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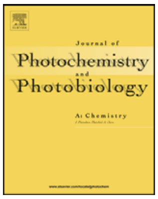

Smart pH sensitive luminescent hydrogel based on Eu(III) β-diketonate complex and its enhanced photostability

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ABSTRACT

A luminescent hydrogel was successfully prepared by immobilizing an europium(III) tetrakis(β-diketonate) complex into a gallate-based hydrogelator. The Eu(III) emission in hydrogel media was switched reversibly "on-off" as a function of pH and the corresponding thermal and photostabilities dramatically increased compared with its solution sample.

1. Introduction

Lately, the design and synthesis of a luminescent signaling system and utilization of metal ions or complexes to control emission through the construction between guest molecules and suitable matrices are emerging areas for the development of luminescent sensors and optical switches [1–6]. With regard to an emission center, lanthanide ions with a long lifetime ranging from sub-microseconds to sub-milliseconds and narrow line emission bands are highly desirable and critical tools in the biological monitoring field because their signals can be easily separated from the fluorescent background [7–9]. As the lanthanides have low extinction coefficients, their direct excitation is not feasible and high absorbance ligands are needed. One well known example of the highly efficient red-emitting complex is $Eu(TTA)_3(phen)$ (HTTA = 2-thenoyltrifluoroacetone and phen = phenanthroline) with a quantum yield of 36.5% [10,11]. Accordingly, much interest is now devoted to how to immobilize the luminescent centers inside specific hosts which have the transparency required for future optical applications. Among numerous matrices, molecular gels, a kind of soft material, have generated enormous interest because they can be transformed from sol to gel stages across a transition temperature T_g. Furthermore, the phenomenon of gelation is considered to be the formation of fibrous nanostructures which become entangled and trap solvents through surface tension, and the orderly aggregated organic molecules may have a totally different influence on the optical properties [12].

In this report, we studied a luminescent hydrogel achieved by a gallic acid derivative **1** doped with an europium(III) β-diketonate complex (Fig. 1). The synthetic gallamide was grafted by three long aliphatic chains and a poly(ethylene glycol) with a terminal hydroxy group which provided hydrophobic and hydrophilic moieties [13]. We previously found a similar compound complexed with dysprosium ions and an on/off switchable emission was observed during the phase transition [14]. Such an europium(III) β-diketonate complex is chosen due to its outstanding luminescent property in quantum efficiency. Additionally, it easily decomposes under pH change because β-diketones exhibit keto-enol tautomerism and the equilibrium is quite sensitive to pH value and also Gunnlaugsson and coworkers very recently reported a pH-sensitive europium complex in an aqueous solution system [15]. Therefore, we studied the photoactive species hosted in a hydrogel network, which will offer potential application in monitoring biological events, preparing soft materials, controlling the movement of the substrate in the media and so on. We foresaw that the luminescence of the doping hydrogel is pH-dependent and the present system, to the best of our knowledge, is the first example of pH driven luminescent low molecular weight hydrogel in which the Eu(III) emission was switched on and off by tuning the pH from basic to acidic.

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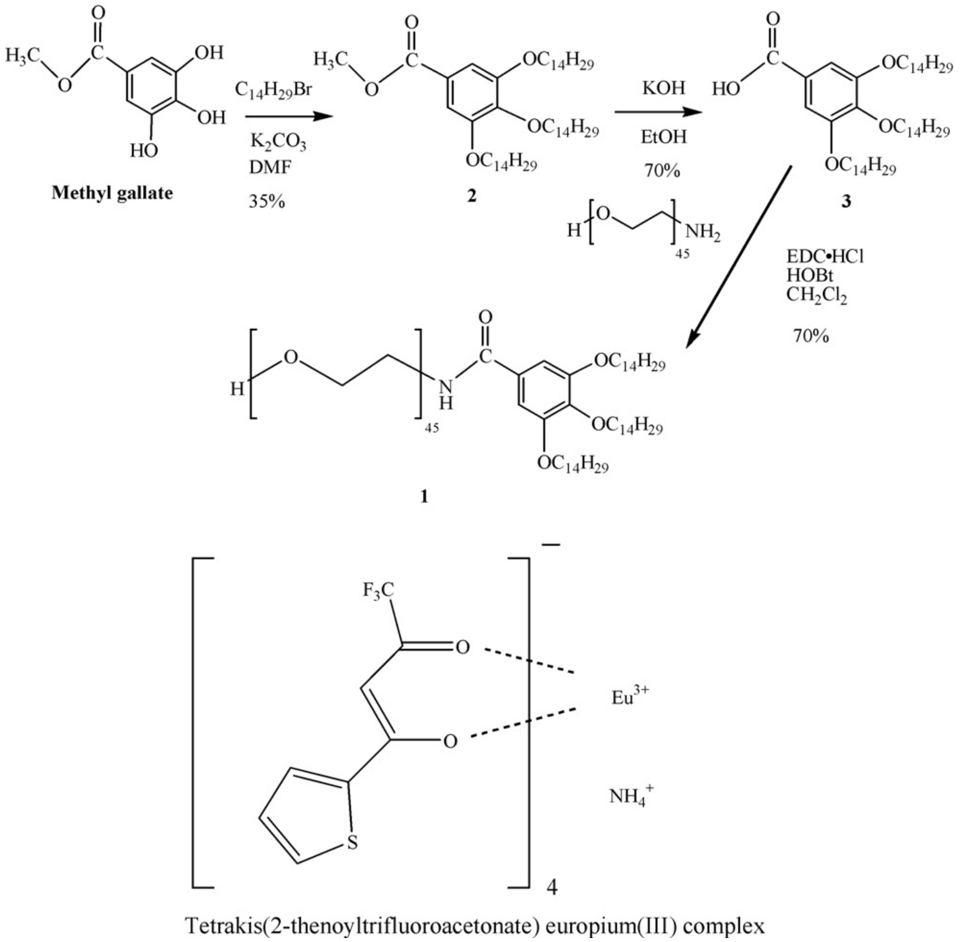

Fig. 1. Synthetic route of hydrogelator compound **1** and structure of europium complex.

2. Experimental

2.1. General

All the starting materials were obtained from commercial suppliers and used as received. DMF was distilled under reduced pressure and other solvents were used as provided. Visible and fluorescence spectra were measured on Hitachi U-3500 and F-4500 spectrometers, respectively. Infrared spectra were measured with a Shimadzu FTIR-8600 spectrometer. Luminescent quantum yields were measured at room temperature using a Hamamatsu photonics absolute PL quantum yield measurement system C9920-02. Elemental analyses were performed at Integrated Center for Science, Ehime University.

Compound **1** was prepared from methyl gallate and PEG 2000 (see Fig. 1). The synthetic procedures were available from the literature [16] and the full data will be reported elsewhere.

2.2. Preparation of $NH_4[Eu(TTA)_4]$ complex

HTTA (0.99 g, 4.0 mmol) was dissolved in boiling ethanol (15 ml) and $NH_3 \cdot H_2O$ (270 μl, 4.0 mmol) was added, then $Eu(CH_3COO)_3 \cdot 4H_2O$ (0.40 g, 1.0 mmol) in ethanol (2 ml) was dropped. After the hot mixture was filtered, orange-red crystals were grown from the filtrate during 2 days of standing to give $NH_4[Eu(TTA)_4]$ (0.947 g, 0.90 mmol, 90% yield): mp 169–171 °C. IR (KBr) 1600 (C=O), 1539, 1411, 1182, 786, 721, 680, 642, 582 cm^{-1}; MS (APCI) found *m/z* 1036 ($[Eu(TTA)_4]^-$); Anal. Found: C, 35.82; H, 2.56; N, 1.42%. Calcd for $C_{32}H_{20}EuF_{12}NO_8S_4 \cdot H_2O$: C, 35.83; H, 2.07; N, 1.31%.

2.3. Preparation of hydrogel and solution samples

$NH_4[Eu(TTA)_4]$ (0.5 mg) was dissolved in DMF (10 μl), then diluted with distilled water (0.5 ml) and compound **1** (68.5 mg) was added. The mixture was slowly heated to 65 °C and turned into a clear solution. The solution was cooled down to room temperature and the gel was formed after standing overnight; the phase transition temperature was about 28 °C. The homogeneous aqueous solution was prepared similarly except for the addition of compound **1**. pH value was controlled by adding NaOH to acidic samples from pH 2 to 11 and the concentration of NaCl was fixed at around 100 mM.

3. Results and discussion

Changes of the Eu(III) emission were evaluated in terms of pH variation. The pH value of the distilled water used was around 4.8, where the $NH_4[Eu(TTA)_4]$-doped hydrogel gave a characteristic red luminescence with irradiation at 402 nm (see solid line in Fig. 2). The emission spectrum consists of five bands from $^5D_0$ to ^7F_J multiplets (J = 0, 1, 2, 3, 4), the most intense band located at 613 nm giving the red-colored emission. According to Binnemans description [17], 82% of the total emission light output came from $^5D_0 \rightarrow {}^7F_2$ transition with high monochromatic purity and Table S1 presents the detailed information. When the hydrogel was soaked in an aqueous

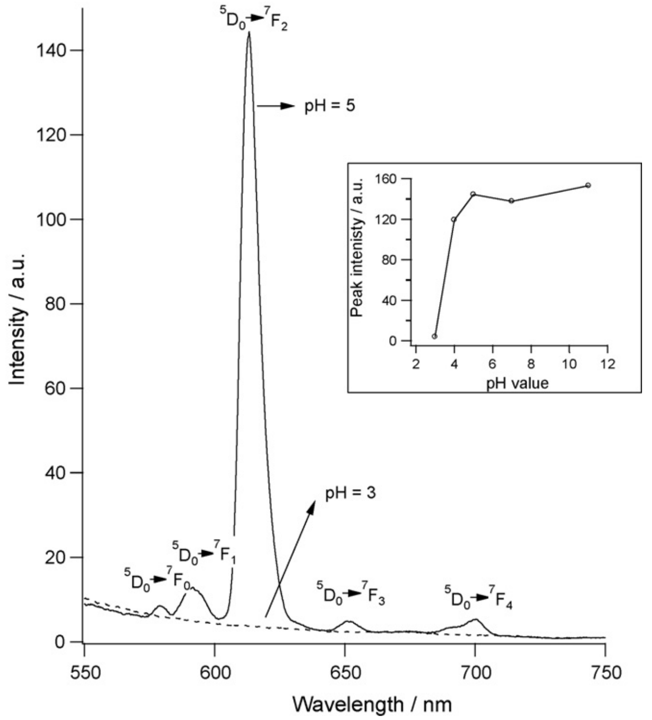

Fig. 2. Emission spectra of europium complex containing hydrogel at pH 3 (broken) and pH 5 (solid) by excitation at 402 nm. Inset: emission peak intensities versus pH value.

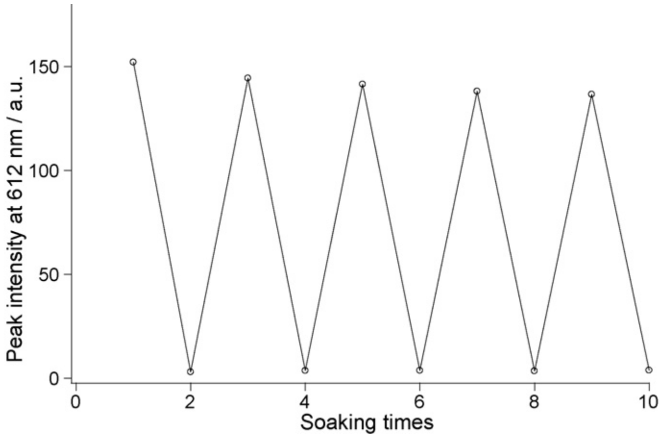

Fig. 4. Emission peak intensities of europium complex containing hydrogel by alternative soaking with acid and base, data in odd and even numbers refer to the values after acidic and basic treatments, respectively. Peak intensities were recorded at $^5D_0 \rightarrow {}^7F_2$ transition by excitation at 402 nm.

acid solution for 1 h, the red emission arising from Eu(III) was completely quenched and switched off (broken line in Fig. 2). Fig. 3b and c provide clear views of the pH dependence of Eu(III) emission. It is obvious that under acidic conditions, europium(III) β-diketonate complexes decompose by protonation of the anionic ligand to give the free neutralized ligand. The resulting non-luminescent hydrogel was treated with water (pH 5) where the red luminescence from Eu(III) was gradually recovered. The detailed emission intensities versus pH value were given in the inset of Fig. 2 and the luminescence intensity does not change greatly after 4–5 cycles (Fig. 4). Therefore, the results show: (1) the emission complex, europium(III) β-diketonate, was dispersed homogenously within the soft matrices, (2) the luminescence in acidic aqueous solution was switched *off*, and (3) in pH over 4, the emission from Eu(III) was switched *on*. In other words, the europium complex in the gallate-based hydrogel is highly sensitive to pH. Additionally, to investigate the influence of surrounding water molecules on the luminescence from europium ions, we measured luminescent quantum yields of $NH_4[Eu(TTA)_4]$-doped hydrogel and its D_2O-gel. The values were 0.16 and 0.17% in H_2O and D_2O-gels, respectively, indicating that outside water molecules should not contribute to the quenching of the $^5D_0$ excited states and the effect of water coordination is insignificant.

The formation and dissociation of complexation between Eu^{3+} and TTA^- within gel matrices were also observed in absorption spectra. As shown in Fig. 5, the emissive hydrogel (pH 5) had three broad bands located at 262, 300 and 336 nm in an ultraviolet light region from 250 to 400 nm (solid line). Especially the band at 336 nm proves the coordination between Eu^{3+} and TTA^- ligands, which was observed as the major peak in the pure $Eu(TTA)_4$ complex (broken line of Fig. 5) and completely disappeared in the non-emissive hydrogel (pH 3, dotted line of Fig. 5).

In a homogeneous and diluted aqueous solution, the Eu(III) complex emission appeared at pH 5 and disappeared at pH 3 as seen in the hydrogel (vide supra). In contrast, the pH-dependent luminescence in a solution at less than 10^{-3} M concentration was totally different from the high reversibility in the gel matrices. Titration of an acid solution with base showed the luminescence was still silent and did not recover. Under high concentration such as 10^{-2} M

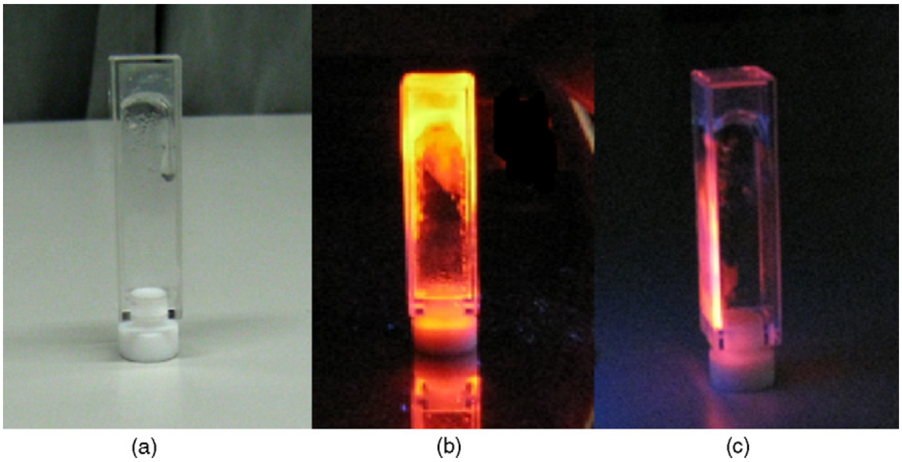
(a) (b) (c)

Fig. 3. Europium complex containing hydrogel under room light (a) and under 254 nm excitation at pH 5 (b) and pH 3 (c).

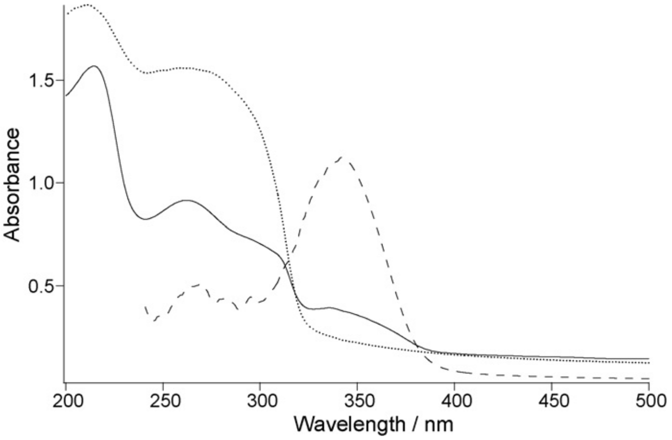

Fig. 5. Absorption spectra of europium complex containing hydrogel under pH 5 (solid line) and pH 3 (dotted line); the dashed line refers to absorption spectrum of Eu(TTA)$_4$ complex in aqueous solution (10^{-5} M in DMF/H_2O = 1/100).

where some precipitates were formed, the europium emission was partially retrieved.

The thermal- and photochemical stabilities of europium complexes are considered to be a very crucial factor in application of luminescent devices [18]. Hydrogels are a new class of soft materials which are attractive because they are permeable to a water system and also provide a unique non-solution environment for real-time sensors. The microenvironments of the hydrogel may exhibit a good shielding effect for the imbedded lanthanide complexes. In order to know more about the effect of such hydrogel matrices on the stability of the europium complex, the temperature-dependent luminescence spectra were measured and compared to those in the aqueous solution.

In the gel system, we can obtain desired red emissions of europium ions from 20 to 55 °C, the luminescence intensity fell slightly from 67 to 62 (Fig. S1). We continued to heat the sample at 55 °C from 30 min to 5 h, the prolonged duration had only a small effect on the europium emissions in the gel state since the peak intensity (62) at 30 min changed slightly to 54 after 5 h. However, in the solution sample, the luminescence intensity (296) at 20 °C was drastically reduced to 85 at 30 °C, then decreased to only 4 at 55 °C (Fig. S2). Hence, it is clear that lanthanide β-diketonates in a solution suffered from poor thermal-stability and the above aqueous sample lost 98% of its emission during the temperature change from 20 to 55 °C. In contrast, the self-assembled soft matter of compound **1** could effectively shield the emitting centers from luminescence quenching and the thermal-stability of Eu(III) β-diketonate was intensively enhanced.

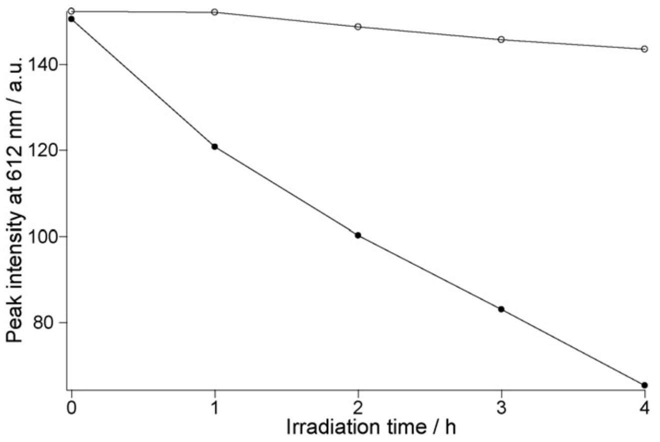

Fig. 6. Emission intensities of europium complex in an aqueous solution (10^{-5} M, filled circle) and in a hydrogel (empty circle) after irradiation with a halide lamp. Peak intensities were recorded at $^5D_0 \rightarrow {}^7F_2$ transition by excitation at 402 nm.

In addition, the Eu(III) β-diketonate complex doped hydrogel displayed an improved photostability in comparison with the same complex dissolved in water. The two samples were exposed under irradiation of a halide lamp (350–750 nm) for 4 h and their photoluminescence spectra show that the solution sample exhibited an almost 50% decrease in intensity while the hydrogel sample remained nearly intact (Fig. 6).

4. Conclusion

In this report, we described photoluminescent Eu(III) β-diketonate complex in hydrogel of synthetic gallamide **1**. This technique can provide the immobilization of luminescent lanthanide complexes in soft matrices. We first realized a reversible on/off switch based on the hydrogel along with the pH change. Of significant importance, the emissions within the hydrogel showed greatly enhanced photo- and thermal-stabilities in comparison with its solution sample.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2008.10.005.

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