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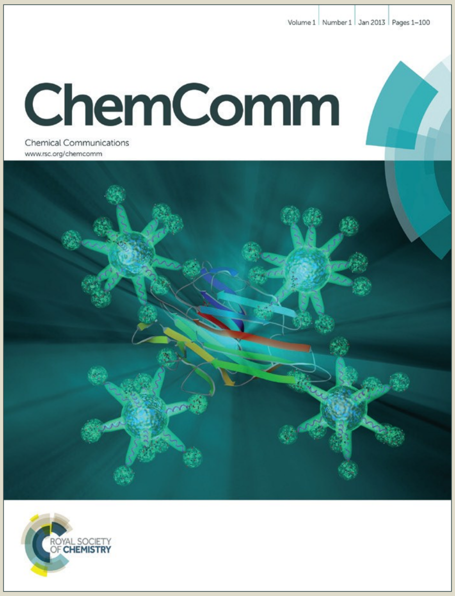

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ARTICLE TYPE

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

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In this work, loading of Eu^{3+}–*β*-diketonate complex into laponite, we herein report an organic-inorganic hybrid pH detection system $Eu^{3+}(TTA)_n$@Lap valid in acid condition, which can serve as highly robust, reliable, rapid responsive and sensitive fluorescent pH detector. In addition, this hybrid pH detector can be easily recovered and reused by simply treating with Et_3N vapor.

pH value is a fundamental physical quantity that governs large amount of manufacturing process and nearly every biological reaction in living cells.[1] Currently, in situ and real time characterization of pH value becomes continuing trend in analysis and diagnostics fields because of their obvious advantages.[2] In medicine, changes or abnormalities in the tissue pH are significant marker of disease, and can also be used to monitor treatment.[3] On the other hand, considerable industrial processes are detected and controlled by pH value. From an ideal point of view, these in situ and real time pH monitor should have the advantages, e.g., little impact on its substrates, rapid response, and wide application. These criterions pose a serious challenge to classical pH meters, such as measurements in metal etching surface, marine research, and aircraft surface.[4] Dramatic efforts have been devoted to the design and construction of novel pH meters. In contrast to other signal output, luminescence is one of the most sensitive and attractive detection signals because they can simultaneously provide the dual function of imaging and pH detecting. Until now, numbers of fluorescence based pH sensors have been reported based on CdSe/ZnS nanocrystals, sensitive dye molecules, core-shell silica nanoparticles, Au nanoshells possessing pH sensitive molecules and DNA.[5] The luminescence of lanthanide ions has been employed as an ideal luminescence probe,[6] which is used to sense molecules and ions based on their specific luminescence properties, such as large Stokes shifts, sharp emission profiles, and long-lived excited states.[7] Although the emission intensities of bare lanthanide ions are weak, the emission intensities increase remarkably after chelate formation with an organic ligand.[8] However, the potential of lanthanide ions as luminescence probe has barely been uncovered, which can be attributed to the poor processability and stability of lanthanide complex. Fortunately, the introduction of inorganic matrices provides an effective and new way for overcoming these defects and laponite[9] has emerged to be an ideal substance candidate.

In our previous work, we have reported for the first time, that the acid environment has significant influence on the luminescence performances of Eu^{3+}–2-thenoyltrifluoroacetate (TTA) complexes.[10] TTA ligand can be protonated under acidic environment, which competes with full coordination to Eu^{3+} ions (Fig. S3). The neutralization of the acid sites can obviously increase the luminescence efficiency due to the formation of complexes with high coordination numbers.[11] This rule is still applicable even the Eu^{3+}–*β*-diketonate complexe is loaded into laponite. Very recently,[12] we present a simple and environmentally friendly two-step strategy to prepare strongly red-light emitting lanthanide-based organic-inorganic hybrid materials by first in situ forming Eu^{3+}–*β*-dikeonate complexes on laponite platelets and subsequently modifying with a silane-functionalized imidazolium salt. The addition of imidazolium salt can remove the abundant protons on the Laponite platelets and fully protect Eu^{3+} ions from the water molecule quenching. These reports are mainly focus on luminescence enhancement by decreasing the proton strength inside the channels of NZL and laponite surface. However, taking full advantage of this feature as pH detector has not been extensively explored. Herein, inspired by the fact that the luminescence performance of Eu^{3+}–*β*-diketonate complexes is sensitive to proton strength, we wish to report a structurally simple, promptly responsive, and widely applicable thin film pH detection system $Eu^{3+}(TTA)_n$@Lap valid in acid condition by adopting the strategy of loading Eu^{3+}–*β*-diketonate complexes to the surface of laponite. Significantly, the thin film can be easily recovered and reused for several recycles upon exposure to Et_3N vapor.

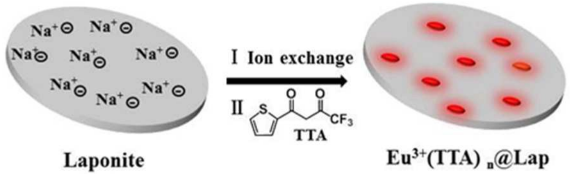

Fig. 1 Schematic of the procedure for preparing of $Eu^{3+}(TTA)_n$@Lap.

The loading of Eu^{3+}–*β*-diketonate to laponite was achieved by a two-step procedure according to our previous work.[12] Firstly, Eu^{3+}@Lap ions were prepared by substituting the positive Na^+ ions of laponite with Eu^{3+} via ion exchanges, followed by addition of TTA in aqueous solution (Fig. 1). The obtained powder denoted as $Eu^{3+}(TTA)_n$@Lap exhibited bright red emission when irradiated by near UV light (Fig. S4), this phenomenon indicate the formation of Eu^{3+}–*β*-diketonate complexes in between the interlayers of laponite. We find that the proportion of TTA to

Eu^{3+}@Lap has significant impact on the luminescence performance of $Eu^{3+}(TTA)_n$@Lap. The luminescence intensity of $Eu^{3+}(TTA)_n$@Lap increased gradually with increasing amount of TTA, which reached its maximum when the quality ratio of TTA to Eu^{3+}@Lap was set as 0.6:1 (Fig. S5). Fig. 2 shows images to give an intuitive impression of the effect. Therefore, the initial amount of TTA to Eu^{3+}@Lap was maintained at 0.6:1 in the following experiments, and the final loading molar ratio of TTA/Eu^{3+} under this condition was determined to be 3.15:1(see the experimental section in ESI).

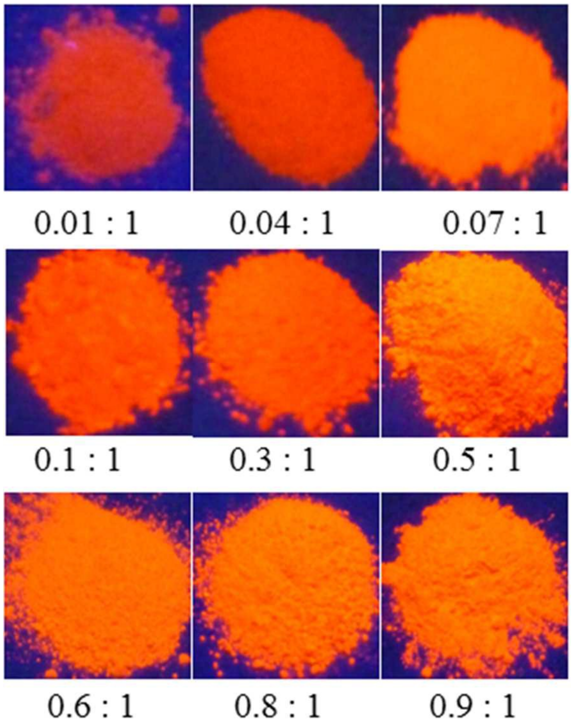

Fig. 2 Images of $Eu^{3+}(TTA)_n$@Lap under 365 nm UV lamp illumination upon different initial amounts of TTA to Eu^{3+}@Lap.

The formation of luminescent Eu^{3+}–*β*-diketonate complexes on Laponite was further confirmed by FT-IR spectra (Fig. S6). The absorption bands at 1655 and 1583 cm^{-1} in the FT-IR spectrum of individual TTA were assigned to C=O and C=C stretching vibrations of TTA, which shifted to 1610 and 1542 cm^{-1}, respectively, in the hybrid material $Eu^{3+}(TTA)_n$@Lap. The shifting to lower frequency is attributed to the coordination of TTA with Eu^{3+} ion. In addition, we also observed the characteristic Si-O stretch of laponite at 1010 cm^{-1}. The aforementioned results jointly demonstrate the successful loading of Eu^{3+}–*β*-diketonate complexes on Laponite.

More interestingly, we found that the $Eu^{3+}(TTA)_n$@Lap can be well dispersed in deionized water and result in stable translucent aqueous suspension (Fig. 3a), which exhibited bright red luminescence under UV irradiation at 365 nm (Fig. 3b). Since the successful preparation of thin films is an important prerequisite for device fabrication. We then explore the possibility of film deposition by our hybrid materials. As expected, luminescent thin film with good transparency was obtained by drop-casting the aqueous suspension of $Eu^{3+}(TTA)_n$@Lap onto a glass slide[13] followed by drying in air at 60°C (Fig. 3c and 3d). SEM images (Fig. S7) reveal the presence of densely and uniformly packed $Eu^{3+}(TTA)_n$@Lap on the glass substrate, side view of the glass slide revealed the height of the coating is 8.6 μm. Subsequently, we investigated the luminescent properties of the $Eu^{3+}(TTA)_n$@Lap thin film. By monitoring the $^5D_0\rightarrow{}^7F_2$ transition, the excitation spectrum (black line in Fig. S8) of the thin film was obtained as a broad band in the range of 240 - 420 nm, which is ascribed to the absorption of the TTA ligand and undoubtedly provides an alternative evidence for the energy transfer process from TTA to Eu^{3+}. The emission spectrum (red line in Fig. S8), excited at 365 nm, gave five sharp lines at 578, 592, 611, 652, and 698 nm, which could be assigned to the $^5D_0\rightarrow{}^7F_J$ (J = 0–4) transitions. Of which, the $^5D_0\rightarrow{}^7F_2$ line at 611 nm dominates the whole spectrum and is responsible for the fluorescence emission in red.

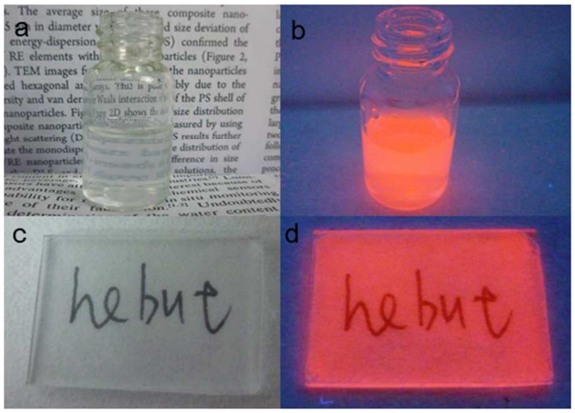

Fig. 3 Digital photographs of $Eu^{3+}(TTA)_n$@Lap dispersed in deionized water under (a) daylight and (b) UV illumination at 365 nm. Images of transparent thin film under (c) daylight and (d) the film under 365 nm UV irradiation.

It has been well-documented that the luminescence property of Eu^{3+}–*β*-diketonate complexes is very sensitive to pH value.[14] Acidic sites usually lead to fluorescence quenching of lanthanide complexes. It is worth expecting that our obtained thin film containing Eu^{3+}–*β*-diketonate complexes can be used for pH detection applicable to acid condition. The luminescence intensity of the thin film was detected after immersed in hydrochloric acid solution with various pH value and then dried in air. The fluorescence intensity of $Eu^{3+}(TTA)_n$@Lap thin film showed remarkable enhancement in accordance with increasing pH values and reached to the balance when pH increased at 5 (Fig. S9). The emission intensity of $Eu^{3+}(TTA)_n$@Lap at 611 nm versus pH is plotted in Fig. 4. It is shown that almost 60-fold luminescence enhancement is observed upon pH change from 1 to 5, suggesting the outstanding sensitivity in such wide pH range. In addition, the luminescence performance change is easily visible by the naked eye on near-UV excitation (Fig. S9, inset). It should be noted that the emission peak of the thin film do not shift within the investigated pH window. In our case, one half of the thin film was immersed in the acidic solution to detect the pH-dependent luminescence performance, whereas the other half of the same film was exposed to air and used as the external reference to eliminate the individual difference among different film samples.

Moreover, response speed to pH changes and commonality must be considered for evaluating the luminescence pH detecting systems. As both the protonation and deprotonation are instantaneously reversible chemical processes, the luminescence change can be completed immediately after immersing in acid solution, which can be considered as a real-time measurement. Meanwhile, it can be seen that the $Eu^{3+}(TTA)_n$@Lap thin film is generic and universally applicable to various acids, ultimately resulting in the fluorescence quenching to the same extent under the comparable experimental conditions. The representative luminescence changes in the presence of other acids, including H_2SO_4 and HNO_3, were listed in Fig. S10. In addition, it is significant to note that the hybrid pH detector can be easily recovered and reused for several recycles without obvious loss in luminescence intensity and pH-responsive hysteresis (Fig. S12 inset). The luminescence performance of the film can be recovered completely after exposure to equilibrated vapor of Et_3N for 2 min, and 6 cycles of the pH-dependent emission were conducted upon alternating immersion in hydrochloric acid with a pH value of 2 and exposure to Et_3N vapor. These results (Fig. S11 and S12) reveal that $Eu^{3+}(TTA)_n$@Lap thin film on the substrate shows good reversibility. In order to fully detection the reversibility, plot of luminescence value versus pH was added by using the same film from pH = 7 to 0 for three cycle and the pH detector show good restorability (Fig. S13).

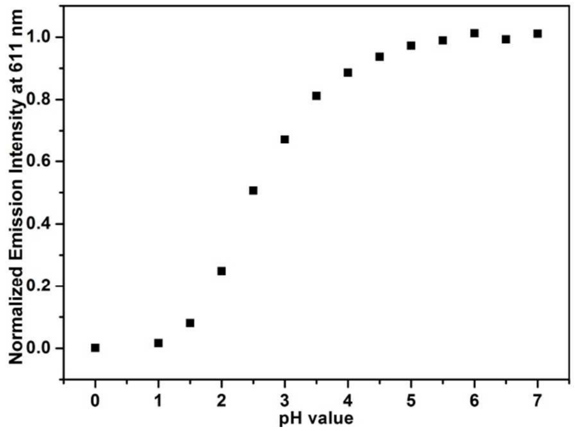

Fig. 4 pH value dependence of the $^5D_0 \rightarrow ^7F_2$ emission of $Eu^{3+}(TTA)_n$@Lap thin film monitored at 611 nm.

In summary, a structurally simple, promptly responsive, and widely applicable thin film pH detector $Eu^{3+}(TTA)_n$@Lap valid in acid condition has been constructed by loading of Eu^{3+}–*β*-diketonate complexes to laponite. The hybrid pH detector is highly sensitive to acid sites over a wide pH range and exhibits pH-dependent luminescence behaviors, which can be observed directly by naked eyes. In addition, the hybrid pH detector can be easily recovered and reused by treating with Et_3N vapor. Considering that laponiteis a very important coating additive, we believe that this host–gust hybrid pH detector will be an appealing alternative for in situ and real time detection of pH in many special areas, such as reaction kettle lining and aircraft/ship surface coating materials.

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Notes and references

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