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

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An isomorphous series of lanthanoid complexes containing tribenzoylmethanide (tbm) and 1,10-phenanthroline (phen) ligands has been synthesised and structurally characterised. These complexes, formulated as [Ln(phen)(tbm)]3 (Ln = Eu3+, Er3+ and Yb3+), were compared with analogous dibenzoylmethanide (dbm) [Ln(phen)(dbm)]3 complexes to investigate the effect of changing β-diketone to β-triketone ligands on the photophysical properties of the complex. The photophysical properties for the Eu3+ complexes were similar for both systems, whereas a modest enhancement was observed for Yb3+ and Er3+ moving from the dbm to the tbm complexes. A detailed study of the NIR photophysical properties was achieved by adapting the integrating sphere method for the calculation of overall quantum yields in the solid state.

Introduction

Luminescent trivalent lanthanoid complexes present characteristic intraconfigurational f-f transitions that result in line-like emission profiles and relatively long-lived excited state lifetime decays. Depending on the specific lanthanoid ion, the emission ranges from the visible to the near-infrared (NIR) spectral region. Particular interest in emission from lanthanoid complexes has arisen due to their wide range of applications from bioimaging to night vision technologies and telecommunication signalling.1–5 However, since f-f transitions are parity- and often spin-forbidden, the use of antenna chromophores is required to enhance their luminescence efficiency. In order to have an effective sensitisation and prevent back energy transfer, the lowest triplet state of the antenna needs to lie at ~3,500 cm−1 above the emitting excited states of the lanthanoid.6,7 Furthermore, high energy oscillators in close proximity to the metal centre, such as O-H, N-H and C-H, are able to quench the NIR and visible lanthanoid emitting states.8 Therefore, extra effort in the design of the lanthanoid emitters has been made in order to favour the energy transfer from the antenna and minimise non-radiative decay pathways.9–11 β-Diketonates have been extensively studied because they strongly bind trivalent lanthanoid ions while being able to sensitise their emission according to their chemical nature. A variety of different structural motifs incorporating β-diketonates can be found in the literature over the last couple of decades.12–16 Various strategies have been followed to improve the luminescence properties of the NIR lanthanoid complexes by means of reducing non-radiative decay pathways. These include the perfluorination and deuteration of the β-diketones, extending their π conjugated systems and, in particular, the use of an ancillary ligand in order to replace coordinating solvent molecules.14,15,17–19

In our previous work, we have reported unusual and improved photophysics for the NIR emitters based on the use of β-triketonates as sensitisers. This characteristic motivated us to further investigate β-triketonates as sensitisers for lanthanoid luminescence.

β-Triketonates are of interest because the additional ketone O-donor atom permits the formation of multinuclear metal assemblies. Our previous studies20–22 with tribenzoylmethanide (tbm) and tris(4-methylbenzoyl)methanide (mtbm) ligands showed that tetranuclear assemblies formed upon reaction of these ligands with various lanthanoid salts and in the presence of alkali
metal hydroxides. When the alkali metal (Ae) was Na\(^+\), K\(^+\) or Rb\(^+\) cations, discrete tetranuclear assemblies [Ln(Ae-HOE\text{t})\text{(tmb)}\text{3}]\text{2}\text{+} formed. By contrast, with Cs\(^+\), polymeric structures of the form [(LnCs\text{(tmb)}\text{3})\text{2}], (Ln = Eu\text{3}\text{+}, Er\text{3}\text{+} and Yb\text{3}\text{+}) were isolated.

For both types of structures, remarkably long-lived lifetimes and improved quantum yields were achieved for NIR-emitting assemblies of Er\text{3}\text{+} and Yb\text{3}\text{+} in comparison to complexes containing \(\beta\)-diketonate ligands, even in cases where the diketone had been perfluorinated or deuterated. While the main reason for this improvement may be the reduction of multiphonon relaxation pathways caused by the removal of the proton on the \(\alpha\)-C atom, other structural effects should be taken into account. In order to do so, a system with similar coordination spheres for both ligands, \(\beta\)-diketone and \(\beta\)-triketone, must be found. Given the flexible geometries of lanthanoid complexes, finding systems with negligible variation of the coordination spheres is not an easy task. Moreover, analogous \(\beta\)-diketone-based Ln\text{3}Ae\text{2} assemblies do not exist and so an alternative need to be proposed.

In the present work, we compare a new family of monomeric \(\beta\)-triketonate complexes containing tmb and phen ligands ([Ln\text(phen\text{tmb})\text{3}], Ln = Eu\text{3}\text{+}, Er\text{3}\text{+} and Yb\text{3}\text{+}), with the analogous previously reported dibenzoylmethanthione (dbm) [Ln\text(phen\text{dbm})\text{3}] complexes. Fortunately, in this case, similarities in composition and structure between the \(\beta\)-diketone and \(\beta\)-triketone complexes were found, making it possible to compare more closely their photophysical properties. The monomeric complexes have been studied by absorption and emission spectroscopies. Furthermore, an adapted method was followed for the calculation of the overall quantum yields for the NIR emitters, providing full characterisation of their photophysical properties. The results show only a small enhancement for the NIR \(\beta\)-triketonate-based complexes, suggesting that structural and composition factors must be considered to explain the remarkable properties of the previously reported tetranuclear complexes.

**Experimental**

**General procedures**

All reagents and solvents were purchased from chemical suppliers and used as received without further purification. The ligand precursor 2-benzoyl-1,3-diphenyl-1,3-propandione (tribenzoylmethane - tmbH\text{4}) was prepared as previously reported.\textsuperscript{20} Hydrated LnCl\text{3} (Ln = Eu\text{3}\text{+}, Er\text{3}\text{+} and Yb\text{3}\text{+}) were prepared following a previously reported method by the reaction of the corresponding Ln\text{2}O\text{3} with hydrochloric acid.\textsuperscript{23} Infrared spectra (IR) were recorded on solid state samples using an Attenuated Total Reflectance (ATR) Perkin Elmer Spectrum 100 FT-IR. IR spectra were recorded from 4000 to 650 cm\text{\text{-1}}; the intensities of the IR bands are reported as strong (s), medium (m), or weak (w), with broad (br) bands also specified. Melting points were determined using a BI Barnsted Electrothermal 9100 apparatus. Elemental analyses were obtained at Curtin University (Australia), or the Université de Montréal (Canada). Nuclear magnetic resonance (\(\text{\text{1}}\text{H}\) and \(\text{\text{13}}\text{C}\) NMR) spectra were recorded using a Bruker Avance 400 spectrometer (400.1 MHz for \(\text{\text{1}}\text{H}\); 100 MHz for \(\text{\text{13}}\text{C}\)) at room temperature. The data were acquired and processed by the Bruker TopSpin 3.1 software. All the NMR spectra were calibrated to the residual solvent signals.

**Selected Equations**

In the case of trivalent europium, the value of the radiative lifetime (\(\tau\text{rad}\)) can be calculated using Eqn 1,

\[ \frac{1}{\tau_{\text{rad}}} = 14.65 \text{s}^{-1} \times n^3 \times \frac{I_{\text{rad}}}{J_{\text{tot}}} \]  

(1)

where the value 14.65 s\text{\text{-1}} is the spontaneous emission probability of the \(\text{\text{5}}\text{F}_2\text{→5}D_0\) transition,\textsuperscript{24} \(I_{\text{rad}}\) is the total integration of the Eu\text{3}\text{+} emission spectrum, \(I_{\text{tot}}\) is the integration of the \(\text{\text{5}}\text{F}_2\text{→5}D_0\) transition and \(n\) is the refractive index of the solvent used or assumed value of 1.5 for the solid state.\textsuperscript{25,26}

The intrinsic quantum yield (\(\Phi_{\text{Ln}}\)) can be calculated using Eqn. 2,\textsuperscript{24} where \(\tau_{\text{rel}}\) is the observed excited state lifetime decay.

\[ \Phi_{\text{Ln}} = \frac{\tau_{\text{rel}}}{\tau_{\text{rad}}} \]  

(2)

The sensitisation efficiency (\(\eta_{\text{sens}}\)) can be determined using Eqn.3:

\[ \eta_{\text{sens}} = \frac{\phi_{\text{Ln}}}{\Phi_{\text{Ln}}} \]  

(3)

Overall quantum yields (\(\Phi_{\text{ref}}\)) in solution can be calculated using the optically dilute method proposed by Crosby and Demas\textsuperscript{27}, using Eqn 4:

\[ \Phi_{\text{Ln}} = \Phi_{\text{ref}} \times \frac{I_{\text{ref}}}{A_{\text{ref}}} \times \frac{R_{\text{tot}}}{R_{\text{ref}}} \]  

(4)

where \(\Phi_{\text{ref}}\) is the photoluminescence quantum yield of the reference, \(I\) is the integrated area under the emission spectrum, \(A\) is the absorbance, \(R\) is the refractive index.

**Photophysical Measurements**

Absorption spectra were recorded at room temperature using a Perkin Elmer Lambda 35 UV/Vis spectrometer. Uncorrected steady-state emission and excitation spectra were recorded using an Edinburgh FLSP980-stm spectrometer equipped with a 450 W xenon arc lamp, double excitation and emission monochromators, a Peltier-cooled Hamamatsu R928P photomultiplier (185–850 nm) and a Hamamatsu R5509-42 photomultiplier for detection of NIR radiation (800-1400 nm). Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by a calibration curve supplied with the instrument.
Overall quantum yields in the solid-state were measured with the use of an integrating sphere coated with Benflex. For the overall quantum yield of Yb³⁺ complexes the use of two different detectors, visible and NIR, is required. Therefore, a correction factor, as the ratio of the measured quantum yield to the reported value for a known sample, needs to be applied. To do that, [Yb(phen)(tta)]₃, where tta is thenoyltrifluoroacetone, with an overall quantum yield of 1.6% in toluene was used as the reference. ²⁸

Overall quantum yields in solution were determined by the optically dilute method ²⁷ using Equation 4. Absorption and emission spectra were measured in 10⁻⁵ M dichloromethane solutions by excitation at 350 nm under the same experimental conditions as the standard; air-equilibrated water solution of [Ru(bpy)₂Cl₂], where bpy is 2,2’-bipyridine, (σ_vσ = 2.8%) ²⁷ for Eu³⁺ and [Yb(phen)(tta)]₃ in toluene (σ_vσ = 1.6%) ²⁸ for the Yb³⁺ complexes. Experimental uncertainties are estimated to be ±10% for quantum yields.

Excited-state decays (t) were recorded on the same Edinburgh FLSP980-stm spectrometer using a microsecond flashlamp. The goodness of fit was assessed by minimising the reduced χ² function and by visual inspection of the weighted residuals. Experimental uncertainties are estimated to be ±10%.

To record the luminescence spectra at 77 K, the samples were placed in quartz tubes (2 mm diameter) and inserted in a special quartz Dewar filled with liquid nitrogen. All the solvents used in the preparation of the solutions for the photophysical investigations were of spectrometric grade.

**Synthesis**

The [Ln(phen)(tta)]₃ (Ln³⁺ = Eu, Er, Yb) were prepared in a similar manner by reaction of tta (50 mg, 0.15 mmol), phen (9 mg, 0.05 mmol) and hydrated LnCl₃ (0.05 mmol) in ethanol (10 mL). Triethylamine (23 µL, 0.15 mmol) was added and the mixture was heated at 50 °C for 30 minutes. The resulting mixture was hot filtered and the filtrate left to stand at ambient temperature. Slow evaporation of the solvent over several days afforded yellow crystals in every case.

**[Eu(phen)(tta)]₃**: 20 mg (0.015 mmol) 30%. M.p. 232-233 °C; elemental analysis calcd (%) for C₇₃H₇₃N₂O₂Eu·H₂O: C, 70.32; H, 4.16 N, 2.10; found: C, 70.54; H, 4.09; N, 2.12. ATR-IR: ν = 3058 w, 3024 w, 1642 m, 1583 s, 1537 s, 1448 m, 1428 m, 1366 s, 1310 m, 1292 m, 1275 m, 1176 w, 1154 m, 1101 w, 1072 w, 1027 w, 1013 w, 1000 w, 968 w, 920 w, 895 m, 863 w, 844 w, 823 w, 810 w, 780 w, 743 m, 729 w, 721 w, 692 m, 667 cm⁻¹ w.

**[Er(phen)(tta)]₃**: 18 mg (0.015 mmol) 28%. M.p. 248-249 °C; elemental analysis calcd (%) for C₇₅H₇₅N₂O₂Er·H₂O: C, 69.52; H, 4.11; N, 2.08; found: C, 69.94; H, 3.65; N, 2.17. ATR-IR: ν = 3058 w, 1642 m, 1565m, 1583 m, 1538 s, 1448 m, 1427 w, 1366 s, 1310 m, 1276 m, 1222 w, 1176 w, 1154 m, 1102 w, 1072 w, 1027 w, 1013 w, 1000 w, 968 w, 920 w, 895 m, 863 w, 844 w, 824 w, 812 w, 780 w, 759 m, 729 m, 723 m, 692 s, 667 cm⁻¹ w.

**PMMA materials**

The lanthanoid complexes were dispersed into PMMA samples as described previously. ³⁰

**Crystallography**

Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction Gemini or Xcalibur diffractometer fitted using Mo Kα or Cu Kα radiation. Following absorption corrections and solution by direct methods, the structures were refined against F² with full-matrix least-squares using the program SHELX-97 or SHELX-2014. ³¹ Unless stated below, anisotropic displacement parameters were employed for the non-hydrogen atoms and hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atom. CCDC-1401032 [Eu(phen)(tta)]₃, CCDC- 3000194 [Er(phen)(tta)]₃, CCDC- 1587889 [Yb(phen)(tta)]₃ and CCDC- 3000195 [Ho(tta)(EtOH)·H₂O·1/2(EtOH)] contain supplementary crystallographic data, and can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

**[Eu(phen)(tta)]₃**: Empirical formula C₇₃H₇₃Eu₂O₁₁ · 5H₂O; MW = 1314.18 Å. Triclinic, Space group P1₁, a = 10.5972(3), b = 13.5765(3), c = 21.3722(5) Å, α = 93.095(2)°, β = 93.095(2)°, γ = 93.095(2)°, V = 3060 w, 3024 w, 1642 m, 1583 s, 1537 s, 1448 m, 1428 m, 1366 s, 1310 m, 1292 m, 1275 m, 1176 w, 1154 m, 1101 w, 1072 w, 1027 w, 1013 w, 1000 w, 968 w, 920 w, 895 m, 863 w, 844 w, 823 w, 810 w, 780 w, 743 m, 729 w, 721 w, 692 m, 667 cm⁻¹ w.

**[Er(phen)(tta)]₃**: Empirical formula C₇₅H₇₅Er₂O₁₁ · 5H₂O; MW = 1329.48 Å. λ = 1.54178. Triclinic, Space group P1₁, a = 10.6127(3), b = 13.4533(4), c = 21.3672(7) Å, α = 93.073(2)°, β = 93.073(2)°, γ = 96.098(2)°, V = 3055.38(16) Å³, Z = 2; p_c = 1.493 Mg/m³, μ = 3.169 mm⁻¹, crystal size 0.12 x 0.12 x 0.12 mm³; δ_min, max = 2.5, 32.73°. Reflections collected = 64852, unique reflections = 20096 [R(int) = 0.0355]. Max. and min. transmission = 0.892 and 0.768. Number of parameters = 811, S = 1.044. Final R indices (I>2σ(I)) R₁ = 0.0287, wR₂ = 0.0605; R indices (all data) R₁ = 0.0356, wR₂ = 0.0633. Largest diff. peak and hole = 0.874 and -0.516 e. Å⁻³.

**[Er(phen)(tta)]₃**: Empirical formula C₇₅H₇₅Er₂O₁₁ · 5H₂O; MW = 1329.48 Å. λ = 1.54178. Triclinic, Space group P1₁, a = 10.6127(3), b = 13.4533(4), c = 21.3672(7) Å, α = 93.073(2)°, β = 102.241(2)°, γ = 96.098(2)°, V = 3055.38(16) Å³, Z = 2; p_c = 1.493 Mg/m³, μ = 3.169 mm⁻¹, crystal size 0.12 x 0.07 x 0.05 mm³; δ_min, max = 3.31, 67.27°. Reflections collected = 26571, unique reflections =
104500 $[R\text{int}] = 0.0484$. Max. and min. transmission = 0.864 and 0.738. Number of parameters = 811, $S = 1.000$. Final $R$ indices ($\geq 2\sigma(\text{I})$) $R1 = 0.0460$, $wR2 = 0.1261$; $R$ indices (all data) $R1 = 0.0561$, $wR2 = 0.1332$. Largest diff. peak and hole = 1.45 and $-0.80$ e. Å$^{-3}$.

$[\text{Yb}(\text{phen})(\text{tbm})]_3$

Empirical formula $C_{66}H_{12}YbN_2O_4$: MW = 1335.26. $\lambda = 0.71073$ Å. Triclinic, Space group $P1$,$\overline{1}$, $a = 12.7746(4)$, $b = 13.4190(4)$, $c = 21.3553(7)$ Å, $\alpha = 93.181(2)^\circ$, $\beta = 102.149(3)^\circ$, $\gamma = 96.363(3)^\circ$. Volume = 2951.16(18) Å$^3$, $Z = 2$; $\rho_c = 1.503$ Mg/m$^3$, $\mu = 1.651$ mm$^{-1}$, crystal size 0.39 x 0.19 x 0.105 mm$^3$; $\theta_{\min, \max} = 2.881$ e. Å$^{-3}$. Number of parameters = 812, $S = 1.037$. Final $R$ indices ($\geq 2\sigma(\text{I})$) $R1 = 0.0389$, $wR2 = 0.0758$; $R$ indices (all data) $R1 = 0.0487$, $wR2 = 0.0799$. Largest diff. peak and hole = 1.805 and $-0.803$ e. Å$^{-3}$.

$[\text{Ho}(\text{tbm})]_3(\text{HOEt})(\text{H}_2\text{O})$

Empirical formula $C_{66}H_{18}YbO_4$: MW = 1234.07. $\lambda = 0.71073$ Å. Triclinic, Space group $P1$,$\overline{1}$, $a = 12.7743(4)$, $b = 13.4190(4)$, $c = 21.3553(7)$ Å, $\alpha = 93.181(2)^\circ$, $\beta = 102.149(3)^\circ$, $\gamma = 96.363(3)^\circ$. Volume = 2951.16(18) Å$^3$, $Z = 2$; $\rho_c = 1.503$ Mg/m$^3$, $\mu = 1.651$ mm$^{-1}$, crystal size 0.39 x 0.19 x 0.105 mm$^3$; $\theta_{\min, \max} = 2.881$ e. Å$^{-3}$. Number of parameters = 812, $S = 1.037$. Final $R$ indices ($\geq 2\sigma(\text{I})$) $R1 = 0.0389$, $wR2 = 0.0758$; $R$ indices (all data) $R1 = 0.0487$, $wR2 = 0.0799$. Largest diff. peak and hole = 1.805 and $-0.803$ e. Å$^{-3}$.

Results and discussion

Tribenzoylmethane (tbmH) was synthesised according to a literature procedure, whereby dibenzoylmethane (dbmH) was reacted with benzoic anhydride in dry diethyl ether.

Previous methods for the synthesis of β-triketonate complexes present two alternatives: the use of alkali hydroxides to form the tetranuclear assemblies, or triethylamine, which results in mononuclear complexes. However, in the latter work reported by Ismail et al., the complex formulated as $[\text{Eu}(\text{tbm})_3(\text{HOEt})(\text{H}_2\text{O})]$ was assigned only from elemental and thermal analyses in the absence of any structural characterisation via X-ray diffraction. In an attempt to synthesise and crystallise analogous mononuclear complexes with the use of triethylamine, hydrated LnCl$_3$ salts (Ln = La$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Ho$^{3+}$, Yb$^{3+}$) were reacted with three equivalents of tbmH and triethylamine in ethanol at 50 °C. An appropriately crystalline product was only obtained in the case of HoCl$_3$, where slow evaporation of the solvent over several days resulted in the formation of yellow single crystals. Analysis of the product by single crystal X-ray diffraction revealed the first structurally characterised mononuclear triketonate structure, $[\text{Ho}(\text{tbm})_3(\text{HOEt})(\text{H}_2\text{O})]$·EtOH, consistent with the composition proposed by Ismail et al. (see Electronic Supporting Information). In the other cases, only amorphous powders were obtained with analogous spectroscopic data.

While this result confirmed the structures first assigned to these complexes, it was necessary to remove solvent molecules from the first coordination sphere to improve their photophysical properties. Hence, $[\text{Ln}(\text{phen})(\text{dbm})]_3$ and $[\text{Ln}(\text{phen})(\text{tbm})]_3$ complexes (Ln = Eu$^{3+}$, Er$^{3+}$, Yb$^{3+}$) were prepared by the addition of tbmH, phen, and hydrated LnCl$_3$ with triethylamine to hot ethanol (Figure 1). After filtration, slow evaporation of the solvent resulted in the formation of suitable crystals for X-ray diffraction for the $[\text{Ln}(\text{phen})(\text{tbm})]_3$ (Ln$^{3+}$ = Eu$^{3+}$, Er$^{3+}$, Yb$^{3+}$). The formulation of the resulting solids was confirmed by elemental analysis and IR spectroscopy.

The previously reported $[\text{Ln}(\text{phen})(\text{dbm})]_3$ complexes were prepared following a slightly modified procedure. Reaction of dbmH, phen, and hydrated LnCl$_3$ with triethylamine in ethanol at 50 °C resulted in pale yellow solids, which were filtered, washed with ethanol and dried in vacuo. The formulation of the resulting solids was supported by elemental analysis, with the consistent inclusion of one equivalent of water, presumably incorporated from atmospheric water upon isolation of the crystals from solution.

X-ray diffraction studies

The $[\text{Ln}(\text{phen})(\text{tbm})]_3$ (Ln = Eu$^{3+}$, Er$^{3+}$, Yb$^{3+}$) complexes are isostructural, crystallising as triclinic structures in the $P1$,-$\overline{1}$ space group (Figure 2). The Ln$^{3+}$ cations are eight-coordinate by six O atoms from three tbm ligands and two N atoms from the coordinated phen molecule. The coordination geometry is best described as a distorted square antiprism. A supramolecular dimer, situated about an inversion centre, is formed through π-stacking of phen ligands of two adjacent complexes, with a distance of ~3.26 Å between the π-stacked planes of the phen ligands. These interactions result in a Ln–Ln distance in a range of 9.21-9.25 Å, a distance which
The [Ln(phen)(dbm)]$_3$ (Ln = Eu$^{3+}$, Er$^{3+}$, Yb$^{3+}$) crystal structures have been previously reported in the literature. Similarly to the [Ln(phen)(tbm)]$_3$ complexes, the Ln$^{3+}$ ion is coordinated by six O atoms from three dbm ligands and two N atoms from the coordinated phen molecule. Unlike the tbm series, the dbm complexes are not isomorphous. Nevertheless, the Ln···Ln distances are greater than 9 Å in all of these complexes and thus cross relaxation pathways are not expected to influence one series of complexes more than the other in the solid state.

Most importantly for this study, the coordination spheres of the complexes of each lanthanoid cation are quite similar. Overlaying the primary coordination sphere structures for the dbm and tbm complexes of each metal gave RMSD for the overlay and the maximum distance between two equivalent atoms (Max. D) as follows: Eu, RMSD 0.1230, Max D 0.1964; Er, RMSD 0.0939, Max D 0.1338; Yb, RMSD 0.2146, Max D 0.3583 Å. The overlaid structures are shown in the Supporting Information. Shape analysis, comparing the distortion from idealised coordination geometries, were consistent with these results, with the Yb pair of complexes showing the greatest differences in structure.

Photophysical investigation

The photophysical properties for [Ln(phen)(tbm)]$_3$ (Ln = Eu$^{3+}$ and Yb$^{3+}$) including excited state lifetime decays ($\tau_{obs}$), calculated radiative lifetime decays ($\tau_r$), intrinsic photoluminescence quantum yields ($\Phi_{LUM}$), overall photoluminescence quantum yields ($\Phi_{LUM, tot}$), and sensitisation efficiency ($\eta_{sens}$) are summarised in Table 2.

The energies of the $^5\pi^*$ excited states of the dbm and tbm ligands were estimated at the 0-phonon transition from the phosphorescence of the Gd$^{3+}$ complexes in a frozen dichloromethane solution at 77 K. These energies were calculated to be 20,350 cm$^{-1}$ and 20,704 cm$^{-1}$, respectively, in agreement with the literature values. The $^5\pi^*$ state energy of the phen ligand has been previously reported at 21,050 cm$^{-1}$ in the presence of hydrated GdCl$_3$. These $^5\pi^*$ states are of high enough energy to sensitise NIR metal-centred emission from Er$^{3+}$ and Yb$^{3+}$. The similarities between the excitation spectra and the absorption profiles of the tbm/dbm ligands and phen ligands support the conclusion that the emission from the lanthanoid cations originates through sensitisation from the coordinated ligands (see Supporting Information). Given the large energy difference between the energy of the $^5\pi^*$ and $^3F_{5/2}$ excited state of Yb$^{3+}$, energy transfer in this case could be mediated by a ligand-to-metal charge transfer state (LMCT). In the case of Eu$^{3+}$, energy transfer will usually occur to the $^5D_0$ (~19,000 cm$^{-1}$) or $^5D_1$ (~19,000 cm$^{-1}$) states. Sato and Wada have reported that for efficient funneling of the energy to the $^5D_1$ state, an energy difference of 1,500 cm$^{-1}$ is sufficient. Therefore in our systems, energy transfer is likely to occur to both excited states.

The measurements were performed on neat solids or with the complexes dispersed within a transparent PMMA matrix following a previously reported procedure. The obtained data were also compared with measurements performed in ca. 10$^{-5}$ M dichloromethane solutions at room temperature and at 77 K. Dichloromethane was used as a non-coordinating solvent, as the structure was not preserved in polar coordinating solvents such as ethanol due to ligand exchange (see Supporting Information). The photophysical properties of [Er(phen)(tbm)]$_3$ were only studied in the solid state as this complex was almost non-emissive from solution at room temperature (see Supporting Information).

Europium Complexes. The combined emission spectra for the Eu$^{3+}$ complexes are shown in Figure 3. The emission spectrum of [Eu(phen)(tbm)]$_3$ in the solid state displays the five characteristic Eu$^{3+}$ emission bands attributed to $^7F_{7/2}$ transitions in the region of 580-750 nm. The low intensity $^7F_{5/2}$ band has a full-width at half-maximum (FWHM) of 35
cm\(^{-1}\), indicative of one unique emitting species.\(^\text{46}\) The \(^7\)F\(_2\leftarrow^5\)D\(_0\) transition is split into three easily distinguishable bands, two of which are very close in energy. This splitting is inherent for a local Eu\(^{3+}\) symmetry lower than D\(_{5h}\).\(^\text{46}\) This is consistent with the observed splitting in the \(^7\)F\(_2\leftarrow^5\)D\(_0\) band and the high integral ratio (13.5) of this band with respect to the \(^7\)F\(_2\leftarrow^5\)D\(_0\). Low symmetry is observed as well in the crystal structure where the ideal square antiprismatic geometry is distorted, with a symmetry lowered due to the N-donor ligand.

The emission spectrum for the \([\text{Eu(phen)(tbm)}]\) in the solid state is in agreement with the literature, showing the five characteristic Eu\(^{3+}\) bands associated with \(^7\)F\(_{J}\leftarrow^5\)D\(_0\) (\(J = 0-4\)) transitions. The \(^7\)F\(_2\leftarrow^5\)D\(_0\) band has a FWHM of 27 cm\(^{-1}\), which again indicates the presence of only one unique emitting Eu\(^{3+}\) centre. The \(^7\)F\(_2\leftarrow^5\)D\(_0\) transition is split in two different bands because of the crystal field effects. The splitting of the band is lower than for \([\text{Eu(phen)(dbm)}]\), revealing higher symmetry in this case, which is in agreement with the results found with the shape analysis, where the \([\text{Eu(phen)(dbm)}]\) complex is less distorted from square antiprismatic geometry compared to the analogous complexes bound to \(\text{tbm}\) (see Supporting Information).\(^\text{39}\)

The \([\text{Eu(phen)(tbm)}]\) excited state decay was found to be monoexponential (see Supporting Information), giving an excited state lifetime (\(\tau_{\text{obs}}\)) value of 0.55 ms. The radiative decay (\(\tau_{\text{r}}\)) could be estimated from the emission spectrum to be 1.03 ms. From these data, the intrinsic quantum yield (\(\Phi_{\text{intr}}\)) was calculated to be 53%. The overall quantum yield was measured to be 45% by an absolute method using an integrating sphere, leading to a sensitisation efficiency (\(\eta_{\text{sens}}\)) of 82%. This value is slightly improved in comparison to our previous report on the assemblies that involved only \(\text{tbm}\) ligands (~70%),\(^\text{21}\) and thus may be due to more efficient sensitisation via the \(\text{phen}\) ligand upon excitation at 350 nm. The values of \(\tau_{\text{obs}}, \tau_{\text{r}},\) and \(\Phi_{\text{intr}}\) for the \([\text{Eu(phen)(dbm)}]\) were found to be very similar to the \(\text{tbm}\) complex at 0.48 ms, 0.96 ms and 50%, respectively, with an overall quantum yield (\(\Phi_{\text{intr}}\)) of 55% and a virtually quantitative sensitisation efficiency,\(^\text{28}\) within experimental error, associated with the quantum yield measurement. These data indicate that the introduction of the extra ketone group at the \(\alpha\)-carbon of the \(\beta\)- diketone does not significantly affect the emission behaviour for Eu\(^{3+}\) complexes, and the photophysical properties for the \(\beta\)- diketone and \(\beta\)- triketone complexes are comparable. This is not surprising, as the \(\alpha\)-CH bond is not an efficient quencher of the \(^5\)D\(_0\) excited state.

As both systems behave similarly across every medium, and the data for the \([\text{Eu(phen)(dbm)}]\) are in agreement with the literature,\(^\text{33}\) only the photophysical properties of the \([\text{Eu(phen)(tbm)}]\) complexes will be discussed from here on.

The emission properties of \([\text{Eu(phen)(tbm)}]\) and \([\text{Eu(phen)(dbm)}]\) in PMMA were studied in order to assess any possible contribution of energy migration between Eu\(^{3+}\) centres in the neat solid. Only in the case of \([\text{Eu(phen)(tbm)}]\) was there an indication of slightly different splitting of emission bands compared to the solid state that may be due to a different geometry of the ligands around the lanthanoids centre in the dispersed medium. The values of \(\tau_{\text{obs}}, \tau_{\text{r}},\) and \(\Phi_{\text{intr}}\)
are 0.43 ms, 1.09 ms, and 43%, respectively. These data show similar values to those in neat solids, suggesting that concentration quenching does not affect the solid-state emission properties.

![Figure 3 - Normalised emission plots for a) [Eu(phen)(tbbm)] and b) [Eu(phen)(dbm)] in solid state (green trace), DCM solution (10-5M) (red trace), 77K (black trace) and PMMA (blue trace), with excitation wavelength at 350 nm.](image)

The [Eu(phen)(tbbm)] complex in dichloromethane solution at room temperature shows characteristic emission from the Eu$^{3+}$ 5D0 state, similar to the spectrum observed in PMMA. All the emission lines were less defined due to higher degrees of freedom of the ligands in solution at room temperature. However, when the solution formed a glass at 77 K, the emission structure was similar to that observed in PMMA with no significant changes. The FWHM of the $^7F_0 \leftrightarrow 5D_0$ transition are 82 cm$^{-1}$ and 26 cm$^{-1}$ at room temperature and 77 K, respectively. In the frozen glass, the $^7F_0 \leftrightarrow 5D_0$ transition is split into three bands, two of them very close in energy comparable to the dispersed medium.

Excited state lifetime decays ($\tau_{\text{em}}$) of [Eu(phen)(tbbm)] in dichloromethane solution were measured to be 0.12 ms and 0.55 ms at room temperature and 77 K, respectively (see Supporting Information). The radiative decay ($\tau_0$), the intrinsic ($\Phi_{\text{In}}$) and overall quantum yield ($\Phi_{\text{Ln}}$) at room temperature were determined to be 1.08 ms, 12% and 0.58%, which leads to a sensitisation efficiency ($\eta_{\text{sen}}$) of 5%. These data are consistent with those reported for [Eu(phen)(dbm)] in dichloromethane solution, suggesting similar behaviour of both systems in solution. The significantly short lifetimes found at room temperature with respect to the 77K may be explained by a more efficient vibrational quenching of the $^3D_0$ excited state favoured due to a higher configurational lability in solution. The reduction in the overall quantum yield, in comparison to that in the solid state, is suggestive of a poor sensitisation efficiency of the ketonates in solution which may suggest quenching of the triplet state of tbbm in agreement with previous literature.\(^{33}\)

These results demonstrate that both β-diketonate and β-triketonate systems behave similarly in every media, thereby confirming that the α-CH bond is not an efficient quencher of the $^3D_0$ excited state. However, the poor emission properties of both systems in solution, in comparison with the neat solids, suggest efficient quenching processes taking place and poor sensitisation properties of these ketonates.

**Ytterbium complexes.** The combined emission spectra for the Yb$^{3+}$ complexes are shown in Figure 4. The emission spectrum of the [Yb(phen)(tbbm)] complex in the solid state shows characteristic NIR emission from the $^2F_{7/2} \leftrightarrow ^2F_{5/2}$. This transition is split into four main bands at 976, 1011, 1029 and 1043 nm due to crystal field effects. The splitting of the $^2F_{7/2} \leftrightarrow ^2F_{5/2}$ transition in the case of the [Yb(phen)(dbm)] is slightly different with three main bands at 976, 1007 and 1039 nm. This may be due to different degrees of distortion between the two coordination spheres, which were the largest differences observed amongst the three pairs of complexes. This is also in accordance with the results found in the shape analysis study, where it was shown that [Yb(phen)(tbbm)] is best described as a distorted square antiprism, while the best description of the geometry for [Yb(phen)(dbm)] is a distorted triangular dodecahedron (see Supporting Information).

The observed lifetime decays ($\tau_{\text{em}}$) for [Yb(phen)(tbbm)] and [Yb(phen)(dbm)] complexes in the solid state were fitted to monoexponential functions, giving values of 15.9 and 11.3 µs, respectively. The excited state lifetime is slightly higher in the case of the [Yb(phen)(tbbm)]. Overall quantum yields ($\Phi_{\text{In}}$) were measured with the help of an integrating sphere using two different detectors: visible and NIR. In order to do so, [Yb(phen)(tta)] with $\Phi_{\text{In}}=1.6\%$,\(^{28}\) was used as a reference to calibrate the system. The value of $\Phi_{\text{In}}$ for the previous reported complex, [Yb(phen)(dbm)] in toluene was found to be 0.62%, in accordance with the literature value of 0.59%\(^{28}\). The $\Phi_{\text{In}}$ of the [Yb(phen)(tbbm)] and [Yb(phen)(dbm)] in the solid state were determined to be 3.64 and 2.91%, respectively, showing a small enhancement for the tbbm complex due to reduction of non-radiative decay pathways.\(^{20}\)

As for the Eu$^{3+}$ complexes, the photophysical properties of the [Yb(phen)(tbbm)] and [Yb(phen)(dbm)] in PMMA were
studied. The emission spectrum of \([\text{Yb}(\text{phen})(\text{tbm})_3]\) shows emission from the \(^2F_{7/2} \leftarrow ^2F_{5/2}\) transition with a slightly different splitting of the band due to small differences in the coordination sphere. The values of observed lifetimes decay (\(\tau_{\text{obs}}\)) are similar to the ones found in the solid state.

These results indicate that the additional ketone group at the \(\alpha\)-carbon of the \(\beta\)-diketone has an effect on the emission behaviour for \(\text{Yb}^{3+}\) complexes, and the photophysical properties for the \(\beta\)-triketonate complexes are slightly enhanced. That is not surprising because the \(\alpha\)-CH bond is an efficient quencher of the \(^2F_{5/2}\) excited state. However, the values found for the monomeric species do not rival the photophysics of the previously reported tetracnuclear assemblies, suggesting that the assemblies present an environment strongly protected from multiphonon relaxation.

**Conclusions**

We report here, three new mononuclear eight-coordinate \(\text{Eu}^{3+}, \text{Er}^{3+}\) and \(\text{Yb}^{3+}\) complexes with tribenzoylmethanide (\(\text{tbm}\)) and phenanthroline (\(\text{phen}\)) ligands, of the general formula \([\text{Ln}(\text{phen})(\text{tbm})_3]\). This work has focussed on a direct comparison with the analogous \([\text{Ln}(\text{phen})(\text{dbm})_3]\) complexes, in order to better understand the effect on the photophysical properties of the replacement of the \(\alpha\)-CH in \(\beta\)-diketonates with an additional ketone functional group to give \(\beta\)-triketonates.

The emission profiles, excited state lifetimes and quantum yields for \(\text{Eu}^{3+}\) revealed similar behaviour for both systems. Particularly short lifetimes were found in solution, suggestive of efficient deactivation pathways of the excited states via non-radiative decay. On the other hand, a small enhancement was observed for \(\text{Yb}^{3+}\) moving from the \(\text{dbm}\) to the \(\text{tbm}\) system, probably because of reduced multiphoton quenching. However, these values do not rival the photophysical properties of the previously reported assemblies\(^{20-22}\), suggesting that simply replacing \(\beta\)-diketonates with \(\beta\)-triketonate ligands in similar complex structures is not likely to enhance photophysical properties. The remarkable properties of the tetracnuclear assemblies presumably are linked to other factors that arise from their structure and composition.

**Conflicts of interest**

The authors declare no conflict of interest.

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Notes and references