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Lanthanoid β-triketonates: a new class of highly efficient NIR emitters for bright NIR-OLEDs

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Abstract. The reaction of hydrated YbCl₃ with potassium tribenzoylmethanide yields new bimetallic tetranuclear Yb³⁺/K⁺ assemblies. These species not only possess the longest excited state lifetime and quantum yield reported for the Yb diketonate family but are also suitable to be incorporated in NIR-OLEDs, whose performance outclasses any other reported lanthanoid-based device with NIR emission.

Research into luminescent species emitting in the visible spectrum and their use for the fabrication of organic light emitting devices (OLEDs), as a replacement for silicon-based technologies, has been extremely active in the past decades. More recently however, there has been growing interest in near-infrared (NIR) emission and associated NIR-OLEDs, as such devices find potential applications in a variety of relevant areas including telecommunication, optical signalling, night-vision devices, bioimaging and light-activated medical therapies. Some elements of the lanthanoid series have NIR emission and, in particular, the NIR luminescence from Yb³⁺ ions is studied due to its characteristic ²F⁵/₂ → ²F⁷/₂ line-like emission at 900-1100 nm. However, a drawback of many of the reported Yb³⁺ species is that their NIR emission is often efficiently quenched by the vibrational overtones of CH bonds within the sensitising ligands. This issue can be counteracted by the preparation of fully fluorinated or deuterated organic antennae or by excluding any high-energy vibrating bonds in close proximity to the Yb³⁺ centre. This strategy however, adds significant complexity to the preparation and optimisation of libraries of targeted sensitising ligands. In this context, diketonates have received much attention as readily accessible chelating O-donor ligands capable of forming stable lanthanoid complexes, which are also suitable to be incorporated in OLEDs. The species reported vary from mononuclear complexes to larger molecular oxo/hydroxo, carbonato, and halogen-bridging clusters.

17 β-Diketonate ligands modified to improve NIR emission have been well investigated. In stark contrast, only three reports on lanthanoid complexes bearing β-triketonate ligands have appeared in the literature. Furthermore, no structural characterisation of lanthanoid complexes bound to β-triketonate nor any investigation of sensitised NIR emission from their corresponding lanthanoid complexes has been reported. Indeed, a search of the CSD indicates that no metal complex of tribenzoylmethanide or triacetylmethanide has ever been structurally characterised, despite these ligands being a seemingly obvious extension of the classic β-diketonate motif.

The aim of this research was therefore to investigate the largely unexplored coordination and photophysical properties of lanthanoid β-triketonate complexes as well as their use in the fabrication of NIR-OLEDs. As a starting point, we focused on the complexation of Yb³⁺ cations with the tribenzoylmethane ligand (LH, Figure 1). Initial attempts to isolate the typical 3:1 ligand/metal mononuclear complex produced instead a bimetallic 2:2 Yb³⁺/K⁺ assembly. This complex displayed a remarkably long excited state lifetime and relatively high...
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chloride and NaH in diethyl ether. The reaction of bimetallic tetranuclear assembly was then stoichiometrically rationalised such that a mixture of hydrated YbCl$_3$ and four equivalents of both LH and KOH were made to react in refluxing ethanol, giving an appreciable yield of ~15% of the bimetallic complex.

![Figure 2](image)

Figure 2. Excitation and emission spectra of [Yb(K-HOEt)(L)$_4$]. The emission spectrum was recorded upon excitation at $\lambda_{ex} = 350$ nm. Inset: excited state decay measured by monitoring the emission at $\lambda_{em} = 1,035$ nm.

[Yb(K-HOEt)(L)$_4$] crystallised as a triclinic structure and comprises of an overall neutral species where the combined 8+ charges of two Yb$^{3+}$ and two K$^+$ cations are counterbalanced by the presence of eight deprotonated anionic ligands. The complex can be viewed as a dimer disposed about a centre of symmetry. The eight-coordinate Yb$^{3+}$ cation adopts a geometry best described as a square antiprismatic or distorted C$_4$ symmetry, bound to four ligands in the bidentate mode typical of diketonate complexes. The third keto-O atoms on three of these ligands are not involved in any close contacts, while the fourth bridges to form the dimer, linking to a centrosymmetrically related K$^+$ ion. The remainder of the coordination sphere of the K$^+$ cation comprises of two O atoms bridging to the Yb$^{3+}$ cation and an ethanol O atom. The Yb--Yb distance was found to be 8.90 Å and it is therefore expected that Yb-Yb energy transfer processes are not likely to occur.$^{26}$

The lowest singlet ('$\Pi\Pi$') and triplet ('$\Pi\Pi$') excited state energies of the ligand (L) were determined from the corresponding Gd$^{3+}$ complex in a frozen ethanol matrix at 77 K and were found to lie at 25,575 cm$^{-1}$ and 20,704 cm$^{-1}$, respectively (see ESI, Figure S5).$^{28}$ The energy difference between the ligand '$\Pi\Pi$' state and the lowest Yb$^{3+}$ excited state '$F_{5/2}$' is 10,454 cm$^{-1}$.$^{29}$ According to previously reported investigations, this value should favour an efficient sensitisation.$^{30}$ However, energy transfer to a higher-energy charge transfer state of Yb$^{3+}$ could also be invoked, which usually requires the energy of the '$\Pi\Pi$' state to be above 29,000 cm$^{-1}$. $^{26,28}$

While measurements in solution suggested that the structure might not maintained upon dissolution (see ESI, Figures S6-7), in the solid state [Yb(K-HOEt)(L)$_4$], displays characteristic Yb$^{3+}$ centred NIR emission (Figure 2) upon excitation in the UV region down to visible light above 400 nm. The emission originates as a consequence of the antenna effect from the L$^-$ ligands, as suggested by the similarity between the excitation (Figure 2) and absorption spectra (see ESI, Figure S4) of the complex and ligand, respectively. The observed luminescence is attributed to the '$F_{5/2} \rightarrow F_{7/2}$, transition of Yb$^{3+}$, which is split into four main bands due to crystal-field effects.$^{29,30}$ The absence of ligand-centred phosphorescence and direct excitation of Yb$^{3+}$ in the emission and excitation spectra, respectively, provides evidence of an efficient energy transfer from the sensitising diketonate ligand.

The observed lifetime decay ($\tau_{obs}$) of [Yb(K-HOEt)(L)$_4$] in the solid state at room temperature is satisfactorily fitted by a monoexponential function (Figure 2, inset), which is indicative of a unique NIR emitting species in the complex in agreement with the presence of an inversion centre. The $\tau_{obs}$ value is 47 µs and, to the best of our knowledge, this excited state decay is remarkably longer than any reported Yb$^{3+}$ complex, in the solid state, belonging to the family of β-diketonate ligands, even where multiphonon relaxation is reduced by the lack of CH bonds. In fact, the highest lifetime reported for Yb$^{3+}$ with perfluorinated β-diketonate ligands in the solid state is 12 µs.$^{20}$

In comparison, the complex [Yb(K-HOEt)(L)$_4$] reported herein utilises a relatively simple ligand possessing CH bonds closer to the Yb$^{3+}$ with a lifetime decay comparable to the above-mentioned examples. The overall quantum yield ($\Phi_{L}^{\text{i.r.}}$) and quantum efficiency ($\Phi_{L}^{\text{exc}}$) for both complexes were estimated assuming 100% sensitisation efficiency ($\Phi_{\text{sens}}$) and radiative lifetime ($\tau_{R}$) for Yb$^{3+}$ of 1.2 ms, as it has been done for analogous Yb$^{3+}$ diketonate species.$^{30,31}$ Under these assumptions, the quantum efficiency (and hence overall quantum yield) is 3.9%.

This value is amongst the highest reported for Yb$^{3+}$ complexes in the solid state; the most comparable values are those reported with experimentally calculated values of radiative lifetime ($\tau_{\text{R}}$), which are usually faster than the assumed $\tau_{\text{R}} = 1.2$ ms.$^{26}$ If we assumed an $\tau_{\text{R}} < 1.2$ ms, the value of $\Phi_{L}^{\text{exc}}$ would increase even further. The investigation into an accurate measurement of the quantum efficiency and quantum yield is currently underway.

![Figure 3](image)

Figure 3. Left: NIR electroluminescence intensity versus applied voltage of the OLED; inset: NIR external efficiency versus current density. Right: Electroluminescence spectrum of OLED.
The complex [Yb(K-HOEt)(L)2] was further assessed as an emissive species for the fabrication of NIR-OLEDs. The devices were fabricated by sublimation on glass substrates pre-coated with indium tin oxide (ITO), semitransparent to the light generated in the emitting layer (EML). The composition of the OLED was as follows: i) ITO anode; ii) 1,3-bis(N-carbazolyl)benzene (mCP, 60 nm); iii) EML [Yb(K-HOEt)(L)2], and mCP in a 1:2 mass ratio (30 nm); iv) 3,5-tris(N-phenyl-benzimidazol-2-yl)benzene (TPBI, 25 nm); v) LiF/Al cathode (0.5 nm of LiF, 100 nm of Al).

Figure 3 shows the plots of electroluminescence (EL) intensity versus voltage and external efficiency versus current density of the studied device. The EL profile is different from that of the solid state, which may be due to loss of solvent during sublimation (see ESI). The external quantum efficiency reaches 0.17% ph/e and the maximum EL voltage and external efficiency versus current density of the studied device showed significant improvement compared to OLEDs based on other lanthanide complexes previously reported where lanthanide complexes were used as emissive species in the composition of the EML. Conclusions

In conclusion, we have reported the synthesis of a novel neutral tetranuclear bimetallic Yb"K" assembly, by combination of Yb" with a triketonate sensitizer in the presence of potassium hydroxide. The Yb" ion in each complex is devoid of directly coordinated solvent and displays characteristic Yb"-centred emission in the solid state. The emission has a long lived lifetime previously unreported in Yb" complexes bearing analogous diketonate ligands in the solid state, even where the ligand was perfluorinated to minimise quenching. A highly efficient NIR-OLED using [Yb(K-HOEt)(L)2], as the source of the emitting layer was fabricated, demonstrating that this species is a suitable precursor in optical materials science. The performance of the device showed significant improvement compared to OLEDs based on NIR emitting lanthanide complexes reported to date, highlighting how the exceptional photophysical properties of the complex can be readily transferred to the device.

Notes and references

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Electronic Supplementary Information (ESI) available: Synthetic details for LH and [Yb(K-HOEt)(L)2]; complete NMR details for LH; X-ray crystallographic data for [Yb(K-HOEt)(L)2] (CCDC 1001908); details for the photophysical measurements, OLED fabrication and characterisation, and thermal analysis. See DOI: 10.1039/b000000x/.

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