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Review of the doctoral dissertation of

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"D-π-A type of chromophores for light amplification and nonlinear optics applications"

Doctoral dissertation of Anna Popczyk, MSc Eng., concerns the study of thiophene derivatives in terms of optical properties that can be used in non-linear and laser optics. The work was created as part of the Cotutelle doctorate in cooperation between the Wrocław University of Technology and the University of Angers and the promoters are, respectively, Prof. Jarosław Myśliwiec and Prof. Bouchta Sahraoui. Both promoters manage teams with a very good international reputation, well-equipped laboratories, and guarantee a high level of work and innovative topics. Anna Popczyk made good use of these opportunities collecting very extensive and diverse research material. She is a co-author of 4 articles in JCR journals, presented her results at several conferences, including the Workshop on Nonlinear Optics Applications in 2018, where she got award for the best oral presentation.

The subject of the work covered a vast research area, ranging from design and synthesis of the chemical structure through measurements of its optical properties to the proposal of applications in sensors and DFB lasers. Part of this work was carried out at the MOLTECH Anjou Laboratory (Angers), included the synthesis of new thiophene derivatives and the characterization of their optically nonlinear properties by measuring the second and third harmonic generation efficiency. In the Nonlinear Optics Laboratory of the Wrocław University of Technology, the optical Kerr effect and random laser action were tested.

The work contains extensive material, well described and systematized, with summaries after larger chapters. I have not found significant errors or inaccuracies and typographical errors do not exceed the number considered indecent. Despite the large volume, the dissertation is read well and is written correctly. The dissertation was divided into a three-chapter literature introduction, a description of the synthesis and measurement methods used in the thesis, and a description of the obtained results and possible applications. A bibliography for each of these sections is provided at the end of the section. The whole is preceded by introductions containing the hypothesis and research tasks of the work. At the end, there is a summary and suggestions for continuing the work. A slightly unusual layout is justified by the large volume (over 180 pages).

20 compounds grouped into 4 families were selected for the study. The role of the reference material played benzothiophene-thiophene aldehyde, and all its derivatives were carefully chosen to have different electron-withdrawing group. As a result, each compound exhibits a different level of intramolecular charge transfer (ICT), what is important in unique physicochemical properties.

The compounds were synthesized and then spectroscopically examined in the solution. The spectra of absorption, emission, photoluminescence quantum yield and in some cases luminescence lifetimes were measured. Additionally, the results of quantum calculations performed by Dr. Anna Grabarz (from Wroclaw University of Science and Technology) provided an explanation of the spectroscopic

transitions and focused primarily on their ICT character. It has been shown that in some cases, in addition to ICT values, other mechanisms also affect the spectra.

The next step was the measurement of optically nonlinear properties in the polymer layers. Second and third order nonlinear susceptibilities and nonlinear Kerr coefficient were measured. It has been shown that for most cases, the change of the dipole moment between the ground and the excited states played a crucial role in the obtained results. However, for some compounds, the measured values did not correspond to the obtained theoretical predictions.

Measurements were also made of the possibility of obtaining random lasing in the tested materials. Shown, by proper choosing compound, it was possible to achieve laser emission from UV through the whole visible spectrum up to the NIR region. These are very interesting and promising results for applications in organic lasers.

The doctoral dissertation was not limited to the synthesis of new compounds and their characterization. A very valuable result that significantly extends is the research to demonstrate the practical application of the compounds. Apart from their use as centers for the second and third harmonics generation, their quite high sensitivity to the environment or certain ions has been shown. It has been shown that they can be used in sensors, such ions as CN- and OH-, which are considered dangerous for the environment and human beings. Finally, it has been proven that some of compound could be useful in the construction of the DFB lasers in the region of NIR.

To sum up, the dissertation contains very extensive material arranged in a logical whole. The thesis of the work about the possibilities offered by push-pull organic chromophores based on the thiophene derivatives and the role of the intramolecular charge transfer controlled by the chemical structure has been proven. It is difficult to predict whether the tested materials will be used commercially. The obtained results, however, contribute significantly to the understanding of the mechanisms and allow for better predictions in the search for new materials. It is also worth mentioning that the work was not limited only to the creation and characterization of new compounds, but also proposed and tested the possibilities of their application.

In conclusion, the dissertation contains a series of diligently conducted studies aimed at. They are important and have a large aspect, not only cognitive, but most of all application. The doctoral student has demonstrated knowledge and skills in the use of various measurement techniques. The dissertation is carefully written and contains interesting conclusions as well as an extensive and properly selected bibliography.

Bearing in mind the reliability of the research carried out and the high scientific and especially practical value of the obtained results, I believe that the reviewed work meets the requirements for doctoral dissertations. Therefore, I am applying for admission of Anna Magdalena Popczyk, MSc. Eng., to the next stages of the doctoral dissertation. At the same time, due to the high level and content, I am also applying for award the doctorate with honors.

M. Kwiecień