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Supporting Information

Water in Organic Solvents: Rapid Detection by a Terbium-based turn-off Luminescent Sensor

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Experimental details

Materials

Terbium (III) chloride hexahydrate ($TbCl_3.6H_2O$, Sigma-Aldrich, 99.9%) and Salicylic acid (SRL, 99.9%) were used directly without further purification. Ultrapure Milli-Q water (18.2 MΩ cm, Ultrapure) was used as the source of water. Methanol (Qualigens, HPLC grade, 99.9%, less than 0.05% water), THF (SDFCL, LR grade, 99.5%), EtOH (Analytical CS reagent, 99.9%), and CH_3CN (SDFCL, HPLC grade, 99.8%) were dried by following literature procedure.[1] The dried solvents were used throughout the entire sets of experiments.

Photo-physical characterizations

UV-Visible spectra were recorded on a Shimadzu-3600 spectrophotometer. Excitation and emission spectra were recorded on a Cary-Varian Eclipse fluorescence spectrophotometer with a high power xenon flash lamp with multichannel scaling (MCS). The quantum yields of Tb-SA in MeOH, and with different percentages of water were measured using an integrating sphere on an Edinburgh FLS 980 fluorescence instrument. The lifetimes of the Tb-SA in MeOH and at different percentages of water were also measured on an Edinburgh FLS 980 fluorescence instrument.

Preparation of Tb (III)/Salicylic acid solution

Terbium (III) chloride (20 mM), salicylic acid (6.4 mM and 0.4 mM) solutions were prepared in dry MeOH and EtOH and stored in sealed round bottom flasks on molecular sieves at room temperature. The optimized concentration of terbium (2.5 mM) and SA (0.1 mM) were used for the preparation of Tb-SA systems. For the preparation of Tb-SA, methanolic solutions of terbium chloride (100 µL, 20 mM) and of SA (12.5 µL, 6.4 mM) were mixed in a test tube (4 mL) and diluted with MeOH (688 µL). For the preparation of Tb-SA with 0.1% of water, 600 µL of terbium chloride (20 mM), 1200 µL of SA (0.4 mM), 2996 µL of MeOH and 4.8 µL of water were added in a glass vial (8 mL). In this way, Tb-SA with various water percentages were prepared by increasing the quantity of water (and reducing the volume of MeOH). To determine water in other solvents (THF, CH_3CN), Tb-SA system was prepared in MeOH, diluted with an equal volume of the other solvents (THF, CH_3CN) because terbium salts were not soluble in these solvents (THF, CH_3CN). For the preparation of Tb-SA at 100% H_2O or D_2O, all the solutions were prepared in in H_2O or D_2O and by using dried terbium chloride salt and salicylic acid.

Optimization of probe concentrations

To optimize the concentrations of Tb(III) and SA in the solution, the relative decrease in emission intensity upon successive addition of water in five systems [Tb-SA], 2.5-0.1 mM (**Figure 1b),** 2.5-0.2 mM (**Figure S1a),** 5-0.1 mM (**Figure S1b),** 5-0.2 mM (**Figure S1c),** and 10-0.2 mM (**Figure S1d)**] were compared. In all these cases, a significant decrease in emission intensity (72%, 72%, 68%, 72%, 72%, and 74%, respectively) was observed with 2% water in the solution. These results made us to choose the system with the lowest concentration of Tb(III) (2.5mM) and SA (0.1 mM) for further studies.

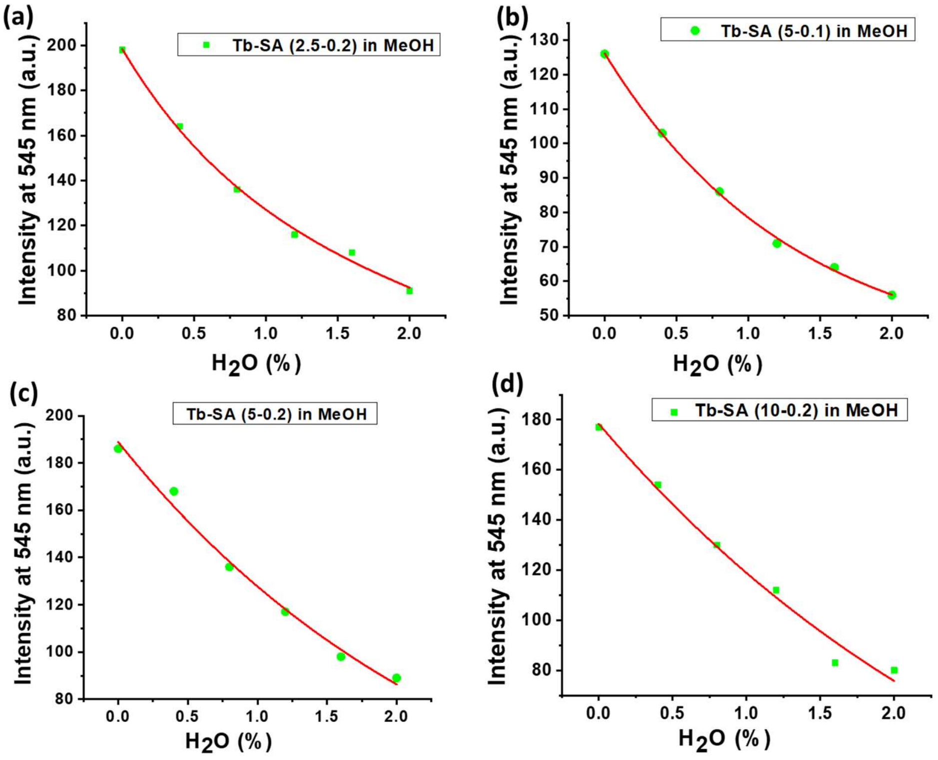
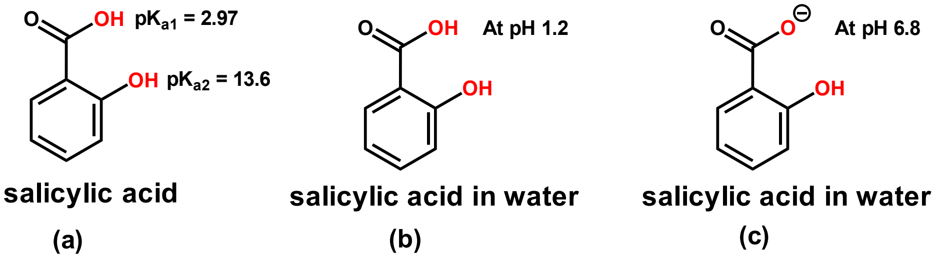


Figure S1 Plots for the decrease in emission at 545 nm by addition of water in Tb-SA at various concentrations of Tb(III) and SA **(a)** 2.5-0.2 mM (**b)** 5-0.1 mM (**c)** 5-0.2 mM (**d)** 10-0.2 mM. mM (λ_{ex} = 305 nm, nm, λ_{em} = 545 nm; slitwidths = 2.5/2.5 nm).

Interaction of SA with Tb(III)

SA ligand remain protonated after Tb-SA complex formation and interaction of SA with Tb(III) was evidenced by absorption studies as discussed below.

The pK_{a1} (-COOH) and pK_{a2} (-OH) of salicylic acid are 2.97 and 13.6, respectively (**Figure S2a**). Therefore, salicylic acid in water at pH 1.2 (below the pK_{a1}) exist in the protonated form (**Figure S2b**) and at pH 6.8 (above the pK_{a1}) exist in the deprotonated form (**Figure S2c**). The λ_{max} in the UV-Vis spectra of salicylic acid in water at pH 1.2 and pH 6.8 found to be 303 nm and 296 nm, respectively (**Figure S3a**). These values are consistent with those reported in the literature.[2] The blue shift at higher pH is documented to be due to the deprotonation of the carboxylic acid moiety.[2] Similarly, at pH 2.2 and pH 8.0 the λ_{max} values are 296 and 303 nm, respectively.[3] This indicated that the increase in pH up to 8.0 did not deprotonate the phenolic -OH obviously because of the higher pK_{a2} of 13.6.



salicylic acid (a) salicylic acid in water (b) salicylic acid in water (c)

Figure S2 (a) Salicylic acid structure indicating pKa1 and pKa2 of carboxylic and phenolic -OH group. (b) protonated form of salicylic acid at pH 1.2 in water. (c) deprotonated form of salicylic acid at pH 6.8 in water.

In our study, the UV-Vis spectral measurement of SA and Tb-SA in MeOH showed λ_{max} of 303 nm and 304 nm, respectively (**Figure S3b**). The observed 1 nm red shift in Tb-SA mixture is insignificant, but may arise from the coordination of SA with Tb^{3+}. Salicylic acid in methanol exists in the protonated form which is supported by the similar UV-Vis spectra of SA and Tb-SA in water at pH 1.2 which is below its pK_{a1}. On the other hand, SA and Tb-SA in water had λ_{max} of 296 nm and 297 nm, respectively, suggesting the deprotonated form of salicylic acid in the system.[2]

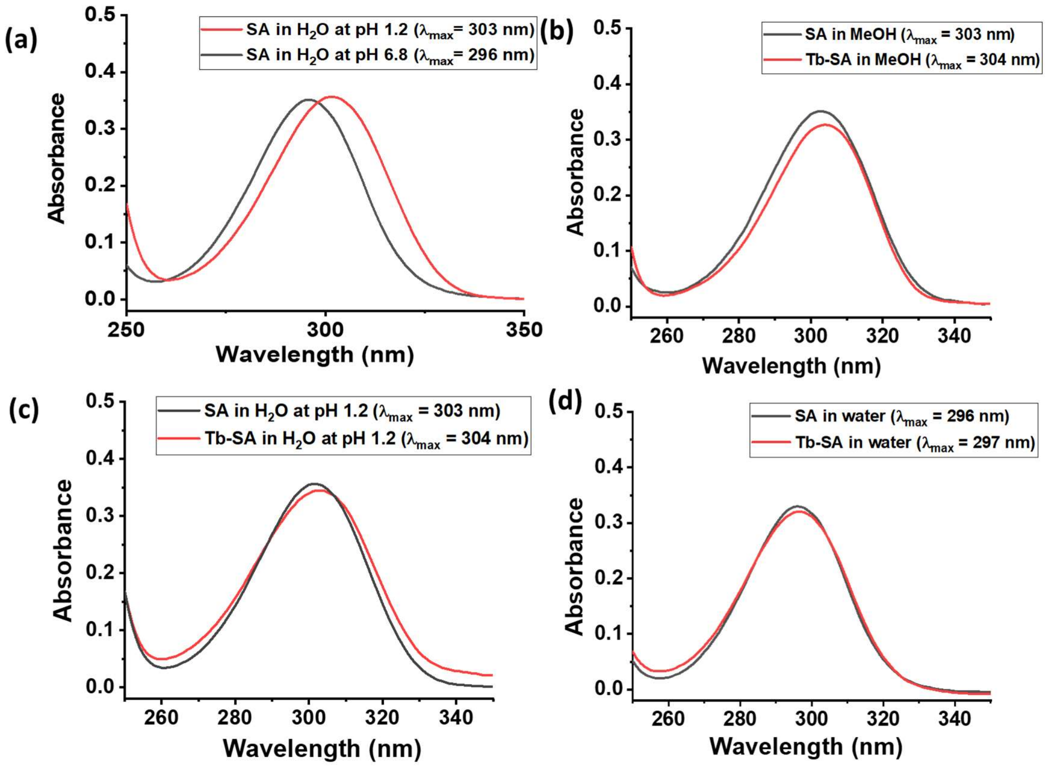


Figure S3. Absorption spectra of (a) SA in water at pH 1.2 and 6.8, (b) SA and Tb-SA in MeOH, (c) SA and Tb-SA in water at pH 1.2, (d) SA and Tb-SA in water (pH 6.8).

Using deuterated solvents

Furthermore, the terbium salt (terbium chloride *hexahydrate*) used to prepare the probe itself contains six water molecules that account for intrinsically ≈ 0.03% of water in a 2.5 mM $TbCl_3.6H_2O$ solution in dry methanol. To minimize the effect of this water, the terbium salt was vacuum dried at 1 mbar for 14 h at about 31 ºC that removed ≈ 83% of water from the hydrated salt (based on weight loss). followed by the addition of CH_3OD to prepare a methanolic terbium solution which was used to prepare the Tb-SA probe solutions. Upon using this probe solution, higher emission intensity (58%) was observed. Moreover, an increase in the lifetime (3.27 ms) and QY (40%) of Tb-SA in CH_3OD (no H_2O/D_2O) compared to the lifetime (1 ms) and QY (22%) of Tb-SA in CH_3OH was observed.

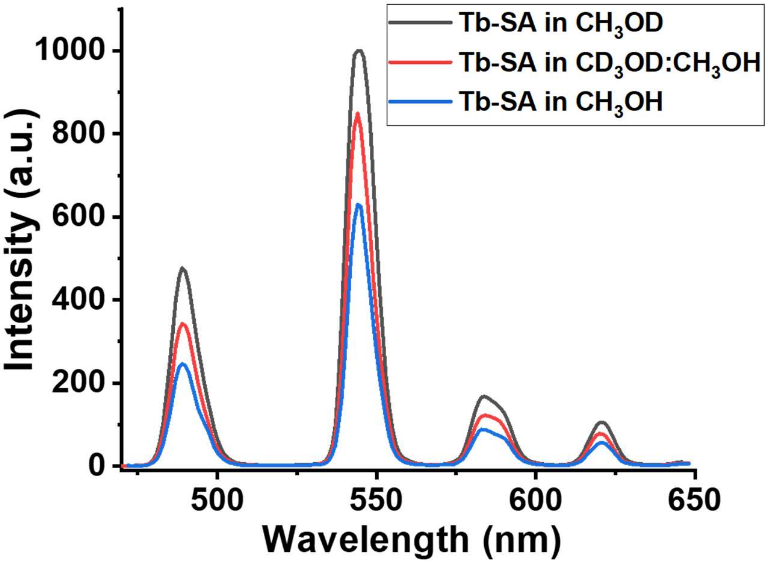


Figure S4. Emission spectra of Tb-SA (2.5/0.1 mM) in CH_3OH (blue), CD_3OD:CH_3OH (1:1) (red) and CH_3OD (black) (λ_{ex} = 305 nm). Lifetime and QY of Tb-SA in CH_3OD (no H_2O/D_2O) were found to be 3.27 ms (Figure S4) and 40%, respectively.

Stability of probe solutions:

Time-dependent emission spectra of Tb-SA in MeOH at higher water concentration, i.e., 0%, 0.4%, 2% and 4% were done (**Figure S5a-d**). We observed a very slighter decrease in the emission spectra with time upon irradiation for 2.5 h. This indicated the stability of the Tb-SA probe solution.

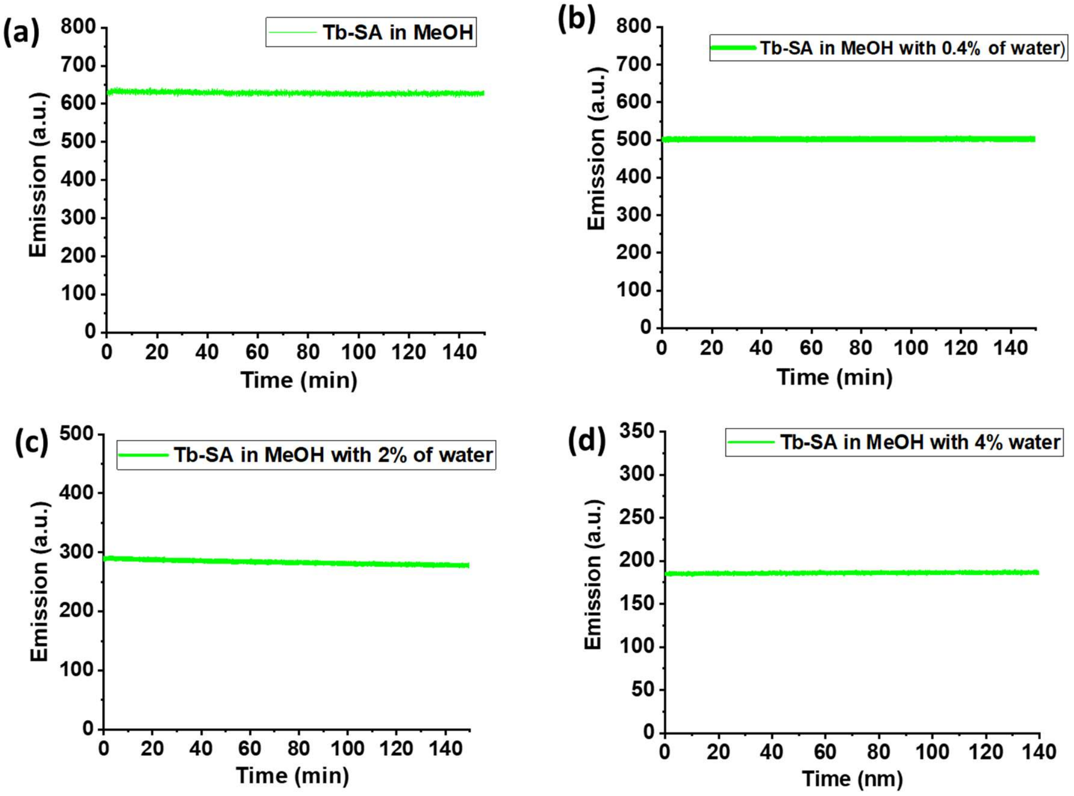


Figure S5 Variation of emission at 545 nm from Tb-SA in (a) MeOH, (b) with 0.4% of water, (c) with 2% of water and (d) with 4% of water. (λ_{ex} = 305 nm, slitwidths = 2.5/5 nm)

Tb lifetime measurements in varying H_2O or D_2O content in Methanol

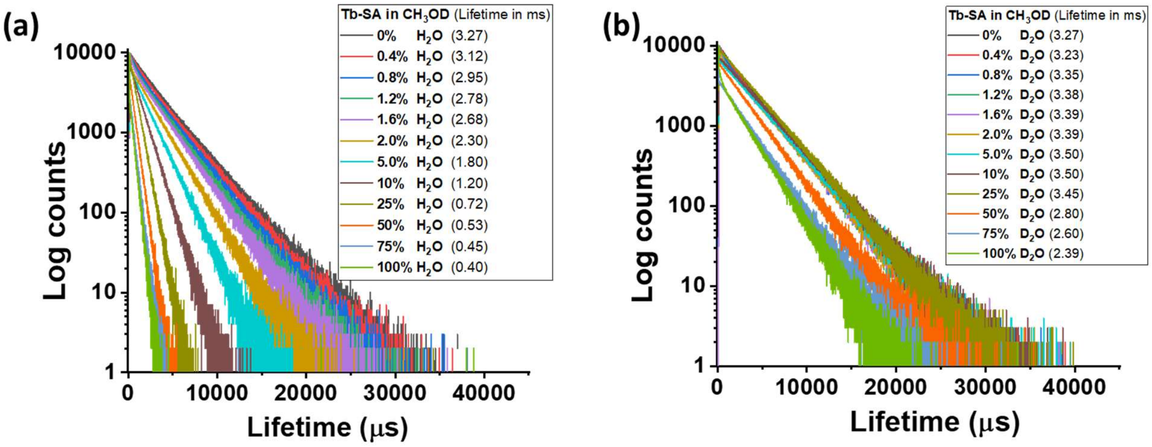
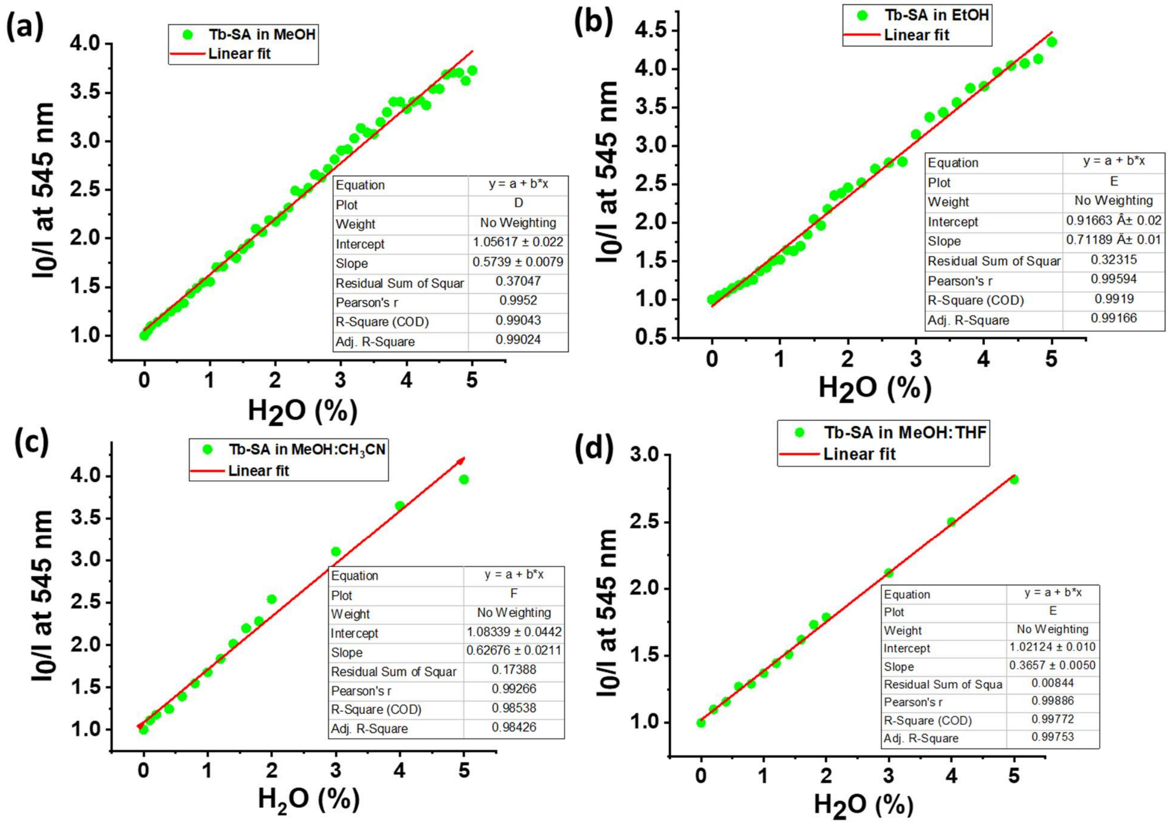


Figure S6 Change in life time of Tb-SA in CH_3OD upon addition of (a) water and (b) D_2O. (λ_{ex} = 305 nm, λ_{em} = 545 nm; slitwidths = 2.5/5 nm).



(a)

Equation	y = a + b*x
Plot	D
Weight	No Weighting
Intercept	1.05617 ± 0.022
Slope	0.5739 ± 0.0079
Residual Sum of Squar	0.37047
Pearson's r	0.9952
R-Square (COD)	0.99043
Adj. R-Square	0.99024

(b)

Equation	y = a + b*x
Plot	E
Weight	No Weighting
Intercept	0.91663 Â± 0.02
Slope	0.71189 Â± 0.01
Residual Sum of Squar	0.32315
Pearson's r	0.99594
R-Square (COD)	0.9919
Adj. R-Square	0.99166

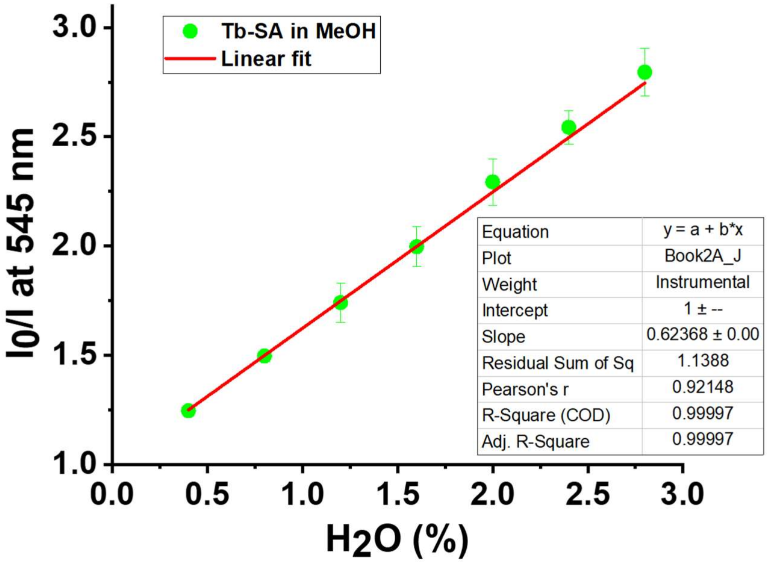
(c)

Equation	y = a + b*x
Plot	F
Weight	No Weighting
Intercept	1.08339 ± 0.0442
Slope	0.62676 ± 0.0211
Residual Sum of Squar	0.17388
Pearson's r	0.99266
R-Square (COD)	0.98538
Adj. R-Square	0.98426

(d)

Equation	y = a + b*x
Plot	E
Weight	No Weighting
Intercept	1.02124 ± 0.010
Slope	0.3657 ± 0.0050
Residual Sum of Squa	0.00844
Pearson's r	0.99886
R-Square (COD)	0.99772
Adj. R-Square	0.99753

Figure S7. Plots for the detection of water by Tb-SA in (a) methanol (b) ethanol (c) acetonitrile and (d) tetrahydrofuran in the range of 0.1-5% of water. [Tb-SA (2.5-0.1 mM), λ_{ex} = 305 nm; λ_{em} = 545 nm].



Equation	y = a + b*x
Plot	Book2A_J
Weight	Instrumental
Intercept	1 ± --
Slope	0.62368 ± 0.00
Residual Sum of Sq	1.1388
Pearson's r	0.92148
R-Square (COD)	0.99997
Adj. R-Square	0.99997

Figure S8. Plots for I_0/I for Tb-SA in MeOH for three data sets with error bars. [Tb-SA (2.5-0.1 mM), λ_{ex} = 305 nm; λ_{em} = 545 nm].

Quantification of water in MeOH

For the quantification of water content (x %) in a MeOH sample (y mL), the following procedure was followed. Based on the 'expected' water content in the sample, the volume y can be adjusted in order to have 0-2% water in the final solution.

1. $TbCl_3$ (20 mM) in MeOH **[600 µL] +** Salicylic acid (0.4 mM) in MeOH **[1200 µL]** + Dry MeOH **[3000 µL] = solution A (I_0)**

2. $TbCl_3$ (20 mM) in MeOH **[600 µL] +** Salicylic acid (0.4 mM) in MeOH **[1200 µL]** + Dry MeOH **[3000 µL-y]** + MeOH sample **[y µL] = solution B (I)**

3. Phosphorescence of solutions A and B were recorded to find the value of I_0 and I respectively. The water content can then be calculated as:

$$x\,(\%) = \frac{4800}{y} \times 1.62\left(\frac{I_0}{I} - 1\right)$$

Quantification of water in EtOH

For the quantification of water content (x %) in a sample of EtOH (y mL), the following procedure was followed:

1. $TbCl_3$ (20 mM) in EtOH **[600 µL] +** Salicylic acid (0.4 mM) in EtOH **[1200 µL]** + Dry EtOH **[3000 µL] = Solution C (I_0)**

2. $TbCl_3$ (20 mM) in EtOH **[600 µL] +** Salicylic acid (0.4 mM) in EtOH **[1200 µL]** + Dry EtOH **[3000 µL-y]** + EtOH sample **[y µL] = Solution D (I)**

3. Phosphorescence of solutions C and D were recorded to find the value of I_0 and I respectively. The water content in EtOH sample can be calculated as:

$$x\,(\%) = \frac{4800}{y} \times 1.34\left(\frac{I_0}{I} - 1\right)$$

Quantification of water in CH_3CN

For the quantification of water content (x%) in a sample of CH_3CN (y mL), following procedure was followed

1. $TbCl_3$ (20 mM) in MeOH **[600 µL] +** Salicylic acid (0.4 mM) in MeOH **[1200 µL]** + Dry MeOH **[600 µL]** + Dry CH_3CN **[2400 µL] = Solution E = I_0**

2. $TbCl_3$ (20 mM) in MeOH **[600 µL] +** Salicylic acid (0.4 mM) in MeOH **[1200 µL]** + Dry MeOH **[600 µL]** + Dry CH_3CN **[2400 µL-y]** + CH_3CN sample **[y µL] = Solution F = I**

3. Phosphorescence of solutions E and F were recorded to find the value of I_0 and I, respectively. The water content in CH_3CN sample can be calculated as:

$$(x, in\ \%) = \frac{4800}{y} \times 1.46\left(\frac{I_0}{I} - 1\right)$$

Quantification of water in THF

For the quantification of water content (x) in a sample of THF (y mL). Following procedure was followed

1. $TbCl_3$ (20 mM) in MeOH **[600 μL] +** Salicylic acid (0.4 mM) in MeOH **[1200 μL]** + Dry MeOH **[600 μL]** + THF **[2400 μL] = Solution G (I_0)**

2. $TbCl_3$ (20 mM) in MeOH **[600 μL] +** Salicylic acid (0.4 mM) in MeOH **[1200 μL]** + Dry MeOH **[600 μL]** + THF **[2400 μL-y]** + THF sample **[y μL] = Solution H (I)**

3. Phosphorescence of solutions G and H were recorded to find the value of I_0 and I, respectively. The water content in THF sample can be calculated as:

$$(x, in\ \%) = \frac{4800}{y} \times 2.68\left(\frac{I_0}{I} - 1\right)$$

References

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[2] I. Nugrahani, B. Tjengal, T. Gusdinar, A. Horikawa, H. Uekusa. *Crystals* **2020**, *10*, 349.

[3] (a) H. Guo, F. He, B. Gu, L. Liang, J. C. Smith. *J. Phys. Chem. A* **2012**, *116*, 11870. (b) M. K. Trivedi, A. Branton, D. Trivedi, H. Shettigar, K. Bairwa and S. Jana. *Nat. Prod. Chem. Res.* **2015**, *3*, 1000186.