American Physical Society Meeting
Baltimore, MD, 13-17 March 2006

Advanced Materials for Solar Energy Utilization

"Bio-inspired constructs for solar energy conversion"

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Bio-inspired catalysts for sustainable large scale energy production and conversion

Photosynthesis (120 TW) employs catalysts that operate with essentially no overpotential. Nature's energy transducing processes are thought to be efficient.

$2H_2O = 4H^+ + 4e^- + O_2$ **oxygen evolving complex**

$H_2 = 2H^+ + 2e^-$ **hydrogenase**

$O_2 + 4H^+ + 4e^- + 4H^+_{(pumped)} = 2H_2O + 4H^+_{(pumped)}$ **complex 4**

These enzymes provide the basic paradigms for fuel cell operation and regeneration of hydrogen and oxygen.

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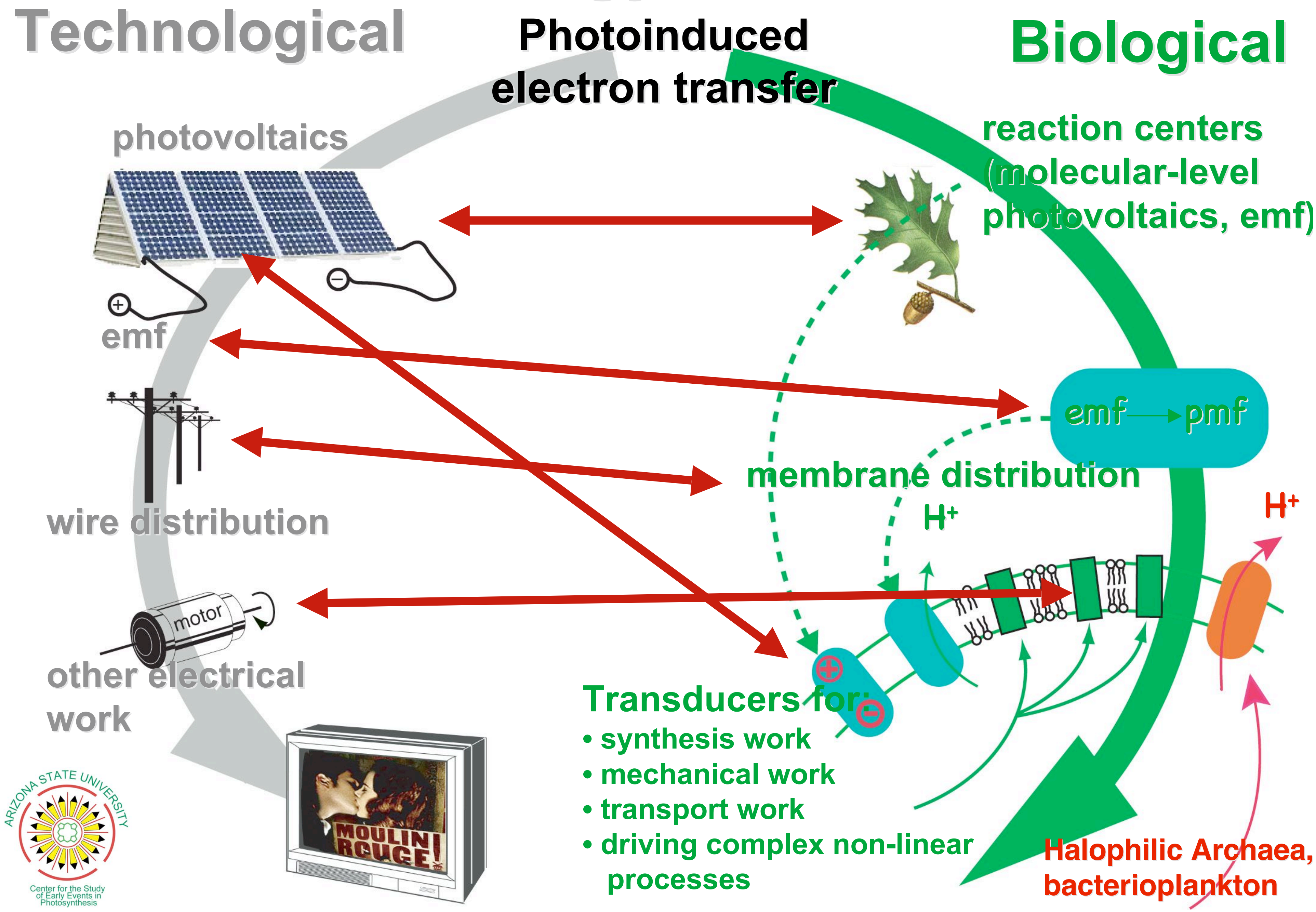
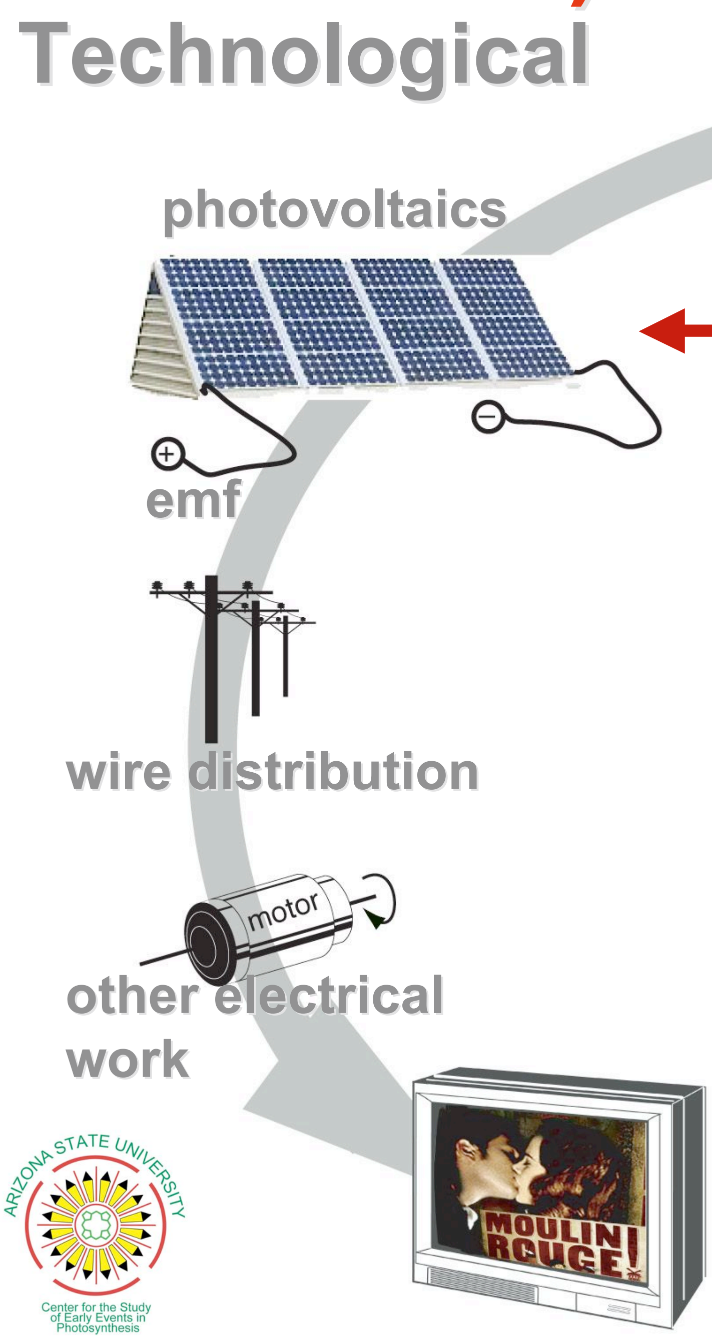
Nature has something to offer

Solar energy conversion

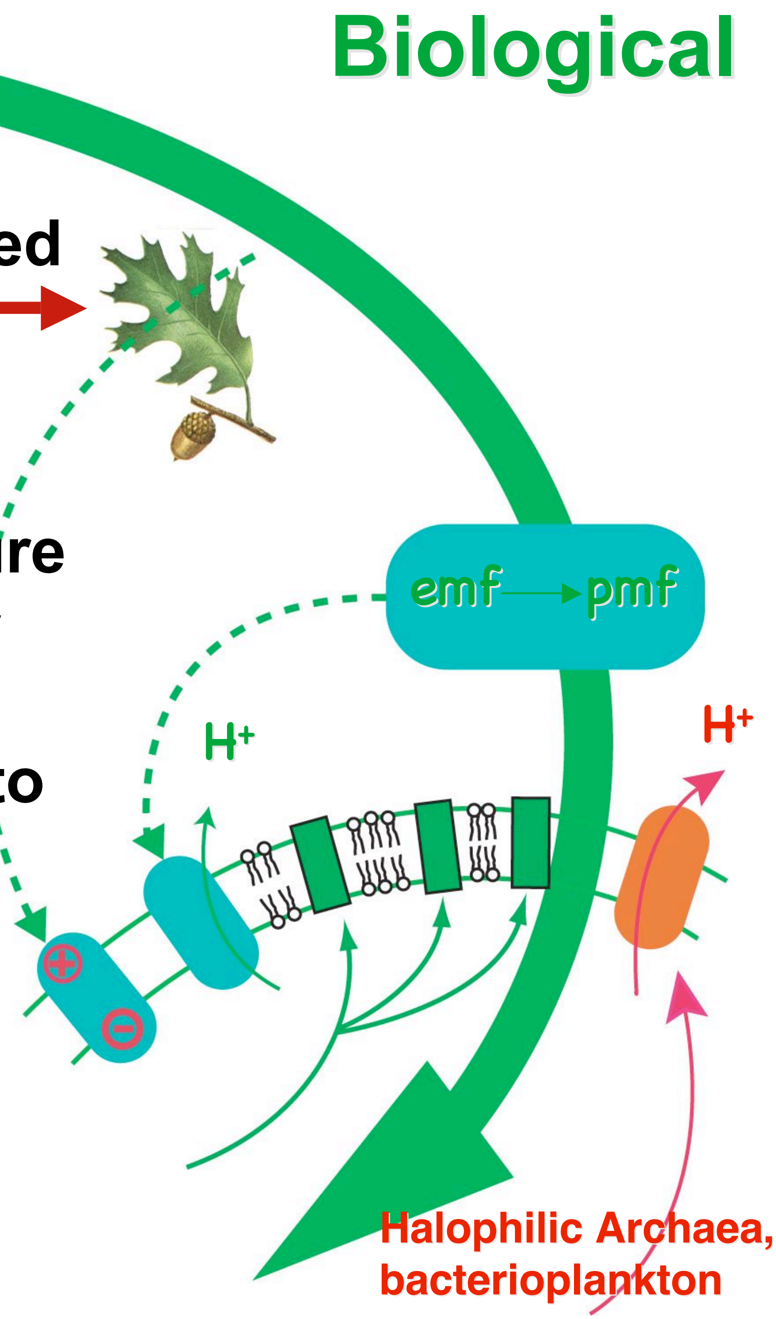


1) Light gathering



Bio-inspired

Spectral coverage
Architecture for energy transfer
Coupling to reaction center



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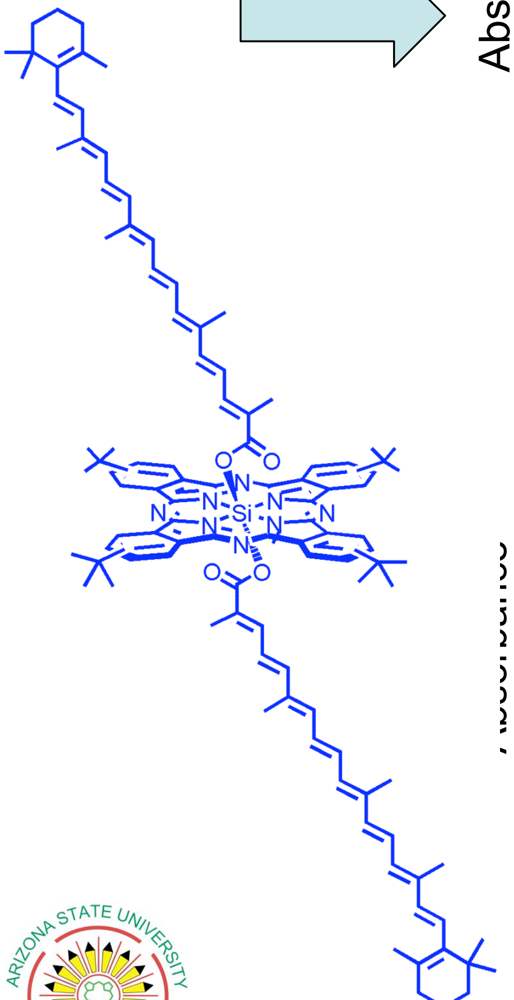
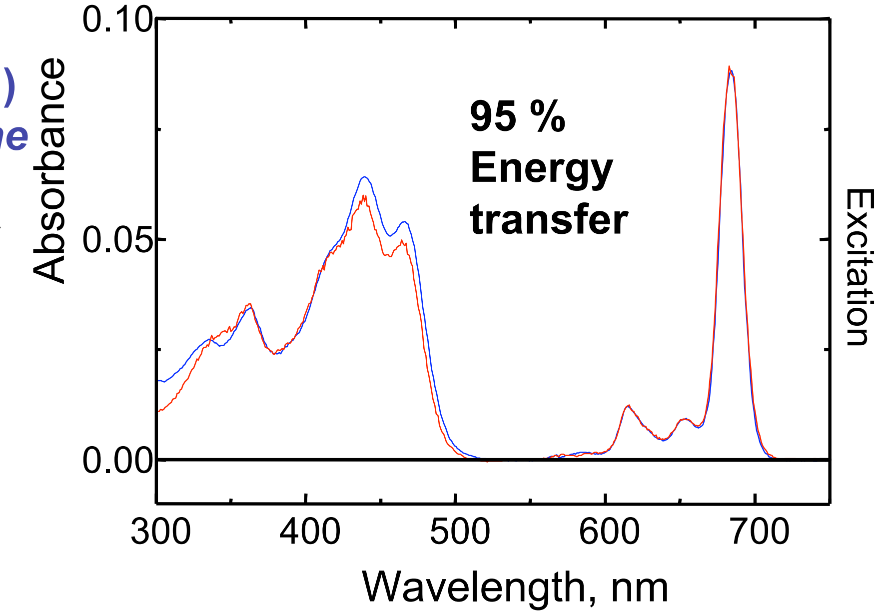
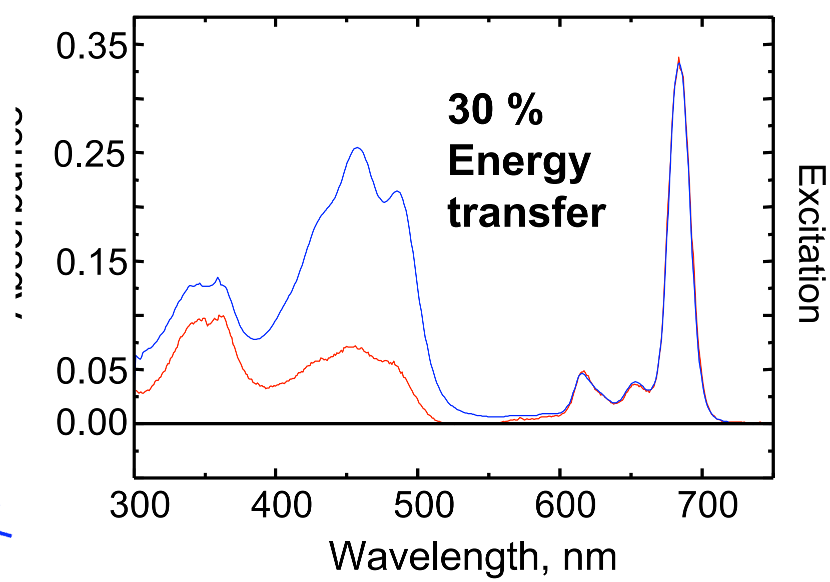
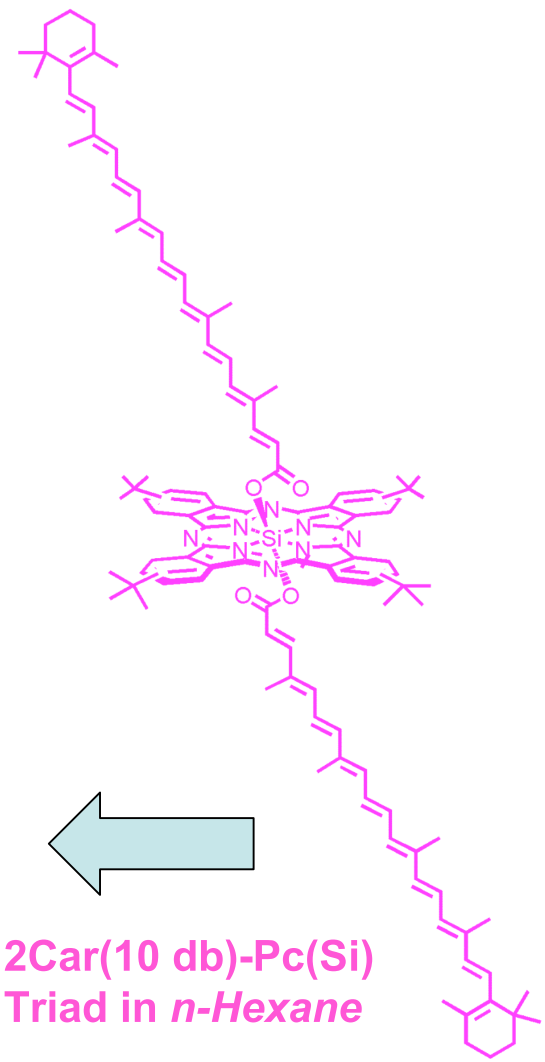
Carotenoid-Phthalocyanine antenna model systems

2Car(9 db)-Pc(Si)
Triad in *n-Hexane*









2Car(10 db)-Pc(Si)
Triad in *n-Hexane*

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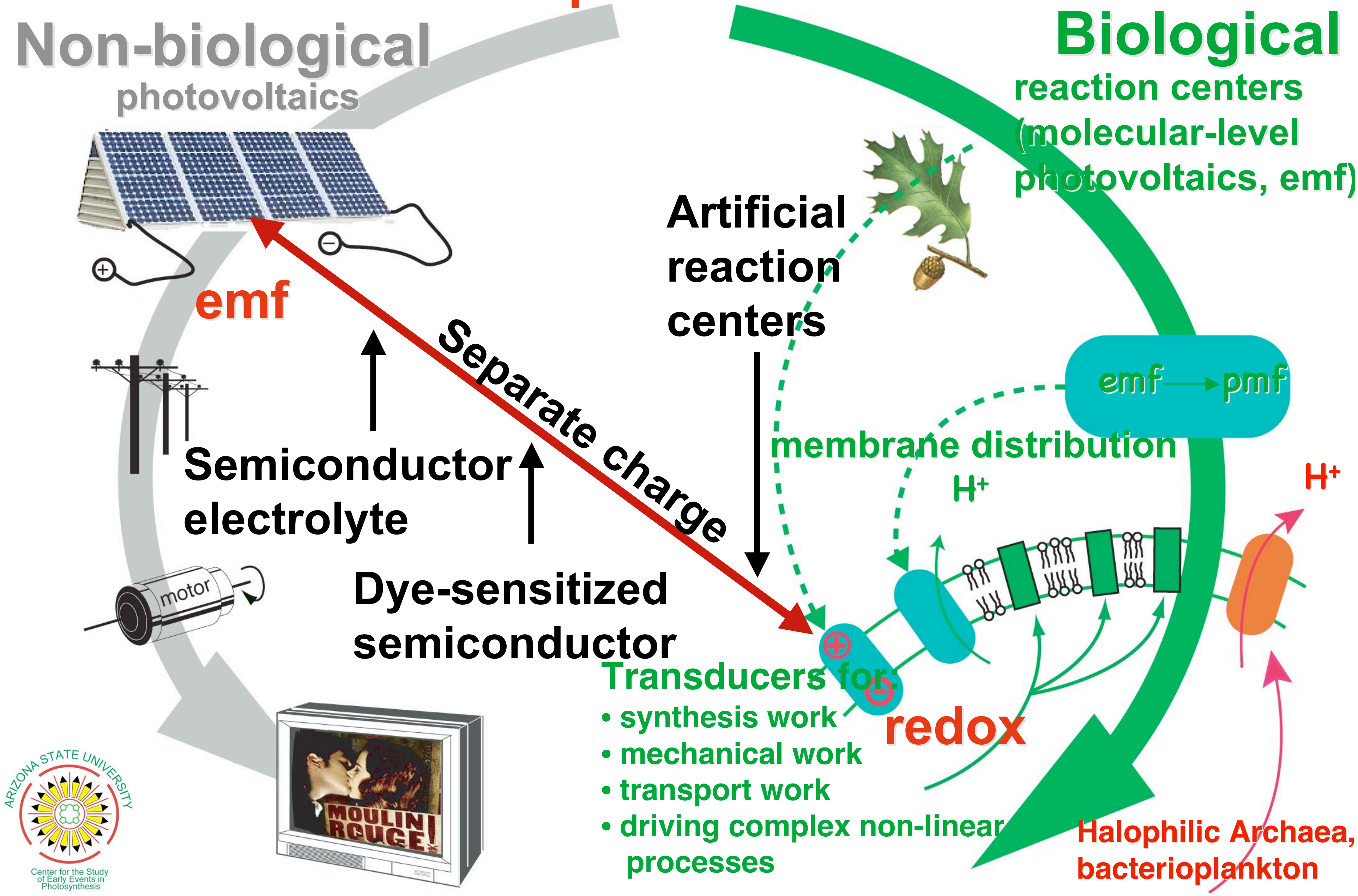
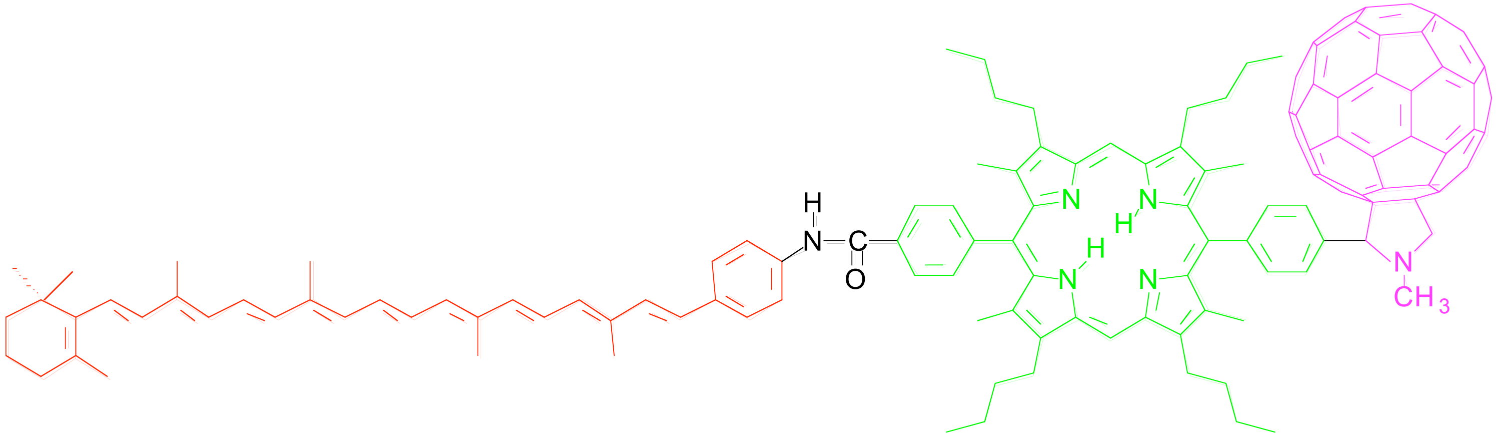
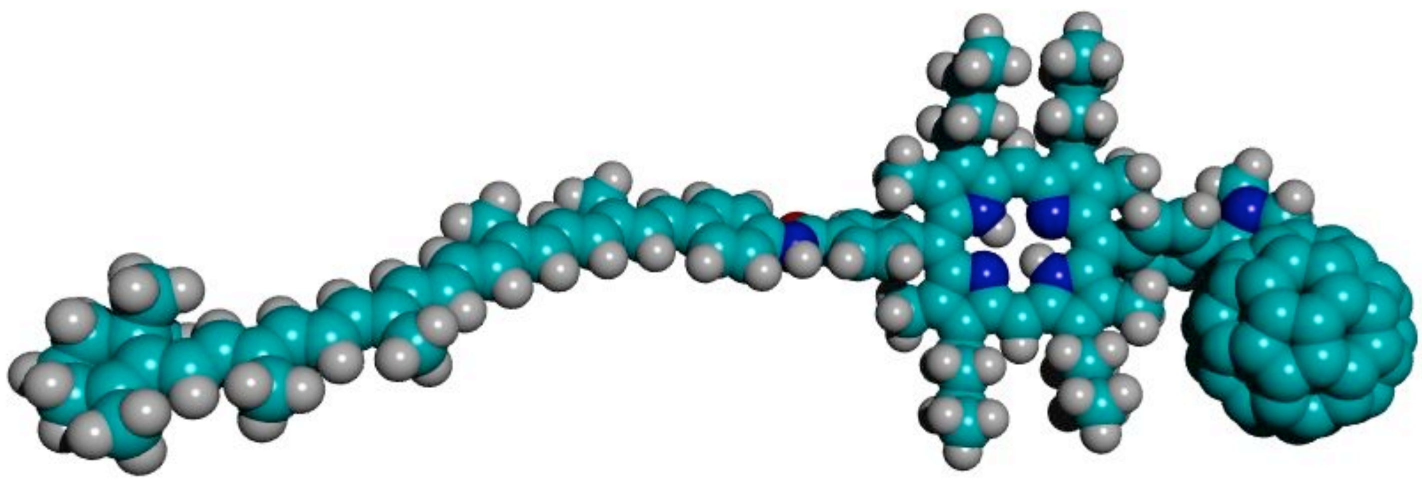
2) Charge separation and the generation of redox potential



A carotenoporphyrin-fullerene triad artificial reaction center





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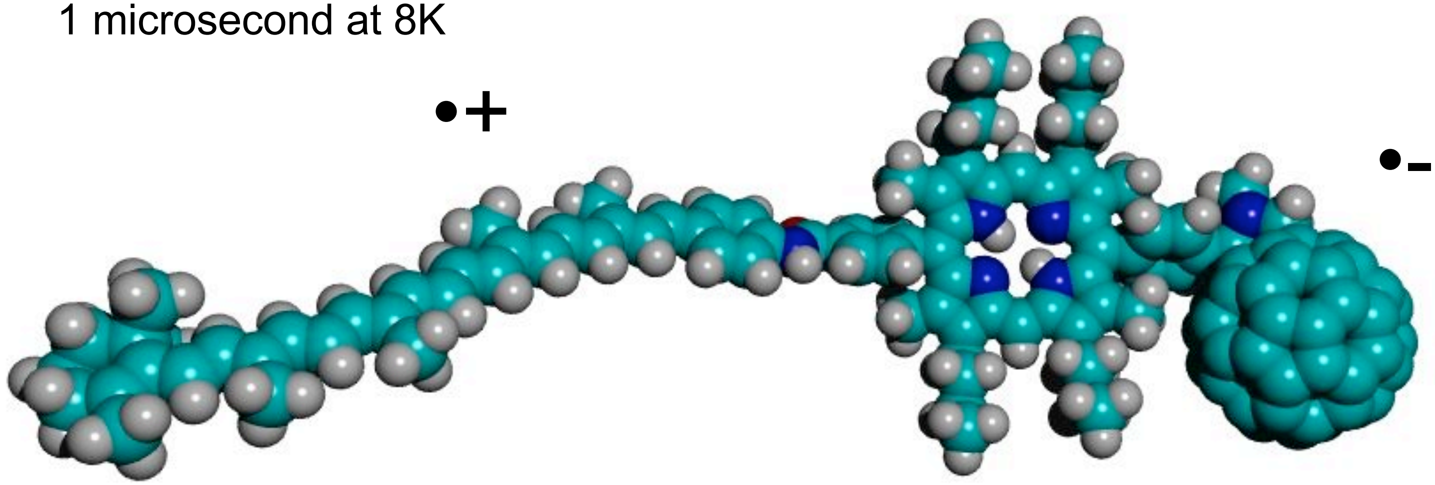
Liddell, P. A.; Kuciauskas, D.; Sumida, J. P.; Nash, B.; Nguyen, D.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1997**, *119*, 1400-1405

Optically excited artificial reaction centers separate charge and convert light energy to electrochemical redox energy

The best C-P-C_{60} triads:
Yield of charge separated state ~ 100%
Stored energy ~1.0 electron volt
Lifetime = hundreds of ns at room temp.
1 microsecond at 8K

$C^{\bullet +}$-P-$C_{60}^{\bullet -}$



Dipole moment ~160 D

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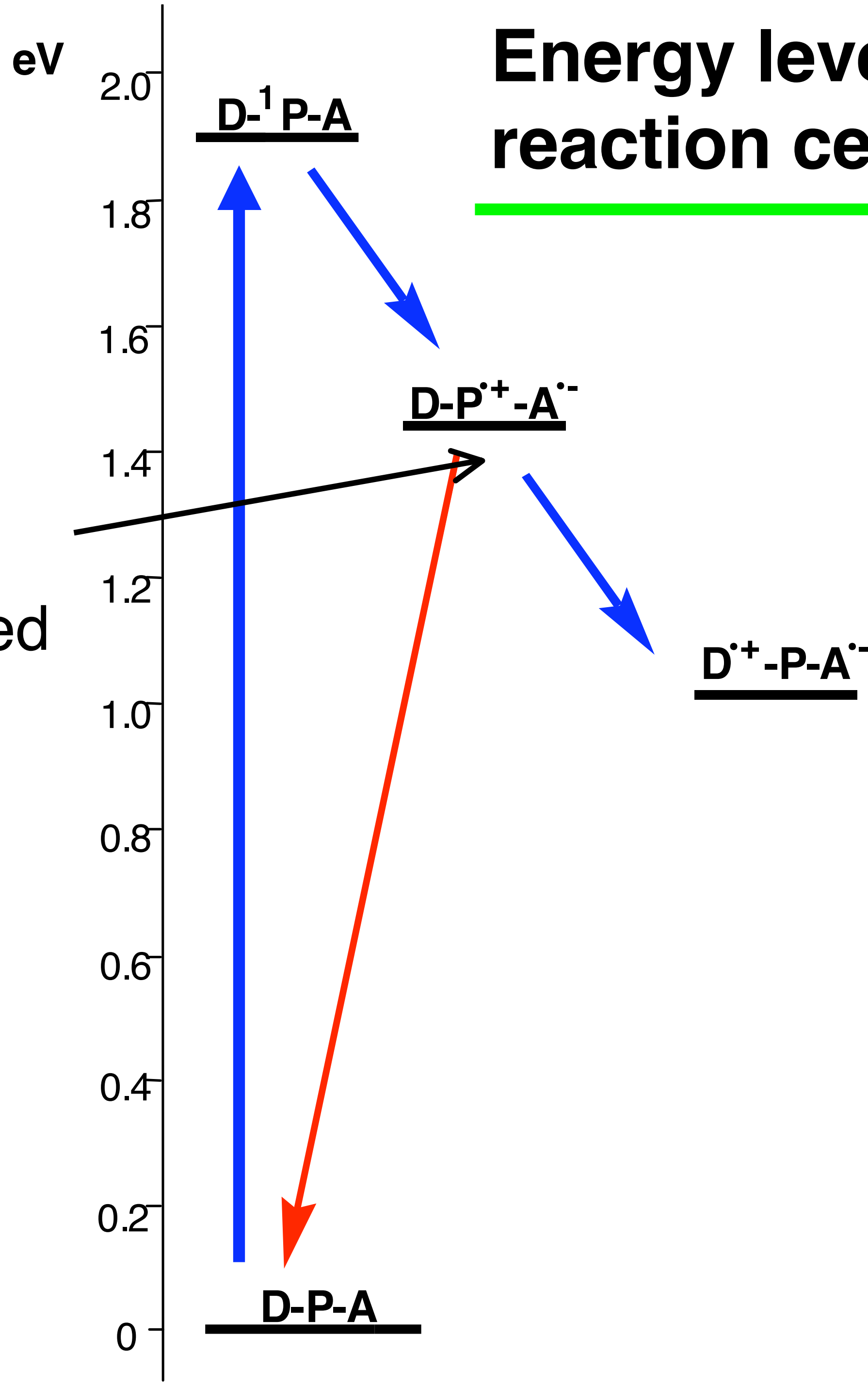
Smirnov, S. N.; Liddell, P. A.; Vlassiouk, I. V.; Teslja, A.; Kuciauskas,D.; Braun,C. L.; Moore, A. L.; Moore, T. A.; and Gust, D. *J. Phys. Chem. A*, **2003**, *107*, 7567-7573

Energy levels for artificial reaction centers

Critical branch point controls yield of final charge separated state as a function of λ, ΔG^o, V_{el}.



Apparently more energy is stored here than at this point in time in reaction centers.

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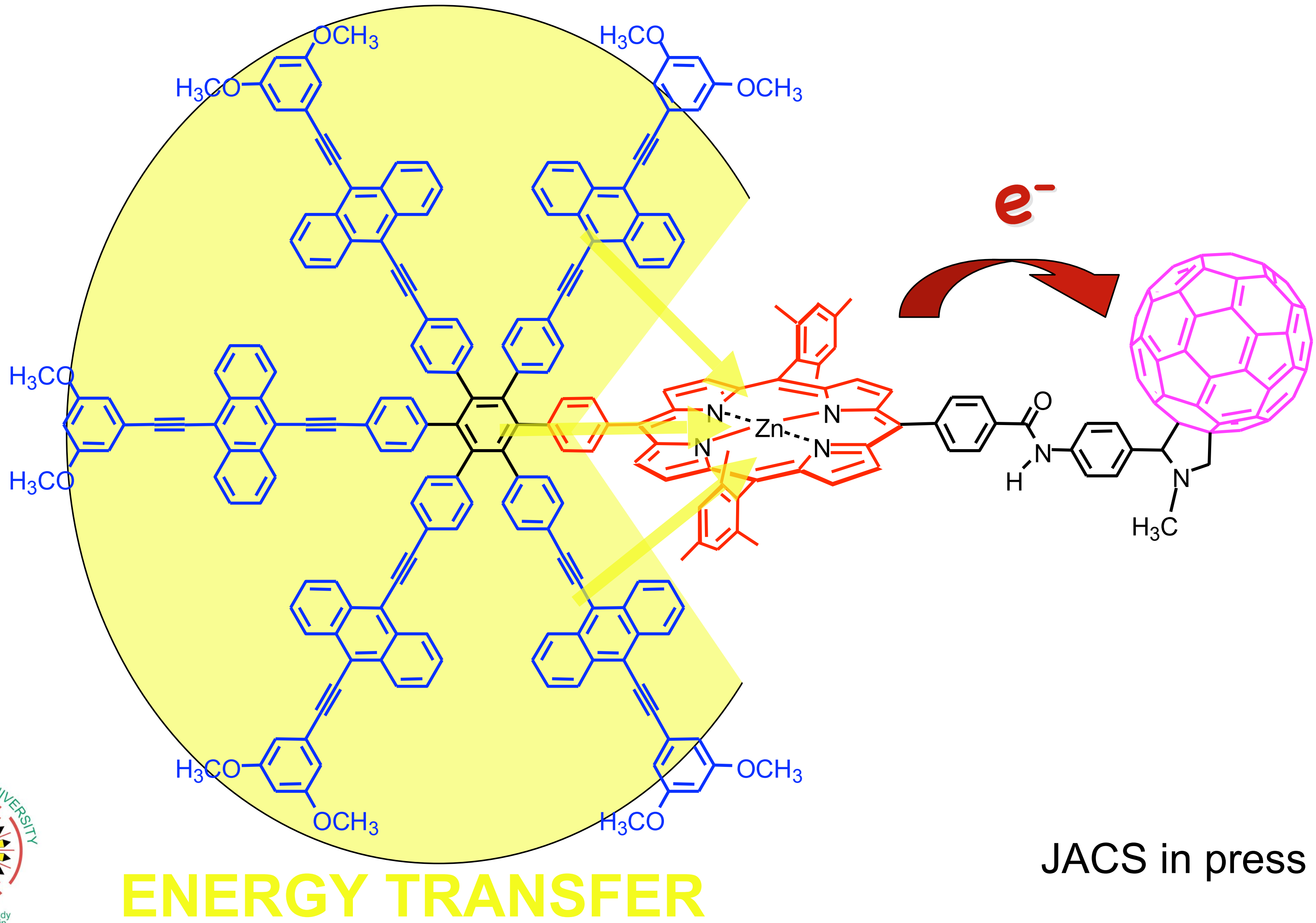
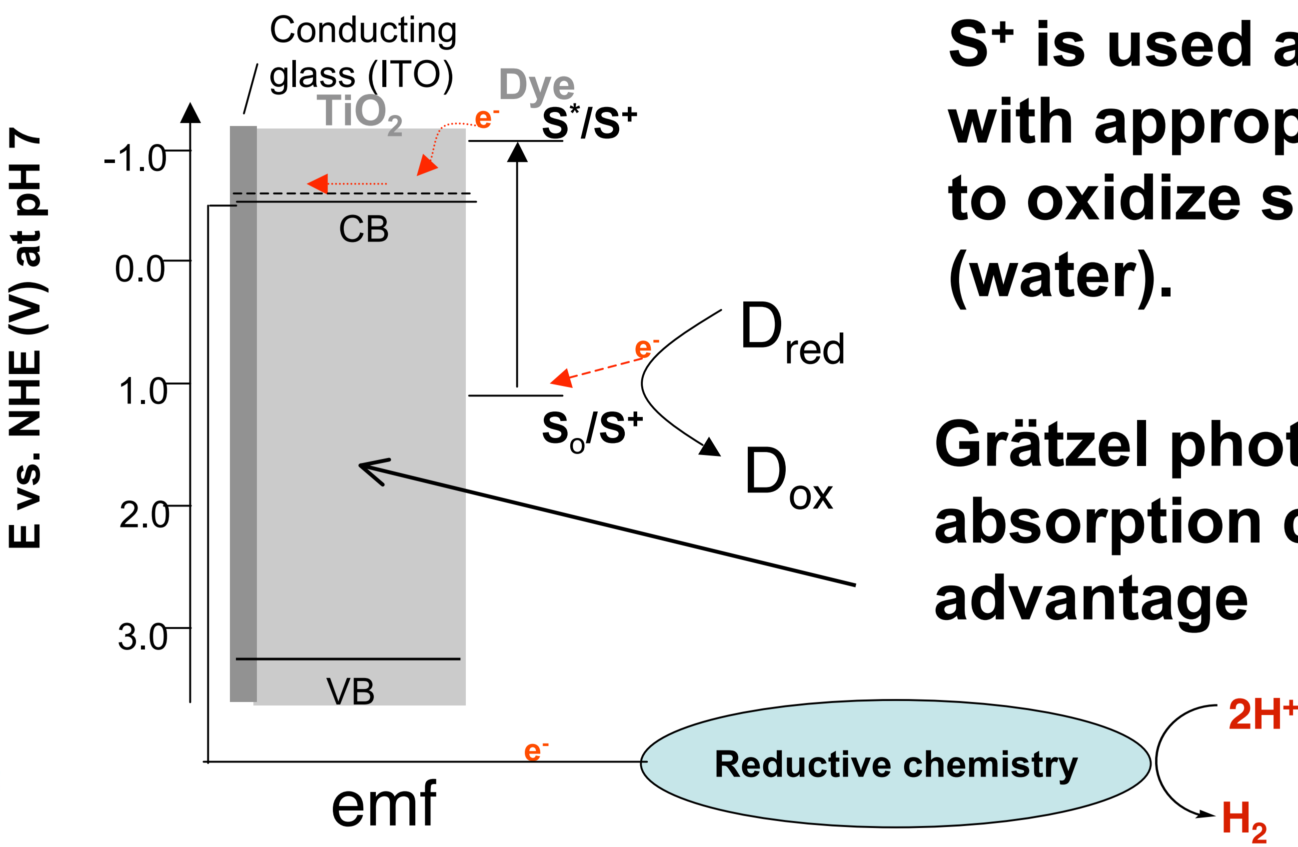
Synthetic coupled antenna - reaction center complexes: a heptad antenna-RC complex



JACS in press

Charge separation with a sensitized semiconductor - emf and redox chemistry

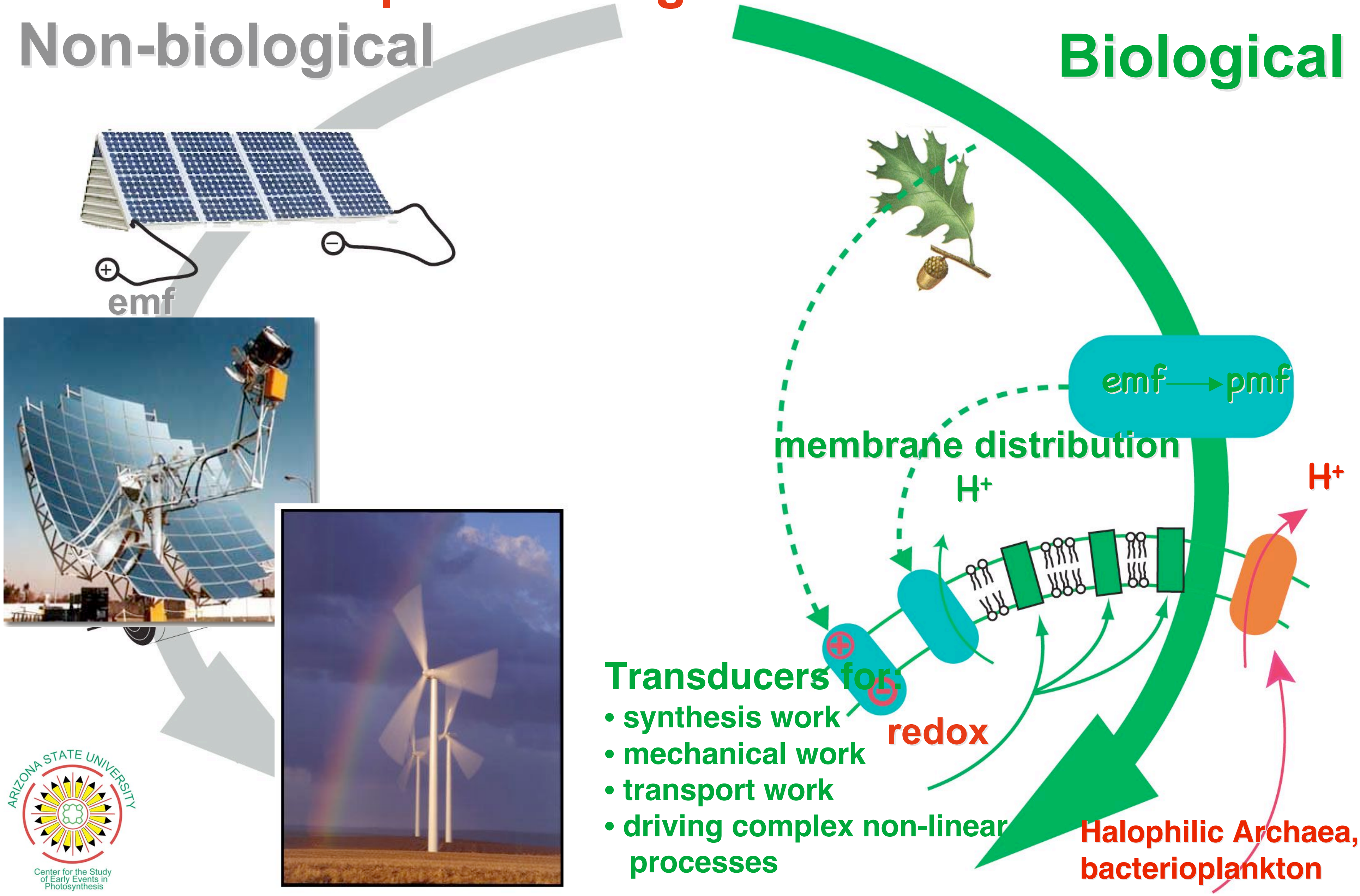
Excited state sensitizer (**S***) injects an electron into the CB of the semiconductor



S^+ is used as an oxidant with appropriate catalyst to oxidize something (water).

Grätzel photoelectrode: absorption cross section advantage

Currently, the best human engineered sustainable processes generate emf



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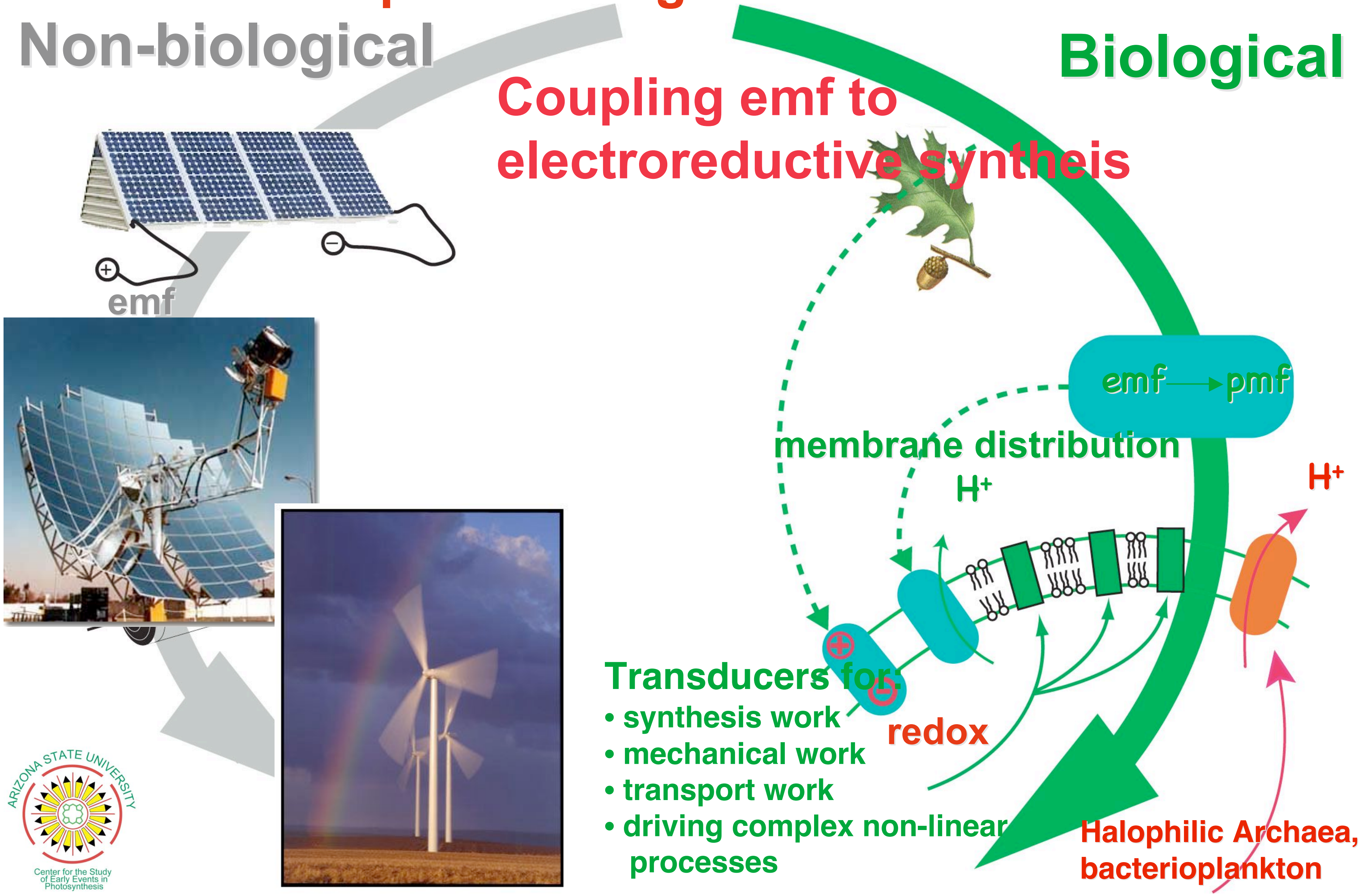

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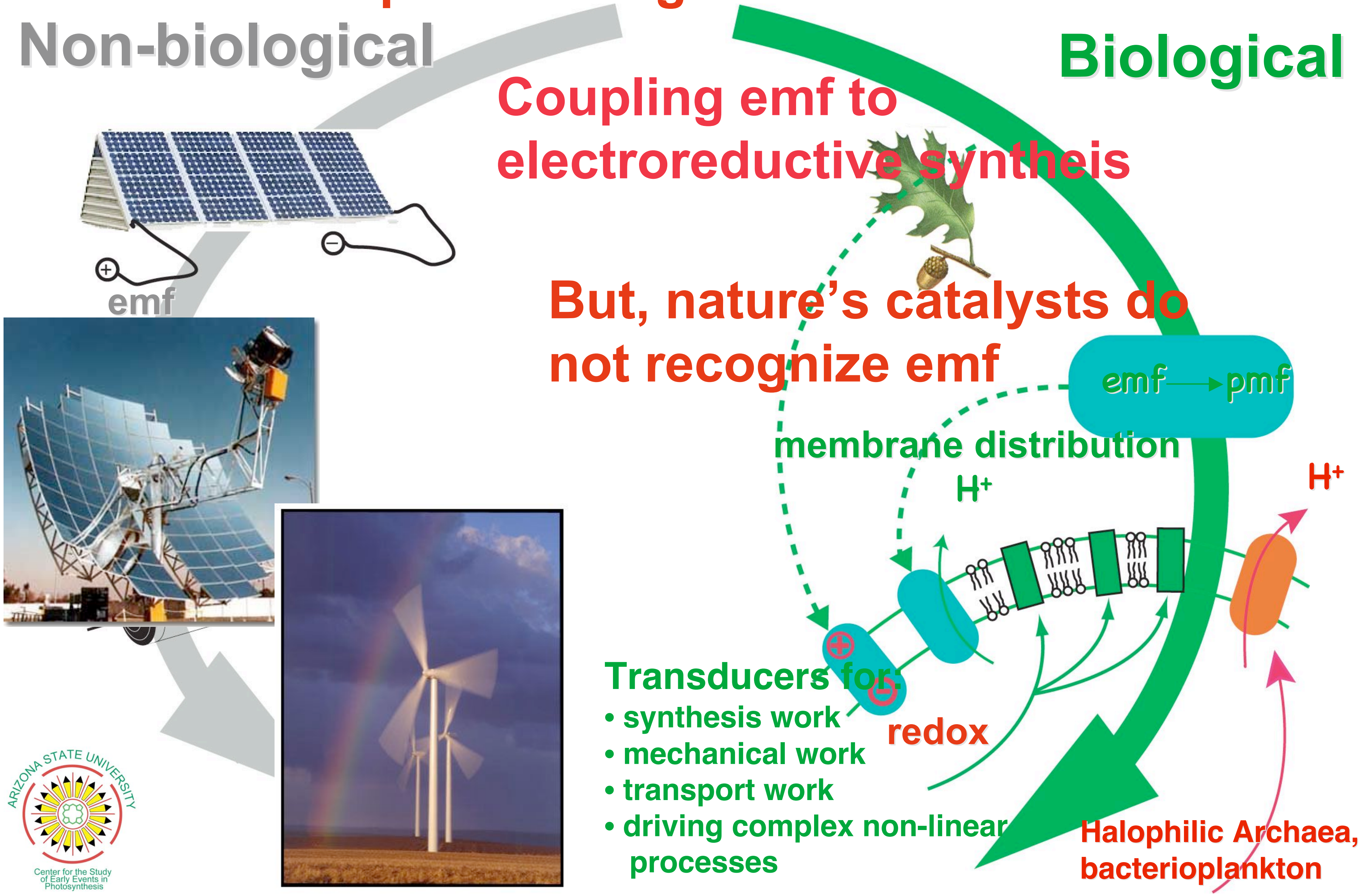

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Coupling sustainable sources of emf to the synthesis of fuel requires at least two chemical processes:

1) A reductant to provide electrons - e.g., H_2O

$$H_2O \longrightarrow O_2 + 4 \text{ electrons} + 4H^+$$

2) An oxidant to receive electrons - e.g., CO_2

$$CO_2 + \text{electrons} + H^+ \longrightarrow CH_3OH, CH_4, \text{etc.}$$

Nature provides catalysts that efficiently direct *<u>chemical potential</u>* along these reaction coordinates. Challenges are to use these catalysts or abstract their catalytic sites in synthetic constructs and couple them to *<u>emf</u>*

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A closer look at Nature's catalysts….

Contrast of bio-catalysts with human-engineered catalysts for mainstream energy transduction

Biological	**Human engineered**
Living organisms use FeS centers, Fe, Cu, Mn and sometimes Ni	Carbon, Pt with alloys and intermetallic compounds, efforts span periodic table
C-C bond cleavage facile.	No good catalysts for C-C bond cleavage in context of low temp fuel cell
Pathways to synthesize MeOH, EtOH, CH_4. etc., from CO_2	Electroreductive synthesis of low efficiency, multiple products
Catalysis involves covalent intermediates with catalytic sites having distinct 3-dimensional architecture to match transition state structures for lowering $\Delta G^{\ddagger}$. Consequence: slow.	Emphasis on surface structure (except bio-inspired ones)
Can use protonmotive force as necessary	Use electromotive force

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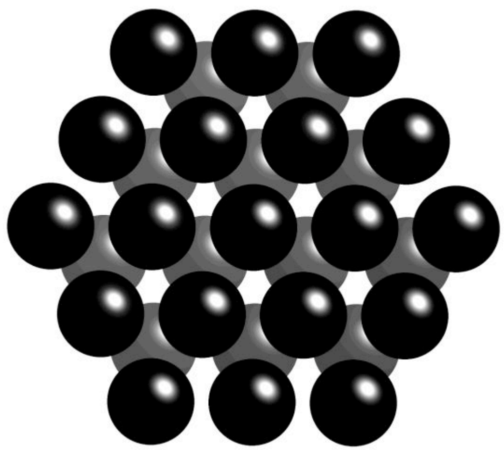
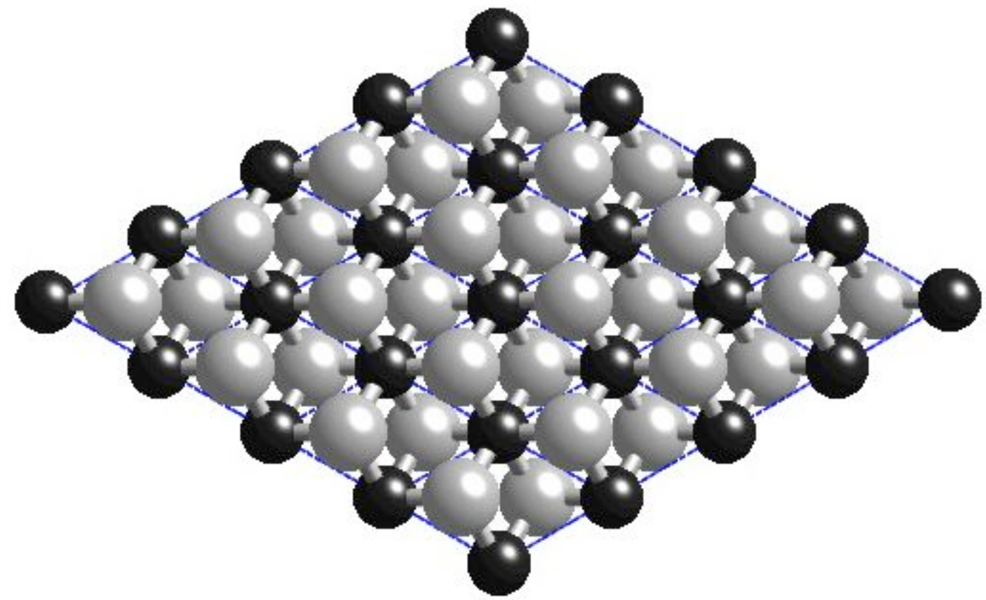
Platinum vs. PtBi



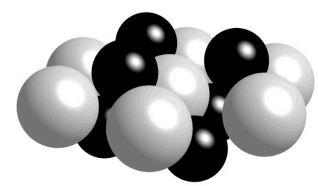
Pt

(111) plane

Pt-Pt 2.77 Å



PtBi



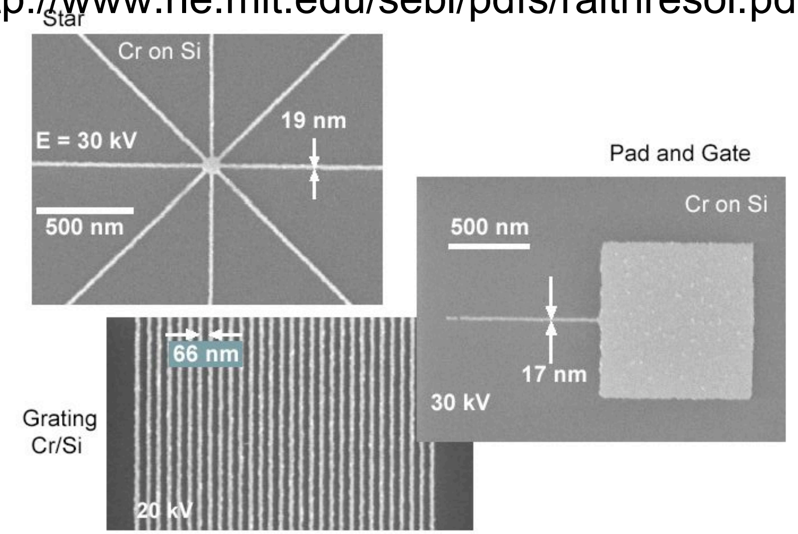
(001) plane

Pt-Pt 4.32 Å

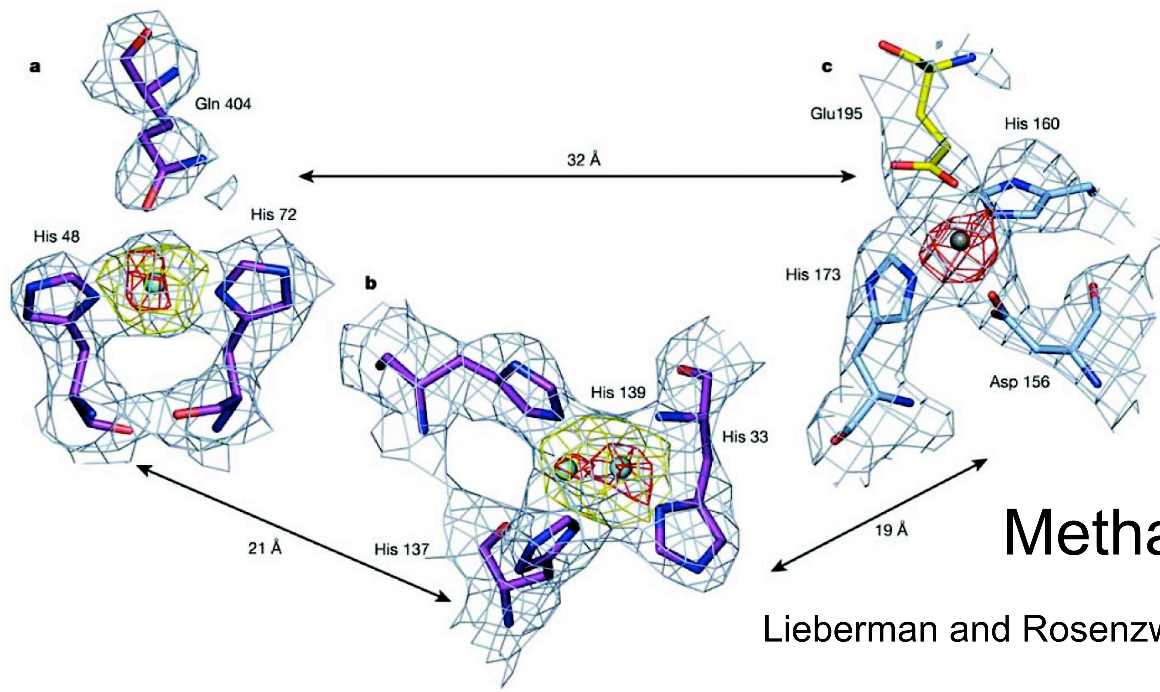
Thanks to Frank DiSalvo

Sub-20-nm Patterning on Raith 150

http://www.rle.mit.edu/sebl/pdfs/raithresol.pdf



Proteins offer true 3-dimensional structures with much higher spatial resolution than human-engineered devices to date and come with a library of catalytic functions refined by a few x 10^9 years of natural selection and can be tuned by molecular biology techniques



Methane monooxygensase

Lieberman and Rosenzweig, *Nature* **434**, 177-182 (2005)

Figure 4 The pMMO metal centres viewed approximately 90° from the orientation shown in Fig. 2a. The distances are measured between metal ions. Anomalous difference Fourier maps calculated using data collected near the copper absorption edge (yellow, 'CuANOM', contoured at 4σ) and near the zinc absorption edge (red, 'Highres', contoured at 4σ) are superimposed on the final $2F_o-F_c$ electron density map (light blue, contoured at 1σ). **a**, The mononuclear copper site. **b**, The dinuclear copper site. **c**, The zinc site.

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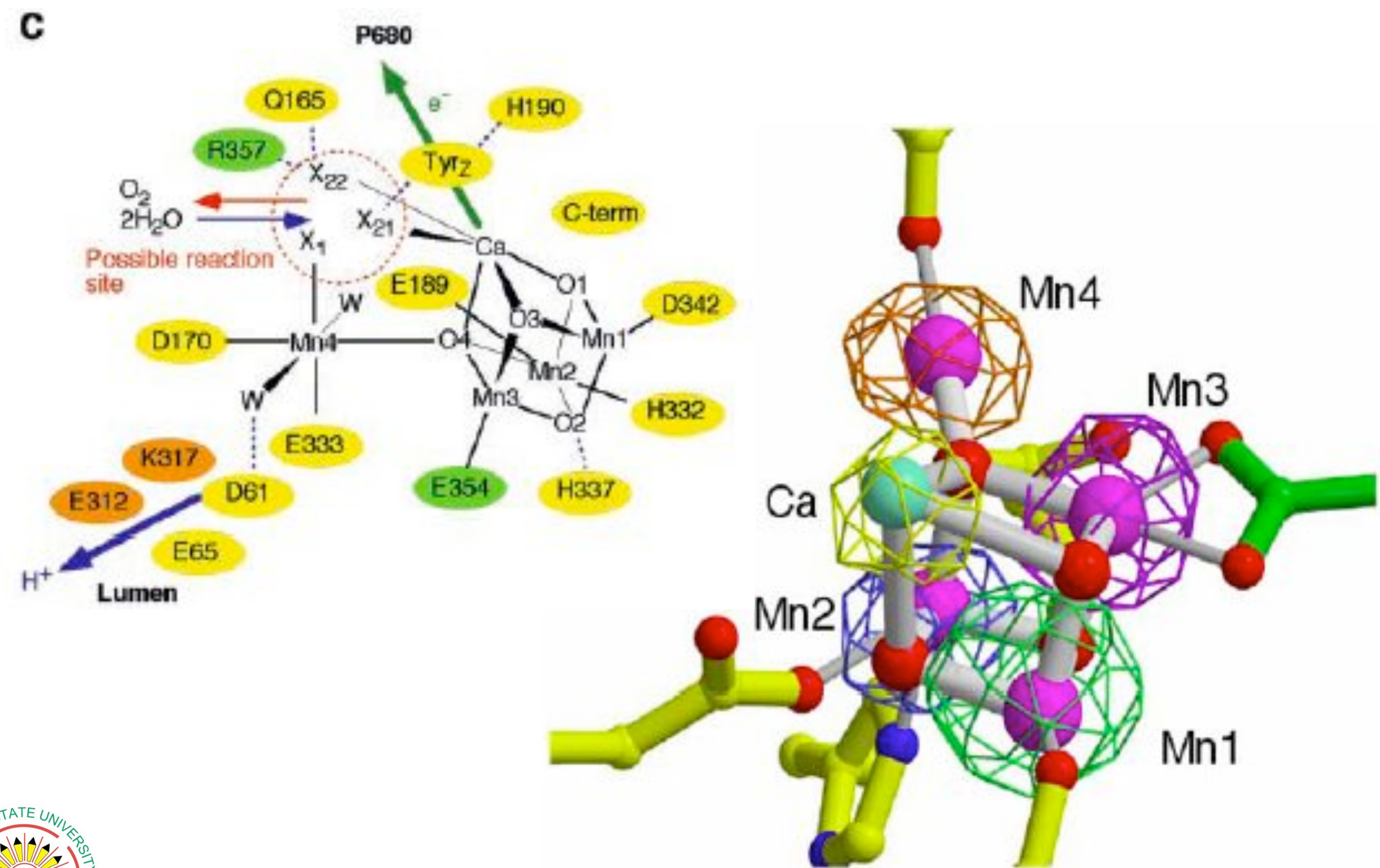
3-dimensional Structure of the oxygen evolving complex



Ferreira et al. *Science* 2004

To couple enzymes to emf an active site - metal interface must be made. Molecular wire, redox relay shuttle, conducting polymer, redox hydrogel, or other means of electrically connecting catalytic site to electrode.

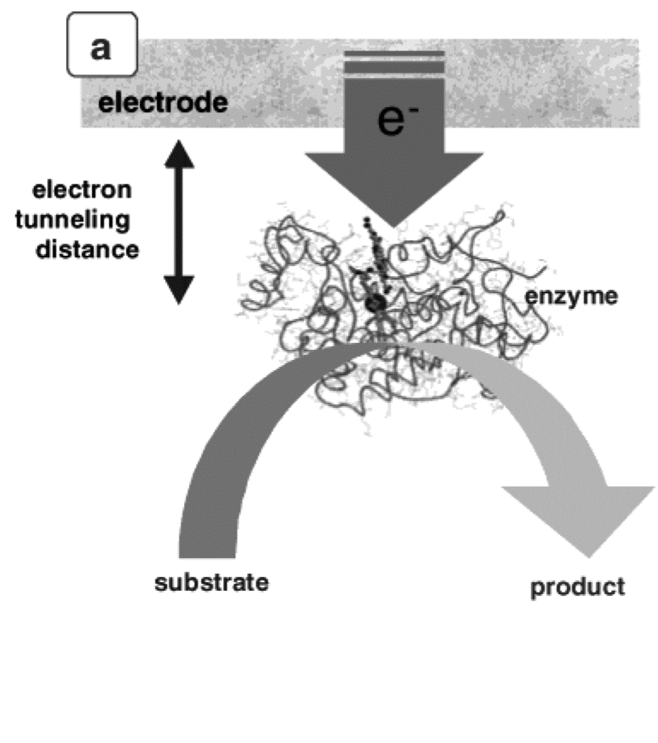


Figure 2. Alternative electron-transfer mechanisms. (a) Direct electron transfer (tunneling mechanism) from electrode surface to the active site of an enzyme. (b) Electron transfer via redox mediator.

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We are encouraged by research demonstrating that significant current can be pushed through a "molecular wire" at low bias. This mechanism could couple sustainable electrical energy to bio-inspired catalysts for synthesis of fuel.

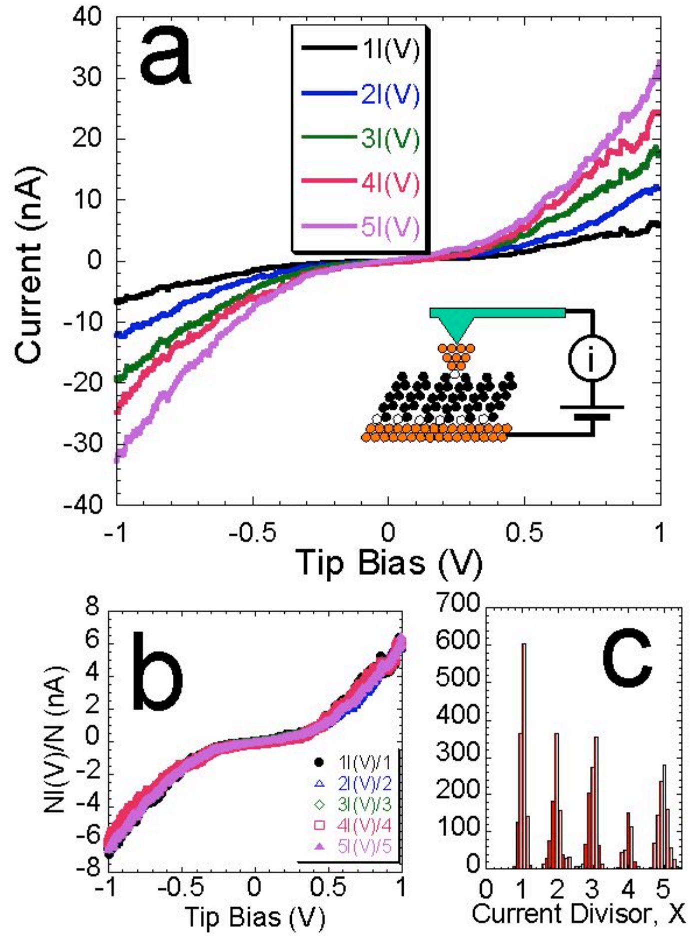
J. He, et al., *J. Amer. Chem. Soc.*, **127**, 1384-1385 (2005).

In single molecule conducting AFM studies of conducting polymers and molecules with low Beta, currents of about 0.1 nA are observed at biases where observations are reversible.

0.1 nA corresponds to ~ $6x10^8$ $e^- s^{-1}$

This easily exceeds by orders of magnitude the turnover number of any enzyme under consideration

Even with a footprint of 100 nm^2, electrodes derivatized with enzyme capable of high k_{cat} could potentially process ~ 10^{21} events/cm^2 per second.



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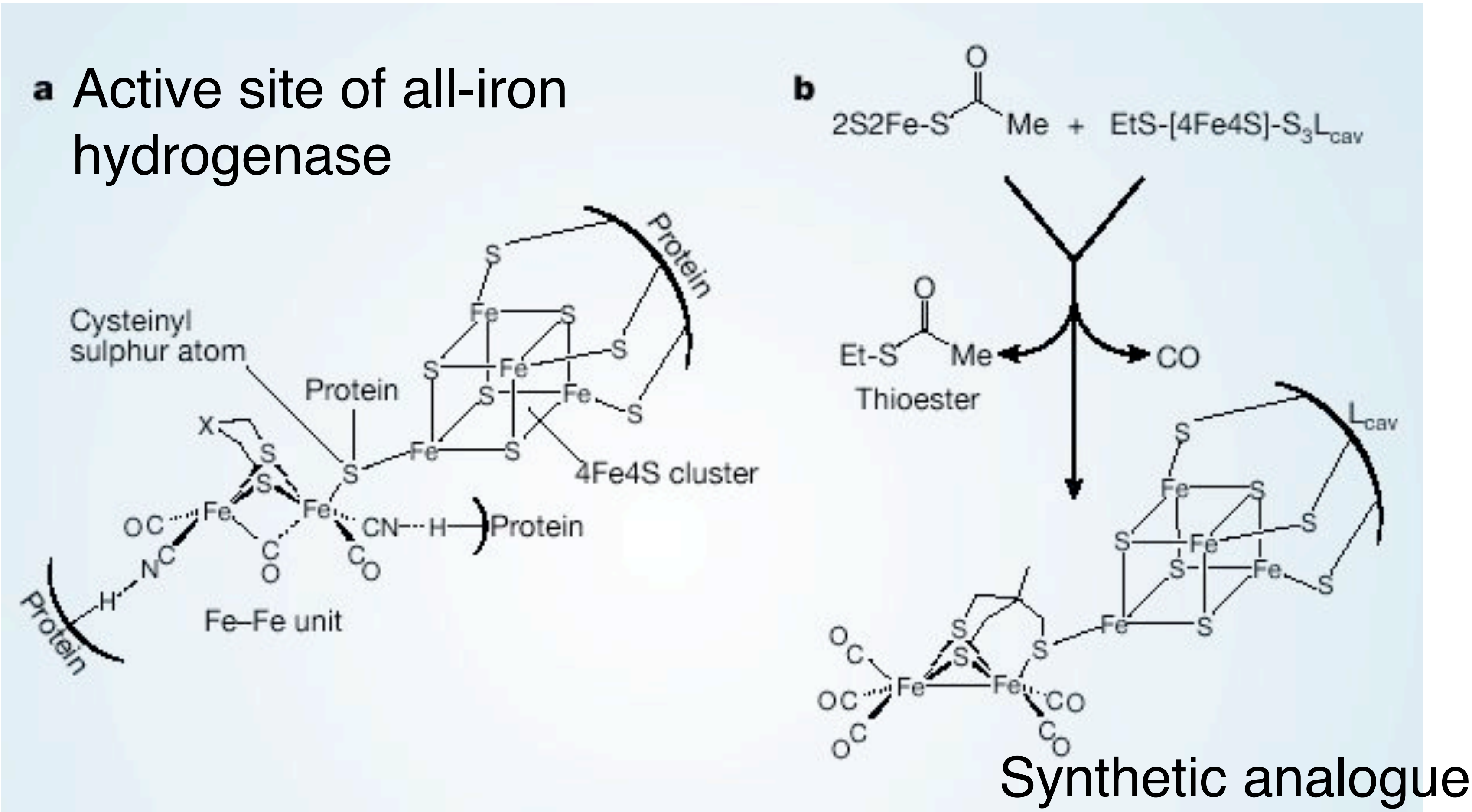
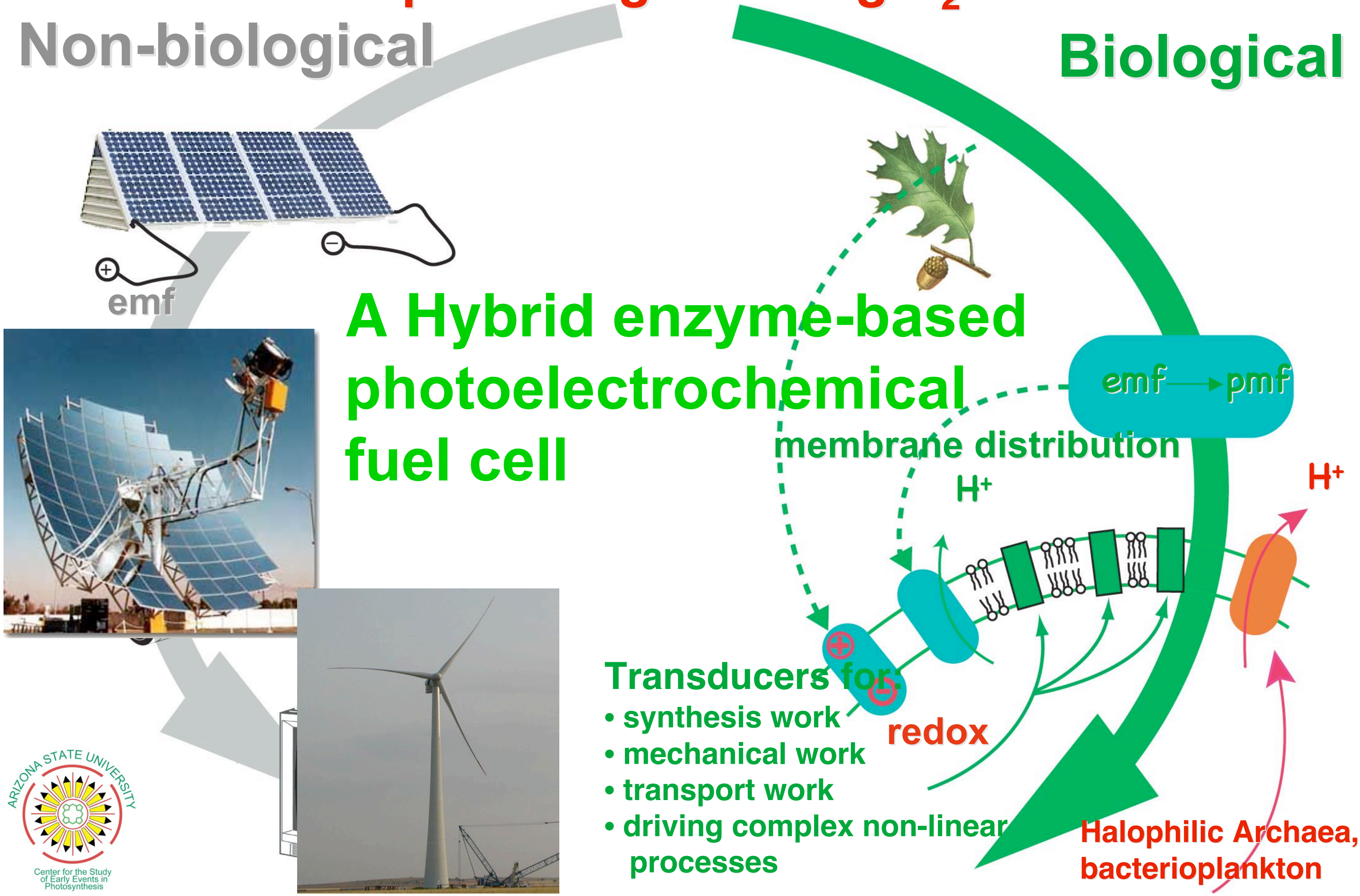
A synthetic active site mimic of iron-only hydrogenase



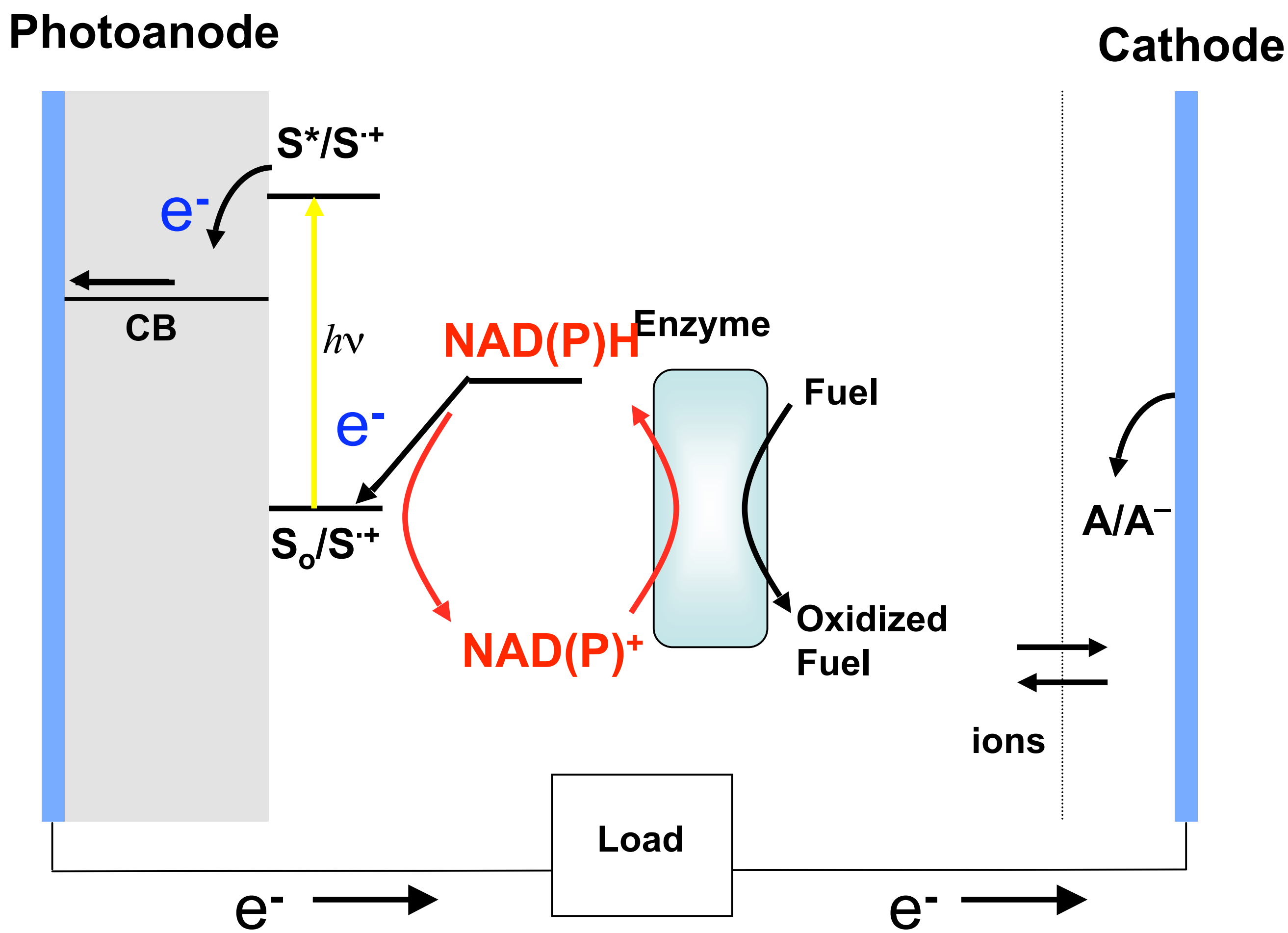
Synthetic analogue shows catalytic H^+ reduction on vitreous carbon electrode

Tard et al., (Pickett), *Nature*, **433**, 610 (2005); N&V **433**, 589 (2005)

A photoelectrochemical fuel cell and reforming process generating H_2



Hybrid Enzyme-Based Photoelectrochemical Fuel Cell



NAD+ is not reduced at the Pt cathode or at the photoanode

Photoelectrochemical Biofuel Cell

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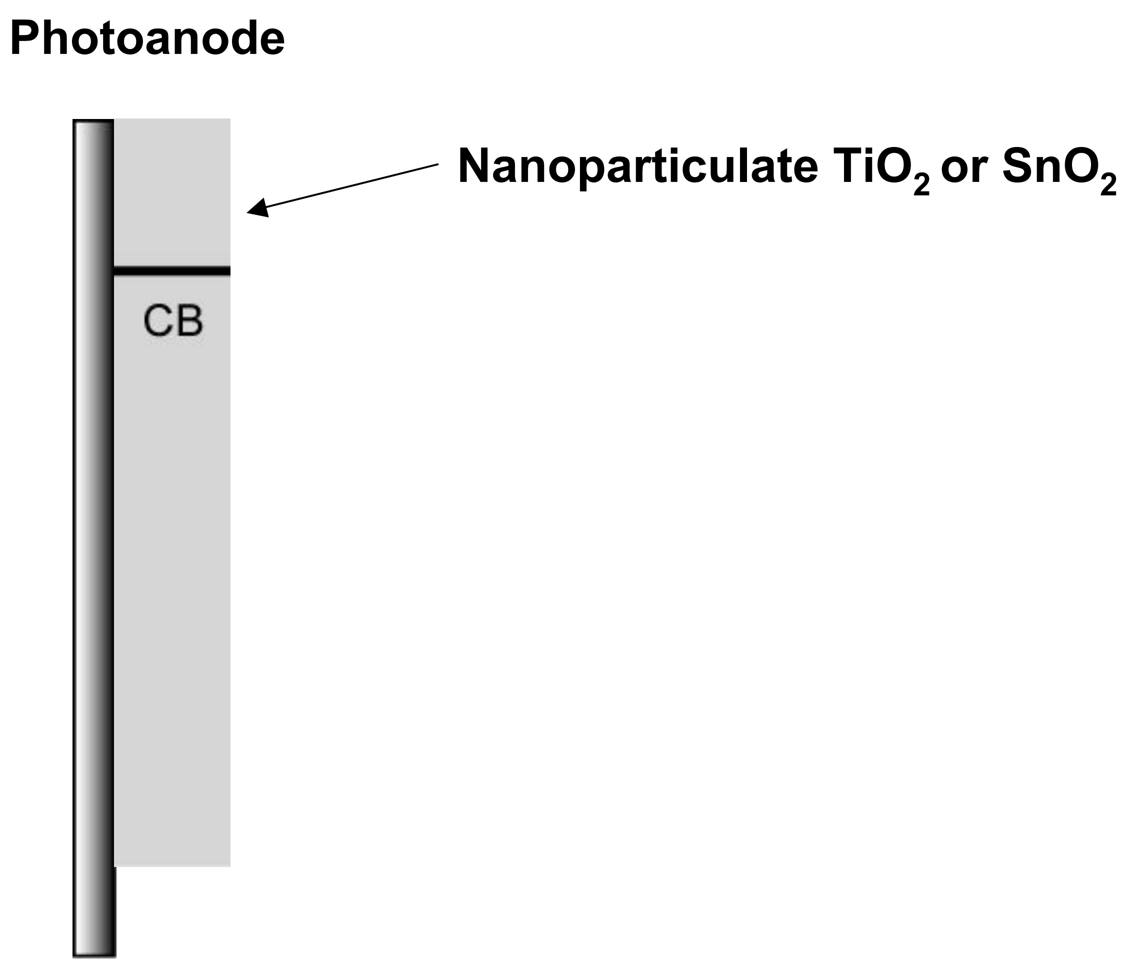
Photoelectrochemical Biofuel Cell



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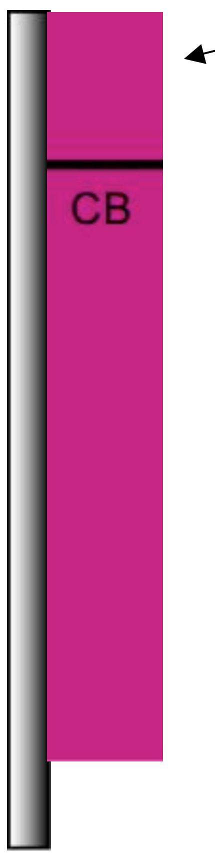
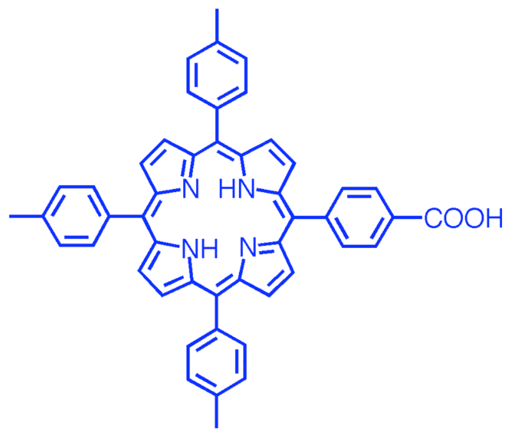
Photoelectrochemical Biofuel Cell

Photoanode

Porphyrin sensitizer





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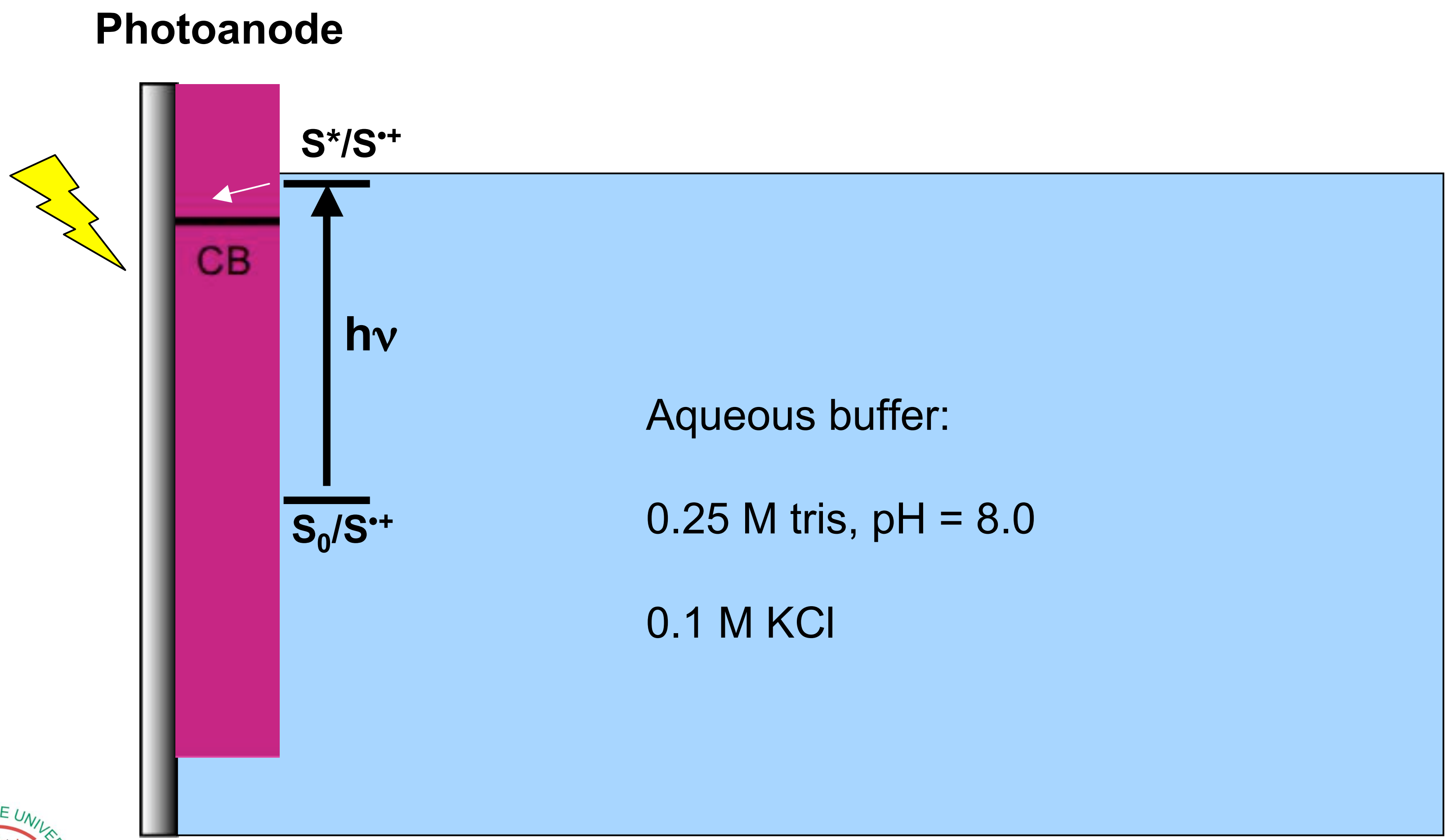
Photoelectrochemical Biofuel Cell



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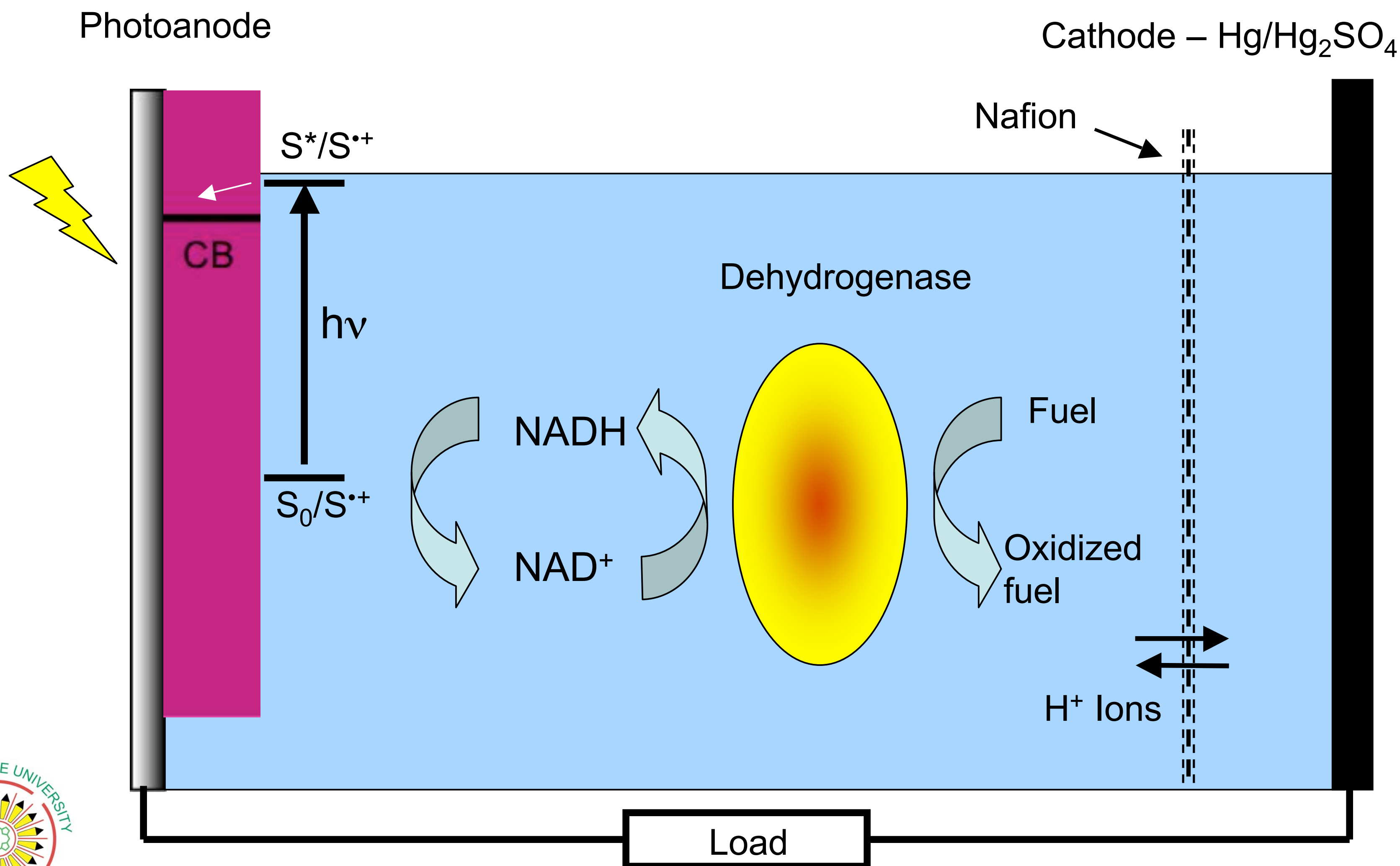
Photoelectrochemical Biofuel Cell



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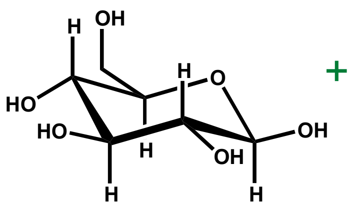
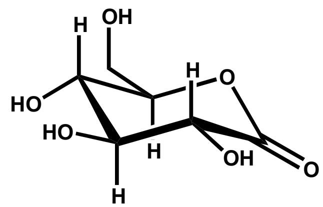
Fuels and Enzymes

β-D-Glucose



+ NAD^+ $\overset{GDH}{\rightleftharpoons}$

β-D-Gluconolactone



+ NADH + H^+

(→ ribulose-6-phosphate + CO_2, starting with glucose-6-phosphate)

$$CH_3OH \xrightarrow[NAD^+]{ADH} H_2C{=}O \xrightarrow[NAD^+]{AldDH} HCOO^- \xrightarrow[NAD^+]{FDH} CO_2$$

$$CH_3CH_2OH \xrightarrow[NAD^+]{ADH} CH_3CH{=}O \xrightarrow[NAD^+]{AldDH} CH_3COOH$$

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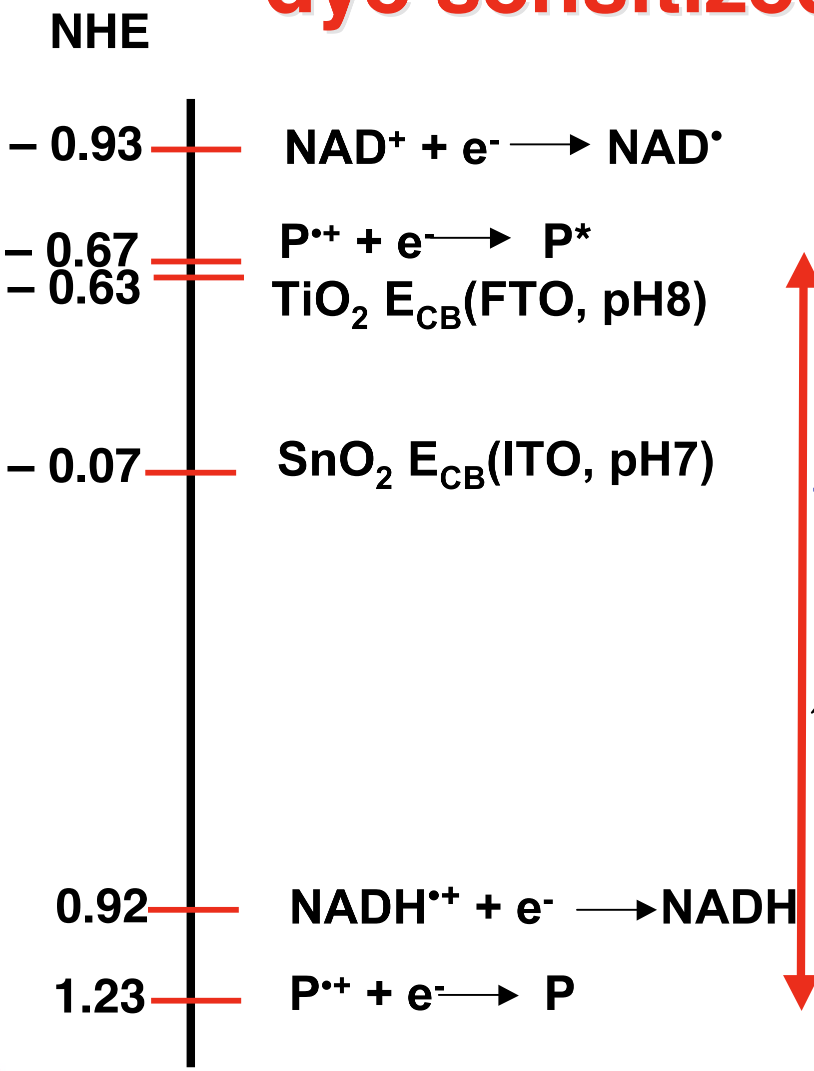
Thermodynamic design parameters for the dye sensitized photoanode



The negative potential of P^* is necessary to inject an electron into the CB of TiO_2

<u>Output poised at ~-0.60 V</u>

The high oxidation potential of P^+ is necessary to oxidize NADH by a 1 electron process

<u>NAD+/NADH poised oxidizing</u>

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Characterization and Analysis of Two-Compartment Bio Fuel Cell Function

- Effect of [enzyme] and [methanol] on I-V curve
- Absorption Spectra
- Light Harvesting Efficiency (LHE)
- Photocurrent
- Incident Photon to Current Efficiency (IPCE)
- Quantum Yield
- Photocurrent-Voltage Curve (I-V Curve)
- Fill Factor (FF)

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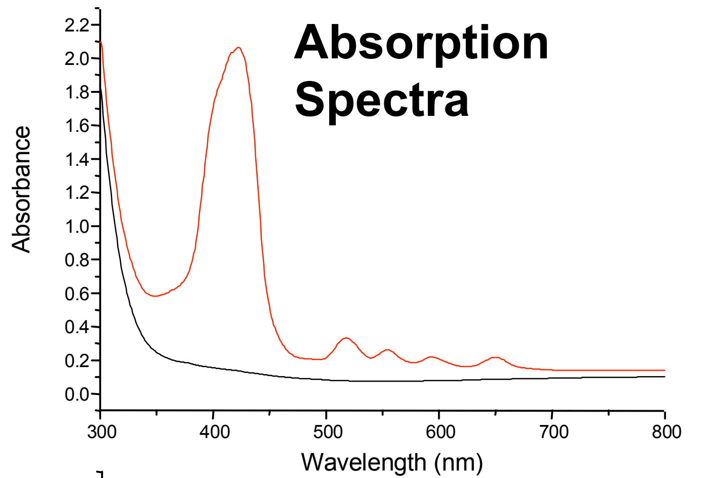
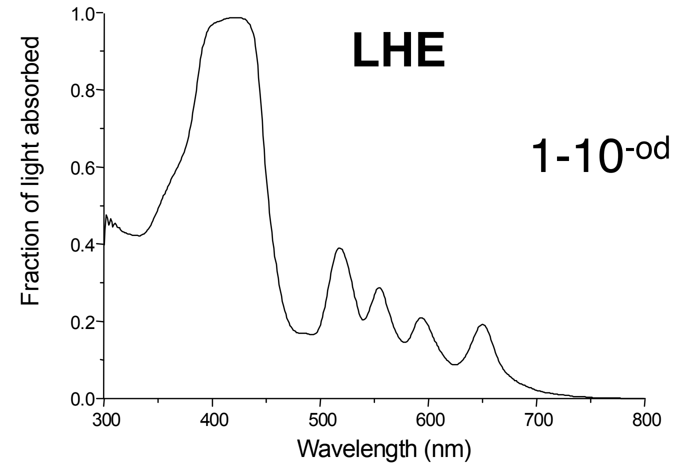
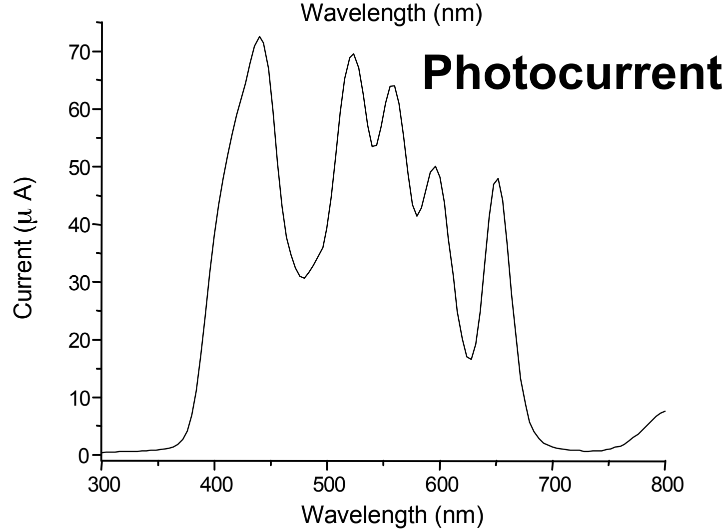
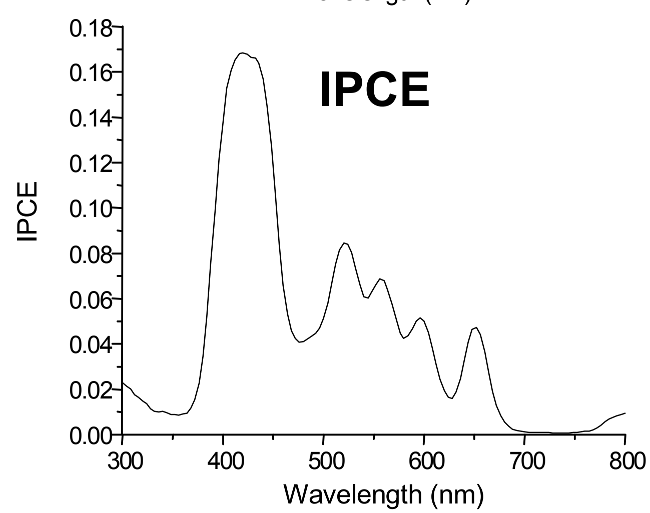
Absorption Spectra, LHE, Photocurrent and IPCE









LHE is calculated from the absorbance spectra. IPCE is obtained by dividing the photocurrent by the light intensity (not shown) at each wavelength.

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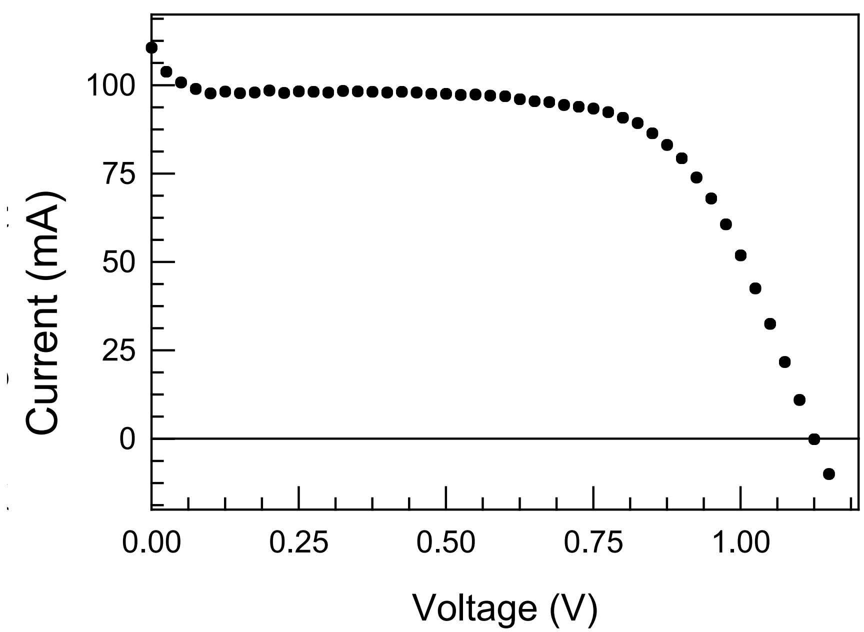
Photobiofuel Cell Performance



λ= 520 nm, 1 mW/cm2, 2 cm^2 electrode area, 4 mM NADH, 0.10 M glucose, GDH

I_{sc} = 55 mA/cm^2
V_{oc} = 1.10 V
P_{max} = 37 mW/cm^2
FF = 0.61

ϕ~ 35% in visible region

Experiment with Arizona Sun
I_{sc} = 900 microamps
V_{oc} = 1.25 V
Solar Power = 106 mW/cm^2

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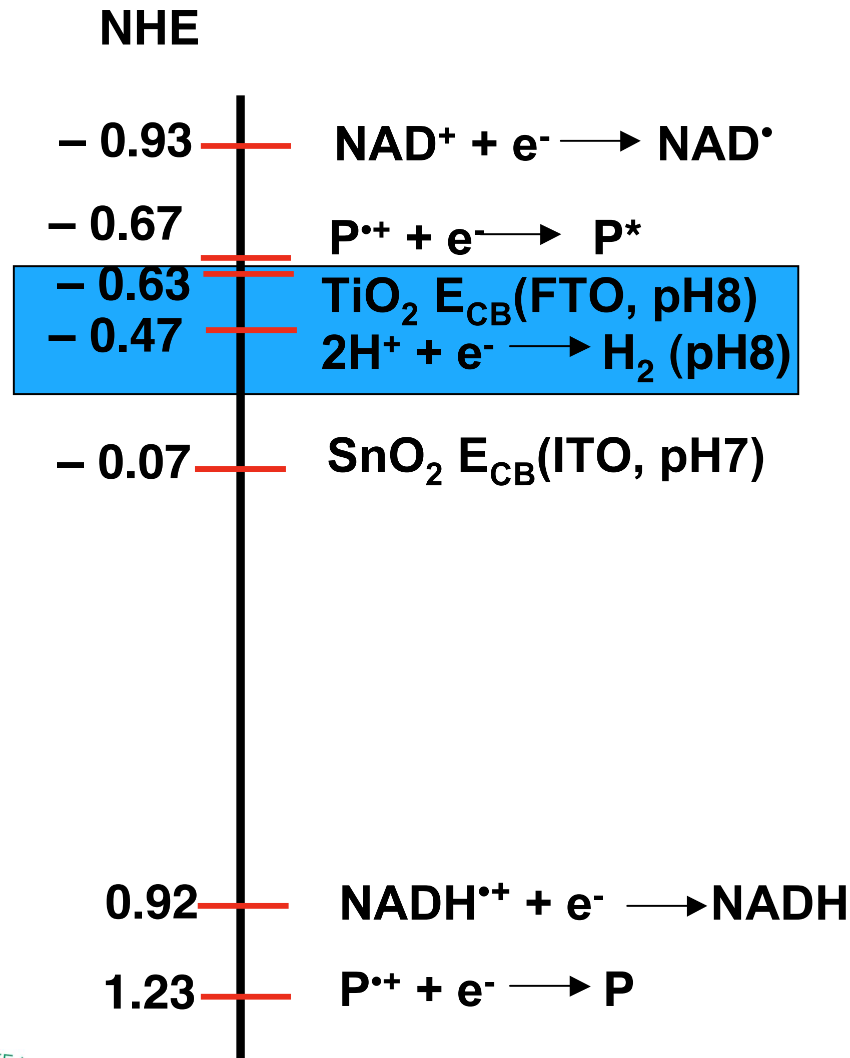
Energetics



N.B., Hydrogen ions can be reduced to H_2 by electrons from the conduction band of TiO_2.

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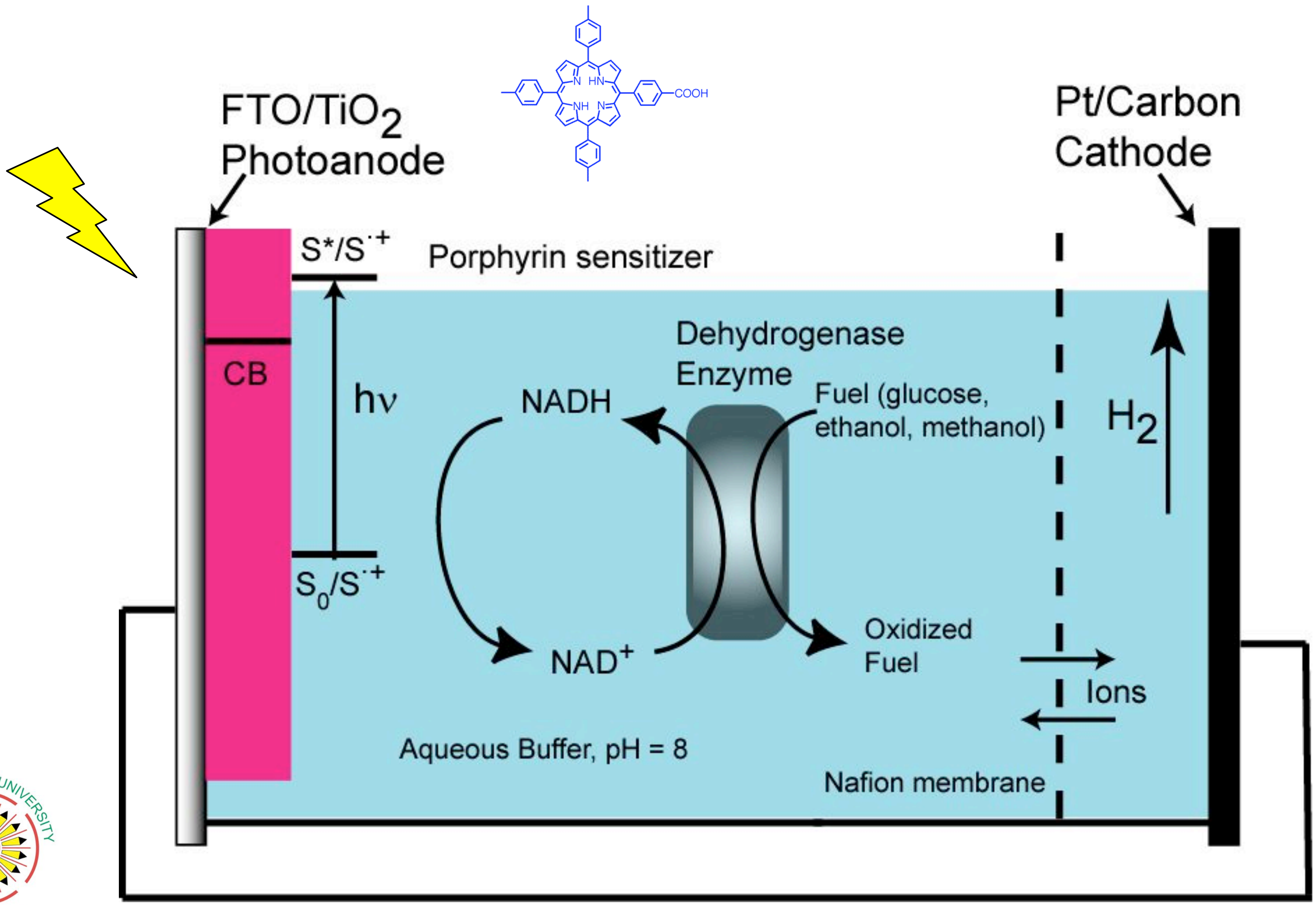
Reforming biomass to H_2



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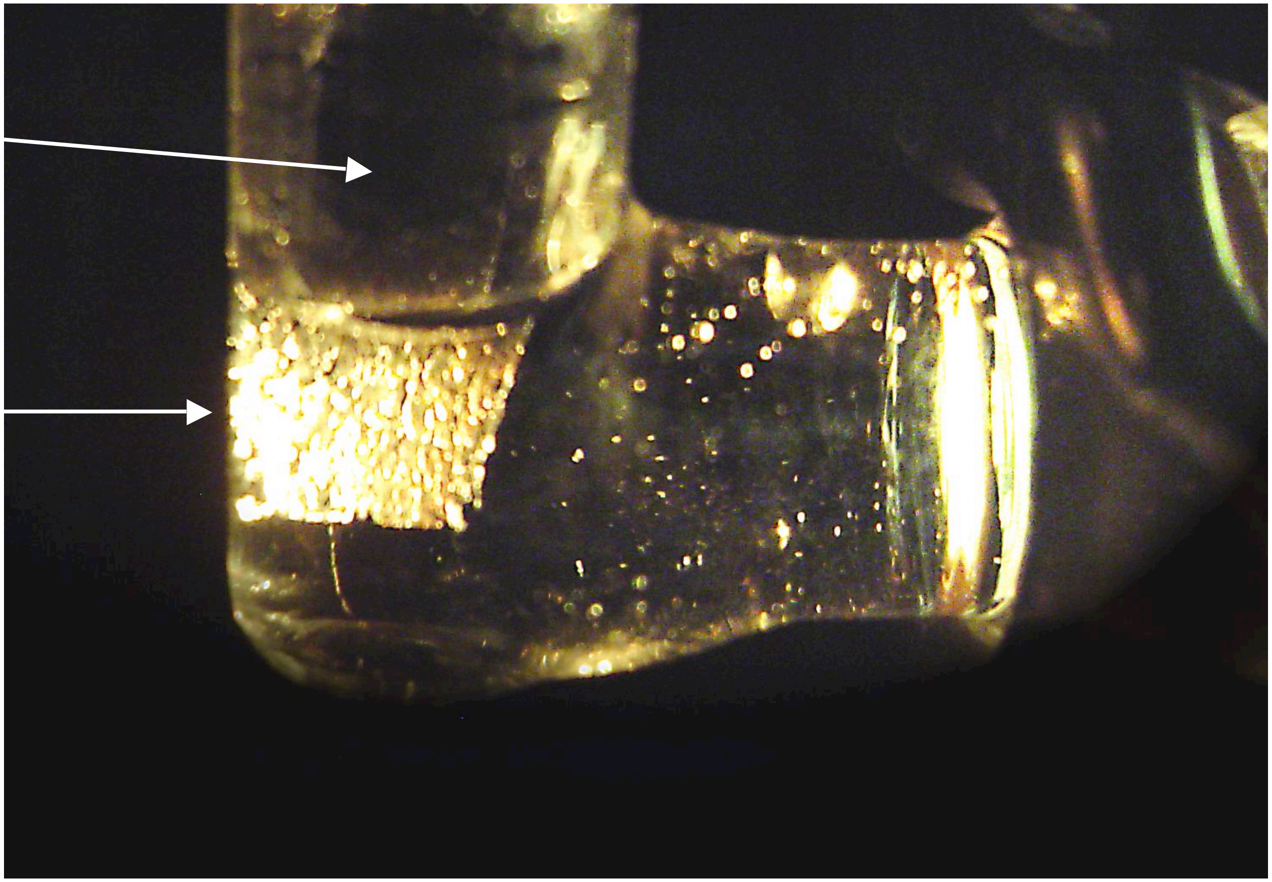
Hydrogen Production

Unwetted Pt Cathode

ETEK Pt/C Cathode



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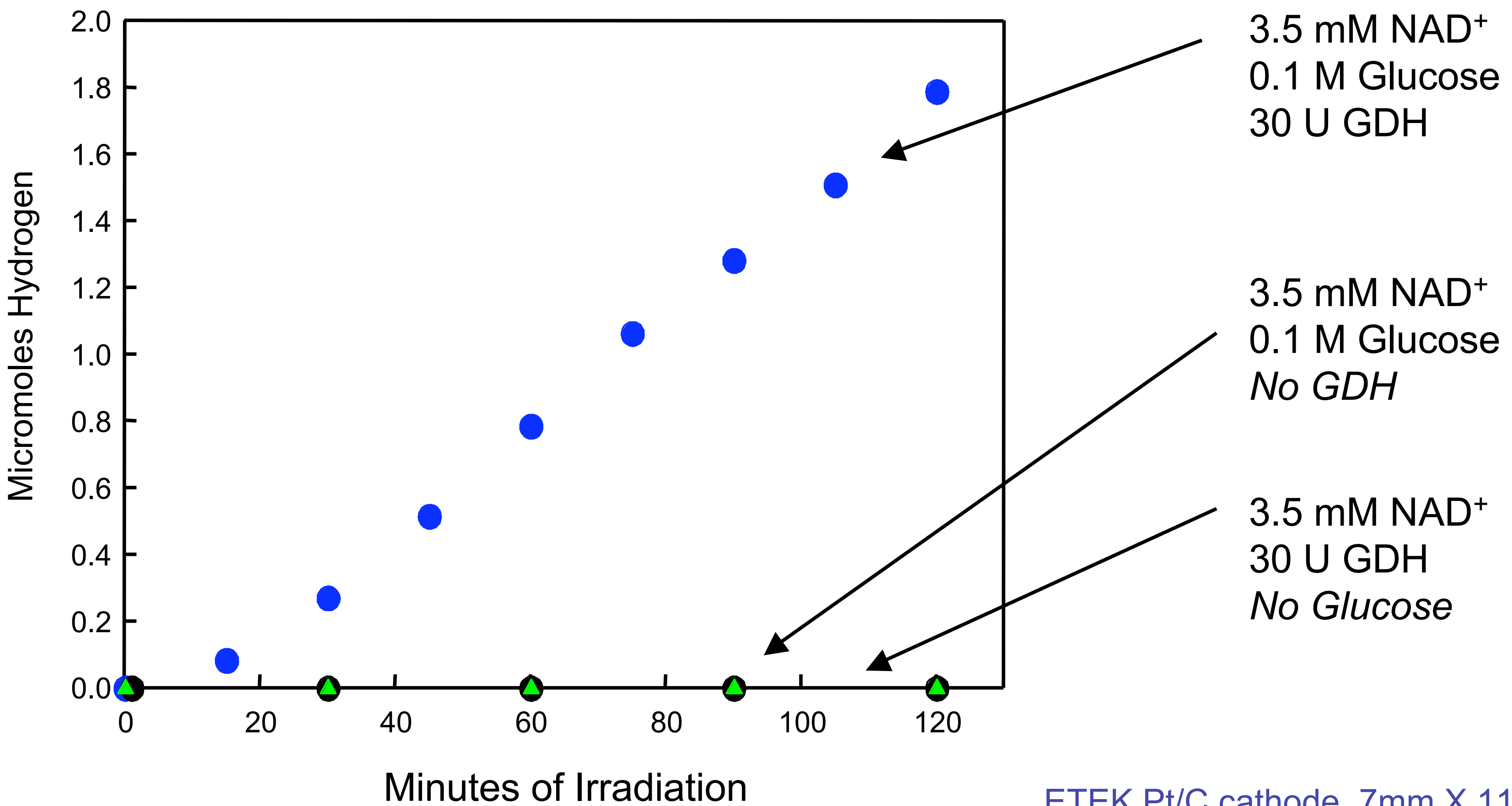
Hydrogen Production



ETEK Pt/C cathode, 7mm X 11 mm, 460<λ<1100 nm
Ar purged

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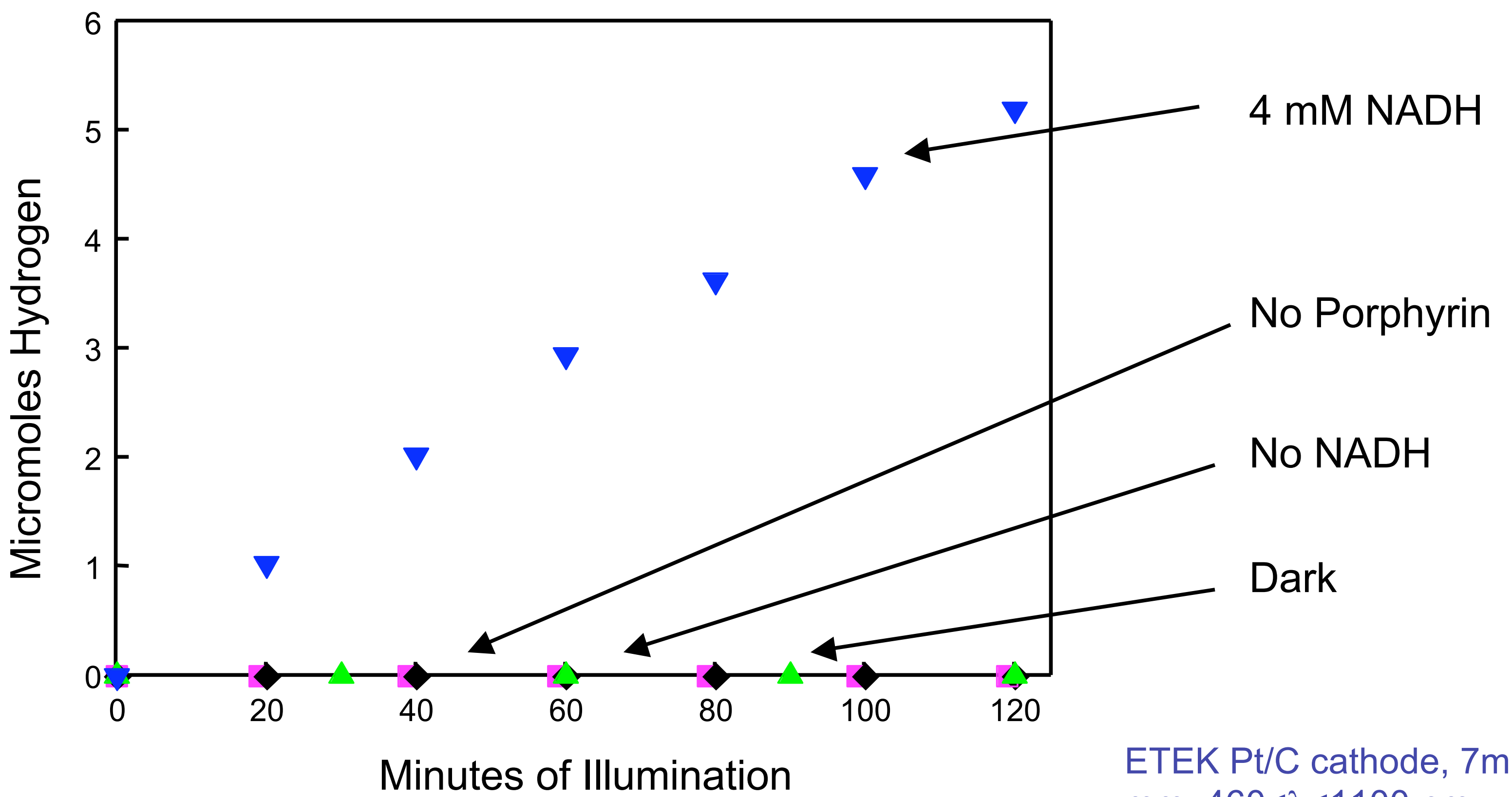
Additional Controls



ETEK Pt/C cathode, 7mm X 11 mm, 460<λ<1100 nm
Ar purged

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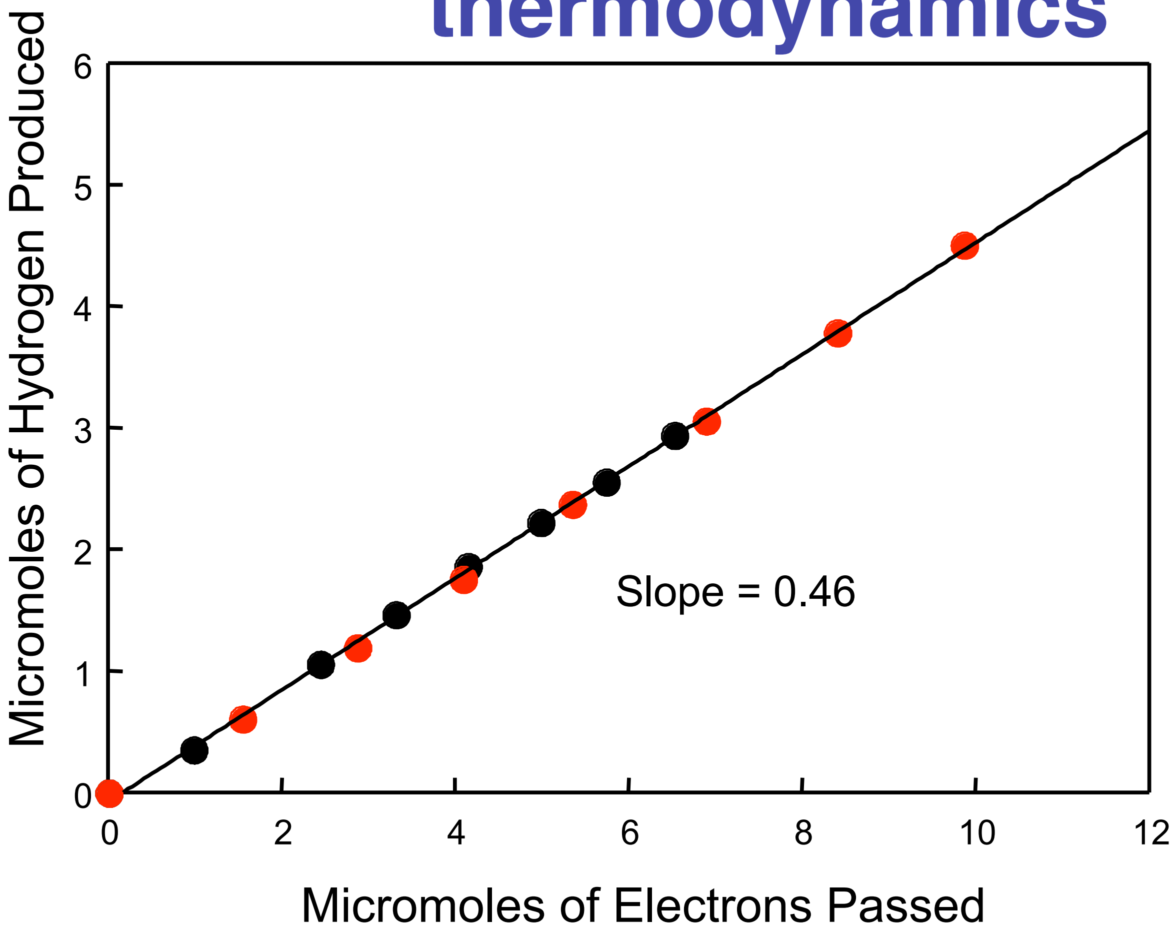
Current efficiency and preliminary thermodynamics



Quantum Yield at 520 nm = 2.5%

ETEK Pt/C cathode, 7mm X 11 mm, 460<λ<1100 nm
Ar purged

The oxidizing side poises NAD^+/NADH oxidizing enough to oxidize ethanol to aldehyde while producing H_2 at pH 8 and 1 atm H_2 gas.

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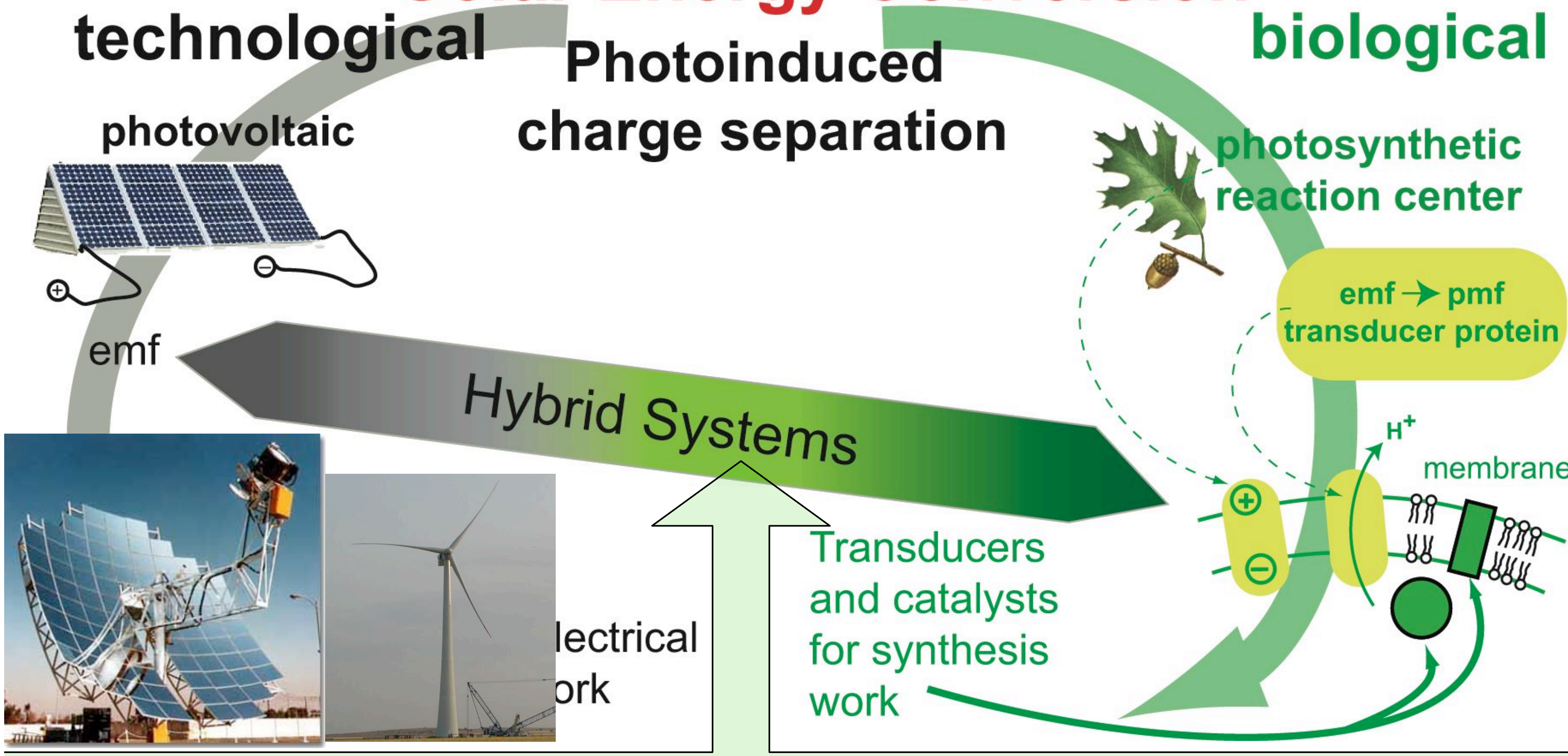
Solar Energy Conversion



The challenge in research towards bio-inspired sustainable energy production and use is the assembly of catalytically active sites of key redox enzymes and others in artificial constructs and electrically coupling them to electrodes thereby harnessing Nature's catalytic prowess to meet human energy needs.

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