



Photo- and thermo-stable luminescent nanocomposite resulting from hybridization of Eu(III)- β -diketonate complexes with laponite



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ABSTRACT

Herein we report the red-emitting nanocomposites via the adsorption of 2-thenoyltrifluoroacetone on the Eu³⁺-containing Laponite that was obtained by substituting the positive Na⁺ ions with Eu³⁺ via an ion exchange procedure. The in-situ formation of luminescent Eu³⁺ complexes is confirmed by Fourier Transform Infrared spectra and luminescent data. X-ray diffraction patterns suggest that at least partial complexes are intercalated within the interlayers of the Laponite. Furthermore, we observed that the solvent used in the ion exchange step shows pronounced influence on the luminescent behaviour of the final nanocomposites. In addition, the luminescent nanocomposite displays high photo- and thermo-stability.

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1. Introduction

Lanthanide complexes, especially lanthanide β -diketonate chelates, display strong emission lines upon UV light irradiation owing to the sensitization of lanthanide ions by the coordinating ligands. Intramolecular energy transfer occurs from the coordinating ligands to the localized intra-4f shell of the lanthanide ions, leading to luminescence with an enhanced quantum yield [1–7]. However, due to their poor thermal stabilities and low-mechanical strength, they have not so far been used extensively in practical applications as tunable solid-state lasers or phosphor devices. A feasible way to overcome these problems is the incorporation of these complexes into matrices [8–14] such as zeolites [15–18], organic-inorganic hybrid networks [11,19,20], and ionic liquids [21,22]. We have reported the encapsulation of lanthanide complexes within the channels of zeolite L crystals and interesting results have been achieved [15,23–26]. The photo- [23] and thermo-stability [26] of lanthanide complexes were obviously enhanced after insertion into the channels of zeolite L; dense, homogeneous, well-oriented, stable, and highly organized luminescent monolayer of zeolite L were obtained with a functional linker, the emitting color of the monolayers can be fine-tuned [25]; the proton strength in channels of zeolite L was also probed by the luminescence feature of the

encapsulated Eu³⁺- β -diketonate complexes [18,27] and the corresponding nanocomposites have been successfully used to detect basic molecules [28]. However, one of the problems using zeolites as the matrices is that the spaces where the guest species are accommodated are believed to be rigid and could not be adjusted according to the size of the accommodated guest species.

Layered clays show obvious advantages for accommodating bulky guest species such as lanthanide complexes because the thickness of interlayer spaces of clays can to some extent be adjusted by the guest species [12,29–31]. Increased interest is currently focused on Laponite (chemical composition Na_{0.7}[Mg_{5.5}Li_{0.3}Si₈O₂₀(OH)₄](H₂O)_n) [32,33], a synthetic layered silicate clay that is in the form of disk-like nanoparticles with a diameter of 25 nm and a thickness of 0.92 nm, consisting of an octahedral sheet of magnesium oxide surrounded by two tetrahedral sheets of silicon oxide. Substitution of Mg²⁺ with Li⁺ yields negatively charged layers, the charge of which is counterbalanced by the corresponding number of cations, typically Na⁺ that are located in the interlayer between the disk-shaped particles. The intercalation of lanthanide complexes in-between the interlayer spaces of Laponite was reported by Kynast [34]. They also investigated the luminescence of the nanocomposite in aqueous solution. We studied the luminescence of ionic complexes on Laponite, however the complexes are mainly on the outer surfaces of the platelets rather than intercalated within the interlayer spaces. Moreover, all the published works have not been involved with the influence of clay on

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the performances of the final luminescent nanocomposite such as the thermo- and photo-stability of the accommodated lanthanide complexes.

In this work, we report a photo- and thermo-stable luminescent nanoparticle through the *in situ* formation of Eu^{3+} - β -diketonate complex ($\text{Eu}^{3+}(\text{TTA})_n$, TTA = 2-thenoyltrifluoroacetate) on the surface of Laponite platelets by loading TTA ligand on the Eu^{3+} -exchanged Laponite. We observe that the solvent during the procedure of loading Eu^{3+} on Laponite plays a great role to determine the luminescence efficiency of the resulting luminescent nanocomposite. Furthermore, the luminescent nanocomposite shows remarkably enhanced photo- and thermo-stability compared with the corresponding pure europium (III) β -diketonate complexes.

2. Experimental

2.1. Material

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 $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ were prepared by dissolving Eu_2O_3 in concentrated hydrochloric acid.

2.2. Preparation of $\text{Eu}^{3+}(\text{TTA})_n@Lap\text{-EtOH}$

Laponite RD (0.5 g) was dispersed in ethanol solution (10 mL), a solution of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (5 mL) was added. The mixture was then stirred at 80 °C for 24 h and the precipitate was recovered by centrifugation, which was further added to TTA (0.150 g) dissolved in ethanol (10 mL). Vigorous sonication of the mixture for 2 h led to the luminescent nanocomposite, which was recovered by centrifugation and washing with ethanol three times, the obtained precipitate was dried in an oven at 80 °C overnight.

2.3. Preparation of $\text{Eu}^{3+}(\text{TTA})_n@Lap\text{-H}_2\text{O}$

$\text{Eu}^{3+}(\text{TTA})_n@Lap\text{-H}_2\text{O}$ was similarly prepared except that ethanol was replaced with water during the step of exchanging Na^+ with Eu^{3+} from Laponite.

2.4. Material characterization

Infrared (IR) spectra were obtained with a Bruker Vector 22 spectrophotometer by using KBr pellets for solid samples from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} and by using ATR (Attenuated Total Reflection) for oily samples from 4000 to 650 cm^{-1} at a resolution of 4 cm^{-1} (16 scans collected). X-ray diffraction patterns were taken on a Rigaku-Dmax 2500 diffractometer using Cu K α 1 radiation. The steady-state luminescence spectra and the lifetime measurements 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. Absolute quantum yield measurements were carried on the aforementioned fluorescence spectrophotometer equipped with an integrating sphere. The fluorescence quantum yield of the sample was obtained according to the manual provided by Edinburgh Instruments.

3. Results and discussion

The intercalation of Eu^{3+} - β -diketonate complexes in-between the interlayers was achieved by a two-step procedure. Eu^{3+} ions were firstly loaded by substituting the positive Na^+ ions via ion exchanges both in ethanol and in water. The ethanol-based procedure produced a precipitate denoted as $\text{Eu}^{3+}@Lap\text{-EtOH}$, while wet gels containing ~80wt% water was obtained when the water-based procedure was used due to the complete delamination of Laponite in water, which we denoted as $\text{Eu}^{3+}@Lap\text{-H}_2\text{O}$. The precipitate and the wet gels were added to an ethanol solution of TTA, respectively, and the mixture was then sonicated for 10 min. The resulting luminescent nanocomposite was recovered by centrifugation, washed with ethanol several times and dried at 80 °C, and denoted as $\text{Eu}^{3+}(\text{TTA})_n@Lap\text{-EtOH}$ and $\text{Eu}^{3+}(\text{TTA})_n@Lap\text{-H}_2\text{O}$, respectively. The Eu^{3+} - β -diketonate complexes were finally formed in-between the interlayers, as revealed by the bright red emission upon near UV excitation shown in Fig. 1. To our surprise, the emission of $\text{Eu}^{3+}(\text{TTA})_n@Lap\text{-H}_2\text{O}$ is much more intense than that of $\text{Eu}^{3+}(\text{TTA})_n@Lap\text{-EtOH}$ (Fig. 1).

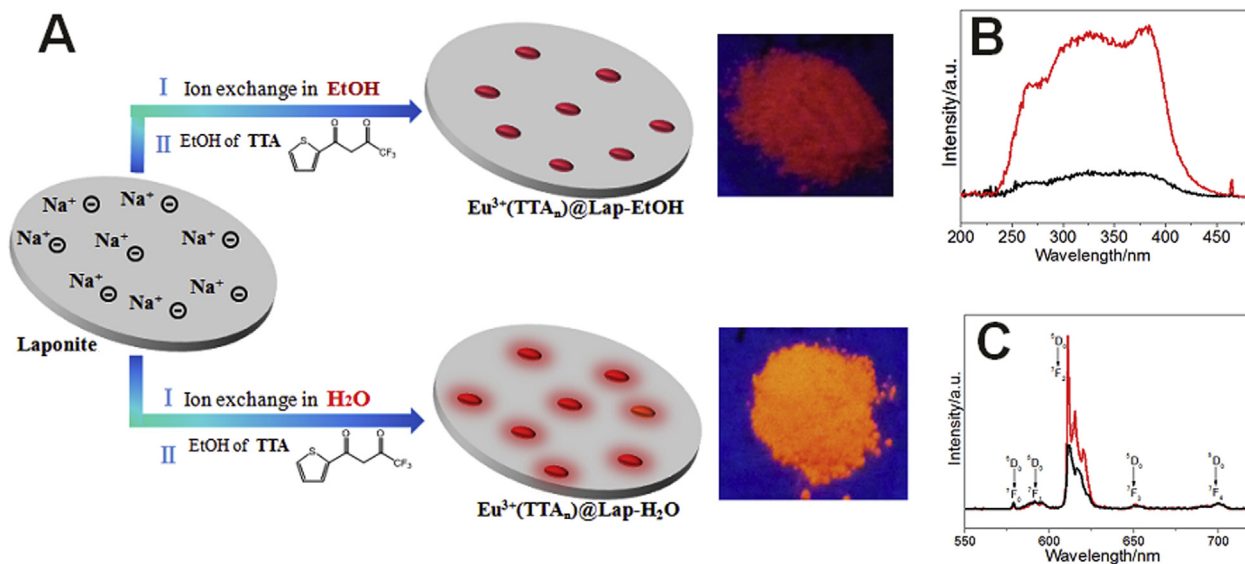


Fig. 1. A) Fabrication process of the luminescent hybrid material in two different solvent (H_2O and EtOH) with photographs of $\text{Eu}^{3+}(\text{TTA})_n@Lap\text{-EtOH}$ and $\text{Eu}^{3+}(\text{TTA})_n@Lap\text{-H}_2\text{O}$ under near UV light illumination. B) Excitation spectra monitored at 612 nm and C) emission spectra excited at 340 nm of $\text{Eu}^{3+}(\text{TTA})_n@Lap\text{-EtOH}$ (black line) and $\text{Eu}^{3+}(\text{TTA})_n@Lap\text{-H}_2\text{O}$ (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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