Electronic Supplementary Information

for

Europium(III)–*β*-Diketonate Complex-containing Nanohybrid Luminescent pH Detector

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Materials and methods

2-Thenoyltrifluoroacetone (TTA) was purchased from Aldrich and used as received. The layered clay (Laponite RD), was purchased from Rockwood Additives Ltd and was used as received without further purification. Aqueous solutions of $EuCl_3 \bullet 6H_2O$ were prepared by dissolving Eu_2O_3 in concentrated hydrochloride acid. Infrared (IR) spectra were obtained with a Bruker Vector 22 spectrometer by using KBr pellets for solid samples from 400-4000 cm^{-1} at a resolution of 4 cm^{-1} and by using ATR (Attenuated Total Reflection) for oily samples from 4000-650 cm^{-1} at a resolution of 4 cm^{-1}(16 scans collected). 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·mm^{-1}), an emission monochromator (600 lines·mm^{-1}), a semiconductor cooled Hamamatsu RMP928 photomultiplier tube.

Experimental Section

Preparation of Eu^{3+} @Lap:

A solution of $EuCl_3 \cdot 6H_2O$ (0.1 M) 5 mL was added to a round-bottom flask contain 0.5 g of Laponite RD. The mixture was then stirred at 80°C for 24 h and the precipitate was collected by centrifugation and washed with deionized water, dried at 45 °C for 6 h. Afterward, the product was ground into a white powder. The supernatant together with deionized water was titrated by ethylenediaminetetraacetic acid (EDTA) with dimethyl phenol orange as indicator. The amounts of Eu^{3+} loaded was determined as 0.099 mmol by subtracting the free Eu^{3+} from the initial amount of $EuCl_3 \cdot 6H_2O$.

Preparation of $Eu^{3+}(TTA)_n$@Lap:

Taking the quality ratio of TTA to Eu^{3+}@Lap is 0.6 : 1 as example. 0.2 g Eu^{3+}@Lap was dispersed in 20 mL deionized water, 0.12 g TTA dissolved in 1 mL ethanol was added. The reaction mixture was sonicated for 0.5 h. The precipitate was collected by centrifugation and washed three times with dichloromethane. The precipitate was then dried at 45 °C for 12 h, resulting in pale yellow solids $Eu^{3+}(TTA)_n$@Lap. Supernatant and dichloromethane was collected and concentrated under the reduced pressure and dried in vacuum, the residue was dissolved in 100 ml ethanol, this stock solution was then diluted 100 times. The amount of TTA loaded on the laponite was determined by measuring the characteristic absorption of TTA at 340 nm of the diluted solution, the photometric standard curve of TTA was obtained with absorption intensity as the ordinate and the TTA concentration in ethanol as the abscissa. Simply subtract the recovered TTA value in this stock solution from the initial amount of TTA to get the amount of TTA loaded on the laponite.

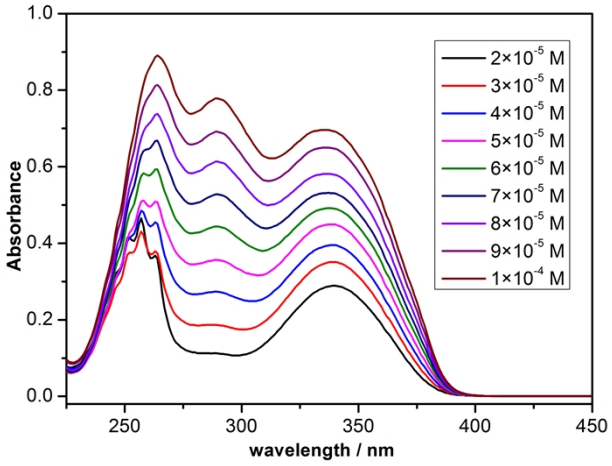

Fig. S1 UV/Vis spectra of TTA at concentration range of 2×10^{-5} M - 1×10^{-4} M.

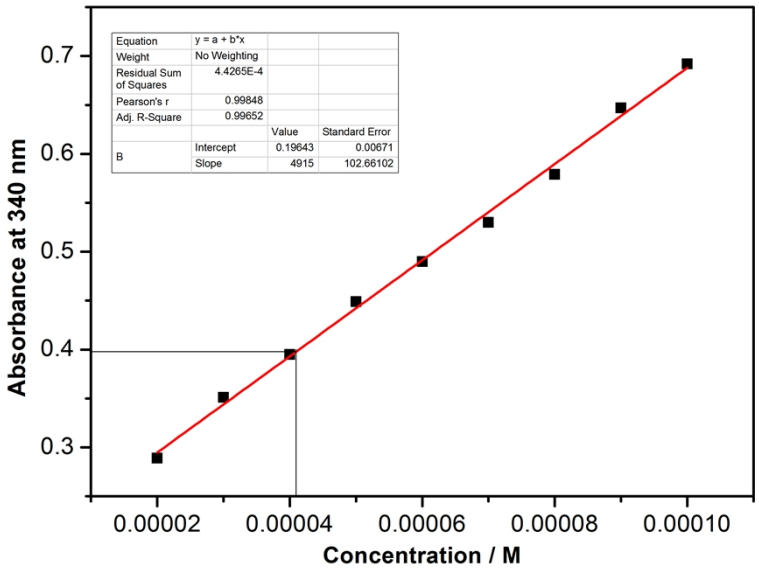

Fig. S2 The photometric standard curve of TTA in EtOH.

Preparation of Luminescent Thin Film

5 mg of $Eu^{3+}(TTA)_n$@Lap was dispersed in 25 ml deionized water. The mixture was sonicated for 0.5 h to obtain a colloidal suspension. The luminescent thin films were obtained by dropping the suspension on glass substrate (Glass substrate were dipped into an acid bath consisting of potassium dichromate and sulfuric acid for 12 h to remove possible organic residues on the surface and washed with copious amounts of deionized water, dried at 80 °C), followed by evaporation of water at 60 °C.

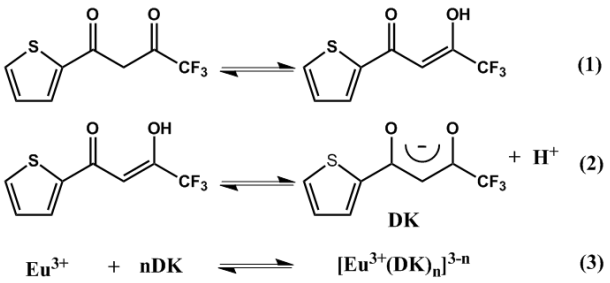

Fig. S3 Formation of Eu^{3+}–β-diketonate complexes.

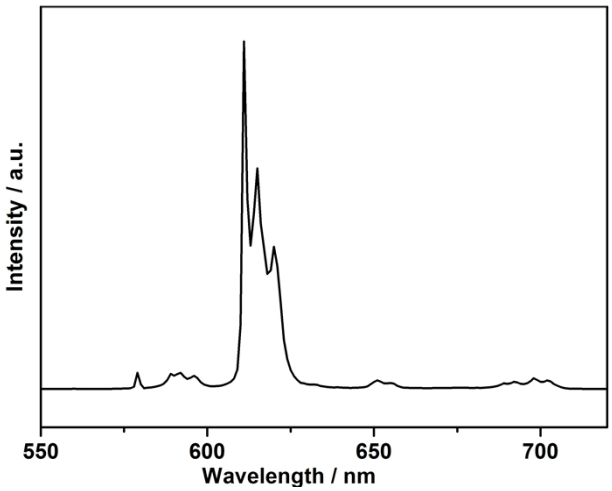

Fig. S4 Fluorescence spectrum of the $Eu^{3+}(TTA)_n$@Lap.(λ_{ex} = 365 nm)

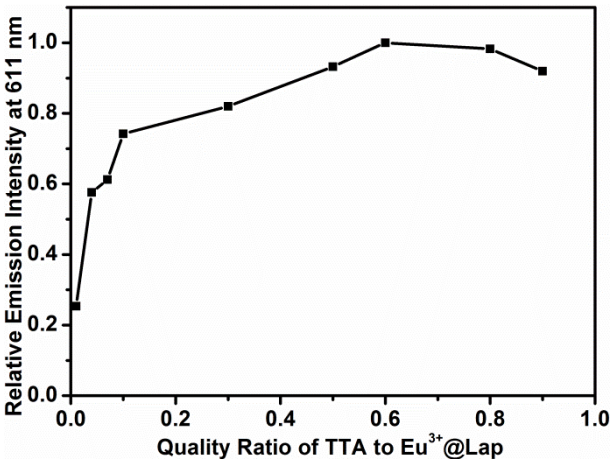

Fig. S5 Luminescence intensity at 611 nm versus the amount of TTA initially added to the reaction mixture containing Eu^{3+}@Lap.

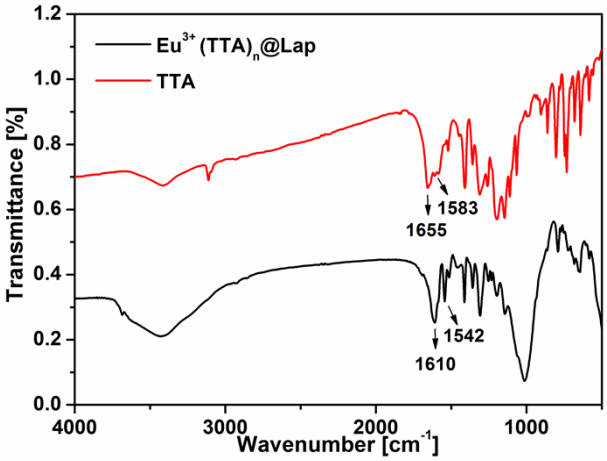

Fig. S6 FT-IR spectrum of $Eu^{3+}(TTA)_n$@Lap and TTA.

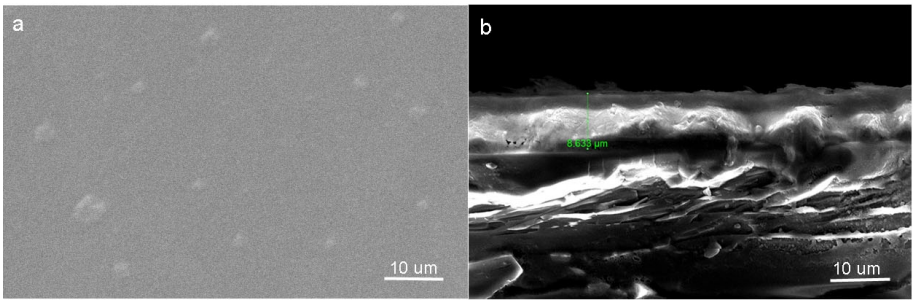

Fig. S7 SEM images of $Eu^{3+}(TTA)_n$@Lap thin film (a is for the top view while b is for the side view).

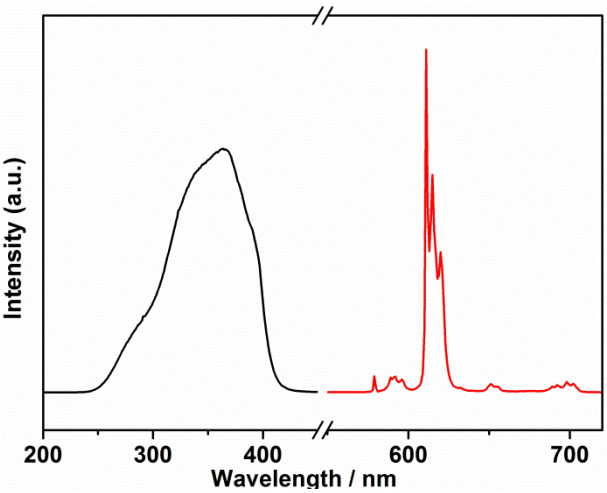

Fig. S8 Excitation (black line) and emission (red line) spectra of the $Eu^{3+}(TTA)_n$@Lap thin film (λ_{ex} = 365 nm).

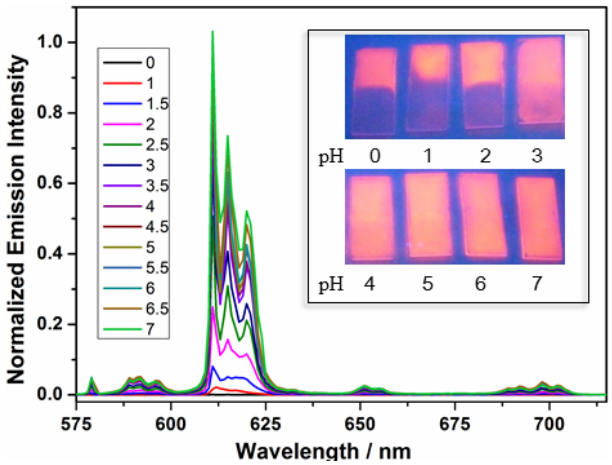

Fig. S9 pH value dependence of normalized emission spectra of $Eu^{3+}(TTA)_n$@Lap thin film. The inset presents partial sample under UV light irradiation in various pH value. (The normalized emission was defined as the ratio of emission value immersed in the acidic solution to the external reference emission value)

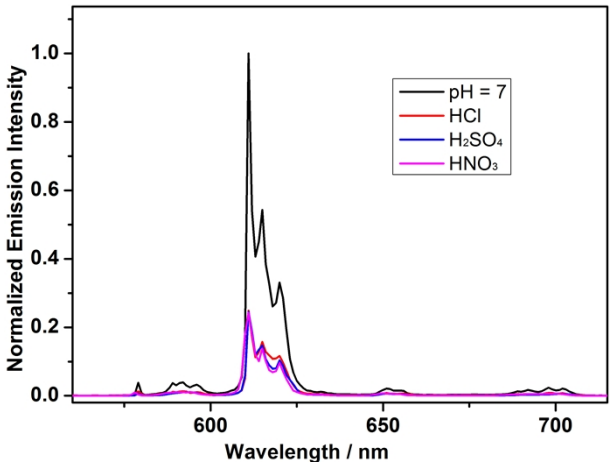

Fig. S10 Normalized emission spectra of $Eu^{3+}(TTA)_n$@Lap thin film response to H_2SO_4, HNO_3 and HCl respectively at pH = 2.

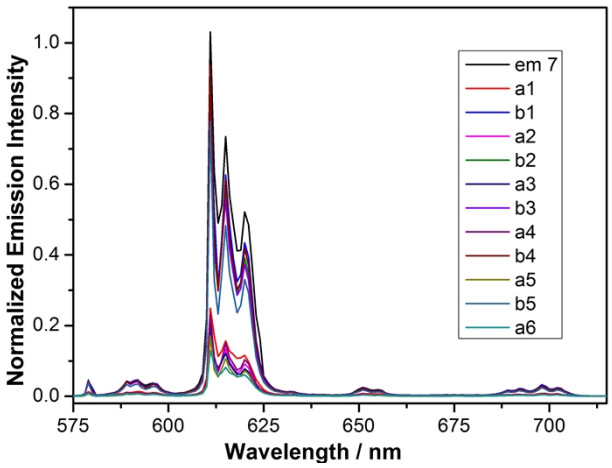

Fig. S11 Normalized emission spectral change of $Eu^{3+}(TTA)_n$@Lap thin film upon alternating immersion in hydrochloric acid and exposure to Et_3N vapor (em 7 present the initial emission spectral of the thin film, a means treated with acid, b means treated with alkaline gas Et_3N).

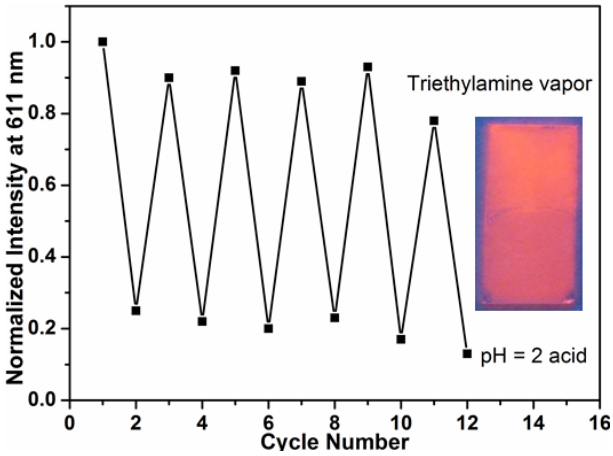

Fig. S12 Normalized emission spectral change of $Eu^{3+}(TTA)_n$@Lap thin film at 611 nm upon alternating immersion in hydrochloric acid and exposure to Et_3N vapor. (After 6 cycle, the hydrochloric acid solution was concentrated under the reduced pressure and dried in vacuum. Then, 5 ml of EtOH was added, no characteristic absorption of TTA was observed in the UV/vis spectra and no obvious Eu^{3+} was detected out from the inductively coupled plasma (ICP) analyses. These results indicated that the $Eu^{3+}(TTA)_n$@Lap is strongly coated on the glass substrate surface and no leaking of TTA and Eu^{3+} was observed.)

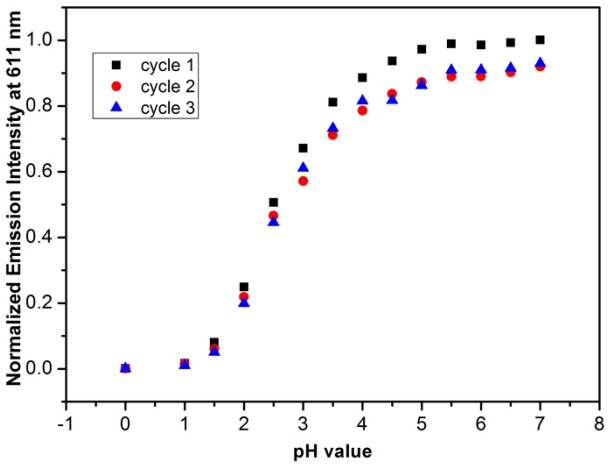

Fig. S13 pH value dependence of the $^5D_0 \rightarrow {}^7F_2$ emission of $Eu^{3+}(TTA)_n$@Lap thin film monitored at 611 nm by using the same film from pH = 7 to 0 for three cycle.