Biohybrids for studying photosynthetic mechanisms and solar fuel production

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Natural photosynthetic energy research is aimed at resolving fundamental mechanisms of photochemical energy conversion in photosynthetic proteins. These basic studies provide us with insight into how to use nature's optimized photochemistry to drive non-native chemical reactions. Currently, we are designing new bio-inspired systems that capture and convert the sun's energy and store it in the energy-rich bond of hydrogen, a clean, carbon-neutral and renewable energy source. Specifically, we are creating a new class of small protein-based photocatalytic complexes that replicate essential design features of photosynthetic reaction centers (RCs) and enable the spectroscopic discernment of the structure and processes crucial to solar-driven proton reduction. In previous work we developed two systems for photocatalytic hydrogen production from water that directly link both a proton reduction catalyst ($[Co(dmgBF_2)_2]$ or $[Co(dmgH)_2pyCl$) and a photosensitizer molecule $[Ru(bpy)_3]^{2+}$ with the small electron transfer proteins, either ferredoxin or flavodoxin. Placement of redox active electron transfer moieties at designed locations in the protein scaffolds enables rapid forward electron transfer and prohibits charge recombination, resulting in strong photocatalytic H_2 generation. Currently, we are expanding these designs using Streptavidin (SA)-biotin interactions to (1) incorporate the light-harvesting protein phycoerythrin from red algae to capitalize on nature's optimized light-capture and energy transfer mechanism and probe photocatalysis using low-energy light (Figure 1A), (2) study protein microenvironmental control of the excited state dynamics of synthetic Cu(I) photosensitizer molecules (Figure 1B).

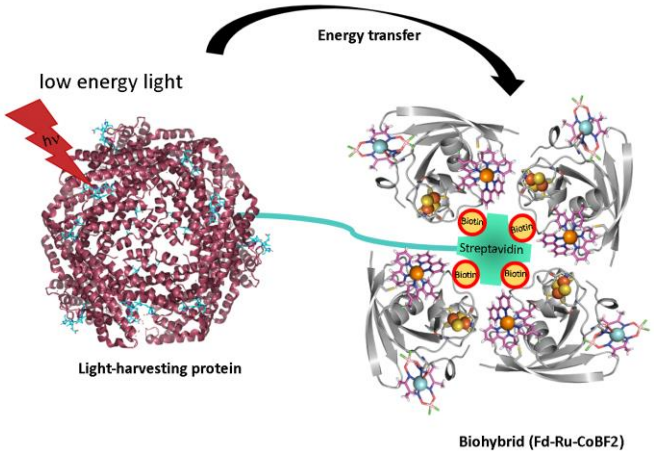

Figure 1A. Biohybrid comprised of a light-harvesting protein and photosensitizer-protein-catalyst complex.

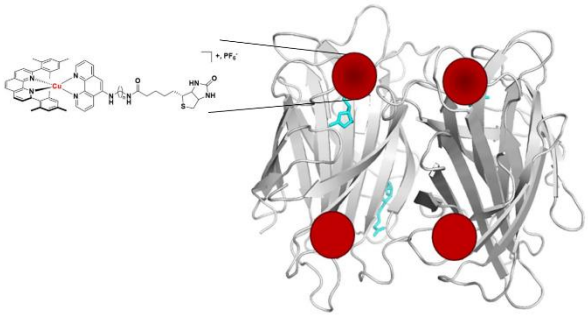

Figure 1B. Cu-C_n-biotin SA hybrid assembly.