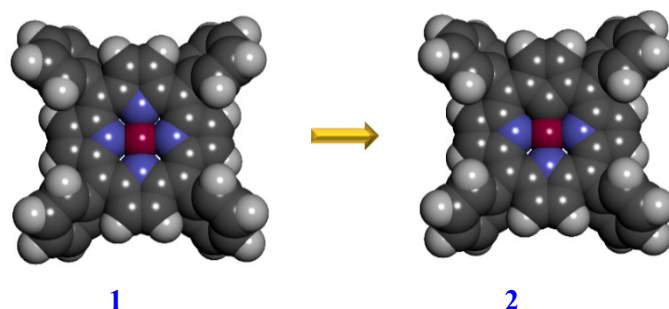


## *Incorporation of a cyclopentadiene unit into meso-aryl substituted porphyrinic frames – a quest for versatile macrocyclic surroundings in organometallic chemistry*

Multiple biochemical roles played by iron protoporphyrin IX have inspired many diverse studies of fundamental scientific significance, triggering a search for suitable porphyrins and metalloporphyrins prearranged to act as biomimetic models. An activation of dioxygen, oxygen atom transfer, direct functionalization of C–H bonds via metal-catalyzed atom/group transfer reactions are the ground-breaking, attractive areas of explorations. All of them require porphyrin or metalloporphyrin participations. Therefore, the development of metalloporphyrinoids continue to be active research areas. In general, advances in metalloporphyrin chemistry are closely tied to developments of synthetic methods of porphyrins. In light of these, it is quite clear why chemists in sophisticated explorations mostly apply in principle *meso*-aryl-substituted porphyrin **1** as their *workhorse tetrapyrrolic macrocycle*. Evidently these molecules preserve the fundamental features of natural porphyrins. They can be easily synthesized in impressive varieties and readily manipulated by virtue of the appropriate external substitution, which in addition provides the required steric protection modelling the shape of a porphyrinic cauldron to allow for instance a control of catalytic stereoselectivity.



The fundamental goal of the presented project is a development of the readily available unique subclass of core-modified porphyrins founded on replacement of a single pyrrole ring in the parent *meso*-aryl-substituted porphyrin **1** by cyclopentadiene yielding *meso*-tetraaryl-21-carbaporphyrin **2**. Subsequently the idea will be extended on expanded macrocycles and ferrocenoporphyrins.

The occurrence of a carbon atom in the inner cavity of macrocycle provides the surrounding, which allows to investigate a specific interaction in particular with paramagnetic metal cations. Importantly, properties of organometallic complexes will be controlled by suitable choices of electronic factors and steric protections provided by cautiously selected external substitution. A specific nature of these carbaporphyrins, resulting from the presence of a carbocycle unit, provides the exceptional opportunity to construct the unique three-dimensional architecture via the formation of  $\pi$ -complexes.

In general a novel class of organometallic molecules is aimed to serve as a perfect versatile macrocyclic surrounding to explore innovative organometallic chemistry. Such an approach is anticipated to provide the essential knowledge concerning mechanisms of organometallic processes addressing also electronic, steric, conformational and mechanistic features crucial for pursued functionalities.

A complete characterization of new molecules will engage wide range of spectroscopic methods. Evidently the NMR spectroscopy will play the fundamental role at all stages of the scientific studies. Typical experiments, aimed to identify the crucial reaction steps, will require the systematic monitoring by NMR spectroscopy at low temperature limit, providing the kinetic and structural insight into the reaction progress. The distinctive macrocyclic environment also creates a long-sought chance to trap the unique dioxygen activation or organometallic intermediates, typically postulated in catalytic processes.

The project in a pursuit of a specific class of core-modified porphyrins with built-in a carbocycle unit will eventually afford a universal macrocyclic platform. These molecule are expected to provide ground-breaking benefits to organometallic chemistry. In a long distance perspective, new organometallic complexes can demonstrate their potential utility in different fields like catalysis, optic data storage or construction of molecular devices.