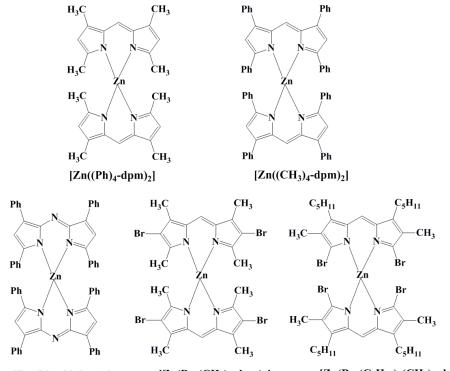
Photochemical and photophysical properties of novel dipyrromethene complexes with zinc

Prokopenko Alexandr¹, Kuznetsova Rimma¹, Aksenova Iuliia¹, Bumagina Natalia²

¹ Tomsk State University, Tomsk, Russia ²G.A. Krestov Institute of Solution Chemistry of the RAS, Ivanovo, Russia

E-mail: alexpr898@gmail.com

Study of dipyrromethene complexes with different structure is one of the most successfully developing areas of modern chemistry. The demand for using a variety of optical devices in modern technology makes it necessary to explore the photonics of new organic luminophores such as coordination complexes of dipyrromethene with p- and d-elements depending on their structure, intermolecular interactions, temperature, etc. In this work was researched dipyrromethene compounds, which can form stable complexes with ions of d-elements. The main advantage complexes of Zn(II) with dipyrromethenes is easy to "self-assembly" in the "soft" conditions on complexing ions in solutions and in biological systems, as well as high sensitivity spectral-luminescence characteristics to changes in the structure of the chromophore and the nature of the solvent. Systematic observation of photochemical and photophysical properties and establishment of their connection with structural features of the complexes are required for successful usage of dipyrromethene complexes and creation of various hi-tech optical devices which are based on them. Therefore, the purpose of the work is to study the spectral-luminescent, sensory properties and stability of different complexes of dipyrromethenes with zinc, the optimal combination of which will indicate the direction of the most effective use of these dyes.



 $[Zn((Ph)_4-N-dpm)_2] \qquad [Zn(Br_2(CH_3)_4-dpm)_2] \qquad [Zn(Br_2(C_5H_{11})_2(CH_3)_2-dpm)_2]$ Figure 1. Structural formulas and denotation of investigated compounds

These complexes (Fig.1) were synthesized in Institute of Solutions Chemistry of the RAS [1]. For this compounds were investigated spectral-luminescent properties in different solvents. It was found that zinc dipyrromethene complexes don't have effective fluorescence but have longlived emission due to increased nonradiative intersystem processes in the excited state [2]. Introduction of heavy atoms into the dipyrromethene core enhances intersystem crossing, which leads to a long-lived emission. For such complexes, we obtained characteristics of the spectra of long-lived emission of frozen ethanol solutions. The matching of the phosphorescence excitation spectra with absorption spectra of halogen-substituted complexes confirm that the phosphorescence belongs to the corresponding complexes. For solid samples based on zinc complexes was found dependency of the long-lived emission intensity of the oxygen concentration in gas flow. The presence of line segment indicates the possibility of the use of these complexes as a basis for creation of optical sensors for oxygen determination. For successful application of such complexes need to know something of their behaviors in different solvents, including when acids and alkalides are present, since the stabilities of fluorophores in acidic/alkaline media are closely related to their applicabilities. The complexes stabilities in the ground and excited states are estimated by spectrophotometric titration of ethanol solutions of compounds using water-ethanol solutions of hydrochloric acid. The results obtained in this work can be used as the basis for the design of optical devices.

References:

- R. T. Kuznetsova, Yu. V. Aksenova, D. E. Bashkirtsev, A. A. Prokopenko, E. N. Tel'minov, G. V. Mayer, N. A. Dudina, E. V. Antina, A. Yu. Nikonova, M. B. Berezin, A. S. Semeikin, High Energy Chemistry, 2015, 49, 16
- [2] N.A. Dudina, A.Yu. Nikonova, E.V. Antina, M.B. Berezin, A.I. V'yugin, Khim. Geterotsikl. Soedin., 2013, 12, 1878