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Sensing of H_2O in D_2O: is there an easy way?†

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We report Tb–Eu based luminescence sensor materials toward H_2O detection in D_2O with the highest sensitivity of 24%/%(H_2O), exceeding the previously reported ones by an order of magnitude. The theoretical description of such sensors based on the terbium–europium systems was performed and proved that the sensitivity is proportional to the number of inner-sphere water molecules.

Heavy water (D_2O) is employed in plenty of applications, such as the solvent for NMR and IR spectroscopy instead of H_2O, which creates a strong band that overlaps with the signals of the studied compounds,[1–3] for hypothermic preservation of the pancreas,[4] as a neutron moderator to slow down the neutrons in nuclear reactors[5–7] and in neutrino detectors.[8–10] The properties of D_2O, important for these applications, suffer dramatically from H_2O impurities, which makes the detection of the H_2O impurity in heavy water an important practical task, where luminescence spectroscopy allows high precision and easiness, though its application to solve this task is very limited. Indeed, since the pioneering work,[11] utilizing a terbium–europium metal–organic framework (MOF) as a sensing system with luminescence intensity ratio LIR = I_{Tb}/I_{Eu} as a water content dependent function, only three publications, devoted to H_2O sensing using terbium–europium compounds, were published,[12–14] including sensing in D_2O,[12,14] and using Tb–Eu MOF systems.[11–13]

Despite a limited number of papers, the study of Tb–Eu complexes with organic ligands for H_2O sensing definitely deserves further attention. Indeed, terbium–europium heterometallic complexes combine high luminescence intensity and fundamentally inevitable sensitivity to water impurity. High luminescence intensity is granted by the special mechanism of lanthanide complex luminescence,[15–22] which includes the luminescence of lanthanide ions from f–f transitions after efficient through-ligand excitation. The sensing properties result from the different efficiencies of the quenching of the luminescence of both ions by water molecules.[19,23–26]

Besides the very limited number of studies devoted to this promising subject, the obtained sensitivity S_r = (1/LIR)(dLIR/dc) (c is the water concentration, LIR is the luminescence intensity ratio; LIR = either I_{Tb}/I_{Eu} in ref. 11 or I_{Eu}/I_{Tb} in ref. 12) of the published systems is rather low. These values were not provided by the authors of ref. 11, 12 and 27 but can be calculated from their data and reach 0.83%/%(H_2O) in the water content range below 10%. We assume that this is due to the fact that in these papers lanthanide complexes are utilized, in which the coordination sphere is significantly filled by organic anionic ligands. At the same time since the sensitivity of these systems is based on the different quenching efficiencies of terbium and europium luminescence by inner-sphere water molecules (n), it is obvious that the higher the n value, the higher is the sensitivity.

In order to increase the sensitivity of the Tb–Eu based sensors we study the mixture of highly water-soluble lanthanide pentafluorobenzoates.[27,28] To estimate the role of the organic ligand in such a system it was compared to the mixture of lanthanide chlorides.

Water-soluble pentafluorobenzoates $Tb(pfb)_3(H_2O)$ and $Eu(pfb)_3(H_2O)$ were synthesized from freshly prepared lanthanide hydroxides and Hpfb[28] and analyzed using PXRD,[29] TGA[30] with the mass-detection of the evolved gases, and IR spectroscopy (see Fig. S1–S3†). Luminescence study of the 25 mM solutions of these complexes in water and in D_2O revealed the ionic luminescence of both europium (Fig. S4a and c†) and terbium ions (Fig. S4b and d†), which was lower in water due to quenching through OH-bonds. The luminescence intensity of D_2O solution compared to that of H_2O solution increased *ca.* 4 times in the case of terbium and *ca.* 16 times in the case of europium, illustrating different sensitivities of the luminescence of these ions toward OH-quenching.

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The excitation spectra of both solutions contain a through-ligand excitation band indicating that the sensitizing anionic pfb⁻ ligand remains in the coordination sphere, which results in the luminescence intensity increase compared with solutions of the corresponding chlorides (Fig. 1).

The lifetimes values (τ_{H_2O} and τ_{D_2O}) of the excited state of $Ln(pfb)_3$ (Ln = Tb, Eu) are much longer in D_2O than in H_2O (Table 1) due to the efficient OH-quenching of both ions. These values allowed the calculation of the number of inner-sphere coordinated water molecules n from the empirical equations.[19,23–26] The obtained data indicate that for both terbium and europium $n = 9$, which is rather high and results from the high dissociation degree.

The search for the optimal Eu : Tb ratio in solution was aimed at obtaining the highest sensitivity toward the water impurity. To achieve this goal the luminescence spectra of the mixtures $[\omega Eu(pfb)_3 + (1 - \omega)Tb(pfb)_3]$ were recorded in both H_2O and D_2O in order to determine the fraction ω which ensures the highest LIR difference ($I_{Eu}(612)/I_{Tb}(545)$) with the solvent change.

The highest LIR difference was observed when $Eu(pfb)_3 : Tb(pfb)_3 = 10 : 1$ (Fig. S5a and b†), which equaled LIR = 1.1 in H_2O and LIR = 6.2 in D_2O. This Eu : Tb ratio was chosen for further studies.

It is important that the lifetime of the terbium excited state decreases when the europium compound is added to the solution. So, the lifetime of $TbCl_3$ solution in D_2O (2.28 ms) decreases down to 0.77 ms upon the addition of $EuCl_3$. This indicates the presence of the efficient terbium-to-europium energy transfer even in such a diluted solution, which affects the luminescence behavior[26,28,31–36] and must be always kept in mind.

To determine the luminescence band ratio dependence on the H_2O concentration we recorded the luminescence spectra of the ($Eu(pfb)_3 : Tb(pfb)_3 = 10 : 1$) solution in D_2O with various impurities of H_2O (Fig. 2). To estimate the sensitivity, the ratio of the intensity of the terbium and europium luminescence bands ($I_{Eu}(612)/I_{Tb}(545)$) was plotted against the ratio of light and heavy water volumes. After a fast decrease, the dependence reaches the plateau at high H_2O contents. It is important that the luminescence switching behavior is highly reproducible (Fig. 2b).

To reveal the role of organic pfb⁻ anions, similar experiments were carried out with lanthanide chlorides. Lifetime measurements demonstrated that the number of inner-sphere water molecules in chloride solutions equals $n = 9$ and, thus, coincides with that of the terbium and europium ions in pentafluorobenzoate solutions. For sensing, the same 10 : 1 $EuCl_3 : TbCl_3$ ratio with the concentration of 25 mM was selected.

The comparison of the luminescence spectra of 25 mM ($10Eu(pfb)_3 + Tb(pfb)_3$) and ($10EuCl_3 + TbCl_3$) solutions reveals that the former system demonstrates a higher luminescence intensity, which is obviously due to the presence of the sensitizing pfb⁻ ligand. Its presence is also indicated by the

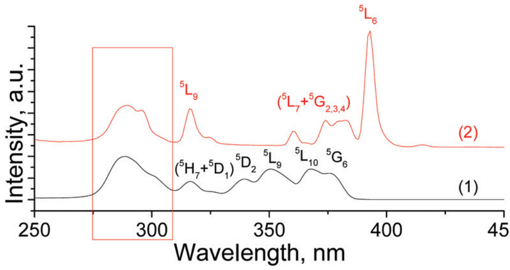

Fig. 1 Normalized excitation spectra in D_2O (25 mM) of $Tb(pfb)_3$ (1) and $Eu(pfb)_3$ (2).

Table 1 Luminescence lifetimes (ms) of the 25 mM solutions of $Ln(pfb)_3$ and $LnCl_3$ (Ln = Tb, Eu) in H_2O and D_2O and the number of inner-sphere lanthanide-coordinated water molecules (n)

	Lifetime		
Complex	H_2O	D_2O	n^a
$Eu(pfb)_3$	0.11	3.32	9.2
$Tb(pfb)_3$	0.42	3.19	8.7
$EuCl_3$	0.12	3.40	8.6
$TbCl_3$	0.40	2.28	9.5

[a] For Eu CCs: $n = 1.05 \cdot \left(\frac{1}{\tau_{H_2O}} - \frac{1}{\tau_{D_2O}}\right)$; for Tb CCs: $n = 4.2 \cdot \left(\frac{1}{\tau_{H_2O}} - \frac{1}{\tau_{D_2O}}\right)$.

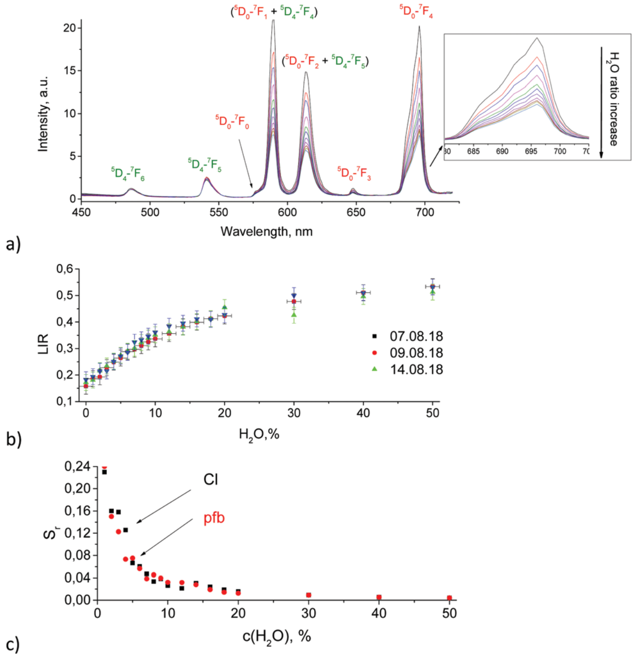

Fig. 2 (a) Luminescence spectra of $Eu(pfb)_3 : Tb(pfb)_3 = 10 : 1$ solution in D_2O (25 mM), where the fraction of H_2O varies from 0 to 10% (terbium bands are assigned in green and europium in red). (b) Dependence of the intensity ratio of the terbium and europium luminescence bands (I^{Tb} (545 nm)/I^{Eu} (612 nm)) on the fraction of H_2O (excitation wavelength is 300 nm) recorded in different days. (c) The sensitivity of both Cl-based and pfb-based systems.

different ratios of the europium luminescence bands in two systems: higher symmetry of the lanthanide coordination environment in a pfb-containing system results in a higher fraction of the hypersensitive $^5D_0$–$^7F_2$ band of europium (*ca.* 612 nm) in its spectrum, than in the spectrum of the chloride mixture. At the same time the intensity of the $^5D_0$–$^7F_1$ magnetic-dipole transition band is higher in both spectra, indicating a predominantly aqueous coordination environment of high symmetry. The presence of the sensitizing pfb$^-$ ligand also results in different ratios of terbium and europium luminescence in two systems. At the same time, when the H_2O content increases, the LIR of the ($10EuCl_3$ + $TbCl_3$) system increases, which is predominantly due to the decrease of the europium luminescence intensity.

The sensitivity of both systems was calculated as the logarithmic derivative of the LIR[36–40] as

$$S_r = \frac{1}{\mathrm{LIR}}\frac{\mathrm{dLIR}}{\mathrm{d}c}$$

where c is the concentration of H_2O, and plotted in Fig. 3. The sensitivity of both systems increases with the decrease of the H_2O content, which is practically very useful, and as expected, exceeds those of previously published data by more than an order of magnitude: it reaches 23%/%(H_2O) for the chloride system and 24%/%(H_2O) for the system based on pentafluorobenzoates.

Despite different luminescence intensities and ratios of Tb and Eu luminescence, the S_r behavior coincides for both systems. This results from the same number of water molecules in the coordination spheres of terbium or europium in both solutions, as well as the same Tb-to-Eu energy transfer efficiency, which resulted from the same Tb–Eu distance in the solution of the same concentration and with the same [Tb : Eu] ratio.

Thus, thanks to the high number of inner-sphere water molecules, the H_2O sensors were obtained with the sensitivity, which exceeds the previously obtained values by an order of magnitude. The sensitivity of both chloride and pentafluorobenzoate systems is the same; however, due to the antenna effect the luminescence intensity is higher for the pentafluorobenzoate system, which is recommended for further applications. It is important that lanthanide pentafluorobenzoates are non-toxic,[28] cheap, and very easy to obtain.

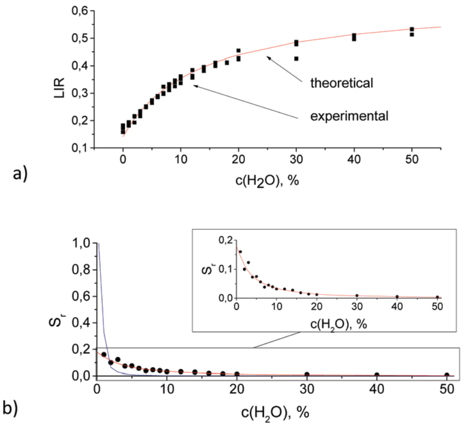

Fig. 3 Theoretical (red lines) and experimental (black scatter) (a) LIR and (b) S_r dependences. Blue line corresponds to the theoretical S_r dependence in the absence of the Tb–Eu energy transfer.

To determine the highest possible sensitivity of the heterometallic terbium–europium compounds as sensors toward H_2O in D_2O the theoretical description of sensing behavior was proposed.

If the mixture of $[\omega\mathrm{Eu}(H_2O)_xL_n + (1-\omega)\mathrm{Tb}(H_2O)_yL_m]$ is used for sensing, where ω and $(1-\omega)$ are the fractions of the components, the luminescence intensity of ions can be evaluated as

$$I = \omega \cdot n \cdot \varepsilon \cdot \mathrm{QY}$$

or

$$I = (1-\omega) \cdot m \cdot \varepsilon \cdot \mathrm{QY}$$

where n (or m) is the number of coordination ligand species, ε is the ligand molar extinction coefficient, and QY is the luminescence quantum yield. The Quantum yield depends on the radiative and nonradiative relaxation rate constants

$$\mathrm{QY} = \eta \cdot \frac{k_{\mathrm{rad}}}{k_{\mathrm{rad}} + k_{\mathrm{nr}}} \text{ in } D_2O \text{ and}$$

$$\mathrm{QY} = \eta \cdot \frac{k_{\mathrm{rad}}}{k_{\mathrm{rad}} + k_{\mathrm{nr}} + k_{\mathrm{OH}}} \text{ in } H_2O$$

here k_{rad} is the radiative constant, k_{nr} is the sum of nonradiative constants, other than OH-quenching, and k_{OH} is the OH-quenching constant. These constants are connected with the observed lifetimes as $(k_{\mathrm{rad}} + k_{\mathrm{nr}}) = \frac{1}{\tau_{D_2O}}$ and $(k_{\mathrm{rad}} + k_{\mathrm{nr}} + k_{\mathrm{OH}}) = \frac{1}{\tau_{H_2O}}$. The luminescence quantum yield in D_2O, containing H_2O of concentration c, can be evaluated by using a similar formula, where k_{OH} depends on H_2O concentration

$$\mathrm{QY} = \eta \cdot \frac{k_{\mathrm{rad}}}{k_{\mathrm{rad}} + k_{\mathrm{nr}} + k_{\mathrm{OH}}(c)}$$

From the empirical equations for innersphere water molecule number determination one can derive the equation for $k_{\mathrm{OH}}(c)$ for both terbium and europium. Indeed, for europium compounds

$$x = 1.05 \cdot \left(\frac{1}{\tau_{H_2O}} - \frac{1}{\tau_{D_2O}}\right) = 1.05k_{\mathrm{OH}}$$

For terbium compounds

$$y = 4.2 \cdot \left(\frac{1}{\tau_{H_2O}} - \frac{1}{\tau_{D_2O}}\right) = 4.2k_{\mathrm{OH}}$$

From this LIR equals

$$\mathrm{LIR}(c) = \frac{I_{\mathrm{Tb}}}{I_{\mathrm{Eu}}} = \frac{1-\omega}{\omega} \cdot \frac{m}{n} \cdot \frac{\eta_{L-\mathrm{Tb}}}{\eta_{L-\mathrm{Eu}}} \cdot \frac{k_{\mathrm{rad}}^{\mathrm{Tb}}}{k_{\mathrm{rad}}^{\mathrm{Eu}}} \cdot \frac{\tau^{\mathrm{Tb}}(c)}{\tau^{\mathrm{Eu}}(c)}$$

Here we assigned

$$\tau^{\mathrm{Ln}}(c) = \frac{1}{k_{\mathrm{rad}}^{\mathrm{Ln}} + k_{\mathrm{nr}}^{\mathrm{Ln}} + k_{\mathrm{OH}}^{\mathrm{Ln}}(c)}$$

Since the equations for europium and terbium differ only in the last term in the denominator, we assigned

$$\zeta = \frac{1-\omega}{\omega} \cdot \frac{m}{n} \cdot \frac{\eta_{L-\mathrm{Tb}}}{\eta_{L-\mathrm{Eu}}} \cdot \frac{k_{\mathrm{rad}}^{\mathrm{Tb}}}{k_{\mathrm{rad}}^{\mathrm{Eu}}}$$

From this

$$\mathrm{LIR}(c) = \zeta \cdot \frac{k_{\mathrm{D_2O}}^{\mathrm{Eu}} + c \cdot \dfrac{x}{1.05}}{k_{\mathrm{D_2O}}^{\mathrm{Tb}} + c \cdot \dfrac{y}{4.2}}$$

where $k_{\mathrm{D2O}}^{\mathrm{Ln}} = k_{\mathrm{rad}}^{\mathrm{Ln}} + k_{\mathrm{nr}}^{\mathrm{Ln}}$.

So, the sensitivity in the absence of the Tb–Eu energy transfer is

$$S_{\mathrm{r}} = \frac{1}{\mathrm{LIR}} \cdot \frac{\mathrm{dLIR}}{\mathrm{d}c} = \frac{\dfrac{x}{1.05} \cdot k_{\mathrm{D_2O}}^{\mathrm{Tb}} - \dfrac{y}{4.2} \cdot k_{\mathrm{D_2O}}^{\mathrm{Eu}}}{\left(k_{\mathrm{D_2O}}^{\mathrm{Eu}} + c \cdot \dfrac{x}{1.05}\right)\left(k_{\mathrm{D_2O}}^{\mathrm{Tb}} + c \cdot \dfrac{y}{4.2}\right)}$$

In this equation when the concentration of H_2O tends to zero ($c \to 0$), we obtain

$$S_{\mathrm{r}} = \frac{x}{1.05 \cdot k_{\mathrm{D_2O}}^{\mathrm{Eu}}} - \frac{y}{4.2 \cdot k_{\mathrm{D_2O}}^{\mathrm{Tb}}}$$

This is a simple equation, according to which S_{r} is expectedly proportional to the number of inner-sphere water molecules (x and y). Therefore, the europium-to-terbium ratio only affects the LIR value, as was observed when comparing chlorides and pentafluorobenzoates. From this equation it also follows that in order to increase the sensitivity it is reasonable to search for new sensors not among MOF materials, as in ref. 11–13, but rather among water-soluble partially dissociating compounds.

Taking into account the terbium-to-europium energy transfer, one can express the LIR as

$$\mathrm{LIR}(c) = \zeta \cdot \frac{k_{\mathrm{D_2O}}^{\mathrm{Eu}} + c \cdot \dfrac{x}{1.05}}{k_{\mathrm{ET}} + k_{\mathrm{D_2O}}^{\mathrm{Tb}} + c \cdot \dfrac{y}{4.2}}$$

where k_{ET} is the constant of terbium-to-europium energy transfer. From this one can similarly obtain an S_{r} expression, which obviously remains proportional to the number of inner-sphere water molecules

$$S_{\mathrm{r}} = \frac{\dfrac{x}{1.05} \cdot \left(k_{\mathrm{ET}} + k_{\mathrm{D_2O}}^{\mathrm{Tb}}\right) - \dfrac{y}{4.2} \cdot k_{\mathrm{D_2O}}^{\mathrm{Eu}}}{\left(k_{\mathrm{D_2O}}^{\mathrm{Eu}} + c \cdot \dfrac{x}{1.05}\right)\left(k_{\mathrm{ET}} + k_{\mathrm{D_2O}}^{\mathrm{Tb}} + c \cdot \dfrac{y}{4.2}\right)}$$

To verify the obtained theoretical description the fitting of the data obtained for the pfb-system using these equations was run, which demonstrated very high accuracy (Fig. 3).

The analysis of the obtained expression shows that further increase of the sensitivity is possible in the absence of the terbium-to-europium energy transfer.

However, to avoid such an energy transfer the metal-to-metal distance should be increased, which means the decrease of the concentration. This will inevitably result in the luminescence intensity decrease. Therefore, for practical applications, where high sensitivity is required together with the high enough luminescence intensity, the system, studied in this paper, namely $\mathrm{Eu(pfb)_3 : Tb(pfb)_3} = 10:1$, is recommended.

In summary, we have developed an easy way toward sensing of H_2O in D_2O thanks to the thoughtful selection of the sensing system. The highest sensitivity of 24%/%(H_2O) was obtained, which exceeds previously obtained values by an order of magnitude. The theoretical description of the H_2O sensors revealed that the sensitivity is proportional to the number of inner-sphere water molecules. The proposed theoretical description can be further modified to describe Tb–Eu-based H_2O sensors in other solvents.

Conflicts of interest

There are no conflicts to declare.

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