Perspectives of Redox-Active Ligands in Artificial Photosynthesis

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Abstract

Organic ancillary ligands can cooperate with metal centers in different ways in molecular catalysts of the very important oxygen evolving reaction. In this overview, we focus on what can be gained of such a cooperation and bring examples on the possible useful outcomes of redox state changes in ancillary ligands. Analogies are also highlighted if apply, with the cooperation between the natural oxygen evolving complex and the redox-mediating Tyrosine-Histidine pairs found in photosystem II.

Introduction

Natural oxygenic photosynthesis is a singular process that has been fundamentally shaping the image of the biosphere on Earth since the advent of the first light-powered life forms. Solar to chemical energy conversion by living organisms involves carbohydrate molecules as chemical energy carrier that capacitate them to fuel their own life processes as needed through cellular respiration (Dau et al. 2017). A substantial part of the photosynthesized organic compounds has been fossilized in millions of years that nowadays represents an essential energy source as fossil fuel and feedstock for the modern human society (Balzani et al. 2008). While in many respect, it means safety and comfort, in other it presents the greatest threat humankind ever faced caused by itself. The extent of greenhouse gas emission, pollutants released into the environment, wasteful thinking about the available resources, these all root from a wrong perception that has prevailed for decades, if not for a century (Pachauri et al. 2015); for we have thought that nature could withstand this increasing load. However, it has become clear that this perception is false. Without feedback (or simply, suitable coupling) neither natural nor artificial functionalities will create a balanced renewable system, no matter how efficient or profitable individual, functional parts were put together. We believe that this is an important, if not the most important piece of knowledge that can be deciphered from natural photosynthesis for its observers, beyond the obvious aim to create artificial systems based on renewable resources (Nocera 2012; Faunce et al. 2013; Pantazis 2021; Osman et al. 2021). Or, should we rather be the plummet that needs to be taken off the scales to rebalance?

Plants harvest solar energy by PS, produce O_2 from water molecules, and as a coupled system, convert CO_2 into carbohydrates in the course of the Calvin cycle (Krewald et al. 2015; Pantazis 2021). A Z-shaped energy diagram is generally used to illustrate the cascade of electron transfer steps. The energy to drive this reaction cascade is supplied by light absorption of P_{680} in PS II, and P_{700} in PS I (Grimes et al. 2008). Indeed, photons are absorbed by the chlorophyll-containing antenna system in the thylakoid membrane as shown in Scheme 1, furnishing PS II with very high quantum efficiency. The excited state molecule P_{680}^+ gives electrons to an external quinone (Q), reducing it to hydroquinone (H_2Q). Electron vacancies are filled by water oxidation producing O_2 as byproduct, carried out by the OEC, which contains an oxo-bridged tetramanganese calcium cluster Mn_4O_5Ca (Krewald et al. 2015).

Several in-depth analysis have been published discussing the structure and operating mechanism of PS II and that of the OEC (McEvoy and Brudvig 2006; Umena et al. 2011; Kärkäs et al. 2014; Shen 2015; Zhang

and Sun 2019; Zabret et al. 2021). Therefore, herein we would like to emphasize only two small details that are worth considering. First, an OEC has a certain average lifetime of ca. 30 minutes under full sunlight; because light quanta induce degradation and the molecular integrity eventually breaks down (Inoue et al. 2011). Thus, the OEC has to be protected but also continuously rebuilt by repair mechanisms strongly coupled to energy conversion. Note that the $\text{Mn}_4\text{O}_5\text{Ca}$ cluster itself binds to the protein and assembles spontaneously from free Mn^{2+} and Ca^{2+} in solution under visible light, a process called photoactivation (Dasgupta et al. 2008).

From the perspective of the many artificial catalytic systems, where the performance-meter is the 'as-long-as-possible-lifespan' a similar feedback mechanism might seem rather contra-productive, since it is operated at the expense of robustness and maximal energy efficiency. Nevertheless, it should make a designer of artificials wonder, why this natural system subsisted a very long evolutionary process, still it probably remains the best practice in energy conversion by Nature. Perhaps it was this feature of the natural OEC that eventually inspired the idea of a Co-based self-healing OER catalyst (Costentin and Nocera 2017) that has to do historically with the century-old attempt of determining the potential for the $\text{Co}^{\text{III/II}}$ couple (Coehn and Gläser 1902). In any case, the electrochemical behavior of cobalt has certainly not changed in a hundred years, which may give cause for optimism in terms of the flexibility of the human approach.

The second detail, which is the starting point of our focused review, is that PS II contains redox active organic co-factors beside the inorganic ones. As integral part of the OEC a redox active tyrosine residue (Tyr-Z) coupled to an H-bonded His-Z unit is found in close proximity to the $\text{Mn}_4\text{O}_5\text{Ca}$ cluster, shuttling PCET and synchronizing the light-induced Kok cycle with the distal transport of the charge carriers between P_{680}^+ and the cluster (Kok et al. 1970). Another tyrosine-histidine pair, Tyr-D and His-D is in redox contact with both Tyr-Z and $\text{Mn}_4\text{O}_5\text{Ca}$. Both redox co-factors are present in every known oxygen evolving organism therefore it is safe to state that no photosynthesis as we witness it today would be possible without these small molecular fragments.

Since the above tyrosine residues may be regarded as a natural archetype (and inspiration) for the utilization of redox cooperating ligands in artificial systems, in the first section we will discuss the role of these small molecular parts in PS II (Styring et al. 2012). Then, artificial catalysts for the OER will be discussed in context of possible analogies to the OEC and the Tyr-His pairs in PS II. Importantly, ancillary ligands may cooperate with metal centers in different ways upon the buildup of oxidizing equivalents to trigger OER catalysis. The outcome of the cooperation can be very different, too. It can increase the stability or the efficiency, but it can also easily seal the fate of a catalyst, leading to rapid decomposition. Therefore, the sections about artificial catalysts have been structured with a focus on the outcome of the redox cooperation by different ancillary ligands.

Effect Of Tyrosine On The Mechanism Of The Natural Oxygen Evolving Reaction

In nature metal co-factors and perhaps to a lesser extent, yet, of comparable effect redox active organic moieties are key components to enzymatic catalysis to facilitate biochemical redox reactions. In this context, the evolutionary role of the phenolic side-chain of tyrosine cannot be over-emphasized. The OEC too, strongly relies on two tyrosine residues found in its protein backbone, Tyr-Z and Tyr-D that are involved in the regulation of the sequential transfer of electrons and protons between P_{680}^{+} and the Mn_4O_5Ca (Siegbahn and Blomberg 2004; McEvoy and Brudvig 2006; Styring et al. 2012; Narzi et al. 2014; Nakamura et al. 2020).

The oxidation of H_2O molecules may take place in four different ways producing $HO^{\bullet}$, H_2O_2 , $O_2^{\bullet-}$, or O_2 , depending on the number of electrons removed. The $4e^{-}$ oxidation pathway (OER) yielding triplet O_2 as product is the lowest in energy although, it is still energetically uphill and the most complex reaction of all at the molecular level, since four O–H bonds from two water molecules have to be broken and an O–O bond has to be formed. This $4e^{-}$ oxidation occurs at the OEC of PS II.

Mechanism of the oxygen producing S-state (or Kok) cycle

Since Kok has proposed that a ‘trapping center, or an associated catalyst’ successively accumulates oxidizing equivalents to link the $1e^{-}$ progression in photo-excitation to the $4e^{-}/4H^{+}$ abstraction from two H_2O molecules to yield O_2 (Kok et al. 1970), the catalytic center has been conceived as progressing in a cycle of five oxidation states, S_0 to S_4 (Scheme 2). In the S_1 state the system is stable in the dark, while O_2 is produced only after reaching the S_4 state, during a single photon-induced $S_4 \rightarrow S_0$ transition. The e^{-}/H^{+} stoichiometry over the four steps corresponds to 1:0:1:2 (Förster and Junge 1985). The photo-induced charge separation in PS II generates the strongest oxidant known in biology, P_{680}^{+} , for which the estimated redox potential is *ca.* +1.2 V vs. NHE (Rappaport and Diner 2008). This potential is enough to drive each of the transitions in the Kok cycle, and ultimately extract electrons from water molecules. At the same time, interfacial tyrosine regulators are required to adjust the sequential charge accumulation in Mn_4O_5Ca .

Outstanding achievements have led to the presently known detailed models for O_2 formation from water by the OEC, including valence and spin state analysis of the Mn ions in the various S-states (Cox et al. 2013; Krewald et al. 2016; Pantazis 2018). In conjunction with spectroscopic and kinetic investigations, structural analysis using femtosecond X-ray pulses, with improved spatial and temporal resolution, selective characterization of the different states resulted in the native structure of PS II (Suga et al. 2015) and the structural analysis of the intermediates in the Kok cycle (Kern et al. 2018).

A thorough overview on the evolution of structural and kinetic models of PS II and OEC has been provided recently (Junge 2019). We rely on the current works cited therein, including the stepwise S-state structural analysis (Krewald et al. 2016; Kern et al. 2018), and further considerations made on Tyr-Z (Nakamura et al. 2020), in order to explain the role of the Tyr-His pairs at the different stages of the Kok cycle.

Structure of the $\text{Mn}_4\text{O}_5\text{Ca}$ cluster (OEC) – initial S-states

The structure of the $\text{Mn}_4\text{O}_5\text{Ca}$ cluster is often depicted as a ‘distorted chair’ since the first atomic resolution crystal structure of PS II has been reported (Umena et al. 2011) (Scheme 3a).

This metal cluster along with the surrounding protein scaffold is very stable, and the expected structural changes during the cycle are subtle (Zhang et al. 2017a), thus the positions of P_{680} , Tyr-Z (and Tyr-D) and the $\text{Mn}_4\text{O}_5\text{Ca}$ cluster vary very little. In states S_0 and S_1 the cluster adopts low spin configurations with $S_T = \frac{1}{2}$ and 0 total spin, respectively. In S_0 the O5 bridge (Scheme 3a) is protonated, one Mn^{III} and the Ca^{2+} ion both have aqua ligands.

All remaining ligands in the first coordination sphere are carboxylates (Glu, Asp and Ala) derived from the so called D1 and CP43 polypeptides except for a nitrogen-donor His ligand of D1, which coordinates to a Mn ion (the peptide ligands were omitted from Scheme 3a). Imaging the changes taking place in the coordination of O5 is of particular importance because spectroscopic results implicated O5 to originate from one of the two reacting substrate water molecules.

The photogenerated cation P680^{++} is coupled to the $\text{Mn}_4\text{O}_5\text{Ca}$ cluster via the intermediary redox active Tyr-Z, which works as a $1e^-$ rectifier (Scheme 2). Initial electron transfer between P680^{++} and Tyr-Z occurs on a nanosecond time scale, whereas the subsequent electron transfer between Tyr-Z^{++} and $\text{Mn}_4\text{O}_5\text{Ca}$ occurs on a micro- to millisecond time scale, depending on the actual S-state. Fast reversible redox transition of Tyr-Z/Tyr-Z $^{++}$ is an intrinsic property originating from the proximal His-Z residue that acts as base, stabilizing the deprotonated Tyr-Z (Scheme 3b), while structured water molecules bound to the Ca^{2+} ion also tune its redox potential. Tyr-Z $^{++}$ is a strong oxidizer with a redox potential greater than +0.9-1.0 V vs. NHE (Vass and Styring 1991). Due to the close proximity of the $\text{Mn}_4\text{O}_5\text{Ca}$ cluster Tyr-Z $^{++}$ is reduced very fast, by means of an S state dependent kinetics, therefore its direct detection is complicated (T. Babcock et al. 1976).

The S_2 -state

The best characterized state of the catalytic cycle is undoubtedly S_2 , in which the cluster is oxidized by $1e^-$ compared to S_1 . The manganese oxidation states in S_2 are $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_3$, leading to an EPR-active $S_T = 1/2$ spin configuration. Importantly, S_2 can adopt a low and a higher spin form ($S_T = 1/2$ for the open cube-like form S_2^A and $S_T = 5/2$ for the closed cube form S_2^B). At this point in the cycle a spin state interconversion takes place on a microsecond timescale under physiological conditions with a low energy barrier for the O5 translocation, thus enabling the conversion of S_2^A to S_2^B that in turn can progress to S_3 (Styring et al. 2012; Pantazis et al. 2012; Bovi et al. 2013). The low spin configuration up to the S_2^A state of the OEC has been suggested to prevent ‘short circuiting’ of the $4e^-$ oxidation at a $2e^-$ level of peroxide formation that may help to increase the lifetime of the OEC (Rutherford 1989). In order to proceed further

from the low spin S_2 Tyr-Z $^{*+}$ state Ca^{2+} is also indispensable, facilitating the S_2^A/S_2^B interconversion and the stabilization of S_3 . Deprotonation of the coordinating water molecule is coupled to the $Mn^{III} \rightarrow Mn^{IV}$ oxidation in S_2^B and it occurs after formation of Tyr-Z $^{*+}$, which reorients the electric dipole of the Mn_4O_5Ca cofactor so that it supports the coupled charge transport (Retegan et al. 2016).

The S_3 - and S_4 -states

In S_3 , all Mn ions adopt oxidation state IV. Note that the structure of S_3 in Scheme 3 may not represent the final state. This is because the S_2 to S_3 transition is a multistep process including manganese oxidation, substrate deprotonation, internal rearrangement and water binding. The resulting S_3 has been described as (Tyr-Z) Mn^{IV}_4 or (Tyr-Z $^{*+}$) $Mn^{IV}_3Mn^{III}$ (Retegan et al. 2014; Cox et al. 2014).

In S_3 two oxygen sites are close to each other and may couple together in the subsequent S_4 state Tyr-Z $^{*+}Mn^{IV}_4$ upon the final photoexcitation. The protonation states of the water-derived ligands have not been established yet for each intermediate and vivid ongoing research aims at resolving the deprotonation sequences (Yang et al. 2021). According to computational studies on the O-O bond formation, it is likely that an oxyl radical is formed in the S_4 state, most probably a terminal oxyl, which subsequently couples with an oxo bridge to form the O-O bond (Siegbahn 2009). Upon O_2 formation the release of the first proton takes place in the time range of 100 μs followed by a slower deprotonation step at 1 ms (Förster et al. 1981). The latter timescale also limits a set of inseparable events from the deprotonation, namely the $1e^-$ transfer to Tyr-Z $^{*+}HisH^+$, the reduction of three manganese ions, the release of O_2 and the uptake of an H_2O molecule. The exact order of these events is subject to ongoing research.

On the role of Tyrosine residues

All these events could take place without Tyr-D, yet, it is found in every natural photosynthesizing species. Tyr-D has a redox potential of *ca.* +0.7-0.8 V vs. NHE (Vass and Styring 1991). This residue is located farther from the cluster than Tyr-Z, and it is very stable in its radical form, it remains in the oxidized state from the first sunlight into the dark night hours. Found in the so called D2 protein of PS II, the oxidized Tyr-D $^{*+} \cdots H^+His-D$ can elevate the potential energy of $P680^{*+}$ via columbic interaction (Rutherford et al. 2004). Thus, the oxidation of Tyr-Z is accelerated and the highly oxidizing charges will be located only in the D1 protein side of PS II, suppressing side events. It was also observed that Tyr-D $^{*+}$ can oxidize the S_0 state to S_1 in the dark, but it can also deactivate the S_2 and S_3 states by reduction, preventing other unwanted reductants from interfering with the S-cycle (Feyziyev et al. 2003). Finally, Tyr-D also plays important role in the repair cycle of PS II, since in the absence of electrons from the Mn_4O_5Ca cluster it can serve as electron hole carrier in equilibrium with P_{680}^{*+} and Tyr-Z $^{*+}$ (Magnuson et al. 1999). As conclusion, nature provides two examples at a time of redox active organic functions that can be paralleled with those existing in artificial systems and to be discussed herein.

Redox Active Ligands In Artificial Water Oxidation Catalysts

General considerations on the mechanism of OER catalysis

Synthetic catalysts for the OER have to deal with the removal of four electrons and four protons from two molecules of water according to Eq. (1).

Transition metal complexes have rich redox chemistry due to their variable d electron configuration making their utilization in catalysts for the OER appealing. Upon reversible 1e^- oxidation of a metal-aqua complex of general formula $[\text{M}^{n+}-\text{OH}_2]$ the aqua ligand becomes more acidic and may lose a proton, thus multiple-site electron-proton transfer (MS-EPT) can generate the corresponding oxidized form, $[\text{M}^{(n+1)+}-\text{OH}]$ (Weinberg et al. 2012). In a next oxidation $[\text{M}^{(n+2)+}=\text{O}]$ can be obtained in a similar fashion (Scheme 4). For example, the aqua-Ru-polypyridyl complexes can reach high oxidation states within a narrow potential range in this way, due to the σ and π -donation character of the $\text{M}=\text{O}$ group (Sala et al. 2014; Matheu et al. 2019).

The possibility of MS-EPT prevents the buildup of positive charges that would otherwise strongly destabilize the oxidized forms and separate the consecutive oxidation steps by high differences in potentials. Instead, the coupling between electron and proton transfer steps allows for a redox leveling that favors rapid kinetics for the whole OER process. An excellent example is the histidine base effect in the Tyr-His pairs of the natural OEC.

Without histidine acting as acceptor site for the proton, electron transfer is unfavorable (it is slowed down by a factor of 200) (Diner et al. 1991) and the oxidation of tyrosine cannot outcompete the reverse electron transfer from $\text{Q}^{\bullet-}$ to P_{680}^{++} (Hoganson et al. 1995) (see the electron transfer chain in Scheme 1). Another example taken from PS II is the proposed MS-EPT reaction in the $\text{S}_0 \rightarrow \text{S}_1$ transition of the Kok cycle (Scheme 3a). This step involves 1e^- oxidation of the $\text{Mn}_4\text{O}_5\text{Ca}$ cluster with electron transfer to Tyr-Z $^{++}$ in concert with two proton transfer events: one taking place from a $\text{Mn}-\text{OH}_2$ moiety to a neighboring aspartate base and another at the electron acceptor site $\text{TyrZ}^{\bullet+}\cdots\text{H}-\text{His}-\text{Z}$ providing $\text{TyrZ}-\text{H}\cdots\text{His}-\text{Z}$.

In addition to the removal of electrons and protons, the oxidation of water to O_2 also requires the formation of an O–O single bond that is generally a purely chemical step in nature and takes place after the second oxidation step of the catalyst. Molecular catalysts for the OER follow two main types of mechanism, depending on whether an external H_2O molecule participates in the formation of the O–O bond, or two M–O units react. The former mechanism corresponds to water nucleophilic attack (WNA), while the interaction of two M–O units is called I2M, as shown in Scheme 5.

This chemical O–O bond formation step that creates a metal-peroxide intermediate is generally regarded as the bottleneck of the overall process, whereas the follow-up reaction steps proceed rapidly towards the closing of the catalytic cycle.

A recent review covered the role of redox active and redox non-innocent ligands in water splitting with a categorization based on the way of activation, i.e., electrochemical, photochemical, or chemical, collecting examples of catalysts for both the HER and OER (Singh and Indra 2020). The same review paid attention to structural mimics and briefly discussed the possible effects of redox active ligands on a catalytic process in general. Another excellent work categorized molecular transition metal OER catalysts as mono- and binuclear complexes, containing redox non-innocent ligands, and emphasized their role in supplying electrons or binding protons at different stages of the corresponding WNA or I2M mechanism, leading to a more efficient reaction (Sutradhar et al. 2021).

Similarly to these previous reviews we follow the definition of a ligand being non-innocent, if it does not allow “the oxidation states of the central atom to be defined” (Jørgensen 1966). According to this definition, intramolecular electron transfer may occur between the ligand and the metal center in complexes containing non-innocent ligands, allowing for different valence tautomers (Tezgrevska et al. 2014). However, *redox active ligands are those, in which well defined changes in the redox state also alter the reactivity of the complex in a favorable direction.* In the case of OER, participation of redox active ancillary ligands in one or more of the oxidation steps is likely, if this change in the electronic structure of the complex makes the concerned steps energetically favorable. Obviously, those ligands, which can accelerate O-O bond forming or reduce the potential barrier in this manner are expected to pay most attention to. At the same time, when ligands intervene the mechanism, it is not always in favor of the catalytic efficiency. Attention should be paid to unexpected effects, as these may occur in new systems, and account for the specific behavior. Such redox activity also contributes to a more complete picture.

Herein we focus on catalysts for the OER, seeking analogies if apply, with the cooperation between the OEC and the Tyr-His pairs found in PS II (with the notion that several redox active ligands have been explored in HER catalysis, see (Singh and Indra 2020)). *We bring representative examples on the possible outcome of the redox state change in ancillary ligands during catalysis, keeping in mind that there may be crosstalk between molecular catalysts and oxides, the other main group of synthetic catalysts for the OER.* The following ligand types will be discussed, irrespective of the metal content, the nuclearity of the complex, or the way of activation:

- i) those accumulating electron vacancy (redox active);
- ii) those serving as internal base to facilitate coupling between electron and proton transfer;
- iii) those participating in the O-O bond formation and get recovered;
- iv) those making the initial complex efficient precursor to true catalyst formation upon redox transformation.

Electron vacancy on the ligand to assist the metal

All-surviving Ruthenium

The first thoroughly characterized molecular catalysts for water oxidation were Ru-polypyridyl complexes, starting with the blue dimer $cis-[(H_2O)Ru^{III}(bpy)_2(\mu-O)Ru^{III}(bpy)_2(OH_2)]^{4+}$ (Gersten et al. 1982) (Scheme 6), although an early work also pointed out that oxygen evolution from water is possible using transition metal complexes as catalysts (Elizarova et al. 1981). Ruthenium complexes are robust, inert towards ligand substitution and their higher oxidation states required for water oxidation are indeed accessible, moreover, typically Ru-based catalysts do not require redox active ligands for efficient operation (Matheu et al. 2019).

The water oxidation mechanism by the blue dimer has been subject to a fruitful debate (Liu et al. 2008; Moonshiram et al. 2012) incorporating electrochemical and chemical activation using Ce(IV) in acidic (pH 1), and also photochemical studies at neutral pH using the $S_2O_8^{2-}/RuL_3^{2+}$ /blue dimer molecular system. In the latter case it has been suggested that the sequential addition of two H_2O molecules to the bipyridine ligands may couple to generate O_2 (Yamada and Hurst 2000; Cape and Hurst 2008). However, this pathway following the $2e^-$ oxidation of the OH^- adducts results in decomposition of bipyridine, ultimately giving CO_2 as a product after several redox cycles, since the partly oxidized rings are kinetically susceptible to further oxidation (Liu et al. 2008).

Upon electrochemical activation of Ru catalysts generally the Ru centers and/or the water-derived ligands eject electrons rather than the ancillary ligands. The blue dimer gets oxidized by a $1e^- + 3e^-$ sequence. The produced $[(O)Ru^V(bpy)_2(\mu-O)Ru^V(bpy)_2(O)]^{4+}$ complex is thermodynamically competent to form a $Ru-O_2H$ intermediate in a WNA step involving one $Ru^V=O$ unit (Scheme 6). Insight into this mechanism allowed for a strategy for utilizing different $[Ru^{II}(NN)_3]^{2+}$ complexes as kinetically facile, external electron-transfer mediators and it was demonstrated that such mediators can enhance the performance of catalytic water oxidation (Concepcion et al. 2008).

Undoubtedly, these achievements inspired several new complexes contributing to the development of mechanistic insights into the molecular catalysis of the OER (Kamdar and Grotjahn 2019). Although ruthenium does not necessitate redox active ligands for catalytic function, quinone ligands were found capable of assisting in Ru-based catalysis (Wada et al. 2001; Kobayashi et al. 2003; Tanaka et al. 2012).

A prominent example is the dinuclear $[Ru^{II}_2(BTPYAN)(Q)_2(OH)_2]^{2+}$ complex (Scheme 6, see abbreviations there) containing two redox active quinone (Q) ligands. The immobilized complex on ITO electrode was capable of electrocatalytic OER at +1.70 V vs. NHE in water (pH 4), producing O_2 by 95% charge efficiency and reaching a TON of 6730. Two features were found indispensable to a successful catalysis: the two hydroxide ligands located close to each other due to the structural constraint by the two terpyridine moieties, and the two Q ligands helping intramolecular coupling of the OH ligands to form the O–O bond. Upon the O–O coupling the quinones act as oxidants via intramolecular electron transfer. In this reaction step $(SQ)Ru^{II}(O-O)Ru^{II}(SQ)$ is formed (SQ is the semiquinonate(-) form of Q) while two protons dissociate from the complex. The SQ ligands undergo oxidation to Q at +0.4 V vs. NHE, furnishing $(Q)Ru^{II}(O-$

$\text{O})\text{Ru}^{\text{II}}(\text{Q})^{2+}$. This is followed by metal oxidation to Ru^{III} at +1.2 V. Valence tautomerism of the produced $(\text{Q})\text{Ru}^{\text{III}}(\text{O}-\text{O})\text{Ru}^{\text{III}}(\text{Q})^{4+}$ complex generates $(\text{Q})\text{Ru}^{\text{II}}(\text{O}=\text{O})\text{Ru}^{\text{II}}(\text{Q})^{4+}$ from which O_2 liberates upon replacement by two H_2O molecules. Note that a theoretical study identified $[\text{Ru}_2(\text{O}_2^-)(\text{Q}^{-1.5})_2(\text{BTPYAN})]$ as a key intermediate and the most reduced catalyst species that is formed by removal of all four protons before $4e^-$ oxidation takes place (Muckerman et al. 2008). The studies on Ru-quinone catalysts signified that the O-O bond formation is attainable at a low oxidation state of the metal and this observation has very important consequences on 1st row TM catalysts.

1st row transition metals

While Ru centers can undergo multiple oxidation steps in a relatively narrow potential range due to effective PCETs, the situation can be very different when water oxidation is carried out using 1st row transition metals. The ligand substitution lability and the access to higher oxidation states demanding high potentials stand as major challenges in the design of catalysts and careful selection of catalytic conditions. Moreover, the release of 4 protons in one catalytic cycle may easily cause ligand protonation and its subsequent dissociation from the metal center as competing process.

Stabilization of the catalytically active form containing a highly oxidized 1st row TMs center demands strong electron donor ligands. However, this requirement can be circumvented if redox-active ligands are utilized that can be reversibly oxidized to cooperate with the metal center in storing electron vacancies needed for the water oxidation reaction. The involvement of ligand redox activity has been documented in complexes bearing rigid, planar macrocyclic, or semi-macrocyclic ligands with extended π -conjugation capable of carrying an open shell electron configuration. Different families of tetra-amidate ligands were used in Fe (Ellis et al. 2010), Co (Du et al. 2018), Ni (Lee et al. 2020) and Cu (Garrido-Barros et al. 2015, 2017, 2020) complexes.

The tetra-amidate macrocyclic ligands in Scheme 7 (TAML complexes) have been studied in details. The first report concerned Fe-TAML complexes that were capable of promoting O_2 -evolution to a highly variable extent, by mixing them with excess Ce(IV) in water at pH 0.7 (Ellis et al. 2010). Loss of activity was associated with oxidative and hydrolytic inactivation pathways of Fe-TAMLs, also confirmed by control reactions using other Fe-ligand combinations. The rate of the biphasic O_2 evolution correlated with the addition of electron-withdrawing substituents to the ligand.

The highest measured TOF was $>1.3 \text{ s}^{-1}$ for the TAML with $\text{R}_1 = \text{R}_2 = \text{Cl}$ and $\text{R}_3 = \text{F}$, that was sufficiently large that it could be limited by the kinetics of bubble formation and release. Later, formation of a key intermediate, $(\text{TAML}')\text{Fe}^{\text{V}}=\text{O}$ with the TAML one-electron oxidized was suggested based on theoretical calculations (Ertem et al. 2012; Liao et al. 2014). In the latter study, this species was proposed to undergo WNA, or nucleophilic attack by a nitrate ion, the water attack being more favored. Notably, according to the results nitrate may function as a co-catalyst by first donating an oxygen atom to the oxo group to form O_2 and a nitrite ion, which can then be re-oxidized to regenerate a nitrate ion. Competing pathways

were suggested to modify the ligand such as water and nitrate attack as well as ligand amide oxidation, leading to the opening of the benzene ring and fast catalyst degradation.

Efficient electrocatalytic OER in neutral aqueous solution was reported by stable Co^{III}-TAML complexes (Scheme 5) that were confirmed as molecular catalysts under the working conditions (Du et al. 2018). The catalytic cycle was examined in detail by electrochemical methods in combination with DFT calculations. As the working potential was increased, the triplet [Co^{III}(TAML⁴⁻)]⁻ complex was first oxidized to [Co^{III}(TAML²⁻)(OH)] via ligand-centered 2e⁻+H⁺ PCET in the presence of water. The oxidation of the TAML moiety was clearly indicated by the changes in the C-C bond length of the benzene ring and the N-aryl ring bond lengths, corresponding to the structural change expected in the oxidation of an *o*-phenylenedicarboxamido ligand to its benzoquinonedicarboxamido form. The resulting [Co^{III}(TAML²⁻)(OH)] was further oxidized to [Co^{IV}(TAML²⁻)=O], which could react with water to form an O-O bond with the help of a buffer anion in a WNA step. The influence of H₂PO₄⁻ on the WNA process revealed by DFT calculation was in good agreement with the observed buffer effect. Analysis of the calculated structure revealed that both the oxo moiety and the cobalt center bear significant spin densities corresponding to a more correct [Co^{III}(TAML²⁻)-O•] assignment. The WNA pathway afforded the quartet hydroperoxo complex, [Co^{II}(TAML²⁻)-OOH] that was oxidized to the superoxo complex [Co^{III}(TAML²⁻)(O₂^{•-})] through a PCET process, to finally release an oxygen molecule and regenerate the resting state [Co^{III}(TAML⁴⁻)]⁻ (Scheme 8). The *k*_{cat} values calculated for the different complexes were very similar, between 7.53-8.81 s⁻¹, but no catalytic activity could be observed for a complex with a non-redox-active ligand homolog (the benzene ring was substituted by an aliphatic bridge), indicating that the redox-active ligand played a critical role in this multi-electron catalytic cycle. This work underlined the interplay of ligand- and metal-centered redox activity could be a benefit for water oxidation catalysts.

A Ni^{II}-TAML (Scheme 7, R₃ = CH₃) was characterized as electrocatalyst of the OER at neutral pH in phosphate buffer (Lee et al. 2020). The HPO₄²⁻ anion served as proton acceptor to accelerate the formation of the O-O bond following atom-proton transfer (APT) pathway. The electrochemical activation of the complex started with a reversible, pH-independent Ni^{II} to Ni^{III} oxidation at +0.68 V vs. NHE, followed by two irreversible oxidation peaks at +1.03 V and +1.51 V vs. NHE. The first irreversible and pH-dependent oxidation was associated with a 2e⁻+H⁺ PCET of [Ni^{III}(TAML⁴⁻)] to produce [Ni^{III}(TAML²⁻)-OH], while the second one was assigned to a [Ni^{III}(TAML²⁻)-OH] to [Ni^{IV}(TAML²⁻)=O] transition. Oxygen evolution took place at 93% Faraday efficiency and the calculated TOF was 0.32 s⁻¹. The first-order dependence of the catalytic current on catalyst concentration clearly indicated a single-site mechanism. The proposed catalytic cycle is shown in Scheme 8.

The above catalysts could possibly exploit the one- and two-electron oxidation of the applied TAML ligand according to Scheme 9 thanks to the available formal *o*-phenylene-/benzosemiquinone-/benzoquinone-dicarboxamido redox forms.

A similar amidate group has been suggested to intervene the redox activation of a mononuclear cobalt(III) complex, $[\text{Co}(\text{dpaq})(\text{Cl})]\text{Cl}$ featuring the pentadentate ligand, $H\text{-dpaq} = 2\text{-[bis(pyridin-2-ylmethyl)]amino-}N\text{-quinolin-8-yl-acetamidate}$ (Biswas et al. 2020). Efficient molecular electrocatalysis was reported to occur at a 500 mV overpotential and pH of 8.0. The redox-active amidate ligand facilitated catalysis through the formation of a reactive oxo-metal species, $[\text{Co}^{\text{IV}}(\text{dpaq}^{++})(\text{O})]^{2+}$ that followed metal oxidation (Scheme 10). According to the mechanism proposal WNA on this putative intermediate formed the O–O bond through a base assisted proton transfer reaction. Interestingly, foot-of-the-wave analysis (FOWA) (Costentin et al. 2012a, b) confirmed the water nucleophilic attack (WNA) mechanism and the high TOF_{max} value in the order of 10^4 s^{-1} obtained by FOWA was comparable to the best performing Ru-based WOCs.

In the case of copper, planar 4N^- donor coordination sites like in TAML are well suited for stabilizing an oxidized Cu^{III} metal center and perhaps this metal has been studied most thoroughly with respect to the utilization of redox active ligands. The $N_1, N_1' \text{-(1,2-phenylene)bis}(N_2\text{-methyloxalamide})$ ('PBOA') ligand family (Scheme 7) demonstrated opportunities in using redox-active ligands to advance Cu-based water oxidation (Garrido-Barros et al. 2015). Introducing electron-donating R_1 and R_2 substituents at the benzene ring of the PBOA ligand allowed reducing the overpotential in electrocatalytic water oxidation by 530 mV.

The energy of the ligand HOMO correlated with the observed overpotential, indicating that the electron-donating substituents increase the overall energy of the HOMO and favor the oxidation of the ligand. DFT analysis revealed a new mechanism progressing towards the rate determining O–O bond formation in single-electron transformations, and generating a peroxide intermediate with no formal M–O bond (Scheme 11). This has led to a new, general mechanistic proposal, the so-called SET-WNA (single-electron transfer water nucleophilic attack) (Funes-Ardoiz et al. 2017).

A derived complex utilizing the ligand 4-pyrenyl-PBOA (py-PBOA) was designed to extend the π -conjugation through its structure (Garrido-Barros et al. 2017). The performance of this catalyst (and the parent complex) has been studied in the homogeneous phase and after immobilization by π -stacking to graphene-based electrodes. In the homogeneous phase the electronic perturbation provided by the pyrene substituent reduced the overpotential by 150 mV and increased the catalytic rate by more than 20 times to achieve a k_{cat} of 128 s^{-1} . Based on spectroscopic investigations on the one-electron oxidized form, the authors addressed the oxidation process to the pyrene moiety in aqueous solution in contrast to the parent complex, in which the oxidation remained metal-centered (the differences are highlighted in red in Scheme 11). This difference was associated with the lower oxidation potential at the ligand site due to the presence of the pyrene group together with the large stabilization to the putatively charged oxidized species in the aqueous environment. Immobilization on a graphene surface provided additional delocalization that improved the catalytic performance of both catalysts, however, the py-PBOA complex was more active. The overpotential of 538 mV, k_{obs} of 540 s^{-1} and $\text{TON} > 5300$ that by a rational design stability of first row TM catalysts can be dramatically increased.

The same group underlined in a later work how crucial it is to elucidate the actual sites affected by consecutive oxidations yielding the different formal oxidation states of the complex and how subtle changes can perturb the delocalization of electron density. For this purpose they developed two new ligands with 13- and 14-membered rings that can be regarded as 'dibenzo-tetraamido macrocycles' ('dibenzo-TAML' in Scheme 7) (Garrido-Barros et al. 2020) in addition to the above discussed semi-macrocyclic 'PBOA' ones. They found that a mere one-atom change in the ring size and change in solvent polarity were enough to shift the delocalization of electron density from the metal over the ligand π -system. Valence tautomerism exerted by the solvent interaction 'evidenced the energetic near degeneration in the frontier orbitals and the subsequent easy access to the different oxidation states, corresponding to metal-centered, d-orbital oxidation or ligand centered oxidation'. For example, the coordinated 13-membered 'dibenzo-TAML' was involved in two $1e^-$ oxidations due to the high delocalization of spins (Scheme 12) resulting in two energetically levelled oxidation steps within an 80 mV potential window. In contrast, this metal-ligand redox cooperativity was missing from the complex with the 14-membered 'dibenzo-TAML' macrocycle (Scheme 5, R = CH(CH₃)₂), where the π -conjugation between both phenylene moieties was broken due to the presence of two dimethylmalonamide bridges with sp³ carbons and the saddle distortion of the ligand.

These subtle changes in the ligand structure fundamentally determined the fate of the catalysts upon electrolytic water oxidation, since the stability of the different spin states of the complex at the different oxidation states relied strongly on the extent of π -delocalization. The complex bearing the larger macrocycle ligand decomposed during catalysis, whereas the one containing the 13-membered macrocycle (Scheme 12) remained stable and highly active thanks to the evidenced redox cooperativity between the metal and the ligand. The highly oxidized reactive form thus has been stabilized due to the delocalization of the accumulated oxidative equivalents (the proposed mechanism and charge delocalization in the different oxidation states are shown in Scheme 12). Importantly, this way the high-energy oxidized states centered only at the ligand, or the metal center have been avoided so that both ligand oxidative degradation and high-valent metal centers requiring large potentials and frequently involved in formation of metal oxides were absent. In addition, the two ligand-based oxidations in a narrow potential window were concluded to be essential to enable water oxidation at neutral pH, where an extra oxidation is required to generate a more active Cu complex. As a result, at neutral pH catalysis proceeded with a k_{obs} of 140 s⁻¹ at an overpotential of only 200 mV.

A comparison was also made in this context with an earlier catalyst featuring electronic delocalization limited to single phenylene moiety (Scheme 7, PBOA ligand, R₁ = R₂ = H) (Garrido-Barros et al. 2015). In this case, water oxidation at pH 12 proceeded via metal oxidation followed by ligand oxidation as with the macrocycle (Scheme 12). However, the acyclic ligand-containing complex was prone to acidic demetallation below pH 10 that prevented its application in water oxidation at neutral pH, in sharp contrast to the macrocyclic complex. This observation underlined the importance of the cooperative metal-ligand design approach for oxidative equivalent accumulation to find more stable and efficient molecular catalyst for redox reactions. The authors also emphasized that attention should be paid to the

analysis of the irreversible pre-catalytic electrochemical oxidation features that may hinder substantial changes in the pre-catalysts upon oxidation and may indicate degradation.

Following simple logic we can conclude that shutting down the redox activity of the metal center in parallel with triggering that of the ligand is possible by appropriate ligand design. Indeed, recently a new family of dianionic [2,2'-bipyridine]-6,6'-dicarboxamide ligands (Scheme 13), substituted with redox-active phenyl or naphthyl moieties have been described (Gil-Sepulcre et al. 2021). The electrocatalytic OER process involving only ligand-based redox events was a consequence of two features of the ligand. First, a $\text{Cu}^{\text{III/II}}$ redox couple at relatively low potentials necessitates highly anionic, strongly σ - and π -donating ligand environment coordinated to the Cu center. In the case the bpy-dicarboxamide ligands two neutral N donors of the bpy and two anionic N donors of the amide groups had insufficient electron-donating capacity to stabilize the oxidized metal center below or at the onset potential of catalysis. The second feature was that two redox-responsive phenyl/naphthyl groups were attached to the ligand conjugated with the amide donors that were able to accommodate two distal electron vacancies. Upon oxidation, one of the aryl-amide groups could be detached from the metal, opening a quasi-equatorial coordination site for an OH^- ligand.

A detailed electrochemical analysis at pH 11.6 revealed a large electrocatalytic current associated with O_2 -evolution at an overpotential of 830 mV for the complex shown in Scheme 13. Experimental and computational results supported a catalytic cycle progressing towards the active form through single-electron transfer steps corresponding to a SET-WNA mechanism, including intramolecular single-electron transfer (I_{SET}) steps (Scheme 13). Upon the first oxidation a triplet Cu^{II} complex is formed with a radical cation mainly centered on one of the aryl-amide moieties. Evidence for this possibly rate limiting ligand-based electron transfer in electrocatalytic OER was provided by the correlation between the substituent effect on the aryl groups and the observed onset potential of catalysis. Accordingly, the k_{obs} values were in the range of $5\text{--}35\text{ s}^{-1}$ and the Faraday efficiencies were between 40 and 76%, both related to the structure of the ligand and the stability of the oxidized moiety. The Cu center served as a scaffold for the two bpy-amide groups bonded to the metal center, and at the same time OH^- coordination and activation could take place. According to the proposed mechanism this Cu-OH group can be attacked by an external hydroxide via a radical-nucleophilic pathway, generating a Cu-(HOOH) species. Since this process involves I_{SET} event between the aryl radical cation and the Cu-OH group, 'the metal center is responsible for placing the two groups sufficiently close so that fast I_{SET} can occur' (Gil-Sepulcre et al. 2021). The role for the aryl substituent was clearly discussed both from a thermodynamic perspective, because it tuned the overpotential for OER catalysis, and from a kinetic perspective, 'because of the low reorganization energy of extended polyacenes' upon electron transfer ensuring fast kinetic processes. Considering the high versatility in ligand design, the low efficiency obtained for the above complexes that is due to competitive deactivation pathways can be solved in the future.

Due to their cyclic π -delocalization porphyrins and corroles are capable of stabilizing electron vacancies. In addition, the two or three negative charges at the N donor groups, respectively, can stabilize the

coordinated metal center in higher oxidation states. Thus, these compounds represent an exciting redox non-innocent and potentially redox-active ligand platform with rich possibilities in derivatization as indicated in Scheme 14. Their advantages have been discussed earlier (Zhang et al. 2017b). In context with the present overview, we emphasize here that metalloporphyrin catalysts for the OER are generally proposed to undergo first a $1e^-$ oxidation concerning the ligand that is followed by $1e^-$ oxidation of the metal center.

Metalloporroles can behave in a similar fashion upon oxidative activation of the OER catalysts (Zhang et al. 2017b). In metalloporroles the stabilization of high-valent metal ions by porroles is viable through a combination of short metal-nitrogen bonds and large metal out-of-plane displacements (Gross 2001). A key difference from metalloporphyrins is the wider prevalence of non-innocent electronic structures and full-fledged porrole $^{2-}$ radicals among metalloporroles (Ghosh 2017). There is gathering evidence that the non-innocent or redox-active behavior of this ligand family is prevalent (Lemon et al. 2016; Schöffberger et al. 2016; Sinha et al. 2018, 2020; Garai et al. 2018; Mondal et al. 2020).

Importantly, these ligand architectures are suitable for surface immobilization through covalent linkers or axial coordination of the metal center by tether ligands grafted onto the surface, or by exploiting their high adsorptivity (Schöffberger et al. 2016), that makes their utilization in (photo)electrodes directly available (Zhang et al. 2017b). Two-electron oxidation of water to form hydrogen peroxide by using metalloporphyrins containing redox silent metal centers like Al, or Sn has been also addressed as viable alternative strategy for artificial photosynthesis systems (Kuttassery et al. 2018) as well as light-driven oxidation of halide anions by metalloporroles (Mahammed and Gross 2015).

Phthalocyanines (PCs) are expected to exhibit advantages like those of porphyrins and porroles in OER catalysis (Scheme 14). For example, photocatalytic water oxidation in the presence of a water soluble Cu^{II} -PC complex was proposed to follow an I2M mechanism in borate buffer at pH 9.5 (Terao et al. 2016). According to computations, upon $1e^-$ oxidation of the complex a PC radical is generated instead of a metal-based electron loss, thus the Cu^{III} oxidation state generally leading to complex photodegradation does not occur. Importantly, competitive ligand exchange between chloride ions and water molecules for the fifth coordination site inhibited the reaction, calling attention to the potential detrimental effect of impurities.

Recent findings on the possible application of metallo-PCs are encouraging. Cu-PC was reported to act as efficient redox mediator for TiO_2 nanorod-based PEC water splitting (Li et al. 2019), moreover, conjugated to carbon quantum dots (CQDs) by π -stacking and then coupled with $BiVO_4$ to construct a hybrid water oxidation photocatalyst $BiVO_4/CQDs/CuPC$ (Xu et al. 2021). A somewhat similar system with Co-PC deployed on $BiVO_4$ was also very recently reported to enhance the photocurrent in PEC oxygen evolution (Shen et al. 2021). Polymeric copper and cobalt PCs (Cu-pPC and Co-pPC) were prepared as thin films on FTO from evaporated metal films via a chemical vapor deposition (CVD) process with 1,2,4,5-tetracyanobenzene and successfully operated in 0.1 M KOH electrolyte to generate O_2 electrocatalytically

(Geis et al. 2016). These and other types of polymers, like metallated azo-naphthalene diimide based redox-active porous organic polymer frameworks (Bhat et al. 2018) are encouraging to envision future applications of such materials. Note on the other hand that the example of a Mn^{II} -PC complex resulting in MnO_x formation upon electrocatalytic water oxidation in unbuffered acetonitrile-water mixture shows that organic ligand platforms may not be suitable under harsh conditions and may undergo hydrolytic degradation (Mousazade et al. 2019).

Ligands capable of a change in both the electronic structure and protonation state

Some ancillary ligands can handle changes in both the protons and electrons in the course of water oxidation catalysis that presents uncommon mechanistic pathways. Some emblematic examples for different ligand design strategies and some recent findings are discussed below.

The 3,5-bis(4-carboxy-1*H*-benzimidazol-2-yl)-1*H*-pyrazole (herein $\text{H}_5\text{bim}_2\text{pz}$) ligand framework was reported to form a mixed valence dinuclear $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$ complex with 4-picolines (pic) occupying the remaining sites (Laine et al. 2015a, b) (Scheme 15).

This complex could carry out WOC both by chemical and photochemical activation and O_2 evolution was observed in high TON of *ca.* 800–890. The strongly electron-donating ligand not only decreased the redox potentials and enabled the higher oxidation states, but it was also involved in proton transfer and exhibited a non-innocent character. The proposed mechanism based on the lowest energy calculated isomers is shown in Scheme 15. A similar ligand design was successful in the case of mononuclear Ru complexes (Kärkäs et al. 2016).

A relatively simple ligand, 6,6'-dihydroxy-2,2'-bipyridine (6,6'-dhbpy) with pendant hydroxyls to mimic the function of Tyr-Z in PS II was applied in a Cu-based electrocatalyst (Zhang et al. 2014). As an effect of the hydroxyl groups, the oxidation of the Cu center was reduced by *ca.* 200 mV, but the k_{obs} of 0.4 s^{-1} was well below that of *ca.* 100 s^{-1} for the parent bpy complex at pH 12 (Barnett et al. 2012). According to DFT calculations, two oxidations preceded the WNA step (Scheme 16). The second one concerned the redox active ligand to yield a radical anion at a calculated potential of +1.4 V vs. NHE. Spin delocalization and stabilization of the corresponding oxidized state were claimed to lower the onset potential, but also to reduce the electrophilic character disfavoring WNA. Importantly, a partially oxidized complex polymer was found on the electrode surface upon electrolysis that could be re-dissolved in pure electrolyte.

Crystallographic studies suggested that a 1-D coordination polymer with μ -OH bridges and an H-bonding network were responsible for the film formation. Importantly, in CVs the catalytic peak current showed a curving-over behavior at high complex concentrations that has been associated with the film formation due to the local pH drop. Although such features are often associated with catalyst decomposition and concomitant metal oxide film formation, coordination polymers may also generate catalytic films (Cui et al. 2016; Mishra et al. 2017; Kuwamura et al. 2018) highlighting that the pH-

dependent behavior and redox transformations of molecular catalysts may change their surface affinity thus promote immobilization.

Finally, 6,6'-dmbpy in 2:1 stoichiometry to Cu^{2+} formed the aqua-coordinated $[(6,6'-(\text{O})_2\text{-bpy})_2\text{Cu}(\text{H}_2\text{O})]^{2-}$ along with homolog bpy compounds (Gerlach et al. 2014). Beside the catalytic water oxidation a competing non-catalytic degradation has been identified and 4,4'-disubstituted analogs were inactive in water oxidation. Thus, the neighboring O^-/OH groups indeed facilitate PCET and H-bonding interactions to promote water oxidation, in addition to the redox non-innocence of 6,6'-(OH)₂-bpy (Burks et al. 2018) in line with findings on the corresponding Ir-complex (DePasquale et al. 2013).

The 3N donor *bis*-aryliminoisoindoline pincer ligands (mentioned both as BAI and ind ligands in the literature) are able to bind metal ions in their neutral or anionic form owing to exocyclic imine functions that can act as internal proton acceptor site (Scheme 17). These rigid ligands occupy three coplanar sites around metal centers and often support both stability and reactivity, because variable coordination sites are available for substrate binding and activation (Scheme 14) (Csonka et al. 2015; Saha et al. 2021).

Recently, Fe- and Cu-BAI complexes were reported to catalyze water oxidation (Al-Zurairi et al. 2020b; Benkó et al. 2021; Al-Zurairi et al. 2021). The $[\text{Fe}^{\text{III}}\text{Cl}_2(\text{tia-BAI})]$ complex ($\text{tia-BAI}^- = 1,3\text{-bis}(2'\text{-thiazolylimino})\text{isoindolate}^-$) (Váradi et al. 2013) was pre-catalyst to efficient water oxidation when immobilized on ITO electrodes and applied in borate buffer at pH 8.3 (Al-Zurairi et al. 2020b). Product analysis indicated >80% Faraday efficiency and a TON of 193. Surface analysis before and after electrolysis, and re-dissolution tests suggested that an immobilized molecular catalyst was responsible for catalysis and de-activation occurred by depletion of the metal. The catalytically active form was claimed to arise by the exchange of chloride ligands to water molecules, while the pincer ligand rendered water-insolubility to the Fe(tia-BAI) assembly. Electrochemical and spectroscopic investigations in homogeneous water-acetone mixtures indicated a single-site molecular catalysis. Both 1e^- ligand oxidation and intramolecular H-atom transfer were suggested to occur as all three forms should be capable of metal binding (Scheme 17). The latter conclusion relied on electrochemical detection of an intermediate in re-dissolved and chloride-free samples from drop-casted ITO that was previously exposed to long-term electrolysis. Interestingly, the ligand exchange occurring in water-organic mixtures could be exploited to develop a material saving electrodeposition method to form chloride-depleted catalyst ad-layers for efficient water oxidation electrocatalysis (Al-Zurairi et al. 2021). Changing the thiazolyl arms in tia-BAI to benzothiazolyl ones increased the durability of the catalytic films, highlighting that the ancillary ligands play a crucial role in the stabilization of surface-adsorbates.

A more insightful, theoretical and experimental study on the possible combined redox-active and proton acceptor role of isoindoline-based pincer ligands was published very recently (Benkó et al. 2021). A pre-catalyst complex, $[\text{Cu}^{\text{II}}(\text{indH})(\text{OCIO}_3)(\text{NCCH}_3)]^+$ with 1,3-*bis*(2'-pyridyl)iminoisoindoline (indH) was immobilized on ITO to generate O_2 electrocatalytically for over 20 hours at pH 10 in carbonate buffer, reaching a TON of 139 with no signs of $\text{CuO}_x/\text{Cu}(\text{OH})_2$ formation. Experimental results in turn indicated

that a $[\text{Cu}^{\text{II}}(\text{ind})(\text{OH})]$ complex form dissolved in the aqueous phase that might be responsible for catalysis. In order to identify the actual catalyst, $[\text{Cu}^{\text{II}}(\text{ind})(\text{OCIO}_3)(\text{OH}_2)]$ was isolated and structurally characterized in the solid state (note that perchlorate dissociated in solution). Spectroscopy and DFT calculations were conducted to reveal a distorted $\{3\text{N},\text{O}\}_{\text{eq}}$ coordination plane around copper in solution in close resemblance to that suggested by others for a similar redox-active ligand containing system (Gil-Sepulcre et al. 2021). In acetonitrile-water solutions, experimental findings supported by DFT calculations suggested that the ind^- ligand was oxidized while the Cu^{II} center remained redox-silent in the proposed catalytic cycle (Scheme 18). Each intermediate was tested with different spin multiplicities and the most stable states were identified.

According to the suggested mechanism, the first PCET step would oxidize the ind^- ligand to produce $[\text{Cu}^{\text{II}}(\text{ind}^*)(\text{OH})]^+$ that is followed by a second oxidation to generate the oxyl form, instead of Cu^{III} . The separation of the two oxidized sites explained the appearance of the second event only after adding H_2O . The redox-silence of Cu^{II} could be attributed to the spatial configuration of the complex, since the steric hindrance made it difficult to form a square planar field around copper and stabilize the $d^8 \text{Cu}^{\text{III}}$ configuration. The oxyl radical was found capable of SET-WNA resulting in $[\text{Cu}^{\text{II}}(\text{indH})(\text{OOH})]^+$. In this step, the oxidized ligand is reduced by the electron from the attacking water molecule and the ancillary ligand could then act as internal proton acceptor before an external base caught the released proton and restored again the anionic ligand form.

The spatial aspect of this proton capture was also considered. Since the $\text{N}\cdots\text{H}(\text{Cu}-\text{O}-\text{OH})$ distance was 4.82 Å in the $[\text{Cu}^{\text{II}}(\text{ind}^-)(\text{HOOH})]^+$ intermediate, it clearly necessitated the assistance of a proton carrier to transport a proton to the ligand N thus it could not be exactly synchronous with the formation of the O–O bond. Note that the $[\text{Cu}^{\text{II}}(\text{ind}^*)(\text{O}^*)]^+$ form contains three unpaired electrons, one at the ind ligand, one at the $d^9 \text{Cu}^{\text{II}}$ center and one at the oxyl ligand giving rise to different available spin multiplicities. Importantly, the calculated energy diagram of the system during the O–O bond formation clearly displayed a cross between the quartet and doublet states with the O–O distance near 2.0 Å.

Ligand participation in O-O bond formation

So far, the participation of ligands in the key O-O bond formation step has been limited to those oxoanions, which may in principle form peroxo-metallo-cycles with transition metals. These ligands are carbonate and borate, both having rich literature on their reactivity as perhydrate and persalt, respectively (Pizer and Tihal 1987; Tsoler 1999; Durrant et al. 2011; Deary et al. 2013; Liu et al. 2021). The presence of these anions by a catalyst in sufficiently high concentration is naturally expected only in electrolytes, thus this section will include electrocatalytic examples.

In a catalytic cycle producing O_2 from two H_2O molecules involving a single-site M-L catalyst and inner-sphere coordination of oxoanions, one can imagine two general pathways. In the cycle on the top of Scheme 19, the aquo-metal assembly (framed form in the middle) is oxidized by $1e^-$ losing also 1H^+ , and the assisting ligand (L^{A} in blue) is coordinated through an oxygen donor.

The next oxidation step concerns L^A , in which a reactive oxyl radical function is formed that in turn attacks the $M^{ox}-OH$, resulting in a peroxo-metallo-cycle and eventually O_2 evolution. The second option is that $M^{ox}-O^{\bullet}$ is generated, as shown in the cycle at the bottom of Scheme 19. In this case, the oxyl attacks a hydroxyl of L^A forming peroxo intermediates. Stabilization of the M^{ox} state generally requires suitable ancillary ligands (L in green, Scheme 19) that can be also an oxoanion as carbonate is known to stabilize higher oxidation states of metal ions in solution. The following examples may fit with one of these two general scenarios, however, as it will be apparent, there are ongoing debates about the dominant mechanisms.

Carbonate

An early report on Cu-based, electrocatalytic water oxidation introduced an astonishingly simple solution equilibrium system. Different copper salts were added to a $NaHCO_3$ buffer at pH 8.2, or 6.7 (satd. with CO_2) and high anodic potentials were applied to an inert (ITO, FTO or GC) working electrode immersed into these solutions yielded O_2 with high charge efficiency (Chen and Meyer 2013). Complex formation between the metal and bicarbonate/carbonate in high excess was clear from the characteristic shifts of the d-d transitions in the electronic spectra. Later, DFT calculations indicated that carbonate is a non-innocent, reactive ligand forming a peroxocarbonate metallo-cycle (Winikoff and Cramer 2014). This mechanism would be compatible with the cycle on the top of Scheme 19. The peroxycarbonate is then oxidized rapidly to yield O_2 and CO_2 . The high reactivity was explained by means of a low energy singlet-triplet splitting in the $3e^-$ oxidized state facilitating the evolution of triplet molecular oxygen. An easy access by carbonate to both mono- and bidentate coordination modes allowing rearrangements that favor the O-O bond formation, and spin delocalization through the Cu-O bonding were pointed out as key features to reach a high catalytic rate.

Alternative proposals argued in favor of reaction steps leading to 'short circuiting' the catalytic cycle at the stage of peroxide formation ($2e^- + 2e^-$ mechanism). According to a combined experimental and theoretical study, it has been suggested that $O_2COO-CO_2^{2-}$ is produced as peroxide product from two Cu^{III} -carbonate complex units (Mizrahi et al. 2018). This means the electrochemical oxidation of Cu^{II} to Cu^{III} upon which no $CO_3^{\bullet -}$ radical anion should occur. Instead, the hydrolysis of $C_2O_6^{2-}$ ($O_2COO-CO_2^{2-}$) gives H_2O_2 that reacts with the Cu^{III} complexes producing O_2 . However, below pH 8.2 the electrocatalytic reaction was found to be first order in copper. This is not in line with the above conclusions that are rather compatible with a second order in copper. Note, on the other hand that second order kinetics in copper has been found in concentrated CO_3^{2-} or HPO_4^{2-}/PO_4^{3-} buffers at pH 10.8, but the rate determining step was the formation of a $CuO-OCu$ intermediate on the analogy to the known copper peroxide chemistry (Lewis and Tolman 2004; Elwell et al. 2017).

There are gathering arguments on the viability of similar mechanistic pathways for other 1st row TMs like cobalt and nickel (Mizrahi and Meyerstein 2019; Patra et al. 2020a, b). In the case of planar $Ni^{II}(1,4,8,11-$

tetraazacyclotetradecane) complexes (TACT, aliphatic 4N donor environment) used in water oxidation electrocatalysis, it was indeed concluded that two axially coordinated carbonate anions are required to stabilize the Ni^{III} oxidation state (Ariela et al. 2017). As a consequence, the concomitant oxidation of $[\text{Ni}^{\text{III}}(\text{TACT})(\text{CO}_3)_2]^-$ to a catalytically active Ni^{IV} species is (a) either preceded by a slow exothermic carbonate-to- H_2O ligand exchange to provide $[\text{Ni}^{\text{IV}}(\text{TACT})(\text{CO}_3)(\text{OH})]^+$, or (b) bond breaking produces $[\text{Ni}^{\text{IV}}(\text{TACT})(\text{CO}_3)_2(\text{O})]^- + \text{CO}_2$ from $[\text{Ni}^{\text{IV}}(\text{TACT})(\text{CO}_3)_2]^-$. In the upcoming steps, the $[\text{Ni}^{\text{IV}}(\text{TACT})(\text{CO}_3)_2(\text{O})]^- + [\text{Ni}^{\text{IV}}(\text{TACT})(\text{CO}_3)_2(\text{OH})]$ coupling would produce a $\text{Ni}^{\text{III}}\text{-O-O-Ni}^{\text{III}}$ species that in turn would release H_2O_2 . If $[\text{Ni}^{\text{IV}}(\text{TACT})(\text{CO}_3)_2(\text{O})]^-$ reacts with an external HCO_3^- , then $\text{O}_2\text{COO-CO}_2^{2-}$ or HCO_4^- is produced, which leads again to H_2O_2 release. All these mechanistic scenarios may be conceived as a ‘short circuiting’ of the $4e^-$ process due to a disfavored metallo-cyclization (see the reaction steps with grey background in Scheme 19), thus the rest of the oxidation steps take place away from the inner-sphere of the original complex.

Whichever is the case, these results underline that carbonate ions are not only ligands that stabilize Ni^{III} , but also active, non-innocent participants in the redox process. Note that the occurrence of a η^2 -peroxomonocarbonate metallo-cycle has been considered for manganese in catalytic epoxidation (Lane et al. 2002) and importantly, the X-ray structure of an $\text{L}_2\text{Fe}^{\text{III}}$ -peroxomonocarbonate complex (Hashimoto et al. 2002) illustrated that such entities should not be eliminated from mechanistic speculations. These redox non-innocent scenarios for carbonate are especially fascinating since L-M compounds involved in water oxidation are known to bind carbonate (Chen et al. 2017; Benkó et al. 2021), and efficient material systems are also known formed with this anion (Ji et al. 2018).

Borate

With respect to borate only a few examples are known to date, including an electrocatalytic system under neutral conditions using copper (Huang et al. 2017), in which this anion was suggested to participate in the O-O bond formation step. Note that the *in situ* formation of a stable ‘Cu-B_i’ catalytic film has been described earlier and its performance was comparable to that of ‘Ni-B_i’, but somewhat lower than that of ‘Co-B_i’ (Yu et al. 2015). In Huang et al.’s study, the addition of borate to a 1 M solution of sulfate resulted in a soluble complex and UV-vis spectrophotometric evidence confirmed a ternary sulfate-Cu-borate catalyst species, in which sulfate acted as ancillary ligand. Electrocatalytic oxygen evolution at pH 7 was stable and no catalytically active deposit could be detected on the surface of the working electrode after several hours of electrolysis. The observed first order dependences in both borate and copper suggested single-site catalysis relying on PCET steps. A KIE close to 1 ruled out the participation of the inner-sphere tetrahydroxyborate ligand in the rate determining step as a proton acceptor. Instead, its effect to enhance the rate of electrocatalysis was associated with its participation in the rate limiting O-O bond formation step as oxygen donor, on the grounds of DFT calculations. This mechanism may be conceived as that shown in Scheme 19 (cycle on the bottom). In the key step, the $2e^-$ oxidized form, $\text{Cu}^{\text{III}}\text{-O}^\bullet$ attacks a

hydroxyl group on the coordinated $(\text{HO})_3\text{BO}^-$ ligand providing an energetically favorable pathway for the O-O bond formation.

In the presence of different N-donor ligands (for example, 2,2'-bipyridine, various tripeptides and a dinucleating peptidomimetic ligand) borate was also reported to coordinate to copper (Huang et al. 2017; Lukács et al. 2019; Ruan et al. 2021). However, the outcome of the electrochemical oxidation seems to depend strongly on the ancillary ligand. In the case of mononucleating tripeptides the formation of $[\text{LCu}^{\text{III}}\text{-OOB}(\text{OH})_3]^{2-}$ has been proposed upon electrochemical oxidation, leading to complex degradation and *in situ* 'CuO' deposition (Lukács et al. 2019). As for the di-copper complex formed with the peptidomimetic ligand results implied that borate coordination occurred upon $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{III}}$ oxidation (Ruan et al. 2021). In the rate determining step the $\text{Cu}^{\text{III}}\text{-O}^\bullet$ attacks the neighboring $(\text{HO})_3\text{B}(\text{O})\text{Cu}^{\text{III}}$ tethered to it by the peptidomimetic ligand. In essence, considering the rate determining chemical step this mechanism corresponds to that shown in cycle on the bottom of Scheme 19 noting that the order of the proton and electron transfers may be shuffled.

Nickel complexes have been scarcely studied in the presence of borate to our knowledge, and even in those cases the complex itself was unstable under catalytic conditions, thus the role of borate has not been discussed (Aligholivand et al. 2019). Recent studies conducted under alkaline conditions (no matter of what buffer was chosen) eventually concluded that Ni complexes undergo degradation and NiO_x is formed under catalytic conditions (Feizi et al. 2018; Garrido-Barros et al. 2019). If one regards this general tendency of the Ni complexes, it is unlikely that with this metal a similar mechanism to that in Scheme 19 may come to light. On the other hand, one might wonder about the role of borate anions in OER catalysis by nickel oxide surfaces. The growth of nickel oxide films from borate electrolyte have been known for long (MacDougall and Graham 1981) and their utilization as efficient heterogeneous OER catalyst was an important milestone in this field (Dinca et al. 2010). The role of borate has been studied in particular (Bediako et al. 2013) and elucidated that in borate-buffered electrolyte borate anions occupy the active surface sites and prior to commence the catalytic cycle their reversible dissociation from the domain edge of NiO_6 octahedra is required. A later study spectroscopically confirmed that an increase in the number of NiO_6 domains is necessary to achieve an efficient OER catalyst (Yoshida et al. 2015). Lately, a $\text{Ni}_3(\text{BO}_3)_2\text{-Ni}_3\text{S}_2$ amorphous-crystalline heterostructure has been identified as an efficient bifunctional catalyst for both HER and OER (Sun et al. 2020). Although the authors constructed schematic models of -OH, -O, and -OOH surface-bound intermediates on varied sites in $\text{Ni}_3(\text{BO}_3)_2$, Ni_3S_2 , and $\text{Ni}_3(\text{BO}_3)_2\text{-Ni}_3\text{S}_2$ in order to calculate the free energy for each elementary step in OER, the possible role of a peroxyborate intermediate was not discussed explicitly.

With respect to other 1st row TMs, a few complexes have been studied in borate with cobalt (Shaghaghi et al. 2021) and iron (Al-Zuraiji et al. 2020a, b, 2021), moreover, Mn_2OBO_3 (manganese-oxoborate) was found to be an efficient surface catalyst under neutral conditions (Elmaci et al. 2021). However, in these cases the possible role of borate in the O-O bond formation step has not been discussed. Based on the

above examples it cannot be excluded that the use of carbonate or borate in PC and PEC systems will reveal a similar, supportive function of these anions in the O-O bond formation step.

Fruitful complex degradation

Some of the uncommon ligands can accumulate electron vacancies; others take part in O-O bond formation and recover by the end of a catalytic cycle. However, many of the ancillary ligands remains an apparently passive scaffold stabilizing the redox rollercoaster of the metal center. Nevertheless, there is a group, where both sets of passive complexing agents (those electronically quasi-passive from the perspective of the catalytic steps) and active ligands (those cooperative in the catalytic steps) occur. This is the field of the precursors, which contribute to the formation of catalytically active surface films.

Among first row transition metal complexes there are hydrolytically unstable formations, or those that are sensitive to the acidification of the solution. In these cases, hydrolytic decoordination of ancillary ligands does not require redox events, but normally this scenario is avoided by proper ligand design.

Another group of compounds has to be activated from their thermodynamic states to give rise to a determinant side-reaction: either upon changing the oxidation state of the metal center or due to the oxidation of the ligand itself (Scheme 20). Under catalytic conditions, degradative side-reactions may affect any of the molecular catalysts to some extent. This has been subject of several studies using advanced *in situ* techniques to reveal the true nature of water oxidation catalysis (Li et al. 2017). Recently, a manuscript summarized the main critical tests that need to be carried out to prove the molecular nature of electrocatalytic processes (Pelosin et al. 2020), demonstrating the usefulness of those on a known pentanuclear iron catalyst (Okamura et al. 2016). The transformation of a metal complex into the corresponding oxide is a major concern from the perspective of drawing structure-activity relationships with respect to the molecular catalyst.

However, if the application of such methodologies is considered vice versa, from the perspective of efficient precursor design, these might prove to be just as useful. Herein we would like to show only a few examples on how redox transformation of the ancillary ligands can lead to an active water oxidation catalyst. Utilization of metal-ligand assemblies may be justified in cases, where special requirements must be met, such as a concentration limit of the precursor, a narrow redox stability of the substrate material, a need for size-control of the deposited catalyst material, or a morphology preserving method.

Ligand degradation through its redox transformation is unequivocal if the identification of any by-product is possible (Lu et al. 2016), but in most cases the initiating event cannot be revealed perfectly, because only a minute part of the molecular catalyst acts as precursor. Just like in the case of copper-diglycylglycine. This copper-tripeptide complex has at least 66 years past in literature with the first known publication in 1955 (Dobbie and Kermack 1955). Year-by-year stability constants, ionic form distributions, as well as other thermodynamic constants and properties have changed, but with a shorter history of its kinetics and reactivity. In fact, it is a water-soluble and stable complex, but it turned out to be precursor to a heterogeneous catalyst in water oxidation (Lukács et al. 2019). In sodium borate solution at its

maximum pH-buffering capacity (pH ~ 9.2) different equilibrium species were identified. Analysis of molecular spectra revealed borate coordination (see also the 'Ligand participation in O-O bond formation section') which allowed a new kinetic route of oxidation. While a purely homogeneous water oxidation catalysis was established at pH ~ 12 (at suitable absolute concentrations), lowering the pH, heterogeneous feature appeared. A black amorphous $\text{Cu}_2\text{O}/\text{CuO}/\text{Cu}(\text{OH})_2$ deposit became responsible for a smaller overpotential. This black 'raspberry' shaped amorphous nanostructure is not unique in the literature as well as its birth from bio-degradable complexes, but it has been unmatched before that the surface might be unstable to overpolarization, since it has a maximum anodic power density. Augmentation of the potential burst a side-reaction ending up in the total destruction of the nanostructure and re-dissolution of the copper-oxide catalyst. The authors investigated and proposed a method to defend the structure. If the deposition was carried out onto a rigid hematite nanostructure it had become polarization-resistant. This study emphasized that the catalytic nanostructure cannot be investigated by neglecting the covered surface, because without physical/chemical defense it may be sensitive to overpolarization.

Another short example involves Ni complexes with substituted PBOA ligands (Scheme 5, PBOA ligand, $\text{R}_1 = \text{R}_2 = \text{CH}_3$ and $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{OCH}_3$) that were investigated as molecular water oxidation catalysts at basic pH. Electrochemical studies revealed that the first oxidation wave corresponded to the $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ redox couple. At pH 10-13 a second oxidation wave was observed due to the generation of a phenyl radical cation associated with the coordination of a hydroxide anion to form $[\text{Ni}^{\text{III}}(\text{PBOA}^*)(\text{OH})]^-$, which was responsible for the O-O bond formation and O_2 release. The dimethyl and methoxy substituted PBOA complexes also exhibited two oxidation processes. The electronic perturbation aroused by the electron-donating ligands resulted in lower overpotentials for water oxidation (0.5 V for the parent PBOA complex, 0.17 V and 0.22 V for the substituted ones, respectively).

While these complexes were stable in basic aqueous solutions from pH 10 to 13, below this pH the protonation of the amidate group caused metal ion release (Garrido-Barros et al. 2019). The $1e^-$ electron oxidized $[\text{Ni}^{\text{III}}(\text{PBOA})]^-$ complex was fully stable within pH 10-12 on the electrochemical time scale, at pH 13 it underwent progressive substitution in four steps leading to $[\text{Ni}^{\text{III}}(\text{OH})_4]^-$. The doubly oxidized phenyl radical cation $[\text{Ni}^{\text{III}}(\text{PBOA}^*)(\text{OH})]^-$ also suffered from hydroxide substitution processes. However, additional degradation occurred through the hydroxylation of the aromatic ring with the OH^- present in the medium that in turn was competing with the O-O bond formation. Based on stability measurements as a function of pH, the authors concluded two possible pathways competing with the homogeneous catalytic process: (a) the formation of the hydroxylated aromatic species with no water oxidation activity and (b) the formation of a catalytically active NiO_x attached to the surface of the electrode with higher overpotential for water oxidation than the molecular catalyst. The dominant process depended on the pH: increase of pH from 10 to 12 promoted NiO_x formation. At pH 13, the amount of the initially active NiO_x decreased, indicating that the material dissolved during a further, slower process. The impact of the applied potential also proved that a slight modification of the different experimental conditions might

influence the stability and the catalytically active form of Ni complexes. During controlled potential electrolysis at +1.05 V vs. NHE (pH ~ 11) no NiO_x formation was detected and the oxygen produced at 94% Faraday efficiency with TON of 3.81. Similar experiments carried out for the 'dimethylated PBOA' complex showed a higher stability and lack of NiO_x at the surface. According to the authors, the high stability of the dimethyl-PBOA complex at pH 11 was first presented in molecular Ni complexes.

Note that the pH-dependent *operando* formation of NiO_x from a *N,N'*-bis(salicylidene)-ethylenediamino-nickel(II) complex was also investigated (Feizi et al. 2018). Here, the applied ligand is often found to play an active role in redox catalysis. However, the complex suffered degradation and the surface deposit containing Ni, P and O in a carbon matrix was formed, and all of these complicated structures clearly showed different activity to simple NiO_x highlighting the unique role of ligand.

No doubt, tunable and well-understood metal oxide formation vs. molecular catalysis may be of use, when size- or morphology control of the deposit is important, when a metal oxide component has to be introduced into a system under controlled conditions, or the surface catalyst regeneration is required without dismantling the cell. Redox-active ligands should not be omitted from the line of options in such cases.

Conclusion And Outlook

Molecular complexes are often regarded as the “chemists’ warm little pond” to allow insight into unexplored details of water oxidation and thus, into artificial photosynthesis. Indeed, these compounds are intrinsically sensitive to degradation; thermodynamics dictates that the harsh oxidative conditions demanded by the endergonic oxygen evolving reaction most often are enough to eventually break up aliphatic bonds or open aromatic rings. Yet, there are examples of ligands accumulating electron vacancies, serving as internal base to facilitate coupling between electron and proton transfer, participating in the O-O bond formation, or allowing true catalyst formation upon redox transformation efficiently. Realization of such phenomena and the concept of self-healing catalytic systems may be guidance for new discoveries and a timely paradigm shift.

This overview is merely a short glimpse at the various catalyst types of an ever-evolving field – artificial photosynthesis. On the timescale of human research, the evolution of the natural system might seem static, but let us not forget that evolution has been in motion since the appearance of the first living organism and our species is only a milestone on the path it follows. How many “futile exercises” shaped the image of biosphere as we may know it today, and how many left a mark that is waiting for a prepared explorer; these provoking questions should inspire us to step forward into unknown.

Abbreviations

APT atom-proton transfer

BDD boron-doped diamond

FTO fluorine-doped tin oxide

GC glassy carbon

HER hydrogen evolving reaction

I2M interaction of two M-O units

ITO indium tin oxide

KIE kinetic isotope effect

MS-EPT multiple-site electron-proton transfer

NP nanoparticle

OEC oxygen evolving complex

OER oxygen evolving reaction

PCET proton-coupled electron transfer

PS II photosystem II

WNA water nucleophilic attack

WOC water oxidation catalyst

Declarations

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Statements & Declarations

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Competing interests

The authors have no relevant financial or non-financial interests to disclose.

Author Contributions

All authors contributed to the conception of and literature analysis in the review. The first draft of the manuscript was written by József S. Pap and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Scheme

Schemes 1-20 are available in the Supplementary Files section.

Supplementary Files

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