

Supporting Information

Additive Effect on the Hot Carrier Cooling in Hybrid Perovskite

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Experiment Section

Materials

Fluorine doped tin oxide (FTO) coated glass substrates, TiO₂ paste, Acetylacetone, Titanium diisopropoxide bis(acetylacetonate) 75% in Isopropyl Alcohol, N-dimethylformamide(DMF, 99%, Sigma-Aldrich), Dimethyl sulfoxide (DMSO, 99%, Sigma-Aldrich), Chlorobenzene (CB, 99.8%, Sigma-Aldrich), Lead iodide(PbI₂, >98%, TCI chemicals), Lead bromide(PbBr₂, >98%, TCI chemicals), Formamidinium (FAI,99.0%,Greatcell), Methylammonium bromide (MABr, 99.95%, Advanced Election Technology Co.,Ltd), 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene(Spiro-OMeTAD, 99.8%, Advanced Election Technology Co.,Ltd), Bis(trifluoromethylsulfonyl)-imide lithium salt (Li-TFSI, 99%, Sigma-Aldrich), Tris(2-(1Hpyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethyl-sulfonyl) imide (FK209, 99%, Greatcell), 4-tert-Butylpyridine(tBP, 99%, Energy Chemical), Acetonitrile (ACN, >99.9%, Sigma-Aldrich), [6,6]-Phenyl C₆₁-butyric acid methyl ester (PC₆₁BM, >99%,Xi'an), TDGA (99%, Energy Chemical).

Solar Cell Fabrication

PSCs were fabricated with a p-i-n structure of fluorine doped tin oxide (FTO)/cp-TiO₂ /mp-TiO₂/perovskite with and without TDGA/Spiro-OMeTAD/Ag. Firstly, the etched glass substrates were put in detergent, deionized water, acetone and ethanol sequentially for ultrasonic cleaning for 20 minutes, and dried in an oven at 70 °C. Next, A TiO₂ precursor solution was prepared using 0.6 mL titanium diisopropoxide bis(acetylacetonate), 0.4 mL acetylacetonate and 9 mL anhydrous ethanol, and under 450

°C and O₂ as the carrying gas, a compact layer of TiO₂ was deposited on cleaned FTO substrate by spray pyrolysis. The commercial TiO₂ paste (30 NRD) was diluted in anhydrous ethanol at a weight ratio of 1/6, 200 nm thick mesoporous TiO₂ layer was spin-coated onto the substrate by spin-coating for 20 s at 5000 rpm with a ramp rate of 2000 rpm s⁻¹. After drying at 100 °C for 10 min, the TiO₂ film was annealed at 450 °C for 30 min under dry air flow to remove organic components. (FAPbI₃)_{0.875}(MAPbBr₃)_{0.075}(CsPbI₃)_{0.05}(PbI₂)_{0.03} perovskite precursor solution was prepared by dissolving 1.30 M PbI₂, 1.19 M FAI, 0.14 M PbBr₂, 0.14 M MABr, and 0.07 M CsI into the DMSO/DMF (1:4 v:v) mixture. The solution was stirred overnight at room temperature. For the molecular additives, add TDCA to the perovskite precursor solution to form a mixed solution containing different concentrations of TDGA. 40 µL of the precursor solution with and without different concentrations of TDGA was deposited on the electron-transporting layer by a consecutive two-step spin-coating process at 2000 rpm for 10 s (ramp rate 200 rpm s⁻¹) and 6000 rpm for 30 s (ramp rate 2000 rpm s⁻¹) in a dry air-filled glove box with a <2% relative humidity. At the time of 15 s prior to the program end, 100 µL of chlorobenzene was quickly dripped onto the spinning film, and the film was then annealed at 120 °C for 1 h. 30 µL of Spiro-OMeTAD solution was then dispersed onto the substrate at 4500 rpm for 30 s (ramp rate 1500 rpm s⁻¹) by dissolving 85mg of Spiro-OMeTAD in 951 µL of chlorobenzene, with the addition of 28.8 µL tBP, 17.8 µL Li-TFSI solution (520 mg/mL in acetonitrile) and 6.5µL FK209-cobalt(III)-TFSI solution (300 mg/mL in acetonitrile). Before Ag deposition, the samples were oxidized overnight in a dark desiccator. Finally, 200 nm of the Ag layer was vaporized at 0.2 Å s⁻¹ in a vacuum evaporator. The mask area of the measured device is 0.0625 cm².

Characterization

The current density-voltage (J-V) characteristics were measured by a Newport solar simulator (model 91160) and a Keithley 2400 source/meter under 100 mW cm⁻² (AM 1.5 G illumination). A certified reference solar cell (Fraunhofer ISE) was used to calibrate the light source for an intensity of 100 mW cm⁻². The steady-state output of short current and PCE were recorded by ITestSystem software under constant bias at the maximum power point and 200 s of continuous sunlight. Incident photon-to-current conversion efficiency

(IPCE) spectra were obtained by a Newport QE measurement fit consisting of a Xenon light source (Spectral Products ASB-XE-175), a monochromator (Spectra Products CM110), and a potentiostat (Lab Jack U6 DAQ board), calibrated by a certified reference solar cell (Fraunhofer ISE). The surface morphology of perovskite films was observed by scanning electron microscope (SEM) model of Rigaku ($\lambda_{\text{CuK}\alpha}=0.154056\text{nm}$). UV-Vis absorption of thin film were tested using ultraviolet, visible, near-infrared spectrophotometer (UV-2600) with an integrating sphere accessory (ISR-2600Plus). Fourier transform infrared spectroscopy (FTIR) spectra for powder were recorded in transmission mode in an FTIR spectrometer (Nicolet iS10, Thermo Fisher). The chemical states of ions were studied by X-ray photoelectron spectroscopy (XPS) of model *K-Alpha*⁺ that purchased from Thermo fisher Scientific. The X-ray light source is monochromatic Al K α source (Mono Al K α) that energy is 1486.6eV, 6mA \times 12KV and scan mode is fixed analyzer Energy (CAE). The surface contamination C1s at 284.8 eV was used for calibrating the results. The steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra of the perovskite thin films were obtained using fluorescence spectrum and TSCPC system respectively by Edinburgh FLS1000 (UK), the sample was excited with 475 nm laser. The space charge limited current (SCLC) was obtained by Qinglang 150 W solar simulator with model Sirius-ss150A and Oriel IV Test Station software in a dark environment, under bias from 0 V to 10 V and current limit at 200mA. The nanosecond transient absorption (TA) spectroscopy was recorded by the pulsed 532nm pump light source obtained by a frequency tripled Nd:YAG laser (a Spectra-Physics Quanta-Ray ProSeries, 10 Hz repetition rate, 10 ns pulse length) pumped an Optical Parametrical Oscillator (OPO) , the white light for probing provided by a LP920 detection system (Edinburgh Instruments) equipped with a pulsed XBO 450 W Xenon Arc Lamp (Osram), the Spectrum detector is composed of an iStar CCD camera (Andor Technology) and a LP980-K photomultiplier tube (PMT) detector connected to a Tektronix MDO 3022 200 MHz 2.5 GS/s oscilloscope. The carrier dynamics of perovskite films with/without TDCA modification was future study using femtosecond transient absorption (fs-TA) spectrometer (Helios). First, an integrated and amplified Ti:Sapphire femtosecond laser generates a beam of 800 nm laser (pulses energy of a 3.5 mJ/pulse, pulse width of \sim 120 fs with a repetition rate of 2 kHz). Then the 800 nm laser

beam was split into two beams through a beam splitter. Among 65% of 800 nm laser pulses energy pass through a spectrally tunable (240–2600 nm) optical parametric amplifier (Newport Spectra Physics) to yield excitation pump pulses (475 nm pump light), another 25% of 800 nm laser pulses energy pass through a 2 mm thick calcium fluoride (CaF_2) crystal to generate the probe pulses (UV–visible and NIR wavelength continuum, white light). Finally, the data was recorded by a computer. All the fs-TA experiments were performed under identical ambient conditions at room temperature.

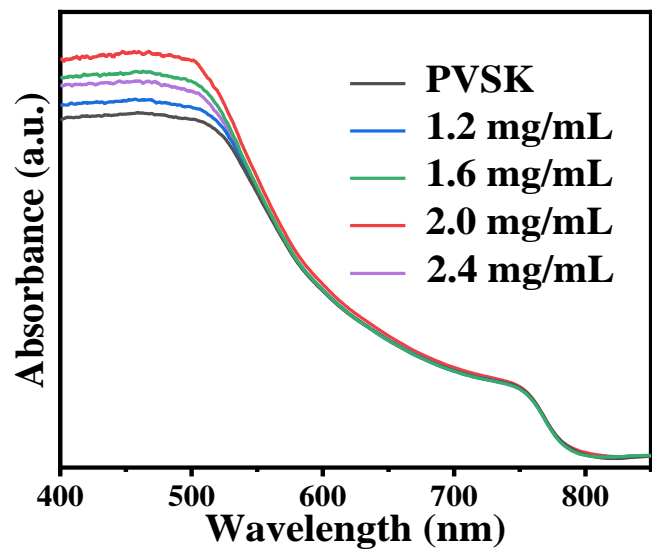


Figure S1. UV-vis spectra of perovskite films with TDGA.

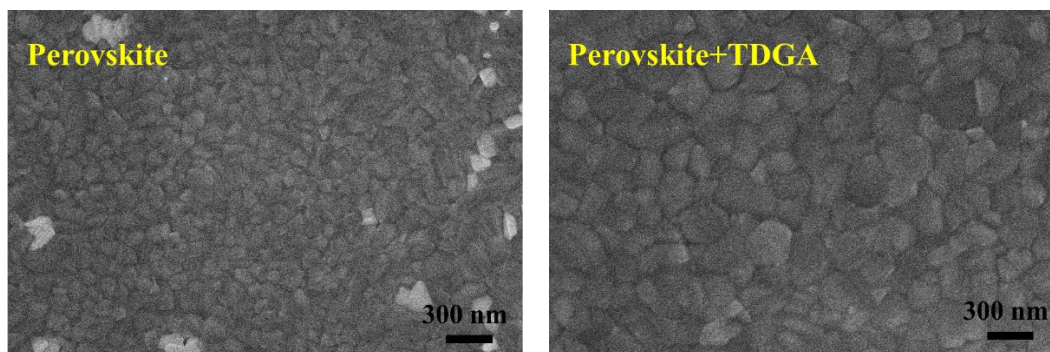


Figure S2. SEM images of perovskite films without and with TDGA.

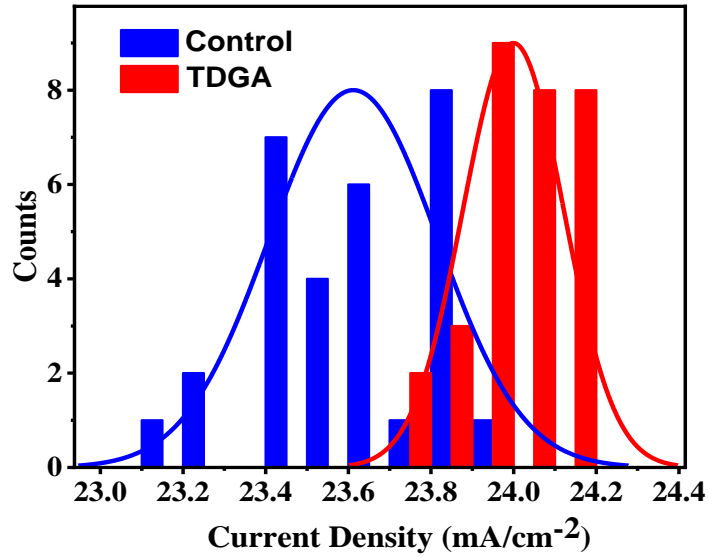


Figure S3. The histograms of J_{sc} distribution of 30 devices without and with TDGA.

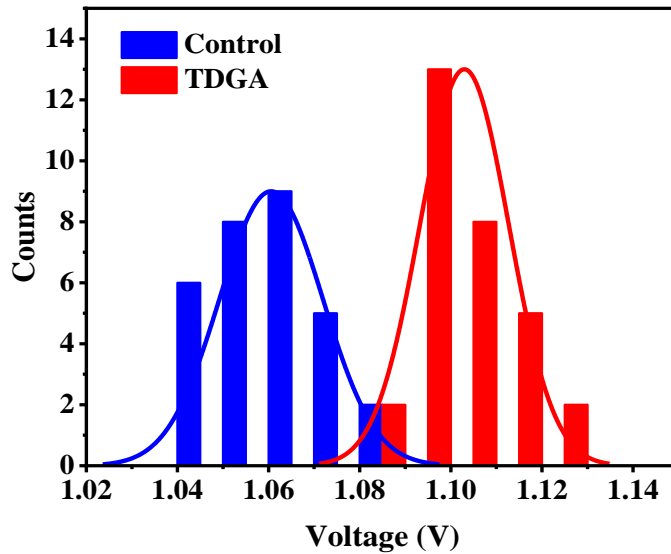


Figure S4. The histograms of V_{oc} distribution of 30 devices without and with TDGA.

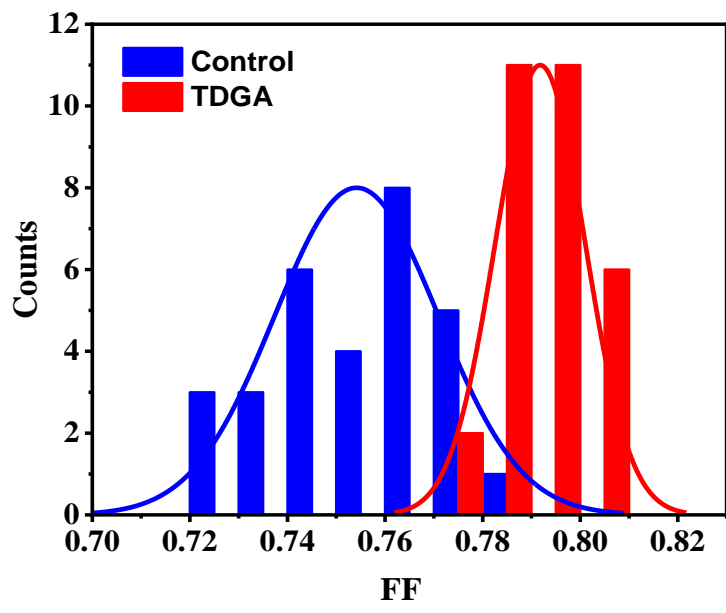


Figure S5. The histograms of FF distribution of 30 devices without and with TDGA.

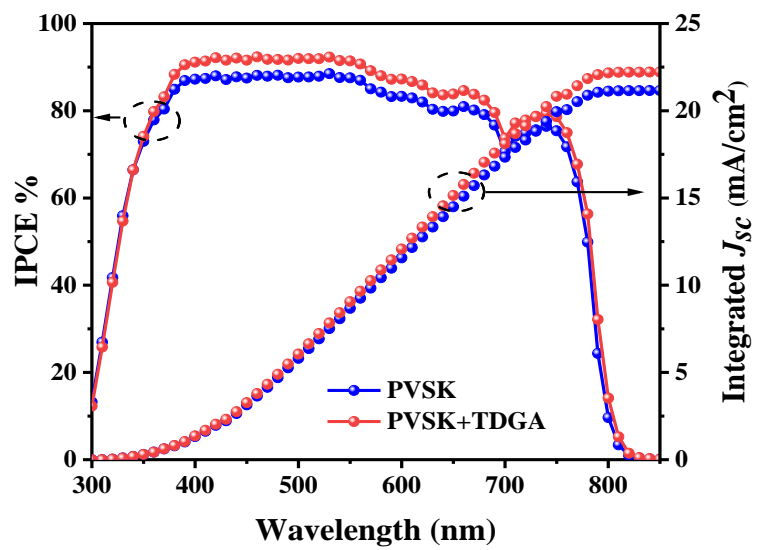


Figure S6. IPCE spectra of device without and with TDGA.

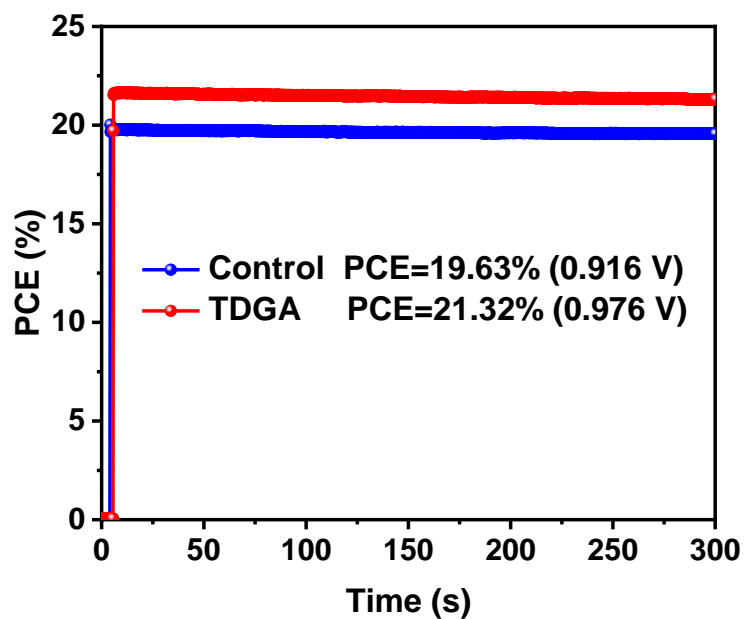


Figure S7. Steady PCE values measured maximum power point for PSCs without and with TDGA.

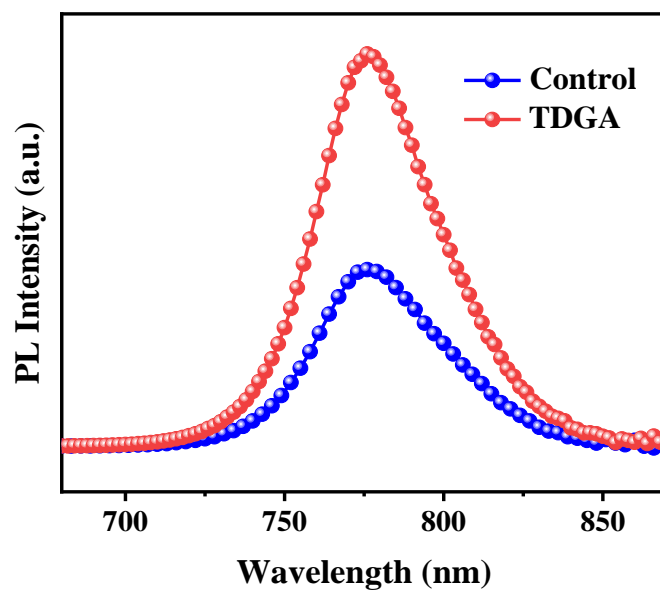


Figure S8. Stable PL spectra of perovskite films without and with TDGA.

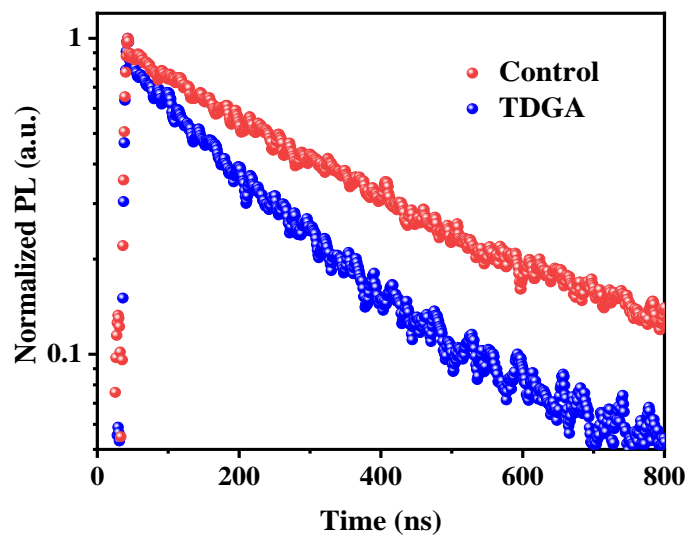


Figure S9. TRPL spectra of perovskite films without and with TDGA.

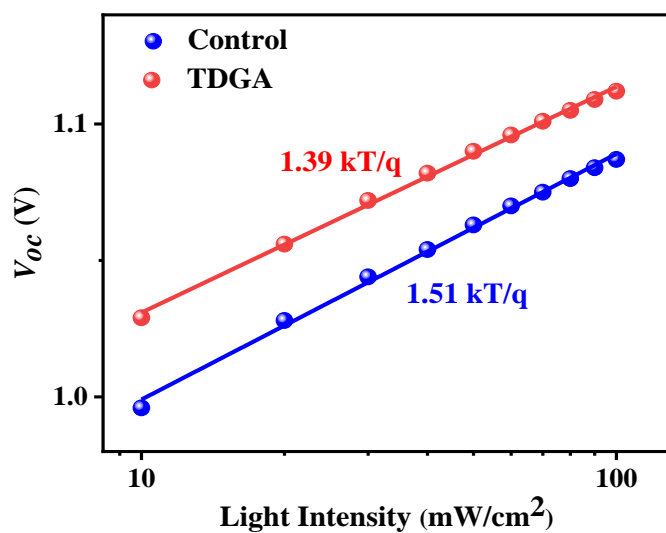


Figure S10. V_{oc} plotted against the light intensity in the device.

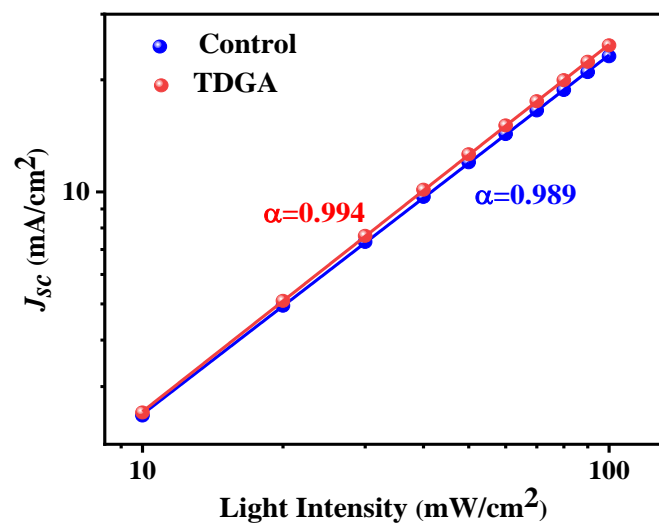


Figure S11. J_{sc} plotted against the light intensity in the device.

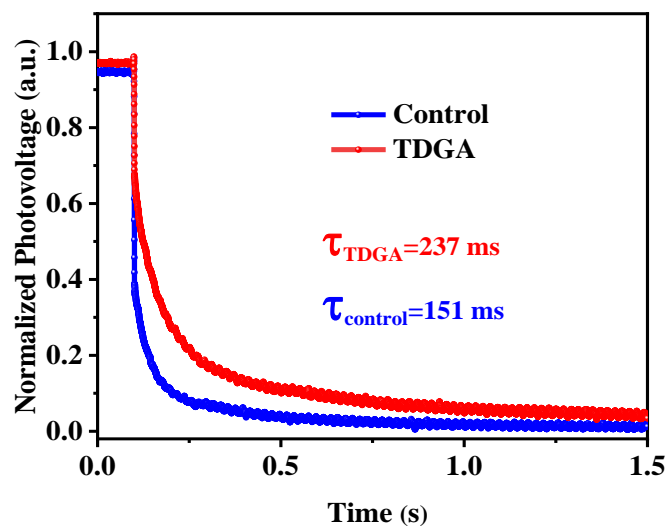


Figure S12. Photovoltage decay curves of these devices.

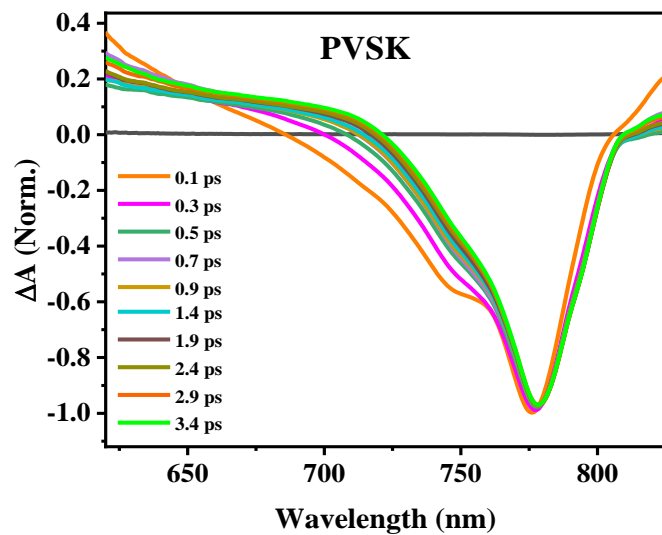


Figure S13. The normalized fs-TA spectrum of pristine perovskite films within delay time from 0.1 to 3.4 ps pumped at 375 nm.

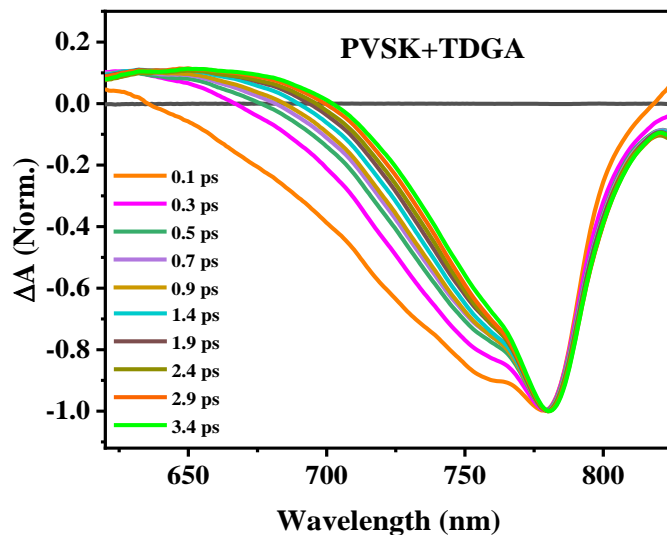


Figure S14. The normalized fs-TA spectrum of pristine perovskite films with TDGA within delay time from 0.1 to 3.4 ps pumped at 375 nm.

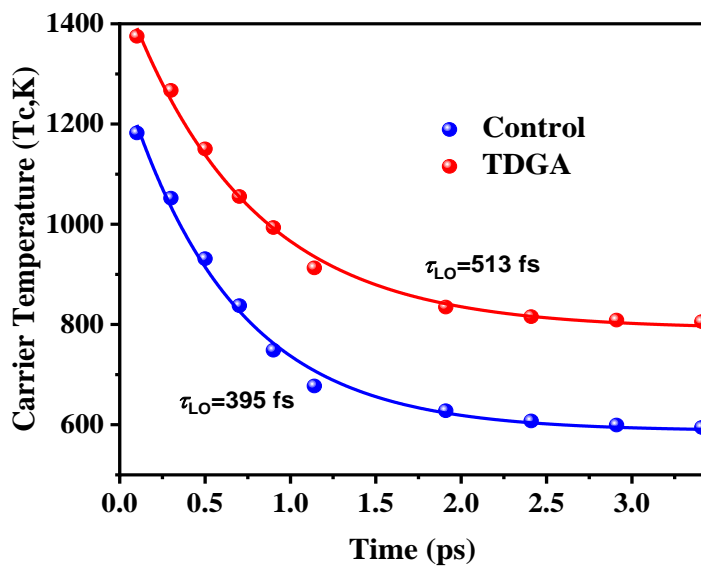


Figure S15. Extracted HCs temperatures with delay time for perovskite films.

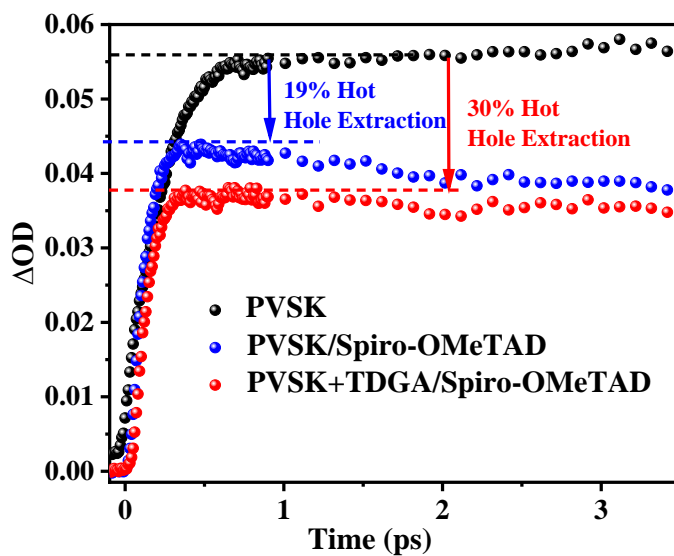


Figure S16. Absolute bleach amplitude at early delay times of perovskite films without and with Spiro-OMeTAD.

Table S1. TRPL fitting parameters of perovskite films without and with TDGA.

Sample	A ₁ (%)	τ_1 (ns)	A ₂ (%)	τ_2 (ns)	τ_{avg} (ns)
Control	5.5	32.5	94.5	196.6	195.1
TDGA	4.2	77.2	95.8	303.2	300.7

Table S2. Dynamic fitting parameters of fs-TAS.

Device	A ₁ (%)	τ_1 (ps)	A ₂ (%)	τ_2 (ps)	A ₃ (%)	τ_3 (ps)	τ_{avg} (ps)
PVSK	43	0.18	44.7	0.18	12.3	5.34	4.31
PVSK+TDGA	20.8	0.17	55.2	5.61	24.2	0.33	5.41