Molecular Engineering of Benzotriazole-based polymer donors for high performance all-polymer solar cells

Jiawei Ru [1], Mengzhen Du,[2] Jieying Cao[2], Xin Liu[2], Hongjun Cheng[2], Lin Hu[2], Qing Guo[1*], Zhihong Xu[3], Chao Li[1], Erjun Zhou [2*]*

[1] School of Materials Science and Engineering, Zhengzhou University, Zhengzhou, 450001, China E-mail: qingg319@zzu.edu.cn

[2] College of Biological and Chemical Engineering, Jiaxing University, Jiaxing 314001, China E-mail: dumengzhen@zjxu.edu.cn; zhouej@nanoctr.cn

[3] College of Chemical and Materials Engineering, Xuchang University, Xuchang, Henan 461000, China

Measurements and characterizations

The relative molecular weights of the polymers were measured by Angilent Technologies PL-GPC 220 high temperature chromatograph with o-dichlorobenzene as the eluent. UV-vis spectra were identified with a Cary 5000 UV-Vis-NIR (Agilent Technologies). Electrochemical CV was conducted on an electrochemical workstation (CHI760E, CH Instruments Ins.) with a Pt disk coated with a polymer film, a Pt plate, and an Ag/AgCl electrode acting as the working, counter, and reference electrodes, respectively, in a 0.1mol/L tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6) acetonitrile solution.

Photovoltaic device fabrication

The OSC devices were fabricated with a configuration of ITO/ PEDOT: PSS/ active layer/ PNDIT-F3N/ Ag. A thin layer of PEDOT: PSS (40 nm, Baytron PH1000) was spin-cast on pre-cleaned ITO-coated glass at 3000 rpm, 30s. After baking at 150℃ for 15 min, the substrates were transferred into glovebox. Optimized devices were prepared under the following conditions. The active layer was dissolved in chloroform (CF) with a D:A ratio of 1:1.2 (w/w). The total concentrations for the J52-F:PY-IT, PE3:PY-IT, and PE3-FCl:PY-IT-based devices were 14, 14, and 14 mg/mL, respectively. For the J52-F and PE3 systems, 1% chloronaphthalene (CN) was added, while 2% CN was added for the PE3-FCl system. Then they were heated and stirred at 90°C for two hours. Afterwards, the active layers were spin-coated from the above solution with 3200rpm for 30s onto the PEDOT: PSS layer, respectively. The thickness of the photoactive layer is in the range of 110-130 nm. Subsequently, **J52-F**, **PE3**, **PE3-FCl**-based devices were annealed at 90 °C for 10 min, respectively. Finally, a PNDIT-F3N (20 nm)/Ag (80 nm) metal top electrode was thermal evaporated onto the active layer under about 3×10^{-4} Pa. The active area of the device was 0.03144 cm^2 defined by shadow mask.

J-V and EQE curves

The *J-V* curves were measured in air with a Keithley 2420 source measure unit. The *J-V* curve was measured using a Zolix Solar IV-150A-ZZU system. The photocurrent was measured under AM 1.5 G illumination at 100 $mW\cdot cm^{-2}$ using a Zolix HPS-300XA solar simulator. Light intensity is calibrated with a Zolix QE-B1 Si-based solar cell. The EQE measurement spectra were measured by a system of QE-R01700390 (Enli Technology Co., Ltd).

Carrier Mobilities

The carrier mobilities of the polymer was investigated by the space charge limited current (SCLC) method. The hole mobility of the blend films was measured with the device structure of ITO/ PEDOT:PSS/ active layer/MoO_3/Al (100 nm), while the electron mobility of the blends was measured with the device structure of ITO/ ZnO/ active layer/ PDINO/Al (100 nm).

The SCLC model is described by modified Mott-Gurney law: [1]

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V2}{L3}$$

where J stands for current density, ε_0 is the permittivity of free space (8.85×10^{-12} C V^{-1} m^{-1}), ε_r is the relative dielectric constant of the transport medium (assuming that of 3.0), μ is the carrier mobility, and L is the thickness of the active layer. V is the internal potential in the device, and $V=V_{app}-V_{bi}$, where V_{app} is the voltage applied to the device, and V_{bi} is the built-in voltage resulting from the relative work function difference between the two electrodes (the V_{bi} values of hole-only and electron-only devices were all selected as 0 V).

AFM characterization: AFM images were obtained on SPM-9700 in the tapping mode.

GIWAXS: Two-dimensional grazing incidence wide angle X-ray scattering (2D-GIWAXS) analyses were measured at the XEUSS SAXS/WAXS equipment. The data were obtained with an area Pilatus 100k detector with a resolution of 195 × 487 pixels (0.172 mm × 0.172 mm). The X-ray wavelength was 1.54 Å, and the incidence angle was 0.2°. The samples were spin-coated onto the PEDOT:PSS/Si substrate.

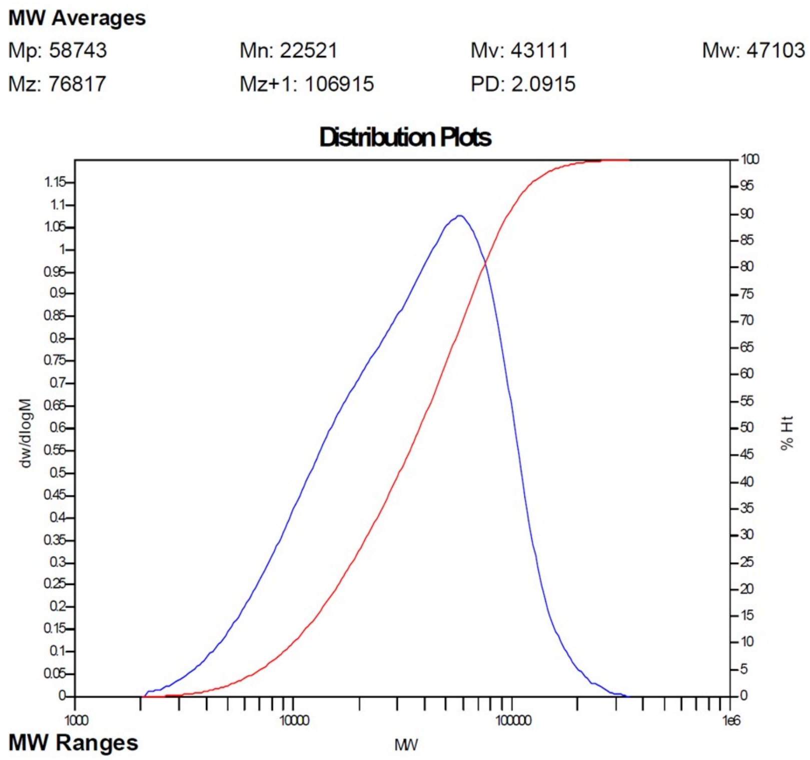

Figure S1. GPC curve recorded at 150^{o}C with o-DCB as eluent for **J52-F**.

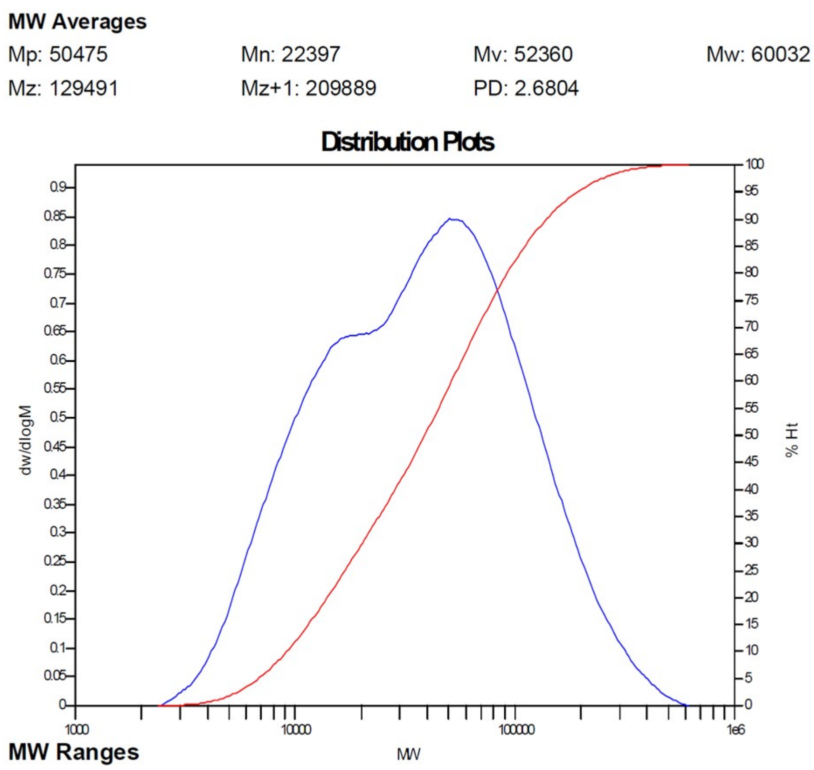

Figure S2. GPC curve recorded at 150^{o}C with o-DCB as eluent for **PE3**.

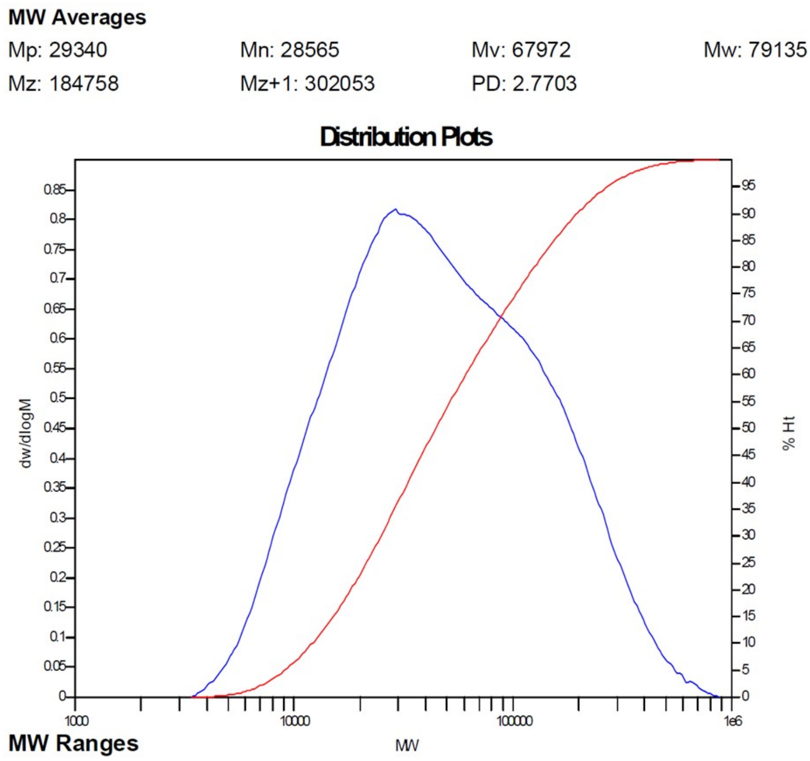

Figure S3. GPC curve recorded at 150^{o}C with o-DCB as eluent for **PE3-FCl**.

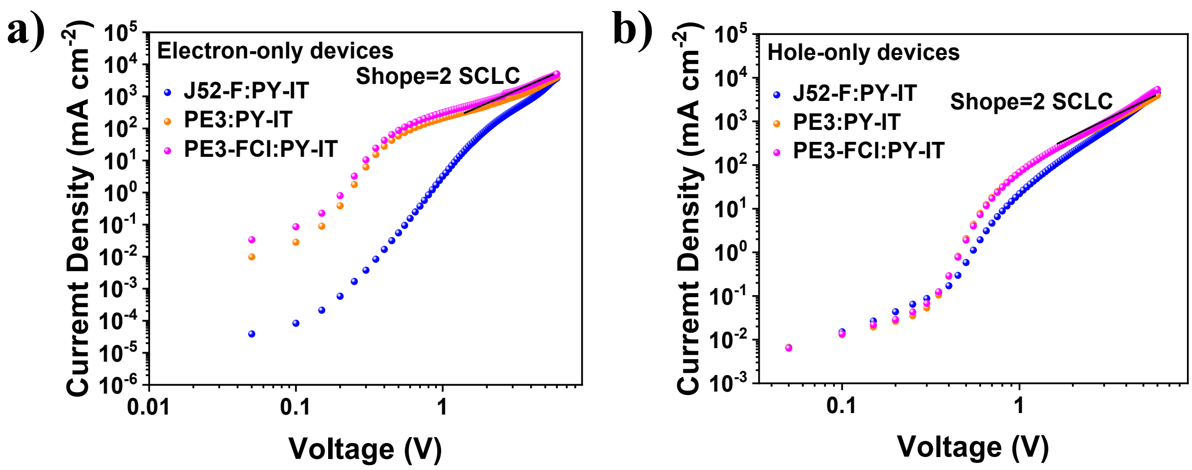

Fig. S4 Electron and hole mobility of three polymer-based devices.

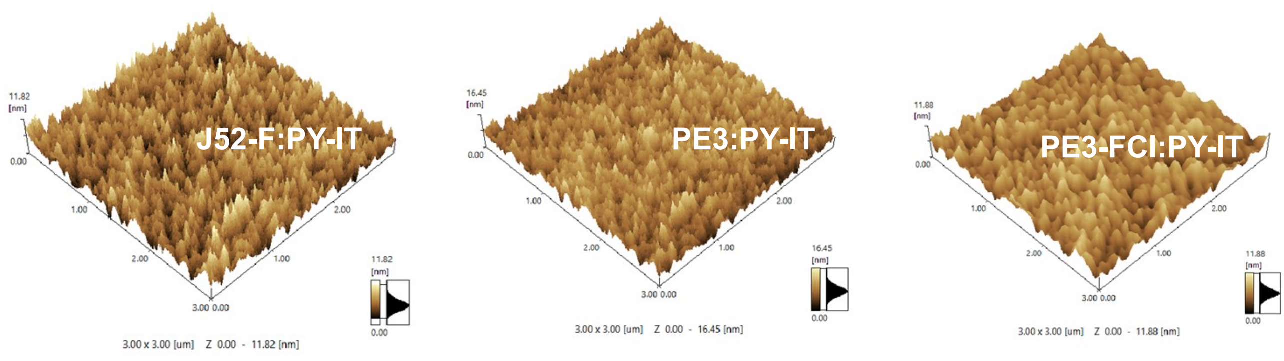

Fig. S5 AFM of 3D height images (3μm×3μm).

Table S1. D/A ratio optimization on the OSCs device performance (CF,1%CN, annealing: 90°C, PNDIT-F3N)

Donor : Acceptor (total concentration)	D/A	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PE3:PY-IT (14mg/mL)	1:1.1	0.901	24.97	73.76	16.59
	1:1.2	**0.905**	**25.45**	**75.71**	**17.43**
	1:1.3	0.912	25.87	73.54	17.35
PE3-FCl:PY-IT (14 mg/mL)	1:1.1	0.909	24.63	70.25	16.75
	1:1.2	**0.915**	**25.89**	**73.47**	**17.40**
	1:1.3	0.917	25.95	72.46	17.13

Table S2. Influence of additives on devices performance.

Donor Acceptor (total concentration)	Additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PE3:PY-IT (14 mg/mL)	**1% CN**	**0.905**	**25.45**	**75.71**	**17.43**
	0.5%DPE	0.884	25.34	63.28	14.19
	1%DPE	0.889	26.53	66.20	15.61
	0.5%DIO	0.880	25.01	70.14	15.43
	1%DIO	0.892	23.01	74.16	15.22
	5mg/ml DIB	0.902	25.42	68.23	15.64
	10mg/ ml DIB	0.905	26.35	70.80	16.88
PE3-FCl :PY-IT (14 mg/mL)	**1% CN**	**0.915**	**25.89**	**73.47**	**17.40**
	0.5%DPE	0.906	26.64	66.64	16.08
	1%DPE	0.903	26.65	65.72	15.81

	0.5%DIO	0.889	24.71	70.21	15.42
	1%DIO	0.892	25.42	69.80	15.83
	5mg/ml DIB	0.899	25.97	62.74	14.48
	10mg/ ml DIB	0.904	26.37	65.61	15.64

Table S3. Influence of additives on device performance.

Donor:Acceptor (total concentration)	Additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PE3:PY-IT (14 mg/mL)	0.5%CN	0.903	26.31	72.65	17.26
	1% CN	**0.905**	**25.45**	**75.71**	**17.43**
	1.5% CN	0.905	25.32	75.08	17.29
	2% CN	0.908	24.93	75.26	17.05
PE3-FCl :PY-IT (14 mg/mL)	0.5%CN	0.916	27.02	68.03	16.83
	1% CN	0.915	25.89	73.47	17.40
	1.5% CN	0.920	25.26	73.59	17.10
	2% CN	**0.915**	**25.75**	**75.23**	**17.73**

Table S4. Statistical table of device parameters of all-PSCs containing BTA-based polymers.

Active layer	V_{OC} (V)	J_{SC} (mA·cm^{-2})	FF (%)	PCE (%)	References
J50 : N2200	0.60	13.92	58.74	4.90	[2]
J51 : N2200	0.83	14.02	70.2	8.27	[2]
J51 : N2200	0.81	13.84	64.27	7.03	[3]
PBTA-BO : N2200	0.87	11.00	75.82	7.24	[4]

PTzBI-Si$_L$: N2200	0.85	13.7	72.2	8.6	[5]
PTzBI-Si$_H$: N2200	0.85	17.2	77.9	11.5	[5]
CD1 : PBN-12	1.17	13.30	64.5	10.04	[6]
J52 : N2200	0.79	16.23	66.68	8.55	[7]
J52-Cl : N2200	0.95	13.71	69.58	9.02	[7]
Nap-SiBTz : N2200	0.84	19.21	70.08	11.66	[8]
J71 : PNDI2OD-T2	0.93	10.2	54.4	5.2	[9]
J71 : PNDI-OT5	0.93	8.1	52.5	4.0	[9]
J71 : PNDI-OT10	0.93	6.2	52.2	3.0	[9]
J71 : PNDI-OT15	0.94	4.9	50.4	2.3	[9]
J71 : PNDI2OD-C8T2	0.94	5.5	50.8	2.6	[9]
J52 : PYBzT	0.851	23.44	56.24	11.22	[10]
J52 : PYBzDT	0.852	21.40	49.01	8.93	[10]
PBDF-NS : PY-IT	0.859	25.24	74.6	16.17	[11]
PTzBI-Si : PIR-C39	0.89	19.6	66.0	11.3	[12]
PTzBI-Si : PRi-C39	0.90	23.1	69.4	14.3	[12]
PTzBI-Si : PRo-C39	0.83	22.1	73.2	13.3	[12]
PTzBI-Si:N2200	0.88	17.62	75.78	11.76	[13]
PTBD-BZ : N2200	0.88	7.99	54.24	3.83	[14]
PTBD-BZ : PNDIOD-30Se	0.91	11.58	60.94	6.42	[14]
PTzBI : N2200	0.82	15.53	69.35	9.07	[15]
J71: PY-IT	0.914	21.44	68.5	13.43	[16]
J71 : PG1	0.99	7.0	51.1	3.5	[17]
PTzBI-oF:PS1	0.92	22.47	66.70	13.8	[18]
PM6 : **PT-YTz**	0.87	26.27	70.59	16.15	[19]
PBDB-T : **PFBTz-TT**	0.85	18.95	63.0	10.14	[20]
PBDB-T : **PZT-** γ	0.89	24.7	71.3	15.8	[21]
J51 : rr-PBN	0.89	10.18	42.5	3.85	[22]
J61 : rr-PBN	0.98	10.99	47.5	5.12	[22]
J91 : rr-PBN	1.06	12.23	51.5	6.67	[22]
PBDB-T : **PZT-C12**	0.92	22.2	63.7	13.1	[23]
PBDB-T : **PZT-C8**	0.91	22.8	65.9	13.8	[23]
PBDB-T : **PZT-C1**	0.91	23.9	68.5	14.9	[23]
PBDB-T : **PYT-Tz**	0.91	23	71.68	15.10	[24]

PBDB-T : **PYV-Tz**	0.88	21.73	67.62	13.02	[25]
PBDB-T : **PBTzO**	0.89	2.90	41.74	1.08	[26]
PBDB-T : **PBTzO-2F**	0.89	18.27	67.37	11.04	[26]
J52-F： PY-IT	0.89	24.62	71.88	15.78	This work
PE3： PY-IT	0.90	25.45	75.71	17.43	This work
PE3-FCl： PY-IT	0.91	25.75	75.23	17.73	This work

Table S5. Electron and Hole Mobility Specific Parameters of Three Polymers.

Blend film	μ_h [cm^{2}v^{-1}s^{-1}]	μ_e [cm^{2}v^{-1}s^{-1}]	μ_h/μ_e
J52-F：PY-IT	3.57×10^{-4}	2.87×10^{-4}	1.24
PE3：PY-IT	3.81×10^{-4}	3.29×10^{-4}	1.15
PE3-FCl：PY-IT	4.09×10^{-4}	3.97×10^{-4}	1.03

Table S6. Detailed GIWAXS data of **J52-F**:PY-IT、**PE3**:PY-IT and **PE3-FCl**.

Film	In-plane				Out-of-plane			
	(100)				(010)			
	q (Å^{-1})	*D* (Å)	FWHM (Å^{-1})	CCL (Å)	q (Å^{-1})	*d* (Å)	FWHM (Å^{-1})	CCL (Å)
J52-F:PY-IT	0.290	21.65	0.162	36.08	1.64	3.76	0.292	20.01
PE3:PY-IT	0.299	21.01	0.060	86.74	1.62	3.87	0.269	21.66
PE3-FCl:PY-IT	0.302	20.83	0.065	89.76	1.632	3.84	0.239	24.469

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