Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Dual stimuli-responsive lanthanide-based phosphors for advanced full-color anti-counterfeiting

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Experimental section

Materials

$Ce(CH_3COO)_3·6H_2O$, $Tb(NO_3)_3·6H_2O$, $Eu(NO_3)_3·6H_2O$, 2, 6-pyridinedicarboxylic acid (DPA), guanosine 5'-monophosphate disodium salt hydrate (GMP), ethylene glycol, diethylene glycol, glycerol and sodium dodecyl sulfate (SDS) were purchased from Aladdin Reagent Co. Ltd. Sodium silicate ($Na_2SiO_3·9H_2O$, Baume degree is 40) were purchased from Usolf Co., Ltd. ethanol was purchased from Sinopharm Chemical Reagent Co., Ltd. Ultrapure water (18.25 MΩ) was prepared with a Milli-Q system. All reagents were used as purchased without further purification.

Synthesis of DPA-Ce, DPA-Tb and DPA-Eu phosphors

$Ce(CH_3COO)_3·6H_2O$ (31.7 mg, 0.1mmol) and DPA (33.4 mg, 0.2 mmol) were dissolved in ethanol (20 mL) and then stirred for 10 s. The obtained pale-yellow suspensions were induced under UV radiation for 20 min to trigger blue emission. DPA-Tb was feasibly obtained by mixing DPA (20.0 mg, 0.12 mmol) and $Tb(NO_3)_3$ $6H_2O$ (45.3 mg, 0.1 mmol) in ethanol (20 mL). DPA-Eu was obtained by mixing DPA (50.1 mg, 0.3 mmol) and $Eu(NO_3)_3·6H_2O$ (44.6 mg, 0.1 mmol) in ethanol (20 mL). The precipitate was collected after being washed with ethanol for three times, which was dried overnight in vacuum at 40 °C.

Synthesis of DPA-Ce-GMP and DPA-Eu-GMP phosphors

DPA-Ce-GMP was synthesized by mixing $Ce(CH_3COO)_3·6H_2O$ (31.7mg, 0.1 mmol) and GMP (40.7 mg, 0.1 mmol) in ultrapure water (20 mL) at room temperature. DPA (33.4 mg, 0.2 mmol) was then added in the mixture and then stirred for 2 min. The obtained DPA-Ce-GMP was UV irradiated for 20 min to emit bright blue fluorescence. DPA-Eu-GMP was synthesized by mixing $Eu(NO_3)_3·6H_2O$ (44.6 mg, 0.1 mmol) and GMP (40.7 mg, 0.1 mmol) in ultrapure water (20 mL) at room temperature. DPA (33.4 mg, 0.2 mmol) was then added in the mixture and then stirred for 2 min. The obtained DPA-Eu-GMP emits bright red fluorescence. To prepare solid powder of DPA-Ce-GMP (or DPA-Eu-GMP), DPA-Ce-GMP (or DPA-Eu-GMP) was mixed with sodium silicate with volume ratio of 1:1 according previous study [S1], followed by microwave heating for 2 min. The as-prepared powder of DPA-Ce-GMP (or DPA-Eu-GMP) was collected after being washed with ethanol for three times.

Preparation of luminescent inks

DPA-Ce-GMP (30 mg), DPA-Tb (20 mg) and DPA-Eu-GMP (25 mg) were separately dispersed in ethanol (2 mL). ethylene glycol (0.6 mL), diethylene glycol (0.2 mL), and glycerol (0.2 mL) were then added into the mixture. SDS (3 mg) was finally added to prepare luminescent inks with appropriate surface tension and dynamic viscosity.

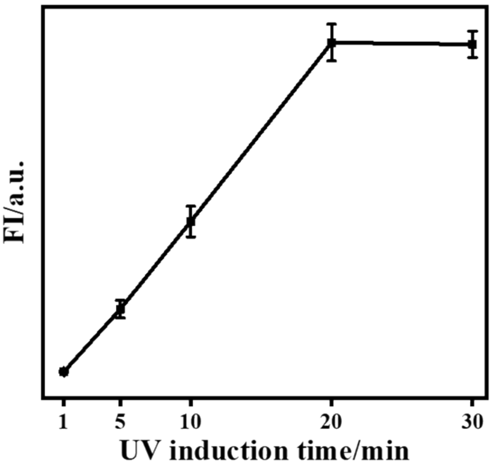

Fig. S1 The fluorescence intensity of DPA-Ce against UV induction time

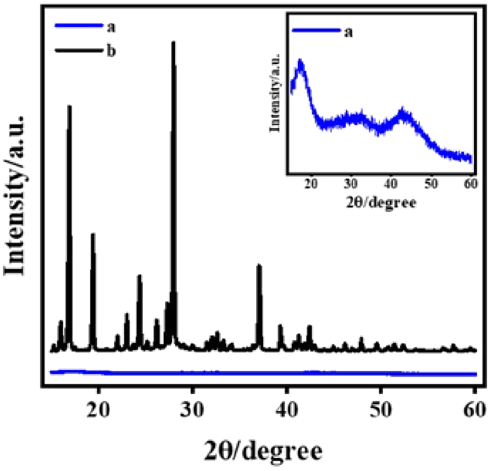

Fig. S2. X-ray diffraction spectra of DPA-Ce (a) and DPA (b). Insert: The individual spectra of DPA-Ce.

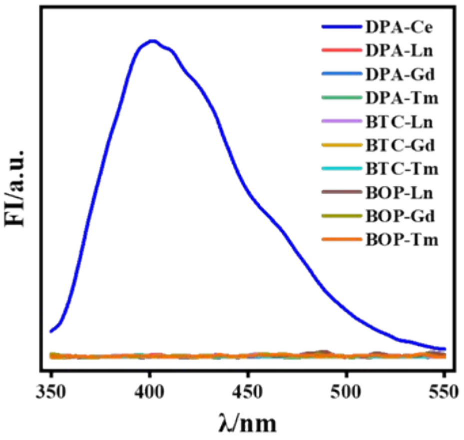

Fig. S3. The fluorescence spectra of DPA-Ce, DPA-Ln, DPA-Gd, DPA-Tm, BTC-Ln, BTC-Gd, BTC-Tm, BOP-Ln, BOP-Gd, BOP-Tm in EtOH after UV induction for 20 min.

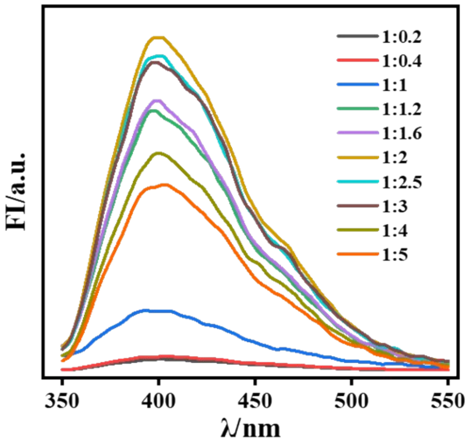

Fig. S4 The fluorescence spectra of DPA-Ce with different ratio of DPA to Ce^{3+}.

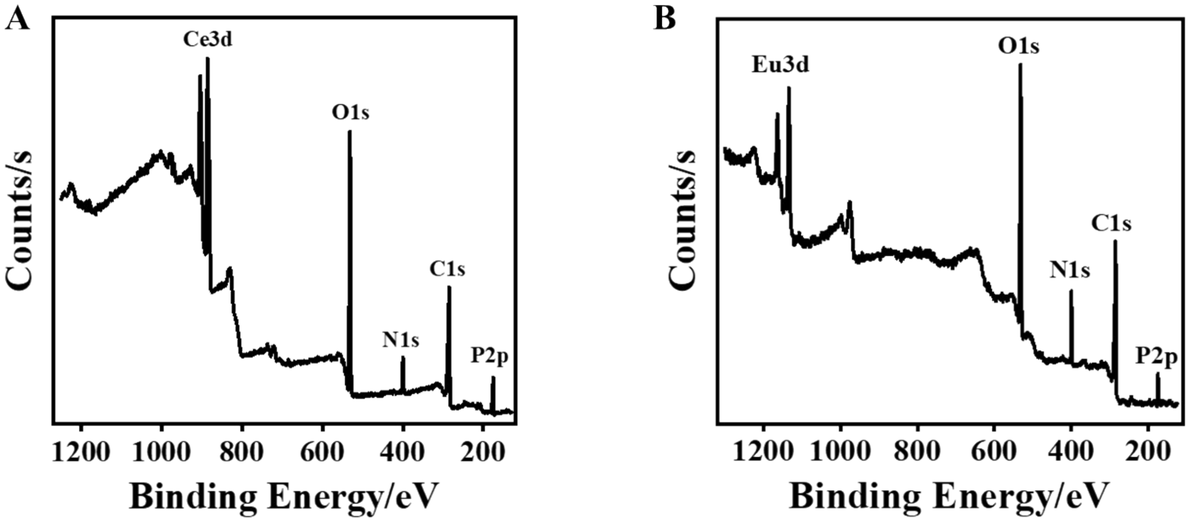

Fig. S5 XPS of DPA-Ce-GMP (A) and DPA-Eu-GMP (B)

XPS experiments for element analysis were implemented to validate the successful preparation of DPA-Ce-GMP (Fig. S5A) and DPA-Eu-GMP (Fig. S5B). Compared with XPS of DPA-Ce, feature peak of P2p is found at 175 eV from the XPS of DPA-Ce-GMP, which is originated from the GMP. Similarly, the feature peaks of Eu $3d_{5/2}$ (1134 eV) and Eu $3d_{3/2}$ (1163 eV) [S2], O1s, N1s, C1s, and P2p are detected from DPA-Eu-GMP. The result confirms the successful preparation of DPA-Ce-GMP and DPA-Eu-GMP

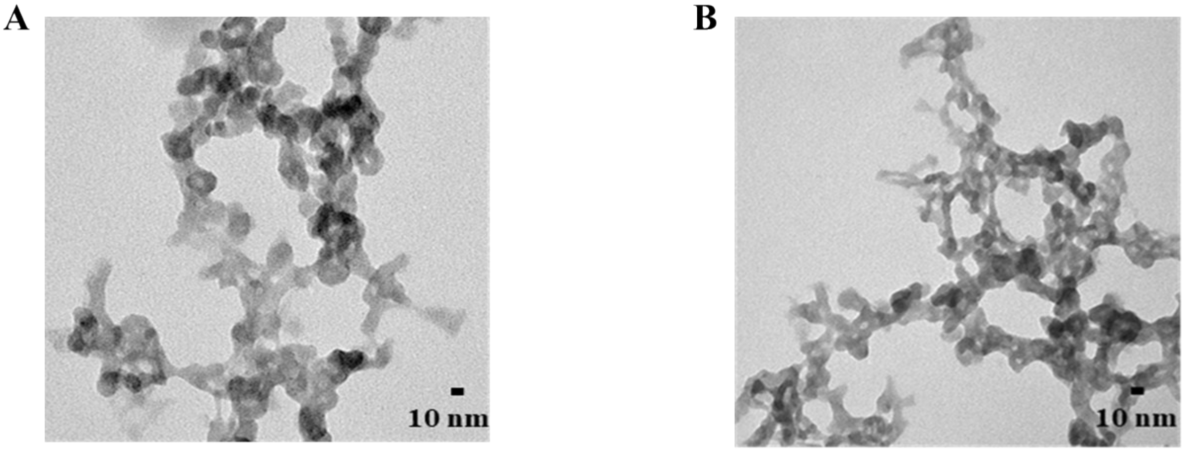

Fig. S6 TEM of DPA-Ce-GMP (A) and DPA-Eu-GMP (B).

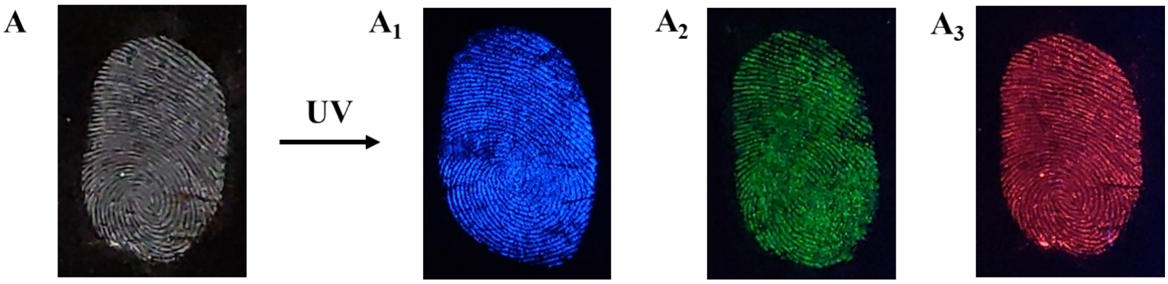

Fig. S7 Images of latent fingerprints on glass slide by depositing the phosphors under day-light (A) and UV light: (A_1) DPA-Ce-GMP, (A_2) DPA-Tb, and (A_3) DPA-Eu-GMP.

References

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S2 D. Xu, W. Y. Chen, M. Q. Zeng, H. F. Xue, Y. X. Chen, X. H. Sang, Y. Xiao, T. Zhang, R. R. Unocic, K. Xiao, L. Fu, *Angew. Chem. Int. Ed.* 2018, 57, 755-759.