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# REPORT ON THE DISSERTATION ENTITLED "DISCRIMINATION OF HOMOLOGOUS AND ISOMERIC DICARBOXYLIC ACIDS BY GOLD NANOPARTICLE-PILLAR[N]PYRIDINIUM ENSEMBLES"

*The basis for issuing the opinion on the doctoral dissertation of Mykola Kravets is the letter of Dr. Hab. Jacek Gregorowicz,(Assoc. Prof. IPC PAS) Deputy Director for Scientific Affairs of the Institute of Physical Chemistry of the Polish Academy of Sciences on March 2, 2023 (SRN.431.11.2022..2023)*

A dissertation submitted by Mr. Mykola Kravets *(hereafter referred to as the Candidate)* consists of a basis for awarding the Doctoral degree. The thesis has been conducted under the supervision of Assoc. Prof. IPC PAS Volodymyr Sashuk at the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw, and it correlates well with the research activities carried out successfully in this team. The report, which I had a pleasure to provide, will be divided into separate sections describing various aspects of the thesis.

1) Thesis content and contribution to the field

The *Thesis* consists of 107 pages, and it has been written using a standard layout. It begins with the Content, followed by the List of scientistic publications, the List of Scientific presentations, the List of Abbreviations, Abstract, Introduction, Result and Discussion, Experimental Part, Conclusions and Future Prospects. The thesis ends with list of References.

The Subchapter 1.1 details various techniques used for discriminating phthalic acid isomers, including colorimetric methods, fluorescence, electrochemical sensors, and other approaches such as gel electrophoresis, hydrogelation, complexation, and DOSY NMR. The subsequent section demonstrates the differentiation of homologous dicarboxylic acids, while the final subsection of the literature review is devoted to distinguishing geometric isomers of these acids. The literary essay commences with a succinct and thematically relevant introduction that offers a clear path for the reader to follow, making it very approachable. Furthermore, it provides 112

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items of theoretical background information that are necessary to comprehend the context of the findings presented in the following sections of the *Thesis*.

Chapter 2 of this *Thesis* describes results and discussion. The *Candidate's* research work aimed to find a universal sensor that could detect as many diacids as possible, and the PhD dissertation narrates the search for nanosensors in three acts. The first act describes the quest for a sensor capable of distinguishing between the three positional isomers of phthalic acids, which was published in a prestigious general chemistry journal, *Chemical Communications*. The authors' scientific research was of exceptional quality, and the editors invited them to design the cover. The *Candidate's* strategic approach was to employ gold nanoparticles (AuNPs), and this hypothesis was validated by obtaining various plasmonic responses, including colours variations. In the second stage of the doctoral thesis, the recognition of homologues of aliphatic carboxylic acids was described. The principle of operation of the sensor is identical, and the plasmonic coupling depends on the length, flexibility and (in)evenness of the aliphatic diacid chain. It is with real satisfaction that I note that the results of these studies described in Section 2.4 have already been published in reputable journal: *Sensors and Actuators B: Chemical*. The high quality of the research tasks described in Section 2.5 was recognized by the reviewers of the *Langmuir* journal, which is commendable for the Doctoral Student, not forgetting, of course, the leading role of the research Supervisor. Furthermore, the publication was rewarded with an invitation to the cover of the journal. The last part of the work was devoted to distinguishing the geometric isomers of the dicarboxylic derivatives ethylene, stilbene and azobenzene. It was observed that the key role is played by the distance between the carboxylic groups. For short dicarboxylic acids, a better plasmonic response is obtained for *trans* isomers, while for *cis* isomers a better plasmonic response is obtained for long dicarboxylic acids.

Chapter 3 contains the results of the conducted research presented in the form of general descriptions of experimental procedures. Noteworthy, the *Candidate* used various analytical techniques such as UV-Vis, NMR and IR spectroscopy, Dynamic Light Scattering and TEM analyses all of which were deeply discussed in experiments described in this *Thesis*. Moreover, these techniques are typically used in various scientific settings, which demonstrates the high commitment of the *Candidate* to carry out the research at the highest level.

The *Thesis* ends with Conclusions and Future Prospects, and References (141 items).

2) Quality of the work

The dissertation showcases the *Candidate's* deep comprehension of the fundamental principles of supramolecular chemistry, as demonstrated by an in-depth analysis. The scientific novelty and effectiveness of the dissertation's objectives are supported by three experimental publications. The quality and originality of the results underwent meticulous assessment by external reviewers and the editorial board. Therefore, it is unnecessary to reiterate and re-evaluate the data's quality by summarizing them again.

3) Presentation

Despite not being a native speaker, the *Candidate's* presentation is excellent. The schematic representations of the obtained results are of high quality, with well-designed figures and graphs. The thesis descriptions and format are clear, and the experimental data are presented concisely and precisely. Additionally, there is a good balance between the various parts of the thesis. It is worth mentioning that the candidate has presented their research findings orally at international conferences on four occasions, indicating their extensive experience as a chemist with a curious and open-minded approach to research.

4) Originality

The scientific novelty presented in this dissertation undoubtedly lies in the development of a simple and highly effective nanosensor, namely, the gold nanoparticle-pillar[n]pyridinium ensembles used for distinguishing homologous and isomeric dicarboxylic acids. It serves as a remarkable example of combining a visionary concept by the Promoter with practical implementation by the Doctoral Student, resulting in incredible scientific outcomes from their collaboration. The dissertation reveals not only the use of nanocooperativity to

discriminate substitution patterns of aromatic acids but also the productive scientific partnership between the *Candidate* and Dr. Iwona Misztalewska-Turkowicz (whom I had the pleasure of reviewing her PhD work several years ago).

5) Summary

The *Thesis* contains original and valuable scientific results of development of discrimination of homologous and isomeric dicarboxylic acids by gold nanoparticle-pillar[n]pyridinium ensembles, which is an important contribution to supramolecular chemistry. The thesis represents a great deal of work. The results are well presented, and their interpretation is at the high scientific level. I find the dissertation of Mr. Mykola Kravets as conceptually very interesting. The work was properly conducted and reported with due care and competence, and the analysis of the experimental results is insightful.

The exceptional scientific activity of the Candidate deserves to be emphasized. In addition to three publications included in the dissertation, he is the co-author of four other papers in recognized journals (*Synthesis, CrystEngComm, Organic & Biomolecular Chemistry, Supramolecular Chemistry*).

The excellent reputation of the *Candidate's* Supervisor, and the research team in which the work was performed had set the expectation for this *Thesis* at the impressive level. And indeed, as expected, the quality of this *Thesis* is not disappointing at any point. I believe that the scope of work presented in this *Thesis* is extremely important and useful not only from a purely scientific point-of-view, but also due to the high application potential of phthalic acids, the industrial use of which will probably increase in the coming years. Despite the low toxicity of phthalic acids, the methods of their detection should be improved to protect the environment.

In view of the above, I believe that the dissertation meets all the requirements and I recommend the Scientific Council of the Discipline of Chemical Sciences at the Institute of Physical Chemistry, Polish Academy of Science to award the candidate the PhD degree. At the same time, due to the high quality of experimental results contained in the doctoral dissertation, innovative

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ideas, which will certainly affect the development of the studied field, I recommend for its distinction.

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