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Łódź 11.06.2021

Review of the doctoral dissertation of M. Sc. Marharyta Vasylieva on "Electrochemical and spectroelectrochemical studies of electronic interactions in donor-acceptor-donor (DAD) and donor-acceptor (DA) systems"

The reviewed dissertation was prepared by M. Sc. M. Vasylieva at the Faculty of Chemistry under the supervision of dr. hab. inż. Przemysław Data, prof. PŚ and submitted as a doctoral dissertation to the Silesian University of Technology in Gliwice.

The submitted thesis was supported by the EXCILIGHT project funded as a part of the Marie Skłodowska-Curie Actions of the European Union's HORIZON 2020 Research and Innovation Programme under grant agreement No 674990. The thesis has been prepared under the supervision of dr. hab. inż. Przemysław Data, prof. PŚ, a specialist in electrochemistry and organic electronics, was the coordinator of the EXCILIGHT project- network providing training for fifteen Early Stage Researchers (PhD students).

The presented research focuses on determining the effects of different donor and acceptor groups on the physical-chemical properties of the selected

compounds. The motivation behind the material selection was the lack of available experimental data in the literature on the electropolymerisation process of the carbazole derivatives. The topic that Doctoral Student undertook is very important, as the alternated donor−acceptor systems are extensively investigated and utilised to design small molecular electron donor materials for organic light-emitting diodes (OLEDs) and organic photovoltaics (OPVs).

The dissertation was split into eight appropriately well-organised chapters. The research objectives have been clearly presented and discussed in relation to the current state-of-the-art in the field. The Author has well explained why the investigation of the mechanism of electrochemical processes involving organic compounds is important for designing the new light-emitting materials for application in OLEDs. However, the doctoral student has paid too little attention to the importance of the estimation of the energy values of HOMO and LUMO levels, and the energy bandgap in the designing of the structures of organic light-emitting diodes and organic photovoltaics, taking into account the electrical processes in optoelectronic devices, as the injection of the charge carriers from the electrodes and the blocking effects of the charge carries. Particularly, the list of publications of the Doctoral Student indicates her involvement in the research devoted to the optimalisation of the device structure by analysing the electrical and optical processes occurring in such devices based on the comparison of the HOMO/LUMO levels of the materials creating the device structure.

The second chapter presents the scope and the object of the research. The object of the study was differently substituted 1-8 naphtalimide, pyridazine, and tetrazine acceptor cores with the varieties of donor groups: carbazole, phenoxazine, a phenothiazine and dimethylacridine.

The next (third) chapter is dedicated to the broad literature review. The description of the fundamentals of electrochemistry and donor and acceptor units, which are the subject of this thesis, has been carefully prepared. The Author has compared the results from electrochemistry with these obtained from DFT calculations, explaining the correlation and the reason for differences between the HOMO and LUMO energy values obtained through these two methods. In this chapter, the Author also presents different electrochemical methods that are usually used to determine the HOMO and LUMO energy levels. In my opinion, this chapter could be nicely complete

with the direct comparison of the cyclovoltammetry and photoemission spectroscopy, as both methods are commonly and alternatively used for the determination of the HOMO and LUMO energy values used in the designing of the OLEDs and OPVs.

The description of the experimental part presents the experimental techniques and the list of the compounds. The compounds' synthesis was detailed in supplements 1 and 2, which are an integral part of this desideration.

Chapter No 5 is dedicated to the results and discussion. The first sub-chapter presents the analysis of the compounds based on the naphthalimide acceptor units. For all investigated compounds, the obtained data from electrochemical investigations have been compared with DFT calculations. Table 1 shows the values of HOMO/LUMO levels for compounds based on the NPTI unit. The values are given to two decimal places, but the Author did not provide information about a possible error. Based on the analysis of the compounds based on the TA acceptor unit (sub-chapter 5.3), the Author has stated that the smallest difference between experimental and calculated LUMO level was in the case of the CBZ-TA compound (0.13 eV) and the highest (0.64 eV), however, the data presented in Figure 67 do not confirm that. I would like to ask the Author for an explanation of this difference.

The last sub-chapter (5.4) presents the influence of the number of electroactive substituent on the electropolymerisation process. The Poly-CBZ-TA and Poly-CBZ-DA were characterised by low conductivity and were unstable under an increase of number of cycles. The NPTI based monomers present the best electropolymerisation properties. From the editorial point of view, the text of this sub-chapter, being a compilation of results, could be prepared more carefully. It should contain some short introduction showing the research's aim and more details concerning the approach to the problem.

In the conclusions (Chapter 6.), the Author has summarised a wide range of analyses. From the editorial point of view, this part of the text summarises different results that could be prepared more systematically and precisely. However, the conclusions do not contain the Author's statement, how her obtained results and data are useful in designing and processing the organic light-emitting diodes and other types of organic, optoelectronic devices (photovoltaics, photodiodes). There is also a lack of

some general guideline for the design of the DAD compounds, which could be good candidates for application in optoelectronic devices, looking at them from the point of view their stability and role in the device structure. Moreover, it would be very valuable if the Author as a specialist in electrochemical techniques, would discuss the limitations of the cyclovoltammetry and other methods used in the frame of her research.

Taking into account the number of analysis and the importance of the provided data, which are very useful for the organic electronic society, I evaluate this thesis positively. I conclude that the submitted dissertation meets the requirements set out in the Act on academic degrees and academic title and on degrees and title in the field of art of March 14, 2003 (Journal of Laws 2003 No. 65, item 595, as amended). Therefore, in my opinion, Mrs Marharyta Vasylieva can be admitted to further procedures necessary to obtain the PhD degree.

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