New approach to increase the sensitivity of Tb-Eu-based luminescent thermometer

Mikhail B. Vialtsev[a,b], Alexander I. Dalinger[a], Egor V. Latipov[a,c], Leonid S. Lepnev[d], Sergey E. Kushnir[a,b], Sergey Z. Vatsadze[a], Valentina V. Utochnikova*[a,b,e]

[a] Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, 1, build.3, 119991, Moscow, Russian Federation

[b] Department of Materials Science, Lomonosov Moscow State University, Moscow 119991, Russia

[c] Institute of Nanotechnology of Microelectronics of the Russian Academy of Sciences, Moscow, Russia

[d] P.N. Lebedev Physical Institute, Leninsky prosp. 53, Moscow, 119992, Russia

[e] SIA Evoled, Puskina iela 1A-24, Riga, LV-1050, Latvia

Contents

Experimental section

Methods

Thermal analyses were carried out on a thermoanalyzer STA 409 PC Luxx (NETZSCH, Germany) in the temperature range of 20–1000 ºC in air atmosphere, heating rate 10 º/min. The evolved gases composition was simultaneously monitored during the TA experiment using a coupled QMS 403C Aeolos quadrupole mass spectrometer (NETZSCH, Germany). The mass spectra were registered for the species with following m/z values: 18 (corresponding to H_2O), 44 (corresponding to CO_2).

Powder X-ray diffraction (PXRD) was performed by using Rigaku D/MAX 2500 [λ(Cu-K_α) = 1,54046 Å; Ni filter] the range of 2Θ 20–60°.

Emission and excitation spectra were measured with a Fluorolog 3 spectrofluorometer over excitation with a xenon lamp. *Luminescence lifetime* measurements were recorded and detected on the same system. Lifetimes were averages of at least three independent measurements. All luminescence decays proved to be perfect single-exponential functions.

Scanning electron microscopy (SEM) and *Energy-dispersive X-ray spectroscopy (EDX).* The microstructures and composition of samples were observed using SEM (Leo Supra 50 VP) attached with EDX (Oxford, X-Max 80).

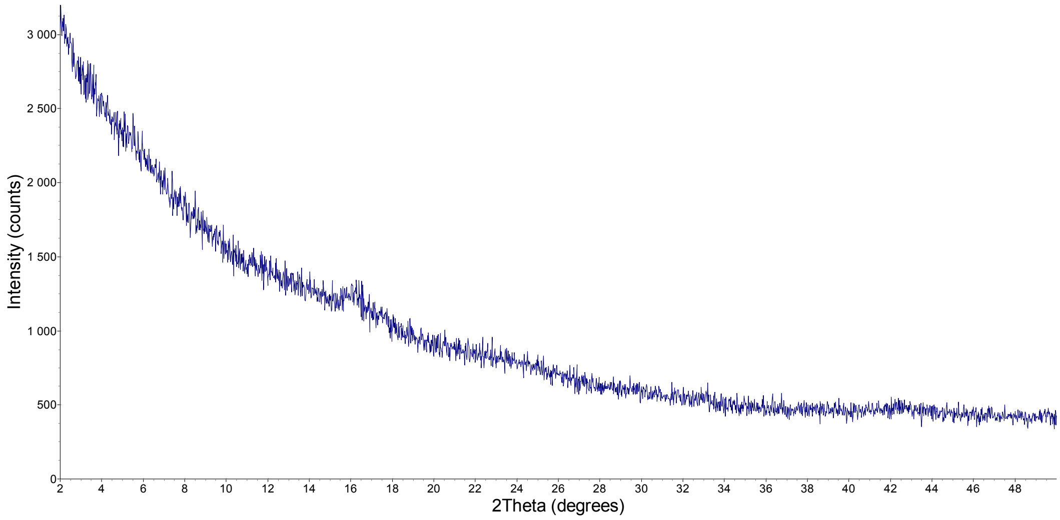
Synthesis of lanthanide complexes

The synthesis of $Tb_xEu_yGd_{1-x-y}(Carb)_3\cdot 4H_2O$ was carried out in water by the exchange reaction between lanthanide chlorides and potassium carboxylates; the homogenization was achieved by co-dissolving of the initial chlorides:

$$HCarb + KOH = K(Carb) + H_2O \quad (1)$$

$$3K(Carb) + xTbCl_3\cdot 6H_2O + yEuCl_3\cdot 6H_2O + (1-x-y)GdCl_3\cdot 6H_2O = Tb_xEu_yGd_{1-x-y}(Carb)_3\cdot 4H_2O + 3KCl \quad (2)$$

PXRD data



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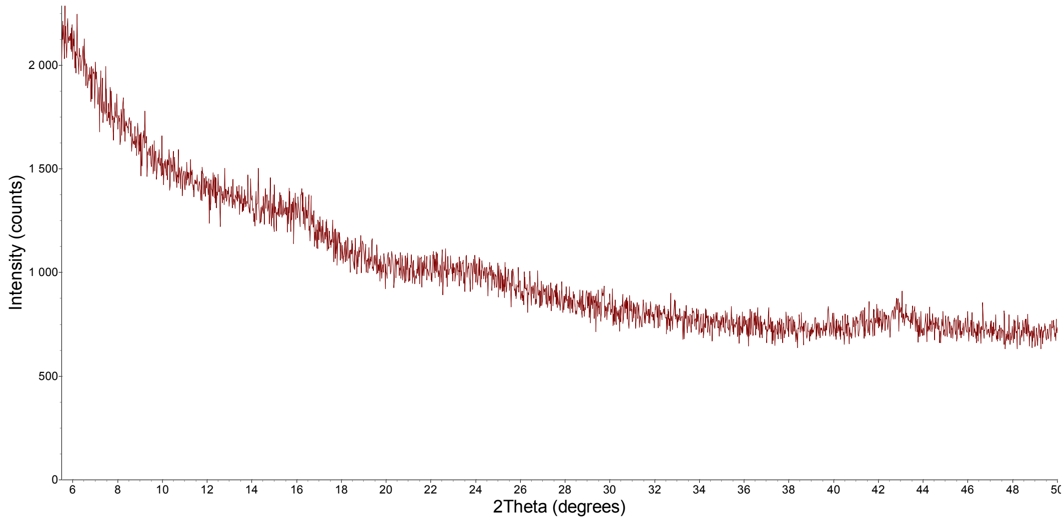

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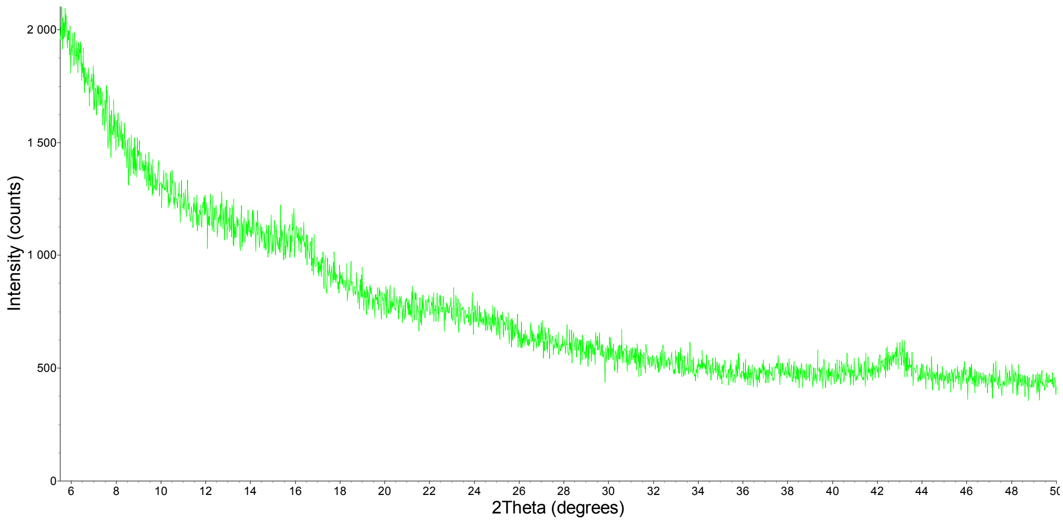

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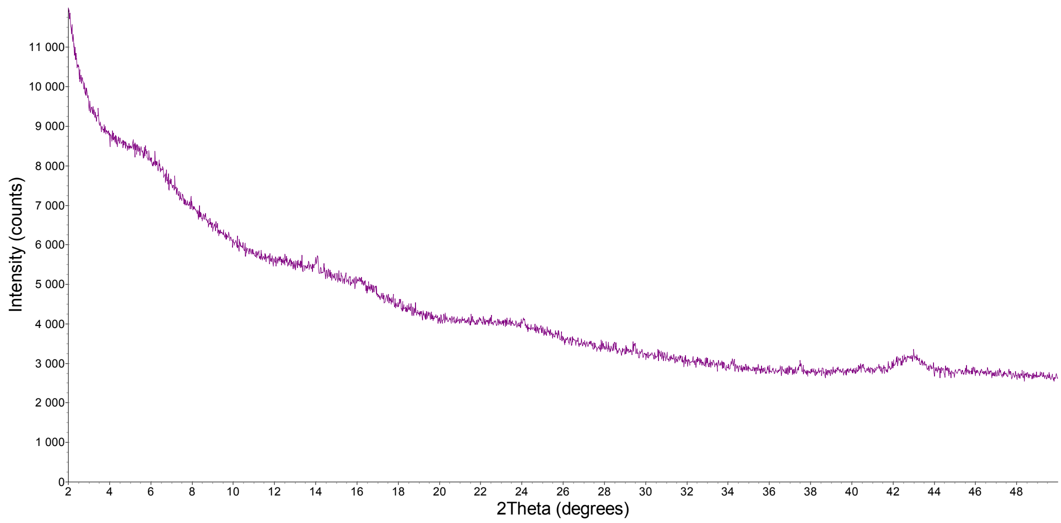
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9 000
8 000
7 000
6 000
5 000
4 000
3 000
2 000
1 000
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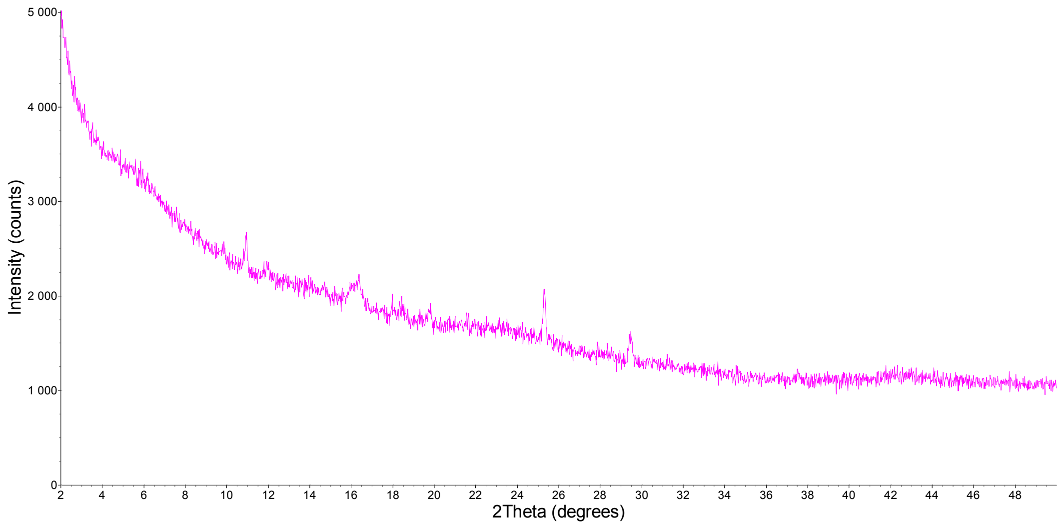
2Theta (degrees)

d)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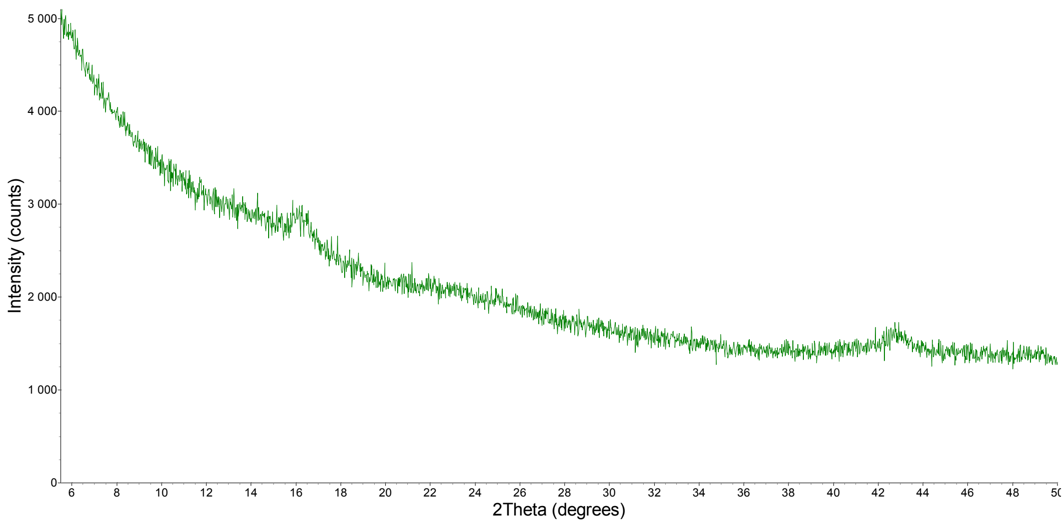
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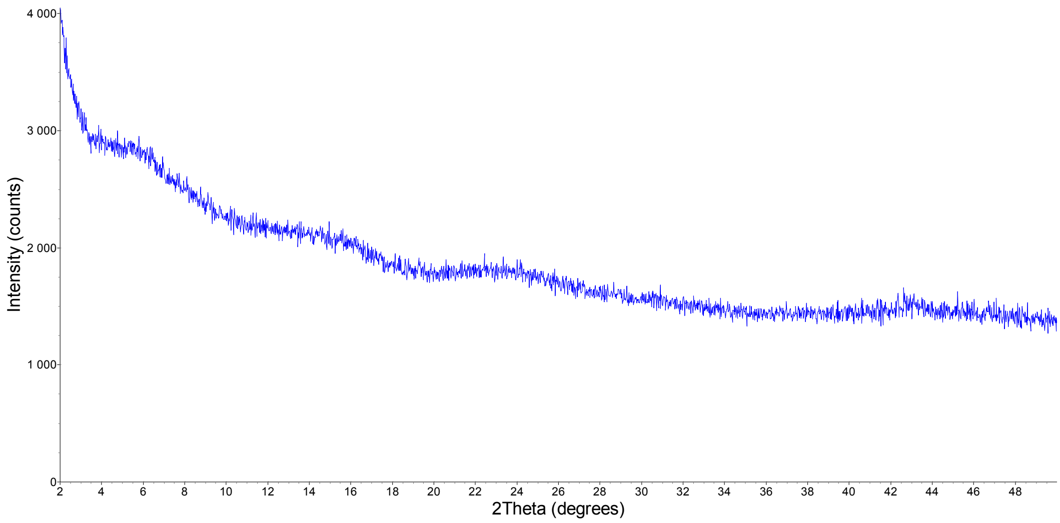

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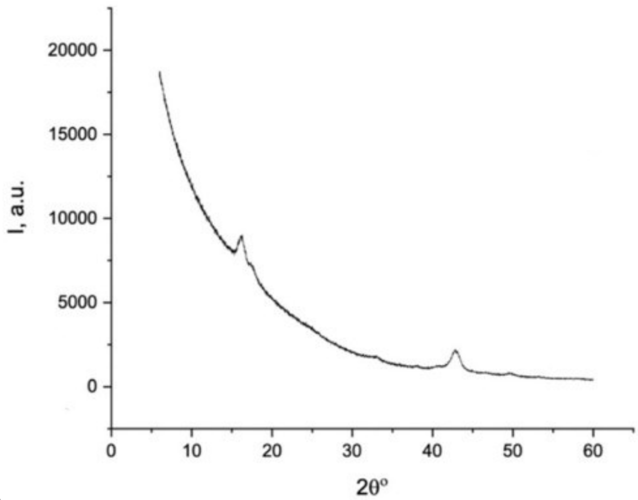


h)

Fig. S1 PXRD data of a) $TbCarb_3 \cdot 4H_2O$; b) $EuCarb_3 \cdot 4H_2O$; c) $Tb_{0.99}Eu_{0.01}Carb_3 \cdot 4H_2O$; d) $Tb_{0.96}Eu_{0.04}Carb_3 \cdot 4H_2O$; e) $Tb_{0.9}Eu_{0.1}Carb_3 \cdot 4H_2O$; f) $Tb_{0.24}Eu_{0.06}Gd_{0.7}Carb_3 \cdot 4H_2O$; g) $Tb_{0.008}Eu_{0.002}Gd_{0.99}Carb_3 \cdot 4H_2O$; h) Mylar film.

Thermal analyses

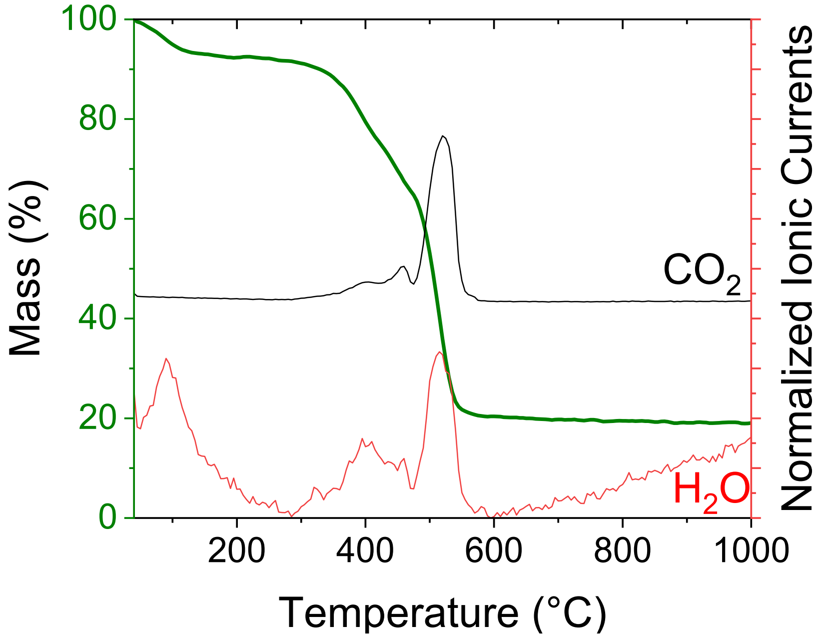


Fig. S2 Thermal analysis with mass-detection of the evolved gases of $Tb_{0.24}Eu_{0.06}Gd_{0.7}Carb_3 \cdot 4H_2O$

EDX and SEM data

The metal ratio in the complexes was determined using EDX. EDX data confirmed the coincidence of the theoretical and experimental terbium-europium-gadolinium ratio in the synthesized terbium-europium-gadolinium carboxylates (Table. S1).

Table. S1 Terbium, europium and gadolinium molar fractions according to EDX data, %

Sample	**Tb**	**Eu**	**Gd**
$Tb_{0.99}Eu_{0.01}(Carb)_3 \cdot 4H_2O$	99	1	0
$Tb_{0.96}Eu_{0.04}(Carb)_3 \cdot 4H_2O$	97	3	0
$Tb_{0.9}Eu_{0.1}Carb_3 \cdot 4H_2O$	91	9	0
$Tb_{0.8}Eu_{0.2}(Carb)_3 \cdot 4H_2O$	81	19	0
$Tb_{0.24}Eu_{0.06}Gd_{0.7}Carb_3 \cdot 4H_2O$	25	4	71
$Tb_{0.08}Eu_{0.02}Gd_{0.9}(Carb)_3 \cdot 4H_2O$	8	2	90
$Tb_{0.024}Eu_{0.006}Gd_{0.97}Carb_3 \cdot 4H_2O$	2	1	97

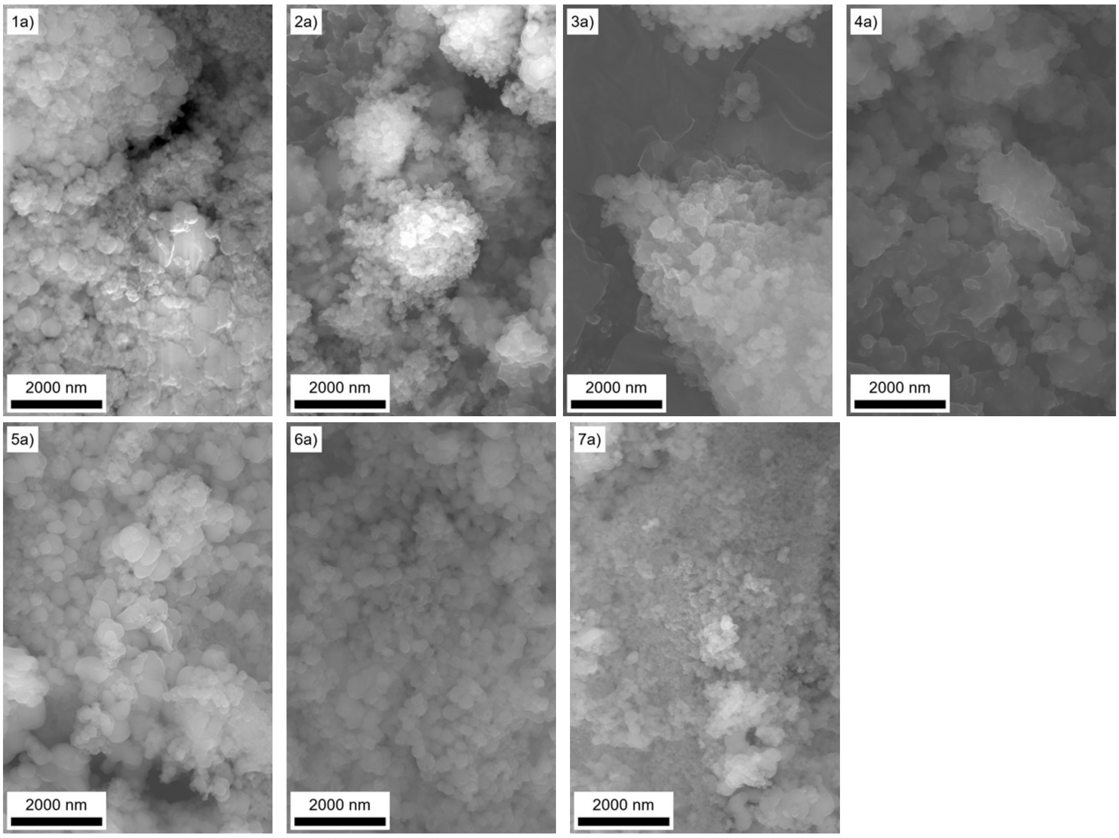
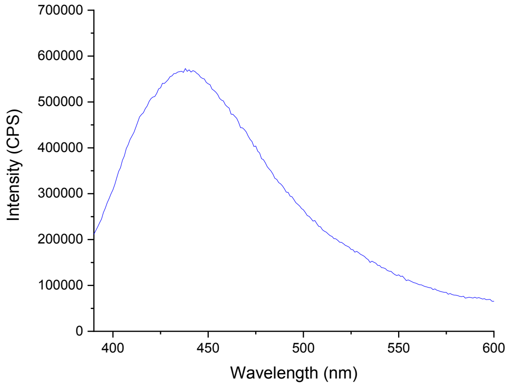


Fig. S3 SEM data of 1) $Tb_{0.96}Eu_{0.04}(Carb)_3 \cdot 4H_2O$; 2) $Tb_{0.9}Eu_{0.1}(Carb)_3 \cdot 4H_2O$; 3) $Tb_{0.8}Eu_{0.2}(Carb)_3 \cdot 4H_2O$; 4) $Tb_{0.24}Eu_{0.06}Gd_{0.7}(Carb)_3 \cdot 4H_2O$; 5) $Tb_{0.08}Eu_{0.02}Gd_{0.9}(Carb)_3 \cdot 4H_2O$ 6) $Tb_{0.024}Eu_{0.006}Gd_{0.97}(Carb)_3 \cdot 4H_2O$; 7) $Tb_{0.008}Eu_{0.002}Gd_{0.99}(Carb)_3 \cdot 4H_2O$

Luminescence data



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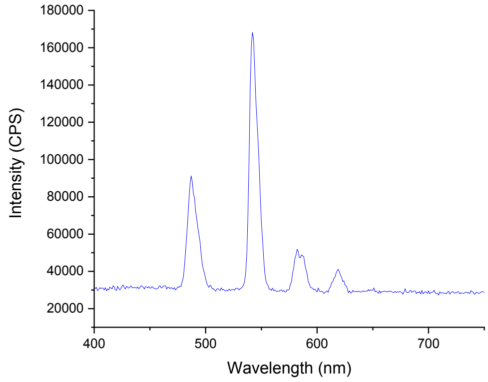

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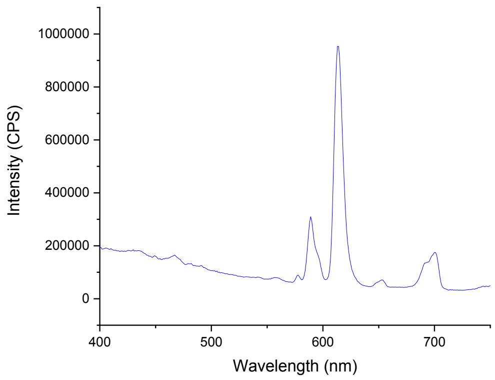

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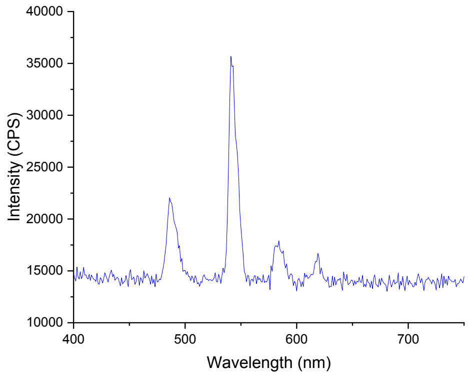

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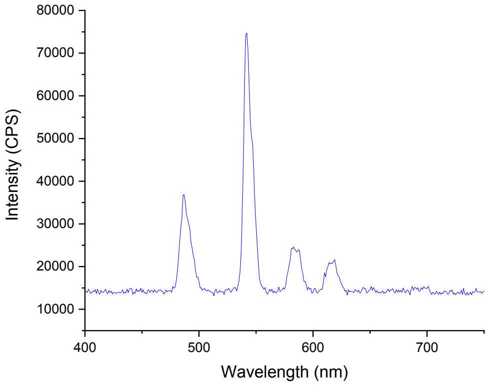

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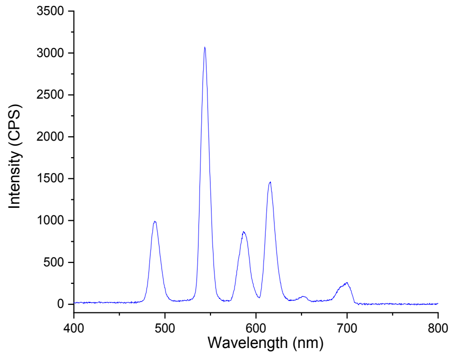

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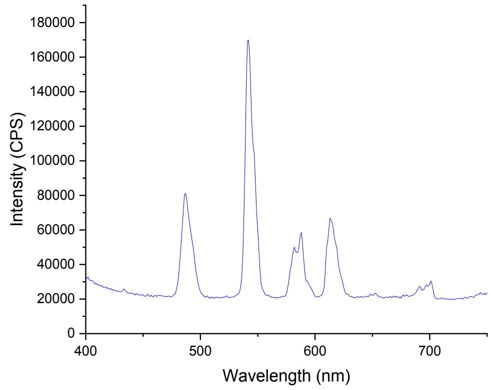

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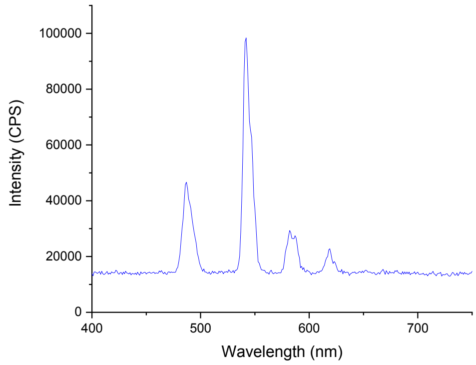

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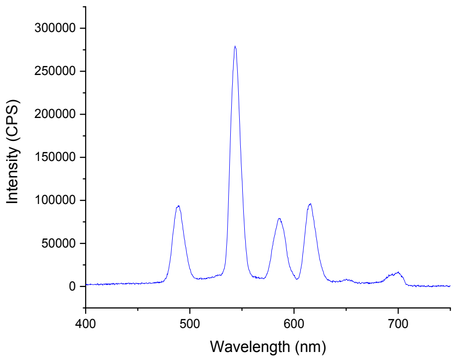

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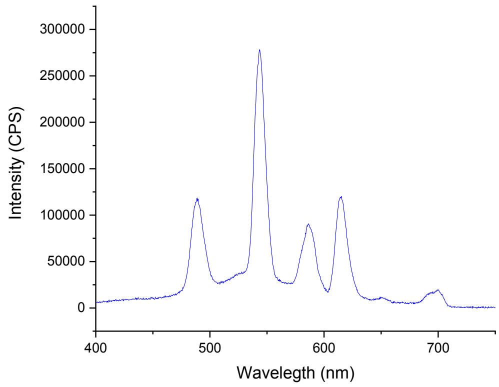

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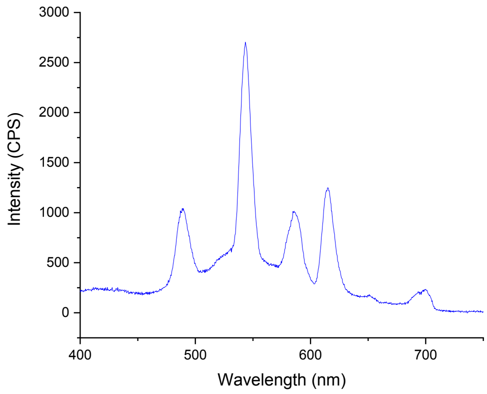

k)

Fig. S4 Luminescence spectra of a) $Gd(Carb)_3 \cdot 4H_2O$; b) $TbCarb_3 \cdot 4H_2O$; c) $EuCarb_3 \cdot 4H_2O$; d) $Tb_{0.99}Eu_{0.01}Carb_3 \cdot 4H_2O$; e) $Tb_{0.96}Eu_{0.04}Carb_3 \cdot 4H_2O$; f) $Tb_{0.9}Eu_{0.1}Carb_3 \cdot 4H_2O$; g) $Tb_{0.8}Eu_{0.2}Carb_3 \cdot 4H_2O$; h) $Tb_{0.24}Eu_{0.06}Gd_{0.7}Carb_3 \cdot 4H_2O$; i) $Tb_{0.08}Eu_{0.02}Gd_{0.9}Carb_3 \cdot 4H_2O$; j) $Tb_{0.024}Eu_{0.006}Gd_{0.97}Carb_3 \cdot 4H_2O$; k) $Tb_{0.008}Eu_{0.002}Gd_{0.99}Carb_3 \cdot 4H_2O$ (λ_{ex}=300 nm, λ_{em}=400...740 nm, room temperature).

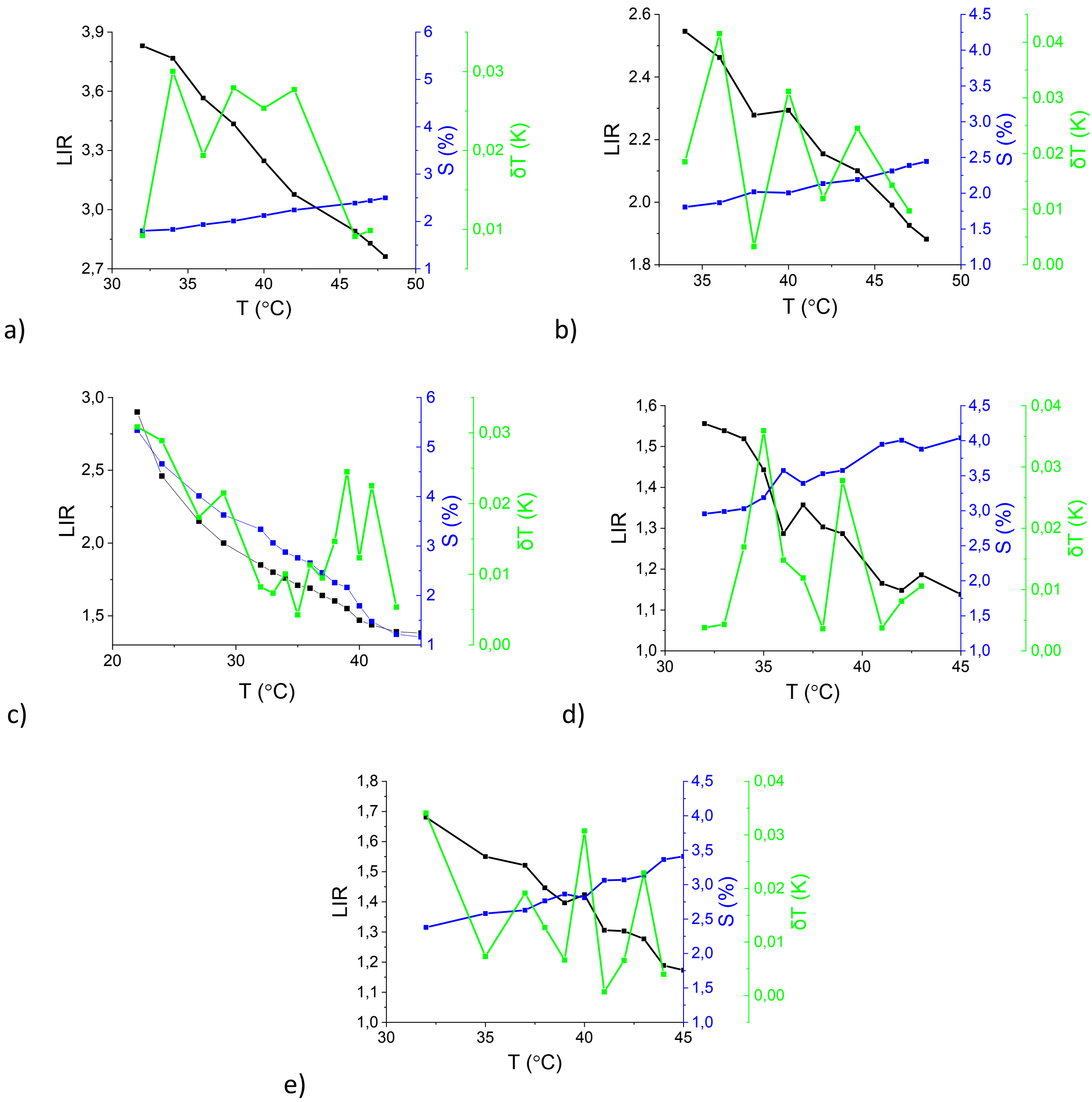

Fig. S5 The LIR = I(545 nm)/I (612 nm), Sr temperature dependence and temperature resolution of a) $Tb_{0.9}Eu_{0.1}Carb_3{\cdot}4H_2O$; b) $Tb_{0.8}Eu_{0.2}Carb_3{\cdot}4H_2O$; c) $Tb_{0.08}Eu_{0.02}Gd_{0.9}Carb_3{\cdot}4H_2O$; d) $Tb_{0.024}Eu_{0.006}Gd_{0.97}Carb_3{\cdot}4H_2O$; e) $Tb_{0.008}Eu_{0.002}Gd_{0.99}Carb_3{\cdot}4H_2O$ suspension (λ_{ex}=300 nm, λ_{em}=400...740 nm, 20-45℃).

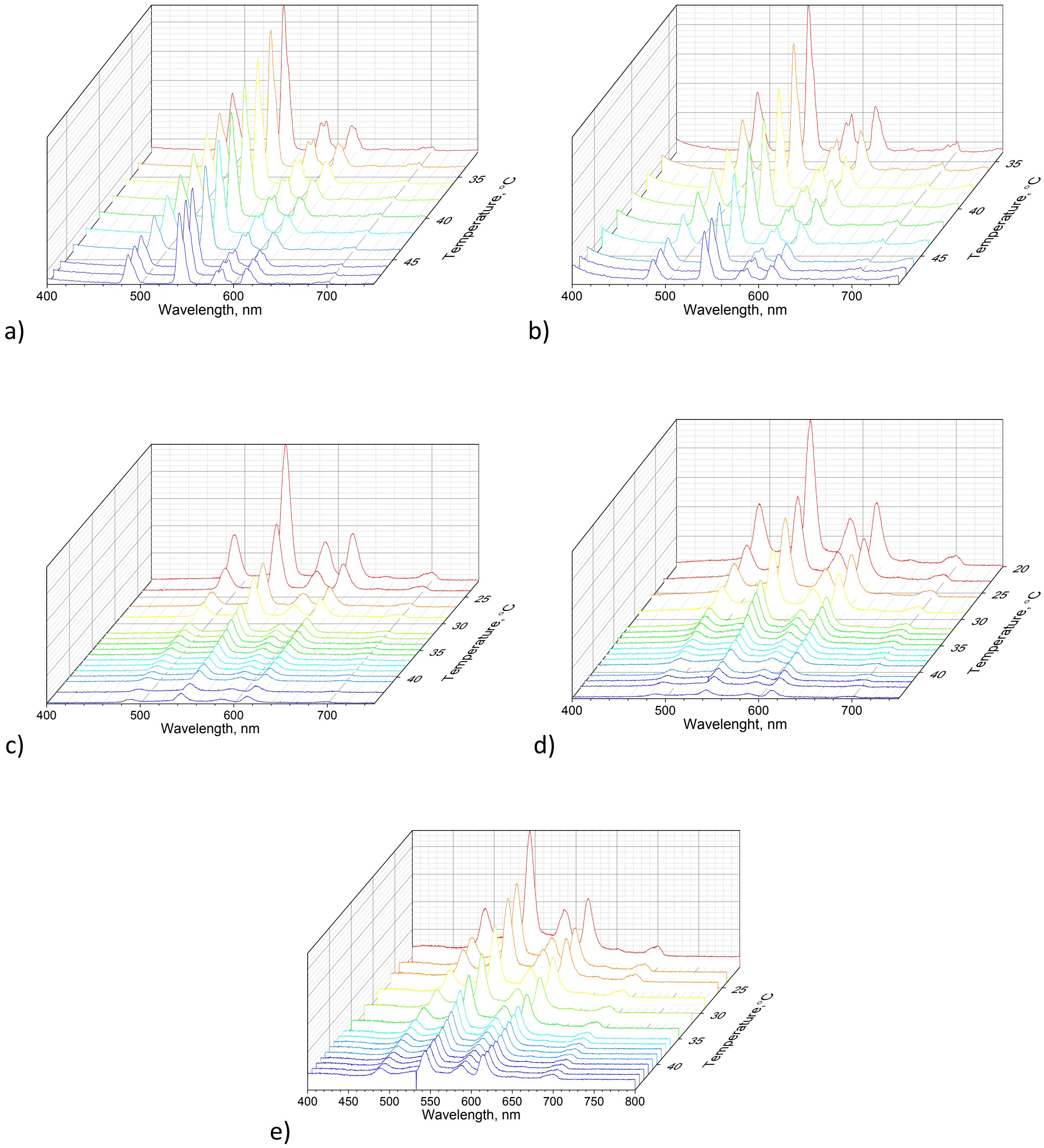

Fig. S6 Luminescence intensities temperature dependence of a) $Tb_{0.9}Eu_{0.1}Carb_3{\cdot}4H_2O$; b) $Tb_{0.8}Eu_{0.2}Carb_3{\cdot}4H_2O$; c) $Tb_{0.08}Eu_{0.02}Gd_{0.9}Carb_3{\cdot}4H_2O$; d) $Tb_{0.024}Eu_{0.006}Gd_{0.97}Carb_3{\cdot}4H_2O$; e) $Tb_{0.008}Eu_{0.002}Gd_{0.99}Carb_3{\cdot}4H_2O$ suspension (λ_{ex}=300 nm, λ_{em}=400...740 nm, 20-45℃).