



Óbuda University, Doctoral School on Material Science
and Technology

"Synthesis and Application of Organic-Inorganic Nanocomposites in Artificial Photosynthesis"

6th semester

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PhD student

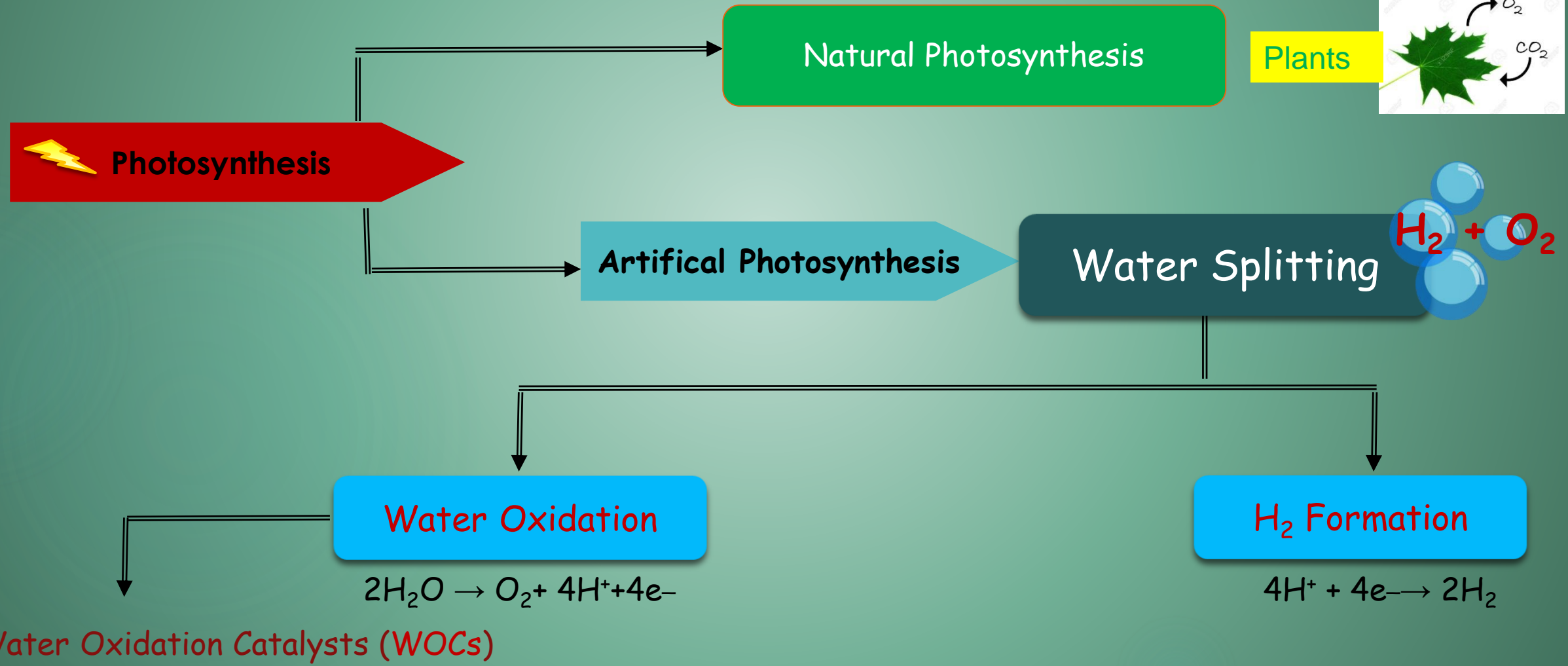
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Overview

Renewable Energy

such as sunlight, wind, rain, tides, waves, and geothermal heat.

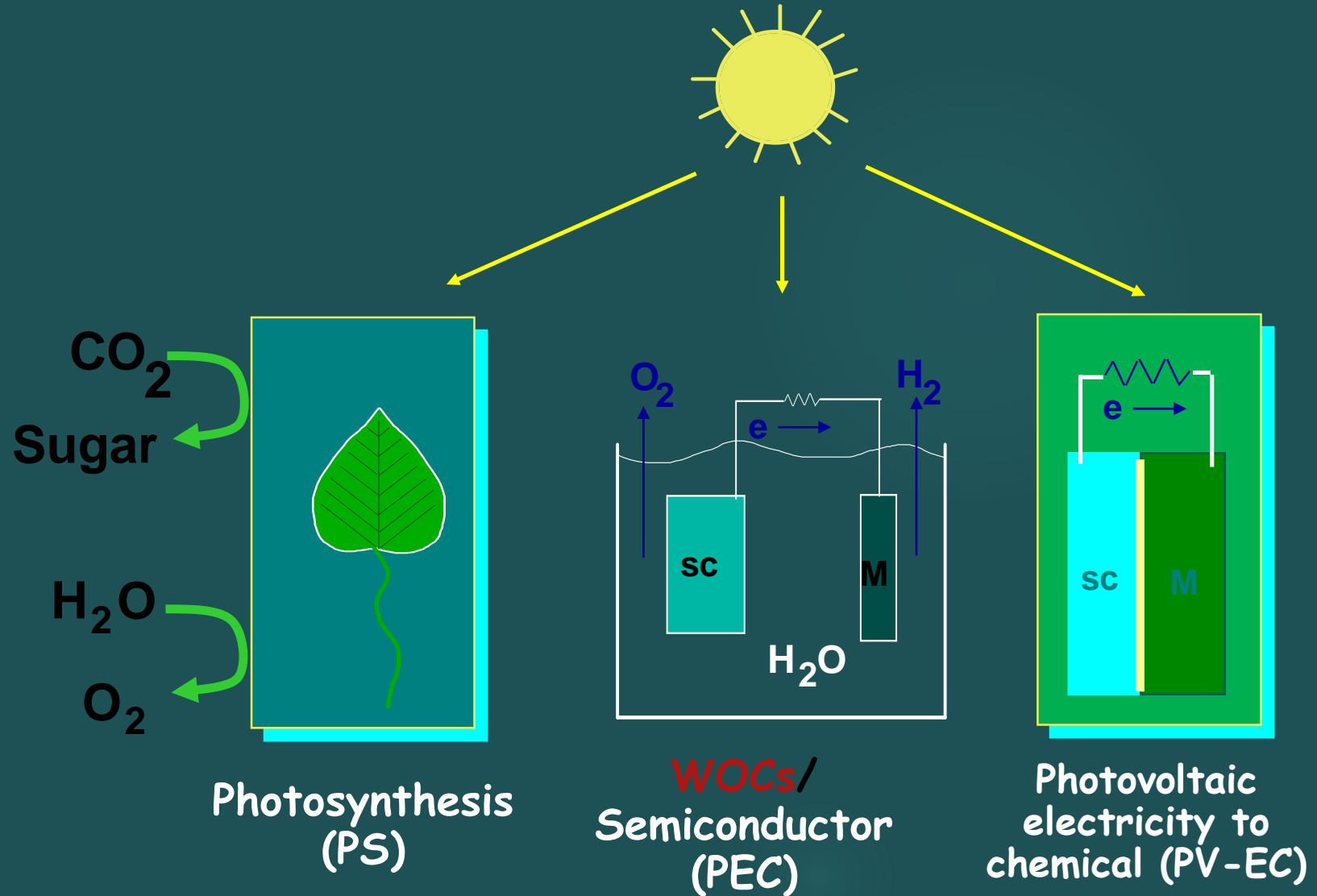


Water Oxidation Catalysts (WOCs)

Solar to Chemical Energy

In this machinery, five major processes: photon absorption, charge separation, electron transfer, water oxidation, and proton reduction have to be combined together to achieve high efficiency.

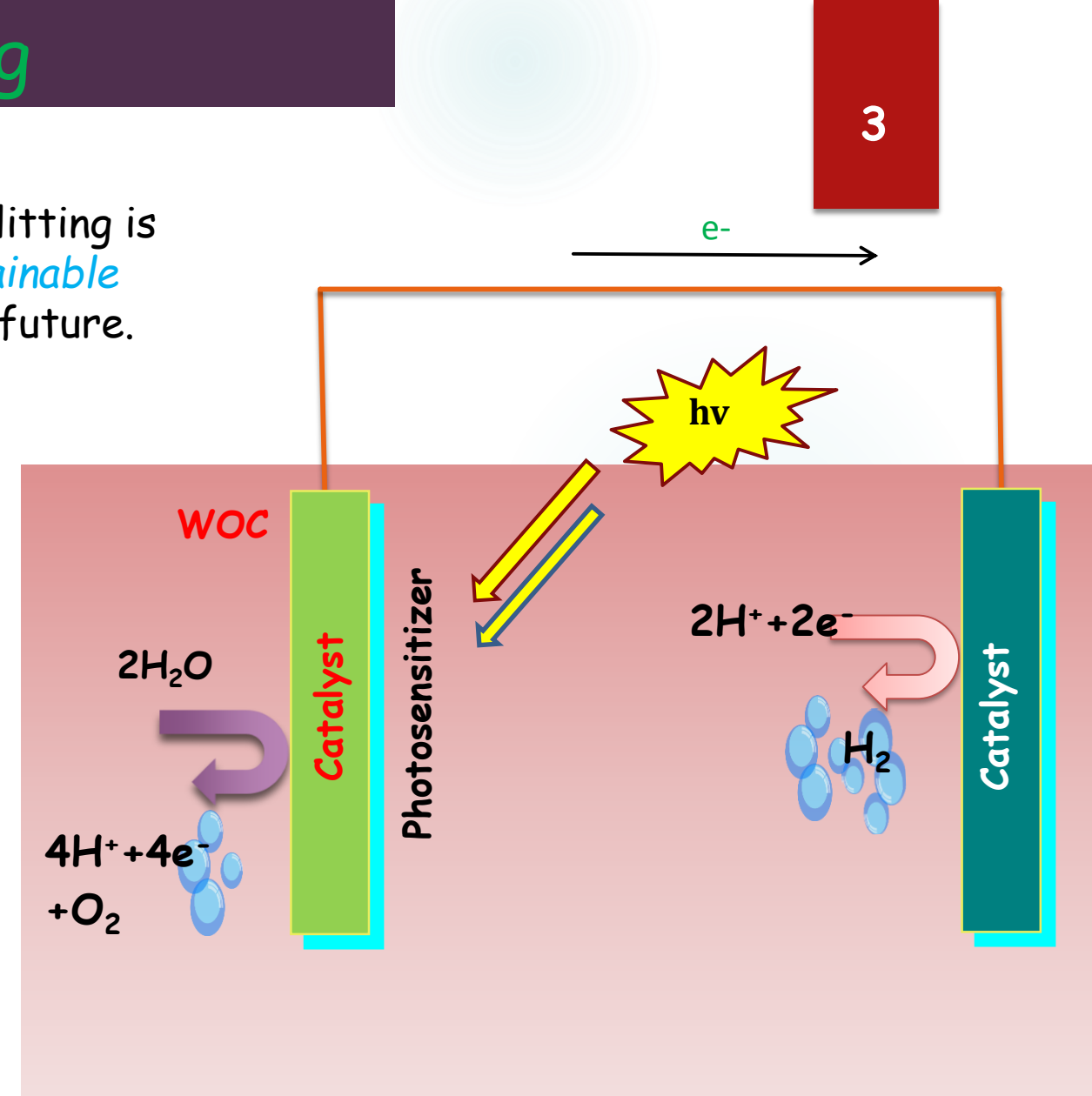
Artificial photosynthesis:
renewable energy storage



Electrochemical Water splitting

Production of **hydrogen** H_2 by electrochemical water splitting is considered as one of *the most promising ways for sustainable energy storage* and hydrogen society realization in the future.

Water oxidation (WO) is currently believed as the bottleneck in the field of electrochemical water splitting and artificial photosynthesis.



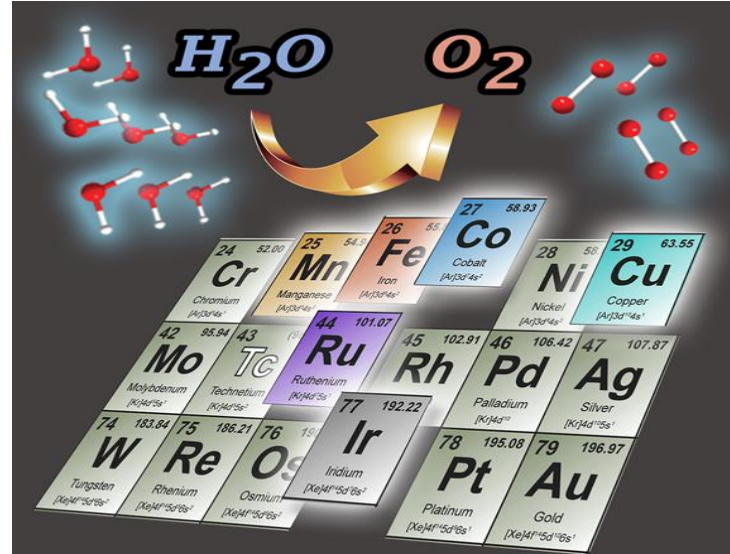
*Enormous efforts have been made in the exploration of water oxidation catalysts (WOCs), including **homogeneous** and **heterogeneous** catalysts.*

Aims of project

4

Main challenges:

find a robust, efficient, and inexpensive catalysts for **Water Oxidation**.



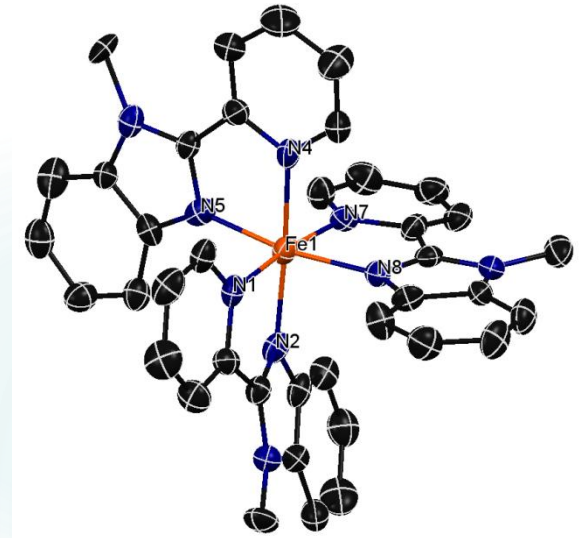
focus on **molecular catalysts** that are:

- insoluble in water,
- show long term stability,
- high catalytic activity and
- affinity for the semiconductor surface, as **ITO, FTO**

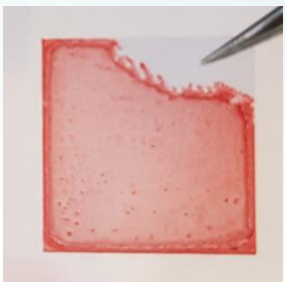
to be applied in electrocatalytic **Water Oxidation(WO)**.

Compare Two Fe^{II} complexes
compatible with electrochemical methods
(homogeneous and heterogeneous conditions)

Fe^(II)(PBI)OTf



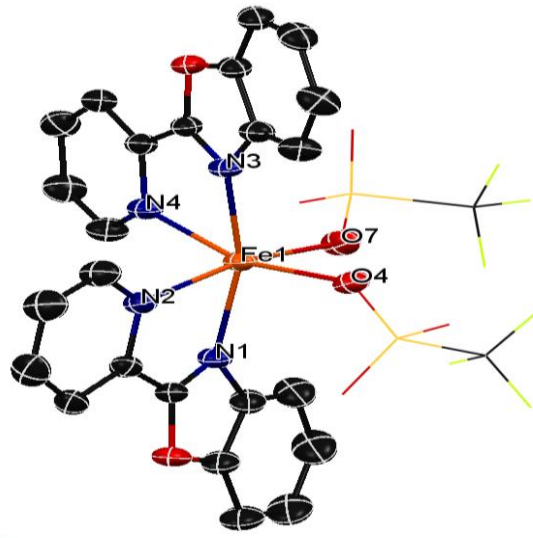
PBI



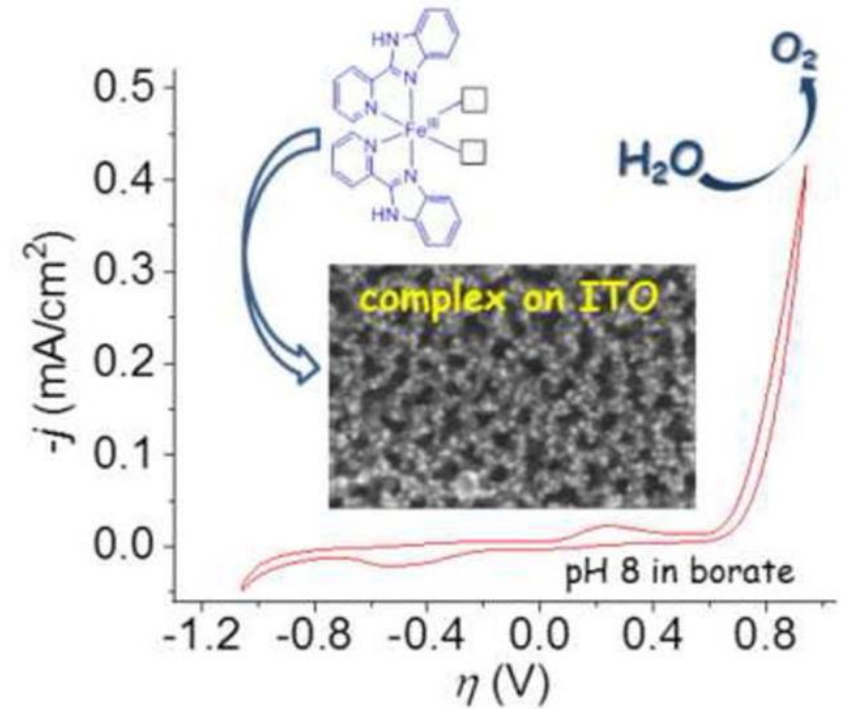
Surface deposition

On indium Tin Oxide (ITO)

Fe^(II)(PBO)OTf



PBO



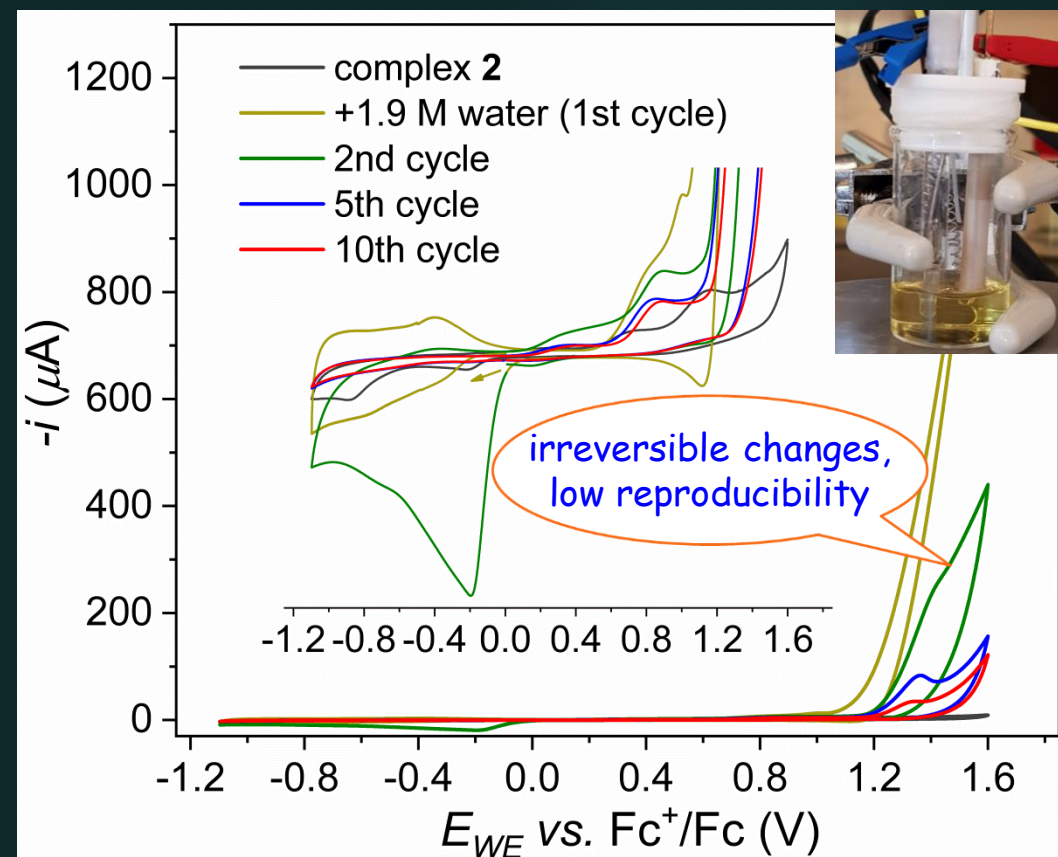
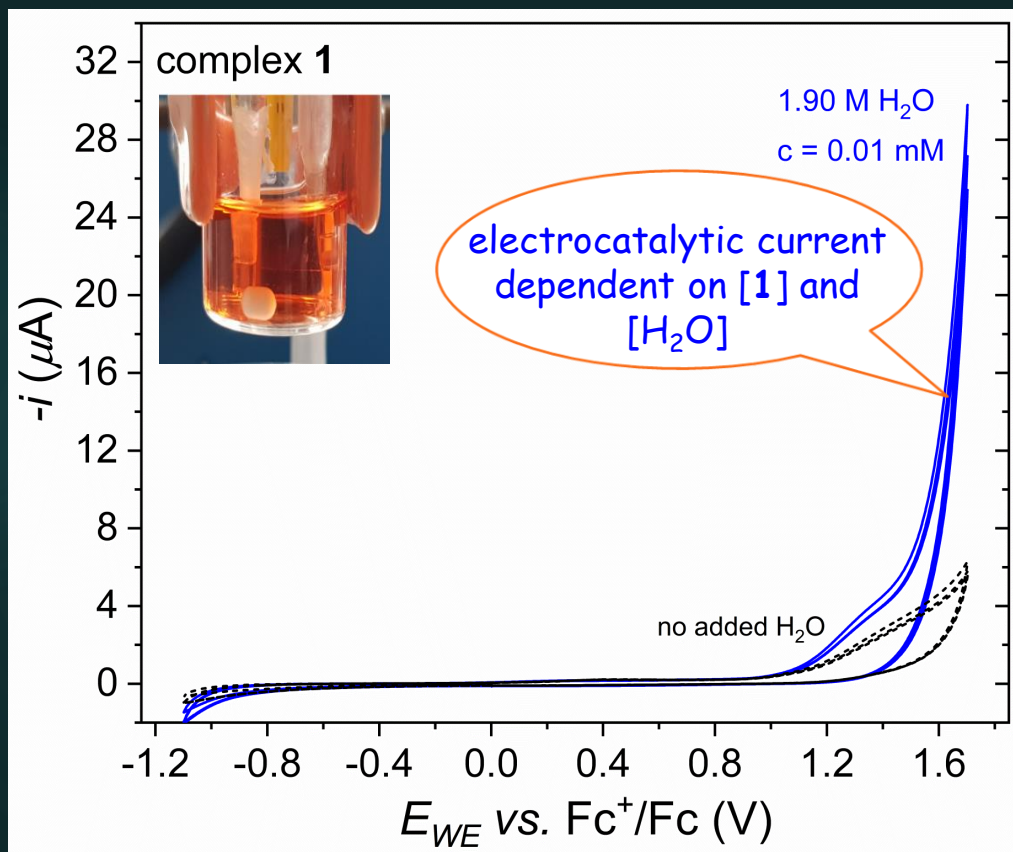
Ligands:

2-(2'-pyridyl)benzimidazole (PBI)

2-(2'-pyridyl)benzoxazole (PBO)

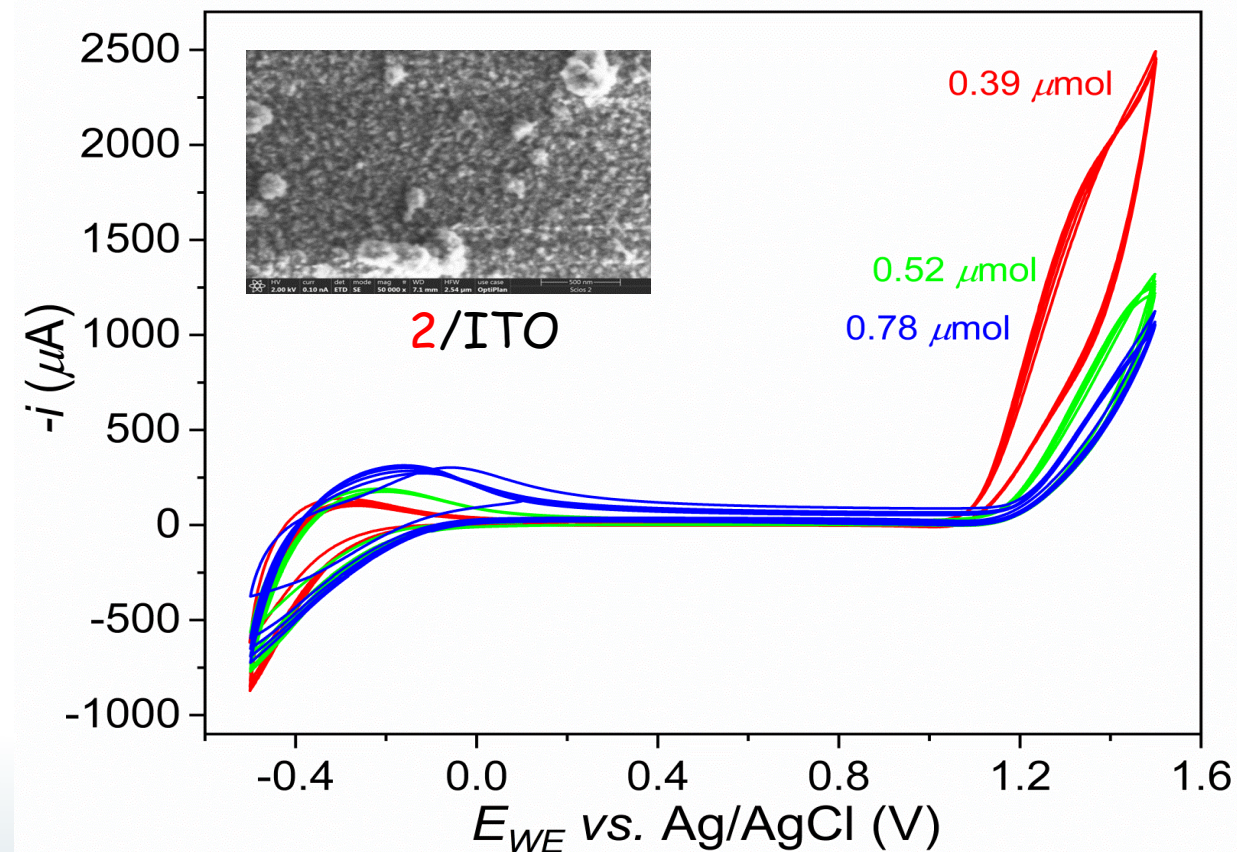
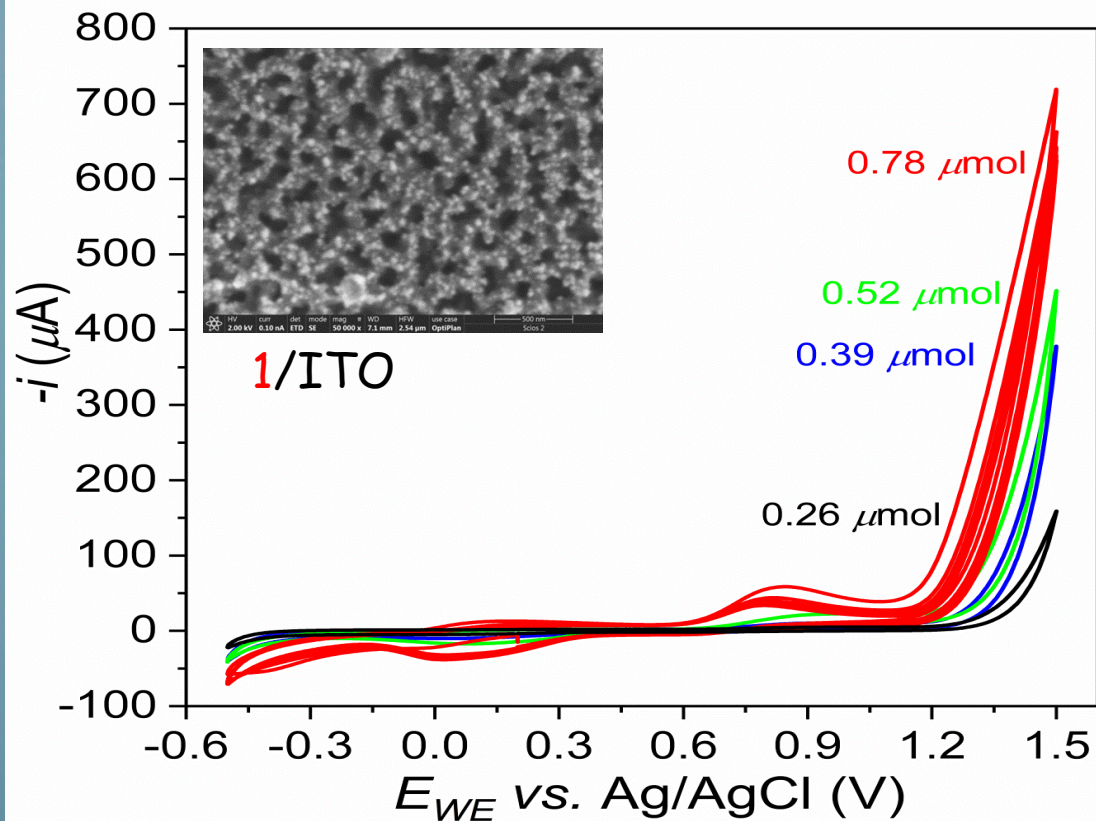
OTf = trifluoromethyl sulfonate anion

The electrocatalytic activity of the complexes was investigated in homogeneous water/acetonitrile mixtures and kinetic analysis revealed considerable activity for both compounds. However, only **1** acts as homogeneous catalyst, **2** undergoes changes (degradation).



Both **1**/ITO and **2**/ITO increased the WOC activity of the electrode in electrocatalytic O_2 evolution in borate buffer at pH 8.3

Cyclic voltammetry with **1**/ITO and **2**/ITO in borate buffer



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Utilization of hydrophobic ligands for water-insoluble Fe(II) water oxidation catalysts – Immobilization and characterization

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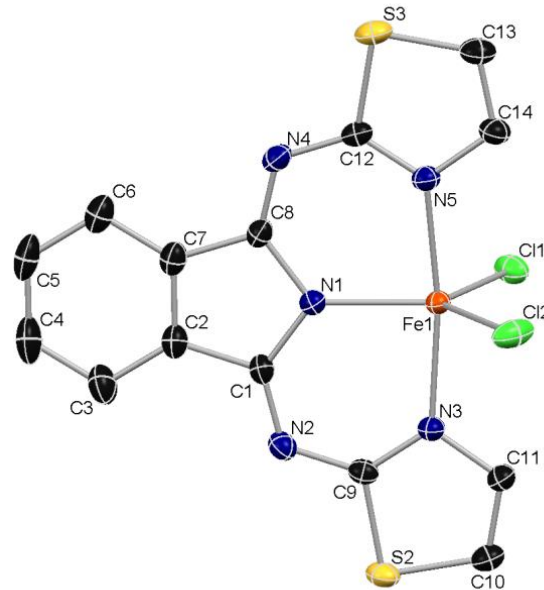
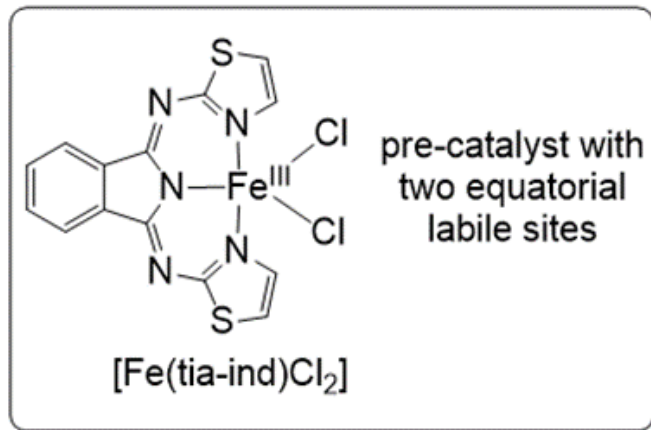
ABSTRACT

Herein, we compare the electrochemical and electrocatalytic properties of two selected, water-insoluble Fe(II) coordination complexes made with the non-symmetric, bidentate ligands, 2-(2'-pyridyl)benzimidazole (PBI) in [Fe(PBI)₂](OTf)₂ (**1**, OTf⁻ = trifluoromethyl sulfonate anion) and 2-(2'-pyridyl)benzoxazole (PBO) in [Fe(PBO)₂](OTf)₂ (**2**). Cyclic voltammetry in water/acetonitrile mixture indicates considerable activity for both compounds. However, only **1** acts as homogeneous catalyst. The complexes have been successfully immobilized on indium-tin-oxide (ITO) electrode surface. The hydrophobic ligands allowed for a simple dip-coating and drop-casting of **1** and **2** onto ITO. Both **1**/ITO and **2**/ITO showed increased activity in electrocatalytic O₂ evolution in borate buffer at pH 8.3. According to scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), moreover, re-dissolution tests, the Fe remains in complex with PBI during electrolysis in the drop-casted, nano-porous films of **1**/ITO. In contrast, the PBO complex in **2**/ITO undergoes a rapid *in situ* decomposition yielding a mineralized form that is responsible for catalysis.

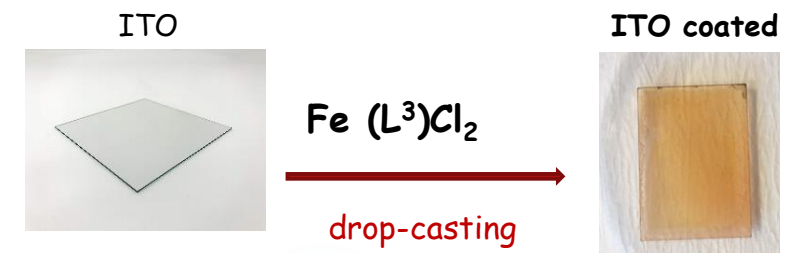
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we successfully synthesized and investigated the electrochemical properties of the five-coordinate complex $[Fe^{III}Cl_2(tia-ind)]$, where $tia-ind = 1,3-bis(2'-thiazolylimino)isoindolate(-)$, as a potential pre-catalyst of water oxidation.

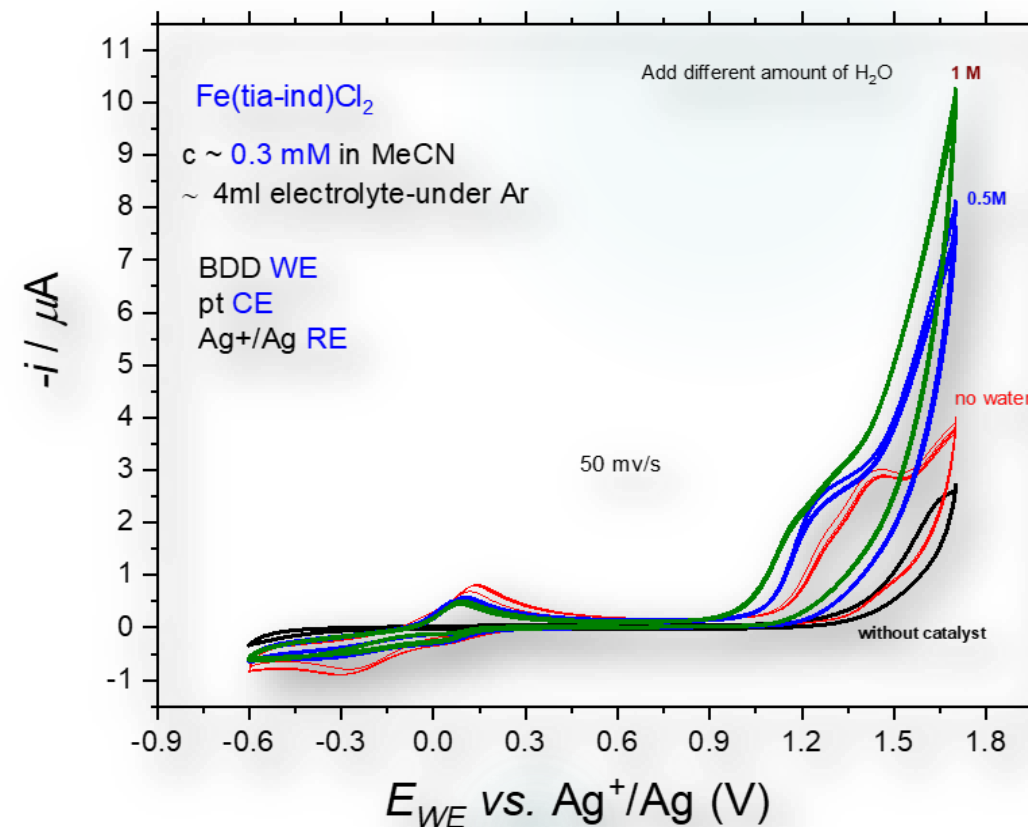
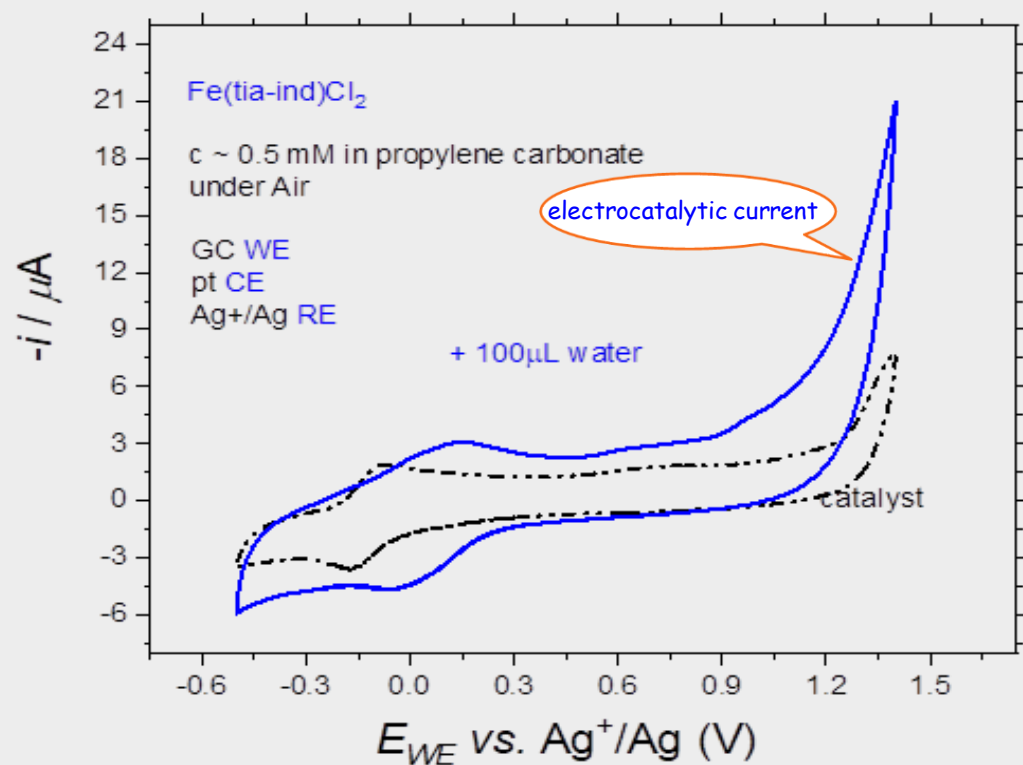
The five-coordinate complex $[Fe^{III}Cl_2(tia-ind)]$



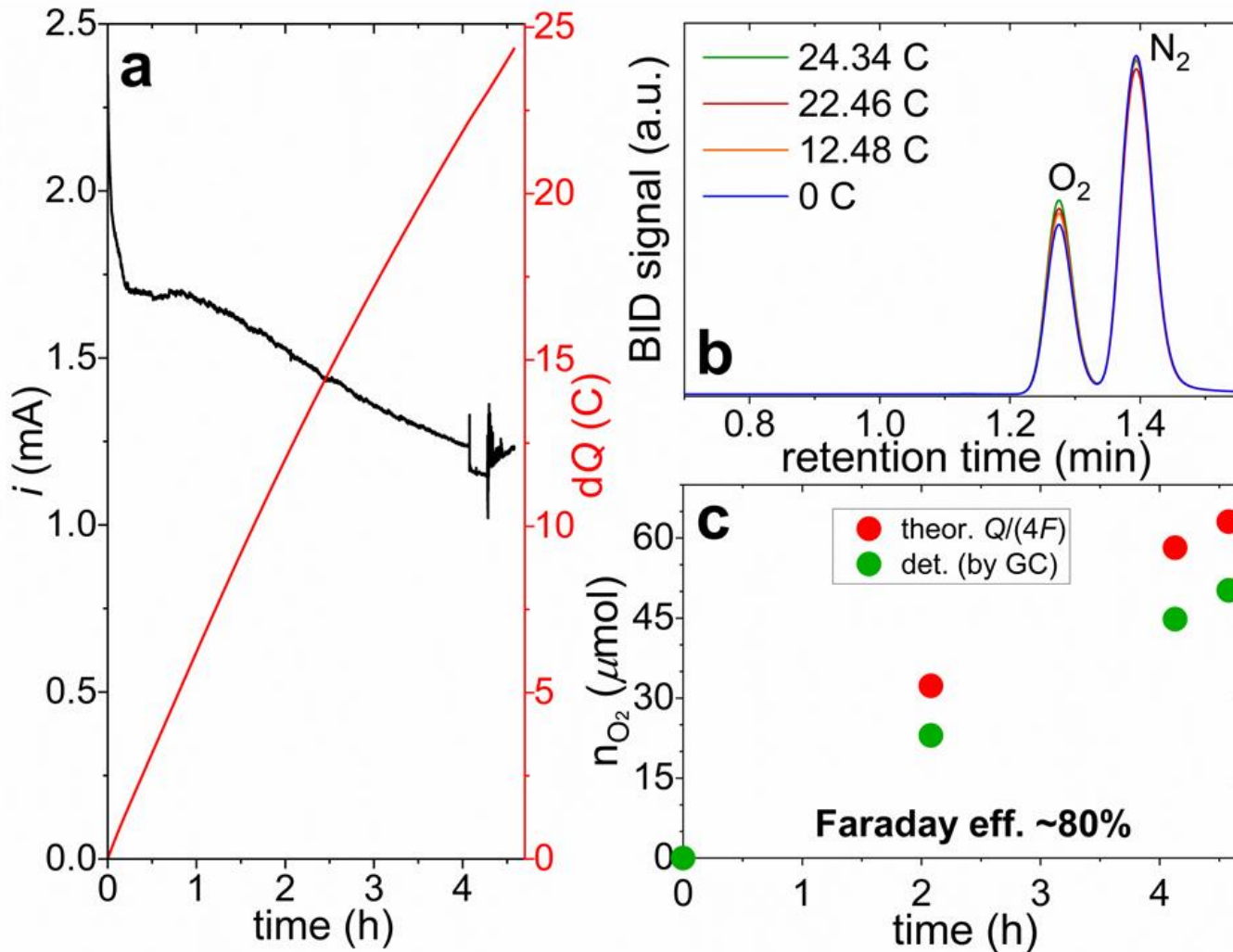
The Fe^{III} complexes have been successfully deposited on indium-tin-oxide (ITO) electrode surface



The electrocatalytic activity of the complexes was investigated in homogeneous water/propylene carbonate mixtures. For example $\text{Fe}^{\text{III}}\text{Cl}_2(\text{tia-ind})$ complex is tested by cyclic voltammetry (CV) as shown in the figures.



Controlled potential electrolysis (CPE) experiments

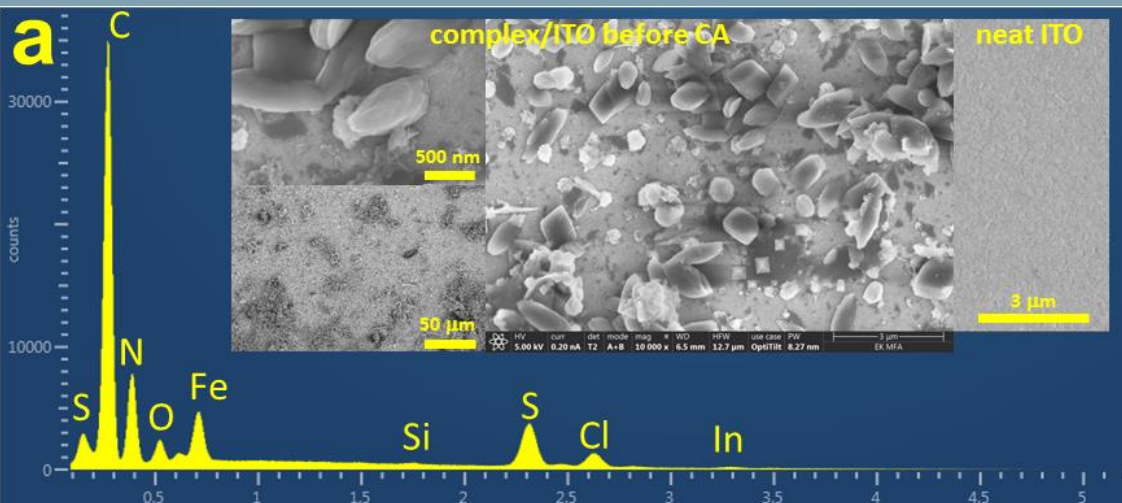


(a) Current (black) and charge (red) during electrolysis performed at +1.4 V vs. Ag/AgCl over 4.5 hours 0.2 M borate buffer, at pH 8.3 ITO working electrode ($0.31 \mu\text{mol}$ complex over 2.37 cm^2) Pt CE separated by a Nafion membrane

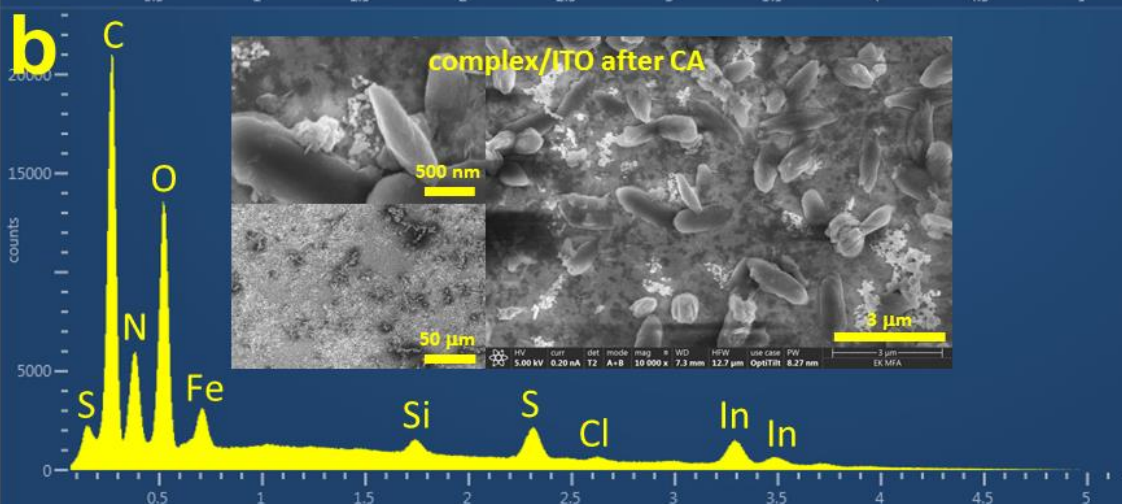
(b) gas chromatograms of headspace samples taken at different stages of electrolysis, the cell was filled with artificial air of known composition

(c) comparison of the theoretical and detected O_2 .

The investigation of the complex/ITO assembly before and after catalysis by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) suggested that a molecular form of catalyst is responsible for water oxidation.



a) EDX spectrum of an as-prepared complex/ITO sample (0.31 mmol over 2.37 cm²), inset: SEM pictures of the sample



(b) EDX spectrum of the sample after **4.5 h** electrolysis at +1.4 V vs. Ag/AgCl in 0.2 M borate buffer at pH 8.3

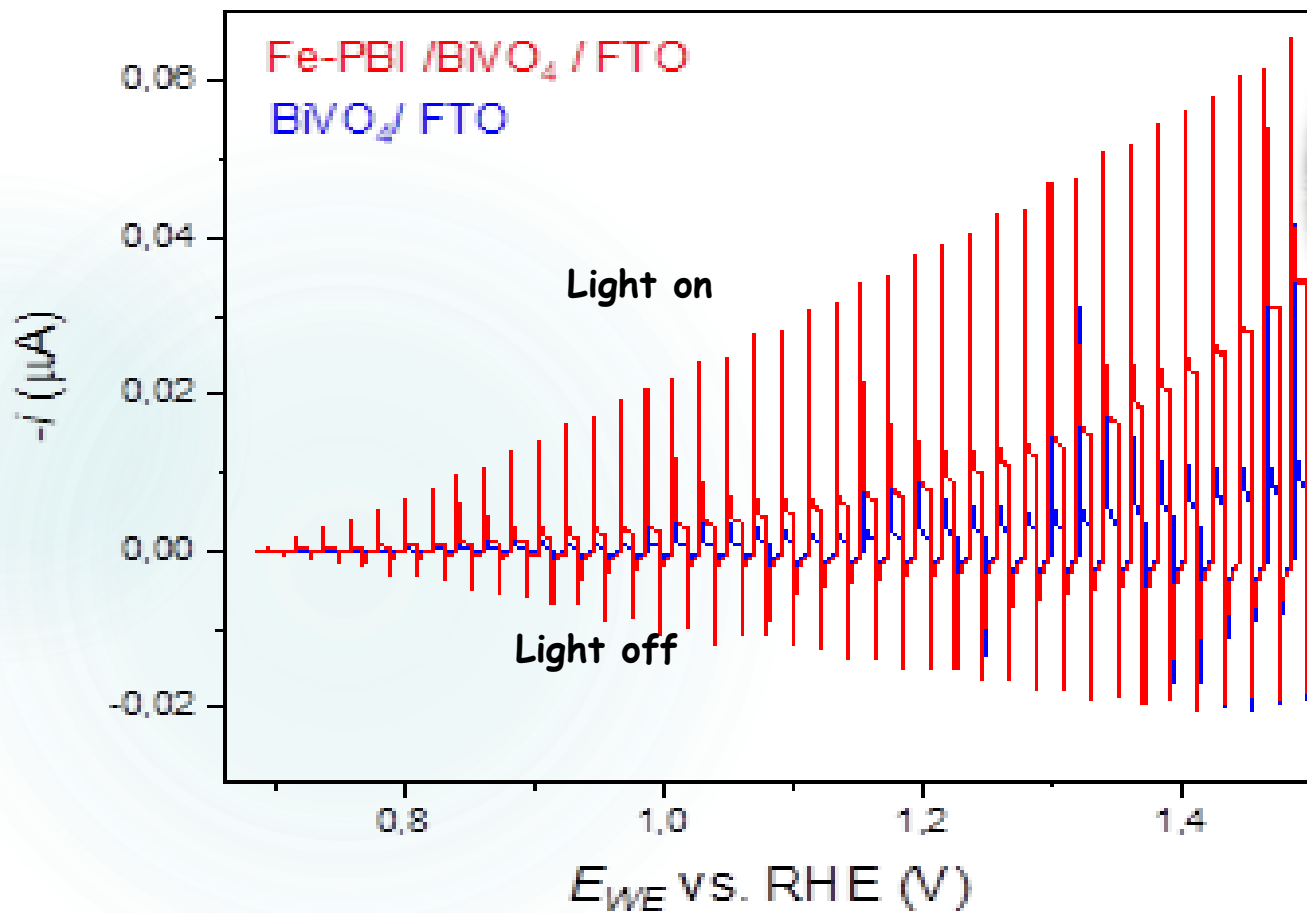
A manuscript has been written up and it is prepared for submission to an IF journal (the COVID-19 delayed our international collaboration for 3 months). The title is "An Iron(III) Complex with Pincer Ligand - Catalytic Water Oxidation through Controllable Ligand Exchange"

Planned of thesis points based on this publication

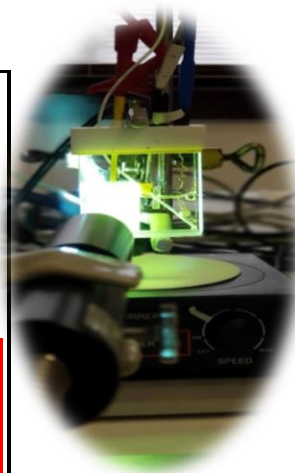
- ❑ **Ligand exchange reactions** between water molecules and ancillary ligands or coordinated anions in catalyst precursors can lead to the cis-di aqua coordination mode that is regarded 'ideal' in water oxidation.
- ❑ **The non-coordinated heteroatoms** in the aromatic ancillary ligands should be sufficiently electron donating in order to support the high oxidation state intermediates occurring in the course of catalysis, otherwise the molecular units become prone to oxidative degradation and mineralization.
- ❑ **Hydrophobic ligands** can aid the immobilization of molecular water oxidation catalysts on oxide surfaces.
- ❑ **No anchoring additive is needed**, hybrid systems that are efficient in water oxidation electrocatalysis can be fabricated by the scalable and simple drop-casting method.

Photoelectrochemical (PEC) water splitting

We are working to test complexes on semiconductor nanomaterial hybrids bismuth vanadate (BiVO_4/FTO) and hematite ($\text{Fe}_2\text{O}_3/\text{FTO}$) involving photoelectrochemical utilization.



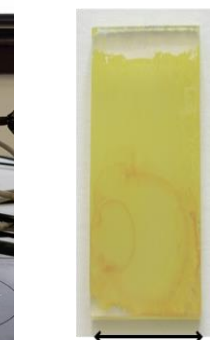
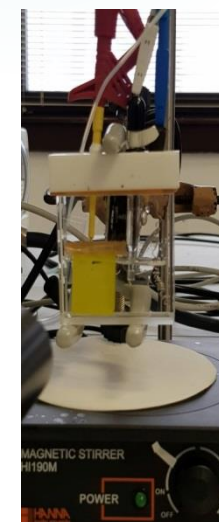
LSV under chopped illumination at $v = 2$ mV/s



drop-casting method: Fe-PBI dissolved in methanol. 50 μL of the solution was layered onto BiVO_4/FTO

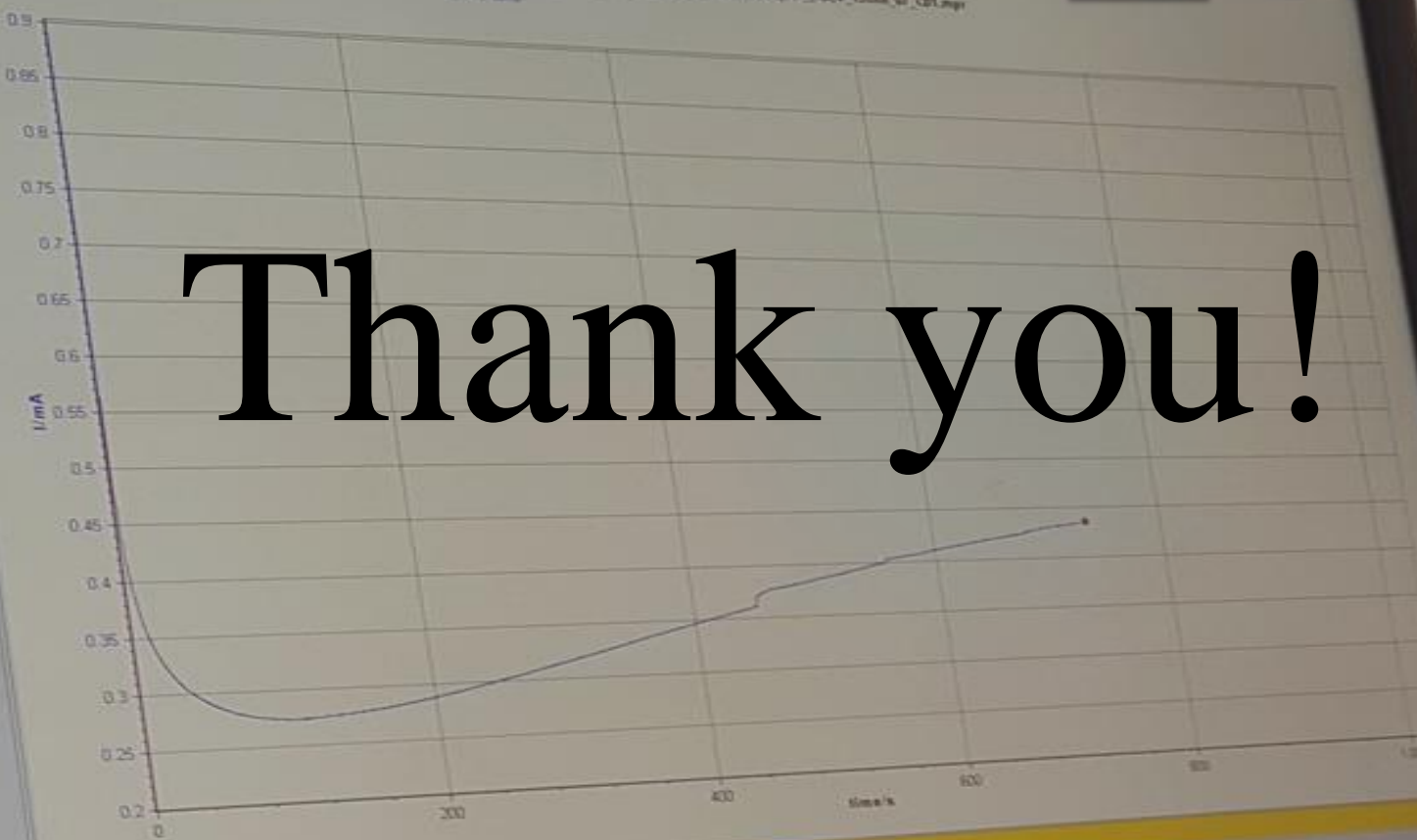


PBI/ Fe_2O_3 / FTO



19 mm
PBI/ BiVO_4 / FTO

Thank you!



SP-150 USB Channel 1 Read mode

Status: Discharge Time: 0:12:14 Evc: 15V I: 435 μ A Buffer: 11 Eoc: 87.34 mV Q-Qo: 75.75 μ Ah I-Range: 1 mA No: 0

-884.8914 26542 μ Ah

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