Electronic Supplementary Information

Cu Substitution Boosts Self-Trapped Exciton Emission in Zinc-Based Metal Halides for Sky-Blue Light-Emitting Diodes

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Chemicals

Zinc bromide ($ZnBr_2$; Macklin, 99%), zinc chloride ($ZnCl_2$; Aladdin, 99%), cuprous bromide (CuBr; Aladdin, 99%), Cuprous chloride (CuCl; Aladdin, 99%), hydrochloric acid (HCl), hydrobromic acid (HBr; ChengDu Chron Chemicals Co,.Ltd, AR), hypophoaphoeous acid (H_3PO_2; Macklin, AR, 50 wt% in water) β-phenylethylamine (PEA; Macklin, GC, 98%) and ethanol (EtOH; Guangdong Guanghua Sci-Tech Co,.Ltd, AR) were used without any purification.

Single-crystal growth of $(PEA)_2ZnX_4$ and Cu:$(PEA)_2ZnX_4$ (X = Cl or Br)

$(PEA)_2ZnX_4$ single crystals were prepared by mixing 2 mmol PEA with 1 mmol ZnX_2 in 6 mL HX and 50 μL H_3PO_2 aqueous solution and stirring the solution at 373 K for 1 h. The stirrer was removed and the solution was cooled and crystallized at room temperature to obtain white transparent fine needle-like crystals, which were washed using ether and dried in vacuum at 343 K for 6 h. For Cu: $(PEA)_2ZnX_4$ single crystals, different proportions of CuX were added using the same method.

Fabrication of the Cu:$(PEA)_2ZnX_4$ thin films

Cu:$(PEA)_2ZnX_4$ single crystals were dissolved in 1 mL ethanol solution to obtain 0.2 mmol/mL of Cu:$(PEA)_2ZnX_4$ solution and stirred at room temperature for 12 h. Subsequently, the solution was transferred into a nitrogen-filled glove box and spin-coated onto ITO at 4000 r.p.m. to obtain Cu:$(PEA)_2ZnX_4$ films.

Device fabrication

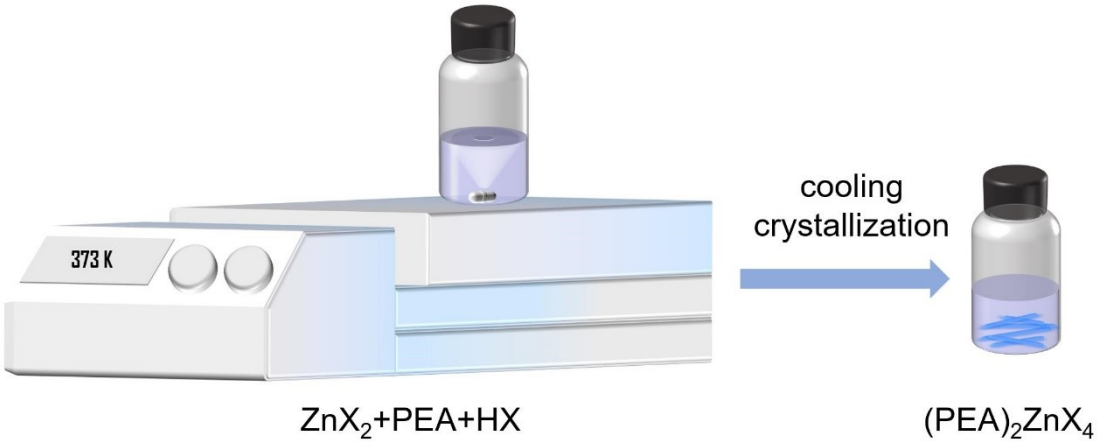
The ITO coated glass substrates were ultrasonically cleaned in detergent, distilled water and ethanol in sequence. The cleaned substrates were treated in oxygen plasma for 10 min. The PEDOT: PSS solution was spin-coated on the ITO substrate at 5200 r.p.m. for 30 s and annealed at 423 K for 15 min. After cooling, the substrates were transferred into a nitrogen-filled glove box and the luminescent layer was prepared by spin-coating the $(PEA)_2ZnX_4$ precursor solution on the PEDOT: PSS layer. Finally, STEs-LEDs were prepared by thermal evaporation of TPBi (40 nm), LiF (1 nm) and Al (100 nm) electrodes.

Calculation

DFT calculations were performed using the Vienna ab initio Simulation Package (VASP) code[1] with the projection-augmented wave method. Structural relaxations and total-energy calculations for all the structures were performed using the generalized gradient approximation (GGA) Perdew–Burke–Ernzerhof (PBE)[2] as the exchange-correlation functional. The cutoff energy of the plane wave is 350 eV and the convergence accuracy is 1 x 10^{-2} eV. The atomic stress convergence criterion for ion relaxation was less than 0.05 eV/Å per atom. Finally, data processing and graphical plotting were performed using VESTA and Origin software.

Characterization

The Single-crystal X-ray diffraction (SCXRD) data were collected by Oxford Gemini S ultra-system with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K. Powder X-ray diffraction (PXRD) data were obtained by Bruker diffractometer. The ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometer (PerkinElmer Instruments, Lambda 750) was used to measure the absorption spectra. The elemental composition and chemical state were identified by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi). The PL and PLE spectra, PLQY, temperature-dependent PL spectra, and PL decay were measured with a Horiba Jobin Yvon fluorolo3 spectrometer and an Edinburgh FLS 1000 fluorescence spectrometer.



Scheme S1. Schematic diagram of the synthesis of $(PEA)_2ZnX_4$ single crystals using the cooling crystallization technique (X = Cl, Br).

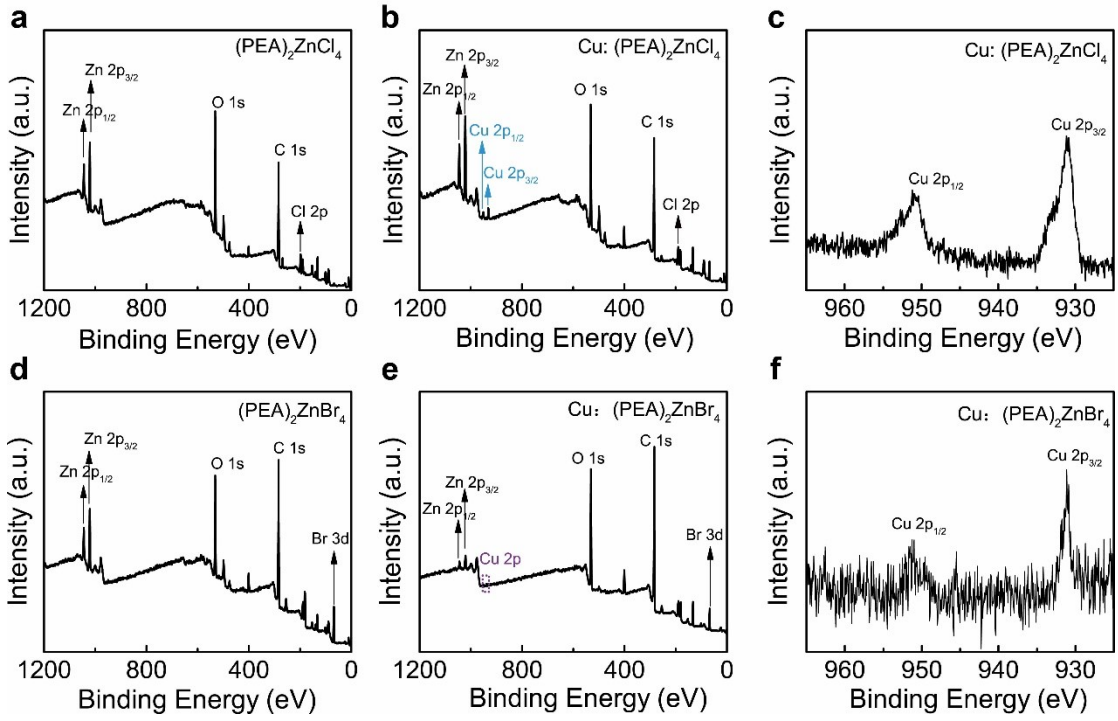


Fig. S1 XPS spectrum of (a) $(PEA)_2ZnCl_4$ (b) Cu:$(PEA)_2ZnCl_4$ (d) $(PEA)_2ZnBr_4$ and (e) Cu:$(PEA)_2ZnBr_4$. High-resolution spectra of (c) Cu:$(PEA)_2ZnCl_4$ and (f) Cu:$(PEA)_2ZnBr_4$ about Cu 2p.

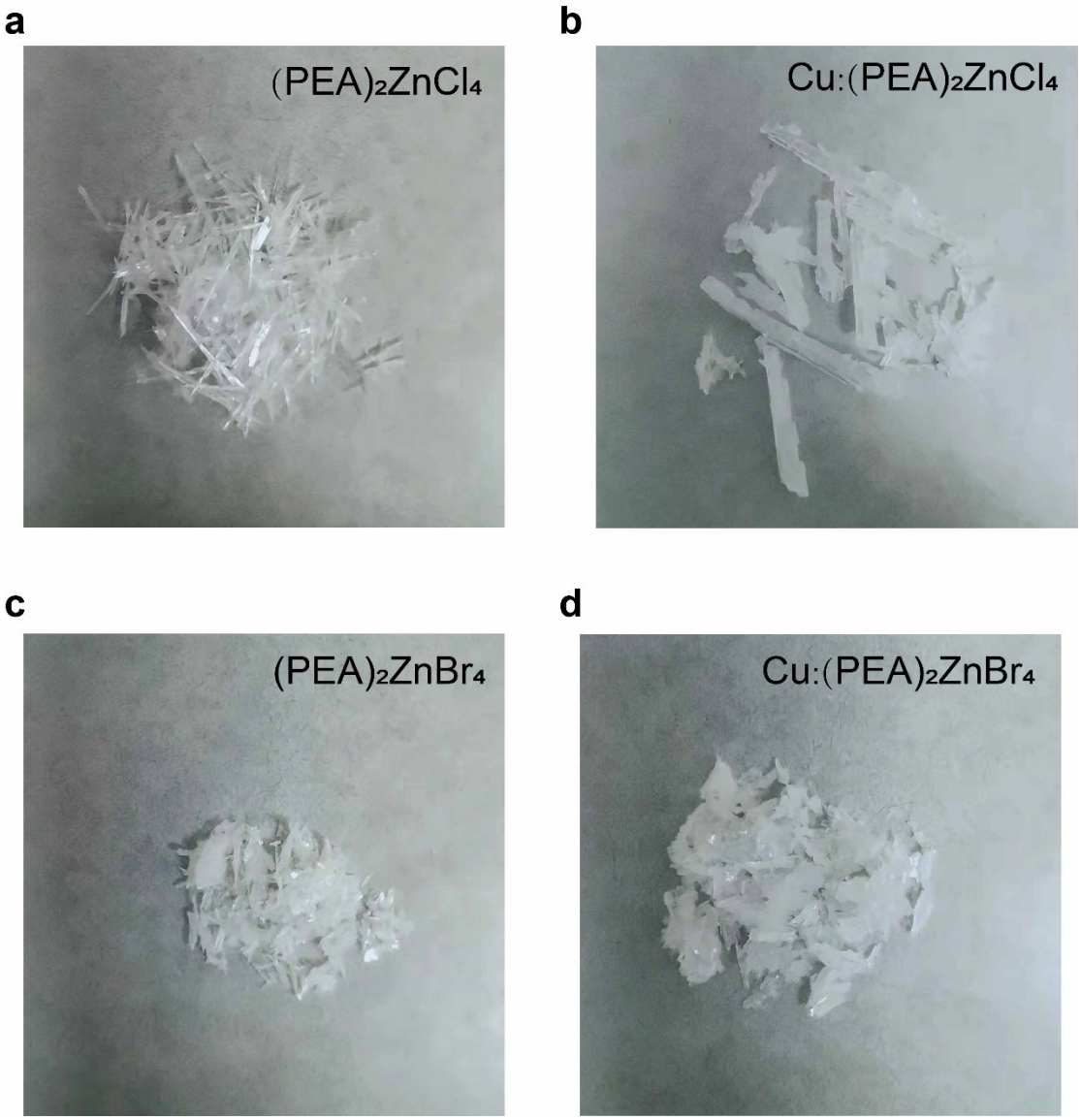


Fig. S2 The photographs of undoped and Cu-doped $(PEA)_2ZnX_4$ single crystals under ambient light.

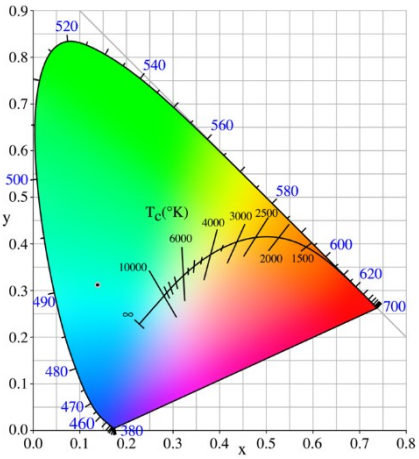


Fig. S3 CIE chromaticity coordinates (0.13, 0.31) of Cu:$(PEA)_2ZnCl_4$ single crystals.

Fig. S4 CIE chromaticity coordinates (0.12, 0.29) of Cu:$(PEA)_2ZnBr_4$ single crystals.

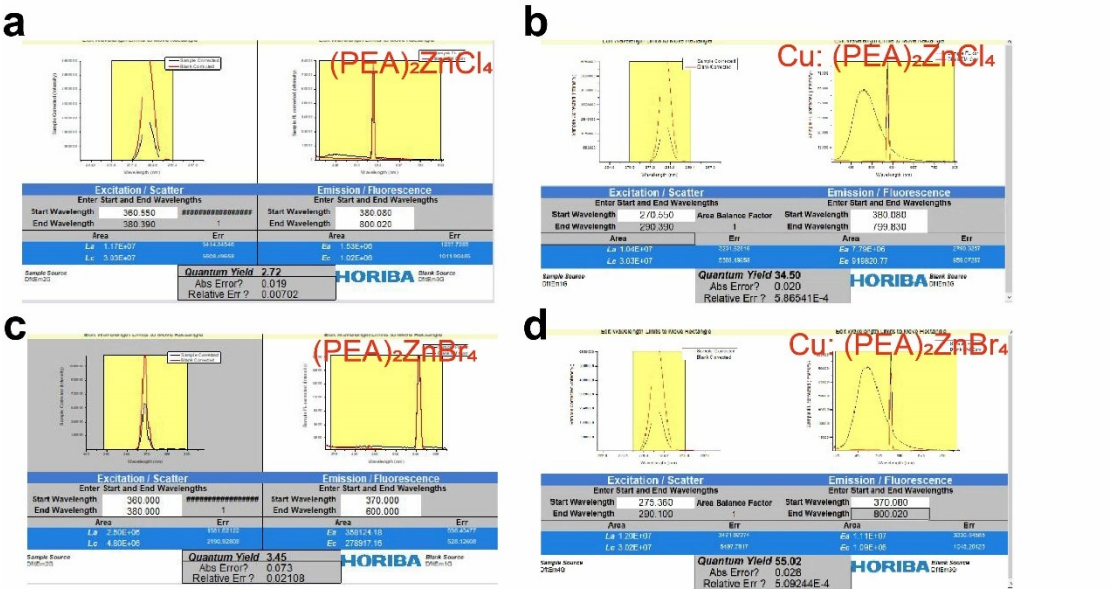


Fig. S5 PLQYs of (a) $(PEA)_2ZnCl_4$ (b) Cu:$(PEA)_2ZnCl_4$ (c) $(PEA)_2ZnBr_4$ (d) Cu:$(PEA)_2ZnBr_4$ single crystals.

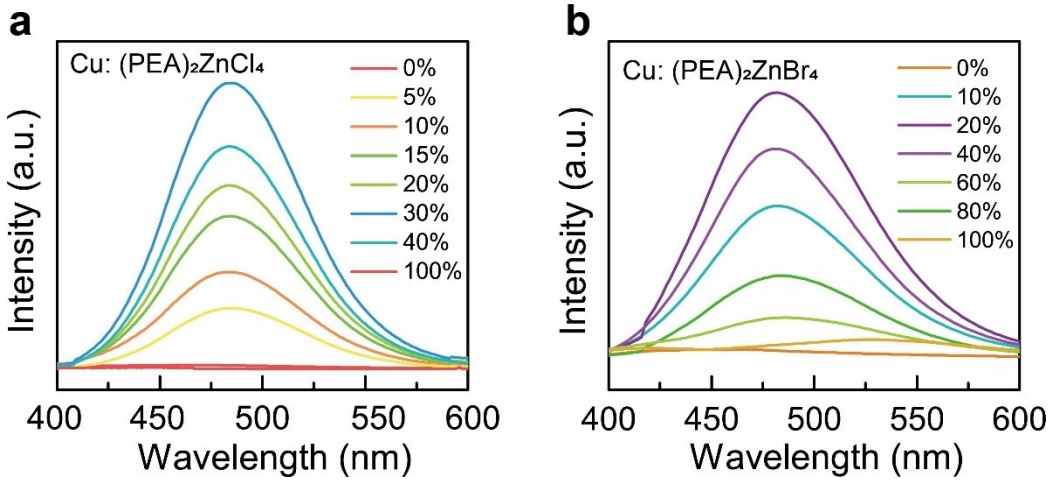


Fig. S6 PL spectra of (a) Cu:$(PEA)_2ZnCl_4$ and (b) Cu:$(PEA)_2ZnBr_4$ (x%= 0~100%, λ_{ex} = 282

nm).

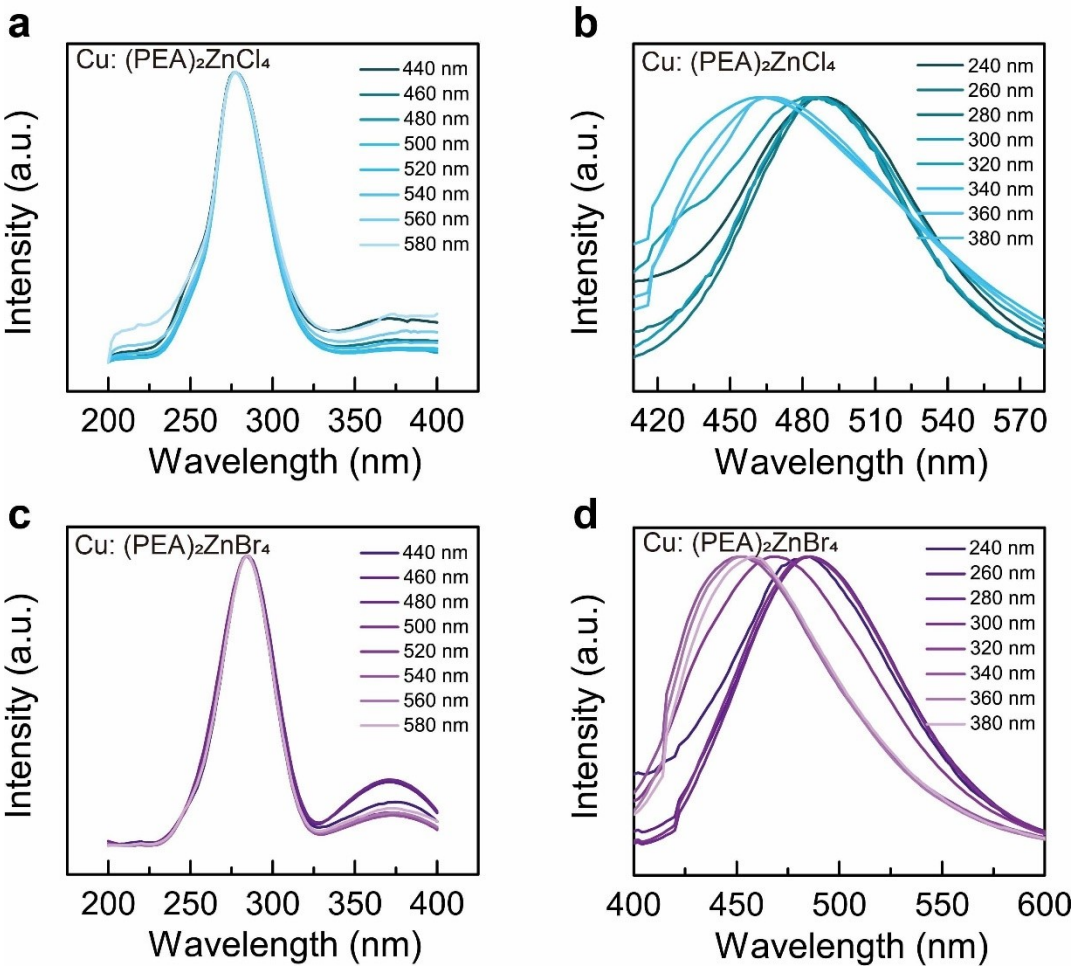


Fig. S7 PLE spectra of (a) Cu:$(PEA)_2ZnCl_4$ and (c) Cu:$(PEA)_2ZnBr_4$ at different emission wavelength (from 440 to 580 nm). PL spectra of (b) Cu:$(PEA)_2ZnCl_4$ and (d) Cu:$(PEA)_2ZnBr_4$ under different excitation wavelength (from 240 to 380 nm).

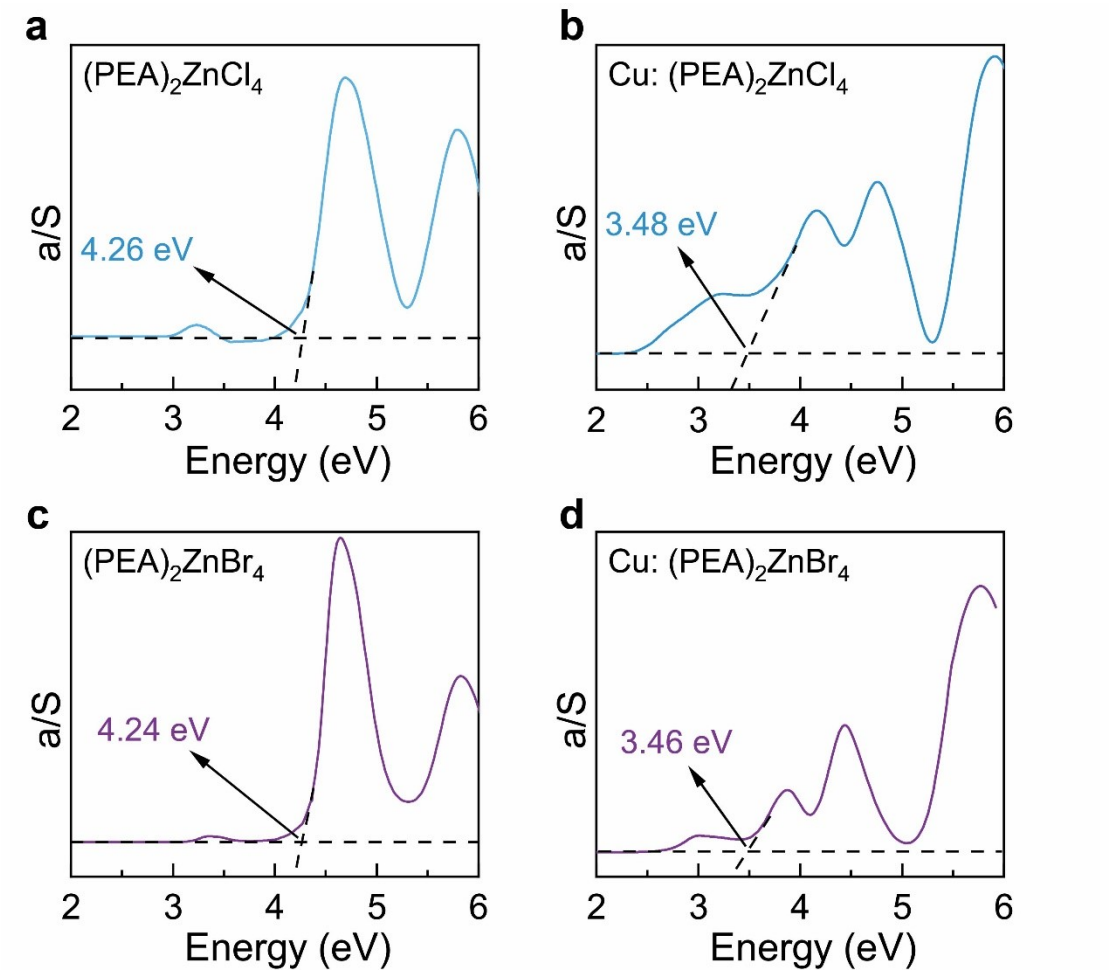


Fig. S8 Band gaps of (a) $(PEA)_2ZnCl_4$, (b) Cu:$(PEA)_2ZnCl_4$, (c) $(PEA)_2ZnBr_4$ and (d) Cu: $(PEA)_2ZnBr_4$.

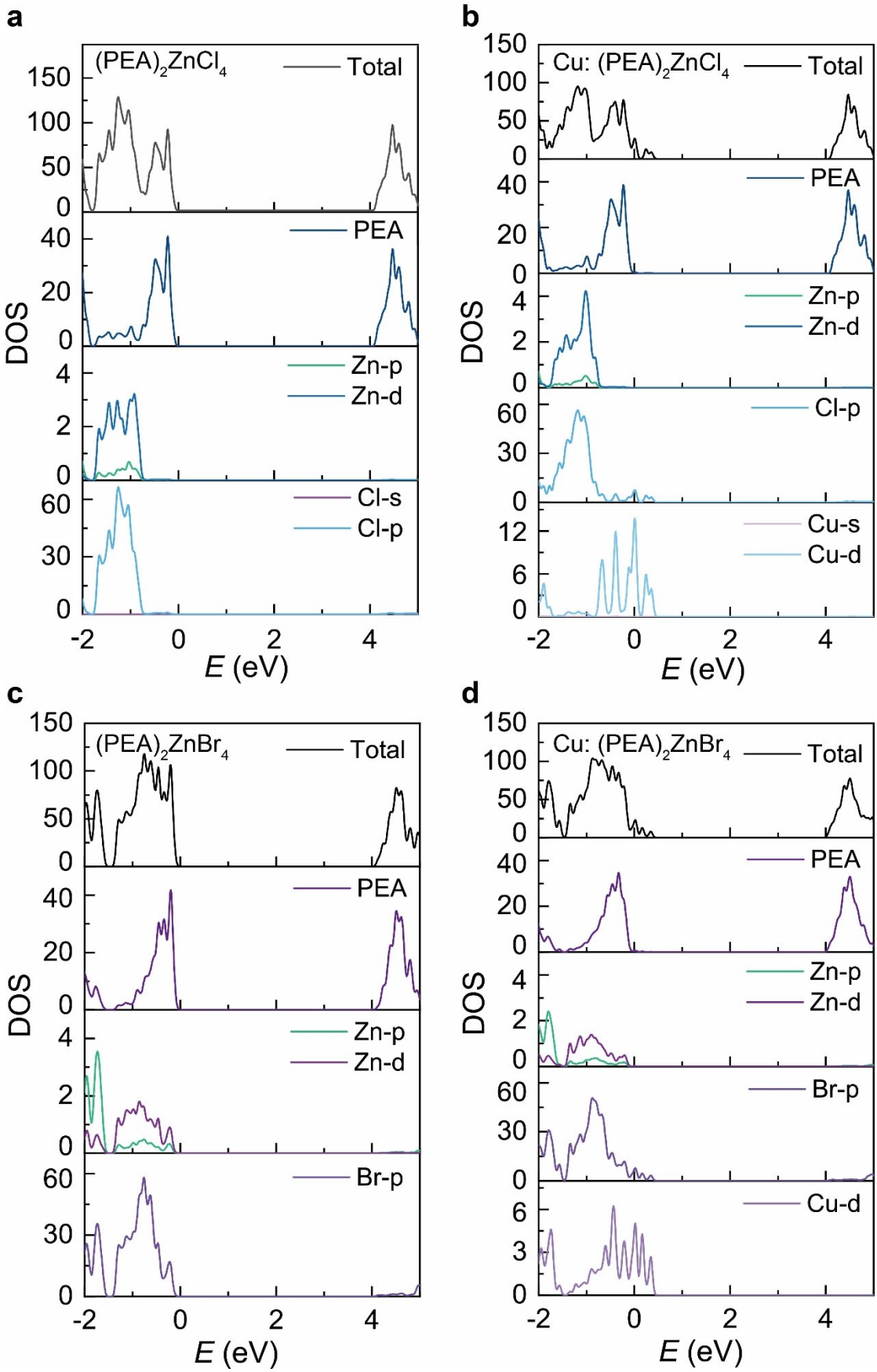


Fig. S9 Density of states of (a) $(PEA)_2ZnCl_4$, (b) Cu:$(PEA)_2ZnCl_4$, (c) $(PEA)_2ZnBr_4$ and (d) Cu:$(PEA)_2ZnBr_4$.

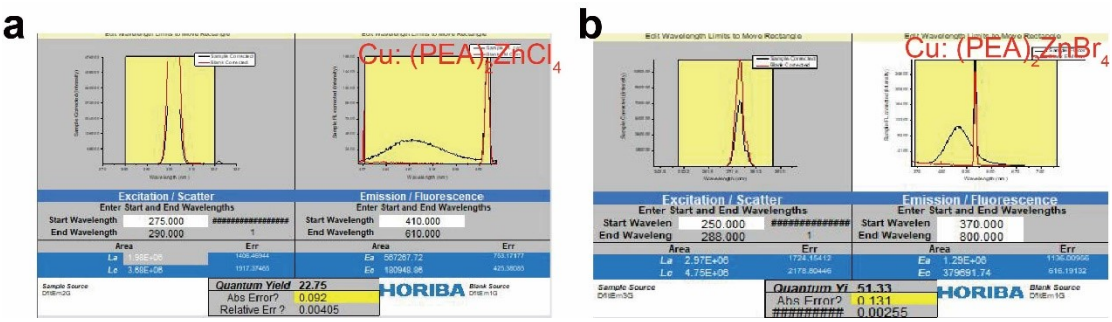


Fig. S10 The PLQYs of (a) Cu:$(PEA)_2ZnCl_4$ (b) Cu:$(PEA)_2ZnBr_4$ thin films.

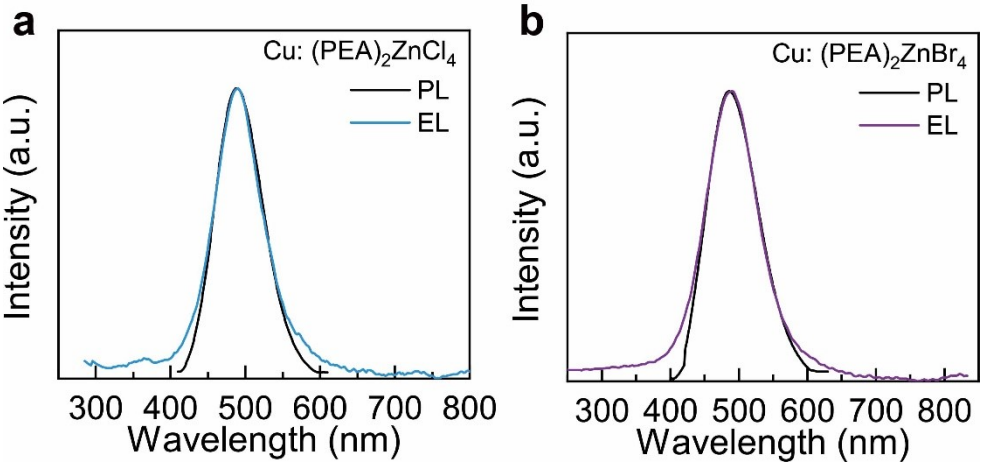


Fig. S11 PL and EL spectra of (a) Cu:$(PEA)_2ZnCl_4$ and (b) Cu:$(PEA)_2ZnBr_4$.

Table S1. Single crystal X-ray data of PEA_2ZnCl_4 and PEA_2ZnBr_4.

Empirical formula	$(C_8H_{12}N)_2ZnCl_4$	$(C_8H_{12}N)_2ZnBr_4$
Formula weight	451.56	629.36
Temperature/K	150	150
Crystal system	monoclinic	monoclinic
Space group	$P2_1/C$	$P2_1/C$
a/Å	7.2646(3)	7.6261(2)
b/Å	24.6566(10)	25.3504(10)
c/Å	11.0924(5)	10.9914(4)
α/°	90	90
β/°	90.623(1)	91.627(1)
γ/°	90	90
Volume/Å^3	1986.76(15)	2124.05(13)
Z	4	4
ρ_{calc}g/cm^3	1.510	1.968
μ/mm^{-1}	1.774	8.681
F(000)	928.0	1216.0
R (reflections)	0.0301 (3621)	0.0299 (3524)
*w*R2 (reflections)	0.0715 (4054)	0.0719 (4325)

Table S2. Photophysical properties of $(PEA)_2ZnX_4$ and Cu:$(PEA)_2ZnX_4$ at room temperature.

Compound	λ (ex, max) nm	λ (em, max) nm	PLQY	stokes shift	FWHM nm
$(PEA)_2ZnCl_4$	372	468	2.7%	96	78
Cu:$(PEA)_2ZnCl_4$	282	488	34.5%	206	75
$(PEA)_2ZnBr_4$	372	454	3.4%	82	82
Cu:$(PEA)_2ZnBr_4$	282	486	55%	204	89

Table S3. The PL lifetimes of $(PEA)_2ZnX_4$ and Cu:$(PEA)_2ZnX_4$ at room temperature.

Compound	A_1	τ_1 (μs)	A_2 (μs)	τ_2	τ_{ave} (μs)
$(PEA)_2ZnCl_4$	0.806	1.07	0.132	7.75	4.58
Cu:$(PEA)_2ZnCl_4$	1.019	24.03			
$(PEA)_2ZnBr_4$	0.870	1.04	0.142	7.83	4.77
Cu:$(PEA)_2ZnBr_4$	0.974	42.67			

Reference

1 G. Kresse, J. Furthmuller, Phys Rev B Condens Matter 1996, 54, 11169.

2 J. P. Perdew, K. Burke, M. Ernzerhof, Phys Rev Lett 1996, 77, 3865.