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PREFACE

Preface to the special issue: photosynthesis-inspired biohybrid and biomimetic systems

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Research of Photosynthesis-Inspired Biohybrid and Biomimetic Systems has gained significant momentum in recent years as an approach to both study and use solar energy in new photon-to-fuel schemes that mimic photosynthesis. This intense interest arises from the incredible opportunity that photosynthesis-inspired biohybrids provide, which is to harness the optimal qualities of both artificial and natural photosynthetic systems by using evolved protein architectures from biology to address synthetic challenges and by incorporating synthetic molecules to creatively probe and utilize Nature's mechanisms.

Photosynthetic organisms harness solar radiation by converting light into chemical energy, ultimately synthesizing energy-rich compounds from abundant but thermodynamically stable inputs like water and CO_2. In natural photosynthesis, light-gathering antenna funnel excitation energy to a core of cofactors housed in the integral membrane reaction center proteins (RCs). Key light-induced RC chemistry involves rapid, sequential electron transfer steps that result in long-lived charge separation across the membrane, establishing an electrochemical potential. This process is intimately tuned to couple efficient light capture, directional electron transfer, and stabilized charge separation to secondary reaction sequences. In this manner, light energy is converted into chemical energy that is subsequently used to drive the chemical reactions required for photosynthesis. A key structural component of RCs is the network of molecular cofactors held by the protein scaffold at appropriate distances and orientations with respect to each other to enable efficient electron transfer. Localized anisotropic protein environments surrounding these redox sites dynamically adjust to promote electron transfer and enable high quantum yield charge separation. Such protein-cofactor interactions have been finely tuned over billions of years to exquisitely manage photon capture and conversion processes in photosynthetic organisms. Thus, photosynthetic systems provide a road map for renewable and clean energy strategies that utilize sunlight. Basic research of Nature's photosynthetic machinery can provide important insight about fundamental mechanisms of photochemical energy conversion that in turn can be used to develop viable photosynthesis-inspired systems for solar energy conversion and solar fuels production.

This foundational work toward understanding natural photosynthesis and its mechanisms that effectively capture and convert solar energy has inspired researchers to construct artificial photosynthetic systems that structurally or functionally mimic parts of the intricate molecular machinery of photosynthesis. For decades, synthetic chemists have used the cascade of donor/acceptor cofactors in RCs as inspiration for designing efficient molecular systems for light-driven charge separation. More recently, artificial photosynthesis has been focused on incorporating both photochemical and catalytic function within new architectures. These systems hope to do what plants do, use solar energy to power the transformation of abundant chemicals such as water and CO_2 into fuels and other useful chemicals. There remain numerous opportunities for successful photocatalysis with constructs composed solely of materials built with chemistry. New efforts, however, combine synthetic approaches with biological matrices to form biohybrid complexes.

This Special Issue is focused on biohybrid research that aims to either replicate or use Nature's photosynthetic schemes. Biohybrid research is truly an interdisciplinary field, leveraging bioinorganic, biochemistry, synthetic, and physical chemistries for hybrid assembly, spectroscopic characterization, and mechanistic studies. The articles showcase how combining protein structure/function with synthetic molecular chemistry imparts creativity and tunability in biohybrid designs to explore the integral functional

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components of solar energy conversion: light harvesting, charge separation, and catalysis.

The first two articles are inspired by photosynthetic light capture chemistry. Ponomarenko et al. examine chirality as a feature for the design of biohybrids with photosensitizer dyes covalently coupled to cysteine residues. The authors find that enantiomer selectivity correlates to timescale for ultra fast photo-induced electron transfer and suggest that enantioselectivity can be used as an additional tuning factor for abiotic cofactor insertion into functional biohybrid designs. Yoneda et al. construct a biohybrid complex of light-harvesting complex 2 (LH2) with site selective attachment of an external chromophore to examine energy transfer pathways and explore possibilities for enhancing the light-harvesting potential of antenna.

Light-induced charge separation is a fundamental attribute of RCs. This aspect is utilized in a biohybrid system in research by Espiritu et al. Using a combination of synthetic Mn oxides with the bacterial RC (bRC), the authors examine the interactions of these clusters with the protein environment and electron transfer to the oxidized primary electron donor P^+, providing a unique model system of the Mn_4CaO_5 cluster of Photosystem II. Botcha et al. provide a biomimetic system comprised of photosensitizer and catalyst that investigate the important details of the photo-induced electron transfer processes fundamental to aqueous photocatalysis of the solar fuel, H_2. Thus this paper addresses the third functional component of solar energy conversion, catalysis—the efficient making and breaking of chemical bonds using sunlight-derived electrons. A similar multimolecular photocatalytic system is encapsulated in a protein cage as described in Chen et al. (https://doi.org/10.1007/s11120-019-00671-4). The protein architecture facilitates photochemical H_2 generation by providing support for supramolecular assembly within a hydrophobic core.

Photosystem I-based systems are among the best photocatalytic H_2-producing hybrids to date. The Photosystem I (PSI) RC has built-in light harvesting, charge separation, and an electron donor/acceptor chain to support multistep reductive chemistry. Gorka and Golbeck share new work in which an [Fe–Fe] hydrogenase is linked via a molecular wire to the phylloquinone sites of PSI through clever bioengineering of the quinone chemistry. Walters and Golbeck re-engineer a ferredoxin protein to act as a coupler between PSI and Pt nanoparticles. In both cases, the optimized photochemistry of PSI drives H_2 production from the linked H_2 catalysts. The latter paper lays the groundwork for extending PSI-based chemistry to *in vivo* H_2-generating systems. Brahmachari et al. use a photosynthetic network involving dynamic protein–protein interactions and interprotein electron transfer in combination with synthetically tuned molecular photosensitizers and tailored catalysts to produce H_2 from light in aqueous solutions.

In addition to articles that describe new research, this Special Issue also features three useful and comprehensive reviews on the state of the art in biohybrid research. Brown and King provide a pertinent overview of the synthetic diversity available through combining nanomaterials with proteins for solar-to-chemical conversion strategies, focusing on fundamental mechanistic studies of molecular scale energy conversion to inspire scale-up technologies. Im et al. provide a review focusing on the chiral and light polarization characteristics of chlorophyll assemblies in biological energy transfer and how these features can be applied to bioinspired scaffold-based artificial antenna systems. Zheng et al. provide a review of visible light-driven enzyme catalytic reactions including CO_2 to CO and formic acid production, N_2 fixation, H_2 production, and fatty acid conversion, highlighting the use of genetically encodable fluorescent protein hybrids.

I wish to acknowledge all authors for their outstanding efforts put forth in their high-quality scientific papers. Furthermore, I would like to express my gratitude to all reviewers for constructive and informative comments. I am grateful to Terry M. Bricker (Editor-in-Chief) for his invitation to edit this Special Issue and for his support throughout the process. My hope is that this Special Issue will inspire the *Photosynthetic Research* community to embrace and explore the novel scientific opportunities afforded by biohybrid research.