

Sensing of H₂O in D₂O: is there an easy way?

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Experimental section

Materials

Commercially available chemicals, including terbium(III) chloride hexahydrate ($\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, 99.999% trace metals basis), europium(III) chloride hexahydrate ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, 99.9% trace metals basis), ammonia solution (Sigma Aldrich), pentafluorobenzoic acid (Hpfb, Sigma Aldrich, 99%) were used without prior purification. Water was preliminary distilled. Ethanol (Sigma Aldrich, 96.0-97.2%) and deuterium oxide (D_2O , Eurisotop, 99.8%) were used without prior purification.

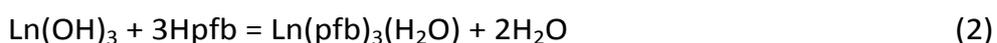
Methods *Thermal analyses* were carried out on a thermoanalyzer STA 409 PC Luxx (NETZSCH, Germany) in the temperature range of 20–1000 °C in air atmosphere, heating rate 10 °/min. The evolved gases composition was simultaneously monitored during the TA experiment using a coupled QMS 403C Aeolos quadrupole mass spectrometer (NETZSCH, Germany). The mass spectra were registered for the species with following m/z values: 18 (corresponding to H_2O), 44 (corresponding to CO_2).

Powder X-ray diffraction (PXRD) was performed by using Bruker D8 Advance [$\lambda(\text{Cu-K}\alpha) = 1.5418 \text{ \AA}$; Ni filter] and Bruker D8 Advance Vario diffractometers [$\lambda(\text{Cu-K}\alpha_1) = 1.54060 \text{ \AA}$; Ge(111)-monochromator] with a step size of 0.020°.

Emission and excitation spectra were measured with a Fluorolog 3 spectrofluorometer over excitation with a xenon lamp. *Luminescence lifetime* measurements were recorded and detected on the same system. Lifetimes were averages of at least three independent measurements. All luminescence decays proved to be perfect single-exponential functions.

Synthesis of lanthanide complexes

To prepare $\text{Ln}(\text{pfb})_3(\text{H}_2\text{O})$ ($\text{Ln} = \text{Tb}, \text{Eu}$) complexes 0.5 mmol of $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved in water. After being stirred magnetically for about 10 min at room temperature, the ammonia solution was added to the mixture upon vigorous stirring. A gelatinous precipitate was gradually formed by stirring at room temperature. After stirring the mixture for 1 hour the precipitate was filtered off and washed several times with distilled water. After that, the precipitate of lanthanide hydroxides was added to a solution of pentafluorobenzoic acid in ethanol. The reaction mixture was vigorously stirred magnetically at room temperature for 1 hour. After the reaction was complete, the unreacted hydroxide was filtered off, and the resulting clear solution was evaporated to dryness on a rotary evaporator. The powder of the lanthanide complex was dissolved in water and recrystallized to separate it from water-insoluble impurities.



PXRD data

Tb(pfb)₃(H₂O) and Eu(pfb)₃(H₂O) complexes were analyzed using PXRD data, they were isostructural to previously published pentafluorobenzoates of terbium and europium (Fig. S1) [1].

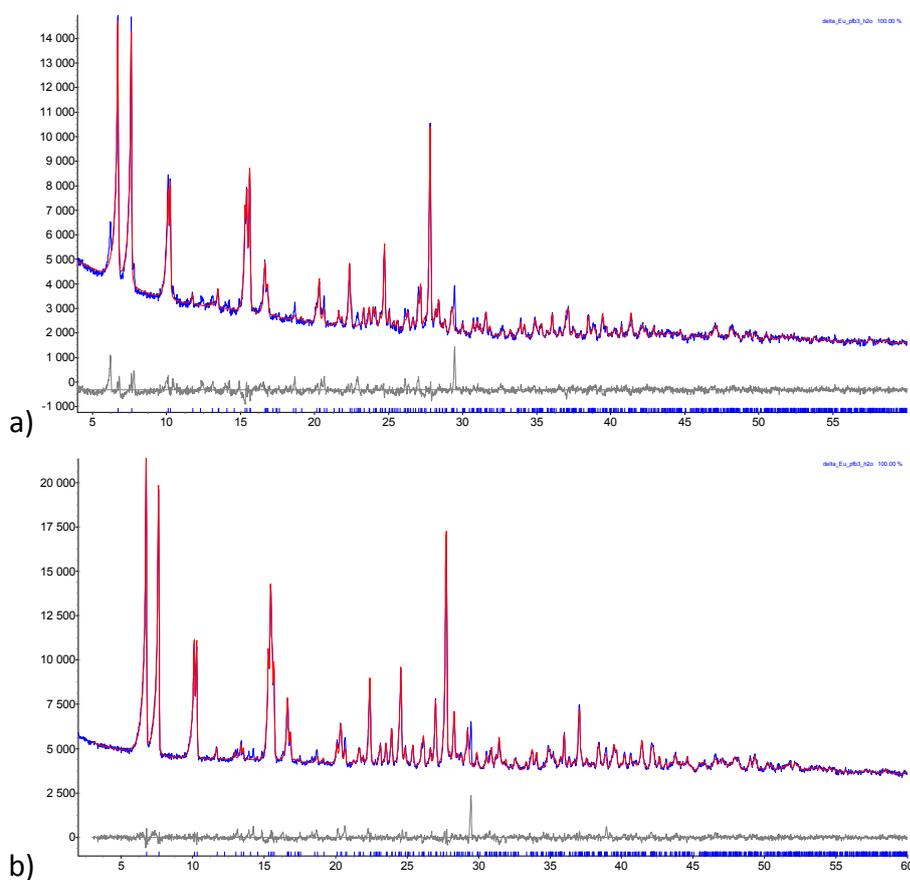


Fig. S1 PXRD data of a) Tb(pfb)₃(H₂O) and b) Eu(pfb)₃(H₂O), fitted using Eu(pfb)₃(H₂O) cif-file from [1].

[1] 28 A.S. Kalyakina, V.V. Utochnikova, I.S. Bushmarinov et al., Chem. A Eur. J., 2016, 21, 17921.

TGA data

The TGA data (Fig. S2) with the mass-detection of the evolved gases witness the formation of monohydrates: according to the ionic current at $M = 18$ (H_2O), the first weight loss step corresponds to the water molecule elimination. The absence of the coordinated ethanol molecule is evidenced by the absence of the maximum on the ionic current of $M = 44$ which is usually present if ethanol is present due to similar molecular weights of CO_2 and ethanol. The coincidence of the experimental weight loss value with the one calculated for the elimination of one water molecules proves the formation of $\text{Ln}(\text{pfb})_3(\text{H}_2\text{O})$.

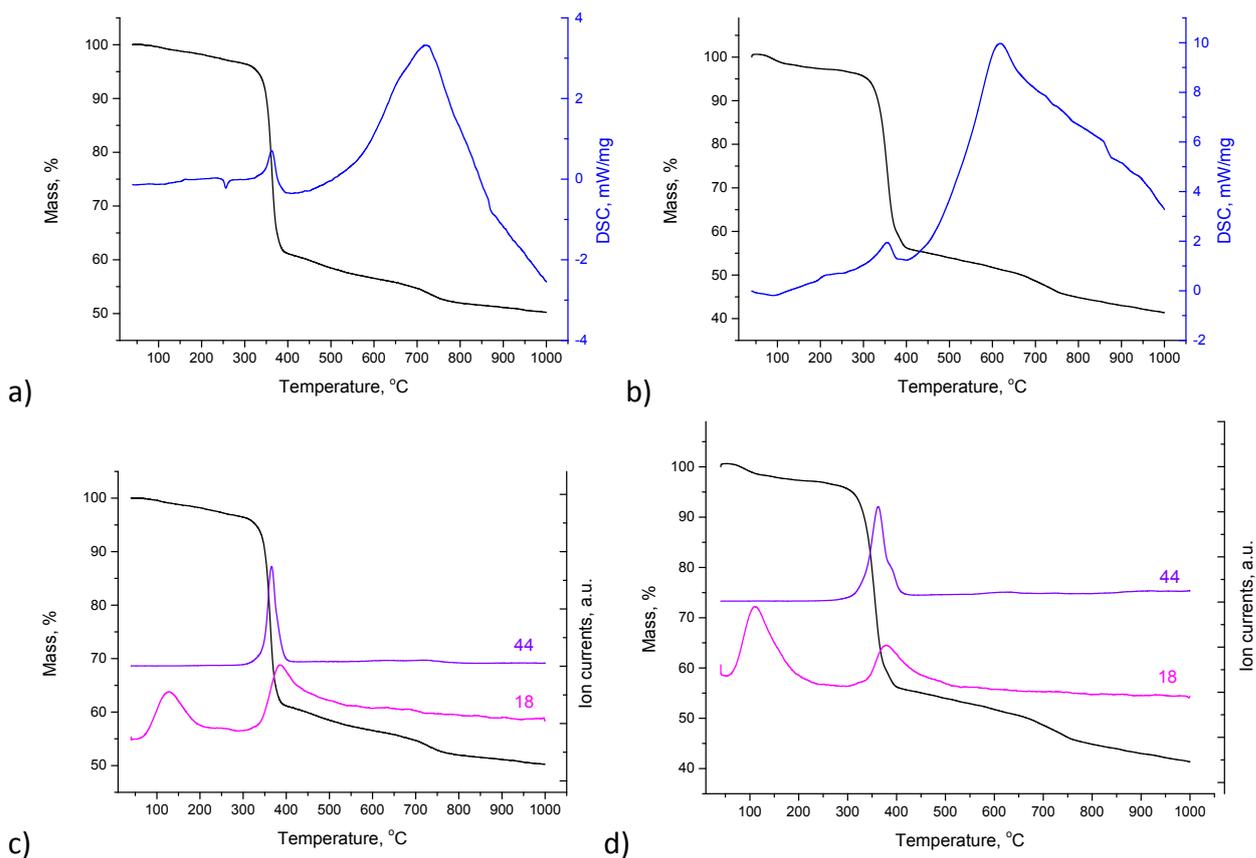
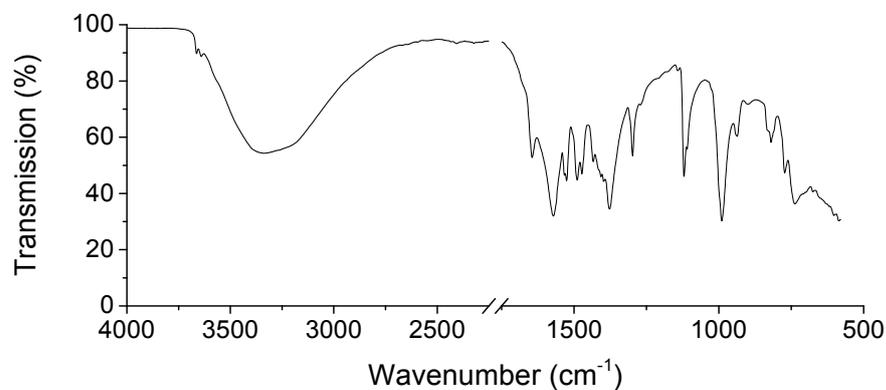


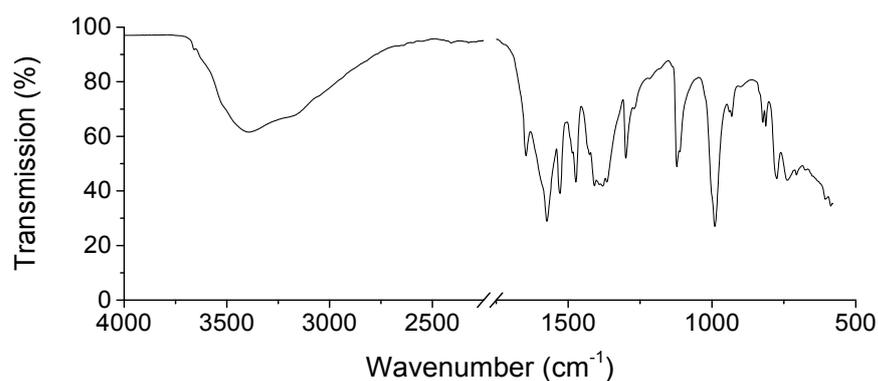
Fig. S2 TGA and DSC data of a) $\text{Tb}(\text{pfb})_3(\text{H}_2\text{O})$, b) $\text{Eu}(\text{pfb})_3(\text{H}_2\text{O})$. Ionic currents are shown in red ($M = 18$) and blue ($M = 44$) in c) $\text{Tb}(\text{pfb})_3(\text{H}_2\text{O})$ and d) $\text{Eu}(\text{pfb})_3(\text{H}_2\text{O})$.

IR spectroscopy data

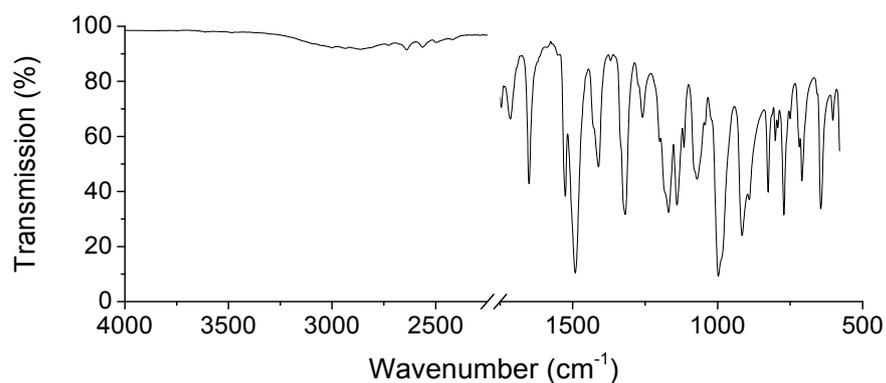
The presence of the water molecule is also supported by the wide band centered at ca. 3500 cm^{-1} in the IR spectra (Fig. S3). The slight shift of other bands, particular of the COO^- band at ca. 1600 cm^{-1} , in lanthanide complex spectra comparing to the Hpfb spectrum indicates the deprotonation during the complex formation.



a)



b)



c)

Fig. S3 IR spectra of a) $\text{Tb}(\text{pfb})_3(\text{H}_2\text{O})$, b) $\text{Eu}(\text{pfb})_3(\text{H}_2\text{O})$, and c) Hpfb.

Luminescence data

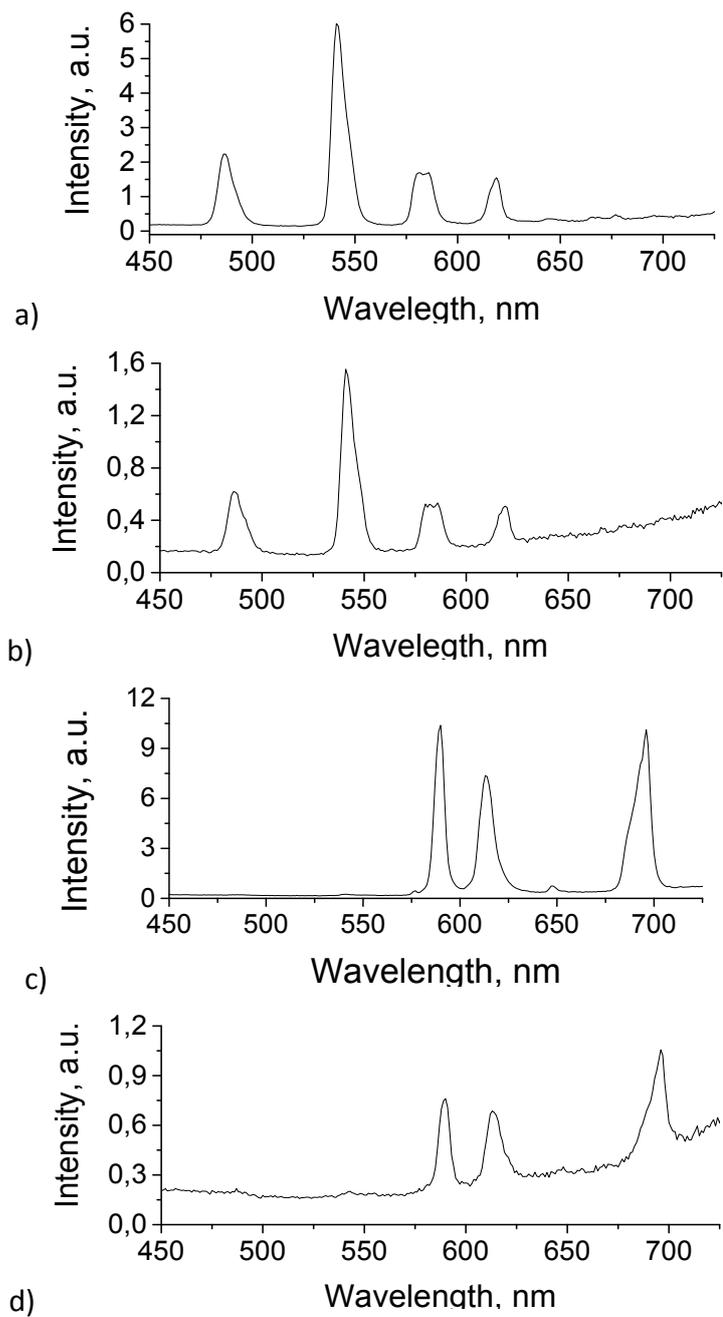


Fig. S4 Luminescence spectra of 25 mM solutions of a) Tb(pfb)₃ in D₂O, b) Tb(pfb)₃ in H₂O, c) Eu(pfb)₃ in D₂O, d) Eu(pfb)₃ in H₂O (excitation wavelength 300 nm).

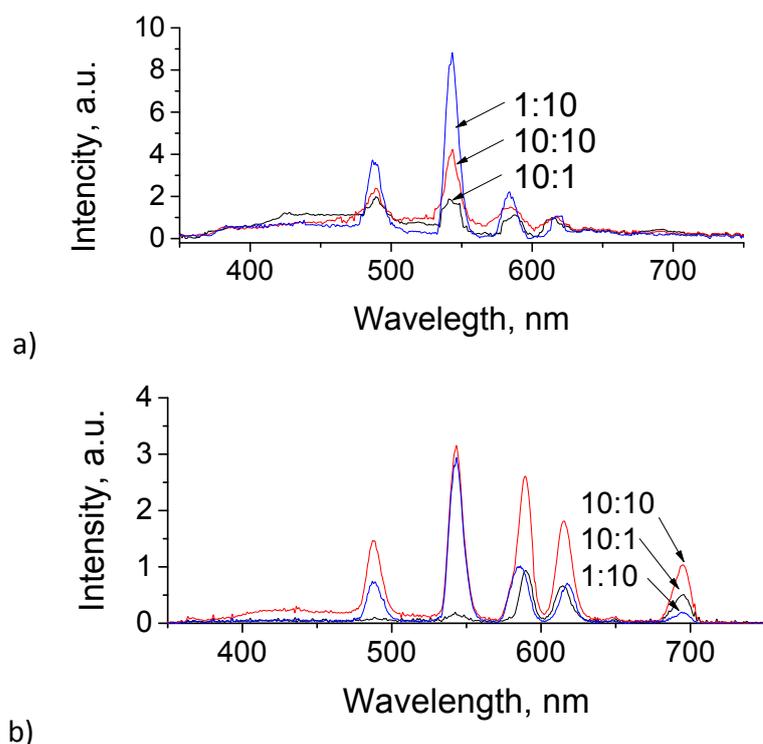


Fig. S5 The luminescence spectra of 25 mM $[\omega\text{Eu}(\text{pfb})_3+(1-\omega)\text{Tb}(\text{pfb})_3]$ solutions with the different Eu:Tb ratio $[\omega:(1-\omega)]$: a) in H_2O b) in D_2O . Excitation wavelength 337 nm.

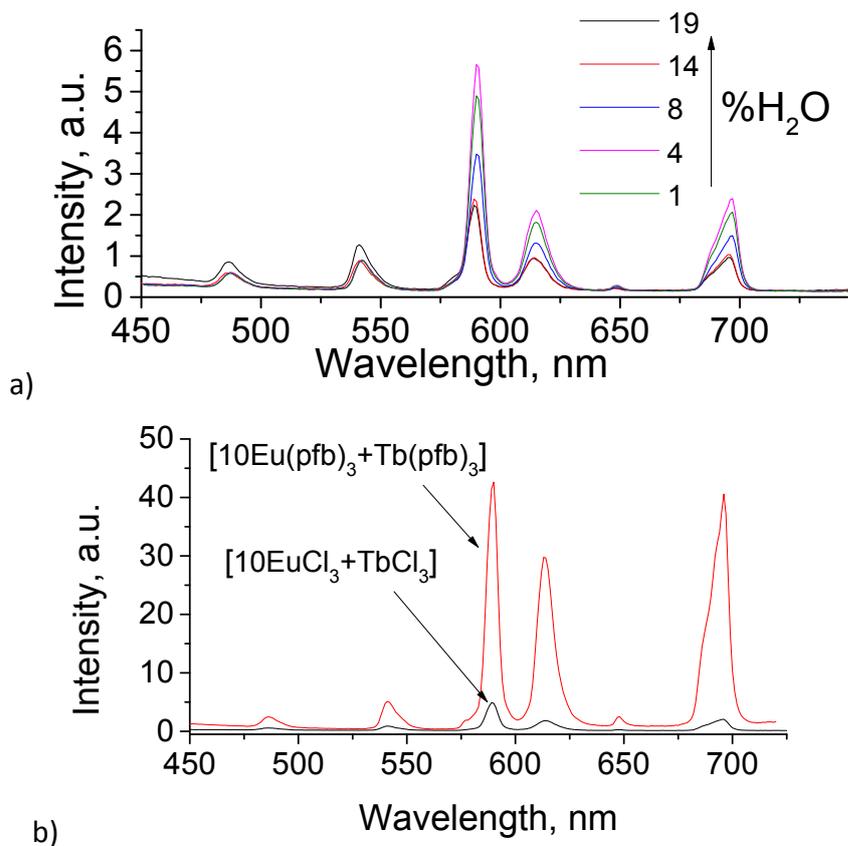


Fig. S6 Luminescence spectra of a) $[10\text{EuCl}_3+\text{TbCl}_3]$ solution in D_2O (25 mM), where fraction of H_2O varies from 1 to 19%, b) $[10\text{EuCl}_3+\text{TbCl}_3]$ (is shown in black) and $[10\text{Eu}(\text{pfb})_3+\text{Tb}(\text{pfb})_3]$ (is shown in red) solution (25 mM) in D_2O with 1% H_2O .

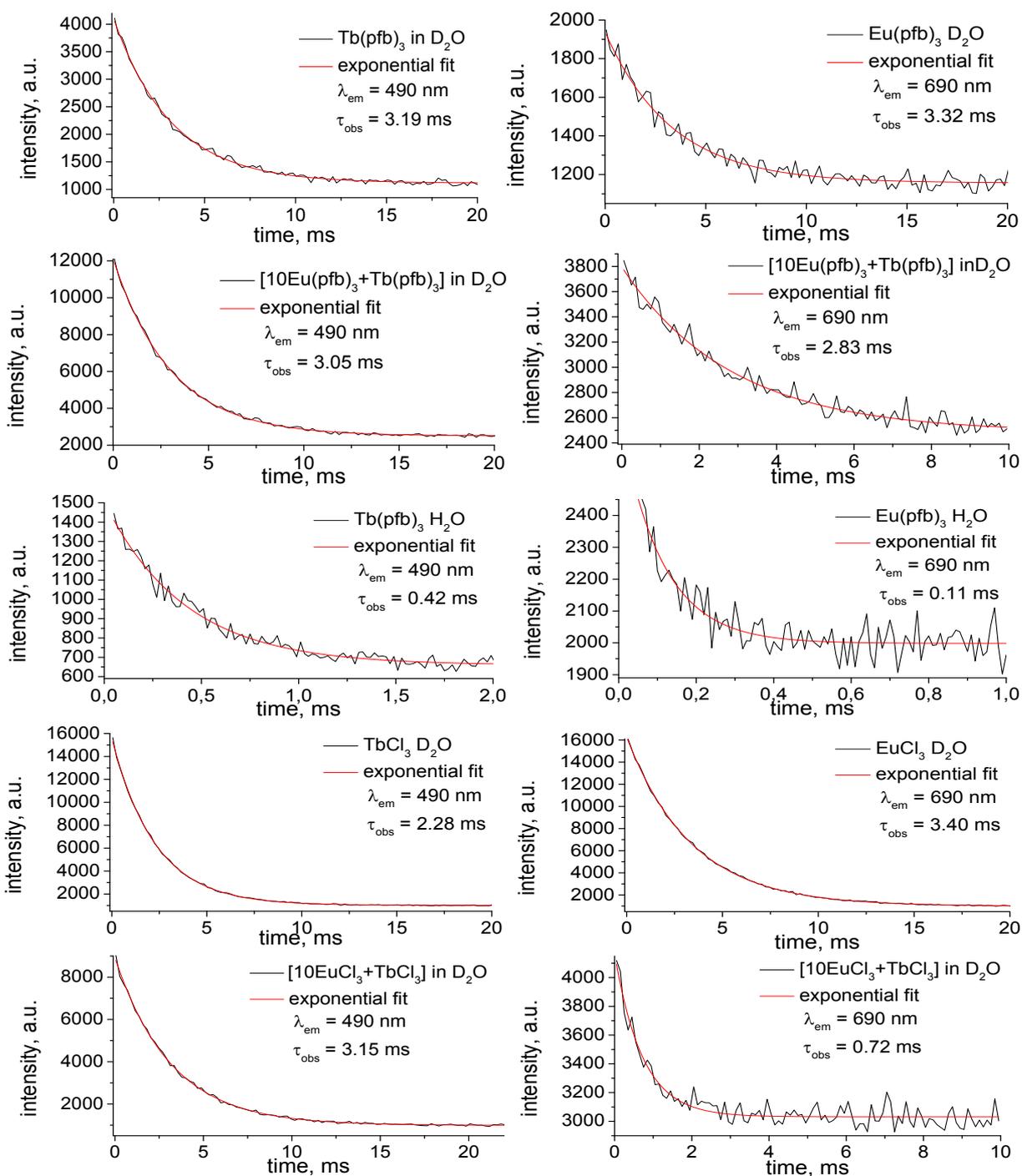


Fig. S7 Observed lifetimes of the excited state of 25 mM solution of $Tb(pfb)_3$, $Eu(pfb)_3$, $[10Eu(pfb)_3 + Tb(pfb)_3]$, $TbCl_3$, $EuCl_3$ and $[10EuCl_3 + TbCl_3]$ in D_2O and H_2O ($\lambda_{ex} = 300$ nm).

Additional data of theoretical description

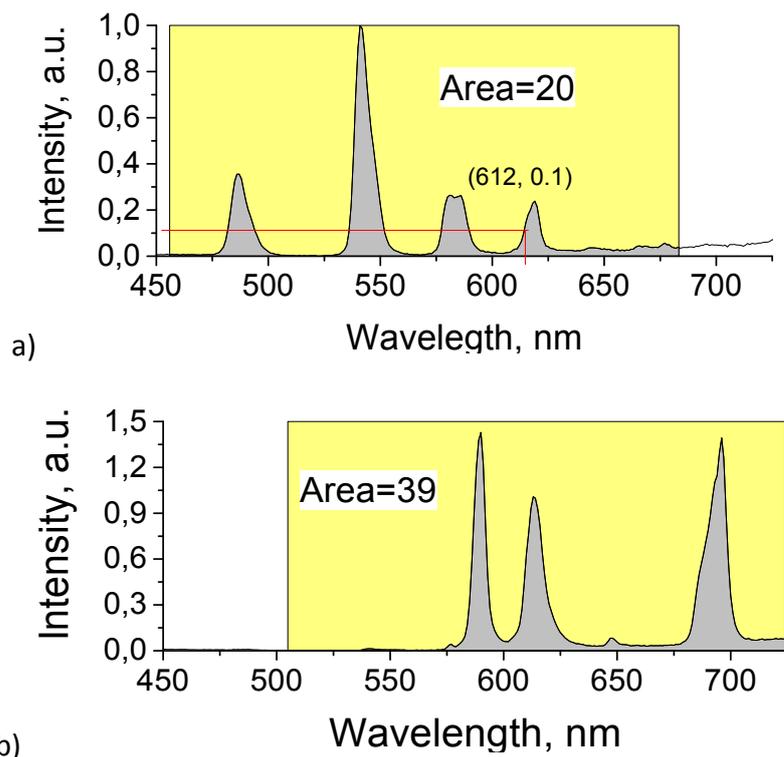


Fig. S8 Luminescence spectra of Tb(pfb)₃ and Eu(pfb)₃ in D₂O (25 mM) (excitation wavelength 300 nm).

To verify the obtained theoretical description the fitting of the data obtained for pfb-system using these equations was run. For this, based on the data shown in Fig. S8, $I(545\text{nm})$ and $I(612\text{nm})$ were expressed from the integral luminescence intensity expressions for $I(\text{Eu})$ and $I(\text{Tb})$ as

$$I_{545} = I_{\text{Tb}}/20$$

$$I_{612} = \frac{I_{\text{Eu}}}{39} + 0.1I_{\text{Tb}}/20$$

Therefore

$$LIR(c) = \frac{I_{545}}{I_{612}} = \frac{39(k_{D_2O}^{\text{Eu}} + c \cdot \frac{x}{1.05}) + 20(k_{ET} + k_{D_2O}^{\text{Tb}} + c \cdot \frac{y}{4.2})/0.1}{20(k_{ET} + k_{D_2O}^{\text{Tb}} + c \cdot \frac{y}{4.2})} + \psi$$

ξ

The obtained experimental data were indeed described with the obtained equation with the fitting parameters $k_{ET}=25 \text{ ms}^{-1}$, $\xi=0.11$ and $\psi=0.14$ (Figure 3).