# Supporting Information

## The first examples of lanthanide selenite-carboxylate compounds: syntheses, crystal structures and properties

Xiao-Feng Guo, Mei-Ling Feng, Zai-Lai Xie, Jian-Rong Li, and Xiao-Ying Huang*

*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China, E-mail: xyhuang@fjirsm.ac.cn*

## 1. More Structural details

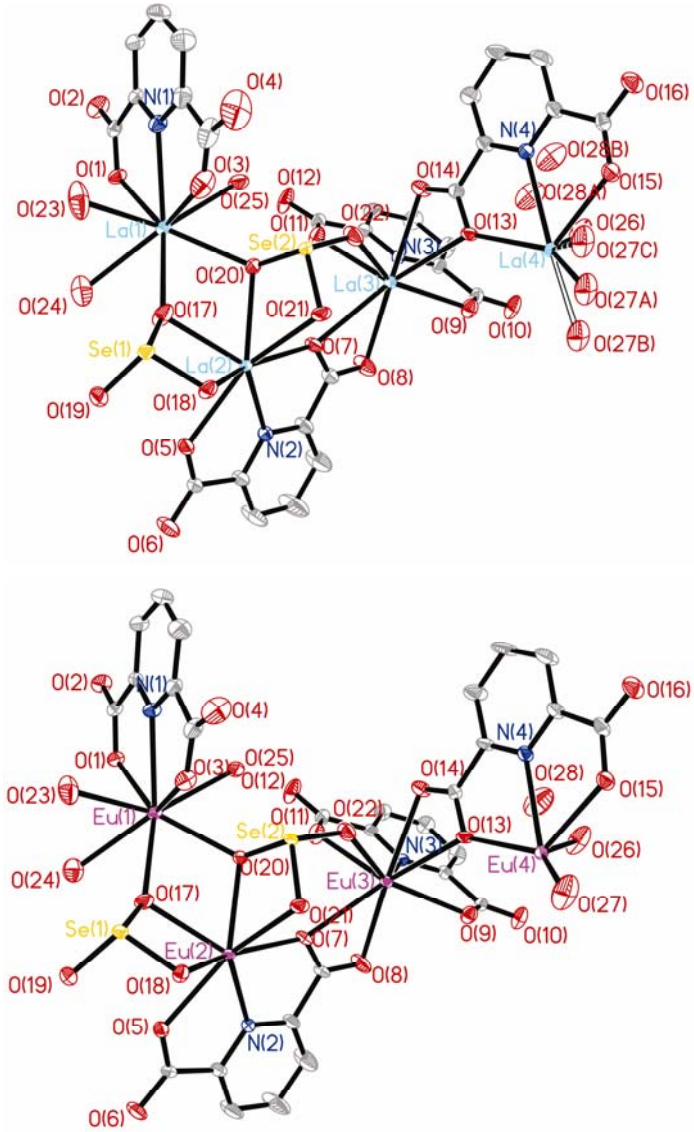


**Fig. S1** *ORTEP* plots of the crystallographically asymmetric units in **1** (top) and **3** (bottom); thermal ellipsoids are given at the 50% probability level; hydrogen atoms are omitted for clarity.

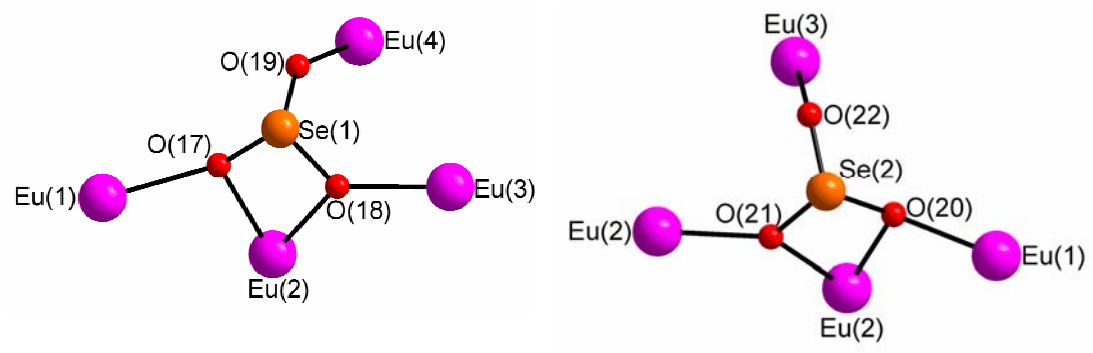


**Fig. S2** Coordination modes of $SeO_3$ groups. The $Se(1)O_3$ group chelates with the Eu(2) ion and bridges to three other Eu(III) ions, Eu(1), Eu(3), Eu(4); whereas $Se(2)O_3$ chelates with the Eu(2) ion and bridges to Eu(1), Eu(2), Eu(3) ions.

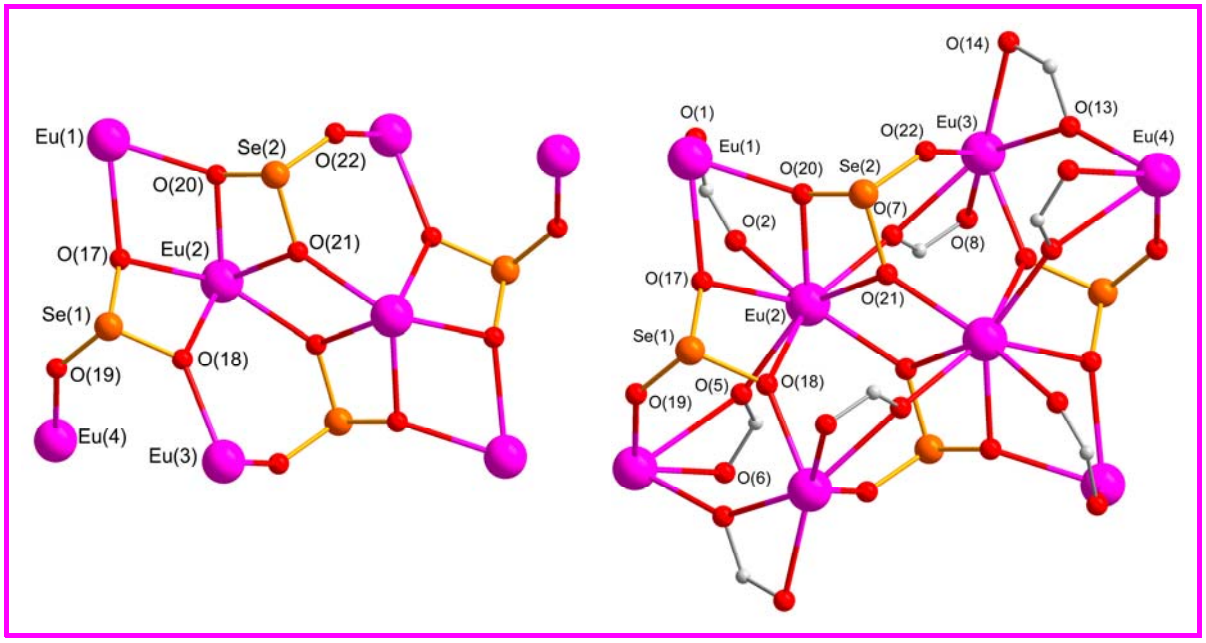


**Fig. S3** Left: The $Eu_8(SeO_3)_4$ core in the cluster. Right: A plot showing that the Eu pairs in the cluster are connected by both $SeO_3^{2-}$ and $CO_2^-$ groups.

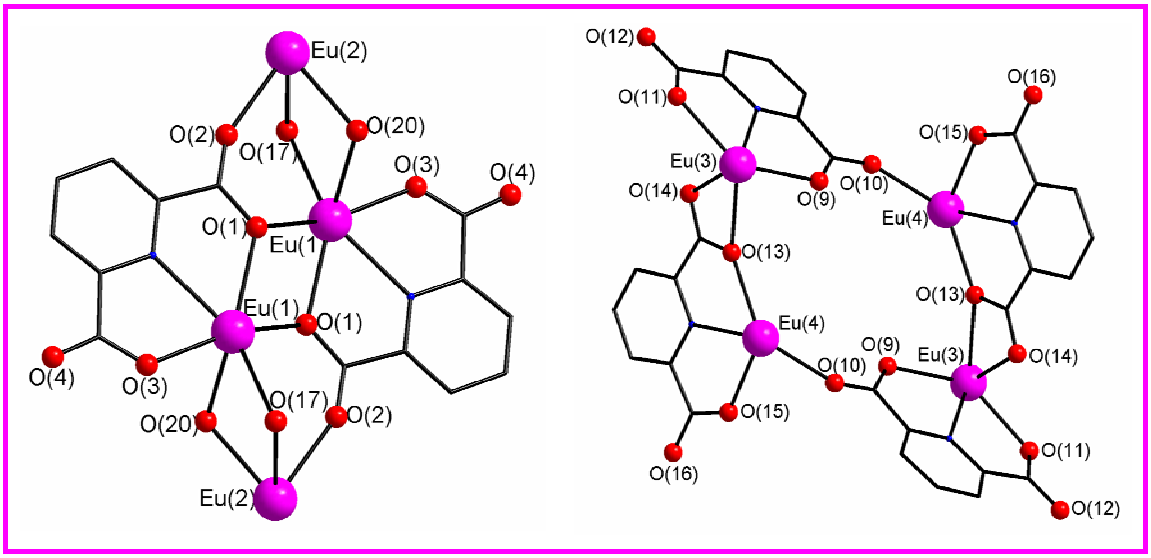


**Fig. S4** The $Eu_2O_2$ rhombic unit (left) and $Eu_4O_2(COO)_2$ 12-membered ring (right) in **3** which connect the clusters into an extended 2D-network along *b* axis and *c* axis, respectively.

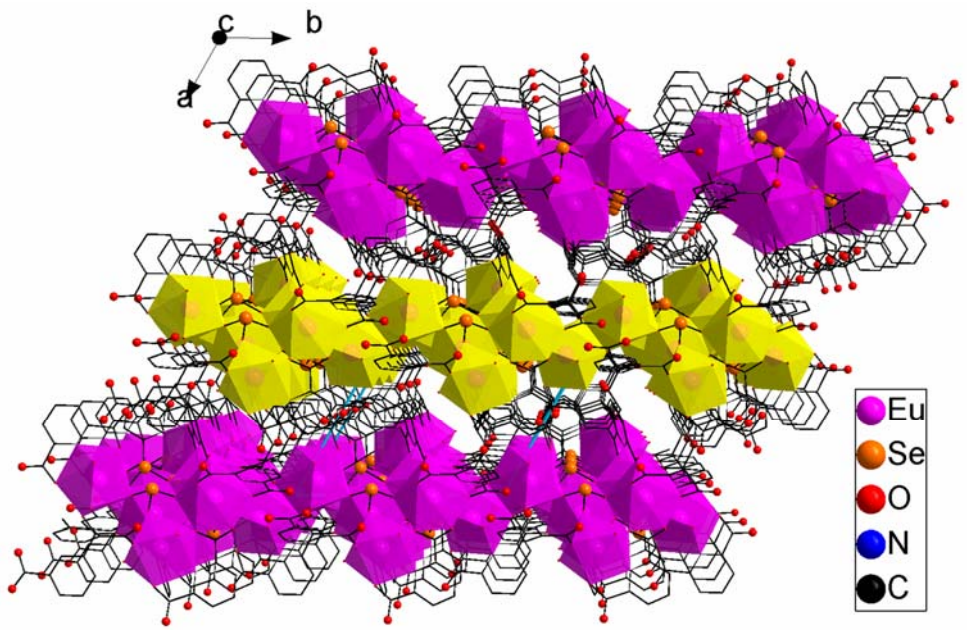


**Fig. S5** Polyhedral view of the packing of layers in compound **3** down the *c*-axis. One of the layers is highlighted in yellow for clarity.

## 2. Physical measurements.

### 2a) IR spectra

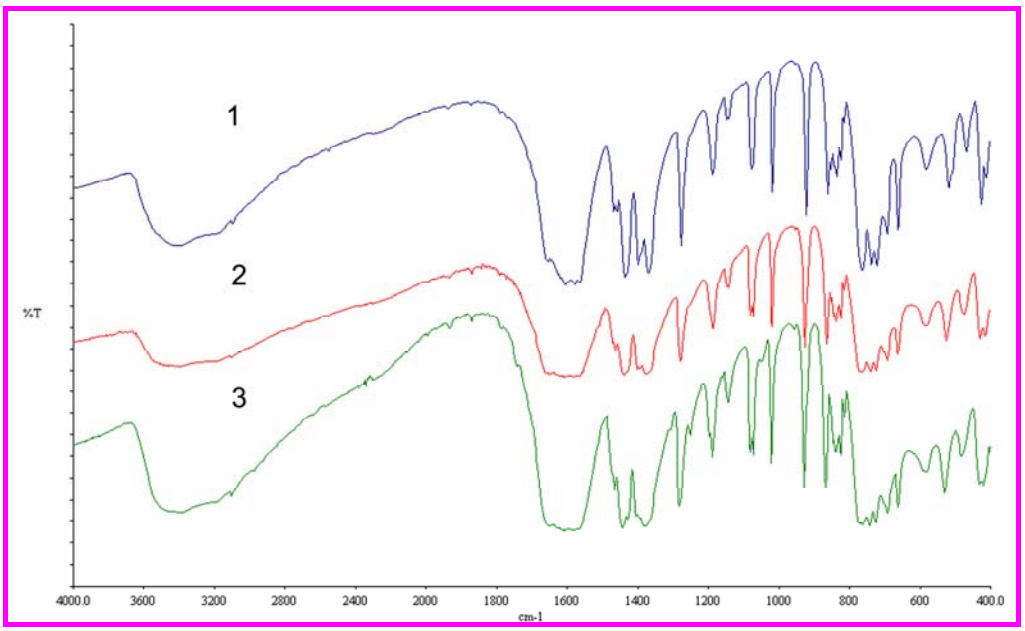


**Fig. S6** IR Spectra of compounds **1** (La), **2** (Nd) and **3** (Eu).

### 2b) PXRD

Powder X-ray diffraction patterns were recorded on a Rigaku Dmax/2500 diffractometer using Cu*Kα* radiation in the angular range of 2θ = 2-50º.

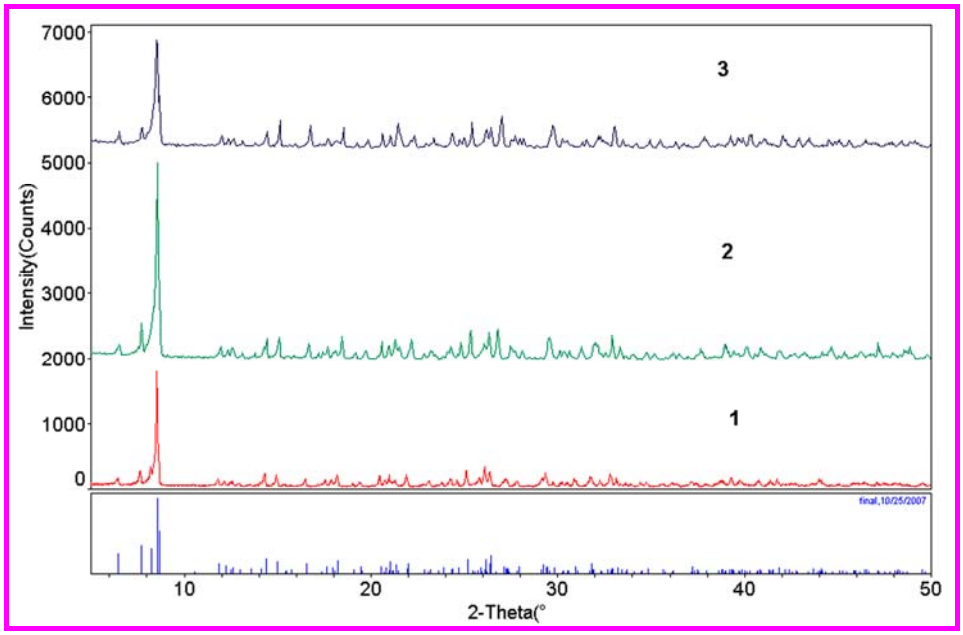


**Fig. S7** The PXRD patterns of compounds **1** (La), **2** (Nd) and **3** (Eu) are in very good agreement with the simulated PXRD pattern calculated from single crystal X-ray data of **3** (bottom), indicating the phase purity of **1** (La), **2** (Nd) and **3** (Eu).

## 3. Dehydration and rehydration process

Thermogravimetric analyses (TGA) were carried out on a METTLER TGA/SDTA851e thermal analyzer from room temperature to 300°C in a ramp rate of 20°C/min and constant temperature at 300°C for approximate 30 mins in a dynamic dry air atmosphere. Powder X-ray diffraction patterns were recorded on a Rigaku Dmax/2500 diffractometer using Cu*Kα* radiation in the angular range of 2θ = 2-50º.

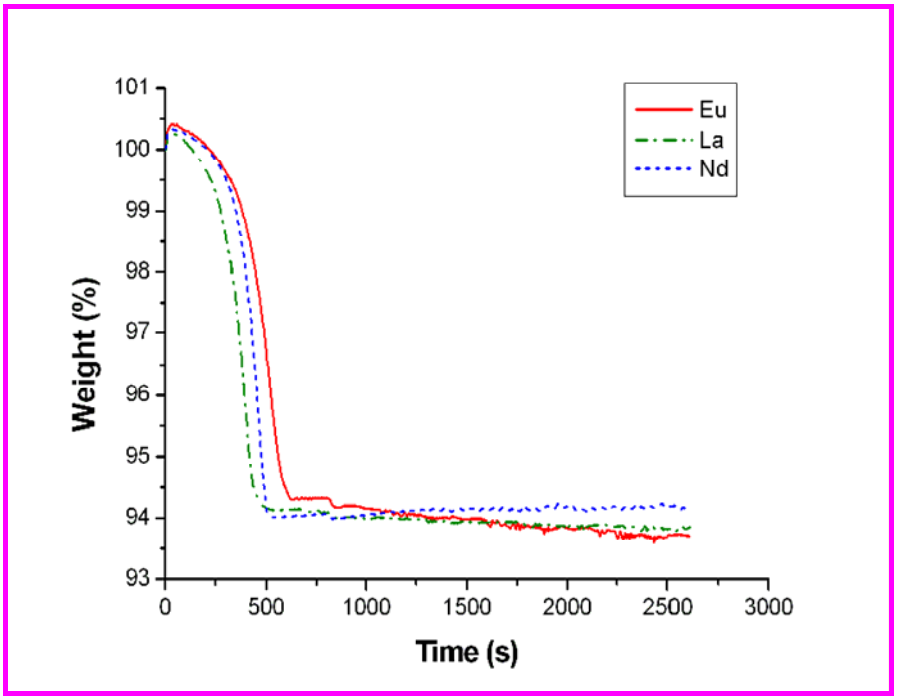


**Fig S8**. The dehydration process of **1** (La), **2** (Nd), and **3** (Eu).

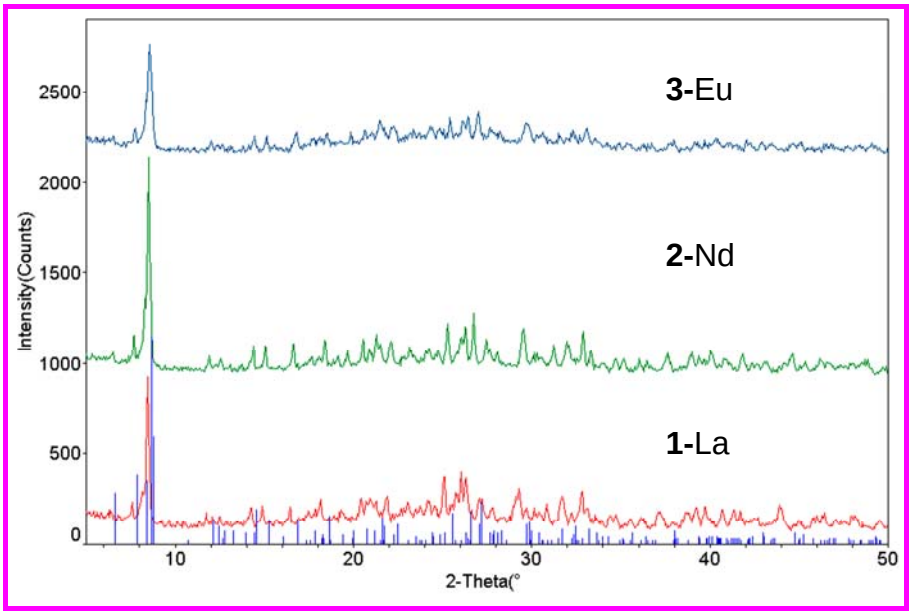


**Fig. S9** Room temperature PXRD patterns for residual of **1** (La), **2** (Nd), and **3** (Eu) after heating at 300°C for approximate 30 mins**;** the simulated PXRD pattern from single crystal X-ray data of **3** (Eu) was plotted at the bottom for comparison.

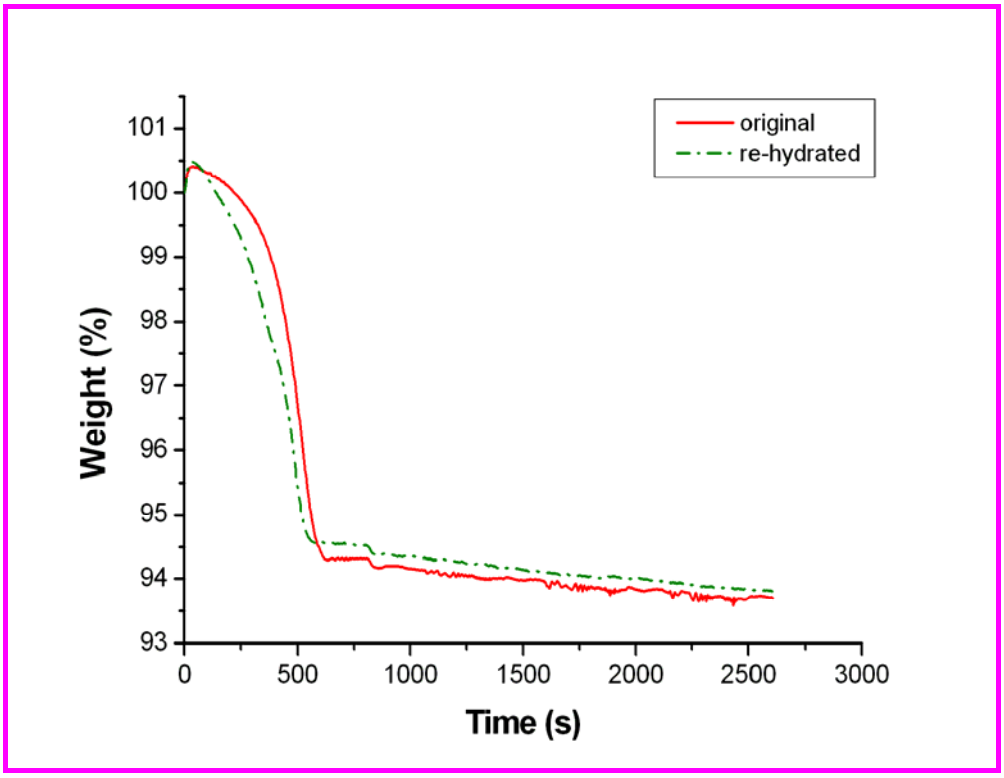


**Fig. S10** The dehydration process of **3** (Eu) by heating at 300 °C for approximate 30 mins. The red curve showed the dehydration process of the original sample. The green curve showed the dehydration process of the rehydrated sample of **3** (Eu) by being exposed to air for twelve days.

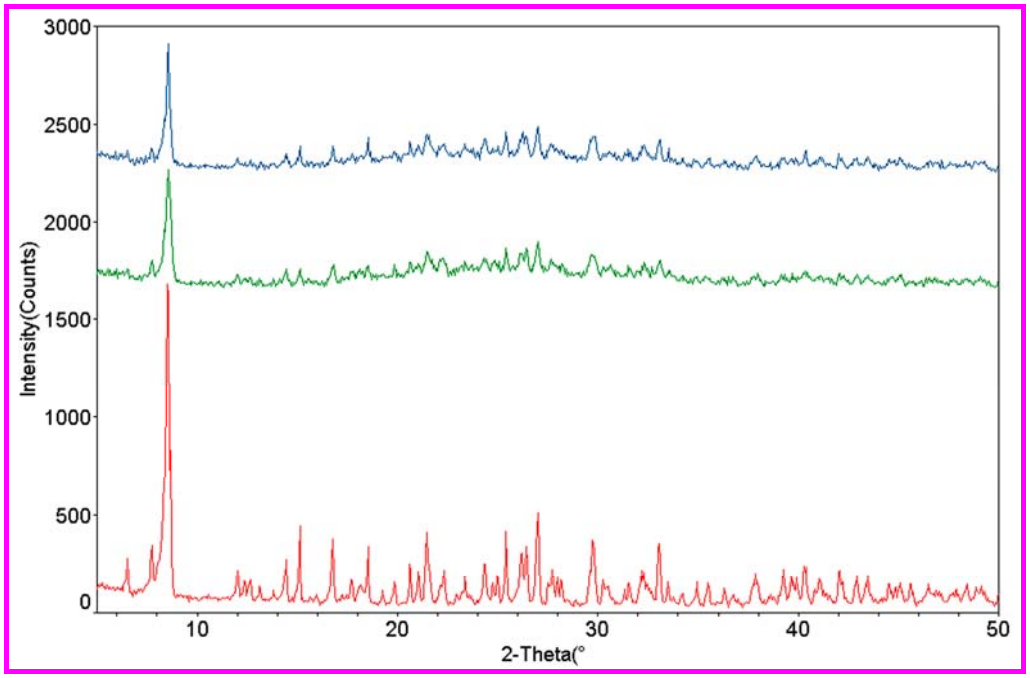


**Fig. S11** Room temperature PXRD patterns of the TGA residual of **3** (Eu). The middle one is for the residue of **3** (Eu) right after heating at 300°C for approximate 30 mins. The residue was rehydrated by being exposed to air for twelve days. The rehydrated sample was heated at 300 °C for approximate 30 mins and the PXRD of the residue was shown at the top. The PXRD pattern of the original pure sample of **3** (Eu) is plotted at the bottom for comparison.