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Photocatalyzed Sulfide Oxygenation with Water as the Unique Oxygen Atom Source

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ABSTRACT: In our research program aiming to develop new ruthenium based polypyridine catalysts for oxidation we were interested in combining a photosensitizer and a catalytic fragment within the same complex to achieve catalytic light driven oxidation. To respond to the lack of such conjugates, we report here a new catalytic system capable of using light to activate water molecules in order to perform selective sulfide oxygenation into sulfoxide via an oxygen atom transfer from H₂O to the substrate with a TON of up to 197 ± 6. On the basis of electrochemical and photophysical studies, a proton coupled electron transfer process yielding to an oxidant Ru(IV)−oxo species was proposed. In particular, the synergistic effect between both partners in the dyad yielding a more efficient catalyst compared to the bimolecular system is highlighted.

INTRODUCTION

In the past decade, a tremendous amount of effort has been devoted to solar energy to chemical energy conversion to promote chemical reactions of interest.¹ To perform such a transformation, ruthenium polypyridine complexes, thanks to their interesting photophysical properties, have emerged as candidates of choice.² Since the pioneering work of Deronzier et al. about 20 years ago, development of photocatalytic systems for organic synthesis has attracted very little attention until now.³ Currently, the necessary search for new energies has stimulated researchers to design new photocatalysts. As a consequence, in the past few years the number of photoredox catalysts has then increased spectacularly in the literature.⁴ Among others, one can cite the very efficient systems reported by T. P. Yoon⁴g and C. R. J. Stephenson ⁴f for [2 + 2] cycloaddition of enones and reductive halogenation, respectively. By combining an inorganic catalyst ([Ru(bpy)₃]²⁺) with a photoredox catalyst with a chiral amine as an organocatalyst to perform efficient enantioselective alkylation of aldehydes, MacMillan et al. reported probably the most elegant example of photoredox catalysis to date.⁴i On the other hand, inspired by photosystem II, some heterogeneous and homogeneous systems were developed to perform one of the most challenging reactions, photooxidation of water into dioxygen.⁵ In most of these cases, a ruthenium polypyridine complex acting as catalyst was associated to ruthenium tris(diimine) complexes as photosensitizers. In such catalytic systems it is proposed that after initiation by light an oxidizing ruthenium oxo species is formed due to an intermolecular electron transfer from the catalyst to the sacrificial electron acceptor via the chromophore. In the field of redox catalysis, such high valent species also oxidize a wide range of organic substrates such as alkanes, alkenes, and sulfides.⁶ In the course of the development of new, eco aware catalytic systems and to achieve efficient catalytic light driven oxygenation of organic substrates, we were interested in the design of a photocatalyst combining a photosensitizer and a catalytic fragment within the same entity in order to promote direct electron transfer between both partners. To the best of our knowledge, only two reports using this approach have been published, both very recently. First, during the course of this work, Rocha and co workers reported the use of a dinuclear ruthenium based complex to perform photocatalytic alcohol oxidation into the corresponding...
aldehyde or ketone. However, unlike sulfide and alkane oxidation, in that case no oxygen atom incorporation into the substrate is required. Very recently we also showed that a similar dyad selectively oxidizes sulfides into sulfoxides. A proton coupled electron transfer (PCET) process was proposed. Involving formation of a Ru(IV)−O species thanks to a proton coupled electron transfer process was proposed.

EXPERIMENTAL SECTION

Materials and Methods. Ru(bpy)₃Cl₂·6H₂O and RuCl₃ were purchased from Strem Chemicals. Bipyrimidine, 2,2′:6,2′-terpyridine, and [Co(NH₃)₅Cl][Cl₂] were obtained from Sigma Aldrich. Solvents used in synthetic procedures were analytical grade. All experiments involving ruthenium complexes were carried out in the absence of light to avoid any racemization process. [(bpy)₂Ru(bpy)₂]²⁺ (designated Ru⁺⁺) recently published by T. J. Meyer while this work was under progress as catalyst for water oxidation using Ce(IV) as oxidant. In this paper we showed that this catalyst also has the ability to selectively photooxidize sulfide into sulfoxide using water as the unique source of oxygen atom (Scheme 1). In particular, a synergistic effect was observed between both partners of the dyad compared to the bimolecular system. Finally, based on electrochemical and photophysical studies and on literature reports a mechanism involving formation of a Ru(IV)==O species thanks to a proton coupled electron transfer process was proposed.
Actinometry experiments were performed using potassium ferrioxalate as an actinometer according to a reported procedure. A 150 W xenon lamp equipped with a monochromator (λ = 436 nm) was used. The light intensity of the monochromatic light was determined as 7.3 × 10⁻¹⁰ einstein·s⁻¹. The variation of the absorbance at 510 nm of the solution as a function of irradiation time is shown in Figure S1, Supporting Information.

The photochemical photooxygenation was performed in a square quartz cuvette (10 mm path length) containing a mixture of catalyst, 4 bromophenyl methyl sulfide substrate, and Co(III) salt in a 0.1:50:100 mM ratio in 0.1 M phosphate buffer (pH 6.8). Formation of the product was monitored by gas chromatography (Autosystem XL) taking aliquots from the reaction mixture and using benzophenone as reference. A quantum yield of 0.32 was determined in the conditions described above.

**Synthesis and Characterization.**

To a solution of [(bpy)₂Ru(bpym)Ru(tpy)Cl][PF₆]₃ (470 mg, 98% yield) was obtained as a green powder. ¹H NMR (300 MHz, acetone-d₆) δ (ppm) = 10.07 (d, 1H, 5.7 Hz), 8.91–8.87 (m, 5H), 8.79–8.68 (m, SH), 8.58 (d, 1H, 5.4 Hz), 8.48 (t, 1H, 1.8 Hz), 8.33–8.16 (m, 9H), 8.08 (dd, 2H, 5.4 Hz, 12.6 Hz), 7.93 (d, 2H, 5.7 Hz), 7.74 (dd, 1H, 6.3 Hz, 6.3 Hz), 7.60–7.63 (m, 2H), 7.58–7.50 (m, 3H), 7.28 (t, 1H, 5.7 Hz), 6.27 (s large, 2H). ESI MS (m/z) (relative intensity) 1216, ([Ru₉cat−OH₂][PF₆]₃−H⁺)⁺ (7); 534.5, ([Ru₇cat−OH₂][PF₆]−H⁺)²⁺ (100). UV–vis (H₂O, λₑₘₙ₅₅₀ nm, ε₉₅₀ nm⁻¹·cm⁻¹): 278 (65 900), 303 (29 900), 331 (12 800), 399 (50 200), 445 (12 500), 610 (6900). Anal. Calcd for [Ru₇cat−OH₂][PF₆]₂: C, 33.54; H, 2.55; N, 9.82.

**Standard Conditions for Photocatalytic Sulfide Oxidation.** A 0.02 mM solution of [Ru₇cat−OH₂][PF₆]₃ in a 0.1 M sodium phosphate buffer at pH 6.8 was prepared and stored at −20 °C.

To 5 mL of this solution in a Schlenk system 1000 equiv of [Co(NH₃)₅Cl]Cl₂ (25 mg, 100 μmol) was added. The solution was degassed for 15 min by Ar bubbling, and then 500 equiv (50 μmol) of substrate was added under an inert atmosphere. The sample was irradiated at 180 W for 24 h. After extraction of the organic products by dichloromethane (x2) and diethyl ether (x2) a known quantity of 3,4,5 trimethoxybenzaldehyde was added as reference. After vacuum distillation, products were characterized and quantified using ¹H NMR spectroscopy by comparison of the integral ratio of the methyl signals of the product and those of the methoxy signals of the reference.

**Synthesis and Characterization of the Catalyst.** In 2009 the synthesis of the Ru₇cat−OH₂ complex was achieved in two steps in moderate overall yield (5%) by condensation of Ru(bpy)₂Cl₂ and [(bpym)Ru(tpy)]²⁺ to yield the Ru₇cat−OH₂ precursor. Subsequent Cl⁻/H₂O exchange was achieved via formation of the [(bpym)Ru(bpy)tpy]OTf⁻ complex (OTF⁻ = trifluoromethanesulfonate) as an intermediate. However, reaction of [(bpym)Ru(bpy)][PF₆]²⁺ (named Ru₇cat) and Ru(tpy)Cl₂ in a refluxing mixture of 2:1 ethanol–water and subsequent direct substitution of the chloro ligand by a water molecule using Ag(OTf) in refluxing water (Scheme 2) proved to be more efficient according the desired Ru₇cat−OH₂ dinuclear complex in higher yield (90% for two steps). The presence of the water molecule as ligand in the final product was confirmed by ¹H NMR in acetone-d₆ as a broad singlet at 6.27 ppm and integrated for two protons. This signal disappeared immediately after addition of a few drops of D₂O as a result of H₂O/D₂O exchange (Figure S1, Supporting Information).

Both dinuclear systems were fully characterized by ¹H NMR spectroscopy, ESI mass spectrometry, and elemental analyses. ESI mass spectra displayed fragments at 1232 and 1216 m/z corresponding to the monocations ([Ru₇cat−OH₂][PF₆]⁻ and ([Ru₇cat−OH₂][PF₆]−H⁺), respectively. The electronic properties of both complexes were investigated and compared to those of the Ru₆cat system (Table 1, Figure S1, Supporting Information) whose transitions were assigned on the basis of literature reports.

Assignments of the bands at higher energy (280–300 nm) were ascribed to ligand centered transitions (1LC) with π–π* transitions. Two metal to ligand charge transfer (MLCT) bands were also observed at lower energy in the visible region of the electronic spectrum.
absorption spectrum at 417 and 475 nm. Addition of the Ru
moieties to the Ruphot, metalloigand resulted in the appearance of an additional transition at 622 and 610 nm for Ru–Ru=Cl and Ru–Ru=OH2, respectively, attributed to the d(Ru–Ru) → π∗(bpym) MLCT transition.10 Substitution of Cl− for H2O results in a significant blue shift of the MLCT of lower energy as a consequence of the destabilization of the dπRu transition level through π donation from Cl− (from 469 to 445 nm and from 622 to 610 nm) in the Ru–Ru=Cl complex.16

**Photocatalytic Oxygenation.** While various oxidants are used to oxidize sulfides into sulfoxides17 very few photocatalytic systems were reported to date to perform such a transformation.8,18 Thus, photooxidation of 4 bromophenyl methyl sulfide to the corresponding sulfoxide by Ru–Ru=OH2 as Catalyst showed almost similar activity with a TON of 131 ± 6 (entry 2) with an excellent selectivity since no other product was formed. Similarly to the experiments showed that in the absence of light (entry 3), catalyst, or electron acceptor no product was formed. Interestingly, those complexes (Ru–Ru=Cl and Ru–Ru=OH2) showed almost similar activity with a TON of about 135 (entries 1 and 2). This may be attributed to the formation of the Ru–Ru=Cl photocatalyst and Ru–Ru=OH2 catalyst by a fast CT/H2O ligand exchange which could occur in the catalytic conditions. Finally, the quantum yield of the photocatalytic oxygenation was determined by actinometry using potassium ferrioxalate as actinometer under irradiation with a monochromatic light (λ = 436 nm; light intensity 7.3 × 10−11 einstein s−1).19 For the catalytic system substrate:Co(III) salt, 0.1:50:100 mM in 0.1 M phosphate buffer (pH 6.8), a quantum yield of 0.32 of the photocatalytic oxygenation was determined.

**Table 1. Spectroscopic Data for [(bpy)2Ru(bpym)][PF6]2 [(Ruphot)[PF6]3], [(bpy)2Ru(bpym)Ru(tpy)Cl][PF6]3 [(Ru–Ru=Cl)[PF6]4], and [(bpy)2Ru(bpym)Ru(tpy)OH2][PF6]4 (Ru–Ru=Cl).[a]

| Compound | λπ−π∗(nm) (ε/M−1 cm−1) | dπRu−π∗(Ru–Ru)(nm) |
|----------|-------------------------|---------------------|
| Ru–Ru=Cl | 283 (53 000)            | 417 (12 300)        |
| Ru–Ru=OH2| 278 (65 900)            | 409 (20 500)        |
| Ru–Ru=OH2| 303 (29 900)            | 445 (12 500)        |
| Ru–Ru=OH2| 331 (12 800)            |                     |

[a] 10 μM in water. b dπRu−π∗(Ru–Ru) transition.

**Table 2. Photocatalytic Oxidation of 4 Bromophenyl Methyl Sulfide[a]

| Entry | Complex:Substrate:Co(III) | Light | TON  |
|-------|---------------------------|-------|------|
| 1     | Ru–Ru=Cl                  |       | 140 ± 10 |
| 2     | Ru–Ru=OH2                 |       | 131 ± 6 |
| 3     | Ru–Ru=OH2                 |       | 0    |
| 4     | Ru–Ru=Cl                  |       | <5   |
| 5     | Ru–Ru=OH2                 |       | <10 ± 2 |
| 6     | Ru–Ru=OH2                 |       | 0    |
| 7     | Ru–Ru=Cl                  |       | 56 ± 4 |
| 8     | Ru–Ru=Cl                  |       | 195 ± 8 |

[a] Complex:Substrate:Co(III) 0.02:10:20 mM in 0.1 M phosphate buffer (pH 6.8) for 24 h. Sun: Xenon lamp (180 W). Moon: in the absence of light. b [Ru–Ru]= [Ru–Ru=OH2] = 0.02 mM. After addition of a second portion of Co(III) salt (1000 equiv) and additional 24 h of irradiation.

**Table 3. Photocatalytic Oxidation of a Variety of Sulfides Using Ru–Ru=OH2 as Catalyst[a]

| Substrate R1 | R1 = phenyl | R1 = 4-bromophenyl | R1 = 2-bromophenyl | R1 = 4-methoxyphenyl | R1 = 4-nitrophenyl | Alcohol | Alkene | cis-cyclooctene |
|--------------|-------------|-------------------|-------------------|--------------------|------------------|--------|--------|---------------|
| S CH3        | 124 ± 4     | 131 ± 6           | 133 ± 4           | 197 ± 6            | 51 ± 5           | 25 ± 3 | 3      | 0             |
| R1 = 4-methoxyphenyl | 197 ± 6 | 51 ± 5           |        |        |        |        |        |               |
| R1 = 4-nitrophenyl |        |        |        |        |        |        |        |               |
| Alcohol      | 25 ± 3      | 3                |        |        |        |        |        |               |
| Alkene       | 3           | 3                |        |        |        |        |        |               |
| cis-cyclooctene | 0        | 0                |        |        |        |        |        |               |

[a] Catalyst: Substrate: Co(III) 0.02:10:20 mM in 0.1 M phosphate buffer (pH 6.8); Xenon lamp (180 W) for 24 h.

The photocatalytic activity of the catalyst Ru–Ru=OH2 was then assayed during oxidation of a variety of sulfides (Table 3). With the exception of the 4 nitrophenyl methyl sulfide, all substrates were efficiently converted into their corresponding sulfoxide with TON ranging from 124 ± 4 to 197 ± 6 and with excellent selectivities since no overoxidation products could be detected. Even though the solubility properties of the various substrates are different in aqueous conditions, it seems that the reactivity is directly correlated to the electronic effect of the para substituent on the substrate. Only 51 ± 5 TON was achieved after 24 h of irradiation with the NO2 electron withdrawing substituent, whereas more than 197 ± 6 TON was obtained when the para substituent is the methoxy electron donating group. In the same conditions, lower catalytic activity was observed during alkenes and alcohol oxidation. As an example, only 25 ± 3 and 3 TON were achieved during oxidation of 1 phenylethanol and trans β methyl styrene into the corresponding ketone and trans epoxide, respectively. No oxidized product could be detected with electron poor alkenes such as cis cyclooctene and methyl trans cinnamate.

The stability of the catalyst toward light was confirmed, first, by irradiation of a solution of the catalyst in phosphate buffer. On the basis of electronic absorption, after 24 h of light exposure more than
70% of the catalyst remains unchanged (Figure S1, Supporting Information). Second, when a second portion of 1000 equiv of Co(III) salt was added to the catalytic mixture after 24 h of irradiation and the resulting solution was irradiated for additional 24 h, the catalytic activity increased about 50% from 131 ± 6 to 195 ± 8 TON (Table 2, entry 8).

**Electrochemical Studies.** The electrochemical behavior of both Ru_{hap}→Ru_{cat}→OH_2 and Ru_{phot}→Ru_{cat}→Cl complexes was investigated in a 0.1 M phosphate buffer (pH 6.8; Figure 1). Data are reported in Rucat vs NHE, respectively (Figure 1). These waves were attributed to oxidation of the Ru_{cat} center by comparison with the oxidation of [Ru(diimine)]^{2+} systems which usually arise at higher potentials (in the range 1.4–1.9 V vs NHE, i.e., +1.51 and +1.46 V vs NHE for the Ru_{hap} and Ru_{phot}→Ru_{cat}→OH_2 complexes, respectively).b For Ru_{phot}→Ru_{cat}→OH_2 the reversibility of the oxidation wave of the catalytic center can be observed at 200 mV.s^{-1} (Figures S9 and S10, Supporting Information). In the CV of the Ru_{phot}→Ru_{cat}→Cl complex a small wave at +0.92 V vs NHE became largely predominant after 2 days was assigned to the aquo species (Figure S11, Supporting Information). It is noteworthy that in such conditions, avoiding light exposure and Co(III) salt, the Cl^−/H_2O ligand exchange proved to be largely slower than in the photocatalytic conditions used for sulfide oxygenation.

An experiment using a rotating disk electrode (RDE, 500 rpm, inset Figure 1) showed unambiguously that oxidation of the Ru_{cat}→Cl subunit is a two electron process yielding a Ru_{cat}→Cl→O species. This was confirmed by analysis of its relative current intensity (integrated area) compared to the one of the Ru_{cat}→Cl reduction, which is one electron process. Moreover, it was also observed that this oxidation potential decreased linearly with pH over the range pH 1–7 with a slope of ~0.056 V/pH unit (Figure S12, Supporting Information). These data are in agreement with a PCET process involving two protons and two electrons avoiding charge build up during oxidation. As a consequence, the oxidation potential of the Ru_{cat}→Cl/O species is lower than that corresponding to the Ru_{cat}→Cl/Ru_{cat}→Cl→Cl couple for which no PCET process is involved, even though the Cl^- ligand is negatively charged and a strong donor.10 Finally, as the potential of the Ru_{phot}→Ru_{cat}→Cl couple is higher than the one of the Ru_{cat}→Cl/Ru_{cat}→Cl→Cl couple in the Ru_{phot}→Ru_{cat}→OH_2 complex oxidation of the Ru_{cat}→Cl→O fragment into a more oxidized Ru_{phot}→Cl→O species by the photogenerated Ru_{phot}→Cl→O (III) is favored.

**Oxygen Atom Transfer from H_2O to the Substrate.** In order to highlight the oxygen atom transfer from the water molecule to the substrate, an isotopic labeling study employing a 1:1 mixture of H_2O and H_2^{18}O was carried out. After the usual extractions the product mixture was analyzed by GC MS, and the results were compared to the unlabeled sulfoxide displaying fragments at m/z 218 and 220 (Figure 2). The mass spectra of the mixture disclosed formation of a 1:1 mixture of both labeled and unlabeled sulfoxide with fragments at m/z 220, 222, and 218, 220 respectively. This result is fully consistent with an oxygen atom transfer from water to the substrate.

**Photophysical Studies.** To gain better insight into the photo physical behavior of the nonemissive dinuclear catalyst transient absorption spectroscopy was employed, exciting into different MLCT bands in the visible region under pseudocatalytic conditions in the absence of Co(III) salt. The excited behavior of model [([bpy])_2Ru(bpy)]^{4+} (named Ru_{phot}→Ru_{phot}→Cl) and Ru_{phot}→Ru_{cat}→Cl was seen to be rather different (Figures 3 and 4). Exciting Ru_{phot}→Ru_{phot}→Cl gave rise to a transient absorption signature attributed to a low lying MLCT state involving the easily reduced bridging ligand and an adjacent ruthenium with a lifetime of 1.8 ns in air equilibrated to a low lying MLCT state involving the easily reduced bridging ligand and an adjacent ruthenium with a lifetime of 1.8 ns in air equilibrated buffer solution. On the other hand, on exciting the dinuclear aquo complex a similar absorption signature is formed showing a similar intermediate based on the Ru_{phot} subunit, regardless of excitation wavelength. The lifetime is only 80 ps (and insensitive to the presence of oxygen). The induced quenching may be attributed to an intramolecular photoinduced electron transfer (PET) reaction as suggested by the catalytic results. However, other quenching mechanisms cannot be entirely ruled out. Assuming the dominant quenching pathway is a PET process from Ru_{cat} to the excited state of the Ru_{phot} subunit, a rate constant of 1.2 × 10^{10} s^{-1} can be estimated, with a small net driving force of ca. -0.1 eV.21 In spite of the short lived excited state under degassed conditions in the presence of 1000 equiv of cobalt salt this excited state lifetime was further shortened to around 50 ps, showing rapid diffusion, approaching the diffusion limit and/or static quenching, permitting electron transfer to the electron acceptor, potentially an important enabler in the catalytic reaction.

**DISCUSSION**

To date, it is well known that [(diimine)Ru(tpy)]→OH_2^{2+} systems have an extensive and well defined catalytic oxidation chemistry involving the high valent [(diimine)Ru(tpy)]→O^{2+} species.80 This system was shown to be particularly efficient for
catalytic oxidation of alcohols, aldehydes, and unsaturated hydrocarbons. Through the pioneering work of T. J. Meyer it was also shown that the molecular assembly of a [(diimine)Ru(tpy)−OH2] based catalyst with a chromophore allowed photodehydrogenation of propanol on TiO2. With the system described here, by combining a photosensitizer and a [(bpy)Ru(tpy)−OH2] like fragment we showed that the sulfoxide can be selectively and catalytically obtained without further overoxidation into the corresponding sulfone with a TON in the range of the ruthenium based bimolecular and binuclear photocatalysts reported by Rocha and very recently by Sun and our group.

Figure 2. Experimental mass spectra of (a) the corresponding sulfoxide obtained using a standard procedure, (b) the corresponding labeled and unlabeled sulfoxides obtained in an unbuffered deoxygenated H216O−H218O 1:1 mixture (instead of the buffered solution), and (c) simulated spectra of unlabeled 4 bromophenyl methyl sulfoxide (top) and 18O labeled 4 bromophenyl methyl sulfoxide (bottom).

Figure 3. (1) (a) Transient absorption spectrum of Ru_{phot}−Ru_{phot}, and (b) calculated excited state absorption of Ru_{phot}−Ru_{phot}. λ_{exc} = 430 nm in aqueous buffer solution. (2) (a) Transient absorption spectrum of Ru_{phot}−Ru_{cat}−OH2, and (b) calculated excited state absorption of Ru_{phot}−Ru_{cat}−OH2. λ_{exc} = 430 nm in aqueous buffer solution.

Figure 4. Kinetics model of transient absorption spectral changes at 430 nm: (a) Ru_{phot}−Ru_{phot} (τ = 1.8 ns), (b) Ru_{phot}−Ru_{cat}−OH2 (τ = 86 ps), and (c) Ru_{phot}−Ru_{cat}−OH2 in the presence of electron acceptor (Co(III) salt 1000 equiv; τ = 57 ps). λ_{exc} = 600 nm in aqueous buffer solution.
recently by us in terms of both the stability and the catalytic efficiency during sulfide oxygenation in the same conditions. This can be attributed to the relative structural homology between both partners. More importantly, the results collected in Table 2 highlight the absolute necessity to associate both partners (chromophore and catalytic fragment) to be able to perform the photocatalytic reaction. Indeed, no product could be detected when they are used independently, whereas up to 56 ± 4 TON was reached by the bimolecular system. The dyad proved to be even more efficient with up to 131 ± 6 TON emphasizing the advantage of combining both partners within a unique photocatalytic entity for a better communication between them. This suggests that the (inter vs intra) molecular electron transfer from the catalyst to the photosensitizer directly impacts the efficiency of the photocatalytic system.

As far as the Ru\textsubscript{phot}−Ru\textsubscript{cat}−Cl precursor is concerned, it was observed that several days are needed for its conversion into its corresponding aquo compound in water in the absence of silver salt (Figure S11, Supporting Information) while a few hours are required for the cation [Ru(tpy)(bpy)Cl]\textsuperscript{+}.\textsuperscript{19a,24} This difference in behavior can be attributed to the significant electron attracting effect of the Ru\textsubscript{phot} moiety as it was noted by the group of C. P. Berlinguette that observed the rate of halide substitution by a water molecule is slower when bpy ligands bearing electron withdrawing substituents were used.\textsuperscript{19a} However, when the Ru\textsubscript{phot}−Ru\textsubscript{cat}−Cl complex was used for sulfide oxidation, an activity comparable to the aquo complex is observed after 24 h. This could be ascribed to the rate acceleration of the Cl\textsuperscript{−}/H\textsubscript{2}O exchange in the photocatalytic conditions affording the aquo photocatalyst from the Ru\textsubscript{phot}−Ru\textsubscript{cat}−Cl precatalyst. However, it was observed that light is not the only parameter allowing this rate enhancement. Indeed, the Ru\textsubscript{phot}−Ru\textsubscript{cat}−Cl system showed high stability (i) after several hours of light irradiation without the presence of the electron acceptor and also (ii) in water in the presence of the sulfide under dark conditions (data not shown). This suggests that all these parameters (light, Co(III), and maybe substrate also) have to be combined to allow this substitution in the experimental time window, leading to formation of the aquo catalyst.

In the four photocatalytic systems based on use of the ([diamine]Ru(tpy)−OH\textsubscript{2}) like compound as catalyst in association with a photosensitizer\textsuperscript{7,8a,b,23} a mechanism involving the two electron oxidation of the catalytic center thanks to a PCET process initiated by photon absorption by the chromophore fragment can be proposed (Scheme 3.). A similar mechanism occurs with the dyad system reported here. Excitation of the Ru\textsubscript{phot} moiety by irradiation in the visible region corresponding to its MLCT absorption initiates an intramolecular electron transfer from the Ru\textsubscript{cat} moiety to Ru\textsubscript{phot} in its excited state, yielding formation of the [Ru\textsubscript{phot}(I)−Ru\textsubscript{cat}(III)−OH (or OH\textsubscript{2})\textsuperscript{3+} or \textsuperscript{4+}] species as it was underlined by the photophysical studies in the absence of Co(III) salt. However, addition of a large excess of electron acceptor resulted in a small but significant diminution of the excited state lifetime (from 80 to 55 ps). Thus, an oxidative quenching involving intervention of a fast intermolecular electron transfer from Ru\textsubscript{phot} in its excited state to the sacrificial electron acceptor generating the [Ru\textsubscript{phot}(III)−Ru\textsubscript{cat}(II)−OH\textsubscript{2}]\textsuperscript{3+} species may be proposed. This mechanism is generally accepted.\textsuperscript{8a} Thanks to the higher Ru\textsubscript{phot} potential relative to the Ru\textsubscript{cat}−OH\textsubscript{2} potential observed by cyclic voltammetry, the resulting Ru\textsubscript{phot}(III) fragment is thermodynamically able to oxidize the neighboring Ru\textsubscript{cat}(II)−OH\textsubscript{2} subunit by an intramolecular electron transfer. A proton is also released from the aquo ligand to avoid unfavorable charge build up during the oxidation process. In light of the reported mechanism for the [Ru(tpy)(bpy)m−OH\textsubscript{2}]\textsuperscript{3+} catalyst (Ru\textsubscript{cat}−OH\textsubscript{2})\textsuperscript{3+},\textsuperscript{13,19a,24} and on the basis of the two electron oxidation observed for the Ru\textsubscript{cat} moiety (Figure 1) a mechanism involving disproportionation of 2 [Ru\textsubscript{phot}(II)−Ru\textsubscript{cat}(III)−OH\textsubscript{2}] into [Ru\textsubscript{phot}(II)−Ru\textsubscript{cat}(IV)−O\textsubscript{4}]+ and [Ru\textsubscript{phot}(II)−Ru\textsubscript{cat}(II)−OH\textsubscript{2}]\textsuperscript{3+} may be proposed. However, a step by step oxidation of the [Ru\textsubscript{phot}(II)−Ru\textsubscript{cat}(II)−OH\textsubscript{2}]\textsuperscript{4+} complex into [Ru\textsubscript{phot}(II)−Ru\textsubscript{cat}(IV)−O\textsubscript{4}]\textsuperscript{4+} by two consecutive PCET processes cannot be entirely ruled out (Scheme 3.). This mechanism was proposed by T. J. Meyer for oxidation of water by Ce(IV) with the same dyad on the basis of electrochemical
studies.10 Surprisingly, the CV of the Ru\textsubscript{phos} - Ru\textsubscript{cat} - OH\textsubscript{2} complex recorded in our laboratory in the same conditions (at pH 4.4; acetate buffer) showed significant differences with the one published (Figure S13, Supporting Information).10 While two waves were observed at +0.75 and +1.2 V vs NHE and attributed to successive one electron oxidation processes Ru(II)−OH\textsubscript{2}→Ru(III)−OH→Ru(IV)=O, a single wave at +1.05 V vs NHE corresponding to a two electron oxidation process was observed in our case. Our data (CV, RDE, and E\textsubscript{p}H experiments) strongly support a two electron two proton (g) Fagnoni, M.; Dondi, D.; Ravelli, D.; Albini, A.; Stephenson, C. R. J. Org. Lett. 2010, 12, 368. (c) Condie, A. G.; Gonzalez Gomez, J. C.; Stephenson, C. R. J. Am. Chem. Soc. 2010, 132, 1464. (d) Yoon, T. P.; Ischay, M. A.; Du, J. Nat. Chem. 2010, 2, 527. (e) Du, J.; Yoon, T. P. J. Am. Chem. Soc. 2009, 131, 14604. (f) Ravelli, D.; Dondi, D.; Fagnoni, M.; Albini, A.; Stephenson, C. R. J. Am. Chem. Soc. 2009, 131, 8756. (g) Ischay, M. A.; Anzovino, M. E.; Du, J.; Yoon, T. P. J. Am. Chem. Soc. 2008, 130, 12886. (h) Fihi, A.; Artero, V.; Razavet, M.; Baffert, C.; Leibl, W.; Fontecave, M. Angew. Chem., Int. Ed. 2008, 47, 564. (i) Nicewicz, D. A.; MacMillan, D. W. C. Science 2008, 322, 77. (j) Renaud, P.; Leong, P. Science 2008, 322, 55. (k) Akiyama, H.; Jiang, J.; Jin, C. W.; Lau, T. C.; Mak, C. K. J. Am. Chem. Soc. 2007, 129, 77. (l) Huynh, M. H. V.; Condie, A. G.; Balzani, V.; Brasme, B. Phys. Chem. Chem. Phys. 2003, 5, 2520. For photocatalytic water oxidation, see ref 5. For photocatalytic oxidation of organic substrates, see refs 7 and 8.

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