Molecular catalytic system for efficient water splitting

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Chapter 1

Introduction to Molecular Complexes for Catalytic Water Splitting

ABSTRACT

During the last few decades, the scientific community has been striving hard to develop new and alternative sources for renewable energy and fuel. Hydrogen or carbon neutral fuels obtained from catalytic water splitting using sunlight offer an attractive solution for a cleaner and greener future. In this pursuit, to establish a simple and superior catalytic system for efficient water oxidation is considered to be a bottleneck, hampering the design, implementation and exploitation of electrochemical and photo-electrochemical devices for light driven energy conversion into hydrogen or low carbon based storable fuels. From metal oxides to composite materials, noble metal complexes to transition metal organometallics, multinuclear to mono site catalysts, various water oxidation complexes (WOC) have been investigated both in a homogeneous environment and on surfaces in photo- or electrochemical conditions. However, a true catalytic system for efficient water splitting, operating with four consecutive proton coupled electron transfer (PCET) steps to generate oxygen and hydrogen with high turnover number (TON) and frequency (TOF) is yet to be achieved. In this introductory chapter an overview is presented for molecular complexes that have been investigated for water oxidation catalysis in homogeneous solution using chemical oxidants, or as heterogeneous species in catalytic electrochemical systems.

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1.1. BACKGROUND

Renewable energy in connection with global environmental change has become an increasingly vital and burning subject, both in political communities and in science, in recent years [1-4]. Growth of the global population and the world economy is expected to double the world's power consumption by 2050 from the present demand of 13 TW [5-7]. On the other hand, the current level of CO_2, a green house gas, has exceeded 387 ppm due to increase in the combustion of carbon based fossil fuels in automobiles and power generation systems [8-10]. Petroleum, coal and natural gas are the primary energy carriers, while at the same time they are the principle sources of CO_2 emissions into the atmosphere [9,11].

Normally, electrons and protons are required to make renewable fuels and they can be obtained from oxidation of water, which is the one and only truly plentiful and attractive candidate to be used as a raw material. Therefore, the best possibility is to utilize abundant solar energy for the production of hydrogen and oxygen from catalytic water splitting [12-14]. At present, there is no efficient system available that makes use of solar energy effectively to produce hydrogen from water catalysis [15-18]. The most intricate task is to develop an easy accessible oxidation catalyst from earth abundant materials that is capable of multielectron water splitting and dioxygen generation at tremendous rate and activity [19,20].

Photosynthesis offers an excellent model for designing an artificial solar energy conversion system for clean fuel generation, where a tetra manganese oxygen evolving complex (OEC) is involved in the process of four electron water oxidation to generate dioxygen and release of four protons in a four step consecutive proton coupled electron transfer cycle. The overall four electron water oxidation reaction is given in Eq. (1):

$$2H_2O_{(l)} \rightarrow 4e^- + 4H^+_{(aq)} + O_{2(g)} \quad (1)$$

Electrons are provided to the reaction center of the photosystem II (PS-II) and ultimately appear as reduced carbon derived products by this process, which is the origin of all biological activities [21]. Thermodynamically, the overall free energy change for the four steps in the tetraelectron water splitting process amounts to 4.92 eV, and the ideal catalyst would exhibit a Gibbs free energy change (ΔG) of 1.23 eV for each step [22]. Assuming the water as the zero point of the energy scale, the Gibbs energies for HO*, O*, and HOO* intermediates (where * represents the catalytic site) generated during ideal catalysis, would be 1.23 eV, 2.46 eV, and 3.69 eV respectively [22,23].

In acidic medium in contact with the catalytic site, the water oxidation proceeds according to the following mechanism (Eqs. 1.1-1.4):

$$2H_2O_{(l)} + [Cat\text{-}(OH_2)]^{2+} \rightarrow [Cat\text{-}(OH)]^{2+} + 2H_2O_{(l)} + H^+ + e^- \quad (1.1)$$

$$\rightarrow [Cat(=O)]^{2+} + 2H_2O_{(l)} + 2(H^+ + e^-) \quad (1.2)$$

$$\rightarrow [Cat\text{-}(OOH)]^{2+} + H_2O_{(l)} + 3(H^+ + e^-) \quad (1.3)$$

$$\rightarrow [Cat\text{-}(OO)]^{2+} + H_2O_{(l)} + 4(H^+ + e^-) \rightarrow [Cat\text{-}(OH_2)]^{2+} + O_{2(g)} + 4(H^+ + e^-) \quad (1.4)$$

Variation of the pH changes the chemical potential of the protons at the catalytic site, and in an alkaline environment the reaction proceeds according to following pathway (Eqs. 1.5-1.8):

$$4OH^- + [Cat\text{-}(OH_2)]^{2+} \rightarrow [Cat\text{-}(OH)]^{2+} + H_2O_{(l)} + 3OH^- + e^- \quad (1.5)$$

$$\rightarrow [Cat(=O)]^{2+} + 2H_2O_{(l)} + 2OH^- + 2e^- \quad (1.6)$$

$$\rightarrow [Cat\text{-}(OOH)]^{2+} + 2H_2O_{(l)} + OH^- + 3e^- \quad (1.7)$$

$$\rightarrow [Cat\text{-}(OO)]^{2+} + 3H_2O_{(l)} + 4e^- \rightarrow [Cat\text{-}(OH_2)]^{2+} + O_{2(g)} + 2H_2O_{(l)} + 4e^- \quad (1.8)$$

A recent X-ray analysis of the photosystem-II has revealed some new structural features showing a water network around PS-II possibly involved in proton channeling from the manganese cluster to the reduction site [24]. Getting inspired from natural principles, there is a continuous effort to design an artificial

photosynthetic assembly based upon harnessing the solar energy and capable of utilizing it efficiently to generate oxygen and hydrogen for water splitting [25,26]. A major task is to establish an efficient and stable oxygen evolving catalyst that displays multielectron oxidation activity for hundred thousands of cycles [27]. There are many water splitting systems based on noble metal complexes, organometallics and inorganic metal oxide catalysts, but none of them have proven good overall efficiency for water splitting [28,29].

In this opening introductory chapter, the advent of molecular catalysts, both mono-site and multi nuclear organometallic complexes, is described, for water oxidation in homogeneous solution, as heterogeneous species using a chemical oxidant and in catalytic electrochemical systems on inert electrode surfaces.

1.2. MOLECULAR COMPLEXES FOR WATER SPLITTING

1.2.1. Early Evolution of Water Oxidation Complexes

The photosynthetic oxygen evolving complex is known to consist of a tetramanganese-oxo cluster active site that is responsible for efficient catalytic water splitting and rapid evolution of oxygen [30]. A number of structures of PS II has been reported, down to 2.9 A° resolution [31-33]. These structures have provided new information on the arrangement of protein subunits and cofactors, but the resolution is not sufficient to reveal the intimate details of the catalytic water splitting centre. The most detailed structure of the OEC of PS II reveals five oxygen atoms serving as oxo-bridges connecting five metal atoms (four Mn and one Ca) and four water molecules bound to the Mn_4CaO_5 cluster [24]. About 1300 water molecules were found in PS-II, providing extensive hydrogen-bonding networks that may serve as channels for protons, water or oxygen molecules.

The quest for a synthetic catalytic water oxidation system began in the 70's with photochemical studies on a di-μ-oxo bridged dinuclear manganese (Mn^{III}-Mn^{IV}) 2,2′-bipyridine (bpy) complex by M. Calvin (Fig. 1.1a), who was awarded

the Noble Prize in chemistry for the discovery of the Calvin-Benson Cycle, in 1961 [34].

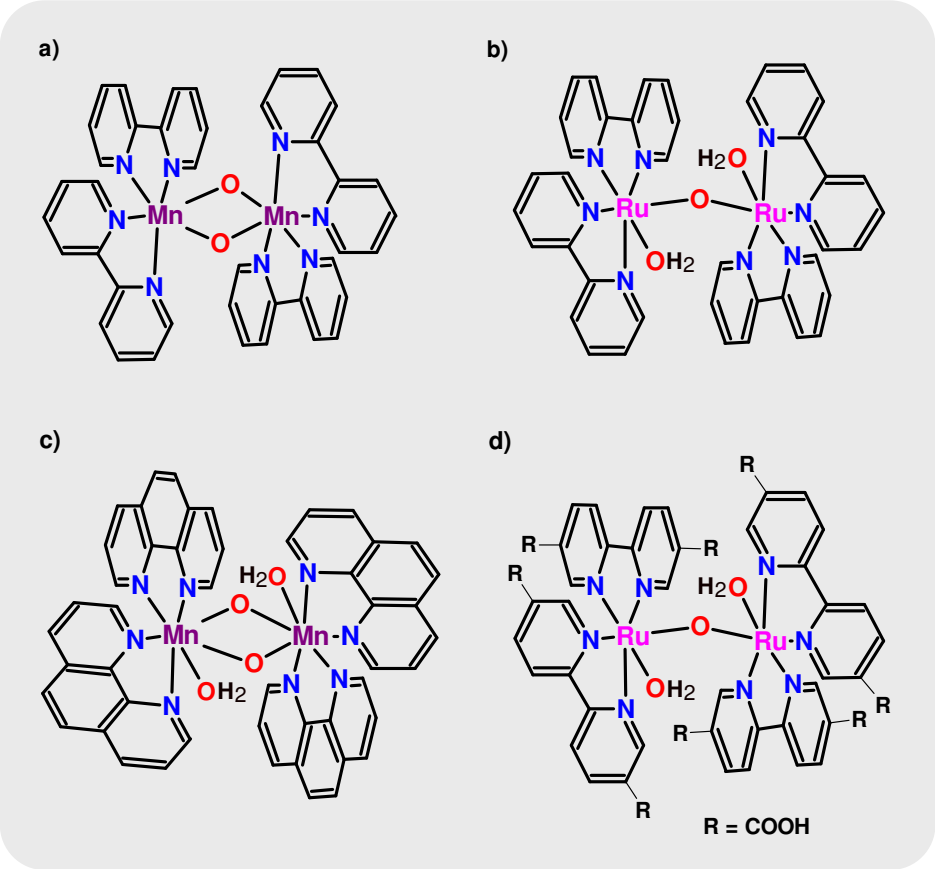


Figure 1.1. Molecular complexes that were proposed as water splitting catalysts at an early stage: **(a)** A binuclear bpy-manganese dimer $[(bpy)_2Mn^{III}(\mu\text{-}O\text{-})_2Mn^{IV}(bpy)_2]^{3+}$; **(b)** the blue dimer $[(bpy)_2Ru^{III}(\mu\text{-}O\text{-})\ Ru^{III}(bpy)_2]^{4+}$, (bpy = 2,2′-bipyridine); **(c)** a phenanthroline di-manganese complex $[(phen)_2Mn^{III}(\mu\text{-}O\text{-})_2Mn^{IV}(phen)_2]^{3+}$ (phen = 1,10-phenanthroline) and **(d)** the dicarboxy-bpy derived $[(R_2\text{-}bpy)_2Ru^{III}(\mu\text{-}O\text{-})Ru^{III}(R_2\text{-}bpy)_2]^{4+}$ binuclear ruthenium catalyst (R_2-bpy = 5,5′-dicarboxy-2,2′-bipyridine).

Later, it was realized that oxygen might have diffused from the atmosphere into the reaction vessel across the Teflon membrane and sensed by the oxygen electrode. As a result, the evidence of oxygen evolution by the manganese dimer complex, which was synthesized two years before as a novel antiferromagnetic

material, remained unclear [35,36]. This first effort was followed by the synthesis of a few dinuclear ruthenium and manganese based oxygen evolving complexes in the next decade (Fig. 1.1) with the same chemical composition of the dinitrogen ligands for the manganese and ruthenium catalysts [37].

1.2.2. Water Oxidation by Manganese Complexes

A well characterized synthetic tetra manganese complex, $Mn_4O_4L_6$ (L = diphenylphosphinate), with a Mn_4O_4 ($2Mn^{III}$, $2Mn^{IV}$) cubane-like core offered a new model of the active site of the photosynthetic water oxidation cluster [38]. It was followed by a synthetic di-terpyridine dimanganese complex, $[(terpy)(H_2O)Mn(\mu\text{-}O)_2Mn(terpy)(H_2O)]^{3+}$, the Mn-terpy dimer, (terpy = 2,2′:6′,2″-terpyridine), and was reported for homogeneous oxygen evolution (Fig. 1.2) in the presence of sodium hypochlorite [39,40]. The maximum turnover number of the di-terpyridine dimanganese complex for oxygen evolution was very low, and a TON=4 was determined in a solution containing sodium hypochlorite (NaClO) and using a one-electron Ce(IV) oxidant that ultimately led to the decomposition of the Mn dimer and the formation of permanganate ions after 6 hours of catalysis [39].

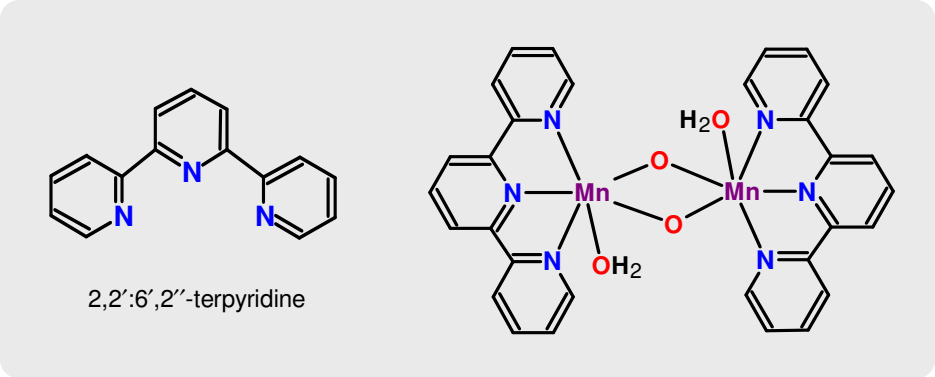


Figure 1.2. A 2,2′:6′,2″-terpyridine (terpy) derived di-μ-oxo di-terpy dimanganese diaqua water oxidation complex, $(terpy)(H_2O)Mn(\mu\text{-}O)_2Mn(terpy)(H_2O)]^{3+}$ (Mn-terpy dimer).

The water oxidation catalyzed by the Mn-terpy dimer complex in an aqueous phase using a Ce(IV) oxidant was also investigated by other groups, but no oxygen

evolution was observed [41,42]. The electrochemical oxidation of the Mn-terpy dimer leads to the formation of an inactive tetranuclear complex from the Mn^{IV}–Mn^{IV} state of the di-manganese catalyst, which confirms that it cannot act as a homogeneous catalyst for water oxidation [43]. Later, Yagi and Narita found that Mn-terpy dimer complexes in the presence of the Ce(IV) oxidant catalytically produce oxygen from water only when adsorbed on kaolin or mica [41]. The maximum TON's for oxygen evolution in heterogeneous conditions were 15-17, obtained in 4 days of continuous catalysis operation of the mica and kaolin adsorbed synthetic terpy-Mn-(μ-O)$_2$-Mn-terpy complex.

1.2.3. Ruthenium Based Water Oxidation Catalysts

A bi-ruthenium tetra aqua tetrakis-bipyridine $[(bpy)_2(H_2O)Ru^{III}(\mu\text{-}O)Ru^{III}(H_2O)(bpy)_2]^{4+}$ with a $Ru^{III}(\mu\text{-}O)Ru^{III}$ core, also known as blue dimer (Fig. 1.1b), is widely considered as the first genuine synthetic homogeneous water oxidation catalyst and was reported by Meyer's group in the early 1980s [44]. Its carboxylic acid substituted derivatives (Fig. 1.1d) are also found to be active for oxygen evolution [45,46]. The turnover frequency and TON's of the blue dimer were reported to be 4.2×10^{-3} per second [47] and 13.2 [48], respectively.

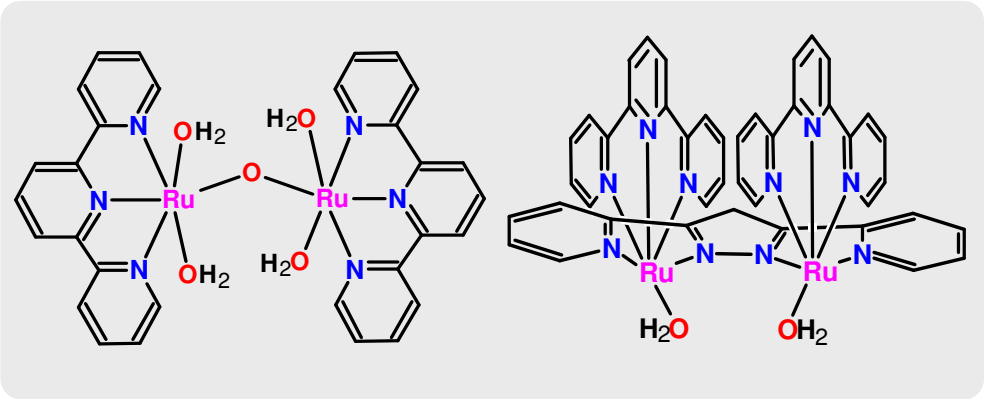


Figure 1.3. (left) A μ-oxo bridged di-terpyridine diruthenium complex, $[(terpy)(H_2O)Ru(\mu\text{-}O)Ru(terpy)(H_2O)]^{4+}$ (terpy = 2,2′:6′,2″-terpyridine) and **(right)** a di-terpyridine diruthenium complex with Hbpp bridging ligand $[Ru_2^{II}(bpp)(terpy)_2(H_2O)_2]^{3+}$, [(Hbpp = 2,2′-(1H-pyrazole-3,5-diyl)bis(pyridine)), for homogeneous water oxidation.

A tetra aqua Ru-terpy dimer $[(terpy)(H_2O)_2Ru(\mu\text{-}O)Ru(terpy)(H_2O)_2]^{4+}$ was synthesized and characterized for homogeneous water splitting in 1998 [49]. The structure was similar to that of the manganese analogue [39] except that it contained only one μ-oxo bridge between two ruthenium centers. Each metal center was ligated to two water molecules and the catalyst deactivated already after 1 turnover (Fig. 1.3). The first structurally and electrochemically well-characterized dinuclear Ru complex with a Hbpp type bridging mode, the terpy-Ru-bpp dimer $[Ru_2^{II}(bpp)(terpy)_2(H_2O)_2]^{3+}$ (Hbpp = 2,2′-(1H-pyrazole-3,5-diyl)bis(pyridine), instead of a Ru-O-Ru motif, was introduced by Llobet and co-workers (Fig. 1.3). Here two Ru metals were deliberately placed in close proximity using a double dinucleating ligand [50].

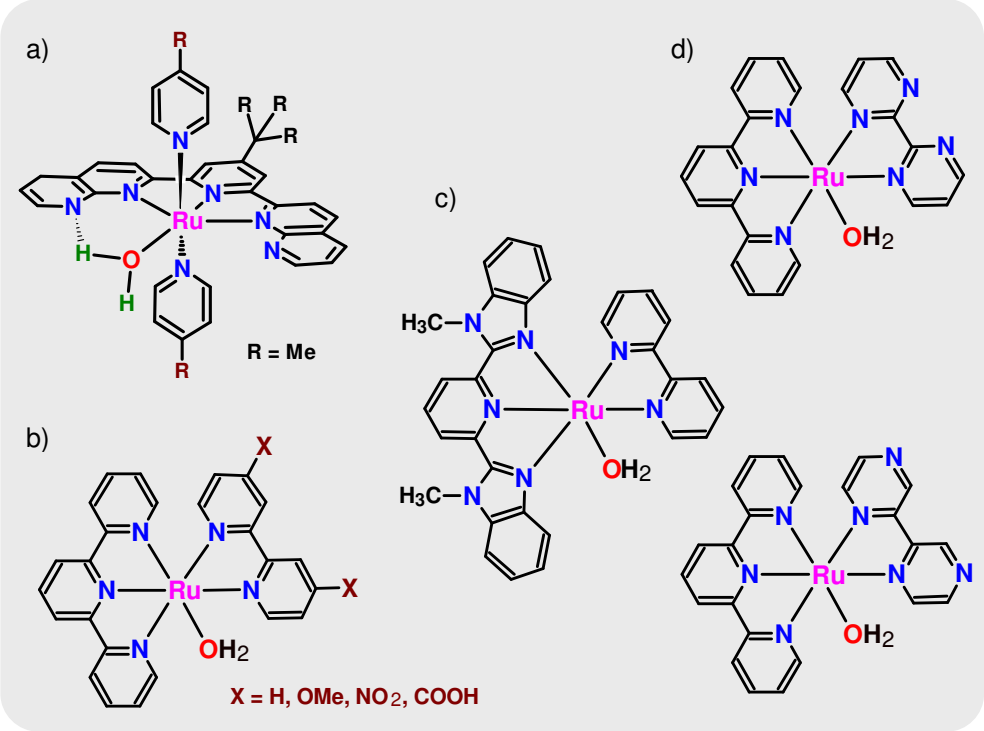


Figure 1.4. (a) A mono ruthenium 4-*tert*-Butyl-2,6-di([1′,8′]-naphthyrid-2′-yl)pyridine based complex introduced in 2005 followed by **(b)** terpy-Ru derived substituted bpy type single Ru catalysts; **(c)** replacement of the terpy ligand with a more bulky 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine (Mebimpy) ligand and **(d)** introduction of tetraaza bpm (2,2′-bipyrimidine) and bpz (2,2′-bipyrazine) type ligands to the Ru-terpy motifs [51-54].

The absence of the μ-oxo bridge in the terpy-Ru-bpp dimer avoids the decomposition and makes it more active than the blue dimer for homogeneous oxygen evolution. Thummel *et al.* introduced a new type of binuclear [51] and a variety of single site ruthenium derived water oxidation complexes [51,52]. A TON up to 600 was achieved in homogeneous solution using a chemical oxidant. In contrast, detailed mechanistic analyses of single-site catalysts with Ru-terpy containing 2,2′-bipyrimidine (bpm), 2,2′-bipyrazine (bpz) motifs [53] and with a 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine (Mebimpy) ligand instead of terpy [54] showed that the TON does not exceed 15 in solution phase catalysis (Fig. 1.4).

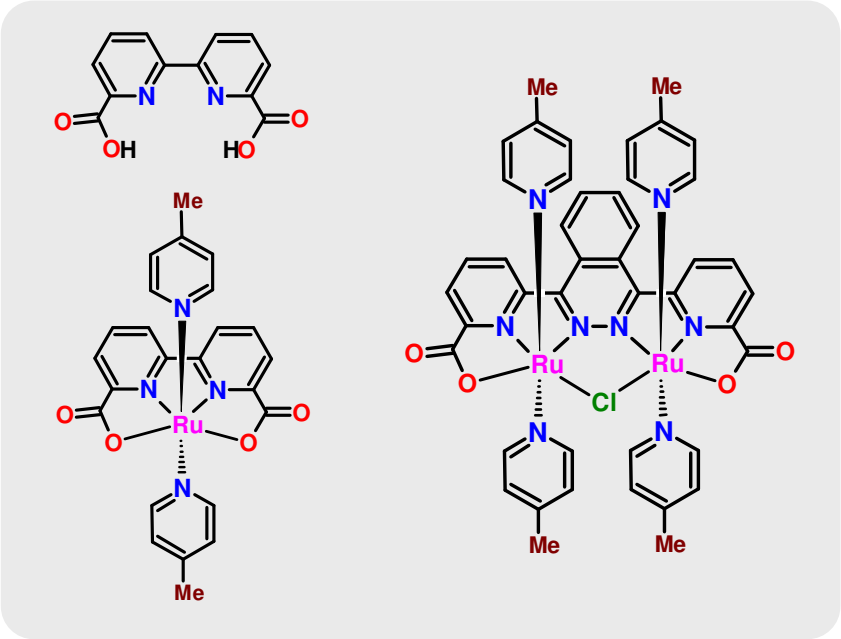


Figure 1.5. (left) A H_2dcabpy ligand derived mono site [(H_2dcabpy)Ru^{II}-(pic)] complex, (H_2dcabpy is 2,2′-bipyridine-6,6′-dicarboxylic acid; pic is 4-picoline) and **(right)** a dinucleating dicarboxylic modified ligand bis(capyptz) based dimeric ruthenium catalyst [bis(capyptz) = 1,4-bis(6′-COOH-pyrid-2′-yl)phthalazine)] [55,56].

Mono ruthenium complex with dicarboxylic acid substituted 2,2′-bpy and 1,10-phenanthroline (phen) ligands were recently studied using Ce(IV), and TON's up to 340 were obtained with TOF's of ~0.1 sec^{-1} [55]. The extended versions of the mono centre complex containing two ruthenium sites were also recently reported

for both chemical and light-driven water oxidation in homogeneous phase (Fig. 1.5). In the presence of an excess amount of Ce(IV), the dinuclear ruthenium complex bis(capyptz)-Ru_2-$(pic)_2$, [bis(capyptz) = 1,4-bis(6′-COOH-pyrid-2′-yl)phthalazine and pic is 4-picoline], produced 10,400 turnovers while generating approximately 20.7 µmol of molecular oxygen in 20 hours reaction time [56]. This is by far, the best TON obtained for a molecular ruthenium catalyst in homogeneous solution.

1.2.4. Iridium Complexes for Water Oxidation

A series of iridium organometallic complexes with general formula cis-$[Ir^{III}(L)_2(H_2O)_2]^+$, [L=2-(2-pyridyl)phenylate anion (2-ph-py)], and related ligands were reported to efficiently catalyze the water oxidation. Up to a TON of 2500 was obtained in the presence of Ce(IV) oxidant in acidic solution (pH <1), though the rate was lower than for the ruthenium analogues [57].

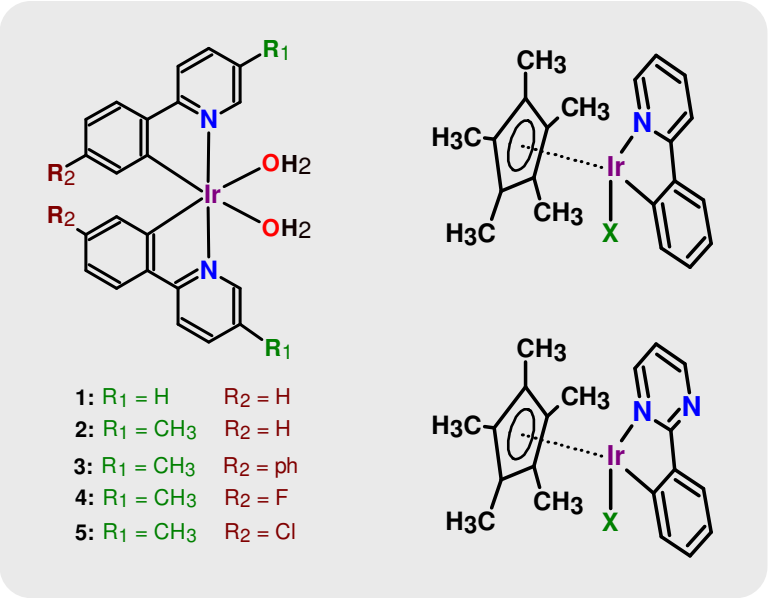


Figure 1.6. (left) Iridium derived $[Ir^{III}(L)_2(H_2O)_2]^+$ [L=2-(2-pyridyl)phenylate anion (2-ph-py)] water oxidation catalysts and **(right)** mono-site half sandwiched Cp*-iridium catalysts for homogeneous water oxidation (X = OTf or Cl).

Recently, Brudvig and Crabtree have prepared single site half sandwiched iridium complexes by combining relatively strong donating Cp* ligands (Cp* is pentamethylcyclopentadiene) with a 2-(2-pyridyl)phenylate type ligand (Fig. 1.6). With this new system, an oxygen generation rate of 0.9 sec^{-1} was achieved in the homogeneous phase [58]. In the next step the 2-ph-py type ligand was replaced with dinitrogen 2,2′-bipyridine, 2,2′-bipyrimidine and 1,10-phenanthroline ligands. To produce a catalytic complex the iridium centre was mono halogenated [59]. In such systems, the chloride at the metal catalytic site may get oxidized and OCl^{-5} or Cl_2 can be formed that may trigger O_2 evolution [58-61].

1.2.5. Other Molecular Oxygen Evolving Complexes

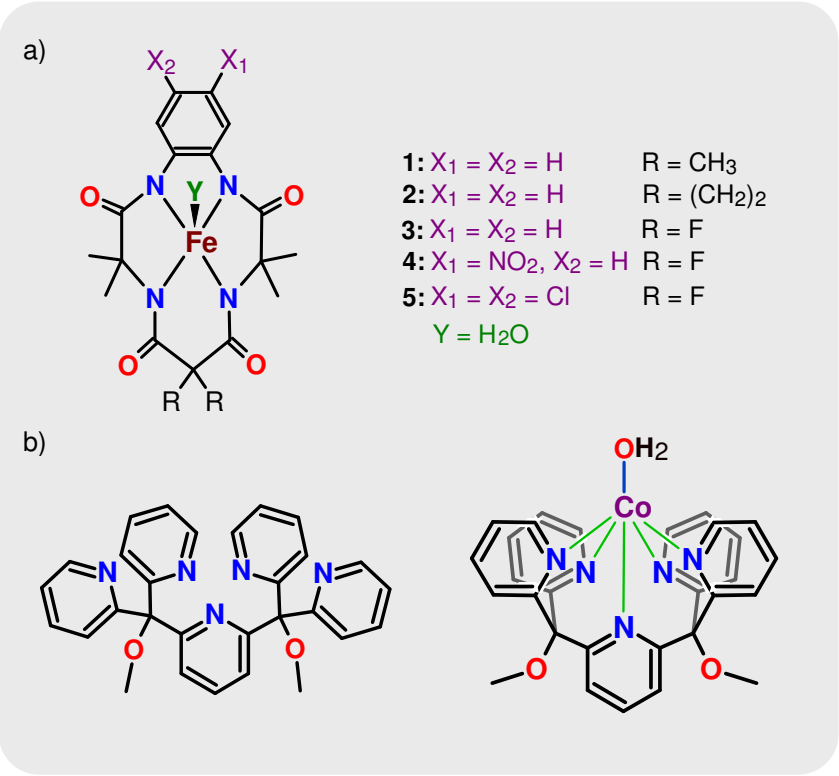


Figure. 1.7. A structural representation of **(a)** Fe^{III}-TAML (TAML = tetraamido macrocyclic ligand) derived complexes; **(b)** 2,6-(bis(bis-2-pyridyl)methoxy-methane)-pyridine (Py5) ligand and a mono cobalt-Py5 $[Co^{II}(Py5)(OH_2)]^{2+}$ complex.

Besides manganese, ruthenium and iridium derived molecular water splitting catalysts, other common transition metal based complexes have also been described that offer effective catalysis for oxygen generation in homogeneous systems [62]. A tetraamido macrocyclic ligand (TAML) based iron-centered complex Fe^{III}-TAML efficiently catalyzes the oxidative conversion of water to molecular oxygen in combination with ceric ammonium nitrate and reaches a turnover frequency of 1.3 per second [63]. A mono cobalt aqua complex with an oxidatively stable pentadentate Py5 ligand $[Co(Py5)(OH_2)](ClO_4)_2$, [Py5 = 2,6-(bis(bis-2-pyridyl)methoxy-methane)-pyridine], has shown catalytic activity for water oxidation in alkaline media (Fig. 1.7). Cyclic voltammetry analysis reveals that the mono cobalt system $[Co^{II}–OH_2]^{2+}$ proceeds by two consecutive PCET conversion steps, first into $[Co^{III}–OH]^{2+}/[Co^{II}–OH_2]^{2+}$ and then to $[Co^{IV}=O]^{2+}/[Co^{III}–OH]^{2+}$ redox couples. The mechanism of O-O bond formation was not yet resolved and is under investigation [64].

1.3. ELECTRO-ASSISTED CATALYTIC SYSTEMS FOR WATER SPLITTING

While there are many reports on solution phase homogeneous water oxidation catalysis, the number of studies involving surface electro-assisted water oxidation assemblies, which have applications in operational electrocatalytic or photo-electrocatalytic devices, is limited [54,65]. The first example of an electrode bound molecular complex appeared almost a decade ago, when a bis(ruthenium–hydroxo) complex, bearing a novel bridging type ligand, 1,8-bis(2,2′:6′,2″-terpyridyl)anthracene (btpyan), was employed in anodic water oxidation experiments (Fig. 1.8). The electrochemical investigation was conducted with the catalyst adsorbed on an indium-doped tin oxide (ITO) electrode at +1.7 V (vs. Ag/AgCl) in a pH=4 solution. More than 33,500 turnovers were obtained in 40 hours of electrolysis [66]. The initial current density was 0.12 mA/cm^2, which dropped significantly during the course of the experiment, indicating breakdown of the electrocatalytic complex [67]. More recently, a Ru(μ-O)Ru terpy dimer

modified with a phosphonate group for anchoring on oxide electrodes, $[(PO_3H_2\text{-terpy})(H_2O)_2Ru^{III}(\mu\text{-}O)Ru^{III}(H_2O)_2(PO_3H_2\text{-terpy})]^{4+}$, ($PO_3H_2$-terpy = 4′-phosphonato-2,2′:6′,2″-terpyridine), was synthesized for electrocatalytic studies of Ru-dimer-based water oxidation chemistry [49,68].

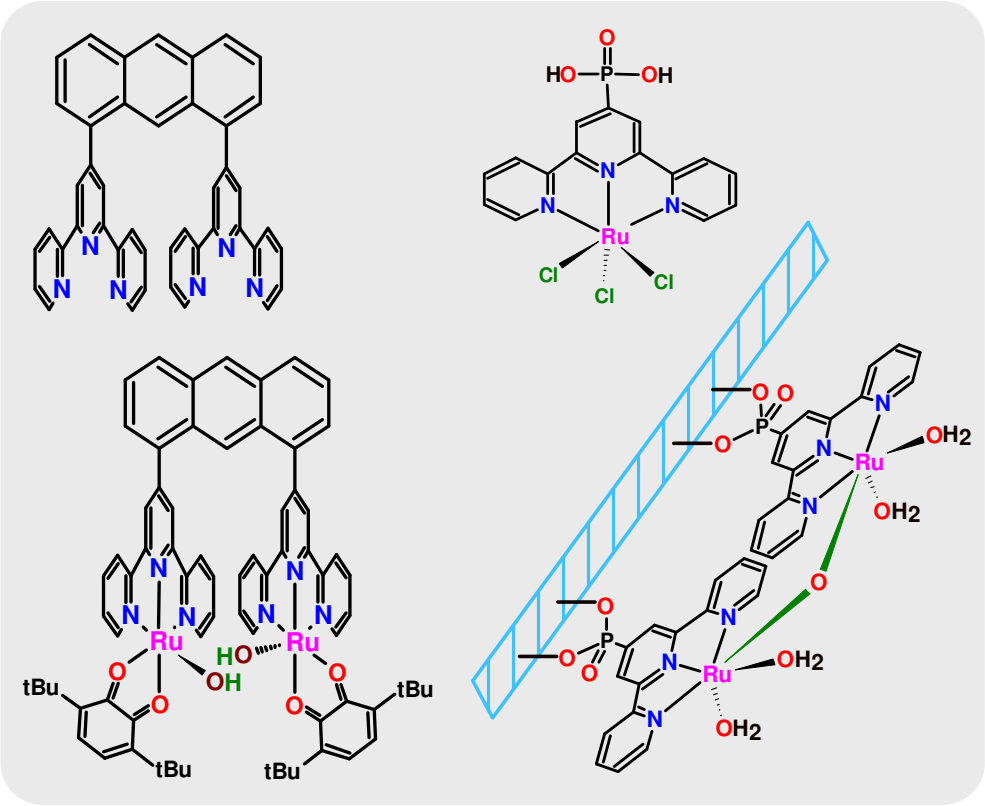


Figure 1.8. (left) A bis(ruthenium–hydroxo) complex, bearing a novel bridging type ligand 1,8-bis(2,2′:6′,2″-terpyridyl)anthracene (btpyan) and **(right)** a surface anchored Ru-terpy dimer $[(PO_3H_2\text{-terpy})(H_2O)_2Ru^{III}(\mu\text{-}O)Ru^{III}(H_2O)_2(PO_3H_2\text{-terpy})]^{4+}$ (PO_3H_2-terpy = 4′-phosphonato-2,2′:6′,2″-terpyridine) for electrocatalytic water oxidation.

The electrocatalytic water oxidation was carried out on catalyst modified ZrO_2 films on fluorine-doped tin oxide (FTO) at 1.5 or 1.25V (vs. Ag/AgCl) and a maximum TON of 3 was obtained with the complex in buffer solution at pH=6.

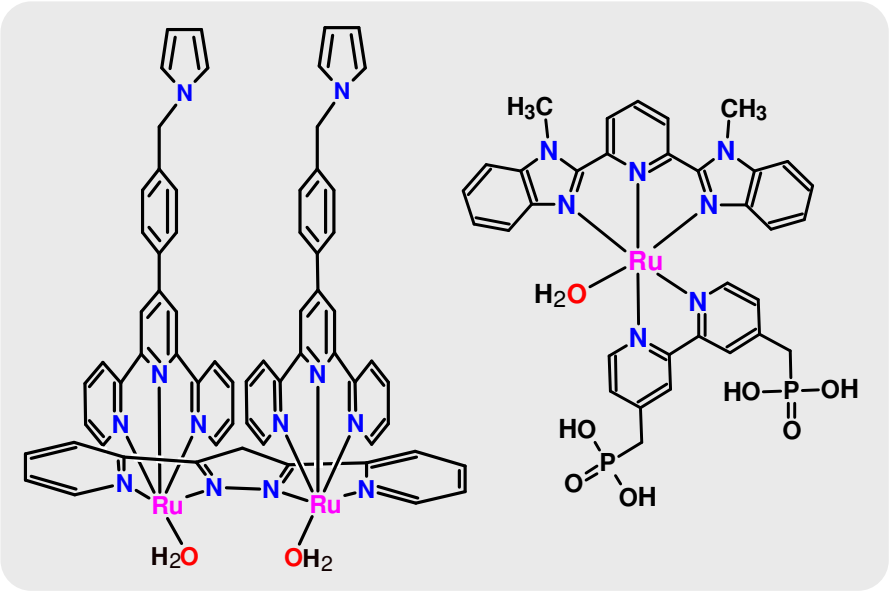


Figure 1.9. (left) A 4′-(para-pyrrolylmethylphenyl)-2,2′:6′,2″-terpyridine (t-terpy) based diruthenium complex with a Hbpp bridging ligand $[Ru_2^{II}(bpp)(t\text{-}terpy)_2(H_2O)_2]^{3+}$,(Hbpp = 2,2′-(1H-pyrazole-3,5-diyl)bis(pyridine), and **(right)** a mono site 2,6-bis(1-methylbenzimidazol-2-yl)-Pyridine (Mebimpy) ligand derived ruthenium complex for electrochemical water oxidation.

Meanwhile, Llobet and co-workers also extended their Hbpp-Ru terpy dimer with an electropolymerizable alkyl pyrrole linker to make a 4′-(para-pyrrolylmethylphenyl)-2,2′:6′,2″-terpyridine (t-terpy) based catalyst for electrochemical water oxidation (Fig. 1.9). The system was relatively efficient, with TON's exceeding 120 at 1.17 V potential (vs. Ag/AgCl) in 0.1 M aqueous triflic acid solution [69]. The extension of the Ru-bpy complex with a 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine ligand was undertaken with the introduction of a 4,4′-dialkyl phosphonate (4,4′-$(H_2O_3PCH_2)_2$-bpy) as a catalytic linker to the 2,2′-bipyridine ligand (Fig. 1.9). Electrochemical water oxidation was detected at 1.85 V (vs. NHE) in pH=5 buffer. Very low turnover rate 0.004 sec^{-1} was observed, with a correspondingly low oxygen yield of 6.5 μmol during 30,000 seconds of the electrolysis run [54].

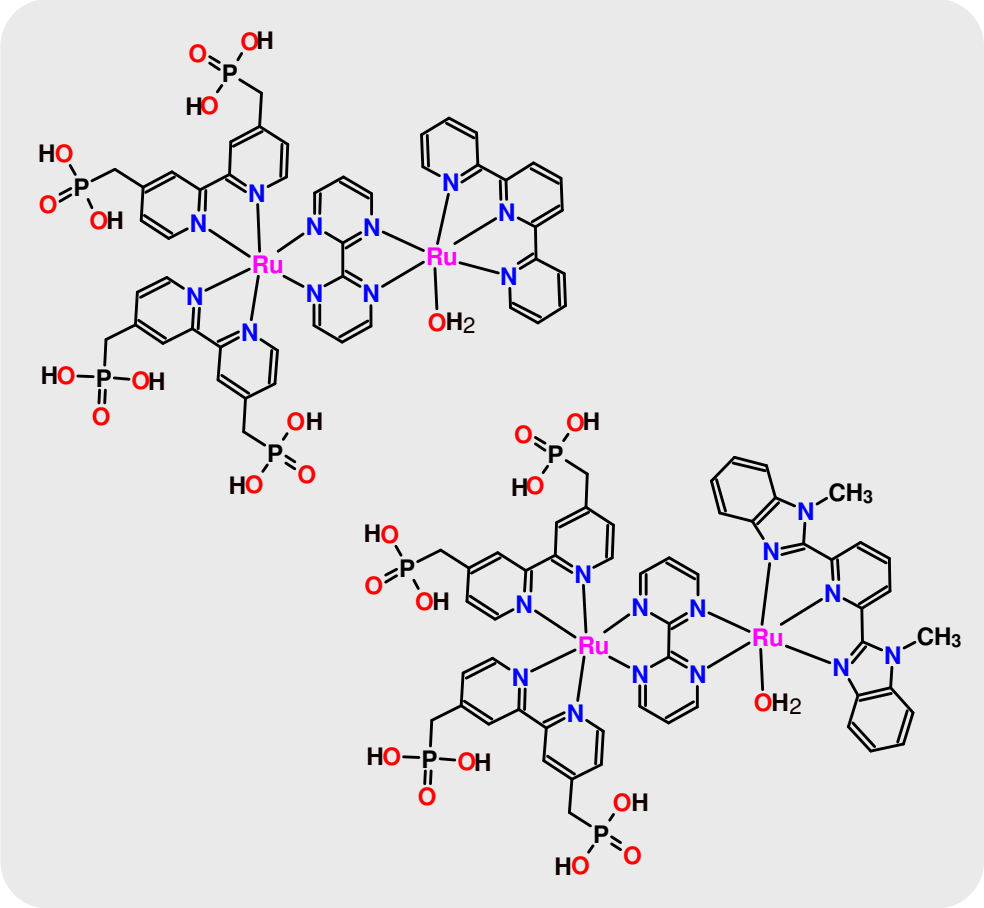


Figure 1.10. A 4,4′-$(H_2O_3PCH_2)_2$-bpy with Ru-tris-bpy type redox mediator modified **(left)** [(bpm)Ru^{II}(terpy)-(OH_2)] complex and **(right)** a [(bpm)Ru^{II}(Mebimpy)-(OH_2)] catalysts for the electrochemical water oxidation [70].

The incorporation of the 4,4′-$(H_2O_3PCH_2)_2$-bpy linker modified Ru-tris-bpy type redox mediator enhances the efficiency of the [(bpm)Ru^{II}(terpy)-(OH_2)] and [(bpm)Ru^{II}(Mebimpy)-(OH_2)] catalytic sites towards water oxidation (Fig. 1.10). In acidic medium at *ca*. 1.80 V (vs. NHE), 28000 turnovers were obtained for the [{4,4′-$(H_2O_3PCH_2)_2$-bpy}$_2$(bpm)Ru^{II}(Mebimpy)-(OH_2)]$^{4+}$ complex on ITO in 1.0 M aqueous $HClO_4$ at turnover rates of 0.6 sec^{-1} with very low current density >50 μA/cm^2 [70]. Very recently, a Cp*-Ir aqua or hydroxo catalyst (blue layer) was generated by anodic deposition in aqueous solution showing current densities up to

1.4 mA/cm^2 at ~1.4 V (vs. NHE) for water oxidation in 0.1M KNO_3 (pH=6) electrolyte solution [71]. This work suggested that organometallic species may be employed as useful precursors in electro-deposition of inorganic heterogeneous catalysts on a fluorine-doped tin oxide electrode for water oxidation. Scanning electron microscopic (SEM) analysis reveals that the thickness of such electrodeposited films is between 1 and 2 μm, and the formation of oxides of iridium on the electrode during electro-deposition and the water oxidation cycle cannot be excluded and requires further experimentation.

1.4. MECHANISM OF WATER OXIDATION

1.4.1. Natural Photosynthesis

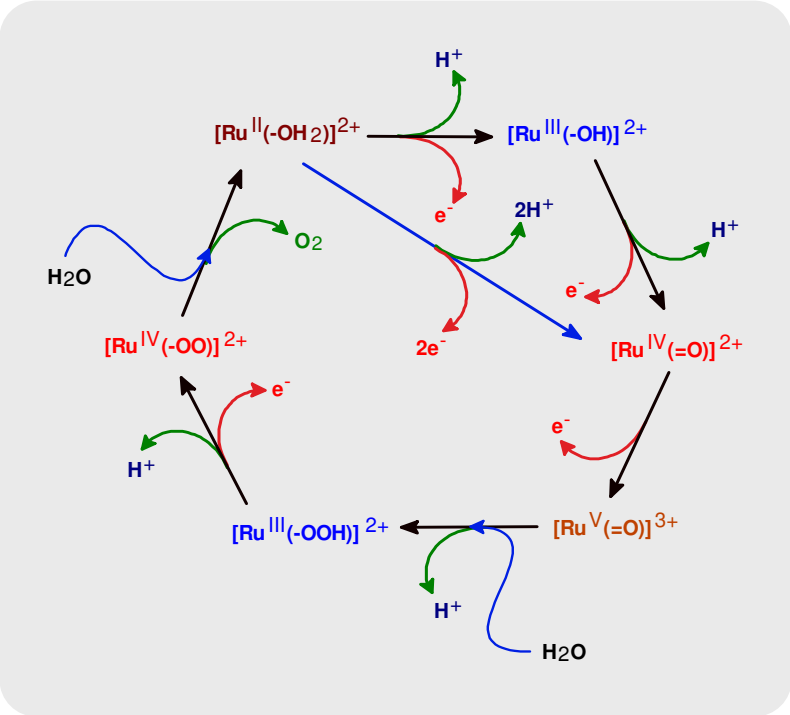
The formation of molecular oxygen in natural photosynthesis is realized by the extraction of four electrons and protons in a four-step proton coupled electron transfer regime from two water molecules at the Mn_4CaO_5 cluster embedded in the photosystem-II [72,73]. Before the oxygen is released, a stepwise increase of the oxidation state of the Mn^{n+} ions permits the accumulation and confinement of the required four oxidizing equivalents. There is no evidence for partial oxidation of water at an early stage in the reaction cycle [74-76]. The consecutive PCET steps enable the accumulation of four redox equivalents while avoiding high energy intermediates during the multi-electron water oxidation cycle [77,78]. Hence the PCET mechanism at the Mn-cluster in the PS-II is a key element for separating electrons and protons from water to produce oxygen with a low overpotential at a high rate for hundred thousands of cycles [78-80].

1.4.2. Artificial Oxygen Evolving Complexes

For mononuclear water oxidation catalysts the oxygen evolution activity is thought to be constrained by a minimum overpotential of ~0.4 V due to a fixed difference of 3.2±0.1 eV in the affinity between the HOO* and the HO* intermediates [22,72]. While many artificial water oxidation catalysts have been scrutinized for

dioxygen generation, detailed mechanistic insight into the reaction mechanisms is still lacking [81-83].

Scheme 1.1. Catalytic water oxidation pathway and dioxygen evolution mechanism by mono nuclear [(terpy)-Ru-(bpm)], [(terpy)-Ru-{$(H_2O_3PCH_2)_2$-bpy}] and [(Mebimpy) -Ru-{$(H_2O_3PCH_2)_2$-bpy}] complexes [54,89]. [terpy = 2,2′:6′,2″-terpyridine, bpm = 2,2′-bipyrimidine, $H_2O_3PCH_2)_2$-bpy = 4,4′-$(H_2O_3PCH_2)_2$-2,2′-bipyridine and Mebimpy = 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine].



For example, several manganese complexes have been described but the mechanism of O-O bond formation is not yet clear [84-86]. In binuclear ruthenium systems the formation of oxygen is realized either by intramolecular O-O bond formation through oxo-oxo coupling at two catalytic sites without HOO* generation, which is prone to catalytic deactivation after a few cycles [87], or by nucleophilic OH_2 attack, generating a higher energy HOO* intermediate in a non-PCET step [88]. Recently reported mono-site ruthenium catalysts are not able to operate along a four step PCET reaction coordinate [18]. The HOO* intermediate

is formed at high overpotential from $[Ru^{V}=O]^{3+}$ type complex (Scheme 1.1) that is generated by an electron removal from $[Ru^{IV}=O]^{2+}$ in a non-PCET rate limiting step [54,89]. Moreover, in the few reports on iridium derived complexes for homogeneous water oxidation catalysis only speculative oxygen formation pathways have been put forward due to lack of experimental evidence, and more investigation is needed to provide insight into the mechanisms of operation [59,90].

1.5. CURRENT SCENARIO AND CHALLENGES

Catalytic water splitting offers an attractive potential solution for the production of environmentally clean energy carriers obtained from renewable materials and abundant solar energy [91,92]. Synthesis and design of complex water oxidation structures, and implementation in a stable four-electron transfer catalytic system, running at high catalytic turnover number and frequency for oxygen evolution, with low activation barrier, moderate overpotential and high current density, remain major challenges in this field [92-95]. A key issue is to devise a molecular complex that exhibits a consecutive proton coupled electron transfer regime during the multi-electron water oxidation cycle. It should be able to efficiently separate electrons and protons from water to produce oxygen with a high rate and sustain production for many hundred thousands of catalytic cycles [94-97]. In addition, the available immobilized oxygen evolving assemblies perform the water oxidation at high overpotential with very small current densities. This hampers their exploitation in electrolysis assemblies and photocatalytic devices for fuel generation [98,99].

1.6. AIM AND STRUCTURE OF THIS THESIS

The aim of this dissertation is to construct and explore artificial oxygen evolving complexes that are synthetically accessible, stable, functionally robust and efficient. To achieve this, a class of mono metal water splitting catalysts is introduced in this manuscript and exploitation of these complexes in homogeneous catalysis and in electrochemical studies with surface immobilized catalyst assemblies has been discussed. The catalysts are comprised of a single centre ruthenium or iridium metal core coordinated to a dinitrogen ligand and stabilized by a cyclic conjugated hydrocarbon (Figs. 1.11-1.13). Homogeneous catalytic water oxidation is performed with a chemical oxidant as catalyst activator. For electro-assisted experiments, the catalyst complexes are functionalized with carboxylic or phosphonic acid linker units on the dinitrogen ligand that serve as anchoring sites for deposition on conducting oxide electrodes.

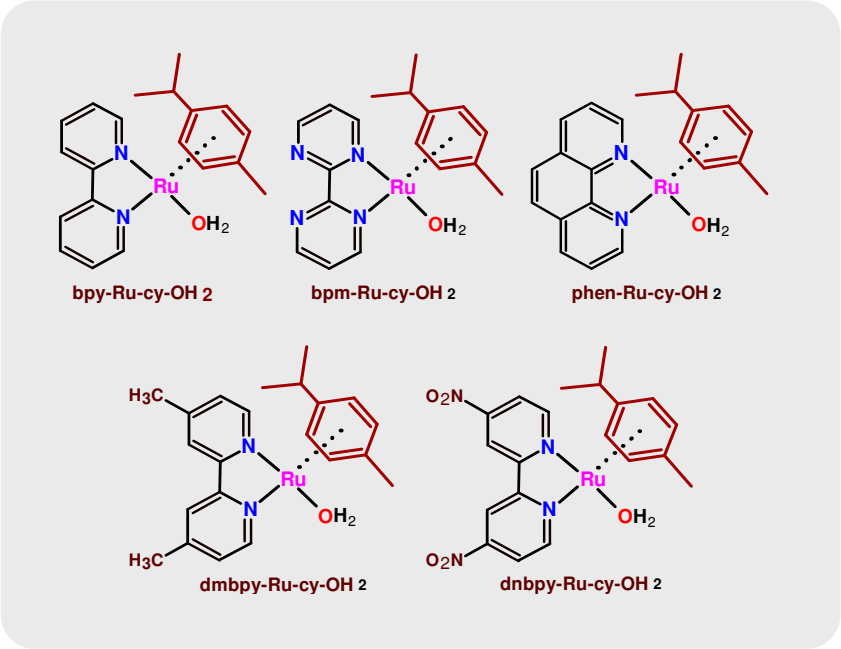


Figure 1.11. Ruthenium *p*-cymene (cy) derived simple and 4,4′-disubstituted-2,2′-bipyridine, 1,10-phenanthroline and 2,2′-bipyrimidine mono nuclear complexes.

The electrochemical methods for water oxidation are described in ***Chapter 2***. The Rotating Ring-Disk Electrode method and On-Line Electrochemical Mass Spectrometry technique, complemented with Surface-Enhanced Raman Spectroscopy, are employed to perform a model study for an existing catalytic system based on Ru-red in solution or adsorbed on the electrode surface.

In ***Chapter 3***, a set of mono site molecular ruthenium complexes is synthesized for homogeneous water splitting catalysis (Fig. 1.11). The complexes are easily accessible, stable in light and air, and appear to follow a four-step proton coupled electron transfer pathway for dioxygen formation.

The extension of the work regarding mono nuclear ruthenium complexes for surface immobilized electrocatalytic water splitting assemblies is described in ***Chapter 4*** (Fig. 1.12). The pH-dependent electrochemical characteristics and the enhancement of oxygen evolution efficiency and rate with the applied electrode potential are also discussed.

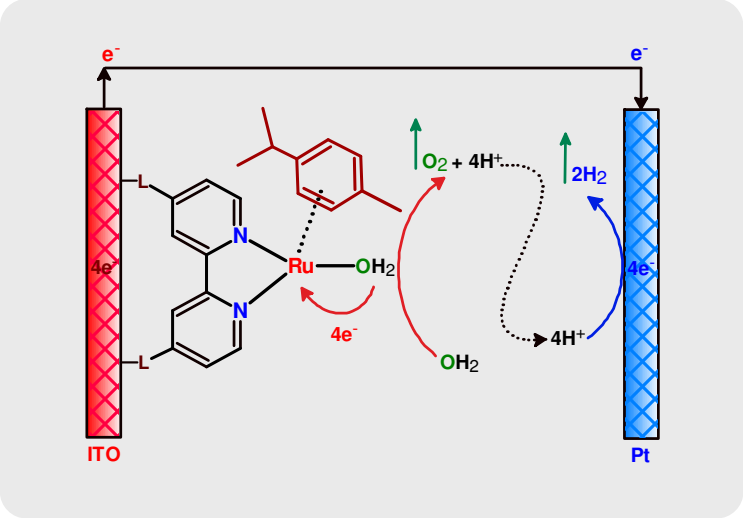


Figure 1.12. A schematic representation of the *p*-cymene-Ru derived 2,2′-bipyridine complexes for water oxidation. The catalyst (Cat.**Ru**–PO_3H_2 or Cat.**Ru**–COOH) is anchored on a conducting oxide surface via linker molecules (L = COOH or PO_3H_2) to drive electro-assisted water oxidation.

Chapter 5 shows the synthesis and catalytic properties of mono iridium complexes, both for homogeneous oxygen evolution catalysis and for surface anchored electro-assisted water oxidation on inert oxide electrodes (Fig. 1.13).

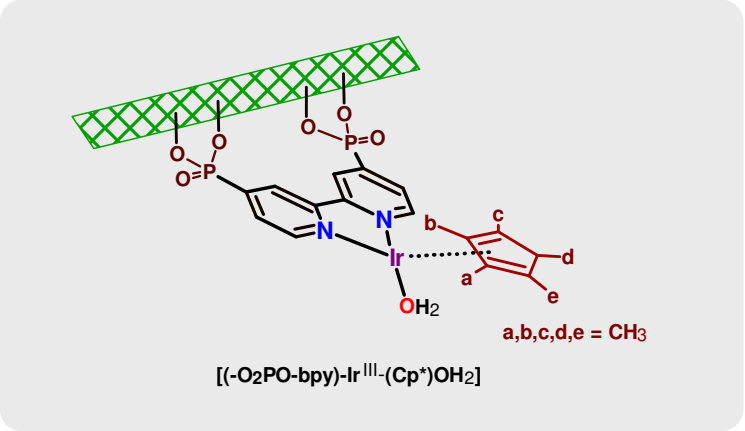


Figure 1.13. A mono iridium-Cp* complex immobilized on a conducting oxide surface (ITO) with linker (L = PO_3H_2) for electro-assisted water oxidation.

Chapter 6 at the end of the thesis describes how this project leads to a future perspective on water splitting catalysis systems for solar fuels generation. Several possibilities, such as the implementation of dinuclear catalysts, or a chromophore sensitized water oxidation system and integrated stand-alone assembly, the "Artificial Leaf", are proposed as future scenarios for the further extension and development of this work. This discussion is followed by a short summary of this dissertation.

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