Supporting Information

Spacer cation enabled dimension control for efficient and wavelengthtunable blue perovskite light-emitting diodes

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1. Experimental Section

1.1. General information

Organic solvents, including anhydrous dimethyl sulfoxide (DMSO), *N*,*N*-Dimethylformamide (DMF), ethanol, and solid chemicals, including lead bromide (PbBr₂), lead chloride (PbCl₂), cesium bromide (CsBr), PVP (Mw = 1300 k), potassium sulfate (K₂SO₄), 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi), NaBr, LiF, and YCl₃ were purchased from Sigma Aldrich. Phenylethylammonium bromide (PEA) was purchased from Greatcell Solar. PEDOT:PSS (Clevios P VP AI 4083) was purchased from Ossila. All the above chemicals were used as received.

1.2. Material synthesis

All reactions sensitive to air and water were performed in an inert (argon) atmosphere using a Schlenk line setup and tubes. All chemical reagents and solvents for synthesis were purchased from Combi-block and used as received.

Biphenylethylammonium bromide (*b*PEA): 2-([1,1'-biphenyl]-4-yl)ethan-1-amine was added into 1 M HBr solution. After stirring for 4 h at room temperature, the solvents were removed under vacuum. Diethyl ether was added to the solid, and the solid products were collected by filtration, and washed several times with diethyl ether. The products were dried under vacuum as a white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.85 (s, 3H), 7.62 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (m, 3H), 3.07 (t, *J* = 7.9 Hz, 2H), 2.90 (t, *J* = 7.9 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 140.21, 139.06, 136.85, 129.67, 129.31, 127.74, 127.26, 126.91, 32.97. HR-MS (ESI) Expected 198.12 [M-Br-H]⁺ Observed 198.12.

1.3. Fabrication of perovskite films

The PEA (0.06 mmol) or *b*PEA (0.06 mmol), CsBr (0.15 mmol), MABr₂ (0.04 mmol), PbCl₂ (0.1 mmol), NaBr (0.02 mmol) were mixed in 1 mL DMSO and stirred for 2 hours at room temperature. GABA (10 mg) was put into the precursor solution, stirred for another 1 hour, and filtered by a 0.22 μ m PTFE filter. Glass slides or indium-doped tin oxide (ITO) coated glass substrates were cleaned by detergent water, DI water, acetone, and isopropanol for 15 mins each under ultrasonication. The substrates were dried with dry air and treated with UV-Ozone for 20 min before depositing any layers. The forementioned precursor solution was spin-coated at 4000 rpm for 90 s and annealed at 110 °C for 5 min (*b*PEA) and 90 °C for 5 min (PEA), respectively. Note that the above-mentioned *b*PEA sample was labelled as Film-D and the resulted device was labelled as Device-D. By varying the precursor solution ratio, different films were prepared from the precursor solutions detailed as follows:

Film-A (*b*PEA:CsBr:YCl₃:PbCl₂:MABr:NaBr = 0.6:1.5:0.1:1:0.4:0.2).

Film-B (*b*PEA:CsBr:YCl₃:PbCl₂:MABr:NaBr = 0.6:1.5:0.07:1:0.4:0.2). Film-C (*b*PEA:CsBr:YCl₃:PbCl₂:MABr:NaBr = 0.6:1.5:0.03:1:0.4:0.2). Film-D (*b*PEA:CsBr:PbCl₂:MABr:NaBr = 0.6:1.5:1:0.4:0.2). Film-E (*b*PEA:CsBr:PbCl₂:MABr:NaBr = 0.6:1.5:1:0.6:0.2).

Film-F (*b*PEA:CsBr:PbCl₂:MABr:NaBr = 0.6:1.5:1:0.4:0.2 with DMSO:DMF = 5:1).

1.4. LED device characterization

The pre-cleaned ITO substrates were treated with UV-Ozone for the next spin-coating fabrication. As purchased PEDOT:PSS solution was mixed with K₂SO₄ at 6 mg/mL concentration and was subsequently spin-coated onto the ITO substrate at 7000 rpm for 30 s and annealed at 150 °C for 20 min. The PEDOT:PSS deposited film was transferred to the nitrogen-filled glove box and PVP in ethanol (2 mg/mL) was spin-coated at 2000 rpm for 45 s and baked at 100 °C for 10 min. Then, the as-prepared perovskite precursor solution was deposited at 4000 rpm for 90 s and annealed for 5 min. For the *b*PEA-based sky-blue (493 nm) PeLED device, a mixture of DMSO and DMF with a volume ratio of 5:1 was used to dissolve all the precursors. The film was transferred to thermal evaporator, and TPBi (40 nm), LiF (1.2 nm), and an Al (100 nm) anode were deposited under high vacuum (< 10⁻⁷ mbar). The active area of each device is defined to be 0.04 cm² by the overlapping area of ITO and Al electrodes.

1.5. Nuclear magnetic resonance (NMR) spectra

NMR spectra were obtained using a Bruker AV 400-MHz spectrometer at room temperature with DMSO- d_6 as the solvent and tetramethylsilane (TMS) as an internal standard.

1.6. Mass spectra

High resolution mass spectrometry was measured in positive electrospray mode (ESI) on an LTQ Orbitrap XL instrument (Thermo Fisher Scientific).

1.7. UV-vis absorption spectra

Thin film absorption spectra were acquired with Agilent UV-Vis-NIR Cary-5000 in transmission mode.

1.8. Photoluminescence (PL) spectra

Steady state PL spectra were measured with an Olympus microscopy (BX 53) integrated with an X-CITE 120Q UV lamp. The filter set contains a bandpass filter (330-385 nm), a dichroic mirror (cutoff wavelength, 400 nm), and a 420 nm long-pass filter. The collected PL signals were analyzed by a spectrometer (SpectraPro HRS-300).

1.9. Photoluminescence quantum yield (PLQY)

Absolute PLQYs were measured with a home-designed system, which consists of a continuouswave laser (375 nm), an integrating sphere, an optical fiber, and a spectrometer (SpectraPro HRS-300). Films used for PLQY measurements were fabricated on optical glass substrates, and an empty glass was used as the background. Spectra used for PLQY were carefully intensity-calibrated using a NIST traceble StellarNet SL1-CAL VIS-NIR Tungsten Halogen lamp to generate the standard curve.

1.10. Grazing incidence wide angle X-ray scattering (GIWAXS)

GIWAXS data were collected at the Advanced Light Source at Lawrence Berkeley National Lab utilizing an incident angle of 0.2°, a sample-detector distance of 3.5 meters and wavelength of 1.24 angstrom (energy 10 keV). The detector used was Pilatus 2M (Dectris, Inc.) and the data were calibrated using silver behenate as a standard via Igor Pro NIKA package.

1.11. Fluorescence lifetime imaging microscopy (FLIM)

Fluorescence lifetime imaging microscopy (FLIM) measurements were performed using a Nikon TE2000 confocal microscope with $60\times/1.2$ NA water immersion objective equipped with Alba Fast FLIM system (ISS). Specifically, samples were excited using 440 nm pulsed laser with modulation frequency of 20 MHz and imaged through 490 ± 20 nm bandpass pass filter followed by MPD APD detectors. After image collection, exponential fitting of FLIM images was performed using Vista Vision software (ISS) to obtain fluorescent lifetimes of each pixel.

1.12. Atomic force microscopy (AFM)

The height topography was obtained with Asylum Research Cypher ES Environmental AFM in ambient air.

1.13. Kelvin probe force microscopy (KPFM)

The KPFM topography and CPD images were obtained with Asylum Research Cypher ES Environmental AFM in ambient air. The surface potential is determined by KPFM relative to a Pt probe. All the KPFM images are processed with subtraction of the background.

1.14. Transmission electron microscopy (TEM)

The TEM images were obtained from transmission electron microscope (JEOL JEM-F200).

1.15. Fourier transform infrared spectrometer (FTIR)

The FTIR spectra were measured on BRUKER VERTEX 70v system.

1.16. Device Characterizations

All LED devices were characterized in a nitrogen-filled glove box. The *J-V* curves were measured using a Keithley 2450 source-measure unit. The devices were swept from zero bias to forward bias at a rate of 0.2 V s^{-1} . A 100 mm integrating sphere coupled with a spectrometer (Enli Technology, LQ-100X) was used for the measurements of luminance (*L*) and electroluminescent spectra.

2. Supplementary figures and related discussion



Fig. S1. Depictions of the single crystal structure for (a-c) (PEA)₂PbBr₄ and (d-f) (*b*PEA)₂PbBr₄. (a,d) View along *b* axis. (b,e) View along *a* axis. (c,f) View along *c* axis. Pb, grey; I, yellow.



Fig. S2. (a) FTIR spectra of PEA powder in KBr (black) and PEA-based perovskite films (red).(b) FTIR spectra of *b*PEA powder in KBr (black) and *b*PEA-based perovskite films.

To further prove the stronger interaction between ligand and Pb²⁺, we carried out FTIR measurements on PEA and *b*PEA powders as well as their perovskite thin films. As shown here, the N-H asymmetric stretching vibration (v_{N-H}) of PEA undergoes a blue-shift of 33 cm⁻¹ from 3431 cm⁻¹ (in PEA powder) to 3464 cm⁻¹ (in PEA-based perovskite), while the N-H bending vibration peak (δ_{N-H}) remains nearly unchanged. This suggests the existence of ligand-Pb interactions. In contrast, the N-H asymmetric stretching vibration (v_{N-H}) of *b*PEA manifests a blue shift of 44 cm⁻¹ from 3430 cm⁻¹ (in *b*PEA powder) to 3474 cm⁻¹ (in *b*PEA-based perovskite), and the symmetric stretching vibration reveals a blue shift of 12 cm⁻¹ from 1500 cm⁻¹ to 1512 cm⁻¹. Apparently, the shifts in *b*PEA samples are significantly larger than that in PEA case, indicating that the *b*PEA cations may have stronger interactions with Pb-lattice.



Fig. S3. (a-b) AFM topography and KPFM CPD images (c-d) of perovskite thin films based on different ligands.

The contact potential difference (CPD) map of PEA-based thin film exhibits substantial heterogeneity in surface potentials, which matches up with the spatial energetic disorders as discussed in the main text. While the CPD map of bPEA film exhibits pronounced uniformity, indicating more homogenous distribution of n-phases and halides.



Fig. S4. The TEM images of (a) PEA and (b) bPEA based perovskites.

To investigate phase distribution in perovskite thin films, we conducted TEM measurement on both PEA and *b*PEA-based samples. As shown in Fig. S4a, the PEA-based film is mainly composed of 3D perovskite bulk crystals and low-dimensional perovskite nanocrystals, which suggests a non-uniform phase distribution in PEA case. In sharp contrast, the *b*PEA-based film is dominated by quasi-2D perovskites with similar layer thickness, indicating that the *b*PEA-based film exhibits a more uniform *n*-phase distribution. These observations corroborate with other characterizations, such as PL, FLIM, KPFM, GIWAXS.



Fig. S5. PL spectra of (a, c) PEA and (b, d) *b*PEA perovskite thin films with different annealing temperatures (a, b) and annealing time (c, d).

We tracked the PL emission of PEA and *b*PEA perovskite thin films at different annealing temperatures (ranging from 30 to 110 °C) and different annealing time (0-30 min). For both PEA and *b*PEA films, as the annealing temperature and time increases, the emission wavelength exhibits a red shift. This suggests the occurrence of crystallization and phase evolution into higher-*n* phases in both cases during the thermal annealing process. More importantly, PEA shows relatively larger red-shift compared with *b*PEA case upon annealing at the same temperature or same duration time, which indicates that the crystallization or phase evolution has been partially suppressed by *b*PEA cations. In other word, the introduction of conjugated spacer cations may retard the crystallization of perovskites, thus leading to the formation of quasi-2D perovskites with uniform phase distribution, improved surface morphology, and reduced defect density.



Fig. S6. (a) Current density versus voltage (*J*–*V*) and luminance versus voltage (*L*–*V*) curves of PeLEDs based on PEDOT:PSS with different additives. (b) EQE versus current density characteristic curves. (c) EL spectra. (d) Peak EQE and corresponding peak wavelengths. The maximum EQE of K₂SO₄ doped PEDOT:PSS system reaches 5.91%, with a peak emission wavelength of 483 nm. In comparison, the maximum EQE for PEDOT:PSS with GABA (Gamma-Aminobutyric Acid) is 4.11% with a peak wavelength of 478 nm; while the maximum EQE of the PEDOT:PSS + ABA (α -aminobutyric acid) system is 0.63%, with a peak wavelength of 467 nm. On this basis, K₂SO₄ is selected as the optimal additive for all the device fabrications as presented in the main text.



Fig. S7. (a) Current density versus voltage (J-V) and luminance versus voltage (L-V) curves. (b) EQE versus current density characteristic curves. (c) EL spectra for *b*PEA-based films. (d) Peak EQE and corresponding peak wavelength for *b*PEA-based films with different additive concentrations. To enhance the device performance, different amount of GABA was added to the perovskite precursor solution. The GABA concentration was set as 10 mg/mL for all the device studies presented in the main text.



Fig. S8. (a) Current density versus voltage (J-V) and luminance versus voltage (L-V) curves. (b) EQE versus current density characteristic curves. (c) EL spectra with different *b*PEA to Pb²⁺ ratios. The performance of *b*PEA device is optimized when the *b*PEA to Pb²⁺ ratio in precursor solution is 0.6.



Fig. S9. (a) Current density versus voltage (J-V) and luminance versus voltage (L-V) curves. (b) EQE versus current density characteristic curves. (c) EL spectra with different NaBr to Pb²⁺ ratios. The performance of *b*PEA device is optimized when the NaBr to Pb²⁺ ratio in precursor solution is 0.4.



Fig. S10. (a) Current density versus voltage (J-V) and luminance versus voltage (L-V) curves. (b) EQE versus current density characteristic curves. (c) EL spectra with different solvent ratios. (d) Peak EQE and corresponding peak wavelength with different solvent ratios. The champion device made from *b*PEA shows EQE of 14.65% with emission at 493 nm when the DMSO to DMF ratio in the precursor solution is 5:1.



Fig. S11. (a) Current density versus voltage (J-V) and luminance versus voltage (L-V) curves. (b) EQE versus current density characteristic curves at different driving voltages. (c) EL spectra. (d) Peak EQE and corresponding peak wavelength with different precursor concentrations. The performance of *b*PEA device is optimized when the precursor solution concentration is 0.10 M.



Fig. S12. (a) Current density versus voltage (J-V) and luminance versus voltage (L-V) curves. (b) EQE versus current density characteristic curves. To determine the ETL used in the device, we employed three different ETLs in the LED devices. For the *b*PEA device, the performance is optimal when TPBi is used as the ETL.



Fig. S13. Current-voltage curves for hole-only LED devices based on PEA (a) and *b*PEA (b) films, and electron-only LED devices based on PEA (c) and *b*PEA (d) films. The trap-filled limit voltage (V_{TFL}) values for both electrons and holes in *b*PEA-based single-carrier devices are lower than that in the PEA case, indicating lower defect densities in the *b*PEA device.

3. Supplementary tables and related discussions

	(bPEA) ₂ PbBr ₄			
CCDC number	2424419			
Chemical formula	$Br_8Pb_2 \cdot 4(C_{14}H_{16}N)$			
Mr	1846.77			
Crystal system, space group	Triclinic, $P\overline{1}$			
Temperature (K)	240			
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.6289 (6), 11.6771 (5), 22.3900 (14)			
$\alpha, \beta, \gamma(^{\circ})$	97.483 (2), 90.784 (2), 90.022 (2)			
$V(Å^3)$	3014.2 (3)			
Ζ	2			
F(000)	1744			
$D_{\rm x} ({\rm mg}{\rm m}^{-3})$	2.035			
Radiation type	Μο Κα			
No. of reflections for cell measurement	9844			
θ range (°) for cell measurement	2.8-28.3			
$\mu (\text{mm}^{-1})$	10.92			
Crystal shape	Plate			
Color	Colourlesss			
Crystal size (mm)	$0.25 \times 0.21 \times 0.04$			
	Bruker AXS D8 Quest			
Diffractometer	diffractometer with PhotonII charge-integrating pixel array			
	detector (CPAD)			
Radiation source	fine focus sealed tube X-ray source			
Monochromator	Triumph curved graphite crystal monochromator			
Scan method	ω and phi scans			
	Multi-scan			
Absorption correction	SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick			
	G.M. & Stalke D. (2015). J. Appl. Cryst. 48, 3-10.			
T_{\min}, T_{\max}	0.055, 0.096			
No. of measured, independent and	53839, 53839, 28364			
observed $[I > 2\sigma(I)]$ reflections				
R _{int}	0.075			
θ values (°)	$\theta_{\text{max}} = 28.3^{\circ}, \ \theta_{\text{min}} = 2.1^{\circ}$			
$(\sin \theta / \lambda)_{\max} (A^{-1})$	0.667			
Range of h, k, l	h = -15-15; k = -14-15; l = -29-29			
Refinement on	F^2			
$R [F^2 > 2\sigma(F^2)], wR(F^2), S$	0.088, 0.335, 1.05			
No. of reflections	53839			
No. of parameters	863			
No. of restraints	2448			
H-atom treatment	H-atom parameters constrained			
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 31.6029P]$			
	where $P = (F_0^2 + 2F_c^2)/3$			
$(\Delta/\sigma)_{\rm max}$	< 0.001			
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	3.46, -3.69			

Table S1. Single crystal X-ray diffraction data of (bPEA)₂PbBr₄

Crystals undergo an apparent phase transformation upon cooling resulting in formation of multiple domains, and deteriorating peak shapes. Attempts were made to process the data below the apparent transformation, but asymmetric peak shape and excessive overlap prevented meaningful analysis of the data. Crystal data were instead collected at -33 degree C, prior to onset of peak shape deterioration.

The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, with the two components being related by a 180 degree rotation around the reciprocal *c*-axis.

Integration proofed problematic due to excessive multiple overlap of reflections, resulting in large numbers of rejected reflections. Attempts were made to adjust integration parameters to avoid excessive rejections (through adjustments to integration queue size, integration box slicing and twin overlap parameters, and omission of box size optimization), which led to less but still substantial numbers of rejected reflections.

With no complete data set obtainable through simultaneous integration of both twin domains, the data were instead handled as if not twinned, with only the major domain integrated, and converted into an hklf 5 type format hkl file after integration using the "Make HKLF5 File" routine as implemented in WinGX. The twin law matrix used was

-1.0000.0000.0000.000-1.0000.0000.0530.4991.000

The Overlap R1 and R2 values used were 0.15, i.e. reflections with a discriminator function less or equal to overlap radius of 0.15 were counted overlapped, all others as single. The discriminator function used was the "delta function on index non-integrality". No reflections were omitted.

The structure was solved using direct methods with the original data before twin correction and was refined using the hklf 5 type file, resulting in a BASF value of 0.331(6).

A refinement using the incomplete data obtained through SAINT and TWINABS gave similar refinement statistics, but with higher overall R values (around 8-9% for R1) and with less well-defined ADPs (two atoms NPD or close to NPD).

No Rint value is obtainable for the hklf 5 type file using the WinGX routine. The value prior to application of twinning is given instead.

The structure is pseudo-C-centered, emulating a smaller triclinic cell with parameters a = 8.236, b = 8.241, c = 22.369, $\alpha = 85.24$, $\beta = 84.18$, $\gamma = 89.74$. C-centered symmetry (in C2/m) is obeyed by the lead and bromide atoms, but broken by the ligands.

The structure also displays pseudo-translation along the b-axis. Exact translation is obeyed by the carbon atoms of the cations, by the lead atoms and the terminal bromide atoms, but is broken by the bridging bromide atoms and the ammonium ions. Ammonium ions are modulated and do not obey exact translation along b. Under omission of twinning apparent electron density is found in the positions created by translation by 0.5 along *b* for the bridging bromides. This apparent electron density vanishes once correction for twinning is included.

Systematic 1:1 disorder is observed for the cations, with two sets of each four cations (with suffixes A-D and E-H, respectively). The two sets are clearly distinct, with different angles with respect to the Pb-Br layer and thus different thicknesses of the anion-cation layer. Cations E-H are reaching out further and are incompatible with their counterparts in a neighboring layer (overlap of phenyl C atoms). For cations A-D no overlap would be observed, but a small gap between layers would result, thus indicating that cations of one type are matched with cations of the other type in the neighboring layer, thus enforcing an exact 1:1 ratio.

The data were investigated for presence of a possible superstructure, with unit cell doubling and ordering of cations, but no supercell reflections were found, indicating that information about cations is not transferred past the Pb-Br layers.

Equivalent bond distances and angles but not torsion angles were restrained to be similar for all cations. Pairs of carbon atoms related by pseudo-translation along b were constrained to have identical ADPs. Ammonium N atoms with similar orientation were constrained to have identical ADPs. Uij components of ADPs for disordered atoms closer to each other than 2.0 Angstrom were restrained to be similar.

Film	Wavelength (nm)	7 1 (ns)	7 ₂ (ns)	7 3 (ns)	$ au_{\mathrm{av}}\left(\mathrm{ns} ight)$
А	467	0.10497	0.10484	0.10491	0.11
В	473	0.21039	1.04883	5.10666	3.15
С	477	0.61426	2.27127	10.15003	5.99
D	483	0.65325	2.42984	10.5107	6.36
Е	487	2.90126	0.88101	11.59974	7.32
F	493	0.32328	1.44209	7.37836	5.34

 Table S2. Fitted time constants of TRPL data from all perovskite films.

4. Summary of ¹H, ¹³C NMR and MS spectra



Fig. S14. ¹H NMR spectrum of *b*PEA in DMSO-*d*₆



Fig. S15. ¹³C NMR spectrum of *b***PEA** in DMSO- d_6



Fig. S16. ¹HR-MS spectrum of **bPEA**