Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for: Mapping the Distribution of Electronic States within the $^5D_4$ and $^7F_6$ Levels of Tb^{3+} Complexes with Optical Spectroscopy

Nicolaj Kofod*,[a] Margrete Juel Henrichsen[a] and Thomas Just Sørensen*[a]

Dr. N. Kofod, M. Henrichsen, Prof. Dr. T. J. Sørensen
Department of Chemistry & Nano-Science Center
University of Copenhagen
Universitetsparken 5, 2100 København Ø, Denmark
E-mail: NK: nicolaj.kofod@chem.ku.dk, TJS: tjs@chem.ku.dk

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$[Tb(H_2O)_9]^{3+}$

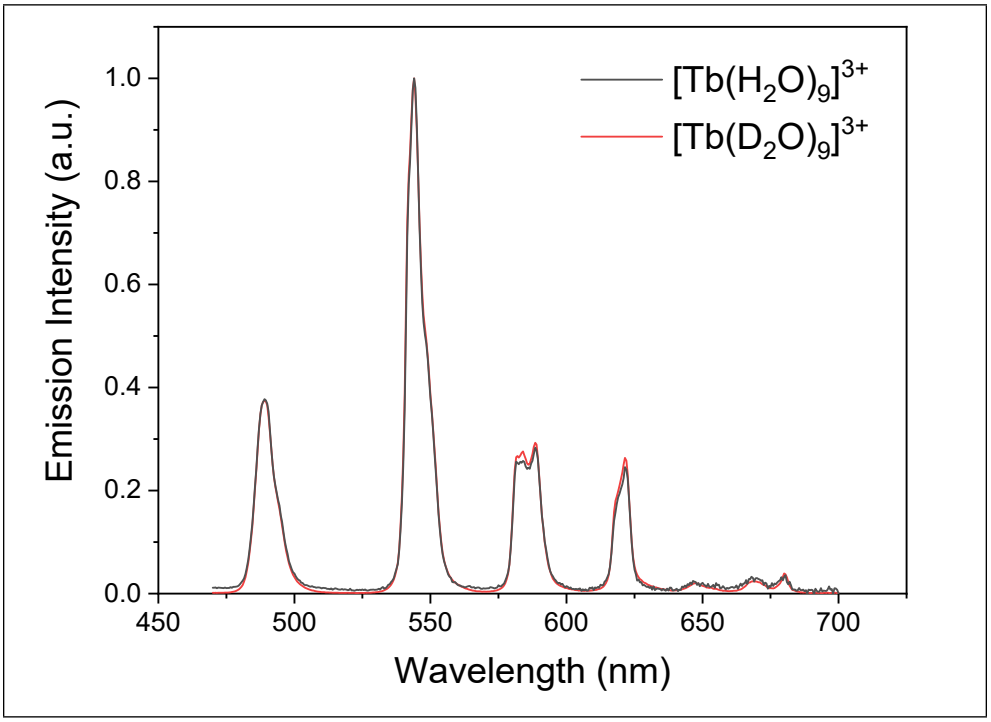

Figure S1. Normalized emission spectra of 0.1 M $Tb(CF_3SO_3)_3$ in H_2O (black) and D_2O (red). Excitation wavelength at 351 nm. Emission and excitation slits were set at 8 and 1 nm respectively.

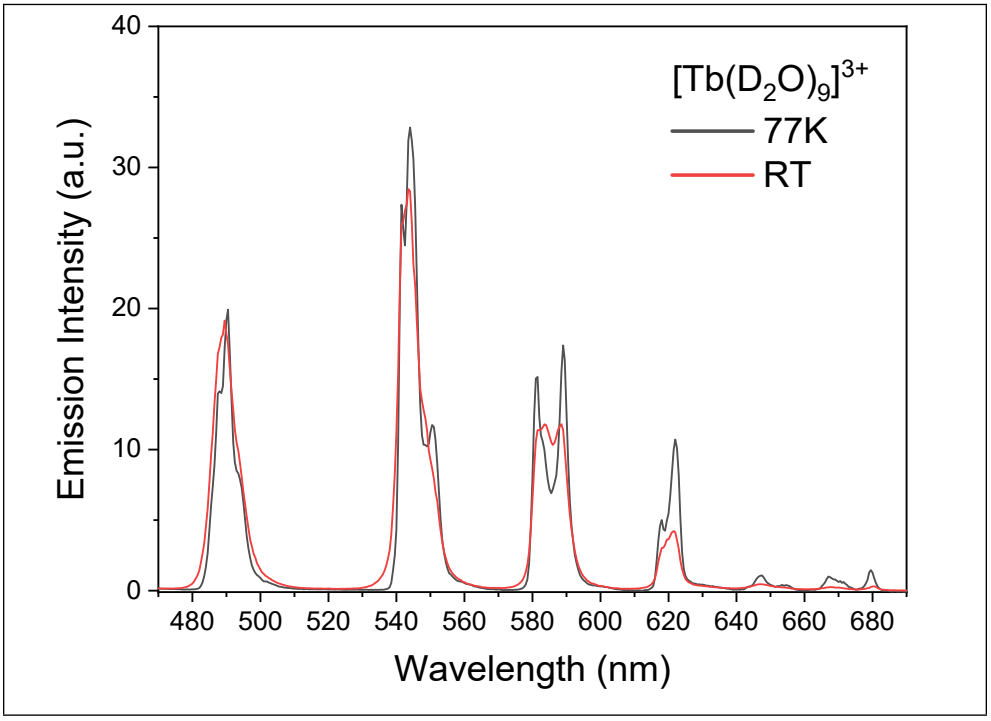

Figure S2. Emission spectra of 0.1 M $Tb(CF_3SO_3)_3$ in D_2O at 77 K (black) and RT (red). Excitation wavelength at 353 nm. Emission and excitation slits were set at 5 nm and 1 nm respectively.

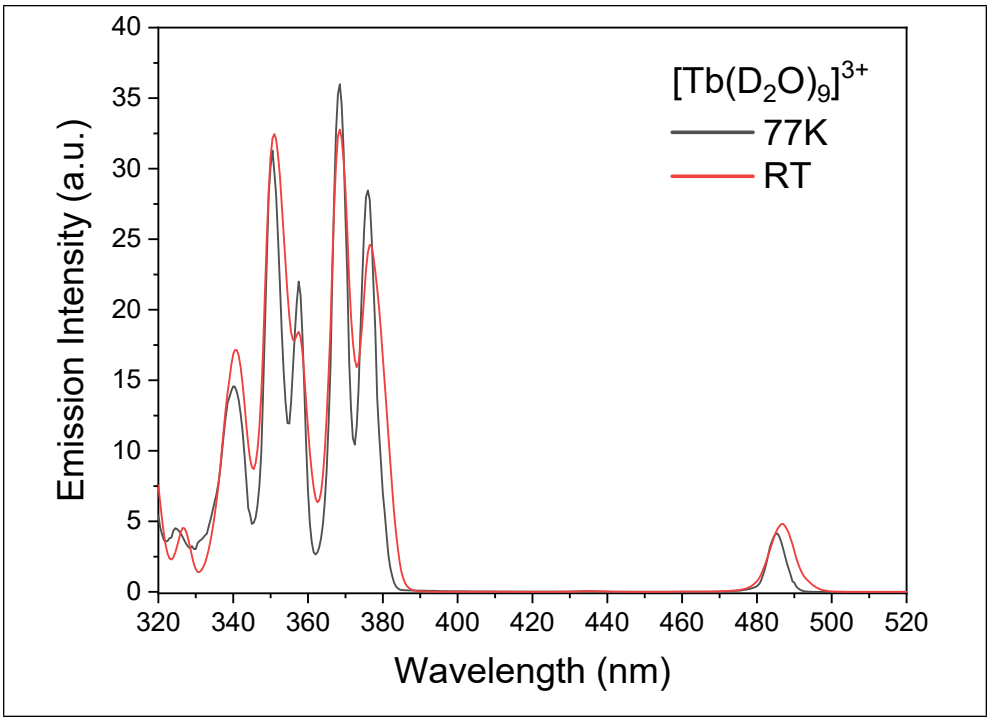

Figure S3. Excitation spectra of 0.1 M $Tb(CF_3SO_3)_3$ in D_2O at 77 K (black) and RT (red). Emission was measured at 544 nm. Emission and excitation slits were set at 8 nm and 2 nm respectively.

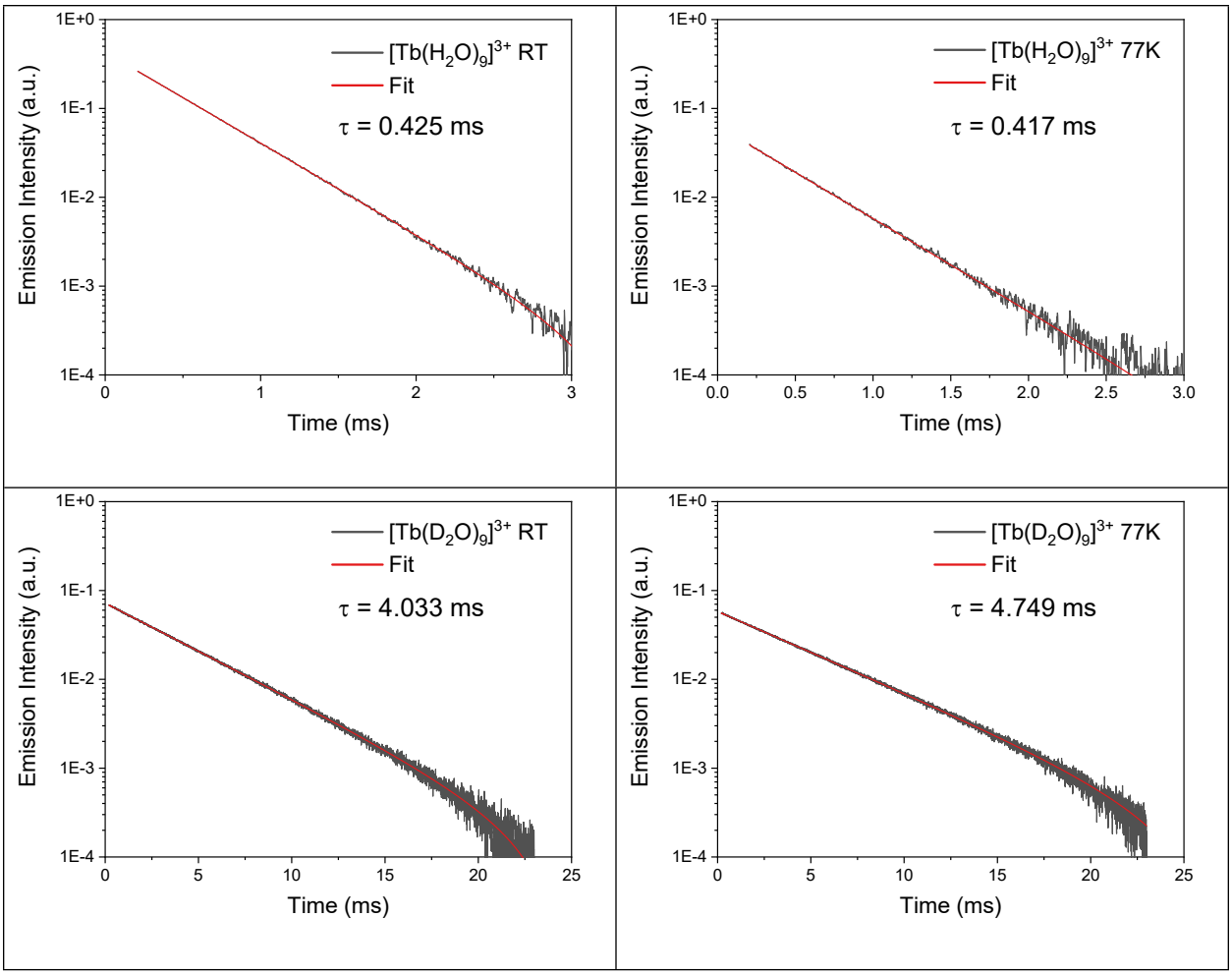

Figure S4. Emission decay traces of 0.1 M $Tb(CF_3SO_3)_3$ in H_2O (top row) and D_2O (bottom row) at RT (left column) and 77 K (right column). The data was fitted with a mono-exponential function (red trace). Excitation was done at 372 nm and emission was measured at 488 nm. Both emission and excitation slits were kept at 5 nm.

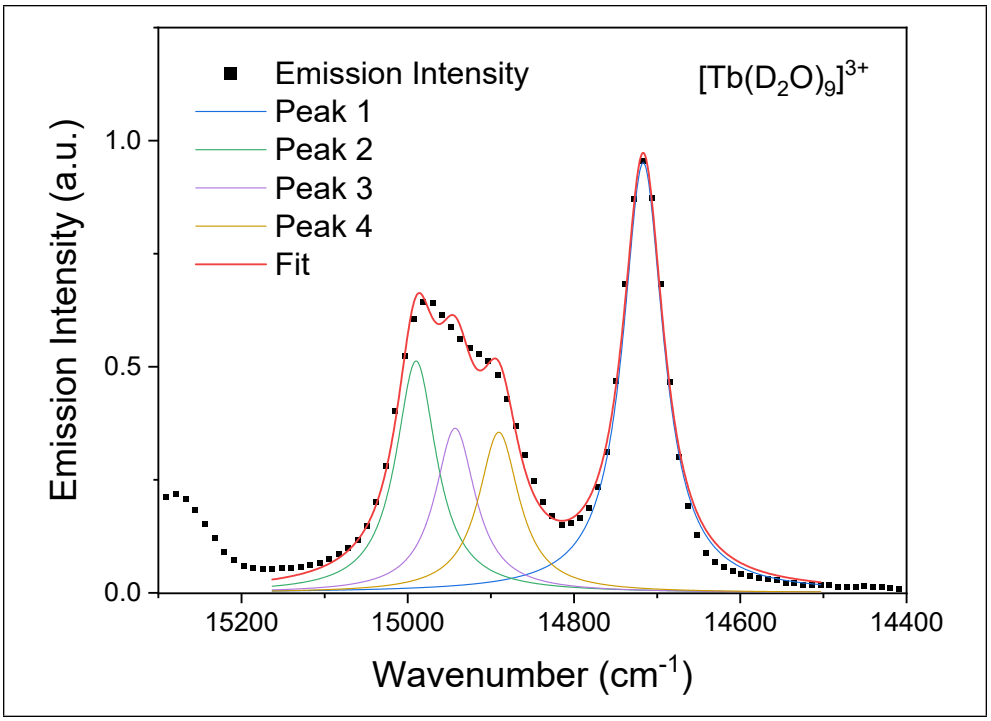

Figure S5. High resolution emission spectra of the $^5D_4 \rightarrow {}^7F_0$ (right) and $^7F_1$ peaks (left) of 0.1 M $Tb(CF_3SO_3)_3$ in D_2O at 77 K. Excitation was done at 372 nm. Excitation and emission slits were kept at 5 nm and 1 nm respectively. The data was fitted with 4 Lorentzian peaks. Fit parameters are given in Table S1.

Table S1. Fit parameters for the emission spectra of the $^5D_4 \rightarrow {}^7F_0$ and $^7F_1$ peaks of 0.1 M $Tb(CF_3SO_3)_3$ in D_2O at 77 K, from Figure S5.

Peak #	Peak Center (cm^{-1})	Peak Width[a] (cm^{-1})	Peak Area
Peak 1	14717 ± 0.5	59.2 ± 1.2	88.5 ± 1.4
Peak 2	14990 ± 1.5	59.2 ± 1.2	47.7 ± 2.3
Peak 3	14943 ± 2.6	59.2 ± 1.2	33.9 ± 2.3
Peak 4	14890 ± 1.9	59.2 ± 1.2	33.0 ± 1.9

[a] Shared parameter

[Tb(EDTA)(H$_2$O)$_3$]$^-$

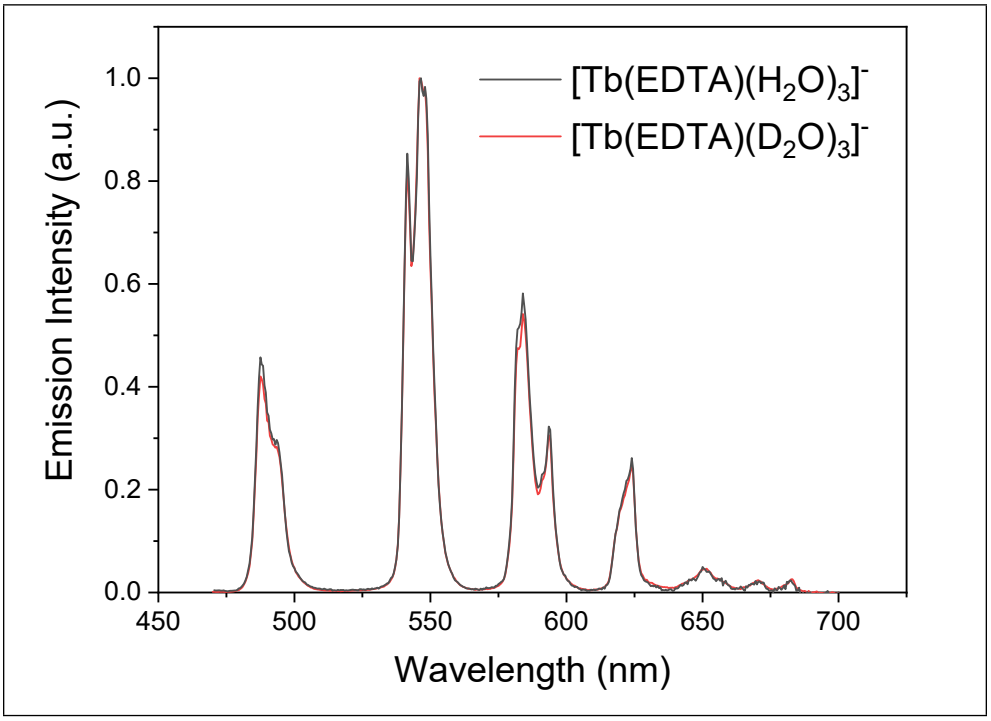

Figure S6. Normalized emission spectra of 0.05 M [Tb(EDTA)(H$_2$O)$_3$]$^-$ in H$_2$O (black) and [Tb(EDTA)(D$_2$O)$_3$]$^-$ in D$_2$O (red). Excitation wavelength at 372 nm. Emission and excitation slits were set at 5 nm and 1 nm respectively.

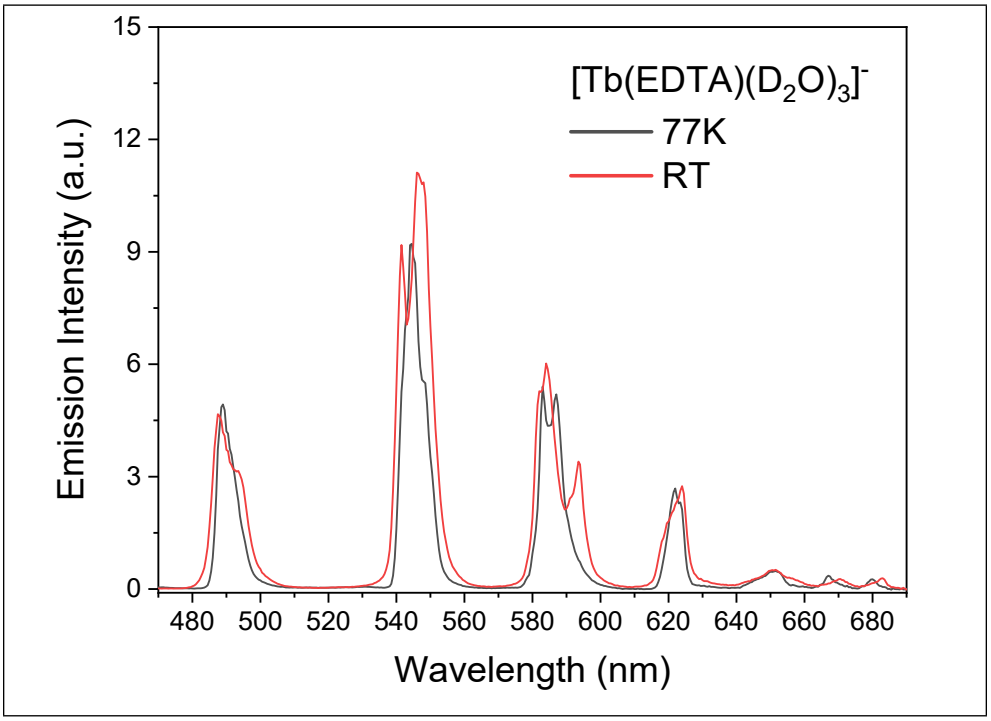

Figure S7. Emission spectra of 0.05 M [Tb(EDTA)(D$_2$O)$_3$]$^-$ in D$_2$O at 77 K (black) and RT (red). Excitation wavelength at 372 nm. Emission and excitation slits were set at 5 nm and 1 nm respectively.

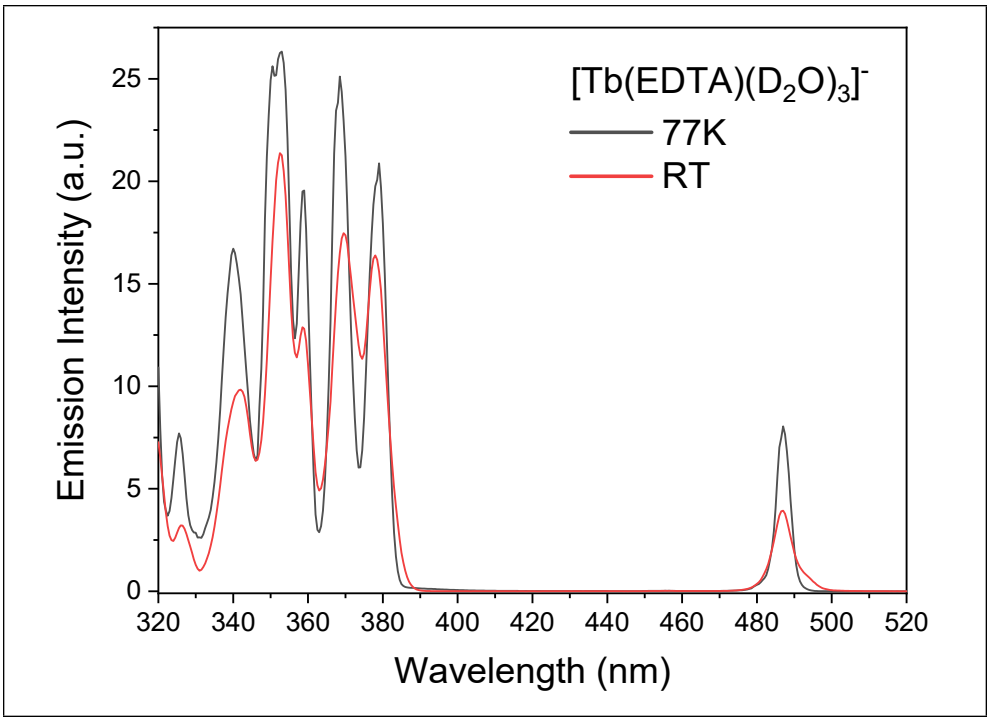

Figure S8. Excitation spectra of 0.05 M $[Tb(EDTA)(D_2O)_3]^-$ in D_2O at 77 K (black) and RT (red). Emission was measured at 545 nm. Emission and excitation slits were set at 3 nm and 3 nm respectively.

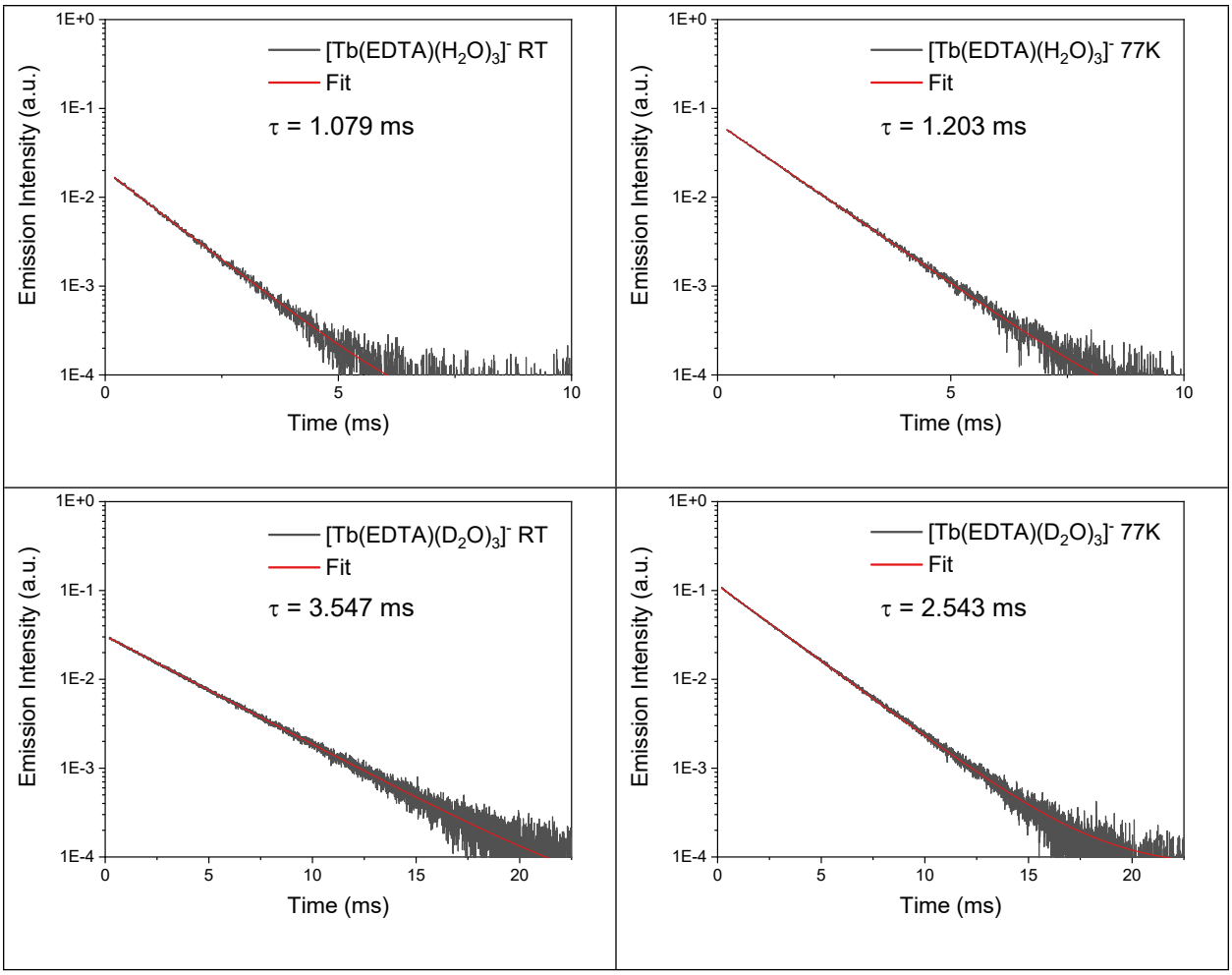

Figure S9. Emission decay traces of 0.05 M $[Tb(EDTA)(H_2O)_3]^-$ in H_2O (top row) and 0.05 M $[Tb(EDTA)(D_2O)_3]^-$ in D_2O (bottom row) at RT (left column) and 77 K (right column). The data was fitted with a mono-exponential function (red trace). Excitation was done at 372 nm and emission was measured at 488 nm. Both emission and excitation slits were kept at 5 nm.

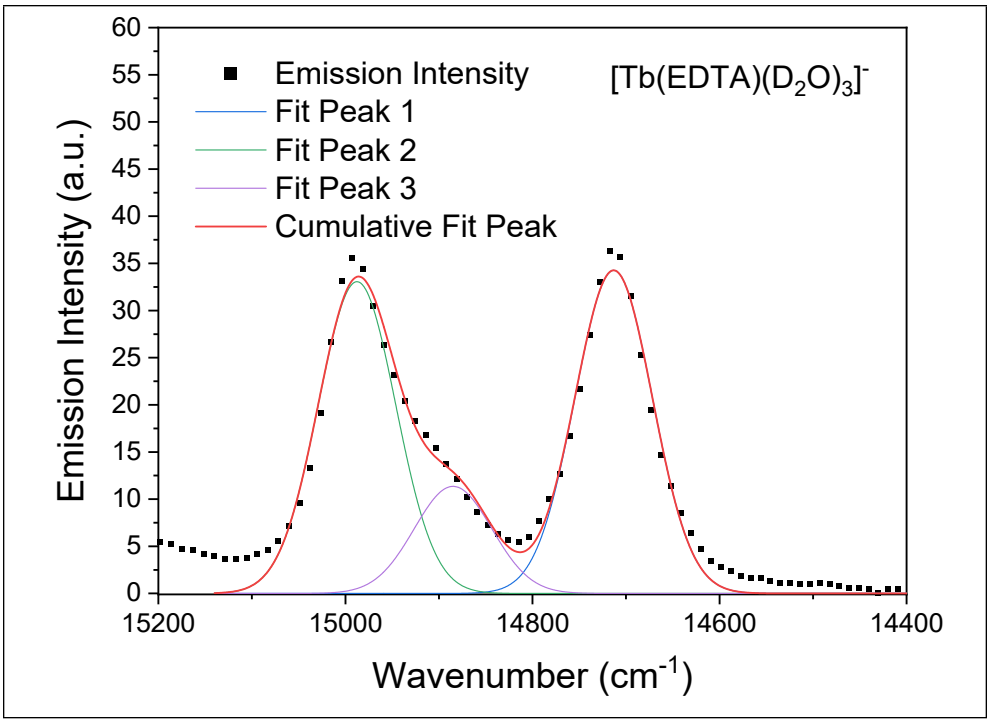

Figure S10. High resolution emission spectra of the $^5D_4 \rightarrow {}^7F_0$ (right) and $^7F_1$ peaks (left) of 0.05 M $[Tb(EDTA)(D_2O)_3]^-$ in D_2O at 77 K. Excitation was done at 372 nm. Excitation and emission slits were kept at 8 nm and 2 nm respectively. The data was fitted with 3 Lorentzian peaks. Fit parameters are given in Table S2.

Table S2. Fit parameters for the emission spectra of the $^5D_4 \rightarrow {}^7F_0$ and $^7F_1$ peaks of 0.05 M $[Tb(EDTA)(D_2O)_3]^-$ in D_2O at 77 K, from Figure S10.

Peak # (RT)	Peak Center (cm^{-1})	Peak Width[a] (cm^{-1})	Peak Area x10^5
Peak 1	14713 ± 0.6	75.2 ± 1.2	43.6 ± 0.56
Peak 2	14990 ± 0.8	75.2 ± 1.2	40.1 ± 0.76
Peak 3	14915 ± 2.6	75.2 ± 1.2	11.8 ± 0.68
[a] Shared parameter			

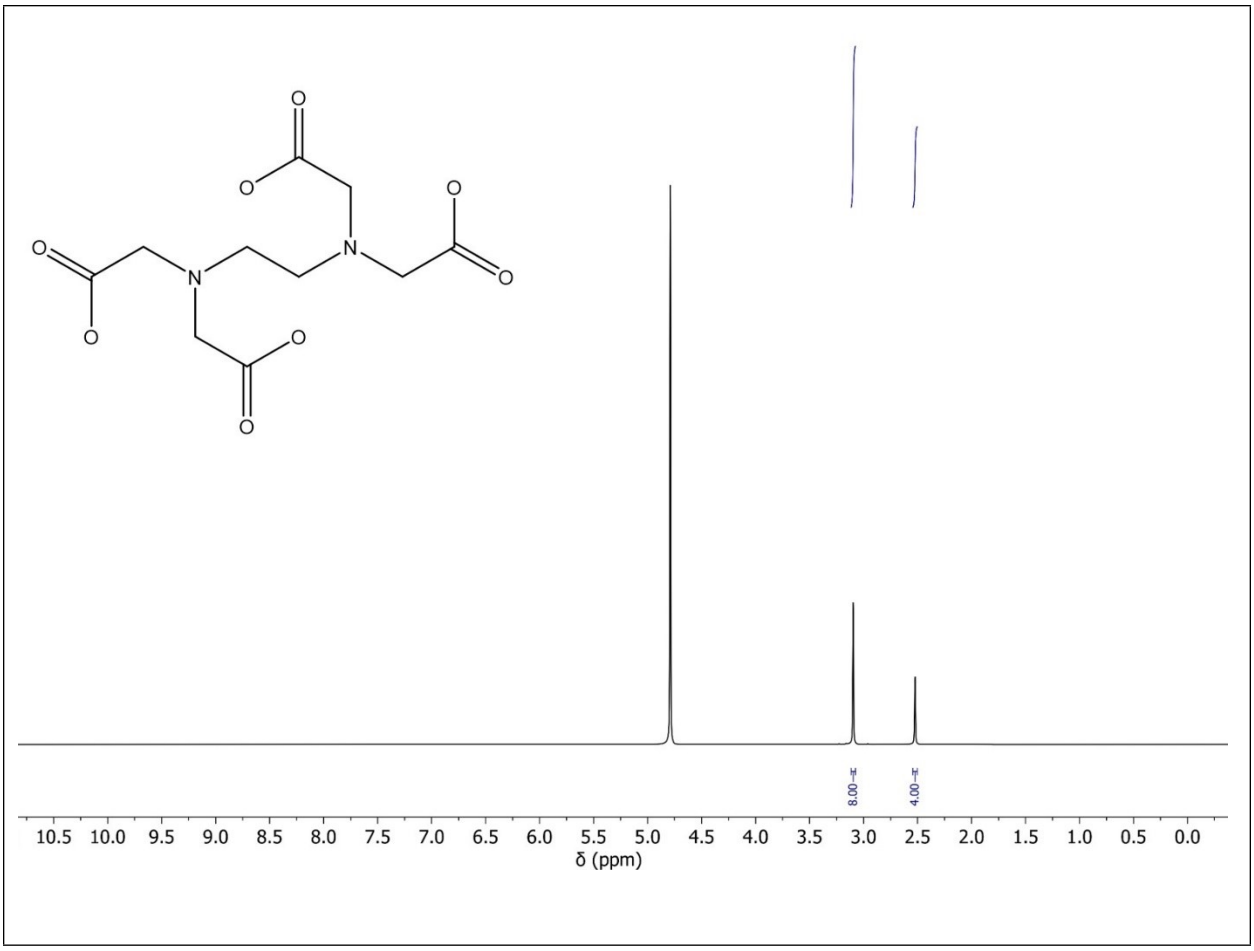

Figure S11. ^{1}H-NMR (500 MHz) of $EDTA^{4-}$ in D_2O. δ 3.10 (s, 8H), 2.52 (s, 4H). pD was adjusted to ~8 using NaOD to make the sample soluble.

$[Tb(DTPA)(H_2O)]^{2-}$

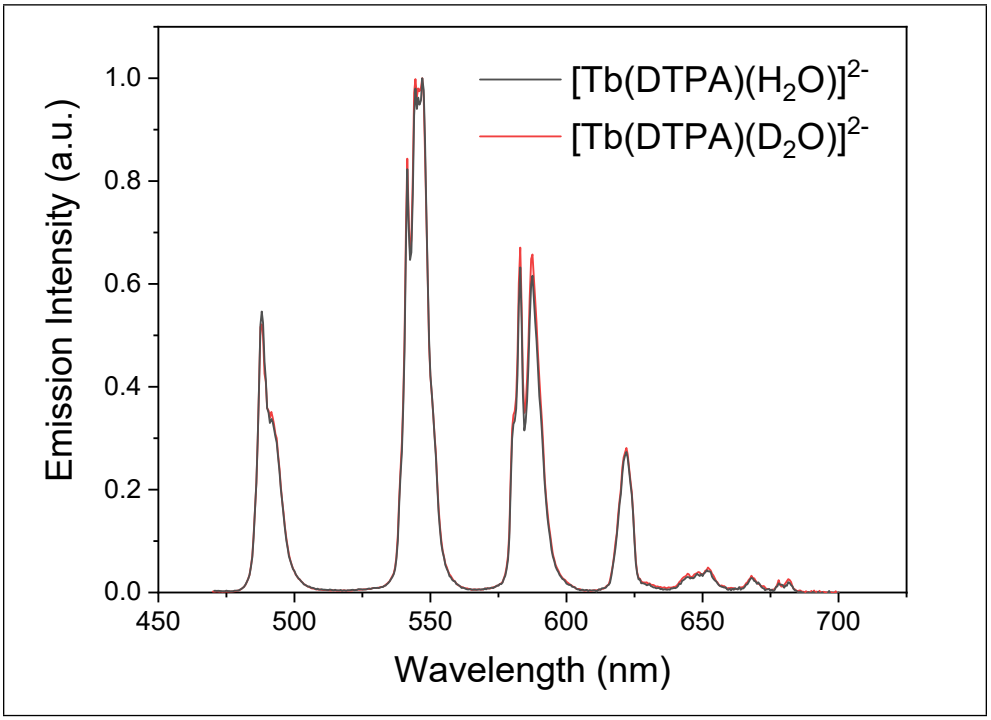

Figure S12. Normalized emission spectra of 0.05 M $[Tb(DTPA)(H_2O)]^{2-}$ in H_2O (black) and $[Tb(DTPA)(D_2O)]^{2-}$ in D_2O (red). Excitation wavelength at 372 nm. Emission and excitation slits were set at 5 nm and 1 nm respectively.

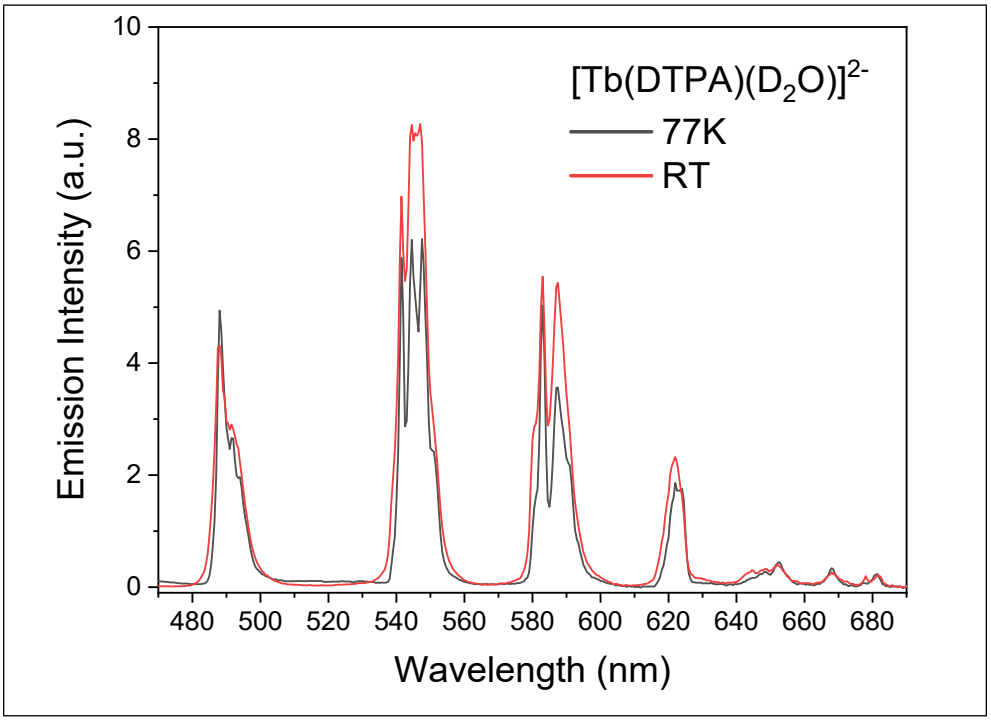

Figure S13. Emission spectra of 0.05 M $[Tb(DTPA)(D_2O)]^{2-}$ in D_2O at 77 K (black) and RT (red). Excitation wavelength at 372 nm. Emission and excitation slits were set at 5 nm and 1 nm respectively.

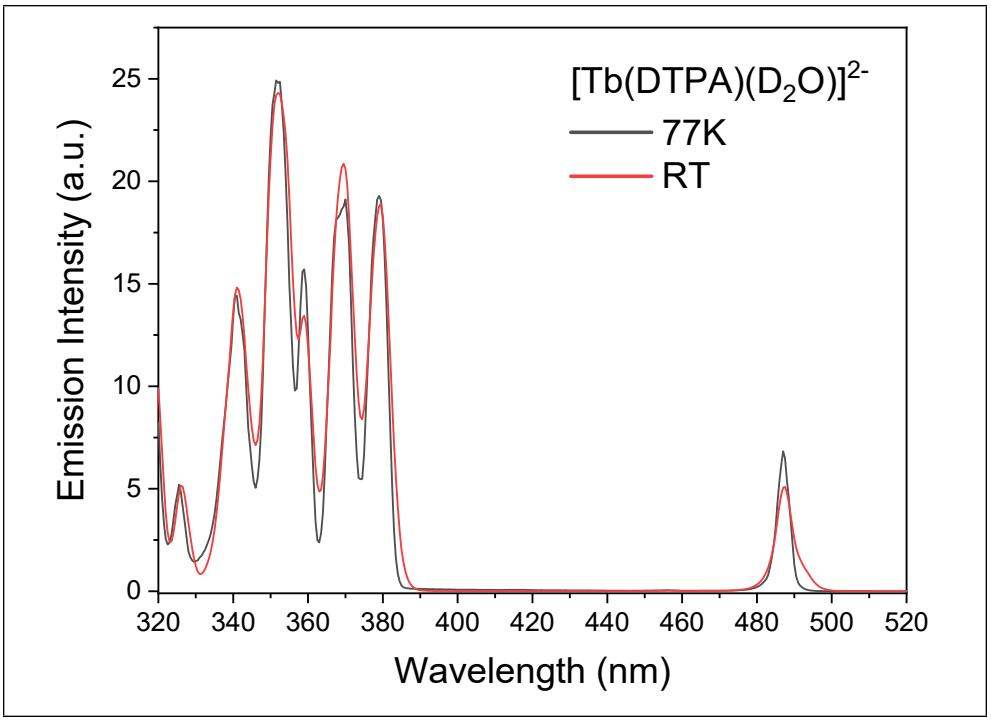

Figure S14. Excitation spectra of 0.05 M of $[Tb(DTPA)(D_2O)]^{2-}$ in D_2O at 77 K (black) and RT (red). Emission was measured at 545 nm. Emission and excitation slits were set at 3 nm and 3 nm respectively.

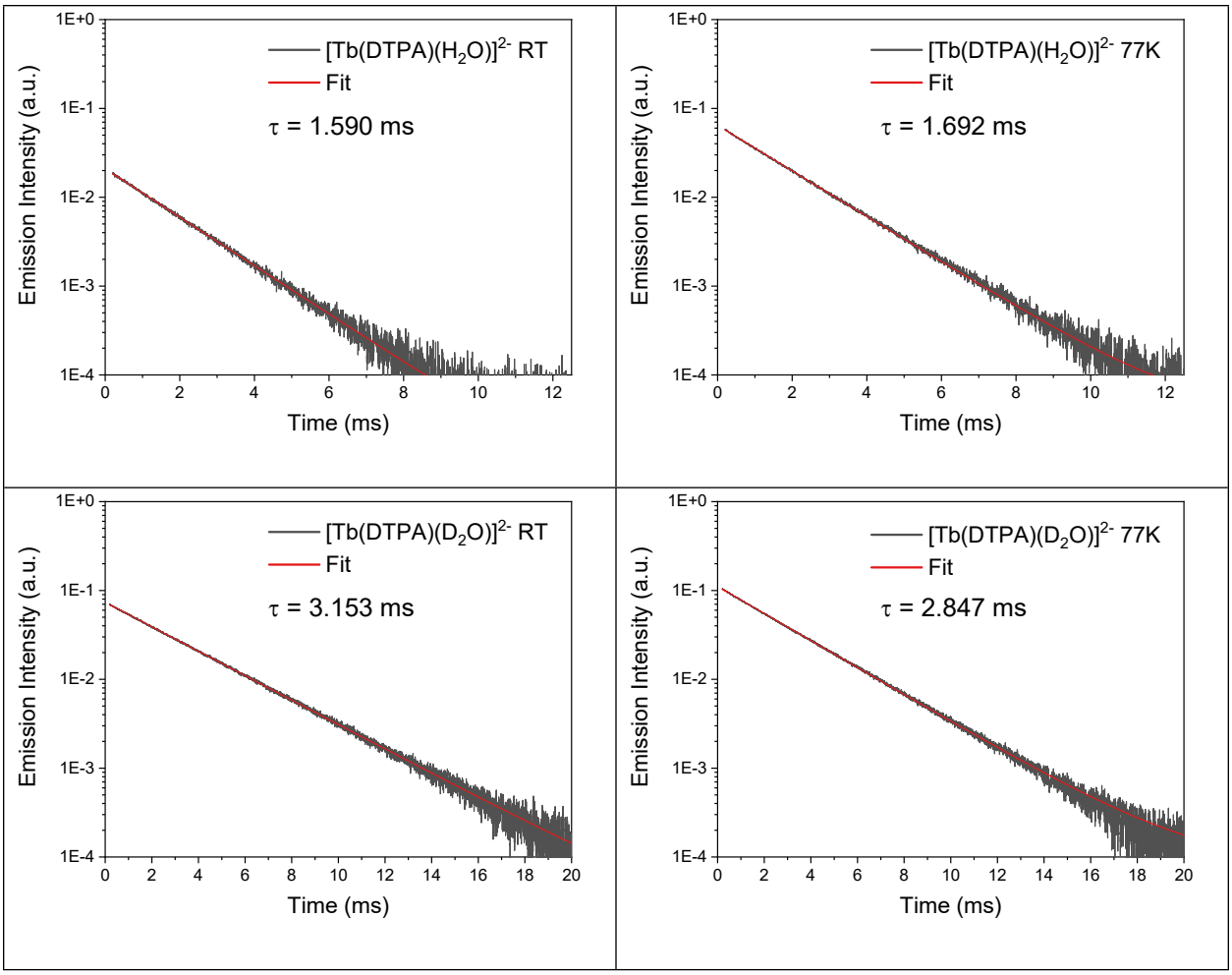

Figure S15. Emission decay traces of 0.05 M $[Tb(DTPA)(H_2O)]^{2-}$ in H_2O (top row) and 0.05 M $[Tb(DTPA)(D_2O)]^{2-}$ in D_2O (bottom row) at RT (left column) and 77 K (right column). The data was fitted with a mono-exponential function (red trace). Excitation was done at 372 nm and emission was measured at 488 nm. Both emission and excitation slits were kept at 5 nm.

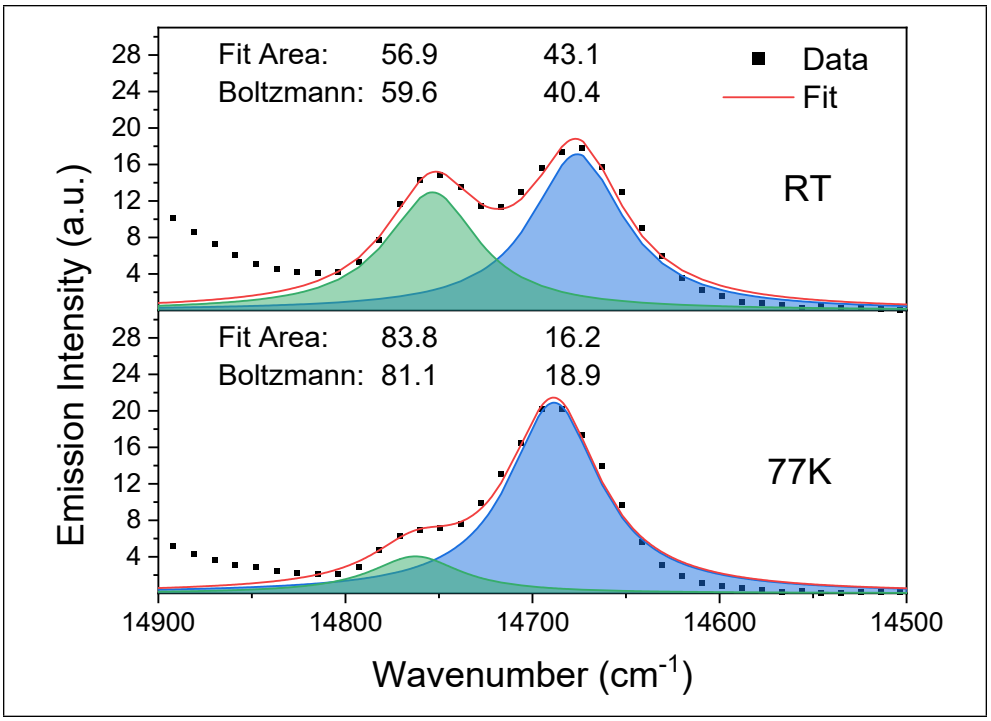

Figure S16. Emission spectra of the $^5D_4 \rightarrow {}^7F_0$ transition of $[Tb(DTPA)(H_2O)]^-$ in D_2O at RT (top) and 77 K (bottom). The area of the fitted peak as well as the calculated Boltzmann distribution for a two state system is given in the figure. Fit parameters are found in Table S3.

Table S3. Fit parameters for the emission spectra of the $^5D_4 \rightarrow {}^7F_0$ and $^7F_1$ peaks of 0.05 M $[Tb(DTPA)(H_2O)]^-$ in D_2O at 77 K and RT from Figure S15.

Peak # (77 K)	Peak Center (cm^{-1})	Peak Width[a] (cm^{-1})	Peak Area x10^5
Peak 1	14688 ± 1.1	59.1 ± 3.3	19.4 ± 0.86
Peak 2	14763 ± 6.0	59.1 ± 3.3	3.75 ± 0.60
Peak # (RT)	Peak Center (cm^{-1})	Peak Width[a] (cm^{-1})	Peak Area x10^5
Peak 1	14676 ± 1.0	59.8 ± 2.2	16.1 ± 0.46
Peak 2	14754 ± 1.3	59.8 ± 2.2	12.2 ± 0.41
[a] Shared parameter			

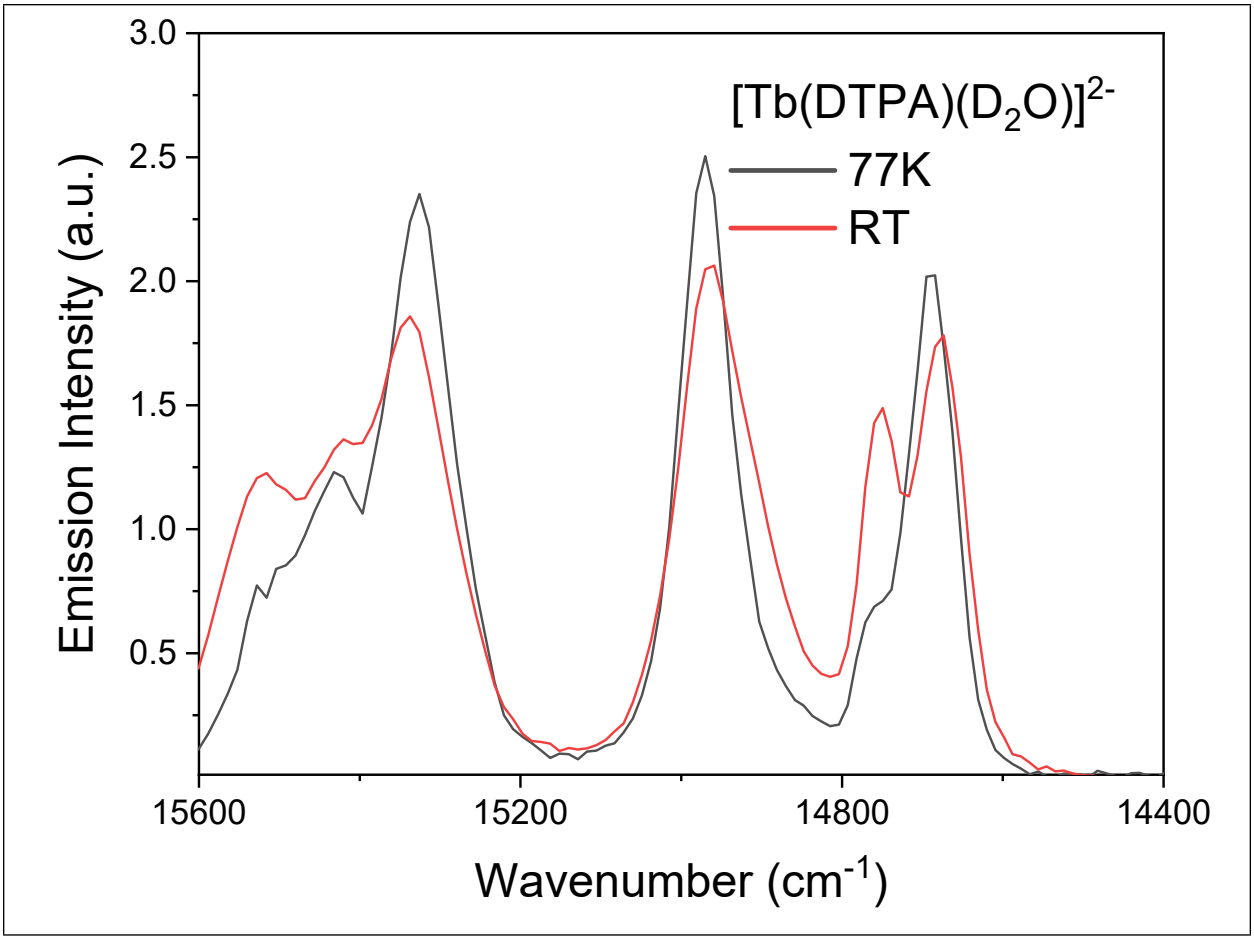

Figure S17. High-resolution spectra of the $^5D_4 \rightarrow {}^7F_{0\text{-}2}$ bands of $[Tb(DTPA)(H_2O)]^-$ in D_2O at 77 K (black) and RT (red).

[Tb(DOTA)(H$_2$O)]$^-$

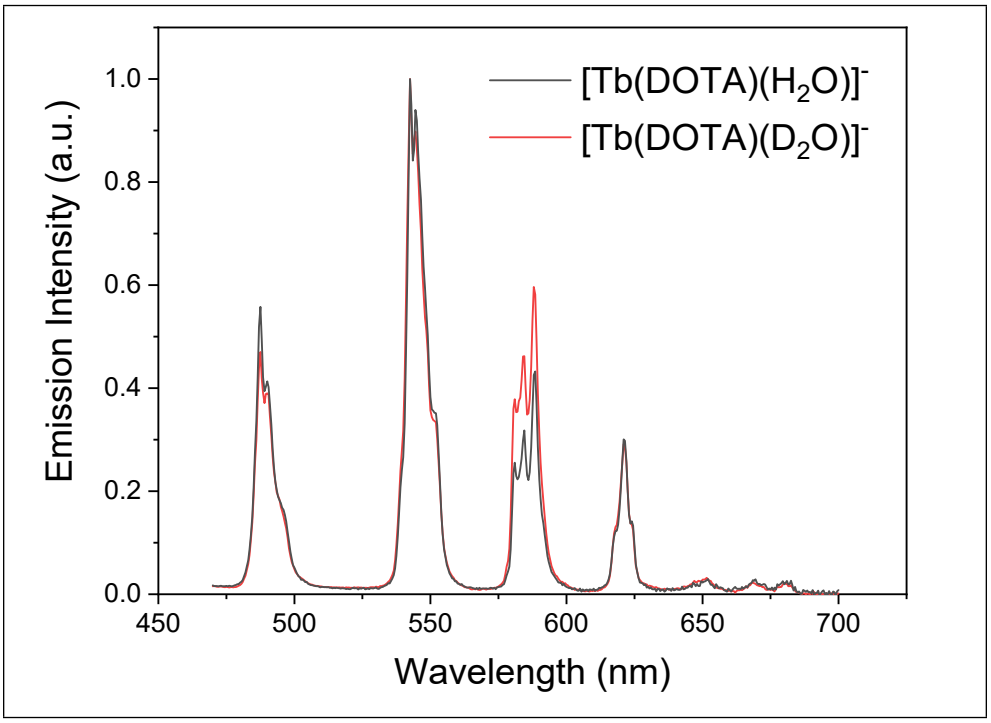

Figure S18. Normalized emission spectra of 0.05 M [Tb(DOTA)(H$_2$O)]$^-$ in H$_2$O (black) and [Tb(DOTA)(D$_2$O)]$^-$ in D$_2$O (red). Excitation wavelength at 372 nm. Emission and excitation slits were set at 8 and 1 nm respectively.

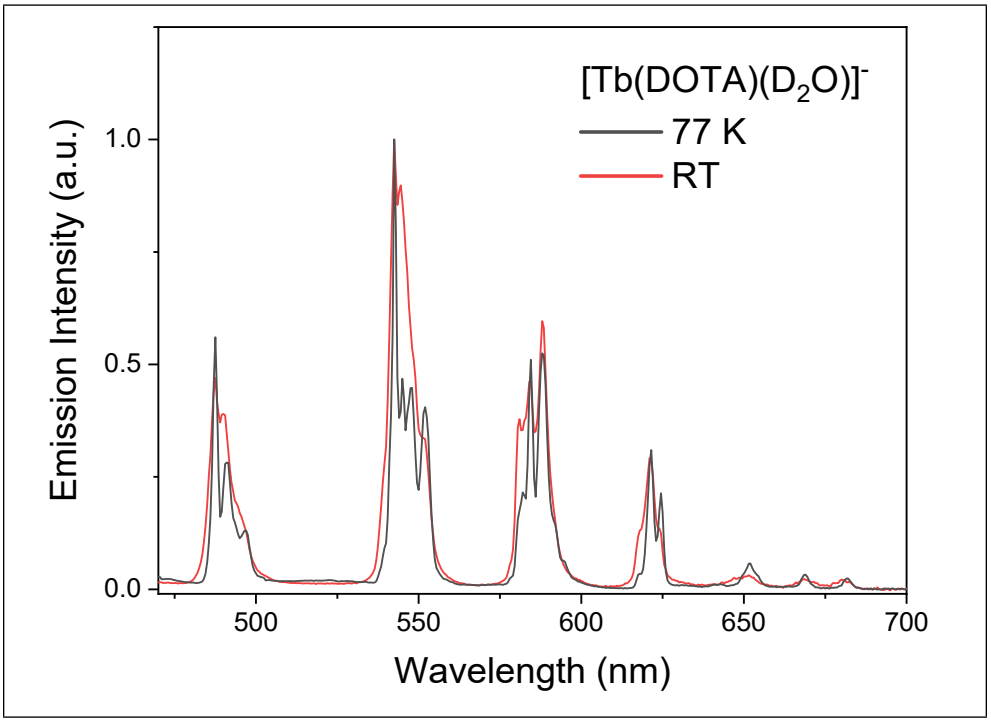

Figure S19. Emission spectra of 0.05 M [Tb(DOTA)(D$_2$O)]$^-$ in D$_2$O at 77 K (black) and RT (red). Excitation wavelength at 372 nm. Emission and excitation slits were set at 5 nm and 1 nm respectively.

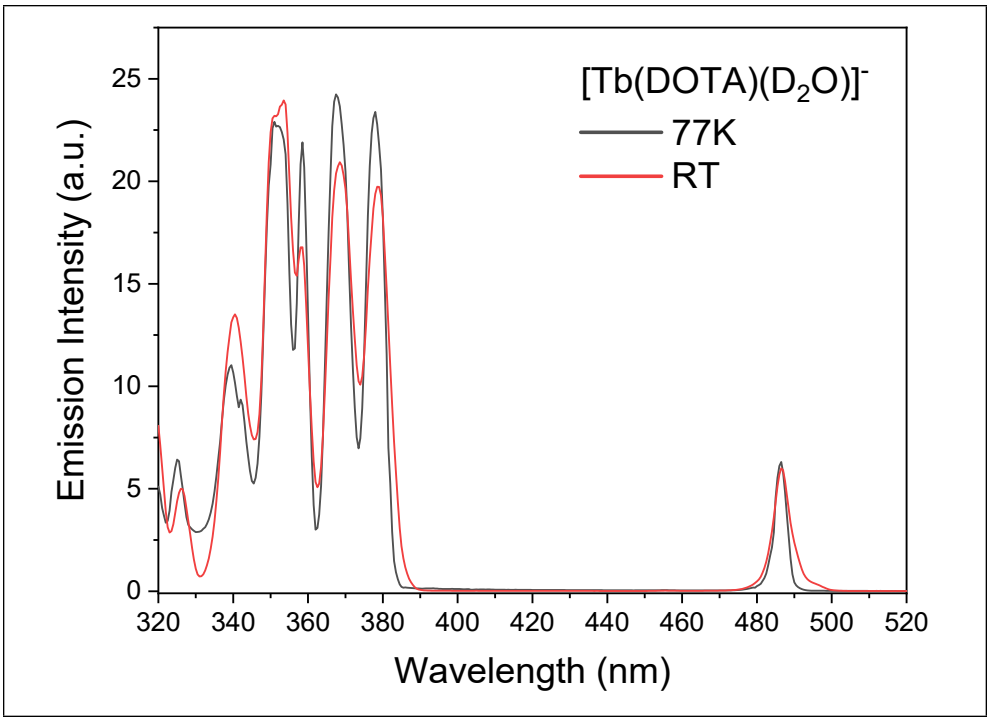

Figure S20. Excitation spectra of 0.05 M $[Tb(DOTA)(D_2O)]^-$ in D_2O at 77 K (black) and RT (red). Emission was measured at 545 nm. Emission and excitation slits were set at 5 nm and 3 nm respectively.

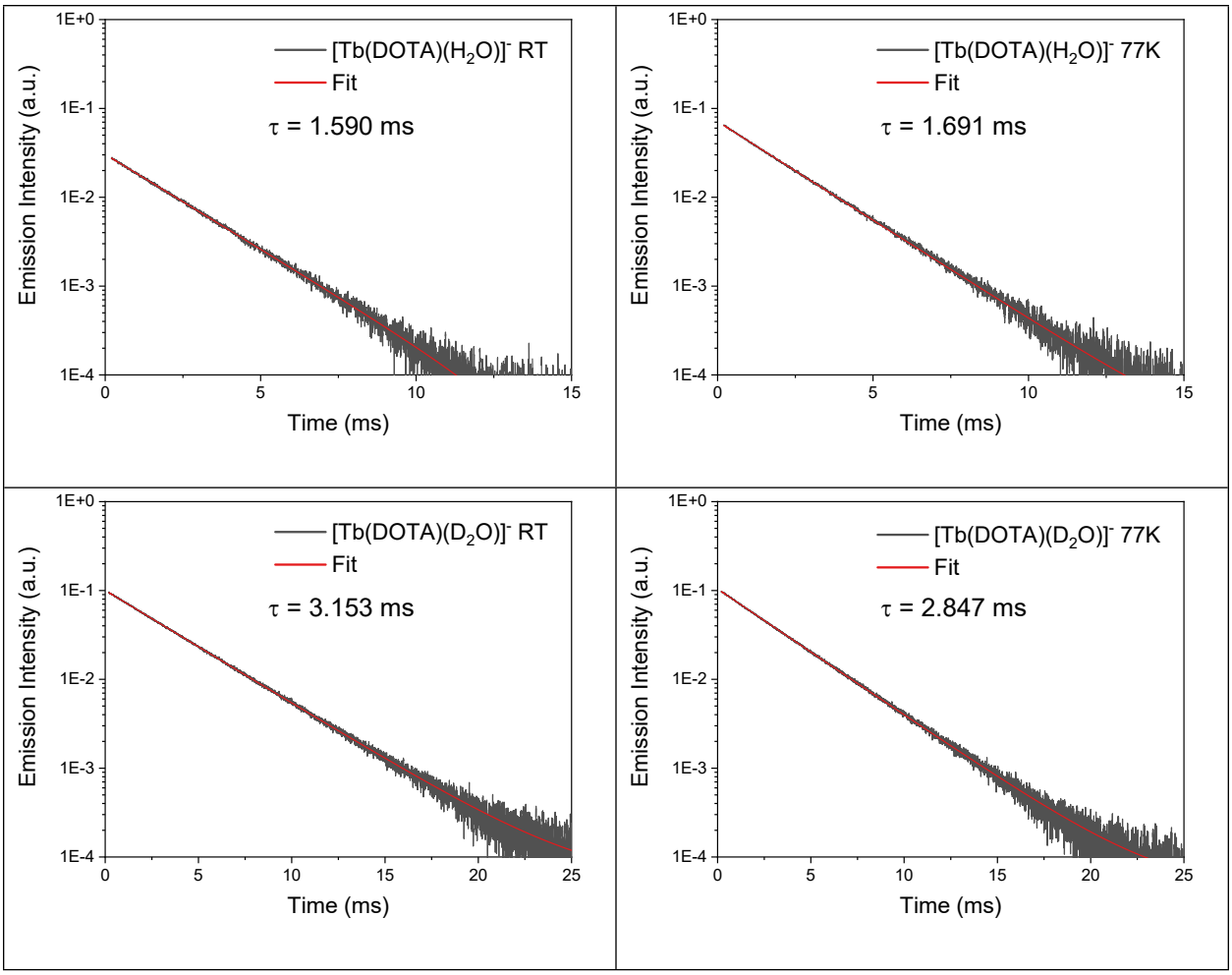

Figure S21. Emission decay traces of 0.05 M $[Tb(DOTA)(H_2O)]^-$ in H_2O (top row) and 0.05 M $[Tb(DOTA)(D_2O)]^-$ in D_2O (bottom row) at RT (left column) and 77 K (right column). The data was fitted with a mono-exponential function (red trace). Excitation was done at 372 nm and emission was measured at 488 nm. Both emission and excitation slits were kept at 5 nm.

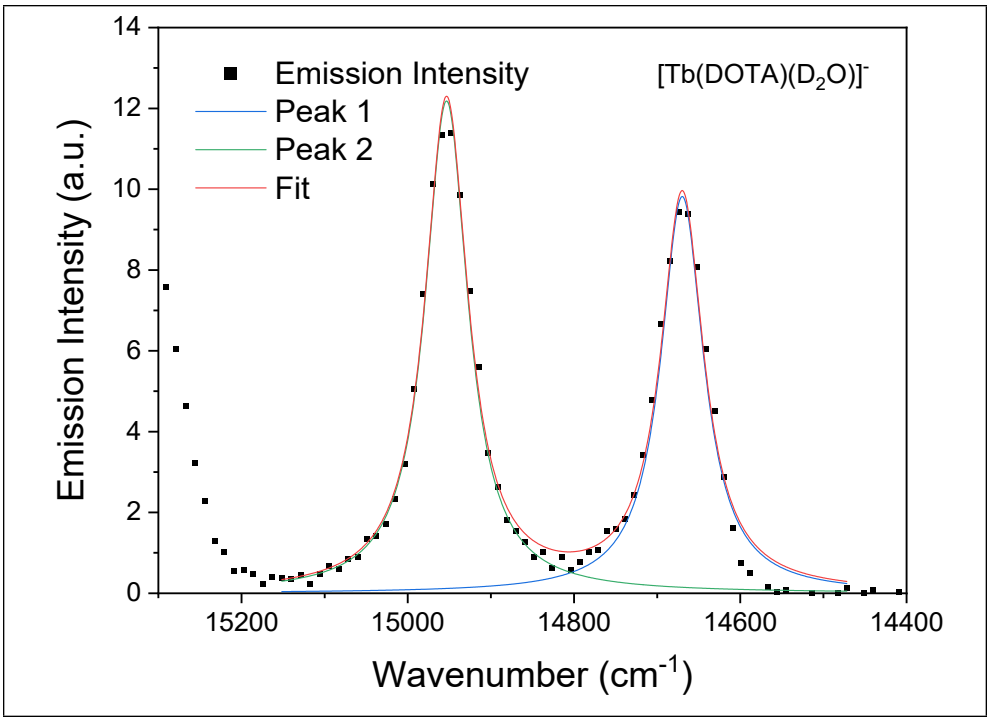

Figure S22. High resolution emission spectra of the $^5D_4 \rightarrow {}^7F_0$ (right) and $^7F_1$ peaks (left) of 0.05 M $[Tb(DOTA)(D_2O)]^-$ in D_2O at 77 K. Excitation was done at 372 nm. Excitation and emission slits were kept at 8 nm and 2 nm respectively. The data was fitted with 2 Lorentzian peaks. Fit parameters are given in Table S4.

Table S4. Fit parameters for the emission spectra of the $^5D_4 \rightarrow {}^7F_0$ and $^7F_1$ peaks of 0.05 M $[Tb(EDTA)(D_2O)_3]^-$ in D_2O at 77 K, from Figure S20.

Peak #	Peak Center (cm^{-1})	Peak Width[a] (cm^{-1})	Peak Area x10^5
Peak 1	14670 ± 0.9	62.8 ± 1.6	9.68 ± 0.23
Peak 2	14953 ± 0.8	62.8 ± 1.6	12.0 ± 0.25
[a] Shared parameter			

Comparisons

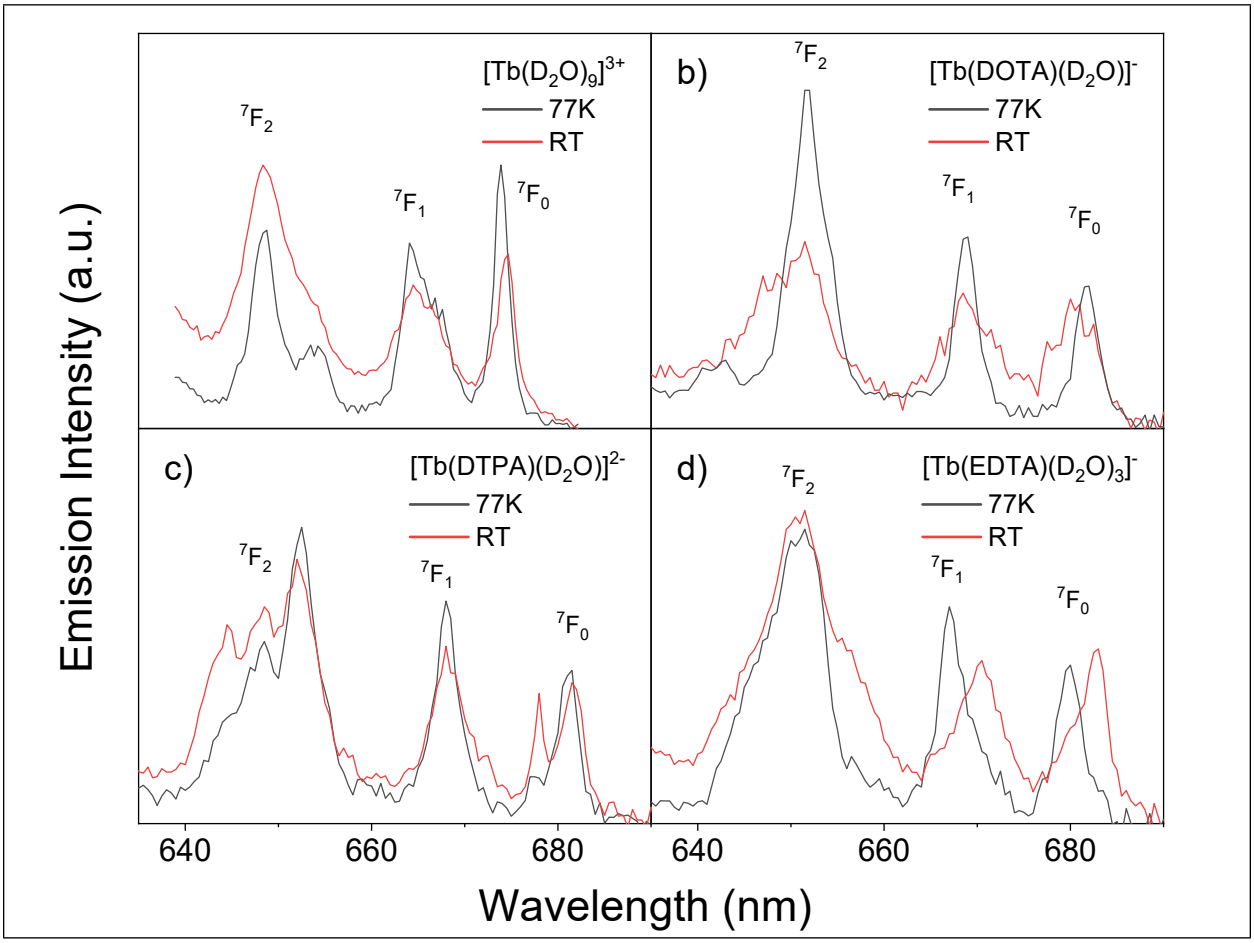

Figure S23. Emission spectra of the $^5D_4 \rightarrow {}^7F_{2\text{-}0}$ transitions of $[Tb(H_2O)_9]^{3+}$ (top left), $[Tb(DOTA)(H_2O)]^-$ (top right), $[Tb(DTPA)(H_2O)]^{2-}$ (bottom left) and $[Tb(EDTA)(H_2O)_3]^-$ (bottom right) measured in D_2O at 77 K (black) and RT (red).