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A Ruthenium(II)–Copper(II) Dyad for the Photocatalytic Oxygenation of Organic Substrates Mediated by Dioxygen Activation**

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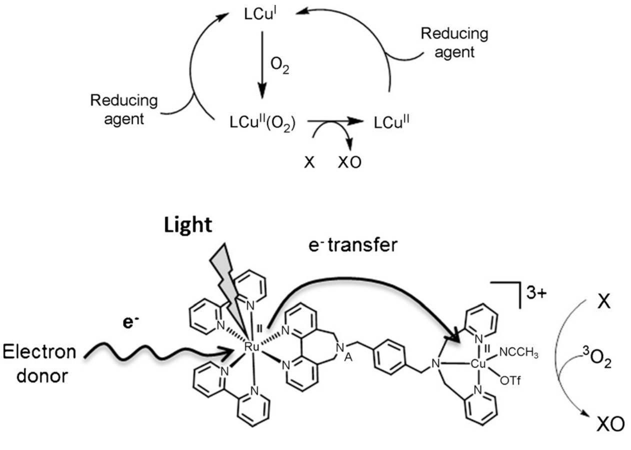
Abstract: *Dioxygen activation by copper complexes is a valuable method to achieve oxidation reactions for sustainable chemistry. The development of a catalytic system requires regeneration of the Cu^I active redox state from Cu^{II}. This is usually achieved using extra reducers that can compete with the $Cu^{II}(O_2)$ oxidizing species, causing a loss of efficiency. An alternative would consist of using a photosensitizer to control the reduction process. Association of a Ru^{II} photosensitizing subunit with a Cu^{II} pre-catalytic moiety assembled within a unique entity is shown to fulfill these requirements. In presence of a sacrificial electron donor and light, electron transfer occurs from the Ru^{II} center to Cu^{II}. In presence of dioxygen, this dyad proved to be efficient for sulfide, phosphine, and alkene catalytic oxygenation. Mechanistic investigations gave evidence about a predominant $^3O_2$ activation pathway by the Cu^I moiety.*

From an environmental point of view, there is a growing interest in designing catalysts capable of using O_2 as oxygen atom source to perform oxidation reactions to avoid strong, toxic, and expensive oxidants.[1] Indeed, O_2 is nowadays considered as an appealing oxidant for sustainable oxidation chemistry. Nature has developed a large panel of metal-containing enzymes to perform selective and efficient oxidation reactions through dioxygen activation.[2] O_2 activation at a metal center generally entails its two-electron reduction to the peroxo state and subsequent O–O bond cleavage. In dinuclear centers, the second metal ion acts as a reductant, while in mononuclear active sites, an external electron donor is required. This is the case for copper metalloenzymes such as dopamine β-monooxygenase (DβM), peptidylglycine α-hydroxylating monooxygenase (PHM), and the recently identified insect tyramine β-monooxygenase (TβM) that are involved in the transformation of various substrates by Cu^I/O_2 chemistry.[3] The catalytic activity is achieved owing to the presence, in close proximity, of a reducing co-factor that allows a regeneration of the active Cu^I species from the final inactive Cu^{II} state (Scheme 1, top). Several bio-inspired mono and dinuclear copper complexes have been reported, but few of them act catalytically in homogeneous conditions.[4] This assessment might originate from the competitive reduction of the active $Cu^{II}(O_2)$ oxidative species (that is, superoxo or peroxo) by the additional sacrificial reductant (Scheme 1, top) that would short-circuit the catalytic cycle. Exploiting our expertise in the development of eco-aware photocatalysts for small molecules activation (such as water[5]), we report herein a unique example of a Ru^{II}-Cu^{II} dyad capable of sulfide and hydrocarbon catalytic oxidations, using O_2 as unique oxygen atom source. The covalent combination of a Ru-based photosensitizer with a Cu^{II} catalyst for O_2 activation and associated with an appropriate sacrificial electron donor



Ru^{II}_{phot}-Cu^{II}_{cat}

Scheme 1. Copper-based oxygen activation/reaction (X: substrate, XO: oxidized substrate).

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allows a controlled delivery of reducing equivalents that overcomes the undesired $Cu^{II}(O_2)$ reduction.

The $[(bpy)_2Ru(bpbpa)Cu(OTf)(CH_3CN)]^{3+}$ (bpy = 2,2′-bipyridine, bpbpa = *N*-(4-((5*H*-dipyrido[3,2-c:2′,3′-e]azepin-6(7*H*)-yl)methyl)benzyl)-1-(pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)methanamine) catalyst reported here, abbreviated as $Ru^{II}{}_{phot}$-$Cu^{II}{}_{cat}$ (Scheme 1, bottom), covalently associates a light-absorbing photosensitizing $[Ru(bpy)_3]^{2+}$-like fragment, known to be an efficient chromophore,[6] and a bio-inspired copper site as the proposed catalytic oxidation locus. It was efficiently prepared in two steps from the reported $[(bpy)_2Ru(bpBr_2)][PF_6]_2$[7] and L-$NH_2$-bpa[8] precursors. The catalytic moiety ($Cu^{II}{}_{cat}$) was synthesized from the L-Pht-bpa protected ligand (Supporting Information, Scheme S1). The syntheses and the characterization for all these compounds (NMR and UV/Vis spectroscopy, elemental analysis, ESI-MS) are provided in the Supporting Information. The nature of the copper subunit coordination sphere is proposed on the basis of the X-ray crystal structure resolved for $Cu^{II}{}_{cat}$ (Supporting Information, Figure S1).

The cyclic voltammogram (CV) of $Ru^{II}{}_{phot}$-$Cu^{II}{}_{cat}$ in CH_3CN shows, in the cathodic region, three successive one-electron processes between −0.7 and −1.7 V *vs* NHE corresponding to the reduction of the bipyridine ligands (Supporting Information, Figure S2). Surprisingly, three waves were observed in the anodic region. On the basis of previous reports and CVs recorded for $Cu^{II}{}_{cat}$ and $[(bpy)_2Ru(bpbpa)]^{2+}$ metalloligand (abbreviated $Ru^{II}{}_{phot}$), the two one-electron quasi-reversible waves at +1.57 V and +0.42 V *vs* NHE were attributed to the Ru^{III}/Ru^{II}[9] and Cu^{II}/Cu^{I} couples, respectively (Supporting Information, Figure S2). Thermodynamically, by considering the redox potential of the excited state of the Ru subunit($E°$ Ru^{III}/Ru^{II*}) of −0.70 V *vs* NHE,[10] an electron transfer from the photoexcited state Ru^{II*} to the Cu^{II} is consequently favorable. The third irreversible oxidation process at +1.44 V vs. NHE (anodic peak given) was assigned to the oxidation of the tertiary amine of the bridging ligand (N_A, Scheme 1).[11] This was further confirmed by comparison with the metal-free bdda molecule[12] (Supporting Information, Scheme S1, Figure S2) showing a similar irreversible pattern with an anodic peak at +1.40 V vs. NHE.

The reliability of the photocatalytic system based on an intramolecular electron transfer between the excited Ru moiety and the vicinal Cu center was probed by EPR and photophysical studies. The photophysical properties of $Ru^{II}{}_{phot}$ and $Ru^{II}{}_{phot}$-$Cu^{II}{}_{cat}$ have been investigated in CH_3CN at room temperature, both in air equilibrated and de-aerated conditions (Supporting Information, Table S1). Both complexes display an intense absorption around 290 nm ($\varepsilon = 60500\ L\,mol^{-1}\,cm^{-1}$ and $\varepsilon = 56\,800\ L\,mol^{-1}\,cm^{-1}$ for $Ru^{II}{}_{phot}$ and $Ru^{II}{}_{phot}$-$Cu^{II}{}_{cat}$, respectively) assigned to π–π^* transitions (Supporting Information, Figure S3). The broad absorption bands around 445 and 455 nm are attributed to the metal-to-ligand charge transfer transition (^{1}MLCT, $d\pi_{Ru}$–$\pi^*{}_{bpy}$).[13] It is worth noting that the Cu-centered d–d transitions for the dyad are not observable owing to their weak extinction coefficient ($\lambda_{max} = 615$ nm and $\varepsilon = 100\ L\,mol^{-1}\,cm^{-1}$ for $Cu^{II}{}_{Cat}$; Supporting Information, Figure S3). Upon excitation in the MLCT absorption band, both $Ru^{II}{}_{phot}$ and $Ru^{II}{}_{phot}$-$Cu^{II}{}_{cat}$ complexes are luminescent, with broad emissions centered at 618 nm (Supporting Information, Figure S4). The presence of the Cu^{II} moiety leads to a 70% drop of the quantum yield in air-equilibrated solution (from 1.05 ns to 0.29 ns) and 60% under Ar (Supporting Information, Table S1). Previous studies on comparable heteropolymetallic complexes featuring $[Ru(bpy)_3]^{2+}$ and polypyridyl-Cu^{II} moieties ascribed the emission quenching to either energy or electron transfer or both processes.[14] This point is discussed along with the transient absorption spectroscopy. The lifetime decay for $Ru^{II}{}_{phot}$ is mono-exponential and air-sensitive, which is characteristic of the ^{3}MLCT excited state radiative decay pathway (Supporting Information, Figure S5).[13] The dyad displays a bi-exponential lifetime decay with a short (16 ns in air equilibrated solution and 31 ns under Ar) and a long component (148–328 ns; Supporting Information, Figure S6). By comparison with the mono-exponential decay determined for $Ru^{II}{}_{phot}$, the latter is ascribed to the radiative deactivation of ^{3}MLCT excited state. Considering i) that energy transfer between the triplet excited state of the ruthenium and the singlet ground state of the copper moieties is a spin-forbidden process; ii) that the weak extinction coefficient of the Cu subunit makes energy transfer a possible but likely minor component of the excited state quenching;[14b,15] and iii) the estimated redox potential of Ru^{II*} ^{3}MLCT excited state (−0.70 V *vs* NHE[10b]) and the redox potential of Cu^{II} (+0.42 V vs. NHE), the quenching is most likely due to an electron transfer from the Ru^{II} ^{3}MLCT excited state to the Cu^{II} moiety (as early observed[14c,16]). Consequently, the short lifetime is ascribed to the decay of the excited state quenched by photoinduced electron transfer (PET). The corresponding rate, estimated to be $2.9\times10^{7}\ s^{-1}$ in argon equilibrated acetonitrile solution for $Ru^{II}{}_{phot}$-$Cu^{II}{}_{cat}$, is artificially increased in air-equilibrated medium ($5.6\times10^{7}\ s^{-1}$), owing to the additional quenching by energy transfer to the triplet ground state of molecular oxygen. The presence of triethanolamine (TEOA, sacrificial electron donor) in the catalytic conditions slightly affects the spectroscopic properties (Supporting Information, Table S1, Figures S3, S4, and S6). All these results enforce the viability of an electron transfer from the excited $Ru^{II*}{}_{phot}$ to the $Cu^{II}{}_{cat}$, rather than a reductive quenching of the $Ru^{II*}{}_{phot}$ by the electron donor (Supporting Information, Scheme S2).

The photo-assisted Cu^{II} reduction in $Ru^{II}{}_{phot}$-$Cu^{II}{}_{cat}$ under catalytic conditions (that is, CH_3CN, $[Ru^{II}{}_{phot}$-$Cu^{II}{}_{cat}] = 10^{-4}$ M, TEOA 200 molar equiv) was probed under Ar-saturated atmosphere by EPR spectroscopy. Spectra were recorded before ($t = 0$ min), and after 1 and 5 min of irradiation with a Xe lamp equipped with a by-pass filter at 450 nm (Figure 1).

At $t = 0$ min, the EPR spectrum is characteristic of a mononuclear copper center in axial symmetry ($g_{\parallel} > g_{\perp}$) with identical features compared to isolated $Cu^{II}{}_{cat}$ (Supporting Information, Figure S7).[17] Upon light exposure of the dyad in the ruthenium MLCT transition region at 298 K, the EPR signal rapidly decreased and completely vanished within 45 min. A complete recovery of the Cu^{II} features was observed upon exposure to air. The decomposition of the dyad has to be precluded, as confirmed by the full conservation of the UV features after 45 min of irradiation of $Ru^{II}{}_{phot}$-

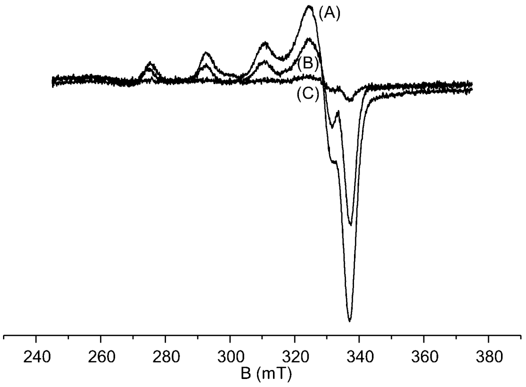


Figure 1. Evolution of the X-band EPR spectra of [$\mathrm{Ru^{II}_{phot}}$-$\mathrm{Cu^{II}_{cat}}$] (10^{-4} M + 200 molar equiv TEOA) in CH_3CN, under argon after irradiation at 450 nm. A) $t=0$, B) $t=1$ min, and C) $t=5$ min at 100 K.

$\mathrm{Cu^{II}_{cat}}$ under the same conditions (10^{-4} M with 200 molar equiv of TEOA; Supporting Information, Figure S8). We thus conclude that the disappearance of the $\mathrm{Cu^{II}}$ signal is due to the formation of a diamagnetic $\mathrm{Ru^{II}_{phot}}$-$\mathrm{Cu^{I}_{cat}}$ species generated by a photoinduced electron transfer (PET).

Two different pathways may be suggested to explain the formation of the $\mathrm{Ru^{II}_{phot}}$-$\mathrm{Cu^{I}_{cat}}$ species from the photogenerated $\mathrm{Ru^{II*}_{phot}}$-$\mathrm{Cu^{II}_{cat}}$ dyad (Supporting Information, Scheme S2). In a reductive process, the $\mathrm{Ru^{II}}$ ^{3}MLCT state is reduced by TEOA leading to a $\mathrm{Ru^{I}_{phot}}$-$\mathrm{Cu^{II}_{cat}}$ intermediate ($\mathrm{Ru^{I}_{phot}}$ is used to symbolize $[\mathrm{Ru^{II}(bpy^{\bullet -})(bpy)(bpbpa)}]^+$). An intramolecular electron transfer from the ruthenium center to the copper ion generates the $\mathrm{Ru^{II}_{phot}}$-$\mathrm{Cu^{I}_{cat}}$ dyad. In a second hypothesis, PET can occur immediately after photon absorption, leading to the formation of $\mathrm{Ru^{III}_{phot}}$-$\mathrm{Cu^{I}_{cat}}$ species. Subsequent reduction of the ruthenium center by TEOA yields to the $\mathrm{Ru^{II}_{phot}}$-$\mathrm{Cu^{I}_{cat}}$ dyad.

Nanosecond time resolved absorption spectroscopy under catalytic conditions was used to discriminate between these two processes. The initial spectrum (black trace, Supporting Information, Figure S9) is characteristic of the ^{3}MLCT excited state of tris(bipyridyl)–ruthenium complex, with an intense positive absorption band at 365 nm corresponding to the formation of the anionic $\mathrm{bpy^{\bullet -}}$ radical. An intense negative signal at 450 nm corresponding to the bleaching of the ground-state ^{1}MLCT absorption is also observed.[18] Both bands display a bi-exponential decay ($\tau^1 = 20$–23 ns and $\tau^2 = 150$–160 ns) of the same magnitude to those observed in luminescence decay ($\tau^1 = 16$ ns and $\tau^2 = 148$ ns). The associate rates ($k_{370} = 3.7\times10^7\,\mathrm{s^{-1}}$, $k_{450} = 4.4\times10^7\,\mathrm{s^{-1}}$) are in agreement with that estimated by time-resolved luminescence spectroscopy with TEOA ($k = 5.9\times10^7\,\mathrm{s^{-1}}$). It is worth noting that the EPR experiment showed that after 45 min of irradiation, no signal corresponding to the $\mathrm{bpy^{\bullet -}}$ radical anion was found at $g = 1.998$ (Supporting Information, Figure S10).[19] Furthermore, a $\mathrm{Ru^{I}}$ intermediate can be ruled out as no characteristic positive absorption band at 510 nm could be detected even in presence of an excess of electron donor.[20] Therefore, this spectroscopic evidence is in agreement with an oxidative quenching of the ^{3}MLCT state leading to a photoinduced electron transfer to the $\mathrm{Cu^{II}}$ from the ruthenium photosensitizer in its excited state.

The $\mathrm{Cu^{II}}$-assisted reduction by the $\mathrm{Ru^{II}}$ photosensitizer havin been established, the photocatalytic activity of $\mathrm{Ru^{II}_{phot}}$-$\mathrm{Cu^{II}_{cat}}$ in oxidation reactions has been evaluated using various substrates under O_2-saturated atmosphere in acetonitrile with TEOA. A blue LED system emitting at 468 nm matching the photosensitizer subunit MLCT transition was used as light source. Irradiation was held for 8 h, corresponding to the maximum conversion for 4-bromothioanisole as test substrate (Supporting Information, Figure S11). Oxidation products were quantified by ^{1}H NMR and the main results are summarized in Table 1. It was observed that most of the sulfides, except 4-nitrothioanisole bearing an electron-withdrawing group, were nearly quantitatively and selectively converted into their corresponding sulfoxides (Table 1, entries 1–4). Whatever the nature of the sulfide, no sulfone was detected even after 24 h of irradiation. Finally, the photocatalyst proved to be also efficient for phosphine and alkene oxidations, affording only phosphine oxide and the major corresponding enone respectively. Yet, while oxidation of cycloalkenes selectively gave the corresponding enone, oxidation of the aromatic indene led to the formation *cis*-diol (36 TON, Table 1, entry 6) and the corresponding dicarboxylic acid (not quantified). In this case, the formation of indenone as a result of the oxidation of the benzylic position was not observed.

Table 1: Catalytic oxidation of sulfides, phosphine, and alkenes by $\mathrm{Ru^{II}_{phot}}$-$\mathrm{Cu^{II}_{cat}}$.[a]

Entry	Substrate	Product	*t* [h]	TON[b]/Conversion [%]
1	PhS	sulfoxide	8	97/ > 98
2	$4\text{-}BrC_6H_4S$	sulfoxide	8	94/ > 98
3	$4\text{-}MeOC_6H_4S$	sulfoxide	8	92/ > 97
4	$4\text{-}O_2NBrC_6H_4S$	sulfoxide	8	10, 28[c]/9, 26[c]
5	Ph_3P	$Ph_3P{=}O$	1.5	100/100
6	indene	*cis*-diol	8	36/100
7	cyclohexene	cyclohex-2-enone	16	57/57
8	*cis*-cyclooctene	cyclooct-2-enone	16	42/42

[a] Standard catalytic conditions: [$\mathrm{Ru^{II}_{phot}}$-$\mathrm{Cu^{II}_{cat}}$] (ca. 0.5 mM), [substrate] (ca. 50 mM], [TEOA] (ca. 100 mM), CH_3CN, RT, LED irradiation (468 nm), O_2 bubbling. All given values are averages of at least two experiments. [b] TON = *n*(product)/*n*(complex). [c] after 24 h of irradiation.

In control experiments performed with 4-bromothioanisole in absence of either light, catalyst or O_2, no oxidation products were detected. Without TEOA, a low amount of sulfoxide was formed (8 TON), suggesting the intervention of a competitive oxidation process (see below). It has to be noted that when O_2 was replaced by air bubbling, the catalyst is still active but yielded a lower conversion (from 98 to 53 %, Table 2, entry 3). More interestingly, the intramolecular electron transfer proved to be more efficient than the intermolecular electron transfer. Indeed, the catalytic activity increased at least four-fold for the dyad compared to the bimolecular combination of $\mathrm{Cu^{II}_{cat}}$ and $[\mathrm{Ru(bpy)_3}]^{2+}$ (Table 2, entry 4). Finally, when the photosensitizer-TEOA pair was

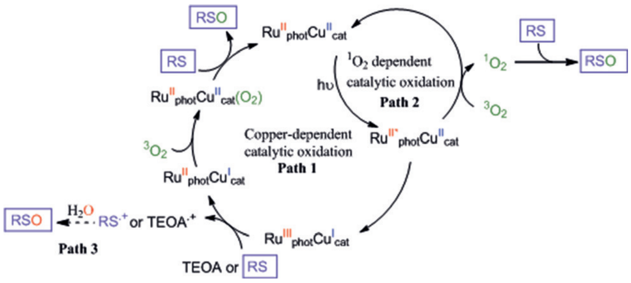
Table 2: Catalytic 4-bromothioanisole oxygenation under various conditions.

Entry	Complex	Electron donor	O_2 source	TON[e]	[%] conv
1[a]	Ru^{II}_{phot}-Cu^{II}_{cat}	TEOA	O_2	94, 300[b]	> 98, 60[b]
2[c]	Ru^{II}_{phot}-Cu^{II}_{cat}	TEOA	O_2	98 (8 h) 195 (22 h) 250 (28 h)	> 98, 98 79
3[a]	Ru^{II}_{phot}-Cu^{II}_{cat}	TEOA	air	53	53
4[d]	$[Ru(bpy)_3]_2^+$ + Cu^{II}_{cat}	TEOA	O_2	25	25
5[a]	Cu^{II}_{cat}	ascorbate or DTT	O_2	0	0
6[a]	Ru^{II}_{phot}	TEOA	O_2	25	25

[a] [complex] (ca. 0.5 mм), [4-bromothioanisole] (ca. 50 mм], [electron donor] (ca. 100 mм). [b] [Ru^{II}_{phot}-Cu^{II}_{cat}] (ca. 0.5 mм), [substrate] (ca. 250 mм], [TEOA] (ca. 500 mм). [c] [Ru^{II}_{phot}-Cu^{II}_{cat}] (ca. 0.5 mм) [4-bromothioanisole] (3 portions of 100 molar equiv spaced by 14 h, then 6 h), [TEOA] (3 portions of 200 molar equiv spaced by 14 h then 6 h). [d] [Ru^{II}_{phot}] = [Cu^{II}_{cat}] (ca. 0.5 mм), [4-bromothioanisole] (ca. 50 mм], [TEOA] (ca. 100 mм). [e] TON = *n*(product)/*n*(complex).

replaced by an excess of dithiothreitol (DTT) or ascorbate, known to reduce transition metals such as cupric ions,[4b,21] no oxidation product was detected (Table 2, entry 5). This highly suggests that, as proposed, the gradual electron delivery to the copper subunit is a prerequisite to the catalytic activity.

The stability of the catalyst was also investigated. Under catalytic conditions, on the basis of electronic absorption, about 50 % of the catalyst remains intact after 8 h of light exposure (Supporting Information, Figure S12). Despite this degradation, a full catalytic activity (up to 195 TON) is still detected upon addition of extra substrate (100 molar equiv) and TEOA (200 molar equiv). The activity then significantly decreased after the third addition, as only 65 additional TON were achieved within 6 h of irradiation (Table 2, entry 2). Furthermore, up to 300 TON (Table 2, entry 1, see footnote [b]) were obtained in the presence of 500 molar equiv of 4-methoxythioanisole and 1000 molar equiv of TEOA (60 % yield).



Scheme 2. Mechanistic pathways for O_2-dependent sulfide oxidations. RS = sulfide; RSO = sulfoxide.

Additional experiments were carried out to obtain mechanistic insights for sulfides oxidation. Based on previous reports, a general mechanism involving three main oxidation pathways can be proposed (Scheme 2). In the first common step, photon absorption by Ru^{II}_{phot}-Cu^{II}_{cat} yields to photo-excited Ru^{II*}_{phot}-Cu^{II}_{cat} which might be able to generate $^1O_2$ by energy transfer (Path 2)[22] and/or Ru^{III}_{phot}-Cu^{I}_{cat} by electron transfer. Subsequent reduction by TEOA generates Ru^{II}_{phot}-Cu^{I}_{cat} able to form a $Cu^{II}(O_2)$ adduct responsible of substrate oxidation by dioxygen activation (Path 1; copper-dependent catalytic oxidation). In that reduction step, sulfide can be used as electron donor yielding to a transient $RS^{\cdot+}$ thiyl radical that further reacts with water (Path 3).[22c,23] The latter process was partly ruled out using $^{18}OH_2$ (1 molar equiv with respect to the substrate), as no labeling was incorporated using only Ru^{II}_{phot}. Independently, the formation of $^1O_2$ during the catalytic cycle was confirmed by using 9,10-dimethylanthracene (a known $^1O_2$ quencher) with the detection of the corresponding endoperoxide product.[24] However, when the reaction was carried out without sacrificial electron donor, thus by-passing the copper-dependent catalytic pathway, only 7 TON were achieved instead of 94 in presence of TEOA. These results confirm the involvement of $^1O_2$ in the sulfide oxidation process, but to a low extent.

Most importantly, the O_2-based process involving the reactivity of a copper oxygen-activated species (Path 1) was clearly established, because when a 1:10 mixture of the reduced Cu^{I}_{cat} (10 μmol) and 4-bromothioanisol in anhydrous acetonitrile was open to air, sulfoxide was formed in 70 % yield with respect to $Cu^{I}_{cat.}$

To conclude, the Ru^{II}_{phot}-Cu^{II}_{cat} dyad reported herein represents, to the best of our knowledge, a unique example of copper-based system capable of performing efficient catalytic oxidation of organic substrates using O_2 as unique oxygen atom source under light irradiation and mild conditions. It represents an interesting alternative to other photoactivable Ru-based systems reported and using $PhI(OAc)_2$, H_2O_2, and H_2O as co-oxidants.[5a,25] This study unambiguously validates our proof-of-concept in which a judiciously chosen association of appropriate photosensitizer and sacrificial electron donor can provide a gradual and controlled electron delivery to a Cu^{II} subunit for its reduction prior to O_2 activation. We also showed the efficient synergistic effect between both partners in the dyad compared to the bimolecular system for which a diffusional contact is required for electron transfer. The deciphering of the reaction pathway for alkene oxidation is under progress.

Keywords: copper · dioxygen · oxygenation · photocatalysts · ruthenium

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