

Professor Jaroslaw Mysliwiec
Wroclaw University of Science and Technology
Wyb. Wyspianskiego 27,
50-370 Wroclaw, Poland
e-mail: jaroslaw.mysliwiec@pwr.edu.pl

**Review of the doctoral thesis
of MSc Paola Zimmermann Crocomo**

Thesis title:

**The intermolecular and intramolecular donor-acceptor charge transfer behavior as a
way to control thermally activated delayed fluorescence emission**

Doctoral thesis of MSc Paola Zimmermann Crocomo has been done under the supervision of Prof. Przemyslaw Data and prepared at Faculty of Chemistry of Silesian University of Technology. The supervising Professor represents the highest standards in the field of broadly understood chemistry and electrochemistry and is well recognized by its achievements in the physical and chemical sciences in the world.

The thesis of Paola Crocomo is placed in the modern discipline of electrochemistry as a part of photonics and optoelectronics. The thesis is written in English and contains 137 pages, adequate references, few dozen figures (including color photographs), several tables to clearly present the obtained results. The work is organized into well balanced in their contents 7 chapters:

1. Introduction
2. Background Theory
3. Materials and Experimental Methods
4. Investigation of Impact of C-C bond Insertion in Donor-Acceptor Structures
5. Electrochemical and Spectroelectrochemical Properties of Dibenzophenazine Based TADF Emitters
6. Photophysical and Spetroelectrochemical Characterization of D-A-D Iminostilbene and Iminodibenzyl Derivatives
7. Photophysical Characterization of Organic Emitters Based on Concaved N-PAHs with Tunable TADF/RTP Properties.

From the chapter contents we can classify this thesis as an experimental one where the optical and electrochemical properties of the new type of compounds are shown. In Chapter 1

we can find information about the main purpose of the PhD thesis which is a) the investigation of TADF and RTP emitters through the characterization by electrochemical and photophysical methods and further application in the manufacture of OLEDs, b) better understanding the distinct emission pathways and the parameters that can influence and optimize such processes.

The Chapter 2 presents the basic concepts of organic emitters, luminescence, electrochemistry, spectroelectrochemistry, etc... It should be mentioned that it is not easy on few pages presents comprehensibly the theory of luminescence and electrochemistry. In my opinion this part of the thesis was done very carefully and gives for the reader all necessary information for further better understanding of experimental results.

The Chapter 3 presents description of materials and techniques used for samples analysis (e.g. time-gated acquisition, cyclic voltammetry, potentiostatic EPR, etc...). Also this part of the thesis was done very carefully and without any critical remarks.

The following chapters are particularly important in which we will find a description of the influence of the chemical structure on the emission properties.

The Chapter 4 is devoted to investigating the effect of C-C bond insertion in donor-acceptor structures. As it was rightly noticed by the Author of the work, the analysis of compounds "A" and "B" resulted in a very didactic comparative study between two molecules containing the same acceptor and donor groups, with only one specific slight difference in structure (an extra bond), leading to different radiative decay pathways.

In chapter 5 and 6 we will find a description of electrochemical and spectroelectrochemical features of Dibenzophenazine, and Iminostilbene/Iminodibenzyl derivatives based emitters respectively. Also this part of the thesis is without any reservation.

The most interesting is Chapter 7, where photophysical characterization of emitters based on concaved N-PAHs with Tunable TADF/RTP properties are shown. The comparative study of emission afforded a better understanding of the tuning between TADF, room-temperature phosphorescence or dual TADF & RTP behaviors, depending on the substituent group on the acceptor's structure, what can be extremely useful information for designing new materials.

The entirety of the presented research results and their description from the substantive point of view are extremely accurate and it is very difficult to find any shortcomings or inaccuracies. A very meticulous work was performed along with an in-depth analysis of the obtained results. Nevertheless, as an very important critical remark, I must write that in a doctoral dissertation, as in any decent and interesting book, characteristic and at the same time

very important endings should be found. In this case, you have the impression and the feeling of a bit of such insufficiency. We have presented 4 types of emitters and described their properties, but there is no answer to the question of what's next and what results from all this, which research path we should follow, in which direction, on what groups of materials, because they are, for example, more promising when it comes to applications in optoelectronics, what can be improved, what can be modified so that e.g. efficiency is greater, stability is better, etc.? In short, each scientific work should contain not only the final summary that is missing here, but more importantly, the conclusions that emerge from the research carried out. Such a discussion should definitely be done and I hope to hear answers to these questions during the defense.

Concluding I can say, that MSc Paola Crocomo is an expert in optical and electrochemical studies of organic compounds. She is a co-author of 8 publications which recently appeared in highly ranked journals such as: Angewandte Chemie (1), Chemistry A European Journal (2), Journal of Materials Chemistry (1), Beilstein Journal of Organic Chemistry (1), Asian journal of Organic Chemistry (1), Journal of sol-gel Science and Technology (1), and Electroanalysis (1). In ISI Web of Knowledge one can find that his papers already have been cited 12 times, which may be a small value, but it is certain that this situation will change a lot in the near future.

The style of the thesis is generally correct. Some technical deficiencies are not decreasing a high quality of the thesis. Reading of the text is smooth and interesting. The quality of the figures is good and all mathematical formula are prepared with care and do not require any changes.

Given the importance of the presented work and the already mentioned reasons, as a referee I state that the scientific quality of the presented thesis is very high. The doctoral thesis formulates the scientific grounds of very interesting properties and possible applications of selected TADF emitters for optoelectronics devices. Therefore I recommend this thesis for being awarded.

The further steps of a procedure for obtaining the title of Doctor of Sciences by MSc Paula Crocomo could be proceeded.

Podpisane odręcznie przez autora

Jaroslaw Mysliwiec