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Covalent Association of a Ruthenium-based Chromophore and a Copper Catalyst: a Synergistic Combination for Sulfides Photooxidation

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Supporting information for this article is given via a link at the end of the document.

Abstract: The development of catalytic systems for the oxidation of organic substrates using renewable sources such as water and dioxygen remains more than ever challenging. In this paper is reported the synthesis and full characterization of a new dyad combining a ruthenium(II)-based chromophore and a bio-inspired copper(II) pre-catalyst. In particular, photo-induced electron transfer from the photosensitized Ru(II) subunit toward the Cu(II) center was highlighted. The photogenerated Cu(I) moiety prove to be, catalytically efficient for the oxidation of sulfides in the presence of ³O₂ and a sacrificial electron source. The beneficial synergistic combination of the two partners when they are covalently linked allows favoring Cu/O₂-based reactions at the expense of a ¹O₂-centered mechanism otherwise.

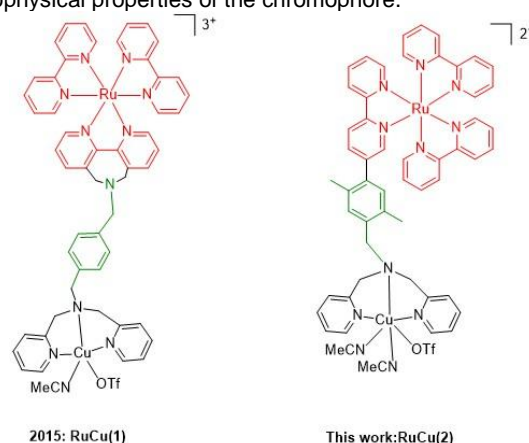
Introduction

For decades, chemists have been inspired by the photosynthetic system capable of producing carbohydrates from H₂O and CO₂, thus converting light energy into chemical energy. Many artificial systems combining a chromophore (mimic of P680 or P700) with a catalyst for oxidation (equivalent to the CaMn₄O₅ cluster), either intra or intermolecularly, have then been developed to perform photocatalyzed reactions. Without doubt, in parallel to protons reduction, photo-oxidation of H₂O into O₂ has been one of the most studied.^[1] However, in 2009, Rocha and coworkers used this strategy for the oxidation of alcohols into ketones or aldehydes by a homodinuclear ruthenium-based dyad involving the formation of an oxidizing Ru^{IV}=O species generated thanks to a proton coupled electron transfer process (PCET).^[2] Later, we showed that the oxygen atom from the water molecule can be transferred to an organic substrate using a dyad combining the Ru(bpy)₃-type subunit as photosensitizer (bpy: 2,2'-bipyridine) with a Ru(tpy)(bpy)OH₂ derivative acting as catalytic partner (tpy: 2,2':6',2''-terpyridine).^[3, 4]

In the same vein, inspired by oxygen-dependent copper oxygenases, we extended this approach aiming at proposing efficient edifices for photocatalytic oxidations. This led to the

report of the first heterodinuclear Ru^{II}-Cu^{II} dyad (**RuCu(1)**, Scheme 1) combining a Ru(diimine)₃-type photosensitizer with a Cu-based catalytic partner for light-driven oxygenation of sulfides, phosphines and alkenes.^[5] Mechanistic investigations gave evidences about a predominant O₂ activation by the Cu^I moiety generated by a photoinduced electron transfer (PET) from the Ru^{II} excited state to Cu^{II}. In this case, we took advantage of the ability of the photosensitizer in its excited state to gradually and on-demand act as electron source.

As an extension of this study, we now report the synthesis, full characterization and catalytic studies of a new heterodinuclear **RuCu(2)** dyad with 2,5-dimethylphenylene as spacer (Scheme 1). The latter, known to ensure a weak electronic coupling between different subunits,^[6, 7] will allow conserving both the electronic properties of the Cu catalytic site and the exceptional photophysical properties of the chromophore.



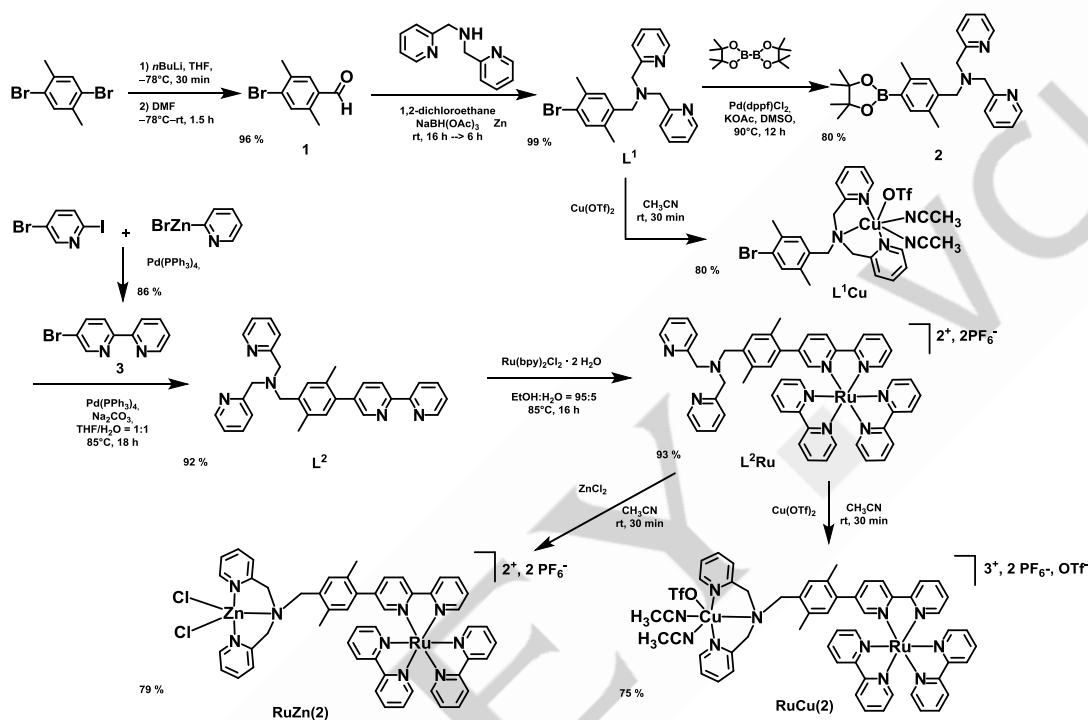
Scheme 1. Chemical representations of the **RuCu(1)** and **RuCu(2)** dyads; OTf = trifluoromethanesulfonate anion.

Results and Discussion

Synthesis

The route depicted in scheme 2 allowed to obtain **RuCu(2)** in 49% overall yield from 1,4-dibromo-2,5-dimethylbenzene after 6 steps. During the course of the synthesis, the mononuclear **L¹Cu** and **L²Ru** together with the dinuclear **RuZn(2)** complexes that will serve later as references for photophysical experiments were synthesized. Reductive amination of **1**^[8] in the presence of bis(picoyl) amine by sodium triacetoxyborohydride^[9] resulted in the formation of **L¹** in very good yield. **L¹** was further metallated with Cu(OTf)₂ in CH₃CN to give **L¹Cu**. The bridging ligand **L²**

was isolated after a sequence of Miyaura borylation^[7] and subsequent Suzuki coupling^[10] with **3** prepared by reaction between 5-bromo-2-iodopyridine and 2-pyridyl zinc bromide.^[11] Reaction of **L²** with Ru(bpy)₂Cl₂ in EtOH / H₂O allowed the isolation of **L²Ru**. The latter finally reacts with Cu(OTf)₂ or ZnCl₂ in CH₃CN to give the desired **RuCu(2)** and **RuZn(2)** dyads, respectively. All the compounds were fully characterized (see supporting information for details).



Scheme 2. Synthetic routes for **L¹Cu**, **L²Ru**, **RuCu(2)** and **RuZn(2)**.

X-ray Crystal Structure of **L¹Cu**

Single crystals of **L¹Cu** suitable for X-ray diffraction studies were grown from diffusion of Et₂O into a solution of **L¹Cu** in CH₃CN. Figure 1 shows a representation of the complex cation together with selected bond lengths and angles. The metal center is hexacoordinated, by three nitrogen atoms from the ligand, two others from exogenous CH₃CN molecules and one triflate oxygen atom. The geometry around the cupric ion is best described as *pseudo* octahedral. The triflate anion and one CH₃CN molecule occupy the axial positions whereas the four nitrogen atoms (N1, N2, N3, N31) define the equatorial plane. The in plane Cu-N distances are in the range of those reported for Cu species in such geometry^[12, 13]. The plane formed has a maximum deviation from the least-squares plane of 0.020 Å and the copper center lies 0.095 Å out of the basal plane toward the apical triflate anion. Finally, as expected for a distorted Jahn-Teller d⁹ metal complex,^[14] the longest distances correspond to the ones between the Cu^{II} ion and the axial ligands (Cu-O1S1 = 2.428(2) Å and Cu1-N32 = 2.587(3) Å).

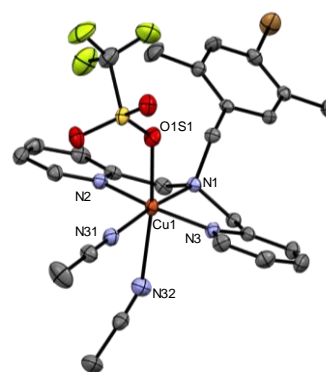


Figure 1. X-ray crystal structure of the cationic unit of **L¹Cu**. Selected bond lengths (Å) and bond angles (deg): Cu1-N1, 2.045(2); Cu1-N2, 1.967(2); Cu1-N3 (1.965(2)); Cu1-N31, 1.989(2); Cu1-O1S1, 2.428(2); Cu1-N32; (2.587(3); N1-Cu1-N3, 83.20(9); N1-Cu1-N2 83.58(9); N2-Cu1-N31, 97.25(10) ; N31-Cu1-N3, 95.52(10); N1-Cu1-O1S1, (100.70(8); N2-Cu1-O1S1, 92.21(9); N3-Cu1-O1S1, 92.72(9); N31-Cu1-O1S1, 86.81(9). All non-H atoms are shown as 30% thermal ellipsoids. H atoms and solvent molecules are omitted for clarity. CCDC number is 2262496; See tables S1-S2 in the supporting information for full details.

Electrochemistry

Cyclic voltammograms of **L¹Cu**, **L²Ru** and **RuCu(2)** recorded in CH₃CN are presented in Figure 2. **L¹Cu** displays a quasi-reversible process at $E_{1/2} = -0.19$ V ($E_{pa} = -0.04$ V and $E_{pc} = -0.32$ V vs $Fc^{0/+}$, $\Delta E_p = 280$ mV) assigned to $Cu^{II} \rightarrow Cu^I$. This value compares well with the one determined for the Cu center of **RuCu(1)** (-0.21 V vs $Fc^{0/+}$) and its mononuclear counterpart (-0.22 V vs $Fc^{0/+}$).^[5]

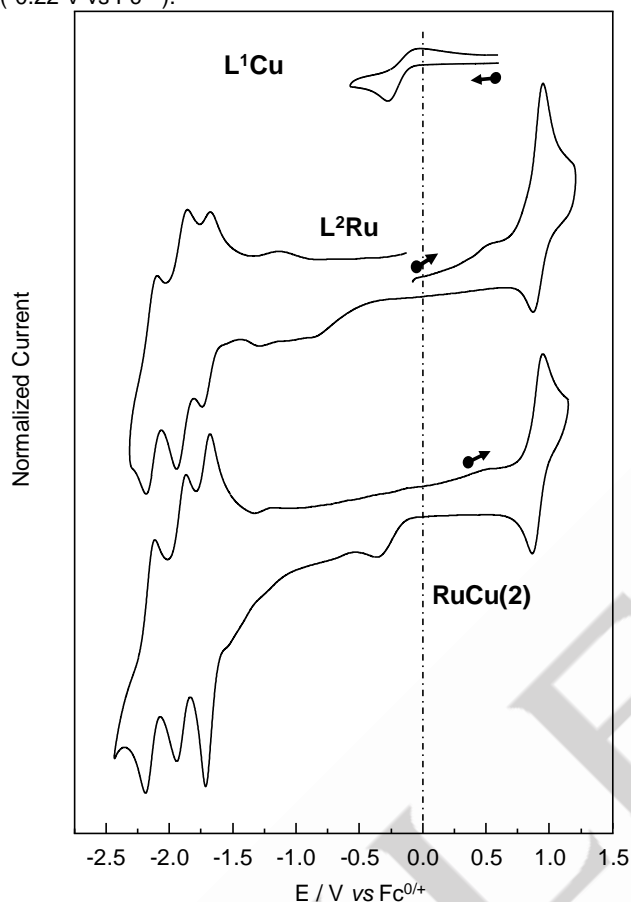


Figure 2. CV curves of **L¹Cu**, **L²Ru** and **RuCu(2)** at 1 mM in CH₃CN + 0.1 M NBu₄PF₆ under Ar at 0.1 V/s on a 3 mm-diameter GCE. Typical currents were of the order of 10–20 μ A and the depicted CV correspond to the n+1 scan.

L²Ru exhibits electrochemical signatures characteristic of Ru(diimine)₃ complexes with a reversible system in the anodic region at $E_{1/2} = 0.91$ V ($E_{pa} = 0.95$, $E_{pc} = 0.87$, $\Delta E_p = 80$ mV,) vs $Fc^{0/+}$ attributed to $Ru^{III/II}$ and three successive events in the cathodic part at $E_{1/2} = -1.70$ V ($E_{pa} = -1.67$ V, $E_{pc} = -1.74$ V, $\Delta E_p = 70$ mV), -1.87 V ($E_{pa} = -1.83$ V, $E_{pc} = -1.91$ V, $\Delta E_p = 80$ mV) and -2.14 V ($E_{pa} = -2.10$ V, $E_{pc} = -2.18$ V, $\Delta E_p = 80$ mV) vs $Fc^{0/+}$, that correspond to the consecutive mono-electronic reductions of the three bipyridine ligands.^[15] These values are comparable to those obtained with **RuCu(1)** and its Ru-based derivative. Finally, the CV curve recorded for **RuCu(2)** is a linear sum of those of **L²Ru** and **L¹Cu**. This result confirms that thanks to the dimethylbenzyl spacer and the methylene groups, the individual electronic properties of both partners are not modified once bound. One can however note that the Cu^{III} redox system ($E_{pc} =$

-0.25 V vs $Fc^{0/+}$) in the dyad became irreversible when recording over the full potential range (-2.3 V to 1.3 V vs $Fc^{0/+}$), while some reversibility (but accompanied with large ΔE_p (700 mV)) can be detected when focusing on the Cu part (Fig. S1 in the supporting information). This could be indicative of disturbed reorganization processes within a large and constrained structure combined to the presence of coordinating CH₃CN.

EPR spectroscopy.

The paramagnetic Cu-containing derivatives **L¹Cu** and **RuCu(2)** display comparable X-band CW-EPR signatures (Figure 3) indicating that the metal centers have nearly identical electronic environments and consequently the same composition of their coordination spheres. Spectra recorded at 25 K are typical for mononuclear Cu^{II} species with axial symmetry. For **L¹Cu**, $g_1 = 2.251$, $g_2 = 2.061$ and $g_3 = 2.058$ and $A_1 = 175$ mT were determined by simulation whereas $g_1 = 2.249$, $g_2 = 2.059$, $g_3 = 2.055$ and $A_1 = 178$ mT were obtained for **RuCu(2)**. These values lie in the range of other reported compounds for which the Cu^{II} centers are coordinated by bis-pyridyl amine groups.^[12]

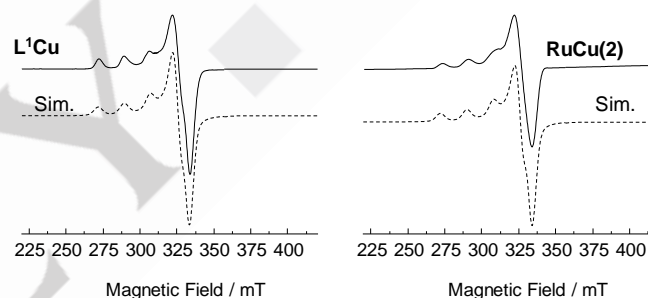


Figure 3. X-band CW-EPR spectra recorded for 1 mM acetonitrile solutions of **L¹Cu** and **RuCu(2)** (solid lines) with simulations (dashed lines). Acquisition parameters: temperature = 25 K; MW frequency = 9.388 GHz (**L¹Cu**), and 9.636 GHz (**RuCu(2)**); MW power = 20 μ W; modulation amplitude = 1.0 mT; conversion time = 163.84 ms.

Photophysical studies.

The electronic absorption spectra of **L¹Cu**, **L²Ru**, **RuZn(2)** and **RuCu(2)**, together with the emission spectra of the Ru-containing species are depicted in Figure 4 (data are gathered in Table 1). In addition to the moderately intense $\pi-\pi^*$ absorption bands centered on the pyridine cycles below 350 nm, the absorption spectrum of **L¹Cu** displays a weak band at 610 nm ($\epsilon = 120$ M⁻¹ cm⁻¹) corresponding to Cu^{II} d-d transitions with a metal ion in an elongated octahedral geometry^[16] consistent with the X-ray crystal structure. For **L²Ru**, **RuZn(2)** and **RuCu(2)**, the spectra feature intense $\pi \rightarrow \pi^*$ bands in the UV range ($\epsilon \sim 80000$ M⁻¹ cm⁻¹) and metal-to-ligand charge transfer (MLCT) bands centered around 450 nm ($\epsilon \sim 15000$ M⁻¹ cm⁻¹) characteristic of Ru^{II} species with three bipyridyl ligands.^[17] As expected, the absence of electronic coupling between the two metallic centers is evidenced by the conservation of the spectral identity, especially in the MLCT region, of the ruthenium-based chromophore upon complexation of the copper moiety.

Table 1. Photophysical data of the different compounds in solution in CH₃CN.

	Absorption	Emission ^[a]		
	$\lambda_{\text{max}} / \text{nm}$ ($\epsilon / \text{M}^{-1} \cdot \text{cm}^{-1}$)	$\lambda_{\text{max}} / \text{nm}$	τ / ns	ϕ
L¹Cu	610 (120)	-	-	-
L²Ru	423 (10900); 453 (13900)	611	950	0.06
RuZn(2)	423 (11000); 453 (13900)	612	950	0.06
RuCu(2)	423 (10250); 453 (12850); 610 (sh, 120)	614	855 (35%) 10 (65%)	0.01

^[a] In deaerated acetonitrile at r. t.

As expected, the **L²Ru** model compound exhibits the typical emission of a ruthenium tris-diimine complex, with a lifetime of 950 ns and a quantum yield of 0.06 in deaerated CH₃CN (Figs. S2-S3 in the supporting information), whereas **L¹Cu** is non emissive. The luminescence energy of **RuCu(2)** remains unchanged compared to **L²Ru**, while its lifetime and quantum yield are significantly decreased in deaerated conditions (Figs. S4-S5 in the supporting information). The presence of two components for the lifetime corresponds to the quenched luminescence (10 ns) and the residual emission (855 ns) from less reactive conformations of the molecule. This quenching is attributed to a likely PET process from the ruthenium subunit to the copper center, which driving force is calculated from the electrochemical and photophysical data to be -0.93 eV. The reference **RuZn(2)** dyad confirms that the copper catalyst subunit of **RuCu(2)** is responsible for the quenching of the emission from the ruthenium part. Indeed, the emission properties of **RuZn(2)** (Figs. S6-S7 in the supporting information) are identical to those of **L²Ru**. Nevertheless, the small overlap between the ruthenium emission and the copper absorption spectra, due to the weak d-d absorption band of **L¹Cu** centered at 610 nm ($\epsilon = 120 \text{ M}^{-1} \text{ cm}^{-1}$) does not allow to completely rule out a quenching also by energy transfer from the chromophore to the Cu moiety. Both processes are probably responsible for the partial ruthenium emission extinction.

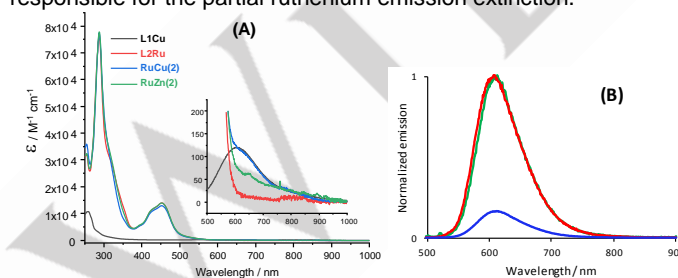


Figure 4. Absorption (a) and emission (b), $\lambda_{\text{exc}} = 453 \text{ nm}$ spectra of **L¹Cu** (black line), **L²Ru** (red line), **RuZn(2)** (green line) and **RuCu(2)** (blue line) recorded in CH₃CN at 298 K. Inset: zoom on the 600 nm region of the absorption spectra.

However, PET was independently evidenced by EPR experiments (Fig. S8 of the supporting information). Irradiation of

RuCu(2) in the presence of an excess of TEOA (200 molar equiv.) resulted in a rapid extinction of the signal corresponding to Cu(II) reduction into Cu(I). In comparison, no change in the EPR spectrum of **L¹Cu** was observed under the same conditions. Addition of oxygen to the medium allowed the Cu(II) features to be recovered.

Photocatalytic oxidation

The catalytic efficiency of **RuCu(2)** was first evaluated for light-driven oxidation of 4-bromothioanisole as a probe substrate under saturated oxygen atmosphere and in the presence of triethanolamine (TEOA) as sacrificial electron donor in CH₃CN (catalyst/substrate/TEOA = 0.5/50/100 mM, 1/100/200 equiv., see supporting information for experimental details). Irradiation was performed using a blue light diode (LED) system emitting at 450 nm corresponding to the energy of the MLCT transition of the chromophore subunit with light intensities ranging from 0 to 24 mW.cm⁻² during 16 h of irradiation. All the products were characterized and quantified by ¹H NMR. Logically, a direct correlation between the irradiation power and the catalytic efficiency was observed. A plateau, corresponding to an almost complete conversion (98 %), is reached for 20 mW.cm⁻² whereas only half is converted into sulfoxide with 10 mW.cm⁻² and one third with 5 mW.cm⁻² (Figure 5a). Unfortunately, limited by the capacity of the setup, higher intensities could not be applied. It has also been observed that, at this optimal intensity, reducing the time of the experiment to 8 h lead to a significant decrease in efficiency with only 42% conversion (Figure 5b).

As it is known that similar dyads combining a light-absorbing [Ru(bpy)₃]²⁺-like fragment and a catalytic partner decomposed progressively during catalysis,^[3] the stability of the dyad was then examined under several conditions. As it can be seen in Figure 5c, the effect of reloading with several portions of both 4-bromothioanisole and TEOA (100 and 200 molar equiv. respectively) every 16 h is spectacular. The dyad showed an exceptional stability since, after each new addition, the substrate was almost entirely consumed in favor of the formation of oxidation products. The efficiency of the dyad was also studied in the presence of larger amounts of substrate and TEOA added all at once. Up to 78 % conversion (388 TON) and 87 % conversion (433 TON) were obtained in the presence of 500 molar equiv. of substrate and 1000 molar equiv. of TEOA after 16h and 48 h of irradiation, respectively. Independently, addition of 1500 molar equiv. of sulfide and 3000 molar equiv. of TEOA resulted in the formation of the sulfoxide in only 35 % conversion (522 TON) after 16h mainly due to the total consumption of O₂ dissolved. This was confirmed since refilling the reaction vessel with O₂ allowed an increase of the conversion up to 53 % (803 TON). Finally, in all cases, at 20 mW.cm⁻², only traces of sulfones (less than 10 %) can be detected.

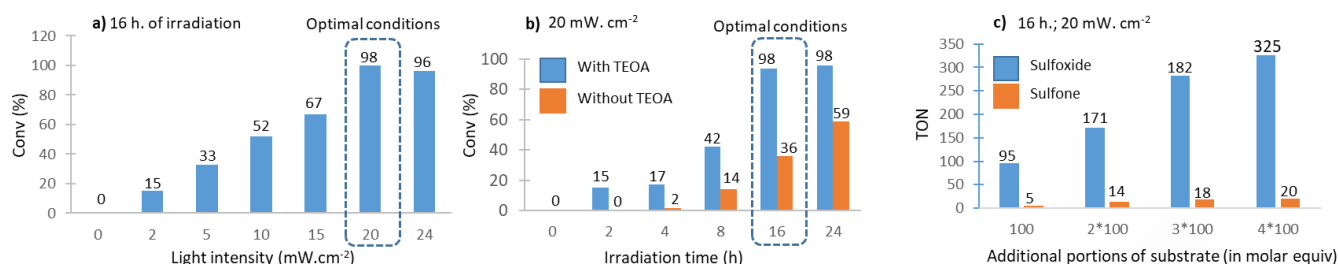


Figure 5. Catalytic efficiency of **RuCu(2)** during 4-bromothioanisole photooxygenation, after 16 h of irradiation using different light intensities [a]; after different irradiation times with (blue) and without (orange) TEOA at 20 mW.cm⁻² [b]; and during successive additions of portions of both substrate and TEOA after 16 h at 20 mW.cm⁻² [c].

Control experiments showed that in absence of light, O₂ or catalyst, no sulfoxide was formed. However, it was observed that, in the optimized conditions but without TEOA (Figure 5b), about a third of 4-bromothioanisole was converted (33-36%) into sulfoxide. This suggests the intervention of a competitive process, as it was observed but to a lesser extent with **RuCu(1)** (Table 2).^[5] This value increases to 59 % after 24 h of irradiation. Based on previous results, one might hypothesized the production of ¹O₂ as oxidative species, generated by energy transfer from photo-excited **RuCu(2)** to ³O₂.^[5, 18] These results indicate that under the optimal conditions, about 1/3 of the oxidation would be due to ¹O₂. This was confirmed by adding to the reaction medium a large excess (15 molar equiv. with regard to the sulfide) of 9,10-dimethylantracene (DMA) known to be an efficient ¹O₂ quencher.^[19] In that case, 71 % conversion were carried out instead of the 98% previously observed, thus confirming the involvement of a competitive ¹O₂-based oxidation competitive reaction pathway (Table 2).

The importance of combining both the chromophore and the catalytic partner within the same binuclear entity was then investigated. Catalytic experiments were carried out with a bimolecular system were [Ru(bpy)₃]²⁺ (as model of the Ru part in **RuCu(2)**) and **L¹Cu** were combined in stoichiometric amount (0.5 mM each). Surprisingly, a nearly total conversion (98 % conversion, table 1) was obtained, as observed for **RuCu(2)**. This result has to be correlated with the fact that [Ru(bpy)₃]²⁺ alone (0.5 mM) proved to be equally efficient (83 % conversion) and that the addition of DMA in the bimolecular mixture prevented any reaction. All together, these results unequivocally show that the oxidation observed with the bimolecular system is exclusively ¹O₂-dependent. This is not the case when the system is organized as a covalent dyad where the main mechanism becomes Cu-centered with PET from the excited Ru subunit to the Cu^{II} center.

Table 2. Photocatalytic oxidation of 4-bromothioanisole (50 mM) by **RuCu(2)**.

	RuCu(2) _{a)}	RuCu(2) _{a)} +DMA ^{[a], [c]}	[Ru(bpy) ₃] ²⁺ _[b]	[Ru(bpy) ₃] ²⁺ + L¹Cu _[b]	[Ru(bpy) ₃] ²⁺ + L¹Cu _{a)} +DMA ^{[b], [c]}
Conv. (%)	98	71	83	95	0

In CH₃CN under O₂ atmosphere for 16 h at 20 mW.cm⁻² with **[RuCu(2)]** = 0.5 mM [a]; **[Ru(bpy)₃]²⁺** = **[L¹Cu]** = 0.5 mM, [b] and 15 molar equiv. of 9,10-dimethylantracene with regard to the sulfide [c].

Finally, the photocatalytic activity of **RuCu(2)** was evaluated using various substrates in the conditions determined above

(Table 3). As expected, electron-donating groups increase the reactivity of

the sulfides in contrast to electron-withdrawing groups. Indeed only 6 % conversion were reached with R = -NO₂ compared to 100 % with R = -OMe. **RuCu(2)** proved also to be chemoselective since using 4-(methylthio)phenylmethanol having both sulfide and primary hydroxyl groups resulted almost exclusively in S-oxygenation (93 % conversion).

Table 3. Photocatalytic oxidation of sulfides by **RuCu(2)**.

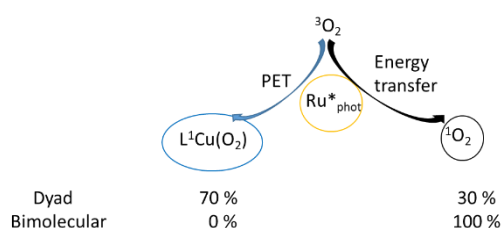
4-RC ₆ H ₄ -S-CH ₃				
R	H	Br	OCH ₃	NO ₂
Product	Sulfoxide	Sulfoxide	Sulfoxide	Sulfoxide
Conv.(%)	100	98	100	6

CH ₂ -OH				
R	CH ₂ -OH			
Product				
Conv.(%)	0	4	93	3

In CH₃CN; [sulfides] = 50 mM; **[RuCu(2)]** = 0.5mM under light irradiation (20 mW.cm⁻²) and O₂ atmosphere after 16 h in the presence of [TEOA] = 100 mM.

Conclusion

In conclusion, we report here the preparation of a new heterodinuclear ruthenium and copper-based dyad, its full characterization and the study of its photocatalytic behavior during light-driven sulfides oxygenation by O₂ activation. Thanks to this study we were able to show and quantify the coexistence of two different oxidation processes; one up to 30 % and involving ¹O₂ generated by energy transfer from the excited chromophore to ³O₂ and a second copper-dependent mechanism involving a PET from the excited chromophore to the Cu^{II} up to 70 %. We also demonstrated that the covalent association of the two entities allowed switching from a 100 % ¹O₂-based process to a predominantly Cu-based catalytic oxidation mechanism controlled by electron transfer.



Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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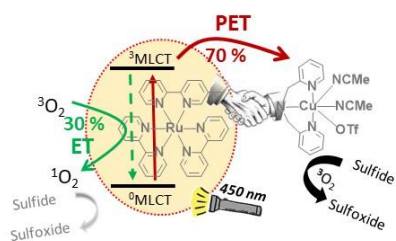
Conflict of Interest

There are no conflicts to declare.

Keywords: photooxidation catalysis • O₂ activation • dyad • photo-induced electron transfer •

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Entry for the Table of Contents



Covalent association of a Ru photosensitizable unit with a Cu-based catalyst prove to be efficient for substrates oxygenation in the presence of molecular O_2 as unique O-atom source and limits the involvement of 1O_2 side pathway.