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Electronic Supplementary Information

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Luminescent Europium(III) Complexes containing an electron rich 1,2,3triazolyl-pyridyl ligand

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Figure S1. ¹H NMR spectrum of 2-(1-*t*-butyl-1*H*-1,2,3-triazol-4-yl)pyridine in CDCl₃ at 298 K.



Figure S2. ¹³C {¹H} NMR spectrum of 2-(1-*t*-butyl-1*H*-1,2,3-triazol-4-yl)pyridine in CDCl₃ at 298 K.

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IR spectrum of $[Eu(\kappa^2-NO_3)_3L_2]$.



¹H NMR spectrum of $[Eu(\kappa^2 - NO_3)_3L_2]$ in acetone- d_6 at 298 K.



IR spectrum of of [Eu(dbm)₃L].



¹H NMR spectrum of [Eu(dbm)₃L] in DMSO-*d*₆ at 298 K.



Comparison of PL spectra ($\lambda_{excitation} = 380 \text{ nm}, \text{ r.t.}$) of [Eu(dbm)₃L] and [Eu(dbm)₃L]@PMMA.

Crystals of X-ray quality of $[Eu(dbm)_3L]$ were obtained by slow evaporation of dichloromethane/acetone solutions in the form of small, pale yellow prisms. The selected specimen was fastened on the goniometer head of an Oxford Diffraction Gemini E four–circle kappa–goniometer diffractometer. The instrument was equipped with a 2K × 2K EOS CCD area detector and sealed–tube Enhance (Mo) and (Cu) X–ray sources. Data collection was performed with the ω –scans technique at room temperature, using graphite–monochromated MoK α radiation ($\lambda = 0.71073$) in a 1024 × 1024 pixel mode and 2 × 2 pixel binning. The diffraction intensities were corrected with respect to absorption, as well as for Lorentz and polarization effects. An empirical multi–scan absorption correction based on equivalent reflections was performed with the scaling algorithm *SCALE3 ABSPACK*. Accurate unit cell parameters were determined by least–squares refinement of 16929 reflections of the highest intensity, chosen from the whole experiment. Raw data collection, data reduction and refinalization were carried out by means of the CrysAlis Pro software suite.¹

The diffraction data set was less than optimal. Although the R_{int} is not too high (0.0436), the I/σ ratio is rather low (7.9), because the sample is only weakly diffracting; the data completeness is also low (0.854) these limitations, as well as disorder (see below) hampered the refinement process. The structure has been solved in the C 2/c space group (Z=16) by means of intrinsic phasing using SHELXT² and refined by full–matrix least–squares methods based on F_o^2 with SHELXL³ in the framework of the OLEX2 software.⁴ The unit cell is rather large (*ca.* 21000 Å³) and the asymmetric unit contains two independent neutral complex molecules (I and II).

About 30% of each molecule is disordered. In particular, the phenyl rings of the dbm units and the tert-butyl residues of the triazolyl-pyridine ligands are disordered over two positions. Alternate positions of involved atoms were refined with site occupation factors constrained to sum to unity. The seven sets of involved atoms were C54-C56, C75-C80; C11-C15; C97-C101, C110-C112; C41-C45; C5-C6, C90-C95; C82-C86; C35-C39, as well as their bounded H atoms. For the above sets the refined sofs were, respectively, 0.695/0.305, 0.660/0.340, 0.542/0.458, 0.764/0.236, 0.567/0.433, 0.519/0.481, 0.530/0.470. Many additional SHELX² restraints /constraints were also applied to the same atoms as well as to those bound to them in affected rings/groups (DELU, DFIX, FLAT, RIGU, SADI, and SIMU) to improve the model, especially to ensure planarity and comparable bond lenghts. After all these treatments, some atoms were still showing rather high thermal motion parameters, but after comparing the results of several modelling attempts, we did not try any further splitting. The proposed selected solution in our opinion represent the best

possible compromise, with all disordered atoms refined anisotropically; H atoms were placed instead in calculated positions and refined as "riding model"

At this point, some solvent accessible voids (124 cubic angstroms) were also present. The voids are inherent to the (somewhat loose) packing and do not contain missing fragments; no PLATON/SQUEEZE (or similar procedure) was used to account for the residual electron density in the voids. We considered the refinement terminated at this stage. Of course, at least part of the above issues can be addressed by recollecting the data at low temperature, and such experiment has already been planned. Anyway, the coordination environment about the Eu centers is unambiguously defined and the chemical identity of the cell content does not appear to be in question. Since the purpose of the structural determination was to identify the molecular structure of the complex, we consider the proposed solution acceptable.

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Distorted square antiprismatic first coordination sphere of Eu^{3+} in $[Eu(dbm)_3L]$.



Overlap of the inner coordination spheres of the two independent molecules found in the asymmetric unit of $[Eu(dbm)_3L]$.



PLE spectra of $[Ln(\kappa^2-NO_3)_3L_2]$ (solid samples). Ln = Eu, red line, $\lambda_{emission} = 616$ nm; Ln = Tb, green line, $\lambda_{emission} = 545$ nm.



PL (red line) and PLE (violet line) spectra of $[Eu(dbm)_3L]$ in CH_2Cl_2 solution.