

***Electronic Supplementary Information (ESI)***

**Red-emitting phosphors  $\text{APF}_6:\text{Mn}^{4+}$  ( $\text{A} = \text{Cs}^+, \text{Rb}^+, \text{K}^+$ ): synthesis,  
luminescent properties and application in solid-state lighting**

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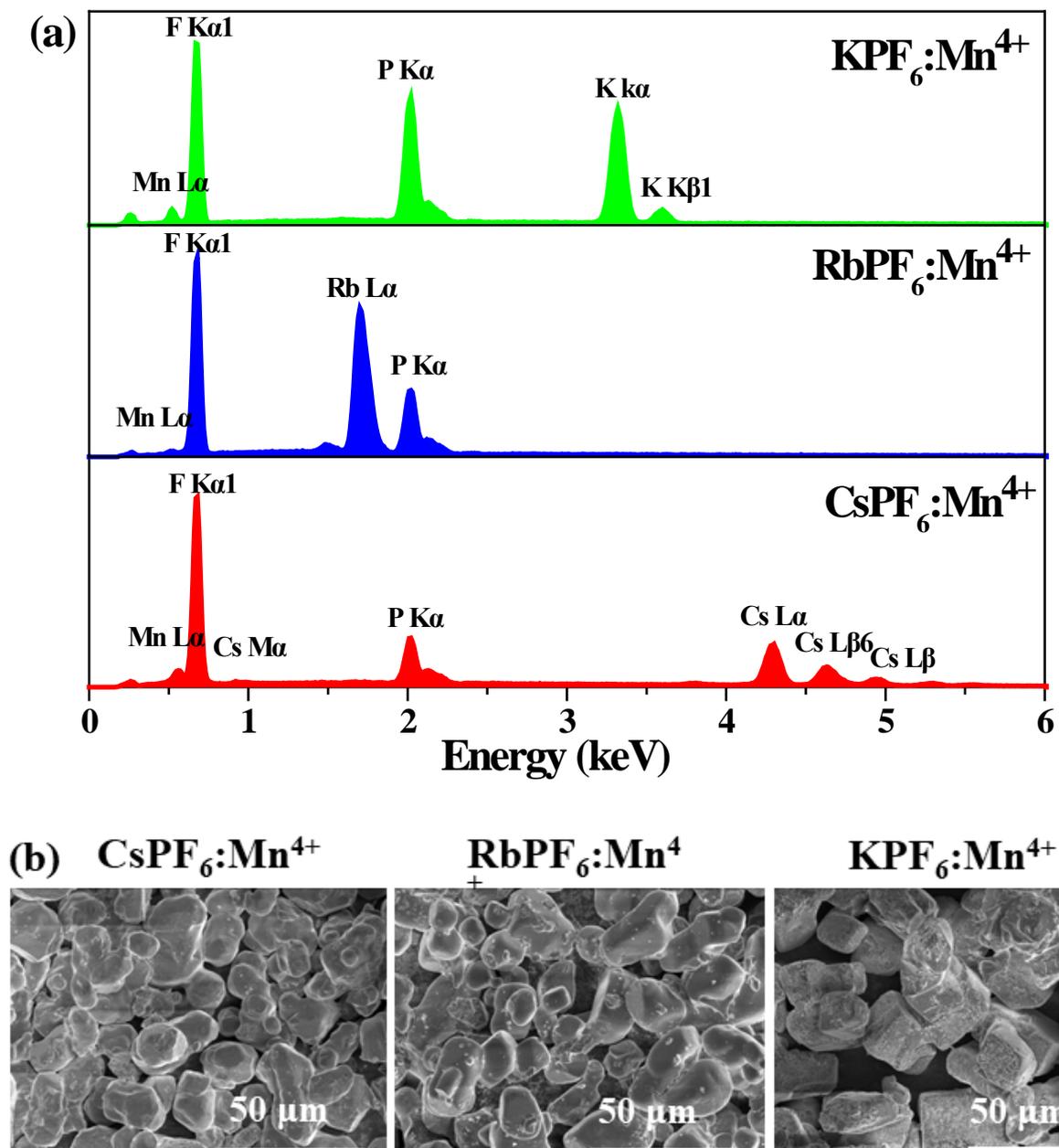


Fig. S1 (a) EDS spectra and (b) SEM images of  $\text{APF}_6:\text{Mn}^{4+}$ .

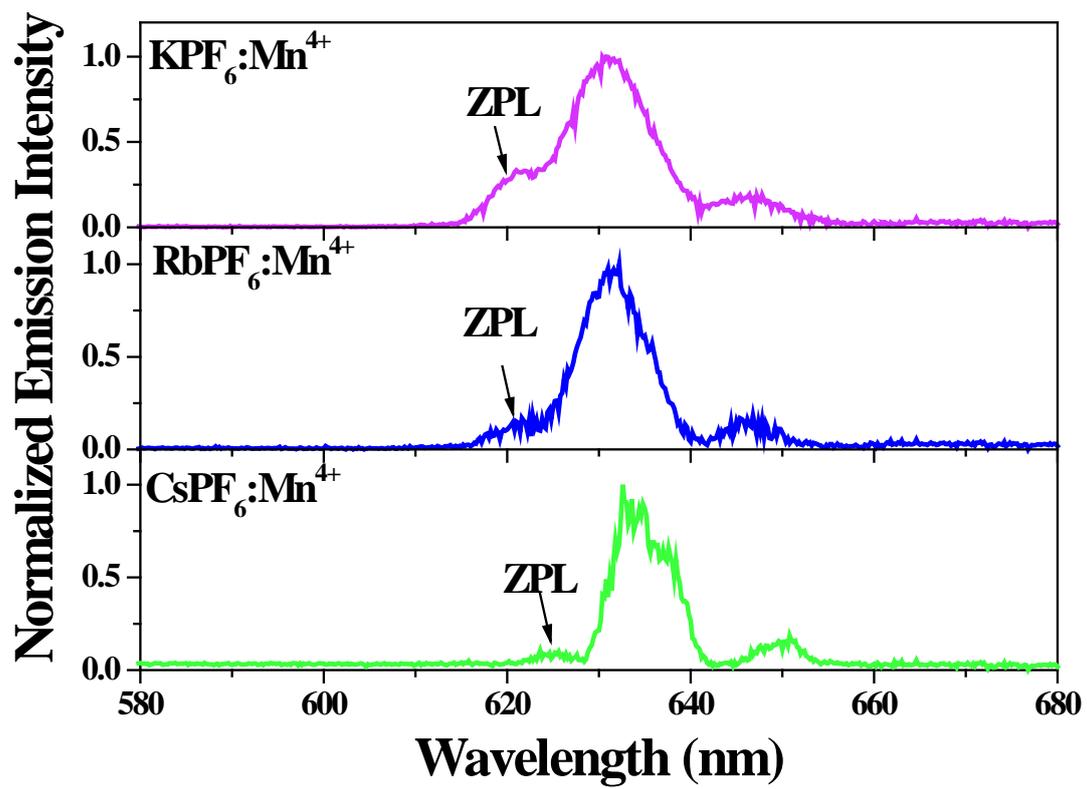


Fig. S2 Emission spectra of APF<sub>6</sub>:Mn<sup>4+</sup> at 77 K

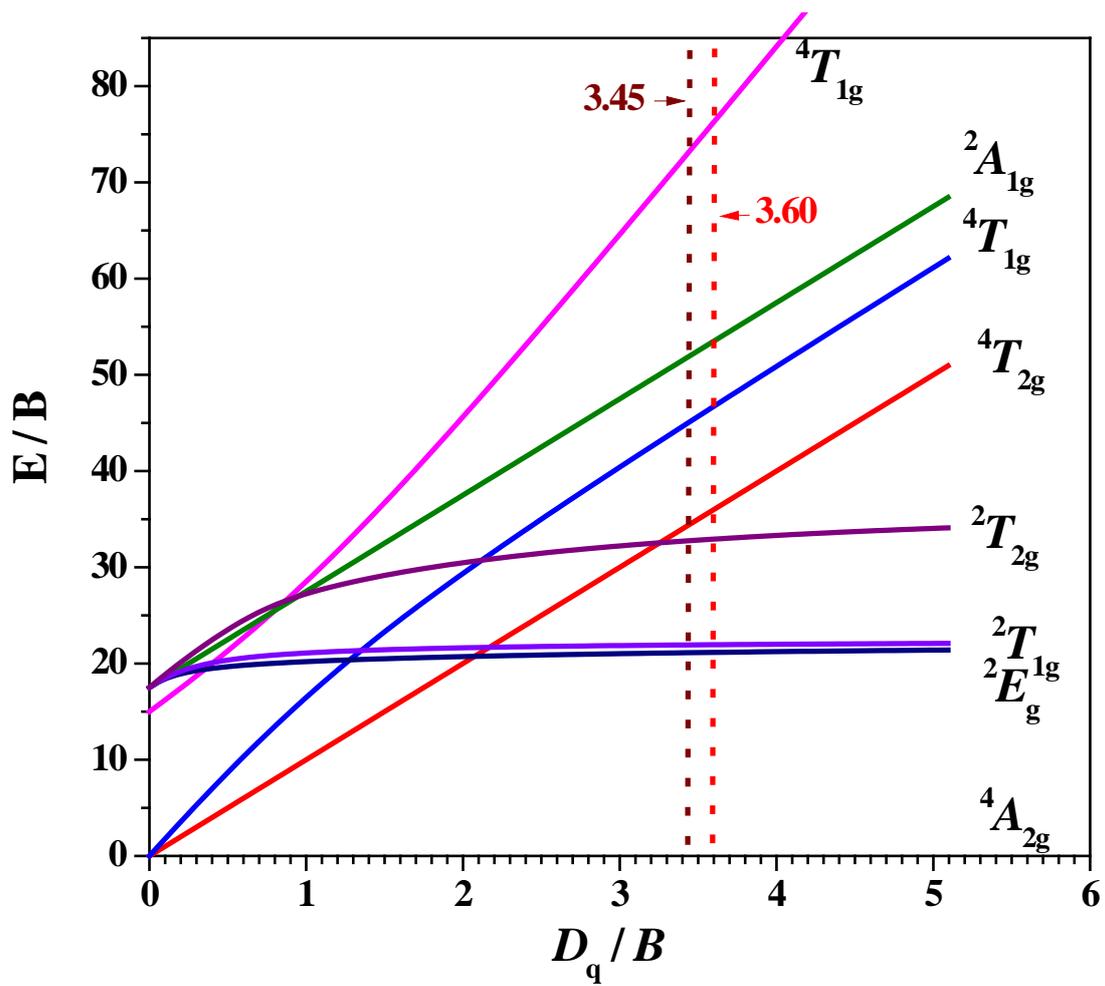


Fig. S3 Tanabe–Sugano energy-level diagram of  $Mn^{4+}$  in an octahedral crystal field.

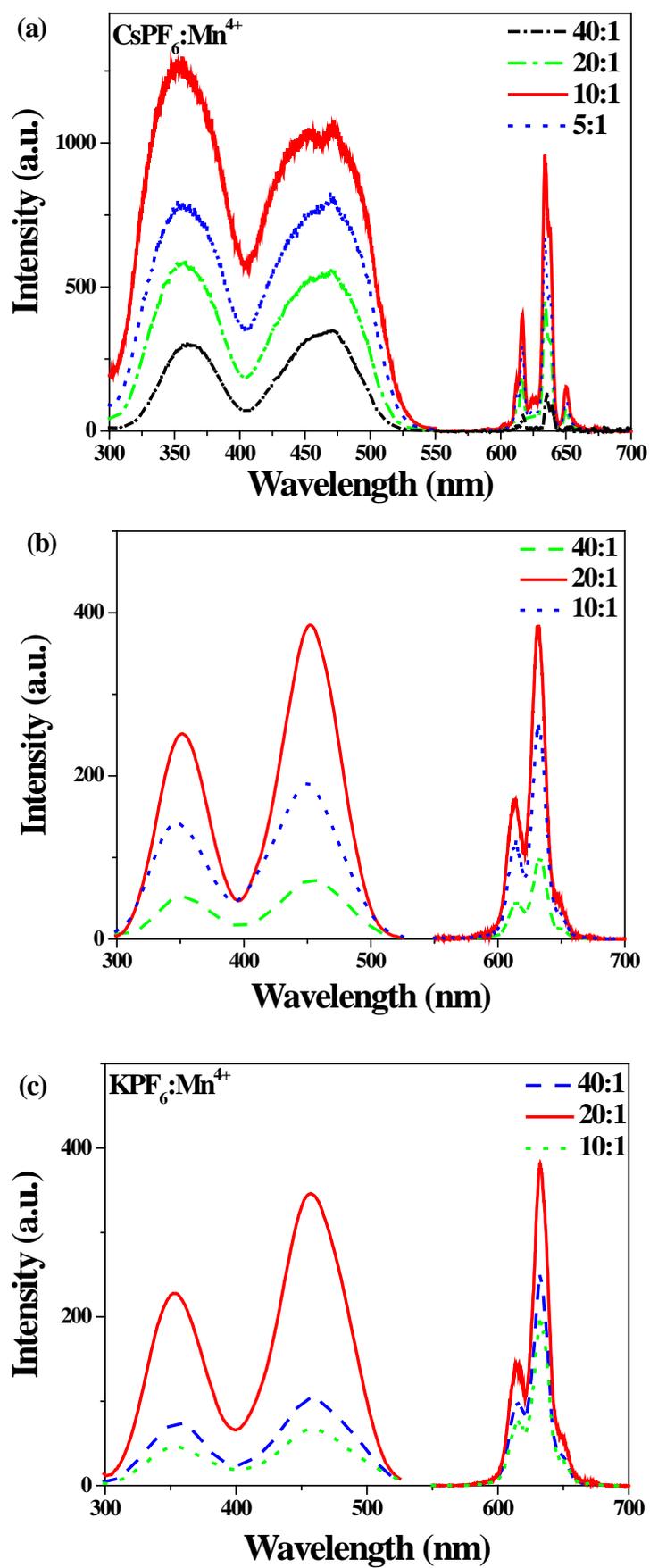
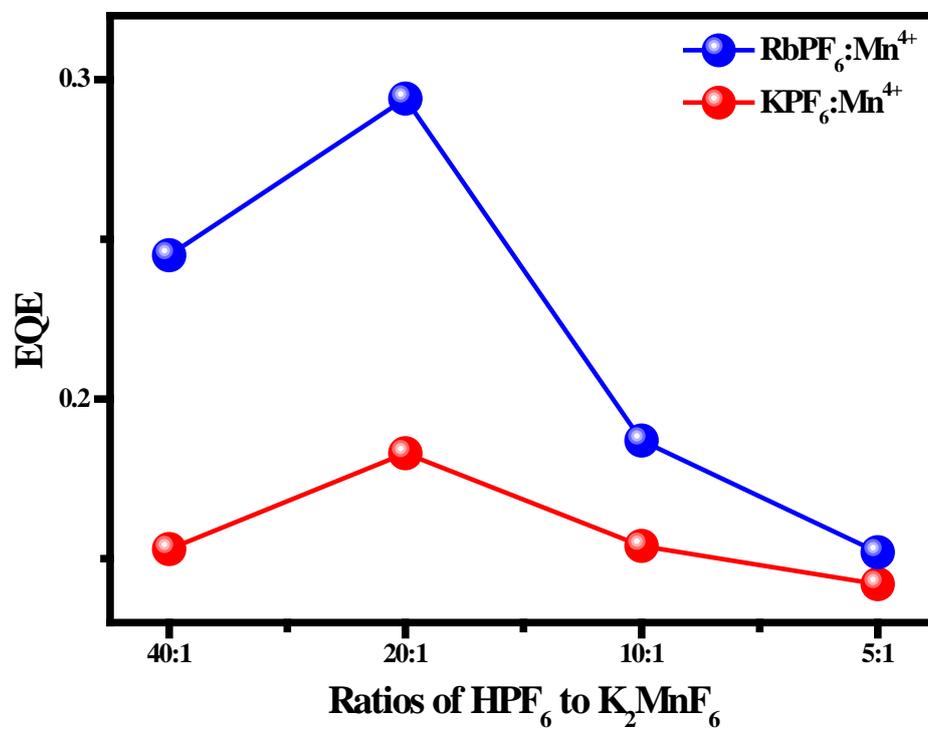
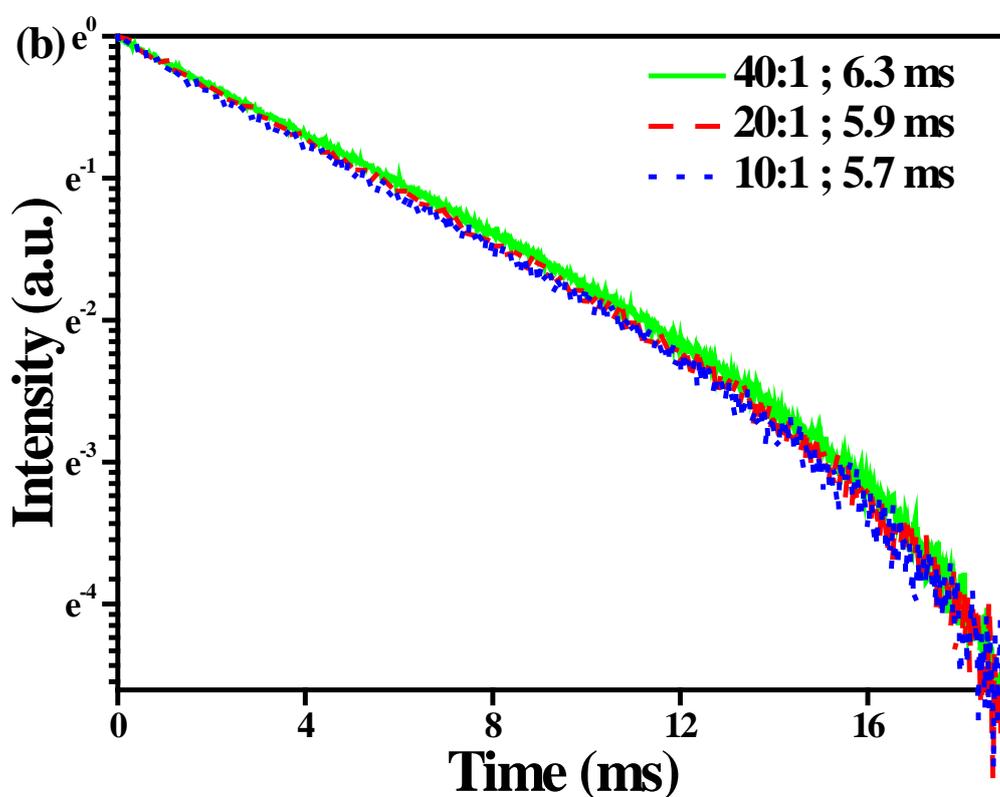
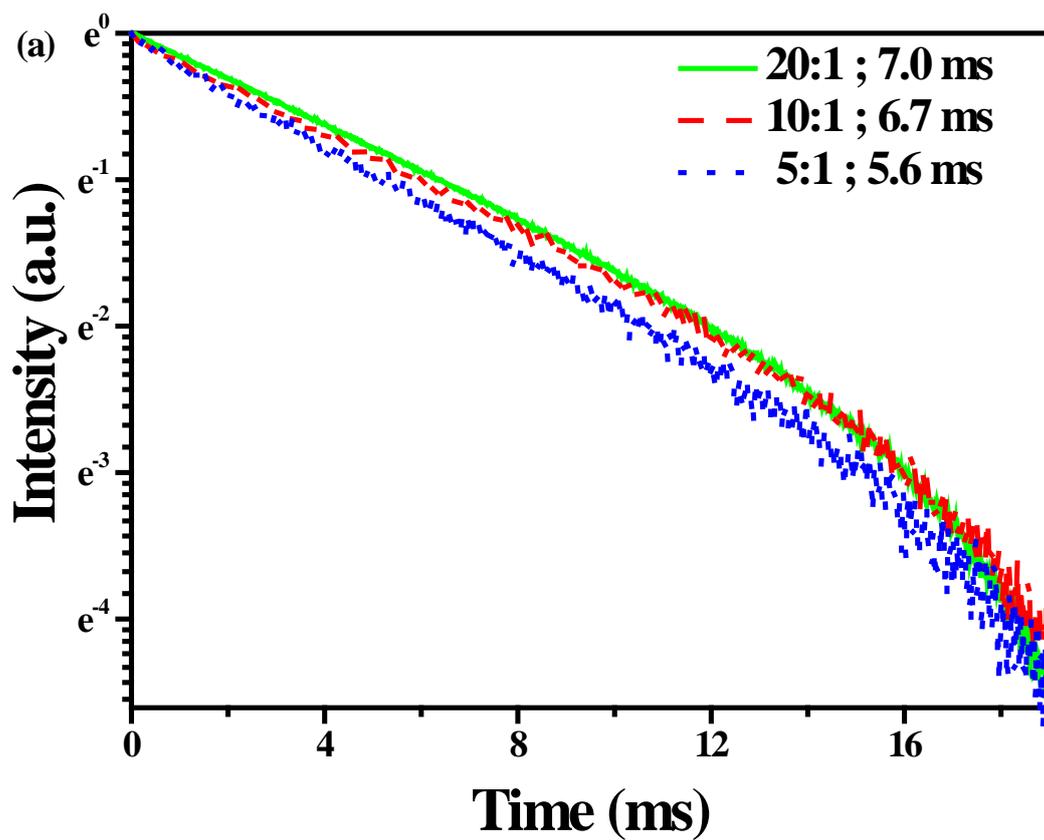


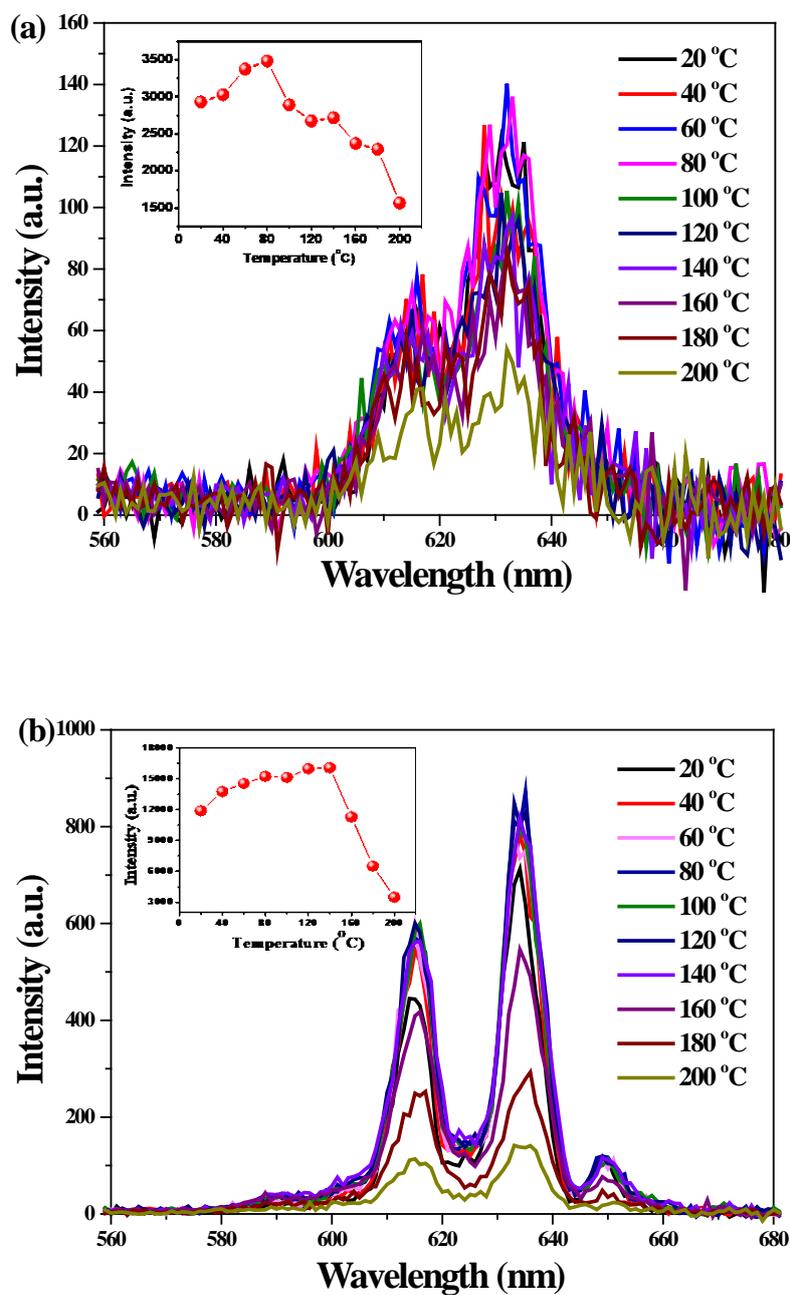
Fig. S4 PL spectra of APF<sub>6</sub>:Mn<sup>4+</sup> with different amounts of Mn<sup>4+</sup>



**Fig. S5** EQE of RbPF<sub>6</sub>:Mn<sup>4+</sup> and KPF<sub>6</sub>:Mn<sup>4+</sup> prepared with different molar ratio of HPF<sub>6</sub> to K<sub>2</sub>MnF<sub>6</sub>



**Fig. S6** Decay curves of transitions  ${}^2E_g \rightarrow {}^4A_{2g}$  of Mn<sup>4+</sup> in (a) RbPF<sub>6</sub>:Mn<sup>4+</sup> and (b) KPF<sub>6</sub>:Mn<sup>4+</sup> prepared with different molar ratios of HPF<sub>6</sub> to K<sub>2</sub>MnF<sub>6</sub> (40:1, 20:1, 10:1)



**Fig. S7** Emission spectra of (a) RbPF<sub>6</sub>:Mn<sup>4+</sup> and (b) KPF<sub>6</sub>:Mn<sup>4+</sup> prepared with the HPF<sub>6</sub>/K<sub>2</sub>MnF<sub>6</sub> molar ratio of 10:1 at different temperatures. The inserted figures are the temperature dependence of emission intensity of RbPF<sub>6</sub>:Mn<sup>4+</sup> and KPF<sub>6</sub>:Mn<sup>4+</sup>

**Table S1** The contents of Mn<sup>4+</sup> in CsPF<sub>6</sub>:Mn<sup>4+</sup> prepared with different molar ratios between HPF<sub>6</sub> and K<sub>2</sub>MnF<sub>6</sub>

Samples	Molar ratios of HPF <sub>6</sub> : K <sub>2</sub> MnF <sub>6</sub>	Doping amount of Mn <sup>4+</sup> (mol %)
1	40 : 1	0.84
2	20 : 1	2.28
3	10 : 1	<b>3.58</b>
4	5 : 1	11.91

**Table S2** The contents of Mn<sup>4+</sup> in RbPF<sub>6</sub>:Mn<sup>4+</sup> prepared with different molar ratios between HPF<sub>6</sub> and K<sub>2</sub>MnF<sub>6</sub>

Samples	Molar ratios of HPF <sub>6</sub> : K <sub>2</sub> MnF <sub>6</sub>	Doping amount of Mn <sup>4+</sup> (mol %)
1	40 : 1	1.13
2	20 : 1	<b>3.18</b>
3	10 : 1	6.55
4	5 : 1	15.59

**Table S3** The contents of Mn<sup>4+</sup> in KPF<sub>6</sub>:Mn<sup>4+</sup> prepared with different molar ratios between HPF<sub>6</sub> and K<sub>2</sub>MnF<sub>6</sub>

Samples	Molar ratios of HPF <sub>6</sub> : K <sub>2</sub> MnF <sub>6</sub>	Doping amount of Mn <sup>4+</sup> (mol %)
1	40 : 1	1.56
2	20 : 1	<b>3.84</b>
3	10 : 1	7.34
4	5 : 1	16.00