Supporting Information for

Highly efficient white-light emission in a polar two-dimensional hybrid perovskite

Sasa Wang,[a, b] Yunpeng Yao,[a] Jintao Kong,[a] Sangen Zhao,[a] Zhihua Sun,[a] Zhenyue Wu,[a, b] Lina Li,*[,a] Junhua Luo*[,a]

[a]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, P. R. China.*
[b]*University of Chinese Academy of Sciences, Beijing, 100049, China.*

Fax: +86-591-63173127; Email: jhluo@fjirsm.ac.cn; lilina@fjirsm.ac.cn

Synthesis of (2meptH_2)$PbBr_4$ (1)

All reagents were used as purchased. 0.005 mol $PbAc_2 \cdot 3H_2O$ (1.8967 g) was dissolved in 20 ml 47% HBr solution, followed by dropwise add of 0.005 mol (0.5811 g) 2-methyl-1,5-diaminopentane (2mept). After stirring and heating for 5 minutes, settled solution was obtained. Upon cooling to atmosphere temperature, we obtained powders of **1**. The powders were then dried under vacuum. Temperature-lowering method was employed to grow single crystals of **1**. Firstly, saturated solution of **1** was prepared at 50 ~ 55 °C, and then preheated to guarantee it is clarify solution at 65 °C. The temperature was lowered with a rate of 1.0 °C/day, colorless crystals of **1** were obtained two weeks later.

Single Crystal Structure Determination

Single-crystal X-ray diffraction was conducted on a SuperNova diffractometer with graphite-monochromatized Mo K_α radiation (λ = 0.71073 Å) at 295 K. Data procession were performed by *CrystalClear* software.[1] The structure of **1** was solved by direct methods and refined by the full-matrix least-squares refinements on F^2 using *SHELXLTL* software package.[2] The non-hydrogen atoms were located by the difference Fourier maps and refined anisotropically. The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on the parent atoms. Crystallographic data and structure refinement for **1** are given in Table S1. The selected Pb–Br bond lengths are given in Table S2.

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) measurement was performed on a Rigaku MiniFlex Ⅱ diffractometer at atmosphere environment (Figure S1). The diffraction patterns were collected in the 2θ range of 5°–40° with a step size of 0.5°/min. The experimental PXRD patterns match fairly well with the calculated data based on the single-crystal structure, which solidly confirm the purity of the as-grown crystals of **1**.

Thermogravimetry (TG) analysis

Thermogravimetry of **1** was carried out on a Netzsch STA 449C thermal analyzer with the heating rate of 10 °C min^{-1} from room temperature to 1000 °C and a nitrogen flow rate

of 30 mL·min^{-1} (Figure S6).

Absorption spectrum measurement

Absorption spectrum of **1** was performed on a Perkin-Elmer Lambda 900 UV–Vis–NIR spectra photometer at room temperature. In which $BaSO_4$ was used as the 100% reflectance reference.

Photoluminescence spectra measurements

Emission spectra of **1** were performed on an Edinbergh FLS980 fluorescence spectrometer. To acquire the photoluminescence quantum efficiency (PLQE) of **1**, an integrating sphere was incorporated into the FLS980 spectrofluorometer. The PLQE was calculated based on the equation: $\eta_{QE} = I_S/(E_R - E_S)$, in which I_S is the luminescence emission spectra of the sample, E_R represents the spectra of the excitation light of the empty integrated sphere, and E_S is the excitation spectra of the excited sample. The lifetime of **1** was measured on an Edinburgh FLS980 fluorescence spectrometer using a picosecond pulsed diode lasers. The dynamics of emission decay were monitored by using the FLS980's time-correlated single-photon counting capability (1,024 channels; 1 μs window) with data collection for 10,000 counts in the maximum channel. Excitation was provided by an Edinburgh EPL-397 ps pulsed diode laser. The CIE chromaticity coordinates and CRI were calculated using the CIE calculator-version 3 software based on the emission spectra.

Second harmonic generation (SHG) Measurement

SHG measurement was performed on microcrystals (150-210 μm) of **1** at room temperature using a pulsed Nd:YAG laser with a wavelength of 1064 nm.

Table S1. Crystallographic Data and Structure Refinement of **1.**

Formula	$C_6H_{18}N_2PbBr_4$
Formula weight (g/mol)	645
Temperature (K)	295
Crystal system	monoclinic
Space group	*Cc*
a (Å)	24.3476(11)
b (Å)	7.8717(4)
c (Å)	8.1932(4)
α (deg)	90
β (deg)	99.000(5)
γ (deg)	90
V (Å3)	1575.27
Z	4
D_{calcd} (g/cm^3)	2.762
F (000)	1160
completeness (%)	99.3%
GOF (F^2)	0.754
R_1 (on F_o^2, I >2s(I))	0.0311
wR_2 (on F_o^2, I >2s(I))	0.0812

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$, $\omega R_2 = [\Sigma[\omega(F_0^2-F_c^2)^2]/\Sigma[\omega(F_0^2)^2]]^{1/2}$

Table S2. The Pb–Br bond lengths of **1**.

Bond	(Å)	Bond	(Å)
Pb1–Br1	2.9750(29)	Pb1–Br4	2.972(3)
Pb1–Br2	2.9859(30)	Pb1–Br1’	2.9836(34)
Pb1–Br3	2.9698(34)	Pb1–Br3’	2.9715(35)

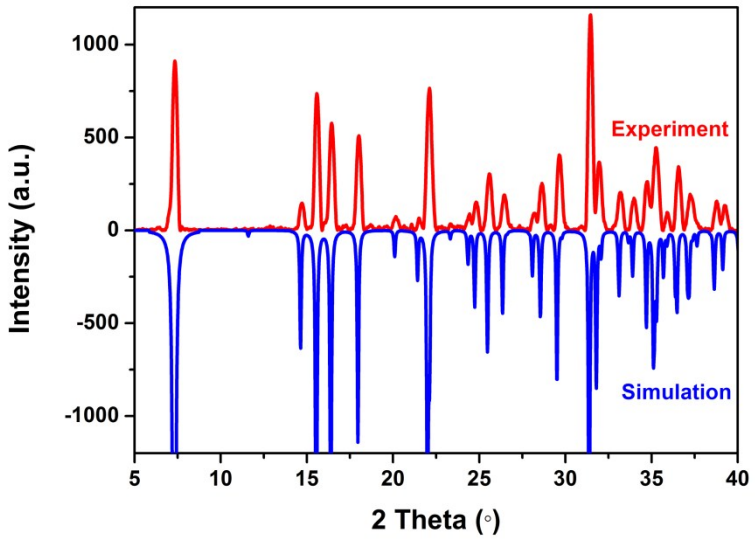

Figure S1. Powder X-ray diffraction patterns of **1.**

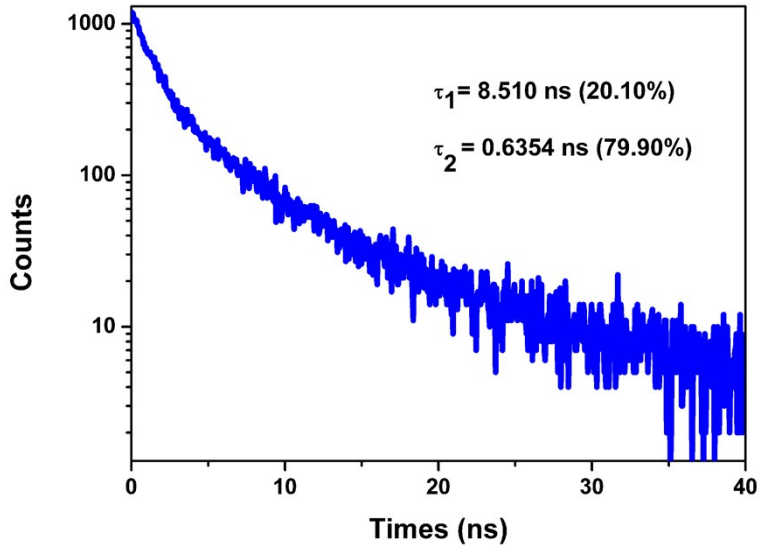

Figure S2. Luminescence decay data of **1**.

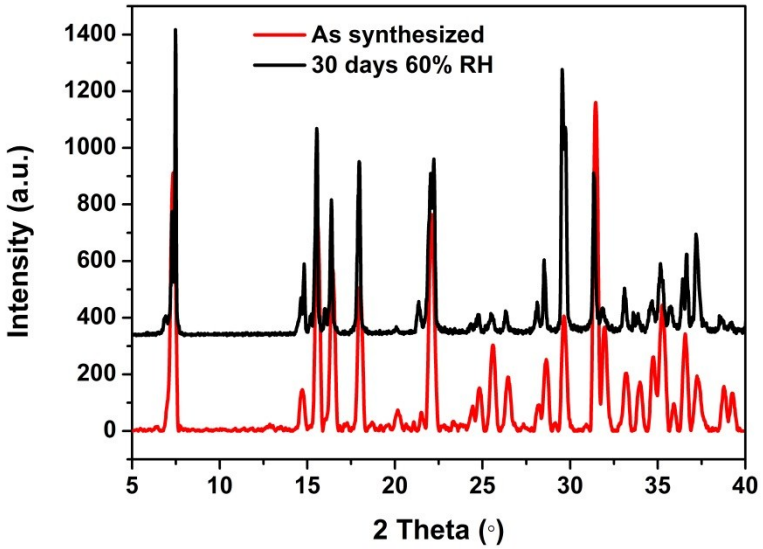

Figure S3. Powder X-ray diffraction patterns of **1** before and after exposured to humidity for 30 days.

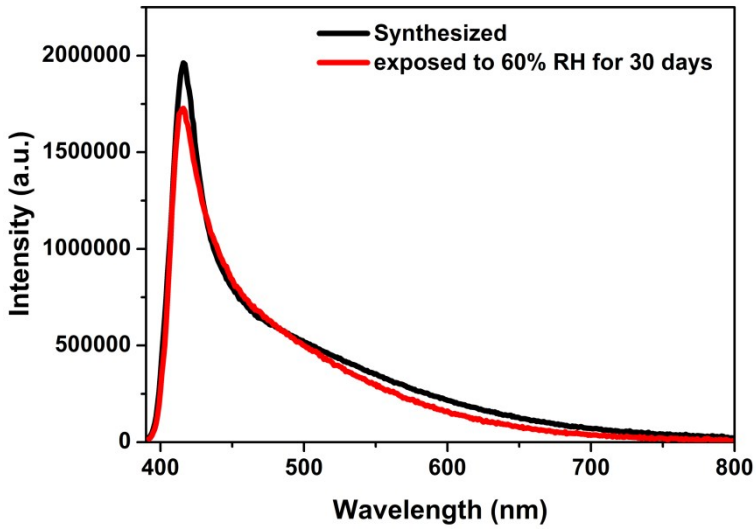

Figure S4. Photoluminescence spectra of **1** before and after exposed to 60% RH for 30 days.

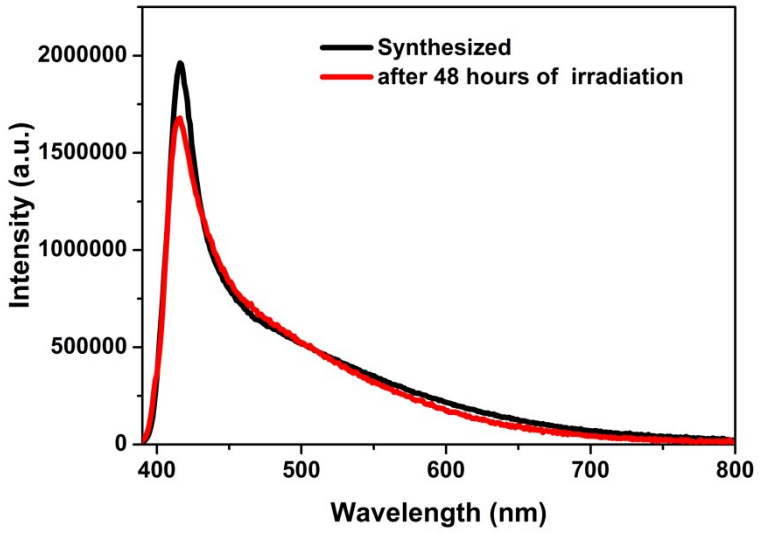

Figure S5. Photoluminescence spectra of **1** before and after irradiated for 48 hours.

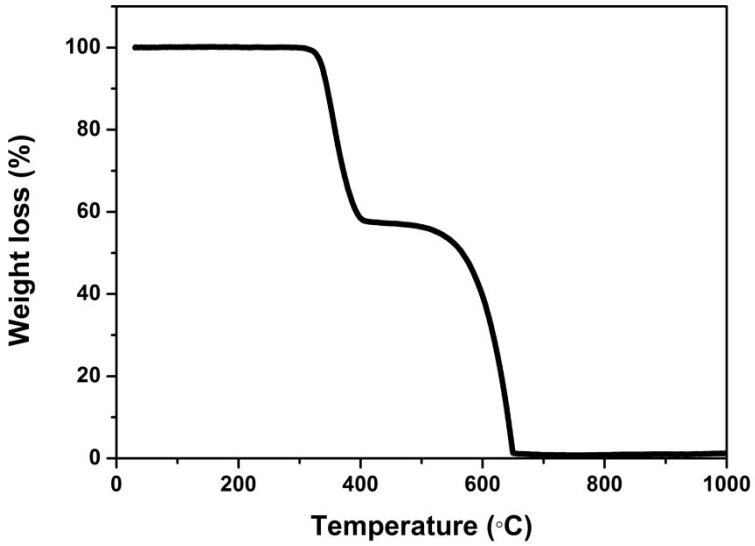

Figure S6. TG curve of **1**.

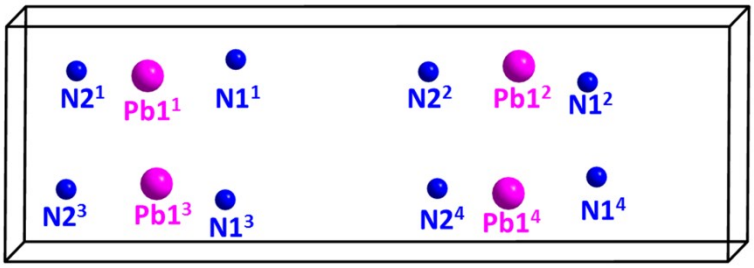

Figure S7. Distribution of Pb and N atoms of $(2meptH_2)PbBr_4$ in a unit cell.

The calculation of μ according to the coordinate charge of the unit cell.

Atoms	Atom coordinate	Coordinate of charge center
Pb	$Pb1^1$(0.8167,0.7508, 0.4643)	(0.5667,0.5,0.7143)
	$Pb1^2$(0.3167,0.7492, 0.9643)	
	$Pb1^3$(0.8167,0.2492,0.9643)	
	$Pb1^4$(0.3167,0.2508,0.4643)	
N	$N2^1$(0.9280,0.7305,0.9470)	(0.5683,0.5,0.7089)
	$N1^1$(0.7085,0.7770,0.9726)	
	$N2^2$(0.4280,0.7695,0.4470)	
	$N1^2$(0.2085,0.7230,0.4726)	
	$N2^3$(0.9280,0.2695,0.4470)	
	$N1^3$(0.7085,0.2230,0.4726)	
	$N2^4$(0.4280,0.2305,0.9470)	
	$N1^4$(0.2085,0.2770,0.9726)	

The dipolarmoment (μ_x) along *x*-axis can be estimated to be:

$(0.5683-0.5667) \times a \times 4e = 0.0016 \times 24.4520 \times 10^{-10}$ m $\times 4 \times 1.6 \times 10^{-19}$ C

$= 0.2333 \times 10^{-29}$ C m

The dipolarmoment (μ_z) along *z*-axis can be estimated to be:

$(0.7089-0.7143) \times c \times \cos(\beta-90) \times 4e = -0.0046 \times 8.1761 \times 10^{-10}$ m $\times 4 \times 1.6 \times 10^{-19}$ C

$= 0.2410 \times 10^{-29}$ C m

The dipolarmoment (μ) of the unit cell can be estimated to be:

$$\mu = \sqrt{\mu_x^2 + \mu_z^2} = 0.3354 \times 10^{-29} \text{ C m}$$

References

1 *Crystal Clear, Version 1.36*; Molecular Structure Corporation and Rigaku: The Woodlands, TX, USA, and Rigaku Corporation: Tokyo, Japan, 2000.

2 G. M. Sheldrick, *SHELXS 97*, Program for Crystal Structure Solution; University of Gottingen: Gottingen, 1997.