

Luminescent solutions and powders of new samarium complexes with N,N',O,O'-chelating ligands

Anastasia V. Kharcheva^a, Kirill S. Nikolskiy^a, Nataliya E. Borisova^b, Alexey V. Ivanov^b,
Marina D. Reshetova^b, Viktor I. Yuzhakov^a, Svetlana V. Patsaeva^a

^aFaculty of Physics, Lomonosov Moscow State University, GSP-1, Leninskie Gory, Moscow, 119991, Russia; ^bChemistry Department, Lomonosov Moscow State University, GSP-1, Leninskie Gory, Moscow, 119991, Russia

ABSTRACT

Imaging techniques in biology and medicine are crucial tools to obtain information on structural and functional properties of living cells and organisms. To fulfill the requirements associated with application of these techniques it appears necessary to design markers with specific characteristics. Luminescent complexes of trivalent lanthanide ions with chelating ligands are of increasing importance in biomedical applications because of their millisecond luminescence lifetime, narrow emission band, high signal-to-noise ratio and minimal photodamage to biological samples. In order to extend the available emission wavelength range the luminescent samarium chelates are highly desirable. In this study the ligands with diamides of 2,2'-bipyridin-6,6'-dicarboxylic acid were used to improve photophysical characteristics of samarium complexes. We report the luminescence characteristics of samarium complexes with novel ligands. All complexes exhibited the characteristic emission of Sm (III) ion with the lines at 565, 597, 605, 645 and 654 nm, the intensity strongly depended on the ligand. Absorption and luminescence excitation spectra of Sm (III) complexes showed main peaks in the UV range demonstrating lanthanide coordination to the ligand. The absolute luminescence quantum yield was measured for solutions in acetonitrile with excitation at 350 nm. The largest luminescence quantum yield was found for the samarium complex **Bipy 6MePy Sm** (3%) being much higher than for samarium complexes reported in the literature earlier. These results prove as well that samarium chelates are potential markers for multiparametric imaging techniques.

Keywords: luminescence, absorbance, rare earth elements, coordination complexes, samarium, luminescence quantum yield.

1. INTRODUCTION

Imaging techniques in biology and medicine are crucial tools to obtain information on structural and functional properties of living cells and organisms. To fulfill the requirements associated with application of these techniques it appears necessary to design markers with specific characteristics.¹⁻³ Design and synthesis of novel luminophores with improved characteristics is a significant task to further development of imaging techniques and their applications in biomedical sciences.⁴⁻⁶ Luminescent complexes of trivalent lanthanide ions with chelating ligands are of increasing importance in biomedical applications.⁷⁻¹⁰ The advantages of these probes over traditional organic fluorophores are their long luminescence lifetime (millisecond order), high signal-to-noise ratio, large Stokes shift, and minimal photodamage to biological samples.

Brightly luminescent Eu (III) complexes with chelating ligands have been extensively studied.¹¹⁻¹³ Recently it was found that chelating ligands with two pyridine rings in their structure provide increased coordination of the ligand to europium ion in luminescent chelating complexes.¹⁴ The complexes of rare earth ions with diamides of 2,2'-bipyridin-6,6'-dicarboxylic acid can be readily soluble in organic solvents and exhibit photoluminescence both in solutions and as the films deposited on the solid support.¹⁵⁻¹⁶ In order to extend the available emission wavelength range the luminescent samarium chelates are highly desirable.

In this study the ligands with diamides of 2,2'-bipyridin-6,6'-dicarboxylic acid were used to improve photophysical characteristics of samarium complexes. The luminescence characteristics of samarium complexes with novel ligands were studied. Investigating the relationship between the structures of organic ligands and the energy levels of samarium ions will give evidences for designing high luminescent lanthanide organic complexes.

1.1. Luminescence of coordination complexes of rare earth elements with organic ligands

Despite the significant decrease in luminescence efficiency compared to that of organic dyes, the rare earth complexes attract much attention of researchers because of the specificity of the mechanism of luminescence which allows for almost monochromatic emission. In these systems rare earth ion luminescence originates from the intramolecular energy transfer through the excited state of the ligand to the emitting level of the lanthanide ion. Electronic spectra of rare earth ions are caused by f-f-transitions in 4f- layer shielded from external fields with closed 5s- and 5p- electron shells providing narrow emission lines with bandwidth down to 10 nm unattainable for traditional organic luminophores. Because f-f transitions are theoretically forbidden, low molar extinction coefficients do not provide an effective luminescence yields upon direct excitation of rare earth ions.

The low probability of the electric dipole f-f transitions on the one hand gives rise to the long lifetimes of the rare earth luminescence, but on the other hand causes the very low molar extinction coefficients which make it difficult to excite directly the rare earth ions by light. To overcome this problem, rare earth ions are chelated with ligands that have intense absorption bands. The ligand sensitized luminescence of rare earth ion typically proceeds in three stages.¹⁷ At the first step light is absorbed by the organic chromophore located close to the lanthanide ion. Then energy is transferred from the organic "antenna" to the excited state of the rare earth ion, and finally the lanthanide ion emits light via the radiative deactivation of the luminescent state to lower lying state. This phenomenon is named the "antenna effect" and proposed that such complexes could be seen as light conversion molecular devices because they are able to transform light absorbed by ligand into emitted light by the ion via an intramolecular energy transfer.¹⁸

This ligand sensitized luminescence is much more effective than the direct excitation of lanthanide emission. Simplified scheme of energy transfer that is usually considered for rare earth coordination complexes is the following: $^1S^*$ (ligand) \rightarrow $^3T^*$ (ligand) \rightarrow Ln*. Intramolecular energy transfer efficiency is determined mainly by tuning the energy gap between $^3T^*$ and the resonance level of the lanthanide ion. Because the position the triplet level depends on the nature of the organic ligand, it is possible to alter the luminescence properties of the complex due to the changing nature of the ligand. Exchanging the central ion of the lanthanide the emission wavelength of luminescence can be varied throughout the entire range of the electromagnetic spectrum from UV to IR.

The energy gap between the excited triplet energy levels of the organic ligands and the lowest excited energy levels of rare earth ions is an important factor to the luminescence of rare earth organic complexes.¹⁹ Although a wide range of sensitized lanthanide complexes have been reported, energy-transfer pathways have not been fully understood for the sensitization of the lanthanide ions.

1.2. Luminescence of samarium complexes and the choice of ligand for coordination

The main luminescence bands of the samarium complexes are presented by the lines corresponding to the $^4G_{5/2} \rightarrow ^6H_J$ ($J=5/2, 7/2, 9/2, 11/2$) transitions, with the highest intensity band being the hypersensitive $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition. The ligand fluorescence emission and the ligand sensitized luminescence of trivalent samarium ions are two competitive processes, and the organic ligand with large conjugated structure may not be beneficial to the energy transfer from the ligand to the central metal ions.

The intensity, splitting and energy of the luminescence bands as well as the relative intensities of different bands for complexes with samarium ion are very sensitive to the symmetry and the detailed nature of the ligand environment.¹⁸ It was proposed that a good organic ligand of samarium ions should have proper triplet energy levels with mediate conjugated structure. Using excitation spectrum for samarium complexes in the solid state it was demonstrated that most of the excitation energy was mainly absorbed by the ligand, and then some absorbed energy was transferred to the central samarium ions, emitting the characteristic lines of the latter, while the ligand keeps its emission itself in shorter wavelengths. The dominant luminescence mechanism for the solid samarium complex was given as luminescence from the triplet state of the ligand to the central samarium ion.¹⁹

The energy gap between the lowest excited state level ($^4G_{5/2}$) and the highest ground state level ($^6F_{11/2}$) of trivalent samarium ions is shorter than that for Eu (III) or Tb (III) ions, and the samarium complex can be easily deactivated by the vibrations of hydroxyl groups of the solvent. The samarium complexes demonstrate lifetimes which are typically longer than that for the hydrated lanthanide precursor indicating the efficient luminescence quenching due to hydroxyl oscillators in the inner coordination sphere of samarium ion in the form of hydrated compounds.²⁰

Different chelating ligands were proposed to study photophysical properties of samarium complexes.²¹⁻²⁵ A bis-pyrrolide macrocyclic ligand [L = trans-calix[2]benzene[2]pyrrole(H)] containing two aromatic phenyl rings in the macrocycle backbone was reacted with SmCl₃(THF)₃ to afford the corresponding [LSmIIICl] complex. Its crystal structure showed the ligand adopting the σ -bonding mode with the pyrrolide moieties and the π -bonding with the two aromatic rings.²³ Steady-state and time-resolved emission spectroscopy and luminescence quantum yield measurements were performed on novel lanthanide complexes with fluorene-based donor-acceptor ligand.²⁴ That ligand construct was based on a donor- π -acceptor architecture with diphenylamino acting as the donor and a fluorenyl π bridge derivatized with a trifluoroacetate moiety acting as both a strong acceptor and the classic bidentate scaffold for complexing metals. The samarium emission was characterized by long luminescent lifetimes of 70 μ s.

In the other study the samarium complexes were applied as probes to study interactions with peptides. The absolute luminescence quantum yield for samarium complexes reported in the literature varied from 0.11 to 0.32%.²⁵ For one of the samarium complexes after its coupling to peptide the luminescence quantum yield increased three times.²⁵

2. OBJECTS AND METHODS

2.1. Synthesis of ligands and samarium complexes

The syntheses of the ligands were performed as reported previously.²⁶ The samarium complexes with chelating ligands were prepared in the following way. The mixture of the ligand and equal amounts of hexahydrate samarium trinitrate in dry acetonitrile (25 ml per 100 mg of a ligand) was boiled for 7-8 hours and slowly cooled to room temperature (for a complete precipitation of the product reaction mixtures were leave to stand overnight). White or pale brown precipitate was filtered under vacuum, washed with a small amount of cold acetonitrile and dried in air.

2.2. Spectral measurements

Luminescence measurements were carried out by Hitachi F-7000 instrument. The emission spectra were corrected for the wavelength dependence of the optical elements of instrumentation and spectral sensitivity of the photomultiplier tube. Spectral measurements were performed for samarium complexes in acetonitrile at concentration of $1 \cdot 10^{-6}$ - $1 \cdot 10^{-4}$ mol/l. Solutions of samarium complexes in acetonitrile were placed in quartz cuvettes and the luminescence properties were measured at 90-degree geometry. Luminescence characteristics of powders of samarium complexes placed in quartz cells were measured at reflection geometry. The luminescence intensities of the samarium complexes with chelating ligands were determined by integrating emission intensity from 550 to 675 nm wavelength range.

UV-Visible absorption spectra of solutions were obtained using a Hitachi U-1900 spectrophotometer in 1 cm path length cells. Absorption spectra for complexes were measured in relation to pure solvent (acetonitrile). Absolute luminescence quantum yields for solutions of samarium complexes in solutions and powders were calculated using classical approach²⁷ against the rhodamine dye solution as a reference.

3. RESULTS AND DISCUSSION

3.1. Absorption spectra of samarium complexes in acetonitrile solutions

The Figure 1 shows the absorption spectra of the samarium (III) complex **BiPy iPr Sm** in acetonitrile solution at three different concentrations ($C = 6.78 \cdot 10^{-6}$, $3.39 \cdot 10^{-5}$, $6.78 \cdot 10^{-5}$ mol/l).

The absorption spectra of all studied samarium complexes in acetonitrile show the short-wavelength maximum centered the range 320-340 nm. We found that in the studied solutions the absorbance values for the complexes followed the Burger-Lambert-Beer law along with increasing the concentration.

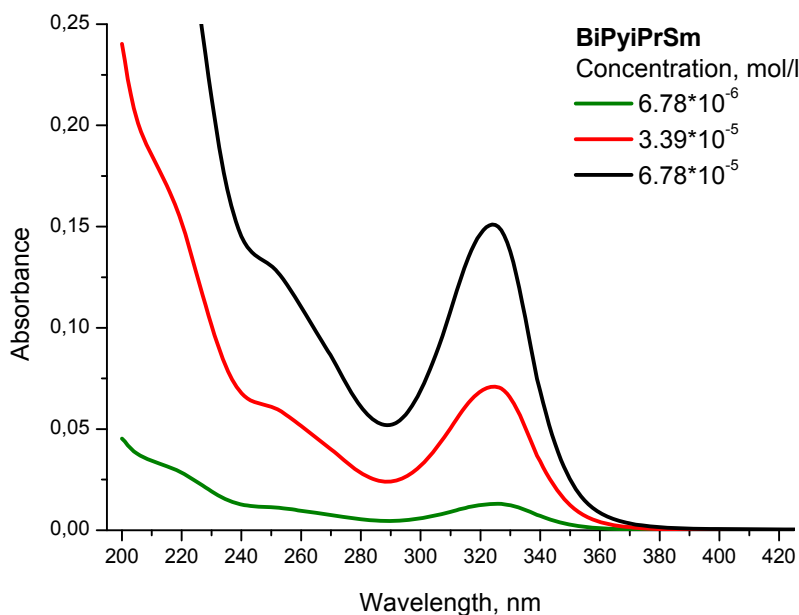


Figure 1. Absorption spectra of the samarium (III) complex **BiPy iPr Sm** in acetonitrile at three concentrations ($C = 6.78 \cdot 10^{-6}$, $3.39 \cdot 10^{-5}$, $6.78 \cdot 10^{-5}$ mol/l).

3.2. Luminescence emission spectra of samarium complexes in solutions and powders

The studied compounds exhibit luminescence emission lines characteristic for the samarium (III) ion binded in the complex. Typical emission spectra of samarium complexes demonstrate the lines centered at 565, 597, 605, 645 and 654 nm. Luminescence intensity strongly depends on the type of the ligand.

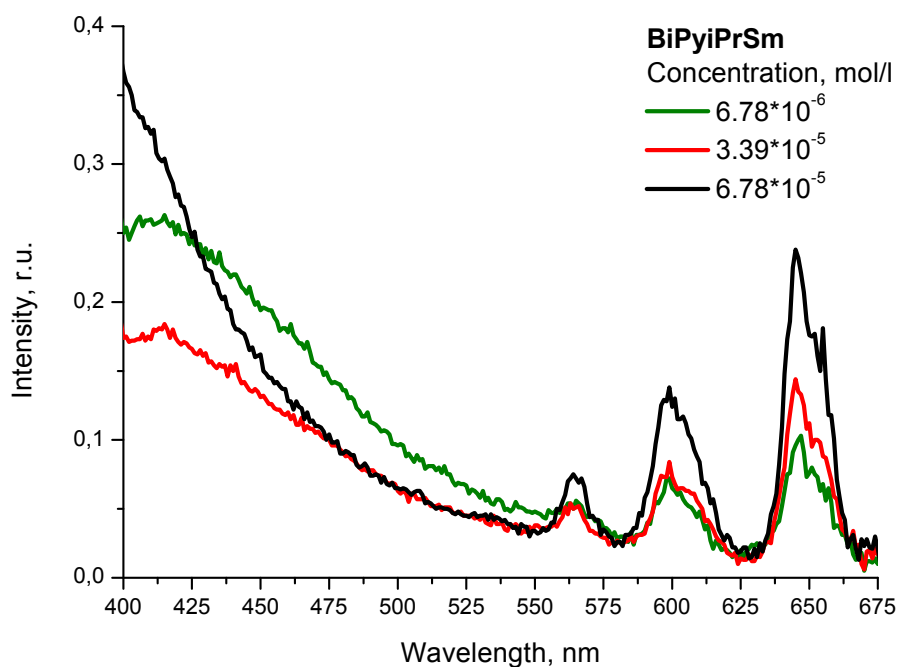


Figure 2. Luminescence spectra of samarium (III) complex **BiPy iPr Sm** in acetonitrile excited at 350 nm at room temperature.

The Figure 2 shows the emission spectra of the samarium (III) complex **BiPy iPr Sm** in acetonitrile solution at various concentrations ($C = 6.78 \cdot 10^{-6}$, $3.39 \cdot 10^{-5}$, $6.78 \cdot 10^{-5}$ mol/l), while Figures 3 and 4 present luminescence spectra of powders of different samarium (III) complexes excited at 350 nm measured at room temperature (Figure 3) and at 77 K (Figure 4). One could note that the intensity of ligand fluorescence is prevailing the emission intensity of samarium ion in solution (see Figure 2). On the contrary the samarium luminescence is dominating in emission spectra for the powders. That gives promising assumptions that the luminescence quantum yield in the solid state will be higher than in solutions.

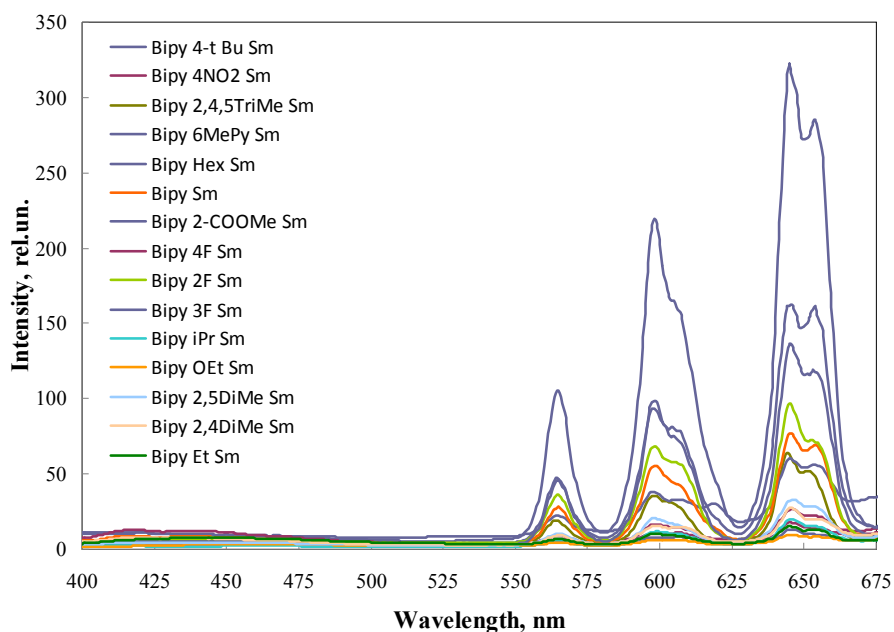


Figure 3. Luminescence spectra of powders of different samarium (III) complexes excited at 350 nm at room temperature.

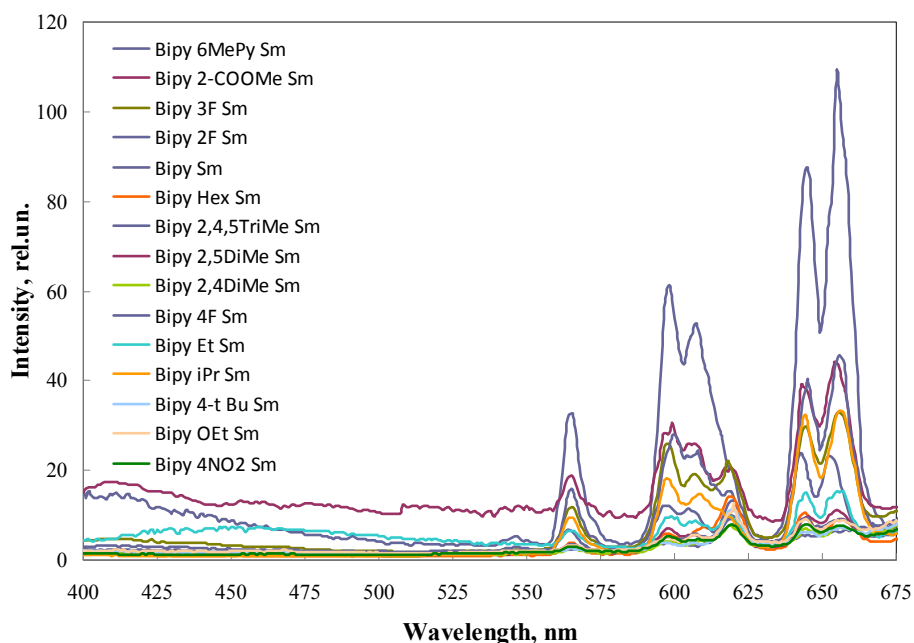


Figure 4. Luminescence spectra of powders of different samarium (III) complexes excited at 350 nm at 77 K.

3.3. Luminescence excitation spectra of samarium complexes in solutions and powders

The luminescence excitation spectra for the studied samarium (III) complexes showed bands correlating to absorption bands of the ligands.

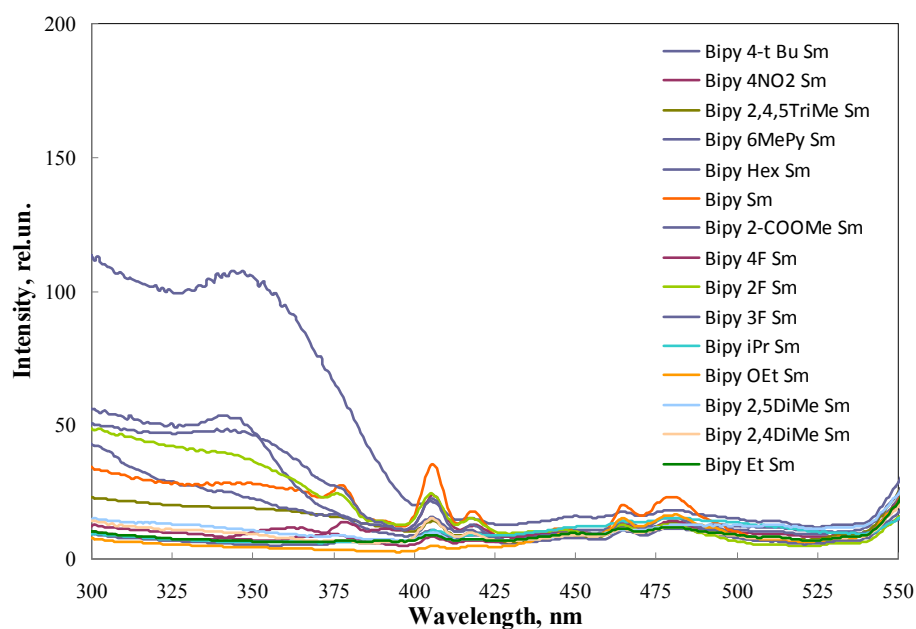


Figure 5. Luminescence excitation spectra of powders of different samarium (III) complexes at room temperature with registration at 565 nm.

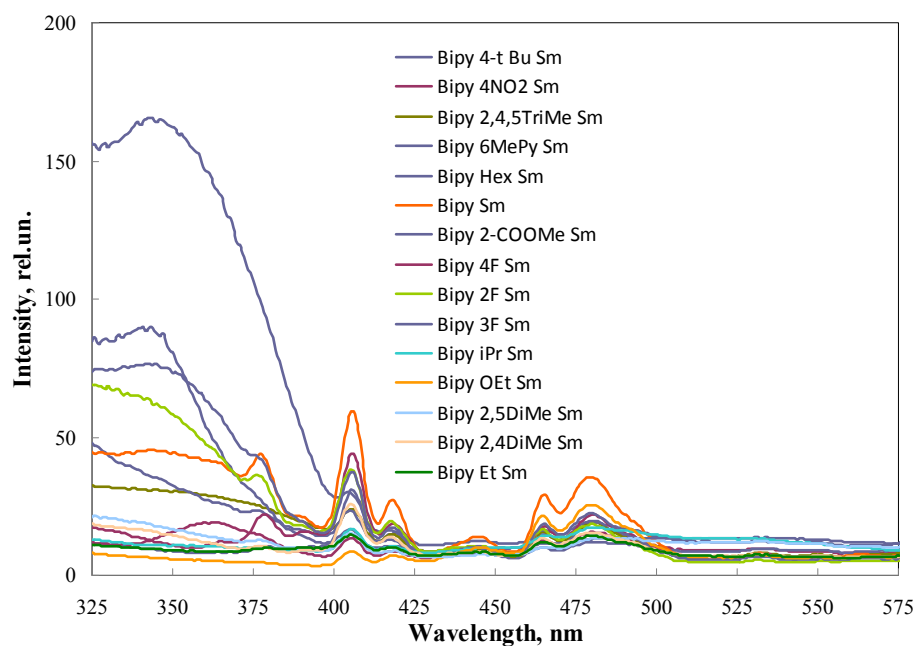


Figure 6. Luminescence excitation spectra of powders of different samarium (III) complexes at room temperature with registration at 605 nm.

3.4. Absolute luminescence quantum yield of samarium complexes in acetonitrile solutions

The overall luminescence quantum yield of the lanthanide coordination complexes is a production of quantum yield resulting from indirect excitation and the efficiency of energy transfer from the organic “antenna” to the centered lanthanide ion.

The absolute luminescence quantum yield was measured for several samarium complexes in relation to that of the rhodamine solution (see Table 1).

Table 1. Absolute luminescence quantum yields of several samarium complexes measured for excitation wavelength 350 nm.

Complex	Absorption wavelength maximum, nm	Absolute luminescence quantum yield, %
Bipy 6MePy Sm	350	3.05
Bipy iPr Sm	325	1.11
Bipy 2Py Sm	300	0.40

The largest yield was found for the complex **Bipy 6MePy Sm** (3.05%). Its value was one order of magnitude higher than the absolute luminescence quantum yield for samarium complexes reported in the literature earlier.^{25,28-30}

4. CONCLUSIONS

In this study the trivalent samarium complexes with chelating ligands based on 2,2'-bipyridylcarbon acid in which structure were introduced additional pyridine moiety, providing increased coordination of the ligand to the metal ion were investigated. These ligands were used to improve photophysical characteristics of samarium complexes. Luminescence characteristics of newly synthesized complexes were studied for compounds dissolved in acetonitrile at various concentrations as well as in the solid state in the form of powders.

All complexes exhibited the characteristic emission of Sm (III) ion with the main lines centered at 565, 597, 605, 645 and 654 nm. Luminescence intensity strongly depended on the type of the ligand. Absorbance and luminescence excitation spectra of complexes showed main peaks in the UV range. The absolute luminescence quantum yield was measured for several compounds dissolved in acetonitrile with excitation at 350 nm, its value varied from 0.4 to 3.05%. The largest luminescence quantum yield (3.05%) was found for the samarium complex **Bipy 6MePy Sm**. Its value was one order of magnitude higher than the quantum yields for samarium complexes reported in the literature earlier.

Investigating the relationship between the structures of organic ligands and the energy levels of samarium ions will give evidence for designing luminescent lanthanide organic complexes. These results prove as well that samarium chelates are potential markers for multiparametric imaging techniques.

The work was supported by an agreement with the Russian Ministry of Education (№ 14.604.21.0082 RFMEFI60414X0082).

REFERENCES

- [1] Karaman, D.S., Burikov, S. A., Dolenko, T. A., Deguchi, T., Mamaeva, V., Hänninen, P.E., Vlasov, I.I., Shenderova, O.A., Rosenholm, J. M., “Functionalization of graphene oxide nanostructures improves photoluminescence and facilitates their use as optical probes in preclinical imaging,” *Nanoscale* 7, 10410-10420 (2015).
- [2] Prabhakar, N., Nareoja, T., von Haartman, E., Karaman, D., Jiang, H., Koho, S., Dolenko, T., Hanninen, P., Vlasov, D., Ralchenko, V., Hosomi, S., Vlasov, I., Sahlgren, C., Rosenholm, J., “Core-shell designs of

photoluminescent nanodiamonds with porous silica coatings for bioimaging and drug delivery II: Application,” *Nanoscale* 5(9), 3713-3722 (2013).

- [3] Haartman, E., Jiang, H., Khomich, A.A., Zhang, J., Burikov, S.A., Dolenko, T.A., Ruokolainen, J., Gu, H., Shenderova, O.A., Vlasov, I.I., Rosenholm, J.M., “Core-shell designs of photoluminescent nanodiamonds with porous silica coatings for bioimaging and drug delivery I: fabrication,” *J. Mater. Chem. B* 1, 2358-2366 (2013).
- [4] Dubinina, T.V., Kosov, A.D., Petrusevich, E.F., Maklakov, S.S., Borisova, N.E., Tomilova, L.G., Zefirov, N.S., “Heteroleptic naphthalo-phthalocyaninates of lutetium: synthesis and spectral and conductivity properties,” *Dalton Transactions* 44, 7973-7981 (2015).
- [5] Shenderova, O., Hens, S., Vlasov, I., Turner, S., Lu, Y.G., Van Tendeloo, G., Schrand, A., Burikov, S. A., Dolenko, T.A., “Carbon-Dot-Decorated Nanodiamonds,” *Part. Part. Syst. Charact.* 31, 580–590 (2014).
- [6] Von Haartman, E., Jiang, H., Khomich, A.A., Zhang, J., Burikov, S.A., Dolenko, T.A., Ruokolainen, J., Gu, H., Shenderova, O. A., Vlasov, I.I., Rosenholm, J.M., “Core-shell designs of photoluminescent nanodiamonds with porous silica coatings for bioimaging and drug delivery I: fabrication,” *J. Mater. Chem. B* 1, 2358-2366 (2013).
- [7] Bünzli, J.-C. G., “Lanthanide luminescence for biomedical analyses and imaging,” *Chem. Rev.* 10(5), 2729-2755 (2010).
- [8] Li, T., Kaercher, S., Roesky, P.W., “Synthesis, structure and reactivity of rare earth metal complexes containing anionic phosphorus ligands,” *Chem. Soc. Rev.* 43, 42-57 (2014).
- [9] Borisova, N.E., Kostin, A.A., Eroshkina, E.A., Reshetova, M.D., Lyssenko, K.A., Spodine, E.N., Puntus, L.N., “Lanthanide complexes with tetradentate n,n',o,o'-dipyridyl-based ligands: Structure, stability, and photophysical properties,” *European Journal of Inorganic Chemistry*, 2219–2229 (2014).
- [10] Alyapyshev, M.Y., Babain, V.A., Tkachenko, L.I., Paulenova, A., Popova, A.A., Borisova, N.E., “New diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid for actinide-lanthanide separation,” *Solvent Extraction and Ion Exchange* 32, 138-152 (2014).
- [11] Richardson, F.S., “Terbium (III) and Europium (III) Ions as Luminescent Probes and Stains for Biomolecular Systems,” *Chem. Rev.* 82, 541-552 (1982).
- [12] Li, Q., Li, T., Wu, J., “Luminescence of Europium (III) and Terbium (III) Complexes Incorporated in Poly (Vinyl Pyrrolidone) Matrix ” *J. Phys. Chem.* 105, 12293-12296 (2001).
- [13] Gai, Y.L., Jiang, F.L., Chen, L., Bu, Y., Su, K.Z., Al-Thabaiti, S.A., Hong, M.C., “Photophysical Studies of Europium Coordination Polymers Based on a Tetracarboxylate Ligand,” *Inorg. Chem.* 52(13), 7658-7665 (2013).
- [14] Kharcheva, A.V., Ivanov, A.V., Borisova, N.E., Kaminskaya, T.P., Patsaeva, S.V., Popov, V.V., Yuzhakov, V.I., “Luminescent solutions and films of new europium complexes with chelating ligands,” *Proc. SPIE* 9448, 11-13 (2015).
- [15] Alyapyshev, M., Babain, V., Borisova, N., Eliseev, I., Kirsanov, D., Kostin, A., Legin, A., Reshetova, M., Smirnova, Z., “2,2'-Dipyridyl-6,6'-dicarboxylic acid diamides: Synthesis, complexation and extraction properties,” *Polyhedron* 29(8), 1998-2005 (2010).
- [16] Kirsanov, D. O., Borisova, N. E., Reshetova, M. D., Ivanov, A. V., Korotkov, L. A., Eliseev, I. I., Alyapyshev, Yu. M., Spiridonov, I.G., Legin, A.V., Vlasov, Yu. G., Babain, V. A., “Novel diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid: synthesis, coordination properties, and possibilities of use in electrochemical sensors and liquid extraction,” *Russian Chemical Bulletin, International Edition* 61 (4), 881—890 (2012).
- [17] Crosby, G.A., Whan, R.E., Freeman, J.J., “Spectroscopic studies of rare earth chelates,” *J. Phys. Chem.* 66, 2493-2499 (1962).
- [18] Bakier, E., Abdel-Mottaleb, M. S. A., “Factors affecting light energy transfer in some samarium complexes,” *International journal of photoenergy* 7, 51-58 (2005).

- [19] Bao-Li, A., Meng-Lian, G., Ming-Xing, L., Ji-Ming, Z., "Synthesis, structure and luminescence properties of samarium (III) and dysprosium (III) complexes with a new tridentate organic ligand," *Journal of Molecular Structure* 687, 1-6 (2004).
- [20] Brito, H.F., Malta, O.L., Felinto, M.C.F.C., Teotonio, E.E.S., Menezes, J.F.S., Silva, C.F.B., Tomiyama, C.S., Carvalho, C.A.A., "Luminescence investigation of the Sm (III)- β -diketonates with sulfoxides, phosphine oxides and amides ligands," *Journal of Alloys and Compounds* 344, 293-297 (2002).
- [21] Kumar, R., Singh, U. P., "Molecular structure, photophysical and thermal properties of samarium (III) complexes," *Journal of Molecular Structure* 875(1), 427-434 (2008).
- [22] Hakala, H., Liitti, P., Peuralahti, J., Karvinen, J., Mukkala, V., Hovinen, J., "Development of luminescent Sm(III) chelates containing hexadentate to nonadentate ligands: synthesis, photophysical properties and coupling to biomolecules," *Journal of Luminescence* 113, 17-26 (2005).
- [23] Ilango, S., Vidjayacoumara, B., Gambarotta, S. "Samarium complexes of a σ - π -pyrrolide/arene based macrocyclic ligand," *Dalton Trans.* 39, 6853-6857 (2010).
- [24] Woodward, A. W., Frazer, A., Morales, A. R., Yu J., Moore, A. F., Campiglia, A. D., Jucov, E.V., Timofeeva, T. V., Belfiel, K. D., "Two-photon sensitized visible and near-IR luminescence of lanthanide complexes using a fluorene-based donor- π -acceptor diketone," *Dalton Trans.* 43, 16626-16639 (2014).
- [25] Hakala, H., Liitti, I., Pukka, K., Peuralahti, J., Loman, K., Karvinen, J., Ollikka, P., Ylikoski, A., Mukkala, V., Hovinen, J., "Novel luminescent samarium (III) chelates," *Inorganic Chemistry Communications* 5, 1059-1062 (2002).
- [26] Kirsanov, D.O., Borisova, N.E., Reshetova, M.D., Ivanov, A.V., Korotkov, L.A., Eliseev, I.I., Alyapyshev, M.Y., Spiridonov, I.G., Legin, A.V., Vlasov, Y.G., Babain, V.A., "Novel diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid: synthesis, coordination properties, and possibilities of use in electrochemical sensors and liquid extraction," *Russian Chemical Bulletin* 61, 881-890 (2012).
- [27] Lakowicz, J.R., [Principles of Fluorescence Spectroscopy], Edition: 3rd Springer Science&Business Media, NY, (2006).
- [28] Rodríguez-Ubis, J.C., Sedano, R., Barroso, G., Juanes, O., Brunet, E., "Lanthanide Complexes of Poliacid Ligands Derived from 2,6-Bis(N-pyrazolyl)pyridine, Pyrazine and 6,6'-Bis(Npyrazolyl)2,2'-bipyridine. Synthesis and Luminescence Properties," *Helv. Chim. Acta* 80, 86-96 (1997).
- [29] Klink, S.I., Hebbink, G.A., Grave, L., Peters, F.G.A., Van Veggel, F.C.J.M., Reinhoudt, D.N., Hofstraat, J.W., "Near-Infrared and Visible Luminescence from Terphenyl-based Lanthanide(III) Complexes bearing Amido and Sulfonamido Pendant Arms," *Eur. J. Org. Chem.*, 1923-1932 (2000).
- [30] Galaup, C., Couchet, J.M., Picard, C., Tisnes, P., "Novel terpyridine macrocyclic complexing agent and luminescence of its neutral Ln(III) complexes (Ln=Eu, Tb, Sm, Dy) in aqueous solution," *Tetrahedron Lett.* 42(36), 6275-6278 (2001).