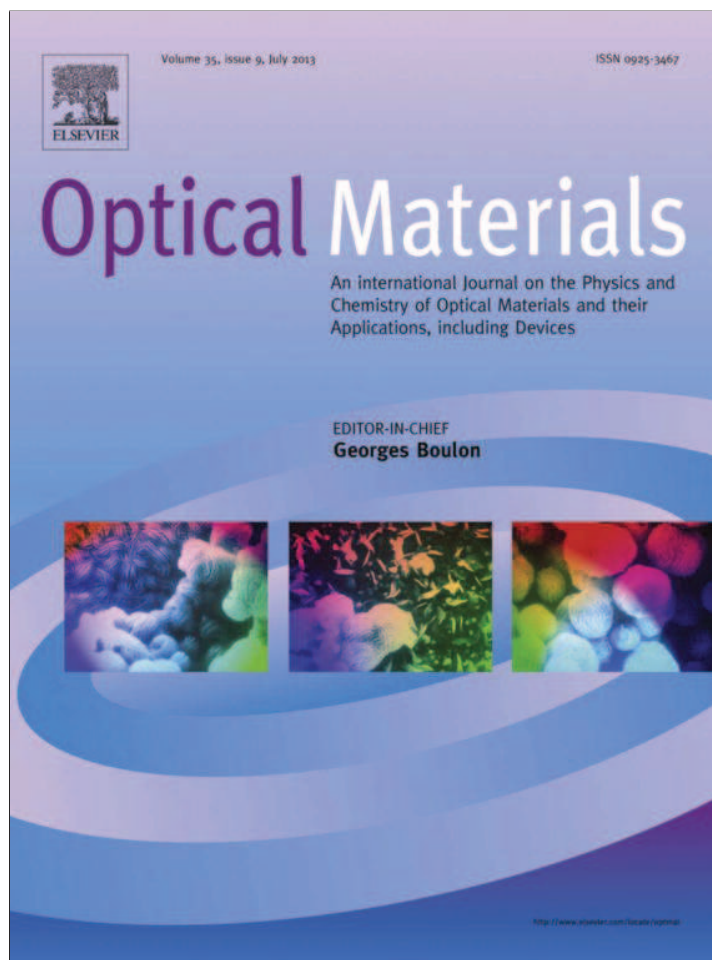


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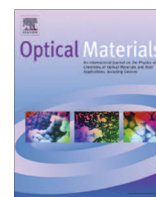


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## Luminescent xerogels obtained through embedding Tb(III) and Eu(III) complexes in silica matrix

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### ABSTRACT

The paper reports the preparation of two luminescent xerogels through embedding in a silica matrix of Tb(III) and Eu(III) complexes using succinimide (SI) and N-hydroxysuccinimide (NHSI) as ligands. In the first stage, Tb(III) and Eu(III) complexes with N-hydroxysuccinimide and succinimide were prepared at 1:3 metal to ligand ratio. Strong luminescent emission was observed only in case of Eu(III)-SI and Tb(III)-NHSI complexes while the Eu(III)-NHSI and Tb(III)-SI complexes exhibited none or weak photoluminescent properties. In the second stage, the selected highly luminescent complexes were embedded in silica matrices via a sol-gel procedure leading to the formation of xerogels with transparent-glassy aspect which keep the remarkable photoluminescence properties of the free complexes. The selected, highly luminescent free complexes and their correspondent silica xerogels were investigated through thermal analysis, powder XRD, SEM, FT-IR and fluorescence spectroscopy. Their excellent photoluminescent properties and excitation spectra, conveniently located in UV-A region, might recommend these materials for applications in optoelectronic devices where photonic conversion layers are required.

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### 1. Introduction

During the last decades there has been a remarkable increase in the interest towards the complexes of lanthanide group elements not only in terms of extending knowledge over their chemical combinations, but mostly due to a high application potential in areas such as OLED color display systems [1], NIR-visible conversion devices [2], energy-efficient lighting systems or as assays in medical imaging [3,4]. The unique spectral properties of the trivalent lanthanide cations ( $\text{Ln}^{3+}$ ) arise from the  $f-f$  transitions within  $4f$  orbitals, which are partially shielded by the  $5s$  and  $5p$  orbitals [5,6]. This leads to minimal interactions with the molecular entities located in the vicinity of the lanthanide cation. The inner shell electronic transitions are barely affected by a certain ligand, thus, characteristic narrow emission bands and excited states lifetimes in millisecond range are achieved. Taking advantage of  $\text{Ln}^{3+}$  cations luminescent properties is not a straightforward task since these properties are mainly governed by Laporte forbidden  $f-f$  transitions, which display relative long (in the microsecond to millisecond range) fluorescence lifetimes but very low extinction coefficients ( $\epsilon < 1 \text{ M}^{-1} \text{ cm}^{-1}$ ) [7]. One possible approach to overcome the weak absorbance of  $\text{Ln}^{3+}$  consists in their coordination by ligands able of energy harvesting and followed by an efficient

transfer to the central  $\text{Ln}^{3+}$  emissive center. The sensitization of the central lanthanide cation may be achieved through coordination of a chromophore-containing ligand in a process also known as “antenna effect” [8]. This chromophore-containing ligand is able to achieve through efficient energy absorption an excited state subsequently transferred to the emitting state of the lanthanide cation which returns to its ground state by photon emission [9]. Due to various factors that influence the efficient energy transfer to the central lanthanide cation, it is unlikely that the same chemical configuration of a certain ligand, effective in a specific case of  $\text{Ln}^{3+}$  cation to be also effective for a different lanthanide cation, as it is also highlighted by the results reported in this study.

In this context, lanthanides complexes investigated in this work, especially those that exhibit remarkable photoluminescence properties, are targeted mainly for applications in optoelectronics. For this purpose, two ligands, N-hydroxysuccinimide ( $\text{HL}^1$ ) and Succinimide ( $\text{HL}^2$ ), were tested for obtaining Eu(III) and Tb(III) complexes. Four complexes were prepared at 1:3 metal/ligand ratio. Strong photoluminescence emission was observed only in case of  $[\text{TbL}_3(\text{H}_2\text{O})_3]$  and  $[\text{EuL}_3(\text{H}_2\text{O})_3]$  complexes which were selected for further embedment in silica matrices. Succinimide and N-hydroxysuccinimide were less investigated as suitable ligands for lanthanide complexes. Although these two compounds were successfully used for preparing alkali or transition metals complexes [10,11], up to date there are no reported studies regarding lanthanide complexes using previously mentioned ligands.

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