Synthesis and luminescence of some rare earth metal complexes

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Abstract: In the present paper the synthesis, photo- and electroluminescent properties of new rare earth metal complexes prepared and studied at the Razuvaev Institute of Organometallic Chemistry during the last decade are reviewed. The obtained compounds give luminescence in UV, visible and NIR regions. The substituted phenolates, naphtholates, mercaptobenzothiazolate, 8-oxyquinolinolate, polyfluorinated alcoholates and chalcogenophosphinates were used as ligands. The synthesis and structure of unusual three–nuclear sulfide–nitride clusters of Nd and Dy are described. The new excitation mechanism of ytterbium phenolates and naphtholates, which includes the stage of reversible reduction of Yb to divalent state and oxidation of the ligands in the excitation process, is discussed.

1 Introduction

The ability of lanthanides to generate long-lived line like luminescence in a broad spectral range makes complexes of these metals attractive for application in various optoelectronic devices and in biomedicine [1, 2]. Compared with organic luminophores, lanthanides present great advantages as emitters in the near-infrared (NIR) region. Below we present some examples of organolanthanide emitters synthesized and studied at the Razuvaev Institute of Organometallic Chemistry (Nizhny Novgorod). However, at the beginning of this paper, luminescent complexes of Sc which also belong to 3-rd group of metals are considered. It should be noted that the scandium compounds did not attract attention as luminophores for a long time because of their inability to generate metal-centered emission due to the absence of f electrons. Aspiring to fill this gap, we synthesized some scandium derivatives and studied their photoluminescent (PL) and electroluminescent (EL) properties. To design the compounds of Sc and other rare earth metals well-known 8-hydroxyquinoline H(q), 2-amino-8-hydroxyquinoline H(q[NH2]) [3, 4], 2-mercaptopbenzothiazole H(mbt) [5], 2-(2-pyridyl)phenol H(pp) [6], 2-(2-benzimidazol-2-yl)phenol H(NON) [7], pentfluorophenol (C6F5OH) [8], fluorinated iso-propanol (HOCH(CF3)2), tert-butanol (HOC(CF3)3), 3-(5-methylbenzoxazol-2-yl)naphthol H(OONMe) [10], 3-(6-methylbenzoxazol-2-yl)naphthol H(OONMe) [10], 3-(2-benzothiazol-2-yl)-2-naphthol H(NpSO3) [11], 3-(2-benzothiazol-2-yl)naphtol H(NpSO3) [11], 3-(2-benzoxazol-2-yl)-2-naphthol H(NpSO3) [11] and new (1-(2-pyridyl)naphth-2-ol H(pn) [6], 2-mercaptobenzothiazolate, 8-oxyquinolinolate, polyfluorinated alcoholates and chalcogenophosphinates were used as ligands. The synthesis and structure of unusual three–nuclear sulfide–nitride clusters of Nd and Dy are described. The new excitation mechanism of ytterbium phenolates and naphtholates, which includes the stage of reversible reduction of Yb to divalent state and oxidation of the ligands in the excitation process, is discussed.

2 Scandium complexes – bright visible luminophores

All the compounds were prepared by reactions of scandium silylamine with the protonated form of respective ligand (Scheme 1). This synthetic approach has an advantage in comparison with conventional reactions of hydrated lanthanide chlorides with ligands in the presence of base because it gives products that are free of coordination water and other neutral groups which can quench luminescence or affect its color. Most of the products were isolated as mononuclear complexes containing three anionic ligands. The only exception is binuclear derivative 1 containing two bridging and four terminal 8-oxyquinolinolate groups [4].

Upon UV excitation, the complex 1 exhibited a strong green PL peaked at 535 nm that was very similar to that of well-known electroluminophore Alq3. To com-
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3 Luminescent lanthanide complexes

Optical properties of lanthanide complexes are related to forbidden electronic transitions between states having an

and current efficiency of 6.2 cd/A were obtained for Sc(OON)₃ (7). The superior EL performance of the cell ITO/TPD/7/Yb were associated with a perfect matching of LUMO energy (~2.65 eV) of the complex and work function (~2.6 eV) of the cathode, facilitating an electron injection towards the emissive layer [7]. In the next stage of the study, the 2-(2-hydroxyphenyl)benzoxazole ligand was modified by substitution of methyl group for proton at the 5- or 6-position of the heterocycle. The obtained complexes 9 and 10 demonstrated similar bathochromic shift in the PL and EL spectra with respect to those of the unsubstituted counterpart 7. It was found that change of the CH₃ group position in the ligands had neither influence on the charge mobility nor on the spectral features of 9 and 10. Under a bias of 22 V, both three-layer devices ITO/TPD/9(10)/Bath/Yb emitted green light at 522 nm with a maximum luminance of about 900 cd/m² [10]. To study the effect of aromatic fragments in the ligands onto the optical properties of the complexes, the naphtholates Sc(NpOON)₃ (11) and Sc(NpSON)₃ (12) were prepared. Being sandwiched between N, N'-bis(3-methylphenyl)-N, N'-diphenylbenzidine (TPD) and spiro-TPD and Bath layers in the diode ITO/spiro-TPD/11/Bath/LiF/Al, the complex gave the best EL characteristics among all scandium emitters: brightness of 8780 cd/m² at 12 V, maximum current and power efficiency of 2.54 cd/A and 1.77 lm/W, respectively, low turn-on voltage (2.7 V) and 11% external quantum yield [11]. It is worth noting that the energy gap between the 1S₁ and 3T₁ levels of Sc(NpOON)₃ was found to be less than 415 cm⁻¹, which allows the correlation of its superior luminescence efficiency with the realization of thermally activated delayed fluorescence (TADF). Later it was found that the doping of the emitting layer with the dye DCM2 (device ITO/PEDOT:PSS/2TNTA(30nm)/TPD(7nm))/11:DCM2(1%)(20nm)/BCP(5nm)/Bpcn(16nm)/LiF(1nm)/Al) increases the brightness of the device up to 26000 cd/m² (16 V) while retaining the emission color [14]. Thus, the emission color and performance of OLEDs based on Sc complexes gave the ground to suggest them in the design of lighting devices. The EL spectra of some compounds and a view of operating at 5 V bias OLED with 11[11] are depicted in Figure 1a,b.
odd parity such that free ions demonstrate weak absorption and also weak long-lived luminescence. The best way to mitigate the forbidden nature of the electric dipole f-f transitions, and hence to attain an intense emission, is a binding of Ln$^{3+}$ ion to organic ligands that results in f-d mixing (the electron transitions between the mixed parity states are not strictly forbidden) induced by electrostatic ligand field which is usually non-centrosymmetric at the ion site [15]. But more importantly, organic ligands act as "antennae" efficiently harvesting and transferring the absorbed light energy to the metal center [16]. The latter phenomenon is called Ln$^{3+}$ luminescence sensitization. Commonly, luminescence sensitization of rare earth organic derivatives is explained in terms of the modified Jablonksi diagram (Figure 2) that includes formation of a singlet ($^{1}S_1$) photoexcited state, intersystem crossing (ISC) and energy transfer (ET) from a triplet ($^{3}T_1$) excited state to resonant 4f* level of the metal ion [17]. According to the empirical rule invented for Eu and Tb complexes, efficient energy transfer occurs when the energy difference between the $^{3}T_1$ state of ligands and the resonant level of the Ln$^{3+}$ ion is around 2500–3500 cm$^{-1}$ [18].

There are four ions demonstrating orange (Sm$^{3+}$), red (Eu$^{3+}$), green (Tb$^{3+}$) and near-white (Dy$^{3+}$) luminescence that have found a practical application in optoelectronics, lighting and medicine. Owing to high energy of the triplet excited state estimated from low temperature phosphorescence of the respective Gd derivatives, the mbt ligands (E$_{3T1}$ = 20 400 cm$^{-1}$), OON (E$_{3T1}$ = 19 700 cm$^{-1}$) and C$_6$F$_5$O (E$_{3T1}$ = 20 408 cm$^{-1}$) are suitable for sensitization of samarium and terbium emission. The complexes 13-18 (Scheme 2) were synthesized by using Ln[N(SiMe$_3$)$_2$]$_3$ precursors and revealed metal-centered PL and EL.

The PL spectra of mercaptobenzothiazolates 13 and 14 consisted of sets of intense sharp peaks corresponding to $^{4}G_{5/2} \rightarrow ^6H_{J}$ (J = 5/2, 7/2, 9/2, 11/2) transitions of Sm$^{3+}$ [19] and $^{5}D_4 \rightarrow ^7F_{J}$ (J = 6-3) transitions of Tb$^{3+}$ (Figure 3a,b). However, the OLED ITO/TPD/14/Yb showed poor EL efficiency of 0.16 cd/A and 0.05 lm/W even at low current density [20]. On the contrary, device performance was much better in the case of phenolates 15 and 16, which presented dinuclear complexes due to additional coordination possibilities of the metal centers caused by their large ionic radii in comparison with that of Sc$^{3+}$. The complex Sm$_2$(OON)$_6$ (15) demonstrated strong metal-centered EL with luminance of 1118 cd/m$^2$ at 19.5 V and maximum power efficiency of 1.16 lm/W [21] while the best published characteristics of Sm containing OLEDs do not exceed 490 cd/m$^2$ value at 15 V [22]. The pentafluorophenolates 17 and 18 possessed modest EL characteristics, yet an unusually strong change in the spectrum and luminescence color with increase in applied voltage was found for the bilayer device based on terbium complex (Figure 3c). The observed phenomenon was explained by shifting of the electron-hole recombination zone from the hole transport layer (HTL)/complex interface towards the emissive layer. As a result, the orange emission from the interfacial HTL/18 electroplex predominated at low bias whereas the compound generated green metal-centered luminescence at high voltage [8]. Due to this effect, similar materials may be employed for the fabrication of voltage-color tunable OLEDs.
In order to discover novel lanthanide optoelectronic materials, a set of chalcogenides and sulfide-nitrides of Nd (21), Sm (19, 20) and Dy (22) were synthesized [12, 13] (Scheme 3). The complexes of Sm and Dy revealed luminescence activity.


The phosphinates of samarium 19 and 20 were obtained by reactions of K(S_2PPh_3) or K(Se_2PPh_3) with anhydrous SmCl_3 in THF medium. Under direct excitation at f-f absorption bands, the complexes displayed metal-centered photoluminescence (PL) in the visible and NIR regions corresponding to 4G_5/2 → 6H_J (J = 5/2, 7/2, 9/2, 11/2, 13/2, 15/2) and 6F_J (J = 1/2, 3/2, 5/2, 7/2, 9/2, 11/2) electronic transitions of Sm^3+. A Judd–Ofelt analysis was performed to estimate PL quantum efficiency (QE), branching ratios (β) and induced-emission cross sections (σ_em) of the compounds. The estimated room-temperature PL QE of 19 and 20 is equal to 1.9 and 0.17%, respectively. It was found that the Judd–Ofelt parameter Ω_2 of dithiophosphinate derivative is significantly greater than that of diselenophosphinate counterpart. This feature is responsible for large values of β (50.98%) and σ_em (4.29 × 10^{-21} cm^2), which suggests the former complex as a good candidate for the development of samarium doped polymethylmethacrylate (PMMA) laser medium acting on the 4G_5/2 → 6H_9/2 transition at 645 nm [12].
The compounds of composition $\text{Ln}_3\text{I}_5(S_2\text{N}_2)(\text{S}_2)(\text{THF})_{10}$ were obtained in the reactions of neodymium and dysprosium iodide-nitrides with sulfur. The inorganic core of the molecules contains the cyclic fragments $\text{Ln}(\mu-\text{S}_2)\text{Ln}$, $\text{LnSNSN}$ and $\text{LnSN}$. Interestingly, ten of fourteen atoms of the core are coplanar while the remaining four $\text{S}_2$ and $\text{I}_2$ atoms lie in other two orthogonal planes. After summarizing the geometric parameters of the molecules, computational data, electron spectroscopy and fluorescence, we assumed the existence of some conjugation in the mentioned heterocycles. The dysprosium complex 22 exhibited metal-centered luminescence at 482 ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$) and 575 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$) in response to UV excitation with $\lambda_{\text{ex}} = 260$ nm (Figure 4) [13]. Recently we have observed monoexponential PL decay for 22 that confirmed the existence of only one luminescent center among three Dy$^{3+}$ ions. Clearly, it belongs to DySNSN cycle.

Alongside the 4f elements showing visible metal-centered luminescence, there are some lanthanides capable of emitting intensive UV light due to f-f (Gd$^{3+}$) or f-d (Ce$^{3+}$, Eu$^{2+}$ and Yb$^{2+}$) electronic transitions. Their complexes are very attractive for design of excitation sources for chemical sensing devices, lithography, optical data recording and biomedicine [23, 24]. Synthesis of such compounds requires employment of anionic ligands having high-lying $^3\text{T}_1$ levels. It was found that fluoroalkoxides respond to these demands. The complexes of Eu and Ce gave UV photoluminescence of moderate intensity (Scheme 4).

The reaction of divalent europium iodide with a potassium salt of hexafluorosopropanol afforded the complex 23 containing two Eu$^{2+}$ and one Eu$^{3+}$ cations. The PL spectrum of the compound showed a band at 330 nm ($\lambda_{\text{ex}} = 230$ nm). Since the used ligand cannot sensitize the Eu$^{3+}$ ion and direct excitation of the ion causes a transition at 612 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition), the observed band was assigned to the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ electronic transition in the Eu$^{3+}$ ion [25]. The cerium derivatives were synthesized using Ce[($\text{SiMe}_3)_2\text{N}$]$_3$ and fluorinated alcohols. Due to the poor air stability of 24 and 26, a neutral 1,10-phenanthroline ligand was introduced in the coordination sphere of each ion in the dinuclear molecules giving rise to the formation of 25 and 27. Insertion of the phenanthroline ligand in the Ce$_2(\text{OR})_6(\text{DME})_4$ caused a red shift of the emission maximum from 370 to 425 nm, whereas the same procedure conducted with butanediolate initiated a slight blue shift (from 410 to 405 nm) and a decrease in PL intensity. Meanwhile the monomer 28 containing two butanediolate and two phenanthroline units emitted at a shorter wavelength in comparison with 26 and 27 [9]. The observed spectral changes confirm the high sensitivity of the frontal molecular orbitals of lanthanide complexes (containing the essential contribution of 5d orbitals) to the nature of the coordination environment. The PL spectra of the obtained UV luminophores are presented in Figure 5.

Recently, much attention has been paid to luminescent materials emitting in the near-infrared region because...
of their potential application in planar waveguide amplifiers for optical fiber telecommunication, NIRD LEDs and detectors, biomedical diagnostics and therapy [1, 2]. Since this spectral region is virtually inaccessible to organic dyes, investigation was focused on the complexes of d and some f metals (mainly trivalent lanthanides including Pr, Nd, Ho, Er, Tm, Yb) emitting in the range from 800 to 3000 nm.

In order to produce effective NIR luminophores, a set of complexes of the mentioned metals with C₆F₅O [8], q [26, 27], mbt [19], OON, SON [28], OON₆Me, OON₅Me [10], NpOON and NpSON [29] ligands were prepared and their PL and EL features were studied. The performance of the most efficient NIR emitting devices based on Nd, Er, Tm and Yb compounds are listed in Table 1. Their spectra are shown in Figure 6.

Importantly, the data show superior EL characteristics for 38 in comparison to complexes of other rare earth metals. A similar trend was pointed out for all ytterbium phenolates and naphtholates having heterocyclic substituents [10, 28, 29]. Optimization of the device (ITO/CuPc/NPD/38/BATH/LiF/Al) led to further increase in the radiation intensity up to 3140 µW/cm² at 13 V [14]. It should be noted that ligands of other types do not allow the obtainment of the EL intensity of Yb³⁺ ions higher than 390 µW/cm² at 12.9 V [30]. The extremely high emission observed cannot be sensitized through the conventional exchange (Dexter) mechanism because the energy gap between the triplet level of the NpSON ligand and the resonant ⁴F₅/₂ level of Yb is too large (more than 5300 cm⁻¹) and the ligand emissive band does not overlap with the Yb absorption band. We believe that in this case an alternative mechanism of excitation of Yb is realized (Scheme 5).

![Scheme 5. Proposed mechanism of EL of the complex 38.](image)

A similar mechanism was proposed previously by Horrocks and coworkers to explain Yb luminescence in the protein matrix [31]. The only difference between that of Horrocks and our scheme is an oxidative state of organic ligands in the starting complexes. In the Horrocks system the ligands are neutral, while in our case the ligands are anions. After photo- or electroexcitation the ligands transfer to an excited state. In this state, a reductive ability of the
ligands becomes enough to reduce the Yb$^{3+}$ to Yb$^{2+}$ transition. A new system is formed containing a divalent Yb and neutral ligand in the form of free radical species. In this system the reductive ability of Yb$^{2+}$ and the oxidative ability of free radical ligands induce the back electron transfer from Yb$^{2+}$ towards the ligand, which leads to the formation of the starting system with trivalent Yb and anionic ligands. However Yb at this stage may be converted in the $^{2}F_{5/2}$ excited state, from which relaxation affords emission with $\lambda = 978$ nm. Since this path allows the excitation of Yb through the redox process, the restrictions on the electronic transition related to the shielding of 4f electrons by 5s and 5p electrons and the Laporte rule are avoided. As a result, the population of $^{2}F_{5/2}$ level is high and is accompanied by very intense emission. On the other hand, the redox mechanism of the luminescence of Yb phenolates and naphtholates is confirmed by the lack of luminescence of Eu analogues. The total energy of the intermediate system is clearly not sufficient to reach the high-lying $^{3}D_{0}$ energy level of Eu$^{3+}$.

4 Conclusions

The conducted studies resulted in the discovery of efficient PL and EL of scandium complexes, which produced promising emissive materials. Investigations in the area of organic ligands sensitizing the luminescence of lanthanides led to the development of Nd, Sm and Yb compounds that yielded record high metal-centered emission. The wavelengths of the emission of the obtained luminophores cover UV, visible and NIR regions. The extremely high EL of Yb substituted phenolates and naphtholates discovered gave ground to the development of a new redox mechanism for the excitation of chelate Yb complexes. Investigation into the design of luminescent lanthanide chalcogenide nanoparticles led to the preparation of unusual three-nuclear iodide-sulfide-nitride clusters of neodymium and dysprosium, the chemical and physical properties of which are currently under study.

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References


