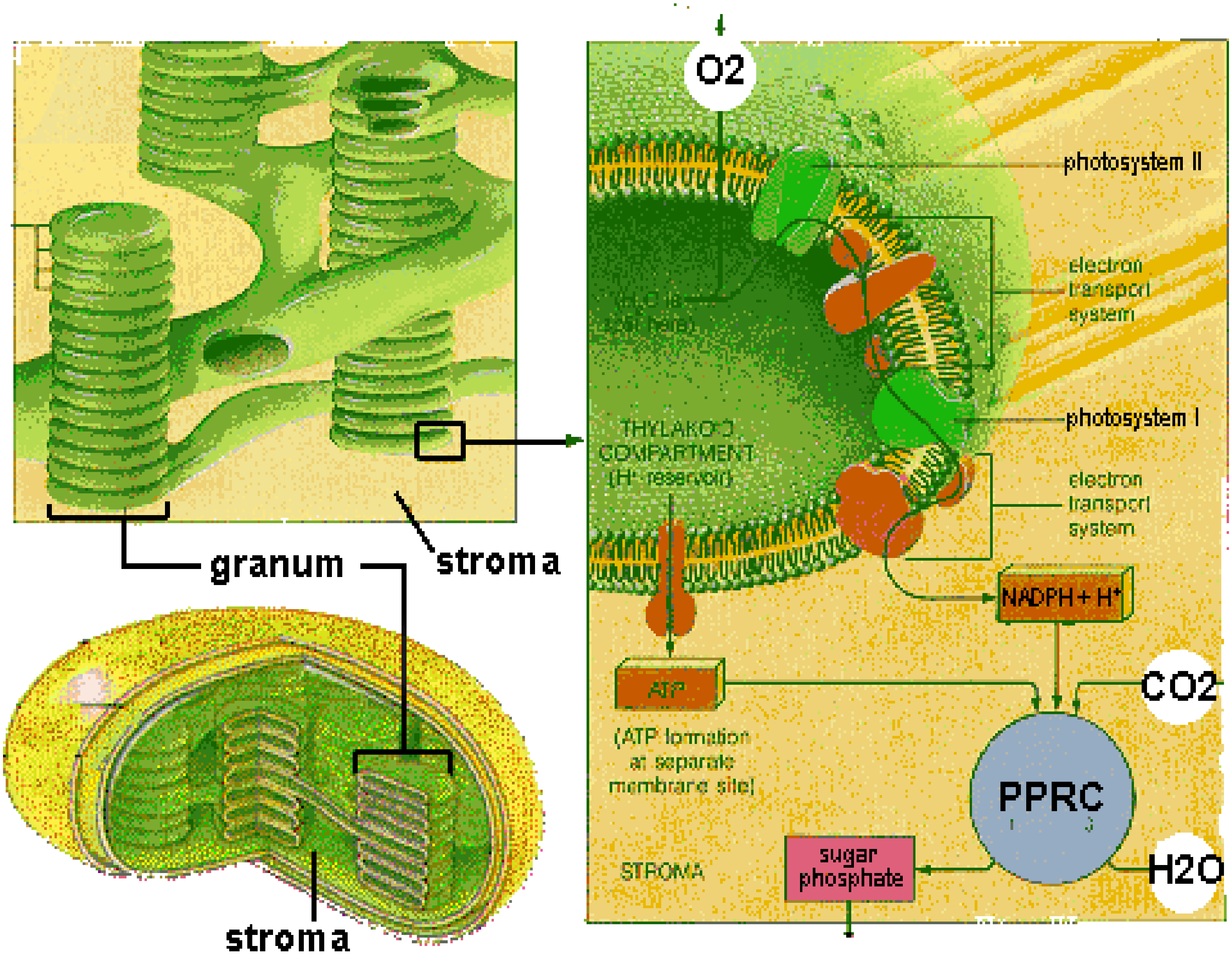
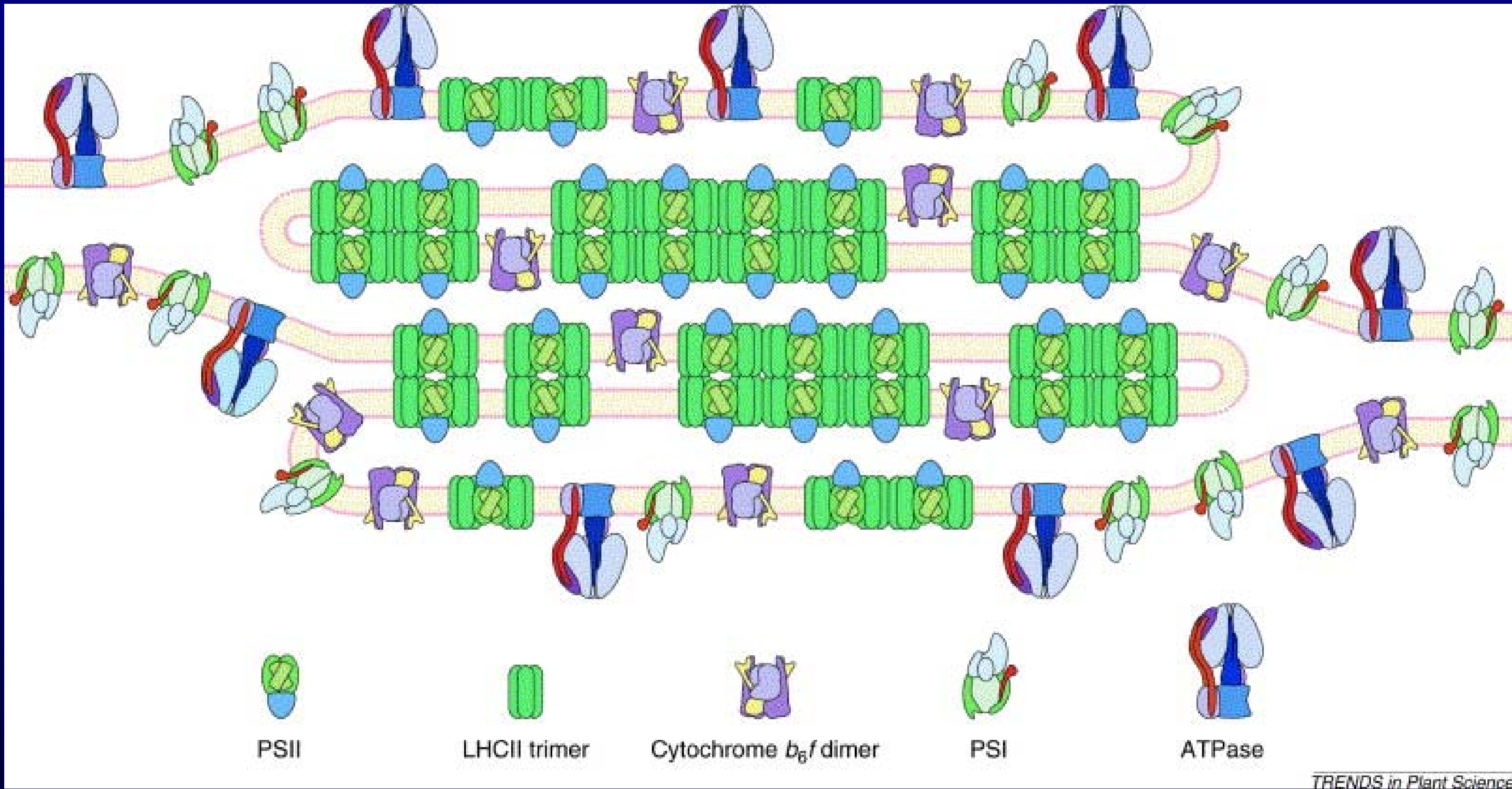
Introduction to Biophysics of Photosynthesis


granum
stroma
stroma
O2
photosystem II
electron transport system
photosystem I
electron transport system
THYLAKOID COMPARTMENT (H+ reservoir)
NADPH + H+
ATP
(ATP formation at separate membrane site)
CO2
PPRC
H2O
STROMA
sugar phosphate

Influence of steric hindrance on grana stacking

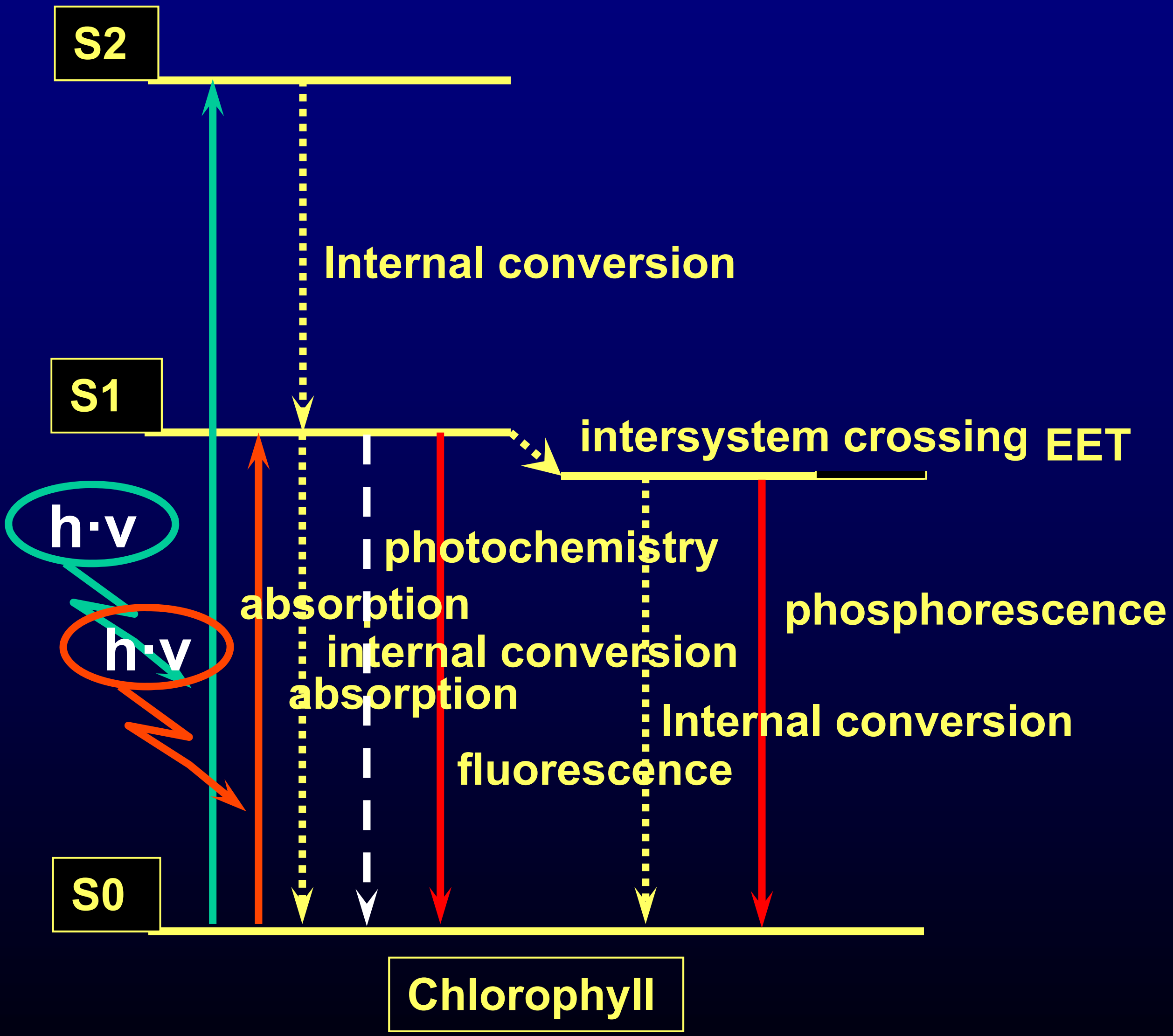


From: Allen JF, Forsberg J (2001) TIBS 6, 317–326

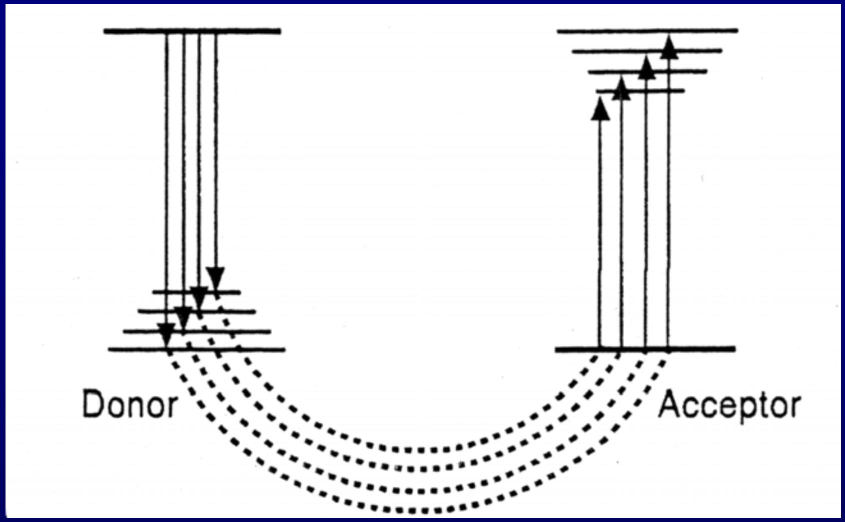
Mechanism of grana stacking

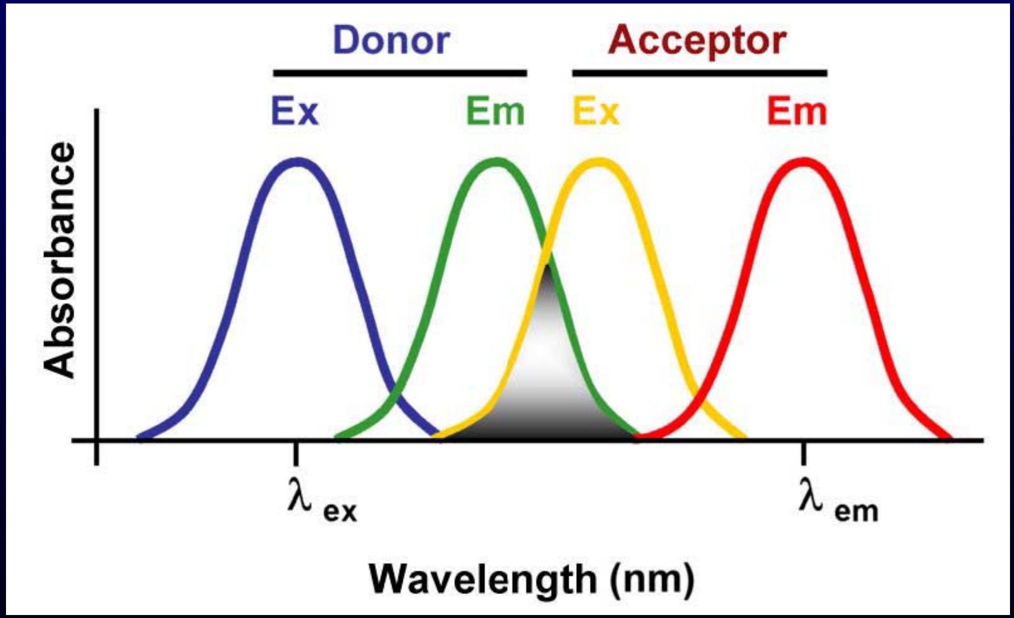
- 1. LHCII tends to aggregate
- 2. thylakoids containing a lot of LHCII will stick together, forming grana. PSIIRC nicely fits in because it does not protrude much out of the membrane
- 3. The more bulky PSIRC and the most bulky ATPase go into stroma regions

Necessary for energy transfer: stable S1-state



Necessary for energy transfer: Overlap of emission/absorption bands



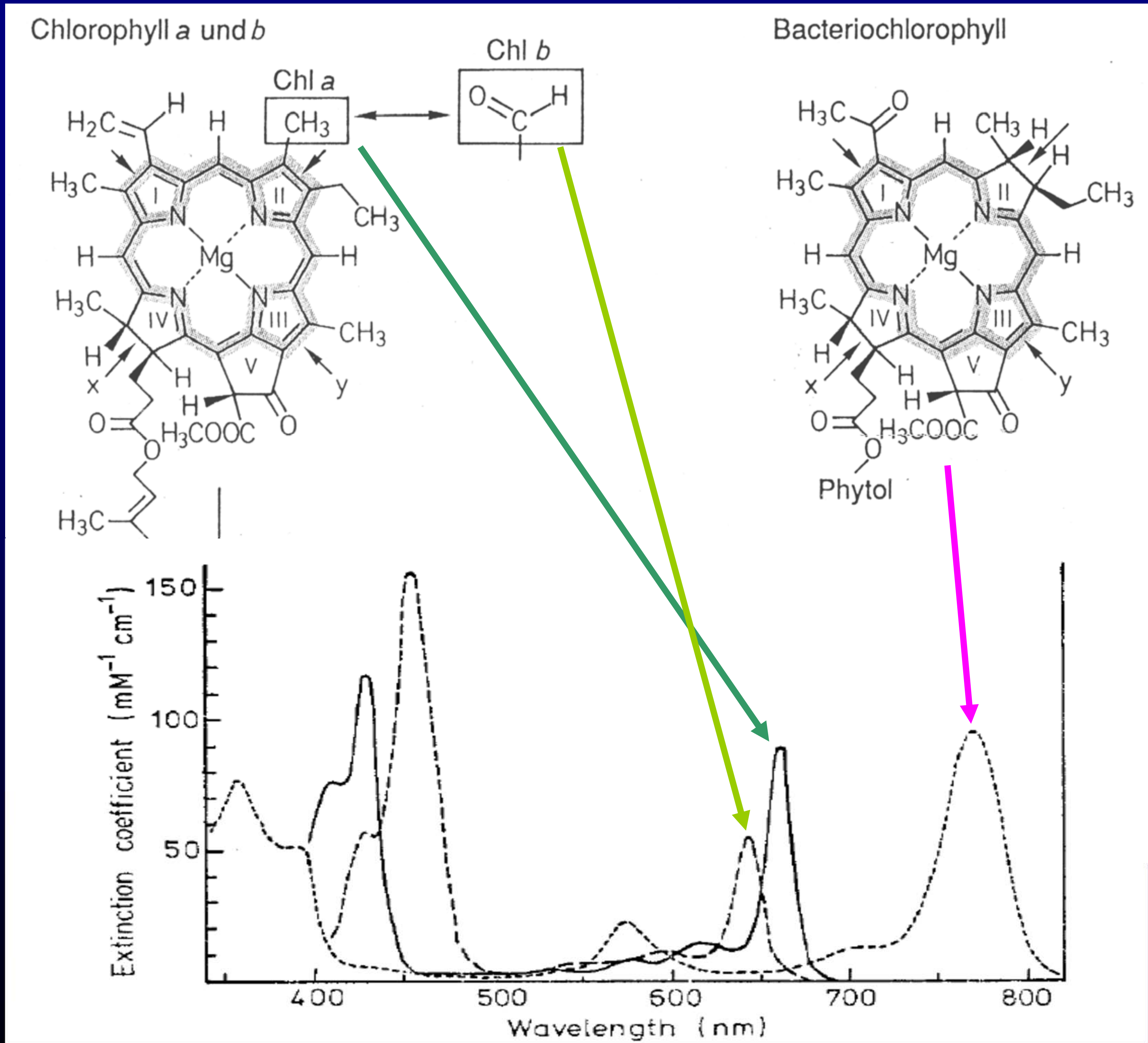


From: bio.libretexts.org

Adjustment of absorption bands by chemical modification

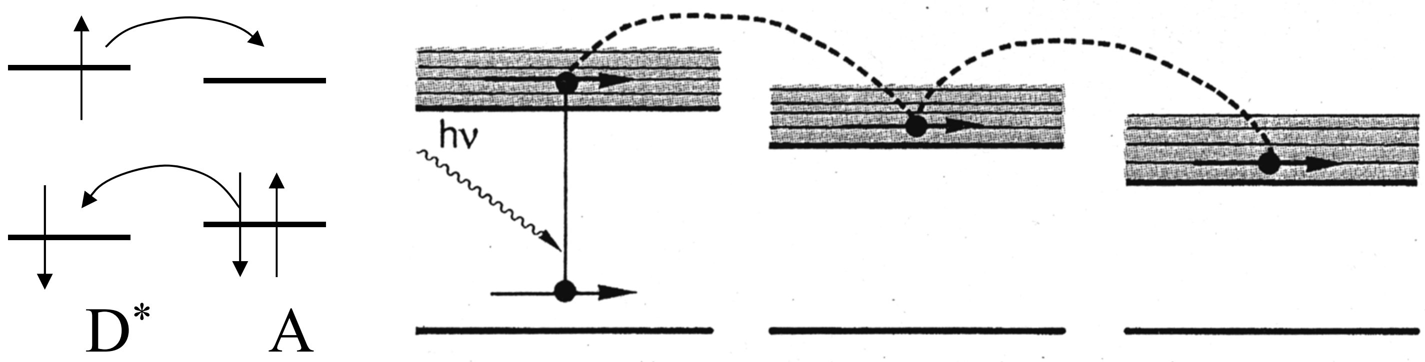
From: Lawlor DW (1990) Thieme, Stuttgart, 377S

From: Barber J (1978) Rep Prog Phys 41, 1158-99

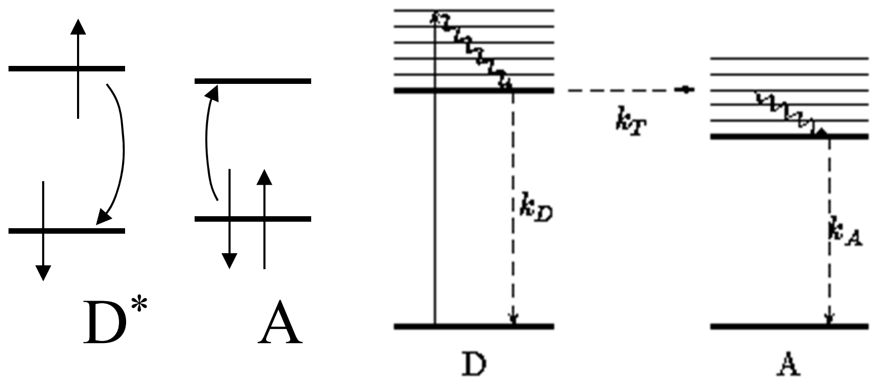


Mechanisms of energy transfer between chlorophylls

Short distance, requires overlap of molecular orbitals (→ only Chls in extremely short distance to each other, e.g. special pair) : direct transfer of S1 excited state (Dexter-Mechanism)



Larger distance, requires overlap of absoprtion/emission spectra: Transfer by induktive Resonance („Förster-Mechanism“)

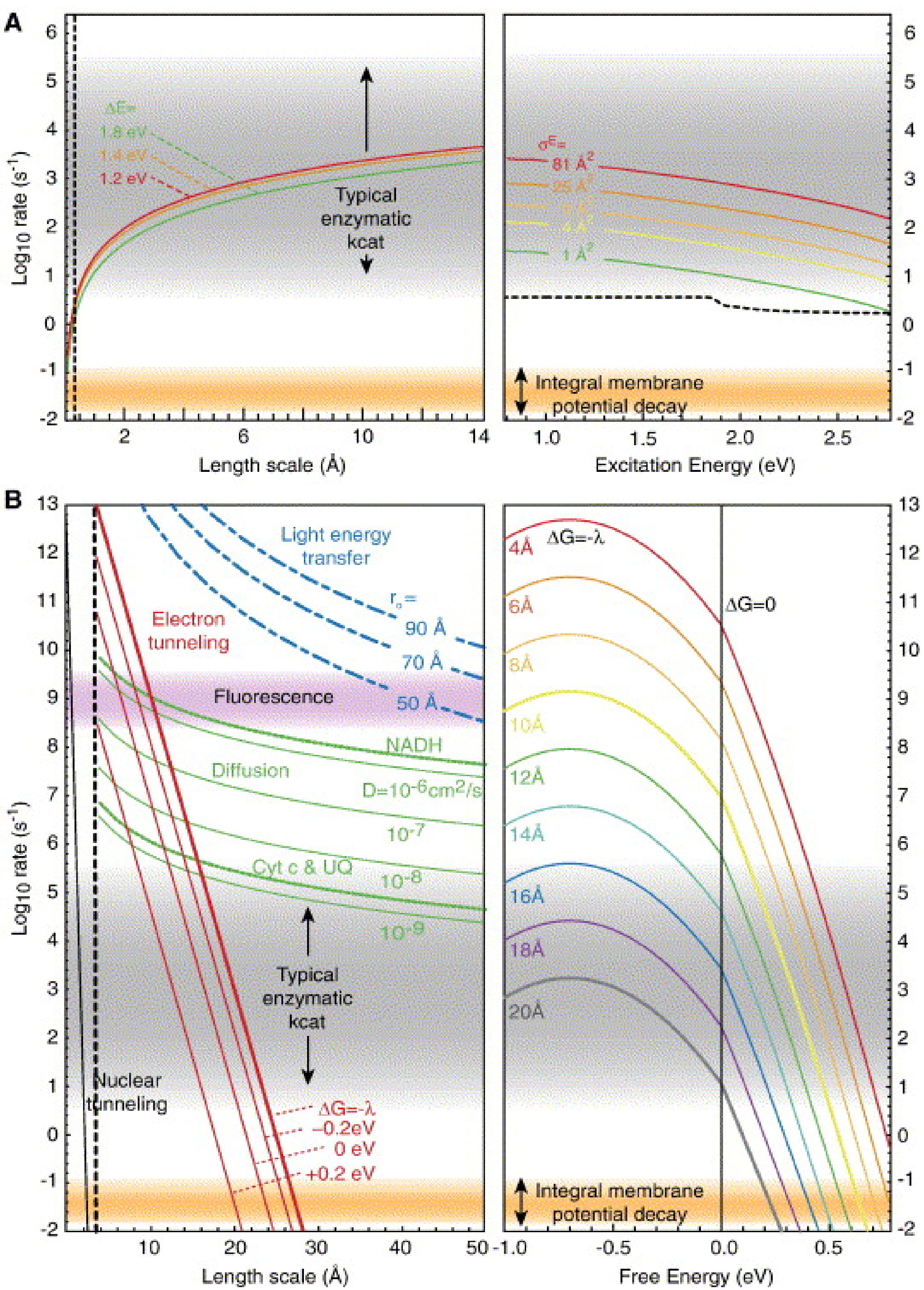


$$\Gamma_{DA} = k_D \left(\frac{R_0}{R}\right)^6$$

$$R_0^6 = 8.8 \times 10^{17} \frac{\kappa^2}{n^4} J$$

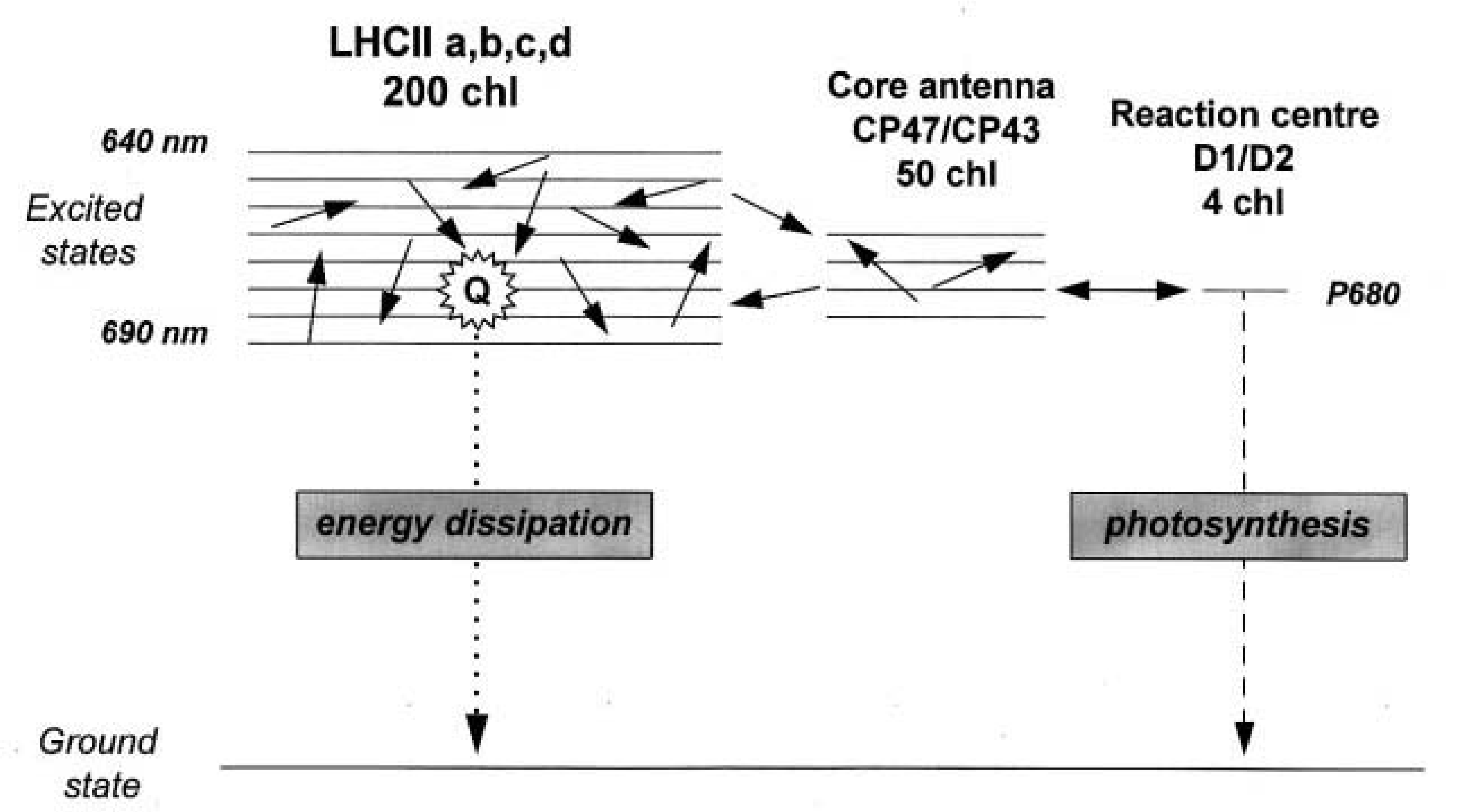
Comparison of other Energy transfer mechanisms

- For all processes, speed of energy transfer decreases with increasing distance.
- This limits the rate and efficiency of enzymatic and non-enzymatic processes. The longer the transfer time, the higher the risk of energy loss by unwanted processes
- Light energy transfer is fast and covers large distances, but required re-absorption and thus is not very efficient
- Electron tunnelling is fast for very short distances, but very slow for longer distances → most relevant <10Å.
- Diffusion speed decreases less with increasing distances, therefore it becomes faster than tunnelling at more than 10-20Å.



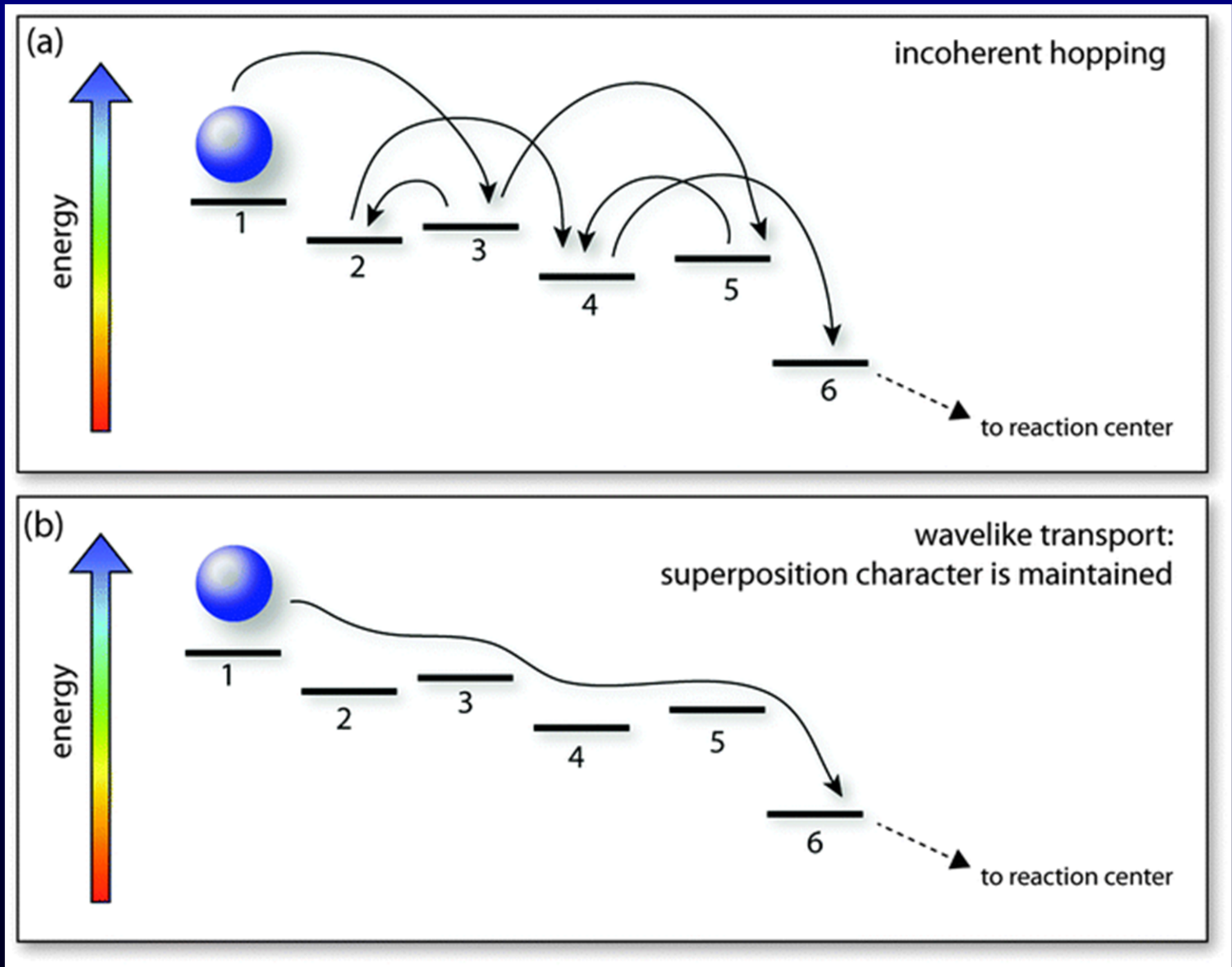
From: Noy D, Moser CC, Dutton PL (2006) BBA Bioen. 1757, 90-105

Energy transfer – funnel principle (II): Scheme in higher plants



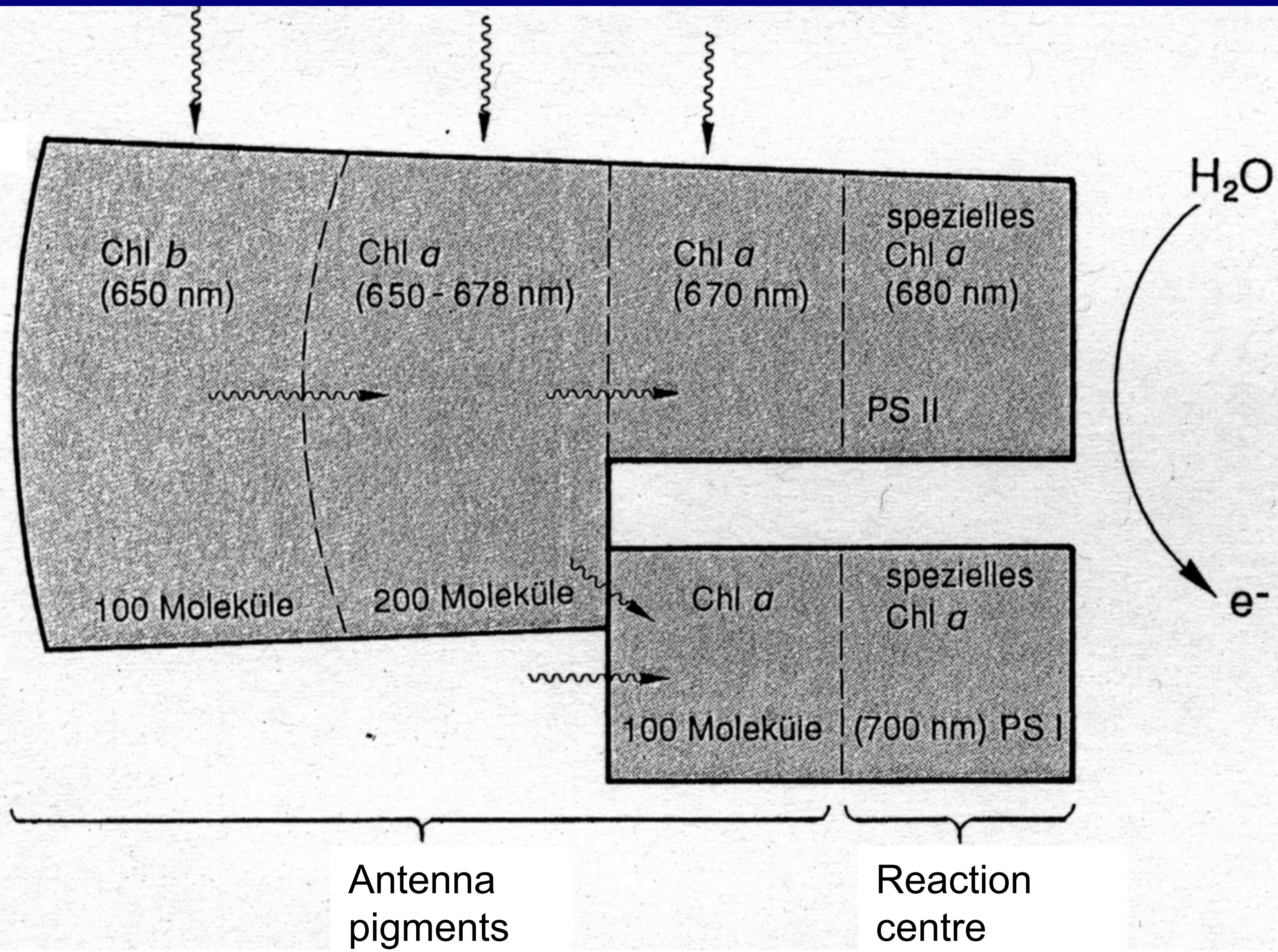
From: Horton P, Ruban AV, Walters RG (1996) Annu Rev Plant Physiol Plant Mol Biol 47: 655-84

Energy transfer – funnel principle (II): debated modern view



From: Collini E (2013) Spectroscopic signatures of quantum-coherent energy transfer. Chemical Society Reviews 42, 4932-4947

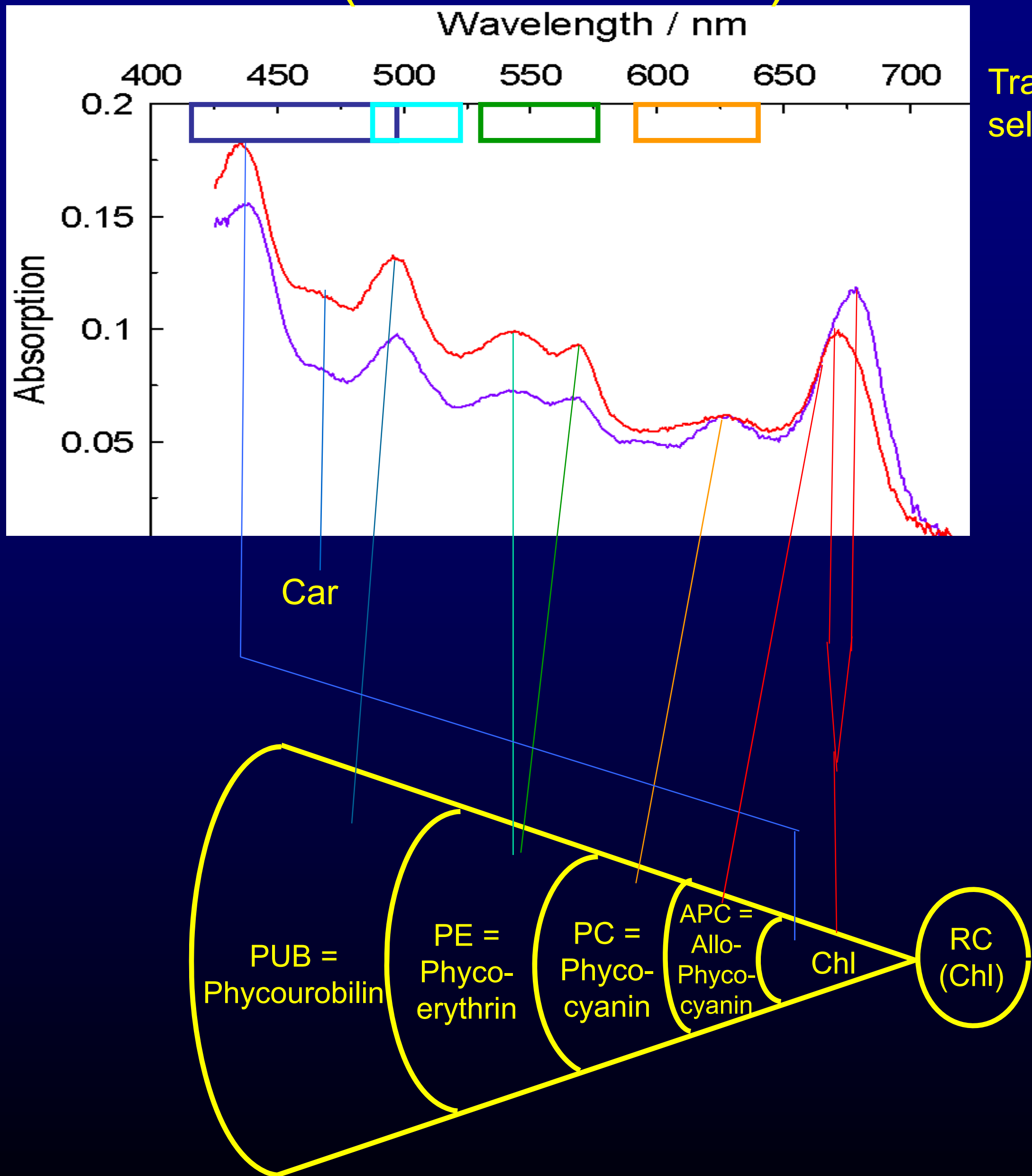
Energy transfer – funnel principle (II): Scheme in higher plants



Absorb shortest wavelengths → absorb longer wavelengths → absorb longest wavelengths

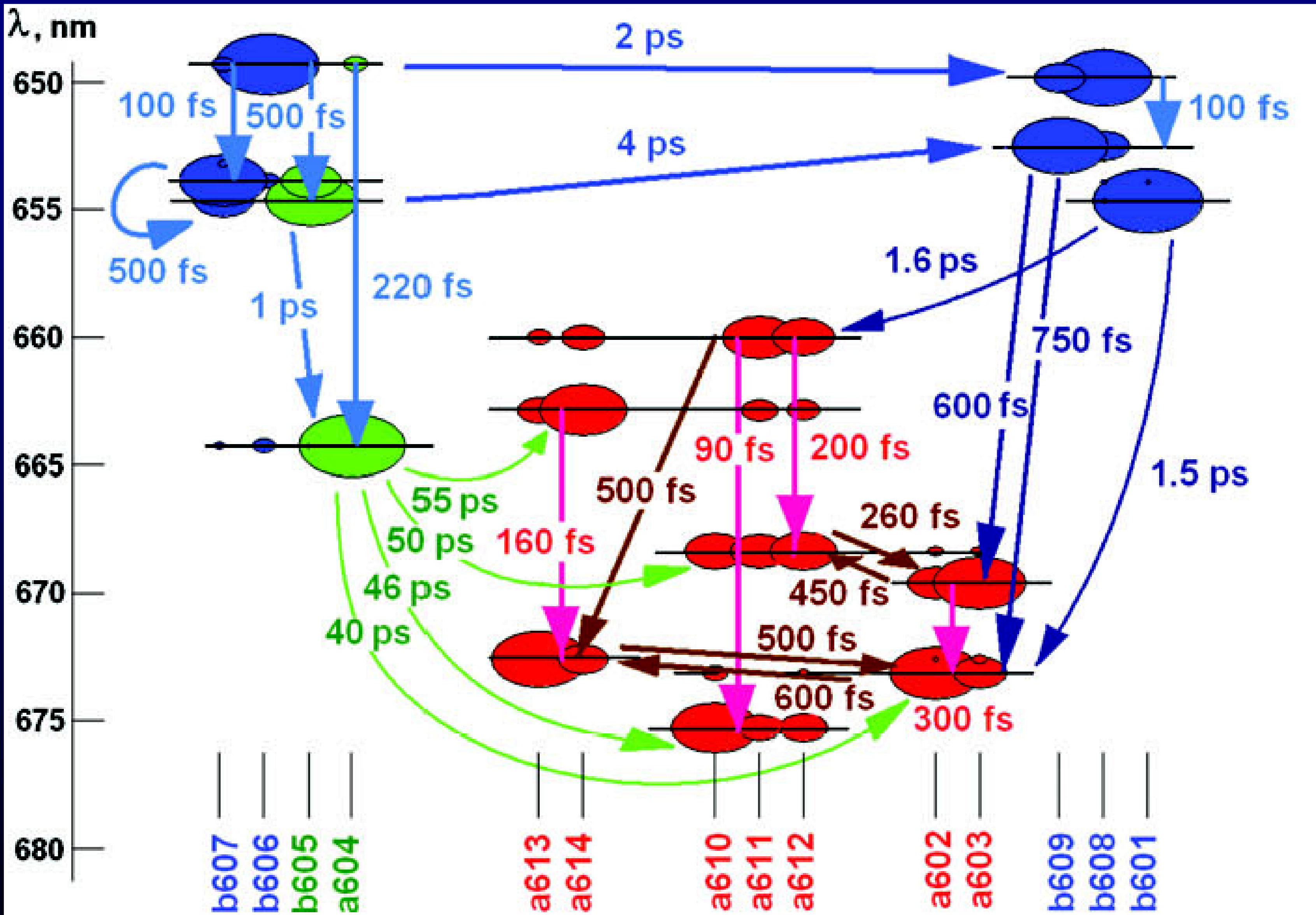
From: Lawlor DW (1990) Thieme, Stuttgart, 377S

Energy transfer – funnel principle (II): Scheme in cyanobacteria (*Trichodesmium*)



Transmission of filters for selective excitation

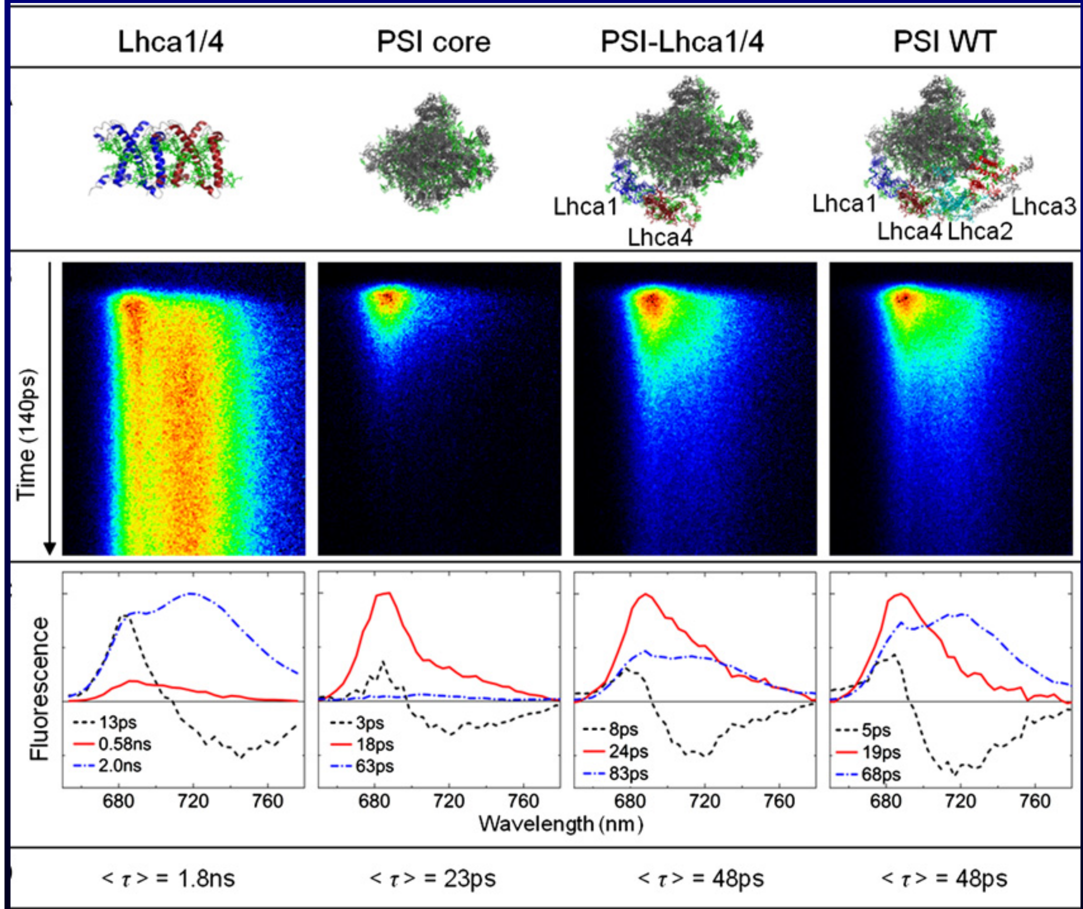
Energy transfer – funnel principle (III): Transfer times between Chls towards & in PSIIRC



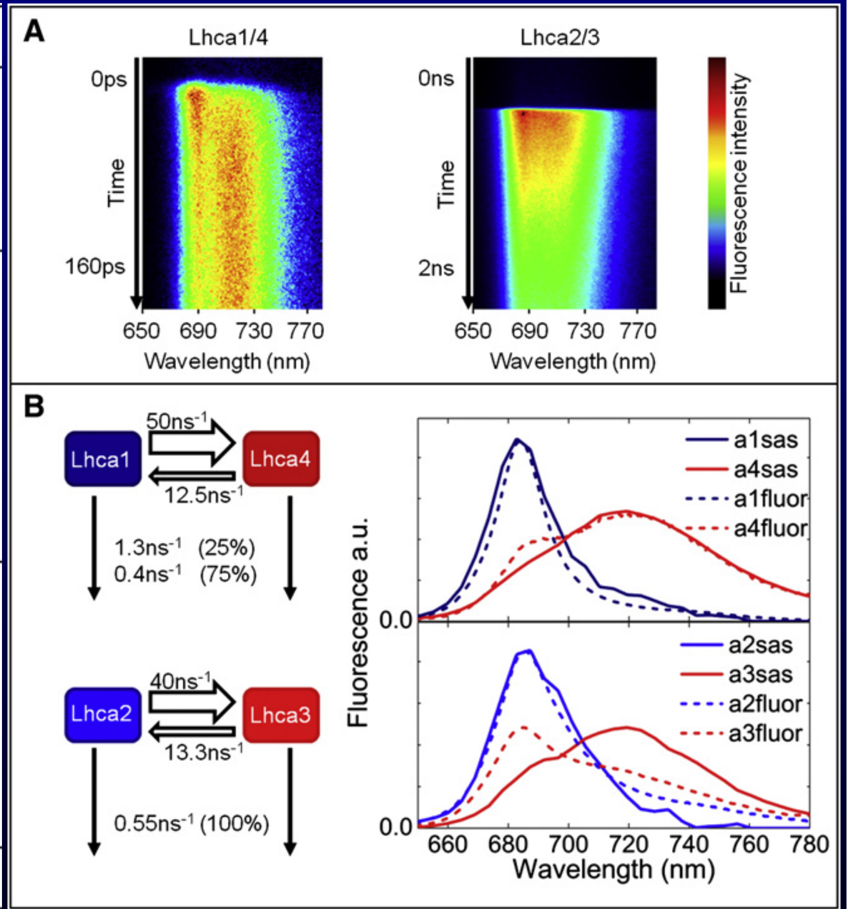
From: vanGrondelle R, Novoderezhkin VI, 2006, PCCP8, 793-807

Photosynthesis related Proteins with metal centres

1. Excitation transfer times between light harvesting complexes



From: Wientjes E_et al (2011) BiophysJ101, 745-54



From: Wientjes E_et al (2011) BiophysJ 100, 1372-80

Photosynthesis related Proteins with metal centres

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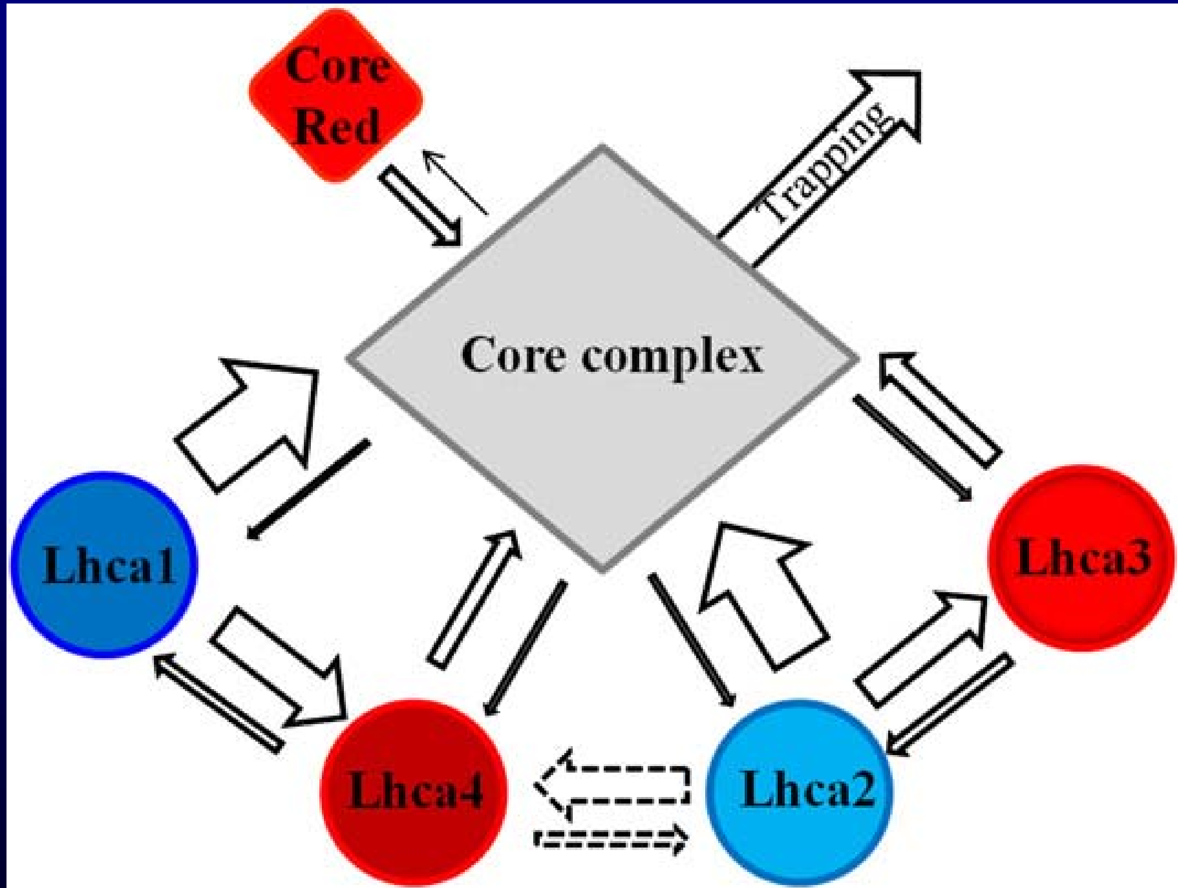
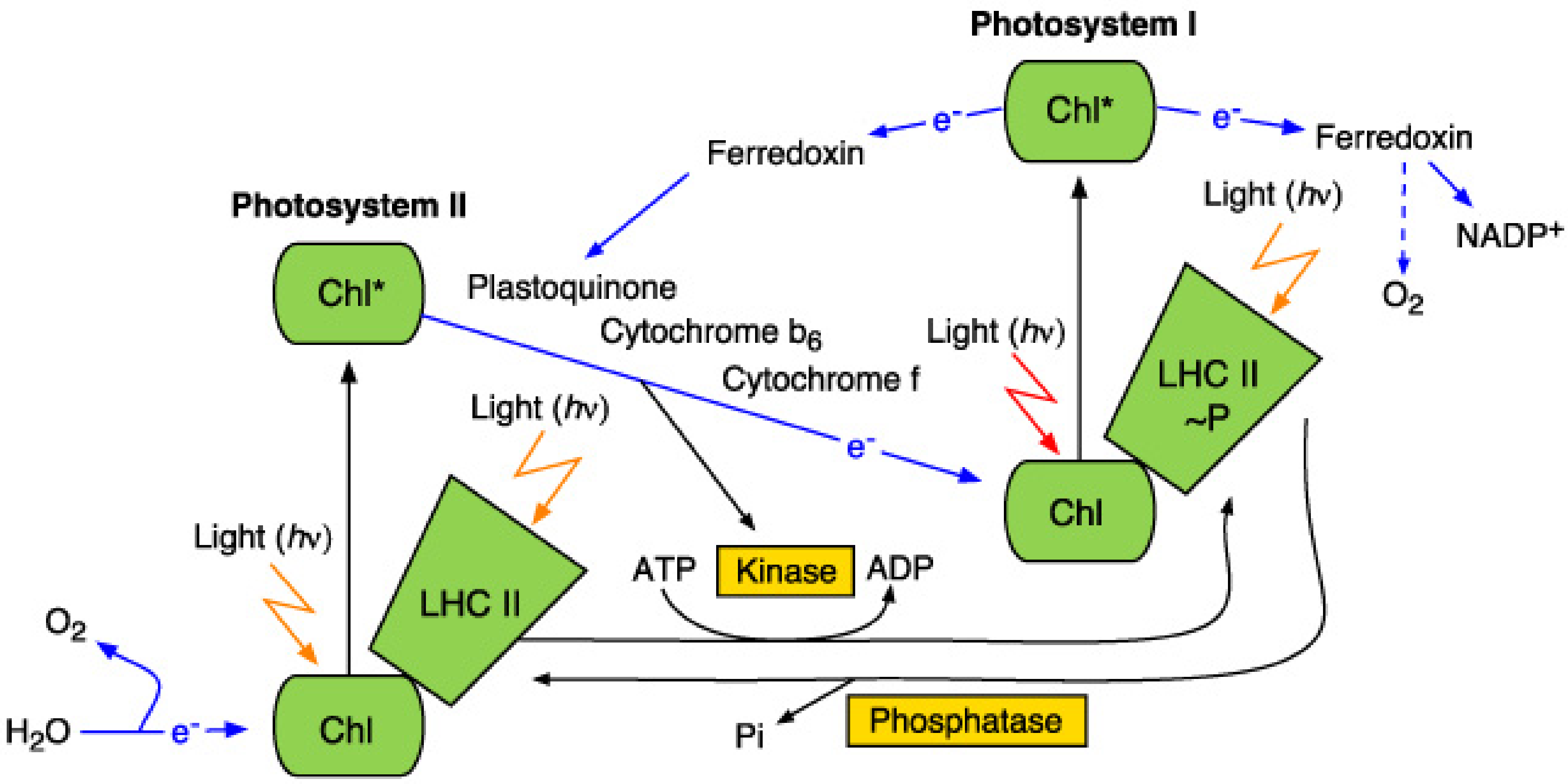


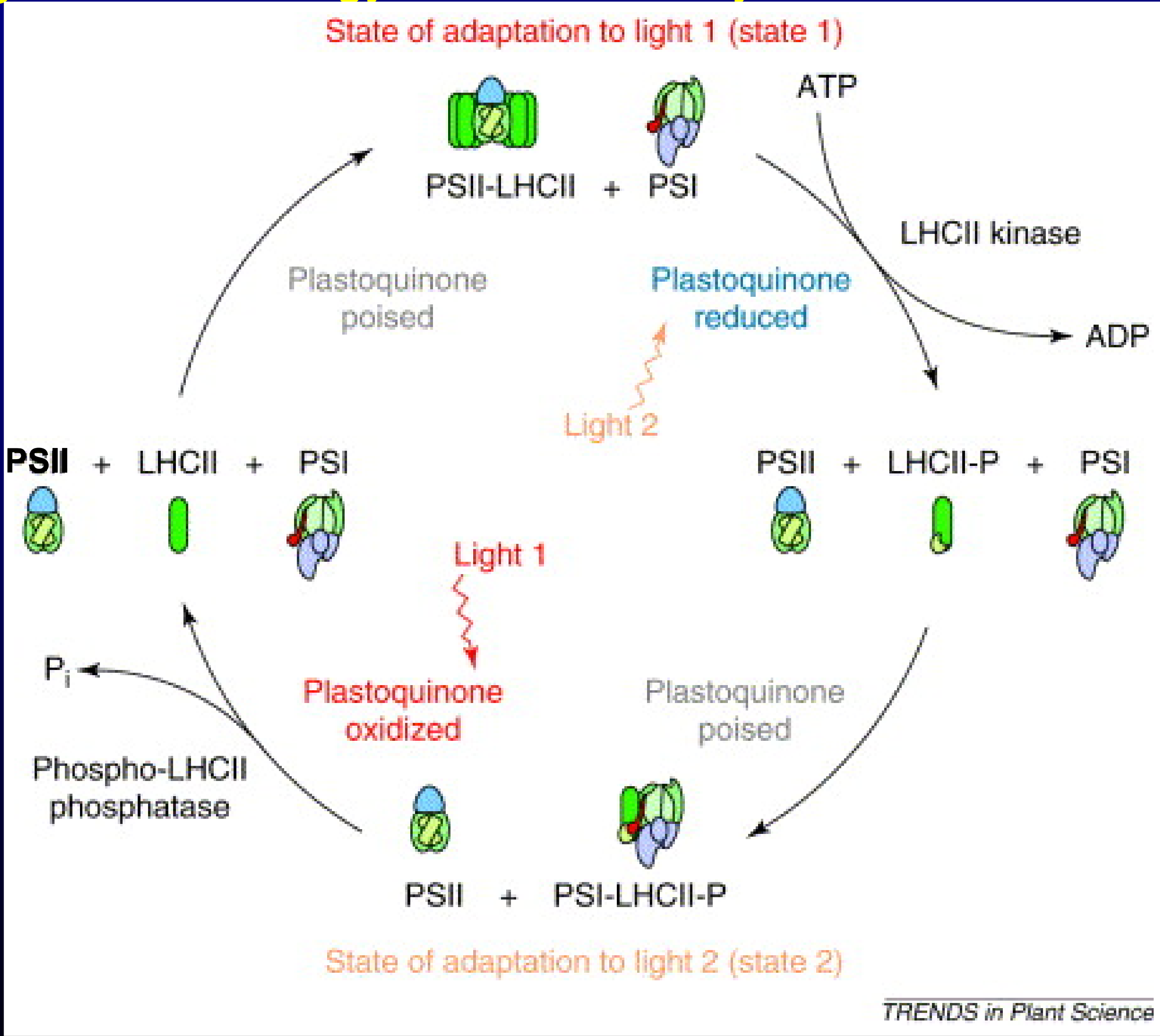
From: Wientjes E_et al (2011) BiophysJ101, 745-54

Regulation of energy transfer (I): the principle of „state transitions“

Higher plants, many algae



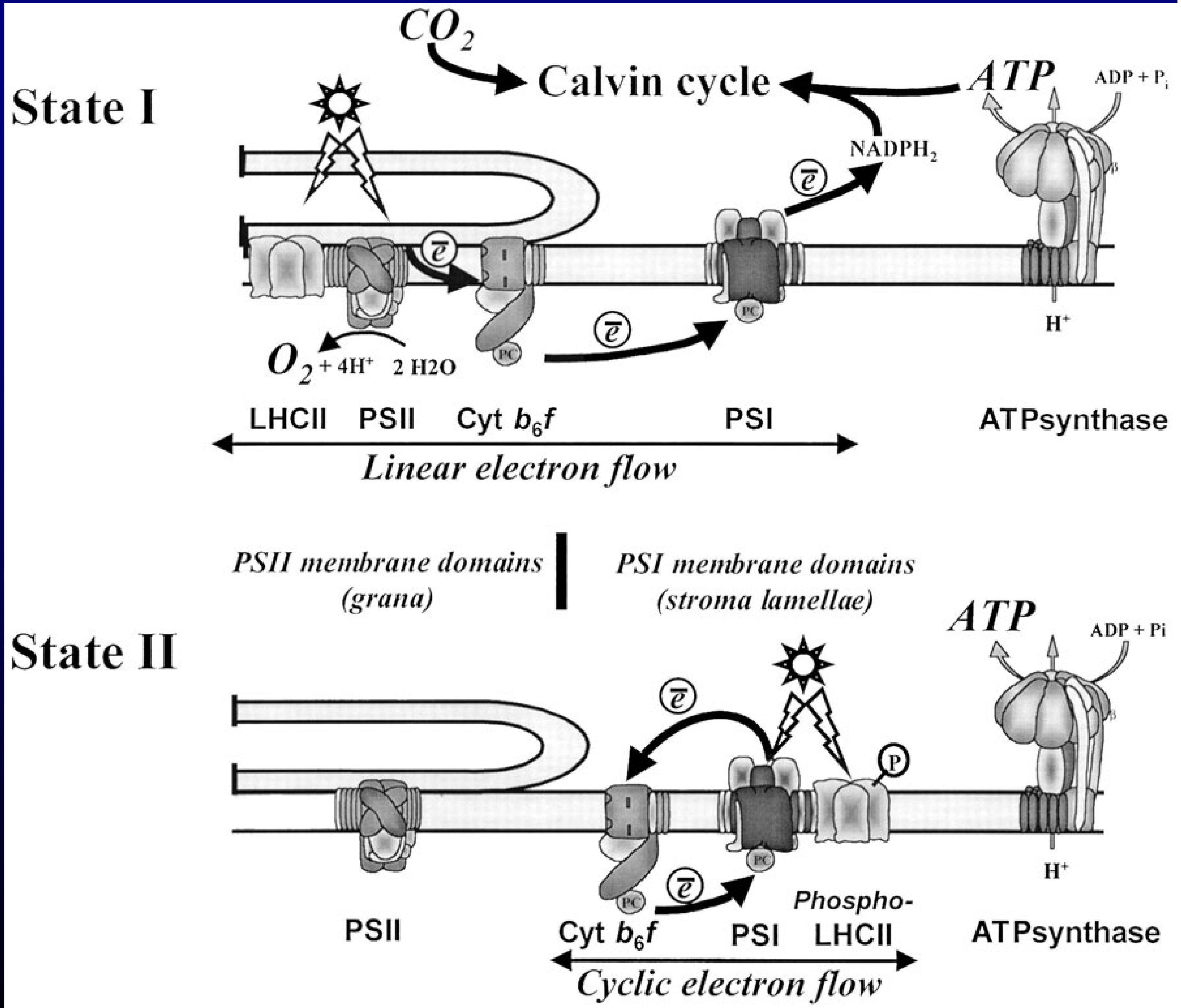
Regulation of energy transfer: The cycle of state transitions



From: Allen JF, Forsberg J (2001) TIBS 6, 317–326

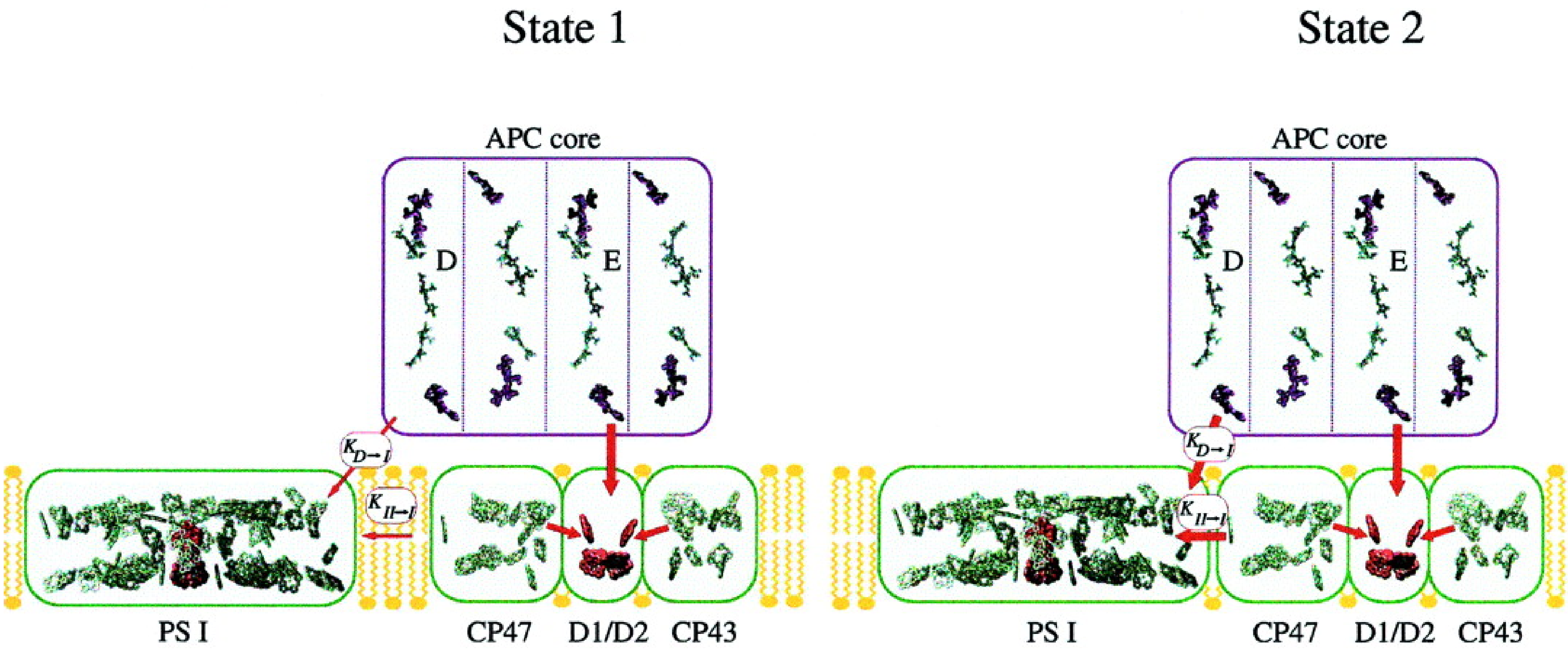
Regulation of energy transfer: another view of „state transitions“

Alternative view of the function of state transitions



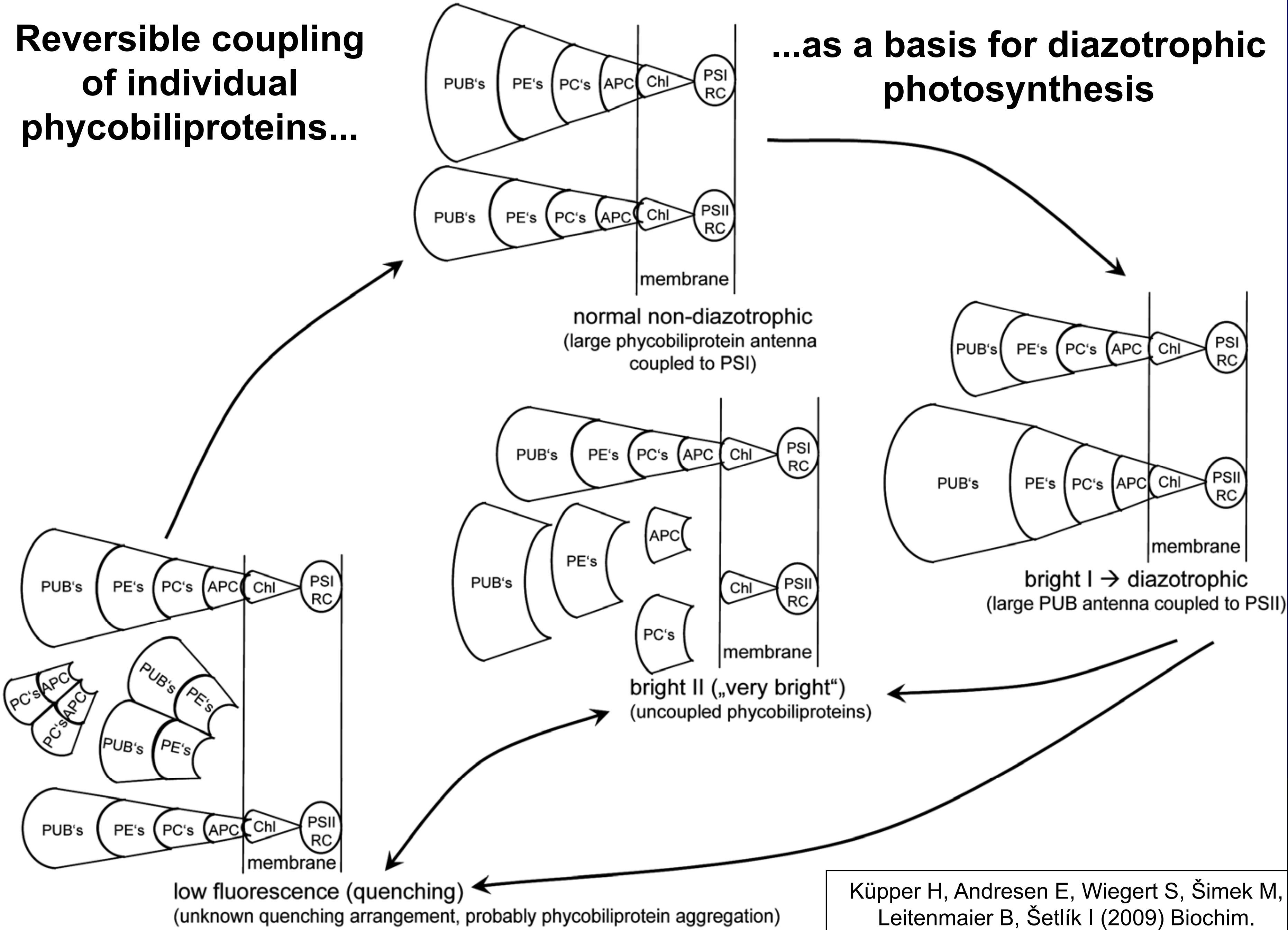
From: Wollman FA (2001) The EMBO Journal (2001) 20, 3623 - 3630

Regulation of energy transfer (I): „state transitions“ in cyanobacteria and red algae



Reversible coupling of individual phycobiliproteins...

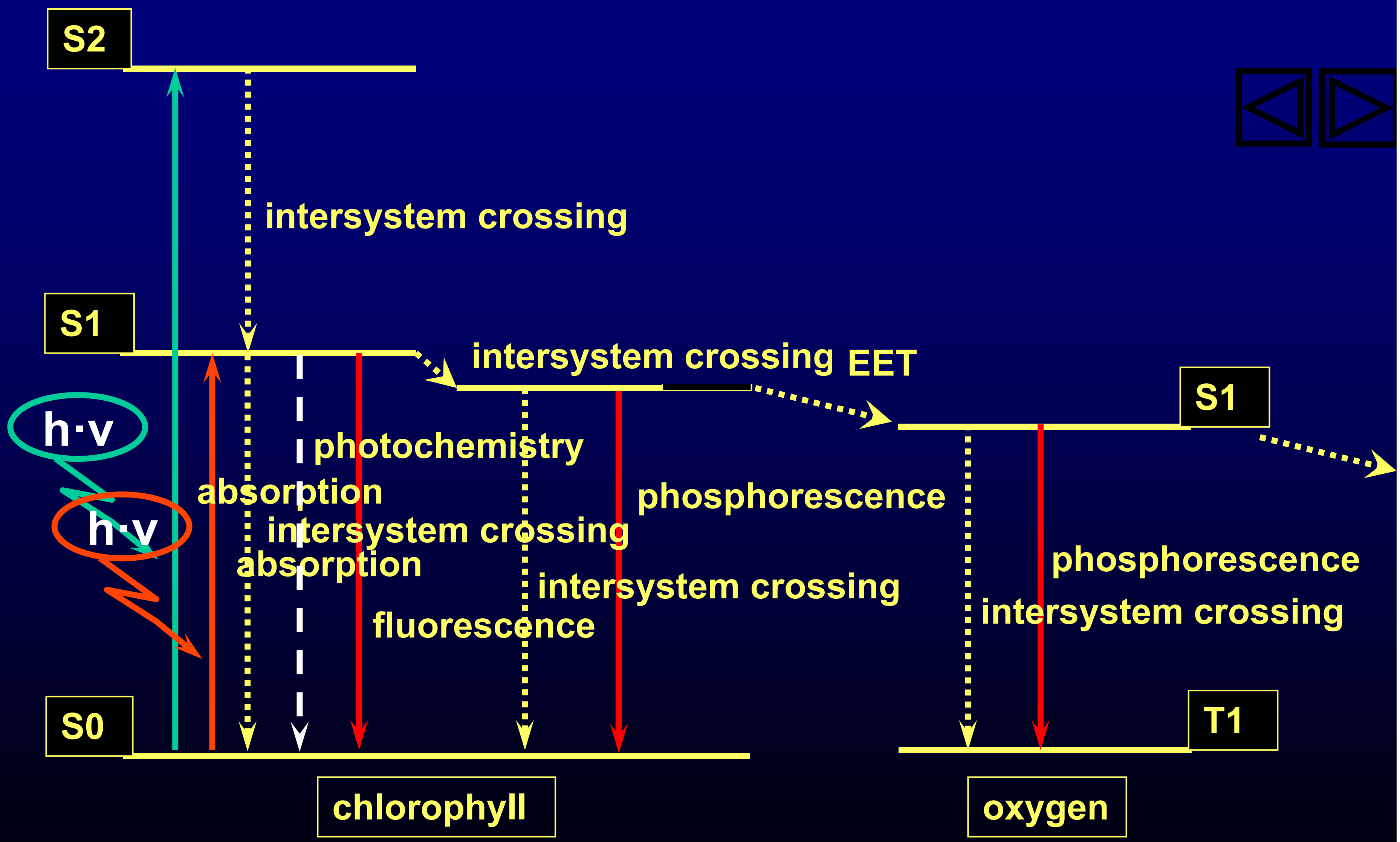
...as a basis for diazotrophic photosynthesis



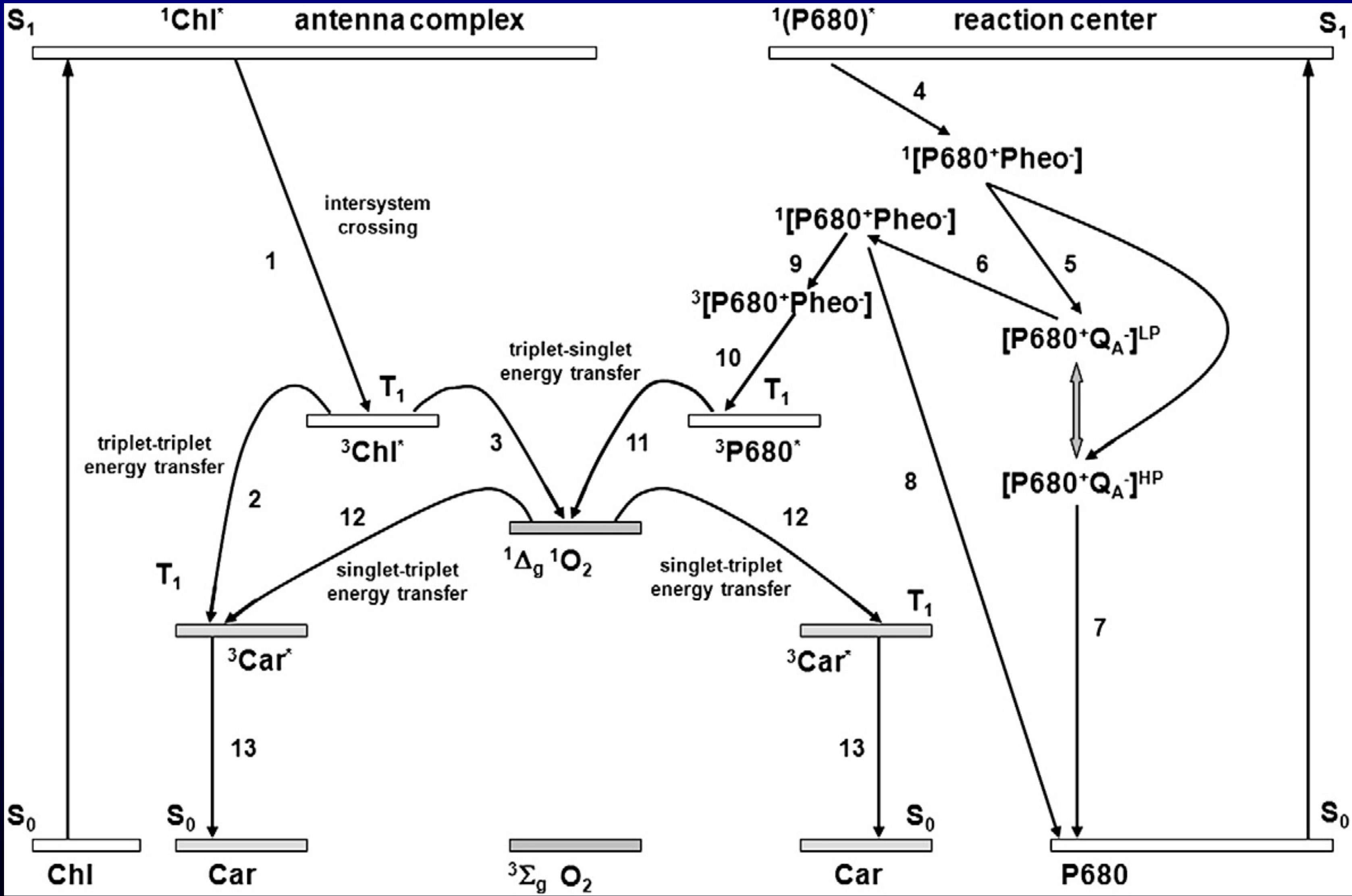
Küpper H, Andresen E, Wiegert S, Šimek M, Leitenmaier B, Šetlík I (2009) Biochim. Biophys. Acta (Bioenergetics) 1787, 155-167

Excitation energy transfer

between chlorophyll derivatives and singlet oxygen

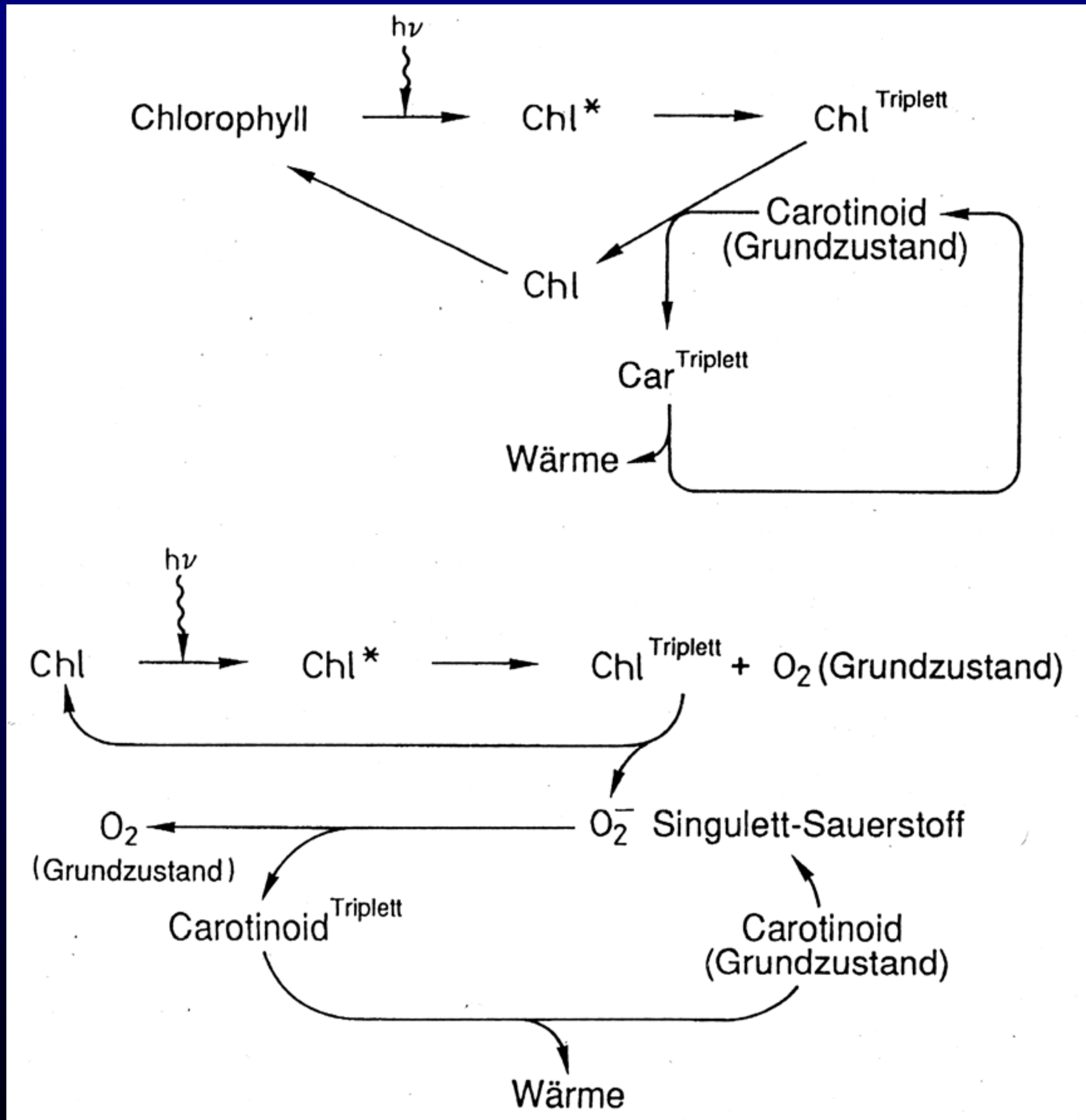


Photosynthesis related Proteins with metal centres
1. LHCII & PSIIRC: generation&quenching of $^1O_2$



From: Pospisil P (2012) Biochimica et Biophysica Acta 1817, 218-31

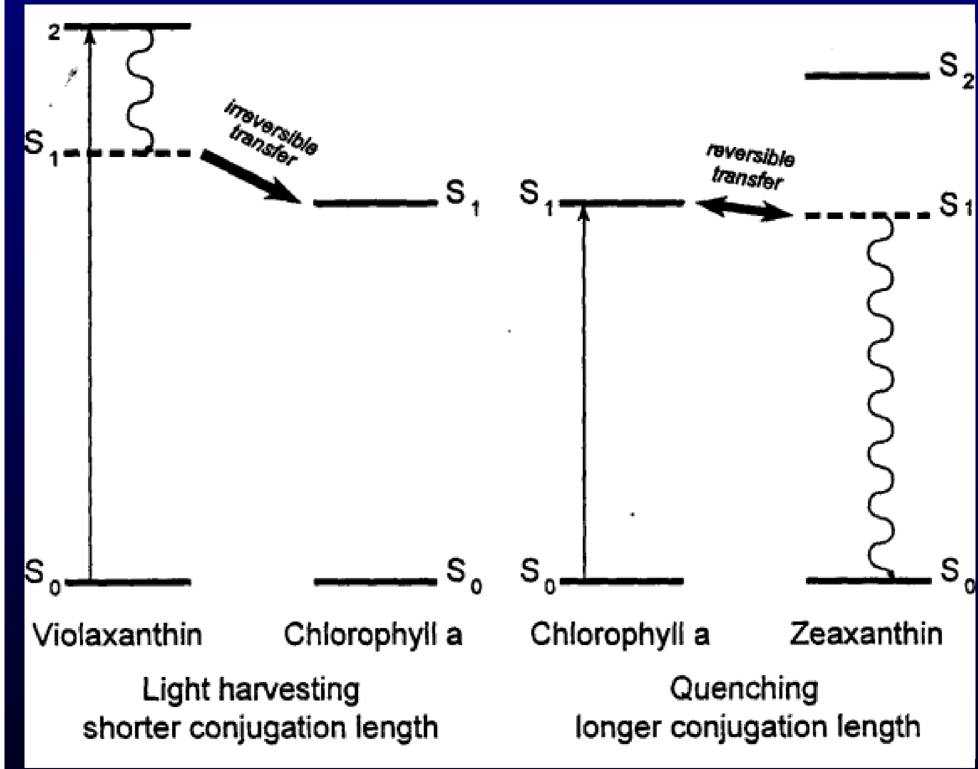
Regulation of energy transfer (II): Mechanisms of protection by carotenoids against singlet oxygen

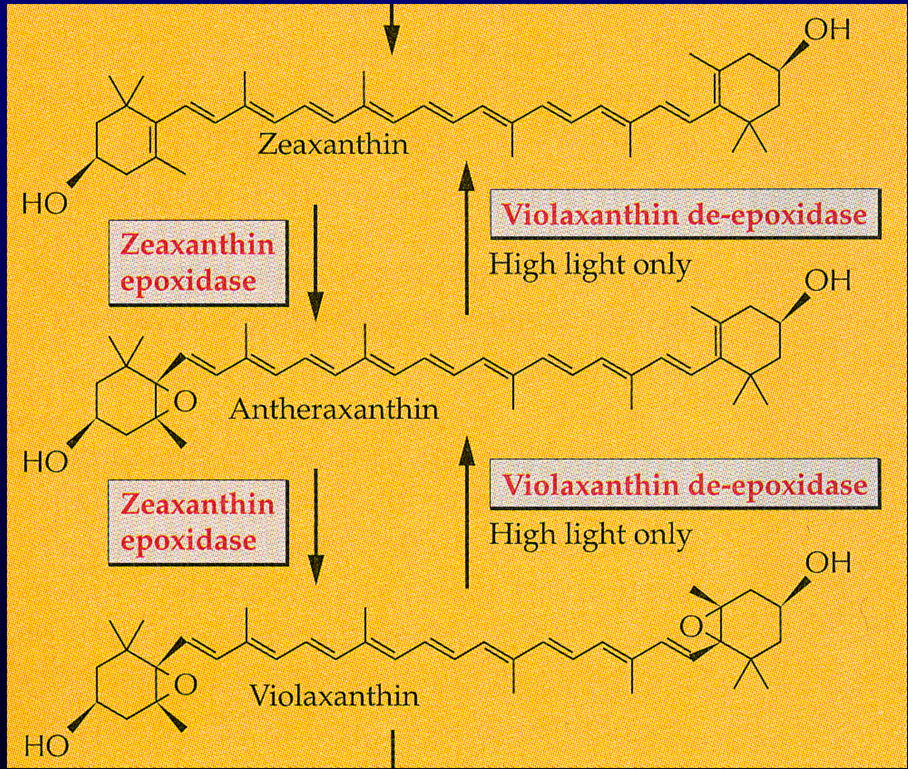


From: Lawlor DW (1990) Thieme, Stuttgart, 377S

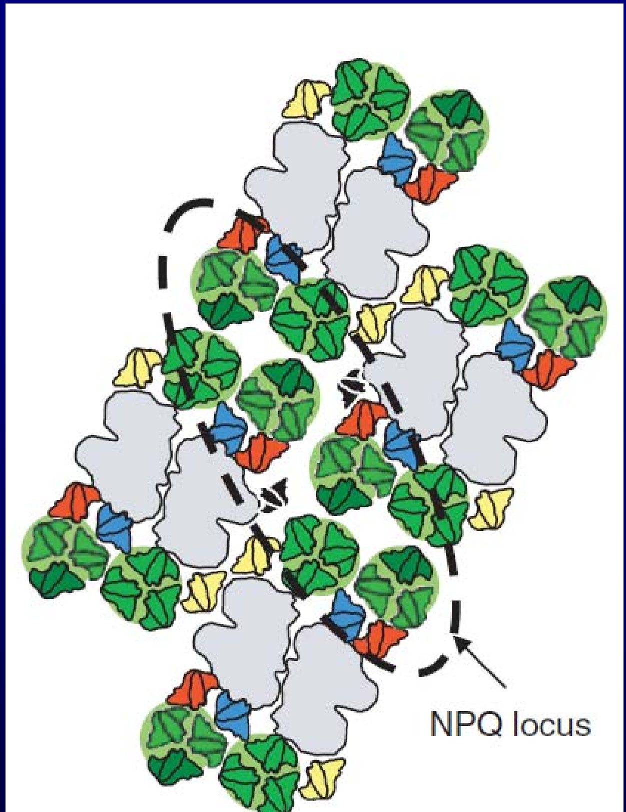
Regulation of energy transfer: xanthophyll cycle

little light much light little light much light

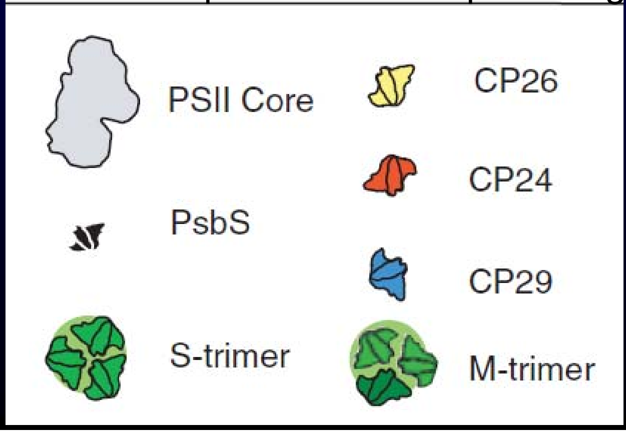


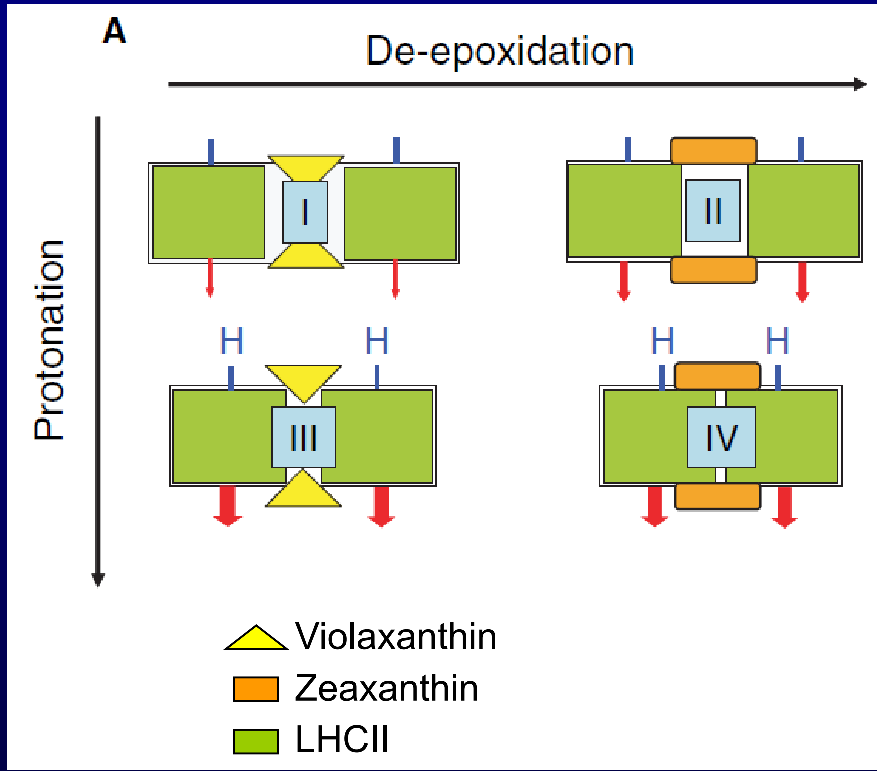


Fast adaptation to irradance changes: combination of LHCII-aggregation with xanthophyll cycle

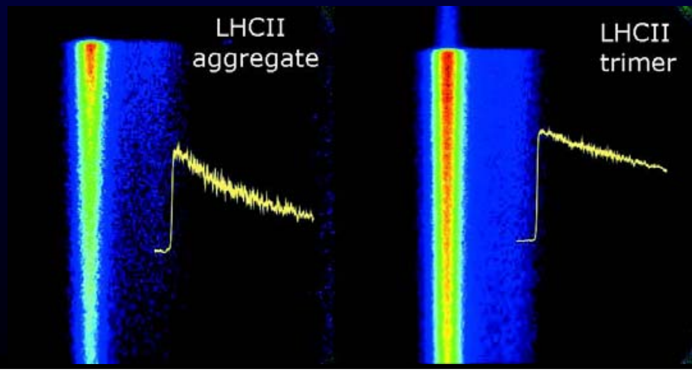


NPQ = non-photochemical quenching



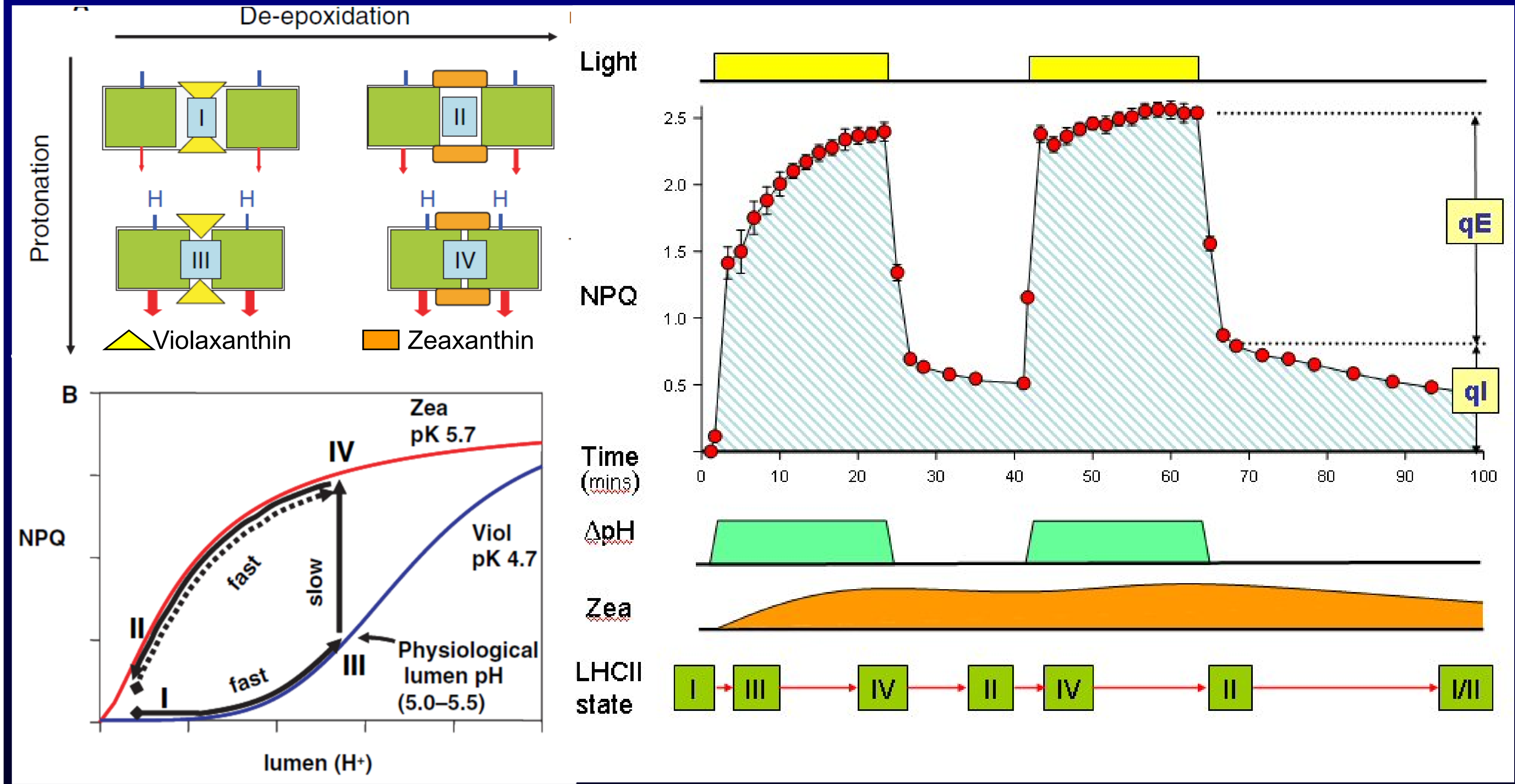


From: http://photosynthesis.peterhorton.eu/research/lightharvesting.aspx
Horton P, Johnson MP, Perez-Bueno ML, Kiss AZ, Ruban AV (2008) FEBS Journal 275, 1069-79



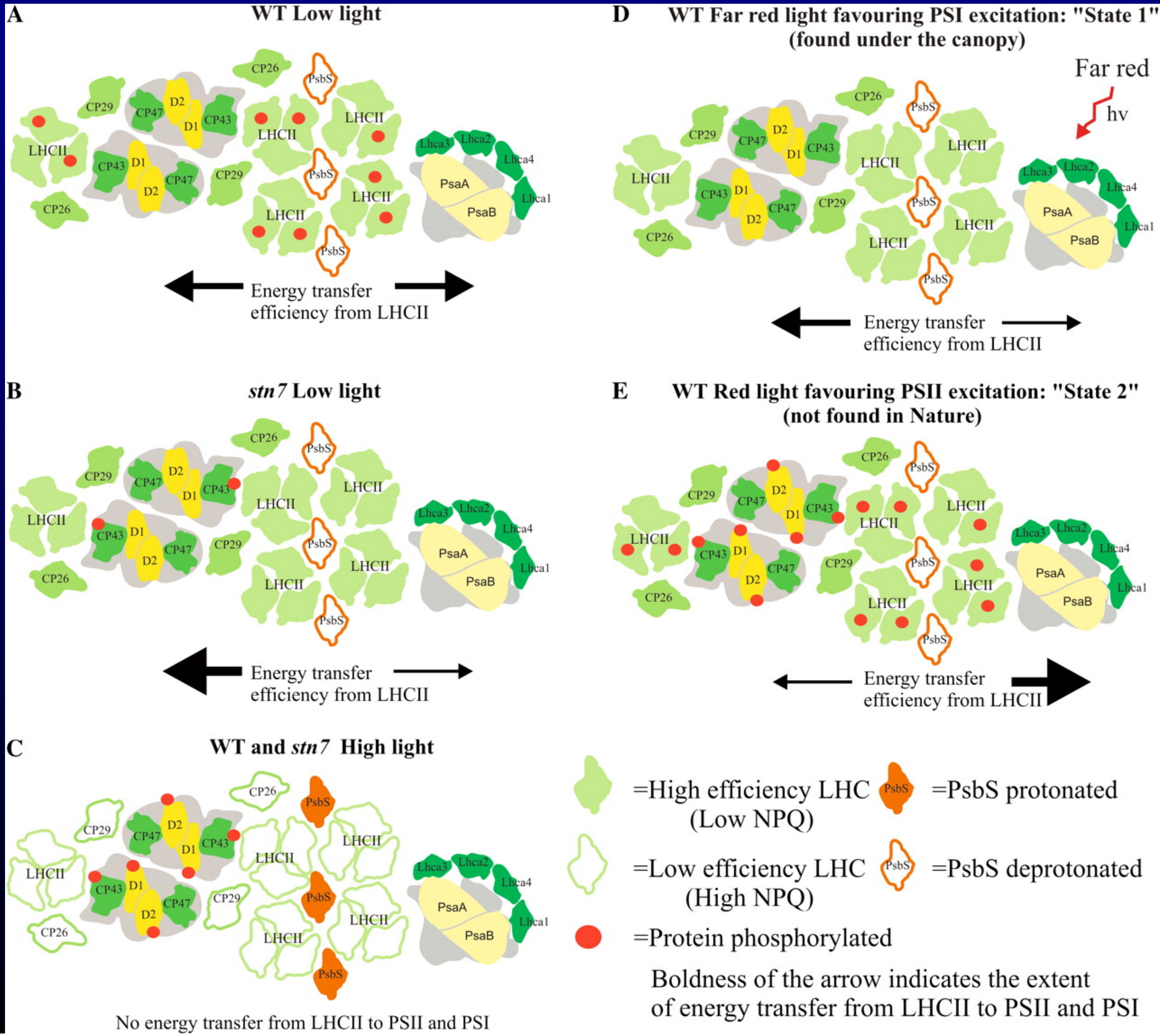
From: http://www.laserlab.vu.nl/en/Research/recearch_projects/the_primary_processes_in_photosynthesis.asp

Fast adaptation to irradance changes: combination of LHCII-aggregation with xanthophyll cycle



From: http://photosynthesis.peterhorton.eu/research/lightharvesting.aspx (Horton lab web page)
Horton P, Johnson MP, Perez-Bueno ML, Kiss AZ, Ruban AV (2008) FEBS Journal 275, 1069-79

Model depicting the differential roles of PSII-LHCII protein phosphorylation in the regulation of excitation energy distribution between PSII and PSI. Such regulation mostly occurs in grana margins where PSII and PSI are in close proximity

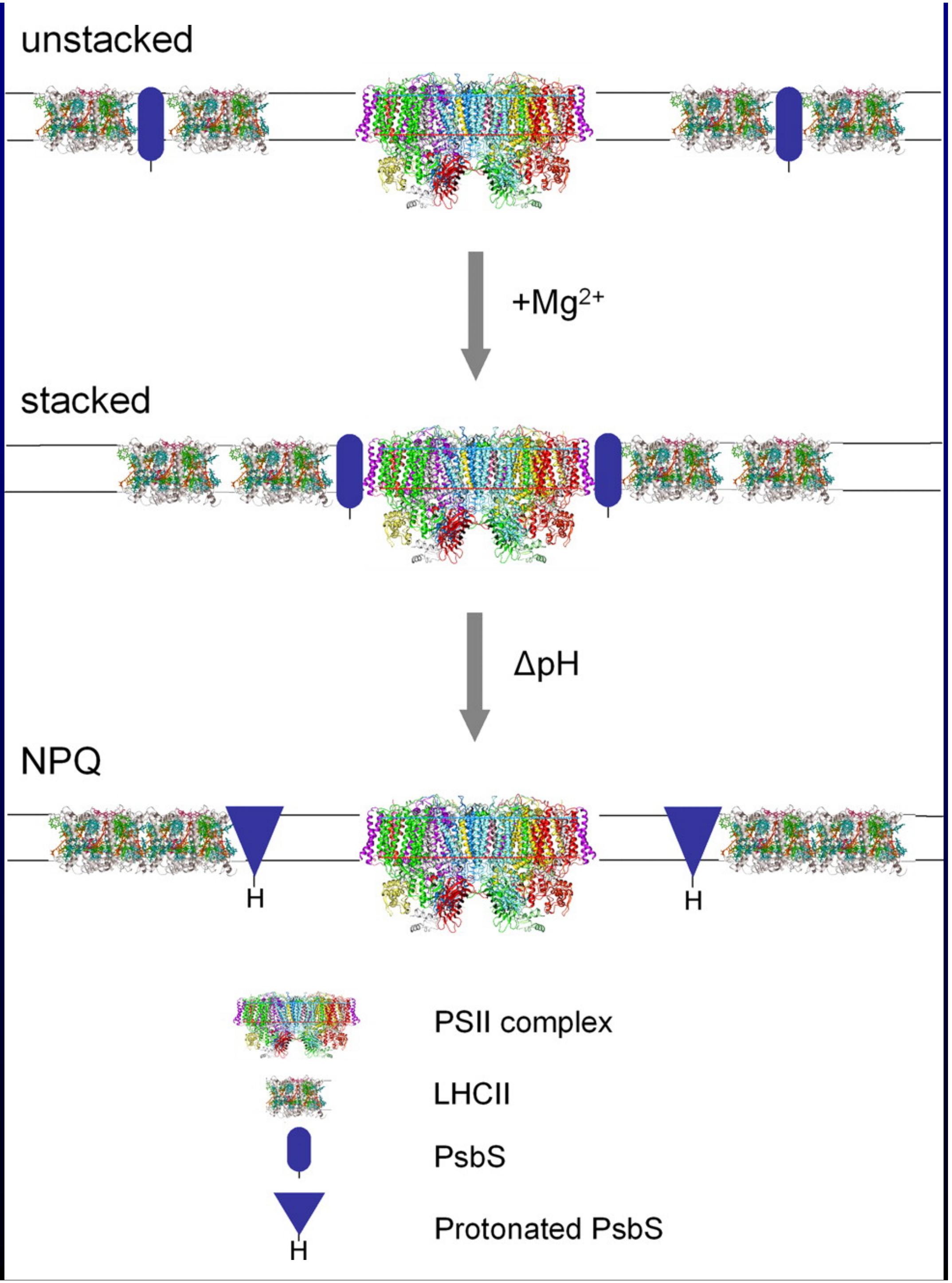


From: Tikkanen M et al. Plant Physiol. 2010;152:723-735

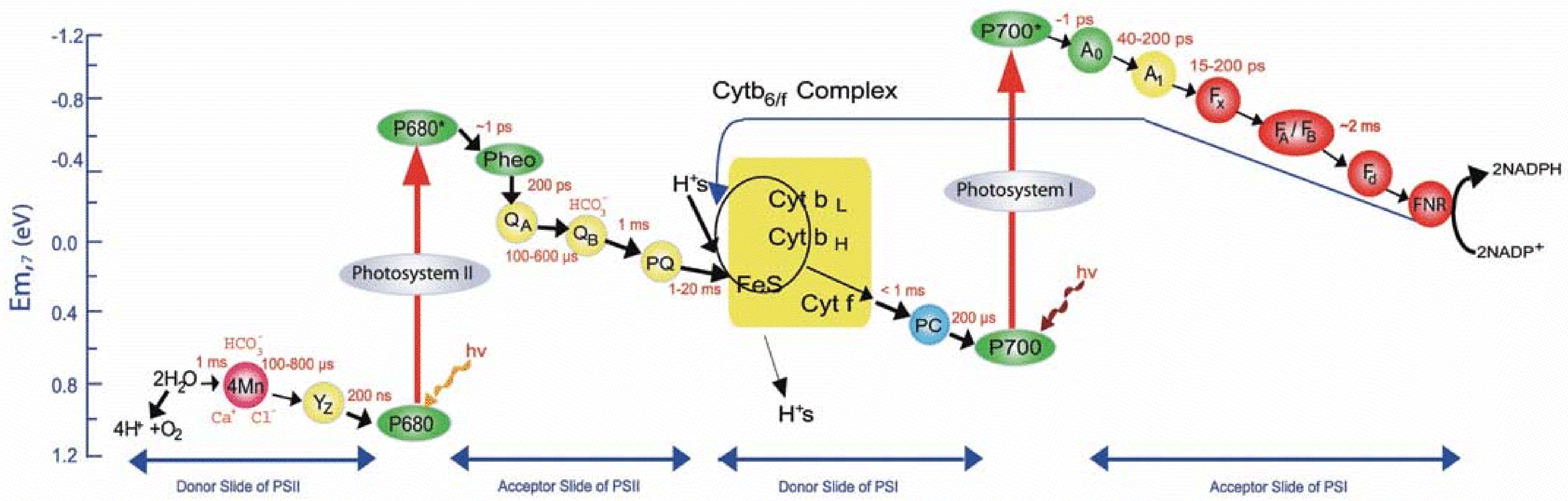
PsbS modulation of the structure and function of the PSII antenna

- At relatively high but not inhibitory light, relatively many unstacked grana exist, where LHCII is not efficiently coupled to PSIIRC
- At low (limiting) light, enhanced grana stacking occurs, regulated via an increase of Mg2+.
- At inhibitory high light, grana unstack again, and in addition protonation of PsbS leads to strong non-photochemical quenching of excitons

Kiss A Z et al. J. Biol. Chem. 2008;283:3972-3978

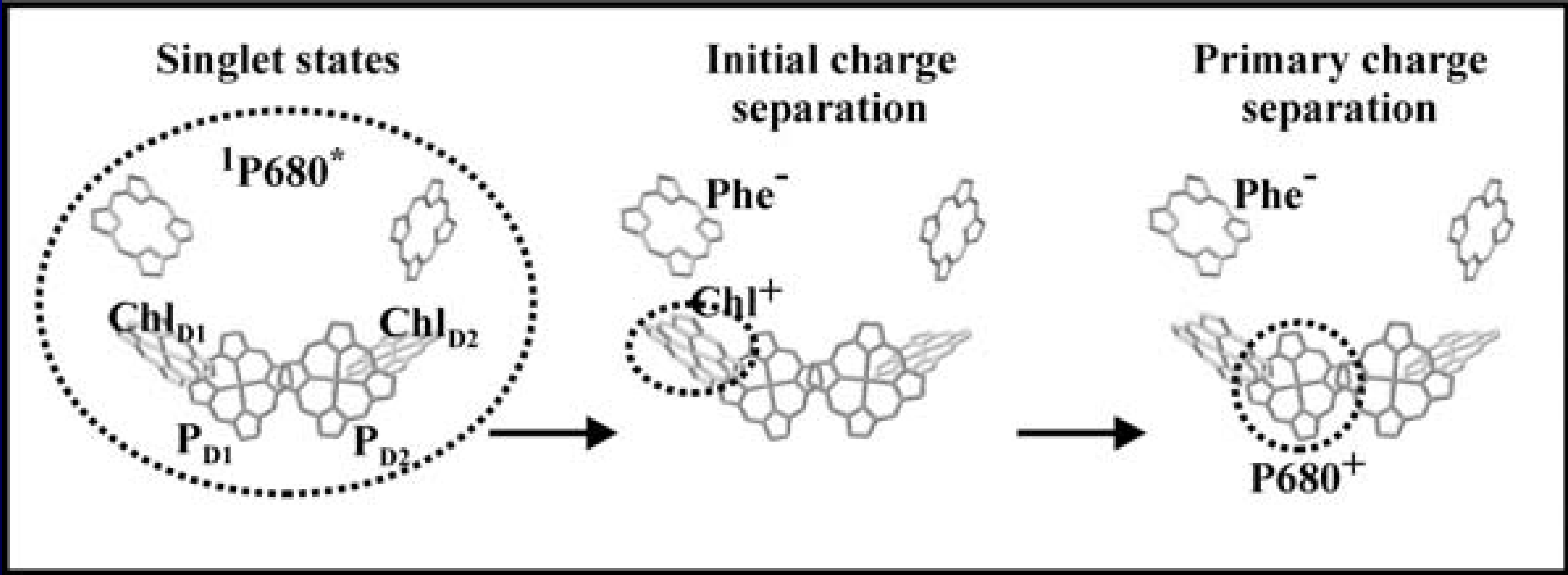


Overview of photosynthetic light reactions the „Z-scheme“



From: accessscience.com

Biophysical aspects of photosynthetic electron transport
A) Photosystem II reaction centre:
special pair chlorophyll and pheophytins

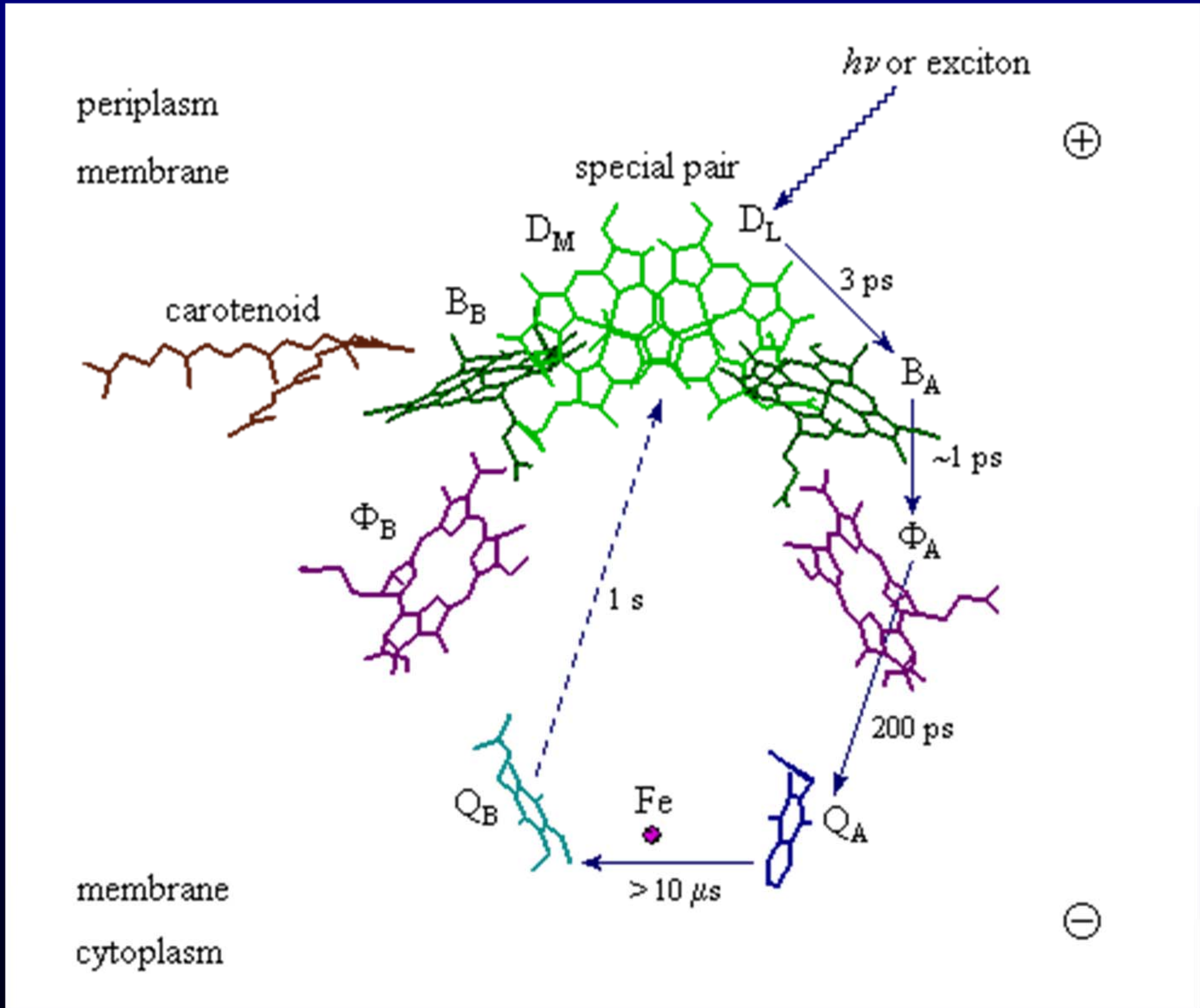


From: Barber J, 2003, QuartRevBiophys36, 71-89

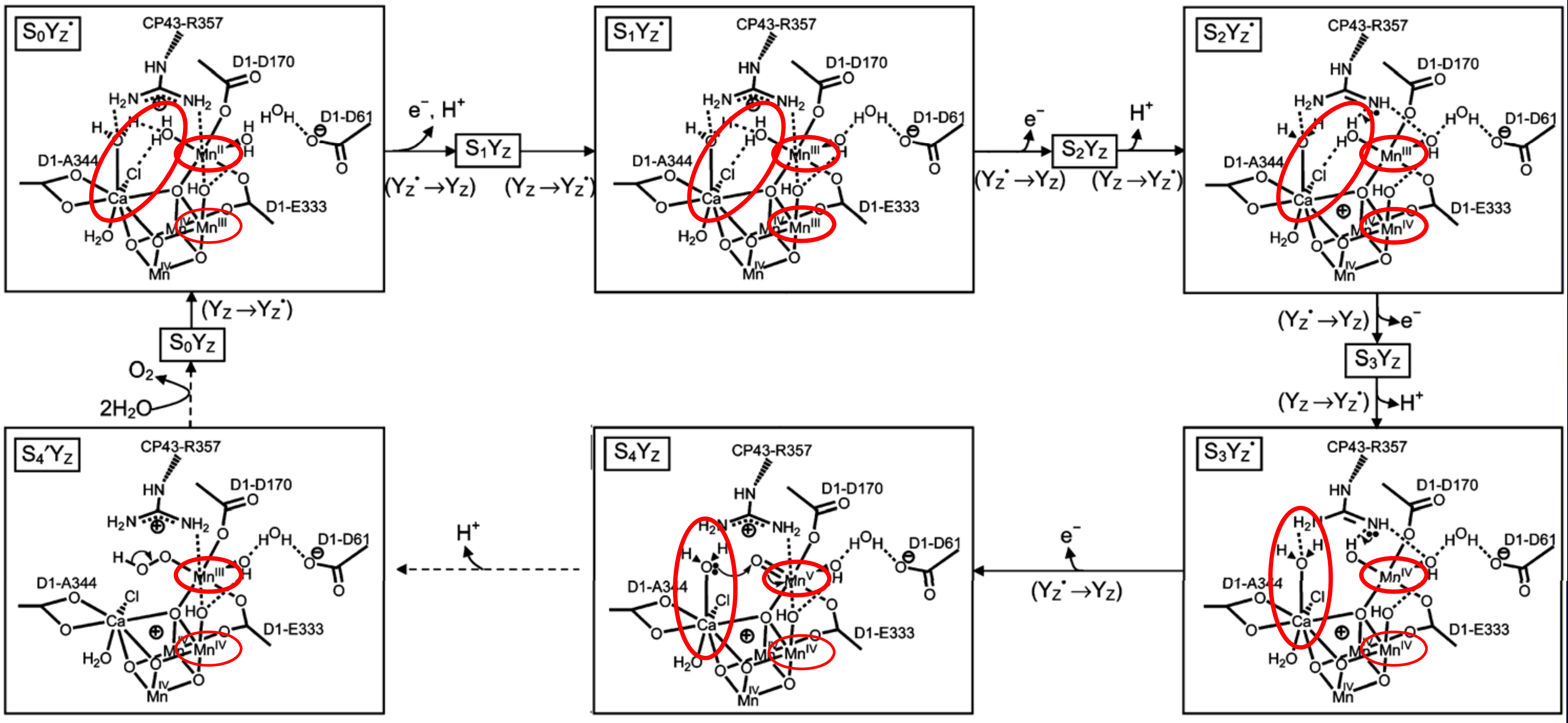
Mechanism of charge separation

- 1. Special pair chlorophylls (=P680) accept excitons from antenna
- 2. Chl$_{D1}$ transfers an electron to Pheo ("initial charge separation")
- 3. Within a few ps, the electron hole in Chl$_{D1}$ is filled from P680 (→ P680$^+$ / Phe$^-$) "primary charge separation"
- (according to other authors, the initial charge separation is in P680, and ChlD1 transfers the electron to Pheo, see next scheme...)

Biophysical aspects of photosynthetic electron transport
A) Photosystem II reaction centre: speeds of electron transfer



Water splitting complex of the photosystem II reaction centre proposed mechanism



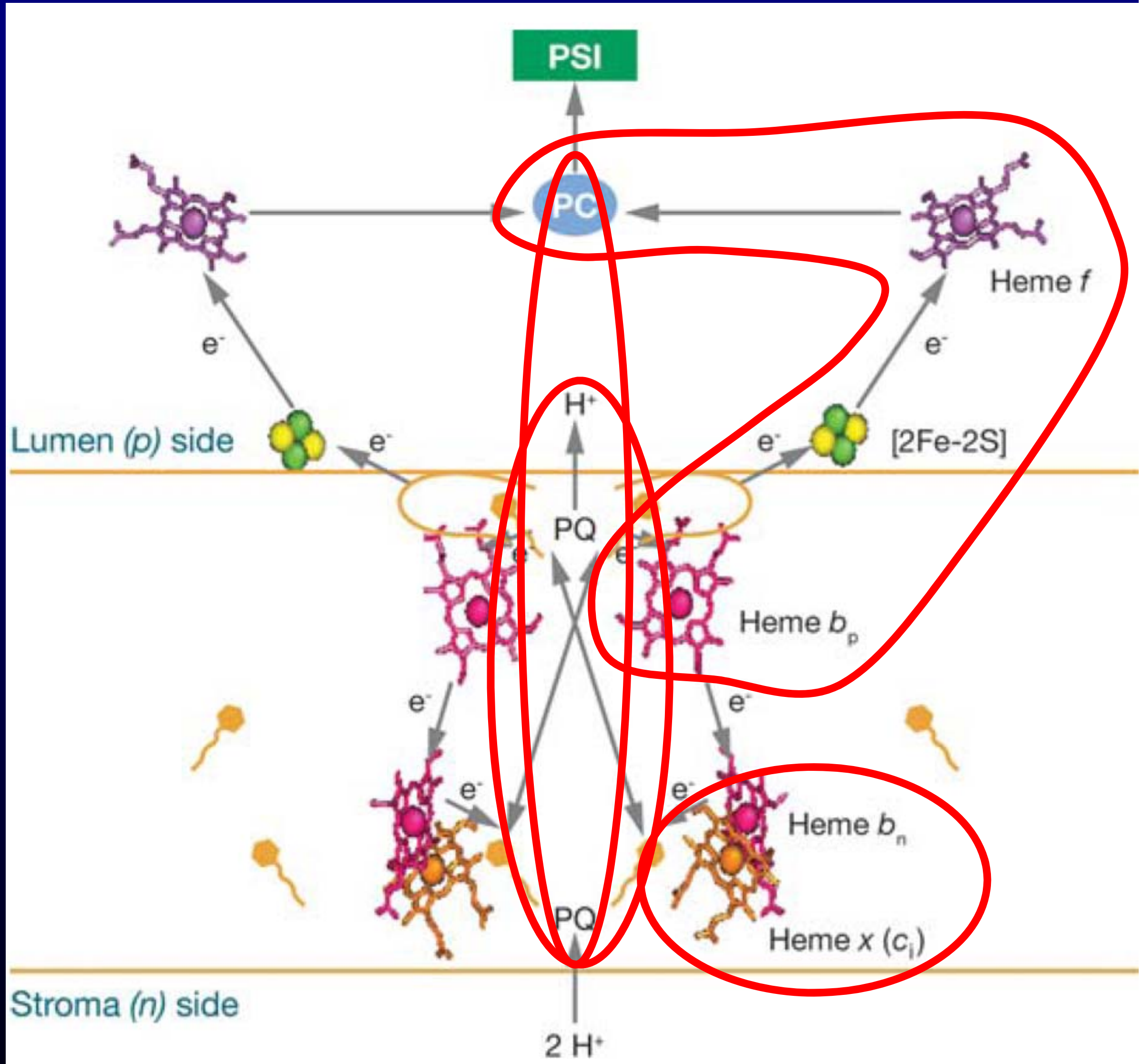
From: McEvoy JP, Brudvig GW, 2006, Chemical Reviews 106, 4455-83

- 2 of the 4 Mn ions are redox-active ($^{3+/4+}$), accepting electrons from water and transferring them to P680
- Ca^{2+} helps in binding the water

Biophysical aspects of photosynthetic electron transport
B) Cytochrome b_6f complex: mechanism

Functional characteristics

- transfers e- from PQ to plastocyanin (PC),
- It uses the difference in potential between Q_B and PC for translocating a proton via 2x2 heme *b* groups and 2x1 heme *x* group
- Electrons are transferred from the heme b groups to PC via a "Rieske" [2Fe2S]-cluster and a heme *f* group
- Cyclic electron transport occurs via coupling of ferredoxin to heme *x*

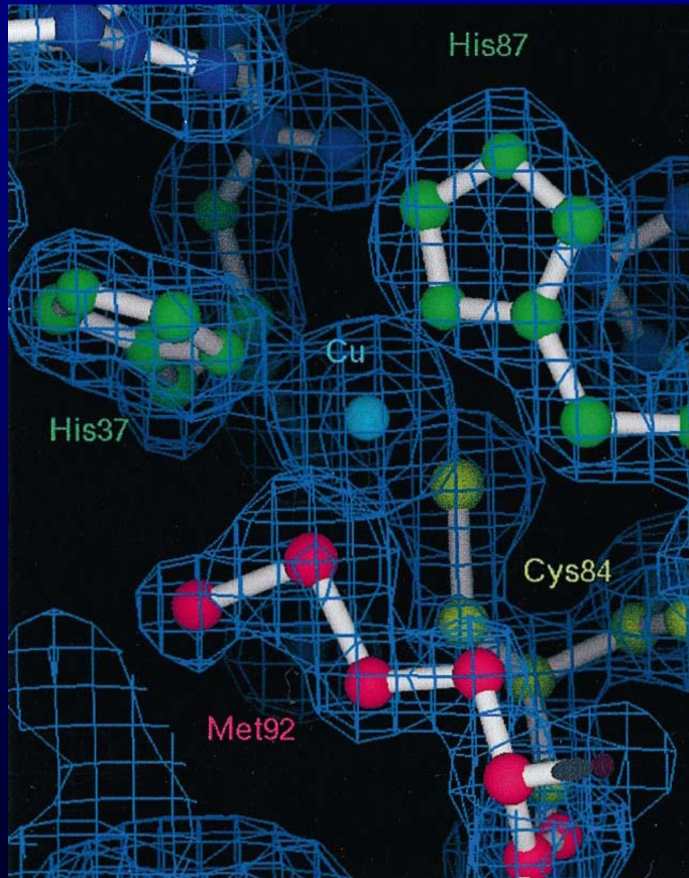


From: Cramer WA, Zhang H, Yan J, Kurisu G, Smith JL, 2006, AnnRevBiochem75_769-90

Biophysical aspects of photosynthetic electron transport
C) Plastocyanin

Functional characteristics

- Oxidised (Cu^{2+}) plastocyanin accepts electron from Cyt_{b6f} complex,
- Reduced (→ Cu^{+}) plastocyanin diffuses to the PSIRC
- Plastocyanin releases the electron (Cu^{+} → Cu^{2+})
- rigid protein structure facilitates fast red/ox-changes, but recent data show that copper binding still causes changes in structure ("induced rack" rather than "entatic state")



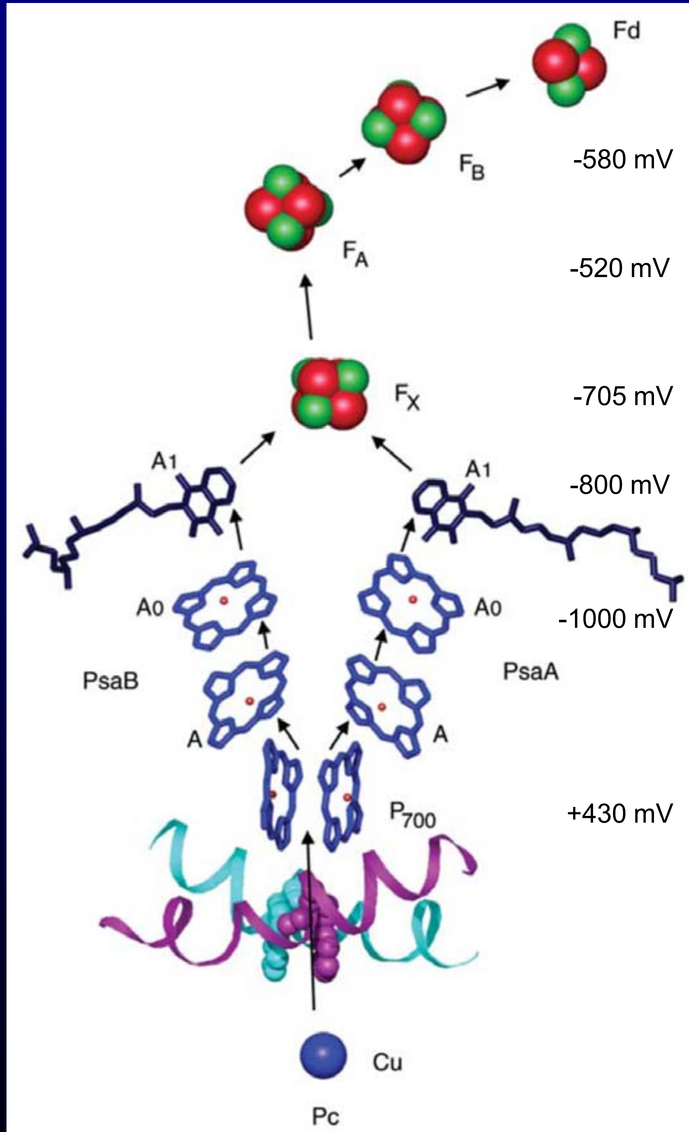
From: Shibata N, Inoue T, Nagano C, Nishio N, Kohzuma T, Onodera K, Yoshizaki F, Sugimura Y, Kai Y, 1999, J Biol Chem. 274: 4225-30

Biophysical aspects of photosynthetic electron transport D) Photosystem I reaction centre

Funtional characteristics:

- primary charge separation:
  special pair (=P700, Chl a / Chl a' heterodimer), releases e^- to A_0 via A (both Chl a)
- e^- transport via A1 (phylloquinone) and the [4Fe4S]-clusters F_x, F_A and F_B to the [4Fe4S]-cluster of ferredoxin
- P700 is re-reduced by plastocyanin

From: Nelson N, Yocum CF, 2006, AnnRevPlantBiol 57, 521-65



All slides of my lectures can be downloaded from my workgroup homepage

Biology Centre CAS → Institute of Plant Molecular Biology → Departments → Department of Plant Biophysics and Biochemistry,

or directly

http://webserver.umbr.cas.cz/~kupper/AG_Kuepper_Homepage.html