Ruthenium– and cobalt–based artificial metalloenzymes for photocatalytic water oxidation in artificial photosynthesis

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Propositions (Stellingen)

Accompanying this thesis

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1. A good protocol for the screening of metal complex-protein interaction is necessary to select the best combination of compounds that produces an artificial protein (*this thesis, Chapter 2*).

2. The binding pocket of the natural cofactor of a protein is not necessarily the best site for the coordination of an artificial cofactor (*this thesis, Chapter 3 and 4*).

3. Even unexplored protein-protein interactions, such as that between bovine serum albumin and bovine carbonic anhydrase, allow for developing artificial photocatalytic enzymatic systems reminiscent of PSII (*this thesis, Chapter 5*).

4. The characterization of an artificial metalloenzyme *before* catalysis is important, but its characterization *after* a photocatalytic reaction is essential as well, as it gives necessary insights on its decomposition pathways (*this thesis, Chapter 3*)

5. Coordination of a ruthenium-based water oxidation catalyst in an enzymatic-like environment can increase the activity of the metal complex toward O_2 evolution. *Noll, N.; Krause, A.-M.; Beuerle, F.; Würthner, F. Nat. Catal.* **2022**, *5* (10), 867–877 and *this thesis, Chapter 4.*

6. Upscaling metalloenzyme-based catalytic systems for industrial application is challenging, but not impossible. *Castro, A. M. de; Ferreira, E.; Portugal, C.; Neves, L. A.; Crespo, J. G. IJMS* **2020**, *21* (8), 2918

7. Using tyrosine radical- or singlet oxygen-scavenging reagents offers a solution to the cross-linking and degradation of artificial metalloenzymes during photocatalytic O_2 evolution. *Sato, S.; Morita, K.; Nakamura, H. Bioconjugate Chem.* **2015**, *26* (2), 250–256.

8. In artificial enzymes used for artificial photosynthesis, the protein scaffolds can improve the catalytic activity of the metal cofactor. *Call, A.; Casadevall, C.; Romero-Rivera, A.; Martin-Diaconescu, V.; Sommer, D. J.; Osuna, S.; Ghirlanda, G.; Lloret-Fillol, J. ACS Catal.* **2019**, *9* (7), 5837–5846 and *this thesis, Chapter 4)*

9. To produce artificial metalloenzymes, one should first choose commercially available proteins to study complex-protein interactions and prove a concept.

10. After a long day of disappointing and failed experiments, a nice meal can make your day brighter. Nice meals should hence be accessible to PhD students, also within the institute.

11. Management and soft-skills courses should be taken by PhD students before teaching bachelor or master courses.

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