Supporting Information

Three-Dimensional Cuprous Lead Bromide Framework with Highly Efficient and Stable Thermochromic Luminescence Property

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Materials and methods

All chemicals were purchased from commercial sources and used as received without further purification. The powder X-ray diffraction experiments were performed on a Bruker D8 Advance X-ray powder diffraction meter operating at 40 kV and 40 mA (CuKα radiation, λ = 1.5418 Å). The 2-theta angular range is from 5 to 80°. The solid state UV-Vis absorption optical spectra for powder sample were collected at PE Lambda 900 UV/Vis spectrophotometer at room temperature in wavelength range of 200−800 nm. The thermogravimetric analysis (TGA) was carried out on a Mettler TGA/SDTA 851 thermal analyzer from room temperature to 800°C under the flow of nitrogen atmosphere. For the photophysical stability test, the samples were directly exposed under the strong UV light irradiation from a 300 W Xe lamp with distance of 10 cm between the Xe lamp and the sample. For the structural stability test, the samples were exposed in moisture air in a sealed glass container with relative humidity of about 75% for three years.

Synthesis of [H$_2$DABCO]$_2$PbCu$_6$Br$_{12}$. Solid powders of PbBr$_2$ (0.1 mmol), CuBr (0.4 mmol), KBr (2 mmol), DABCO (0.1 mmol) were dissolved in mixed solution of tert-butyl alcohol (3 mL) and hydrobromic acid (5 mL, 47%), and the mixture was stirred for one hour and then sealed in 25 mL Teflon-lined stainless steel reactor. The reactor was firstly heated at 140 °C for 5 days and then slowly cooled to room temperature with cooling rate of 5 °C·min^{-1}. After the filtration, block-shaped crystals were obtained and subsequently determined as [H$_2$DABCO]$_2$PbCu$_6$Br$_{12}$. After crystal structural determination, crystals of compound [H$_2$DABCO]$_2$PbCu$_6$Br$_{12}$ were collected in 21% yield based on PbBr$_2$, and then washed, dried and preserved in vacuum. Elemental analysis calculated for C$_{12}$N$_4$H$_{28}$Cu$_6$PbBr$_{12}$: C, 8.12; N, 3.16; H, 1.59 %; found: C, 8.29; N, 3.25; H, 1.12 %.

X-ray Crystallography. The single crystal data of title compound was collected on the Bruker

Apex II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) at room temperature. The crystal structures were solved by direct method and refined based on F^2 using SHELXTL-97 program.[1] All the non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms of organic molecules were positioned geometrically and refined isotropically. Structural refinement parameters of [H$_2$DABCO]$_2$PbCu$_6$Br$_{12}$ are summarized in Table S1 and important bond lengths are listed in Table S2-S3.

Photoluminescent property characterizations. The PL spectra were performed on an Edinbergh FLS980 fluorescence spectrometer. The photoluminescence quantum efficiency (PLQE) was achieved by incorporating an integrating sphere into the FLS980 spectrofluorometer. The PLQE was calculated based on the equation: η_{QE} = $I_S/(E_R$ - $E_S)$, which I_S represents the luminescence emission spectrum of the sample, E_R is the spectrum of the excitation light from the empty integrated sphere (without the sample), and E_S is the excitation spectrum for exciting the sample. The time-resolved decay data were carried out using the Edinburgh FLS980 fluorescence spectrometer with a picosecond pulsed diode laser. The average lifetime was obtained by exponential fitting. The power-dependent photoluminescence spectra were measured using the 375 nm (LE-LS-375-140TFCA, 1-140 mW). The CIE chromaticity coordinates and CRI were calculated using the CIE calculator software based on the emission spectra.

Calculation Details.   Single-crystal structural data of the title compounds were directly used for the theoretical calculations. The density of states for title compounds are calculated by with the total-energy code CASTEP.[2] The total energy was calculated with density functional theory (DFT) using Perdew−Burke−Ernzerhof (PBE) generalized gradient approximation.[3] The interactions between the ionic cores and the electrons were described by the norm-conserving pseudopotential.

Hence, the C-$2s^22p^2$, N-$2s^22p^3$, H-$1s^1$, Cu-$3d^{10}4s^1$, Pb-$6s^26p^2$ and Br-$4s^24p^5$ were adopted as valence electrons. The number of plane waves included in the basis sets was determined by a cutoff energy of 320 eV, and the numerical integration of the Brillouin zone is performed using Monkhorst-Pack k-point sampling of 3×2×3. Other calculating parameters and convergence criteria were set by the default values of the CASTEP code.
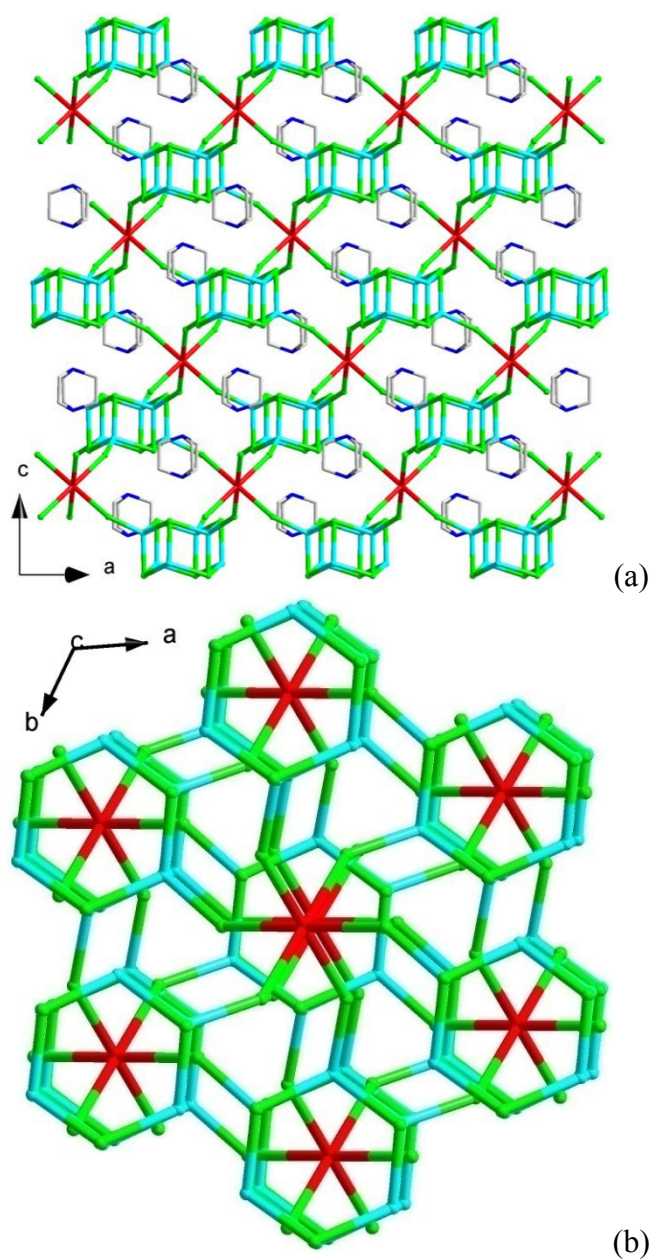

(a)

(b)

Fig. S1. The 3D framework of [H$_2$DABCO]$_2$PbCu$_6$Br$_{12}$ viewed along the b-axis (a) and c-axis (b).

(a)

(b)

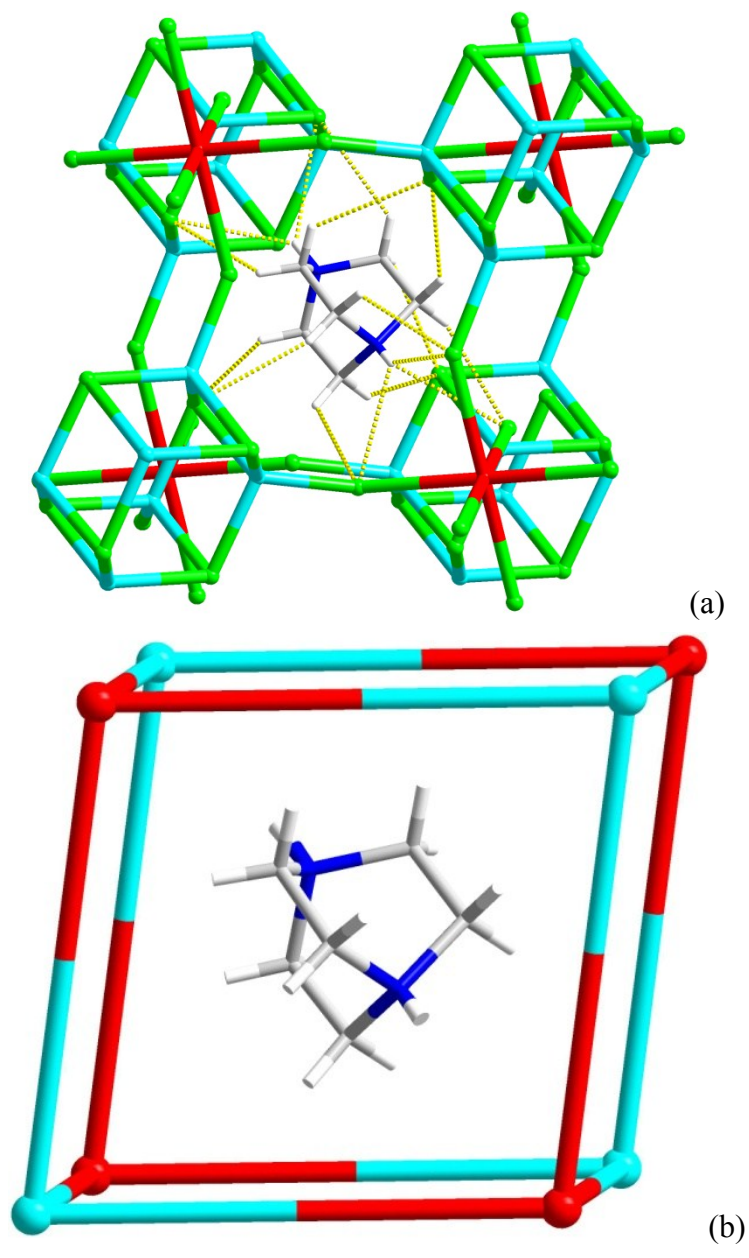**Fig. S2**. The nanocage composed of four [Cu_6Br_6] SBUs and four [$PbBr_6$] octahedrons (a), and the simplified diagram in which the light blue and red spheres represent [Cu_6Br_6] SBU and [$PbBr_6$] octahedron, respectively (b).

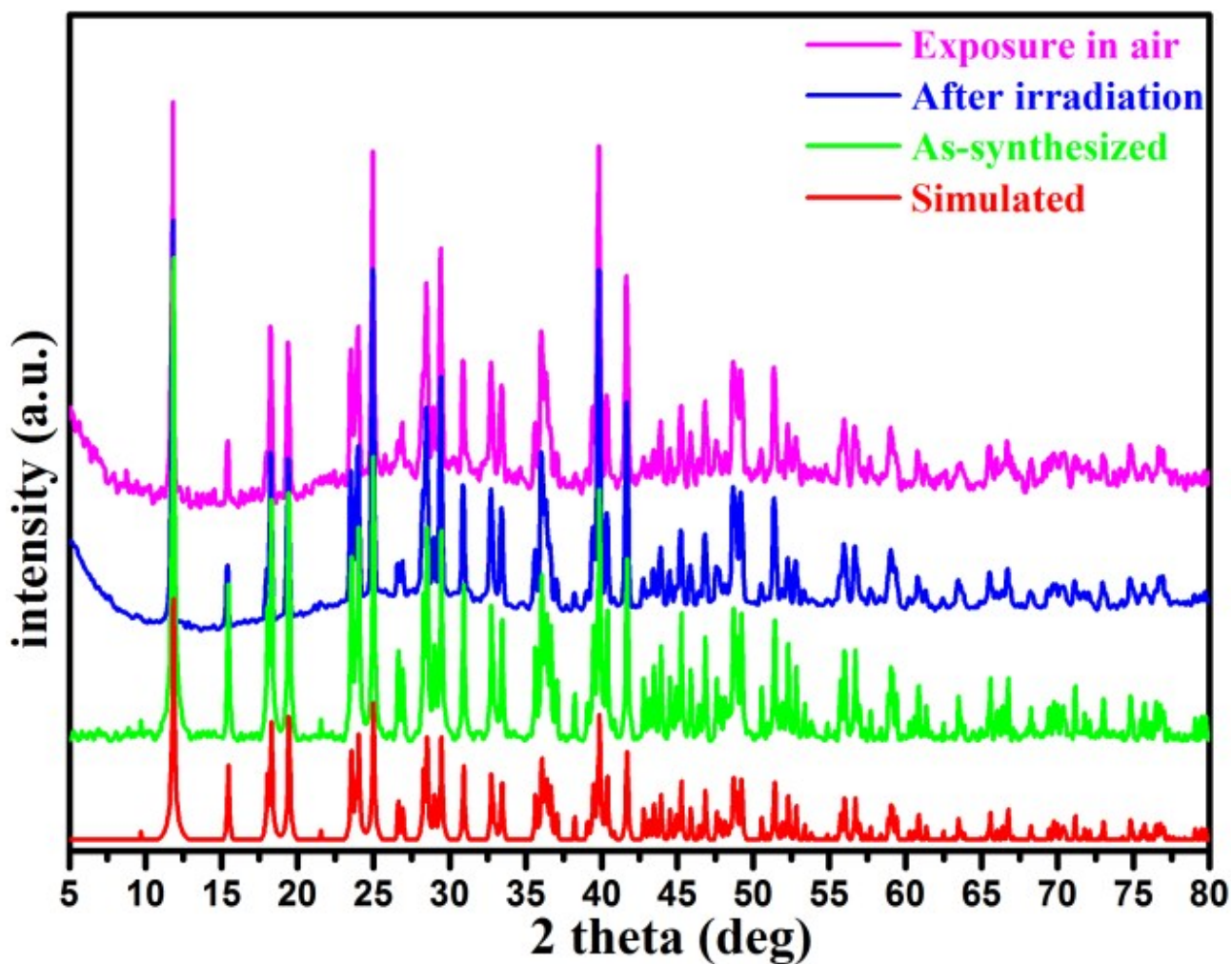**Fig. S3.** The simulated and as-synthesized XRD patterns of $[H_2DABCO]_2PbCu_6Br_{12}$ as well as the crystals after irradiation for 48 hours or exposure in air for three years.

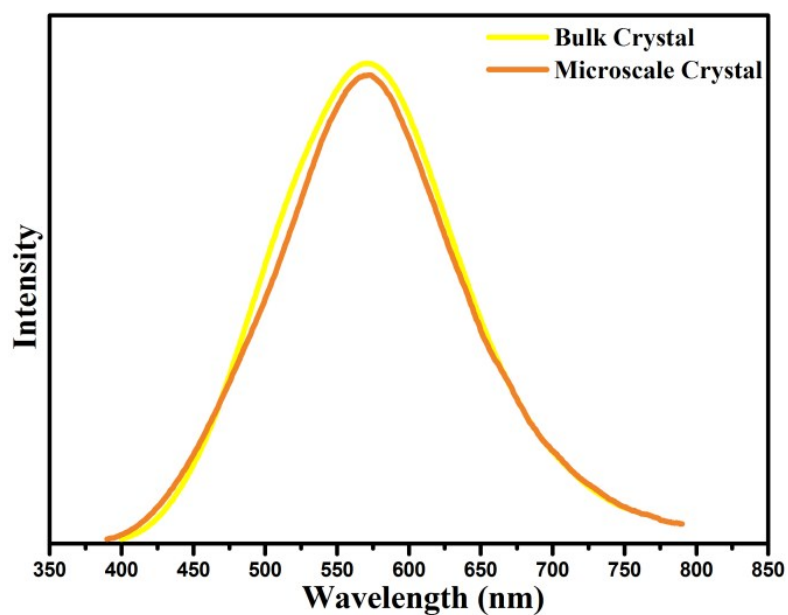**Fig. S4**. Photoluminescence spectra of bulk crystals and grinded microscale crystals for

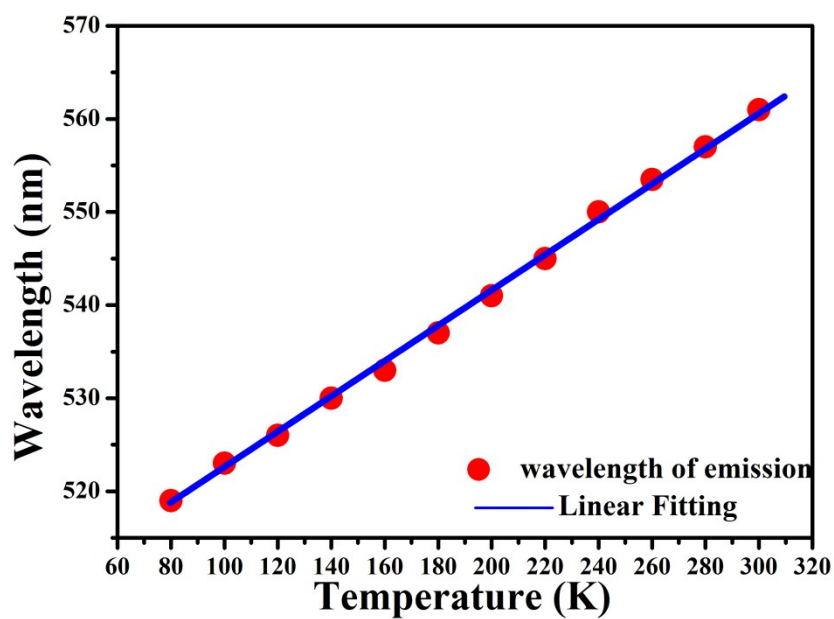$[H_2DABCO]_2PbCu_6Br_{12}$ measured at room temperature.

Fig. S5. The experimental and fitted relationship of maximum emission peak and temperature for

$[H_2DABCO]_2PbCu_6Br_{12}$.

$\Gamma_0 = 374.2 \pm 18$ meV

$\Gamma_{phonon} = 77$ meV
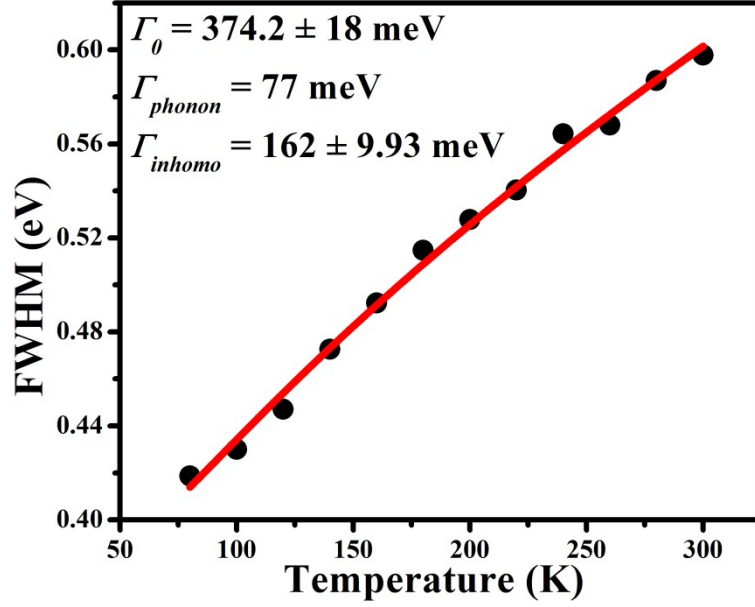
$\Gamma_{inhomo} = 162 \pm 9.93$ meV

Fig. S6. The experimental and theoretical fitting of temperature-dependent FWHM. The temperature-dependent FWHM can be used to estimate the electron-phonon coupling according to the follow equation:

$$\Gamma(T) = \Gamma_0 + \Gamma_{phonon}(e^{E_{LO}/k_B T} - 1)^{-1} + \Gamma_{inhomo}e^{-E_b/k_B T}$$

where Γ_0 is the FWHM of 0 K, Γ_{LO} represents the energy of the longitudinal-optical phonon, and E_b is the average binding energy of the trap states. Γ_{phonon} and Γ_{inhomo} represent the relative contributions of electron-phonon coupling and trapped states that induced inhomogeneous broadening.

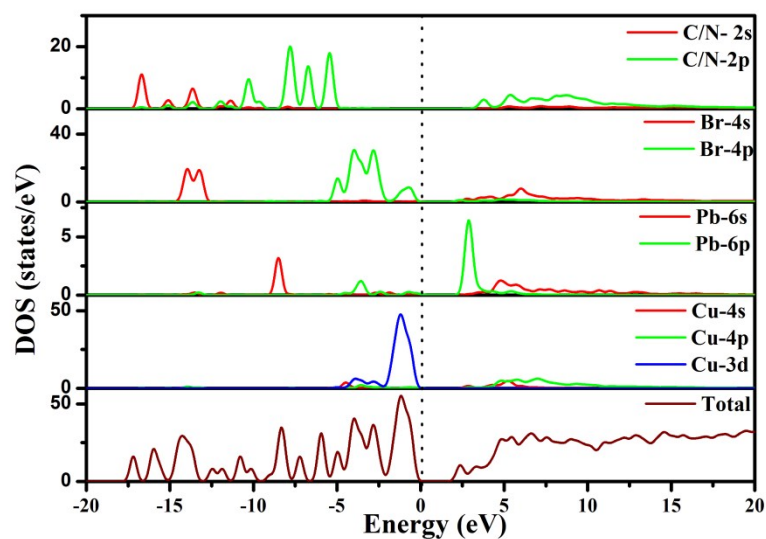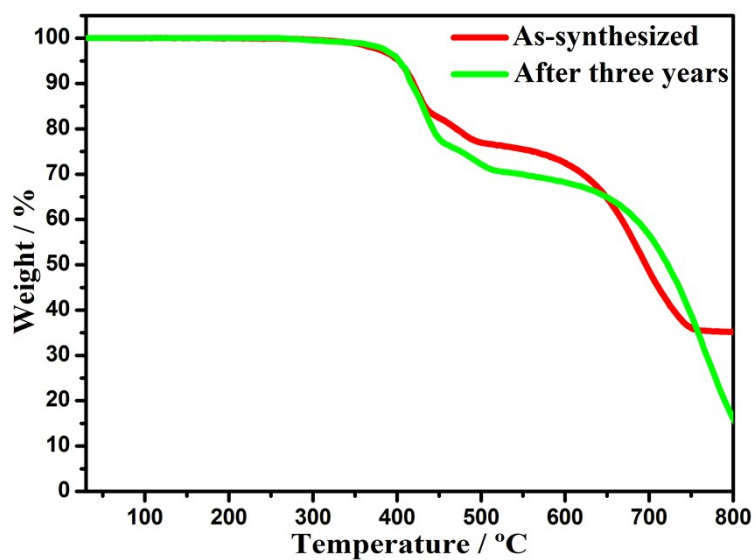**Fig. S7**. The calculated total and partial density of states of $[H_2DABCO]Cu_6PbBr_{12}$.

Fig. S8. The thermogravimetric analysis curves of as-synthesized sample (red) and exposure treated

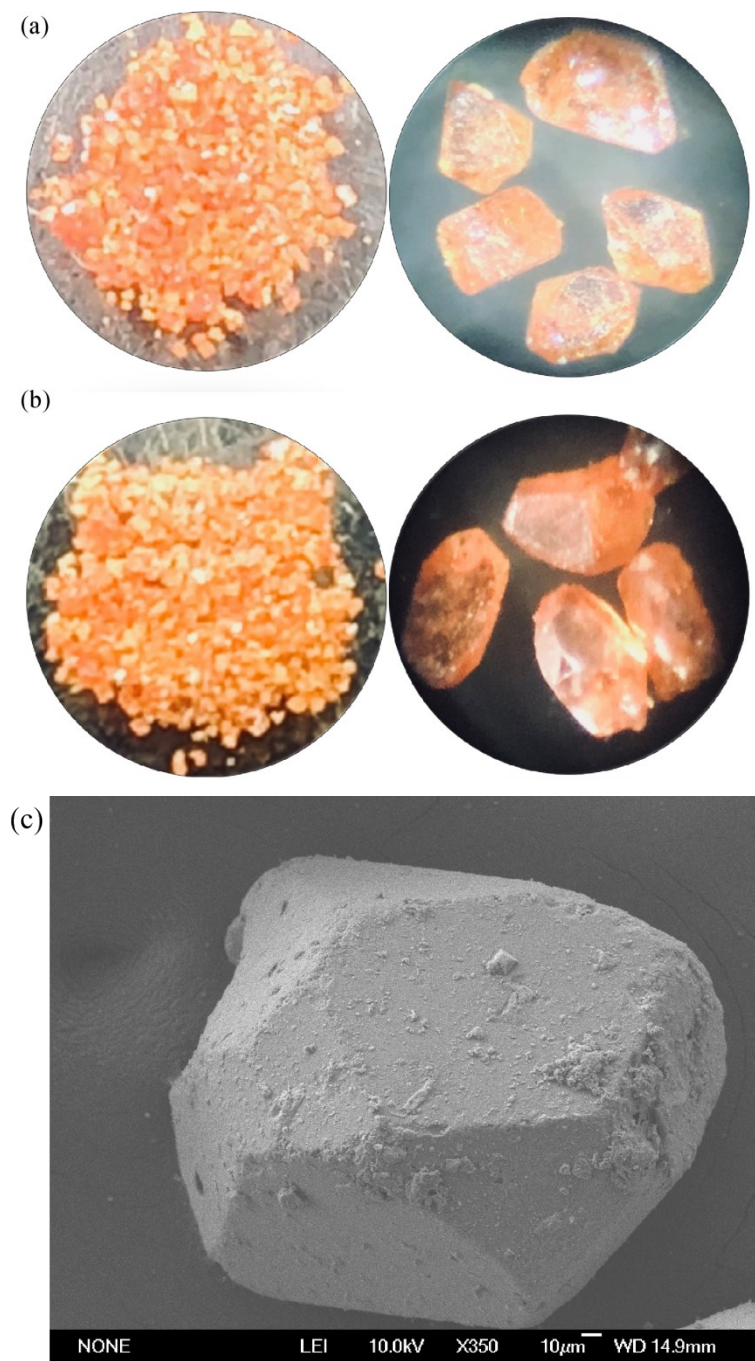sample in moisture air for three years (green) for $[H_2DABCO]_2Cu_6PbBr_{12}$.

Fig. S9. The optical photos of as-synthesized crystals (a), and exposure treated crystals in moisture air for three years (b) as well as the SEM picture (c).
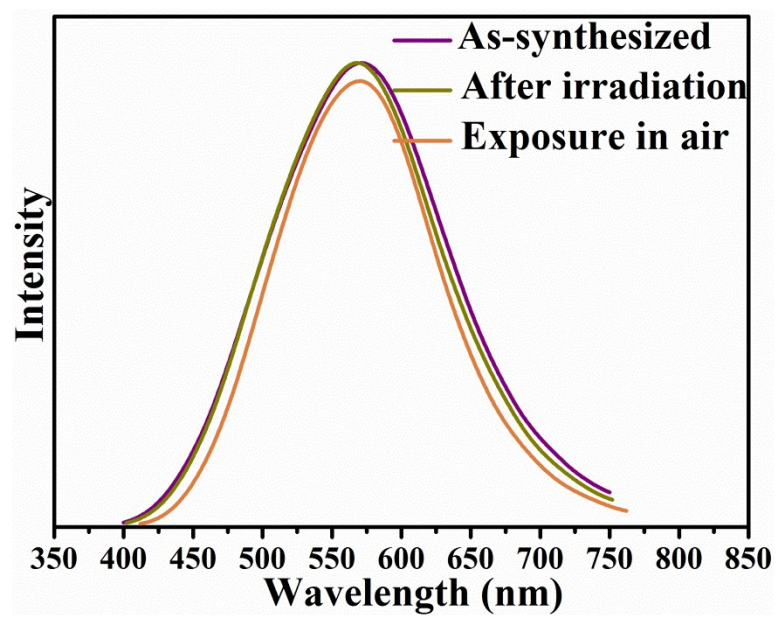
Fig. S10. Comparison of the emission spectra of as-synthesized crystals, after irradiation under UV light for 48 hours and exposure in air for three years.

Table S1. Crystal Data and Structural Refinements for [H_2DABCO]$_2$Cu$_6$PbBr$_{12}$.

Chemical formula	$C_{12}N_4H_{28}Cu_6PbBr_{12}$
fw	1775.73
Space group	R-3 (No. 148)
a/Å	11.4530(15)
b/Å	11.4530(15)
c/Å	22.637(3)
V(Å^3)	2571.5(6)
Z	3
D_{calcd} (g·cm^{-3})	3.440
Temp (K)	298(2)
μ (mm^{-1})	22.541
F(000)	2412
Reflections collected	9703
Unique reflections	1313
Reflections ($I>2\sigma(I)$)	1176
GOF on F^2	1.101
R_1,wR_2 ($I > 2\sigma(I)$)[a]	0.0260/0.0616
R_1,wR_2 (all data)	0.0305/0.0630
$\Delta\rho_{max}$ (e/Å^3)	2.002
$\Delta\rho_{min}$ (e/Å^3)	-0.959

[a] $R_1 = \sum||F_o| -|F_c||/\sum|F_o|$, $wR_2 = \{\sum w[(F_o)^2 -(F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

Table S2. Selected bond lengths (Å) and band angles (°) for [H_2DABCO]$_2PbCu_6Br_{12}$.

Pb(1)-Br(2)#1	3.0020(5)	Cu(1)-Br(2)	2.4144(9)
Pb(1)-Br(2)#2	3.0020(5)	Cu(1)-Br(1)	2.4709(9)
Pb(1)-Br(2)	3.0020(5)	Cu(1)-Br(1)#6	2.5287(10)
Pb(1)-Br(2)#3	3.0020(5)	Cu(1)-Br(1)#7	2.5452(10)
Pb(1)-Br(2)#4	3.0020(5)	Cu(1)-Cu(1)#8	3.0108(11)
Pb(1)-Br(2)#5	3.0020(5)	Cu(1)-Cu(1)#7	3.0108(11)
Br(2)#1-Pb(1)-Br(2)#2	180.00(3)	Br(2)#2-Pb(1)-Br(2)#4	94.516(16)
Br(2)#1-Pb(1)-Br(2)	94.517(16)	Br(2)-Pb(1)-Br(2)#4	94.516(16)
Br(2)#2-Pb(1)-Br(2)	85.483(16)	Br(2)#3-Pb(1)-Br(2)#4	180.00(2)
Br(2)#1-Pb(1)-Br(2)#3	94.516(16)	Br(2)#1-Pb(1)-Br(2)#5	85.483(16)
Br(2)#2-Pb(1)-Br(2)#3	85.484(16)	Br(2)#2-Pb(1)-Br(2)#5	94.517(16)
Br(2)-Pb(1)-Br(2)#3	85.484(16)	Br(2)-Pb(1)-Br(2)#5	180.0
Br(2)#1-Pb(1)-Br(2)#4	85.484(16)	Br(2)#3-Pb(1)-Br(2)#5	94.517(16)
Br(2)-Cu(1)-Br(1)	112.61(3)	Br(2)#4-Pb(1)-Br(2)#5	85.483(16)
Br(2)-Cu(1)-Br(1)#6	104.88(3)	Br(2)-Cu(1)-Br(1)#7	115.41(3)
Br(1)-Cu(1)-Br(1)#6	110.25(3)	Br(1)-Cu(1)-Br(1)#7	107.58(3)
		Br(1)#6-Cu(1)-Br(1)#7	105.82(3)

Symmetry transformations used to generate equivalent atoms: #1 *x-y, x, -z*; #2 *-x+y, -x, z*; #3 *-y, x-y, z*; #4 *y,-x+y,-z*; 5 *-x, -y, -z*; #6 *-y, x-y*-1, *z*; #7 *x-y*-1/3, *x*-2/3, *-z*+1/3; #8 *y*+2/3, *-x+y*+1/3, *-z*+1/3.

Table S3. Hydrogen bonds data for [H_2DABCO]$_2PbCu_6Br_{12}$.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(1)-H(1B)· ··Br(1)	0.97	2.92	3.5529	124
C(2)-H(2A)· ··Br(2)	0.97	2.91	3.5397	123

Table S4. Summarized theoretical fitting parameters based on temperature-dependent FWHM for previously reported lead halides.

Compounds	Γ_0 [meV]	Γ_{phonon} [meV]	Γ_{inhomo} [meV]	E_{LO} [meV]	E_b [meV]	Ref
$(2meptH_2)PbCl_xBr_{4-x}$	580 ± 2	88 ± 3	157 ± 12	12 ± 3	32 ± 1	4
TJU-4	494 ± 9	49 ± 3	72 ± 5	13 ± 2	19 ± 3	5
$(H_2O)(C_6H_8N_3)_2Pb_2Br_{10}$	419	150	49	18	14.5	6
$(C_4H_{14}N_2)_2In_2Br_{10}$	352 ± 0.5	25	178	24.2	.....	7
$[H_2DABCO]_2Cu_6PbBr_{12}$	**374.2 ± 18**	**77**	**162 ± 9.93**	**25.9**	**28.1**	**This work**

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