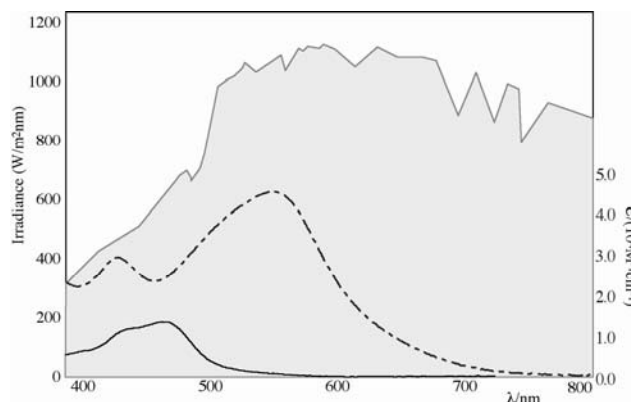Photo-induced water oxidation with tetra-nuclear ruthenium sensitizer and catalyst: A unique 4x4 ruthenium interplay triggering high efficiency under visible light irradiation

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Electronic Supplementary Information

Fig. S1 Comparison between solar spectrum at the sea level (visible region, grey area) and the acetonitrile absorption spectra of **1** (dashed-dotted) and of Ru(bpy)$_3^{2+}$ (solid line).

10

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 luminescence lifetime of a deoxygenated acetonitrile solution of [Ru(bpy)$_3$]$^{2+}$ in a cuvette (the measuring compartment) to which the oxygen evolved in a second cuvette containing the photocatalytic mixture (reaction compartment) was transferred, by using a gas-tight syringe. A quantitative calibration curve was used.

$$[O_2]_t = [(\tau^0/\tau_t) - 1]/k_q\, \tau^0 \tag{1}$$

20 In eq. 1, τ^0 and τ_t are the luminescence lifetime 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 25 acetonitrile, approximated to 10^9 s^{-1}.

Photochemical quantum yield for oxygen production was obtained by eq. 2, on exciting at 550 nm.

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

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

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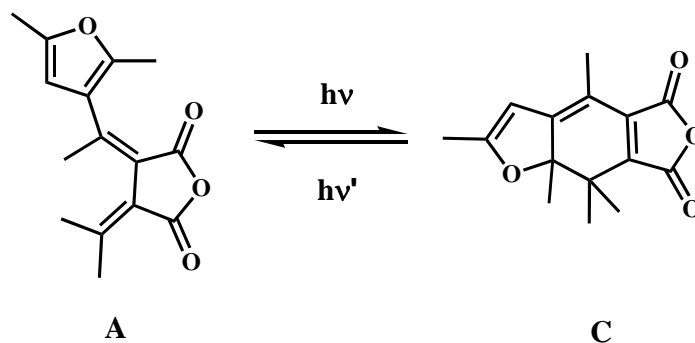
The number of moles of incident photons were calculated using eq. 3.

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

10 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), t is the time of irradiation and ϕ is the quantum yield of the photocyclization reaction, calculated for the irradiation wavelength using eq. 4.

15 $\phi_\lambda = 0.178 - 2.4 \times 10^{-4} \cdot \lambda$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (4)$

Equipment

Absorption spectra were recorded by a Jasco V560 spectrophotometer. Luminescence lifetimes were determined by time-correlated single-photon-counting Edinburgh OB900 spectrometer (light pulse:
20 Hamamatsu PL2 laser diode, pulse width 59 ps at 408 nm). For the light irradiation, a home-made system based on a halogen lamp (50 W) was used. Excitation wavelengths were selected with a cut-off filter (for the esperiments shown in Fig. 1 of the paper) and with band-pass filters (for the photochemical quantum yield determinations).