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A Dyad as Photocatalyst for Light-Driven Sulfide Oxygenation with Water As the Unique Oxygen Atom Source

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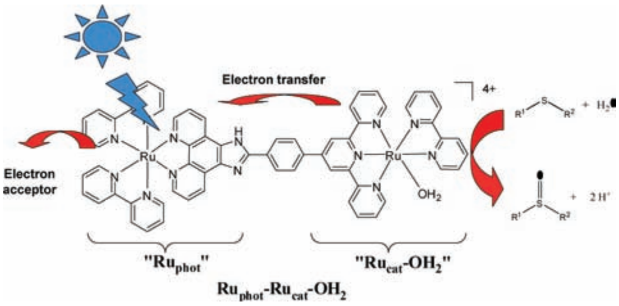
S *Supporting Information*

ABSTRACT: With the objective to convert light energy into chemical oxidation energy, a ruthenium-based dyad constituted of the assembly of a photosensitizer and a catalytic fragment was synthesized. Upon irradiation with blue LEDs, and in the presence of an electron acceptor, the complex is able to catalyze selective sulfide oxygenation involving an oxygen atom transfer from water to the substrate. Electrochemical and photophysical studies highlighted a proton-coupled electron transfer (PCET) to access to a high valent oxidant Ru(IV) oxo species.

Today, due to the running out of petrol and gas stocks combined with the pollution of the atmosphere, soils, and seas, the development of new catalytic solutions is becoming of paramount importance.[1] In order to perform oxygenation reactions, the use of water as an oxygen atom source appears to be an ideal solution. However, its activation by a metal is required, as photosystem II does using light energy to drive the oxidation of water.[2] Herein, we showed that the sulfide oxygenation reaction using water as an oxygen atom source can be light-driven using a sacrificial electron acceptor thanks to the use of a fully characterized ruthenium-based dyad constituted of a photosensitizer covalently bound to a polypyridyl ruthenium fragment as the oxygenation catalyst.[3]

The catalyst reported here ($[(bpy)_2Ru(tpphen)Ru(bpy)(OH_2)]^{4+}$, named $Ru_{phot}-Ru_{cat}-OH_2$, Scheme 1), is constituted of (i) a light-absorbing photosensitizing $[Ru(bpy)_3]^{2+}$-like fragment known to an efficient chromophore and (ii) a catalytic reaction center $[Ru(tpy)(bpy)(OH_2)]^{2+}$ (abbreviated by $Ru_{cat}-OH_2$) known to achieve organic substrate oxidation through its $[Ru(tpy)(bpy)(O)]^{2+}$ oxidized form.[4] Its synthesis and the characterization data of all of the compounds are reported in the Supporting Information.

Scheme 1. A Dyad As Photocatalyst for Sulfide Oxygenation Using Water As the Unique Oxygen Atom Source



The photocatalytic activities of the complex $Ru_{phot}-Ru_{cat}-OH_2$ (20 μM) were evaluated during sulfide oxidation in a deoxygenated 0.1 M phosphate buffer at a pH of 6.8 using $[Co(NH_3)_5Cl]Cl_2$ as an electron acceptor. 4-Bromophenyl methyl sulfide was used as a probe substrate, and a blue light emitting diode (LED) system of low wattage (less than 3 W) and emitting at 468 nm, which corresponds to the MLCT transition of the photosensitizer subunit, was used as a source of light. After 24 h of irradiation, for which maximum conversion was observed (Supporting Information), the reaction products were extracted and quantified by ^1H NMR spectroscopy.[5] The main results are reported in Table 1. First, they show that higher photocatalytic activity was observed for the $Ru_{phot}-Ru_{cat}-OH_2$ complex than for its chloro homolog since up to 201 turnover numbers (TON) were achieved compared to 81 with the $Ru_{phot}-Ru_{cat}-Cl$ complex, as a consequence of the slow Cl^-/H_2O exchange, even under light exposure (entries 1 and 2). This result emphasizes the role of the Ru_{cat} moiety as a catalyst during the catalytic process. Second, higher conversion was observed when the catalysis was performed with a catalyst/substrate/Co(III) 1:200:400 ratio (entries 1 and 4), affording the sulfoxide with an initial rate of about 10 TON h^{-1} (Supporting Information). It was also shown that basic (pH 10.7) or acidic (pH 4.4) conditions resulted in lower catalytic activity, probably as a consequence of the amphoteric property of the imidazole moiety of the bridging ligand (entries 4–6).[6] Control experiments showed that, in the absence of light, a catalyst, or an electron acceptor, no product was detected. Surprisingly, the photosensitizer Ru_{phot}, though devoid of a $Ru_{cat}-OH_2$ entity, showed a non-negligible catalytic activity with 36 TON after 24 h (entry 7). Slightly better activity was also observed with the $[Ru(tpy)(bpy)(OH_2)]^{2+}$ complex, represented by the $Ru_{cat}-OH_2$ fragment (entry 8). However, both activities remained far from that of the dinuclear complex. Finally, the stoichiometric combination of both constituents of the dyad, namely Ru_{phot} and $Ru_{cat}-OH_2$ (20 μM each), led to the formation of the sulfoxide with 71 TON, probably as a result of the combined activities of both complexes (entry 9). These important results emphasize more efficient communication between both partners in the dyad compared to the bimolecular system. Such a synergetic effect was not shown in the nice

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Table 1. Photocatalytic Oxidation of 4-Bromophenyl Methyl Sulfide Using a Blue LED System As a Source of Light[a]

entry	complex	cat./subs./Co(III) ratio	pH	TON (conv %)
1	$Ru_{phot}-Ru_{cat}-OH_2$	1:500:1000	6.8[c]	201 (40)
2	$Ru_{phot}-Ru_{cat}-Cl$	1:500:1000	6.8[c]	81 (16)
3	$Ru_{phot}-Ru_{cat}-OH_2$	1:500:1000	*d*	18 (9)
4	$Ru_{phot}-Ru_{cat}-OH_2$	1:200:400	6.8[c]	132 (66)
5	$Ru_{phot}-Ru_{cat}-OH_2$	1:200:400	4.4[b]	83 (42)
6	$Ru_{phot}-Ru_{cat}-OH_2$	1:200:400	10.7[e]	10 (5)
7	Ru_{phot}	1:200:400	6.8[c]	36 (18)
8	$Ru_{cat}-OH_2$[f]	1:200:400	6.8[c]	45 (23)
9	Ru_{phot} + $Ru_{cat}-OH_2$[f]	1:1:200:400[g]	6.8[c]	71 (36)

[a] Photocatalytic oxidations performed in aqueous conditions with [catalyst] = 0.02 mM for 24 h. [b] A 0.1 M Sodium acetate buffer (pH 4.4). [c] A 0.1 M phosphate buffer (pH 6.8). [d] Reaction performed in unbuffered deoxygenated water. [e] A 0.1 M sodium carbonate buffer (pH 10.7). [f] $Ru_{cat}-OH_2$ is $[Ru(tpy)(bpy)(OH_2)]^{2+}$. [g] $[Ru_{phot}] = [Ru_{cat}-OH_2] = 0.02$ mM

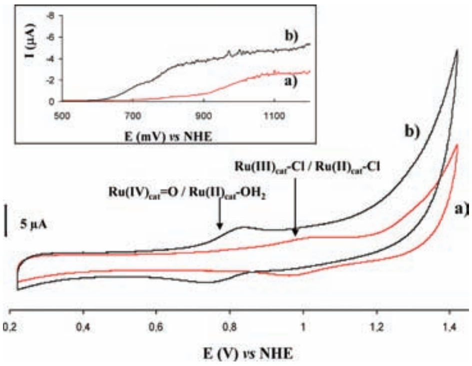


Figure 1. Cyclic voltammograms and RDE experiments (inset) of (a) $Ru_{phot}-Ru_{cat}-Cl$ and (b) $Ru_{phot}-Ru_{cat}-OH_2$ complexes (0.43 mM in a 85:15 mixture of 0.1 M sodium phosphate buffer (pH 6.8) and acetonitrile).

multicomponents system reported very recently by Nam and coworkers.[7] Finally, a quantum yield of 0.09 of the photocatalytic oxygenation was determined using chemical actinometry under irradiation with monochromatic light ($\lambda = 436$ nm; Supporting Information). The absorption spectrum of the reaction mixture performed at the end of the photocatalytic process shows that, after 24 h of illumination, about 40% of the catalyst was recovered (Supporting Information).

In order to collect mechanistic information, electrochemical and photophysical studies were undertaken. The cyclic voltammograms of $Ru_{phot}-Ru_{cat}-OH_2$ showed one reversible oxidation process at +0.79 V vs NHE (Figure 1). This wave was attributed to the oxidation of the Ru_{cat} center since oxidation of the Ru_{phot} complex arises at a higher potential (Supporting Information), as for $[Ru(diimine)_3]^{2+}$ cations.[8] By comparison with the oxidation of the $Ru_{cat}-Cl$ moiety, which is a one-electron process arising at +1.00 V vs NHE,[4a,9] experiments achieved with a rotating disk electrode (RDE; 1000 rpm) showed unambiguously that the electrochemical oxidation of the $Ru(II)_{cat}-OH_2$ moiety corresponds to a two-electron process yielding to the $Ru(IV)_{cat}=O$ species (Figure 1, inset). A different behavior was reported for the $[Ru(tpy)(bpy)(OH_2)]^{2+}$ complex ($Ru_{cat}-OH_2$), for which two one-electron oxidation waves attributed to the Ru(III)/Ru(II) and Ru(IV)/Ru(III) couples were observed.[10]

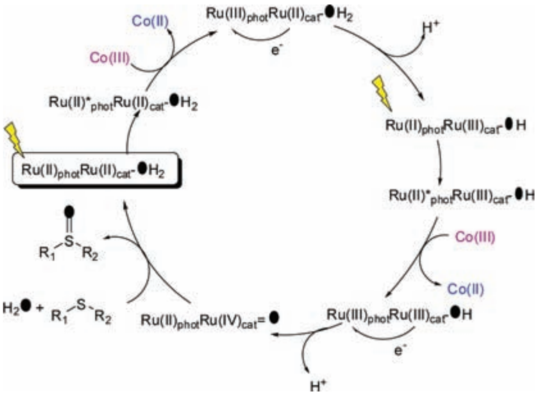
Moreover, the Pourbaix diagram of the $Ru_{phot}-Ru_{cat}-OH_2$ species showed that the observed two-electron oxidation process involving the $Ru(IV)_{cat}=O/Ru(II)_{cat}$ couple is dependent on the pH by approximately 59 mV per pH unit over the range pH 2−8 (Supporting Information). These results are in agreement with a PCET process involving two protons and two electrons avoiding a charge buildup during the oxidation process. As a consequence, the oxidation potential of the $Ru(IV)_{cat}=O/Ru(II)_{cat}-OH_2$ couple is lower than that corresponding to the $Ru(III)_{cat}-Cl/Ru(II)_{cat}-Cl$ couple for which no PCET process is involved, even though the Cl^- ligand is negatively charged and a strong donor.[9,11] Finally, as a consequence of the higher oxidation potential of the photosensitizing subunit compared to that of $Ru(IV)_{cat}/Ru(II)_{cat}$, the versatile oxidant $Ru(IV)_{cat}=O$ species is expected to be formed if a $Ru(III)_{phot}$ entity can be photogenerated.

The oxygen atom transfer from the water molecule to the substrate was then highlighted by an isotopic labeling experiment in a phosphate buffer containing 33% $H_2{}^{18}O$. Under such conditions, a 2:1 mixture of unlabeled and labeled sulfoxide was obtained. This was also proved by performing the reaction in pure degassed unbuffered water in order to preclude the intervention of the phosphate anion as a potential oxygen atom source in the oxidative process (entry 3, Table 1). In such conditions, an increase of the acidity of the solution during the course of the catalysis may explain the lower activity as a consequence of the shift of the redox potential of the Ru_{cat} center to a higher value as observed in the Pourbaix diagram.

The luminescence of $Ru_{phot}-Ru_{cat}-OH_2$ and of the Ru_{phot} model compound was then measured in a 0.1 M degassed phosphate buffer (pH 6.8) in the absence of the Co(III) salt. The data showed that the Ru_{phot} complex exhibited a characteristic emission for tris(diimine)Ru(II) compounds,[8] centered at 604 nm, with a monoexponential lifetime of 812 ns and a quantum yield of 0.011 (Supporting Information). The luminescence spectra of $Ru_{phot}-Ru_{cat}-OH_2$ show two weak emission maxima at about 613 and 710 nm attributed to the deactivation of the Ru_{phot} moiety and of the Ru_{cat} part of the complex, respectively. The lower energy of the second emission is explained by the presence of the terpyridine ligand and the π-donating OH_2 ligands. At this wavelength, the luminescence quantum yields were estimated to be about 10^{-4}. Moreover, the coordination of the $Ru_{cat}-OH_2$ moiety to the chromophore Ru_{phot} resulted in a partial quenching of the Ru_{phot} emission with a rate constant of 1.2×10^8 M^{-1} s^{-1} involving an energy transfer toward Ru_{cat}. Indeed, the driving force of a potential reductive electron transfer from Ru_{cat} to Ru_{phot} was calculated to be ca. 0 eV. This is also supported by the spectral overlap between emission of Ru_{phot} and absorption of $Ru_{cat}-OH_2$ within the dyad.

In the presence of a large excess of $[Co(NH_3)_5Cl]Cl_2$ (400 equiv), continuous photolysis of a solution of $Ru_{phot}-Ru_{cat}-OH_2$ in a deoxygenated 0.1 M phosphate buffer was then performed with a 250 W xenon lamp equipped with a 460 nm band-pass filter. Electronic modifications of the mixture were followed by UV−visible spectroscopy (Supporting Information). While in the absence of irradiation, the absorption spectrum of the mixture remains stable over hours, upon irradiation, a decrease of both MLCT bands in the visible domain was mainly observed. This was attributed to the concomitant reduction of the Co(III) salt in its low soluble Co(II) form and the oxidation of one or both

Scheme 2. Proposed Reaction Mechanism for the Photocatalytic Oxygenation of Sulfide by $Ru_{phot}-Ru_{cat}-OH_2$



of the ruthenium center(s) at the Ru(III) or Ru(IV) level at least. During the 2 h experimental time, significant decomposition of the complex has to be precluded, as was observed under catalytic conditions. This observation is of importance, giving evidence for an electron transfer from the dyad to the electron acceptor upon light irradiation. In the absence of any substrate, the subsequent reduction of the photooxidized ruthenium center(s) cannot be achieved. These results show that the cobalt salt is able to short-circuit the energy transfer from the Ru_{phot} excited state to the $Ru(II)_{cat}-OH_2$ moiety observed in the absence of the electron acceptor, by an electron transfer. As a consequence, oxidation of the $Ru(II)_{cat}$ subunit by the transient photogenerated $Ru(III)_{phot}$ moiety can be performed.

In conclusion, we reported here the proof of concept of a photocatalyst constituted by the coupling of a light-absorbing photosensitizing fragment and catalytic reaction center within the same entity for sulfide oxygenation using water as the oxygen atom source. On the basis of the mechanism proposed by the groups of Fukuzumi and Nam[7] and thanks to the electrochemical and photophysical results, associated with the photocatalytic activity of the $Ru_{phot}-Ru_{cat}-OH_2$ complex, the catalytic mechanism shown in Scheme 2 is suggested. The absorption of two photon equivalents by Ru_{phot} initiates two PCET processes from the $Ru(II)_{cat}$ moiety to the Co(III) salt, resulting in the formation of the oxidizing $Ru(II)_{phot}Ru(IV)_{cat}{=}O$ species.[12] The aquo form of the catalyst is then recovered after an oxo transfer to the substrate. These results should represent an important consideration in the design of future catalysts for various light-driven oxidation reactions using water as an oxygen atom source. In the near future, replacement of the commonly used electron acceptor Co(III) salt will be a requirement to converge toward a more eco-aware photocatalytic system.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed synthetic procedures, NMR spectra of compounds, absorption spectra of the complexes, electrochemical studies, photocatalytic oxygenation results, and isotopic labeling experiment. This material is available free of charge via the Internet at http://pubs.acs.org

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(5) The catalytic activity of $Ru_{phot}-Ru_{cat}-OH_2$ was then assayed during the oxidation of a variety of sulfides under the optimized conditions (Supporting Information). All of the sulfides were selectively converted into their corresponding sulfoxides with TON ranging from 13 to 132. In all cases, no evidence for the formation of the sulfones could be obtained.

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(12) Involvement of a sulfide radical cation arising from a direct oxidation of the sulfide by the photogenerated Ru(III)phot species is a pathway to reject. Indeed, high potentials (>2−2.7V vs NHE) are required to carry out such an oxidation. (a) Devyatova, N. F.; Kurbangalieva, A. R.; Yanilkin, V. V.; Chmutova, G. A. *Russ. Chem. Bul., Int. Ed.* **2009**, *58*, 908. (b) Yamamoto, K.; Shouji, E.; Suzuki, F.; Kobayashi, S.; Tsuchida, E. *J. Org. Chem.* **1995**, *60*, 452. The potential of the Ruphot(III)/Ruphot(II) couple is **only** +1.46 V vs NHE. Moreover, no trace of products from radical decomposition was found.

■ NOTE ADDED AFTER ASAP PUBLICATION

There were errors in the third column of Table 1 in the version of this paper published July 27, 2011. The correct version published August 1, 2011.