ABSTRACT
research publications series

«Phosphorescent transition metal complexes:
new approach to the synthesis and practical applications»

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This series of research publications was aimed to elaboration of synthetic approach and investigation of new types of organometallic complexes, which demonstrate unique photophysical characteristics and high potential for application in such areas as OLED technology, nonlinear optics, bio-analytics and biomedical imaging.

Pioneer works devoted to the synthesis supramolecular luminescent heterometallic complexes of copper subgroup have been published in 2008-2010 years and the series of publications presented here (2012-2016) we formulated general strategy of the preparation of compounds with predetermined photophysical properties, which is based on experimental studies of luminescent characteristics of the compounds obtained, investigation of the properties dependence on the composition, structure and state of matter, as well as on theoretical modeling of their electronic structure.

The compounds presented in this series of publication display extremely high luminescent quantum yields (up to 100%),[22, 34] variable emission wavelengths,[1, 3, 7, 35] fine tunable dependence of phosphorescence characteristics on oxygen concentration[5, 9] and other small molecules,[2, 4] dual luminescence,[5] nonlinear optical properties,[15, 23] *stimuli-responsive* characteristics[2, 8, 12, 13] and ability for covalent and non-covalent conjugation with biomolecules.[11, 15, 17, 26, 27]. These findings pave the way to a wide range of practical application in the design of electroluminescent devices,[6, 20] sensors,[2,12] as well as for the use in biomedical experiments as phosphorescent probes in luminescent microscopy.

A unique feature of these coordination compounds consists in the presence in their structure the polymetallic coordination core, which is stabilized by a network of metallophilic bonding.[1, 10, 20, 22, 24, 25, 28] This non-covalent interactions are simultaneously the driving force for self-assembly of these compounds. Thus the key idea of this synthetic project was a combination of self-assembling metallophilic interactions with structurally directing role of polydentate template phosphine and alkynyl ligands, which made possible to synthesize the compounds with predetermined composition and structure! It was also found that this self-assembled and very stable structure may serve as a nucleus of polymetallic nanoparticles with given composition that largely determines their useful properties.[21, 33]

The experimental data obtained and theoretical analysis of the complexes electronic structure showed that their photophysical characteristics depend on both composition/nature of coordinating metal core and donor-acceptor properties of the ligand environment because excited state responsible for emission includes metal ion orbitals and orbitals of organic ligands. This

observations form a basis for an alternative approach to modification of luminescent properties of the final compounds. Under the framework of this approach it is possible to keep invariable the nature of coordinating centre in mono- and polynuclear complexes and simultaneously to vary electronic characteristics of ligands,[1, 3, 7, 14, 18, 29, 35] thus manipulating the energy of excitation, emission wavelength and excited state lifetime.

A considerable part of the studies presented here was aimed at the synthesis of compounds suitable for application in bioimaging, where the biomolecules (peptides, enzymes) were used as "outer-sphere ligands" to increase solubility of hydrophobic complexes in physiological media and their biocompatibility.

The results of these studies were presented in 35 papers published in international high-rank journals, some of them[4, 11, 19] have been places at the journals Cover-page as the best publications of the corresponding issues. The authors also gave numerous lectures at the Russian and international scientific conferences and have got one patent.