

## Supporting Information

### Reversible multiplexing optical information storage and photoluminescence switching in Eu<sup>2+</sup> doped fluorophosphate-based tunable photochromic materials

Yang Lv<sup>1,2</sup>, Shaoan Zhang<sup>2</sup>, Zhenzhang Li<sup>3</sup>, Yahong Jin<sup>1,5,\*</sup>, Haoyi Wu<sup>1</sup>,  
Guifang Ju<sup>1</sup>, Li Chen<sup>1</sup>, Zhengfa Hu<sup>1,4</sup>, Yihua Hu<sup>1,4\*</sup>

<sup>1</sup>*School of Physics and Optoelectronic Engineering, Guangdong University of Technology, WaiHuan Xi Road, No. 100, Guangzhou 510006, China*

<sup>2</sup>*School of Optoelectronic Engineering, Guangdong Polytechnic Normal University, Zhongshan Avenue No. 293 West, Tianhe District, Guangzhou, 510665, China*

<sup>3</sup>*College of Mathematics and Systems Science, Guangdong Polytechnic Normal University, Zhongshan Avenue No. 293 West, Tianhe District, Guangzhou, 510665, China*

<sup>4</sup>*Synergy Innovation Institute for Modern Industries of Dongyuan and GDUT, Heyuan 517025, China*

<sup>5</sup>*Department of Chemistry, The Hong Kong University of Science and Technology, Kowloon, 999077, Hong Kong, China*

#### Corresponding author:

Fax: +86 20 39322265;

Tel: +86 20 39322262;

E-mail: yhjin@gdut.edu.cn (Y. Jin)

E-mail: huyh@gdut.edu.cn (Y. Hu)

---

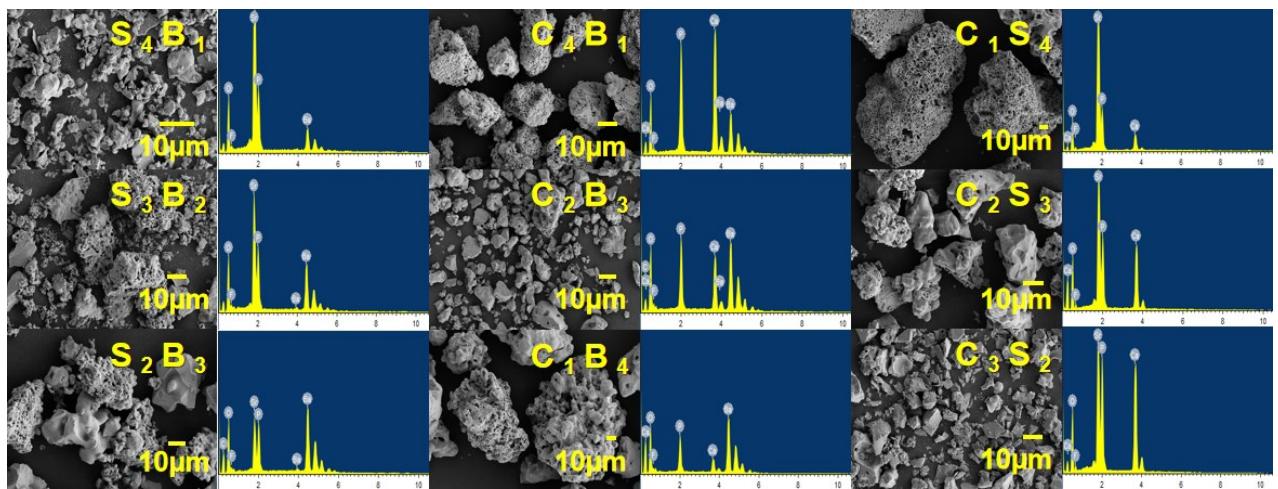


Fig. S1 SEM images of the samples  $S_4B_1$ ,  $S_3B_2$ ,  $S_2B_3$ ,  $C_4B_1$ ,  $C_2B_3$ ,  $C_1B_4$ ,  $C_1S_4$ ,  $C_2S_3$  and  $C_3S_2$ , together with the EDS spectra (the right side).

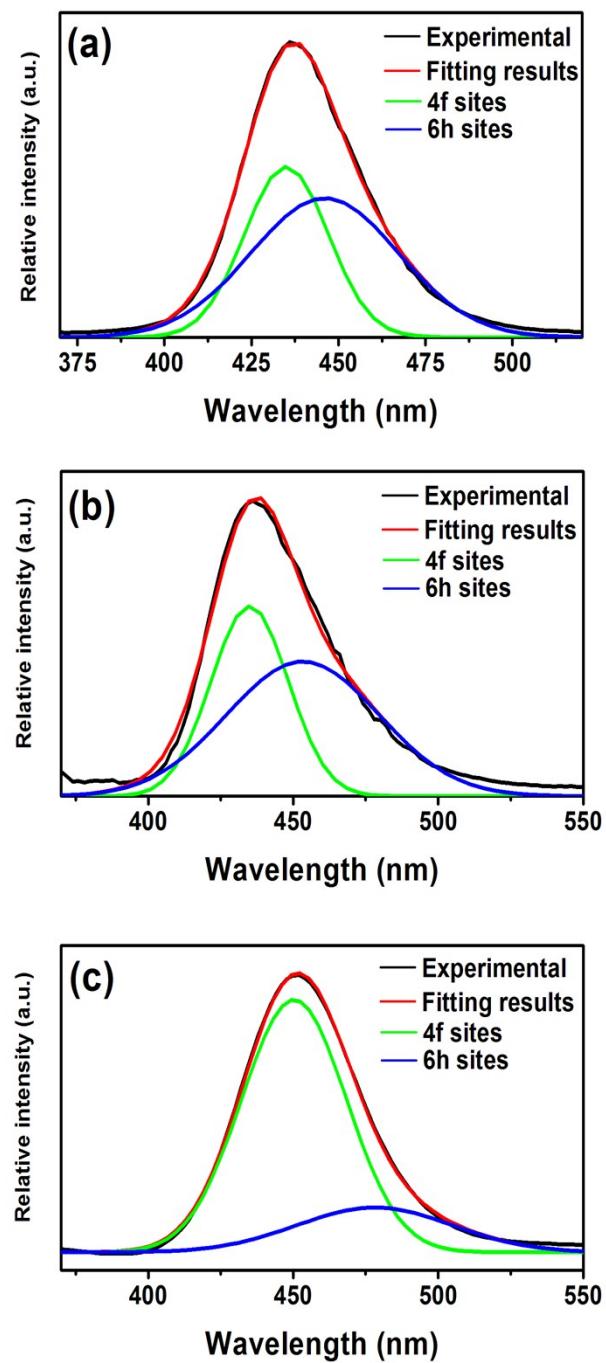


Fig. S2 The Gaussian fitting results of samples (a) S5, (b) B5, (c) C5.

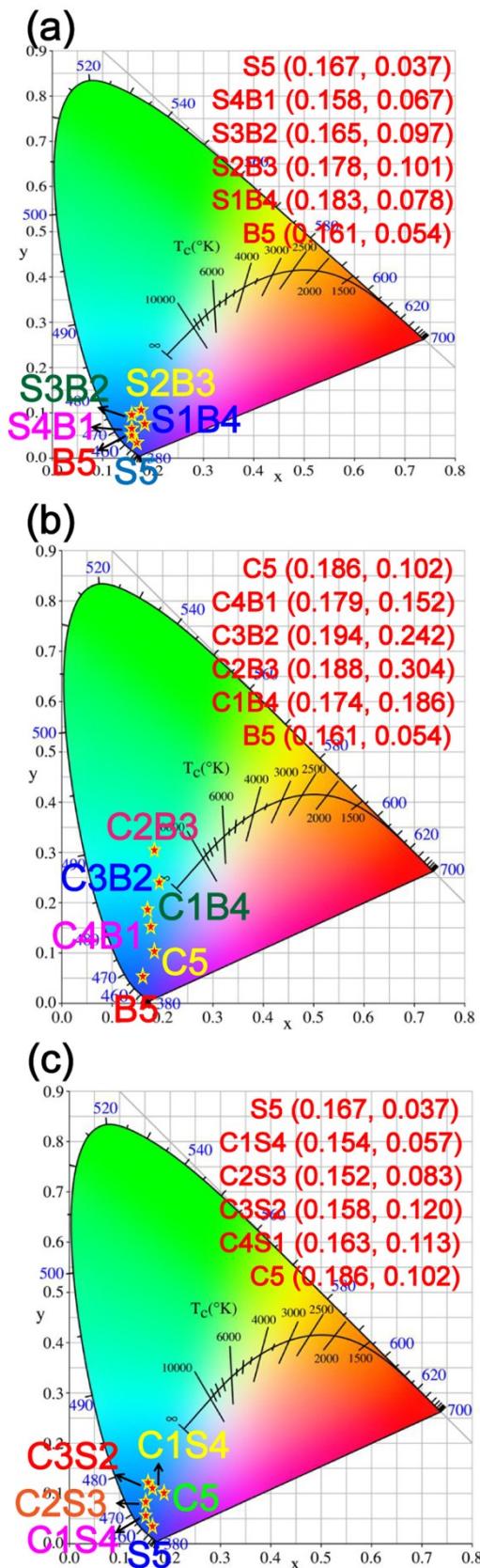


Fig. S3 CIE chromaticity of (a)  $(\text{Sr}, \text{Ba})_5(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$ , (b)  $(\text{Ca}, \text{Ba})_5(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$ , (c)  $(\text{Ca}, \text{Sr})_5(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$ .

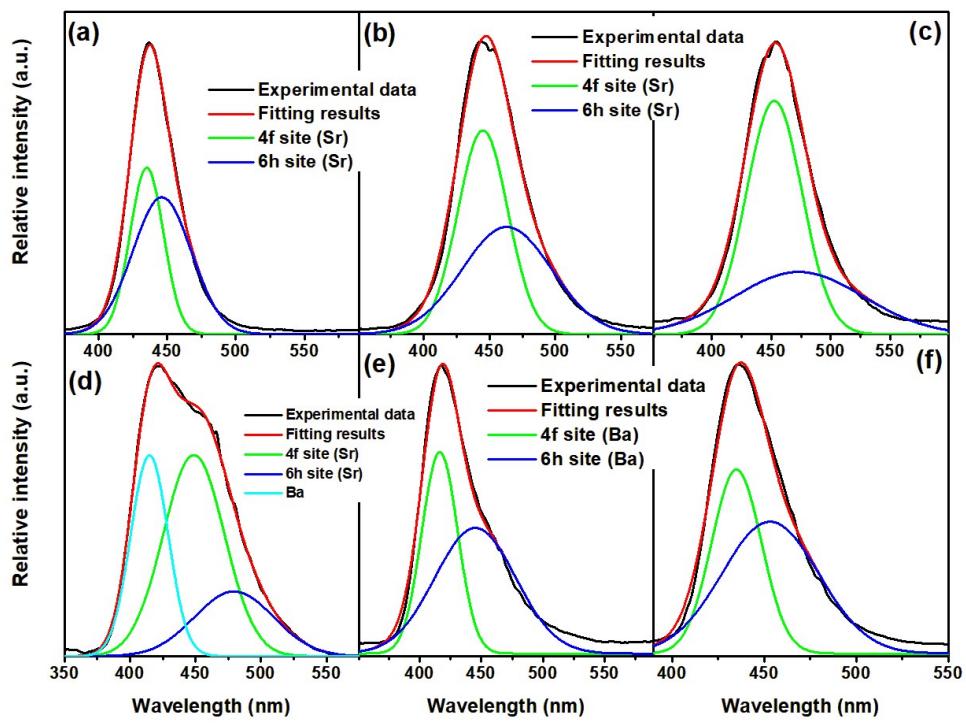


Fig. S4 The Gaussian fitting results of  $(\text{Sr}, \text{Ba})_5(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$  solid solution (a)S<sub>5</sub>, (b)S<sub>4</sub>B<sub>1</sub>, (c)S<sub>3</sub>B<sub>2</sub>, (d)S<sub>2</sub>B<sub>3</sub>, (e)S<sub>1</sub>B<sub>4</sub>, (f)B<sub>5</sub>.

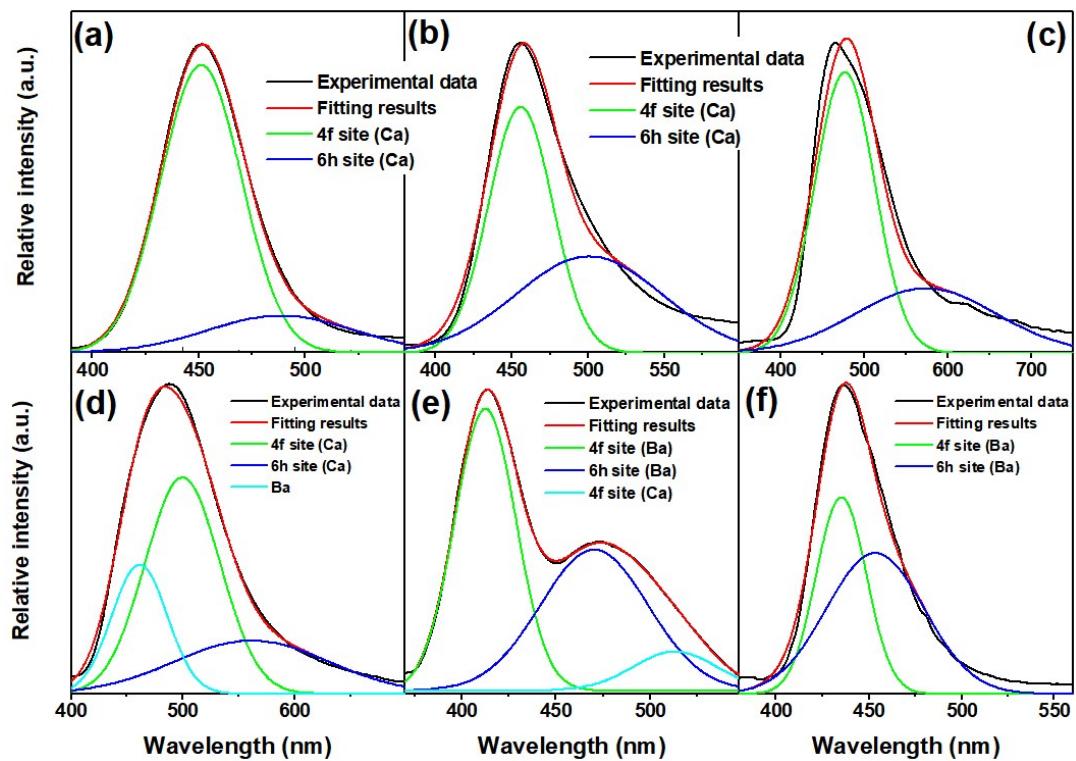


Fig. S5 The Gaussian fitting results of  $(\text{Ca}, \text{Ba})_5(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$  solid solution (a)C<sub>5</sub>, (b)C<sub>4</sub>B<sub>1</sub>, (c)C<sub>3</sub>B<sub>2</sub>, (d)C<sub>2</sub>B<sub>3</sub>, (e)C<sub>1</sub>B<sub>4</sub>, (f)B<sub>5</sub>.

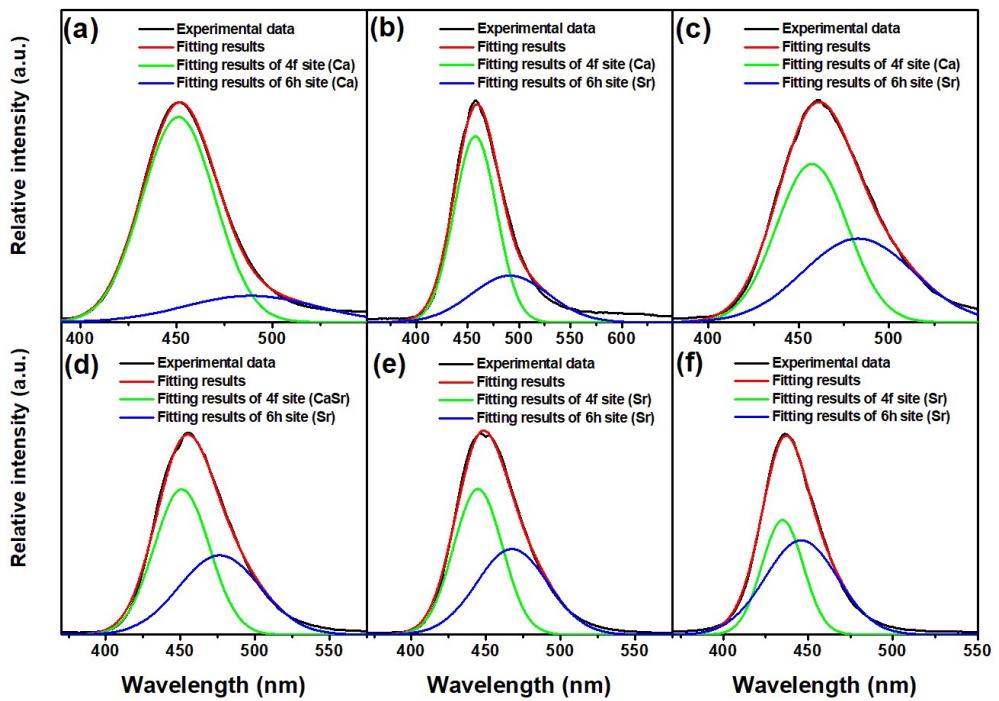


Fig. S6 The Gaussian fitting results of  $(\text{Ca}, \text{Sr})_5(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$  solid solution (a)C<sub>5</sub>, (b)C<sub>4</sub>S<sub>1</sub>, (c)C<sub>3</sub>S<sub>2</sub>, (d)C<sub>2</sub>S<sub>3</sub>, (e)C<sub>1</sub>S<sub>4</sub>, (f)S<sub>5</sub>.

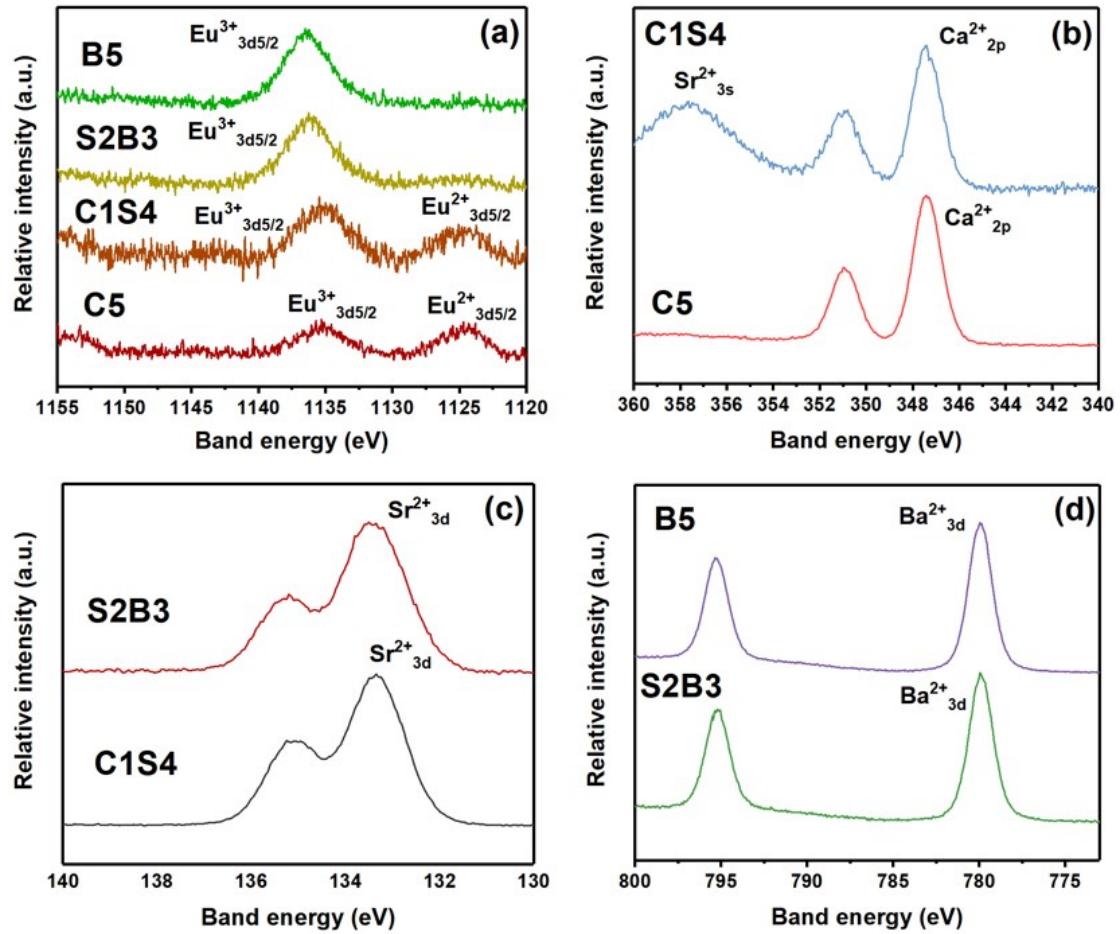


Fig. S7 XPS spectra of (a) Eu ions in  $C_5$ ,  $C_1S_4$ ,  $S_2B_3$  and  $B_5$ , (b)  $\text{Ca}^{2+}$  ion in  $C_5$  and  $C_1S_4$ , (c)  $\text{Sr}^{2+}$  ion in  $C_1S_4$  and  $S_2B_3$ , (d)  $\text{Ba}^{2+}$  ion in  $S_2B_3$  and  $B_5$ .

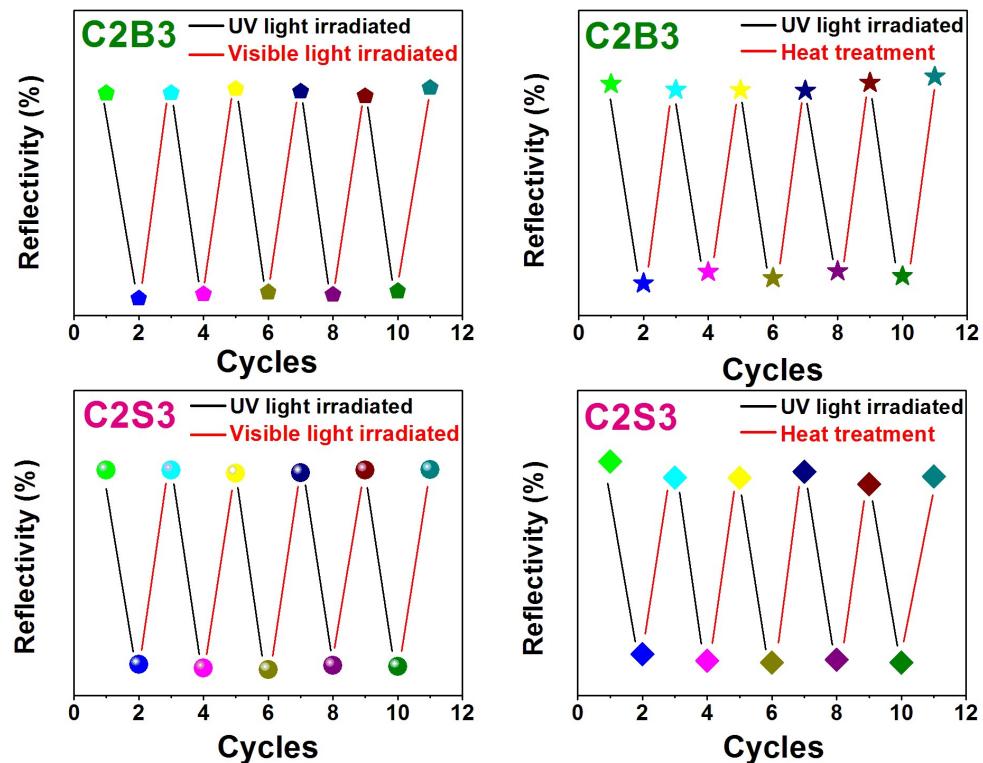


Fig. S8 The representative samples C2B3 and C2S3 after UV light and visible light/heat treatment for several cycles.

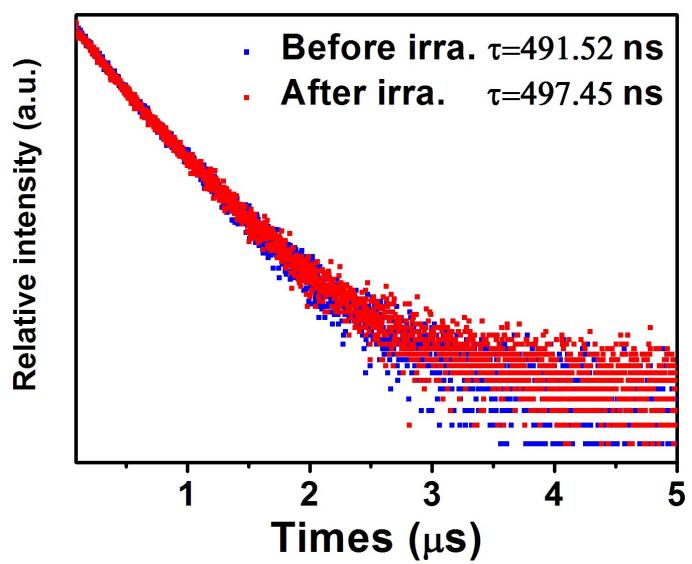


Fig. S9 Fluorescence lifetimes of  $C_5$  before and after UV light irradiation.

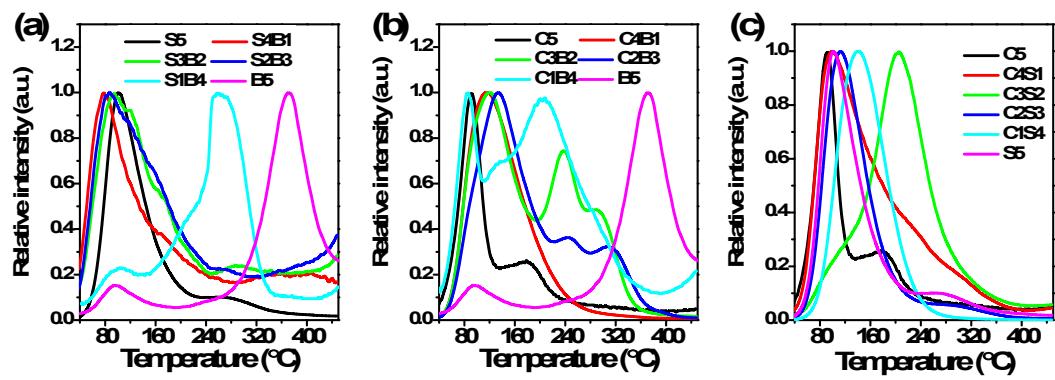


Fig. S10 TL spectra of (a)  $(\text{Sr}, \text{Ba})_5(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$ , (b)  $(\text{Ca}, \text{Ba})_5(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$ , (c)  $(\text{Ca}, \text{Sr})_5(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$ .

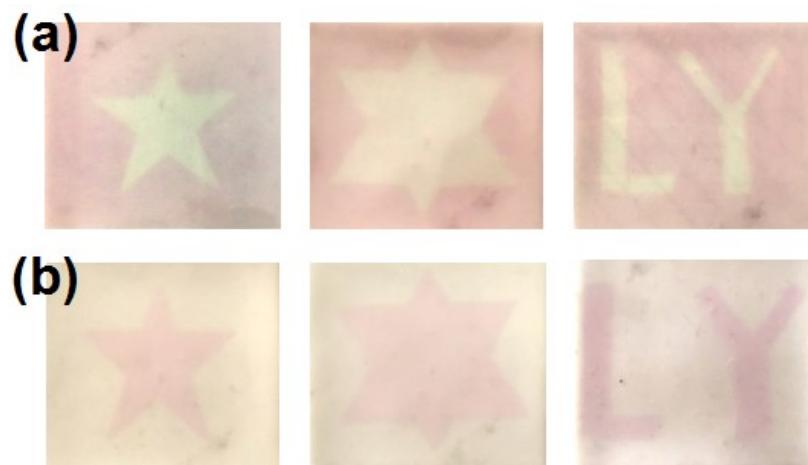


Fig. S11 (a) PC flexible films cover by the mask of patterns (pentagram and hexagram) and letters (L and Y) upon UV light irradiation (or colored PC flexible films cover by the hollow mask upon 365 nm light irradiation), (b) PC flexible films cover by the hollow mask of patterns (pentagram and hexagram) and letters (L and Y) upon UV light irradiation (or colored PC flexible films cover by the mask upon 365 nm light irradiation).

**Table S1 Atomic percentage of as-prepared samples based on EDS measurement**

Sample	Atomic percentage (%)					
	Ca	Sr	Ba	P	O	F
$\text{Ca}_5(\text{PO}_4)_3\text{F}$	19.7	0	0	12.7	61.3	6.4
$\text{Ca}_4\text{Ba}(\text{PO}_4)_3\text{F}$	15.6	0	6.3	13.8	57.8	6.5
$\text{Ca}_3\text{Ba}_2(\text{PO}_4)_3\text{F}$	10.2	0	9.4	13.4	59.5	7.5
$\text{Ca}_2\text{Ba}_3(\text{PO}_4)_3\text{F}$	6.4	0	9.9	9.7	45.7	5.3
$\text{Ca}\text{Ba}_4(\text{PO}_4)_3\text{F}$	3.9	0	18.4	12.6	59.0	6.1
$\text{Ba}_5(\text{PO}_4)_3\text{F}$	25.2	0	0	13.4	55.3	6.1
$\text{Sr}\text{Ba}_4(\text{PO}_4)_3\text{F}$	0	3.9	18.2	13.1	59.4	5.4
$\text{Sr}_2\text{Ba}_3(\text{PO}_4)_3\text{F}$	0	4.4	8.3	6.4	34.3	3.0
$\text{Sr}_3\text{Ba}_2(\text{PO}_4)_3\text{F}$	0	13.7	9.0	13.6	57.4	6.3
$\text{Sr}_4\text{Ba}(\text{PO}_4)_3\text{F}$	0	17.3	3.9	12.0	59.8	7.0
$\text{Sr}_5(\text{PO}_4)_3\text{F}$	0	22.9	0	11.8	59.6	6.6
$\text{Ca}\text{Sr}_4(\text{PO}_4)_3\text{F}$	3.5	17.8	0	11.5	60.1	7.2
$\text{Ca}_2\text{Sr}_3(\text{PO}_4)_3\text{F}$	8.7	10.7	0	11.0	62.7	6.9
$\text{Ca}_3\text{Sr}_2(\text{PO}_4)_3\text{F}$	11.3	7.9	0	12.4	60.9	7.5
$\text{Ca}_4\text{Sr}(\text{PO}_4)_3\text{F}$	17.8	3.7	0	12.0	60.9	5.6

**Table S2 Element proportion of ICP-MS measurement**

Sample	Element proportion				Emissio range	peak
	Ca	Sr	Ba	Eu		
$\text{Ca}_5(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$	4.996	0	0	0.004	385~550 nm	451 nm
$\text{Ca}_3\text{Ba}_2(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$	2.908	0	2.087	0.005	375~750 nm	464 nm
$\text{CaBa}_4(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$	0.987	0	4.011	0.003	370~600 nm	414 nm
$\text{Ba}_5(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$	0	0	4.997	0.003	390~580 nm	436 nm
$\text{Sr}_2\text{Ba}_3(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$	0	1.937	3.059	0.004	365~600 nm	424 nm
$\text{Sr}_4\text{Ba}(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$	0	3.914	1.081	0.004	365~575 nm	447 nm
$\text{Sr}_5(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$	0	4.996	0	0.004	375~525 nm	436 nm
$\text{Sr}_4\text{Ca}(\text{PO}_4)_3\text{F}:\text{Eu}^{2+}$	1.151	3.845	0	0.003	380~550 nm	449 nm