Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2023

## **Supporting Information**

## Continuous Synthesis of All-inorganic Low-dimensional Bismuth-based Metal

# Halides Cs<sub>4</sub>MnBi<sub>2</sub>Cl<sub>12</sub> from Reversible Precursors Cs<sub>3</sub>BiCl<sub>6</sub> and Cs<sub>3</sub>Bi<sub>2</sub>Cl<sub>9</sub> under

#### **Phase Engineering**

Chunli Zhao<sup>1</sup>, Yuan Gao<sup>1,2\*</sup>, Jianbei Qiu<sup>1,2\*</sup>

<sup>1</sup>Faculty of Material Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

<sup>2</sup>Key Lab. of Advanced Materials of Yunnan Province, Kunming 650093, China

### **Corresponding Author**

\*E-mail: Yuan Gao (1251719335@qq.com); Jianbei Qiu (qiu@kust.edu.cn).



**Figure S1.** (a) Crystal structure of  $Cs_3BiCl_6$ . (b) XRD pattern of  $Cs_3BiCl_6$  compared to the simulated pattern (PDF#22-0171). (c) Crystal structure of  $Cs_3Bi_2Cl_9$ . (d) XRD pattern of  $Cs_3Bi_2Cl_9$  compared to the simulated pattern (PDF#70-0990).



Figure S2. The XRD patterns of  $Cs_3BiCl_6$  / $Cs_3Bi_2Cl_9$  and their continuous phase transformation after adding CsCl and BiCl\_3, respectively.



Figure S3. XRD patterns of  $Cs_3BiCl_6$  as precursor, after adding  $CsCl+MnCl_2.H_2O+BiCl_3$ , and synthesized  $Cs_4MnBi_2Cl_{12}$  phosphor.



Figure S4. XRD patterns of  $Cs_3Bi_2Cl_9$  as precursor, after adding  $CsCl+MnCl_2.H_2O$ , and synthesized  $Cs_4MnBi_2Cl_{12}$  phosphor.



Figure S5. XPS spectra of Mn in Cs<sub>4</sub>MnBi<sub>2</sub>Cl<sub>12</sub> phosphor.



Figure S6. (a) The EDS spectrum of  $Cs_3BiCl_6$ . (b) The EDS spectrum of  $Cs_3Bi_2Cl_9$ . (c) The EDS spectrum of  $Cs_4MnBi_2Cl_{12}$ , respectively.



Figure S7. Selected diffraction peaks near  $23.5^{\circ}$  of  $Cs_4Mn_{1-x}Cd_xBi_2Cl_{12}$  (x=0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0).



Figure S8. The measurement results of the optimal PLQY of (a)  $Cs_4MnBi_2Cl_{12}$  and (b)  $Cs_4Mn_{0.3}Cd_{0.7}Bi_2Cl_{12}$ .



**Figure S9.** PL decay curves by monitoring Visible emission ( $\lambda_{em} = 950 \text{ nm}$ ) for the Cs<sub>4</sub>MnBi<sub>2</sub>Cl<sub>12</sub> and Cs<sub>4</sub>Mn<sub>0.3</sub>Cd<sub>0.7</sub>Bi<sub>2</sub>Cl<sub>12</sub> phosphor.



Figure S10. Temperature-dependent PL spectra for Cs<sub>4</sub>Mn<sub>0.3</sub>Cd<sub>0.7</sub>Bi<sub>2</sub>Cl<sub>12</sub>.



Figure S11. Schematic energy-level diagram illustrating the possible energy-transfer mechanism in  $Cs_4Mn_{0.3}Cd_{0.7}Bi_2Cl_{12}$  sample under UV excitation.



Figure S12. Thermogravimetric analysis graph of  $Cs_4Mn_{0.3}Cd_{0.7}Bi_2Cl_{12}$ .



Figure S13. XRD patterns of the fresh  $Cs_4Mn_{0.3}Cd_{0.7}Bi_2Cl_{12}$  sample and after exposing in air for 50 days.



Figure S14. The (a) XRD patterns and (b) photoluminescence of thermal stability of the  $Cs_4Mn_{0.3}Cd_{0.7}Bi_2Cl_{12}$  under 373 K heat.