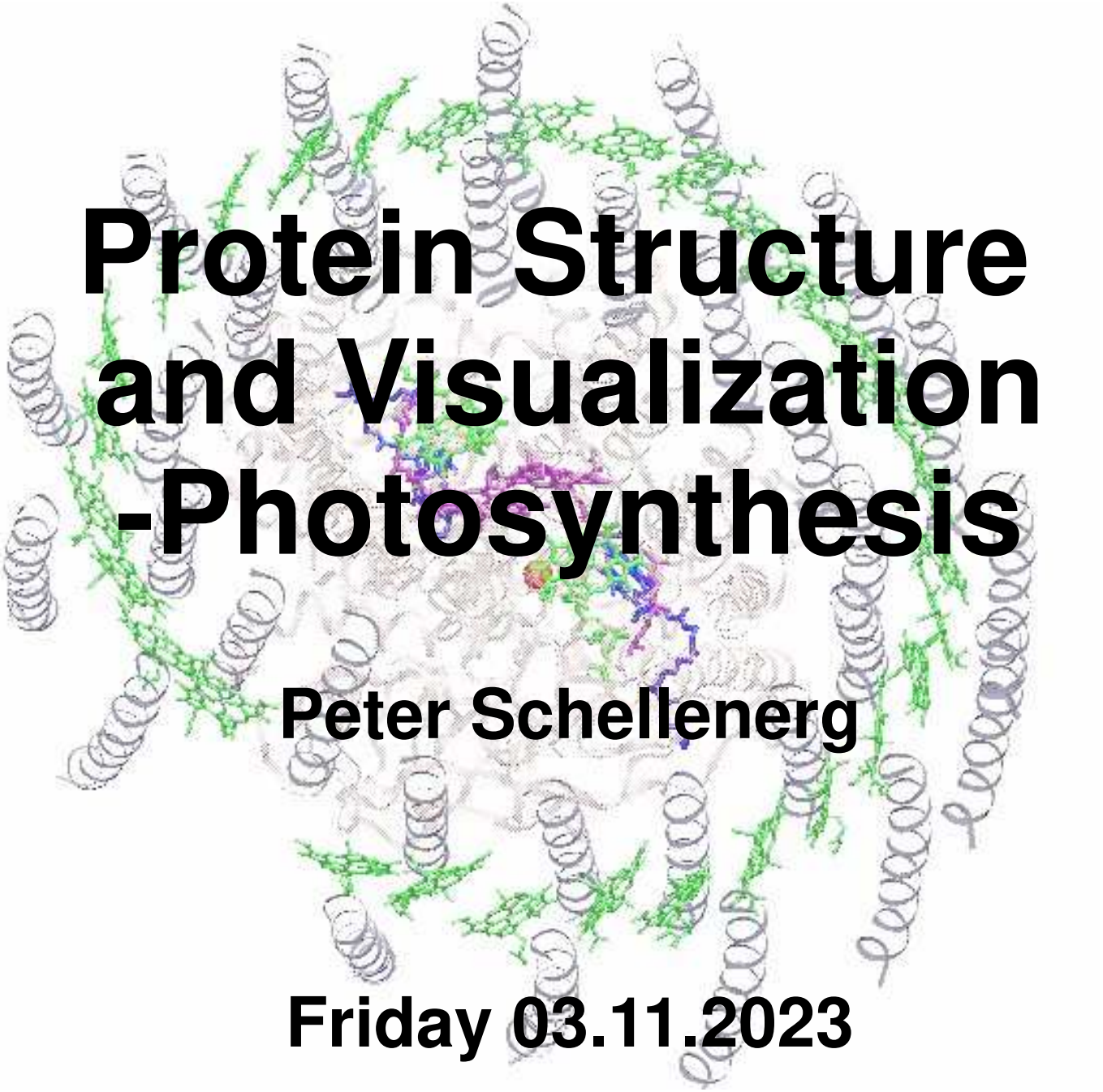
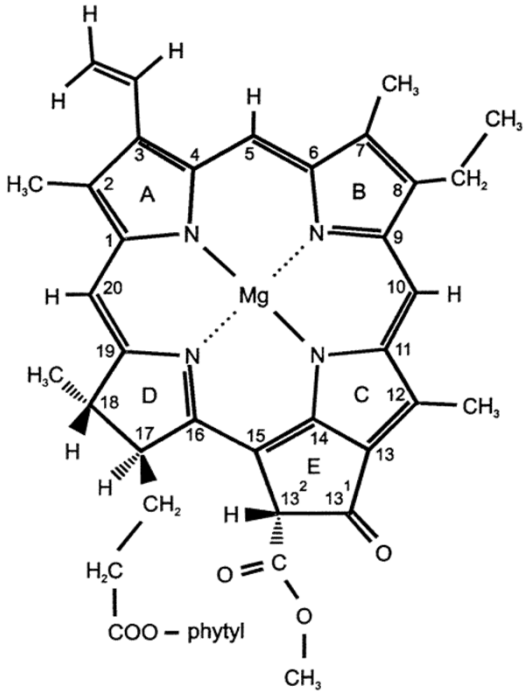


Protein Structure and Visualization -Photosynthesis

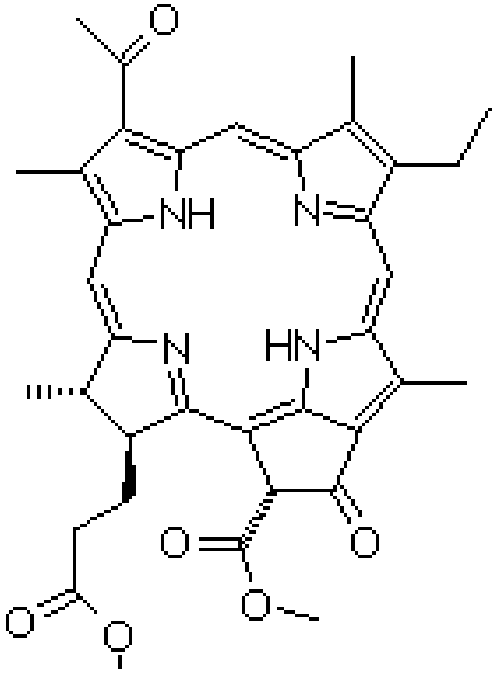
Peter Schellenerg

Friday 03.11.2023

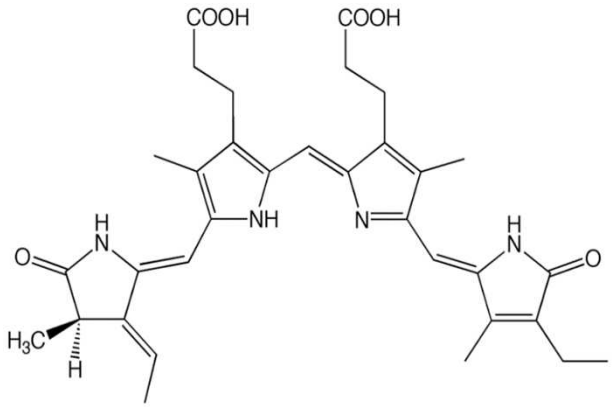
Cofactors for light absorption



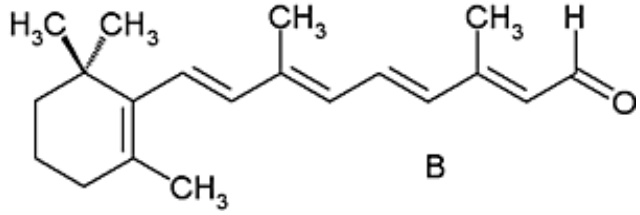
Chlorophyll: Photosynthesis



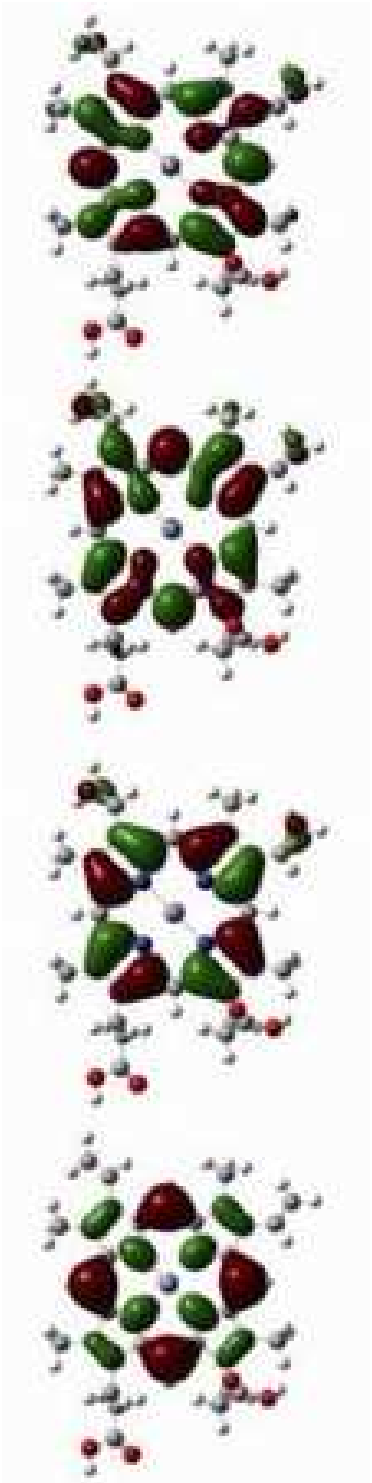
Pheophytin: Photosynthesis



Open tetrapyrolls: light detection, Photosynthesis



Retinal: light detection, Photosynthesis, Singulet-Oxygen Quencher

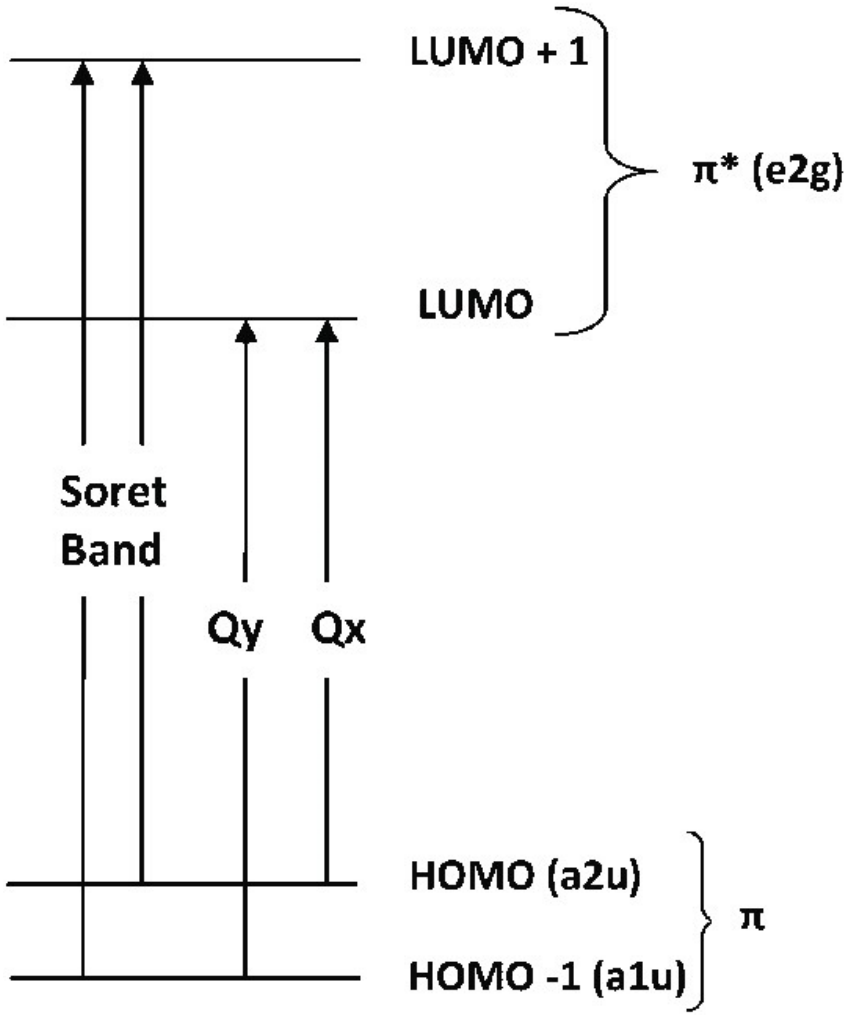


LUMO +1

LUMO

HOMO

HOMO -1



Photosynthesis

Reaction centers: Recieve and translate excitation energy into electrical potential across a membrane

-Bacterial non-oxygenic reaction centers

-Reaction centers of cyanobacteria and plants (oxygenic)
(Evolutionary time tag: minimum 2.8 billion years old)

Antenna pigments: Absorb light, transform its wavelength and eventually transfer to the reaction center

Structures of Reaction Centers

R. viridis is a model!

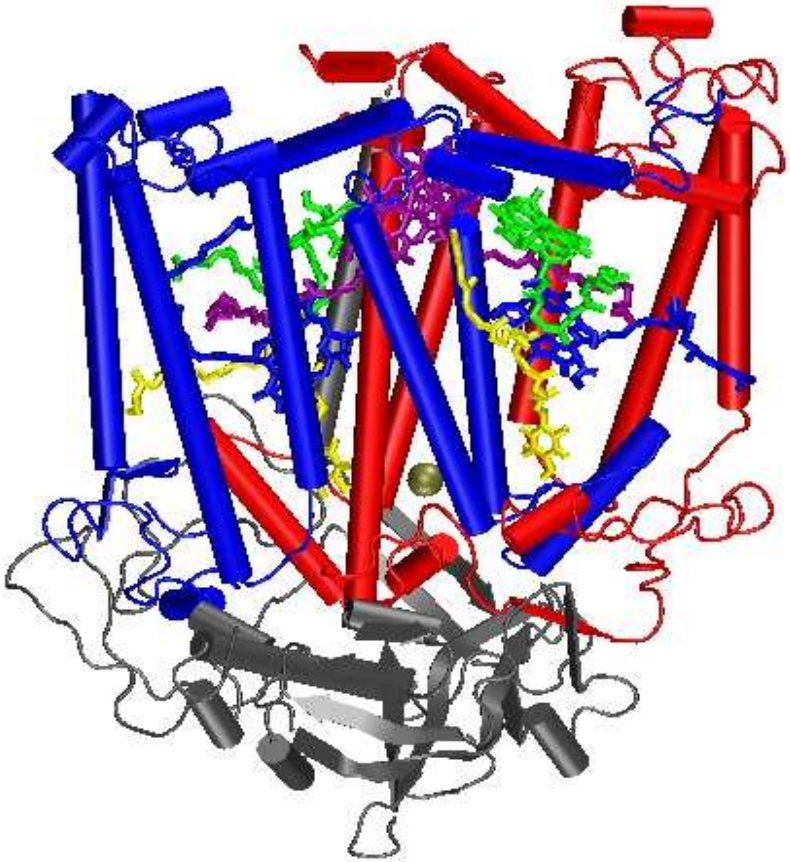
More important: R. sphaeroides

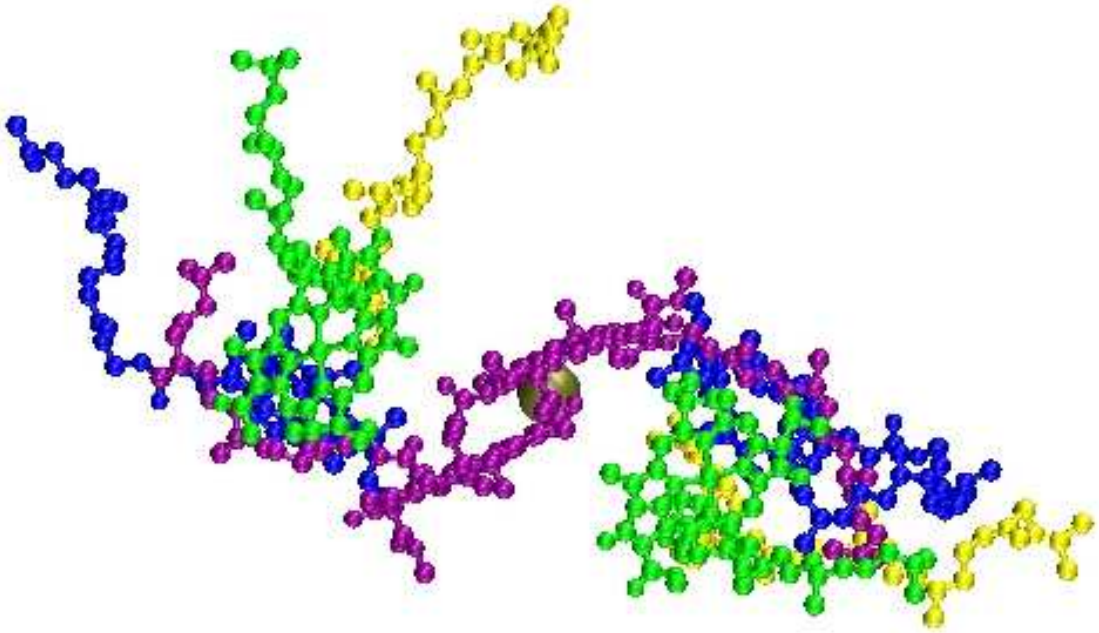
Membrane proteins (as always) are resistant to crystallization (and X-ray diffraction studies)

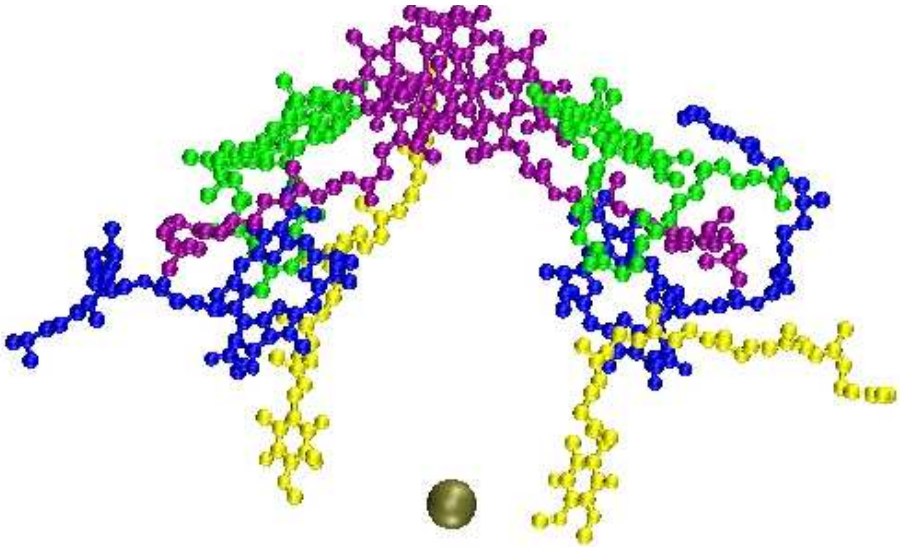
Deisenhofer, Michel and Huber solved *R.viridis* structure in 1984 (Nobel Prize same year!)

Four peptides: L, M, H (and cytochrome)

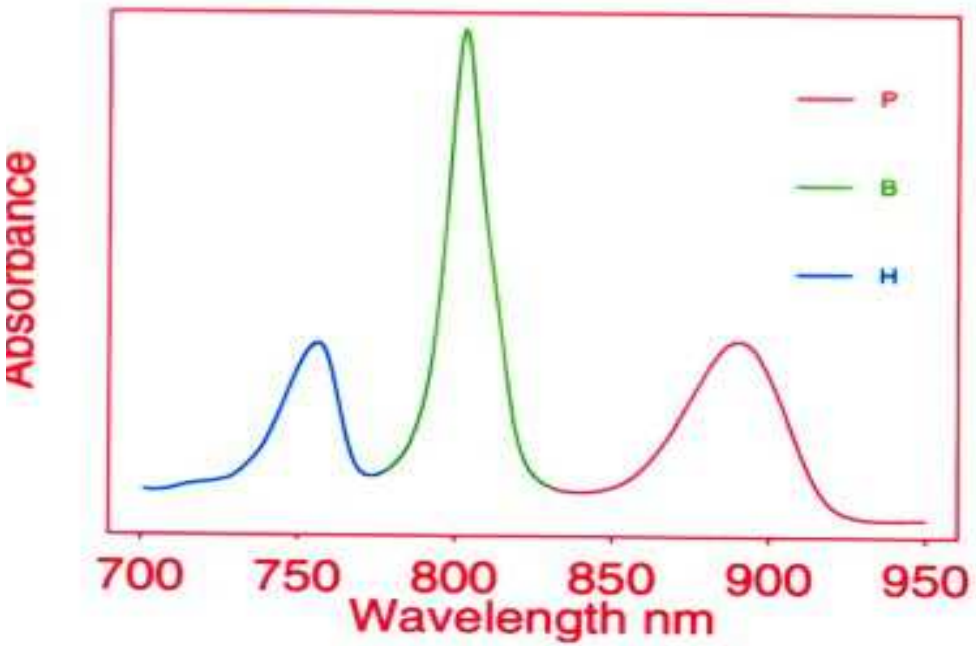
No electron transfer appears to occur through M



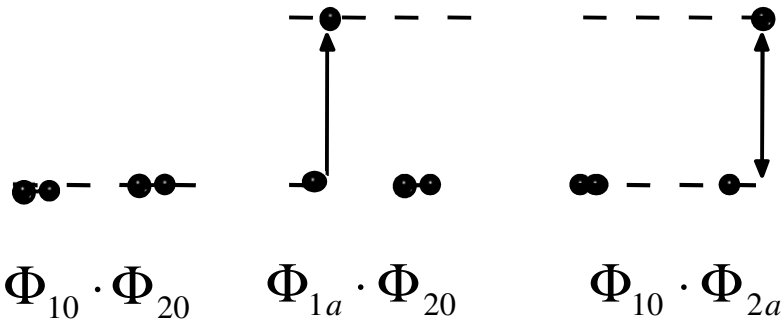


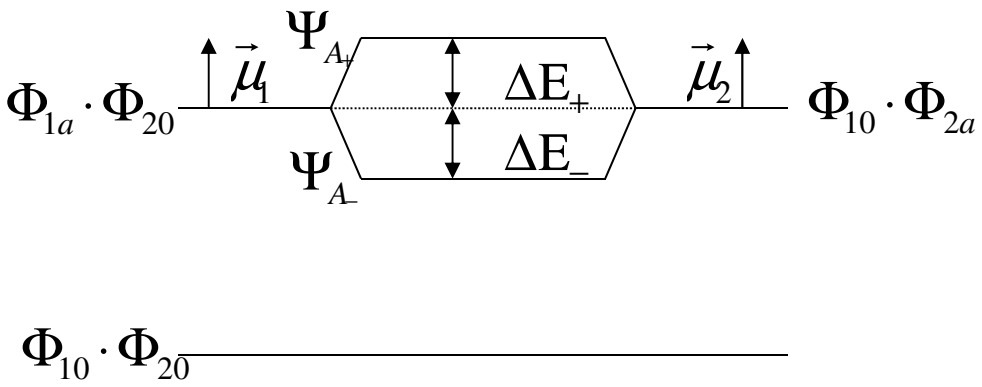


Absorption spectrum



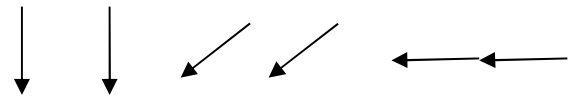
Special Pair: A Dimer of Interacting Monomers





$$\Psi_{A_+} = \frac{1}{\sqrt{2}}\left(\Phi_{1a}\cdot\Phi_{20} + \Phi_{10}\cdot\Phi_{2a}\right) \qquad \Psi_{A_-} = \frac{1}{\sqrt{2}}\left(\Phi_{1a}\cdot\Phi_{20} - \Phi_{10}\cdot\Phi_{2a}\right)$$

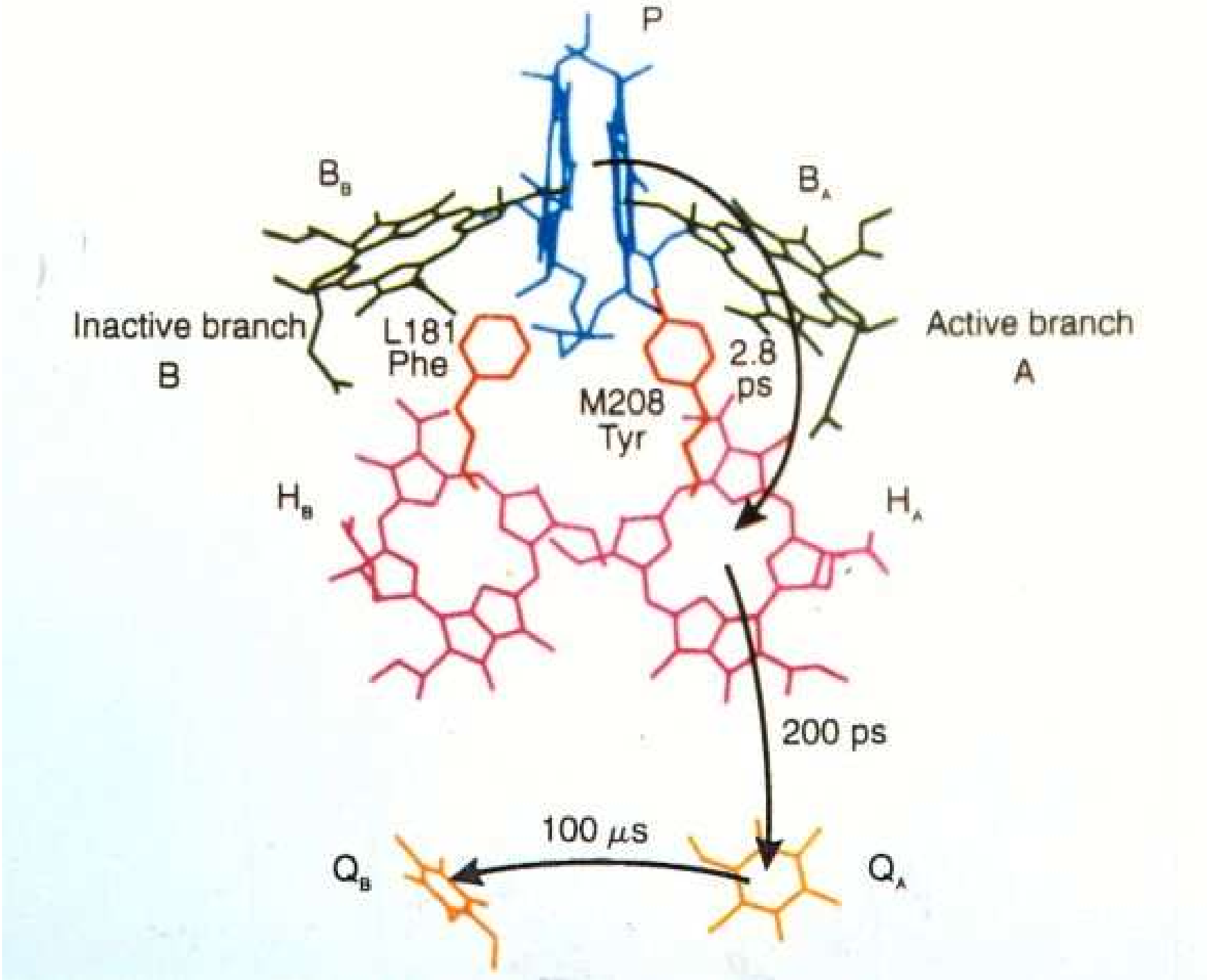
$$V_{WW} = \frac{\vec{\mu}_1\cdot\vec{\mu}_2}{r_{12}}\left(1-3\cos^2\theta\right)$$



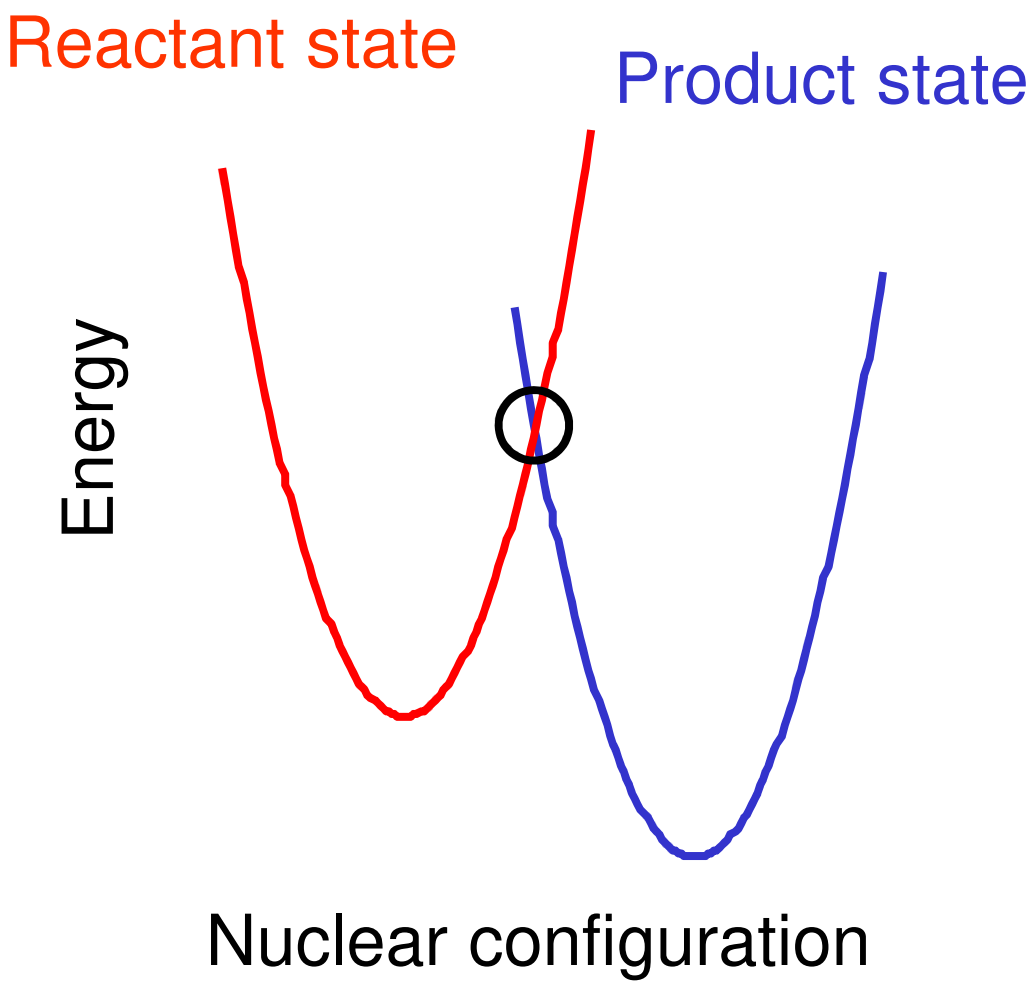
$$\Delta E_+ = \left\langle \Psi_{A_+} \middle| V_{WW} \middle| \Psi_{A_+} \right\rangle = +\Delta E$$
$$\Delta E_- = \left\langle \Psi_{A_-} \middle| V_{WW} \middle| \Psi_{A_-} \right\rangle = -\Delta E$$

Splitting into two lines

Charge separation in bacterial reaction centers



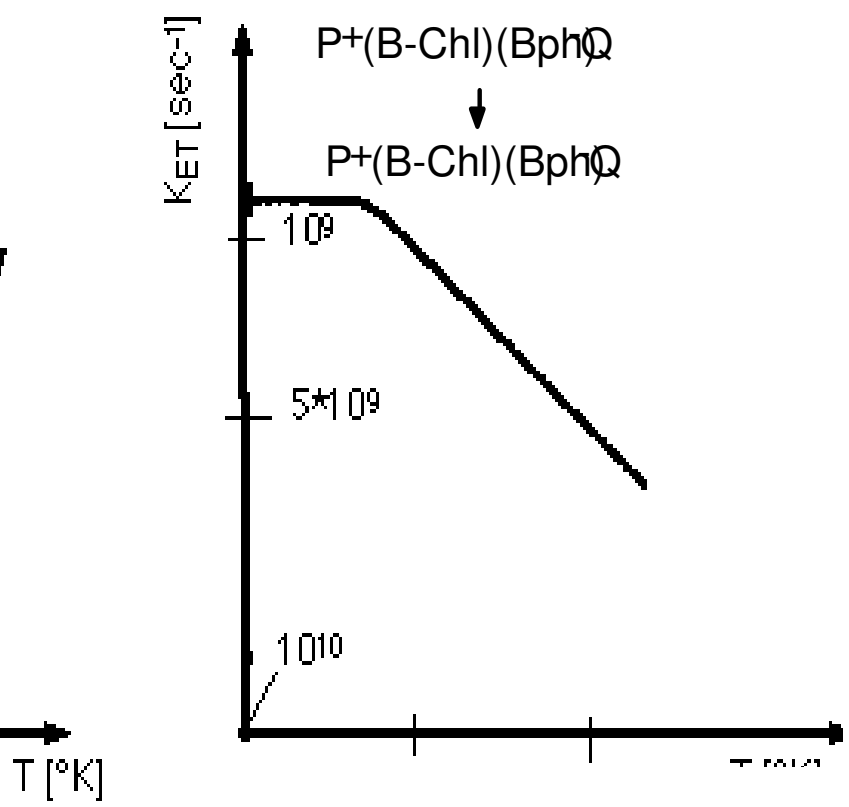
Charge separation analog to electronic transition – Marcus theory

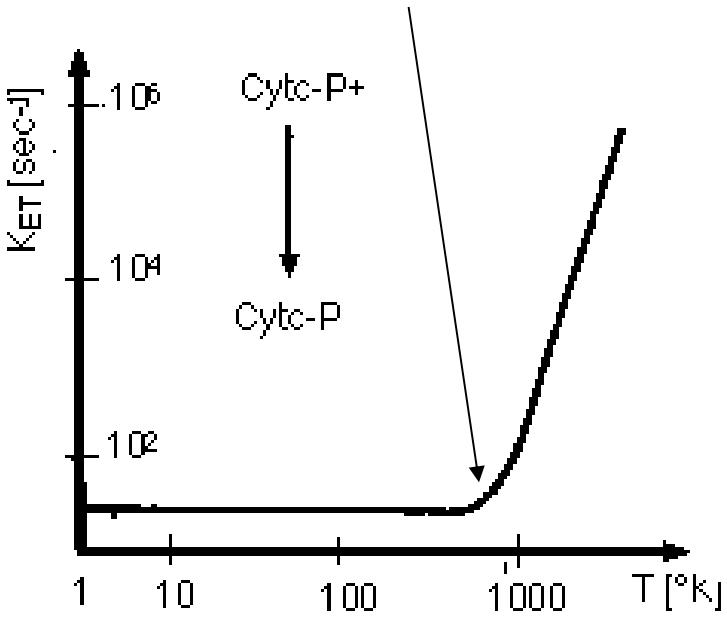


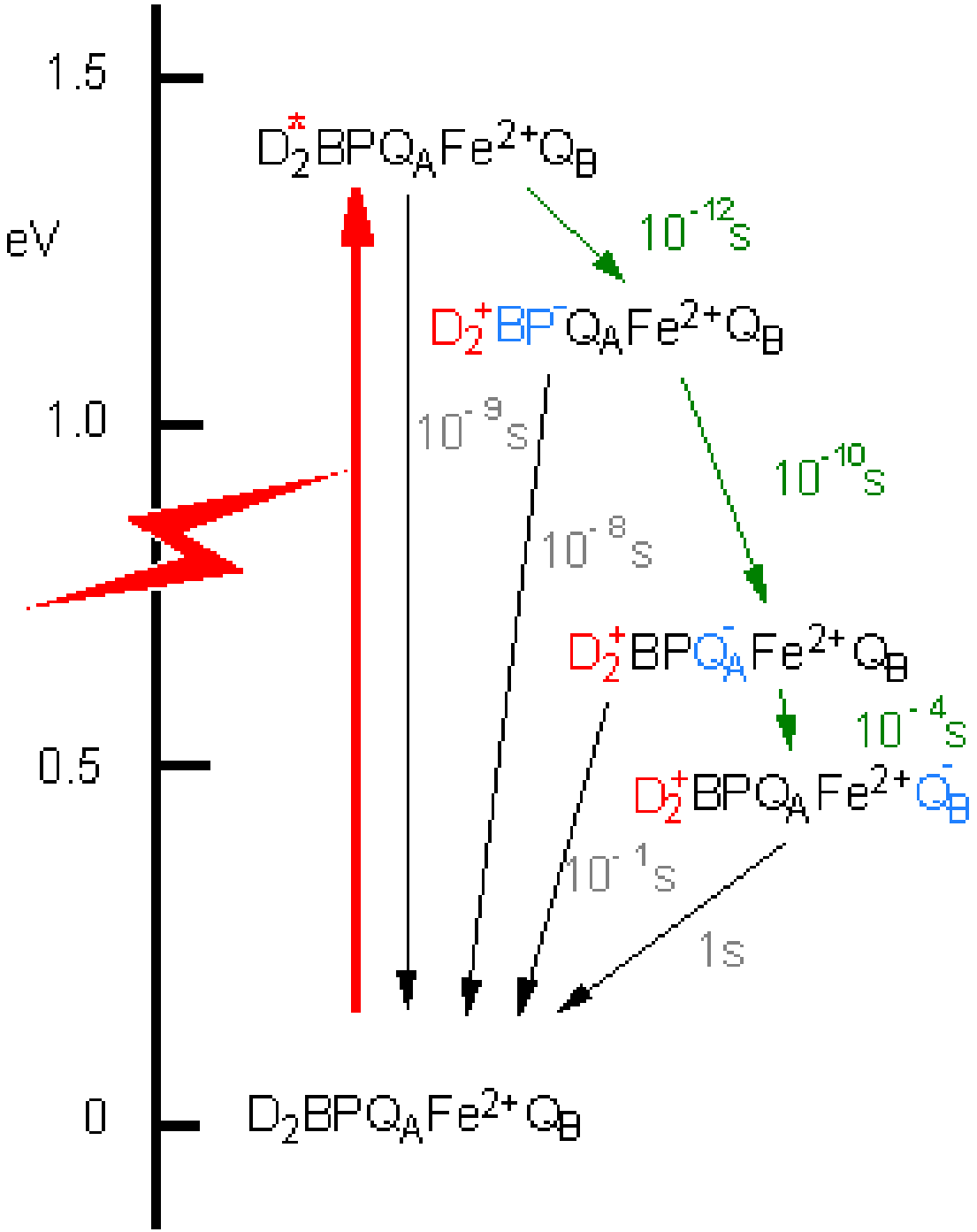
The Franck-Condon principle applies: electrons move much faster than nuclei. No change in nuclear configuration during the electron transfer: transition is vertical.

There is also energy conservation during the transition: transition is horizontal.

Conclusion: electron transfer only occurs in nuclear configuration at crossing point.


P+(B-Chl)(BphQ
P+(B-Chl)(BphQ
KET [sec-1]
10⁹
5*10⁹
10¹⁰
T [°K]


KET [sec-1]
10⁶
10⁴
10²
Cytc-P+
Cytc-P
1
10
100
1000
T [°K]


1.5
1.0
0.5
0
eV
D2*BPQAFe2+QB
D2+BP-QAFe2+QB
D2+BPQA-Fe2+QB
D2+BPQAFe2+QB-
D2BPQAFe2+QB
10-12s
10-9s
10-10s
10-8s
10-4s
10-1s
1s

Oxygenic Photosynthesis

PSI (P700) and PSII (P680)

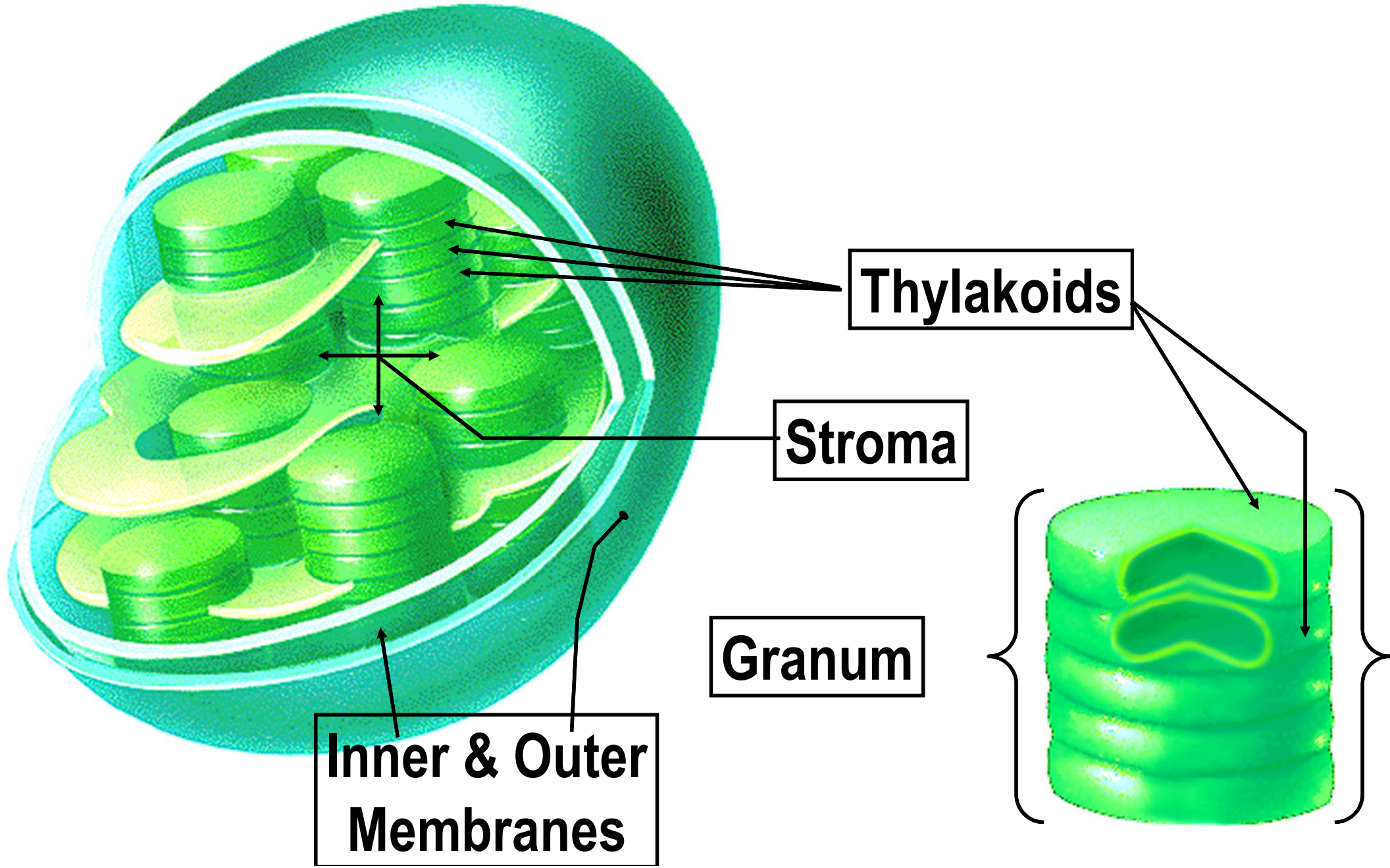
All chlorophyll is part of either LHC, PSI or PSII

PSI absorbs at 700 nm

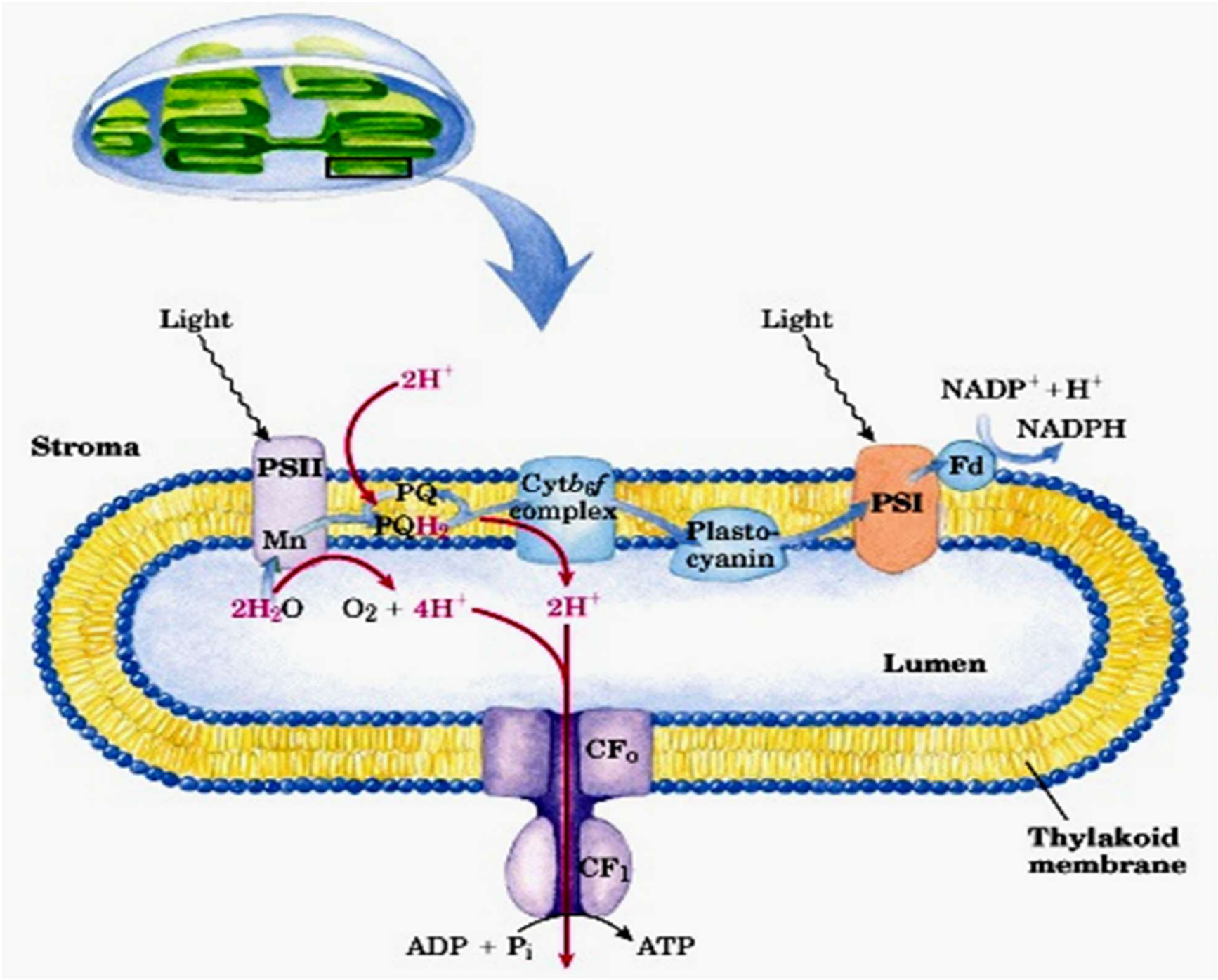
PSII absorbs at 680 nm

Chloroplasts given light at 680 and 700 nm simultaneously yield more O_2 than the sum of amounts when each is used alone

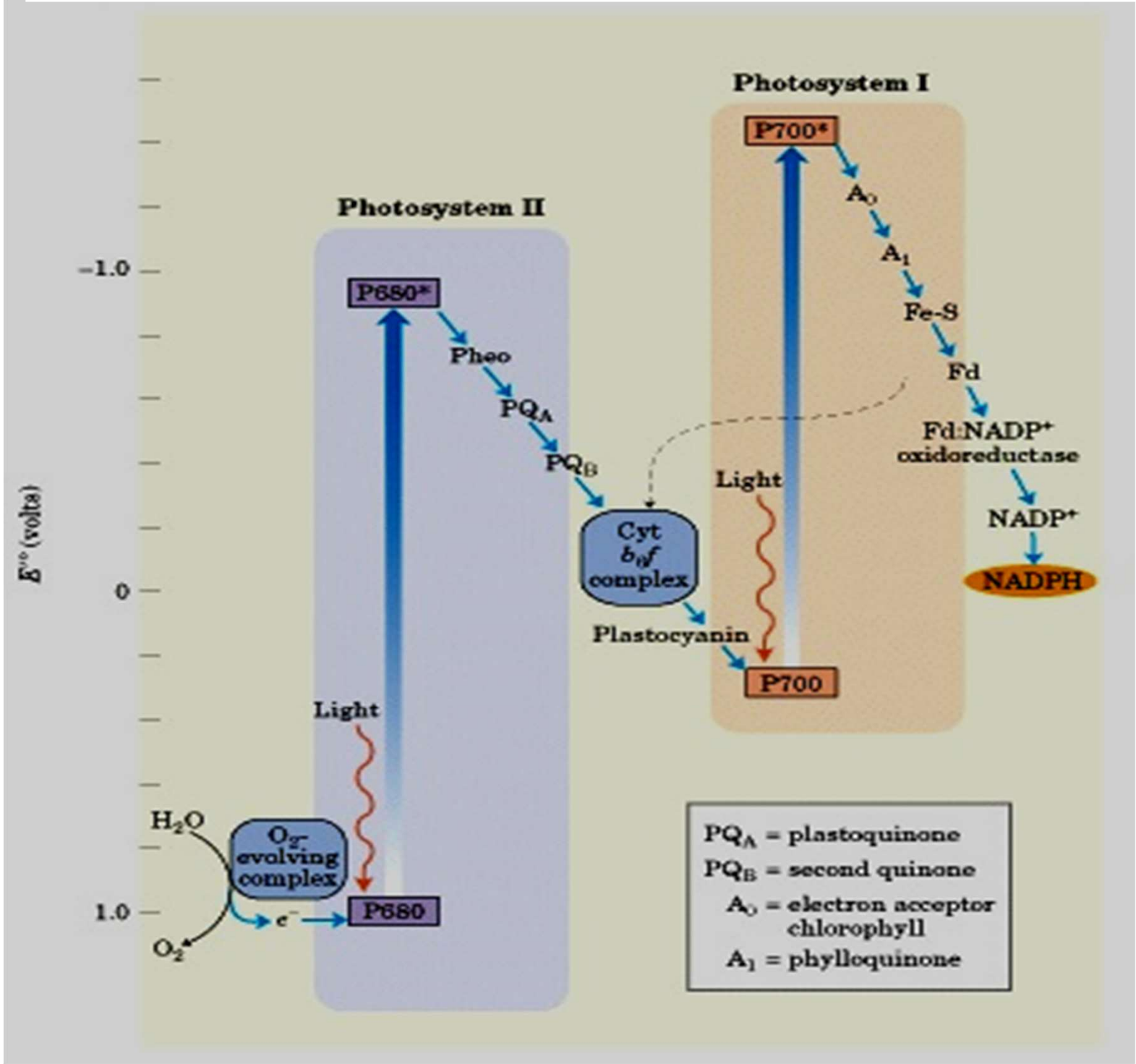
Site of Photosynthesis in Plants



Enlargement



The Z- scheme of oxygenic photosynthesis



What does each photosystem do?

PSII oxidizes water (termed “photolysis")

PSI reduces $NADP^+$

ATP is generated by establishment of a proton gradient as electrons flow from PSII to PSI

Oxygen evolution by PSII

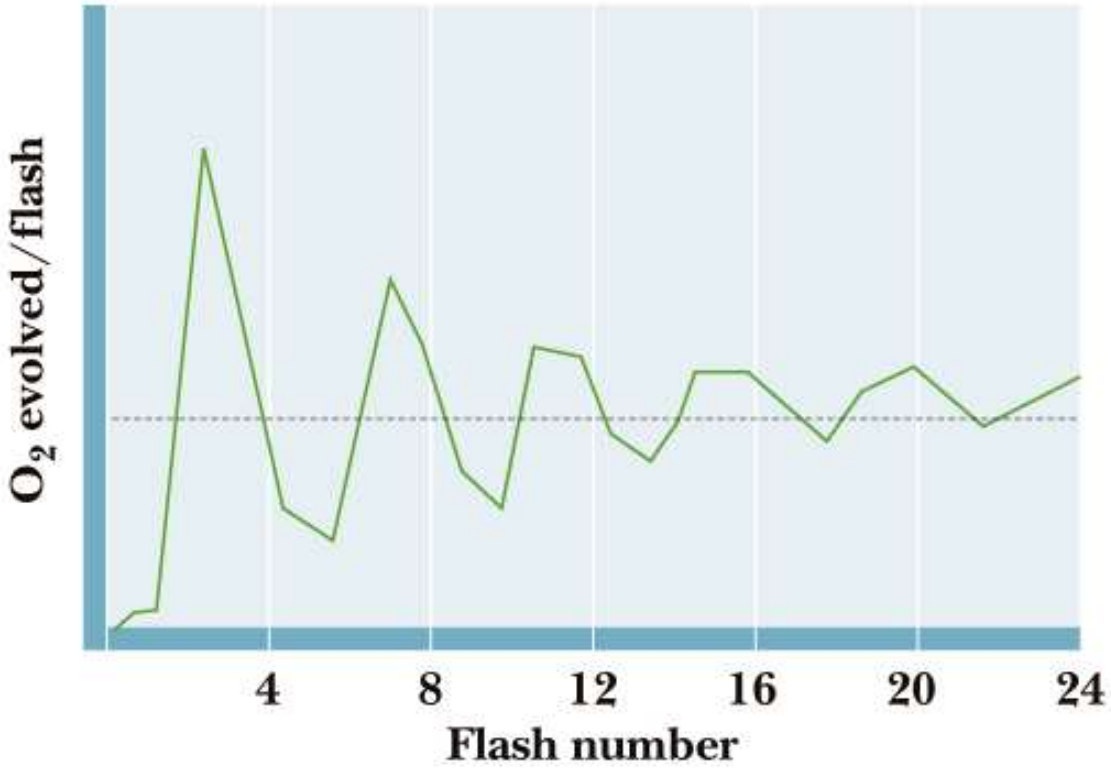
requires accumulation of four oxidizing equivalents

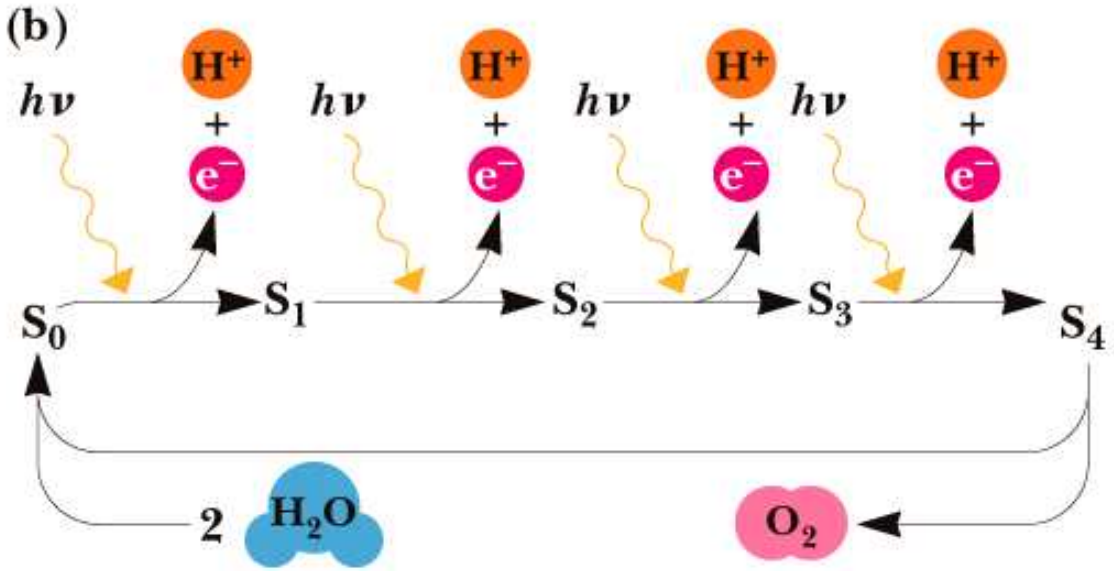
PSII (P680) cycles through five oxidation states

1 e^- is removed in each of four steps

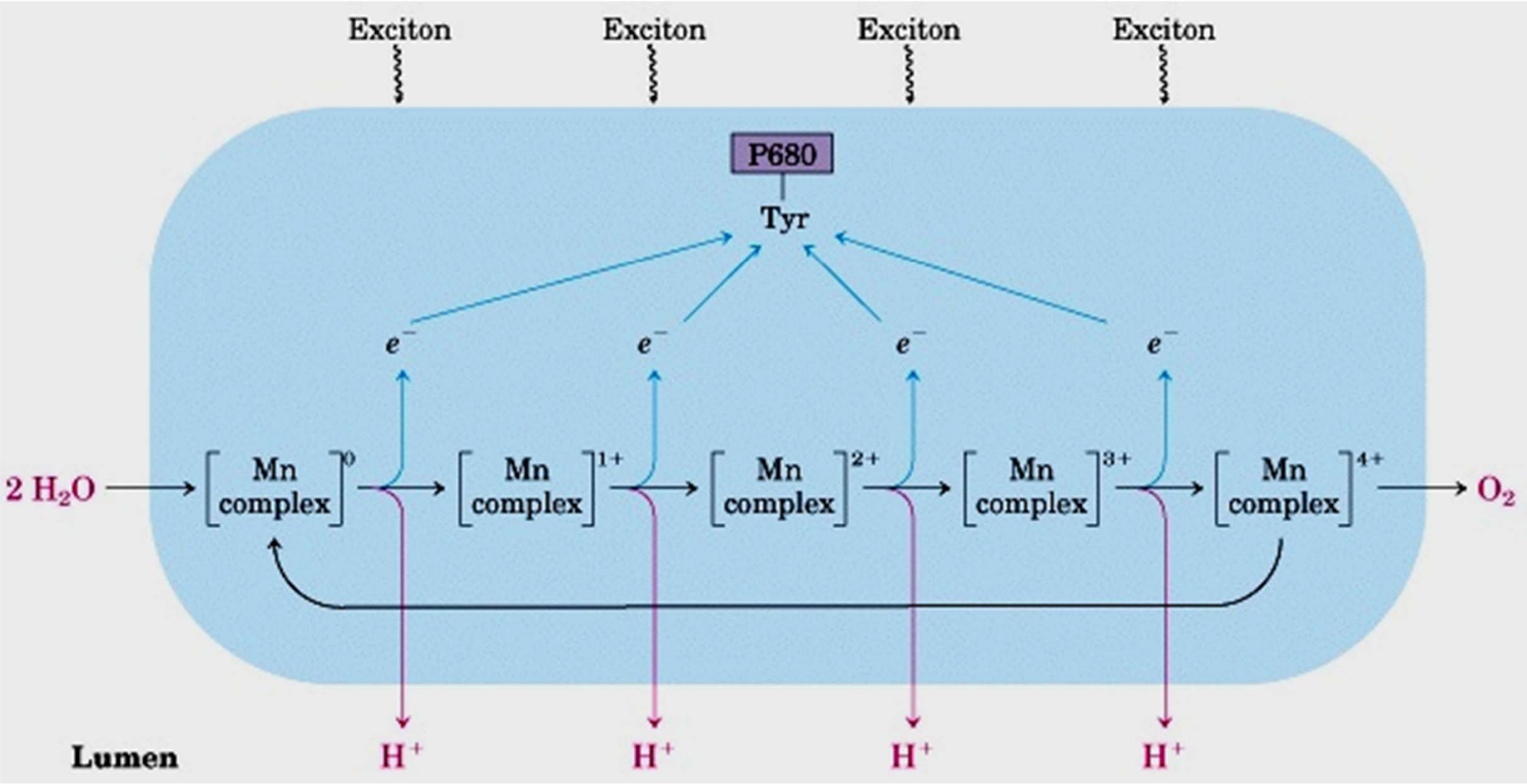
Fifth step involves H_2O oxidized to $O_2 + 4H^+$

Flash dependent oxygen development





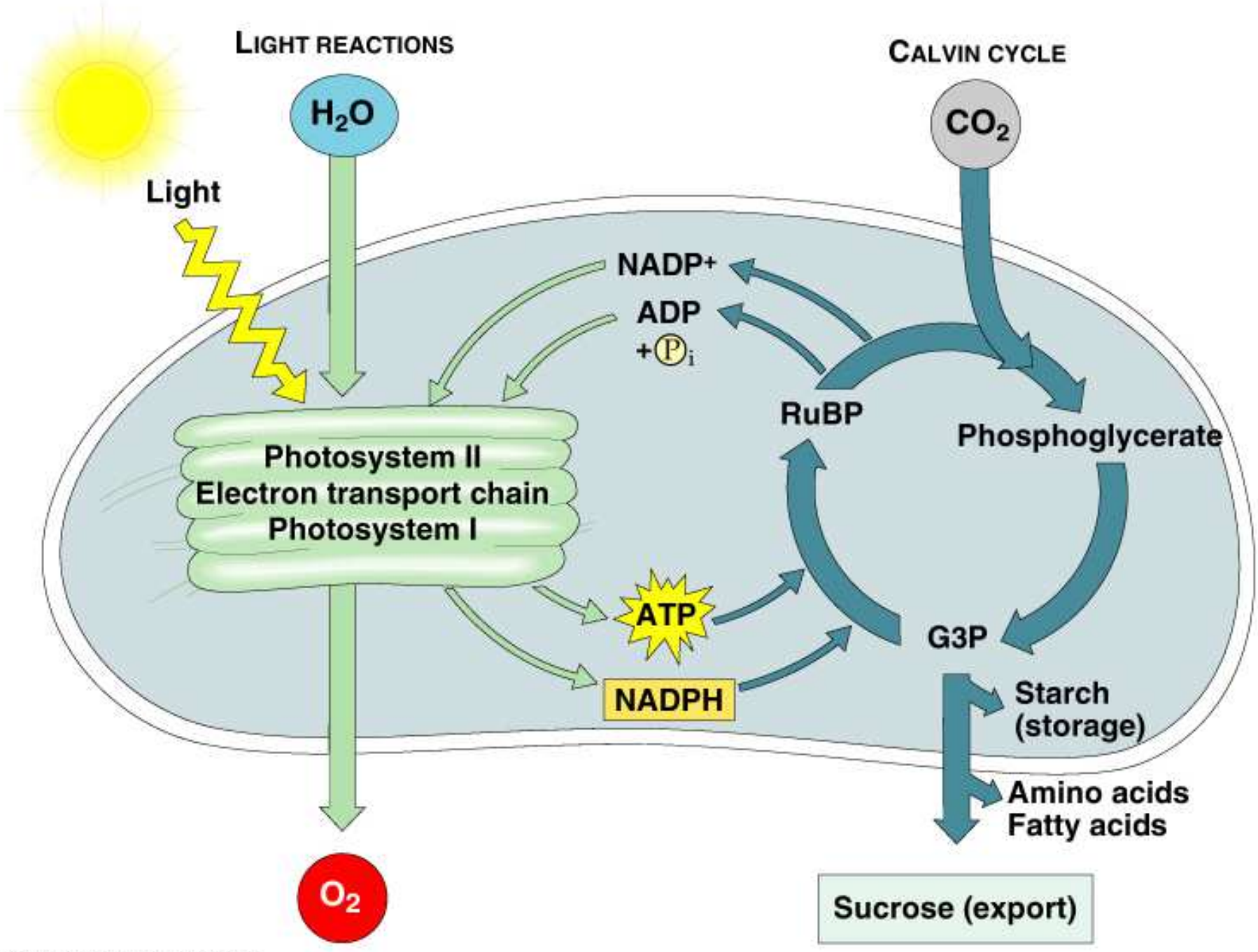
Oxygen Evolving Complex



$Mn(II)Mn(III)\ Mn(IV)_2$ $Mn(III)\ Mn(IV)_3$ $Mn(IV)_3\ Mn(V)$

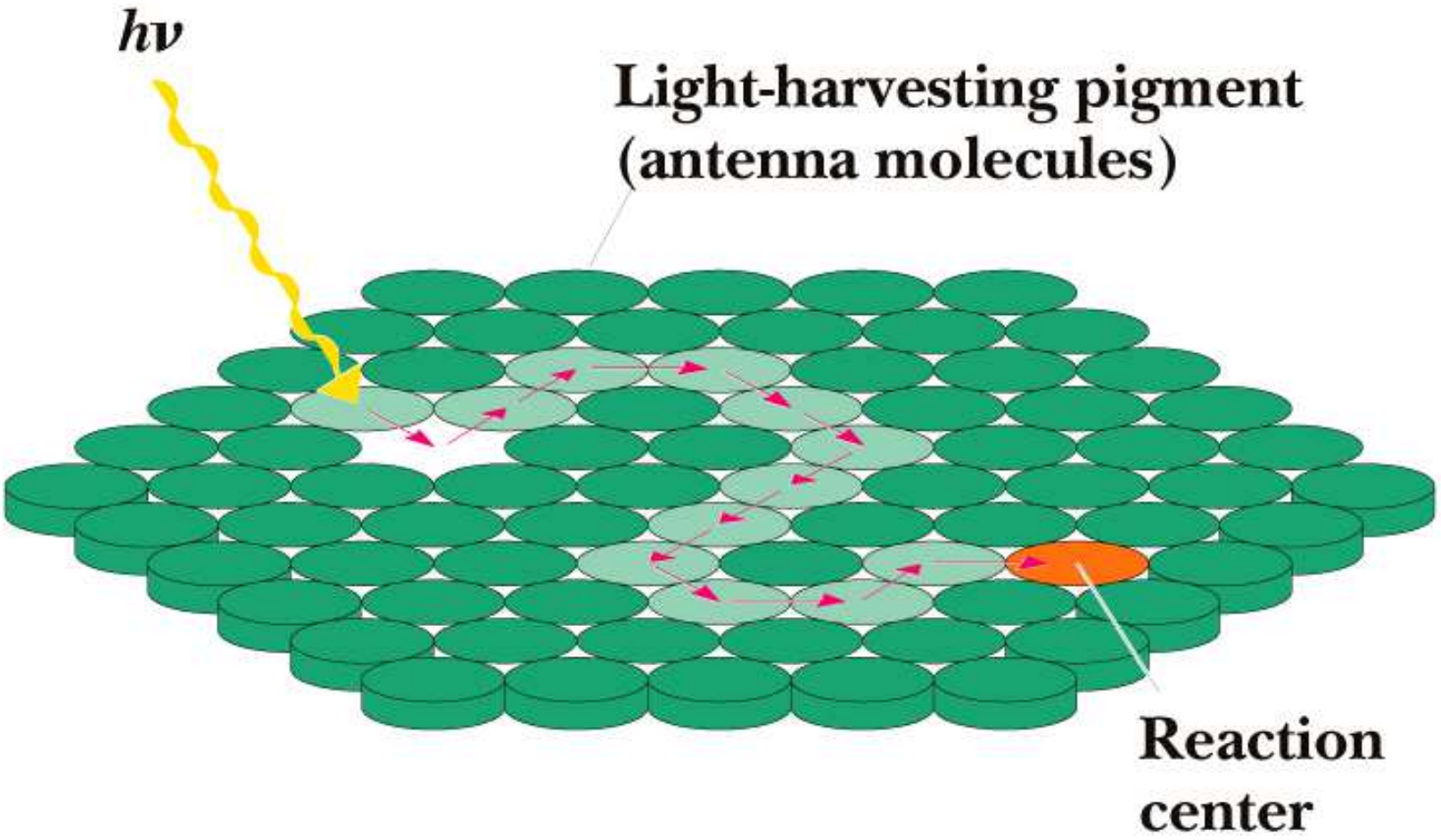
$Mn(III)_2\ Mn(IV)_2$ $Mn(IV)$

Overall scheme

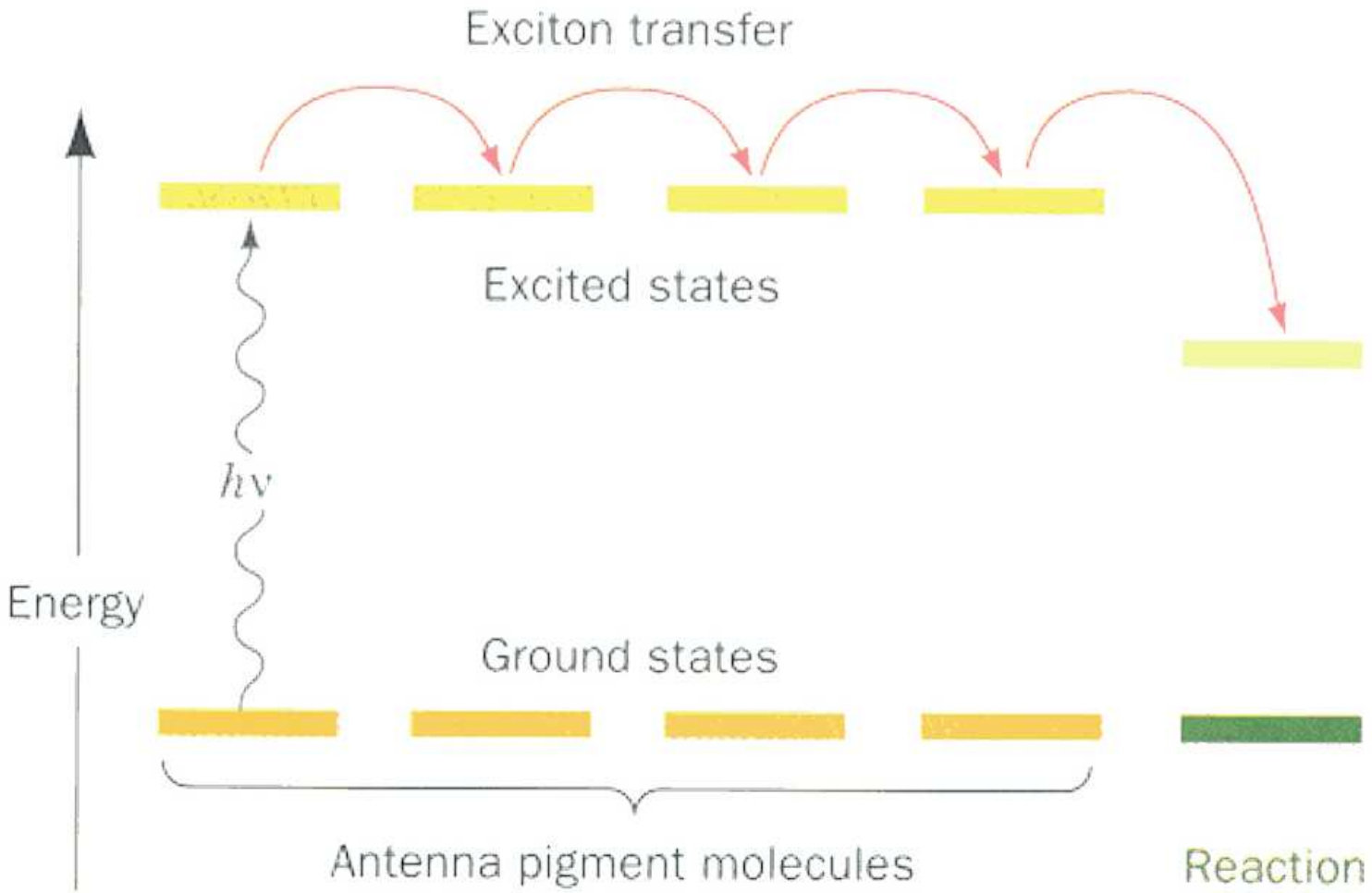


Antenna functional scheme

Garrett & Grisham: Biochemistry, 2/e
Figure 22.9

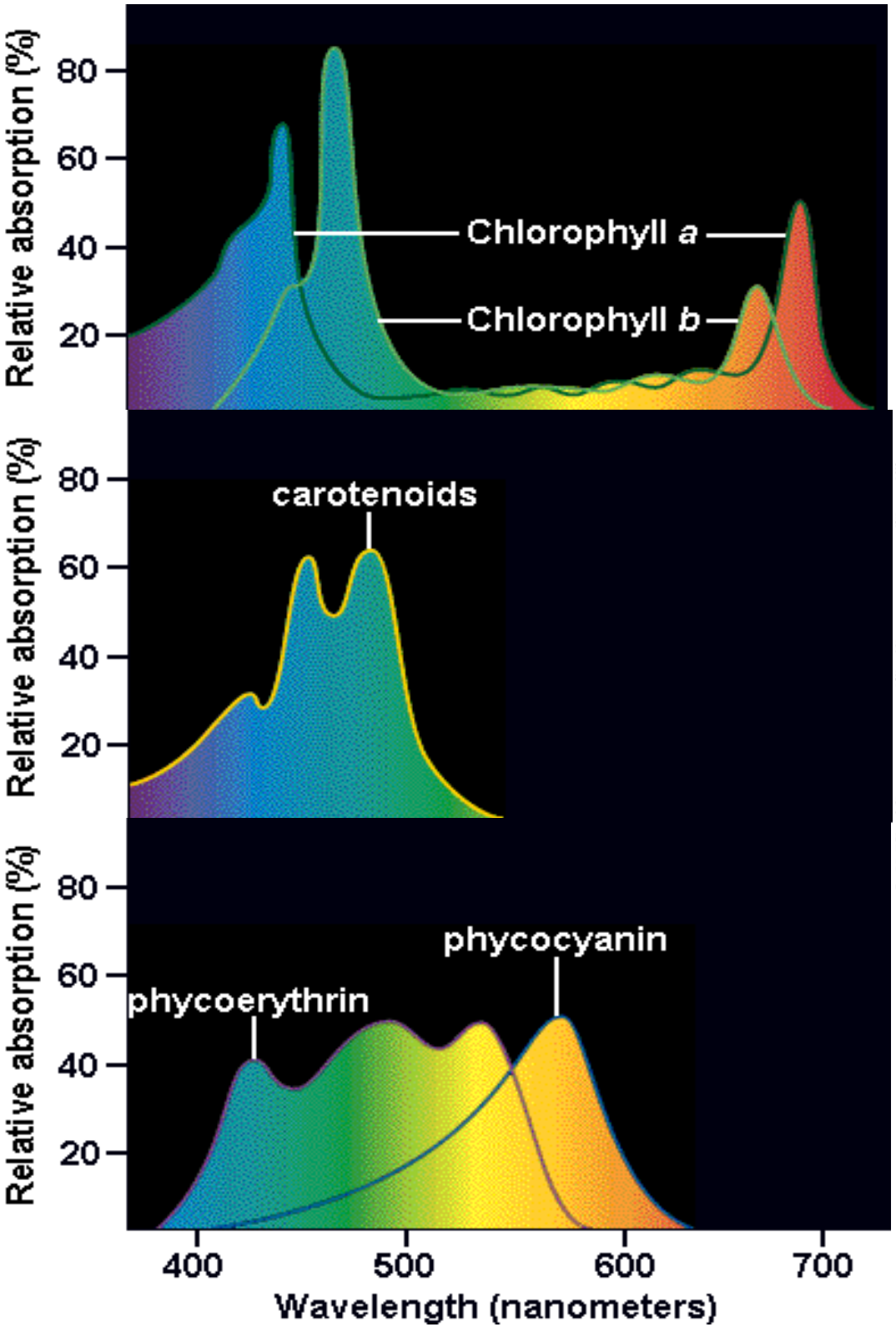


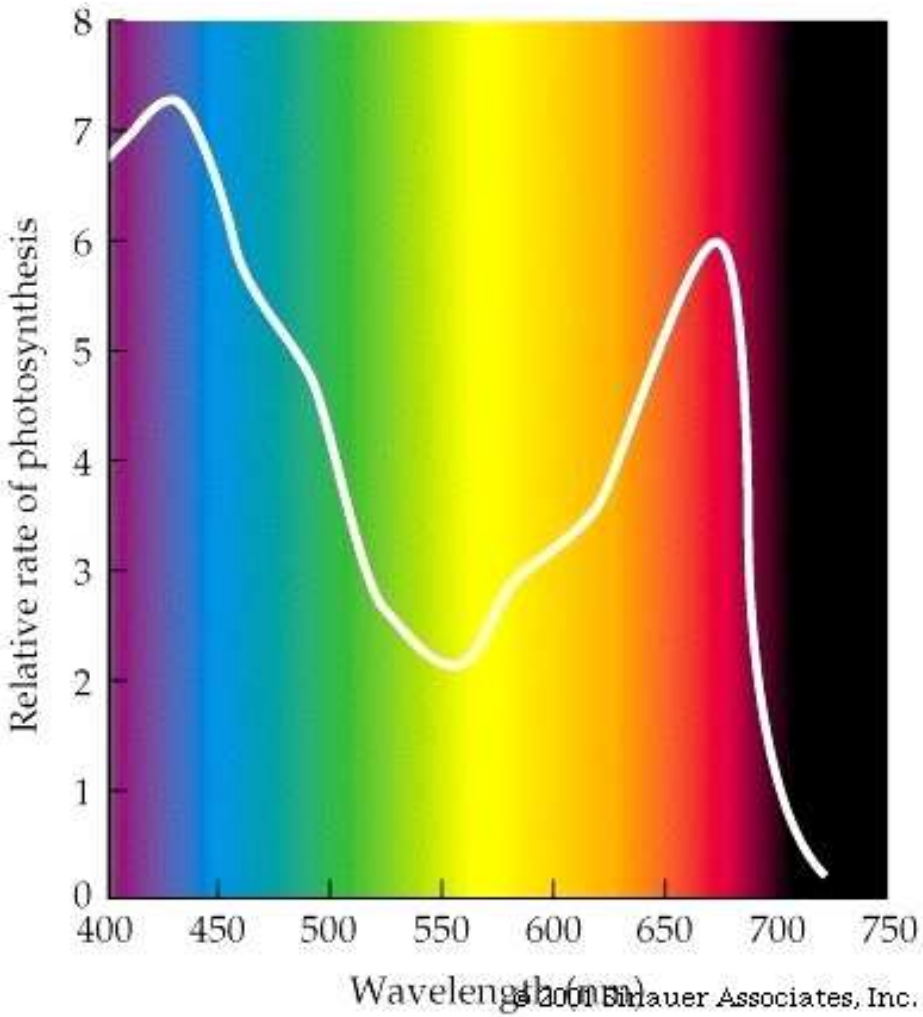
The excitation is trapped by the reaction centre chlorophyll because its lowest excited state has a lower energy than those of the antenna pigment (chlorophyll) molecules.



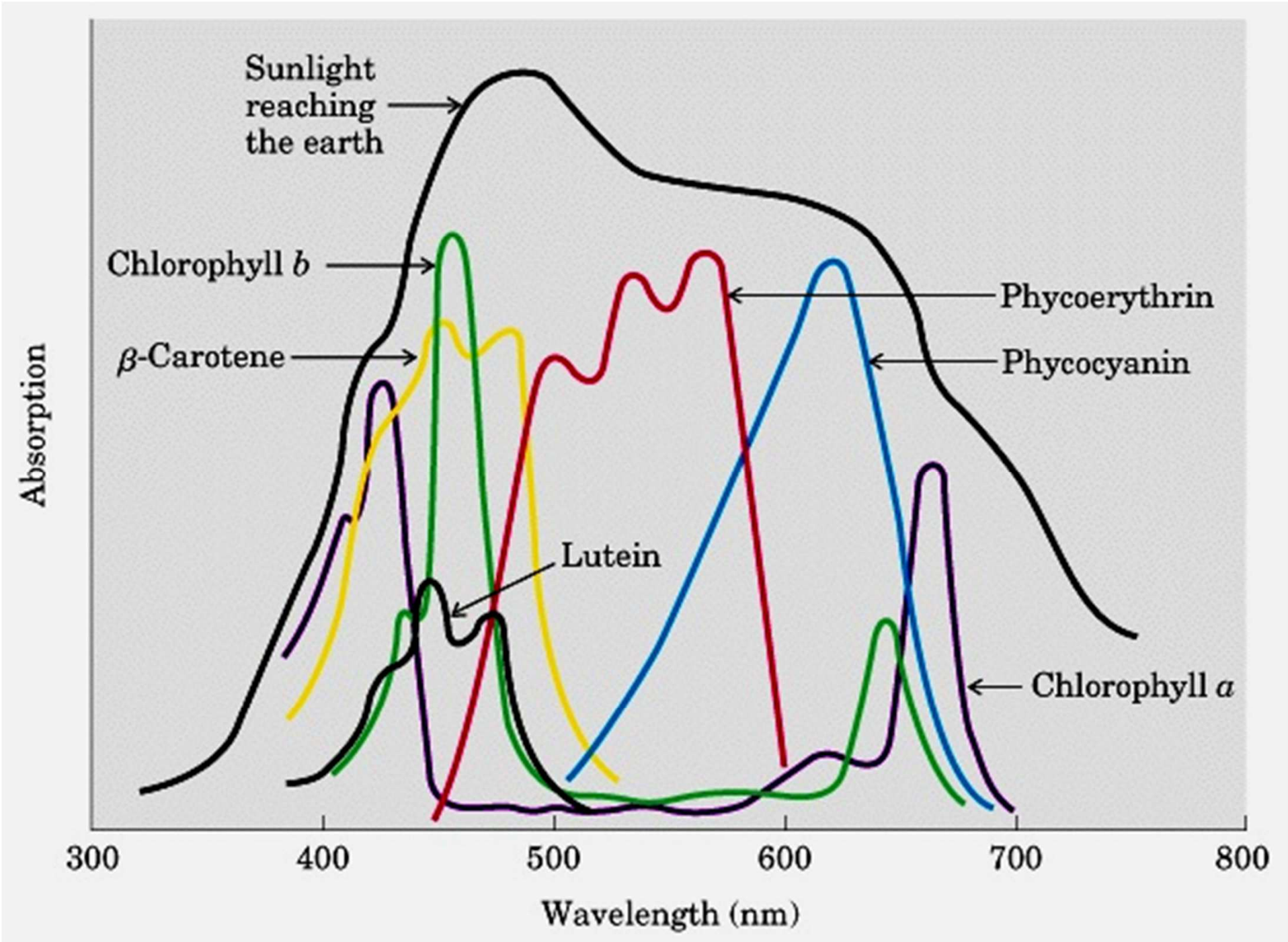
At the reaction centre, the excited state chlorophyll loses an electron (becomes oxidized) by photooxidation, to an acceptor molecule.

Spectral coverage

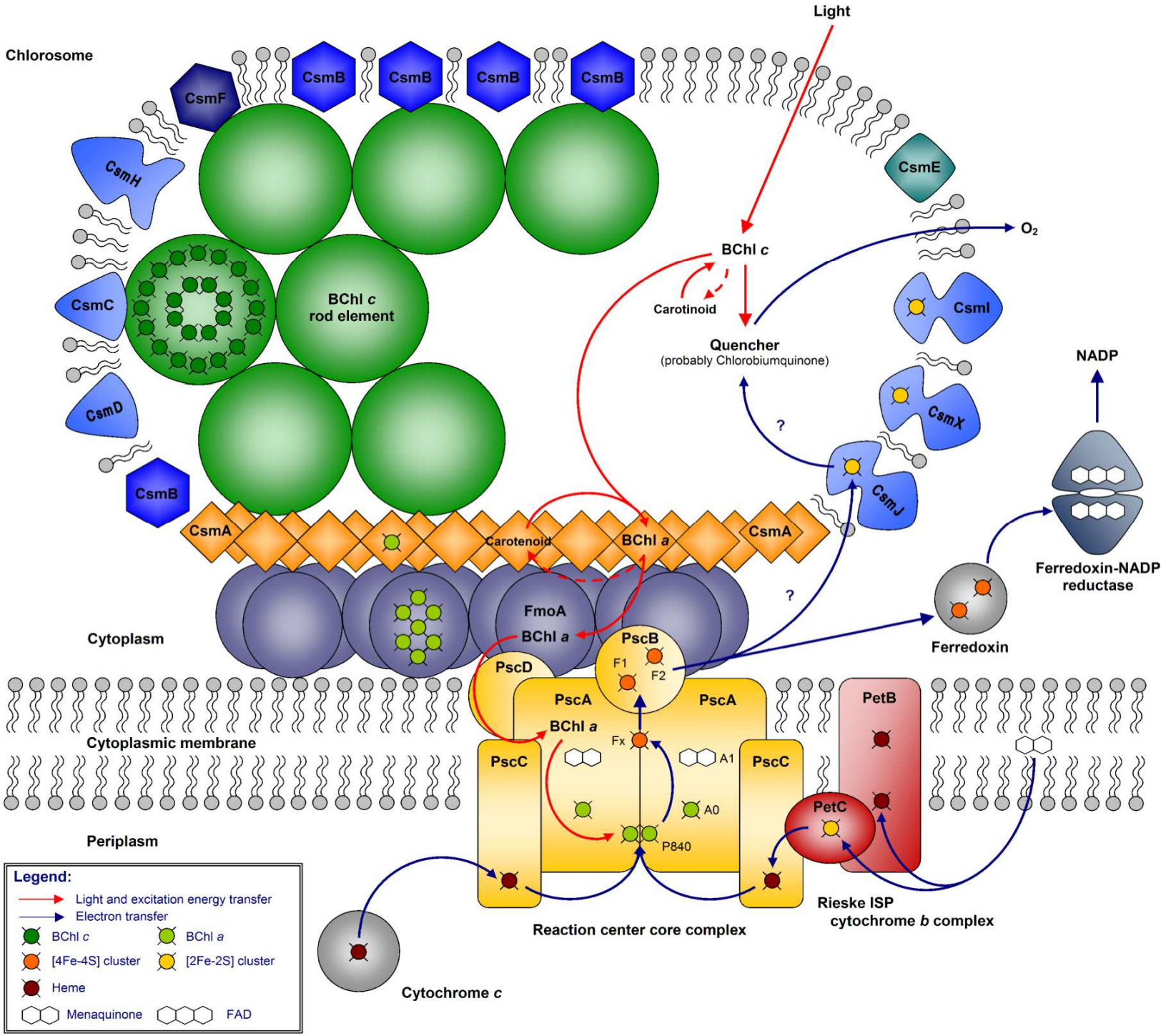




Solar spectrum and absorption of chromophores



Chlorosomes



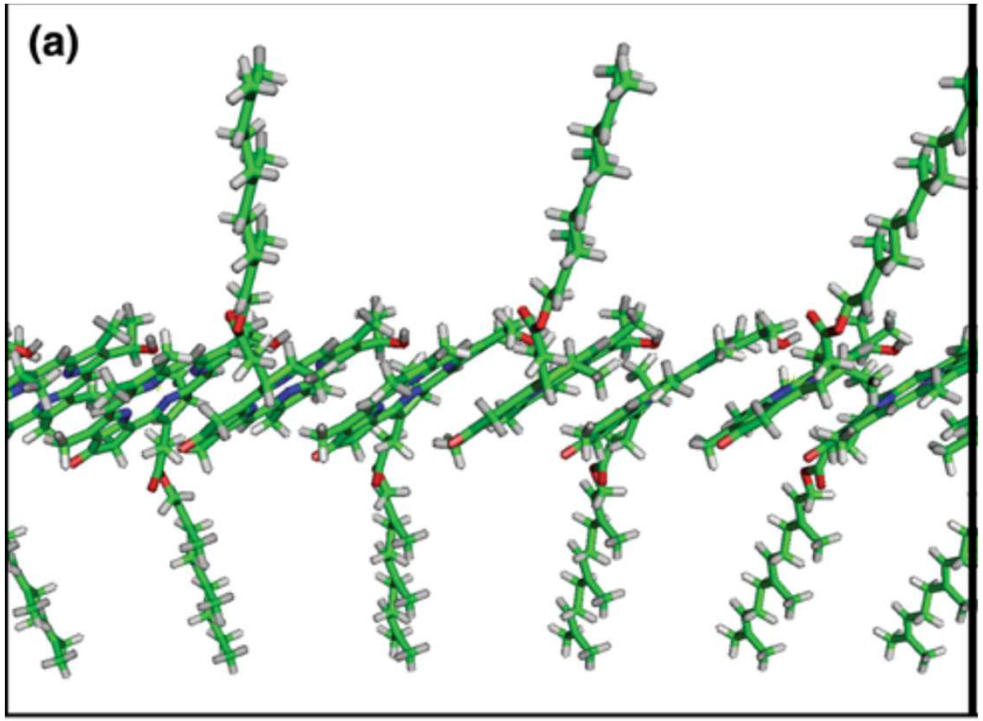
80% BChl

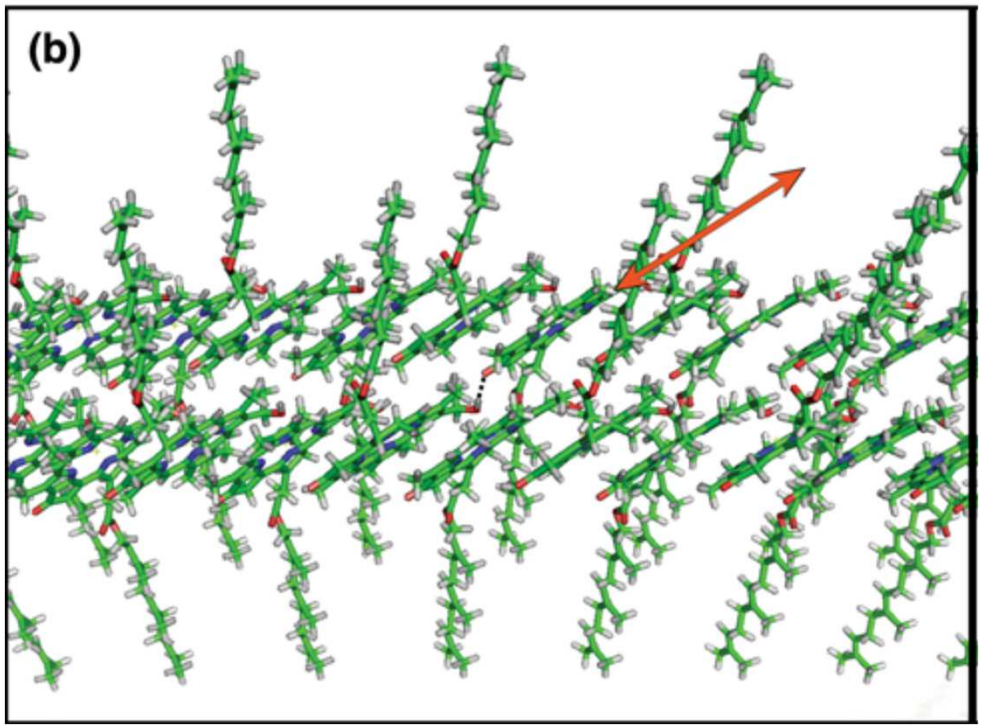
6% Carotinoids

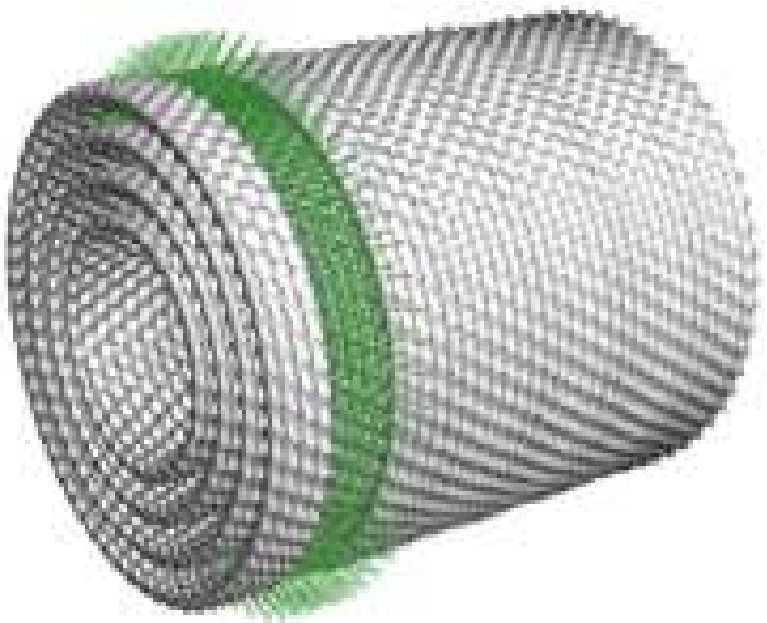
6% Lipids

2% Protein

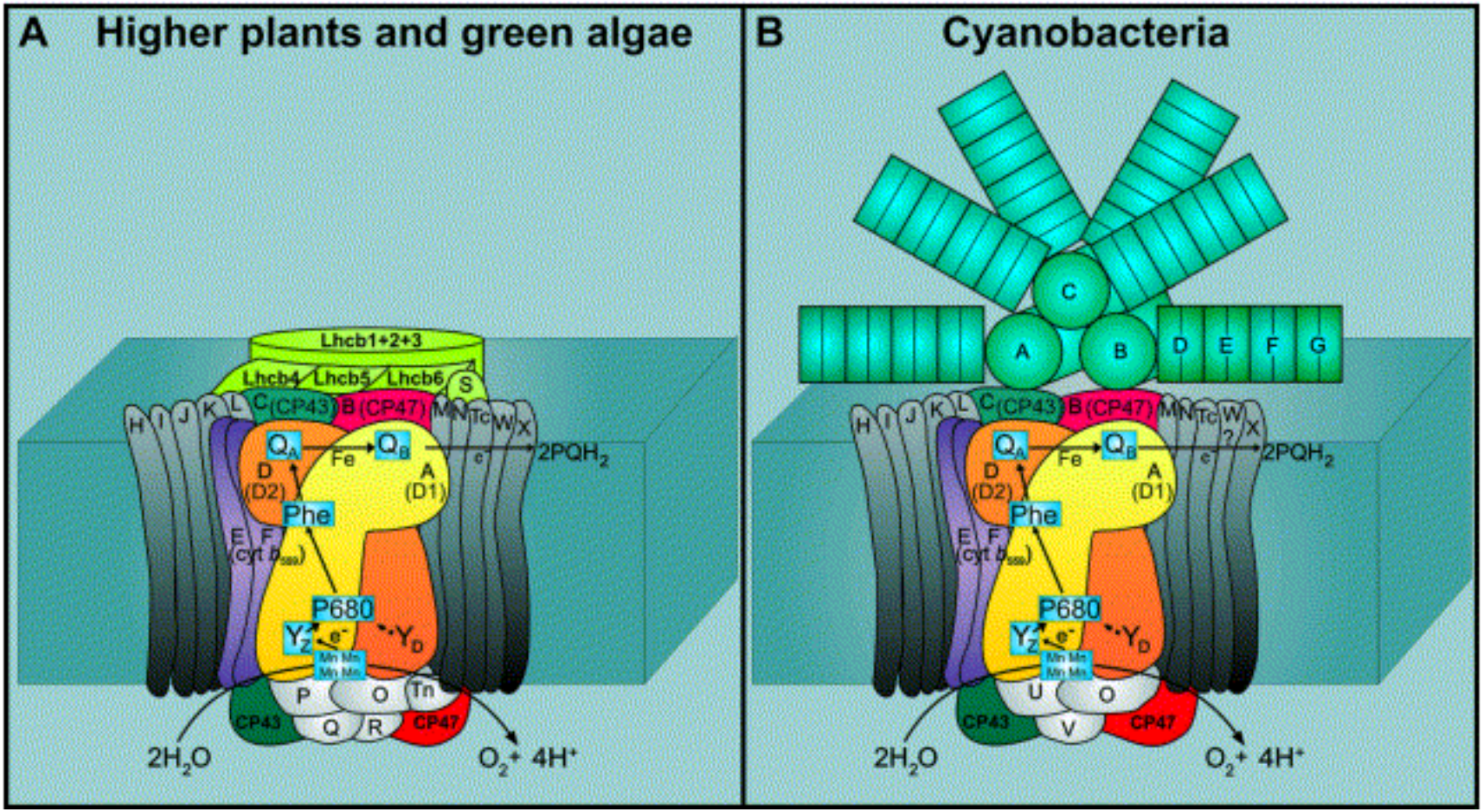
Chlorosome BChl: syn-anti self-aggregation



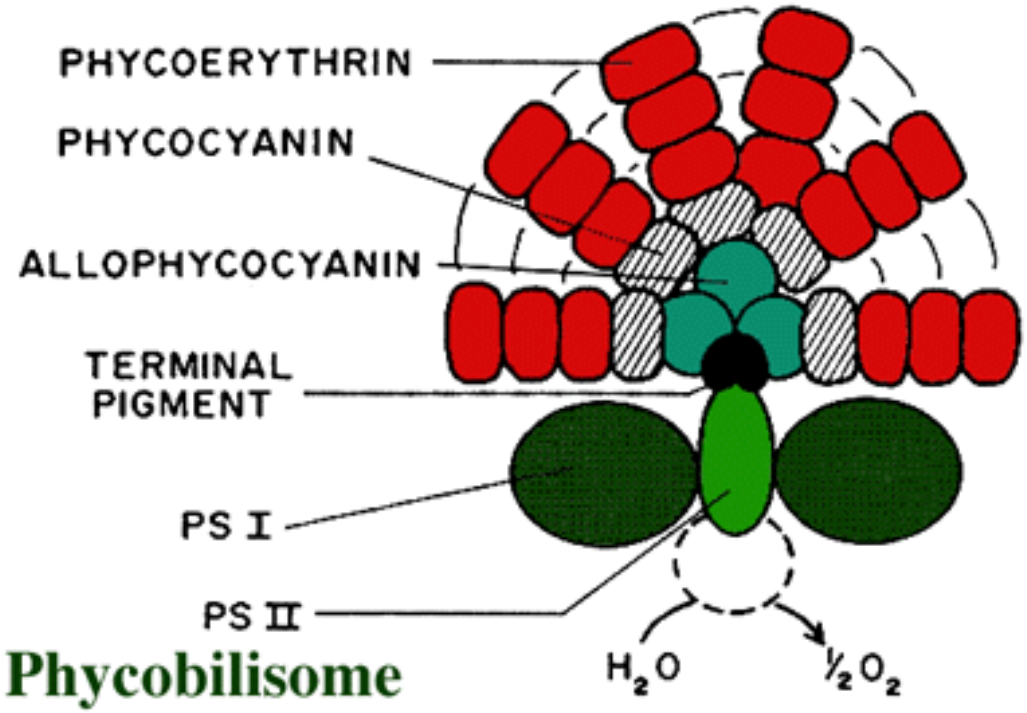


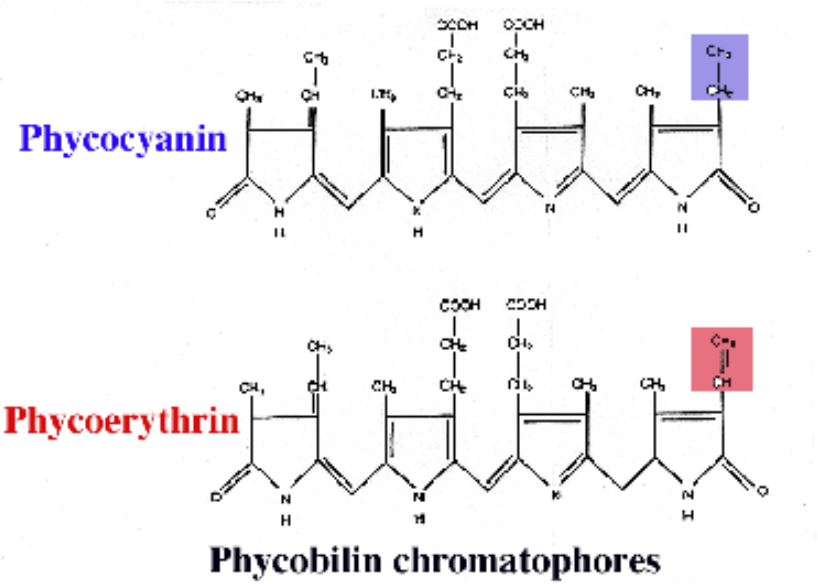


Organization of Photosystem II



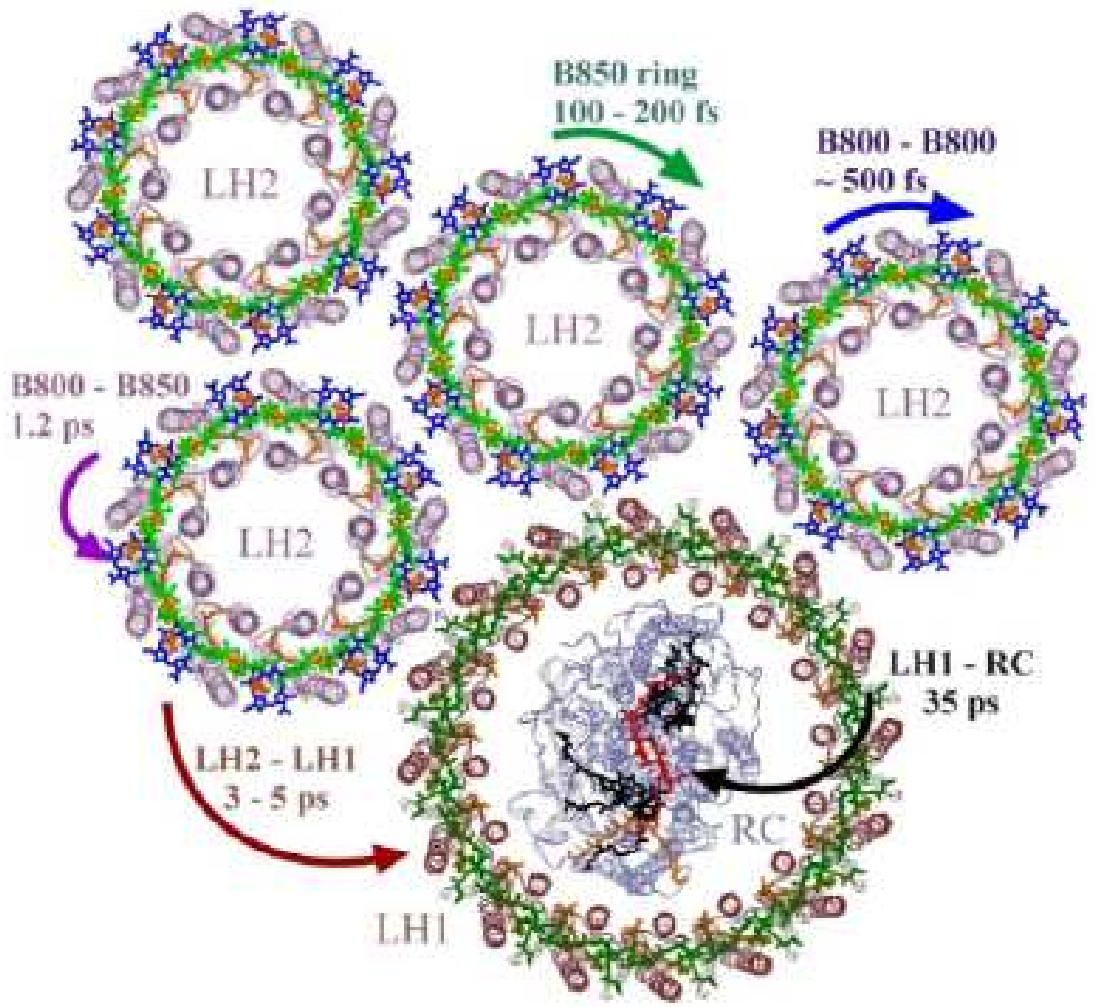
Phycobilisomes





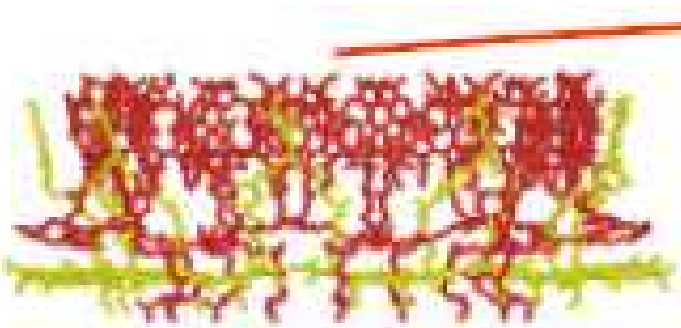
Excitonic interaction and excitation transfer

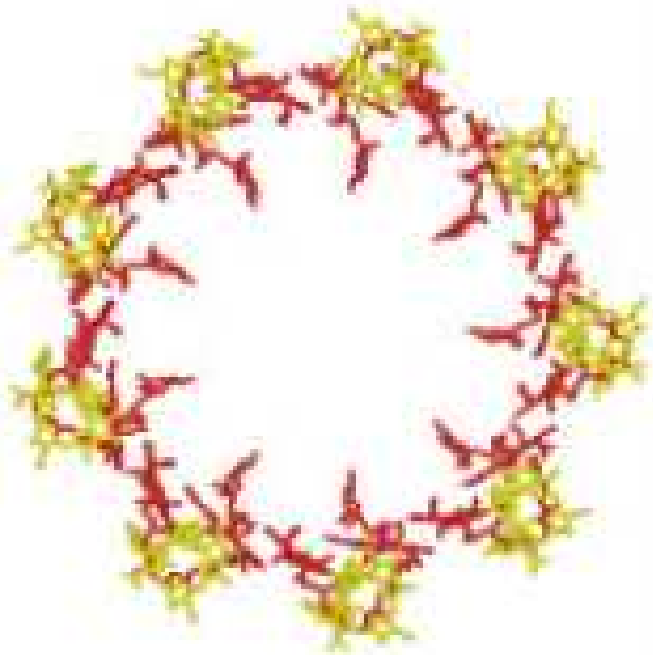
The excitation energy is transfered between the LH2 rings, to the LH1 antenna, and finally to the reaction center. Below are estimates of the times involved.

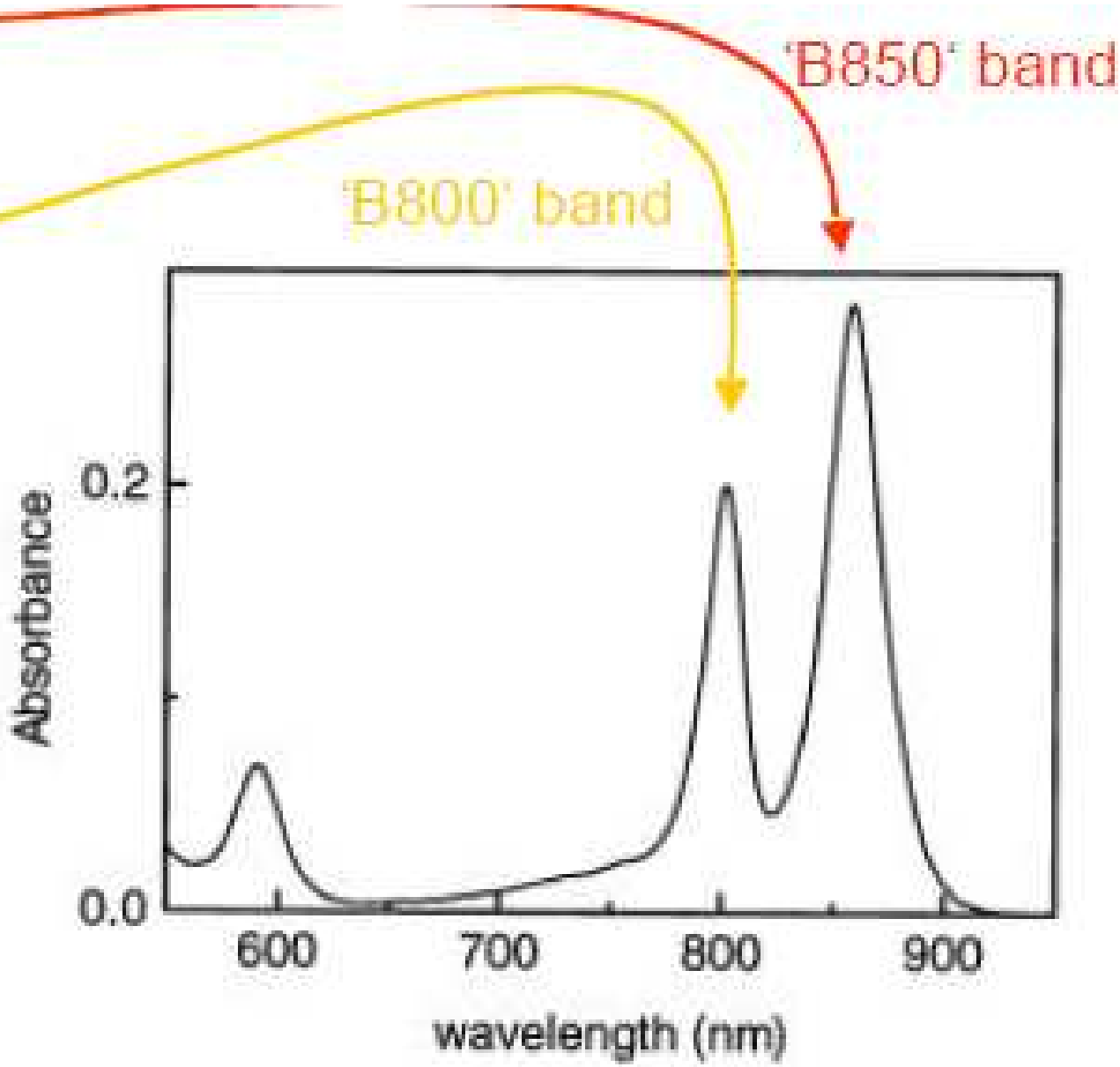


For the longer transfer times, Förster transfer mechanism is invoked, while for the fast transfer times, coherent energy transfer is the mechanism.

Spectral assignments of LH-II



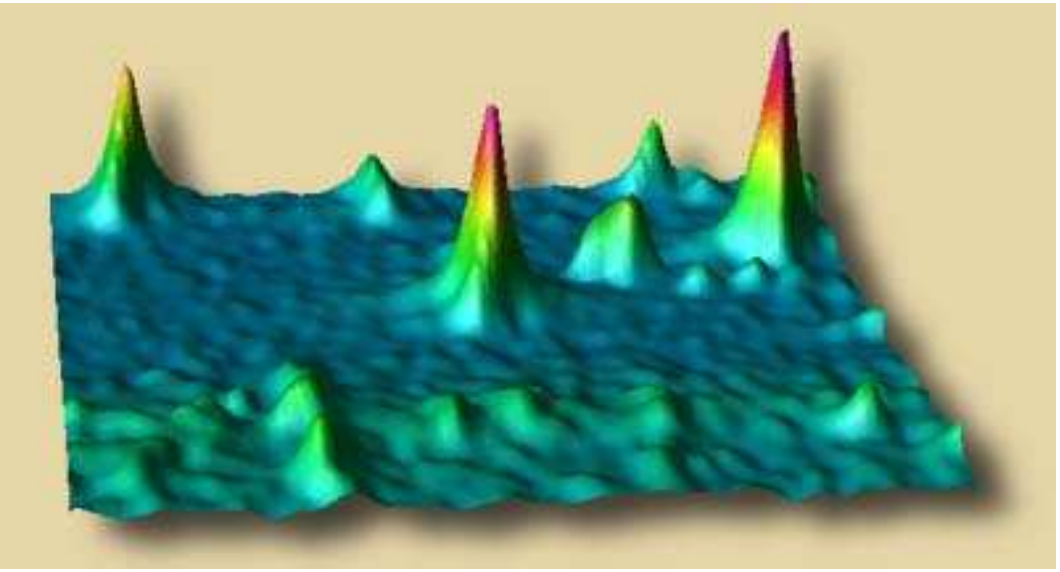


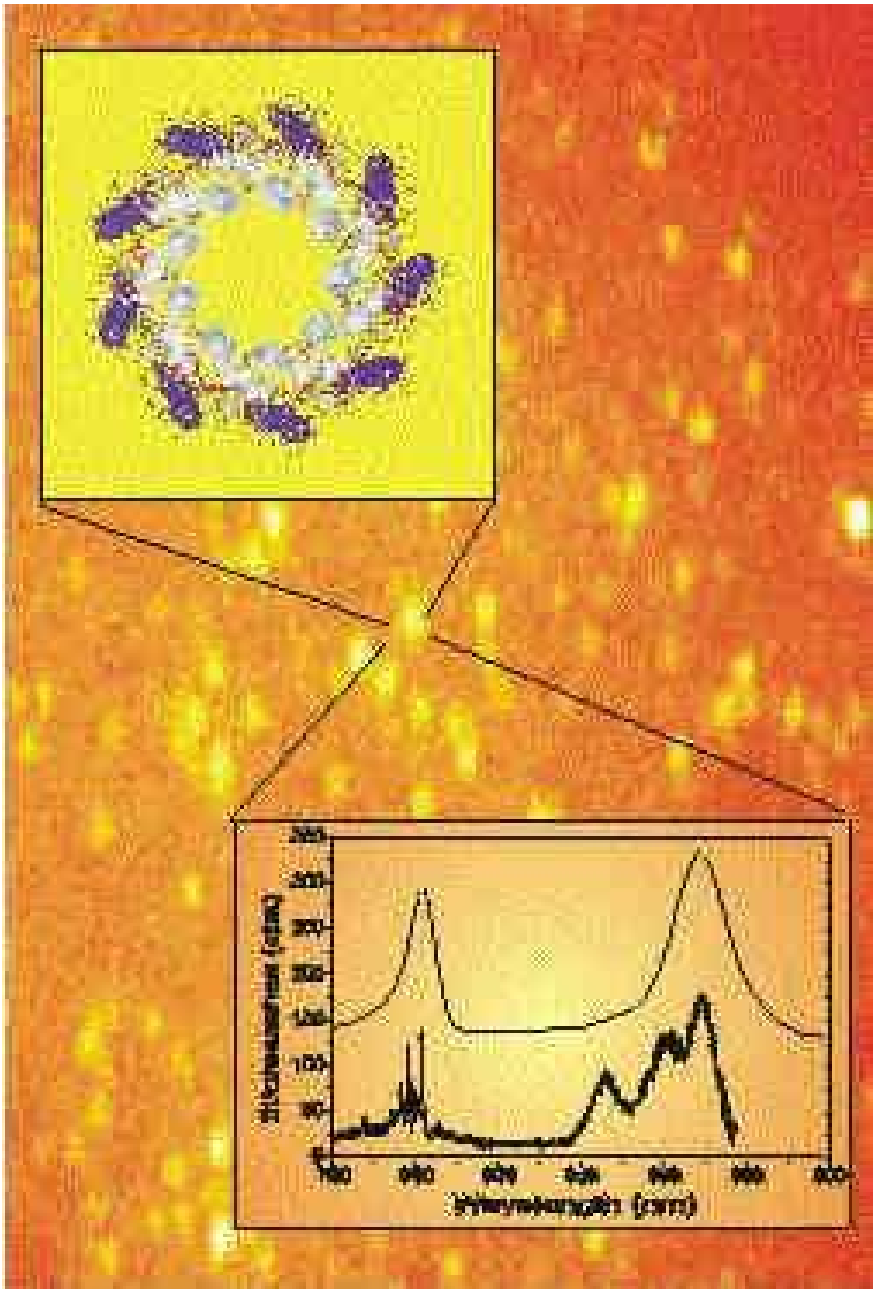


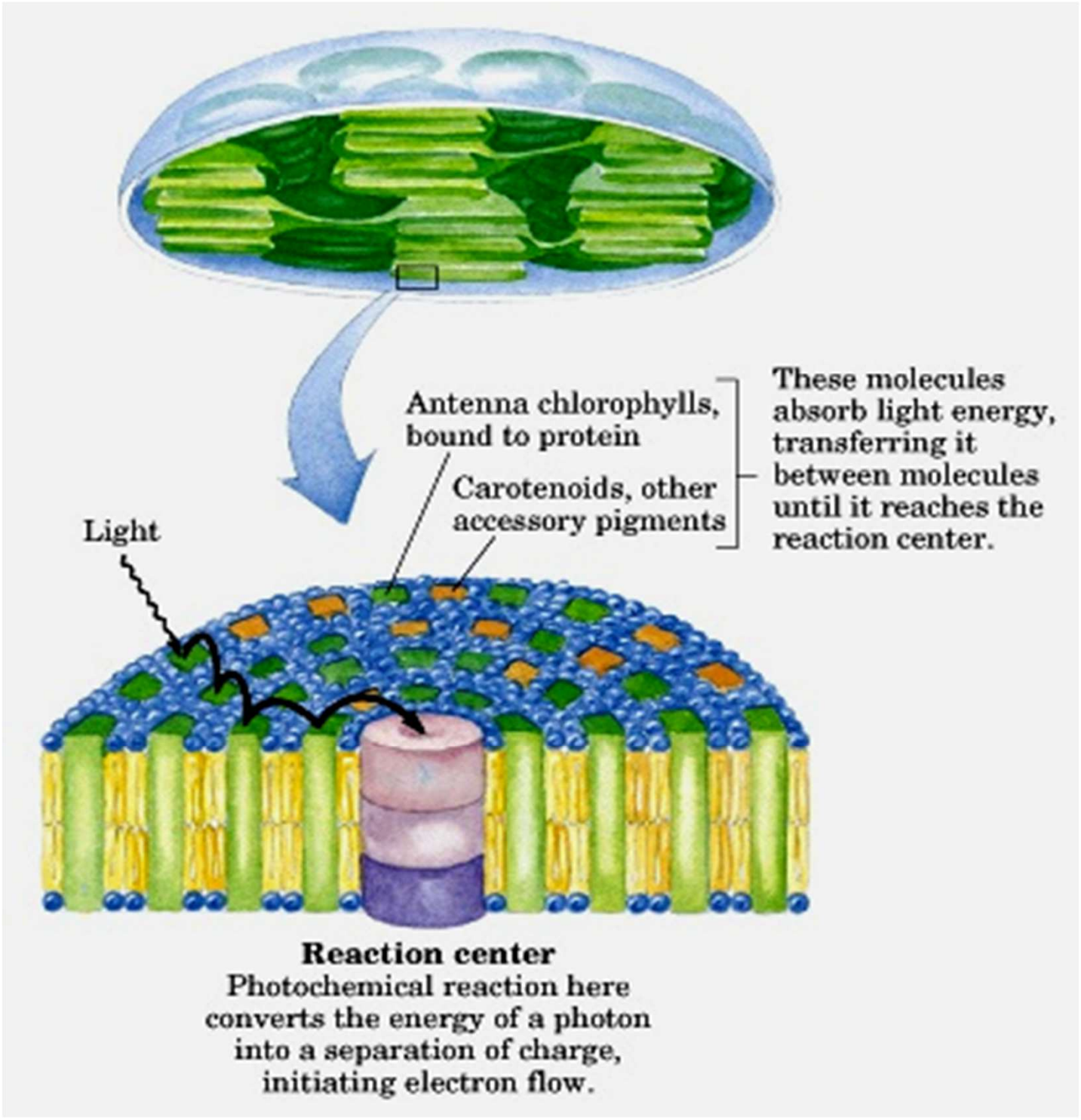
(From PhD Thesis John Kennis, RUL, september 1997)

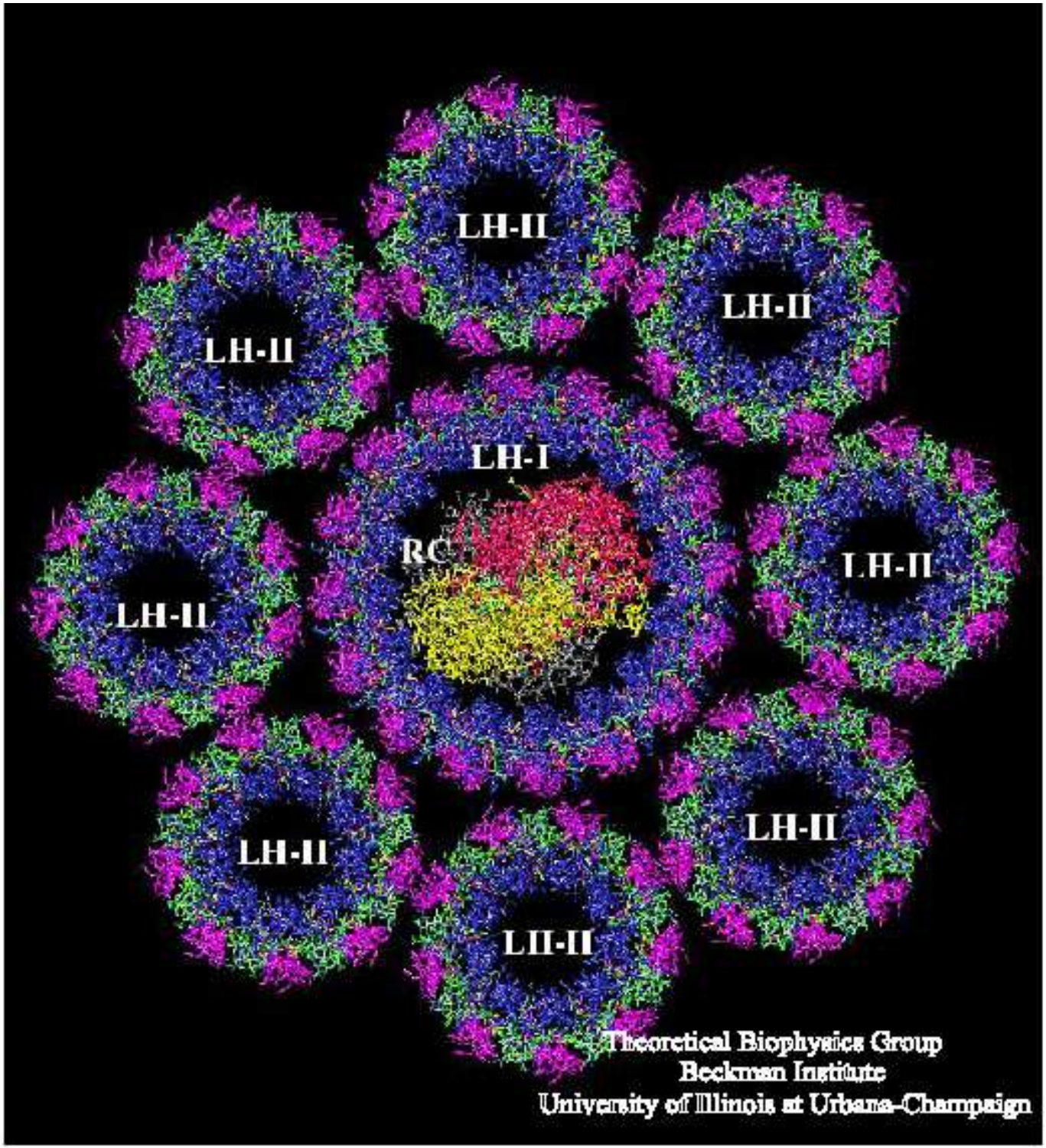
Single molecule spectroscopy

Photosynthetic antenna pigment: Light harvesting complex II

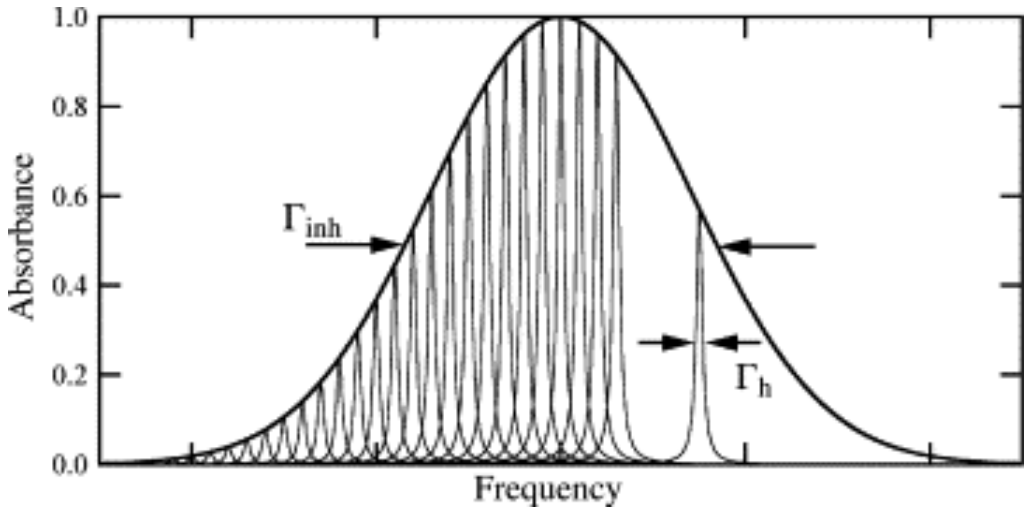


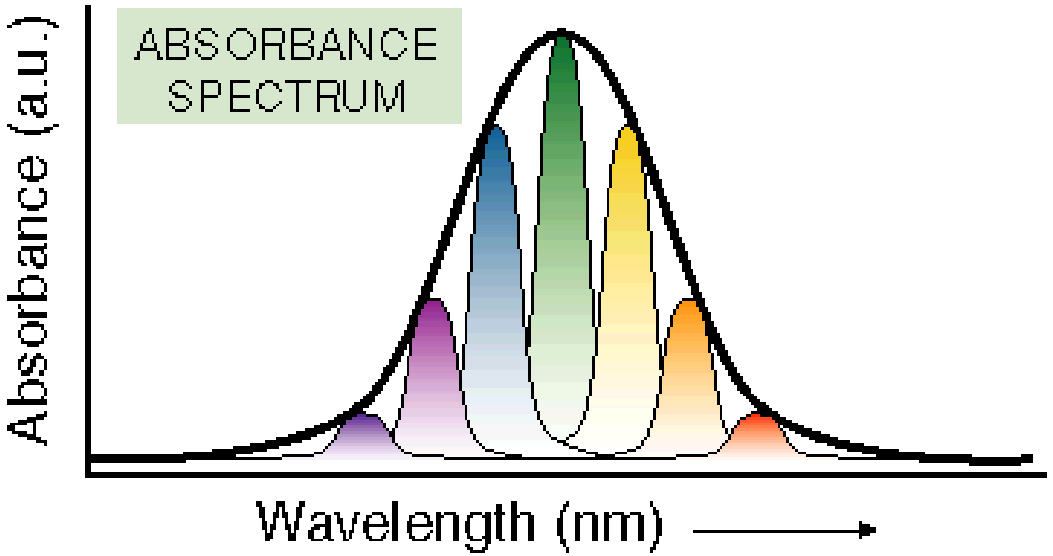



Antenna chlorophylls, bound to protein
Carotenoids, other accessory pigments
These molecules absorb light energy, transferring it between molecules until it reaches the reaction center.
Light
Reaction center
Photochemical reaction here converts the energy of a photon into a separation of charge, initiating electron flow.

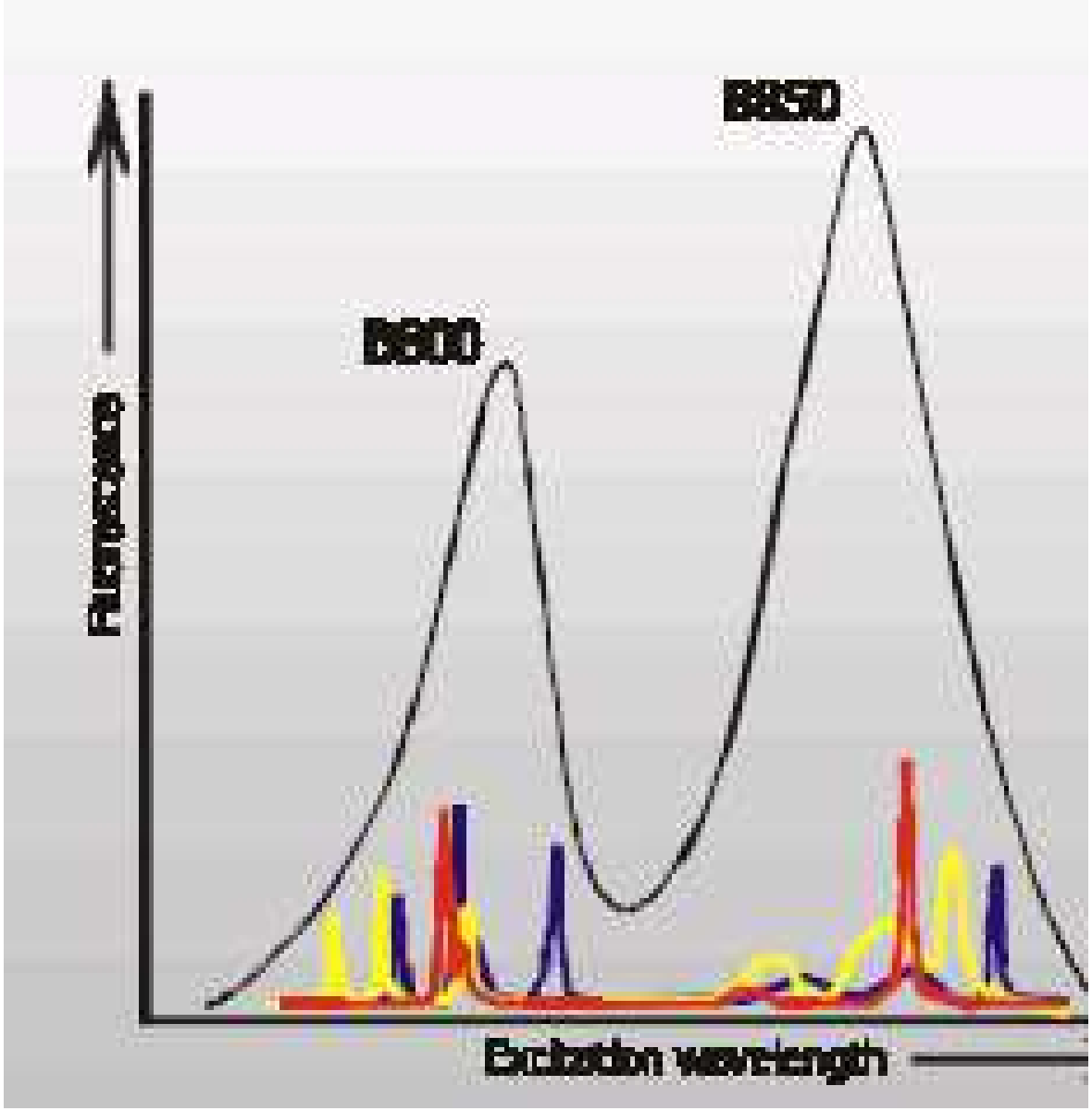

LH-II
LH-II
LH-II
LH-I
RC
LH-II
LH-II
LH-II
LH-II
LII-II
Theoretical Biophysics Group
Beckman Institute
University of Illinois at Urbana-Champaign

Homogeneous vs. Inhomogeneous broadening





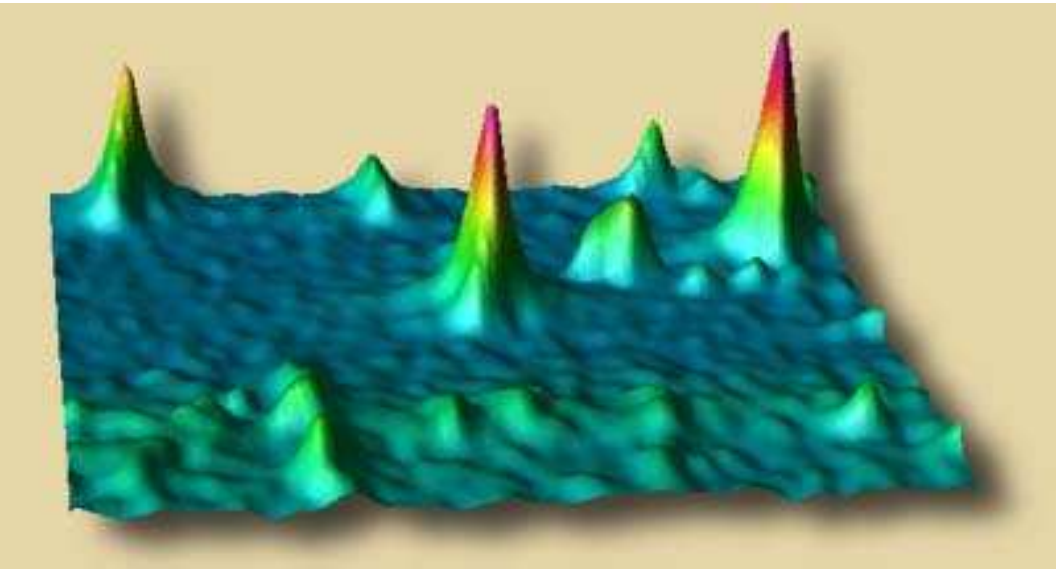
Inhomogenously or homogenously broadened spectrum ?

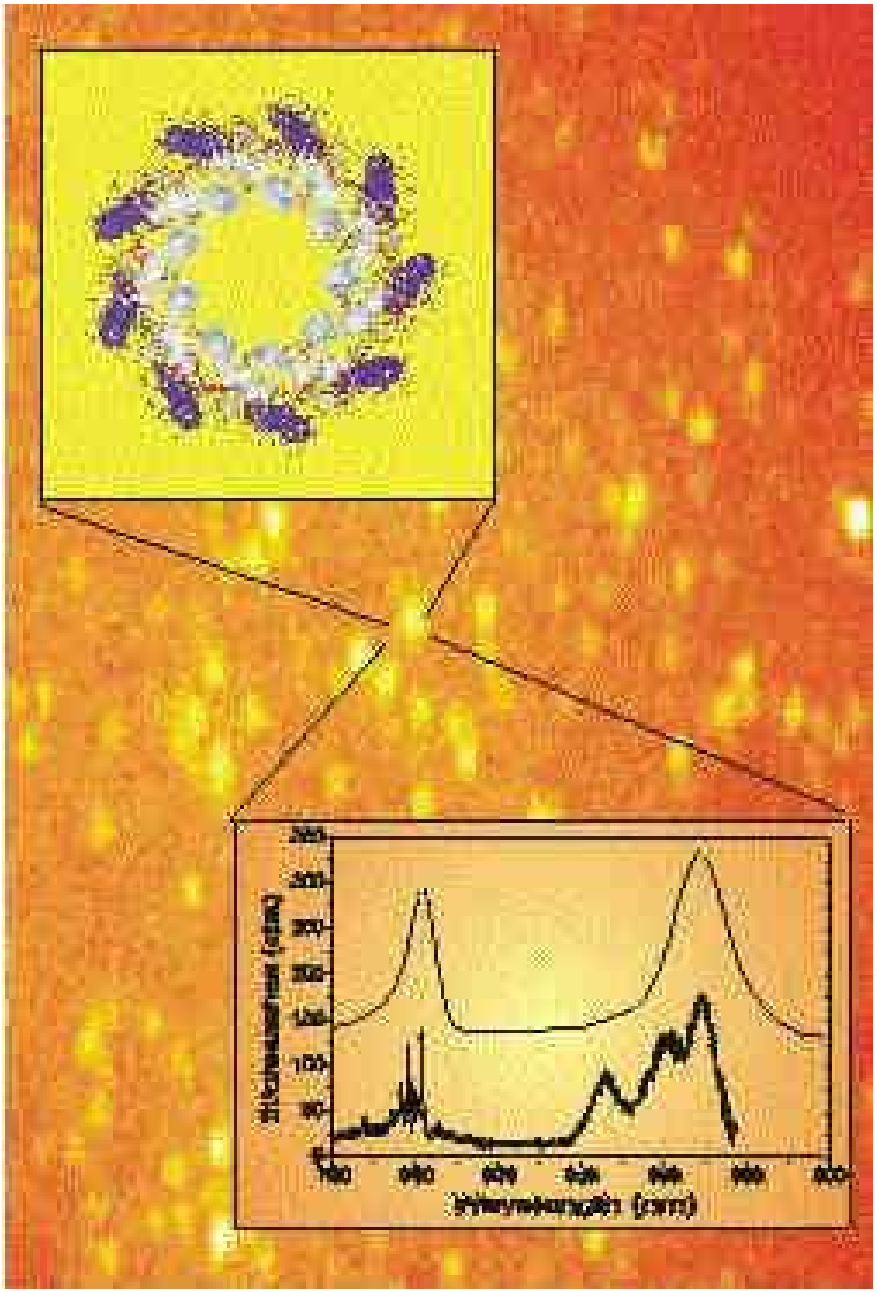


Thomas Schmidt et al
Leiden
Les Houches Seminar

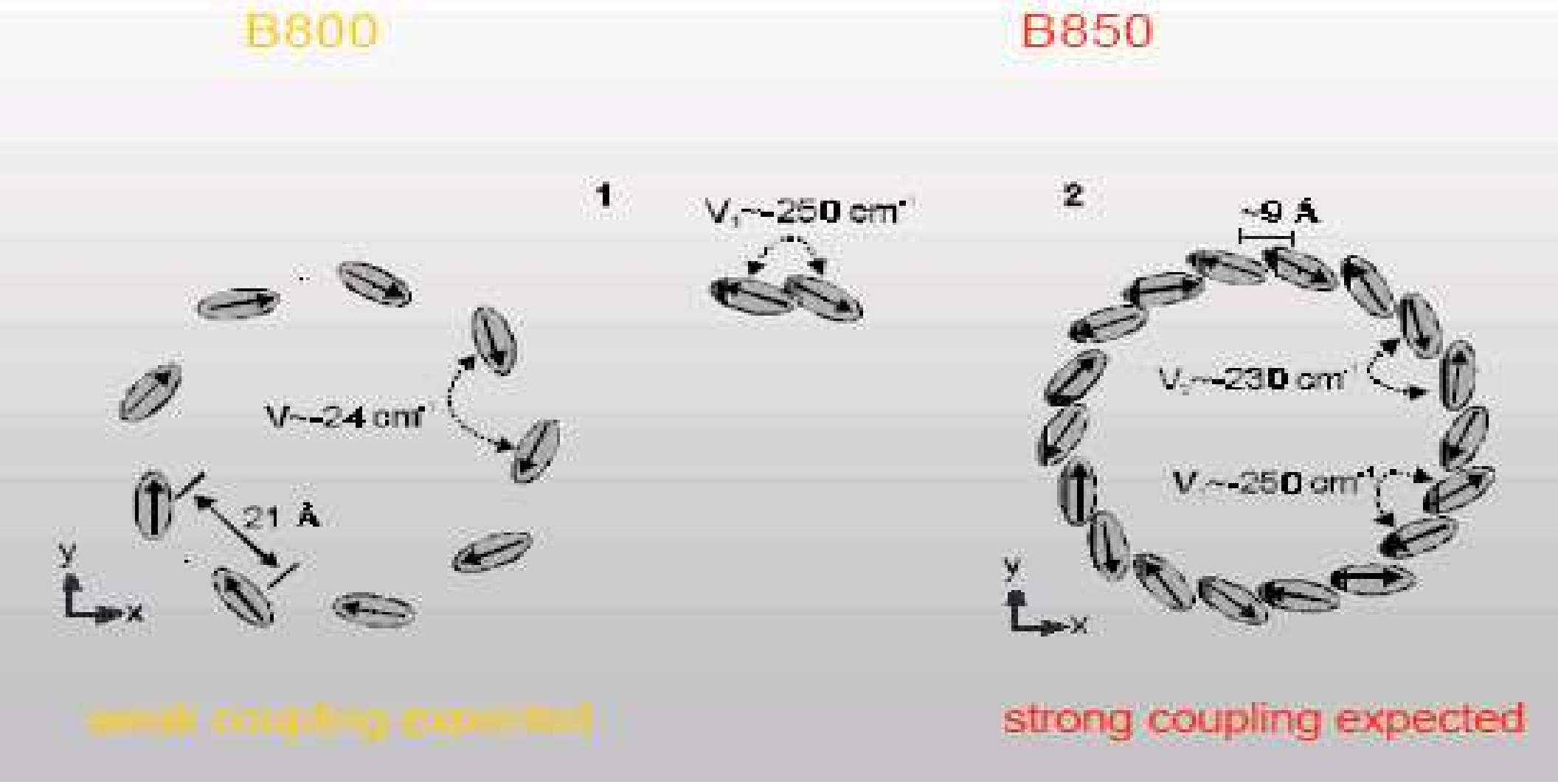
Single molecule spectroscopy

Photosynthetic antenna pigment: Light harvesting complex II



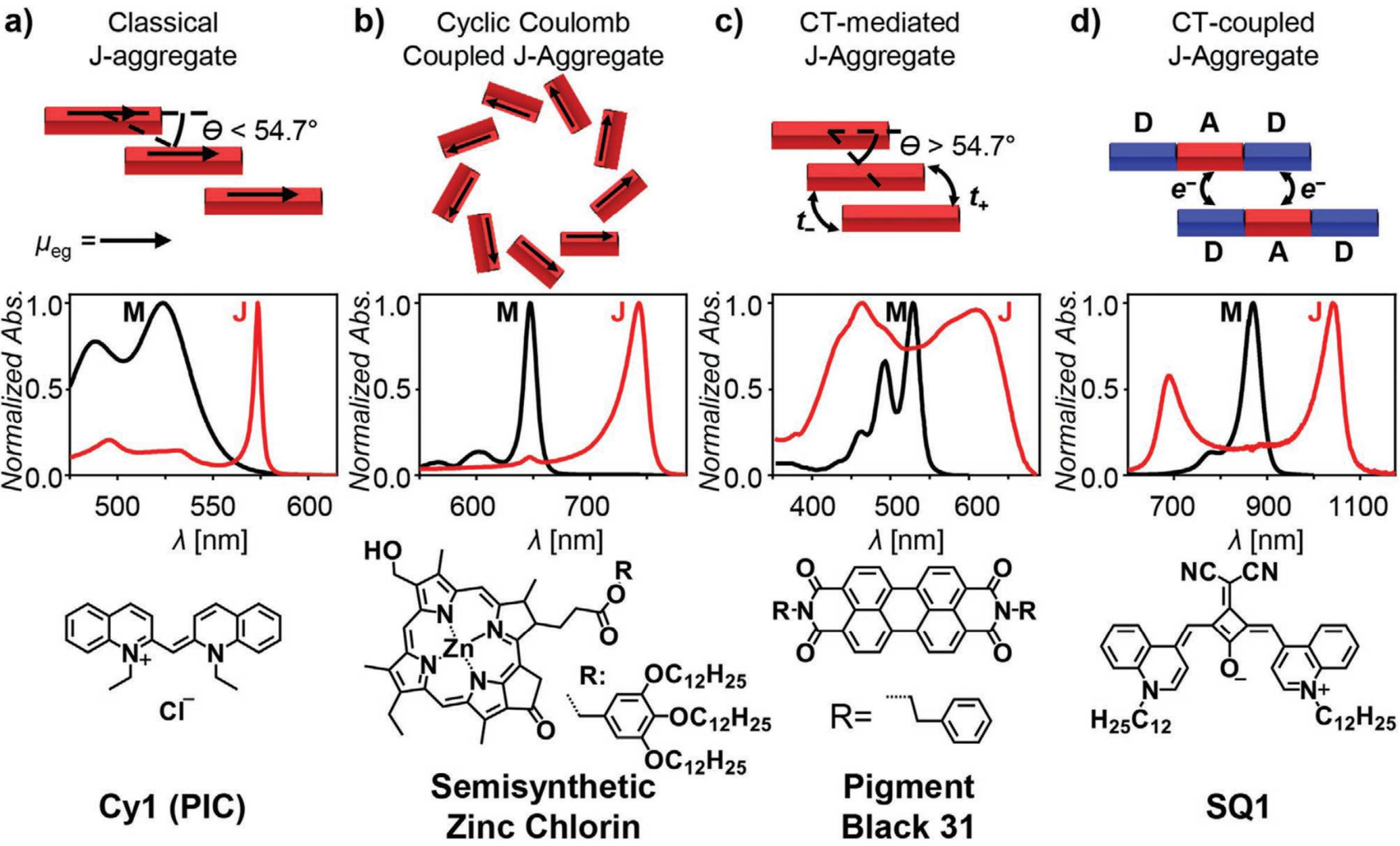


B800 is weakly coupled, B850 is strongly coupled eg. in an excitonic state



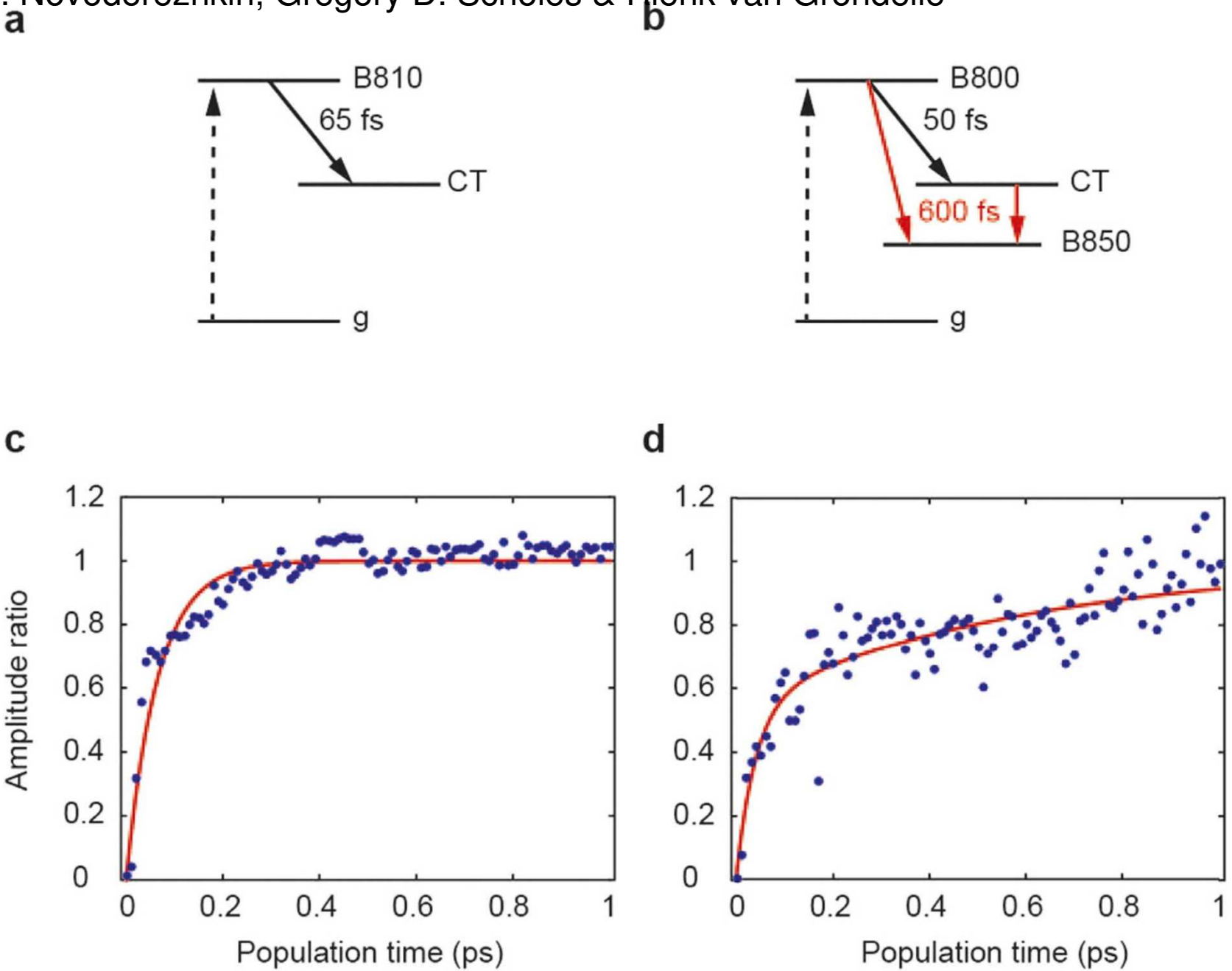
Thomas Schmidt et al
Leiden
Les Houches Seminar

Aggregate arrangements



Dark states in LH2 revealed by 2-dimensional spectroscopy

Marco Ferretti, Ruud Hendrikx, Elisabet Romero, June Southall, Richard J. Cogdell, Vladimir I. Novoderezhkin, Gregory D. Scholes & Rienk van Grondelle



Classification of spectroscopic Aggregates