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Two-dimensionalbenzo[1,2-b:4,5-b']difuran-based wide bandgapconjugated polymers for efficient fullerene-free polymer solar cells

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Abstract

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Wide bandgap conjugated polymers are important to provide complementary absorption with the state-of-the-art narrow bandgap nonfullerene electron acceptor to reach the maximum utilization of the solar photons. In this work, two wide bandgap two-dimensional conjugated polymers PBDFT-Bz and PBDFF-Bz based on benzo[1,2b:4,5-b']difuran building block were designed and synthesized. The optical bandgaps of PBDFT-Bz and PBDFF-Bz were found to be 1.90 eV and 1.85 eV, respectively. PBDFF-Bz with 2-ethylhexylfuranyl side chains possesses the lower HOMO energy level, and the denser π - π stacking than that of PBDFT-Bz with 2-ethylhexylthienyl side chains. The fullerene-free PBDFF-Bz:ITIC-based polymer solar cell (PSC) showed a PCE of 9.46% with a J_{sc} of 15.02 mA/cm², a V_{oc} of 0.94 V and a FF of 67%; while the PCE would be further improved to 10.28% with an enhanced J_{sc} of 16.57 mA/cm², a V_{oc} of 0.94 V and a FF of 66% by using m-ITIC as electron acceptor. Under the same condition, PBDFT-Bz:m-ITIC device gave a PCE of 9.84% with a J_{sc} of 16.63 mA/cm^2 , a V_{oc} of 0.85 V and a FF of 70%. In addition, it is exciting that PBDFF-Bz based devices show the small energy loss (E_{loss}) of 0.63 eV, while PBDFT-Bz based devices have the E_{loss} of 0.72 eV. These results are among the best fullerene-free devices with the BDF-based polymers and demonstrate that the BDF is a very promising candidate for the highly efficient polymer solar cells.

Introduction

Polymer solar cells (PSCs) have achieved the significant advancements in the past decade.¹⁻⁴ The power conversion efficiencies (PCEs) have underwent a rapid increment to over 13% for binary PSCs⁵ and exceeded over 14% for ternary PSCs⁶ with the rapid developments of new materials and continuous innovations of the device engineering. Especially, the design of new materials plays the decisive role in pursuing higher PCEs for PSCs. Among the new emerged materials, the success of non-fullerene acceptors in PSCs in recent years have provided the great opportunity to pursue the promising photovoltaic performances for the practical applications. Currently, the PCEs of the fullerene-free PSCs havereachedover 13%, which is comparable or even higher than its PC71BM-based counterparts.^{5, 7} Up to date, various non-fullerene acceptors, such as NDI-, PDI- and IDT-based small molecules or polymers, have been designed and developed for PSCs with the impressive device performances.^{8, 9} However, compared with the boomings of the efficient non-fullerene acceptors, the highly efficient donor polymers are mainly limited to such as PTB7,¹⁰ PTB7-Th,¹¹ PBDT-TS1¹² and PffBT4T-2OD,¹³ etc. Furthermore, the current high performance nonfullerene acceptors are mostly from the A-D-A type small molecules, such as ITIC, m-ITIC and IEIC, with the narrow bandgaps of ~ 1.50 eV and the main absorption bands of 600– 800 nm, which have a large overlap in absorption range with the above highly efficient donor polymers. It is well known that an ideal active layer containing the donor and acceptor blend should possess the complementary absorption so as to reach the

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maximum utilization of the solar photons. For instance, the ITIC or m-ITIC acceptors with absorption at longer wavelength region will require the wide bandgap donor polymer with a strong absorption at the shorter wavelength region to avoid the interference upon absorbing sunlight. Therefore, in pursuing the highly efficient fullerene-free PSCs, the developments of the wide bandgap polymer donors have become one of the most important strategies and are also highly demanded to harvest the solar photons efficiently. For examples, Yan et al. reported that the wide bandgap copolymer PffT2-FTAZ-2DT with a band-gap of 1.91 eVshowed the good complementary absorption with IEIC and provided a PCE of 7.3%.¹⁴ Li and Zhang et al. have also synthesized a series of wide bandgap copolymers based on BDT and difluorobenzotriazole (Bz), i.e. PBDTT-Bz (J52),¹⁵ J60,¹⁵ J61,¹⁵ J71,¹⁶ J91¹⁷ etc with the bandgaps of $\sim 1.8-2.0$ eV, and exhibited the PCEs of up to 11% with ITIC or m-ITIC as the electron acceptors.

Benzo[1,2-b:4,5-b']difuran (BDF), a furan-based derivative, has recently received considerable attention in the developments of conjugated polymers for PSCs. Compared with BDT unit, the furan-based BDF possesses the advantages of i) more planar structure as the smaller oxygen size of furan unit;¹⁸ ii) the lower highest occupied molecular orbital (HOMO) energy level as the strong elecronegativity of oxygen atom;¹⁹ iii) the denser π - π stacking behavior.²⁰ In addition, the furan unit is also available from the biorenewable sources with the low cost.^{21, 22} However, the current BDF-based polymers for PSCs in either the availabilities of the numbers of polymers

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or the device performances still largely lag behind the BDT-based counterparts.^{DQ: 101039/C7TA10976H} examples, Beaujuge et al. developed the one-dimensional (1D) BDF-based polymer PBDFTPD with a best PCE of 7.4%.²³ Sun et al. designed and synthesized a twodimensional (2D) BDF polymer PBDF-T1, which showed a promising PCE of 9.43%.²⁴

To further nourish BDF-based polymers for PSCs, herein, we designed and synthesized two wide bandgap 2D polymers PBDFT-Bz and PBDFF-Bz (Fig. 1) with 4,8-bis-(5-(2'-ethylhexylthien-2-yl))benzodifuran (BDFT) and 4,8-bis-(5-(2'ethylhexylfuran-2-yl)benzodifuran(BDFF) as the donor unit, respectively, and fluorobenzotriazole (Bz) as the acceptor unit. The optical bandgaps of PBDFT-Bz and PBDFF-Bz were measured to be 1.90 eV and 1.85 eV, respectively. Also, we found that PBDFF-Bz possesses the lower HOMO energy level and stronger $\pi - \pi$ stacking than that of PBDFT-Bz. The photovoltaic performances of both polymers were investigated in the fullerene-free PSCs with ITIC or m-ITIC as the electron acceptors. The fullerene-free PSCs based on PBDFT-Bz:m-ITIC showed a PCE of 9.84% with a high J_{sc} of 16.63 mA/cm², a V_{oc} of 0.85 V and a FF of 70%. With the advantageous properties of PBDFF-Bz, the PCE of fullerene-free PSC based on PBDFF-Bz;m-ITIC was further improved to 10.28% with a J_{sc} of 16.57 mA/cm², a V_{oc} of as high as 0.94 V and a FF of 66%, which is very competitive with the BDT-based counterparts. The energy losses of PBDFT-Bz and PBDFF-Bz-based devices were 0.72 eV and 0.63 eV, respectively. The optimized PBDFF-Bz-based device is among the best devices with a V_{oc} of over 0.9 V and the PCE of more than 10%. The results demonstrate that the BDF-

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based polymers are the very promising candidates for the highly efficient polymer solar

cells.



Fig. 1.The chemical structures of PBDFT-Bz, PBDFF-Bz, non-fullerene small molecule acceptors ITIC and m-ITIC.

Discussion

Synthesis

The synthetic routes of monomers and polymers are depicted in Scheme 1. The BDFT and BDFF were synthesized by the common method from 2-(2'ethylhexyl)thiophene and 2-(2'-ethylhexyl)furan, respectively.²⁵⁻²⁷ The procedure for synthesizing the distannyl monomers 2,6-bis(trimethylstannane)-4,8bis(5-(2ethylhexyl)thiophene)benzo[1,2-b:4,5-b']difuran (BDFT-T) and 2,6-bis (trimethylstannane)-4,8-bis(5-(2-ethylhexyl)furan)benzo[1,2-b:4,5-b']difuran (BDFF-T) were displayed in the experimental section. The monomer 4,7-bis(5-bromothiophen-2-yl)-5,6-difluoro-2-(2-hexyldecyl)-4,5-dihydro-2H-benzo [d][1,2,3]triazole(Bz-Br) was prepared by following the literature procedure.¹⁵ Finally, PBDFT-Bz and PBDFF-Bz were synthesized via Palladium-catalyzed Stille polycondensation of BDFT-T or BDFF-T with Bz-Br. The obtained polymers were precipitated in methanol and then purified by soxhlet extraction to remove the impurities and oligomers. Both polymers

could be easily dissolved into chloroform, chlorobenzene and dichlorobenzene at room View Article Online Disport And Control C

temperature, which makes them to be facile for the solution process. The molecular weights of polymers were measured using gel permeation chromatography (GPC) with polystyrene as standard and 1,2,4-trichlorobenzene as eluent at 180 °C. The number average molecular weights (M_n) of polymers are 30.2 kDa and 27.5 kDa for PBDFT-Bz and PBDFF-Bz, respectively, with polydispersity indexes (PDIs) of 1.85 and 2.45 (Table 1). Thermogravimetric analysis shows that both polymers present good thermal stability with a 5% weight-loss temperature at around 385°C under N₂ atmosphere (Fig. S1).



Scheme 1. Synthetic routes of monomers and polymers.

Optical properties

The UV–vis absorption spectra of PBDFT-Bz, PBDFF-Bz, ITIC and m-ITIC in film states are displayed in Fig. 2a and the absorption spectra of PBDFT-Bz and PBDFF-Bz in chlorobenzene solution are shown in Fig. S2. As displayed in Fig. 2a, it

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can be seen that PBDFT-Bz and PBDFF-Bz show similar absorption profile with the strong intramolecular charge transfer (ICT) between BDF and Bz units at longer wavelength. The well-defined 0-1 and 0-0 absorption peaks of PBDFT-Bz are observed at 558 nm and 605 nm, whereas the two absorption peaks of PBDFF-Bz redshift to 566 nm and 612 nm, respectively. The slight bathochromicshift in PBDFF-Bz film is mainly ascribed to the better coplanarity of BDFF unit than that of BDFT unit in PBDFT-Bz, which is because of the smaller torsion angle of alkylfurylside chain to BDF backbone for BDFF than that of alkylthienyl side chain to BDF backbone for BDFT. The above phenomenon has also been proved by DFT calculations (Fig.S3) and other BDF-based copolymers.²⁸ PBDFT-Bz and PBDFF-Bz in film states show absorption edges at 651 nm and 671 nm, respectively, which correspond to the optical bandgaps of 1.90eV and 1.85eV, which match well with the non-fullerene small molecular acceptor ITIC or m-ITIC (~1.50 eV) as discussed above. Fig. 2a also shows the absorption spectra of ITIC and m-ITIC, and it could be found that the absorption of PBDFT-Bz and PBDFF-Bz present well complementation with that of ITIC or m-ITIC, which cover the most solar photons from 400 to 800 nm and will be more favorable to enhance the J_{sc} of PSCs.



Fig.2. a) UV-vis spectra of PBDFT-Bz, PBDFF-Bz, ITIC and m-ITIC in film states; b) Energy levels diagram of PBDFT-Bz, PBDFF-Bz, ITIC and m-ITIC.

Polymer	Mn (KDa)	PDI	Td (°C)	λ (fil 0-1	max m) 0-0	Abs (onset) (nm)	Eg ^{opt} (eV) (film)	HOMO (eV) ^a	LUMO (eV) ^a	Eg ^{cv} (eV) (film)
PBDFT-Bz	30.2	1.85	395	558	607	651	1.90	-5.35	-3.29	2.06
PBDFF-Bz	27.5	2.45	383	569	612	671	1.85	-5.48	-3.48	2.00

Table 1.Molecular weights and physicochemical properties of PBDFT-Bz and PBDFF-Bz

^aCalculated from cyclic voltammetry

Electrochemical properties

To investigate the electrochemical properties of both polymers, cyclicvoltammetry (CV) was performed to determine the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels. The CV curves of two polymers are shown in Fig.S4. The HOMO and LUMO energy levels are estimated according to equation $E_{HOMO} = -e(V_{ox} + 4.8 - V_{ferro})$ and $E_{LUMO} = -e(V_{red} + 4.8 - V_{ferro})$,²⁹ respectively, where V_{ox} and V_{red} are the onset of oxidation and reduction potentials of polymers in film states versus Ag/AgCl, and V_{ferro} is the deviation potential of FeCp2. Therefore, the HOMO and LUMO energy levels are calculated to be -5.35 eV and -3.29 eV for PBDFT-Bz, and the HOMO and LUMO energy levels of PBDFF-Bz downshift to -5.48 eV and -3.48 eV, respectively, as the result of the strong

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elecronegativity of the alkyfuryl side chain. The HOMO energy levels of both PBDFT-Bz and PBDFF-Tz are ca. 0.14-0.27 eV lower than their BDT counterpart PBDTT-Bz (J52) (E_{HOMO}=-5.21 eV).¹⁵ It is well known that the open-circuit voltage of PSCs is directly dependent on the HOMO energy level of the donor when fabricating PSCs using the same acceptor. Therefore, the lower-lying HOMO energy levels of PBDFT-Bz and PBDFF-Bz than that of PBDTT-Bz (J52) will be expected to acquire higher V_{oc} in PSCs. Fig. 2b shows the energy levels diagram of PBDFT-Bz, PBDFF-Bz, ITIC and m-ITIC. As shown in Fig. 2b, the LUMO energy offsets between two polymers and ITIC/m-ITIC are $\sim 0.34-0.57$ eV, which could be enough to provide the driving force for efficient excition dissociation.³⁰ It is interesting that the HOMO energy offsets between two polymers and ITIC/m-ITIC are found to be only ~0.04-0.19 eV, which is usually thought not to be enough for exciton dissociation in the fullerene-based PSCs. However, recent studies have showed that the smaller or even approximate zero HOMO energy offsets in the fullerene-free PSCs are still able to facilitate the exciton dissociation efficiently.³¹⁻³⁵ Most importantly, as dispalyed in the photoluminescence (PL) spectra (Fig. S5), for the neat polymer films, they show broad and strong emission in the range of 550-850 nm when they were excited at 550 nm. However, the emission of polymer:m-ITIC blend films were totally quenched, indicating the effective electron transfer from PBDFF-Bz or PBDFT-Bz to the m-ITIC.



Fig.3. a) J-V curves and b) EQE spectra of devices based on polymer/acceptor (ITIC or m-ITIC)(1:1.5, w/w); c) the plots of E_{loss} against V_{oc}; d) the plots of PCE against E_{loss}.

Photovoltaic properties

The photovoltaic performances of PBDFT-Bz and PBDFF-Bz were investigated with the conventional architecture of ITO/PEDOT:PSS/polymer:ITIC or m-ITIC/PFN/Al. The optimized donor:acceptor (D:A) weight ratio was 1:1.5 with the polymer concentration of 10mg/mL in chlorobenzene. The detailed device fabrication was listed in the supporting information.

The current density–voltage (J–V) curves of the PSCs under the illumination of AM1.5G, 100 mW/cm² are shown in Fig. 3a. The corresponding photovoltaic performance are summarized in Table 2. It can be seen that the device based on PBDFT-

Bz and ITIC (1:1.5, w:w) obtained a PCE of 9.26% with a V_{oc} of 0.85 V, a J_{sc} of 15.36 mA/cm² and a FF of 70 %, which is much higher than the PCE of 5.18% for its BDT counterpart PBDTT-Bz (J52):ITICbased device under its best condition.¹⁵ As displayed in Table 2, the obvious advantage of PBDFT-Bz:ITIC based device is its high V_{oc} than that of PBDTT-Bz (J52):ITIC based device, which is due to the low E_{HOMO} value of PBDFT-Bz. In addition, the E_{HOMO} of PBDFF-Bz is much lower than that of PBDTT-Bz (J52), therefore it can be found that the V_{oc} of PBDFF-Bz:ITIC based device further improved to0.94V. The PCE of PBDFF-Bz:ITIC device reaches to 9.46% with a J_{sc} of 15.02 mA/cm² and a FF of 67%.

Table 2. Photovoltaic parameters of polymers/acceptor measured under the illumination of simulated AM 1.5G conditions (100 mW/cm²).

D:A	V _{oc} (V)	$J_{\rm sc}$ (mA/cm ²)	FF (%)	PCE (%)	E _{loss} (eV)	J _{sc} (mA/cm ²) (integrated)	Ref
PBDFT-Bz:ITIC	0.85	15.56	70	9.26 (9.08) ^a	0.72	15.41	This work
PBDFT-Bz:m-ITIC	0.85	16.63	70	9.84(9.62) ^a	0.72	15.97	This work
PBDFF-Bz:ITIC	0.94	15.02	67	9.46(9.28) ^a	0.63	14.76	This work
PBDFF-Bz:m-ITIC	0.94	16.57	66	10.28(10.02) ^a	0.63	15.81	This work
PBDTT-Bz(J52):ITIC	0.73	13.11	59	5.18	0.84	12.48	[13]
PBDTT-Bz(J52):m-ITIC	0.70	17.16	50	5.98	0.87	16.33	[14]

^athe average value from 20 devices.

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It has demonstrated that m-ITIC, the analogue acceptor of ITIC, possessed higher film absorption coefficient, larger crystalline coherence and higher charge carrier mobility,³⁶ which was expected to contribute to a higher J_{sc} so as to win a higher PCE for PSCs. As expected, PBDFT-Bz:m-ITIC based device fabricated under the same condition as the best device based on PBDFT-Bz:ITIC, exhibited a better PCE of 9.84%

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with an enhanced J_{sc} of 16.63 mA/cm² and a V_{oc} of 0.85 V and a FF of 70%. More excitingly, a very promising PCE of as high as 10.28% with an improved J_{sc} of 16.57 mA/cm², a V_{oc} of 0.94 Vand a FF of 66% was achieved for PBDFF-Bz:m-ITIC based devices. It is notable that the significant improvements on the m-ITIC based devices, were mainly resulted from the increased J_{sc} compared to that of ITIC-based devices, which was in consistent with the physicochemical properties of m-ITIC. It is also noted that the performances of ITIC- and m-ITIC-based devices for both polymers are significant higher than that of their BDT counterpart PBDTT-Bz (J52) (Table 2), which indicates that polymers based on BDF and difluorobenzotriazole possess more potential for application in fabricating highly efficient PSCs.

External quantum efficiencies (EQEs) curves of ITIC- and m-ITIC-based devices for both polymers under best condition are shown in Fig. 3b. As shown in Fig. 3b, owing to the complementary absorption of polymer donor (PBDFT-Bz or PBDFF-Bz) with acceptor (ITIC or m-ITIC), the broad EQE spectra from 300 to 800 nm could be clearly observed with the maximum value of 67.25-75.53%, which demonstrates highly efficient photon harvesting and charge collection in the active layers. Meanwhile, the broad and strong EQEs spectra of all devices indicate polymer donors and acceptor in each device both make contributions to the overall current. Especially, the EQE value of more than 60% between 550 nm and 750nm demonstrates that the exction are effectively dissociated between the interfaces, even though there is a smaller HOMO energy offset between polymer donors and acceptors. The calculated J_{se} s by integrating

View Article Online the EQE curve with an AM 1.5 G reference spectrum are 15.41 and 15.97mA/cm² for PBDFT-Bz:ITIC and PBDFT-Bz:m-ITIC based devices, respectively. Whereas the calculated J_{scs} are obtained to be 14.76 and 15.81mA/cm² for PBDFF-Bz:ITIC and PBDFF-Bz:m-ITIC-based devices, respectively. The calculated and observed higher $J_{\rm sc}$ s in m-ITIC devices are contributed to the higher film absorption coefficient and higher charge carrier mobility of m-ITIC than that of ITIC. It is also noted that PBDFF-Bz devices with either ITIC or m-ITIC acceptors possess a slightly lower J_{sc} than that of PBDFT-Bz, which is partly ascribed to the lower hole mobility of PBDFF-Bz based devices. The hole mobility was measured using space charge limited current (SCLC) method with a hole-only diode architecture of ITO/PEDOT:PSS/active layer/MoO_x/Ag. The result exhibited a hole mobility (μ_h) of 0.85×10⁻⁴ cm²V⁻¹s⁻¹ for PBDFF-Bz:m-ITIC based device, while PBDFT-Bz:m-ITIC based device gave a higher μ_h of $2.26 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (Fig. S6).

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It is well known that there is a trade-off between J_{sc} and V_{oc} in pursing higher PCEs, and minimizing the photon energy loss (E_{loss}) is one of the critical issues to further improve the photovoltaic performance of PSCs. The E_{loss} is defined as $E_{loss} = E_g$ – eV_{oc} ,³⁷ and is usually greater than 0.7 eV in PSCs.³⁸ Fig. 3c and 3d showed the E_{loss} against V_{oc} and PCE against E_{loss} from the reported BDT (or BDF)-alt-Bz based devices in comparison with PBDFT-Bz and PBDFF-Bz based devices with either ITIC or m-ITIC as the acceptors. And the corresponding data were summarized in Table S1.The E_{loss} of PBDFT-Bz device is calculated to be 0.72 eV, while PBDFF-Bz device has the

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 E_{loss} of 0.63 eV. More excitingly, as seen fromFig. 3c and 3d, it can be found that PBDFF-Bz based device is among the best devices with the high V_{oc} of over 0.9 V and the PCE of more than 10% with smaller E_{loss} . The result demonstrates that the side engineering through alkylfuryl side chain replacing alkylthienyl side chain did provide a facile strategy to decrease E_{loss} for fabricating highly efficient polymer solar cells.



Fig.4.AFM height images (a, d), AFM phase images (b, e) and TEM images (c, f) of PBDFT-

Bz:m-ITIC or PBDFF-Bz:m-ITIC blend films.

The morphologies of PBDFT-Bz:m-ITIC and PBDFF-Bz:m-ITIC blend films were investigated by the tapping-mode atomic force microscopy (AFM)and the transmission electron microscopy (TEM). The AFM and TEM images of the blend filmsare shown in Fig.4. As shown inFig. 4a and 4b, the blend film of PBDFT-Bz:m-ITIC presents an uniform and smooth surface with a root-mean-square (RMS) roughness of 1.68 nm. While a relatively coarse surface with RMS roughness of 2.32 nm is found for PBDFF-Bz:m-ITIC blend film, indicating that the PBDFF-Bz and m-ITIC possess relatively worse miscibility in comparison with that of PBDFT-Bz and mITIC, which should be due to the relatively denser stacking behavior of PBDFF-Bz than ^{View Article Online} that of PBDFT-Bz (Fig.S7). The TEM images (Fig. 4c,f) of PBDFT-Bz:m-ITIC and PBDFFTBz:m-ITIC blend films show similar well-distributed interpenetrated nanofibrillar structures, which are beneficial for achieving high J_{sc} and FF,^{39, 40} which

is in line well with the results of J-V measurement.

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Fig. 5. 2D GIWAXS patterns and profiles of active layers based on PBDFT-Bz:m-ITIC (a,c) and

PBDFF-Bz:m-ITIC (b,d) prepared under optimal condition.

The intermoleular orientations and nanostructural orders of the polymer:m-ITIC blend films were investigated by grazing incident wide-angle X-ray scattering (GIWAXS). Fig.5 shows the 2D GIWAXS patterns (a, b) and corresponding 1D cuts (c, d) along in-plane and out-of-plane direction of PBDFT-Bz:m-ITIC (a, c) and

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PBDFF-Bz:m-ITIC (b, d) blend films. As displayed in Fig. 5, the blend films of rcratosymetric PBDFT-Bz:m-ITIC and PBDFF-Bz:m-ITIC present the identical 2D GIWAXS patterns $and profiles, in which the stronger diffraction peaks for <math>\pi$ - π stacking at q = 1.89 Å⁻¹(d=3.32 Å) and 1.87 Å⁻¹(d=3.36 Å) in the out-of-plane were observed for PBDFT-Bz:m-ITIC and PBDFF-Bz:m-ITIC blend films, respectively. Besides, four lamellar peaks at q (0.31~1.45 Å⁻¹) were also found in the out-of-plane for PBDFT-Bz:m-ITIC and PBDFF-Bz:m-ITIC blend films. It can find that both polymer:m-ITIC blend films show the very similar intermolecular orientations and nanostructural orders with the preferred face-on orientation. Even though both PBDFT-Bz:m-ITIC and PBDFF-Bz:m-ITIC-based films exhibited the strong crystallinity and π - π stacking, the PBDFT-Bz:m-ITIC-based film had a smaller π - π stacking distance of 3.32Å than that of the PBDFF-Bz:m-ITIC (3.36 Å), which may be in consistent with the observed higher hole mobility of the PBDFT-Bz:m-ITIC-based film.

Conclusion

In summary, we have designed and synthesized two novel wide bandgap 2D polymers PBDFT-Bz and PBDFF-Bz with 4,8-bis-(5-(2'-ethylhexylthien-2-yl)) benzodifuran and 4,8-bis-(5-(2'-ethylhexylfuran-2-yl)benzodifuran as the donor units, respectively. The optical and electrochemical properties of both polymers were investigated, and it is found that PBDFF-Bz possesses the slightly red-shifted absorption and the lower HOMO energy level. The XRD and GIWAXS measurements were also used to study the polymer chains packing behaviors. The fullerene-free PSCs

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of both polymers with ITIC or m-ITIC as the electron acceptors were fabricated to investigate the photovoltaic performances. The fullerene-free PSCs based on PBDFT-BZ:ITIC or m-ITIC showed a PCE of 9.26% and 9.84%, respectively, with a V_{oc} of 0.85V, the J_{sc} of 15.56 and 16.63 mA/cm², and a FF of 70%. The PCE of PBDFF-Bz:ITIC-based device was found to be 9.46%, however, the PCE of PBDFF-Bz:m-ITIC was further improved to 10.28% with a J_{sc} of 16.57 mA/cm², a V_{oc} of as high as 0.94 V and a FF of 66% as the result of the stronger absorption and better charge carrier mobility of m-ITIC than that of ITIC. These promising photovoltaic performances are very competitive with their BDT counterpart PBDTT-Bz (J52). The results demonstrate that the furan-based BDF polymers would be very promising polymers for PSCs with the rational molecular designs.

Experimental section

Materials

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Compound Bz-Br was synthesized from the literature method.⁴¹ ITIC and m-ITIC were purchased from 1-Materials Inc and used without further purification. Other chemicals were used directly unless otherwise indicated.

Synthesis of BDFT: To a solution of compound 1 (1.73 g, 8.8 mmol) in dry THF (20 mL) in ice bath, n-BuLi (11.0 mmol, 4.4 mL, 2.5M in hexane) was slowly added within 10mins. After the mixture was kept at 0°C for 2 h, the mixture was removed to room temperature and stirred 1h. The compound 3 (0.60 g, 3.20 mmol) in THF (10mL) was added in one portion into the above mixture. After the mixture was stirred at room

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temperature for 2h, SnCl₂-2H₂O (6.0g) solution was added in one portion. After the mixture was stirred at room temperature for 1h, the mixture was poured into water and extracted with 3×30 mL hexane. The organic phase was washed with water and dried over Na₂SO₄. After removing solvent, the crude product was purified via column chromatography with petroleum ether as eluent. Finally, the product was dried under vacuum to obtain a pale yellow oil (1.44 g, 82.4% yield). ¹H-NMR (400 MHz, CDCl₃, δ /ppm):7.78 (d, *J* = 2.8 Hz, 2H), 7.68 (d, *J* = 3.2 Hz, 2H), 7.37 (d, *J* = 2.8 Hz, 2H), 6.90 (d, *J* = 3.2 Hz, 2H), 1.68 (m, 2H), 1.34 (m, 16H), 0.91 (t, *J* = 6.8 Hz, 12H).

Synthesis of BDFF: To a solution of compound 1 (2.63 g, 14.61 mmol) in dry THF (25 mL) in an ice bath, n-BuLi (18.26 mmol, 7.3 mL, 2.5M in hexane)was slowly added within 10mins. After the mixture was kept at 0°C for 2 h, the mixture was removed to room temperature and stirred for 1h. The compound 3(1.00 g, 5.31 mmol) in THF (10mL) was added in one portion into the above mixture. After the mixture was stirred at room temperature for 2h, SnCl₂-2H₂O (9.96g, 3.30mL ConcHCl/13.28mL H₂O) solution was added in one portion. After the mixture was stirred at room temperature for 1h, the mixture was poured into water and extracted with 3×30 mL hexane. The organic phase was washed with water and dried over Na₂SO₄. After removing solvent, the crude product was purified via column chromatography with petroleum ether as eluent. Finally, the product was dried under vacuum to obtain a pale yellow oil (1.37 g, 85.6% yield). ¹H-NMR (400 MHz, CDCl₃, δ /ppm):7.80 (d, *J* = 2.0 Hz, 2H), 7.57 (d, *J*

 $= 2.0 \text{ Hz}, 2\text{H}), 7.27 \text{ (d, } J = 3.2 \text{ Hz}, 2\text{H}), 6.27 \text{ (d, } J = 3.2 \text{ Hz}, 2\text{H}), 2.79 \text{ (d, } J = \overset{\text{DOI:30}}{4.8} \overset{\text{View Article Online}}{\text{Hz}}, 4\text{H}), 1.81 \text{ (m, 2H)}, 1.38 \text{ (m, 16H)}, 0.92 \text{ (t, } J = 7.2 \text{ Hz}, 12\text{H}).$

Synthesis of BDFT-T: To a solution of compound 5 (1.04 g, 1.89 mmol) in dry THF (15 mL) at -78 °C was added n-BuLi (5.68 mmol, 2.27 mL, 2.5M in hexane). After the mixture was kept at -78 °C for 1 h, trimethyltin chloride (5.68 mmol, 5.68 mL, 1M in hexane) was added. Then the solution was stirred at room temperature overnight. The mixture was extracted with 3×30 mL hexane after pouring into water. The organic phase was washed with water and dried over Na₂SO₄. After removing solvent, the crude product was recrystallized in ethanol and dried under vacuum to obtain a pale yellow solid (1.00 g, 61.2% yield). ¹H-NMR (400 MHz, CDCl₃, δ /ppm): 7.76 (s, 2H), 7.34 (d, J = 3.2 Hz, 2H), 6.88 (d, J = 3.2 Hz, 2H), 2.84 (d, J = 3.6 Hz, 4H), 1.68 (m, 2H), 1.34 (m, 16H), 0.91 (t, J = 6.8 Hz, 12H), 0.49 (s, 18H). ¹³C-NMR(CDCl₃, ppm): 154.51, 146.80, 142.51, 140.66, 135.62, 131.17, 118.00, 117.30, 112.29, 40.26, 39.93, 32.04, 28.69, 25.26, 22.99, 14.11, 10.78.

Synthesis of BDFF-T:To a solution of compound 4 (0.80 g, 1.55 mmol) in dry THF (15 mL) at -78 °C was added n-BuLi (4.66 mmol, 1.86 mL, 2.5M in hexane). After the mixture was kept at -78 °C for 1 h, trimethyltin chloride (4.66 mmol, 4.66 mL, 1M in hexane) was added. Then the solution was stirred at room temperature overnight. The mixture was extracted with 3×30 mL hexane after pouring into water. The organic phase was washed with water and dried over Na₂SO₄. After removing solvent, the crude product was recrystallized in ethanol and dried under vacuum to obtain a pale yellow

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solid (0.86 g, 64.9% yield). ¹H-NMR (400 MHz, CDCl₃, δ/ppm): 7.71 (s, 2H), ^{DCls10.1039/C7TA10976H} J = 3.2 Hz, 2H), 6.27 (d, J = 3.2 Hz, 2H), 2.79 (d, J = 3.6 Hz, 4H), 1.81 (m, 2H), 1.36 (m, 16H), 0.92 (t, J = 6.8 Hz, 12H), 0.50 (s, 18H). ¹³C-NMR(CDCl₃, ppm): 166.12, 152.18, 144.49, 135.34, 127.04, 125.54, 123.32, 117.80, 108.45, 41.46, 34.12, 32.46, 29.73, 28.96, 25.60, 23.09, 14.24, 10.94.

Synthesisof PBDFF-Bz: BDFF-T (210 mg, 0.250 mmol) and Bz-Br (175 mg, 0.250 mmol) were charged into a 25 mL round bottom flask with a condenser under N_2 protection. After degassed twice, dry chlorobenzene (8 mL), Pd₂(dba)₃ (5 mg) and P(o tol_{3} (10 mg) were added into the flask consequently. The resulting mixture was further degassed twice, then heated to 135 °C for 48 h. The reaction was end-capped with 1.00 mmol of 2-bromothiophene and 1.05 mmol of 2-tributylstannylthiophene in order. The mixture was poured into methanol and the precipitate was collected. Then the mixture was dissolved in chloroform (100 mL) and got a flash silica column with chloroform as eluent. A majority of the solvent was removed under pressure and the residue, which was about 8-10 mL, was deposited into acetone (100 mL). The crude product was purified by soxhlet extraction with hexane and chloroform for 12h in order. The chloroform fraction was precipitated in methanol (100 mL). Finally, the pure polymer was collected by filtration, dried under vacuum at 50 °C overnight and obtained as brown solid (232.8 mg, 88.5% yield). M_n=27.5 kDa; M_w=67.4 kDa; PDI=2.45.¹H-NMR (400 MHz, CDCl₃, δ/ppm):8.00-7.70 (m, 4H), 7.24-7.20 (m, 4H), 6.24 (m, 2H), 4.74 (m, 2H), 2.80-2.27 (m, 5H), 1.42-1.30 (br, 42H), 0.92-0.87 (br, 18H).

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Synthesis of PBDFT-Bz: PBDFT-Bz was synthesized following the similar procedure^{DOI:10:10:1039/C7TA10976H} with PBDFF-Bz. Finally, PBDFT-Bzwas obtained as a brown solid (246.1 mg, 90.8% yield). GPC (THF): M_n=30.2 kDa; M_w=55.9 kDa; PDI=1.85.¹H-NMR (400 MHz, CDCl₃, δ/ppm):8.02-7.69 (m, 4H), 7.42-7.20 (m, 4H), 7.15-6.80 (m, 2H), 4.74 (m, 2H), 2.80-2.31(m, 5H), 1.69-1.30(br, 42H), 0.91-0.76 (br, 18H).

Supporting Information

Electronic supplementary information (ESI) available: Characterization methods, the detailed device fabrications, thermogravimetric analysis, DFT calculations, the absorption of PBDFT-Bz and PBDFF-Bz in solution, CV curves, the photoluminescence spectra, SCLC curves.

Conflicts of interest

There are no conflicts to declare.

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