

Molecules of macrocyclic ligands usually have a certain number of donor sites, i.e. atoms that can combine with a metal ion, all of which are directed to the inside of the macrocyclic ring. Therefore, they are usually only able to connect in one way, using all donors to coordinate one ion. Porphyrins and related systems, containing four nitrogen atoms inside a flat ring formed from four pyrrole rings connected by single-carbon methine bridges, invariably bind to cations of different charges using all four nitrogen donors. There is no donor atom in a typical porphyrin on the circumference of a macrocyclic ring unless it is attached there in the form of a substituent.

The so-called inverted, or N-confused porphyrin (NCP), which has an elemental composition identical to porphyrin (i.e. is its isomer), is slightly different from it in structure. The difference is to replace one of the nitrogen atoms inside the porphyrin with a carbon atom, and one of the carbon atoms at periphery with a nitrogen atom. Such a change causes different properties of compounds with metals, but also gives the possibility of interaction with them by this external nitrogen atom. NCP also shows a special reactivity of this so-called *confused* pyrrole, allowing for relatively easy modification of the interior and periphery of this porphyrin. In the cycloaddition reaction, two additional carbons and one nitrogen can be introduced at this location with the formation of an additional, porphyrin-coupled imidazole ring. In this way, imidazocarbachlorine (ImCC) is formed, a hybrid ligand that, in addition to the macrocyclic functionality typical of porphyrins, gains additional donor site in the form of conjugated imidazole. The well-exposed imidazole nitrogen atom in ImCC can be used to construct coordination compounds containing an external metal ion. This ion can combine two or more ImCC units, as well as molecules containing a metal ion in a macrocyclic cavity (MImCC), leading to systems with different and desirable properties and unprecedented structures. The subject of research in this project will be to investigate the interactions between metal ions in such systems, mediated by the macrocyclic ligand and the impact of these interactions on the properties of the system, such as the ease of electron transfer/reception (redox properties), the interaction of electron spins on metals (magnetic properties) or the absorption and emission of electromagnetic radiation, as well as catalytic properties.

The introduction of an alkyl substituent on the external imidazole nitrogen atom in complexes of some metals (e.g. trivalent silver) causes the compound to be cationic in nature, and the imidazole carbon located between nitrogen atoms in the porphyrin-coupled ring can be easily carried out into the state of carbene, i.e. divalent carbon with strong ability to coordinate metals at low oxidation states, e.g. gold(I) or rhodium(I). Systems of this type are known for their ability to accelerate many reactions in organic chemistry, i.e. they are catalysts for these reactions. This project will investigate a number of such compounds for their catalytic properties.

The coordination compound alkylated on an imidazole nitrogen atom with a divalent metal in the coordination cavity is a system of zwitterion or a dipolar ion: the positive charge is located on imidazole (mainly on the nitrogen atom), and the negative charge is distributed on the macrocyclic ring. Owing to this distribution of charge, the molecules attract each other and form supramolecular structures, both in the solid state and in solution. Such an arrangement also favors the transfer of electrons from molecule to molecule, not only because of their proximity, but also because each of them contains a donor part, having an excess of electric charge (macrocyclic ring) and an acceptor part, with a high ease of receiving charge (imidazole). It should be expected that the systems constructed in this way will have interesting electrical properties and can be used as semiconductor materials. These issues will also be the subject of research in this project.