Politechnika Wrocławska

Wydział Chemiczny, Instytut Materiałów Zaawansowanych

Wrocław, 05.09.2022

Referee's Report on the Ph.D. thesis entitled
"Characterisation of donor-acceptor system as materials for organic optoelectronics"
written by MSc. Aleksandra Nyga.

Ph.D. thesis presented by MSc. Aleksandra Nyga is mostly devoted to the studies of the phenomena of singlet oxygen photogeneration in the organic charge transfer compounds and its impact on the optoelectronic devices. The research and thesis preparation of MSc Nyga was conducted under the joint supervision of Professor Przemysław Data and DSc Agata Blacha-Grzechonik.
The studies have been performed at the Faculty of Chemistry, Silesian University of Technology.

The subject of the presented PhD thesis is in line with the latest trends in the research of new functional materials for use in the production of modern devices such as OLEDs, displays, light modulators, energy storage and other optical devices. Although the subject started a few decades ago there is still room for improvements and new discoveries which makes the topic timely and worth exploring.

The reviewed doctoral dissertation shows an interdisciplinary approach, combining physical chemistry and materials engineering, which is currently more and more common in the case of experimental work in the discipline of chemical sciences. Dissertation is presented in the form of the 30 page long introduction to the topic and a series of 5 original papers published in the international, peer-reviewed journals, namely: Applied Materials Today, Chemical Communications, Applied Surface Science, Materials Advances and Materials. A. Nyga is the first author of the papers included in the thesis.
Literature overview presented as an introduction part of the thesis contains only 41 citations which seems to be very modest taking into account the maturity, importance and richness of the explored field. However, the first paper introduced in the manuscript is a review article with 150 citations in it which makes me believe that the MSc Nyga is familiar with the works in the scope. Four other papers are research papers in the highly reputable journals with high IF, which were peer-reviewed.

In my opinion, the most important achievements of A.Nyga doctoral dissertation consist of:

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budynek A-2 /A-3

1. Discovery of the relationship between various types of D-A molecules with singlet oxygen production;
2. Studies and understanding of competing radiative and non-radiative processes in the collection of the standard photoactive materials;
3. Propositions of the application of the studied materials as antibacterial coatings.

From the editorial point of view, the work has a layout characteristic of experimental doctoral dissertations based on the already published works: after abstracts in English and Polish, there is a list of the publications of the PhD student, followed by a glossary. Next, short foreword with the purpose of the research is followed by the modest literature overview on the organic materials used in the optoelectronics, containing the information needed in the further parts of the thesis. Aim of the work is presented on the half of the page clearly emphasising the main novelty being the investigation of the singlet oxygen photogeneration on the D-A materials. Research methodology consisted of electrochemical, spectroscopic and spectroelectrochemical characterisation of selected D-A systems namely: cyclic voltammetry, EPR spectroelectrochemistry, UV-Vis-NIR spectroelectrochemistry, layers formation, electrochemical polymerisation (for two selected systems) and spin-coating details for one molecule as well as chemical grafting for other molecule. Finally, the details of the singlet oxygen photogeneration are described. This paragraph is followed by 14-page long presentation of the results and its discussion.

The entire doctoral thesis consists of 44 pages plus 5 original papers and is written in English.
The results in the experimental part are supported with the graphics and in the body text and presented in the form of figures and tables.

The role of the reviewer is to point out some flaws which are quasi impossible to avoid while we are not native speakers. I will list just a few, nevertheless their do not diminish overall quality of the thesis. As examples:
Page 5 – approach to study (not to studying);
Page 6 – last sentence incomprehensive due to its length and word order;
Page 8 – the formatting,
Page 9 – M5, incoherent citation (full name of the 2nd author)
Page 10 – O3, incoherent punctuation
Page 15 – “process appears”
Page 16 – “Another possibilities are so-called blends (..)”
etc.

However, I have a few questions that I would like to have answered during the discussion:

1. What was the materials selection key?
2. The main deposition techniques are spin-coating, chemical grafting and electrochemical methods. Can you name any other techniques suitable for the material deposition? What would make chosen methods superior over other available techniques?
3. What was the thickness of the studied layers and what was its influence on the singlet oxygen production?
4. The research were done at room temperature. What would be the influence of the temperature on the photophysical properties of the presented materials?
5. There was a polymerisation process observed for the germanium derivative on the gold and platinum electrodes - what was the origin of this process?
Summarizing, the evaluation of the studies conducted as part of the doctoral dissertation, I believe that the research tools used by the PhD student to characterize the new materials exhibiting singlet oxygen production were appropriately selected and applied. Obtained results and their analysis were presented in a logical, comprehensible and clear manner and discussed based on the current state of knowledge.

I appreciate the doctoral dissertation of MSc. Aleksandra Nyga. I would like to again emphasize that the PhD student is a first co-author of 5 papers published in a peer-reviewed journals and 3 other papers, out of the main scope of the thesis, but in the terms of the overall studies in the field of optoelectronics.
I assume that in the 5 articles her contribution is dominant, in the next papers she is also the first, second and third author, respectively which makes her role also important. She took part in the realization of the First TEAM project financed by the Foundation for Polish Science and she was a scholarship holder of the above mentioned project, which, I believe, is also a significant achievement. I did not find the information about the conference participation or research training which may be due to the pandemic.

To sum up, the PhD student, based on her research, brought new information about the photophysical properties of D-A organic systems in terms of the possibility of singlet oxygen production and propagation as well as has shown a scientific maturity level corresponding to the PhD student status.

Thus A. Nyga achieved the goal set at the beginning of her doctoral dissertation contributing to the extension of the existing knowledge in the field of optoelectronics and establishing the role of the singlet oxygen on the D-A materials.

The doctoral dissertation submitted for review by MSc. Aleksandra Nyga therefore presents an original solution to a scientific problem, confirms the

candidate's general theoretical knowledge in the field of chemistry and the ability to conduct scientific research. The dissertation meets the customary and statutory requirements for doctoral dissertations in the Act of July 20, 2018 - Law on Higher Education and Science.

Therefore, I would like to propose the Chemical Sciences Discipline Council of the Silesian University of Technology to admit the PhD student to the next stages of the doctoral dissertation defence.

Dr hab. inż. Katarzyna Matczyszyn, professor PWr