

A Novel Luminescent Organogel Containing Dysprosium Ions Quenched by Gel-to-sol Transition

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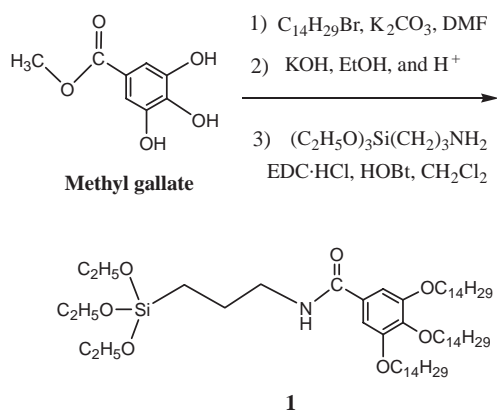
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A synthetic amphiphilic gallamide bearing three hydrophobic tetradecyl chains and a hydrophilic triethoxysilyl group formed a gel in ethanol at room temperature, which complexed with dysprosium ions to show an “on–off” switchable emission property at the phase-transition point (ca. 48 °C).

The tremendous interest induced by organogels is due to a combination of their future industrial application such as cosmetics or polymeric soft matter matrices and capability of growing from a homogenous solution into a delicate fine structure within common organic solvents.^{1–3} There have also been some successful efforts particularly in regard to metallo gels, owing to the study of metallophilicity that directed the formation of gels and the exploration of spectroscopic properties exhibited by a series of transition-metal complexes.^{4–6}

Lanthanide elements are well known for their unique luminescence properties but with very low absorption coefficients. In order to enhance the light absorption cross section, an antenna effect mechanism in which the lanthanide ion was coordinated with suitable organic chromophores was adopted.⁷ Numerous investigations have been reported that such sensitizers as β -diketonates and aromatic carboxylic acids are able to transfer their energy to rare earth ions effectively.^{8–12} Additionally, the Ln^{3+} –aromatic acid complexes showed a higher thermal stability than β -diketonates probably due to their infinite chain structure of chelation.¹⁰ Among all the lanthanide ions, Eu^{3+} and Tb^{3+} were frequently focused on owing to their red and green emission whereas other lanthanid complexes are less studied. Recently, dysprosium ion attracted much interest because of its characteristic blue (around 480 nm) and yellow emission (around 570 nm).

We, therefore, designed and synthesized a novel organogelator equipped with an aromatic ring, compound **1** based on



Scheme 1. Synthesis of compound **1**.

methyl gallate (Scheme 1). The presence of three long aliphatic alkyl chains in compound **1** not only reinforced the self-association properties of the amide functional groups but also decreased its solubility in polar solvents like ethanol and methanol. To overcome this problem, we attempted to introduce triethoxysilyl moiety ($\text{Si}(\text{OEt})_3$) which can be used as a sol–gel processable silicate precursor.¹³

Compound **1** was fully dissolved in CHCl_3 , CH_2Cl_2 , or THF and readily formed the stable gel with white color in ethanol (30 mg mL^{-1}) or methanol (32 mg mL^{-1}) at room temperature. The sol–gel transition in ethanol took place at around 48–50 °C. After several warming and cooling cycles, the supramolecular architecture of the organogel was regarded to be still thermoreversible owing to the repeated formation of robust white gel. The NMR spectra showed that triethoxysilyl groups were not hydrolyzed under the mild warming conditions and that the monomeric form of compound **1** remained stable (data not shown).

Enlightened by the latest publications,^{14,15} lanthanide could bind well to a carboxylic acid and is potentially coordinated with the amide group in compound **1**. We investigated the coordination ability of compound **1** in ethanol. At a low concentration ($1 \times 10^{-5} \text{ M}$) of compound **1**, dysprosium ions were not sensitized by its photoexcited state and no emission from the metal ions over 450 nm was observed at all (Figure S1), indicating that no complex of **1** with Dy^{3+} was formed in the homogeneous solution.

At a high concentration ($3.1 \times 10^{-2} \text{ M}$) of **1** in ethanol, the gel formed as mentioned above to give a red-shifted and broadened absorption band (from 261 to 275 nm see Figure S1). Addition of 0.1 equivalent of $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ did not disturb the formation of gel and afforded visible emission (Figure S2). The partial coordination was substantiated by the infrared spectra (Figure S3). Two sharp emission peaks were located at the blue (480 nm) and yellow regions (573 nm) which corresponded to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2,13/2}$ transitions of dysprosium ions, respectively (Figure 1). Up to 47 °C, the emission bands changed slightly to show the gel’s stability. Moreover, in the gel state (up to 47 °C), the peak of fluorescence excitation spectra remains almost unchanged in its intensity and shifts from 318 to 322 nm (Figure S4). This band is common in the excitation band of dysprosium complex,¹⁶ providing evidence that $\text{Dy}-\text{O}$ coordination exists inside the organogels. But when heated over T_{gel} , the $\text{Dy}-\text{O}$ coordination collapsed and the emission peaks at 480 and 573 nm disappeared; the characteristic Dy^{3+} emission thus vanished completely and we achieved the “on” and “off” states of the fluorescence by adjusting the temperature. To the best of our knowledge, to date there have been very few cases involving the organogels in conjunction with lanthanide ions;¹⁷ this is the first example of a lanthanide optical switch type low-molecular-weight organogel controlled by temperature variation.

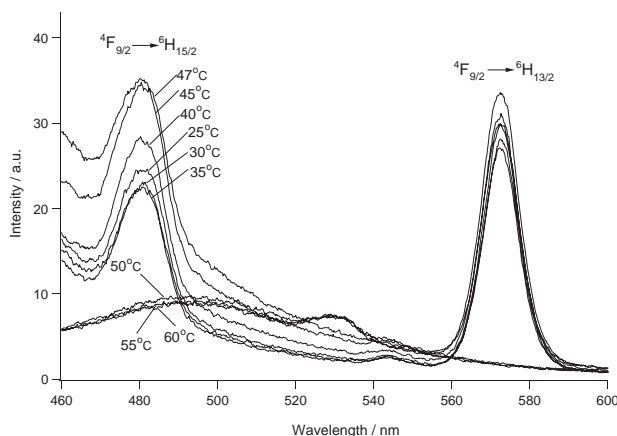


Figure 1. Temperature dependence of emission spectra of EtOH-gel of **1** containing Dy³⁺ ($\lambda_{\text{ex}} = 319 \text{ nm}$).

It is worth pointing out that the luminescence of a lanthanide-containing organogel can be used as a tool to examine the nature of the metal binding in this system. The substantial reduction found in the dysprosium-based emission cannot be observed in the corresponding terbium-activated organogel in which the luminescence has decreased gradually during the heating process (Figure S5).¹⁸ The difference is ascribable to the fact that the unique and loose coordination bonds of **1** with Dy³⁺ are easily thermally broken whereas the too strong coordination interactions between **1** and Tb³⁺ cause the gel to lose its stimuli-responsive properties. Both the emission bands observed in **1**-Dy³⁺ were completely reversible upon cooling and heating. The proposed mechanism for the unique emission property is described as follows: Firstly, the gel formation is a hierarchical process requiring a combination of hydrophobic segregation and hydrogen bonding; the long alkyl chain hydrophobic interactions especially separate dysprosium ions to rule out the possible concentration quenching of the metal ions. Secondly, the immobilization of the solvent ethanol in the gel is critical to decrease the influence of vibration of hydroxy groups on the emission of lanthanide ions. Thirdly, compound **1** shows higher selective recognition to terbium ions in contrast to fragile coordination ability toward dysprosium ions, the “on” and “off” phenomenon was the result of relatively weak interactions between the amide groups and Dy³⁺.

In summary, a novel low-molecular-weight amphiphilic organogelator **1** was synthesized and evaluated for its gel capability in alcohol. More importantly, the amide group (CONH) in synthetic **1** plays dual role: (1) it can establish intermolecular association through hydrogen bonds in order to form the resulting gels and (2) optical centers such as lanthanide ions will generate new photoluminescence properties due to the coordination with its carbonyl groups. Since lanthanide elements have high coordination numbers (8–12) and poor steric requirements for coordination, we incorporated a small amount of Dy(NO₃)₃·6H₂O into compound **1** (molar ratio of compound **1**/Dy³⁺ = 10/1). Blue luminescence from the Dy³⁺-containing organogels

was obtained, and interesting emission properties of dysprosium ions were surprisingly observed for the first time below the order–disorder phase-transition temperature (48 °C). In brief: i) only in the gel state, could compound **1** coordinate and transfer its excited energy to Dy³⁺, and ii) an on/off switch for dysprosium fluorescence could be easily realized by heating the gel to above T_{gel} . At present we have no information on how lanthanide ions interact with growing fibrillar morphology, and much more must be learned in this burgeoning field. In the present systems, we grafted a triethoxysilyl group on compound **1**, which will be hydrolyzed and incorporated into inorganic matrices in the future, then we might expect to obtain stable hybrid soft matter inducing phosphorus light.

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- 18 Another reason explaining the gradually decreasing terbium luminescence might be the back energy transfer from Tb(III) emitting level to the triplet state of compound **1** due to their close overlap of the spectra.