Cooperative effects in homogenous water oxidation catalysis by mononuclear ruthenium complexes†

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The homogenous water oxidation catalysis by [Ru(terpy)(bipy)Cl]+ (1) and [Ru(terpy)(Me2bipy)Cl]+ (2) (terpy = 2,2':6,2''-terpyridine, bipy = 2,2'-bipyridine, Me2bipy = 4,4'-dimethyl-2,2'-bipyridine) under the influence of two redox mediators [Ru(bipy)]2+/3+ (3) and [Ru(phen)(Me2bipy)]2+/3+ (4) (phen = 1,10-phenanthroline) was investigated using Ce4+ as sacrificial oxidant. Oxygen evolution experiments revealed that mixtures of both 2–4 and 2–3 produced more molecular oxygen than catalyst 2 alone. In contrast, the combination of mediator 4 and catalyst 1 resulted in a lower catalytic performance of 1. Measurements of the temporal change in the intensity of a UV transition at 261 nm caused by the addition of four equivalents of Ce4+ to 2 revealed three distinctive regions—suggested to correspond to the stepwise processes: (i) [RuIV=O]2+/3+ → [RuIV=O]3+; (ii) [RuIV=O]3+ → [RuII(=O)(OH)]2+/3+; and (iii) [RuIII(=O)(OH)]2+/3+ → [RuI(=O)H]2+.

UV-Visible spectrophotometric experiments on the 1–4 and 2–4 mixtures, also carried out with four equivalents of Ce4+, demonstrated a faster [Ru(phen)2(Me2bipy)]2+/3+ → [Ru(phen)2(Me2bipy)]3+ reduction rate in 2–4 than that observed for the 1–4 combination. Cyclic voltammetry data measured for the catalysts and the mixtures revealed a coincidence in the potentials of the RuII/RuIII redox process of mediators 3 and 4 and the predicted [RuIV=O]2+/3+[RuIV=O]3+ potential of catalyst 2. In contrast, the [RuIV=O]2+/3+[RuIV=O]3+ process for catalyst 1 was found to occur at a higher potential than the RuIV/RuIII redox process for 4. Both the spectroscopic and electrochemical experiments provide evidence that the interplay between the mediator and the catalyst is an important determinant of the catalytic activity.

Introduction

The splitting of water into oxygen and hydrogen using sunlight has a great potential for developing an alternative renewable energy source that will help to overcome the looming shortfall in fossil fuels. However, despite the promise, to achieve water splitting (2H2O → O2 + 2H2) a substantial energy input additional to the thermodynamic requirement (1.23 V or 267 kJ mol−1 per mole of H2 produced) is needed to compensate for losses arising from, for example, cell resistance and various activation barriers. In this regard, the mechanistically complex water oxidation half reaction (2H2O → O2 + 4H+ + 4e−) presents particular challenges as it involves the extraction of four electrons and four protons from two water molecules and the formation of a stable diatomic O=O bond. Thus, efficient catalysts need to be developed such that the energy required to drive the water-splitting reaction is as close as possible to the thermodynamic value (1.23 V). There has been much interest in this field of research and efforts have been made to develop heterogeneous photocatalysts as well as photo-electrocatalysts for water splitting.1 Single semiconductors or combinations of semiconductors with appropriate valence and conduction band positioning (Z-scheme) have been used to split water directly and more active catalysts have been introduced to enhance performance (these include metals and a variety of transition metal oxides).1,2 In parallel with these studies, there has been a long-standing interest in molecular catalysts that oxidise water or reduce water, with a focus on the former being driven in part by the fact that a tetramanganese cluster in water oxidation complex (WOC) of photosystem II is the only catalyst known to catalyse water oxidation in nature.3 Amongst the range of molecular water oxidation catalysts that have been reported,4 however ruthenium complexes have been investigated for several decades now and, in contrast to some purported molecular catalysts incorporating other transition metals, there is
clear evidence that such complexes are indeed molecular catalysts operating in homogeneous solution and when attached to surfaces.\textsuperscript{5–9} Initially, the focus was on dinuclear complexes owing to the discovery that the ruthenium blue dimer (cis,cis-[[bipy]₂(H₂O)RuH₂(μ-O)RuOH₂(bipy)]\textsuperscript{4⁺}; bipy = 2,2’-bipyridine) catalysed this reaction,\textsuperscript{6} and a mechanistic understanding of the pathways leading to oxygen formation was developed from these studies.\textsuperscript{7} More recently, mononuclear ruthenium complexes have also been shown to catalyse water oxidation.\textsuperscript{5,8}

ruthenium complexes have also been shown to catalyse water oxidation.\textsuperscript{5,8} These mononuclear ruthenium complexes have largely been investigated using Ce\textsuperscript{4⁺} as a sacrificial oxidant,\textsuperscript{5,8,9,11} and although investigations of the interactions between potential photosensitisers (or dyes) and the ruthenium catalysts is very important for the development of a light-induced water-splitting system, to date only a handful of reports have focussed on this aspect in homogeneous systems.\textsuperscript{9,10} For example, the catalytic rate of Ce\textsuperscript{4⁺}-assisted water oxidation by the blue dimer in homogeneous solution was enhanced by a factor of \textasciitilde30 on addition of mediators such as [Ru(bipy)₂]L\textsuperscript{2⁺}, where L = 2,2’-bipyridine, 2,2’-bipyrimidimine and 2,2’-bipyrazine.\textsuperscript{9} In a more recent report, a covalently-linked mediator/catalyst dinuclear complex [(bipy)₂Ru(4-Mebpy-4’-bimpy)(terpy)(OH₂)]\textsuperscript{2⁺} or [Ru\textsuperscript{II}Ru\textsuperscript{IV}O₂] (4-Mebpy-4’-bimpy = 4-(methylbipyridin-4’-yl)-N-benzimid-N’-pyridine; terpy = 2,2’:6’:2’-terpyridine) displayed a faster catalytic rate than the individual mononuclear complex [Ru(terpy)(Mebim-py)(OH₂)]\textsuperscript{2⁺} (Mebim-py = 2-pyridyl-N-methylbenzimidazole).\textsuperscript{10}

The relative lack of investigations focussing on cooperativity between ruthenium catalysts and redox-active ruthenium poly-pyridyl complexes has led us to study the interplay between two tris(diimine)ruthenium complexes [Ru(bipy)₂]\textsuperscript{2⁺} (3) and [Ru(phen)₂(Me₂bipy)]\textsuperscript{2⁺} (4) (phen = 1,10-phenanthroline, Me₂bipy = 4,4’-dimethyl-2,2’-bipyridine) as redox mediators and two closely-related mononuclear catalysts [Ru(terpy)(bipy)-Cl]\textsuperscript{2⁺} (1) and [Ru(terpy)(Me₂bipy)Cl]\textsuperscript{2⁺} (2) in Ce\textsuperscript{4⁺}-activated homogeneous water oxidation catalysis. Building on previous related investigations of mononuclear complexes of type [Ru(terpy)-(xbipy)(H₂O)]\textsuperscript{2⁺} (xbipy = derivatives of 2,2’-bipyridines with various substitutions on the 4,4’ position),\textsuperscript{11} we report an investigation of the influence of redox mediators 3 and 4 on water oxidation mononuclear catalysis by 1 and 2 (Scheme 1).

**Results and discussion**

Following our reports describing the synthesis of the stereochemically-resolved \(\Delta\)[Ru(phen)₂(Me₂bipy)]\textsuperscript{2⁺} and the non-chiral [Ru(terpy)(Me₂bipy)Cl]\textsuperscript{2⁺} for the study of their biological activity,\textsuperscript{12,13} in the present work we adopted the same synthetic pathway to obtain complexes 1 and 2. These compounds were prepared by refluxing mixtures of [Ru(terpy)Cl₃] and 2,2’-bipyridine or 4,4’-dimethyl-2,2’-bipyridine in ethanol–water (4 : 1), while 4 was obtained from the reaction between [Ru(phen)₂Cl₂] and 4,4’-dimethyl-2,2’-bipyridine in ethanol–water (1 : 1). Size-exclusion chromatography was used to separate each complex from the unreacted starting material and any oxidised ruthenium by-products. The purity of the compounds was confirmed by \(^1\)H NMR spectroscopy.

A series of oxygen evolution experiments using catalysts 1 and 2 as a 1 : 1 mixture with either 3 or 4 at the concentration 73 \(\mu\)M was carried out in an air-tight vessel using 0.1 M HClO₄ solution as the reaction medium and (NH₄)₂[Ce(NO₃)₆] (0.073 M or 1000 equivalents) as the oxidant. The molecular oxygen evolved from the reaction was detected in the headspace over the course of several hours by a Clark-type micro-sensor. The oxygen measurement for the individual catalysts revealed that 2 produced approximately 16 \(\mu\)mol oxygen after six hours whereas 1 produced twice as much (30 \(\mu\)mol). In order to test the effect of the redox mediators 3 and 4 on the catalytic performance of 1 and 2, the oxygen evolution of each catalyst in the presence of the mediators was investigated. Upon mixing with 4 in a 1 : 1 ratio, oxygen production catalysed by 1 was found to decrease slightly to 23 \(\mu\)mol over the six hours of testing. In contrast, the addition of mediator 4 to catalyst 2 resulted in a significant increase in oxygen production from 16 \(\mu\)mol to 38 \(\mu\)mol over the same period. No molecular oxygen could be detected from a control experiment using only mediator 4 (Fig. 1). The enhancement of the catalytic properties of 2 affected by the redox mediator prompted us to perform further analyses in order to elucidate the mode of interaction between the tris(diimine)ruthenium(II) complexes...
and the catalyst. Our initial investigations using UV-Visible, 
$^1$H NMR and electrochemical techniques are discussed in the
following sections.

The changes in the UV-Visible spectrum of the individual
catalysts and the mixtures, before and after the addition of
four equivalents of Ce$^{4+}$, were studied in 0.1 M HClO$_4$. The
initial UV-Visible spectrum of catalyst 2 (before Ce$^{4+}$ was
added) showed three absorption bands (480 nm, 313 nm and
281 nm). The absorption at 480 nm, assigned as MLCT (metal-
to-ligand charge transfer) band, was found to disappear upon
addition of four equivalents of Ce$^{4+}$ (Fig. 2, panel a). This
spectral assignment has been reported earlier for the reaction
of the closely-related [Ru(terpy)(bpm)(OH$_2$)]$^{2+}$ complex with
Ce$^{4+}$ in 0.1 M HClO$_4$.$^8$ The addition of two equivalents of Ce$^{4+}$
to the solution of [Ru(terpy)(bpm)(OH$_2$)]$^{2+}$ resulted in the two
oxidation steps that could be followed spectroscopically:

$$[\text{Ru}^{II} - \text{OH}_2]^{2+} + \text{Ce}^{4+} \rightarrow [\text{Ru}^{III} - \text{OH}]^{2+} + \text{Ce}^{3+}$$  \hspace{1cm} (1)
$$[\text{Ru}^{III} - \text{OH}]^{+} + \text{Ce}^{4+} \rightarrow [\text{Ru}^{IV} - \text{O}]^{2+} + \text{Ce}^{3+}$$  \hspace{1cm} (2)

Further addition of one equivalent of Ce$^{4+}$ to the
[Ru$^{IV}$$=$$O]^{2+}$ species (or three equivalents to [Ru$^{III}$$-$$OH_2]^{2+}$) trig-
gerated three stepwise redox processes. Three distinctive regions
based on the absorbance changes at 283 nm were observed
and attributed to the reactions given in eqn (3)–(5).$^8$

$$[\text{Ru}^{IV} - \text{O}]^{2+} + \text{Ce}^{4+} \rightarrow [\text{Ru}^{V} - \text{O}]^{3+} + \text{Ce}^{3+}$$  \hspace{1cm} (3)
$$[\text{Ru}^{V} - \text{O}]^{3+} + \text{H}_2\text{O} \rightarrow [\text{Ru}^{III} - (\text{OOH})]^{2+} + \text{H}^+$$  \hspace{1cm} (4)
$$[\text{Ru}^{III} - (\text{OOH})]^{2+} \rightarrow [\text{Ru}^{III} - \text{OH}_2]^{2+}$$  \hspace{1cm} (5)

The transient [Ru$^{V}$$=$$O]$^{3+}$ ion has been proposed to react
further with water to give what is tentatively assigned as the
[RU$^{III}$$-$$OOH]^{2+}$ species which slowly decays to [Ru$^{III}$$-$$OH_2]^{2+}$. 

Fig. 1 (Top) Oxygen evolution from the reaction between the com-
plexes and Ce$^{4+}$ in 0.1 M HClO$_4$ detected in the headspace. (Bottom)
Turnover numbers (TONs). Blue = 2–4 mixture; green = 1 only; black = 1–4 mixture; orange = 2–3 mixture; purple = 2 only; red = 4 only. The
error bars of the full and crossed lines are in grey. In all cases, the con-
centration of each complex and Ce$^{4+}$ were 73 µM and 0.073 M,
respectively.

Fig. 2 Spectral changes before and after addition of four equivalent
Ce$^{4+}$ in (a) 2 only; (b) 2–4 mixture and (c) 1–4 mixture. In all cases the
complex concentration was 24 µM.
possibly by releasing O₂. In the present investigation, three regions were indeed observed at the slightly lower wavelength (261 nm), compared with 283 nm in the previous study, suggesting that catalyst 2 also undergoes the stepwise redox processes described by eqn (3)–(5) after the addition in this case of four equivalents of Ce⁴⁺ (see Fig. 3, top panel). Oxygen can be released if further Ce⁴⁺ is added to the peroxido species [Ru³⁺–OOH]²⁺ according to eqn (6) and (7). This was demonstrated in the present study by using an excess (1000 equivalents) of Ce⁴⁺ in the oxygen evolution experiment mentioned earlier.

$$[\text{Ru}^{III}-(\text{OH})]^{2+} + \text{Ce}^{4+} \rightarrow [\text{Ru}^{IV}-(\text{O}_2)]^{2+} + \text{Ce}^{3+} + H^+ \quad (6)$$

$$[\text{Ru}^{IV}-(\text{O}_2)]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Ru}^{II}-(\text{OH}_2)]^{2+} + \text{O}_2 \quad (7)$$

The UV-Visible spectrum of the mixture of catalyst 2 and 4 before the Ce⁴⁺ addition showed the MLCT band at 455 nm and three other bands in the UV regions (313, 281 and 264 nm). As observed for the individual catalyst, the MLCT band also disappeared upon adding the oxidant (Fig. 2, panel b). In addition to the three redox processes observed for the individual catalyst, oxidation of the mixture with four equivalents of Ce⁴⁺ is also expected to trigger the formation of [Ru(phen)₂(Me₂bipy)]³⁺ according to eqn (8).

$$[\text{Ru}(\text{phen})_2(\text{Me}_2\text{bipy})]^{3+} + \text{Ce}^{4+} \rightarrow [\text{Ru}(\text{phen})_2(\text{Me}_2\text{bipy})]^{3+} + \text{Ce}^{3+} \quad (8)$$

As in the study with 2 alone, the absorbance changes at 261 nm was also monitored for the 2–4 mixture to see whether the features associated with (3), (4) and (5) could be identified on the same time scale. These features were absent (Fig. 3, bottom) partly because of the coincidental rise in a strong ligand-centred absorption at 264 nm as is typically observed in this region for similar tris(diimine)ruthenium(II) complexes. Alternatively, it is possible that the oxidation step (3) is greatly accelerated by [Ru(phen)₂(Me₂bipy)]³⁺ such that it could not be detected on the minute time scale. The acceleration of reaction (3) by [Ru(phen)₂(Me₂bipy)]³⁺ (see eqn (9)) during the oxidation of 2 by Ce⁴⁺ is consistent with the enhanced oxygen production by 2 in the presence of 4, as shown in Fig. 1.

$$[\text{Ru}(\text{phen})_2(\text{Me}_2\text{bipy})]^{3+} + [\text{Ru}^{IV} = \text{O}]^{2+} \rightarrow [\text{Ru}^{IV} = \text{O}]^{3+} + [\text{Ru}(\text{phen})_2(\text{Me}_2\text{bipy})]^{2+} \quad (9)$$

A ¹H NMR experiment was carried out on the mixture of 2–4 in D₂O–CD₃CN to further probe the processes occurring on addition of Ce⁴⁺ (Fig. 4). The characteristic C6 proton resonance of the bipy ligand, located between 9 to 10 ppm, is affected by the adjacent chlorido or aqua ligand in [Ru(terpy)(x(bipy)Cl)]⁺ or [Ru(terpy)(x(bipy)[OH₂])]²⁺. It is a useful tool to identify the presence of [Ru⁴⁺–Cl]⁻ or [Ru⁴⁺–OH₂]²⁻ species. As shown in Fig. 4, the C6 proton 9.45 ppm of 4 disappears on addition of Ce⁴⁺ to the mixture because of the formation of paramagnetic higher-valency ruthenium species. Over a period of 180 minutes, [Ru⁴⁺–OD₂]⁻ was clearly generated as indicated by the disappearance of the C6 proton signal.

The spectrum of the mixture before Ce⁴⁺ addition shows a proton resonance at 9.45 ppm, attributed to the C6 Me₂bipy proton adjacent to the chlorido ligand in [Ru(terpy)(Me₂bipy)Cl]⁺ (2). The proton resonance located nearby (9.4 ppm) is attributed to the corresponding C6 proton of Me₂bipy of the solvation.
product, [Ru(terpy)(Me₂bipy)(OD₂)]^{2+}. Integration of the two proton resonances reveals that the mixture contains approximately 90% [Ru(terpy)(Me₂bipy)Cl]^{2+} and 10% [Ru(terpy)(Me₂bipy)(OD₂)]^{2+}. Both proton resonances disappear following the addition of Ce⁴⁺. The spectrum measured at 180 minutes after the addition of Ce⁴⁺ shows the appearance of the C6 proton at 9.4 ppm, suggesting that the [Ru(terpy)(Me₂bipy)(OD₂)]^{2+} was regenerated but not [Ru(terpy)(Me₂bipy)Cl]^{2+}.

Although the stepwise processes (3) to (5) in the 2–4 mixture could not be identified from the UV-Visible spectral data, process (5) or the regeneration of [RuII–OH₂]^{2+} (or the deuterated forms) was evident from the time-course ¹H NMR data.

In order to investigate the kinetics of the reduction of [Ru(phen)₃(Me₂bipy)]^{3+} to the initial [Ru(phen)₃(Me₂bipy)]^{2+} state with respect to catalyst 1 and 2, the absorbance changes at 264 nm in 1–4 and 2–4 mixtures after Ce⁴⁺ addition were monitored. The UV-Visible spectrum of catalyst 2 before Ce⁴⁺ addition showed no absorption below 270 nm (Fig. 2), and thus the strong 264 nm band is more specific for [Ru(phen)₃(Me₂bipy)]^{2+} and was chosen for the kinetic evaluation. As can be seen from Fig. 5 (top panel), the absorbance changes at 264 nm reflecting the regeneration of [Ru(phen)₃(Me₂bipy)]^{2+} follow first-order exponential kinetics and the rate constants for the [Ru(phen)₃(Me₂bipy)]^{3+} to [Ru(phen)₃(Me₂bipy)]^{2+} reduction in the 2–4 and 1–4 combinations were 1.11 (±0.03) × 10⁻⁴ s⁻¹ and 5.2 (±0.2) × 10⁻⁴ s⁻¹, respectively (Fig. 5, bottom panel). The faster rate of reduction of [Ru(phen)₃(Me₂bipy)]^{3+} to [Ru(phen)₃(Me₂bipy)]^{2+} in the 2–4 combination in comparison to 1–4 suggests that the redox processes of 2 and 4 under Ce⁴⁺ activation may be inter-dependent, thus supporting the cooperative interaction given in eqn (9). In contrast to the ‘cooperative’ effect in the 2–4 mixture, 1 and 4 appear to consume Ce⁴⁺ independently, such that a ‘competitive’ effect leads to a slight decrease in the oxygen evolution performance of 1 (Fig. 1). Accordingly, in this case 4 merely reacts with some of the available Ce⁴⁺ but the [Ru(phen)₃(Me₂bipy)]^{3+} complex produced is not capable of oxidising the catalyst 1 from [Ru⁴⁺–O₂]⁰ to [Ru⁴⁺–O]⁰ state.

The cyclic voltammograms of 1, 2, 3 and 4 as individual complexes and in mixtures were measured in CH₃CN–0.1 M HClO₄ (1 : 6) at the concentration 0.48 mM and the data are presented in Fig. 6, 7 and Table 1. The Ru⁴⁺/Ru³⁺ oxidation potentials (Eₚa vs. NHE) of 1 and 2 of 0.97 V and 0.93 V, respectively, lie within the range of those reported for closely-related complexes. The Ru⁴⁺/Ru³⁺ oxidation potentials (Eₚa vs. NHE) for 3 and 4 were observed at 1.37 V and 1.39 V, respectively. There were no significant differences in these potentials when measured as mixtures of complexes.

A close analysis of the cyclic voltammetry of the individual catalysts reveals a significant increase in current starting from 1.37 V (Fig. 6, bottom) in 2 which, as described in eqn (2) and (3), may be attributed to the formation of [Ru⁴⁺–O₂]²⁻ and [Ru⁴⁺–O]³⁻ leading to the onset of water oxidation. The redox waves of the [Ru⁴⁺–O₂]²⁻ and [Ru⁴⁺–O]³⁻ are generally not well-defined as they coincide with the onset of water oxidation. On the other hand, the cyclic voltammetry of 1 reveals that the oxidation processes occurs at much higher potential (1.55 V). The predicted [Ru⁴⁺–O₂]²⁻ and [Ru⁴⁺–O]³⁻ species that are accessible at a reasonably lower potential in 2 may be ‘switched on’ by both redox mediators 3 and 4 as the Ru⁴⁺/Ru³⁺ potentials of the two complexes occur in the same range. In contrast, this may be more difficult for catalyst 1 because the higher potential results in a slight increase in the reaction driving force. This postulate is consistent with both the oxygen evolution and the UV-Visible spectrophotometric data presented earlier.

The significant difference in the oxygen evolution performance of 2 in the presence of 3 and 4 is interesting (Fig. 1), and worthy of further comment. From the electrochemistry point of view, although the anodic potentials (Eₚa) of both 3 and 4 are identical, the cathodic potential (Eₚc) of 4 was significantly lower (see Table 1). When compared with [Ru(bipy)]³⁻, it is feasible that the [Ru(phen)₃(Me₂bipy)]²⁻/³⁻ redox process in the acidified, and predominantly aqueous, solution may be accompanied by structural changes that lead to electro-
acceleration of the oxidation of [RuIV\textsuperscript{2+}] by [Ru(phen)\textsubscript{2}(Me\textsubscript{2}bipy)]\textsuperscript{3+} (eqn (9)), we tentatively propose that this may be due to a greater thermodynamic stability of [Ru(phen)\textsubscript{2}(Me\textsubscript{2}bipy)]\textsuperscript{3+} compared with [Ru(bipy)]\textsuperscript{3+} to [Ru(bipy)]\textsuperscript{2+}, and a concomitantly faster oxidation of RuIV to RuV oxidations leading to the onset of water oxidation.

The proposed mechanism for the homogenous catalysis by the recently-reported dinuclear complex [(bipy)\textsubscript{2}Ru(4-Mebpy-bimpy)Ru(terpy)(OH\textsubscript{2})\textsuperscript{4+}, referred to as [Ru\textsubscript{a}\textsuperscript{II}–Ru\textsubscript{b}\textsuperscript{II}–OH\textsubscript{2}]\textsuperscript{3+}, followed by Ce\textsuperscript{4+} (eqn (10)), an intra-molecular electron transfer between the two ruthenium centres leads to a redox equilibrium described in eqn (11).\textsuperscript{10} Further reactions (eqn (12)–(14)) follow what was described earlier in eqn (4), (6) and (7).

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\begin{align*}
[\text{Ru}_a\textsuperscript{II}–\text{Ru}_b\textsuperscript{II}–\text{OH}_2]^{3+} + 3\text{Ce}^{4+} & \rightarrow [\text{Ru}_a\textsuperscript{III}–\text{Ru}_b\textsuperscript{IV}–\text{OH}_2]^{2+} + 3\text{Ce}^{3+} + 2\text{H}^{+} \\
\text{Ru}_a\textsuperscript{II}–\text{Ru}_b\textsuperscript{V}–\text{OH}_2]^{5+} + \text{H}_2\text{O} & \rightarrow [\text{Ru}_a\textsuperscript{II}–\text{Ru}_b\textsuperscript{III}(\text{OOH})]^{4+} + \text{H}^{+}
\end{align*}
\]
Experimental section

Materials and synthesis

[Ru(bipy)$_2$Cl$_2$] and (NH$_4$)$_2$[Ce(NO$_3$)$_6$] were purchased from Sigma Aldrich and used as received. All other chemicals were sourced from commercial suppliers and used without further purification except where otherwise indicated.

The synthesis and characterisation of the two precursors [Ru(terpy)Cl$_3$] and [Ru(phen)$_2$Cl$_2$]$_{16,17}$ and the [Ru(phen)$_2$(Me$_2$bipy)]Cl$_2$$_{][12}$ [Ru(terpy)(Me$_2$bipy)Cl]Cl and [Ru(terpy)(bipy)Cl]Cl complexes$^{13}$ have been reported previously and the same methods were used in the present work. In a typical synthesis, solid [Ru(terpy)Cl$_3$] (0.20 g, 0.45 mmol) and appropriate amounts of the ligands (0.084 g, 0.45 mmol for Me$_2$bpy and 0.071 g, 0.38 mmol for bipy) were refluxed in EtOH-H$_2$O (4 : 1 ; 40 ml) for 4 h. After cooling, the solvent mixture was evaporated to dryness. The crude product was dissolved in methanol and loaded onto a Sephadex LH-20 exclusion column and the pure compounds were separated from the impurities using methanol as the eluent.

Yield of [Ru(terpy)(Me$_2$bipy)Cl]Cl 0.16 g (60%). To prepare [Ru(phen)$_2$(Me$_2$bipy)][Cl$_5$, [Ru(phen)$_2$Cl]$_2$ (0.20 g, 0.38 mmol) and Me$_2$bipy (0.069 g, 0.38 mmol) were refluxed in EtOH-H$_2$O (1 : 1, 30 ml) for 6 h, after which the bright orange solution was evaporated to dryness and loaded onto a Sephadex LH-20 column. The pure [Ru(phen)$_2$(Me$_2$bipy)]Cl$_2$ compound was separated from the impurities using methanol as the eluent. The yield was 0.24 g (90%).

The $^{1}$H NMR data of the compounds were consistent with those reported in the literature.$^{12,13}$

Methods

Oxygen evolution

Oxygen measurements were performed using a Unisense OXY-500 microsensor connected to a Unisense OXY Meter. The sensor was calibrated using air and argon for 100% O$_2$ and 0% O$_2$, respectively. The signal was processed using Sensor Trace software. To measure oxygen evolution by the individual complexes and the mixtures (1 : 1 complex to redox mediator), each complex and redox mediator (0.51 μmol) was suspended in 0.1 M HClO$_4$ (6 ml) in an air-tight vessel. Argon was then purged to obtain zero oxygen reading. A solution of (NH$_4$)$_2$[Ce(NO$_3$)$_6$] (0.28 g, 0.51 mmol) in 0.1 M HClO$_4$ (1 ml) was charged through a septum after the reading had stabilised for 20 min. The final concentrations of the complexes and the Ce$^{4+}$ in the vessel were 73 µM and 0.073 M, respectively. The oxygen sensor was measured in the headspace and the signal was collected for 6 to 10 h.

UV-Visible spectrophotometry

UV-Visible spectra were recorded on a Varian Cary 300 spectrophotometer. To measure the spectra of either individual complexes or the mixture of complexes, each compound (0.51 μmol) was dissolved in distilled water (0.5 ml) and 0.1 M HClO$_4$ (6.5 ml) was then added. A 1 ml aliquot was taken from

Conclusions

This study has provided evidence of the enhancement of the water oxidation catalytic properties of 2 under the influence of the redox mediator 4, [Ru(phen)$_2$(Me$_2$bipy)]$^{3+}$. The ability of 4 to accelerate the critical oxidation of the catalyst, [Ru$^{IV}$$\equiv=O$]$^{2+}$ → [Ru$^{V}$]=$^{3+}$, may be due in part to the slightly better potential match between the two redox events when compared to [Ru(bipy)$_2$Cl]$^{3+}$ (3). Work is currently underway to further probe such electron transfer processes using ruthenium catalysts and mediators appropriate for immobilisation on electrode surfaces. This accessibility of the electron transfer between the redox mediator (dye) and the catalyst is significant for the design of catalytic assemblies for the photo-induced oxidation of water. For example, mediator-catalyst assemblies can be attached to, for example, dyed-titania semiconductor films to construct photoanodes capable of splitting water with visible light.$^{15}$

In keeping with this study, an (inter-molecular) electron transfer between [Ru(phen)$_2$(Me$_2$bipy)]$^{3+}$ in 4 and [Ru$^{IV}$$\equiv=O$]$^{2+}$ in 2 was demonstrated in the present study suggesting a similar mechanism of the cooperative effect proposed in Fig. 8.

$[\text{Ru}^{II} \rightarrow \text{Ru}^{III} (\text{OOH})]^4+ + \text{Ce}^{4+} \rightarrow [\text{Ru}^{II} - \text{Ru}^{IV} (\text{O}_2)]^4+ + \text{Ce}^{5+} + \text{H}^+ \quad (13)$

$[\text{Ru}^{II} \rightarrow \text{Ru}^0 (\text{O}_2)]^4+ + \text{H}_2\text{O} \rightarrow [\text{Ru}^{II} - \text{Ru}^{III} - \text{OH}_2]^4+ + \text{O}_2 \quad (14)$

Fig. 8. (Top) Proposed mechanism of the mediator/catalyst cooperative effect observed in the 2–4 mixture.$^9,10$ The catalytic mechanism involving only Ce$^{4+}$ is given in the bottom diagram.$^8$ The green colour indicates the catalyst and the red indicates the redox mediator.
this stock into a 1 cm path length cuvette and 1.95 ml of 0.1 M HClO₄ was added. The initial spectrum was recorded prior to adding 0.05 ml [NH₄]₂[Ce(NO₃)₆] in 0.1 M HClO₄. The concentration of the complex and [NH₄]₂[Ce(NO₃)₆] in the cuvette were 24 µM and 97 µM, respectively. The spectra were then recorded in 2, 5, 10 and 15 min intervals for 15 h.

°F NMR experiment

°¹H NMR experiments were performed on a Bruker Avance 400 MHz. Solid [Ru(terpy)(Me₂bipy)Cl]Cl (2.0 mg, 3.4 mol) and [Ru(phen)(Me₂bipy)Cl]₂ (2.4 mg, 3.4 µmol) were dissolved in CD₃CN (0.2 ml) in an NMR tube and was topped up by 0.1 M HClO₄ in D₂O (0.6 ml). The concentration of each complex was 4.22 mM. The initial spectrum was recorded prior to adding the solid (NH₄)₂[Ce(NO₃)₆] (7.4 mg, 14 mol). The spectrum was then recorded every 10 min for the first 30 min then every 30 min for additional 2.5 h.

Electrochemistry

Electrochemical measurements were performed on a VSP Biologic potentiostat connected to a three-electrode system. Cyclic voltammetry of the individual complexes and the mixtures were measured in CH₃CN (0.2 ml) in an NMR tube and was topped up by 0.1 M HClO₄ (1 : 6) at the scan rate 50 mV s⁻¹ on a glassy carbon working electrode. A platinum wire was used as an auxiliary electrode and Ag/AgCl electrode was used as the reference. The concentration of each complex in all cases was 0.48 mM. The observed potentials were corrected relative to NHE.

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Notes and references


