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Luminescent amine sensor based on europium(III) chelate

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ABSTRACT

The effect of methylamine vapor on luminescence of Eu(III) tris-benzoylacetonate (**I**) immobilized in thin-layer chromatography plates has been investigated. It has been revealed that interaction of **I** with analyte vapor results in increase of the intensity of Eu(III) luminescence. The mechanism of the effect of methylamine vapors on intensification of the Eu(III) luminescence has been suggested using the data of IR spectroscopy and quantum chemistry calculations. The mechanism of luminescence sensitization consists in bonding of an analyte molecule with a water molecule into the coordination sphere of Eu(III). As a result, the bond of a water molecule with the luminescence centre weakens, rigid structural fragment including europium ion, water and methylamine molecules forms. The presence of such fragment must naturally promote decrease of influence of OH-vibrations on luminescence of the complex **I**.

1. Introduction

There is an increasing demand for ammonia and amine sensing systems. Some organic molecular compounds such as ammonia and amines series have become serious pollution sources of groundwater, soils, and other security applications due to their high toxicity [1,2].

Recently, one has been observed intensification of the studies in the field of development of polyfunctional materials characterized by optical chemosensor properties [3–5]. Analysis of literature data shows that metal compounds, particularly lanthanide-containing complexes with luminescence properties, are promising compounds for the production of optical chemosensors [6–7,8].

The photophysical properties of lanthanide-containing compounds (their long lifetimes, narrow emission bands, large Stokes shifts, and high photostability) make them very promising candidates to be used in the receptor units of sensor devices [9,10]. Some of the lanthanide transitions are hypersensitive, and thus lanthanides create a good basis for sensors that follow changes in signal intensity as a result of alterations in the chemical or physical environment. The luminescence of the europium(III) and terbium(III) complexes is especially sensitive to changes in the structure and coordination environment of ions and depends substantially on the interaction with the analyte. The intensive luminescence and characteristic Stark structure of Eu^{3+} luminescence spectra allows registering fine changes in the structure of the coordination sphere of a rare-earth ion upon surrounding impact [11–12,13]. Luminescent lanthanide-containing complex compounds can be applied as optical chemosensors in detection of anions, cations, gases etc. [11,12]. One should mention that the works related to application of complex lanthanide compounds as optical chemosensors in detection of vapors of volatile organic compounds are rather infrequent [5,6].

Given their adverse effects on human health and environment, sensitive recognition of amine vapors is highly desirable [2]. Introduction volatile organic amines are used in various fields that include chemical and food industries [14].

Though these amines find wide applications in various fields, they are often found to be highly toxic to human health as well as potential harmful agents for environment. Therefore, development of novel materials that can based to detect these volatile organic amines at trace level, rapidly and efficiently, is one of the active field of research in chemistry and material science [2,15].

As we have established earlier [16–19], the action of ammonia and amine vapors on europium(III) tris-β-diketonates yields the 1.5–10-fold increase of the Eu(III) luminescence intensity. In the course of the above studies(, the present work was devoted to examining the effect of methylamine vapor on luminescence of Eu(III) tris-

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benzoylacetonate immobilized in thin-layer chromatography plates and refining detailed mechanism of interaction of the analyte with the lanthanide-containing sensor.

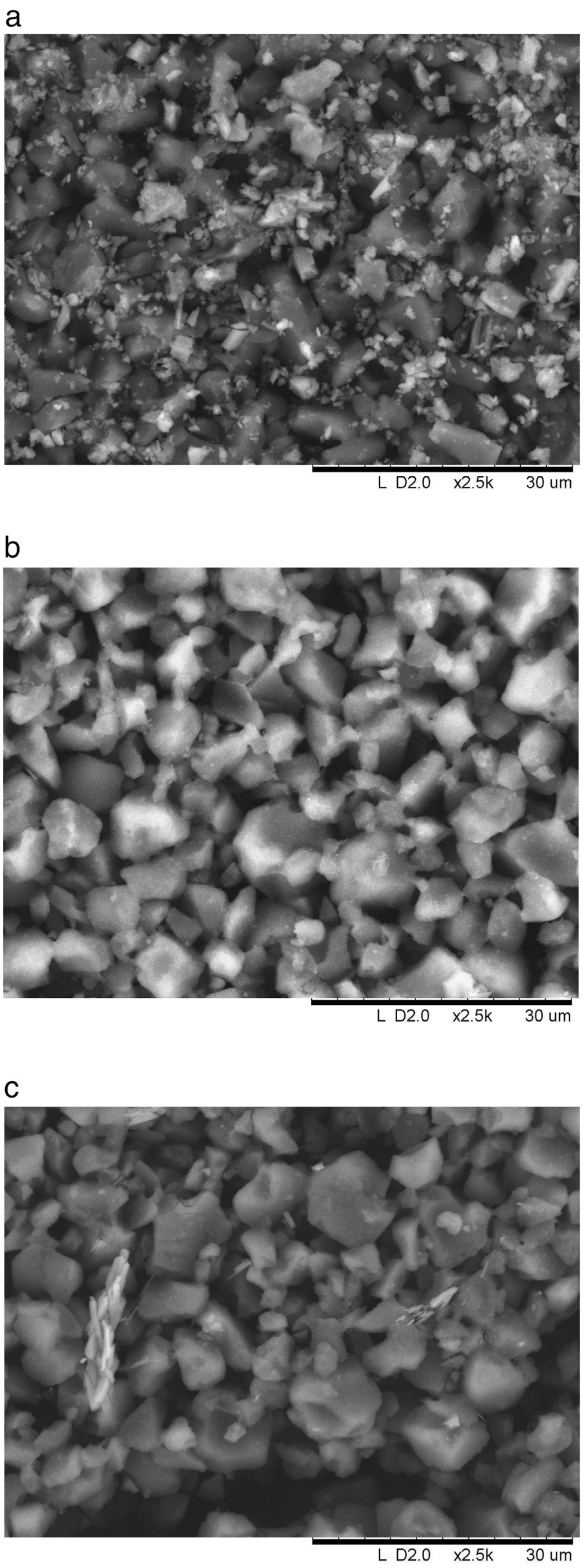

Fig. 1. SEM-photographs of Eu(III) tris-benzoylacetonate complexes: a) **I**; b) **II**; c) **III.**

2. Experimental

2.1. Materials and Methods

Europium(III) tris-benzoylacetonate, $Eu(Ba)_3 \cdot 2H_2O$ (**I**) was synthesized according to the technique described in Ref. [20]. Thin-layer chromatography plates PTSKh-AF-A (Sorbfil Co) were used as matrices for immobilization. Samples on thin-layer chromatography plates were fabricated by depositing the Eu(III) tris-benzoylacetonate solution in acetone (**II**) and benzene (**III**) ($C = 10^{-3}$ mol/l) on the matrix followed by holding for 30 min until complete solvent evaporation. As reference sample we used crystalline powder of $Eu(Ba)_3 \cdot 2H_2O$ complex (**I**), which was smeared on thin-layer chromatography plates.

Morphology studies of obtained complexes were performed by SEM Hitachi TM1000 (Japan). Because thin-layer chromatography plates composed of non-uniform sized silica particles it is difficult to recognize structural features of obtained samples. In order to perform morphology studies, samples were prepared by the same procedure but with the use plane silica substrate.

Studies of the complexes sensor characteristics were performed using a Horiba Fluorolog 3 spectrofluorimeter equipped with a specially developed hermetic chamber of a volume of 700 cm^3. The required level

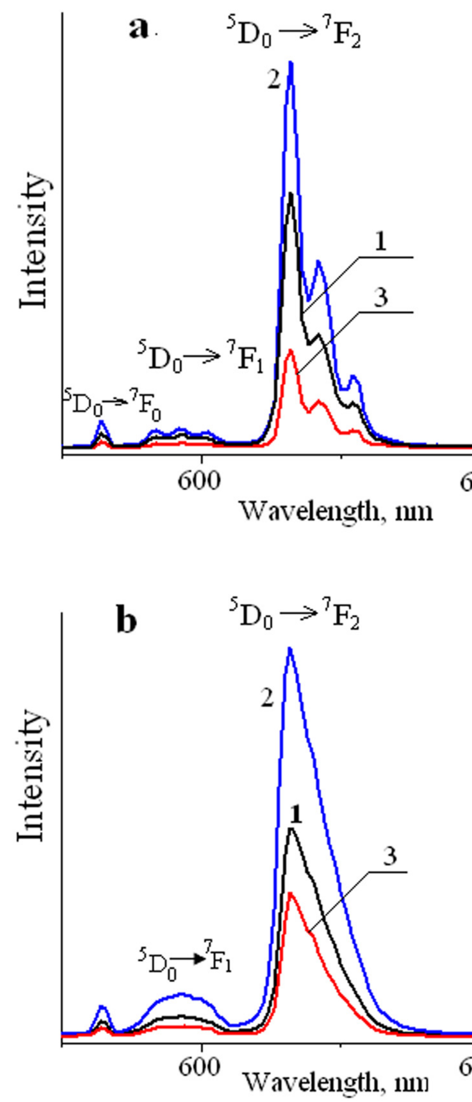

Fig. 2. Luminescence spectra ($\lambda_{ex} = 380$ nm) of the complex $Eu(Ba)_3 \cdot H2O$: a – **I**, b – **III** adsorbed on thin-layer chromatography plates: (1) initial sample, (2) in the presence methylamine vapours, (3) in the presence water vapours at 300K.