Thiazole Functionalized Terpolymer Donors Obtained *via* Random Ternary Copolymerization for High-Performance Polymer Solar Cells

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EXPERIMENTAL SECTION

1. Materials and Instruments

All reagents and chemicals were commercially available. Monomer of BDT-2F and materials PM6 and Y6 were purchased from Solarmer Co., Ltd. (Beijing, China). Monomer of BDD was purchased from Derthon Co., Ltd. Monomer of E-Tz was purchased from Energy Chemical., Ltd. 1,8-diiodooctane (DIO) and chloronaphthalene (CN) additive were supplied by Sigma Aldrich. The Phen-NaDPO was purchased from Bellingway Technology Co., Ltd. ^{1}NMR spectra were recorded on a Bruker Ascend 400 MHz spectrometer using $CDCl_3$ and CD_2Cl_2 as the solvent. Molecular weight and polydispersity index of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene as standard (PL-GPC220, using trichlorobenzene (TCB) as eluent at a flow rate of 1.0 mL/min at 150 °C. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 with a heating rate of 20 K/min under nitrogen. The cyclic voltammetry was recorded with a computer controlled PP211 electrochemical workstation using polymer films on platinum electrode (1.0 cm^2) as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (0.1 M) as the reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile at a scanning rate of 20 $mV \cdot s^{-1}$. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc^+) redox couple (4.8 eV below the vacuum level). The HOMO and LUMO levels were calculated using the equations: E_{HOMO} = -e (E_{ox} + 4.8

- $E_{Fc/Fc+}$) V, E_{LUMO} = -e (E_{red} + 4.8 - $E_{Fc/Fc+}$).[1-3] AFM using a Digtial Instrumental Nanoscope 31 operated in the tapping mode, the film was prepared as the same as device fabrication to ensure the reliability and authenticity. AFM sample preparation: The ITO glass substrates were cleaned followed by ultrasonic treatment in detergent deionized water, acetone, and isopropyl alcohol for 30 min. each. After treating with plasma for 3 min. PEDOT:PSS layer spin-cast on top of the ITO substrates at 4000 rpm for 20 s and heated at 160 °C in ambient atmosphere for 30 min. Active layer was spun at 2800 rpm for 30 s from the solution of polymers:Y6 at weight ratio of 1:1.3 with a total concentration of 17 mg ml^{-1} in chloroform, and then thermal annealed at 100 °C for 10 min. TEM sample preparation: The ITO glass substrates were cleaned followed by ultrasonic treatment in detergent deionized water, acetone, and isopropyl alcohol for 30 min. each. After treating with plasma for 3 min. PEDOT:PSS layer spin-cast on top of the ITO substrates at 4000 rpm for 20 s and generated at 160 °C in ambient atmosphere for 30 min. Active layer were spun at 2800 rpm for 30 s from the solution of polymers:Y6 at weight ratio of 1:1.3 with a total concentration of 17 mg ml^{-1} in chloroform, and then thermal annealed at 100 °C for 10 min. And then the film was extracted in water and put on the copper grid. The current–voltage ($J^{1/2}$–V) curves evaluated by SCLC method was fitted by $J = 9\varepsilon_0\varepsilon r\mu V^2/8L^3$, where ε_0 is the permittivity of free space and constant at 8.85×10^{-12} F/m, εr is the dielectric constant of the polymer and it is assumed to be 2, μ is the charge mobility, V is the applied voltage across the device, and L is the thickness of the active layer.

2. Synthesis of polymers

Four polymers were synthesized using a palladium-catalyzed Stille coupling reaction. OPz1: 0.1 mmol (940.5mg) monomer of BDT-2F and 0.095 mmol (72.8mg) bromide monomer of BDD and 0.005 mmol (1.58mg) E-Tz; OPz2: 0.1 mmol (940.5mg) monomer of BDT-2F and 0.09 mmol (69mg) bromide monomer of BDD and 0.01 mmol (3.15mg) E-Tz; OPz3: 0.1 mmol (940.5mg) monomer of BDT-2F and 0.08 mmol (61.3mg) bromide monomer of BDD and 0.02 mmol (6.3mg) E-Tz; OPz4: 0.1 mmol (940.5mg) monomer of BDT-2F and 0.1 mmol (31.5mg) E-Tz, were dissolve in dry toluene (10 mL). $Pd(PPh_3)_4$ (8% mmol 9.2mg) was added into the mixtures after being flushed with argon for five minutes. Then, the reaction mixtures were purged with argon for another 10 min. The reactions were stirred at 110 °C (preheat) for 4 h. The obtained copolymers were purified by Soxhlet extraction (the solvent using methanol, acetone and n-hexane and chloroform, respective), and the primary polymers followed by a fast silica gel column chromatography with chloroform as solvent to remove the oligomers and other impurities. The polymer was then precipitated in methanol (60 mL) and dried under vacuum for 12 h before use. The yields are around 60%.

BDD: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):7.37 (d, 1H), 6.99(d, 1H), 3.31 (m, 2H), 1.68 (m, 1H), 1.22-1.41 (m, 9H), 0.9 (m, 6H).

BDT-2F: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):7.67 (s ,1H), 6.99 (s, 1H), 3.25 (d, 2H), 1.45 (m, 1H), 1.25-1.36 (m, 9H), , 0.9-0.98 (m, 6 H), 0.42 (t, 9H)

E-Tz: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.45 (t, 2H), 1.41-1.6 (m, 3H).

PM6: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 (1H), 7.0 (1H), 3.51 (m, 7.7 H), 2.82 (m, 16.26 H), 0.88-1.56 (m, 264.4H).

OPz1: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (1.41H), 6.93 (1.18H), 4.78 (1H), 2.75 (39.29H), 0.8-1.5 (3627.54H).

OPz2: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (1.33H), 6.93 (1.29H), 4.78 (1H), 2.75 (m, 40.04H), 0.8-1.5 (m, 421H).

OPz3: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (0.41H), 6.93 (0.41H), 4.36 (1H), 3.22 (m, 5.32 H), 2.75 (m, 7.5H), 0.8-1.5 (m, 135.4H).

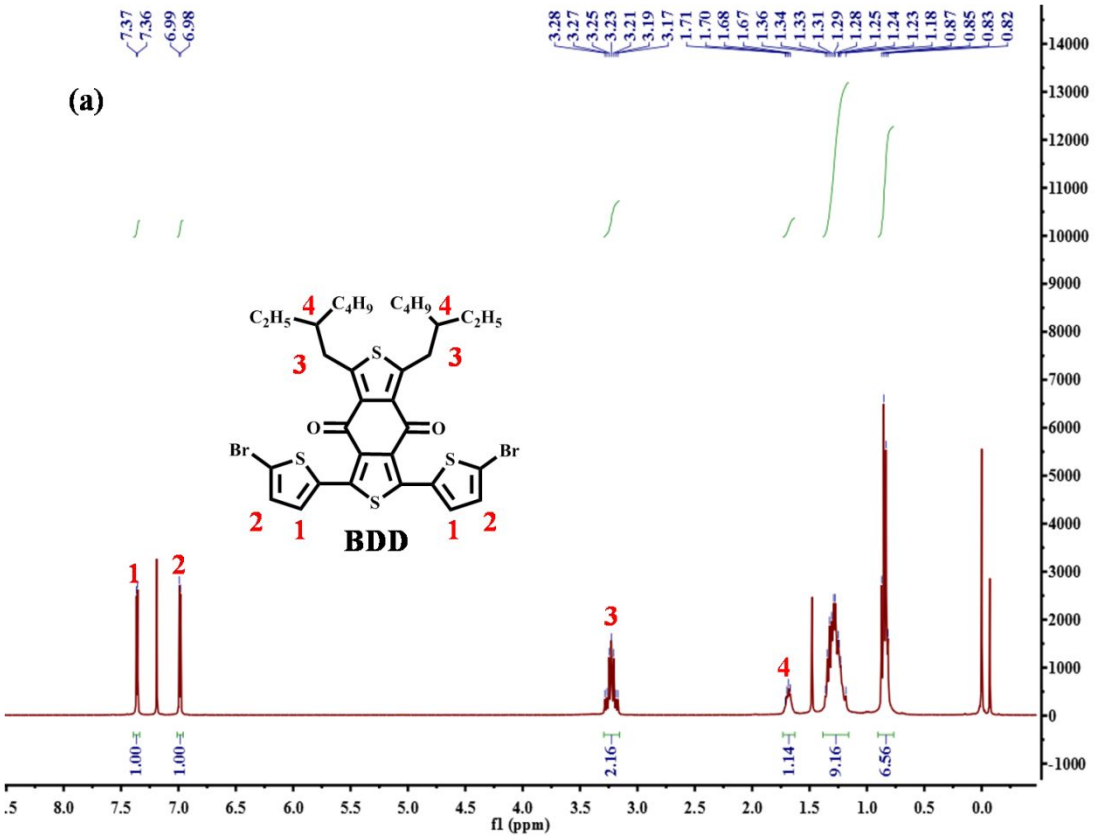
OPz4: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.44 (1H), 2.82 (m, 2.54 H), 0.8-1.5 (m, 37.79H).

Elemental analysis calcd (%) for OPz1: C = 66.84%, H = 6.31%, S = 20.96%, N% 0.06% . Found: C= 66.52%, H= 6.26%, S = 20.96%, N% = 0.07%.

Elemental analysis calcd (%) for OPz2: C = 66.69%, H = 6.29%, S = 20.96%, N% 0.12% . Found: C= 67.36%, H= 6.8%, S = 20.83%, N% = 0.12%.

Elemental analysis calcd (%) for OPz3: C = 66.24%, H = 6.18%, S = 21.23%, N% 0.24% . Found: C= 64.84%, H= 7.21%, S = 20.85%, N% = 0.28%.

Elemental analysis calcd (%) for OPz4: C = 62.80%, H = 6.04%, S = 20.44%, N% 1.79% . Found: C= 62.40%, H= 5.86%, S = 20.30%, N% = 1.82%.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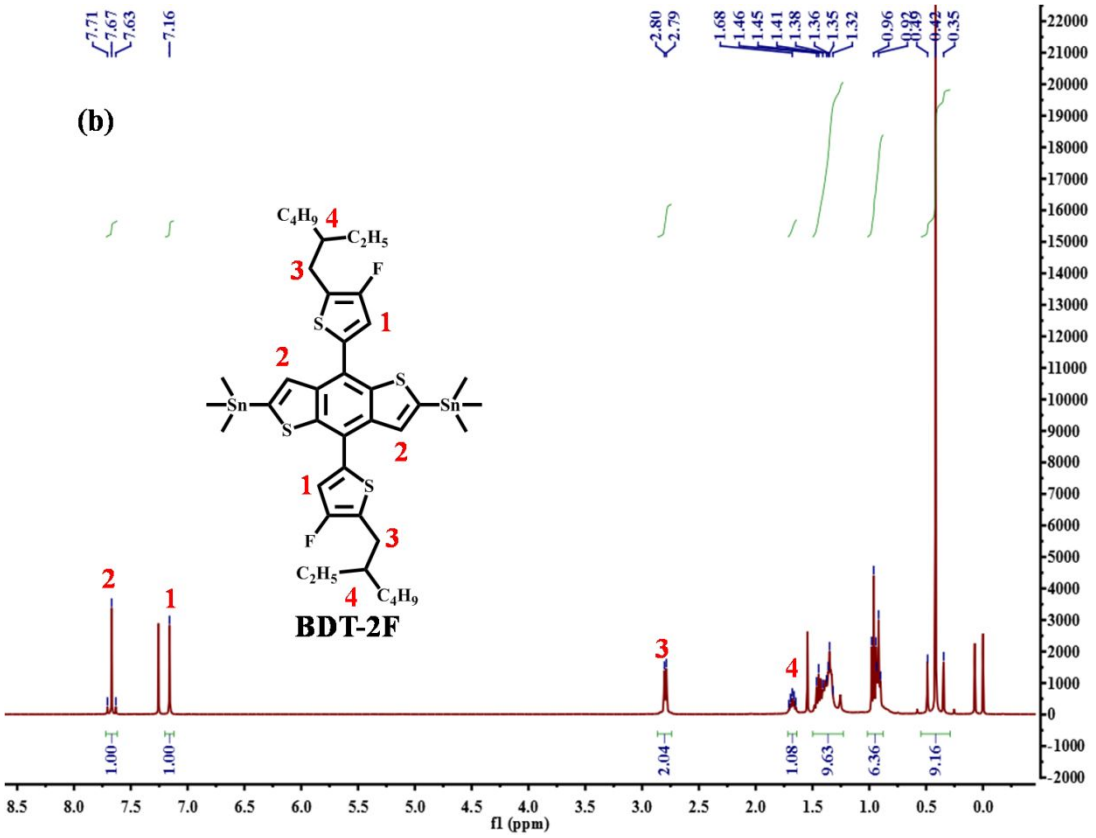
BDD
fl (ppm)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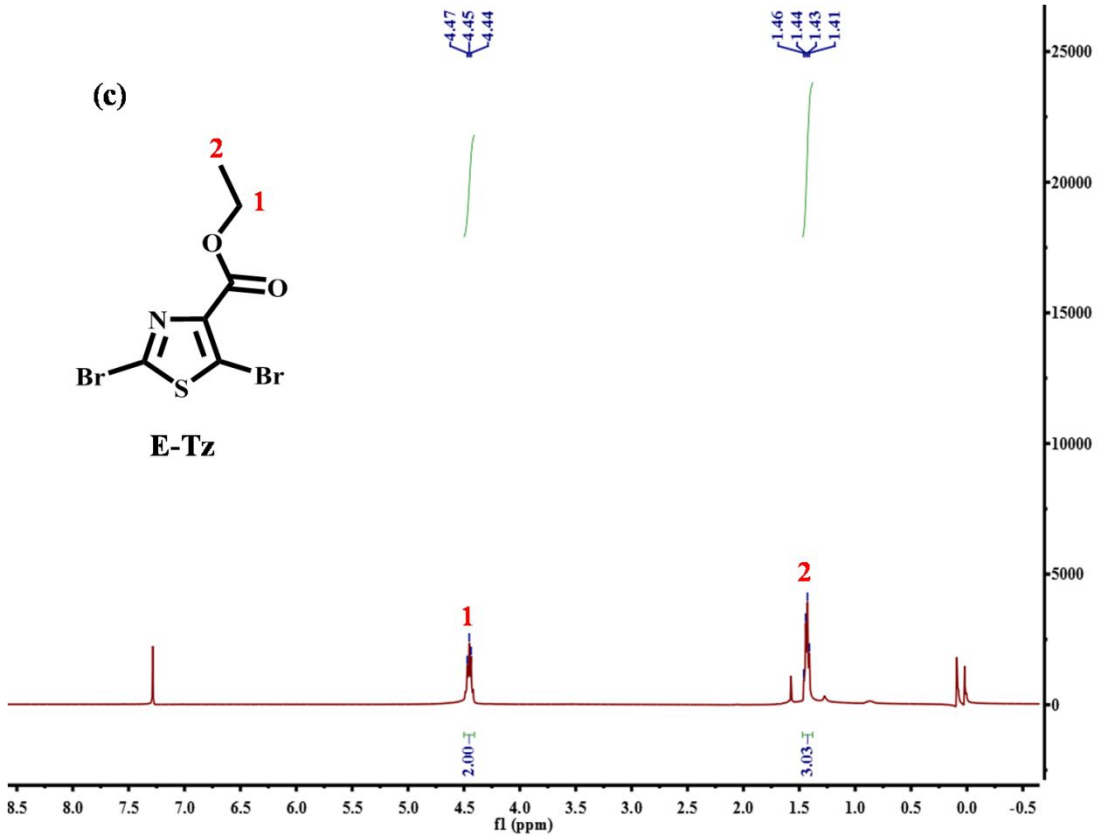
BDT-2F
fl (ppm)


(c)
E-Tz
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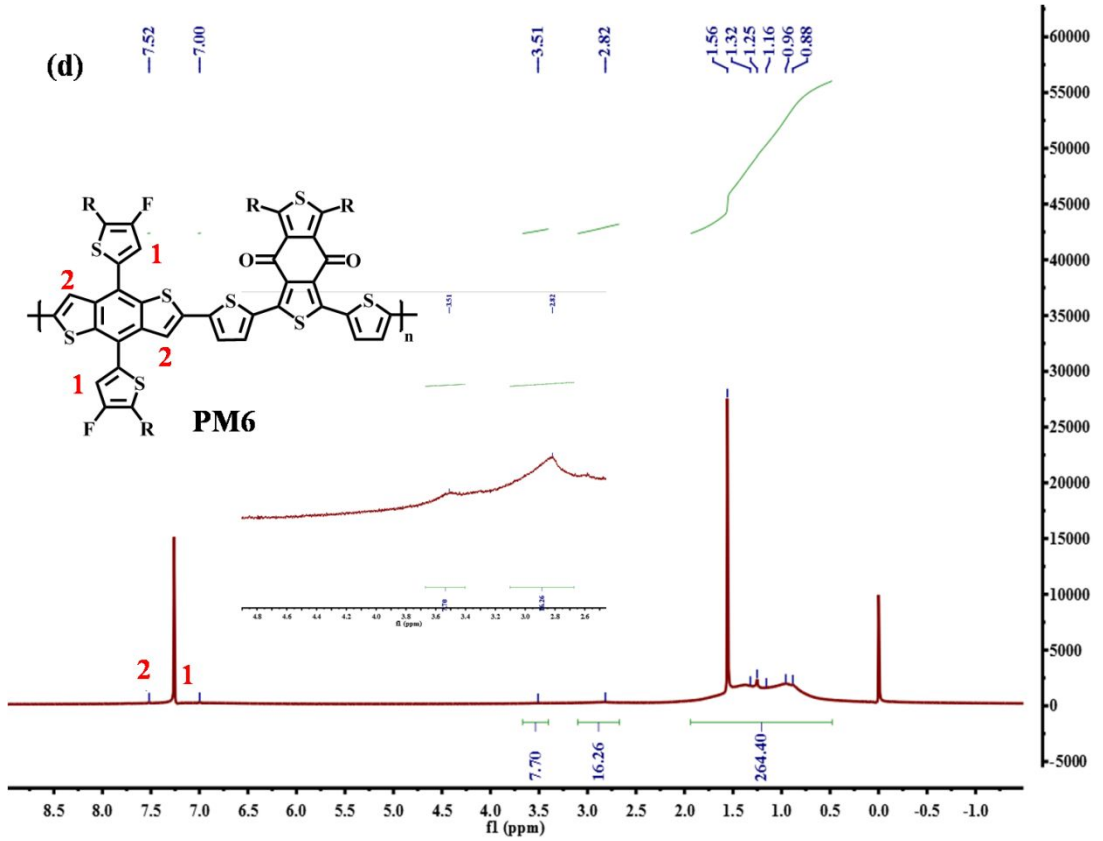
4.45
4.44
1.46
1.44
1.43
1.41
2.00
3.03
fl (ppm)


(d)
PM6
7.52
7.00
3.51
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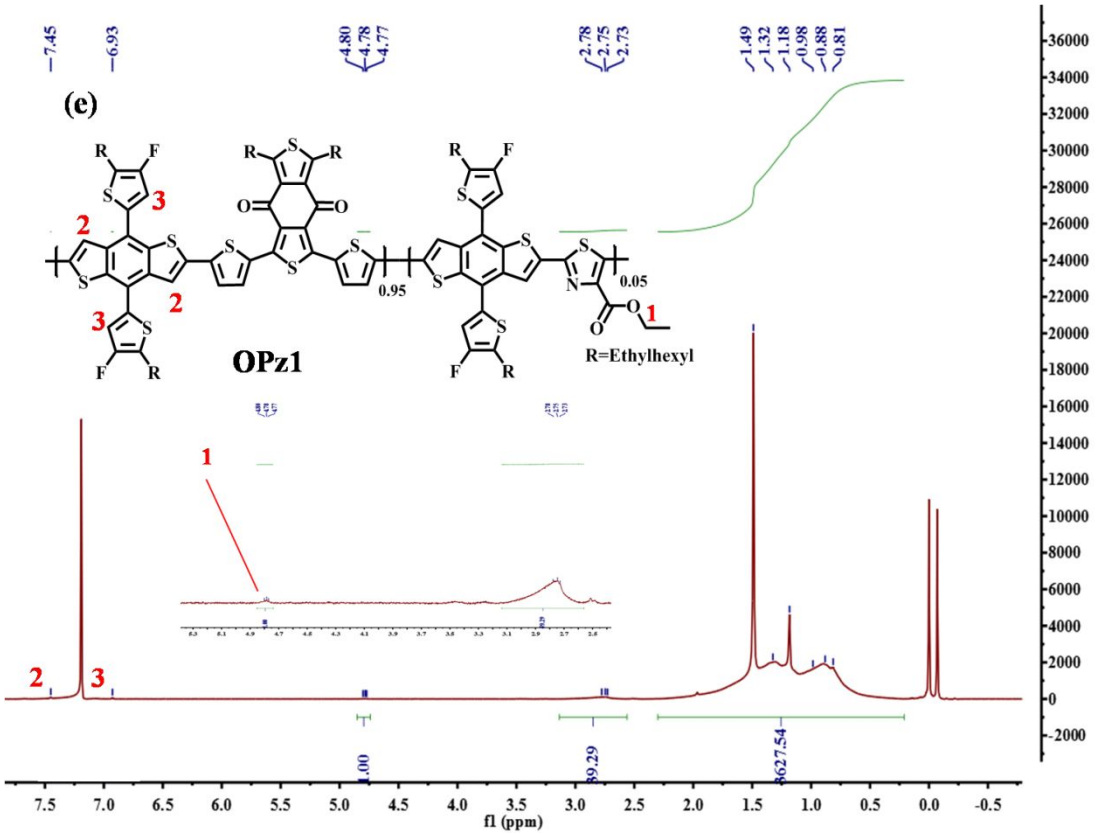
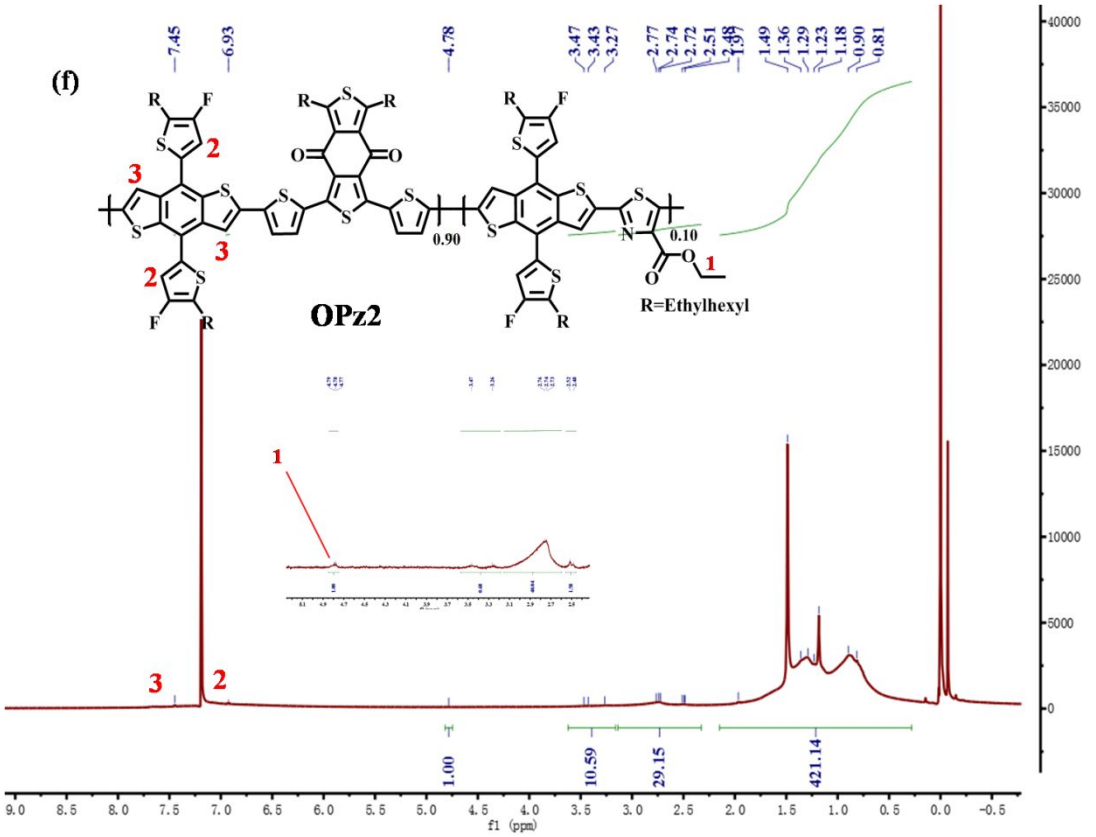
7.70
16.26
264.40
fl (ppm)


(e)
OPz1
R=Ethylhexyl
0.95
0.05
f1 (ppm)


(f)
OPz2
R=Ethylhexyl
0.90
0.10
f1 (ppm)

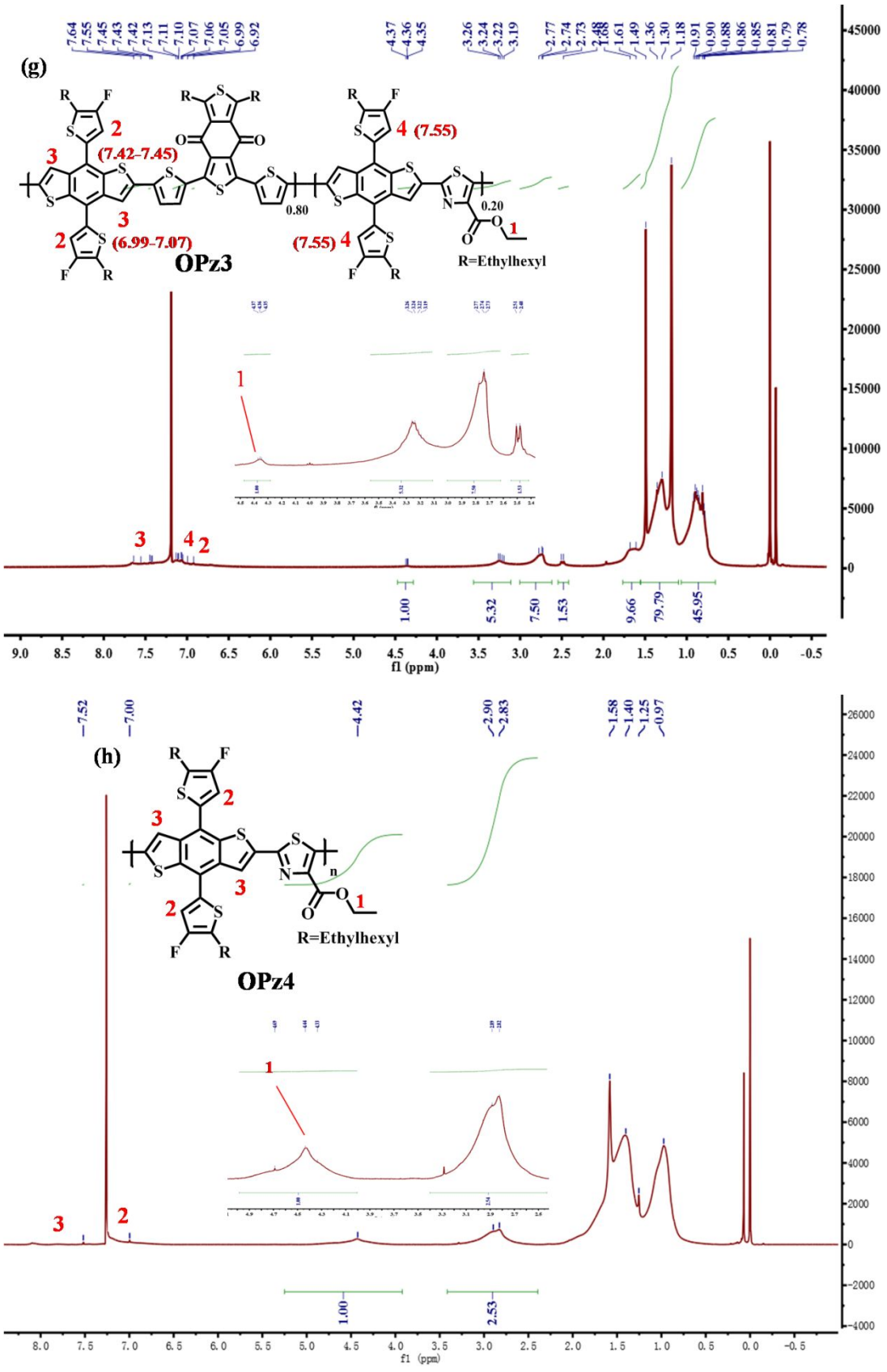


Figure S1. ^{1}H MNR data of the initial monomers and final copolymers in this work.

3. Device Fabrication

Traditional devices based on polymers and Y6 were fabricated according to following procedure. The ITO glass substrates were cleaned followed by ultrasonic treatment in detergent deionized water, acetone, and isopropyl alcohol for 30 min. each. After treating with plasma for 3 min. PEDOT:PSS layer spin-cast on top of the ITO substrates at 4000 rpm for 20 s and generated at 160 °C in ambient atmosphere for 30 min. Active layer were spun at 2800 rpm for 30 s from the solution of polymers:Y6 at weight ratio of 1:1.3 with total concentration of 17 mg ml^{-1} in CF as solvent, and then thermal annealing with 100 °C for 10 min. The Phen-NaDPO (DPO) as the electron-transporting layer, was spin coated on the active layer by 2,000 rpm for 20s from an isopropyl alcohol solution (0.5 mg/ml). Finally, drying Ag layer with a thickness of about 90 nm were deposited onto the active layer under vacuum of about 2×10^{-6} Torr. The surface area of the OPV cells is 11 mm^2, and the active layer was processed at room temperature condition.

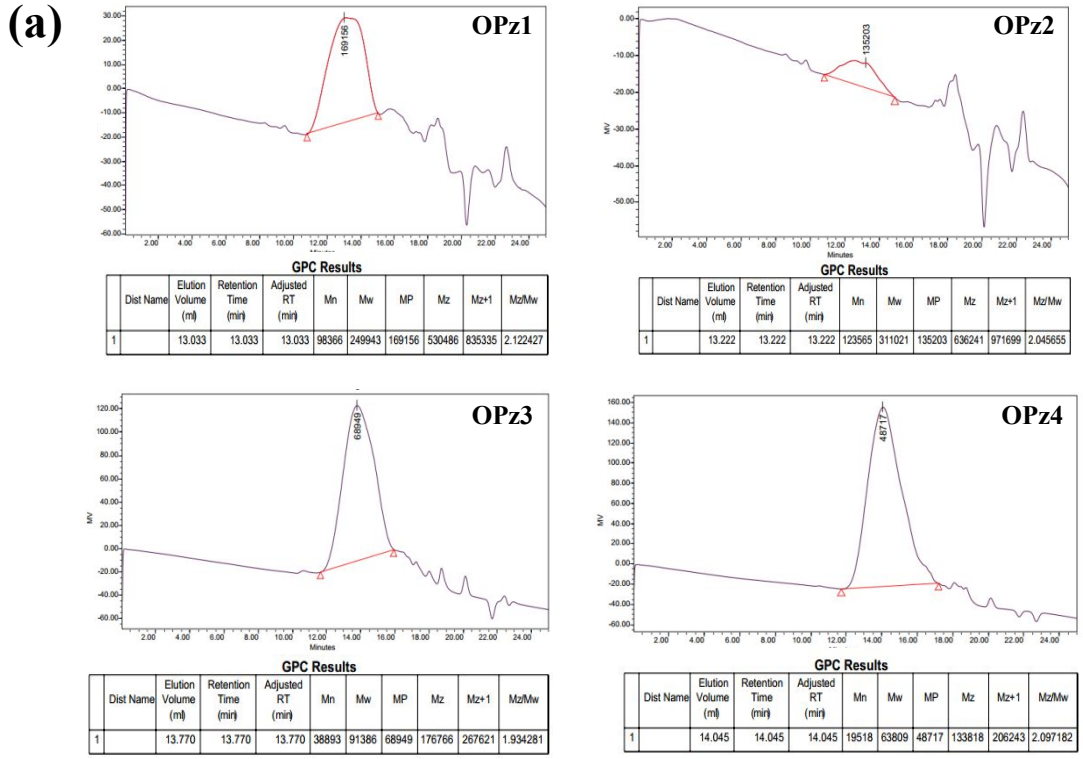


Figure S2. The gel permeation chromatography (GPC) measurements of PM6, OPz1, OPz2, OPz3 and OPz4. (a) In tetrahydrofuran (THF) at room temperature. (b) In trichlorobenzene (TCB) at high temperatures (150 ^{o}C).

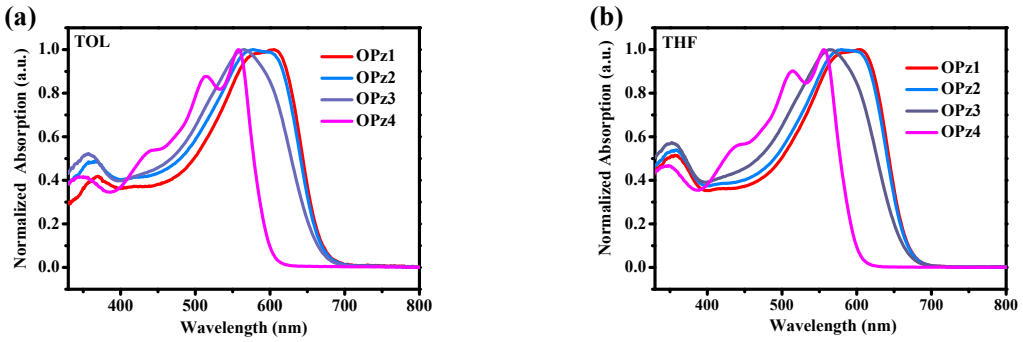


Figure S3. Solution absorption spectra of the polymers in tetrahydrofuran and toluene.

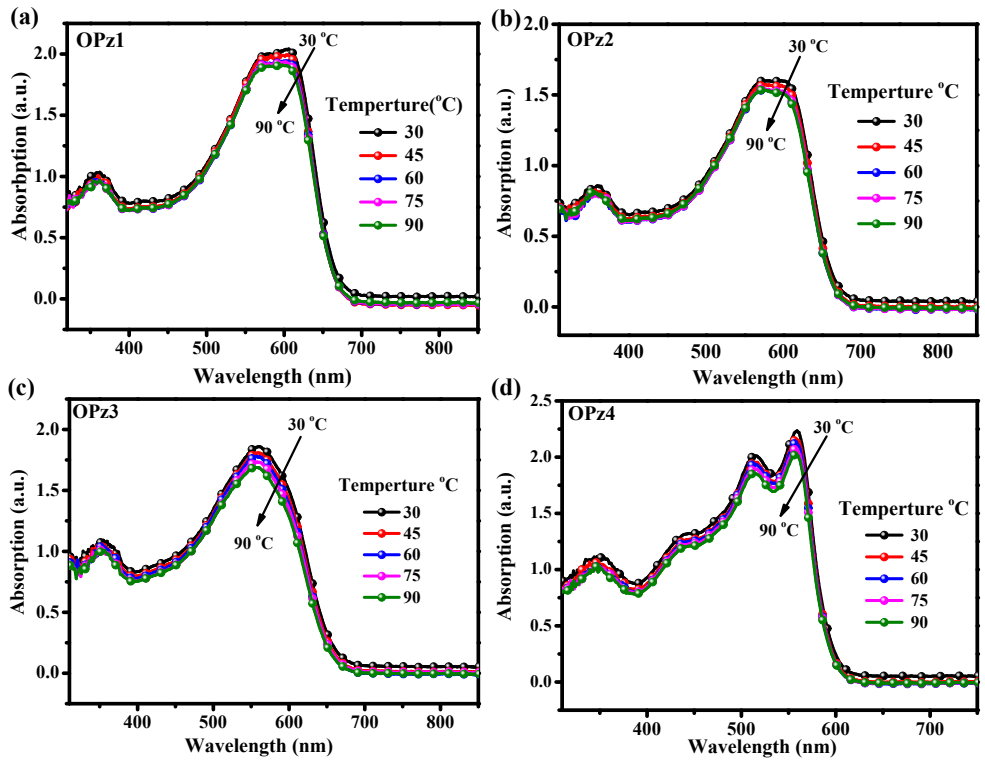


Figure S4. The UV-vis absorption of OPz1, OPz2, OPz3 and OPz4 in chlorobenzene at different temperatures.

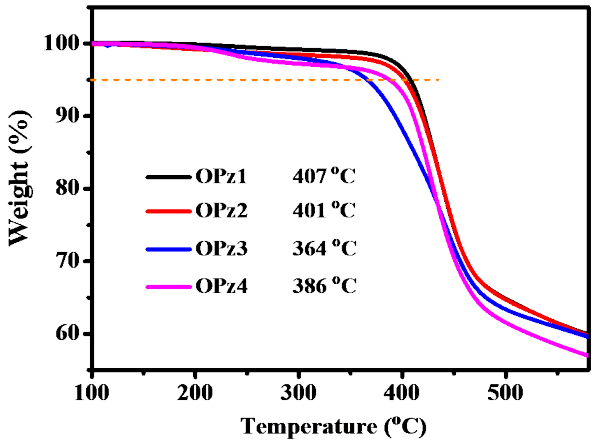


Figure S5. The thermal stability of OPz1, OPz2, OPz3 and OPz4.

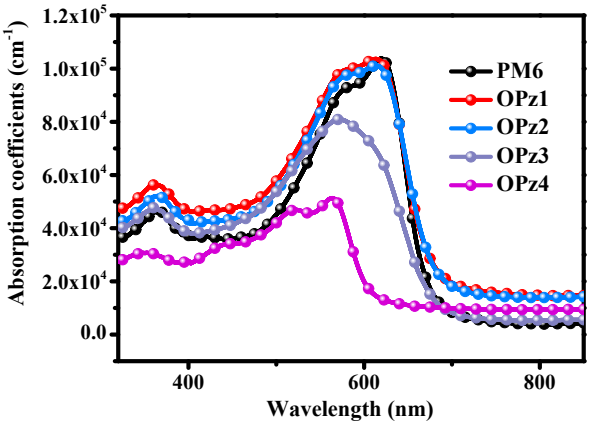


Figure S6. The maximum absorption coefficients for PM6, OPz1, OPz2, OPz3 and OPz4.

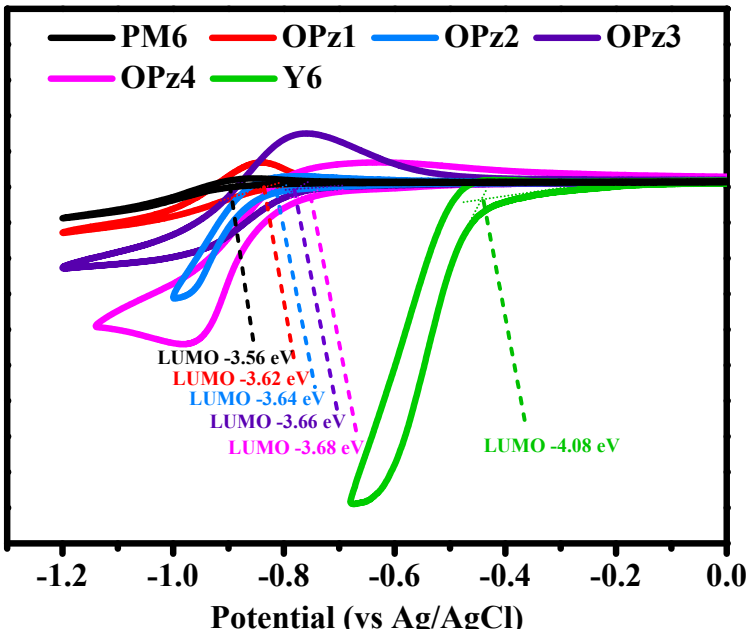


Figure S7. The LUMO energy levels of PM6, OPz1, OPz2, OPz3, OPz4 and Y6 obtained by CV measurements.

Table S1. The detailed device optiming processes of OPz1:Y6-based device.

Active layer	Conc. (mg/ml)	D/A	Annealing Temp.(°C)	Additive (vol %)	V_{oc}(V)	J_{sc} (mA cm^{-2})	FF (%)	PCE$_{best}$ (%)
OPz1: Y6	16	2:1	none	none	0.860	23.40	65.07	13.09
		1.5:1	none	none	0.860	23.47	65.99	13.32
		1:1	none	none	0.880	24.38	63.01	13.52
		1:1.2	none	none	0.865	24.50	63.52	13.38
		1:1.3	none	none	0.871	24.05	66.57	13.93
		1:1.5	none	none	0.870	24.30	59.99	12.69
		1:2	none	none	0.870	21.81	63.23	12.04
	17	1:1.3	none	none	0.871	24.83	66.07	14.41
	18	1:1.3	none	none	0.871	24.07	66.45	14.07
	17	1:1.3	130	CN (0.5%)	0.870	24.21	67.0	14.11
	17	1:1.3	120		0.870	25.15	65.33	14.54
	17	1:1.3	110		0.870	24.96	66.49	14.43
	17	1:1.3	100		0.870	25.19	68.72	15.23
	17	1:1.3	90		0.871	24.12	68.03	14.42
	17	1:1.3	80		0.871	24.10	66.31	14.13
	17	1:1.3	100	CN (0.8%)	0.870	25.37	73.70	16.28
	17	1:1.3		CN (1.0%)	0.863	25.41	70.52	15.41

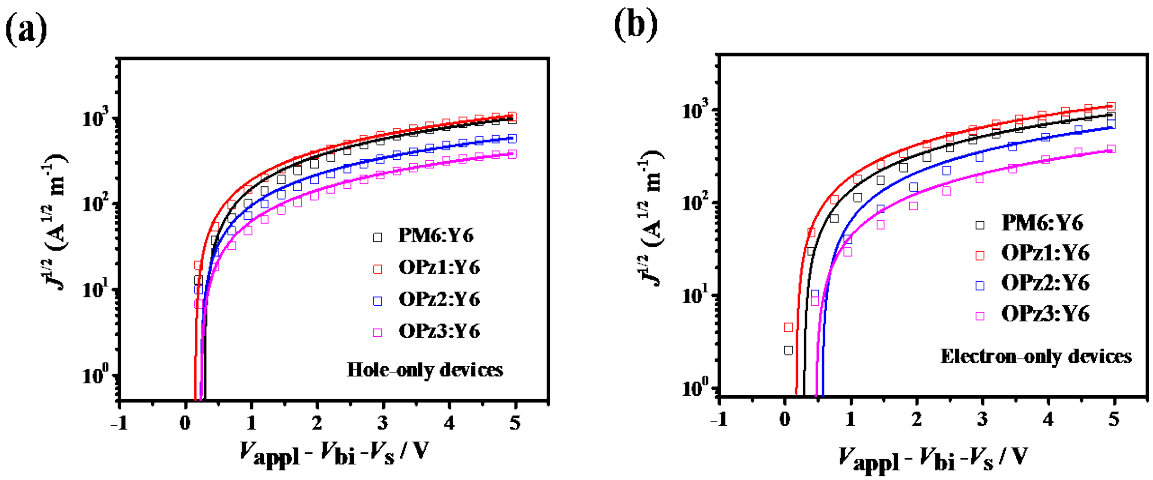


Figure S8. The charge mobilities of OPz1-based, OPz2-based, OPz3-based and OPz4-based devices(fitted curves).

Table S2. The charge mobilities of the devices.

Devices	Hole mobilities(μ_h) (cm^2 V^{-1} s^{-1})	Electron mobiliyies (μ_e) (cm^2 V^{-1} s^{-1})	μ_h / μ_e	Thickness (nm)	
				μ_h	μ_e
PM6:Y6	6.32×10^{-4}	4.98×10^{-4}	1.26	115	120
OPz1:Y6	6.76×10^{-4}	5.48×10^{-4}	1.23	110	117
OPz2:Y6	5.25×10^{-4}	2.74×10^{-4}	1.91	113	122
OPz3:Y6	2.28×10^{-4}	9.38×10^{-5}	2.43	108	115

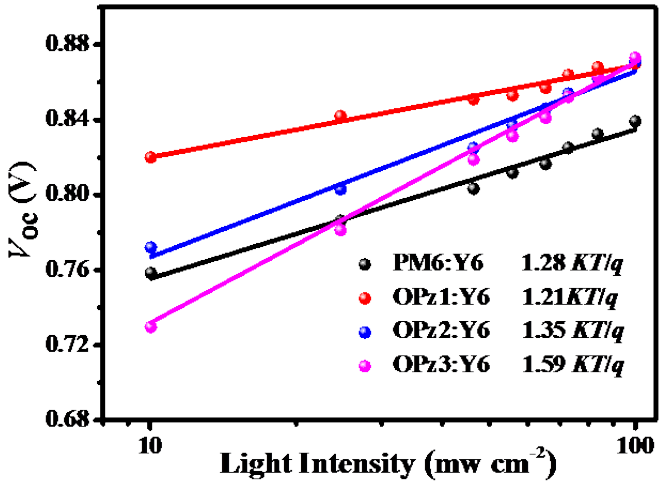


Figure S9. The V_{oc} versus light intensity for PM6:Y6, OPz1:Y6, OPz2:Y6 and OPz3:Y6 devices.

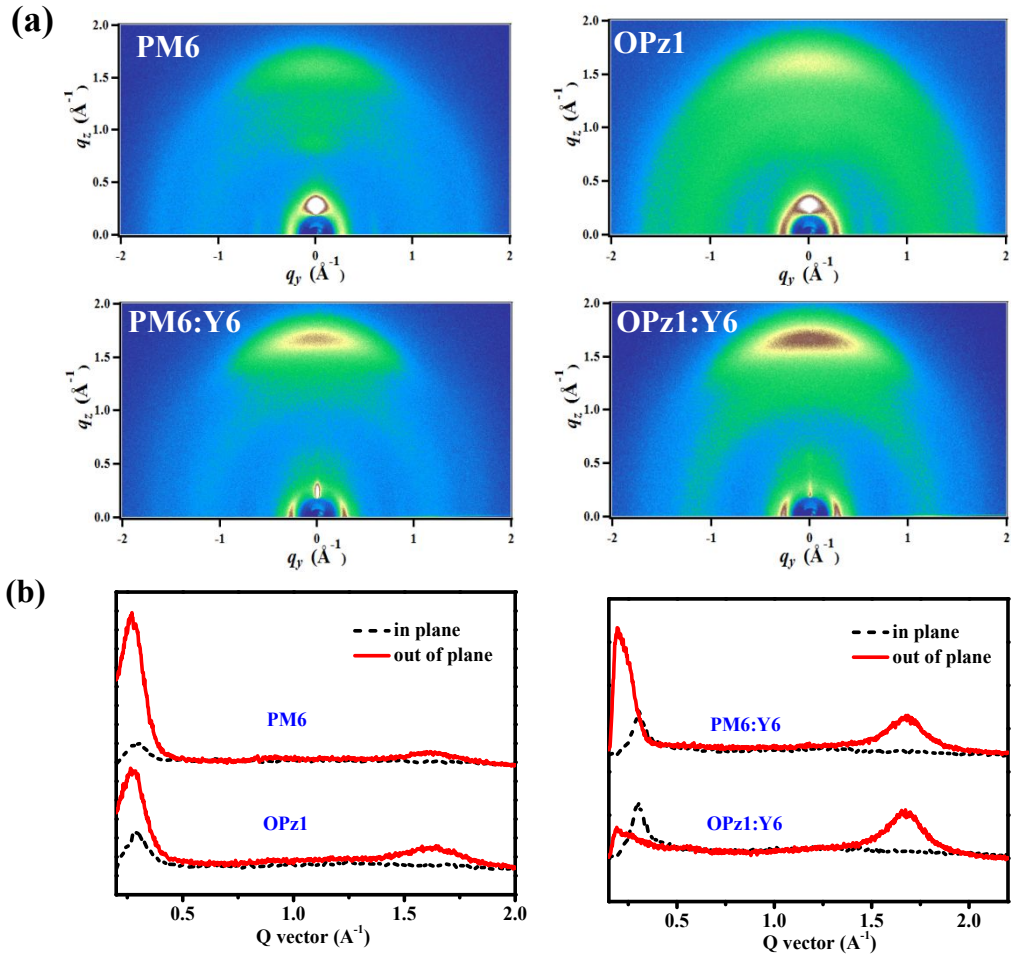


Figure S10. (a) GIWAXS images of PM6, and OPz1 neat and blend film. (b) GIWAXS intensity profiles along the in-plane (dotted line) and out-of-plane (solid line) directions.

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