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Luminescent PMMA Films and PMMA@SiO₂ Nanoparticles with Embedded Ln³⁺ Complexes for Highly Sensitive Optical Thermometers in the Physiological Temperature Range

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Abstract: Luminescent materials doped with Ln³⁺ ions have attracted in recent years a large amount of attention for their applications as optical thermometers based both on down shifting and upconversion processes. This study presents research done on development of highly sensitive optical thermometers in the physiological temperature range based on PMMA (poly(methyl methacrylate)) films doped with two series of visible Ln³⁺ complexes (Ln³⁺ = Tb³⁺, Eu³⁺ and Sm³⁺) and silica (SiO₂) nanoparticles (NPs) coated with these PMMA films. The best performing PMMA films doped with Tb³⁺ and Eu³⁺ complexes, was the **PMMA[TbEuL₁tppo]1** film (L₁ = 4,4,4-trifluoro-1-phenyl-1,3-butadionate and tppo = triphenylphosphine oxide), which showed good temperature sensing S_r = 4.21% K⁻¹ at 313 K, while for the PMMA films doped with Tb³⁺ and Sm³⁺ complexes, was the **PMMA[TbSmL₂tppo]3** film (L₂ = 4,4,4-trifluoro-1-(4-chlorophenyl)-1,3-butadionate) showed S_r = 3.64% K⁻¹ at 313 K. Additionally, SiO₂ nanoparticles coated with the best performing films from each of the series of PMMA films (Tb-Eu and Tb-Sm) and their temperature sensing properties were studied in water showing excellent performance in the physiological temperature range (**PMMA[TbEuL₁tppo]1@SiO₂** S_r = 3.84% °C at 20 °C and **PMMA[TbSmL₂tppo]3@SiO₂** S_r = 3.27% °C at 20 °C) and the toxicity of these nanoparticles on human cells was studied showing that they are not toxic.

Introduction

Temperature is one of the fundamental thermodynamic properties that can influence physical, chemical or biological processes.^[1] The accurate and precise measurement of temperature is needed for different industrial, technological developments and scientific research such as aerospace, automotive, metrology, electronics, cell biology, nanomedicine and biomedicine.^[2-10] In biotechnological applications and biological research the reactivity and dynamics of the biomolecules are correlated with temperature. Elevated temperature in an organism can indicate that there is a physiological disorder, such as illness.^[7] For example, cancer cells show a higher temperature than normal cells. The reason for this difference in temperature is the higher metabolism of cancer cells.^[11,12] One of the ways to measure temperature in cells is employing luminescent thermometry measurements as they are non-contact, give a real-time response and have precision on the molecular level.^[13]

Organic dyes have been extensively used for this purpose, yet they show certain drawbacks such as short excited-state lifetimes, small Stokes shifts, broad emission bands, photobleaching and additionally their emission intensity depends on the local environment.^[7,14-18] Alternatively, lanthanide (Ln³⁺) ions have large Stokes shifts, narrow and sharp emission bands, long excited-state lifetimes, and their luminescence properties are less dependent on the local environment, and therefore very attractive for luminescent sensing applications.^[19-23] Lanthanide emission is based on the parity forbidden 4f-4f transitions and direct excitation of Ln³⁺ is therefore an inefficient process because of the low molar extinction coefficients. To avoid this limitation Ln³⁺ can form complexes with organic ligands, where these ligands can act as sensitizers to increase the absorption of light and transfer the absorbed energy to the lanthanide ions. Organic molecules,

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Supporting information for this article is given via a link at the end of the document. It contains synthesis of lanthanide β-diketonate complexes, crystal data and refinement details, FTIR, ESI-MS and TGA-DTA data, photoluminescence properties discussion and discussion temperature dependent samples not discussed in manuscript.

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which can be employed as sensitizers are for example heterocyclic, aromatic carboxylates or β -diketonates as ligands.^[24-26] The long excited-state lifetimes of lanthanide probes versus the short excited-state lifetimes of organic dyes present a clear advantage in biological experiments: the fluorescence of a typical organic molecule will be observable for about the same amount of time as the autofluorescence of biomolecules, whereas the emitted light of a Ln^{3+} probe is longer lived. So, when Ln^{3+} probes can be made to bind selectively to certain parts of tumor cells, these can be very precisely located using the longer-lived lanthanide luminescence.

Lanthanide molecular structures based on β -diketonate complexes retain high color purity and quantum yields. β -diketonate ligands possess high energetic singlet and triplet levels, which makes them suitable for exciting the Ln^{3+} . Furthermore, they have a strong affinity to form stable complexes with Ln^{3+} as they are hard Lewis bases and Ln^{3+} are hard Lewis acids. With Ln^{3+} they mostly form tris complexes, leaving two vacant coordination sites, which can be occupied by water molecules or by additional neutral ligands. This creates the opportunity to change the chemical properties just by changing the coordination environment. Furthermore, these compounds can be easily processed into complex matrices such as organic polymers, silica glasses or other materials.^[27]

In this work, we report on the synthesis, photoluminescence and sensing properties of poly(methyl methacrylate) (PMMA) films and silica (SiO_2) nanoparticles (NPs) coated with PMMA films doped with luminescent tris- β -diketonate lanthanide complexes. The lanthanide β -diketonate complexes with 4,4,4-trifluoro-1-phenyl-1,3-butadionate (L_1) or 4,4,4-trifluoro-1-(4-chlorophenyl)-1,3-butadionate (L_2) ligands were isolated as water-free molecules where the neutral triphenylphosphine oxide (tpo) molecules complete the coordination sphere. The complexes of Eu^{3+} and Tb^{3+} are new complexes reported in this study, while the complexes of Sm^{3+} were reported in our previous study.^[28] The best performing complexes, selected on the basis of their photoluminescent properties and emission quantum yields, were incorporated as dopants in transparent and flexible PMMA films.^[29] PMMA was chosen as a homogenous material in which two different complexes could be doped to obtain ratiometric thermometers. In particular, doping was carried out with two systems consisting of $\text{Tb}^{3+} - \text{Eu}^{3+}$ and $\text{Tb}^{3+} - \text{Sm}^{3+}$ mixed-metal complexes, which were already proved to show promising

temperature sensing properties in physiological range.^[30] While the $\text{Tb}^{3+} - \text{Eu}^{3+}$ system is an already popular thermometer in the physiological temperature range,^[5,13,31-34] the $\text{Tb}^{3+} - \text{Sm}^{3+}$ system is rarely investigated despite its promising potential, due to the difficulty to obtaining intense Sm^{3+} emission at temperatures above room temperature.^[35,36] Finally, to explore the potentiality of these materials to be used as thermometers in biological applications, SiO_2 nanoparticles coated with doped PMMA films were investigated.

Results and Discussion

Preparation and optimization of doped PMMA films. The optimized synthesis of the doped PMMA films is described in the Experimental Section. The polymerization of PMMA and the condition for doping the lanthanide complexes into the polymer were firstly optimized. In the first attempts different solvents were used to dissolve PMMA (acetonitrile and methanol, pure acetonitrile, dichloromethane and chloroform). Chloroform was identified as the best solvent to co-dissolve PMMA and the complexes. The second step of optimizing the film preparation was finding the optimal ratio between the two complexes $\text{Ln}_1(\text{L}_{1(2)})_3(\text{tpo})_2$ and $\text{Ln}_2(\text{L}_{1(2)})_3(\text{tpo})_2$ ($\text{Ln}_1 = \text{Tb}^{3+}$ and $\text{Ln}_2 = \text{Eu}^{3+}$ or Sm^{3+}), which would give desired luminescent properties (see the PL studies of complexes in SI), and would allow the final materials to be used for temperature sensing properties, in **Table 1** are given the optimized ratios of Ln_1 to Ln_2 complexes in PMMA films. The films were obtained by slow solvent evaporation at 30 °C in Petri dishes with a diameter of 70 mm. Transparent films with Ln^{3+} complexes were obtained (**Figure 2**). The photoluminescence characterization was carried out before the samples were investigated for temperature-dependent luminescence sensing. The short discussion of the results obtained for the photoluminescence properties of the PMMA films is given in SI (**Figures S32-35** and **Tables S3-S4**).

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Figure 2. PMMA Ln³⁺-doped films (a) the transparent film **PMMA[Ln₁Ln₂L₁(2)tpo]3**; (b) the **PMMA[TbEuL₁tpo]1** under a UV lamp with excitation at 365 nm and (c) the **PMMA[TbSmL₂tpo]3** under a UV lamp with excitation at 365 nm.

Table 1. Molar ratio of doped lanthanide complexes (Ln₁ = Tb³⁺, Ln₂ = Eu³⁺/Sm³⁺) after optimization in PMMA films, with general formula of LnL₁tpo and LnL₂tpo complexes.

Samples	Ln ₁	Ln ₂
PMMA[TbEuL ₁ tpo]1	12	1
PMMA[TbEuL ₁ tpo]2	16	1
PMMA[TbEuL ₁ tpo]3	20	1
PMMA[TbEuL ₂ tpo]1	30	1
PMMA[TbEuL ₂ tpo]2	34	1
PMMA[TbEuL ₂ tpo]3	38	1
PMMA[TbSmL ₁ tpo]1	4	1
PMMA[TbSmL ₁ tpo]2	6	1
PMMA[TbSmL ₁ tpo]3	10	1
PMMA[TbSmL ₂ tpo]1	4	1
PMMA[TbSmL ₂ tpo]2	12	1
PMMA[TbSmL ₂ tpo]3	16	1

PMMA coated SiO₂ nanoparticles. Two different methods of coating the SiO₂ nanoparticles (NPs) were investigated. As a model fil, the **EuL₁tpo** doped PMMA was used. The first method was based on the sonication of the suspension of SiO₂ NPs with PMMA for 30 min. The second method consisted of a vigorous stirring on the suspension of SiO₂ NPs with PMMA for 30 min., in both methods chloroform was used as solvent. After the sonication or stirring, the SiO₂ NPs were separated from the solution by centrifugation and left for one day to dry in air. Next, the NPs were washed once with a methanol/water mixture to remove all residuals of the synthesis. The luminescent properties of coated SiO₂ NPs were then studied, and the intensity of the emitted light provided an indication of the homogeneity and thickness of the coating layer. Results on PMMA@SiO₂ NPs samples showed that the second method was more efficient in the coating of the silica nanoparticles. The stirring process was further prolonged to 2 hours to ensure complete coating of the SiO₂ NPs.

SEM and TEM images of the PMMA@SiO₂ NPs are shown in **Figure 3**. After the coating process there was no visible change in the size and shape of the particles, ranging from 150 to 500 nm in diameter (**Figures S19–22** in SI). Upon higher magnification, a thin coating with a thickness of about 7 nm can be observed on the particle surface (see **Figure 3d**).

Figure 3. SEM and TEM images of SiO₂ NPs coated with a **PMMA[TbEuL₁tpo]1** film: (a) dispersion of the particles; (b) magnification of the SiO₂ NPs by SEM; (c) particles and (d) magnification of the surface of SiO₂ NPs showing PMMA coating by TEM.

Luminescent thermometry. Luminescent thermometers can be based on different principles, such as the measurement of luminescence lifetimes, of shifts of the emission peaks or of the changes of the luminescence intensity of one or more emission peaks.^[2,37] In this case, luminescent thermometry based on emission intensity was chosen. There are two types of ratiometric emission intensity thermometry methods. The difference is based on the number of emission centers present in the materials. Single center ratiometric based luminescent thermometers are based on a single emission center, in which both emission peaks are generated from two different excited levels which are in thermal equilibrium of the same emitting center. As these levels are thermally coupled for these type of thermometers external thermal calibration of the thermometric parameter is needed. The calibration process requires an independent measurement using for example a thermocouple or infrared-camera, which allows the intensity-to-temperature conversion. The dual center based luminescent thermometers overcome these disadvantages by possessing two emitting centers. In this type of thermometers, the emitting center can be thermally coupled but in most cases they are not, and for this reason it is not needed to have external calibration of the thermometric parameter.^[22] In this study, the ion pairs of Tb³⁺ – Eu³⁺ and Tb³⁺ – Sm³⁺ as systems for dual center ratiometric thermometers were chosen. For calculation of the thermometric parameter Δ **Equations 1 and 2** were used.^[38]

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$$\Delta = \frac{I_1}{I_2} \quad (1)$$

$$\Delta = \frac{\Delta_0}{1 + \alpha \exp\left(-\frac{\Delta E}{k_B T}\right)} \quad (2)$$

where I_1 ($\text{Tb}^{3+} = {}^5\text{D}_4 \rightarrow {}^7\text{F}_5$) and I_2 ($\text{Eu}^{3+} = {}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ or $\text{Sm}^{3+} = {}^5\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$) are integrated intensities of the transitions, Δ_0 is the Δ ($T = 0$ K), α presents the ratio between nonradiative (W_0 at $T = 0$ K) and radiative (W_R) rates, and ΔE is the activation energy for the nonradiative pathway. The S_r indicates the relative change of the thermometric parameter per degree of the temperature change (% K^{-1}) and was calculated using the following Equation 3:

$$S_r = 100\% \left[\frac{1}{\Delta} \frac{\partial \Delta}{\partial T} \right] \quad (3)$$

which is inversely proportional to the thermometric parameter (Δ) and the variation of the thermometric parameter ($\partial \Delta$) per temperature variation (∂T). The S_r is used for thermometer comparison of different materials and it is independent from the nature of the thermometer. The maximal value of the relative sensitivity for the measured temperature range can be presented as S_m .

The performance and stability of the thermometer is estimated by cycling the temperature in the given temperature interval ensuring that the thermometer reaches the thermal equilibrium for each measurement. It can be described by Equation 4:

$$R = 1 - \frac{\max(|\Delta_c - \Delta_i|)}{\Delta_c} \quad (4)$$

where the Δ_c is the mean thermometric parameter extracted from the calibration curve and Δ_i is the value of each thermometric parameter measurement.^[22]

The temperature uncertainty δT is one of the important parameters in the assessment of the performance of the desired thermometer. δT can be calculated using Equation 5:

$$\delta T = \frac{1}{S_r} \frac{\delta \Delta}{\Delta} \quad (5)$$

Temperature dependent luminescence of PMMA[Ln₁Ln₂L₁₍₂₎tppo] films (Ln₁ = Tb³⁺, Ln₂ = Eu³⁺ or Sm³⁺). The temperature-dependent luminescence was measured in the physiological temperature region, which was extended down to 253 K (-20 °C) for the samples of this series as there is an interest for fundamental studies of the biological, biochemical and physiological processes happening in the cells when they are frozen and during defrosting it is needed to accurately measure the temperature while these processes are monitored. For the PMMA[TbEuL₁₍₂₎tppo] films six samples for the were studied for their temperature-dependent luminescence properties: three with L₁ and three with L₂ ligands. Among the PMMA[TbEuL₁tppo]1 and therefore it will be discussed in detail, while the other two samples are discussed in detail in the SI (Figures S36-37).

The integrated areas under the peaks used for these samples are: for Tb³⁺ the ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition peak, observed between 533 and 558 nm and for Eu³⁺ the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition peak, observed between 604 and 630 nm.

Figure 4. (a) Emission map of PMMA[TbEuL₁tppo]1 film, measured in 253-353 K range (step 10 K); (b) plot representing the calibration curve for PMMA[TbEuL₁tppo]1. The point show the experimental Δ parameter and solid line is the best fit of the experimental points using Equation 2; (c) plot showing the relative sensitivity S_r values at different temperatures (253-353 K), the solid line is intended as a guide.

An emission map of PMMA[TbEuL₁tppo]1, measured in the temperature range from 253 K to 353 K, is presented in Figure 4a. The I_{543}/I_{614} intensity ratio of the integrated areas under the peaks for PMMA[TbEuL₁tppo]1 was calculated and plotted in Figure 4b, for the indicated temperature range in which the sample shows monotonic behavior. The data points were fitted with Equation 2, yielding $\Delta E = 3537 \text{ cm}^{-1}$ ($R^2 = 0.9993$). The calculated energy difference between the emitting level of Tb³⁺ (${}^5\text{D}_4 = 20500 \text{ cm}^{-1}$) and emitting level of Eu³⁺ (${}^5\text{D}_0 = 17300 \text{ cm}^{-1}$) which is $\Delta E = 3200 \text{ cm}^{-1}$. In Figure 4c the relative sensitivity S_r is presented as calculated for different temperatures. The maximum value of $S_r = 4.21\% \text{ K}^{-1}$ obtained at 313 K indicates that this sample has one of the highest S_r values in the physiological temperature range reported to date (Table 2).

For the films from the PMMA[TbEuL₂tppo] series, the best results were obtained for the sample PMMA[TbEuL₂tppo]3. The detailed discussion of the temperature-dependent luminescence of this sample and the other two samples in the series are presented in SI. For the PMMA[TbEuL₂tppo]3 sample the maximal value of the relative sensitivity $S_r = 4.04\% \text{ K}^{-1}$ was obtained at 313 K.

Similarly, six PMMA[TbSmL₁₍₂₎tppo] films were investigated for the temperature-dependent luminescence properties and their

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ability to work as temperature sensor. For both ligands L_1 and L_2 three samples were investigated.

The integrated peaks used for these samples were at 543 nm ($^5D_4 \rightarrow ^7F_5$) for the Tb^{3+} ion, which was integrated in the range between 533 and 558 nm and the Sm^{3+} ion peak at 643 nm ($^5G_{5/2} \rightarrow ^6H_{9/2}$) integrated in the range 630–660 nm.

For the samples from the **PMMA[TbSmL₁tpo]** series out of the three investigated samples the best results were obtained from **PMMA[TbSmL₁tpo]1** which is in detailed discussion of this sample and for other two samples in SI. For the **PMMA[TbSmL₁tpo]1** sample the maximal relative sensitivity $S_r = 3.45\% K^{-1}$ at 313 K was obtained.

In the series of the samples with general formula **PMMA[TbSmL₂tpo]** the sample showing the best results is **PMMA[TbSmL₂tpo]3** will be discussed in the manuscript, while other two samples are discussed in the SI (**Figures S44–45**).

An emission map of the **PMMA[TbSmL₂tpo]3**, measured in the temperature range from 253 K to 343 K, is presented in **Figure 5a**. The I_{543}/I_{643} intensity ratio of the integrated areas under the peaks for **PMMA[TbSmL₂tpo]3** was calculated and plotted in **Figure 5b** for the indicated temperature range and the shows monotonic behavior. Fitting of the data points was done using **Equation 2**, yielding $\Delta E = 3274\text{ cm}^{-1}$ ($R^2 = 0.9994$). the calculated energy difference can be best matched with the energy difference between the triplet level ($T_1 = 24000\text{ cm}^{-1}$) of the tpo ligand and emitting level of Tb^{3+} ($^5D_4 = 20500\text{ cm}^{-1}$) which is $\Delta E = 3500\text{ cm}^{-1}$. In **Figure 5c** the relative sensitivity S_r is presented, calculated for the different temperatures. The maximum value of $S_r = 3.64\% K^{-1}$ obtained at 313 K indicates that this sample is a very good temperature in the physiological range. In **Table 2** a comparison of the materials reported here with known materials from literature is presented.

Figure 5. (a) Emission map of **PMMA[TbSmL₂tpo]3** film, measured in 253–343 K range (step 10 K); (b) plot representing the calibration curve for **PMMA[TbSmL₂tpo]3**. The point show the experimental Δ parameter and solid line is the best fit of the experimental points using **Equation 2**; (c) plot showing the relative sensitivity S_r values at different temperatures (253–343 K), the solid line is intended as a guide.

Table 2. Comparison of the sensitivity of the reported thermometers with the sensitivity of other luminescent thermometers performing in the physiological temperature range. The materials, temperature range (K), and maximal relative sensitivity value (S_m) have been overviewed.

Materials	Range (K)	S_m (% K^{-1})	Ref.
[Eu _{0.53} Tb _{0.47} (tfac) ₈] ²⁻ Na ₂ ⁺	273–373	2.70 (353 K)	30
[Tb _{0.90} Sm _{0.10} (tfac) ₈] ²⁻ Na ₂ ⁺	280–360	2.30 (360 K)	30
Eu _{0.50} Tb _{0.50} DPA-PMO	260–460	1.56 (360 K)	35
Sm _{0.95} Tb _{0.05} DPA-PMO	280–460	2.38 (340 K)	35
BPY-PMO@Tb,Sm(acac) ₃ _10_90	253–333	4.93 (253 K)	36
Tb _{0.92} Eu _{0.08} -HPIDC-OX	303–473	0.6 (473 K)	39
[Ln(ad) _{0.5} (phth)(H ₂ O) ₂] (Ln = 5Eu ^{III} : 10Tb ^{III})	303–423	1.21 (303 K)	40
Tb@UiO-66-Hybrid film	303–353	2.76 (303 K)	41
Eu@UiO-66-Hybrid film	303–403	4.26 (363 K)	41
Ca _{8.98} Mg _{1.5} (PO ₄) ₇ ·x (Eu ²⁺ , Eu ³⁺)	293–473	1.192 (383 K)	42
[Tb _{0.97} Eu _{0.03} (L)(ox)(H ₂ O)]	250–340	1.38 (340 K)	43
Eu _{0.05} -Tb _{1.95} -PDC	298–333	1.37 (333 K)	44
Tb _{0.8} Eu _{0.2} BPDA	293–328	1.19 (313 K)	45
(Tb/Eu-TPTZ)PMMA	298–373	2.98 (373 K)	46
ZJU-88J-perylen	293–353	1.28 (293 K)	47
PMMA[TbEuL₁tpo]1	253–353	4.21 (313 K)	This work
PMMA[TbEuL₁tpo]2	253–353	3.99 (313 K)	This work
PMMA[TbEuL₁tpo]3	253–353	3.81 (313 K)	This work

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PMMA[TbEuL ₂ tpo]1	253-343	3.57 (293 K)	This work
PMMA[TbEuL ₂ tpo]2	253-343	3.78 (303 K)	This work
PMMA[TbEuL ₂ tpo]3	253-343	4.04 (313 K)	This work
PMMA[TbSmL ₁ tpo]1	253-373	3.45 (313 K)	This work
PMMA[TbSmL ₁ tpo]2	253-353	3.15 (313 K)	This work
PMMA[TbSmL ₁ tpo]3	253-343	2.93 (313 K)	This work
PMMA[TbSmL ₂ tpo]1	253-373	3.39 (333 K)	This work
PMMA[TbSmL ₂ tpo]2	253-333	3.50 (323 K)	This work
PMMA[TbSmL ₂ tpo]3	253-343	3.64 (313 K)	This work

The results for the Tb³⁺ – Eu³⁺ materials from this study have shown very good relative sensitivities compared to other Tb³⁺ – Eu³⁺ materials reported in literature (Table 2). They are much more sensitive, even up to 7 times. While the results for samples based on the Tb³⁺ – Sm³⁺ system shown that their relative sensitivity is slightly higher compared to the similar systems with only one material (reference 36), it has nevertheless shown higher sensitivity. Comparison of our samples with different systems, such as hybrid systems or organic dyes, shows similar or higher sensitivity, even up to 4 times.

To show the potential of the thermometer materials for real applications, stability test were carried out, where the samples were subjected to three heating/cooling cycles. The stability tests for samples PMMA[TbEuL₂tpo]3 (a) and PMMA[TbSmL₁tpo]1 (b) are presented in Figure 6 showing a repeatability of up to 95% for PMMA[TbEuL₂tpo]3 and up to 97% for PMMA[TbSmL₁tpo]1. The temperature uncertainty for these two compounds has been calculated and it is presented in SI (Figure S46). The proposed energy transfer mechanism based on the results obtained for samples from both systems are presented in Figure 7.

Figure 6. Temperature cycling test for PMMA[TbEuL₂tpo]3 (a) and PMMA[TbSmL₁tpo]1 (b) in the temperature range 253 K to 373 K. The dashed lines are intended as a visual guide.

Figure 7. Energy level diagram presenting the mechanism of the energy transfer in (a) PMMA[TbEuL₂tpo] films, PMMA[TbEuL₂tpo]@SiO₂ NPs, (b) PMMA[TbSmL₁tpo] films and PMMA[TbSmL₁tpo]@SiO₂ NPs. Labels are: S₀ and S₁ singlet ground level and singlet excited level, T₁ triplet

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level, ET is the energy transfer to the lanthanide ions by the ligands, BT energy back transfer. ΔE represents the energy gap and is indicated (a) in purple is for both series of samples and (b) in purple for samples **PMMA[TbSmL1tpo]** and in dark blue for samples **PMMA[TbSmL2tpo]**.

Temperature sensing of PMMA coated SiO₂ NPs in water. For SiO₂ NPs coated with PMMA films containing lanthanide complexes, the temperature sensing capability was studied in water in the 5 °C (278 K) to 50 °C (323 K) temperature range. It is known that water is an efficient quencher of the luminescence properties of the lanthanide ions through vibrational quenching.^[27] For this reason it is taken as a case study for these preliminary measurements. Cells, as well as the whole human body consist of water up to 70%. However, cytosol, besides water, also contains salts, proteins and other biomolecules which were not taken into consideration at this point of study. This as well as *in vitro* temperature sensing studies will be a part of future investigations. As coating four PMMA films were selected, two samples with the best performing temperature sensing properties from the Tb³⁺ – Eu³⁺ and two from Tb³⁺ – Sm³⁺ systems and one of each from both systems were taken from the series of the films, which consisted of sample derivatives with L₁ and L₂ complexes. The integrated areas of the peaks, which were used for calculations in both systems are given in the last section. The stability of the PMMA coated SiO₂ NPs was investigated after having been dispersed in water for one month. It was observed that the emission intensity of the Ln³⁺ complexes embedded in PMMA film was reduced by about 20% compared to the initial measurements. The decrease in the emission intensity can be due to partial diffusion of water molecules in the PMMA polymer, which can then partially quench the Ln³⁺ emission.

Figure 8. (a) Emission map of **PMMA[TbEuL1tpo]1@SiO₂** NPs measured in 5-50 °C range (step 5 °C); (b) plot representing the calibration curve for **PMMA[TbEuL1tpo]1@SiO₂**. The point show the experimental Δ parameter and solid line is the best fit of the experimental points using Equation 2; (c) plot showing the relative sensitivity S_r values at different temperatures (5-50 °C), the solid line is intended as a guide.

An emission map of the **PMMA[TbEuL1tpo]1@SiO₂**, measured in the temperature range from 5 °C to 50 °C, is presented in **Figure 8a**. The I_{543}/I_{614} intensity ratio of the integrated areas under the peaks for **PMMA[TbEuL1tpo]1@SiO₂** was calculated and plotted in **Figure 8b**, for the mentioned temperature range in which the sample shows monotonic behavior. The data points could be well fitted using Equation 2, yielding $\Delta E = 3143 \text{ cm}^{-1}$ ($R^2 = 0.9936$). The calculated energy difference can be well matched with the energy difference between the emitting level of Tb³⁺ ⁵D₄ (20500 cm⁻¹) and the emitting level of Eu³⁺ ⁵D₀ (17300 cm⁻¹). In **Figure 8c** the relative sensitivity S_r calculated for the different temperatures is presented. The maximal value of $S_r = 3.84\% \text{ } ^\circ\text{C}^{-1}$ was obtained at 20 °C indicates that this sample shows very good thermometric behavior as highlighted by the comparison with literature values, reported in **Table 3**.

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Figure 9. (a) Emission map of **PMMA[TbSmL₂tpo]1@SiO₂** NPs measured in 5–50 °C range (step 5 °C); (b) plot representing the calibration curve for **PMMA[TbSmL₂tpo]1@SiO₂**. The point show the experimental Δ parameter and solid line is the best fit of the experimental points using Equation 2; (c) plot showing the relative sensitivity S_r values at different temperatures (5–50 °C), the solid line is intended as a guide.

An emission map of the map of the **PMMA[TbSmL₂tpo]3@SiO₂**, measured in the temperature range from 5 °C to 50 °C, is presented in **Figure 9a**. The I_{543}/I_{643} intensity ratio of the integrated areas under the peaks for **PMMA[TbSmL₂tpo]3@SiO₂** has been calculated and plotted in **Figure 9b**. The sample shows monotonic behavior in the indicated temperature range. The data points could be well fitted using Equation 2, yielding $\Delta E = 2533 \text{ cm}^{-1}$ ($R^2 = 0.9987$). The calculated energy difference again matched well with the energy difference between the emitting level of $\text{Tb}^{3+} {}^5\text{D}_4$ (20500 cm^{-1}) and emitting level of $\text{Sm}^{3+} {}^5\text{G}_{5/2}$ (17900 cm^{-1}). In **Figure 9c** the relative sensitivity S_r calculated for the different temperatures is presented, showing a maximum value of $S_r = 3.27\% \text{ } ^\circ\text{C}^{-1}$ at 20 °C which is

among the best performing thermometers in water for this system (**Table 3**).

Table 3. Comparison of the sensitivity of our thermometers with the sensitivity of other luminescent thermometers performing in the physiological temperature range. The materials, temperature range (°C), and maximal relative sensitivity value (S_m) have been overviewed =.

Materials	Range (°C)	S_m (%°C ⁻¹)	Medium	Ref.
BPY-PMO@Tb,Sm(acac) ₃ 20_80	5-50	2.72 (5°C)	In solution	36
ZJU-88J-perylene	20-80	1.28 (20°C)	In solution	47
ZJU-28-DPASD-1	20-60	3.39 (60°C)	In solution	48
[Tb(dipicCbz) ₃] ³⁻	25-79	3.40 (35°C)	In solution	49
THA@EuNMOF@Fe/TA	20-60	0.6 (60°C)	In tissue	50
Eu _{0.058} Tb _{0.942} BPT	20-80	7.22 (80 °C)	Solid-state	51
Tb _{0.99} Eu _{0.01} (BDC) _{1.5} (H ₂ O) ₂	25-47	0.31 (45 °C)	In solution	52
PMMA[TbEuL₁tpo]1@SiO₂	5-50	3.84 (20°C)	In solution	This work
PMMA[TbEuL₂tpo]3@SiO₂	5-50	3.05 (20 °C)	In solution	This work
PMMA[TbSmL₁tpo]1@SiO₂	5-50	2.93 (15 °C)	In solution	This work
PMMA[TbSmL₂tpo]3@SiO₂	5-50	3.27 (20 °C)	In solution	This work

The results obtained for the samples in this study show similar or higher sensitivity compared to the examples from the literature, except for one example (reference [51]) which was measured in the solid-state. Our samples based on the $\text{Tb}^{3+} - \text{Eu}^{3+}$ system have shown to be over 12 times more sensitive compared to samples based on the same system, and the samples based on the $\text{Tb}^{3+} - \text{Sm}^{3+}$ system have shown to be sensitive up to 1% more than the most sensitive example presented up to today.

The temperature uncertainty δT was calculated for the above-mentioned samples remains below 1K in the whole studied temperature range, confirming the excellent behavior of these thermometers, as illustrated in **Figure 10**. For the **PMMA[TbEuL₁tpo]1@SiO₂** NPs (**Figure 10a**) the temperature uncertainty δT is more consistent and it is in the range from 0.015 to 0.03 °C, while for the **PMMA[TbSmL₂tpo]3@SiO₂** NPs (**Figure 10b**) the δT is in the range from 0.1 to 0.24 °C. The difference in the δT comes from the intensity of the emission peaks which are used for ratiometric temperature sensing in these two systems. In the physiological temperature range the emission intensity of the Sm^{3+} peak at 643 nm (${}^5\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$) is significantly lower compared to the emission intensity of the Eu^{3+} peak at 614

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nm ($^5D_0 \rightarrow ^7F_2$), which leads to a possibly higher uncertainty due to a rise of the background noise during the temperature readout for the thermometers based on the $Tb^{3+} - Sm^{3+}$ system compared to the ones based on the $Tb^{3+} - Eu^{3+}$ system.

Figure 10. Calculated temperature uncertainty ΔT for $PMMA[TbEuL1tpo]1@SiO_2$ NPs (a) and $PMMA[TbSmL2tpo]3@SiO_2$ NPs (b).

Toxicity test. To fully assess the potential use of PMMA coated SiO_2 NPs for biological applications cytotoxicity tests were conducted on living cells. Normal human dermal fibroblastic cells (NHDF cells) were used for these experiments. The results of the viability test demonstrated that the samples $PMMA[TbEuL1tpo]1@SiO_2$ and $PMMA[TbSmL2tpo]3@SiO_2$ NPs are non-toxic (Figure 11). At rather high concentrations of 1, 0.5 and 0.1 mg per well the particles have shown toxicity towards fibroblastic cells. Cell viability at these concentrations ranges from 20 to 40% which shows a toxic effect. The violation of cell adhesion and morphology was indicated by round cell morphology at 1, 0.5, and 0.1 mg per well concentrations (Figure 11b). At 0.05 mg per well concentrations, cells start to attach better, a higher number of cells have a spindle-shaped morphology, which is inherent in NHDF cells. ANOVA analysis showed a strong difference between the control at 1, 0.5 and 0.1 mg per well concentrations. Most likely at these concentrations nanoparticles tend to conglomerate which can lead to mechanical pressure on the cells and stop the cell adhesion. At concentrations of 0.05 mg per well and lower the cell viability is

75% or higher (Figure 11a), which is considered as almost non-toxic.^[53]

Figure 11. (a) The cell viability (%) after exposure to different concentrations of $PMMA[TbEuL1tpo]1@SiO_2$ and $PMMA[TbSmL2tpo]3@SiO_2$ NPs. An asterisk (*) indicates significant differences from the control cell group. The statistical analysis was performed by ANOVA followed by the Tukey test ($p < 0.05$). (b) Fluorescence microscopy images of cells at different SiO_2 coated NP concentrations (cells are green). Scale bar is 250 μm .

Conclusions

Thin PMMA films and PMMA coated SiO_2 NPs thermometers doped with tppo derivatives of lanthanide β -diketonate complexes showed very good temperature sensing properties in the physiological temperature range. The thermometers were based on two ion pair systems, a $Tb^{3+} - Eu^{3+}$ and a $Tb^{3+} - Sm^{3+}$ pair in specific, where lanthanide ions were doped in the PMMA polymer in different ratios to form a series of samples with L₁ and L₂ complexes. The results obtained for the PMMA films in both systems showed promising results for this temperature range, where for the $Tb^{3+} - Eu^{3+}$ pair the maximal values of S_r were in the range from 3.57 to 4.21% K^{-1} , reaching the highest obtained value of $S_r = 4.21\% K^{-1}$ at 313 K for the sample $PMMA[TbEuL1tpo]1$. For the second system, the $Tb^{3+} - Sm^{3+}$ pair, the maximal values of S_r were in the range from 2.93 to 3.64% K^{-1} , with the highest value of $S_r = 3.64\% K^{-1}$ at 313 K found for the $PMMA[TbSmL2tpo]3$ sample. The best performing samples, one from each series of PMMA films, were used for coating SiO_2 NPs and the results showed that the relative sensitivity are similar as in the films, with only slightly lower maximal S_r values. The value of $S_r = 3.84\% ^\circ C^{-1}$ at 20 $^\circ C$ was retrieved for the $PMMA[TbEuL1tpo]1@SiO_2$ sample, while the $PMMA[TbSmL2tpo]3@SiO_2$ sample showed $S_r = 3.27\% ^\circ C^{-1}$ at 20 $^\circ C$. The obtained results of the relative sensitivity reported for PMMA films place amongst the highest values for the physiological temperature range in both solid-state and in water, as coating of SiO_2 NPs. The promising results of toxicity test gives

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opportunity for the future work with *in vitro* and *in vivo* measurements of temperature with PMMA coated SiO₂ NPs.

Experimental Section

Preparation of PMMA films doped with [Ln₁(L₁₍₂₎)₃(tppo)₂] and [Ln₂(L₁₍₂₎)₃(tppo)₂] complexes (Ln₁ = Tb³⁺, Ln₂ = Eu³⁺ or Sm³⁺). The PMMA films were prepared as follows: 100 mg of poly(methyl methacrylate) (PMMA) was weighed and placed in a 25 mL vial. It was dissolved in 10 mL of chloroform and stirred at room temperature for 15 min. The lanthanide complex Ln₁(L₁₍₂₎)₃(tppo)₂ and Ln₂(L₁₍₂₎)₃(tppo)₂ (Ln₁ = Tb³⁺ and Ln₂ = Eu³⁺ or Sm³⁺) solution was prepared by dissolving different ratios of Ln₁ and Ln₂ complexes in 3 mL of chloroform with a total concentration of the complexes in the range of 1.67·10⁻³ mol/L to 1.67·10⁻² mol/L depending of the ratio used for lanthanide complexes, in order to obtain different intensity ratio of emission peaks of Ln₁ and Ln₂. The solution of the lanthanide complexes was added dropwise to the PMMA solution and left to stir for 2 hours. After this time the solution was transferred into a Petri dish and a heating plate at 30 °C was used to evaporate the chloroform and obtain clear films.

Preparation of SiO₂ nanoparticles coated with PMMA[Ln₁Ln₂L₁₍₂₎tppo] films. The silica NPs were synthesized by a procedure previously established in our group.^[54] The coating of the SiO₂ NPs was done as follows. In 5 mL of chloroform 50 mg of PMMA[Ln₁Ln₂L₁₍₂₎tppo] was dissolved and 40 mg excess of PMMA was added and left to stir for 30 min at room temperature. At the same time 70 mg of SiO₂ NPs were dispersed in 3 mL of chloroform, and after 30 min of stirring the SiO₂ NPs suspension was added to the solution of PMMA[Ln₁Ln₂L₁₍₂₎tppo] and left to stir for 2 hours. Afterwards the suspension was transferred to a 15 mL centrifuge tube and centrifuged for 5 min at 5000 rpm to separate the SiO₂ NPs from the rest of the PMMA solution. The PMMA solution was decanted and the PMMA[Ln₁Ln₂L₁₍₂₎tppo]@SiO₂ NPs were left to dry in open air for one day. The next day the NPs were washed once with a methanol/water mixture (1/1, v/v) to wash the residuals of unreacted PMMA. After washing and decanting of the washing solvent the nanoparticles were left to dry in open air for one day.

The details of the characterization of the PMMA films doped with [Ln₁Ln₂(L₁₍₂₎)₃(tppo)₂] and the SiO₂ NPs coated with PMMA [Ln₁Ln₂L₁₍₂₎tppo] films can be found in the SI.

CCDC 1964128-1964132 contain the supplementary crystallographic data of the molecular structures obtained for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/contents/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

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Entry for the Table of Contents

Layout 1:

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Designing highly sensitive ratiometric luminescent thermometers: From lanthanide complexes to PMMA coated SiO₂ nanoparticles.

Dimitrije Mara,^{*,[a,b]} Anna M. Kaczmarek,^{*,[a]} Flavia Artizzu,^[a] Anatolii Abalymov,^[c,d] Andre G. Skirtach,^[c] Kristof Van Hecke^[a] and Rik Van Deun^[a]

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Luminescent PMMA Films and PMMA@SiO₂ Nanoparticles with Embedded Ln³⁺ Complexes for Highly Sensitive Optical Thermometers in the Physiological Temperature Range