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

Serena Silvi,[a] Edwin C. Constable,[b] Catherine E. Housecroft,[b] Jonathon E. Beves,[b] Emma L. Dunphy,[b] Massimiliano Tomasulo,[c] Françisco M. Raymo*[c] and Alberto Credi*[a]

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Photoluminescence in the far red spectral region and photosensitised generation of singlet oxygen, with associated near-IR emission, are reversibly controlled by near-UV or violet light in a communicating ensemble of molecular switches.

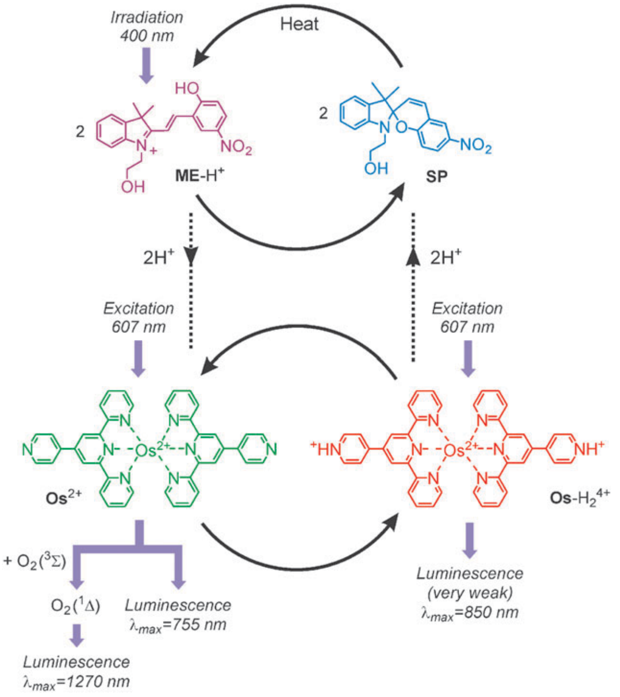
Photochemical switches are molecular or supramolecular species in which properties or functions can be switched on and off by light.[1,2] The design and preparation of molecule-based systems in which optical outputs can be modulated reversibly in response to optical inputs is a scientifically stimulating objective,[3] with potential outcomes in fields such as materials science and information and communication technology.

As shown by biological structures,[4] the type and utility of the functions that can be obtained with photochemical switches depend on the degree of complexity and organisation of the chemical species that receive and process the photons. In the frame of artificial systems, one approach is that of linking together, either by weak interactions or covalent bonds, a discrete number of molecular components.[5] Along this line, a large number of multicomponent (supramolecular) systems exhibiting photoinduced functions such as light harvesting,[6] charge separation,[6] catalysis,[7] control of acid–base properties,[8] drug delivery,[9] logic operations,[10] and molecular mechanical motions,[5,11] have been investigated.

A different modular approach for constructing photochemical molecular devices with predetermined functionalities relies on the combined operation of *structurally unlinked* but *functionally connected* molecular switches. Recently, we applied this strategy to develop prototypes of molecule-based memories,[12] simple mechanical machines,[13] and logic gates.[14]

Here we describe the design and operation of a chemical ensemble in acetonitrile solution which employs a near-UV or violet light input to control a photoluminescence output in the far-red spectral region. This system can also be used to switch on or off the generation of oxygen in the lowest singlet excited state, which in turn exhibits phosphorescence in the near infrared (NIR).

The ensemble is composed of a reversible merocyanine-type photoacid and an osmium polypyridine complex that functions as a two-state luminescent switch (Scheme 1). On irradiation with near-UV or violet light (*e.g.*, 400 nm), **ME-H**$^+$ is converted into the spiropyran **SP** and releases a proton into the solution.[15] The **Os**$^{2+}$ species is an $[\mathrm{Os(pytpy)_2}]^{2+}$ complex (pytpy = 4′-(pyridin-4-yl)-2,2′:6′,2″-terpyridine).[16] Upon the addition of two equivalents of acid, **Os**$^{2+}$ is converted into the **Os**-$\mathrm{H_2}^{4+}$ species, protonated on the pendant pyridyl nitrogen atoms, which possesses different absorption and luminescence properties.[16] Specifically, on protonation both the intensity and lifetime of the luminescence from the triplet metal-to-ligand charge-transfer (MLCT) state are strongly quenched, and the band maximum is red shifted (**Os**$^{2+}$: $\lambda_{\max} = 755$ nm, $I_{\mathrm{rel}} = 100$, $\tau = 115$ ns; **Os**-$\mathrm{H_2}^{4+}$: $\lambda_{\max} = 843$ nm, $I_{\mathrm{rel}} = 3$, $\tau = 20$ ns).† We envisaged that the protonation state of the osmium complex could be controlled by light using **ME-H**$^+$ as a photoacid,



Scheme 1 Structures and coupled operation of the **ME-H**$^+$/**SP** photoacid system and the **Os**$^{2+}$/**Os**-$\mathrm{H_2}^{4+}$ switch in MeCN solution by means of photoinduced proton exchange.

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[a] *Dipartimento di Chimica "G. Ciamician", Università di Bologna, via Selmi 2, 40126 Bologna, Italy. E-mail: alberto.credi@unibo.it; Fax: +39 051 2099456*
[b] *Department of Chemistry and Swiss Nanoscience Institute, University of Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland. E-mail: edwin.constable@unibas.ch*
[c] *Center for Supramolecular Science, Department of Chemistry, University of Miami, 1301 Memorial Drive, Coral Gables, FL 33146-0431, USA. E-mail: fraymo@miami.edu; Fax: +1 305 2844571*

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because **SP** and **ME**-H^+ exhibit smaller and larger pK_a values than that of the pyridinium ion, respectively.[12,13]

The UV–visible absorption spectrum (Fig. 1, curve ***a***) of a MeCN solution containing 8.4 μM $\mathbf{Os}^{2+}$ and 18 μM **ME**-H^+ is essentially identical to the sum of the spectra of separated components. The sharp and intense bands at $\lambda < 350$ nm are due to ligand-centered (LC) transitions of the metal complex, the band with $\lambda_{max} = 401$ nm is ascribed to the absorption of **ME**-H^+, and the bands with $\lambda_{max} = 487$ and 670 nm are, respectively the ^{1}MLCT and ^{3}MLCT absorption bands typical of $\mathbf{Os}^{2+}$.[16] The luminescence spectrum (inset of Fig. 1, curve ***a***) shows a band with $\lambda_{max} = 755$ nm, assigned to emission from the ^{3}MLCT state of $\mathbf{Os}^{2+}$.

From the absorption spectrum reported in Fig. 1, curve ***a***, it can be noticed that (i) **ME**-H^+ can be photoexcited with good selectivity in the spectral region around 400 nm, and (ii) exclusive excitation of the metal complex is possible at $\lambda > 500$ nm, regardless of its protonation state. Irradiation of the solution at 400 nm causes profound changes in the absorption and luminescence spectra of the solution (Fig. 1). At the photostationary state (Fig. 1, curves ***b***), obtained after 60 min of irradiation in our conditions,† the **ME**-H^+ absorption band at 401 nm has disappeared completely, an absorption shoulder at *ca.* 350 nm has grown up, and the MLCT absorption bands of the metal complex have become more intense and bathochromically shifted. The MLCT luminescence intensity and lifetime are quenched by factors of ~30 and 6, respectively. A careful comparison with the spectra of separated **SP** and **Os**-H_2^{4+} suggests that (i) the **ME**-H^+ species has been photoconverted to **SP**, and (ii) the protonated complex **Os**-H_2^{4+} has been obtained (Scheme 1). Upon leaving the solution for five days in the dark at room temperature the original absorption and luminescence spectra are restored (Fig. 1, curves ***c***), indicating that thermal equilibration with regeneration of $\mathbf{Os}^{2+}$ and **ME**-H^+ has occurred (Scheme 1).

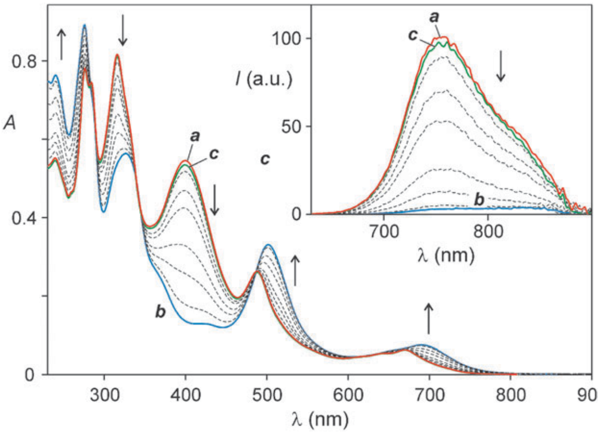

Fig. 1 Absorption and (inset) luminescence spectra (air equilibrated MeCN, r.t.) of a solution containing 8.4 μM $\mathbf{Os}^{2+}$ and 18 μM **ME**-H^+ (***a***). The dashed lines show the absorption and (inset) luminescence changes observed on irradiation of the solution at 400 nm until a photostationary state containing **Os**-H_2^{4+} and **SP** is reached (***b***). In particular, spectra ***a*** and ***b*** in the inset are ascribed to emission from the $\mathbf{Os}^{2+}$ and **Os**-H_2^{4+} species, respectively. Thermal re-equilibration (five days in the dark at r.t.) regenerates the original spectra (***c***). For the luminescence spectra, excitation was performed at an isosbestic point at 607 nm.

Interestingly, the switching between $\mathbf{Os}^{2+}$ and **Os**-H_2^{4+} is accompanied by a significant change in the emission intensity (Fig. 1, inset),[16] indicating that in this system a luminescence signal in the far red spectral region can be switched off by a light input at the opposite extremity of the visible spectrum, and switched on again by heating. As noted above, the optical output reading can be performed with excitation at $\lambda > 500$ nm (in our experiments, $\lambda_{exc} = 607$ nm) and thus it does not interfere with the switching process. In fact, cycling experiments performed on the same solution indicate that the luminescence switching is reversible.†

Another interesting feature of this system arises from the fact that the lifetime of the ^{3}MLCT excited state is substantially shortened on going from $\mathbf{Os}^{2+}$ to **Os**-H_2^{4+}.[16] Therefore, the chance that such an excited state becomes involved in bimolecular events is greatly diminished upon protonation of the metal complex. It follows that the photoinduced proton transfer between **ME**-H^+ and $\mathbf{Os}^{2+}$ could be used to implement light control on the efficiency of bimolecular photosensitisation processes that originate from the osmium species.

To demonstrate the feasibility of this idea, we relied on the fact that the ^{3}MLCT excited state of oligopyridine complexes of Ru(II) and Os(II)[17] is able to generate singlet oxygen ($^1\Delta$) with good efficiency by energy transfer to the triplet ground state ($^3\Sigma$) of O_2.[18,19] Hence, we investigated the formation of singlet oxygen (monitored by its characteristic phosphorescence at 1270 nm) in air equilibrated solutions upon excitation of the osmium species in the ^{3}MLCT absorption band (λ = 600–780 nm).‡ The experiment can be described in terms of the following sequence of reactions (S_0 denotes the electronic ground state of the osmium complex):

$$\mathbf{Os}\ (S_0) + h\nu\ (600\text{–}780\ \text{nm}) \rightarrow \mathbf{Os}\ (^3\text{MLCT}) \qquad (1)$$

$$\mathbf{Os}\ (^3\text{MLCT}) + O_2\ (^3\Sigma) \rightarrow \mathbf{Os}\ (S_0) + O_2\ (^1\Delta) \qquad (2)$$

$$O_2\ (^1\Delta) \rightarrow O_2\ (^3\Sigma) + h\nu'\ (1270\ \text{nm}) \qquad (3)$$

In fact, we found that in air equilibrated MeCN solution $\mathbf{Os}^{2+}$ photosensitises the formation of O_2 ($^1\Delta$) with a quantum yield $\Phi_\Delta = 0.41$ upon excitation at 607 nm. Conversely, no luminescence at around 1270 nm, indicative of the presence of singlet oxygen, was observed in the case of **Os**-H_2^{4+}.

We then performed the photosensitisation experiments with the osmium complex in the presence of the **ME**-H^+ photoacid. The results are summarised in Fig. 2. Upon 607-nm excitation of an air equilibrated MeCN solution containing 8.4 μM $\mathbf{Os}^{2+}$ and 18 μM **ME**-H^+, we observed the singlet oxygen phosphorescence band shown in Fig. 2, curve ***a***. Irradiation of the solution at 400 nm for 60 min generates the **Os**-H_2^{4+} and **SP** species; for this solution we detected no emission peak in the NIR range, as shown in Fig. 2, curve ***b***. Successive thermal re-equilibration of the solution regenerates $\mathbf{Os}^{2+}$ and **ME**-H^+, and the singlet oxygen phosphorescence can again be seen upon excitation of the metal complex (Fig. 2, curve ***c***).

As noted above, the output reading in this system can be performed non-destructively on excitation with $\lambda > 500$ nm

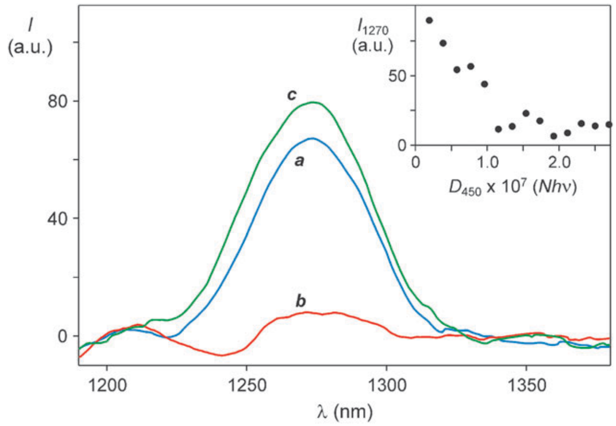

Fig. 2 Near-infrared phosphorescence spectra (λ_{exc} = 607 nm) of an air equilibrated MeCN solution containing 8.4 μM **Os**$^{2+}$ and 18 μM **ME**-H$^+$ (***a***), and of the same solution after exhaustive irradiation at 400 nm (***b***) and successive re-equilibration for five days at r.t. (***c***). The inset shows the O_2 ($^1\Delta$) phosphorescence intensity at 1270 nm for a solution containing **Os**$^{2+}$ (12 μM) and **ME**-H$^+$ (24 μM) as a function of the dose of light absorbed by the osmium complex at 450 nm. Note that in this experiment the same wavelength is employed for both irradiating the photoacid and exciting the Os species.

because light in this spectral range is not absorbed by the photoacid. However, an interesting behaviour arises if the solution is irradiated at a wavelength absorbed by both the **ME**-H$^+$ species and the osmium complexes. We chose 450 nm because at this wavelength **Os**$^{2+}$ and **Os**-H_2^{4+} have the same absorption coefficient.† In fact, starting from the **ME**-H$^+$/**Os**$^{2+}$ state, the NIR phosphorescence band of singlet oxygen is initially observed, but it progressively fades out on increasing the irradiation time (*i.e.*, the dose of light absorbed by the Os complex) because of the transformation of **ME**-H$^+$ into **SP** and concomitant conversion of **Os**$^{2+}$ into the shorter-lived **Os**-H_2^{4+} species (Scheme 1). Therefore, the photosensitised formation of O_2 ($^1\Delta$) takes place at low doses of light, whereas it becomes inefficient at high doses (Fig. 2, inset). Such a behaviour could be useful for the design of self-regulating systems[20] for applications, *e.g.*, in photodynamic therapy.

In summary, the coupled operation of the acid–base switchable complex **Os**$^{2+}$ and the photoacid system **ME**-H$^+$/**SP** has enabled us to devise a chemical ensemble in which a violet light input controls (a) a photoluminescence output in the far red spectral region, and (b) the photosensitised generation of singlet oxygen—and associated NIR phosphorescence—with self-regulating behaviour.

This molecular switching ensemble exhibits a number of interesting features, namely: (i) it can process input and output optical signals in the visible region; (ii) at the same time, a near-UV light input can control a light output in the near IR, thus bypassing the whole visible range; (iii) the outputs correspond to wavelengths in a spectral region (far red/near infrared) that is interesting, for instance, in communication technology and diagnostics; (iv) the photoluminescence output reading can be performed in a non-destructive manner; (v) owing to its reversibility and stability, the system can be cycled for several times without appreciable loss of signal, and (vi) the reset is thermally driven and thus it does not imply the addition of chemicals and accumulation of byproducts. The main limitation of this system in view of real applications is the very slow thermal reset, which however could be exploited to implement memory effects.[12]

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Notes and references

‡ The excitation spectra show that, as expected, the lowest excited state (^{3}MLCT) of these Os complexes is obtained with unit efficiency regardless of the wavelength of the absorbed light.

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