Towards photocatalytic water splitting in homogeneous solutions using molecular metalloporphyrin photosensitizers and catalysts

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PROPOSITIONS (STELLINGEN)

Accompanying the thesis

Towards Photocatalytic Water Splitting in Homogeneous Solutions Using Molecular Metalloporphyrin Photosensitizers and Catalysts

1. In order to realize full photocatalytic water splitting, it is imperative to find effective electron relays coupling the water oxidation and hydrogen evolution half-reactions. (*C. Wang, et al., Nat. Chem.* ***2021****, 13, 358-366*)

2. Porphyrin is a versatile ligand scaffold for building molecular catalysts, both for water oxidation and hydrogen evolution. (*This thesis and R. Cao, et al., Chem. Rev.* ***2017****, 117, 3717-3797*)

3. The design and fine-tuning opportunities available for molecular photosensitizers and catalysts represent a significant advantage over heterogeneous photoactive materials. (*S. Masaoka, et al., Chem. Soc. Rev.* ***2021****, 50, 6790-6831*)

4. The classical metal complex $[Ru(bpy)_3]^{2+}$ is used too often as a standard photosensitizer in the development of new catalysts for water oxidation or hydrogen evolution. (*This thesis, Chapter 2 & 3 and K. B. Yoon, et al., ACS catal.* ***2016****, 6, 8361-8369*)

5. Fine-tuning the electron-density of a catalytic center by using appropriate substituents allows for balancing the driving forces of catalytic water oxidation vs. that of the electron transfer from the catalyst to the photo-oxidized photosensitizer. (*This thesis, Chapter 2*)

6. It is not necessary to functionalize hydrogen-evolving catalysts with electron-donating groups to enhance their catalytic activity. (*This thesis, Chapter 3*)

7. A well-designed molecular photosensitizer balances the redox potentials of its ground-state and excited state. (*This thesis, Chapter 4*)

8. Details of the photocatalytic mechanism must be known to predict which influence substituting the photosensitizer or catalyst with electron-donating or electron-withdrawing groups will have on the photocatalytic properties of the system. (*Thesis, Chapter 2, 3 & 4*)

9. An experimental set-up for studying photocatalysis is easy to use but not easy to design.

10. A successful duplicate experiment may not solve all your problems, but it will bring the confidence you need.

11. Balance needs to be found in many aspects of life, not only in photocatalysis.