Gdańsk, September 8th,2025 r.

Review

of the doctoral dissertation of M.Sc. **Martyna Mańka**,
entitled
"Amino-functionalized MOF based thin films as sensory platforms for detection of aldehydes"

Aldehydes are among the most essential compounds in chemistry, and, probably alongside sulfuric acid (VI), which is considered the *"blood of the chemical industry"*, they have extensive applications in the chemical, pharmaceutical, and material industries. Unfortunately, they are also regarded as toxic and carcinogenic substances, which makes it necessary to develop sensitive and selective methods for their detection in the environment and in technological processes. Traditional analytical techniques, such as gas chromatography or UV-Vis spectroscopy, although precise, often require complicated equipment, sampling, and long analysis times. One alternative for the fast and selective detection of aldehydes is metal-organic frameworks (MOFs). MOFs are most often synthesized by the solvothermal or hydrothermal method, consisting of the reaction of a metal salt with an organic ligand (e.g., dicarboxylic acid, imidazole) in an organic or aqueous solvent at elevated temperature and pressure. Alternative methods include microwave, ultrasonic, electrochemical, or mechanochemical synthesis, which enable the production of materials with controlled morphology and crystal size. The materials obtained in this way are characterized by high stability against external factors, porosity, a huge specific surface area, and possibilities for chemical functionalization. These unique MOF properties allow the design of sensors capable of fast and selective detection, including aldehydes.

The doctoral dissertation submitted to me for evaluation of the M.Sc. Martyna Mańka, entitled "*Amino-functionalized MOF based thin films as sensory platforms for detection of aldehydes*," was prepared at the Faculty of Chemistry of Adam Mickiewicz University in Poznań in cooperation with the Institute of Supramolecular Science and Engineering of the University of Strasbourg. The role of supervisors of this dissertation was entrusted to Prof. Violetta Patroniak from the Faculty of Chemistry of AMU and Dr. Artur Ciesielski (HDR, Strasbourg). In addition, the role of co-supervisor was held by Dr. Marta Fik-Jaskółka from the Faculty of Chemistry of AMU. Such a scientifically distinguished group of supervisors guarantees its high substantive quality. The dissertation is written traditionally. Part of the material included in the dissertation was published in the form of one short article in *Chem. Comm.*

Due to the research being carried out in international scientific cooperation, the dissertation was written in English. Additionally, it includes summaries both in Polish and French. The summary contained in this dissertation (regardless of the language in which it was written) is, in my opinion,

Prof. Mariusz Makowski,
University of Gdańsk, Faculty of Chemistry,
Head of the Department of Bioinorganic Chemistry,
ul. Wita Stwosza 63, 80-308 Gdańsk, Poland
tel. +48 58 523 50 55, email: mariusz.makowski@ug.edu.pl

very extensive. The doctoral student essentially writes what is contained in the individual chapters here. After the pages devoted to summaries, there are several items of the cited literature included in them. I will devote a few sentences later in my review to the issue of including cited reference items in the evaluated dissertation.

Then, two pages are devoted to the symbols and abbreviations included in the dissertation. To tell the truth, there are quite a lot of them, and it is difficult for the reader to remember them all. Two of the abbreviations seem to be unfortunate. The doctoral student states that pK_a is the *"acid dissociation constant"*, and ACE is "absorbance caused enhancement." pK_a is the negative decimal logarithm of the acid dissociation constant of a given compound. At the same time, ACE may be confused with the Angiotensin-Converting Enzyme, commonly used in biochemistry. The table of contents is the next three and a half pages.

The most extensive part of the dissertation, as many as 81 pages, is Chapter 1, entitled Introduction (divided into subsections). One of the subsections of this part of the dissertation is entitled "*Motivations and aim of the thesis.*" I believe that the aim and motivation of the research should be emphasized more strongly in a doctoral dissertation, even in the form of a separate chapter. Chapter 1 contains the most important general information about MOFs, their synthesis methods, stability to pH changes, and their applications as sensors for electrochemical and fluorescence detection of various substances in the human environment. The motivation and aim (subsection 1.7) of the research carried out by the doctoral student is (in general) the development of sensors for the electrochemical detection of aldehydes. The doctoral student proposes to seek a solution to her problem in two classes of compounds, i.e., four zeolitic imidazolate frameworks (ZIFs) and 3 MOFs functionalized with 2-aminoterephthalic acid consisting of Ni, Cu, and Co metal ions. The doctoral student proposes to obtain and examine 4 ZIFs, in which the structures contain Zn and Co ions and are coordinated by 2-methylimidazole or 2-aminobenzimidazole. Of course, the products obtained in this way will be structurally and morphologically characterized, in terms of stability to physicochemical factors, and tested for aldehyde detection, by first preparing appropriate layers of electrode material used for detection. Finally, this chapter contains 403 references cited in this part of the dissertation, listed on 25 pages. Chapter 1 is carefully written, with good quality illustrations and their descriptions. However, the title of the slightly more than 1-page subsection 1.1 *Brief introduction to coordination chemistry* is at least an overstatement. The reader expects basic information on the (physico)chemistry of coordination compounds, properties, crystal field theory, etc., and receives information that coordination compounds have long been known and used. This subsection would undoubtedly have gained in value if the doctoral student had explained why imidazole readily forms monodentate coordination bonds with nickel and cobalt ions.

Chapter 2 (32 pages) is, according to the author of the dissertation, a description of the techniques used for the chemical characterization of MOFs. I very much like that at the beginning of each chapter, the reader is informed what is included in it. However, the doctoral student probably meant to write here that she describes physical (physicochemical) as well as analytical and computational methods to confirm the structure, morphology, durability, and electrochemical properties of MOFs. This chapter is written quite well. Some fragments are very extensive; they could even be used as instructions in academic textbooks, and others, such

Prof. Mariusz Makowski,
University of Gdańsk, Faculty of Chemistry,
Head of the Department of Bioinorganic Chemistry,
ul. Wita Stwosza 63, 80-308 Gdańsk, Poland
tel. +48 58 523 50 55, email: mariusz.makowski@ug.edu.pl

as subsection 2.2.2 *Structural simulations*, in my opinion, does not contain any relevant information on DFT, remaining at a very high level of generality. I am aware that the doctoral student did not perform the calculations herself, but commissioned them to a collaborating person. However, she could have asked for a more extensive description, supported by some application examples, as was done in the later part of the dissertation. The whole of Chapter 2 contains a lot of equations. However, the doctoral student provides the units of the described quantities selectively. The final dimension of the given physical quantity should have been used consistently. This would improve readability. In subsection 2.5 *Materials*, there is information about the origin of the materials necessary for the synthesis of ZIFs and MOFs. Now I will refer to the cited references, which I mentioned earlier. Namely, in 2.6 *References*, there are 58 items numbered from the beginning. The numbers of these items do not correspond to numbers 1–58 in the previous subsection 1.7. However, I noticed that the items in Chapter 2 correspond to the 58 items from subsection 1.7, only renumbered here. What was the purpose of this procedure? This remark also applies to the references included later in Chapters 3 and 4. In a classical doctoral dissertation as well as in publications, it is customary to place the cited literature at the very end of the dissertation.

The results section is divided into two chapters, 3 and 4, respectively. Both chapters are written similarly. They differ only in the subclasses of the MOFs obtained and studied. The doctoral student describes in Chapter 3 (31 pages) the synthesis of 4 ZIFs with linkers 2-methylimidazole and 2-aminobenzimidazole with zinc (ZIF-8 and NH_2-ZIF-7) and cobalt (ZIF-67 and NH_2-ZIF-9). For these compounds, she performed a whole series of structural and morphological studies (Powder X-ray, DFT, FT-IR, XPS, and SEM). TGD measurements confirmed high thermal stability. Specific surface area (SSA) and pore structure were estimated based on nitrogen adsorption and desorption isotherms. The compounds were also exposed to aldehydes to test the durability of the obtained ZIFs. Based on the collected results in Tables 3.4–3.7, the doctoral student stated that the ZIF systems synthesized using 2-aminobenzimidazole with nickel and cobalt ions show the highest sensitivity to the detection of the three aldehydes tested. I want to ask for an explanation of how to understand the sensitivity and LOD (Limit of Detection) values given in Tables 3.4–3.7. What is the difference between them? On page 143, third line from the top, there is the sentence "*As shown in Table x (...)*". I did not find Table x in the dissertation. Table 3.8 contains the results of detecting tap water spiked with aldehydes. The introduced amounts of contamination with formaldehyde, acetaldehyde, and benzaldehyde were known. The experiment aimed to determine the effectiveness of the ZIF detectors used. In all the cases presented in the Table, aldehyde detection was above 95%. These are very high values. But if one looks at these values in comparison with RSD (I assume that means Relative Standard Deviation). In chromatographic methods, values with RSD < 2% are considered satisfactory. In the presented Table 3.8, apart from one case, RSDs are close to values of 10, which may indicate a problem with repeatability. Please comment. RSD is defined as the ratio of the standard deviation divided by the arithmetic mean of the measurement, and of course, the whole multiplied by 100%. If the measurement was performed (repeated) several times, such information should be included in the result tables. Subsection 3.5 is a collection of conclusions from the studies for ZIFs and a description of the perspective of further optimization of ZIF electrochemical sensors and the extension of their environmental and biological applications.

Prof. Mariusz Makowski,
University of Gdańsk, Faculty of Chemistry,
Head of the Department of Bioinorganic Chemistry,
ul. Wita Stwosza 63, 80-308 Gdańsk, Poland
tel. +48 58 523 50 55, email: mariusz.makowski@ug.edu.pl

The scheme of Chapter 4 (27 pages) is the same as in Chapter 3, with the difference that the doctoral student obtains and studies another subclass of 3 MOFs functionalized with 2-aminoterephthalic acid, consisting of Ni, Cu, and Co metal ions. Then the obtained MOFs undergo the same physicochemical procedures, and their effectiveness is tested. The advantage of the MOFs studied here is lower detection limits than in the case of ZIFs, i.e., nM vs μM. The results are collected in Tables 4.10, 4.11, and 12.4 (it should be 4.12). All the studied MOFs showed the highest sensitivity to formaldehyde. Interestingly, the LODs shown in these tables are three orders of magnitude lower than in the case of ZIFs, indicating better suitability for practical applications. Interestingly, in Table 4.5, there are "recovery" values > 100%, which means detecting more aldehyde than was spiked into the tap water. Moreover, in all cases, it was possible to reduce the RSD values compared to the ZIFs. This indicates better repeatability of the experiment. Please comment. As in the previous chapter, there is no information on measurement errors. Subsection 4.5 contains, similarly to 3.5, conclusions and perspectives from the studies in 4.5.

The summary of the conducted research, the conclusions drawn from it, and the research perspectives are collected on the following five pages. Additionally, it is provided with subsection *5.1 References* with six items, which, by numbering, as in Chapters 2–4, do not fit.

The following pages are the *"Statement of work"*, information about the achievements of the M.Sc. Martyna Mańka and statements of co-authors regarding their contribution to the *Chem. Comm.* publication. Based on these materials, I do not doubt that the doctoral student carried out most of the research conducted in the dissertation. She also contributed to the development of the research concept. Ms. Martyna Mańka is a co-author of two papers, one of which is from outside the subject of the doctoral dissertation. She presented the research results at three conferences, including one oral presentation. In addition, the doctoral student completed three internships at the University of Strasbourg, with a total duration of 17.5 months, was a contractor on the Sonatina-6 grant, and led two projects from AMU, as well as being a recipient of a French government scholarship from 2022 to 2025. The research presented in this dissertation, as well as the results, fulfill the criteria of scientific novelty. The material contained in the dissertation constitutes an original contribution to the development of material chemistry related to the search for electrochemical sensors for pollutant detection. The doctoral student achieved all the research objectives set in the dissertation. The remarks contained in the review are of a discussion character and in no way diminish the high scientific value of the results obtained. The dissertation constitutes an original solution to the stated research problem and meets all requirements for doctoral theses as defined by the Polish Act of July 20, 2018, "Law on Higher Education and Science".

Therefore, I recommend that the Scientific Council of the Discipline of Chemical Sciences at the University of Adam Mickiewicz in Poznań allows M.Sc. Martyna Mańka to proceed to the following stages of the doctoral examination process in the field of natural sciences, in the discipline of chemical sciences.

Prof. Mariusz Makowski,
University of Gdańsk, Faculty of Chemistry,
Head of the Department of Bioinorganic Chemistry,
ul. Wita Stwosza 63, 80-308 Gdańsk, Poland
tel. +48 58 523 50 55, email: mariusz.makowski@ug.edu.pl