Elucidation of the mechanism of singlet oxygen formation by selected photosensitizers

V. Planetová[1*], Š. Budzák[2], P. Boháč[1], J. Bujdák[1, 3], M. Pribus[1,4]

[1] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, SK- 845 36, Slovak Republic
[2] Department of Chemistry, Matej Bel University, Banská Bystrica, SK-974 01, Slovak Republic
[3] Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Bratislava, SK-842 15, Slovak Republic
[4] Department of Microbiology and Virology, Faculty of Natural Sciences, Comenius University in Bratislava, Bratislava, SK-842 15, Slovak Republic
** Corresponding author:* viktoria.planetova@savba.sk

Keywords: Singlet oxygen, TD-DFT, halogenated fluorescein dyes, spectral properties.

Singlet oxygen is a highly reactive species that plays a role in a variety of chemical reactions and processes, which makes it widely used in many fields ranging from photooxidation, DNA damage, photodynamic therapy to polymer science. [1] In our research, we specifically focus on the use of singlet oxygen production by functional materials composed of an organic dye and a layered silicate, which are used as antibacterial surfaces. Although singlet oxygen is a much-studied system, the actual mechanisms of its formation have not been adequately described yet. In our work, we attempt to gain a deeper insight into the role of selected organic photosensitizers in molecular oxygen activation.

Photosensitizers are molecules with the ability to absorb light energy and transfer it to molecular oxygen, resulting in various photochemical reactions. [2] Our study focuses on fluorescein and its halogen-derivatives, 4,5,6,7-tetrachloroflorescein, 4,5,6,7-tetrachloro-2ʹ,4ʹ,5ʹ,7ʹ-tetrafluoroflorescein,4,5,6,7-tetrachloro-2ʹ,4ʹ,5ʹ,7ʹ-tetrachloroflorescein, phloxine B and Rose Bengal. In the present work, we have tried to approach the understanding of the mechanism of singlet oxygen formation by a combination of experimental and theoretical chemistry methods. The photochemical properties and the ability of photosensitizers to generate singlet oxygen were investigated using UV-Vis and fluorescence spectroscopy. Computational chemistry methods TD-DFT are a useful tool as they help to elucidate electronic transitions and behaviour in excited states. We used the programs ORCA and Gaussian to simulate the geometries, vibrationally resolved absorption and emission spectra, and fluorescence decay rates. The results were then compared with experimentally measured spectra.

The knowledge gained may help explain the unique photophysical properties of halogenated fluorescein dyes. A better understanding of the mechanism of singlet oxygen formation itself could support the development of efficient dye/layered silicate antibacterial materials in the future.

References:

[1] DEROSA, Maria C.; CRUTCHLEY, Robert J. Photosensitized singlet oxygen and its applications. Coordination Chemistry Reviews, 2002, 233: 351-371.

[2] YOO, Je-Ok; HA, Kwon-Soo. New insights into the mechanisms for photodynamic therapy-induced cancer cell death. *International review of cell and molecular biology*, 2012, 295: 139-174.