RSC Advances



View Article Online

PAPER

Check for updates

Cite this: RSC Adv., 2021, 11, 34735

Temperature sensing in Tb³⁺/Eu³⁺-based tetranuclear silsesquioxane cages with tunable emission[†]

Karina Nigoghossian, 💿 ** Alena N. Kulakova, ^{bc} Gautier Félix, 🕞 * Victor N. Khrustalev, ^{cd} Elena S. Shubina, 💿 ^b Jérôme Long, 💿 * Yannick Guari, 🗔 * Saad Sene, ^a Luís D. Carlos, 몓 ^e Alexey N. Bilyachenko 몓 *^{bc} and Joulia Larionova 💼 **

New luminescent cage-like tetranuclear silsesquioxanes [NEt₄][(Ph₄Si₄O₈)₂(Tb₃Eu)(NO₃)₄(OH)(EtOH)₃(H₂O)]-

4(EtOH) (1) and [NEt₄]₂[(Ph₄Si₄O₈)₂(Tb₂Eu₂)(NO₃)₆(EtOH)₂(MeCN)₂] · 4(MeCN) (2) present a tunable thermosensitive

 Tb^{3+} -to- Eu^{3+} energy transfer driven by Tb^{3+} and Eu^{3+} emission and may be used as temperature sensors

operating in the range 41–100 °C with excellent linearity ($R^2 = 0.9990$) and repeatability (>95%). The thermometer performance was evidenced by the maximum relative sensitivity of 0.63% °C⁻¹ achieved at 68 °C.

Received 8th September 2021 Accepted 18th October 2021

DOI: 10.1039/d1ra06755a

rsc.li/rsc-advances

Introduction

Cage-like metallasilsesquioxanes (CLMSs) are an exciting family of molecule-based architectures of kaleidoscopic structural diversity built from metal ions or lanthanides and silsesquioxane ligands.^{1,2} Their design benefits from both coordination and sol-gel chemistries, and for this reason these compounds are also described as hybrid organic-inorganic materials.^{1,3} Indeed, the presence of silses quioxanes, $(RSiO_{1,5})_n$ (where n = 6, 8, 10, 12, ...), permits construction of inorganic Si-O-Si skeletons as a basic structural unit realizing cyclic and polycyclic types of matrixes, which offer to these architectures chemical stability, mechanical robustness, thermal stability, and the possibility to form a cage-like topology providing porosity and host-guest properties.4 Moreover, these ligands can provide several modes of metal ion coordination, which explains the important diversity of structural arrangements of polyhedral cages, which can be designed in various shapes including adamantane, cooling tower, birdcage, cube, drum, sandwichlike, Asian lantern, and others.^{1,2} On the other hand, the presence of various metal ions (for instance Mg²⁺, Ca²⁺, Al³⁺, Sn⁴⁺,

etc.), transition metal ions (such as $Pt^{2+/4+}$, Cr^{3+} , Mn^{2+} , Ti^{3+} , Fe^{3+} , Ni²⁺, Cu²⁺ or their combinations) or lanthanides (such as Yb³⁺ Nd³⁺, Er³⁺, Ce³⁺, Eu³⁺, Sm³⁺ or Pr³⁺) usually situated in the core of CLMSs not only ensures the assembly of the whole architecture but also brings functional physical and chemical properties.5 Among those, CLMSs have been widely investigated as molecule-based models for catalysis6 or as a particular family of molecule-based magnets.7 Unexpectedly, the optical properties of CLMSs have been investigated only scarcely. We can cite only one work reporting on luminescence in a mononuclear Eu³⁺ based CLMS, but its crystal structure has not been clarified.8 In this line of thought, we recently reported on the first series of luminescent tetranuclear lanthanide ions containing CLMSs presenting Ln³⁺ characteristic emission and interesting magnetic properties.9,10 However, the employment of CLMSs as temperature emissive sensors has never been reported up to now.

Indeed, accurate temperature measurements are an important issue for innovative technologies in a wide range of fields, including electronics, photonics, and biology. The conventional thermometers require close contact between the probe and the specimen, which hampers temperature sensing with high spatial resolution. Luminescent thermometry enables remote sensing by monitoring the emission of a probe.11 Several types of luminescent materials can be used for temperature sensing, including Ln3+-based complexes, semiconductor nanocrystals (quantum dots), and organic dyes.11 The former allows designing thermometry self-referencing methods based on the luminescence intensity ratio (LIR) of two distinct Ln³⁺ transitions,12 which are not affected by variations in probe concentration, excitation power, detection system, and others.¹¹ Among them, materials based on a solid solution of Eu³⁺/Tb³⁺ materials have widely been proposed as temperature sensors13-16 using the LIR between Tb^{3+} green and Eu^{3+} red emissions (${}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{5}$ and ${}^{5}\text{D}_{0} \rightarrow$ ${}^{7}F_{2}$ transitions, respectively). The nature of the host lattice and ligands highly affects the temperature dependence of both

[&]quot;ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France. E-mail: karina. nigoghossian@umontpellier.fr; joulia.larionova@umontpellier.fr

^bNesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova str., 28, Moscow, 119991, Russia. E-mail: bilyachenko@ineos.ac.ru

[&]quot;Peoples' Friendship University of Russia (RUDN), Miklukho-Maklay Str., 6, Moscow, 117198, Russia

^dZelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, Moscow 119991, Russia

^ePhantom-g, Physics Department and CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, 3810-193, Portugal

[†] Electronic supplementary information (ESI) available. CCDC 2094637 and 2002352. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1ra06755a

emissions. The ratiometric Eu³⁺/Tb³⁺ luminescent thermometers are designed from a simple physical mixture of mononuclear complexes of both Ln³⁺ (ref. 13-16) or as a solid solution of mono or polynuclear complexes containing both Ln3+ in the same compound.¹⁷⁻¹⁹ In the latter case, the proximity of Ln³⁺ emitting centers enables energy transfer (ET) among them, which affects the green-to-red LIR. Therefore, the thermometric parameter (LIR) can be adjusted by varying the Ln³⁺ composition, and serve as an interesting strategy to optimize the thermometer performance.19

In this work, we report on tunable emission of tetranuclear CLMSs, linked to the Tb^{3+} -to-Eu³⁺ energy transfer (ET), which may be used for temperature sensing. The investigation on the sensing properties reveals great stability and repeatability after multiple heating/cooling cycles. This important stability to photobleaching and a relatively high working temperature (to 100 °C) are ensured by the presence of a siloxane matrix, which plays a protective role.

Results and discussion

The synthesis of [NEt₄] [(Ph₄Si₄O₈)₂(Tb₃Eu)(NO₃)₄(OH)(EtOH)₃(H₂O)]· 4(EtOH) **1** and $[NEt_4]_2[(Ph_4Si_4O_8)_2(Tb_2Eu_2)(NO_3)_6(EtOH)_2(MeCN)_2]$. 4(MeCN) 2 compounds has been performed by adapting the previously described procedure consisting in a two-step reaction involving, first: the in situ formation of phenylsiloxanolate [PhSi(O)ONa]x species with their following self-assembling reaction with Et_4NCl and the corresponding $\rm Tb^{3+}$ and $\rm Eu^{3+}$ salts with the $\rm Tb^{3+}/\rm Eu^{3+}$ ratio equal to 3/ 1 for 1 and 2/2 for 2, respectively. X-ray diffraction analysis performed on single crystals of 1 and 2 indicates that these compounds crystalize in the $P\bar{1}$ space group (Table S1, ESI[†]). The crystal structure of 2 is similar to those previously published pure Eu and Tb analogues.9

Briefly, the molecular structure may be described as a $(Tb_{1-x}Eu_xO_2)_4$ core (where x = 0.25 for 1 and 0.50 for 2) caught between two tetraphenylcyclotetrasiloxanolates and assembled in a prism-like polyhedron (Fig. 1, S1, S3 and S4, ESI[†]). The cores are constituted by four statistically distributed Tb/Eu ions linked through oxygen atoms forming a distorted square. In both compounds, there are two different eight coordinated Tb/ Eu sites, which adopt a distorted square antiprism geometry. Each lanthanide ion in 1 is coordinated by four bridging oxygens and three oxygens from terminal nitrate and ethanol. The tetranuclear cycle encapsulates also an hydroxyl group situated in the centre. In 2, one lanthanide site is coordinated by four bridging oxygen atoms and four oxygen atoms from two terminal nitrate ligands, while another is linked to four bridging oxygens, three oxygens from one terminal nitrate, and one ethanol and nitrogen from acetonitrile. The main distances and angles are given in ESI (Table S2[†]). The anionic CLMS molecules are aligned along the *b* axis and alternated with Et_4N^+ cations (Fig. S2 and S5, ESI⁺). The atomic Tb/Eu ratio determined by SEM-EDX is equal to 3:1 and 1:1 for 1 and 2, respectively, confirming the expected Tb/Eu ratio in the core of CLMSs (Table S3, ESI[†]). The thermogravimetric analysis indicates that the complexes 1 and 2 start to decompose from 240 $^\circ\mathrm{C}$ (Fig. S6, ESI[†]).

The morphological characterisations have been performed by Scanning Electronic Microscopy (SEM), which indicates the



Fig. 1 Two different views of molecular structure of 1 (a) and (b). Hydrogen atoms and crystallized ethanol molecules have been omitted for clarity; (c) representation (Tb_{0.75}Eu_{0.25}O₂)₄O core of 1 showing the coordination geometry of Tb/Eu sites. Color code: green Tb/Eu; yellow Si; red O; blue N; grey C.

presence of microparticles in samples (Fig. 2 and S7, ESI†). The profile curve permitting to probe the chemical analysis indicates the homogeneity of sample.

The magnetic measurements performed for both compounds are perfectly coherent with the presence of 75 and 50% occupation of Tb³⁺ ions (⁷F₆, $S = 3, L = 3, g = 3/2, \chi T = 11.82 \text{ cm}^3 \text{ K mol}^{-1}$) for 1 and 2, respectively, since Eu^{3+} is diamagnetic (Fig. S8, ESI^{\dagger}).

The photoluminescence of CLMSs in the solid-state was first investigated at room temperature. The excitation spectra of 1 were recorded by monitoring the main emissions of Eu³⁺ at



Fig. 2 SEM images for sample 1 with different magnifications.

612 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) and Tb³⁺ at 543 nm (${}^{5}D_{4} \rightarrow {}^{7}F_{5}$) (Fig. 3a). The diverse observed lines are assigned to intra-4f transitions of Eu³⁺ (ref. 20) and Tb³⁺.²¹ Its luminescence properties are similar to those of previously published single Eu³⁺ or Tb³⁺ containing CLMSs.⁹ The maximum intensity of excitation for Eu³⁺ red emission is located at 394 nm, which corresponds to the Eu³⁺ transition ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$. As for Tb³⁺ green emission, the highest excitation intensity is observed at 378 nm, which is attributed to the transition ${}^{7}F_{6} \rightarrow {}^{5}G_{6}, {}^{5}D_{3}$. The Tb³⁺-to-Eu³⁺ ET is evidenced by the presence of the Tb³⁺ transition lines in the excitation spectra monitored in the Eu³⁺ emission (at 612 nm).

The emission spectra of 1 were measured under excitation at 394 nm and 378 nm (Fig. 3b). Upon 394 nm irradiation, the Eu³⁺ ion is selectively excited to the 5L6 energy level, and, subsequently, non-radiative relaxations lead to the population of the ${}^{5}D_{0}$ emitting state. The Eu ${}^{3+}$ transitions are then observed from ⁵D₀ to ⁷F_I (I = 0-4) manifold. The excitation at a higher energy state, under 378 nm irradiation, leads to the emissions of Tb³⁺ from ⁵D₄ to ⁷F₁ (I = 6-2) manifold, as well as Eu³⁺ transitions $({}^{5}D_{0} \rightarrow {}^{7}F_{I} J = 0-4)$. This result indicates an intramolecular Tb³⁺-to-Eu³⁺ ET considering the relatively short distances between lanthanides in the CLMS core (the shortest direct Ln³⁺- ${\rm Ln}^{\rm 3+}$ distance in 1 is 3.5087 Å and the shortest ${\rm Ln}^{\rm 3+}\text{-}{\rm Ln}^{\rm 3+}$ distance through the bridging oxygen atom is 4.6616 Å, Table S2 and Fig. S1, ESI⁺).²² Furthermore, the observation of the very weak transition ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ at 579 nm visible in both emission spectra (insets of Fig. 3b), indicates low symmetry of the Eu³⁺

coordination environment. The presence of one sharp peak at this region suggests rather a single chemical environment.²³

The excitation and emission spectra of 2 show some differences in comparison with 1 (Fig. S9, ESI⁺). In particular, the emission spectrum under excitation at 378 nm exhibits lower green-to-red (543 to 612 nm) LIR in comparison with 1. The relative higher red emission at lower Eu³⁺ amount for 1 also suggests that the intramolecular Tb³⁺-to-Eu³⁺ ET occurs to the detriment of Tb³⁺ emission ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (543 nm), which is in agreement with the literature.^{17,19}

The Tb³⁺-to-Eu³⁺ ET has previously been reported in inorganic^{24,25} and molecular luminescent materials.^{17,26-28} Its occurrence and its efficiency highly depends on the crystal structure, the presence of relatively short intra or intermolecular Tb³⁺...Eu³⁺ distances and/or the nature of ligands.²⁷ Indeed, the efficient Tb³⁺-to-Eu³⁺ ET occurred under direct excitation of Tb^{3+} (ref. 26) or through an antenna effect in Eu³⁺/ Tb³⁺ coordination polymers having relatively short intramolecular distances between lanthanide ions.²⁸ Alternatively, in coordination polymers built from Tb³⁺ and Eu³⁺ β-diketone complexes linked through a bridging phosphine oxide the presence of organic bridging ligands allowed the ET to occur despite the long distances between the lanthanides (13.6 Å). In fact, the Tb³⁺-to-Eu³⁺ ET rates depends on the operative multipolar and exchange mechanisms that are a function of the distance between the two ions $(R_{\rm L})$. While for the former, the dipole-electric electric dipole, electric dipole-electric



Fig. 3 Room temperature (a) excitation spectra of 1 monitored at $\lambda_{em} = 612$ (top) and $\lambda_{em} = 543$ nm (bottom), and (b) emission spectra of 1 performed with $\lambda_{ex} = 394$ (top) and $\lambda_{ex} = 398$ nm (bottom). Eu³⁺ and Tb³⁺ transitions are written in red and green, respectively. Inserts: high-resolution emission spectra for the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition.

quadrupole, and electric quadrupole-electric quadrupole rates depend on $R_{\rm L}^{-6}$, $R_{\rm L}^{-8}$ and $R_{\rm L}^{-10}$, respectively, the exchange transfer rate decreases exponentially with increasing $R_{\rm L}$. In this later case, the exchange mechanism becomes significant for Tb³⁺-to-Eu³⁺ separations lower than 4 Å.²²

In order to confirm the presence of an intramolecular Tb³⁺to-Eu³⁺ ET in 1 and 2, the luminescence of a physical 3:1 mixture of powders of two previously published (Et₄N)₂[(-PhSiO₂)₈Tb₄(NO₃)₆(EtOH)₂(MeCN)₂] and (Et₄N)₂[(PhSiO₂)₈Eu₄(NO₃)₆(EtOH)₂(MeCN)₂]⁹ was investigated (ratio Tb : Eu = 3 : 1, as confirmed by SEM-EDX, Table S3, ESI[†]). The excitation spectra (Fig. S10a, ESI[†]) monitored for Eu³⁺ red emission (612 nm) and Tb³⁺ green emission (at 543 nm) have a similar profile as observed for 1. The emission spectra under 394 and 378 nm are presented on Fig. S10b, ESI.[†] Under 394 nm-excitation, the expected Eu³⁺ transitions are observed (⁵D₀ \rightarrow ⁷F₀₋₄). The excitation at 378 nm leads mainly to Tb³⁺ emissions, while some low intensity Eu³⁺ emission bands can also be detected due to the less-efficient intermolecular ET. This fact reinforces the evidence of an intramolecular ET in 1 and 2 occurring due to the short distances between the donor (Tb^{3+}) and the acceptor (Eu³⁺) ions.²² Therefore, the emissive levels of Tb³⁺ and Eu³⁺ (⁵D₄ and ⁵D₀, respectively) are close enough in energy, thus permitting this Tb³⁺-to-Eu³⁺ ET. The observation of Eu^{3+} red emission (at ~612 nm) via Tb³⁺ excitation (at ~350-380 nm), where the Eu³⁺ emission occurs to the detriment of the Tb³⁺ radiative decay, clearly proves this fact. In order to investigate the possibility to use our CLMSs as emissive thermometers, the luminescence has been investigated at different temperatures. Fig. 4 shows the spectra of 1 measured under 365 nm excitation from 40 to 100 °C, and the corresponding LIR between Tb³⁺ and Eu³⁺ emissions (at 543 nm and 612 nm, respectively). The wavelength ranges used to compute the integrated areas are 530–565 nm (Tb³⁺: ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$) and 603– 637 nm (Eu³⁺: ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$). The error bars represent the standard deviation of average values obtained upon three consecutive temperature cycles (Fig. S11, ESI[†]). The temperature-dependent variation of the parameter LIR (I_{543}/I_{612}) shows a linear correlation, indicative of a self-referencing temperature sensor. The calibration parameters are presented in Table S4 (ESI[†]) along with several metric parameters that provide the thermometric performance in the operating temperature range. The regression coefficient (R^2) revealed an excellent calibration linearity $(R^2 = 0.9990)$ in the temperature range 41–100 °C. We also verified the repeatability, which corresponds to the variability among the measurements, which is indicated by the relative standard deviation (RSD). Therefore, satisfactory repeatability was observed as the maximum RSD among measurements values was lower than 5%. The relative thermal sensitivity (S_r) is the parameter that allows the comparison of thermometric performance among different types of thermometers.^{29,30} The S_r represents the variation of the experimental parameter (LIR in the present case) per degree of temperature, expressed as:

$$S_{\rm r}(T) = |\partial {\rm LIR}(T)/\partial T|/{\rm LIR}(T).$$

The maximum S_r value estimated from the calibration data was found to be 0.63% °C⁻¹ at 68 °C, which is close to a frequently considered high relative thermal sensitivity (~1% °C⁻¹),³¹ and in proximity with S_r values reported for mixed Eu³⁺/ Tb³⁺ compounds.¹⁹ Temperature uncertainty (or thermal resolution, δT) is the smallest temperature change that can be detected.³¹ This value is related to S_r as follows:

$$\delta T = |\delta \text{LIR}(T)/\text{LIR}(T)|/S_{r}(T),$$

where $\delta \text{LIR}(T)$ is the standard deviation in the LIR(T) obtained upon several heating cycles. According to this, the minimal thermal resolution is 0.04 °C. Therefore, the temperature sensor proposed here works reliably in temperature operating range 41–100 °C. Note that the Tb³⁺ emission intensity decreased around 20% of its initial value upon temperature increase (Fig. S11, ESI†). On the other hand, the Eu³⁺ transition showed an increase of about 10% of its initial value.

Compound 2 also shows the features making it interesting as self-referencing temperature sensor (Fig. S12, ESI[†]), but with lower sensitivity (Table S4, ESI[†]).

The thermal behavior of the emission spectra of CLMSs containing only Eu^{3+} ((Et_4N)₂[(PhSiO₂)₈ $Eu_4(NO_3)_6(EtOH)_2(MeCN)_2$]) or



Fig. 4 (a) Emission spectra ($\lambda_{ex} = 365$ nm) of 1 at different temperatures; and (b) corresponding LIR between the emissions at 543 nm and 612 nm. The solid line represents a linear fitting. Integrated areas: 530–565 nm (Tb³⁺: ⁵D₄ \rightarrow ⁷F₅) and 603–637 nm (Eu³⁺: ⁵D₀ \rightarrow ⁷F₂). The error bars correspond to standard error of mean determined from three consecutive temperature cycles.

Paper

Tb³⁺ ((Et₄N)₂[(PhSiO₂)₈Tb₄(NO₃)₆(EtOH)₂(MeCN)₂]) in the same temperature range is shown in Fig. S13 and S14 (ESI[†]), respectively. The slight decrease in Tb³⁺ emission intensity with temperature (Fig. S14[†]) is related to the increase of nonradiative energy transfer from the Tb³⁺ ion to the ligands to the detriment of the radiative emission. The thermal effect on Tb³⁺ emission observed for **1** in the presence of Eu³⁺ suggests an additional energy transfer pathway among emitting centers probably arising due to the presence of the hydroxyl bridge in the center of the cage **1** and also due to the shorter intermolecular Tb/Eu···Tb/Eu distances (see Fig. S1 and S4, ESI[†]). As the thermal effect on Tb³⁺ emission is more relevant in the presence of Eu³⁺, we consider that the ET Tb³⁺ → Eu³⁺ has improved the thermal sensitivity of Tb³⁺ emission, and therefore enabled the application of the heteronuclear Tb³⁺/Eu³⁺ CLMSs for luminescent thermometry.¹⁹

Conclusions

In summary, two tetranuclear Tb³⁺/Eu³⁺ based silsesquioxane cages with a prism-like topology have been synthesized and characterized. The morphological characterisations performed by means of SEM indicate the presence of microparticles in samples as well as their homogeneity. The compounds exhibit the terbium and europium characteristic green and red emissions. The relatively short intramolecular distances between the lanthanide atoms in the cores of CLMSs have enabled the intramolecular Tb³⁺-to-Eu³⁺ energy transfer, as evidenced by the europium emissions observed under excitation in the terbiumexcited levels. The tetranuclear structure has enabled the design of the compounds with well-defined Eu³⁺ and Tb³⁺ molar ratio, and therefore the control of the intrametallic interactions. The relative intensity of the red Eu³⁺ emission (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) increases along with the relative amount of the Eu³⁺ with respect to the green Tb^{3+} one $({}^{5}D_{4} \rightarrow {}^{7}F_{5})$ because of the increased ET effect. In this sense, a better thermal sensitivity in 1 in comparison with 2 can be attributed to its lower relative intensity of Eu3+ red emission. On the other hand, the thermal sensitivity of Tb³⁺ emission increased in the presence of Eu³⁺ in the heteronuclear CLMSs in comparison with the homonuclear Tb³⁺-based one, because of the occurrence of an additional nonradiative ET pathway. The Tb³⁺/Eu³⁺-based CLMSs were then proposed as self-referenced temperature sensors based on the LIR of Tb³⁺and Eu³⁺ transitions (${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$). The sensor 1 showed an excellent linearity in the temperature range 41-100 °C with the maximum relative thermal sensitivity of 0.63% $^{\circ}C^{-1}$ at 68 °C, which indicates its successful performance. Its important stability to photobleaching at a relatively high working temperature (100 °C) is certainly due to the presence of the siloxane matrix, which plays a protective role. This work opens great perspectives for the design of new class of CLMSs-based temperature sensors.

Experimental procedures

Materials

Phenyltrimethoxysilane (98%), Et₄NCl (\geq 98%), Eu(NO₃)₃·6H₂O (99.9% trace metals basis), Tb(NO₃)₃·6H₂O (99.9% trace metals basis), ethanol and acetonitrile were purchased from Merck and used as received.

Synthesis

The synthesis of compounds 1 and 2 has been performed in a similar way. A mixture of PhSi(OMe)₃ and NaOH was dissolved in 30 mL of ethanol. The resulting solution was heated to reflux for 1.0 h. Afterwards the mixture of $Tb(NO_3)_3 \cdot 6H_2O$ and $Eu(NO_3)_3 \cdot 6H_2O$ in proportions 3/1 for 1 and 2/2 for 2 and Et_4NCl dissolved in 30 mL of CH₃CN were added at once. The resulted mixture was heated to reflux for 3 h. Filtration of the mixture from the insoluble part gave a non-colored solution. Slow evaporation of solvents (ethanol/CH₃CN) gave in a period of 5–10 days a bunch of crystalline material. The single crystals suitable for a single crystal X-ray diffraction were collected. The crystal products were dried in vacuum to perform elemental analysis and to calculate the yield.

Compound $(Et_4N)[(PhSiO_{1.5})_8(Tb_{0.75}Eu_{0.25}O_{1.5})_4(O)(NO_{2.5})_4(-EtOH)_4]$ (1). Reactants loadings: PhSi(OMe)₃ (0.186 g, 0.8 mmol), NaOH (0.032 g, 0.8 mmol), Tb(NO₃)₃·6H₂O (0.131 g, 0.3 mmol), Eu(NO₃)₃·6H₂O (0.045 g, 0.1 mmol), Et₄NCl (0.066 g, 0.4 mmol). Yield = 38.24% (0.87 g).

Anal. calcd for $C_{62}H_{81}N_5O_{33}Si_8Tb_3Eu: \% C 32.69, \% H 3.58, \% N 3.07. Found: \% C 29.68, \% H 3.39, \% N 3.01. IR in KBr pellets (cm⁻¹): 3448 (w), 3073 (s), 3050 (s), 3005 (s), 1624 (w), 1593 (s), 1500 (w), 1430 (s), 1384 (s), 1314 (w), 1129 (s), 1027 (m), 997 (s), 945 (w), 813 (s), 785 (s), 747 (s), 705 (s), 678 (s), 646 (s), 576 (s), 548 (s), 499 (s), 467 (s).$

Scanning Electronic Microscopy (SEM) image is shown in Fig. S14 (ESI[†]).

Compound

 $(Et_4N)_2[(PhSiO_{1.5})_8(Tb_{0.5}Eu_{0.5}O_{1.5})_4(O)(NO_{2.5})_6(EtOH)_2(MeCN)_2]$ (2). Reactants loadings: PhSi(OMe)₃ (0.186 g, 0.8 mmol), NaOH (0.032 g, 0.8 mmol), Tb(NO₃)₃·6H₂O (0.091 g, 0.2 mmol), Eu(NO₃)₃·6H₂O (0.089 g, 0.2 mmol), Et₄NCl (0.066 g, 0.4 mmol). Yield = 25.83% (0.34 g).

Anal. calcd for $C_{72}H_{98}N_{10}O_{36}Si_8Tb_2Eu_2$: % C 34.23, % H 3.91, % N 5.54. Found: % C 33.72, % H 3.83, % N 5.29. IR in KBr pellets (cm⁻¹): 3437 (w), 3484 (w), 3074 (s), 1617 (w), 1593 (s), 1500 (w), 1430 (s), 1384 (s), 1316 (s), 1129 (s), 1058 (m), 997 (s), 950 (w), 746 (s), 704 (s), 678 (s), 576 (s), 497 (s), 467 (s).

Characterizations

Morphological characterizations and quantifications of Eu, Tb and Si elements were performed by using Scanning electron microscope and Energy Dispersive X-ray Analysis (SEM-EDX) on a FEI Quanta FEG 200 instrument. The powders were deposited on an adhesive carbon film and analyzed under vacuum. The quantification of the heavy elements was carried out with the INCA software, with a dwell time of 3 µs. IR spectra (KBr pellets) were recorded using PerkinElmer Spectrum Two FT-IR Spectrometer. The N, C, H elemental analyses were carried out in the microanalytical laboratory of the IOC RAS (Moscow) by means of a Carlo Erba Model 1106 elemental analyzer with an accepted tolerance of 0.4 unit on carbon (C), hydrogen (H), and nitrogen (N).

The emission and excitation spectra were at first evaluated at room (298 K) and low (77 K) temperatures using a spectrofluorimeter Edinburgh FLS-920. The excitation source was a 450 W Xe arc lamp. The spectra were corrected for detection and optical spectral response of the spectrofluorimeter. In the second step, the emission spectra were measured as a function of temperature. The temperature setup included a thermal element (Heidolph, MR Hei-Tec (EU), 825 W, plate diameter 145 mm), a thermal camera (Optris PI 450i, accuracy \pm 0.01 °C), an excitation source and a detector. The powder sample was placed on a cover glass (14 mm dia.) at the center of the heating source. The thermal camera was positioned at an angle of 30° relative to the sample to work as a temperature standard controller. A UV LED operating at 365 nm (ThorLabs M365L2) was used to excite the samples (I = 0.7 A) by irradiating at a distance of 15 mm from the sample surface. The spectrometric detector and the excitation source were coupled by using a multimode fiber. The fiber excitation output and detector were located at the top of sample. A long pass filter (in-line fiber optic filter mount, ThorLabs FOFMS/M, 450 nm, 20 µm) was placed in light path between sample and detector to avoid artefacts arising from excitation source. The emission spectra were recorded in the temperature range from 20 to 110 °C. At each temperature step, a period of 10 min was given to allow the temperature to stabilize, and then 10 emission spectra were recorded from an average of 10 consecutive spectra with an integration time of 100 ms.

UV-visible-NIR absorption spectrum was measured using a spectrophotometer Specord 210 Plus (Analytik Jena AG, Germany).

Magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer working between 1.8– 350 K with the magnetic field up to 7 Tesla. The sample was prepared in an ambient condition. The data were corrected for the sample holder and the diamagnetic contributions calculated from the Pascal's constants.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the RFBR (project 19-53-15008). J. La., K. N., G. F., Y. G. and J. Lo. thank the University of Montpellier and CNRS for financial support (project PRC2287 Premium 2019-2021), as well as for the project MAGCELL which was co-financed by the European Union (European Regional Development Fund) as part of the support of interdisciplinary or innovative research projects in S3 fields of the Occitanie region. The work was also developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/ 50011/2020, financed by Portuguese funds through the FCT/ MEC and, when appropriate, co-financed by FEDER under the PT2020 Partnership Agreement. Authors are grateful to Platform of Analysis and Characterization (PAC) of ICGM for magnetic and X-Ray diffraction measurements. J. La. and A. N. K. are grateful for Vernadski program (Embassy of France in Russian Federation). Elemental analyses were performed with the financial support from the Ministry of Science and Higher Education of the Russian Federation and using the equipment of the Center for Molecular Composition Studies of INEOS RAS.

This paper was supported in part by the RUDN University Strategic Academic Leadership Program (A. N. K., A. N. B. and V. N. K.).

References

- 1 H. W. Roesky, G. Anantharaman, V. Chandrasekhar, V. Jancik and S. Singh, *Chem.-Eur J.*, 2004, **10**, 4106.
- 2 V. Lorenz and F. T. Edelmann, *Adv. Organomet. Chem.*, 2005, 53, 101; M. M. Levitsky, B. G. Zavin and A. N. Bilyachenko, *Russ. Chem. Rev.*, 2007, 76, 847; M. M. Levitsky and A. N. Bilyachenko, *Coord. Chem. Rev.*, 2016, 306, 235.
- 3 R. Murugavel, A. Voigt, M. G. Walawalkar and H. W. Roesky, *Chem. Rev.*, 1996, **96**, 2205–2236.
- 4 R. Duchateau, *Chem. Rev.*, 2002, **102**, 3525; M. M. Levitsky,
 Y. V. Zubavichus, A. A. Korlyukov, V. N. Khrustalev,
 E. S. Shubina and A. N. Bilyachenko, *J. Clust. Sci.*, 2019, **30**, 1283.
- 5 F. Edelmann, P. Jutzi and U. Schubert, *Silicon Chemistry: From the Atom to Extended Systems*, ed. P. Jutzi and U. Schubert, 2007, p. 383; K. Sheng, Y.-N. Liu, R. K. Gupta, M. Kurmoo and D. Sun, *Sci. China: Chem.*, 2021, **64**, 419.
- 6 M. Levitskii, V. Smirnov, B. Zavin, A. Bilyachenko and A. Y. Rabkina, *Kinet. Catal.*, 2009, 50, 490; E. A. Quadrelli and J.-M. Basset, *Coord. Chem. Rev.*, 2010, 254, 707; K. Wada and T.-A. Mitsudo, *Catal. Surv. Asia*, 2005, 9, 229; M. M. Levitsky, A. N. Bilyachenko and G. B. Shul'pin, *J. Organomet. Chem.*, 2017, 849–850, 201; M. M. Levitsky, A. I. Yalymov, A. N. Kulakova, A. A. Petrov and A. N. Bilyachenko, *J. Mol. Catal. A: Chem.*, 2017, 426, 297.
- 7 M. M. Levitsky, A. N. Bilyachenko, E. S. Shubina, J. Long,
 Y. Guari and J. Larionova, *Coord. Chem. Rev.*, 2019, 398, 213015.
- 8 S. Marchesi, F. Carniato and E. Boccaleri, *New J. Chem.*, 2014, **38**, 2480.
- 9 A. N. Kulakova, A. N. Bilyachenko, M. M. Levitsky, V. N. Khrustalev, E. S. Shubina, G. Félix, E. Mamontova, J. Long, Y. Guari and J. Larionova, *Chem.-Eur. J.*, 2020, 26, 16594.
- 10 A. N. Kulakova, K. Nigoghossian, G. Félix, V. N. Khrustalev,
 E. S. Shubina, J. Long, Y. Guari, L. D. Carlos,
 A. N. Bilyachenko and J. Larionova, *Eur. J. Inorg. Chem.*, 2021, (27), 2696–2701.
- 11 C. D. S. Brites, P. P. Lima, N. J. O. Silva, A. Millán, V. S. Amaral, F. Palacio and L. D. Carlos, *Nanoscale*, 2012, 4, 4799.
- 12 C. D. S. Brites, S. Balabhadra and L. D. Carlos, *Adv. Opt. Mater.*, 2019, 7, 1801239.
- R. Piñol, C. D. S. Brites, R. Bustamante, A. Martínez, N. J. O. Silva, J. L. Murillo, R. Cases, J. Carrey, C. Estepa, C. Sosa, F. Palacio, L. D. Carlos and A. Millán, *ACS Nano*, 2015, 9, 3134; A. M. Kaczmarek, D. Esquivel, B. Laforce, L. Vincze, P. Van Der Voort, F. J. Romero-Salguero and R. Van Deun, *Luminescence*, 2018, 33, 567.
- 14 L. B. Guimarães, A. M. P. Botas, M. C. F. C. Felinto, R. A. S. Ferreira, L. D. Carlos, O. L. Malta and H. F. Brito, *Materials Advances*, 2020, 1, 1988.

- 15 C. D. S. Brites, P. P. Lima, N. J. O. Silva, A. Millán, V. S. Amaral, F. Palacio and L. D. Carlos, *Adv. Mater.*, 2010, 22, 4499.
- 16 C. J. Salas-Juárez, R. E. Navarro, A. Pérez-Rodríguez, U. Orozco-Valencia and R. Acevesm, *Sens. Actuators, A*, 2020, **315**, 112293.
- 17 M. Hatanaka, Y. Hirai, Y. Kitagawa, T. Nakanishi, Y. Hasegawa and K. Morokuma, *Chem. Sci.*, 2017, **8**, 423.
- 18 Y. Cui, H. Xu, Y. Yue, Z. Guo, J. Yu, Z. Chen, J. Gao, Y. Yang,
 G. Qian and B. Chen, *J. Am. Chem. Soc.*, 2012, 134(9), 3979.
- 19 V. Trannoy, A. N. Carneiro Neto, C. D. S. Brites, L. D. Carlos and H. Serier-Brault, *Adv. Optical Mater.*, 2021, **9**, 2001938.
- 20 W. T. Carnall, P. R. Fields and K. Rajnak, *J. Chem. Phys.*, 1968, **49**, 4450.
- 21 W. T. Carnall, P. R. Fields and K. Rajnak, *J. Chem. Phys.*, 1968, **49**, 4447.
- 22 O. L. Malta, J. Non-Cryst. Solids, 2008, 354, 4770;
 A. N. Carneiro Neto, R. T. Moura, A. Shyichuk, V. Paterlini,
 F. Piccinelli, M. Bettinelli and O. L. Malta, J. Phys. Chem. C,
 2020, 124, 10105; P. A. Tanner, L. Zhou, C. Duan and
 K.-L. Wong, Chem. Soc. Rev., 2018, 47, 5234; D. L. Dexter
 and J. H. Schulman, J. Chem. Phys., 1954, 22, 1063;
 G. Blasse and B. C. Grabmaier. Luminescent materials,
 Springer, Berlin, 1994.

- 23 J. Kai, D. F. Parra and H. F. Brito, *J. Mater. Chem.*, 2008, **18**, 4549.
- 24 V. Khudoleeva, L. Tcelykh, A. Kovalenko, A. Kalyakina,
 A. Goloveshkin, L. Lepnev and V. Utochnikova, *J. Lumin.*,
 2018, 201, 500.
- 25 T. Li, P. Li, Z. Wang, S. Xu, Q. Bai and Z. Yang, *Dalton Trans.*, 2015, 44, 16840; M. Jiao, N. Guo, W. Lü, Y. Jia, W. Lv, Q. Zhao, B. Shao and H. You, *Dalton Trans.*, 2013, 42, 12395; T. K. Anh, T. Ngoc, P. T. Nga, V. T. Bitch, P. Long and W. Stręk, *J. Lumin.*, 1988, 39, 215.
- 26 E. Chelebaeva, J. Long, J. Larionova, R. A. S. Ferreira,
 L. D. Carlos, F. A. Almeida Paz, J. B. R. Gomes, A. Trifonov,
 C. Guérin and Y. Guari, *Inorg. Chem.*, 2012, 51, 9005.
- 27 C. Piguet, J. C. G. Bünzli, G. Bernardinelli, G. Hopfgartner and A. F. Williams, *J. Am. Chem. Soc.*, 1993, **115**, 8197.
- 28 A. R. Ramya, D. Sharma, S. Natarajan and M. L. P. Reddy, *Inorg. Chem.*, 2012, **51**, 8818.
- 29 *Thermometry at the Nanoscale*, ed. L. D. Carlos and F. Palacio, Nanoscience & Nanotechnology Series, 2015.
- 30 A. Bednarkiewicz, L. Marciniak, L. D. Carlos and D. Jaque, *Nanoscale*, 2020, **12**, 14405.
- 31 C. D. S. Brites, A. Millán, and L. D. Carlos, In *Handbook on the Physics and Chemistry of Rare Earths*, ed. J. C. G. Bünzli and V. K. Pecharsky, Elsevier B.V., Amsterdam, 2016, vol. 49, p. 339.