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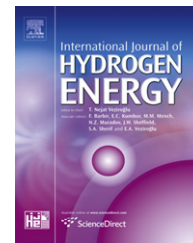
Biomimetic molecular water splitting catalysts for hydrogen generation

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ARTICLE INFO

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 free fuels obtained from catalytic water splitting using sunlight offer an attractive solution for a cleaner and greener future. In this pursuit, to establish effective molecular catalytic systems for efficient water oxidation is considered to be a bottleneck, hampering the design, implementation and exploitation of electrochemical and photo-electrochemical modular devices for light driven energy conversion into hydrogen-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 (WOCs) have been investigated both in a homogeneous environment and on surfaces in photo- or electrochemical conditions. However, a truly biomimetic catalytic system that matches the performance of photosystem-II for efficient water splitting, operating with four consecutive proton coupled electron transfer (PCET) steps to generate oxygen and hydrogen for hundred thousands of cycles at high rate is yet to be achieved. We here present an overview of biomimetic molecular complexes that have been investigated recently for water oxidation catalysis in homogeneous solution using chemical oxidants, or as heterogeneous species for catalytic electrochemical systems.

1. Introduction

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]. In parallel, the current level of CO_2, a green house gas, has exceeded 387 ppm owing to the increasing combustion of carbon-based fossil fuels in automobiles and power generation systems [8–10].

Petroleum, coal and natural gas are the primary supplies of energy, 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 for the production of hydrogen and oxygen from catalytic water splitting utilizing abundant solar energy [12–14]. At present, there is no efficient system available that makes use of solar energy effectively to produce hydrogen from water catalysis [15–17]. A most

challenging task is to develop an easy accessible oxidation catalyst from earth abundant materials that is capable of multielectron water splitting and dioxygen generation at a high rate and with optimal activity. This parallels the development of electro-assisted water splitting with oxide-based systems [6,18—20].
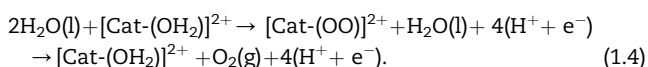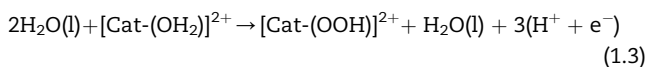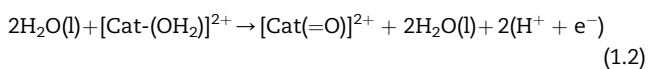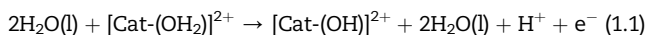
Photosynthesis offers an excellent model for designing an artificial solar energy conversion system for clean fuel generation, where a tetramanganese oxygen evolving complex (OEC) is involved in the process of four electron water oxidation to generate dioxygen [16]. The overall four electrons water oxidation reaction is given in Eq. (1).

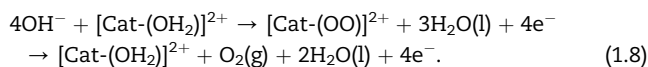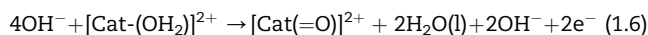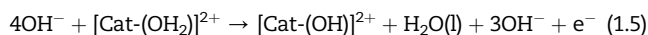$$2H_2O(l) \rightarrow 4e^- + 4H^+(aq) + O_2(g) \qquad (1)$$
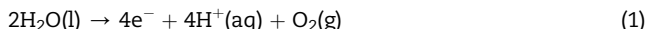
Electrons are provided to the reaction center of the photo-system-II (PS-II) in four consecutive proton coupled electron transfer steps and ultimately appear as reduced carbon derived products that form the basis of almost all biological activities [21]. The most detailed structure of the OEC of PS=II, with a resolution down to 1.9 Å, has revealed many structural details involving five oxygen atoms serving as oxo-bridges connecting the five metal atoms (four Mn and one Ca) and four water molecules bound to the Mn_4CaO_5 cluster. About 1300 water molecules were found in PS-II, providing extensive hydrogen-bonding networks that may serve as channels for protons from the manganese cluster to the reduction site [22—24].

Getting inspiration 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 from water splitting [25,26]. A major task is to establish an efficient and stable oxygen evolving catalyst that displays multi-electron 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 these systems has proven effective with good overall efficiency for water splitting [28,29].

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 of adsorption of the intermediates generated during ideal catalysis would be 1.23 eV, 2.46 eV, and 3.69 eV for HO*, O*, and HOO*, respectively [30,31]. In acidic medium in contact with the catalytic site, the PCET water oxidation proceeds along a reaction coordinate with four consecutive redox couples

$$2H_2O(l) + [Cat\text{-}(OH_2)]^{2+} \rightarrow [Cat\text{-}(OH)]^{2+} + 2H_2O(l) + H^+ + e^- \quad (1.1)$$

$$2H_2O(l) + [Cat\text{-}(OH_2)]^{2+} \rightarrow [Cat\text{-}(=O)]^{2+} + 2H_2O(l) + 2(H^+ + e^-) \qquad (1.2)$$

$$2H_2O(l) + [Cat\text{-}(OH_2)]^{2+} \rightarrow [Cat\text{-}(OOH)]^{2+} + H_2O(l) + 3(H^+ + e^-) \qquad (1.3)$$

$$2H_2O(l) + [Cat\text{-}(OH_2)]^{2+} \rightarrow [Cat\text{-}(OO)]^{2+} + H_2O(l) + 4(H^+ + e^-) \rightarrow [Cat\text{-}(OH_2)]^{2+} + O_2(g) + 4(H^+ + e^-). \qquad (1.4)$$

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

$$4OH^- + [Cat\text{-}(OH_2)]^{2+} \rightarrow [Cat\text{-}(OH)]^{2+} + H_2O(l) + 3OH^- + e^- \quad (1.5)$$

$$4OH^- + [Cat\text{-}(OH_2)]^{2+} \rightarrow [Cat\text{-}(=O)]^{2+} + 2H_2O(l) + 2OH^- + 2e^- \quad (1.6)$$

$$4OH^- + [Cat\text{-}(OH_2)]^{2+} \rightarrow [Cat\text{-}(OOH)]^{2+} + 2H_2O(l) + OH^- + 3e^- \quad (1.7)$$

$$4OH^- + [Cat\text{-}(OH_2)]^{2+} \rightarrow [Cat\text{-}(OO)]^{2+} + 3H_2O(l) + 4e^- \rightarrow [Cat\text{-}(OH_2)]^{2+} + O_2(g) + 2H_2O(l) + 4e^-. \qquad (1.8)$$

To avoid higher energy intermediates around neutral pH, a good water oxidation catalyst should release four electrons and protons in four consecutive proton coupled electron transfer steps [32]. With four PCET steps (1.1—1.8), a trans-formation of the reaction to a pH-independent reference frame provides a unified picture that is particularly useful when aiming for the design of complex device topologies [31,32]. We here describe the advent of both mono-site and multinuclear molecular complexes that have been reported for catalyzing water oxidation in homogeneous solution, as heterogeneous species using a chemical oxidant, and in catalytic electrochemical systems.

2. Molecular complexes for biomimetic water splitting

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 [33]. The quest for a synthetic catalytic water oxidation system began in the 70's with photochemical studies of a di-μ-oxo bridged dinuclear manganese (Mn^{III}—Mn^{IV}) 2,2′-bipyridine (bpy) complex by M. Calvin, who received the noble prize in chemistry for the discovery of the Calvin-Benson Cycle, in 1961 [34]. 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 for oxygen evolution by the binuclear manganese 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 binuclear ruthenium and manganese-based oxygen evolving complexes in the next decade (Fig. 1) using the same collection of di-nitrogen ligands for manganese and ruthe-nium complexes [37].
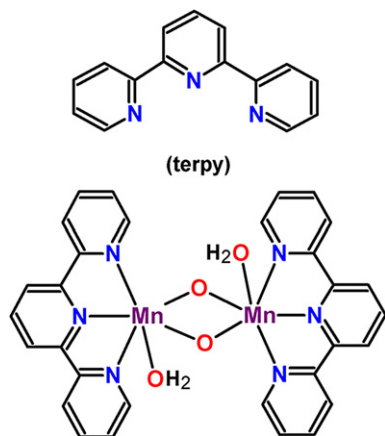
2.2. Water oxidation by manganese complexes

A well characterized synthetic tetramanganese complex, $Mn_4O_4L_6$ (L = diphenylphosphinate), with a Mn_4O_4 ($2Mn^{III}$,
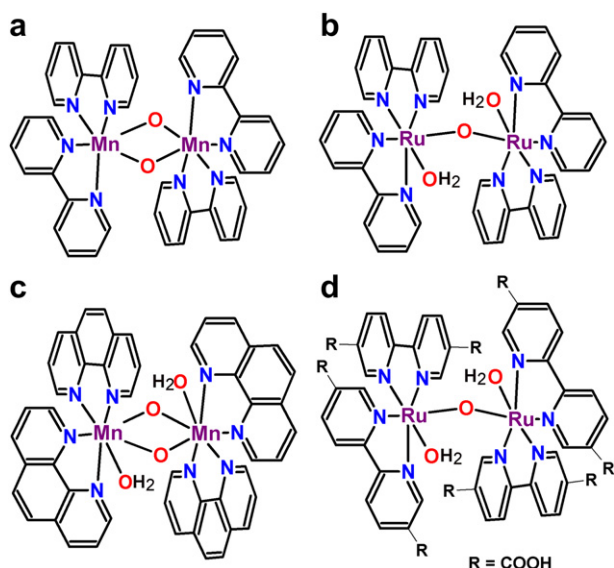
Fig. 1 – Molecular complexes that were proposed as water splitting catalysts at an early stage: (a) A binuclear bpy-manganese dimer [(bpy)$_2$Mn^{III}(μ-O)$_2$Mn^{IV}(bpy)$_2$]$^{3+}$, (b) the blue dimer [(bpy)$_2$Ru^{III}(μ-O)Ru^{III}(bpy)$_2$]$^{4+}$, (bpy = 2,2′-bipyridine), (c) a phenanthroline dimanganese complex [(phen)$_2$Mn^{III}(μ-O)$_2$Mn^{IV}(phen)$_2$]$^{3+}$ (phen = 1,10-phenanthroline) and (d) the dicarboxy-bpy derived [(R$_2$-bpy)$_2$Ru^{III}(μ-O-)Ru^{III}(R$_2$-bpy)$_2$]$^{4+}$ binuclear ruthenium catalyst (R$_2$-bpy = 5,5′-dicarboxy-2,2′-bipyridine).

2Mn^{IV}) cube-like core offered a new model of the active site of the photosynthetic water oxidation cluster [38]. Two years later, a synthetic di-terpyridine dimanganese complex, [(terpy)(H$_2$O)Mn(μ-O)$_2$Mn(terpy)(H$_2$O)]$^{3+}$ (terpy = 2,2′:6′,2″-terpyridine) (Mn dimer), was reported for homogeneous oxygen evolution (Fig. 2) in the presence of sodium hypochlorite [39,40]. The maximum turnover number (TON) of the di-terpyridine dimanganese complex for oxygen evolution was low, and a TON of 4 was determined in a solution containing

Fig. 2 – 2,2′:6′,2″-terpyridine (terpy) derived di-μ-oxo di-terpy dimanganese diaquo water oxidation complex, [(terpy)(H$_2$O)Mn^{III}(μ-O)$_2$Mn^{IV}(terpy)(H$_2$O)]$^{3+}$ (Mn dimer).

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 h [39].

The water oxidation catalysis by the Mn 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 dimer is thought to lead to the formation of an inactive tetranuclear complex from the Mn^{IV}–Mn^{IV} state of the Mn dimer, which would explain why 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 when adsorbed on kaolin or mica [41]. The maximum TON's for oxygen evolution in heterogeneous conditions were 15–17, and were reached after 4 days of continuous catalysis operation of the mica and kaolin adsorbed synthetic Mn-(μ-O)$_2$-Mn complex (Fig. 2). Recently, a synthetic [Mn$_3$CaO$_4$]$^{6+}$ cubane using a trinucleating ligand architecture has been reported that structurally models the trimanganese–calcium–cubane subsite of the OEC [44]. Structural and electrochemical characterization reveals potential roles of calcium in facilitating higher oxidation states at manganese cluster but the catalytic water splitting using this complex is not investigated.

2.3. Ruthenium-based water oxidation catalysts

The bi-ruthenium tetra aqua tetrakis-bipyridine [(bpy)$_2$(H$_2$O)Ru^{III}(μ-O)Ru^{III}(H$_2$O)(bpy)$_2$]$^{4+}$ with a Ru^{III}(μ-O)Ru^{III} core, also known as blue dimer (Fig. 1b), is widely considered the first genuine synthetic homogeneous water oxidation catalyst and was reported by Meyer et al. in the early 1980's [44]. Its carboxylic acid substituted derivatives (Fig. 1d) are also found to be active for oxygen evolution [45,46]. The turnover frequency (TOF) and TON of the blue dimer were reported to be 4.2×10^{-3} per second [47] and 13.2 [48], respectively. A tetra aqua terpy-Ru dimer, [(terpy)(H$_2$O)$_2$Ru(μ-O)Ru(terpy)(H$_2$O)$_2$]$^{4+}$ (terpy = 2,2′:6′,2″-terpyridine), was synthesized and characterized for homogeneous water catalysis in 1998 [49]. Its structure resembles the organization of the manganese analogue [39] except that it contains only one μ-oxo bridge between two ruthenium centers. Each center is ligated with two water molecules and the catalyst deactivates already after 1 turnover (Fig. 3a). The first structurally and electrochemically well-characterized dinuclear Ru complex with a Hbpp type bridging mode [Ru$_2^{II}$(bpp)(trpy)$_2$(H$_2$O)$_2$]$^{3+}$, [Hbpp = 2,2′-(1H-pyrazole-3,5-diyl)bis(pyridine)], instead of a Ru–O–Ru motif, was introduced by Sens et al. (Fig. 3b). Here two Ru metals have been deliberately placed in close proximity using a dinucleating ligand [50]. The absence of the μ-oxo bridge in the catalyst avoids the decomposition by reductive cleavage and makes it more active than the blue dimer for homogeneous oxygen evolution.

Thummel et al. introduced a new type of binuclear and a variety of single-site ruthenium derived water oxidation complexes (Fig. 4). A TON up to 600 was achieved in homogeneous solution using a chemical oxidant [51,52]. In contrast, detailed mechanistic analyses of single-site catalysts with a Ru-terpy with 2,2′-bipyrimidine (bpm), 2,2′-bipyrazine (bpz) motif and with a 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine
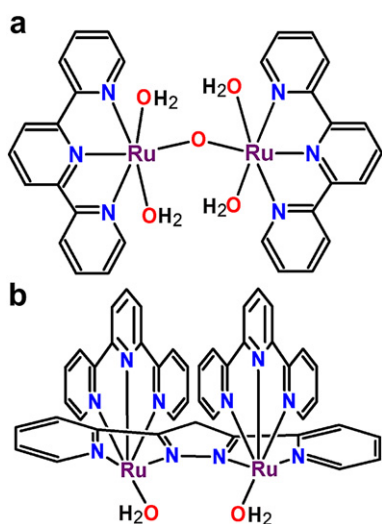
Fig. 3 − (a) A μ-oxo bridged di-terpyridine diruthenium complex, [(terpy)(H₂O)Ru^{III}(μ-O)Ru^{III} (terpy)(H₂O)]$^{4+}$ (terpy = 2,2':6',2''-terpyridine) and (b) a di-terpyridine diruthenium complex with Hbpp bridging ligand [Ru$_2^{II}$(bpp)(trpy)₂(H₂O)₂]$^{3+}$, [Hbpp = 2,2'-(1H-pyrazole-3,5-diyl)bis(pyridine)], for homogeneous water oxidation.

(Mebimpy) ligand instead of terpy showed that the TON does not exceed 15 in solution phase catalysis (Fig. 4c and d) [53,54]. Mono-ruthenium complexes with dicarboxylic acid substituted 2,2'-bpy and 1,10-phenanthroline (phen) ligands

were recently studied (Fig. 5a) using Ce(IV), and TON's up to 340 were obtained with TOF's of ∼0.1 per sec [55].

Extended versions of the mono-center complex containing two ruthenium sites were also reported recently for both chemical and light driven water oxidation in the homogeneous phase (Fig. 5b). In the presence of an excess amount of Ce(IV), the dinuclear ruthenium complex bis(capyptz)-Ru₂-(pic)₂, [bis(capyptz) = 1,4-bis(6'-COOH-pyrid-2'-yl)phthalazine and pic is 4-picoline], produce 10,400 TON's while generating approximately 20.7 μmol of molecular oxygen in 20 h reaction time [56]. This is by far the best TON obtained for a molecular ruthenium catalyst in homogeneous solution.

2.4.   Iridium complexes for water oxidation

A series of iridium organometallic complexes with general formula cis-[Ir^{III}(L)₂(H₂O)₂]$^+$ [L = 2-(2-pyridyl)phenylate anion (2-ph-py)] and related ligands have been reported to efficiently catalyze the water oxidation (Fig. 6a). Up to 2500 TON's have been reported in the presence of Ce(IV), though the rate was lower than for the ruthenium analogues [57]. 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 (2-ph-py) type ligand (Fig. 6b). With this new system, an oxygen generation rate of 0.9 per second was achieved in the homogeneous phase [58]. In a next step the 2-ph-py type ligand was replaced with di-nitrogen bpy and bpm. To produce a catalytic complex the metal was mono halogenated [59]. The chloride at the iridium catalytic site may
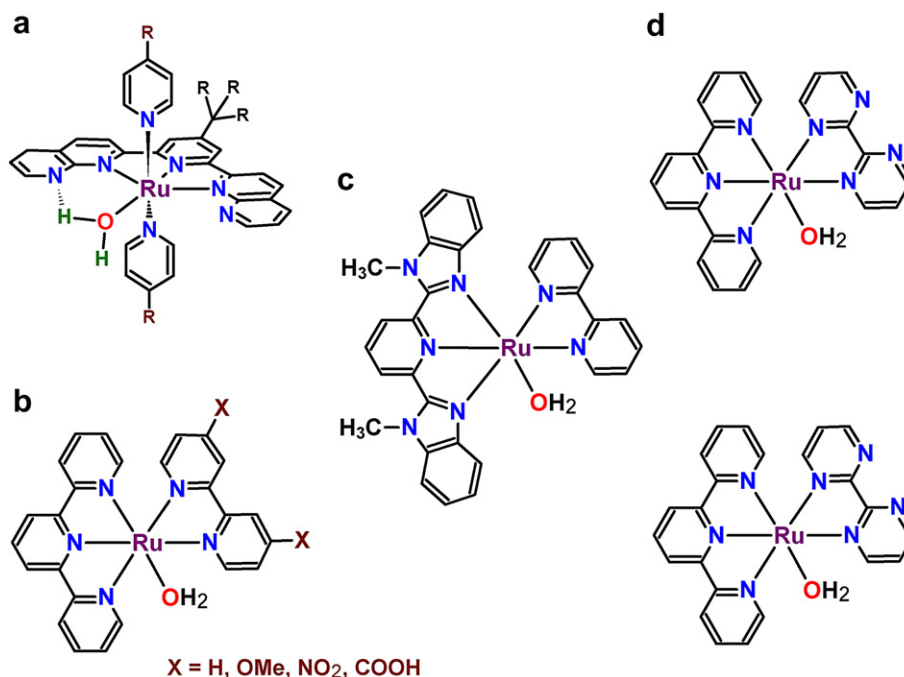
Fig. 4 − (a) A mono-ruthenium 4-*tert*-Butyl-2,6 di([1',8']-naphthyrid-2'-yl)pyridine based complex was introduced in 2005 followed by (b) terpy-Ru derived substituted bpy type single Ru catalysts. (c) Replacement of the terpy ligand with a more bulky 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine (Mebimpy) ligand and (d) introduction of tetraaza bpm and bpz type ligands to the Ru-terpy motifs [51−54].
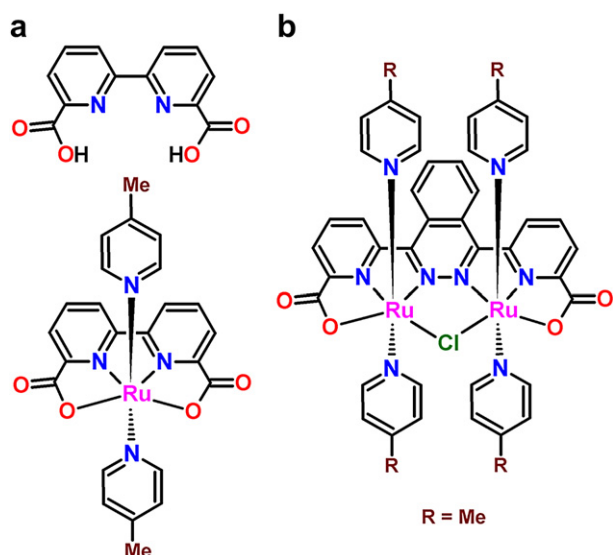
Fig. 5 – (a) A H$_2$dcabpy ligand derived mono-site [(H$_2$dcabpy)Ru^{II}-(pic)] complex, (H$_2$dcabpy is 2,2′-bipyridine-6,6′-dicarboxylic acid; pic is 4-picoline) and **(b)** a dinucleating dicarboxylic modified ligand bis(capyptz) based dimeric ruthenium catalyst [bis(capyptz) = 1,4-bis(6′-COOH-pyrid-2′-yl)phthalazine)] [55,56].

become oxidized to OCl^{-5}, or Cl$_2$ can be formed that may accelerate O$_2$ evolution [58–61].

2.5. Other molecular oxygen evolving complexes

Besides manganese, ruthenium and iridium derived molecular water splitting catalysts, other common transition metal-based complexes have recently been described that offer effective catalysis for oxygen generation in homogeneous
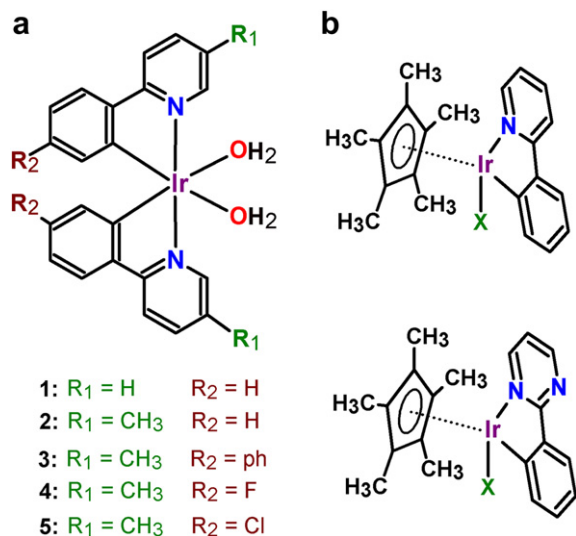

Fig. 6 – (a) First [Ir^{III}(L)$_2$(H$_2$O)$_2$]$^+$ [L = 2-(2-pyridyl)phenylate anion (2-ph-py)] derived water oxidation catalysts and **(b)** mono-site half sandwiches Cp*-iridium catalysts for homogeneous water oxidation (X = OTf or Cl).

systems. A tetraamido macrocyclic ligand (TAML) based iron-centered complex Fe^{III}-TAML has been reported that 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 [62]. 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. 7). Cyclic voltammetry analysis reveals that the mono-cobalt system [Co^{II}–OH$_2$]$^{2+}$ reacts by two PCET conversion redox couples, first [Co^{III}–OH]$^{2+}$/[Co^{II}–OH$_2$]$^{2+}$ and then [Co^{IV}=O]$^{2+}$/[Co^{III}–OH]$^{2+}$. O–O bond formation was not yet reported and is under investigation [63]. Recently, environmentally benign iron-based coordination complexes with nitrogen surroundings have shown high efficiency during a period of hours for homogeneous water oxidation to give molecular oxygen. Turnover numbers in excess of 350 and 1000 were obtained using cerium ammonium nitrate at pH=1 and sodium periodate at pH=2, respectively [64]. The next step will be aimed at coupling the Fe-system with the photochemical and electrochemical oxidation assemblies for sustained water oxidation based on cheap and abundant materials.

3. Electro-assisted molecular catalytic systems for water splitting

3.1. Ruthenium-based electrochemical water oxidation assemblies

While there are many reports on solution phase water splitting, the number of studies involving surface catalytic electro-assisted water oxidation assemblies that have applications in

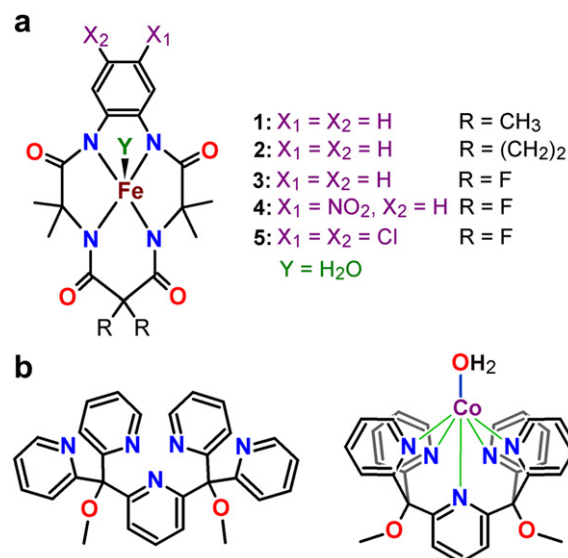**Fig. 7 – (a)** Structural representation of (a) Fe^{III}-TAML (TAML = tetraamido macrocyclic ligand) derived complexes. **(b)** 2,6-(bis(bis-2-pyridyl)methoxy-methane)-pyridine (Py5) ligand and a cobalt-Py5 [Co^{II}(Py5)(OH$_2$)]$^{2+}$ complex.

operational electrocatalytic or photoelectrocatalytic 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. 8a). The electrochemical investigation was conducted on the catalyst adsorbed on an indium-doped tin oxide (ITO) electrode at +1.7 V (vs. Ag/AgCl) in a pH=4.0 solution. More than 33,500 turnover numbers were obtained in 40 h 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 μ-oxo ruthenium(II) terpy dimer [49] modified with a phosphonate group for anchoring on oxide electrodes, [(PO$_3$H$_2$-terpy)(H$_2$O)$_2$Ru^{III}(μ-O)Ru^{III}(H$_2$O)$_2$(PO$_3$H$_2$-terpy)]$^{4+}$ (PO$_3$H$_2$-terpy = 4′-phosphonato-2,2′:6′,2″-terpyridine), was synthesized for electrocatalytic studies of μ-oxo dimer-based water oxidation chemistry (Fig. 8b) [68].

The electrocatalytic water oxidation was carried out on catalyst modified ZrO$_2$ films on fluorine-doped tin oxide (FTO) at 1.5 or 1.25 V (vs. Ag/AgCl) and a maximum TON of 3 was obtained with the complex in buffer solution at pH = 6. Meanwhile, Mola et al. 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-trpy) based catalyst for electrochemical water oxidation (Fig. 9a). The system was efficient, with TON's exceeding 120 at 1.17 V in a 0.1 M aqueous triflic acid solution (vs. Ag/AgCl) [69].

The extension of the Ru-bpy complex with a 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine ligand was realized with the introduction of a 4,4′-dialkyl phosphonate (4,4′-(H$_2$O$_3$PCH$_2$)$_2$-bpy) motif as a catalytic linker to the 2,2′-bpy (Fig. 9b). The water electrocatalysis started at 1.85 V (vs. NHE) in pH=5 buffer, but with a very low turnover rate of 0.004 s^{-1} and low oxygen yield of 6.5 μmol during 30,000 s of water electrolysis [54]. The incorporation of the 4,4′-(H$_2$O$_3$PCH$_2$)$_2$-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. 10). In acidic medium at ca. 1.80 V (vs. NHE), 28,000 turnover numbers were obtained for [{4,4′-(H$_2$O$_3$PCH$_2$)$_2$-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 s^{-1} with very low current density [70]. The high TON for the immobilized catalysts relative to the corresponding materials in solution underlines the importance of proper interfacing when designing biomimetic catalytic devices. Natural photosynthesis uses separate modules for light harvesting, charge separation, and catalysis. The size and mutual arrangement of these modules is important to arrive at a high efficiency of conversion, by matching of length, time, and energy scales [71]. Similarly, in the design and synthesis of biomimetic devices knowledge of the
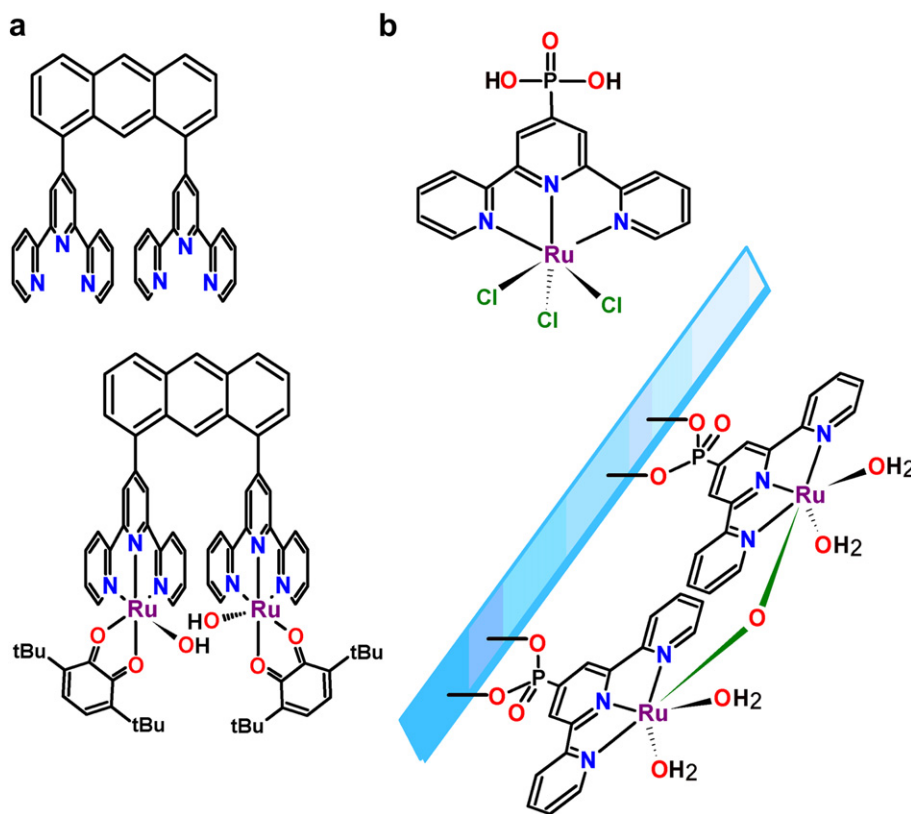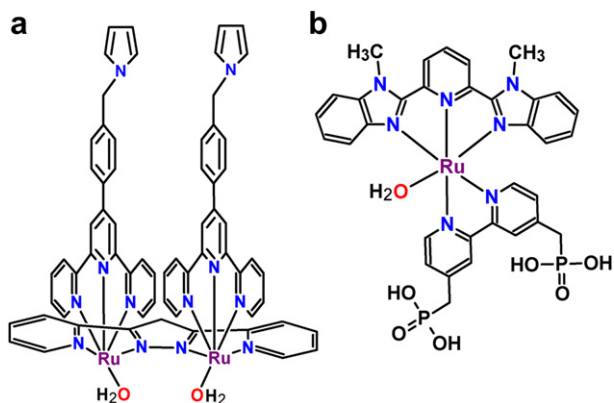

Fig. 8 – (a) A bis(ruthenium–hydroxo) complex, bearing a novel bridging type ligand 1,8-bis(2,2′:6′,2″-terpyridyl)anthracene (btpyan) and (b) a surface anchored terpy-Ru dimer [(PO$_3$H$_2$-terpy)(H$_2$O)$_2$Ru^{III}(μ-O)Ru^{III}(H$_2$O)$_2$(PO$_3$H$_2$-terpy)]$^{4+}$ (PO$_3$H$_2$-terpy = 4′-phosphonato-2,2′:6′,2″-terpyridine) for electrocatalytic water oxidation.

Fig. 9 – (a) 4′-(para-pyrrolylmethylphenyl)-2,2′:6′,2″-terpyridine (t-trpy) based diruthenium complex with Hbpp bridging ligand [Ru$_2^{II}$(bpp)(t-trpy)$_2$(H$_2$O)$_2$]$^{3+}$[Hbpp = 2,2′-(1H-pyrazole-3,5-diyl)bis(pyridine)], and (b) mono-site 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine (Mebimpy) ligand derived ruthenium complex, for electrochemical water oxidation.
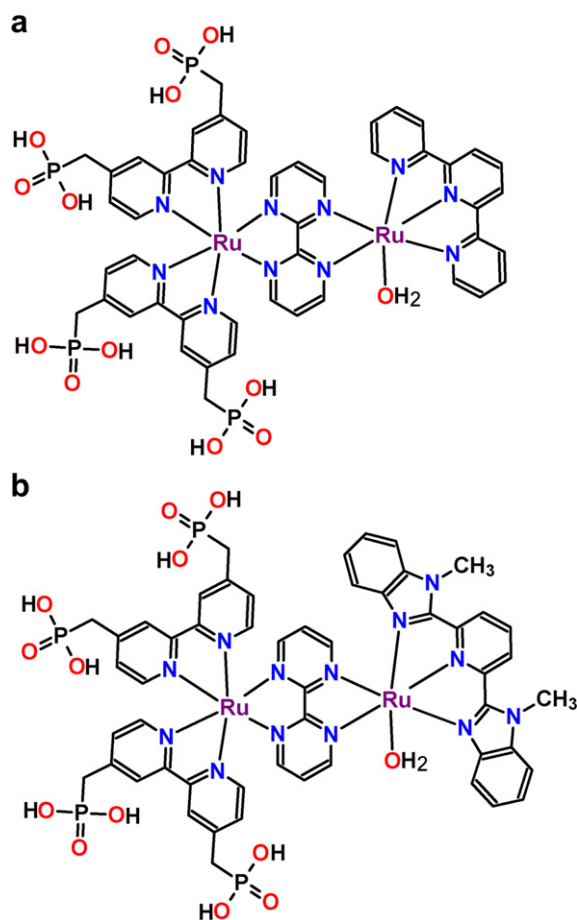
Fig. 10 – (a) A 4,4′-(H$_2$O$_3$PCH$_2$)$_2$-bpy with Ru-tris-bpy type redox mediator modified (left) [(bpm)Ru^{II}(terpy)-(OH$_2$)] complex and (b) a [(bpm)Ru^{II}(Mebimpy)-(OH$_2$)] catalysts for electrochemical water oxidation [70].

principles of operation for natural photosynthetic systems will serve to determine the optimal separation between a catalyst and its supporting electrode, by an electron tunneling barrier that can kinetically stabilize essential intermediates, thereby enhancing the operation of a catalyst module [72].

3.2. Electrochemical water oxidation by manganese and cobalt complexes

Light-assisted electro-oxidation of water was studied by a tetranuclear Mn-oxo cluster [Mn$_4$O$_4$L$_6$]$^+$, (L is MeOPh$_2$PO$_2^-$) suspended in a Nafion membrane coated on a conductive electrode. The cluster generates a sustained photocurrent, oxygen gas, and protons at 1.2 V (vs. NHE) when illuminated with visible light and produced >1000 catalytic cycles in aqueous electrolyte at pH = 6.5. Recently, the [Mn$_4$O$_4$L$_6$]$^+$ water oxidation catalyst within a Nafion membrane was combined with a TiO$_2$-supported [Ru^{II}(bpy)$_2$-(COO)$_2$-bpy] light sensitizer light-driven water oxidation. The Ru^{II}-tris-bpy dye injects an electron into the conduction band of TiO$_2$ on light excitation, and the electron flows into an external circuit. This generates [Ru^{III}(bpy)$_2$-(COO)$_2$-bpy]$^+$, a potent oxidant (E$_P^{red}$ = +1.4 V vs. NHE) which is able to carry out a one-electron oxidation. A photo-electrochemical multilayer device system based on this Mn-oxo molecular catalyst has been constructed (Fig. 11) which, like PS-II, oxidizes water using only visible light and no external bias [73]. A detailed elucidation of the catalytic mechanism in the Nafion membrane was obtained recently by in situ Mn K-edge X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM), providing strong evidence for the dissociation of the Mn-cluster within the Nafion polymer matrix to generate Mn^{II} type compounds which can be electro-oxidized to Mn$^{III/IV}$ oxide forms and can be responsible for water oxidation [74].

The Mn-oxo cubane water oxidation electrocatalysis work was further extended by introducing a Co$_4$O$_4$ cubane complex Co$_4$O$_4$(OAc)$_4$(py)$_4$ for photochemical or electrochemical oxygen evolution. Electrochemistry of the new cobalt-oxo complex reveals one electron reversible redox couple at E$_{1/2}$ = 0.71 V (vs. Ag/AgCl) in acetonitrile corresponding to the Co^{III}, Co^{IV} transition [75]. Light illumination in an photochemical experimental setup with Co-cubane catalyst sensitized with [Ru(bpy)$_3$]$^{2+}$ in Na$_2$S$_2$O$_8$ solution generated 40 TON after 60 min with a TOF of 0.02 per second.

3.3. Iridium complex derived anodic water oxidation

Very recently, a Cp*-Ir aqua or hydroxo catalyst (blue layer) was generated by anodic deposition in aqueous solution. The catalyst operates with a current density up to 1.4 mA/cm^2 at ~1.4 V (vs. NHE) for water oxidation in 0.1 M KNO$_3$ (pH=6) electrolyte solution [76]. This work suggests that organometallic species may be employed as useful precursors in electrodeposition of inorganic heterogeneous catalysts on a fluorine-doped tin oxide electrode for water oxidation reaction. SEM analysis reveals that the thickness of such electrodeposited films is between 1 and 2 μm.
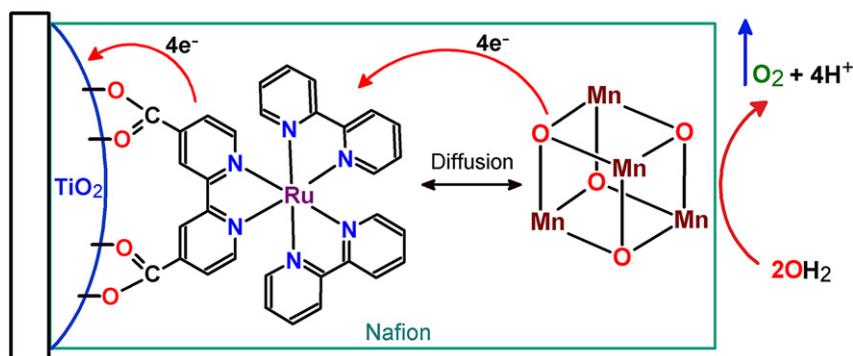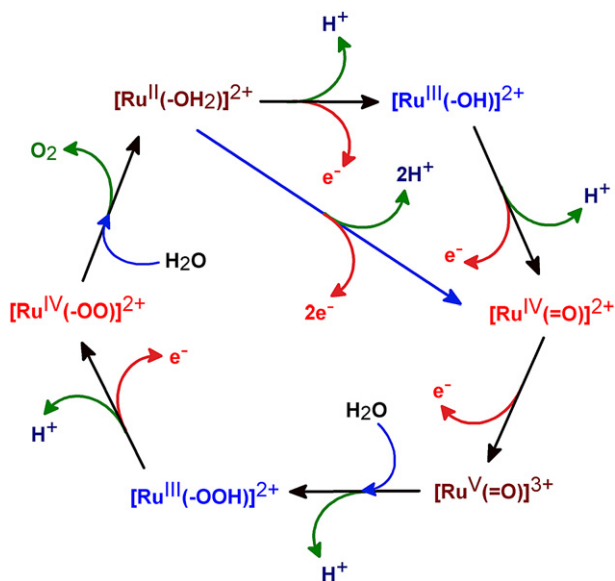
Fig. 11 − A molecular Mn-oxo catalyst-based photo-electrochemical multilayer device system embedded in a Nafion membrane on a TiO$_2$ layer sensitized with a [Ru^{II}(bpy)$_2$-(COO)$_2$-bpy] dye.
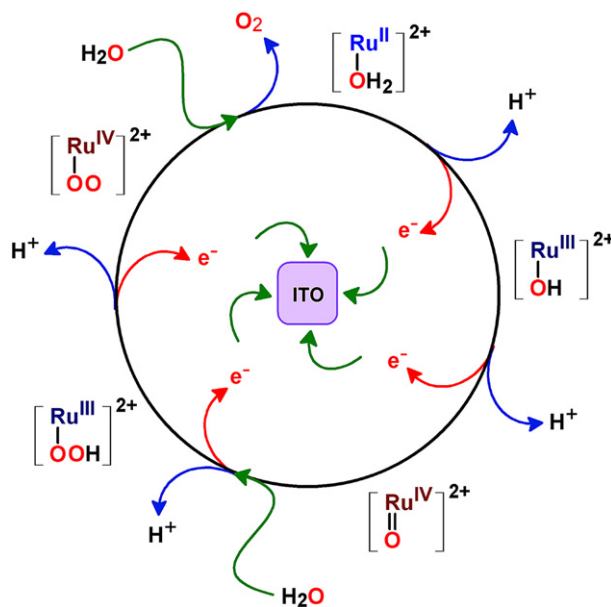
4. Polyoxometalate derived water oxidation system

The first example of a polyoxometalate (POM) derived diruthenium-substituted electrocatalyst for oxygen generation was tested on a gold surface in pH = 8 phosphate buffer solution [77]. The close proximity of the Ru−Ru atoms at 0.318 nm is considered to be a key factor to generate molecular oxygen. This work was followed by two reports that describe tetra-ruthenium core derived POM catalysts for water oxidation using Ce(IV) or [Ru(bpy)$_3$]$^{2+}$ as one electron oxidants for catalysis initiation [78,79]. Recently, a tetra-cobalt POM catalyst with Co$_4$O$_4$-core [Co$_4$(H$_2$O)$_2$(PW$_9$O$_{34}$)$_2$]$^{10−}$ was investigated

showing a high TOF ≥ 5 in pH = 8 solution using [Ru(bpy)$_3$]$^{2+}$ as oxidant but the catalytic TON's were only 75 in the homogeneous phase [80]. However, a very recent electrochemical study provides compelling evidence for the formation of a heterogeneous CoO$_x$ species as the WOC, instead of a homogeneous Co-based POM system for oxygen evolution [81].

Scheme 2 − Catalytic water oxidation and oxygen evolution pathway by mononuclear ruthenium catalyst operating with four PCET steps avoid the a higher oxidation state [Ru^V(=O)]$^{3+}$ species when the oxidation states of the metal ion alternate through Ru^{II}/Ru^{III}/Ru^{IV}−Ru^{III}/Ru^{IV}/Ru^{II} while maintaining an overall charge of +2 [98−101]. Such a process can occur if there is rapid association of a second water molecule, following non rate-limiting internal rearrangements to generate [Ru^{III}-(OOH)]$^{2+}$ and [Ru^{IV}-(OO)]$^{2+}$ complexes by two successive PCET steps in the second half of the catalytic mechanism and eventually dioxygen release with simultaneous water molecule exchange to recharge the system for the next catalytic cycle for water splitting and molecular oxygen evolution.

Scheme 1 − Catalytic water oxidation pathway and dioxygen evolution mechanism by mono-catalytic site [(terpy)-Ru-(bpm)], [(terpy)-Ru-{(H$_2$O$_3$PCH$_2$)$_2$-bpy}] and [(Mebimpy)-Ru-{(H$_2$O$_3$PCH$_2$)$_2$-bpy}] complexes proceeding along a higher oxidation state [Ru^V(=O)]$^{3+}$ intermediate [54,103]. [terpy = 2,2′:6′,2′′-terpyridine, bpm = 2,2′-bipyrimidine, (H$_2$O$_3$PCH$_2$)$_2$-bpy = 4,4′-(H$_2$O$_3$PCH$_2$)$_2$-2,2′-bipyridine and Mebimpy = 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine].

5. Mechanism of water oxidation

5.1. Natural PS-II

Formation of molecular oxygen is realized by the extraction of four electrons and protons in a four-step PCET regime from two water molecules at the Mn_4CaO_5 cluster embedded in the photosystem-II [82]. Before the beginning of water oxidation, the stepwise increase in the oxidation state of the Mn^{n+} gives rise to the accumulation of the four oxidizing equivalents. There is no evidence for partial oxidation of water at an early state in the reaction cycle [83–85]. The consecutive PCET steps enable the accumulation of four redox equivalents while circumventing high energy intermediates during the multi-electron water oxidation cycle [32,86]. For the Mn-cluster in the PS-II PCET is considered one of the key elements for separating electrons and protons from water to produce oxygen at a high rate for hundred thousands of cycles [86–88].

5.2. Biomimetic oxygen evolving complexes

In mononuclear artificial biomimetic systems, the maximum oxygen evolution activity is thought to be constrained by a minimum overpotential of ∼0.4 V. In these systems the cycle proceeds through an HOO* intermediate, and there is a constant difference of 3.2 ± 0.1 eV in the affinity between the HOO* and the HO* intermediates [31,82]. Many artificial water oxidation catalysts have been scrutinized for dioxygen generation but detailed mechanistic insight is difficult to obtain [89–91]. 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 few cycles [92], or by nucleophilic OH_2 insertion generating a higher energy HOO* intermediate in a non-PCET step [93]. Recently reported mono-site ruthenium catalysts are also unable to construct a four-step PCET mechanism [17], where an HOO* intermediate is formed at high overpotential from a $[Ru^V=O]^{3+}$ species (Scheme 1) that is generated by an electron transfer pathway in a non-PCET rate-limiting step [54,94]. As mentioned earlier, there are few reports regarding iridium derived complexes for homogeneous water splitting catalysts describing a speculative oxygen formation pathway but the experimental evidences about the mechanistic insight are yet to be investigated [59,95]. In addition, several manganese complexes have been described, and also for these compounds the mechanism of O–O bond formation is not studied in much detail [29,96,97].

By continuous learning from natural systems, it will be possible to continue the development of new mono-metal water splitting catalysts, both for homogeneous study as well as surface immobilized assemblies. Complexes that are stable and efficient and show a consecutive four-step proton coupled electron transfer pathway for molecular oxygen generation are currently envisaged, where advanced proton management is exploited to stabilize a divalent catalyst complex during the entire four-electron water oxidation pathway by cycling through $Ru^{II/III/IV}$–$Ru^{III/IV/II}$ states with two water molecules coordinating sequentially while maintaining an overall charge +2 as shown in Scheme 1 [98,99].

In Scheme 2, a stable divalent $[Ru^{II}-(OH_2)]^{2+}$ molecular species allows for two consecutive PCET steps. Subsequent insertion of a second water molecule re-establishes the proton

Table 1 – Water oxidation catalysts system for homogeneous and electrochemical oxygen evolution by molecular complexes.

Catalysts	System	Conditions	TOF, J[a]	TON	Refs.
Blue dimer	Homogeneous, aqueous	Ce(IV)	0.0042 s^{-1}	13	[44]
Mn_4O_4 cubane complex	Heterogeneous, photo- & photo-electrochemical	1.0 V (Ag/AgCl) Xe lamp	–	1000	[38,73,74]
Mn-terpy dimer	Homogeneous, aqueous	Ce(IV) in NaClO	–	4	[39]
Ru-terpy dimer	Homogeneous, aqueous	Ce(IV) in $HClO_4$	–	∼1	[49]
PO_3H_2-terpy-Ru dimer	Heterogeneous, pH = 6	1.5 V (Ag/AgCl)	–	3	[68]
Ru_2-Hbpp.terpy	Homogeneous, aqueous	Ce(IV) in triflic acid	–	∼15	[50]
Ru_2-Hbpp.t-trpy	Heterogeneous, pH = 1	1.17 V (Ag/AgCl) in triflic acid	–	120	[69]
Ru_2-Btpyan	Heterogeneous, pH = 4	ITO +1.7 V (Ag/AgCl)	0.12 mA/cm^2	33,500	[66,67]
Terpy-Ru(N–N)[b]	Homogeneous, aqueous	Ce(IV) in 0.1 M acids	∼0.02 s^{-1}	∼600	[52]
Mebimpy-Ru(N–N)[c]	Heterogeneous, pH = 5	1.85 V (NHE) in 0.1 M acetate buffer	0.36 s^{-1} 14.8 µA/cm^2	11,000	[54]
Tpy-Ru(N–N)Ru(bpy)$_3$L[d]	Heterogeneous, pH = 1	1.80 V (NHE) in 0.1 M $HClO_4$	0.3 s^{-1} 6.7 µA/cm^2	8900	[70]
Cp*-Ir-(ph-py)Cl[e]	Homogeneous, aqueous	Ce(IV) in $MeCN/H_2O$	0.9 s^{-1}	1500	[58]
Fe^{III}-TAML[f]	Homogeneous, pH = 0.7	Ce(IV) in H_2O	1.3 s^{-1}	∼12	[62]
$[Co_4O_4]$ cubane	Photochemical	$[Ru(bpy)_3]^{2+}$ in $Na_2S_2O_8$ solution	0.02 s^{-1}	40	[75]
Co_4O_4–POM[g]	Homogeneous, pH = 8	$[Ru(bpy)_3]^{2+}$	∼5 s^{-1}	75	[80]
Fe-tetradentate N-ligand	Homogeneous, pH = 1,2	Ce(IV) in H_2O	$150–850$ h^{-1}	∼1000	[64]

a J = current density (in mA/cm^2).
b N–N is di-nitrogen ligands.
c Mebimpy is 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine and N–N is 4,4′-dialkyl phosphonate-2,2′-bipyridine [4,4′-$(H_2O_3PCH_2)_2$-bpy].
d Tpy-Ru(N–N)Ru(bpy)$_3$L is [{4,4′-$(H_2O_3PCH_2)_2$-bpy}$_2$Ru^{II} (bpm)Ru^{II}(tpy)-(OH$_2$)]$^{4+}$.
e Cp* is pentamethylcyclopentadiene and ph-py is 2-(2-pyridyl)phenylate.
f TAML is tetraamido macrocyclic ligand.
g $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ complex.

management for the second half of the cycle and the activated form retains a double positive charge during the course of the whole catalytic cycle. In this way, the higher oxidation state rate-limiting ruthenium intermediates (Ru^V or Ru^{VI}) are avoided by generating $[Ru^{III}-(OOH)]^{2+}$ and $[Ru^{IV}-(OO)]^{2+}$ via two successive proton coupled electron transfer events as well. Dioxygen is released from the $[Ru^{IV}-(OO)]^{2+}$ species on the addition of another water molecule, and this regenerates the $[Ru^{II}-(OH_2)]^{2+}$ complex for the next catalytic cycle for water oxidation. The catalytic system described above manifests the first example of a robust, fast and long lasting mono-metal molecular complex that shows new and simple structural design for an efficient artificial photosynthetic device by constructing four PCET steps [98–101].

6.   Conclusions and future outlook

Hydrogen can be made a renewable and personalized energy source if obtained from catalytic water splitting using sunlight as driving force on the top of our roofs [102–104]. Development of a novel and competent photocatalytic water oxidation assembly is a key task for establishing an artificial photosynthetic system. Present systems of molecular complexes for water splitting catalysis and the associated technology are based on newly born science learning. Many things need to be explored in this research field to get better understanding of the basic principles of water oxidation and oxygen formation mechanism, designing new stable ligands and develop robust organometallics [80,105]. The research interests in the field of water oxidation science are expanding from homogeneous catalysis to electrochemical water oxidation, as presented by various examples of mono-site and multinuclear molecular complexes in this review. A list of molecular complexes for water oxidation in homogeneous solution and for electrochemical oxygen evolution is given in Table 1, which summarizes various features of the molecular oxygen evolving complexes developed during water oxidation research. Both mononuclear and multisite catalytic systems have not yet reached a state where the water oxidation generates more than 100,000 of turnovers for molecular oxygen at a rapid rate [106–108]. After developing an efficient molecular water oxidation catalytic system, the next task will be to build integrated light triggered stand alone water splitting catalytic assemblies that generate oxygen and hydrogen at moderate rate and turnover without external driving force [109–111].

Acknowledgements

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