Lanthanoid Complexes Supported by Retro-Claisen Condensation Products of $\beta$-Triketonates

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

dmtbmH

Figure S1 $^1$H NMR of the dmtbmH molecule in CDCl$_3$

Figure S2 $^{13}$C NMR of the dmtbmH molecule in CDCl$_3$
$\text{ettbmH in CDCl}_3$

**Figure S3** $^1$H NMR of the $\text{ettbmH}$ molecule in CDCl$_3$

**Figure S4** $^{13}$C NMR of the $\text{ettbmH}$ molecule in CDCl$_3$
butbmH in CDCl₃.

Figure S5: ¹H NMR of the butbmH molecule in CDCl₃.

Figure S6: ¹³C NMR of the butbmH molecule in CDCl₃.
$\textit{t-butbmH}$ in $\text{CDCl}_3$.

Figure S7 $^1\text{H}$ NMR of the t-bu$\text{bmH}$ molecule in $\text{CDCl}_3$

Figure S8 $^{13}\text{C}$ NMR of the t-bu$\text{bmH}$ molecule in $\text{CDCl}_3$
Absorption profiles

$\textit{dm}^{\textit{tbm}H}$

![Absorption profile of $\textit{dm}^{\textit{tbm}H}$ and $\textit{dm}^{\textit{tbm}-}$ in excess of KOH from $10^{-5}$M solutions in EtOH](image)

*Figure S9 Absorption profiles of $\textit{dm}^{\textit{tbm}H}$ (black trace) and $\textit{dm}^{\textit{tbm}-}$ in excess of KOH (blue trace) from $10^{-5}$M solutions in EtOH.*

$\textit{et}^{\textit{tbm}H}$

![Absorption profile of $\textit{et}^{\textit{tbm}H}$ and $\textit{et}^{\textit{tbm}-}$ in excess of KOH from $10^{-5}$M solutions in EtOH](image)

*Figure S10 Absorption profiles of $\textit{et}^{\textit{tbm}H}$ (black trace) and $\textit{et}^{\textit{tbm}-}$ in excess of KOH (blue trace) from $10^{-5}$M solutions in EtOH.*
Figure S11 Absorption profiles of butbmH (black trace) and butbm in excess of KOH (blue trace) from 10^{-5}M solutions in EtOH.

Figure S12 Absorption profiles of t-butbmH (black trace) and t-buttbm in excess of KOH (blue trace) from 10^{-5}M solutions in EtOH.
Figure S13 Emission of ligand dm\text{tbm}H (black trace) and its Gd\textsuperscript{3+} complex (red trace) in an ethanol matrix at 77 K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red).

Figure S14 Emission of ligand dm\text{dbm}H (black trace) and its Gd\textsuperscript{3+} complex (red trace) in an ethanol matrix at 77 K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red).
**Figure S15** Emission of ligand ettbmH (black trace) and its Gd$^{3+}$ complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red). Inset shows deconvolution of the Gd$^{3+}$ complex emission curve.

**Figure S16** Emission of ligand etdbmH (black trace) and its Gd$^{3+}$ complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red).
**Figure S17** Emission of ligand $\text{butbmH}$ (black trace) and its Gd$^{3+}$ complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red).

**Figure S18** Emission of ligand $\text{bubdmH}$ (black trace) and its Gd$^{3+}$ complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red).
Figure S19 Emission of ligand t-bu\text{bm}H (black trace) and its Gd\textsuperscript{3+} complex (red trace) in an ethanol matrix at 77K. The asterisks denote the estimated position for the 0-phonon transition for the determination of the energy of the singlet state (black) and triplet state (red). Inset shows deconvolution of the Gd\textsuperscript{3+} complex emission curve.

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

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

<table>
<thead>
<tr>
<th>LIGAND</th>
<th>$^1\pi\pi^*$ (cm⁻¹)</th>
<th>$^3\pi\pi^*$ (cm⁻¹)</th>
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<tbody>
<tr>
<td>TBM</td>
<td>25,575</td>
<td>20,620</td>
</tr>
<tr>
<td>DBM</td>
<td>26,110</td>
<td>20,580</td>
</tr>
<tr>
<td>mTBM</td>
<td>24,957</td>
<td>20,790</td>
</tr>
<tr>
<td>mDBM</td>
<td>25,974</td>
<td>20,576</td>
</tr>
<tr>
<td>etTBM</td>
<td>25,189</td>
<td>20,202</td>
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<tr>
<td>etDBM</td>
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<td>20,790</td>
</tr>
<tr>
<td>dmTBM</td>
<td>24,509</td>
<td>20,790</td>
</tr>
<tr>
<td>dmDBM</td>
<td>25,974</td>
<td>20,633</td>
</tr>
<tr>
<td>buTBM</td>
<td>25,156</td>
<td>20,790</td>
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<tr>
<td>buDBM</td>
<td>25,840</td>
<td>20,537</td>
</tr>
<tr>
<td>t-buTBM</td>
<td>25,126</td>
<td>20,844</td>
</tr>
<tr>
<td>t-buDBM</td>
<td>26,007</td>
<td>20,709</td>
</tr>
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</table>
NMR stability studies

tbmH

Figure S21 $^1$H NMR of the tbmH molecule and one equivalent of KOH over 5 days in MeOD

mtbmH

Figure S22 $^1$H NMR of the mtbmH molecule and one equivalent of KOH over 5 days in MeOD
**Figure S23** $^1$H NMR of the dmtbmH molecule and one equivalent of KOH over 5 days in MeOD

**Figure S24** $^1$H NMR of the ettbmH molecule and one equivalent of KOH over 5 days in MeOD
Figure S25: $^1$H NMR of the ettbmH molecule and one equivalent of KOH over 5 days in EtOD.

**ButbmH**

Figure S26: $^1$H NMR of the butbmH molecule and one equivalent of KOH over 5 days in MeOD.
**t-butb mh**

Figure S27 $^1$H NMR of the t-butb mh molecule and one equivalent of KOH over 5 days in MeOD

**tbmH + LuCl₃**

$^1$H-NMR studies of the most stable $\beta$-triketone (tbmH) in MeOH were also performed in the presence of LuCl₃. As it can be seen in Figure S28, after addition of 1 equivalent of LuCl₃ in a tbm solution, appearance of multiple species can be observed. While some coordination of the $\beta$-triketonate can be identified, new peaks are also present assigned to $\beta$-diketonate and benzoate probably in both coordinated and non-coordinated forms.

Figure 28. $^1$H NMR of the tbmH molecule and one equivalent of KOH (a) and after addition of 1 equivalent of LuCl₃ in MeOD
X-ray crystal structures

Figure S29 X-ray crystal structure of the t-butmH molecule where the hydrogens are omitted for clarity.

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

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

Plots

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

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

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>COC-7</th>
<th>CTPR-7</th>
<th>Complex</th>
<th>TTD-8</th>
<th>SAPR-8</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.87456</td>
<td>1.74336</td>
<td>5</td>
<td>2.05306</td>
<td>1.19826</td>
</tr>
<tr>
<td>2</td>
<td>0.83017</td>
<td>1.65397</td>
<td>6</td>
<td>1.97817</td>
<td>0.8581</td>
</tr>
<tr>
<td>3</td>
<td>0.54534</td>
<td>1.95295</td>
<td>8</td>
<td>1.56109</td>
<td>0.57236</td>
</tr>
<tr>
<td>4</td>
<td>0.92305</td>
<td>0.77807</td>
<td>9</td>
<td>1.71699</td>
<td>1.34692</td>
</tr>
<tr>
<td>7</td>
<td>1.23820</td>
<td>0.63934</td>
<td>10</td>
<td>1.0359</td>
<td>1.29566</td>
</tr>
</tbody>
</table>

Normalised excitation and emission plots

Figure S33 Excitation (black trace) and emission spectra (red trace) for complex 1 with excitation wavelength at 350nm in the solid state.
Figure S34 Excitation (black trace) and emission spectra (red trace) for complex 3 with excitation wavelength at 350nm in the solid state.

Figure S35 Excitation (black trace) and emission spectra (red trace) for complex 4 with excitation wavelength at 350nm in the solid state.
Figure S36 Excitation (black trace) and emission spectra (red trace) for complex 5 with excitation wavelength at 350nm in the solid state.

Figure S37 Excitation (black trace) and emission spectra (red trace) for complex 6 with excitation wavelength at 350nm in the solid state.
Figure S38 Excitation (black trace) and emission spectra (red trace) for complex 7 with excitation wavelength at 350nm in the solid state.

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

\textit{Eu}^{3+}

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

\textit{Yb}^{3+}

Figure S41 Lifetime decay at 980nm for complexes 3 (black trace), 4 (red trace), 6 (blue trace), 7 (green trace) in the solid state at 298K.
References
(1) Llunell, M.; Casanova, D.; Cirera, J.; Alemany, P.; Alvarez, S. Shape version 2.1
   29.