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

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The reaction of hydrated YbCl_3 with potassium tribenzoylmethanide yields a new bimetallic tetranuclear $\text{Yb}^{3+}/\text{K}^+$ assembly. This species not only possesses the longest excited state lifetime and quantum yield reported for the Yb^{3+} diketonate family but is 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.^{1,2} 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.^{1,3–7} Some elements of the lanthanoid series have NIR emission and, in particular, the NIR luminescence from Yb^{3+} ions is studied due to its characteristic $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ line-like emission at 900–1100 nm.^{8,9} However, a drawback of many of the reported Yb^{3+} species is that their NIR emission is often efficiently quenched by the vibrational overtones of CH bonds within the sensitising ligands.³ This issue can be counteracted

by the preparation of fully fluorinated or deuterated organic antennae,^{3,10} or by excluding any high-energy vibrating bonds in close proximity to the Yb^{3+} centre.^{11,12} This strategy, however, adds significant complexity to the preparation and optimisation of libraries of targeted sensitising ligands. In this context, β -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.^{1,13–17} β -Diketonate ligands modified to improve NIR emission have been well investigated.^{18–20}

In stark contrast, only three reports on lanthanoid complexes bearing β -triketonate ligands have appeared in the literature.^{21–23} 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 CSD²⁴ 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 focussed on the complexation of Yb^{3+} cations with the tribenzoylmethane ligand (LH, Fig. 1). Initial attempts to isolate the typical 3 : 1 ligand/metal mononuclear complex produced instead a bimetallic 2 : 2 $\text{Yb}^{3+}/\text{K}^+$ assembly. This complex displayed a remarkably long excited state lifetime and relatively high quantum yield when compared to the parent β -diketonate complexes of Yb^{3+} , despite the presence of multiple CH bonds within the ligands.

The tribenzoylmethane ligand LH (2-benzoyl-1,3-diphenyl-1,3-propanedione) was prepared following a slightly modified procedure,²⁵ in which dibenzoylmethane was reacted with benzoyl chloride and NaH in diethyl ether. The reaction of LH with hydrated YbCl_3 in the presence of KOH in ethanol

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† Electronic supplementary information (ESI) available: Synthetic details for LH and $[\text{Yb}(\text{K-HOEt})(\text{L})_4]_2$; complete NMR details for LH; X-ray crystallographic data for $[\text{Yb}(\text{K-HOEt})(\text{L})_4]_2$; details for the photophysical measurements, OLED fabrication and characterisation, and thermal analysis. CCDC 1001908. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc04961f

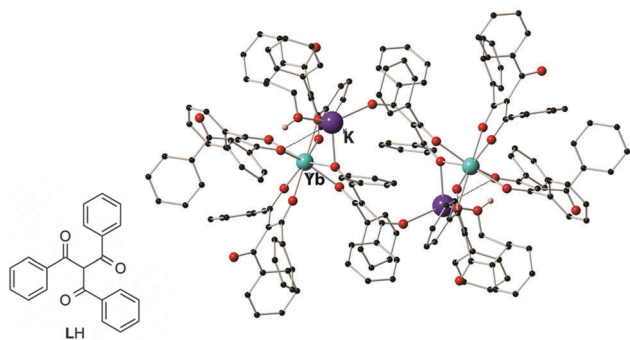


Fig. 1 Ligand **LH** and X-ray crystal structure of $[\text{Yb}(\text{K-HOEt})(\text{L})_4]_2$. H atoms, aside from ethanol OH, are omitted for clarity.

resulted in the formation of the complex $[\text{Yb}(\text{K-HOEt})(\text{L})_4]_2$ (Fig. 1). The synthesis of this 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 $\sim 15\%$ of the bimetallic complex.

$[\text{Yb}(\text{K-HOEt})(\text{L})_4]_2$ 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 $\mu\text{-O}$ atoms bridging to the Yb^{3+} cation and an ethanol O atom. The $\text{Yb} \cdots \text{Yb}$ distance was found to be 8.90 \AA and it is therefore expected that $\text{Yb}\text{-Yb}$ energy transfer processes are not likely to occur.²⁶

The lowest singlet ($^1\pi\pi^*$) and triplet ($^3\pi\pi^*$) 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 $25\,575 \text{ cm}^{-1}$ and $20\,704 \text{ cm}^{-1}$, respectively (see ESI,† Fig. S5).²³ The energy difference between the ligand $^3\pi\pi^*$ state and the lowest Yb^{3+} excited state $^2\text{F}_{5/2}$ is $10\,454 \text{ cm}^{-1}$. According to previously reported investigations, this value should favour an efficient sensitisation.^{3,27} However, energy transfer to a higher-energy charge transfer state of Yb^{2+} could also be invoked, which usually requires the energy of the $^3\pi\pi^*$ state to be above $19\,000 \text{ cm}^{-1}$.^{26,28}

While measurements in solution suggested that the structure might not be maintained upon dissolution (see ESI,† Fig. S6 and S7), in the solid state $[\text{Yb}(\text{K-HOEt})(\text{L})_4]_2$ displays characteristic Yb^{3+} centred NIR emission (Fig. 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 (Fig. 2) and absorption spectra (see ESI,† Fig. S4) of

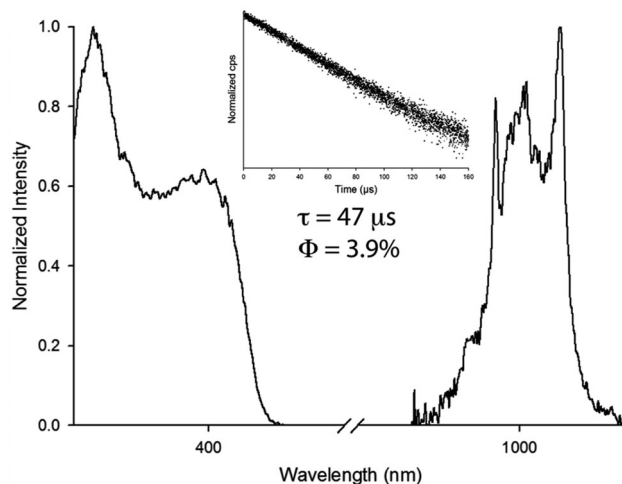


Fig. 2 Excitation and emission spectra of $[\text{Yb}(\text{K-HOEt})(\text{L})_4]_2$. The emission spectrum was recorded upon excitation at $\lambda_{\text{ex}} = 350 \text{ nm}$. Inset: excited state decay measured by monitoring the emission at $\lambda_{\text{em}} = 1035 \text{ nm}$.

the complex and ligand, respectively. The observed luminescence is attributed to the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ 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 triketonate ligand.

The observed lifetime decay (τ_{obs}) of $[\text{Yb}(\text{K-HOEt})(\text{L})_4]_2$ in the solid state at room temperature is satisfactorily fitted by a monoexponential function (Fig. 2, inset), which is indicative of one unique NIR emitting species in the complex in agreement with the presence of an inversion centre. The τ_{obs} value is $47 \mu\text{s}$ and, to the best of our knowledge, this excited state decay is remarkably longer than any reported β -diketonate- Yb^{3+} complex in the solid state, 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 $12 \mu\text{s}$.²⁰

In comparison, the complex $[\text{Yb}(\text{K-HOEt})(\text{L})_4]_2$ 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 ($\Phi_{\text{Ln}}^{\text{L}}$) and quantum efficiency ($\Phi_{\text{Ln}}^{\text{Ln}}$) for both complexes were estimated assuming 100% sensitisation efficiency (η_{sens}) and radiative lifetime (τ_{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 (τ_{R}), which are usually faster than the assumed $\tau_{\text{R}} = 1.2 \text{ ms}$.²⁶ If we assumed an $\tau_{\text{R}} < 1.2 \text{ ms}$, the value of $\Phi_{\text{Ln}}^{\text{L}}$ would increase even further. The investigation into an accurate measurement of the quantum efficiency and quantum yield is currently underway.

The complex $[\text{Yb}(\text{K-HOEt})(\text{L})_4]_2$ was further assessed as an emissive species for the fabrication of NIR-OLEDs. The devices

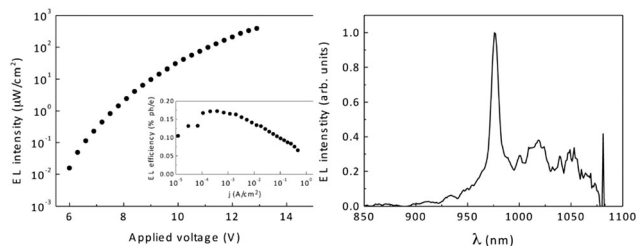


Fig. 3 Left: NIR electroluminescence intensity versus applied voltage of the OLED; inset: NIR external efficiency versus current density. Right: electroluminescence spectrum of OLED.

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 $[\text{Yb}(\text{K-HOEt})(\text{L})_4]_2$ and mCP in a 1:1 mass ratio (30 nm); (iv) 1,3,5-tris(*N*-phenyl-benzimidazol-2-yl)benzene (TPBi, 25 nm); (v) LiF/Al cathode (0.5 nm of LiF, 100 nm of Al).

Fig. 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 intensity is $390 \mu\text{W cm}^{-2}$ at 12.9 V, which originates exclusively from the Yb^{3+} -centred NIR emission peaked at 976 nm. To the best of our knowledge, the performance of this device is better than any other NIR-OLED previously reported where lanthanoid complexes were used as the emissive species in the composition of the EML.^{14,32–34}

In conclusion, we have reported the synthesis of a novel neutral tetranuclear bimetallic $\text{Yb}^{3+}/\text{K}^+$ assembly, by combination of Yb^{3+} with a triketonate sensitizer in the presence of potassium hydroxide. The Yb^{3+} ion in each complex is devoid of directly coordinated solvent and displays characteristic Yb^{3+} -centred emission in the solid state. The emission has a long lived lifetime previously unseen in Yb^{3+} complexes bearing analogous diketonate ligands in the solid state, even where the ligand was perfluorinated to minimise quenching. A highly efficient NIR-OLED using $[\text{Yb}(\text{K-HOEt})(\text{L})_4]_2$ 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 lanthanoid complexes reported to date, highlighting how the exceptional photophysical properties of the complex can be readily transferred to the device.

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