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Review Report on Doctoral Dissertation of M.Sc. Welisson de Pontes Silva

entitled

*„Design, Synthesis, and Investigation of the Photophysical and Electrochemical Properties of Selected Conjugated Molecules Belonging to Various Classes of Compounds”*the work done at the Silesian University of Technology in Faculty of Chemistry
under the supervision of prof. dr hab. inż. Mieczysław Łapkowski and the auxiliary supervision
of dr inż. Radosław Motyka

The issues taken in the doctoral dissertation of M.Sc. Welisson de Pontes Silva include the synthesis of new organic semiconductors and investigations of their selected properties, that is electrochemical and photophysical to study structure-properties relationship and determining the possibilities of applications in new generation of organic light emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) or in photovoltaic cells.

Over the past decades, there has been tremendous progress in the synthesis of organic semiconductors, which has contributed to their commercial applications in various optoelectronic devices. However, intensive work is still being carried out aimed at obtaining materials with the most favorable properties, and at the same time allowing cheap industrial production of electronic devices.

The initial literature report on the utilization of organic semiconductors was presented in Tang and Van Slyk's 1987 paper, describing the first fabricated organic light emitting diode. This marked a significant milestone in the advancement of a new generation of displays and lighting technologies. Presently, OLEDs are integral components of commonly manufactured screens and displays, offering unique features not easily achievable by other types of luminescent diodes. These advantages include excellent color reproduction, high contrast and brightness, and the capability to create flexible devices. Nonetheless, there is still potential for enhancing OLED

parameters and cost-effectiveness. A key issue in development of OLED technology is organic material as well as device architecture. Conventional diodes, suffer from limited internal quantum efficiency which may not exceed 25% due to the inability of applied organic compounds to utilize dark triplet excitons. To increase the efficiency of the OLEDs new materials able to harvest all electrically generated excitons are desired. Currently, attention is paid on thermally activated delayed fluorescence materials as a promising metal-free organic emitters due to their potential for achieving 100% theoretical internal quantum efficiency of OLED through a reverse intersystem crossing process. The developing efficient TADF materials is a significant and challenging issue. Into this current strand of research is the doctoral dissertation of M.Sc. Silva.

Evaluating of the layout of the PhD thesis it can be concluded that the dissertation has a nonstandard composition. General information includes acknowledgements, abstracts, lists of figures, tables, and schemes and list of abbreviations with symbols. The main part consists of 13 chapters. Chapter 1 is two-page introduction containing also the aim of work. Chapter 2 (13 pages) presents the theoretical foundation of the research, encompassing the description of electronic transitions in organic emitters, OLEDs, TADF, aggregation-induced fluorescence (AIE), and the molecular design of TADF compounds. However, there is a lack of information concerning materials for organic photovoltaics (OPV). In the next six chapters (Chapters 3-8), the PhD student describes the obtained results, with each chapter dedicated to a specific group of synthesized compounds. Each of these chapters comprises a brief introduction, a description of the synthesis and structural characterization of the prepared compounds, an analysis of electrochemical and photophysical properties, conclusions, and experimental details. Chapter 9 consists of a two-page section providing general conclusions. Chapter 10 comprises a two-page section dedicated to the experimental part. This section presents the applied materials and equipment for UV-vis absorption, photoluminescence (PL), and electrochemical measurements, along with the details of theoretical calculations. Chapter 11 presents the References section, listing a total of 154 articles. Chapter 12 is Appendices with NMR and HRMS spectra of synthesized compounds. Chapter 13 contains scientific achievements of Candidate including list of publications and conference presentations, participations in grants/projects and internship details.

The applied literature within the dissertation is current, and the literature items are properly selected. However, there is a noticeable deficiency in the review of literature specifically focused on the particular group of synthesized compounds. The compounds are new but built from blocks utilized for preparation of TADF molecules and it should have received more attention. Instead of this each chapter from Chapters 3-8 in short Introduction section the PhD Student unnecessarily repeats the same information on basic and already discussed issues in Chapter 2, e.g. OLEDs, their importance and construction of organic emitters.

Investigations presented by the M.Sc. Silva in his doctoral dissertation concern synthesis and characterization of 6 groups of new compounds consisting of selected donor-acceptor (A) and electron-donor (B) building blocks towards application in OLEDs or in photovoltaic devices. The proper selection such blocks should let to obtain spatially separated the frontier molecular orbitals (FMOs) and small singlet-triplet energy gap which allow efficient reverse intersystem crossing process in TADF materials. As acceptor core M.Sc. Silva used derivatives of acenaphthopyridinopyrazine (NQPy), perylene (PDA, PTE), naphthalene benzimidazole (BTNA), diquinoxalines (DQ), pyridobenzotriazole (PyBTZ), diphenazine (NQ), triphenyl phosphanimine (Ph₃PN) and benzopyridoimidazoisoquinolinone (PyNA). The A units were connected by N-C or C-C cross-coupling reactions with selected D blocks resulted in D-A, D-A-D and D-A-A-D configurations of synthesized 35 compounds, which were divided into 6 groups. Three groups of molecules based on NQPy, perylene and BTNA were designed considering the localization of FMOs and energy of the lowest singlet and triplet states estimated using density functional theory (DFT) and time-dependent DFT, respectively. It is important to emphasize the fact of the complexity of the synthesis of compounds with the designed chemical structure, which involved several steps and in most cases purification by column chromatography. The Doctoral Student received compounds with good or very good yield. He applied appropriate research methods to determine both the chemical structure of the synthesized compounds and to study selected properties. The chemical structure of synthesized molecules was confirmed by NMR spectroscopy and high resolution mass spectrometry (HMRS).

The electrochemical behavior and FMOs energy of studied compounds was investigated by cyclic voltammetry (CV) in solution. Based on onset oxidation and reduction potentials read from voltammograms, the HOMO and LUMO energy and resulting energy band gap were estimated. M.Sc. Silva compared in tables the calculated and obtained from CV, FMOs energy, however, a comment concerns series with perylene units, where the noticeable differences are seen, was missing. In the case of some compounds (DQ-DPA, DQ-DMAC, DQ-DPAC) electrochemical polymerization was occurred. The HOMO and LUMO energies of the resulting polymers would be expected to be reported for comparison with monomers. The Author only mentioned lower oxidation potential for polymers in comparison to monomer. In my opinion, the electrochemical data should be presented in greater detail, including the indication of both oxidation and reduction potentials along with their onsets. This would allow for the demonstration and commentary on the reversibility, quasi-reversibility, or irreversibility of electrochemical processes. This approach would help eliminate vaguely specific statements such as: “*The first oxidation process was more clearly reversible...*” , „*While it was more irreversible for ...*”. The effect of donor and acceptor structure on FMOs energies was demonstrated and investigated

compounds exhibited E_g in the range of 1.05 – 2.83 eV and the lowest E_g was found for perylene derivatives (1.05-1.67 eV).

Photophysical investigations comprised UV-vis absorption and photoluminescence characterization. UV-vis absorption measurements were conducted in dichloromethane (DCM) solution. The tables compiled the position of the maximum absorption band, molar absorption coefficient, and their values, which could be incorporated into the discussion. PL properties of all compounds were studied considering emission range and PL quantum yield (PLQY) in DCM and in toluene. In the case of NQ, DQ, Ph₃PN, PyNA and PyBTZ derivatives PL solvatochromic investigations were extended to other solvents differing in polarity such as methylcyclohexane, tetrahydrofuran, and acetonitrile. The photoluminescent behavior of two groups with NQPy and PyNA units were examined in THF/water mixtures with different water fractions to study AIE phenomena. The PL properties of most of molecules except for PyBTZ and Ph₃PN derivatives were also investigated in solid state in Zeonex matrix, which is important for practical applications. In order to investigate the efficiency of reverse intersystem crossing (RISC) process crucial for TADF materials, PL spectra (in Zeonex matrix and in toluene for NQ and DQ derivatives) were registered also in degassed conditions and observed increment in PLQY, which confirms TADF behavior or no increase in emission intensity was analyzed. Considering the ability of investigated compounds as TADF materials, one might have expected a comparison of the theoretically estimated the energy (for series with NQPy, perylene and BTNA units) of the lowest singlet and triplet states with observed PL increment or its lack in experimental research.

The synthesized compounds exhibited various ability for light emission including AIE, and efficiency of RISC process both in solution and in solid state. The maximum of PL band ranging from 473 to 667 nm. The molecules based on perylene unit proved to be inefficient emitters and the PhD Students concluded that they can be good materials for organic PV. In the case of Ph₃PN and PyNA the PL quantum yield was not measured. In toluene solution the higher PLQY in comparison with more polar DCM was observed (series of NQPy and PyBTZ). Compounds (with NQPy and BTNA structure) molecularly dispersed in Zeonex matrix showed PLQY in the range of 1-38.6%. The highest quantum yield in the series of NQPy revealed molecules with such substituent as phenoxazine (BTNA-PXZ) 38.6%, dimethyl acridine (NQPy-DMAC) 34.5%, phenothiazine (NQPy-PTZ) 30.1% and diphenyl acridine (NQPy-DPAC) 30.7%. Lower PLQY in the range of 1-16.4% exhibited molecules based on BTNA and the highest PL quantum yield was found for BTNA-p-PXZ and BTNA-m-PTZ. Considering the goal of the work focusing on develop the new TADF materials, as the most promising, based on estimated increase in PLQY measured in degassed conditions, are compounds from series (i) DQ and NQ derivatives substituted with phenothiazine, dimethyl acridine and phenoxazine which exhibited in toluene PL

intensity increment from 1.93 to 3.01% in relation to PLQY registered in air atmosphere, (ii) NQPy with dimethyl and diphenyl acridine units showing 2.56 and 1.81% increment in PLQY and (iii) BTNA bearing phenothiazine structure (increase of 1.66%). In the case of PyNA molecule there is a lack of information about PLQY in Zeonex matrix, only PL spectra are presented in Fig. 8.8. The carried out investigations by Candidate have the character of basic research, however the application potential of some of compounds seems to be worth checking out in OLEDs.

In summarizing the presented discussion of the results, it is noteworthy to emphasize that M.Sc Silva not only analyzes the obtained results in the context of the structure of the donors used but also makes efforts to explain the observed phenomena. However, taking into account that the same donor units were used for preparation of various D-A systems differing in acceptor structure for example phenothiazine was a donor in DQ, NQ, PH₃PN, PyBTZ, PTE, PDA, BTNA and NQPy series the effect of acceptor structure could be analyzed.

The PhD Student has demonstrated a knowledge and considerable research experience. The stated aim of the work has been successfully accomplished. The acquisition of such comprehensive research material enables the tracing and identification of numerous relationships between the donor and acceptor structures in various series of compounds and between series. However, the conclusion provided for each series of compounds are rather general, they could be more detailed. The same concerns the Chapter 9. General Conclusions. I expect that the conclusions presented during the dissertation defense will be more specific and less general.

The interpretation of the research results does not raise any substantial objections. However, some comments are needed for the presented description:

- The evaluated dissertation contains an unexpectedly high number of repetitions. The introductions to each Chapter 3-8 feature repetitive information regarding the aim of synthesizing the compounds, which are already known from the purpose of the work. Additionally, the introductions specify the scope of the PhD Student's work, being always the same *“In this chapter the author was responsible for all the molecular design, synthesis, structural characterizations (NMRs), and partially for the electrochemical and photophysical investigations.”* The meaning of partial participation in electrochemical and photophysical research could be clarified. At the end of the Introduction in Chapters 3-8, there is a repetition of information about the performed investigations.

Each subsection in each chapter concerns electrochemical investigations contains the same information *“The electrochemical properties of the NQPy-Donors were investigated by cyclic voltammetry (CV) to estimate the ionization potential (IP) and electron affinity (EA) (from onset oxidation (E_{ox}) and reduction (E_{red}) potentials), that are correlated with the HOMO (E_{HOMO}) and LUMO (E_{LUMO}) energy levels, respectively, using the following equations: $E_{HOMO} = -(E_{ox}$*

+ 5.1); $ELUMO = -(E_{red} + 5.1)^{78}$ ”, albeit with different compound names. The same concerns the basic photophysical analysis carried out in the same conditions. The thesis should form a cohesive whole rather than being a collection of independent chapters.

The structures of the same compounds are also repeated, e.g. the chemical structure of NQPy derivatives is shown in Fig. 3.1 and repeated in Scheme 3.1. and similar for others. Some results are also repeated – HOMO, LUMO and E_g calculated from CV measurements are given in tables and repeated in figures.

- The approach to entering abbreviations for certain terms is unclear. After introducing an abbreviation, there is no need to repeat it with the full name again for example “*by cyclic voltammetry (CV)*” or “*dichloromethane (DCM)*”. List of abbreviations and symbols is not completed, some important symbols are omitted (e.g. LUMO or DFT) and some are unnecessarily introduced because they are not repeated in the text. Moreover, the unit “eV” should not be treated as a symbol.
- Why does the Author, writing about absorption spectra, give the UV-vis range in parentheses “*The absorption spectra (UV-Vis)...*”?
- The data concerning PL in the CBP matrix in Table 6.2 should not be included, as they are not discussed, and this matrix is not mentioned in the work.
- The column description concerns PL quantum yield registered in degassed conditions in all tables is not clear “*PLQY x Incerase (%)*”. In Table 5.2. the explanation of b and c symbols is the same “*b Obtained in zeonex matrix. c obtained in zeonex matrix*”.
- In the Experimental section, information regarding the preparation of compounds in the solid state in Zeonex matrix and the degassing of samples should be provided.
- Not all literature items are cited uniformly (for example ref. 129, 1450 and in some cases there is a lack of pages of cited article (for example ref. 45, 59, 88, 91, 94, 107, 108, 109, 114, 120, 123, 129, 134).

The research work conducted by M.Sc. Welisson de Pontes Silva demanded a combination of theoretical knowledge in the field of organic semiconductors and practical skills in it's the preparation and characterizations, particularly for their applications in organic electronics, primarily in OLED technology. The obtained results are important for basic studies and make a significant contribution to the development of knowledge of organic conjugated compounds. Scientific achievement of M.Sc. Silva includes 3 articles published in international journals from the JCR list, and one of them is related to the PhD thesis. The Candidate also indicated activity in the international conferences in the form of posters presentation. He precipitated in a few projects

(PRELUDIUM 20, OPUS 16, OCTA, Grant supporting academics starting their scientific activity in a new research field and Research tasks carried out by young scientists SBM (BKM)).

Taking above into account, I conclude that the presented doctoral dissertation meets the requirements set out in Art. 187 of the Act of July 20, 2018 Law on higher education and science. Therefore, I am applying for admission of M.Sc. Welisson de Pontes Silva to further stages of the doctoral proceeding.

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