Visible and Near-Infrared Emission from Lanthanoid β-Triketonate Assemblies Incorporating Cesium Cations

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Supporting Information

ABSTRACT: The reaction of the β-triketonate ligands tris(4-methylbenzoyl)methanide and tribenzoylemethanide with the trivalent lanthanoids Eu³⁺, Er³⁺, and Yb³⁺ in the presence of Cs⁺ afforded polymeric structures where the repeating units are represented by bimetallic tetranuclear assemblies of formulation \( \{[\text{Ln(Cs)}(\beta\text{-triketonate})]_4\}_\infty \). The only exception is the structure formed by the reaction of tris(4-methylbenzoyl)methanide, Yb³⁺, and Cs⁺, which yielded a polymeric assembly where the repeating units are mononuclear Yb³⁺ complexes bridged by Cs⁺ cations. Photophysical measurements on the obtained materials confirmed efficient sensitization from the ligand excited states to the 4f⁸ excited states of the three lanthanoids. According to transient absorption data, Er³⁺ and Yb³⁺ are sensitized via energy transfer from the triplet state of the β-triketonate ligands. On the other hand, energy transfer to Eu³⁺ seems to occur via an alternative pathway, possibly directly via the singlet state or through ligand to metal charge transfer states. The emission measurements confirm efficient sensitization for all three lanthanoids and bright near-infrared emission for Er³⁺ and Yb³⁺, a characteristic that seems to be linked to the specific chemical structure of the β-triketonate ligands.

INTRODUCTION

The photophysical properties of trivalent lanthanoid cations are currently the focus of extensive investigation, stemming from their potential application in a variety of fields including optical displays, night vision devices, telecommunication signaling, life science, and counterfeiting technologies.1–6 Lanthanoid cations cannot be directly excited in an efficient manner, a limitation that arises from ℓ–f transitions being parity and often spin forbidden.7–10 Therefore, efficiently luminescent lanthanoid complexes are obtained by exploiting sensitization through π-conjugated ligands. These ligands act as antennas by absorbing energy more efficiently and subsequently transferring this energy to populate the 4f⁸ lanthanoid excited states. The general rules that govern efficient sensitization are well established and usually rely on the energy difference between

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particularly important for those lanthanoid elements emitting near-infrared (NIR) radiation (e.g., Nd³⁺, Er³⁺, and Yb³⁺), which are more susceptible than visible emitters (e.g., Eu³⁺ and Tb³⁺) to these quenching phenomena.

β-Diketonate ligands have been extensively investigated in lanthanoid coordination chemistry. In fact, these types of ligands easily chelate the strongly oxophilic lanthanoid cations. Research in this domain has yielded a wide variety of structural motifs, ranging from mononuclear complexes to architecturally more sophisticated discrete oxo/hydroxo clusters. Indeed, not only have β-diketonate ligands been useful in stabilizing a wide variety of structures but also their chemical composition can include aromatic moieties that favor the efficient sensitization of lanthanoid cations.

In comparison to β-diketonates, β-triketonate ligands have been scarcely considered in lanthanoid coordination chemistry, with only a handful of examples being reported during the 1960s. This lack of investigation is rather surprising, especially when one considers that these systems can be easily obtained by starting from ubiquitously available β-diketonates and well-established synthetic procedures based on Claisen-type condensation reactions. We have therefore endeavored to fill this gap and investigate the potential of β-triketonates for the synthesis of luminescent lanthanoid complexes. Our initial results highlighted the serendipitous discovery of discrete bimetallic tetranuclear assemblies of formulation [Ln(Ae·HOEt)(tbm)]₄₂ (Ae⁺ = Na⁺, K⁺, or Rb⁺) assemblies, where Ae⁺ is an alkali-metal cation and tbm⁻ is the tribenzoylmethanide ligand. Our studies have shown that this assembly is consistently obtained upon variation of the lanthanoid cation (Eu³⁺, Er³⁺, and Yb³⁺), alkali-metal cation (Na⁺, K⁺, or Rb⁺), and alcoholic solvent (ethanol or n-butanol). Despite the structural novelty of these species, the most remarkable discovery occurred on investigating the photophysical properties of these lanthanoid assemblies.

While the luminescent properties in the case of Eu³⁺ were similar to those of analogous complexes bound to diketonate ligands, exceptional NIR emission was recorded for assemblies of Er³⁺ and Yb³⁺. In particular, these assemblies exhibited remarkably elongated excited state lifetime decays, with values usually obtained from complexes bound to deuterated or fluorinated organic ligands designed to minimize quenching via multiphonon relaxation. Furthermore, we demonstrated how these assemblies can be exploited as material precursors for the fabrication of near-infrared organic light emitting devices (NIR-OLEDs).

In this work, we focus on completing the series, synthesizing lanthanoid assemblies incorporating Cs⁺ as the alkali-element cation. Furthermore, we extend our investigation by using the new ligand tris(4-methylbenzoyl)methane (mtbmH) alongside the previously employed tribenzoylmethane (tbmH). Studying mtbmH is an initial step toward establishing how chemical modifications of the ligand might influence the specific structure of the species obtained. As in our previous studies, the resulting assemblies have been investigated by means of absorption and emission spectroscopy to characterize their photophysical properties. Additional transient absorption experiments have been conducted using simpler model complexes in an effort to further elucidate the detailed sensitization pathways that characterize lanthanoid species bound to β-triketonate ligands.

## RESULTS AND DISCUSSION

### Synthesis of the Lanthanoid Assemblies

The mtbmH ligand was synthesized following the same procedure previously reported for tbmH. The same methodology used for the preparation of discrete tetranuclear [Ln(Ae·HOEt)-tbm]₄₂ (Ae⁺ = Na⁺, K⁺, Rb⁺) assemblies, 1 equiv of hydrated LnCl₃ (Ln³⁺ = Eu³⁺, Er³⁺, Yb³⁺) was made to react
with 4 equiv of either \( \text{tbmH} \) or \( \text{mtbmH} \) in the presence of 4 equiv of \( \text{CsOH} \) in ethanol (Figure 1). In general, slow evaporation of the solvent over several days resulted in the deposition of crystals suitable for X-ray diffraction. The formulation of all the isolated species was further confirmed by means of elemental analysis and IR spectroscopy. In particular, the former revealed the presence of various degrees of solvation, which is typical for these bimetallic \( \text{Ln}^{3+}/\text{Ae}^{3+} \) assemblies.

Structural characterization revealed the formation of unique coordination polymers with formulation \( \left\{ [\text{Ln(Cs)(tbm)}]_2 \right\}_n \) (\( \text{Ln}^{3+} = \text{Eu}^{3+}, \text{Er}^{3+}, \text{Yb}^{3+} \)) or \( \left\{ [\text{Ln(Cs)(mtbm)}]_2 \right\}_n \) (\( \text{Ln} = \text{Eu}^{3+}, \text{Er}^{3+} \)), upon reaction of \( \text{LnCl}_3 \) with \( \text{CsOH} \) and either \( \text{tbmH} \) or \( \text{mtbmH} \) (Figure 1). In each case, the repeating unit of these polymeric species was found to be a tetranuclear assembly analogous to the previously reported species obtained when the alkali metal was \( \text{Na}^+, \text{K}^+, \) or \( \text{Rb}^+ \) \(^{29,31} \). On the other hand, reaction of \( \text{YbCl}_3 \) with \( \text{mtbmH} \) and \( \text{CsOH} \) yielded a different coordination polymer that was identified as \( [\text{Yb(Cs-HOEt)}(\text{mtbm})]_n \) (Figure 1). In this case, the repeating unit can be more appropriately described as mononuclear \( \text{Yb}^{3+} \) complexes linearly bridged by \( \text{Cs}^+ \) cations.

Notably, when crystals obtained from the reaction of hydrated \( \text{EuCl}_3 \) and \( \text{mtbmH} \) were analyzed, a second product was also identified by the presence of crystals having a different morphology with respect to those belonging to \( \left\{ [\text{Eu(Cs)-(mtbm)}]_2 \right\}_n \). This byproduct was identified as a linear polymer where mononuclear \( \text{Eu}^{3+} \) complexes bearing bis(4-methylbenzoyl)methanide ligands (\( \text{mdbm}^- \)) were linked by \( \text{Cs}^+ \) cations, \( [\text{Eu(Cs-2HOEt)}(\text{mdbm})]_n \). This arrangement is analogous to a previously published structure formed by lanthanoid cations and dibenzoylmethanide. \(^{32} \) The presence of this species seems to indicate possible retro-Claisen reactivity of the triketonate ligands under the alkaline reaction conditions, with formation of the analogous diketonate species. This hypothesis is supported by the fact that the \( ^1\text{H} \) NMR spectrum of \( \text{mtbmH} \) does not show the presence of \( \text{mdbmH} \) (see the Supporting Information).

Analogous reactions were attempted by substituting \( \text{CsOH} \) with \( \text{Cs}_2\text{CO}_3 \); however, no lanthanoid-containing species could
be identified upon deposition of the crystals. In fact, only the formation of the cesium-containing coordination polymer \(\text{Cs}(\text{tbm})_n\) was identified (see the Supporting Information for a description of this structure). The use of \(\text{Cs}_2\text{CO}_3\) was therefore not further explored.

**X-ray Diffraction Studies.** The repeating units of the three \([\text{Ln}(\text{Cs})(\text{tbm})_4]_n\) (\(\text{Ln}^{3+} = \text{Eu}^{3+}, \text{Er}^{3+}, \text{Yb}^{3+}\)) polymers were analogous to those of previously reported \(\text{Ln}^{3+}/\text{Ae}^{3+}\) assemblies. A \(\text{Ln}^{3+}/\text{Cs}^{+}\) dimer is formed by two \(\text{Ln}^{3+}\) and two \(\text{Cs}^{+}\) metal centers surrounded by eight anionic triketonates (Figure 2). Each \(\text{Ln}^{3+}\) ion is eight-coordinate, with the four \(\text{tbm}^{-}\) ligands binding in a bidentate mode. The third O-keto atoms of two of the ligands, O(23,43), are not involved in any contact, one O-keto atom, O(33), bridges to a \(\text{Cs}^{+}\) ion to form the dimer, and the fourth, O(13), bridges to a neighboring \(\text{Cs}^{+}\) to form the polymeric structure. In the previously reported dimeric structures, this last position in the coordination sphere of the \(\text{Ae}^{3+}\) cation was occupied by the O atom of an ethanol molecule. Here, an EtOH molecule is found in the lattice, with a hydrogen bond formed with the keto O(43) atom. The remainder of the coordination sphere of the \(\text{Cs}^{+}\) comprises three \(\mu\)-O atoms (one each from ligands 1–3) bridging to the \(\text{Ln}^{3+}\) cation.

The structures of the two \([\text{Ln}(\text{Cs})(\text{mtbm})_4]_n\) \((\text{Ln}^{3+} = \text{Eu}^{3+}, \text{Er}^{3+})\) polymers are unsolvated and are structurally similar to the \(\text{tbm}^{-}\) coordination polymers (Figure 3). The tetranuclear \(\text{Ln}^{3+}/\text{Ae}^{3+}\) dimeric assembly is again observed, with the polymeric structure formed by coordination to the \(\text{Cs}^{+}\) cations. The specifics of these bridging interactions between the tetranuclear assemblies do differ. On comparison of the two \(\text{Eu}^{3+}\) polymeric structures, in the \(\text{mtbm}^{-}\) system, the closest approaches between aromatic rings and the \(\text{Cs}^{+}\) cations occur within the tetranuclear assembly (\(\text{Cs}^{+}::\cdot\cdot\cdot\text{C}(216,316), 3.324, 3.521; \text{C}s^{+}::\cdot\cdot\cdot\text{centroid}(2,3), 3.926, 4.257 \text{\AA}\)), consistent with an attractive interaction. In contrast, the closest such approaches occur between the tetranuclear assemblies in the \(\text{tbm}^{-}\) polymers (\(\text{Cs}^{+}::\cdot\cdot\cdot\text{C}(115), 3.580 \text{\AA}; \text{Cs}^{+}::\cdot\cdot\cdot\text{centroid}, 3.542 \text{\AA}\)). This results in a \(\text{Cs}^{+}::\cdot\cdot\cdot\text{Cs}^{+}\) distance between linked tetranuclear assemblies of 7.332 \text{\AA} in the \(\text{tbm}^{-}\) system, in comparison to 8.168 \text{\AA} in the \(\text{mtbm}^{-}\) system.

The \([\text{Yb}(\text{Cs})(\text{mtbm})_4]_n\) polymer crystallized with a significantly different structure (Figure 4). This species is comprised of one \(\text{Yb}^{3+}\) and one \(\text{Cs}^{+}\) that are counterbalanced by four anionic \(\text{mtbm}^{-}\) ligands. Each \(\text{Yb}^{3+}\) is octacoordinated and bound to four ligands in a bidentate mode. The third keto-O atoms on three of the ligands are not coordinated, while the fourth, O(13), is bridging to the \(\text{Cs}^{+}\) cation. The bridging interaction also involves a close approach with the second ring of the first ligand, with a \(\text{Cs}^{+}::\cdot\cdot\cdot\text{centroid}\) distance of 3.473 \text{\AA}.

The \([\text{Eu}(\text{Cs})(\text{HOEt})_2(\text{mdbm})_4]_n\) species (Figure 5), presumably formed due to a retro-Claisen reaction of \(\text{mtbm}^{-}\) in the presence of \(\text{CsOH}\) and hydrated \(\text{EuCl}_3\), is a coordination polymer analogous to previous reports. Each subunit comprises one octacoordinate \(\text{Eu}^{3+}\) and one \(\text{Cs}^{+}\) counterbalanced by four deprotonated ligands. The \(\text{Cs}^{+}\) is coordinated to two molecules of solvent and six \(\mu\)-O atoms bridging to the \(\text{Eu}^{3+}\).
The emission properties were recorded in the solid state, as we have previously demonstrated that these assemblies do not persist in polar coordinating solvents and are generally insoluble in nonpolar solvents.29 This was also the case for species bound to the mtbm ligand, as the substitution with a simple methyl group does not appear to be sufficient to impart solubility in common noncoordinating solvents. In each case, the emission of the various species originates as a consequence of the antenna effect, an argument that is supported by the broad excitation spectra that are analogous to the correspondence of the excited states of Eu3+, Er3+, and Yb3+ (the last possibly via charge transfer excited states).16,36

The emission spectra of \([\text{Eu(Cs)}(\text{tbm})_4]_2\) and \([\text{Eu(Cs)}(\text{mtbm})_4]_2\) show the characteristic Er3+-based NIR centered linelike bands in the region 850–750 nm (Figure 6), corresponding to the \(\text{F}_1 \leftarrow \text{D}_0 (J = 0–4)\) transitions. The \(\text{F}_0 \leftarrow \text{D}_0\) peak appears narrow (full width at half-maximum smaller than \(\sim 30 \text{ cm}^{-1}\)), albeit of very weak intensity, indicating that the emission originates in each case from a unique Eu3+ and is in agreement with the fact that the two Eu3+ cations in each assembly unit are related by an inversion center.29,37

The magnetic dipole allowed transition, \(\text{F}_1 \leftarrow \text{D}_0\), appears to be split into two bands in the case of \([\text{Eu(Cs)}(\text{tbm})_4]_2\) and into three bands (with two being quasi-degenerate) for \([\text{Eu(Cs)}(\text{mtbm})_4]_2\). This trend suggests slightly different degrees of distortion between the two coordination spheres,37 which is supported by the results found in the shape analysis study, where \([\text{Eu(Cs)}(\text{mtbm})_4]_2\) is more distorted than \([\text{Eu(Cs)}(\text{tbm})_4]_2\) with respect to an ideal triangular dodecahedron (see the Supporting Information). Slight differences can also be observed in the splitting of the hypersensitive \(\text{F}_2 \leftarrow \text{D}_0\) peaks.

Excited state lifetime decay values (\(\tau_{\text{obs}}\)) were measured to be 355 and 424 \(\mu s\) for \([\text{Eu(Cs)}(\text{tbm})_4]_2\) and \([\text{Eu(Cs)}(\text{mtbm})_4]_2\) respectively. In both cases, the decays were satisfactorily fitted with monoexponential functions. From the emission spectra, the values of the radiative lifetimes could be estimated at 0.660 and 0.798 ms for \([\text{Eu(Cs)}(\text{tbm})_4]_2\) and \([\text{Eu(Cs)}(\text{mtbm})_4]_2\) respectively. The overall quantum yields of the compounds were measured with values of 0.51 and 0.57 for \([\text{Eu(Cs)}(\text{tbm})_4]_2\) and \([\text{Eu(Cs)}(\text{mtbm})_4]_2\) respectively. From these data, the intrinsic quantum yields, as a ratio of \(\tau_{\text{obs}}/\tau_0\), could be calculated at 0.54 and 0.53, providing information on the sensitization efficiency for the tbm (0.57) and mtbm ligand (0.64).

Taken together, the photophysical data for the two Eu3+ species indicate that in these complexes energy transfer from the t bm and mtbm ligands is quite efficient and is in line with the previously reported Eu3+ assemblies obtained with Na+, K+, and Rb+.25

The emission spectra of both \([\text{Er(Cs)}(\text{tbm})_4]_2\) and \([\text{Er(Cs)}(\text{mtbm})_4]_2\) show the characteristic Er3+-based NIR emission in the 1450–1650 nm spectral region. This peak is attributed to the spin-allowed \(4f_{13/2} \leftarrow 4f_{15/2}\) transition (Figure 7). The peak appears structured as a consequence of the crystal field effect exerted by the ligands.39 The fine structure of the splitting is slightly different, which is ascribed to a different degree of distortion in the coordination sphere around the Er3+ centers in the two species (see the Supporting Information).

The values of \(\tau_{\text{obs}}\) were measured to be 7 \(\mu s\) for both \([\text{Er(Cs)}(\text{tbm})_4]_2\) and \([\text{Er(Cs)}(\text{mtbm})_4]_2\). Both decay

Table 1. Photophysical Data for the Complexes in the Solid State

<table>
<thead>
<tr>
<th>complex</th>
<th>(\tau_{\text{obs}} (\mu s))</th>
<th>(\tau_0 (\text{ms}))</th>
<th>(\Phi_{\text{lab}}^\text{exc})</th>
<th>(\Phi_{\text{lab}}^\text{em})</th>
<th>(\eta_{\text{exc}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Eu(Cs)}(\text{tbm})_4]_2)</td>
<td>355</td>
<td>0.660</td>
<td>0.54</td>
<td>0.31</td>
<td>0.57</td>
</tr>
<tr>
<td>([\text{Eu(Cs)}(\text{mtbm})_4]_2)</td>
<td>424</td>
<td>0.798</td>
<td>0.53</td>
<td>0.37</td>
<td>0.64</td>
</tr>
<tr>
<td>([\text{Er(Cs)}(\text{tbm})_4]_2)</td>
<td>7</td>
<td>0.660</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Er(Cs)}(\text{mtbm})_4]_2)</td>
<td>7</td>
<td>0.660</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Yb(Cs)}(\text{tbm})_4]_2)</td>
<td>46</td>
<td>1.200</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Yb(Cs)}(\text{mtbm})_4]_2)</td>
<td>19</td>
<td>1.200</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

"Literature \(\tau_0\) for Er3+. "Literature \(\tau_0\) for Yb3+. Measured with the use of an integrating sphere.

Figure 6. Normalized emission plots for \([\text{Eu(Cs)}(\text{tbm})_4]_2\) (red trace) and \([\text{Eu(Cs)}(\text{mtbm})_4]_2\) (black trace), with excitation wavelength at 350 nm. Inset: highlight of the peaks corresponding to the \(\text{F}_1 \leftarrow \text{D}_0\) transition.

Figure 7. Normalized emission plots for \([\text{Er(Cs)}(\text{tbm})_4]_2\) (red trace) and \([\text{Er(Cs)}(\text{mtbm})_4]_2\) (black trace), with excitation wavelength at 350 nm.
profiles were satisfactorily fitted by monoexponential functions (after deconvolution from instrumental response). This value provides an estimation of the intrinsic quantum yield $\Phi_{Ln}^{\text{In}}$ of 0.01. As in the case of the previously published assemblies bearing Er$^{3+}$ and Na$^+$, K$^+$, or Rb$^+$, $\tau_{\text{obs}}$ is longer than the average excited state lifetime values for Er$^{3+}$ diketonate species (1–2 $\mu$s) and is within the range of Er$^{3+}$ species that have complexes with perfluorinated and deuterated ligands (6–11 $\mu$s at 58–98% $\alpha$-deuteration).39,40

Characteristic NIR emission from both $\{\text{Yb}(\text{Cs})(\text{tbm})_{4}\}_n^2$ and $\{\text{Yb}(\text{Cs}-\text{HOEt})(\text{mtbm})_{4}\}_n$ was observed in the 900–1100 nm region, corresponding to the spin-allowed $^2F_{7/2} \leftrightarrow ^2F_{5/2}$ transition (Figure 8). This transition is split into four main bands due to crystal field effects and shows emission from hot bands as a shoulder in the 930–960 nm region.7 As in the previous cases, slight differences in the fine splitting of the band are ascribed to a variable degree of distortion for the two Yb$^{3+}$ centers (see the Supporting Information).38

The observed lifetime decays $\tau_{\text{obs}}$ were fitted to a monoexponential function and gave values of 46 and 19 $\mu$s for $\{\text{Yb}(\text{Cs})(\text{tbm})_{4}\}_n^2$ and $\{\text{Yb}(\text{Cs}-\text{HOEt})(\text{mtbm})_{4}\}_n$ respectively. If the radiative lifetime is assumed to be 1200 $\mu$s (which is the standard assumption for Yb$^{3+}$ diketonate complexes, but experimental data are known to range between 500 and 1200 $\mu$s),7,41,42 the complexes would have intrinsic quantum yield values of 0.04 and 0.01, respectively. The value of $\tau_{\text{obs}}$ for $\{\text{Yb}(\text{Cs})(\text{tbm})_{4}\}_n^2$ is still relatively high in comparison to those of Yb$^{3+}$ diketonate compounds (4–5 $\mu$s),43 and it is analogous to the previously reported series of Yb$^{3+}$/Ae$^+$ (Ae$^+$ = Na$^+$, K$^+$, Rb$^+$) assemblies.29 This new result suggests that the presence of the molecule of ethanol coordinated to Ae$^+$ in the tetranuclear assemblies is not a dominant factor for nonradiative deactivation of the $^2F_{5/2}$ excited state of Yb$^{3+}$. Interestingly, the $\{\text{Yb}(\text{Cs}-\text{HOEt})(\text{mtbm})_{4}\}_n$ species has a composition similar to that of the tetranuclear assemblies, but its excited state lifetime is halved. On the basis of the previous consideration, it might be excluded that the shorter value of $\tau_{\text{obs}}$ for $\{\text{Yb}(\text{Cs}-\text{HOEt})(\text{mtbm})_{4}\}_n$ will be due to multiphonon relaxation caused by the molecule of ethanol coordinated to the Cs$^+$ cation. Given that energy migration is unlikely due to the distance between Yb$^{3+}$ centers,5 the difference in excited state lifetime decays could be caused by a shorter value of $\tau_R$ for $\{\text{Yb}(\text{Cs}-\text{HOEt})(\text{mtbm})_{4}\}_n$ and this aspect is currently under investigation.

To gain a more detailed insight into the kinetics involved in the sensitization process for the triketonate ligands, we have also performed transient absorption (TA) measurements on the femtosecond time scale, which have proven useful in understanding the excited state properties for diketonate species.44−47 However, as noted earlier, we have shown that the tetranuclear assemblies do not persist in polar coordinating solvents,29 which necessitated these measurements to be

![Figure 8](image-url)

**Figure 8.** Normalized emission plots for $\{\text{Yb}(\text{Cs})(\text{tbm})_{4}\}_n^2$ (red trace) and $\{\text{Yb}(\text{Cs}-\text{HOEt})(\text{mtbm})_{4}\}_n$ (black trace), with excitation wavelength at 350 nm.

![Figure 9](image-url)

**Figure 9.** TA spectra (left) of Gd$^{3+}$ complexes of mtbm$^-$ (top) and tbm$^-$ (bottom), along with corresponding decay kinetic plots (middle) and decay associated difference spectra (right).
performed using simpler model complexes. To that end, solutions of the 

perform the rate of electronic energy transfer from the excited 

The lack of an observed T1 → T0 signal suggests that ISC to 

### CONCLUSION

This work has focused on synthesizing bimetallic assemblies 

The photophysical properties were investigated by means of 

The calculated rate constants are on the order of 10^10 s^{-1} and reveal that both the 

For the corresponding Eu^{3+} complexes, a close analysis of the 

The excited state difference spectra (ΔOD) at early time delays reveal a negative ground 

The corresponding kinetic plots for the observed ΔOD dynamics integrated over 10 nm data intervals from 350 to 650 nm are 

Notably, the data for the Gd^{3+} complexes of 

Table 2, together with the decay associated difference spectra (DADS) shown in Figure 9.

Calculating the rate of electronic energy transfer from the excited 

For both the 

and 

ligands, while the initial ΔOD spectra obtained at early time delays were similar to those for the other complexes, the broader spectral feature appearing at ca. 650 nm due to 

However, in the present work these assemblies are the 

When Na^+, K^+, and Rb^+ were used as alkali-element cations.

When comparing the tetranuclear assemblies in the solid state 

previously reported study 

The analogous simple model complexes in solution. 

when comparing the tetranuclear assemblies in the solid state 

When comparing the tetranuclear assemblies in the solid state 

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ligands, while the initial ΔOD spectra obtained at early time delays were similar to those for the other complexes, the broader spectral feature appearing at ca. 650 nm due to 

However, in the present work these assemblies are the
efficient and fast energy transfer from the triplet excited state of the ligand after ISC. On the other hand, the transient absorption data for Eu⁴⁺ seems to suggest an alternative energy transfer pathway, occurring either directly via the ligand singlet state or through the population of an intermediate LMCT state. The emission profiles, excited state lifetimes, and quantum yield data for the Eu⁴⁺ species confirm efficient sensitization and relatively high quantum yields, with values in line those for previously reported Eu⁴⁺ diketonate complexes. On the other hand, the NIR emission of Er³⁺ and Yb³⁺ highlights rather elongated excited state lifetimes with respect to analogous diketonate species, similar to those previously observed for assemblies of these elements, tribenzoylmethanide, and Na⁺, K⁺, or Rb⁺. This work concludes the series of Ln¹⁻/泌 assemblies and reinforces our previous results confirming that these species constitute viable building blocks for the preparation of efficient NIR emitters.

### EXPERIMENTAL SECTION

#### General Procedures.
All reagents and solvents were purchased from chemical suppliers and used as received without further purification. The ligand tribenzoylmethane (tbtmH) was prepared as previously reported.38 Hydrated LnCl₃ (Ln = Eu³⁺, Er³⁺, Yb³⁺) was prepared by the reaction of Ln₂O₃ 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 (ATR) PerkinElmer Spectrum 100 FT-IR instrument. IR spectra were recorded from 4000 to 650 cm⁻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 Bowl Stearic Electrothermal 9100 apparatus. Elemental analyses were obtained at Curtin University, Bentley, Australia. Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance 400 spectrometer (400.1 MHz for ¹H; 100 MHz for ¹³C) 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 (τᵣ) and intrinsic quantum yield (Φᵢₛₑₜₜₑₓₜₑₓ), can be calculated with the equations:

\[
\frac{1}{\tau_R} = 14.65 \text{s}^{-1} \times \lambda \times \frac{I_{\text{MAX}}}{I_{\text{MD}}} \tag{1}
\]

\[
\Phi_{\text{IN}} = \frac{\tau_{\text{SDBS}}}{\tau_R} \tag{2}
\]

In eq 1, the refractive index (n) of the solvent is used (assumed value of 1.5 in the solid state). The value 14.65 s⁻¹ is the spontaneous emission probability of the 7F₁ ← 5D₀ transition reported previously. Iₕₑₓ is the total integration of the Eu³⁺ emission spectrum, and Iₕₑₓ is the integration of the 7F₁ ← 5D₀ transition. The sensitization efficiency (ηₑₛₑₜ) can be determined using eq 3:

\[
\eta_{\text{SDBS}} = \frac{\Phi_{\text{IN}}}{\Phi_{\text{IN}} - \Phi_{\text{IN}}} \tag{3}
\]

#### Photophysical Measurements.
Absorption spectra were recorded at room temperature using a PerkinElmer Lambda 35 UV/vis spectrometer. Uncorrected steady-state emission and excitation spectra were recorded using an Edinburgh FLS980-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. Quantum yields were measured with the use of an integrating sphere coated with BenFlect.48 Experimental uncertainties are estimated to be ±15% for quantum yields.

Excited-state decays (r) were recorded on the same Edinburgh FLS980-stm spectrometer using a microsecond flashlamp. The goodness of fit was assessed by minimizing the reduced χ² function and by visual inspection of the weighted residuals. Experimental uncertainties are estimated to be ±8% for lifetime determinations.

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 of the solvents used in the preparation of the solutions for the photophysical investigations were of spectrometric grade.

#### Transient Absorption Measurements.
The excitation source utilized for femtosecond transient absorption measurements was an amplified laser system (Spitfire ACE, Spectra Physics) delivering 800 nm laser pulses of 110 fs duration and a 1 kHz repetition rate. Approximately 0.1 m of this output was attenuated and focused onto a 15 mm CaF₂ window mounted on an automated z-stage translation mount to generate a white light continuum probe pulse from 350 to 650 nm. The remainder of the laser fundamental was coupled to an OPA system (Topas Prime, Light Conversion) which was tuned to deliver excitation pulses at 340 nm. The pump pulse polarization was set to magic angle with respect to the probe, and ground and excited state difference spectra (∆ΔΔD) at various delay times were measured using a femtosecond TA spectrometer (Helios, Ultrafast Systems) incorporating two 512 pixel CCD sensors as the sample and reference channel. Sample absorbances were ca. 0.4 over the 2 mm path length cell used, and these were continuously stirred mechanically. No detectable changes were observed in the UV–vis absorption spectra of the complex at the completion of transient absorption studies, indicating no decomposition. The instrument response function (IRF) had a full width at half-maximum (fwhm) of ca. 200 fs, measured experimentally by a Gaussian fit to the scattered laser excitation profile, and spectra were corrected for the chip of the probe pulses. The resulting time traces were analyzed globally using commercially available software (Igor, Version 6.1.2.1, WaveMetrics). Experimental uncertainties are estimated to be ±10% for lifetime determinations.

#### Synthesis of Bis(4-methylbenzoyl)methane (mdbmH).
The mdbmH precursor was synthesized following a slightly modified procedure.49 Ethyl 4-methylbenzoate (500 mg, 3 mmol) and 4-acetylbenzene (400 mg, 3 mmol) were combined in 40 mL of THF. To this solution, a suspension of NaH (60% in mineral oil, 144 mg, 3.6 mmol) was added.49 The synthesis of bis(4-methylbenzoyl)methane was complete after 2 h. After this time, the solvent was removed under reduced pressure and the remaining solid 4-methylbenzyl chloride was immediately added to diethyl ether (20 mL). NaH (60% in mineral oil, 144 mg, 3.6 mmol) was combined in 20 mL of diethyl ether, and the suspension was maintained at 0 °C. The mixture was then cooled to 0 °C for 4 h. The solid product was then collected by filtration, and the solution was washed with ethyl acetate (3 × 15 mL), and the combined organic phase was then separated. After filtration, the crude product was then dried over MgSO₄. The solvent was removed under reduced pressure and the target compound was isolated following purification via recrystallization in ethanol as a yellow solid. Yield: 80%. The spectroscopic data match those previously reported.49

#### Synthesis of Tris(4-methylbenzoyl)methane (mtbmH).
4-Methylbenzoic acid (625 mg, 4.8 mmol) was added to thionyl chloride (5 mL) and heated at reflux for 2 h. After this time, the solvent was removed under reduced pressure and the remaining solid 4-methylbenzyl chloride was immediately added to diethyl ether (20 mL). NaH (60% in mineral oil, 144 mg, 3.6 mmol) and mmdbmH (300 mg, 1.2 mmol) were combined in 20 mL of diethyl ether, and the suspension was maintained at 0 °C. The solution was added to a solution of 4-methylbenzyl chloride in diethyl ether dropwise. After the addition, the mixture was stirred under a nitrogen atmosphere at 40 °C for 16 h. The formed precipitate was filtered and washed with a HCl solution (1 M). The solid was then dried under reduced pressure for several hours and afforded the target compound as a white solid. Yield: 60.0%. M.p: 233–234 °C. Anal. Calcd for C₂₅H₂₂O₃: C, 80.67; H, 5.93. IR (ATR): ν: 2920 w, 1685 s, 1669 s, 1446 s, 1406 w, 1376 w, 1316 m, 1284 s, 1159 m, 1059 m, 1046 w, 1046 w, 1376 w, 1316 m, 1284 s, 1260 s, 1128 w, 1181 s, 1123 w, 1020 m, 1011 m, 957 w, 906
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X-ray Crystallography. Crystallographic data for the structures were collected at (200) K on an Oxford Diffraction Gemini Xcalibur diffractometer fitted with 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-2014.

X-ray Data Refinement. [Eu(Cs)(tbm)2]0.60 empirical formula C91H60CsO12Yb, C2H6O; MW = 1601.67, colorless needle, 0.17 × 0.12 × 0.03 mm, triclinic, space group P1, a = 16.8240(4) Å, b = 16.1806(4) Å, c = 17.9760(4) Å, α = 83.7682(16)°, β = 75.1762(16)°, γ = 83.4000(2)°; V = 4144.49(17) Å3, D0 = 1.425 g/cm3, μ = 1.509 mm−1, F(000) = 1806, Mo Kα radiation, λ = 0.71073 Å, T = 100(2) K, 2θmax = 134.9°, 60010 reflections collected, 21797 unique reflections (Rint = 0.0041), final GOF = 1.003, R1 = 0.0370, wR2 = 0.0455, wR2 = 0.0029, R indices based on 21086 reflections with I > 2σ(I) (refinement on F2), Δρmax = 1.059 e Å−3, 1027 parameters, 0 restraints.

[Yb(Cs)(tbm)2]0.60 empirical formula C91H60CsO12Er, C2H6O; MW = 1777.64, colorless needle, 0.20 × 0.12 × 0.05 mm, triclinic, space group P1, a = 16.8243(4) Å, b = 16.1806(4) Å, c = 17.9760(4) Å, α = 83.7682(16)°, β = 75.1762(16)°, γ = 83.4000(2)°; V = 4144.49(17) Å3, D0 = 1.425 g/cm3, μ = 1.509 mm−1, F(000) = 1806, Mo Kα radiation, λ = 0.71073 Å, T = 100(2) K, 2θmax = 134.9°, 60010 reflections collected, 21797 unique reflections (Rint = 0.0041), final GOF = 1.003, R1 = 0.0370, wR2 = 0.0455, wR2 = 0.0029, R indices based on 21086 reflections with I > 2σ(I) (refinement on F2), Δρmax = 1.268 e Å−3, 1006 parameters, 6 restraints.

[Eu(OH3)(mtbm)]0D.00 empirical formula C2H7H2CsEuO6ζ0; MW = 1829.68, colorless prism, 0.23 × 0.15 × 0.06 mm, monoclinic, space group C2/c, a = 29.9314(14) Å, b = 8.4707(3) Å, c = 26.1468(11) Å, β = 105.325(5)°, V = 6393.53(15) Å3, D0 = 1.436 g/cm3, μ = 11.859 mm−1, F(000) = 2808, Cu Kα radiation, λ = 1.54178 Å, T = 100(2) K, 2θmax = 134.3°, 15957 reflections collected, 5670 unique reflections (Rint = 0.0039), final GOF = 1.021, R1 = 0.0650, wR2 = 0.1834, R indices based on 4887 reflections with I > 2σ(I) (refinement on F2), Δρmax = 2.82 e Å−3, 397 parameters, 4 restraints.

[Yb(OH3)(mtbm)]0D.00 empirical formula C2H7H2CsEuO6ζ0; MW = 1829.68, colorless prism, 0.23 × 0.15 × 0.06 mm, monoclinic, space group C2/c, a = 29.9314(14) Å, b = 8.4707(3) Å, c = 26.1468(11) Å, β = 105.325(5)°, V = 6393.53(15) Å3, D0 = 1.436 g/cm3, μ = 11.859 mm−1, F(000) = 2808, Cu Kα radiation, λ = 1.54178 Å, T = 100(2) K, 2θmax = 134.3°, 15957 reflections collected, 5670 unique reflections (Rint = 0.0039), final GOF = 1.021, R1 = 0.0650, wR2 = 0.1834, R indices based on 4887 reflections with I > 2σ(I) (refinement on F2), Δρmax = 2.82 e Å−3, 397 parameters, 4 restraints.

[Cs(tbm)]0D.00 empirical formula C91H60CsO12Yb, C2H6O; MW = 460.25, colorless prism, 0.63 × 0.48 × 0.20 mm, monoclinic, space group P21/c, a = 7.0986(1) Å, b = 15.2205(1) Å, c = 16.782(1) Å, β = 99.9287(16)°, V = 1786.18(29) Å3, D0 = 1.76 g/cm3, μ = 1.78 mm−1, F(000) = 904, Mo Kα radiation, λ = 0.71073 Å, T = 100(2) K, 2θmax = 77.9°, 6872 reflections collected, 10666 unique reflections (Rint = 0.0234), final GOF = 1.103, R1 = 0.0180, wR2 = 0.0449, R indices based on 9419 reflections with I > 2σ(I) (refinement on F2), Δρmax = 0.84(8) e Å−3, 335 parameters, 0 restraints.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00928.

Details of 1H and 13C spectra for mtbmH, absorption profiles for mtbmH and mtbml in ethanol, emission profiles for mtbmH and the Gd(III) complex of mtbmH from a frozen ethanol solution at 77 K, transient absorption spectra of Ln3+ (Ln3+ = Eu3+, Er3+, Yb3+) complexes of tbml and mtbmH, along with corresponding decay kinetic plots and decay associated difference spectra, geometrical parameters for the complexes using shape analysis, and normalized excitation and emission plots for the assemblies in the solid state (PDF)

Accession Codes
CCDC 1539972-1539979 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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