

## **Photocontrolled reversible modulation of lanthanide luminescence in mesoporous silica nanospheres by photochromic diarylethenes**

Qing-Feng Li <sup>a</sup>, Hongjun Xia <sup>a</sup>, Erqing Li <sup>b</sup>, Jin-Tao Wang <sup>a\*</sup>, Zhenling Wang <sup>c\*</sup>

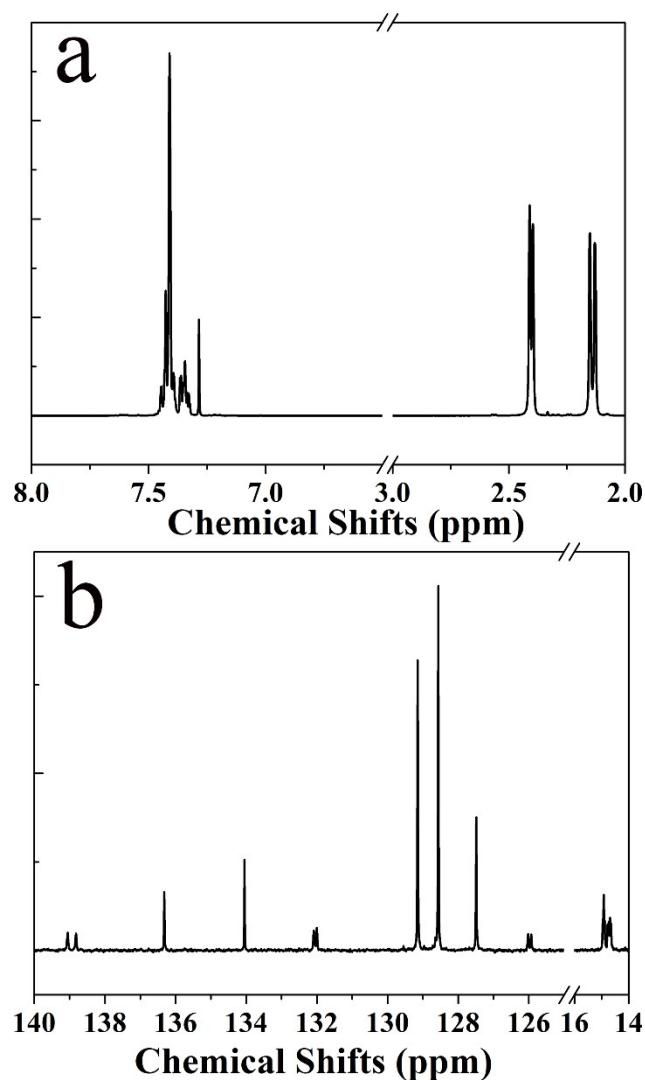
<sup>a</sup> Henan Key Laboratory of Rare Earth Functional Materials, International Joint Research Laboratory for Biomedical Nanomaterials of Henan, Zhoukou Normal University, Zhoukou, 466001, Henan, PR China.

<sup>b</sup> College of Chemistry, Green Catalysis Center, Zhengzhou University, Zhengzhou 450001, PR China.

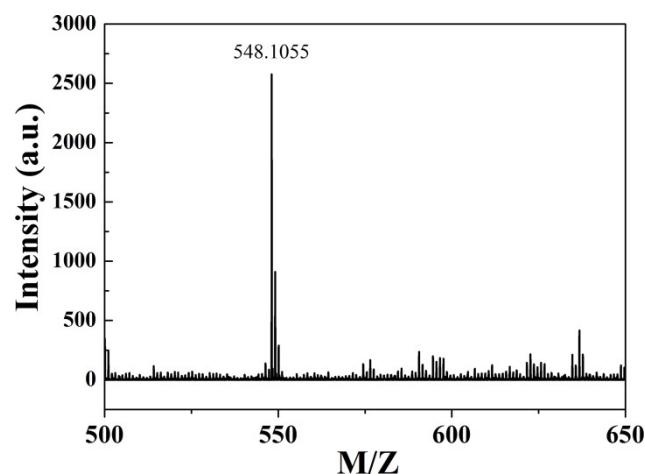
<sup>c</sup> College of Materials Engineering, Henan International Joint Laboratory of Rare Earth Composite Materials, Henan University of Engineering, Xinzheng, 451191, PR China.

\*Corresponding author

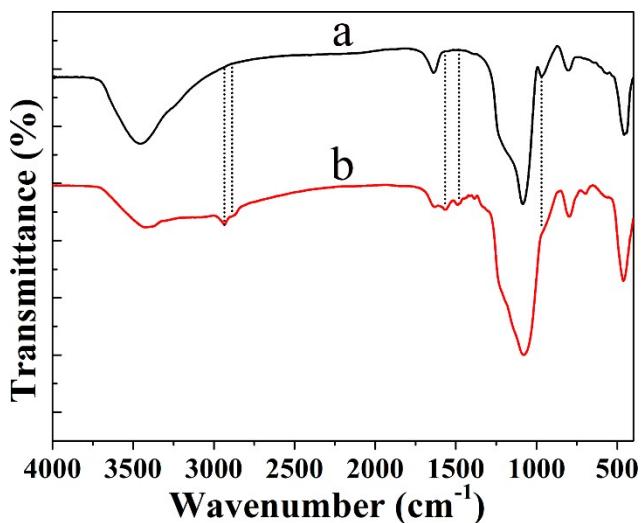
E-mail: wangjintao2565@126.com (J. T. Wang), zlwang2007@hotmail.com (Z. Wang).



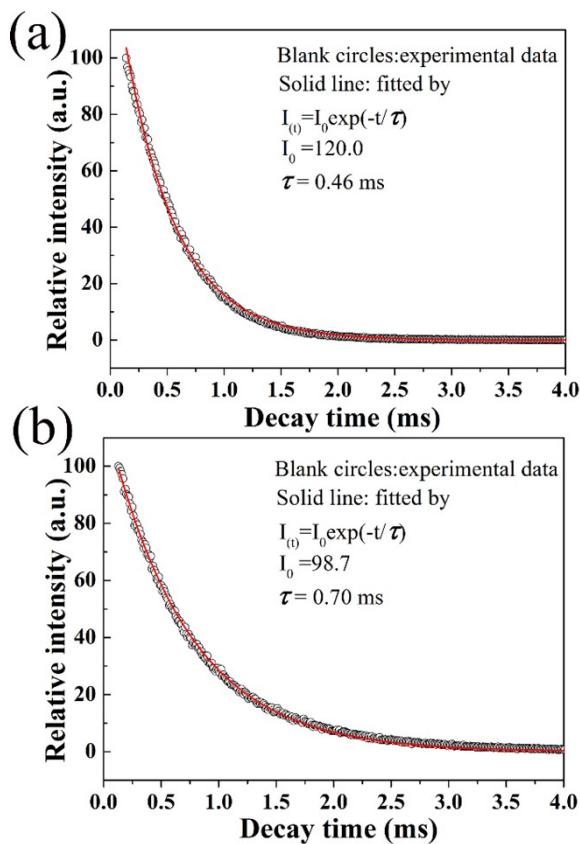
**Fig. S1** <sup>1</sup>H-NMR (a) and <sup>13</sup>C-NMR (b) of open-form BTHFC. <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>) δ ppm: 7.45-7.30 (10H, m), 2.40 (6H, d), 2.15 (6H, d). <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>) δ ppm: 139.0, 138.8, 136.2, 134.0, 132.1, 132.0, 129.1, 128.5, 127.5, 126.0, 125.9, 14.9, 14.7.



**Fig. S2** High resolution mass spectrum (HR-MS) of open-form BTHFC. (M<sup>+</sup>=548.1055)



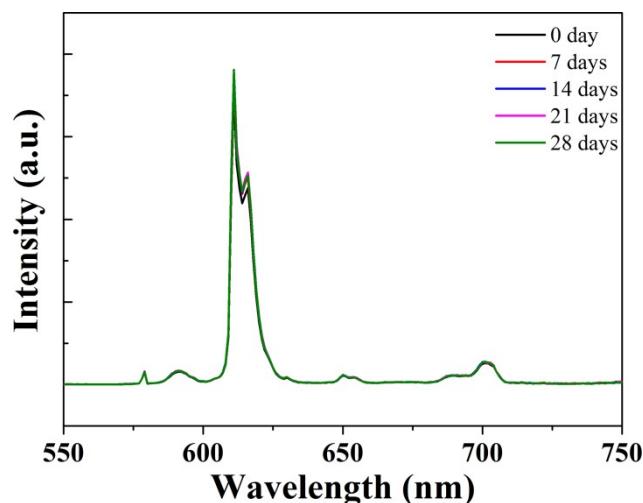
**Fig. S3** FT-IR spectra of MSNs (black line) and NH<sub>2</sub>-MSNs (red line). The peak near 3420 cm<sup>-1</sup> and 1630 cm<sup>-1</sup> can be assigned to the stretching vibration of O-H and bending vibration of H-O-H, respectively (Fig. S3a and b). The results indicate the presence of adsorbed water molecules in the samples. The peak located at 1485 cm<sup>-1</sup> is ascribed to the scissoring vibrations of CH<sub>2</sub>- (Fig. S3b).<sup>1</sup> Moreover, the stretching of Si-C is also observed at 695 cm<sup>-1</sup> (Fig. S3b).<sup>2</sup>



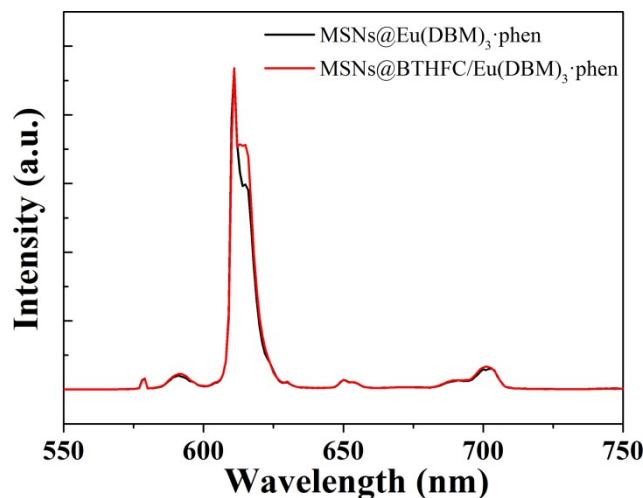
**Fig. S4** The luminescence lifetime curves of Eu(DBM)<sub>3</sub>·phen(a) and NH<sub>2</sub>-MSNs@Eu(DBM)<sub>3</sub>·phen (b).

**Table S1** The lifetimes and quantum yields of Eu(DBM)<sub>3</sub>·phen and NH<sub>2</sub>-MSNs@Eu(DBM)<sub>3</sub>·phen.

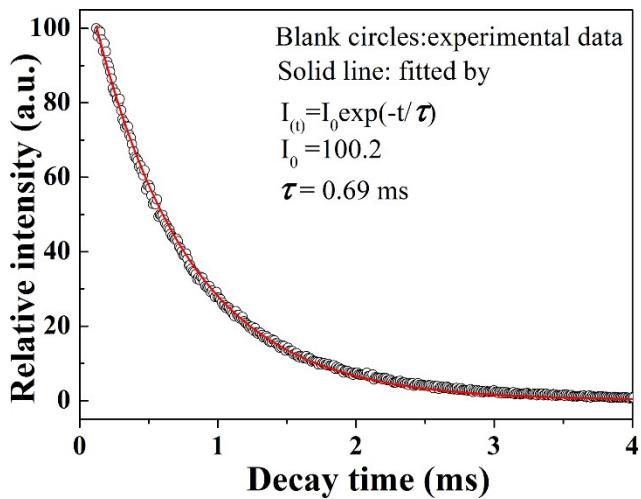
Samples	Lifetimes (ms)	Quantum yields (%)
Eu(DBM) <sub>3</sub> ·phen	0.46	32.7
NH <sub>2</sub> -MSNs@Eu(DBM) <sub>3</sub> ·phen	0.70	12.5
NH <sub>2</sub> -MSNs@BTHFC/Eu(DBM) <sub>3</sub> ·phen	0.69	12.2



**Fig. S5** The luminescence intensity changes of NH<sub>2</sub>-MSNs@Eu(DBM)<sub>3</sub>·phen within 4 weeks.



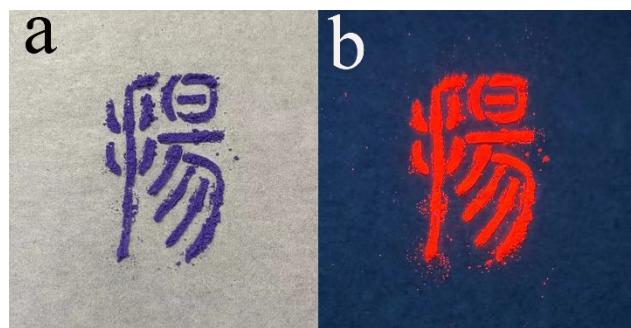
**Fig. S6** Emission spectra of NH<sub>2</sub>-MSNs@Eu(DBM)<sub>3</sub>·phen and NH<sub>2</sub>-MSNs@BTHFC/Eu(DBM)<sub>3</sub>·phen.



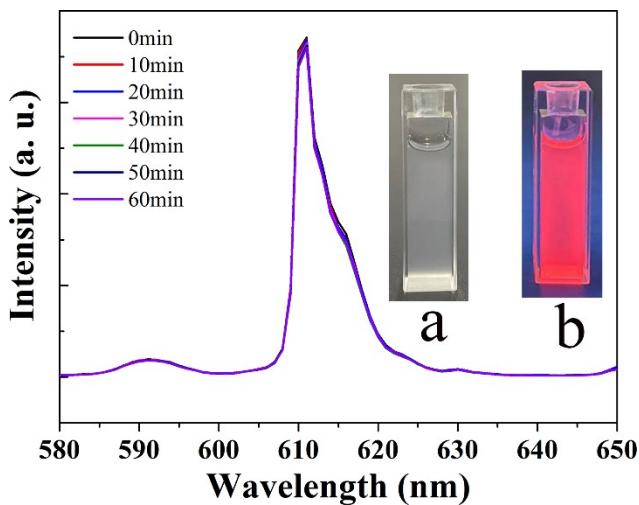
**Fig. S7** The luminescence lifetime curves of  $\text{NH}_2\text{-MSNs@BTHFC/Eu(DBM)}_3\cdot\text{phen}$ .

**Table S2** The size of pores, BET surface area and total volume of pores of MSNs,  $\text{NH}_2\text{-MSNs}$  and  $\text{NH}_2\text{-MSNs@BTHFC/Eu(DBM)}_3\cdot\text{phen}$ .

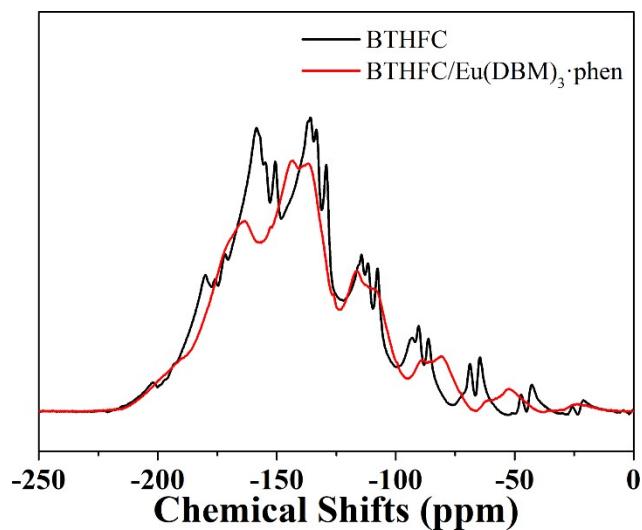
Sample	Size of pores (nm)	BET surface area ( $\text{m}^2 \text{ g}^{-1}$ )	Total volume of pores ( $\text{cm}^3 \text{ g}^{-1}$ )
MSNs	22.5	452	2.54
$\text{NH}_2\text{-MSNs}$	21.4	366	1.96
$\text{NH}_2\text{-MSNs@BTHFC/Eu(DBM)}_3\cdot\text{phen}$	21.0	319	1.67



**Fig. S8** The photographic images of  $\text{NH}_2\text{-MSNs@BTHFC/Eu(DBM)}_3\cdot\text{phen}$  after irradiation with the 254 nm UV lamp (a), The luminescence images of  $\text{NH}_2\text{-MSNs@BTHFC/Eu(DBM)}_3\cdot\text{phen}$  under the 365 nm UV lamp (b).



**Fig. S9** The emission spectra of  $\text{NH}_2\text{-MSNs@BTHFC/Eu(DBM)}_3\cdot\text{phen}$  dispersion (0.5 mg/mL) and corresponding photographic image under daylight (a) or under the 365 nm UV lamp (b). This result showed that the luminescence intensity of  $\text{NH}_2\text{-MSNs@BTHFC/Eu(DBM)}_3\cdot\text{phen}$  in aqueous solution remained stable within 1 h.



**Fig. S10** Solid-state  $^{19}\text{F}$  NMR spectra of BTHFC and BTHFC/Eu(DBM) $_3\cdot\text{phen}$  (the molar ratio of BTHFC and Eu(DBM) $_3\cdot\text{phen}$  is 1:1).

#### Reference

1. P. Premila, C. Subbu, S. Rajendran and K. S. Kumar, *Appl. Surf. Sci.*, 2018, 449, 426-434.
2. P. G. Song, Y. Shen, B. X. Du, Z. H. Guo and Z. P. Fang, *Nanoscale*, 2009, 1, 118-121.