

18.42% efficiency polymer solar cells enabled by terpolymer donors with optimal miscibility and energy levels

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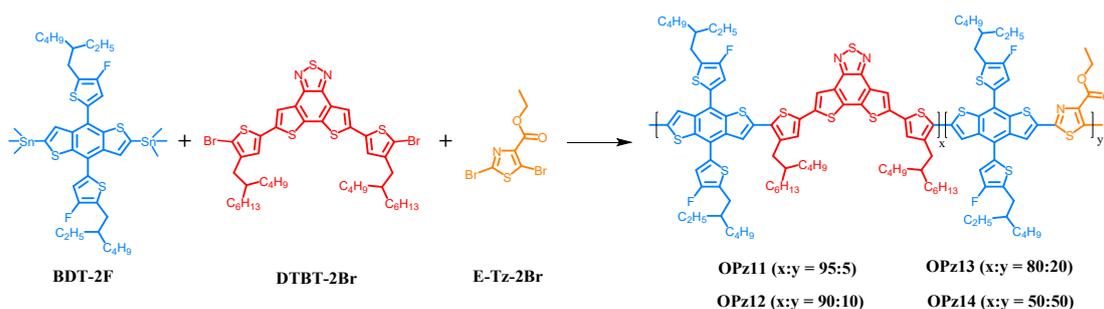
EXPERIMENTAL SECTION

1. Materials and Instruments

All reagents and chemicals are commercially available. Monomer of BDT-2F and materials Y6 are purchased from Organtec.Ltd (Beijing, China). Monomer of DTBT is purchased from Derthon Co., Ltd. Monomer of E-Tz is purchased from Energy Chemical. ^{13}C NMR spectra are recorded on a Bruker Ascend 400 MHz spectrometer using CDCl_3 as the solvent. Molecular weight and polydispersity index of the polymer are determined by high temperature gel permeation chromatography (GPC) analysis with polystyrene as standard (Agilent PL-GPC220 differential refractometer using trichlorobenzene (TCB) as eluent at a flow rate of 1.0 mL/min at 150 °C, and tested from Shiyanjia Lab (www.shiyanjia.com). Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 with a heating rate of 20 K/min under nitrogen. AFM using a Digital Instrumental Nanoscope 31 is operated in the tapping mode, the film was prepared as the same as device fabrication to ensure the reliability and authenticity. The cyclic voltammetry is recorded with a computercontrolled PP211 electrochemical workstation using polymer films on platinum electrode (1.0cm²) as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (0.1 M) as thereference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) in acetonitrile at a scanning rate of 20 mV·s⁻¹. The HOMO and LUMO energy levels are calculated using the formula: $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8 - E_{\text{Fc/Fc}^+}) \text{ eV}$, $E_{\text{LUMO}} = -(E_{\text{red}} + 4.8 - E_{\text{Fc/Fc}^+}) \text{ eV}$; $E_{\text{opt p}} = 1240/\lambda_{\text{onset}}$. The current–voltage ($J^{1/2}$ – V) curves evaluated by space charge-limited

current (SCLC) method was fitted by $J = 9\epsilon_0\epsilon_r\mu V^2/8L^3$, where ϵ_0 is the permittivity of free space and constant at 8.85×10^{-12} F/m, ϵ_r 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. The contact angles of the films were measured on a DSA-100 (KRUSS Germany) contact angle meter. The grazing incidence X-ray scattering (GIWAXS) measurement was carried with Pohang Accelerator Laboratory beamline using an In-Vacuum Undulator 20B source (11.08 keV) and a 2D CCD Detector (Rayonix SX165, USA). The incidence angle was 0.12°. The samples for GIWAXS measurements were fabricated on silicon substrates using the same recipe for the devices. The surface area of the OPV cells is 0.11 cm² and process the active area at room temperature.

2. Synthesis of polymers



Four polymers are synthesized using a palladium-catalyzed Stille coupling reaction. All terpolymers are obtained from the reaction at 110 °C for 4 h under nitrogen and using toluene as the solvent with mixed catalyst of Pd₂(dba)₃ and P(o-tolyl)₃. Then, the crude polymers are purified by Soxhlet extraction and successively extracted with methanol, acetone, n-hexane, dichloromethane/chloroform (1:1), chloroform to

remove oligomers and other impurities, and finally extracted with chlorobenzene to collect the product polymers.

OPz11: 0.1 mmol monomer of BDT-2F and 0.095 mmol bromide monomer of DTBT and 0.005 mmol E-Tz;

OPz12: 0.1 mmol monomer of BDT-2F and 0.09 mmol bromide monomer of DTBT and 0.01 mmol E-Tz;

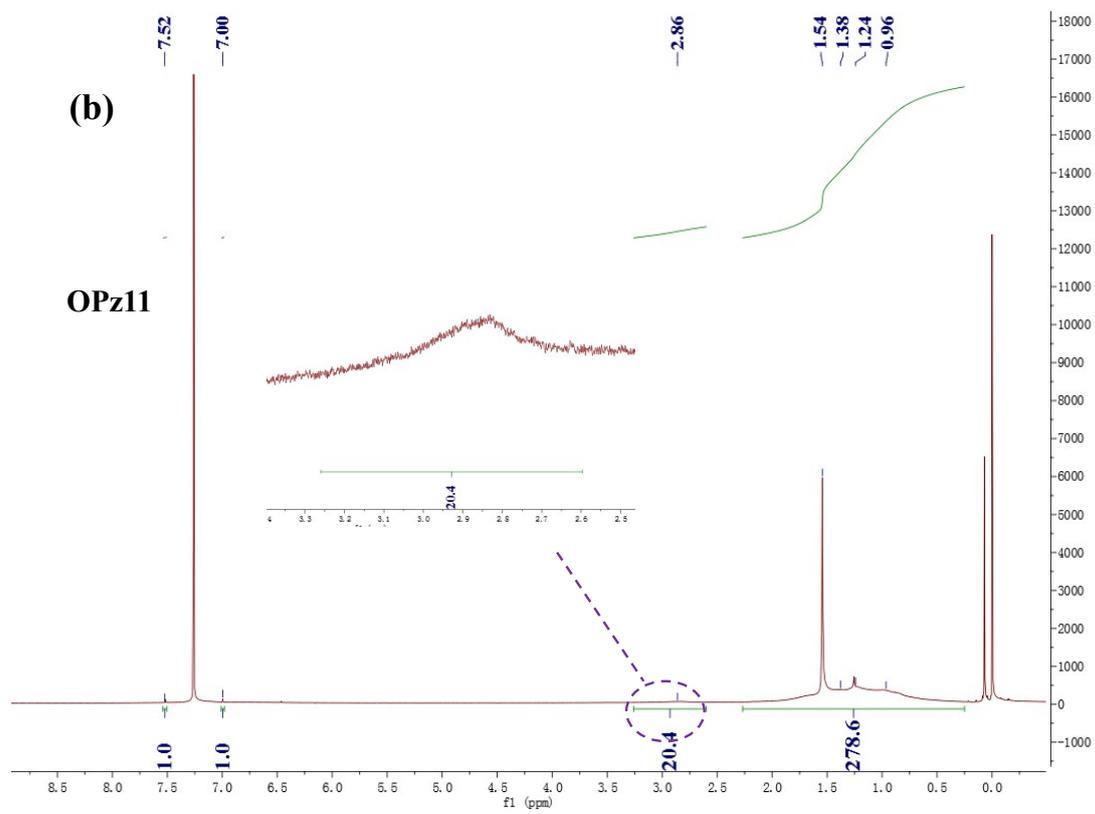
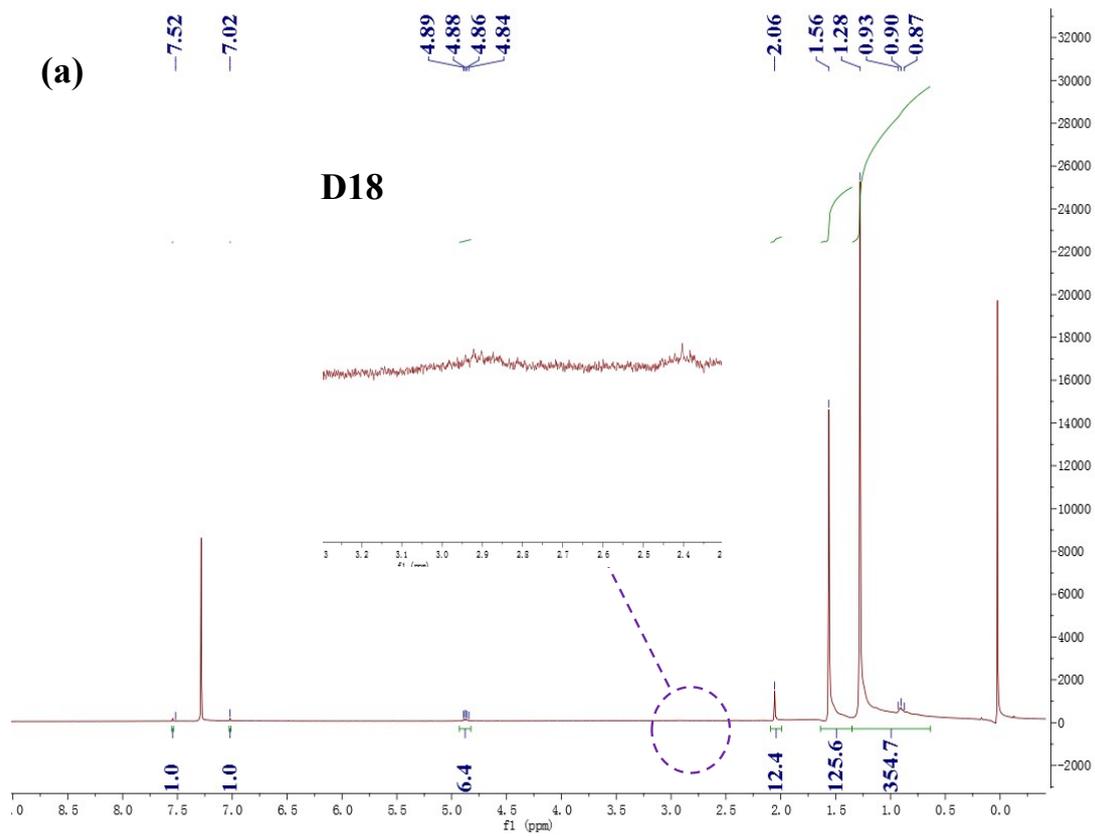
OPz13: 0.1 mmol monomer of BDT-2F and 0.08 mmol bromide monomer of DTBT and 0.02 mmol E-Tz;

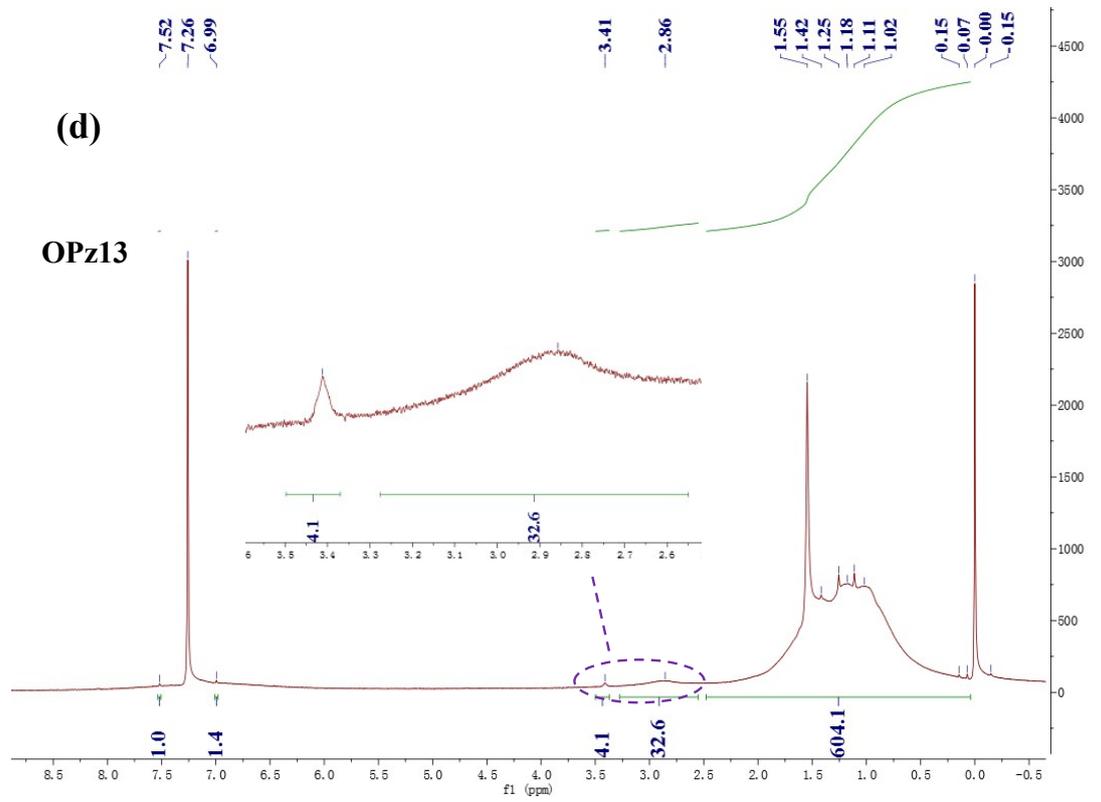
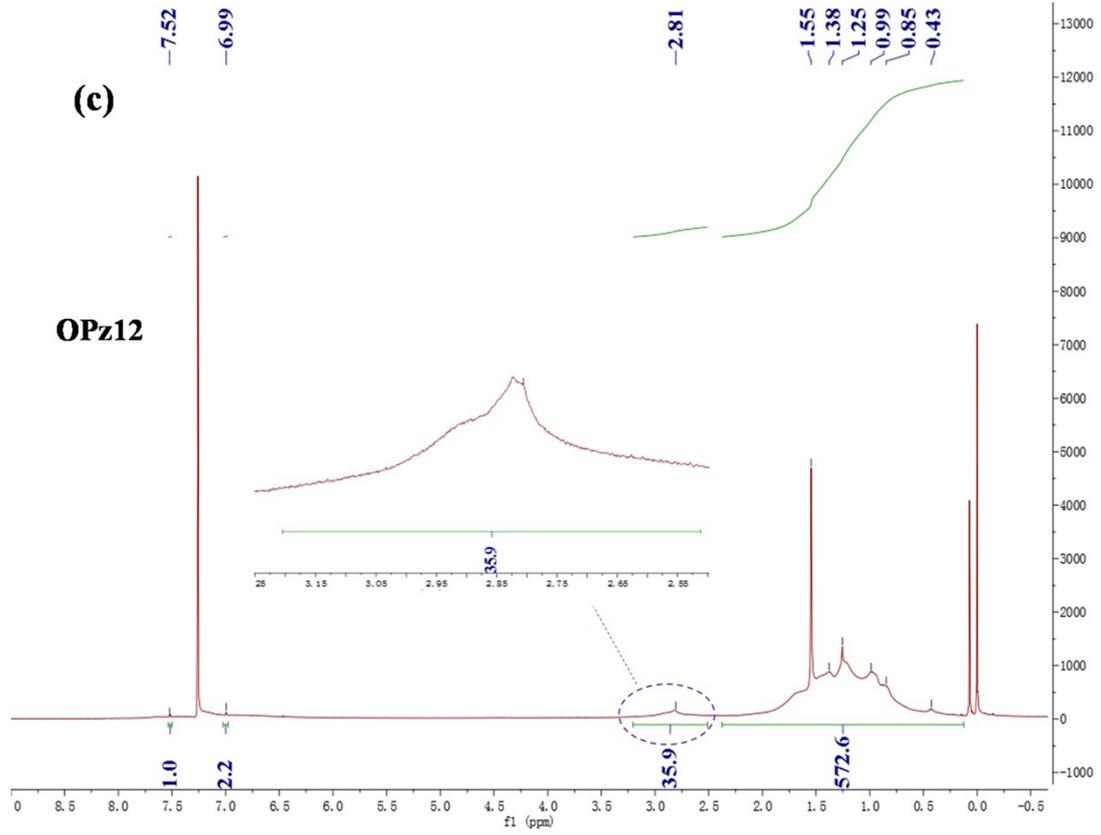
OPz14: 0.1 mmol monomer of BDT-2F and 0.05 mmol E-Tz and 0.05 mmol DTBT, are dissolve in toluene (8 mL).

$\text{Pd}_2(\text{dba})_3$ (2% mmol) and $\text{P}(\text{o-tolyl})_3$ (8% mmol) as catalyst were 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 for 4 h. The obtained copolymers were purified by Soxhlet extraction (the solvent using methanol, acetone and n-hexane, chloroform:dichloromethane (1:1), chloroform and chlorobenzene, respective) to remove the oligomers and other impurities. The polymer extracted from chlorobenzene was then precipitated in methanol (60 mL) and dried under vacuum for 6 h before use. The yields for OPz11 is around 65%, for OPz12 is around 68%, for OPz13 is around 70%, and for OPz14 is around 72%.

3. Device Fabrication

Traditional devices based on polymers and Y6 are fabricated according to following procedure. The ITO glass substrates are 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 120 °C in ambient atmosphere for 15 min (the film thickness ~30 nm). The best devices are preparation by spin-coating blend films with D/A ratio of 1:1.2 and donor concentration of 6 mg/ml and CF as processing solvent without any additives. The mixed solution are stirred for 4 h under 100 °C, and then cooled down to room temperature and stirred for 10 min before spin coating. Active layer are spun at 4000 rpm (the film thickness ~145 nm) and then solvent annealing with CF for 30 s. After spun the PDIN (2 mg/ml, 0.3% acetic acid, the film thickness ~30 nm) layer at 5000 rpm for 30 s. Finally, drying Ag layer with a thickness of about 90 nm are deposited onto the active layer under vacuum of about 2×10^{-6} Torr.





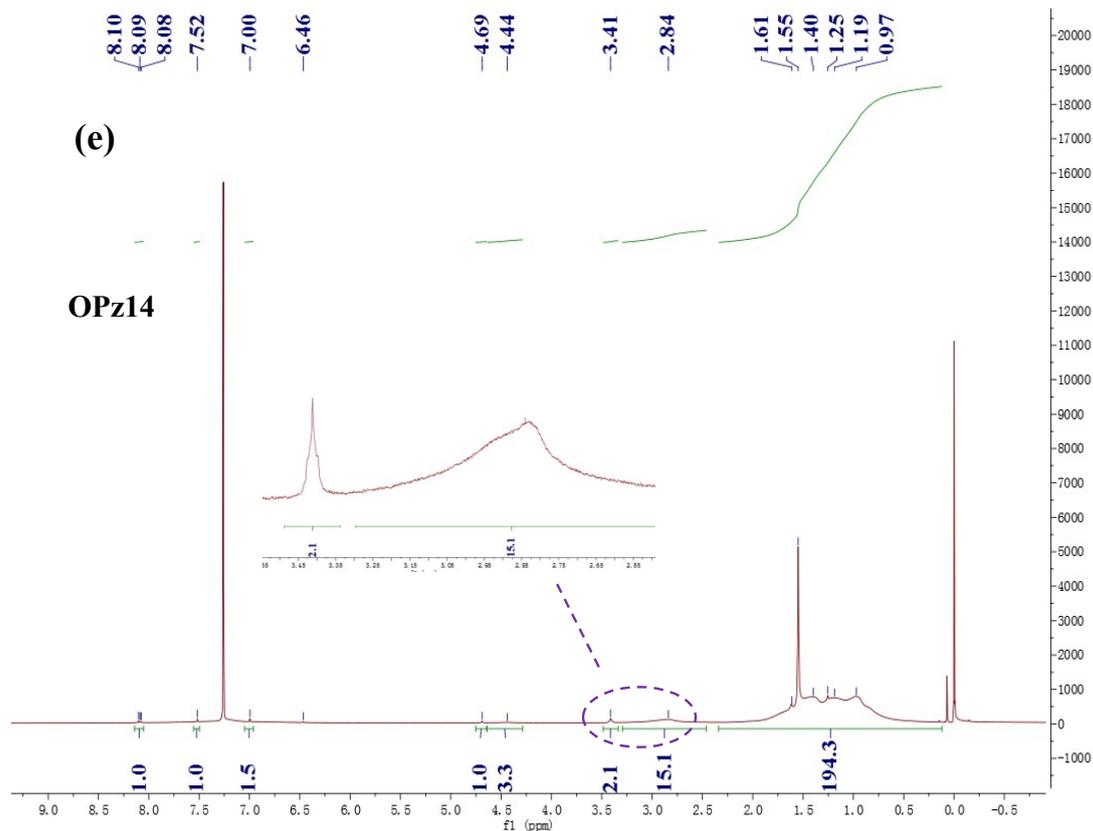


Fig. S1. ^1H NMR data of the copolymers in this work (a) D18; (b) OPz11; (c) OPz12; (d) OPz13; (e) OPz14.

Table S1. The device based on PCEs achieving 18% in recent reported.

Donor	Acceptor	Strategy	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	Ref.
PM7 and PCE10	TiF-4Cl ₂ COi8DFIC and PC ₇₀ BM	Tandem	1.64	14.59	78.0	18.71	Adv. Funct. Mater. 2021, 31, 2103283
PTQ10	m-BTP-PhC6 and PC ₇₁ BM	Ternary	0.869	26.99	80.6	18.89	Adv. Mater. 2021, 2105301
D18-Cl	Y6 and PC ₇₁ BM	Ternary	0.860	27.04	77.67	18.06	Adv. Funct. Mater. 2021, 31, 2102694
PM6	Y6 and AQx-3	Ternary	0.870	26.82	77.20	18.01	Adv. Mater. 2021, 33, 2100830
PM6	BO-4Cl and Y6-1O	Ternary	0.855	27.46	79.0	18.52	Adv. Funct. Mater. 2021, 2107827
PM6	BTP-eC9 and L8-BO-F	Ternary	0.853	27.35	80.0	18.66	Adv. Mater. 2021, 33, 2101733
PT-RI-4F	CH1007 and	Ternary	0.820	28.15	77.80	18.0	Adv. Energy Mater. 2021,

	PC ₇₁ BM						11, 2101768
PBQ _x -TF	eC9-2Cl	Binary	0.868	25.90	78.6	17.70	Adv. Mater. 2021, 33, 2102420
PBQ _x -TF	eC9-2Cl and F-BTA3	Ternary	0.879	26.70	80.90	19.0	
PB2T	BTP-eC9 (new acceptor)	Binary	0.916	10.30	53.10	4.99	Adv. Energy Mater. 2021, 11, 2101705
PB2T and PBDB-TF		Ternary	0.860	26.60	79.90	18.60	
PM6	L8-BO (new acceptor)	Hole transporting layer optimization	0.890	26.37	79.94	18.77	Angew.Chem. Int. Ed. 2021, 60,22554–22561
PM6	Y6-BO (new acceptor)	Binary (Post-optimization)	0.840	27.70	76.60	18.0	Adv. Energy Mater. 2021,11, 2102000
PM6	L8-BO (new acceptor)	Binary (firstly reported)	0.870	25.72	81.50	18.32	NatureEnergy, 2021, 6, 605
PM6	L8-BO (new acceptor)	Binary (Post-optimization)	0.893	26.03	80.0	18.60	Mater. 2021, 33, 2102420
PM6	L8-BO (new acceptor)	Binary (Post-optimization)	0.893	26.11	80.6	18.74	Adv. Funct. Mater. 2021, 2108797
PM6	BTP-eC9 (new acceptor)	Binary (firstly reported)	0.839	26.20	81.1	17.80	Adv. Mater. 2020, 32, 1908205
PM6	BTP-eC9 (new acceptor)	Binary (Post-optimization)	0.848	27.12	80.79	18.58	ACS Energy Lett. 2021, 6, 10, 3582–3589
PMZ-10	Y6	Binary	0.834	27.96	78.20	18.23	Adv. Funct. Mater. 2021, 2109271
PM6	Y-BO-FCI (new acceptor)	Binary	0.850	26.42	77.92	17.52	doi.org/10.1039/D1EE01832A
PNTB6-Cl	N3 (new acceptor)	Binary	0.857	26.58	77.30	17.59	Energy Environ. Sci., 2021,14, 5919-5928
PM6	BTP-4F-P2EH (new acceptor)	Binary (new acceptor)	0.880	25.85	80.08	18.22	Adv. Energy Mater. 2021, 2102596
PBDTT1Cl	Y18-1F (new acceptor)	Binary	0.870	27.70	71.35	17.10	doi.org/10.1002/adma.202105483
D18	Y6	Binary	0.859	27.70	76.60	18.22	Science Bulletin. 2020, 65, 272
OPz11 (New donor)	Y6	Binary (firstly reported)	0.865	27.02	78.71	18.42	this work

Table S2. The element analysis results of the terpolymers in this work.

Materilas	N %(theoretical)	C %(theoretical)	H %(theoretical)	S %(theoretical)	The actual ratios of E-Tz unit (N%-baed)
D18	2.00 (2.02)	67.75 (67.39)	7.58 (7.11)	21.29 (20.76)	0

OPz11	2.04 (2.03)	67.43 (67.10)	7.54 (7.00)	20.92 (20.94)	4.98%
OPz12	2.07 (2.02)	67.27 (66.95)	7.28 (6.97)	20.52 (20.94)	9.75%
OPz13	2.01 (2.01)	67.10 (66.77)	7.22 (6.91)	20.48 (20.92)	20.00%
OPz14	1.93 (1.95)	66.10 (65.67)	7.08 (6.59)	20.40 (20.80)	50.52%

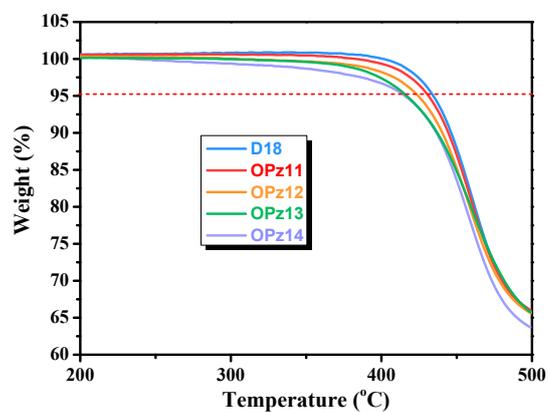


Fig. S2. The thermal stability of D18, OPz11, OPz12, OPz13 and OPz14.

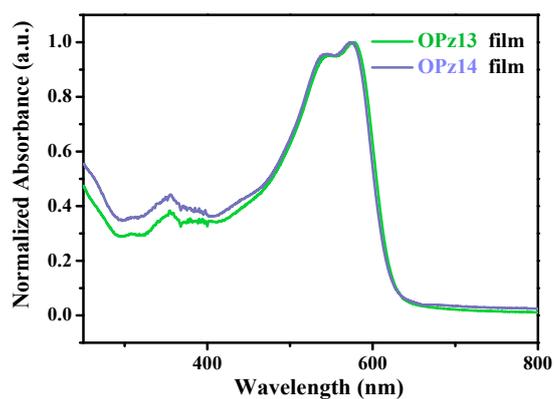


Fig. S3. The absorption of OPz13 and OPz14 film.

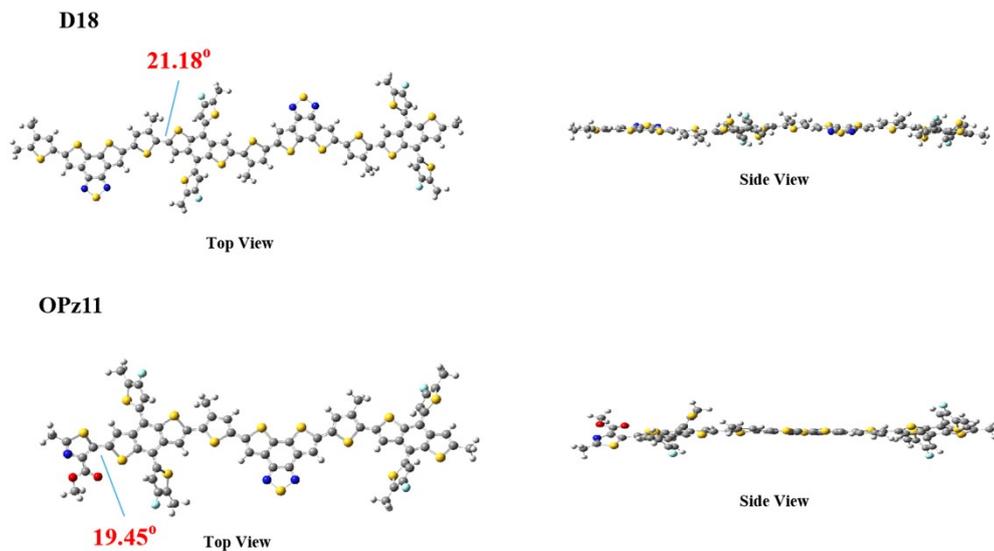


Fig. S4. The planarity and conjugation of the backbones for D18 and OPz11.

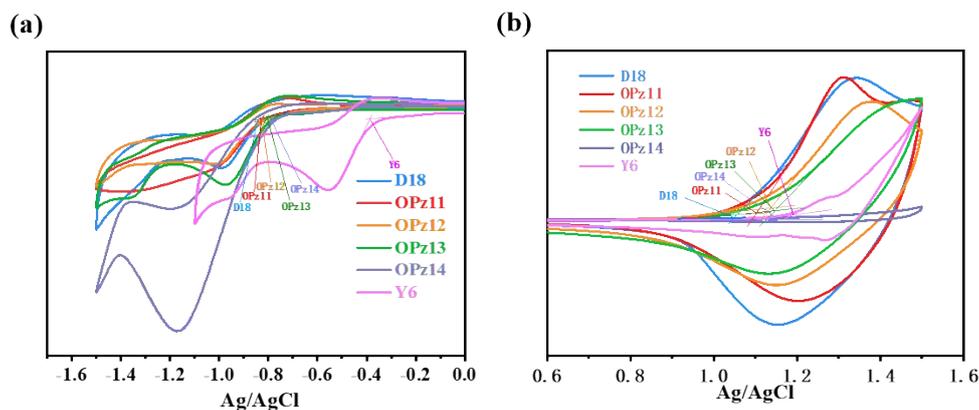


Fig. S5. The electrochemical cyclic voltammetry results of the terpolymers a) reduction curves and b) oxidation curves.

Table S3. The optical and electrochemical properties of OPz13 and OPz14.

Copolymers	M_n (kg/mol)	M_w (kg/mol)	\bar{D}	λ_{max} [nm]	λ_{edge}^a [nm]	$E_g^{opt\ b}$ [eV]	E_{HOMO}^c [eV]	E_{LUMO}^c [eV]
OPz13	60.56	117.91	1.95	575	618	2.00	-5.63	-3.71
OPz14	33.02	133.43	1.85	573	617	2.01	-5.65	-3.73

^{a)} Calculated from the onset absorption of thin films; ^{b)} $E_g^{opt} = 1240 / \lambda_{onset}^{film}$ (eV); ^{c)} Obtained from CV measurements.

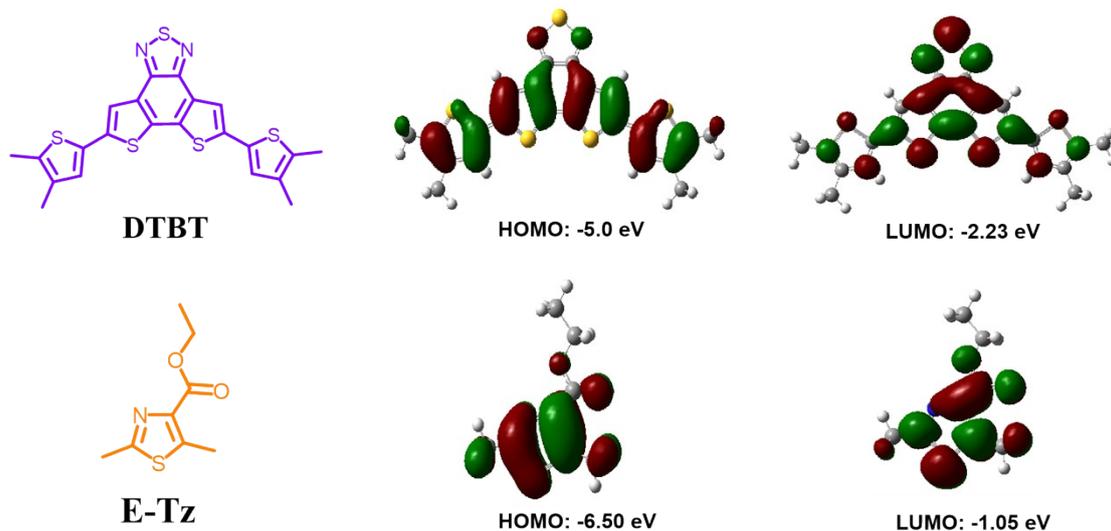


Fig. S6. The density functional theory calculations of monomers DTBT and E-Tz.

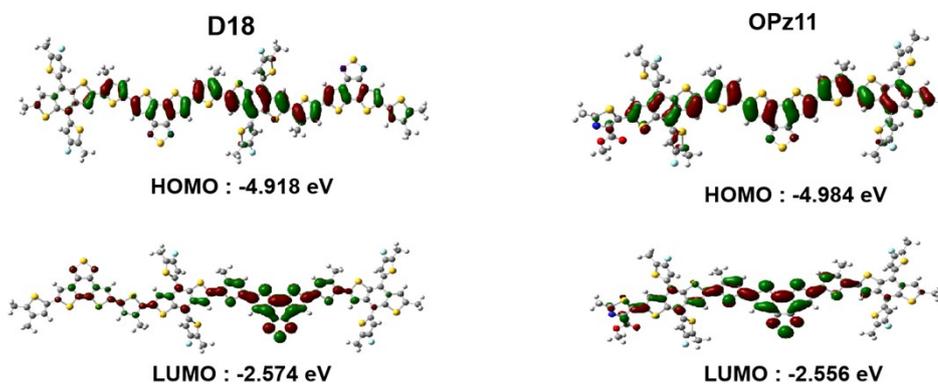


Fig. S7. The molecular backbone conformations and the HOMO and LUMO electron distributions for D18 and OPz11.

Table S4. The detailed device optimizing processes of OPz11:Y6-based device.

Active layer	Stirring temperature (°C)	Donor Concentration (mg/ml)	D/A	Spin coating rate (r)	Solvent annealing	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{best} (%)
OPz11:Y6	50 °C (Poorly dissolves)	6.2	1:1.6	3000	CS ₂ 30 s	860.1	25.97	72.35	16.16
		6	1:1.6	3000	CS ₂ 30 s	864.2	25.17	72.70	15.82
		5.5	1:1.6	3000	CS ₂ 30 s	861.8	25.36	74.12	16.21
		5	1:1.6	3000	CS ₂ 30 s	868.3	25.89	73.17	16.44
		5	1:1.4	3000	CS ₂ 30 s	859.0	26.06	72.73	16.27
			1:1.2	3000	CS ₂ 30 s	861.0	25.59	74.87	16.50
			1:1	3000	CS ₂ 30 s	861.2	25.72	72.71	16.11
			1:1.2	3000	CF 30 s	871.3	26.18	73.26	16.71
	100 °C (Dissolves well)	5	1:1.2	3000	CF 30 s	856.8	26.30	76.86	17.33
		5	1:1.2	4000	CF 30 s	863.1	26.0	78.34	17.57
		5.5	1:1.2	4000	CF 30 s	866.0	26.81	77.13	17.92
		6	1:1.2	4000	CF 30 s	865.3	27.03	78.71	18.42
			1:1.2	4500	CF 30 s	867.2	26.48	78.86	18.10
			1:1.2	3000	CF 30 s	867.2	26.99	76.75	17.97
		6.2	1:1.2	4000	CF 30 s	865.3	26.73	77.81	17.99
		6.5	1:1.2	4000	CF 30 s	865.3	26.77	76.9	17.78
	5000			CF 30 s	863.0	26.05	77.9	17.52	

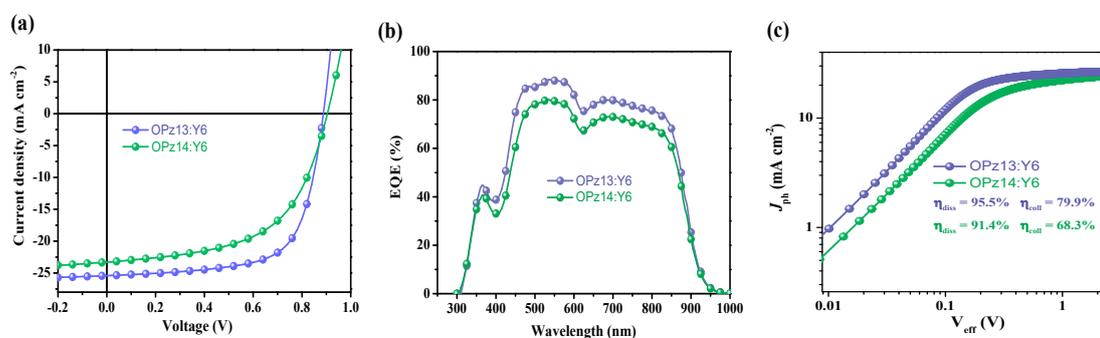


Fig. S8. a) The best J - V characteristics of OPz13:Y6 and OPz14:Y6 devices; b) the corresponding EQE spectra; c) the J_{ph} versus V_{eff} for OPz13:Y6 and OPz14:Y6 devices.

Table S5. The photovoltaic parameters of OPz13 and OPz14 with Y6 under the illumination of AM 1.5 G, 100 mW cm⁻².

Active layer	V_{oc} [mV]	J_{sc} [mA cm ⁻²]	FF [%]	J_{EQE} [mA cm ⁻²]	PCE ^a [%]
OPz13:Y6	888.2	25.42	67.78	25.16	15.29
OPz14:Y6	905.9	23.29	56.36	22.76	11.87

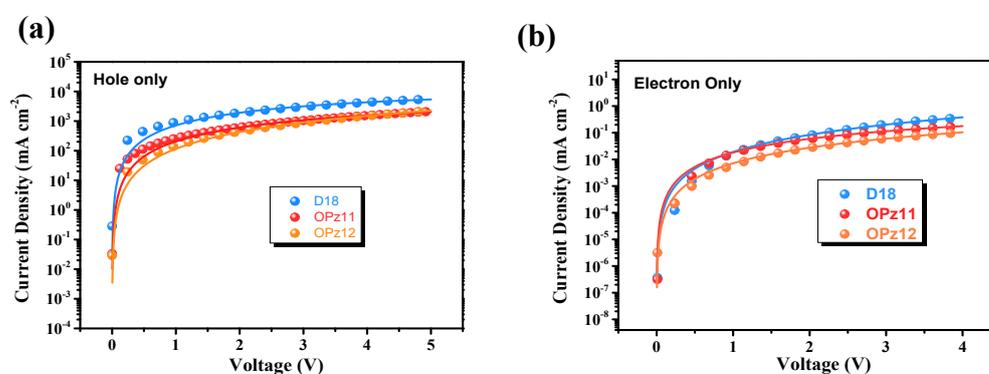


Fig. S9. The charge mobilities of D18-based, OPz11-based, OPz12-based devices (fitted curves).

Table S6. The charge mobilities of devices.

Mobility	Hole	Electron	Hole/electron
D18	2.02×10^{-3}	9.36×10^{-4}	2.16
OPz11	1.68×10^{-3}	8.18×10^{-4}	2.05
OPz12	8.53×10^{-4}	2.78×10^{-4}	3.06

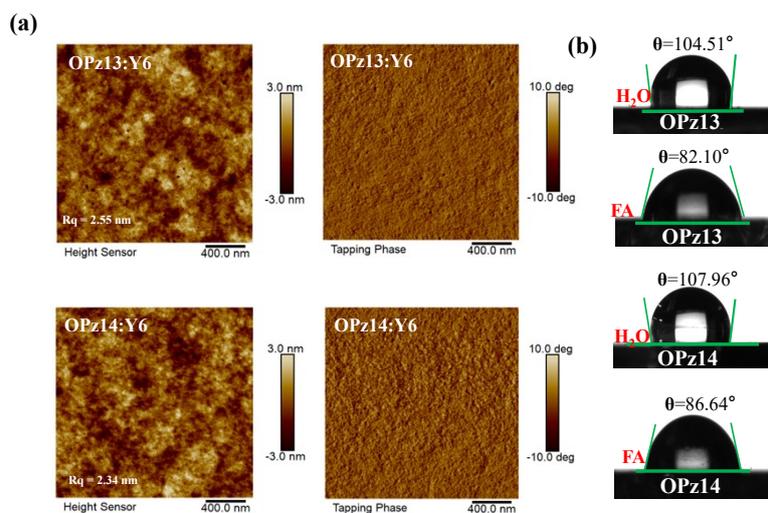


Fig. S10. a) AFM height and phase images; b) the contact angel measurements with H₂O and formamide (FA) for terpolymers OPz13 and OPz14, respectively.

Table S7. Summarized contact angles of the materials.

Films	Contact Angle (deg)	
	a) H ₂ O	b) formamide,FA
D18	109.51	86.92
	109.24	87.12
	109.97	86.44
	Average :109.57(±0.37)	
OPz11	105.42	83.36
	105.66	83.23
	105.32	83.96
	Average :105.47(±0.18)	
OPz12	103.23	81.60
	103.07	81.14
	103.40	81.79
	Average :103.23(±0.17)	
OPz13	104.57	82.16
	104.32	82.35
	104.64	81.80
	Average :104.51(±0.16)	
OPz14	107.91	83.95
	Average :82.10(±0.28)	

	107.78	83.60
	108.19	83.36
	Average :107.96(± 0.21)	Average :83.64(± 0.30)
Y6	93.57	71.68
	93.67	71.64
	93.60	71.81
	Average :93.61(± 0.05)	Average :71.71(± 0.09)

^{a)}Deionized water; ^{b)} formamide;

Table S8. Summarized average contact angles and surface free energy parameters of the materials

Films	Contact Angle (deg)		surface free energy, γ (mN m ⁻¹)
	^{a)} H ₂ O	^{b)} formamide,FA	
D18	109.57(± 0.37)	86.83(± 0.35)	21.67
OPz11	105.47(± 0.18)	83.52(± 0.39)	22.47
OPz12	103.23(± 0.17)	81.52(± 0.33)	23.16
OPz13	104.51(± 0.16)	82.10(± 0.28)	23.48
OPz14	107.96(± 0.21)	83.64(± 0.30)	24.50
Y6	93.61(± 0.05)	71.71(± 0.09)	27.94

^{a)}Deionized water; ^{b)} Formamide;

Table S9. The miscibility calculation results from surface free energy of the materials.

Film	$\Delta\delta$ ($\times K$)
D18:Y6	0.40
OPz11:Y6	0.29
OPz12:Y6	0.22
OPz13:Y6	0.19
OPz14:Y6	0.11

Table S10. Summary of the crystal coherence length for blend films.

Blend film	Lattice plane	Peak location (\AA^{-1})	d-spacing (\AA)	Coherence length (\AA)
		q_z	q_z	q_z
D18:Y6	010	1.713	3.666	32.57
OPz11:Y6	010	1.710	3.673	31.71
OPz12:Y6	010	1.708	3.677	31.29