Supporting Information

Synergistic Mixed Halide and Additive Strategy for Efficient Pure Red Quasi-2D Perovskite Light-Emitting Diodes

Fanyuan Meng[a]*, Shengxuan Shi[a], Zhao Chen[b], Boyang Li[a], Xianfei Lu[a], Qi Feng[a], Yan Chen[a]*, Shi-Jian Su[c]*

[a] School of Applied Physics and Materials, Wuyi University, Jiangmen, 529020, China

[b] Key Laboratory of Basic Pharmacology of Ministry of Education and Joint International Research Laboratory of Ethnomedicine of Ministry of Education, School of Pharmacy, Zunyi Medical University, Zunyi, 563000, China.

[c] State Key Laboratory of Luminescent Materials and Devices, Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Wushan Road 381, Guangzhou 510640, China.

*E-mail addresses: mengfanyuan@wyu.edu.cn, ychen08@163.com, mssjsu@scut.edu.cn

Experimental Section

Materials: phenylethylammonium iodide (PEAI, 99.5%), Cesium iodide (CsI, 99.999%), lead bromide ($PbBr_2$, 99.999%), lead iodide (PbI_2, 99.999%), and N,N'-Bis(3-methylphenyl)-N,N'-bis(phenyl)benzidine (TPD, 99.0%) were procured from Xi'an Yuri Solar Co., Ltd. Tris(4-carbazoyl-9-ylphenyl)amine (TCTA, 99.8%), lithium fluoride (LiF, 99.99%), and Molybdenum(VI) Oxide (MoO_3, 99.998%) were obtained from Lumtec. Rubidium iodide (RbI, 99.9%) was purchased from Macklin. N,N-Dimethylformamide (DMF, 99.8%), Dimethyl sulfoxide (DMSO), and chlorobenzene (CB) were acquired from Sigma Aldrich. All chemicals were employed as received, without any additional purification.

Perovskite Precursor Preparation: The pristine perovskite precursor solutions were synthesized by dissolving PEAI, RbI, CsI, $PbBr_2$, and PbI_2 in a molar ratio of 0.7:0.1:1:0.53:0.47 with a DMSO:DMF (1:4, v:v) mixed solvent. For the TDA-modified perovskite precursors, TDA was incorporated into the pristine precursor solution at a molar ratio of 0.055: 0.7:0.1:1:0.53:0.47 for defect passivation. The concentration of Pb^{2+} in perovskite precursor solution was maintained at 0.095 M. All precursor solutions were stirred under nitrogen atmosphere in a glovebox at 40 °C for 8 hours prior to utilization.

Device Fabrication: The PeLEDs were fabricated following a well-established procedure. The patterned ITO glasses were ultrasonically cleaned with detergent, deionized water, and ethyl alcohol, and then baked at 120°C for 20 min. The ITO substrates were treated with O_2 plasma for 10 min and transferred into a nitrogen-filled glove box. The LiMg-ZnO (14 mg mL^{-1}) in ethanol solvent was spin-coated at 3000 rpm for 30 s and then baked at 140 °C for 20 min. Here, PEI (0.5 mg mL^{-1}) in ethanol solvent was spin-coated at 3000 rpm for 30 s and then baked at 80 °C for 5 min. Naturally cool to room temperature, the pristine and TDA-modified perovskite precursor solution was spin-coated onto the above substrates at 3000 rpm for 50s. Next, TPD (1 mg mL^{-1}) in 1,4-dioxane solvent was spin-coated at 3000 rpm for 20 s and then baked at 100 °C for 2 min. Finally, TCTA (30 nm), MoO_3 (7.0 nm), and Al (130 nm) were evaporated with a high-vacuum deposition system. The emission area of these PeLEDs was 2 mm × 2 mm by the overlapping area of the ITO and Al electrodes. Current density-voltage (*J-V*) curves were measured by using a dual-channel Keithley 2400 instrument. The EL spectra, current efficiency, and EQE were measured by using an integrating sphere, a multi-channel analyzer PMA-12, and

an external quantum efficiency measurement system (C9920-12, Hamamatsu Photonics, Japan). Before taking out the glove box for EQE testing, all the PeLEDs were easily encapsulated with a UV-cured epoxy resin.

Thin Film and Device Characterizations: UV-vis absorption spectra were acquired using a SHIMADZU/UV-3600 PLUS spectrophotometer. XRD spectra were measured by a multipurpose SmartLab SE Japan Rigaku system. The Fourier transform infrared spectroscopy (FTIR) measurement was conducted by using Thermo Scientific Nicolet iS5. X-ray photoelectron spectroscopy (XPS) was obtained on an Thermo Scientific Nexsa G2 system. SEM images were taken with a ZEISS/SIGMA500 system. PL spectra were measured using an Edinburgh FL980 fluorescence spectrophotometer with a 375 nm xenon lamp as the excitation light source. Time-resolved PL decay spectra were measured with an Edinburgh FL980 fluorescence spectrophotometer with a 371.6 nm ps diode laser as the excitation light source. PLQYs of the perovskite films were measured by a commercialized PLQY measurement system from Ocean Optics with a 375 nm LED as the excitation light source.

Calculation of radiative & non-radiative decay rate:

The TRPL spectra were fitted by a triexponential function following the Equations S1 below:

$$y = \sum A_i \exp\left(-\frac{t}{\tau_i}\right) \quad \text{(S1)}$$

Where i = 1, 2, 3, the A_1, A_2, and A_3 are the normalized pre-exponential factors, and τ_1 is the fast decay time constant, τ_2, and τ_3 are the lifetimes of the slow decay component.

The average PL lifetime (τ_{avg}) can be calculated by the following equation S2:

$$\tau_{avg} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \quad \text{(S2)}$$

The radiative recombination rate (k_r) and the nonradiative recombination rate (k_{nr}) were obtained using the following Equation S3 and S4:

$$k_r = \frac{PLQY}{\tau_{avg}} \tag{S3}$$

$$k_{nr} = \frac{1}{\tau_{avg}} - k_r \tag{S4}$$

The relationship between PLQY and EQE can be expressed as Equation S5:

$$\eta_{EQE} = \eta_b \times \eta_{IQE} \times \eta_{out} \tag{S5}$$

wherein, η_b is the charge carrier-balance efficiency, η_{IQE} is the PLQY of the perovskite film, and η_{out} is the light out-coupling efficiency.

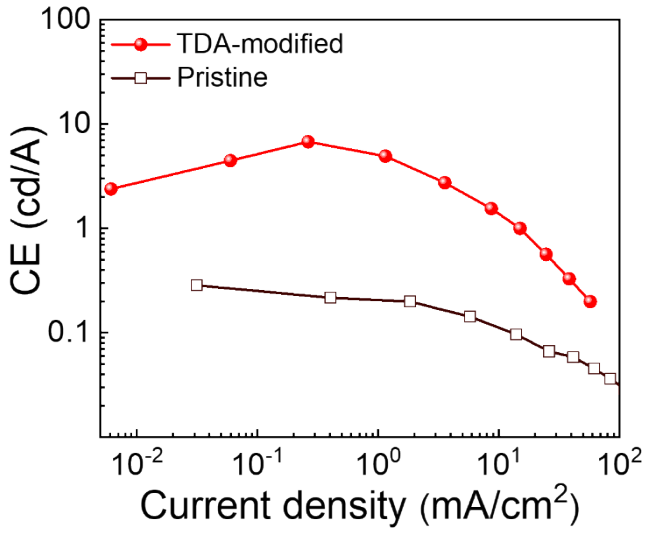

Fig. S1 Current efficiency-current efficiency (*CE-J*) curves of TDA-modified and Pristine PeLEDs.

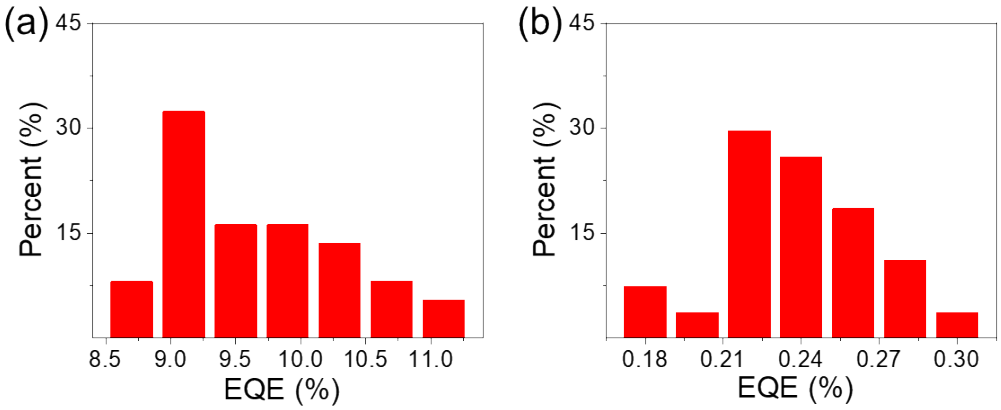

Fig. S2 Statistical EQE performance. (a) TDA-modified PeLEDs with an average EQE of 9.67% from 28 devices, and (b) pristine perovskite with an average EQE of 0.24% from 31 devices.

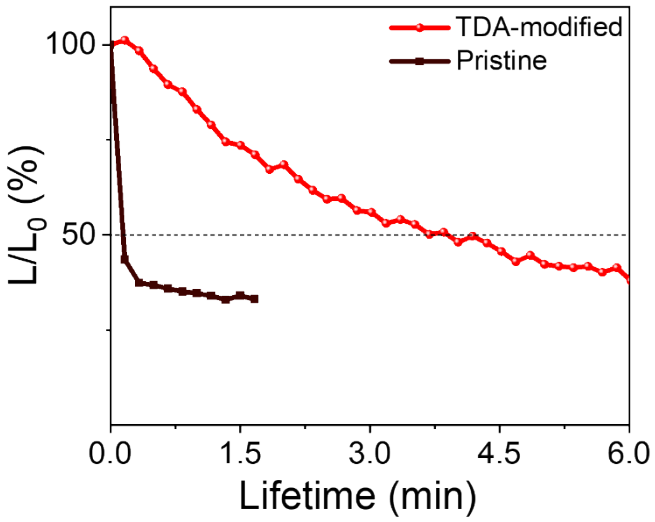

Fig. S3 T_{50} lifetime of the TDA-modified and Pristine PeLEDs.

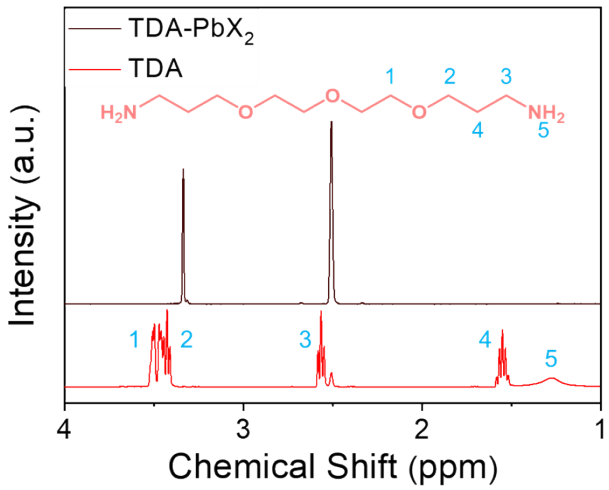

Fig. S4 ^{1}H nuclear magnetic resonance (NMR) spectroscopy of pure TDA additive and its mixture with PbX_2.

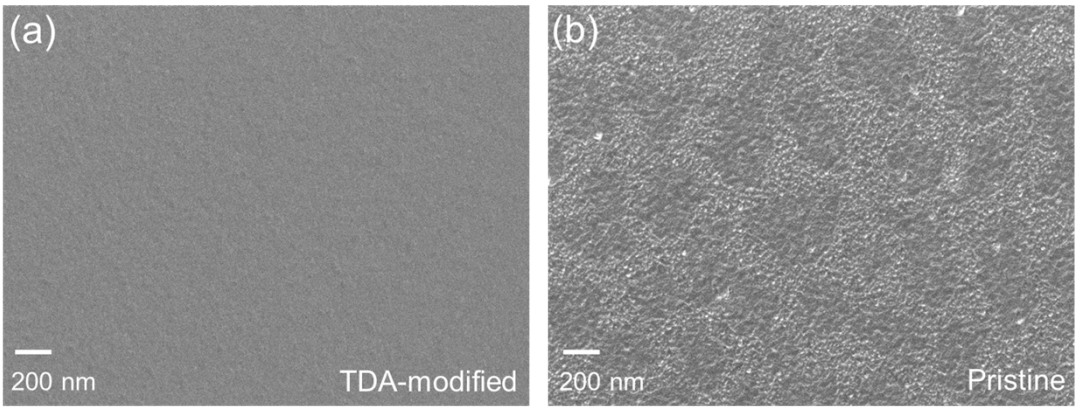

Fig. S5 The SEM images of (a) TDA-modified and (b) pristine perovskite films.

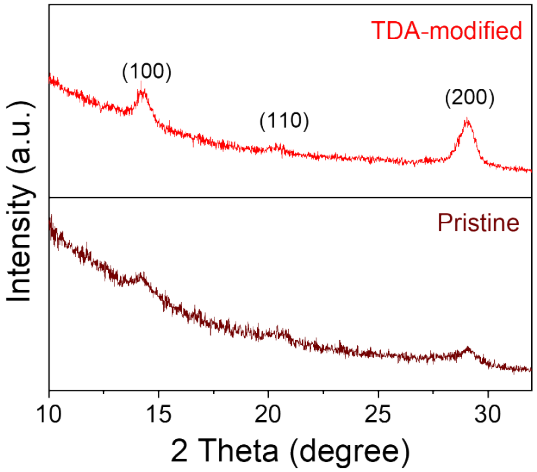

Fig. S6 XRD spectra of TDA-modified and pristine perovskite films.

Table S1. Performance summary of pristine and TDA-modified PeLEDs.

Light-Emitting layers	V_{on} (V)	CE_{max} (cd/A)	EQE_{max} (%)	EL (nm)	CIE_x	CIE_y
Pristine	2.5	0.22	0.25	638	0.713	0.312
TDA-modified	2.25	6.76	12.39	650	0.711	0.290

Table S2. TRPL fitting parameters of pristine and TDA-modified perovskite films.

Light-Emitting layers	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	τ_{avg} (ns)
Pristine	2137.23	0.94	299.68	4.3	27.92	22.14	5.39
TDA-modified	933.4	6.56	827.94	25.05	130.54	100.28	46.86

Table S3. PL average lifetimes (τ_{avg}), PLQY, radiative decay rates (k_r), and nonradiative decay rates (k_{nr}) of the pristine and TDA-modified perovskite films.

Light-Emitting layers	τ_{avg} (ns)	PLQY (%)	k_r (10^6 s^{-1})	k_{nr} (10^6 s^{-1})	k_r: k_{nr}
Pristine	5.39	11.9	22.08	163.45	0.14
TDA-modified	46.86	66.2	39.26	7.21	5.45