Supporting information

Efficient Sky-blue Perovskite Light-Emitting Diodes by Regulating the Quantum Wells Distribution of Quasi-2D Perovskites with Suppressing Lattice Distortion

*Zixun Tang, Yuhang Guo, Zexu Li, Qian Wang, Yingying Fu, Zhiyuan Xie**

Z. Tang, Y. Guo, Z. Li, Q. Wang, Y. Fu, Z. Xie

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

E-mail: xiezy_n@ciac.ac.cn (Z. Xie)

Z. Tang, Y. Guo, Z. Li, Q. Wang, Z. Xie

School of Applied Chemistry and Engineering, University of Science and Technology of China, Hefei 230026, P. R. China

E-mail: xiezy_n@ciac.ac.cn (Z. Xie)

Experimental details

Materials and Reagents

Lead bromide ($PbBr_2$, 99.99%), cesium bromide (CsBr, 99.99%), ethylammonium bromide (EABr, 99.99%), propylammonium bromide (PABr, 99.99%), butylammonium bromide (BABr, 99.99%) and phenethylammonium bromide (PEABr, 99.99%) were purchased from Xi'an Yuri Solar Co., Ltd. Dimethyl sulfoxide (DMSO, 99.8%) was purchased from Thermo Fisher Scientific. Metformin (Met, 95%) was purchased from Shanghai Macklin Biochemical Corp. Potassium dihydrogen phosphate (KH_2PO_4, 99.5%) was purchased from Aladin. Poly (sodium 4-styrenesulfonate) (PSS-Na, average Mw ≈ 70 000) was purchased from Sigma-Aldrich. TPBi and LiF were obtained from Luminescence Technology Corp. Patterned ITO glass substrate with a sheet resistance of 7Ω was obtained from Advanced Election Technology Company. PEDOT: PSS (Clevios P VP AI 4083) was purchased from Heraeus. All chemicals were used as received.

Quasi-2D Perovskites Preparation and Characterization

Taking the quasi-2D perovskites prepared with mixed EA/PEA ligands as an example, a mixture of CsBr (17.0 mg), $PbBr_2$ (36.7 mg), EABr (7.5 mg) and PEABr (10.1 mg) with a molar ratio of 0.8:1:0.6:0.5 was dissolved in 1 mL DMSO to form the precursor solution and the concentration of Pb^{2+} was approximately kept at 0.1 mmol mL^{-1}. The precursor solutions for other quasi-2D perovskites prepared with PA/PEA and BA/PEA ligands were prepared following the same procedure. The CsBr:$PbBr_2$:PEA molar ratio for the quasi-2D perovskite prepared with PEA ligand is

0.8:1:1.1. As to the precursor solution for perovskite prepared by EA of 1.0, a mixture of CsBr (21.3 mg), $PbBr_2$ (36.7 mg) and EABr (12.6 mg) with a ratio of 1:1:1 was dissolved in 1 mL DMSO to form the precursor solution. The precursor solutions for perovskite prepared with EA, PA, BA with different ratio were prepared following the same procedure. The precursor solution was stirred at 45°C for 2h and cooled to room temperature before use. Quasi-2D perovskites are prepared by spin-coating the precursor solution onto the PEDOT:PSS layer at 4000 rpm for 60 s and annealed at 80 °C for 10 min. In the case of modified-EA/PEA (m-EA/PEA), 30 μL Met solution in DMSO with a concentration of 50 mg mL^{-1} was added to 1 mL precursor solution and the solution was stirred for 20 min before use.

Out-of-plane X-ray diffraction was conducted on a Rigaku Smart Lab with Cu Kα source (λ=1.54056 Å), where the perovskite samples were placed in a simple package to prevent oxygen and moisture. Steady-state PL spectra were measured on an Edinburgh FLS980 PL spectrometer with an excitation wavelength of 375 nm. UV-vis absorption spectra were recorded with an Agilent Cary 60 spectrophotometer. The fs-TA experiment was carried out on an ultrafast pump-probe system. A pump light with a 100 nJ pulse was used to excite the sealed quasi-2D perovskite samples. The SEM images of the perovskites were measured with a ZEISS Sigma 300 SEM at 3 kV. The AFM height images were measured with Bruker Dimension ICON AFM in peak force mode.

PeLEDs Fabrication and Characterization

The PeLEDs have a structure of ITO/PEDOT:PSS (70 nm)/quasi-2D perovskite

(25 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm). The PEDOT:PSS hole-transport layer is spin-coated from the PEDOT:PSS solution, which is prepared by mixing the 80 mg mL^{-1} PSS-Na aqueous solution and the commercial PEDOT AI 4083 aqueous solution with a volume ratio of 1:1. The KH_2PO_4 modified PEDOT:PSS solution is prepared by mixing the 80 mg mL^{-1} PSS-Na aqueous solution, the commercial PEDOT AI 4083 aqueous solution and 100 mg mL^{-1} KH_2PO_4 water solution with a volume ratio of 46%:50%:4%, and the solutions were stirred for at least 20 min before use.

The patterned ITO glass substrates were subjected to a routine cleaning procedure and were dried with nitrogen gas flow. After the patterned ITO glass substrate was treated with UV ozone for 40 min, the PEDOT:PSS layer was spin-coated at 5000 rpm and annealed at 130 °C for 20 min. the perovskite layers were spin-coated on the PEDOT:PSS layer in a nitrogen-filled glove box. The electron-transport layer of TPBi (40 nm) and the cathode of LiF (1 nm)/Al (100 nm) were sequentially deposited in a vacuum chamber below a base pressure of 7.0×10^{-7} Torr. The emissive area of each cell is about 14 mm^2, defined by the overlapping of ITO and Al electrodes. The current density-voltage-luminance (J-V-L) characteristics of the PeLEDs were measured using a Keithley 2400 source meter and a calibrated silicon photodiode. EL spectra and stability test were recorded with spectroradiometer CS2000A.

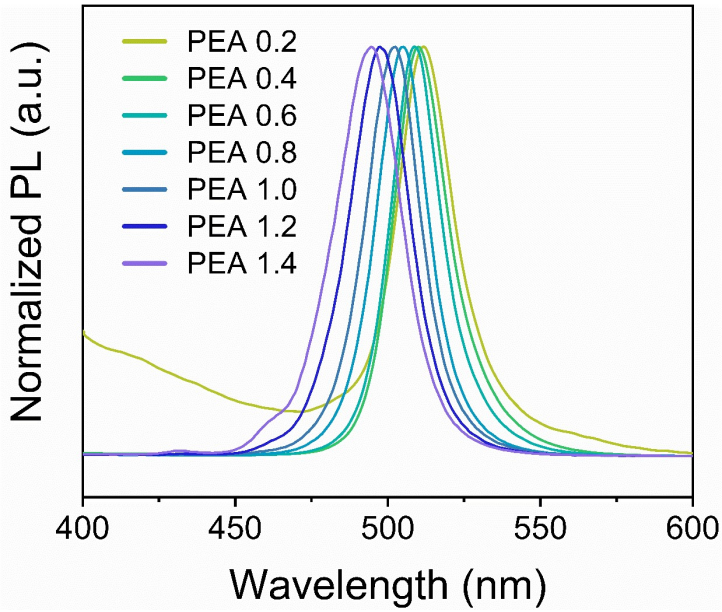

Fig. S1 Normalized PL spectra of the quasi-2D perovskites prepared with various PEA molar ratios in the PEABr:CsBr:$PbBr_2$ (1:1:x) precursor solutions.

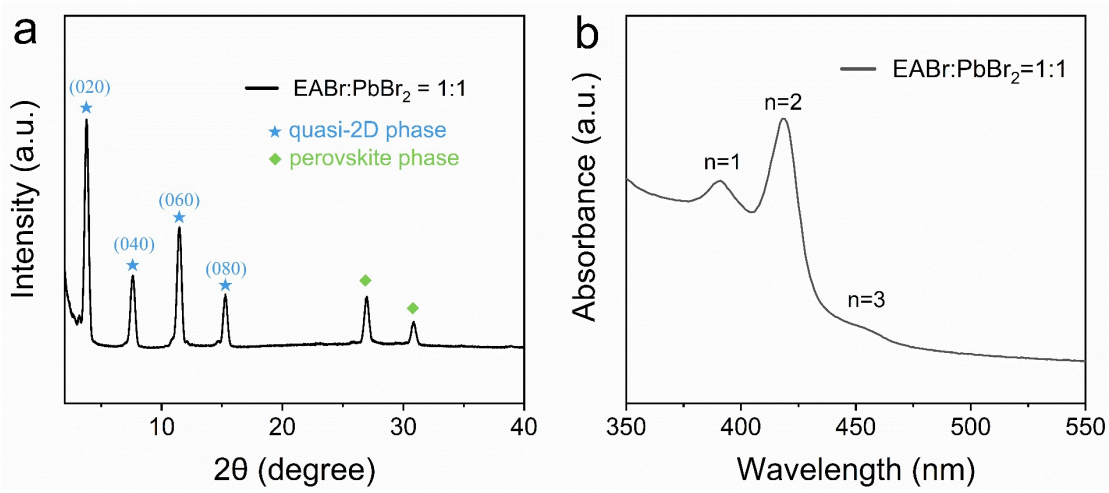

Fig. S2. (a) XRD pattern and (b) absorbance spectrum of the perovskites prepared with the $PbBr_2$:EABr (1:1) precursors without CsBr.

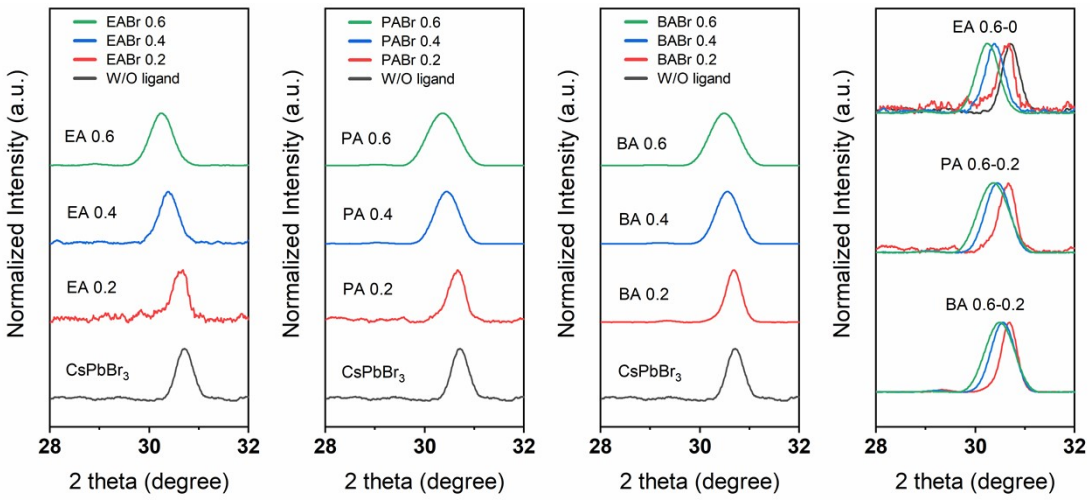

Fig. S3 XRD patterns of the perovskites prepared with EA, PA and BA organic ligands. The molar ratio of organic ligand is from 0.2 to 0.6.

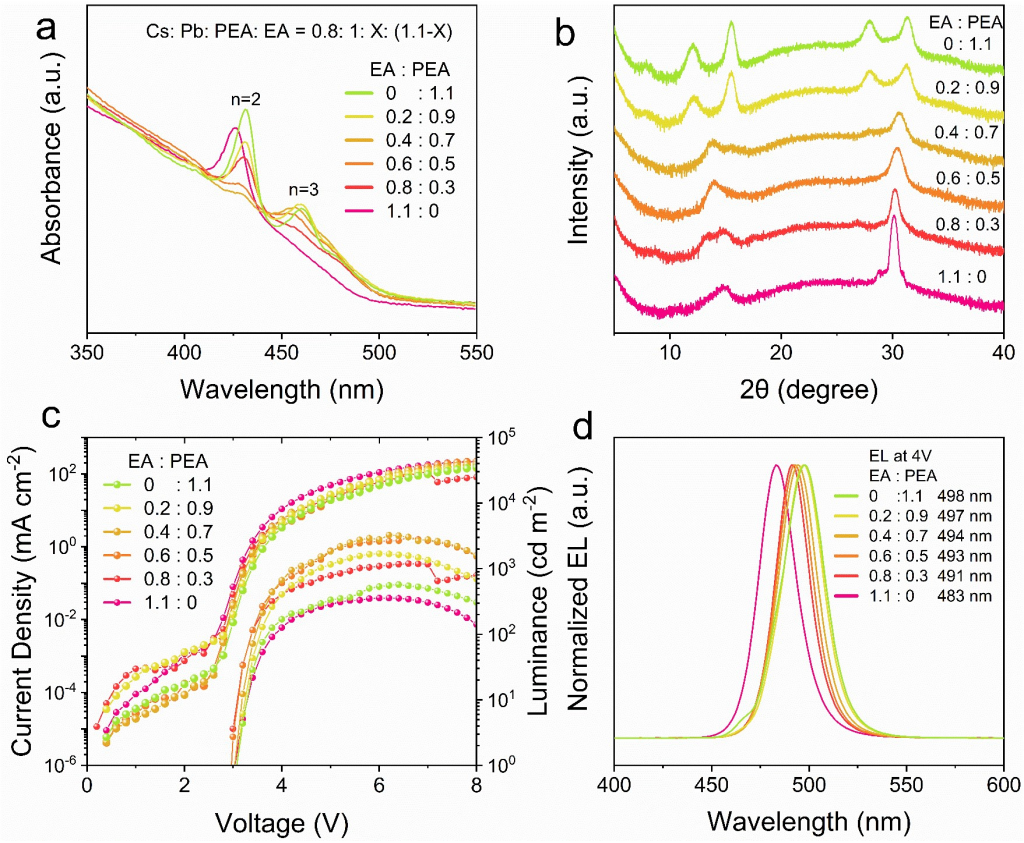

Fig. S4 (a) Absorbance spectra and (b) XRD patterns of the quasi-2D perovskites prepared with different ratios of mixed PEA and EA ligands. The ratio of CsBr:$PbBr_2$ is 0.8:1. (c) J-V-L characteristic curves and (d) normalized EL spectra of the sky-blue PeLEDs based on the quasi-2D perovskites prepared with different ratios of mixed PEA and EA ligands.

Table S1 EL performance of sky-blue PeLEDs based on the quasi-2D perovskites prepared with different ratios of mixed PEA and EA ligands. The ratio of CsBr:$PbBr_2$ is 0.8:1.

Ratio of PEA:EA	L_{max} (cd m^{-2})	CE_{max} (cd A^{-1})	EQE_{max} (%)	V_{on} (V)	EL peak@4V (nm)	FWHM (nm)
0: 1.1	357	1.55	1.39	3.2	483	22
0.3: 0.8	1189	11.77	8.13	3.0	491	20
0.5: 0.6	3027	19.46	12.95	3.0	493	21
0.7: 0.4	3250	12.65	7.93	3.2	494	23
0.9: 0.2	1698	10.57	6.02	3.2	497	24
1.1: 0	571	9.86	5.60	3.2	498	26

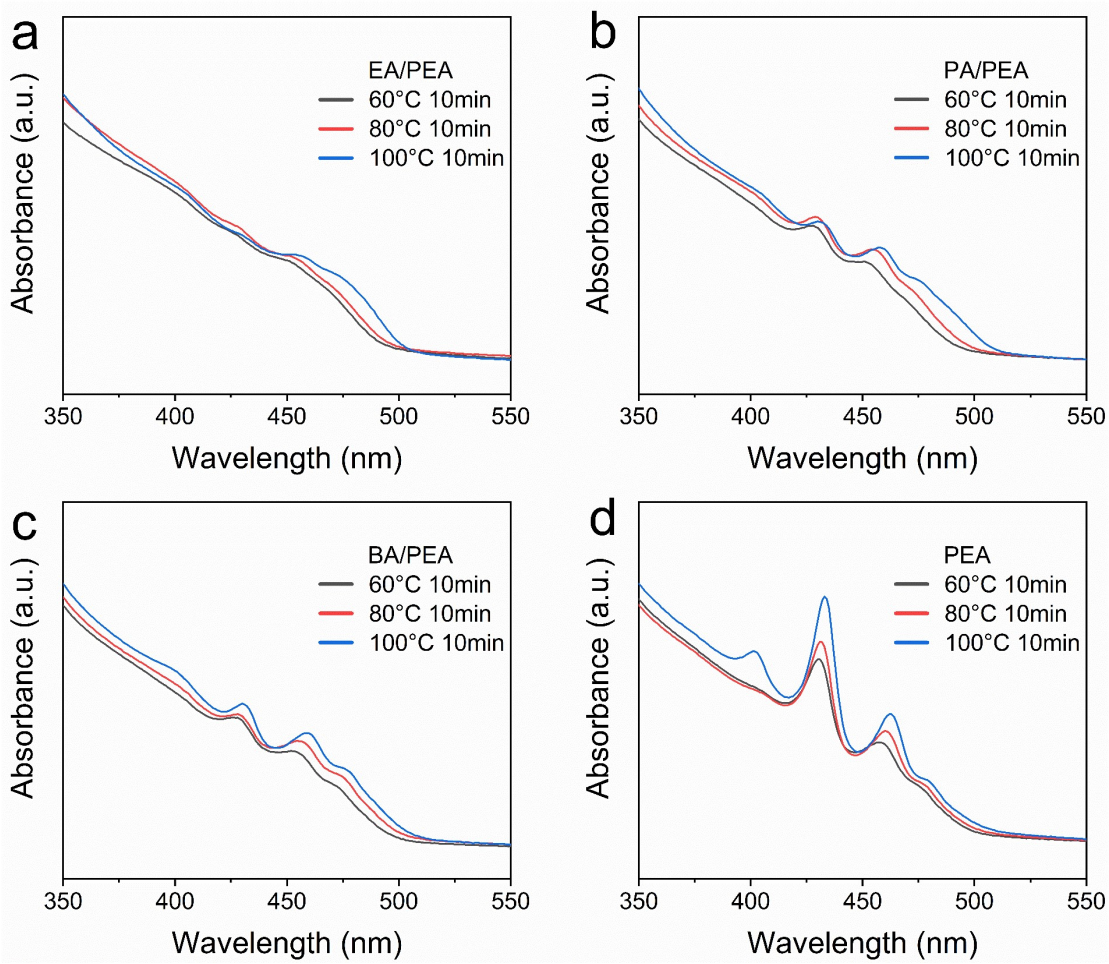

Fig. S5 Absorbance spectra of the quasi-2D perovskites prepared with the EA/PEA, PA/PEA, BA/PEA and PEA ligands annealed at different temperatures.

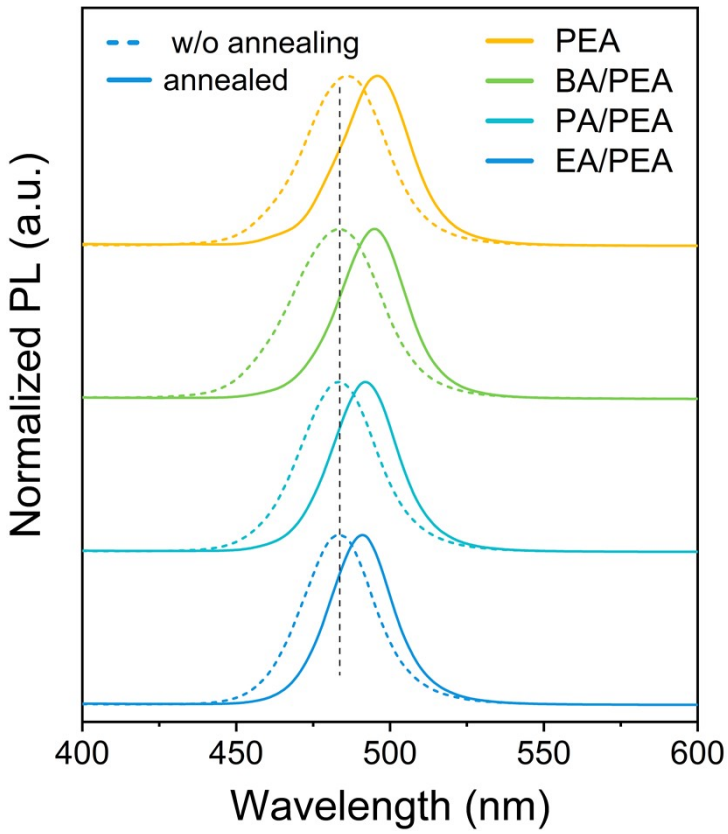

Fig. S6 PL spectra of the quasi-2D perovskites prepared with the EA/PEA, PA/PEA, BA/PEA and PEA ligands before and after annealed at 80°C for 10 min.

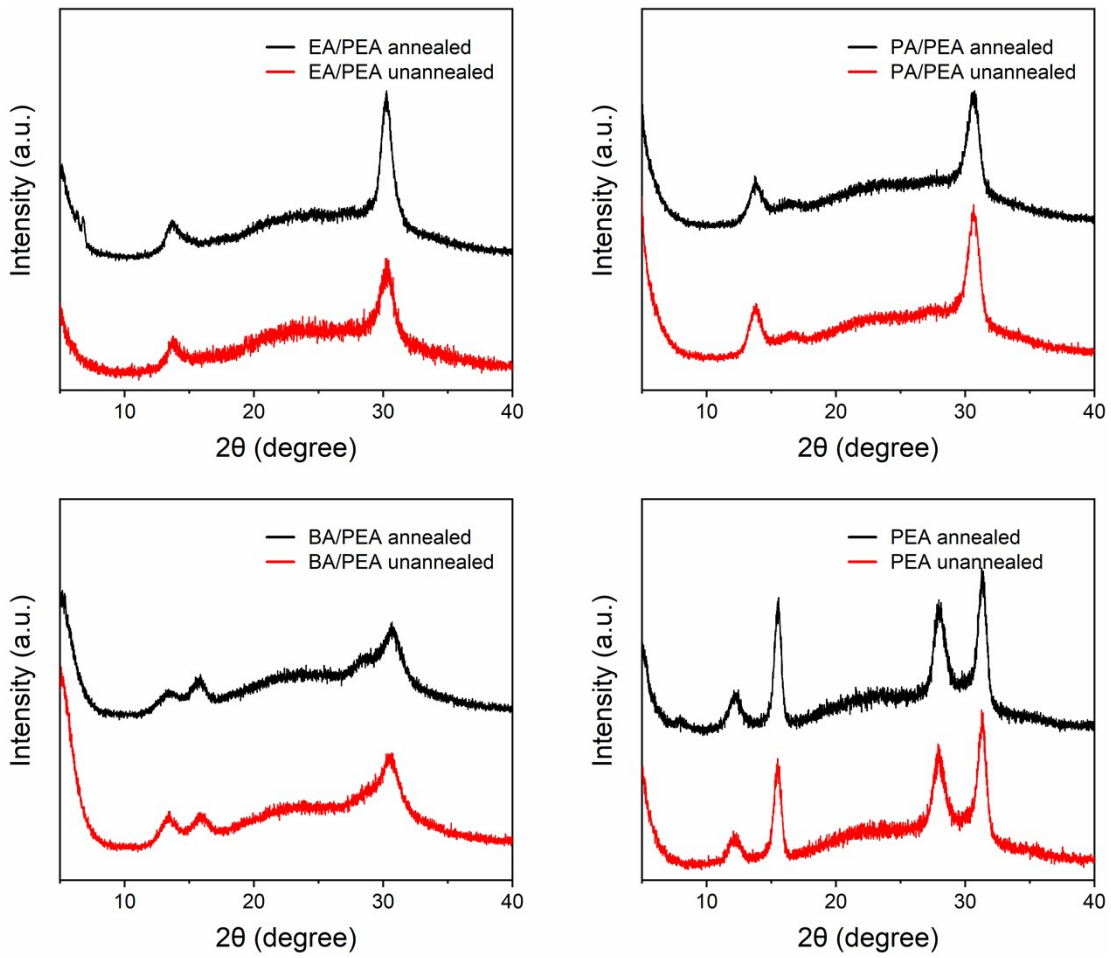

Fig. S7 XRD patterns of quasi-2D perovskite prepared with the EA/PEA, PA/PEA, BA/PEA and PEA as ligands before and after annealing at 80 °C for 10 min.

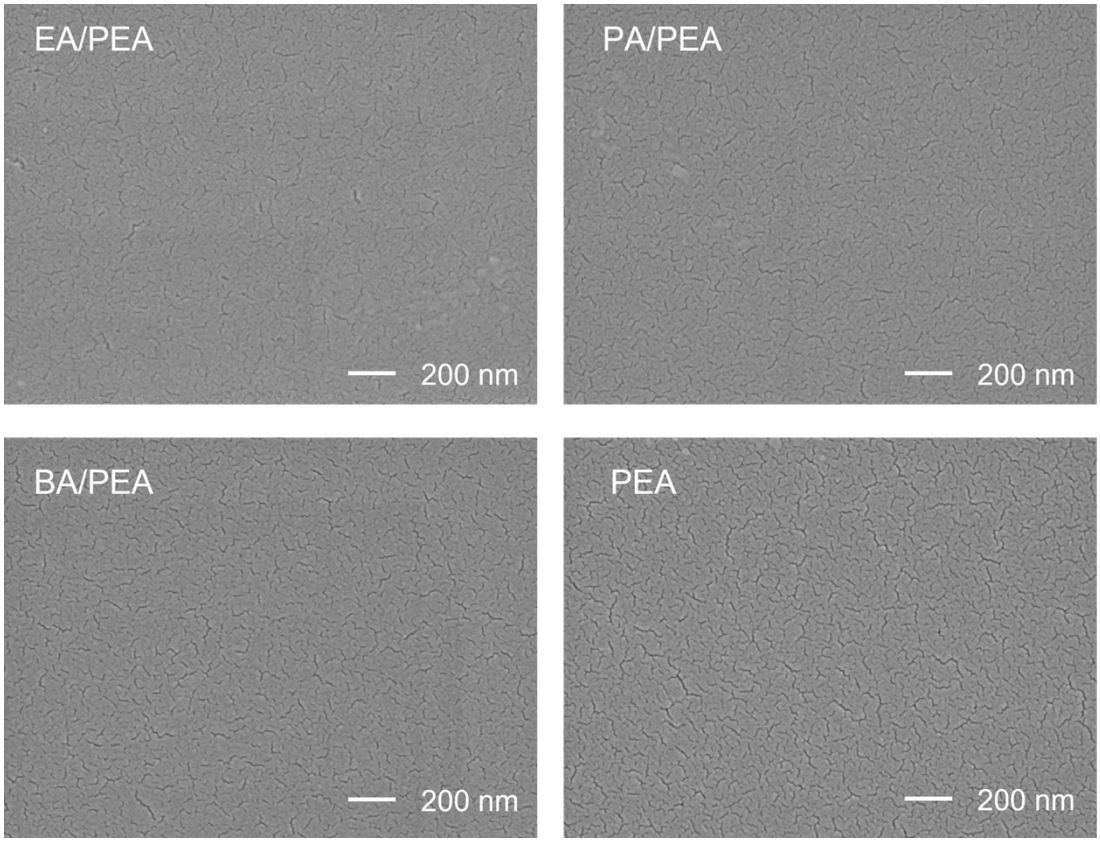

Fig. S8 SEM images of the quasi-2D perovskite emissive layers prepared with the EA/PEA, PA/PEA, BA/PEA and PEA as ligands, respectively. The scale bar is 200 nm.

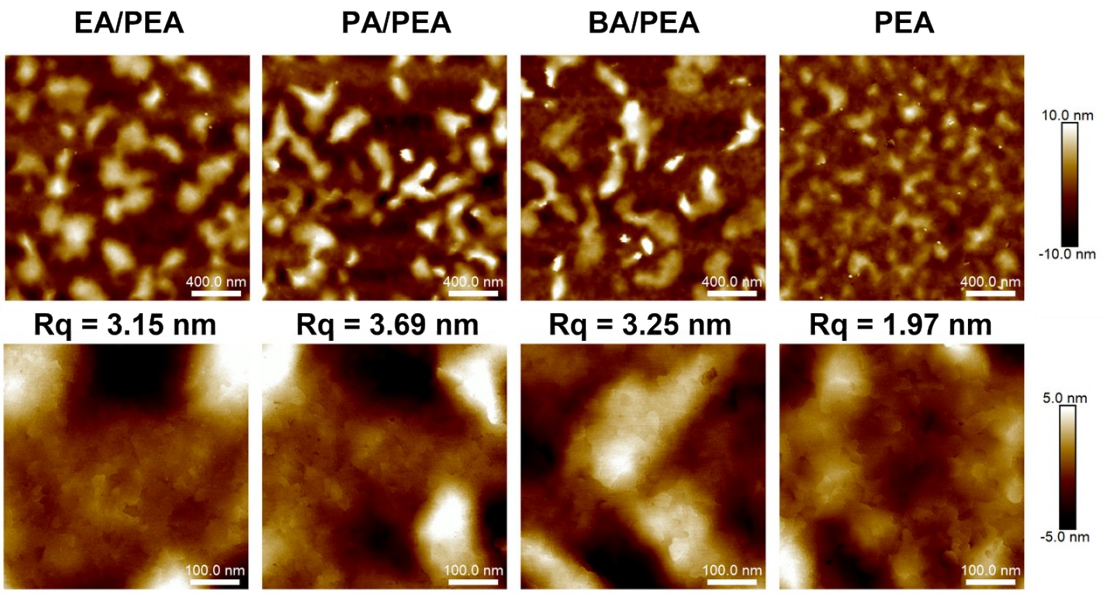

Fig. S9 AFM height images of the quasi-2D perovskite emissive layers prepared with the EA/PEA, PA/PEA, BA/PEA and PEA as ligands, respectively. The scale bar is 400 nm (top) and 100 nm (bottom).

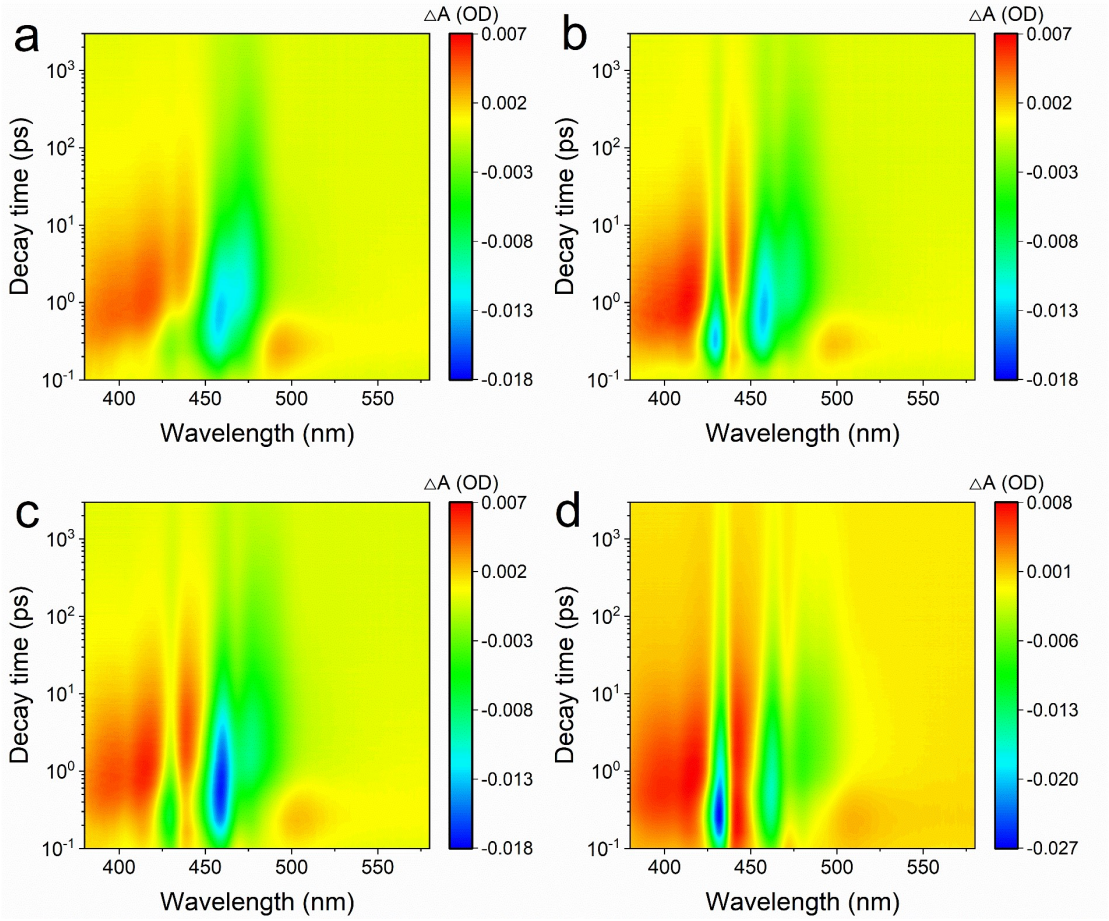

Fig. S10 Time-wavelength-dependent TA maps of the quasi-2D perovskites prepared with different ligands of EA/PEA, PA/PEA, BA/PEA and PEA, respectively.

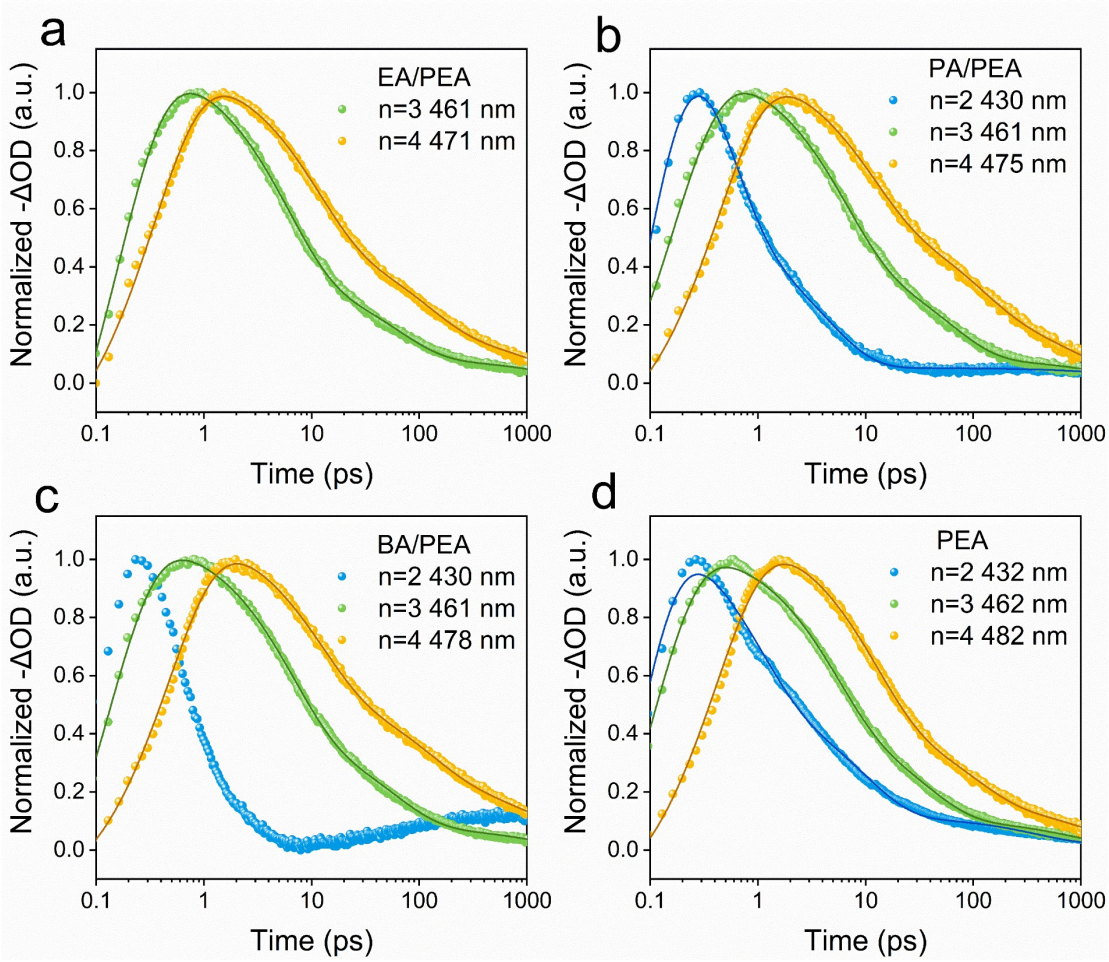

Fig. S11 TA kinetics traces of the quasi-2D perovskites prepared with different ligands of EA/PEA, PA/PEA, BA/PEA and PEA, respectively, probed at different wavelengths.

Table S2 Fitted parameters of the decay kinetics of different QWs in various perovskites.

	Wavelength (nm)	τ_{et} (ps)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
EA/PEA	GSB (n=3) 461 nm	0.16	5.78	62.56	1270.48
	GSB (n=4) 471 nm	**0.36**	10.81	111.39	1032.37
PA/PEA	GSB (n=2) 430 nm	0.09	0.47	4.36	2876.70
	GSB (n=3) 461 nm	0.17	6.16	60.42	1259.28
	GSB (n=4) 475 nm	**0.45**	10.77	104.00	740.99
BA/PEA	GSB (n=3) 461 nm	0.13	6.26	58.06	995.95
	GSB (n=4) 478 nm	**0.49**	11.51	114.39	844.98
PEA	GSB (n=2) 432 nm	0.07	0.97	9.79	389.49
	GSB (n=3) 462 nm	0.11	4.94	36.04	767.11
	GSB (n=4) 482 nm	**0.43**	11.65	95.60	1025.21

$$A(t) = a_1\exp\left(-\frac{t}{\tau_1}\right) + a_2\exp\left(-\frac{t}{\tau_2}\right) + a_3\exp\left(-\frac{t}{\tau_3}\right) - c_1\exp\left(-\frac{t}{\tau_{et}}\right)\#$$

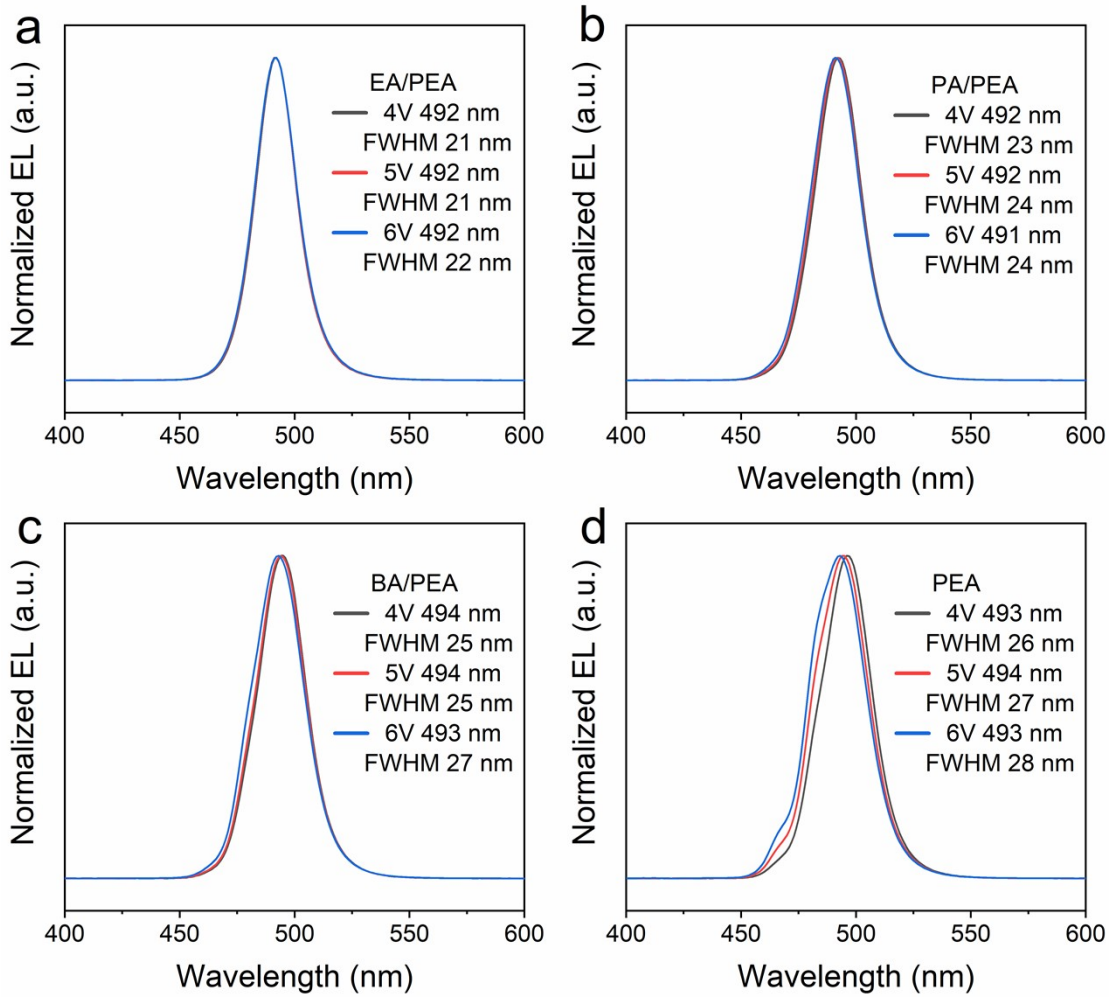

Fig. S12 Normalized EL spectra of the sky-blue PeLEDs based on various quasi-2D perovskites at driving voltages of 4V, 5V and 6V.

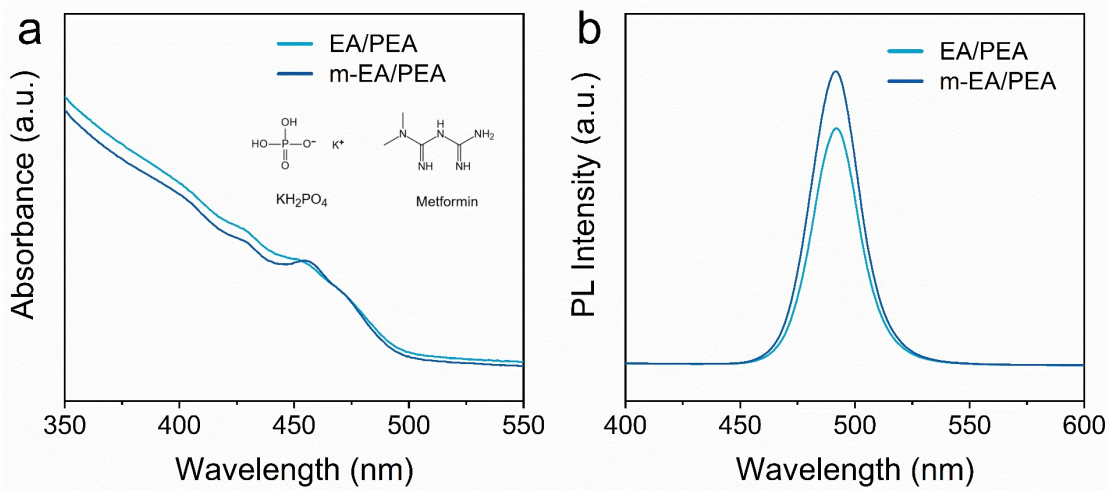

Fig. S13 (a) Absorbance and (b) PL spectra of the quasi-2D perovskites based on the mixed EA/PEA ligands without or with modification of KH_2PO_4 and Metformin.