

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

*Yueyue Gao,^{a,c,#} Zhen Wang,^{b,#} Jianqi Zhang,^b Hong Zhang,^a Kun Lu^{*b} Fengyun Guo,^a
YulinYang,^c Liancheng Zhao,^a Zhixiang Wei^b and Yong Zhang^{*a}*

^aSchool of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001,
China

*Email - yongzhang@hit.edu.cn

^bCAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology,
Beijing 100190, China

*Email - lvk@nanoctr.cn

^cSchool of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin
150001, China

[#]These authors contributed equally to this work.

1. Experimental Section

1.1. Characterization method

UV-vis spectra was studied via Beijing Purkinje General-TU-1901 spectrophotometer. ^1H -NMR spectra was collected on a Bruker AV 400 spectrometer operating at 400 MHz in deuterated chloroform solution with TMS as reference. Cyclic voltammetry was conducted in acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate with a scan rate of 100 mV/s. The polymer film (casted atop ITO), Ag/AgCl and Pt mesh were used as working electrode, reference electrode and counter electrode, respectively. Gel permeation chromatography (GPC) measurements was performed on Agilent PL-GPC 220 instrument with high temperature chromatograph, using 1,2,4-trichlorobenzene as the eluent at 180 °C. Thermogravimetric analysis (TGA) was carried out by a Q600 Simultaneous TG-DSC instrument under N_2 with a heating rate of 20 °C/min. The X-ray diffraction (XRD) was performed at room temperature with a D8 DISCOVER spectrometer using a general area detector. Atomic force microscopy (AFM) images were obtained using a NanoMan VS microscope in the tapping mode. Transmission electron microscopy (TEM) images of the polymer:m-ITIC blend films were recorded using a JEOL JEM-1400 transmission electron microscope operated at 120 keV. Grazing incidence wide-angle X-ray scattering (GIWAXS) experiments were conducted at XEUSS SAXS/WAXS system at the National Center for Nanoscience and Technology (NCNST, Beijing). Samples were prepared on PEDOT:PSS modified ITO glasses, and then exposed to X-ray beam (wavelength 1.54 Å) in a 0.2° incident angle for 12 hours.

1.2. Device fabrication and characterization

Polymer solar cells were fabricated with the structure of ITO/PEDOT:PSS/polymer:ITIC or m-ITIC/PFN/Al. The patterned ITO glass substrates (15Ω/sq) were successively cleaned with detergent, deionized water, ethanol and isopropyl alcohol, subsequently stored in isopropyl alcohol before use. PEDOT:PSS (Heraeus Clevis P VP A 4083) was spin cast from aqueous

solution at 4000 rpm for 40 s (40 nm), then dried at 150 °C for 15 min in air. When fabricating NF-PSCs, a solution of polymer:ITIC or m-ITIC mixture in chlorobenzene (CB) (the concentration of 10 mg/mL for polymer) was spun coated at 2000 rpm for 30 s at the top of PEDOT:PSS layer to form the active layer. Following, the concentration of 0.2 mg/mL PFN solution in methanol was spun cast at 2500 rpm for 35 s at the top of active layer to form the cathode interfacial layer. Finally, an aluminum layer (100 nm) were deposited atop the cathode interfacial layer at the vacuum condition of 3×10^{-6} Pa by thermal evaporation method. The active area of the devices was 0.04 cm². Current density-voltage ($J-V$) characteristics were measured using a Keithley 2400 Source Measure Unit. Solar cell performance used an Air Mass 1.5 Global (AM 1.5 G) solar simulator (Class AAA solar simulator, Model 94063A, Oriel) with an irradiation intensity of 100 mW/cm², which was measured by a calibrated silicon solar cell and a readout meter (Model 91150V, Newport). EQEs spectra was measured by using a QEX10 Solar Cell EQE measurement system (PV measurements, Inc). The light intensity was calibrated to 100 mW/cm² using a calibrated silicon solar cell with a KG5 filter, which has been previously standardized as the National Renewable. Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere of N₂ dry glovebox.

Hole-only diode was fabricated using the architecture of ITO/PEDOT:PSS/active layer/MoO_x/Ag. Mobilities were extracted by fitting the current density-voltage ($J-V$) curves using space charge limited current (SCLC) method. The $J-V$ curves of the devices were plotted as $\log J$ versus V using the equation $J = 9 \epsilon_0 \epsilon_r \mu_h V^2 / 8L^3$ for holes, where J was the current density, L was the film thickness of active layer, μ_h was the hole mobility, ϵ_r was the relative dielectric constant of the transport medium, ϵ_0 was the permittivity of free space (8.85×10^{-12} Fm⁻¹), V is the internal voltage in the device and $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} was the applied voltage to the device and V_{bi} was the built-in voltage due to the relative work function difference of the two electrodes.

2. Thermal properties

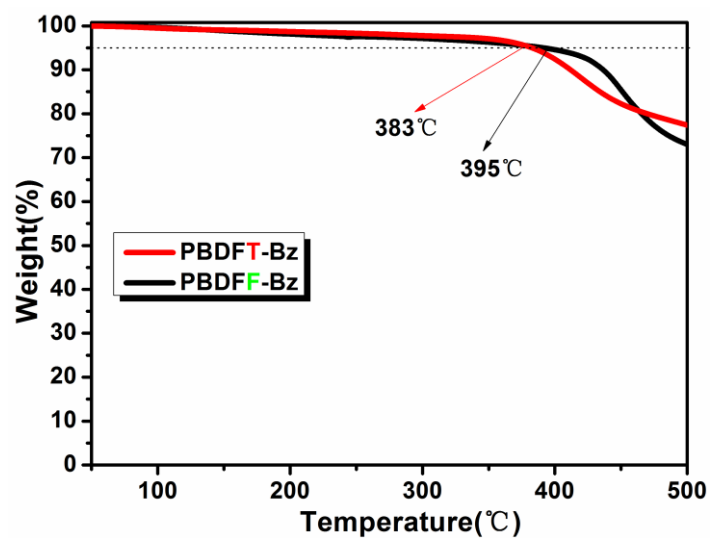


Fig.S1. Thermogravimetric analysis of PBDFT-Bz and PBDFE-Bz.

3. Optical properties

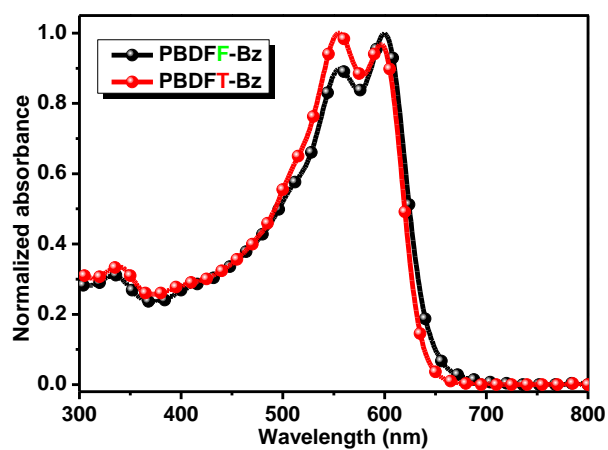


Fig.S2. UV-vis spectra of PBDFT-Bz and PBDFE-Bz in chlorobenzene solution

4. DFT calculation

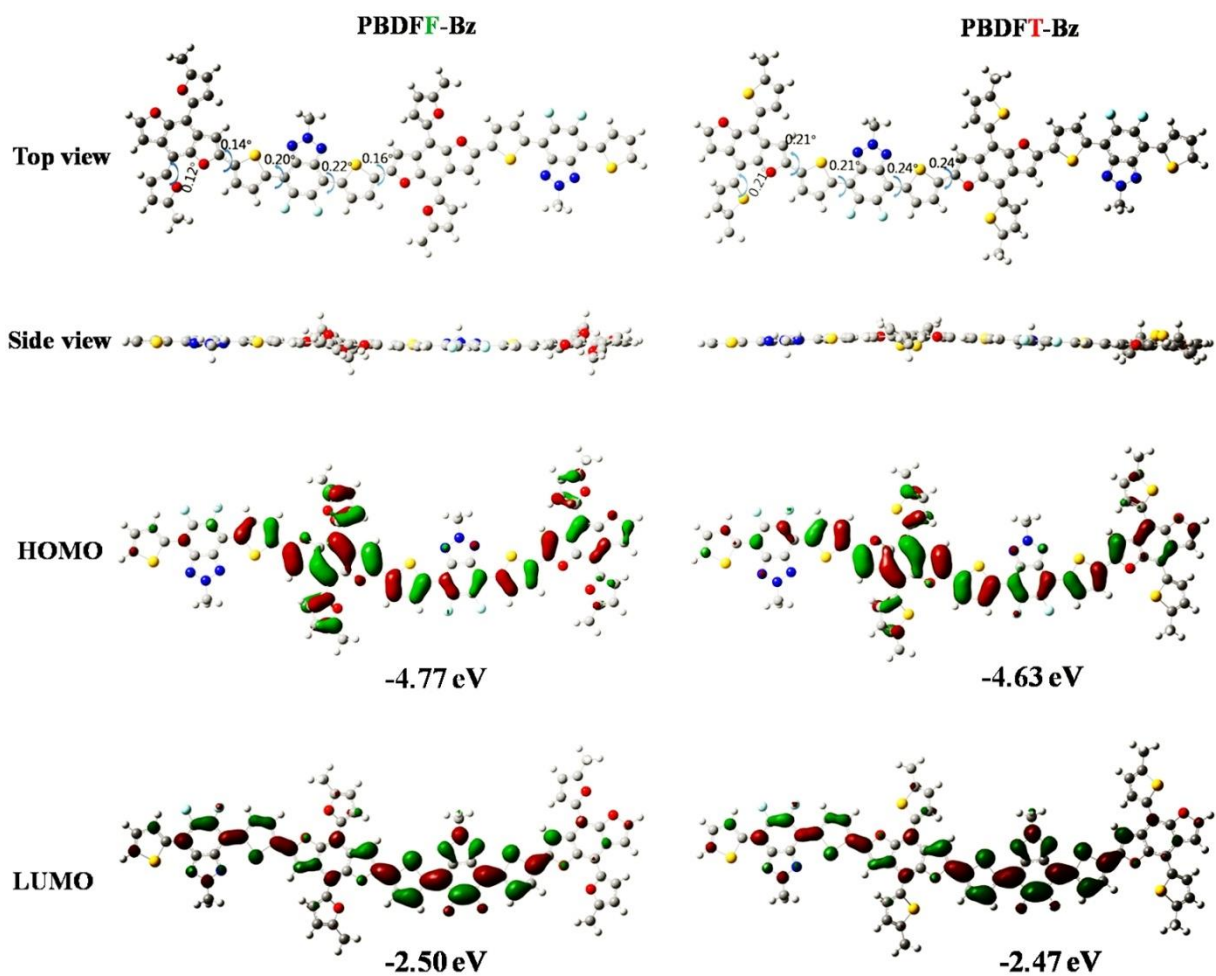
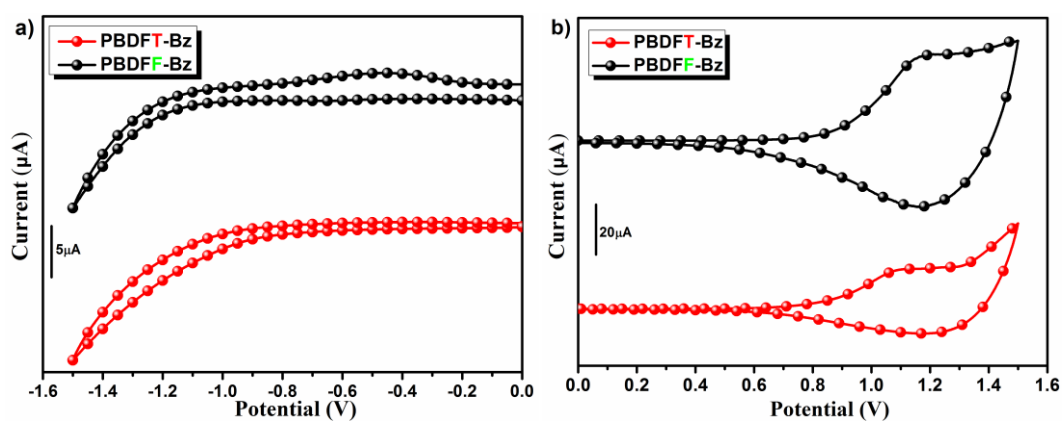


Fig.S3. Optimized geometries and HOMO and LUMO electron density distributions of PBDFE-Bz and PBDFE-Bz by DFT with the B3LYP/6-31G* basis set.

5. Electrochemical properties



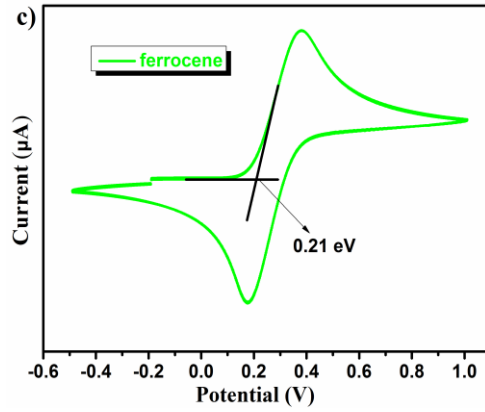


Fig.S4. The CV profiles of PBDFT-Bz and PBDFF-Bz. a) the potentials of reduction; b) the potentials of oxidation; c) the CV profiles of ferrocene in acetonitrile solution

6. Photoluminescence characteristics

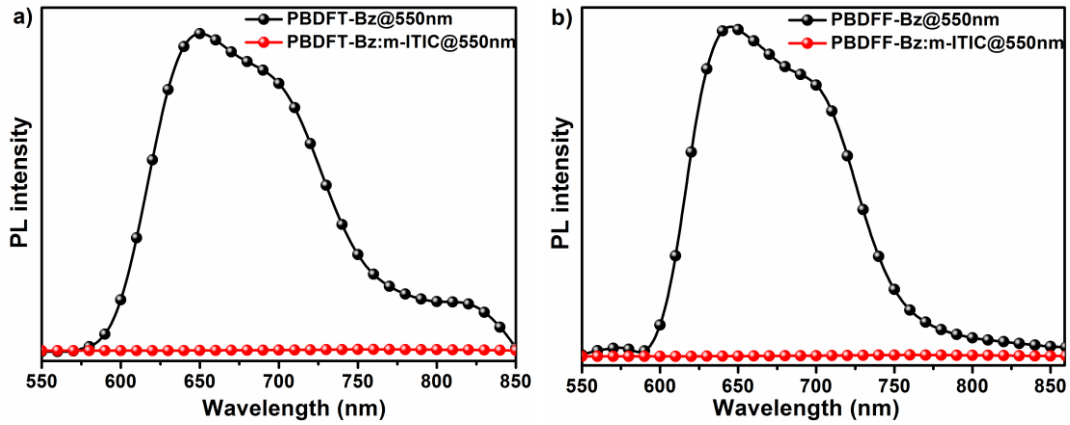


Fig.S5. The PL spectra of a) PBDFT-Bz and PBDFT-Bz/m-ITIC blend; b) PBDFF-Bz and PBDFF-Bz/m-ITIC blend (excited at 550 nm)

7. Hole mobilities

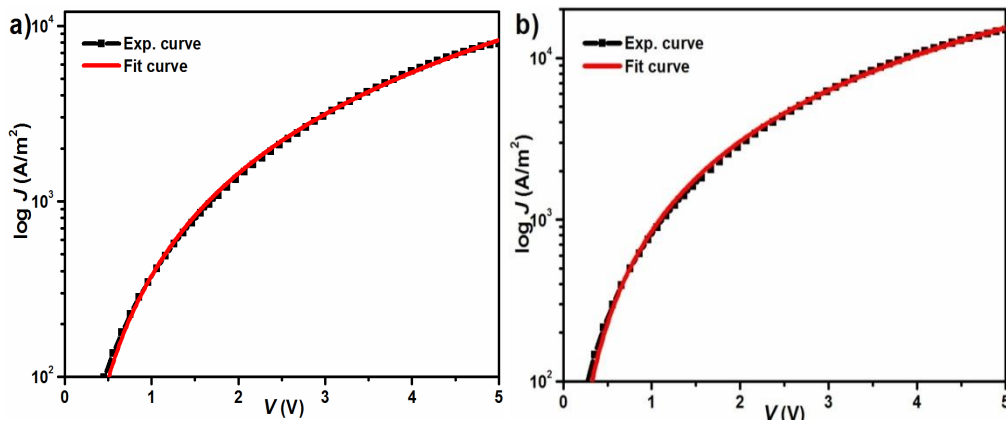


Fig.S6. The $\log J$ - V characteristics of hole-only diodes based on PBDFT-Bz (a) and PBDFF-Bz (b).

Table S1. The photovoltaic parameters and E_{loss} of polymer solar cells based on BDT (or BDF) and benzotriazole.

D:A	$E_g(D)$ (eV)	$E_g(A)$ (eV)	V_{oc} (V)	E_{loss} (eV)	PCE (%)	Ref
PBDTDTBTz:PC ₇₀ BM	1.95	2.00	0.61	1.34	1.70	[1]
PBDTBTz:PC ₇₀ BM	2.00	2.00	0.61	1.39	1.40	[1]
PBnDT-HTAZ:PC ₆₀ BM	1.98	2.00	0.70	1.28	4.36	[2]
PBnDT-FTAZ:PC ₆₀ BM	2.00	2.00	0.79	1.21	7.10	[2]
PBDT-HBTA:PC ₇₀ BM	1.88	2.00	0.58	1.30	2.43	[3]
PBDT-FBTA:PC ₇₀ BM	1.91	2.00	0.75	1.16	6.00	[3]
PBDTFBZO:PC ₇₀ BM	1.83	2.00	0.91	0.92	6.25	[4]
PBDTFBZS:PC ₇₀ BM	1.81	2.00	0.88	0.93	7.74	[4]
PTIPSBDT-DFDTBTz:PC ₇₀ BM	2.00	2.00	0.89	1.11	2.92	[5]
P1:PC ₆₀ BM	1.73	2.00	0.93	0.80	1.58	[6]
P2:PC ₆₀ BM	1.74	2.00	0.95	0.79	6.12	[6]
PBDTT-BTAZT-1:PC ₇₀ BM	1.65	2.00	0.75	0.90	6.64	[7]
PBDTT-BTAZT-2:PC ₇₀ BM	1.62	2.00	0.75	0.87	5.96	[7]
J52:ITIC	1.86	1.57	0.74	0.83	5.18	[8]
J60:ITIC	2.22	1.57	0.91	0.66	8.97	[8]
J61:ITIC	2.29	1.57	0.89	0.68	9.53	[8]
J71:ITIC	1.96	1.57	0.94	0.63	11.43	[9]
J81:m-ITIC	1.93	1.57	0.96	0.61	11.05	[10]
J91:m-ITIC	2.00	1.57	0.97	0.60	11.63	[11]
PSBZ:ITIC	1.93	1.57	0.89	0.68	10.5	[12]
PBDFT-Bz:m-ITIC	1.90	1.57	0.85	0.72	9.84	this work
PBDFF-Bz:m-ITIC	1.85	1.57	0.94	0.63	10.28	this work

8. X-ray diffraction (XRD)

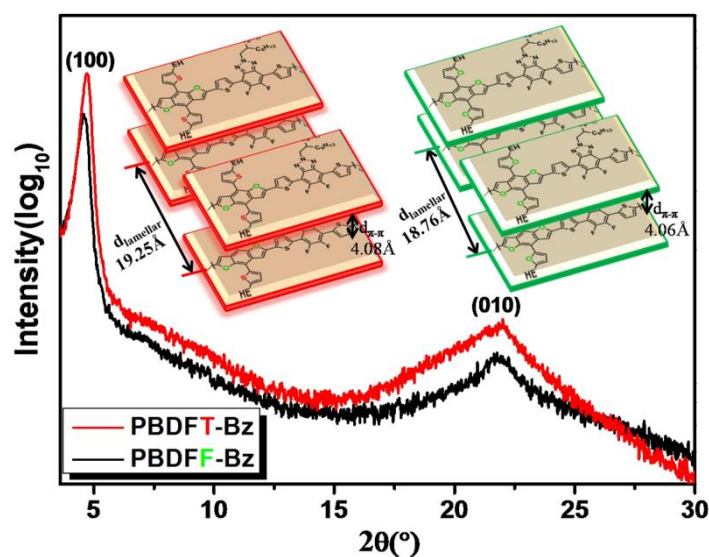


Fig.S7. XRD patterns of pristine PBDFT-Bz and PBDFF-Bz in film state (inset-illustration of the $d_{lamellar}$ and $d_{\pi-\pi}$ between polymers molecules).

References

- [1] Z. Zhang, B. Peng, B. Liu, C. Pan, Y. Li, Y. He, K. Zhou, Y. Zou, *Polym. Chem.* **2010**, *1*, 1441
- [2] S. C. Price, A. C. Stuart, L. Yang, H. Zhou, W. You, *J. Am. Chem. Soc.* **2011**, *133*, 4625.
- [3] J. Min, Z.-G. Zhang, S. Zhang, Y. Li, *Chem. Mater.* **2012**, *24*, 3247.
- [4] K. Li, Z. Li, K. Feng, X. Xu, L. Wang, Q. Peng, *J. Am. Chem. Soc.* **2013**, *135*, 13549.
- [5] C. E. S. Ji-Hoon Kim, In-Nam Kang, Won Suk Shin, Zhi-Guo Zhang, Yongfang Li, Do-Hoon Hwang et al, *Bull. Korea. Chem. Soc.* **2014**, *35*, 1356.

- [6] A. Casey, J. P. Green, P. Shakya Tuladhar, M. Kirkus, Y. Han, T. D. Anthopoulos, M. Heeney, *J. Mater. Chem. A* **2017**, *5*, 6465.
- [7] P. Zhou, Y. Yang, X. Chen, Z.-G. Zhang, Y. Li, *J. Mater. Chem. C* **2017**, *5*, 2951.
- [8] H. Bin, Z. G. Zhang, L. Gao, S. Chen, L. Zhong, L. Xue, C. Yang, Y. Li, *J. Am. Chem. Soc.* **2016**, *138*, 4657.
- [9] H. Bin, L. Gao, Z. Zhang, Y. Yang, Y. Zhang, C. Zhang, S. Chen, L. Xue, C. Yang, M. Xiao, Y. Li, *Nat. Commun.* **2016**, *7*, 13651.
- [10] H. Bin, L. Zhong, Y. Yang, L. Gao, H. Huang, C. Sun, X. Li, L. Xue, Z.-G. Zhang, Z. Zhang, Y. Li, *Adv. Energy. Mater.* **2017**, *8*, 1700746.
- [11] L. Xue, Y. Yang, J. Xu, C. Zhang, H. Bin, Z. G. Zhang, B. Qiu, X. Li, C. Sun, L. Gao, J. Yao, X. Chen, Y. Yang, M. Xiao, Y. Li, *Adv. Mater.* **2017**, *29*, 1703344.
- [12] Q. Fan, W. Su, X. Guo, Y. Wang, J. Chen, C. Ye, M. Zhang, Y. Li, *J. Mater. Chem. A* **2017**, *5*, 9204.