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EXCITED STATE ABSORPTION-BASED PHOTOCHEMISTRY IN MESO-TETRA(4-PYRIDYL) ZINC PORPHYRIN

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Excited state absorption (ESA) stands as a selective, and noninvasive excitation mechanism for the photochemical modification of porphyrin structures. Our group has recently explored the use of ESA to controllably photo-protonate and photo-aggregate pyridyl- and phenyl-substituted free-base porphyrins in chloroform [1,2,3]. This is possible because ESA operating in the visible can replace the UV excitation of porphyrins, enabling the molecules to access high-energy excited states capable of triggering the decomposition of chlorinated solvents through an oxi-reduction reaction, which finally leads to the release of protons in solution and favors the modification of the macrocycle and its outlying ligands [1,2,3]. In the present work, we investigated ESA-driven photochemical reactions in a metalloporphyrin model (the meso-tetra(4-pyridyl) zinc (II) porphyrin (ZnTPyP)) dissolved in the chloroform: methanol (9:1 v/v) binary

solvent. By means of steady-state and time-resolved optical spectroscopy techniques, it is observed that the initial solution evolves into a complex molecular system after pulsed irradiation. Three distinct types of ESA-driven photoproducts are verified, being the first specie assigned to the photo-protonation of the outlying meso-substituents of ZnTPyP; the second to the possible photolysis of ZnTPyP, and the third to the formation of a ground-state complex between photolyzed and remnant unmodified ZnTPyP molecules. The data also suggest the occurrence of Forster resonance energy transfer between remnant ZnTPyP and the formed complex. Finally, optimal conditions for these ESA-based photochemical reactions are addressed, where it is found that solvent, critical concentration, and irradiation conditions play key roles in the observed results. The work was funded by CNPq, CAPES, FAPESPA e INEO.

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