Photochemical switching of luminescence and singlet oxygen generation by chemical signal communication

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Supporting Information

1 Materials and methods

1.1 Chemicals. Acetonitrile (Merck Uvasol™) and triflic acid (CF_3SO_3H, Fluka) were used as received. $[Ru(bpy)_3](PF_6)_2$ was available from previous investigations.[1] The syntheses of **Os**$^{2+}$ and **SP** can be found in refs. 2 and 3, respectively.

1.2 Preparation of the solutions. Solutions containing **Os**$^{2+}$ and **ME**-H^{+} were obtained by mixing **Os**-H_2^{4+} with **SP**, and subsequent equilibration in the dark at room temperature. The **Os**-H_2^{4+} species, in its turn, was afforded by adding two equivalents of CF_3SO_3H to the **Os**$^{2+}$ complex. The conversion extent of the **Os**-H_2^{4+}/**SP** mixture into the **Os**$^{2+}$/**ME**-H^{+} one was estimated from the absorption and luminescence spectra and, in the conditions employed, was larger than 90%.
In a typical experiment, 9.3 µM **Os**-H_2^{4+} was mixed with 20 µM **SP** and left in the dark at room temperature for 5 days. After equilibration the solution contained contained 8.4 µM **Os**$^{2+}$ and 18 µM **ME**-H^{+}.

1.3 Absorption and luminescence experiments. The absorption spectra were recorded with a Perkin Elmer λ45 spectrophotometer; the luminescence spectra were recorded with either a Perkin Elmer LS50 spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier, a SPEX Jobin-Yvon Fluorolog τ-3 equipped with a Hamamatsu R928 photomultiplier or an Edinburgh Analytical Instruments (EAI) FLS920 equipped with a Hamamatsu R928 photomultiplier for the UV-visible region and a germanium detector cooled at 77 K for the NIR region. Air equilibrated acetonitrile (Merck Uvasol™) solutions with concentrations ranging from 5×10^{-6} to 1×10^{-4} M were examined in 1-cm spectrofluorimetric quartz cells at room temperature. Luminescence spectra were recorded on excitation in isosbestic points and were corrected for the monochromator-detector spectral response. Luminescence lifetime measurements were obtained by the time-correlated single-photon counting technique using an EAI FLS920 apparatus equipped with a cooled (ca. –20 °C) Hamamatsu R928-P photomultiplier tube; the excitation pulse (fwmh 800 ps) was obtained by a pulsed diode laser (406 nm, Picoquant). Data correlation and manipulation were carried out using the EAI F900 software version 6.35. Emission lifetimes were calculated using a single-exponential fitting function; a Levenberg–Marquardt algorithm with iterative reconvolution as implemented in the EAI F900 software was used. The reduced χ^2 and residual plots were used to judge the quality of the fits. The experimental error on the wavelength values was ±1 nm, and that on absorbance, luminescence intensity and lifetime values was estimated to be ±5%.

1.4 Relative luminescence intensities and quantum yields. The I_{rel} parameters discussed in the paper are relative luminescence intensities obtained from the area under the corresponding luminescence spectra, performed in the same experimental conditions. An arbitrary value of 100 was chosen for the **Os**$^{2+}$ species. The luminescence quantum yield of **Os**$^{2+}$ ($\Phi = 0.013$) was determined by the optically dilute method at room temperature in air-equilibrated MeCN solutions using $[\mathrm{Ru(bpy)_3}]^{2+}$ ($\Phi_{\mathrm{ref}} = 0.059$) as reference compound.[4] As evidenced by the dashed line in Figure S2, the luminescence band of **Os**-$\mathrm{H_2}^{4+}$ is likely to extend in a spectral region ($\lambda > 850$ nm) where the sensitivity of the photomultiplier drops. Therefore, the relative luminescence intensity of this species – albeit much smaller than that of **Os**$^{2+}$ – could not be accurately determined; a lower-limiting value is reported.

1.5 Quantum yield of singlet oxygen production. The quantum yield of singlet oxygen production (Φ_{Δ}) is calculated using a relative method, by comparison with a standard of known quantum yield, $[\mathrm{Ru(bpy)_3}]^{2+}$, in air equilibrated MeCN solution.[5]

1.6 Photochemical experiments. Irradiation experiments were carried out by using the Xe arclamp-monochromator ensemble of a Perkin Elmer LS50 spectrofluorimeter. The light intensity at 400 nm, measured by ferrioxalate actinometry, was 5×10^{-9} Einstein min^{-1} on a 3-mL volume.

2 Absorption spectra of the Os complexes

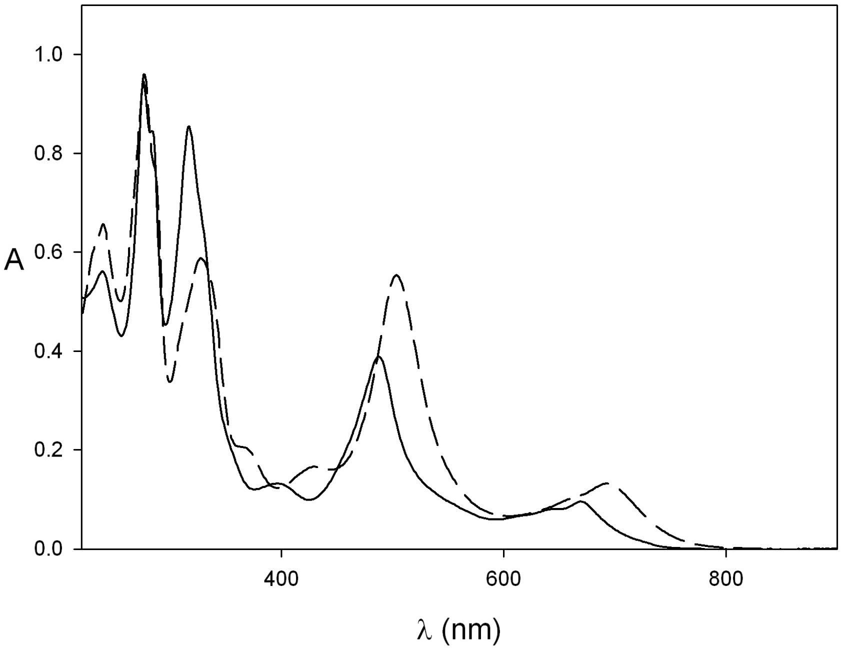

Figure S1. Absorption spectra of 13 μM solutions of $\mathbf{Os}^{2+}$ (solid line) and $\mathbf{Os}\text{-}H_2{}^{4+}$ (dashed line) in MeCN at room temperature.

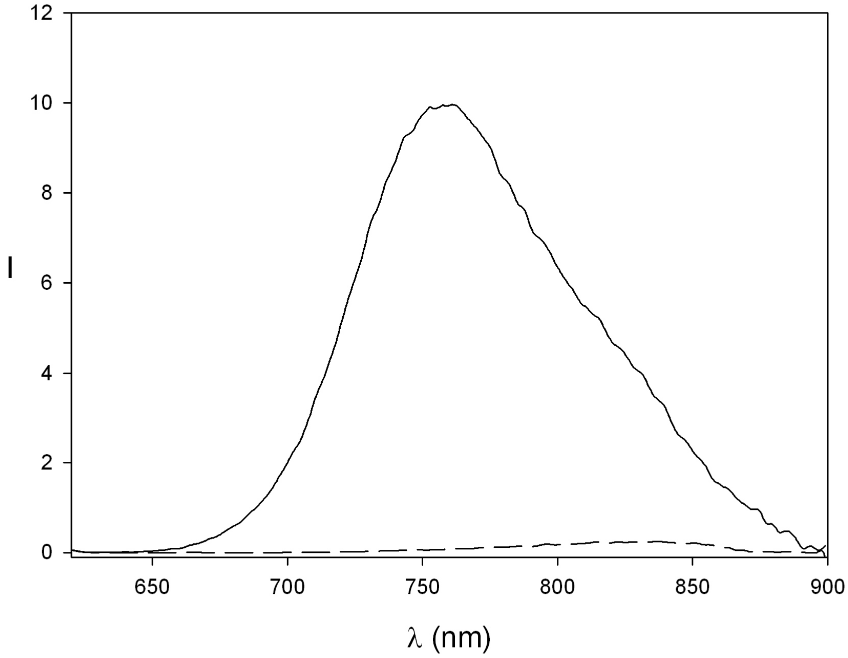

Figure S2. Luminescence spectra of 13 μM solutions of $\mathbf{Os}^{2+}$ (solid line) and $\mathbf{Os}\text{-}H_2{}^{4+}$ (dashed line) in MeCN at room temperature. Excitation was performed in an isosbestic point at 607 nm.

3 Cycling experiment

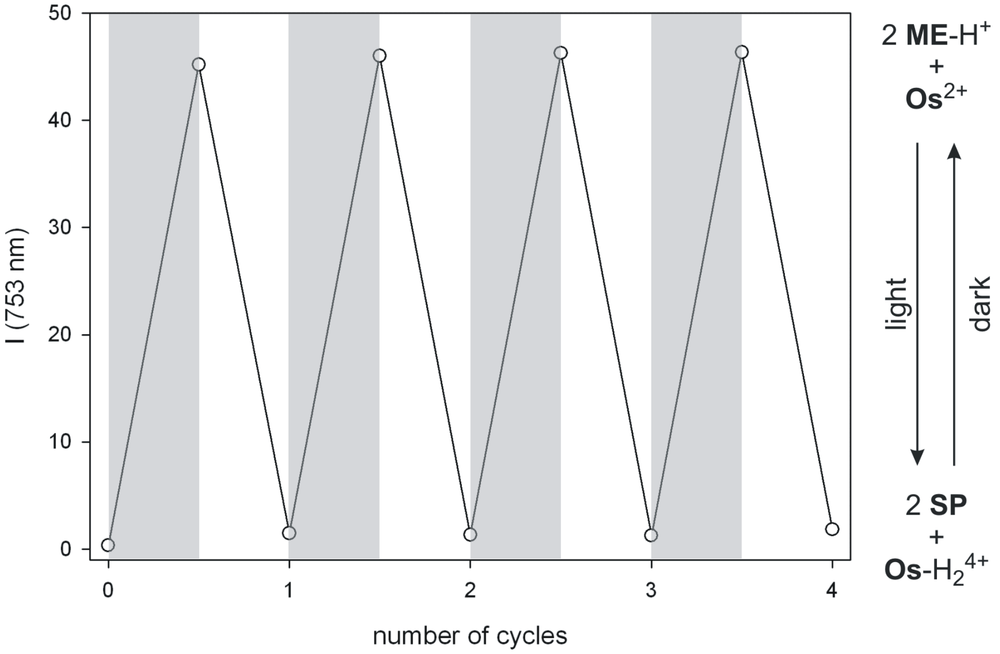

Figure S3. Emission intensity values at 753 nm upon several equilibration-irradiation cycles performed on a solution containing 7.2 μM **Os**-H_2^{4+} and 2 equivalents of **SP**. Equilibration (grey areas) was performed by leaving the solution for 5 days in the dark at room temperature. Irradiation (white areas) was carried out at 400 nm until a photostationary state was reached.

References

1 V. Balzani, M. Clemente-León, A. Credi, B. Ferrer, M. Venturi, A. H. Flood and J. F. Stoddart, *Proc. Natl. Acad. Sci. USA*, 2006, **103**, 1178.

2 E. C. Constable and A. M. W. Cargill Thompson, *J. Chem. Soc., Dalton Trans.*, 1994, 1409.

3 F. M. Raymo, S. Giordani, A. J. P. White and D. J. Williams, *J. Org. Chem.*, 2003, **68**, 4158.

4 *Handbook of Photochemistry – Third Edition*, eds. M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, CRC Press, Boca Raton, FL, 2006.

5 (a) F. Wilkinson, *J. Phys. Chem. Ref. Data*, 1993, **22**, 113; (b) C. Tanielian, C. Wolff and M. Esch, *J. Phys. Chem*, 1996, **100**, 6555.