ARTIFICIAL PHOTOSYSTHESIS: MIMICKING BIOLOGICAL SOLAR ENERGY CONVERSION

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Bacterial photosysthetic energy conversion begins with absorption of light by an antenna followed by singlet-singlet energy transfer to a reaction center, where photoinduced electron transfer generates a trans-membrane change-separated state. The energy stored in this state is used to produce a trans-membrane proton gradient that in turns is employed to synthesize ATP which fills the energy needs of the organism. We have prepared synthetic molecular systems consisting of two to five covalently linked components (porphyrines, quinones, carotenoid polyenes) that mimic photosynthetic antenna function and undergo photoinduced electron transfer to produce energitic, long-lived charge-separated states in high quantum yield. One of these artificial reaction centers, a molecular triad (C-P-Q) consisting of a porphyrin moiety (P) linked to a quinone (Q) and to a carotenoid polyene (C), has been synthesized and incoporated unidirectionally into the lipid bilayer membranes of liposomes.

Time-resolved fluorescence experiments reveal that excitation of C-P-Q in these membranes leads to electron transfer from the porphyrine excited singlet state to give $C\text{-}P^{+}\text{-}Q^{-}$. A subsequent electron transfer from the carotenoid to the porphyrine radical cation yields the long-lived species $C^{+}\text{-}P\text{-}Q^{-}$. A collateral electron carrier in the bilayer, 2,5-diphenylbenzoquinone, has been found to act as a trans-membrane proton shuttle driven by the intramolecular redox potential of $C^{+}\text{-}P\text{-}Q^{-}$. The photoinduced trans-membrane proton transport was monitored by a fluorescent, pH-sensitive dye located in the aqueous interior of the liposomes. Irradiation of the porphyrine moiety of the triad at 650nm led to acidification of the inside of the liposomes. The pH gradient was stable for several hours, and could be relaxed by addition of a proton ionophore.