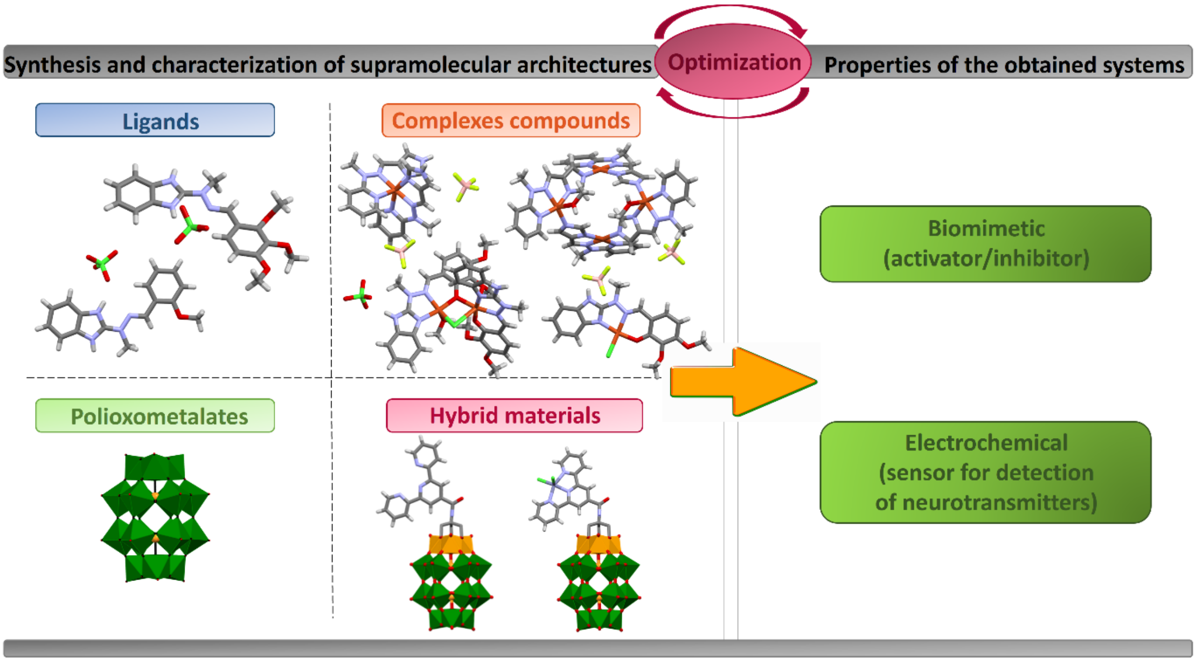
„Multicore supramolecular architectures as multitasking systems”

mgr Daria Anna Nowicka

ABSTRACT

The scientific objective of this dissertation, entitled "**Multicore supramolecular architectures as multitasking systems**" is:

1) Design, synthesis and structural-spectroscopic characterization of supramolecular architectures of *d*-electron metal ions, polyoxometalates and hybrid materials
2) Study of the biomimetic and electrochemical properties of the obtained compounds, taking into account the influence of the organic backbone of the ligand, aldehyde, metal ion, counter ion, solvent, temperature and molar ratio of the substrates on the multifunctionality of the obtained supramolecular architectures.



The dissertation includes five scientific publications that describe the synthesis and structural-spectroscopic characterization of supramolecular systems in the form of *d*-electron metal complex compounds, polyoxometalates and hybrid materials. Developing synthetic strategies by properly designing the structures of supramolecular architectures is crucial for the resulting systems to effectively exhibit biomimetic and electrochemical properties.

The first publication in the series describes the first example in the literature of oxidative *O*-demethylation occurring with the participation of a Cu(II) center based on an imine ligand without the addition of strong oxidants such as peroxides. The paper presents the self-organization processes of three N,N,O-donor ligands of the Schiff base type **L1** [$C_{18}H_{20}N_4O_3$], **L2** [$C_{16}H_{16}N_4O$] and **L3** [$C_{18}H_{20}N_4O_2$] with respect to Cu^{2+} ions in the presence of selected cations: Mn^{2+}, Na^+ and anions: Cl^-, ClO_4^-, which are to act as biomimetics of the enzyme oxidative demethylase. The presence of a C-O-C bond in the ligand skeleton structure is particularly important. Based on this, the reaction of oxidative *O*-demethylation was studied, which involves the removal of a methyl group attached to an oxygen atom, leading to the formation of a hydroxyl group. Optimization of the reaction allowed the influence of various factors on the obtained products to be determined, which in turn enabled the development of a strategy leading to the obtaining of a demethylated product under mild reaction conditions. In this publication, six complex compounds is presented: **K1** [$Cu(L1)Cl_2$], **K2** [$Cu((L1)-CH_3)Cl$], **K3** [$Cu_2((L1)-CH_3)_2Cl(MeOH)$]$ClO_4$, **K4** [$Cu(L2)Cl_2$], **K5** [$Cu(L3)Cl_2$] and **K6** [$Cu(L3)_2Cl(ClO_4)$]MeOH. Oxidative *O*-demethylation was observed only for compounds based on the **L1** ligand using appropriate reaction conditions. When a chlorate(VII) anion is added to the **K1** complex, the **L1** ligand is demethylated at the metal center, resulting in the formation of **K2** and **K3** complexes with the demethylated ligand.

The second and third publications show the self-assembly of the N,N,N-donor ligand of the Schiff base type **L4** [$C_{10}H_{11}N_5$] in the presence of $Cu(CH_3CN)_4BF_4$ and $Cu(BF_4)_2 \cdot xH_2O$ salts to form the multicore complex compound **K7** [$Cu_4((L4)-H)_4(BF_4)_2(MeOH)_2$]$(BF_4)_2$ and the monometallic complex **K8** [$Cu(L4)_2$]$(BF_4)_2$, respectively. The resulting supramolecular systems were used to modify the surface of the gold electrode, and it was verified whether the electrode so modified could serve as a conducting element in an electrochemical sensor for detecting neurotransmitters present in living organisms (dopamine and epinephrine). The structure of the studied supramolecular systems allowed their adsorption on the gold surface without the use of thiol moieties, which, despite their numerous and well-known disadvantages, such as susceptibility to pH changes, oxidants and organic solvents, are widely used in gold surface modification due to the ease of S-Au binding. Another advantage is that gold electrodes modified in this way can be used for independent detection of dopamine and epinephrine, as well as for their detection in the presence of interfering agents (ascorbic acid and uric acid) under aqueous, i.e. near physiological conditions. The use of the proposed voltammetric sensors can help control the content of neurotransmitters in living organisms increasing the chance of faster detection of neurodegenerative diseases.

The fourth publication deals with hybrid materials **H1** – **H3** obtained by a reaction between the pyridine ligand **L5** [$C_{20}H_{19}N_3O_2$] with the R^1-C(=O)-O-R^2 grouping, where R^1 – $C_{17}H_{14}N_3$, R^2 – C_2H_5, or its complexes **K9** [$Zn(L5)Cl_2$] or **K10** [$Zn(L5)_2$](ClO_4)$_2$ and a modified Wells-Dawson-type polyoxometalate **WD-POM** $(TBA)_4H_2[H_2NC(CH_2O)_3P_2V_3W_{15}O_{59}]\cdot 3C_3H_7NO$ containing the R^3-NH_2 grouping. This publication focuses on selecting an appropriate route to synthesize the desired products, studying stability and interactions with nucleic acids.

The last publication in the series is a review publication covering the broad topic of Wells-Dawson-type polyoxometalates, their structure, types of modifications, functionalization possibilities using the introduction of organic substituents, including ligands or their complexes, species in environments with different pH values, and application possibilities in fields such as catalysis, magnetism, medicine and as other functional materials.