Supporting information for

## Precise Incorporation of Transition Metals into Organolead Oxyhalide Crystalline Materials for Photocatalysis

Lu Zhang, ‡ Wen Ma, ‡ Chen Sun, Lei Fang, Xueling Song and Honghan Fei\*

<sup>a</sup> School of Chemical Science and Engineering, Shanghai Key Laboratory of Chemical Assessment and Sustainability, Tongji University, Shanghai 200092, P. R. China

**Corresponding Author** 

fei@tongji.edu.cn

## **Experiment section**

*Materials.* Starting materials and solvents were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, TCI, et al) and used without further purification. Pb(NO<sub>3</sub>)<sub>2</sub>, KBr, MAc<sub>2</sub>·4H<sub>2</sub>O (M=Zn, Ni, Mn, Co), ethylene glycol and MeOH were purchased from Adamas and Sigma, respectively.

*Synthesis of TJU-18(Pb/Mn)*. A mixture of 0.1 mmol of  $Pb(NO_3)_2$  (0.0331 g), 0.8 mmol of KBr (0.0952 g), 0.1 mmol of MnAc<sub>2</sub>·4H<sub>2</sub>O (0.0245 g), and 1 ml of ethylene glycol were added into a 20 ml Teflon lined stainless steel autoclave. Then the autoclave reactor was sealed and heated statically at 160 °C for 6 days in an oven. Upon the autoclave cooling to room temperature, the product was washed repeatedly with ethanol and then dried to obtain yellow block-shaped crystals. The molecular weight of Pb<sub>8</sub>MnBr<sub>9</sub>O<sub>8</sub>H(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> (TJU-18(Pb/Mn)) is 2644.84 g/mol.

*Synthesis of TJU-18(Pb/Co)*. A mixture of 0.2 mmol of Pb(NO<sub>3</sub>)<sub>2</sub> (0.0662 g), 0.3 mmol of KBr (0.0357 g), 0.1 mmol of CoAc<sub>2</sub>·4H<sub>2</sub>O (0.0245 g), and 1 ml of ethylene glycol were added into a 20 ml Teflon lined stainless steel autoclave. Then the autoclave reactor was sealed and heated statically at 140 °C for 4 days in an oven. Upon the autoclave cooling to room temperature, the product was washed repeatedly with ethanol and then dried to obtain pink purple block-shaped crystals. The molecular weight of Pb<sub>8</sub>CoBr<sub>9</sub>O<sub>8</sub>H(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> (TJU-18(Pb/Co)) is 2648.83 g/mol.

*Synthesis of TJU-18(Pb/Ni)*. A mixture of 0.1 mmol of Pb(NO<sub>3</sub>)<sub>2</sub> (0.0331 g), 0.15 mmol of KBr (0.0179 g), 0.05 mmol of NiAc<sub>2</sub>·4H<sub>2</sub>O (0.0124 g), and 1 ml of ethylene glycol were added into a 20 ml Teflon lined stainless steel autoclave. Then the autoclave reactor was sealed and heated statically at 140 °C for 4 days in an oven. Upon the autoclave cooling to room temperature, the product was washed repeatedly with ethanol and then dried to obtain light green block-shaped crystals. The molecular weight of Pb<sub>8</sub>NiBr<sub>9</sub>O<sub>8</sub>H(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> (TJU-18(Pb/Ni)) is 2648.59 g/mol.

*Synthesis of TJU-18(Pb/Zn)*. A mixture of 0.2 mmol of Pb(NO<sub>3</sub>)<sub>2</sub> (0.0662 g), 0.3 mmol of KBr (0.0357 g), 0.1 mmol of ZnAc<sub>2</sub>·4H<sub>2</sub>O (0.0245 g), and 1 ml of ethylene glycol were added into a 20 ml Teflon lined stainless steel autoclave. Then the autoclave reactor was sealed and heated statically at 140 °C for 4 days in an oven. Upon the autoclave cooling to room temperature, the product was washed repeatedly with ethanol and then dried to obtain colorless block-shaped crystals. The molecular weight of Pb<sub>8</sub>ZnBr<sub>9</sub>O<sub>8</sub>H(C<sub>2</sub>H<sub>4</sub>)<sub>3</sub> (TJU-18(Pb/Zn)) is 2655.29 g/mol.

**Powder X-ray Diffraction (PXRD)**. PXRD analysis was performed using on a BRUKER D2 PHASER X-ray diffractometer equipped with a Cu sealed tube ( $\lambda = 1.54184$  Å) at 30 kV and 10 mA. The diffraction patterns were scanned at ambient temperature, with a scan speed of 1 sec/step, a step size of 0.02° in 20, and a 20 range of 8~40°.

Single Crystal X-ray Diffraction (SCXRD). A single crystal of TJU-18 suitable for X-ray analysis was chosen under an optical microscope (NIKON ECLIPSE LV100N POL), and carefully mounted onto a glass fiber. The crystal structure of the asprepared single crystal was analyzed by a Bruker SMART APEX II CCD area detector X-ray diffractometer at 279(2) K, applying a graphite-monochromated Mo-K $_{\alpha}$  radiation  $(\lambda = 0.71073 \text{ Å})$  from a fine-focus sealed tube operated at 50 kV and 30 mA. An empirical absorption correction was applied. The data were corrected for Lorentzpolarization effects. The crystal structure was solved by direct methods and expanded The model was refined by full-matrix least-squares analysis of  $F^2$  against routinely. All non-hydrogen atoms were refined with anisotropic thermal all reflections. displacement parameters. Thermal parameters for hydrogen atoms were tied to the isotropic thermal parameter of the atom to which they are bonded. The used programs included APEX-II v2.1.4,<sup>S1</sup> SHELXTL v6.14,<sup>S2</sup> and DIAMOND v3.1e.<sup>S3</sup> Further details of crystallographic data and structural refinement are summarized in Table S1. Simulated powder patterns were calculated by Mercury software applying the crystallographic information from the SCXRD results.

*Fourier-transform Infrared (FT-IR) spectrum*. FT-IR spectra were recorded using a BRUKER ALPHA spectrophotometer with a wavenumber range of  $4000 \sim 400 \text{ cm}^{-1}$  with a resolution of 2 cm<sup>-1</sup>.

*Thermogravimetry Analysis (TGA).* TGA analysis was carried out on a TGA Q500 differential thermal analyzer. The samples were heating in  $N_2$  stream (60 mL/min) from room temperature to 800°C with a heating rate of 10°C/min.

*Ultraviolet-visible (UV-vis) Diffuser Reflectance Spectra*. UV-vis diffuse reflectance characterization was performed on a Agilent Carry 5000 spectrophotometer equipped with an integrating sphere, using 100% BaSO<sub>4</sub> as reflectance standard for all measurements.

*Time-resolved Photoluminescence*. Time-resolved emission data was collected at room temperature using steady state/transient state fluorescence/phosphorescent spectrometer equipped with time-correlated single photon counting (TCSPC) system (FLUOROLOG-3-11). Excitation light with the specific wavelength was provided by an EPL-360PS pulsed diode laser. The average lifetime was calculated according to the following equation:

 $\tau_{avg} = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} \quad i=1,2,3...$ 

where  $a_i$  represents the amplitude of each component and  $\tau_i$  represents the decay time.

*X-ray Photoelectron Spectra (XPS)* The date were recorded on an AXIS ULTRA ALD spectrometer to analyze the valence state of elements in cryatalline materials.

*Electrochemical Measurements.* The working electrode was prepared by loading different catalysts on the ITO conductive glass. Specifically, 5 mg of catalyst was firstly dispersed in a mixture containing H<sub>2</sub>O (500  $\mu$ L), ethanol (500  $\mu$ L) and 5 wt.% Nafion solution (10  $\mu$ L) under ultrasonic condition for 30 min to obtain a mixture. Then, an ITO slide was coated with 5  $\mu$ L of slurry with an area of 0.5 cm<sup>2</sup> and dried at 60 °C for 6 hours to serve as the working electrode. The electrochemical impedance spectra (EIS) analysis and photocurrent response were measured on a Chenhua CHI-760E electrochemical workstation using a standard three-electrode cell with a Pt foil as the counter electrode, an Ag/AgCl electrode as the reference electrode, an aqueous Na<sub>2</sub>SO<sub>4</sub> solution (0.1 mol·L<sup>-1</sup>) as the electrolyte solution. All of the electrochemical data were collected under 300 W Hg lamp without any cutoff filter.

**Photocatalytic Experiments.** Typically, 10 mg of photocatalyst was dispersed in 10 mL CH<sub>3</sub>CN and 10  $\mu$ L (0.1 mmol) benzylamine under ultrasonication. And then the suspension was injected into the photoreactor, sealed with O<sub>2</sub> balloon (1 atm) and followed by the 300 W Hg lamp irradiation. After the reaction, the solution was concentrated, and analyzed by 'H NMR.

*Recyclability of Oxidative Coupling of Benzylamine over TJU-18.* After the reaction indicated above, the reaction solution was centrifuged at 12000 rpm for 2 min after each cycle and washed with  $CH_3CN$  2 times. Then the catalyst was reused for the subsequent run with fresh benzylamine (0.1 mmol) under the optimized reaction conditions.

*Theoretical band calculation.* The single crystal data of TJU-18(Pb/Zn) and TJU-18(Pb/Mn) were directly used to calculate the electronic band structure in Castep software. The total energy was calculated with density functional theory (DFT) using Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation. The interactions between the ionic cores and the electrons were described by the norm-conserving pseudopotential. Other calculating parameters and convergence criteria were set by the default values of the CASTEP code.

*Effective mass calculation.* The electronic structures were computed by Vienna ab initio Simulation package (VASP) of density functional theory (DFT). The projector augmented wave (PAW) model with Perdew–Burke–Ernzerhof (PBE) function was employed to describe the interactions between core and electrons. An energy cutoff of 450 eV was used for the planewave expansion of the electronic wave function. The Brillouin zones of all systems were sampled with gamma-point centered Monkhorst–Pack grids. A  $3 \times 3 \times 2$  Monkhorst Pack k-point setup were used for slab geometry optimization. The force and energy convergence criterion were set to 0.02 eV Å<sup>-1</sup> and  $10^{-5}$  eV, respectively.

## **Supporting Tables and Figures**

	TJU-18(Pb/Mn)	TJU-18(Pb/Co)	
Empirical formula	C <sub>6</sub> H <sub>13</sub> Br <sub>9</sub> MnO <sub>8</sub> Pb <sub>8</sub>	C <sub>6</sub> H <sub>13</sub> Br <sub>9</sub> CoO <sub>8</sub> Pb <sub>8</sub>	
Formula weight	2643.81	2647.80	
Temperature(K)	279(2)	279(2)	
Wavelength(Å)	0.71073	0.71073	
Crystal system	monoclinic	monoclinic	
Space group	P2/n	P2/n	
<i>a</i> (Å)	9.667(4)	9.6100(19)	
<i>b</i> (Å)	9.179(4)	9.175(2)	
<i>c</i> (Å)	18.133(8)	17.977(4)	
α (°)	90	90	
$\beta$ (°)	92.309(16)	92.612(7)	
γ (°)	90	90	
V (Å), Z	1607.6(12), 2	1583.3(6), 2	
$\rho_{calc}$ (g cm <sup>-3</sup> )	5.492	5.554	
F(000)	2216.0	2220.0	
2θ range /deg	4.976-54.994	6.142-52.808	
Crystal size (mm <sup>3</sup> )	0.2×0.19×0.05	0.3×0.15×0.06	
Limiting indices	$-12 \le h \le 12$	$-12 \le h \le 11$	
	$-11 \le k \le 11$	$-11 \le k \le 11$	
	$-23 \le l \le 23$	$-22 \le l \le 22$	
Reflections collected	30047	26721	
Independent reflections	3663	3239	
Absorption correction	Empirical	Empirical	
Data/restraints/parameters	3663/6/146	3239/30/147	
Goodness-of-fit on $F^2$	1.073	1.295	
Final R indices [I>2sigma(I)]	$R_1 = 0.0485$	$R_1 = 0.0976$	
	wR <sub>2</sub> =0.1278	wR <sub>2</sub> =0.2759	
R indices (all data)	$R_1 = 0.0548$	$R_1 = 0.1019$	
	wR <sub>2</sub> =0.1329	wR <sub>2</sub> =0.2823	

 Table S1. Crystallographic data and structural refinement for TJU-18

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

	TJU-18(Pb/Zn)		TJU-18(Pb/Mn)	
effective mass*	electron	hole	electron	hole
G→Z	-1.977	-2.793	118.532	12.822
G→B	-2.020	-1.968	0.243	0.540
G→A	-5.674	-43.016	7.287	31.011

**Table S2.** Calculated effective mass ( $m_0$  unit) in the different directions of the holes and electrons of TJU-18(Pb/Zn) and TJU-18(Pb/Mn).

\* Effective mass is obtained by fitting a third order polynomial, which yields the mass values that are less sensitive to the employed k-points.



**Figure S1.** Crystallographic view of a single  $[Pb_8Br_8O(OH)]^{5+}$  layer connected with Pb-Br bond. (Pb light blue, Br orange).



**Figure S2.** Thermogravimetric analysis of TJU-18(Pb/Mn), TJU-18(Pb/Co), TJU-18(Pb/Ni), TJU-18(Pb/Zn).



**Figure S3.** PXRD patterns of TJU-18(Pb/Mn) before and after 24 h in different relative humidity.



**Figure S4.** Kubelka-Munk plot of TJU-18(Pb/Mn), the extrapolation of the linear region estimates the bandgap value of  $\sim$ 3.27 eV.



**Figure S5.** Kubelka-Munk plot of TJU-18(Pb/Co), the extrapolation of the linear region estimates the bandgap value of ~3.25 eV.



**Figure S6.** Kubelka-Munk plot of TJU-18(Pb/Ni), the extrapolation of the linear region estimates the bandgap value of ~3.23 eV.



**Figure S7.** The estimated VB of ~1,10 eV, ~1.50 eV ~1.07 eV and ~1.02 eV for TJU-18(Pb/Mn), TJU-18(Pb/Co), TJU-18(Pb/Ni), TJU-18(Pb/Zn), respectively.



Figure S8. Density of states of TJU-18(Pb/Zn).



Figure S8. Density of states of TJU-18(Pb/Mn).



Figure S10. Photoluminescence decay curves of TJU-18(Pb/Mn).



Figure S11. Photoluminescence decay curves of TJU-18(Pb/Co).



Figure S12. Photoluminescence decay curves of TJU-18(Pb/Ni).



Figure S13. <sup>1</sup>H NMR spectrum of benzylamine (600 MHz, CD<sub>3</sub>CN).



**Figure S14.** <sup>1</sup>H NMR spectrum of (*E*)-N-benzyl-1-phenylmethanimine (600 MHz, CD<sub>3</sub>CN).



1.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3. f1 (ppm)

**Figure S15.** <sup>1</sup>H NMR spectrum of benzylamine catalyzed by TJU-18(Pb/Zn) (600 MHz, CD<sub>3</sub>CN).



**Figure S16.** <sup>1</sup>H NMR spectrum of benzylamine catalyzed by TJU-18(Pb/Zn) in different cycles (600 MHz, CD<sub>3</sub>CN).

## References

- S1. APEX-II, 2.1.4, Bruker-AXS: Madison, WI, 2007.
- S2. *SHELXTL, Crystal Structure Determination Package*, Bruker Analytical X-ray Systems Inc.: Madison, WI, 1995~99.
- S3. Brandenburg, K.; Putz, H., Diamond, Crystal Impact, Bonn, Germany, 2007.