“Development of methods for the directed synthesis of copper subgroup luminescent metal complexes with a predetermined structure”

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Annotation

A series of research works by Shakirova J. R. is devoted to the development of the methods for the synthesis of the luminescent copper subgroup homo- and heterometallic compounds, based on the rational choice of cluster and frame-forming ligands. A key feature of this approach is simultaneous use of rigid ligands with a given geometry of coordinating centers and special types of aurophilic/metallophilic interactions, which, ultimately, allow obtaining the final products with predetermined structure, stoichiometry and properties. In publications devoted to these studies, the effectiveness of the proposed synthetic approaches is demonstrated by the example of several classes of coordination compounds.

The research on the synthesis of homo- and heterometallic alkynyl gold(I) complexes have demonstrated the effectiveness of using metallophilic interactions in the design and synthesis of polynuclear compounds, which form polymeric structures of various nature in the solid phase (European Journal of Inorganic Chemistry, 2017, Vol. 36, P. 4180-4186, ZAAC, 2018, Vol. 644, No. 5, P. 308-316). Solid-phase samples of the obtained compounds are intensely phosphorescent, and in some cases demonstrate extremely high quantum yields up to 95% that make possible to use them as emitters in OLED devices.

The advantages of the synthesis of compounds with a predetermined structure by using the combination of sterically rigid polyphosphines and aurophilic/metallophilic interactions were clearly demonstrated by the author in the studies related to the synthesis of the phosphorescent homo- and heterometallic complexes based of copper subgroup metals. (J. Phys. Chem. C, 2016, Vol. 120, No. 44, P. 25541–25547; Inorg. Chem., 2014. Vol. 53. No. 9. P. 4705 - 4715). Complexes of this class are bright phosphors, and their luminescence parameters can be tuned up by variations in the geometry of the ligands and composition of the cluster core, as well as by introducing substituents with different donor characteristics into the ligands. For some of these compounds, a unique ability to change the emission parameters being exposed to organic solvents vapors (methanol, acetone, tetrahydrofuran) was discovered and studied that paves the way to design of sensor materials and solid-state devices for sensing these solvents in the gas phase (Fig. 1).

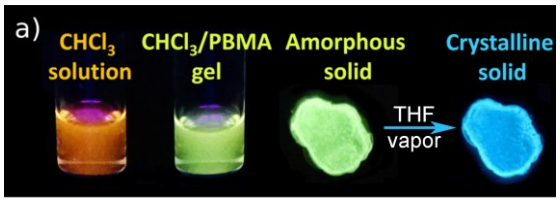

Figure 1. The change in the gold complex emission in the solid phase under the influence of THF vapor.

The combination of cluster-forming ligands ($tBuN^{2-}$, S^{2-}, tris(diphenyl)phosphinomethane) and template sterically rigid polyphosphines or acetylenes allowed the directed synthesis of a new class of homometallic and heterometallic gold(I) complexes with three-dimensional architecture of two types: cylindrical metal frames based on linear diphosphines and acetylenes, as well as several tetrahedral homo- and heterometallic complexes (Dalton Trans., 2014. Vol. 2014. No. 43. P. 6236 - 6243, Dalton Trans., 2017, Vol. 46, P.2516 - 2523, Angew. Chem . Int. Ed., 2018, Vol. 57, P. 14154-14158) (Fig. 2).

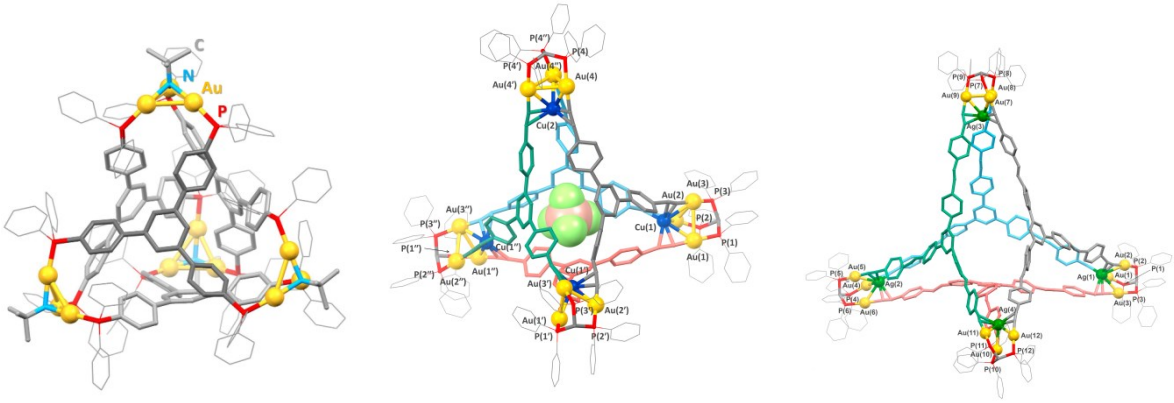

Fig. 2. Structures of homo- and heterometallic tetrahedral cluster complexes.

A unique ability of direct exchange of copper(I) ions for silver(I) ions in the structure of the cluster cor, was found in the obtained heterometallic ensembles, that results in the change in the nature of the emission center and shift of the luminescence band to the blue region (Fig. 3).

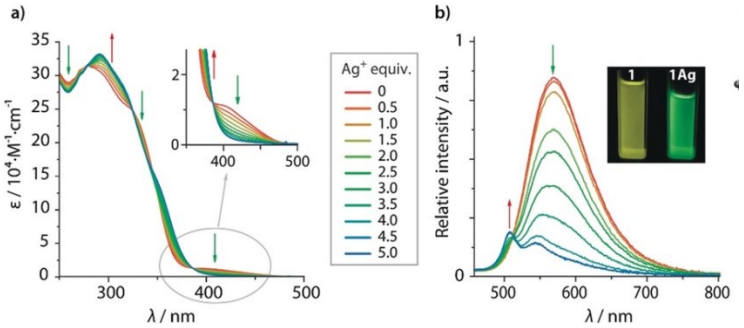

Fig. 3. Changes in absorption (a) and emission (b) upon interaction of gold-copper complex with the $AgCF_3SO_3$ salt in acetonitrile.

The studies performed by J. R. Shakirova and submitted for participation in St. Petersburg State University competition for scientific works in the category “For Contribution to the Science of Young Researchers” make a significant contribution to the development of a strategy for the directed synthesis of highly efficient phosphors, which are potentially applicable in the OLED technology and as sensors to various classes of organic compounds. The scientific value of the results is fully confirmed by their publication in high-rank international scientific journals. Of the 7 articles published by the present time 6 appeared in the journals of the first quartile; their total impact factor is 33,435.

Personal contribution of Shakirova J.R. into the research presented consists in the development of design ideas for targeted complexes, their synthesis, measurement and interpretation of spectral data, studies of the photophysical properties of the obtained compounds, and preparation of materials for publication.