Synthesis of photosensitizers supported on gel-type and macroreticular polystyrene with antimicrobial photodynamic properties

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Reactive oxygen species (ROS) generated by photosensitization are widely used in a variety of areas, from photocatalysis to photodynamic therapy of cancer and antimicrobial photodynamic inactivation of bacteria. In the first realm, production of fine chemicals can be achieved by means of oxygenation reactions.^[1] In the second area, elimination of cancerous cells or inactivation of pathogens can be done by the appropriate choice of irradiation conditions and photosensitizer.^[2]

A vast number of photocatalytic and photodynamic agents has been reported so far in the literature.^[3] Hexanuclear clusters of molybdenum $[Mo_6X_8L_6]$ (X = Cl, Br, I; *L* is a ligand) have been recently studied as generators of singlet oxygen ($^{1}O_2$).^[4,5] Hence, in comparison to other families of photosensitizers, molybdenum clusters remain a less known group of ROS generating photosensitizers, with unexplored applications in photochemical synthesis and photobiology.

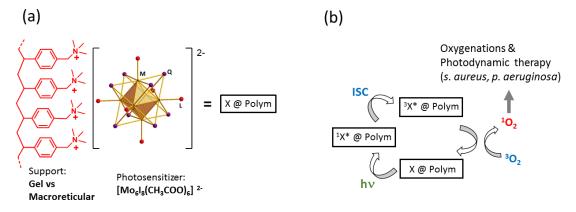


Figure 1. (a) Schematic representation of the photosensitizer $[Mo_6I_8(CH_3COO)_6]^{2-}$ supported on polystyrene (gel type or macroreticular); (b) Photocatalytic cycle leading to the generation of singlet oxygen for photo-oxygenations or for antimicrobial photodynamic therapy.

Here we describe the activity of cluster $[Mo_6I_8(CH_3COO)_6]^{2-}$ supported on two types of polystyrene matrices (Figure 1) as photosensitizer for oxygenations involving 1O_2 . Also it is described the photodynamic antimicrobial activity against *Staphylococcus aureus* and *Pseudomonas aeruginosa*. Special attention will be paid to the effect of the nature of the support (low cross-linking gel-type polymer *vs* high-cross-linking macroreticular resin) on the photochemical and photobiological performance of the new materials.^[6]

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References:

[1] E. L. Clennan, A. Pace, *Tetrahedron* **2005**, 61, 6665.

- M. R. Hamblin, *Curr. Opin. Microbiol.* 2016, 33, 67; I. J. MacDonald, T.J. Dougherty, J. *Porphyrins. Phthalocyanins*, 2001, 5, 105; P. R. Ogilby, *Chem. Soc. Rev.* 2010, 39, 3181; Singlet Oxygen: Applications in Biosciences and Nanosciences. S. Nonell (ed.), C. Flors (ed.), Royal Society of Chemistry, 2016.
- [3] S. S. Lucky, K. C. Soo, Y. Zhang, Chem. Rev. 2015, 115, 1990.
- [4] K. Kirakci, P. Kubat, M. Dusek, K. Fejfarova, V. Sicha, J. Mosinger, K. Lang, *Eur. J. Inorg. Chem.* **2012**, 3107.
- [5] M. Mikhailov, K. Brylev, P. Abramov, E. Sakuda, S. Akagi, A. Ito, N. Kitamura, M. Sokolov, *Inorg. Chem.* **2016**, 55, 8437.
- [6] A. Beltrán, M. Mikhailov, M. N. Sokolov, Vanesa Pérez-Laguna, A. Rezusta, M. J. Revillo, F. Galindo, J. Mater. Chem. B. 2016, 4, 5975.