Dr Roger Hiorns, HDR

Directeur de Recherche, CNRS,

IPREM (UMR 5254, EPCP)

Hélioparc Pau Pyrénées,

2 av. Président Angot

64053 Pau, France

Email: roger.hiorns@univ-pau.fr

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Subject: referee report on the PhD of Aleksandra Nyga

Aleksandra Nyga's PhD is entitled, 'Characterisation of donor-acceptor systems as materials for organic optoelectronics', consists of around 44 pages of text organised in six chapters, followed by four papers published and one submitted.

The document is introduced with a short Abstract which sets up well the main objective of this work, that is to study the ability of organic acceptor(A)-donor(D) based conjugated materials to develop, or not, singlet oxygen. The abstract also points out that this is an original way of looking at molecules and adds to the growing number of parameters that can be used to study such materials. This referee is persuaded by this being an important step and one that is not often enough considered in the general literature.

It should be noted that this thesis is essentially based on the papers that have come from the work that have been produced, submitted, and in most cases already published. Those journals have medium high to extremely high impact factors, and that the work has already been published during the PhD is an impressive record.

The very short introduction is well written with excellent English. It well lays out the generation of singlet oxygen and its importance in the degradation of organic electronic materials. The importance of the underlying and fundamental chemical reactions within which framework organic electronics must work is clearly and well stated, and the resulting upshot, that some materials are better suited to singlet oxygen development and others to optoelectronic devices is well framed. At this point is could be said that the referee would have appreciated some diagram that could schematically show the various chemical pathways that might occur with respect to the generation of singlet oxygen and the subsequent degeneration (or not) or the materials.

There then follows a general review of organic electronics. Again, as in the introduction references are well chosen, with a mixture of reviews and extremely recent works. The system electronics are well if briefly explained, again well framing the current understanding of excitational and vibrational states, with radiative and non-radiative loses well explained. And here the diagrams are well used to explain the processes that occur, identifying the general photosensitizing action of numerous organic materials. Figure 3 is well used although it would have been nice to explain what the names stand for, or at least give a better idea of the range of molecules that they studied. Otherwise, this part is very clear.

The third short chapter gives the aims and scope of the work, identifying the molecules chosen. It would have been nice to see more reasoning as to why these specific systems were chosen, although it can be recognized that this is not the main reasoning behind the work.

The fourth chapter gives the methodology of the experimental details, with a clear identification and description of the methods used. Figure 4 is particularly appreciated. A very minor point is in the CV, for how long was argon bubbling performed? That said, a much more interesting discussion might be had around the phrase, 'it does not matter whether it is obtained by chemical or electrochemical processes'.

This referee would have preferred some schemes to help follow the processes of chemical grafting, such as that of Figure 5. But overall, this chapter is extremely clear and very helpful.

Chapter 5 is the main part of the document, prior to the papers, having fifteen or so pages. The table 2 is much appreciated, relating names to structures, applications and method used for deposition. Again, it is not quite clear why the structures in Figure 7 were chosen for the studies. That said the following study and discussion of the CV curves of the materials is excellent and very interesting. This tied to the spectroscopic characterisations, which correlate very well oxidative events with the qualities of the materials during doping processes, and pinpoint, should this referee understand correctly, to reactive species which are well-delocalised. Extremely interesting and of great interest for further discussion.

There then follows a consideration of materials used in OPVs, notably based on C_{60}, but also mixtures of PCBM with P3HT, and separately, chemically grafted porphyrin and phenothiazine materials are considered. The subsequent investigation of singlet oxygen production is very interesting with a clear explanation of the strategy used avoiding direct methods but rather UV-visible spectroscopy and chemical traps, with this process exploited for PGeZ. It would have been interesting to see a short discussion on the possibility of quantitative studies with respect to the molar generation of singlet oxygen and the material itself, rather than the relative decrease of alpha-terpine absorbances at 266 nm, even if not possible. That said, the kinetics of the system for P3HT:PCBM are extremely well described and followed.

Interestingly the work also extends to a consideration of antimicrobial properties of the materials via their singlet oxygen generation under white light.

Chapter 6 concludes this general summary of the work prior to the presentation of the papers, and resonates with the rest of the work by indicating that this well understudied area, the generation of singlet oxygen can relate to the structure, and design, of the materials, can be importance and relevancy to future work. It is hoped that this pioneering work will become much more routine when considering the new classes of materials such as non-fullerene acceptors and so on.

The first paper, submitted, gives a wide review of the work on small molecules and their ability, or not, to generate singlet oxygen. An excellent explanation of the singlet oxygen structure itself is given, along with its impact and physical processes with molecular materials, distinguishing type 1 and 2 processes. Applications, and detection methodologies are discussed with excellent discrimination between direct and indirect methods. The crucial role of singlet oxygen with a range of molecules and applications is excellently covered. In sum, this paper more than makes up for any lack of details in the first part of the PhD dissertation and is an excellent review paper.

The second paper, recently published in Chem. Comm., considers in-depth the electronic structure of an A-D-A based organogermanium compound, and the reasons for its choice become much clearer. There is an extraordinary complementarity of data. The referee would have appreciated the inclusion of the Supporting Information.

The third paper deals with the singlet oxygen generation of a selenophene-based material generated electrochemically. A full battery of complementary characterisations is employed, and the use of indirect methods well applied. By way of these methodologies, an extraordinary step is taken by way of optimising the structures towards the generation of singlet oxygen. An in-depth appreciation of the structural impact on singlet oxygen generation is given.

The fourth paper considers P3HT:PCBM systems, and an extremely complementary range of techniques are employed to explore the generation of singlet oxygen by various ratios of P3HT to PCBM. The paper is extremely well written, and fully discloses the methodologies and results. While quantum yields are given it's not entirely clear to this referee how the *absolute* efficiency of the materials might be calculated.

The fifth paper considers the applicability of ROS generation by the aforementioned porphyrin and azure A, attached by way of a siloxane to glass, against Gram-negative bacteria. Using an excellent complementary range of techniques, again the balance in components is well-attained to maximise ROS generation under white light, leading to a compelling story for these materials.

Moreover, it is expected that this technology, and understanding of ROS generation will be of considerable use not only in optimisation of materials *per se*, but also in finding ideally paired materials to reduce singlet oxygen generation for long-term stability of materials in OLED and OPV applications.

To sum, the work done here clearly demonstrates the considerable scientific maturity of the candidate, having strengths in a wide range of techniques, coupled with the expertise and understanding of complex physical processes that clearly draw together properties and structure of classic and novel organic materials.

It is therefore the strong recommendation of this referee that this work goes forward for the award of a doctorate from the Silesian University of Technology.

Yours sincerely,

Roger Hiorns

IPREM-EPCP – UMR 5254
Institut des Sciences analytiques et de Physico-Chimie pour l'Environnement et les Matériaux - *Equipe de Physique et Chimie des Polymères*
Université de Pau et des Pays de l'Adour
Technopole Hélioparc – 2, av. Pdt Angot – 64053 PAU Cedex 09
Tél. : 05 59 40 76 00 – Fax : 05 59 40 77 44 – Site web : www.iprem-epcp.univ-pau.fr