Supporting Information

Photobleaching resistant polymer supported hexanuclear molybdenum iodide cluster for photocatalytic oxygenations and photodynamic inactivation of *Staphylococcus aureus*

Alicia Beltrán,[a] Maxim Mikhailov,[b] Maxim N. Sokolov*[,b,c] Vanesa Pérez-Laguna,[d] Antonio Rezusta,[d] María José Revillo,[d] Francisco Galindo*[,a]

[a] *Universitat Jaume I, Departamento de Química Inorgánica y Orgánica, Avda.Sos Baynat s/n, 12071, Castellón, Spain.*
E-mail: francisco.galindo@uji.es

[b] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 Acad. Lavrentiev Prosp., 630090 Novosibirsk, Russia.*
E-mail: caesar@niic.nsc.ru

[c] *Novosibirsk State University, 2 Ul. Pirogova, 630090, Novosibirsk, Russia*

[d] *Department of Microbiology - Miguel Servet University Hospital. Universidad de Zaragoza. IIS Aragón, Zaragoza, Spain*

Materials and Methods

Synthesis of 1@PS. 1g of washed Amberlite IRA 900 resin (**PS**, Sigma-Aldrich, chloride form, particle size of the beads: 650-820 μm), was suspended in 50 mL of absolute EtOH containing 1.5 mg of dissolved cluster **1**. The suspension was stirred overnight at room temperature, filtered and the polymer washed exhaustively with 100 mL of absolute EtOH. UV-vis absorption measurements before and after the overnight period indicated quantitative exchange of chloride by the octahedral molybdenum anion. The emission

spectrum of the solid confirmed the presence of **1** bounded to the matrix (maximum λ_{em} = 680 nm, with excitation at 400 nm). The emission of **1@PS** was recorded with a Spex Fluorolog 3-11 apparatus equipped with a 450W xenon lamp, operated in the front-face mode. The sample was introduced into a quartz cell, sealed and purged with nitrogen prior to measurements. Excitation was set at 400 nm.

Photooxygenation reactions.

(a) Homogeneous photocatalysis. In open erlenmeyer flasks 50 mL solutions of photosensitizer **1** ($2x10^{-5}$ M) and substrate (10^{-4} M **DMA**, 10^{-4} M **DPA**, $4x10^{-5}$ M **FA** or 10^{-4} M **DHN**) were prepared and irradiated, with stirring, with a LED lamp (22W, see emission in Figure S1) placed 3 cm away from the reaction vessel. In one case solar light was also used in order to illustrate the generality of the photooxidation. The evolution of the photoreactions was monitored over time by means of UV-vis absorption spectrophotometry. The initial points of the kinetic traces were fitted to a pseudo-first order model ($\ln C/C_0 = - k_{obs} \cdot t$).

(b) Heterogeneous photocatalysis. 500 mg of **1@PS** were suspended in 50 mL of acetonitrile containing 10^{-4} M **DMA**. This suspension was allowed to equilibrate overnight. After equilibration no sign of adsorption of **DMA** to the polymer nor leaching of the photocatalyst out of the support was detected. Irradiations were conducted as indicated above, with continuous stirring. After complete reaction of **DMA** (30 min) the polymer was filtered off and resuspended in 50 mL of freshly prepared **DMA** solution (10^{-4} M) in acetonitrile, and irradiated again, up to seven cycles.

Photodynamic studies.

Staphylococcus aureus ATCC 29213 strain was obtained from the American Type Culture Collection (ATCC; Rockville, MD). Columbia Blood Agar (BA) was purchased from Oxoid. Microorganisms were grown aerobically in BA medium at 35ºC for 24 h. Stock inoculum suspensions were prepared in bidistilled water and adjusted to optical densities corresponding to 0.5 McFarland containing > 10^8 cell/mL. A Showtec LED Par 64 Short lamp was used for the irradiations. Irradiation was performed up to a fluence of 120 J/cm^2 with a blue LED lamp (maximum emission at 460 nm, 0.013 W/cm^2, see emission in Figure S2) at a distance of 17 cm for 12 minutes and 49 seconds every 10 J/cm^2. Three groups of microorganisms were prepared for the irradiations (and other three as controls in the darkness): 5mL of the initial suspensions with the desired McFarland value of *S. aureus* were dropped into different RODAC plates and then (a) 200 mg of **1@PS** or (b) the same amount of control **PS** or (c) no polymer, were added. The final concentration in the experiments was 40 mg polymer/mL. All the groups were prepared and handled under light-restricted conditions. The six groups were subjected to shaking during the whole time of the photodynamic treatment. The antimicrobial effect was determined by counting the number of colony-forming units (CFU) / mL at different light fluences up to a maximum of 120 J/cm^2. A criterion of 6 log10 unit decrease from the starting inoculum was adopted to define bactericidal activity. Bacterial cultures were incubated at 35 ºC for 24 h. CFU counting was performed using Flash and Go automatic colony counter.

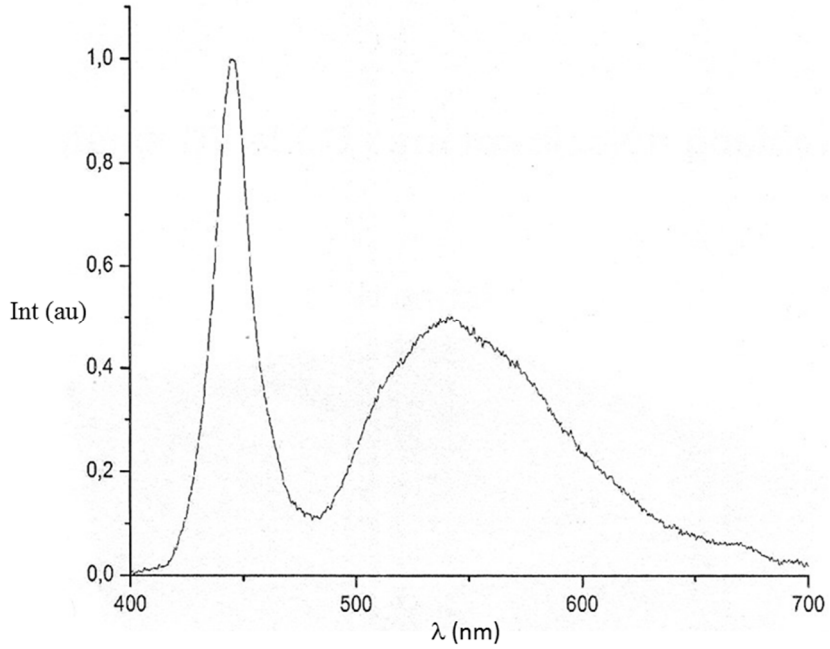

Figure S1. Emission spectrum of the LED lamp used for the photooxygenation reactions.

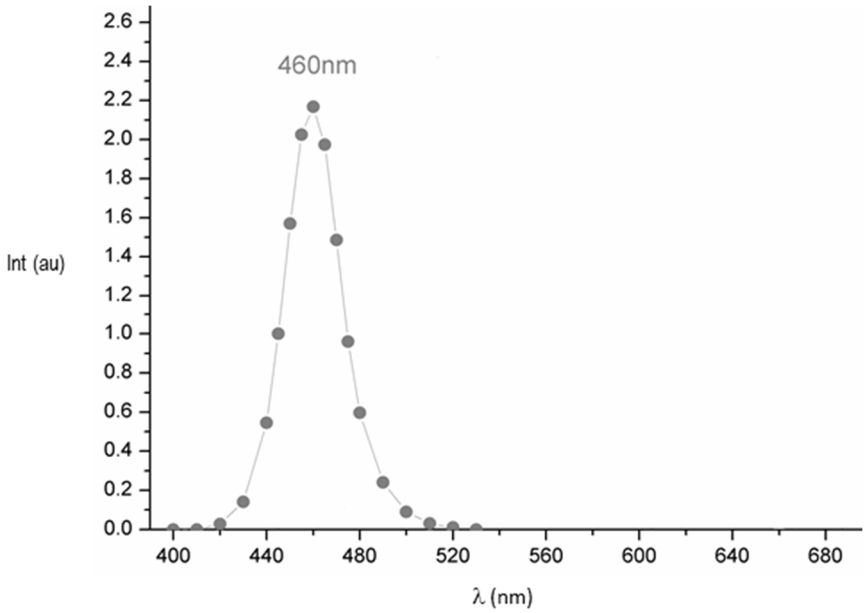

Figure S2. Emission spectrum of the LED lamp used for the photobiological assays.

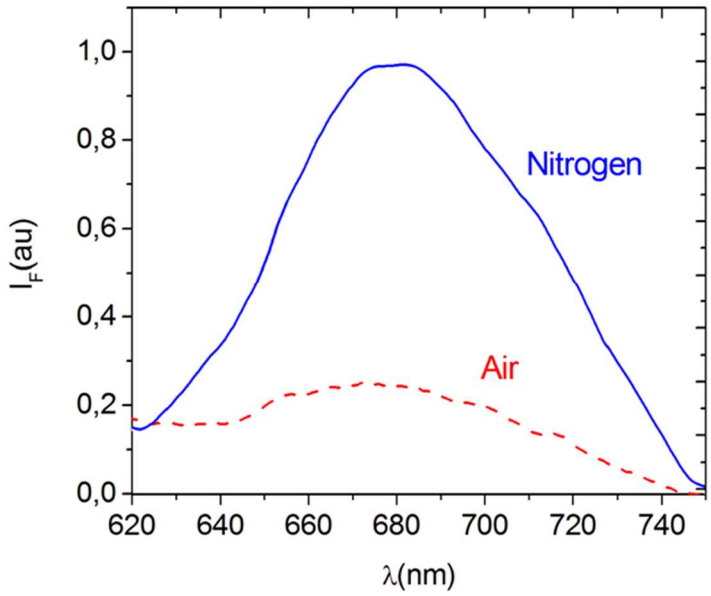

Figure S3. Emission spectrum of **1@PS** under nitrogen (blue line) and the same sample after exposure to air for 10 seconds (red dashed line). Excitation at 400 nm.

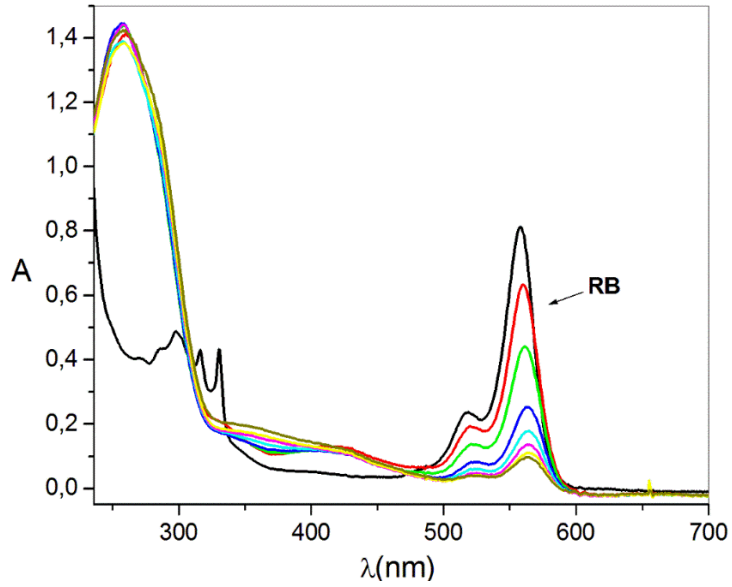

Figure S4. Photobleaching of Rose Bengal (**RB**): reaction of **DHN** $2x10^{-5}$M in EtOH photocatalysed by **RB** 10^{-5}M (times: 0, 15, 30, 45, 60, 75, 90 and 120 min).

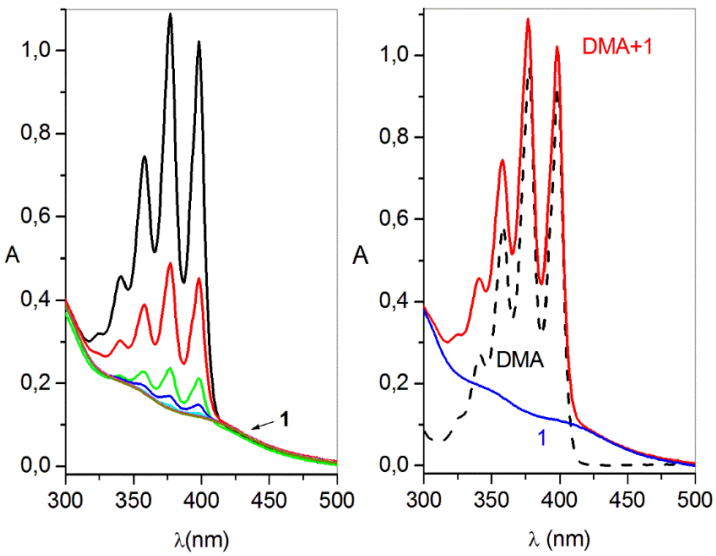

Figure S5. Photostability of **1**. Left: photoreaction of **DMA** 10^{-4}M in CH_3CN in the presence of **1** $2x10^{-5}$M (0, 1, 2, 3, 4, 5, 10 and 15 min). Note the constant absorption of **1** at $\lambda > 400$ nm. Right: absorption spectra of **DMA** 10^{-4}M, **1** $2x10^{-5}$M and mixture of **DMA** and **1** at those concentrations, in CH_3CN.

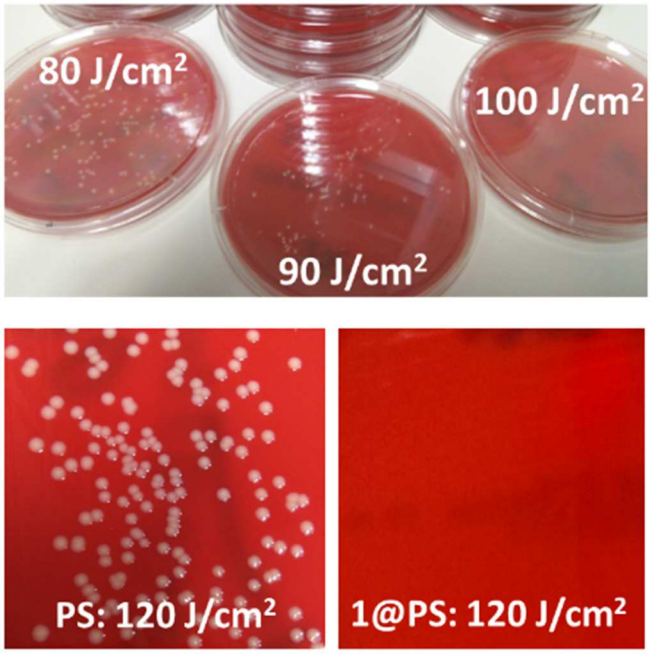

Figure S6. Photodynamic inactivation of *S. aureus*. Top: **1@PS** irradiated at different light fluences (note complete disappearance of colonies of *S. aureus* at 100 J/cm^2). Bottom: Comparison between control **PS** (left, no photodynamic effect) and total elimination of pathogens with **1@PS** (right) irradiated at 120 J/cm^2.