Luminescent PMMA films and SiO_2 nanoparticles functionalized with Ln^{3+} complexes for highly sensitive ratiometric optical temperature sensors in the physiological range

GHENT UNIVERSITY

XStruct BIO-INORGANIC CHEMISTRY

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Luminescent Lanthanide Lab f-element coordination chemistry

Synthesis of Ln^{3+} complexes

The complexes were synthesized according to the following procedure with a Ln^{3+} : $L_{1(2)}$ ratio 1: 3 ,(with Ln^{3+} = Sm^{3+}, Eu^{3+} and Tb^{3+} and L_1 = 4,4,4-trifluoro-1-phenyl-1,3-butadiene or L_2 = 4,4,4-trifluoro-1-(4-chlorophenyl)-1,3-butadiene). The ligands were firstly deprotonated with an equimolar amount of NaOH. After obtaining the tris β-diketonate complexes the water molecules were replaced with the neutral co-ligand triphenylphosphine oxide (tppo). The obtained complexes were crystalized and crystals were analyzed with single crystal X-ray diffraction.

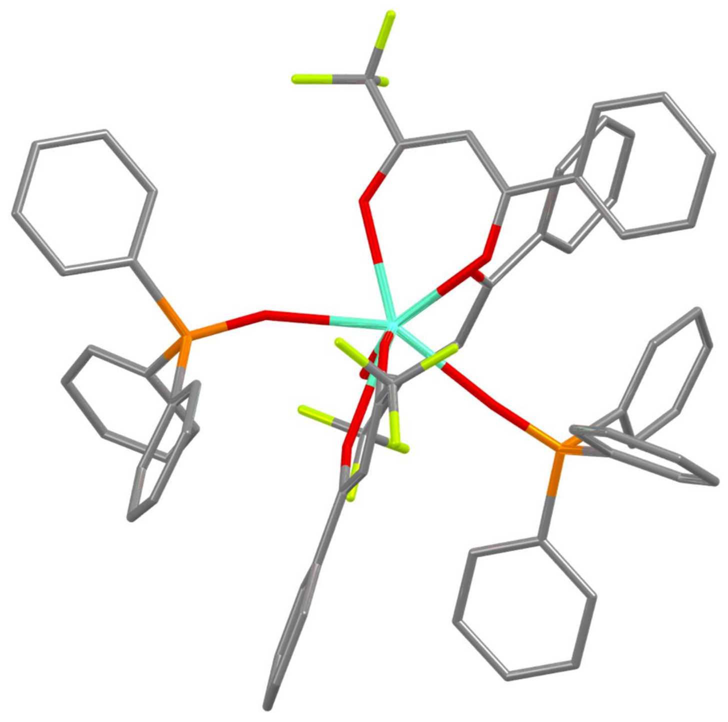

Fig 1. Molecular structure of complex LnL_1tppo

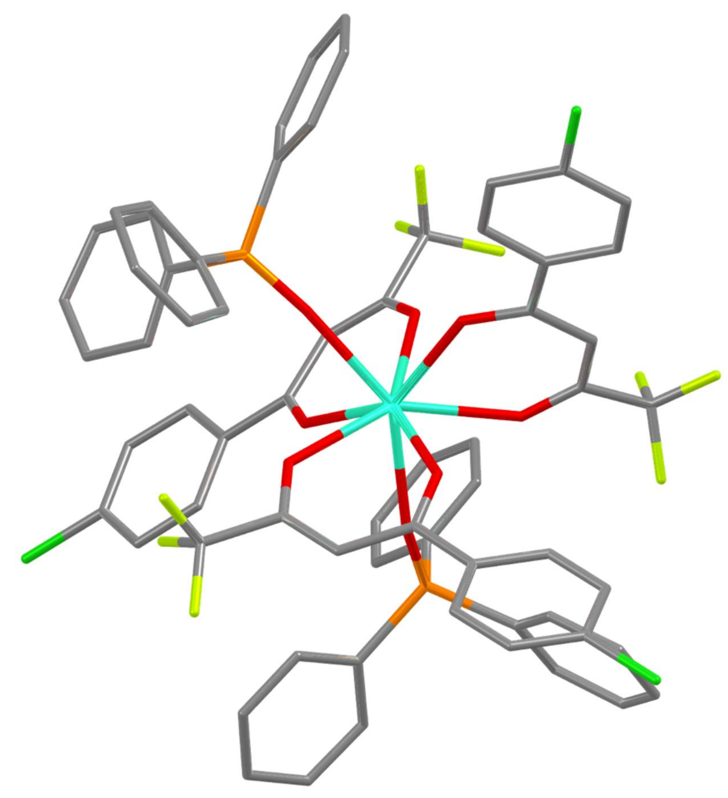

Fig 2. Molecular structure of complex LnL_2tppo

Luminescence properties of Ln^{3+} complexes

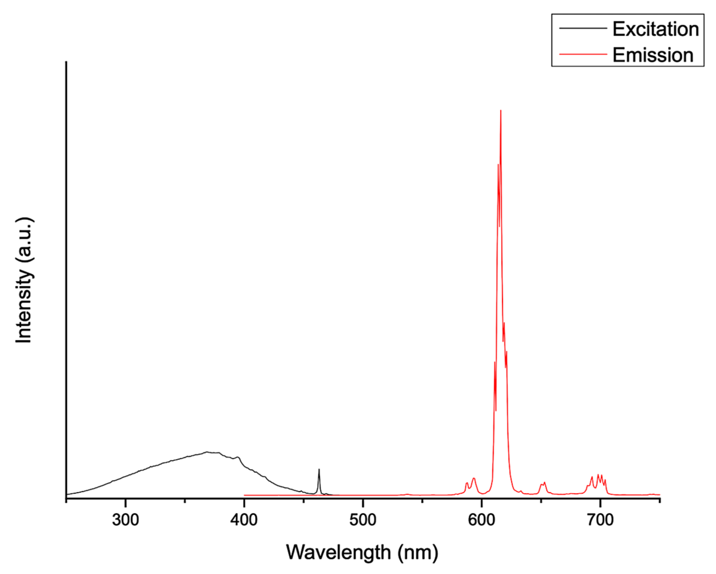

Fig 3. PL spectra of EuL_1tppo

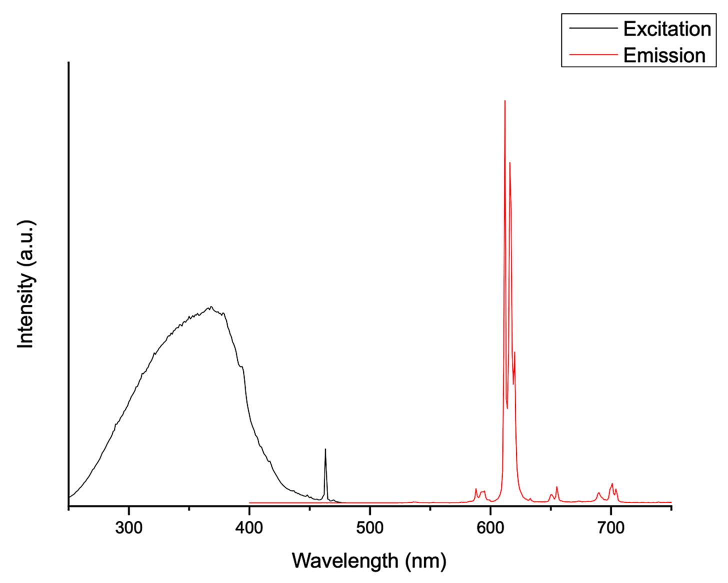

Fig 4. PL spectra of EuL_2tppo

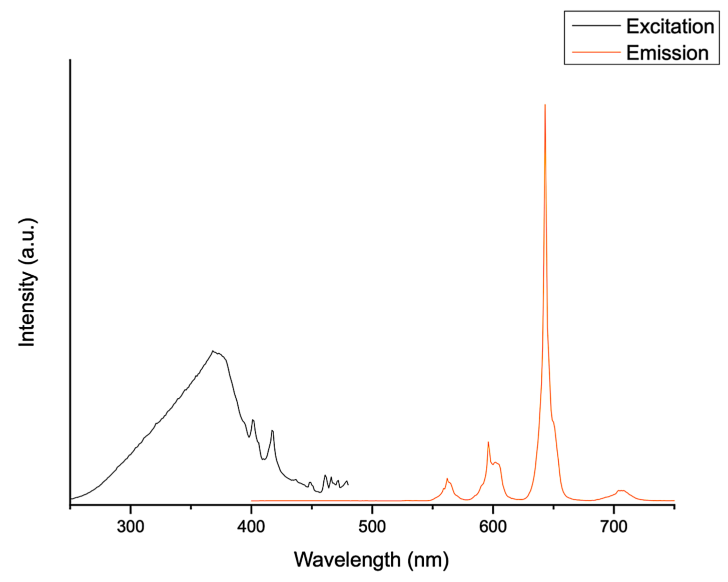

Fig 5. PL spectra of SmL_1tppo

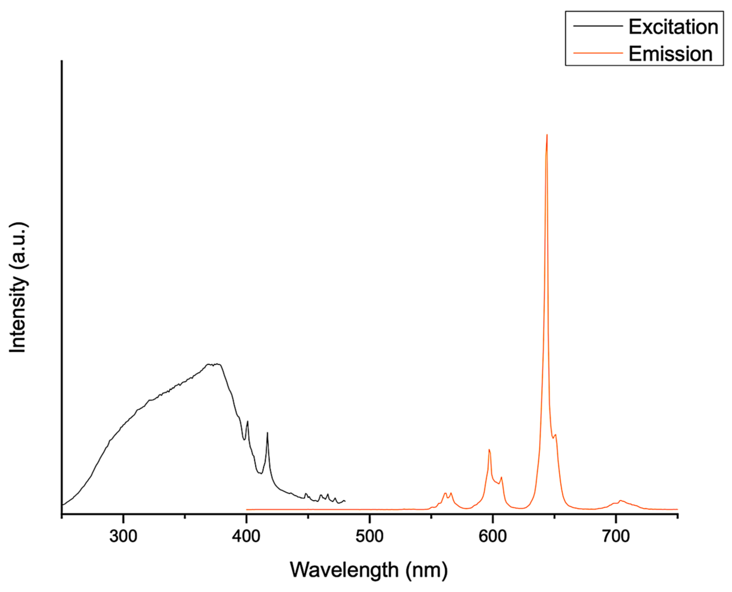

Fig 6. PL spectra of SmL_2tppo

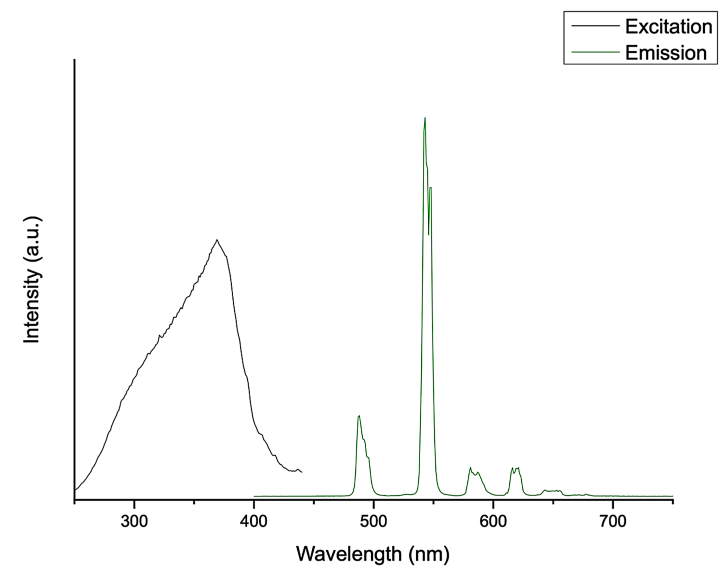

Fig 7. PL spectra of TbL_1tppo

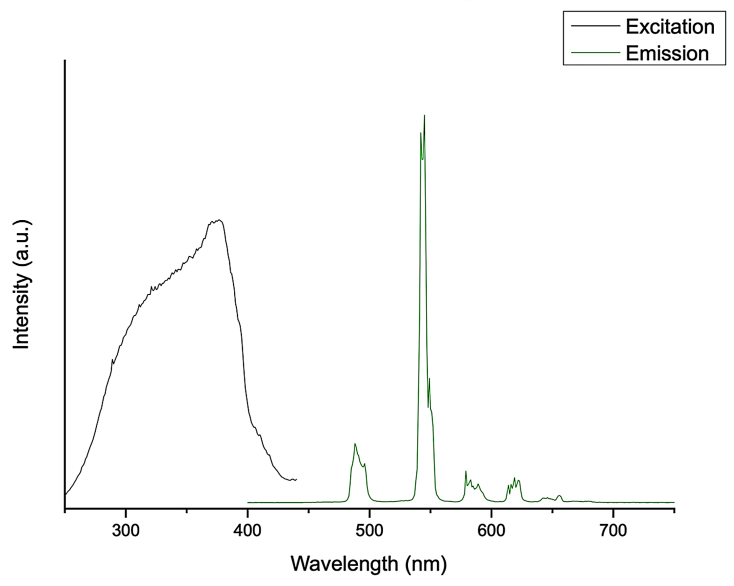

Fig 8. PL spectra of TbL_2tppo

Preparation of PMMA films and SiO_2-coated nanoparticles

The PMMA films were prepared as follows: PMMA was dissolved in 5 mL of CH_2Cl_2 and stirred at room temperature. To this solution was added a CH_2Cl_2 solution of the $LnL_{1(2)}$tppo complexes (Tb-Eu or Tb-Sm) in different molar ratios to obtain luminescent PMMA films.

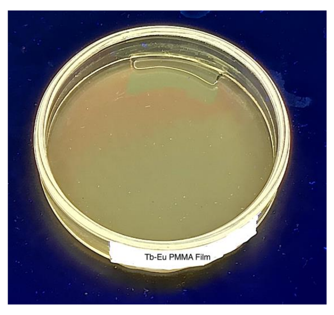

Fig 9. Sample of Tb-Eu PMMA film under UV lamp λ_{exc} = 365 nm

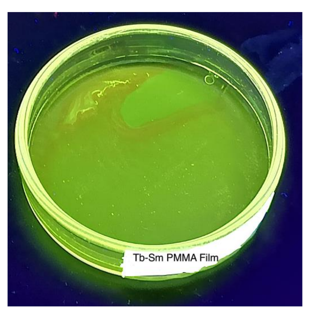

Fig 10. Sample of Tb-Sm PMMA film under UV lamp λ_{exc} = 365 nm

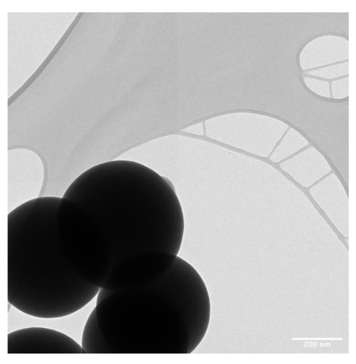

Fig 11. TEM image of SiO_2 nanoparticles and PMMA coating

Preparation of SiO_2 coated nanoparticles was done as following, firstly we have prepared the silica nanoparticles by the synthesis procedure that was already established in our group.[1] The silica nanoparticles were suspended in CH_2Cl_2 for some time before they were transferred to the PMMA-$LnL_{1(2)}$tppo CH_2Cl_2 solution and stirred for one hour. After time passed the mixture was transferred to centrifuge tubes and centrifuged to separate the SiO_2 nanoparticles from the rest of the mixture.

Temperature sensing of PMMA films

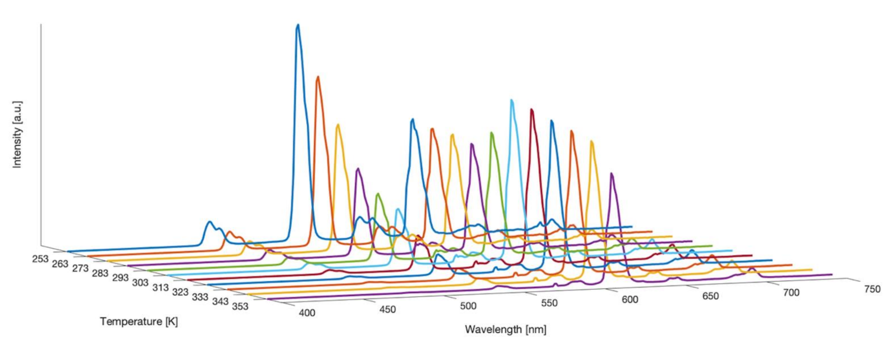

Fig 12.Emission spectra in the temperature range from 253 K to 353 K [$Tb_{0.83}Eu_{0.17}L_1$tppo]-PMMA film[2]

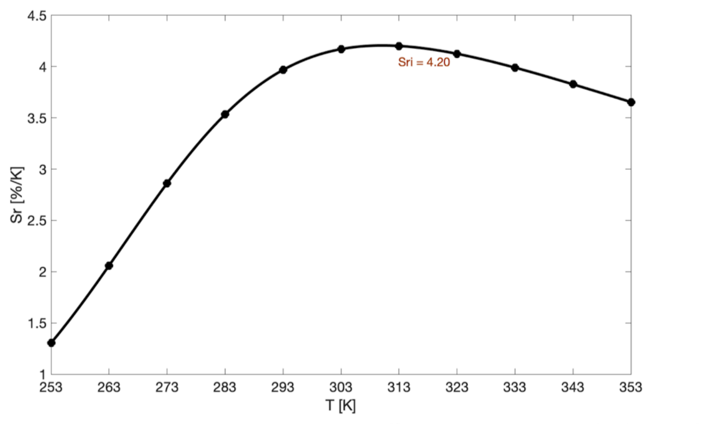

Fig 13. Plot showing relative sensitivity at different temperatures (253-353 K) for [$Tb_{0.83}Eu_{0.17}L_1$tppo]-PMMA film

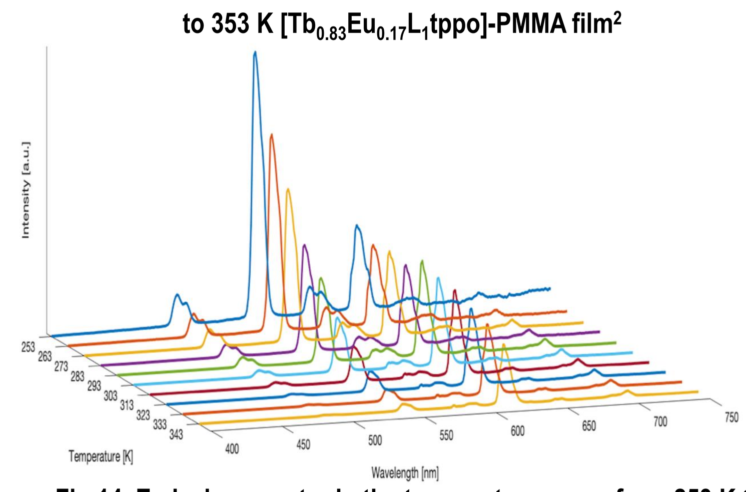

Fig 14. Emission spectra in the temperature range from 253 K to 343 K [$Tb_{0.92}Eu_{0.08}L_2$tppo]-PMMA film

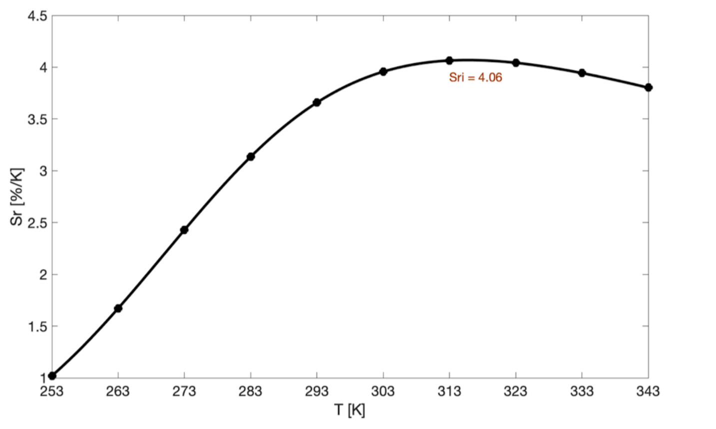

Fig 15. Plot showing relative sensitivity at different temperatures (253-343 K) for [$Tb_{0.92}Eu_{0.08}L_2$tppo]-PMMA film

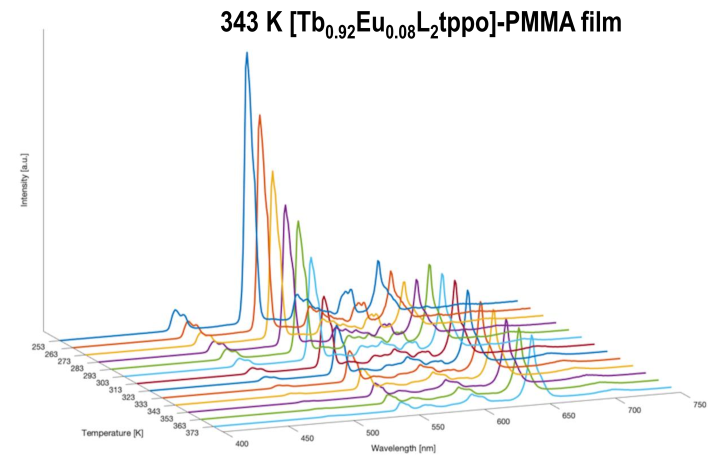

Fig 16.Emission spectra in the temperature range from 253 K to 373 K [$Tb_{0.5}Sm_{0.5}L_1$tppo]-PMMA film

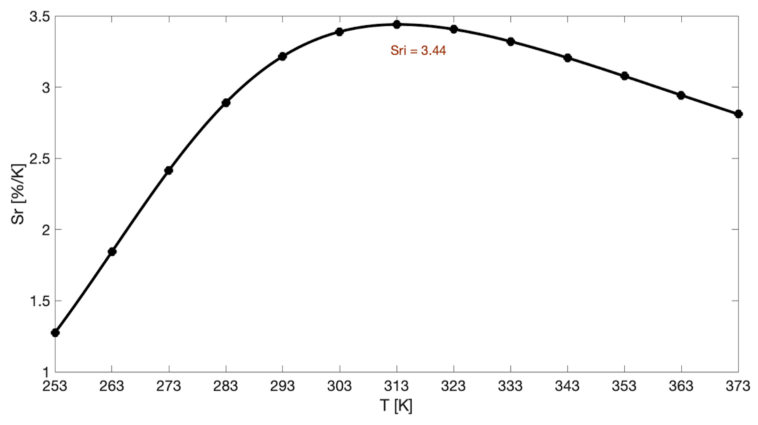

Fig 17. Plot showing relative sensitivity at different temperatures (253-373 K) for [$Tb_{0.5}Sm_{0.5}L_1$tppo]-PMMA film

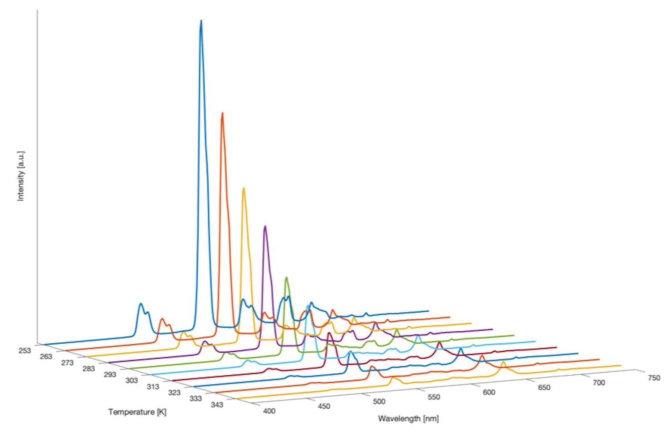

Fig 18. Emission spectra in the temperature range from 253 K to 343 K [$Tb_{0.81}Sm_{0.19}L_2$tppo]-PMMA film

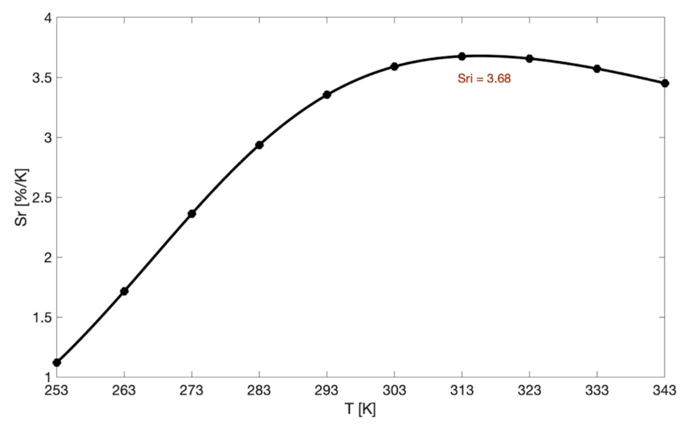

Fig 19. Plot showing relative sensitivity at different temperatures (253-343 K) for [$Tb_{0.81}Sm_{0.19}L_2$tppo]-PMMA film

Temperature sensing of coated SiO_2 nanoparticles in H_2O

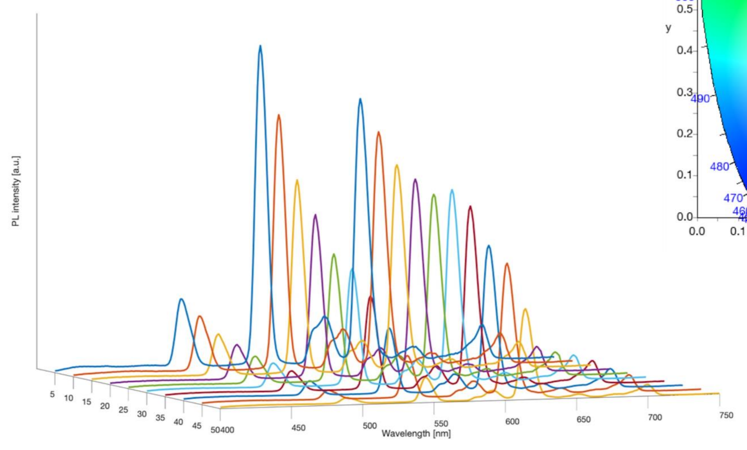

Fig 20.Emission spectra in the temperature range from 5 °C to 50 °C [$Tb_{0.83}Eu_{0.17}L_1$tppo]-PMMA@SiO_2

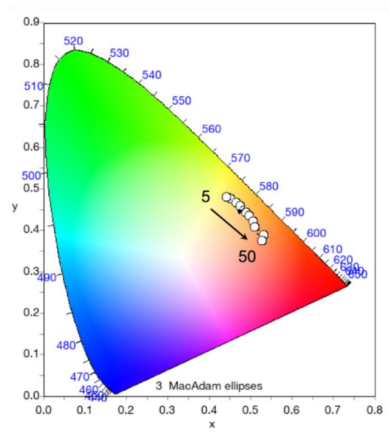

Fig 21. CIE chromaticity diagram showing color change with change of temperature for [$Tb_{0.83}Eu_{0.17}L_1$tppo]-PMMA@SiO_2

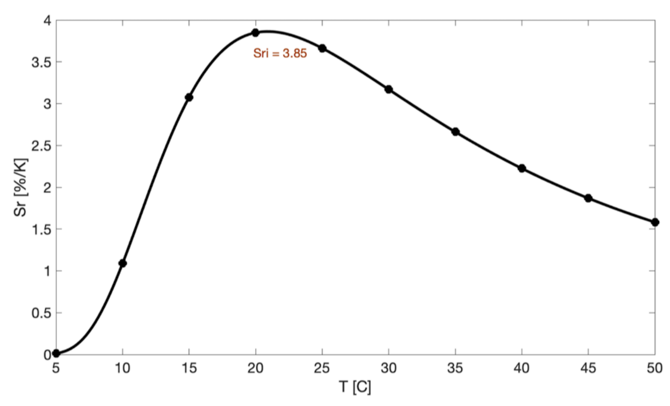

Fig 22. Plot showing relative sensitivity at different temperatures (5-50 °C) for [$Tb_{0.83}Eu_{0.17}L_1$tppo]-PMMA@SiO_2

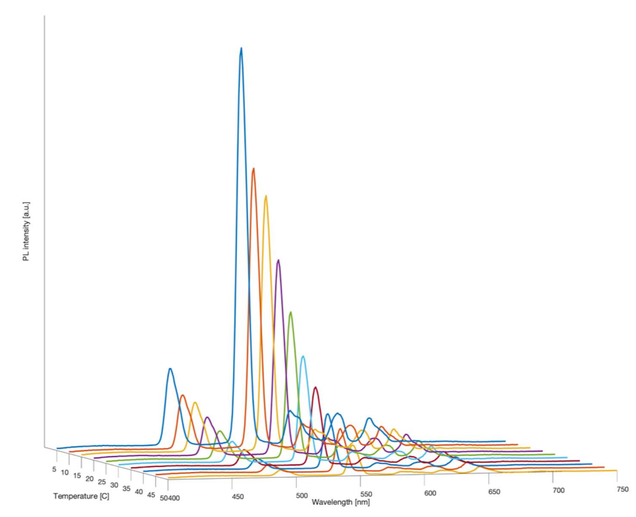

Fig 23. Emission spectra in temperature range from 5 °C to 50 °C [$Tb_{0.81}Sm_{0.19}L_2$tppo]-PMMA@SiO_2

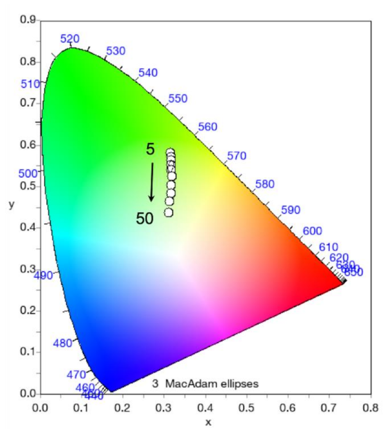

Fig 24. CIE chromaticity diagram showing color change with change of temperature for [$Tb_{0.81}Sm_{0.19}L_2$tppo]-PMMA@SiO_2

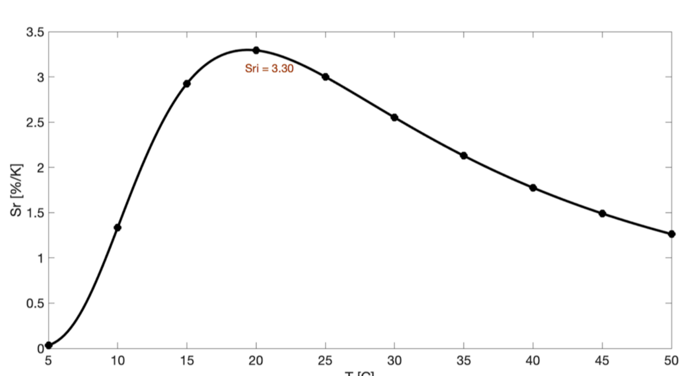

Fig 25. Plot showing relative sensitivity at different temperatures (5-50 °C) for [$Tb_{0.81}Sm_{0.19}L_2$tppo]-PMMA@SiO_2

Conclusion

We have obtained five new crystal structures of $LnL_{1(2)}$tppo complexes (Ln^{3+} = Sm^{3+}, Eu^{3+} and Tb^{3+}) which were characterized with single crystal X-ray diffraction and photoluminescence. Further these complexes were doped in PMMA films in different ratios (Tb-Eu and Tb-Sm) which yielded luminescent PMMA films with high relative sensitivity in the physiological temperature range. Also we have managed to coat SiO_2 nanoparticles with PMMA films of the best performing films for Tb-Eu and Tb-Sm samples and afterwards to test temperature sensing in water where we have managed to reproduce the sensitivity of PMMA films.

1. F. Artizzu, D. Loche, D. Mara, L. Malfatti, A. Serpe, R. Van Deun, M . F. Casula, Lightning up Eu^{3+} luminescence through remote sensitization in silica nanoarchitetures, *J. Mater. Chem. C*, 2018, **6**, 7479-7486.
2. A. M. Kaczmarek, R. Van Deun, M. K. Kaczmarek, TeSen-tool for determining thermometric parameters in ratiometric optical thermometry, *Sensor. Actuator. B Chem.*, 2018, **273**, 696-702.