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## Gelation and luminescence of lanthanide hydrogels formed with deuterium oxide†

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Gel formations and efficient lanthanide luminescence appeared in deuterium oxide (D<sub>2</sub>O) medium instead of light water (H<sub>2</sub>O), and their solvation possibilities by using luminescence lifetimes were discussed. The lanthanide ions in the hydrogel of **1** obtained by H<sub>2</sub>O (abbreviated as H<sub>2</sub>O-Ln**1**; Ln = Eu, Tb, and Gd) in our previous report act as the coupling part between neighbor molecules for the bundle structure. Here, D<sub>2</sub>O also acts as a medium to form the lanthanide-hydrogel of **1**, and increases intensities of luminescence for Tb, because a soft crystalline state reducing resonance thermal relaxation is realized. The gel-formation and luminescence band positions of Ln**1** in D<sub>2</sub>O corresponded to those in H<sub>2</sub>O. From the observation of luminescence lifetimes in H<sub>2</sub>O and D<sub>2</sub>O, the number of coordinating water molecules on Eu and Tb were estimated to be around 3 or 4 for both. The luminescence intensity of Eu**1** did not increase even in D<sub>2</sub>O, due to a blue shift of the excited triplet state of **1**, as compared to that in H<sub>2</sub>O.

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## Introduction

Deuterium oxide is a key matrix to induce ff-emission regarding trivalent lanthanide (abbreviated to Ln) complexes.<sup>1–5</sup> For instance, Bruce *et al.* cordially explained the influence of the vibrational mode of a hydrogen/deuterium-oxygen for the enhancement or quenching of luminescence of Ln<sup>3+</sup> such as Tb<sup>3+</sup> and Eu<sup>3+</sup> in their coordination compounds. The ff-emissions of Ln<sup>3+</sup> are sensitized by the antenna effect by the coordination of  $\pi$ -electronic systems with high absorption coefficient. Lanthanide luminescent materials have recently attracted considerable attention, due to their brightness and sharp bands.<sup>1–4</sup> For instance, trivalent Tb in a complex exhibits green emission, which originates from ff transitions that have no influence on any organic ligands because they exist independently in the core of the atom.<sup>5</sup> Organic ligands act as photo-antennas to provide the excitation energy to the central metal. Additionally, the luminescence intensities of Tb complexes show temperature dependence, due to reverse energy transfer.<sup>6</sup>

The combination of two hetero Ln ions such as Tb and Eu with organic components can accomplish colour mixing of luminescence, and induce inter-metal energy transfer from Tb to Eu by UV excitation of the ligand moiety.<sup>7–9</sup> Such a stepwise energy transfer is also useful for developing luminescent sensors or devices. Recently, we reported mixed Tb/Eu systems in chain-structured complexes consisting of helical Ln complexes (abbreviated as LnL; Ln = Eu or Tb) linked by analogues of 1,4-benzenedicarboxylate (abbreviated as bdc).<sup>10</sup> The initial compound LnL-bdc showed no inter-metal energy transfer between the energy donor (ligand) and acceptor (centre metal ion), whereas bdc substituted with NH<sub>2</sub>- or OH- induced inter-metal energy transfer in the chain complexes, and resulted in reddish-orange emission even with a 1 : 1 mixture of EuL and TbL, due to its amorphous structure.

It was reported that the intensity change of lanthanide luminescence is affected by O–H/O–D or C–H/C–D vibrational mode, due to harmonic resonance with the luminescent level in lanthanide ions.<sup>11,12</sup> It is known that the quenching mechanism for trivalent Eu and Tb involves resonance of the third and fourth overtones of O–H vibrations (*ca.* 3400 cm<sup>–1</sup>) in H<sub>2</sub>O, respectively.<sup>13–15</sup> We recently reported the effect of deuterium on the luminescent components of H/b-phenanthroline complexes with Eu, Tb, and Tm complexes, according to the appearance of polymorphism detected by the synchrotron X-ray powder diffraction (XRPD).<sup>13</sup>

A water-soluble lanthanide complex of helicate structure with  $\pi$ -electronic systems and two carboxyl groups, LnL<sup>COOH</sup> also showed the change in luminescent intensity, when using D<sub>2</sub>O instead of H<sub>2</sub>O.<sup>16</sup> LnL<sup>COOH</sup> retains its molecular and spectral stability in a wide pH range of 2.6–9.7.

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To overcome the quenching problem related to Tb or Eu in H<sub>2</sub>O, some investigators reported using a capsulated molecular structure to prohibit solvent molecules from reaching Ln ions.<sup>17,18</sup> A Ln complex (Ln = Eu, Tb, Dy, and Sm) with a 2-hydroxyisophthalamide derivative with a multidentate ligand has water solubility, and shows a 60% luminescence quantum yield for Ln = Tb, even in water.<sup>17</sup> Cluster-type Zn complexes with Ln [Zn<sub>8</sub>(ad)<sub>4</sub>(BPDC)<sub>6</sub>O·2Me<sub>2</sub>NH<sub>2</sub>, 8DMF, 11H<sub>2</sub>O] (ad = adeninate; BPDC = biphenyldicarboxylate; DMF = dimethylformamide) form the metal-organic frameworks and show Ln luminescence even in water.<sup>18</sup>

Supramolecular gels, which are formed by self-assembly of small molecules, have attracted interest in recent decades because of their wide applicability.<sup>19,20</sup> Some luminescent lanthanide complexes in organogels and hydrogels have been developed and reported for applications such as paintable luminescent thermo sensors and color tunable LED fibers.<sup>21–28</sup> We also recently succeeded in obtaining bright luminescent Tb complexes with tris-urea-based hydrogelator **1** in H<sub>2</sub>O.<sup>29</sup> The gelator shown in Fig. 1 has multiple roles in hydrogel formation, by coordinating with cations such as protons, divalent calcium, trivalent Ln ions, and serving as a photo-antenna to transfer excitation energy to Ln ions. Compound **1** also shows Ln selectivity in luminescence; the hydrogel of the lanthanide complex with **1** obtained with H<sub>2</sub>O (abbreviated as H<sub>2</sub>O-Ln1; Ln = Eu, Tb, and Gd) shows different luminescence quantum yields based on the Ln; for H<sub>2</sub>O-Eu1 and H<sub>2</sub>O-Tb1, the quantum yields are <0.1% and 5.4%, respectively. It was recently revealed that the abovementioned lanthanide-including hydrogels of **1** act as media for organic fluorophores such as Rhodamine 6G,<sup>30</sup> and the interaction between the gelator and fluorophore was clearly enhanced in the luminescence as well as its lifetime.

Heavy water (D<sub>2</sub>O) has been considered to be nearly equivalent to light water (H<sub>2</sub>O), due to its physical properties in supramolecular hydrogels. Therefore, nuclear magnetic resonance (NMR) and small-angle neutron scattering (SANS) experiments have been performed in D<sub>2</sub>O as an alternative to H<sub>2</sub>O.<sup>31</sup> The similarities and dissimilarities of D<sub>2</sub>O and H<sub>2</sub>O are still unclear, and more study is required to clarify them. Here, we report a heavy water effect in the luminescence of a series of

D<sub>2</sub>O-Ln1 based on measurements of electronic absorption, excitation, and luminescence spectra. Furthermore, the inter-metal energy transfer between Eu and Tb was induced in D<sub>2</sub>O-Ln1. The luminescence lifetime and quantum yield were also measured to evaluate the luminescence efficiency in these hydrogels with Ln.

## Results and discussion

### Hydrogel formation and structure of D<sub>2</sub>O-Ln1

#### Viscoelastic features of hydrogels D<sub>2</sub>O-Ln1 and H<sub>2</sub>O-Ln1.

The viscoelastic properties of the hydrogels D<sub>2</sub>O-Tb1 and H<sub>2</sub>O-Tb1 were measured using a rheometer. The concentrations of **1** and Tb(OTf)<sub>3</sub> in hydrogels were fixed at 10 mM and 30 mM, respectively. The hydrogels D<sub>2</sub>O-Tb1 and H<sub>2</sub>O-Tb1 showed similar linear viscoelastic frequency sweep responses (Fig. 2a). Both the storage modulus (*G'*) and the loss modulus (*G''*) were almost independent of the frequency from 0.1 to 10 rad s<sup>−1</sup>. For both samples, *G'* was about twelve times larger than *G''*. The *G'* values for the hydrogels D<sub>2</sub>O-Tb1 and H<sub>2</sub>O-Tb1 at 1.0 rad s<sup>−1</sup> were 42.8 and 42.7 kPa, respectively. Previously, we reported that the *G'* value for H<sub>2</sub>O-Tb1 at 1.0 rad s<sup>−1</sup> was 8.1 kPa.<sup>29</sup> This result was obtained by measuring a relatively large hydrogel using a flat plate geometry (25 mm). Several pieces of the hydrogel were present in the measured sample. In the present study, we prepared the hydrogel in an aluminium cup (14 mm diameter) as a single continuous sample.<sup>30</sup> This unbroken sample exhibited a larger *G'* value. As shown in Fig. 2b, strain amplitude sweeps of D<sub>2</sub>O-Tb1 and H<sub>2</sub>O-Tb1 demonstrated elastic responses. The linear viscoelastic region of D<sub>2</sub>O-Tb1 was extensive, in comparison to that of H<sub>2</sub>O-Tb1.

**SEM and EDX measurement of hydrogels of Tb/Eu1.** Energy dispersive X-ray (EDX) spectroscopy of the xerogel produced from a 1 : 1 mixture of hydrogels containing Eu1 and Tb1 is shown in Fig. 3. The peaks for Eu and Tb appear at 1.15 and 1.25 keV, respectively. The component ratios of elements are C, 73.8%; N, 9.8%; O, 13.8%; Tb, 1.9%; and Eu, 1.7%. Tb and Eu are localized on the fiber in equal amounts, which is consistent with the results of a previous study.<sup>29</sup>

### Luminescence properties of D<sub>2</sub>O-Ln1

**Luminescence spectra of D<sub>2</sub>O-Tb1 and D<sub>2</sub>O-Eu1.** D<sub>2</sub>O-Tb1, a gel complex with trivalent Tb ions, was obtained as a hydrogel. Under UV light, the luminescence was a greenish colour to the naked eye. Electronic absorption spectra of D<sub>2</sub>O-Ln1 (Ln = Tb,

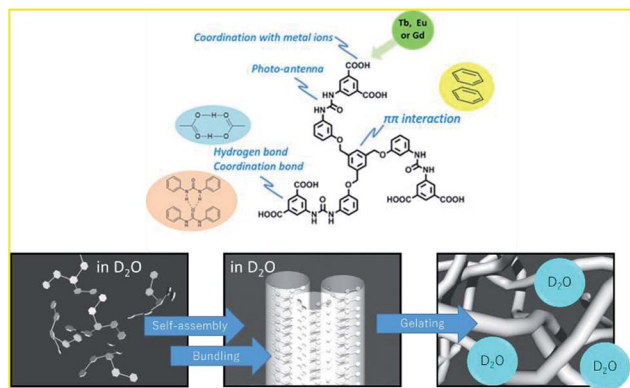


Fig. 1 Role of substances of **1** in the metal gelation (top), and schematic representation of gel formation in D<sub>2</sub>O (bottom).

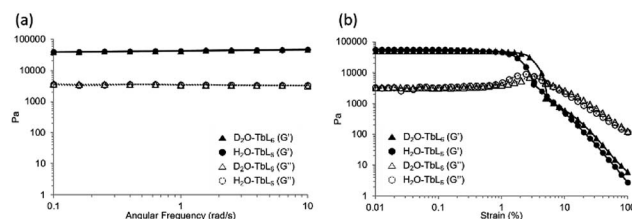


Fig. 2 *G'* and *G''* values for D<sub>2</sub>O-Tb1 (triangles) and H<sub>2</sub>O-Tb1 (circles) (a) with a frequency sweep; (b) with a strain sweep.



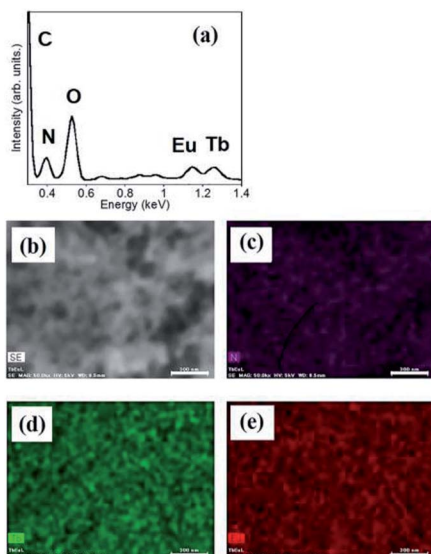


Fig. 3 EDX spectrum (a), SEM image (b), and element maps ((c) N; (d) Tb and (e) Eu) of the xerogel obtained from hydrogels by mixing of Eu1 and Tb1. Scale bar shows 100  $\mu\text{m}$ .

Eu, and Gd) were measured (Fig. 4) to compare the electronic properties with those found previously for  $\text{H}_2\text{O-Ln1}$ . The bands at 288 and 323 nm and their shapes for  $\text{D}_2\text{O-Ln1}$  correspond well to those for  $\text{H}_2\text{O-Ln1}$ , meaning that their  $\pi$ -electronic states with  $\text{D}_2\text{O}$  completely matched those with  $\text{H}_2\text{O}$ . Additionally, the  $\text{D}_2\text{O}$  hydrogel of **1** without metal also shows the corresponding absorption band. This means that these metallo-hydrogels have similar  $\pi$ -electronic structures.

Luminescence spectra of  $\text{D}_2\text{O-Tb1}$  and  $\text{D}_2\text{O-Eu1}$  are shown in Fig. 5.  $\text{D}_2\text{O-Tb1}$  shows sharp luminescence bands at 489, 544, 583, and 621 nm assigned to the  $^5\text{D}_4 \rightarrow ^7\text{F}_6$ ,  $^5\text{D}_4 \rightarrow ^7\text{F}_5$ ,  $^5\text{D}_4 \rightarrow ^7\text{F}_4$ , and  $^5\text{D}_4 \rightarrow ^7\text{F}_3$  transitions, respectively. The excitation spectra monitored at these luminescence band positions correspond to those for the electronic absorption spectra (Fig. S1†). Luminescence and excitation bands for  $\text{D}_2\text{O-Tb1}$  reproduced those of  $\text{H}_2\text{O-Tb1}$ , indicating that gelator **1** coordinates to the Ln ions while maintaining a suitable distance, to induce excitation energy transfer even in  $\text{D}_2\text{O-Tb1}$ .

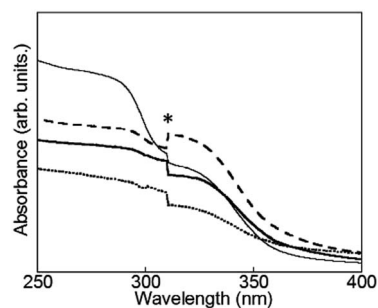


Fig. 4 Electronic absorption spectra of  $\text{D}_2\text{O-Tb1}$  (solid line),  $\text{D}_2\text{O-Eu1}$  (dotted line),  $\text{D}_2\text{O-Gd1}$  (dashed line), and  $\text{D}_2\text{O-H1}$  (thin line). \* Due to apparatus.

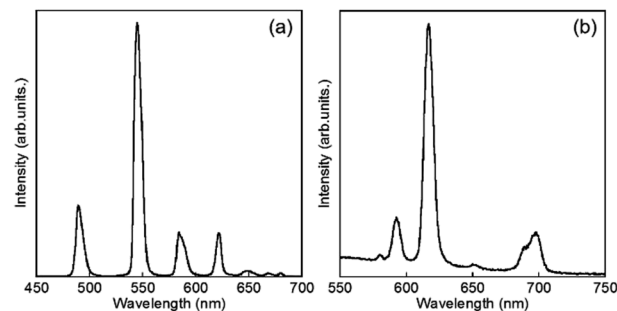


Fig. 5 Luminescence spectra of  $\text{D}_2\text{O-Tb1}$  (a) and  $\text{D}_2\text{O-Eu1}$  (b).  $\lambda_{\text{ex}} = 323 \text{ nm}$ .

To evaluate the luminescence of  $\text{D}_2\text{O-Tb1}$  quantitatively, luminescence quantum yields and lifetimes were measured and are summarized in Table 1. From the luminescence decay curves monitored at 545 nm for both  $\text{D}_2\text{O-Tb1}$  and  $\text{H}_2\text{O-Tb1}$  (Fig. 6), it is clear that the luminescence decay for Tb in  $\text{D}_2\text{O-Tb1}$  was much slower than that for  $\text{H}_2\text{O-Tb1}$ . This indicates that the luminescence rate is influenced by the vibrational mode of the water medium. Based on the decomposition of the decay curves,  $\text{D}_2\text{O-Tb1}$  has at least three luminescent components, whereas the corresponding components in  $\text{H}_2\text{O-Tb1}$  were shorter than those in  $\text{D}_2\text{O-Tb1}$ . Surprisingly, the longest luminescence lifetime was for  $\text{D}_2\text{O-Tb1}$ . A typical value in terbium complexes in the solid state is *ca.* 1.5–1.7 ms. Thus, deuterium oxide accelerates Tb luminescence efficiently in the gel of  $\text{D}_2\text{O-Tb1}$ , and this is known as the heavy water effect. The luminescence quantum yield for  $\text{D}_2\text{O-Tb1}$  is twice that for  $\text{H}_2\text{O-Tb1}$ , which also supports the above conclusion. Thus, heavy water acts as an accelerator for Tb luminescence even in hydrogels.

$\text{D}_2\text{O-Eu1}$  also exhibits luminescence bands at 580, 592, 616, 650, and 697 nm, which are assigned to the  $^5\text{D}_0 \rightarrow ^7\text{F}_6$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_5$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_4$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_3$ , and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transitions, respectively. These band positions are mostly the same for  $\text{H}_2\text{O-Eu1}$  (Fig. S2†). The luminescence quantum yields for Eu in  $\text{D}_2\text{O-Eu1}$  and  $\text{H}_2\text{O-Eu1}$  are quite low (Table 1). The luminescence decay profile for  $\text{D}_2\text{O-Eu1}$  was divided into two components, whose lifetimes are longer than those of  $\text{H}_2\text{O-Eu1}$ . This is in contrast to the two gel complexes with Tb, and may be also due to the vibrational mode of water as the medium.

The number of coordinating water molecules on Ln ions in hydrogels can be estimated using the experimental Horrocks' equation for the lifetime:<sup>32–35</sup>

Table 1 Luminescence quantum yields and lifetimes for  $\text{D}_2\text{O-Tb1}$  and  $\text{D}_2\text{O-Eu1}$  compared to those with light water<sup>28</sup>

	Quantum yields	Lifetimes/ms (amp); $\lambda_{\text{ex}} = 340 \text{ nm}^c$		
		$\tau_1$	$\tau_2$	$\tau_3$
$\text{D}_2\text{O-Tb1}$	10% <sup>a</sup>	0.20(14%)	0.83(41%)	1.7(45%)
$\text{H}_2\text{O-Tb1}$	5.4% <sup>a</sup>	0.08(8%)	0.37(37%)	0.70(54%)
$\text{D}_2\text{O-Eu1}$	<0.1% <sup>b</sup>	0.32(25%)	1.06(75%)	—
$\text{H}_2\text{O-Eu1}$	<0.1% <sup>b</sup>	0.10(23%)	0.22(77%)	—

<sup>a</sup>  $\lambda_{\text{obs}} = 450\text{--}700 \text{ nm}$ . <sup>b</sup>  $\lambda_{\text{obs}} = 550\text{--}750 \text{ nm}$ . <sup>c</sup>  $\lambda_{\text{mon}} = 545$  and  $616 \text{ nm}$  for Tb and Eu, respectively.



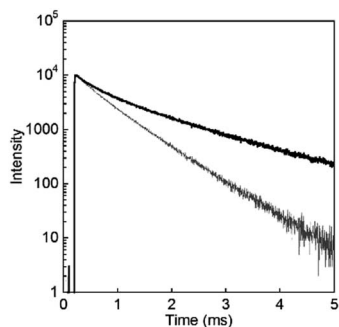


Fig. 6 Luminescence decay profiles for D<sub>2</sub>O-Tb1 (solid line) and H<sub>2</sub>O-Tb1 (thin grey line).  $\lambda_{\text{mon}} = 545$  nm and  $\lambda_{\text{ex}} = 323$  nm.

$$q^{\text{Ln}} = x(1/\tau_{\text{H}_2\text{O}} - 1/\tau_{\text{D}_2\text{O}}) \quad (1)$$

where,  $q^{\text{Ln}}$  is the number of water molecules coordinating to a Ln ion,  $x$  is a fixed number (1.02 for Eu and 4.2 for Tb), and  $\tau_{\text{H}_2\text{O}}$  and  $\tau_{\text{D}_2\text{O}}$  are the average luminescence lifetimes (eqn (2)) observed in H<sub>2</sub>O and D<sub>2</sub>O, respectively:<sup>36</sup>

$$\tau = (a_1\tau_1^2 + a_2\tau_2^2)/(a_1\tau_1 + a_2\tau_2) \quad (2)$$

Here,  $\tau_n$  and  $a_n$  are the  $n^{\text{th}}$  observed luminescence lifetime and its amplitude, respectively. We used the values in Table 1, and  $q_{\text{Tb}}$  and  $q_{\text{Eu}}$  were calculated as 3.7 and 3.1, respectively. Both metal ions in hydrogels will bind three or four water molecules. Thus, the O-H or O-D vibrational mode will directly affect the energy transfer efficiency or excitation energy relaxation, including non-radiative processes in these hydrogels.

To clarify the energy relaxation process for the water vibrational mode, ligand-centred emissions such as fluorescence and phosphorescence were observed. Fig. 7 shows fluorescence spectra of D<sub>2</sub>O-H1 and phosphorescence spectra of D<sub>2</sub>O-Gd1. The compounds D<sub>2</sub>O-H1 and D<sub>2</sub>O-Tb1 also formed stable hydrogels similar to D<sub>2</sub>O-Tb1. The use of Gd ion instead of a luminescent Ln ion is the conventional means for the determination of the singlet and triplet states as the energy donor in the  $\pi$ -electron system.<sup>37</sup> In our previous report, the fluorescence and phosphorescence bands for **1** using the hydrogel H<sub>2</sub>O-Gd1 were at 363 and 465 nm, respectively.<sup>29</sup> The corresponding bands appear at 363 (27 500 cm<sup>-1</sup>) and 477 (21 000 cm<sup>-1</sup>) nm,

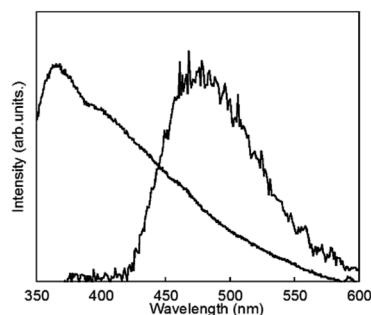


Fig. 7 Fluorescence spectrum of D<sub>2</sub>O-H1 (shorter wavelength band and phosphorescence spectrum at 77 K) and of D<sub>2</sub>O-Gd1 (longer wavelength band) localized on **1** ( $\lambda_{\text{ex}} = 323$  nm).

respectively, in the present compounds. The 477 band acts as an energy donor to Tb or Eu in hydrogels. The phosphorescence band position for D<sub>2</sub>O-Gd1 is lower than that for H<sub>2</sub>O-Gd1 by 12 nm, and may affect the energy transfer efficiency of D<sub>2</sub>O-Eu1 which has acceptor bands around 394 or 416 nm.<sup>38</sup> Additionally, H<sub>2</sub>O-Tb1 and D<sub>2</sub>O-Tb1 show broad luminescence bands in laser Raman spectra at 637 (15 700 cm<sup>-1</sup>) and 625 (16 000 cm<sup>-1</sup>) nm, respectively (Fig. 8). These bands do not correspond to the fluorescence and phosphorescence in Fig. 6, suggesting that the luminescence bands are caused by strong intermolecular interactions by the formation of supramolecular hydrogels. It is noteworthy that the band position for self-assemblies of the gelator covers the Eu luminescence bands. In other words, the O-D vibrational mode intensified the luminescence of Tb in D<sub>2</sub>O-Tb1. In contrast, the weakened luminescence for Eu in D<sub>2</sub>O-Eu1 was caused by the O-D vibration in deuterium oxide and by superimposition of the emission of self-assembly in the gelator and luminescence of Eu.

**Luminescence spectra of D<sub>2</sub>O-Tb/Eu1.** Metal-to-metal excitation energy transfer between Tb and Eu suggests metal-metal interaction, by the measurement of their luminescence. We prepared the 1 : 1 mixed hydrogels of Eu and Tb with **1** in H<sub>2</sub>O and D<sub>2</sub>O, abbreviated as H<sub>2</sub>O-Tb/Eu1 and D<sub>2</sub>O-Tb/Eu1, respectively. From the EDX measurement as described above, nitrogen in **1** was also found at the similar position with the metal ions. This supports luminescence effects such as inter-metal interactions between Tb and Eu in the mixed hydrogel of Eu1 and Tb1.

Fig. 9 shows luminescence spectra of hydrogels containing Tb and Eu ions in a 1 : 1 ratio, which are abbreviated as H<sub>2</sub>O-Tb/Eu1 and D<sub>2</sub>O-Tb/Eu1 for light and heavy water, respectively. Bands at 544, 545, 584, 585, 620, 650(sh), and 679(sh) nm, assigned to the overlap of ff transitions of Tb<sup>3+</sup> and Eu<sup>3+</sup>, are observed for H<sub>2</sub>O-Tb/Eu1. The corresponding bands for D<sub>2</sub>O-Tb/Eu1 appear at 544, 584, 590, 615, 649, and 696 nm, respectively.

The luminescence decay profile of H<sub>2</sub>O-Tb/Eu1 was monitored at both the emission band positions of Tb and Eu (Fig. S3† and Table 2). The decay curve of H<sub>2</sub>O-Tb/Eu1 monitored at 545 nm for Tb was divided into three luminescent components, and that at 616 nm for Eu into two. In the luminescence decay profile monitored at 616 nm for H<sub>2</sub>O-Tb/Eu1, the luminescence rise curve for Eu was obtained and resulted in the time as 0.15 ms because the time range corresponds to the decay time of

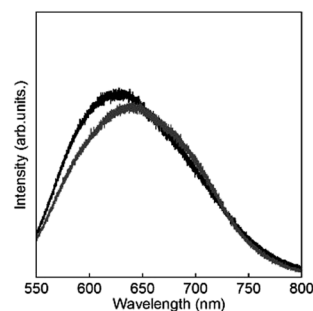


Fig. 8 Luminescence spectra of D<sub>2</sub>O-Tb1 (black line) and H<sub>2</sub>O-Tb1 (grey line) observed by Raman spectroscopy ( $\lambda_{\text{ex}} = 532$  nm).





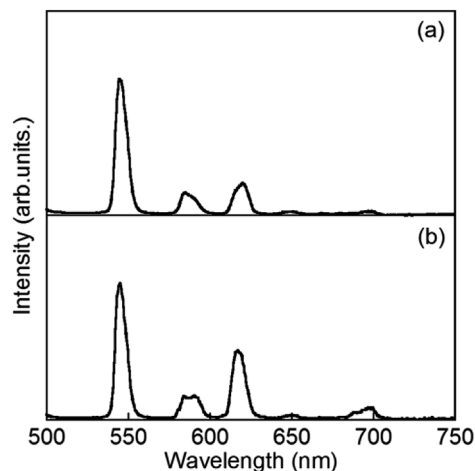


Fig. 9 Luminescence spectra of H<sub>2</sub>O-Tb/Eu1 and D<sub>2</sub>O-Tb/Eu1 ( $\lambda_{\text{ex}}$  = 323 nm).

0.19 ms for Tb. These results are consistent with Tb<sup>3+</sup> ions transferring the excitation energy to Eu<sup>3+</sup> in the mixed metal hydrogels. It also demonstrated that Tb and Eu would exist sufficiently close together, so as to promote metal-to-metal energy transfer in gels.<sup>39</sup> Similar metal-to-metal energy transfer was also observed in the xerogel obtained from hydrogels with both Tb and Eu. It should note to worth that the number of luminescent decay component of Eu in D<sub>2</sub>O-Tb/Eu1 is one; however, the rise in luminescence lifetime of 0.29 ms is higher than that in H<sub>2</sub>O-Tb/Eu1. It suggests that the metal-to-metal energy transfer from Tb to Eu in the gel with D<sub>2</sub>O is more efficient than that with H<sub>2</sub>O.

The total luminescence quantum yield of Tb/Eu1 was observed in the Tb and Eu emission region (500–750 nm). The quantum yield of D<sub>2</sub>O-Tb/Eu1 was 2%, which is higher than that of H<sub>2</sub>O-Tb/Eu1 and xerogel (<0.1%). These trends support the above discussion.

The xerogel obtained from hydrogels of Tb/Eu1 showed the luminescence spectra and quantitative properties similar to those of the initial compound. It is also consistent that heavy water in this hydrogel system plays a role in enhancing lanthanide luminescence and inter-metal energy transfer. The increase in the  $\phi$  value for the xerogel at 77 K means the increase in forwarded energy transfer from **1** to the Tb ion, because of the existence of thermal equilibrium between the donor and acceptor levels in the Tb complexes.<sup>7,9,40</sup>

The energy diagram for Tb/Eu1 systems is shown in Fig. 10. The excited triplet state of **1** acts as an energy donor to the terbium with less contribution of backward energy transfer.<sup>29</sup> However, the energy difference between **1** and the Eu ion is not suitable for efficient energy transfer. The mixing of Tb and Eu in the hydrogel formed with D<sub>2</sub>O accomplished acceleration of Eu emission by Tb, through metal–metal energy transfer in D<sub>2</sub>O-Tb/Eu1.

## Experimental

### Sample preparation

The gelator **1** and the gel containing Ln ions and D<sub>2</sub>O were prepared as given in the previous paper using H<sub>2</sub>O.<sup>29,30</sup> Lanthanide-containing hydrogels were obtained from light water and D<sub>2</sub>O (Isotech Inc.), and lanthanide nitrates were used as the sources of metal ions (Ln = Eu, Tb and Gd). The 1 : 1 mixed hydrogels using Eu and Tb were also obtained by the mixing of europium nitrate and terbium nitrate equivalently. To obtain a metal-free hydrogel, hydrochloride and D<sub>2</sub>O were used.

### Apparatus

Rheological measurements were carried out on a DHR-2 rheometer (TA Instruments), using a flat plate geometry (8 mm). Electronic absorption and luminescence spectra were

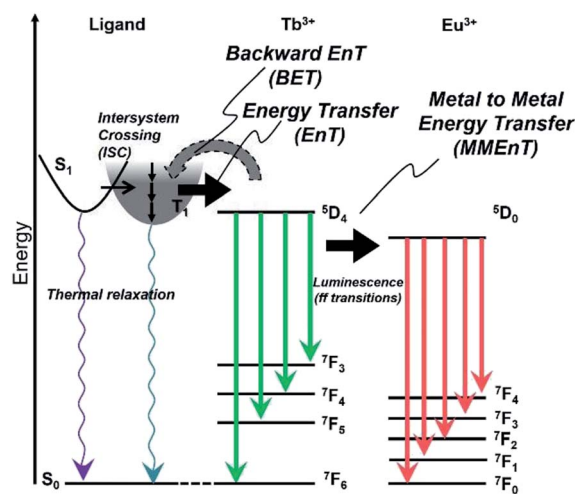


Fig. 10 Schematic representation of energy diagram for **1** and Tb-sensitizing of the Eu luminescence in hydrogels.

Table 2 Photophysical properties of mixed-metal systems in hydro/xerogels.  $\lambda_{\text{ex}}$  = 340 nm<sup>d</sup>

	Quantum yield <sup>a</sup>	Lifetimes/ms (amp.)
H <sub>2</sub> O-Tb/Eu1	<0.1%	0.53 (40%), <b>0.19</b> (30%), 0.018 (30%) <sup>b</sup> 0.51 (24%), 0.20 (76%), <b>-0.15</b> <sup>c</sup>
D <sub>2</sub> O-Tb/Eu1	2%	1.20 (35%), <b>0.41</b> (33%), 0.034 (32%) <sup>b</sup> 1.40 (100%), <b>-0.29</b> <sup>c</sup>
Xerogel of Tb/Eu1	<0.1%	0.47 (36%), <b>0.14</b> (28%), 0.026 (36%) <sup>b</sup> 0.50 (22%), 0.23 (78%), <b>-0.081</b> <sup>c</sup>

<sup>a</sup>  $\lambda_{\text{obs}}$  = 450–700 nm. <sup>b</sup>  $\lambda_{\text{mon}}$  = 545 nm for Tb. <sup>c</sup>  $\lambda_{\text{mon}}$  = 616 nm for Eu. <sup>d</sup> Minus values in lifetimes represent the rise times of luminescence.



recorded using a Shimadzu 3600S UV-VIS-NIR spectrophotometer and a Horiba Jovin-Yvon Fluorolog 3-22 spectrofluorometer, respectively. Luminescence quantum yields and lifetimes were measured by a Hamamatsu 9920-02 absolute photoluminescence quantum yield spectrometer and Quantaaurus tau fluorescence lifetime spectrometer, respectively. SEM images were obtained using an Ultra-55 scanning electron microscope (Carl Zeiss AG) equipped with a secondary in-lens electron detector, together with a QUANTAX detector (Bruker Corporation) for EDX. The micro Raman spectra were obtained using Renishow *via* a Reflex spectrometer equipped with a 532 nm diode laser, calibrated to the 520.5 cm<sup>-1</sup> line of silicon.

## Conclusion

Three types of lanthanide ions aggregate to form hydrogels with **1**, even in heavy water. The viscoelastic property of the hydrogel D<sub>2</sub>O-Tb**1** was identical to that of H<sub>2</sub>O-Tb**1**, whereas deuterium oxide in the gel D<sub>2</sub>O-Tb**1** enhanced the efficiency of ff emission of Tb ion. There was no influence on the luminescence of D<sub>2</sub>O-Eu**1** by heavy water. The fluorescence and phosphorescence bands localized on **1** were observed using D<sub>2</sub>O-H**1** (metal free; prepared by using hydrochloride) and D<sub>2</sub>O-Gd**1**, respectively. Raman spectra supported the weak luminescence of Eu in this system. Finally, Eu emission was enhanced in the mixed hydrogel D<sub>2</sub>O-Tb/Eu**1** through inter-metal energy transfer. These results will provide new aspects for designing hydrogels in heavy water.

## Conflicts of interest

There are no conflicts to declare.

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