

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

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Electronic Supplementary Information

General Remarks

All reagents and solvents were purchased from Sigma Aldrich and used as received without further purification. The synthesis of 2-benzoyl-1,3-diphenyl-1,3-propanedione (**LH**) was adapted from a previously published procedure.¹ Hydrated YbCl_3 was prepared by the reaction of Yb_2O_3 with hydrochloric acid, followed by evaporation of the solvent under reduced pressure. Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Avance 400 spectrometer (400.1 MHz for ^1H ; 100 MHz for ^{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. The assignment of the individual peaks was confirmed by 2D COSY, HSQC and HMBC experiments. 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^{-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 Barnsted Electrothermal 9100 apparatus. Thermogravimetric Analysis/Differential Thermal Analysis (TGA/DTA) were recorded using a TA Instruments SDT 2960. Elemental analyses were obtained at Curtin University (Australia) for **LH**, and the Elemental Analyses Services at Université de Montréal (Canada) for complex $[\text{Yb}(\text{K}\cdot\text{HOEt})(\text{L})_4]_2$.

Synthetic Details

Synthesis of 2-benzoyl-1,3-diphenyl-1,3-propanedione (LH)

The synthesis of (LH) was adapted from a procedure reported by Guthrie *et al.*¹ Dibenzoylmethane (0.5 g, 2.23 mmol) was added to a suspension of sodium hydride (0.09 g, 2.23 mmol) in diethyl ether (10 mL) and the resulting mixture stirred at RT for 3 hours. Benzoyl chloride (260 μ L, 2.23 mmol) was added drop wise to the mixture and left to stir at RT overnight. Ethanol (2 drops), water (2 mL), and HCl (5M, 2 mL) were added to the mixture and the solid filtered and washed with water to afford a white solid (620 mg, 85%). M.p. 221-223 °C (lit. 226-231).¹ Anal. Calcd for C₂₂H₁₆O₃·0.1(H₂O): C, 80.03; H, 4.95. Found: C, 79.87; H, 4.86. ATR-IR: ν 3329 w, 3065 w, 2002 w, 1979 w, 1913 w, 1819 w, 1787 w, 1667 s, 1595 s, 1581 s, 1492 w, 1448 s, 1401 w, 1324 m, 1311 w, 1285 s, 1260 m, 1194 s, 1181 s, 1158 w, 1102 w, 1077 w, 1030 w, 1000 s, 975 w, 393 w, 840 m, 763 s, 691 s cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 7.57 (6H, t, J = 7.2 Hz, phenyl CH), 7.68-7.72 (3H, m, phenyl CH), 8.02 (6H, d, J = 7.3 Hz, phenyl CH), and 8.11 (1H, s, CH) ppm. ¹³C NMR (100 MHz, DMSO-d₆): δ 65.05 (CH), 128.63 (phenyl CH), 129.03 (phenyl CH), 134.12 (phenyl C), 135.37(phenyl CH), and 193.71 (CO) ppm. In the ¹H-NMR spectrum only a trace amount of the enol tautomer of the LH ligand is visible; the assignment corresponds to the keto tautomer of the ligand as drawn in Figure 1.

Synthesis of [Yb(K·HOEt)(L)₄]₂

To a mixture of LH (68 mg, 0.21 mmol) and hydrated YbCl₃ (20 mg), an aqueous KOH solution (1 M, 206 μ L, 0.21 mmol) was added. Ethanol (10 ml) was added and the mixture heated at reflux for 30 minutes. The resulting mixture was filtered and the filtrate left to stand at ambient temperature. Slow evaporation of the solvent over 8 days afforded yellow block-like crystals (21 mg, 15%). M.p. 240-242°C. Anal. Calcd for C₁₈₀H₁₃₂Yb₂K₂O₂₆·2(H₂O): C, 68.17; H, 4.32. Found: C, 68.13; H, 3.91. ATR-IR: ν 3655 w, 3567 w, 3057 w, 1645 m, 1613 w, 1585 s, 1548 s, 1492 m, 1448 m, 1374 s, 1311 m, 1279 m, 1180 w, 1152 m, 1073 w, 1028 w, 1014 w, 999 w, 925 w, 898 m, 824 w, 780 w, 749 m, 694 m, 669 w cm⁻¹.

X-ray Crystallographic Data

Diffraction data were collected using a Bruker Microstar equipped with a Platinum 135 CCD detector, a Helios optics, a kappa geometry goniometer, and a rotating anode source for Cu K α radiation. Cell refinement and data reduction were achieved using APEX2. Absorption corrections were applied using SADABS. The structure was solved by direct methods using SIR2011,² and refined on F^2 by full-matrix least squares using Olex2.1.4.³ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated upon their parent atoms using the riding model, except the hydrogen atom of the ethanol molecule (OH), which was determined using residual electron density. All hydrogen atoms were refined isotropically. The structure of [Yb(K·HOEt)(L)₄]₂ is shown in Figure S1.

[Yb(K·HOEt)(L)₄]₂. Empirical formula C₁₈₀H₁₃₂Yb₂K₂O₂₆; $MW = 3135.13$. Triclinic, Space group $P\bar{1}$, $a = 14.1075(12)$, $b = 14.4693(12)$, $c = 17.9695(14)$ Å, $\alpha = 102.772(4)^\circ$, $\beta = 90.083(4)^\circ$, $\gamma = 91.038(4)^\circ$, Volume = 3576.6(5) Å³, $Z = 1$; $\rho_c = 1.456$ Mg/m³, $\mu = 3.494$ mm⁻¹, crystal size 0.286 x 0.091 x 0.078 mm³; $\theta_{\min, \max} = 2.52, 70.38^\circ$. Reflections collected = 254230, unique reflections = 13465 [$R(\text{int}) = 0.0685$]. Max. and min. transmission = 0.753 and 0.479. Number of parameters = 950, $S = 1.062$; Final R indices [$I > 2\sigma(I)$] $R1 = 0.0589$, $wR2 = 0.1549$; R indices (all data) $R1 = 0.0634$, $wR2 = 0.1622$; Largest diff. peak and hole 2.638 and -1.931 e. Å⁻³.

The average Yb...O distance is consistent with the literature for Yb³⁺ complexes bearing diketonate ligands.⁴ Given the potential for the hydroxyl group of the potassium-bound ethanol molecule to deactivate emission from the Yb³⁺ centre through non-radiative processes, the environment of the hydroxyl group was examined in some detail. The Yb...O distance is 5.72 Å (Figure S2). Consideration of the atom-atom distances about the ethanol O atom suggested it is not involved in classical H-bond interactions. Analysis of the Hirshfield surface⁵ of the ethanol molecule in the complex, however, revealed that there is a OH... π interaction in complex [Yb(K·HOEt)(L)₄]₂ (Figure S3), which may restrict the hydroxyl vibrations.

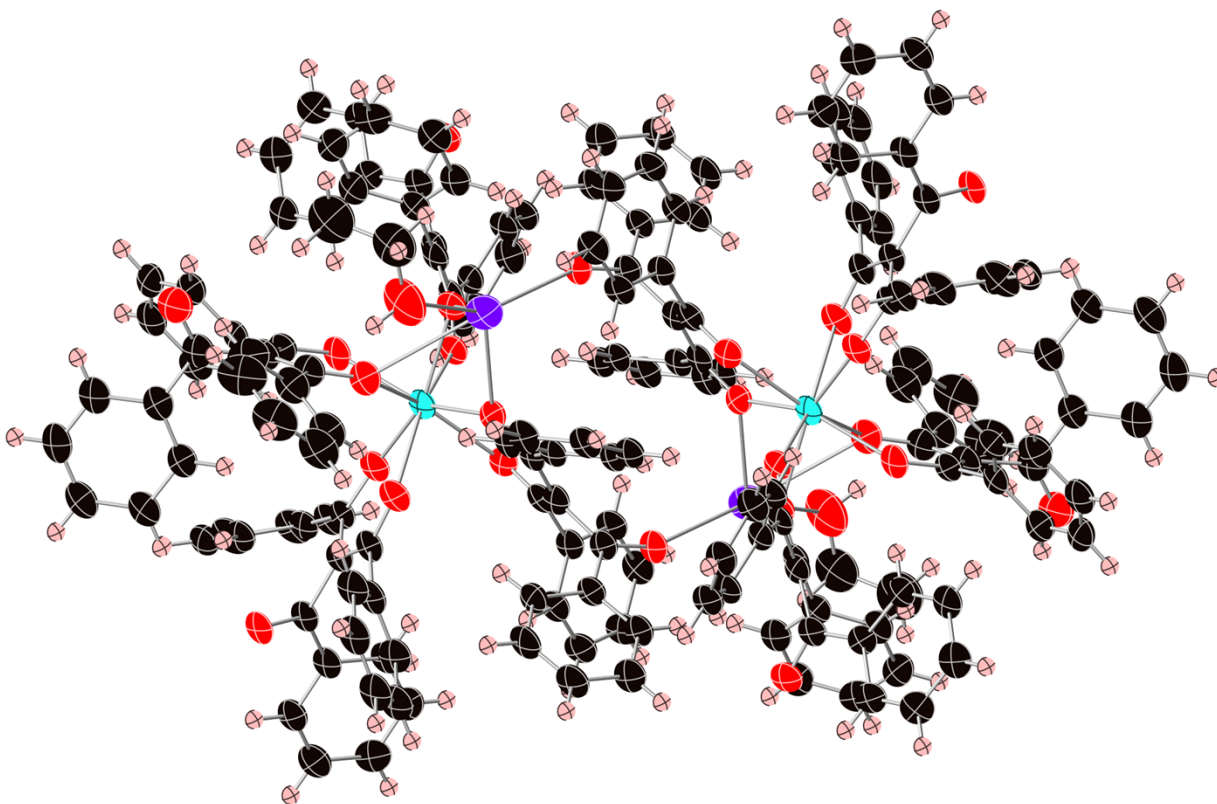


Figure S1. Structure of $[\text{Yb}(\text{K}\cdot\text{HOEt})(\text{L})_4]_2$ (Yb^{3+} - teal, K^+ - purple) with ellipsoids drawn at the 50% probability level.

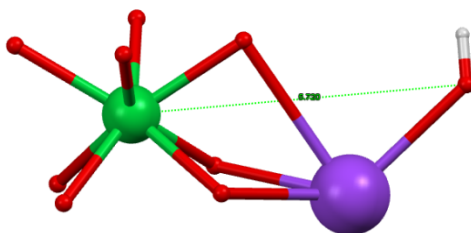


Figure S2. View of the coordination sphere of the Yb^{3+} centre (green) in $[\text{Yb}(\text{K}\cdot\text{HOEt})(\text{L})_4]_2$; the $\text{Yb}\cdots\text{O}(\text{ethanol})$ distance in the complex $[\text{Yb}(\text{K}\cdot\text{HOEt})(\text{L})_4]_2$ is 5.72 Å.

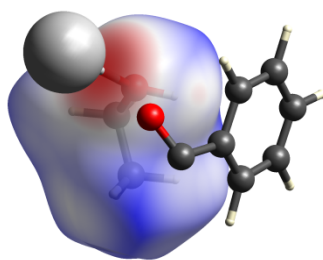


Figure S3. Hirshfeld surface of the ethanol molecule in complex $[\text{Yb}(\text{K}\cdot\text{HOEt})(\text{L})_4]_2$. Red coloration is indicative of a close approach to atoms outside of the surface. The strongest interaction is the coordination to the K^+ cation, with an additional $\text{OH}\cdots\pi$ interaction clearly observed.

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-stm spectrometer equipped with a 450 W xenon arc lamp, double excitation and emission monochromators 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.

Excited state decays (τ) were recorded on the same Edinburgh FLSP980-stm spectrometer using a microsecond flashlamp with the above-mentioned R5509-42 photomultiplier as the detector. The goodness of fit was assessed by minimising the reduced χ^2 function and by visual inspection of the weighted residuals.

To record the luminescence spectra at 77 K, the samples were put in quartz tubes (2 mm diameter) and inserted in a quartz Dewar filled with liquid nitrogen. All the solvents used in the preparation of the solutions for the photophysical investigations were of spectrometric grade.

UV-visible Absorption Spectra of LH and L⁻

The absorption spectra were recorded for LH and L⁻ (deprotonated by excess 1M KOH) in ethanol (Figure S4). These spectra illustrate two bands attributed to $\pi\pi^*$ transitions occurring within the conjugated framework of the ligand. The molar absorptivity of the lower energy band centred at 340 nm is increased in intensity in L⁻ due to the lower energy associated with increased conjugation in the deprotonated ligand.

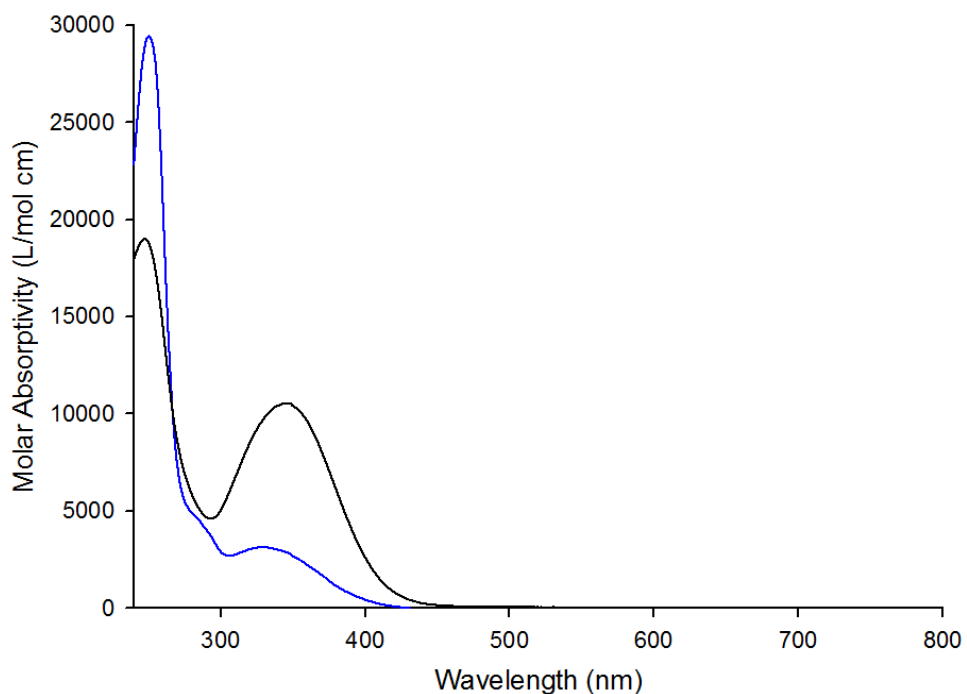


Figure S4. Absorption profile of LH (blue line), and L⁻ (black line, in the presence of an excess of KOH) in ethanol.

Ligand Emission and Triplet State Energy Determination

Emission of LH was measured in a frozen matrix in ethanol at 77 K and compared to the emission of L⁻ (deprotonated with triethylamine) as a Gd³⁺ complex under the same experimental conditions. The lowest singlet excited state was determined as the highest energy sharp band in both spectra. The lowest triplet state energy was then determined to be the first major band of a new set of three bands in the Gd³⁺ sample (Figure S5).

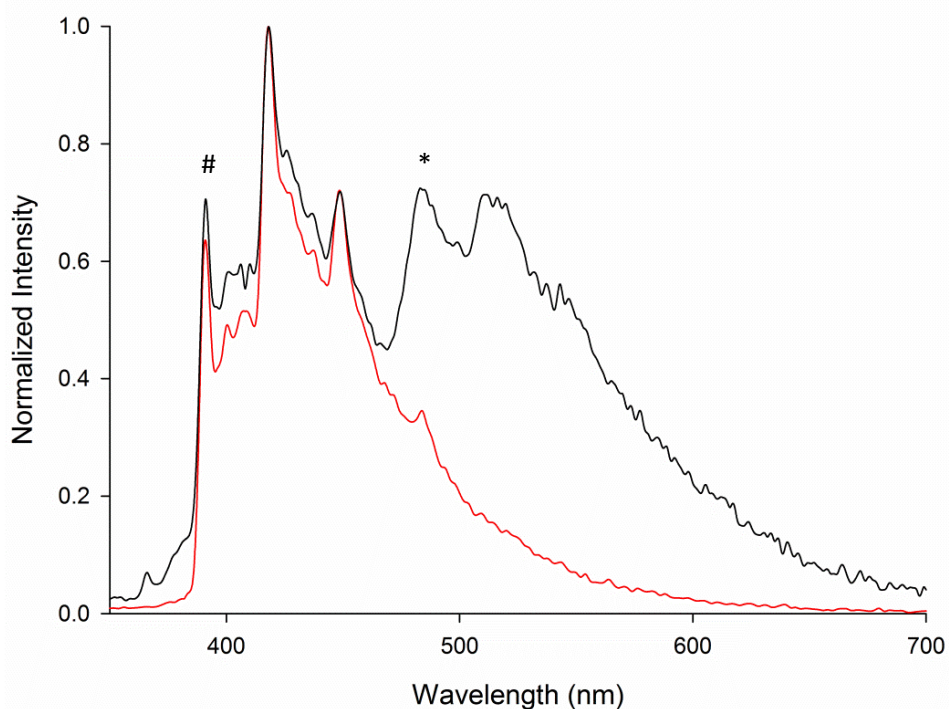


Figure S5. Emission of ligand LH (red line) and its Gd³⁺ complex (black line) in an ethanol matrix at 77K. The # symbol indicates the 0-phonon transition for the singlet excited state, whereas the * symbol indicates the 0-phonon transition for the triplet excited state.

Yb³⁺ Centred Emission in Solution

The emission profile of the complex [Yb(K·HOEt)(L)₄]₂ was measured in ethanol at 298 K (Figure S6) and 77 K (Figure S7). At 298 K, the emission spectrum shows a typical major line-like band at 970 nm with broadened shoulders between 930 and 1070 nm. The band is attributed to the metal-centred Yb³⁺ transition $^2F_{5/2} \rightarrow ^2F_{7/2}$ split due to crystal-field interaction. The rather featureless nature of the band might be attributed to a non-rigid coordination sphere possibly due to the lability of the ligands in the ethanol solution. On the other hand, the high energy shoulder is attributed to emission from “hot” excited states. At 77 K the intense peak centered at 970 nm is again present, albeit visibly sharper, and in this case the splitting of the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition is structured due to the more rigid environment within the frozen ethanol medium. The structure in the emission bands is different from the solid state emissions of the crystalline samples, and hence it is believed that the tetranuclear assembly [Yb(K·HOEt)(L)₄]₂ might not be preserved after dissolution. The resulting complex in solution is likely to be a mixture of equilibrium complexes.

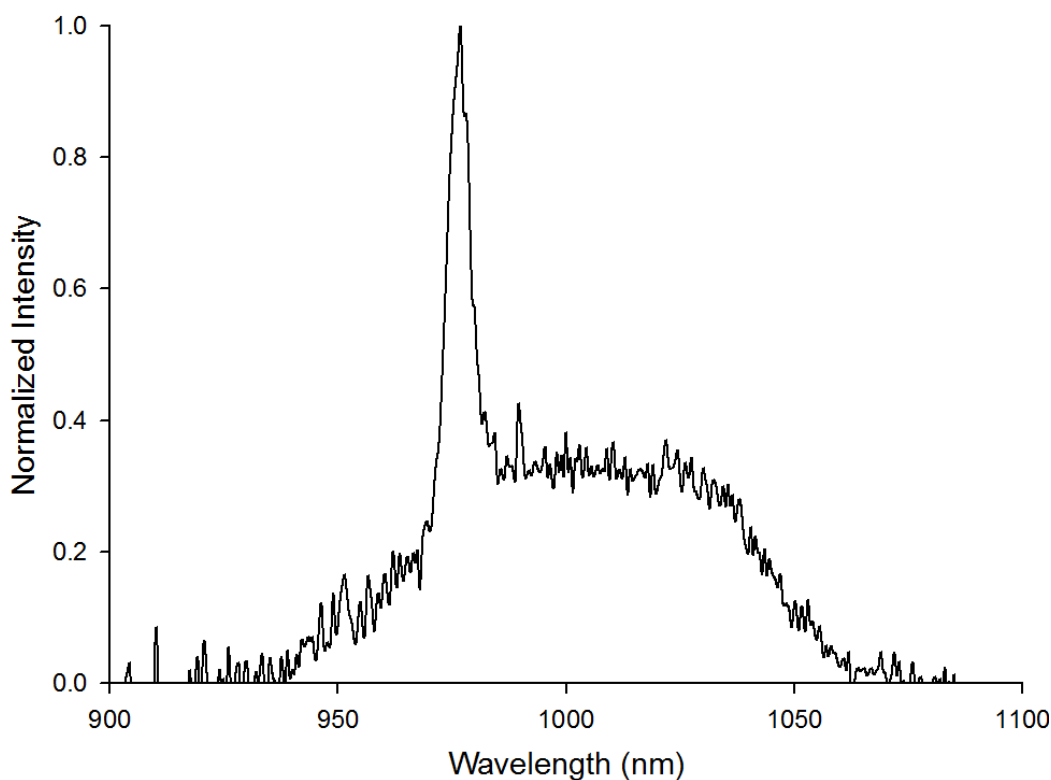


Figure S6. Emission profile of [Yb(K·HOEt)(L)₄]₂ in ethanol at 298 K.

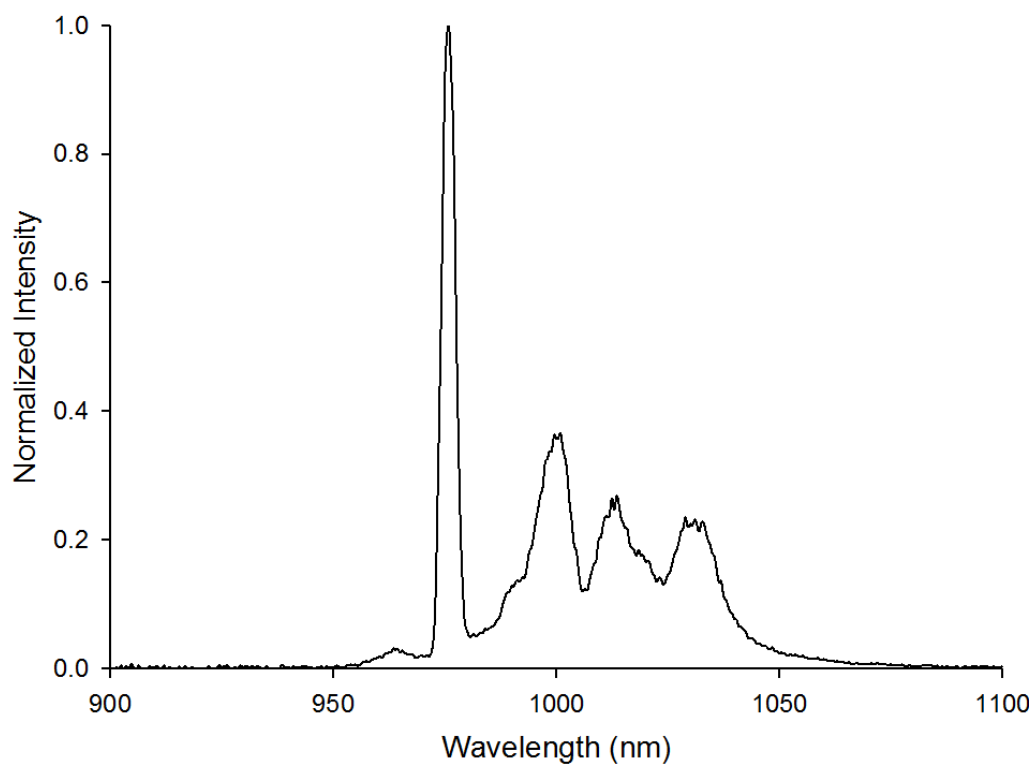


Figure S7. Emission profile of [Yb(K·HOEt)(L)₄]₂ in ethanol at 77 K.

OLED Device Fabrication and Characterisation

Organic Light Emitting Diodes (OLEDs) were fabricated by growing a sequence of thin layers on clean glass substrates pre-coated with a layer of indium tin oxide (ITO), 120 nm thick, with a sheet resistance of 20 Ω per square. A 2 nm-thick hole-injecting layer of MoO_x was deposited on top of the ITO by thermal evaporation under high vacuum of 10⁻⁶ hPa. All remaining layers were deposited in succession by thermal evaporation under high vacuum, followed by thermal evaporation of the cathode layer consisting of 0.5 nm thick LiF and a 100 nm thick aluminium cap. Hole transporting layer (1,3-bis(N-carbazolyl)benzene, mCP), emitting layer and electron transporting layer (1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene, TPBi) were of 60 nm, 30 nm, 25 nm thicknesses, respectively. The emitting layer (EML) was evaporated by co-deposition of [Yb(K·HOEt)(L)₄]₂ and mCP in 1:1 mass ratio. TGA/DTA was carried out at atmospheric pressure under N₂ atmosphere to understand the thermal stability of the [Yb(K·HOEt)(L)₄]₂ complex. There is a mass loss between 180-210°C consistent with the loss of coordinated ethanol molecules. The desolvated complex is then thermally stable until 300°C, which is above the temperature during the device fabrication.

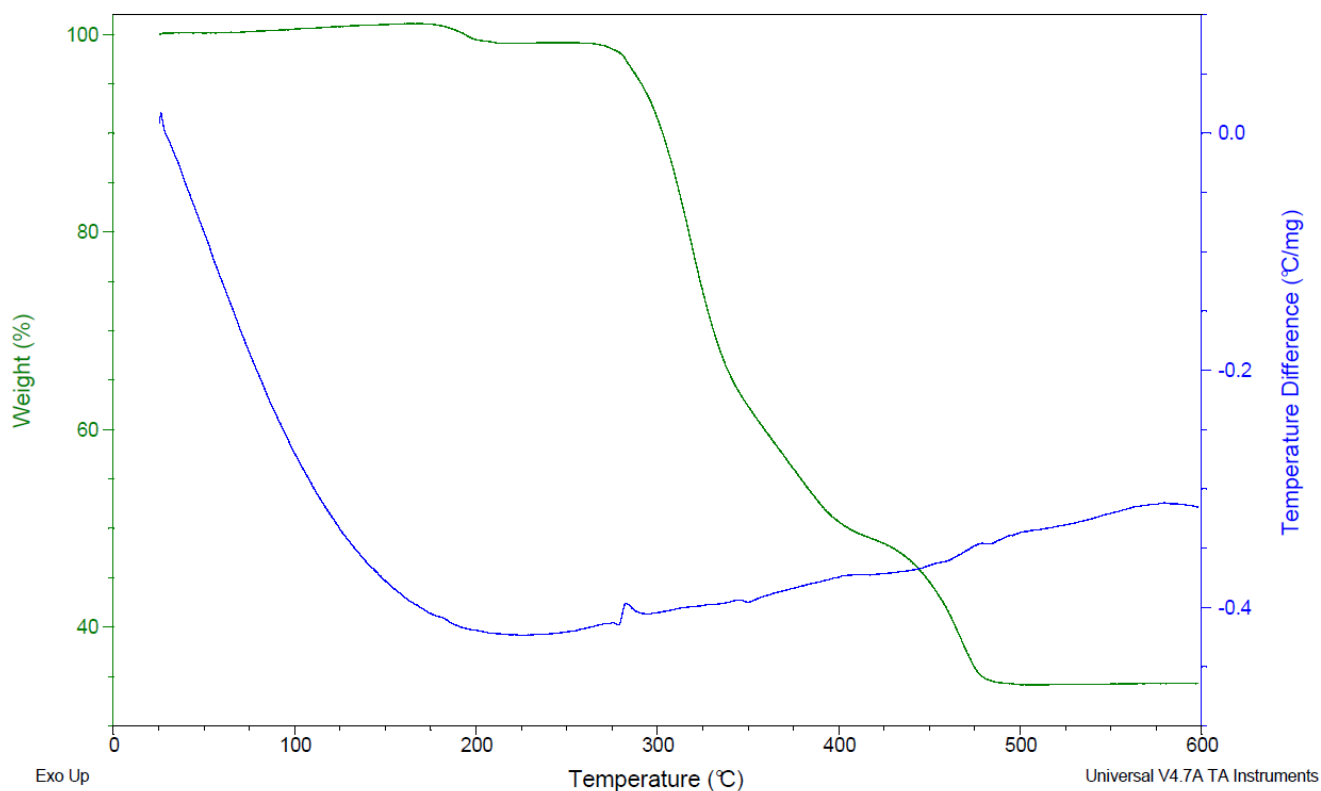


Figure S8. TGA/DTA of $[\text{Yb}(\text{K}\cdot\text{HOEt})(\text{L})_4]_2$.

The current–voltage characteristics were measured with a Keithley Source-Meter unit, model 236, under continuous operation mode, while the light output power was measured with an EG&G power meter, and electroluminescence (EL) spectra recorded with a StellarNet spectroradiometer. All measurements were carried out at room temperature under an argon atmosphere and were reproduced for many runs, excluding chemical reaction with oxygen or moisture.

References

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