Supporting Information

Site-Sensitive Energy Transfer Modes in Ca$_3$Al$_2$O$_6$: Ce$^{3+}$/Tb$^{3+}$/Mn$^{2+}$ Phosphors

Jilin Zhang$^{a,b,*}$, Yani He$^{a,b}$, Zhongxian Qiu$^{a,b}$, Weilu Zhang$^{a,b}$, Wenli Zhou$^{a,b}$, Liping Yu$^{a,b}$, Shixun Lian$^{a,b,*}$

$^a$ Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), Hunan Normal University, Changsha 410081, China.

$^b$ Key Laboratory of Sustainable Resources Processing and Advanced Materials of Hunan Province College, Hunan Normal University, Changsha 410081, China.

*Corresponding Authors: Fax and Tel: +86 731 88865345; E-mail:
chemzhangjl@163.com (Jilin Zhang), shixunlian@gmail.com (Shixun Lian).
**Figure S1.** The comparison of PLE spectra of Tb$^{3+}$/Mn$^{2+}$ and PL spectra of Ce$^{3+}$ in Ca$_3$Al$_2$O$_6$, showing different spectral overlap manners.

**Figure S2.** PLE spectra of Ca$_{3(0.96-y)}$Al$_2$O$_6$: 0.06Ce$^{3+}$, 0.06Li$^+$, 3yTb$^{3+}$ 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$^{3+}$, suggesting energy transfer from Ce$^{3+}$ to Tb$^{3+}$. An additional band at ~367 nm appears when $y$ is higher than 0.04. This phenomenon indicates the existence of purplish-blue Ce$^{3+}$ and the transfer of its energy to Tb$^{3+}$ with a high content. Furthermore, the excitation bands at about 245, 263 and 283 nm are consistent with that of Tb$^{3+}$ single-doped one.
Figure S3. PLE spectra of Ca\textsubscript{3(0.96-z)}Al\textsubscript{2}O\textsubscript{6}: 0.06Ce\textsuperscript{3+}, 0.06Li\textsuperscript{+}, 3zMn\textsuperscript{2+} 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\textsuperscript{3+} to Mn\textsuperscript{2+}. In addition, a shoulder band at ~370 nm and several bands in 400-600 range appear, which originate from d-d transitions of Mn\textsuperscript{2+} itself.