

## Electronic Supplementary Information

### The key role of accurate lattice parameters in revealing subtle structural differences – a case study in the system [Ln(phen/phen-d<sub>8</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>]

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#### a) Synthesis

All batches were prepared according to the following general procedure: 65 mg of the lanthanide nitrate (europium(III) nitrate hexahydrate, 3N5, Kanto Chemical or terbium(III) nitrate hexahydrate, 3N5, Kanto Chemical) were dissolved in 1.5 ml ethanol, then 70 mg 1,10-phenanthroline monohydrate (min. 99.0%, Wako) were added and the resulting slurry was stirred for 10 minutes at ambient temperature. The product was filtered off, washed with ethanol and dried under vacuum, resulting in yields of about 92%. For the syntheses of the deuterated compounds ethanol-d<sub>6</sub> (99.5 Atom% D, ISOTEC) was used as the solvent and 1,10-phenanthroline-d<sub>8</sub> (min. 98 Atom% D, ISOTEC) as the ligand. Elemental analyses (Micro Corder JM10, J-Science Lab) confirmed the gross compositions, FAB mass spectrometry (MStation, MS-700A, JEOL) showed that the samples prepared with phen-d<sub>8</sub> retained the deuterium upon storage.

#### b) Synchrotron Powder Diffraction

In order to obtain accurate lattice parameters of the investigated phases, powder patterns were recorded on the large Debye-Scherrer camera, installed at the BL02B2 beamline at SPring-8 [1], that is equipped with an image plate detector. The samples were gently ground and filled to 0.3 mm Mark tubes (Hilgenberg). Data were collected by exposing a BAS-MS 2040 imaging plate (Fuji Photo Film Co., Ltd.) to the diffracted beam for 5 min at 300 K. The wavelength of the primary beam ( $\lambda=1.00224$  Å) was determined from a CeO<sub>2</sub> sample (NIST standard 674a,  $a=5.4111(1)$  Å).

All powder data were treated with the GSAS program [2]. For the structure refinement of Eu<sup>H</sup>-IIa the starting geometry was imported from the ordered model of modification II [3]. To overcome the low reflection/parameter ratio strict restraints were applied to the phenanthroline and nitrate ligands. The position, i.e. the *y*-coordinate, of europium as well as all metal-ligand bonds were allowed to vary freely. The isotropic displacement parameters of atoms of the same type were constrained and

those of hydrogen were set to 1.2 times the value of their basis atoms. The refinement converged at  $R_{wp}=0.034$ ,  $\chi^2=1.83$ ,  $R_{Bragg}=0.051$  (Figure S1).

The so obtained structure, together with the atom parameters of Eu<sup>H</sup>-I [4] and Tb<sup>H</sup>-I [5] were used in the refinement of the lattice parameters (Le Bail fit; parameters varied: lattice parameters, zero shift, profile, background) and the following quantitative phase analyses (parameters varied: scale factors, background; see Figure S2 for an example plot) of the two-phase batches. In the case of the samples containing the terbium complex in modification IIa the atom parameters of Eu<sup>H</sup>-IIa were used for the quantitative phase analyses, since i) no data of sufficient quality, i.e. a single-phase batch of Tb<sup>H/D</sup>-IIa, was obtained to refine the structure properly and ii) the structural differences between the europium and terbium complex in modification IIa were considered to have a negligible effect on the phase analysis.

### c) Tables

**Table S1** Lattice parameters (Å, °) of the various modifications of Ln<sup>H/D</sup> as obtained by Le Bail fits (space group *C2/c* (no. 15) and *Z*=4 for all phases)

Phase	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$	<i>V</i>
Eu <sup>H</sup> -I [4]	11.165(1)	17.972(2)	13.052(1)	100.565(7)	2574.6(4)
[3]	11.156(1)	17.960(1)	13.057(1)	100.51(1)	2572.1(3)
Eu <sup>D</sup> -I <sup>a</sup>	11.1610(1)	17.9425(2)	13.0326(1)	100.519(1)	2565.99(5)
Eu <sup>H</sup> -II [3]	9.515(1)	15.455(1)	17.176(1)	93.45(1)	2521.3(3)
Eu <sup>H</sup> -IIa <sup>a</sup>	9.52609(8)	15.4672(2)	17.2278(2)	93.458(1)	2533.77(5)
Eu <sup>D</sup> -IIa <sup>a</sup>	9.51735(7)	15.4544(2)	17.2015(1)	93.437(1)	2525.53(5)
Tb <sup>H</sup> -I [5]	11.155(1)	17.914(2)	13.026(1)	100.549(9)	2559.0(4)
<sup>a</sup>	11.1521(4)	17.9037(6)	13.0226(4)	100.505(4)	2556.6(1)
Tb <sup>D</sup> -I <sup>a</sup>	11.1477(4)	17.8808(5)	13.0063(4)	100.496(2)	2549.2(2)
Tb <sup>H</sup> -IIa <sup>a</sup>	9.4995(1)	15.4717(1)	17.1750(3)	93.479(1)	2519.62(9)
Tb <sup>D</sup> -IIa <sup>a</sup>	9.4902(2)	15.4555(6)	17.1489(4)	93.458(2)	2510.7(1)

<sup>a</sup> this work

**Table S2** Selected dihedral angles ( $^{\circ}$ ) in the three  $\text{Eu}^{\text{H}}$  modifications

Modification	phen-phen	$\text{NO}_3^{\text{a}}-\text{NO}_3^{\text{a}}$	$\text{NO}_3^{\text{a}}-(\text{Eu}1-\text{O}1-\text{O}2)$	$\text{NO}_3^{\text{b}}-\text{C-plane}$
I [4]	42.91(3)	42.5(2)	0.7(2)	87.4(2)
II [4]	60.4(2)	28.4(7)	13.4(7)	12.0(4)
IIa <sup>c</sup>	61.09(8)	25.3(5)	11.9(5)	11.5(4)

<sup>a</sup> Spanned by N3-O1-O2-O3 and <sup>b</sup> N4-O4-O5

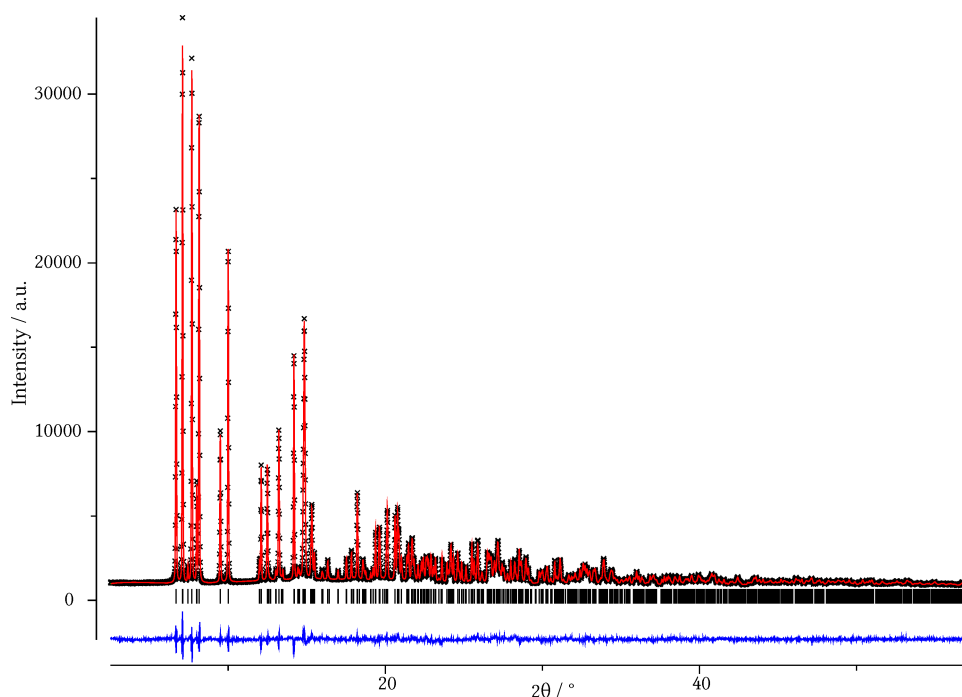
<sup>c</sup> this work

**Table S3** Coordinative bond lengths ( $\text{\AA}$ ) in the three  $\text{Eu}^{\text{H}}$  modifications

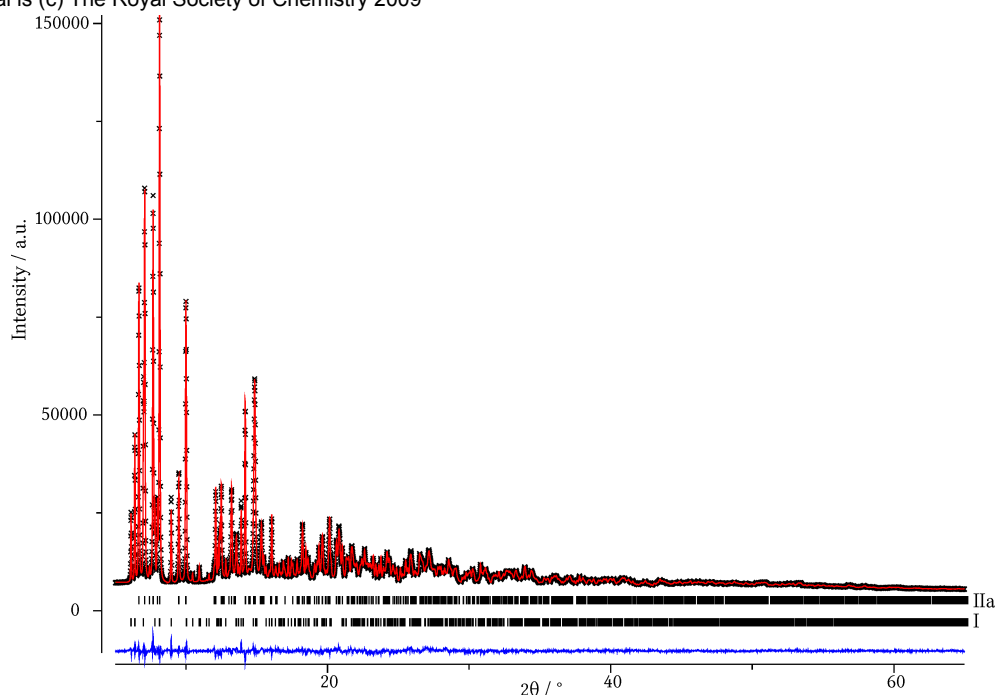
Modification	Eu1-N1	Eu1-N2	Eu1-O1	Eu1-O2	Eu1-O4
I [4]	2.593(2)	2.541(2)	2.540(2)	2.497(2)	2.495(2)
II [3]	2.58(1)	2.529(9)	2.511(7)	2.524(8)	2.480(9)
IIa <sup>a</sup>	2.586(4)	2.534(4)	2.509(6)	2.552(6)	2.490(5)

<sup>a</sup> this work

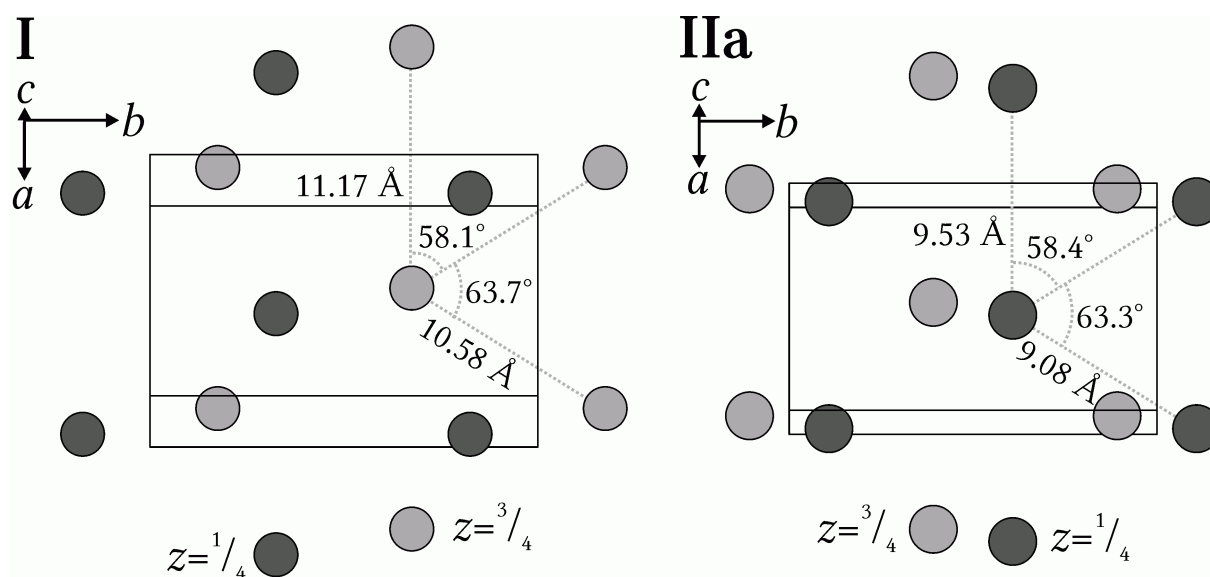
#### d) Figures



**Figure S1** Final Rietveld plot of the structure refinement of  $\text{Eu}^{\text{H}}\text{-IIa}$  ( $\lambda=1.00224 \text{ \AA}$ ,  $R_{\text{wp}}=0.034$ ,  $\chi^2=1.83$ ). The Bragg reflections' positions are marked with vertical bars, the difference curve is shown at the bottom.



**Figure S2** Quantitative phase analysis of the Eu<sup>D</sup> batch. ( $\lambda=1.00224 \text{ \AA}$ ,  $R_{wp}=0.021$ ,  $\chi^2=4.31$ ). The Bragg reflections' positions are marked with vertical bars, the difference curve is shown at the bottom



**Figure S3** Two pseudo-hexagonal layers of Eu atoms in the crystal structure of  $[\text{Eu}(\text{phen})_2(\text{NO}_3)_3]$  projected onto the C-plane, shown for modification I and IIa.

e) Literature on organometallic lanthanide compounds containing deuterium

(as deposited in the Cambridge Structural Database, CSD Version 5.29, November 2007)

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