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Molecular catalytic system for efficient water splitting

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Propositions/Stellingen

To the dissertation (behorende bij het proefschrift)

Molecular Catalytic System for Efficient Water Splitting

Khurram Saleem Joya

1. A successful integration of a molecular water splitting complex and a hydrogen evolution catalyst with a multi-junction photovoltaic system would be the future stand-alone solar to fuel conversion technology for personalized energy conversion and storage using water as the raw material.
2. Electrochemical methods combined with *in situ* spectroscopic analysis to get more insight into the surface catalytic processes provide convincing evidence that Ru-red is not a viable water oxidation catalyst.

(This thesis, Chapter 2)

3. Cyclic conjugated hydrocarbons that stabilize a $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$ species in mono ruthenium water oxidation complexes, can enable a third proton coupled electron transfer step by facilitating rapid insertion of a water molecule for the second half of the four electron water oxidation cycle.

(This thesis, Chapter 3 and 4)

4. In mono ruthenium complexes, catalytic turnover frequencies up to 80 per second can be obtained for prolonged periods.

(This thesis, Chapter 4)

5. Pre-aqua induction of the mono-site $\text{Cp}^*\text{-Ir}$ derived dinitrogen ligand complexes does not produce a hygroscopic species.

(This thesis, Chapter 5)

– J. D. Blakemore *et al.* *J. Am. Chem. Soc.* **2010**, 132, 16017–16029.

6. The surface enhancement of the catalytic performance of $[\text{cyRu}(\text{N-N})\text{OH}_2]^{2+}$ and $[\text{Cp}^*\text{Ir}(\text{N-N})\text{OH}_2]^{2+}$ catalysts indicates that the unidirectional water oxidation avoids wasteful side reactions and products.

(This thesis, Chapter 4 and 5)

7. In water splitting, the choice to make is whether to focus on a cheap but inferior catalyst, or on a relatively costly but efficient molecular material.
8. The polypyridyl ligands in ruthenium water oxidation complexes favour the oxidative formation of $[\text{Ru}^{\text{V}}=\text{O}]^{3+}$ before the second water insertion, thereby avoiding the OH_2 ligation with $[\text{Ru}^{\text{IV}}=\text{O}]^{2+}$.

(This thesis, Chapter 3 and 4)

- J. J. Concepcion *et al.* *J. Am. Chem. Soc.* 2010, 132, 1545–1557.
- D. J. Wasylenko *et al.* *J. Am. Chem. Soc.* 2010, 132, 16094–16106.

9. Mononuclear bpy-cy based water oxidation catalysts offer promising potential for self-repair by electro-deposition and self-assembly in stand-alone applications to address the fundamental chemical paradox of water splitting.
10. There exists an empirical limit to what a Pakistani graduate student can order from Sigma Aldrich.
11. Active reaction is better than a pre-emptive action.
12. The road to success is usually the road least travelled and is always “under construction”.
13. The greatest pleasuring challenge in my life is doing what people say: “It’s impossible”.

(Leiden University, 2011)