Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics
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Supporting Information

Luminescence and Upconversion from Thulium (III) Species in Solution

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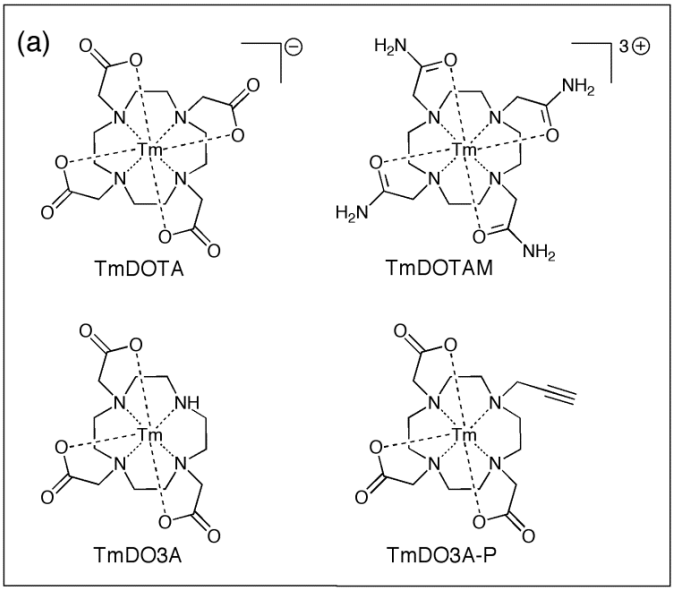

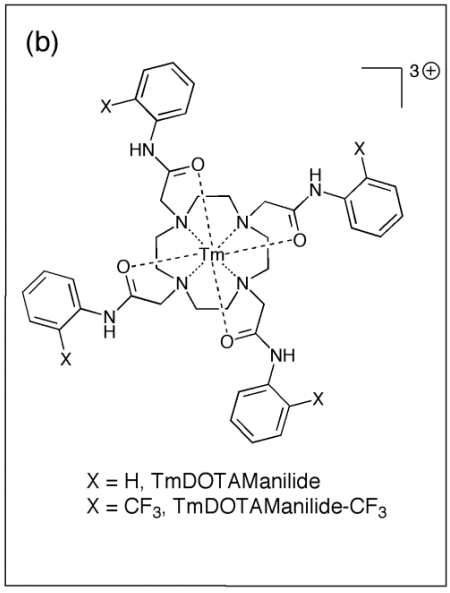

2. Absorption Spectra

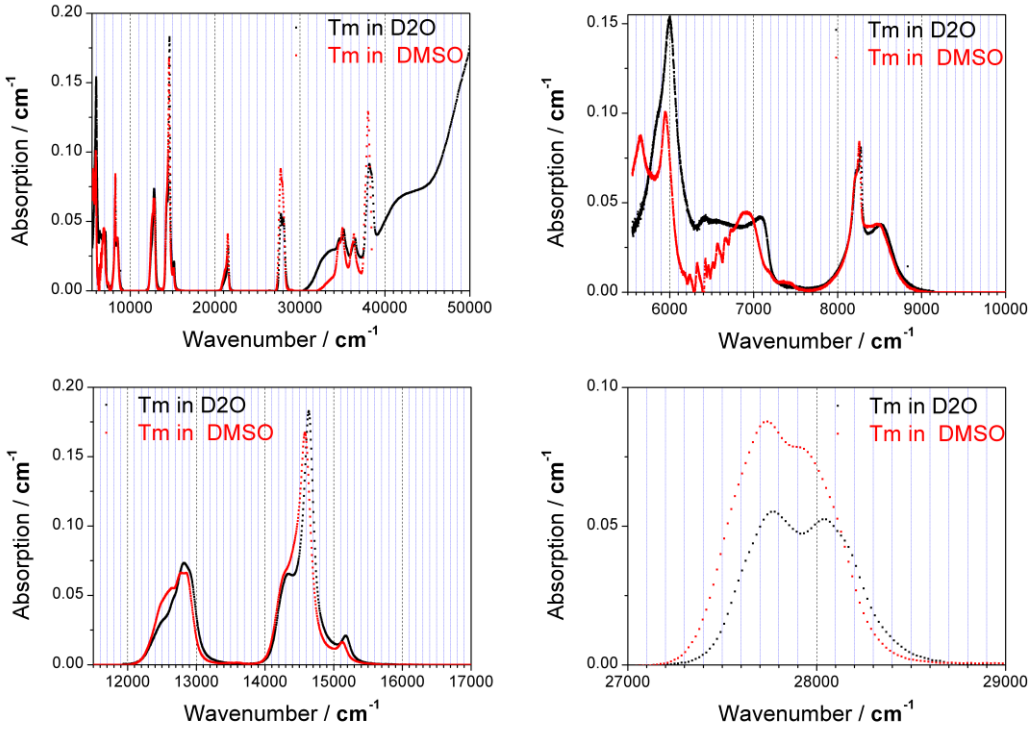

Figure S1. Absorption spectra of thulium trifluoromethanesulfonate ($Tm(OTf)_3$) (tin D_2O (black) and d_6-DMSO (red) showing the full spectrum (top left) and expanded regions. The feature at ca. 7000 cm^{-1} is associated with trifluoromethanesulfonate.

3. Time-Correlated Single Photon Counting (TCSPC) traces and fits

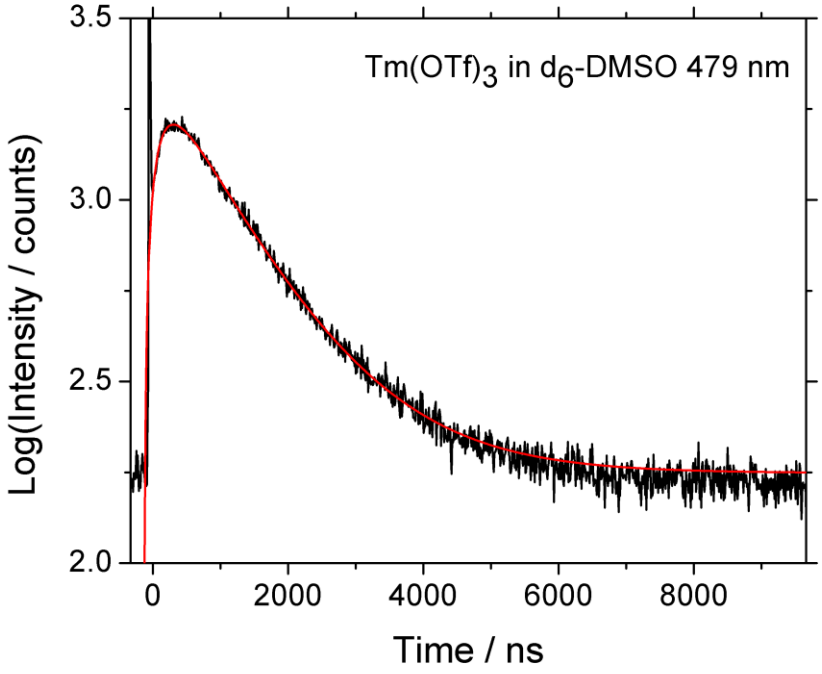

Figure S2. TCSPC trace of $Tm(OTf)_3$ in d_6-DMSO recorded at 479 nm with 364 nm excitation showing negative time delays.

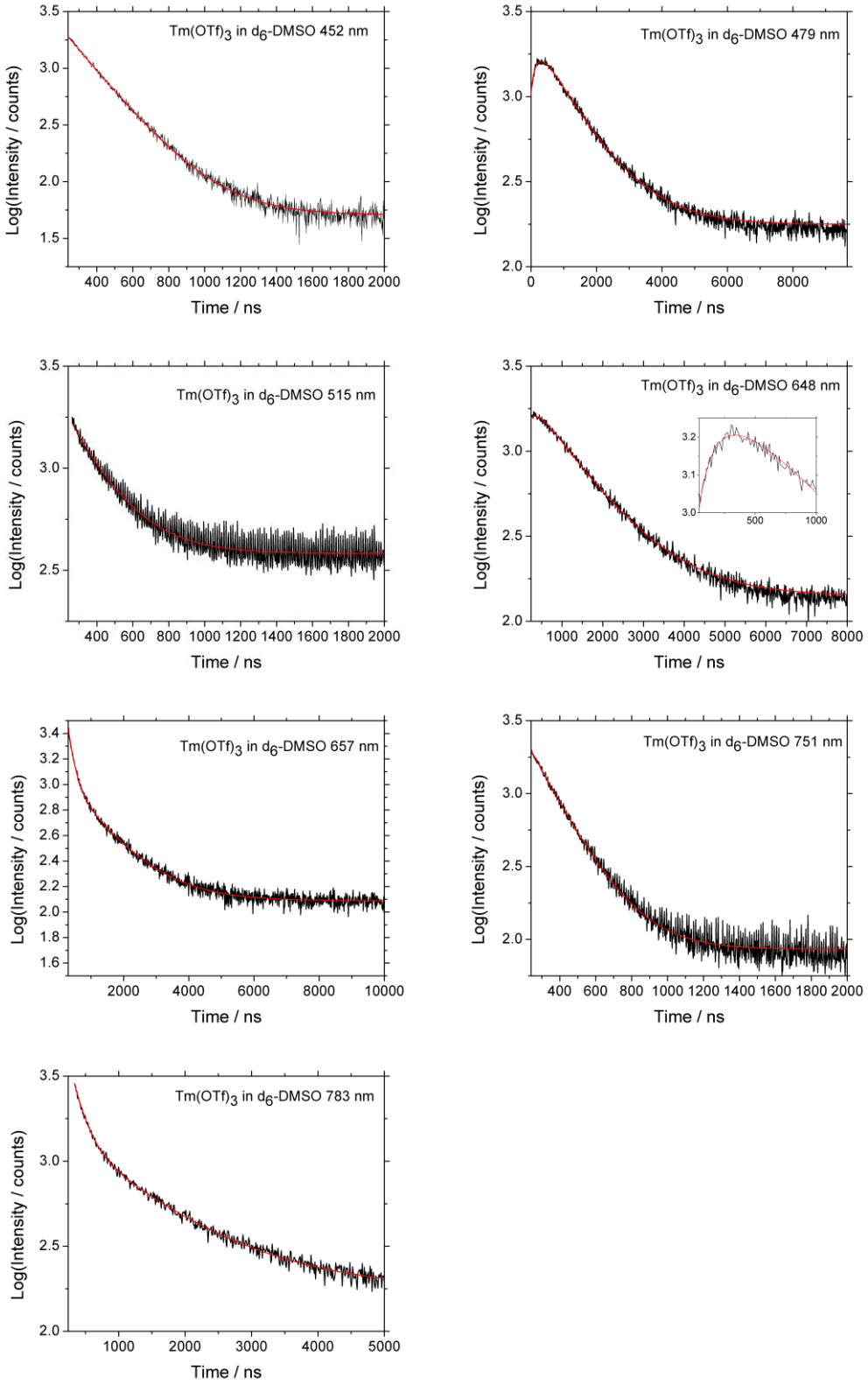

Figure S3: Black line: TCSPC traces of $Tm(OTf)_3$ in d_6-DMSO with 364 nm excitation. Red line: The fit of the data resulting from a tail fit for emission at 452, 515, 657, 751 and 783 nm, and a reconvolution fit for the rise and decay behaviour at 479 and 648 nm.

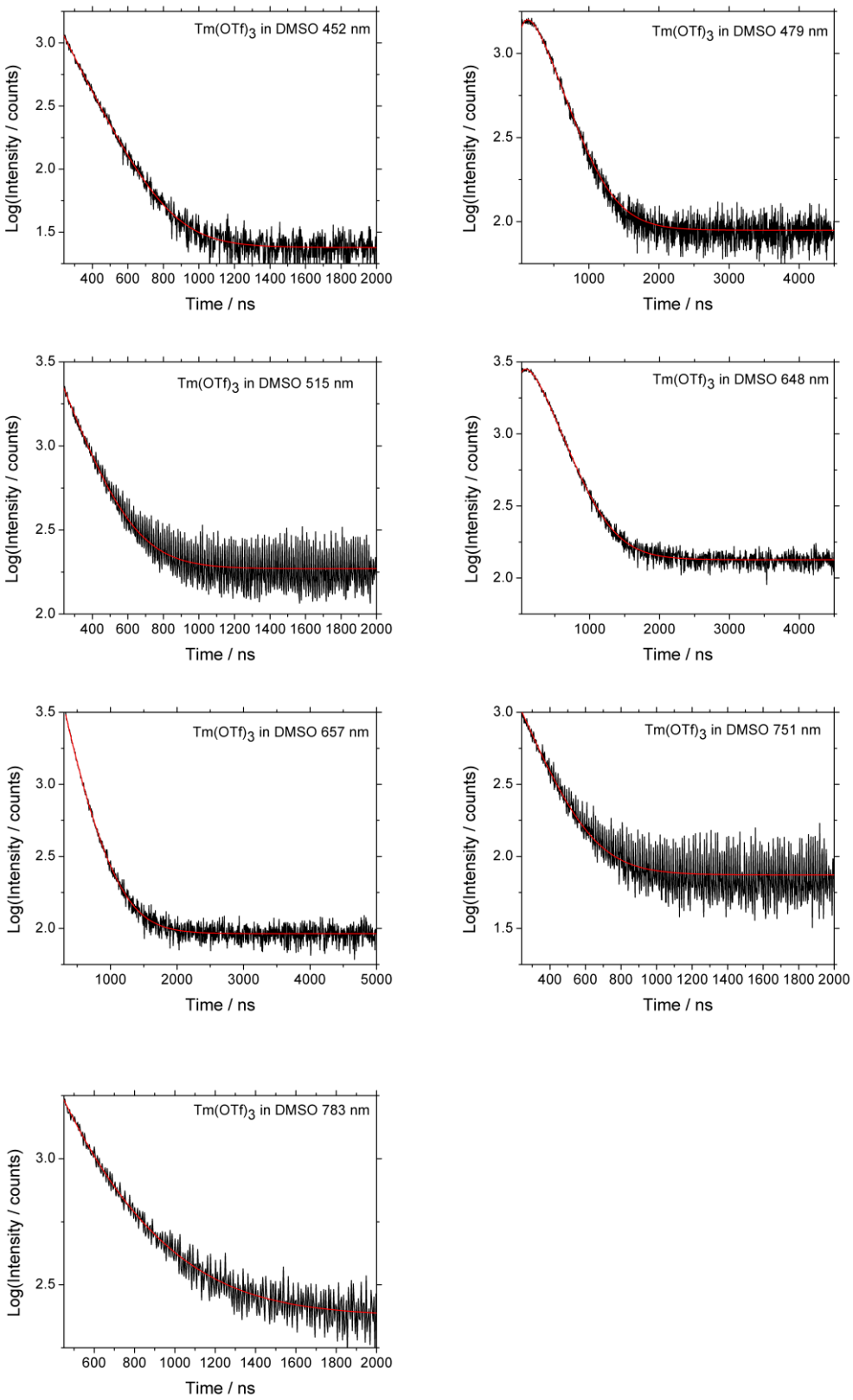

Figure S4: Black line: TCSPC traces of $Tm(OTf)_3$ in DMSO with 364 nm excitation. Red line: The fit of the data resulting from a tail fit for emission at 452, 515, 657, 751 and 783 nm, and a reconvolution fit for the rise and decay behaviour at 479 and 648 nm.

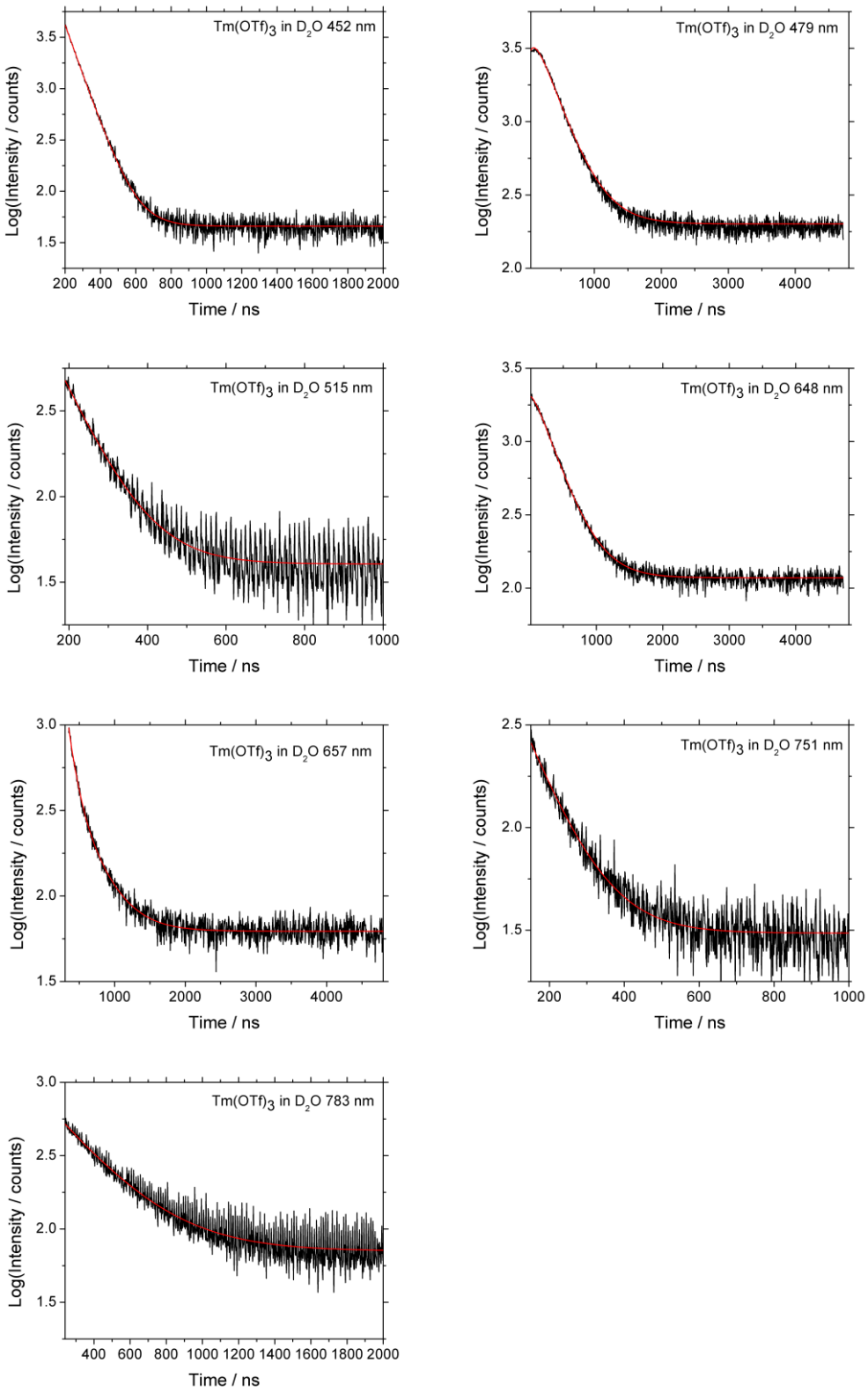

Figure S5: Black line: TCSPC traces of $Tm(OTf)_3$ in D_2O with 364 nm excitation. Red line: The fit of the data resulting from a tail fit for emission at 452, 515, 657, 751 and 783 nm, and a reconvolution fit for the rise and decay behaviour at 479 and 648 nm.

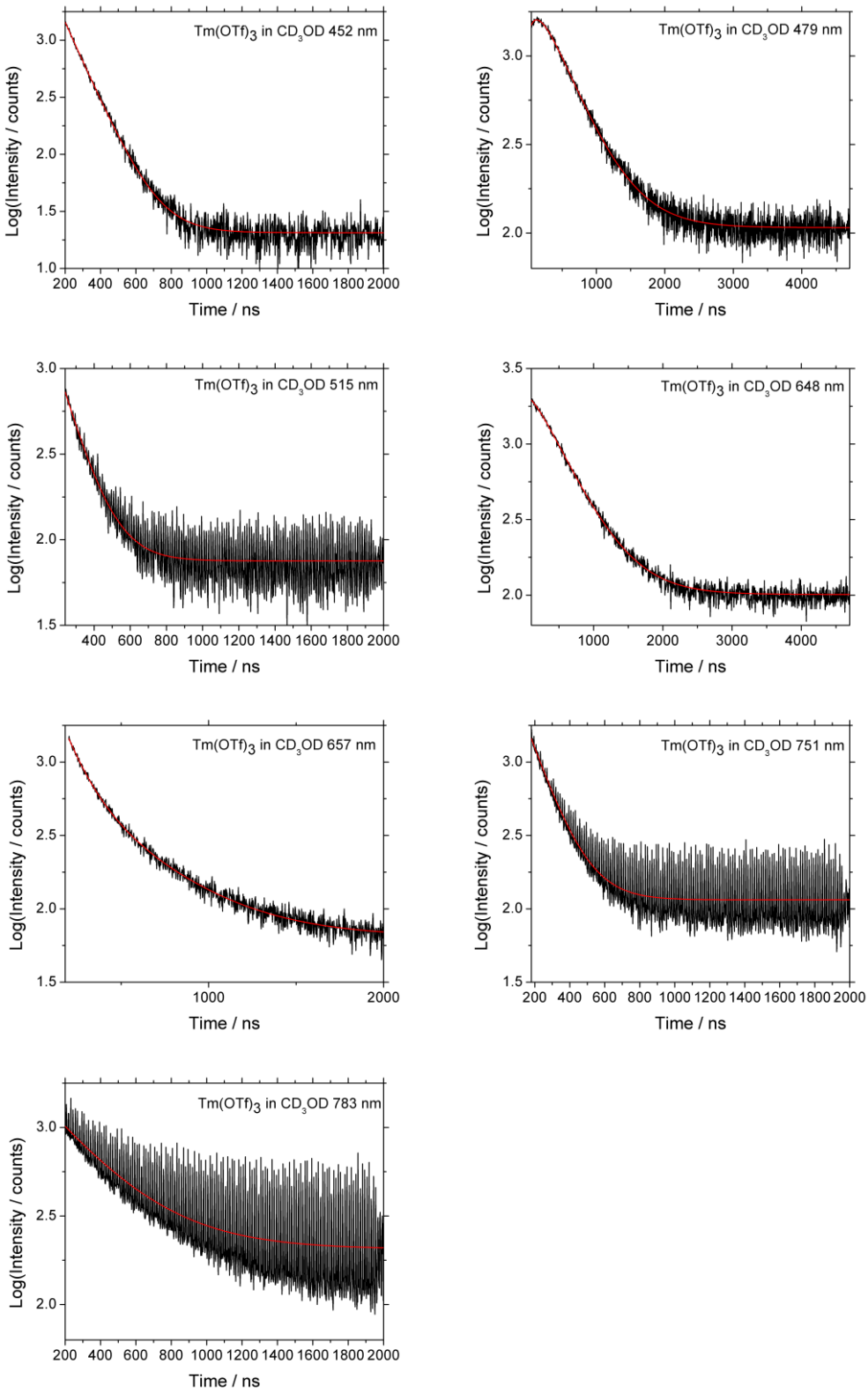

Figure S6: Black line: TCSPC traces of $Tm(OTf)_3$ in CD_3OD with 364 nm excitation. Red line: The fit of the data resulting from a tail fit for emission at 452, 515, 657, 751 and 783 nm, and a deconvolution fit for the rise and decay behaviour at 479 and 648 nm.

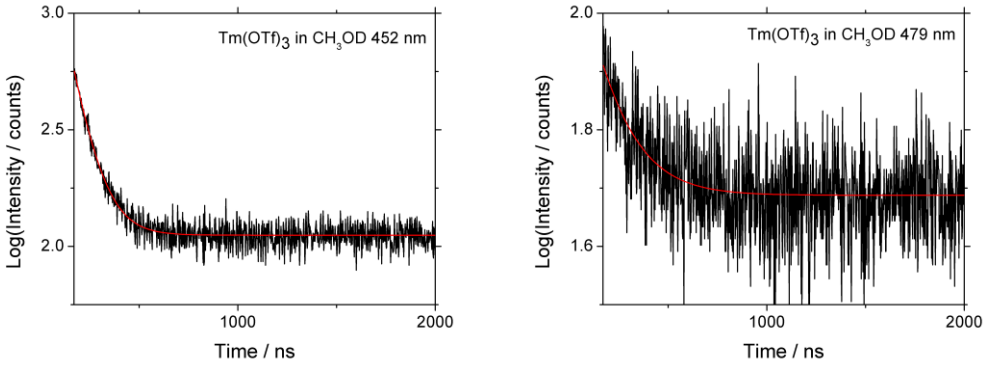

Figure S7: Black line: TCSPC traces of $Tm(OTf)_3$ in CH_3OD with 364 nm excitation. Red line: The fit of the data resulting from a tail fit for emission at 452 nm, and a reconvolution fit for the rise and decay behaviour at 479 nm.

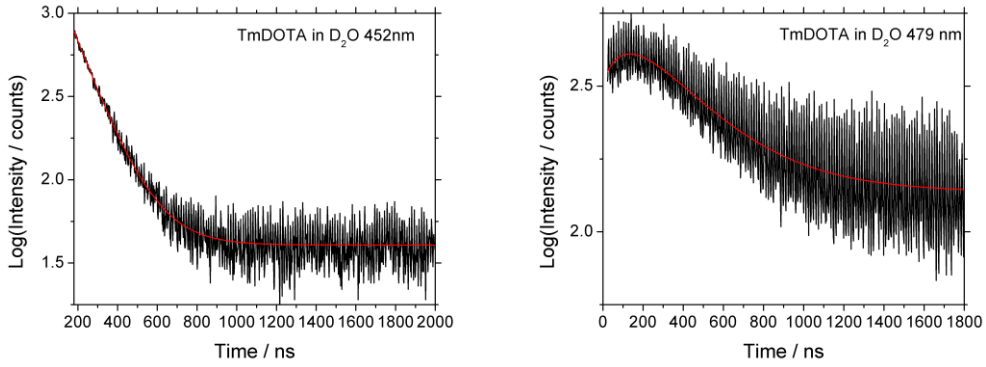

Figure S8: Black line: TCSPC traces of $[Tm.DOTA]^-$ in D_2O with 364 nm excitation. Red line: The fit of the data resulting from a tail fit for emission at 452 nm, and a reconvolution fit for the rise and decay behaviour at 479 nm.

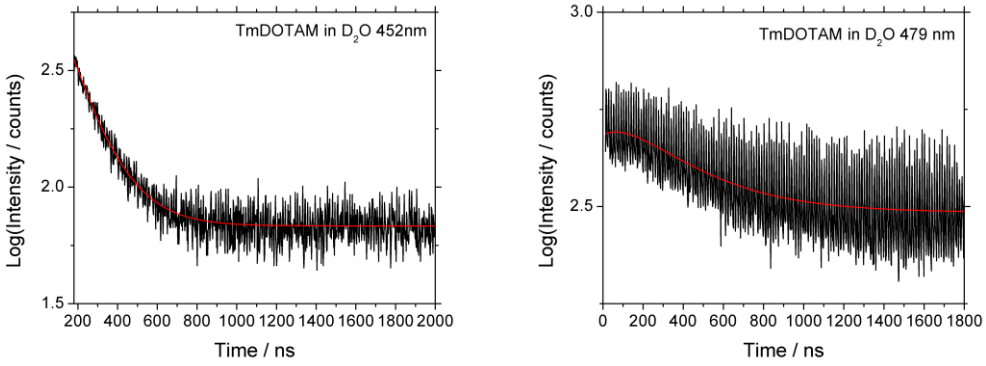

Figure S9: Black line: TCSPC traces of $[Tm.DOTAM]^{3+}$ in D_2O with 364 nm excitation. Red line: The fit of the data resulting from a tail fit for emission at 452 nm, and a reconvolution fit for the rise and decay behaviour at 479 nm.

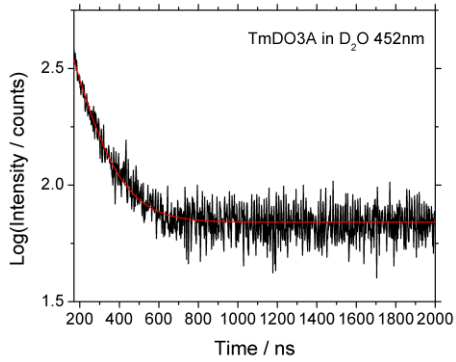

Figure S10: Black line: TCSPC trace of [Tm.DO3A] in D_2O with 364 nm excitation. Red line: The fit of the data resulting from a tail fit for emission at 452 nm.

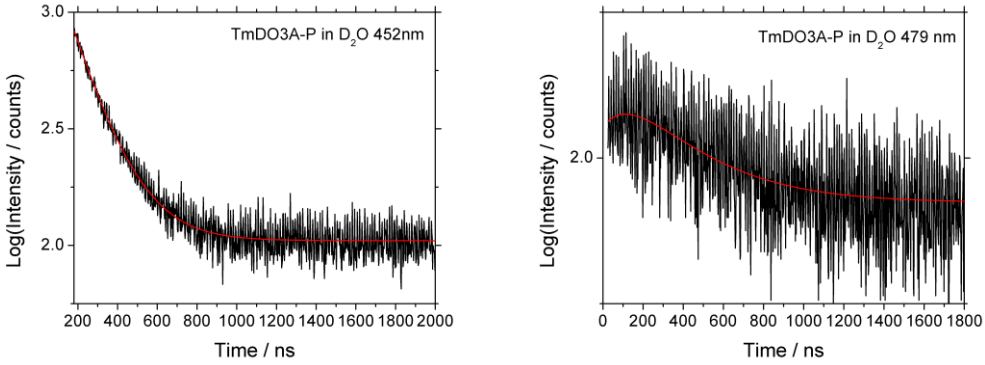

Figure S11: Black line: TCSPC traces of [TmDO3A-P] in D_2O with 364 nm excitation. Red line: The fit of the data resulting from a tail fit for emission at 452 nm, and a reconvolution fit for the rise and decay behaviour at 479 nm.

4. Emission Spectra

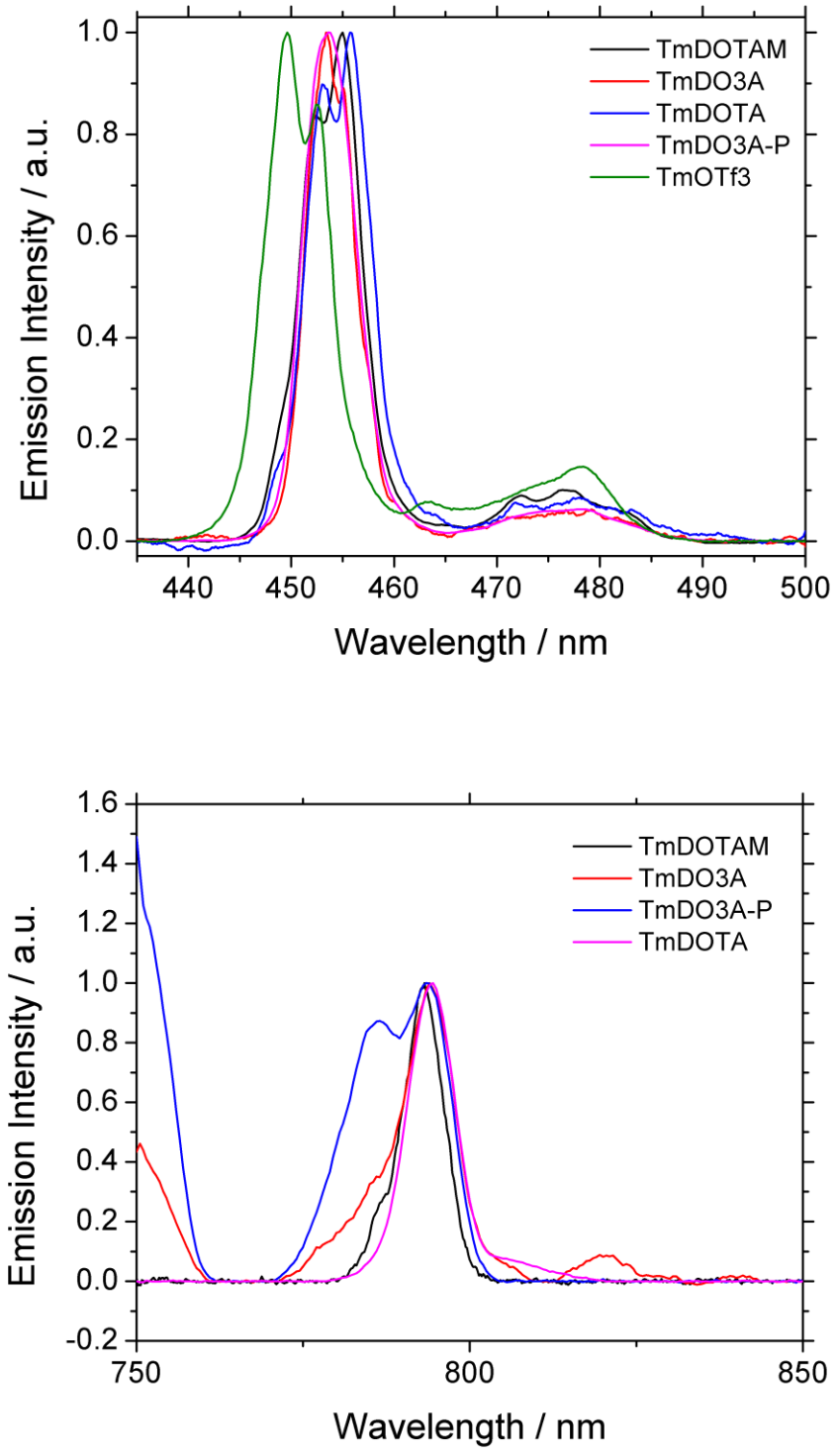

Figure S12: Overlaid emission spectra of $Tm(OTf)_3$, TmDOTAM, TmDO3A, TmDO3A-P and TmDOTA in D_2O upon excitation at 360 nm.

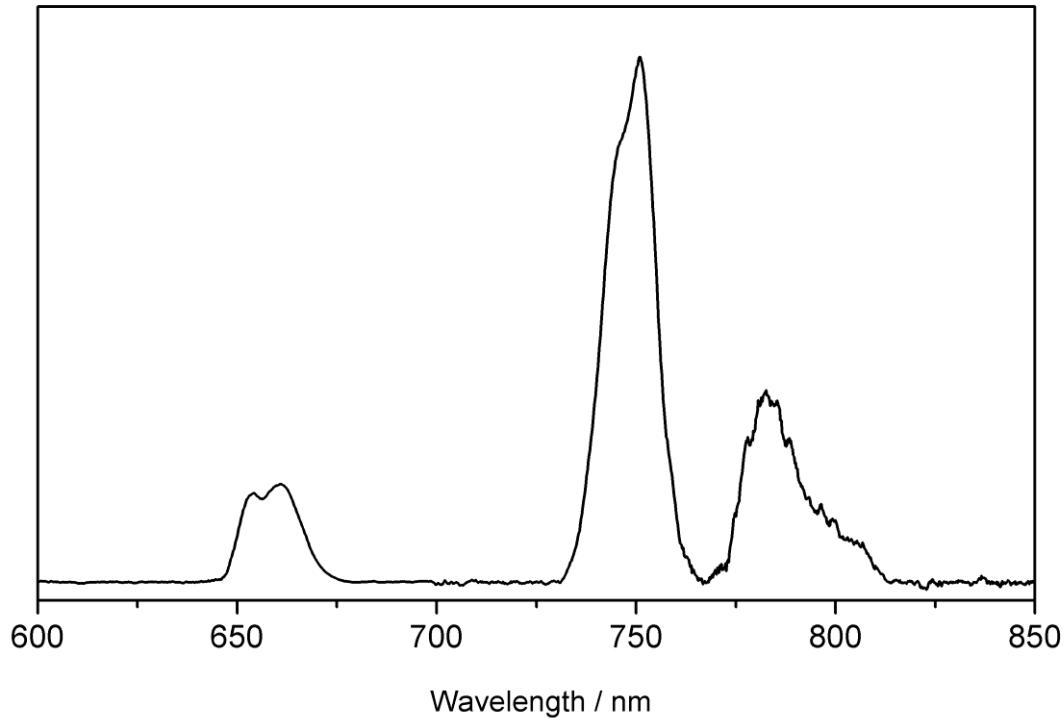

Figure S13: Emission from $^1D_2$, of $Tm(OTf)_3$ in d_6-DMSO, obtained by subtraction of the emission spectrum on 465 nm excitation from the spectrum on 360 nm excitation.

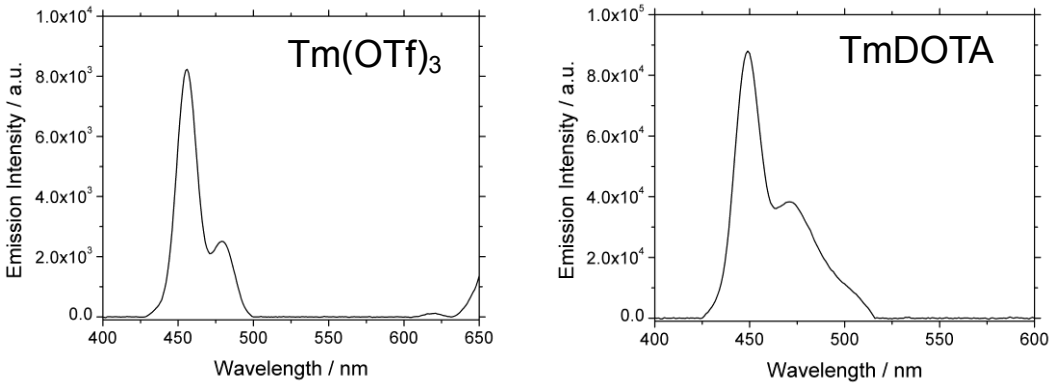

Figure S14. Two photon emission spectra, exciting into $^1D_2$ at 728 nm, of $Tm(OTf)_3$ in d_6-DMSO and $[Tm.DOTA]^-$ in D_2O.