

## Supporting Information

### **Self-catalytic synthesis of metal oxide nanoclusters@mesoporous silica composites based on successive spontaneous reactions at near neutral condition**

Fang Cui, Tieyu Cui \*

*The Academy of Fundamental and Interdisciplinary Science, Harbin Institute of Technology, Harbin 150080, People's Republic of China*

---

\*Corresponding author. Tel.: (+86)451-86403646  
E-mail address: [cuit@hit.edu.cn](mailto:cuit@hit.edu.cn) (Tieyu Cui)

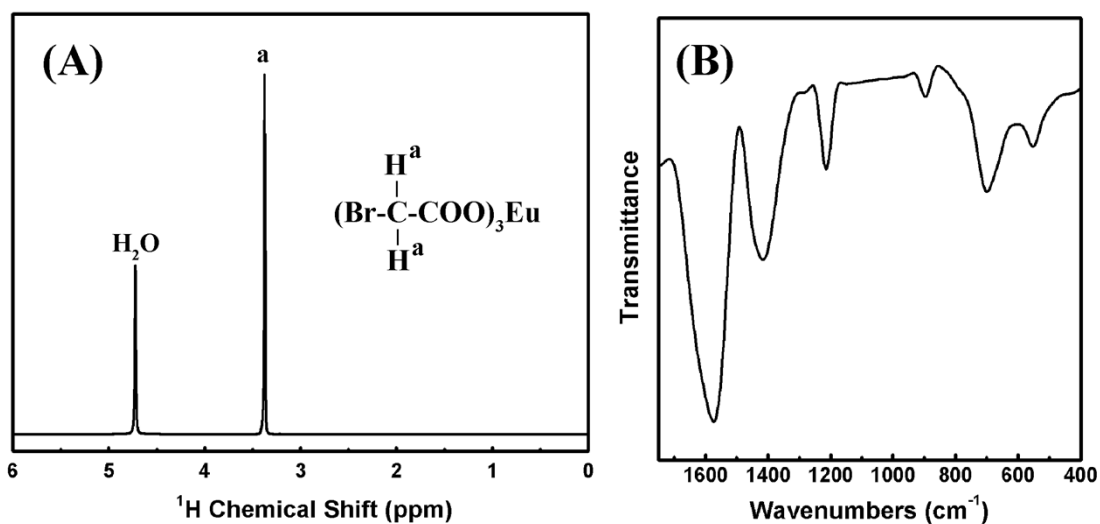
## Experimental Section

**Materials.**  $\text{Eu}_2\text{O}_3$  powder, bromoacetic acid (BA), tetraethylorthosilicate (TEOS, >99%) and absolute ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, PR China). (3-Aminopropyl)triethoxysilane (APTES, 99%) was purchased from Fluka. All these chemicals were of analytical reagent grade and used as received. The water used in the experiments was deionized with a resistivity of  $18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$ .

**Synthesis of EuBA.** In a typical synthesis,  $\text{Eu}_2\text{O}_3$  powder (8.8 g, 0.025 mol) was mixed with BA (22.0 g, 0.158 mol) in 100 mL absolute ethanol and the mixture was continuously stirred for at least 4 hours at 60 °C. The synthesized EuBA is insoluble in ethanol and is therefore precipitated from the solution. After cooling to room temperature, the white deposits were then collected by centrifugation and washed several times with absolute ethanol to remove the unreacted BA. To remove the trace quantities of unreacted  $\text{Eu}_2\text{O}_3$ , which may be mixed with EuBA, a small quantity of water was added to the white powder to dissolve EuBA. After filtration, the filter liquor was rotary evaporated and exposed to high vacuum at 40 °C to remove some of the water, and then the remainder was cooled to separate out the white powder of EuBA. The resulting white powder was collected by filtration and dried in a vacuum oven at room temperature for 24 h.

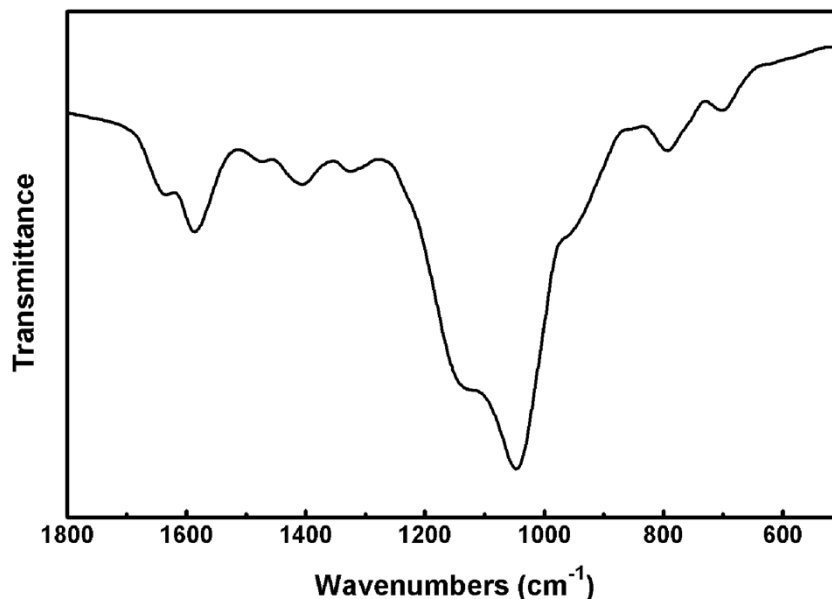
**Synthesis of  $\text{Eu}_2\text{O}_3$  NCs@mSiO<sub>2</sub>.** In a typical synthesis, a ethanol solution containing APTES (4.474 g, 20.0 m mol) and TEOS (0.694 g 3.33 m mol) were added dropwise in a water-ethanol mixture (30 mL water/30 mL ethanol) containing EuBA (3.788 g, 6.66 m mol) at room temperature. Then the mixture was continuously stirred for 24 h at room temperature. The generated white deposits were collected by centrifugation and washed with absolute ethanol for 4 times. After that, the white powder was dried in a vacuum oven at room temperature for 12 h. Finally, the white powder of the organic/inorganic hybrid silica was calcined at 550 °C for 30 min to obtain the  $\text{Eu}_2\text{O}_3$  NCs@mSiO<sub>2</sub> composites.

**Characterization.** FTIR data were collected on an AVATAR 360 FT-IR infrared spectrophotometer.  $^1\text{H}$  NMR spectrum was recorded in  $\text{D}_2\text{O}$  using a Bruker AVANCE500 500MHz NMR spectrometer. TEM and STEM images, EDS spectrum and EDX element mappings were obtained by employing a FEI Tecnai G2 F30 transmission electron microscope, using an accelerating voltage of 300 kV. The pore size distribution measurements were performed on a Micromeritics ASAP 2010 M analyzer. Fluorescence measurements were performed with the assistance of a SHIMADZU RF-5301 spectrofluorimeter.



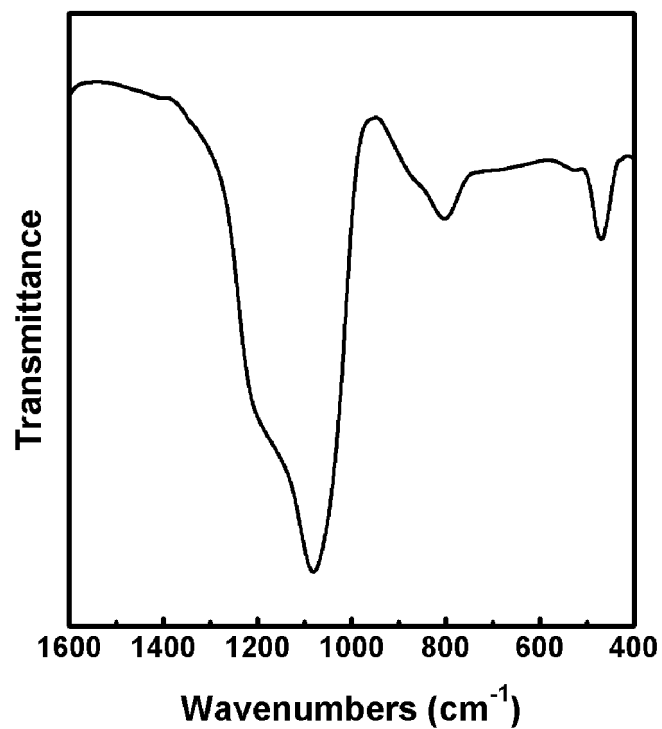
**Fig. S1**  $^1\text{H}$  NMR spectrum (A) and FTIR spectrum (B) of EuBA.

In the  $^1\text{H}$  NMR spectrum (Fig.S1(A)), the chemical shift at 3.38 ppm is assigned to the methylene protons of EuBA. FTIR spectrum (Fig.S1(B)) reveals three strong bands of the carboxylate groups at  $1574\text{ cm}^{-1}$ ,  $1374\text{ cm}^{-1}$  and  $707\text{ cm}^{-1}$  for the antisymmetric stretching vibration, symmetric stretching vibration and deformation vibration, respectively. In addition, the two bands at  $1416\text{ cm}^{-1}$  and  $550\text{ cm}^{-1}$  are assigned to the variable-angle vibration of the  $-\text{CH}_2-$  groups and the C-Br vibration respectively.



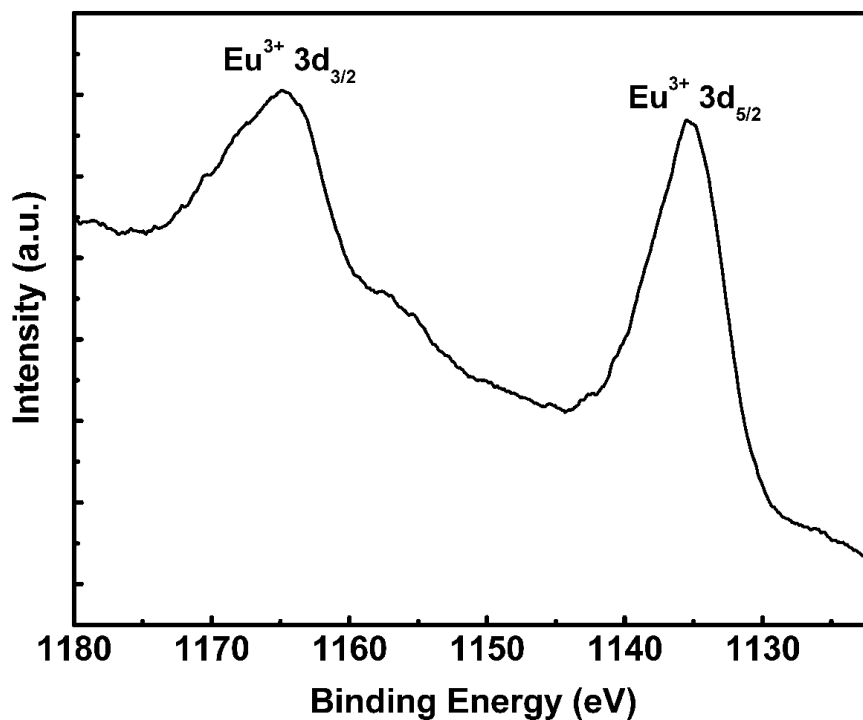
**Fig. S2** FTIR spectrum of the organic/inorganic hybrid silica materials.

FTIR spectrum (Fig. S2) provides evidence for the formation of the expected organic/inorganic hybrid silica materials through spontaneous nucleophilic substitution and subsequent self-catalytic hydrolyzation and polycondensation reactions. Firstly, the C-N stretch of the primary amine ( $1167\text{ cm}^{-1}$ ) of APTES and the C-Br vibration ( $550\text{ cm}^{-1}$ ) of EuBA virtually disappear, whereas the expected C-N stretch of secondary amine ( $1128\text{ cm}^{-1}$ ) is obviously present, which confirm the occurrence of nucleophilic substitution reaction between the terminal bromine groups of EuBA and the amine groups of APTES. Secondly, the variable-angle vibration of the protonated amine groups appears at  $1634\text{ cm}^{-1}$ , further confirming the nucleophilic substitution reaction. Thirdly, the Si-O-Si stretching band appearing at  $1047\text{ cm}^{-1}$  confirms the formation of Si-O-Si networks within the hybrid materials. Fourthly, the presence of the Si-C stretching band ( $793\text{ cm}^{-1}$ ) demonstrates the organic alkyl chains are covalently bonded to the Si-O-Si networks. Fifthly, three strong bands at  $1587\text{ cm}^{-1}$ ,  $1406\text{ cm}^{-1}$  and  $702\text{ cm}^{-1}$  are attributed to the antisymmetric stretching, symmetric stretching and deformation vibration of the carboxylate, which clearly demonstrate that the europium carboxylate groups are well-protected in the process of hydrolyzation and polycondensation reaction because of the near neutral reaction condition.



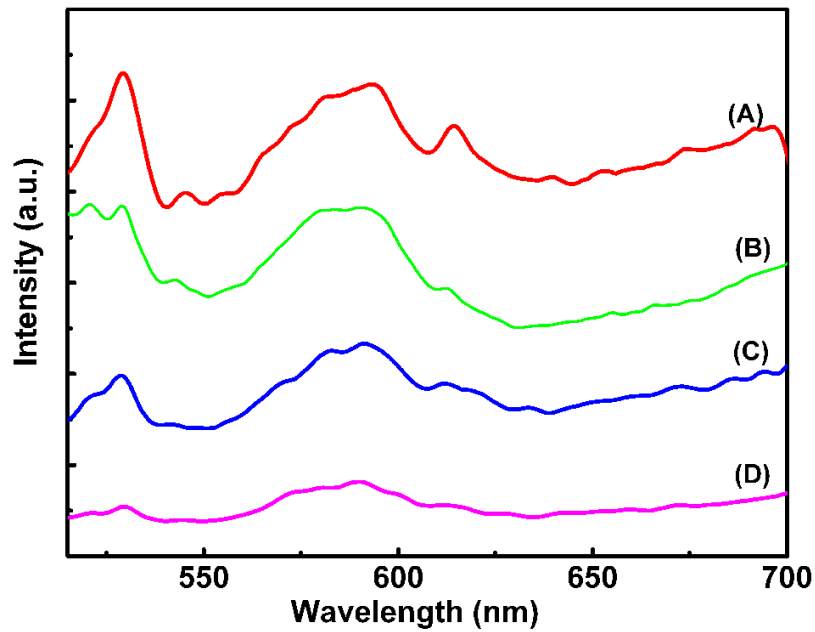
**Fig. S3** FTIR spectrum of the Eu<sub>2</sub>O<sub>3</sub> NCs@mSiO<sub>2</sub> composites.

The FTIR spectrum reveals bands of the Si-O-Si stretch at 1081 cm<sup>-1</sup> for antisymmetric stretch and at 802 cm<sup>-1</sup> for symmetric stretch. The band of the Eu<sub>2</sub>O<sub>3</sub> vibration appears at 470 cm<sup>-1</sup>.



**Fig. S4** XPS spectrum of Eu (3d) levels in the  $\text{Eu}_2\text{O}_3$  NCs@mSiO<sub>2</sub> composites.

The XPS spectrum of the  $\text{Eu}_2\text{O}_3$  NCs@mSiO<sub>2</sub> composites recorded in the energy region of the Eu(3d) transition is presented in Fig. S4. The two peaks appears at 1135.1 eV and 1164.7 eV are assigned to the  $\text{Eu}^{3+}_{5/2}$  ( $3d4f^6$ ) configuration and  $\text{Eu}^{3+}_{3/2}$  ( $3d4f^6$ ) configuration, respectively.



**Fig. S5** Emission spectra of the Eu<sub>2</sub>O<sub>3</sub> NCs@mSiO<sub>2</sub> composites prepared at different molar ratios of EuBA : APTES : TEOS. From top to bottom: 1: 3: 0 (A), 1: 3: 0.5 (B), 1: 3: 2 (C) and 1: 3: 5 (D). ( $\lambda_{\text{ex}} = 394 \text{ nm}$ )

The luminescent intensity of the composites increases with increasing the amounts of Eu<sub>2</sub>O<sub>3</sub>, while the major peak positions in the emission spectra are basically identical to each other.