Supporting Information

Luminescence and Upconversion from
Thulium (III) Species in Solution

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Contents

1. Structures of complexes

2. Absorption Spectra

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

4. Emission Spectra

1. Structures of complexes

![Chemical structures](image)

(a) TmDOTA
(b) TmDOTAM
TmDO3A
TmDO3A-P

X = H, TmDOTAMnile
X = CF₃, TmDOTAMnile-CF₃
2. Absorption Spectra

Figure S1. Absorption spectra of thulium trifluoromethanesulfonate (Tm(OTf)₃) (in D₂O (black) and d₆-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$_2$O 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$_3$OD 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$_3$OD 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$_2$O 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$_2$O 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.D03A] in D$_2$O 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 [Tm.D03A-P] in D$_2$O 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$_2$O 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$_2$O.