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## COMMUNICATION

## Supramolecular Luminescent Hydrogels Based on $\beta$ -Amino Acid and Lanthanide Ions Obtained by Self-Assembled Hydrothermal Reactions

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**Using the hydrothermal method, we obtained new hydrogels based on lanthanide ions and iminodiacetic acid. The hydrogels of europium and terbium show reddish and greenish luminescence, respectively. A mixed system Eu/Tb gel was prepared and the luminescent properties were studied.**

Supramolecular hydrogels are important and versatile colloidal materials<sup>1a</sup>. They are a new class of soft materials usually formed by solvent molecules, such as water, that are trapped in nanofibers or microfibers cross-linked in a supramolecular 3D network of the organic<sup>1b</sup>. There are several published review articles that describe the synthesis of hydrogels, their characterizations<sup>1c,1d,1e,1f</sup> and their potential applications in several areas, such as tissue engineering<sup>2a</sup>, biomaterials<sup>2b</sup>, controlled drug release<sup>2c</sup> and others. Small organic molecules that can gel aqueous solvents are named hydrogelators, and the driving forces of these processes are the supramolecular interactions, such as van der Waals interactions,  $\pi$ - $\pi$  stacking, and, most importantly, hydrogen bonds between the water molecules and the organic molecules<sup>1a,1b</sup>. Many classes of organic molecules have been used as gelator agents, including polymeric structures<sup>3a</sup>. However, biomolecules, such as cholesterol-based, carbohydrate-based, aminoacids and peptides have a special interest due to the biocompatibility for applications as biotechnological materials<sup>3</sup>.

On the other hand, organic-inorganic hybrid materials with lanthanide ions are in evidence<sup>4a</sup>. The luminescent properties of the lanthanide ions, especially europium (red emission) and terbium (green emission) trivalent ions have been extensively explored<sup>4b</sup>. Due to their electronic structure, the Ln<sup>3+</sup> ions present line-like emission spectra and long luminescence life time, having applications in areas such as light emission molecular devices<sup>4c</sup>, optical materials<sup>4d</sup>, forensic science<sup>4e</sup>, etc. In this context, the incorporation of lanthanide luminescent ions in supramolecular hydrogels could be an interesting method to generate new optical materials.

Some works have reported synthesis of hydrogels that contain Ln<sup>3+</sup> ions, successfully<sup>5</sup>. For example, Huang and co-workers synthesized hybrid hydrogels based on europium ions

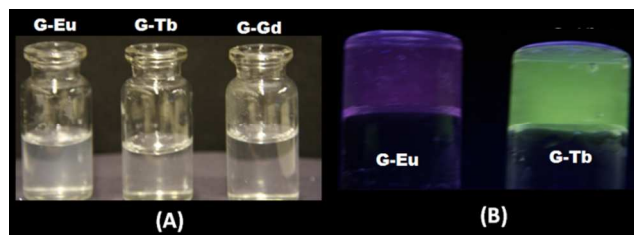
and the cholate ligand with interesting luminescent properties as a function of the lanthanide concentration<sup>5a</sup>. Another recent report by Wang, showed a reversible luminescent hydrogel induced by changes the pH<sup>5b</sup>.

This communication describes the synthesis and characterization of three new hydrogels based on lanthanide ions (Eu<sup>3+</sup>, Gd<sup>3+</sup>, and Tb<sup>3+</sup>) using iminodiacetic acid (H<sub>2</sub>IDA) as an organic gelator. H<sub>2</sub>IDA is a  $\beta$ -aminoacid that is an important precursor in the synthesis of herbicides<sup>6a</sup>. This compound also has been extensively used for the synthesis of porous coordination polymers<sup>6b</sup> and chelating agents for metal capture<sup>6c</sup>. Although other high molecular mass  $\beta$ -aminoacid derivatives were used as gelators<sup>3d</sup>, this is the first report of the utilization of the iminodiacetic acid to produce hydrogels.

The gels were obtained using the hydrothermal synthesis method starting from the lanthanide oxide and an aqueous solution of iminodiacetic acid (pH=5, adjusted with NaOH). The temperature of the reaction was 120°C and the time reaction was six days. The samples obtained were named G-Eu, G-Gd, and G-Tb, for each lanthanide ion used. Figure 1a shows the hydrogels obtained with Eu<sup>3+</sup>, Tb<sup>3+</sup>, and Gd<sup>3+</sup>. No residue of the reagents was observed, which indicates that all lanthanide oxide and iminodiacetic acid were incorporated in the gel structure. Using UV-light (Figure 1b) is possible to observe the reddish and greenish luminescence of the europium and terbium samples, respectively. When the reaction was performed in three days, it was possible to obtain the same hydrogels, however, with some residue of the lanthanide oxide not incorporated in the structure. In this way, the hydrothermal process seemed to be a good method to synthesize gels with high degree of transparency. Once this method is very employed to produce gel systems based on carbon materials<sup>7</sup>, to the best of our knowledge, there are no previous reports on hydrogel synthesis using low molecular weight  $\beta$ -aminoacid and lanthanide compounds using the hydrothermic method. It was also possible to obtain those lanthanide-hydrogels using hydrothermal reaction assisted by microwave.

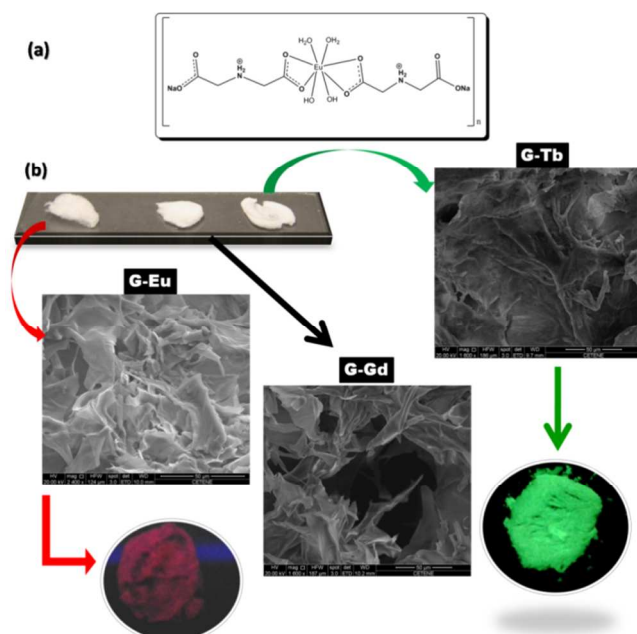
The samples were lyophilized and the resulting solids (Figure 2) were characterized by analytical methods. The elementary analysis (Table S1, supporting information) indicated an empirical formula [LnNa(HIDA)<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]

(Ln = Eu<sup>3+</sup>, Gd<sup>3+</sup>, and Tb<sup>3+</sup>). This composition was in good agreement with the alkaline pH observed in the hydrogels and the atomic lines found in the SEM-EDS of the solids (Figure 2 and Figures S1-S3, supporting information).



**Figure 1.** (a) Hydrogels of Eu, Tb, and Gd, and (b) the luminescence properties of G-Eu and G-Tb.

The infrared (IR) spectra of the dried gels (Figure S4, supporting information) show all of the vibrational bands corresponding to iminodiacetic acid. The IR spectrum of the europium sample revealed broad absorption bands centered at 3420 cm<sup>-1</sup> related to the asymmetric O-H stretching. The bands related to the carboxyl groups appeared at 1594 cm<sup>-1</sup> (asymmetric stretching) and 1413 cm<sup>-1</sup> (symmetric stretching). These signals were displaced by 124 cm<sup>-1</sup> and 17 cm<sup>-1</sup>, respectively, in comparison to the free ligand, which indicates a coordination bond with the Eu<sup>3+</sup> ions. The IR spectra of the other samples were similar. All signals were in agreement with the literature<sup>6b</sup>.

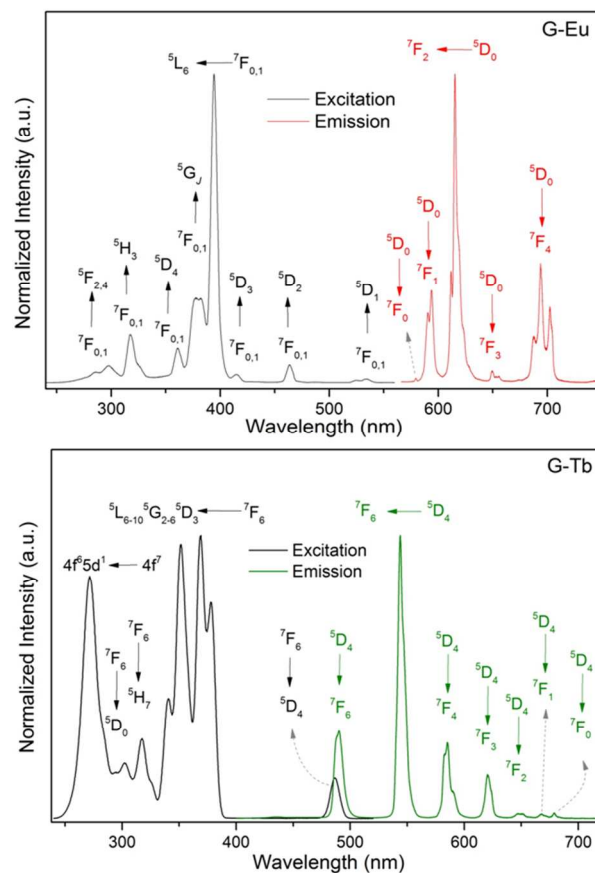


**Figure 2.** (a) Chemical composition of lanthanide hydrogels. (b) Lyophilized sample, SEM images and the luminescence properties of the lyophilized solid G-Eu and G-Tb.

The luminescent properties of the G-Eu and G-Tb samples were investigated and the results are shown in Figure 3. The excitation spectrum of G-Eu (Figure 3a, black line) shows line-like signals between 240–580 nm, which is related to the intra-*f-f* transitions of the Eu<sup>3+</sup> ions<sup>8a</sup>. The emission spectrum (Figure 3a, red line) shows the characteristic signals corresponding to the <sup>7</sup>F<sub>J</sub> ← <sup>5</sup>D<sub>0</sub> (*J* = 0–4) of the Eu<sup>3+</sup> ions<sup>8a</sup>. The <sup>7</sup>F<sub>2</sub> ← <sup>5</sup>D<sub>0</sub> transition (at 616 nm) showed the most intense peak (49% of

the integrated spectrum) and was primarily responsible for the reddish color of the photoluminescence. According to the selection rules, the <sup>7</sup>F<sub>0</sub> ← <sup>5</sup>D<sub>0</sub> transition (centered at 579 nm) is observed in low symmetry group points around the Eu<sup>3+</sup> ion<sup>8b</sup>. The presence of a single peak in this transition indicates that there were predominantly Eu<sup>3+</sup> ions with the same local symmetry. The profile for mono-exponential decay for the lifetime curve (Figure S5, supporting information) confirms these observations<sup>8b</sup>. The lyophilized sample was rehydrated and the same emission profile (Figure S6, supporting information) like the one in as-synthesized G-Eu was observed, showing the reversibility of the gel process.

The excitation (λ<sub>em</sub> = 543nm) and emission spectra (λ<sub>exc</sub> = 378nm; Figure 3b) of the G-Tb were collected at room temperature. In the excitation spectrum (Figure 3b, black line), the peaks between 290 nm and 500 nm are related to the intra-*f-f* transitions of the Tb<sup>3+</sup> ions<sup>9a</sup>. The emission spectrum (Figure 3b, green line) shows the typical signals for compounds containing Tb<sup>3+</sup> ions associated with the <sup>7</sup>F<sub>J</sub> ← <sup>5</sup>D<sub>4</sub> (*J* = 0–6) transitions<sup>9b</sup>. The most intense peak at 543 nm (51% of the integrated spectrum) corresponded to the <sup>7</sup>F<sub>5</sub> ← <sup>5</sup>D<sub>4</sub> transition and was primarily responsible for greenish photoluminescence observed in the G-Tb gel. The radiative decay curve of the <sup>5</sup>D<sub>4</sub> emitting state (Figure S7, supporting information) exhibited a di-exponential behavior (τ<sub>1</sub> = 1.08 ms; A<sub>1</sub> = 5.7 × 10<sup>7</sup> and τ<sub>2</sub> = 1.83 ms; A<sub>2</sub> = 4.64 × 10<sup>7</sup>), indicating the existence of two Tb<sup>3+</sup> ions chemically different in appreciable amounts<sup>9c</sup>.

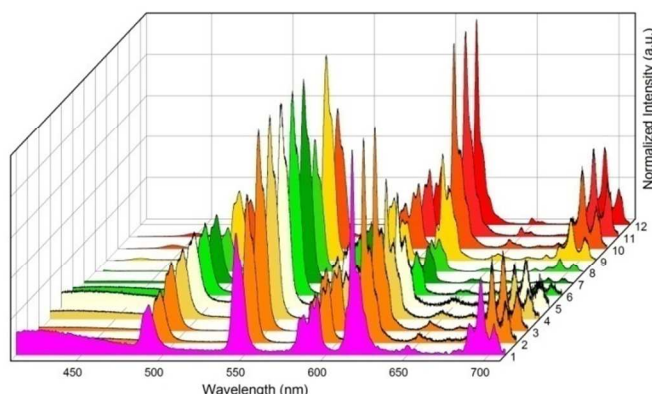


**Figure 3.** Excitation and emission spectra of the (a) G-Tb and (b) G-Eu gels.

The experimental values of the intensity parameters  $\Omega_2$  and  $\Omega_4$ , radiative ( $A_{\text{RAD}}$ ) and non-radiative ( $A_{\text{NRAD}}$ ) decay rates, lifetime, and emission quantum efficiency ( $\square$ ) for G-Eu are shown in Table S2. The high  $A_{\text{NRAD}}$  value in comparison to the  $A_{\text{RAD}}$  value, and the low lifetime indicate that the relaxation processes were governed by multiphonon and non-radiative decay mechanisms, such as O-H oscillators of water molecules in the first coordination sphere of the  $\text{Eu}^{3+}$  ions<sup>10a</sup>.

Using the same procedure, a mixed gel that contained europium and terbium ions, G-Tb<sub>0.5</sub>Eu<sub>0.5</sub>, was also prepared. The emission spectra for the gel sample were collected at room temperature upon excitation at (1) 310 nm, (2) 315 nm, (3) 320 nm, (4) 325 nm, (5) 330 nm, (6) 335 nm, (7) 340 nm, (8) 360 nm, (9) 375 nm, (10) 385 nm, (11) 390 nm, and (12) 395 nm (Figure 4). These spectra and the CIE chromaticity diagram<sup>10b</sup> of this sample are shown in Figure S8.

The CIE chromaticity diagram reveals that the lanthanide-mixed gel showed different emission colors when irradiated with different wavelengths of UV light, indicating that the coordinates and color can be tuned to green ( $x = 0.329$ ,  $y = 0.491$ ) to red ( $x = 0.861$ ,  $y = 0.316$ ). Point 5 ( $x = 0.372$ ,  $y = 0.369$ ) shows coordinates close to the ideal white color established by the CIE (0.33, 0.33), suggesting that the material is promising for the production a full color system, started the variation of the molar ratio of the lanthanide ions<sup>10c</sup>. The excitation spectra of G-Tb<sub>0.5</sub>Eu<sub>0.5</sub> monitored at 543 nm had similar characteristics to those shown in Figure 3b, except for the absence of the  $4f^65d^1 \leftarrow 4f^7$  transition. However, while monitoring the emission at 616 nm (Figure S9 in supporting information), in addition to the typical transitions of europium, new peaks were also observed. These new signals suggest an energy transfer between the  $\text{Tb}^{3+}$  to  $\text{Eu}^{3+}$  ions<sup>10d</sup>. In the lifetimes decay (Figure S10, supporting information), we noticed that when the sample was irradiated at 380 nm, both the  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions had identical profiles to the G-Eu and G-Tb samples. This behavior indicates no energy migration of the  $\text{Tb}^{3+}$  ions to  $\text{Eu}^{3+}$  ions excited in this wavelength (i.e. ions show independent photophysical properties). However, when the sample was excited at 352 nm, two lifetimes emission for europium are observed. This suggests a radiative emission of the europium ions due to the direct excitation and energy transfer between the lanthanide ions. These results indicate the existence of three crystalline domains in the material: two containing  $\text{Eu}^{3+}$  ions or  $\text{Tb}^{3+}$  ions and the third containing  $\text{Eu}^{3+}$  ions and  $\text{Tb}^{3+}$  co-doped.



**Figure 4.** Emission spectra upon excitation at (1) 310 nm, (2) 315 nm, (3) 320 nm, (4) 325 nm, (5) 330 nm, (6) 335 nm, (7) 340 nm, (8) 360 nm, (9) 375 nm, (10) 385 nm, (11) 390 nm, (12) 395 nm.

## Conclusions

In this work, we obtained new supramolecular hydrogels based on lanthanide ions (Eu, Tb, and Gd) and iminodiacetic acid using the hydrothermal reaction. The gels showed reversible hydration processes and dehydration. The IR analysis confirmed the presence of the ligand and the metal composition was verified by EDS analysis. Samples containing europium and terbium showed the typical excitation and emission peaks that are characteristic of the  $f-f$  transitions for ions. The mixed Eu/Tb compound presents interesting luminescent properties.

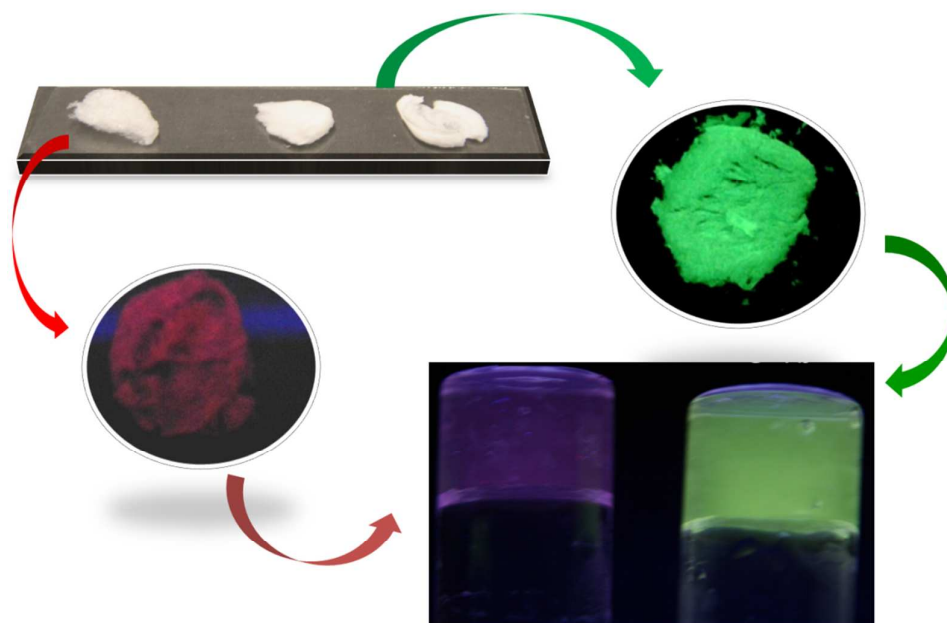
## Notes and references

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Hydrothermal synthesis of four new supramolecular hydrogel based on lanthanide ions with promising properties for RGB systems.