Óbuda University, Doctoral School on Material Science and Technology

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

5th semester

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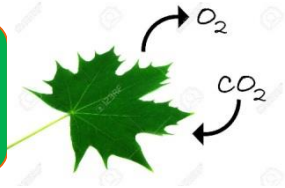
HUNGARIAN ACADEMY OF SCIENCES

Sustainable Energy

Natural Photosynthesis



Artifical Potosynthesis → Water Splitting → $O_2 + H_2$

Water Oxidation the most challenging process

can be generated in a pure form by the splitting of water.

Photoelectrochemical water splitting (PEC)

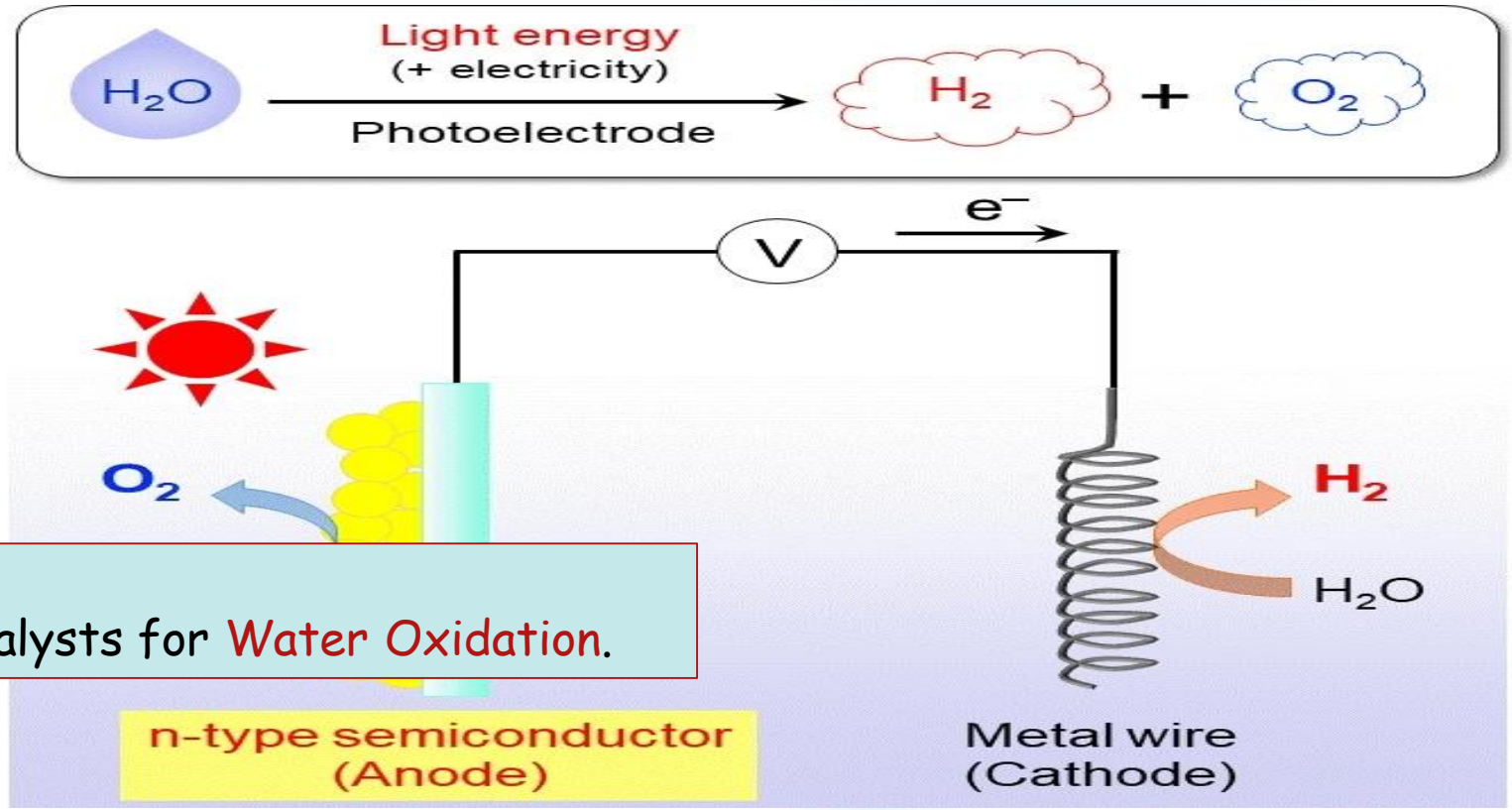
offers a promising path for sustainable generation of hydrogen fuel

A brief introduction

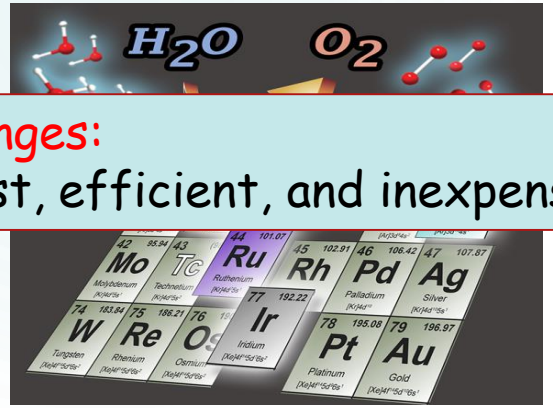
Water splitting

Water oxidation (WO)

is an energyetically uphill transformation (multi-electron process coupled with multiple proton transfers) to produce H_2



Water oxidation Catalysts (WOCs)



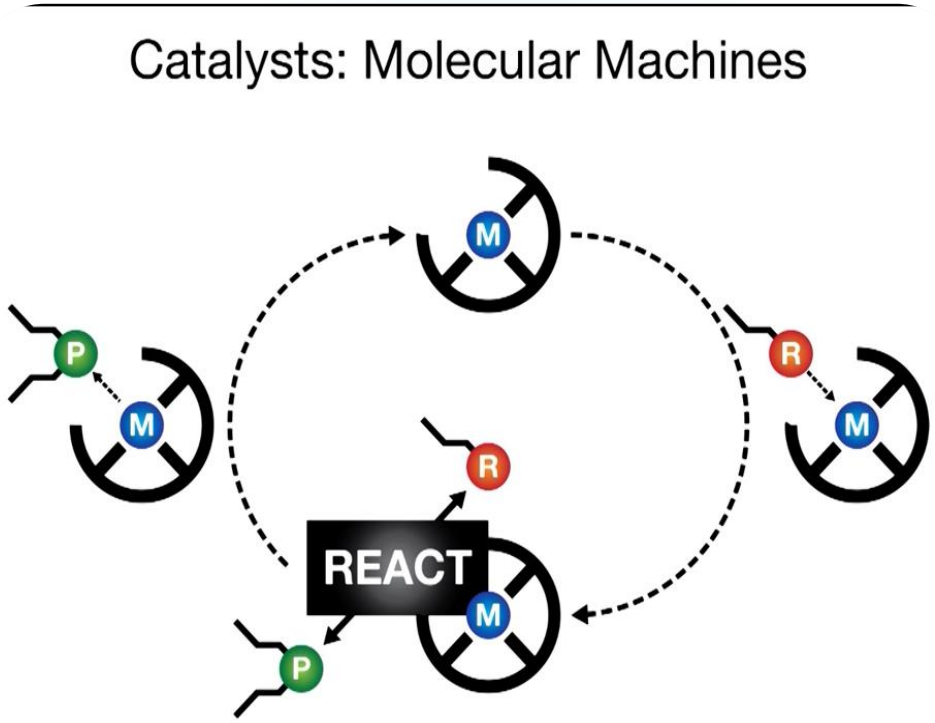
Main challenges:
find a robust, efficient, and inexpensive catalysts for Water Oxidation.

https://www.azocleantech.com/news.aspx?newsID=26683

Catalysis

Catalysts lower the activation barrier of a reaction

- Catalysts play very important roles in both half-cell reactions of water splitting:
- Hydrogen Evolution Reaction (HER)
- Oxygen Evolution Reaction (OER)



Our work focuses on molecular catalysts that are:

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

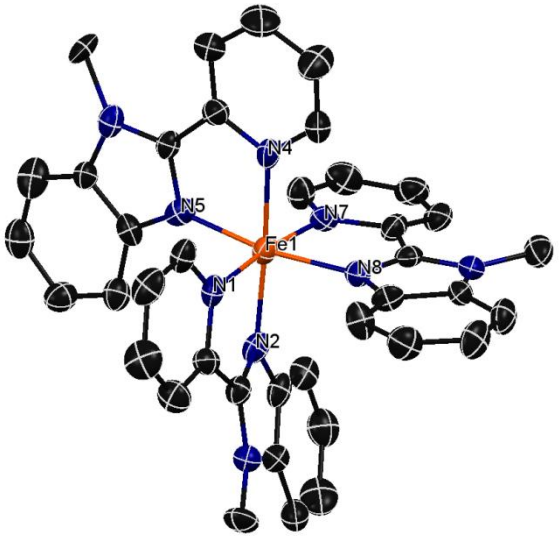
to be applied in electrocatalytic Water Oxidation(WO).

Our work

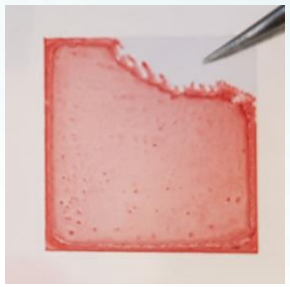
Compare Two Fe^{II} complexes

compatible with electrochemical methods
(homogeneous and heterogeneous conditions)

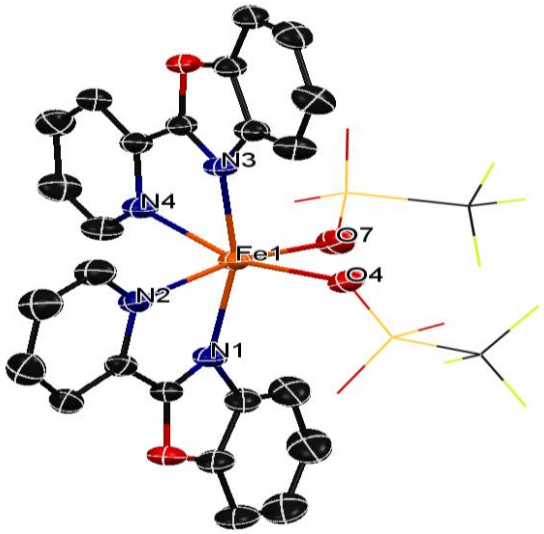
$Fe^{(II)}(PBI)OTF$



PBI



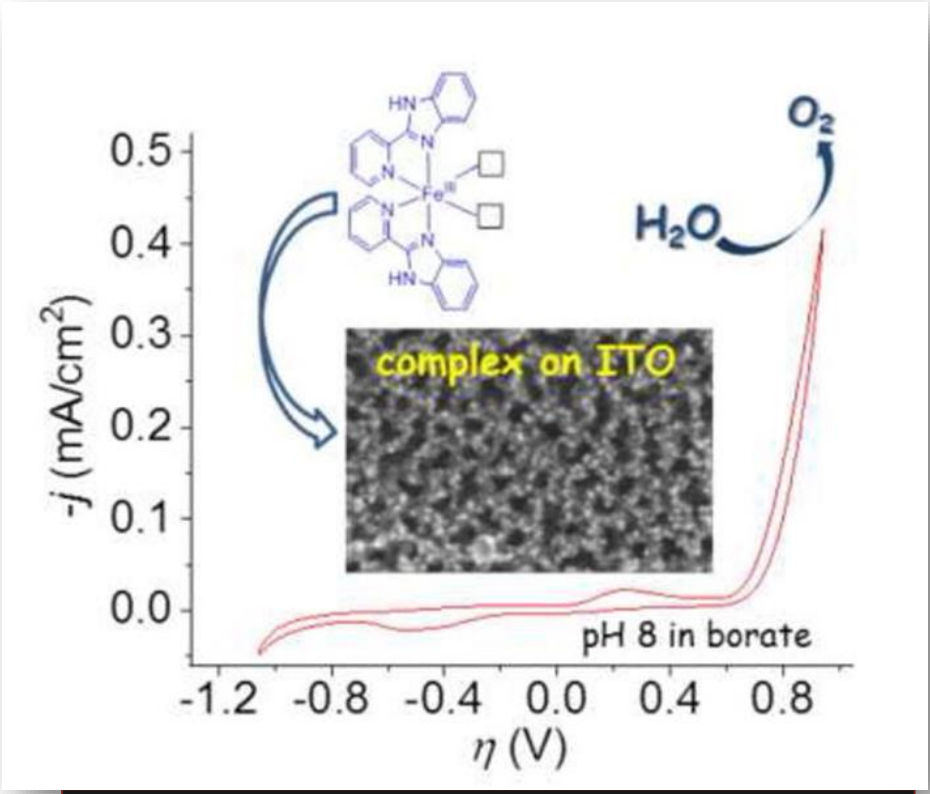
$Fe^{(II)}(PBO)OTF$



PBO

Surface deposition

On indium Tin Oxide (ITO)



Ligands:
2-(2'-pyridyl)benzimidazole (PBI)
2-(2'-pyridyl)benzoxazole (PBO)

OTf = trifluoromethyl sulfonate anion

Work is Published

Journal of Catalysis

open access

Journal Metrics

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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 $[Fe(PBI)_3](OTf)_2$ (**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 O_2 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.

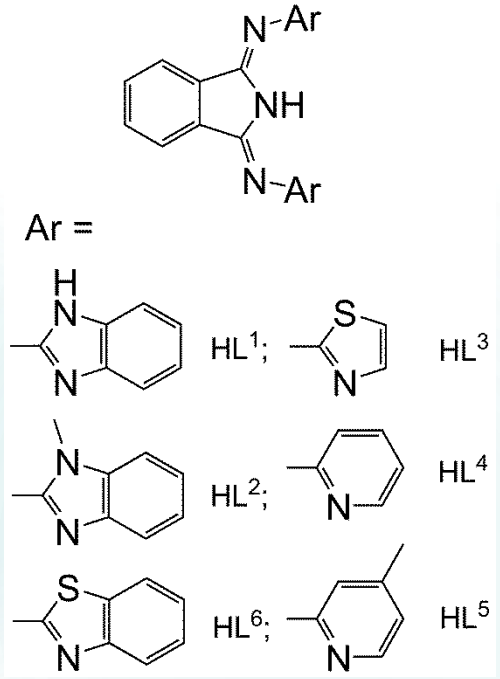
Planned of thesis points based on this publication

- 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.

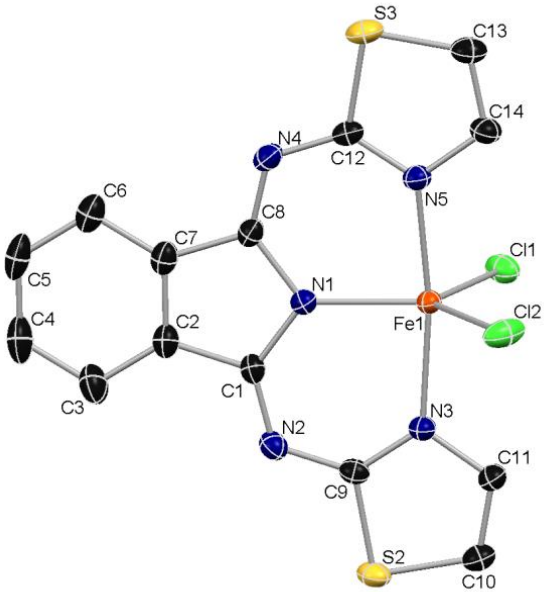
- Hydrophobic ligands can aid the immobilization of molecular water oxidation catalysts on oxide surfaces.
- No anchoring additive is needed, hybrid systems that are efficient in water oxidation electrocatalysis can be fabricated by the scalable and simple drop-casting method.

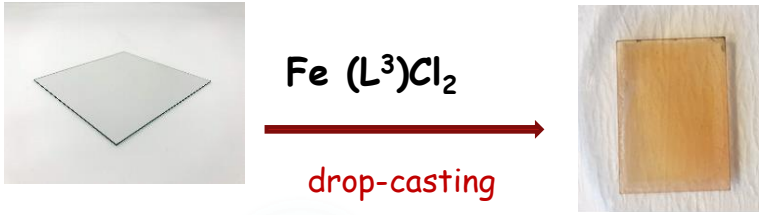
Our current work

We are investigating some complexes (as $Fe^{III}(L^3)Cl_2$*) with aromatic isoindoline-based ligands, which coordinate to iron in a meridional fashion.*



An example of complexes

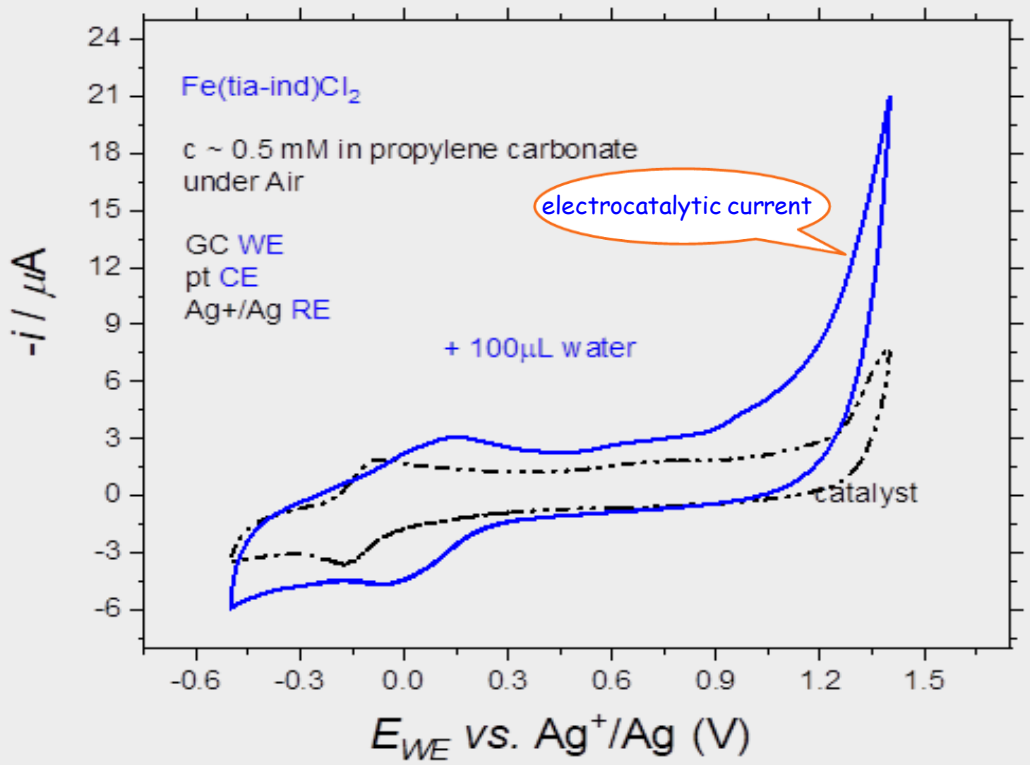


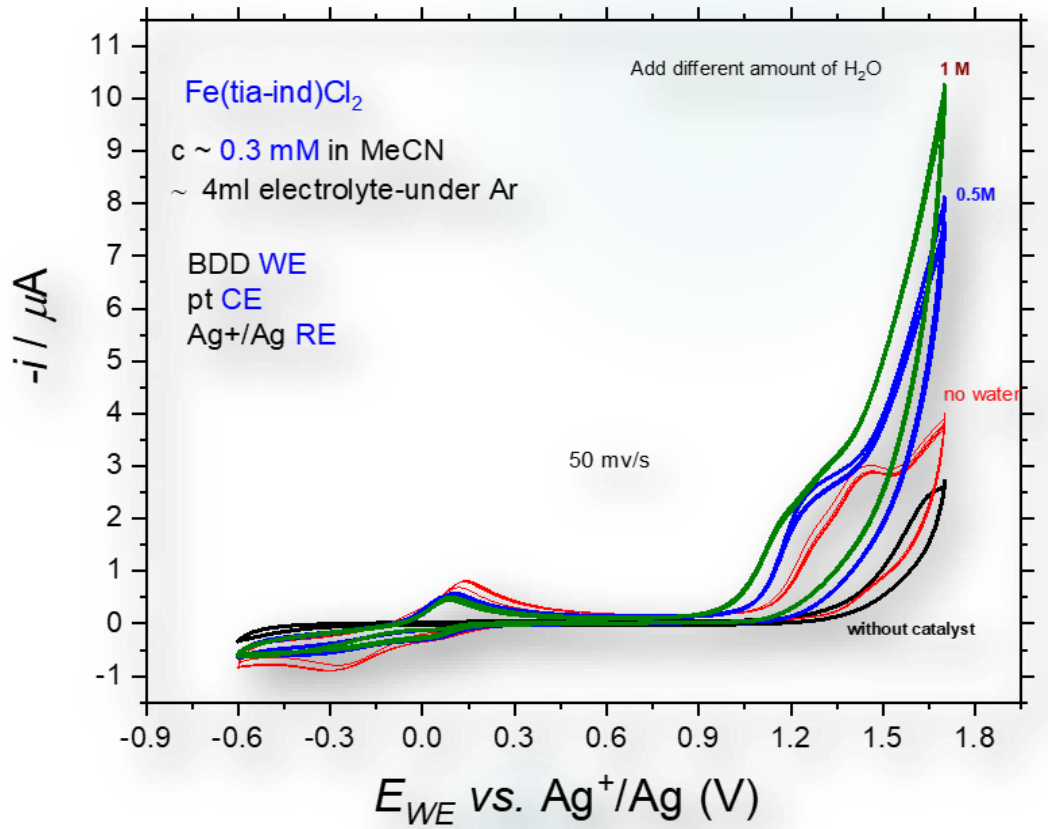


The Fe^{III} complexe have been successfully deposited on indium-tin-oxide (ITO) electrode surface

Homogeneous Catalysis

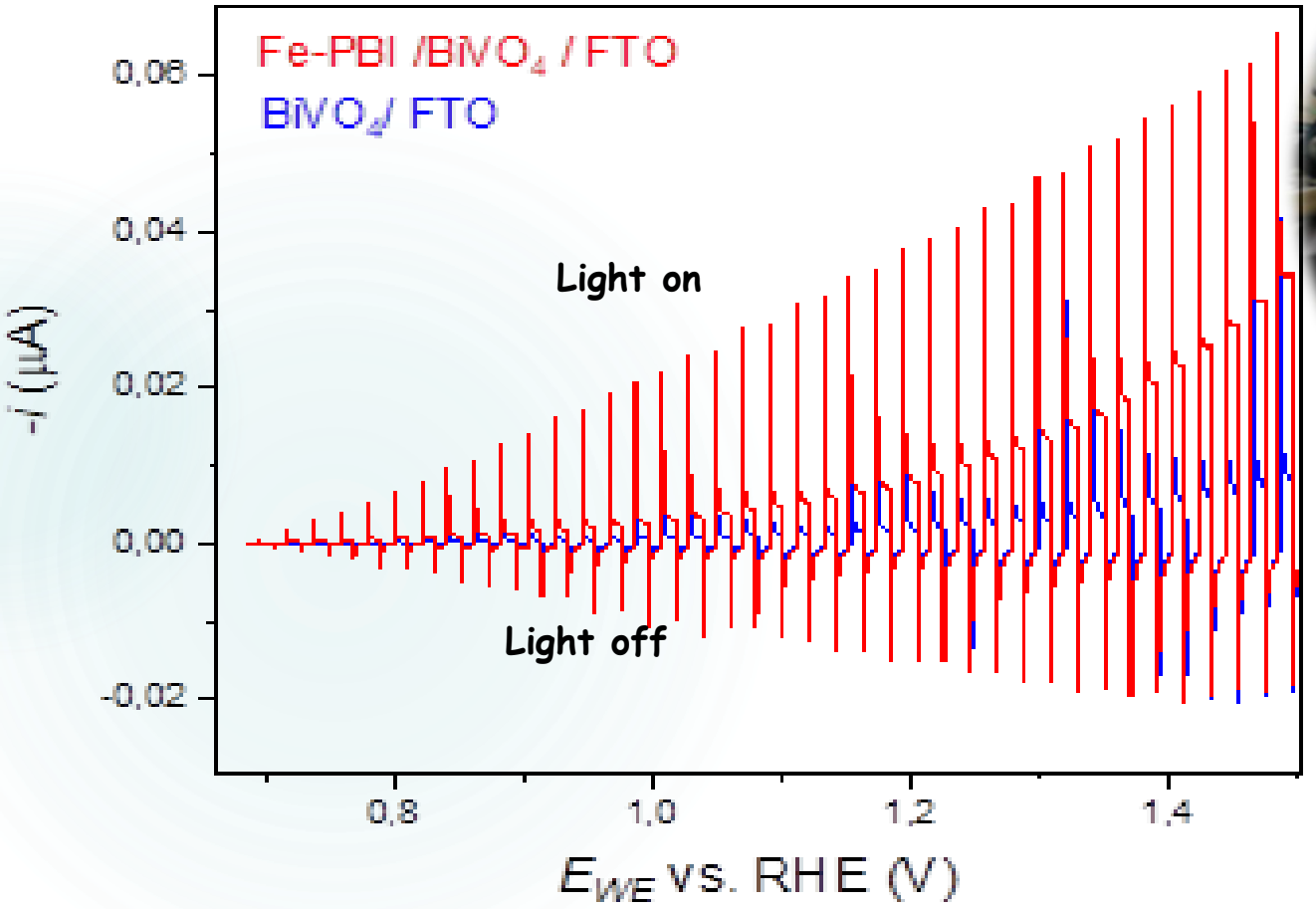
The electrocatalytic activity of the complexes was investigated in homogeneous water/propylene carbonate mixtures. For example $Fe^{III}(L^3)Cl_2$ complexe is tested by cyclic voltammetry (CV) as shown in the figures.



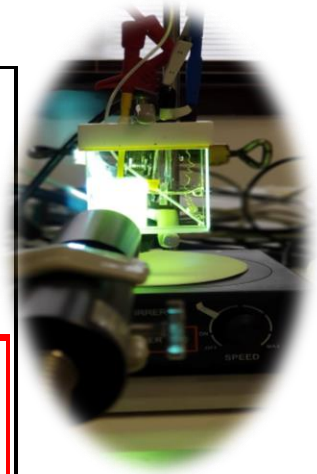


Photoelectrochemical (PEC) water splitting

We are working to test complexes on semiconductor nanomaterial hybrids bismuth vanadate ($BiVO_4$/FTO) and hematite (Fe_2O_3/FTO) involving photoelectrochemical utilization.

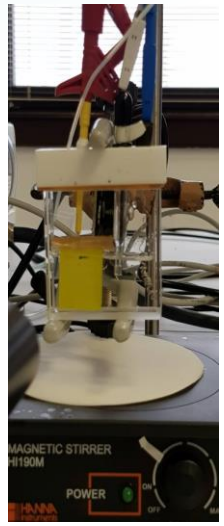


LSV under chopped illumination at v = 2 mV/s



drop-casting method: Fe-PBI dissolved in methanol.
50 μL of the solution was layered onto BiVO4/ FTO

PBI/Fe_2O_3 / FTO



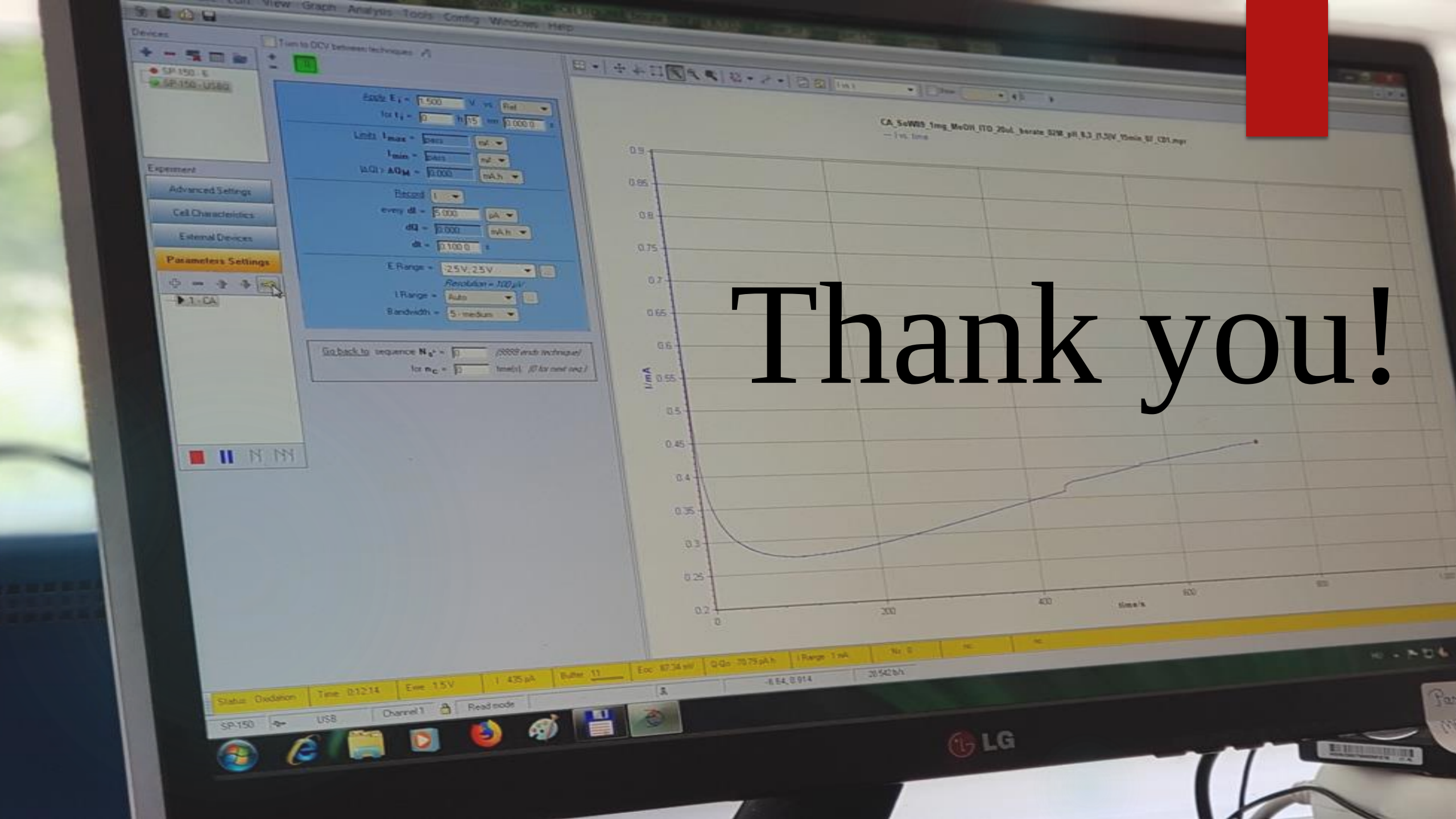
PBI/$BiVO_4$ / FTO

Our Future Work and Activities

- **Two Journals with impact Factor:**

- ✓ Further investigations are planned with aromatic isoindoline-based ligands, which coordinate to iron in a meridional fashion.
- ✓ Tests will be conducted on molecular catalyst/semiconductor nanomaterial hybrids involving photoelectrochemistry.

- **The 4th International Symposium on Energy and Environmental Photocatalytic Materials (EEPM4) Xi'an, China, March 20-23, 2020.**
- **15th Pannonian International Symposium on Catalysis,Sep.2020, Jastrzębia Góra, Poland.**


Thank you!