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Supporting Information

Regulating the Crystallization Dynamics through Hydrogen Bonding

for High Efficiency Tin Halide Perovskite Solar Cells

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Experimental Section

Materials

N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), aniline (>99%, Adamasbeta), dimethyl sulfoxide (DMSO, 99.9%, Sigma-Aldrich), chlorobenzene (CB, 99.8%, Sigma-Aldrich), isopropanol (IPA, 99.5%, Adamas-beta), formamidinium iodide (FAI, 99.9%, Great-Cell), methylammonium bromide (MABr, 99.9%, Great-Cell), tin (II) iodide (SnI₂, 99.99%, Adamas-beta), tin fluoride (SnF₂, 99%, Sigma-Aldrich), phenethylammonium iodide (PEAI, >99.5%, Xi'an Polymer Light Technology Corp.), tin powder (Sn, 99.8%, Sigma-Aldrich), poly (3,4-ethylene dioxythiophene)-poly (styrene sulfonate) (PEDOT: PSS, 4083, CleviousTM HTL Solar), bathocuproine (BCP, >98%, Adamas-beta), silver (Ag, 99.9%, Trillion Metals), indium tin oxide (ITO, 7-9 Ω sq⁻¹, Advanced Election Technology CO.Ltd). All the commercial materials were purchased and used directly without any other processing.

C₆₀-ETPA synthesis¹:

 C_{60} (0.366 g, 0.5 mmol) and 2eq. of (2-ethylhexyl)glycine, 1 eq. of 4-(bis(4methoxyphenyl)amino)benzaldehyde were dissolved in 60 ml of 1,2-DCB. The mixture was heated for 2 h at 120 °C under nitrogen atmosphere with intense stirring. After cooled down and the solution was removed under pressure. The crude product was purified through column chromatography (petroleum ether/ethyl acetate = 9/1 vol/vol) to obtain C₆₀-ETPA (0.108 g; yield: 29.5%) as a brown solid. 1H NMR (400 MHz, Chloroform-d) δ 7.58 (s, 2H), 7.38 (s, 1H), 7.15 (d, J = 8.8 Hz, 1H), 6.99 (dd, J = 21.0, 8.2 Hz, 5H), 6.81 (d, J = 8.5 Hz, 4H), 5.08 (d, J = 9.3 Hz, 1H), 4.99 (s, 1H), 4.06 (d, J = 9.4 Hz, 1H), 3.80 (s, 6H), 3.10 (t, J = 11.5 Hz, 1H), 2.52 (t, J = 9.9 Hz, 1H), 2.05 – 1.98 (m, 2H), 1.46 (s, 9H), 1.36 (s, 4H), 1.31 (s, 6H), 1.26 (d, J = 15.3 Hz, 1H), 1.07 (q, J = 7.5 Hz, 2H), 1.00 (s, 5H), 0.92 (s, 1H), 0.10 (s, 17H). HR-MS: (ESI) m/z: C₉₀H₃₈N₂O₂; calculate: 1178.2766; found: 1178.2933.

Device Fabrication

ITO glass was carefully cleaned with detergent, deionized water, ethanol, acetone, and

isopropyl for 20 min, sequentially. Then, the cleaned ITO substrates were blown dry with N₂ and exposed to UV light for 15 min. PEDOT: PSS was spin-coated on the ITO substrate at 4000 rpm for 50 s followed with 30 min annealing at 140 °C under ambient conditions. For the preparation of perovskite precursor solution, 128.9 mg FAI, 28.0 mg MABr, 372.5 mg SnI₂, 15.7 mg SnF₂ and 5 mg Sn⁰ were dissolved in 1 ml (DMF : DMSO = 4 : 1, v : v) solvent and stirring overnight. The aniline was added into the precursor solution with a concentration of 0.36 mM. 12% PEAI was added before spincoating. After being filtered with 0.22 µm PTFE filters, 45 µL precursor solution was spin-coated on the prepared substrate at 8000 rpm for 60 s. At 10 s after the start of spin-coating, 150 µL CB was dropped on the film. And then the film was annealed at 80 °C for 10 min. Next, 50 µL C₆₀-ETPA (20 mg ml⁻¹ in CB) was coated on the film at 2000 rpm for 30 s followed by annealing at 70 °C for 10 min. Then 90 µL BCP (5 mg ml⁻¹ in IPA) was spin-coated at 6000 rpm for 30 s and annealed at 70 °C for 10 min. Finally, the Ag electrode (100 nm) was evaporated at a speed of 2 A s⁻¹ under a high vacuum level.

Equations for device characterization

The microstrain of the perovskite film was calculated from XRD data by Williamson-Hall plot with the following equation:²

$$\beta_T \cos\theta = \frac{\kappa\lambda}{D} + 4\varepsilon\sin\theta \tag{1}$$

where θ refers to the peak position in radians, λ is the X-ray wavelength with the value of 0.15406 nm, K means shape factor (0.9), D refers to the average crystal size and $\beta_{\rm T}$ corresponds to the full-width half maximum, respectively.

The carrier mobility could be estimated by Photo-CELIV measurement and calculated with the equation:³

$$\mu_e = \frac{2d^2}{3At_{max}^2 [0.36(\frac{\Delta j}{j_0})] + 1}$$
(2)

where d is the film thickness, A is related to extraction speed, t_{max} , Δj , are correspond

to the maximum extraction time and extraction peak, and j_0 , refers to displacement current.

The value of V_{TFL} could be obtained from the fitting curves shown in SCLC plot so that the trap density was calculated by the following equation:⁴

$$N_t = \frac{2\varepsilon\varepsilon_0 V_{TFL}}{eL^2} \tag{3}$$

where L, ε , $\varepsilon 0$ belongs to the film thickness, the relative dielectric constant and the permittivity of vacuum, respectively.

In addition, the built-in potential (V_{bi}) could be obtained by the Mott-Schottky measurement with the following equation:⁵

$$\frac{A^2}{C^2} = \frac{2(V_{bi} - V)}{q\varepsilon\varepsilon_0 N_d} \tag{4}$$

where V, A, C corresponds to the applied potential, the effective area, and the capacitance, respectively.

To get the DOS and n, first, the differential capacitance C is calculated at each V_{oc} value as:⁶

$$C = \frac{\Delta Q}{\Delta V_{oc}} \tag{5}$$

where ΔQ is the short-circuit photogenerated charge integrated from the TPC results, and the ΔV_{oc} under different light intensity can be obtained from the OCVD test results. Then, DOS can be derived from the capacitance using the equation:⁷

$$DOS = \frac{C}{Le^2} \tag{6}$$

where C is the chemical capacitance, L is the thickness of the perovskite film, and e is the elementary charge.

Characterization

The Fourier transform infrared (FTIR) spectra were detected by a Fourier transform infrared spectroscopy (Bruker). KBr powder was ground and pressed into flakes. Then aniline or aniline + FAI was dropped onto the flaked KBr for FTIR measurement. For

FTIR spectra of FAI, the FAI powder was mixed with KBr and thoroughly ground. The mixed powder was pressed into flakes for measurement. X-ray diffraction (XRD) analysis was measured by a MiniFlex 600 (Rigaku) X-ray diffractometer with Cu Ka radiation ($\lambda = 0.15406$ nm, 40 kV, 100 mA). The UV-vis absorption spectra were probed by UV-2600 (Shimadzu). The steady photoluminescence (PL) and timeresolved photoluminescence (TRPL) were collected by PTI QuantaMaster 8000 (HORIBA) with a pulsed source at 510 nm laser. J-V characteristics were performed by solar simulator (San-EI Electric, 3A) under standard AM 1.5G (1000 W m⁻²) illumination in N2 atmosphere (calibration with silicon wafer (AK-200, KONICA MINOLTA, INC.) before testing). The devices were measured from -0.1 to 0.85 V with a 200 mV/s scan speed and 20 ms setting time The space charge limited current (SCLC) measurement was conducted by Keithley 2400 source meter in the voltage range of -0.1~3 V. The external quantum efficiency (EQE) was measured by QE-R (Enlitech). The transient photocurrent (TPC), transient voltage (TPV), Mott-Schottky (M-S), Photo-CELIV, dark state J-V, and impedance spectroscopy (IS) were tested by Paios 4.0 system with a 60 mW LED light source (FLUXiM). For Mott-Schottky (M-S) measurements, the positive and negative electrodes of the solar cell were connected with the Paios 4.0 system test port. Then the solar cell was tested at a fixed frequency of 20 kHz in the voltage range of -0.1~2 V. For Photo-CELIV tests charge carriers were created by an 60 mW LED pluse, and the charges extracted by the voltage ramp of 0.1 V/µs with illumination duration of 100 µs. For DOS characterization by Paios 4.0 system, The offset voltage set in the transient photocurrent (TPC) method was 0.85 V for the aniline devices and 0.82 V for the control devices, respectively. The carriers were generated by the pulsed light and then the light was turned off to simultaneously measure the attenuation of a voltage signal. The light-pulse length, the setting time and the follow-up time were all 100 ms. The sweep variable was absolute light intensity which was from 0% to 100% with 10 steps. The effective area of the device is 0.096 cm^2 .



Fig. S1. The perovskite film images of (a) control, (b) with aniline dripping and (c) after aniline post-treatment.



Fig. S2. Photograph of SnI_2 solution (1M) dissolved in aniline after stirring overnight.



Fig. S3. XRD patterns of the control and perovskite film with aniline.



Fig. S4. The fitting curves of the (a) control and (b) aniline perovskite films; (c) microstrain plot of control and aniline film.



Fig. S5. Top-view SEM images of (a) control and (b) aniline film; cross-sectional SEM images of (c) control and (d) aniline devices.



Fig. S6. The ultraviolet-visible absorption spectra of perovskite films.



Fig. S7. Photo-CELIV plots of the (a) (c) control and (b) (d) aniline device.



Fig. S8. SCLC plots of hole-only devices with a structure of ITO/PEDOT: $PSS/FA_{0.75}MA_{0.25}SnI_{2.75}Br_{0.25}/Spiro-OMeTAD/Ag.$



Fig. S9. The steady-state PL spectra of perovskite films.



Fig. S10. The box diagram of (a) PCE, (b) V_{oc} , (c) J_{sc} and (d) FF for 20 devices.



Fig. S11. The normalized PCE of control and aniline devices (a) under N_2 atmosphere for 1440 h and (b) in air (RH ~70%, without encapsulation) for 24 h.



Fig. S12. The TPC and TPV curves of (a) (b)control (c) (d) and aniline device.



Fig. S13. DOS in the bandgap calculated from TPV and TPC measurements.



Fig. S14. Dark state *J*-*V* curves of control and aniline device.



Fig. S15. Mott-Schottky curves of control and aniline device.



Fig. S16. EIS curves of control and aniline device.



Fig. S17. TPV curves of the control and aniline device.



Fig. S18. The light intensity dependence of $V_{\rm oc}$.

	2θ (°)	FWHM (°)	D (nm)	δ*10 ⁻³ (nm ⁻²)	4sinθ	βcosθ
	14.282	0.111	72.130	0.192	0.497	0.00192
Contro l	28.563	0.132	62.103	0.259	0.987	0.00223
	43.303	0.162	52.761	0.359	1.476	0.00263
	14.281	0.111	72.130	0.192	0.497	0.00192
Aniline	28.561	0.127	64.548	0.240	0.987	0.00212
	43.298	0.148	57.751	0.300	1.476	0.00240

Table S1. The detailed microstrain calculation parameters of the perovskite films.

 Table S2. The fitted PL lifetime from TRPL spectra of the control and aniline perovskite films.

	\mathbf{A}_{1}	$\tau_1(ns)$	\mathbf{A}_{2}	$\tau_2(ns)$	$ au_{avg}(ns)$
Control	0.87	5.86	0.13	11.01	6.99
Aniline	0.76	8.26	0.24	20.30	13.52

Table S3. Detailed photovoltaic performance parameters of the control device and device with aniline.

	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
	757	20.20	67.57	10.34
Control	(765±18.12)	(18.55±0.87)	(66.43±1.93)	(9.32±0.48)
Aniline	788	21.77	70.16	12.04
	(808±20.37)	(19.87±0.75)	(68.61±1.66)	(11.00±0.42)

Light Intensity	$V_{\rm oc}$ (V)	$\Delta V_{ m oc}$ (V)	Q (nC)	C (nF)	DOS (10 ¹⁷ cm ⁻³ eV)
11.10%	0.697	0.116	9.00874	77.66155172	2.970272463
22.20%	0.741	0.072	9.402203	130.5861528	4.994446351
33.30%	0.761	0.052	9.89502	190.2888462	7.277857668
44.40%	0.776	0.037	10.418401	281.5784054	10.76935195
55.6%	0.787	0.026	11.085151	426.3519615	16.30641498
66.70%	0.796	0.017	11.87573	698.5723529	26.71785687
77.80%	0.802	0.011	12.91472	1174.065455	44.90374209
88.90%	0.808	0.005	14.31063	2862.126	109.4659307
100.00%	0.813	0	16.67476		

 Table S4. The calculated DOS of the control device.

Light Intensity	$V_{\rm oc}$ (V)	$\Delta V_{ m oc}$ (V)	Q (nC)	C (nF)	DOS (10 ¹⁷ cm ⁻³ eV)
11.10%	0.75	0.102	7.61352	74.64235294	2.854799068
22.20%	0.789	0.063	7.94079	126.0442857	4.820736421
33.30%	0.809	0.043	8.17903	190.21	7.274842088
44.40%	0.822	0.03	8.35922	278.6406667	10.65699411
55.6%	0.831	0.021	8.52956	406.1695238	15.53451
66.70%	0.838	0.014	8.66979	619.2707143	23.68485703
77.80%	0.844	0.008	8.8218	1102.725	42.17522865
88.90%	0.847	0.005	8.98515	1797.03	68.72987476
100.00%	0.852	0	9.12921		

 Table S5. The calculated DOS of the aniline device.

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