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JAGIELLONIAN
UNIVERSITY
IN KRAKOW

Marian Smoluchowski

Institute of Physics

Referee's Report on the Ph.D. Thesis entitled
"Charge transfer compounds as sources of laser light"
written by MSc. Eng. Martyna Durko-Maciąg

Ph. D. thesis written by MSc. Eng. Martyna Durko-Maciąg is devoted to study the phenomena of light amplification of organic charge transfer compounds - new materials with potential applications, and was conducted under supervision of Professor Jarosław Myślwiec and Doctor Julien Massue. The research has been done at the Faculty of Chemistry, Wroclaw University of Technology in Poland as well as French National Center for Scientific Research and University of Strasbourg in France, as a part of the program of interdisciplinary cross-institutional post-graduate studies KNOW in the field of Biotechnology and Nanotechnology (BioTechNan). The reviewed doctoral dissertation is interdisciplinary in nature, combining chemistry and material engineering, which is now becoming more and more common in the case of experimental work in the discipline of chemical sciences.

The subject of this 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 displays, light modulators, energy storage and optical devices, including lasers. Although the first lasers were constructed in the 1960s and many devices using them have been created so far (from everyday use pointers, printers or readers through devices in industry like engraving or cutting machines for both aesthetic medicine, imaging and therapies, e.g. cancer treatments), extensive research on the search for materials with appropriate parameters that would reduce the cost of their production are still attractive. Currently, many types of lasers are used, differing in power (from very low to high), mode of operation (pulsed, continuous), the range of radiation (infrared, visible, ultraviolet) and finally the active medium. Although commercially available lasers are based on inorganic materials, the organic materials can be also used to produce lasers, working as solutions or guest-host systems. One type of laser based on organic material is distributed feedback (DFB) laser in which the active area of the device contains an element with a periodic structure (1D, 2D or 3D) forming an interference mesh that provides optical feedback to the laser. Lasers of this type are attractive due to their compact design, which makes it possible to use them in integrated systems. However, organic DFB lasers have not yet been commercialized, although they are easy to tune and exhibit large cross-section of stimulated emission. So, organic compounds and dye-polymer systems have a high application potential (although they are less stable than inorganic ones), because

Professor Dr. Monika Marzec
Head of Department of Advanced Materials Engineering
Liquid Crystals Group: http://www.zinm.if.uj.edu.pl/liquid-crystals
e-mail: Monika.Marzec@uj.edu.pl
tel. +48 12 66 44 549

ul. St. Łojasiewicza 11
PL 30-348 Kraków
tel. +48(12) 664-47-03
fax +48(12) 664-49-06
e-mail: fizyka@uj.edu.pl

their physicochemical properties can be easily changed by modifying the chemical structure and the technology of organic materials is easier and cheaper then inorganic ones. Therefore, it becomes very important to characterize new organic materials by finding the dependence of their properties on the chemical structure and the interactions between components in guest-host systems.

As part of the doctoral dissertation, MSc. Eng. M. Durko-Maciąg investigated the properties of organic Excited-State Intramolecular Proton Transfer (ESIPT) chromophores, focused on the light-matter interactions, in terms of their use as a source of laser radiation. PhD student chose 18 non-commercial compounds exhibiting Excited-State Intramolecular Proton-Transfer phenomena (sixteen 2-(2'-hydroxyphenyl)benzazole derivatives – HBX and two Schiff bases), from which she synthesized 3 compounds on her own. This choice is justified because both the molecular structure of these compounds and the confirmed ESIPT behavior indicate their light-enhancing potential. The studies of the properties were done in dilute solutions and solid guest-host systems, where potassium bromide and two polymers (PMMA and PS) were used as host matrices. In my opinion, the most important achievements of M. Durko-Maciąg's doctoral dissertation include:

1. Discovery of the relationship between substitution with different heteroatom in HBX derivatives and fluorescence energy - the highest for nitrogen substitution (HBI) and the lowest for sulfur substitution (HBT).

2. Demonstration that for all studied compounds there is a large Stokes shift due to proton transfer in the excited state as well as confirmation the existence of the ESIPT phenomenon in a thin layer of polymer matrices doped with the studied chromophores.

3. Showing that aggregation induced emission enhancement (AIEE) is characteristic only for six of eighteen studied organic chromophores while for others the quenching of emission caused by aggregation takes place, with complete quenching for two Schiff bases.

4. Showing that, apart from Schiff bases, all sixteen HBX derivatives placed in a polymer matrix (thin films) are capable of stimulated emission, where population inversion can be achieved by a four-level system based on ESIPT photocycle.

5. Demonstration for the first time the stimulated emission in the anionic form of the ESIPT chromophores.

6. Demonstration that DFB lasers with tuneability exceeding the profile of random lasing action (> 39 nm) can be produced on the basis of thin layers of HBX-doped polymers.

Summarizing the evaluation of the research conducted as part of the doctoral dissertation, I believe that the research tools used by the PhD student to characterize the new commercially unviable materials exhibiting Excite-State Intramolecular Proton-Transfer phenomena were appropriately selected and applied. The obtained results and their analysis were presented in a logical, comprehensible and clear manner and discussed based on the current state of knowledge. Such a large number of tested materials allowed to find out the correlation between the chemical

structure and/or the surrounding matrix and the photophysical properties of ESIPT compounds, including lasing ability. I highly appreciate the doctoral dissertation of MSc. Eng. Martyna Durko-Maciąg. Both the way of presenting the research results and the methods of their analysis prove the great knowledge of the PhD student. I would also like to emphasize that the PhD student is a co-author of 6 papers published in a peer-reviewed journals and one paper under review. These articles have 5-9 authors and this number of authors involved in research is typical of interdisciplinary work, because contemporary research is based on collaboration between different scientists and research institutes. M. Durko-Maciąg is the first author in 3 of these 7 papers, so I can assume that in these articles her contribution is dominant, in the next two she is the second and third author, which also indicates her significant contribution. PhD student presents his scientific results in the form of oral presentation at two international conferences and participated in research in the framework of 5 projects financed by the Polish National Science Center (OPUS, SONATA, POLONEZ).

From the editorial point of view, the work has a layout characteristic of experimental doctoral dissertations: after abstracts in Polish and English, there is a short foreword with the purpose of the research following by the theoretical part containing all the necessary information needed in the further parts of the thesis. Then there is the experimental part with the description of the studied materials and their synthesis as well as the description of the research methods used, followed by the presentation and discussion of the results, which is the most extensive part of the work. The thesis ends with conclusions in which the perspectives are also described. The biography is provided after each chapter. The list of symbols and abbreviations is provided at the beginning, which is helpful while reading the thesis. Dissertation is complemented by the inclusion of two appendixes (Details of the synthesis - Apendix A and Author's research achievements - Apendix B). The entire doctoral thesis consists of 166 pages (144 numbered with Arabic numerals, 14 with Roman numerals, and the rest without numbers) and is very well written in English. In this case, writing the thesis in English is fully justified, because one of the supervisors is not of Polish nationality. The results in the experimental part are very well discussed in the body text and presented in the form of high-quality figures and tables. I consider it a very good move to include a summary after each chapter as it highlights the most important results from each part of the thesis. I also would like to emphasize that the synthesis of the samples as well as their characterisation required work, effort and accuracy from the PhD student, which I really appreciate. The thesis is prepared very carefully and a few editorial errors are not worth mentioning.

The role of the reviewer is to point out mistakes or possible discussion issues, but the work is so well prepared that it is difficult to indicate them. However, I have three questions that I would like to have answered during the discussion:

1. PhD student found that by changing the polymer matrix it is possible to tune the final stimulated emission. Were there considered other kind of polymers to be doped with studied chromophores? Is it possible to use for example biodegradable polymers, like PLA or PCL?
2. The thin layers of doped polymer were prepared by drop casting. Were other kind of methods tested? I mean spin-coating or H-dipping. Is it possible that thin layers obtained by various methods will exhibit different photophysical properties?

3. The research were done at room temperature. Is it possible that the temperature can influence photophysical properties of polymer doped thin layers?

Summarizing, the PhD student, based on her research, brought new information about the photophysical properties of commercially unavailable organic chromophores (ESIPT) in terms of the possibility of amplifying light through stimulated emission in a four-level system and opportunity to tune their properties by chemical substitution or/and type of host system. Thus M. Durko-Maciąg achieved the goal set at the beginning of her doctoral dissertation contributing to the extension of the existing knowledge in the field of light-enhancing organic materials and showed for the first time that the stimulated emission in the anionic form of the ESIPT material takes place. The doctoral dissertation submitted for review by MSc. Eng. Martyna Durko-Maciąg, 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 independently conduct scientific work. The dissertation more than meets the customary and statutory requirements for doctoral dissertations in the Act of July 20, 2018 - Law on Higher Education and Science. Therefore, I am applying to the Chemical Sciences Discipline Council of the Wroclaw University of Science and Technology to admit the PhD student to the next stages of the doctoral dissertation.

At the same time, taking into account the very rich experimental material, the high level of research as well as the editorial level of the dissertation, and the scientific achievements of the PhD student, I would like to request the award of Martyna Durko-Maciąg's doctoral dissertation.