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Evaluation of the Doctoral Thesis of Ms. Emma ROBINS

Photodynamic therapy is a treatment modality which is now approved in several countries for several indications, but that remains insufficiently known and used, which is a pity given its advantages free of many drawbacks. Yet there is still improvement for better photosensitizing systems, which is tacked by the PhD works of Ms Emma Robins.

The Doctoral Thesis of Ms. Emma ROBINS is entitled “Design, optimisation, and characterisation of two- and multi-photon absorption photosensitizers for their potential application in photodynamic therapy”. It is made of four chapters, a conclusion and some annexes.

The first chapter is about lignin nanoparticles loaded with photosensitising porphyrins. Three porphyrins (tetra hydroxy free base, treta hydroxy Zn, and tetra acetylated free base) have been encapsulated and the resulting nanoparticles have been thoroughly characterised. The study of their photoproperties with one and two photon conditions is complete and very interesting. The NLO section is particularly well and clearly written. The effect of the self-assembly / agglomeration of these nanohybrids occurring in bulk dispersions on the two-photon excited fluorescence of these nanoparticles is demonstrated, and the fact that various forms of nanoparticles loaded with porphyrins co-exist is evidenced, which is of great interest given that the field is still in its infancy.

The second chapter focuses on the NLO properties of Foscan, a commercially available photosensitiser of great interest, and of three Foscan-derived photosensitisers. Two

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photon excitation measurements have been performed and are very well presented. The quality and clarity of the figures has been particularly appreciated. The effect of the power and of the solvent has been investigated and showed that simple modifications can lead to significant improvements of two photon absorption properties. The fact that formulation / encapsulation of poorly water-soluble photosensitisers into lignin nanoparticles improves their photo-properties demonstrates well the potential of these biosourced nanoparticles for photodynamic therapy.

The third chapter details the syntheses of potential aPDT photosensitisers that have been performed during the time of these research. The design of the targeted porphyrins conceived to exhibit improved two photon photoproperties is well explained with appropriate contextualisation in the existing state-of-the-art. The synthetic strategy of these targeted molecules that have asymmetric substitution pattern is well presented and discussed. Advanced chemical synthesis techniques have been successfully used, such as chemistry on the porphyrin macrocycle (such as iodination, organometallic coupling). The characterisations have been well completed, even though they are presented in an unusual manner.

The fourth chapter presents photo experiments conducted on naphthiporphyrins. The extension of the porphyrinoids macrocycle and the introduction of heteroatoms is expected to improve their properties. Three different heteroatoms (S, Se and Te) have been selected and the study showed this strategy dramatically shifts the absorption of these compounds towards near-infrared wavelengths, the most efficient heteroatom for this being tellurium. The results in this chapter open new directions in the development of photosensitisers excitable in the phototherapeutic window.

The conclusion summarizes well the works achieved during this PhD works as well as their importance in the current scientific context.

All these works as well as the Doctoral Thesis manuscript itself, and the publications out of them, are of very good quality and level. Therefore, I am delighted to deliver a very positive opinion for the defense and I am looking forward to it.

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