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A semisynthetic peptide-metalloporphyrin responsive matrix for artificial photosynthesis

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Summary

In nature, photosynthesis is a complicated process and a diversity of strategies is used by different organisms. Under low light conditions, light energy can be transferred from the antenna to a reaction center with nearly 100% efficiency. The high yield of natural photosynthesis inspires scientists to replicate the natural process of photosynthesis and build artificial photosynthesis systems to convert CO₂ and H₂O into fuel and chemicals with sunlight. In this thesis, I focus on building an artificial light-harvesting system to explore how a chiral responsive matrix can be formed and if the harvested light energy can be transferred with nearly 100% to an acceptor. **Chapter 1** presents a general introduction to the semi-artificial light-harvest system that is studied in this thesis and that is derived from the CsmA protein from the baseplate of the *Chlorobaculum tepidum*.

In **Chapter 2** the tCsmA, a truncated version of the CsmA, has been successfully applied to form a protein scaffold and bind with the chromophore ZnPP using a dialysis procedure specifically developed for this purpose. The photochemical properties such as the molar extinction coefficient, and the stoichiometry of the tCsmA-ZnPP complex, are determined. Structural information is obtained by cryo-EM, and validated with LD and CD optical spectroscopy, and SEC. The results show that the complex forms an extended periodic 7₂ helical structure composed of well-ordered tetramer units. The ZnPP are oriented perpendicular to the long axis of the peptide helix and subject to strong dipole-dipole couplings in the self-assembly. And almost 100% harvested energy can be transferred to the acceptor cation radical methyl viologen. The excitation-energy transfer rate of the complex was increased from the ns⁻¹ scale monomeric ZnPP in solution compared to the ps⁻¹ scale for the complex, which is comparable to natural light-harvesting antenna systems.

Chapter 3 presents a detailed study on the mechanism of the self-assembly of the tCsmA-ZnPP complex. The high pH of the dialysis buffer, the net charge of the complex, an α -helical peptide structure, and the binding of ligand are shown to be important for modulating the self-assembly of truncated CsmA and ZnPP. The hydrophobic effect, the salt bridges or the

dipole-dipole interactions of chromophores drive the complex to form an ordered chiral matrix. In addition, a minor fraction of para-crystalline sheets similar to the natural baseplate was observed by cryo-EM. The baseplate structure is provoked by untwisting of the helical structure and possible formation of salt bridges between antiparallel peptide strands with arrays of dimeric ZnPP coordinated to the histidyl between the strands.

The 3D structure of the helical tCsmA-ZnPP assembly was solved by single particle analysis and is discussed in **Chapter 4**. In the helical structure, two strands of tCsmA twist and form a hydrophobic core, to embed the ZnPP coordinated to the imidazole group of the histidine. The helix is built from antiparallel strands of tCsmA with the monomers organized in a head to tail manner within each strand. In this case, the ZnPP interact and form a tetrameric unit. The charged residues are on the outside of the helices and form salt bridges to stabilize helical filaments that form bundles. In the baseplate structure, the ZnPP shows a vertical orientation to the plate.

To complement the peptide synthesis, in **Chapter 5** protein expression in *E.coli* is explored. Without a large fusion tag, tCsmA rapidly degrades. With a TRX tag the stability can be improved, but the sample precipitates making further treatment difficult. With the MBP tag a strongly associated soluble tCsmA-MBP construct is obtained. While SEC can separate the tCsmA and MBP with the help of 6 M GuHCl, and the tCsmA denatures, a small fraction of tCsmA was recovered during the dialysis. This paves the way for further improvement towards obtaining recombinant variants of tCsmA for *e.g.* isotope labeling of samples for NMR studies.