

Electronic Supplementary Information for:

Layer-by-layer processing enabled alloy-like ternary organic solar cells to achieve 17.9% efficiency

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1. Experiment Section

Materials Preparation:

PM6, PTO2 and PDINN were commercially available from Beijing Ogetake Technology Ltd. N3 was commercially available from EflexPV Ltd. Hole transport materials PEDOT:PSS was commercially available from Xi'an Polymer Light Technology Corp. Other related materials and solvents were bought from Alfa Chemical Inc. or Sigma-Aldrich Corp and used directly (without extra treatment).

Device Fabrication:

All devices were fabricated with a conventional structure of ITO/PEDOT:PSS/active layer/PDINN/Ag. The glass substrates covered with ITO were sequentially sonicated in deionized water, ethanol, acetone and ethanol solvents for 30 minutes, then dried with nitrogen and placed in an ultraviolet ozone box treatment for 20 minutes to improve the surface environment. Next, the PEDOT:PSS was spin coated on the ITO substrates with 4000 rpm for 30s, and then the substrates were annealed at 150 °C for 15 minutes. Afterward, the substrates were transferred into the glovebox. For BHJ OSCs, PM6:N3, PTO2:N3 and PM6:PTO2:N3 were dissolved in chloroform to prepare a 16 mg/ml blend solution, respectively, and the weight ratio between donor and acceptor was kept at 1:1.2. The solution was placed in a nitrogen atmosphere and stirred for more than 12 hours, and then was spin coated on the PEDOT: PSS layer with 3300 rpm for 50s to form an active layer based on BHJ structure. For layer-by-layer (LbL) OSCs, PM6, PTO2 and PM6:PTO2 were dissolved in chlorobenzene to prepare solution

at a concentration of 7 mg/ml, in which the weight ratio between PM6 and PTO2 was kept at 1:0, 0.9:0.1, 0.85:0.15, 0.8:0.2, and 0:1 respectively. N3 was dissolved in chloroform to prepare solution at a concentration of 8 mg/ml. After stirring overnight, the donor and acceptor were sequentially spin-coated to form an active layer based on LbL structure. Among them, the spin-coating rate and spin-coating time for depositing PM6 as well as PM6:PTO2 is 1200 rpm, 50s, and for N3 is 2000 rpm, 50s. Ultimately, PDINN was dissolved in methanol to prepare solution of 1mg/ml, and then was spin-coated on the active layer with 3000 rpm for 40s. Ultimately, Ag was deposited about 100 nm under vacuum conditions of 5×10^{-4} Pa. The hole-only devices were fabricated with a structure of ITO/PEDOT:PSS/active layer/MoO₃/Au, while the electron-only devices were fabricated with a structure of ITO/ZnO/active layer/PDINN/Ag. The UPS devices were fabricated with a structure of ITO/material (PM6/PTO2/N3/PM6:PTO2(0.85:0.15)). The active area of the devices is approximately 0.023cm².

Characterization and Measurements:

The simulated solar light (100 mW cm⁻² AM 1.5 G) was provided by a Newport Oriel Sol3A solar simulator. Our simulator was corrected by using a standard monocrystalline silicon reference cell. The device's basic photovoltaic properties, carrier mobilities, J_{ph} - V_{eff} curves, and the light intensity dependence of J_{SC} and V_{OC} were measured by a Keithley 2400. The UV-vis absorption spectra were measured on a Hitachi U-3010 UV-vis spectroscopy. The EQE spectra were measured by QTEST HIFINITY5 solar cell IPCE test system. The photoluminescence spectra were measured on a Hitachi F-4600 spectrophotometer. The contact angles of neat films were measured by a Kruss DSA100 drop shape analyzer. The ultraviolet photoelectron spectroscopy (UPS) was measured on a Escalab Xi+ X-ray photoelectron spectrometer. The surface morphology of the films was investigated by an FEI Tecnai G2 F20 transmission electron microscope and Bruker Dimension Icon atomic force microscope. The GIXRD was measured on a Bruker D8 ADVANCE diffractometer platform. Film-depth-dependent light absorption spectra (FLAS) is conducted by a home-made setup. Low-pressure (less than 20Pa) oxygen plasma was used for the incremental etching of the film. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) are performed using a TOF-SIMS instrument (ION TOF-SIMS 5).

2. Supplementary Figure Section

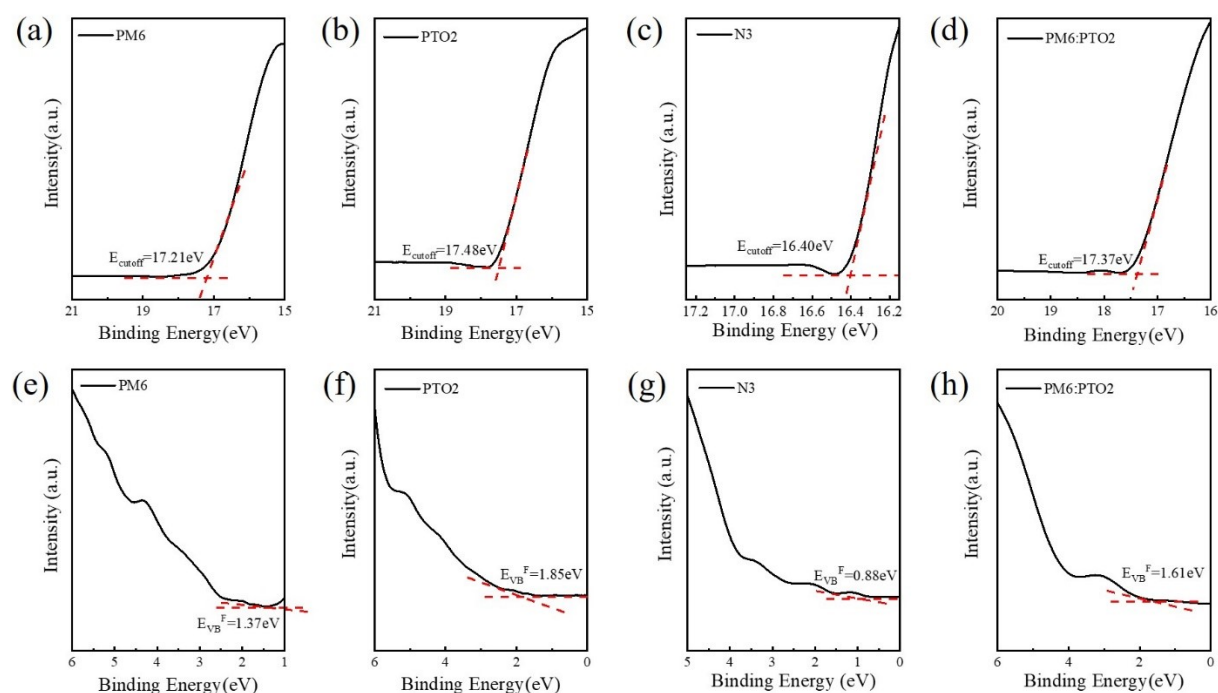


Fig. S1 Ultraviolet photoelectron spectroscopy (UPS) measurements of (a), (e) PM6, (b), (f) PTO2, (c), (g) N3 and (d), (h) PM6:PTO2 (0.85:0.15).

Table S1. Properties of optical absorption and molecular energy level in neat PM6, PM6:PTO2(0.85:0.15), PTO2, N3.

Material	Absorption onset [nm]	E_g^{opt} [eV] ^(a)	$HOMO$ [eV] ^(b)	$LOMO$ [eV] ^(c)
PM6	674	1.84	-5.38	-3.54
PM6:PTO2	670	1.85	-5.46	-3.61
PTO2	646	1.92	-5.59	-3.67
N3	905	1.37	-5.70	-4.33

^a calculation based on film absorption onset. ^b HOMO values obtained from UPS measurements.

^c calculation based on $E_{LOMO} = E_{HOMO} + E_g^{opt}$.

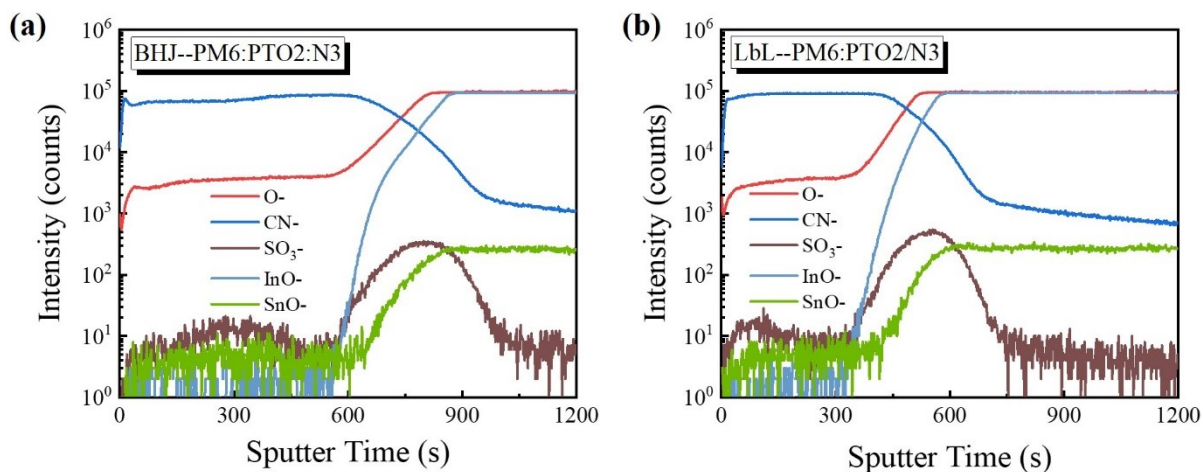


Fig. S2 ToF-SIMS measurement of devices based on the above systems.

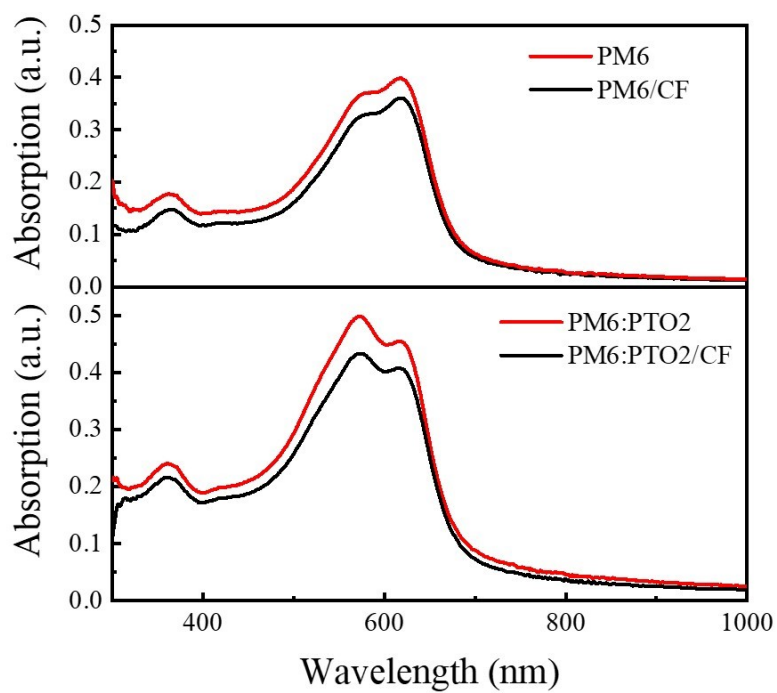


Fig. S3 Washout experiments of PM6 (CB) and PM6:PTO2 (CB) by CF solvent.

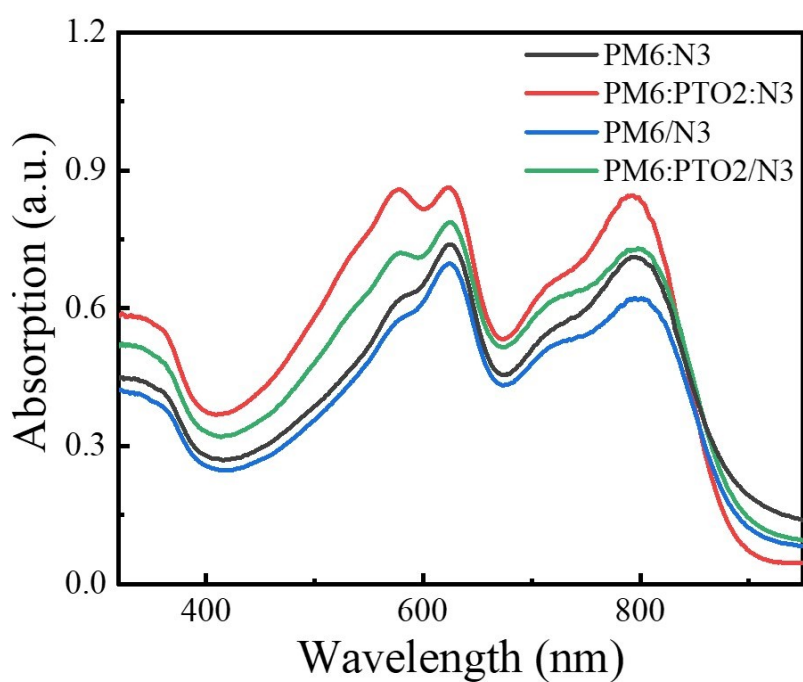


Fig. S4 Normalized absorption spectra of BHJ and LbL structure hybrid films.

Table S2 Summary of contact angles (θ), surface tensions (γ), and Flory-Huggins interaction parameters (χ) for PM6, PTO2 and N3 films.

Surface	$\theta_{water} [^\circ]$	$\theta_{diiodomethane} [^\circ]$	$\gamma [mN m^{-1}]$	$\chi [PTO2, D/A]$
PTO2	100.4	45.3	36.89	/
PM6	103.9	50.4	34.05	0.06
N3	94.3	40.9	39.54	0.21

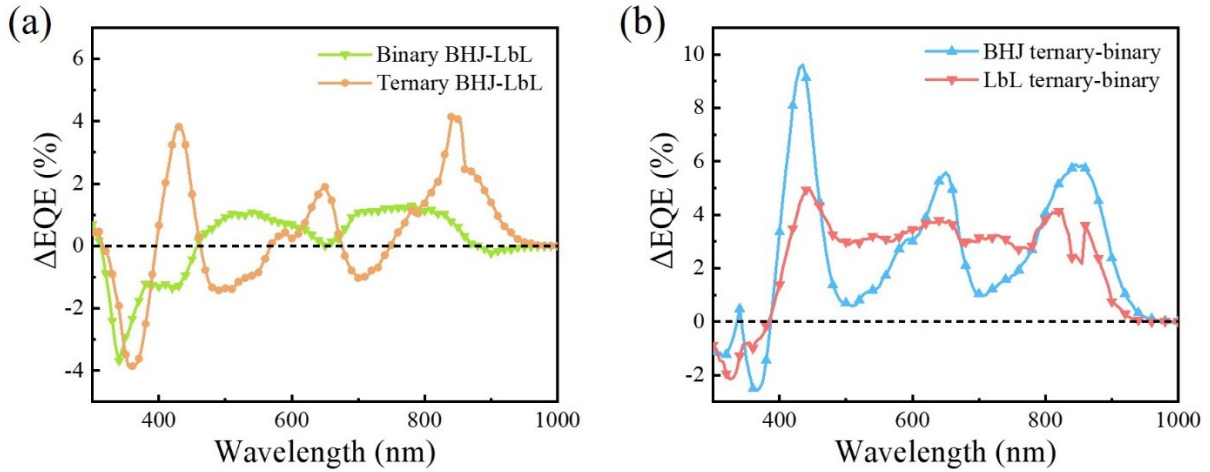


Fig. S5 The ΔEQE values of (a) BHJ and LbL devices for the same binary system and the same ternary system and (b) binary and ternary system for the same BHJ structure and the same LbL structure.

Table S3. μ_h , μ_e and μ_h/μ_e values of binary OSCs and ternary OSCs with different structures.

Device structure	Active layer	$\mu_h (cm^2 v^{-1} s^{-1})$	$\mu_e (cm^2 v^{-1} s^{-1})$	μ_h/μ_e
BHJ	PM6: N3	7.68×10^{-4}	4.71×10^{-4}	1.63
	PM6: PTO2: N3	8.50×10^{-4}	5.27×10^{-4}	1.61
LbL	PM6/N3	7.11×10^{-4}	5.70×10^{-4}	1.25
	PM6: PTO2/N3	8.46×10^{-4}	7.08×10^{-4}	1.19

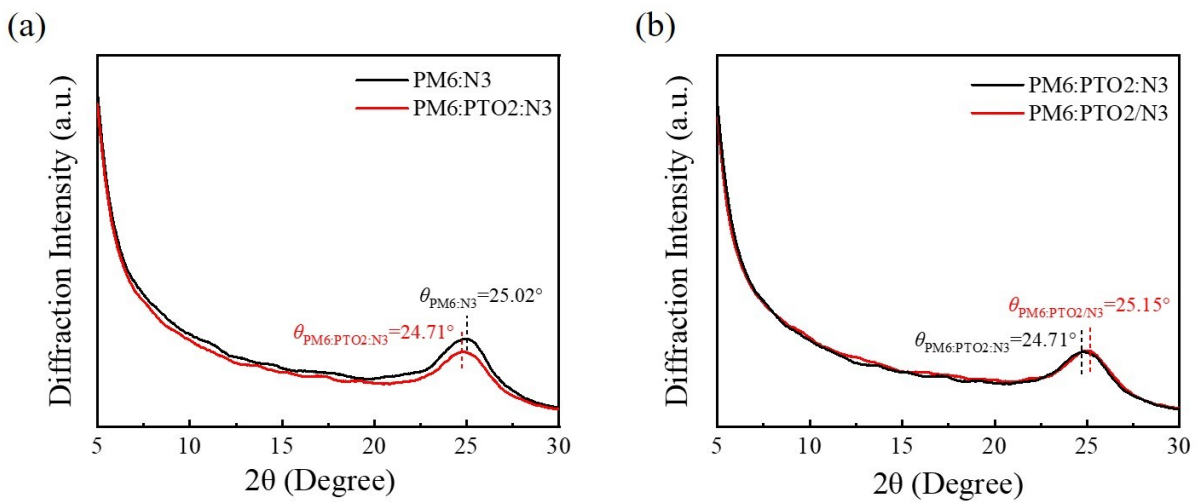


Fig. S6 Smooth GIXRD curves of binary and ternary films of different structures on silicon wafers. (a) Binary BHJ film with ternary BHJ film. (b) Ternary BHJ film with ternary LbL film.

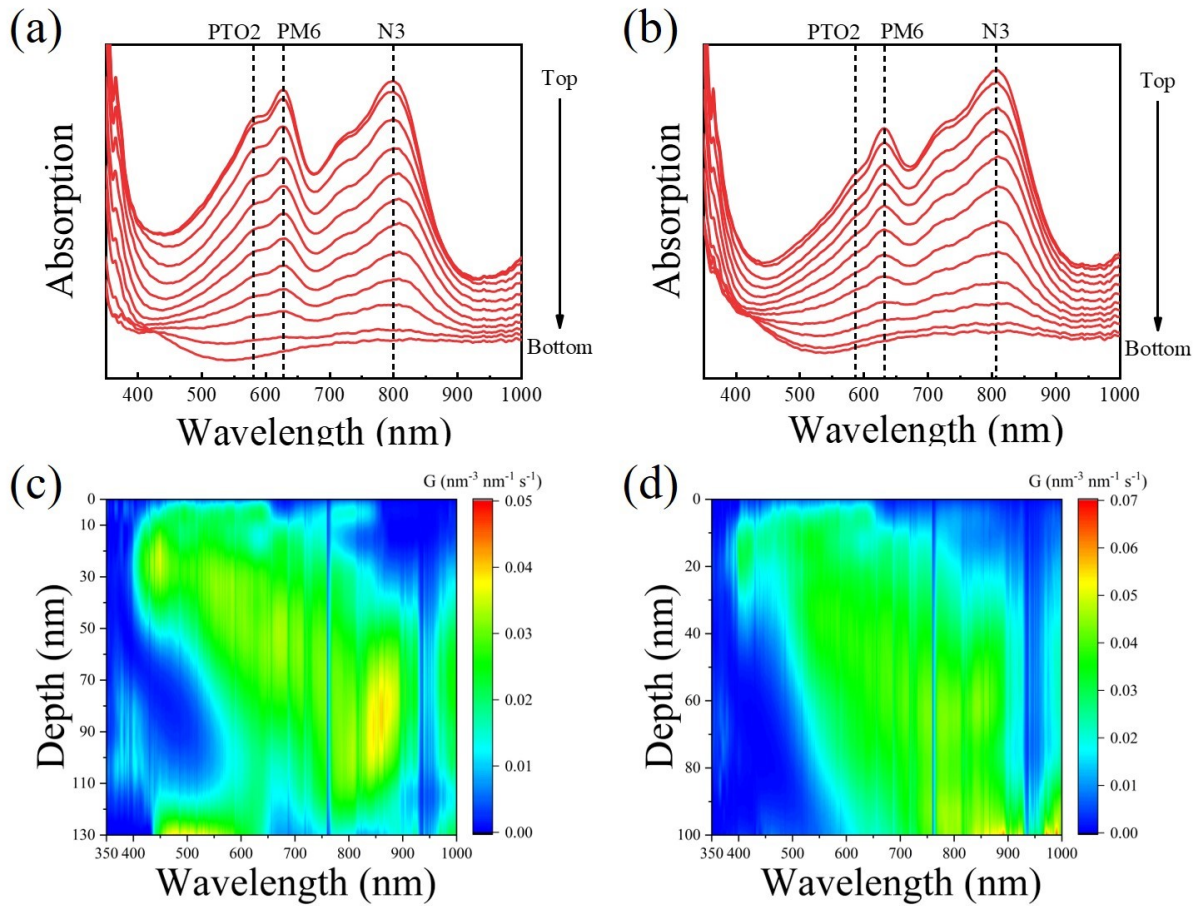


Fig. S7 Film-depth-dependent absorption spectroscopy of PM6, PTO2 and N3 films based on a) BHJ structure and b) LbL structure. Exciton generation rate distribution of PM6, PTO2 and N3 films based on a) BHJ structure and b) LbL structure.