

# Polydioxothiadiazoles: new platform for true molecular multivalency

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## Abstract

The development of modern materials, with properties that can be freely adapted to needs and changed over a wide range in the finished material, requires new, original molecular platforms that are the source of desired functionalities. The ability to modify the final characteristics of the material without interfering with its structure through post-synthetic adaptations is associated with savings and allows such materials to be used not only as a structural element, but also as switches or sensors. The unique nature of molecular materials allows for the use of rational molecule design to combine multiple functionalities within a single molecular architecture and maintain these material characteristics regardless of its physical size down to individual molecules. In the age of intense miniaturization of technology, materials whose properties do not strongly depend on size are becoming the subject of intense research, paving the way for new fields of knowledge such as spintronics or quantum technologies. The search for new, original molecular structures that provide a wide range of functionalities is of strategic importance for the further advancement of materials science. In the context of limited availability of certain raw materials such as rare earth metals and growing environmental awareness, it is desirable to design solutions incorporating abundant and harmless elements. For this reason, purely organic “soft” materials are now being implemented in areas generally associated with ceramics, alloys or inorganic crystals.

The aim of this doctoral dissertation was to develop and characterize a new family of organic molecules with potential significance in the construction of multifunctional molecular materials. The 1,1-dioxo-1,2,5-thiadiazole system was adopted as an archetypal structure, whose physicochemical properties such as high chemical and thermal stability, electrochemical activity, and the ability to form stable anion radicals were decided to be used in the construction of a new heterocyclic platform with comparable, ultimately better functionalities. To achieve this, it was necessary to propose an architecture that would not only harness the benefits of dioxothiadiazoles but also ensure the presence of other desirable traits such as the ability to

bind with metal ions. The simplicity of the new system and a short synthetic path enabling the real application of the new material were also of importance. Work on the new family of compounds began with the recognition of previous achievements in the chemistry of compounds containing the 1,1-dioxo-1,2,5-thiadiazole motif - thanks to this, it was possible to choose the preferred synthetic pathway leading to the target polydioxothiadiazole analogs. A literature review also showed that there are no published examples of compounds containing more than one dioxothiadiazole group. Based on the understanding of simple derivatives of 1,1-dioxo-1,2,5-thiadiazoles efforts were made to obtain molecules with more than one such moiety in their structure.

The basis of the doctoral thesis consists of two publications **P1** and **P2**, the first of which was published in a peer-reviewed scientific journal (IF=4.6) and the second is currently under review and is also deposited in the Chemrxiv open repository.

In the first publication (**P1**), the current state of knowledge about the physicochemical properties of systems containing a heterocyclic 1,1-dioxo-1,2,5-thiadiazole fragment in their structure was presented. Structural data available in the Cambridge Structural Database were discussed and a correlation was shown between the length of individual bonds determined from single crystal diffraction experiments (SCXRD) and the valence state of the dioxothiadiazole skeleton. A summary of characteristic signatures of 1,1-dioxo-1,2,5-thiadiazoles in popular spectroscopic techniques such as NMR, IR or UV-vis was also given. Moreover, the publication contains a collection of all synthetic methods and conditions used to date to obtain 1,1-dioxo-1,2,5-thiadiazole derivatives, and typical reactivity for this system was presented. An important part of this work is the analysis of the electrochemical properties of such molecules with an indication of the possibility of obtaining dianions as a result of reduction and the absence of side processes and high reversibility of electrochemical transformations. For monoanions of dioxothiadiazoles, a summary of research on their magnetism was presented both in the context of simple alkali metal salts as well as complexes and coordination networks with *d*-block metal ions.

The second publication (**P2**) is dedicated to the synthesis and characterization of the first compound from a new family of polydioxothiadiazoles. It is the benzo[1,2-*c*:3,4-*c'*:5,6-*c''*]tris([1,2,5]thiadiazole) 2,2,5,5,8,8-hexaoxide or **tripak**. It is a molecule consisting solely of three dioxothiadiazole units, thus being an ideal realization of a polydioxothiadiazole. **Tripak** is a flat, heteroaromatic molecule consisting of 21 atoms, occurring natively in the form of a

dianion. The exceptionally rich electrochemical activity of **tripak** allows for the reversible, sequential exchange of up to 6 electrons, and the molecule has been isolated and structurally characterized in five out of six available valence states. The exchange of electrons by the **tripak** skeleton has a dramatic effect on its physicochemical properties, and the half-potentials of the relevant redox reactions span over more than 3V of electrochemical potential, making **tripak** both a strong oxidizer or reducer depending on its valence state. The very fact that certain valence states of **tripak** (monoanion and neutral form) are available as a result of oxidation distinguishes it from simple dioxothiadiazole derivatives for which the native forms are neutral and additional valence states are available only through reduction.

In the frame of perspectives, a second molecule obtained in the same synthesis is presented - *4H,8H*-benzo[1,2-*c*:4,5-*c'*]bis([1,2,5]thiadiazole)-4,8-dione 2,2,6,6-tetraoxide or **dipak**. It is a system containing two dioxothiadiazole rings with physicochemical properties in many aspects similar to **tripak**. **Dipak** presents rich electrochemical activity allowing access to many valence states. Due to the presence of two C=O bonds in its structure, it is susceptible to further functionalization. It is also a system complementary to **tripak** in the context of constructing molecular materials involving metal ions due to different geometry and type of atoms available for coordination. An outline of further research on polydioxothiadiazole systems with more complex architecture was also presented.

The research presented in this doctoral thesis was conducted in the Organometallic Molecular Materials Group, Faculty of Chemistry of the Jagiellonian University and in the research group of Prof. Selvan Demir, Department of Chemistry, Michigan State University, Lansing, Michigan, USA. A six-month research stay in the United States was made possible by thanks to a scholarship awarded by the Kosciuszko Foundation for the period 10.2020 - 04.2021. Work on new systems based on the dioxothiadiazole motif was carried out as part of the PRELUDIUM 20 project (No. 2021/41/N/ST5/04375) funded by the National Science Center.