Final Scientific/Technical Report

February 20, 2007

Grant Title: Biomimetic Energy Transduction: Artificial Photosynthesis in a Stabilized Lipid Membrane Coupled to a Semiconductor

Agency: U.S. Department of Energy

Grant Number: DE-FG02-02ER15378

Dates: 9/15/02–3/31/06

Amount: \$650,000

Principal Investigators: S. Scott Saavedra
Neal R. Armstrong

Affiliation and Performance Site: Department of Chemistry,
University of Arizona,
Tucson, AZ 85721-0041

A. Summary

This research program explored development of artificial, biomimetic photosynthetic assemblies that perform the initial steps of bacterial photosynthesis, visible light absorption, charge separation, and vectorial proton pumping, in a planar supported lipid bilayer (PSLB), coupled to a semiconductor electrode. The creation of a light-driven, transmembrane proton pump interfaced to an electrically active support is significant because at the most basic level, the development of a proton motive force (pmf) across a biological membrane is one of the essential elements of biological energy conversion.

Our efforts were primarily focused on: *i*) development of the individual components of our proposed architecture for solar energy conversion, shown in Figure 1, and *ii*) establishing the feasibility of transmembrane proton pumping (TMPP) in this architecture. In collaboration with Devens Gust, Tom Moore, and Ana Moore at Arizona State University, we have demonstrated, for the first time, both chemically- and photo-driven TMPP across a single PSLB, with embedded photoactive triads and quinone shuttles, coupled to an electroactive waveguide through a conducting polymer layer. Only the most significant results are discussed below. More detailed accounts of the research supported in whole or part by this grant have appeared or will appear in publications.¹⁻¹³

Figure 1 – Schematic view of our energy conversion concept -- a planar ITO electrode is modified with a hydrophilic, self-assembled conductive polymer (SA-CP, ca. 5 nm thick) cushion (e.g. polyaniline), on which is deposited a planar supported lipid bilayer (PSLB, 5 nm thick) that is stabilized by cross-linking polymerization, and incorporates artificial photosynthetic reaction centers (C-P-Q triads) and diffusive quinones (Q). Upon light absorption, the C-P-Q triad (structure shown in (b)) undergoes electron transfer to produce the charge separated C^+-P-Q^- , which reduces Q at the outer interface and oxidizes it at the inner interface. Thus Q shuttles protons from the outer electrolyte across the membrane to the space occupied by the water-swollen polymer cushion – each triad acts as a closed-loop photoelectrochemical system (i.e. electrons are conserved within the PSLB). The ITO film (ca. 25-100 nm thick) is the upper layer of a unique spectroelectrochemical planar waveguide. Broadband planar waveguide ATR spectroscopy, performed under potential control or during potentiometric characterization of the biomimetic process, is used to characterize key structural and functional properties of the multilayer architecture.

B. Transduction of an ion gradient across a PSLB coupled to an electroactive waveguide through a conductive polymer film.

A number of liposome-based systems have been developed that allow for chemically- or light-induced transport of ions into or out of the vesicle interior.¹⁴⁻²⁸ Liposomal architectures, however, are not readily interfaced to a solid-state transducer. Formation of ion gradients across planar supported membranes, “wired” to substrate electrodes,^{29, 30} may ultimately allow utilization of the potential energy to drive other electrochemical processes. We made a significant step toward this goal by developing a spectroelectrochemical transduction platform (Figure 2a) that provides for simultaneous electrochemical and spectroscopic detection of a proton gradient across a PSLB.¹

The PSLB is coupled to a planar ITO electrode through a self-assembled, conducting polymer (SA-CP) multilayer composed of alternating layers of poly(aniline) (PANI) and poly(acrylic acid) (PAA),^{4, 9} deposited using the layer-by-layer (LbL) self-assembly method.^{31, 32} The water-swollen (PANI/PAA)₂ layer (ca. 50 Å thick): *i*) planarizes the ITO surface; *ii*) is physically and chemically compatible with deposition of a continuous PSLB (whereas bare ITO is not); and *iii*) serves as an ionic reservoir for charge transported across the PSLB. At near-neutral pH, three major forms exist in equilibrium in the (PANI/PAA)₂ layer (Figure 2b):^{33, 34} Two are partially oxidized, the protonated emeraldine salt (ES) and the deprotonated emeraldine base (EB). The third is fully reduced leucoemeraldine (LE). LE is transparent at visible wavelengths, whereas the absorbance of EB and ES in the 400-900 nm range is pH-dependent. Although PANI films are typically doped into their conductive ES forms at low pH, PAA co-deposition renders PANI electroactive and pH-responsive at near-neutral pH.^{4, 9, 35, 36} Thus the ITO/(PANI/PAA)₂ layer can function as both a potentiometric pH sensor and an absorbance pH indicator. The construction and extensive characterization of these layers is described in two publications.^{4, 9}

Figure 2 – (a) Schematic of a PSLB supported on ITO/(PANI/PAA)₂. Ascorbic acid in the aqueous superstrate reacts with membrane-bound BQ, generating BQH₂, which diffuses across the lipid bilayer and undergoes a second redox reaction, donating two protons and two electrons to the (PANI/PAA)₂ layer. (b) Coupled equilibria between the three dominant forms of PANI in the PANI/PAA layer, near neutral pH. When the (ES+EB)/LE ratio is held constant by potential control, proton transport shifts the ES/EB equilibrium, which is spectroscopically characterized. Potentiometric experiments at open-circuit are used to sense the reduction of EB+ES to LE.

Redox-driven proton pumping was used to test the architecture (Figure 2a). A lipid-soluble shuttle molecule, 1,4-diphenyl-2,5-benzoquinone (BQ),¹⁵ was inserted into a PSLB composed of egg phosphatidylcholine that was deposited on ITO/(PANI/PAA)₂ by vesicle fusion. Charge transport across the PSLB is initiated when ascorbic acid (AA) in the superstrate solution reacts with membrane-bound BQ. The product, BQH₂, diffuses across the membrane where it is re-oxidized by either the ES or EB forms of PANI, donating two protons and two electrons to the ionic reservoir.¹⁹ To monitor the process spectroscopically, the ITO/glass electrode was used as a broadband electroactive planar optical waveguide to perform attenuated total reflectance (ATR) spectroscopy.^{4, 9, 37} Multiple internal reflections along the length of the substrate provide a large optical pathlength, allowing small absorbance changes in the (PANI/PAA)₂ layer to be measured over a bandwidth of ca. 300 nm. During the spectroscopic measurement, the potential of the ITO electrode is held constant, which fixes the ([EB]+[ES])/[LE] ratio (i.e., re-oxidization of BQH₂ generates a current in the overall circuit). Proton transport across the PSLB converts EB to ES, producing a red shift in the ATR spectrum. Typical spectra acquired before and after

AA injection into the superstrate solution are shown in Figure 3. The increase in [ES], caused by BQ-mediated proton transport across the PSLB, produced a spectral shift of 12 nm, which from pH-spectral calibration data¹ corresponds to a $\Delta\text{pH} = -1.1$ units at the ITO/(PANI/PAA)₂ interface. From estimates of the pK_a for ITO/(PANI/PAA)₂ and the number of proton acceptor sites in the ionic reservoir, a transmembrane proton flux of 74 pmol/minute is calculated.¹ This value equates to a transport rate of 0.07 s^{-1} per BQ, which agrees well with previous estimates of diffusion-limited, charge transport by benzoquinone and its structurally related analogs in lipid bilayers.^{14, 18, 21, 23}

C. Light-driven, transmembrane proton pumping.

We next showed the feasibility of using light to drive TMPP across the same type of waveguide-supported PSLB assembly.¹⁰ These experiments were performed using an artificial photosynthetic reaction center consisting of covalently linked carotenoid, porphyrin, and quinone moieties (C-P-Q triad, Figure 4) synthesized by our Arizona State University (ASU) collaborators. Previous work by the groups of Gust, Moore, and Moore¹⁵ demonstrated that illumination of a suspension of C-P-Q-containing liposomes leads to electron transfer from photo-excited P to Q, generating C-P⁺-Q⁻, followed by a secondary electron transfer (hole capture by C) to yield the charge separated state, C⁺-P-Q⁻. In the membrane, BQ is reduced and protonated at the outer bilayer surface, and oxidized and deprotonated at the inner bilayer surface, regenerating the ground state, neutral C-P-Q. On the nanometer scale, this process can be viewed as a closed-loop photoelectrochemical process driving a quinone-based, proton-transporting redox loop that produces a transmembrane proton gradient (i.e., a proton motive force or pmf).

Figure 3 - Absorbance spectra acquired before (A) and 10 min after (B) injection of AA over a PSLB containing BQ, and the difference spectrum ($C = B - A$). The decrease in absorbance in the 450-650 nm region results from BQ-mediated proton transport across the PSLB.

Figure 4 – Structure of the C-P-Q triad.

To demonstrate light-driven TMPP with these triads, a PSLB containing 2 mol% BQ was deposited by vesicle fusion on ITO/(PANI/PAA)₂. C-P-Q triads were then inserted into the PSLB from a THF/buffer solution. The photoelectrochemical process was driven by illumination with a 150 watt Xe lamp, filtered to provide green-NIR output. TMPP was first demonstrated using potentiometric detection. The closed-loop redox reactions involving BQ and photo-excited C-P-Q donate protons to the (PANI/PAA)₂ layer, shifting the EB/ES equilibrium *without* altering the $([\text{EB}] + [\text{ES}])/[\text{LE}]$ ratio; under these conditions, the change in cell potential is proportional to $0.0592 \log(\Delta a_{\text{H}^+})$ in the water-swollen CP layer.¹ A positive shift in cell potential of 12 mV was observed during 10 min of illumination (Figure 5a), which equates to a pH drop of 0.28 units, corresponding to a transmembrane proton flux of 22 pmol/minute. When the illumination was blocked, the cell potential slowly decreased, which is likely due to slow leakage of protons back across the PSLB.³⁸ When either BQ or C-P-Q was absent in the PSLB, potential shifts upon illumination were not observed. ATR difference spectra, acquired at constant cell potential as a function of illumination time, are shown in Figure 5b. A negative absorbance change, accompanied by a red shift in λ_{max} of the absorbance band, was observed due to protonation of EB to generate ES, similar to the

results obtained with redox-driven, TMPP (Figure 3). While the incident light quantum efficiency for the process appears to be low, these results clearly *establish the feasibility* of using photon energy to generate a pmf across a PSLB interfaced to an electrically-active support. This is an essential first step toward creation of useful molecular devices, e.g. sensors and energy conversion devices, based on membrane-based, artificial photosynthetic processes.

Figure 5 - (a) Potentiometric detection of light-driven, transmembrane proton transport. The ITO/(PANI/PAA)₂/PSLB architecture used here is identical to that depicted in Figure 2a, except that the C-P-Q triad is present in the PSLB and light (rather than reaction with AA) is used to drive proton transport. (b) ATR difference spectra (versus the absorbance spectrum before illumination) for the triad- and BQ-doped PSLB. Spectra 1-5 were acquired after illumination for 2, 4, 6, 8, and 10 min, respectively.

D. CP/sol-gel composite layers.

As an alternative to (PANI/PAA)₂ layers for coupling PSLBs to ITO, we have created ITO substrates coated with porous sol-gel glass (PSG) layers that are doped with CP nanowires. The sol-gel method is a low-temperature process used to synthesize optically transparent, amorphous bulk glasses and thin films.³⁹ The reaction proceeds by hydrolysis of alkoxide precursors followed by polycondensation of the hydroxylated units to form a microporous glass. The chemical and physical properties of the glass (e.g. pore size distribution, surface chemistry, optical transparency) can be systematically adjusted by varying the precursor composition and processing parameters.⁴⁰⁻⁴³ In addition: *i*) The surface roughness of a PSG glass layer deposited by dip- or spin-coating can be quite low (<5 Å rms) depending on the fabrication method (see below). *ii*) Relative to polymer cushions (such as (PANI/PAA)₂), PSLBs adhere more strongly to glass surfaces, particularly PSLBs composed of cross-linked dienoyl lipids.⁶

For the purposes of this project, the sol-gel must be electrically conductive. A number of groups have described methods to prepare conductive sol-gel materials by entrapping a monomer, e.g. aniline, in a microporous sol-gel coated on a conductive substrate followed by electrochemical polymerization.⁴⁴⁻⁴⁷ In a recent paper,³ we described use of this approach to prepare sol-gels “wired” with poly(3,4-ethylenedioxythiophene) (PEDOT), a polymer used in our previous work with electropolymerized CP thin films.^{7,8} EDOT monomer is introduced either by dissolving it

Figure 6 - SEM image of two “emergent” PEDOT wires (b and c) which have grown from the ITO substrate, up through the sol-gel matrix (a), which is 200-300 nm thick.

in the sol or by soaking the PSG layer in an EDOT solution. In Figure 6, a scanning electron microscograph of a cross-sectioned sol-gel layer illustrates PEDOT wires grown through a PSG layer that has been spin-coated on ITO. Electrochemical experiments showed that the PEDOT behaves as an array of nano-electrode wires templated in a 300 nm thick, insulating sol-gel layer.³

More recently, we extended this concept to create PSG layers doped with PANI nanowires in a manner that allows subsequent fusion of a PSLB (Figure 7).¹³ A TEOS sol-gel layer (ca. 300 nm thick) was first deposited on ITO, followed by electropolymerization of aniline, followed by deposition of a second TEOS layer (ca. 50 nm thick) that covers the protruding PANI nanowires, generating a smooth, hydrophilic glass surface. Both sol-gel layers are porous, which allows the PANI nanowires to rapidly equilibrate when the pH of the buffer in contact with the upper PSG layer is changed. The potentiometric response is ca. 30 mV/pH unit (Figure 7b), and this response is *completely blocked* after a PSLB is fused onto the glass surface. These results demonstrate the feasibility of developing PANI/sol-gel composite materials as structurally rigid CP layers for coupling PSLBs to ITO substrates for lipid membrane-based solar energy conversion applications.

Figure 7 – (a) Schematic drawing of a PSLB on PANI-doped sol-gel layers on ITO, and height AFM images of the oxide layer surfaces. The ITO surface (lower AFM image; rms = 13.7 Å) is coated with the first sol-gel layer, followed by aniline electropolymerization. PANI nanowires protrude above the sol-gel (middle AFM image). Application of the second sol-gel layer creates a smooth surface (rms = 2.2 Å) onto which egg-PC vesicles are fused to form the PSLB. (b) In the absence of the PSLB, the potentiometric response of the electrode to buffers of varying pH is ca. 30 mV/decade (blue symbols). The pH response is blocked (red symbols) after deposition of the PSLB, demonstrating its low permeability to protons.

E. Polymeric PSLBs.

A variety of biomimetic supramolecular structures that rely on charge separation and/or ion transport across a fluid lipid membrane have been constructed for use in chemical sensors, biosensors, and energy storage/conversion media (e.g.^{16, 24, 48, 49}). However, in a fluid-phase membrane, the lipids are associated only by relatively weak, noncovalent forces; thus these structures lack chemical, thermal, and mechanical stability relative to, for example, alkylsiloxane self-assembled monolayers.^{5, 6, 50-52} This lack of stability is a major impediment to technological implementation of lipid membranes in molecular devices, particularly when operation for extended periods is desired.^{50, 53, 54} Polymerization of the lipid monomers is the strategy we are pursuing to overcome this problem. We have been investigating cross-linking polymerization of dienoyl-functionalized lipids (Figure 8) in an effort to create PSLBs with enhanced physical and chemical stability. Several parameters thought to affect poly(PSLB) structure and stability were examined, including a comparison of UV photopolymerization and redox-initiated radical polymerization, and the number and location of the polymerizable moieties in the lipid monomer. The

results are described in several manuscripts.^{6, 55-57} Briefly: Both UV-initiated and redox-initiated radical polymerization of PSLBs composed of bis-functionalized lipids produce cross-linked poly(PSLB)s that are stable to dissolution in surfactants, a condition that would destroy a fluid membrane. In some cases, these materials are even stable to repeated drying/rehydration and immersion in organic solvents, despite the absence of a covalent tether between the membrane and the underlying substrate. Insolubility is attributed to a high degree of cross-linking coupled with multivalent interactions between polymer segments and the substrate surface. These poly(PSLB)s appear to possess both the stability and inertness required for application in a number of emerging biomimetic energy conversion technologies.

Figure 8 - Polymerizable dienoyl lipids: mono-SorbPC (**1**), bis-SorbPC (**2**), mono-DenPC (**3**), bis-DenPC (**4**).

F. Ion permeability of poly(lipids).

We have developed a liposome-based assay, based on entrapment of a calcium-sensitive fluor,¹² to evaluate the permeability of poly(lipid) bilayers to ions and create a feedback loop between synthesis of new lipids and their evaluation. The design of the assay permits measurement of both the permeability of poly(lipids) to Ca^{2+} (a convenient ion to monitor in these systems) through defects in the bilayer, as well as assessment of the viability of insertion of a lipid-soluble ionophore into the lipid bilayer to diffusively transport Ca^{2+} . Both properties are important for development of artificial photosynthetic poly(lipid) membranes, i.e. to transport protons across the membrane, the quinone shuttle must be capable of diffusing through the poly(lipid) network, and the defect density in the membrane must be low enough to prevent significant back-leakage of the transported protons.

Initially we focused on characterizing the properties of liposomes formed from sorbyl-lipids (e.g. **1** and **2** in Figure 8). As noted above, these lipids were found to form the most stable poly(PSLBs).⁶ However, after polymerization poly(SorbPC) liposomes were found to be highly permeable to Ca^{2+} (data not shown).¹² Creation of a polymeric network in the center of the bilayer appears to perturb the packing of the lipid tails, creating ion-permeable defects.

We next synthesized and evaluated lipids in which one or two sorbyl groups are linked to the head group of the molecule (structures not shown). This strategy is based on the hypothesis that head group polymerization should minimally perturb tail group packing and thus minimally perturb the characteristic ion impermeability of the membrane. The results obtained were encouraging but still inadequate for the purposes of this project:¹² *i*) Ca^{2+} impermeability is maintained after UV photopolymerization; however the degree of polymerization is low. It appears that the polymerization of sorbyl groups is relatively inefficient at low concentration⁵⁸ unless they are organized in a liquid-crystalline phase, consistent with recent results reported by Meijer's group.⁵⁹ *ii*) A neutral sorbyl head group is not sufficiently hydrophilic to form the lamellar phase. Stable liposomes can be formed only when these lipids are mixed with a large mole fraction (e.g. 0.5) of a lamellar-forming lipid such as dioleoylphosphatidylcholine (DOPC), which negates the stability provided by polymerization.

Den-functionalized lipids (**3** and **4**, Figure 8), offer a “middle ground” - formation of polymeric networks adjacent to the glycerol backbone in each leaflet of the bilayer should not significantly perturb the chain packing in the center of the bilayer. Our most recent results support this hypothesis.¹² The Ca^{2+} impermeability of bis-DenPC liposomes is maintained after UV photopolymerization (Figure 9), comparable to that of fluid liposomes composed of egg phosphatidylcholine. Furthermore, introduction of ionomycin, a Ca^{2+} ionophore (MW = 747), facilitates Ca^{2+} transport into the poly(liposomes). *Thus after lipid polymerization*, an ion gradient is maintained across the bilayer, lipid-soluble molecules can be inserted into the bilayer, and they can diffusively transport ions across the bilayer.

Figure 9 - Results from a fluorescence assay for Ca^{2+} permeability and transport across liposomal membranes. Calcium Green (CG), a Ca^{2+} -sensitive fluor, was entrapped in bis-DenPC (**4**, Fig. 8), liposomes, which were then photopolymerized. When the concentration of Ca^{2+} in the solution was increased from 1.7 nM to 39 μM (left arrow), a small increase in CG fluorescence was observed, due to a small amount of residual CG in solution (i.e., not entrapped). When ionomycin, a lipophilic Ca^{2+} ionophore, was injected into the solution (right arrow), a larger increase in CG fluorescence was observed, due to ionomycin-mediated transport of Ca^{2+} into the liposome interior. Identical results were obtained for unpolymerized (fluid) bis-DenPC liposomes. Thus both ion impermeability and diffusive transport by a membrane-bound ionophore are maintained after lipid polymerization.

G. University of Arizona Personnel Who Played a Significant Role in the Project

Senior: S. Scott Saavedra, Neal R. Armstrong, Henry K. Hall

Postdoctoral Research Associates: Hadj El Andaloussi, Gemma D. D’Ambruoso, Liying Wang

Technical Staff: Ronald J. Wysocki

Graduate and Undergraduate Students: Eric E. Ross, Todd W. McBee, Saliya Ratnayaka, Chenhao Ge, Walter J. Doherty, Brooke Beam, Tony Spratt, Fathima Marikkar

H. Publications Supported in Whole or Part by DE-FG02-02ER15378

1. McBee, T.; Wang, L.; Ge, C.; Beam, B.; Moore, A. L.; Gust, D.; Moore, T. A.; Saavedra, S. S.; Armstrong, N. R., Characterization of Proton Transport Across a Waveguide-Supported Lipid Bilayer. *J. Amer. Chem. Soc.* **2006**, 128, 2184-2185.
2. Doherty, W. J.; Simmonds, A. G.; Mendes, S. B.; Armstrong, N. R.; Saavedra, S. S., Molecular ordering in monolayers of an alkyl-substituted perylene-bisimide dye by attenuated total reflectance ultraviolet-visible spectroscopy. *Applied Spectroscopy* **2005**, 59, (10), 1248-1256.
3. Doherty, W. J.; Armstrong, N. R.; Saavedra, S. S., Conducting polymer growth in porous sol-gel thin films: Formation of nanoelectrode arrays and mediated electron transfer to sequestered macromolecules. *Chemistry of Materials* **2005**, 17, 3652-3660.
4. Ge, C.; Doherty III, W. J.; Mendes, S. B.; Armstrong, N. R.; Saavedra, S. S., Voltammetric and Waveguide Spectroelectrochemical Characterization of Ultrathin Poly(Aniline)/Poly(Acrylic Acid) Films Self-Assembled on Indium-Tin Oxide. *Talanta* **2005**, 65, 1126-1131.
5. McBee, T. W.; Saavedra, S. S., Stability of lipid films formed on gamma-aminopropyl monolayers. *Langmuir* **2005**, 21, (8), 3396-3399.

6. Ross, E.; Rozanski, L.; Spratt, T.; Liu, S.; O'Brien, D. F.; Saavedra, S. S., Planar supported lipid bilayer polymers formed by vesicle fusion. 1. Influence of diene monomer structure and polymerization method on film properties. *Langmuir* **2003**, 19, 1752-1765.
7. Doherty, W.; Wysocki, R. J.; Armstrong, N. R.; Saavedra, S. S., Potential-Modulated, Attenuated Total Reflectance Spectroscopy of Poly(3,4-Ethylenedioxythiophene) (PEDOT) and Poly(3,4-Ethylenedioxythiophene Methanol) (PEDTM) Copolymer Films on Indium-Tin Oxide. *J. Phys. Chem. B* **2006**, 110, 4900-4907.
8. Doherty, W.; Wysocki, R. J.; Armstrong, N. R.; Saavedra, S. S., Electrochemical Copolymerization and Spectroelectrochemical Characterization of 3,4-Ethylenedioxythiophene (EDOT) and 3,4-Ethylenedioxythiophene Methanol (EDTM) Copolymers on Indium-Tin Oxide. *Macromolecules* **2006**, 39, 4418-4424.
9. Ge, C.; Armstrong, N. R.; Saavedra, S. S., pH Sensing Properties of Poly(Aniline) Ultrathin Films Self-Assembled on Indium-Tin Oxide. *Analytical Chemistry* **2007**, 79, 1401-1410.
10. McBee, T.; Wang, L.; Ge, C.; Beam, B.; Moore, A. L.; Gust, D.; Moore, T. A.; Saavedra, S. S.; Armstrong, N. R., Photo-Driven Proton Transport Across a Planar Supported Lipid Bilayer Interfaced to a Semiconductor Electrode. Manuscript in preparation.
11. Marikkar, F.; Brumbach, M.; Wang, L.; Lawler, M.; Beam, B.; Saavedra, S. S.; Armstrong, N. R., Layer-by-Layer Self-Assembly of Poly(Aniline)/Poly(Acrylic Acid) Films on ITO Substrates with Optimized Work Functions and Electron Transfer Rates to Probe Molecules. Manuscript in preparation.
12. Ratnayaka, S. R.; El Andaloussi, H.; D'Ambruoso, G. D.; Wysocki, J., R. J.; Hall, H. K.; Saavedra, S. S., Calcium Permeability and Ionomycin-Mediated Transport Across Polymerized Dienoyl Liposomes. Manuscript in preparation.
13. Ge, C.; Armstrong, N. R.; Saavedra, S. S., Porous sol-gel thin films on ITO templated with electrochemically grown poly(aniline) nanowires as a pH-responsive support for a planar lipid bilayer. Manuscript in preparation.

I. Additional References

14. Robinson, J. N.; Cole-Hamilton, D. J., Electron-Transfer across Vesicle Bilayers. *Chemical Society Reviews* **1991**, 20, (1), 49-94.
15. Steinberg-Yfrach, G.; Liddell, P. A.; Hung, S. C.; Moore, A. L.; Gust, D.; Moore, T. A., Conversion of light energy to proton potential in liposomes by artificial photosynthetic reaction centres. *Nature* **1997**, 385, 239-241.
16. Steinberg-Yfrach, G.; Rigaud, J. L.; Durantini, E. N.; Moore, A. L.; Gust, D.; Moore, T. A., Light-driven production of ATP catalysed by F0F1-ATP synthase in an artificial photosynthetic membrane. *Nature* **1998**, 392, (6675), 479-482.
17. Bennett, I. M.; Farfano, H. M. V.; Bogani, F.; Primak, A.; Liddell, P. A.; Otero, L.; Sereno, L.; Silber, J. J.; Moore, A. L.; Moore, T. A.; Gust, D., Active transport of Ca²⁺ by an artificial photosynthetic membrane. *Nature* **2002**, 420, (6914), 398-401.
18. Stanish, I.; Lowy, D. A.; Lee, Y.; Fang, J.; Wong, E.; Ray, R. I.; Singh, A., Structural and electrochemical characterization of immobilized polymerized electroactive vesicles. *Journal of Physical Chemistry B* **2004**, 108, (1), 127-135.
19. Hinkle, P. C., A Model System for Transmembrane Redox Reactions. *Methods In Enzymology* **1979**, 55, 541-544.
20. Hinkle, P. C., Electron-Transfer across Membranes and Energy Coupling. *Federation Proceedings* **1973**, 32, (9), 1988-1992.
21. Futami, A.; Hurt, E.; Hauska, G., Vectorial Redox Reactions of Physiological Quinones.1. Requirement of a Minimum Length of the Isoprenoid Side-Chain. *Biochimica Et Biophysica Acta* **1979**, 547, (3), 583-596.

22. Coutts, D.; Paterson, R., Photochemically Activated Electron-Transport across Unilamellar Liposomes Using Coenzyme-Q10 and Vitamin-K1 as Carriers. *Journal of Membrane Science* **1986**, 27, (2), 275-281.
23. Hauska, G., Plastoquinone and Ubiquinone as Translocators of Electrons and Protons through Membranes - Facilitating Role of Isoprenoid Side-Chain. *Febs Letters* **1977**, 79, (2), 345-347.
24. Luo, T. J. M.; Soong, R.; Lan, E.; Dunn, B.; Montemagno, C., Photo-induced proton gradients and ATP biosynthesis produced by vesicles encapsulated in a silica matrix. *Nature Materials* **2005**, 4, (3), 220-224.
25. Khairutdinov, R. F.; Hurst, J. K., Light-driven transmembrane ion transport by spiropyran - Crown ether supramolecular assemblies. *Langmuir* **2004**, 20, (5), 1781-1785.
26. Khairutdinov, R. F.; Hurst, J. K., Cyclic transmembrane charge transport by pyrylium ions in a vesicle-based photocatalytic system. *Nature* **1999**, 402, (6761), 509-511.
27. Khairutdinov, R. F.; Hurst, J. K., Cyclic transmembrane charge transport mediated by pyrylium and thiopyrylium ions. *Journal of the American Chemical Society* **2001**, 123, (30), 7352-7359.
28. Lei, Y. B.; Hurst, J. K., Photoregulated potassium ion permeation through dihexadecyl phosphate bilayers containing azobenzene and stilbene surfactants. *Langmuir* **1999**, 15, (10), 3424-3429.
29. Burgess, J. D.; Rhoten, M. C.; Hawkrige, F. M., Cytochrome c oxidase immobilized in stable supported lipid bilayer membranes. *Langmuir* **1998**, 14, 2467-2475.
30. Naumann, R.; Baumgart, T.; Graber, P.; Jonczyk, A.; Offenhausser, A.; Knoll, W., Proton transport through a peptide-tethered bilayer lipid membrane by the H⁺-ATP synthase from chloroplasts measured by impedance spectroscopy. *Biosensors & Bioelectronics* **2002**, 17, (1-2), 25-34.
31. Decher, G.; Eckle, M.; Schmitt, J.; Struth, B., Layer-by-layer assembled multicomposite films. *Current Opinion in Colloid & Interface Science* **1998**, 3, (1), 32-39.
32. Decher, G., Fuzzy nanoassemblies: Toward layered polymeric multicomposites. *Science* **1997**, 277, (5330), 1232-1237.
33. Huang, W. S.; Macdiarmid, A. G., Optical-Properties of Polyaniline. *Polymer* **1993**, 34, (9), 1833-1845.
34. Chiang, J. C.; MacDiarmid, A. G., Polyaniline - Protonic Acid Doping of the Emeraldine Form to the Metallic Regime. *Synthetic Metals* **1986**, 13, (1-3), 193-205.
35. Li, D.; Jiang, Y.; Li, C.; Wu, Z.; Chen, X.; Li, Y., Self-assembly of polyaniline/polyacrylic acid films via acid-base reaction induced deposition. *Polymer* **1999**, 40, (25), 7065-7070.
36. Raitman, O. A.; Katz, E.; Buckmann, A. F.; Willner, I., Integration of polyaniline/poly(acrylic acid) films and redox enzymes on electrode supports: An in situ electrochemical/surface plasmon resonance study of the bioelectrocatalyzed oxidation of glucose or lactate in the integrated bioelectrocatalytic systems. *Journal of the American Chemical Society* **2002**, 124, (22), 6487-6496.
37. Doherty III, W. J.; Donley, C. L.; Armstrong, N. R.; Saavedra, S. S., A broadband spectroelectrochemical ATR instrument for molecular adlayer studies. *Appl. Spectrosc.* **2002**, 56, 920-927.
38. Deamer, D. W.; Nichols, J. W., Proton Hydroxide Permeability of Liposomes. *Proceedings of the National Academy of Sciences of the United States of America-Biological Sciences* **1983**, 80, (1), 165-168.
39. Brinker, J.; Scherer, G., *Sol-Gel Science*. Academic: New York, 1989.
40. Raman, N. K.; Anderson, M. T.; Brinker, C. J., Template-based approaches to the preparation of amorphous, nanoporous silicas. *Chemistry of Materials* **1996**, 8, (8), 1682-1701.
41. Collinson, M. M.; Howells, A. R., Sol-gels and electrochemistry: Research at the intersection. *Analytical Chemistry* **2000**, 72, (21), 702A-709A.
42. Lev, O.; Wu, Z.; Bharathi, S.; Glezer, V.; Modestov, A.; Gun, J.; Rabinovich, L.; Sampath, S., Sol-gel materials in electrochemistry. *Chemistry of Materials* **1997**, 9, (11), 2354-2375.
43. Avnir, D., Organic-Chemistry within Ceramic Matrices - Doped Sol-Gel Materials. *Accounts of Chemical Research* **1995**, 28, (8), 328-334.

44. Ballarin, B.; Facchini, M.; Dal Pozzo, L.; Martini, C., Comparison of different porous sol-gel matrices: template synthesis of polythiophene. *Electrochemistry Communications* **2003**, 5, (8), 625-631.
45. Verghese, M. M.; Ramanathan, K.; Ashraf, S. M.; Kamalasanan, M. N.; Malhotra, B. D., Electrochemical growth of polyaniline in porous sol-gel films. *Chemistry of Materials* **1996**, 8, (4), 822-824.
46. Roux, S.; Audebert, P.; Pagetti, J.; Roche, M., Electropolymerization of carboxylic acid functionalized pyrrole into hybrid zirconium-silicon oxopolymer sol-gel coatings. *New Journal of Chemistry* **2002**, 26, (3), 298-304.
47. Roux, S.; Audebert, P.; Pagetti, J.; Roche, M., Electrochemical growth of conducting polymer into zirconium oxopolymers sol-gel coatings. *Journal of Sol-Gel Science and Technology* **2003**, 26, (1-3), 435-439.
48. Schmidt, C.; Mayer, M.; Vogel, H., A Chip-Based Biosensor for the Functional Analysis of Single Ion Channels. *Angew. Chem. Int. Ed.* **2000**, 39, 3137-3140.
49. Cornell, B. A.; Braach-Maksyvtis, V.; King, L. G.; Osman, P. D. J.; Raguse, B.; Wieczorek, L.; Pace, R. J., A Biosensor that uses Ion Channel Switches. *Nature* **1997**, 387, 580-583.
50. Holden, M. A.; Jung, S. Y.; Yang, T. L.; Castellana, E. T.; Cremer, P. S., Creating fluid and air-stable solid supported lipid bilayers. *J. Am. Chem. Soc.* **2004**, 126, (21), 6512-6513.
51. Cremer, P. S.; Boxer, S. G., Formation and spreading of lipid bilayers on planar glass supports. *J. Phys. Chem. B* **1999**, 103, 2554-2559.
52. Sackmann, E., Supported membranes: Scientific principles and practical applications. *Science* **1996**, 271, 43-48.
53. Fang, Y.; Frutos, A. G.; Lahiri, J., Membrane protein microarrays. *Journal of the American Chemical Society* **2002**, 124, (11), 2394-2395.
54. Halter, M.; Nogata, Y.; Dannenberger, O.; Sasaki, T.; Vogel, V., Engineered lipids that cross-link the inner and outer leaflets of lipid bilayers. *Langmuir* **2004**, 20, (6), 2416-2423.
55. Ross, E. E.; Bondurant, B.; Spratt, T.; Conboy, J. C.; O'Brien, D. F.; Saavedra, S. S., Formation of self-assembled, air-stable lipid bilayer membranes on solid supports. *Langmuir* **2001**, 17, 2305-2307.
56. Ross, E.; Rozanski, L.; Spratt, T.; Liu, S.; O'Brien, D. F.; Saavedra, S. S., Planar supported lipid bilayer polymers formed by vesicle fusion. 2. Adsorption of bovine serum albumin. *Langmuir* **2003**, 19, 1766-1774.
57. Conboy, J. C.; Liu, S. C.; O'Brien, D. F.; Saavedra, S. S., Planar supported bilayer polymers formed from bis-diene lipids by Langmuir-Blodgett deposition and UV irradiation. *Biomacromolecules* **2003**, 4, (3), 841-849.
58. Matsumoto, A.; Horie, A.; Otsu, T., Synthesis and Thermal-Properties of Poly(Adamantyl Sorbate). *Makromolekulare Chemie-Rapid Communications* **1991**, 12, (12), 681-685.
59. Masuda, M.; Jonkheijm, P.; Sijbesma, R. P.; Meijer, E. W., Photoinitiated polymerization of columnar stacks of self-assembled trialkyl-1,3,5-benzenetricarboxamide derivatives. *Journal of the American Chemical Society* **2003**, 125, (51), 15935-15940.