Prof. dr hab. Bronisław Marciniak
Faculty of Chemistry
Adam Mickiewicz University, Poznan

Poznań 18.06.2024

Review of the PhD dissertation

"Spectroscopy, photophysics, tautomerism and photodegradation of amino and nitro derivatives of porphycene"

Idaresit Mbakara

The presented dissertation has been prepared within the International Doctoral Studies of the Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw, Poland. It has been conducted under the supervision of professor Jacek Waluk. The subject of the thesis is a continuation and further extension of a very successful research on spectroscopy and tautomerization of porphycenes that has been developed for several years by professor Waluk and his group. The thesis covers the study of spectral, photophysical and photochemical properties including phototautomerization and photodegradation of various amino and nitro derivatives of porphycene. The research topic correlates well with the current prevailing trends in modern photochemistry as a fundamental research with a strong grounding in the applied chemistry, particularly emphasizing research on new materials in the photodynamic therapy.

The dissertation contains 154 pages and comprises of 11 chapters divided into two Sections: Section I (Chapter 1-4) and Section II (Chapters 5-11). Chapter 1 is an introduction to the study presented in the thesis and contains literature data on structure, properties, reactivity and applications of porphycenes. Chapter 2 provides the justification for the research presented in the thesis and contains goals, methodology, potential impact and scope of thesis. In Chapter 3, some basic concepts of photochemistry and photophysics are presented. Chapter 4 describes the methodology of research (materials, methods and techniques for steady-state and time-resolved experiments and theoretical calculations). The compounds investigated in the dissertation were synthesized by organic chemists dr. A. Gajewska and dr. A. Listkowski (see Chapter 4, section Materials - samples, page 56).

Chapters 1-4 are written in a very clear manner and constitute a good introduction for readers of this thesis, including those who are not experts in the field. In particular, I like the

chapter 2 describing motivation and goals of the research with the list of questions (presented on page 32) to be answered.

The main part of thesis (results and discussion) is presented in Section II (Chapters 5-11). In Chapter 5, the spectroscopic and photophysical properties and tautomerism of amino and nitro porphycenes are presented. In Chapter 6, the spectroscopic and photophysical properties and tautomerism of 2-nitro- 7,12,17-tri-tert-butylporphycene are discussed. Chapter 7 describes the study of degradation and photodegradation reactions of amino porphycenes. Chapter 8 presents results and discussion about photostability of 9-substituted porphycenes as potential agents for photodynamic therapy. Chapter 9 describes the results for pull, push and push-pull porphycene derivatives of 9,19- disubstituted porphycenes. In Chapter 10, the position effect in meso-tetraphenyl derivatives of porphycene when a nitro group is placed in β or β' position is discussed. Finally, Chapter 11 presents summary of the results obtained and gives future recommendations. In the last part of thesis a chapter with 248 references is included.

Part of the thesis (*vide* page IV) has been already published in prestigious journals (Physical Chemistry Chemical Physics 2022, 24, 29655- 29666; Journal of Porphyrins and Phthalocyanines 2023, 27, 1457-1464; Journal of Porphyrins and Phthalocyanines 2023, 27, 563- 568) and two more articles are in preparation.

I would like to admit that the dissertation contains a lot of very interesting and new results presented in a logical and clear manner, and the text is written in precise English. The thesis is presented in a good and simple way. The quality of figures, tables and equations is high, and the text is written in a simple manner. There is a good balance between various chapters and various parts of the thesis. The references are carefully chosen and indicate Ms. Mbakara's broad knowledge in the topics covered in her PhD thesis.

In order to perform all experiments presented in the thesis, various steady-state and time-resolved techniques were used e.g. UV vis absorption and emission spectroscopies, steady-state fluorescence anisotropy, magnetic circular dichroism spectroscopy, transient absorption spectroscopy (ns and fs), fluorescence decay measurements (using Time Correlated Single Photon Counting technique). In addition, the quantum chemical calculations (DFT) were performed to interpret experimental results. The above-mentioned techniques and methods indicate that Ms. Mbakara is an experienced and mature researcher.

Below, there are minor Reviewer's comments concerning dissertation::

1. A list of abbreviations and symbols used would be very helpful for general readers who are not familiar with the specific terminology in the field.

2. Based on the Glossary of Terms Used in Photochemistry (Pure and Applied Chemistry 2007, 79, 293) I suggest to use the term *Absorbance* instead of *Optical Density* (e.g. p. 57 in the thesis)
3. A term **b** in eq 4.14 (page 65) was not defined. It should be:
   b = $\Phi_b \times (1000\varepsilon l/N_{av}V)$
4. A sentence on page 113, line 7, top : "Error! Reference source not found" should be removed.
5. During the PhD defense I would like to clarify meanings of two terms used in the thesis: *photobleaching* and *photodegradation* (e.g. pages 64 and 109).

Personally, I think the greatest achievements of the thesis are the following:

- a detailed description of spectral and photophysical properties of a new series of porphycenes (substituted with electron-donating (NH_2) and electron-withdrawing (NO_2) groups) considered as potential photosensitizers in photodynamic therapy. These properties and parameters include: UV-vis absorption and emission spectra and photophysical parameters such as fluorescent quantum yields, lifetimes of the lowest excited singlet and triplet states, quantum yields of singlet oxygen generation in solvents of various polarity,
- application of fluorescent anisotropy, magnetic circular dichroism (MCD) combined with theoretical calculations to assign the absorption bands of porphycenes studied,
- establishing that amino porphycenes emit only single fluorescence and that previously observed double or triple emissions originate from the products of photodegradation,
- observation of a large difference (three-order of magnitude) in photostability quantum yields of amino and nitro porphycenes,
- taking into account photostability, singlet oxygen yields and triplet lifetimes of nitro-porphycenes (e.g. 9-nitroporphycene, 2-nitro- 7,12,17-tri-tert-butylporphycene, 9-nitro-2, 7,12,17-tetra-n-propylporphycene, and 3-nitro- 9,10,19,20-tetraphenylporphycene) were suggested to be good candidates for efficient sensitizers in the photodynamic therapy
- observation of large differences in the photophysical parameters (such as fluorescence quantum yields and singlet oxygen quantum yields) for nitro derivatives of porphycene substituted in 2 or 3 position, and assignment of these effects to the steric interaction between the nitro group and the adjacent phenyl group,

- suggestion of further experiments to be performed in future studies on porphycene derivatives and their application in the photodynamic therapy.
-

In summary, taking into account that Ms. Idaresit Mbakara's PhD thesis: (i) contains original and valuable scientific results that were discussed and interpreted on a high scientific level, (ii) concerns a very attractive subject in modern photochemistry with potential application in the photodynamic therapy, (iii) was published, in part, in widely recognized journals in the field of chemistry (more publications in preparation), (iv) was written in a clear and logical way and carefully edited, I recommend it to the Scientific Council of the Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw, Poland for a full acceptance.

Bronisław Marciniak