Lanthanoid Complexes Supported by Retro-Claisen Condensation Products of *β*-Triketonates

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Supplementary Information

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

*dm**tbm**H*

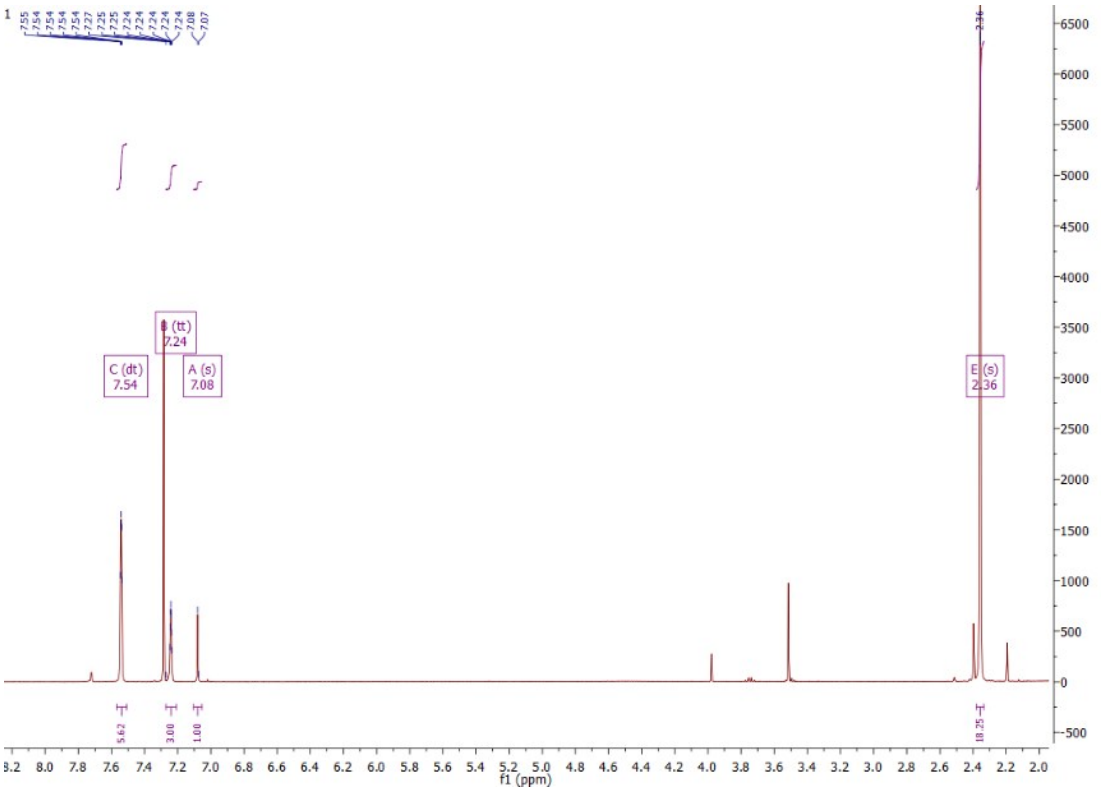

*Figure S1 ^{1}H NMR of the dm**tbm**H molecule in $CDCl_3$*

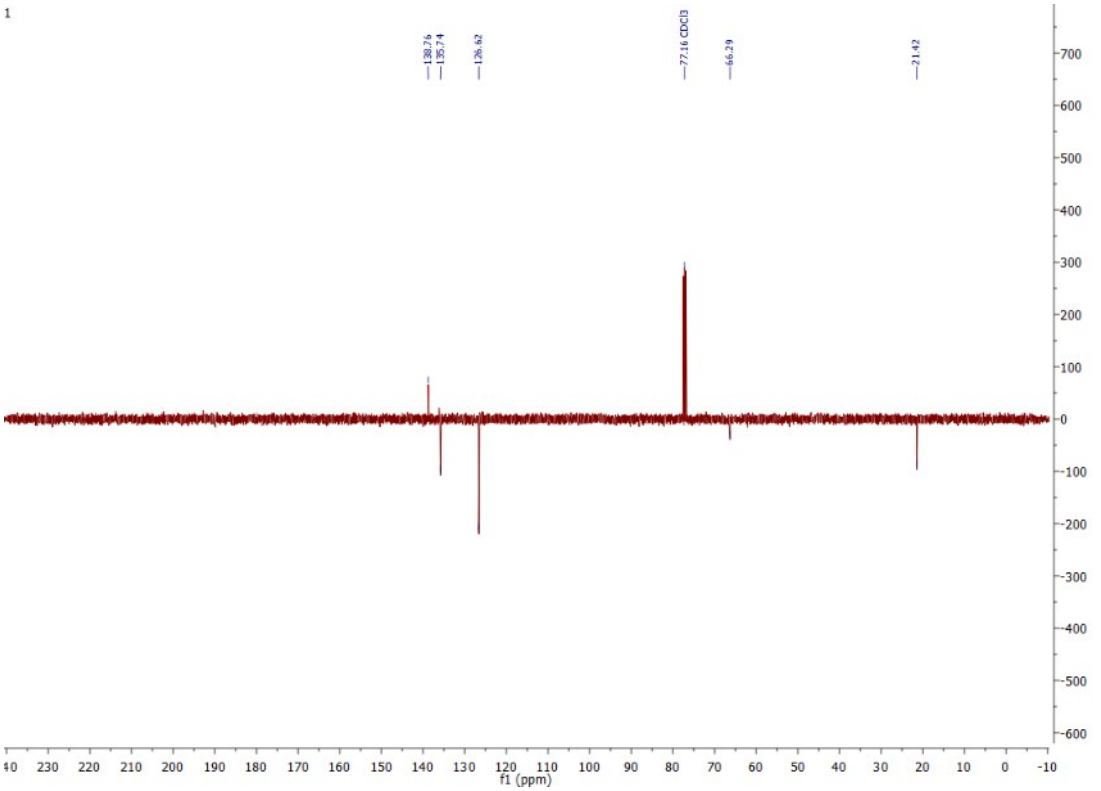

*Figure S2 ^{13}C NMR of the dm**tbm**H molecule in $CDCl_3$*

*et**tbm**H in $CDCl_3$*

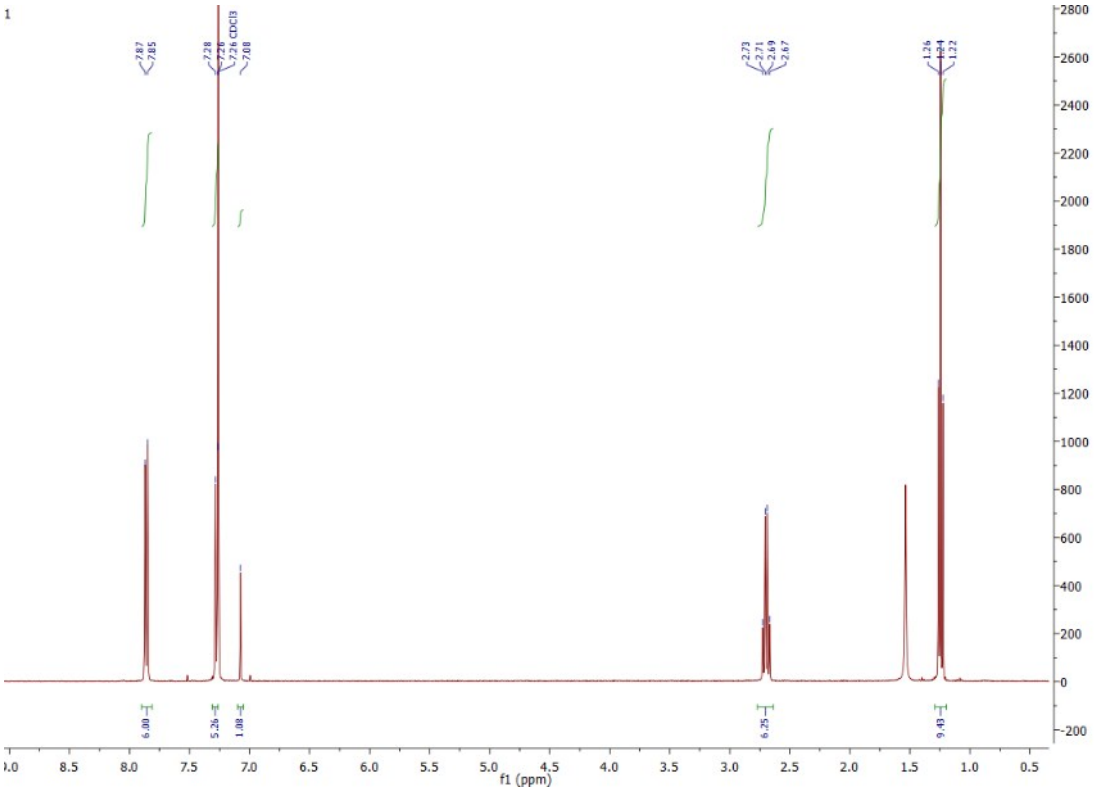

*Figure S3 ^{1}H NMR of the et**tbm**H molecule in $CDCl_3$*

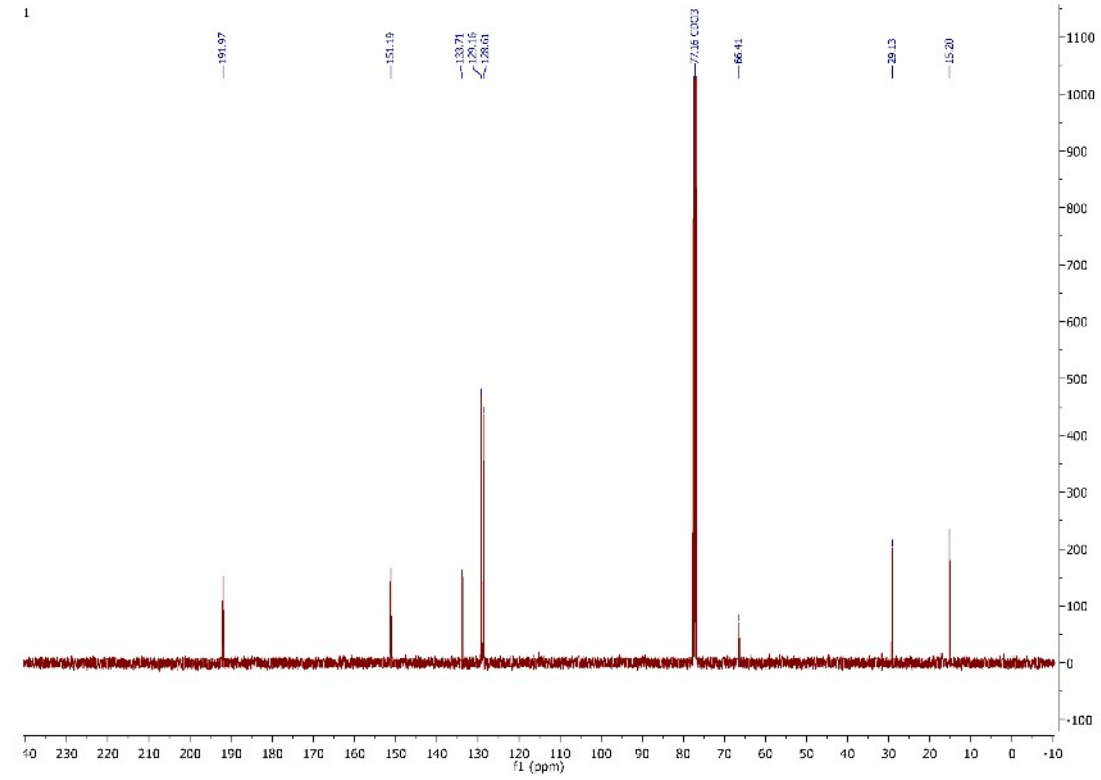

*Figure S4 ^{13}C NMR of the et**tbm**H molecule in $CDCl_3$*

*but**bm**H in $CDCl_3$.*

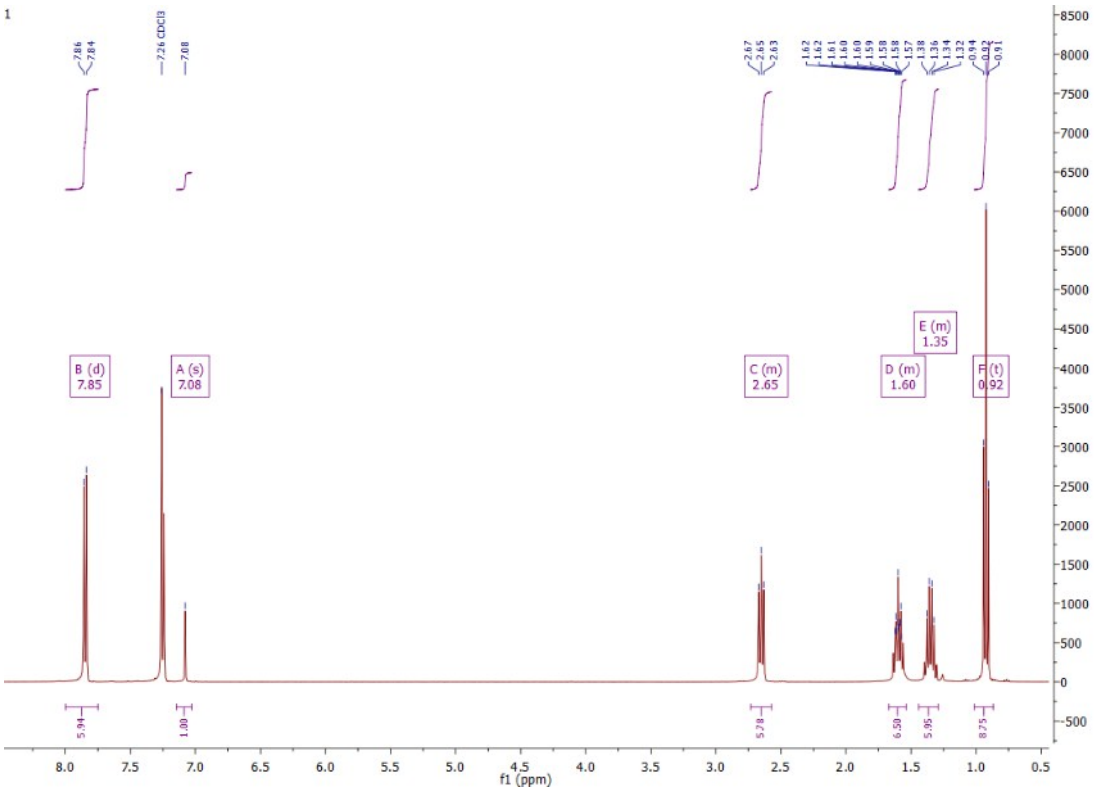

*Figure S5 ^{1}H NMR of the but**bm**H molecule in $CDCl_3$*

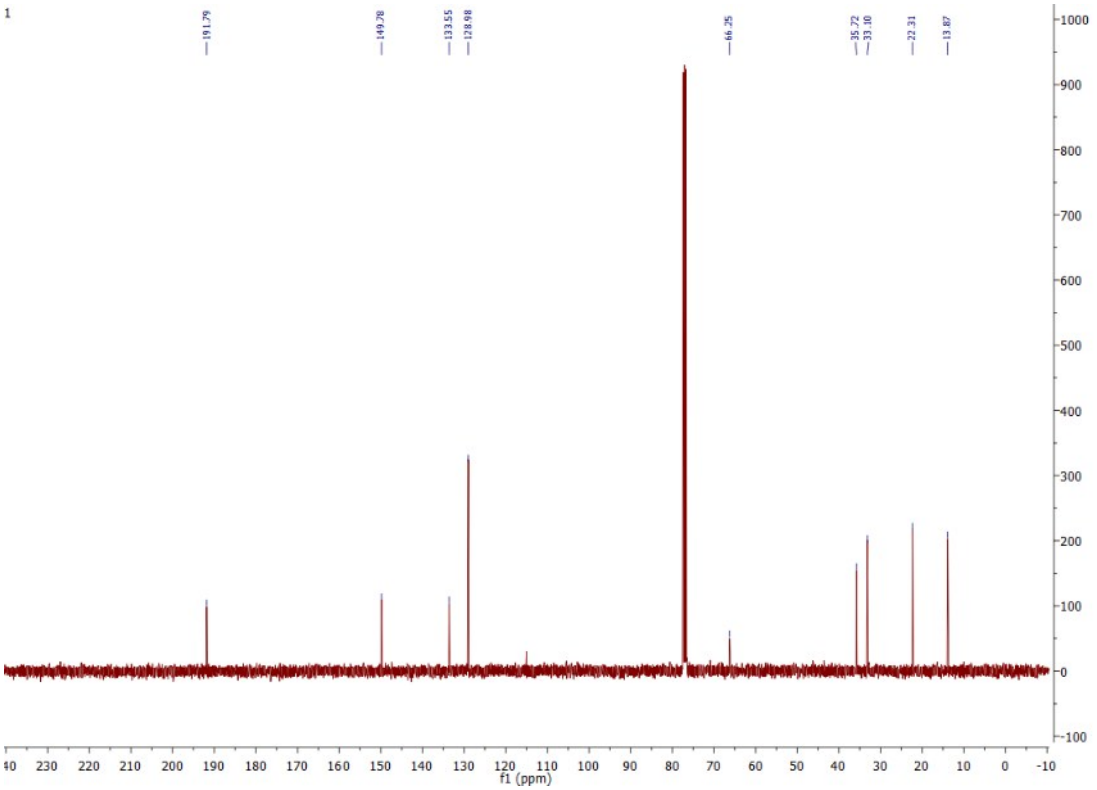

*Figure S6 ^{13}C NMR of the but**bm**H molecule in $CDCl_3$*

*t-bu**tbm**H in $CDCl_3$.*

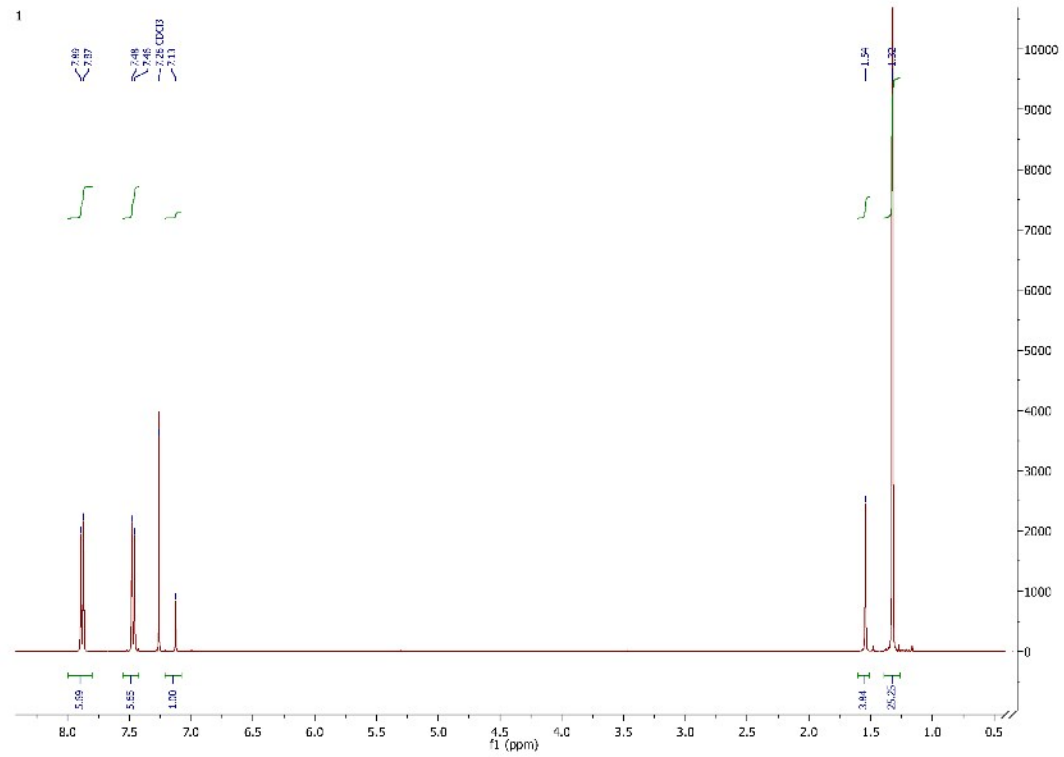

*Figure S7 ^{1}H NMR of the t-bu**tbm**H molecule in $CDCl_3$*

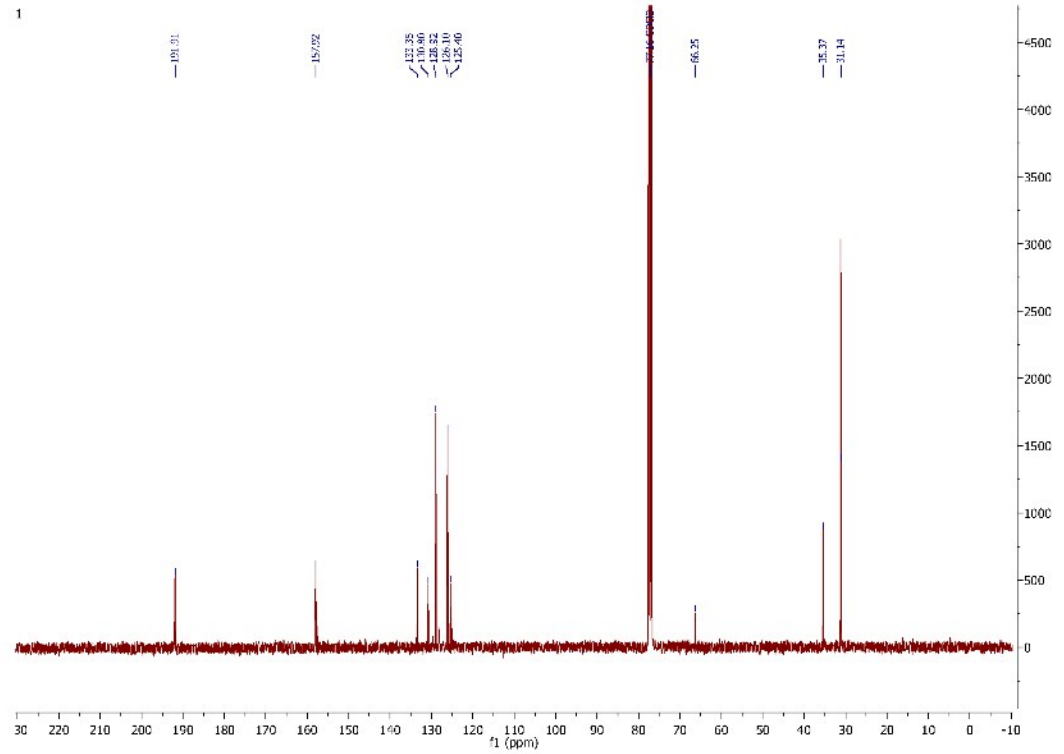

*Figure S8 ^{13}C NMR of the t-bu**tbm**H molecule in $CDCl_3$*

Absorption profiles

*dm**tbm**H*

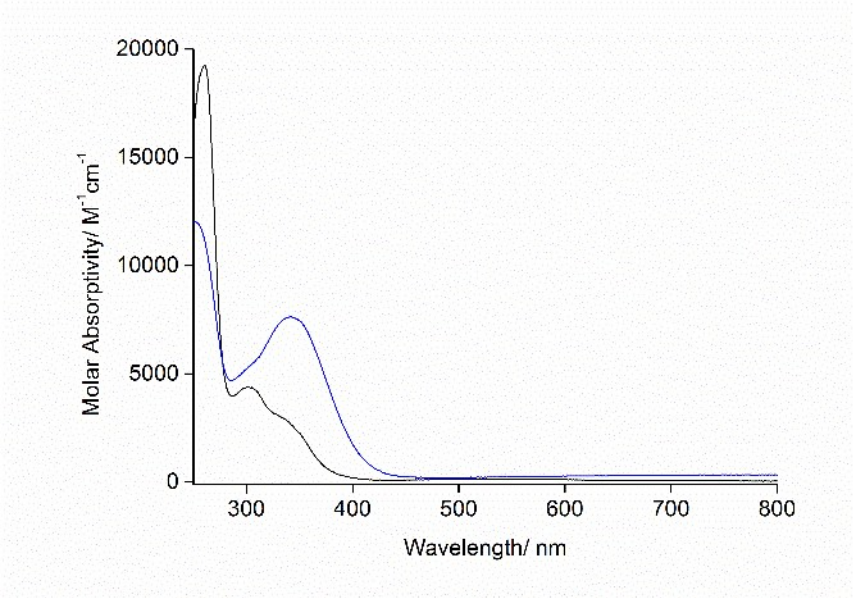

*Figure S9 Absorption profiles of dm**tbm**H (black trace) and dm**tbm*⁻ *in excess of KOH (blue trace) from 10⁻⁵M solutions in EtOH*

*et**tbm**H*

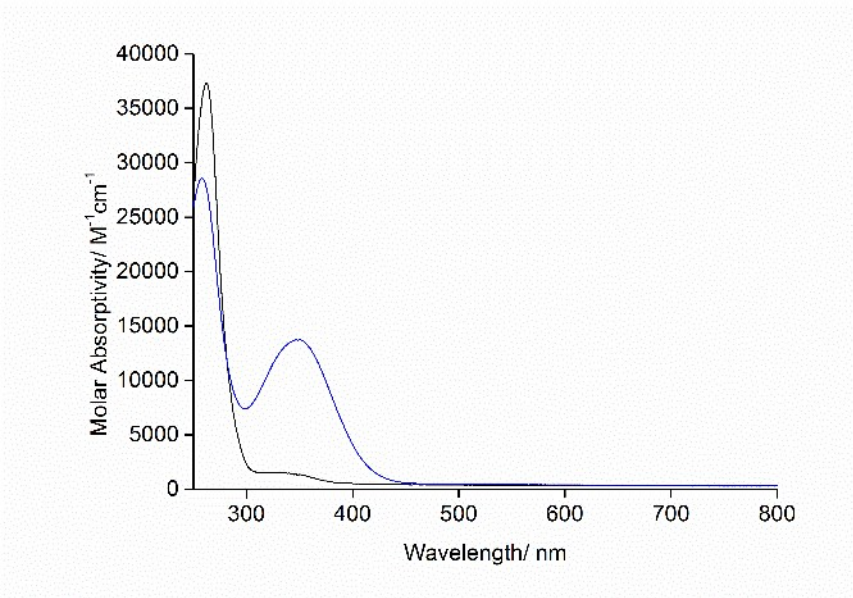

*Figure S10 Absorption profiles of et**tbm**H (black trace) and et**tbm*⁻ *in excess of KOH (blue trace) from 10⁻⁵M solutions in EtOH*

*bu**tbm**H*

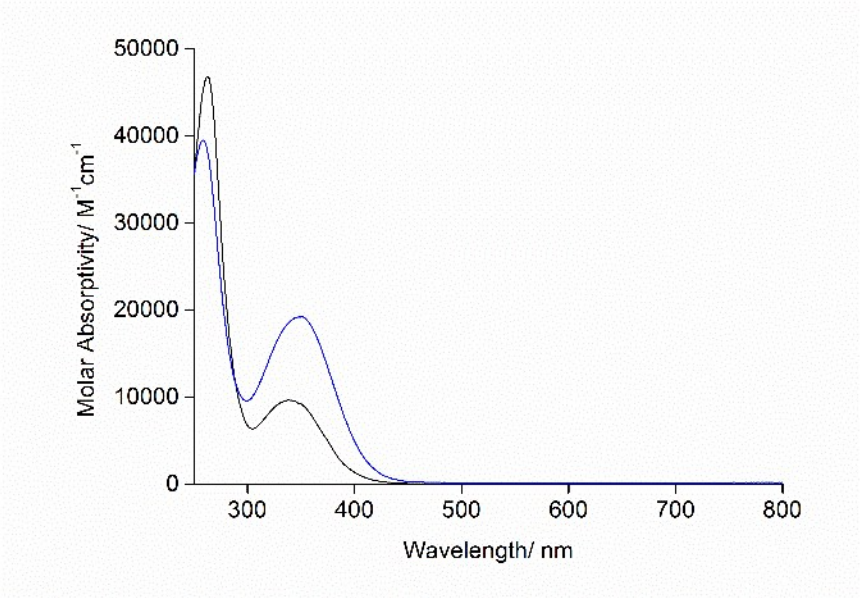

*Figure S11 Absorption profiles of bu**tbm**H (black trace) and bu**tbm**- in excess of KOH (blue trace) from 10-5M solutions in EtOH*

*t-bu**tbm**H*

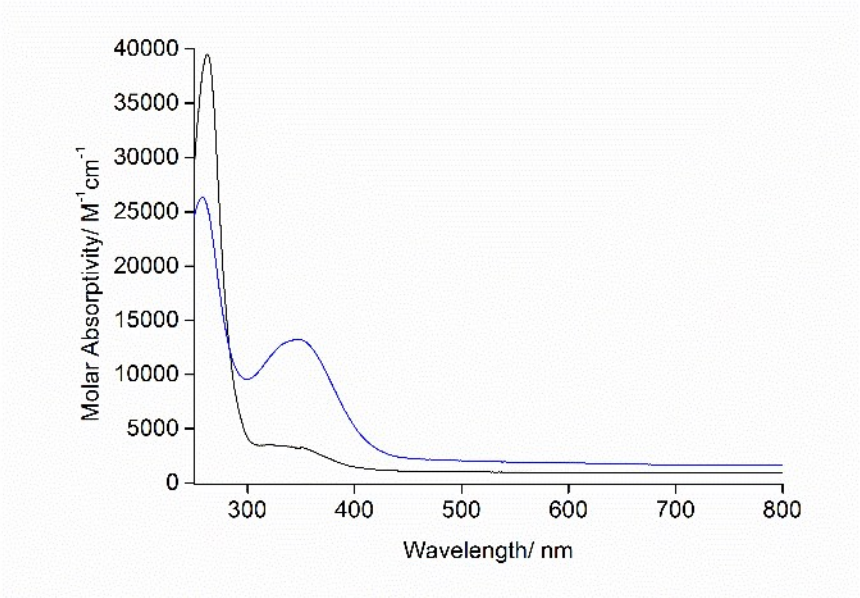

*Figure S12 Absorption profiles of t-bu**tbm**H (black trace) and t-bu**tbm**- in excess of KOH (blue trace) from 10-5M solutions in EtOH*

Emission plots of Gd^{3+} complexes at 77 K

*dm**tbm**H/ dm**dbm**H*

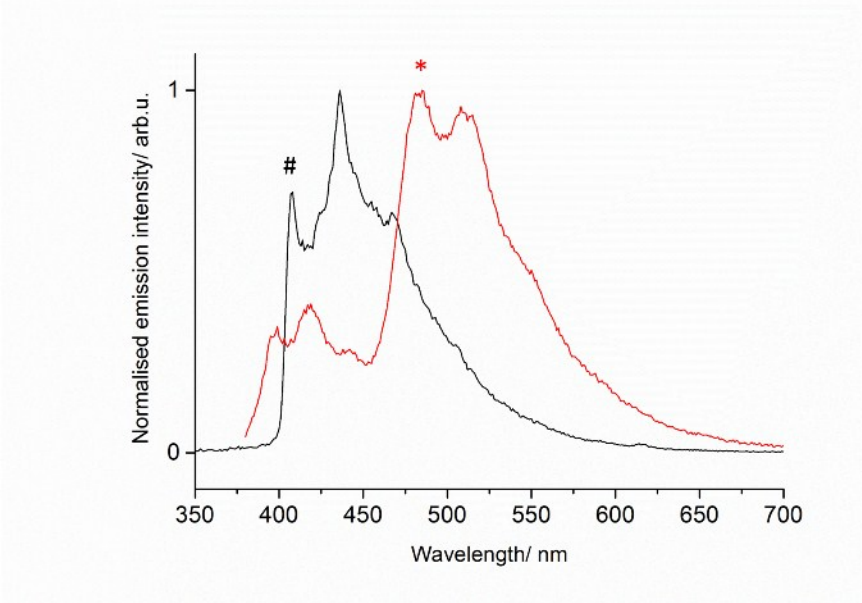

*Figure S13 Emission of ligand dm**tbm**H (black trace) and its Gd^{3+} complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red).*

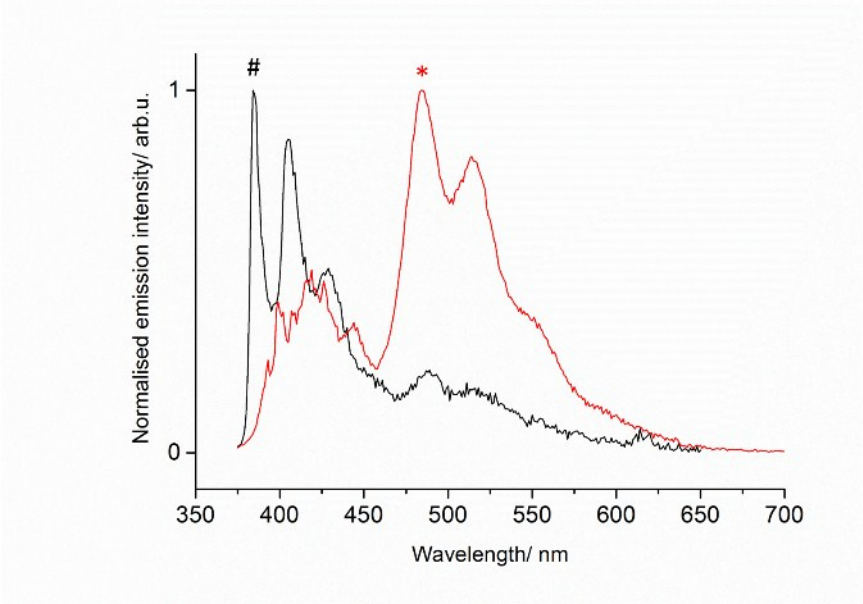

*Figure S14 Emission of ligand dm**dbm**H (black trace) and its Gd^{3+} complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red).*

*et**tbm**H/et**dbm**H*

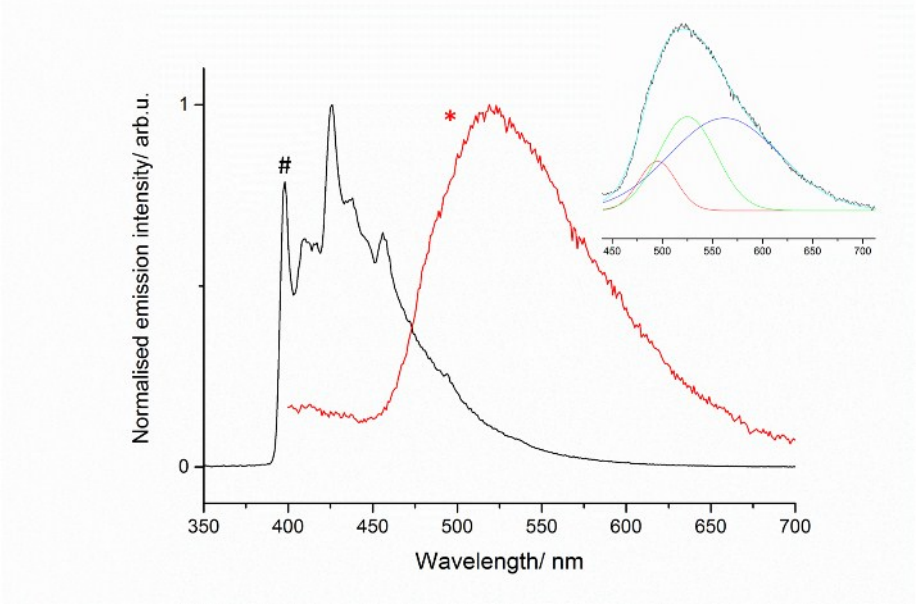

*Figure S15 Emission of ligand et**tbm**H (black trace) and its Gd^{3+} complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red). Inset shows deconvolution of the Gd^{3+} complex emission curve.*

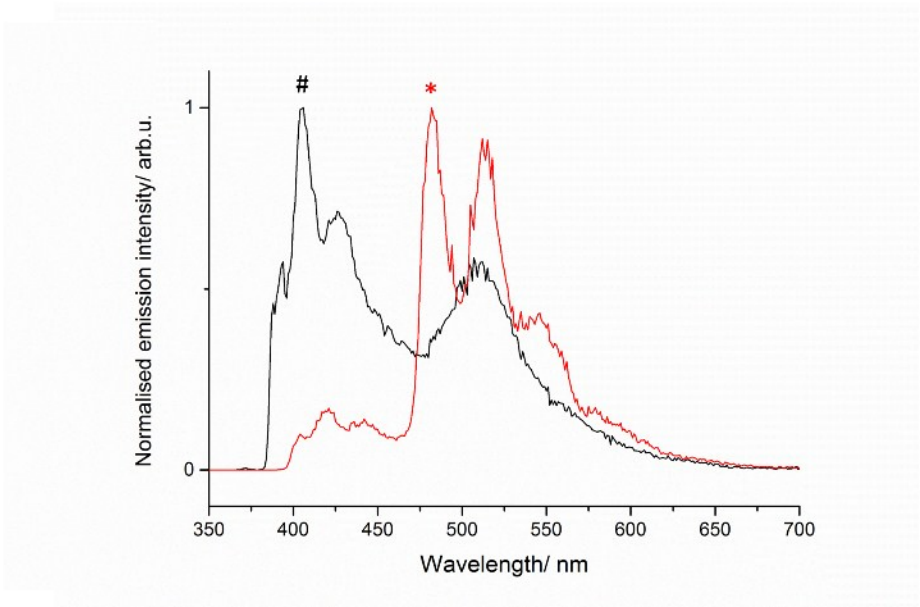

*Figure S16 Emission of ligand et**dbm**H (black trace) and its Gd^{3+} complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red).*

*bu**tbm**H/ bu**dbm**H*

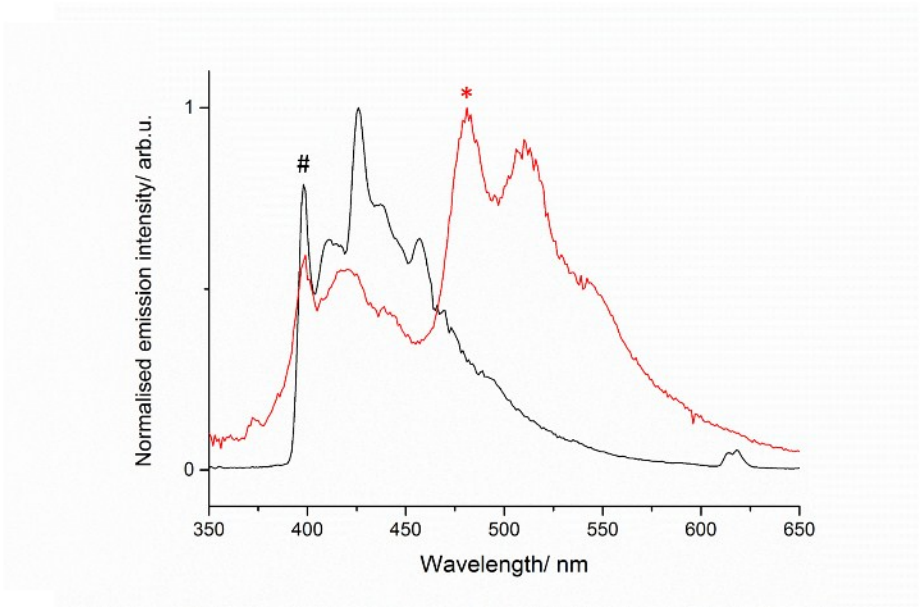

*Figure S17 Emission of ligand bu**tbm**H (black trace) and its Gd^{3+} complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red).*

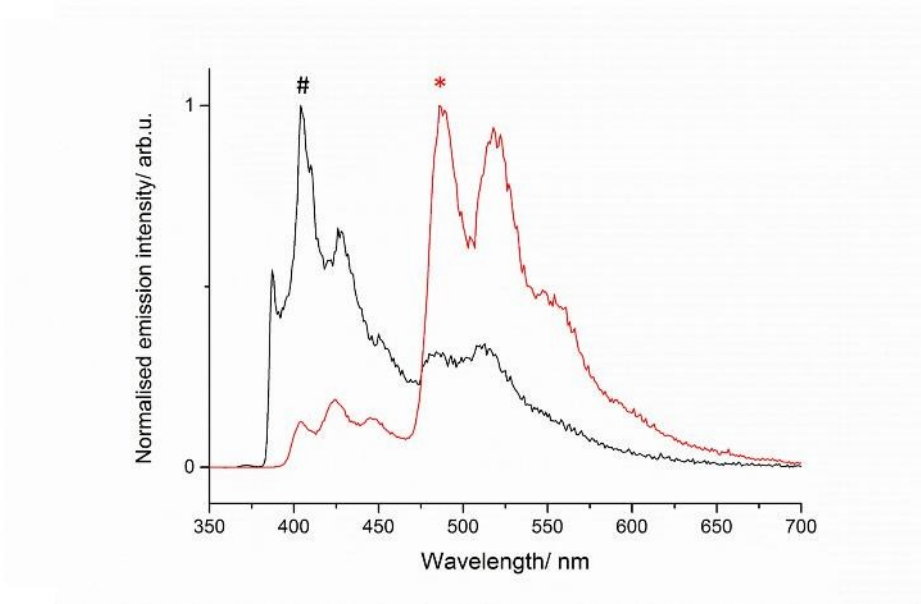

*Figure S18 Emission of ligand bu**dbm**H (black trace) and its Gd^{3+} complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red).*

*t-bu**tbm**H/ t-bu**dbm**H*

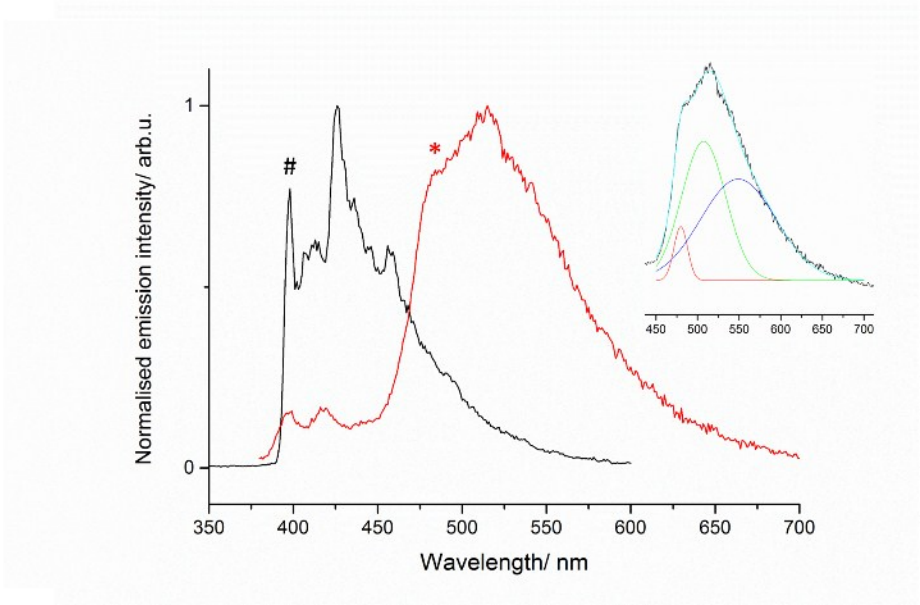

*Figure S19 Emission of ligand t-bu**tbm**H (black trace) and its Gd^{3+} complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red). Inset shows deconvolution of the Gd^{3+} complex emission curve.*

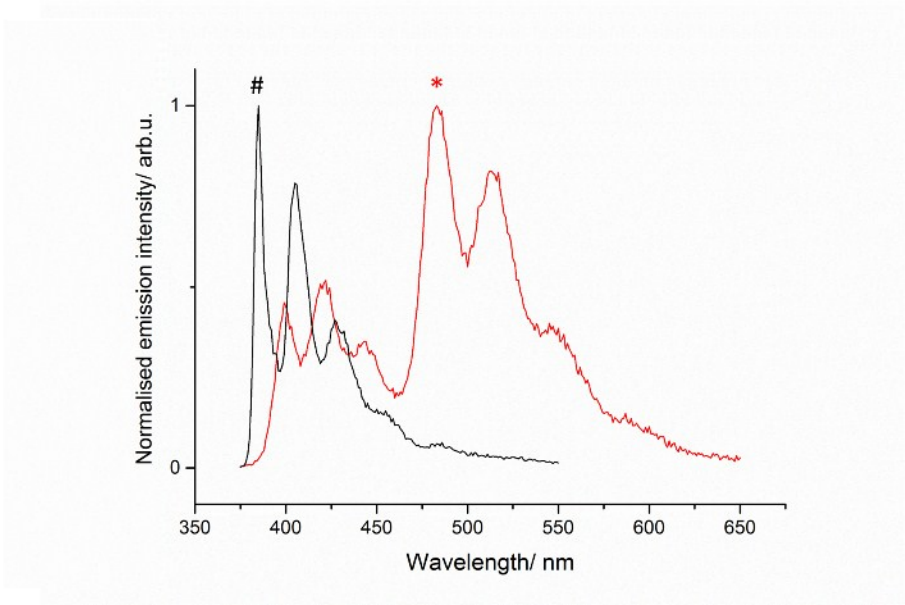

*Figure S20 Emission of ligand t-bu**dbm**H (black trace) and its Gd^{3+} complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red).*

Energy values for singlet and triplet states of ligands

Table S1.- Energy values for singlet and triplet states of correspondent β-triketones and β-diketones.

LIGAND	$^1\pi\pi^*$(cm^{-1})	$^3\pi\pi^*$(cm^{-1})
TBM	25,575	20,620
DBM	26,110	20,580
mTBM	24,957	20,790
mDBM	25,974	20,576
etTBM	25,189	20,202
etDBM	25,445	20,790
dmTBM	24,509	20,790
dmDBM	25,974	20,633
buTBM	25,156	20,790
buDBM	25,840	20,537
***t*-buTBM**	25,126	20,844
***t*-buDBM**	26,007	20,709

NMR stability studies

tbmH

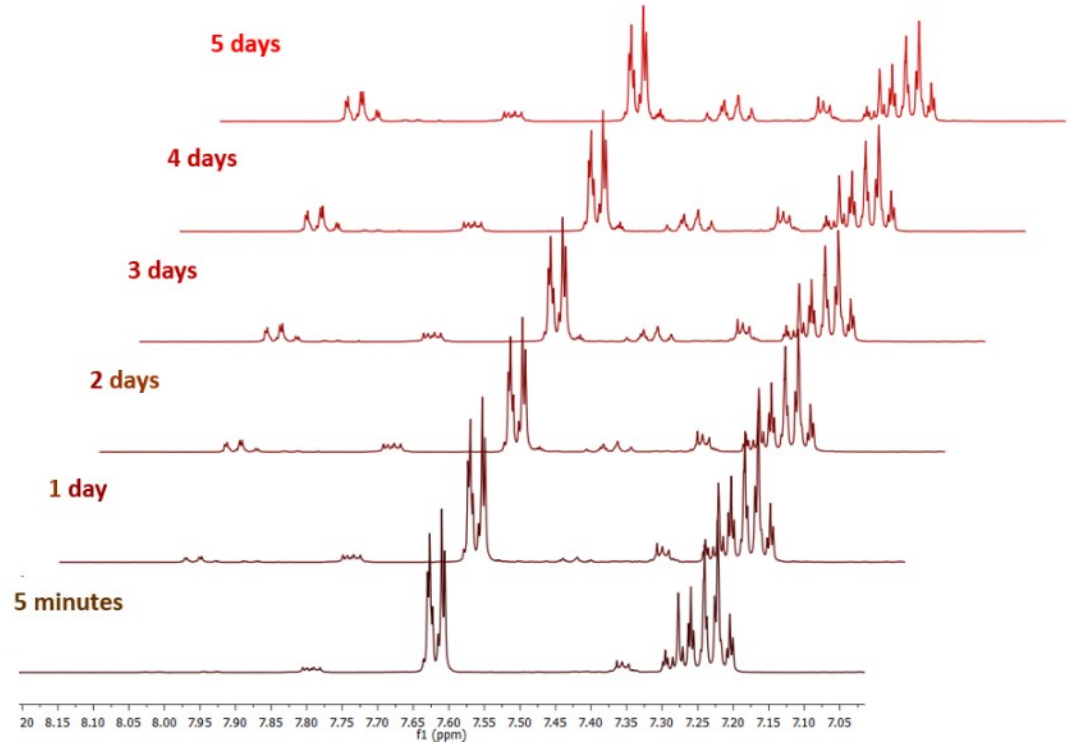

*Figure S21 ^{1}H NMR of the **tbm**H molecule and one equivalent of KOH over 5 days in MeOD*

*m**tbm**H*

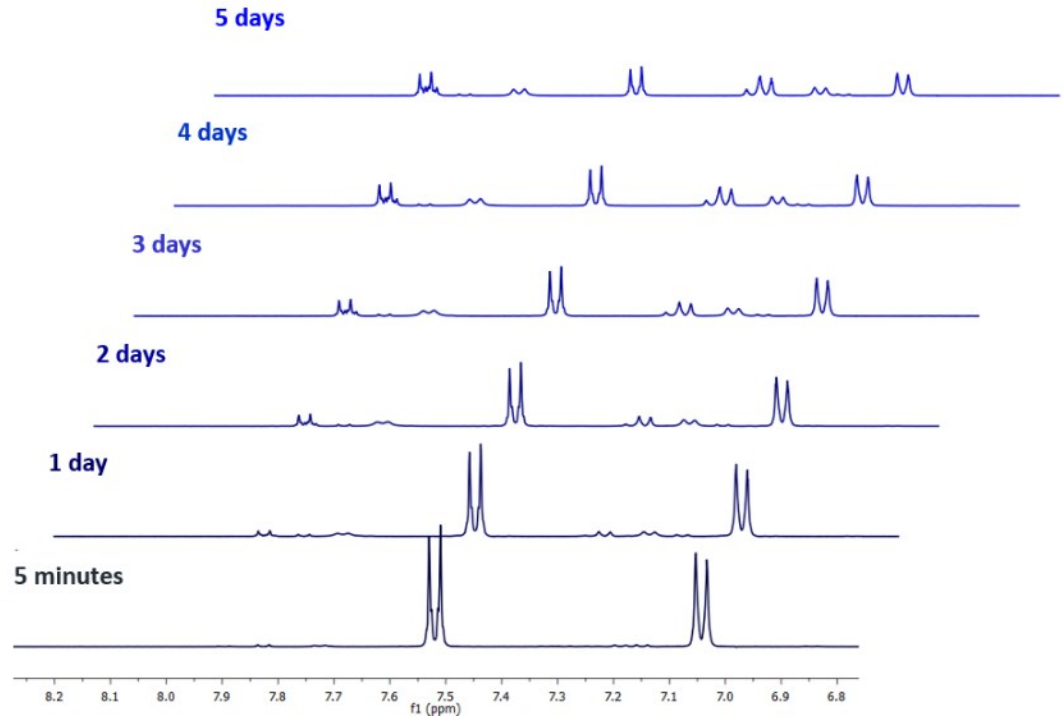

*Figure S22 ^{1}H NMR of the m**tbm**H molecule and one equivalent of KOH over 5 days in MeOD*

*dm**tbm**H*

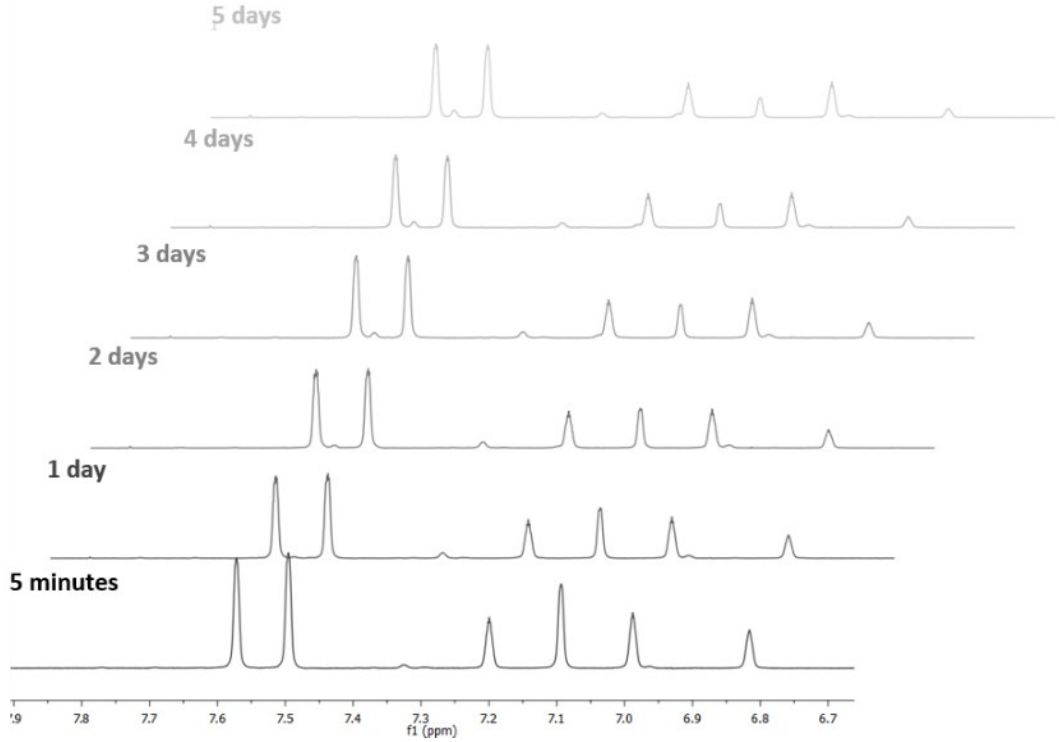

*Figure S23 [1]H NMR of the dm**tbm**H molecule and one equivalent of KOH over 5 days in MeOD*

*et**tbm**H*

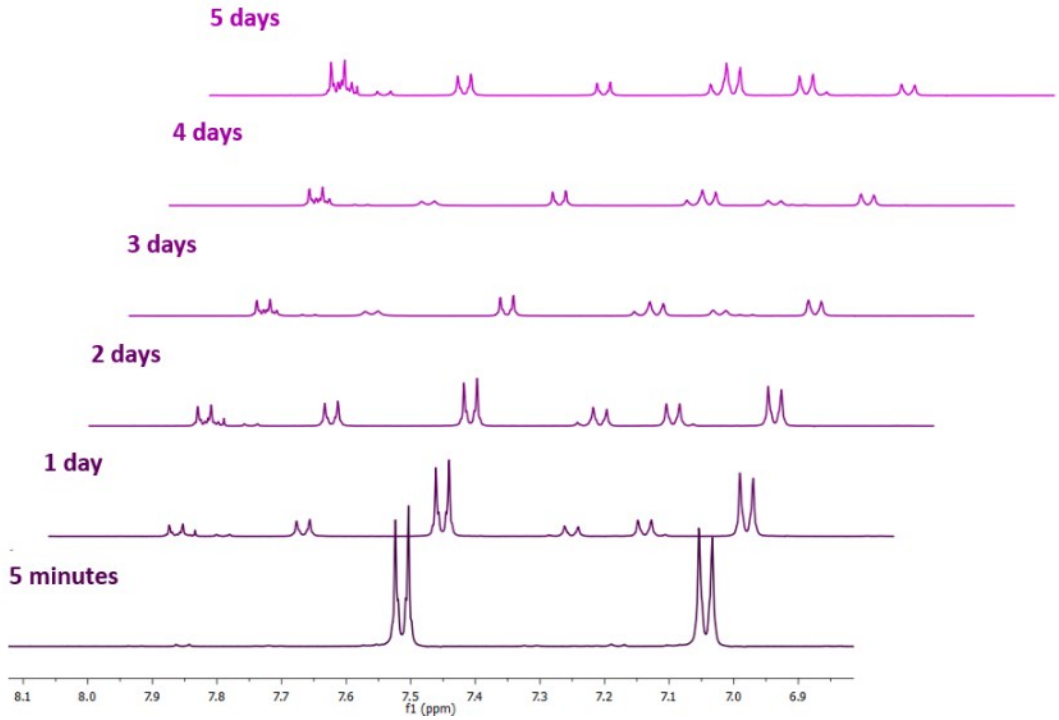

*Figure S24 [1]H NMR of the et**tbm**H molecule and one equivalent of KOH over 5 days in MeOD*

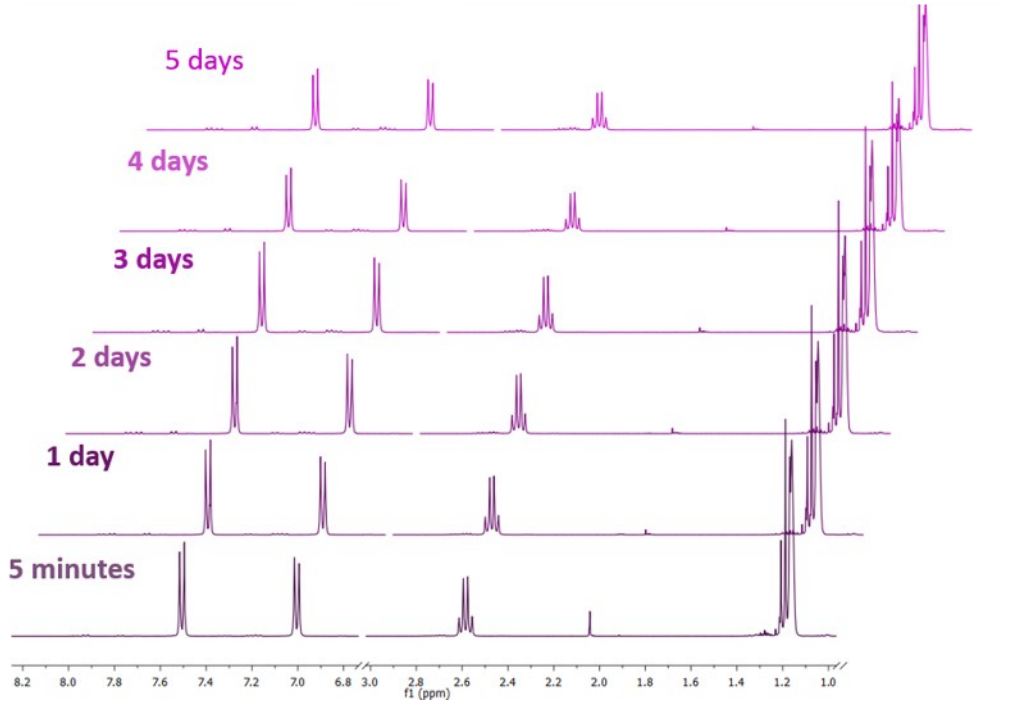

*Figure S25 [1]H NMR of the et**tbm**H molecule and one equivalent of KOH over 5 days in EtOD*

*but**bm**H*

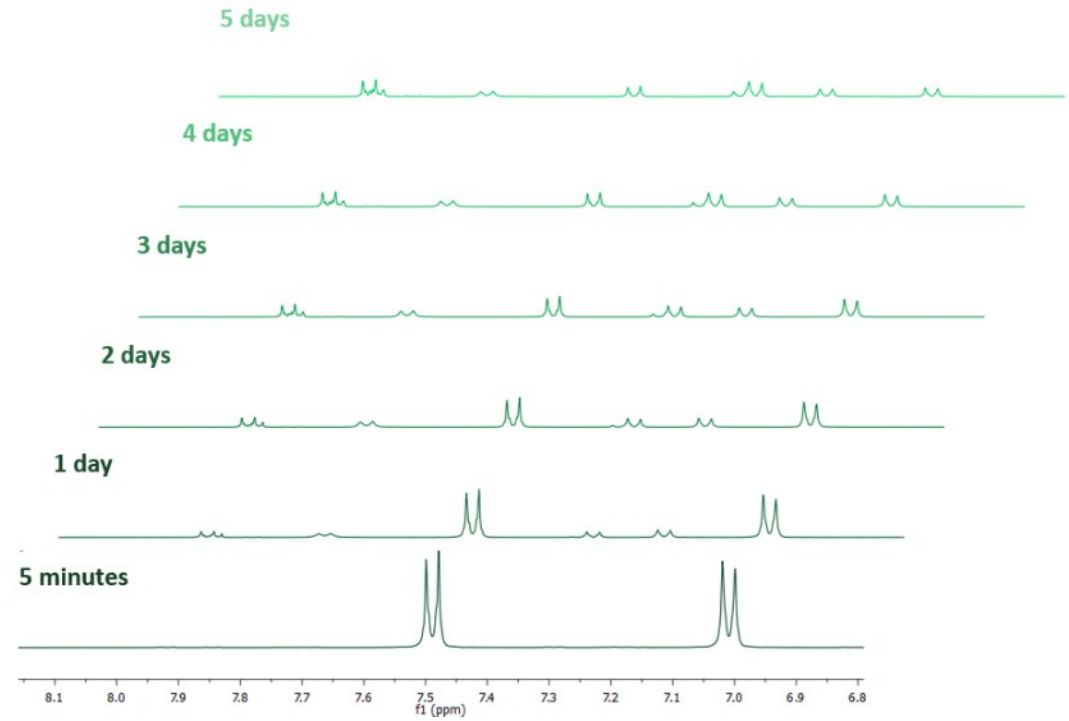

*Figure S26 [1]H NMR of the bu**tbm**H molecule and one equivalent of KOH over 5 days in MeOD*

*t-bu**tbm**H*

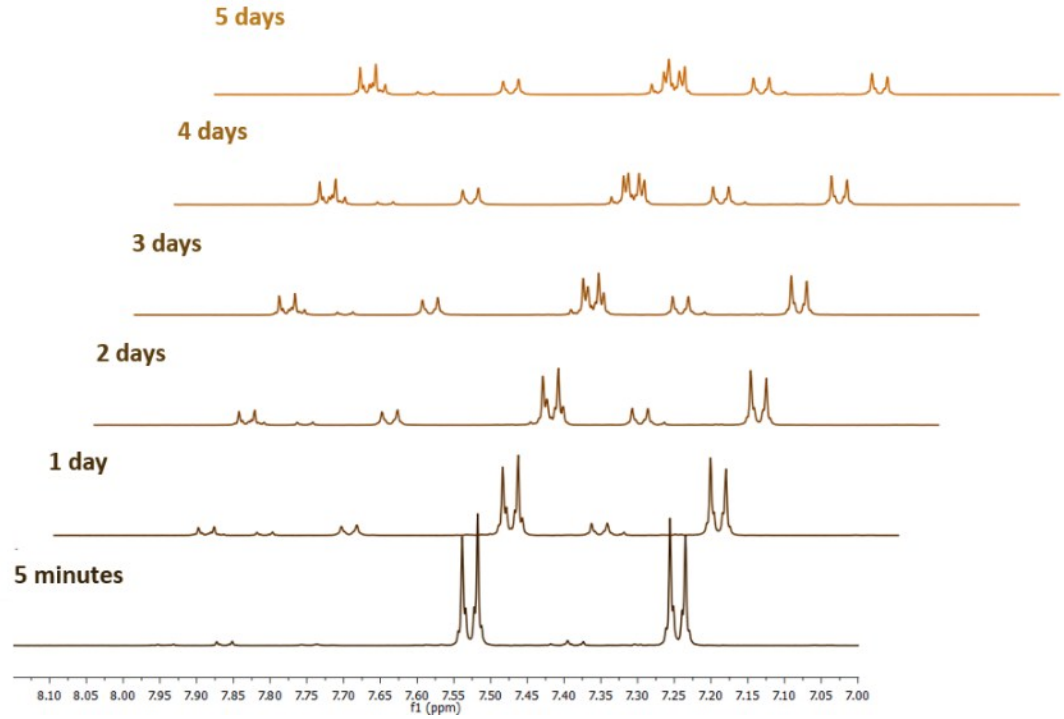

*Figure S27 [1]H NMR of the t-bu**tbm**H molecule and one equivalent of KOH over 5 days in MeOD*

***tbm**H + $LuCl_3$*

[1]H-NMR studies of the most stable *β*-triketone (**tbm**H) in MeOH were also performed in the presence of $LuCl_3$. As it can be seen in Figure S28, after addition of 1 equivalent of $LuCl_3$ in a **tbm** solution, appearance of multiple species can be observed. While some coordination of the *β* -triketonate can be identified, new peaks are also present assigned to *β*–diketonate and benzoate probably in both coordinated and non-coordinated forms.

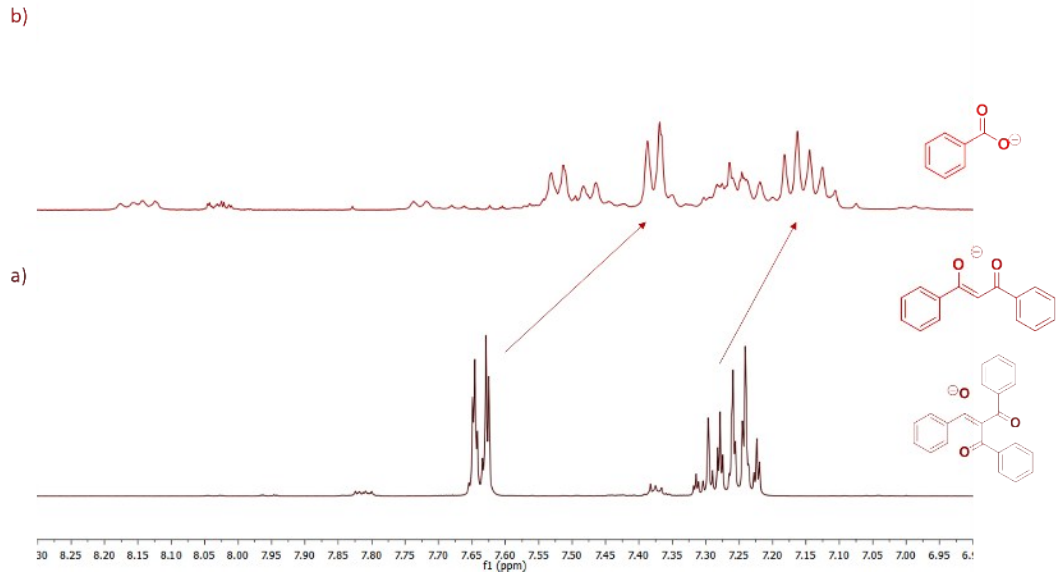

*Figure 28.- [1]H NMR of the **tbm**H molecule and one equivalent of KOH (a) and after addition of 1 equivalent of $LuCl_3$ in MeOD*

X-ray crystal structures

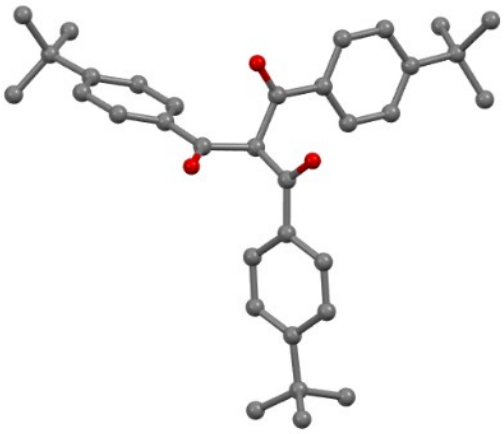

*Figure S29 X-ray crystal structure of the t-bu**tbm**H molecule where the hydrogens are omitted for clarity.*

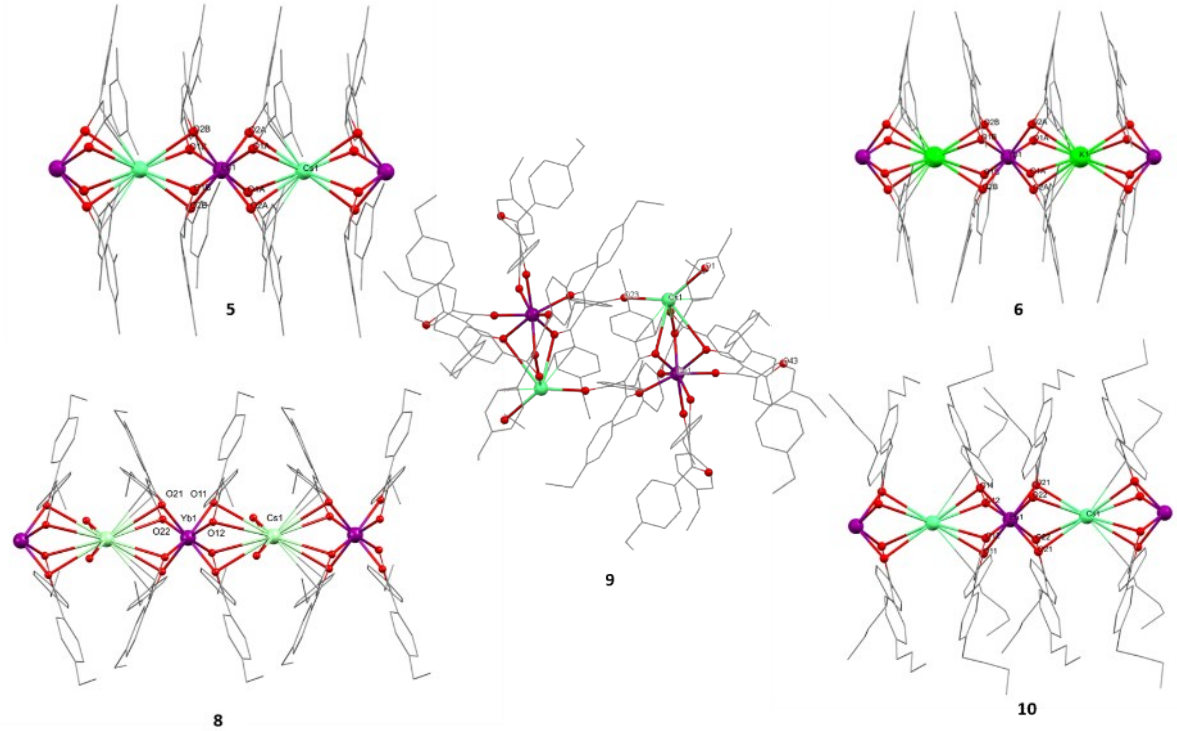

*Figure S30 X-ray crystal diffraction of complexes **5**,**6**,**8**,**9** and **10** where hydrogens are omitted for clarity.*

Shape analysis

Geometrical parameters for the coordination sphere of the lanthanoid cations in the complexes **1**-**10** were determined. The analysis was carried out considering the degree of distortion with respect to the two closest ideal geometries using software developed by Alvarez et al.[1] that allows a mathematical calculation of continuous shape measures (CShM)[2] relative to the ideal geometries shown in the x- and y- axes.

Plots

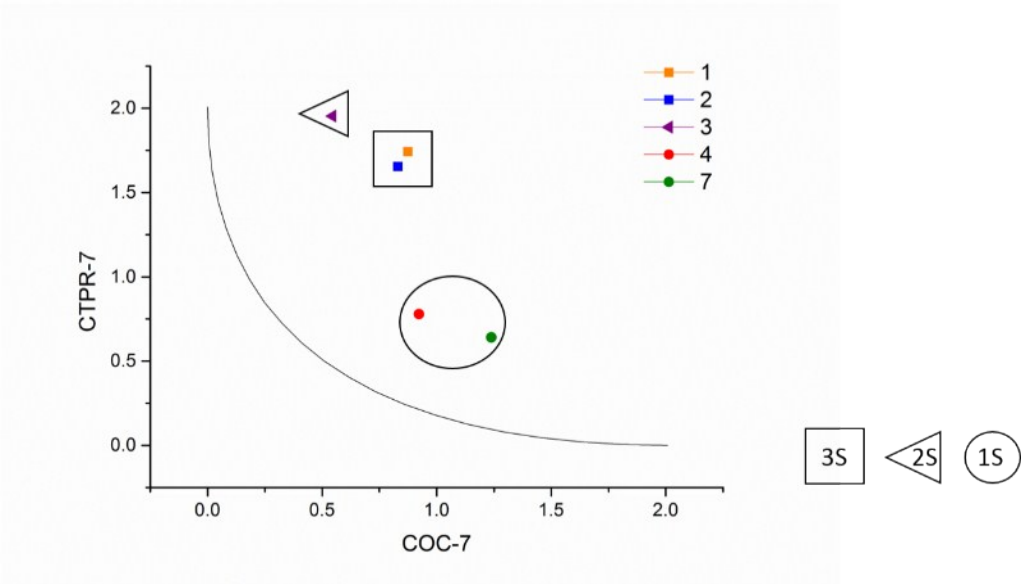

Figure S31 Determination of the geometrical parameters for the coordination sphere of the lanthanoid cations in complexes 1 (orange trace), 2 (blue trace), 3 (purple trace), 4(red trace) and 7 (green trace), with respect to two ideal seven coordinated geometries: capped octahedron (COC) and capped trigonal prism (CTPR).

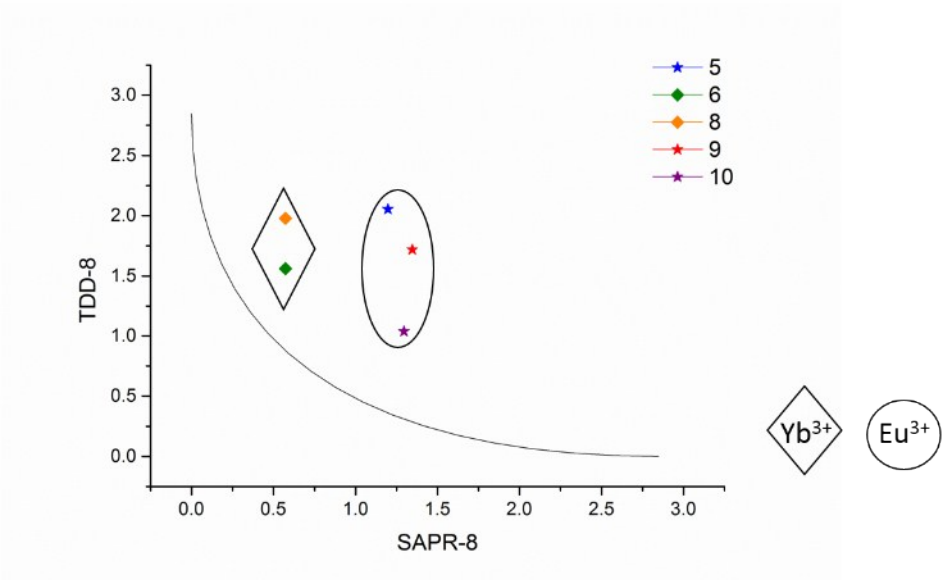

Figure S32 Determination of the geometrical parameters for the coordination sphere of Eu^{3+} (star) and Yb^{3+} (diamond) in complexes 5 (blue trace), 6 (green trace), 8 (orange trace), 9 (red trace) and 10 (purple trace), with respect to two ideal eight coordinated geometries: triangular dodecahedron (TDD) and square antiprism (SAPPR).

Coordination parameters data

Table 2.- CSh) values of the complexes against the reference capped octahedron (COC) and capped trigonal prism (CTPR) and triangular dodecahedron (TDD) and square antiprism (SAPPR) for the seven and eight coordinated geometries, respectively.

Complex	COC-7	CTPR-7	**Complex**	TTD-8	SAPR-8
1	0.87456	1.74336	**5**	2.05306	1.19826
2	0.83017	1.65397	**6**	1.97817	0.8581
3	0.54534	1.95295	**8**	1.56109	0.57236
4	0.92305	0.77807	**9**	1.71699	1.34692
7	1.23820	0.63934	**10**	1.0359	1.29566

Normalised excitation and emission plots

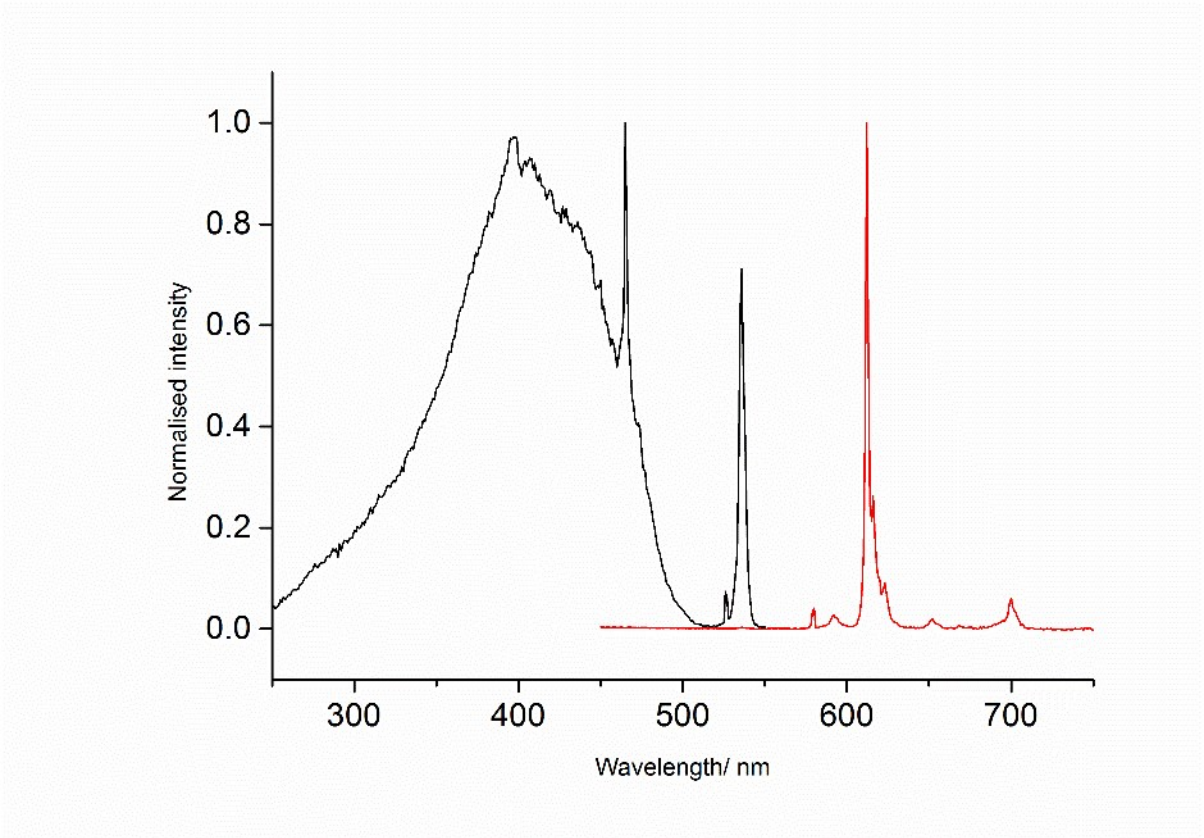

*Figure S33 Excitation (black trace) and emission spectra (red trace) for complex **1** with excitation wavelength at 350nm in the solid state.*

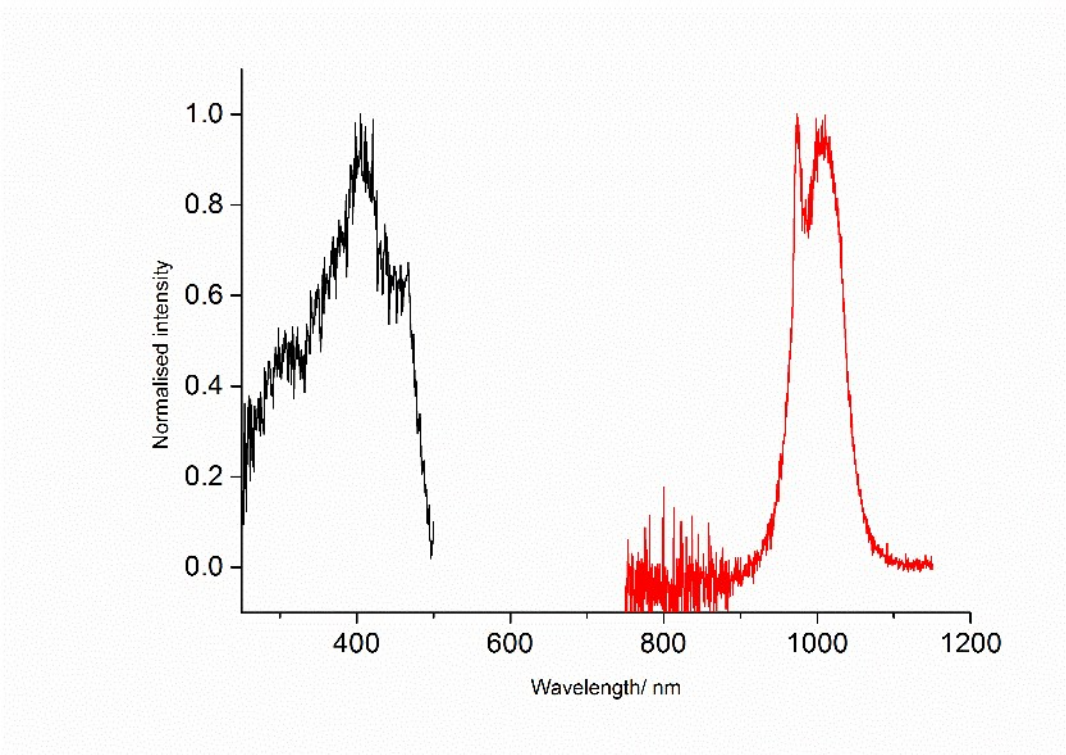

*Figure S34 Excitation (black trace) and emission spectra (red trace) for complex **3** with excitation wavelength at 350nm in the solid state.*

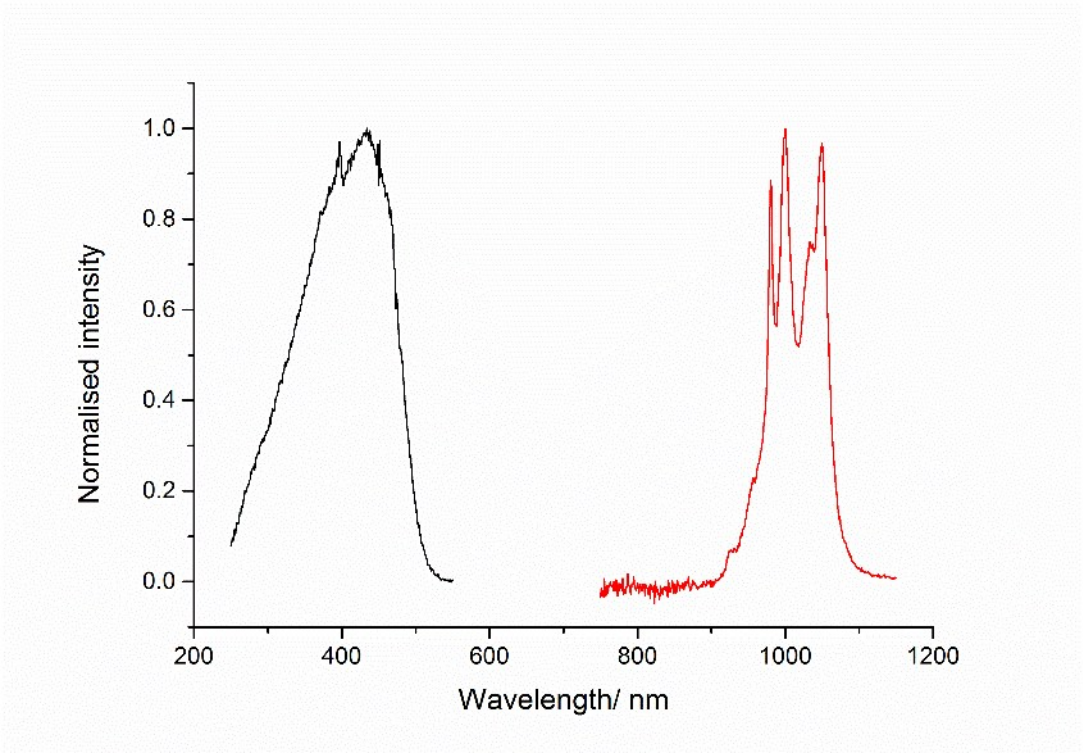

*Figure S35 Excitation (black trace) and emission spectra (red trace) for complex **4** with excitation wavelength at 350nm in the solid state.*

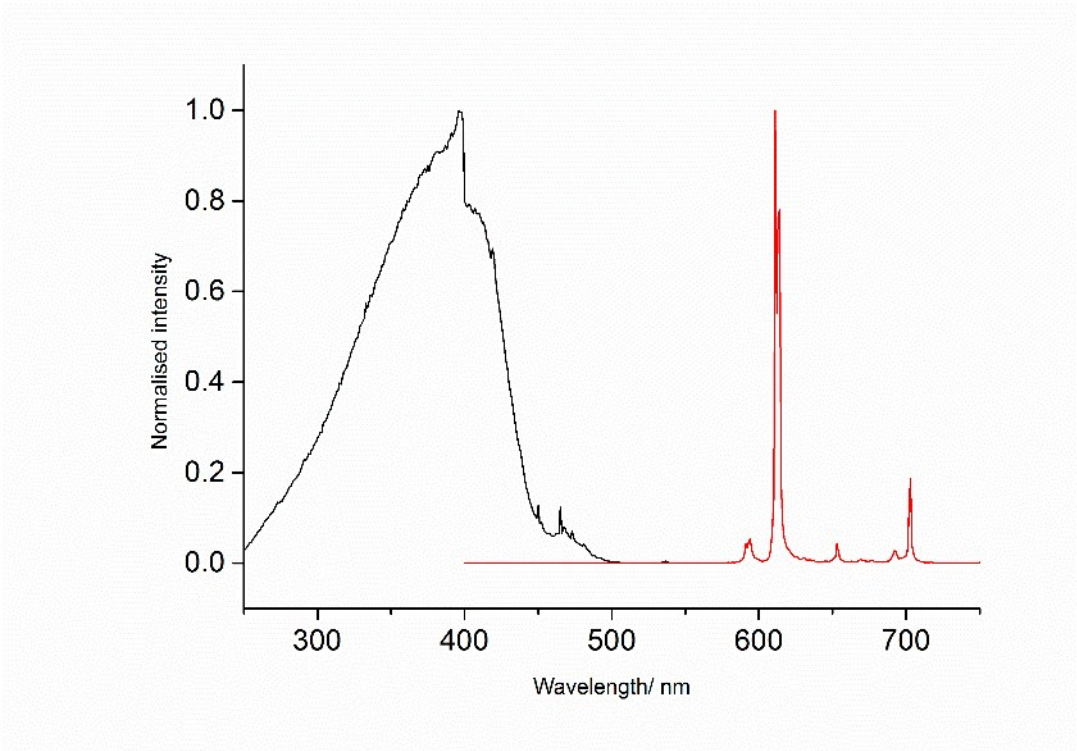

*Figure S36 Excitation (black trace) and emission spectra (red trace) for complex **5** with excitation wavelength at 350nm in the solid state.*

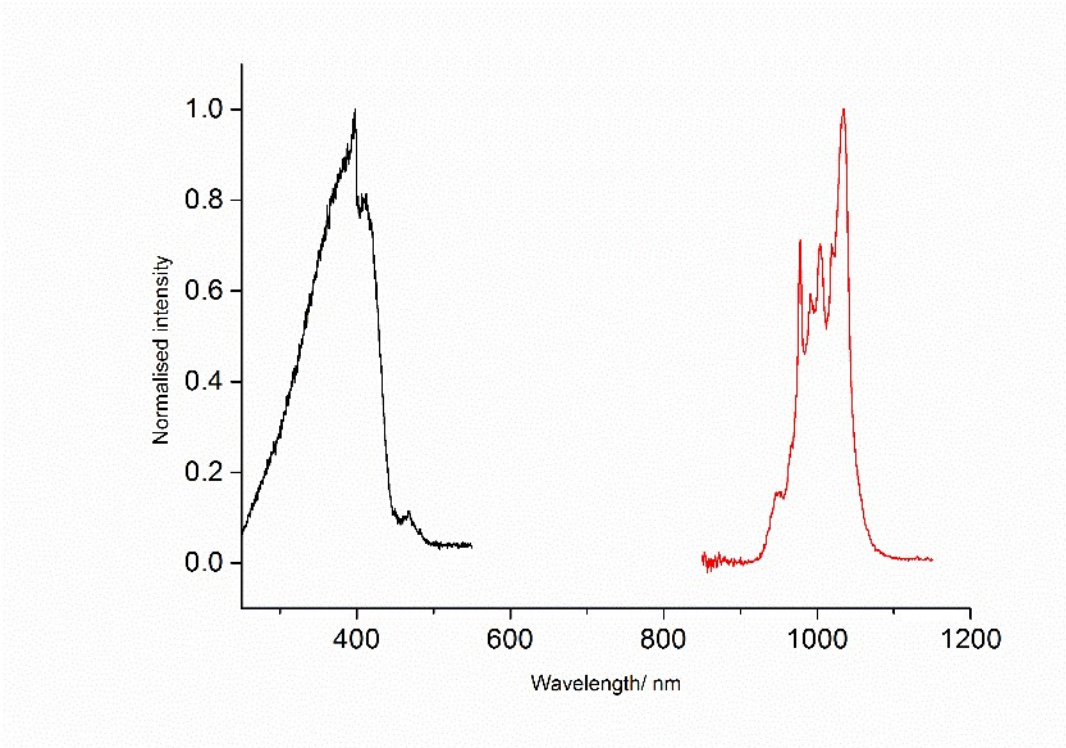

*Figure S37 Excitation (black trace) and emission spectra (red trace) for complex **6** with excitation wavelength at 350nm in the solid state.*

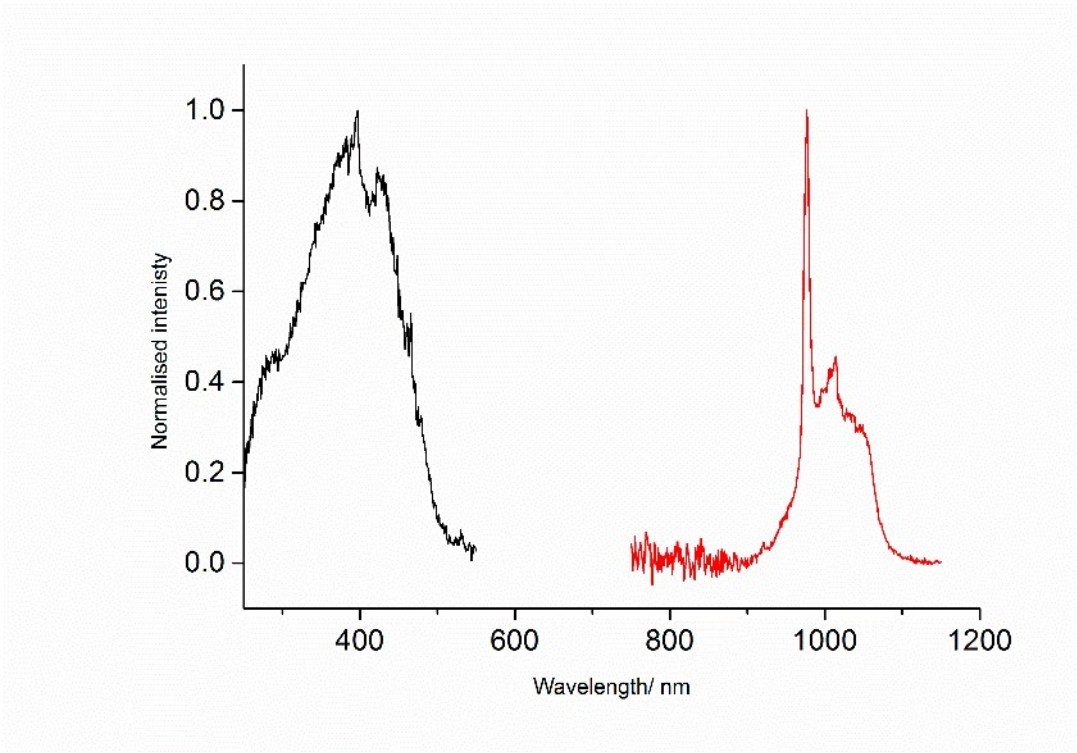

*Figure S38 Excitation (black trace) and emission spectra (red trace) for complex **7** with excitation wavelength at 350nm in the solid state.*

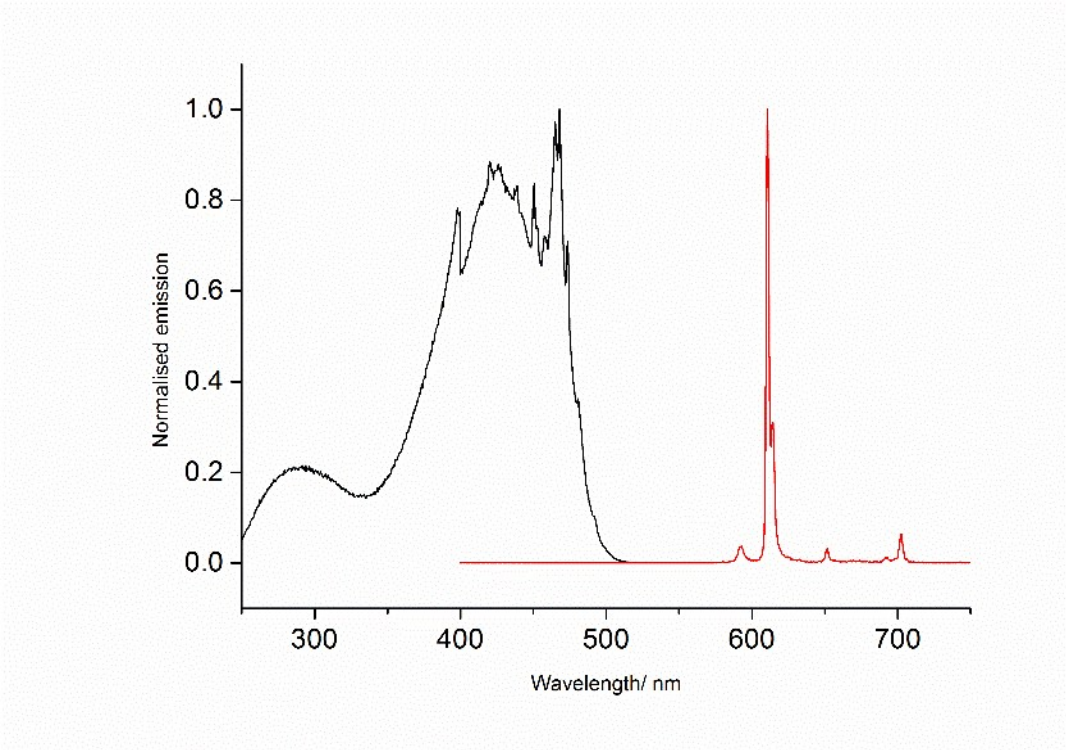

*Figure S39 Excitation (black trace) and emission spectra (red trace) for complex **10** with excitation wavelength at 350nm in the solid state.*

Excited lifetime decay plots

Eu^{3+}

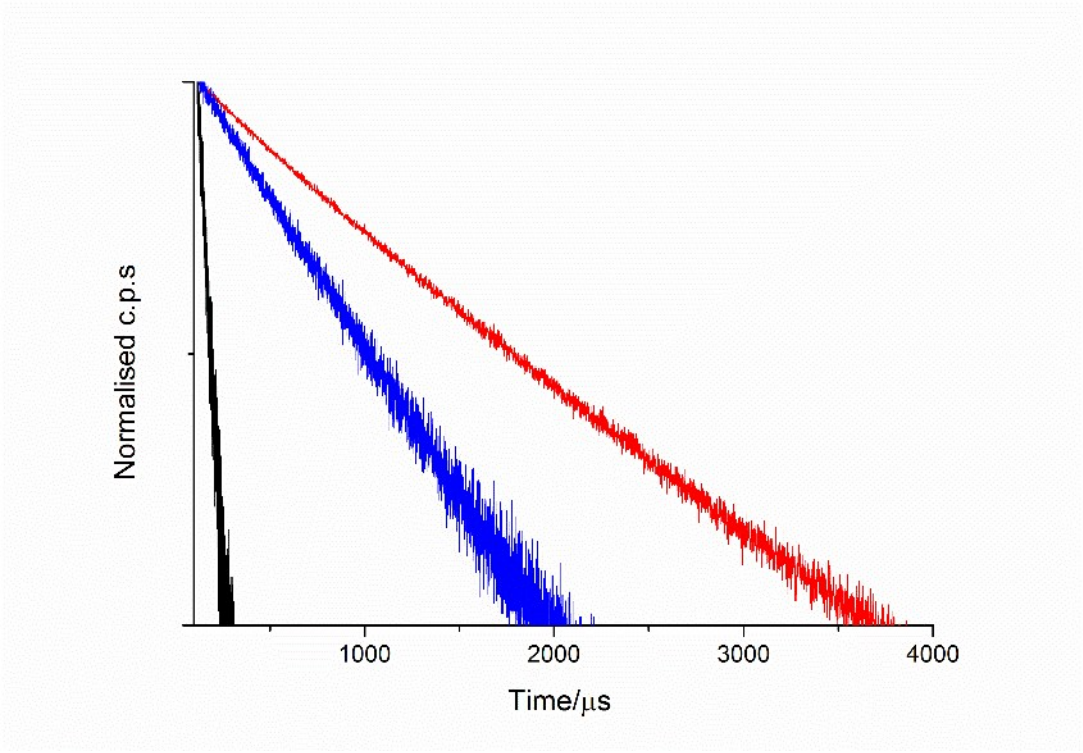

*Figure S40 Lifetime decay at 612nm for complexes **1** (black trace), **5** (red trace), **10** (blue trace) in the solid state at 298K.*

Yb^{3+}

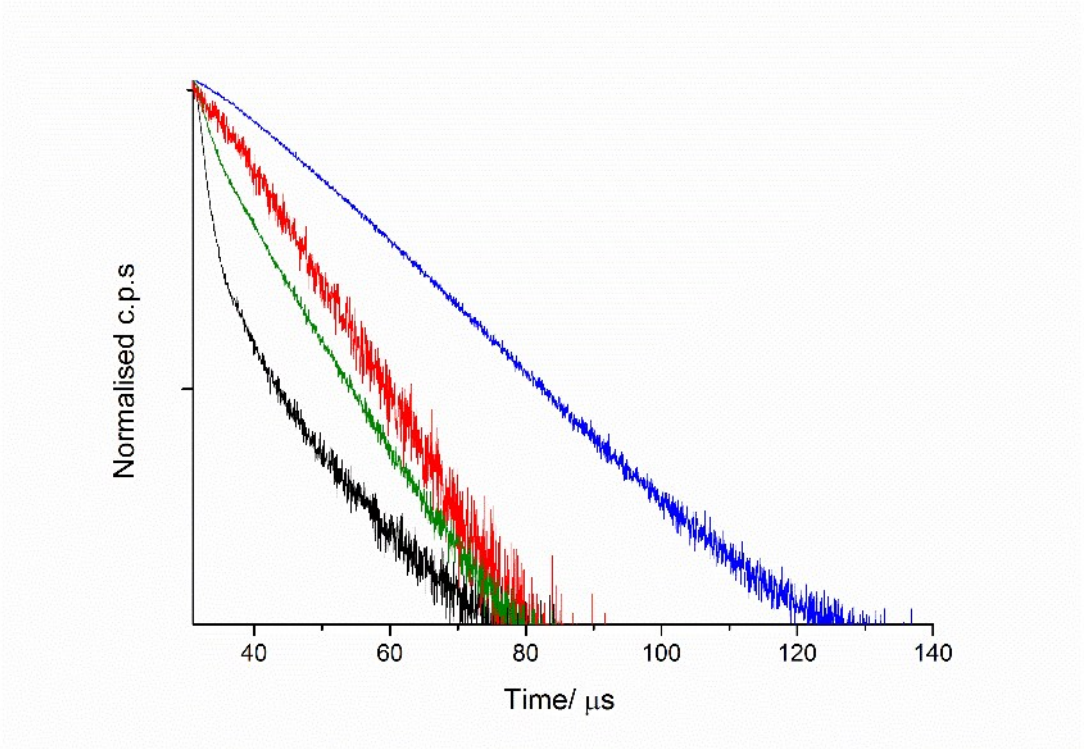

*Figure S41 Lifetime decay at 980nm for complexes **3** (black trace), **4** (red trace), **6** (blue trace), **7** (green trace) in the solid state at 298K.*

References

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(2) Alvarez, S.; Alemany, P.; Casanova, D.; Cirera, J.; Llunell, M.; Avnir, D. *Coord. Chem. Rev.* **2005**, *249*, 1693–1708.