Photoinduced water oxidation sensitized by a tetranuclear Ru(II) dendrimer

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SUPPORTING INFORMATION

Evolved oxygen measurement and quantum yield determination

The amount of O_2 evolution was calculated by Stern-Volmer equation (eq. 1), following the reduction in the emission intensity of a deoxygenated acetonitrile solution of $[Ru(bpy)_3]^{2+}$ in a cuvette (the measuring compartment) to which was quantitatively conveyed the oxygen evolved from a second cuvette containing the photocatalytic mixture, under light irradiation (reaction compartment). The measuring cuvette was kept in a spectrofluorimeter and the emission intensity was continuously monitored at 620 nm (excitation wavelength, 450 nm). The two compartments were connected one another by a cannula. All the system (the two compartments and the connecting cannula) were carefully deoxygenated. A needle was inserted in the measuring compartment cuvette to allow for gas diffusion. Control experiments performed without irradiating the reaction compartment cuvette showed that luminescence intensity of the above described "measuring compartment" cuvette was fully stable for more than 1 h, that is more than the time of the reported photocatalytic experiments.

$$[O_2]_t = [(I^0/I_t) - 1]/k_q \, \tau^0 \qquad (1)$$

In eq. 1, I^0 and I_t are the luminescence intensity of the measuring compartment cuvette before photocatalytic activity (t_0 time) and at time t, respectively; $[O_2]_t$ is the concentration of molecular oxygen in the measuring compartment cuvette at the time t, responsible for energy transfer quenching of the Ru(II) complex emission; τ^0 is the emission lifetime of $[Ru(bpy)_3]^{2+}$ in deoxygenated acetonitrile (1.0 μs) in absence of any quencher; k_q is assumed to be the diffusion constant in acetonitrile, approximated to $10^9 \, s^{-1}$.

Quantum yield for oxygen production was obtained by eq. 2.

$$\Phi(O_2) = \text{(moles of oxygen)/(moles of photons absorbed)} \qquad (2)$$

The moles of photons absorbed were calculated by considering the photon output of the irradiation lamp (on its turn measured by using Aberchrome 540 (**A**, see Figure) as photochromic actinometer, see ref. 13 of the article for further details) and the absorption of the solution.

A   **C**
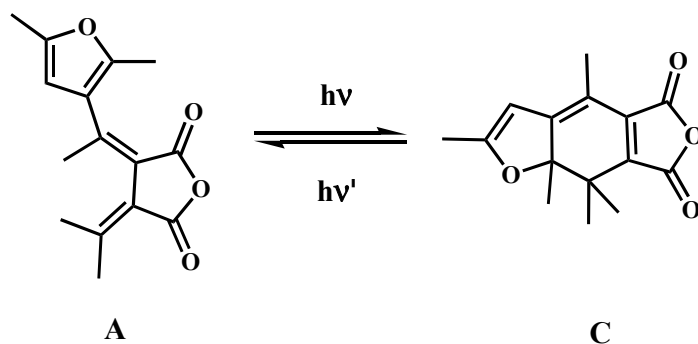
The number of moles of incident photons were calculated using eq. 3.

$$\frac{Nh\nu}{t} = \frac{\Delta A \times V}{\phi_\lambda \times \varepsilon \times t \times F}$$ (3)

where ΔA is the decrease in absorbance at 494 nm of a solution of **A** in dry toluene (after a suitable period of irradiation with UV light to obtain the closed form **C**), F is the mean fraction of light absorbed at the irradiation wavelength, ε is the molar absorption coefficient of C (8200 M^{-1} cm^{-1} at 494 nm) and t is the time of irradiation and ϕ is the quantum yield of the photocyclization reaction, calculated for the irradiation wavelength using eq. 4.

$$\phi_\lambda = 0.178 - 2.4 \times 10^{-4} \cdot \lambda$$ (4)