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## **Supplementary Information**

## Sn<sup>2+</sup> doping-induced large extra vibrational energy of excited state for

## efficient blue emission in Cs<sub>2</sub>SnCl<sub>6</sub>: Bi

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Figure S1. The XRD Rietveld refinement of  $Sn^{2+}$ : 0.08% Bi and  $Sn^{4+}$ : 0.04% Bi.



Figure S2. PL spectra for PLQY of Cs<sub>2</sub>SnCl<sub>6</sub>: Bi at room temperature.



Figure S3. PL spectra of the  $Cs_2SnCl_6$ : Bi samples synthesized by  $SnCl_2$  or  $SnCl_4$  precursor.



Figure S4. (a) PLQY and (b) PL spectra of the samples synthesized by different ratio of  $Sn^{2+}$  and  $Sn^{4+}$  in precursor solutions.



Figure S5. Full-scan XPS spectra of Sn<sup>4+</sup>: Bi@H<sub>3</sub>PO<sub>2</sub> and Sn<sup>4+</sup>: Bi.



Figure S6. PL intensity of  $Sn^{4+}$ : Bi and  $Sn^{4+}$ : Bi@H<sub>3</sub>PO<sub>2</sub> at different temperatures under UV light.



Figure S7. Integrated PL intensity as a function of temperature of (a)  $Sn^{2+}: 0.08\%$  Bi and (b)  $Sn^{4+}: 0.04\%$  Bi.