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Luminescence of cryptate-type Eu^{3+} complexes incorporated in inorganic and ormocer sol–gel matrices

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Abstract

Two new complexes of Eu-bipyridine (Eu-AA and Eu-BB) were incorporated into sol–gel derived thin films based on zirconia oxide and organically modified sol–gel hybrid zirconia–silica–urethane ormocer (ZSUR).

The absorption and the emission intensities of the composites were compared to the intensity of the Eu oxide doped films and to the other complexes studied recently. The site symmetry of the Eu complexes and Eu oxide in used matrices were studied as well. The intensification of fluorescence, as compared to europium oxide, value was increased by a factor of 64 in amido–amino complex (Eu-AA), and of 2044 in fluorine complex (Eu-BB) as a result of efficient charge transfer from the combined ligand-europium state to europium high ligand levels. The lifetimes from the $^5D_0$ state of the complexes are measured and the results explained.

Keywords: Eu complexes; Sol–gel matrices; Absorption and luminescence spectra; Lifetime measurements; 2,2′-Bipyridine; 3,3′-Biisoquinoline-2,2′-dioxide

1. Introduction

Sol–gel derived glassy materials are of great importance based on their wide applications in non-linear optics and optical switching, catalysis, solar energy collectors, chemical and biological sensors [1–6]. Rare earth (RE) doped sol–gel matrices are of current interest because of their potential as laser materials and phosphors. When europium oxide, or other europium inorganic salts are doped into sol–gel films, only a weak emission is observed due to low oscillator strength of the RE ions. In addition, the low luminescence intensity of the samples prepared at room temperature result from nonradiative relaxations originated from the interaction of the hydroxyl ions of residual water. The luminescence intensities of RE can be strongly increased by incorporating the ions into a complex as a result of charge transfer from strongly absorbing ligands to the RE [7]. Several authors describe the use of the sol–gel method to incorporate complexes of RE elements into a glassy matrix [8–18]. The interest in lanthanide complexes is related to the huge Stokes-shift between absorption and emission, the potentially long life time of the excited state, the narrow line emission and strong binding with biological molecules. These properties enable at least in principle optical measurements with high signal to noise ratio; the light emitted is in or near the visible region and thus can be detected by standard techniques.

Rare earth ions can form stable complexes with heterocyclic ligands which exhibit excellent luminescence properties attributed to the "antenna effect" which denotes an efficient energy transfer from the triplet state of an absorbing coordinated organic molecule (the sensitiser) to a chelated RE ion (the activator). Much effort has been done not only to prepare different classes of organic

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ligands, but also to find suitable host matrices in order to enhance the luminescence intensity and improve thermal-, photo- and mechanical stabilities necessary for their potential applications as lasers, phosphors and so on [19,20].

It has been shown that organic complexes of rare earths doped in zirconia and zirconia-GLYMO had much higher fluorescence properties with respect to comparable inorganic salts as reported recently [8,9,16]. In this context, it was of interest to study the new complexes of Eu(III) within the sol–gel matrices based on zirconia and inorganic–organic hybrid zirconia–silica–urethane (ZSUR).

Since acyclic Eu(III) complexes are sussceptible for the luminescence quenching in protic media, our attention was focused on Eu(III) cryptates which proved to be kinetically stable in water and alcohols. In this work we have used two of the Lehn's-type cryptates: one composed of three 2,2′-bipyridine units appended with two carboxamido–amine sidearms [21], and the second – comprising two 2,2′-bipyridine units and one 3,3′-biisoquinoline-2,2′-dioxide unit [22] that is known to be particularly good sensitizer for Eu(III) emission.

2. Experimental

2.1. Materials

The following materials were used for preparation of the final matrix of zirconia and zirconium–silica–polyurethane (ZSUR) matrices:

Tetramethoxysilane-TMOS (3-isocyanatopropyl)triethoxysilane-ICTEOS, zirconium (IV) *n*-propoxide (70% solution in 1-propanol) were obtained from Fluka; 3-glycidoxypropyl trimethoxysilane-GLYMO, chloro benzene, Poly(ethylene glycol)-PEG, 2-methoxyethanol – from Aldrich were used as received without further purification; ethanol, *n*-propanol of analytical grade (Riedel-de Haen), acetonitrile, glacial acetic acid, nitric acid (analytical grade, Frutarom, Israel), and triply distilled water were used for solution preparations. Chemglass CGQ-0640-01 (USA) quartz slides were used as substrates for the film deposition.

Preparation of the complex Eu-AA ({6,6′-[*N*,*N*′:*N*,*N*′-bis(2,2′-bipyridine-6,6′-dimethyl)bis(aminomethyl)]-5,5′-bis(2-aminoethylcarboxamido)2,2′-bipyridine}europium-(III)chloride) and Eu-BB ({1,1′-[*N*,*N*′:*N*,*N*′-bis(2,2′-bipyridine-6,6′-dimethyl)bis(aminomethyl)]3,3′-biisoquinoline-2,2′-dioxide}europium(III)trifluoromethanesulfonate) was performed according to the literature [21,22], respectively.

2.2. Sample preparation

2.2.1. Zirconium *n*-propoxide was hydrolyzed using a procedure similar to that reported in the literature [8,9].

2.2.2. The synthesis and preparation scheme of the final solution of ZSUR based on ZrO_2 matrix, ESOR and DURS solutions was reported recently [6,15].

The DURS-oligomer solution was synthesized separately by reacting isocyanatopropyl triethoxysilane (ICTEOS) and polyethylene glycol (PEG-600) with the molar ratio (2:1). The reagents were stirred in chlorobenzene at boiling temperature under reflux for 3 h. The residual solvent was evaporated and the DURS hybrid material oligomer was obtained.

The ESOR solution was obtained from TMOS and GLYMO CH_3OH:H_2O:CH_3COOH (15.0:12.8:7.2:2.4), at room temperature for 2 h then GLYMO was added and stirred for 3 h at room temperature.

Than hydrolyzed ZrO_2 was added to hydrolyzed sol of ESOR and DURS.

The nominal molar ratio in the final sol was: $SiO_2:ZrO_2 = 69:31$; and of urethane to epoxy was 24:76.

2.2.3. 0.36 mol% of Eu AA-$(bipy)_3(CONHCH_2CH_2)_2 * EuCl_3$–(1) complex (0.0045 mM) was dissolved in 2 mL acetonitrile and 0.5 mL of acetic acid with stirring and heating 15 min at reflux. Then the solution was cooled to room temperature and added 1.24 mM hydrolyzed zirconia and stirred during 30 min. The films were obtained by the dip-coating technique with a withdrawal speed of 20 cm/min, dried at 40 °C for 30 min and heated at 150 °C for 1 h. The described procedure prevents decomposition of the complexes—as can be seen from the spectroscopic data.

2.2.4. 0.012 mM of Eu-AA was dissolved in 3 mL of acetonitrile as described above and after cooling was added to 3.33 mM ZSUR colloidal sol.

The films were obtained by the dip-coating technique and were treated as described above.

2.2.5. 0.5 mol% of Eu-BB-$(biqi)O_2(bpy)_2 * Eu(TF)_3$–(2) complex was also incorporated in zirconia and ZSUR films using the same technology as described in (3) and (4).

2.2.6. 1 mol% of Europium nitrate (0.0163 mM) was dissolved in 2 mL of methoxyethanol and added to 5 mL of hydrolyzed zirconium oxide (1.55 mM) in propanol. The films were obtained as described above.

2.3. Optical measurements

Steady state luminescence and its excitation spectra were measured at room temperature using JASCO FP770 spectrofluorimeter.

The absorption spectra in the UV–Vis region were recorded at room temperature using Shimadzu UV–Vis spectrometer.

Since the samples have exhibited different intensities they had to be measured at three different sensitivities of the photomultiplier. Therefore a calibration was performed and we have observed that the ratio of the medium sensitivity to the high sensitivity is 11.62 at the 618 nm. The results, for comparison, can be seen from Fig. 2 (sensitivity-medium 5/5) and Fig. 3 (sensitivity-high 5/5) performed for the same emission spectra of Eu-AA complex-0.36% in zirconia. The ratio of the low sensitivity to the medium sensitivity is the same 11.62 at the 618 nm.