Probing the effect of β-triketonates in visible and NIR emitting lanthanoid complexes

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Characterisation of the [Ln(phen)(dbm)$_3$] complexes

[Eu(phen)(**dbm**)$_3$]: M.p. 141-143 °C, ATR-IR: *v* = 3057 w, 1593 s, 1545 s, 1476 s, 1404 s, 1306 m, 1283 m, 1218 m, 1177 w, 1067 m, 1023 m, 840 w, 782 w, 743 m, 719 s, 684 s, 659 m cm^{-1}. Elemental analysis calcd (%) for $C_{57}H_{41}N_2O_6Eu{\cdot}H_2O$: C, 67.12; H, 4.25; N, 2.75; found: C, 66.74; H, 3.90; N, 2.68. The characterisation matched with reported literature.[1]

[Er(phen)(**dbm**)$_3$]: M.p. 153-155 °C, ATR-IR: *v* = 3057 w, 1594 s, 1548 s, 1513 s, 1477 m, 1456 s, 1411 s, 1286 w, 1177 w, 1065 m, 1023 m, 941 w, 837 m, 741 m, 718 s, 685 s cm^{-1}. Elemental analysis calcd (%) for $C_{57}H_{41}N_2O_6Er{\cdot}H_2O$: C, 66.13; H, 4.19; N, 2.71; found: C, 66.33; H, 3.95; N, 2.68. The characterisation matched with reported literature.[2]

[Yb(phen)(**dbm**)$_3$]: M.p. 172-174 °C , ATR-IR: *v* = 3058 w, 1594 m, 1549 s, 1514 s, 1477 m, 1455 s, 1412 s, 1393 s, 1311 m, 1286 m, 1219 m, 1177 m, 1023 m, 942 w, 784 w. 740 m, 718 s, 685 s cm^{-1}. Elemental analysis calcd (%) for $C_{57}H_{41}N_2O_6Yb{\cdot}H_2O$: C, 65.77; H, 4.16; N, 2.69; found: C, 65.79; H, 3.67; N, 2.67. The characterisation matched with reported literature.[3]

X-ray diffraction studies of [Ho(tbm)$_3$(EtOH)(H$_2$O)]·EtOH

The [Ho(**tbm**)$_3$(EtOH)(H$_2$O)]·EtOH complex (Figure 1) crystallised as a triclinic *P***Error!** structure. The Ho^{3+} cation is eight-coordinate with six O atoms from three bidentate **tbm** ligands, an O atom from a coordinated water molecule, and another O atom from a coordinated ethanol molecule (Figure S1). The coordination geometry is best described as a distorted square antiprism (see Shape Analysis), with one square face consisting of two O atoms from one ligand, and one oxygen atom from a second ligand plus the ethanol molecule, while the other face is similarly coordinated bearing a water molecule in place of the ethanol. There are interesting intermolecular hydrogen bonding interactions which characterise the complex. The OH group of the coordinated ethanol molecule interacts with the O atom of a co-crystallised solvent ethanol. This in turn hydrogen bonds to a third keto O atom of another complex. This occurs in both complexes to form a hydrogen bonded pair with a Ho···Ho distance of 7.93 Å. As well as this interaction, the bound water molecule in each complex binds with a third keto O atom of a *β*-triketonate bound of a different complex, forming a distinct hydrogen bonded pair with a Ho···Ho distance of 8.42 Å. The result is a one-dimensional polymer of hydrogen-bond linked coordination complexes.

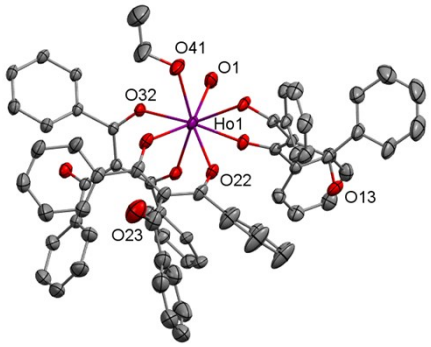

*Figure S1 - Molecular plot of the [Ho(**tbm**)$_3$(EtOH)(H$_2$O)]·EtOH complex. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.*

Shape analysis plot

Geometrical parameters for the coordination sphere of the lanthanoid cations in the complexes [Ln(**phen**)(**dbm**)$_3$] and [Ln(**phen**)(**tbm**)$_3$] were determined. The analysis was carried out considering the degree of distortion with respect to two ideal geometries, square antiprism and triangular dodecahedron (see figure S2), using software developed by Alvarez et al.[4] that allows a mathematical calculation of continuous shape measures (CShM)[5] relative to the ideal geometries shown in the x- and y- axes.

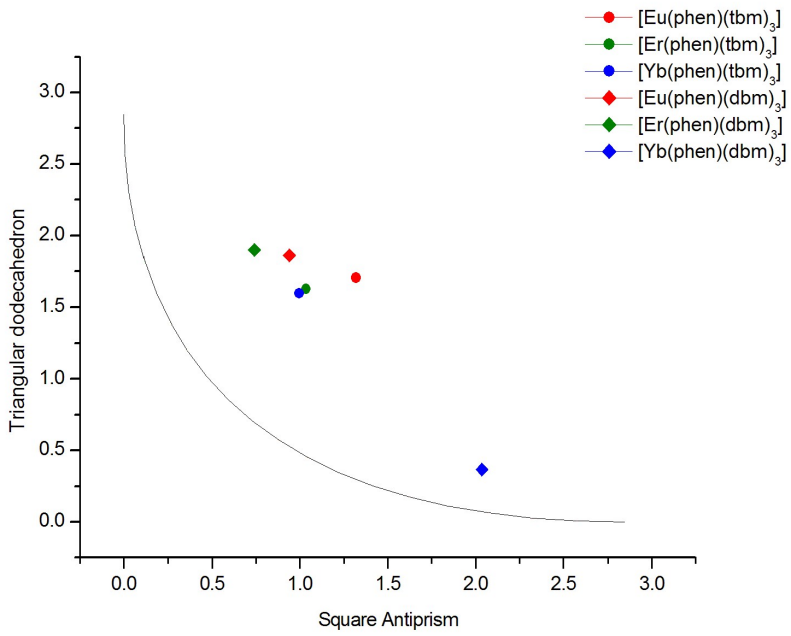

*Figure S2. Shape analysis comparison between Square Antiprism and Triangular Dodecahedron geometries for [Ln(**phen**)(**dbm**)$_3$] and [Ln(**phen**)(**tbm**)$_3$] complexes.*

Table S1.- CShM values for complex according to Square Antiprism(SAPR-) and Triangular dodecahedron (TTD-8)*

Complex	**SAPR-8**	**TTD-8**
[Eu(**phen**)(**tbm**)$_3$]	1.32	1.704
[Eu(**phen**)(**dbm**)$_3$]	0.94	1.86
[Yb(**phen**)(**tbm**)$_3$]	0.996	1.597
[Yb(**phen**)(**dbm**)$_3$]	2.036	0.365
[Er(**phen**)(**tbm**)$_3$]	1.035	1.626
[Er(**phen**)(**dbm**)$_3$]	0.74	1.9

First coordination sphere overlay

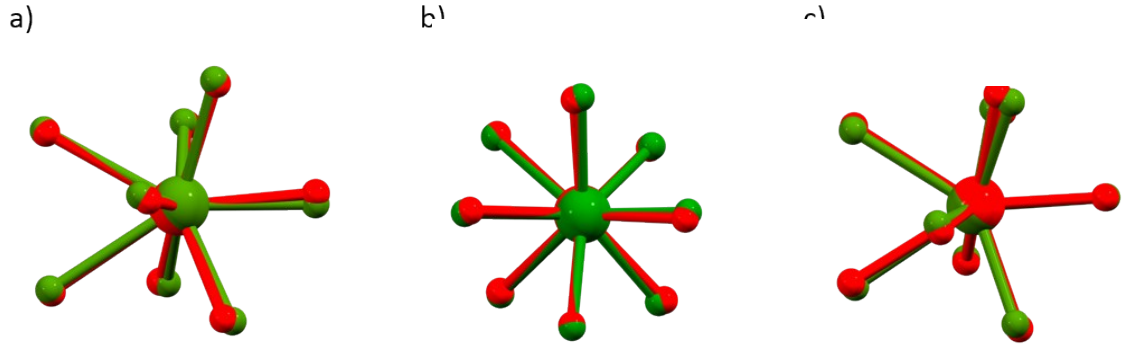

*Figure S3.- First coordination sphere overlay for complexes a) [Eu(**phen**)(**tbm**)$_3$]/ [Eu(**phen**)(**dbm**)$_3$], b) [Er(**phen**)(**tbm**)$_3$]/ [Er(**phen**)(**dbm**)$_3$] and c) [Yb(**phen**)(**tbm**)$_3$]/ [Yb(**phen**)(**dbm**)$_3$]*

[Eu(phen)(tbm)$_3$] emission studies in EtOH

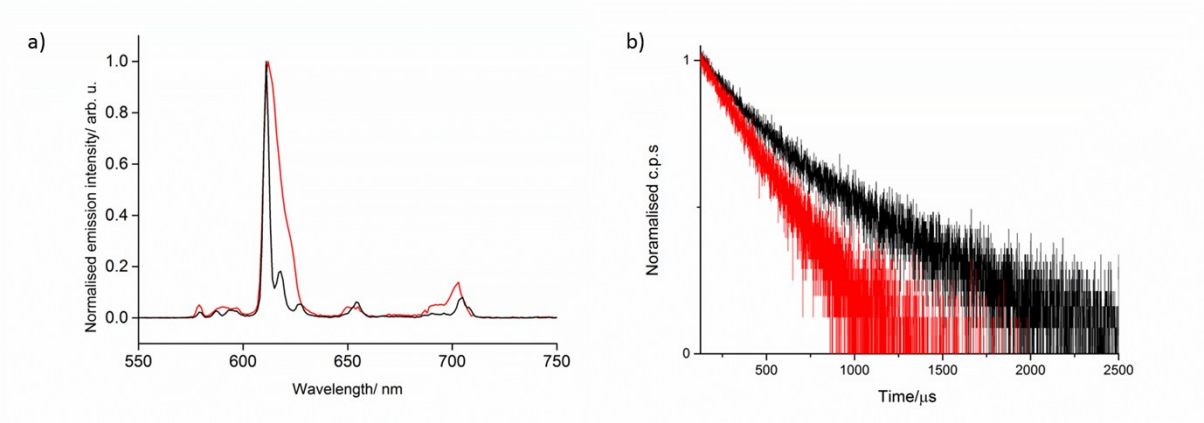

*Figure S4. Normalised emission plot (a) and excited lifetime decays (b) for [Eu(**phen**)(**tbm**)$_3$] in EtOH fresh solution (black trace) and after an hour (red trace).*

Normalised excitation and excited lifetime decay plots for [Ln(phen)(tbm)$_3$] and [Ln(phen)(dbm)$_3$], Ln= Eu^{3+}, Yb^{3+}

The similarities found between the absorbance profile of **tbm** and the excitation spectrum of the complexes, suggest efficient energy transfer from the ligand to the lanthanoid ion. The red shift found in the excitation spectrum for the samples in PMMA and solid state may be due to aggregation occurring in these states.

Same results were found for the **dbm**. However, in this case a pronounce red shift was found between the ligand and the dbm complexes, respectively. This shift may be present due to coordination to the lanthanoid ion, in agreement with literature data.[6]

[Eu(phen)(tbm)$_3$]

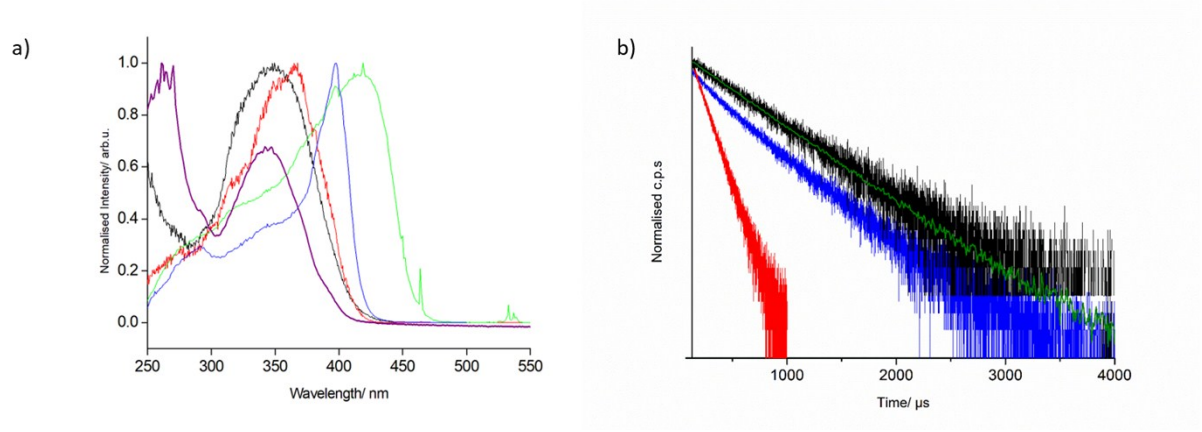

*Figure S5. Normalised excitation (a) and lifetime decay (b) for [Eu(**phen**)(**tbm**)$_3$] in DCM-RT (red trace), 77 K (black trace), PMMA (blue trace) and solid state (green trace) media. . Trace in purple represents the normalised absorbance of **tbm** to highlight the similarities with the excitation spectrum.*

[Eu(phen)(dbm)$_3$]

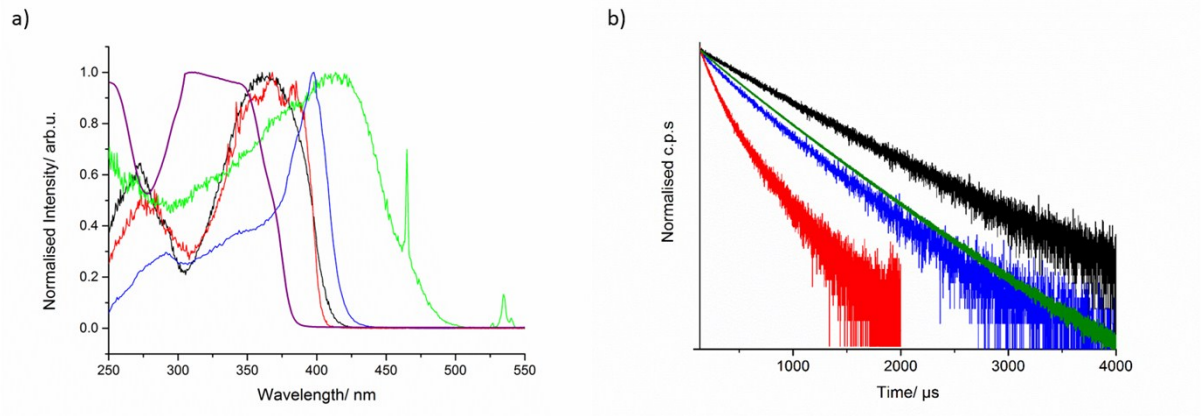

*Figure S6. Normalised excitation (a) and lifetime decay (b) for [Eu(**phen**)(**dbm**)$_3$]in DCM-RT (red trace), 77 K (black trace), PMMA (blue trace) and solid state (green trace) media. . Trace in purple represents the normalised absorbance of **dbm** to highlight the similarities with the excitation spectrum.*

[Yb(phen)(tbm)$_3$]

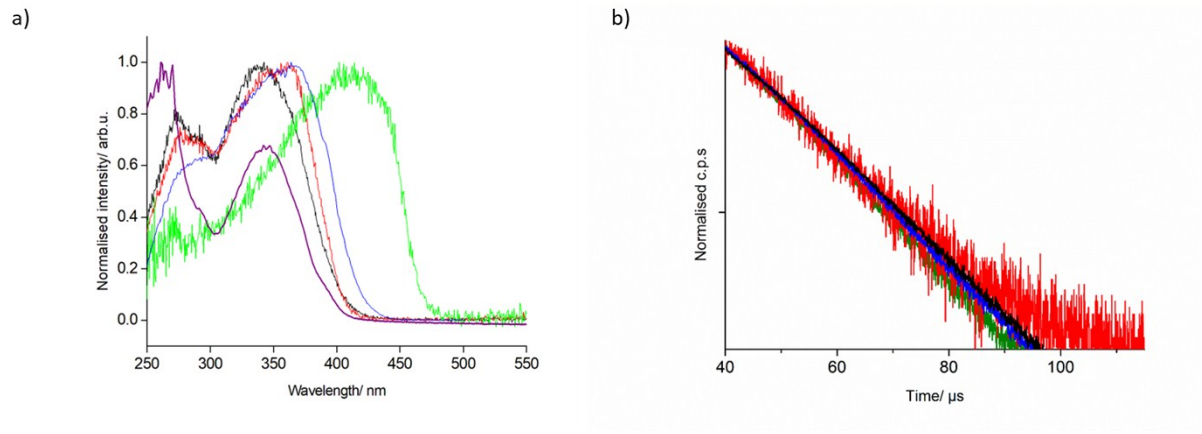

*Figure S7. Normalised excitation (a) and lifetime decay (b) for [Yb(**phen**)(**tbm**)$_3$] in DCM-RT (red trace), 77 K (black trace), PMMA (blue trace) and solid state (green trace) media. Trace in purple represents the normalised absorbance of **tbm** to highlight the similarities with the excitation spectrum.*

[Yb(phen)(dbm)$_3$]

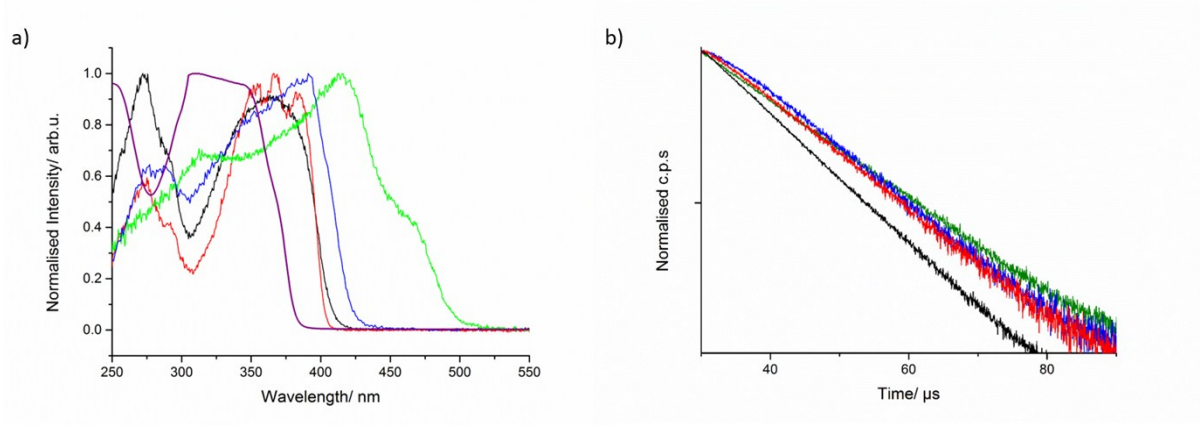

*Figure S8. Normalised excitation (a) and lifetime decay (b) for [Yb(**phen**)(**dbm**)$_3$] in DCM-RT (red trace), 77 K (black trace), PMMA (blue trace) and solid state (green trace) media. . Trace in purple represents the normalised absorbance of **dbm** to highlight the similarities with the excitation spectrum.*

Photophysical properties of Er^{3+}complexes

The emission spectra of both [Er(**phen**)(**tbm**)$_3$] (red trace) and [Er(**phen**)(**dbm**)$_3$] (black trace) in the solid state display NIR emission from the $^4I_{15/2}\leftarrow{}^4I_{13/2}$ transition in the λ=1420 to 1620 nm range (See figure S9). The structure of the emission band varies slightly from both complexes due to relatively different crystal field effects evidenced by shape analysis.

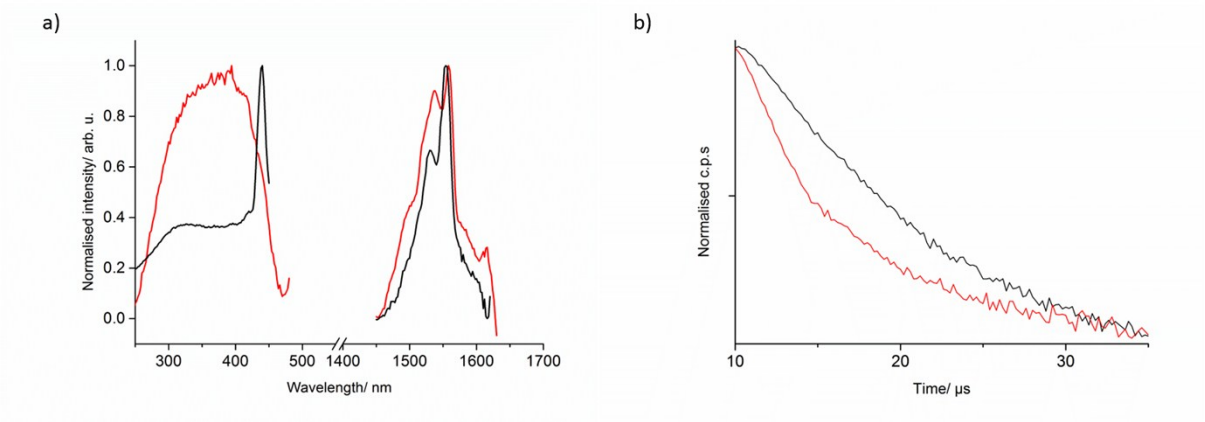

*Figure S9. Excitation-emission spectra (a) and lifetime decay (b) of [Er(**phen**)(**tbm**)$_3$] (red trace) and [Er(**phen**)(**dbm**)$_3$] (black trace) in the solid state at room temperature.*

The observed emission decays for both complexes, [Er(**phen**)(**tbm**)$_3$] and [Er(**phen**)(**dbm**)$_3$], in the solid-state were fitted to a monoexponential function, with the lamp component of the decay removed, giving values of 1.8 and 3.2 µs, respectively. The solid-state radiative decay for the Er^{3+} complexes is assumed to be 660 µs.[7] With this in consideration, the intrinsic quantum yield could be calculated to be 0.48% and 0.27%, respectively.

Table S2. Photophysical data for the Er^{3+} complexes in the solid state.

Complex	τ_{obs} (µs)	τ_R (µs)	Φ_{Ln}^{Ln} (%)
[Er(**phen**)(**dbm**)$_3$]	1.8	660[a]	0.27
[Er(**phen**)(**tbm**)$_3$]	3.2	660[a]	0.48

[a]*Literature* τ_R for Er^{3+} [7]

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