Energy Transfer Between Eu$^{3+}$ and Nd$^{3+}$ in Near-Infrared Emitting β-Triketonate Coordination Polymers

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Isomorphous β-triketonate-based lanthanoid polymers containing tris(4-methylbenzoyl)methanide (mtbm) and Rb+ with formula, $[\text{Ln}(\text{Rb})(\text{mtbm})]_{n}$, (Ln = Eu$^{3+}$ and Nd$^{3+}$) have been synthesised and structurally characterised. The photophysical properties for the Nd$^{3+}$ complex presented long lifetimes and relatively high quantum yields in comparison with analogous β-diketonate complexes. Mixed lanthanoid complexes were also formed and their luminescence properties studied, with effective sensitisation of the $^4F_{3/2}$ of Nd$^{3+}$ via the $^2D_{5/2}$ of Eu$^{3+}$, which is to the best of our knowledge the first example of Eu$^{3+}$ to Nd$^{3+}$ sensitisation in a coordination complex or polymer.

Introduction

Much attention has been paid to materials incorporating trivalent lanthanoid cations due to their unique photophysical properties such as their line-like emission spectra and their long-lived excited state lifetimes as a result of intraconfigurational $f$-$f$ transitions. In addition, their emission colours range from the UV to the near infrared (NIR), and it is exclusively characteristic of the specific lanthanoid cation (e.g. red emission from europium or green emission from terbium). The NIR region of particular interest due to potential applications in a wide range of fields including, night vision devices, telecommunication signalising and life science.1-6 Despite the listed advantages, trivalent lanthanoid cations cannot be directly excited with high efficiency, as intraconfigurational $f$-$f$ transitions are parity and often spin forbidden. Therefore, π-conjugated ligands are routinely used as sensitiser because of their high efficiency in absorbing light with consequent energy transfer to lanthanoid excited states. This alternative pathway, which is termed antenna effect, is well established and is generally rationalised as energy transfer from the triplet state of the conjugated ligands, populated via intersystem crossing due to the strong spin-orbit coupling of the lanthanoid elements, to the excited energy levels of the lanthanoid.7,8 Furthermore, in the design of emissive lanthanoid complexes it is also necessary to avoid high energy vibrations in close proximity to the metal centre, such as in the presence of OH and NH bonds. The activation of vibrational modes of these bonds acts as efficient quenchers for lanthanoid excited states. In the case of NIR emission, which is of particular interest here, CH bonds can also become a source of quenching.7 β-Diketones with aromatic substituents, such as dibenzoylethelene, have commonly been used as antenna ligands because of their good chelating properties and their ability to effectively sensitise the trivalent lanthanoid excited states, particularly in the solid state.9 Of the potential near-IR emitting systems, Nd$^{3+}$ diketonate complexes have been studied in less detail than the Yb$^{3+}$ and Er$^{3+}$ compounds. Reported quantitative data (quantum yields, lifetimes) are very limited, despite the fact that a variety of β-diketonate Nd$^{3+}$ complexes can be found in the literature over the last couple of decades.10-17 As for all of the near-IR emitting systems, the design of the β-diketonate Nd$^{3+}$ complexes typically involves two main strategies to improve photophysical properties: i) lowering the triplet state of the antenna in order to favour the energy transfer to Nd$^{3+}$ and ii) minimising the nonradiative relaxation pathways.13,14

In extending the coordination chemistry of luminescent lanthanoid β-diketonate complexes, we have been exploring recently the use of β-triketonate molecules as antenna ligands for lanthanoids. These ligands have been found to support the formation of unique assemblies which present particularly enhanced ytterbium and erbium emission properties. Our previous studies with tris-benzylmethanate (tbbm) and tris(4-methylbenzoyl)methane (mtbbm) resulted in the isolation of tetranuclear assemblies and polymeric structures of formulation $[\text{Ln}(\text{AeHOEt})(\text{tbbm})]_{w}$ (Ln$^{3+} = \text{Eu}^{3+}$, Er$^{3+}$, Yb$^{3+}$ / Ae* = Na+, K+, Rb+)/18,19 and $[(\text{Ln}),(\text{tbbm})(\text{mtbbm})]_{n}$ (Ln$^{3+} = \text{Eu}^{3+}$ and Er$^{3+}$), respectively. In contrast, our initial attempts to isolate the corresponding neodymium analogues were not successful and their photophysical properties remained unknown.

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In this work, we report the successful extension of these studies to neodymium-containing assemblies using both \textit{tbmH} and \textit{mtbmH} ligands in presence of RbOH and CsOH. The syntheses, crystal structures and emission properties of the resulting assemblies are reported.

Furthermore, since the structure of these complexes were found to be similar for the different lanthanoids, we have studied the formation of mixed assemblies for the purpose of investigating energy transfer processes or multiple emission from the same material. Excited states of a lanthanoid have been previously explored to sensitize excited states of another lanthanoid.\textsuperscript{21-24} This approach is well established for certain pairings with NIR emitters, for example sensitisation of erbium luminescence \textit{via} energy transfer from the \textsuperscript{2}F\textsubscript{5,2} excited state of trivalent ytterbium,\textsuperscript{25-27} or ytterbium luminescence \textit{via} visible emitters such as terbium or europium.\textsuperscript{28,29} In contrast, to our knowledge, neodymium sensitisation via other lanthanides has not been reported in coordination complexes. Only three examples have been reported where Eu/Nd energy migration was used to determine the lanthanoid-lanthanoid distance following pure Forster mechanisms.\textsuperscript{30-32} However, these studies are focused on the quenching of the europium excited states but do not report any associated near-IR emission from the neodymium centres. This sensitisation process for neodymium emission has been seen in the case of Eu/Nd doped glasses,\textsuperscript{33,34} so should also be possible in the comparatively well-defined structure of a coordination complex. Indeed, this study presents the first example of a coordination complex with effective lanthanoid-lanthanoid energy transfer from the \textsuperscript{5}D\textsubscript{0} of Eu\textsuperscript{3+} to the \textsuperscript{4}P\textsubscript{0} of Nd\textsuperscript{3+}, leading to dual emission.

**Experimental**

**General procedures**

All reagents and solvents were purchased from chemical suppliers and used as received without further purification. The ligand tribenzoylmethane (\textit{tbmH}), was prepared as previously reported.\textsuperscript{31} Hydrated LnCl\textsubscript{3} (Ln = Eu\textsuperscript{3+}, Yb\textsuperscript{3+}) was prepared by the reaction of Ln\textsubscript{2}O\textsubscript{3} with hydrochloric acid (5 M), followed by evaporation of the solvent under reduced pressure. Infrared spectra (IR) were recorded on solid-state samples using an attenuated total reflectance Perkin Elmer Spectrum 100 FT-IR. IR spectra were recorded from 4000 to 650 cm\textsuperscript{-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 B1 Barnsted Electrothermal 9100 apparatus. Elemental analyses were obtained at Curtin University, Australia. Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance 400 spectrometer (400.1 MHz for \textsuperscript{1}H; 100 MHz for \textsuperscript{13}C) at 300 K. The data were acquired and processed by the Bruker TopSpin 3.1 software. All of the NMR spectra were calibrated to residual solvent signals.

**Selected Equations**

The values of the radiative lifetime (\(\tau_\text{R}\)), and intrinsic quantum yield (\(\Phi_{\text{In}}\)), can be calculated with the following equations:\textsuperscript{36}

\[
\frac{1}{\tau_\text{R}} = 14.65 \text{ s}^{-1} \times n^{3} \times \frac{I_{\text{Tot}}}{I_{\text{MD}}} \quad (\text{eq. 1})
\]

In equation 1, the refractive index (\(n\)) of the solvent is used (assumed value of 1.5 in the solid state), the value 14.65 s\textsuperscript{-1} is the spontaneous emission probability of the \(\text{^2}F_\text{i} \leftrightarrow \text{^2}D_\text{0}\) transition reported previously. \(I_{\text{Tot}}\) is the total integration of the Eu\textsuperscript{3+} emission spectrum, and \(I_{\text{MD}}\) is the integration of the \(\text{^2}F_\text{i} \leftrightarrow \text{^2}D_\text{0}\) transition.

\[
\Phi_{\text{In}}^{\text{Ln}} = \frac{\tau_{\text{tot}}}{\tau_\text{R}} \quad (\text{eq. 2})
\]

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

\[
\eta_{\text{sens}} = \frac{\Phi_{\text{In}}^{\text{Ln}}}{\Phi_{\text{In}}^{\text{Eu}} \Phi_{\text{In}}^{\text{Nd}}} \quad (\text{eq. 3})
\]

The rate of energy transfer (\(K_{\text{ET}}\)) and quantum efficiency of energy transfer (\(\Phi_{\text{ET}}\)) can be calculated according to the following equations:

\[
k_{\text{ET}} = \frac{1}{\tau_\text{Q}} - \frac{1}{\tau_\text{U}} \quad (\text{eq. 4})
\]

\[
\Phi_{\text{ET}} = 1 - \frac{\tau_\text{Q}}{\tau_\text{U}} \quad (\text{eq. 5})
\]

In equations 4-5, \(\tau_\text{Q}\) and \(\tau_\text{U}\) are the \(\text{^2}D_\text{0}\) decay lifetime of Eu\textsuperscript{3+} in the presence or absence of the quencher (Nd\textsuperscript{3+}), respectively.

For dipole-dipole exchange mechanisms or Forster the donor-acceptor distance (\(R_{0}\)) can be calculated following equation 6:

\[
\Phi_{\text{FRET}} = \frac{1}{1 + \left(\frac{R_0}{R_0}\right)^6} \quad (\text{eq. 6})
\]

Where \(R_0\) is the critical distance for a 50% transfer, being tabulated to be 9.05 Å for the Eu\textsuperscript{3+}-Nd\textsuperscript{3+} pair.\textsuperscript{35}

**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-s-tm 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 (\(\Phi_{\text{In}}^{\text{Ln}}\)) were measured with the use of an integrating sphere coated with BenFlect.\textsuperscript{36} In the case of the NIR, overall quantum yields were measured using two different detectors and \(\text{[Yb(phen)(tta)]}_3\) in toluene (\(\Phi_{\text{In}}^{\text{Ln}} =

2 |
Excited-state decays (τ) were recorded on the same Edinburgh FLS-P890-stm spectrometer using a microsecond flashlamp. The goodness of fit was assessed by minimizing the reduced $\chi^2$ function and by visual inspection of the weighted residuals.

**Synthesis**

**Di(4-methylbenzoyl)methane (mdbm)**

The mdbm precursor was synthesized following a previously reported procedure.²₀

**Lanthanoid assemblies**

RbOH (21 mg, 0.02 mmol) was added to a mixture containing mdbmH (74 mg, 0.20 mmol) and hydrated LnCl₃ (18 mg, 0.05 mmol) in ethanol (10 mL). The mixture was heated at reflux for 30 minutes and filtered over a glass frit while still hot. The filtered solution was then left undisturbed at ambient temperature and slow evaporation of the solvent over several days afforded crystals suitable for X-ray diffraction.

**Crystallography**

Crystallographic data for the structures were collected at 1297 s, 1277 s, 1181 w, 1151 m, 1084 m, 1062 m, 1015 w, 1000 w, 940 s, 924 w, 890 i, 810 i, 675 s, 615 m, 532 m, 504 w, 448 s, 435 w, 414 s, 390 m, 360 w, 350 w, 320 m, 290 m, 250 w, 220 w, 200 w, 180 w, 160 w, 150 w, 120 w, 110 w, 100 w, 90 w, 80 w, 70 w, 60 w, 50 w, 40 w, 30 w, 20 w, 10 w, 5 w, and 1 w. The non-hydrogen atoms were modelled as being disordered over two sets of sites with occupancies constrained to 0.5 and with the non-hydrogen atoms refined with geometries restrained to ideal values. The water molecule hydrogen atoms were refined with geometries restrained to ideal values. The water molecule hydrogen atoms were refined with geometries restrained to ideal values. The water molecule hydrogen atoms were refined with geometries restrained to ideal values.

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\[\text{[Nd(Cs-2H2OEt)(tmbm)₄]}: C₃₂H₂₂CsNdO₂, M = 1262.23, crystal size 0.26 \times 0.084 \times 0.053 \text{ mm}³, monoclinic, space group C2/c, a = 27.4726(6), b = 8.29060(10), c = 25.4388(6) Å, \ \delta = 108.315(2)^°, V = 5500.5(2) Å³, Z = 4, D_\text{c} = 1.524 \text{ g/cm}³, \ \mu_{\text{c}} = 12.772 \text{ mm}⁻¹, F_{\text{obs}} = 2540, \ \text{Cu Ka radiation, } \lambda = 1.54178 \text{ Å, } 2\theta_{\text{max}} = 134.6^°, 29516 reflections collected, 4906 unique (R_{\text{int}} = 0.0436). \ \text{Final Goof} = 1.090, R₁ = 0.0386, wR₂ = 0.1095, R indices based on 4314 reflections with I > 2\sigma(I), \ |\Delta \rho|_{\text{max}} = 2.5 \text{ e Å}⁻³, 349 parameters, 0 restraints. CCDC 1829216.

\[\text{[Cs(tmbm)]₄}: C₉H₂₂CsO₄, M = 502.33, crystal size 0.240 \times 0.057 \times 0.042 \text{ mm}³, monoclinic, space group P2₁/c, a = 8.41028(14), b = 31.2556(4), c = 8.01519(14) Å, \ \delta = 102.777(2)^°, V = 2054.77(6) Å³, Z = 4, D_\text{c} = 1.624 \text{ g/cm}³, \ \mu_{\text{c}} = 14.245 \text{ mm}⁻¹, F_{\text{obs}} = 1000, \ \text{Cu Ka radiation, } \lambda = 1.54178 \text{ Å, } 2\theta_{\text{max}} = 134.6^°, 17616 reflections collected, 3671 unique (R_{\text{int}} = 0.0558). \ \text{Final Goof} = 1.037, R₁ = 0.0455, wR₂ = 0.1174, R indices based on 3361 reflections with I > 2\sigma(I), |\Delta \rho|_{\text{max}} = 2.4 \text{ e Å}⁻³, 265 parameters, 0 restraints. CCDC 1829217.

Results and discussion

The tmbmH and tmbmH molecules were synthesised according to the previously reported methodology. Following a similar procedure to that previously reported for the preparation of \{[Ln(Cs)(tmbm)]₂\} \((\text{Ln}^{3+} = \text{Eu, Er, Yb})\) and \{[Ln(Cs)(mtbm)]₂\}, \((\text{Ln}^{3+} = \text{Eu, Er})\), one equivalent of hydrated LnCl₃ \((\text{Ln}^{3+} = \text{Eu, Nd})\) was made to react with four equivalents of tmbmH and four equivalents of RbOH in ethanol. Slow evaporation of the solvent resulted in the formation of suitable crystals for X-Ray diffraction revealing the formation of coordination polymers with formula \{[Ln(Rb)(tmbm)]₂\}, where Ln³⁺ = Eu(1), Nd(2). The compositions of the isolated species were further confirmed by elemental analysis and IR spectroscopy. The resulting solids are isolated with variable degrees of solvation which has been found previously for these Ln³⁺/Ae⁺ based complexes.\(^{19,20}\)

The Eu³⁺/Nd³⁺ mixed assemblies were synthesised in a similar fashion to the \{[Ln(Rb)(tmbm)]₂\} except for the use of mixtures of hydrated EuCl₃ and NdCl₃ in molar ratios of Nd³⁺ of 0.25 (3), 0.50 (4) and 0.75 (5).

Analogous syntheses were attempted with CsOH and NdCl₃ in order to assess the effect of the different alkaline base in the mixed systems. However, only the cesium-containing coordination polymer \{[Cs(tmbm)]₄\} was deposited (see supplementary information).\(^{20}\)

When the same procedure was followed for the hydrated NdCl₃ and tmbmH with RbOH or CsOH, the formation of assemblies with formula \{[Nd(Rb)(tmbm)]₂\} and \{[Nd-Cs-2H2OEt(tmbm)]₄\} were found, respectively. The \{[Nd(Rb)(tmbm)]₂\} complex presents a similar structure to the previously reported tetranuclear assemblies.\(^{19}\) In contrast, the isolation of the \{[Nd-Cs-2H2OEt(tmbm)]₄\} linear polymer shows the second example of a possible in situ retro-Claisen condensation reaction of tmbmH in the presence of CsOH and hydrated NdCl₃ resulting in the formation of a δ-diketonate complex similar to previously reported examples (see supplementary information).\(^{20}\) The hypothesis that the triketonate ligands undergo a retro-Claisen condensation reaction under these reaction conditions is currently under investigation and the results will be presented elsewhere.

Finally, when the same procedure was attempted with YbCl₃, a dimeric structure was crystallised with formula \{[Yb(tmbm)]₃(H₂O)]₂\} (see supplementary information). Due to difference in composition and symmetry of this structure in comparison with the polymeric species of complexes 1 and 2, Yb³⁺ was not further investigated for the purpose of this study.

Crystal structures

The structures of the two \{[Ln(Rb)(tmbm)]₂\} \((\text{Ln}^{3+} = \text{Nd, Eu})\) complexes are isomorphous and structurally similar to the Cs-based polymers with formula \{[Ln(Cs)(tmbm)]₂\}, \((\text{Ln}^{3+} = \text{Eu}, \text{Er})\).\(^{20}\) The units formed of two Ln³⁺, two Rb⁺ metal centres and eight tmbm ligands are isomorphous to the previously reported tetranuclear assemblies.\(^{18}\) The Ln³⁺ is eight coordinated, with four tmbm ligands coordinated by two of the O-keto atoms in a bidentate mode. In this case, the third O-keto of two of the ligands is linked to Rb⁺ cations forming the tetranuclear assembly and the polymer, respectively (Figure 1).

[Image 304x220 to 553x406]

Figure 1 Representation of the X-Ray structure of 2, \{[Nd(Rb)(tmbm)]₂\}, where hydrogens have been omitted for clarity.

Here, a H₂O molecule is found in the lattice with two hydrogen bonds formed with two keto O(22) and O(31). Intermolecular interactions between chains are present where the lanthanoid centres sit at distances longer than 14Å (see supplementary information). The geometry of the eight coordinate Ln³⁺ is best
described as triangular dodecahedron (see supplementary information).

The structure of the [Nd(Rb·HOEt)(tmbm)]₄ is isomorphous to the previously published tetrannuclear assemblies where the eight coordinated Nd⁺³ adopts a geometry best described as distorted triangular dodecahedron (Figure 2).

The photophysical data for complexes 1-6 including excited state lifetime decay (τobs), calculated radiative decay (τr), intrinsic photoluminescence quantum yield (Φln), overall photoluminescence quantum yield (Φln), and sensitisation efficiency (ηsens), are reported in Table 2. The emission properties were recorded in the solid state due to the low stability of the complexes in polar solvents and poor solubility in nonpolar solvents as previously demonstrated for analogous systems.¹⁸

As shown before, the energy of the mtbm and tmbm triplet states (21,140 cm⁻¹ and 20,704 cm⁻¹)¹⁸,²⁰ are sufficiently high to sensitise the ⁶D₀ (~17,200 cm⁻¹) of Eu³⁺, the ⁷F₅/₂ (~10,200 cm⁻¹) of Yb³⁺ and the ⁹I₁₃/₂ (~6,566 cm⁻¹) of Er³⁺. Therefore, energy transfer to the ⁴F₅/₂ (~11,260 cm⁻¹) state of Nd⁺³ is also expected. In fact, each emission spectrum shown herein is the result of an effective antenna effect, a conclusion that is supported by the broad excitation spectra which match with the absorption profile of the corresponding ligands.

The emission spectrum of [[Eu(Rb)(mtbm)]₄] (1) shows the characteristic Eu³⁺ emission bands attributed to the ⁷F₆←⁵D₇(J=0-6) region 580-820 nm (Figure 3).⁴⁰,⁴¹ The ⁷F₅/₂←⁵D₃ transition is strictly forbidden by the selection rules and is only observable for low symmetry complexes. The lack of this band in our system suggests a higher symmetry than Csᵥ, Cᵥ or Cᵥ. The magnetic dipole-allowed band (⁷F₅/₂←⁵D₃) is split into two sublevels inherent to tetragonal crystal fields. This is in agreement with the splitting of the hypersensitive band (⁷F₆←⁵D₃) in four sublevels. The splitting of the main transitions is in accordance with the shape analysis which suggests that the local symmetry of the Eu³⁺ cation is best described as a distorted triangular dodecahedron.

| 1 [[Eu(Rb)(mtbm)]₄] | 2 [[Nd(Rb)(mtbm)]₄] | 6 [Nd(Rb·HOEt)(tmbm)]₄ |
|---------------------|---------------------|---------------------|
| Ln-O                | 2.327(2)-2.405(2)   | 2.363(2)-2.444(2)   | 2.390(2)-2.450(2) |
| Ae-O                | 2.816(2)-2.983(2)   | 2.817(2)-2.989(2)   | 2.822(2)-3.051(2) |
| Ae(1)-Ae(2)         | 8.119(5)            | 8.131(5)            | 8.305(6)          |
| Ae(1)-Ae(2')        | 8.799(5)            | 8.801(5)            | -                 |
| Ln(1)-Ln(2)         | 9.491(5)            | 9.539(5)            | 8.938(5)          |
| Ln(1)-Ln(2')        | 11.090(6)           | 11.092(9)           | 13.891(6)         |
| Ln(1)-Ae(1)         | 4.094(4)            | 4.104(3)            | 4.134(3)          |
| Ln(1)-Ae(2)         | 8.184(5)            | 8.816(9)            | 7.599(3)          |
| Ae(2)-Ln(1')        | 8.814(5)            | 8.208(7)            | -                 |
| Ln(1)-Ln(1')        | 14.938(7)           | 14.990(7)           | 14.053(9)         |

Table 1. Selected bond lengths and intermetallic distances (Å) for complexes 1, 2 and 6.

³subsequent units and * different chain

Photophysical investigation

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Figure 2 Representation of the X-Ray structure of 6, [Nd(Rb·HOEt)(tmbm)]₄, where hydrogens have been omitted for clarity except those on the solvent EtOH molecule.

| Normalised emission intensity, arb. u. |
|---------------------|---------------------|---------------------|
| Wavelength/ nm |

Figure 3 Normalised emission plot for [[Eu(Rb)(mtbm)]₄] (red trace) and [[Nd(Rb)(mtbm)]₄] (black trace) in the solid state, with excitation wavelength at 350nm. Inset: highlight of the splitting of the magnetic dipole transition for the Eu³⁺ complex.
Excited state decay was fitted to a monoeponential function giving a value of observable lifetime ($\tau_{\text{obs}}$) of 507 $\mu$s. From the emission spectrum, the radiative decay ($\tau_{\text{r}}$) was calculated to be 0.86 ms. With an integrating sphere, the overall quantum yield ($\Phi_{\text{ET}}(%)$) was measured as 31%. From these data, the intrinsic quantum yield ($\Phi_{\text{in}}(%)$) could be calculated to be 59% with a sensitisation efficiency of 52%.

These data are of the same order as the previously reported $\Phi_{\text{ET}}(%)$ for the Nd$^{3+}$ emitter. The exchange in the alkaline base has little impact on the photophysical properties.

The emission spectrum of [(Nd(Rb)(mbtm)$_2$)$_2$]$_n$ (2) shows the characteristic Nd$^{3+}$ emission bands from the $^7F_{J} \leftrightarrow ^{5}D_{J}$ transitions at 910, 1060 and 1350 nm, respectively (Figure 3). These bands are structured as a consequence of the crystal field effect from the ligands. The excited state decay was measured to be 11 $\mu$s after deconvolution from instrumental response. This value of $\tau_{\text{obs}}$ is relatively high in comparison to the previously reported $\beta$-diketone compounds$^{21,28}$ and of the same order of magnitude as highly conjugated systems where the triplet state is lowered in energy to better match the emissive lanthanoid excited state energy.$^{14,41}$

Although it is known that the radiative decay for Nd$^{3+}$ ranges from 0.2 to 0.5 ms,$^{4}$ a standard value of 0.27 ms is generally accepted for the Nd$^{3+}$ complexes in the solid state.$^{16}$ The intrinsic quantum yield can therefore be estimated to 4.2%. The overall quantum yield using an integrating sphere following previously reported procedure for the use of two different detectors$^9$ was found to be 1.34%, with a sensitisation efficiency of 32%. These data suggest that reducing non-radiative decays due to the removal of the C-H bond is an effective way to enhance the photophysical properties of the Nd$^{3+}$ emitters.

As the structures for Eu$^{3+}$ and Nd$^{3+}$ are isomorphous, [[Ln(Rb)(mbtm)$_2$]$_2$]$_n$ mixtures of both lanthanoids were prepared (3-5) in order to investigate sensitisation of the $^4F_{3/2}$ of Nd$^{3+}$ via the $^5D_0$ of Eu$^{3+}$ (Figure 4).

The emission spectra of the mixed complexes show the characteristic emission bands from the $^7F_{J} \leftrightarrow ^{5}D_{J}$ (J = 0-6) of Eu$^{3+}$ in the visible region (580-820 nm) and the $^7F_{J} \leftrightarrow ^{5}D_{J}$ (J = 9/2, 11/2, 13/2) Nd$^{3+}$ bands in the NIR region (850 -1400 nm) with identical splitting in comparison with the pure complexes 1 and 2, respectively. This suggests that the structure is preserved with the mixed lanthanoid polymers. The intensity of the Nd$^{3+}$ emission bands increases when the molar ratio of Nd$^{3+}$ is higher (Figure 5). The lifetime of the excited state of Eu$^{3+}$ is shortened as the amount of Nd$^{3+}$ increases, from 507 $\mu$s for 1 to 335 $\mu$s, 183 $\mu$s and 143 $\mu$s for 3, 4 and 5, respectively. From these numbers, the highest energy transfer quantum efficiency can be calculated to be 72% for complex 5. Overall quantum yields were measured, finding decreasing values for Eu$^{3+}$ of 17.5%, 6.55% and 1.44% for complexes 3-5, respectively (see table 2). In the case of Nd$^{3+}$, both lifetime and overall quantum yield values seem to be reduced by the presence of Eu$^{3+}$. These results indicate possible quenching of the $^4F_{3/2}$ of Nd$^{3+}$ by the $^7F_2$ of Eu$^{3+}$ as previously suggested in literature.$^{44}$ However, the ratio of this energy transfer was calculated to be only 20% which is perhaps the main difference.
from previous Eu/Nd coordination compounds where no neodymium emission was reported.

Typically, energy transfer between lanthanide centres is considered for distances longer than 9 Å because of slow energy migration.\(^{44}\) In fact, if a purely dipole-dipole exchange mechanism is considered, the donor–acceptor distance can be calculated to be 7.7 Å following equation 6, for a quantum efficiency of energy transfer (\(\Phi_{\text{ET}}\)) of 0.72 for complex 5. However, in our system and when considering one polymeric chain, the shortest distance between two lanthanide centres is 9.5 Å. Therefore, the sensitisation to \(4f^*\) states of Nd\(^{3+}\) from the \(5D_0\) of Eu\(^{3+}\) for complexes 3-5 seems not to be a pure Förster mechanism, and a ligand-mediated Dexter mechanism may have some contribution.\(^{45,46}\)

For control experiments, equimolar mechanically-ground mixtures of 1 and 2 were studied. The lifetime of the \(5D_0\) of Eu\(^{3+}\) was found to be 356 µs, shorter than the pure complex 1 (\(\tau_{\text{obs}} = 507\) µs) and longer with respect to the solution-phase mixed equimolar complex 4 (\(\tau_{\text{obs}} = 507\) µs). These data suggest that there is energy transfer between chains occurring at 30% of efficiency. Taking into consideration the long Ln–Ln distances between chains (~15 Å) based on the crystal structure, the energy transfer process may occur via intermolecular interactions (see supplementary information).

Finally, the emission spectrum of [Nd(Rb-HOEt)(tmbm)]\(_2\) (6) shows the three characteristic Nd\(^{3+}\) bands from the \({}^{7}I_{5/2}\leftrightarrow{}^{5}I_{J}\) \((J=9/2, 11/2, 13/2)\) similarly to the \([\text{Nd}({\text{Rb}})(\text{tmbm})]_n\), \(1\) (see supplementary information). The values of lifetime (\(\tau_{\text{obs}}\)), intrinsic quantum yield (\(\Phi^{\text{intr}}\)) and overall quantum yield (\(\Phi^{\text{tot}}\)) were found to be 8.85 µs, 3.3% and 0.58%, respectively. The main difference with complex 2 arises from a lower overall quantum yield, maintaining the values of lifetime and intrinsic quantum yields, which suggests that the sensitisation process from tmbm to the \(4f^*\) accepting states of Nd\(^{3+}\) is not as efficient as in the tmbm based complexes.

**Conclusions**

In this report the study of \(\beta\)-triketonate based lanthanoid complexes has been extended to Nd\(^{3+}\), presenting new examples of tetranuclear assemblies ([Nd(Rb-HOEt)(tmbm)]\(_2\)) and coordination polymers with formula ([Nd(Rb)(tmbm)]\(_2\))\(_n\). The fact that isomorphous structures were found for the tmbm and Eu\(^{3+}\) ([([Nd(Rb)(tmbm)]\(_2\))\(_n\)], opened up the possibility to synthesise mixed lanthanoid complexes with the aim of achieving \(f-f\) energy transfer. Indeed, an example of a mixed tmbm based lanthanoid coordination polymer with efficient sensitisation from the \(5D_0\) of Eu\(^{3+}\) to the \(4F_{1/2}\) of Nd\(^{3+}\) was formulated. The emission studies of the pure and mixed complexes show particularly good photophysical properties in the case of Nd\(^{3+}\) via both mechanisms; standard antenna and \(f-f\) sensitisation.

**Conflicts of interest**

There are no conflicts to declare.

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