Supporting Information

Tailored Synthesis of an Unprecedented Pb-Mn Heterometallic Halide Hybrid with Enhanced Emission

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Experimental details

Materials and Chemicals: (*R*)-3-Aminopiperidine dihydrochloride ($C_5H_{14}Cl_2N_2$, 98%, Chemical Book), lead (Ⅱ) acetate trihydrate ($Pb(Ac)_2{\cdot}3H_2O$, 99.5%, Aladdin), manganese (Ⅱ) monoxide (MnO, 99.5%, Aladdin), hydrochloric acid (HCl, 36.46%, SCR), Barium sulfate ($BaSO_4$, AR, Aladdin). All the chemicals were bought and used without further purification.

Synthesis and crystal growth: Crystalline materials of **1** were synthesized by adding $C_5H_{14}Cl_2N_2$ (0.346 g, 2 mmol) to the concentrated aqueous HCl solution (20 mL) of the $Pb(Ac)_2{\cdot}3H_2O$ (1.89 g, 5 mmol). A colorless solution was obtained by heating to boiling under constant magnetic stirring. After cooling to room temperature, we obtained colorless microcrystals of **1**. Crystalline materials of **2** were synthesized by adding $C_5H_{14}Cl_2N_2$ (0.346 g, 2 mmol) to the concentrated aqueous HCl solution (20 mL) of $Pb(Ac)_2{\cdot}3H_2O$ (0.75 g, 2 mmol) and excess MnO (2 g, 28 mmol). Through heating to boiling under constant magnetic stirring, a yellow solution was obtained. Finally, yellow crystals of **2** were obtained after the solution cooling to 40 ℃. Notably, without MnO, the same proportion ($C_5H_{12}N_2$ and $Pb(Ac)_2{\cdot}3H_2O$ were mixed at 1:1 molar ratio) results in colorless needle like crystals as we reported before.[1] The obtained microcrystals of **2** were washed three times using anhydrous ether then dried under vacuum at 50 ℃ overnight for further characterizations.

Structural Characterization: Single crystal X-ray diffraction (SCXRD) was performed on a Bruker D8 diffractometer with Mo *K*α radiation (λ = 0.71073). Crystal structures of **1** and **2** were solved by direct methods and then refined by the full-matrix least-squares refinements on F^2 using a *SHELXLTL* 97 software package. All the non-hydrogen atoms were refined anisotropically based on all reflections with $I > 2\sigma(I)$, and the H atoms were generated by geometrical considerations and placed at their idealized positions. Powder X-ray diffraction (PXRD) patterns were collected on a MiniFlex 600, Rigaku, using a Cu *K*α rotating anode. Element analysis was performed using a Jobin Yvon Ultima-2 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Thermogravimetric (TG) measurement was conducted on a Netzsch STA 449C thermal analyser in the temperature range of 40 ~ 1100 ℃ and recorded at heating rate of 10 ℃ min^{-1}.

Optical Characterization: The absorption spectra were collected using a PerkinElmer Lambda 900 UV-vis spectrophotometer with an integrating sphere and $BaSO_4$ was used as the 100% reflectance reference. The excitation spectra, photoluminescence spectra and emission decay of **1** and **2** were acquired at room temperature on a FLS980 spectrofluorometer (Edinburgh Instruments). The PLQEs were obtained using a

FSP920-C spectrometer (Edinburgh Instruments) and were calculated by the equation: $\eta_{QY} = I_S/(E_R - E_S)$, in 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.

Calculations of band structure: The calculations of band structures and density of states were performed using *ab initio* first-principle density functional theory method within the total-energy code *CASTEP* program. For the calculations of **1**, the exchange and correlation effects were treated by Perdew-Burke-Ernzerh for solids in the generalized gradient approximation. The core-electrons interactions between the ionic cores and the electrons were described by the norm-conserving pseudo potentials. For the calculations of **2**, Ceperley and Alder (1980) data as parameterized by Perdew and Zunger (1981) in the local density approximation was used to deal exchange and correlation effects. The core-electrons interactions between the ionic cores and the electrons were described by ultrasoft pseudo potentials. Moreover, the spin-orbit coupling effect was taken into account for the band structure calculations of **2**.

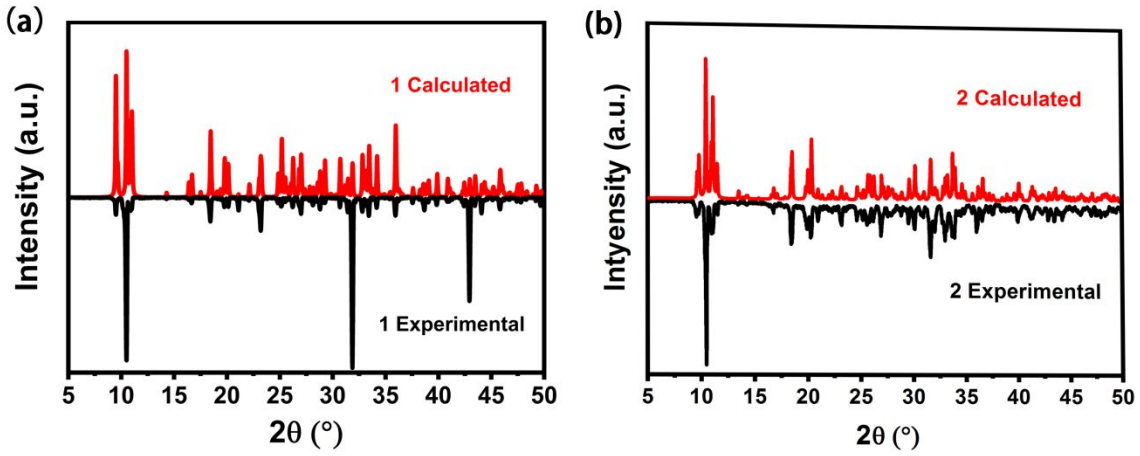

Figure S1. Patterns of the powder X-rays diffraction (PXRD) match well with the simulated ones, verifying the purity of the bulk phase of **1** and **2**.

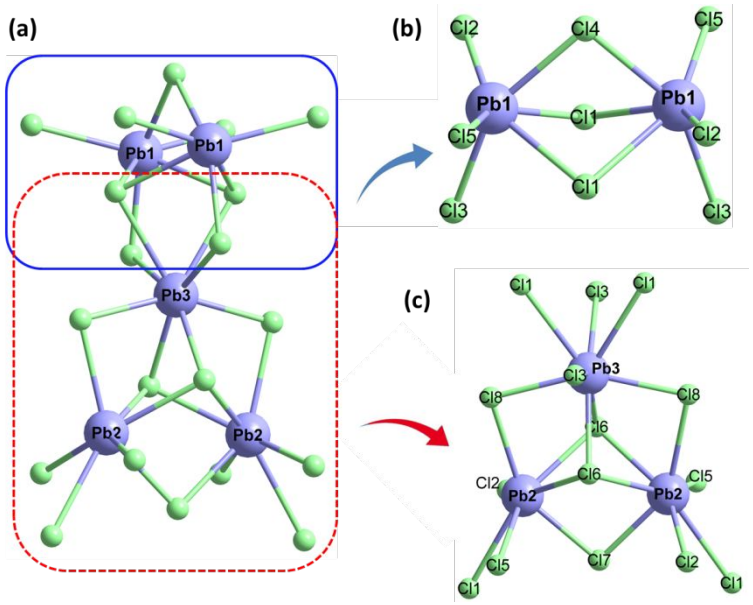

Figure S2. (a) A structural motif of the inorganic part for **1**. The Pb_2Cl_9 dimer (b) and the firm Pb_3Cl_{15} trimer (c) in the structural motif**.**

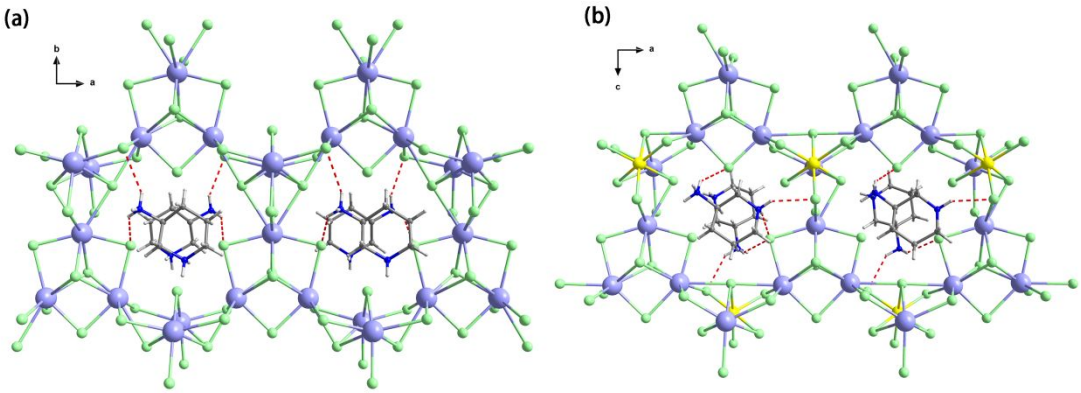

Figure S3. The N-H···Cl hydrogen-bonding interactions between organic cations and inorganic metal halide net of **1** (a) and **2** (b).

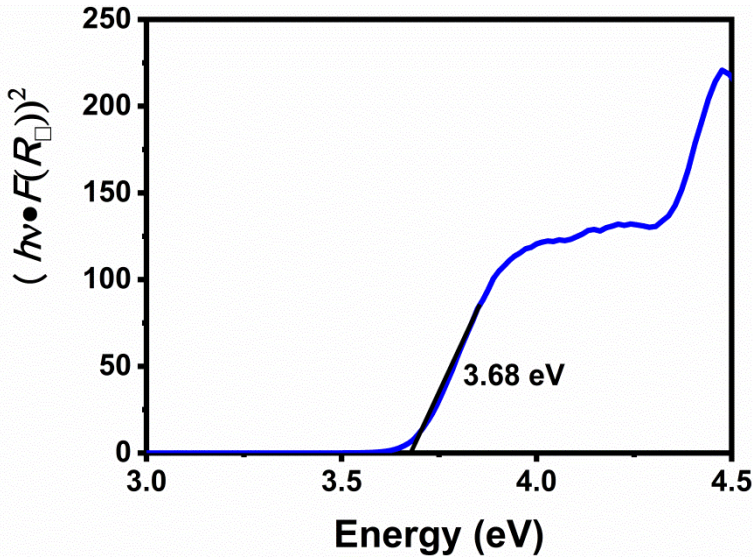

Figure S4. Tauc plot for **1**.

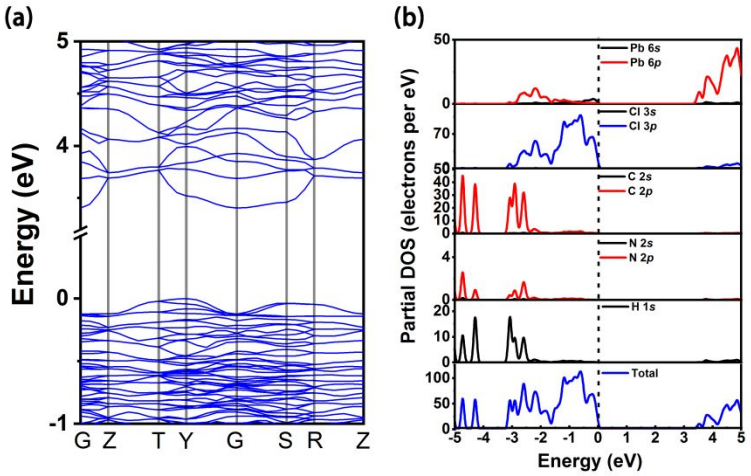

Figure S5. (a) The calculated band structure of **1**. (b) The partial density of states (PDOS) of **1**.

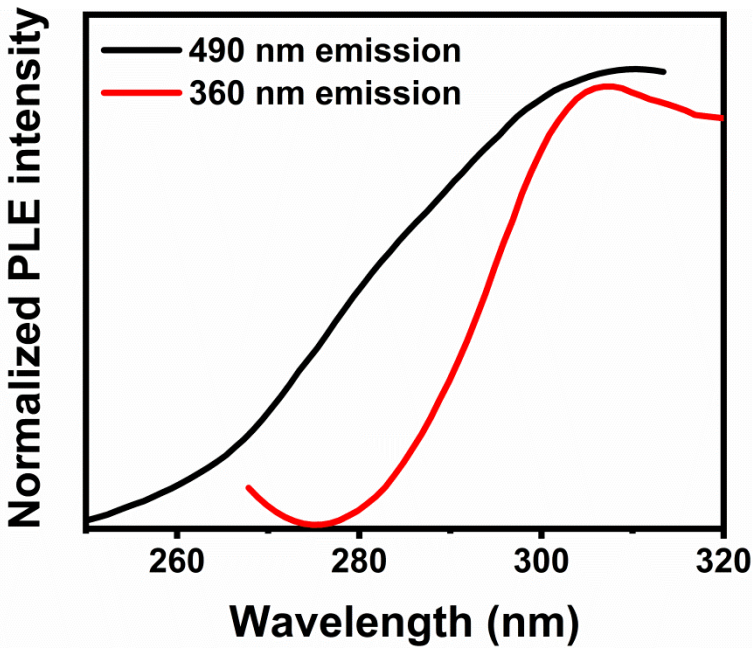

Figure S6. Excitation spectra for the 360 and 490 nm emissions of **1**.

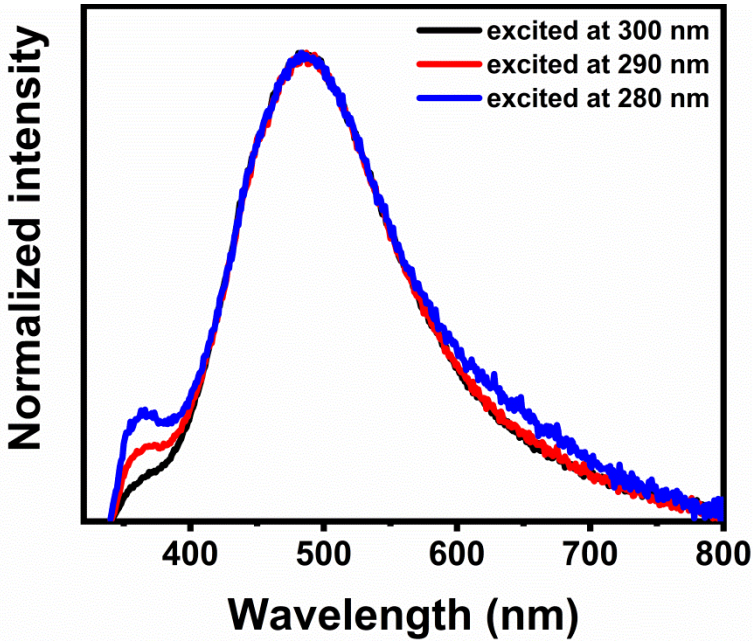

Figure S7. Emission spectra of **1** at different excitation wavelengths.

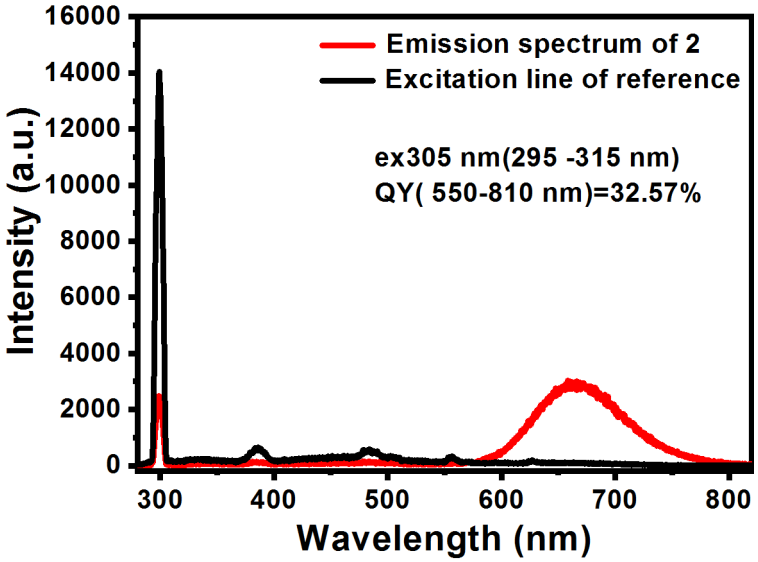

Figure S8. Excitation line of reference and emission spectrum of freshly synthesized **2** with the excitation wavelength of 305 nm collected by an integrating sphere.

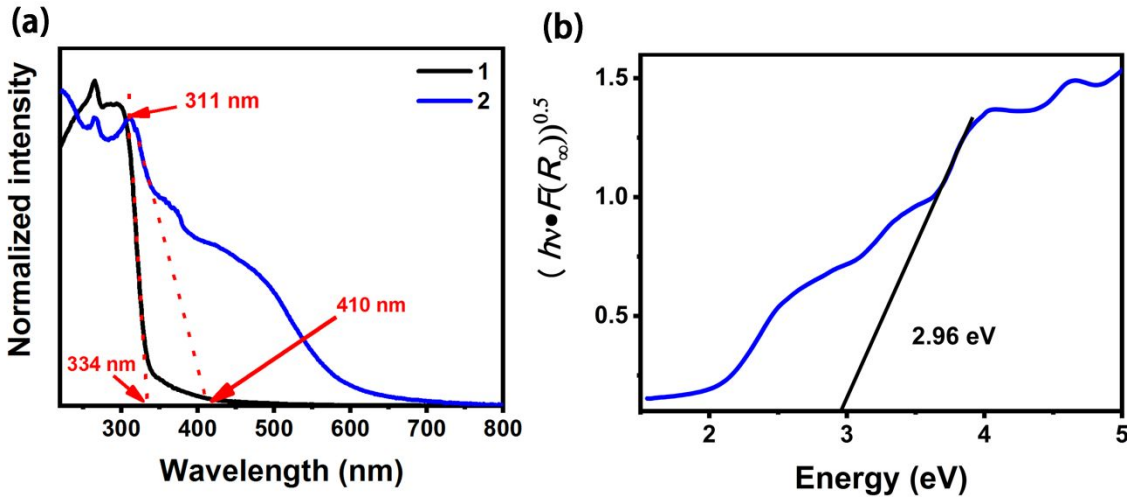

Figure S9. (a) normalized absorption spectra of **1** and **2**. (b) Tauc plot for **2**.

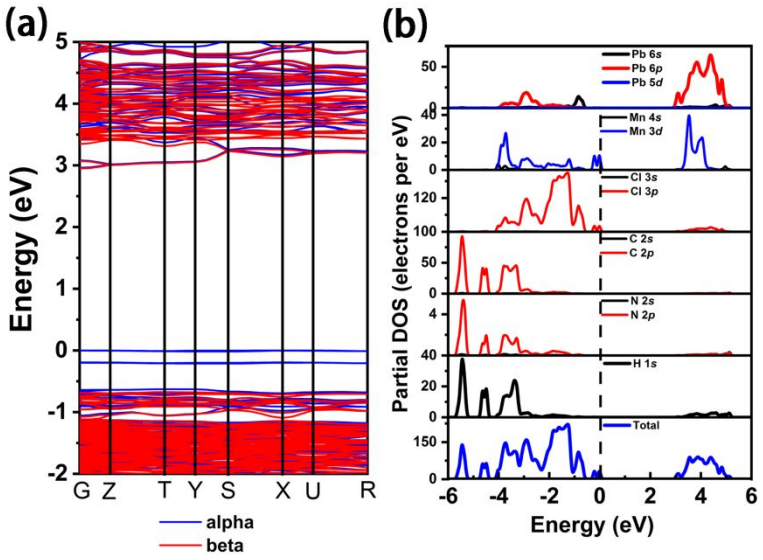

Figure S10. (a) The calculated band structure of **2**. (b) The partial density of states (PDOS) of **2**.

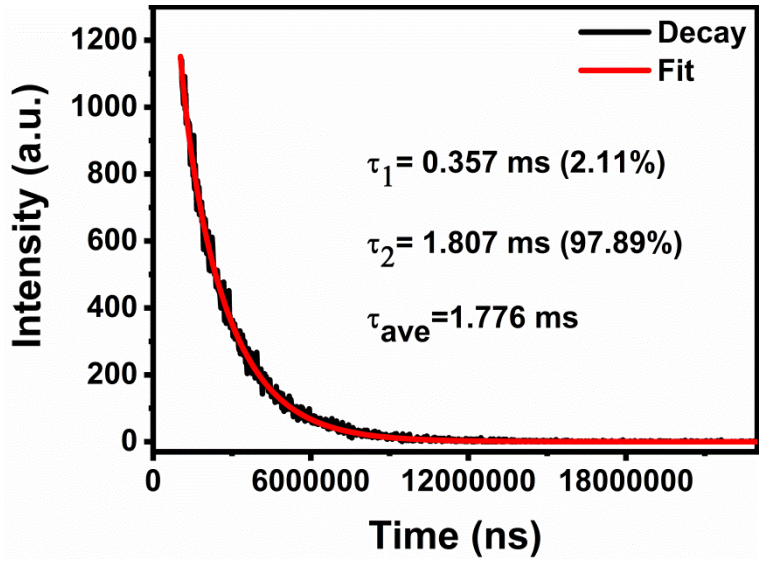

Figure S11. Photoluminescence decay of **2** (measured at 678 nm) at room temperature.

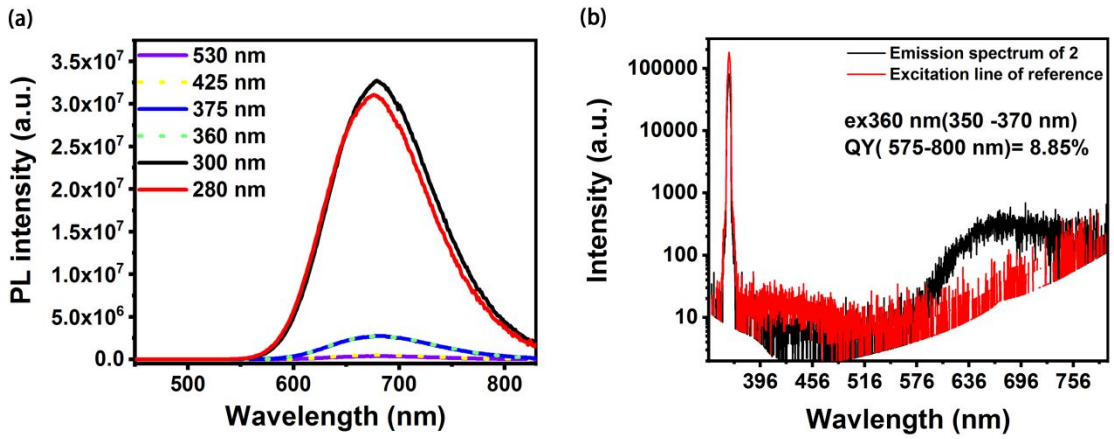

Figure S12. (a) Emission spectra of **2** upon different excitation wavelengths. (b) Excitation line of reference and emission spectrum of freshly synthesized **2** with the excitation wavelength of 360 nm collected by an integrating sphere.

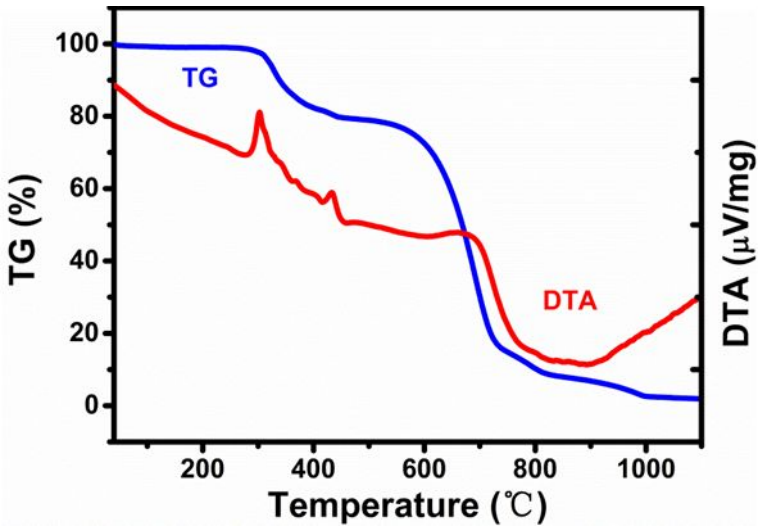

Figure S13. TG and DTA heating curves of **2**.

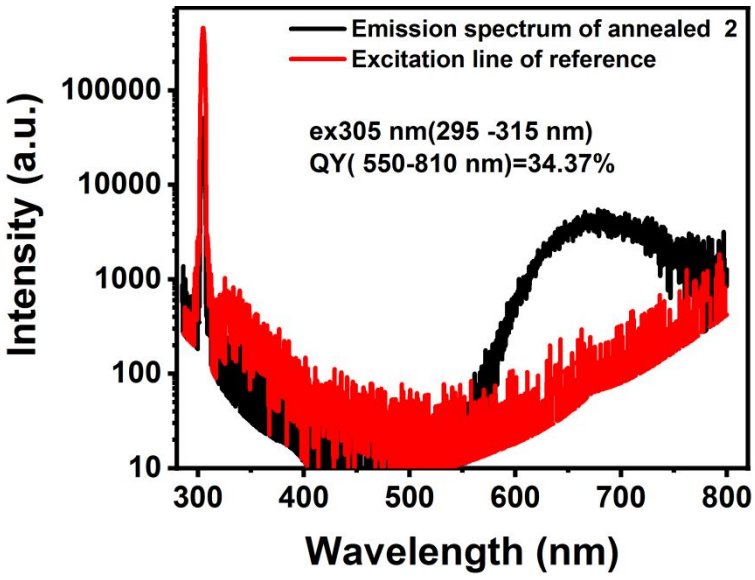

Figure S14. Temperature evolution for PL emission spectra of heterometallic halide hybrid **2**.

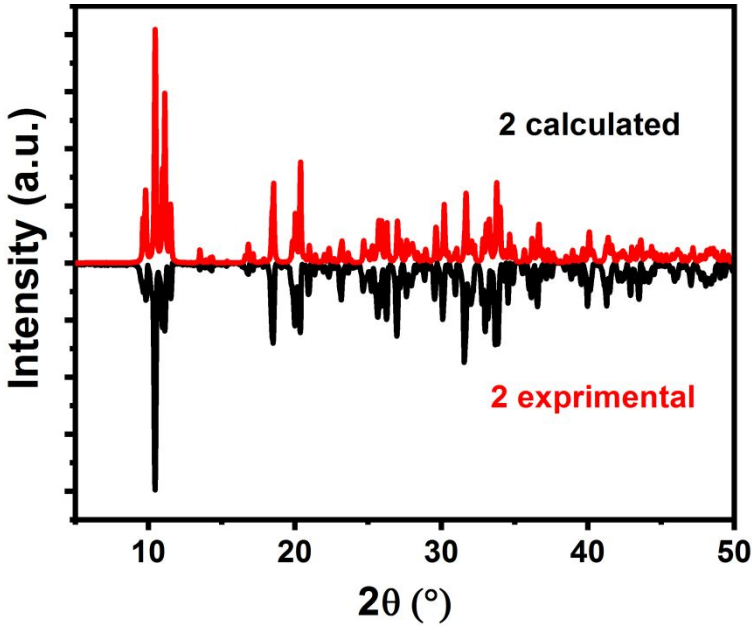

Figure S15 PXRD pattern of **2** after annealed at 120 °C for 10 hour .

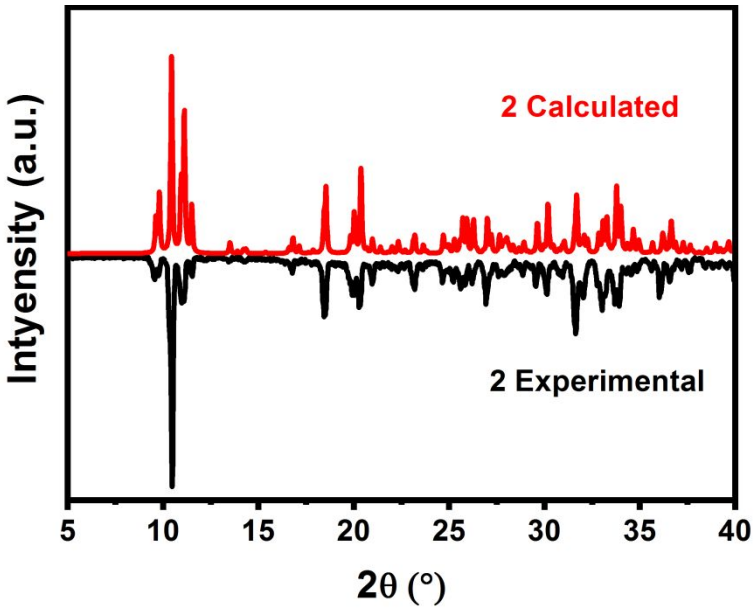

Figure S16. PXRD pattern of **2** after exposed to ambient condition for three month.

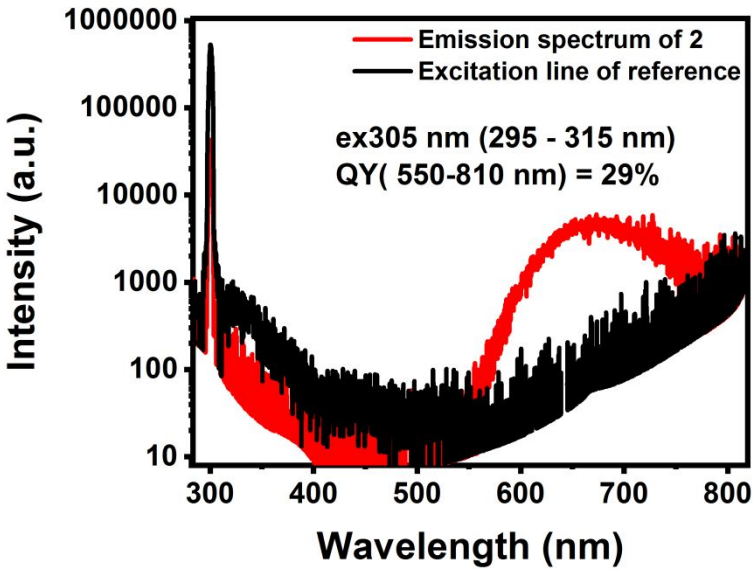

Figure S17. Excitation line of reference and emission spectrum of **2** exposed to ambient condition for three month collected by an integrating sphere.

Table S1. Crystal data and structure refinement for **1** and **2**.

Identification code	**1**	**2**
Formula	$(C_5H_{14}N_2)_2Pb_5Cl_{14}$	$(C_5H_{14}N_2)_2Pb_4MnCl_{14}$
Formula weight (g/mol)	1734.60	1584.36
Temperature (K)	285.15	200.15
Crystal system	orthorhombic	orthorhombic
Space group	$C222_1$	$P2_12_12_1$
a (Å)	10.7997(4)	10.3435(3)
b (Å)	18.2694(6)	16.9247(6)
c (Å)	16.8270(6)	18.3660(7)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	90.00	90.00
Volume (Å^3)	3320.0(2)	3215.16(19)
Z	4	4
ρ_{calc} (g/cm^3)	3.470	3.273
F(000)	3048.0	2828.0
Radiation	Mo K_α (λ = 0.71073)	Mo K_α (λ = 0.71073)
S	4.38 to 50.06	4.44 to 52.74
limiting indices	$-12 \le h \le 12$, $-20 \le k \le 21$, $-19 \le l \le 20$	$-11 \le h \le 12$, $-21 \le k \le 19$, $-22 \le l \le 22$
Reflections collected/unique	9839/2931	19997/6190
Data/restraints/parameters	2931/57/152	6190/114/301
GOF	1.083	1.011
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0453, wR_2 = 0.0977	R_1 = 0.0475, wR_2 = 0.1146
Final R indexes [all data]	R_1 = 0.0624, wR_2 = 0.1058	R_1 = 0.0576, wR_2 = 0.1257

Table S2. Bond lengths for **1**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Pb3	Cl6	2.872(5)	Pb1	Cl1	2.991(10)
Pb3	Cl6[1]	2.872(5)	Pb1	Cl1[4]	2.926(11)
Pb3	Cl1[2]	3.215(5)	Pb1	Cl4	2.901(5)
Pb3	Cl1[3]	3.215(5)	Pb1	Cl2	2.849(9)
Pb3	Cl8[1]	2.851(5)	Pb1	Cl5	3.002(9)
Pb3	Cl8	2.851(5)	Pb1	Cl3	2.784(6)
Pb3	Cl3[2]	3.215(7)	Pb2	Cl1[4]	3.202(5)
Pb2	Cl6[1]	2.927(10)	Pb2	Cl8	3.076(5)
Pb2	Cl6	3.007(10)	Pb2	Cl2[4]	2.900(12)
Pb2	Cl7	2.842(5)	Pb2	Cl5	3.050(11)

Symmetry transformations used to generate equivalent atoms:

[1]-x,+y,1/2-z; [2]-1/2+x,-1/2+y,+z; [3]1/2-x,-1/2+y,1/2-z; [4]1-x,+y,1/2-z

Table S2. Bond lengths for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pb1	Cl13[1]	3.168(5)	Pb4	Cl10	2.931(5)
Pb1	Cl7	2.923(6)	Pb4	Cl4[4]	2.830(6)
Pb1	Cl3	2.875(5)	Pb4	Cl9	2.947(6)
Pb1	Cl5	2.988(5)	Cl13	Mn1	2.587(6)
Pb1	Cl2	2.889(6)	Cl11	Mn1	2.725(7)
Pb1	Cl1	2.883(6)	Mn1	Cl10	2.624(5)
Pb2	Cl7	2.967(5)	Mn1	Cl8	2.442(7)
Pb2	Cl3	2.950(5)	Mn1	Cl14	2.448(5)
Pb2	Cl5	2.932(5)	Mn1	Cl12	2.508(7)
Pb2	Cl6	2.848(5)	Pb3	Cl1	2.864(5)
Pb2	Cl10	3.134(5)	Pb3	Cl10[2]	3.123(5)
Pb2	Cl8	3.023(7)	Pb3	Cl12[2]	3.192(7)
Pb2	Cl9	3.003(7)	Pb3	Cl4	2.850(6)
Pb3	Cl3	3.015(5)	Pb4	Cl13	2.926(6)
Pb3	Cl5	2.872(5)	Pb4	Cl11	2.961(6)
Pb3	Cl6	2.970(5)	Pb4	Cl2[3]	2.905(5)

Symmetry transformations used to generate equivalent atoms:

[1]1/2-x,-1-y,-1/2+z; [2]1+x,+y,+z; [3]1/2-x,-1-y,1/2+z; [4]-1+x,+y,+z

(1) Y. Peng, Y. Yao, L. Li, Z. Wu, S. Wang and J. Luo,White-light emission in a chiral one-dimensional organic–inorganic hybrid perovskite, *J. Mater. Chem. C*, **2018**, *6*, 6033−6037.