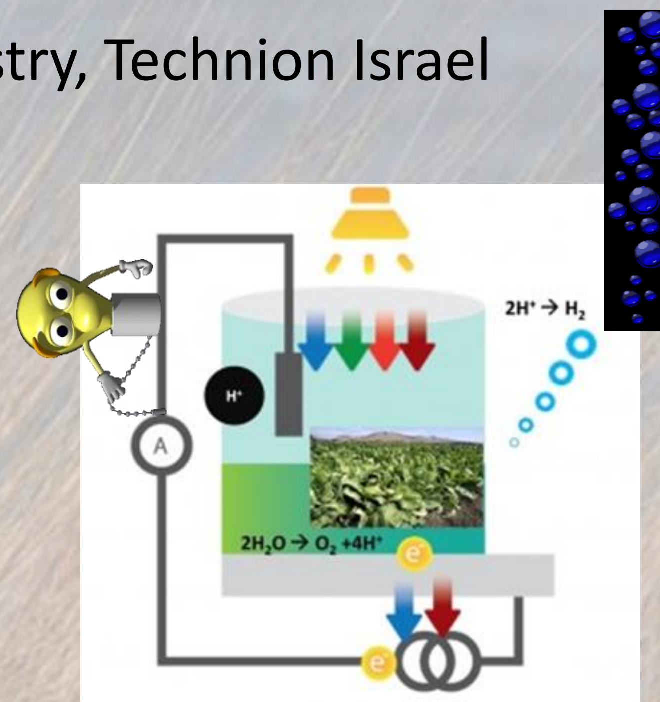
Utilizing Photosynthetic Complexes for Solar Energy Conversion: Building a Bio-generator

Noam Adir - Schulich Faculty of Chemistry, Technion Israel



Solar Fuels I-Core

GTEP Grand Technion Energy Program | Securing Israel today. Transforming Israel's tomorrow.

Schulich Faculty of Chemistry Technion – Israel Institute of Technology

שוליך הפקולטה לכימיה ע"ש
הטכניון - מכון טכנולוגי לישראל

TECHNION Israel Institute of Technology

March 8, 2018

Acknowledgements

The Lab

Avital Lahav
Dvir Harris
Shira Bar Zvi
Itay Goldschmid
Maayan Swissa
Tarek Tarabeh
Tünde Töth

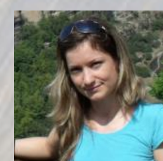
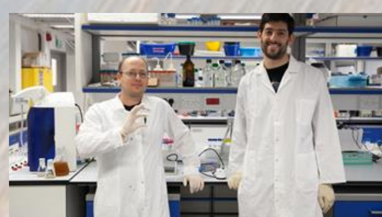
Past Members

Dan Kallmann
Roy Pinhassi
Faris Salama
Gadiel Saper

Ruhr Universitat Bochum

Wolfgang Schuhmann



Technion

Gadi Schuster, Biology
Shirly Larom, Biology
Varda Livneau, Biology
Avner Rothschild, Materials


Funding: ISF, I-CORE, BSF, DFG-DIP, GTEP

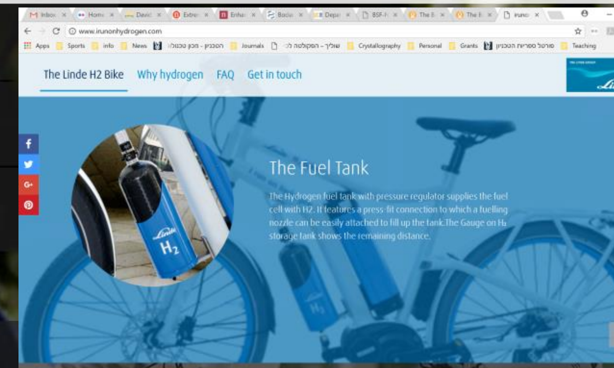
The Driving Force for our Research

The Driving Force for our Research

The Linde H2 Bike | Why hydrogen | FAQ | Get in touch

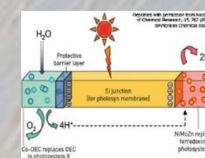
Frame material	Aluminium
Gears	Shimano deore M610
Tyres	Schwalbe Big Ben 55-559/26 x 2.15
Rims	Sun Ringle Track 26"
Pedals	Wellgo Co98 Blk

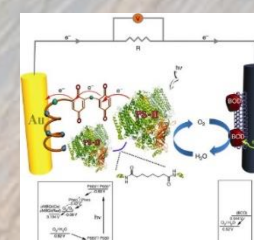
H2 SYSTEM	
Weight of fuel cell system	3.7 kg
Max. working pressure of cylinder	340 bar
Storage capacity	33gr H2, corresponding to 1,000 Wh
Range per cylinder filling	> 100 km
Fuelling time	1 – 6 min
Fuel cell lifetime	5 years
Fuel cell efficiency	~ 50%
Buffer battery	60 Wh

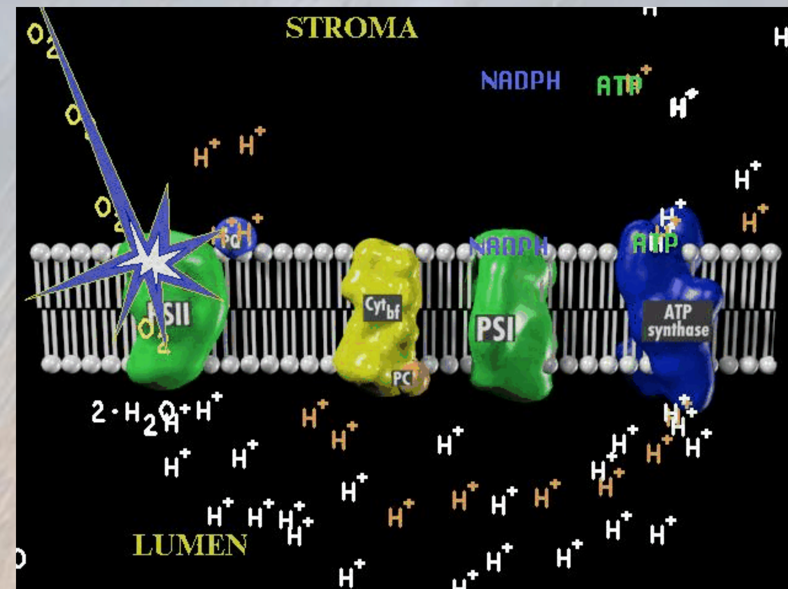


Photosynthesis for solar energy conversion
Present and Future Technologies

- Biomass (combus
- Biofuels (combus
- Artificial photosy
  compounds, hea
- Photosynthetic c
  complexes, chem
  electrochemical s

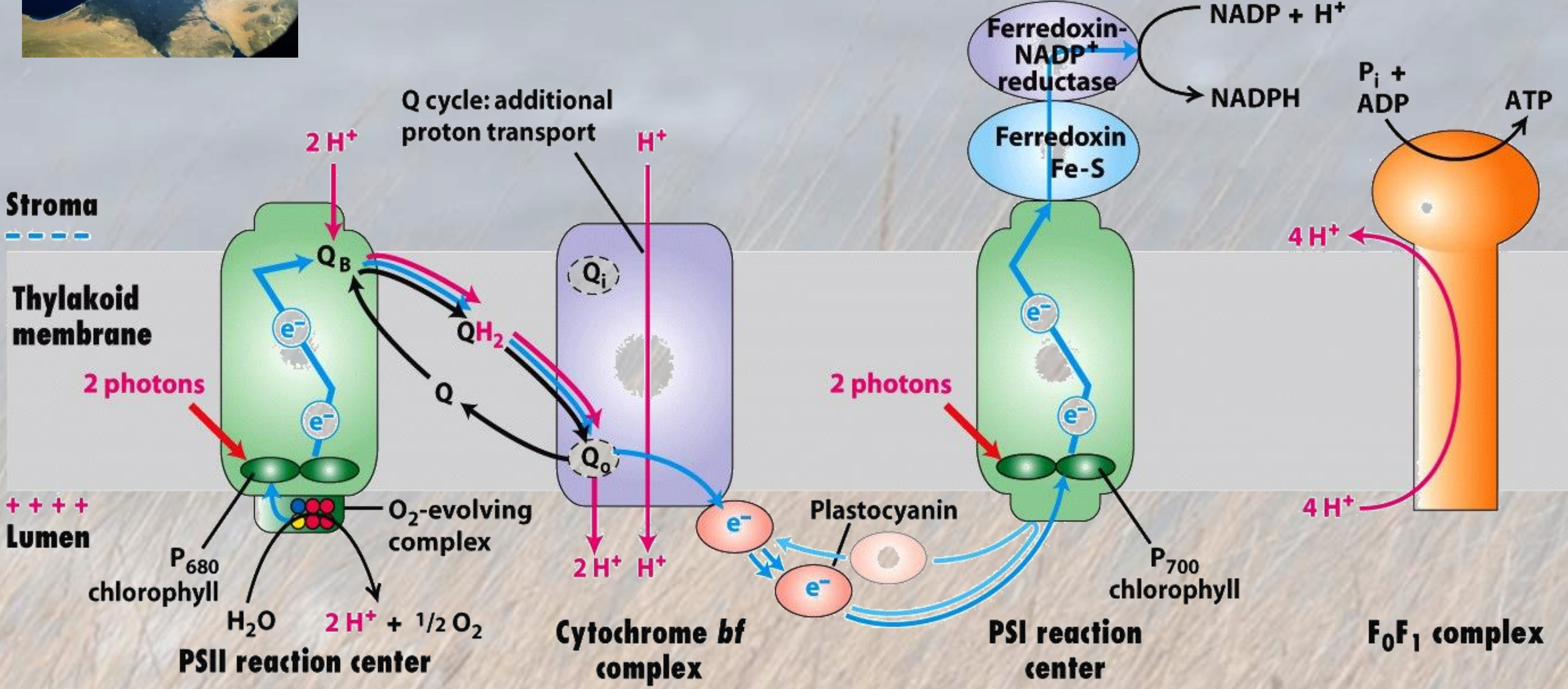





STROMA
NADPH
ATP
PSII
Cyt bf
PC
PSI
ATP synthase
LUMEN


P.7

The Oxygenic Photosynthetic membrane

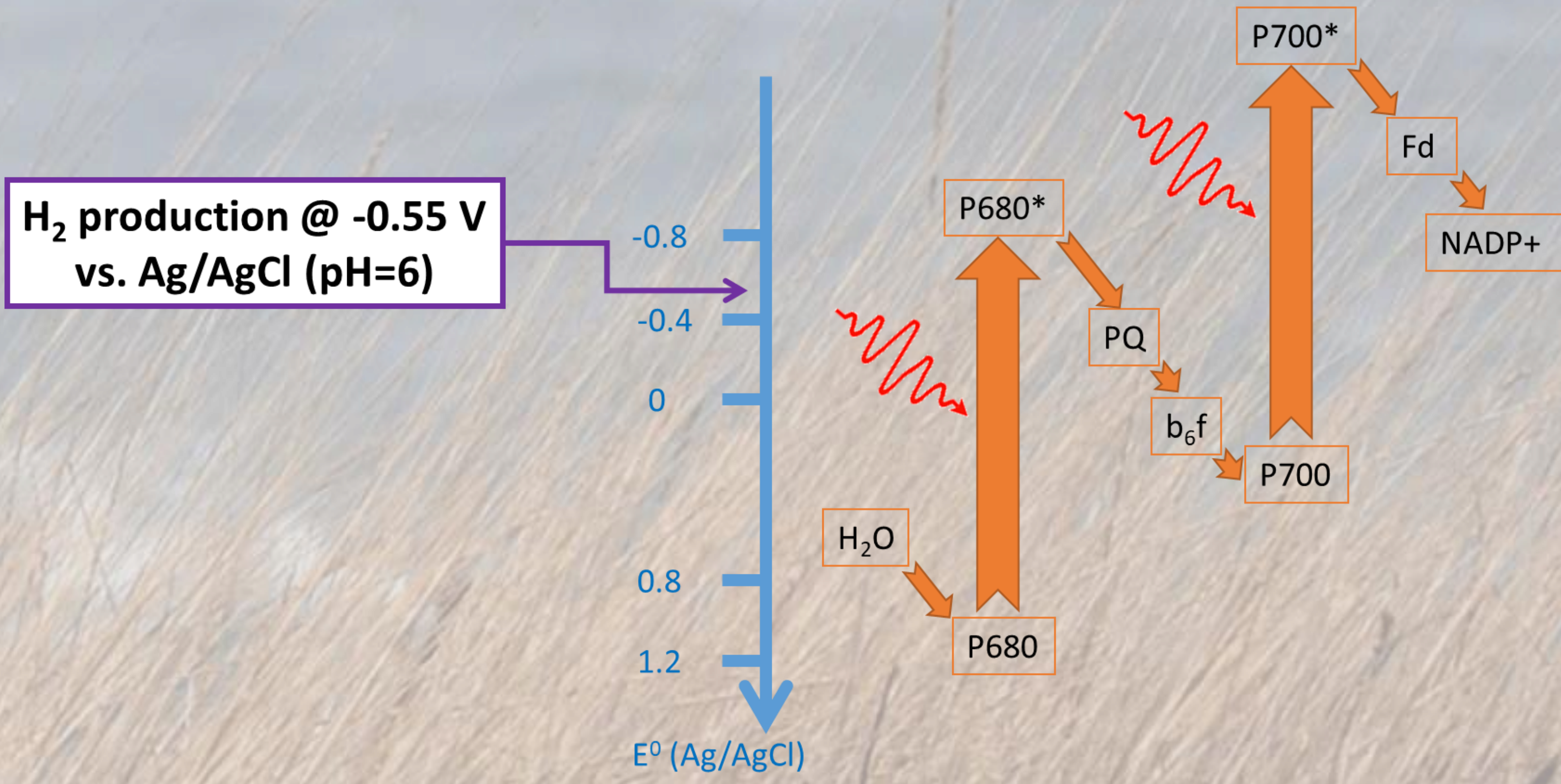


http://www.studyblue.com/notes/note/n/bio-final/deck/26494

20-200mA/mg chlorophyll at full activity

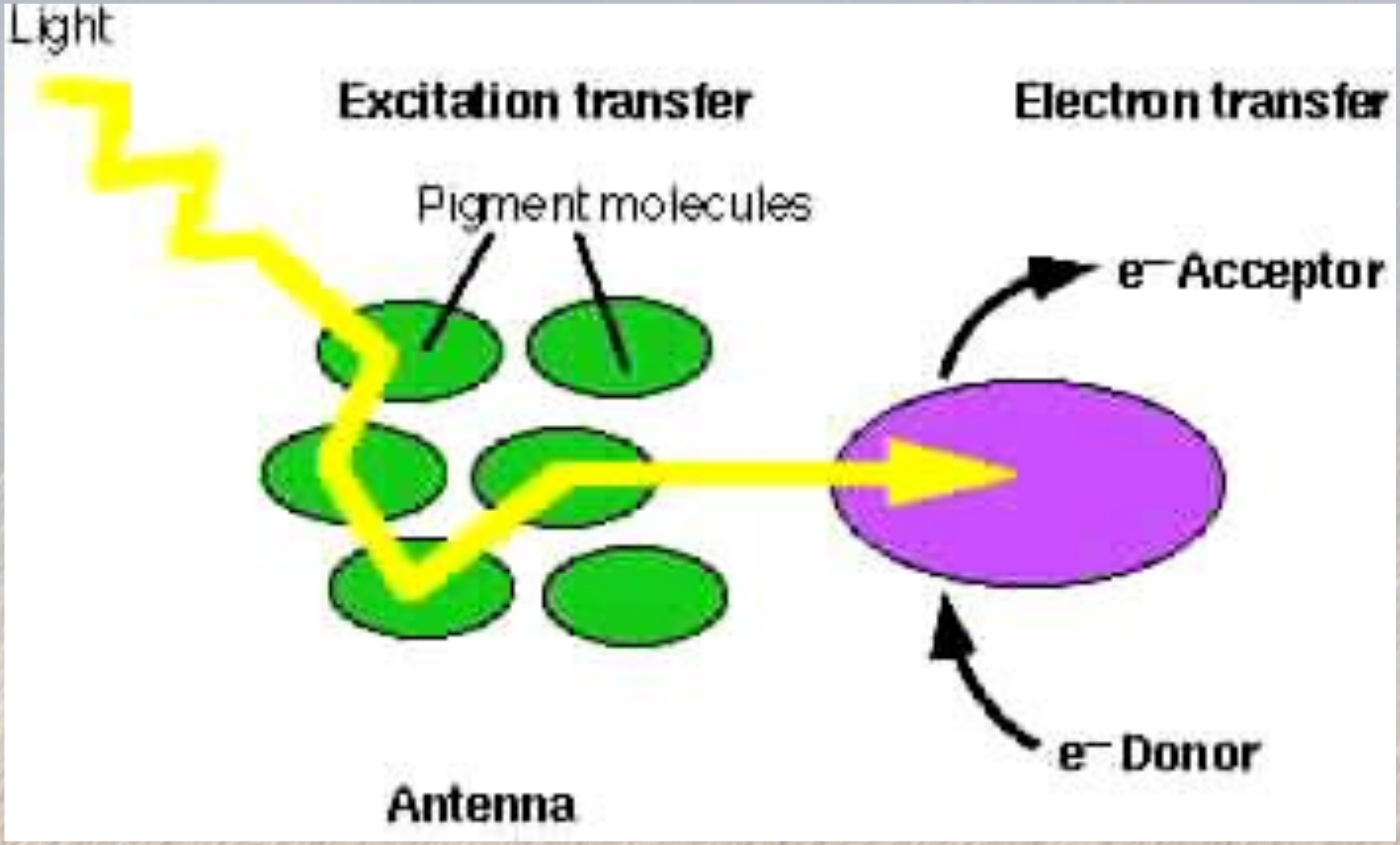
1 mg chlorophyll = ~ 1 leaf

Oxygenic Photosynthesis provides the strongest oxidant (PSII) and most negative reductant (PSI) in Nature

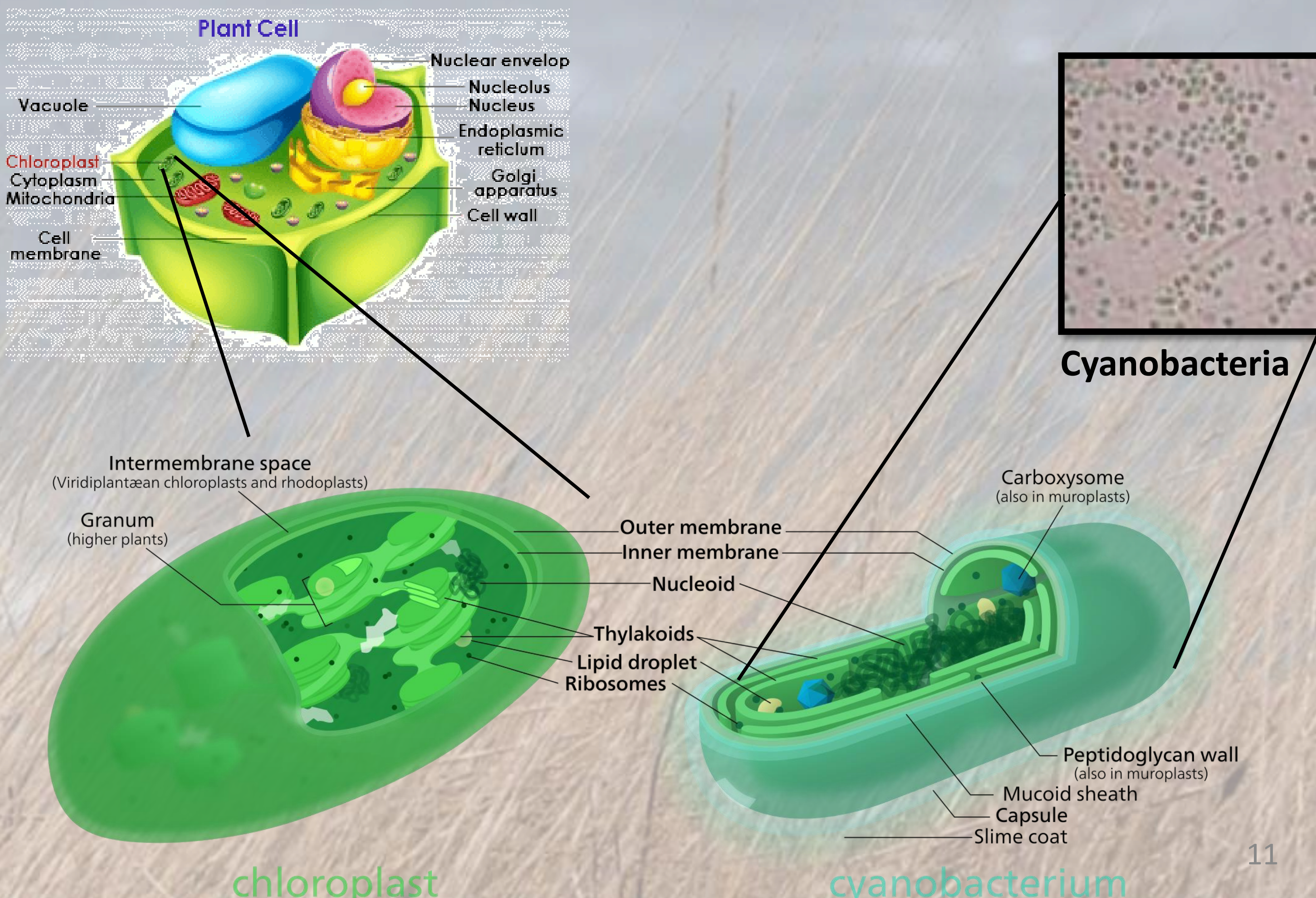


Z diagram of the electron transport in the photosynthesis process

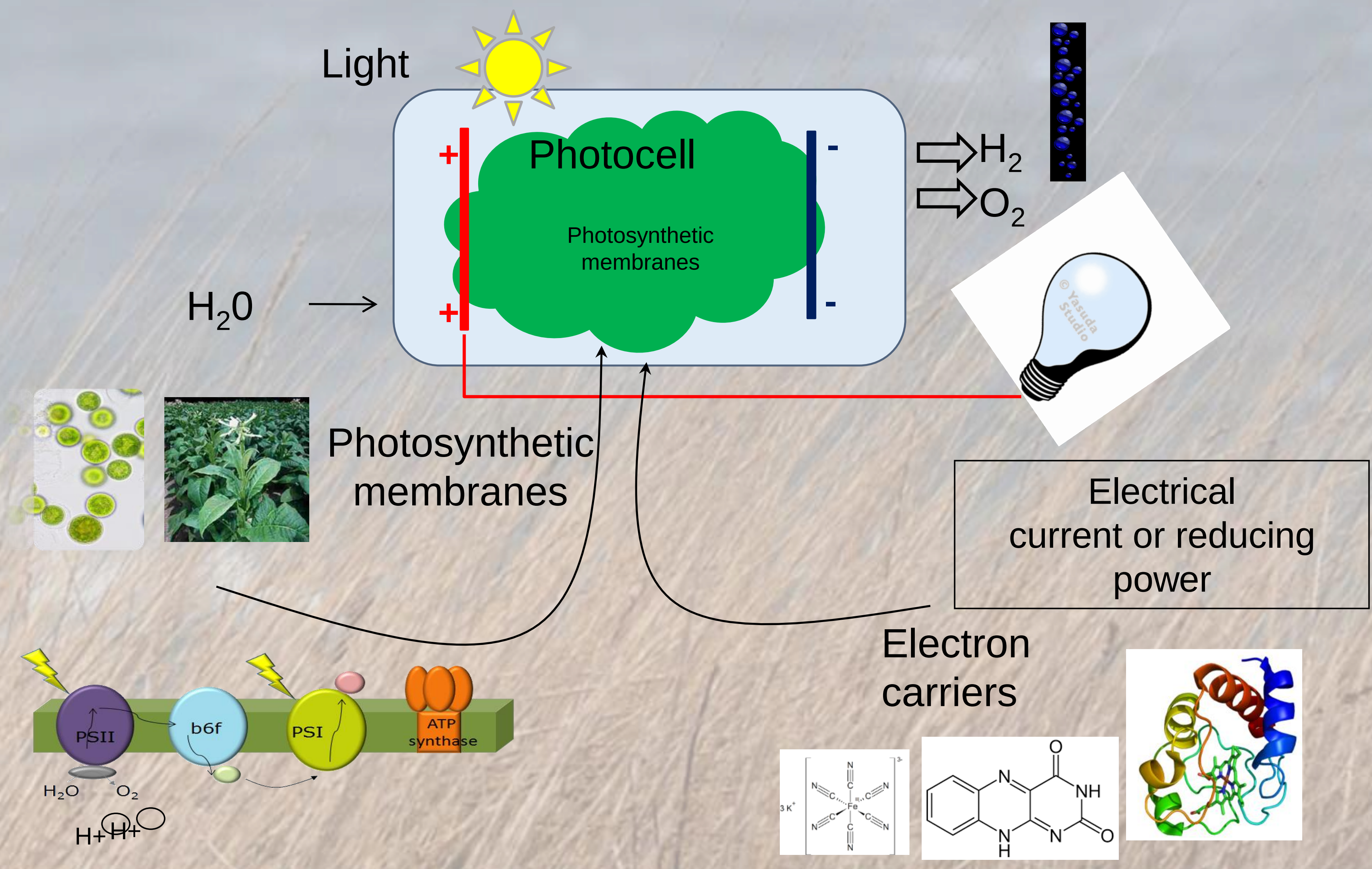
Photosynthesis works well from low to high light intensities – giant antennas with dynamic EET control



The photosynthetic apparatus is "sealed" within compartments and performed in membranes



Green machines for harnessing photosynthesis for solar energy conversion to hydrogen



Prerequisites for the engineering of a useful bio-generator

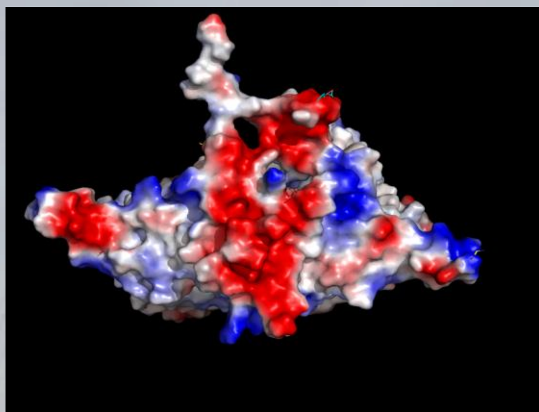
1. A Photoautotrophic organism – so that it can be grown cheaply in large quantities.
2. Normal Photosynthetic rates.
3. No expensive, polluting isolation or synthetic steps.
4. Stability for **a useful amount of time.**

Cyanobacteria

Algae

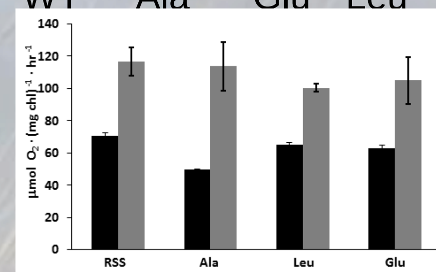
Plants

Our original idea –shuttling electrons from a mutated PSII with a protein mediator



Goal #1: Identification of mutation site

Strain	Generation time (h)
WT	19 ± 3
RSS	21 ± 4
Ala	22 ± 3
Glu	25 ± 3
Leu	30 ± 8

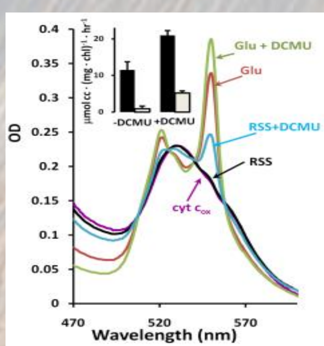


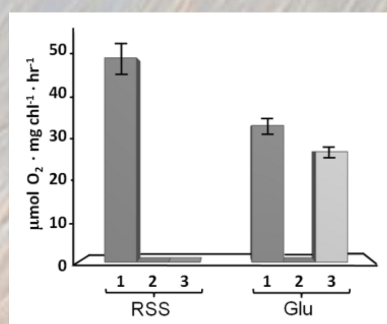
O_2 evolution *in vivo*

H_2O to DCPIP, *in vitro*

Shirely Larom
Faris Salama

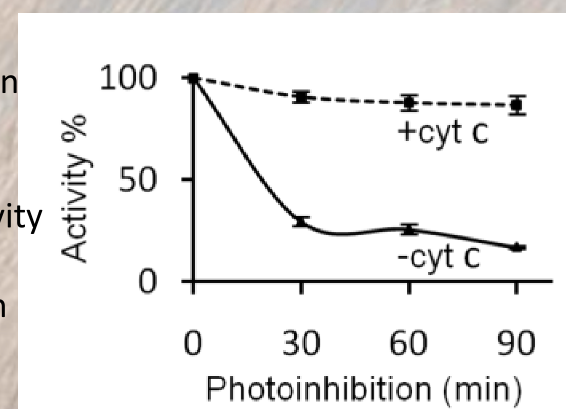
Goal #2: Site directed mutagenesis creates photoautotrophic mutants with near-normal growth and photosynthetic activity rates





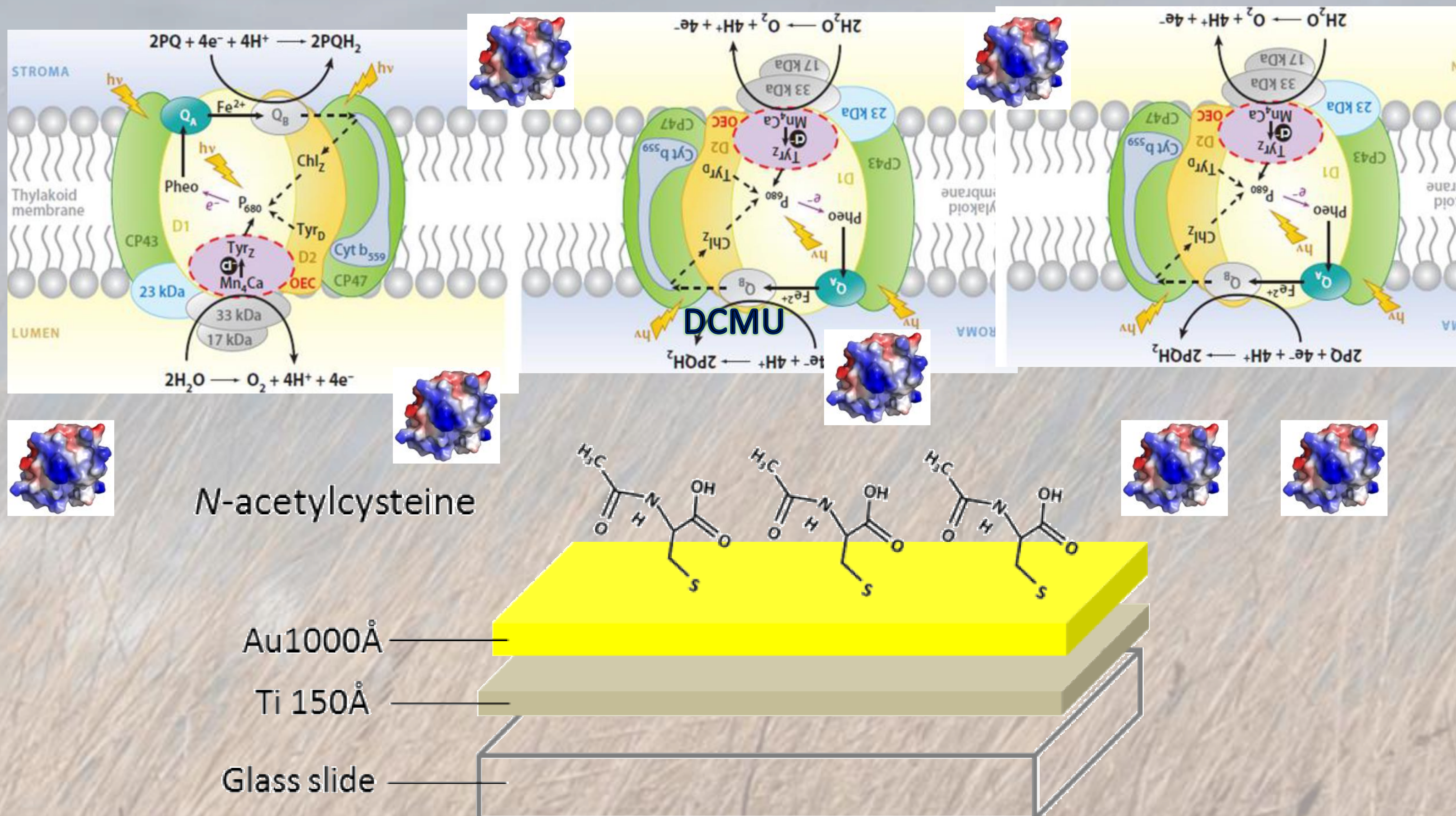
Goal #3: Membranes from mutants reduce cytochrome c in the presence of DCMU (inhibitor) and are fully active

Goal #4: Electron transfer to cytochrome c protects PSII activity from photoinhibition



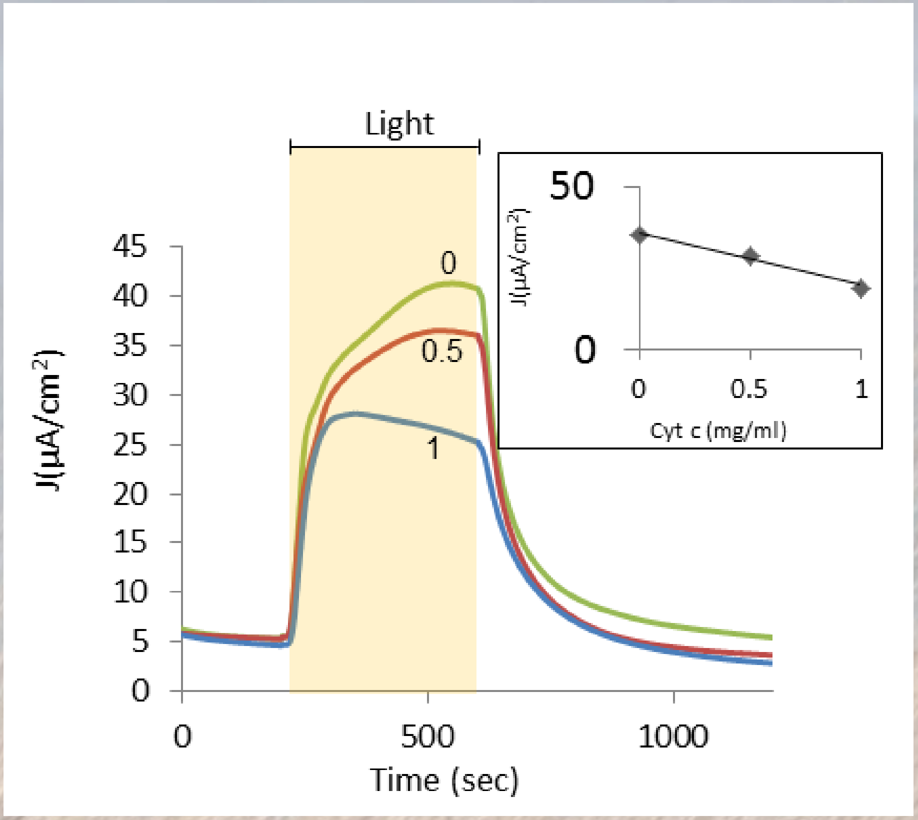
Larom S. et al., PNAS (2010)

Our original idea – cyt. c shuttles electrons from PSII



Larom *et al. Photosynthesis Research* 2015

Photocurrent generation is greater in the absence of cytochrome c.



Dependence of photocurrent in BPEC -1 on Cyt c concentration. Photo-chronoampermetric measurement was performed to Glu membranes in the presence of DCMU with the addition of 0, 0.5 or 1mg/ml cytochrome c. Insert: The photocurrent decreases linearly with cyt c concentration.

Larom *et al. Photosynthesis Research* 2015

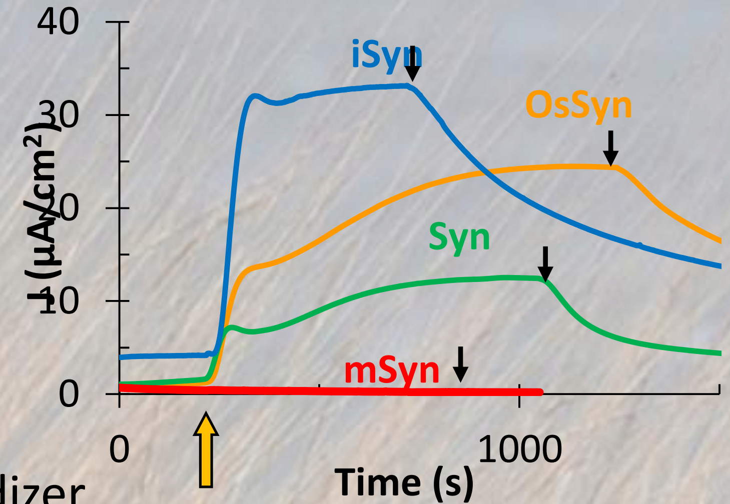
Gently treated cyanobacteria generates the maximum and the fastest photo-current

Syn
- Growth media

OsSyn
- Osmotic Shock

iSyn
- Microfluidizer

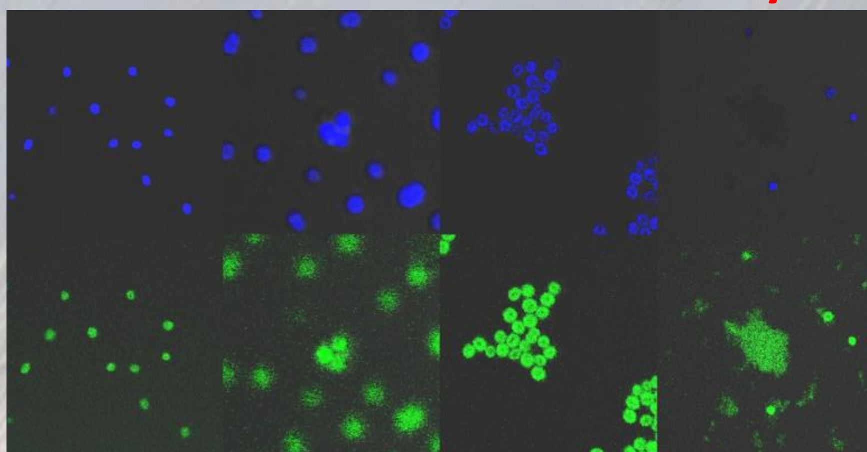
mSyn
- French-press

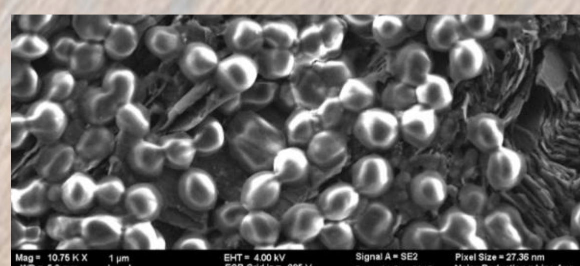


No treatment or too strong treatment ⟹ no current

Saper *et al. under review* 2018

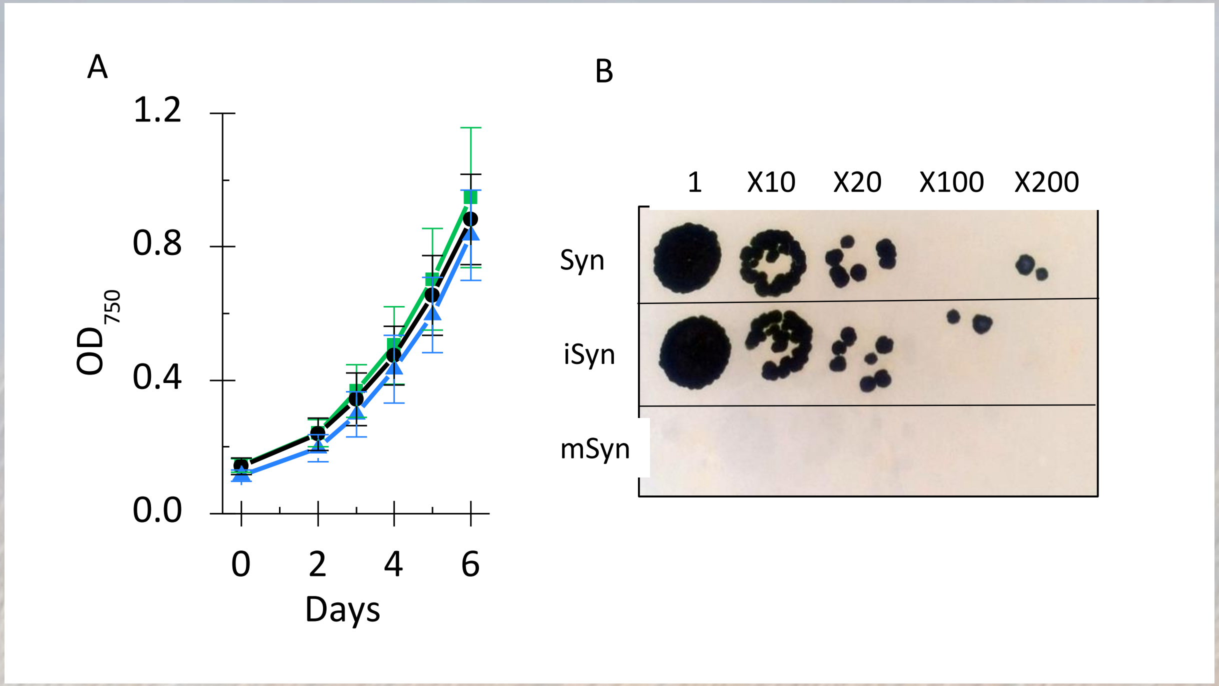
Low pressure microfluidic treatment does not fully break the cell membranes





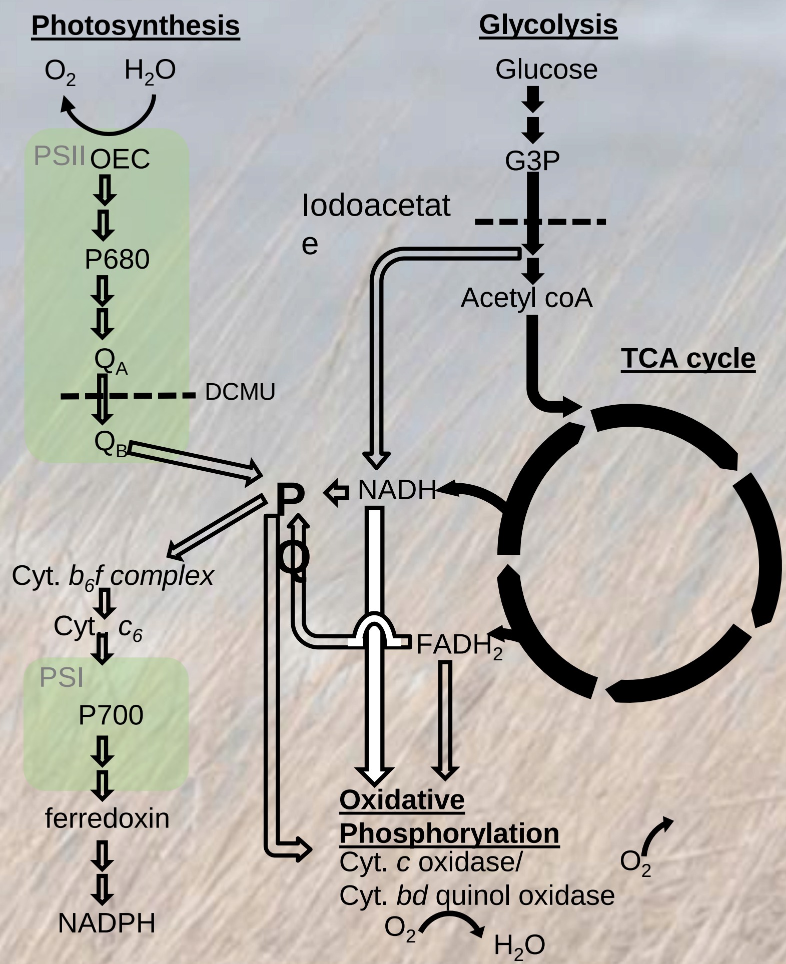
- Syn: Growth media
- OsSyn: Osmotic Shock
- iSyn: Microfluidizer
- mSyn: French press

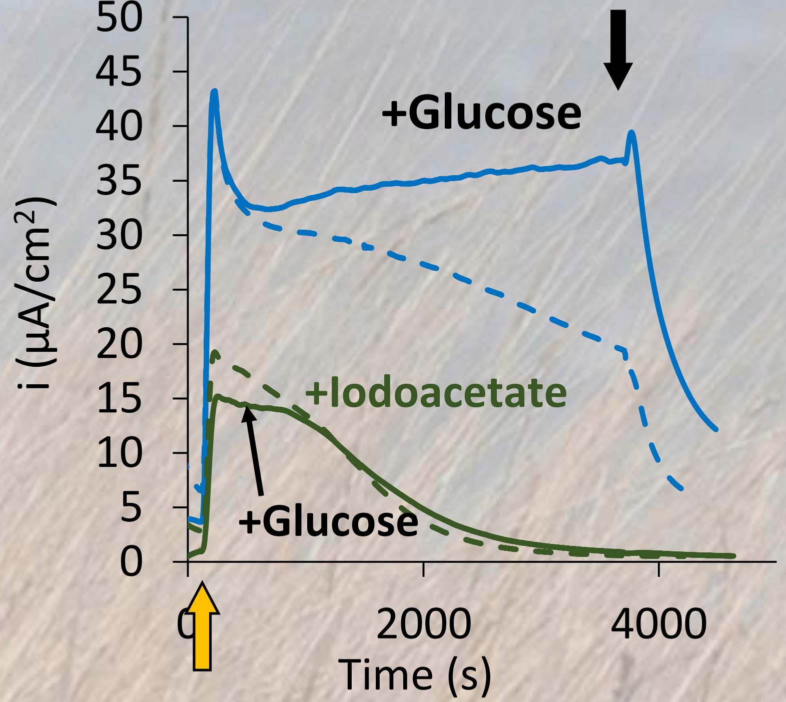
iSyn are living and multiplying cells.



(A) Growth curve of Syn (green), iSyn (black) and iSyn that were illuminated for 30 min in the BEPC (blue), in liquid medium was examined by the absorption at 750nm. The vertical lines show the standard deviation values (n=5). (B) Colony formation test for Syn, iSyn and photosynthetic membranes (mSyn). Syn, iSyn and mSyn were plated at serial dilutions on agar plate containing growth medium. The equivalent amount of cells or membranes containing 1 ng of chlorophyll was plated in the lanes marked 1.

Major electron source is the respiratory system - carbohydrates oxidation





A soluble diffusive mediator smaller than 3 kD is secreted

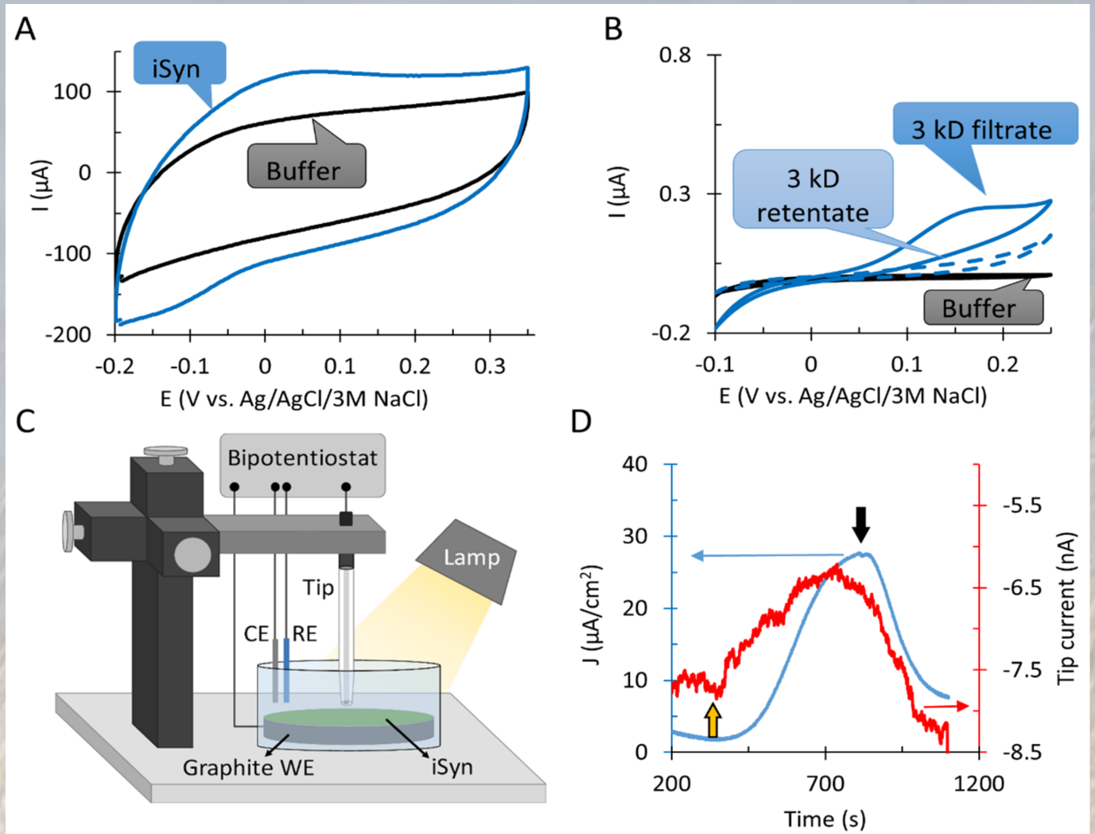
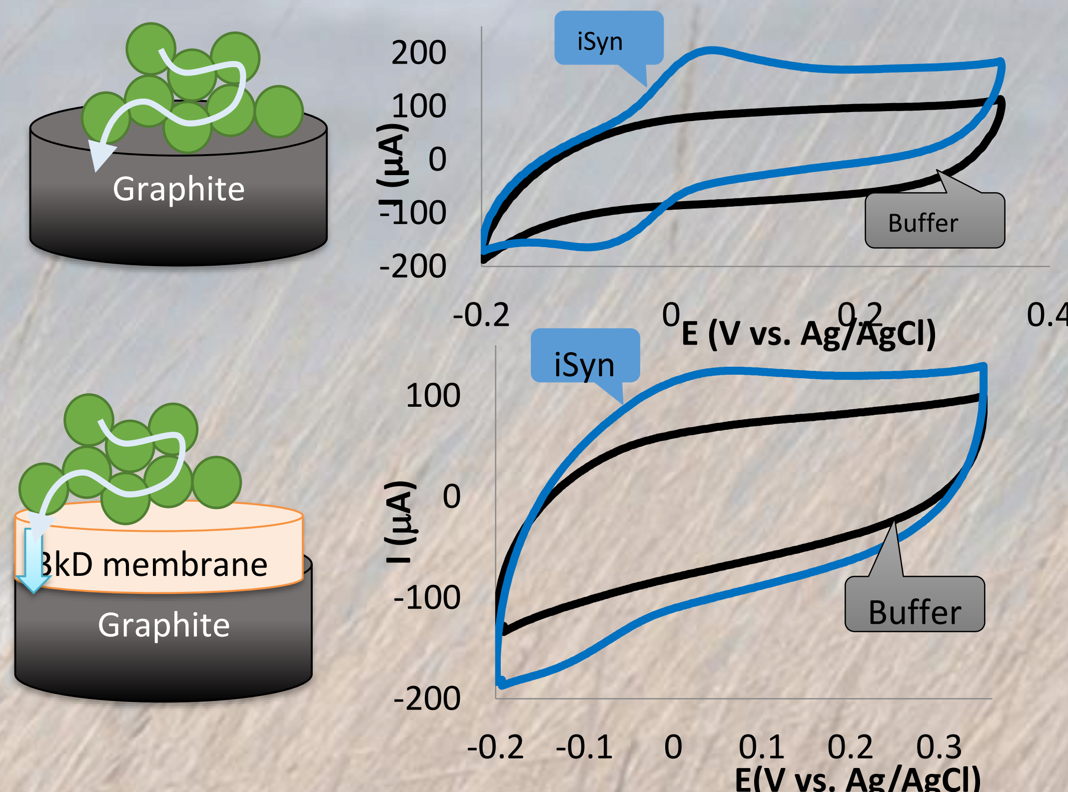


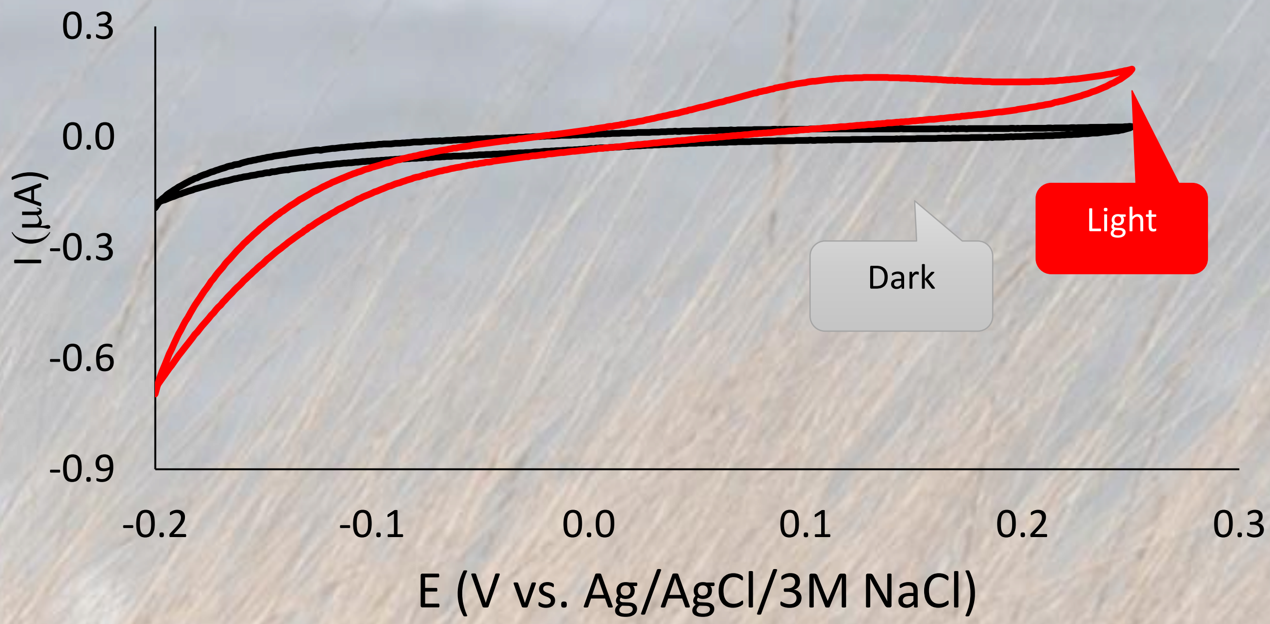
Figure 4: iSyn electron transfer to the BPEC is via a diffusive endogenous mediator. (A) CV in the light for buffer (black) and the iSyn (blue) separated by a 3 kD membrane on the graphite electrode. (B) CV of supernatant fraction from centrifuged iSyn cells separated by filtration (see SI Methods for details). Filtrate (solid blue line), retentate (dashed blue) and buffer (black). (C) Illustration of the scanning electrochemical microscopy set up. iSyn settled on the working electrode (WE) electrode. The counter electrode (CE) is platinum, and the reference electrode (RE) a Ag/AgCl/3M KCl. The tip is a carbon-based microelectrode with a mixture of bilirubin oxidase (BOD) embedded in an Os-complex modified polymer matrix. All electrodes are connected to the bipotentiostat. (D) CA of the iSyn (blue) and the BOD tip current (red) measuring the oxidation of the mediator at a distance of 30 µm from the graphite electrode.

With Wolfgang Schuhmann
Ruhr Univ. Bochum

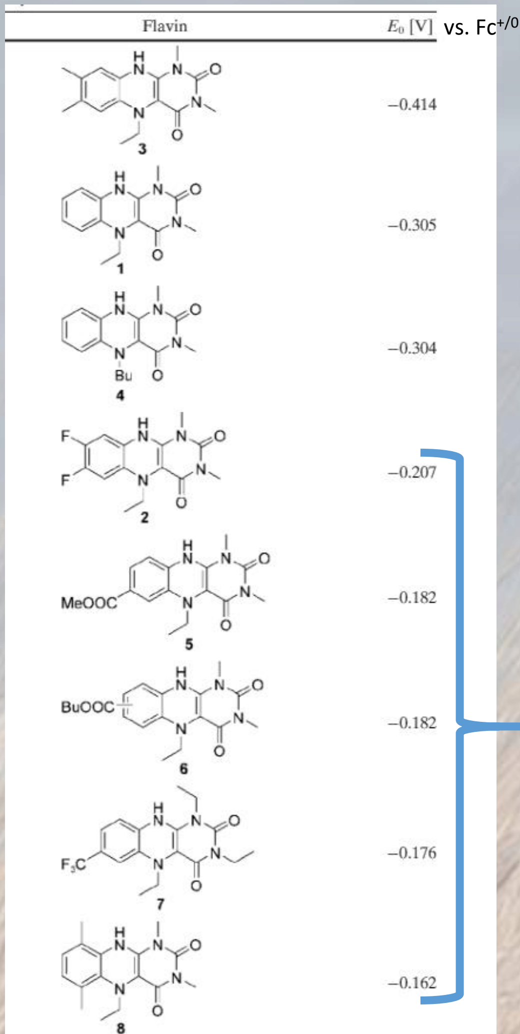
Electron transfer via a diffusive mediator smaller than 3 kD

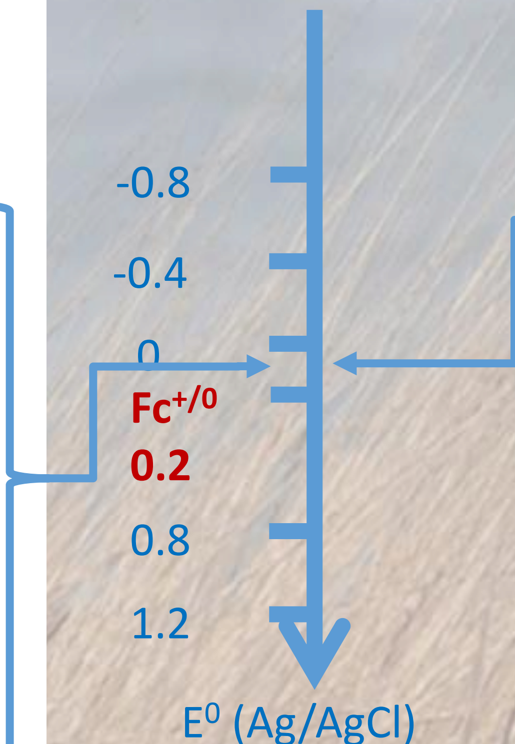


The mediator release is light induced



The mediator is probably a quinone or a flavin derivative



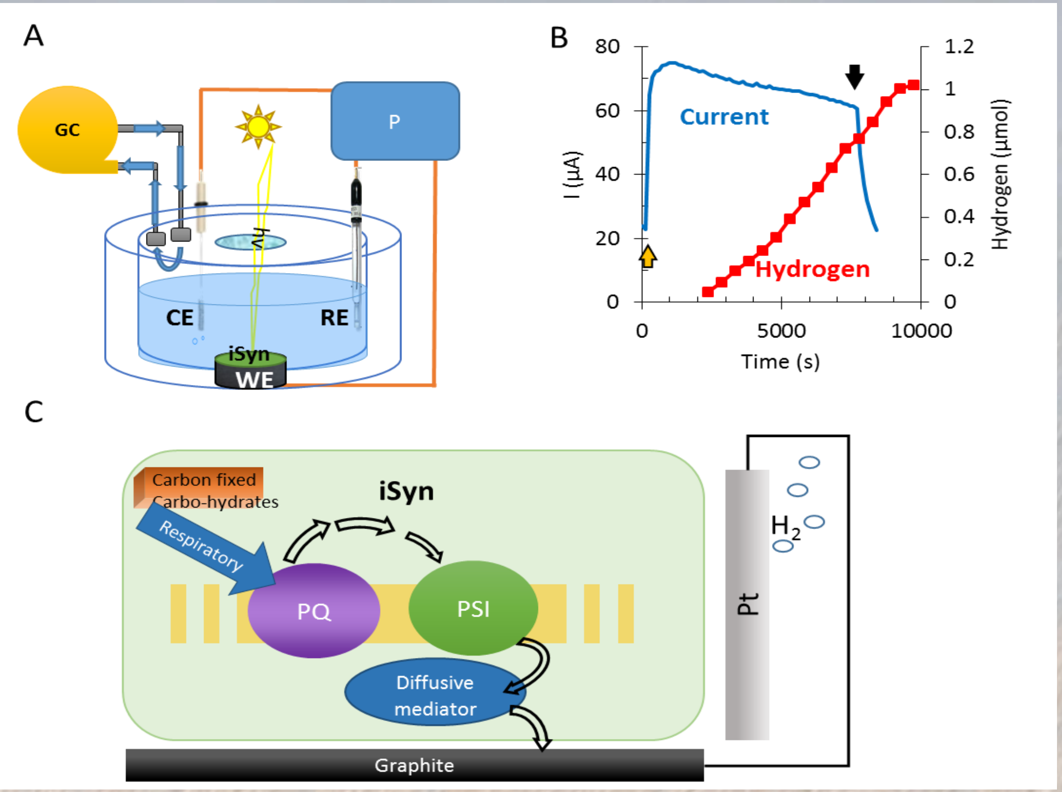


Compound	Solubility (mg/L)	E_{ox} (mV)
1,4-benzoquinone	1.11 E+04 (SRC)	278
2,6-dimethyl-1,4-benzoquinone	7.88 E+03 (SRC)	137
Tetramethyl-1,4-benzoquinone	4.43 E+02(SRC)	-37
Phenyl-1,4-benzoquinone	1.14 E+03 (SRC)	229
2,3-dimethoxy-5-methyl-1,4-benzoquinone	1.11 E+04 (SRC)	156
2,6-dimethoxy-1,4-benzoquinone	7.06 E+04 (SRC)	166
2-hydroxymethyl-6-methoxy-1,4-benzoquinone	2.85 E+05 (C)	158

https://www.google.ch/patents/WO2003033726A1?cl=en

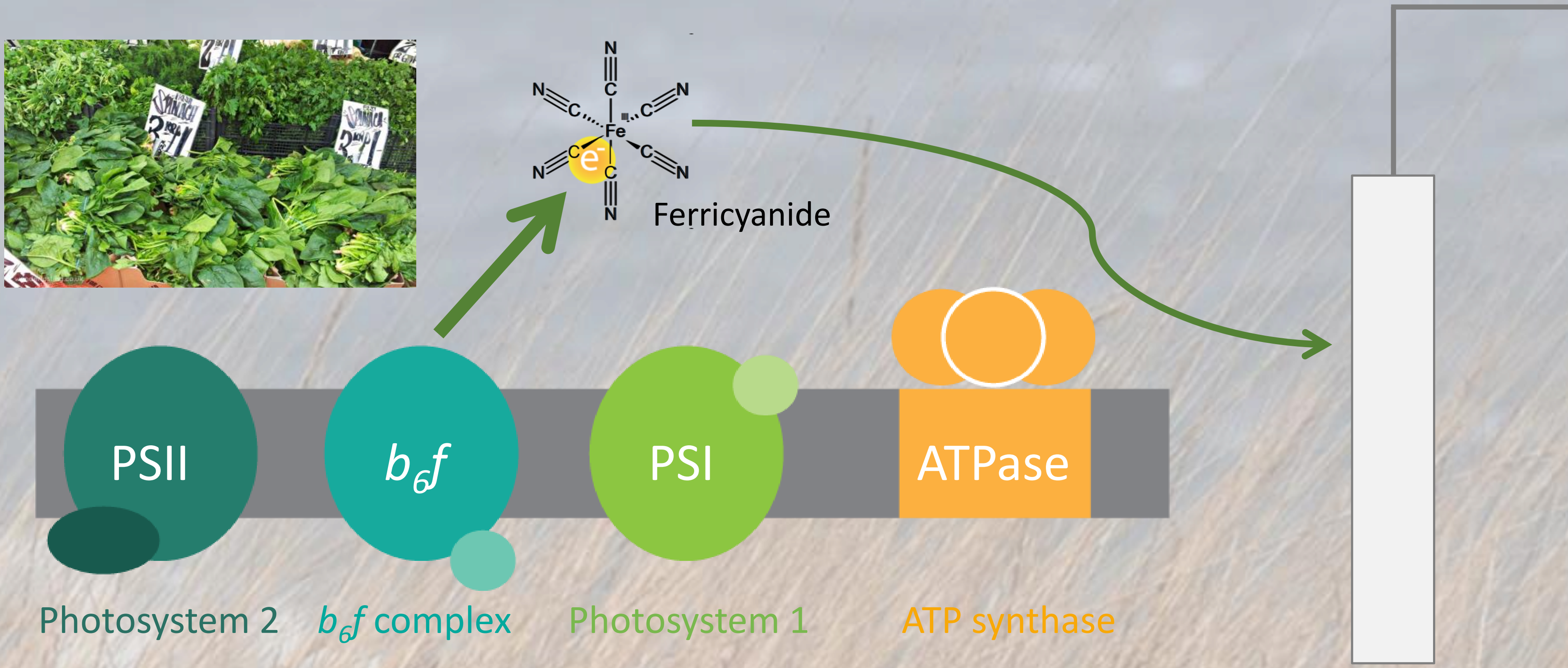
Lindén, Auri A., et al. "Preparation and Redox Properties of N, N, N-1, 3, 5-Trialkylated Flavin Derivatives and Their Activity as Redox Catalysts." *Chemistry–A European Journal* 11.1 (2005): 112-119.

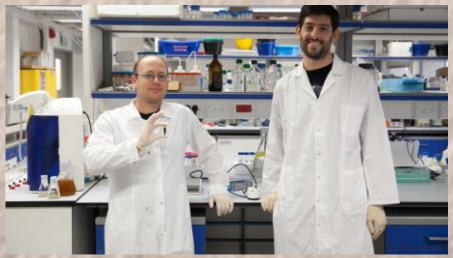
Hydrogen is evolved on the cathode at a lower voltage than in water electrolysis.



(A) Schematic drawing of the working set up for the hydrogen evolution measurements. The CA was measured at 50 mV (vs. Ag/AgCl/3M NaCl) which corresponds to a voltage of 650 mV between the anode and cathode. (B) Simultaneous CA measurement of photocurrent (blue) and GC measurement of hydrogen production (red) measured as a function of time for the iSyn at 50 mV (vs. Ag/AgCl/3M NaCl). (C) Schematic drawing of the electron flow from carbohydrates (internal or external) via the respiratory, light driven activity of PSI, and an endogenous diffusive mediator to form hydrogen gas. The multiple electron transfer steps between the PQ and PSI are shown as multiple curved arrows for simplicity.

Plant thylakoids require a mediated electron transfer - ferricyanide

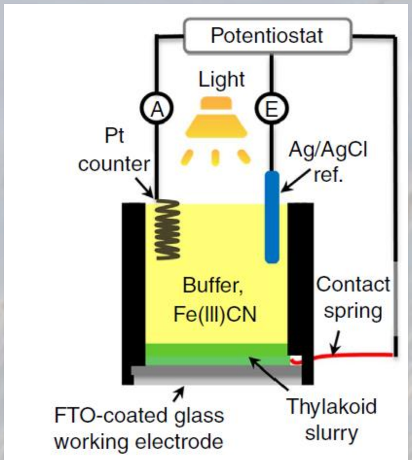




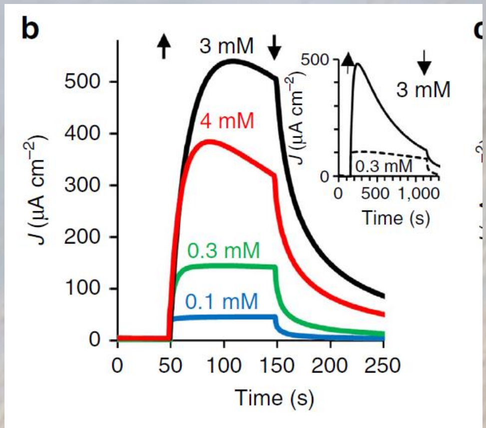
Roy Pinhassi Dan Kallmann Gadiel Saper

Plant membranes provide high currents and H_2 in BPEC with 0.5V bias.

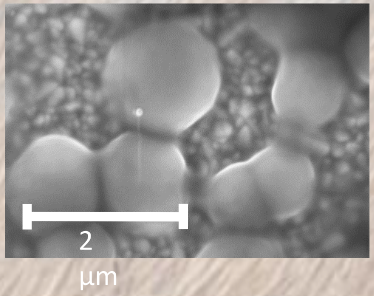
Ferricyanide mediates currents of up to 0.5mA/cm2 (100mg chlorophyll). Membranes are not physically attached to electrode and can be easily replaced for extended use.



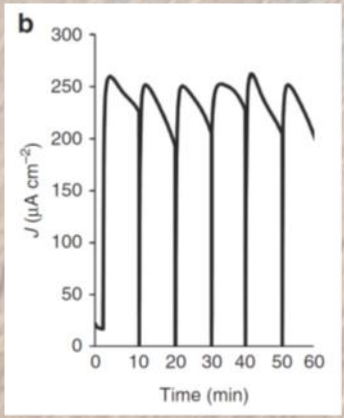
The BPEC cell.



Photocurrent, measured at an electrode potential of 0.5VAg/AgCl, as a function of time during exposure to solar-simulated light. The inset shows the long-term photocurrent stability in high (3 mM, full line) and low (0.3 mM, dashed line) Fe(III)CN concentrations. The arrows indicate light turn on (up) and off (down) points.



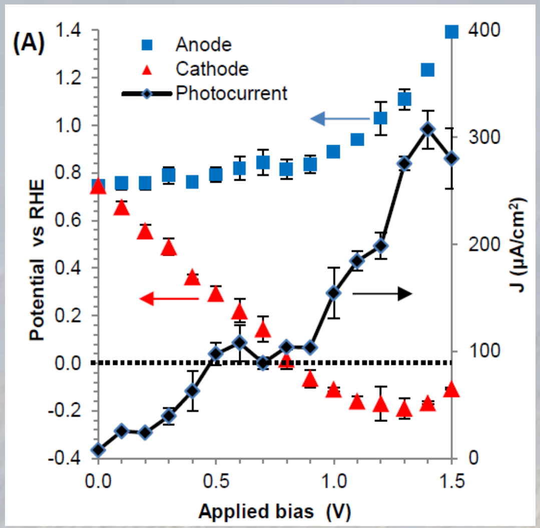
Scanning electron microscopy image of the spinach membranes on the surface of a FTO coated glass electrode.



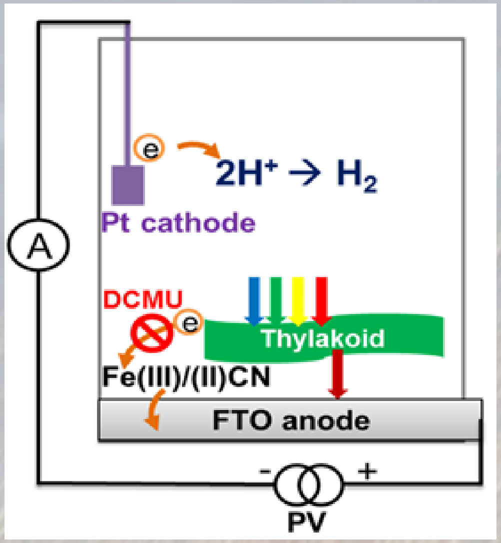
Batch mode of operation wherein damaged thylakoids were replaced with fresh ones every 10 min. All the other cell components were reused.

Pinhassi *et al.* Nature Communications 2016

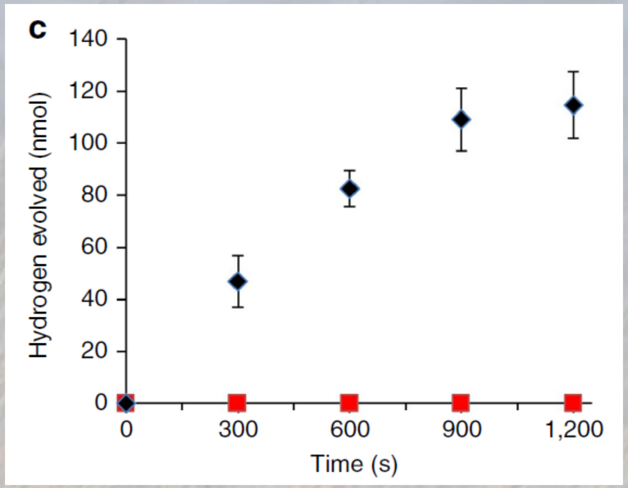
Plant membranes provide high currents and H_2 in a stand alone BPEC.



Photocurrent (black curve) and anode (blue squares) and cathode (red triangles) potentials as a function of the applied bias between the anode and cathode. The dashed line represents a potential of 0V RHE



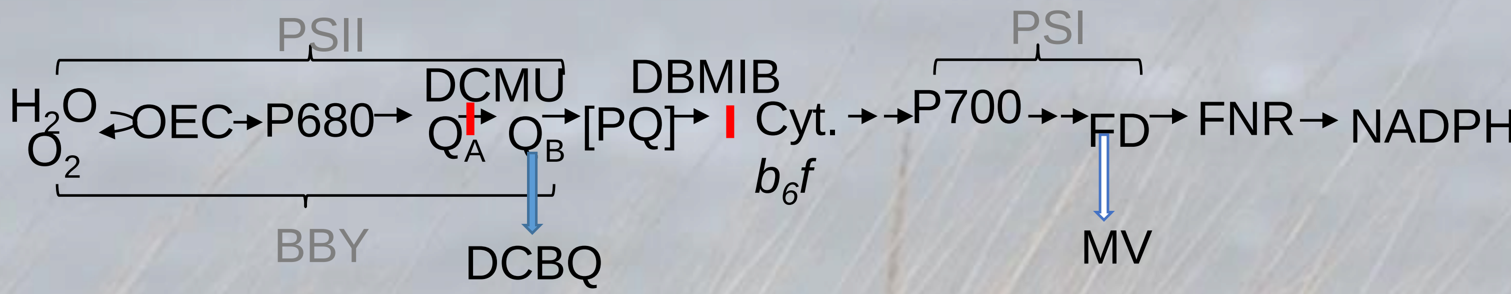
A tandem stand-alone H_2 evolution BPEC with PV absorbing IR

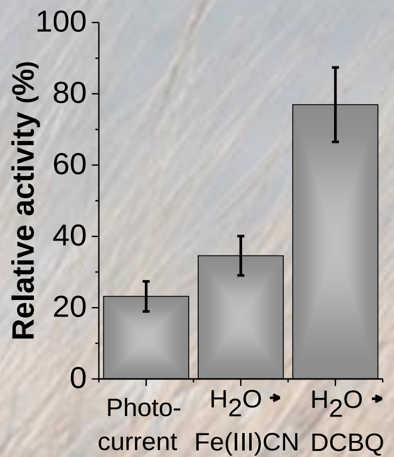


Hydrogen evolution at the cathode in the presence (red squares) or absence (black diamonds) of the herbicide DCMU

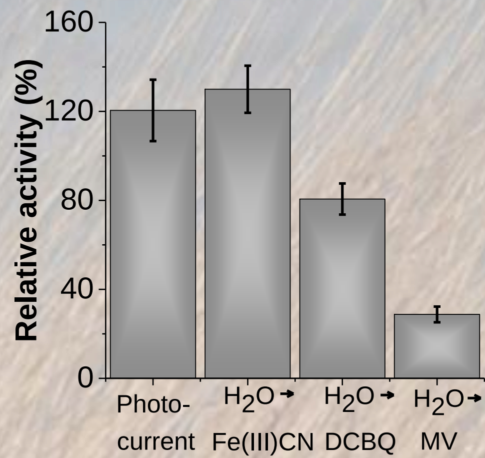
Pinhassi *et al.* Nature Communications 2016

PQ pool is the electron donor to Fe(III)CN

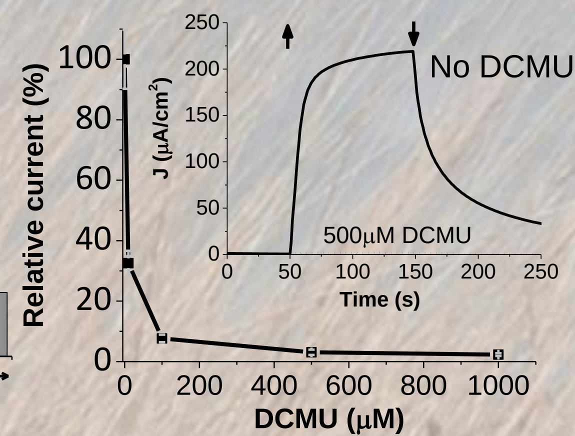




PSII enriched Thylakoids (BBY)



5 µM DBMIB



Summary: Electron transfer to the electrode from plants and from cyanobacteria

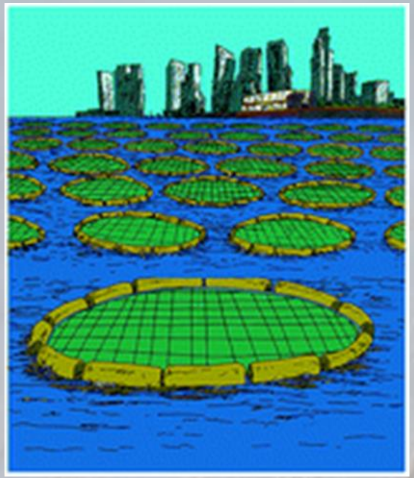
Plants

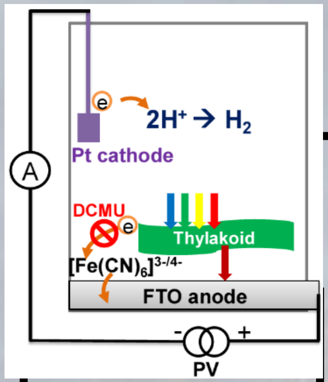
- Simple preparation of the spinach thylakoids
- Demand for an exogenous mediator
- High potential (300 mV vs. Ag/AgCl)
- Current of 0.5 mA*cm^{-2}
- Short life-time
- Electron source: water
- Electron extraction site: PQ pool – cyt B_6F complex
- FTO and PV cell enable stand alone BPEC without added bias

Cyanobacteria

- Simple preparation of the cells
- Transfer of electrons utilizing an endogenous mediator
- Low potential (50 mV vs. Ag/AgCl). Requires small added bias for H2 production.
- Current of 31 µA*cm^{-2}
- Live cells: current provided for extended life-time.
- Electron source: carbohydrates
- Electrons flow from PSI to the electrode (auto-mediation)
- Dark current – utilize as bio-energy storage system.

Where would we use such a BPEC?





At home

Off the grid

Mars?

Thank you for keeping our world a better place!