

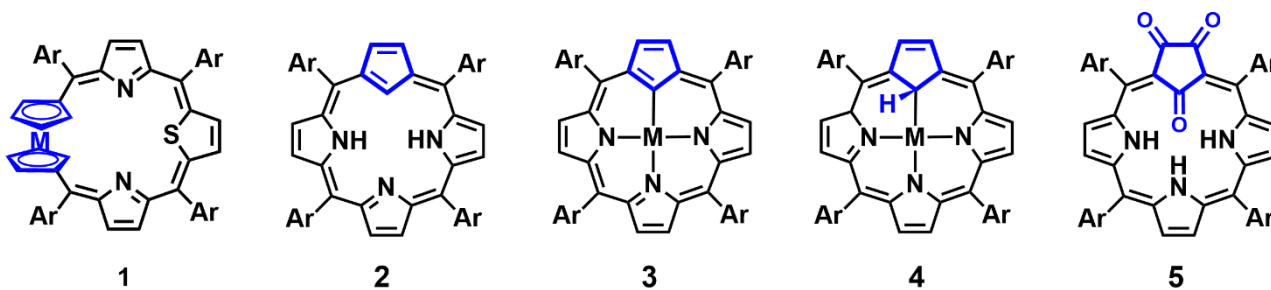
## Carbaporphyrinoids – macrocyclic ligands in organometallic chemistry

Lechośław Latos-Grażyński

University of Wrocław, Wrocław, POLAND

e-mail: lechośław.latos-grazyński@chem.uni.wroc.pl

Redesign of archetypical porphyrin frame, introducing of CH unit(s) in place of one of pyrrolic nitrogen atoms, created an original class of macrocycles – carbaporphyrinoids, which reveal fascinating properties in terms of their electronic structure, aromaticity and their potential ability to bind metal ions. Carbaporphyrinoids realize the specific concept of macrocyclic ligand construction by fusing the structural frame of porphyrin and carbon donor(s) **1-5**, introduced by appropriately chosen moieties.



The entrapment of metal ions in a coordination core of carbaporphyrinoids creates an efficient protection of the metal-carbon bond and allows to stabilize extremely rare oxidation/electronic states in organometallic environments. These macrocycles enforce the specific intramolecular reactivity, skeletal rearrangements and frequently exotic coordination architectures: For instance Metallocenoporphyrinoid **1** demonstrates a hitherto unknown facet of porphyrinoid aromaticity, namely the possibility of including a *d*-electron subunit in  $\pi$ -electron conjugation pathways. The contraction *p*-phenylene – embedded in *p*-benzporphyrin – to cyclopentadiene, mediated by transition metal cations produced complexes of 21-carbaporphyrin **3**. Incorporation of a cyclopentadiene moiety into the *meso*-tetraarylporphyrin framework, using 1,3-bis(arylhydroxymethyl)ferrocene as a synthon, resulted in the rational synthesis of *meso*-tetraaryl-21-carbaporphyrin **2**. The molecular design preserves all essential virtues of the original tetrapyrrolic architecture of *meso*-tetraarylporphyrin, including the perfect match between the ionic radii of inserted metal cations and the size of the macrocyclic (C<sub>3</sub>NNN) core, and steric protection provided *meso*-aryl substituents as shown in **3**. The protonation of the inner core reveals an adjustable (trigonal versus tetrahedral, **3** vs. **4**) geometry. Oxygenation of **3** yielded aromatic 21-carbaporphyrin-2,3,21-trione **5**.