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Chemical, Electrochemical and Photochemical Molecular Water Oxidation Catalysts

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ABSTRACT

Hydrogen release from the splitting of water by simply using sunlight as the only energy source is an old human dream that could finally become a reality. This process involves both the reduction and oxidation of water into hydrogen and oxygen, respectively. While the first process has been fairly overcome, the conversion of water into oxygen has been traditionally the bottleneck process hampering the development of a sustainable hydrogen production based on water splitting. Fortunately, a revolution in this field has occurred during the past decade, since many research groups have been conducting an intense research in this area.

Thus, while molecular, well-characterized catalysts able to oxidize water were scarce just five years ago, now a wide range of transition metal based compounds has been reported as active catalysts for this transformation. This review reports the most prominent key advances in the field, covering either examples where the catalysis is triggered chemically, electrochemically or photochemically.

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1. Introduction

Nature has always been a source of inspiration for human kind. The astonishing complexity and perfection of the biochemical processes occurring every second within our natural environment still amaze us every day. Sunlight, a free and inexhaustible energy source, is efficiently used every day by green plants, algae and cyanobacteria in order to produce energetically rich biomolecules. The emulation of this process in the sense of storing the energy of sun into the bonds of a chemical fuel would be a solution for our global energy demand. Moreover, if the combustion of this fuel was carbon free, the whole process would constitute a clean approach for fighting against climate change. From this point of view, the use of sunlight in order to split water into oxygen and hydrogen has become one of the most brilliant feasible ideas during the last three decades, since hydrogen combustion only produces energy and water, thus closing the whole cycle in a perfectly sustainable manner.

The molecular machinery involved in photosynthesis consists in two families of electronically coupled protein complexes, named Photosystem I (PSI) and Photosystem II (PSII), embebed within the thylakoid membrane of green plant and algae chloroplasts and cyanobacteria. During photosynthesis, 4 protons and 4 electrons are detached in PSII from 2 H_2O molecules after the absorption of 4 sunlight photons by chlorophyll P_{680}, generating O_2 and a gradient of electrons and protons that are used by PSI to generate 2 NADPH and 3 ATP molecules. These constitute the necessary reducing equivalents and energy needed during the Calvin-Benson cycle for generating carbohydrates from CO_2 outside of the thylakoid membrane at later stages of the photosynthetic process [1, 2].

From a chemical point of view, the most important process takes place at the Oxygen Evolving Centre (OEC) of PSII, where the oxidation of H_2O happens in the absence of light in a Mn_4CaO_5 cluster shown in Fig. 1. In this cluster, five acidic amino acids, one His and one Ala coordinate the Mn and Ca atoms. In addition, four H_2O molecules are also present in the cluster, two of which binding to the Ca ion [3]. Although the exact mechanism of water oxidation is still a mater of intense debate, it is accepted that during the so-called S-cycle or Kok-cycle four electrons are released from the Mn_4CaO_5 cluster, provoking the oxidation of the Mn ions and the formation of an O-O bond from two water molecules [4,5,6].

Following the oxidation of H_2O within the OEC-PSII, the released electrons are then transferred to the $Tyr_ZO\cdot$ radical (Tyr161) formed after oxidative quenching of the excited P_{680}*, which at the same time is stabilized by the presence of a proximal His190 [7, 8]. Afterward, the electrons flow from Tyr_Z through an electronic transport channel that consecutively involves P_{680}, pheophytin and plastoquinones A and B, until finally reaching PSI [9].

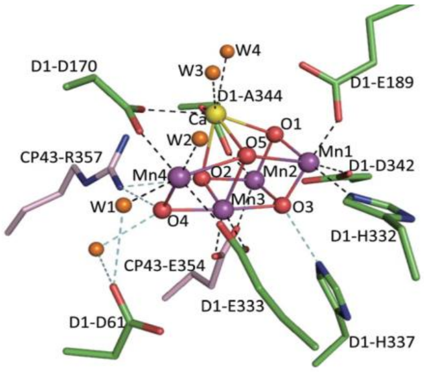

Fig. 1. X-Ray structure of the OEC-PSII at 1.9 Å resolution. Reprinted with permission from Macmillan Publishers Ltd: Nature, Y. Umena, K. Kawakami, J.R. Shen, N. Kamiya, N. Nature 473 (2011) 55–60, copyright (2011).

It has been hypothesized that the oxo ligands in OEC are needed for the neutralization of the positive charges of the Mn ions [10]. Furthermore, it has been suggested that the Ca ion may play a significant role as a Lewis acid during water oxidation by modifying the nucleophilicity of its bounded H_2O molecules [11]. Indeed, Stranger *et al.* have recently shown that in the Sr(II) analogue of PSII, the region containing the alkaline earth metal and its associated H bonding network is closely related to the substrate water binding and O-O bond formation [12]. Furthermore, very recently, with the use of femtosecond X-ray laser spectroscopy, a series of snap shots of PSII at 5 Å resolution during the dark state (S_1) and the putative excited state (S_3) have shown that the Mn_4CaO_5 cluster elongates, accompanied by changes in the protein environment, allowing for binding of a second substrate water molecule between Mn4 (see Fig. 1) and the rest of the cluster [13].

Inspired, but not constrained, by nature, chemists have designed artificial molecular systems in order to capture light with the aim of using this energy to oxidize water and at the same time employ the released electrons to form hydrogen from water protons, since water cannot be directly excited by the electromagnetic radiation of the sun. Therefore, three different chemical components are needed for this purpose: a light harvesting device (or photosensitizer, P), a water oxidation catalyst (WOC) and a hydrogen evolving catalyst (HEC). These three components can be assembled in a photo-electrochemical cell (PEC), such as the one drawn in Fig. 2 [14, 15, 16]. This cell needs to be robust, and contains a proton-exchange membrane (PEM) that allows diffusion of protons to the cathode and, at the same time, physically separates the anodic and the cathodic compartments, thus avoiding the potential hazardous recombination of H_2 and O_2 to form back water. Besides, the cell should work harmonically and should also be economically viable.

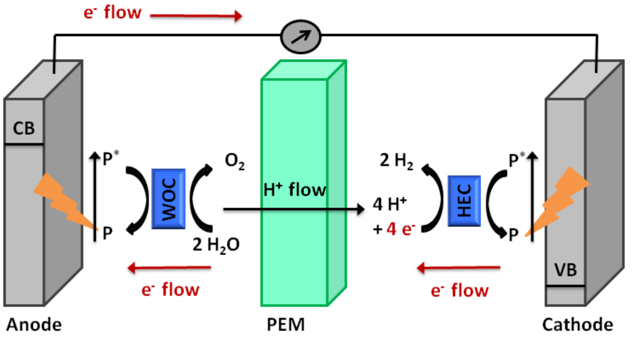

Fig. 2. Schematic representation of a photo-electrochemical cell (PEC) designed for water splitting using sunlight. P: photosensitizer, WOC: water oxidation catalyst, HEC: hydrogen evolving catalyst, PEM: proton-exchange membrane, CB: conduction band, VB: valence band.

Excellent works have demonstrated the viability of hydrogen production from protons by using molecular catalysts [17,18,19,20, 21]. However, the development of efficient WOCs has been, up till the last decade, continuously hampered by the complex mechanistic and thermodynamic unfavorable nature of this reaction that involves the removal of 4 H^+ and 4 e^- from two H_2O molecules together with the formation of an O-O bond. In spite of the inherent difficulties, the field is nowadays effervescent, with numerous research groups involved and an awesome amount of papers describing new and improved WOCs appearing every year.

This review highlights the main achievements obtained in chemically, electrochemically and photochemically-driven molecular WOCs. Additionally, the inclusion of the latter on real PECs will also be described, and the future goals in the field will be briefly discussed.

2. Chemically and electrochemically-driven water oxidation catalysis

As stated before, the detailed knowledge of the structure of the Mn_4CaO_5 cluster of PSII has clearly become a source of inspiration for the generation of artificial catalysts based on transition metal ions that oxidize water to oxygen. In order to chemically activate a transition-metal catalyst for successfully oxidize water, the use of a sacrificial chemical oxidant is compulsory. A salt of Ce(IV) has been by far the most employed one. It should be noticed that although the generation of light-driven systems is the final goal in the field, the use of these chemical oxidants allows a simple and fast way of assessing the catalyst performance. However, the applicability of chemically-driven molecular WOCs in real and sustainable PECs for the photo-production of H_2 (Fig. 2) is impractical because the sacrificial chemical oxidant is irreversibly consumed, has a non-innocent character (since it is an indiscriminate oxidant) and is energetically inefficient (usually presenting high overpotentials).

Within this context, the use of electrochemically-driven WOCs addresses some of the above-mentioned issues, allowing the control of the applied overpotential. Therefore, in the way from chemical to light-driven WOCs potentially applicable in the modular construction of real PECs, electrochemically-driven systems have been developed as a step forward in this field. However, the direct application with a potentiostat of a redox potential through an electrode to an homogeneous catalyst usually ends up with a diffusion/electron-transfer (catalyst-electrode) controlled catalytic system [22]. In order to overcome this hurdle, the WOCs can be anchored onto the electrode surface, thus providing the necessary catalyst-support electric connection for the efficient electron removal and collection taking place during the oxidation process. The anchoring approach constitutes a step further towards the final incorporation of WOCs into feasible PECs. However, these hybrid systems must be stable against the oxidative and acidic conditions employed, and there must also exist a fast catalyst-electrode electron transfer when pursuing long-term reliable PECs.

The following subsections will point the most relevant examples reported until now of chemically and electrochemically-driven molecular WOCs.

2.1. Manganese and other first-row transition metal complexes

Since manganese is the transition metal selected by nature in the OEC to carry out the oxidation of H_2O, it has been the focus of much attention for chemists in the past decade. However, reliable examples of robust and active Mn molecular WOCs chemically triggered by pure electron transfer oxidants like Ce(IV) are still scarce. Several Mn-based systems coupled to oxo-transfer oxidants were reported to evolve oxygen from water, but their potential performance as catalase mimics [23,24,25] or transformation into Mn-oxide particles [26] introduced controversy on their real molecular nature. However, Styring and Kurz were the first authors to demonstrate that a dinuclear complex containing an anionic N_6O ligand in front of the oxo-transfer oxidant HSO_5^- was able to generate O_2 exclusively from the solvent (water) and not from the oxidizing agent, although unfortunately the compound underwent fast degradation during the reaction [27]. Three years later, Åkermark and collaborators could finally describe a stable Mn-based chemically-driven WOC, which consisted in a dinuclear complex containing an anionic chelating N_2O_3 ligand (**1**, Fig. 3) [28]. This complex yielded at pH 7.2 a turnover number (TON) of 25 with a turnover frequency (TOF) of 1.6 min^{-1} in the presence of $[Ru(bpy)_3]^{3+}$ (bpy = 2,2'-bipyridine) as the sacrificial chemical oxidant.

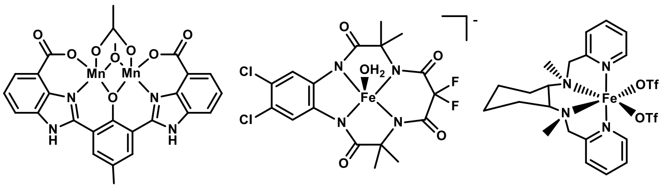
1 **2** **3**

Fig. 3. Structure of some of the most relevant chemically-driven Mn and Fe molecular WOCs.

Iron compounds have also been described as active molecular WOCs. Thus, in a pioneering work, Bernhard and co-workers reported a set of Fe(III) complexes containing highly oxidatively rugged tetraamido macrocyclic ligands, the best of which giving an initial TOF above 78 min^{-1} and an overall TON above 16 in the presence of Ce(IV) at pH 0.7 [29] (**2**, Fig. 3). Later on, Lloret-Fillol, Costas and co-workers described several octahedral Fe(II) complexes containing diverse tetradentate ligands, the best of which resulted in a TON of 360 and TOF of 14 min^{-1} when employing Ce(IV) as sacrificial oxidant, and a TON above 1050 and a TOF of 3.7 min^{-1} if using $NaIO_4$ as sacrificial oxidant (**3**, Fig. 3) [30]. The homogeneous *vs.* heterogeneous nature of the catalytic species of related Fe(II) complexes depending on the acidic or basic conditions employed was later on investigated by Nam, Llobet and Fukuzumi [31].

Regarding cobalt compounds, Hill *et al.* reported in 2010 the synthesis of an all-inorganic polyoxometalate (POM) complex with a cuban-like structure ($[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$), Co_4-POM, with a closely related structure to that of the Ru_4-POM catalyst **16** (*cf* Fig. 8 in next subsection), which resulted to be very active and stable in chemically-driven water oxidation catalysis, yielding a TON above 1000 and a TOF of 300 min^{-1} when employing $[Ru(bpy)_3]^{3+}$ as sacrificial oxidant at pH 8 [32].

With respect to electrochemically-driven water oxidation catalysis, Mn, Co and Cu complexes have given promising results. Thus, Smith *et al.* have very recently reported a mononuclear Mn(II) complex able to electrocatalytically oxidize water at pH 12.2 with a TON between 16 and 24 and a faradaic efficiency of 74-81% under a 0.8 V overpotential (**4**, Fig. 4) [33]. Also, Berlinguette and co-workers have reported the remarkably high WO activity of a single-site Co-aqua complex (**5**, Fig. 4) [34], in which the catalytic process took place with low overpotentials (*ca.* 0.5 V) when electrochemically triggered in a pH range of 7.6-10.3. Another interesting example was reported by Stahl and Llobet, consisting in a dinuclear Co complex isostructural to complex **8** shown in Fig. 5 with the only exception that Ru(II) ions were replaced by Co(II) ions (*cf* next subsection). This bimetallic species yielded 77% faradaic efficiency after applying 0.9 V overpotential at pH 2 [35].

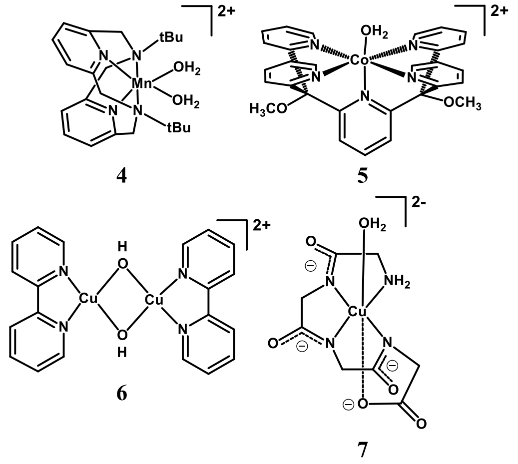

Fig. 4. Structure of selected electrochemically-driven Mn, Co and Cu molecular WOCs.

Complexes based on the cheap and earth-abundant Cu ion have been the last first-row transition metal species reported as electrocatalysts for the oxidation of water. Initially, a simple Cu-bpy complex was reported by Mayer to oxidize water by applying a 0.75 V overpotential at pH 13, with a TOF of 6000 min^{-1} and 90% faradaic efficiency (**6**, Fig. 4) [36]. Then, a mononuclear complex related to **6**, $[Cu(bpyOH)(OH)_2]$, has recently been reported by Lin *et al.* to oxidize water at 0.64 V overpotential and pH 12.4, yielding a TOF of 24 min^{-1} and a TON above 400 [37]. Another interesting example is the Cu mononuclear polypeptide complex (**7**, Fig. 4) described by Meyer, showing at pH 11 and 0.72 V overpotential similar TOF values than **6** [38].

2.2. Ruthenium complexes

The first molecular Ru complex acting as a chemically-driven WOC was the so-called blue-dimer (*cis,cis*-$\{[Ru(bpy)_2(H_2O)]_2(\mu\text{-}O)\}^{4+}$) reported 32 years ago by Meyer [39]. It consisted in an oxo-bridged dinuclear compound in which each Ru atom was bound to two bpy ligands and an exchangeable water solvent molecule. Inspired by the results of Meyer, 22 years later Llobet reported a much more stable and faster chemically driven-WOC in which the flexible and somehow unstable oxo bridge was replaced by the anionic and more rigid 3,5-bis-(2-pyridyl)pyrazole (Hbpp) bridge, a tetra-N-dentate ligand. Also, for each Ru atom a 2,2':6',2''-terpyridine (trpy) ligand replaced the two bpy ligands (**8**, Fig. 5) [40,41]. In the presence of Ce(IV) and under optimized conditions, catalyst **8** showed TON and TOF values of 512 and 0.78 min^{-1}, respectively [42,43].

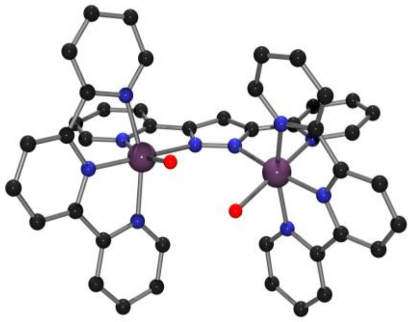

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Fig. 5. X-Ray structure of *in,in*-$\{[Ru(trpy)(H_2O)]_2(\mu\text{-}bpp)\}^{3+}$ reported by Llobet [40]. Color code: Ru, purple; N, blue; O, red; C, black. All H atoms have been removed for clarity.

From that moment on, a revolution in the research of Ru-based chemically and electrochemically-driven WOCs took place, with significant advances in the reported TOF and TON values as well as in the understanding of the pathways through which they form O-O bonds (detailed and exhaustive information can be found in references [44,45,46,47]). Thus, their ability to reach a wide range of oxidation states within a small potential range, as well as their relative stability, especially when polypyridylic ligands are present, have been the main reasons why Ru-based complexes have been by far the most studied chemically and electrochemically triggered WOCs. Hence, only the most relevant results will be explained below.

Following the idea of combining two Ru atoms with a rigid bridging ligand, Thummel and collaborators reported a symmetrical complex with a TON of 689 (**9**, Fig. 6) [48].

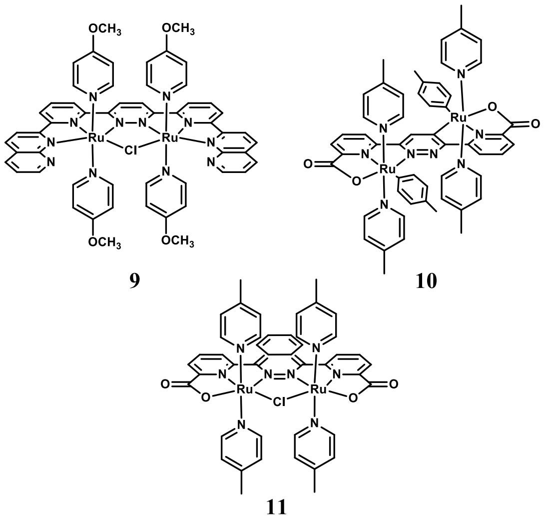

Fig. 6. Structure of some of the most relevant chemically-driven dinuclear Ru WOCs reported to date.

A year later, Sun and Åkermark introduced two negatively charged carboxylate groups within the bridging pyridyl scaffold, provoking an increase in the TON up to 1690 (*trans*-catalyst **10,** Fig. 6) [49]. Another year later, the same authors replaced the central pyridazine group by a phtalazine moiety (**11,** Figure 6), thus forcing a *cis* configuration, constituting the most robust chemically-driven dinuclear Ru WOC reported until now (TON and TOF values of 10400 and 72 min^{-1}, respectively) [50].

In addition to dinuclear Ru catalysts, during the last decade dozens of mononuclear Ru complexes have been also tested as chemically-induced WOCs because of their simpler and more versatile synthesis compared to the arduous reactions required to synthesize dinuclear compounds. Especially interesting are the complexes shown in Fig. 7. Thus, Thummel and co-workers reported a Ru-N_5Cl complex (**12**, Fig. 7) showing a TON of 1170 [51], whereas Sun and co-workers described two Ru-N_4O_2 compounds with spectacular TON and initial TOF values (550 and 13.8 min^{-1} for **13** and 2000 and above 2500 min^{-1} for **14**, respectively, Fig. 7) [52]. In the last two cases it is believed that the reason for their impressive performance is due to the Ru high oxidation states stabilization by the negatively charged carboxylate ligands [53]. Within the same family of complexes, the most impressive results have been obtained with another Ru-N_4O_2 complex reported by Llobet and Sun (**15**, Fig. 7), with a water oxidation activity comparable to that of PSII (TON of 50000 and TOF of 18000 min^{-1}). In this case, the π-π interaction among catalyst molecules provoked by the bicyclic nature of their isoquinoline ligands favors an extremely fast O-O bond formation through a bimolecular coupling of two M-O active sites [54].

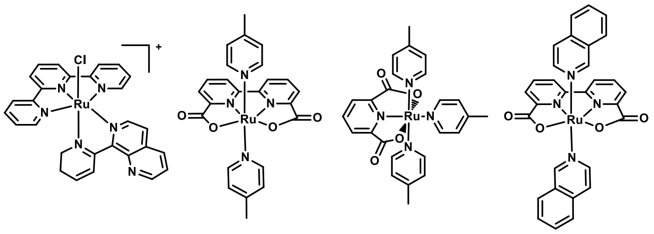
12 **13** **14** **15**

Fig. 7. Structure of selected chemically-driven mononuclear Ru WOCs reported to date.

Finally, with the aim of avoiding the frequently observed degradation of the surrounding organic ligands due to the highly oxidizing conditions used in chemically-driven water oxidation catalysis, which is one of the main deactivation pathways of molecular WOCs, Bonchio, [55] on the one hand and Hill on the other [56] independently reported in the same year the synthesis of a Ru_4-POM catalyst (**16**, Fig. 8). This catalyst resulted very stable against degradation, and thus its TON was only dependent on the amount of sacrificial chemical oxidant employed, while its TOF resulted to be 7.5 min^{-1}.

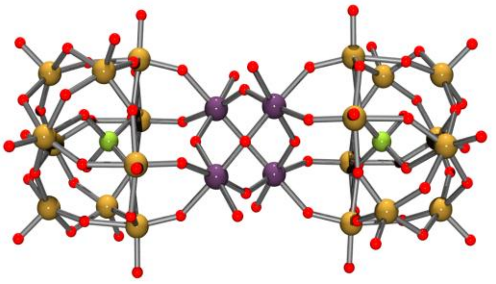
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Fig. 8. X-Ray structure of $[Ru_4O_4(OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$. Color code: Ru, purple; O, red; Si, green; W, yellow. All H atoms have been removed for clarity.

Once embedded into conductive/semi-conductive materials through either covalent or noncovalent interactions, several Ru-based molecular complexes have proven to be active electrocatalysts for water oxidation. One relevant example is a dinuclear Ru-Hbpp complex analogous to **8** (Fig. 5) reported by Llobet and collaborators with the only difference of adding a pyrrole group within the trpy ligand; *i.e.*, trpy was replaced by t-trpy (t-trpy = 4'-(*p*-pyrrolylmethylphenyl)-2,2':6',2''-terpyridine), which enabled its electro- and co-electropolymerization (**17**, Fig. 9) onto fluorine-doped tin oxide (FTO/poly-**17** and FTO/poly-(**17**-*co*-cobaltabisdicarbollide)) [57]. The resulting co-electropolymerized hybrid materials were capable of oxidizing water with a TON of 120 and a TOF of 1.44 min^{-1}, clearly showing the benefits of site-isolation and dilution of the catalyst at the electrode surface in order to avoid catalyst-catalyst deactivation pathways through oxidative degradation.

Tanaka and co-workers employed noncovalent interactions to directly deposit a molecular dinuclear Ru-WOC into an indium tin oxide (ITO) electrode (ITO-**18**, Fig. 9) [58 , 59]. This hybrid material generated oxygen with an exceptional TON of 33500 at pH 4 but with a high overpotential (0.905 V). Unfortunately, the catalyst experimented significant leaching after 40 h. Four years ago, Bonchio, Prato and collaborators reported the electrostatic immobilization of the Ru-POM catalyst **16** (Fig. 8) into modified ITO electrodes, in which functionalized carbon nanotubes bearing polycationic dendrimeric substituents were used in order to improve the electrical contact between **16** and the electrode [60]. The resulting nano-hybrid material oxydized water at pH 7 with a TOF of 5.1 min^{-1} at low overpotentials (0.35-0.60 V). More recently, Sun and collaborators reported a molecular Ru catalyst derivative of **13** (**19**, Fig. 9), in which its pyrene moieties allow the immobilization of **19** on mutilwalled carbon nanotubes (MWCNT) by noncovalent π-π interactions. The MWCNT-modified ITO showed at pH 7 and 0.28 V overpotential a TON of 11000, a TOF of 18 min^{-1} and a 96% faradaic efficiency [61]. Finally, Llobet, Escriche, Sala and co-workers very recently reported the use of another dinuclear Ru-Hbpp complex analogous to **8** (Fig. 5) where positively charged pyridinium moieties were employed to electrostatically immobilize the catalyst ($\{[Ru(L1^+)]_2(\mu\text{-bpp})(\mu\text{-Cl})\}^{4+}$, $L1^+$ = 4′-(-p-(Pyridin-1-ylmethyl)phenyl)-2,2′:6′,2′-terpyridine) onto several inorganic oxides such as SiO_2 or FTO-TiO_2 and the polymeric Nafion, obtaining different degrees of stability and performance [62].

As stated above, another strategy for obtaining electrochemically-triggered WOCs consists in the covalent tethering of the molecular catalyst onto the surface of conductive/semi-conductive solid supports. This approach has been mainly examined by Meyer and co-workers, who anchored the mononuclear $[Ru(Mebimpy)(4,4'\text{-}(CH_2PO_3H_2)_2bpy(OH_2)]^{2+}$ complex (Mebimpy = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine) on FTO, ITO and nanoITO [63,64]. At pH 5, this material electro-catalytically oxidizes water with a TON of 11000 and a TOF of 21.6 min^{-1} during 8 h. The next step forward was the demonstration that a redox-mediator, such as $[Ru(bpy)_2(B)]^{2+}$ (B = bpy or a bpy derivative), could drive water oxidation to an adjacent Ru mononuclear molecular WOC. Molecular assemblies were prepared and anchored onto ITO, FTO and FTO-TiO_2, showing constant catalytic activity, and the best system resulted in a TON of 28000 and a TOF of 36 min^{-1} (ITO-**20**, Fig. 9) [65]. Also, recent works on the covalent anchoring of Ru molecular WOCs on carbon surfaces have shown very promising results. Thus, Sun and co-workers have anchored an aryl azide derivative of **14** (**21**, Fig. 9), showing a TOF of 4.38 min^{-1} at pH 7 and 0.3 V overpotential [66].

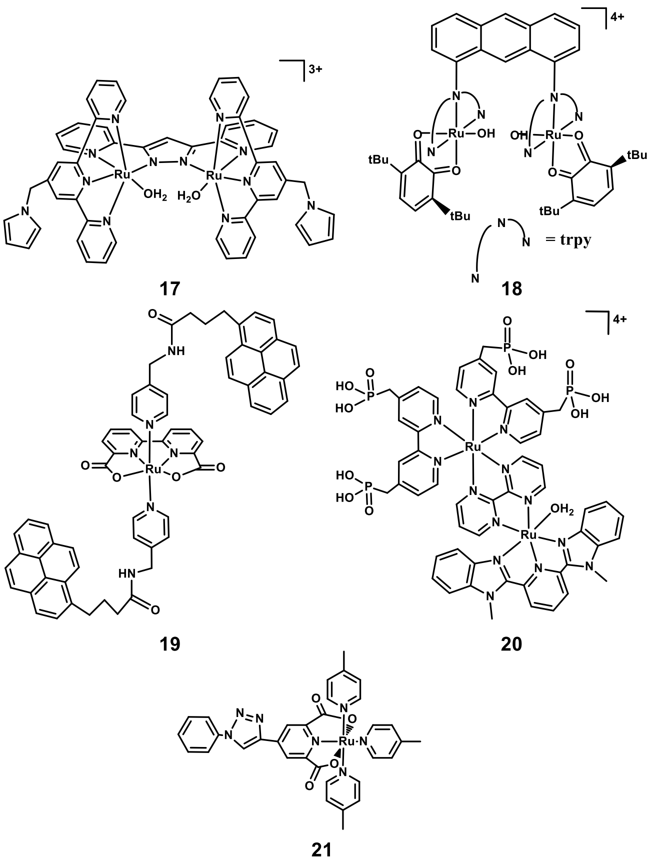

Fig. 9. Structure of selected electrochemically-driven Ru molecular WOCs.

2.3. Iridium complexes

Despite the considerably high price of this precious metal (about 20 USD/g versus the 2 USD/g of ruthenium or the 0.007 USD/g of copper), during the last six years interesting Ir-based molecular WOCs have been also reported. Originally, relevant examples in the presence of Ce(IV) as sacrificial oxidant at acidic pH were described by Bernhard and co-workers, yielding a TON of 2760 (**22**, Fig. 10) [67], and by Crabtree, Brudvig and Eisenstein, obtaining an initial TOF of 20 min^{-1} (**23**, Fig. 10) [68].

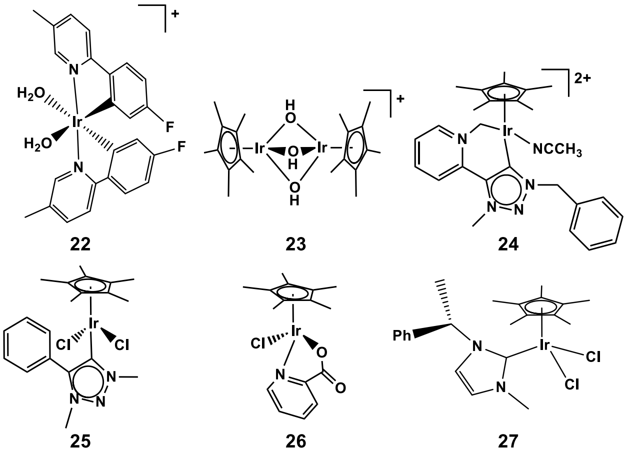

Fig. 10. Structure of selected chemically-driven Ir molecular WOCs.

Later on, Bernhard and Albrecht introduced abnormally bound N-heterocyclic carbenes as ligands for Ir, obtaining remarkable results, with a TOF of 1.4 min^{-1} and a TON around 10000 after 5 days in the presence of Ce(IV) for **24** [69], and a TOF of 2 min^{-1} and a TON of 22800 after 10 days in analogous conditions for **25** [70] (Fig. 10). In 2012, Macchioni and Llobet reported the fastest molecular Ir WOC in the presence of Ce(IV) based on pyridinecarboxylate ligands (initial TOF of 287 min^{-1}, complex **26**, Fig. 10) [71]. A year later, Lloret-Fillol, inspired in Albrecht and Bernhard's previous works, reported the most robust chemically-driven molecular Ir WOC (**27**, Fig. 10), with a TON of 400000 and a TOF of 150 min^{-1}. These authors also showed the improved performance of Ir molecular catalysts when using $NaIO_4$ as the sacrificial chemical oxidant instead of Ce(IV) [72].

Despite the sound results reported until now with this metal, a serious controversy about the molecular or colloidal/heterogeneous nature of the active species opened in 2011. Grotjahn, Rheingold and co-workers reported that after Ce(IV) addition to several molecular iridium complexes iridium oxide nanoparticles were quickly formed, thus possibly being the real active species under these conditions [73]. Analogous nanoparticles were also detected by Crabtree and collaborators from **23** when using $NaIO_4$ as the sacrificial oxidant [74]. Furthermore, Macchioni et. *al* thoroughly studied the decomposition pathways that the Ir-Cp* type of complexes can undergo (see as an example complexes **23**-**27**), involving the C-H activation of one of the Me groups of the Cp* ligand and accounting for the putative formation of CO_2 and/or acetic, formic and/or glycolic acids as degradation products [75].

Finally, Ir molecular WOCs have also been studied under electrochemical conditions (**23** and **28** [76], and **29** [77], Fig. 11). Crabtree and collaborators have analyzed the nature of the final catalytically active species in the case of **28** and **29**, concluding that, for the former, amorphous iridium oxide formation takes place, generating an astonishingly active and stable material able of performing water oxidation at 0.2 V overpotential during several days, while for the latter no sign of deposition was found, thus pointing to an homogeneous nature [77], which had also been corroborated in the case of chemically-triggered water oxidation [74].

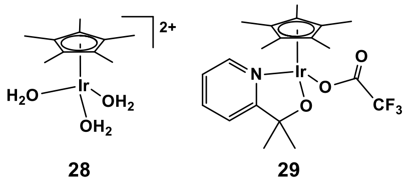

Fig. 11. Structure of selected electrochemically-driven Ir molecular WOCs.

3. Photochemically- and photoelectrochemically-driven water oxidation catalysis and first examples of PECs

Three different approaches can be addressed when trying to perform water oxidation with the use of light. The first one consists in building up a three-component system containing a photosensitizer (P), a molecular WOC and a sacrificial electron acceptor (SEA). $S_2O_8^{2-}$ or $[Co(NH_3)_5Cl]^{2+}$ have been the most used SEAs, although $[Co(bpy)_3]^{3+}$ or $[Co(phen)_3]^{3+}$ have also been employed (phen = phenantroline). On the other hand, $[Ru(bpy)_3]^{2+}$ and derivatives have been by far the most used compounds as Ps thanks to their strong visible absorbance, long excited-state lifetimes and high redox potentials. When absorbing light, P reaches its excited state (P*) and transfers an electron to the SEA, thus generating an oxidized P^+ form, which in turn provokes the oxidation of the WOC and the set off of the catalytic cycle. Thus, the absorption of photons ends up generating the active form of the WOC, able to produce O_2 from water. One of the main problems related to these systems is the stability of P due to the extreme reactivity of singlet oxygen formed during photocatalysis.

The second approach consists in the use of covalent dyad P-WOC or triad P-WOC-P supramolecular assemblies. In this case the two metal complexes, each one responsible for a different chemical function, are covalently bound within the same metal complex. In some cases, these dyads and triads have shown improved performances than the related three-component systems [45,78].

Finally, the third chemical approach is based on anchoring both the P and the WOC onto a n-type semiconductor surface, thus producing a photoanode [45,79].

The following final subsections will describe the most relevant examples reported until now of photochemically or photoelectrochemically-driven WOCs (mainly molecular compounds) and their performance when included within a PEC.

3.1. Iridium compounds

The first PEC for water splitting was developed in 2009 by Mallouck and collaborators [80]. However, in this work they did not use any molecular Ir WOC, but IrO_2 nanoparticles, which were connected to TiO_2 by an heteroleptic $[Ru(bpy)_3]^{2+}$ derivative acting as P and containing both malonate and phosphonate groups, which are chemically selective for IrO_2 and TiO_2, respectively. In this system, the TON was 16 and the quantum yield (ϕ, the number of photons used to generate oxygen with respect to the total amount of photons) was 0.09.

Brudvig and Crabtree carried out the use for the first time of a molecular Ir WOC in a real PEC in 2011 [81]. In this work, a Cp* derived complex acting as WOC (**30**, Fig. 12) and a porphyrin acting as P, both containing a carboxylate group for their attachment to TiO_2 nanoparticles, generated a photocurrent after illumination when using a small external bias.

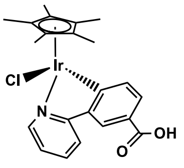

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Fig. 12. Structure of the photoelectrochemically-driven Ir molecular WOC developed by Brudvig and collaborators [81].

A year later, Albrecht and co-workers also checked the photoelectrochemical activity of the molecular Ir WOC **25**. Nevertheless, the results were not as spectacular as when it had been driven chemically, mainly because of the lack of stability as well as pH dependent activity concerns [70].

3.2. Ruthenium compounds

Ru complexes, especially those including polypyridylic ligands, have been by far the most studied molecular WOCs in light-driven water oxidation because of their stability and versatility, as already stated in section 2.2. Thus, a selection of the most relevant works will be presented below.

In 2009, Hill and Lian used the tetranuclear Ru-POM catalyst (**16**, Fig. 8), obtaining a TON of 350 and a ϕ of 0.09 when employing $[Ru(bpy)_3]^{2+}$ as P and $S_2O_8^{2-}$ as the sacrificial electron-acceptor [82]. A year later, a TON of 80 and an outstanding ϕ of 0.30, at this point the highest ever achieved with a molecular assembly in light-driven water oxidation catalysis, implying that 60% of the photons were used to generate O_2, was measured by Campagna, Bonchio and Puntoriero with a tetranuclear Ru dendrimer as P and $S_2O_8^{2-}$ as SEA [83].

In 2010, Sun and collaborators obtained for catalyst **10** (Fig. 6) an outstanding TON of 1270 using $S_2O_8^{2-}$ as SEA [84], and in the same year they reported the first example of PEC employing a Ru molecular WOC [85]. In this work, catalyst **13** (Fig. 7) was immobilized into Nafion and a $[Ru(bpy)_3]^{2+}$ phosphonate derivative used as P was anchored onto FTO-TiO_2. TON and TOF values were 16 and 0.45 min^{-1}, respectively, and a small extern voltage was needed for a correct performance of the whole system. The same authors recently improved this system in 2013 by anchoring a silane-functionalized derivative of **13** onto a TiO_2 surface, which also contained a phosphonate $[Ru(bpy)_3]^{2+}$ derivative as P [86]. After 500 seconds of illumination, a TON of 498 and a TOF of 60 min^{-1} were obtained with regards to O_2 formation, accounting for a 83% faradaic efficiency, thus constituting the best reported PEC until now based on a molecular WOC.

Very recently, since 2012, Ru molecular dyads and triads have also been tested in light-driven water oxidation catalysis. Some of the most promising examples are a triad based on **13** in which the catalyst is bound through its two *trans*-pyridine groups to $[Ru(bpy)_3]^{2+}$ via an amide bond (**31**, Fig. 13), described by Sun and Li to produce a TON of 38 and a TOF of 4.7 min^{-1} [78], a dyad prepared by Sun *et al.* also inspired in **13** in which the catalyst binds through its terminal carboxylate group and a Zr(IV) ion to a phosphonate derivarive of $[Ru(bpy)_3]^{2+}$ (**32**, Fig. 13), yielding a faradaic efficiency of 4.1% [87], and a dyad reported by Thummel and collaborators, in which a bis-pyridyl-naphthyridine bridge connects a Ru(trpy)-based catalyst and a Ru(bpy)-based P (**33**, Fig. 13), obtaining a TON of 134 after 6 hours of irradiation [88].

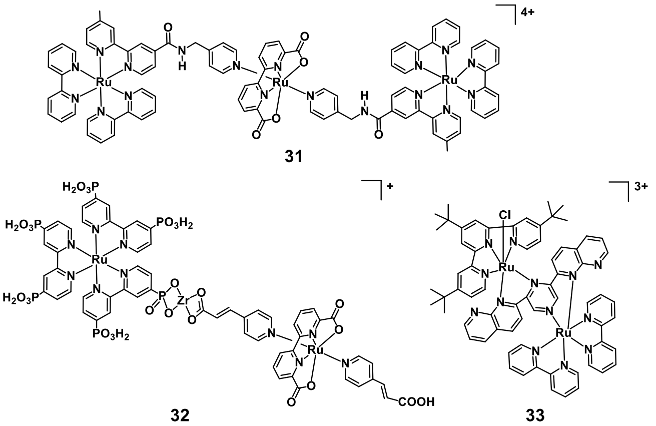

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Fig. 13. Structure of the most relevant Ru molecular dyads and triads used in light-driven water oxidation catalysis.

3.3. Manganese, cobalt and vanadium compounds

Again, biologically relevant first row transition metal ions have also been tested in molecular-based light-induced water oxidation catalysis. Thus, in 2010 Spiccia and collaborators reported the use of a bioinspired $[Mn_4O_4L_6]^+$ cluster (*cf.* Fig. 1) implanted into a nafion membrane that acted as WOC in combination with a carboxylate $[Ru(bpy)_3]^{2+}$ derivative onto FTO-TiO_2 acting as P, constituting the first example of a PEC including a Mn molecular WOC [89]. They obtained a TON of 13 and a TOF of 0.78 min^{-1} without the aid of any external bias. However, the same author reported a year later that this Mn-oxo cluster decomposes upon light irradiation, generating a mixed Mn(III/IV)-oxide material that could be the real catalyst in this system [90]. Interestingly, this year 2014 a stable Mn_4-POM ($[Mn^{III}_3Mn^{IV}O_3(CH_3COO)_3(A\text{-}\alpha\text{-}SiW_9O_{34})]^{6-}$) in light-driven water oxidation catalysis has been reported by Bonchio *et al.*, yielding a TON of 5.2 and a TOF of 0.17 min^{-1} when employing $[Ru(bpy)_3]^{2+}$ as P and $S_2O_8^{2-}$ as SEA, although the ϕ is still low [91].

Regarding cobalt compounds, Lian and Hill reported in 2011 that the Co_4-POM catalyst $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ is very active and stable in light-driven water oxidation catalysis, yielding a TON of 220 and a ϕ of 0.15 when employing $[Ru(bpy)_3]^{2+}$ as P and $S_2O_8^{2-}$ as the SEA [92]. A year later, in 2012, Sakai and collaborators used a Mo-based POM with a di-Co(III) core ($[Co_2Mo_{10}O_{38}H_4]^{6-}$) that yielded a TON of 154 and a ϕ of 0.15 at pH 8 when employing $[Ru(bpy)_3]^{2+}$ as P and $S_2O_8^{2-}$ as the SEA [93]. This year 2014, Hill *et al.* have reported an isostructural Co_4-POM catalyst to the one used in 2011 with the only difference that the 2 PO_4 units have been replaced by 2 VO_4 units ($[Co_4(H_2O)_2(VW_9O_{34})_2]^{10-}$, **34**, Fig. 14), thus generating an exceptionally fast WOC under analogous conditions, yielding a TOF above 60000 min^{-1}, a ϕ of 0.34 and a final O_2 yield twice as high as the former Co_4-POM [94].

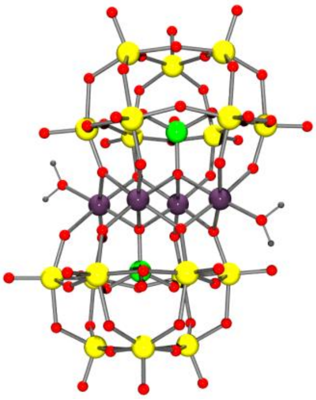

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Fig. 14. X-Ray structure of $[Co_4(H_2O)_2(VW_9O_{34})_2]^{10-}$. Color code: Co, violet; V, green; W, yellow; O, red; H, gray.

Finally, very recently Santoni, Scandola and Campagna have reported for the first time a V-based POM ($[V_6O_7(OCH_3)_{12}]^-$) able to perform photoinduced water oxidation in the presence of $[Ru(bpy)_3]^{2+}$ as P and $S_2O_8^{2-}$ as the SEA with a ϕ of 0.20 [95].

4. Final remarks

The imperative need of a clean and renewable energy source to replace the contaminating fossil fuels has provoked the appearance of a lot of research studies in light-driven water oxidation catalysis. Within the field, the oxidation of water into O_2 has been recognized as the bottleneck process hampering a sustainable and commercially viable production of H_2. Fortunately, the tremendous efforts performed in the field for the last ten years have been rewarding. Thus, we have gone from a unique to hundreds of active WOCs whose kinetic rates have increased in more than 4 orders of magnitude, with some catalysts that have already reached the figures of the natural OEC. Therefore, with efficient and robust catalysts on hand, water oxidation does not longer represent the bottleneck step for the construction of a commercial PEC for the photo-production of H_2. However, the difficulty in arranging the P-WOC, P-anode and anode-cathode electronic connections in a way that fast electron transfer can occur at every step while charge recombination is avoided, still hampers the final goal. Even nowadays, it is still difficult to obtain P-WOC systems able to keep the electron flow in the right direction. Therefore, although efficient WOCs, HECs and Ps have been described to date, more work needs to be done in order to obtain PECs with improved electronic connections and significantly enhanced performances.

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