Simple furan-based polymers featuring self-healing function enable efficient eco-friendly organic solar cells with high stability

Luwen Shang[1], Shengchun Qu[2], Yingying Deng[1], Yueyue Gao[1,], Gentian Yue[1], Furui Tan[1,*], Shenghua He[1], Zhijie Wang[2,*], Zhangguo Wang[2]*

[1]Key Laboratory of Photovoltaic Materials, Henan University, Kaifeng 475004, P. R. China.

Email:gaoyueyue@henu.edu.cn; frtan@henu.edu.cn

[2]Key Laboratory of Semiconductor Materials Science, Beijing Key Laboratory of Low Dimensional Semiconductor Materials and Devices, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, P. R. China.

Email: wangzj@semi.ac.cn

1. Experimental section

1.1 Materials

Anhydrous toluene and tetrahydrofuran (THF) were used after being dried over sodium/benzophenone. P3HT, $PC_{71}BM$, PTB7-Th and ITIC were purchased from Solarmer Inc company. PM6 and Y6 were purchased from Zhiyan Company (Nanjing, China). PCBO-12 was prepared according to the reported work.[1] Unless otherwise noted, other chemicals with chemically pure grade were purchased from Energy Chemical (Shanghai, China) and used as received without further purification.

1.2. Materials characterization

AVANCE III HD 400 MHz instrument using deuterochloroform ($CDCl_3$) as solvent and tetramethylsilane as reference was implemented to obtain the ^{1}H-NMR spectra. Spectrum Two infrared spectrometer was adopted to get the IR spectra. The gel permeation chromatography (GPC) with polystyrene as a standard and THF as the eluent at room temperature was performed with the assistance of Agilent PL-GPC 50, which was applied to determine the molecular weight (M_n/M_w) and polydispersity index (*PDI*) of target polymers. The absorption spectra were studied via UH4150 UV-Vis-NIR spectrophotometer. TAQ600 simultaneous TG-DSC instrument was used for thermogravimetric analysis (TGA) measurements (heating rate of 10 °C/min under N_2). X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra) was applied to investigate the composition and chemical structure of the photoactive layer post-treated with different condition. Bruker DEKTAK XT step profiler was applied to measure the thickness of the photoactive layer. CHI600E electrochemical workstation accompanied with a computer was used to carry out the cyclic voltammetry (CV) measurement, where the polymer film coated upon ITO served as the working electrode, platinum wire as the counter electrode and Ag/AgCl as the reference electrode, respectively. It is noted that the CV measurement was conducted with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile as electrolyte, and with the protection of N_2.

The relative dielectric constants (ε_r) of the PFO3 and PFO4 film were tested via capacitance (C)−voltage (V) measurements via CHI600E electrochemical workstation with a device structure of ITO/ZnO/sample/MoO_3/Ag and frequency range of 10^3−10^5 Hz. The ε_r is evaluated via the equation: $C = \varepsilon_0\varepsilon_r S/d$, where ε_0, S, and d represent the vacuum permittivity (8.85×10^{-12} Fm^{-1}), device area (0.0314 cm^2), and thickness of the tested film, respectively.

1.3. Device fabrication

The devices were fabricated with an inverted structure of ITO/ZnO (30 nm)/polymer:PCBO-12/MoO_3 (~8 nm)/Ag (90 nm). The laser patterned ITO-coated glasses (~12 Ω/sq) were successively cleaned by ultrasonic treatment in detergent, deionized water, acetone and isopropanol for 30 mins. Then, the ITO-coated glasses were quickly dried with nitrogen-flow, and treated with UV-ozone for 15 mins. Next, the ZnO precursor solution was spin-coated upon the ITO-coated glass with 4500 rpm for 30 s.[2] Following, the film was annealed at 220 °C for 40 mins in air, and then was further treated with UV-ozone for 10 mins. Meanwhile, the polymer:PCBO-12 (1:2.5, by weight) blends with a concentration of 5.5 mg/mL and 6.0 mg/mL for PFO3 and PFO4, respectively, were dissolved in ethanol/water (85:15, by volume) and kept stirring at 60 °C for overnight. Before spin-coating, 1.0 % p-anisaldehyde was added into the above solution and consecutively stirred at 60 °C for at least 1.0 h. Then, the polymer:PCBO-12 solution was quickly spin-coated upon the ZnO film via 1300 rpm for 40s, and annealed at 100 °C for 20 mins. To eliminate the residual water, the photoactive layer was dried under high vacuum conditions (10^{-5} Pa) for overnight. Finally, MoO_3/Ag (~8 nm/90 nm) was successively evaporated onto the photoactive layer under pressure of ~8.0×10^{-5} Pa. The active area of devices was defined by the shadow mask with 3.14 mm^2.

1.4. Device characterization

The current density-voltage (*J-V*) curves of devices were obtained using a Keithley 2400 source-meter when devices were illuminated under AM 1.5G illumination of 100 mW/cm^2 (Newport, Class A), where the light intensity was adopted a NREL-certified monocrystal silicon cell for calibration prior to measuring. The scan rate was fixed at 50 mV/s from −0.5 V to 1.0 V with 10 mV voltage steps. In the process of the measurement of *J-V*, the device was placed in inert atmosphere (~28 °C, V_{O2}≤1ppm, V_{H2O}≤1ppm). The active area (0.0314 cm^2) was determined using an aperture shade mask. The incident photon-to-electron conversion efficiency (IPCE) spectra were measured with a commercial photo modulation spectroscopic setup that included a Xenon lamp, an optical chopper, a monochromator, and a lock-in amplifier operated by a PC computer. Meanwhile, a calibrated Si photodiode was used as a standard in the IPCE measurement.

A self-designed system under dark was applied to conduct the TPC and TPV measurements, in which the photocurrent or photovoltage decay process was recorded by a digital oscilloscope (Tektronix, DPO 7104).

The charge mobility was characterized via the space charge limited current (SCLC) method, where single-carrier devices with structure of ITO/MoO_3 (10 nm)/polymer:PCBO-12/MoO_3 (5 nm)/Ag (90 nm) or ITO/ZnO (30 nm)/ polymer:PCBO-12/Ca (10 nm)/Al (100 nm) were fabricated for measuring the hole and the electron mobilities, respectively. The *J–V* curves for the hole-only or electron-only devices were measured and fitted to calculate the mobility based on the following equation.

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^3}$$

And J, L, μ, ε_r and ε_0 in the above equation represent the current density, the film thickness of the active layer, the charge (hole or electron) mobility, the relative dielectric constant of PTs, and the permittivity of free space (8.85×10^{-12} Fm^{-1}), respectively.

The photocurrent density (J_{ph}) versus the effective voltage (V_{eff}) curves was applied to investigate the exciton dissociation and charge collection properties, in which $J_{ph} = J_L - J_D$, where J_L and J_D are photocurrent densities under illumination and dark conditions, respectively.[3] $V_{eff} = V_0 - V_{bias}$, where V_0 is the voltage at which J_{ph} is zero and V_{bias} is the applied external bias voltage. The value of exciton dissociation probability P_{diss} could be calculated via $P_{diss} = J_{ph}/J_{sat}$, where J_{sat} is the saturation photocurrent density).

Multimode 8 scanning probe microscope in tapping mode was applied to get the AFM height and phase images of the photoactive layer. TEM patterns were acquired on JEOL JEM-2100 microscope (accelerating voltage, 200 kV), where the sample was prepared by spin-casting polymer:PCBO-12 solution onto copper grids attached to glass under optimized device fabricating conditions. Grazing incidence wide-angle X-ray scattering (GIWAXS) experiments were performed at South China University of Technology in China. The photoactive layer for the GIWAXS measurements were prepared on ZnO-coated ITO substrate according to the optimized device conditions.

1.5. Material synthesis

Synthesis of 2

The 3-furoicacid (1.12 g, 10 mmol) and glacial acetic acid (60 mL) were placed into a 250 mL three-necked flask equiped with reflux condensing tube and tail gas receiver. Then, the Br_2 solution in acetic acid (1M, 55 mL) was carefully added to the flask through drop funnel dropwise at room temperature. After that, the mixture was slowly warmed and consecutively stirred at ~90 °C for overnight. Subsequently, the mixture was poured into 200 mL deionized water, and then the saturated solution of $Na_2S_2O_3$ in deionized water was slowly added to the mixture to decolorize. After dehydration and evaporation of the solvent, the crude product was purified by recrystallization from deionized water to obtain compound 2 with 2.31 g (85.6%). ^{1}H-NMR (400 MHz, DMSO-d6, δ ppm): 13.32 (*s*, 1H), 7.41 (*s*, 1H).

Synthesis of 3 for PFO3

The compound 2 (1.08 g, 4.0 mmol), DMAP (0.19 g, 1.6 mmol), DCC (1.03 g, 5 mmol) and CH_2Cl_2 (30mL) were placed into a 100 mL single-necked flask. Then, triethylene glycol monomethyl ether (3.28g, 20 mmol) in CH_2Cl_2 (10mL) was added dropwise into the flask. Following, the mixture was stirred at ~ 25 °C for overnight under N_2 atmosphere. After that, the mixture was poured into deionized water (50 mL), and then extracted with CH_2Cl_2 (3×30 mL). The organic phase was dried with anhydrous $MgSO_4$ and the solvent was removed. Finally, the crude product was purified by column chromatography on silica gel using hexane/ethyl acetate (6:5) as eluent, and compound 3 was obtained with 1.35 g (81.1%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): δ 6.67 (*s*, 1H), 4.33 (*t*, 2H), 3.81 (*t*, 2H), 3.56 (*m*, 8H), 3.30 (*s*, 3H).

Synthesis of 3 for PFO4

The compound 2 (1.11g, 4.1 mmol), DMAP (0.18 g, 1.5 mmol), DCC (1.03 g, 5 mmol) and CH_2Cl_2 (30mL) were placed into a 100 mL single-necked flask. Then, tetraethylene glycol monomethyl ether (4.17g, 20 mmol) in CH_2Cl_2 (10mL) was added dropwise into the flask. Following, the mixture was stirred at ~25 ^oC for overnight under N_2 atmosphere. After that, the mixture was poured into deionized water (50 mL), and then extracted with CH_2Cl_2 (3×30 mL). The organic phase was dried with anhydrous $MgSO_4$ and the solvent was removed. Finally, the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (6:4) as eluent, and compound 3 was obtained with 1.52 g (80.6%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): δ 6.64 (*s*, 1H), 4.31 (*t*, 2H), 3.80 (*t*, 2H), 3.54 (*m*, 8H), 3.30 (*s*, 3H).

Synthesis of 5

The CuI (2.86g, 15.0 mmol), *t*-BuOK (2.58g, 23.0mmol), diethylene glycol monomethyl ether (18.02g, 150.0 mmol) and DMF (60 mL) were placed into a 250 mL three-necked flask equiped with reflux condensing tube and droplet funnel with constant pressure. After the mixture was stirred at room temperature for 2.0h, the 3-bromofuran (10.36g, 70mmol) in DMF (30mL) was added into the flask dropwise via the droplet funnel. Then, the mixture was heated until ~100 ^oC, and stirred for 24.0 h at this temperture. After that, the mixture was poured into water (100mL) and extrated with CH_2Cl_2 (3×50 mL). The organic phase was further washed successively with water (3×50 mL) and saturated NaCl solution in water. Following, the organic solution was dried with anhydrous $MgSO_4$ and the solvent was removed. Finally, the crude product was purified by vacuum distillation to obtain compound 5 with 10.43 g (80.0%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): δ 7.01 (*s*, 1H), 6.89 (*d*, 1H), 6.05 (*d*, 1H), 4.31 (*t*, 2H), 3.79 (*t*, 2H), 3.53 (*m*, 4H), 3.30 (*s*, 3H).

Synthesis of 6

The compound 5 (1.86g, 10.0 mmol) and anhydrous THF (20mL) were palced into a 50 mL single-necked flask. After the flask was vacuumed and refilled with N_2 three times, the flask was placed into the bath full of the mixture of liquid nitrogen and ethanol, whose temperature was about −78 °C, and stirred for ~0.5 h under the N_2 atmosphere. Then, n-BuLi (21.1 mmol, 13.2 mL, 1.6 M in hexane) was injected into the flask via 15 mL injection syringe dropwise. After finished, the mixture was further stirred at −78 °C for 1.0 h. Following, trimethyltin chloride (21 mmol, 21 mL, 1M in hexane) was injected into the flask via 10 mL injection syringe dropwise, then the mixture was stirred at −78 °C for 1.0 h. After that, the flask was gradually warmed to room temperature and stirred for ~6.0 h. The mixture was poured into the water and extracted with diethyl ether (3×30 mL). The organic solution was dried with anhydrous Na_2SO_4 and the solvent was removed under vacuum. Subsequently, the mixture was quickly passed through a plug of aluminium oxide pretreated with triethylamine, and further purified by vacuum distillation to obtain compound 6 with 4.21 g (82.4%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): δ 6.26 (*s*, 1H), 4.28 (*t*, 2H), 3.75 (*t*, 2H), 3.51 (*m*, 4H), 3.30 (*s*, 3H), 0.29 (*s*, 18H).

Synthesis of PFO3

The compound 3 (104 mg, 0.25 mmol) and compound 6 (128 mg, 0.25 mmol) were placed into a single-neck bottom-flask (25 mL), and the flask was vacuumed and refilled with N_2 three times. Following, $Pd_2(dba)_3$ (5 mg) and $P(o\text{-}tol)_3$ (10 mg) were quickyly added into the flask, and the falsk was once again vacuumed and refilled with N_2 three times. Then, toluene (10 mL) and DMF (1.5mL) were quickly injected into the flask via injection syringe. Subsequently, the mixture was heated at 110 ^{o}C for 16 h. Afterwards, 1.00 mmol phenyltri-n-butyltin (home-made) was injected into the flask and the mixture was consecutively stirred for 1.0 h. Then, 1.05 mmol 2-bromobenzene was also injected into the flask and the mixture was further consecutively stirred for 1.0 h. After the reaction was finished, the mixture was poured into hexane and further purified by Soxhlet extraction with hexane, dichloromethane, and chloroform. The extracted solution in chloroform was precipitated into hexane, centrifuged with hexane (3×10 mL), and then dried under vacuum overnight to obtain PFO3 (89.0 mg, 80.2%). GPC (THF): Mn=13.2 KDa; Mw=24.1 KDa; PDI=1.83. ^{1}H-NMR (300 MHz, $CDCl_3$, δ ppm): 7.51 (m, H), 7.23(m, H), 3.77-3.62(br, 16H), 3.42(br, 6H), 1.24(m, 6H). FTIR (cm^{-1}): 849, 1103, 1278, 1453, 1614, 2882, 2940, 2970, 3093, 3438. Calcd for $C_{21}H_{30}O_{10}$: C, 57.01; H, 6.83; O, 36.16; Found (%): C, 57.20; H, 6.91.

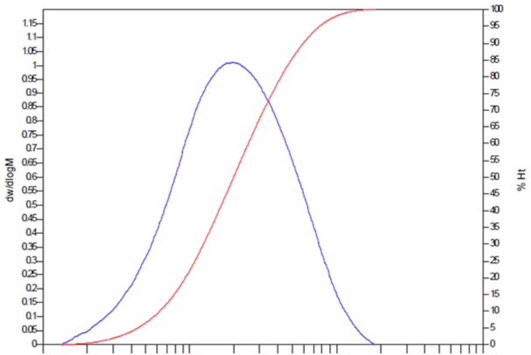


Fig. S1 The pattern of GPC measurement of PFO3.

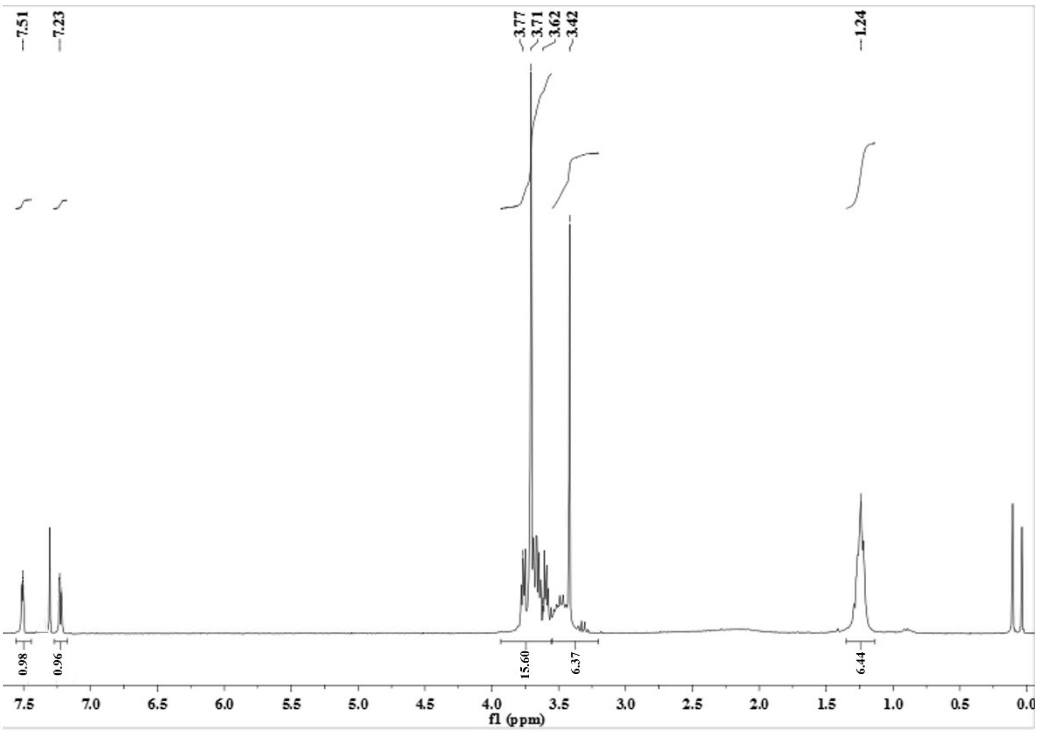


Fig. S2 ^{1}H-NMR spectroscopy of PFO3.

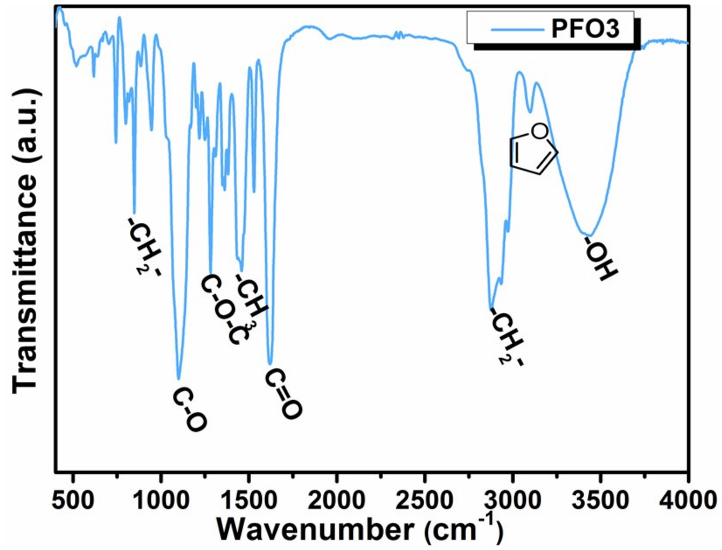


Fig. S3 FTIR spectroscopy of PFO3.

Synthesis of PFO4

The compound 3 (115 mg, 0.25 mmol) and compound 6 (128 mg, 0.25 mmol) were placed into a single-neck bottom-flask (25 mL), and the flask was vacuumed and refilled with N_2 three times. Following, $Pd_2(dba)_3$ (5 mg) and $P(o\text{-}tol)_3$ (10 mg) were quickyly added into the flask, and the falsk was once again vacuumed and refilled with N_2 three times. Then, toluene (10 mL) and DMF (1.5mL) were quickly injected into the flask via injection syringe. Subsequently, the mixture was heated at 110 ^{o}C for 16 h. Afterwards, 1.00 mmol phenyltri-n-butyltin (home-made) was injected into the flask and the mixture was consecutively stirred for 1.0 h. Then, 1.05 mmol 2-bromobenzene was also injected into the flask and the mixture was further consecutively stirred for 1.0 h. After the reaction was finished, the mixture was poured into hexane and further purified by Soxhlet extraction with hexane, dichloromethane, and chloroform. The extracted solution in chloroform was precipitated into hexane, centrifuged with hexane (3×10 mL), and then dried under vacuum overnight to obtain PFO4 (99.7 mg, 81.7%). GPC (THF): Mn=11.5 KDa; Mw=20.1 KDa; PDI=1.75. ^{1}H-NMR (300 MHz, $CDCl_3$, δ ppm): 7.50(m, H), 7.22(m, H), 3.74-3.63(br, 20H), 3.54(br, 6H), 1.23(m, 6H). FTIR (cm^{-1}): 847, 1102, 1285, 1460, 1612, 2873, 2924, 2976, 3102, 3420. Calcd for $C_{23}H_{34}O_{11}$: C, 56.78; H, 7.04; O, 36.17; Found (%): C, 57.02; H, 7.10.

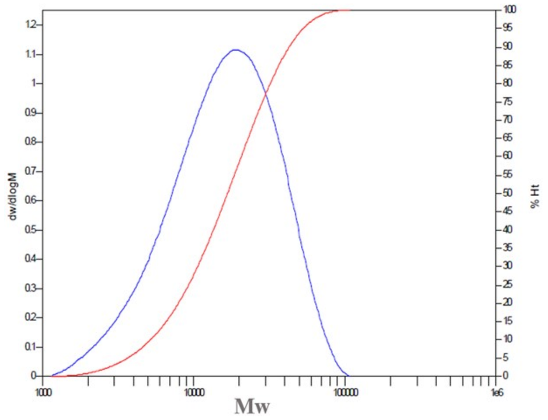


Fig. S4 The pattern of GPC measurement of PFO4.

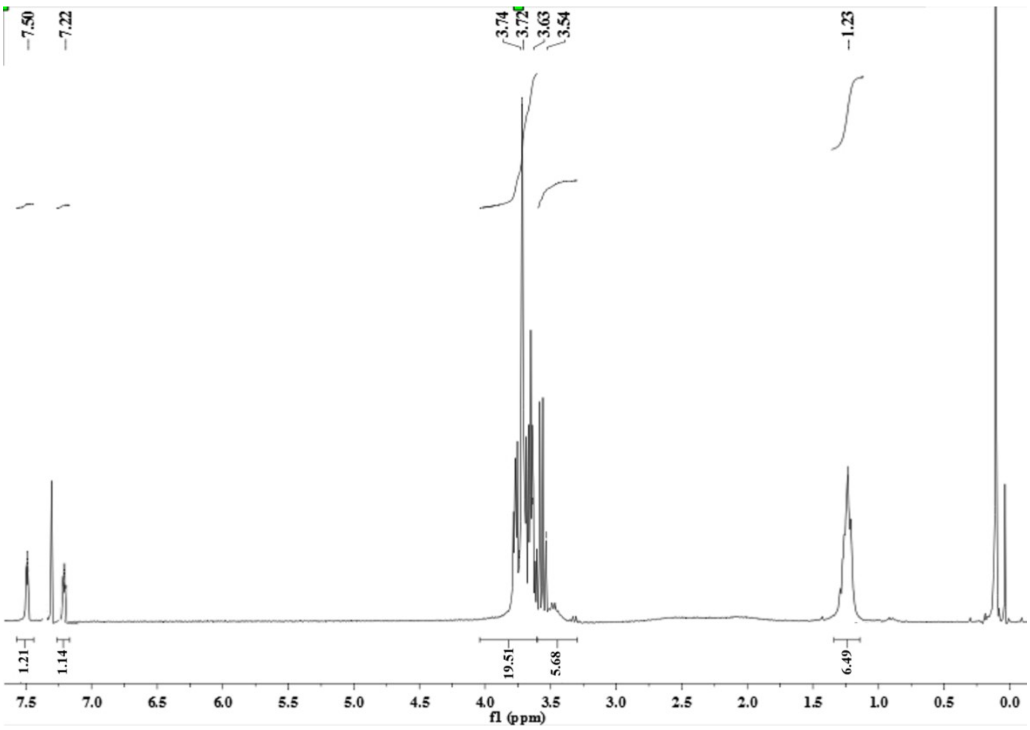


Fig. S5 ^{1}H-NMR spectroscopy of PFO4.

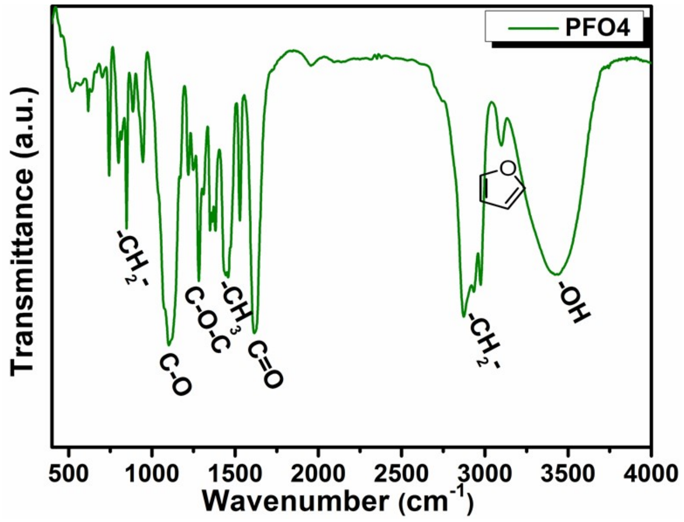


Fig. S6 FTIR spectroscopy of PFO4.

2. Result and discussion

Table S1 The toxicological properties of representative solvents uesd in OSCs.

Solvent	Toxicity	Median lethal dose (mouse)	Allowable concentration in air (ppm)	Environmental friendliness
Dichlorobenzene	++++++	500mg/kg (rabbit)	50	Worst
Chloroform	+++++	1194mg/kg	50	Worst

Chlorobenzene	++++	1445mg/kg	75	Worst
o-xylene	++	1500 mg/kg	100	Worse
Toluene	+++	5000mg/kg	100	Worse
Tetrahydrofuran	++	1650mg/kg	250	Medium
Alcohol/Water	no	no	no	Good

Table S2 The price of the commercial raw materials in the preparation of PFO3 and PFO4.

Raw materials	CAS	Price (RMB)	Source
3-furoicacid	488-93-7	1000/100g	Beijing Ouhe Technology CO., LTD in China
3-bromofuran	22037-28-1	485/25g	Energy Chemical crop in China
Bromine	7726-95-6	198/100mL	Energy Chemical crop in China
Acetic acid	64-19-7	98/500mL	Energy Chemical crop in China
Diethylene glycol monomethyl ether	111-77-3	30/100mL	Energy Chemical crop in China
Triethylene glycol monomethyl ether	112-35-6	43/100mL	Energy Chemical crop in China
Tetraethyleneglycol monomethyl ether	23783-42-8	189/25g	Energy Chemical crop in China
n-butyllithium	109-72-8	175/500mL	Energy Chemical crop in China
Trimethyltin chloride	1066-45-1	950/100mL	Energy Chemical crop in China
dimethylaminopyridine	1122-58-3	61/100g	Energy Chemical crop in China
dicyclohexylcarbodiimide	538-75-0	58/100g	Energy Chemical crop in China
$Pd_2(dba)_3$	51364-51-3	850/5g	Energy Chemical crop in China
$P(o\text{-}tol)_3$	6163-58-2	85/25g	Energy Chemical crop in China
CuI	7681-65-4	95/100g	Energy Chemical crop in China
t-BuOk	865-47-4	45/100g	Energy Chemical crop in China
Anhydrous THF	109-99-9	30/500mL	Prepared in our laboratory

Na_2SO_4	7757-82-6	55/500g	Local manufacturers
Anhydrous toluene	108-88-3	50/500mL	Prepared in our laboratory
DMF	68-12-2	90/500mL	Energy Chemical crop in China
$Na_2S_2O_3$	10102-17-7	50/500g	Local manufacturers
Dichloromethane	75-09-2	50/500mL	Local manufacturers
Ethyl acetate	141-78-6	60/500mL	Local manufacturers
$MgSO_4$	7487-88-9	25/500g	Local manufacturers
Chloroform	67-66-3	50/500mL	Local manufacturers
Hexane	110-54-3	25/500mL	Local manufacturers
Deionized water		10/5L	Local manufacturers
Silical gel (200~300 mesh)		30/kg	Yantai Xincheng Silicone Materials Co.,LTD in China

Table S3 The statistics of the material cost of PFO3 with 1.0 gram.

	Raw materials	Commercial cost (RMB)	Need amount (g)	Total cost (RMB)
Step 1	3-furoicacid	1000/100g	1.12	11.2
	Bromine	198/100mL	55 mL	108.9
	Acetic acid	98/500mL	60 mL	11.76
	Deionized water	10/5L	200 mL	0.4
	$Na_2S_2O_3$	50/500g	15	1.5
	Compound 2	85.6% yield	2.31	57.9
Step 2	Compound 2		1.08	62.5

	dimethylaminopyridine	61/100g	0.19	0.12
	dicyclohexylcarbodiimide	58/100g	1.03	0.60
	Dichloromethane	50/500mL	30 mL	3.0
	Triethylene glycol monomethyl ether	43/100mL	3.28	1.41
	Dichloromethane	50/500mL	10 mL	1.0
	Deionized water	10/5L	50 mL	0.1
	Dichloromethane	50/500mL	90 mL	4.5
	Hexane	25/500mL	800 mL	40
	Ethyl acetate	60/500mL	600 mL	72
	Compound 3	81.1%yield	1.35	137.2
Step 3	CuI	95/100g	2.86	2.72
	t-BuOk	45/100g	2.58	1.16
	Diethylene glycol monomethyl ether	30/100mL	18.02	5.41
	DMF	90/500mL	60 mL	10.8
	3-bromofuran	485/25g	10.36	201
	DMF	90/500mL	30 mL	5.4
	Dichloromethane	50/500mL	150 mL	15
	Deionized water	10/5L	100 mL	0.2
	Compound 5	80.0%yield	10.43	23.2
Step 4	Compound 5		1.86	43.2

	THF	30/500mL	20	1.2
	n-butyllithium	175/500mL	13.2 mL	4.62
	Trimethyltin chloride	950/100mL	21 mL	199.5
	diethyl ether	100/500mL	60 mL	12
	Compound 6	82.4%yield	4.21	61.9
Step 5 for polymerization	Compound 3	137.2/g	0.104	14.27
	Compound 6	61.9/g	0.128	7.92
	$Pd_2(dba)_3$	850/5g	0.005	0.85
	$P(o\text{-}tol)_3$	85/25g	0.010	0.034
	Anhydrous toluene	50/500mL	10 mL	1.0
	DMF	90/500mL	1.5 mL	0.27
	Hexane	25/500mL	30 mL	1.5
	PFO3	80.2%yield	0.089	290.37RMB/g (44.83 $/g)

Table S4 The statistics of the material cost of PFO4 with 1.0 gram.

	Raw materials	Commercial cost (RMB)	Need amount (g)	Total cost (RMB)
Step 2	Compound 2		1.11	64.3
	dimethylaminopyridine	61/100g	0.18	0.11
	dicyclohexylcarbodiimide	58/100g	1.03	0.60
	Dichloromethane	50/500mL	30 mL	3.0

	Tetraethyleneglycol monomethyl ether	189/25g	4.17	31.5
	Dichloromethane	50/500mL	10 mL	1.0
	Deionized water	10/5L	50 mL	0.1
	Dichloromethane	50/500mL	90 mL	4.5
	Hexane	25/500mL	800 mL	40
	Ethyl acetate	60/500mL	400 mL	48
	Compound 3	80.6%yield	1.52	127.0
Step 5 for polymerization	Compound 3	127.0/g	0.115	14.61
	Compound 6	61.9/g	0.128	7.92
	$Pd_2(dba)_3$	850/5g	0.005	0.85
	$P(o\text{-}tol)_3$	85/25g	0.010	0.034
	Anhydrous toluene	50/500mL	10 mL	1.0
	DMF	90/500mL	1.5 mL	0.27
	Hexane	25/500mL	30 mL	1.5
	PFO4	1.7%yield	0.0997	262.63RMB/g (40.55 $/g)

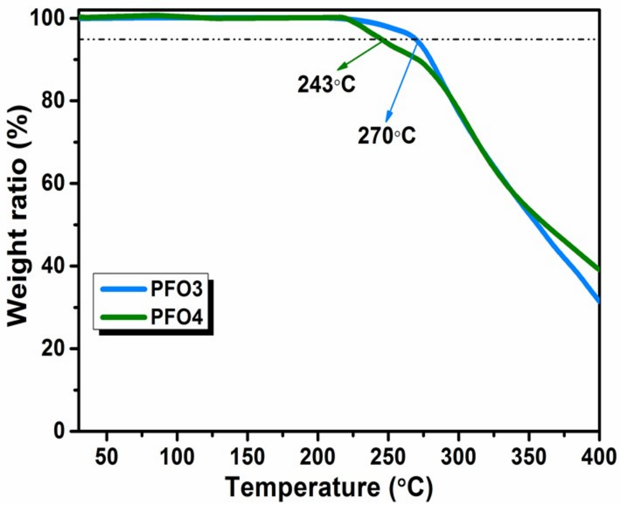
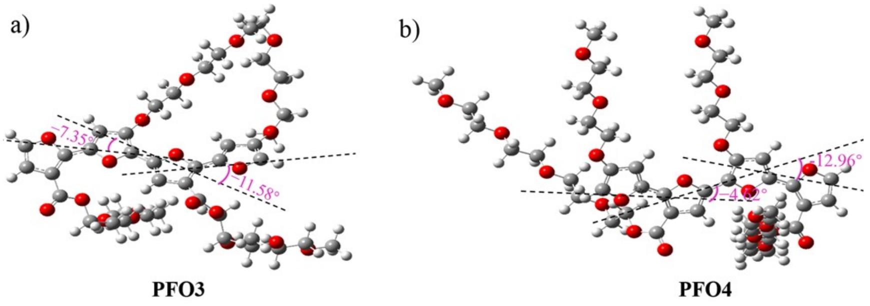


Fig. S7 The thermal gravimetric curves of PFO3 and PFO4.



PFO3

PFO4

Fig. S8 The top view of PFO3 and PFO4 obtained from DFT calculation.

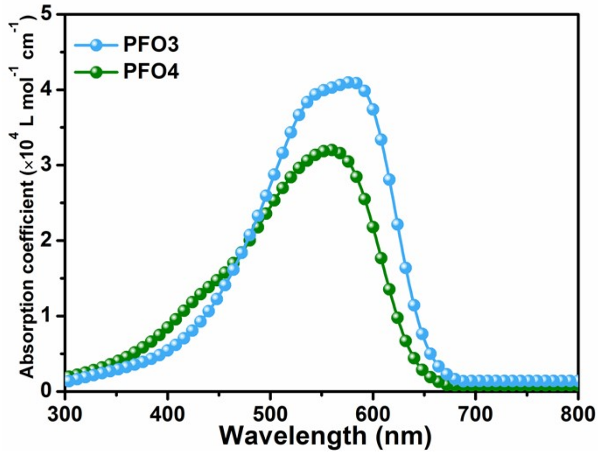


Fig. S9 The UV-Vis absorption spectra of PFO3 and PFO4 in ethanol solution.

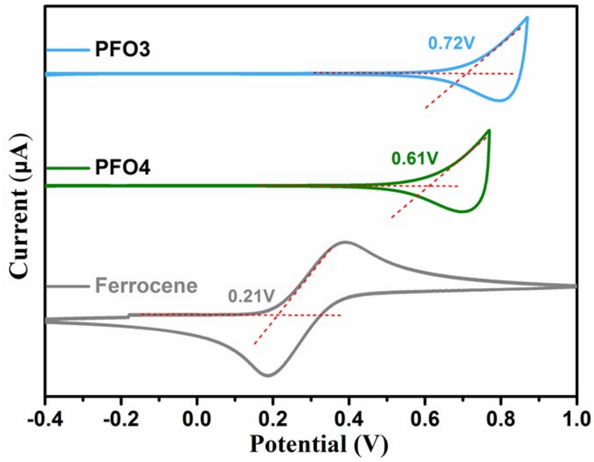
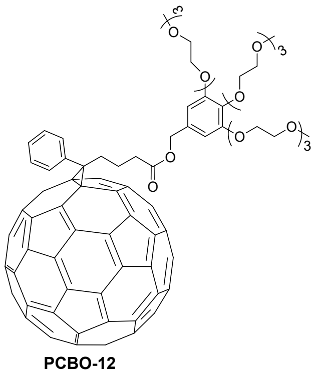


Fig. S10 The cyclic voltammetric curves of PFO3, PFO4 and ferrocene.



PCBO-12

Fig. S11 The chemical structure of PCBO-12.

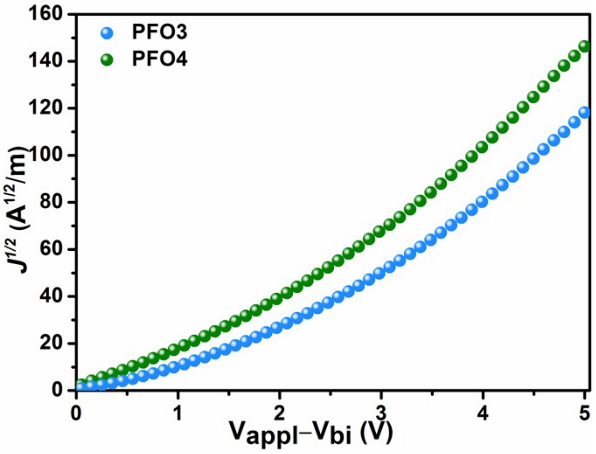


Fig. S12 The $J^{1/2}$-V characteristics of hole-only devices (ITO/MoO_3/polymer/MoO_3/Ag) based on PFO3 or PFO4 pristine film processed with ethanol and thermally annealed at 100 °C for 20 min (Note that the pristine PFO3 film was dried under high vacuum conditions (10^{-5} Pa) overnight before measurement for eliminating the influence of the residual water)

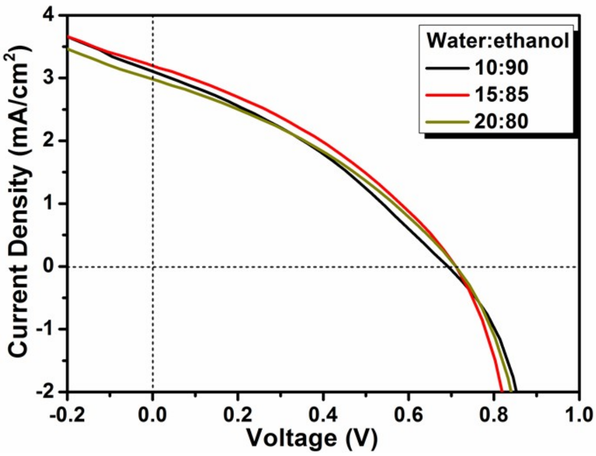


Fig. S13 $J-V$ curves of PFO3:PCBO-12 devices with different ratio between water and ethanol as process solvent (other condition is that the concentration of PFO3 is 5.5 mg/mL, the ratio of D:A is 1:2.5 by weight, and dried under high vacuum conditions (10^{-5} Pa) overnight before thermal deposition of MoO_3).

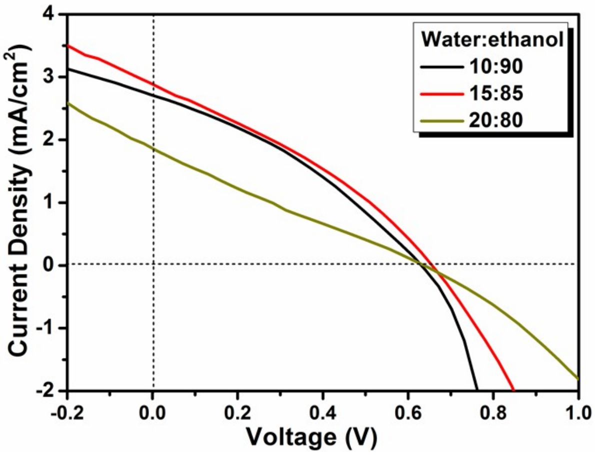


Fig. S14 $J-V$ curves of PFO4:PCBO-12 devices with different ratio between water and ethanol as process solvent (other condition is that the concentration of PFO4 is 6.0 mg/mL, the ratio of D:A is 1:2.5 by weight, and dried under high vacuum conditions (10^{-5} Pa) overnight before thermal deposition of MoO_3).

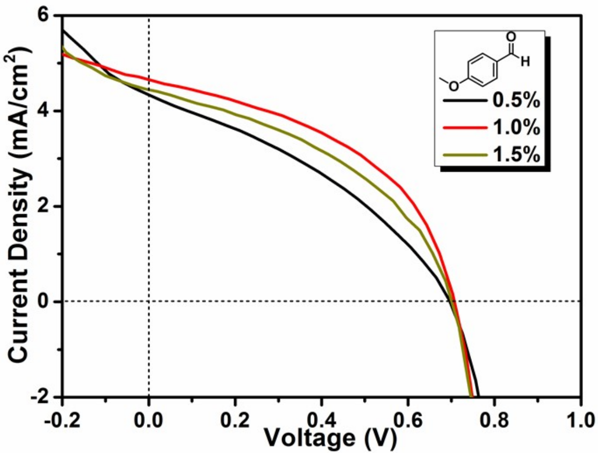


Fig. S15 *J*−*V* curves of PFO3:PCBO-12 devices with different concentration of p-anisaldehyde additive (other condition is that the concentration of PFO3 is 5.5 mg/mL, the ratio of D:A is 1:2.5 by weight, the ratio of water:ethanol is 15:85, and dried under high vacuum conditions (10^{-5} Pa) overnight before thermal deposition of MoO_3).

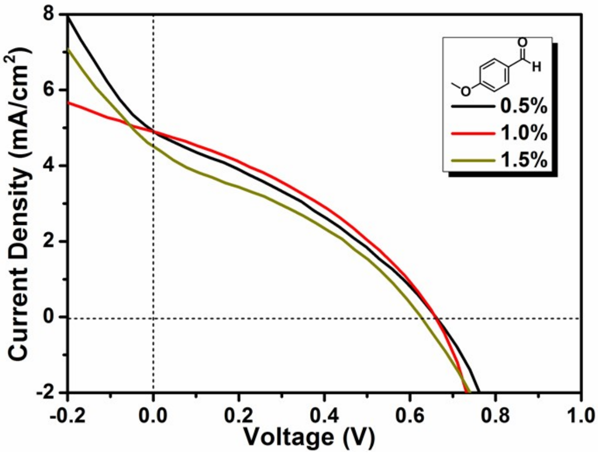


Fig. S16 *J*−*V* curves of PFO4:PCBO-12 devices with different concentration of p-anisaldehyde additive (other condition is that the concentration of PFO4 is 6.0 mg/mL, the ratio of D:A is 1:2.5 by weight, the ratio of water:ethanol is 15:85, and dried under high vacuum conditions (10^{-5} Pa) overnight before thermal deposition of MoO_3).

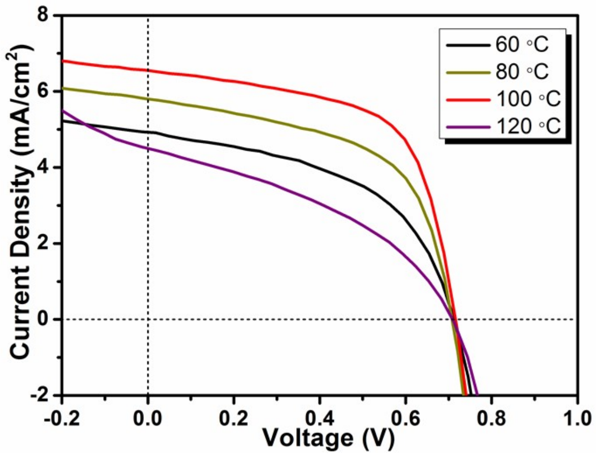


Fig. S17 *J*−*V* curves of PFO3:PCBO-12 devices with different thermal annealing temperature (other condition is that the concentration of PFO3 is 5.5 mg/mL, the ratio of D:A is 1:2.5 by weight, the ratio of water:ethanol is 15:85, 1.0% of the sdditive and dried under high vacuum conditions (10^{-5} Pa) overnight before thermal deposition of MoO$_3$).

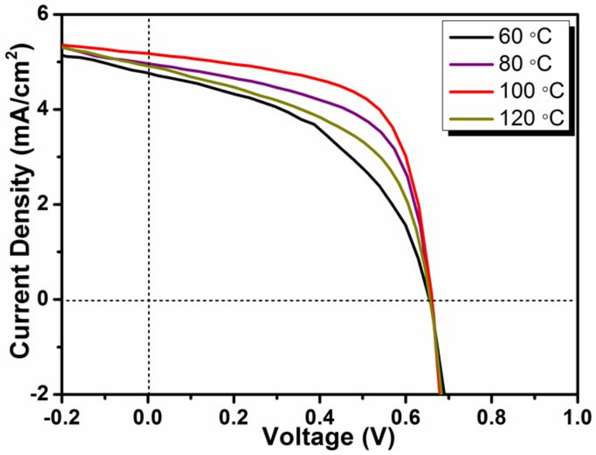


Fig. S18 *J*−*V* curves of PFO4:PCBO-12 devices with different thermal annealing temperature for 20 mins (other condition is that the concentration of PFO4 is 6.0 mg/mL, the ratio of D:A is 1:2.5 by weight, the ratio of water:ethanol is 15:85, 1.0% of the sdditive and dried under high vacuum conditions (10^{-5} Pa) overnight before thermal deposition of MoO$_3$).

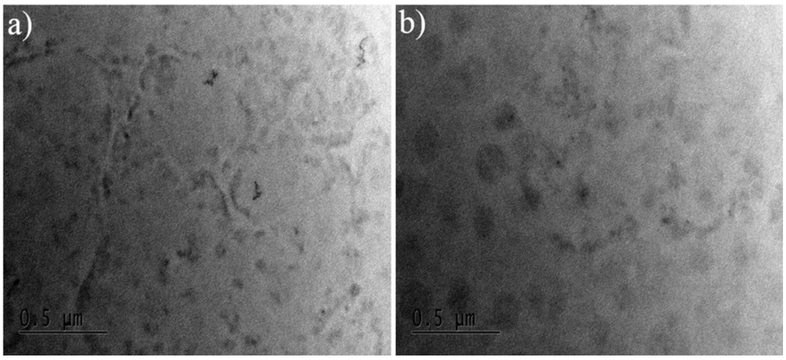


Fig. S19 TEM images of a) PFO3:PCBO-12 film and b) PFO3:PCBO-12 film processed with ethanol.

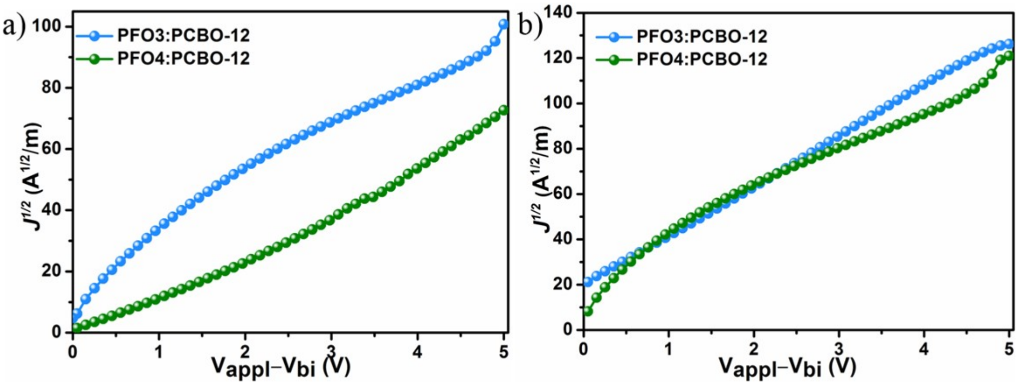


Fig. S20 The $J^{1/2}$-V characteristics of hole-only devices (ITO/MoO$_3$/polymer:PCBO-12/MoO$_3$/Ag) and electron-only devices (ITO/ZnO/polymer:PCBO-12/Ca/Al), and the condition for the preparing the blend film is as same as the condition of optimized devies.

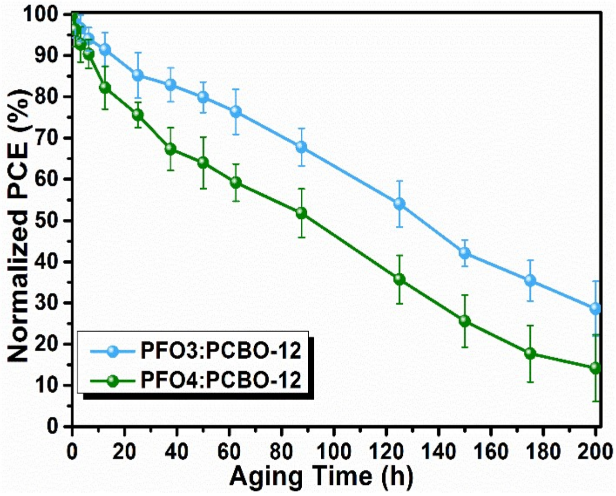


Fig. S21 The stability of optimized devices under high humid environment (relative humidity of ~60%) for different time.

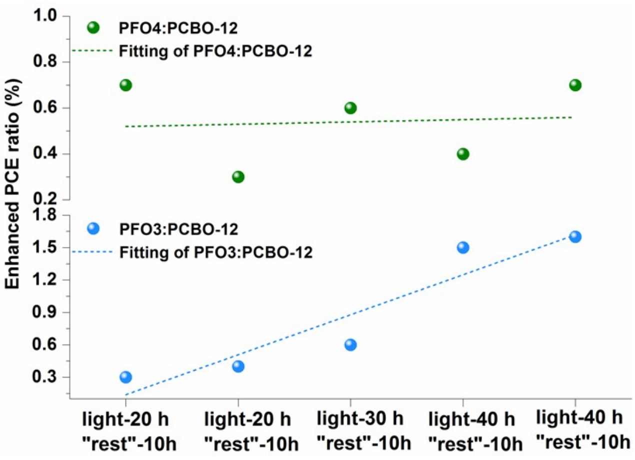


Fig. S22 The enhanced PCE ratio of devices based on PFO3:PCBO-12 and PFO4:PCBO-12 after every interval of 10 h under darkness.

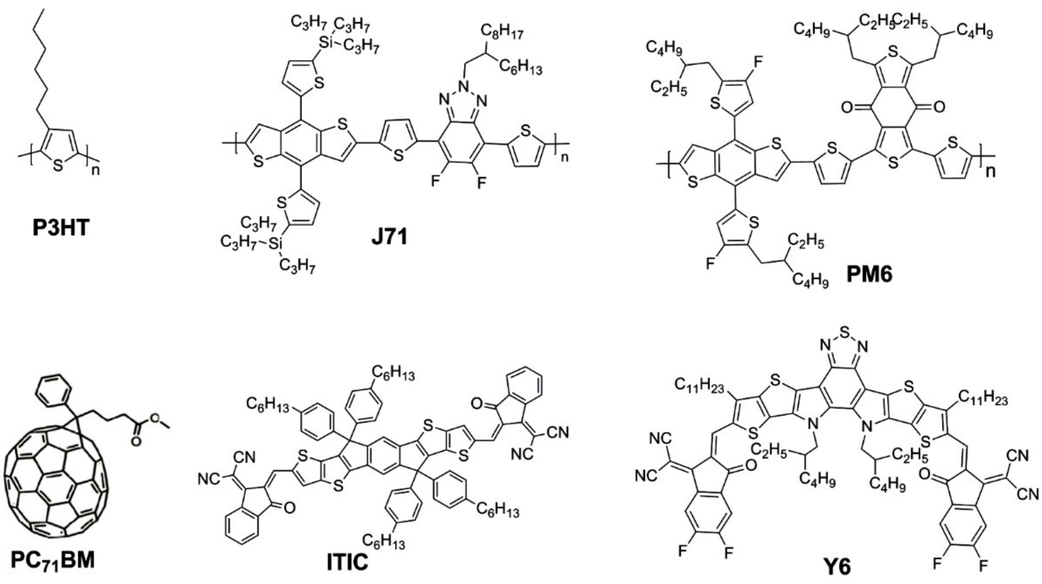


Fig. S23 The chemical structure of other three photovoltaic systems without abundant OEG side chains.

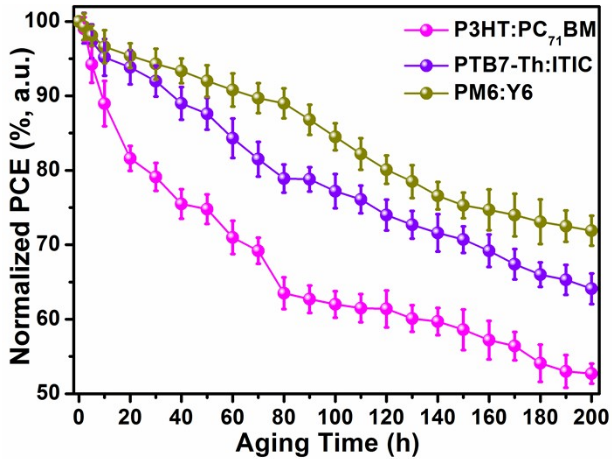


Fig. S24 The stability of devices based on three different photovoltaic systems with continuous light-soaking for 200 h in inert atmosphere.

Table S5 The remained PCE ratio of devices with continuous light-soaking (*CLS*) or discontinuous light-soaking (*DLS*) for same illumination time of 200 h in air.

Photoavtive layer	Remained PCE ratio (*CLS*)	Remained PCE ratio (*DLS*)	Variation PCE ratio $\left(\frac{PCE_{DLS} - PCE_{CLS}}{PCE_{CLS}}\right)$
P3HT:PC$_{71}$BM	52.6%	53.6%	1.9%
PTB7-Th:ITIC	64.2%	65.0%	1.2%
PM6:Y6	71.7%	72.6%	1.3%
PFO3:PCBO-12	64.5%	81.6%	26.5%
PFO4:PCBO-12	51.2%	69.1%	35.0%

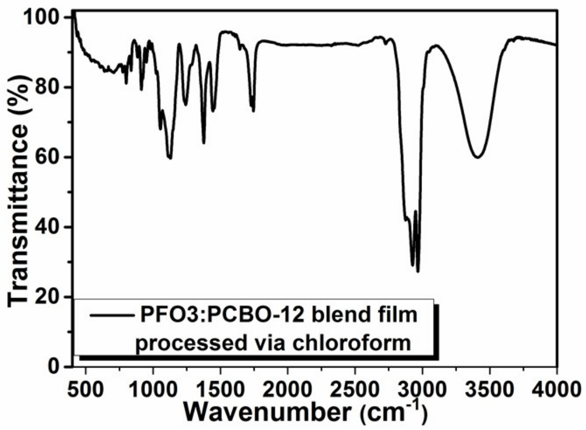


Fig. S25 The FTIR spectroscopy of PFO3:PCBO-12 blend film.

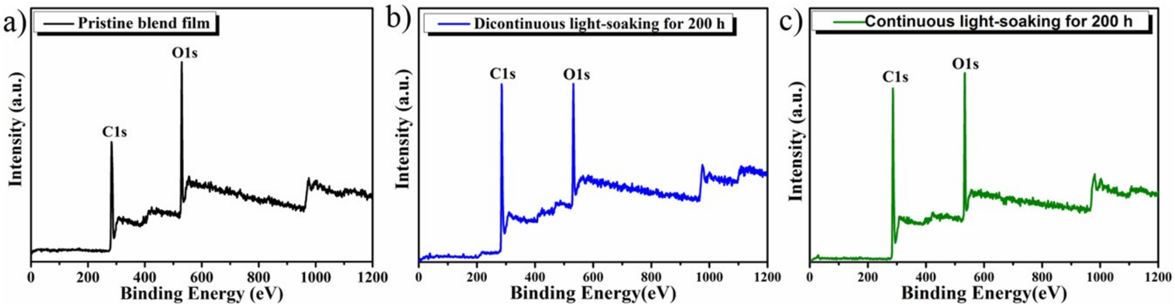


Fig. S26 The XPS spectra of a) the PFO3:PCBO-12 blend film, b) the aged DCLS-PFO3:PCBO-12 film, c) the aged CLS-PFO3:PCBO-12 film.

Reference

1. Y. Kim, J. Choi, C. Lee, Y. Kim, C. Kim, T. L. Nguyen, B. Gautam, K. Gundogdu, H. Y. Woo and B. J. Kim, *Chem. Mater.*, 2018, **30**, 5663-5672.
2. Y. Sun, J. H. Seo, C. J. Takacs, J. Seifter and A. J. Heeger, *Adv. Mater.*, 2011, **23**, 1679-1683.
3. C. Jiao, Z. Guo, B. Sun, Y.-q.-q. Yi, L. Meng, X. Wan, M. Zhang, H. Zhang, C. Li and Y. Chen, *J. Mater. Chem. C*, 2020, **8**, 6293-6298.