## **Supporting Information**

Site-Sensitive Energy Transfer Modes in  $Ca_3Al_2O_6$ :  $Ce^{3+}/Tb^{3+}/Mn^{2+}$  Phosphors

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Fiugre S1. The comparison of PLE spectra of  $Tb^{3+}/Mn^{2+}$  and PL spectra of  $Ce^{3+}$  in

Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>, showing different spectral overlap manners.



**Figure S2**. PLE spectra of  $Ca_{3(0.96-y)}Al_2O_6$ : 0.06Ce<sup>3+</sup>, 0.06Li<sup>+</sup>, 3*y*Tb<sup>3+</sup> monitored at 542 nm. Excitation bands contain several bands. The highest one is at ~305 nm with a shoulder at ~335 nm, which belongs to *f-d* transition of Ce<sup>3+</sup>, suggesting energy transfer from Ce<sup>3+</sup> to Tb<sup>3+</sup>. An additional band at ~367 nm appears when *y* is higher than 0.04. This phenomenon indicates the existence of purplish-blue Ce<sup>3+</sup> and the transfer of its energy to Tb<sup>3+</sup> with a high content. Furthermore, the excitation bands at about 245, 263 and 283 nm are consistent with that of Tb<sup>3+</sup> single-doped one.



**Figure S3**. PLE spectra of  $Ca_{3(0.96-z)}Al_2O_6$ : 0.06Ce<sup>3+</sup>, 0.06Li<sup>+</sup>, 3*z*Mn<sup>2+</sup> monitored at 635 nm. The excitation bands mainly two bands at 305 and ~ 335 nm, which are similar as that monitored at 470 nm. These results suggest energy transfer from greenish-blue Ce<sup>3+</sup> to Mn<sup>2+</sup>. In addition, a shoulder band at ~370 nm and several bands in 400-600 range appear, which originate from *d-d* transitions of Mn<sup>2+</sup> itself.