**Luminescent PMMA films and SiO2 nanoparticles functionalized with Ln3+ complexes for highly sensitive ratiometric optical temperature sensors in the physiological range**

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Optical thermometry based on luminescence is an expanding field of research because non-contact temperature sensing can have different applications, such as for bioimaging in the physiological temperature region, in the cryogenic temperature region for space and aeronautics applications, or in industry where it is necessary to have good sensing properties in precisely defined temperature ranges [1]. Lanthanide β-diketonate complexes have been extensively investigated in the past, as they are cheap, easy to synthesize and they tend to form highly stable complexes with lanthanide ions. Lanthanide β-diketonate complexes have been used as NMR shift reagents, also they are good precursors for further synthesis in some more complex matrixes (such as sol-gels, polymers, etc.), used as OLEDs and as temperature probes because of their distinct luminescence properties [2].

Here, we report novel structures of different homonuclear complexes (Ln3+ = Eu3+, Tb3+ and Sm3+) with two different β-diketonate ligands and one neutral ligand. The β-diketonate ligands (L) used for the synthesis of the complexes are 4,4,4-trifluoro-1-phenyl-1,3-butadione (bfa) and 4,4,4-trifluoro-1-(4-chlorophenyl)-1,3-butadione (Clbfa) and the neutral monodentate ligand triphenylphosphine oxide (tphpo). The complexes show distinct luminescence properties such as color purity and high quantum yield, which gave us the idea to process these complexes in different matrixes and try to make functional thermometers for use in the physiological temperature range.

The complexes were doped into poly(methyl-methacrylate) (PMMA) at different ratios to obtain PMMA thin films that could be used as luminescent thermometers. We have two series of PMMA films, first with Ln(bfa)3(tphpo)2 complexes and second with Ln(Clbfa)3(tphpo)2 complexes. In the series we have two different subseries: one with Tb3+-Eu3+ ions and another with Tb3+-Sm3+. We have obtained a series of Eu-Tb and Sm-Tb thermometers with different ratio between the lanthanide complexes. The best performing sample from the Eu-Tb series shows a maximal value of Sr = 4.38% K-1 at 303 K in the 253-353 K region, as for best performing sample for the Sm-Tb series shows a maximal value of Sr = 3.85% K-1 at 313 K in the 253-343 K region. The best PMMA films were coated on SiO2 nanoparticles and were studied in water in the 5-50 °C temperature range. The Eu-Tb sample shows a maximal value of Sr = 4.14 % C-1 at 20 °C and for the Sm-Tb sample a maximal Sr = 3.81 % C-1 at 20 °C.

REFERENCES

[1] C. D. S. Brites, A. Millan, L. D. Carlos, *Lanthanides in Luminescent Thermometry*, *Handbook of the Physics and Chemistry of Rare Earths*, 2016.

[2] K. Binnemmans, *Rare-earth beta-diketonates, Handbook of the Physics and Chemistry of Rare Earths,* 2005.