

Supporting Information

Air-Stable Ternary Organic Solar Cells Achieved by Using Fullerene Additives in Non-Fullerene Acceptor-Polymer Donor Blends

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Table of Contents

Optical absorption spectroscopy	2
ET18 HOMO-LUMO characterization	3
Solar cell fabrication and characterization	4
Light stability	5
Atomic force microscopy.....	6
Grazing-incidence wide-angle x-ray scattering	6
Transient Absorption (TA) Spectroscopy	7
Integrated photocurrent device analysis (IPDA).....	8
References.....	9

Optical absorption spectroscopy

Absorption spectra were recorded from thin films obtained by spin coating (1500 rpm) a chloroform solution (5.0 mg/mL) onto glass slides on a Perkin Elmer LAMBDA 1050 UV-vis spectrophotometers. The normalized absorption spectra binary and ternary blends show two dominant absorption peaks (Figure S1).

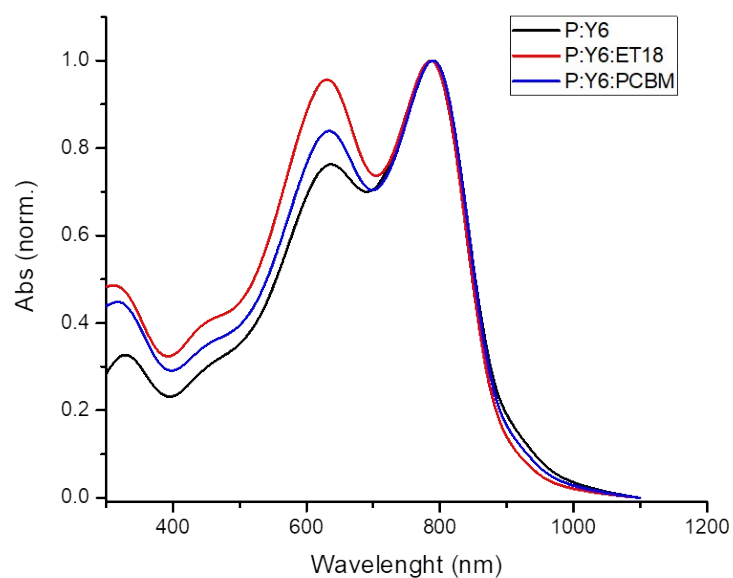


Figure S1. Absorption spectra of the binary blend (black), the **ET18** based ternary blend (red) and **PCBM** based ternary blend (blue)

ET18 HOMO-LUMO characterization

Ultraviolet photoelectron spectroscopy (UPS) was conducted on a Thermo Scientific ESCALAB 250Xi at a base pressure of 2×10^{-8} mBar, using a He I line at $h\nu = 21.21$ eV while the sample is biased at -5 V. A plasma cleaned gold film was also used as a reference.

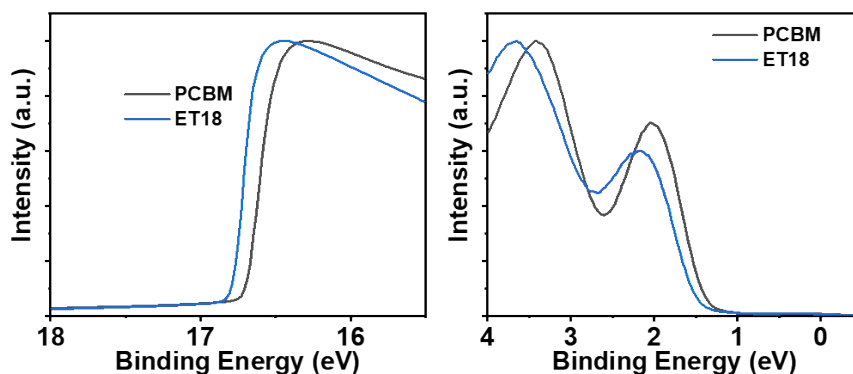


Figure S2. UPS spectra of PCBM and ET18 films.

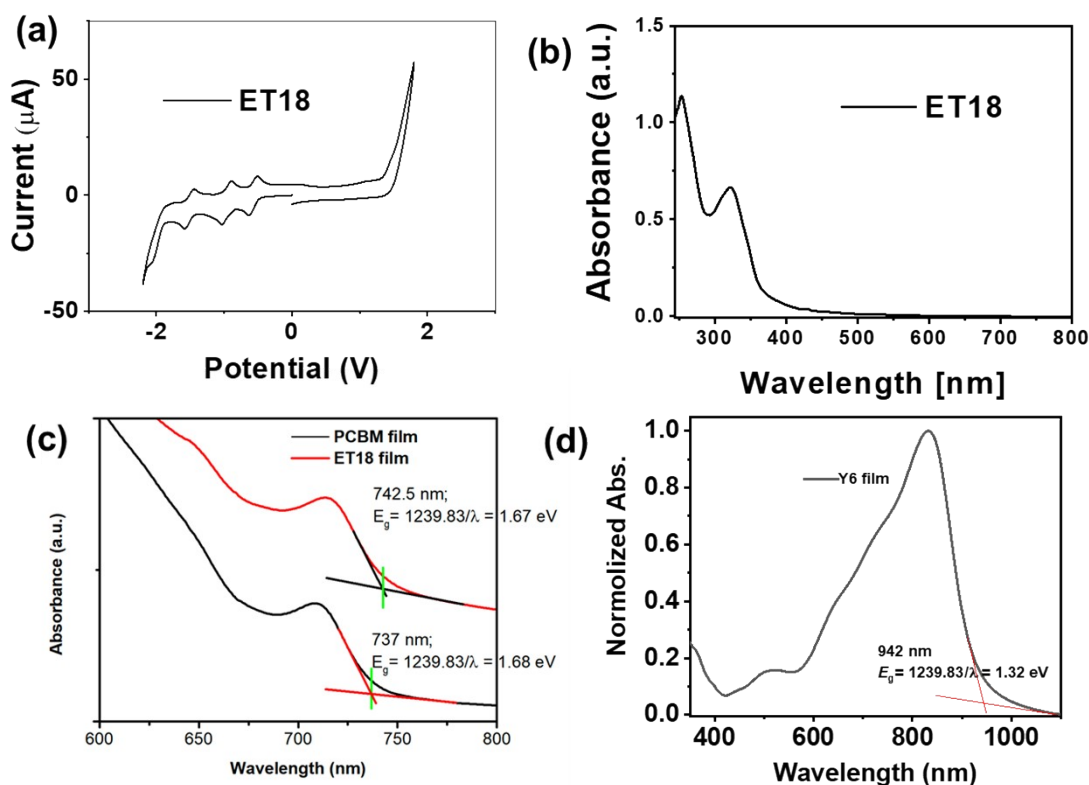


Figure S3. Cyclic voltammogram of ET18 in oDCB-CH₃CN (4:1v/v), 0.1 M TBAClO₄ at a scan rate of 200 mV/s (a). UV-vis spectra of a ET18 thin film (b); UV-vis spectra of a ET18, PCBM (c) and Y6 (d) thin films for bandgap calculation. Note, for Y6 HOMO energy measured by UPS was taken from the reference 68 in the main text (ACS Energy Lett. 2020, 5, 1780).

Solar cell fabrication and characterization

The inverted device architecture used in this study is ITO /ZnO /polymer:Y6:optionally fullerene derivative /MoO₃ /Ag. Pre-patterned ITO-coated glass wafers (Thin-film Devices, Inc.) with a sheet resistance of $\approx 20 \Omega/\text{sq}$ were used as substrates. The substrates were cleaned by sonicating them in water, acetone, methanol, and isopropanol, in that order.

For the electron transporting layer (ETL), ZnO precursor solution is prepared by dissolving 220 mg of zinc acetate dehydrate (Sigma Aldrich) and 62 mg of 2-ethanolamine (Sigma Aldrich) in 2 mL 2-methoxyethanol (Sigma Aldrich), then stirred overnight at room temperature. The ZnO precursor was filtered using an 0.45 μm PVDF filter and the resulting solution was spin-coated on ITO at 7000 rpm followed by thermal annealing for 20 min at 170 °C. Y6 (99.9 %) was purchased from Derthon Optoelectronic Materials Science Technology Co LTD. The active layer solution (total concentration = 14 mg/mL) was then spin-coated onto the ZnO layer by spinning at 3000 rpm, and then annealed for 10 minutes at 130 °C in an argon glove box or in air. The final thickness of the active layer is approximately 120 nm. The hole transporting layer (MoO_x) and top electrodes were using a thermal evaporator (pressure $\approx 6 \times 10^{-6}$ Torr) and shadow masks to obtain an active layer area of 6 mm². First, a 10-nm-thick layer of molybdenum oxide interlayer was evaporated followed by another 100-nm-thick layer of silver electrode. All the devices were measured under a simulated AM1.5G irradiation (100 mW cm⁻²) illuminated with a standard ABET Sun 2000 Solar Simulator in the air. A standard silicon solar cell was used to calibrate the light intensity. The voltage was scanned from 1.20 V to -0.20 V. The EQE measurements were carried out using an Oriel model QE-PV-SI instrument in ambient conditions. No preconditioning was applied for any characterization. A calibrated silicon solar cell was used as a reference.

Light stability

Light soaking stability tests were conducted by storing the devices without encapsulation in a flowing N₂ box and then exposing them to a 5000 K white LED source (EverWatt, EW-HB-06-V-150W) with 100 mW/cm² intensity. The light intensity was also calibrated with an NREL-certified monocrystalline Si photodiode coupled to a KG3 filter to bring the spectral mismatch to unity. The working temperature of the device in the light soaking condition was ≈58 °C.

Atomic force microscopy

Atomic force microscopy (AFM) was measured on a Dimension Icon scanning probe microscope (Bruker Dimension FastScan AFM) in standard tapping mode. The blend thin films were prepared in the same way as the photovoltaic devices and spun cast on Si substrates.

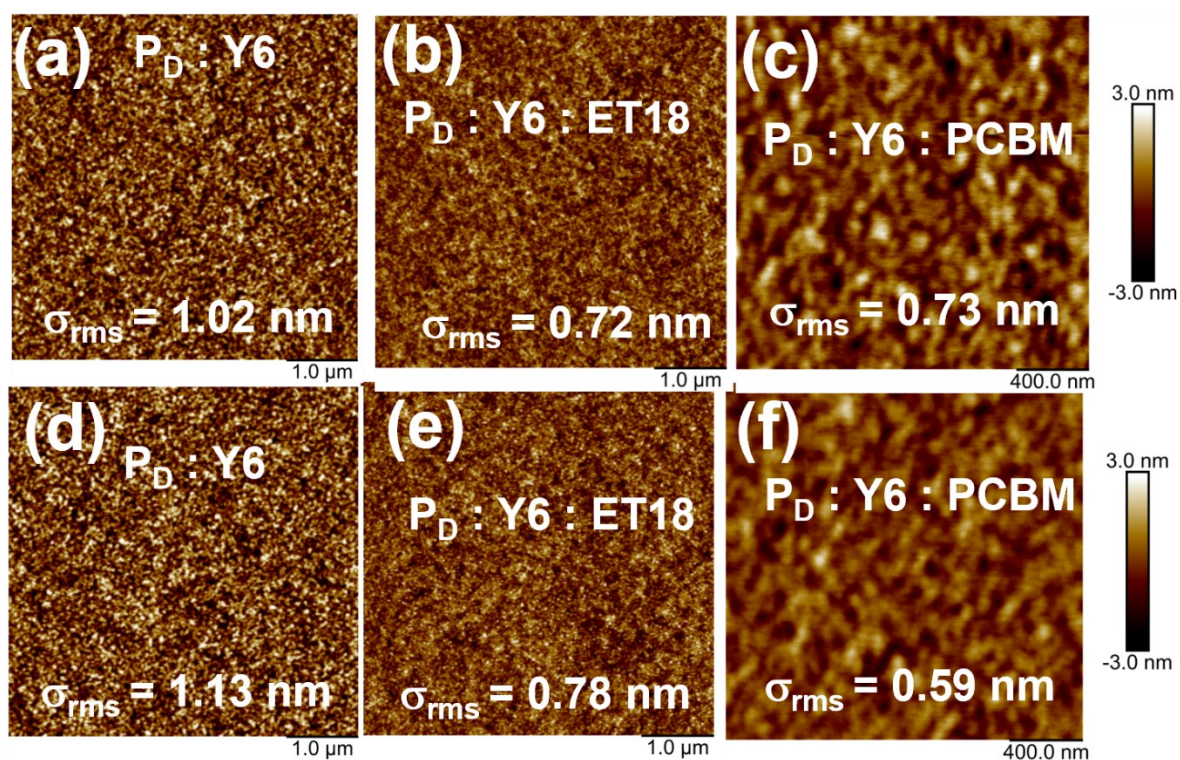


Figure S4. AFM images of the indicated binary and ternary blends freshly prepared (a, b, c) and aged for 6 months (d, e, f).

Grazing-incidence wide-angle x-ray scattering

Grazing-incidence wide-angle x-ray scattering (GIWAXS) measurements were performed at beamline 8ID-E at the Advanced Photon Source at Argonne National Laboratory. The samples were irradiated at incidence angles from 0.130° to 0.140° in vacuum at 10.915 keV for two summed exposures of 2.5 s each. Signals were collected with a Pilatus 1M detector located at a distance of 228.16 mm from the samples. Blend films for GIWAXS were prepared using the same procedure as used in OSC devices. The neat films were prepared by spin coating 14 mg/mL blend solutions in chloroform on Si substrates (20 mm x 20 mm) and annealed as in the case of solar cell fabrication.

Table S1. Summary of GIWAXS d-spacings and correlation lengths in in-plane direction.

	In-plane			In-plane		
	q (100) (Å ⁻¹)	d (100) (Å)	Correlation length (Å)	q (010) (Å ⁻¹)	d (010) (Å)	Correlation length (Å)
P_D:Y6	0.3042	20.65	54.90	1.4435	4.35	40.76
P_D:Y6-aged	0.3065	20.49	45.29	-	-	-
P_D:Y6:ET	0.3031	20.72	65.68	1.3822	4.54	18.04
P_D:Y6:ET-Aged	0.3028	20.74	64.99	1.3967	4.49	20.05
P_D:Y6:PCBM	0.3048	20.61	58.40	1.3703	4.58	14.34
P_D:Y6:PCBM-Aged	0.3048	20.61	58.10	1.3804	4.55	13.64

Table S2. Summary of GIWAXS d-spacings and correlation lengths in out of plane direction.

	Out of plane			Out of plane		
	q (100) (Å ⁻¹)	d (100) (Å)	Correlation length (Å)	q (010) (Å ⁻¹)	d (010) (Å)	Correlation length (Å)
P_D:Y6	-	-	-	1.7493	3.59	32.46
P_D:Y6-aged	-	-	-	1.7449	3.60	27.48
P_D:Y6:ET	-	-	-	1.7503	3.59	28.92
P_D:Y6:ET-Aged	-	-	-	1.7457	3.60	30.81
P_D:Y6:PCBM	-	-	-	1.7459	3.60	32.76
P_D:Y6:PCBM-Aged	-	-	-	1.7532	3.58	33.12

Transient Absorption (TA) Spectroscopy

All the films were spin-coated on 25 mm × 25 mm clean glass substrate (VWR) in the Ar-filled glovebox using the same procedure as for optimized OSC devices. Transient absorption (TA) experiments for thin films were performed as described previously.¹ Briefly, ≈40% of the output of a 1 kHz amplified Ti:sapphire system at 827 nm (1 W, 100 fs, Spitfire, Spectra Physics) is used to pump a laboratory-constructed optical parametric amplifier that is then tuned to the specific excitation wavelength. The pump is depolarized to minimize polarization-specific dynamics. The probe in the fsTA experiment is generated using 10% of the remaining output by driving continuum generation in a sapphire plate (430-850 nm) or a proprietary crystal from Ultrafast Systems (850-1600 nm). In the nsTA experiment, the probe is generated in a separately delayed broadband laser system (EOS, Ultrafast Systems, LLC). Pump and probe are spatially and temporally overlapped at the sample. The transmitted probe is detected on a commercial spectrometer (customized Helios-EOS, Ultrafast Systems, LLC).

Before kinetic analysis, the fsTA data are background/scatter-subtracted and chirp-corrected, and the visible and NIR data sets are spectrally merged (Surface Explorer 4, Ultrafast Systems, LLC). The kinetic analysis was performed using home-written programs in MATLAB and was based on a global fit to selected single-wavelength kinetics. The time-resolution is given as $w = 300$ fs (full width at half maximum, FWHM); the assumption of a uniform instrument response across the frequency domain and a fixed time-zero (t_0) is implicit in global analysis.

The kinetic data from multiple different wavelengths are fit using the global analysis described below. Each wavelength is given an initial amplitude that is representative of the spectral intensity at time t_0 and varied independently to fit the data. The time/rate constants and t_0 are shared between the various kinetic data and are varied globally across the kinetic data to fit the model(s) described in the cited work ref.¹

Integrated photocurrent device analysis (IPDA)

For IPDA measurements were carried in ambient conditions by using a 100 mW/cm² simulated AM 1.5G light source and filters, using the procedure outlined previously.²⁻⁴ J-V characteristics were measured by using a Keithley 2400 source-measurement unit controlled by home-built NI LabView programs. Impedance measurements were done using a Solartron 1260 impedance analyzer using an AC amplitude of 100 mV (frequency range: 100 Hz - 5 MHz). The filter wheel, LabView programs, and ZPlot programs were controlled by homemade Autoit scripts provided here: <https://github.com/MikeHeiber/AutoItScripts/tree/master/Hersam%20Lab>.

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