Assessment of doctoral thesis

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Study program: **Biophysics, chemical and macromolecular physics** at FMP CU

Title: **Charge carrier transport in conjugated polymers with controlled morphology**

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A. Relevance of the chosen topic and its scientific and practical importance

The submitted work investigates, in the first place, the charge transport and related phenomena in conducting polymers - polypyrrole (Ppy), poly(p-phenylenediamine) (PPDA) and polyaniline (PA), and their composites. In addition, electro-chromic properties are studied of Fe(II) metallo -supramolecular polymers based on unimers composed of thieno[3,2-b]thiophene central unit and various linkers. These systems show a high practical application potential e.g. in the field of flexible optoelectronics. Despite the extensive research devoted to the energy and charge transport phenomena in the aforementioned polymers, there are still a number of unresolved problems resulting (but not only) from the complicated microstructure of these only loosely organized systems. The careful, well organized experimental research summarized in the submitted thesis provides very valuable contribution to this topic. The obtained results point also the way to some practical applications, the characteristic utility figures of the studied systems being in some instances equal or superior to the values achieved to date.

The subject of the submitted dissertation is highly topical and internationally significant from a research and practical point of view.

B. Content of the dissertation and its structure, formal aspects of the work

The dissertation is written in English, and has the form of commented set of seven papers of the author (enclosed in Appendix) published in respected international impacted journals. For two of these seven publications the author is the first author. The commentary part consists of 70 numbered pages including the Content of the thesis, chapter 1 - Introduction, chapter 2 - Experimental and characterization techniques, chapter 3 – Results and discussion, and chapter 4 – Conclusions. These parts are supplemented by Biography containing 130 references cited in text, List of Figures, List of Tables, List of Abbreviations, and List of publications of the author.

The first chapter is divided in three parts. The first one provides a general overview of the history, structure, preparation, main properties and possible applications of conductive polymers, with focus on the studied systems. Separate subsections are devoted to description of mechanisms influencing the electronic band structure and its hybridization, and the influence of polymer doping. The second part deals with detail description of charge transport models relevant for the studied systems and role of temperature, charge transfer rate and applied voltage frequency. Finally, the third part provides

basic theoretical grounds for description of electronic structure and electrochromic properties of metallo-supramolecular polymers.

The second chapter describes the experimental techniques and procedures applied in the study. Independent subsections are devoted to the main applied techniques: methods DC conductivity measurement, broad-spectrum impedance spectroscopy and methods used for spectro-electrochemical characterization; this list is then supplemented by other 8 additional experimental techniques used.

The third chapter is the key part of the thesis providing overview of the achieved results and discussion of these. The chapter is split in three parts: 3.1 Conductivity of conducting polymers and charge transport mechanism dealing gradually with PPy–MoS composites, 1-D PPy nanostructures prepared by using four different organic dyes templates and PANI thin films stabilized with PVP and doped by PA and HCl; 3.2 Impedance studies of conducting polymer-clay composites; 3.3 Electrochromic properties of iron(II) metallo-supramolecular polymers.

The fourth chapter Conclusions gives then summary of the main results achieved.

In spite of the considerable amount of the research conducted, the structure of the dissertation text is logical and clear, readable, and provides a comprehensive overview of the methodological procedures and the results achieved. Formally, the text of the thesis is very carefully prepared, with a minimum of typos and fulfils all the requirements laid on the dissertation theses.

C. Objectives of the dissertation, chosen methods and solution procedures

In the submitted text, the objectives and goals of the dissertation are not explicitly formulated. However, these implicitly follows from the whole content: collection of precise, well specified experimental data, interpretation of the mechanisms behind the obtained results leading to broadening of general knowledge of the studied materials, and, since of the apparent application potential, maximization of the potential utility parameters (electric conductivity, thermal stability, optical contrast, ..).

The methods and approaches applied in the performed research are fully adequate to the goals and objectives of the research.

D. Achieved results

A large number of time-consuming experiments were performed during the PhD project and a large set of valuable results were obtained, presented in a systematic way in Chapter 3. in line with the predictions of theoretical models and results obtained by other research groups around the world.

I consider the most valuable result to be the clear demonstration of the connection between the molecular orientation of the Ppy chains polymerized in presence of organic dyes and the resulting conductivity, the finding of a suitable experimental procedure that demonstrates this effect on two differently microstructured (nanorods/nanotubes versus globular arrangement) systems, and the use of the obtained knowledge to achieve a DC specific electrical conductivity value of 175 S cm^{-1} which is nowadys the highest DC conductivity obtained for the powder PPy reported in the literature.

The achieved results represent an internationally significant contribution to basic research and characterization of conducting polymers and their composites and create a good basis for possible further applications.

E. Questions and comments on the content of the dissertation

I would like to ask the following additional questions about the content of the dissertation:

- In Fig. 10, a schematis of the van der Pauw (vdP) metod used in the performed measurements is shown. The typical sample arrangement of the vdP method contains radial notches mutually rotated by 90 degrees. Were they applied? If not, why?
- The linear four probe method provides values of electric conductivity along the direction defined by the row of electrodes. Since the films might show some anisotropy, was also the directional dependence tested? If yes, what was the result?
- Was there any particular reason for which the four dyes (AB25, AB129, safranine and phenosafranin) have been selected?
- Last sentence on the page 33: "In the presence of Acid Blue 25, PPy nanowires were formed, while in the presence of Acid Blue 129 globular morphology was preserved (Fig. 18).". Can you try to provide some interpretation of such morphological behaviour observed for the systems with dyes, taking in account possible interactions between the dye moieties and the growing polymer?
- Since the extend of performed research is considerable, I'm just curious to ask about the own author's contribution to the obtained results.

F. Final evaluation

The submitted dissertation represents a significant contribution to the topic in its content and results achieved on an international scale and demonstrates the prerequisites of the Udit Acharya for independent creative scientific work.

I recommend the thesis for defense and in case of success I propose to award the author the scientific degree of Ph.D.

In Kamenice, June 9, 2023

doc. Ing. Ladislav Kalvoda, CSc.

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