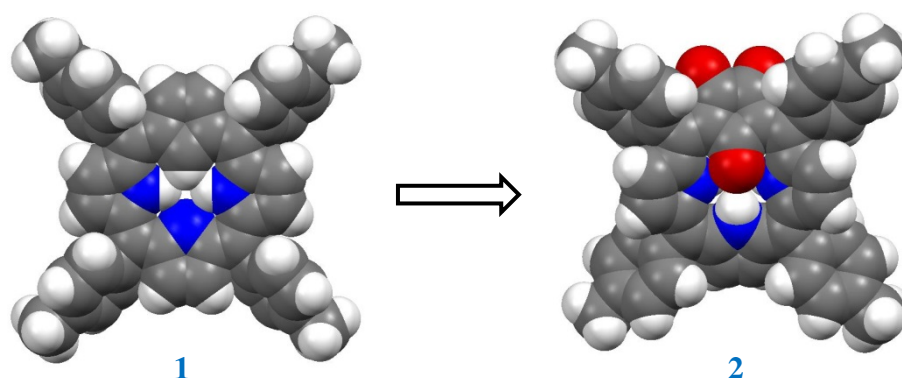


21-carbaporphyrin-2,3,21-trione - a cyclopentane-1,2,4-trione moiety entrapped into the *meso*-tetraarylporphyrin framework. Synthesis, reactivity and peripheral annulation

Porphyrins are aromatic macrocycles built with four pyrrolic subunits connected with each other by methine bridges that create a framework with an inner cavity suitable for metal cation insertion. Their complexes with iron (heme) ions play a fundamental role in the biochemical processes related to the activation and transportation of molecular oxygen. Formally, these compounds can be modified by replacing one of the pyrrolic nitrogen atoms with a carbon atom to obtain carbaporphyrinoids. An alternative strategy for forming carbaporphyrinoids is the incorporation of the carbocyclic unit into the porphyrinoid architecture. Studies carried on carbaporphyrinoids indicated their intriguing reactivity in the area of coordination and organometallic chemistry. They also provided an insight into the features of three-dimensional aromaticity and unique conformational balances. An excellent example of extraordinary chemistry of carbaporphyrinoids are metal mediated contractions (Pd(II), Au(III), Rh(III)) from benzene to cyclopentadiene ring in the *p*-benzoporphyrin framework leading to 21-carbaporphyrin. The synthesis of *meso*-tetraaryl-21-carbaporphyrin **1**, the first macrocycle with a cyclopentadiene subunit entrapped in the *meso*-tetraarylporphyrin architecture, was recently developed in the Porphyrin group at the Faculty of Chemistry of the University of Wrocław (*Angew. Chem. Int. Ed.*, **2019**, 58, 6089) and it provides significant motivation for further exploration of the chemistry of 21-carbaporphyrin and its derivatives. This research project will focus on post-macrocylic chemistry of porphyrinoids and carbaporphyrinoids which is unique for porphyrinoids and carbaporphyrinoids.



This research proposal focuses on the reactivity of 21-carbaporphyrin-2,3,21-trione **2**, a *meso*-tetraaryl-21-carbaporphyrin **1** derivative with an embedded cyclopenta-1,2,4-trione motif formed from cyclopentadiene subunit of 21-carbaporphyrin **1**. Due to its nontrivial structure, it is expected that the new group of compounds presented in the research proposal would possess not only interesting chemical, but also physicochemical properties. The first stage will not only focus on elaboration of synthetic routes leading to 21-carbaporphyrin-2,3,21-trione **2** starting from 21-carbaporphyrin **1**, but also on isolation and characterization of intermediate forms occurring in this process. The second stage is going to explore the reactivity of the β, β' -positions of cyclopenta-2,3,4-trione unit with aliphatic and aromatic diamines. These modifications will lead to the expansion of π -electron system of the macrocycle altering the reactivity and spectroscopic features of the initial compound. Moreover, the coordination chemistry for these derivatives will be tested in stage three. Experiments on controlled removal of the centrally located oxygen atom in reducing environments leading to 21-carbaporphyrin-2,3-dione complexes are also being considered. The last stage is devoted to contraction and expansion reactions of the cyclopentadiene subunit into 4-, 6- and 7- membered rings. The new library of 21-carbaporphyrin **1** derivatives will significantly impact the development of 21-carbaporphyrins chemistry. The similarity of regular geometry of *meso*-tetraarylporphyrin and *meso*-tetraaryl-21-carbaporphyrin **1** suggests its potential usage in creating optical materials or functional devices and introducing new tools to control their functionality due to a different coordination core.

All of the obtained products will be characterized by nuclear magnetic resonance spectroscopy (NMR) experiments, mass spectrometry (MS), ultraviolet-visible (UV-Vis) and x-ray crystallography.