Electronic Supplementary Information for

A trifluorothymine interlayer reduces the degradation of perovskite and controls the cracks of hole transport layers Yutong Ren, Lifei He, Bing Zhang, Tianyu Li, Yi Yuan, Jing Zhang, and Peng Wang*

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1. Experimental section

1.1. Materials

Chlorobenzene (CB, 99.8%, Acros Organics), 4-tert-butylpyridine (TBP, 96%, Aldrich), acetone (≥ 99.5%, Energy Chemical), ethanol (99.7%, Aladdin), isopropanol (IPA, \geq 99.9%, Energy Chemical), aluminum oxide (Al₂O₃ nanoparticles, particle size < 50 nm, 20 wt% in IPA, Aldrich), poly(9-vinylcarbazole) (PVK, average M_n 25,000–50,000, Aldrich), polymethyl methacrylate (PMMA, average $M_{\rm w} \sim 120,000$, Aldrich), titanium diisopropoxide bis(acetylacetonate) (TIACA, 75% in IPA, Aldrich), acetylacetone (ACAC, > 99.0%, TCI), TiO₂ paste (30NR-D, Greatcell Solar), PbI₂ (99.99%, TCI), PbBr₂ (99.99%, TCI), formamidinium iodide (FAI, 99.0%, Greatcell Solar), methylammonium bromide (MABr, 99.0%, Greatcell Solar), CsI (99.0%, TCI), CsBr (> 99.9%, Xi'an Polymer Light Technology Corp.), dimethyl sulfoxide (DMSO, 99.9%, Aldrich), N,N-dimethylformamide (DMF, 99.8%, Aldrich), [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, 99%, Aldrich), poly(3,4ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS, 1.3-1.7% solution in water, Xi'an Polymer Light Technology Corp.), phenethylammonium iodide (PEAI, 98%, TCI), theophylline (98%, TCI), caffeine (98%, TCI), theobromine (98%, TCI), uracil (98%, Energy Chemical), thymine (98%, Energy Chemical), trifluorothymine (TFT, 98%, Energy Chemical), spiro-OMeTAD (≥ 99.8%, Xi'an Polymer Light Technology Corp.), and PTAA (average $M_{\rm p}$ 5,000–10,000, Xi'an Polymer Light Technology Corp.) were purchased from commercial sources and used without further purification. Pentafluorophenylethylammonium iodide (FEAI),¹ 4-(CFPEAI),² trifluoromethyl phenethylammonium iodide 4-tert-butylpyridinium bis(trifluoromethanesulfonyl)imide (BPTFSI),³ and T5H-BMCA⁴ were prepared according to the literature methods.

1.2. General instrumentation

The water contact angle of thin film was measured with a Dropmeter 100P contact angle meter. Transmission polarization optical microscope (POM) images were recorded on a SDPTOP CX40P system. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra were collected on a Vertex 70 FTIR spectrometer (Bruker). X-ray photoelectron spectra (XPS) were measured with K-Alpha+ instrument (Thermo Scientific). Time-resolved photoluminescence (TRPL) decay was measured with a Life-Spec-II fluorescence spectrometer (Edinburgh Instruments Ltd). Impedance spectra (IS) measurements were performed on an AutolabPGSTAT302N electrochemical workstation. The devices were tested in the dark at a set of forward bias potentials, with the frequency range from (10 Hz - 3 MHz). A voltage perturbation of 15 mV was applied. Ultraviolet-visible (UV-Vis) absorption spectra were measured with a Cary 8454 spectrophotometer (Agilent Technologies). X-ray diffraction (XRD) patterns were measured with a SmartLab diffractometer (Rigaku), using Cu K α radiation ($\lambda = 0.15418$ nm) operated at 7200 W power (40 kV, 180 mA). Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) measurement was carried out with a TOF-SIMS 5-100 spectrometer (ION-TOF GmbH). Top-viewed surface morphologies were recorded on a SU-70 field emission scanning electron microscope (Hitachi). Fluorescence optical microscope (FOM) images were recorded with an ECLIPSE Ti-U system (Nikon).

1.3. Fabrication, sealing, and disassembly of solar cell

Fluorine doped tin oxide (FTO) glass was rinsed in turn with detergent, deionized water, acetone, and ethanol by sonication. On the surface of FTO was deposited a compact TiO_2 (c- TiO_2) layer via spray pyrolysis, by use of an ethanolic solution containing TIACA and ACAC. Next, a mesoporous TiO_2 (m- TiO_2) layer with a thickness of ~

200 nm was coated by spin-coating an ethanolic solution of TiO_2 colloid, which was formulated with the commercial 30NR-D TiO₂ paste. The as-prepared film was sintered at 450 °C to produce the TiO₂-coated FTO electrode. The precursor solution for (CsPbI₃)_{0.05}(MAPbBr₃)_{0.075}(FAPbI₃)_{0.875}(PbI₂)_{0.03} perovskite was made by adding 1.34 M of PbI₂, 0.11 M of PbBr₂, 1.23 M of FAI, 0.11 M of MABr, and 0.07 M of CsI into the mixed DMSO and DMF (v/v, 1/4). The precursor solution for (CsPbI₃)_{0.05}(MAPbBr₃)_{0.075}(FAPbI₃)_{0.875} perovskite was made by adding 1.30 M of PbI₂, 0.11 M of PbBr₂, 1.23 M of FAI, 0.11 M of MABr, and 0.07 M of CsI into the mixed DMSO and DMF (v/v, 1/4). The precursor solution for (CsPbI₃)_{0.05}(CsPbBr₃)_{0.075}(FAPbI₃)_{0.875} perovskite was made by adding 1.30 M of PbI₂, 0.11 M of PbBr₂, 1.23 M of FAI, 0.11 M of CsBr, and 0.07 M of CsI into the mixed DMSO and DMF (v/v, 1/4). The perovskite layer was deposited by use of the anti-solvent method via two-step spin-coating. The first step was carried out at 1000 rpm for 10 s with a ramp rate of 200 rpm s⁻¹. The second step was at 6000 rpm for 30 s with a ramp rate of 2000 rpm s⁻¹. In the second step, 150 μ L of CB was dripped at the time of 15 s prior to the end of spinning. The spin-coated film was annealed at 120 °C for 1 h to produce the perovskite layer. Next, 50 μ L IPA solution of TFT (2 mg mL⁻¹) was dropped on the top of the perovskite film at 2500 rpm for 25 s. The CB solution for HTL (~ 60 nm) was then spin-coated at 5000 rpm for 30 s with a ramp rate of 2000 rpm s⁻¹. The small-molecule based HTL solution was formulated with 35 mg mL⁻¹ of T5H-BMCA or spiro-OMeTAD, 6.18 mg mL⁻¹ of BPTFSI, and 132 mM of TBP. The polymer based HTL solution was formulated with 20 mg mL⁻¹ of PTAA, 3.53 mg mL⁻¹ of BPTFSI, and 132 mM of TBP. The gold electrode (~ 120 nm) was thermally evaporated using a shadow mask at a vacuum of $\leq 1 \times 10^{-4}$ Pa. The device was kept in dry air (< 3% RH) overnight, covered with a waterproof adhesive tape, and further sealed with an epoxy adhesive (3M). The active area of our cells is ~ $0.5 \times 0.5 \text{ cm}^2$. For some characterizations, the encapsulation materials, gold electrode, and even HTL were removed.

1.4. Fabrication of single-carrier devices and trap density measurement

For electron-only device, the TiO₂ and perovskite layers were the same as PSCs. Next, a CB solution of PCBM (20 mg mL⁻¹) was spin-coated on the top of perovskite layer at 2000 rpm for 40 s. Finally, a silver layer at a thickness of 120 nm was thermally evaporated in high vacuum ($\leq 1 \times 10^{-4}$ Pa). For hole-only device, a 40-nm-thick layer of PEDOT:PSS was first deposited on the top of pre-cleaned indium tin-oxide (ITO) glass. Onto the PEDOT:PSS layer was deposited the perovskite layer and the T5H-BMCA based HTL layer in turn. Finally, a gold layer at a thickness of 120 nm was thermally evaporated in high vacuum ($\leq 1 \times 10^{-4}$ Pa). Dark current–voltage (*I–V*) curves in the range of 0 to 3 V were measured with a 2400 source meter (Keithley).

1.5. Aging of solar cell

The operation stability of PSCs was measured via maximum power point (MPP) tracking of PSCs at 60 °C under continuous illumination of one sun equivalent LED, with a PVLT-G8001M-256H test system in a nitrogen-filled glovebox. The MPP data were updated every 15 min using a standard perturb and observe method. The sealed cells were stored in the air-filled FD56 oven (Binder, Germany) at 85 °C to evaluate the thermal stability of PSCs. The environmental relative humidity was ~ 40%.

1.6. Measurement of photocurrent-voltage characteristic and external quantum efficiency

We measured the photocurrent density–voltage (J-V) characteristic by use of a Keithley 2400 source meter. The test was automated with Labview 14.0. A Sirius-SS150A solar simulator (Zolix, China) was employed to supply the AM1.5G simulated sunlight. A black metal mask (aperture area, 0.16 cm²) was used to define the photoactive area. We used an Omni- λ 300 monochromator (Zolix, China) collocated with an 150 W xenon lamp

(Zolix, China) to supply monochromatic light for external quantum efficiency (EQE) measurement. A Keithley 2400 source meter was utilized to record photocurrent. A Hamamatsu S1337-1010BQ silicon diode calibrated at the National Institute of Metrology, China was used to measure the monochromatic light intensity.

1.7. Calculation of TFT adsorbed on perovskite

The DFT calculations at the GGA:revPBE-D3/DZ level of TFT adsorbed on perovskite and the periodic energy decomposition analysis were performed with ADF BAND package. The perovskite model system was constructed by a $4\times4\times3$ FAPbI₃ perovskite slab orientated along the 110 direction for the PbI₂-terminated surface.

2. References

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3. Additional data



Fig. S1 Temporal evolution of water contact angle (θ) and polarized optical microscopy (POM) image upon dripping a water droplet on the spin-coated TFT film on glass. The concentration of TFT in hot IPA is 35 mg mL⁻¹. The size of POM image is 400 μ m × 200 μ m.



Fig. S2 Chemical structures of (a) T5H-BMCA and (b) BPTFSI.



Fig. S3 Tauc plot of the CsMAFA based perovskite films without and with TFT modification. E_{g}^{opt} refers to the optical gap.



Fig. S4 X-ray diffraction patterns. Diffraction intensities are normalized with respect to the (110) plane of perovskite.



Fig. S5 ATR-FTIR spectra. Curve a is for the TFT-modified perovskite, and curve b is for the TFT-modified perovskite after washing with chlorobenzene via spin-coating.



Fig. S6 Steady-state PL spectra of CsMAFA based perovskite films without and with TFT modification. Excitation wavelength: 670 nm.



Fig. S7 TRPL traces of fresh and aged perovskite samples without and with TFT modification. The black lines refer to the biexponential fittings of normalized PL as a function of time (t). The 1000 h aging was performed at room temperature.

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sample	status	τ_1 [ns]	A_{l}	τ_2 [ns]	A_2	$\overline{ au}$ [ns]
Al ₂ O ₃ /CsMAFA	fresh	332.6	0.18	1401.2	0.82	1208.9
	aged	301.7	0.22	1048.5	0.78	884.2
Al ₂ O ₃ /CsMAFA/TFT	fresh	337.2	0.10	1908.1	0.90	1751.0
	aged	322.4	0.18	1830.1	0.82	1558.7

^{*a*} τ_1 and τ_2 refer to the time constants of fast and slow decays, A_1 and A_2 refer to the relative amplitudes of fast and slow decays, and $\overline{\tau}$ refers to the amplitude-averaged time constant which can be calculated by equation $\overline{\tau} = A_1\tau_1 + A_2\tau_2$. The 1000 h aging was performed at room temperature.



Fig. S8 TRPL traces of fresh and aged perovskite films without or with TFT modification. The black lines refer to the biexponential fittings of normalized PL as a function of time (t). Note from panel b that the change of inert polymer from PVK to PMMA does not alter PL decay kinetics. The 1000 h aging was performed at 85 °C.

Table S2 Fitting parameters of TRPL decays^a

sample	status	τ_{1} [ns]	A_{l}	τ_2 [ns]	A_2	$\overline{ au}$ [ns]
$\Delta l_{a} O_{a} / C_{s} M \Delta F \Delta / PVK / \Delta u/sealant$	fresh	282.3	0.45	1964.5	0.55	1207.5
	aged	98.1	0.55	1532.2	0.45	743.4
ALO./C.MAFA/TFT/PVK/Au/sealant	fresh	489.1	0.22	2102.2	0.78	1747.3
	aged	340.1	0.44	2366.8	0.56	1475.1

^{*a*} τ_1 and τ_2 refer to the time constants of fast and slow decays, A_1 and A_2 refer to the relative amplitudes of fast and slow decays, and $\overline{\tau}$ refers to the amplitude-averaged time constant which can be calculated by equation $\overline{\tau} = A_1\tau_1 + A_2\tau_2$. The 1000 h aging was performed at 85 °C.



Fig. S9 Bode plots of dielectric permittivity as a function of frequency (*f*) for the TFT-modified and unmodified perovskite films in the dark.



Fig. S10 J-V curves at the forward and reverse scans of representative PSCs (a) without TFT and (b) with TFT modification, under the irradiation of AM1.5G simulated sunlight (100 mW cm⁻²).



Fig. S11 Box plots of photovoltaic parameters: (a) $J_{\rm SC}$, (b) $V_{\rm OC}$, (c) FF, and (d) PCE.



Fig. S12 (a) Photon flux of AM1.5G solar spectrum and (b–e) J_{SC}^{EQE} plotted as a function of wavelength of (b) the fresh PSC without TFT, (c) the fresh PSC with TFT, (d) the aged cell without TFT, and (e) the aged cell with TFT. The aging was carried out at 85 °C for 1000 h with an environmental relative humidity of ca 40%.



Fig. S13 The PCE evolution at 60 °C via MPP tracking under the irradiation of continuous AM1.5G equivalent light-emitting diode. Error bars refer to the average deviations of 4 cells.

Interlayer	HTM	Source	$J_{\rm SC}[{\rm mA~cm^{-2}}]$	$V_{\rm oc}$ [V]	FF [%]	PCE [%]	Retention rate at 85 °C
4 h 11	Spiro-OMeTAD	Ref 1	24.74±0.46	1.187±0.01	77.0±2	22.61±0.58	not reported
theophylline	T5H-BMCA	This work	24.48±0.07	1.125±0.005	76.2±0.6	21.0±0.3	78% @ 1000h
	Spiro-OMeTAD	Ref 1	24.63±0.39	1.168±0.02	75.0±1	21.58±0.69	not reported
caffeine	T5H-BMCA	This work	24.45±0.12	1.120±0.005	75.2±0.6	20.6±0.4	73% @ 1000h
41	Spiro-OMeTAD	Ref 1	24.36±0.43	1.151±0.02	70±3	19.63±0.65	not reported
theobromine	T5H-BMCA	This work	24.41±0.16	1.090±0.010	70.3±0.8	18.7±0.5	75% @ 1000h
	Spiro-OMeTAD	Ref 2	25.2	1.18	78.4	23.32	not reported
PEAI	PTAA	Ref 2	24.49	1.10	71.40	19.15	82% @ 500h
	T5H-BMCA	This work	24.50±0.05	1.125±0.005	76.6±0.6	21.1±0.3	69% @ 1000h
EFAL	Spiro-OMeTAD	Ref 3	25.8	1.096	78.4	22.2	not reported
FEAI	T5H-BMCA	This work	24.45±0.09	1.120±0.005	75.6±0.8	20.7±0.4	71% @ 1000h
CEDEAL	Spiro-OMeTAD	Ref 4	15.45	1.23	84.65	16.07	not reported
CFPEAI	T5H-BMCA	This work	24.48±0.04	1.120±0.010	76.6±0.6	21.0±0.4	75% @ 1000h
TFT	T5H-BMCA	This work	24.50±0.03	1.150±0.005	78.0±0.4	22.0±0.2	90% @ 1000h

Table S3 Parameters of perovskite solar cells^a

^{*a*} The photovoltaic parameters were measured at the AM1.5G conditions for PSCs, which were covered with a black metal mask with an aperture area of 0.16 cm². Ref 1: R. Wang, J. Xue, K.-L. Wang, Z.-K. Wang, Y. Luo, D. Fenning, G. Xu, S. Nuryyeva, T. Huang, Y. Zhao, J. L. Yang, J. Zhu, M. Wang, S. Tan, I. Yavuz, K. N. Houk and Y. Yang, *Science*, 2019, **366**, 1509. Ref 2: Q. Jiang, Y. Zhao, X. Zhang, X. Yang, Y. Chen, Z. Chu, Q. Ye, X. Li, Z. Yin and J. You, *Nat. Photonics*, 2019, **13**, 460. Ref 3: Y. Liu, S. Akin, L. Pan, R. Uchida, N. Arora, J. V. Milić, A. Hinderhofer, F. Schreiber, A. R. Uhl, S. M. Zakeeruddin, A. Hagfeldt, M. I. Dar and M. Grätzel, *Sci. Adv.*, 2019, **5**, 2543. Ref 4: S.-C. Chen, D. Wang and Q. Zheng, *Sol. RRL*, 2020, **4**, 2000321.

PSC	$J_{ m SC} [{ m mA~cm^{-2}}]$	$V_{\rm oc}$ [V]	FF [%]	PCE [%]
w/o TFT/fresh	24.48 ± 0.03	1.110 ± 0.005	76.3 ± 0.6	20.6 ± 0.4
with TFT/fresh	24.51 ± 0.02	1.135 ± 0.010	77.5 ± 0.4	21.6 ± 0.3
w/o TFT/aged	18.02 ± 0.51	1.040 ± 0.030	50.6 ± 3.1	9.5 ± 1.1
with TFT/aged	22.11 ± 0.22	1.065 ± 0.010	61.6 ± 1.8	14.5 ± 0.6

Table S4 Photovoltaic parameters of fresh and aged PSCs with spiro-OMeTAD^a

^{*a*} The photovoltaic parameters were measured at the AM1.5G conditions for PSCs, which were covered with a black metal mask with an aperture area of 0.16 cm². The aging was carried out for 1000 h at 85 °C. Errors are from 4 fresh and aged cells.

Table S5 Photovoltaic parameters of fresh and aged PSCs with PTAA^a

PSC	$J_{ m SC} [{ m mA~cm^{-2}}]$	$V_{\rm oc}$ [V]	FF [%]	PCE [%]
w/o TFT/fresh	24.46 ± 0.04	1.070 ± 0.015	71.9 ± 0.8	18.8 ± 0.5
with TFT/fresh	24.48 ± 0.03	1.095 ± 0.005	75.6 ± 0.4	20.3 ± 0.2
w/o TFT/aged	20.62 ± 0.41	1.010 ± 0.015	54.4 ± 2.1	11.3 ± 0.8
with TFT/aged	22.53 ± 0.22	1.060 ± 0.010	64.7 ± 1.5	15.4 ± 0.6

^{*a*} The photovoltaic parameters were measured at the AM1.5G conditions for PSCs, which were covered with a black metal mask with an aperture area of 0.16 cm². The aging was carried out for 1000 h at 85 °C. Errors are from 4 fresh and aged cells.

Table S6 Photovoltaic parameters of $(CsPbI_3)_{0.05}(MAPbBr_3)_{0.075}(FAPbI_3)_{0.875}$ based PSCs before and after aging^{*a*}

PSC	$J_{\rm SC}$ [mA cm ⁻²]	$V_{\rm oc}$ [V]	FF [%]	PCE [%]
w/o TFT/fresh	24.50 ± 0.03	1.110 ± 0.015	75.7 ± 0.6	20.6 ± 0.4
with TFT/fresh	24.51 ± 0.02	1.130 ± 0.010	78.0 ± 0.3	21.6 ± 0.3
w/o TFT/aged	21.67 ± 0.22	1.080 ± 0.015	64.2 ± 1.4	15.0 ± 0.7
with TFT/aged	23.51 ± 0.16	1.120 ± 0.010	69.8 ± 1.0	18.4 ± 0.5

^{*a*} The photovoltaic parameters were measured at the AM1.5G conditions for PSCs, which were covered with a black metal mask with an aperture area of 0.16 cm². The aging was carried out for 150 h at 85 °C. Errors are from 4 fresh and aged cells.

PSC	$J_{\rm SC} [{ m mA~cm^{-2}}]$	$V_{\rm oc}$ [V]	FF [%]	PCE [%]
w/o TFT/fresh	24.02 ± 0.14	1.090 ± 0.015	74.9 ± 1.0	19.6 ± 0.6
with TFT/fresh	24.12 ± 0.09	1.120 ± 0.010	76.6 ± 0.3	20.7 ± 0.3
w/o TFT/aged	21.08 ± 0.24	1.070 ± 0.020	62.8 ± 2.1	14.2 ± 0.9
with TFT/aged	22.96 ± 0.13	1.110 ± 0.010	67.3 ± 1.1	17.1 ± 0.5

Table S7 Photovoltaic parameters of $(CsPbI_3)_{0.05}(CsPbBr_3)_{0.075}(FAPbI_3)_{0.875}$ based PSCs before and after aging^{*a*}

^{*a*} The photovoltaic parameters were measured at the AM1.5G conditions for PSCs, which were covered with a black metal mask with an aperture area of 0.16 cm². The aging was carried out for 150 h at 85 °C. Errors are from 4 fresh and aged cells.



Fig. S14 Plot of $J_{\rm SC}\,$ as a function of $J_{\rm SC}^{\rm EQE}$.

Table S8 Fitting parameters of TRPL decays^a

cell	status	τ_1 [ns]	A_{1}	τ_2 [ns]	A_2	$\overline{ au}$ [ns]
TiO ₂ /CsFAMA/T5H-BMCA	fresh	8.1	0.54	35.3	0.46	20.6
	aged	23.8	0.61	104.3	0.39	55.2
TiO./CsEAMA/TET/T5H BMCA	fresh	7.2	0.52	35.6	0.48	20.8
110 ₂ /CSFAMA/111/13H-DMCA	aged	15.9	0.68	64.1	0.32	31.3

^{*a*} τ_1 and τ_2 are the time constants of fast and slow decays, A_1 and A_2 are the relative amplitudes of fast and slow decays, and $\overline{\tau}$ is the amplitude-averaged time constant which is calculated by equation $\overline{\tau} = A_1\tau_1 + A_2\tau_2$. The aging was carried out at 85 °C for 1000 h with an environmental relative humidity of ca 40%.