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Electronic Supporting Information

Europium complexes with dinitropyrazole: unusual luminescence thermal behavior and irreversible temperature sensing

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Experimental Section

Materials and methods

All solvents and chemicals were purchased from commercial sources.

Thermal analysis was carried out on a thermoanalyzer STA 449 F1 jupiter (NETZSCH, Germany) in the temperature range of 40–1000 °C in air and at a heating rate of 10° min^{-1}. The evolved gases were simultaneously monitored during the TA experiment using a coupled QMS 403 Aëolos Quadro quadrupole mass spectrometer (NETZSCH, Germany). The mass spectra were registered for the species with the following m/z values: 18 (corresponding to H_2O), 44 (corresponding to CO_2), 45 (corresponding to C_2H_5OH) and 31 (corresponding to CH_3O). The **IR spectra** were recorded on an Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer as powdered at ATR. **Powder X-ray diffraction (PXRD)** was performed by using Bruker D8 Advance [λ(Cu-Kα) = 1.5418 Å; Ni filter] with a step size of 0.020°. The patterns were indexed by using SVD-Index[27] as implemented in the TOPAS 4.2 software.[28] Then, the powder patterns were refined by using the Pawley method. The registration of **luminescence spectra** and the measurement of **quantum yields** were carried out on a Fluorolog FL3-22 (HORIBA) spectrometer at room temperature, excitation was performed through a ligand, and the absolute method in the integration sphere was used.

Total X-ray scattering data for pair distribution function (PDF) analysis were collected at 100K on Bruker D8 Quest diffractometer equipped with Bruker C14 Photon III detector and Incoatec IμS 3.0 microfocus sealed tube (Mo-Kα radiation, λ=0.71073 Å) in the 2θ range of 2.7−150° (Q range 0.4−17.1 $Å^{-1}$). The powder sample was fixed onto 100 μm nylon cryoloop within the droplet of nujol oil and placed into cryostream, the empty loop with nujol was measured

as background prior to sample. Azimutal integration of 2D frames and data merging were performed in CrysAlisPro software [1]. Instrument calibration was performed against LaB_6 powder (NIST SRM 660c) pattern measured in the same instrumental conditions. PDF calculations were done with PDFgetX3 [2] using the Q-range of 0.58 to 10.6 Å-1. The simulation of PDF was carried out with DiffPy-CMI package [3]. Atomic coordinates for simulation were taken from the DFT models.

DFT calculations of $EuL_3(H_2O)_3$, $EuL_4(H_2O)^-$ and Eu_2L_6 species in vacuum were performed using Firefly 8.2 package [4] based on density functional theory (DFT) at the hyper-GGA level (PBE0 functional). For the light atoms (C, O, N, H), 6-31G(d, p) basis set was used. For the Eu atoms, the energy-consistent Stuttgart/Cologne quasi-relativistic pseudopotential (large core including f-electrons) and corresponding optimized valence basis set was applied [5]. Geometry optimization of each molecule was performed for several times using the different starting points with random initial atomic displacements. Final geometry of the lowest energy was checked for the absence of imaginary frequencies of normal vibrations by Hessian calculation. The TDDFT calculation was performed for $EuL_4(H_2O)^-$ anionic species within the same PBE0 functional and basis set, the first 100 singlet-singlet excitations were taken into account.

Literature

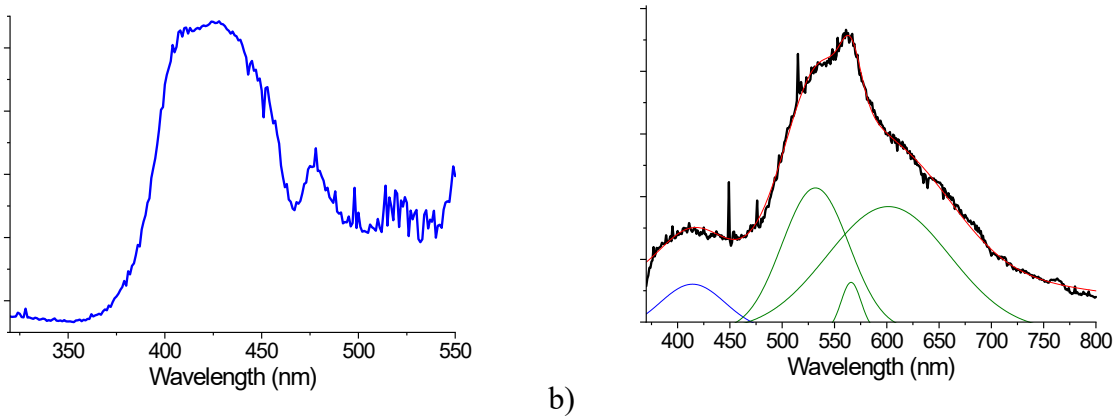
1 CrysAlisPro Software System, Version 1.171.40.1a Rigaku Oxford Diffraction, http://www.rigaku.com.

2 P. Juhás, T. Davis, C. L. Farrow, S. J. L. Billinge and IUCr, *urn:issn:0021-8898*, 2013, **46**, 560–566.

3 P. Juhás, C. Farrow, X. Yang, K. Knox, S. Billinge and IUCr, *urn:issn:2053-2733*, 2015, **71**, 562–568.

4 Alex A. Granovsky, Firefly 8.2 package, http://classic.chem.msu.su/gran/firefly/index.html.

5 Stuttgart/Cologne energy-consistent (ab initio) pseudopotentials, http://www.tc.unikoeln.de/PP/clickpse.en.html.



a) b)

Figure S1. a) Excitation spectrum of solid HL at 77K (λ_{em}=562 nm). b) Deconvoluted emission spectrum of solid HL at 77K (λ_{ex}=320 nm).

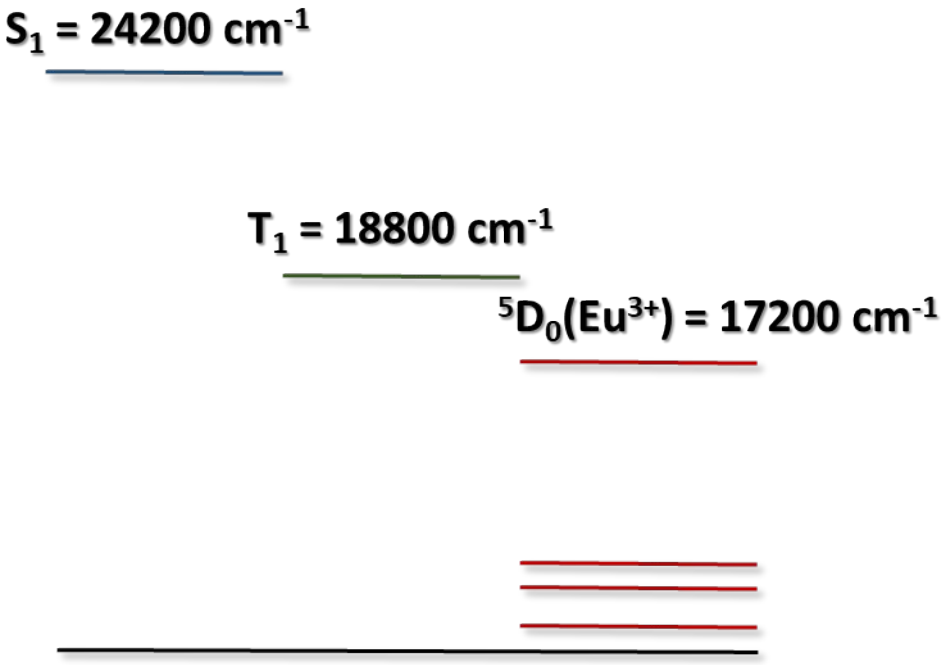


Figure S2 A diagram depicting the relative position of the ligand and Eu excited states energy levels