Materials, Electronics and Renewable Energy

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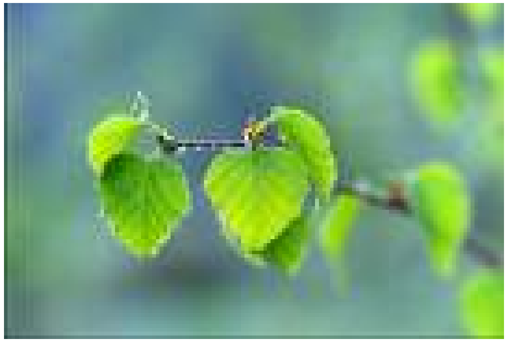
Photosynthesis

Physics – Chemistry energy conversion table:

1 eV = 1.6×10^{-19} J is equivalent to 96 kJ/mol

Photosynthesis:



$$6CO_2 + 6H_2O + \text{photons} \rightarrow C_6H_{12}O_6 + 6O_2$$

- Capture of sunlight by light-absorbing 'antennae' molecules
- transfer of excitons to the 'reaction centre'
- charge separation across a 'semiconductor heterojunction'
- chemical reactions driven by net positive charge (e.g. oxidation product causes reduction of water to oxygen)
- chemical reactions driven by negative charge: (e.g. formation of hydroquinones from quinones as intermediate chemical feedstocks)
- generation of ATP from ADP and NADPH from $NADP^+$
- ATP and NADPH used in the Calvin cycle to convert CO_2 to glucoses

Many different systems:

not all of them are green… colour is selected according to available sunlight – bacterial systems come in many colours (as seen in coral reefs..)

not all of them produce oxygen: purple bacteria use a wide range of reductants such as hydrogen sulphide, other organic matter (sewage ponds..)

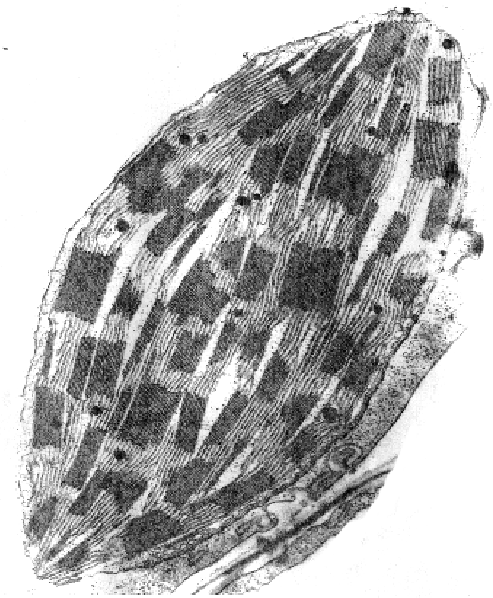
Efficiency losses in photosynthesis:

- Absorption only at wavelengths < 700 nm
- Shockley-Queisser limit (1.8 eV) ~ 24%
- Efficiency of converting 1.8 eV photons into glucose = 27% (9 - 10 photons required per molecule)
- 24% × 27% = 6.5%
- Not all photons absorbed (plants are green, not black)

⇒ net efficiency ~ 5%

Further losses reduce realised efficiencies to typically below 1%:

- shading
- seasonal growing conditions (winter, rainfall, excess sunlight)



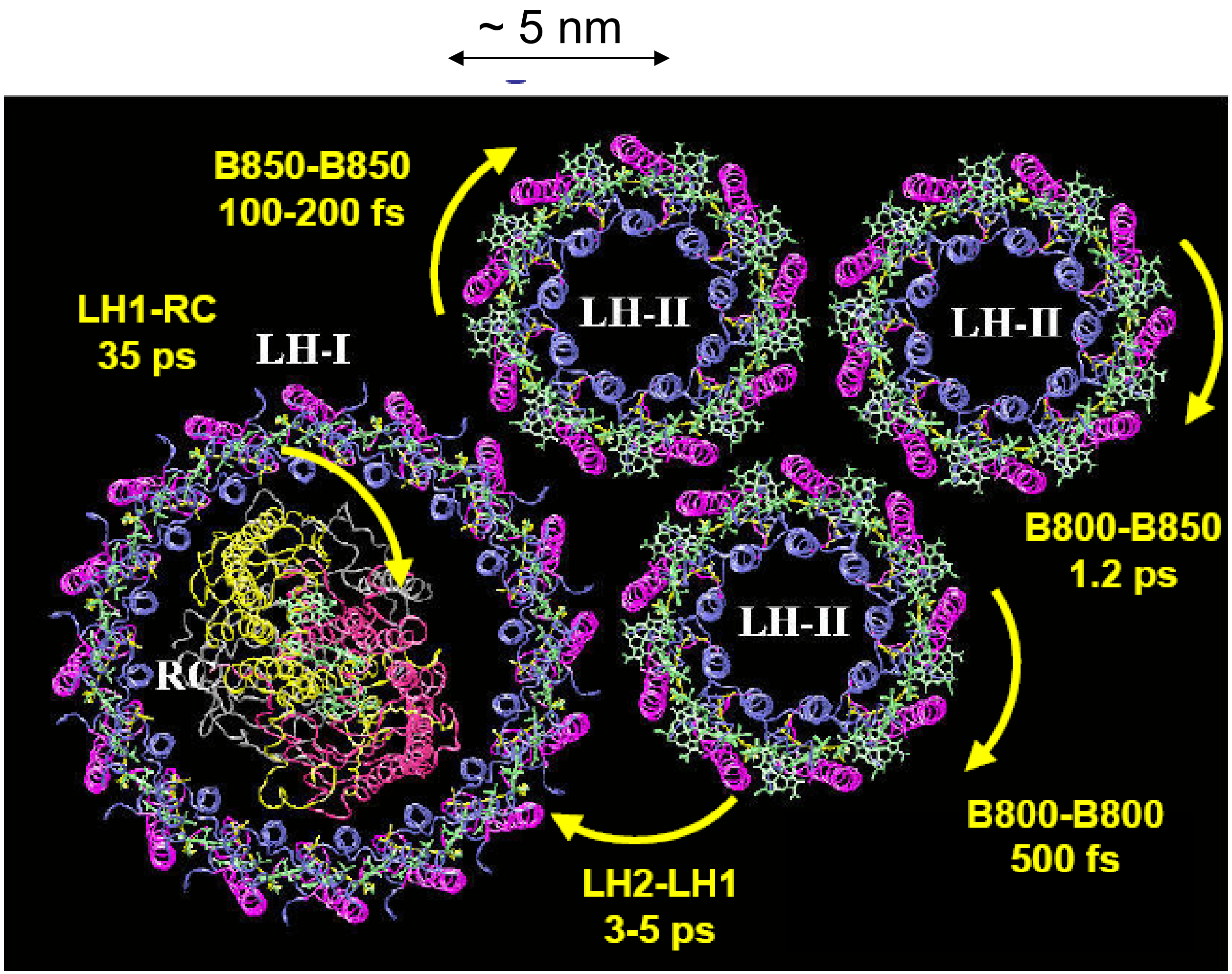
Chloroplast

Separate question: Efficiency of capture of carbon in plant matter:

constant CO_2 concentration in the atmosphere implies steady state in the pre-industrial past?

Many mechanisms for re-generation of CO_2. Plant respiration, plant decay, combustion etc.

The photosystem: two different light-harvesting complexes, LH-I and LH-II. Charge separation at the reaction centre, RC



Electronic energy transfer cascade to reaction centre.

Up to 200 chromophores per reaction centre.

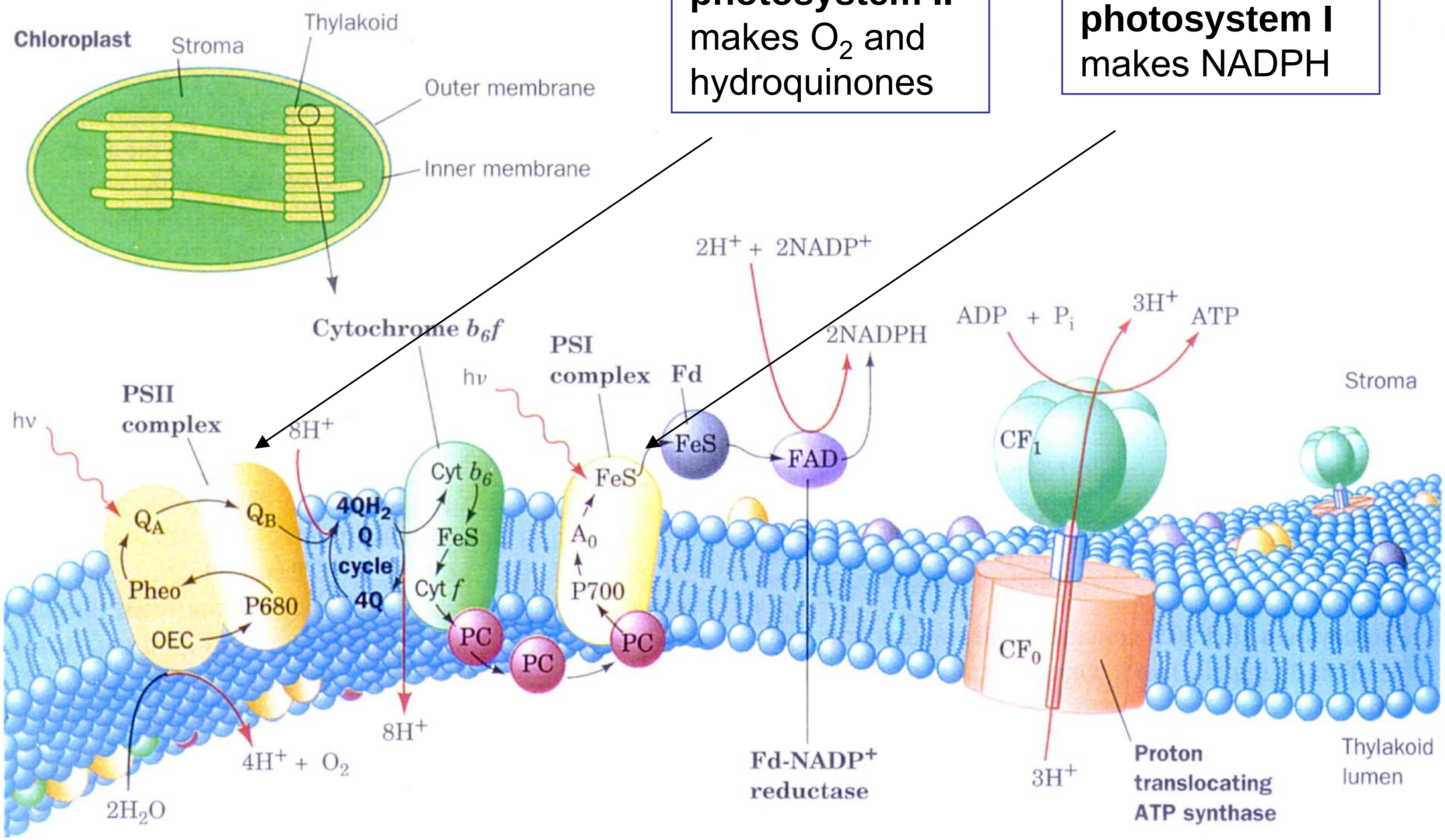
Concept common to all photosynthetic organisms; detailed structure varies

Top view of bacterial photosynthetic membrane
Green = chlorophylls

Green plant photosynthesis:

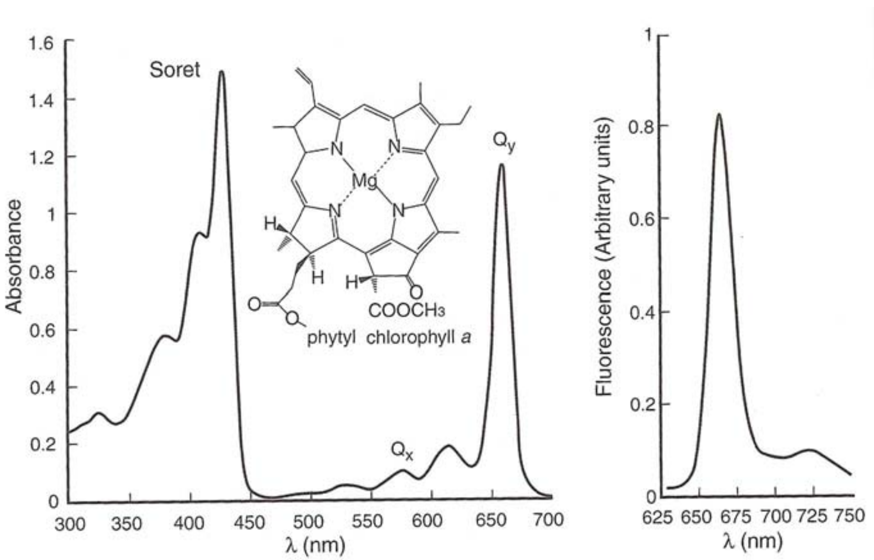
photosystem II makes O_2 and hydroquinones

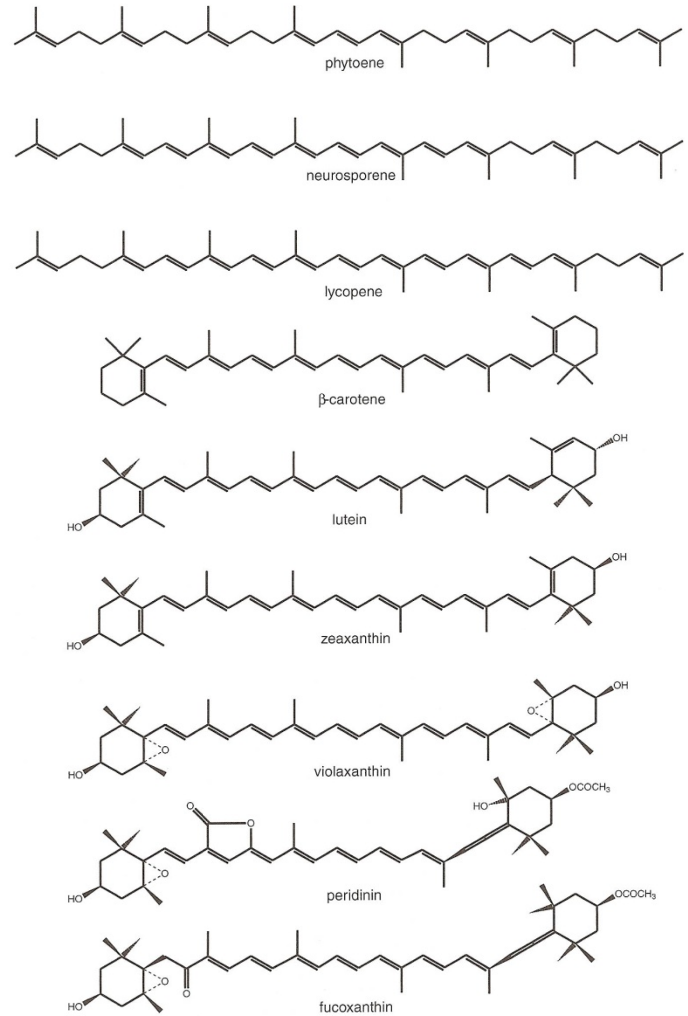
photosystem I makes NADPH



Light-harvesting antennae:

Typically a few hundred light-absorbing molecules. These are varied and include chlorophylls and carotenes.





various carotenoid molecules used in photosynthesis

Why bother with antennae?

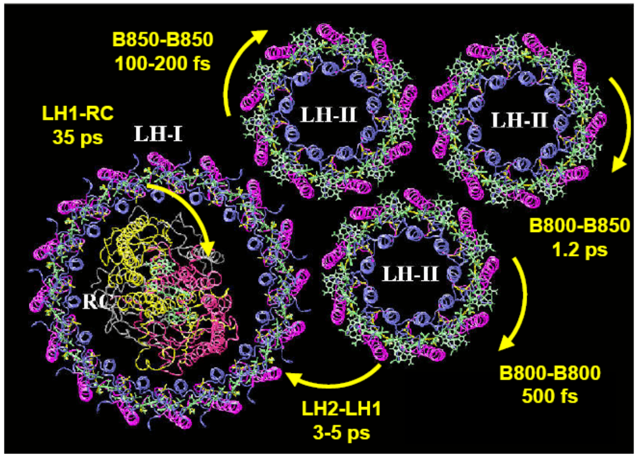
about 10 photons/s absorbed under full sunlight in one chlorophyll. Much slower than rate at which the RC can operate

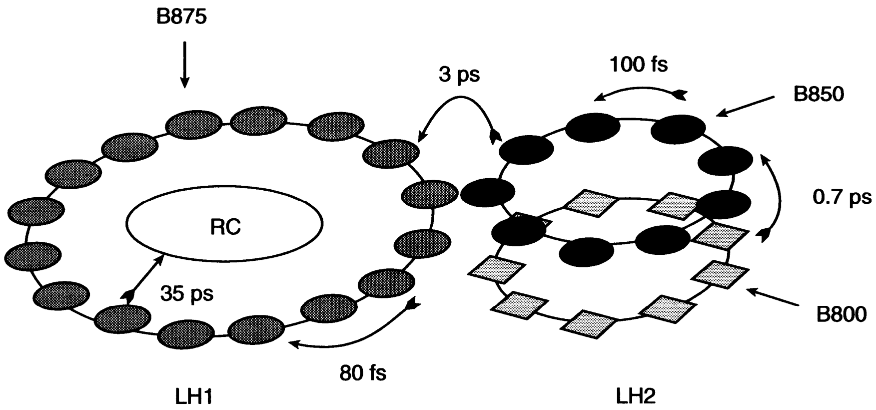
Energy transfer

Antennae molecules:

- absorb incident photons (creating molecular excitons)

- transfer exciton energy quickly towards the reaction centre (avoiding non-radiative decay channels).



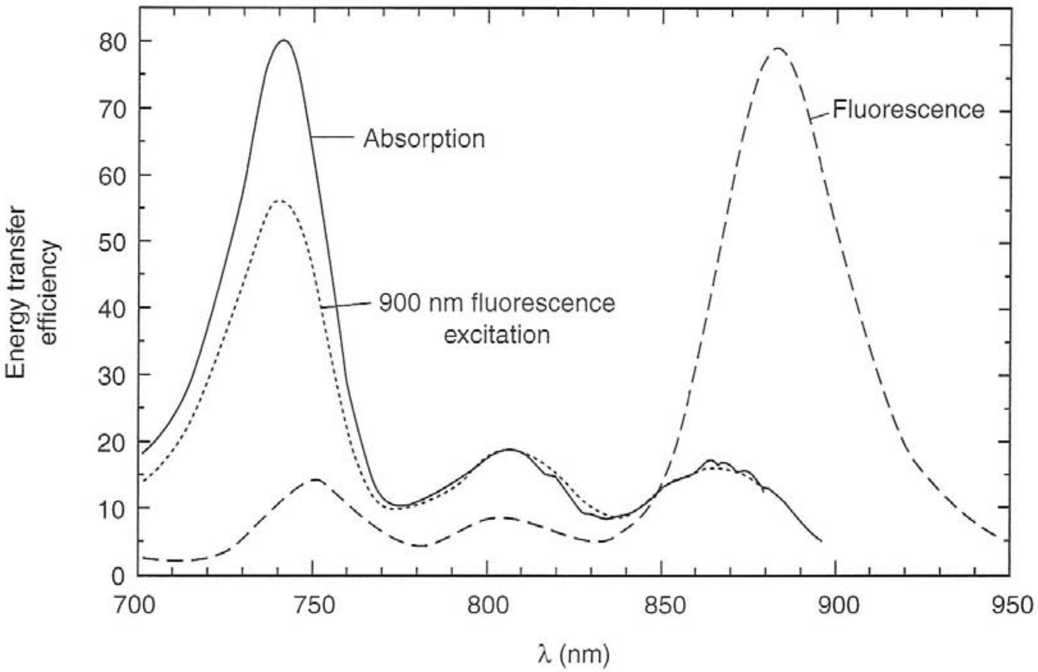


- Exciton delocalisation within rings is very rapid (exciton-exciton coupling)
- Transfer from B800 to B850 in LH2, from LH2 to LH1, and from LH1 to the reaction centre is by Förster transfer
- "Downhill" energy transfer to give overlap of absorption and emission spectra
- Distances carefully controlled by protein structure to control rates.
- Avoid very close contact – wavefunction tunnelling leads to non-radiative states

Optimum separations are around 1 nm (giving transfer times of a few ps)

Forster Energy Transfer:

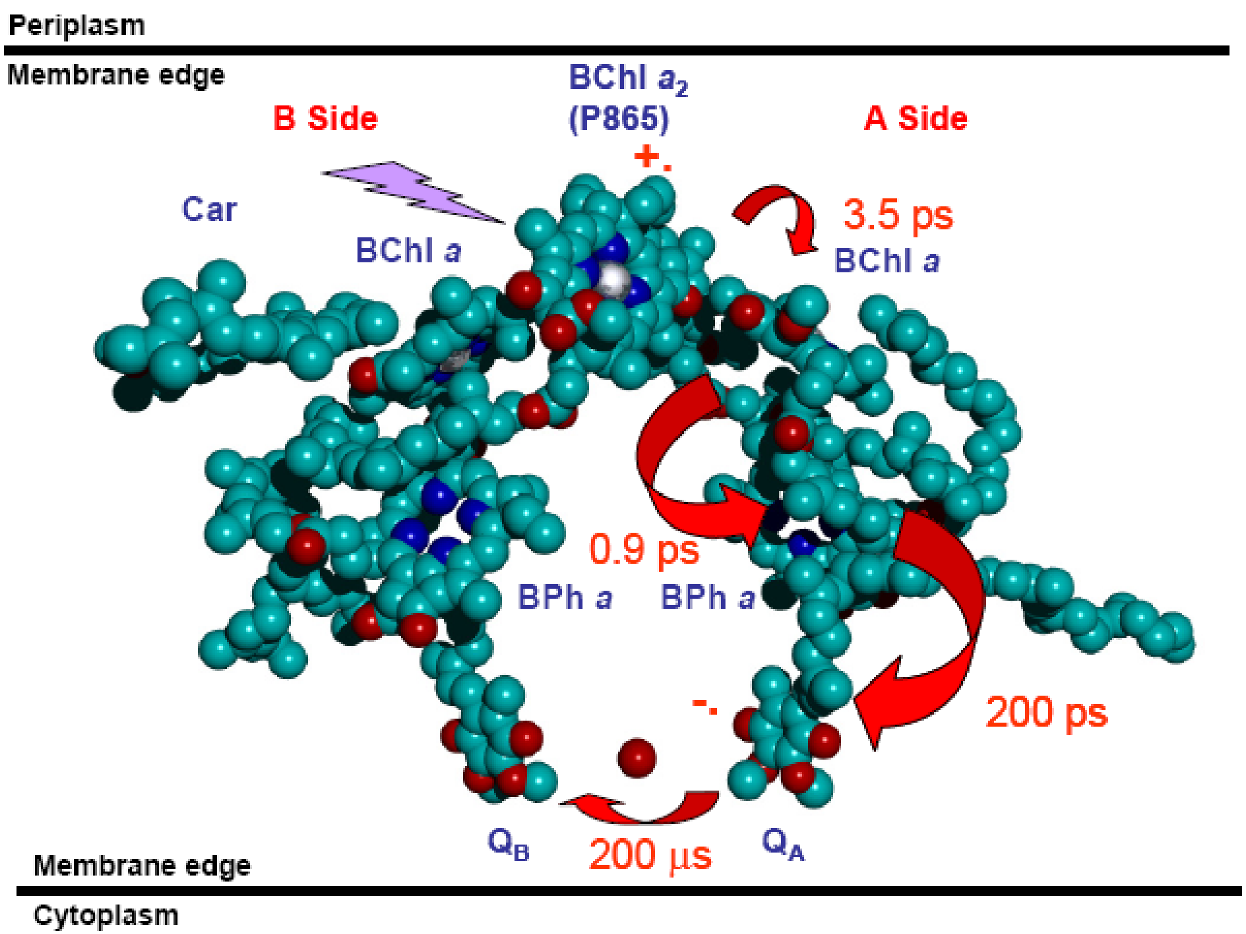
Green bacterium *cloroflexus aurantiacus*



bacteriochlorophyll c absorbs near 740 nm and transfers energy to bacteriochlorophyll a which absorbs at around 800 nm

resulting emission at 900 nm is from bacteriochlorophyll a

The reaction centre



Side view of bacterial reaction centre, with protein not shown

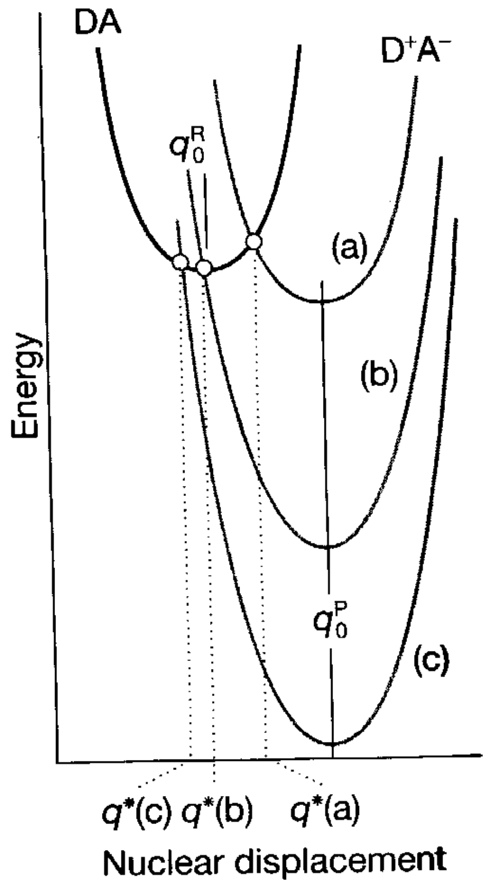
Exciton transfers from antennae to pair of chlorophylls which are arranged to have the correct exciton energy to collect from the antennae

– usually labelled by this energy (in nm)

– note that this energy is different for bacterial systems versus green plants

electron transfer 'across the heterojunction' – in green plants to a 'pheophytin'. subsequent transfers to lower-energy sites

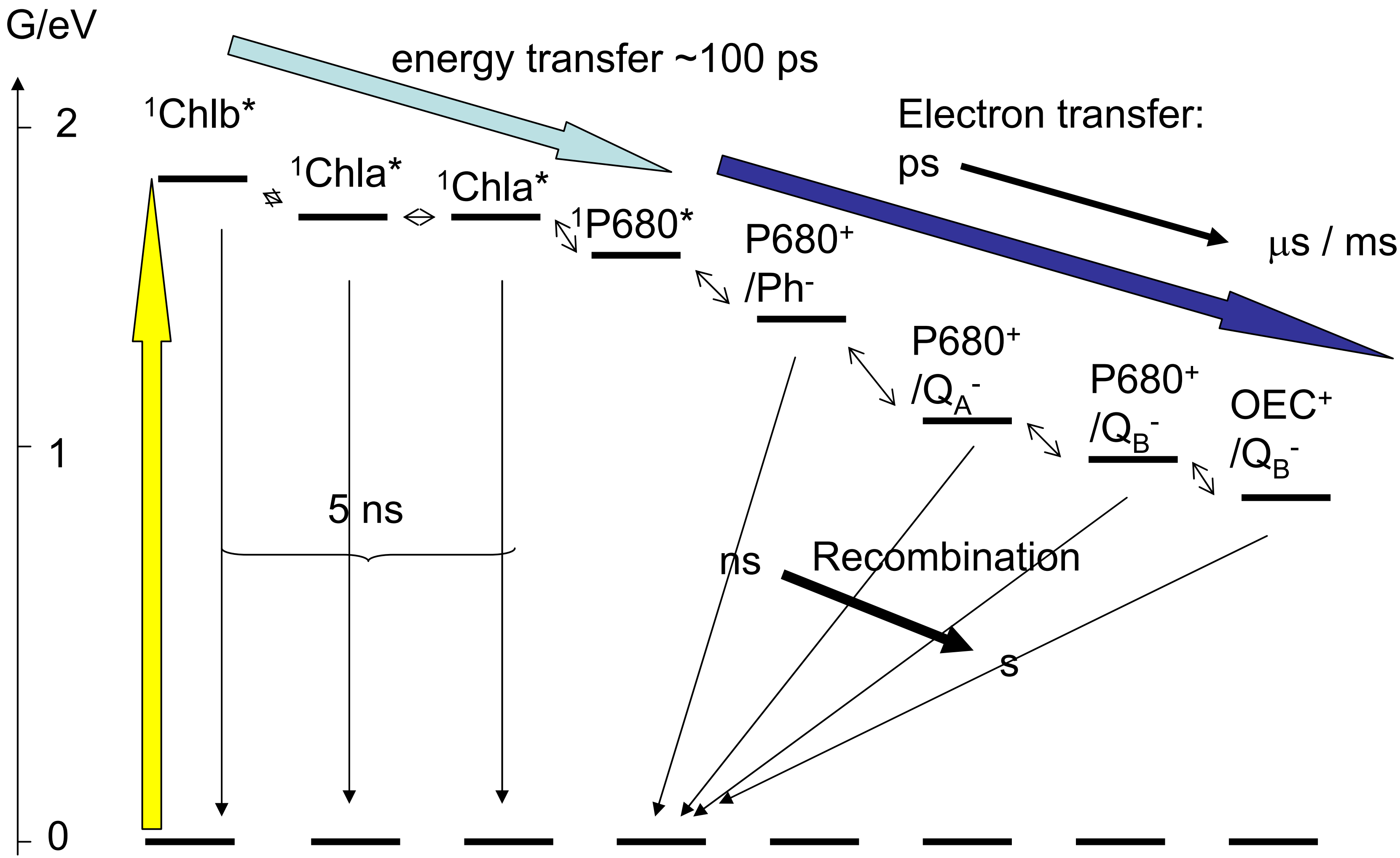
Marcus Theory



$$k_{transfer\quad rate} \propto V_{tunnelling}^{2} e^{-\left(\frac{(\Delta G^0+\lambda)^2}{4\lambda k_B T}\right)}$$

- Photosynthetic reaction centres evolved such that:
  - Non-polar interior (λ ≤ 1 eV)
  - Forward reactions activationless: $|\Delta G^0| = \lambda$: fast
  - Reverse reactions in inverted region: $|\Delta G^0| > \lambda$: slow

Energetics versus kinetics: green plants



Jim Barber et al, Imperial College, 2004

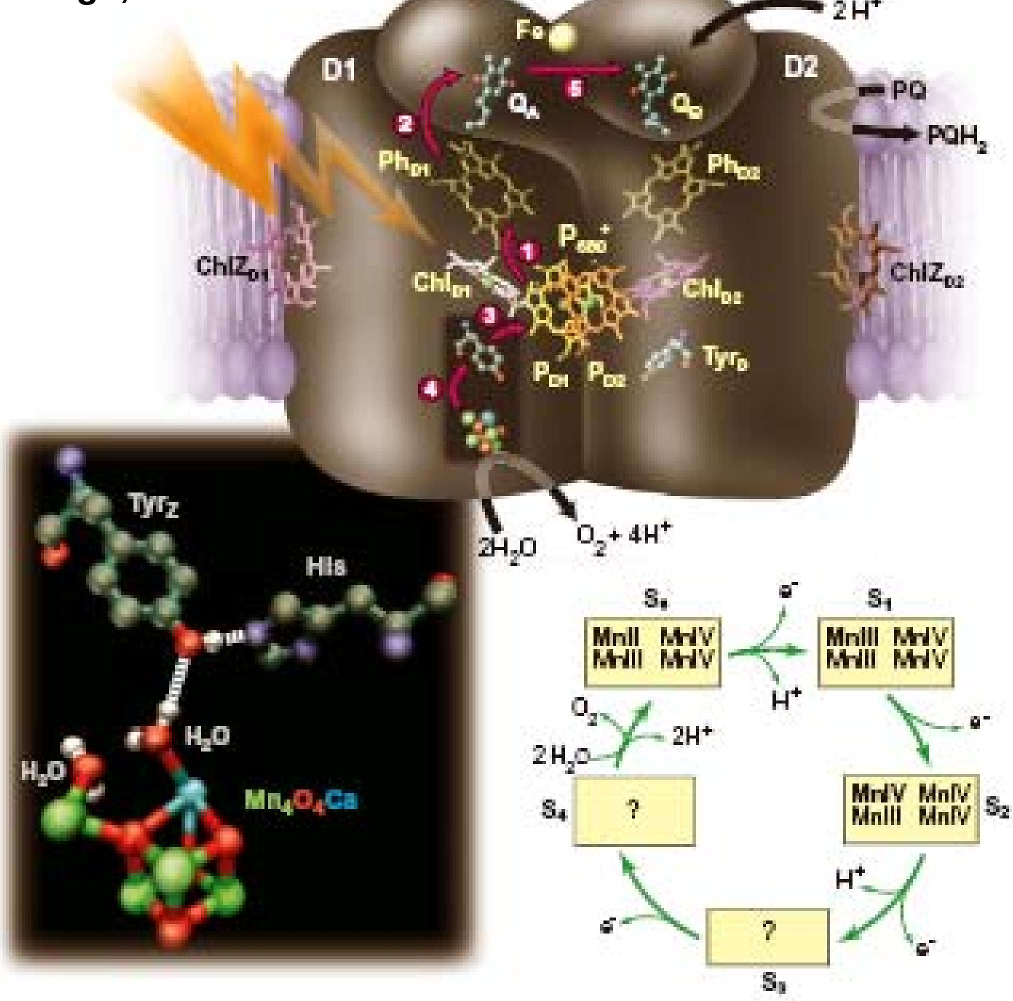


image due to Rutherford and Boussac, Science **303** 1782 (2004)

Water photolysis in PSII:

oxygen is produced by electrolysis of water (not from CO_2). $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Step1: charge separation (2 to 20 ps) between chlorophyll Chl_{D1} and pheophytin, Ph_{D1}. Cation stabilised on chlorphyll P_{D1} (designated $P680^+$)

Step 2: Ph_{D1} transfers electron to quinone Q_A (lowers energy and prevents reverse reaction)

Step 3: $P680^+$ oxidises (20 ns) tyrosine, which loses a proton to neighbouring hystadine.

Step 4: tyrosine oxidises (30 μs) the Mn cluster (S_1 to S_2).

Step 5: Q_A- transfer electron to second quinone, Q_B.

Cycle repeated with successive photon absorptions:

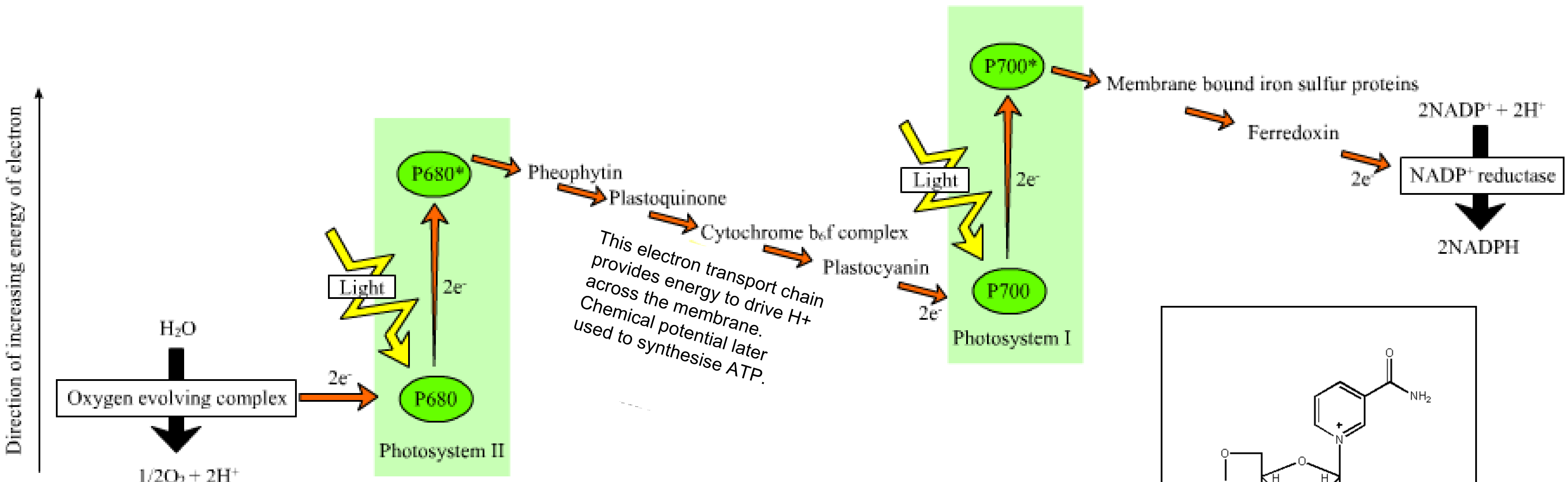
- second electron on Q_B produces hydroquinone: $Q_B + 2e + 2H^+$ -> hydroquinone.
- four photon cycles required to remove four electrons from the Mn cluster, to liberate O_2

The ‘Z-scheme’

Green plants couple the operations of photosystem II and photosystem I…..

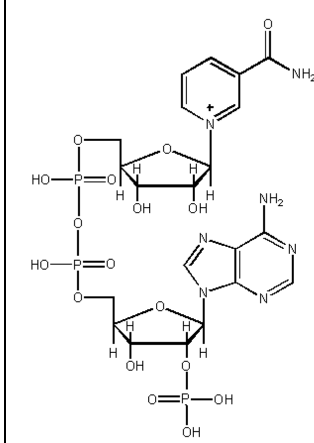
Net reaction is $2H_2O + 2NADP^+ \rightarrow O_2 + 2NADPH + 2H^+$

highly-reducing $P700^+$ transfers electron via iron-sulphur complexes, to reduce $NADP^+$ to NADPH



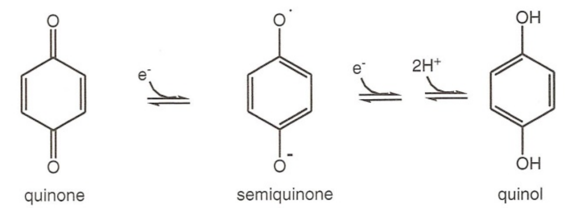
PSII reduces water to O_2 and and makes hydroquinones

electron from PSII – released from the hydroquinones via the cytochrome complex is eventually used to re-reduce P700 in PSI

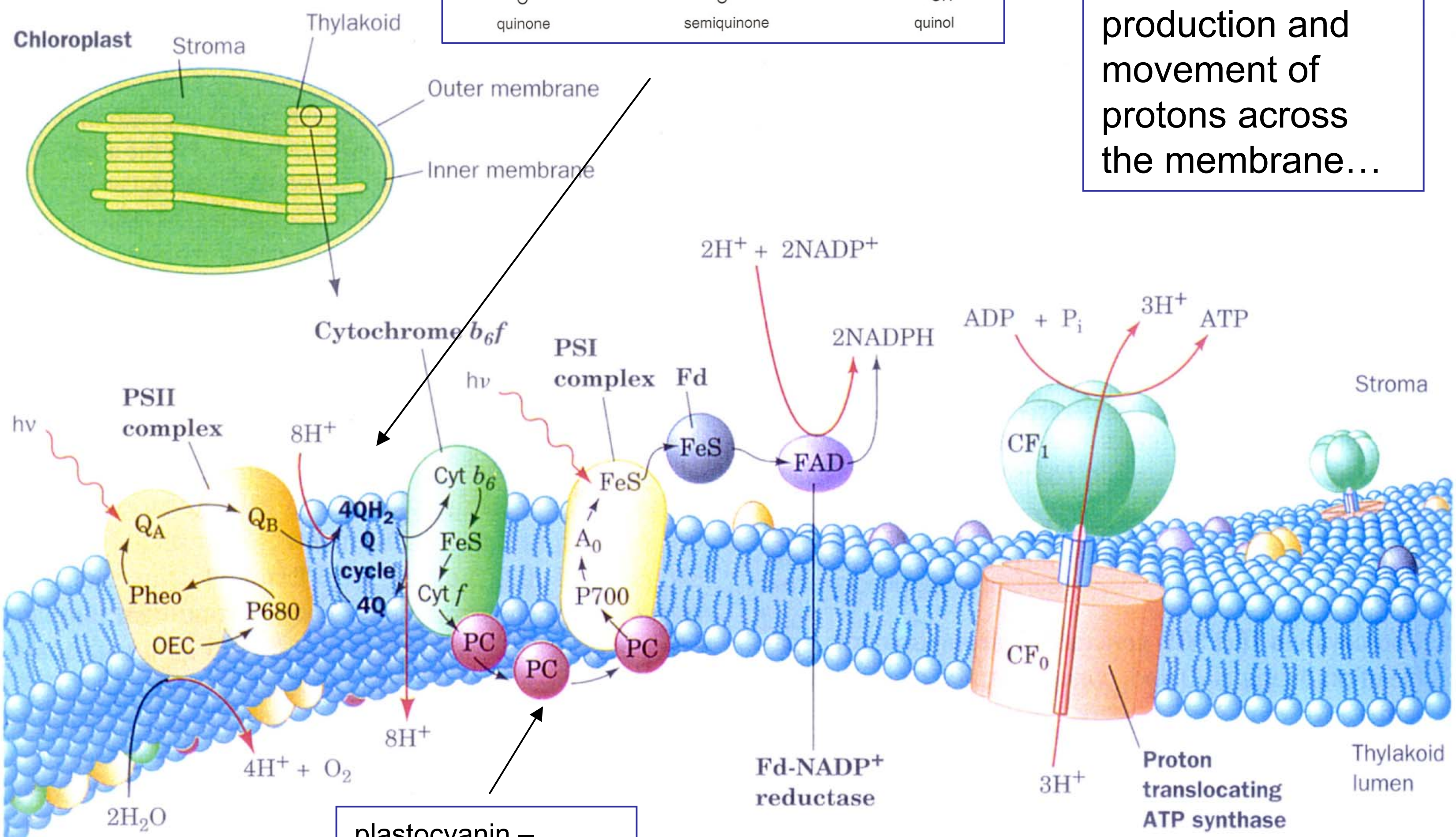


$NADP^+$

Green plant photosynthesis:



note: multiple production and movement of protons across the membrane…



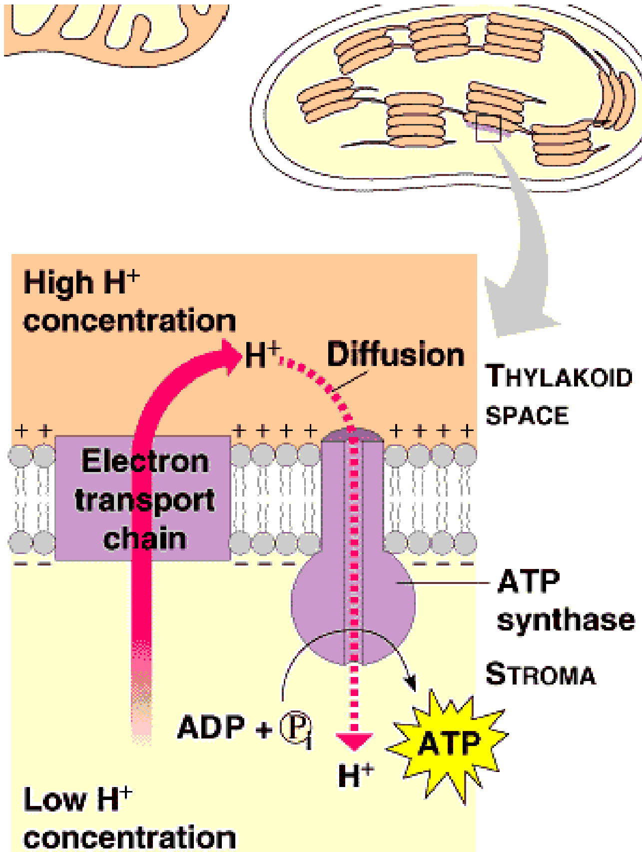
plastocyanin – reduces P_{700}^+ to P_{700}

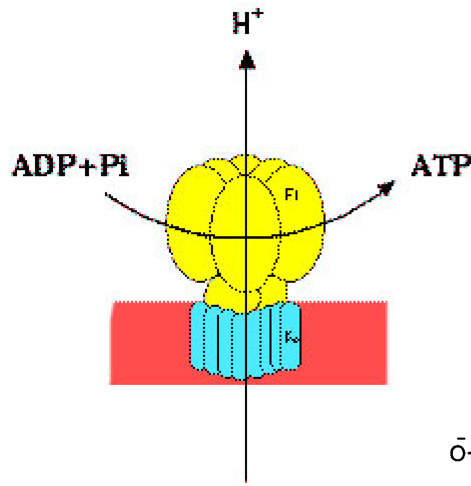
Proton Pump used to produce ATP from ADP:

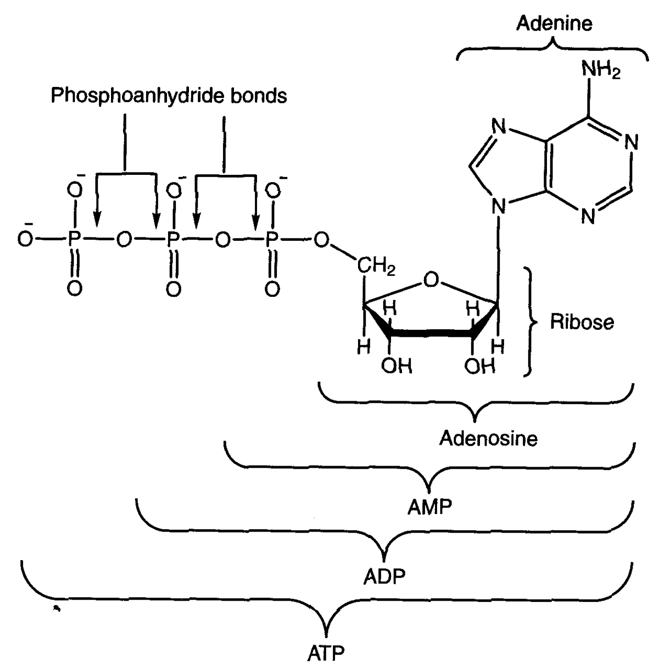
Recall from electrochemistry

$\mu = RT \ln[H^+]$

Concentration difference gives available energy



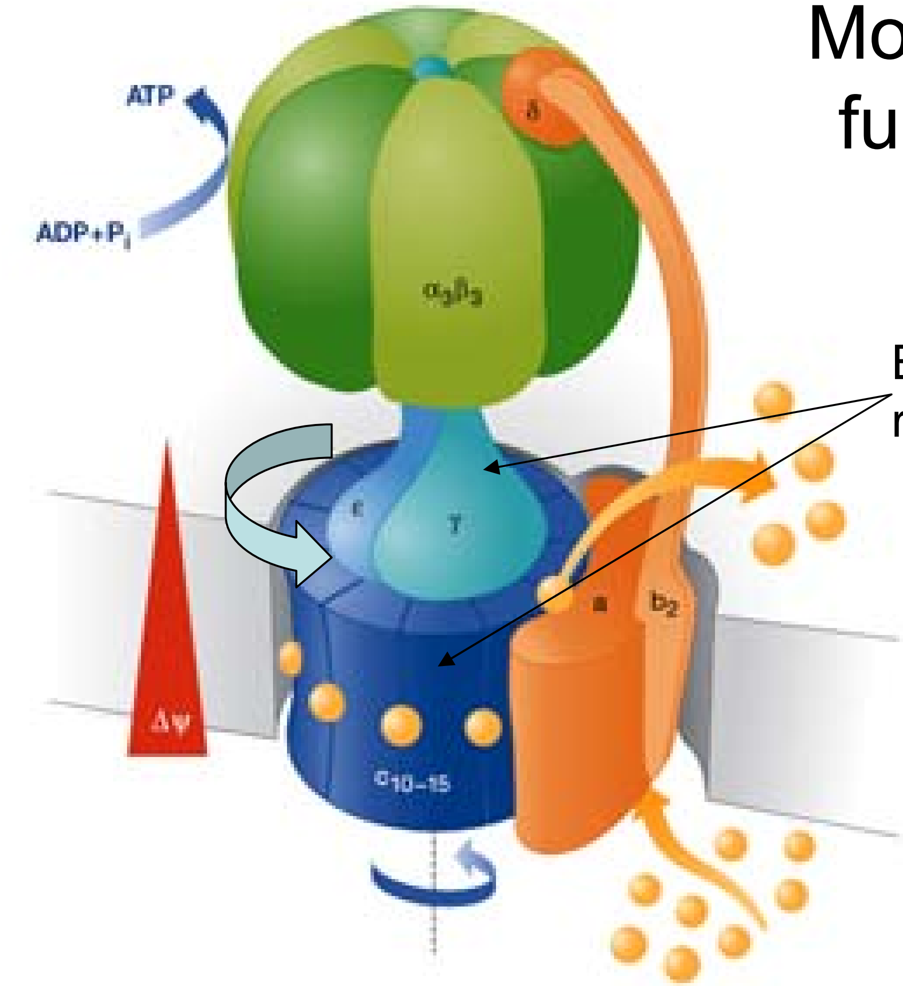




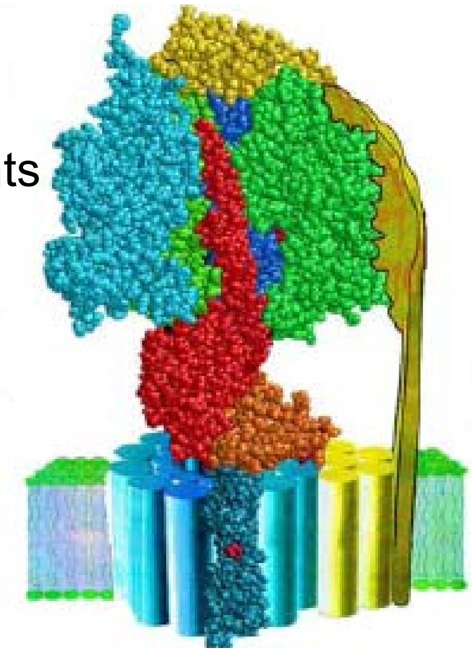
ATP - adenosine triphosphate

ADP – adenosine diphosphate

Molecular function

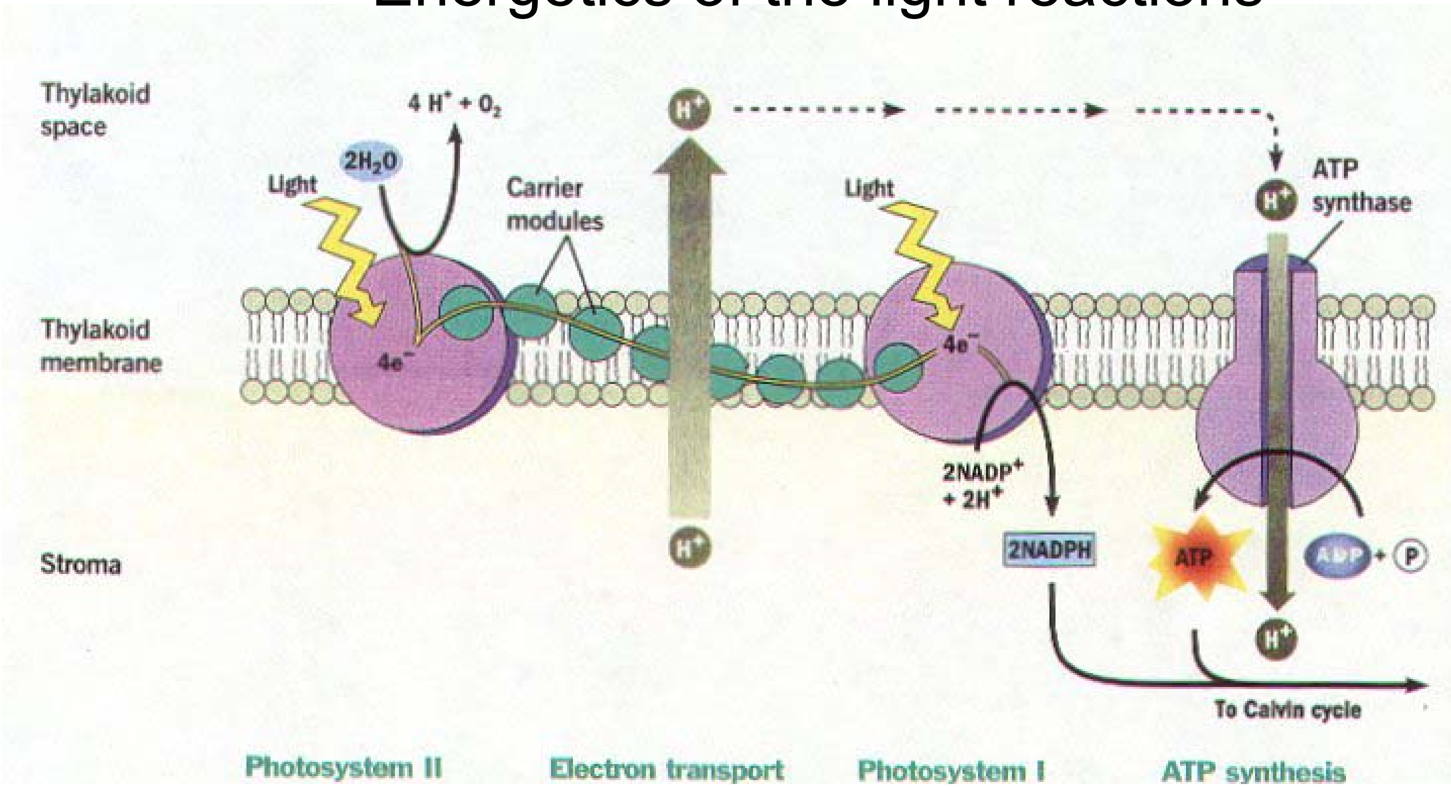


Blue components rotate



- Proton binding / release from transmembrane protein (F_0) drives rotation of circular *c* subunits, and drive shaft (γ) relative to *a,b* scaffold
- Drive shaft motion applies mechanical force to stationary $\alpha\beta$ subunits, driving ADP binding, reaction to ATP and ATP unbinding

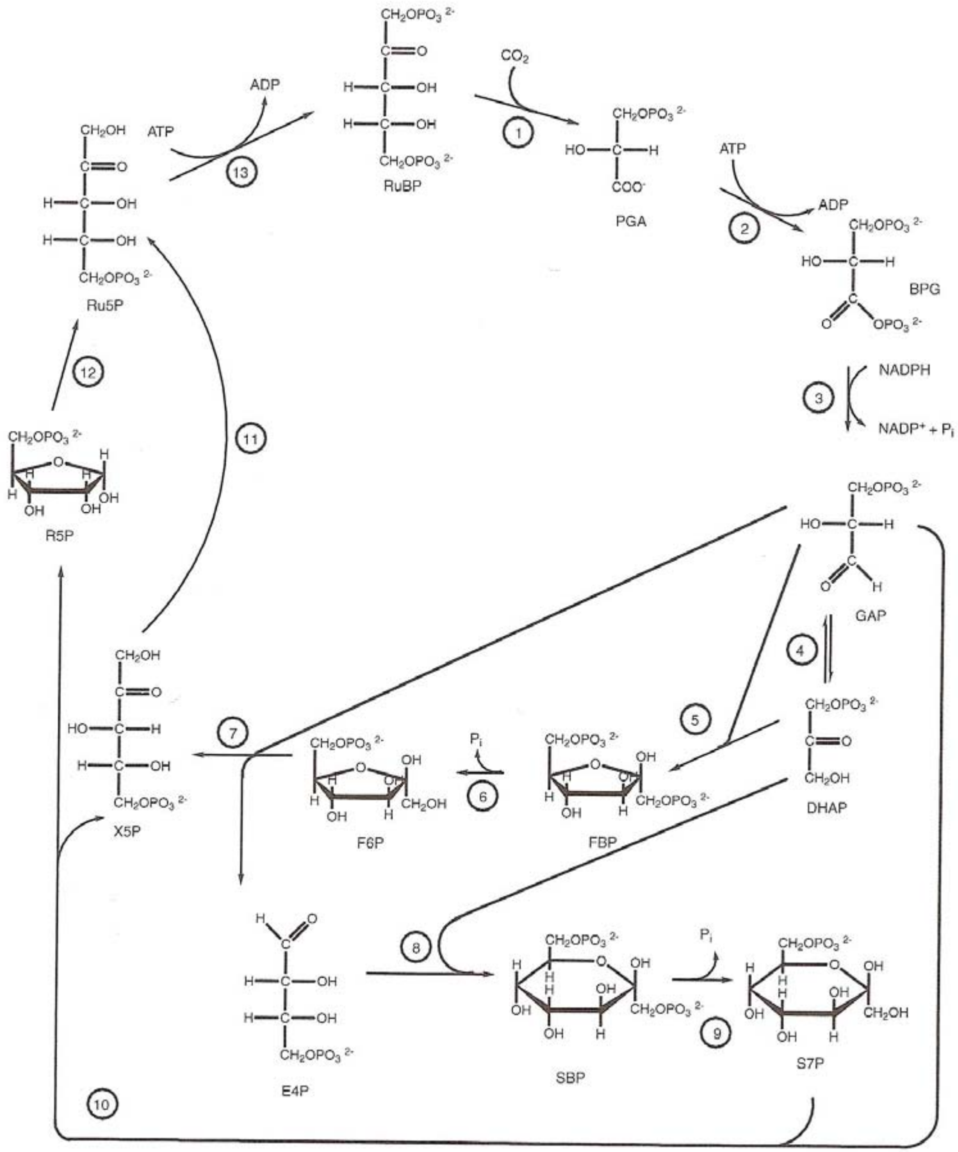
Energetics of the light reactions



8 photons (1360 kJ mol^{-1}) pump 4 e$^-$ (Q.E.=1)

- $2H_2O + 2NADP^+ \rightarrow O_2 + 2NADPH + 2H^+$
- ΔG_r ~ 500 kJ mol^{-1} (only approx as dependent on concentration)
- 6 protons pumped: ~ 250 kJ mol^{-1}
- Overall monochromatic energy conversion efficiency ~ 55 %
- Remaining energy losses in ATP synthesis and dark reactions of carbon fixation – optimum optical to biomass energy conversion efficiency 34%
- Reduced further to ~27% since Q.E.<1 (9-10 photons required)

Chemistry: Carbon metabolism - the Calvin cycle



NADPH and ATP provide the chemical energy required to fix CO_2 and convert to glucoses.

Enzyme for this chemistry: Rubisco

present in large quantities in plant matter (accounts for much of the protein in the plant leaf)

C_3 and C_4 plants: number of carbons in first product in the cycle is usually 3, but is 4 in some (more advanced) plants (maize, sugar cane).

Rubisco also fixes O_2 – this is a wasteful reaction – perhaps rubisco developed at a time when oxygen was not present in the atmosphere? Some plants have elaborate CO_2-concentrating mechanisms. Management of water loss is also important.