# Integration of Photosynthetic Complexes into Novel Biomolecular Electronic Devices

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The amount of energy consumed globally is astounding and continues to grow each year, and unfortunately most of our energy sources are not renewable. Average annual solar irradiance at the earth's surface represents 10,000 times the annual global energy consumption, which makes photovoltaic devices very enticing as an alternative to current technology in energy sources. The principle barrier to widespread use of photovoltaic power sources has been cost per unit energy i.e. low conversion efficiency and high production cost of devices. The careful use of photosynthetic proteins as nano-scale generators may alleviate the cost and boost the efficiency of photovoltaic devices.

A photocell has three main functions 1) absorb the maximum number of photons, 2) split photons into charge, and 3) conduct charge out of the device. Using proteins as scaffolding for chromophores such as chlorophyll affords two major advantages over existing technology. First, increased spatial resolution or more absorption per unit area compared with current technology, and secondly, proteins create a functional 3-D arrangement of molecules. These two factors taken together can lead to 2-3 orders of magnitude of improvement. Photosystem I is and ideal choice for this application for numerous reasons. The large tightly coupled antenna complex contains ~ 175 chlorophyll/PSI, and the efficiency of charge separation is nearly unity in its native environment. The final electron acceptors are quite stable, have a low potential (<0.6V), and are well outside the insulating transmembrane domain, which isolates charge separation. Re-reduction of P700 occurs via a soluble protein, plastocyanin, and this can easily be integrated into the device as well. Along with the previous properties, PSI is easily and cheaply isolated and extremely robust.

Currently we have immobilized PSI and bacterial reaction center (RC) with hexahistidinyl tags onto gold derivatized with Ni-NTA and confirmed a uniform orientation with AFM. RC layered with ETL:C60 then ETL:BPC and finally with Ag have shown photovoltaic activity although with low efficiency. Other groups have pursued similar goals in wet electrochemical cells, and the photocurrent spectrum of our devices agree well with published RC absorption spectra and those of wet electrochemical cells. In similar experiments PSI oriented with the opposite topology has shown light dependent current capabilities. Once again the photocurrent spectra of PSI agrees very well with the solution spectrum of chlorophyll. The stability of these devices has been greatly enhanced by the addition of short surfactant peptides while the PSI is being dehydrated. Using a fluorescence assay the stability of the PSI complex was found to be greater that three weeks in the solid state.

Strategies for improvement of the device fall into three categories: 1) increasing the optical cross-area by incorporation of high efficiency light harvesting mega-structures such as phycobilisomes and chlorosomes from cyanobacteria and green bacteria. 2) Explore the use of high-absorbing, synthetic antenna that may be both easily fabricated and highly stable. 3) Incorporation of a surface plasmon layer with exceptionally high energy transfer efficiency to permit a substantial increase in light harvesting via a lateral use of either natural or synthetic antennae structures. 4) Improve the steady-state electron transfer kinetics by accelerating the re-

reduction of P700 by integration of its natural reductant, plastocyanin via cross-linking or overlay.


1) Kiley, P., Zhao, X., Vaughn, M., **Baldo, M.A., Bruce, B.D., and Shuguang Zhang** (2005) Self-assembling Peptide Detergents Stabilize Isolated Photosystem I on a Dry Surface for an Extended Time. PloS Biology, **3(7),** 230-237.

2) Yu, A.A., Stoney, P.R., Norvillez, J.E., Vaughn, M., Pacsial, E.J., **Bruce, B.D., Baldo, M.,** and Stellacci, F. (2005) A Simple Atomic Force Microscopy Method The Visualization Of Polar And Non-Polar Parts Organic Films. J. Exp. Nanoscience, 1:1, 1-11.

3) Das, R., Kiley, P.J., Segal, M., Norville, J., Yu, A.A., Wang, L.Y., Trammell, S.A., Reddick, L.E., Kumar, R., Stellacci, F., Lebedev, N., Schnur, J., **Bruce, B.D., Zhang, S.G., and Baldo, M.** (2004) Integration of photosynthetic protein molecular complexes in solid-state electronic devices. Nano Lett. **4(6):** 1079-1083.