From Photosynthetic Organisms to Abiotic Solar Energy Conversion, and Back

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Sunlight is an abundant source of free and clean energy that has been used by plants for billions of years through the process of photosynthesis. This fundamental process sustains plant life by converting sunlight energy, water, and carbon dioxide effectively into oxygen and chemical energy stored in organic material. Thus, photosynthesis is the primary source of all useful forms of biochemical energy as well as the inspiration for those who seek clean and renewable alternatives for fossil fuels. Our group aims at designing and constructing molecular scale solar energy conversion systems based on the engineering guidelines of the photosynthetic apparatus using general biological architecture and building blocks: organic and inorganic cofactors embedded within specific protein scaffolds. Such systems may be assembled in a non-biological context as stand-alone energy conversion devices, or expressed genetically and maintained in living organisms such as bacteria, plants and algae. The valuable insights into the fundamentals of design, assembly, and regulation of bioenergetic systems, gained through this endeavor, will open the way for (a) stand-alone energy conversion and light-activated devices, such as protein-based solar cells that make use of biological elements in a non-biological context, and (b) genetically engineering photosynthetic organisms by coupling the photosynthetic

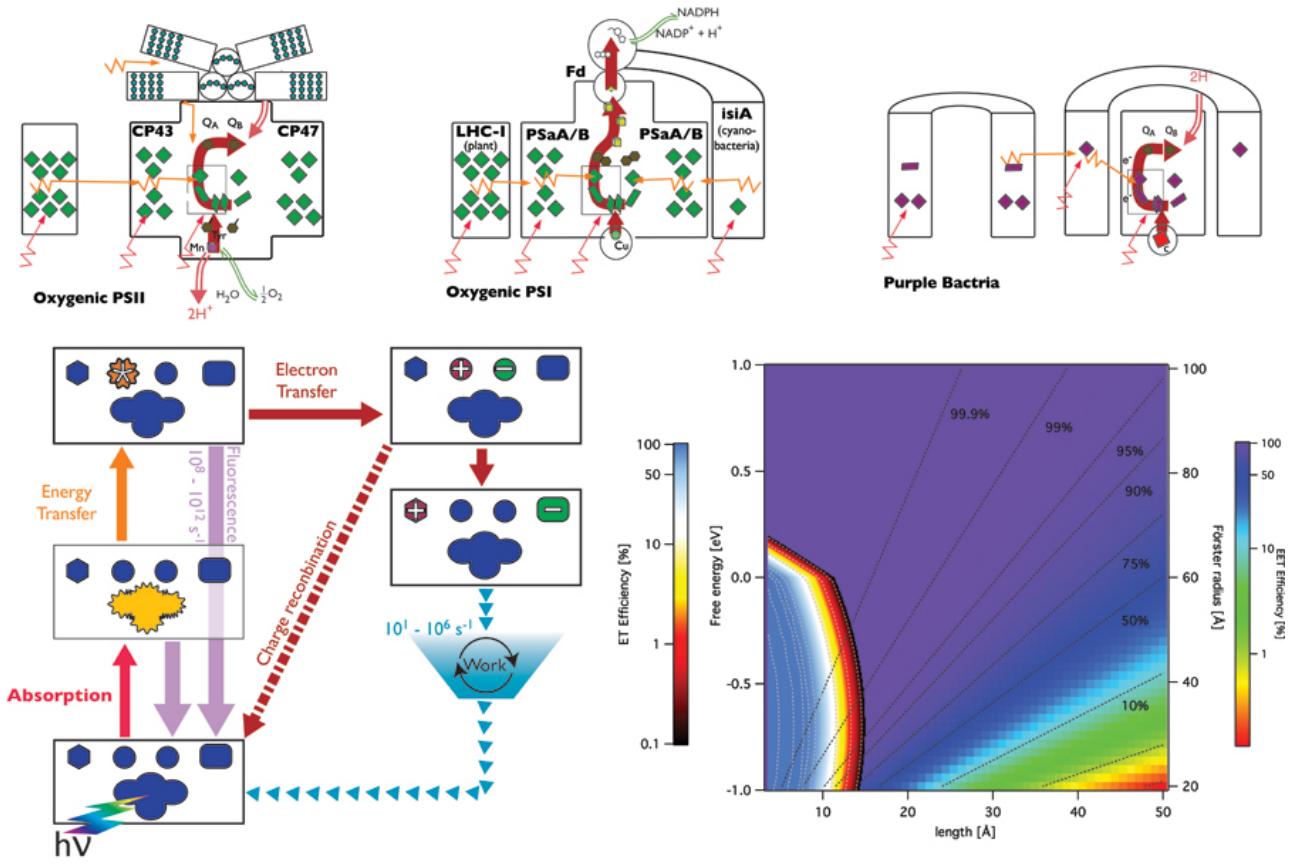

Fig. 1 *Photosynthetic proteins including the two oxygenic photosystems, PSI and PSII, as well as the purple bacterial photoystem (top) are large multi-protein, multi-cofactor complexes. Yet, their engineering that has been favored by blind natural selection is comparatively simple and resilient, and does not require an atom-by-atom examination to appreciate its functional design. Instead, we consider the fundamental physical processes that are involved in the energy conversion relay as shown here for the simplest generic photosystem (bottom left). Transfer efficiency is simply determined by the ratio between energy- and electron-transfer rates and the inherent decay rates (fluorescence, charge recombination, catalytic turnover). The latter exhibit distinctive rates, which impose time constraints on the integrated design. Intercofactor distances are the predominant determinants of energy- and electron-transfer rates whereas other factors such as reaction free energy and Förster radius (an empirical measure of dipole strength), respectively, have minor effects. Altogether, these parameters determine distinct landscapes of transfer efficiencies, as shown here (bottom right) for a typical fluorescence decay rate of 10^9 s^{-1}, and ranges of distances, free energies, and Förster radii.*

apparatus to naturally unrelated catalytic and metabolic processes, thereby conferring novel and more useful energy harvesting properties to the organism.

Engineering guidelines of photosynthetic solar energy conversion

The vast structural and functional information database of photosynthetic enzymes includes in addition to detailed kinetic records from decades of research on physical processes and chemical reaction-pathways, a variety of high and medium resolution crystal structures of key photosynthetic enzymes. Recently, we have examined this database from an engineer's point of view with the long-term goal of reproducing the key features of natural photosystems in novel biological and non-biological solar energy conversion systems. Our surveys reveal that the basic physics of the transfer processes, namely, the time constraints imposed by the rates of incoming photon flux and the various decay processes allow for a large degree of tolerance in the engineering parameters. Furthermore, the requirements to guarantee energy and electron transfer rates that yield high efficiency in natural photosystems are largely met by control of distance between chromophores and redox cofactors. This underlines a critical challenge for projected de novo designed constructions, that is, the control of spatial organization of cofactor molecules within dense arrays of different cofactors, some well within 1 nm from each other.

Applying photosynthetic engineering guidelines in de novo designed protein-pigment complexes

The basic physics of energy and charge transfer processes can tolerate a broad range of structural and environmental variation. Therefore, applying the same engineering guidelines of photosynthetic and respiratory redox enzymes in de novo designed molecular systems is a viable strategy for customizing novel functional proteins that reproduce

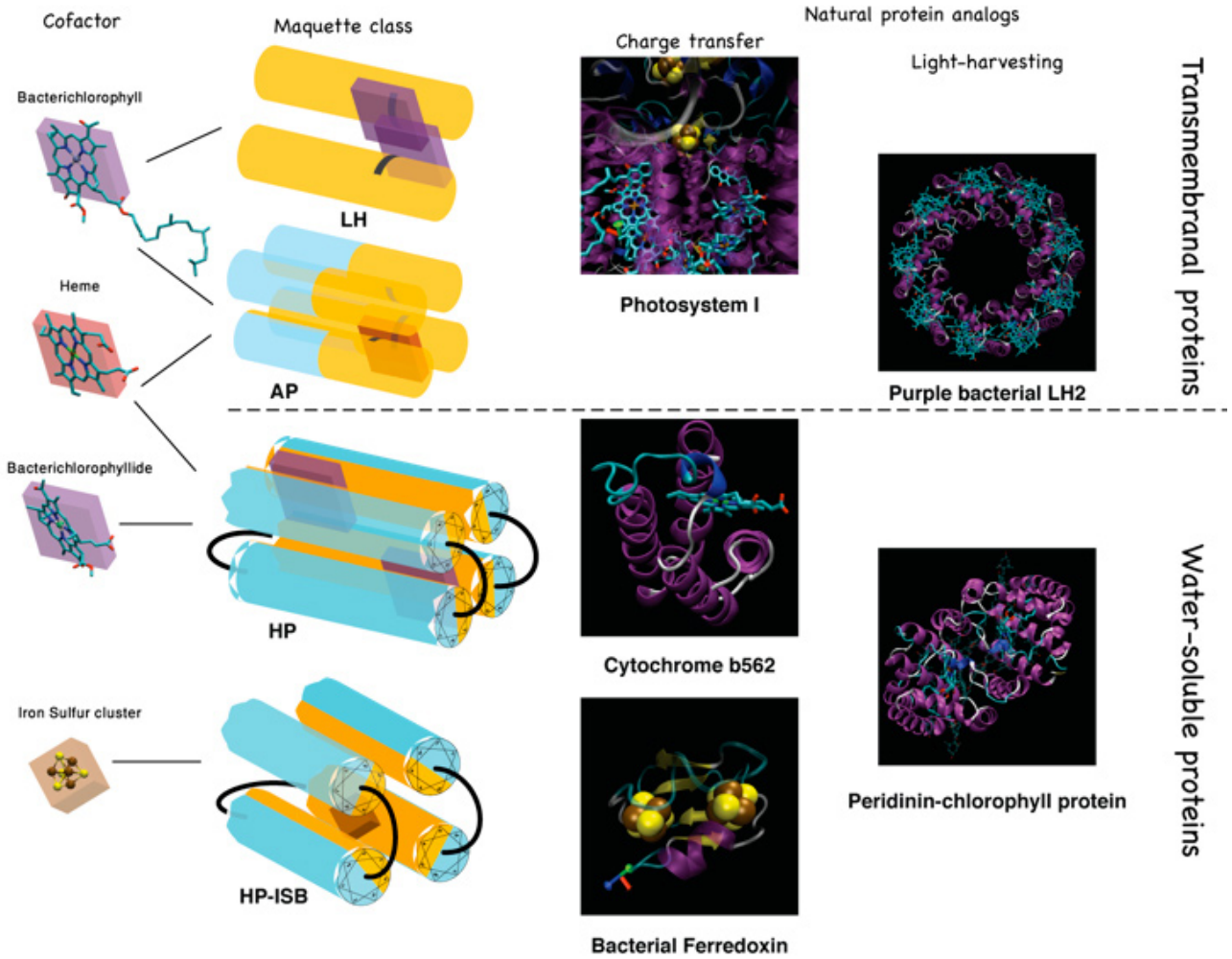

Fig. 2 *Protein maquettes designed and investigated in the lab, their typical cofactors and examples of their natural protein analogs. LH, AP, HP, and HP-ISB stand for transmembranal purple bacterial light harvesting complex analogs, amphiphilic, water-soluble, and iron-sulfur binding maquette classes, respetively. Cyan and orange represent hydrophilic and hydrophobic faces of the protein helices, respectively.*

the essential features of their natural enzyme analogs with minimal structural complexity. These proteins are called maquettes by analogy to the three dimensional sketches used by artists and architects for capturing the essence of their large and elaborate works. Thus, we aim at constructing photosynthetic protein maquettes.

Complying with the distance requirements implies controlling and organizing cofactors within a protein environment at sub-nanometer accuracy, which is still a significant challenge of protein design. Yet, we demonstrate that much progress can be achieved without resorting to rigorous and computationally intensive protein design algorithms. Instead, we apply simple guideline of protein design to robust and proven templates, and optimize our designs by an iterative learning and application strategy. Particularly, we focus on water-soluble (HP, for hydrophilic) and amphiphilic (AP) variants of the well-established four-helix bundle template that can be functionalized for binding a variety of pigments and redox cofactors including modified chlorophylls (Chls) and bacteriochlorophylls (BChls). Other useful templates are based on the small transmembranal BChl-binding proteins of purple bacterial light harvesting complexes. By judicious modification of BChls we were able to obtain a variety of protein-pigment complexes that may be used as functional modules of a more elaborate and complex system. Currently we are designing and constructing a system that can carry out photoinduced charge separation in a manner similar to natural photosystems namely, light absorption by a light-harvesting module and efficient energy transfer to a charge separation module.

Prospective: de novo designed protein-pigment complexes in vivo

Building devices based on amino-acids and modified natural organic and inorganic cofactors offers significant benefits including inexpensive production through expression in bacterial systems, high yield and high purity as well as considerable versatility and adaptability to various construction requirements and external conditions. Additionally, a unique and important benefit of such protein-based systems is the potential of genetically expressing and assembling those in living cells, thereby providing new possibilities for bioreactors for prescribed products. As a first step in this direction, we are designing protein maquettes that can be used as redox partners to natural protein complexes. Here again, the key for functionality is bringing the redox cofactors close enough to allow efficient electron transfer. Thus, rather than designing specific protein-protein interactions, we employ simple and global considerations such as matching the overall charge and polarity of the estimated interaction interface of the maquettes to the native binding site. Alternatively, short maquettes sequences may be fused to the native proteins by recombinant DNA techniques, circumventing the need to design specific protein-protein interaction interfaces.

Selected publications

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