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Intramolecular Hydrogen Bonds Assist to Control Quasi-2D Perovskite Quantum Well Distribution for Efficient Pure-blue Perovskite Light-emitting Diodes

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Experimental section

Materials and Reagents

Lead bromide ($PbBr_2$, 99.99%), ethylammonium bromide (EABr, 99.99%), cesium bromide (CsBr, 99.99%), lithium bis(trifluoromethanesulphonyl)imide (LiTFSI, 99.99%), ethylenediamine dihydrobromide (EDADBr, 99.5%), phenethylammonium bromide (PEABr, 99.99%) and 2-Fluorophenylethylammonium bromide (*o*-F-PEABr, 99.99%) were purchased from Xi'an Yuri Solar Co., Ltd. Dimethyl sulfoxide (DMSO, 99.8%) was purchased from Thermo Fisher Scientific. Guanidinium dihydrogen phosphate (GAH_2PO_4, 99.9%) 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 substrates with a sheet resistance of 7Ω were obtained from Advanced Election Technology Company. PEDOT: PSS (Clevios P VP AI 4083) was purchased from Heraeus. All chemicals were used as received.

Blue Quasi-2D Perovskites Preparation and Characterization

Taking the quasi-2D perovskite prepared with *o*-F-PEA ligands as an example, a mixture of CsBr, FABr, $PbBr_2$, $PbCl_2$, $SrBr_2$, EDADBr, EABr and *o*-F-PEABr with a molar ratio of 1: 0.1: 0.6: 0.4: 0.02: 0.025: 0.3: 0.7 was dissolved in 1 mL DMSO to form the precursor solution and the concentration of Pb^{2+} was approximately kept at 0.06 mmol mL^{-1}. The precursor solutions for quasi-2D perovskites prepared with PEABr 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 annealing at 65 °C for 20 min. All the experimental operations mentioned above were completed in a nitrogen-filled glove box, including weighing the chemical with an electronic analytical balance, adding solvent to prepare precursor solution, spin-coating and annealing processes for preparing quasi-2D perovskite films.

Out-of-plane X-ray diffraction was conducted on a Rigaku Smart Lab with Cu Kα source (λ=1.54056 Å). Steady-state PL spectra were measured on an Edinburgh FLS980 PL spectrometer with an excitation at 360 nm. UV-vis absorption spectra were recorded with an Agilent Cary 60 spectrophotometer. *In-situ* absorption spectra during spin-coating were measured by a self-built test-system, absorption spectra were collected by an Ocean Optics spectrophotometer. The fs-TA experiment was carried out on an ultrafast pump-probe system. A pump light with a 40 nJ pulse was used to excite the sealed quasi-2D perovskite samples. The SEM images of the perovskites were obtained with a ZEISS Sigma 300 SEM at 3 kV.

Blue PeLEDs Fabrication and Characterization

Blue PeLEDs have a structure of ITO/modified PEDOT:PSS (70 nm)/blue quasi-2D perovskite (20 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 100 mg mL^{-1} PSS-Na aqueous solution, 100 mg mL^{-1} LiTFSI aqueous solution, 100 mg mL^{-1} GAH_2PO_4 aqueous solution and the commercial PEDOT AI 4083 aqueous solution with a volume ratio of 40:5:5:50. 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 treated with UV ozone for 40 min before use. The modified PEDOT: PSS layer was spin-coated on the patterned ITO glass substrates at 5000 rpm for 30 s and annealed at 130 °C for 20 min. The blue perovskite precursor solutions 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 J-V-L characteristics of the PeLEDs were measured using a Keithley 2400 source meter and a calibrated silicon photodiode in a nitrogen-filled glove box. EL spectra and stability tests were recorded with spectroradiometer CS2000A in air condition.

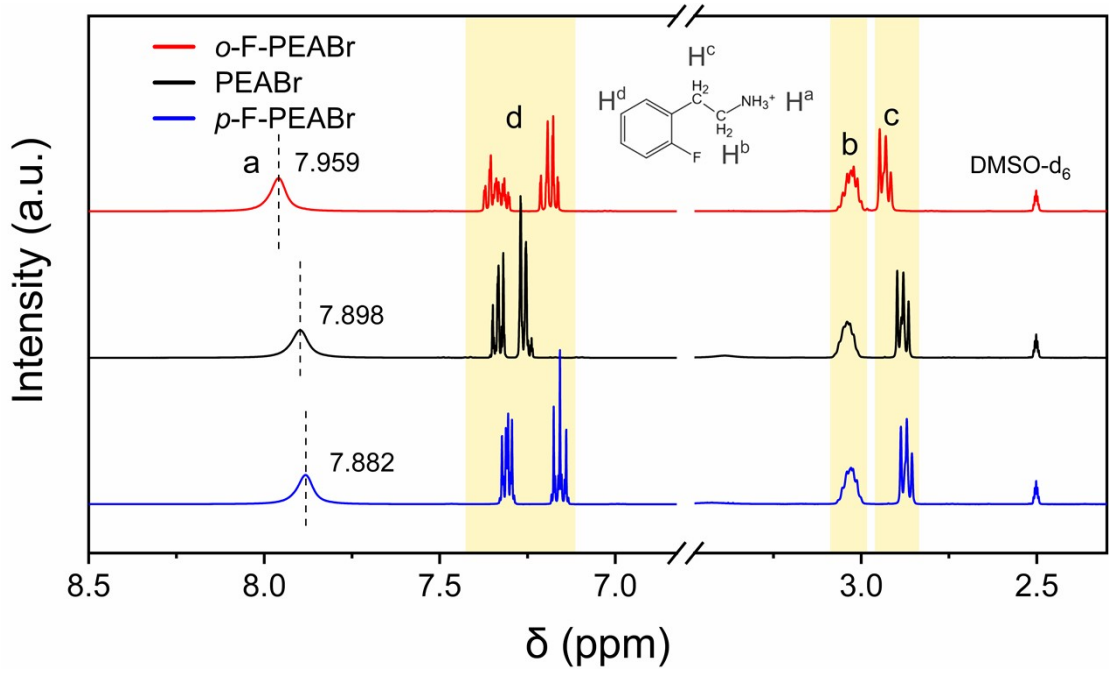

Fig. S1. H^1-NMR spectra of *o*-F-PEABr, PEABr and *p*-F-PEABr dissolved in DMSO-d_6, respectively.

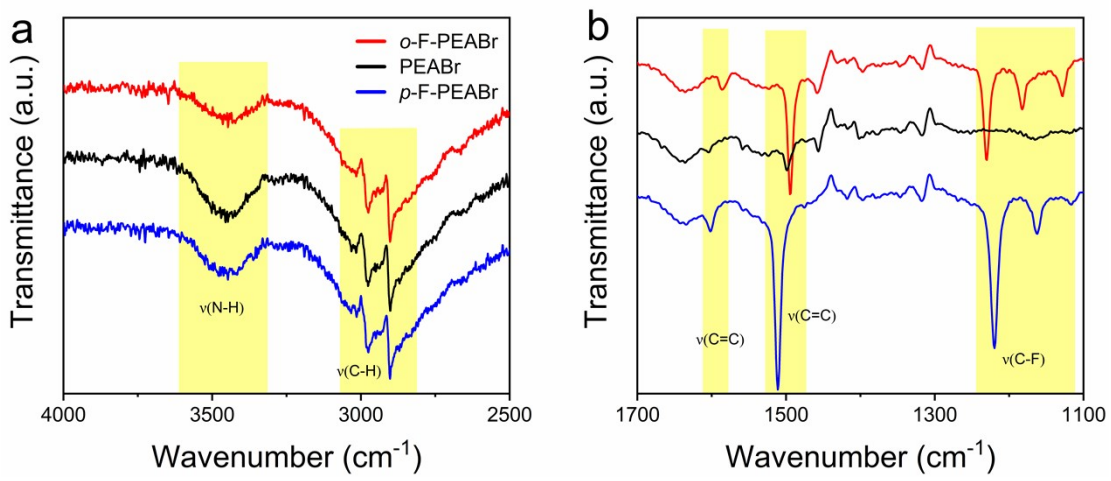

Fig. S2. FTIR spectra of *o*-F-PEABr, PEABr and *p*-F-PEABr dissolved in DMSO at different wavenumber ranges, respectively.

Table S1. Fitted parameters of the decay kinetics of different components in quasi-2D perovskites prepared with *o*-F-PEABr and PEABr ligands.

	component	τ_{et} (ps)	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
o-F-PEABr	n=3 (440 nm)	0.14	0.35	3.03	60.30
	n≥4 (459 nm)	0.31	6.31	36.89	411.13
PEABr	n=3 (440 nm)	0.17	0.51	4.97	105.18
	n≥4 (459 nm)	0.33	7.13	41.61	477.04

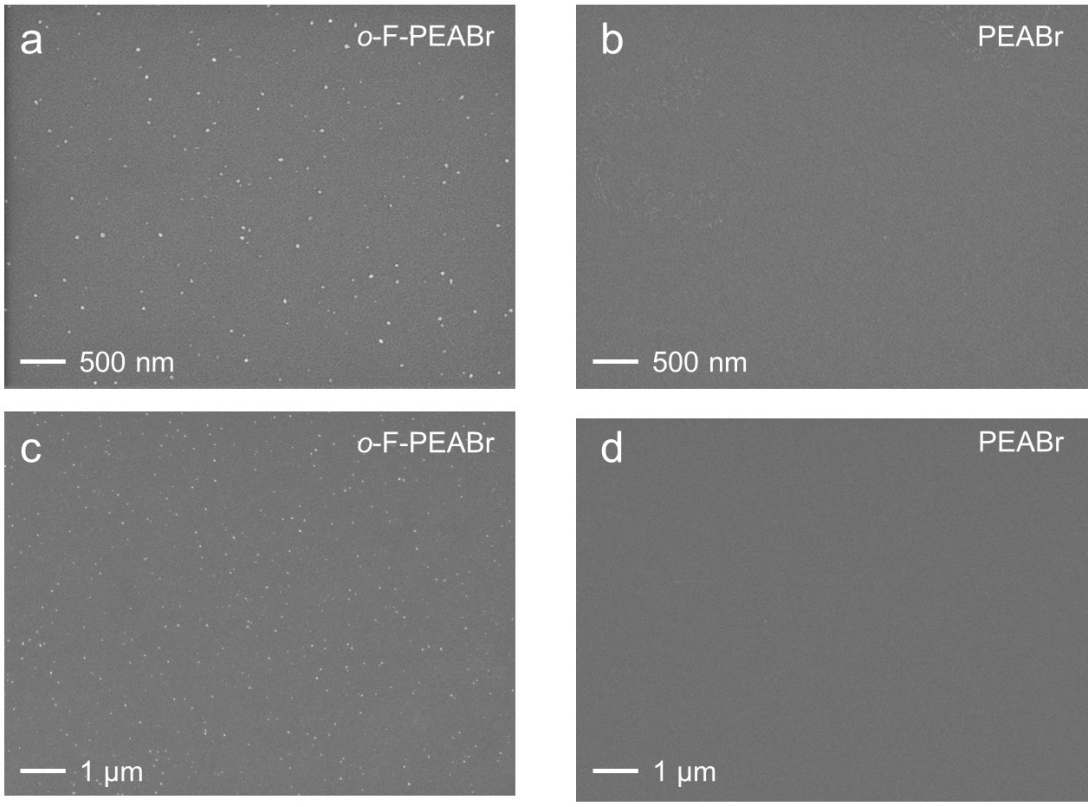

Fig. S3. SEM images of the quasi-2D perovskite emissive layers prepared with (a,c) *o*-F-PEABr and (b,d) PEABr ligands, respectively.

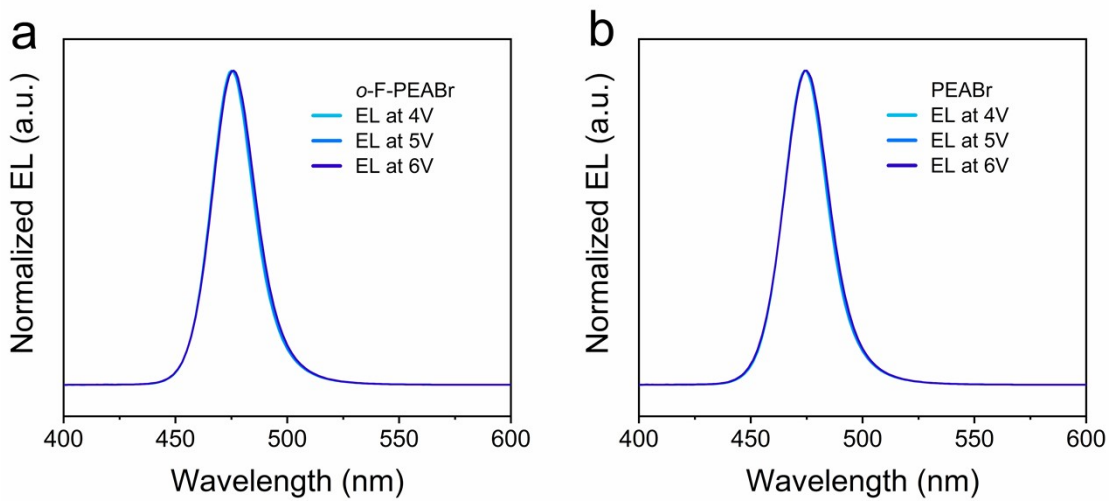

Fig. S4. EL spectra of the blue PeLEDs based on quasi-2D perovskites prepared with (a) *o*-F-PEABr and (b) PEABr ligands at different driving voltages.

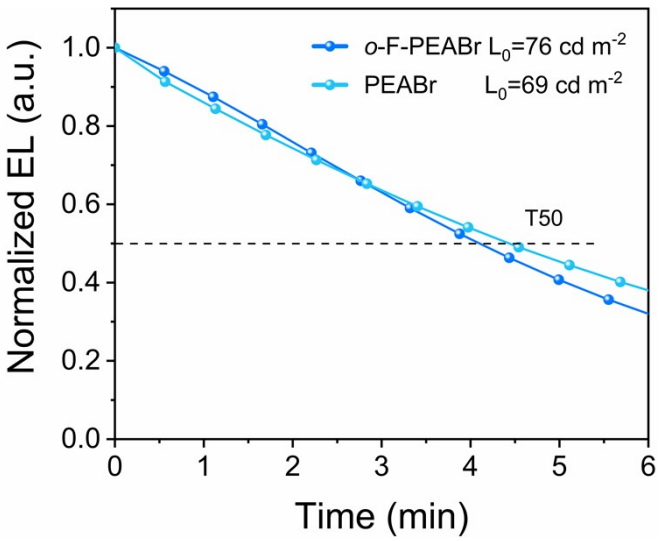

Fig. S5. Stability test of the blue PeLEDs based on quasi-2D perovskites prepared with *o*-F-PEABr and PEABr ligands.

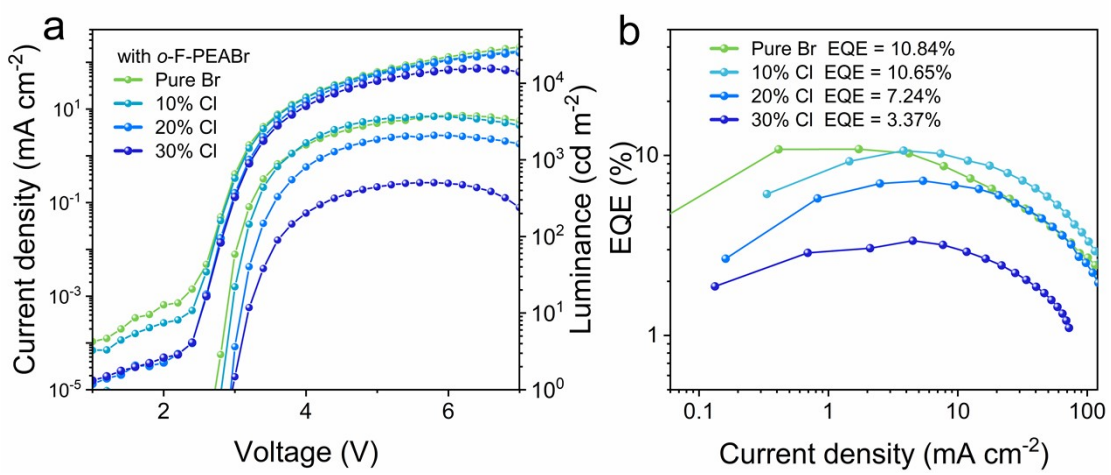

Fig. S6. (a) Current density-Voltage–Luminance characteristic and (b) EQE–Current density curves of the blue PeLEDs prepared with different Cl/(Br+Cl) ratios using *o*-F-PEABr as ligands.

Table S2. EL performance of the blue PeLEDs based on the quasi-2D perovskite emissive layers prepared with different Cl/(Br+Cl) ratios using o-F-PEABr as ligands.

	V_{on} (V)	L_{max} (cd m^{-2})	CE_{max} (cd A^{-1})	EQE_{max} (%)	EL peak (nm)	FWHM (nm)	CIE (x,y)
Pure Br	2.8	3782	14.20	10.84	487	24	(0.077, 0.265)
Cl 10%	3.0	3641	11.49	10.65	482	23	(0.091, 0.189)
Cl 20%	3.0	2039	6.13	7.24	475	22	(0.111, 0.113)
Cl 30%	3.0	505	2.00	3.37	466	22	(0.130, 0.064)

L_{max} denotes the maximum luminance. CE_{max} and EQE_{max} are the maximum current efficiency and EQE, respectively. V_{on} is the turn-on voltage, at which a luminance of 1 cd m^{-2} is achieved.

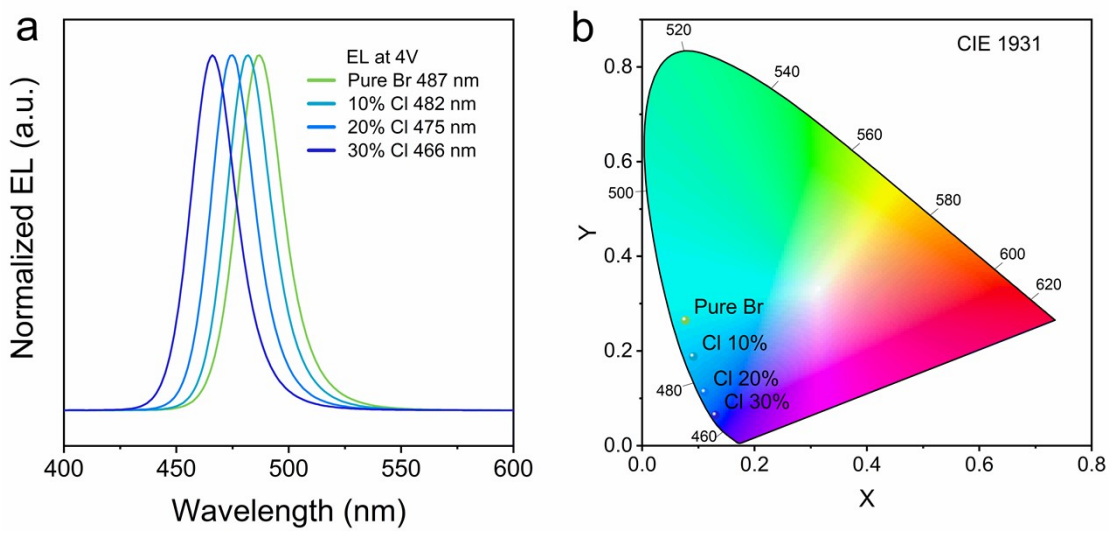

Fig. S7. (a) EL spectra at 4V and (b) CIE values of the blue PeLEDs prepared with different Cl/(Br+Cl) ratios using *o*-F-PEABr as ligands.