

# Performance of near-IR luminescent xerogel materials covalently bonded with ternary lanthanide ( $\text{Er}^{\text{III}}$ , $\text{Nd}^{\text{III}}$ , $\text{Yb}^{\text{III}}$ ) complexes

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## Abstract

A series of near-infrared (NIR) luminescent ternary lanthanide (Ln = Er, Nd, Yb) complexes covalently linked to xerogels by a chelate ligand 5-(*N,N*-bis-3-(triethoxysilyl)propyl)ureyl-1,10-phenanthroline (phen-Si) were synthesized in situ via a sol–gel method. The obtained xerogel materials (named xerogel-bonded Ln complex) are rigid, and appear homogeneous confirmed by SEM images. Upon excitation at the maximum absorption wavelength of the ligands, all these xerogel materials with different lanthanide complex concentration show the characteristic NIR luminescence of the corresponding lanthanide ion, as a result of the efficient energy transfer from the ligands to the lanthanide ion. For the xerogel-bonded Er complex, the full width at half maximum (FWHM) of the  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  transition is 76 nm, which enables a wide gain bandwidth for the optical amplification. Based on the Judd–Ofelt theory, the radiative properties of the xerogel-bonded Nd complex (with Nd/Si molar ratio of 1/11 in the reaction) were studied.

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**Keywords:** NIR luminescence; Covalently bonded; Ternary lanthanide complex; Xerogel material; Judd–Ofelt theory

## 1. Introduction

Recently, much attention has been paid to near-infrared (NIR) luminescence of trivalent lanthanide complexes, such as Yb(III), Er(III) and Nd(III), due to their potential applications from biomolecule labeling in luminescent bioassays (based on Yb complexes) [1,2] to functional materials for optical telecommunication network (based on Er complexes) [3–5] and laser systems (based on Nd complexes) [6–8]. For practical applications, it is advantageous to embed these NIR luminescent complexes in a stable rigid matrix. Sol–gel derived hybrid materials have attracted much interest for photonic applications, as they potentially combine the optical quality of silica, its thermal stability and mechanical strength, together with the optical characteristics of active organic molecules [9–12]. The obvious advantages of the sol–gel method include the mild reaction conditions, the feasibility to control the com-

position easily and the convenient preparation routes [13–16]. Therefore, sol–gel hybrid materials are potential hosts for NIR-luminescent lanthanide complexes. In the recent years, more effort has been devoted to covalent grafting of the ligands to the backbone of sol–gel via Si–C bonds, because the solubility and homogeneous distribution of lanthanide complexes in the material can be improved by covalently linking the complexes to the matrix [17–21]. Recently, our group has reported the synthesis of functionalized 1,10-phenanthroline ligand 5-(*N,N*-bis-3-(triethoxysilyl)propyl)ureyl-1,10-phenanthroline (phen-Si), through which the binary europium phenanthroline complex was covalently attached to the silica-based network [22]. And Binnemans et al. reported the covalent grafting of some ternary lanthanide complexes to the sol–gel via the phen-Si ligand by a ligand exchange reaction [23,24]. Yet, in the previous reports the optical properties of the luminescent sol–gel materials have not been studied in detail.

In the present paper, the NIR-luminescent xerogel materials covalently bonded with lanthanide complex via the recently developed in situ approach [13–15] were synthesized and the

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luminescent properties of the materials have been demonstrated in detail. The NIR-luminescent materials (denoted xerogel-bonded Ln complex(*N*), where *N* is the Ln/Si molar ratio in the reaction) consist of ternary lanthanide complexes [Ln(dbm)<sub>3</sub>phen; Ln = Er, Nd, Yb; dbm = dibenzoylmethanate] covalently bonded to the sol–gel matrix by the phen–Si ligand. No cracks were observed in the obtained xerogels. And the xerogel materials were very rigid. The NIR-luminescence behavior of these materials with different lanthanide complex concentrations has been studied. Based on the Judd–Ofelt theory and the experimental absorption spectrum, the optical properties of the xerogel-bonded Nd complex(1/11) have been investigated.

## 2. Experimental

### 2.1. Materials

Tetraethoxysilane (TEOS, Aldrich), 3-(triethoxysilyl)-propyl isocyanate (Aldrich), fuming nitric acid and absolute ethanol were used as received. The solvent chloroform (CHCl<sub>3</sub>) was used after desiccation with anhydrous calcium chloride. Ytterbium oxide (Yb<sub>2</sub>O<sub>3</sub>, 99.99%), neodymium oxide (Nd<sub>2</sub>O<sub>3</sub>, 99.99%) and erbium oxide (Er<sub>2</sub>O<sub>3</sub>, 99.99%) were purchased from Yue Long Chemical Plant (Shanghai, China). 1,10-Phenanthroline monohydrate (Phen·H<sub>2</sub>O, 99%, A.R.), and dibenzoylmethane (Hdbm, C.P.) were bought from Beijing Fine Chemical Co. (Beijing, China). LnCl<sub>3</sub> (Ln = Er, Nd, Yb) was obtained by dissolving Ln<sub>2</sub>O<sub>3</sub> in hydrochloric acid.

### 2.2. Synthesis of the xerogel-bonded Ln complex (Ln = Er, Nd, Yb)

The starting reagent 5-amino-1,10-phenanthroline (denoted as phen-NH<sub>2</sub>) was prepared according to the procedure described in the literature [25]. The modified phenanthroline (phen-Si) was synthesized by the reaction of phen-NH<sub>2</sub> and 3-(triethoxysilyl)-propyl isocyanate in CHCl<sub>3</sub> as described in ref. [21]. Analysis: calculated for C<sub>32</sub>H<sub>51</sub>N<sub>5</sub>O<sub>8</sub>Si<sub>2</sub>: C, 55.5; H, 7.4; N, 10.0%. Found: C, 55.0; H, 7.1; N, 10.9%. NMR (CDCl<sub>3</sub>), δ 0.520 (4H, m); 1.133 (18H, t); 1.606 (4H, m); 3.223 (4H, q); 3.687 (12H, q); 7.270 (2H, brs); 7.680 (2H, m); 7.855 (1H, s), 8.238 (2H, m); 9.225 (2H, m).

Phen-Si was dissolved in ethanol, and then TEOS and deionized water (acidified with HCl, pH = 2) were added under stirring. An appropriate amount of Hdbm and LnCl<sub>3</sub> ethanol solution were introduced into the starting solution consecutively. The molar ratio of phen-Si:TEOS:H<sub>2</sub>O:Ln<sup>3+</sup>:Hdbm was 1:*x*:4*x*:1:3 (*x* = 25 and 9). The mixed solution was stirred for about 4 h at room temperature to ensure homogeneous mixing and achieve a single phase, and then placed in a cuvette. The precursor solution converted to wet gel after several days of gelation at 45 °C and then was continuously dried to obtain a transparent monolithic xerogel. The lanthanide complexes were supposed to be in situ synthesized during the corresponding sol-to-xerogel conversion accompanied with the evaporation of HCl, respectively. Monolithic xerogel samples were ground for the luminescence and SEM measurements. The obtained powder

materials were washed with acetone and ethanol for removal of the surplus Ln<sup>3+</sup> ion and Hdbm, and all of the complexes in the materials were attached to the matrix by the functionalized phen groups. The obtained materials were denoted as xerogel-bonded Ln complex(*N*), where *N* is the Ln/Si molar ratio in the initial mixture, and it is 1/27 and 1/11 when *x* equals 25 and 9, respectively. Before the luminescence measurements were made, the materials were powdered again and dried under vacuum for 24 h at 80 °C.

### 2.3. Characterization

All measurements were carried out at room temperature. Scanning electron micrographs were obtained using a JSM-6700F microscope operating at 10.0 kV. FT-IR spectra were measured within a 4000–400 cm<sup>-1</sup> region on an American Bio-Rad Company model FTS135 infrared spectrophotometer with the KBr pellet technique. The fluorescence spectra were recorded on an Edinburgh Analytical Instruments FLS920 equipped with a stablespec-Xenon lamp (450 W) as the light source with the samples in solid state as powder. The time-resolved measurements, for xerogel-bonded Yb complex(1/11) was made on the same instrument (monitored at 980 nm), for xerogel-bonded Er complex(1/11) was done on an Edinburgh Instruments Combined Luminescence Lifetime and Steady State Spectrometer FLS920 equipped with a μF900 Lamp (monitored at 1535 nm), and for xerogel-bonded Nd complex(1/11) was done by using the third harmonic (355 nm) of a Spectra-physics Nd:YAG laser with a 5 ns pulse width and 5 mJ of energy per pulse as the source, an emission monochromator (Acton 2758) equipped with a Hamamatsu R5108 photomultiplier tube and the data were analysed with a LeCroy WaveRunner 6100 1 GHz Oscilloscope (monitored at 880 nm). The xerogel sample, 5.30 mm in diameter and 5.26 mm in thickness, was applied to the optical absorption measurement. The spectral optical density  $OD(\lambda) = 0.4343l\rho\sigma(\lambda)$  of the xerogel-bonded Nd complex(1/11) was recorded using a Shimadzu UV-3101 PC at room temperature, where *l* is the thickness of the xerogel,  $\sigma(\lambda)$  the absorption cross-section and  $\rho$  is the concentration of Nd<sup>3+</sup> ion in the xerogel. The corresponding concentration is calculated to be  $3.0 \times 10^{20}$  Nd/cm<sup>3</sup>, using the expression  $\rho = (nN)/(\pi(R/2)^2l)$ , where *n* is the molar number of Nd<sup>3+</sup> ion, *N* is  $6.02 \times 10^{23}$  and *R* is the diameter.

## 3. Results and discussion

Because of the presence of numerous hydroxyl groups (in Si–OH and H<sub>2</sub>O) that act as nonradiative channels for the excited states of the lanthanide ions, the observation of NIR luminescence by lanthanide ions in silica sol–gel material is not common compared with that of the visible luminescence by Eu(III) and Tb(III), etc. The concentration of hydroxyl groups is high in gels and has strong quenching properties toward the luminescence of lanthanide complexes. The most common method to decrease the degree of quenching is to calcine the sol–gel materials at high temperature (>900 °C). However, the sensitizer ligands usually decompose at such high calcination tempera-

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