# Electronic Supplementary Information for:

## Remarkable photoluminescence on Europium (II)-doped phosphate

### cyan@red emitting phosphors with highly dispersed luminescence

#### centers

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#### **Experimental Section**

**Chemicals and Materials.** The raw materials used in this work were commercially available CaCO<sub>3</sub> (AR), Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (AR), and Eu<sub>2</sub>O<sub>3</sub> (99.99%) from Shanghai Aladdin Biochemical Technology Co., Ltd, China. Nitric acid (HNO<sub>3</sub>, AR) and ammonium hydroxide (NH<sub>4</sub>OH, AR) were purchased from Baiyin Chemical Reagent Factory, China. All chemicals were used without further purification.

**Preparation.** In the synthesis of  $Ca_4(PO_4)_2O$  host, the stoichiometric amounts of raw materials were weighed and mixed thoroughly in an agate mortar. Then, the powder mixtures were placed in an alumina crucible and sintered at 1400 °C for 5 hr in tubular furnace under a flow condition of 3% H<sub>2</sub>/N<sub>2</sub> gas (100 mL/min) or in air. A series of Ca<sub>4-x</sub> (PO<sub>4</sub>)<sub>2</sub>O:  $xEu^{2+}$  (x = 0 - 0.2) phosphors were prepared by the simple deposition-precipitation (DP) method and subsequent heat-treatment. The precursor solution of  $Eu^{3+}$  ions can be obtained by addition of  $Eu_2O_3$  (0 - 0.55 mmol) in 50 mL aqueous solution (pH =  $\sim$ 2, adjusted by nitric acid) and pH of the precursor solution was then adjusted to  $\sim 6$  by adding ammonium hydroxide solution. During a typical deposition-precipitation process, 2 g of Ca<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>O host was immersed in the precursor solution of  $Eu^{3+}$  ions (pH = ~2 or ~6) with vigorous magnetic stirring under ambient conditions. And then, pH value of the solution was adjusted to ~10 by addition of ammonia. The obtained precipitate was separated by centrifugation, washed with deionized water for several times and dried at 60 °C. After sintering at 1400 °C under a reducing atmosphere, the samples were cooled with the furnace and the final phosphor powders were generated. The phosphor for comparison was

prepared at 1400 °C under a reducing condition of 3%  $H_2/N_2$  through a traditional solid-state reaction (SSR) method.

**Characterization.** The phase purity of the samples were analyzed by powder X-ray diffraction (XRD; XRD-7000S, Shimadzu) patterns with Cu K $\alpha$  radiation ( $\lambda$  = 0.15374 nm) operating at 40 kV and 20 mA using a step size of 0.02° (20) and a count time of 1 second per step. Photoluminescence (PL) spectra were recorded by a HITACH F-7000 fluorescence spectrophotometer with a 150 W Xe-lamp as the excitation source. The samples were packed into a sample holder and all the measurements were carried out at room temperature. The excitation and emission slits were both set at 2.5 nm. The photoluminescence decay curves of Eu<sup>2+</sup> doped phosphors were recorded recorded at the excitation and emission wavelengths of 460 nm and 640 nm on a spectrofluorometer (HJY, TRIAX550) with a laser source (Horizon, OPO system, 10 Hz). All the measurements were performed at room temperature. The structure, surface morphology and crystal crystalline planes of phosphors were examined by field emission electron microscopy (FESEM, JSM-7800F, JEOL) and high-resolution transmission electron microscopy (HRTEM, JEM-2100F) fitted with a field emission gun at an accelerating voltage of 200 kV (JEOL). Surface elemental mapping of the samples were analyzed by an energy dispersive Xray spectrometer (EDS) in conjunction with TEM. X-ray photoelectron spectroscopy (XPS) was performed to analyze the surface elements of powders by Thermofisher ESCALAB 250Xi, using monochromated Al source. All binding energies were referenced to the C1s peak at 284.6 eV.



**Fig. S1** (a) XRD patterns of  $Ca_{4-x}(PO_4)_2O$ :  $xEu^{2+}$  (x = 0.02-0.2) phosphors prepared by DP method (pH 6) and standard data (JCPDS 25-1137) for  $Ca_4(PO_4)_2O$  crystal. (b) The magnified XRD patterns in the 2 $\theta$  range of 28.5 - 30.5° for  $Ca_{4-x}(PO_4)_2O$ :  $xEu^{2+}$ (x = 0.02-0.2) phosphors prepared by DP method (pH of precursor solution was ~6). (c) Schematic crystal structure illustration of  $Ca_4(PO_4)_2O$  projected on the (001) plane.

As evidenced in Fig. S1a, all diffraction peaks of Eu<sup>2+</sup>-doped Ca<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>O phosphors can be well indexed to those of the monoclinic Ca<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>O phase (JCPDS no. 25-1137) with lattice constants of a = 7.023(1) Å, b = 11.986(4) Å, c = 9.473(2) Å and  $\beta$  $= 90.90(1)^{\circ}$  in space group P2<sub>1</sub>. The magnified XRD patterns in the 20 range of 28.5 -30.5° in Fig. S1b (ESI) shows a peak shift to lower diffraction angle with increasing Eu<sup>2+</sup> concentration (x), which reveals the expansion of unit cell due to the substitution of Ca<sup>2+</sup> ions by Eu<sup>2+</sup> ions with larger ionic radii.



**Fig. S2** Photoluminescence intensity and emission band as a function of  $Eu^{2+}$  content (x) for Ca<sub>4-x</sub>(PO<sub>4</sub>)<sub>2</sub>O: xEu<sup>2+</sup> (x = 0.02-0.2) phosphors prepared by DP method (pH 6).



**Fig. S3** Decay curves (excited at 460 nm, monitored at 641 nm) of the phosphors (x=0.07) synthesized by SSR, DP (pH 6) and DP (pH 2) method, respectively. The luminescence decay curves can be fitted into a two-exponential decay exponential function  $[I = I_0 + A_I \exp(-t/\tau_I) + A_2 \exp(-t/\tau_2)]$ , where *I* and  $I_0$  represents luminescent intensities at time 0 and *t*,  $A_I$  and  $A_2$  are constants,  $\tau_I$  and  $\tau_2$  are rapid and slow components of lifetime, respectively. The average decay times ( $\tau^*$ ) can be determined using the equation of  $\tau^* = (A_I \tau_I^{2+} A_2 \tau_2^{2}) / (A_I \tau_I^{+} A_2 \tau_2)$ .



**Fig. S4** Decay curves (excited at 345 nm, monitored at 498 nm) of TTCP:  $0.07\text{Eu}^{2+}$ -DP (pH 2) phosphor. The luminescence decay curves can be fitted into a twoexponential decay exponential function  $[I = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)]$ , where *I* and  $I_0$  represents luminescent intensities at time 0 and *t*,  $A_1$  and  $A_2$  are constants,  $\tau_1$ and  $\tau_2$  are rapid and slow components of lifetime, respectively. The average decay times ( $\tau^*$ ) can be determined using the equation of  $\tau^* = (A_1\tau_1^2 + A_2\tau_2^2) / (A_1\tau_1 + A_2\tau_2)$ .



**Fig. S5** FESEM images of (a) TTCP: 0.07Eu<sup>2+</sup>-DP (pH 2), (b) TTCP: 0.07Eu<sup>2+</sup>-DP (pH 6) and (c) TTCP: 0.07Eu<sup>2+</sup>-SSR.



Fig. S6 XRD patterns of TTCP:  $0.07Eu^{2+}$ -DP (pH 2) phosphor and standard data (JCPDS 25-1137) of Ca<sub>4</sub>(PO<sub>4</sub>)<sub>2</sub>O crystal.



**Fig. S7** Survey scan spectra of TTCP: 0.07Eu<sup>2+</sup> phosphors prepared by (a) DP method (pH 2), (b) DP method (pH 6) and (c) SSR method, respectively.



**Fig. S8** Photoluminescence emission spectra of TTCP: 0.07 Eu-DP (pH = 2) samples excited by different NUV light. Inset is correlated color temperature (CCT) and color rendering index (CRI, Ra) under excitation at 345 nm, 370 nm and 390 nm, respectively. The CRIs were evaluated according to CIE 13.3 CIE 13.3-1995 (Method of Measuring and Specifying Colour Rendering Properties of Light Sources).



**Fig. S9** Commission Internationale de L'Eclairage (CIE) chromaticity diagram of TTCP: 0.07Eu<sup>2+</sup>-DP (pH 2) phosphor excited at (a) 345 nm (0.3863, 0.4089), (b) 370 nm (0.4423, 0.4169), (c) 390 nm (0.4835, 0.4186) and (d) 460 nm (0.6099, 0.3884), respectively.