Politechnika Wrocławska

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**Referee report for a PhD thesis submitted by MSc Mykola Kravets**
**entitled: „ Discrimination of homologous and isomeric dicarboxylic acids by gold nanoparticle-pillar[n]pyridinium ensembles"**
**prepared under the supervision of: dr hab. Volodymyr Sashuk (Assoc. Prof. IPC PAS)**

The PhD thesis of Mr Mykola Kravets is a 107 pages long document comprising "Abstracts", "Introduction", "Results and Discussion", "Experimental part" and "Conclusions and Future Prospects" chapters followed by "References" list. The thesis is clearly organized, with good quality of presented figures and very helpful schemes presenting discussed ideas.

Abstracts in English and Polish introduce the topic of the dissertation, which is a development of a supramolecular nanosensor designed to discriminate homologous and isomeric dicarboxylic acids. The sensor comprises of gold nanoparticle-pillar[n]pyridinium (P4P with n=4 or P6P with n=6) ensembles, which exhibit surface plasmon resonance (SPR) in the visible range of wavelengths, with the position (and thus the color of the solution) dependent on the distance between nanoparticles. Thus, in principle, the aim is to develop a colorimetric sensor with visual discrimination of selected diacids. The first part of the research work is devoted to phthalic acids, which are positional isomers, then aliphatic dicarboxylic acids, which are chemical homologs and the third part is devoted to geometric isomers: dicarboxylic derivatives of ethylene, stilbene and azobenzene. The application of plasmonic noble metal nanoparticles in colorimetric sensors of small molecules has been broadly studied since the first works of Chad Mirkin and co-workers in 1990ties (Elghanian et al. "Selective Colorimetric Detection of Polynucleotides Based on the Distance-Dependent Optical Properties of Gold Nanoparticles" Science 1997, 277, 1078– 1081). However, as there is a great need for portable sensor technologies (in medical diagnostics, field-testing applications etc.), this topic is still broadly and actively investigated, especially as the sensors based on plasmonic gold/silver nanoparticles address many of the requirements of portable and colorimetric sensors: they are robust, simple to use and can be made low cost. Moreover, with a proper functionalization of nanoparticles, they may provide very high selectivity and sensitivity, which can be the foremost motivation in applications like the one described in the thesis, where gold nanospheres are tested for the detection and discrimination of dicarboxylic acids. In the introductory part of the thesis, Mr Kravets presents a broad overview of the literature about existing chemical sensors with colorimetric, fluorescent, electrochemical and other detection methods. The chapter is divided to sensors specific for phthalic acid isomers, dicarboxylic acid homologs and dicarboxylic acid geometric isomers. I appreciate that more than 100 articles are cited here, but it will be very helpful for a reader to conclude each part with the summary: what is already achieved and what are the main challenges still remaining to overcome. The author provides broad introduction to the structures of compounds with confirmed dicarboxylic acid - binding property, although screening for an appropriate compound for binding of dicarboxylic acids is not a central part of the thesis. Unfortunately, there is no introduction to plasmonics and its application in colorimetric sensors. We a few references are cited about sensors of dicarboxylic acids with plasmonic nanospheres (compounds 8, 26, 27), but there is no clear information why the application of plasmonic nanoparticles is beneficial in sensing and more beneficial than already existing chemosensors. I hope Mr Kravets can comment on that during his defense.

In the first experimental chapter recognition of various phthalic acids is described, where naked gold nanoparticles are post-synthesis stabilized with P4P molecules. This simple strategy enables to produce P4P@AuNPs as a core of nanosensor. The author investigated the temporal stability of decorated NPs, which is an important issue in case of such systems. Throughout the thesis the exact time point when the presented measurements are performed is well documented, also in the mixtures of NPs with dicarboxylic acids. Upon mixing with phthalic acid (1,2-acid), isophthalic acid (1,3-acid) and terephthalic acid (1,4-acid) different colorimetric response was observed: the initially red color changed to pink, blue and violet, for 1,2-acid, 1,3-acid and 1,4-acid, respectively. The combination of dynamic light scattering (DLS) and transmission electron microscopy (TEM) characterization of nanoparticle diameters and inter-particle distances enabled the author to propose a mechanism of the interaction between P4P-stabilized nanoparticles and the investigated phthalic acids. As a control experiment, nanoparticles stabilized with 11-mercapto-N,N,N-trimethylundecan-1-aminium chloride (TMA) were prepared and mixed with the investigated phthalic acids. Similar changes of colors were observed regardless of the phthalic acid used in this case, what was confirmed with UV-Vis absorption spectra. Thus, the discrimination between 1,2-acid, 1,3-acid and 1,4-acid was not possible in case of TMA ligand. Surprisingly, DLS measurements showed no changes in nanoparticles diameter, so is there any explanation of simultaneous large change in SPR position and no change in the average hydrodynamic size of nanoparticles?

In the next paragraph recognition of dicarboxylic acids homologs with P4P-stabilized and P6P-stabilized nanoparticles is described. Most of the acids introduced changes in color and position of SPR band possible to distinguish respective long and short acids in case of P4P ligands, but not for P6P ligands. Chromaticity diagrams and UV-Vis spectroscopy was required in this case to precisely distinguish between diacids of various length (number of carbon atoms). The results were supported with TEM analysis where the distance between nanoparticles was evaluated. Here, I would suggest to present the average interparticle distance with the standard deviation.

In the third paragraph, recognition of geometric isomers of three compounds were described: butendioic acid, azobenzene-4,4'-dicarboxylic acid (ADA) and stilbene-4,4'-dicarboxylic acid (SBDA). The author describes also experiments which aim at controlling nanoparticle self-assembly by light. The topic of photo-switchable assembly of nanoparticles has been developed for many years (eg. by R. Klajn and co-workers), but still various aspects of photochromic molecules isomerization in the presence of nanoparticles are not resolved. In the dissertation, in solutions of NPs with both, ADA and SBDA, UV and visible light illumination cycles produced reversible changes in the hydrodynamic radius of NPs' aggregates. The author also points out differences in the response of ADA and SBDA, where the former one produced gradual increase in the size of aggregates with each additional illumination cycle. The authors suggest that the observed differences come from the slight difference in pH of the solutions and "nonspecific" aggregation. However, the efficiency of photoisomerization may vary when photochromes are attached to/adsorbed on nanoparticles and I wonder if it was measured by the author how UV-Vis spectra change in a photochromic dye range after each illumination cycle (at least for ADA, which has absorption bands in longer range of wavelengths). Is it possible to determine the efficiency of photoisomerization and the content of trans- and cis- in a photostationary state?

The "Results" chapter is followed by "Experimental part", where materials and methods applied in the described experiments are listed, together with the protocols of spectroscopic/microscopic measurements. The last paragraph summarizes the results and very briefly mentions future prospects (in one sentence). It will be interesting to hear from the author which of his results satisfy the initial requirements posed for the dicarboxylic acid sensors and in which case application of nanoparticles is beneficial in comparison to organic sensors described in the previously cited literature. As the field of plasmonic nanoparticles is rich in various shapes and sizes, is it possible to improve the nanosensors performance if other nanoparticles morphologies are applied than the nanospheres presented in the thesis?

Overall, the dissertation is well written and I did not find any grammar/spelling errors, so I appreciate the additional work devoted to polish the language of the thesis. The thesis presents an original contribution to the knowledge on discrimination of dicarboxylic acids and plasmonic colorimetric nanosensors. A high quality of the presented results is confirmed by their publication in renown journals (Chemical Communications, Langmuir, Sensors and Actuators B: Chemical). This, together with three other publications which Mr Kravets co-authored, is a very good publication record for a PhD student and promising starting point towards further research work (if this is what the author wish to continue).

I find the thesis interesting and communicating original findings in actively studied topic of nanosensors based on plasmonic nanoparticles. Mr Kravets proved with the research described in the thesis that he can adopt appropriate research methods and draw meaningful conclusions to address scientific challenges defined at the beginning of his thesis. Hence, I conclude that the thesis presented by Mr Kravets meets all the requirements for doctoral dissertations included in the Act "art. 187 ustawy z dnia 20 lipca 2018 r. - Prawo o szkolnictwie wyższym i nauce (Dz. U. z 2022 r. poz. 574 ze zm." and I submit the application to the Scientific Council of Institute of Physical Chemistry, Polish Academy of Sciences for the admission of Mr Kravets to further stages of the doctorate.

J. Olesiak-Bańska