## **Supporting information**

## Narrow-band red-emitting KZnF<sub>3</sub>: Mn<sup>4+</sup> fluoroperovskite: insights into electronic/vibronic transition and thermal quenching behavior

Tao Hu,<sup>a</sup> Hang Lin,<sup>a,\*</sup> Fulin Lin,<sup>a,b</sup> Yan Gao,<sup>a</sup> Yao Cheng,<sup>a</sup> Ju Xu,<sup>a</sup> Yuansheng Wang<sup>a,\*</sup>

<sup>a</sup> CAS Key Laboratory of Design and Assembly of Functional Nanostructures, and Fujian Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002 (P. R. China);

<sup>b</sup> Xiamen Institute of Rare-earth Materials, Haixi Institutes, Chinese Academy of Sciences, Xiamen, Fujian 361000 (P. R. China)



Fig. S1 SEM image of KZnF3: Mn<sup>4+</sup>



Fig. S2 PL spectra of KZnF<sub>3</sub>:  $Mn^{4+}$  and  $K_2SiF_6$ :  $Mn^{4+}$ 



Fig. S3 PLE spectra of KZnF<sub>3</sub>: Mn<sup>4+</sup> and KZnF<sub>3</sub> by monitoring at 633 nm and 400 nm emission, respectively. The dash peaks are the two Gaussian-fitted peaks for KZnF<sub>3</sub>: Mn<sup>4+</sup>



Fig. S4 The enlarged view at ZPLs of  $K_2 TiF_6$ :  $Mn^{4+}$  and  $KZnF_3$ :  $Mn^{4+}$  at 10 K



Fig. S5 Schematic illustration of the influence of  $Mn^{4+}$ :  ${}^{4}T_{2g}$  location on thermal activation energy  $\Delta E$  of  $Mn^{4+}$