Supporting Information

Ferrocene as Highly Volatile Solid Additive in Non-Fullerene Organic Solar Cells with Enhanced Photovoltaic Performance

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Materials

PBT1-C-2Cl, PBT1-C, IT-4F, 3TP3T-4F, FOIC, PBI-Se and J52-Cl were synthesized as reported previously.¹⁻⁸ PM6 was purchased from Solarmer Inc. Y6 was purchased from hyperchemical Inc. Ferrocene was purchased from energy chemical Inc. Chlorobenzene, chloroform and 1,8-diiodooctanewere purchased from Sigma-Aldrich.

Measurements

UV-vis absorption spectra of neat and blend films were acquired with a UV-vis spectrophotometer (Shimadzu UV-2600). Device current density-voltage (*J-V*) characteristics were recorded using a Keithley 2400 Source Measure Unit. The photocurrent was tested under AM 1.5G illumination at 100 mWcm⁻² using a solar simulator (Class AAA solar simulator, Model 94063A, Oriel). The light intensity was calibrated using a standard Si solar cell and a readout meter (Model 91150V, Newport). The EQE spectra were acquired from a QEX10 Solar Cell EQE measurement system (PV measurement, Inc.). GIWAXS was carried out at the Advanced Light Source on beamline 7.3.3, Lawrence Berkeley National Lab (LBNL). AFM measurement was performed on a Dimension Icon AFM (Bruker) in a tapping mode under ambient conditions. All of the blends were thermal annealed to achieve optimum conditions before GIWAXS and AFM measurements. FT-IR spectra were recorded using a Nicolet Avatar 360 FI-IR spectrometer. And the materials to be tested in chloroform solution were dried on pressed KBr slices. XRF spectra were recorded using an energy dispersive X-ray spectrometer (Shimadzu EDX-GP). And the materials to be tested in chloroform solution were dried on silicon wafers.

Device fabrication

Prepatterned ITO-coated glass substrates were cleaned with detergent and ultrasonicated in deionized water, acetone and isopropanol for 20 min each and subsequently dried in an oven overnight. PM6:Y6 was fabricated based device with conventional device structure of ITO/PEDOT:PSS/PM6:Y6/PNDIT-F3N/Ag. PEDOT:PSS (Heraeus Clevios P VP. AI 4083, filtered at 0.45 µm) was spin-cast onto the ITO surface at 4000 rpm for 30 s (the thickness is about 40 nm), and baked at 150 °C for 15 min in air. Devices based on PM6:3TP3T-4F, PBT1-C-2Cl:IT-4F, PM6:PBI-Se, PBT1-C:FOIC, and J52-Cl:IT-4F were fabricated with inverted structure of

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ITO/ZnO/active layers/MoO₃/Ag. ZnO precursor was prepared by dissolving 1 g zinc acetate dihydrate and 280 µL ethanolamine in 10 mL 2-methoxyethanol under stirring for 12 h for the hydrolysis reaction. ZnO precursor solution was spin cast on the top of ITO substrates at 4000 rpm for 30 s and then baked at 200 °C for 15 min under ambient condition. Then the active layers were spin-coated from CB or CF solutions in a N₂-filled glove box. For devices using solvent additives, DIO or CN with different volume ratio was added into the solution. As for devices adopted ferrocene as solid additive, 5% ferrocene (weight ratio to the blend) was introduced to PBT1-C-2Cl:IT-4F, PM6:PBI-Se, PBT1-C:FOIC blends, while 6% ferrocene (weigh ratio to the blend) was added into PM6:Y6, PM6:3TP3T-4F and J52-Cl:IT-4F blends. Subsequently, the blend films processed with solvent additive were heated at 100 °C for 10 min, while blends with ferrocene were thermally annealed at 100 °C for 15 min. For PM6:Y6 based device, the methanol solution of PNDIT-F3N (0.5 mg mL⁻¹) was spin-cast on the BHJ layer at 1500 rpm. Finally, 90 nm Ag layer was thermally deposited under the vacuum condition of 2×10^{-4} Pa. While for devices using inverted structure 7 nm MoO_3 and 90 nm Ag layer was thermally deposited under the vacuum condition of 2×10^{-4} Pa. The active area is 4.0 mm². The optimal thicknesses of PM6:Y6 devices without any additive, processed with CN and ferrocene are around 105, 106 and 108 nm, respectively. For stability test, the devices were put under continuous100 mW cm⁻² simulated 1.5 Global (AM 1.5 G) solar simulator (Enli Technology Co., Ltd, SS-F5-3A). The light intensity was calibrated by a standard Si solar cell (SRC-2020, Enli Technology Co., Ltd). The temperature was kept at room temperature. Thermogravimetric analysis (TGA) was measured on a Pyris 1 TGA under a nitrogen flow. The heating rate is 10 °C min⁻¹ and the temperature was held at 100 °C for 15 min.

Carrier Mobility Measurements

Carrier mobility was measured using the space-charge-limit current (SCLC) method. The electron mobility was determined with the device structure of ITO/ZnO/Active layer/PFN-Br/Al and the hole mobility was determined with the device structure of ITO/PEDOT:PSS/Active layer/MoO₃/Al. The devices were fabricated under the optimized conditions for the different processing methods. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, according to the equation: $J = 9\epsilon_0\epsilon_r\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, ϵ_r is the relative dielectric constant of the transport medium,

and ε_0 is the permittivity of free space. The carrier mobility can be calculated from the slope of the $J^{0.5} \sim V$ curves.

TRPL Measurement

Fluorescence decay dynamics were recorded by TCSPC (Becker&Hickl, SPC-150). The excitation wavelength is 400 nm and monitor wavelengths are 700 and 900 nm for PM6 and Y6, respectively. A laser power of ca. 20 μ J cm⁻² was adopted. The laser spot diameter is 2 μ m.

Computational Details

The geometries of PM6, Y6 and ferrocene as well as the complexes of PM6/ferrocene and Y6/ferrocene were optimized by density functional theory (DFT) with the B3LYP functional and the basis set of SDD for Fe and 6-31G(d,p) for other types of atoms. The binding energies of PM6 and Y6 with ferrocene were further calculated by DFT with the B3LYP functional and the basis set of SDD for Fe and 6-311+G(d, p) for other types of atoms. In the calculations, the alkyl side chains were removed for simplicity. All the calculations were carried out by using Gaussian16 program⁹.



Figure S1. UV-vis absorption of (a) ferrocene (b) PM6 (c) Y6 and (d) PM6:Y6 blend processed under different conditions.



Figure S2. Scanning copy of the certification report for the PM6:Y6 device processed with ferrocene from National Institute of Metrology (NIM), China.



Figure S3. Histogram of the PCE parameter in 40 devices processed with different conditions.



Figure S4. Current density-voltage (*J-V*) characteristics of PM6:Y6 devices with different amount of ferrocene.

Table S1. Summary of photovoltaic parameters of PM6: Y6 devices with different amount of ferrocene.

Weight ratio of	V _{oc}	J _{sc}	FF	PCE ^(a)
ferrocene to the blend	(V)	(mA cm ⁻²)		(%)
5%	0.838 ± 0.002	26.08±0.26	0.75±0.01	16.82 (16.43)
6%	$0.838 {\pm} 0.002$	26.71±0.20	0.76 ± 0.01	17.40 (17.01)
8%	$0.838 {\pm} 0.002$	26.59±0.23	0.73 ± 0.01	16.67 (16.30)

(a) Average values with standard deviation were obtained from 10 devices.

Additive	TA time	$V_{\rm oc}$ (V)	J _{sc} (mA cm ⁻²)	FF	PCE ^{a)} (%)
CN	5 min	0.832±0.002	25.79±0.23	0.74±0.01	16.27(15.88)
	10 min	0.831±0.002	26.00±0.25	0.74±0.01	16.40(15.99)
	15 min	0.830±0.002	25.81±0.22	0.73±0.01	16.03(16.58)
ferrocene	5 min	0.832±0.002	26.22±0.25	0.76±0.01	16.97(16.58)
	10 min	0.832±0.002	26.49±0.21	0.76±0.01	17.15(16.75)
	15 min	0.832±0.002	26.71±0.20	0.76±0.01	17.29(16.88)

Table S2. Summary of the photovoltaic parameters of CN and ferrocene processed PM6:Y6 devices with different thermal annealing times.

a) Average values with standard deviation were obtained from 10 devices.



Figure S5. Representative current density–voltage (J–V) characteristics of (a) CN and (b) ferrocene processed PM6:Y6 devices with different thermal annealing times under AM 1.5G illumination (100 mW cm⁻²).

 Table S3. Summary of photovoltaic parameters of ferrocene processed PM6:Y6 devices with different thermal annealing times.

Active layer	TA time	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	PCE ^{a)} (%)
	1 min	0.834±0.002	26.50±0.23	0.75±0.01	16.98(16.69)
PM6:Y6	2 min	0.833±0.002	26.19±0.28	0.75±0.01	16.80(16.42)
(ferrocene)	5 min	0.832±0.002	26.22±0.25	0.76±0.01	16.97(16.58)
	10 min	0.832±0.002	26.49±0.21	0.76±0.01	17.15(16.75)
	15 min	0.832±0.002	26.71±0.20	0.76±0.01	17.29(16.88)

^{a)} Average values with standard deviation were obtained from 10 devices.



Figure S6. Representative current density–voltage (J–V) characteristics of ferrocene processed PM6:Y6 devices with different thermal annealing times under AM 1.5G illumination (100 mW cm⁻²).



Figure S7. (a-e) *J-V* characteristics of devices processed with different processing methods based on PM6:3TP3T-4F, PBT1-C-2CI:IT-4F, PM6:PBI-Se, PBT1-C:FOIC, and J52-CI:IT-4F blends, and (f-j) the corresponding EQE spectra.



Figure S8. 2D GIWAXS patterns for (a,b) PM6 with different conditions (c) IP and (d) OOP line-cut profiles of GIWAXS images.



Figure S9. 2D GIWAXS patterns for (a,b) Y6 with different conditions (c) IP and (d) OOP line-cut profiles of GIWAXS images.

	FWHM (Å ⁻¹)	CCL (Å)	Intensity
PM6	0.359	15.75	57.09
PM6 Fc	0.360	15.71	56.54
Y6	0.243	23.27	82.31
Y6 Fc	0.238	23.76	114.88
PM6:Y6 w/o	0.252	22.44	205.98
PM6:Y6 CN	0.248	22.80	214.74
PM6:Y6 Fc	0.250	22.62	334.77

Table S4. The full width at half-maximum (FWHM) of the out-of-plane (010) diffraction peaks and the corresponding crystal coherence lengths (CCLs) for the neat and blend films under different conditions.



Figure S10. Tapping-mode AFM height images of (a,b) PM6 and (c,d) Y6 processed with different conditions.



Figure S11. (a-e) AFM height images of ferrocene processed blend films under light illumination over different time periods.



Figure S12. Charge mobilities of the blend films under different conditions. (a) Hole-only devices and (b) electron-only devices.



Figure S13. PL spectra of (a) PM6, (b) Y6, and (c) PM6:Y6 films with different conditions.



Figure S14. TRPL spectra of (a) PM6, (b) Y6, and (c-d) PM6:Y6 films under different conditions (excitation wavelength of 400 nm and monitor wavelengths of 700 and 900 nm for PM6 and Y6. The maximum signature of TRPL spectra was normalized.



Figure S15. AFM height images of ferrocene processed blend films with different thermal annealing times.



Figure S16. Thermogravimetric Analysis (TGA) plot of ferrocene containing blend at a scan rate of 10.0 $^{\circ}$ C min⁻¹ and in the heating process, the temperature was held for 15 min at 100 $^{\circ}$ C.



Figure S17. (a,b) Optimized PM6-ferrocene complex structures and the corresponding binding energy. (c,d) Optimized Y6-ferrocene complex structures and the corresponding binding energy.

ITO glass silicon wafer			-
	0 s	8 s	22 s
Fc blank	-		
	41 s	56 s	71 s

Figure S18. Volatilization process of ferrocene on the ITO glass and silicon wafer (thermal annealed at 100 °C).

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