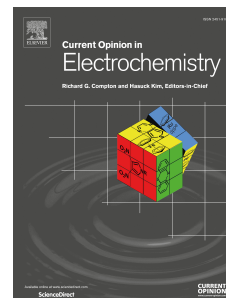


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Electronic, mechanistic and structural factors that influence the performance of molecular water oxidation catalysts anchored on electrode surfaces

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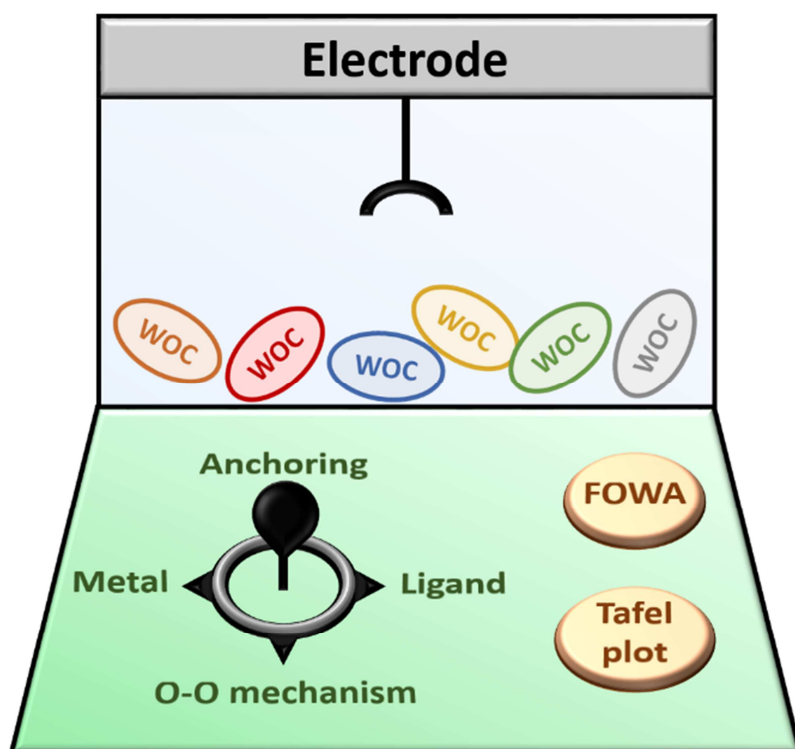
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Graphical Abstract



Abstract

To harness solar energy to generate fuels powerful anodes for the water oxidation reaction need to be developed. During the last decade an extensive number of molecular water oxidation catalysts based on transition metals have been reported and in some cases these molecular catalysts have been anchored on conductive surfaces generating molecular anodes. In this review, we analyze the factors that influence the performance of these molecular anodes, which are largely related to their mechanism of O-O bond formation and the nature of the anchoring functionality.

Introduction

Our society urgently needs renewable energy sources to replace fossil fuels [1]. The only source of unlimited and renewable energy is the sun that in one day provides, at the surface of planet earth, all the energy that the humanity uses in a year [1]. One attractive way to harness this energy is the use of technologies that mimic natural photosynthesis by harvesting solar energy to generate fuels. These technologies could use sunlight energy to drive the water oxidation reaction ($2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$) and the H^+ or CO_2 reduction reactions. The products of the reduction reactions are H_2 or reduced CO_2 compounds respectively, that are named “solar fuels” and that can be stored and used as a replacement for fossil fuels [1,2,3,4].

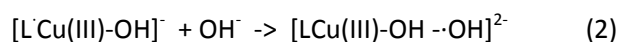
To come up with useful devices for the generation of solar fuels, each component of the device including light harvesting and catalysts materials and/or molecules, need to work efficiently and in harmony. It is thus important to understand the behavior of all the components individually before a device can be successfully assembled [1,5,6]. In the oxidation site, the anodic material can be built using a molecular water oxidation catalyst anchored on conductive surface [2,7,8]. During the last decade an extensive number of molecular water oxidation catalysts based on transition metals have been reported and in some cases even a detailed mechanistic description has been carried out [2,9,10,11,12,13,14,15]. Furthermore, some of these molecular catalysts have been anchored on the surface of conductive and semiconductive materials to generate molecular anodes and photoanodes respectively for the water oxidation reaction [7,8,16,17,18,19].

Herein we report on the electronic, mechanistic and structural factors that influence the performance of a molecular water oxidation catalyst once it is anchored on a solid support. This is an essential information needed for the successful design of molecular photo(electroanodes) to be used in practical artificial photosynthesis devices.

Homogeneous water oxidation catalysts

A large number of molecular catalysts have been described in the last years using different transition metals and ligands, including mononuclear and binuclear complexes, see Charts 1 and 2 for the most representative ligands and metal complexes described in the literature [12]. The highest activities in terms of turnover number (*TON*) and turnover frequency (*TOF*) have been achieved with the Ruthenium complexes $\{[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{L3})_2]_2(\mu\text{-L9py})\}$, **1**, $[\text{Ru}^{\text{IV}}(\text{O})(\text{L12COO})(\text{L1})_2]$, **2**, and $[\text{Ru}^{\text{IV}}(\text{O})(\text{L11})(\text{L2})_2]$, **3** [10, 20, 21]. Ru complexes have been the main focus in the molecular water oxidation field development during the last years along with Ir complexes including the precursor $[\text{Ir}^{\text{III}}(\text{L6})(\text{L7})(\text{Cl})]$, **4**, and its catalytically active derivatives. Some first-row transition metal complexes have also been reported as potential water oxidation catalysts although in most cases the initial complex degrades to its corresponding oxide that is the real active catalyst. An example of rugged first row water oxidation catalyst that does not degrade during turnover is the Copper complex, $[\text{Cu}^{\text{II}}(\text{L13})]^{2-}$, **5**, that has also been anchored on solid supports [7,11,22].

The mechanism through which the metal complexes oxidize water to produce oxygen in solution has been a subject of study since the appearance of the first well characterized molecular catalyst the “blue dimer” [13,23,24]. The mechanisms are studied by means of kinetic and spectroscopic techniques, ^{18}O labeling experiments and complemented with theory calculations, in most cases based on Density Functional Theory (DFT) [2,12,13,15,20,21,24]. A key feature for the design of molecular water oxidation anodes is the pathway followed for the O-O bond formation after the activation of the transition metal complex via a series of electron transfers (ET) and/or proton coupled electron transfers (PCET) steps as shown in Figure 1. When the O-O bond formation is made via the interaction of H_2O (or OH^-) solvent molecule to an activated M-O species the pathway is named Water Nucleophilic Attack (WNA). Within the WNA we can distinguish two different cases as shown on the upper part of Figure 1 for complexes **2** and **5**. The main difference between the two is that in the **WNA** the formation of the hydroperoxido intermediate takes place via a concerted two electron pathway in a single step (equation 1) while for the **SET-WNA** the hydroperoxido formation occurs via two one electron transfer steps, with the subsequent formation of a two centers-three electrons (2c-3e) intermediate, as shown in equations 2-3,[25] In equation 1, L refers to the set of auxiliary ligands attached to the Ru center whereas in equations 2-3 represents the amidate ligand of complex **5**.



All the Ru complexes that have been described so far follow the WNA whereas the Cu ones follow the SET-WNA. [9,10,20,21,25]

The other main pathway that leads to the formation of oxygen-oxygen bonds is the so-called Interaction of 2 M-O units (I2M) that is described in the lower part of Figure 2 and that can take place in an *inter*- or an *intra*-molecular manner. Complex **3** is an example of the **inter-I2M** [26] path whereas the dinuclear complex $\{[\text{Ru}^{\text{II}}(\text{H}_2\text{O})(\text{L12H})]_2(\mu\text{-L9H})\}^{3+}$, **6**, is an example of the **intra-I2M** [27] as can be observed in Figure 1.

Electrochemical measurements, such as cyclic voltammetry (CV), provide a powerful tool to extract thermodynamic and kinetic information in electrocatalytic processes. Particularly, Savéant and coworkers developed the foot-of-the-wave (FOWA) analysis tool that allows the calculation of rates in the absence of a perfect S-shape CV response once considered the chemical and electron transfer steps involved in the rate determining step. Furthermore, FOWA uses the initial points of the catalytic wave, which are much less affected by side reactions. [28,29] This methodology has been applied to the electrocatalytic water oxidation to extract rate constants and *TOF* values [30]. In addition, the obtained kinetic parameters allow to obtain catalytic Tafel plots that relate the calculated *TOF* with the overpotential of the electrocatalytic process. Therefore, Tafel plots are useful for benchmarking the performance of water oxidation catalysts since one can easily identify the fastest one by comparing their *TOF* values at the same overpotential. Moreover, the change in the slope from an inclined to a flat line represents the minimum overpotential at which those catalysts operate at maximum *TOF*.

Figure 2 shows the catalytic Tafel plots for catalysts **1**, **2**, **3** and **5**. A number of conclusions can be drawn from the careful examination of the catalytic Tafel plots of the best water oxidation catalysts in solution.

At high overpotentials ($\eta > 0.7$ V) **1**, **2** and **5** reach TOF_{MAX} of 50 s^{-1} , 7700 s^{-1} and 6.2 s^{-1} respectively, Table 1. Catalyst **2** shows the highest rate that is almost two orders of magnitude higher than that of any other molecular catalyst and that of the naturally occurring reaction in the photosystem II [31]. The slope of the three plots at $\eta < 0.55$ V are parallel because in the three complexes the rds (rate determining step) is first order with regard to the initial metal complex concentration. Besides these kinetic analysis, the mechanism is further supported by ^{18}O labeling experiments and/or DFT calculations (WNA for **1** and **2** and SET-WNA for **5**, Table 1). [7,10,20] The Tafel plot of **3** shows that this metal complex requires only $\eta > 0.3$ V to oxidize water at a $TOF_{MAX} = 53\text{ s}^{-1}$, being one of the lowest overpotentials reported for molecular catalysts. In this case the kinetic analysis shows that the rds is second order with regard to the initial catalyst concentration, [**3**], a fact that is reflected in the slope of the red line at $\eta < 0.3$ V that obviously is not parallel to the slope of the other complexes.

On the other hand, it is worth noticing that in many cases the absence of detailed electrochemical description of the water oxidation catalysts prevents a proper FOWA analysis and thus a benchmarking via catalytic Tafel plots is not possible. Further, in some cases the initial complex is not even the active catalyst but a precursor that is transformed into something that becomes active. This is the case of catalyst precursor **4** displayed in Figure 2 and other (pre)catalysts reported in the literature [32,33,34,35,36].

Molecular anodes for water oxidation

Molecular anodes can be defined as conductive materials containing a molecular catalyst attached to the surface, that retain its molecularity during turnover. The link between the material and the catalyst is provided by a functional group that acts as an anchoring point and is attached to an auxiliary ligand without modifying the intrinsic coordination properties of the original complex [37]. Initial efforts in this direction focused on including carboxylate or phosphonate as anchoring groups so that the resulting complex was attached to a conductive metal oxide electrode by a covalent M-O bonding, as in the case of $\{[\text{Ru}^{\text{II}}(\text{OH}_2)(\text{L1})_2(\mu\text{-L10})]\}^{\text{het}}$, **1**^{het} [38,39]. However, the poor stability induced by hydrolytic M-O cleavage in aqueous conditions, particularly at low pH has prevented its widespread use. The use of stabilizing coatings based on porous and thin layers of Al_2O_3 or TiO_2 on top of molecular photoanodes has been explored to increase the longevity of this type of linkages, a strategy that has also been employed in the design of dye sensitized solar cells [40,41,42]. In addition, silyl groups have also been used as

alternative anchoring group employed in the case of the Ir catalyst $[\text{Ir}(\mathbf{L8})(\mathbf{L6})(\text{Cl})]$, $\mathbf{4}^{\text{het}}$ [43], which features stronger M-O bonds and enhances its stability [44]. The latest advances in the development of molecular anodes include the use of inexpensive and conductive carbon-based electrodes where complexes are anchored by either covalent C-C bonds as is the case of complex $[\text{Ru}^{\text{IV}}(\text{O})(\mathbf{L11})(\mathbf{L5})_2]$, $\mathbf{3}^{\text{het}}$, [45] or π - π stacking as shown for $[\text{Ru}^{\text{IV}}(\text{O})(\mathbf{L12COO})(\mathbf{L4})_2]$, $\mathbf{2}^{\text{het}}$; and $[\text{Cu}(\mathbf{L14})]$, $\mathbf{5}^{\text{het}}$ [7,8,17,18].

As discussed in detailed in the previous section, another important aspect in the performance of molecular anodes is the mechanism of the O-O bond formation step. The mechanism is important due to translational mobility restrictions imposed by the catalyst-electrode linkage. In the case of the WNA, SET-WNA and intra-I2M mechanisms, the catalyst does not require a translational movement and thus the anchoring process should not interfere in the O-O bond formation step. One example of this situation is $\mathbf{1}$, which catalyzes the water oxidation through WNA mechanism in the homogeneous phase [20]. Figure 2 allows the comparison of the electrocatalytic performance of $\mathbf{1}$ to that of its anchored counterpart $\mathbf{1}^{\text{het}}$. The two complexes show analogous catalytic Tafel plots ($\mathbf{1}$, $TOF_{\text{MAX}} = 50 \text{ s}^{-1}$; $\mathbf{1}^{\text{het}}$, $TOF_{\text{MAX}} = 47 \text{ s}^{-1}$, see also Table 1), indicating that the restricted mobility does not affect the performance of $\mathbf{1}^{\text{het}}$.

The fastest water oxidation catalyst up to date, $\mathbf{2}$, also follows a WNA mechanism in solution [10]. Its heterogenized counterpart, $\mathbf{2}^{\text{het}}$, results in a molecular anode that its rate is analogous to homogenous counterpart ($\mathbf{2}$, $TOF_{\text{MAX}} = 7700 \text{ s}^{-1}$; $\mathbf{2}^{\text{het}}$, $TOF_{\text{MAX}} = 8000 \text{ s}^{-1}$) [8]. The combination of fast kinetics and the WNA mechanism not only allows to generate molecular anodes that reach a million turn over in the dark [8], but also molecular photoanodes that reach 1 mA/cm^2 of photocurrent for several hours under illumination [17].

It is also interesting to analyze the behavior of catalysts following an inter-I2M mechanism, which require a dimerization step during the O-O bond formation from two different molecules. Such a mechanism is drastically hindered upon anchoring the molecular catalyst on the surface of the electrode. This fact can either cause the total loss of catalytic activity or force the catalyst to switch to a WNA type of mechanism. A good example of this case is $\mathbf{3}$, which in homogeneous phase catalyzes the water oxidation through an inter-I2M mechanism [21]. When this catalyst is anchored, $\mathbf{3}^{\text{het}}$ loses the mobility required to dimerize and promotes the water oxidation through a WNA mechanism at a much lower rate ($\mathbf{3}$, $TOF_{\text{MAX}} = 53 \text{ s}^{-1}$; $\mathbf{3}^{\text{het}}$, $TOF_{\text{MAX}} = 1.9 \text{ s}^{-1}$). [45] The high energetic paths that the catalyst must follow due to the restricted mobility are now comparable to those of its oxidative degradation that lead to the irreversible formation of RuO_2 . Thus during the initial turnovers both the molecular and the RuO_2 catalysts coexists at the surface of the electrode, but as the catalytic reaction proceeds the molecular

catalyst completely depletes. After a few turnovers the only active species remaining at surface of the electrode is RuO₂.

An even more interesting case arises from the anchoring of **5**, a copper-based complex bearing a tetraamidate ligand with a redox non-innocent character [9]. In homogeneous phase, this complex promotes the O-O bond formation by SET-WNA mechanism. The incorporation of a pyrene functional group in the phenyl ring of the ligand generates complex **5**^{het} where the pyrene functionality is linked to the surface of graphene by non-covalent π - π interactions [7]. The resulting molecular electrode performs catalytic water oxidation at higher rates, nearly two orders of magnitude, than its homogeneous analogue (**5**, $TOF_{MAX} = 6.2 \text{ s}^{-1}$; **5**^{het}, $TOF_{MAX} = 560 \text{ s}^{-1}$). This constitutes the first example where the anchored catalyst performs much better than its homogenous counterpart. This large increase in reaction rate is due to the fact that the graphene surface is now becoming an integral part of the ligand attached to the metal center via the π - π stacking interaction. This in turn reduces the energy of activation at the rate determining step that in this case is the electron transfer from the metal catalyst to the electrode surface.

Concluding remarks

An important challenge in the field of water splitting with sunlight for the generation of solar fuels is the construction of an efficient device. For this purpose, it is imperative to develop rugged and highly performant electro- and photo-anodes for the oxidation of water to dioxygen. A potential option to achieve this consists on the anchoring of molecular water oxidation catalysts into the surface of conductive or semiconductive materials.

In the present report we have focused our attention on the anchoring of molecular WOCs into graphitic or metal oxide type of surfaces. This generates molecular electroanodes with a range of different performances as compared to the initial molecular catalyst in homogeneous phase. The performance of these catalysts anchored on surfaces is strongly related to the mechanism of O-O formation followed by the different catalysts.

- Catalysts **1** and **2** whose O-O mechanism is a WNA have exactly *the same* performance in homogeneous phase than in heterogeneous phase as can be graphically observed in the Tafel plots of Figure 2.

- On the other hand, catalyst **3** whose O-O bond formation mechanism is I2M in homogeneous phase has to switch to a WNA when anchored on solid supports, due to mobility restrictions and thus its rates **decrease** in heterogeneous phase as also shown in Figure 2. In addition, due to this mobility restriction, it ends up degrading to RuO₂.
- Lastly, catalyst **5** undergoes O-O bond formation via a SET-WNA and when anchored into the surface of the graphene electrode **increase** its TOF_{max} by nearly two orders of magnitude with regard to the same catalyst in homogeneous phase, as can again be graphically observed in Figure 2. This is due to the graphene involvement as part of the auxiliary ligands bonded to the Cu center.

These changes of catalyst behavior and performance from homogeneous to heterogeneous phase just described, is nicely observed in the combined Tafel plots displayed in Figure 2.

Finally, the chemistry described and discussed in this review manifests the importance of mechanistically understanding the pathways for O-O bond formation in homogeneous phase in order to assess the suitability of anchoring such a catalyst onto solid surfaces. In addition, the nature of the electrode surface and the linkage between catalyst and electrode can strongly influence the performance and stability of the anchored catalyst.

Conflict of interest statement

No conflicts.

Acknowledgements

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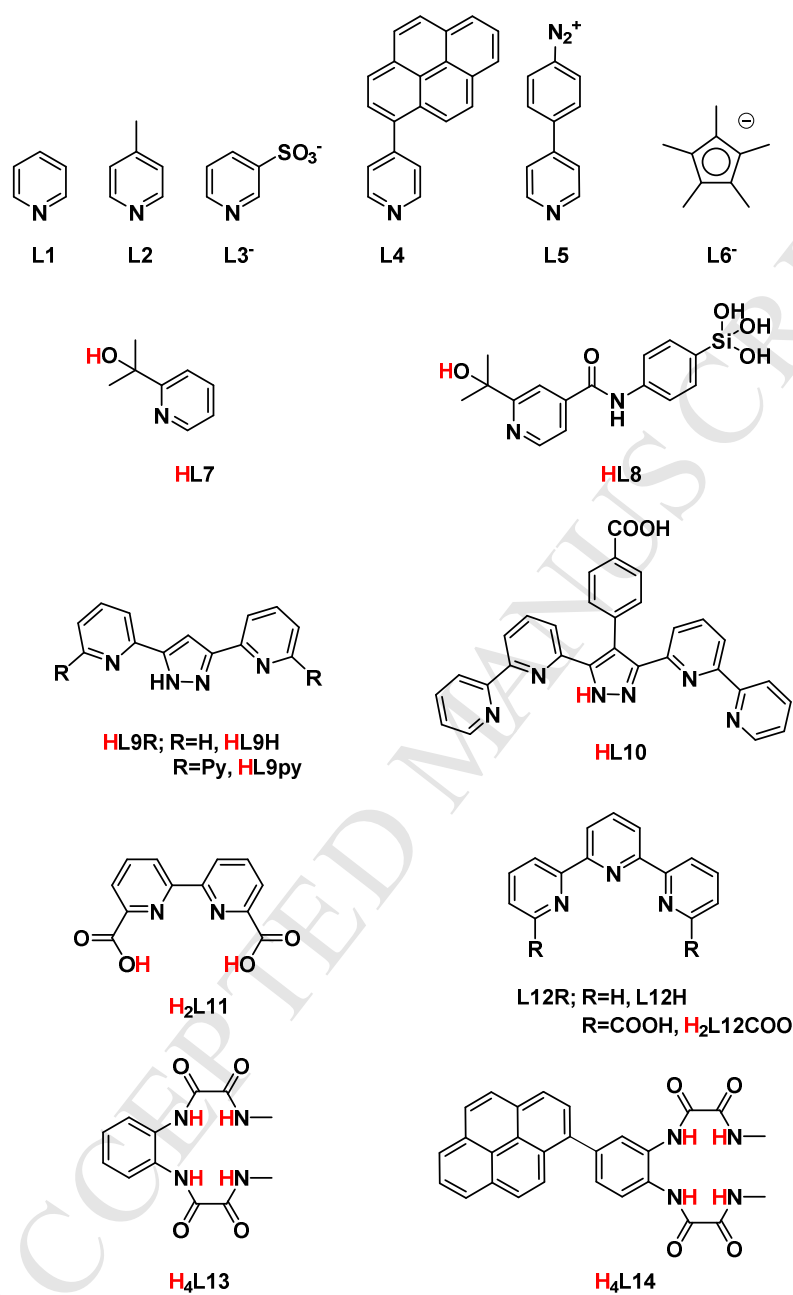


Chart 1. Organic ligands discussed in this report.

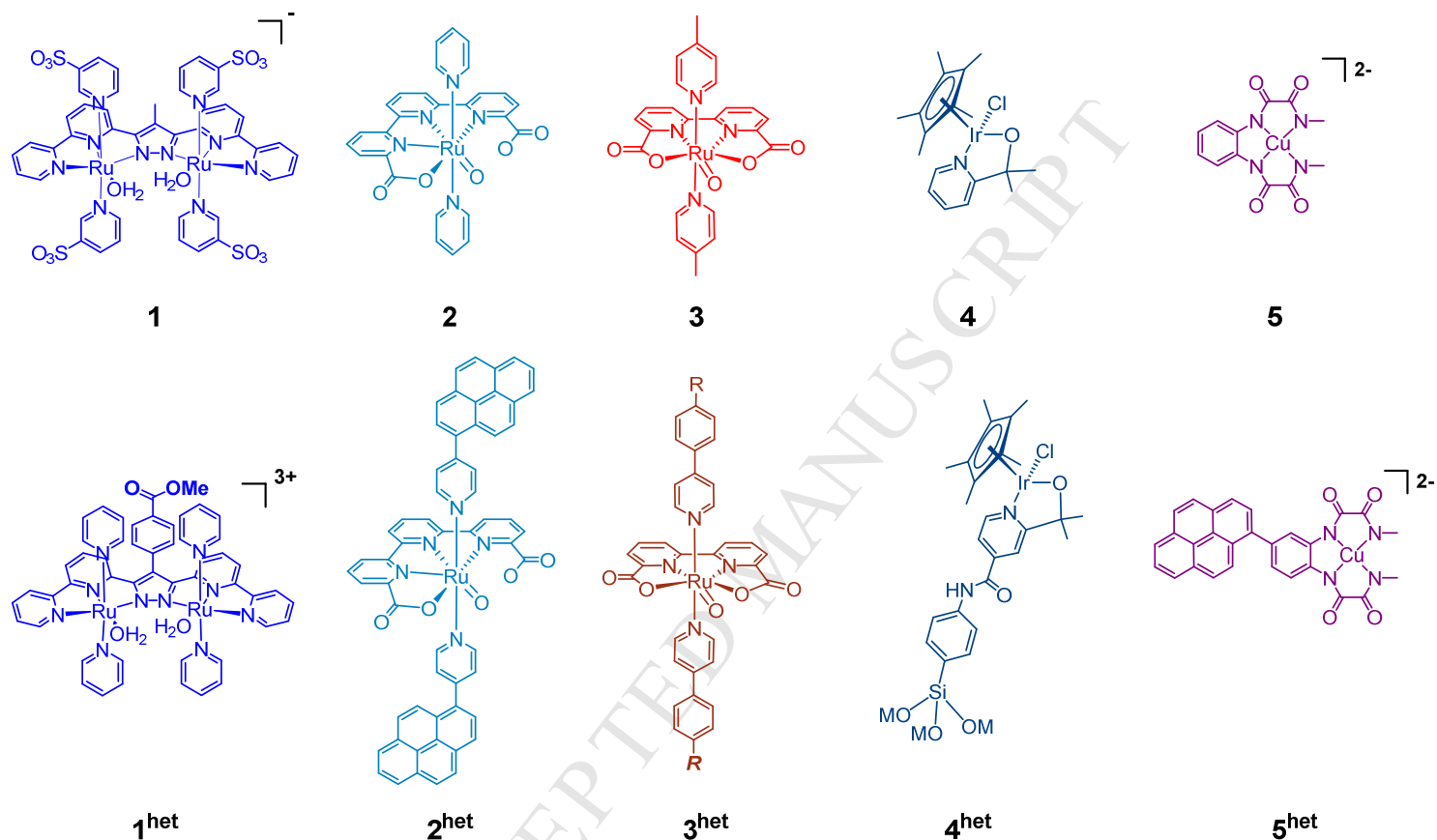


Chart 2 Drawing of representative homogeneous water oxidation complexes (**1-5**) and their heterogenized derivatives (**1^{het}-5^{het}**). The water oxidation mechanism elucidated for **1-5** is indicated by their color: blue, WNA; purple, SET-WNA; and red, inter-I2M. "M" represents the Metal at the surface of the electrode. For the heterogenized catalyst **3^{het}** R is either H or C from the glassy carbon surface generated after the diazonium electrografting.⁴⁵

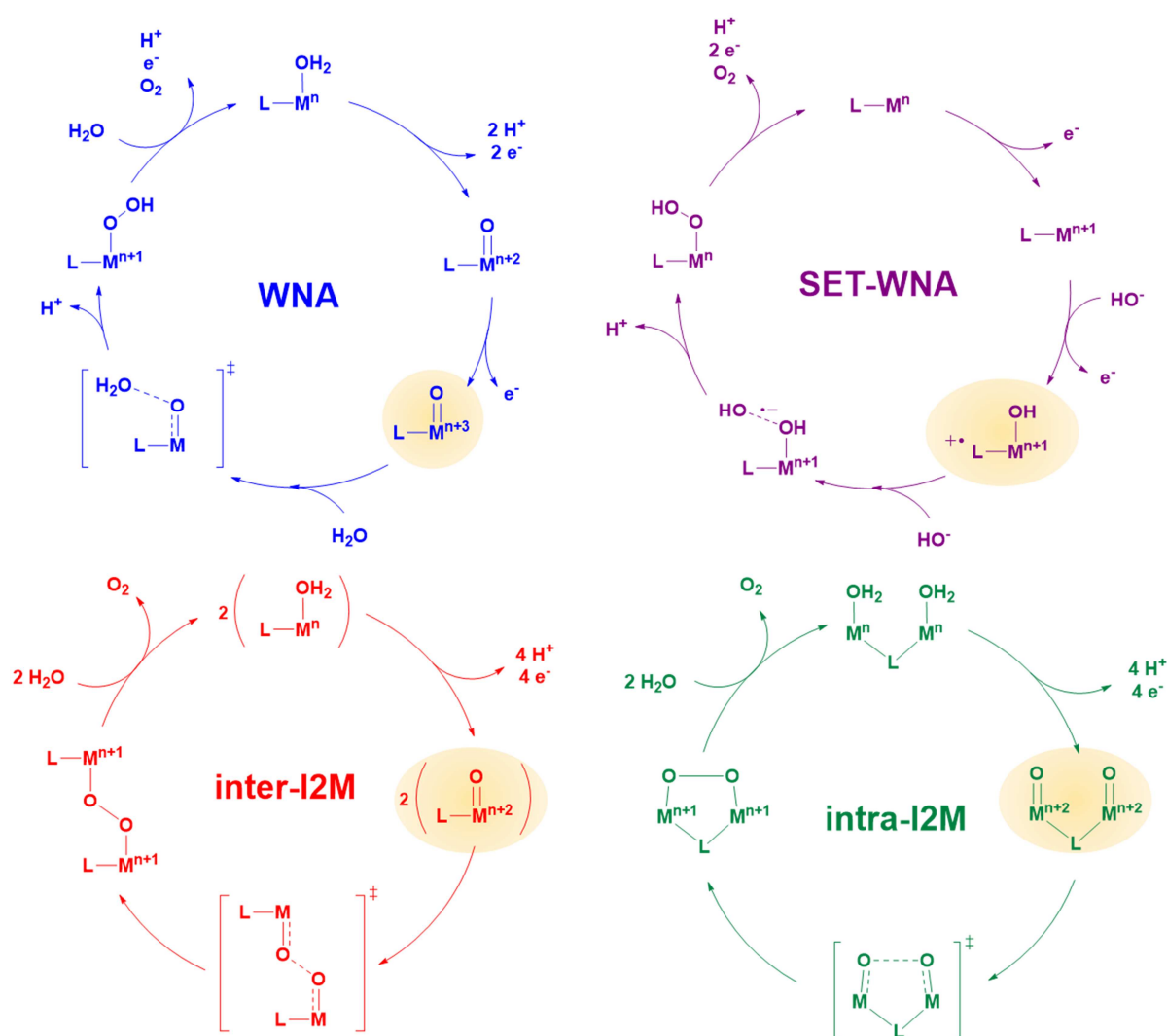


Figure 1. Examples of O-O bond formation mechanism followed by transition metal complexes. Top left, WNA followed by complex **2**. Top right, followed by **5**. Bottom left, followed by **3**. Bottom right, followed by **6**. The superscript $n+i$ stands for the formal oxidation state of the metal center, regardless the partial or total radical character of the M-O bond. L represents the different auxiliary ligands bonded to the metal center. The yellow circle highlights the oxidized activated species that can promote the O-O bond formation.

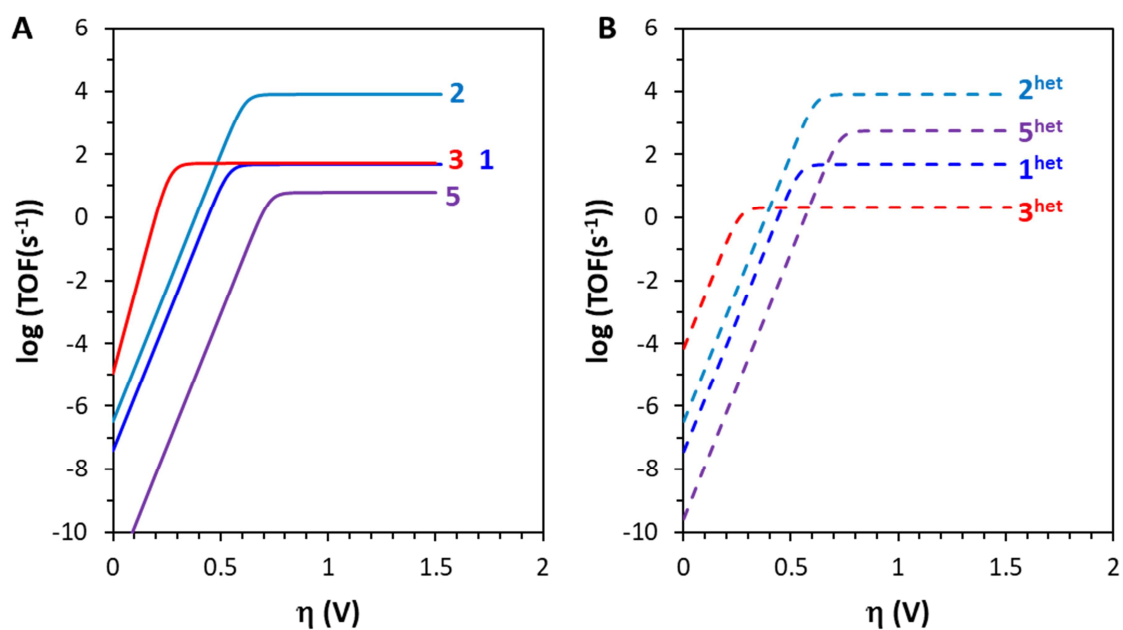


Figure 2. A) Catalytic Tafel plot of **1** at pH = 1.0, **5** at pH = 12.0 and **2** and **3** at pH = 7.0. The concentration used for calculating **3** was 1 mM. B) Catalytic Tafel plot of **1^{het}** at pH = 1.0, **5^{het}** at pH = 12.0 and **2^{het}** and **3^{het}** at pH = 7.0. Due to the restrained mobility on the electrode, a first order kinetics with regard to the catalysts was assumed in all heterogenized complexes. All plots were built using the literature values (see Table 1) and using the equations from reference 30.

Table 1. Kinetic parameters for the molecular catalysts in solution and deposited on electrodes.

<i>Complex</i>	<i>pH</i>	<i>Mechanism</i>	$TOF_{MAX} [s^{-1}]_{hom}$	$TOF_{MAX} [s^{-1}]_{het}$	$k_D [s^{-1} M^{-1}]^{[a]}$	<i>Reference</i>
1	1.0	WNA	$5.0 \cdot 10^1$	---	---	29
1^{het} [b]	1.0	WNA	---	$4.7 \cdot 10^1$	---	37
2	7.0	WNA	$7.7 \cdot 10^3$	---	–	10
2^{het}	7.0	WNA	---	$8.0 \cdot 10^3$	---	8
3 [c]	7.0	inter-I2M	$5.3 \cdot 10^1$		$1.7 \cdot 10^5$	21
3^{het}	7.0	WNA		1.9	–	44
5	12.0	SET-WNA	6.2	--	–	9
5^{het}	12.0	SET-WNA	---	$5.6 \cdot 10^2$	---	7

[a] Dimerization constant for inter-I2M mechanism, [b] We have performed the foot-of-the-wave analysis of the reported data in reference 38.⁴⁶ [c] TOF_{MAX} calculated with **[3]** = 1 mM.

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