZnO electron transporting layer. The J-V characteristics of the optimized PSCs under simulated air mass (AM) 1.5G illumination (100 mW cm<sup>-2</sup>) are shown in Fig. 5a with relevant performance parameters collected in Table 3,

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and the external quantum efficiency (EQE) spectra of the optimal cells are illustrated in Fig. 5b.

Polymer PffBX-3 exhibited a PCE of 2.44% with a  $J_{sc}$  of 6.65 mA cm<sup>-2</sup>, a  $V_{oc}$  of 0.75V and a FF of 48.9%. The optical absorption of PffBX-3 approaches 854 nm, which indicates that a high  $J_{sc}$  maybe could be attained in PSCs. However, PffBX-3 showed excessive aggregation at both 30 °C and 100 °C (Fig. S11b), leading to poor blend film morphology revealed by atomic force microscopy (AFM) and transmission electron microscopy (TEM) imaging, which was not favorable to achieve efficient charge transport and collection in the related devices, as well as to induce to low  $J_{sc}$ . For the polymer PffBT-3, it was found that both  $J_{sc}$  and PCE were drastically improved by adding 1,8-octanedithiol (ODT) additive, as a result of increasing film crystallinity as revealed by grazing incidence X-ray diffraction (GIXD) and AFM imaging. PffBT-3 exhibited a higher PCE of 10.12% with a remarkable  $J_{sc}$ of 21.46 mA cm<sup>-2</sup>, a  $V_{oc}$  of 0.67 V, and a large fill factor (FF) of 70.9%. The performance of polymer PffBT-3 is improved probably because the film morphology is better than that in previous report.<sup>20</sup> To our best knowledge, the  $J_{sc}$  and PCE are among the highest value for fullerene-based PSCs with a bandgap < 1.50 eV. A small  $V_{oc}$  of 0.55 V and a low  $J_{sc}$  of 13.03 mA cm<sup>-2</sup> with a PCE of 3.65% is obtained for polymer PffBSe-3, the low  $J_{sc}$  is likely to be attributed to the low charge carrier mobility and poor morphology. The PffBX-2 showed better solubility than PffBX-3, leading to proper blend film morphology, hence making the  $J_{sc}$ and PCE in PSCs higher than that of PffBX-3. The PffBT-2 and PffBSe-2 exhibited a  $J_{sc}$  of 20.01 and 13.30 mA cm<sup>-2</sup>, respectively, similar to that of PffBT-3 and PffBSe-3. However, the *FFs* were significantly reduced by a big margin (> 10%) probably because of the low charge

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carrier mobility and poor blend film morphology. As a result, the PCE was decreased to 7.42%<sup>1006E</sup> and 2.32% for the PffBT-2 and PffBSe-2-based PSCs, respectively.

**Table 3.** Device performance parameters of BHJ PSCs fabricated under the optimalconditions.The solar cells feature an inverted structure ofITO/ZnO/polymer:PC71BM(1:1.5)/MoO3/Ag and 3% (volume) of 1,8-octanedithiol (ODT) isused as the processing additive.

Polymer	$\mu_{ m h,SCLC}$	$\mu_{e, SCLC}$	Thickness	$V_{oc}$	$J_{ m sc}$	FF	PCE <sup><i>a</i></sup>
	$[\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}]$	$[cm^2V^{-1} s^{-1}]$	[nm]	[V]	$[mA cm^{-2}]$	[%]	[%]
PffBX-2	$7.70 \times 10^{-5}$	$1.08 \times 10^{-3}$	129	0.74	13.03	57.1	5.47 (5.42)
PffBX-3	$3.52\times 10^{4}$	1.36 ×10 <sup>-3</sup>	151	0.75	6.65	48.9	2.44 (2.23)
PffBT-2	$9.93 \times 10^{\text{-5}}$	$7.85\times10^{4}$	181	0.65	20.01	57.2	7.42 (7.28)
PffBT-3	$2.68 \times 10^{-3}$	$8.64 \times 10^{-4}$	210	0.67	21.46	70.9	10.12 (9.81)
PffBSe-2	$4.45\ \times 10^{\text{-5}}$	$6.88 \times 10^{-4}$	138	0.53	13.30	33.3	2.32 (2.11)
PffBSe-3	$2.63 \times 10^{-5}$	$1.28 \times 10^{-4}$	117	0.55	13.57	49.3	3.65(3.41)

<sup>*a*</sup> Data represent the best performing device with the average PCEs from > 15 devices shown in parentheses.

In terms of performance parameters, the PffBT-based polymer semiconductors showed  $V_{oc}$ s of 0.66-0.67 V, indicating the minimum effects of branch point of side chains on the  $V_{oc}$ s. The PffBX-based PSCs showed the largest  $V_{oc}$ s of 0.74-0.75 V, which verified its lowest-lying  $E_{HOMO}$  in the polymer series. The PffBT-based polymers showed larger  $V_{oc}$  of (0.65-0.67 V) than that (0.53-0.55 V) of PffBSe-based polymers. The  $V_{oc}$ s of PffBX-based PSCs were well consistent with the  $E_{HOMO}$  of these polymer donors. In term of device performance, the chalcogen atom exerted a great influence on the  $V_{oc}$ s and PCEs of the PffBZ-based polymers. The branch point of alkyl side chain had a strong influence on the morphology and mobility (space charge limited current), thus making PCEs in PSCs different.



View Article Online DOI: 10.1039/D0NJ01006E



**Fig. 5** (a) J-V curves and (b) EQE spectra of PffBZ-based polymer solar cells fabricated under the optimized condition.

The EQE spectra (Fig. 5b) reveal that PffBT-3 exhibited higher EQE values than PffBX-3 and PffBSe-3, with the highest EQE value of nearly 75%, indicating that this polymer had a high  $J_{sc}$  in PSCs. The PffBX and PffBT-based polymers showed broad photo-response from 300 to 850 nm, but the PffBSe-based polymers exhibited an EQE spectrum with a longer wavelength of 950 nm in the EQE curve. These results were in good consistency with the optical absorption spectra of these polymers. The integral  $J_{sc}$  deduced from the EQE spectra was well matched with that obtained from the J-V measurements with a mismatch < 5%, indicating its good reliability of PSC performance.

#### Charge carrier mobilities in blend polymer films.

Charge carrier mobilities of the polymer:PC<sub>71</sub>BM blend films were characterized by using the space charge limited current (SCLC) method<sup>56</sup> with a device structure of ITO/PEDOT:PSS/Polymer:PC<sub>71</sub>BM/MoO<sub>3</sub>/Ag and ITO/ZnO/Polymer:PC<sub>71</sub>BM/Ca/Al for

hole-only and electron-only device, respectively (see Table 3, Fig. S15 and S16). The defived outcode hole-only and electron-only device, respectively (see Table 3, Fig. S15 and S16). The defived outcode SCLC hole mobility ( $\mu_{h,sclc}$ ) was 7.70 × 10<sup>-5</sup>, 3.52×10<sup>-4</sup>, 9.93 × 10<sup>-5</sup>, 2.68 × 10<sup>-3</sup>, 4.45 × 10<sup>-5</sup>, and 2.63 × 10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (Table 2) for PffBX-2, PffBX-3, PffBT-2, PffBT-3, PffBSe-2, and PffBSe-3-based blend films, respectively. Among all blend films, the  $\mu_{h,sclc}$  of PffBT-3:PC<sub>71</sub>BM blend was the highest. The SCLC electron mobility ( $\mu_{e,sclc}$ : 8.64 ×10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) of PffBT-3 blend was slightly lower than that of PffBX-3 (1.36 × 10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), but it was greater than that of other polymer blends, possibly because PffBX-based polymers showed the lowest  $E_{LUMO}$  among the PffBZ-based polymers. The high SCLC mobility of PffBT-3:PC<sub>71</sub>BM blend was benefitted to the highest  $J_{sc}$  among PffBX-based PSCs. The PffBSe-3:PC<sub>71</sub>BM blend showed the lowest  $\mu_{h,sclc}/\mu_{e,sclc}$  of (2.63 × 10<sup>-5</sup>/1.28 × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), which prohibited the transport and collection of charge carrier, hence leading to low  $J_{sc}$  in PSCs.



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**Fig. 6** AFM phase images and TEM images of the active layers (a, g) PffBX-2:PC<sub>71</sub>BM, (b, f)<sup>View Article Online PffBX-3:PC<sub>71</sub>BM, (c, i) PffBT-2:PC<sub>71</sub>BM, (d, j) PffBT-3:PC<sub>71</sub>BM, (e, k) PffBSe-2:PC<sub>71</sub>BM, and (f, l) PffBSe-3:PC<sub>71</sub>BM. The films are prepared by using the optimal conditions for PSCs (3vol% ODT).</sup>

#### Film morphologies and their correlations with device performance

AFM and transmission electron microscopy (TEM) were used to investigate the surface and bulk morphologies of the polymer:PC<sub>71</sub>BM blend films (Fig. 6, S17, and S18). The root mean square (RMS) roughness of all these polymers:PC71BM blend films increased after it is added with ODT addition (Fig. S18), and the RMS roughness of PffBX-2:PC71BM, PffBX-3:PC71BM, PffBT-2:PC<sub>71</sub>BM, PffBT-3:PC<sub>71</sub>BM, PffBSe-2:PC<sub>71</sub>BM, and PffBSe-3:PC<sub>71</sub>BM blend films was increased to 22.67, 21.28, 19.38, 11.67, 4.53, and 9.88 nm, respectively, indicating that the film crystallinity of the blend films was increased by adding ODT addition.<sup>20,57</sup> It can be seen from Fig. 6 and Fig. S18 that PffBT-3:PC<sub>71</sub>BM blend film exhibited a smoother surface with a lower RMS roughness than PffBT-2:PC<sub>71</sub>BM blends. The low RMS roughness of PffBT-3:PC71BM blend film is beneficial to exciton dissociation at the polymer:PC<sub>71</sub>BM interface and charge transport. Consequently, the polymer PffBT-3 showed a higher J<sub>sc</sub> and FF than PffBT-2. The RMS roughness of PffBSe-2:PC<sub>71</sub>BM and PffBSe-3:PC<sub>71</sub>BM blend films is the lowest among the PffBZ-based polymers:PC<sub>71</sub>BM blend film, which was likely to be attributed to their low crystalline and good solubility. After ODT was added, the phase separation at nanoscale with interpenetrating network clearly occurred in TEM images of PffBZ-based polymers:PC71BM blend film, which enabled these

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polymers:PC<sub>71</sub>BM-based devices have higher PCEs in PSCs than polymers:PC<sub>71</sub>BM without being added with ODT (see Fig. 6, Fig. S17 and Table S4). Among all PffBZ-based polymers, the TEM images of PffBX-3:PC<sub>71</sub>BM, PffBSe-2:PC<sub>71</sub>BM, and PffBSe-3:PC<sub>71</sub>BM suggested that some PC<sub>71</sub>BM-rich domains were formed. The domains formed in the polymers:PC<sub>71</sub>BM blend films were detrimental to exciton diffusion and separation, thus leading to low  $J_{sc}$  values. The PffBT-3:PC<sub>71</sub>BM blend film showed the longest nanoscale fibril among PffBZ-based polymers, which probably enhanced mixing, efficient exciton and charge transport between PffBT-3 and PC<sub>71</sub>BM, thus leading to high  $J_{sc}$  in PSCs.



Fig. 7 2D–GIXD images of pure film (annealing at 250 °C) and blend film.

The interchain packing structure of PffBX-based polymers in pure and blend films were analyzed by 2D–GIXD. X-ray diffraction pattern and the corresponding linecut profiles are depicted in Fig.7 and S19, and the relevant data are summarized in Table S5. For the pure film, GIXD diffractograms of PffBX-2 exhibited remarkably strong lamellar diffraction reaching to the (300) peak with a *d*-spacing of 1.75 nm both in-plane (IP) and out of plane

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(OOP) orientation. A obvious  $\pi - \pi$  stacking peak was seen in OOP direction, and the  $\pi - \pi$ stacking located at 1.62  $A^{-1}$  give a stacking distance of 0.39 nm, indicating the high crystallinity of PffBX-2 film. A weak  $\pi$ - $\pi$  stacking peak was also seen in IP direction, indicating the coexistence of edge-on crystalline orientation. This edge-on backbone orientation was benefitted from charge transport in transistor devices. The crystal coherence length (CCL) calculated from in-plane (IP) and OOP direction were 21.0 and 11.4 nm, respectively (Table S9). The pure PffBX-3 film showed obvious lamellar diffractions reaching to the (300) peak at the IP direction and the (100) peak at the OOP direction with a longer d-spacing of 1.85 nm versus to the d-spacing (1.75 nm) of PffBX-2 film, which suggested that the bulky 2-propylheptan-1-oloxy chain on TRTOR unit led to an increase in interchain distance of PffBX-based polymers. A similar phenomenon could also be seen among PffBT and PffBSe-based polymers. The pure PffBX-3 film showed a face-on dominant orientation with a  $\pi$ - $\pi$  stacking distances of  $\sim 0.39$  nm, and had a long crystal size (24.6 nm) at the IP direction, which was of disadvantage to charge transport at the edge-on orientation in transistor devices. The PffBT-based polymer films showed a different microstructure from PffBX-based polymers. The pure PffBT-2 and PffBT-3 films showed remarkably strong lamellar diffractions reaching to the (300) peak with the *d*-spacing of 1.75 and 1.80 nm, respectively. Both the PffBT-based polymer films exhibited stronger  $\pi^{-\pi}$ stacking peaks in OOP direction than PffBX-based polymer films, and the  $\pi^{-\pi}$  stacking located at 1.57-1.59 Å<sup>-1</sup> displayed a stacking distances of  $\sim$ 0.40 nm. The PffBSe-based polymer films had the strong lamellar diffractions progressing up (300) peaks with large

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crystal size (17-19 nm) at the OOP direction, which indicated the high crystallinity of PffBSe-based polymer films.

All the PffBZ-based blend films showed similar diffractions as in pure film. The PffBX:PC<sub>71</sub>BM-based blend film exhibited obvious diffraction at the (100) and (200) peaks, leading to high crystallinity of PffBX:PC71BM-based blend films. Both PffBX-2:PC71BM and PffBX-3:PC<sub>71</sub>BM blend films exhibited obvious  $\pi$ - $\pi$  stacking peak in OOP direction, indicating a face-on orientation. The crystal coherence length (CCL) calculated from IP direction is about 21.7-24.0 nm possibly because of increased interchain interaction and strong aggregation of PffBX-based polymers. The PffBT:PC71BM-based blend films had a distinct diffraction peak among these polymers, and the PffBT-3:PC<sub>71</sub>BM blend film showed the strongest  $\pi$ - $\pi$  stacking at the OOP direction among the PffBZ-based blend films, the  $\pi$ - $\pi$ stacking peak located at 1.59  $\text{\AA}^{-1}$  (corresponding to a stacking distance of 0.39 nm), the diffraction pattern indicated that the PffBT-3 in blend film took an edge-on crystalline orientation, which was beneficial to charge transport and result in high  $J_{sc}$  and FF in PSCs.<sup>58,59</sup> causing polymer PffBT-3 to demonstrate high performance in PSCs. PffBSe:PC<sub>71</sub>BM-based blend film did not show obvious  $\pi$ - $\pi$  stacking peak at the OOP and IP direction, which indicated that these two polymers:PC71BM blend films showed poor crystallinity, and thus obtained low performance in PSCs.

## Conclusion

In conclusion, a series of narrow bandgaps (1.33–1.47 eV) PffBZ-based polymers incorporating TRTOR as the electron donor units and ffBZs as the electron acceptor units

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synthesized and characterized. The five new copolymers were compared compared computationally and experimentally with the previously reported copolymer PffBT-3. As the chalcogen atomic size in ffBZs increased, the HOMOs of copolymers were raised and accompanied by better solubility. By comparing different chalcogen atom containing PffBZ-based PSC devices, a decreased trend in  $V_{oc}$  was found to be accompanied by the increase in heteroatom size of chalcogen atom. Although the  $V_{oc}$  decreased, high-performing PSCs were obtained with PCEs of 2.44 %, 10.12%, and 3.65% for PffBX-3, PffBT-3, and PffBSe-3, respectively. The PCEs of PffBT-3 was the highest among polymer semiconductors containing a head-to-head linkage and polymer semiconductors with  $E_{g}^{opt}$ smaller than 1.50 eV. The optical and electrochemical properties were very similar for PffBZ-based polymers with different branch position chain, but the morphologies of the polymer:PC<sub>71</sub>BM blend films were very different, resulting in different PCEs in PSCs. The high planarity backbone of TRTOR causes the polymers PffBX-2, PffBX-3, PffBT-2, PffBT-3, PffBSe-2, and PffBSe-3 to exhibit hole mobilities of 0.14, 0.084, 0.55 1.58, 0.12, and 0.21 cm<sup>2</sup> V<sup>-1</sup>s<sup>-1</sup> in the OTFT devices, respectively. The correlations between structure, property and device performance in this work offer useful insights for constructing ffBZ-based polymer semiconductors in organic electronics.

#### **Conflict of Interest**

The authors declare no conflict of interest.

## Acknowledgements

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This work was financially supported by the National Natural Science Foundation of the Strike Online

(No. 21676054), Fundamental Research Funds for the Central Universities (No. 2242018K40041), Scientific Research Foundation of Graduate School of Southeast University (No. 3207049713).

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Colour graphic (size:  $4 \text{ cm} \times 7.53 \text{ cm}$ )

A series of difluorobenzochalcogenadiazole-bithiophene copolymers are developed

for high-performance organic semiconductors.