Doctoral (Ph.D.) dissertation

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“Application of Water-Insoluble Iron Complexes in Water Oxidation”

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I. Introduction

In combination with the finite natural reserves of fossil fuels, our continuously growing energy demand has expedited the development of alternative renewable energy resources. Additionally, the combustion of fossil fuels increases carbon dioxide (CO_2) emissions, which have fundamental adverse effects on the global climate, regarded as the primary contributor to global warming.

Artificial photosynthesis (AP), aiming to harvest solar energy, can produce clean, sustainable, and large-scale energy carriers through water splitting and generating hydrogen gas as renewable chemical fuel. Water splitting by AP attracted distinguished attention from researchers, and it is considered the most encouraging method for producing hydrogen (H_2) as fuel and oxygen (O_2) as a side-product. H_2 is a potential fuel for the future because its energy density suits many applications. To achieve efficient AP, developing inexpensive, highly active, and stable catalysts for both hydrogen production (Hydrogen Evolving Reaction, HER) and water oxidation (Oxygen Evolving Reaction, OER) is inevitable in the first place. However, it is standing as a problem since nowadays, the catalysts in practice utilize noble metals like Pt or Ir.

The fundamental challenge is the rational design and development of more cost-efficient catalysts for each reaction in order to create a device proficient at completing the whole water splitting process. Water oxidation catalysts (WOC) are intended to improve the OER efficiency, thus aiding solar-to-chemical energy conversion. Efforts have resulted in promising findings by applying different first-row transition metal-based electrocatalysts that can help to develop catalysts suitable for industrial and practical applications to replace noble metal-based materials.

According to the above objective, many recent studies focus on molecular systems based on transition metals (TMs) suitable as WOCs due to their structural versatility, transparent catalytic mechanisms, and ultimate atomic efficiency concerning catalytic centers. Among these TMs, Fe is an abundant and less toxic element in Earth's crust, having rich redox chemistry for the activation of O_2 in biological systems and versatile catalytic applications. Fe-based compounds can be envisioned as efficient electrocatalysts for the OER, too.

Consequently, in my dissertation, I concentrated on first-row transition metals; thus, Fe complexes with hydrophobic, robust heterocyclic ligands have been utilized in this work. The primary aim was to evaluate the redox behavior and intrinsic catalytic activity for water oxidation; thus, the Fe complexes were first investigated and characterized by electrochemical and spectroscopic methods in homogeneous organic/water mixtures to help select those are capable of OER electrocatalysis. The second aim was to discover simple methods (such as drop-casting, dip-coating, and electrodeposition) for the immobilization of the selected candidates on semiconducting materials in order to fabricate hybrid systems.

II. Experiential Work

A. Synthesis and characterization of the Fe complexes

Known complexes with different ancillary ligands have been selected that served as precursors for the catalytically active species. These ligands were:

(**a**) non-symmetric, readily available bidentate ligands, i.e., 2-(2’-pyridyl)benzimidazole (PBI) in $[Fe(PBI)_3](OTf)_2$ (**1**, OTf^- = trifluoromethyl sulfonate anion), 2-(2’-pyridyl)benzoxazole (PBO) in $[Fe(PBO)_2(OTf)_2]$ (**2**) (Fig. 1);

(**b**) pincer ligands like in the [Fe^{III}Cl$_2$(tia-BAI)] complex (**3**, where tia-BAI$^-$ = 1,3-*bis*(2'-thiazolylimino)isoindolinate(−)) and the [Fe^{III}Cl$_2$(btia-BAI)] complex (**4**, where btia-BAI$^-$ = 1,3-*bis*(2'-benzthiazolylimino)isoindolinate(−)) (Fig. 1). These ligands could be synthesized following a solvent-free literature method by simply melting together phthalocyanine and the appropriate aromatic amine.

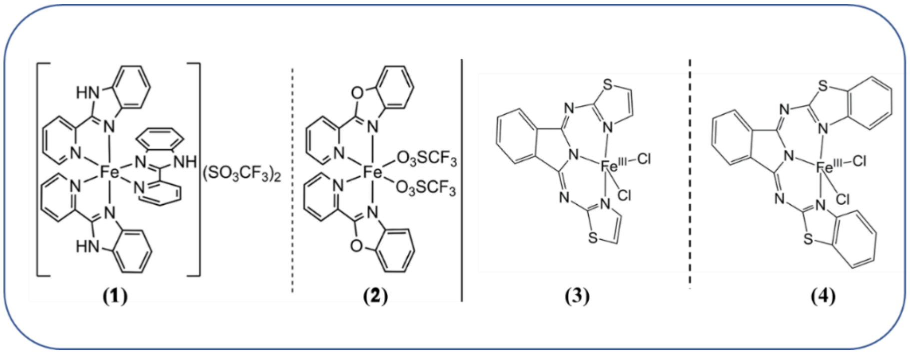

Figure 1 Molecular structure of the precursor Fe complexes **1-4** utilized in OER electrocatalysis.

High purity products required re-crystallization from methanol. FT-IR in the solid phase and UV-vis spectroscopy in solution and comparison of the data to those reported in the literature confirmed the expected complexes (the immobilized complexes were later analyzed by XPS, which also showed the expected compositions). Thus, These simple and efficient synthesis methods allowed high yields (ca. 65-90%) produced the wished complexes selectively with relatively low waste.

B. Homogeneous electrocatalysis

I investigated the electrochemical behavior of **1-4** in water/organic mixtures to reveal their intrinsic molecular properties. I compared the redox reactivity in the presence or absence of added water that was relevant to their later electrocatalytic application. Inert solvents have been applied that were miscible with water (acetonitrile, acetone). A standard 3-electrode setup was applied, where the working electrode was glassy carbon or boron-doped diamond, the counter-electrode was Pt, and the reference electrode was Ag/Ag$^+$. The experiments were carried out under Ar atmosphere. The experimental methods included LSV, CV, SWV, CA/CPE, and EIS.

C. Heterogeneous electrocatalysis

I applied different procedures (DIP, DC, and ED, as shown in Fig. 2) to immobilize the complexes on a semiconductor surface. In Fig. 2, methods (A-C) include DC and DIP with/no Nafion, whereas method D shows the ED method. I demonstrated with 4 (Fig. 1) the effectiveness of ED (Fig. 2, method D) in fabricating catalytically active layers. In the case of the electrodeposition of complexes 3 and 4, dichloromethane was applied as a solvent. In this case, the limited solubility of **4** in the obligate solvent mixtures prevented the use of any other immobilization methods.

The immobilized samples were used in electrocatalytic (CPE) experiments to produce O$_2$. All CPE experiments were carried out in 0.2 M borate buffer (pH ~ 8.3) or in some cases in 0.1 M carbonate using a 3-electrode configuration containing ITO, or FTO, Pt, and Ag/AgCl as working, counter, and reference electrodes, respectively. SEM, EDX, and XPS were used to analyze the complex/ITO(FTO) assemblies before and after electrolysis. Re-dissolution tests were carried out in the case of **1**/ITO and **3**/ITO to investigate the nature of the catalyst in organic solution after long-term CPE.

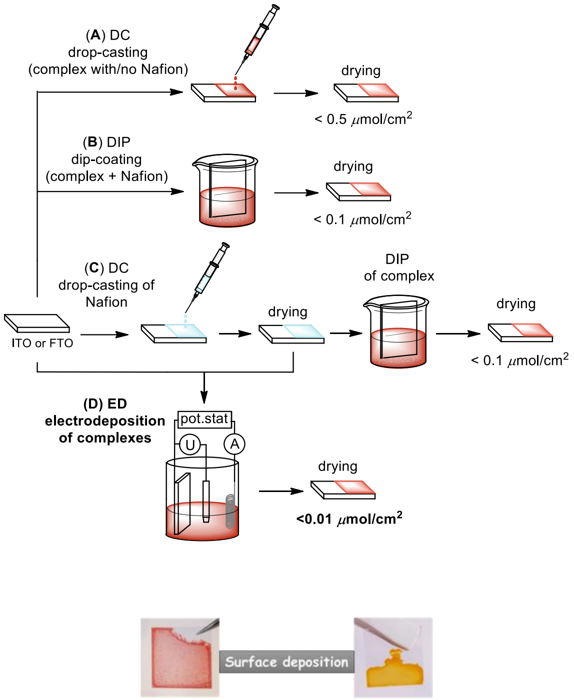

Figure 2 Schematic presentation of the different deposition methods and some illustrative pictures of the resulting modified electrodes.

III. Scientific results and thesis points

The results of my work are summarized in the following thesis points concerning the ultimate objective of finding Fe-based molecular catalysts for the oxygen-evolving reaction (OER, or water oxidation). I selected known Fe complexes containing non-symmetric NN' bidentate (complexes **1** and **2**) or NN'N pincer ligands (complexes **3** and **4**) and utilized those candidates successfully in water oxidation electrocatalysis as a new application.

1. I demonstrated for the first time that the non-coordinated heteroatoms (or groups) of non-symmetric bidentate heterocyclic ligands sufficiently electron-donating to support higher oxidation states of the Fe center could support water oxidation catalysis (ref. 1).

The strikingly different redox behavior caused by two different, non-symmetrical, heterocyclic bidentate ligands with analog structures and NN' binding mode in the two corresponding complexes highlights a determinant electronic effect of the non-coordinated heteroatoms. The relative electron-withdrawing nature of O in PBO compared with NH in PBI makes the PBI ligand a stronger donor. Therefore, the replacement of a non-coordinated O-atom in the ligand heterocycle (complex **2**) with an NH group (complex **1**) (Fig. 1) enhances the redox stability. Specifically, oxidation products occurring upon water oxidation catalysis are expectedly degradation-prone in the presence of a weaker donor ancillary ligand like PBO. This leads to a non-homogeneous behavior of **2** in water/acetonitrile, moreover, mineralization of the deposited complex on the ITO surface. Complex **1,** on the other hand, is an efficient precursor to an $Fe(PBI)_2$ assembly-based molecular catalysis.

2. I confirmed that the catalytically active form involved in water oxidation is generated by ligand exchange in the case of Fe complexes made with non-symmetric NN' bidentate or NN'N pincer ligands. This ligand exchange allows the coordination of H_2O molecules and determines the effectiveness of the immobilized catalyst. The ancillary ligand controls the favorable geometry, while the applied solvent strongly influences the exchange (refs. 1 and 2).

In the case of **1** (Fig. 1), the NN' ancillary ligand allows *cis*-diaqua coordination that favors efficient catalysis. In the case of the rigid NN'N pincer ligands (Fig. 1, complexes **3** and **4**), two equatorial sites become available for H_2O coordination, leading to the catalytically active form. The presence of water induces the ligand exchange, but the organic solvent is also essential: methanol is preferable over acetonitrile or dichloromethane. The solvent effect is more pronounced in the case of the NN'N ligand scaffold. Consequently, selecting the solvent for drop-casting can be crucial for gaining an active immobilized catalyst.

3. I found that Fe complexes exhibiting tridentate NN'N or bis-bidentate NN' ancillary ligand environments follow WNA mechanism in mixed water/organic solvent, where the rate-limiting step is the nucleophilic attack of a water molecule at a single Fe center (refs. 1 and 2).

Detailed kinetic investigations in water/organic solvent mixtures using complex **1** support single-site catalysis for the electrocatalytic O_2-evolution, since the observed rate-dependence is first order in both the H_2O- and the catalyst-concentration. In the case of complex **3,** the electrochemical detection of a proposed peroxidic intermediate also hints at a single-site mechanism. The KIE values in both cases are consistent with a rate-limiting, multiple-site electron-proton transfer WNA step.

4. I discovered that the NN'N pincer ligands could behave as redox-active compounds and carry a single electron vacancy stabilized by an extended π-delocalization (refs. 2 and 5).

The free tia-BAIH ligand undergoes oxidation at a similar potential like the Fe^{III} complex formed with it (**3**); therefore, the first $1e^-$ oxidation in the catalytic cycle is assigned as $[Fe^{III}(OH)(H_2O)(\text{tia-BAI})]^{1+}$ to $[Fe^{III}(OH)(H_2O)(\text{tia-BAI}^\bullet)]^{2+}$. This fact implies that a ligand-based $1e^-$ oxidation occurs in **3 and** plays a role in water oxidation catalysis.

5. I found that water-insoluble Fe complexes utilizing hydrophobic ancillary ligands with a two-way effect, i.e., control of the complex stability in the course of catalysis and strong attachment to the surface by secondary interactions, represent a viable strategy to fabricate molecular catalyst/anode hybrids (refs. 1-3).

Controlled potential electrolysis experiments using the drop-casted and dip-coated complex/electrode samples showed that hydrophobic ligands could be utilized to favor a stable surface attachment of the molecular architectures. I performed electrolysis to achieve several turnovers in O_2 production without considerable desorption of the metal-ancillary ligand moieties in the case of complexes **1** and **3**. This strategy is also promising when hybrid molecular co-catalyst/semiconductor carrier photoelectrodes are considered. Importantly, by this strategy, the application of additional immobilizing agents like Nafion can be avoided.

6. I introduced electrodeposition (ED) as a new method for the pincer ligand containing Fe complex precursors that affords a catalytically active, chloride-depleted catalyst coating that is non-homogeneously distributed on ITO and FTO electrodes (refs. 3-4).

The simple DC and DIP methods can be limited by the solubility of the complex, as complex **4** illustrates. In this case, ED may represent a more atom-efficient immobilization method that is morphology-preserving with respect to the carrier. The ED method is based on utilizing a chloride precursor complex $[Fe^{III}Cl_2(NN'N)]$, which is dissolved in an organic electrolyte and undergoes chloride/aqua ligand exchange upon the addition of water. Compared to the amount of the catalyst immobilized by DC and DIP in combination with Nafion, lower amounts in samples fabricated by ED are available by at least an order of magnitude that can be just as stable in long-term CPE. SEM analysis of the deposits from **3** and **4** confirmed a patchy distribution of the compound. The charge transfer resistance related to the electrocatalytic OER, determined by EIS, also demonstrates inhomogeneity of the deposited catalyst and a clear advantage of ED over the DC and DIP carried out using Nafion.

7. I revealed that extending the molecular structure of the Fe complex by introducing aromatic groups on the periphery of the NN'N polycyclic pincer ligands increases the surface stability of electrodeposited samples (ref. 3).

Polycyclic ligands would be beneficial to supporting surface stability of the immobilized complexes in the aqueous electrolyte and further investigate the role of ligand oxidation in electrocatalytic OER. Electrodeposition may be a fruitful immobilization method, even in the case of precursors that are only soluble in solvents that are practically immiscible with water. The example of complex **4** offers the same metal-binding geometry and donor pattern as 3 but contains fused aromatic rings on the periphery to provide a better surface affinity, illustrating that such molecular design enhances the stability of the complex/electrode assembly. This strategy can be beneficial for future co-catalyst/semiconductor hybrids in advanced PEC systems.

IV. Related publications

1. **Sahir M. Al-Zuraiji,** Tímea Benkó, Levente Illés, Miklós Németh, Krisztina Frey, Attila Sulyok, József S. Pap: *Utilization of hydrophobic ligands for water-insoluble Fe(II) water oxidation catalysts – Immobilization and characterization*
   Journal of Catalysis 381 (2020) 615-625. **IF = 7.920** Cited: 8(5)

2. **Sahir M. Al-Zuraiji,** Dávid Lukács, Miklós Németh, Krisztina Frey, Tímea Benkó, Levente Illés, József S. Pap: *An Iron(III) Complex with Pincer Ligand—Catalytic Water Oxidation through Controllable Ligand Exchange*
   Reactions 1 (2020) 16–36. **IF = n.a.** Cited: 4(2)

3. **Sahir M.Al Zuraiji,** Tímea Benkó, Krisztina Frey, Zsolt Kerner, József S.Pap: *Electrodeposition of Fe-Complexes on Oxide Surfaces for Efficient OER Catalysis*
   Catalysts 11 (2021) 577. **IF = 4.146.** Cited: 3(2)

4. József S. Pap, **Sahir M. Al-Zuraiji**: *Immobilization and Characterization of Water-insoluble Fe Complexes as Molecular Catalysts For Water Oxidation*
   12th ICEEE – 2021 "Global Environmental Development & Sustainability: Research, Engineering & Management," November 18–19, 2021 RKK – Óbuda University, Budapest, Hungary.
   Proceedings book (8 pages), ISBN: 978-963-449-256-6.
5. **Sahir M. Al-Zuraiji**, József S. Pap: *Redox-active ligands in Fe complexes and their use in water oxidation catalysis*
   Engineering Symposium at Bánki (ESB 2021), http://bgk.uni-obuda.hu/esb/2021/
   Proceedings book (6 pages), ISBN:

V. Conference presentations

1. **Sahir M. Al-Zuraiji**, Tímea Benkó, József S. Pap: *Application of water-insoluble Fe(II) complexes with hydrophobic bidentate N-donor ligands in electrocatalytic water oxidation*
   European Materials Research Society (E-MRS) Spring Meeting, Materials for Energy, symposium A – Latest advances in solar fuels, https://www.european-mrs.com/latest-advances-solar-fuels-emrs
   May 27-31, 2019, Nice, France. (**poster A.3.11**)

2. József S. Pap, **Sahir M. Al-Zuraiji**: *Immobilization and Characterization of Water-insoluble Fe Complexes as Molecular Catalysts For Water Oxidation*
   The 12th ICEEE-2021 International Annual Conference on "Global Environmental Development & Sustainability: Research, Engineering & Management."
   18th – 19th of November 2021, Budapest – Hungary. (**oral presentation**)

3. József S. Pap, Tímea Benkó, Krisztina Frey, **Sahir M. Al-Zuraiji**, Márta M. Móricz, Shaohua Shen: *How First Row Transition Metal Complexes Can Be Utilized to Improve Water Oxidation in (Photo)Electrocatalytic Hybrid Systems?*
   The "5th International Conference on New Photocatalytic Materials for Environment, Energy, and Sustainability" (NPM-5) & The "6th International Conference on Photocatalytic and Advanced Oxidation Technologies for the Treatment of Water, Air, Soil and Surfaces" (PAOT-6)
   Proceedings (p. 70), ISBN number: 978-963-306-789-5 (**oral presentation**)