Supporting Information

Exploring 0D Lead-Free Metal Halide with Highly Efficient Blue Light Emission and High-Sensitivity Photodetection

Yu-Yin Wang,[a] Huai-Yuan Kang,[a] Shao-Ya Zhang,[a] Hao Qu,[a] Lin Zhu,[a] Dan Zhao,[a] Xian-Feng Li,*[b] Xiao-Wu Lei[a] and Cheng-Yang Yue*[a]

a. School of Chemistry, Chemical Engineer and Materials, Jining University, Qufu, Shandong, 273155, P. R. China, Email: yuechengyang@126.com

b. Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. E-mail: xianfeng.li@kit.edu

Experimental section

1.1. Materials

The chemical materials and reagents were commercially purchased from the Aladdin chemical company and directly used in the preparation reaction without any further purification or other physical processes. $ZnBr_2$ (99%), F-PPA = $C_{10}H_{14}N_2F$ (1-(2-Fluorophenyl)piperazine, 98%), hypophosphorous acid (H_3PO_2, AR, 50 wt. % in H_2O), and hydrobromic acid (HBr, 45%).

2.1 Synthesis of **(F-PPA)$ZnBr_4$**.

Single crystal of **(F-PPA)$ZnBr_4$** was facilely prepared through solution evaporation method at room temperature by utilizing the corresponding organic salts and inorganic salts as precursor materials. To grow the single crystals of **(F-PPA)$ZnBr_4$**, a mixture of $ZnBr_2$ (0.4 mmol, 0.1 g), iso-Propyl alcohol (3 mL) and 1-(2-Fluorophenyl)piperazine (0.4 mmol, 0.072 g) was combined in a blended solution of hydrobromic acid (HBr, 1 mL, 35%) and hypophosphorous acid (1 mL). The obtained solution was stirred at room temperature for 20 minutes, then transferred to a 25 mL glass vial, and heated at 80 °C for 5 days in the oven. Following filtration and ethanol washing, large-size colorless crystals of **(F-PPA)$ZnBr_4$** with a were obtained. After the single crystal XRD, the crystal structure of **(F-PPA)$ZnBr_4$** is confirmed.

2.2 Photodetector preparation

Based on the grown single crystal, a photodetector with a planar configuration was fabricated (the substrate is the glass). To be more specific, the crystals were polished by dried silk as the surface conditions of hybrid perovskite crystals have a strong effect on optoelectronic properties. Then, the crystal surface was covered by Au-conductive paste to do photoelectricity tests.

3.1 Characterizations.

The powder XRD data of **(F-PPA)$ZnBr_4$** were acquired using a Bruker D8 Advance diffractometer operating at 40 kV and 40 mA, with Cu-Kα radiation (λ = 1.5418 Å). The solid state UV-vis absorption spectrum was performed on PE Lambda 900 UV-Vis spectrophotometer at room temperature (RT) over a wavelength range of 200 to 800 nm. TGA was conducted using a Mettler TGA/SDTA 851 thermal analyzer in nitrogen (N_2) atmosphere covering temperatures from RT to 800 °C.

The substrate is the glass and the crystals were fabricated after polished by using dried silk. Then, the crystal surface was covered by silver-conductive paste to do photoelectricity tests. Moreover,

the electrode spacing is 400 μm and electrode length is about 2.5 mm.

UV/Vis spectrum measurements were performed to explore the optical absorption properties of **(F-PPA)$ZnBr_4$**. As is known to all, the absorption characteristics near band edge of a material are closely related to the band gap type, direct or indirect band gap. As shown in the Fig. S12, the absorption edge of **(F-PPA)$ZnBr_4$** is clearly shown in the ultraviolet spectrum region with a wavelength of 350–450 nm.

The indirect band gap was carried out and fitted with the single exponential function:

$$(\alpha h\nu)^2 = B(h\nu - E_g)$$

α is the absorption coefficient, B is a constant, hν is the photon energy, h is Planck's constant =$4.1356676969\times10^{-15}$ eV·s, ν is the incident photon frequency and E_g is the semiconductor band gap width (band gap). According to the formula, it is not difficult to find that $(\alpha h\nu)^2$ is linear with $h\nu$, and B is a constant, which does not affect the intercept. Therefore, we can make a curve with these two values, and extrapitate the straight part of the curve to the X-axis, that is, when Y is 0, the intersection point is the indirect band gap.

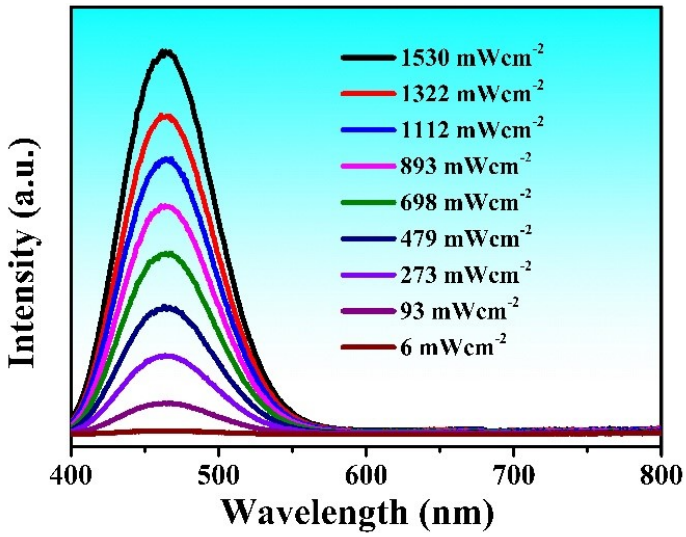

Fig S1. The PL spectra of **(F-PPA)$ZnBr_4$** depending on the excitation power density.

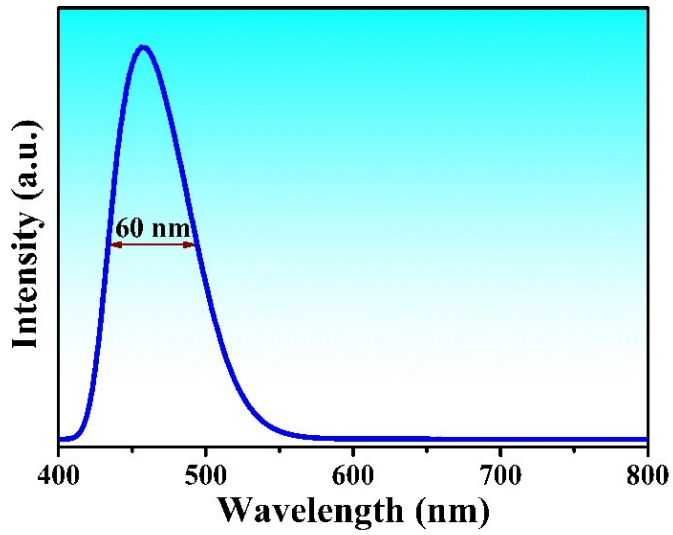

Fig S2. The FWHM in the emission spectrum of **(F-PPA)ZnBr$_4$**.

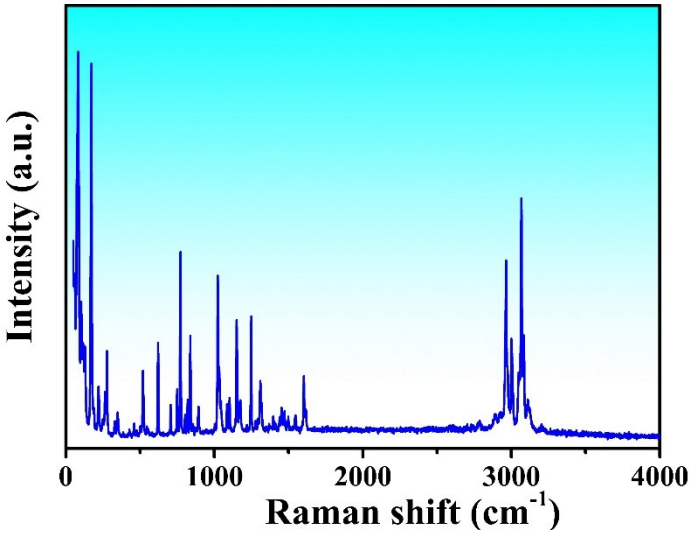

Fig S3. The entire Raman spectrum of **(F-PPA)ZnBr$_4$** excited by 365 nm laser.

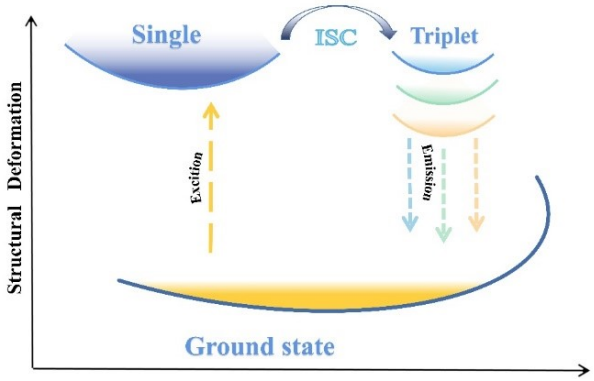

Fig S4. Blue emission mechanism of **(F-PPA)ZnBr$_4$**.

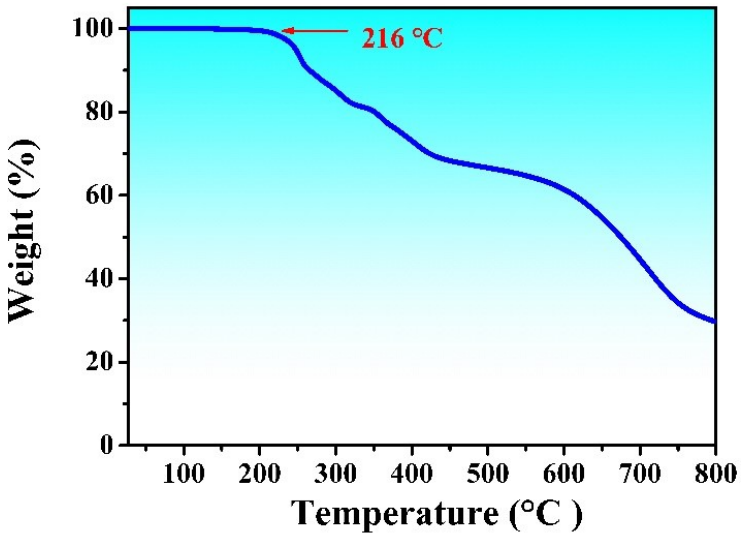

Fig S5. Thermogravimetric (TG) curve of **(F-PPA)$ZnBr_4$** crystals.

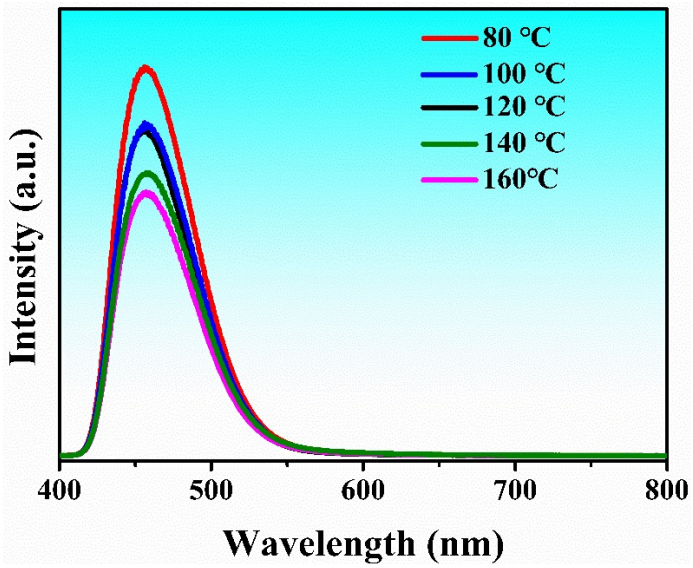

Fig S6. The experimental PL emission spectra of **(F-PPA)$ZnBr_4$** after constant heating at different temperature.

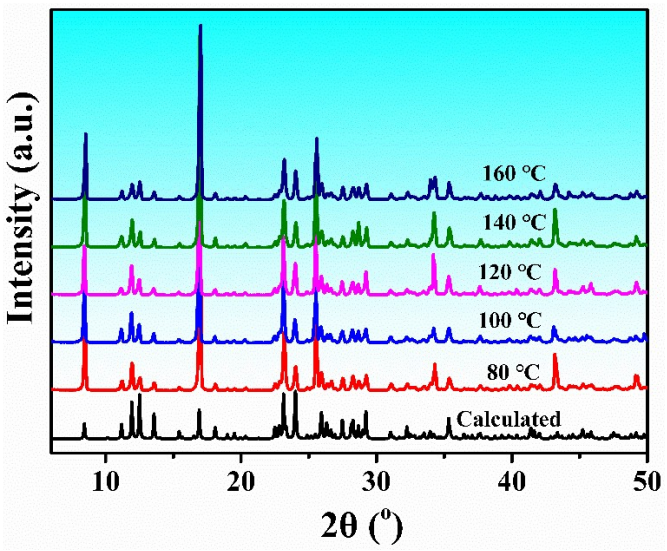

Fig S7. The experimental PXRD patterns of **(F-PPA)ZnBr$_4$** after constant heating at different temperature.

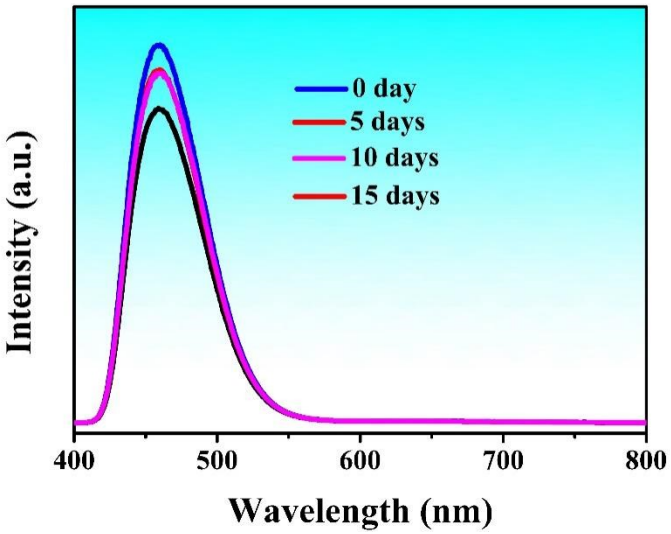

Fig S8. Comparison of the PL emission spectra **(F-PPA)ZnBr$_4$** before and after storing in humid air for 15 days.

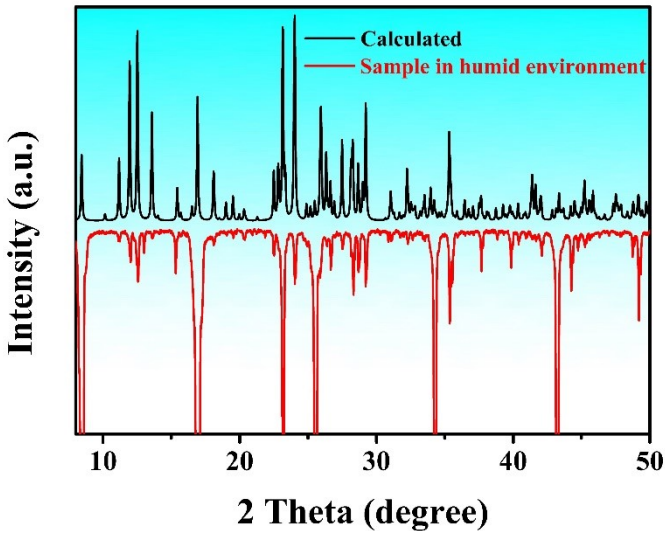

Fig S9. The experimental PXRD patterns of **(F-PPA)ZnBr$_4$** after storing in humid air for 15 days.

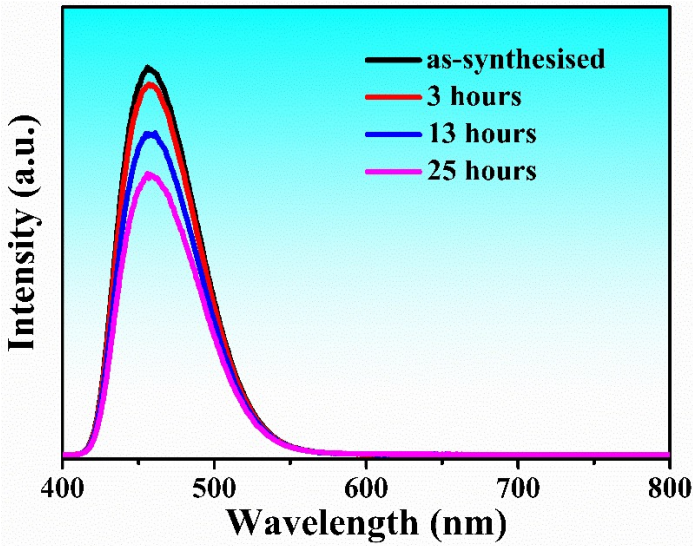

Fig S10. The PL emission spectra of **(F-PPA)ZnBr$_4$** after constant illumination of strong Xe lamp light at different hours.

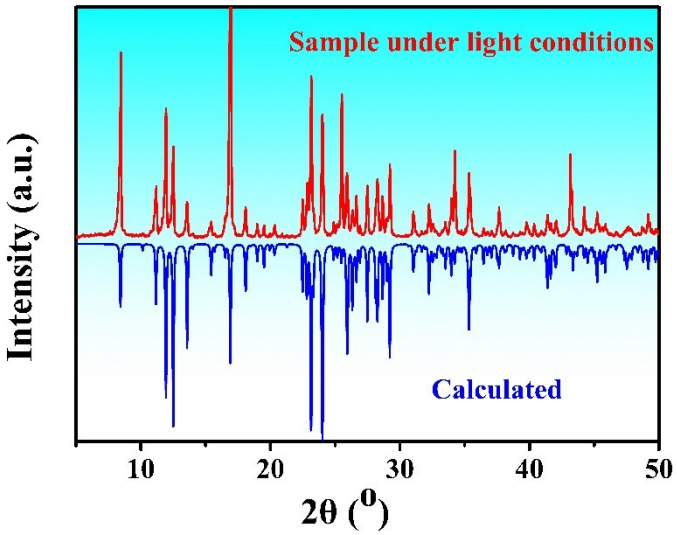

Fig S11. PXRD patterns after Xe lamp illumination and PXRD after synthesis.

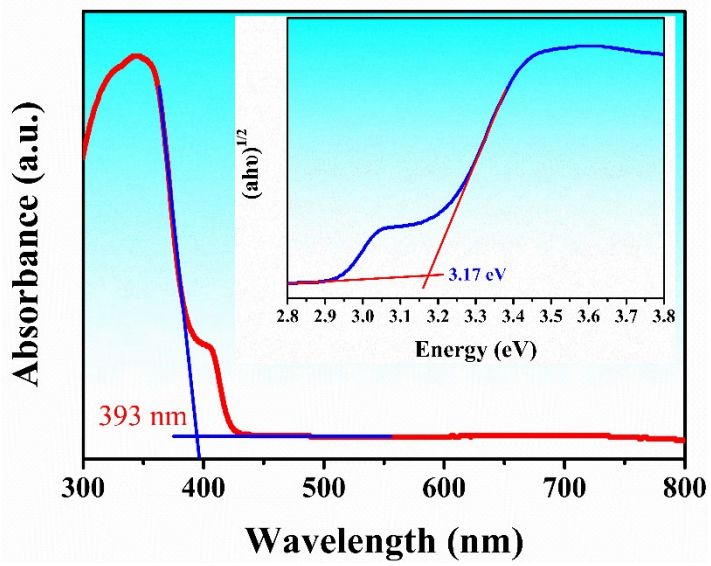

Fig S12. UV/Vis absorption spectra of **(F-PPA)ZnBr$_4$**. Inset is the calculated band gap based on experiment.

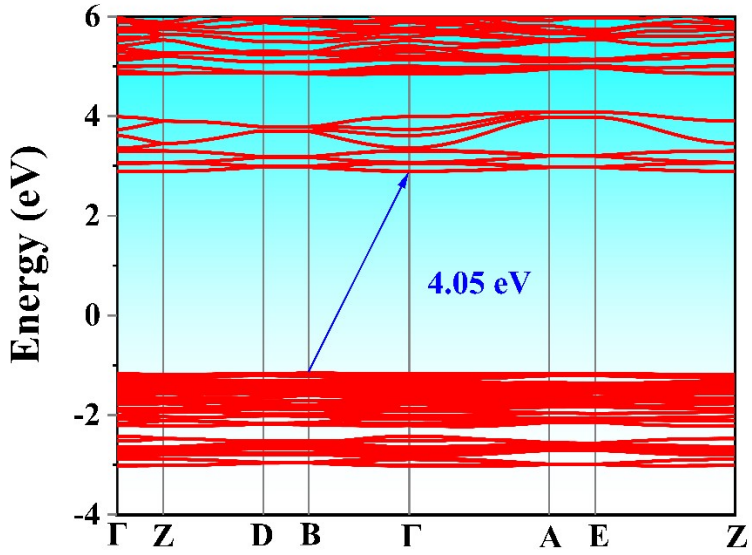

Fig S13. Theoretically calculated **(F-PPA)ZnBr$_4$** band structure.

Table S1. Crystal Data and Structural Refinements for **(F-PPA)ZnBr$_4$** single crystal.

Compound	**(F-PPA)ZnBr$_4$**
CCDC number	2302288
Empirical formula	$C_{10}H_{14}N_2FZnBr_4$
Formula weight	566.24
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	8.0955(3)
b (Å)	20.9526(8)
c (Å)	9.8012(3)
α (°)	90
β (º)	102.2500(10)
γ (°)	90
V (Å^3)	1624.64(10)
Z	4
ρ_{calcd} (g·cm^{-3})	2.315
Temperature (K)	273.15
μ (mm^{-1})	11.344
F (000)	1068.0
Reflections collected	25662
Theta range for data collection (°)	4.676 to 56.606
Index ranges	-10 ⩽ h ⩽ 10, -27 ⩽ k ⩽ 27, -13 ⩽ l ⩽ 12
Independent reflections	4032 [R_{int} = 0.0606, R_{sigma} = 0.0454]
Data/restraints/parameters	4032/0/164
Goodness-of-fit on F^2	1.019
Final R indexes (I > 2σ(I))[a]	R_1 = 0.0342, wR_2 = 0.0773
Final R indexes [all data]	R_1 = 0.0652, wR_2 = 0.0890

[a] $R_1 = \Sigma\left||F_0|-|F_c|\right| / \Sigma|F_0|$, $wR_2 = [\Sigma(F_0^2 - F_c^2) / \Sigma w(F_0)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and bond angles (°) for **(F-PPA)ZnBr$_4$**.

Br1-Zn1	2.4550(7)	Br2-Zn1-Br1	108.92(3)
Br2-Zn1	2.4172(6)	Br3-Zn1-Br1	105.42(2)
Br3-Zn1	2.4007(6)	Br3-Zn1-Br2	110.29(2)
Br4-Zn1	2.3781(7)	Br4-Zn1-Br1	104.06(2)
		Br4-Zn1-Br2	109.48(3)
		Br4-Zn1-Br3	118.11(3)

[1]1/2+X,1/2-Y,1-Z; [2]1/2-X,1/2-Y,1-Z