

Electronic Supplementary Information

Highly efficient non-fullerene organic solar cells enabled by a delayed processing method using a non-halogenated solvent

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1. Methods

Materials. PM6 and BTP-BO-4Cl were purchased from Solarmer Material Inc. BV was synthesized according to previous report.¹ Other reagents and solvents used were purchased from commercial sources and used as received.

Material characterization. UV-vis-NIR spectra were obtained on a Shimadzu UV-2700 spectrophotometer. GIWAXS measurements were conducted at the National Synchrotron Light Source II, Brookhaven National Lab, Suffolk, Upton, New York, America. All the pristine films GIWAXS measurements were processed from their respective solutions immediately as the solutions cooled to room temperature. The blend films for GIWAXS measurements were prepared by spin-coating active blend solutions same as the device conditions on top of a silicon wafer. AFM images were obtained by using a Bruker Inova atomic microscope in tapping mode. TEM images were obtained by using a ZEISS LIBRA 200 FE transmission electron microscope.

Device fabrication. The patterned indium tin oxide (ITO, sheet resistance = $15\ \Omega$ square⁻¹) glass substrates were sequentially ultrasonicated with detergent, deionized water, acetone, and isopropanol. Then, the ITO glasses were treated with UV for 30 min in a UV-ozone chamber. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) (Bay P VP. Al 4083, Bayer AG) was filtrated through a 0.45 μ m nylon filter and then spin-coated on the cleaned ITO substrates at 5000 rpm for 60 s to form a thin layer (35 nm). The PM6:BTP-BO-4Cl (1:1.2, w/w, 22 mg/mL in CB or 17.6 mg/mL in Tol), PM6:IT-4F (1:1, w/w, 16 mg/mL in Tol) and PM6:Y6 (1:1.2, w/w, 17.6 mg/mL in Tol) solution were prepared. PM6:BTP-BO-4Cl and PM6:IT-4F were stirred

under 60 °C, while PM6:Y6 were stirred under 80 °C for at least 3 hours before used. For *n*-doped devices, 0.4 wt% of BV was added into the above active blend solutions. After delayed at room temperature for different times, the solutions were then spin-coated on the substrates at a speed of 2500 rpm for 30 s to form a ~110 nm thickness of active layer. The substrates were then thermal annealed at 100 °C for 5 min. PFN-Br (0.5 mg/mL in methanol) was spin-coated on the top of the active layer to form a thin cathode interlayer (~5 nm). Finally, aluminum electrode (Al, 100 nm) was deposited under high vacuum ($\sim 10^{-5}$ Pa) in an evaporation chamber. The device area was exactly fixed at 4.00 mm². Hole-only devices were fabricated with a structure of ITO/PEDOT:PSS/PM6:BTP-BO-4Cl/MoO₃/Au. After active layer preparation as depicted above, a 10 nm of MoO₃ layer was evaporated before the evaporation of Au (100 nm) electrode. Electron-only devices were fabricated with a structure of ITO/ZnO/PM6:BTP-BO-4Cl/PFN-Br/Al. Diethyl zinc (2M in toluene diluted by tetrahydrofuran) was spin-coated on the top of ITO glass at 5000 rpm under dry air flow and baked under 180 °C for 30 min. PFN-Br (0.5 mg/mL in methanol) was spin-coated before and after active layer deposition. Then, Al (100 nm) was deposited under high vacuum ($\sim 10^{-5}$ Pa) in an evaporation chamber.

Device Characterization. The *I-V* characterization was performed on a computer-controlled Keithley 2400 Source under AM1.5G (100 mW cm⁻²) using a solar simulator (XES-70S1, SAN-EI), which was calibrated by a standard Si solar cell (AK-200, Konica Minolta, INC.). The EQE values were measured with an QE-R solar quantum efficiency test system (Enlitech Co., Ltd., Taiwan, China).

2. Supplementary Figures

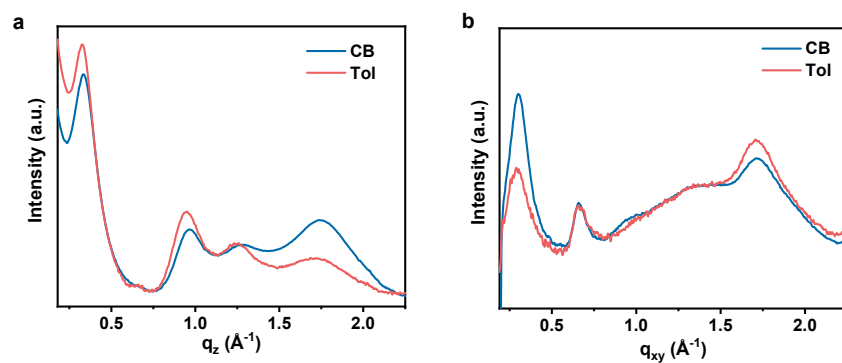


Fig. S1 (a) OOP and (b) IP diffraction profiles of PM6 processed by CB and Tol solutions.

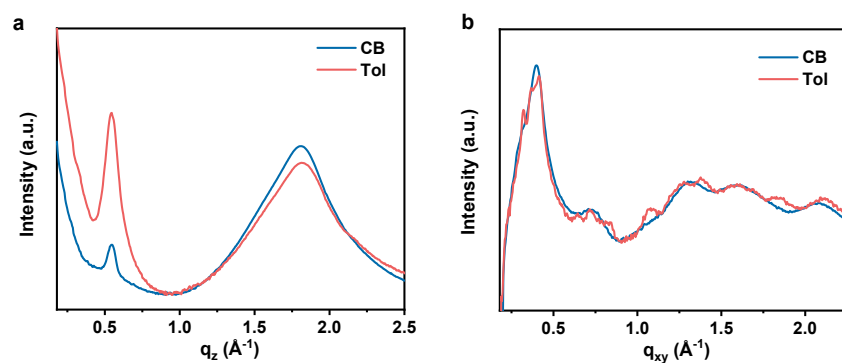


Fig. S2 (a) OOP and (b) IP diffraction profiles of BTP-BO-4Cl processed by CB and Tol solutions.

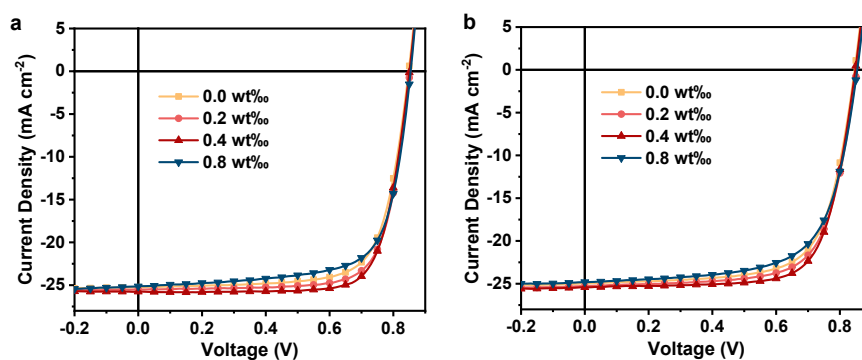


Fig. S3 J - V curves of PM6:BTP-BO-4Cl-based devices processed from (a) CB and (b) Tol solutions with different amount of BV additive.

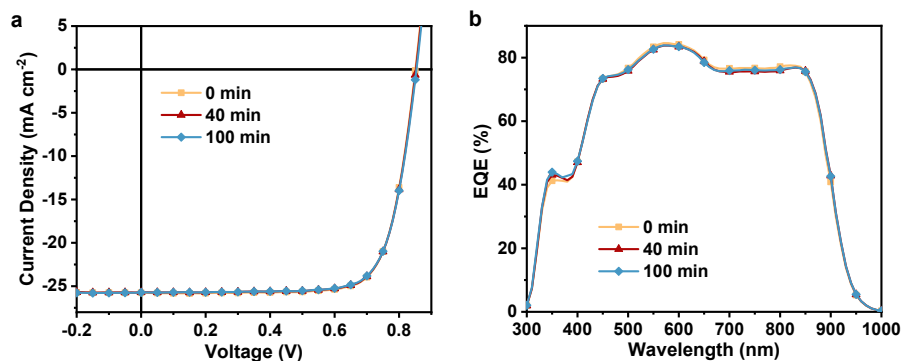


Fig. S4 (a) J - V curves and (b) EQE curves of PM6:BTP-BO-4Cl-based devices processed from different time delayed CB solutions.

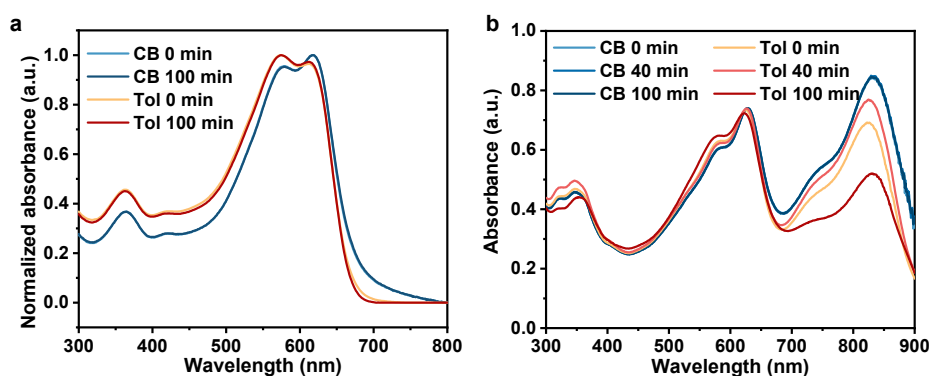


Fig. S5 (a) Normalized absorption profiles of the pristine PM6 films casted from CB or Tol solutions with different delayed processing times. (b) UV-vis-NIR absorption profiles of the PM6:BTP-BO-4Cl blend films casted from CB or Tol solutions with different delay times.

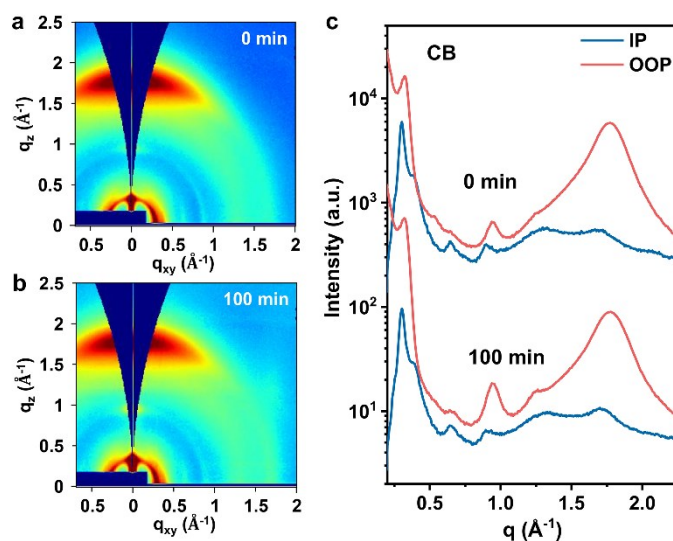


Fig. S6 (a,b) GIWAXS patterns of PM6:BTP-BO-4Cl films casted from CB solutions with different delay times. (c) The corresponding IP and OOP line-cuts.

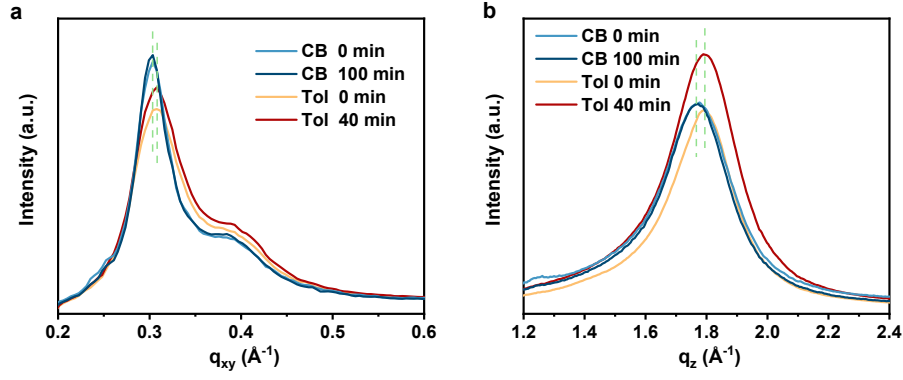


Fig. S7 (a) (100) diffraction in the in-plane direction and (b) (010) diffraction in the out-of-plane direction of PM6:BTP-BO-4Cl films casted from CB or Tol solutions with different delay times.

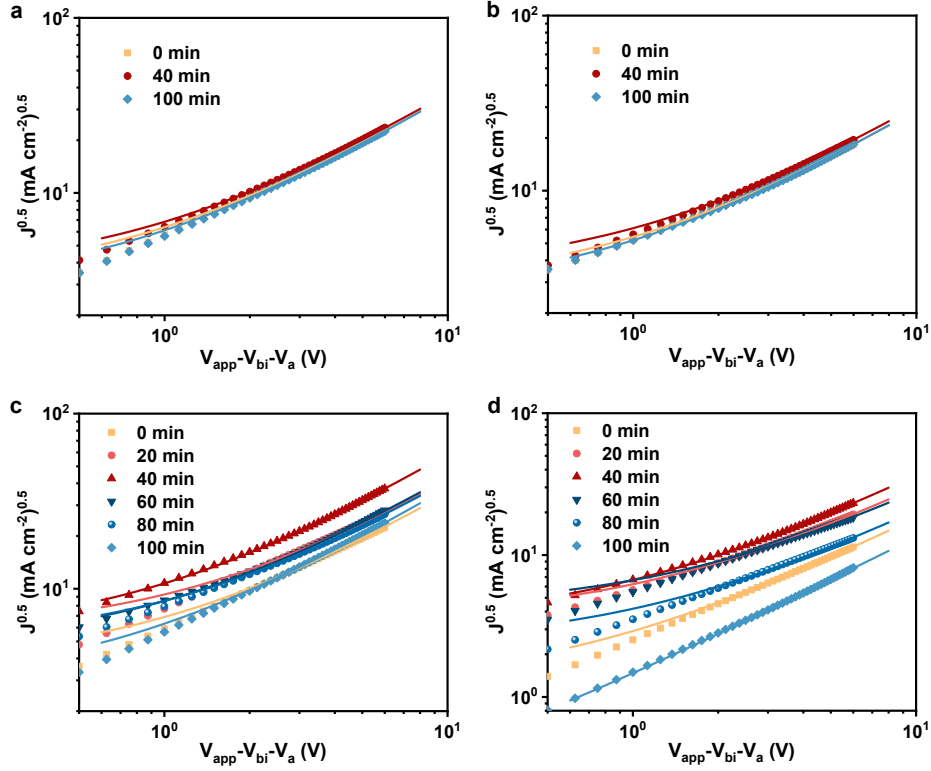


Fig. S8 J - V curves of the (a,c) hole-only devices and (b,d) electron-only devices based on PM6:BTP-BO-4Cl processed from (a,b) CB and (c,d) Tol solutions with different delay times.

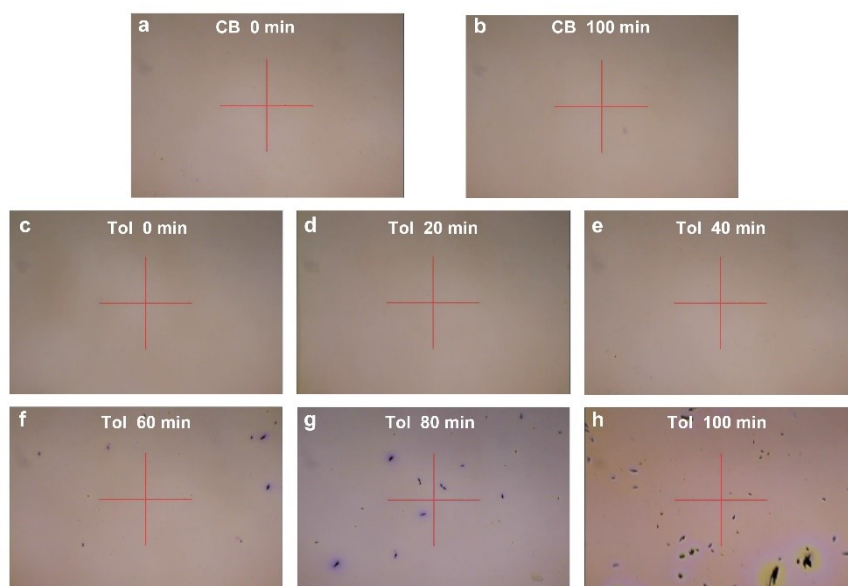


Fig. S9 Optical micrographs of PM6:BTP-BO-4Cl films casted from (a, b) CB solutions and (c-h) Tol solution with different delay times.

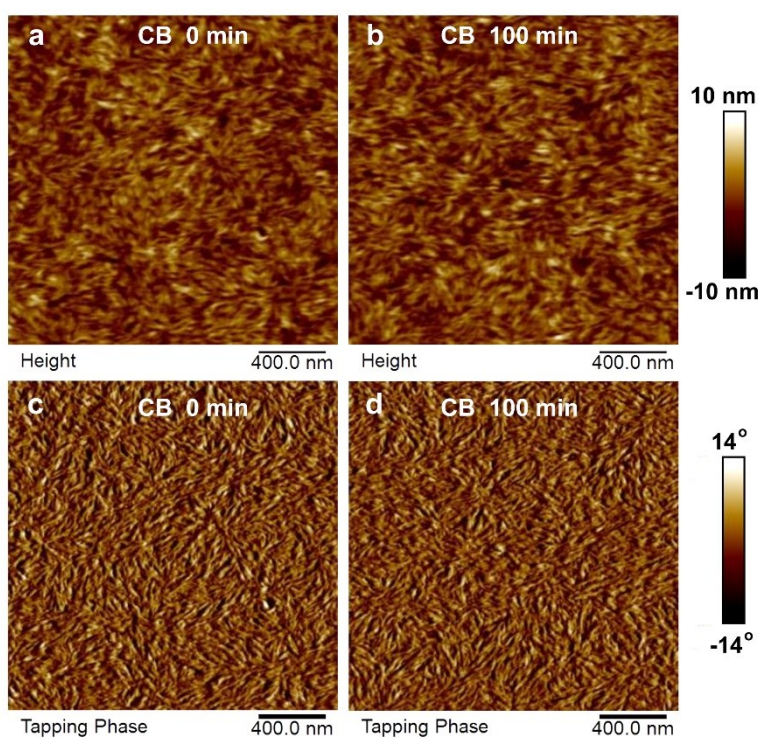


Fig. S10 AFM (a, b) height and (c, d) phase images of PM6:BTP-BO-4Cl films casted from CB solutions with different delay times.

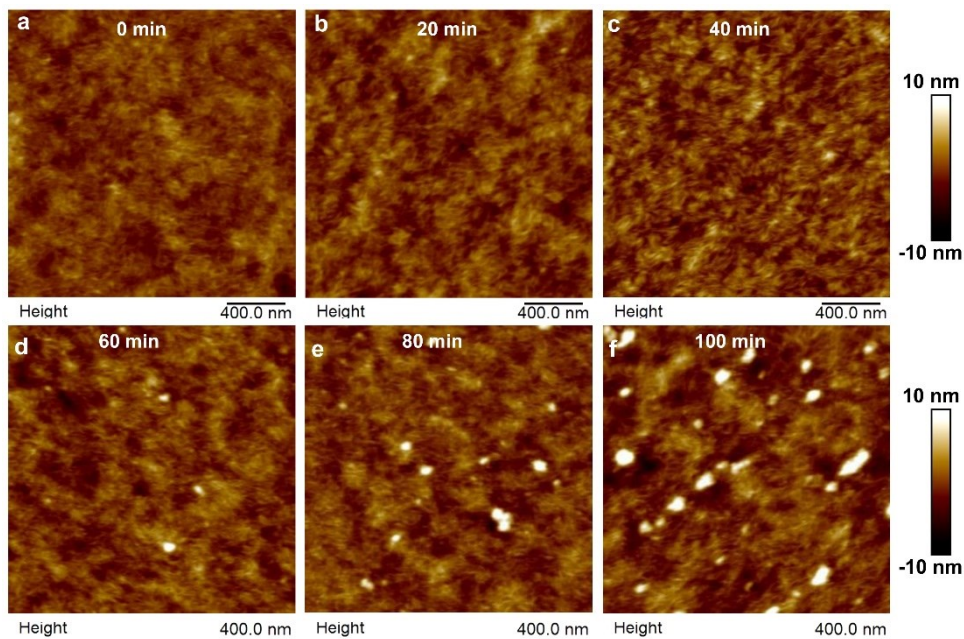


Fig. S11 AFM height images of PM6:BTP-BO-4Cl films casted from Tol solutions with different delay times.

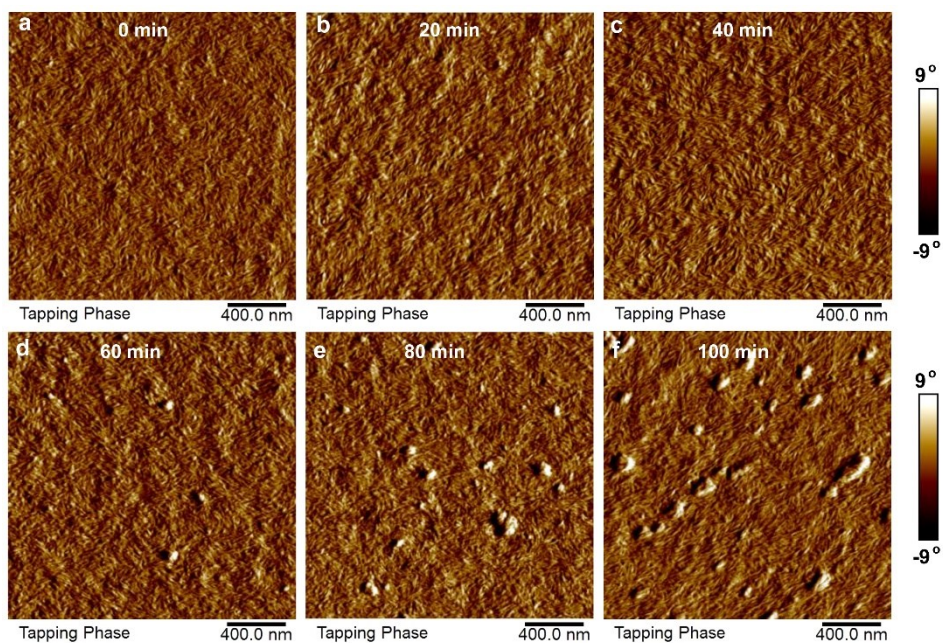


Fig. S12 AFM phase images of PM6:BTP-BO-4Cl films casted from Tol solutions with different delay times.

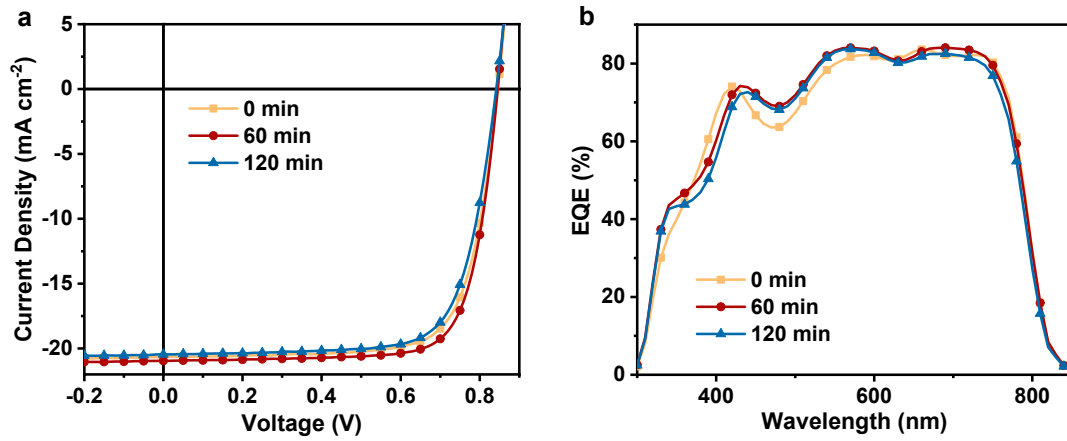


Fig. S13 Delay time dependent (a) J - V curves and (b) EQE curves of PM6:IT-4F-based PSCs processed from Tol solutions.

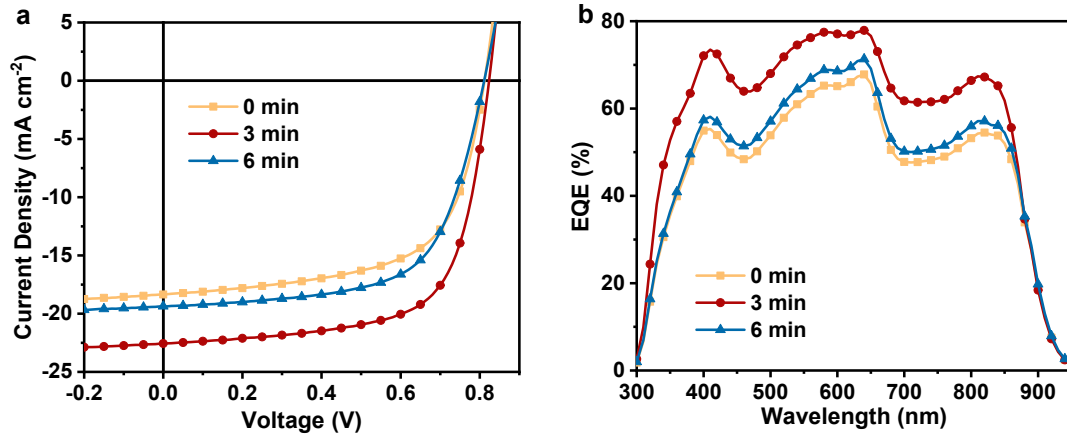


Fig. S14 Delay time dependent (a) J - V curves and (b) EQE curves of PM6:Y6-based PSCs processed from Tol solutions.

3. Supplementary Tables

Table S1 Contact angle of water and ethylene glycol droplet.

Material	Solvent	θ_{water} (°)	θ_{EG} (°)	γ (mN m ⁻¹)
PM6	CB	107.28±0.06	85.83±0.65	18.15
PM6	Tol	107.71±0.08	85.57±0.66	17.92
BTP-BO-4Cl	CB	99.53±0.50	71.88±0.17	24.07
BTP-BO-4Cl	Tol	101.75±0.18	72.32±0.57	25.71

Table S2 Photovoltaic parameters of the PSCs with/without BV additive CB or Tol solutions without delayed processing.

Solvent	BV (wt%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
CB	0	0.846	25.24	73.2	15.63
CB	0.2	0.852	25.51	75.1	16.32

CB	0.4	0.851	25.76	76.5	16.77
CB	0.8	0.855	25.14	71.2	15.30
Tol	0	0.847	24.98	69.7	14.75
Tol	0.2	0.853	25.27	70.5	15.20
Tol	0.4	0.848	25.41	72.8	15.69
Tol	0.8	0.854	24.81	67.4	14.28

Table S3 Photovoltaic parameters of the PSCs processed from CB solutions with different delay times.

Delay time (min)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	J_{EQE} (mA cm ⁻²)	FF (%)	PCE (%)
0	0.851	25.76	25.33	76.5	16.77
40	0.852	25.70	25.21	76.3	16.71
100	0.854	25.72	25.26	76.2	16.74

Table S4 Delay time dependent charge carrier mobilities of PM6:BTP-BO-4Cl processed from CB or Tol solutions.

Delay time (min)	Solvent	Hole mobility μ_h ($\times 10^{-4}$ cm ² V ⁻¹ s ⁻¹)	Electron mobility μ_e ($\times 10^{-4}$ cm ² V ⁻¹ s ⁻¹)	μ_h/μ_e
0	CB	3.57	2.23	1.60
40	CB	3.73	2.41	1.55
100	CB	3.61	2.32	1.56
0	Tol	3.29	0.97	3.39
20	Tol	4.38	2.02	2.16
40	Tol	5.84	3.86	1.51
60	Tol	4.97	1.91	2.60
80	Tol	4.38	1.11	3.95
100	Tol	4.07	0.58	7.02

Table S5 Delay time dependent photovoltaic parameters of PM6:IT-4F and PM6:Y6 based PSCs processed from Tol solutions.

Blend	Delay time (min)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	J_{EQE} (mA cm ⁻²)	FF (%)	PCE (%)
PM6:IT-4F	0	0.846	20.65	20.18	74.0	12.93
PM6:IT-4F	60	0.845	20.95	20.56	76.1	13.48
PM6:IT-4F	120	0.842	20.46	20.04	73.3	12.63
PM6:Y6	0	0.813	18.35	17.96	62.6	9.35
PM6:Y6	3	0.823	22.56	22.09	67.5	12.53
PM6:Y6	6	0.811	19.37	18.91	64.1	10.07

4. References

- 1 D. Kiriya, M. Tosun, P. Zhao, J. S. Kang and A. Javey, *J. Am. Chem. Soc.*, 2014, **136**, 7853-7856.