

Photo-generation of free radicals by TiO₂ nanoparticles, fullerenes and functionalized fullerenes

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In this work we investigated, with Electron Paramagnetic Resonance (EPR) using the spin-trapping methodology, the photogeneration of free-radicals by nanoparticles of TiO₂, fullerene (C₆₀) and functionalized fullerene bearing tetrazole groups. The main motivation for this study was the potential application of these materials in Photodynamic Therapy (PDT), a topic treatment against skin cancer and infections caused by parasites, and photocatalysis. For this purpose, TiO₂ (P25 Degussa) non-aqueous suspensions and fullerene solutions, in the presence of the spin-trap N-tertbutyl- α -phenil-nitrone (PBN), were illuminated with UVA light and the resulting paramagnetic PBN-spin adducts identified and quantified. For the TiO₂ suspensions in isopropyl myristate, a solvent commonly used in the cosmetic industry, a hyperfine triplet spectrum (¹⁴N, with I = 1 and a_N = 1.48mT) due to PBN-O₂⁻ adducts indicated that O₂⁻ was the main free radical formed under UVA illumination (366nm 5W). These results were corroborated by experiments using the superoxide dismutase enzyme (SOD) and were reproduced for other solvents. The amount of free radical produced was quantified by EPR after calibration using a nitroxide stable paramagnetic radical (4-hydroxi-tempo). Important parameters for the PDT like illumination times and concentrations were also investigated. In the second part of this work, we used the same methodology for solutions of fullerene and a functionalized fullerene bearing tetrazol groups, recently synthesised, [1] (see Fig. 1).

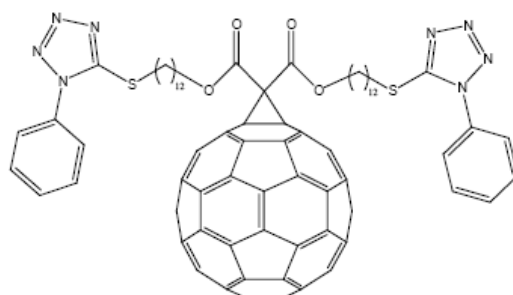


Fig. 1 – Bis[12-(1-phenyl-1H-tetrazole-5-ylsulfanyl)dodecyl]1,2-Methano[60]fullerene-61,61-dicarboxylate, a new fullerene-based photosensitizer for use in PDT.

Under similar illumination conditions of the TiO₂ suspensions we showed also that the formation of superoxide (O₂⁻) radicals was the dominant process. The amount of radicals generated in the three cases was compared and the new tetrazol-fullerene derivative showed the highest efficiency among them.

Keywords: TiO₂, fullerenes, PDT, photocatalysis, EPR, spin-trapping, free radicals
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[1] L.J. dos Santos et al., *Journal of Photochemistry and Photobiology*, submitted April 2008.