

Electronic Supplementary Information
for

Smart Luminescent Hydrogel with Superior Mechanical Performance based on Polymer Networks Embedded with Lanthanide Containing Clay Nanocomposite

*Bin Li,^a Yan Qin,^b Zhiqiang Li,^{*a} Ying Zhang^{*a} and Huanrong Li^{*a}*

^aNational-Local Joint Engineering Laboratory for Energy Conservation in Chemical Process Integration and Resources Utilization, Tianjin Key Laboratory of Chemical Process Safety, School of Chemical Engineering and Technology, Hebei University of Technology, Guangrong Dao 8, Hongqiao District, Tianjin 300130, P. R. China.

^bInner Mongolia Yitai Coal Based New Materials Research Institute Co., Ltd., High Tech Industrial Park, Ordos, 010700, P. R. China.

E-mail: zhiqiangli@hebut.edu.cn; yzhang@hebut.edu.cn; lihuanrong@hebut.edu.cn

Materials and methods

The layered clay (LAPONITE® XLG), was purchased from Rockwood Additives Ltd and was used directly without further purification. 2,6-Pyridinedicarboxylic acid was purchased from Aladdin Scientific Ltd, acrylamide (AAm), N, N'-methylenebis(acrylamide) (MBA) and 2,2-diethoxyacetophenone (DEAP) were purchased from J&K Scientific Ltd. The Eu content was measured by inductively coupled plasma optical emission spectrometry (ICP-OES). The FTIR spectra were recorded on a Bruker Vector 22 spectrometer from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} . X-ray powder diffraction (XRD) research were completed with an X-ray powder diffractometer (BRUKER D8 Focus) complying with Cu Ka radiation ($\lambda = 1.5418 \text{ \AA}$), operating at 40 kV and 40 mA. SEM images were obtained using a Nova NanoSEM 450 at an acceleration voltage of 15 kV. Mechanical performances were determined according to CMT6104. The measurements of tensile properties were carried out at a crosshead speed of 100 mm/min. Compression properties were carried out at a crosshead speed of 6 mm/min. The steady-state luminescence spectra were measured on an Edinburgh Instruments FS920P near-infrared spectrometer, with a 450 W xenon lamp as the steady-state excitation source, a double excitation monochromator (1800 lines $\cdot\text{mm}^{-1}$), an emission monochromator (600 lines $\cdot\text{mm}^{-1}$), a semiconductor cooled Hamamatsu RMP928 photomultiplier tube.

Preparation of Eu-DPA@clay nanocomposite

The Eu@clay was readily prepared according to our previous work.¹ Eu-DPA@clay nanocomposite was prepared by the following method. Eu@clay (1.0 g) was dispersed in 10 mL of deionized water and stirred for 30 minutes. DPA (54.2 mg, 0.1 mmol) was added to 10 ml of deionized water, and the pH was adjusted to 8 with NaOH (1 M) and then added gradually. The mixture was stirred magnetically at 80 °C for 12 hours. The obtained colloidal product was centrifuged to remove excess DPA, and the final product was washed several

times with a mixture of ethanol and water, and dried under vacuum. The content of Eu^{3+} loaded was measured by ICP-OES is 0.029 mmol for 1.0 g Eu-DPA@clay nanocomposite.

Preparation of Eu-DPA@clay nanocomposite hydrogel

The Eu-DPA@clay nanocomposite (60 mg) was dispersed in 1 mL deionized water, and ultrasonicated to obtain a completely exfoliated nanosheet solution. Then acrylamide (150 mg) it was added. MBA (30 μL , 10mg/mL) were added into the above pregel solution. Then, the photoinitiator DEAP (1 μL) was added. The mixed solution was bubbled with nitrogen for 10 min to eliminate the dissolved oxygen. Finally, the oxygen-free pregel solution was injected into a square container (20×10 mm) and was placed under mercury lamp for 1 h by radical-copolymerization to obtained gel. Hydrogels with other different Eu-DPA@clay contents were prepared using the same method as described above.

Luminescence on/off switch behavior tests.

For the reversible luminescence response to acid/base stimuli, the Eu-DPA@clay nanocomposite hydrogel film was put into 0.1 M HCl solution for 60 s. After luminescence was quenched, the hydrogel film was transferred to Tris-HCl buffer solution of pH=8 for 60 s to restore luminescence. This cycle was repeated for 5 times.

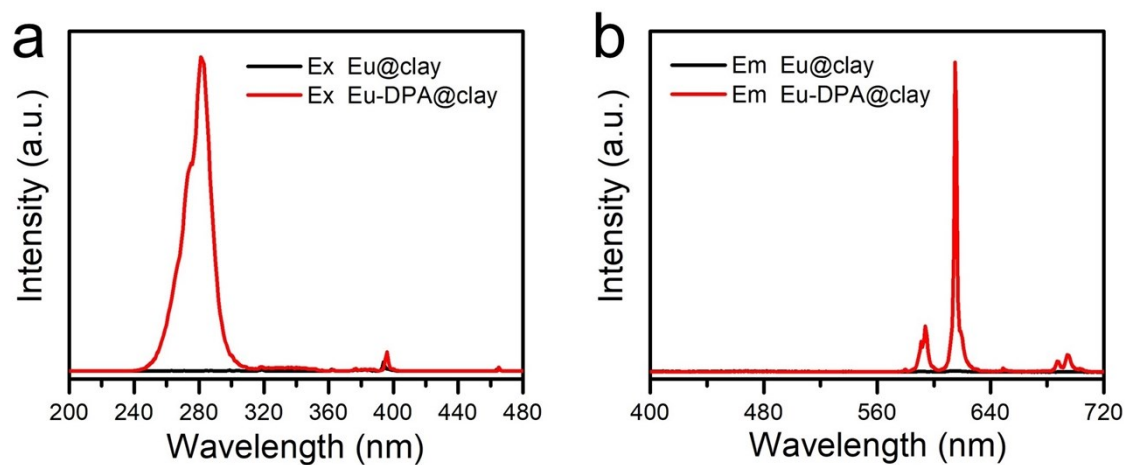


Figure S1. (a) The excitation spectrum of Eu@clay and Eu-DPA@clay nanocomposite (monitored at 615 nm); (b) The emission luminescence spectrum of Eu-DPA@clay nanocomposite (excited at 280 nm).

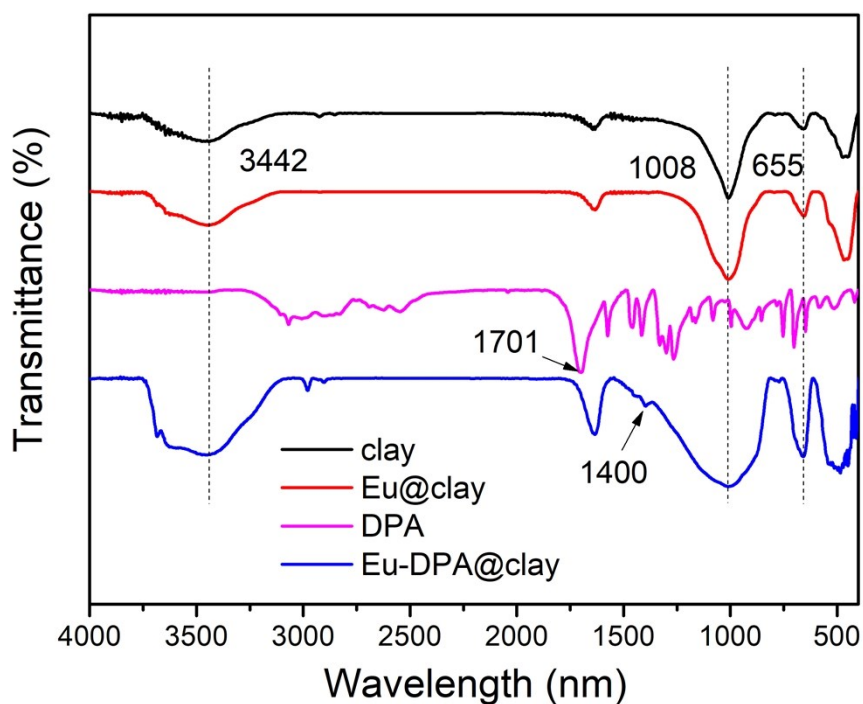


Figure S2. FTIR spectra of pure clay, Eu@clay, Eu-DPA@clay and pure DPA.

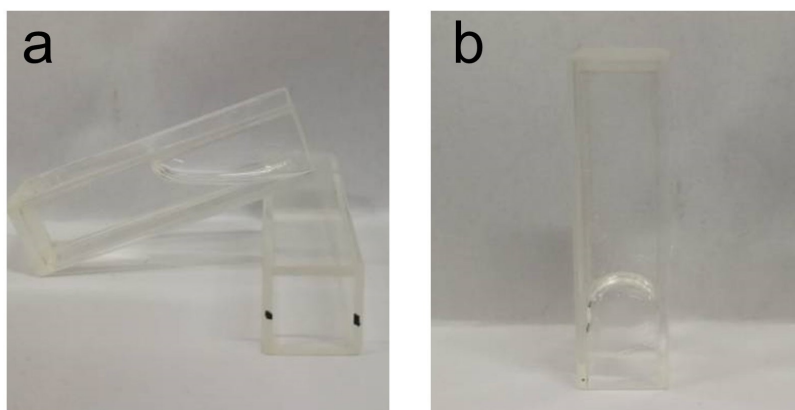


Figure S3. Photographs of Eu-DPA@clay aqueous disperse system with Eu-DPA@clay content of 4.8 wt% (a) and 6.3 wt% (b)

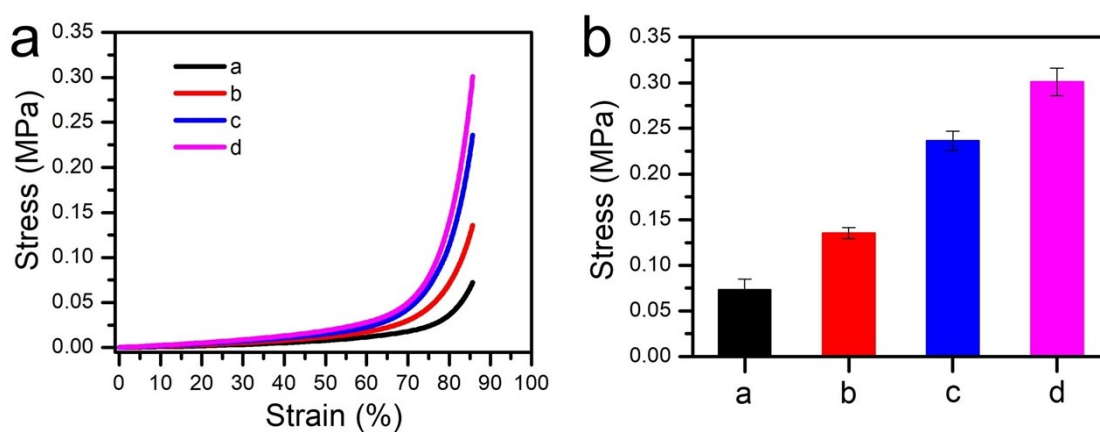


Figure S4. (a, b) Compressive stress-strain curves and bar charts of the stress of the nanocomposite hydrogel with different contents of Eu-DPA@clay nanosheets. (The Eu-DPA@clay nanocomposite contents represented by a, b, c and d are 0, 1.7, 3.3 and 4.8 w% respectively)

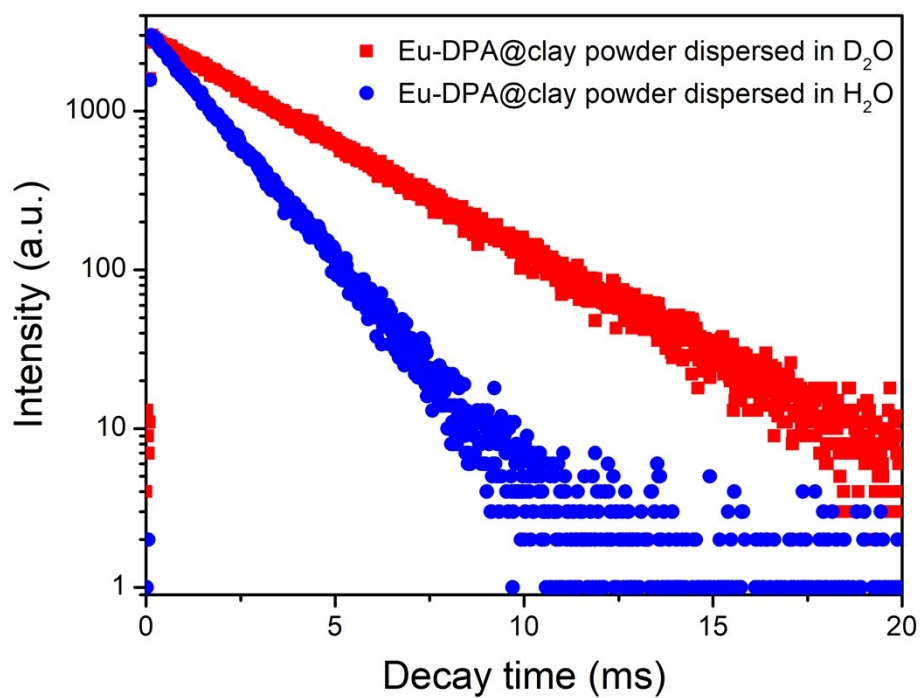


Figure S5. The decay curves of Eu-DPA@clay dissolved in D₂O and H₂O. (excited at 280 nm and monitored at 615 nm)

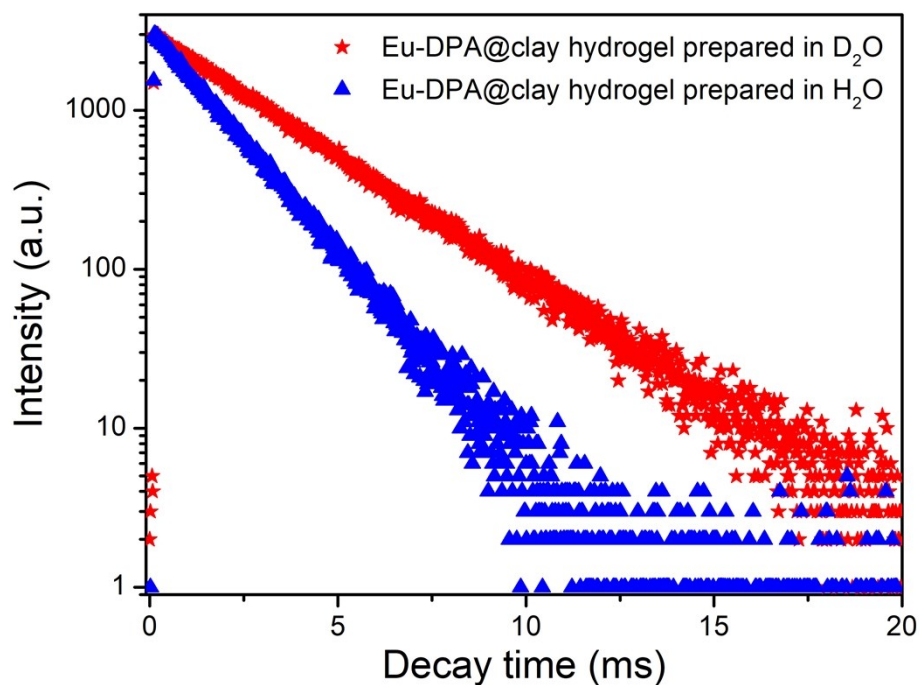


Figure S6. The decay curves of Eu-DPA@clay nanocomposite hydrogel prepared in D₂O and H₂O. (excited at 280 nm and monitored at 615 nm)

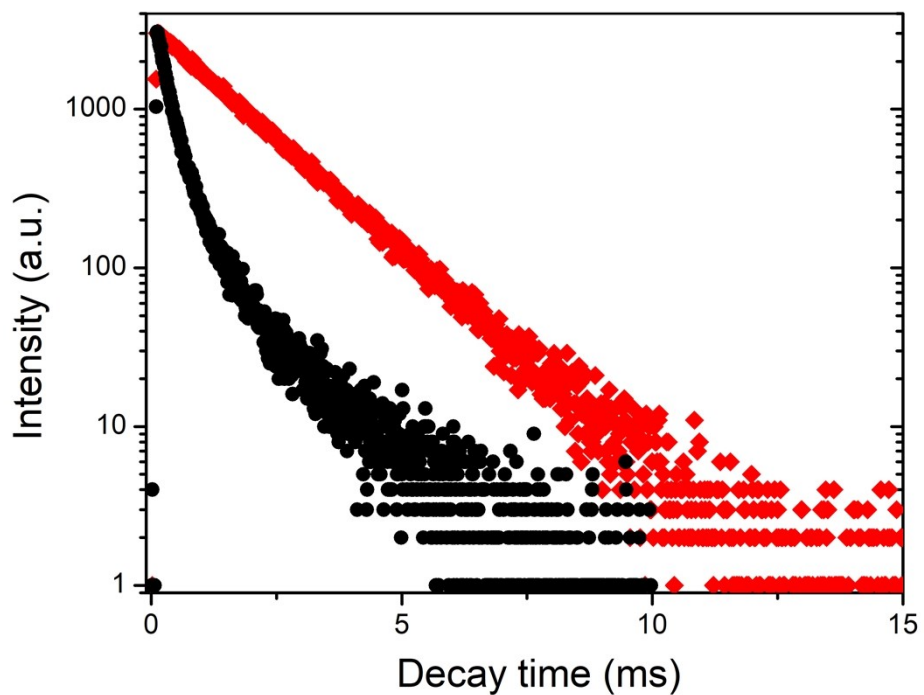


Figure S7. Luminescence decay curves of the Eu-DPA@clay nanocomposite hydrogel before and after treated with HCl.

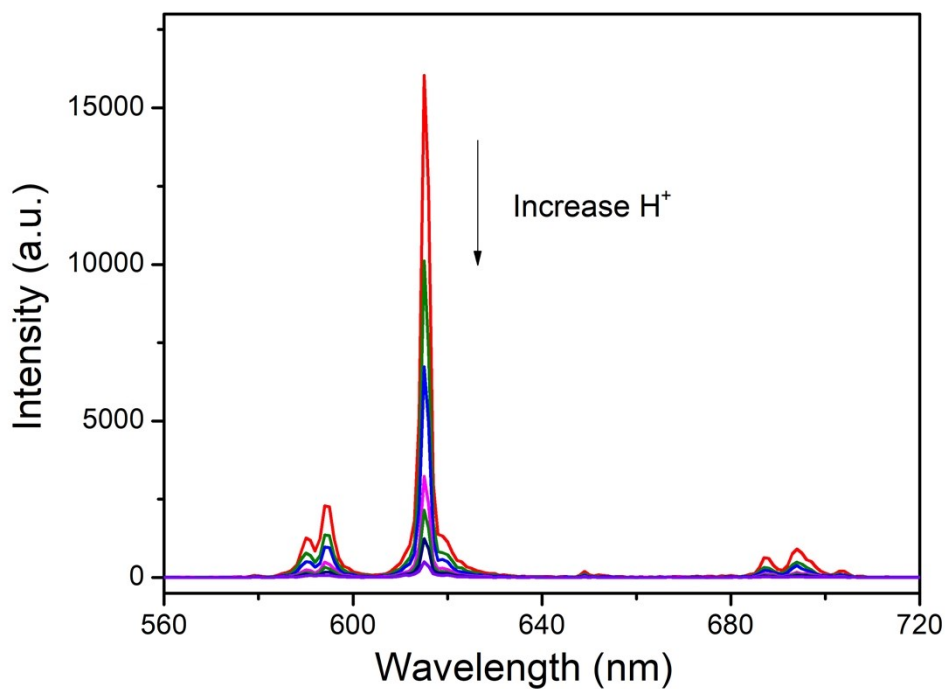


Figure S8. Gradual decrease in the luminescence intensity of the Eu-DPA@clay nanocomposite hydrogel by increasing HCl concentration from 0 to 0.1 M.

References

- 1 D. Yang, Y. Wang, Y. Wang, Z. Li, H. Li, *ACS Appl. Mater. Interfaces*, 2015, **7**, 2097-2103.