## Thick-Film All-Polymer Organic Solar Cells: Non-Halogen Solvent Processing for Efficient and Stable Photovoltaics

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**Device characterization**. The current density-voltage(J-V) curves of all devices were measured by Keithley 2400 Source Meter under AM 1.5G (100 mW cm-2) equipped with an Enlitech solar simulator. A standard silicon reference cell with a KG5 filter was used for calibration to ensure the light intensity during testing. The device area (3.95 mm<sup>2</sup>) was identified using an optical microscope(Olympus BX51). Both of the light intensity studies and dark J-V measurements were also performed by this system. The measurements of external quantum efficiencies (EQEs) were measured using the Enlitech QE-S EQE system, with a standard Si diode for calibration. Besides, a 300 W

lamp from Enlitech was utilized to generate monochromatic light. Impedance spectroscopy measurement was performed by a commercially available Paios system (FLUXiM AG).

**Transient photovoltage (TPV) and transient photocurrent (TPC) measurements**: In the TPV and TPC measurements, devices are tested under specific lighting and electrical conditions. For TPV, the device is subjected to background light bias provided by a focused Quartz Tungsten-Halogen Lamp, simulating working device conditions where the voltage matches the open-circuit voltage ( $V_{OC}$ ) under solar illumination. Photo-excitations are introduced using 8 ns laser pulses (Oriental Spectra, NLD520) at a wavelength of 518 nm, with a spectral width of 3 nm. A digital oscilloscope is used to record the voltage changes at open-circuit conditions. In contrast, TPC measurements are conducted under short-circuit conditions using the same excitation wavelength, but without background light bias.

## **Deep Level Transient Spectroscopy Measurement**

To gain information on trap state density, we carried out current-based deep-level transient spectroscopy (DLTS) measurement. The experiment is carried at a reverse bias voltage of -3.0 V lasting from 0.1 to 10 µs after applying a voltage step to the devices. Using the result of the measurement, the trap state density,  $N_t$ , can be calculated based on the equation:

$$j_{te}(t) = 2 \times \frac{1}{\tau_{te}} \times q \times d \times N_t \times exp^{[to]}(-\frac{t}{\tau_{te}})$$

where  $j_{te}(t)$  is the trap emission current,  $\tau_{te}$  the catch-trap emission time constant, q the elementary charge, d the film thickness, and  $N_t$  the trap state density.

## Film-depth-dependent light absorption spectroscopy (FLAS) and composition distribution:

Film-depth-dependent light absorption spectra were acquired using an in situ

spectrometer (PU100 crafted by Shaanxi Puguang Weishi Co. Ltd.) (Shaanxi, China), with a soft plasma-ion source. Which generates soft ions with power supply (100 W) accompanying with an input oxygen pressure of approximately 10 Pa. to etch film surface incrementally while preventing the materials underneath the surface, a spectrometer will real-time monitor. According to the Beer-Lambert's film-depth-dependent absorption spectra were extracted to reveal the composition distribution of the material at various depth.

The thickness measurement: The stylus-based surface profiler is used for measuring surface topography, providing accurate information about height and roughness. The device scans the sample's surface with a stylus, monitoring its movement to detect small variations in surface contours. In this study, the profiler is primarily used to measure the thickness of the devices. Incorporating with software, the sensor captures the surface variations with high sensitivity. The output electrical signal from the sensor is processed and displayed in the software, showing detailed surface topography, including peaks and valleys, which reflect various surface features.

**In situ UV-Vis absorption measurement:** In situ UV-Vis absorption measurements were conducted using a DU-100 system. The optical fiber was precisely aligned to focus the light on the center of the film. The measurements were taken with a sampling interval of 40 ms and an integration time of 5 ms per sample point. To ensure smooth and accurate absorption curves, the average sampling time was adjusted between 4 and 7 iterations, allowing for optimal data collection.

Atomic force microscopy (AFM): AFM measurements were conducted by a Scanning Probe Microscope Dimension 3100 in tapping mode, under ambient conditions at room temperature. All film samples were spin-cast on glass/ITO substrates.

**Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements:** GIWAXS were performed at beamline BL16B1 at the Shanghai Synchrotron Radiation Facility (SSRF). Samples were prepared on Si substrates using identical solutions as those used in devices. The 10k eV X-ray beam was incident for 30s at a grazing angle of 0.15°, which maximized the scattering intensity from the samples. The scattered Xrays were detected using a Dectris Pilatus 1 M photon counting detector. 2D images were azimuthally averaged to obtain the reported one-dimensional (1D) scattering profiles using the Nika package. The coherence length was calculated using the Scherrer equation: CCL =  $2\pi K/FWHM$ , where K is a dimensionless shape factor, normally with a value of 0.9. FWHM is the full with at half maximum of peak and  $\theta$  is Bragg's angle (scattering angle).

## **Experimental procedures**

All devices fabricated with conventional structure were а (ITO/PEDOT:PSS/PM6/PJ1-7/PNDIT-F3N/Ag). The following are the experimental procedures. ITO-glass substrates were cleaned by sequential sonication in a detergent solution, followed by sonication in deionized water, and finally in isopropyl alcohol twice, with each step lasting 15 minutes. After cleaning, the substrates were dried at 120°C on a hot plate. Next, the substrates were treated with ultraviolet/ozone for 15 minutes. Following this, an aqueous PEDOT:PSS solution was spin-coated onto the cleaned ITO substrates at 6,000 rpm. The films were then annealed at 150°C for 15 minutes in air, resulting in a film thickness of approximately 30 nm. The following steps were carried out in a nitrogen-filled glovebox. For the active layer, PM6 and PJ1- $\gamma$ were dissolved separately in toluene and stirred at 60°C for 50 minutes before spin coating. Additionally, chloronaphthalene (CN) was added to the PJ1- $\gamma$  solution. Notably, for the 200 nm and 300 nm layers, the same concentration of additive was also added to the donor solution. The active layer was spin-coated on top of the PEDOT:PSS layer, then thermally annealed at 100°C for 5 minutes. Next, PNDIT-F3N in methanol with a concentration of 0.5 mg/mL, containing 0.5% acetic acid, was spin-coated on top of the active layer at 3,000 rpm for 30 seconds. Finally, 100 nm of Ag was thermally evaporated under high vacuum through a shadow mask to form the anode.

In our study, we fabricated devices with different thicknesses (100 nm, 200 nm,

and 300 nm). For the device with a 100 nm thickness, the PM6 solution was first spincoated from a 7.5 mg/mL toluene solution at 4,000 rpm for 30 seconds. The acceptor layer was then deposited on top of the donor layer from a 10 mg/mL toluene solution containing 2% CN, using the same spin speed of 4,000 rpm for 30 seconds. For the 200 nm device, the donor concentration was 9 mg/mL, the acceptor concentration was 10 mg/mL, and 2% CN was added, with a spin speed of 3,500 rpm. For the 300 nm device, both the donor and acceptor concentrations were 12 mg/mL with 6% CN, and the spin speed was set to 3,000 rpm.

PJ1-γ PM6/PJ1-y Spin coating speed PM6 layer PM6 layer after layer (nm) layer rinsing (nm) (rpm) (nm)100 nm 4000/4000 58 82 50 97 200 nm 3500/3500 110 95 172 300 nm 3000/3000 150 151

 Table S1. Thickness of different layer.



Figure S1. J-V measurement of toluene-casted devices with varying active-layer thickness employing blend-casting.



Figure S2. EQE measurement of toluene-casted devices with varying thickness fabricated by blend-casting.

Table S2. Photovoltaic parameters for PM6/PJ1-y devices fabricated by blend-casting

Thickness	$V_{\rm OC}\left({ m V} ight)$	$J_{SC}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
100 nm	0.933	26.09 (24.47) <sup>a</sup>	66.53	16.20
200 nm	0.923	24.39 (23.43) <sup>a</sup>	64.44	14.51
300 nm	0.910	24.23 (23.18) <sup>a</sup>	46.11	10.17

a: Integrated current densities from EQE spectra.



Figure S3. DLTS measurement of devices with varying active-layer thickness fabricated.



Figure S4. Photo-CELIV measurement of SqP devices with different active-layer thickness.



**Figure S5.** lg ( $J_{SC}$ ) versus lg ( $P_{light}$ ) curves of all-polymer solar cell with different thickness.



Figure S6. Impedance spectra curves of all-polymer solar cell with different thickness.



Figure S7. The equivalent circuit for fitting impedance spectroscopy.

Table S3.	Fitting parameters	of impedance	spectroscopy	using	equivalent circuit	•
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Thickness	$R_{S}[\Omega]$	CPE-T [nF]	CTE-P	$R_{CT}[\Omega]$
100 nm	21.51	6.51	0.932	2215
200 nm	26.76	6.67	0.942	2842
300 nm	31.82	12.4	0.875	3068



**Figure S8.** Depth-dependent integrated generation rate curves of the PM6/PJ1- $\gamma$  device with different active layer thicknesses.



Figure S9. In situ UV-vis absorption spectra of SqP film using chloroform solvent.



**Figure S10.** *J*-*V* curves for PM6/PJ1- $\gamma$  devices using chloroform as the main solvent.

**Table S4.** Photovoltaic parameters for PM6/PJ1- $\gamma$  devices fabricated with chloroform solvent.

Thickness	$V_{\rm OC}\left({ m V} ight)$	$J_{SC}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
100nm	0.937	23.86	72.33	16.17
200nm	0.928	23.51	66.49	14.51
300nm	0.915	19.62	60.22	10.82



Figure S11. AFM height images (size 5  $\mu$ m x 5  $\mu$ m) of the PM6/PJ1- $\gamma$  films with different active layer thicknesses.



Figure S12. The 2D GIWAXS pattern of three SqP films.



**Figure S13.** Scattering cut-line profiles of 2D GWAXS for three SqP films: a) out-ofplane, b) in-plane.

Thickness	Direction	q (Å-1)	<i>d</i> -spacing (Å)	FWHM (Å <sup>-</sup> 1)	CCL (Å)
100 nm	IP	0.283	22.2	0.07	80.78
	OOP	1.659	3.79	0.249	22.71
200 nm	IP	0.278	22.6	0.066	85.68
	OOP	1.691	3.72	0.223	25.36
300 nm	IP	0.281	22.2	0.052	108.75
	OOP	1.665	3.77	0.215	26.3

Table S5. 2D GIWAXs pattern of SqP films with varying thickness



Figure S14. The normalized PCE of SqP devices over heating time under 80°C.