# **Supporting Information**

# Broadband Near-Infrared Persistent Luminescence of Ba[Mg<sub>2</sub>Al<sub>2</sub>N<sub>4</sub>] with Eu<sup>2+</sup> -Tm<sup>3+</sup> after Red Light Charging

Jumpei Ueda\*<sup>+</sup>, Julius L. Leaño Jr.<sup>‡,∫,∞</sup>, Cyril Richard<sup>§</sup>, Kazuki Asami<sup>+</sup>, Setsuhisa Tanabe<sup>+</sup>, Ru-Shi Liu<sup>‡,◊</sup>

<sup>†</sup>Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

<sup>‡</sup> Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

<sup>f</sup>Nanoscience and Technology Program, Taiwan International Graduate Program, Academia Sinica, and National Taiwan University, Taipei 106, Taiwan

<sup>∞</sup> Philippine Textile Research Institute, Department of Science and Technology, Taguig City 1631, Philippines

<sup>§</sup>Unité de Technologies Chimiques et Biologiques pour la Santé (UTCBS); UMR 8258 CNRS; U 1022 Inserm; Université Paris Cité, Faculté des Sciences Pharmaceutiques et Biologiques, Paris, F-75270 cedex 06, France; Chimie-ParisTech, Paris F-75231 cedex 05, France

<sup>6</sup> Department of Mechanical Engineering and Graduate Institute of Manufacturing Technology National Taipei University of Technology Taipei 106, Taiwan

#### Tm-L<sub>3</sub> edge X-ray absorption near edge structure (XANES)

The Tm- $L_3$  edge was profiled from the synchrotron x-ray absorption near-edge structure in transmission mode at the BL17C1 beamline at NSRCC, Taiwan. The solid state approach involving high pressure and temperature under a reducing atmosphere could render the Tm<sub>2</sub>O<sub>3</sub> input from Tm<sup>3+</sup> to the reduced form Tm<sup>2+</sup>, as Eu<sup>3+</sup> is converted to Eu<sup>2+</sup> in the reaction. The Tm- $L_3$ -edge XANES reveals that the single Tm peak at 8650 eV corresponds to Tm<sup>3+</sup> with no indication of having Tm<sup>2+</sup>. Thus, emission of Tm<sup>3+</sup> charged via energy transfer from Eu<sup>2+</sup> account for the observed broadening to the NIR region of the observed emission.

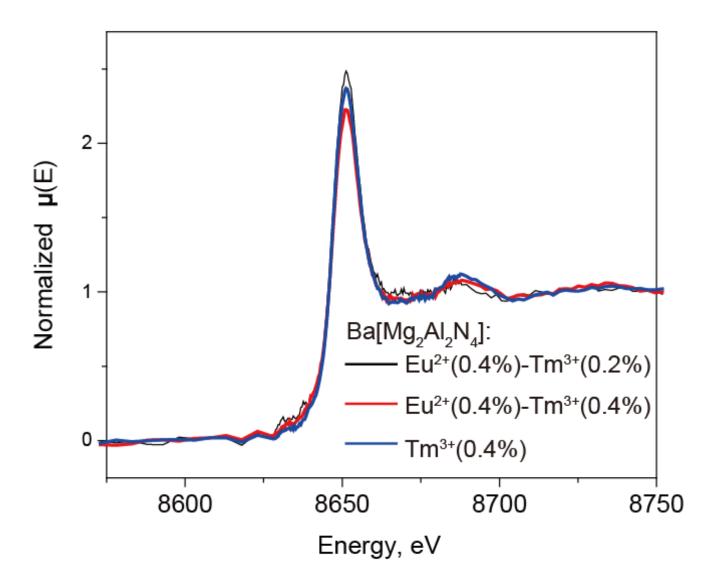


Figure S1. Tm L<sub>3</sub>-edge X-ray Absorption at Near-Edge Spectra of Ba[Mg<sub>2</sub>Al<sub>2</sub>N<sub>4</sub>]:Eu<sup>2+</sup>, Eu<sup>2+</sup>-Tm<sup>3+</sup>

## Luminescence decay curves for energy transfer.

Figure S2 shows luminescence decay curves of Ba[Mg<sub>2</sub>Al<sub>2</sub>N<sub>4</sub>]:Eu<sup>2+</sup>, Eu<sup>2+</sup>-Tm<sup>3+</sup>. The lifetime of Eu<sup>2+</sup>:5d in Eu<sup>2+</sup>-Tm<sup>3+</sup>-doped samples is slightly shorter than Eu<sup>2+</sup>-singly-doped sample.

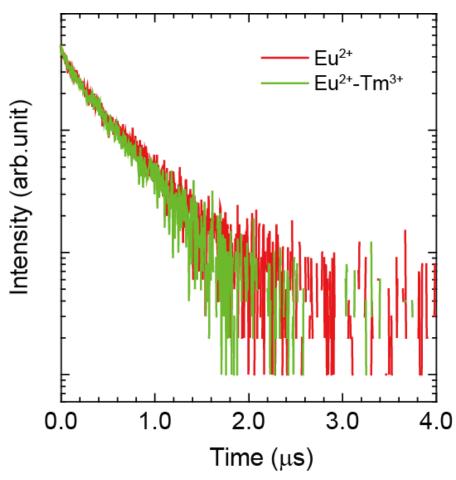


Figure S2. Luminescence decay curve monitoring 680 nm excited by 470 nm pico-second LED

### Thermoluminescence (TL) glow curves

TL glow curves of Ba[Mg<sub>2</sub>Al<sub>2</sub>N<sub>4</sub>]:Eu<sup>2+</sup>, Eu<sup>2+</sup>-Tm<sup>3+</sup> were measured after UV excitation as shown in Figure S3. Both TL glow curves are almost the same as each other. The Tm<sup>3+</sup> ion works as NIR luminescence, but not as trap center. The TL glow band has the peak temperature of 180 K and ranges up to around 350K. The peak temperature is not the best for the persistent phosphors at ambient temperature, but the small contribution at around 300 K in the TL glow curves is enough strong for detecting the persistent luminescence at room temperature for approximately 1 hour.

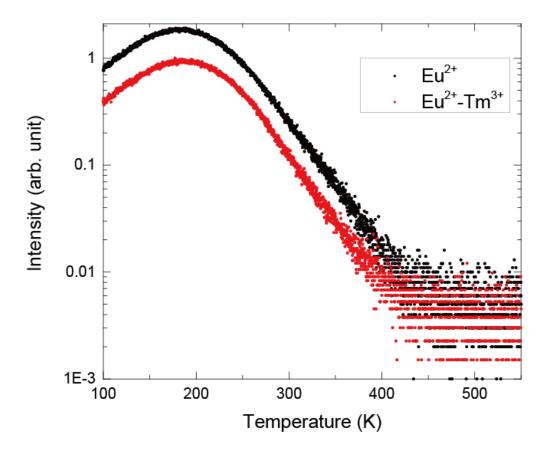
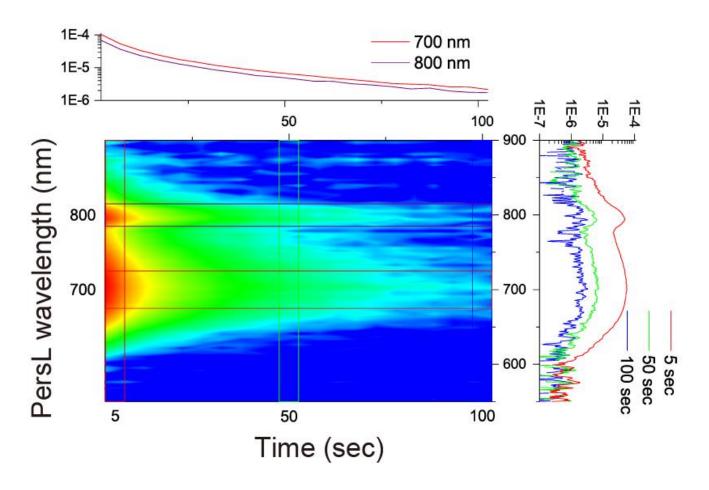


Figure S3. TL glow curves of Ba[Mg<sub>2</sub>Al<sub>2</sub>N<sub>4</sub>]:Eu<sup>2+</sup>, Eu<sup>2+</sup>-Tm<sup>3+</sup> after UV excitation

### Time course of PersL spectra.

The contour plot of the persistent luminescence time versus the persistent luminescence wavelength. The *y*-axis of the plot is persL wavelength and the *x*-axis is time in seconds. The persistent decay profiles of the emission peaks at 700 and 800 nm are plotted in the graph (top) is almost the same as each other. In addition, the PersL spectra at 5, 50 and 100 sec after ceasing 660 nm excitation shows  $Eu^{2+}$  and  $Tm^{3+}$  persistent luminescence bands, and spectral shape does not change. These results show that  $Tm^{3+}$ PersL is caused by energy transfer from  $Eu^{2+}$ .



**Figure S4.** Time course of PersL spectra of Ba[Mg<sub>2</sub>Al<sub>2</sub>N<sub>4</sub>]:Eu<sup>2+</sup>-Tm<sup>3+</sup> after 660 nm charging.

# Charging properties for Ba[Mg2Al2N4]:Eu<sup>2+</sup>

The charging wavelength vs emission wavelength contour plot for persistent luminescence intensity in Ba[Mg<sub>2</sub>Al<sub>2</sub>]N<sub>4</sub>:Eu<sup>2+</sup>. The persistent luminescence of Eu<sup>2+</sup>:5d-4f transition was observed after UV to red light charging. In the PersL excitation spectrum, the host exciton band below 400 nm and Eu<sup>2+</sup>:4f-5d band in the ranger from 400 to 700 nm were observed.

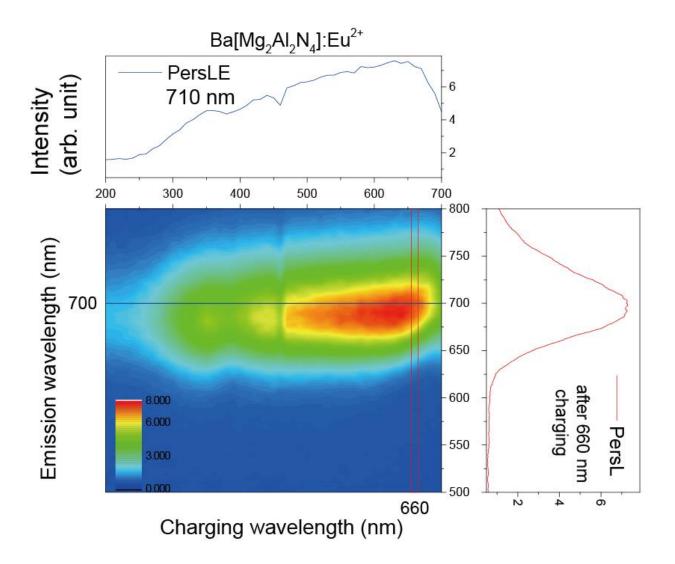


Figure S5. Charging wavelength vs emission wavelength contour plot for persistent luminescence intensity in  $Ba[Mg_2Al_2N_4]:Eu^{2+}$ .