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Paper

Oxidation catalysis via visible-light water activation of a $[Ru(bpy)_3]^{2+}$ chromophore BSA-metallocorrole couple

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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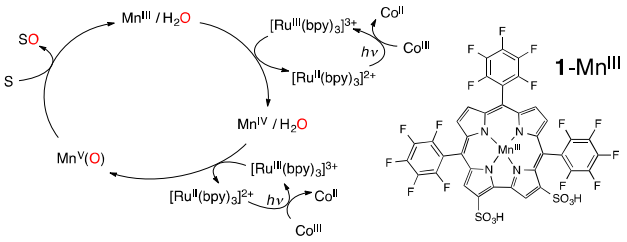
Light induced enantioselective oxidation of an organic molecule with water as the oxygen atom source is demonstrated in a system where chirality is induced by a protein, oxygen atom transfer by a manganese corrole, and photocatalysis by ruthenium complexes.

Introduction

The introduction of benign components into the field of chemical catalysis has been of great interest in recent years. For example, systems where the reactants and free energy used for a chemical reaction come from clean and abundant sources such as water and light are of great interest in the development of new catalytic oxidation processes.[1,2] Association of these "cleaner" methodologies with the use of biological scaffolds, such as proteins, in order to induce selectivity or increase its yield in particular oxidation reactions, would lead to very appealing systems not only for their future implementation in industry but also as fundamental interdisciplinary research models.[3-10]

In this paper we report the visible light driven oxidation of an organic substrate using a system that associates a $[Ru^{II}(bpy)_3]^{2+}$ chromophore with a bis sulfonato Mn^{III} corrole/Bovine Serum Albumin (BSA) artificial metalloenzyme. A Mn-bound water molecule is activated as to form the high-valent manganese-oxo species that performs oxygen atom transfer (OAT) to sulfide (Scheme 1).



Scheme 1. Reaction scheme for the light driven oxidation of an organic substrate by water in the presence of a catalyst/protein conjugate, a Ru chromophore and a Cobalt-based sacrificial electron acceptor. The structure of the applied **1**-Mn^{III} corrole catalyst is shown on the right. For experimental conditions see experimental section. Protons released during light induced activation of H_2O are omitted for clarity.

Ruthenium trisbipyridyl type complexes have been widely used as visible light sensitizers in bimolecular and heterodinuclear photocatalytic systems, for oxidizing a wide range of substrates ranging from water to organic molecules.[11-14] The mechanism of action (Scheme 2) relies on visible light absorption by a MLCT band (400-500 nm) which produces a long-lived activated Ru^{II} species (Ru^{II*}) that can be oxidatively quenched by a myriad of sacrificial electron acceptors on the route to $[Ru^{III}(bpy)_3]^{3+}$.[15] The oxidation potential of the latter complex, 1.30 V *vs.* SCE, can then be used to activate an adjacent catalyst. For multi-electron catalytic processes, this series of events has to be repeated until the necessary accumulation of holes has been achieved at the catalytic center.

$$Ru^{II} + h\nu \rightarrow Ru^{II*} \quad (1)$$
$$ea + Ru^{II*} \rightarrow ea^{-} + Ru^{III} \quad (2)$$
$$Ru^{III} + BSA\text{-}Mn^{III} + H_2O \rightarrow Ru^{II} + BSA\text{-}Mn^{IV}(OH) + H^{+} \quad (3)$$
$$Ru^{II} + h\nu \rightarrow Ru^{II*} \quad (4)$$
$$ea + Ru^{II*} \rightarrow ea^{-} + Ru^{III} \quad (5)$$
$$Ru^{III} + BSA\text{-}Mn^{IV}(OH) \rightarrow Ru^{II} + BSA\text{-}Mn^{V}(O) + H^{+} \quad (6)$$
$$BSA\text{-}Mn^{V}(O) + S \rightarrow BSA\text{-}Mn^{III} + SO \quad (7)$$

Scheme 2. Reaction pathway for the oxidation of a substrate *via* light induced activation of a water molecule assisted by the BSA-Mn^{III} hybrid catalyst. The substrate, electron acceptor and photosensitizer are denoted as S, ea and Ru^{II}, respectively.

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† Electronic Supplementary Information (ESI) available: [Additional data including flash photolysis, UV/Visible and mass spectrometry experiments.]. See DOI: 10.1039/x0xx00000x

Among the possible catalysts to be used, metal complexes of the amphipolar bis-sulfonato corrole **1** (Scheme 1) are interesting candidates. This kind of trianionic ligands can indeed be complexed to different metal ions leading to versatile catalysts towards the oxidation of different substrates such as sulfides, olefins and water.[16-20] Additionally, **1**-Mn^{III} and **1**-Fe^{III} complexes have been shown to bind tightly to serum albumin proteins.[21] These non-covalent conjugates have shown good TON in the enantioselective oxidation of thioanisole and the *R*-modafinil precursor by hydrogen peroxide.[19,22]

Given these precedents we set out to assay the oxidation of organic substrates using visible light and water as the energy and O-atom sources, respectively. Under these experimental conditions, continuous visible light activation of $[Ru(bpy)_3]^{2+}$, in the presence of $[Co^{III}(NH_3)_5Cl]^{2+}$ as sacrificial electron acceptor, and **1**-Mn^{III} as catalyst embedded in BSA, yields the active form **1**-Mn^{V}=O which has been shown to be responsible for the oxidation of sulfides.[17]

Experimental

Mn corrole (**1**-Mn^{III}) was prepared as previously published.[23] $[Ru^{II}(bpy)_3]^{2+}$, $[Ru^{III}(NH_3)_6]^{3+}$, $[Co^{III}(NH_3)_5Cl]^{2+}$ and thioanisole were obtained from Aldrich and used as received.

Light activated oxidation reactions: In a typical photo-oxidation reaction, to a 800 µL of a degassed phosphate buffer solution (PBS) (10 mM, pH 7.4) containing 14 mM $[Co^{III}(NH_3)_5Cl]^{2+}$, 0.30 mM BSA and 0.06 mM **1**-Mn^{III}, were added 130 µL of 3.04 mM $[Ru^{II}(bpy)_3]^{2+}$ in PBS buffer, and 11 µL of thioanisole. The solution was degassed by 3 freeze/thaw cycles and the samples were illuminated with a 450 nm diode during 10 minutes. The final concentrations of each component were 12 mM $[Co^{III}(NH_3)_5Cl]^{2+}$ (240 eq), 0.25 mM BSA (5 eq), 0.05 mM **1**-Mn^{III} (1 eq), 0.42 mM $[Ru^{II}(bpy)_3]^{2+}$ (8.5 eq), and 100 mM thioanisole (2000 eq)

Control experiments in the absence of protein were performed maintaining the above concentrations. Control experiments in the absence of chromophore or catalyst were done by substituting the corresponding solution by the equivalent volume of PBS solution.

The content of each vial was eluted through a short (3 cm) silica plug to which 100 µL 10^{-2} M acetophenone solution in acetonitrile acting as internal standard had been previously added. The column was washed with 2 mL ethyl acetate in order to elute all the components. The aqueous phase of the resulting filtrate was removed and the organic phase was dried using Na_2SO_4 prior to GC analysis. In order to determine the enantiomeric excess, the solvent was evaporated and the residue was redissolved in the minimum amount of isopropanol prior to injection in HPLC.

Quantification of products: GC analysis was performed on a Shimadzu GC 2010 Plus fitted with a Zebron ZB Semi Volatiles column (30 m x 0.25 mm x 0.25 µm). For detection of thioanisole and its oxidation products, the applied temperature gradient was: from 100°C to 130°C at 5°C/min, then 130°C to 300°C, 50°C/min, which was held constant for 3 min. The injector and FID temperature were set at 300°C. The internal standard used was acetophenone and the elution times were (min): acetophenone (4.03), thioanisole (4.32), thioanisole sulfoxide (7.56), thioanisole sulfone (8.04).

HPLC analysis of the enantiomers was done on a Perkin Elmer HPLC equipped with a chiral Chiracel OD-H column to determine the enantiomeric excess of the sulfoxide obtained. The eluent was hexane: isopropanol (95:5 v/v), and the flow rate was 1 ml min^{-1}.

Laser flash photolysis: Transient absorption spectra and kinetic measurements were performed on an Edinburgh Instruments LP920 Laser Flash Photolysis Spectrometer system that incorporated a Continuum OPO for sample excitation (~7 ns pulse duration). The OPO was pumped by a Continuum Surelite Q-switched Nd:YAG laser operating at 355 nm. Samples were excited by 460 nm wavelength pulses at ~10 mJ laser energy. The LP920 system uses a 450 W Xenon arc lamp as source for the probe light for the transient absorption measurements. For kinetic measurements in the 10 ns—1 ms time range, the Xenon arc lamp was pulsed. Detection was performed either via a Czerny-Turner blazed 500 nm monochromator (bandwidth: 1-5 nm) coupled with a Hamamatsu R928 photomultiplier tube (kinetic mode), or via a 500 nm blazed spectrograph (bandwidth: 5 nm) coupled with a water-cooled ICCD nanosecond Andor DH720 camera (spectral mode). Samples, purged with argon for 10 minutes prior to each experiment, had an absorbance of ~0.40 at the excitation wavelength. The presented transient absorption spectra were typically the average of 20-50 measurements. Experiments in the presence of reversible electron acceptor were performed using 20 mM $[Ru^{III}(NH_3)_6]^{3+}$ which lacks any absorption band in the visible.

Results

The UV/Vis spectrum of $[Ru^{II}(bpy)_3]^{2+}$ is dominated by a MLCT band with an absorbance maximum at 450 nm (ε = 14600 M^{-1} cm^{-1}). **1**-Mn^{III} shows a typical Soret absorption band at 400 nm (ε_{400} = 34000 M^{-1} cm^{-1}), a sharp solvent dependent strong absorption at 480 nm, and Q bands around 600 nm (ε_{600} = 11600 M^{-1} cm^{-1}) (Figure 1). Under the experimental conditions of 10:1 Ru:Mn, illumination with 450 nm light leads to the absorption of 85% of the incident light by the ruthenium chromophore, which initiates the photochemical events. Absorption of visible light by **1**-Mn^{III} is not deleterious for the reaction sequence since the excited state of Mn-corrole decays in < 10 ns (instrumental resolution), preventing the catalyst from interacting with the electron acceptor (Supporting Information Figure SI.1). The use of more equivalents of Mn-corrole was disregarded in order to avoid a light-filtering effect of the chromophore.

To test the OAT of **1**-Mn^{V}(O) corrole to sulfides **1**-Mn^{III} was oxidized by *m*-CPBA (Figure 1, right) to the corresponding **1**-Mn^{V}(O). This results in the bleaching of the 600 nm Q band leading to an absorption spectrum dominated by a 520 nm Q band and a 400 nm Soret band.[17,18] Addition of thioanisole to **1**-Mn^{V}(O) leads to regeneration of the spectrum of **1**-Mn^{III}. This

observation is a proof that the active species in the catalytic cycle is **1**-Mn^{V}(O), as previously described.[17]

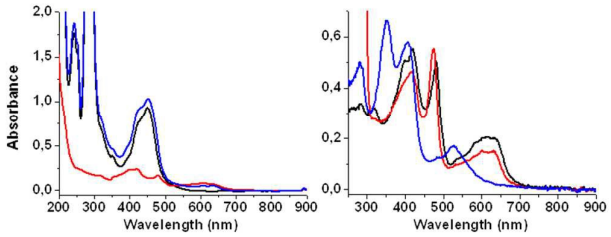

Figure 1: Left) UV/Vis spectra in acetonitrile of 70 μM $[Ru^{II}(bpy)_3]^{2+}$ (black trace), 7 μM **1**-Mn^{III} (red trace), and 10:1 equivalents mixture of $[Ru^{II}(bpy)_3]^{2+}$ and **1**-Mn^{III} (blue trace) in acetonitrile. Right) UV/Vis spectra of 20 μM **1**-Mn^{III} (black trace), **1**-Mn^{V} (blue trace) obtained after addition of 8 eq. *m*-CPBA, and **1**-Mn^{III} obtained after addition of 1000 eq. thioanisole to **1**-Mn^{V} (red trace).

Laser flash photolysis experiments of either a 1:1 $[Ru^{II}(bpy)_3]^{2+}$:**1**-Mn^{III} solution in water or a 10:1 $[Ru^{II}(bpy)_3]^{2+}$:BSA-**1**-Mn^{III} solution indicated that the excited state of $[Ru^{II}(bpy)_3]^{2+}$ is not quenched by interaction with the catalyst either in solution or as part of the protein conjugate (Eq. 1, Supporting Information Figure SI.2). It still displayed its typical emission features at 610 nm with a lifetime of 600 ns. Addition of $[Ru^{III}(NH_3)_6]^{3+}$ as an external electron acceptor lead, after light excitation, to a charge separated state composed of $[Ru^{III}(bpy)_3]^{3+}$ and $[Ru^{II}(NH_3)_6]^{2+}$ (Eq. 2, Supporting Information Figure SI.3). This state, identified by the MLCT bleaching at 450 nm, had a lifetime of *ca.* 250 μs in the absence of further reactions. However, in the presence of **1**-Mn^{III} it underwent a electron transfer reaction with the catalyst, to generate the **1**-Mn^{IV} species (Supporting Information Figure SI.4, spectrum at 50 μs). This becomes apparent from the bleaching of the 600 nm Q-band and the absorption at 480 nm (Fig. 2) stemming from the loss of **1**-Mn^{III}, as well as by the recovery of the Ru^{II} MLCT band at 450 nm arising from the **1**-Mn^{III} → $[Ru^{III}(bpy)_3]^{3+}$ charge transfer (Eq. 3, Figure 2). Except for the spectroscopic changes at 450 nm, due to the Ru photosensitizer, the differential absorption features shown in Figure 2 were very similar to those observed for a **1**-Mn^{III} to **1**-Mn^{IV} conversion (Supporting Information Figure SI.4). Consistent with the transient absorption, kinetic studies revealed that the formation of complex **1**-Mn^{IV} had a rise time of 89 μs, as observed by the bleach at 640 nm, and a lifetime of 530 μs as seen by the recovery of the original **1**-Mn^{III} 640 nm absorption, (Supporting Information Figure SI.5).

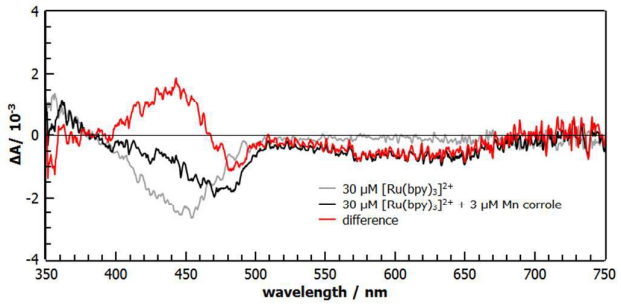

Figure 2: Transient absorption of a solution of 30 μM $[Ru^{II}(bpy)_3]^{2+}$ and 20 mM $[Ru^{III}(NH_3)_6]^{3+}$ (—) , and of a solution of 30 μM $[Ru^{II}(bpy)_3]^{2+}$, 20 mM $[Ru^{III}(NH_3)_6]^{3+}$ and 3 μM **1**-Mn^{III} (—) in CH_3CN:H_2O (70:30) solvent 100 μs after laser pulse at 460 nm (—). OD(460) = 0.4, laser energy 2mJ. Resulting difference spectrum (—).

Similar results were obtained studying the system where **1**-Mn^{III} was embedded in BSA (BSA-**1**-Mn^{III}), although the extent of the bleach was significantly lower, denoting a lower yield in oxidized catalysts. (Supporting Information Figure SI.6).

Photo-driven oxidation catalysis of thioanisole was performed by irradiation at 460 nm of a reaction mixture containing $[Co^{III}(NH_3)_5Cl]^{2+}$ as electron acceptor, $[Ru^{II}(bpy)_3]^{2+}$ as chromophore, BSA-**1**-Mn^{III} conjugate as catalyst, and thioanisole as substrate (see experimental section for details). With the BSA-**1**-Mn^{III} catalyst, methylphenylsulfoxide was obtained as the sole product with a TON of 21 ± 7 as shown by GC analysis which corresponds to *a* 20% yield with respect to $[Co^{III}(NH_3)_5Cl]^{2+}$. Interestingly, an enantiomeric excess ranging between 12-16% in favor of the R isomer was observed. Most important, when 19 % $H_2{}^{18}O$ was introduced in the solvent mixture, 20% of the resulting sulfoxide contained ^{18}O as shown by the peaks observed in GC/MS at m/z 143.0386 $[M + H]^+$ and 165.0216 $[M + Na]^+$. This confirmed that the inserted O-atom in the oxidation product originates from water molecules of the solvent medium (Supporting Information Figure SI.7).

When non-conjugated **1**-Mn^{III} was used as catalyst, methylphenylsulfoxide was also obtained as the major product, in a slightly better yield than in the case of BSA-**1**-Mn^{III} [32 ± 3 TON, 27% % *vs.* $[Co^{III}(NH_3)_5Cl]^{2+}$, together with some sulfone (TON = 1.6)]. As observed in the previous case, ^{18}O insertion was also evidenced when $H_2{}^{18}O$ was used in the solvent mixture. Removal of any single component in both sets of experiments yielded no catalysis.[24]

Discussion

Formation of bioconjugates composed of albumin with **1**-Mn and analogous metal complexes of the same corrole and their functions in various applications has been widely studied.[19,22,25-29] The use of a 5:1 protein:**1**-Mn^{III} ratio assures for the complete incorporation of the **1**-Mn^{III} catalyst into the strong binding pocket of albumin. Induction of enantiomeric excess by using this kind of biocatalyst has been demonstrated by Gross et al. for the oxidation of sulfides by H_2O_2.[21,22]

10 eq. $[Ru^{II}(bpy)_3]^{2+}$ *vs.* **1**-Mn^{III} were used in the reaction mixture in order to favor light absorption by the former

species (ε_{450} = 14600 M^{-1} cm^{-1}) acting as a chromophore rather than by the **1**-Mn^{III} catalyst (ε_{450} = 18000 M^{-1} cm^{-1}). The electron acceptors used in this study were either $[Ru^{III}(NH_3)_6]^{3+}$, a reversible electron acceptor with no absorbance in the visible region of the spectrum, which is convenient in the kinetic studies, or $[Co^{III}(NH_3)_5Cl]^{2+}$, an irreversible electron acceptor used for catalytic studies in which electrons must be removed permanently from the reaction medium in order to yield the high valent catalytically active species. Additionally, this acceptor is known to be able to quench the excited state of ruthenium chromophores while not interfering with the ground state of the catalyst, which would lead to dark oxidation reactions independent of irradiation. Laser flash photolysis experiments show that the **1**-Mn^{III} species, although being a strong chromophore, lacks a sufficient excited state lifetime in order to react with the electron acceptor and to start a parallel electron transfer pathway. Additionally, under the conditions used in this work, $[Ru^{II}(bpy)_3]$* is not quenched by either energy transfer to, or excited state electron transfer from **1**-Mn^{III}. Thus, the full 600 ns lifetime of the excited state remaines available for reacting with the electron acceptor in order to form the $[Ru^{III}(bpy)_3]^{3+}$ species needed to initiate the catalytic cycle. This species has $E_{1/2}$ = 1.30 V *vs.* SCE and is capable of performing the Mn^{III} to Mn^{IV} oxidation. Corrole-Mn complexes have Mn^{IV}/Mn^{III} redox potentials in the 0.57 to 0.64 V range, depending on ring substitution,[17] and the axial ligand- a water molecule under our conditions. The second oxidation step is usually a macrocyclic ring oxidation rather than a metal centered oxidation, unless the macrocyclic rings are so electron deficient that metal oxidation becomes prominent. For complexes similar to **1**-Mn^{III} but lacking the electron withdrawing sulfonato substituents, the $E_{1/2}$ of the $Mn^{V}(O)/Mn^{IV}(O)$ redox couple has been shown to be 0.13 V *vs.* SCE.[17] Thus, formation of the active **1**-$Mn^{V}(O)$ intermediate following two successive light induced electron/proton activations of a water molecule in the presence of **1**-Mn^{III} and $[Ru^{II}(bpy)_3]^{2+}$ is a plausible scenario (see Scheme 2, eq. 3 and 6). This highly oxidizing species has been demonstrated to perform the oxidation of thioanisole into its sulfoxide product.

Compared to TON and ee's values found using H_2O_2 as oxidant and O-atom source, the turnover numbers and ee's observed in this work are modest.[22] This might be explained by the myriad of different competitive reactions that can happen in this system. Indeed, small deviations from the ideal scenario (two consecutive reaction sequences consisting in light absorption, oxidative excited state quenching and electron transfer) may lead to deactivating pathways which nonetheless consume the electron acceptor. For example, the reaction between the oxidized chromophore $[Ru^{III}(bpy)_3]^{3+}$ and either the **1**-Mn^{III} or **1**-Mn^{IV} embedded complexes might be hampered by the protein scaffold. Such a limitation is indicated by the transient absorption monitoring of the BSA-**1**-Mn^{III} conjugate which shows that the photogenerated BSA-**1**-Mn^{IV} does not accumulate to a large extent (Supporting Information Figure SI.6). Hence, the photoinduced generation of the subsequent active BSA-**1**-$Mn^{V}(O)$ intermediate is necessarily limited and the TON observed with the biohybrid system are decreased with respect to the molecular analogue. Along this line, it should be noted that the light induced oxidation of the heme in P450 could not be achieved by $[Ru^{II}(bpy)_3]^{2+}$, unless the ruthenium photosensitizer was covalently attached to the protein surface.[30] Note that BSA contains an important number of cysteine residues which could be easily oxidized and block the oxidation of the catalyst by the $[Ru^{II}(bpy)_3]^{2+}$ chromophore.[31] However, our experimental conditions (larger amount of thioanisole *vs* cysteine) have been devised in order to minimize side reactions with the protein.

Nevertheless, the most important advance is that water is the oxygen atom source in the currently introduced system. This was proven via the addition of 20% $H_2{}^{18}O$ to the reaction mixture, which led to an equivalent amount of ^{18}O labelled reaction products. (Supporting Information Figure SI.7). This observation testifies that the O-atom inserted into the product originates from water, *i.e.*, that the activation of water is at the heart of the photo-induced oxidation reaction of thioanisole. By implication, this leads to the conclusion that the active form **1**-$Mn^{V}(O)$ of the molecular catalyst is generated following a mechanism akin to the one depicted in Scheme 1.

Conclusions

We demonstrate the light driven activation of a Mn-corrole unit by visible light activation *via* a ruthenium chromophore. The resulting oxidized form of the catalyst is capable of the selective oxidation of thioanisole into its corresponding sulfoxide. Sulfide oxidation mediated by the BSA-**1**-Mn^{III} conjugate results in a significant enantiomeric excess. The presence of $H_2{}^{18}O$ in the reaction medium leads to the insertion of ^{18}O in the product, thus confirming the role of water as the O-atom source in the reaction. This work shows that oxidation catalysis can be performed in aqueous medium without any chemical oxidant and using visible light as only energy input.

Acknowledgments

JPM and FB thank the Labex CHARMMMAT, the ANR (project ANR Blanc Cathymetoxy) and the EU-COST Action CM1003. ZG thanks ISF for financial support.

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Oxidation catalysis via visible-light water activation of a $[Ru(bpy)_3]^{2+}$ chromophore BSA-metallocorrole couple

Table of contents entry:

Light induced enantioselective oxidation of thioanisole with water as the oxygen atom source is catalyzed by a Mn-corrole-BSA artificial metalloenzyme in the presence of a photoactivable ruthenium complex.