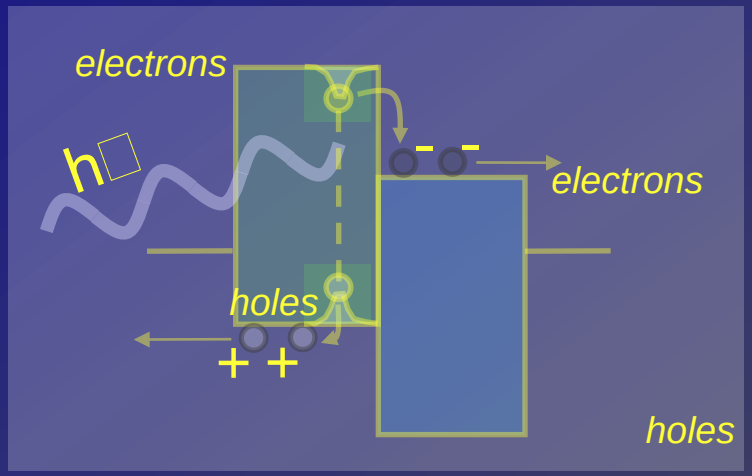
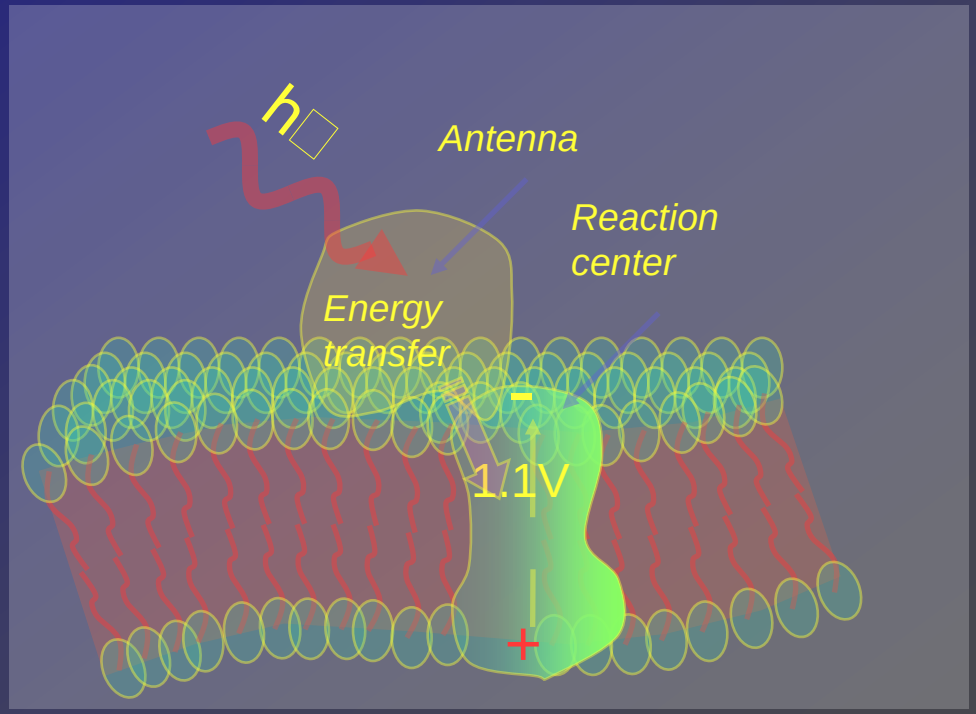
Putting Photons to Work:
Two Parts *Nature* & One Part *Material Science*!





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Current Photovoltaic Devices have global limitations on critical metal components.

Not sustainable from economic, geological, and geo-politicial perspective.

Table I. Material constrained PV expansion potentials

Solar cell	Metal	Baseline					Modified 2020
		Metal requirements* (g/m^2)	Reserves 1998† (Gg)	Refinery production 1997† (Mg/yr)	S_{MC}§ (TWp)	G_{MC}¶ (GWp/yr)	G_{MC}‖ (GWp/pr)
CdTe	Cd	6·3	600	20000	9	310	500
	Te	6·5	20	290	0·3	5	20
CIGS	Se	4·8	70	2200	1·4	46	300
	Ga	0·53	110	54	20	10	400
	In	2·9	2·6	290	0·09	7	70
aSiGe	Ge	0·44	2	63	0·5	14	200
Dye-sensitised	Ru	0·1	6	11	6	11	20

Prog. Photovolt. Res. Appl. 8, 61±76 (2000)

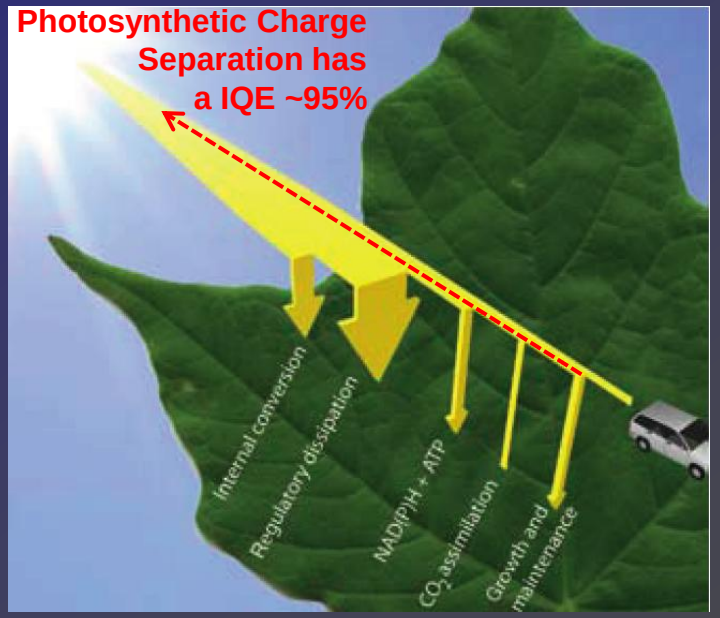
Currently have 0.001 TWp PV capacity we now need ~10.0 TWp, by year 2050 we will need >50 TWp capability.

Possibly only Dye-sensitised PV has this potential!

External Quantum Efficiency (EQE) of plant growth & biomass accumulation is very low ~0.10%. Two orders of magnitude < than Si-based PV.

Table I: Annual Biofuel Production and Energy Conversion Efficiency by Photosynthetic Organisms and Electrical Energy Production by a Photovoltaic Cell.

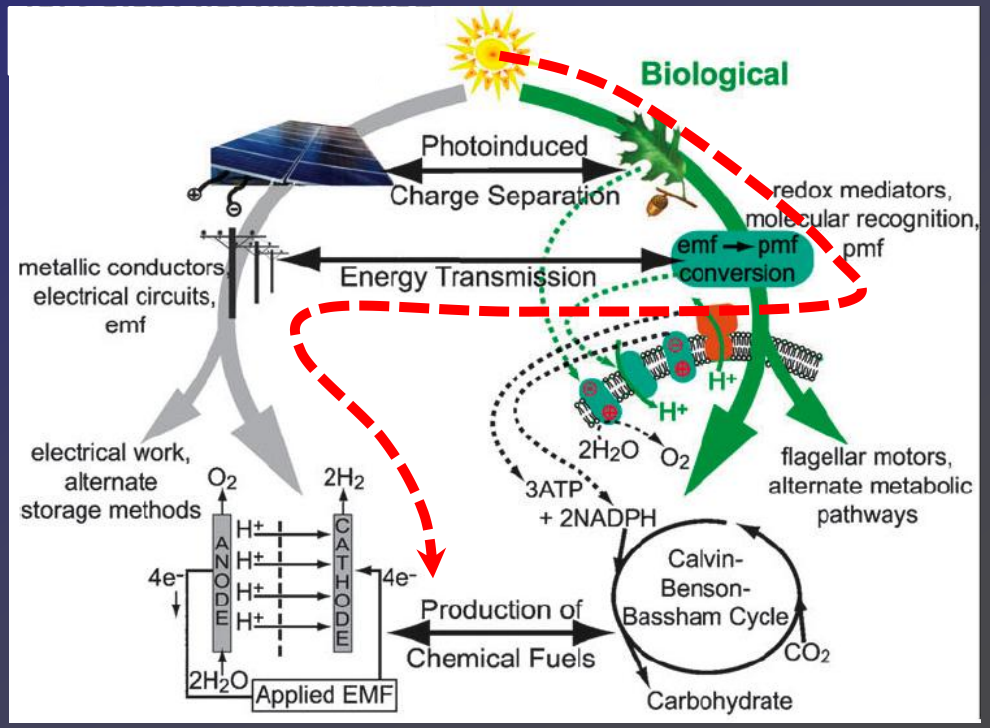
Oil Producer	Fuel Production [kg/(ha year)]	Energetic Equivalent [kWh/(ha year)]	ECE (%)
Oil palm	3,600–4,000	33,900–37,700	0.16–0.18
Jatropha	2,100–2,800	19,800–26,400	0.09–0.13
Tung oil tree (China)	1,800–2,700	17,000–25,500	0.08–0.12
Sugarcane	2,450	16,000	0.08
Castor oil plant	1,200–2,000	11,300–18,900	0.05–0.09
Cassava	1,020	6,600	0.03
Microalgae	91,000	956,000	4.6
Si-based PV cell		3×10^6	14.3



Possibly we can use plants or algae as self-organizing "biofactories" to produce the photosynthetic reaction centers that can be used "outside" the constraints of plant growth and reproduction.

From ONE growth cycle potentially can provide MANY photocycles!

Can we take a biological "shortcut" to usable solar energy with the *"green"* components, and without the production of "brown" or "black" biomass?



Outline of Talk

- Introduction to sustainable energy needs
- Bio-derived Photosynthetic Photovoltaics (*not mimetic*)
  - Introduction to biological self-assembly & photosynthesis
  - Attractive properties of PSI
  - 1st Photosynthetic Photovoltaic Device: *proof-of-principle*
  - Strategies for stabilization and thermostability
- Harvest more light- Increase OD (2D ⇨ 3D) & Extend Spectra
  - Methods to increase optical cross-section
  - Attraction of LSCs
  - Properties of natural phycobilisomes
  - Formation of PBS:acrylamide hydrogels
  - Demonstration of efficient light harvesting
  - Pathway to improvements
- Self-assembled Hydrogen Evolving nanoparticles

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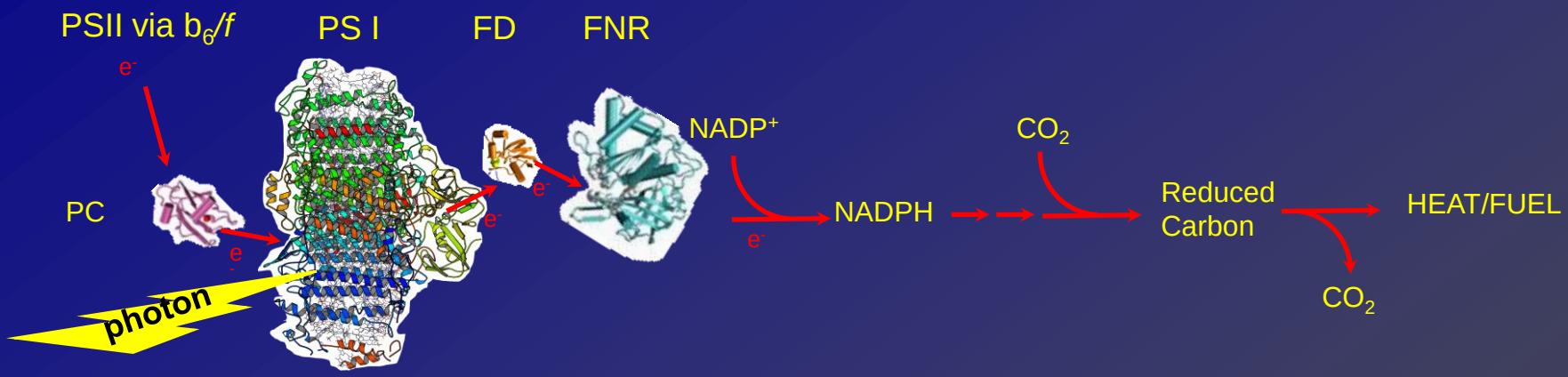
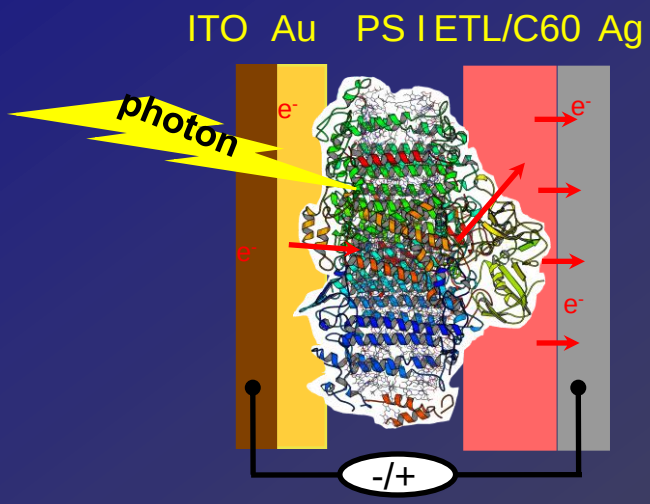
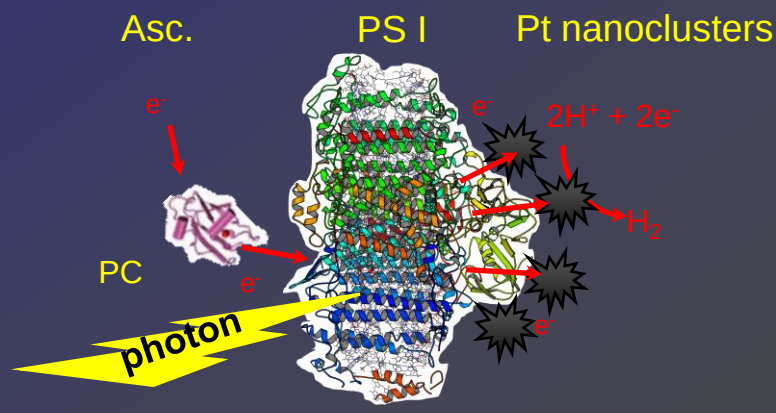
Redirecting the role of PSI for applied photosynthesis





PS I in a solid-state, photovoltaic device



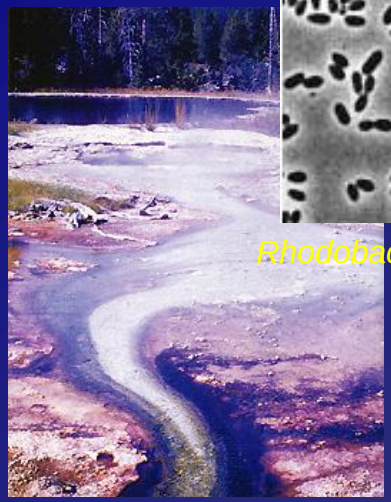
PS I as a hydrogen-evolving nanoparticle

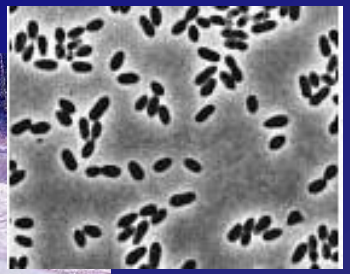
The proof of principle:

Can photosynthetic reaction centers be integrated into solid-state devices such that they preserve their functionality and become coupled electronically to organic semi-conductors?

DEVICE FABRICATION

ORIENTATION AND ASSEMBLY OF PHOTOSYNTHETIC COMPLEXES

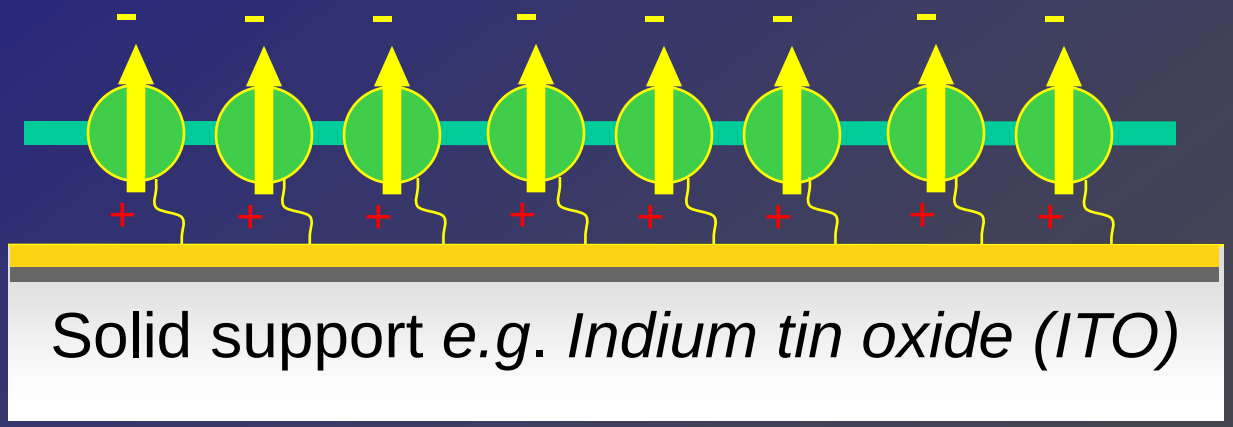




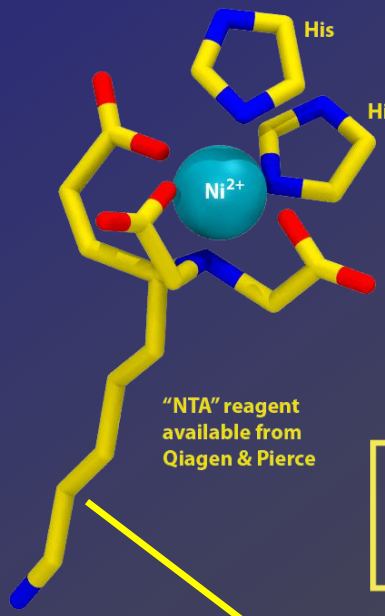
Rhodobacter sphaeroides

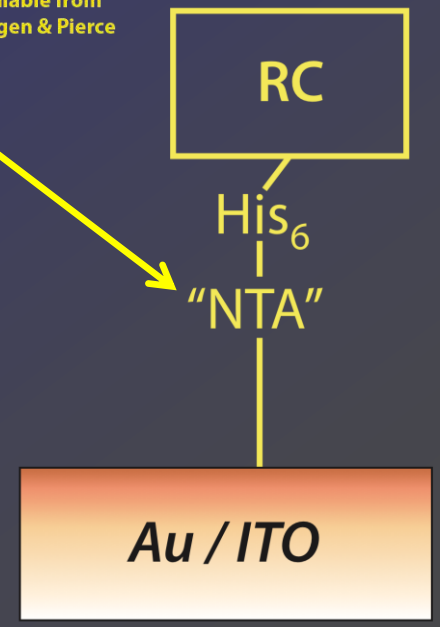
spinach

- Harvest protein complexes from plants or bacteria
- Tether complexes to solid support
- Orient complexes with uniform charge transfer vector



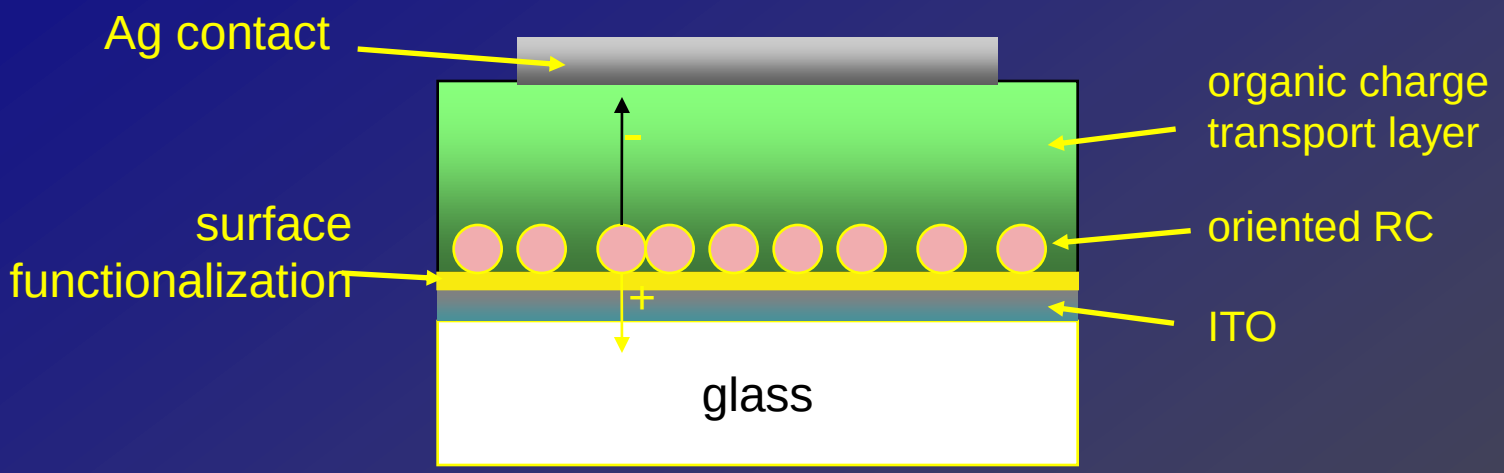
From tagged reaction center

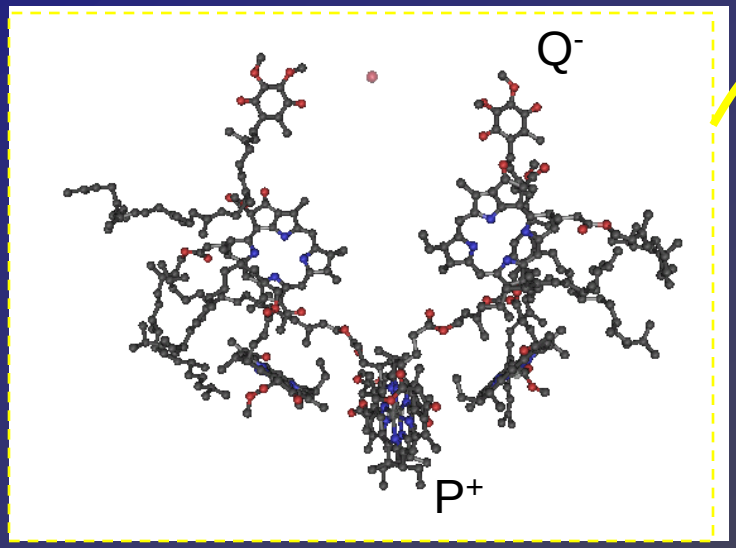


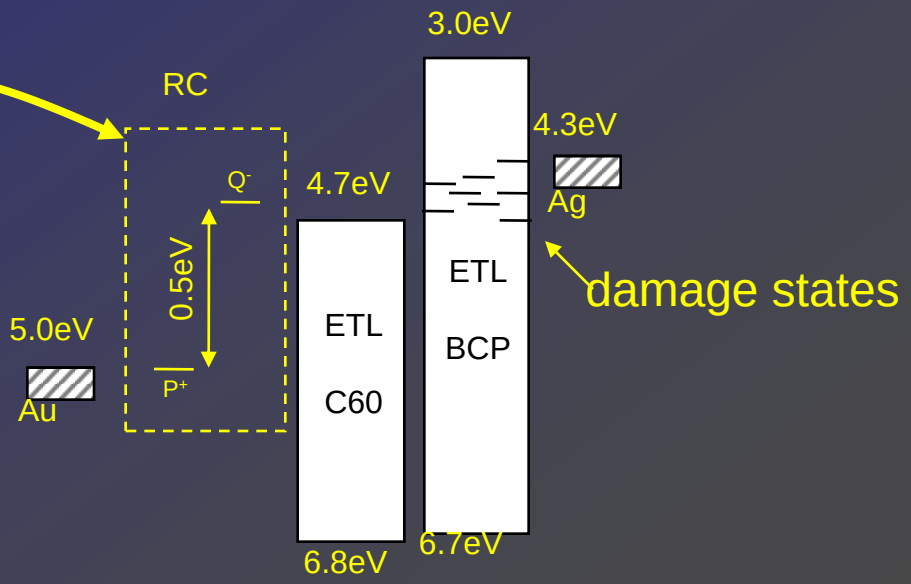


REACTION CENTER DEVICE INTEGRATION

Evaporate *organic semiconductor* over assembled RC film

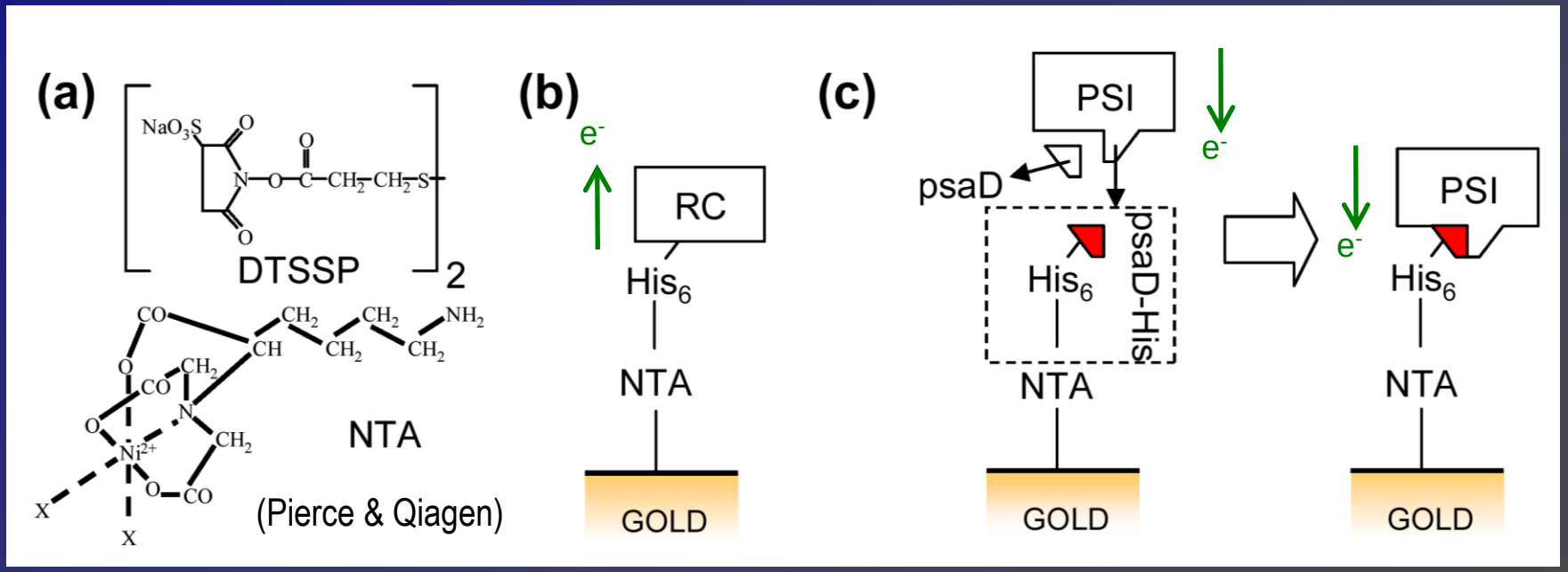




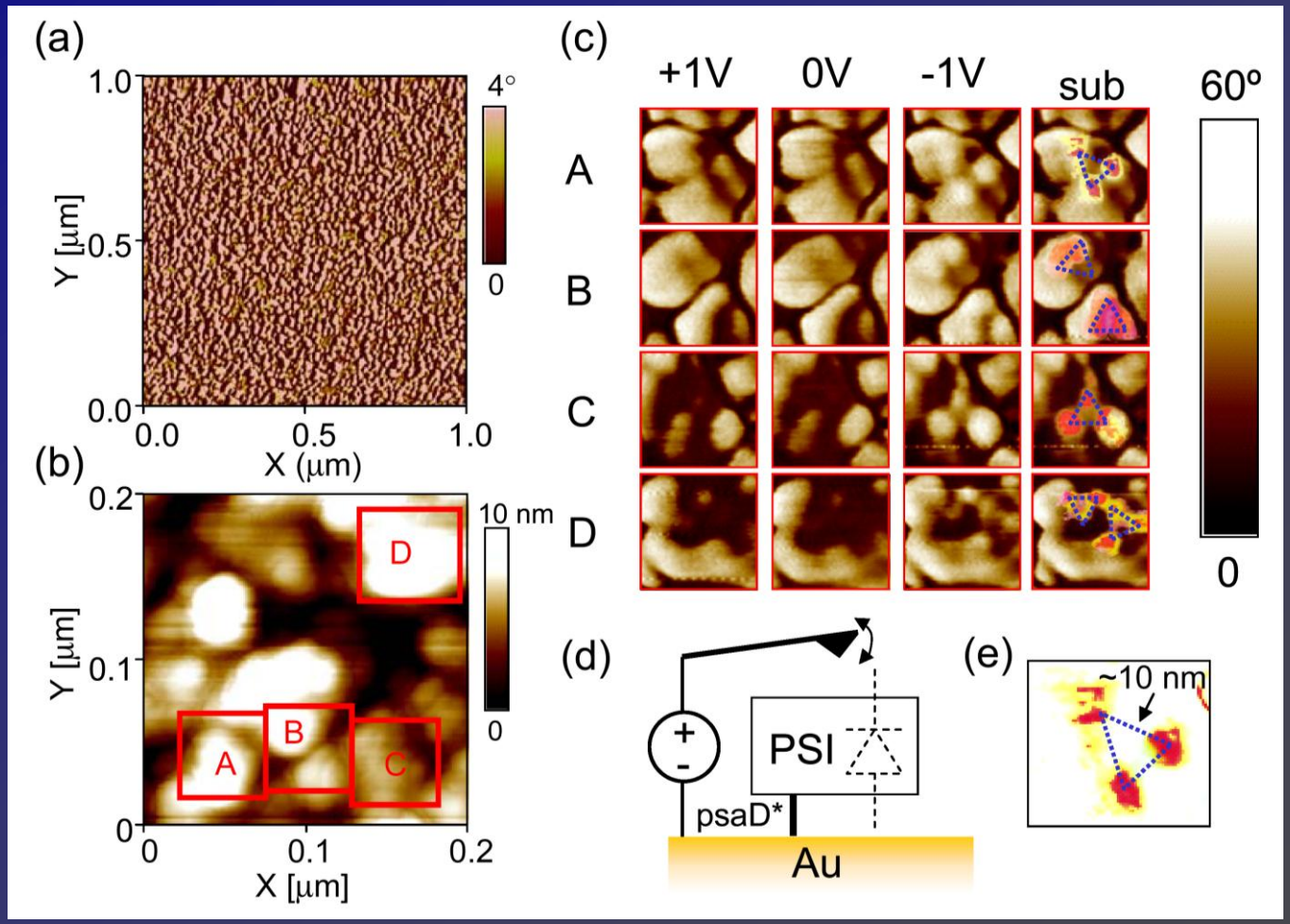


Nano Letters, June '04

Strategy for immobilizing and orienting reaction centers and PSI onto the device surface: ability to *in vitro* exchange psaD and psaE is key for future plans. Note opposite orientation of the charge separation.

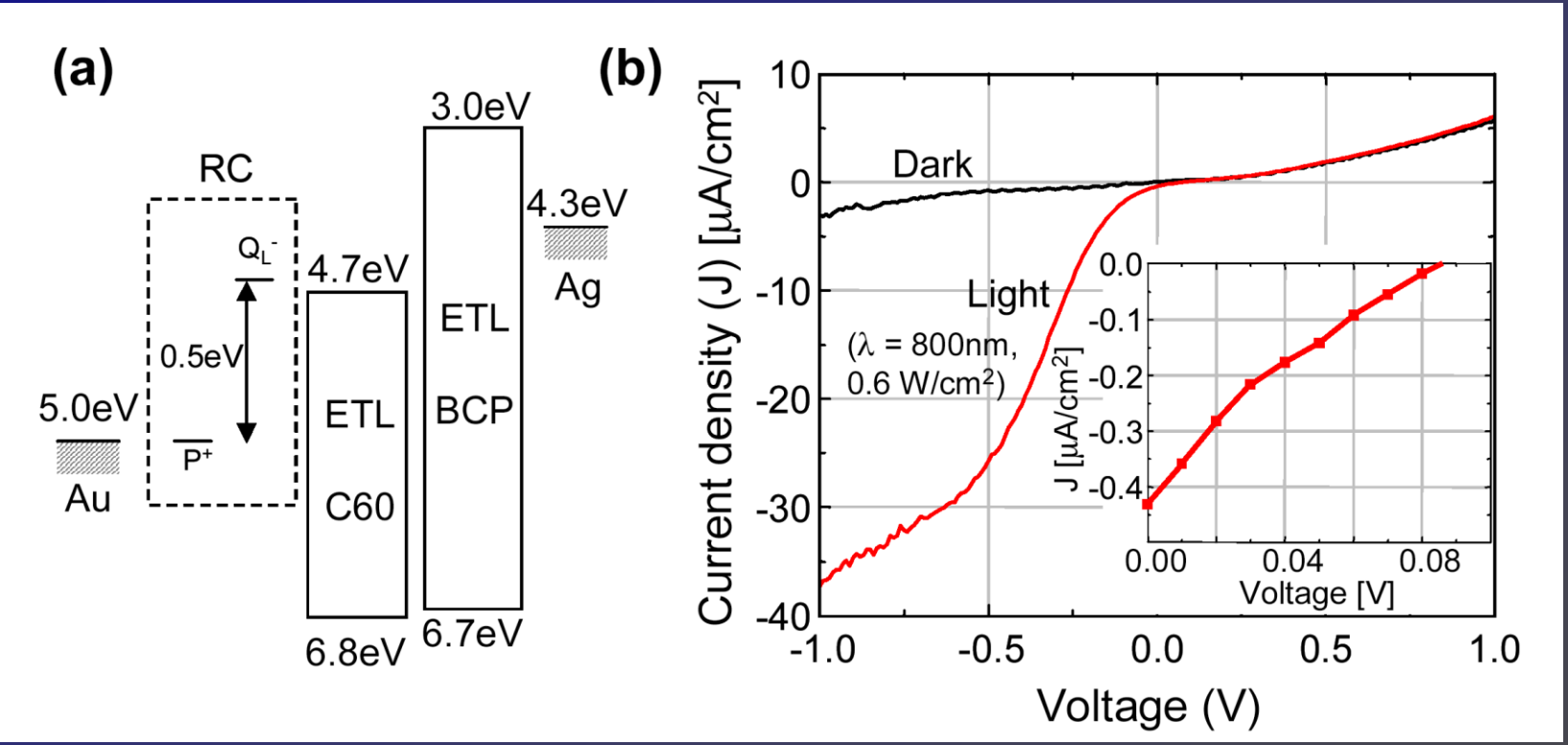


Characterization of self-assembled photosynthetic PSI complexes by atomic force microscopy (AFM). Confirms the orientation with P700 dimer face UP.

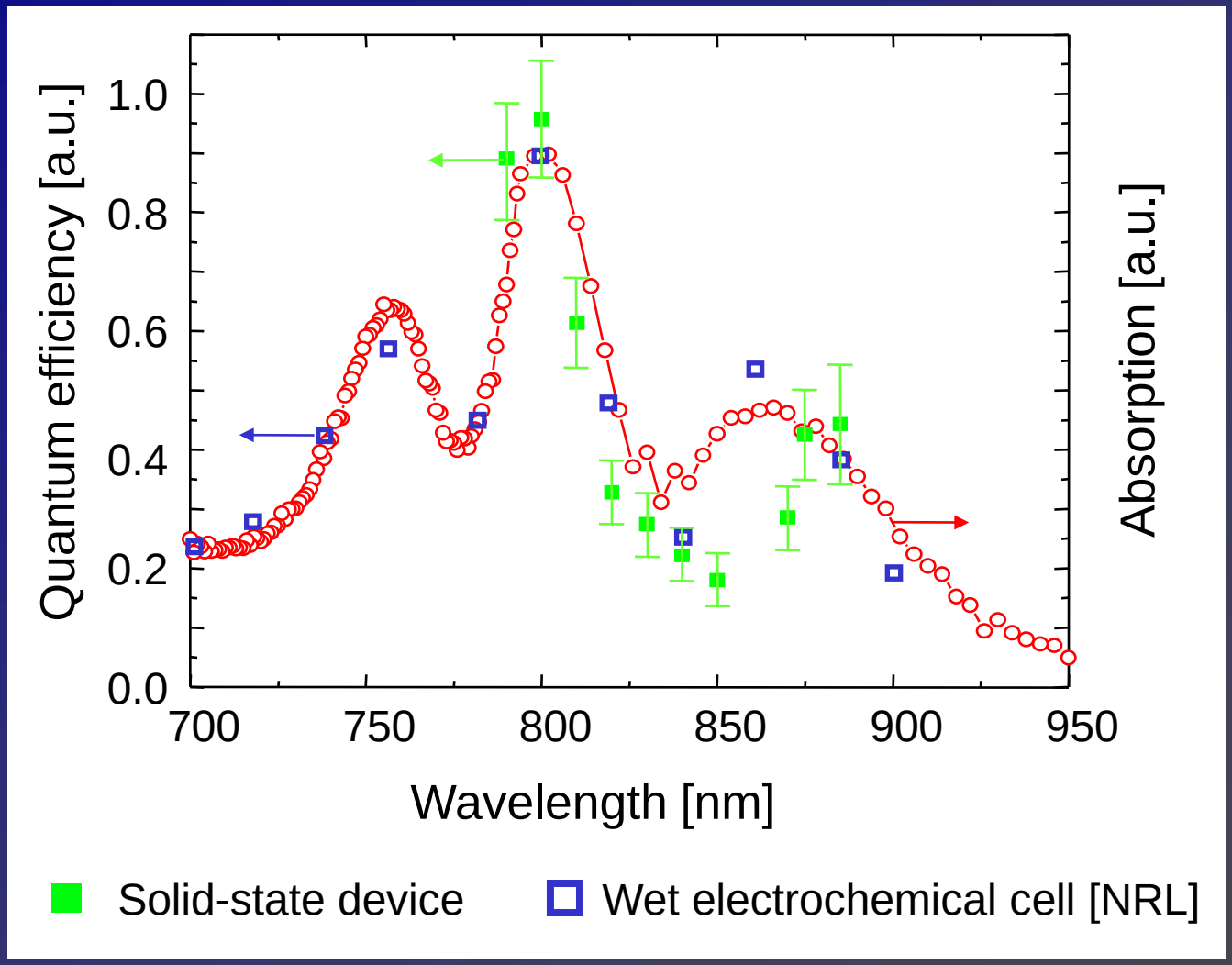


The increase in phase in the -1 V scan corresponds to an increase in the attractive forces between the tip and the sample and indicates the presence of a positive charge trapped on the surface of PSI, mostly likely at the special pair, P700.

The solid state bacterial reaction center does in fact show Light driven photovoltaic activity yet with low efficiency.



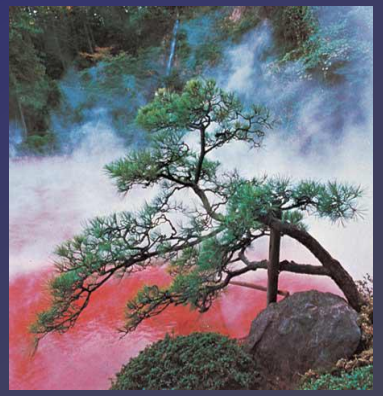
RESULTS: *Photocurrent spectrum confirms integration of RCs.*

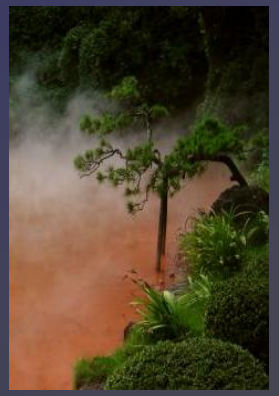


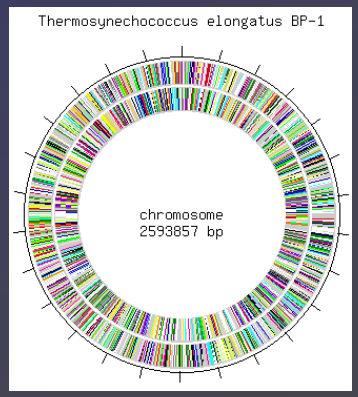
Internal quantum efficiency = 12%

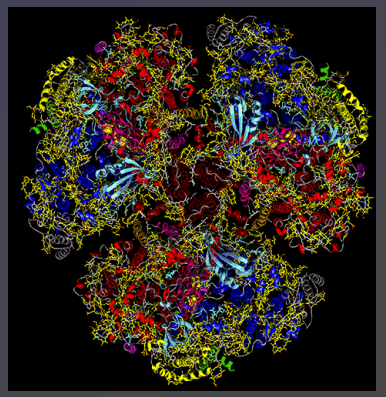
Nano Letters, June '04

Thermosynechoccus elongatus BP1: thermophilic cyanobacteria, transformable, fully sequenced, and high-resolution crystal structures (from Beppu Hot Springs, Japan)

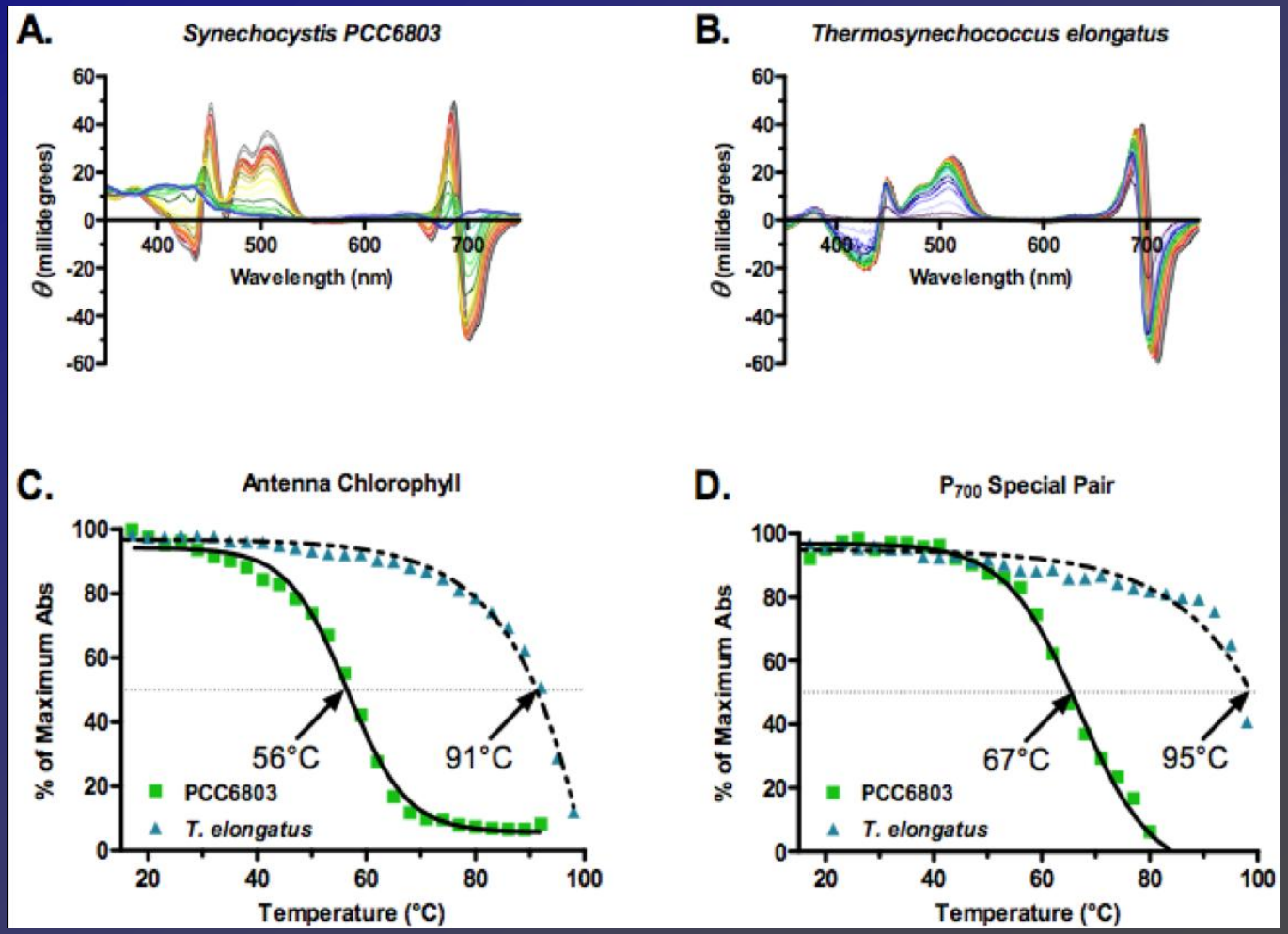




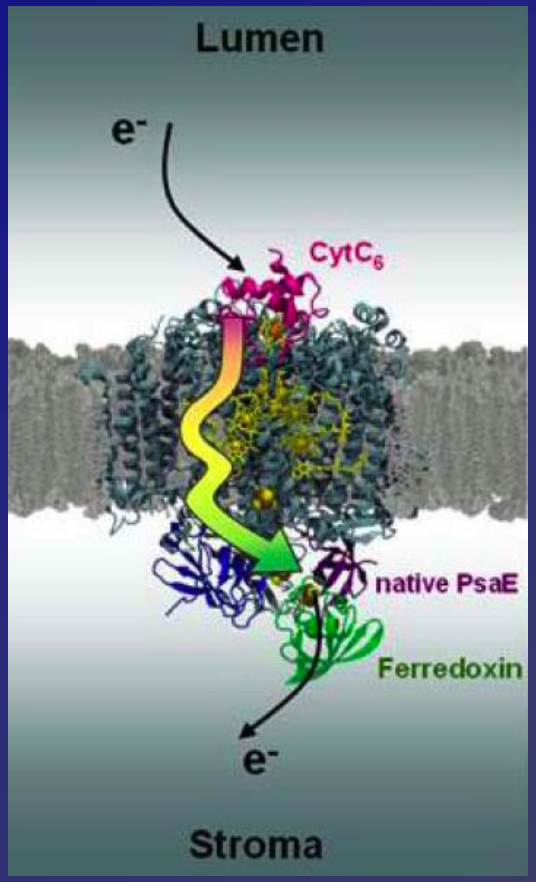


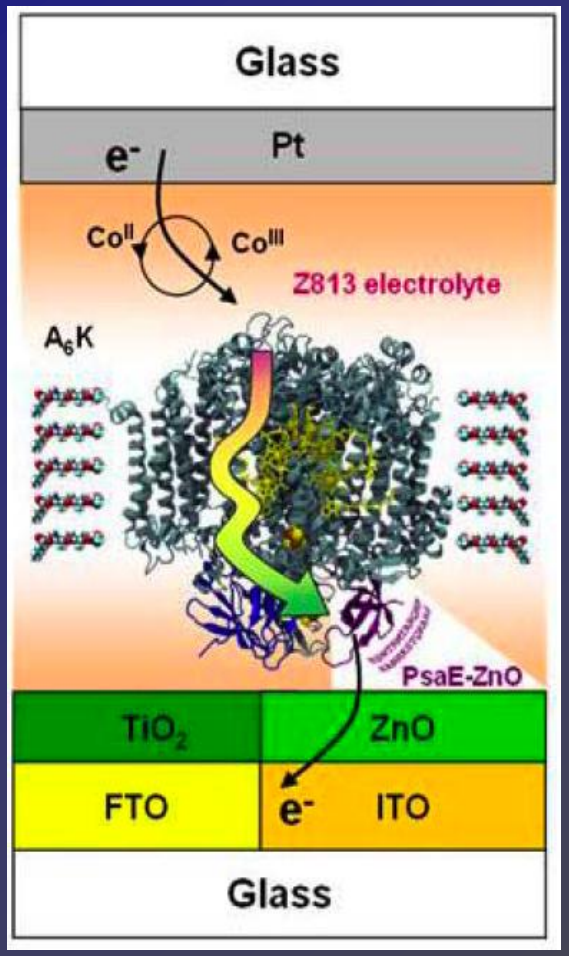


Trimeric PSI isolated from *T. elongatus* is very thermostable with bulk Chl and P700 stable to 91°C and 95°C, respectively. (>30° more stable than PCC6803)



Need to bioengineering psaD/E to contain an exposed ZnO-binding domain allow PSI to self assemble in an oriented onto ZnO-nanotubes.





- By screening a random peptide library (4 x 10^7 clones) in attached FimH in *E. coli to ZnO*
- ZnO- Binding Domain was identified (RSNTRMTARQHRSANHKSTRARS)
- Putative motif, RXXRS Binds only to oxide and shows homology to Zn-dependent helicase
- (Kjaergaard *et al.* (2000) App. Env. Microbiology)
- Engineered onto the N-terminus of psaD & psaE and expressed in E. coli.

ZnO-PSI nanophotovoltaic device have very promising performance:

-Fill factors up to 71%

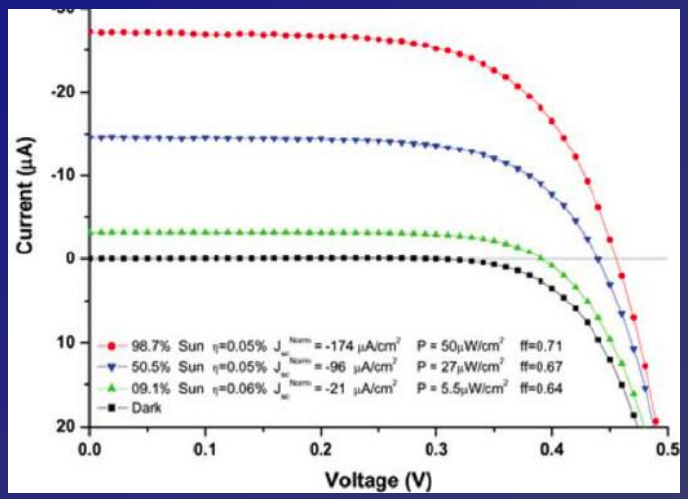
-Generating open circuit photovoltages up to 0.5V

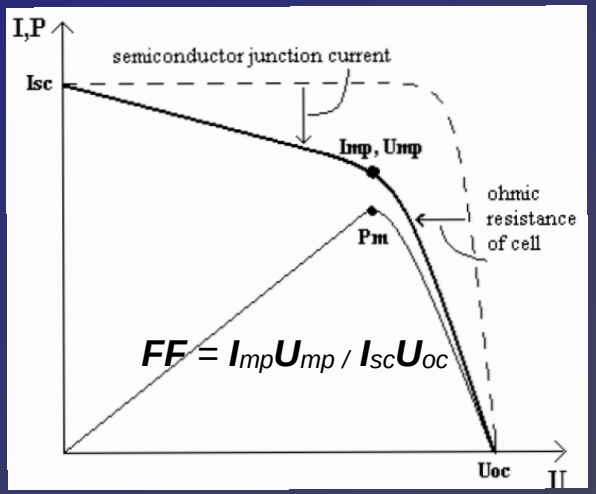
-Normalized photocurrent densities up to 362 μA/cm^2

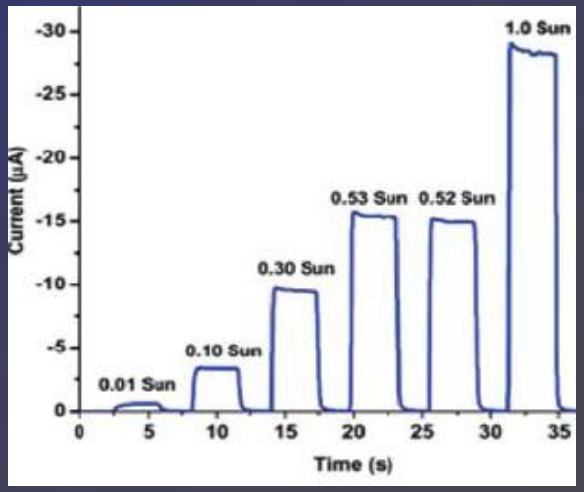
-Power outputs up to 81 μW/cm^2

-Functions in low light and quite linear up to 1.0 Sun.

- -Several orders better than the gold surface system



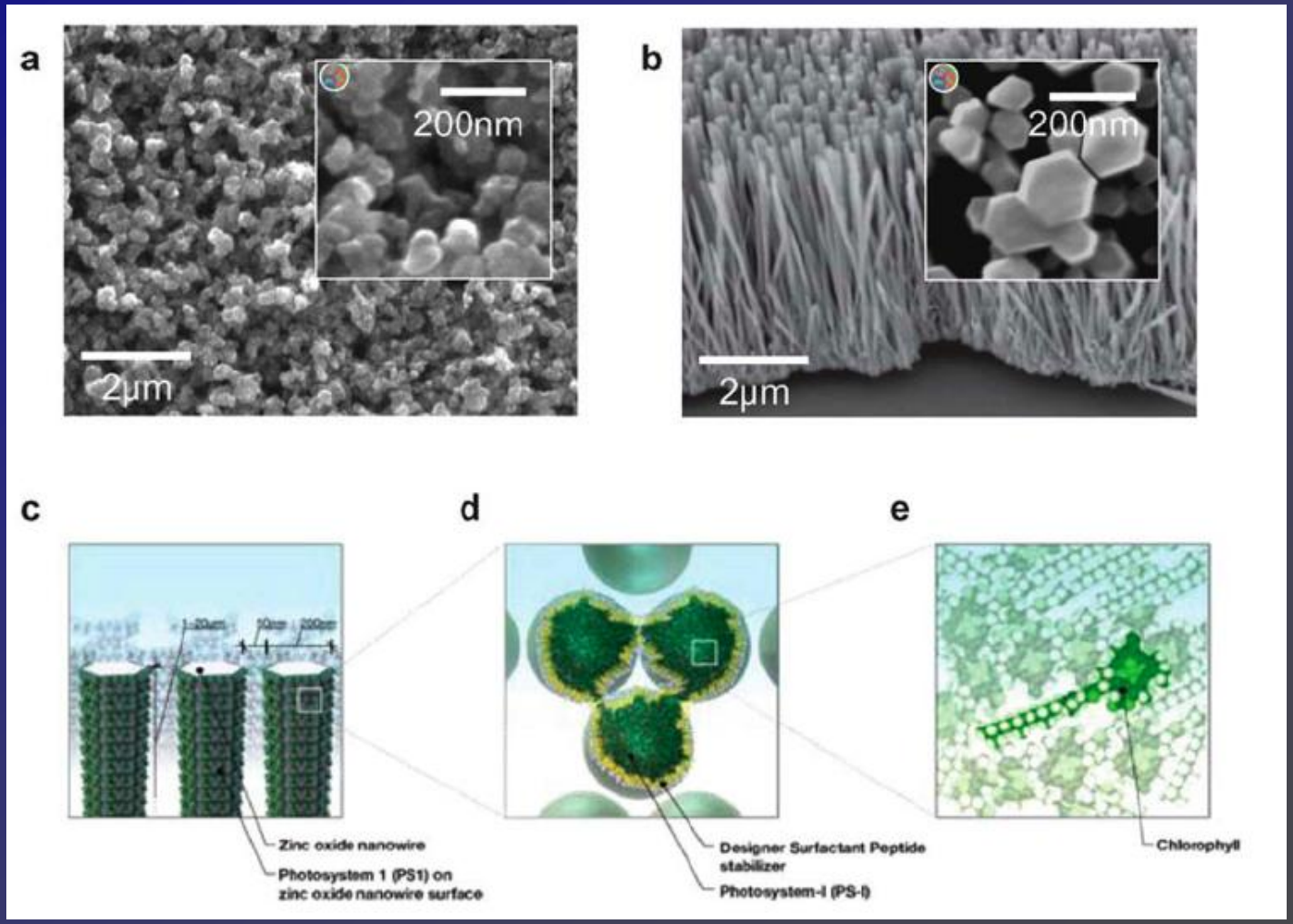




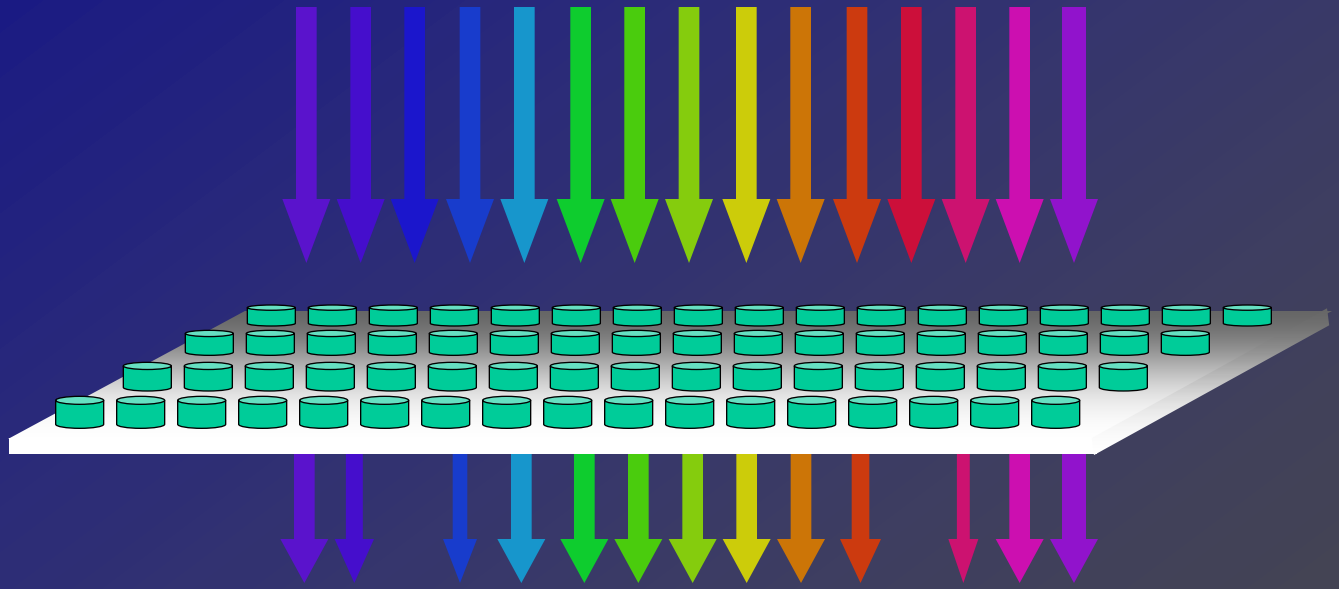
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

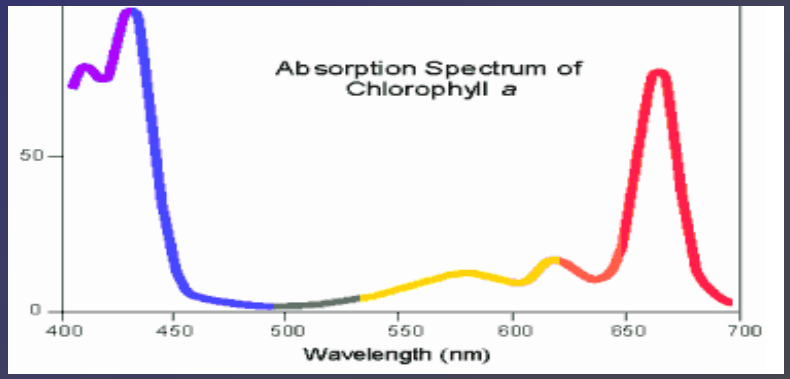
work conducted in lab of:
Prof. Michael Grätzel
Laboratory of Photonics and Interfaces
Ecole polytechnique fédérale de Lausanne

If we could easily coat nanotubes with PSI we could provide huge increase in surface area plus have a self-organizing device design an “artists view” of such a coating!

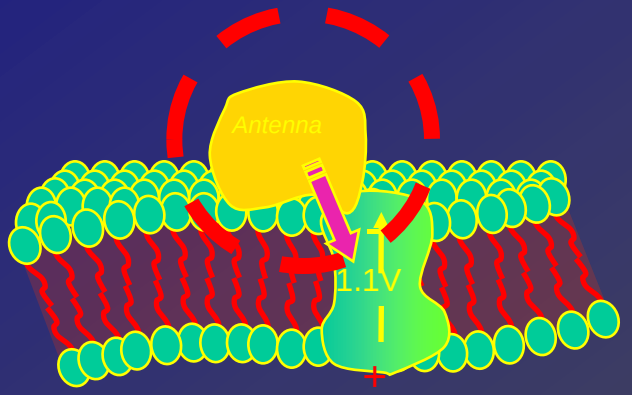


Most of visible light is either transmitted/reflected giving the PSI devices very low External Quantum Efficiency (EQE).



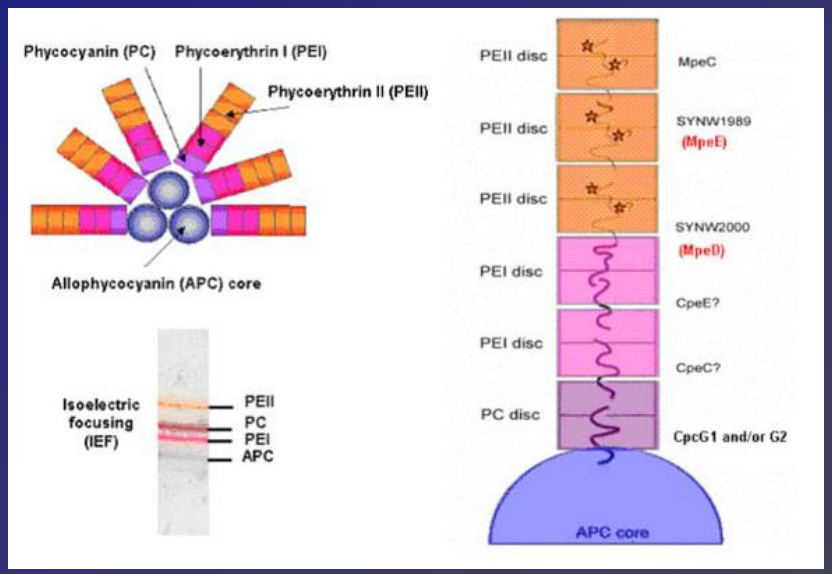


Can we use the solutions Nature created to harvest more light over a wider spectral range?



Marine cyanobacteria see little light and forfeit most red spectra due to water absorbance.

- sits above membrane
- divided into segments, 480-660 nm
- chromophores positioned by proteins
- 1500 chromophores per phycobilisome.



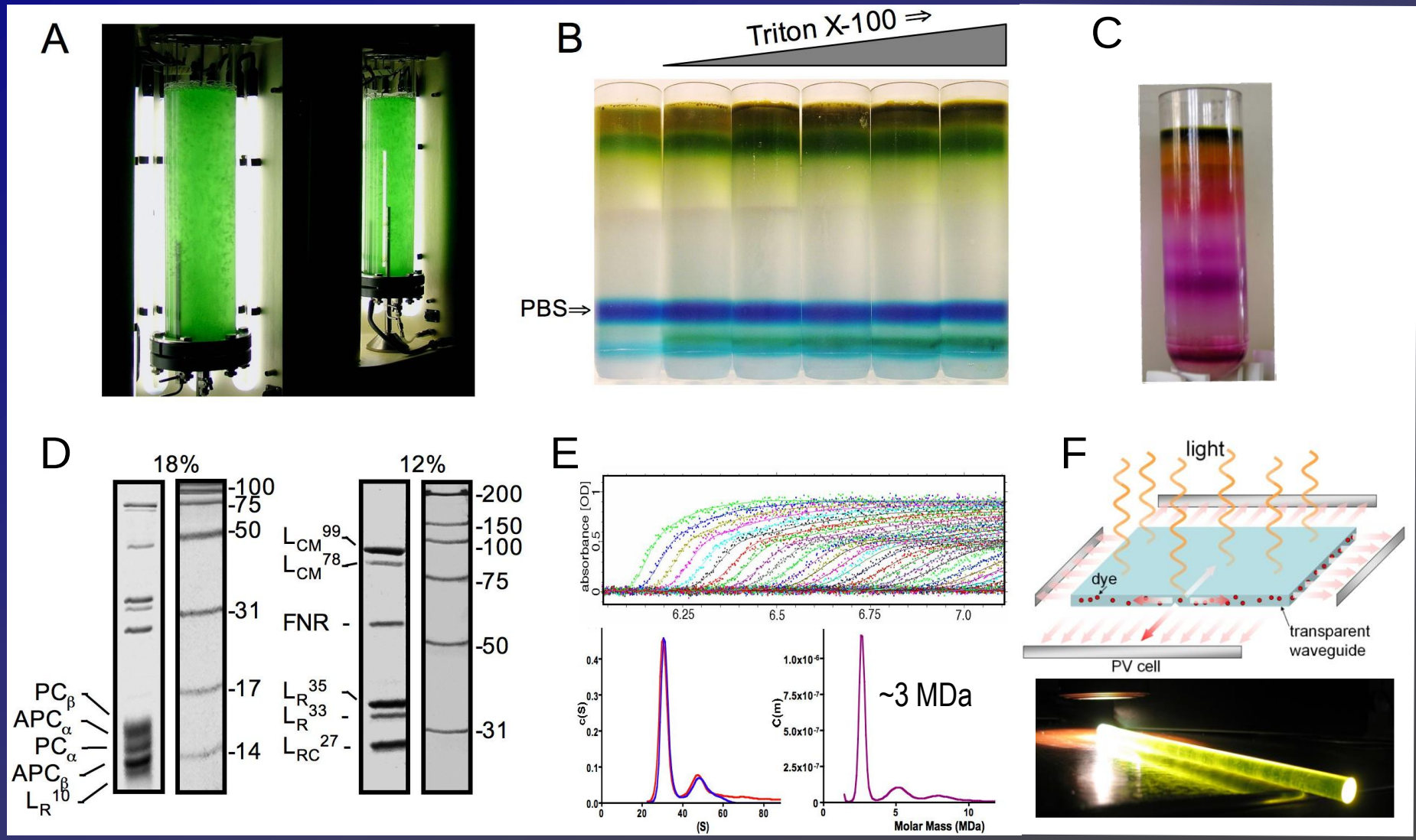
Advantages:

1. Extremely high quantum yield of fluorescence (up to 98%)
2. Precise control over transition dipole moment orientation.

Disadvantages:

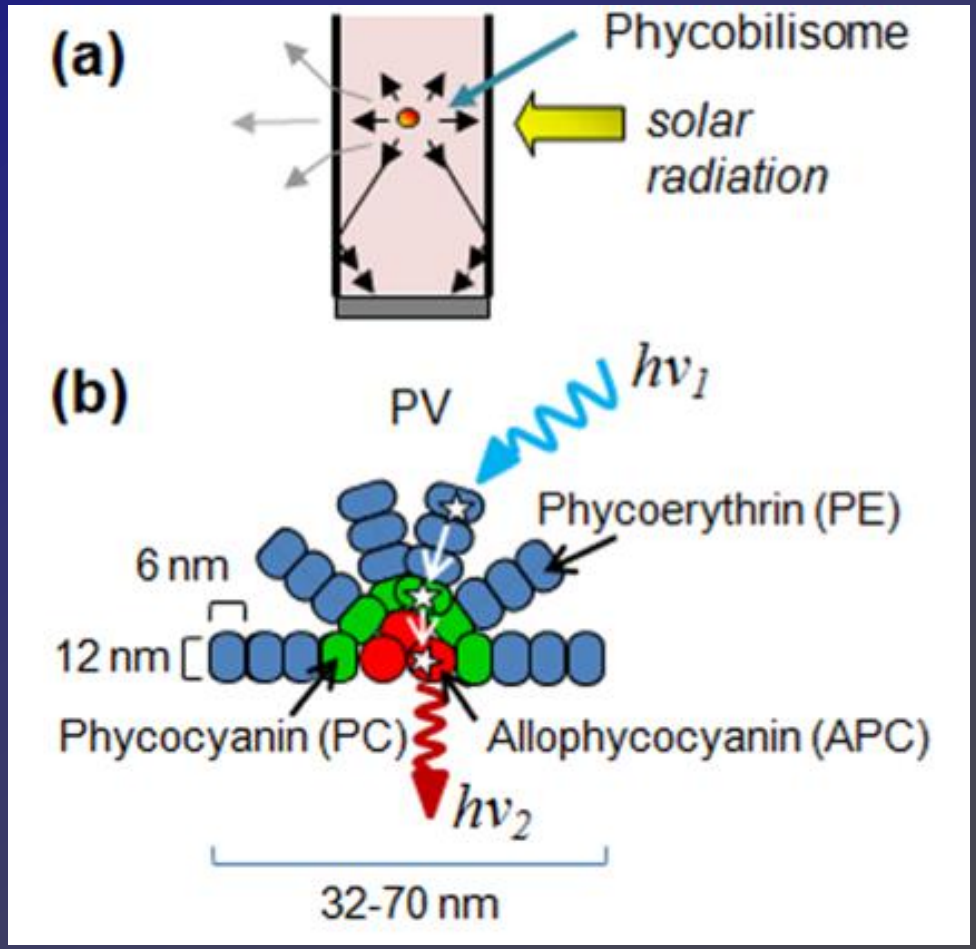
- relatively low density of chromophores
- May be hard to attach onto thin films
- Requires high salt for tight energy coupling

Isolation of Intact Phycobilisomes from *Synechocystis* WH 6803 & *Synechococcus* PCC 7803

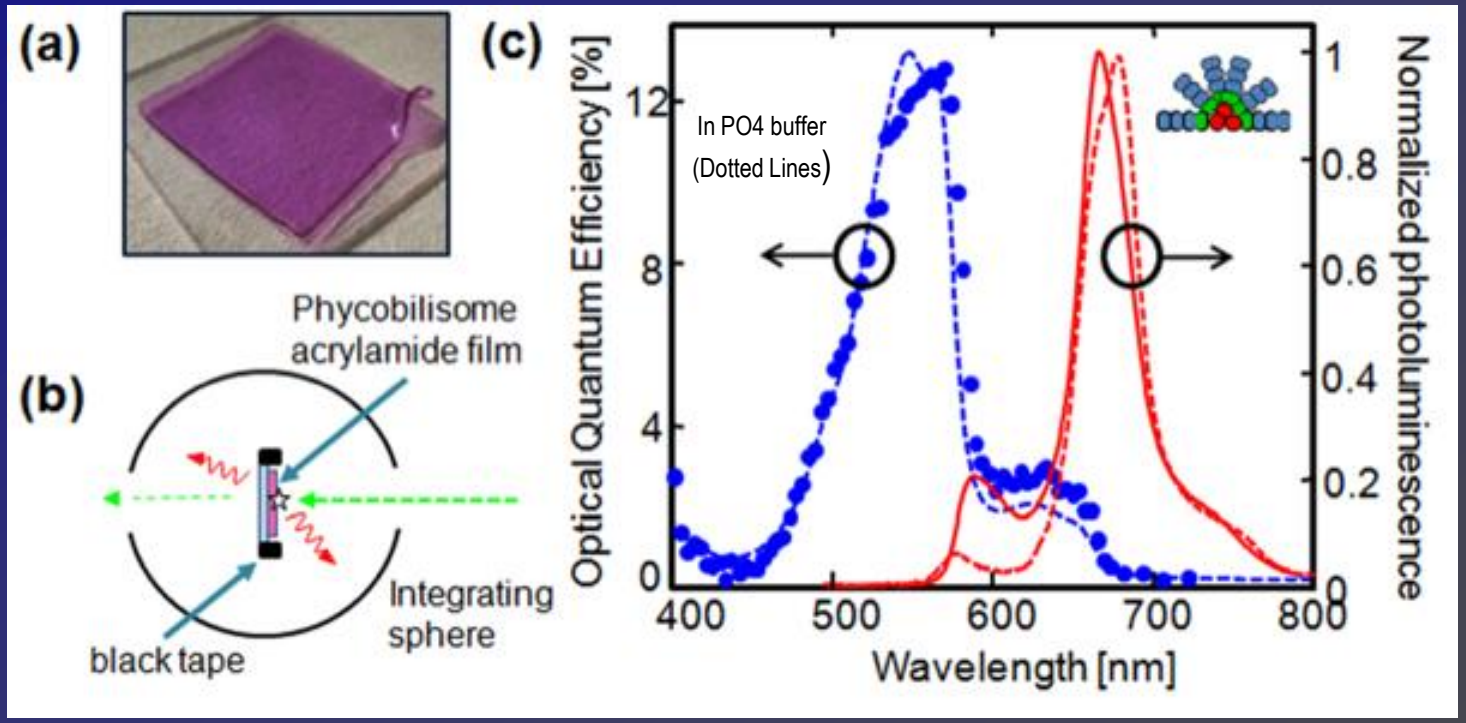


PBS are sequentially organized *dye clusters* with high efficiency energy transfer from phycoerythrin (PE_{540}) to allophycocyanin (APC_{685}).

This may permit them to function as effective solar concentrators!

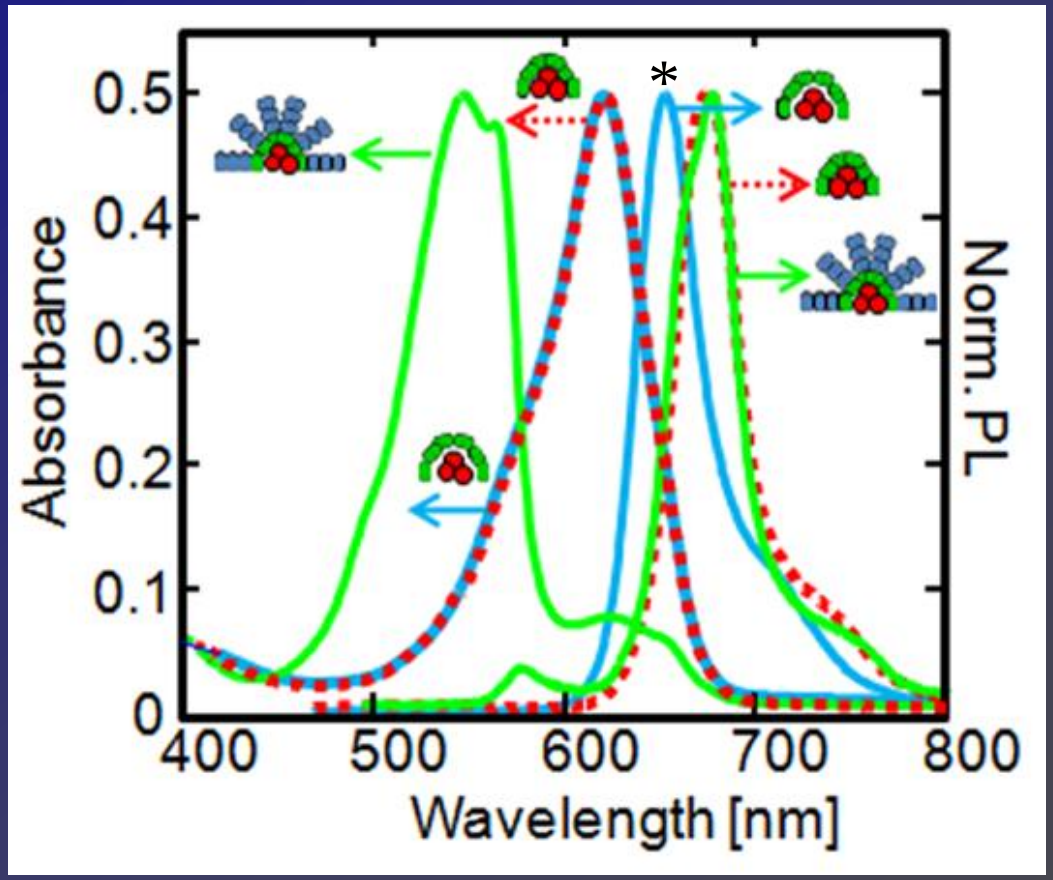


Optical properties (absorbance and fluorescence) of PBS stabilized in acrylamide film are very similar to PBS in high PO4 buffer.



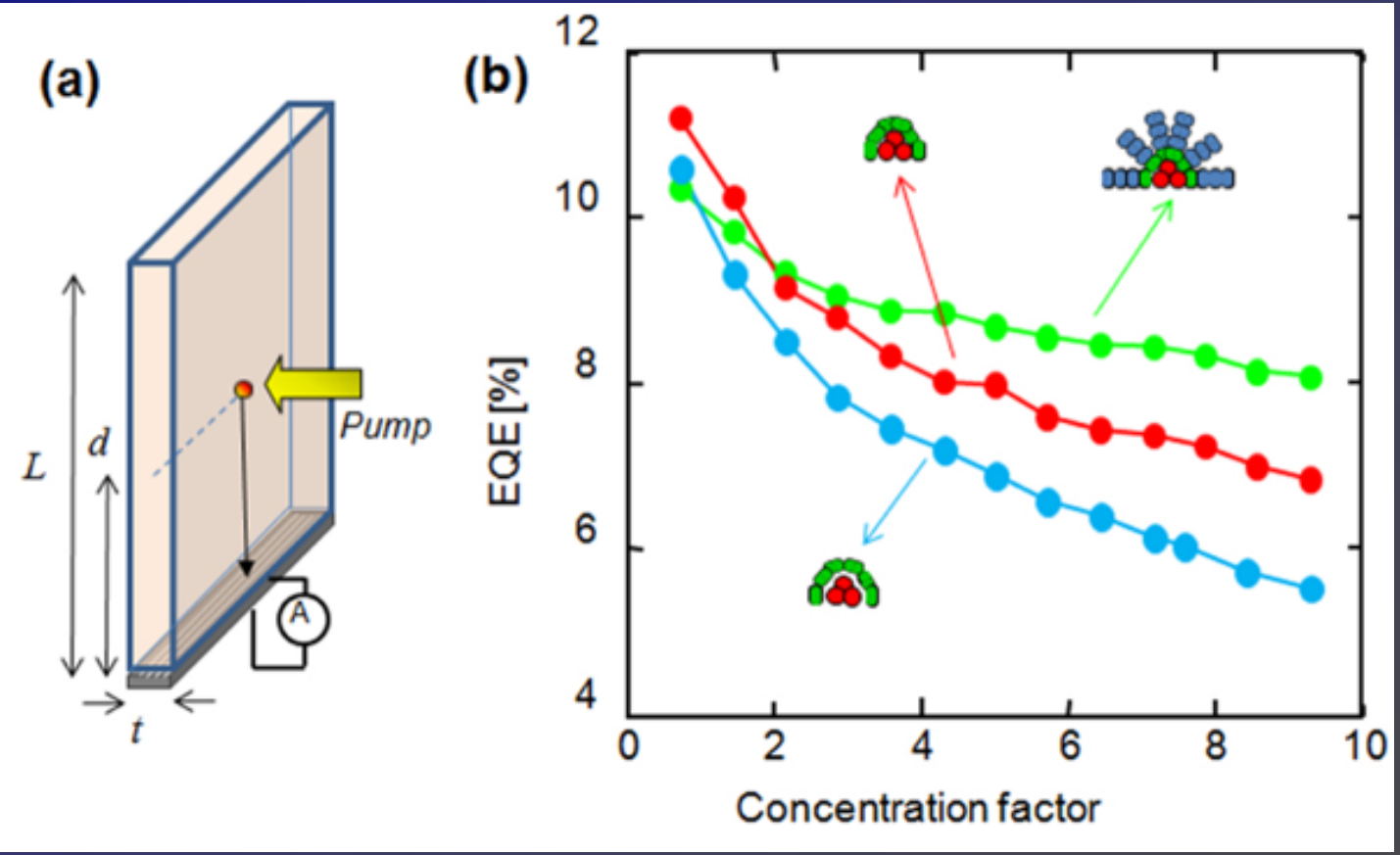
The gel immobilized PBS maintain their internal energy transfer.
*Simply combining free PC & APC fails to demonstrate effective energy transfer in gel (behaving as distinct dyes).

Native PE:PC:APC complex provides ~150 nm Stokes shift.



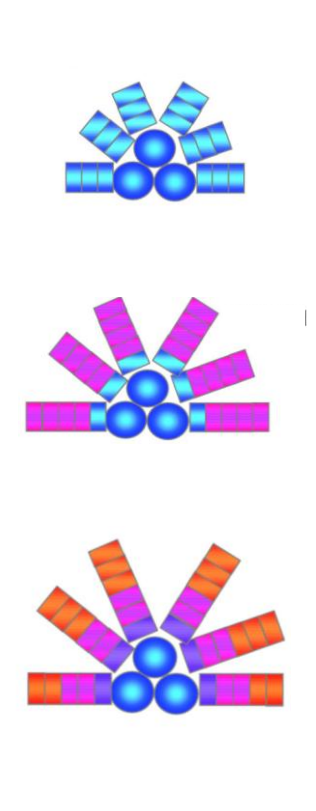
By increasing the blue absorbing pigments (PE) and maintaining tight energy coupling, the gel immobilized PBSs maintain high quantum yield while providing a high concentration factor as LSC.
Our device was only 11 x11 mm (L) & 0.5 mm thick (t)

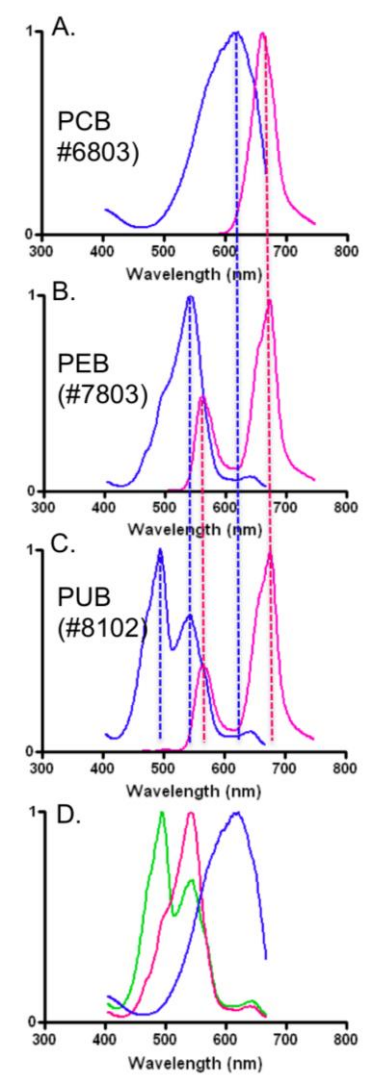
$G = L/4t$ = 11 concentration factor. Make wider and thinner!!

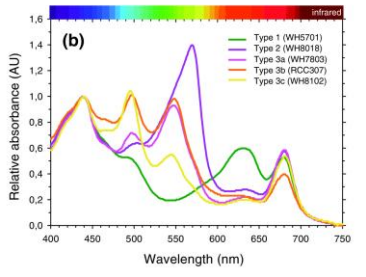


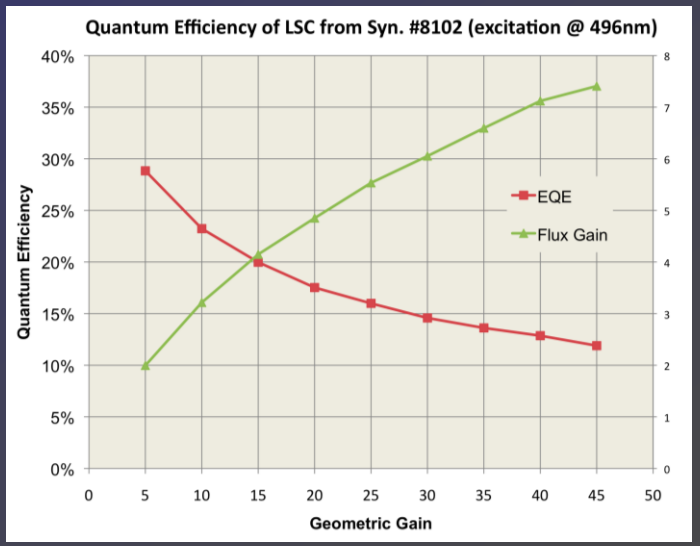
Does Nature Do Better? YES

Modeling of LSC devices w/ phycouribilin PBSs from *Synechococcus* WH8102 yields a device with EQE of >12% with conc. factors of >45!!

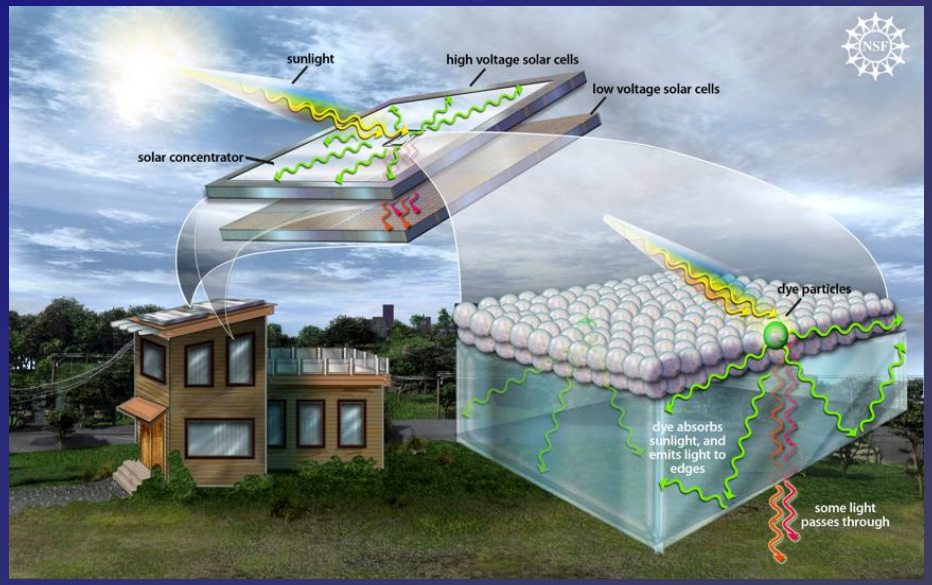


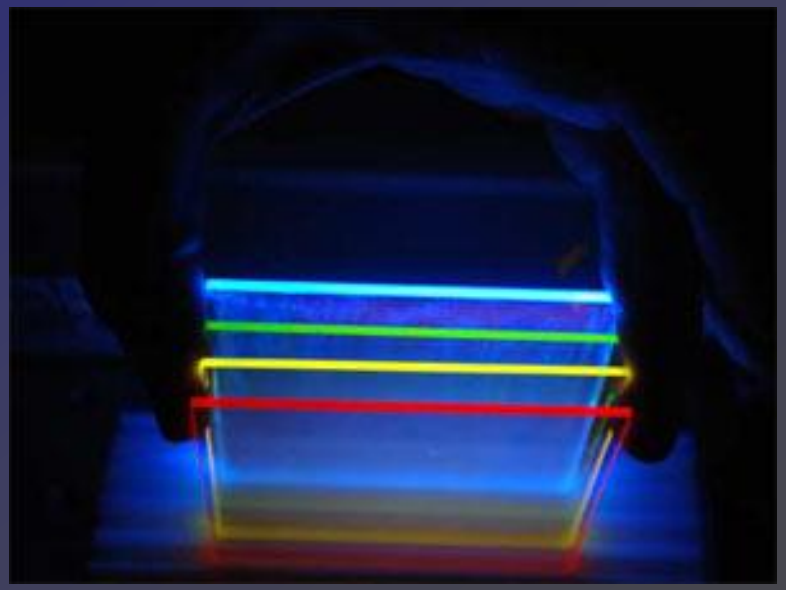






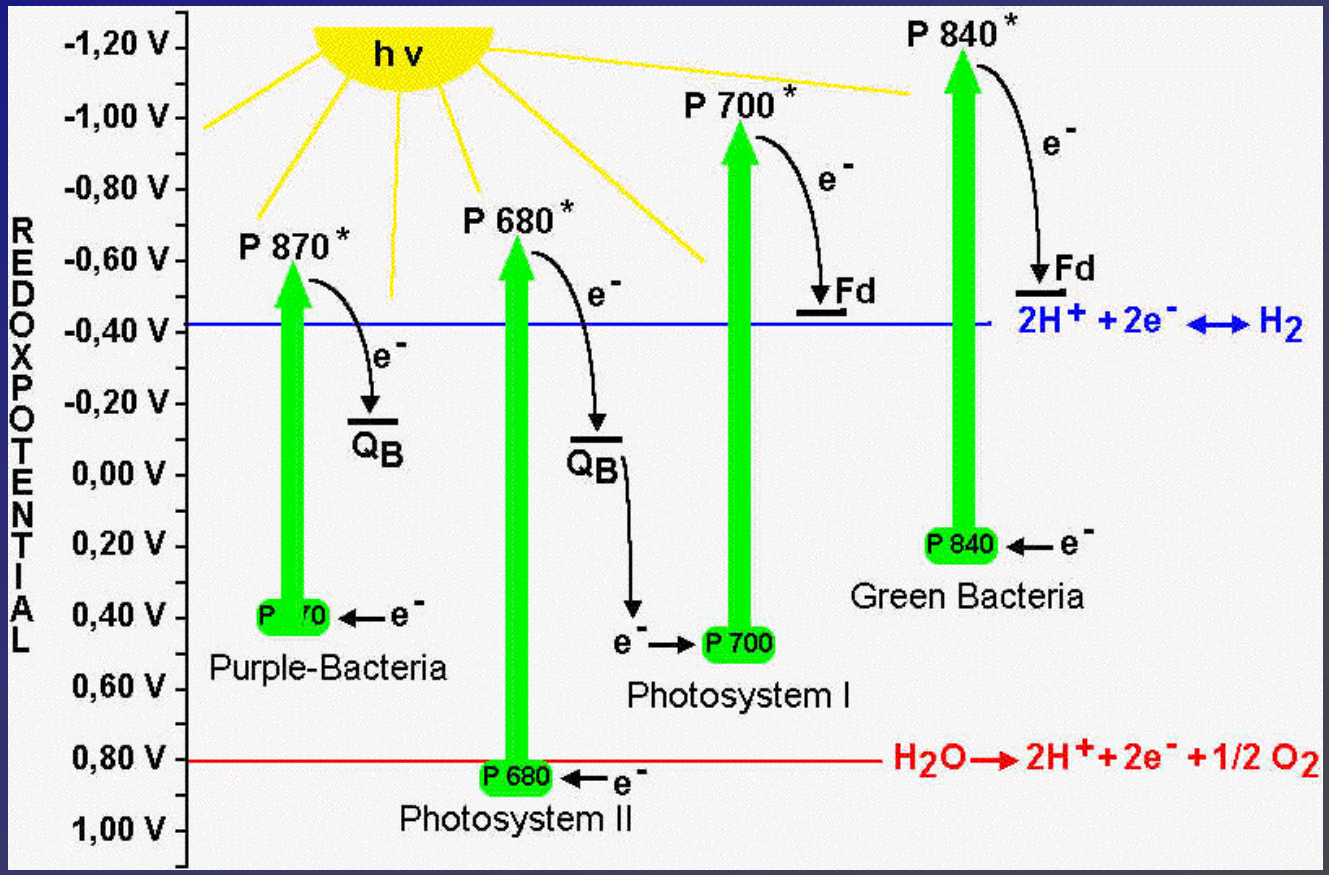
Our MIT collaborators have a new company, Covalent Solar to develop & market LSC based on organic dyes.



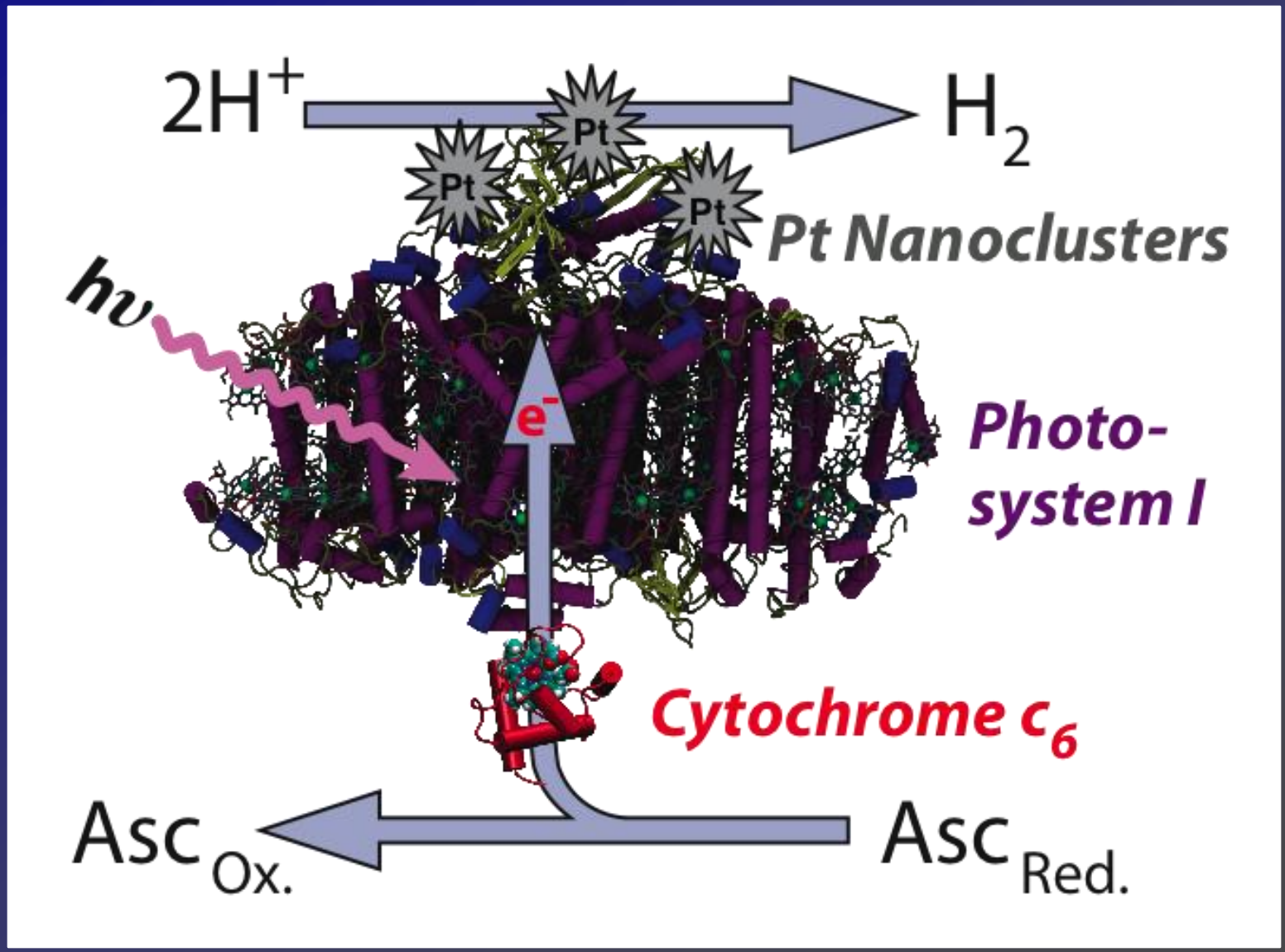


http://www.covalentsolar.com/About_Us.html

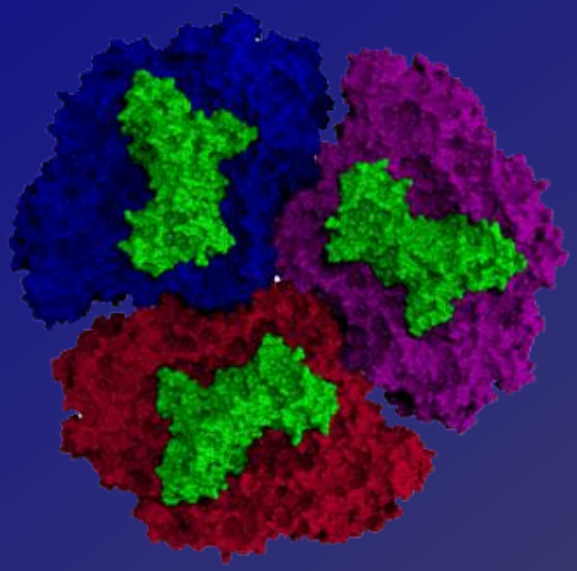
Only green bacteria and oxygenic organisms via PSI have the redox “strength” to directly produce hydrogen.



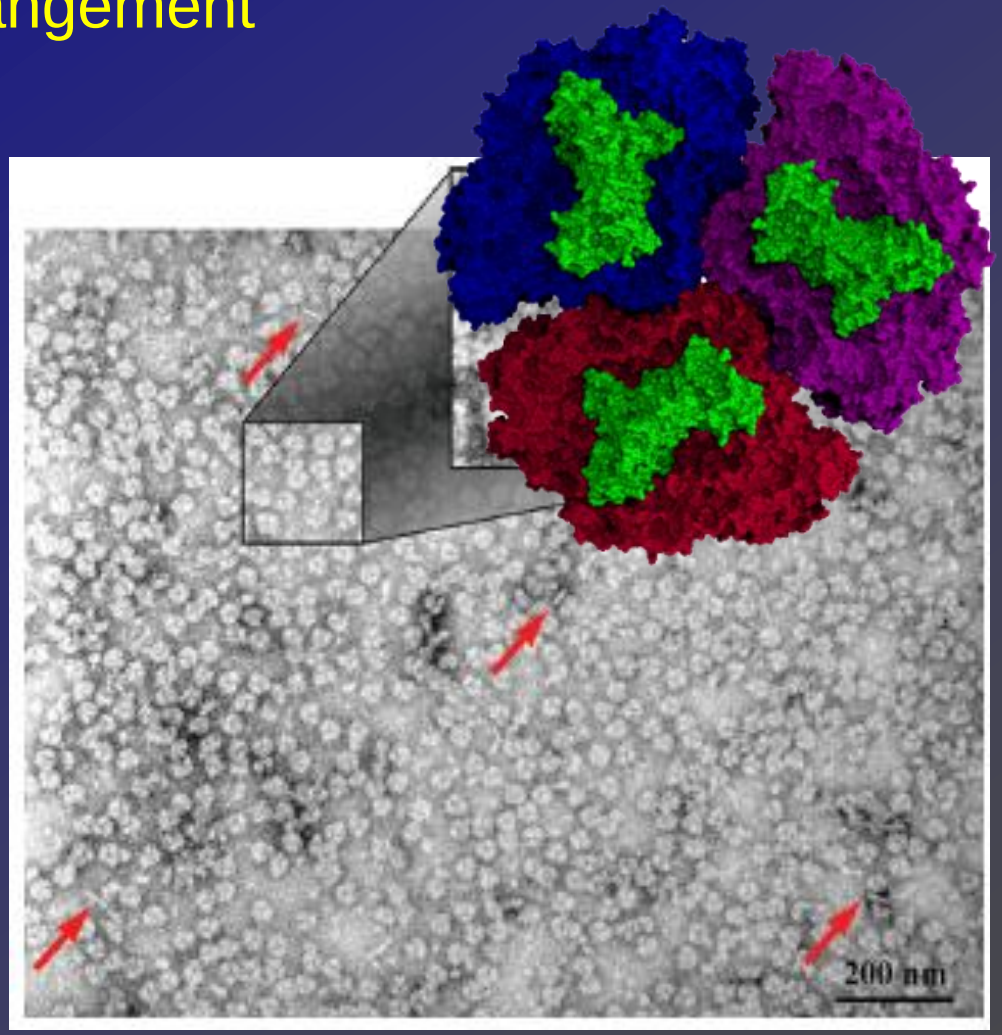
System Overview:



Confirmation of Trimeric Arrangement



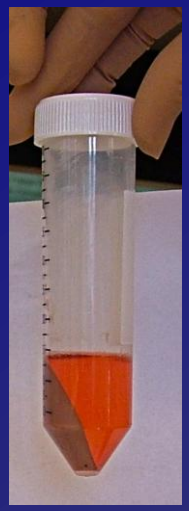
PSI trimer structure as determine by Jordan et al. Each monomer is depicted as red, blue and purple solvent accessible surfaces and the stromal humps shown in green

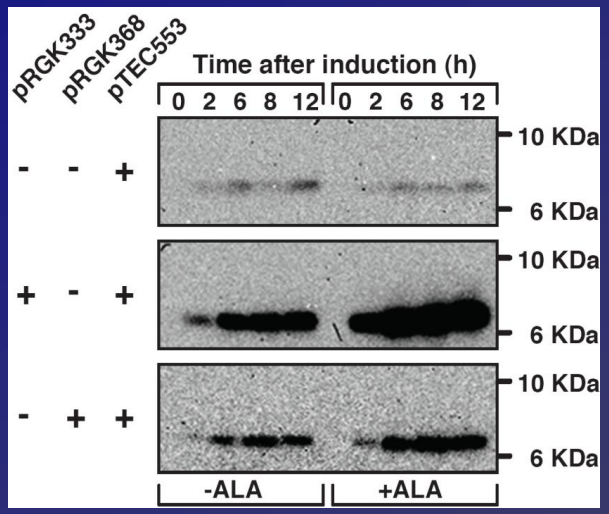


Transmission electron microscopy (TEM) on the purified complexes.
The red arrows show PSI trimers sitting on the edge.

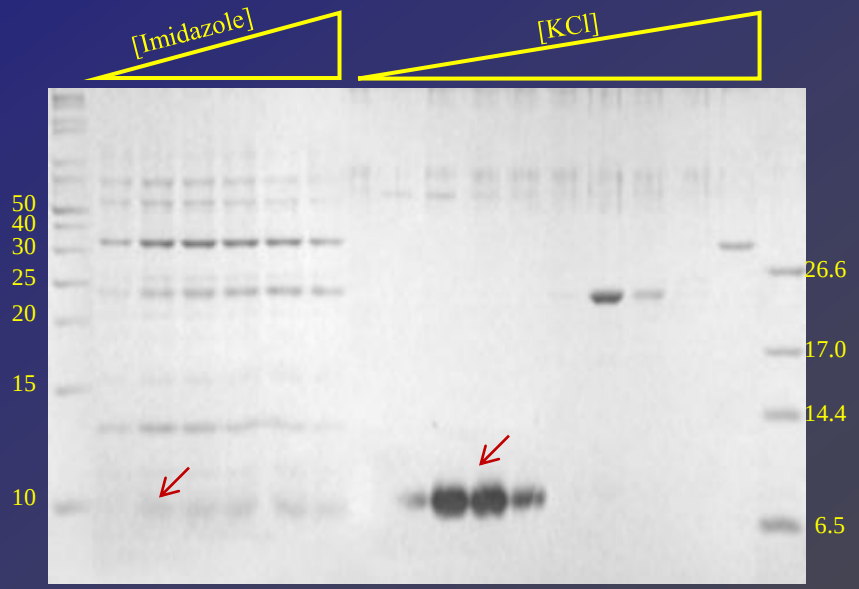
Optimization of Cytochrome c_6 using System I in *E. coli*

Immobilized Metal Affinity Chromatography (IMAC) &
High Pressure Liquid Chromatography (HPLC)





Heme stain of cyt c_6.



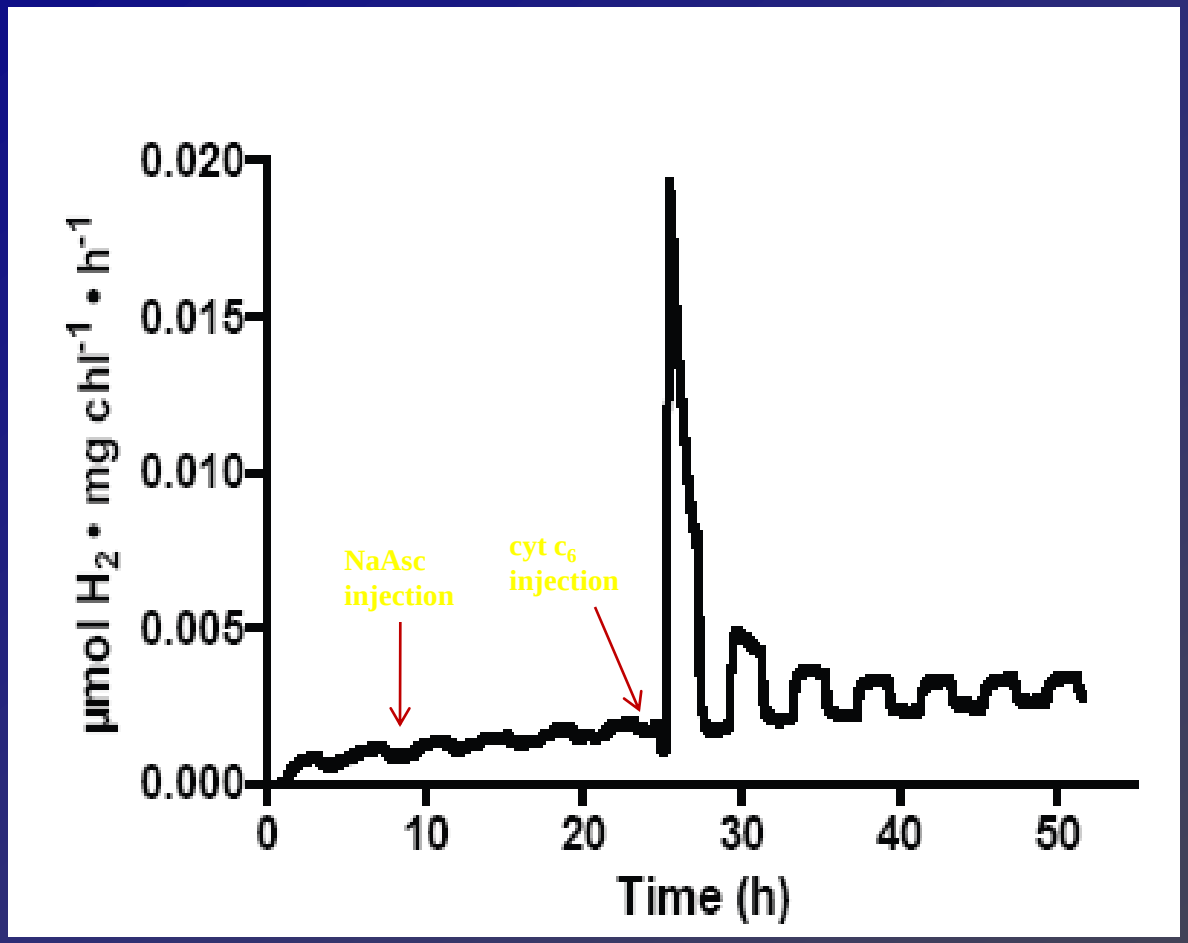
Low pressure IMAC HPLC anionic exchange

- Tris-tricine SDS-PAGE.
- IMAC purification after lysing the *E. coli* cell shows contaminant (endogenous *E. coli* protein).
- In HPLC purification cyt c_6 elutes first and the contaminants elutes later.

- pET-TEC553 and pRGK333 are system I heme insertion gene.
- pET-TEC553 and pRGK368 are system II heme insertion gene.
- Amino-levulinic acid (ALA) is a heme biosynthethic precursor.
- 7 – 10 mg/l of culture.

Determination of the Rate-limiting Step in PSI-mediated Hydrogen Evolution

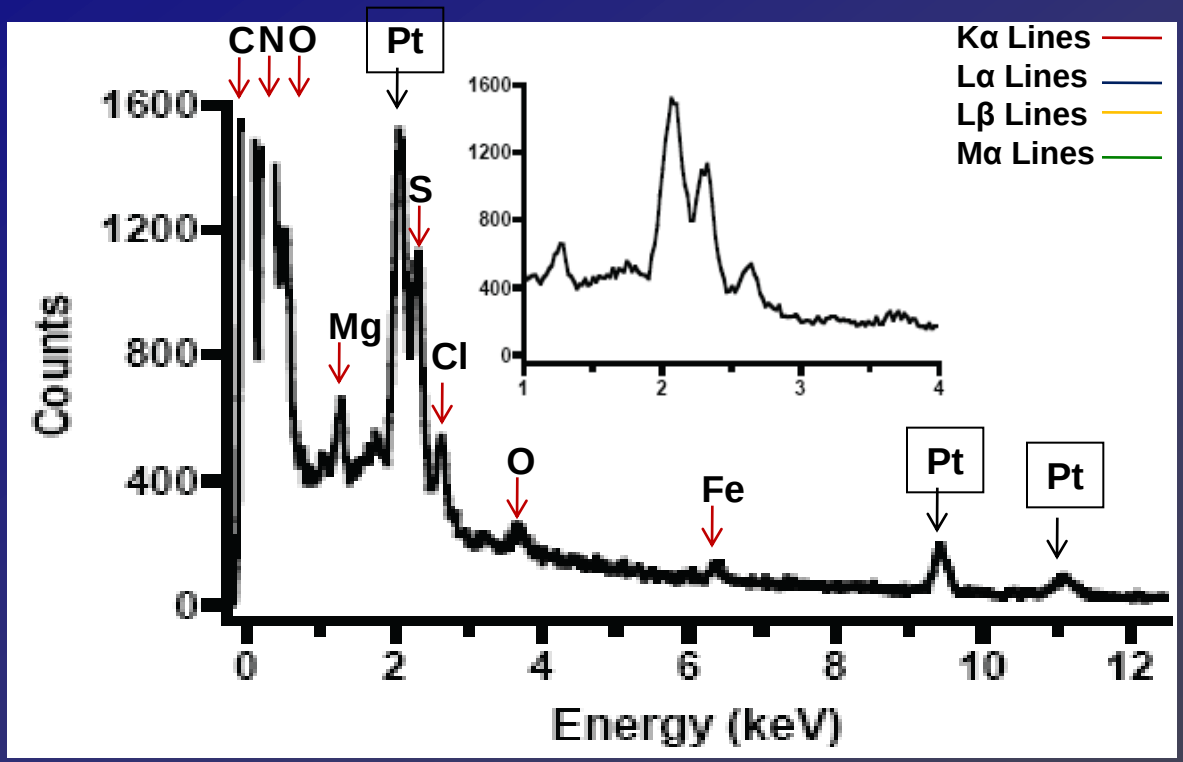
Sequence of addition experiment



- Addition of cyt c_6 supported a rapid burst of hydrogen.
- Decreased sharply to about 25%.
- We conclude that this rapid H_2 evolution was support by a large pool of fully reduced cyt c_6 which becomes depleted by the next light cycle.
- After 13 L/D cycle, the PSI was re-isolated via sucrose density gradient ultracentrifugation and dialyzed overnight.

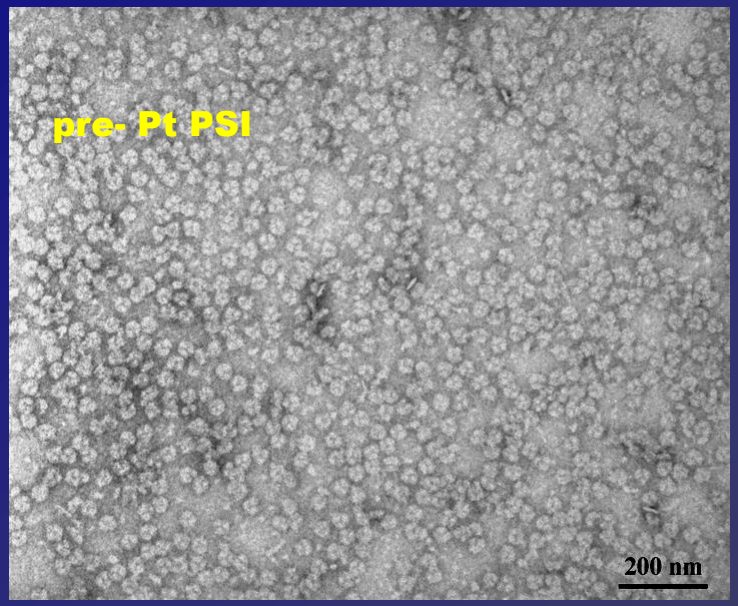
PSI at a Chl concentration of 80 µg/ml and 0. 5mM $[PtCl_6]^{2-}$ in 20mM MES buffer pH 6.4 were added at time t = 0. 1 mM NaAsc was injected through a side port into the photo-reactor at t = 7.18 h in the dark.282 µmol cyt c_6 was then added into the system at time t = 24.58 h in the dark.

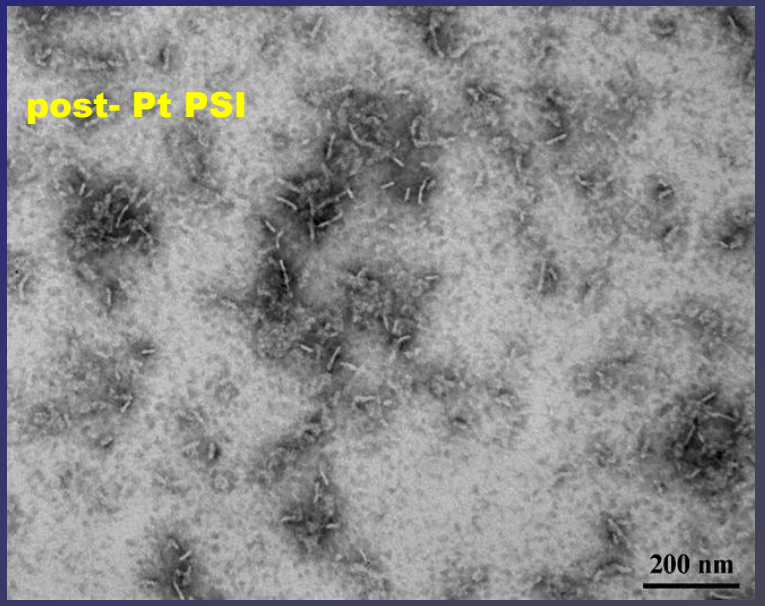
Energy-dispersive X-ray Spectroscopy of re-isolated PSI Confirms presence of tightly associated Pt Nanoclusters

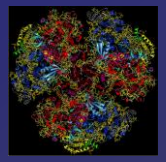


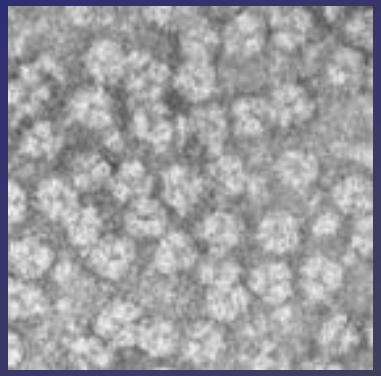
- It is clear that this sample contains platinum as indicated by the energy levels of the x-rays at 2.05 keV (Mα line), 9.44 keV (Lα line) and 11.25 keV (Lβ line).

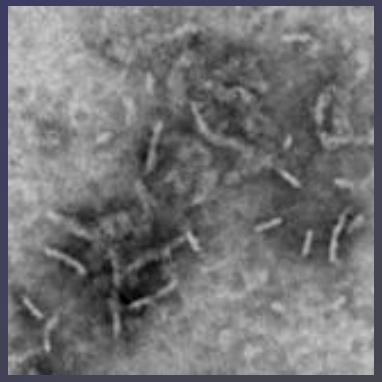
Upon platinization *T. elongatus* shifts from a well dispersed nanoparticle to some “cross-linked” aggregate structure.



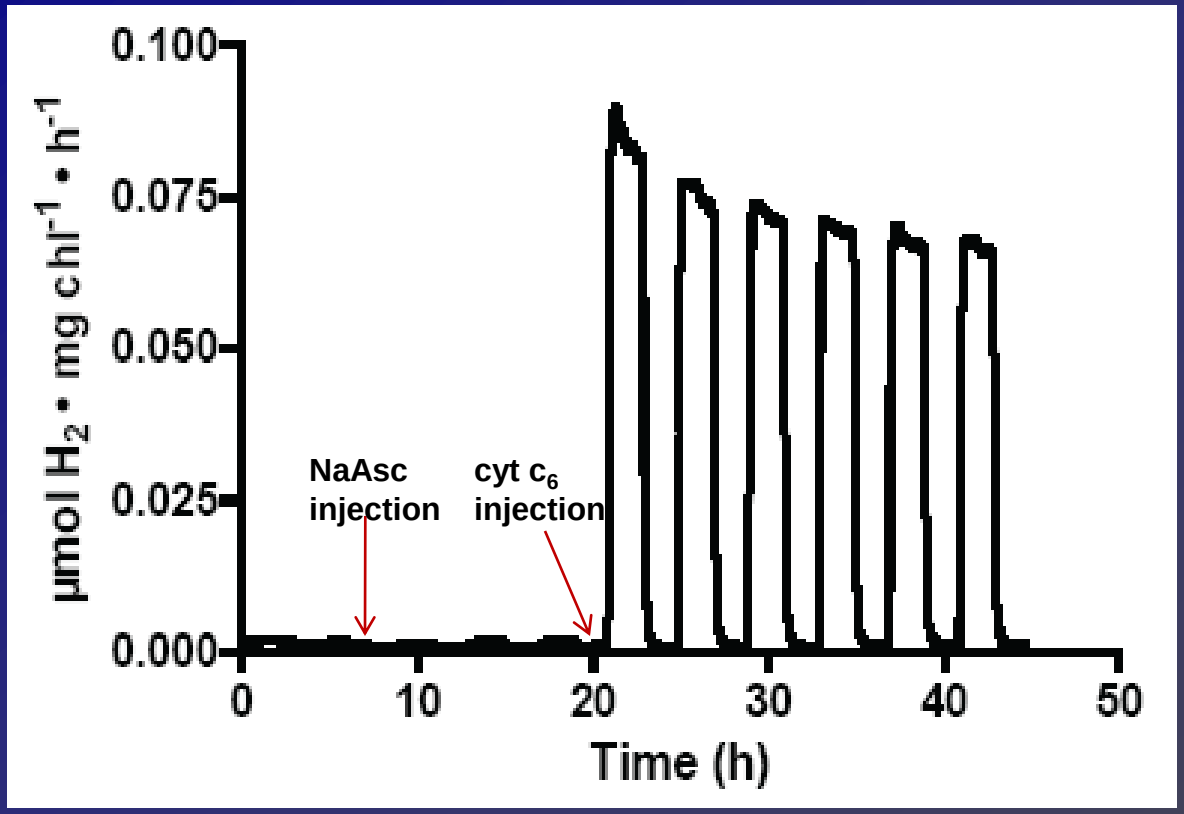








A second sequence of addition experiment on platinized–PSI complex indicates no cytochrome c cross-linking

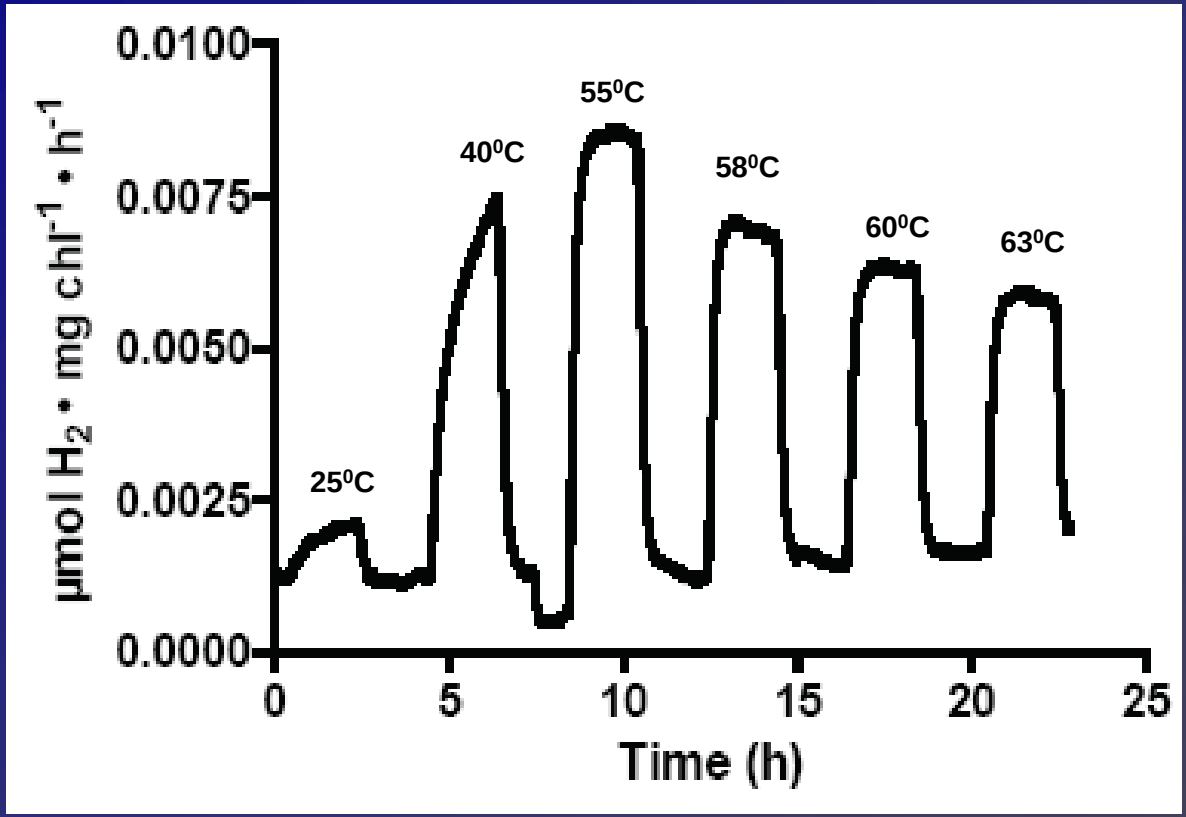


cyt c_6-free platinized PSI was initially added at time t = 0. 1 mM sodium ascorbate were added at time t = 7.5 h and cyt c_6 was then added at time t = 20.09 h.

- H_2 evolution rate increase approximately 80- fold following the addition of cyt c_6.
- Our result indicates that the initial treatment results in a stable form of platinum integration into PSI.
- We observe a decay in the H_2 evolution.

Evaluation of Thermostability, Kinetic Limitations and Sustainability.

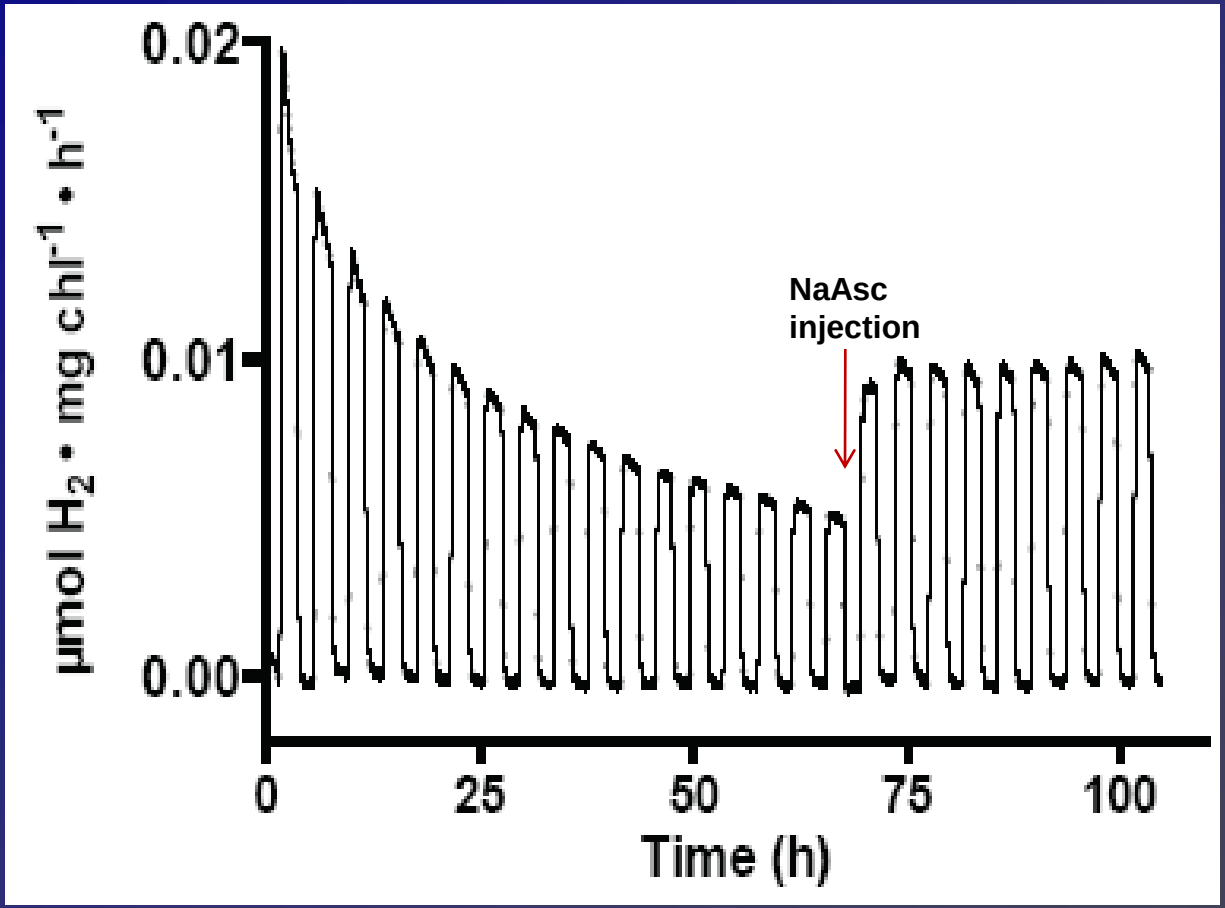
Temperature-activity measurement on dialyzed PSI prep



An external water bath was used to incrementally increase the temperature during successive 2 h light on/off cycles allowing the reaction to equilibrate during the dark cycles.

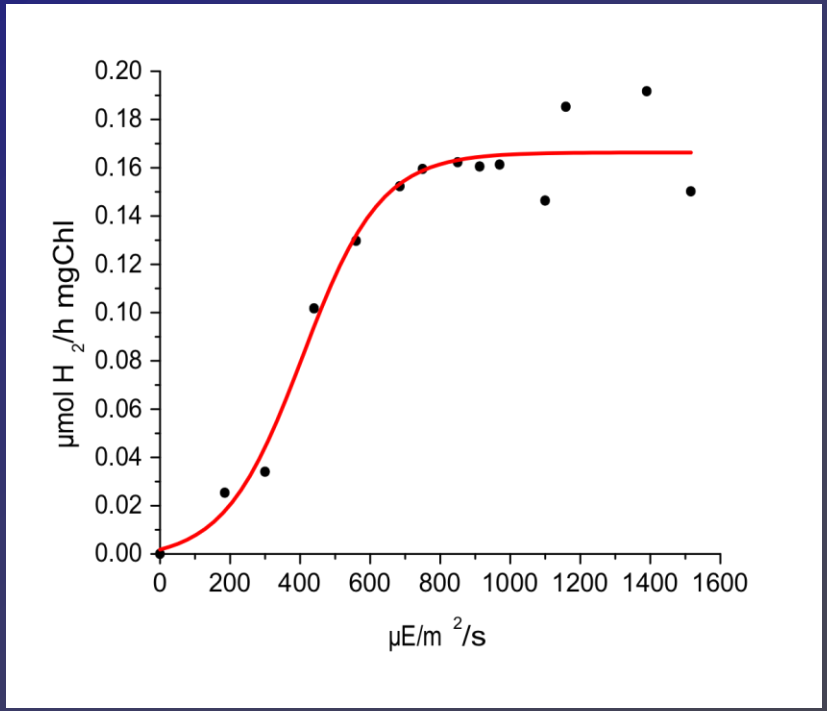
- The highest rate of hydrogen evolution was observed at 55^{0}C.
- This decay suggests that there is some systemic component that is loosing its activity during multiple L/D cycle.
- NaAsc is the only consumable component that was added in excess to facilitate the re-reduction of cyt c_6.

Decay appears to be due to both catalytic “poisoning” and potential NaAsc consumption

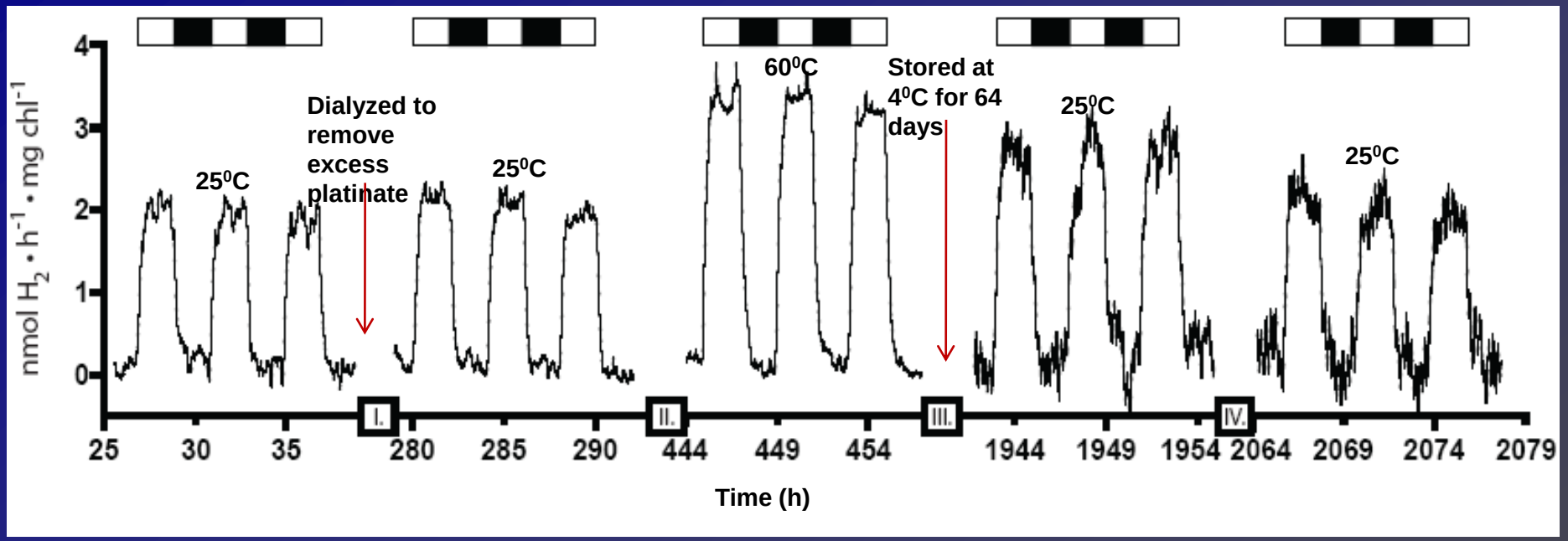


- Injected a new aliquot of 1 mM NaAsc at t = 68h.
- H_2 evolution rate increase by ~80% and is stable and free from decay fold following the addition of cyt c_6.
- This rates remained stable for another 35 light/dark cycle (data not shown).

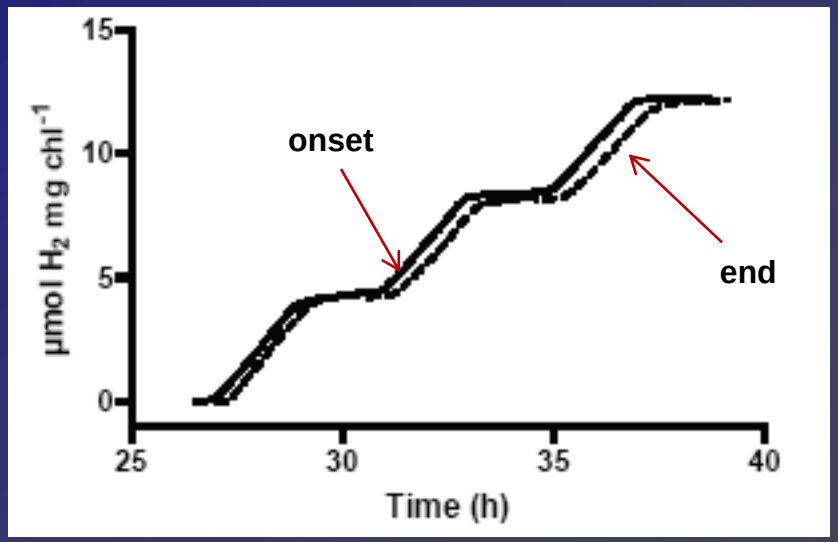
Platinized PSI demonstrates a light dependent hydrogen production with a plateau of ~800 μE/m^2/s PAR. Saturating light does not appear to inhibit activity. H2 yield is now limited by some other step besides photon capture, possibly PSI re-reduction by cyt c_{553}.



Long-term (3-month) stability of Platinized PSI hydrogen evolution

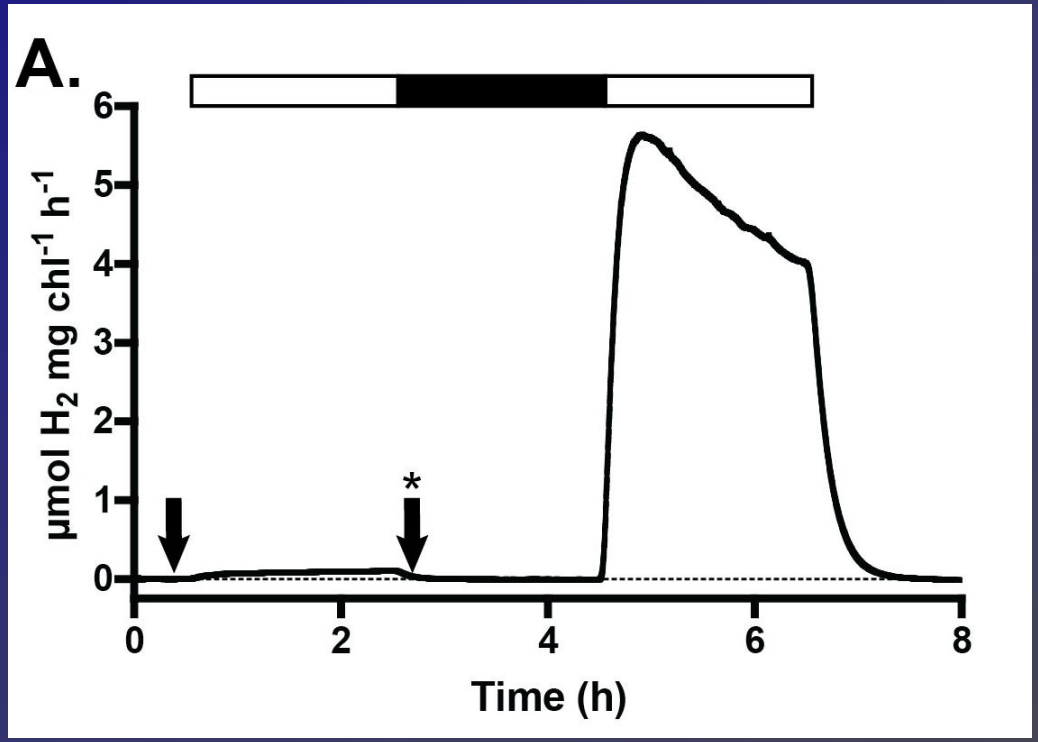


Average values of H_2 evolution at 25⁰C



- H_2 evolution at 60⁰C increased by 80%.
- Our PSI preparation maintain operational stability for extended time periods >90 days

Peak rates of hydrogen evolution (~6 µmole H_2/mg chl a/hr)



Peak rates of hydrogen evolution. Platinized PSI complexes (5 µg chl/ml), 100 mM NaAsc, and 4.4 µM cyt c6 in 20mM MES buffer pH 6.4. White light from a halogen bulb light source was used at an intensity of about 1200µE/m2/s. Cyt c6 was added into the system at time t = 2.8 h in the dark as indicated with an arrow.

If scalable, how does yield comparison with other BioEnergy strategies?

Fuel	Specific Fuel Value (equivalent yield in liters gasoline/hectare/day)
Soybean biodiesel	1.42
Corn ethanol	5.43
Switchgrass ethanol	12.1
Bio-Pt H_2	300.8

Pimentel, D. & Patzek, T. Ethanol Production Using Corn, Switchgrass, and Wood; Biodiesel Production Using Soybean and Sunflower. *Natural Resources Research* **14**, 65-76 (2005).
Pimentel, D. in Encyclopedia of Physical Science and Technology, Vol. 2, Edn. 3rd. (ed. R. Meyers) 159-171 (Academic, San Diego, CA; 2001).

Conclusions:

- PSI can be platinized through a self-assembly process.
- Platinized PSI photo-reduces protons to hydrogen
- Process requires cytochrome c to couple sacrificial donor (Asc)
- Hydrogen evolution is functional up to ~65°C.
- Platinized PSI is active for > 3months
- If scalable, yield is currently greater than biomass conversion.
- Many *easy* opportunities for improved yield.
- Need truly sustainable electron donor-PSII!
- Hydrogenase may have higher yield and sustainability?

The NIRT Team Members:

-UTK-

Biochemistry, Cellular and Molecular Biology

- Wang Qiang: Phycobilisome stabilization
- Michael Vaughn: Photosystem I isolation
- David McWilliams: Mass spectrometry
- Sarah Wright: Analytical ultracentrifugation

Chemical & Biomolecular Engineering

- Mehrsa Raeiszadeh: Modeling of Kinetics
- Ifeyinwa Iwuchukwu: O_2 uptake & H_2 Evolution
- Dibyendu Mukherjee: PSI Immobilization
- Paul Willard, Cyanobacteria
- Bamin Khomami, co-PI
- Paul Frymeir, co-PI

Chemistry

- Mark Dadman, co-PI
- Jimmy Mays, co-PI

Microbiology

- Natalie Myers: Cytochrome c expression , Cyanobacteria Transformation

-MIT-

Electrical Engineering and Computer Science

- Tim Heidel: Solid state antennas, ET
- Michael Segal: Spin resonances: theory
- Jon Mapel: LSC
- Kemal Celebi: Dipole radiation modeling
- Kelley Rivoire: Spin resonances: device fabrication
- Mike Currie: Integration of photosynthetic complex
- C.L. Mulder, LSC
- L. Theogarajan, LSC
- Jon Mapel: LSC
- *Marc Baldo , Co-PI*

Biomedical Engineering

- Andreas Mershin, TiO nanotubes
- *Shugwang Zhang, Co-PI*

-ORNL-

- Barbara Evans: Chemical Crosslinking
- Jennifer Millsaps: H_2 Evolution measurement
- Hugh O'Neill: PI
- Elias Greenbaum: PI

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- UTK Office of Research SARIF Program
- Sustainable Energy and Education Research Center
- NSF Sustainable Science Program
- DARPA
- Intel

Thank you!
Questions?