

Photophysical properties of asymmetric and water-soluble dinuclear lanthanide complexes of poly glycol chain functionalized-benzoic acid derivative: Experimental and theoretical approaches

G. Z. Bosshard^a, G. A. Brito^a, J. H. S. K. Monteiro^b, A. de Bettencourt-Dias^b, I. O. Mazali^a, F. A. Sigoli^a

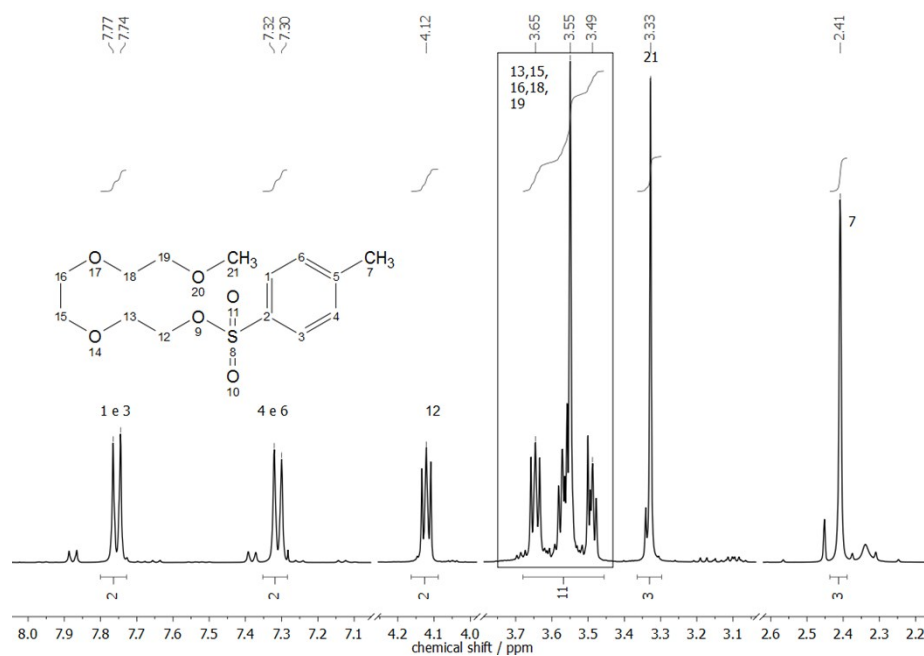
^a Laboratory of Functinal Materials, Institute of Chemistry, Unicamp, Campinas -SP, Brazil.

^b Department of Chemistry, University of Nevada, Reno-NV, USA.

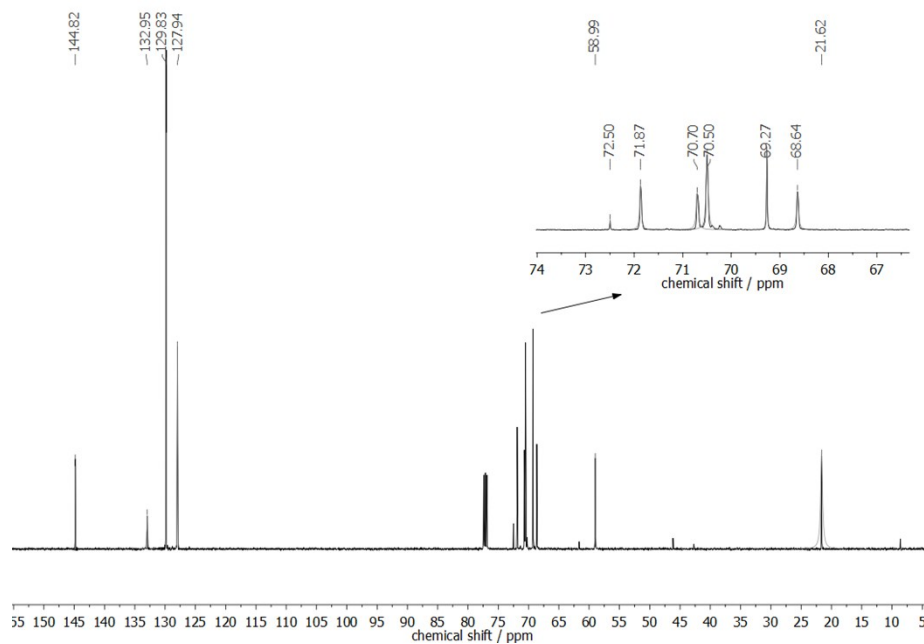
Table of contents

1. ¹ H and ¹³ C-NMR.....	2
2. Mass spectra	5
3. Fit of the emission lifetime decay curve	7
4. TGA	8
5. Phosphorescence emission time resolved spectra	8
6. Emission decay curves	9
7. Time resolved emission spectrum of solid [Eu ₂ (mee) ₆ (H ₂ O) ₂]	12

1. ^1H and ^{13}C -NMR



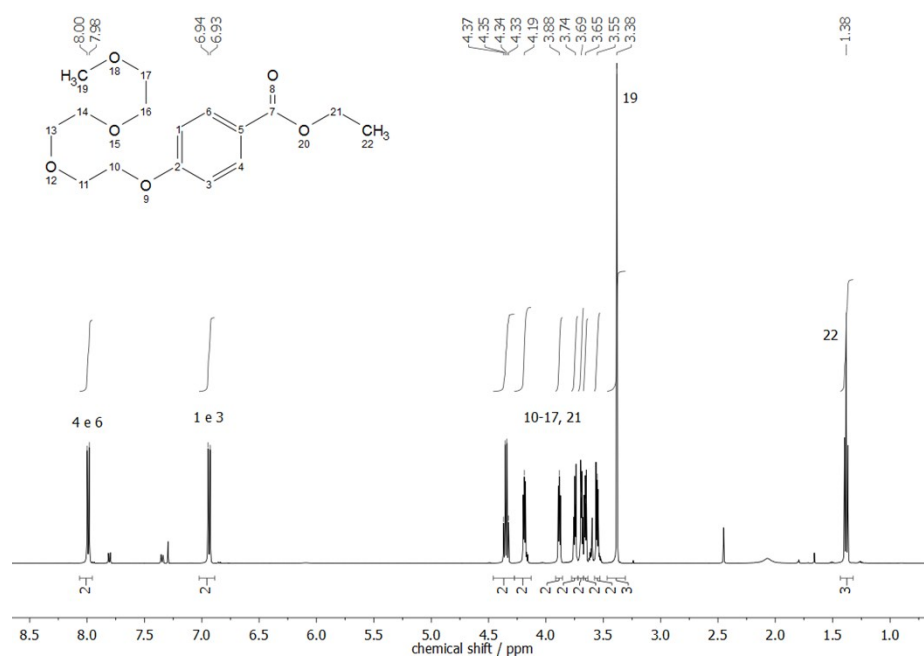
(a)



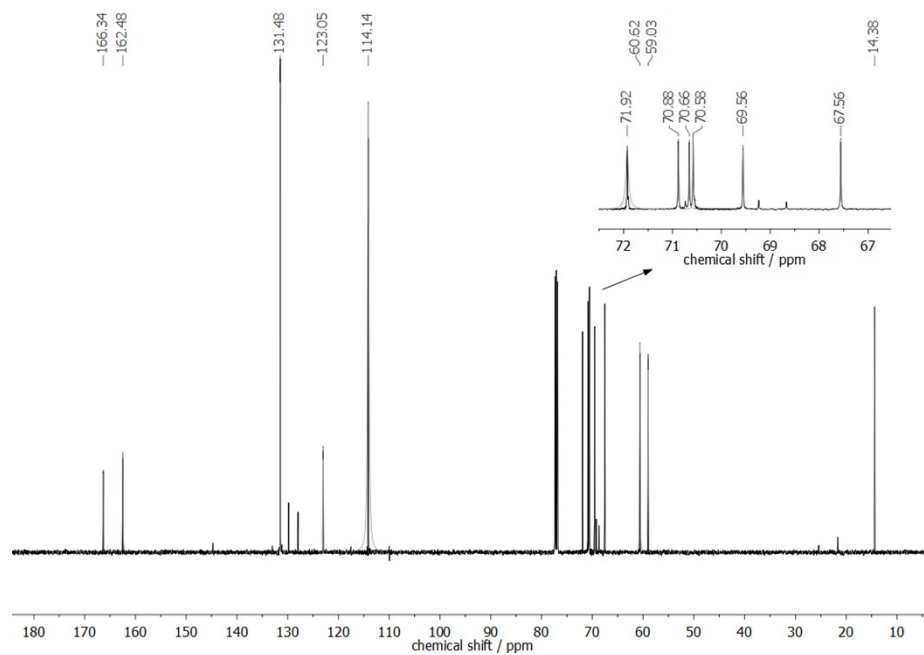
(b)

Figure S1. ^1H and ^{13}C -NMR spectra of 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (**1**).

(a) ^1H -NMR. (b) ^{13}C -NMR.

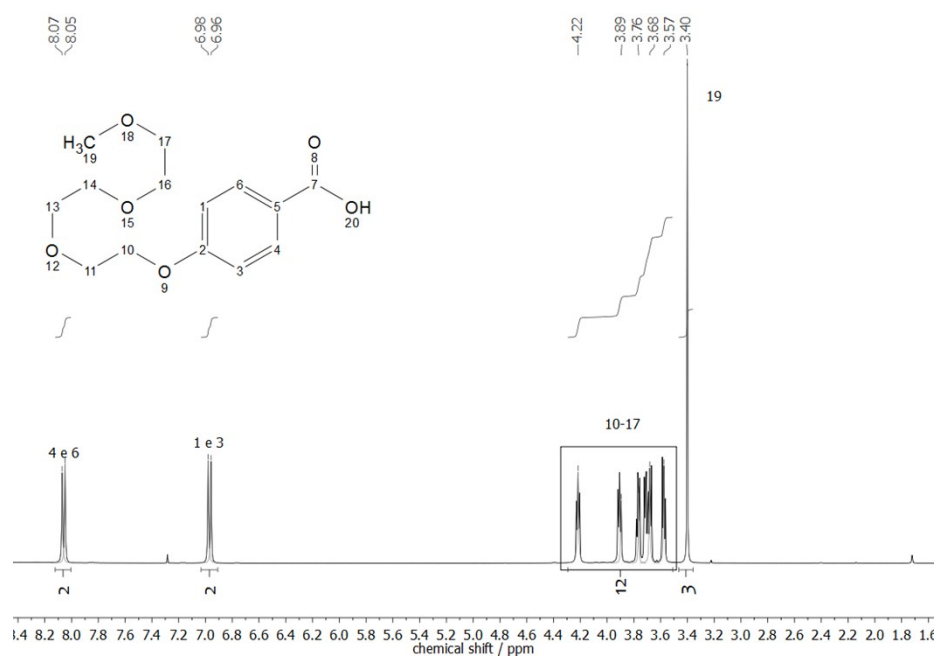


(a)

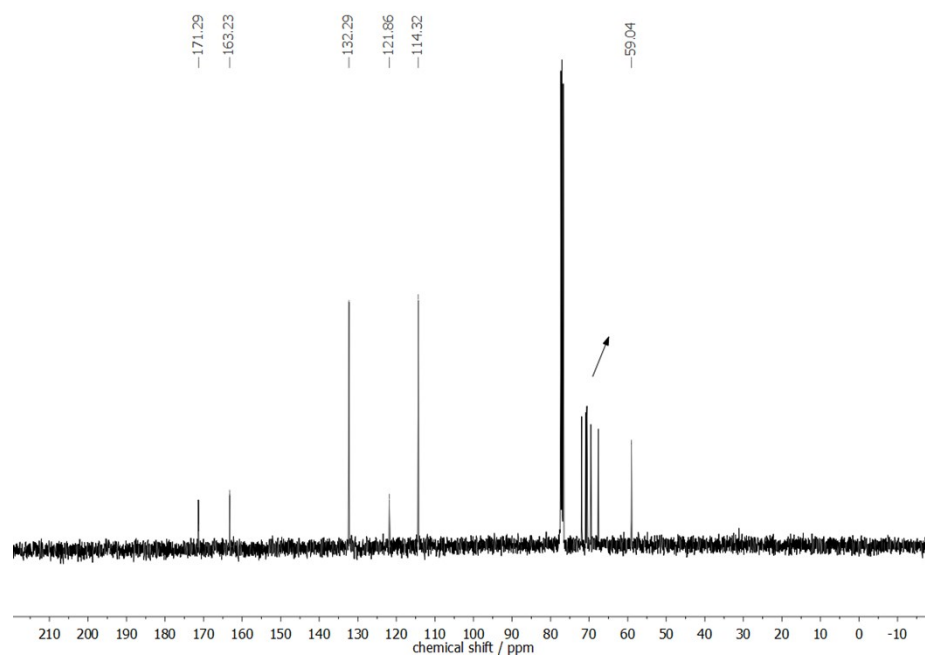


(b)

Figure S2. ^1H and ^{13}C -NMR spectra of methyl 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoate (**2**). (a) ^1H -NMR. (b) ^{13}C -NMR.



(a)



(b)

Figure S3. ^1H and ^{13}C -NMR spectra of 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoic acid (**Hmee**). (a) ^1H -NMR. (b) ^{13}C -NMR.

2. High Resolution Mass Spectroscopy

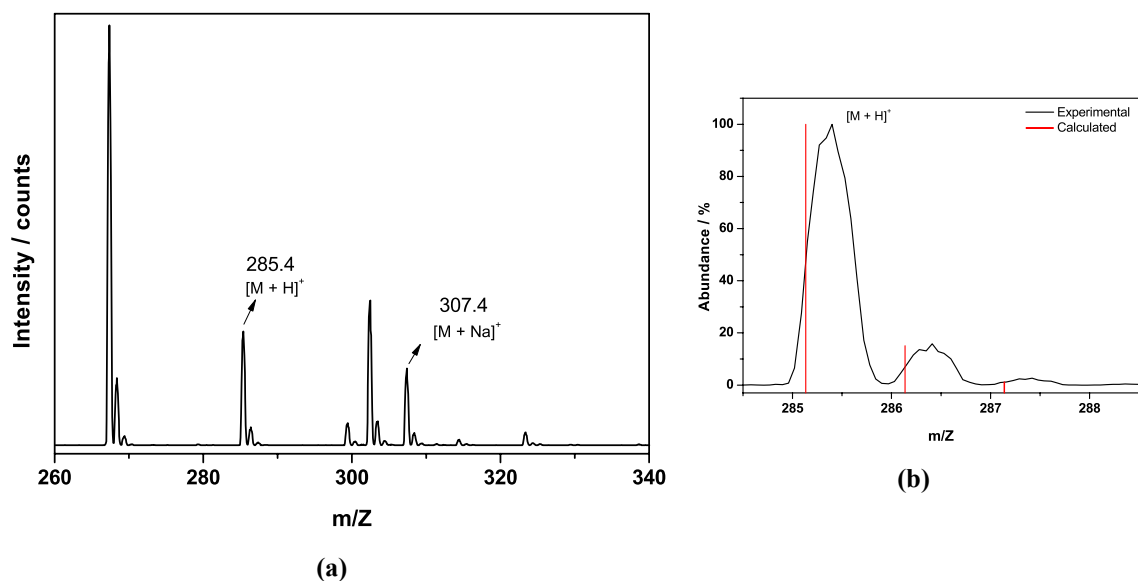


Figure S4. High resolution mass spectrum of 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzoic acid (**Hmee**). (a) Full spectrum. (b) Isotopic pattern.

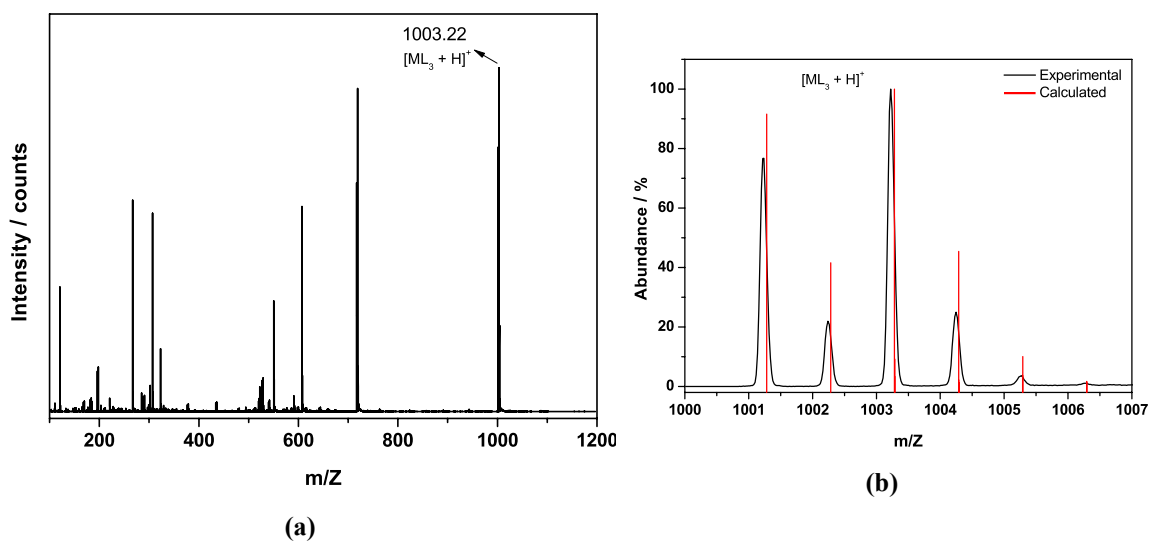


Figure S5. High resolution mass spectrum of europium complex. (a) Full spectrum. (b) Isotopic pattern.

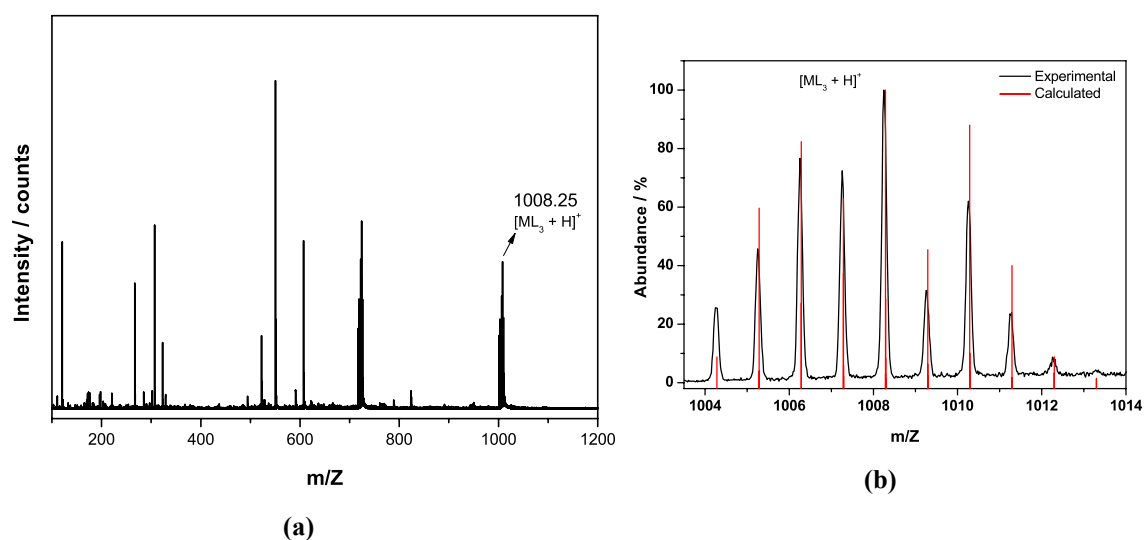


Figure S6. High resolution mass spectrum of gadolinium complex. (a) Full spectrum. (b) Isotopic pattern.

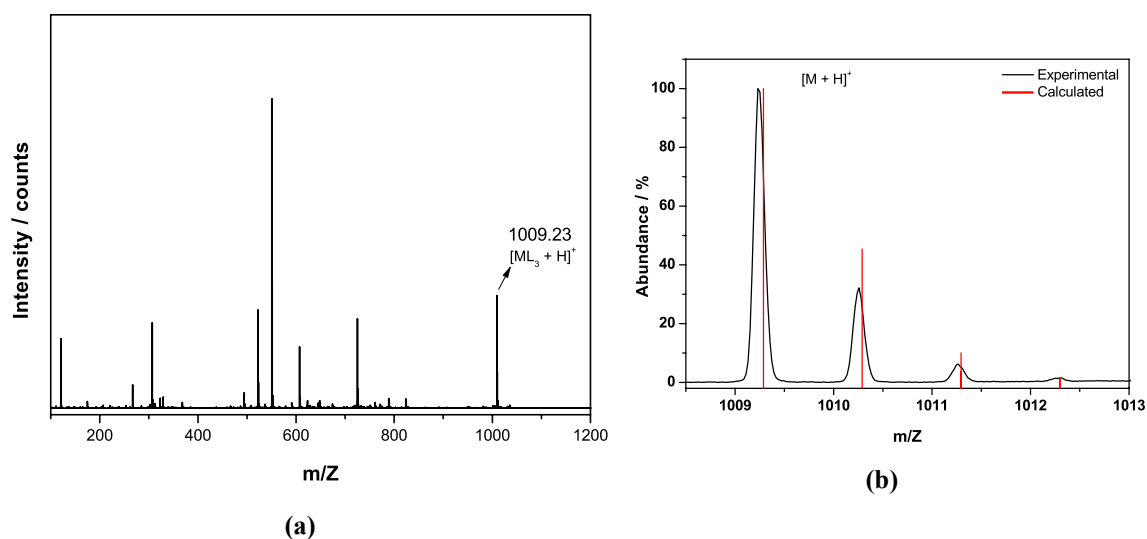


Figure S7. High resolution mass spectrum of terbium complex. (a) Full spectrum. (b) Isotopic pattern.

Table S1. Comparison between experimental and calculated mass/charge of the complexes.

Motifs	m/z _{exp}	m/z _{calc}
1Eu: 3mee	1003.22	1003.28
1Gd: 3mee	1008.25	1008.29
1Tb:3mee	1009.24	1009.29

3. Fit of the emission lifetime decay curve

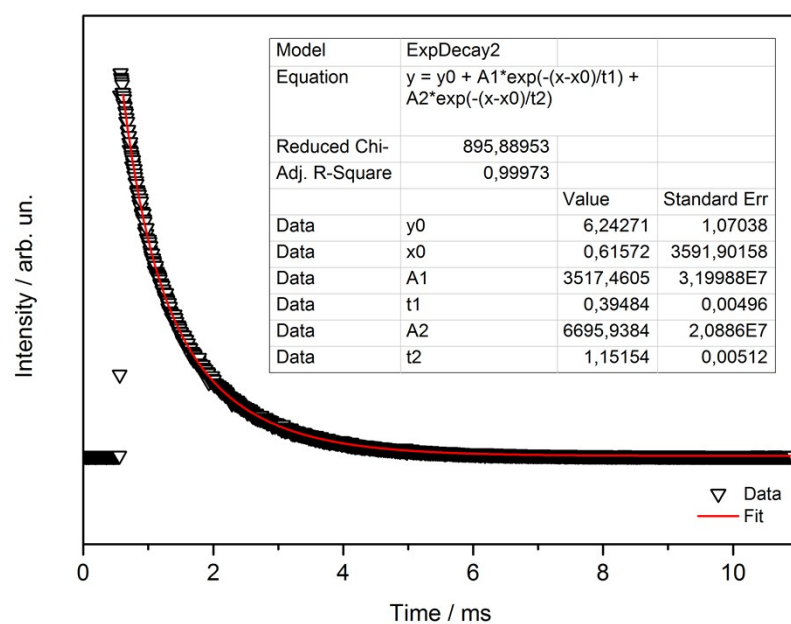


Figure S8: Fit of the emission decay curve of the solid europium(III) complex.

4. Thermogravimetric Analyses - TGA

The TGA curves of complexes are shown in Figure S9.

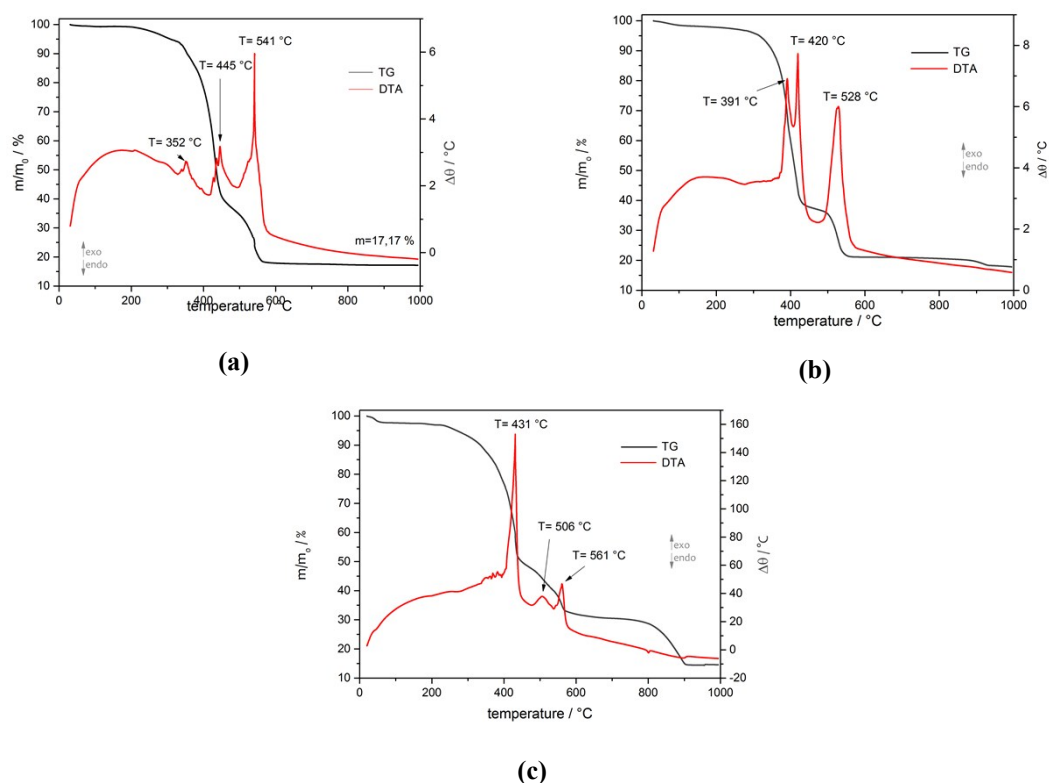


Figure S9. Thermogravimetric analysis of (a) europium (b) terbium and (c) gadolinium complexes.

5. Phosphorescence emission time resolved spectra

The energy of the triplet level (T) of the ligands were determined from the time resolved emission spectra, of analogous gadolinium(III) complexes obtained at 77 K, Figure S10a. From the phosphorescence spectra, the energies of the triplet states were determined

fitting a tangent at the highest energy band edge or the peak of the highest band obtained from the deconvolution of the phosphorescence spectra, Figure S10b-c.

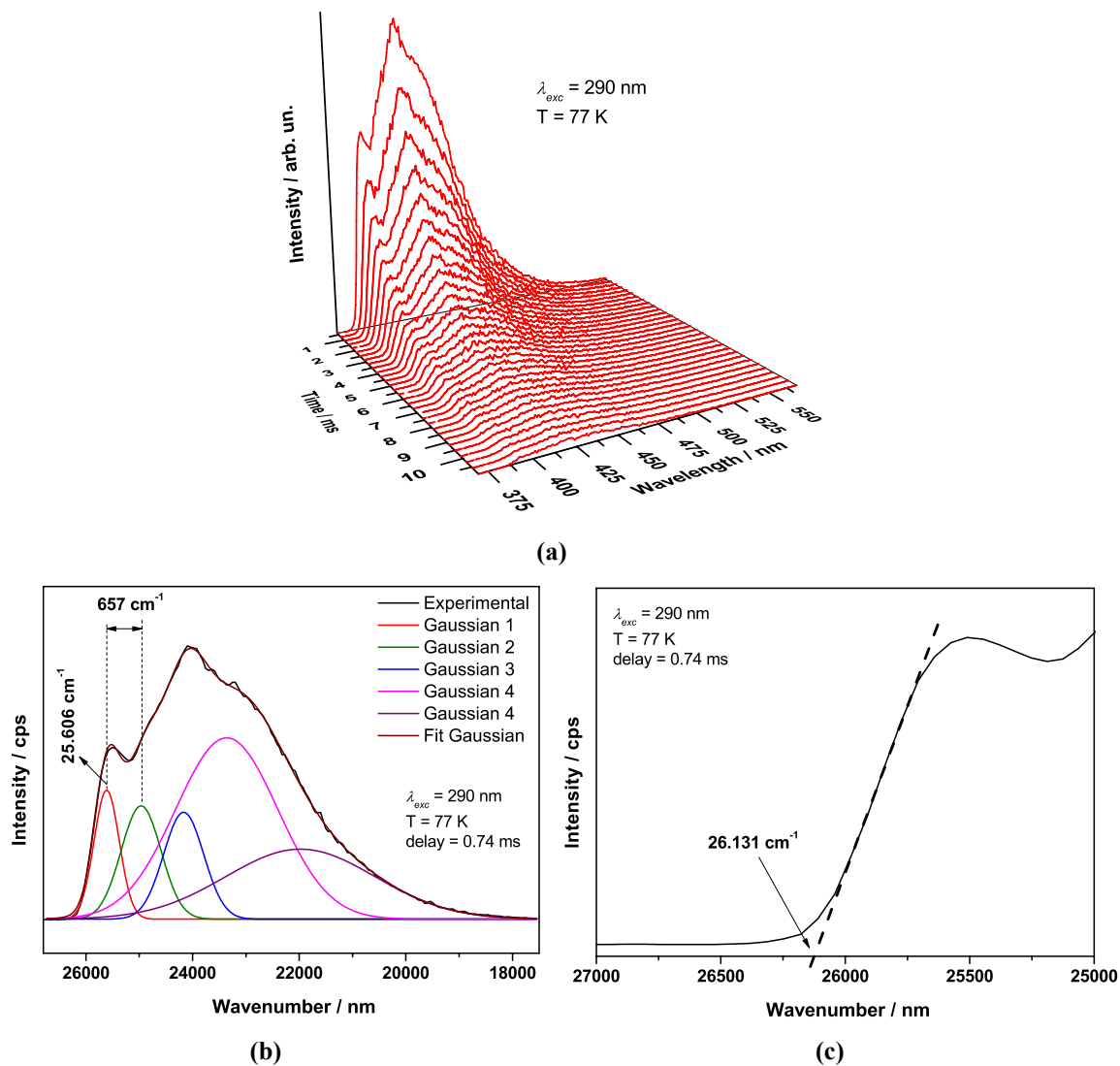


Figure S10. Phosphorescence emission spectra obtained at 77 K. (a) Time resolved emission spectrum. (b) Deconvolution of the phosphorescence emission band. (c) Edge of the phosphorescence emission band.

6. Emission decay curves

The emission decay curves of the europium(III) and terbium(III) complexes are shown in Figures S11 and S12, respectively.

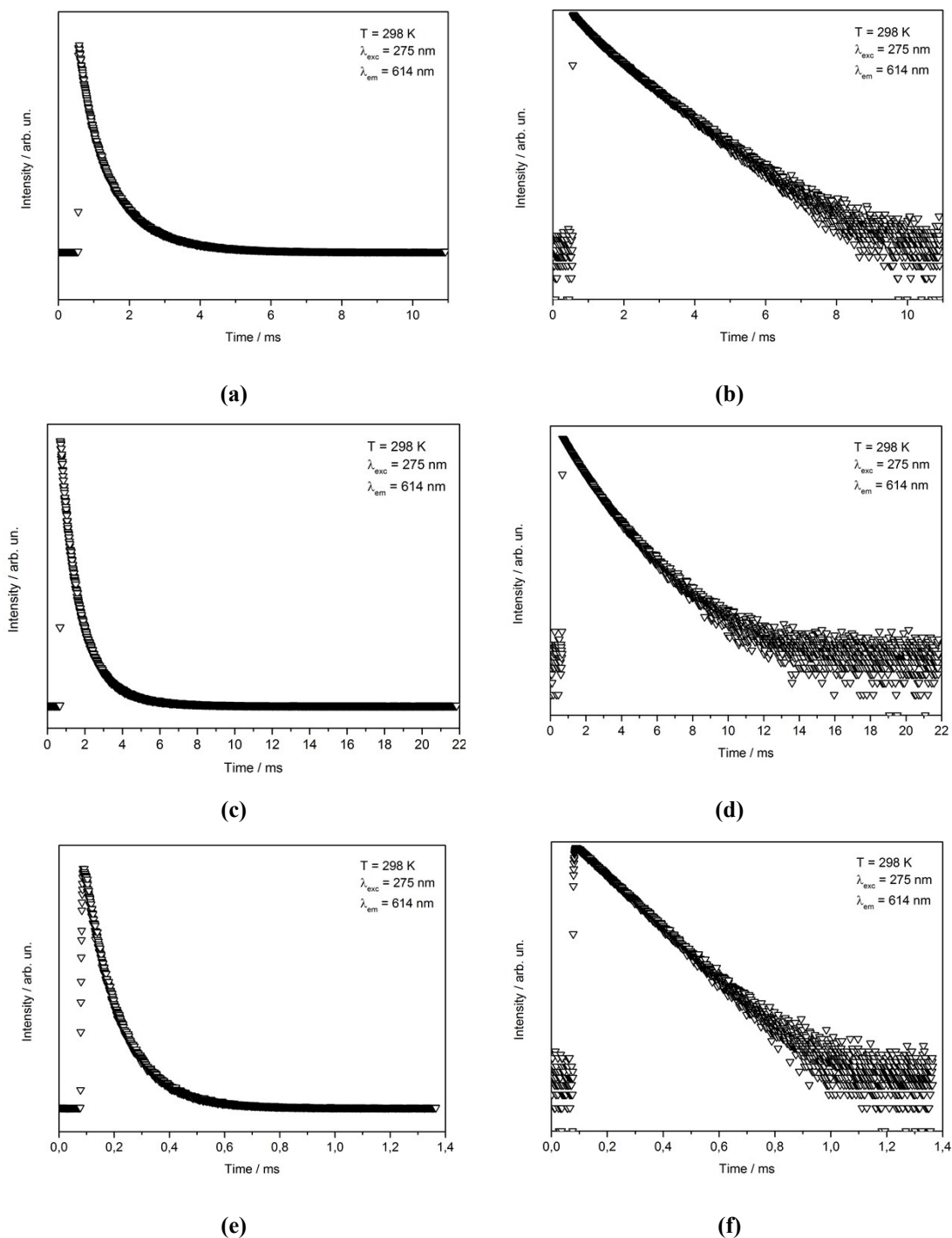


Figure S11. Emission decay curves of the europium(III) complexes and linearization. (a) and (b) Solid state. (c) and (d) Acetonitrile solution. (e) and (f) Water solution.

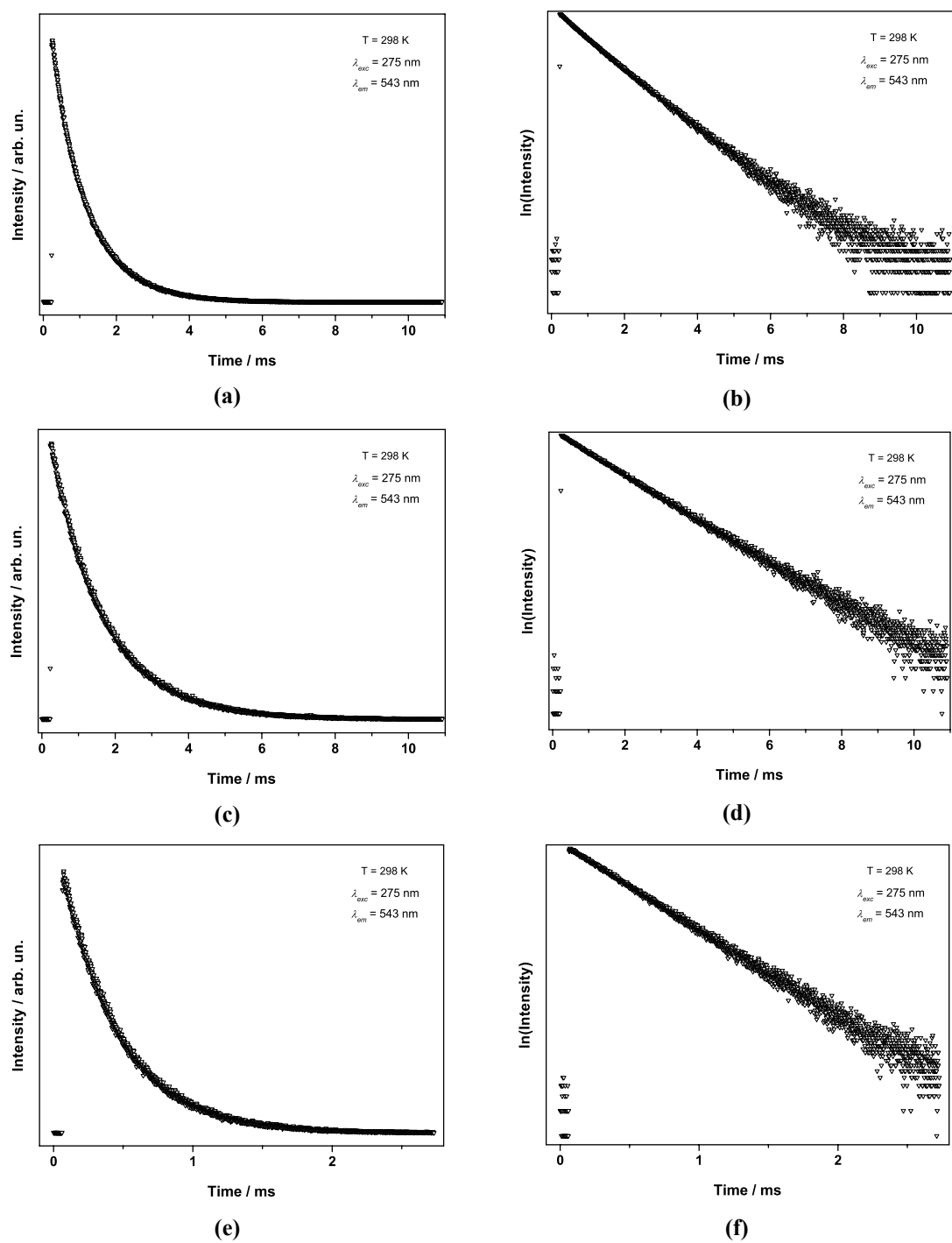


Figure S12. Emission decay curves of the terbium(III) complexes and linearization. (a) and (b) Solid state. (c) and (d) Acetonitrile solution. (e) and (f) Water solution.

7. Time resolved emission spectrum of solid $[\text{Eu}_2(\text{mee})_6(\text{H}_2\text{O})_2]$

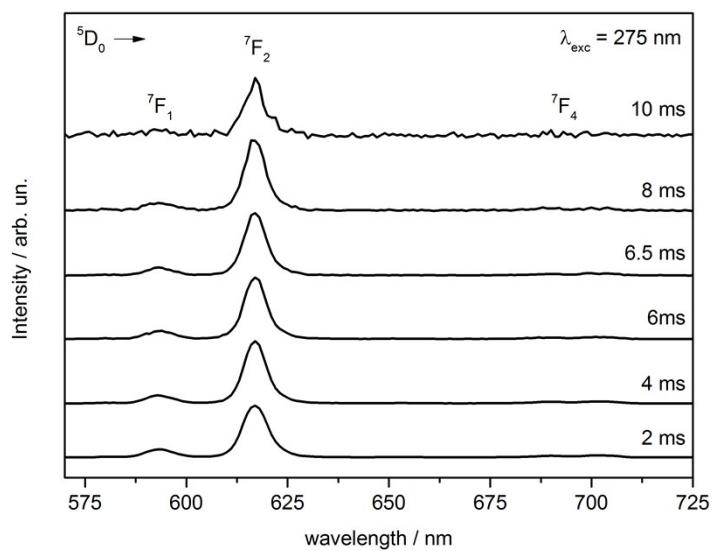


Figure S13: Time resolved emission spectra of the complex $[\text{Eu}_2(\text{mee})_6(\text{H}_2\text{O})_2]$.