

# Organic ammonium salt assisting crystallization and defect passivation of quasi-two-dimensional pure blue perovskite at the buried interface

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## Materials

Xi'an Yuri Solar Co., Ltd provided PbBr<sub>2</sub> (≥99.99%), PbCl<sub>2</sub> (≥99.9%), MDABr<sub>2</sub> (≥98%), EABr (≥99.5%), EACl (≥99.5%), CsBr (≥99.9%), PEABr (≥99.5%) and 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzamide-azole) (TPBi). Heraeus provided PEDOT: PSS (Clevious PVP Al 4083). LiF was purchased from the Aladdin company. Alfa Aesar manufactures the dimethyl sulfoxide (DMSO) solvent. Chlorobenzene (CB, 99.8%) was purchased from Macklin. Without additional purification, all items were used as they were received.

## Preparation of the precursor solutions

The precursor solution of the quasi-2D PEA<sub>2</sub>[(Cs<sub>0.4</sub>EA<sub>0.4</sub>MDA<sub>0.1</sub>)<sub>2</sub>]Pb<sub>3</sub>(Br<sub>0.8</sub>Cl<sub>0.2</sub>)<sub>10</sub> perovskite was prepared by dissolving PEABr, CsBr, EABr, MDABr<sub>2</sub>, PbBr<sub>2</sub> and PbCl<sub>2</sub> in DMSO at a molar ratio of 2:1.6:1.6:0.4:2:1. All combined solutions were then swirled for the entire next day at room temperature. Before usage, the perovskite precursor solutions were filtered using 0.22 μm PTFE syringe filters.

## Device Fabrication

The m-PEDOT: PSS (PEDOT: PSS doped with PSS-Na) solution was spin-coated at 3000 rpm for 40 s on a precleaned ITO-coated glass substrate before being annealed at 150° for 15 min. The substrates were then placed in an N<sub>2</sub>-filled glovebox. The perovskite precursor solutions were spin-coated on an m-PEDOT: PSS layer for 60 s at 5000 rpm, and the resulting films were annealed at 70° for 10 min. Finally, the substrates were transferred to a vacuum thermal evaporation chamber to deposit TPBi (36 nm), LiF (0.6 nm), and Al (100 nm) layer by layer under the pressure of 5 × 10<sup>-4</sup> pa. The device area was 9 mm<sup>2</sup>, as determined by the overlap area between the ITO and Al electrodes.

## DFT Calculations

The Cambridge Serial Total Energy Package (CASTEP) in Materials Studio was utilized to calculate the structural optimization and electronic structure. The generalized gradient approximation (GGA) function of the Perdew–Burke–Ernzerhof (PBE) functional was used to calculate the structural optimization of perovskite. The calculation was expanded by using the ultrasoft pseudopotential, the cut-off energy was set as 435.4 eV, and the total energy was converged to 2.0–5.0 eV. The

structural optimization was optimized until the force tolerance was less than  $0.05 \text{ eV\AA}^{-1}$ , the stress tolerance was kept less than  $0.1 \text{ GPa}$ , and the displacement tolerance was kept less than  $0.002 \text{ \AA}$ .

### Characterization

Absorbance spectra were measured with a visible spectrophotometer (UV3600i-plus). Steady-state photoluminescence (PL) emission spectra were recorded on a Hitachi F4500 fluorescence spectrophotometer equipped with an Xe lamp coupled to a monochromator. X-ray diffraction patterns (XRD) were collected using a powder diffractometer with D/max 2200 V X-ray with  $\text{Cu K}\alpha$  radiation. Time-resolved photoluminescence (TRPL) and Photoluminescence Quantum Yield (PLQY) of the film were achieved via FLS1000. The current density–voltage curves were obtained using a Keithley 2410 Source Meter. Atomic Force microscopy (AFM) measurements were performed using the scanning probe microscope Bruker (Bruker Multimode 8). An X-ray photoelectron spectrometer was tested by a routine measurement with an ESCALAB 250Xi, Thermo Fisher Scientific. The Hitachi 4800 was used for scanning electron microscopy (SEM) measurements. Transient absorption (TA) spectra were carried out by Ultrafast transient absorption/two-photon fluorescence Spectroscopy (Titanium gemstone Femtosecond laser) (Vitara-Legend Elite-Helios); the excitation wavelength was  $350 \text{ nm}$  and the excitation intensity was  $30 \mu\text{W}$ . Newport 1830-R optical power meters equipped with a calibrated 918D photodiode and Keithley 2400 Source were used to record the current density–voltage–luminance (J–V–L) characteristics and electroluminescence (EL) spectra. The UPS was tested using Thermo Fly's ESCALAB 250Xi and the excitation energy is  $21.22 \text{ eV}$ . Unless otherwise specified, all measurements were taken at room temperature and the devices were not encapsulated.

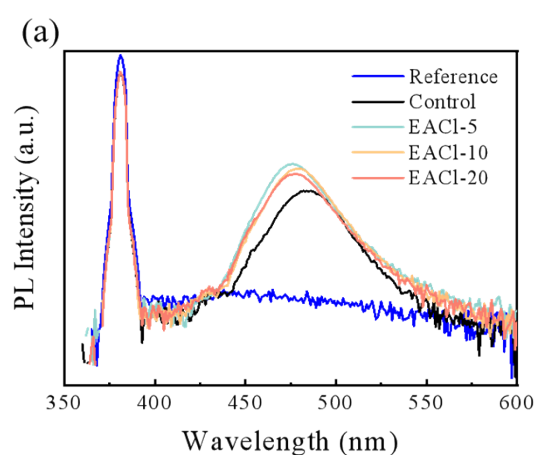


Figure S1. PLQY spectra of perovskites at different concentrations of EACl modification.

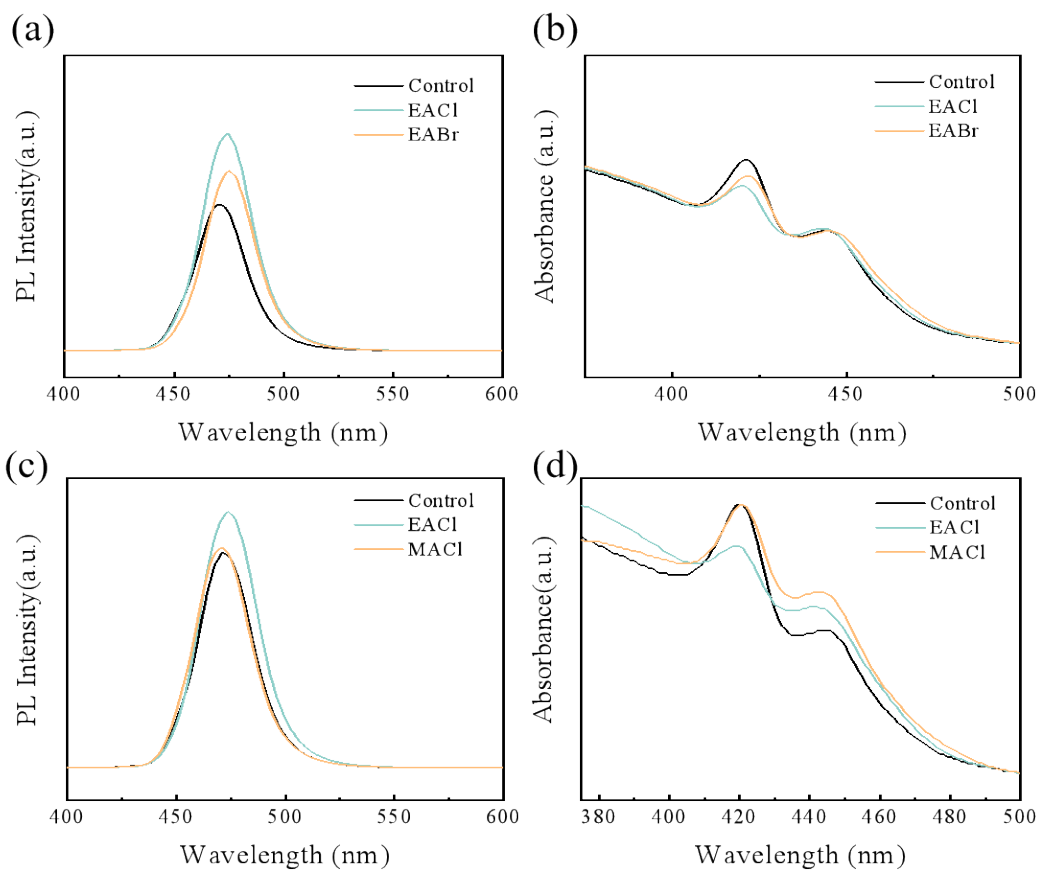


Figure S2. Optical properties of perovskites modified with different organic ammonium salts. (a) and (c) PL spectra. (b) and (d) Absorption spectra.

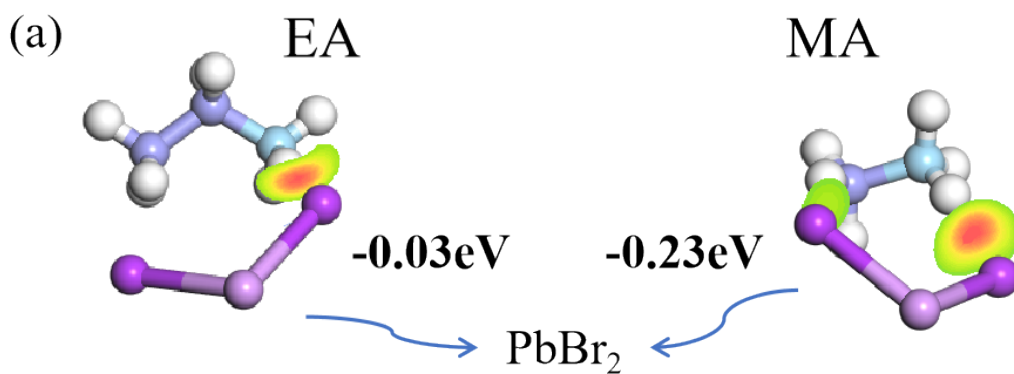


Figure S3. (a) Binding energy of ethylamine and methylamine with  $\text{PbBr}_2$  calculated by DFT calculation

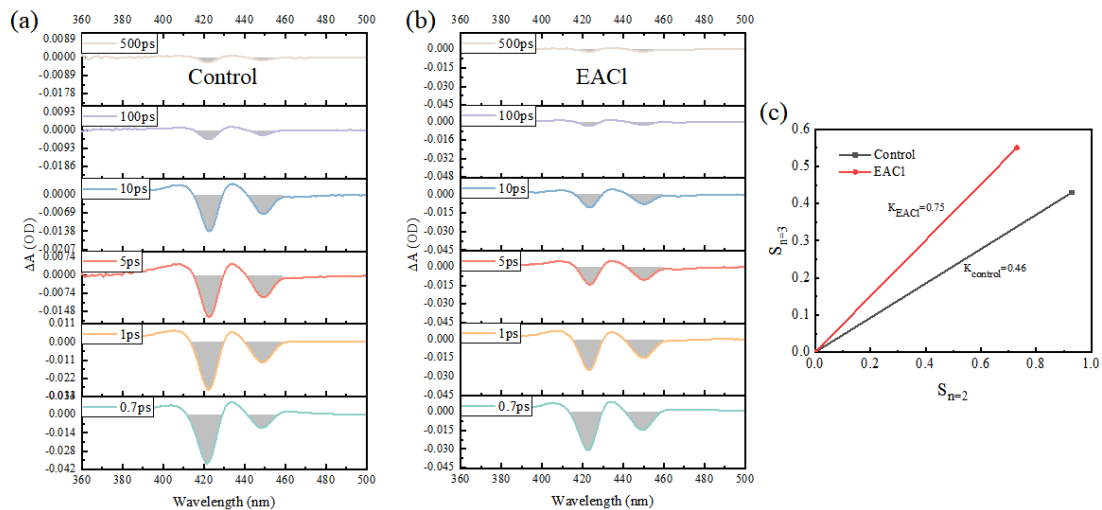


Figure S4. The relative contents of different phases estimated from the TA spectra. (a) Control. (b) EACI. (c) The relative ratio of  $n=3$  to  $n=2$ .

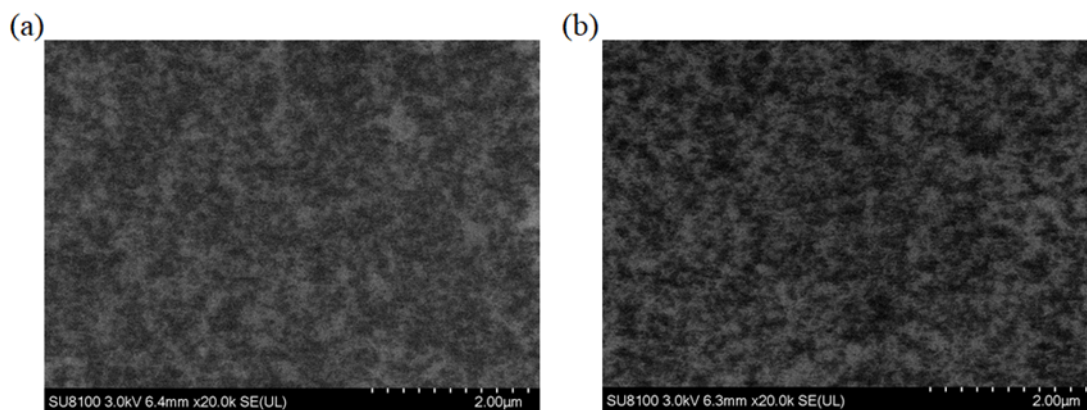


Figure S5. PEDOT:PSS film surface under SEM test. (a) Control (b) EACI .

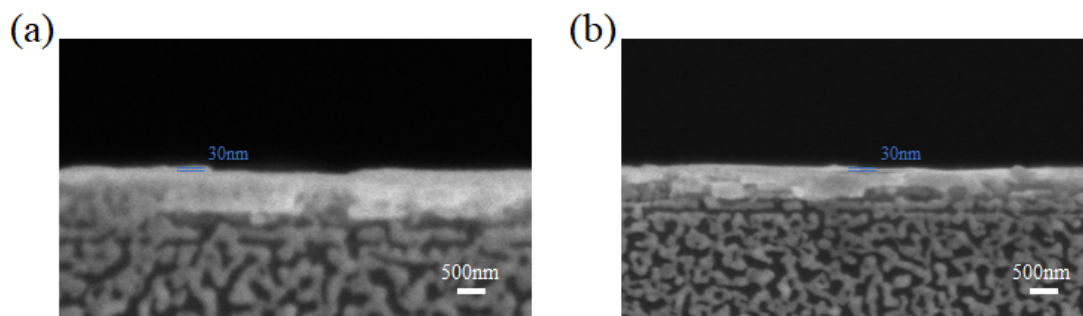


Figure S6. Cross-sectional SEM images with Control (a) and EACI-modified (b) perovskite films.

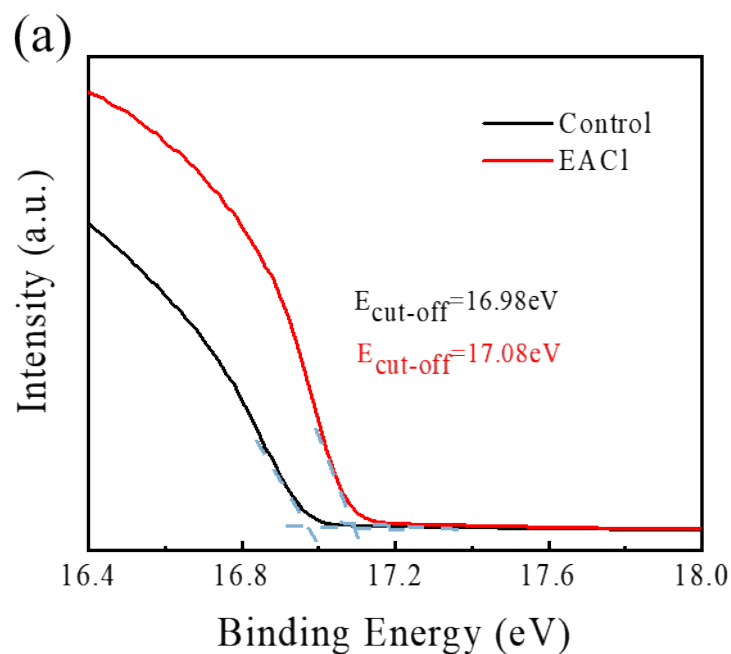


Figure S7. (a) Ultraviolet photoelectron spectroscopy(UPS) of PEDOT: PSS.

Table S1. Fitting parameters of time-resolved photoluminescence attenuation transients obtained of perovskites at different concentrations of EACl modification.

EACl concentration (mg/ml)	$\tau_1$ (ns)	$A_1$ (%)	$\tau_2$ (ns)	$A_2$ (%)	$\tau_3$ (ns)	$A_3$ (%)	$\tau_{\text{ave}}$ (ns)
0	1.32	66.74	4.33	30.55	20.98	3.26	7.35
5	6.85	20.83	1.82	85.26	34.09	1.78	9.28
10	1.25	72.47	5.37	27.09	28.29	3.74	11.37
20	1.51	67.77	4.98	33.45	25.23	3.52	9.01

Table S2. Solubility of MACl and EACl in DMSO.

	MACl (mg/ml)	EACl (mg/ml)
Solubility in DMSO	~350	~300

Table S3. The content of each element in the PEDOT: PSS film tested by XPS.

	C 1s (%)	O 1s (%)	Cl 2p (%)	N 1s (%)
Control	73.28	24.58	0.59	1.55
EACl	72.71	24.64	0.65	2.00

Table S4. XRD parameters of perovskites at different concentrations of EACl modification.

	Control	EACl-5	EACl-10	EACl-20
Peak intensity (a.u.)	208	331	218	265
FWHM(°)	1.17	0.78	1.03	0.88

Table S5. EL performance of the PeLEDs with different EACl doping concentrations.

Device	$L_{\max}$ (cd/m <sup>2</sup> )	$V_{\text{on}}$ (V)	EQE(%)	$\lambda_{\text{EL}}$ (nm)
Control	64.29	3.6	1.14	472
EACl-5	110.14	3.4	1.40	476
EACl-10	80.89	3.6	1.58	473
EACl-20	38.38	3.8	1.01	471