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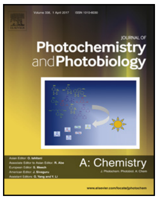

Invited paper

Regulation of the luminescence efficiency of europium benzoates by $-OH$ and $-NO_2$ substituents and alkali metal counterions

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ABSTRACT

Methods for the design of visible-light excitable europium nitrosalicylates having a high efficiency and “monochromaticity” of the luminescence are proposed. A series of europium-alkali metal 3,5-dinitrosalicylates and 5-nitrosalicylates with the general formula $M_5Eu(Lig)_4{\cdot}nH_2O$ ($M = Li^+, Na^+, K^+, Cs^+$), as well as 3-nitrosalicylates, was investigated using optical spectroscopy. The optimization of relative energies of the lowest excited singlet and triplet states of the ligands to achieve the best photophysical characteristics is provided by the proper arrangement of $-OH$ and $-NO_2$ groups on the aromatic ring and a suitable choice of the counterion. The excitation energy transfer processes to the Eu^{3+} ion were analyzed. The effect of the triplets lying in close proximity to the $^5D_0$ state for 5- and 3-nitrosalicylates and to the $^5D_1$ state for 3,5-dinitrosalicylates on the Eu^{3+} luminescence efficiency was demonstrated. The europium-lithium 3,5-dinitrosalicylate has an optimum triplet position relative to the $^5D_1$ state to supply the most efficient energy transfer to the $^5D_0$ state of Eu^{3+} ion and the brightest red emission. The luminescence intensity of this compound exceeds that for the europium benzoate ~60 times at 77 K and ~25 times at 295 K. Thermal quenching properties of the compounds shown by the temperature behavior of the luminescence intensity and the $^5D_0$ lifetime are entirely similar. The proper combination of the sizes of the Ln^{3+} ion, ligand and counterion is necessary for the formation of a perfect structure of the complex with the most symmetrical Eu^{3+} luminescence center. It was found that the compound $Li_5Eu(5\text{-}NSal)_4{\cdot}4H_2O$ is characterized by an intense “monochromatic” red-light emission with the 7 cm^{-1} half-width for the 612.2 nm line related to the $^5D_0$-$^7F_2$ transition.

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1. Introduction

In the present paper, we demonstrate methods for the design of visible-light excitable highly luminescent europium nitrosalicylates. It is known that the nitro group assumes the role of the quencher of luminescence of lanthanide compounds [1–7]. Luminescence intensity of Eu^{3+} and Tb^{3+} nitrobenzoates including compounds with auxiliary heterocyclic diimine ligands is lower by a factor of ~10^2 in comparison with the benzoates [1]. A low sensitization efficiency of Ln^{3+} luminescence in nitrobenzoates is caused by a dissipation of the excitation energy through the ligand $S_{n\pi^*}$ excited state corresponding to the transition between the $-NO_2$ oxygen lone pairs orbital and the π^* orbital of nitrobenzoate ligand. The introduction of the hydroxy group to the second position of the 3,5-dinitrobenzoate results in an enhancement of the Eu^{3+} luminescence intensity by three-four orders of magnitude [8]. At the same time, the placing of only the 2-hydroxy group in the benzoate ligand ensures a drop in the Eu^{3+} luminescence intensity by one order of magnitude at 77 K and complete lack of luminescence at 295 K due to nonradiative processes through the ligand-metal charge transfer (LMCT) state [9]. The presence of both $-OH$ electron-donating and $-NO_2$ electron-withdrawing substituents on the aromatic ring gives rise to the intraligand charge transfer (ILCT) and the appearance of a broad excitation band in the UV region with a long-wavelength edge at 500–520 nm [8]. Spread of the luminescence excitation of lanthanide compounds into a visible region [10–13] can be important for biological applications.

The appropriate choice of an outer-sphere counterion can provide an additional tuning of the photophysical characteristics. In particular, up to a tenfold increase in the luminescence efficiency of europium complexes can be achieved [8,14]. The variation of counterions modifies also the structure of the europium nearest surroundings that is reflected in the Stark splitting of the Eu^{3+} electronic states [14–17].

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There are very scant data on the investigation of lanthanide nitrosalicylates. In the paper [18], the formation of the complexes between the La^{3+} ion and 5-nitrosalicylate ligand was studied. The authors indicated the coordination of the ligand via salicylate sites. X-ray data on the structures of lanthanide nitrosalicylates are not available in the Cambridge Structural Database except for a tetranuclear La^{3+} complex with 3,5-dinitrosalicylate and 1,10-phenanthroline [19,20]. At the same time, crystal structures and physical properties of nitrosalicylates of transition metals are thoroughly studied [20–25] because of their antibacterial, anticonvulsant and anti-inflammatory activities.

This work focuses on a comparative study of the processes of the excitation energy transfer to the Eu^{3+} ions in the series of europium-alkali metal 3,5-dinitrosalicylates, 5- and 3-nitrosalicylates. The methods of optimization of energies of the lowest singlet and triplet electronic states of the ligands relative to the electronic states of the Eu^{3+} ion consisting in the proper arrangement of $-OH$ and $-NO_2$ groups on the aromatic ring and a suitable selection of counterions (Li^+, Na^+, K^+, Cs^+, NH_4^+) are discussed to provide a maximum luminescence efficiency. The relationship between the thermal processes of the back energy transfer from the $^5D_1$ and $^5D_0$ levels of the Eu^{3+} ion to the ligand triplet, luminescence intensity, and $^5D_0$ lifetime is considered. Herein we also investigate the effect of sizes of the ligands and alkali metal cations on the structure of the Eu^{3+} nearest surroundings to obtain a high color purity of the luminescence.

2. Experimental

2.1. Compounds

The 3,5-dinitrosalicylates $M_5Eu(3,5\text{-}DNSal)_4\cdot nH_2O$ ($M = Li^+$ (**1**), Na^+ (**2**), K^+ (**3**), Cs^+ (**4**)) and $Li_5Gd(Eu)(3,5\text{-}DNSal)_4\cdot nH_2O$ (**1a**) were examined. The europium 5-nitrosalicylates $M_5Eu(5\text{-}NSal)_4\cdot nH_2O$ ($M = Li^+$ (**5**), Na^+ (**6**), K^+, Cs^+, NH_4^+), 3-nitrosalicylates $M_aEu(3\text{-}NSal)_b\cdot nH_2O$ ($M = Li^+$ (**7**), Na^+, K^+, Cs^+ (**8**)) and 3,5-dinitroanthranilates $M_5Eu(3,5\text{-}DNAnthr)_4\cdot nH_2O$ ($M = Li^+$ (**9**), Na^+) were also synthesized and investigated. All of the reagents used for the syntheses were purchased from Sigma-Aldrich and were analytical grade. The reagents were used without further purification. All solvents were purified by standard techniques.

First, lanthanide hydroxides were prepared. To obtain hydroxide $LnCl_3\cdot 6H_2O$ was dissolved in a small volume of double-distilled water. 3N NaOH solution in water was added with stirring to the $LnCl_3\cdot 6H_2O$ solution (molar ratio 3:1). The formed gel-like precipitate of $Ln(OH)_3$ was separated by centrifugation (7000 RPM for 15 min). The precipitate was washed 3–4 times with double-distilled water and centrifuged after each wash.

The complexes were obtained by the dropwise addition of a water solution of lithium, sodium or potassium hydroxides, or cesium carbonate, or a liquid ammonia to a warm water mixture of freshly prepared lanthanide hydroxide and nitrosalicylic acid. A molar ratio of Ln^{3+}: nitrosalicylic acid: M^+ was equal to 1:4:5. The reaction mixture was kept in a warm water bath with continuous stirring for one-two hours, and then it was left for 24 h or more at room temperature. A yellow precipitate was filtered, washed with isopropanol and ethylic ether, and then it was dried in a vacuum exiccator. The final products are homogeneous powdery substances.

Our attempts to grow crystals of europium nitro- and dinitrosalicylates from a solution were unsuccessful. However, it is known that crystals of nitrosalicylates of Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, and other double-charged metal ions can be obtained using both a slow evaporation from the solution [21–24] and hydrothermal reactions [20,25].

Results of the elemental analysis for 3,5-dinitrosalicylates: **1** (Calc.: N-8.57; C-25.72; H-2.47%. Found.: N-8.6; C-25.9; H-2.29%), **2** (Calc.: N-9.01; C-27.05; H-1.03%. Found.: N-8.84; C-26.90; H-1.48%), **3** (Calc.: N-8.7; C-26.11; H-0.94%. Found.: N-8.53; C-26.21; H-1.2%) and **4** (Calc.: N-6.44; C-19.34; H-0.58%. Found.: N-6.07; C-19.35; H-0.7%). Results of the elemental analysis for 5-nitrosalicylates: **5** (Calc.: N-5.7; C-34.21; H-2.05%. Found.: N-5.59; C-34.57; H-2.3%) and **6** (Calc.: N-5.1; C-30.59; H-2.2%. Found.: N-4.93; C-30.72; H-2.09%). We did not obtain europium 5-nitrosalicylates containing the large alkali metal ions K^+, Cs^+ and NH_4^+, and all of 3-nitrosalicylates with their individual composition. That was shown by multicentered or broadened Eu^{3+} luminescence spectra. Probably, steric effects resulting from inconsistencies of sizes of anions and counterions in the crystal lattice in analogy to europium tetrakis dibenzoylmethanates with different counterions [26], or presence of substitutional crystal defects as in europium-sodium-salicylaldehydes [27] lead to the formation of nonequivalent Eu^{3+} centers.

A list of the compounds under study with the exception of multicentered 5-nitrosalicylates with K^+, Cs^+, NH_4^+, 3-nitrosalicylates with K^+, Na^+ and 3,5-dinitroanthranilate with Na^+ is given in Table 1. Data of the analysis confirm the composition of the compounds indicated in this table. The experimental data for 3,5-dinitrosalicylates can also correspond to another composition $M_3Eu(Lig)_3\cdot nH_2O$, which was previously indicated in the paper [8].

2.2. Optical spectroscopy

Luminescence and luminescence excitation spectra of the europium compounds were measured on a FSL 920 spectrometer from Edinburgh Instruments, a SLM Aminco SPF 500 spectrofluorimeter and a LOMO ISP-51 spectrometer with the recording photoelectron cassette FEC-2/3648. The luminescence spectra were recorded at ~8 cm^{-1} resolution. The registration of the Eu^{3+}

Table 1

Europium compounds under investigation, energy of the lowest triplet state of the ligand E_T, values $\Delta_1 = E_T - E(^5D_0)$ and $\Delta_2 = E_T - E(^5D_1)$[a], Eu^{3+} luminescence intensity I and lifetime τ of $^5D_0$ state, $\lambda_{exc} = 365$ nm.

No.	Compound	E_T (cm^{-1})	Δ_1 (cm^{-1})	Δ_2 (cm^{-1})	$^5D_0$ (cm^{-1})	I_{77K} (a.u.)	I_{295K} (a.u.)	I_{295K}/I_{77K}	τ_{77K} (ms)	τ_{295K} (ms)	τ_{295K}/τ_{77K}
1	$Li_5Eu(3,5\text{-}DNSal)_4\cdot 12H_2O$	~19470	2250	520	17222	585	235	0.4	0.83	0.38	0.46
2	$Na_5Eu(3,5\text{-}DNSal)_4\cdot 4H_2O$	18870	1645	−80	17227	355	95	0.27	2.26	0.81	0.36
3	$K_5Eu(3,5\text{-}DNSal)_4\cdot 2H_2O$	19070	1840	120	17231	290	25	0.09	1.18	0.18	0.15
4	$Cs_5Eu(3,5\text{-}DNSal)_4\cdot H_2O$	19020	1780	70	17241	155	13	0.08	0.69	0.08	0.12
5	$Li_5Eu(5\text{-}NSal)_4\cdot 4H_2O$	18800	1570	−150	17230	225	70	0.31	0.61	0.24	0.39
6	$Na_5Eu(5\text{-}NSal)_4\cdot 6H_2O$	17670	435	−1280	17235	75	No lum		0.52	No lum	
7	$Li_aEu(3\text{-}NSal)_b\cdot nH_2O$	17280	45	−1650	~17255	35	Low lum		0.69	Low lum	
8	$Cs_aEu(3\text{-}NSal)_b\cdot nH_2O$				~17266	8	No lum		0.22	No lum	
9	$Li_5Eu(3,5\text{-}DNAnthr)_4\cdot nH_2O$				17255	Yellow	Low lum		0.38	Low lum	
	$Eu(Benz)_3\cdot 2.5H_2O$	~24500	7250	5550	17250	10	9	0.9	0.47	0.44	0.94

[a] $E(^5D_1\ Eu^{3+}) = 18950\ cm^{-1}$.

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