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EVALUATION OF THE PH.D. THESIS ENTITLED

"High(t)-Rate Supercapacitors Based on Conducting Poly(3,4-ethylenedioxythiophene)"
presented by

MSc. Iryna Ivanko
to the Charles University, Faculty of Science, Department of Physical and Macromolecular Chemistry

The present Ph.D. Thesis written by MSc. Iryna Ivanko under the supervision of Ing. Elena Tomšík, Ph.D. is concerned with the topic of synthesis and characterization of conducting polymers namely poly(3,4-ethylenedioxythiophene), (PEDOT), with the aim of constructing functional materials. This is a topic of high current research interest due to enormous practical potential of conducting polymers.

In her work MSc. Ivanko tackled this scientific question by 3 different approaches: chemical oxidation, electrochemical polymerization and a new method, namely acid-assisted polymerization of 3,4-ethylenedioxythiophene to synthesize PEDOT with interesting new properties. In the first case an effect of methanoate ion on polymer chains hydration during polymerization as well as self-assembly into semicrystalline structure was investigated. Moreover, it was demonstrated that the hydrated PEDOT chains undergo rearrangements under the electrochemical treatment with the formation of anisotropic structure, and unique photoluminescence properties. In the case of electrochemical polymerization, the ability of intramolecular electrostatic interaction between PEDOT and supporting electrolytes (HCOOH, H_3PO_4, NaCl) was investigated. It was found that a crucial role in enhancing the electroactive properties of PEDOT are playing H-bonding and Coulomb interaction, prompting the concentration of localized cation radicals. Those promising new findings lead to the construction of symmetrical supercapacitor with significantly improved performance in terms of specific capacity, energy and power as compared to the published data. Acid-assisted polymerization of EDOT, a new method developed by Ph.D. candidate allows for the preparation of stable and soluble short oligomer chains of PEDOT in its neutral form that can self-assemble into small nanoobjects and further to form larger globular aggregates. This discovery opens possibilities for obtaining reproducible conducting polymer films for practical applications.

These rather complex polymeric species were investigated by a combination of a large variety of physico-chemical techniques for structural characterization such as electrochemical impedance spectroscopy, electron paramagnetic resonance, cyclic voltammetry, differential scanning calorimetry, thermogravimetric analysis, matrix-assisted laser desorption/ionization time-of-flight, nuclear magnetic resonance spectroscopy, X-ray diffraction and X-ray photoelectron

spectroscopy, just to mention few. This enabled Ph.D. candidate to achieve many valuable and interesting findings and to formulate important hypothesis and conclusions.

The research results were extensively published in internationally recognized high impact journals. The Thesis is based on six papers published in, *2x Macromolecules, 2x J. Mater. Chem. C, Macromol. Chem. Phys., Adv. Funct. Mater., Sens. Actuators B Chem*. Iryna Ivanko is the first author of five of these papers and simultaneously corresponding author in one of them, which is showing Ph.D. candidates significant engagement in the formation of these articles. In any case, a brief description of the contribution of all co-authors to the common articles should be specified as it is done in paper published in *Sens. Actuators B Chem* (CRediT authorship contribution statement).

I have marginal comments and some questions to the thesis:

- For a better readability, I would appreciate a schematic depiction of some chemical reactions, intermediates or so as they are discussed in section State of the art.
- Description in text: Fig.12(a) and Fig.12(b) do not correspond to any figure caption. Some grammar mistakes can be found, for example p.43 “The reason of it that last fellfield the next requirements:”, p.46: repetition: “as well and, and shown”
- Supporting information for all Appendices should be included in the Thesis as some of the descriptions in the main body of the Thesis correlate with information included in it. See foe example p. 44 “Using SEM, it was proved PEDOT-HQ polymerized…”
- p. 24 “The nature of two other peaks is still unknown to us…” What kind of measurements/experiments would you recommend to solve the question of additional peaks?
- Is caption of Figure 5 in Appendix 3 correct? Please provide detailed information on how Mw and Rh for polymer particles was determined? What is the wavelength of the laser light source used? This is interesting in the context of light absorbing polymers, where light scattering investigation and data analysis should be performed with special care.
- Based on your experience of different methods of PEDOT synthesis, what is the most suitable synthesis for the supercapacitor applications and way is it so?

In summary I can only express my positive opinion about the research work presented in the Thesis, both with respect to the quantity of the results obtained and the quality with which they were analyzed. That represents a significant contribution in material science of polymers and meets all criteria that can be expected for Ph.D. work to the highest level. Therefore, I strongly support its acceptance for public defense and awarding MSc. Iryna Ivanko the Ph.D. title.

Prague 7. February 2022 Eng. Mariusz Uchman, Ph.D.