Supporting Information

A core-shell model of polymetallic hybrid metal halides

Dongjie Tian, [a,b,c] Jie Lin, [a] Adel Mesbah, [b] Jiajing Zhou, [a] Mianji Yang, [a] Romain Gautier*[d] and Xi Chen*[a]

[a.] *Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China, E-mail: xichen@xmu.edu.cn*
[b.] *Université Claude Bernard Lyon 1, CNRS, IRCELYON, Villeurbanne F-69626, France*
[c.] *College of Sciences, Henan Agricultural University, Zhengzhou 450002, China*
[d.] *Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, Nantes F-44000, France, E-mail: romain.gautier@cnrs-imn.fr*

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Experimental Procedures

Materials. All experiments were carried out in the air atmosphere with standard Schlenk technology. 2-(piperazin-1-yl) ethan-1-amine, $PbBr_2$, $MnCl_2{\cdot}4H_2O$ and HBr (47% solution in H_2O) were purchased from Meryer (Shanghai) Chemical Technology Company. All solvents (acetone and diethyl ether) were purchased from Sinopharm Chemical Reagent Company and stored in accordance with standard procedures.

Synthesis of 1. [1] 2-(piperazin-1-yl)ethan-1-amine (0.046 g, 0.36 mmol) and $PbBr_2$ (0.132 g, 0.36 mmol) were mixed in an appropriate amount of HBr (47%, in H_2O) and heated to reflux (the reactants dissolve completely). The reaction system was cooled slowly. After 24 h, yellowish block crystals were formed. Then wash with cold acetone, bulk crystals of **1** were obtained. Isolated yield: 0.082 g, 46% yield. ^{1}H NMR (500 MHz, DMSO-*d6*), δ (TMS, ppm): 9.01 (s, 2H), 7.97 (s, 3H), 3.37-3.17 (m, 12H). ^{13}C NMR (125 MHz, DMSO-*d6*), δ (TMS, ppm): 52.90, 48.67.

Synthesis of 2-0. [2] 2-(piperazin-1-yl)ethan-1-amine (0.067 g, 0.52 mmol), $PbBr_2$ (0.191 g, 0.52 mmol) and $MnCl_2{\cdot}4H_2O$ (0.412 g, 2.08 mmol) were mixed in an appropriate amount of HBr (47%, in H_2O) and heated to reflux (the reactants dissolve completely). The reaction system was immediately cooled using an ice-water bath. Orange solid powder was formed. Then wash with cold acetone, **2-0** were obtained. Isolated yield: 0.287 g, 43% yield. ^{1}H NMR (500 MHz, DMSO-*d6*), δ (TMS, ppm): 9.03 (s, 2H), 7.99 (s, 3H), 3.38-3.19 (m, 12H). ^{13}C NMR (125 MHz, DMSO-*d6*), δ (TMS, ppm): 52.74, 48.53.

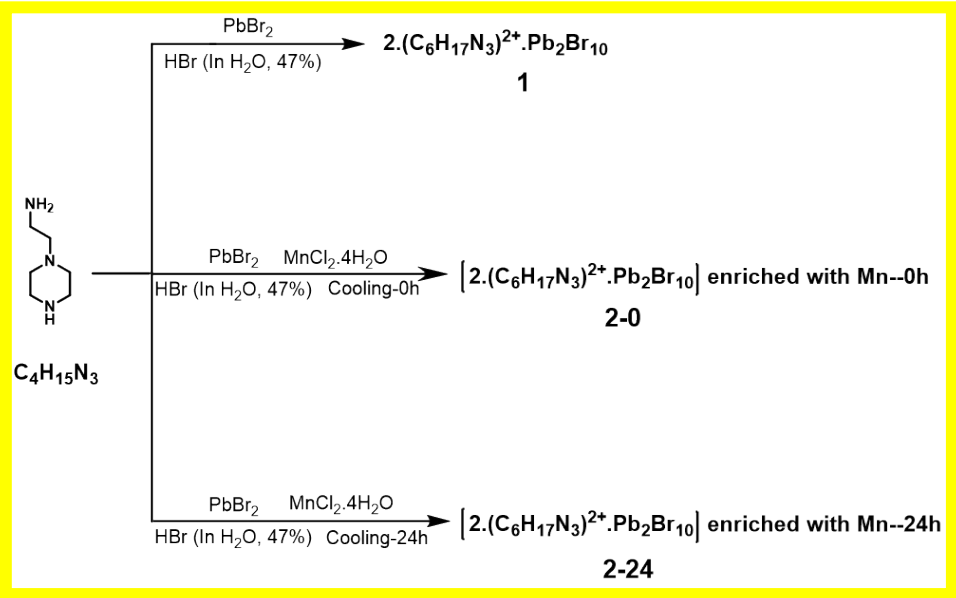
Synthesis of 2-24. 2-(piperazin-1-yl)ethan-1-amine (0.077 g, 0.60 mmol), $PbBr_2$ (0.219 g, 0.60 mmol) and $MnCl_2{\cdot}4H_2O$ (0.472 g, 2.38 mmol) were mixed in an appropriate amount of HBr (47%, in H_2O) and heated to reflux (the reactants dissolve completely). The reaction system was cooled slowly to room temperature for 24 hours. Orange block crystals were formed. Then wash with cold acetone, **2-24** were obtained. Isolated yield: 0.385 g, 50% yield. ^{1}H NMR (500 MHz, DMSO-*d6*), δ (TMS, ppm): 9.02 (s, 2H), 7.98 (s, 3H), 3.37-3.18 (m, 12H). ^{13}C NMR (125 MHz, DMSO-*d6*), δ (TMS, ppm): 52.86, 48.63.

Physical measurements. Full sphere data were collected on single crystals with good quality using a synergy Diffraction Micro-focus spot diffractometer with graphite-monochromatized Cu Kα radiation (λ = 1.54184 Å), operating at 50 kV and 1 mA under N_2 flow. Crystal data were integrated and corrected for absorption (numerical) using the CrysAlispro programs. Crystal structures were solved by direct methods and refined by full-matrix least-squares on F_2 using the OLEX2 program package. [3] Powder X-Ray Diffractometer (PXRD) analysis was performed using a Rigaku Smart-Lab-SE X Powder X-Ray Diffractometer (Cu Kα graphite, λ = 1.5406 Å) operating at 40 kV/20 mA. The collected data were refined using the le-bail method using the Full prof suite program. [4]Scanning electron micrographs (SEM) images and mapping characterization were obtained by a Hitachi S-4800 scanning electron microscope. ^{1}H NMR and ^{13}C NMR spectra were measured using a Bruker Bio-Spin GmbH in ppm downfield from Me_4Si. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fisher Scientific Escalab 250Xi spectrometer equipped with a monochromatized aluminum source (Al Kα = 1486.8 eV) and charge compensation gun. TGA was recorded from R.T. to 800℃with the 10 K min^{-1} in nitrogen atmosphere on a TA Instruments SDT Q600 in a N_2 atmosphere.

[CCDC 2206169 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.]

Optical Measurements. Optical diffuse reflectance measurements were performed using a CACY5000 UV-Vis NIR spectrometer operating in the 200−800 nm region at room temperature and $BaSO_4$ as the 100% reflectance reference. The reflectance data were converted to absorption according to the Kubelka−Munk equation: [5] $\alpha/S = (1 - R)^2 (2R)^{-1}$, where R is the reflectance, α and S are the absorption and scattering coefficients, respectively. Steady-state and time-resolved photoluminescence (TRPL) spectra were acquired using Edinburgh FS5 spectrophotometer equipped with a xenon lamp and a TCSPC module (diode laser excitation at λ = 365 nm) and an integrating sphere for absolute PLQY determination. The spectra were corrected for the monochromator wavelength dependence and photomultiplier response functions provided by the manufacturer.

Results and Discussion



Scheme S1. The synthesis process of **1**, **2-0** and **2-24**.

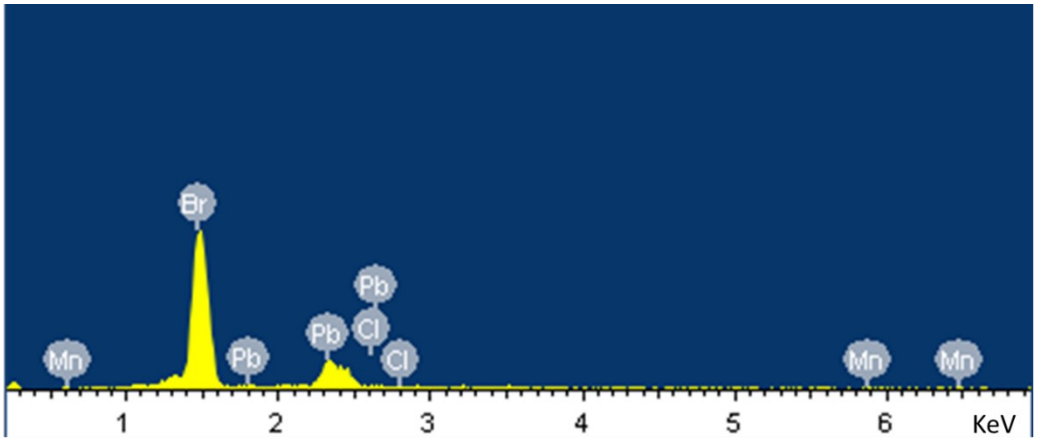


Figure S1. The EDX data of **2-24.**

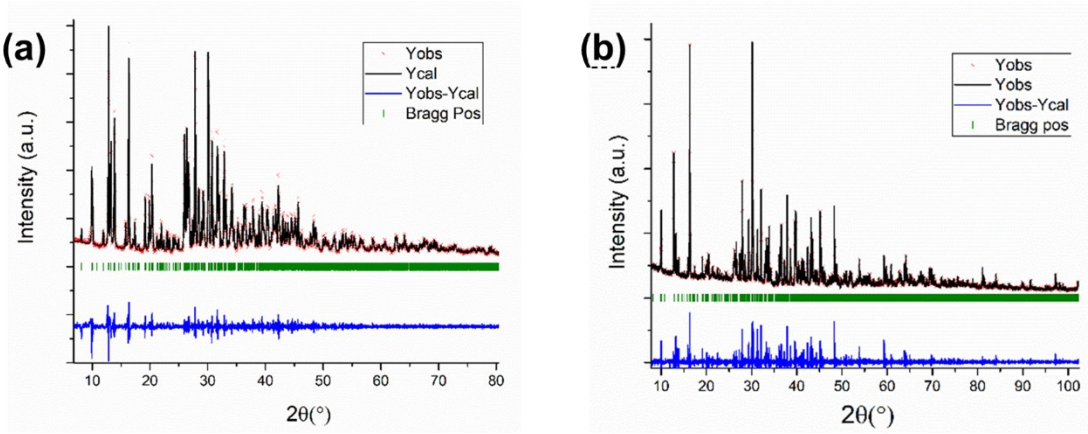


Figure S2. Observed, calculated, and the difference patterns after the profile (le-bail) refinement of the compounds **2-0** (top) and **2-24** bottom).

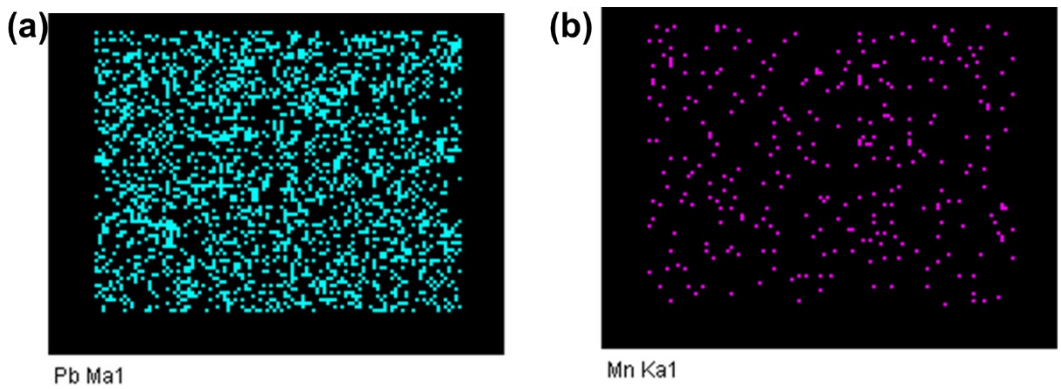


Figure S3. Element mapping of Mn (a) and Pb (b) in **2-0.**

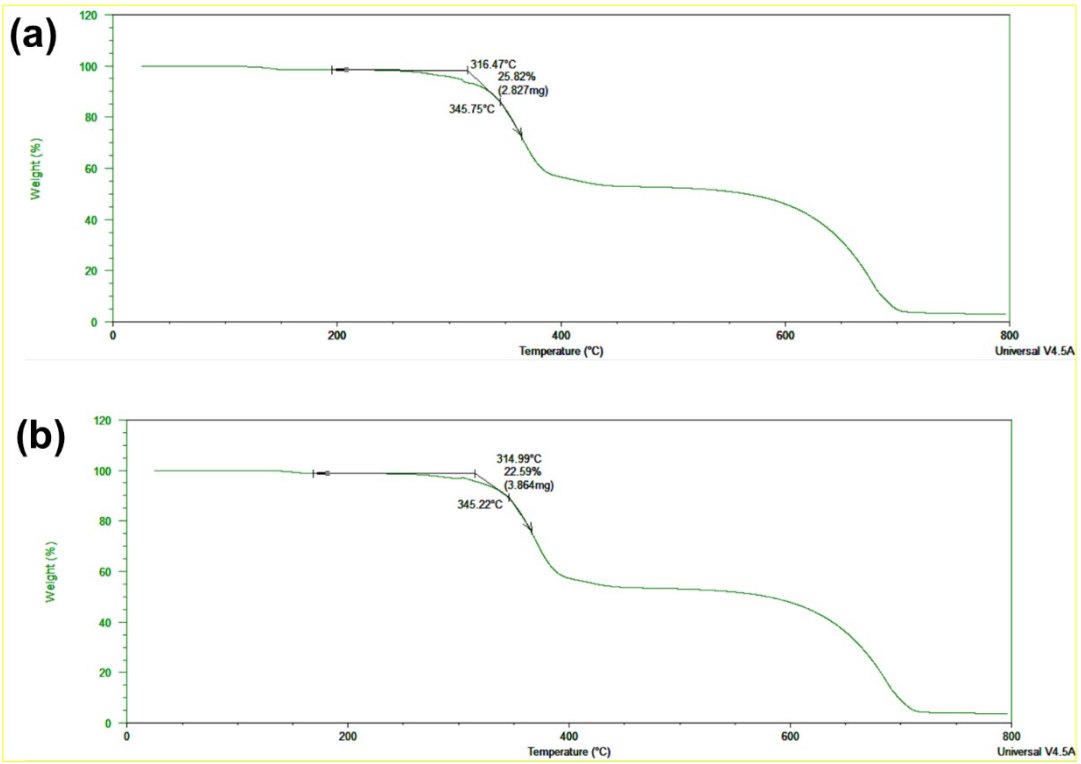


Figure S4. Thermogravimetric Analysis of **2-0** (top) and **2-24** (bottom)**.**

Table S1. The unit cell data of **1** and **2-24** refined using single crystal data at 100K and from powder data at RT**.**

Sample	**1 (100K)**	**2-24 (100K)**	**1 (RT)**	**2-0 (RT)**	**2-24**
a (Å)	13.77	13.74	13.9018(17)	13.8504(2)	13.8631(4)
b (Å)	17.52	17.50	13.9018(17)	17.5660(3)	17.5341(5)
c (Å)	13.77	13.75	13.8567(13)	13.8402(2)	13.8169(3)
β (°)	96.2	96.2	96.14(1)	96.15	96.13(1)
V (Å3)	3304	3286	3364.88(61)	3347.84(9)	3339.41(15)

Table S2. Crystal data and structure refinement for **1**.

	1	**2-24**
Formula	$C_{12}H_{37}N_6Pb_2Br_{10}{\cdot}H_2O$	$C_{12}H_{37}N_6Pb_2Br_{10}$:Mn
Mr(g/mol)	1494.95	1491.93
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Z	4	4
Temp.(K)	150	100
μ(mm^{-1})	22.287	34.086
a/(Å)	13.7743(4)	13.7379(1)
b/(Å)	17.5198(7)	17.4999(1)
c/(Å)	13.7748(4)	13.7514(1)
α/(º)	90.00	90.00
β/(º)	96.25	96.25
γ/(º)	90.00	90,00
V/Å³	3304.43(19)	3286,36(4)
*R*1(I >σ(I))	0.0356	0.0369
*wR*2(all data)	0.0831(6748)	0.1062(6326)

Table S3. Lifetime decay of **1**, **2-0** and **2-24**.

Sample	**τ_1/ns**	**τ_2/ns**	**τ_3/ns**	**τ/ns**
1	120.9	134.3	147.7	135.2
2-0	54.3	60.3	66.3	60.7
2-24	76.7	85.2	93.8	85.8

References

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