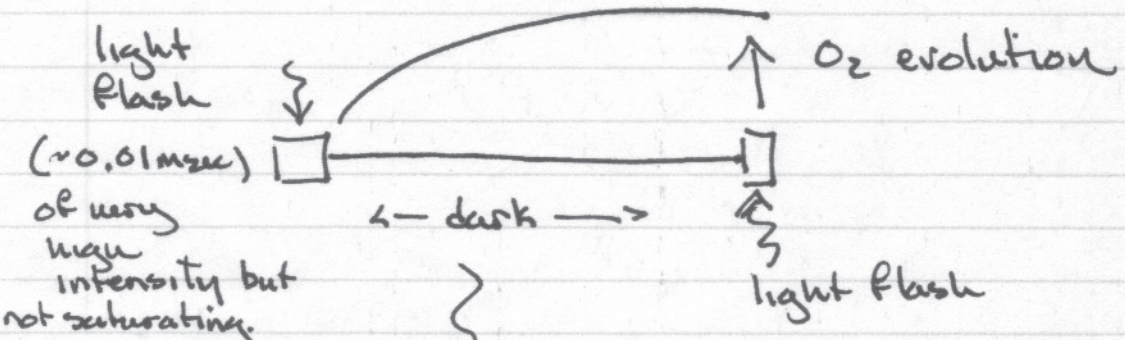
LIGHT HARVESTING.

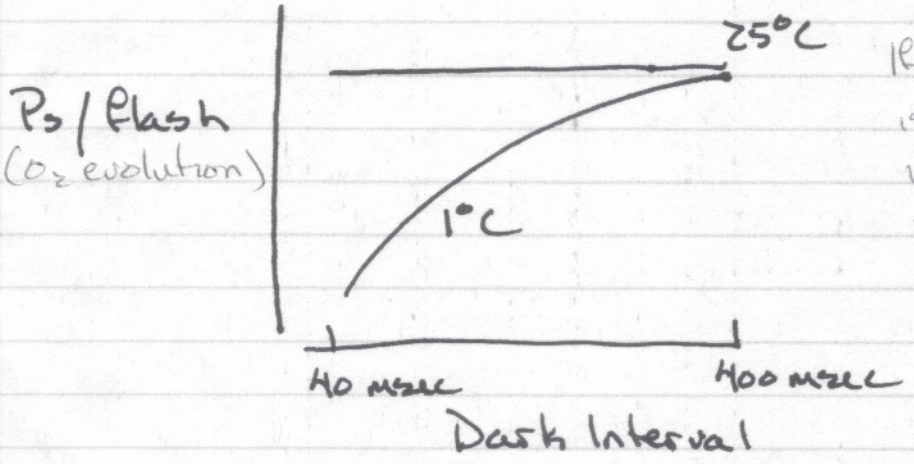
In Emerson and Arnold's classic experiments published in 1932, they examined the effect of light and dark on photosynthesis measured as oxygen evolution.



At 25°C, 40 msec of dark was sufficient time ~~of saturable~~ for oxygen evolution to ~~max~~ reach some maximal level. That is, sufficient time for the process of O_2 evolution to be complete

However, at 1°C, the dark reaction time required to reach maximal O_2 production was significantly longer: 400 msec.

As long as the dark period was long enough, O_2 evolution was temperature independent.



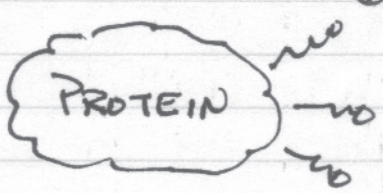
If the dark duration is long enough, inhibition of respiration with CN^- has no effect on the O_2 produced per light flash.

Blankenship notes that the idea that ≥480 chlorophyll molecules were required for 1 O_2 molecule evolved was, historically, unexpected. The assumption was one chlorophyll molecule functioned independently in the light reaction to produce oxygen.

An additional complexity is the arrangement of chlorophyll in the chloroplast.

Because chlorophyll has a hydrophobic phytol 'tail' it was originally thought to occur in the lipid phase of the thylakoid membranes. After all, it is readily extractable using solvents such as acetone and methanol.

However, when detergent extraction is used, the detergent replaces the lipids surrounding the proteins



When these are electrophoresed on gels, the chlorophyll migrates with specific proteins. For example, photosystem-related proteins and LHCP (light-harvesting chl a/b protein).

From these disparate observations arises the concept of light-harvesting 'antenna', complexes of protein and chlorophyll.

Dark Reactions of Photosynthesis[1]

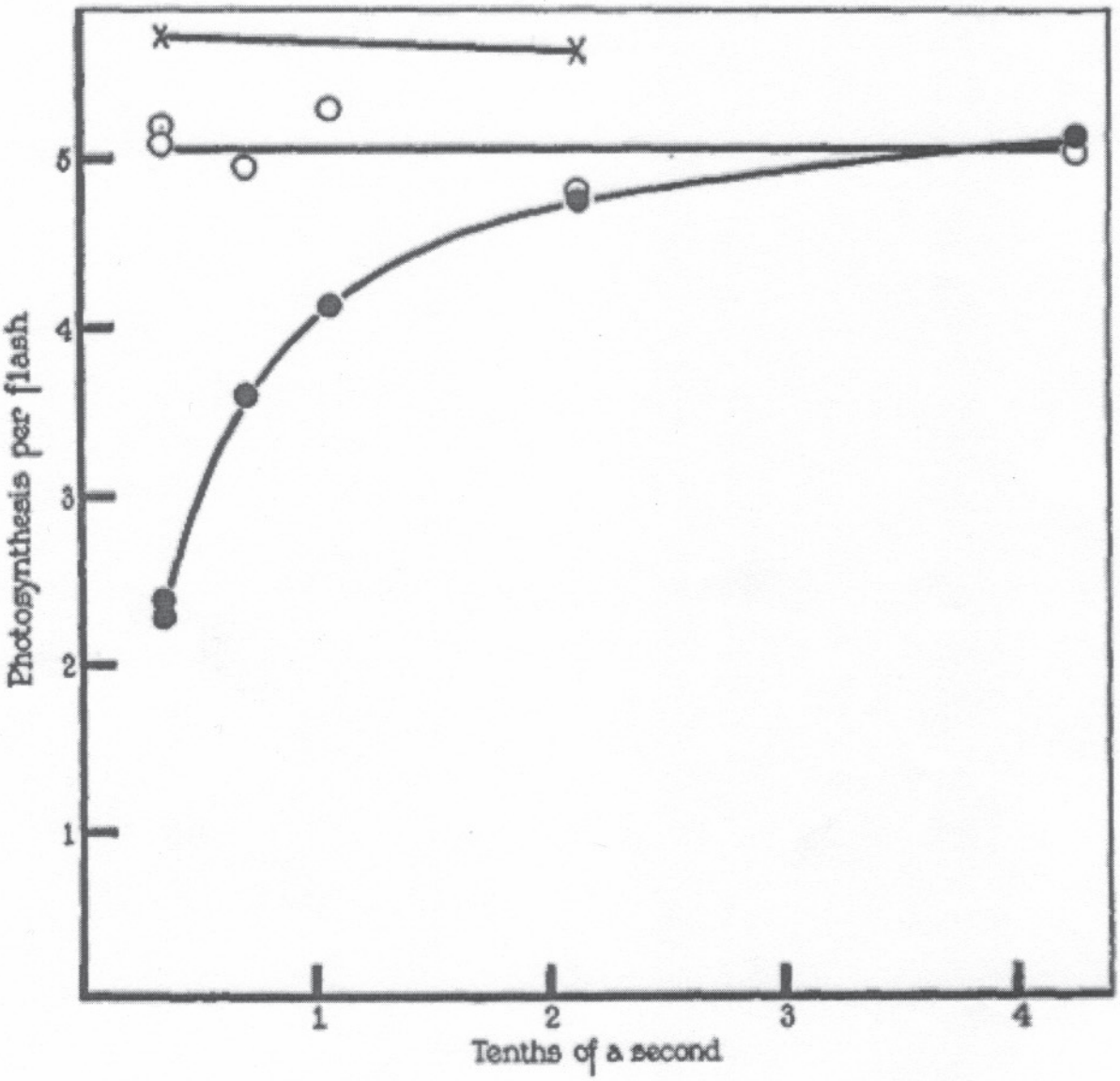


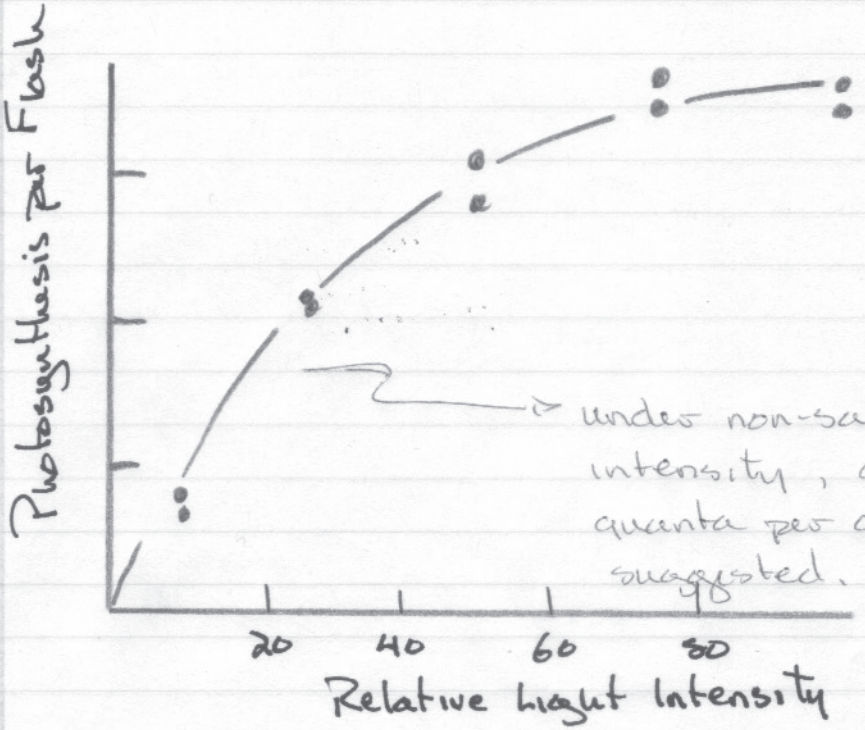
FIG. 8. The effect of dark time on yield of photosynthesis per flash of light. Open circles are points made at 25°C., solid circles at 1.1°C. The crosses are a check made at 25°C.

Source: R Emerson and W Arnold 1932. A separation of the reactions in photosynthesis by means of intermittent light. Journal of General Physiology 16:391–420.

[1] The light flash duration was no more than $2 \cdot 10^{-5}$ sec.

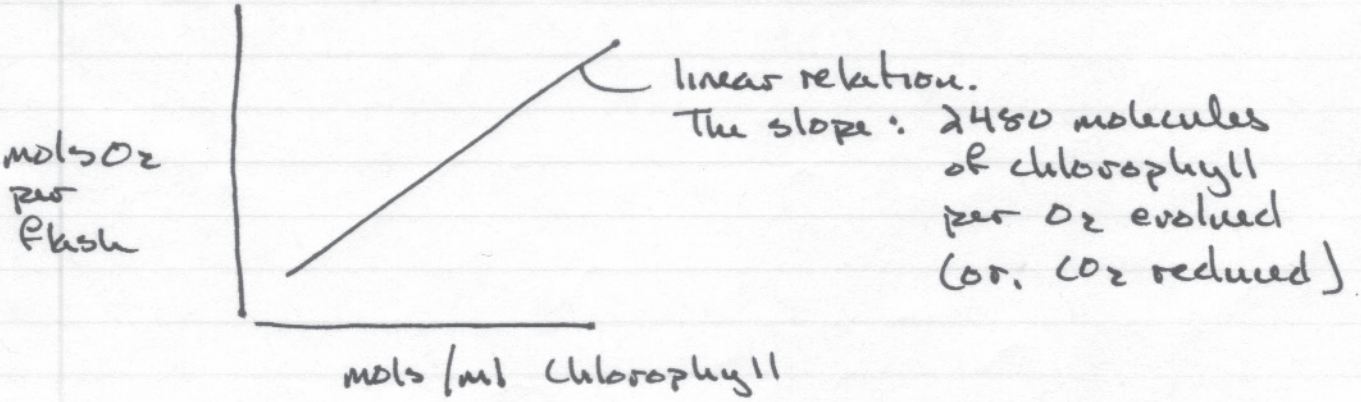
In a subsequent paper, Emerson and Arnold explored the photochemical reactions in greater detail.

First, the determined the effect of light intensity (that is, photon flux) on O_2 evolution per flash.



Source:
Emerson, R, W. Arnold
1932 The photo-chemical reaction in photosynthesis
J. Gen Phys.
16: 191-205.

Knowing the saturating light intensity, they examined the dependence of photosynthesis on the concentration of chlorophyll



The physical justification for "antennae" that harvest light resides in part upon 'order of magnitude' calculations of photon-absorbing events.

- photon flux for photosynthetically active wavelengths (400-700 nm) is about:

$$2000 \text{ } \mu\text{mol } m^{-2} \text{ sec}^{-1}$$

at full sunlight intensity.

- the average chlorophyll concentration in chloroplasts is about 30 mol chlorophyll m^{-3}

- in a chloroplast ~ 2 μm thick, about 30% of the photosynthetically active light is absorbed.

So:

$$\frac{(0.3)(2000 \times 10^{-6} \text{ mol photons } m^{-2} s^{-1})}{(30 \text{ mol chl } m^{-3})(2 \cdot 10^{-6} \text{ m})} = \left(\frac{10 \text{ mol photon}}{\text{mol chl sec}}\right)$$

OR,

10 photons per chl per sec. or | an absorption event every 0.1 sec |

The average processing time per reaction center is about 0.005 sec ⊕ [This value comes from Emerson and Arnold's work: 240 msec at room temperature]

Depending on the number of chlorophylls associated with each reaction center, most absorption events will be unused.

(next page)

⊕ Nobel PS 1991 Hillroy page 273

So if a 2500 Chl group produces $1 O_2$

$(2500)(10 \text{ photons})(0.005) = 125$ excitations of which only one can be used

2500 Chl "group"

10 photons chl^{-1} sec^{-1}

processing time sec

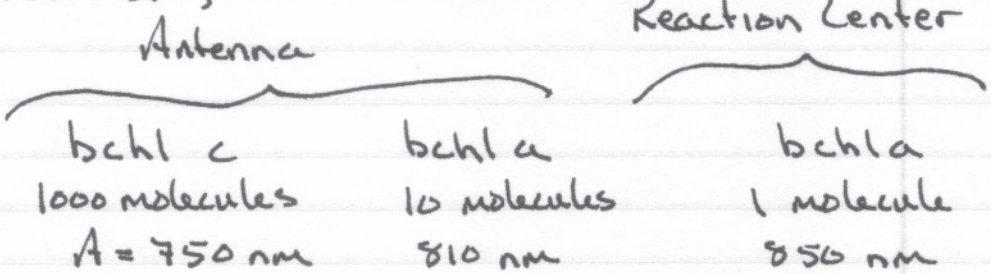
On the other hand, in attenuated light, less than maximal sunlight, the antenna concept makes more sense.

A light intensity that is 1% of full sunlight: there would be 1.25 excitations: Spot on.

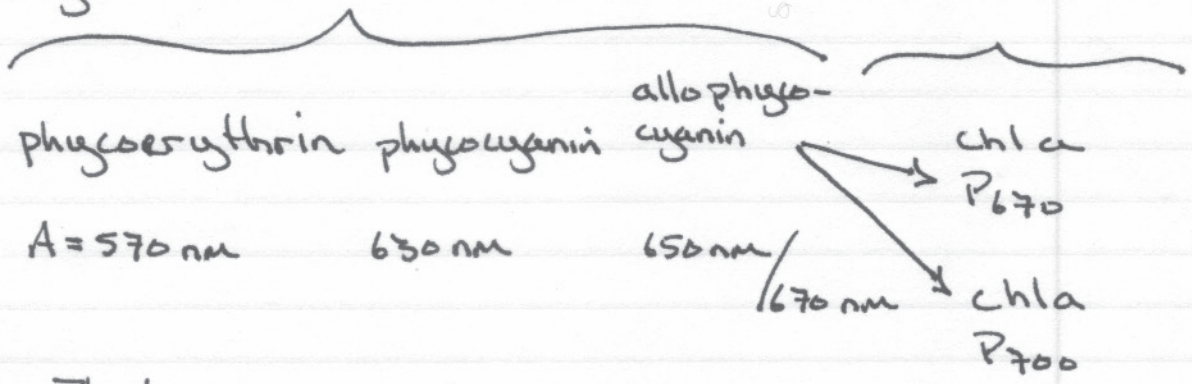
- The other perspective on the issue of justifying "light-harvesting" antenna is that reaction centers, with their multitude of proteins is expensive, thus there was an evolution of "economy".

Light-harvesting complexes vary considerably depending upon the photosynthetic organism.

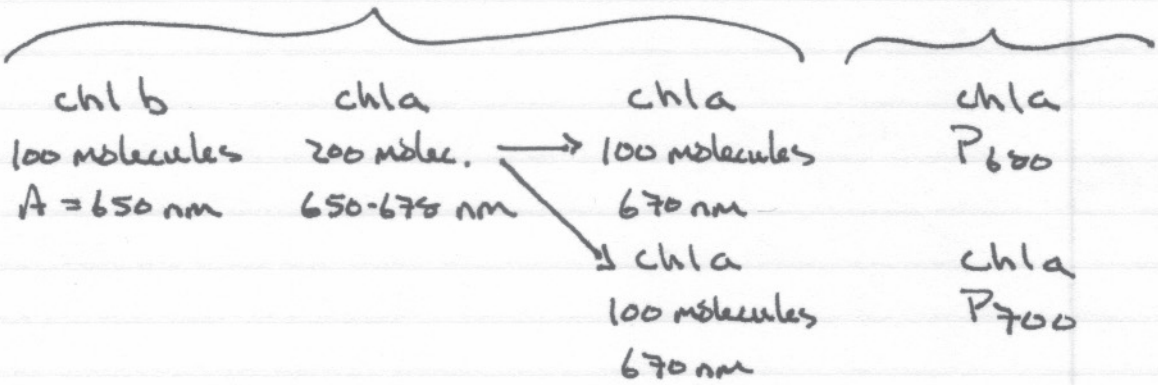
Photosynthetic bacteria (Chlorobium)



Cyanobacteria
Red Algae



Higher Plants



Total chl: 400 molecules
If there are 8 photons / $1O_2$

(1) 8 "hits" in 2480 chl molecules
(OR) / (2) 1 hit = 1 photochem event
So, 8 - 1 'hits' in $\frac{2580}{8} = 300$ chl molecules in group.

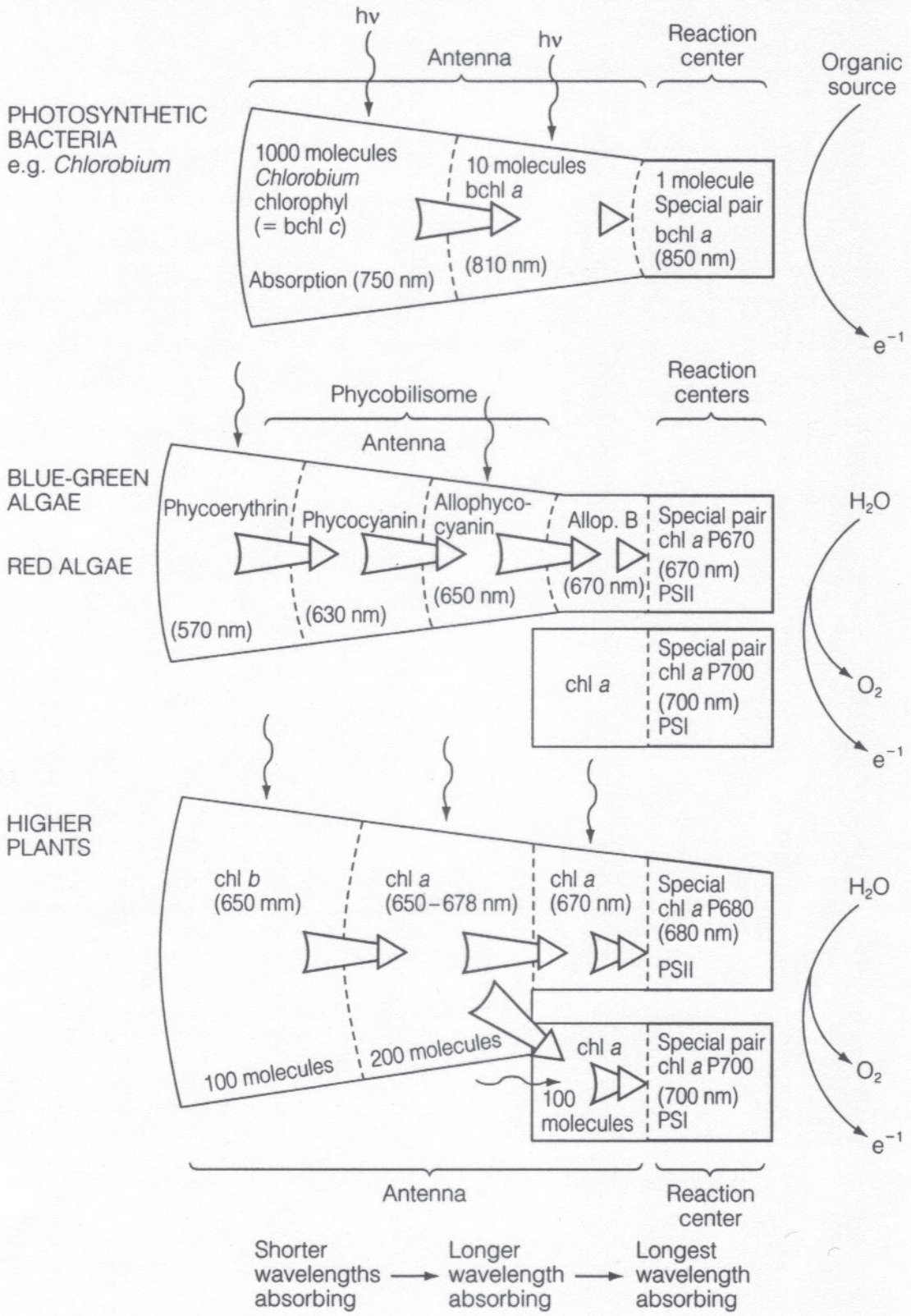
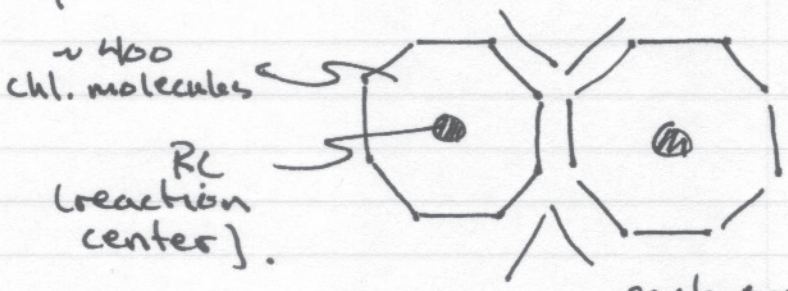


Figure 3.1. Energy absorption (~~▶) and excitation transfer (⇒) between pigments in the light-harvesting antenna and to the photochemical reaction centers of different photosynthetic organisms

Source: Lawlor, DW (2001) Photosynthesis. 3[d] edition. Springer-Verlag

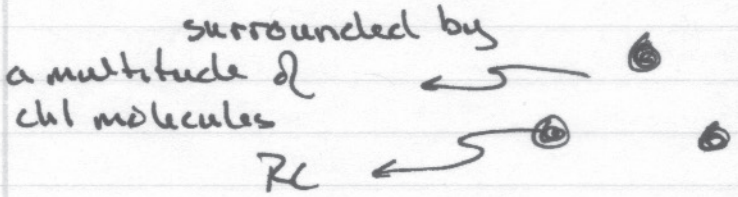
The original concept of antenna function was based on two functionally distinct models

one was the 'puddle' model (separate units model)

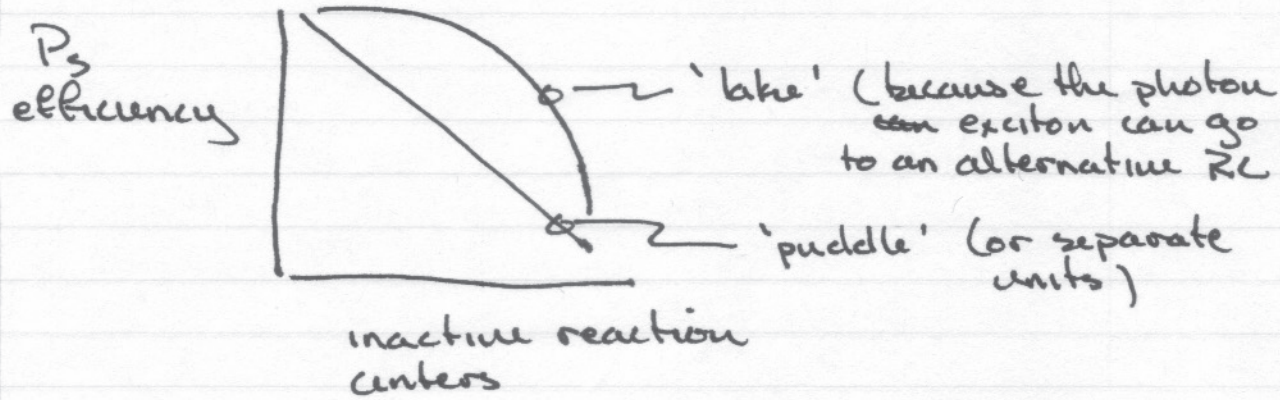


each separate and distinct.

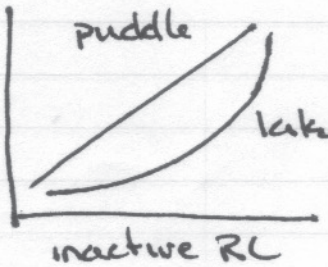
The other was the 'lake' model



These two models will exhibit a different dependency on the number of active reaction centers



If P_3
inefficiency is measured by fluorescence



The structures of light-harvesting complexes are not completely understood.

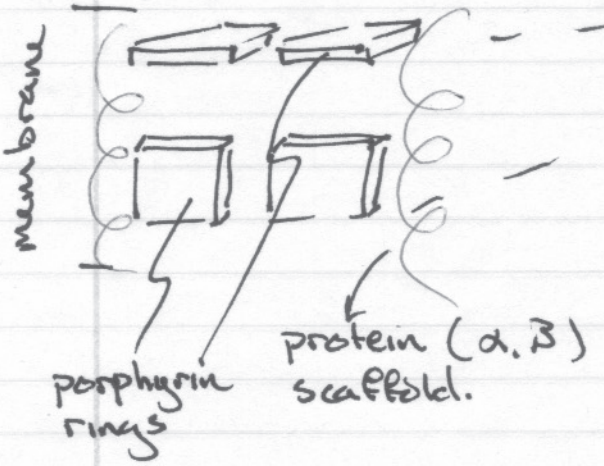
As is often the case, the most detailed structures are from fairly "simple" organisms, such as the purple bacteria.
For example; LH2

proteins	pigments
α	3 · bchl
β	1 · carotenoid.

subunit

→ 8 or 9 subunits aggregate to form a ring-shaped unit.

The porphyrin rings are localized very specifically



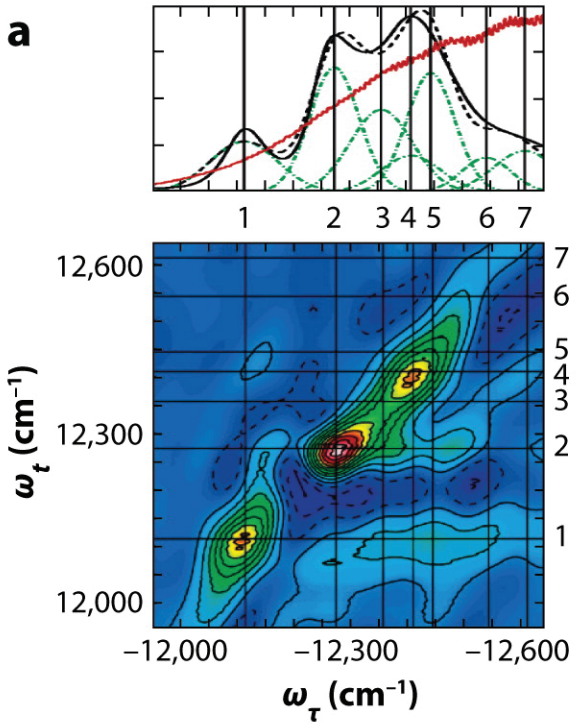
exciton transfer between the bchl is fast: $80 \cdot 10^{-15}$ sec.
transfer to the reaction center is slower: $35 \cdot 10^{-12}$ sec.

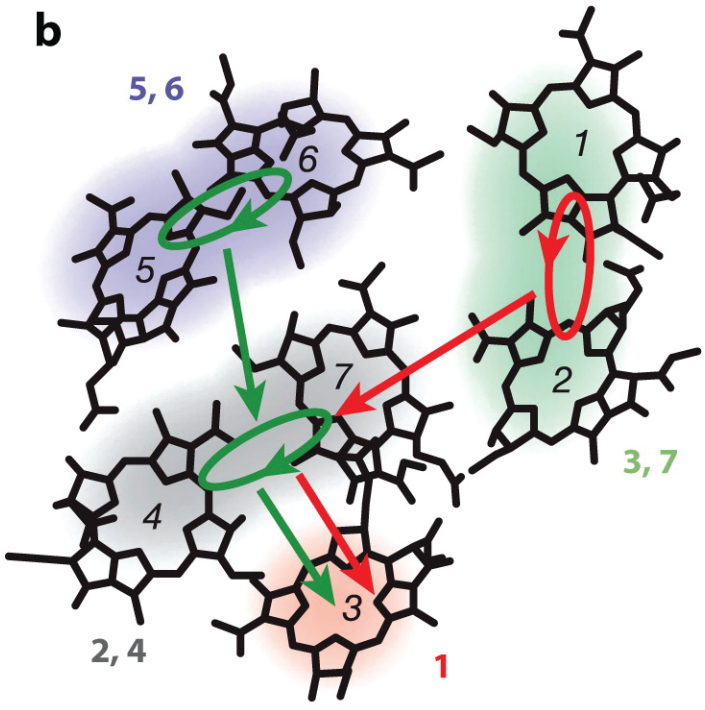
LH1 is similar, but with the reaction center in the "hole" in the antenna donut.

Quantum Photosynthesis

$$\left|\Psi_\alpha\right\rangle = \sum_{n=1}^{N} \phi_n^\alpha \left|n\right\rangle$$

Exciton delocalization and energy flow in the Fenna-Matthews-Olson (FMO) complex





Cheng Y-C, Fleming GR. 2009.
Annu. Rev. Phys. Chem. 60:241–62

Quantum Photosynthesis

Why I refuse to teach quantum tunneling mechanisms in Photosynthesis

$$\tau_{DA} = \frac{2\pi}{\hbar} \sum_{m \in D} \sum_{n \in A} \frac{e^{-E_m^D / k_B T}}{\sum_{l \in D} e^{-E_l^D / k_B T}} \left| V_{mn}^{DA} \right|^2 \int dE S_m^D(E) S_n^A(E)$$

Even so, it's a source of recent excitement amongst physicists, so I do feel a need to discuss it in a limited way.

The basic idea is that an exciton created by a photon interacting with a light-absorbing pigment is not located at a unique place but instead can be located in multiple places at once. This is known as *coherence*. In addition, an exciton may be *entangled* with another exciton, so that their fates are intertwined. There's no simple way to describe this, and the math is really harsh (see above for an example). The net outcome is that quantum effects can increase the *efficiency* of energy transfer. Now, these kinds of effects have been well established for many decades in biological pigments (hemes for example[1]), but the experimental proof used pigments at very cold temperatures (liquid nitrogen or even colder). There was no expectation that the effects could be demonstrated at normal physiological temperatures because thermal motions at the time scale of quantum effects are very strong and would short-circuit any quantum effect. It came as a surprise when quantum effects in *Rhodopseudomonas* light harvesting complexes were demonstrated at room temperature, and even more so when it was observed in other light harvesting complexes as well[2].

Is this important? To a physicist, yes. And, as a biologist, I have fun telling my physicist colleagues that biological organisms discovered quantum physics 4000 million years ago. But from the viewpoint of photosynthesis, it's probably not all that important. Exciton transfers relies on *normative* mechanisms, entanglement does not provide anything better from the viewpoint of selective pressure in evolution. One place where it might be important is in organisms adapted to survive at extremely low light intensities where every photon counts. But even here, why not just increase the absorptive area by using more pigments?

What is important is its potential importance in artificial photosynthesis. Simple systems --much simpler than those required by biological organisms-- could use the greater efficiency of quantum effects to maximize energy harvesting[3].

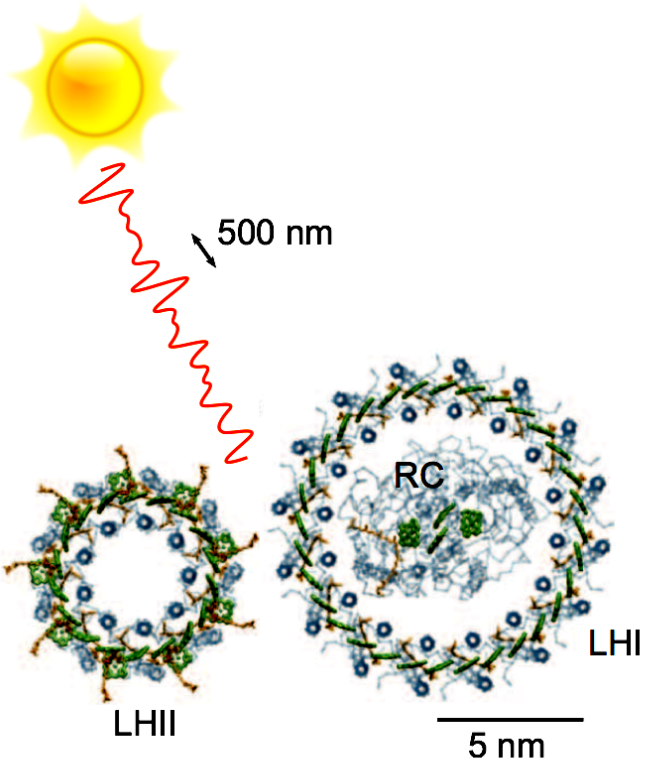
---

[1] Don De Vault and Britton Chance (1966) Studies of photosynthesis using a pulsed laser I. Temperature dependence of cytochrome oxidation rate in Chromatium. Evidence for tunneling. Biophysics Journal 6:825–847.

[2] Collini E, Wong CY, Wilk KE, Curmi PMG, Brumer P & Scholes GD (2010) Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature. Nature 463:644-647.

[3] Lubner CE, Applegate AM, Knörzerb P, Ganago A, Bryant DA, Happe T, Golbeck JH (2011) Solar hydrogen-producing bionanodevice outperforms natural photosynthesis. PNAS 108:20988-20991.

a. Sunlight: incoherent, stationary

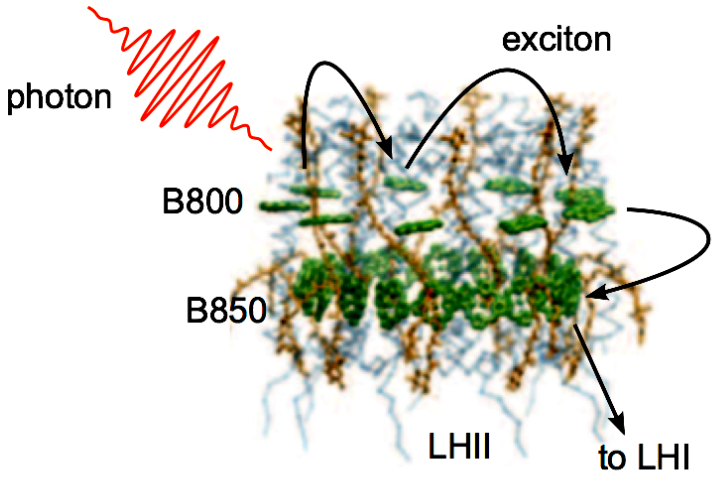


arXiv:1210.5022

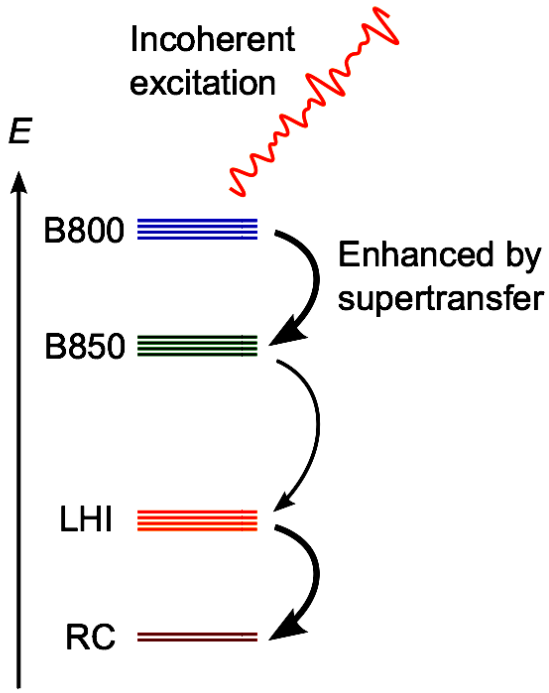
Does coherence enhance transport in photosynthesis?

Ivan Kassal, Joel Yuen-Zhou, Saleh Rahimi-Keshari

b. An inaccurate picture:



c. A more accurate picture:



No light pulses
No localised excitation
No wavelike transport
Microscopic coherence doesn't help

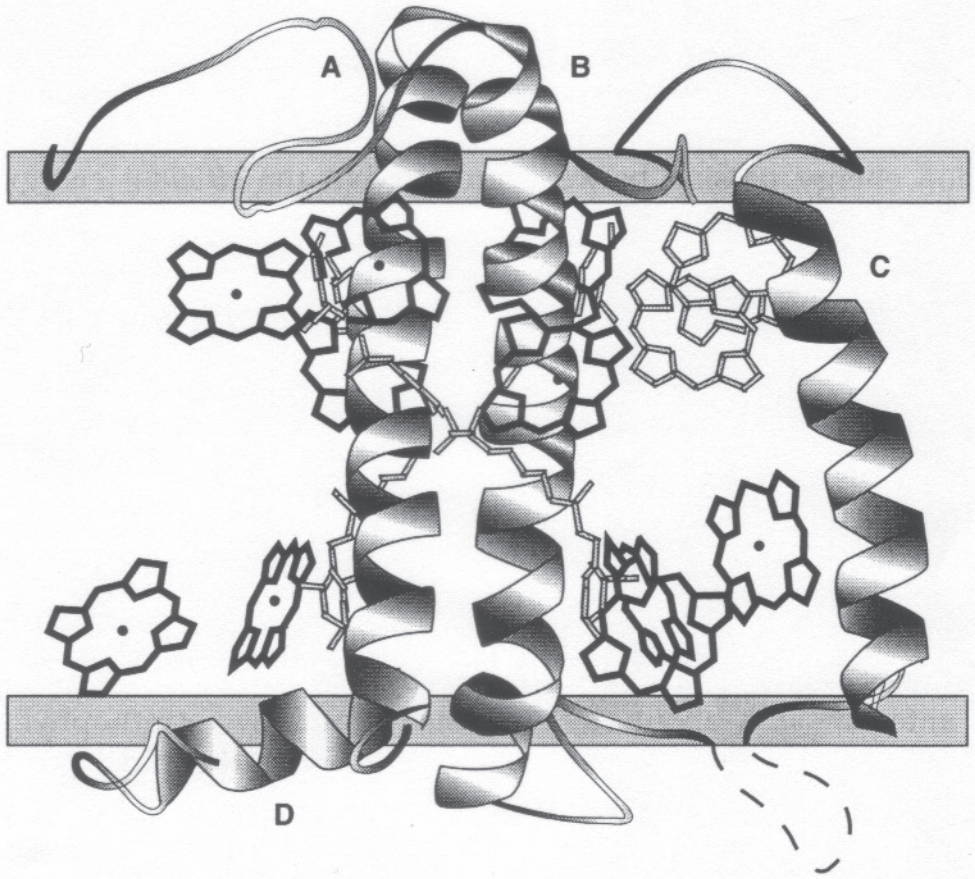
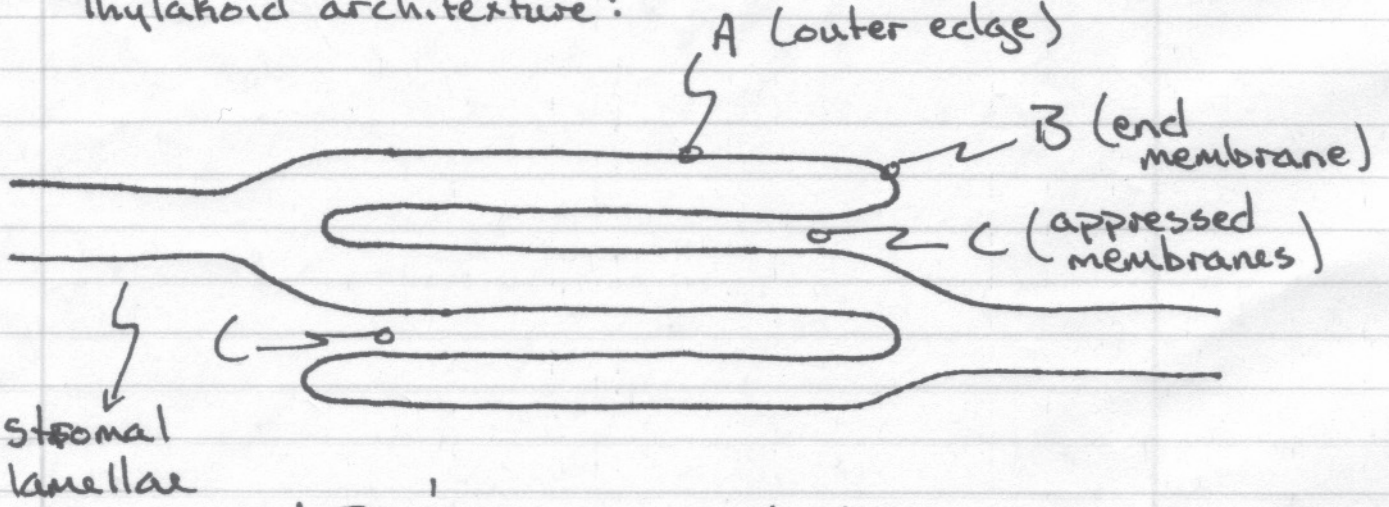


Figure 4.11. Simplified structure of LHCII determined by electron crystallography, showing the three protein chains spanning the thylakoid membrane, and the locations of chlorophyll molecules (Reprinted with permission from *Nature*, Kühbrandt *et al*., Atomic model of plant light-harvesting complex by electron crystallography. 1994; **367**: 614–621. Copyright 1994, Macmillan Magazines Limited)

Source: Lawlor, DW (2001) Photosynthesis. 3[d] edition. Springer-Verlag

In addition to a primary role in light-harvesting, the light-harvesting complexes can play an additional role in regulating the delivery of exciton energy to the various components of photosynthesis.

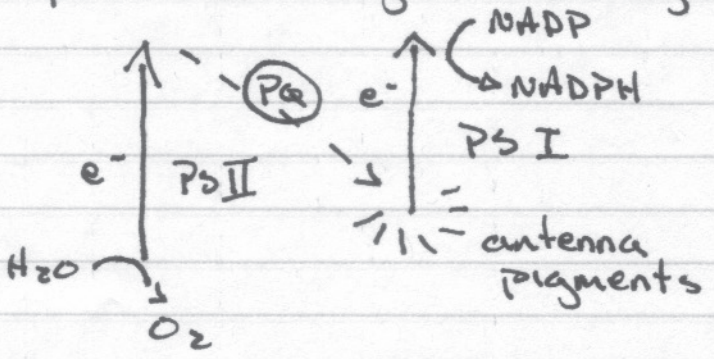
Thylakoid architexture:



A, B & C: Grana stack.

In low salt conditions, granal stacks are lost (instead the membranes look onion-like)
Stacking recovers with the addition of divalent cations (M^{2+}), and requires the light-harvesting complex (LHC). (most LHC is located in the granal stacks).

In higher plants and algae: Two light steps



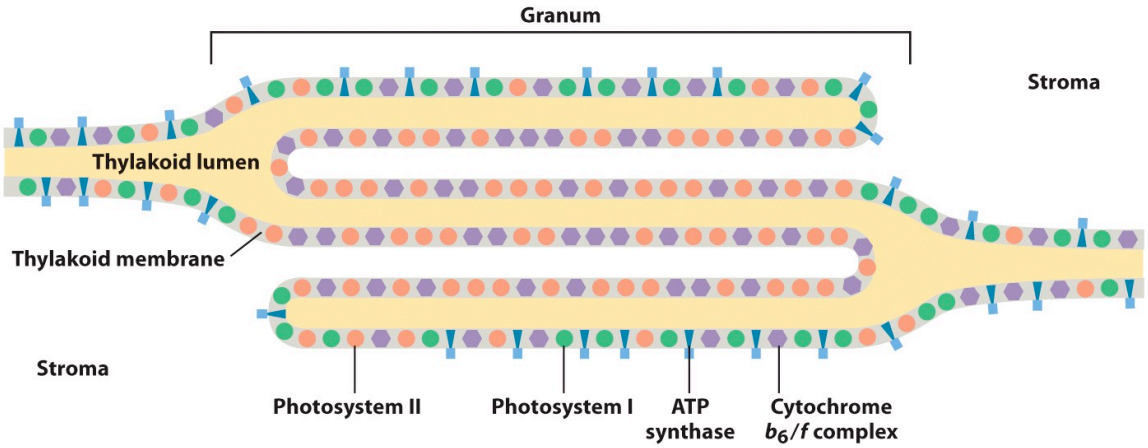


Figure 7-13a
Raven Biology of Plants, Eighth Edition

Organization and structure of the four major protein complexes of the thylakoid membranes (a) Photosystem II is located primarily in the grana thylakoids, and Photosystem I and ATP synthase almost entirely in the stroma thylakoids and the outer portions of the grana. The cytochrome b_6/f complexes are distributed evenly throughout the membranes. The spatial separation of the photosystems requires mobile electron carriers such as plastoquinol and plastocyanin to shuttle electrons between the separated membrane complexes. (b) The structure of the four major protein complexes and the soluble proteins of the photosynthetic apparatus.

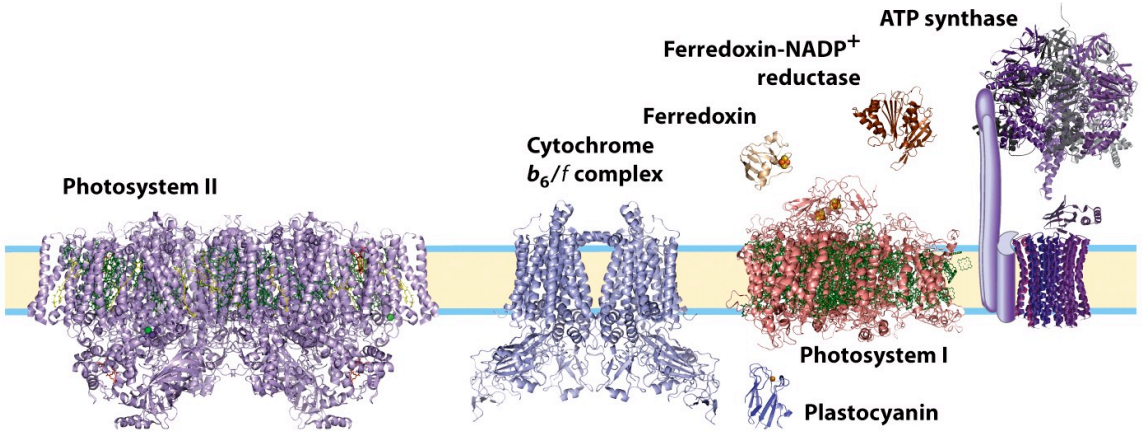


Figure 7-13b
Raven Biology of Plants, Eighth Edition

Figure 7-13 Organization and structure of the four major protein complexes of the thylakoid membranes (a) Photosystem II is located primarily in the grana thylakoids, and Photosystem I and ATP synthase almost entirely in the stroma thylakoids and the outer portions of the grana. The cytochrome b_6/f complexes are distributed evenly throughout the membranes. The spatial separation of the photosystems requires mobile electron carriers such as plastoquinol and plastocyanin to shuttle electrons between the separated membrane complexes. (b) The structure of the four major protein complexes and the soluble proteins of the photosynthetic apparatus.

The relative contributions of PS I and PS II vary depending upon light and metabolic conditions:

State 1 — high efficiency of PS I e⁻ transport (less granal stacking)

↕

State 2 — high efficiency of PS II e⁻ transport (more granal stacking)

The poize between State 1 & 2 is controlled by the control of granal stacking (*), mediated by LHC

(*) Component of photosynthesis	Appressed	Non-Appressed
ATP synthetase	—	+
PS II	+	—
PS I	+	+

The sensor is the reduced state of PQ (plasto-quinone): PQH_2

↓ (+) Kinase

LHC ⟶ LHC-(P)

↓

decreased stacking leading to increased contribution of PS I, and decrease in PQH_2 (because NADP → NADPH)

Light-Harvesting Complex Regulation of PS I and PS II Photosynthesis[1]

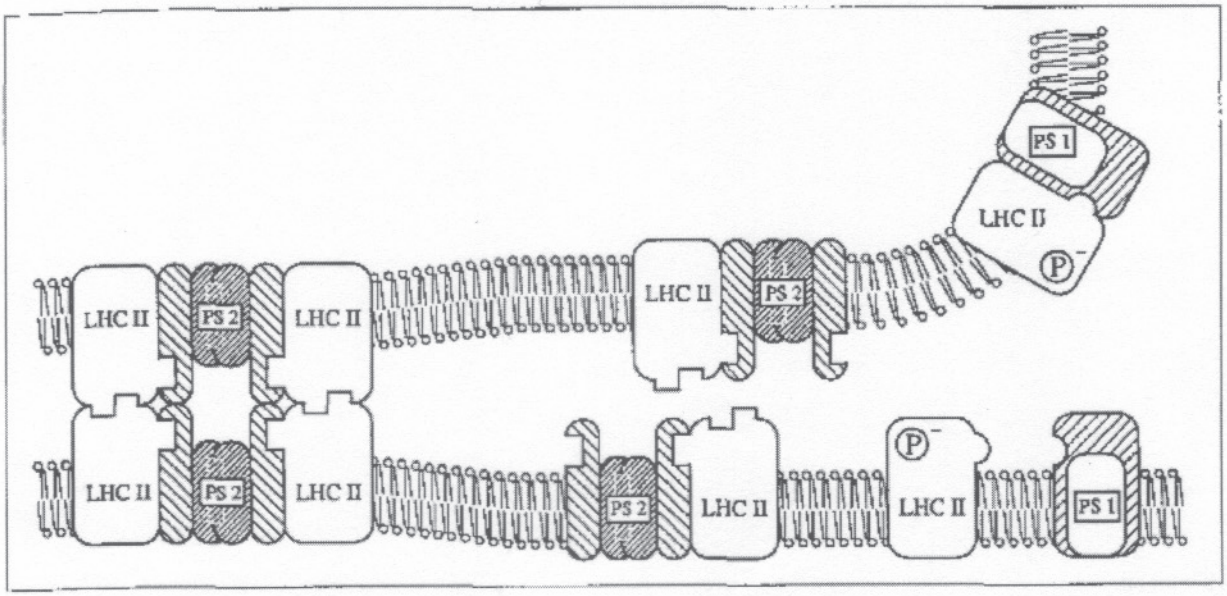


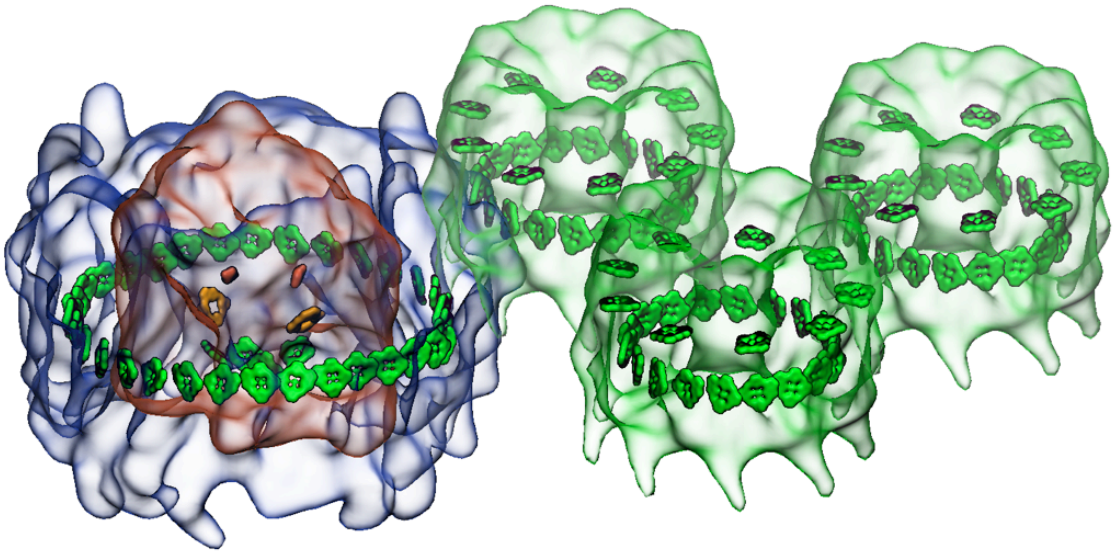
Figure 6

The molecular recognition model for phosphorylation-induced changes in the organization of the chloroplast thylakoid. PSII centres may be connected laterally and transversely for excitation energy transfer by docking of LHCII complexes with the PSII core antenna system (diagonally hatched) and with each other (left-hand side). This brings the acceptor side of PSII reaction centres into opposition. Phospho-LHCII has a decreased affinity for the PSII core (lateral protein–protein interactions) and for itself (transverse protein–protein interactions), and therefore becomes free to diffuse independently of PSII within the membrane, eventually to dock instead with the PSI antenna system (right-hand side). In contrast to the surface charge model (Fig. 1), only thermal energy is required for dissociation of phospho-LHCII from PSII. The connectivity and antenna size of PSII units are decreased, and the loss of adhesion contact surfaces may cause some transverse separation of adjacent thylakoids of the grana stack. A proportion of PSII reaction centres ceases to be in opposition. The altered shape of the block representing LHCII is intended to convey a structural change in the surface exposed domain (Fig. 5), electrostatic blocking of protein–protein interactions by the phosphate groups, or a combination of both.

---

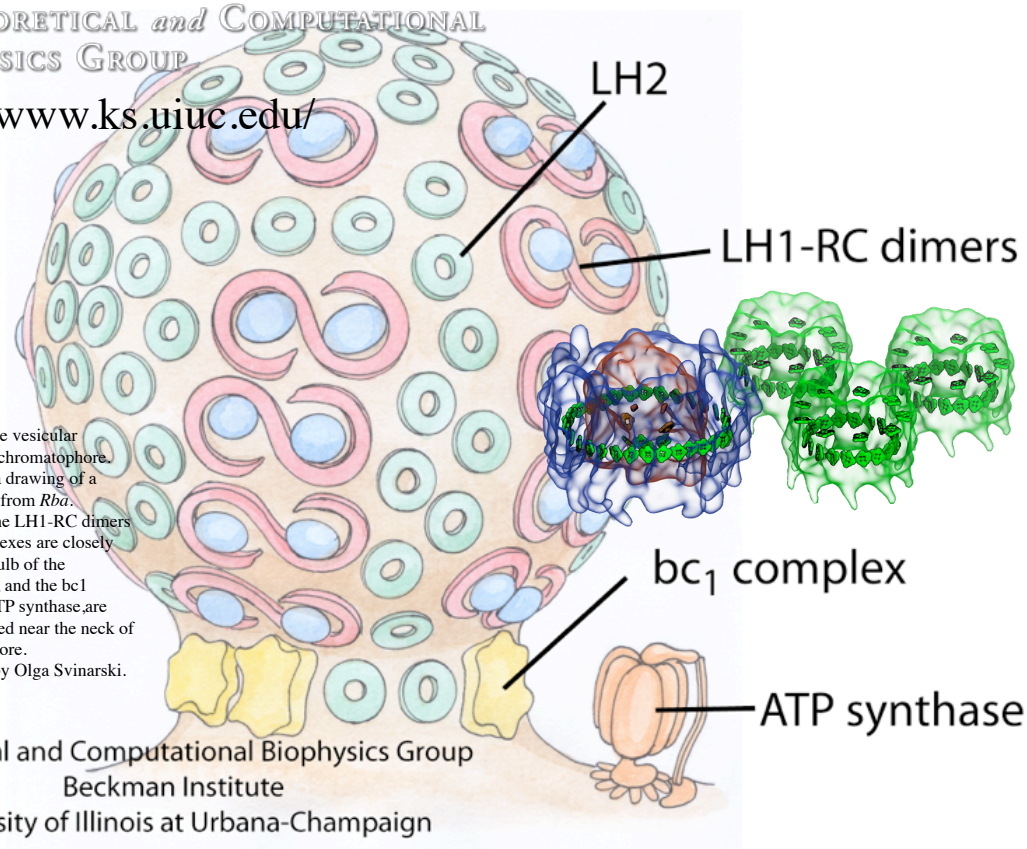
[1] Source: JF Allen 1992. How does protein phosphorylation regulate photosynthesis? TIBS 17: 12–17.

LHC-1 Reaction Center and LHC2s
http://www.ks.uiuc.edu/



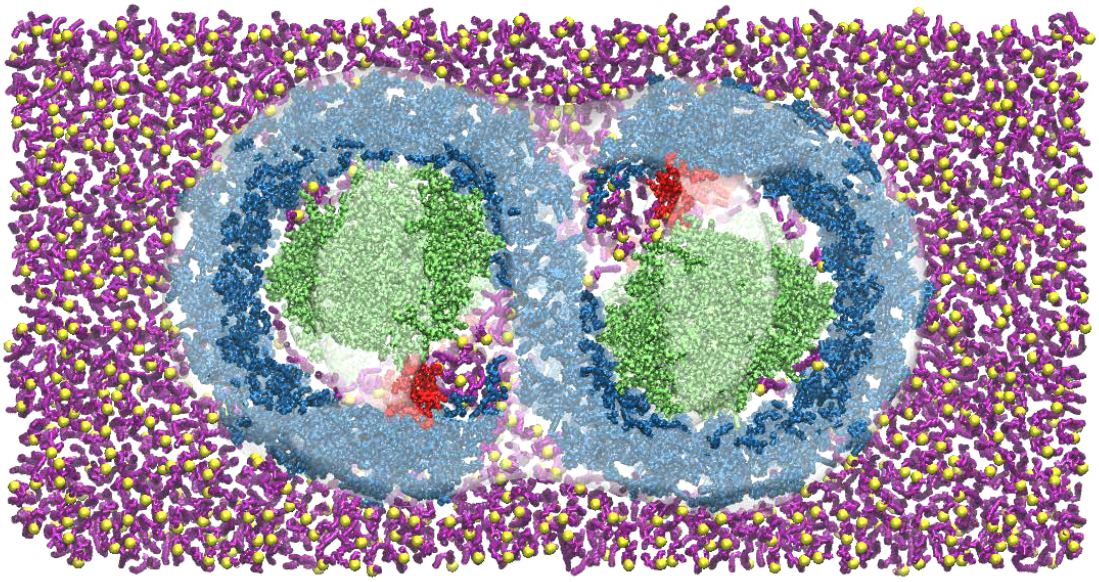
Theoretical and Computational
Biophysics Group

http://www.ks.uiuc.edu/

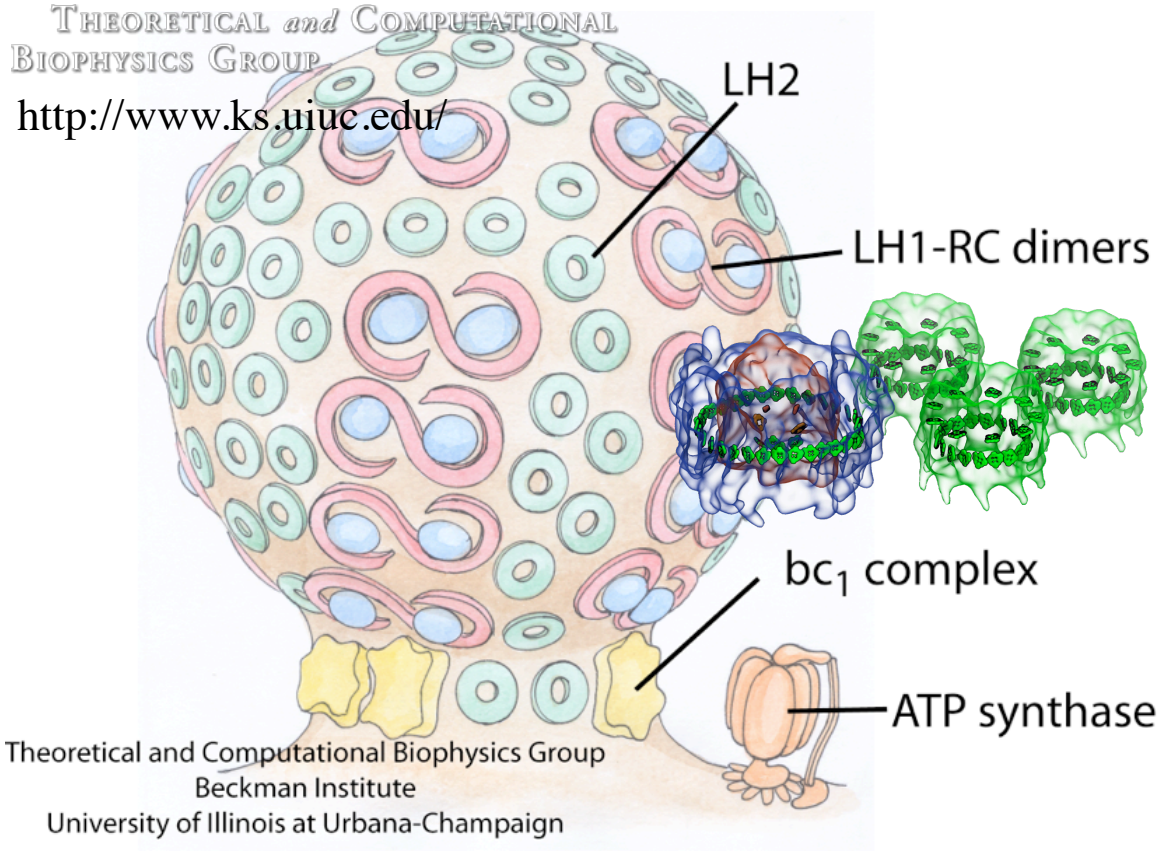


Schematic of the vesicular photosynthetic chromatophore. Shown here is a drawing of a chromatophore from *Rba. sphaeroides*. The LH1-RC dimers and LH2 complexes are closely packed in the bulb of the chromatophore, and the bc1 complex and ATP synthase,are tentatively placed near the neck of the chromatophore.
Picture drawn by Olga Svinarski.

Reaction Centers and Light-Harvesting Complexes within the Chloroplast Membrane



Jen Hsin, James Gumbart, Leonardo G. Trabuco, Elizabeth Villa, Pu Qian, C. Neil Hunter, and Klaus Schulten. Protein-induced membrane curvature investigated through molecular dynamics flexible fitting. Biophysical Journal, 97:321-329, 2009. (PMC: 2711417)

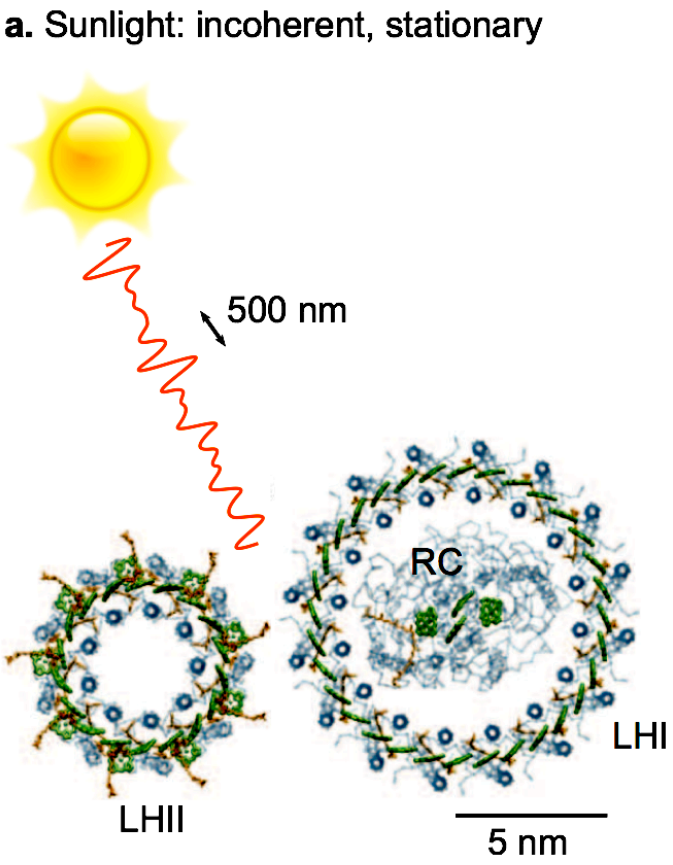


quantum photosynthesis

Why I refuse to teach quantum tunneling mechanisms in Photosynthesis

$$\tau_{DA} = \frac{2\pi}{\hbar} \sum_{m \in D} \sum_{n \in A} \frac{e^{-E_m^D / k_B T}}{\sum_{l \in D} e^{-E_l^D / k_B T}} \left| V_{mn}^{DA} \right|^2 \int dE S_m^D(E) S_n^A(E)$$

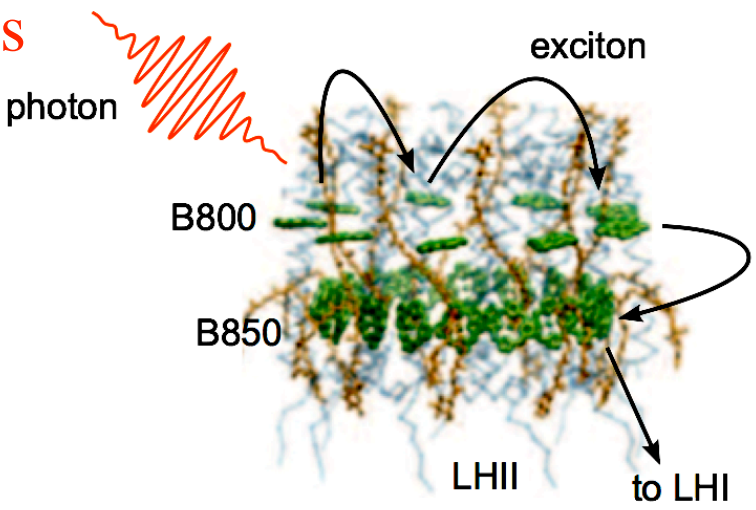
quantum photosynthesis



Kassel, Yuen-Zhou and Rahimi-Keshari (2012) Does coherence enhance transport in photosynthesis? arXiv:1210.5022v1

quantum photosynthesis

b. An inaccurate picture:

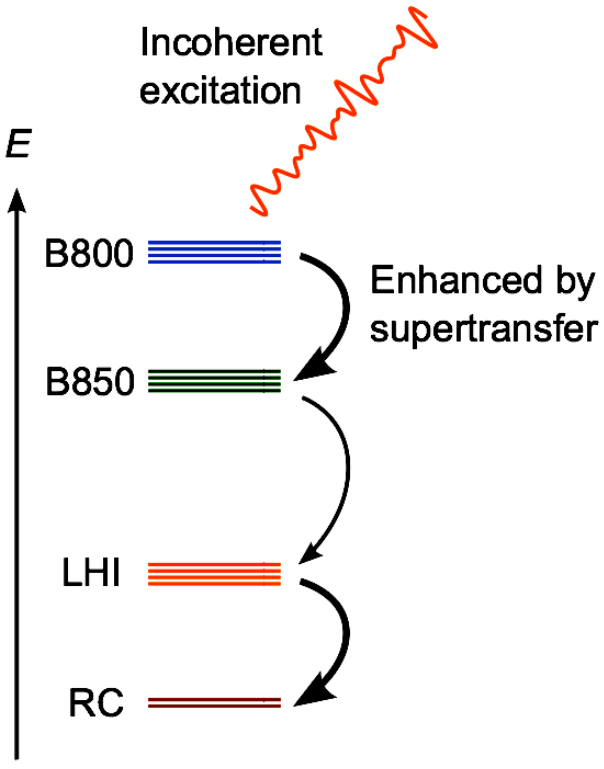


Kassel, Yuen-Zhou and Rahimi-Keshari (2012) Does coherence enhance transport in photosynthesis? arXiv:1210.5022v1

No light pulses
No localised excitation
No wavelike transport
Microscopic coherence doesn't help

quantum photosynthesis

c. A more accurate picture:

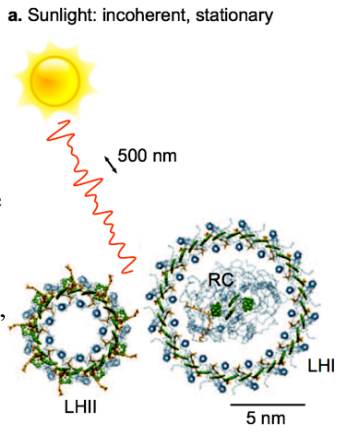


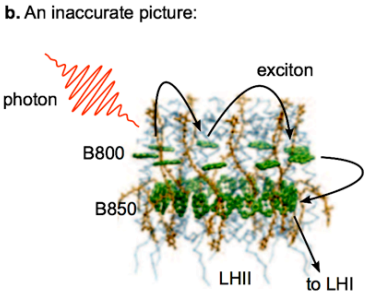
Kassel, Yuen-Zhou and Rahimi-Keshari (2012) Does coherence enhance transport in photosynthesis? arXiv:1210.5022v1

quantum photosynthesis

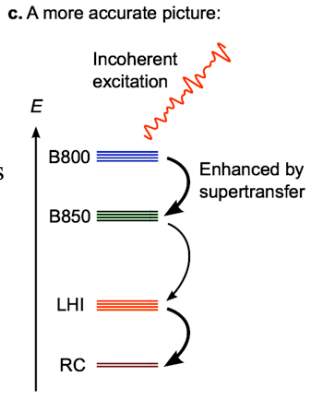
Recent observations of coherence in photosynthetic complexes have led to the question of whether quantum effects can occur in vivo, not under femtosecond laser pulses but in incoherent sunlight and at steady state, and, if so, whether the coherence explains the high exciton transfer efficiency. […]two partially coherent mechanisms—ENAQT and supertransfer—can enhance transport even in sunlight and thus constitute motifs for the optimisation of artificial sunlight harvesting.

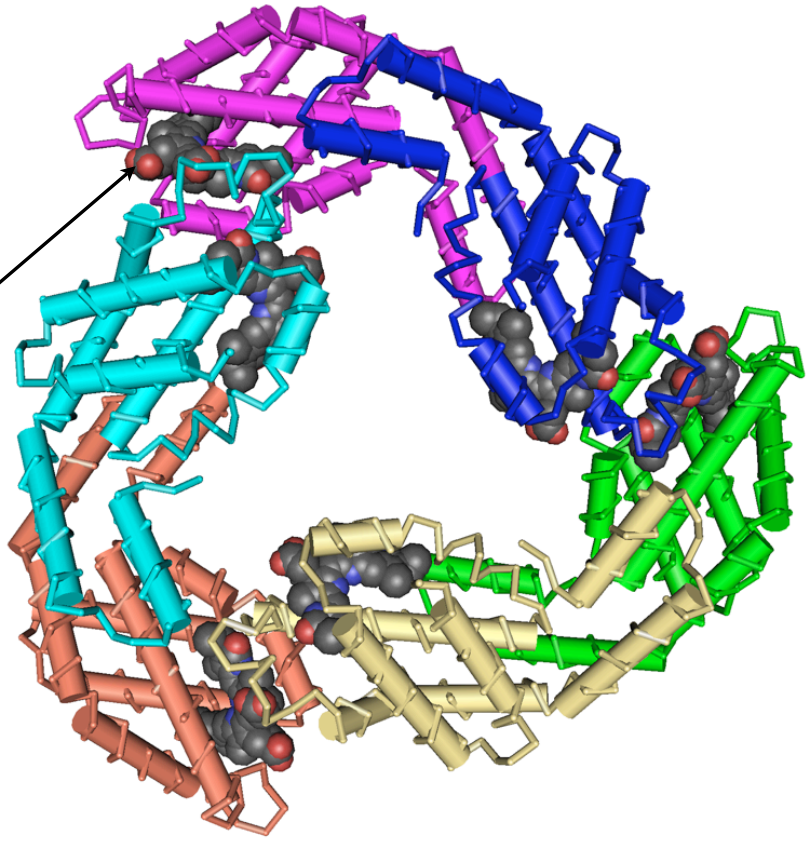
Kassel, Yuen-Zhou and Rahimi-Keshari (2012) Does coherence enhance transport in photosynthesis? arXiv:1210.5022v1





No light pulses
No localised excitation
No wavelike transport
Microscopic coherence doesn't help





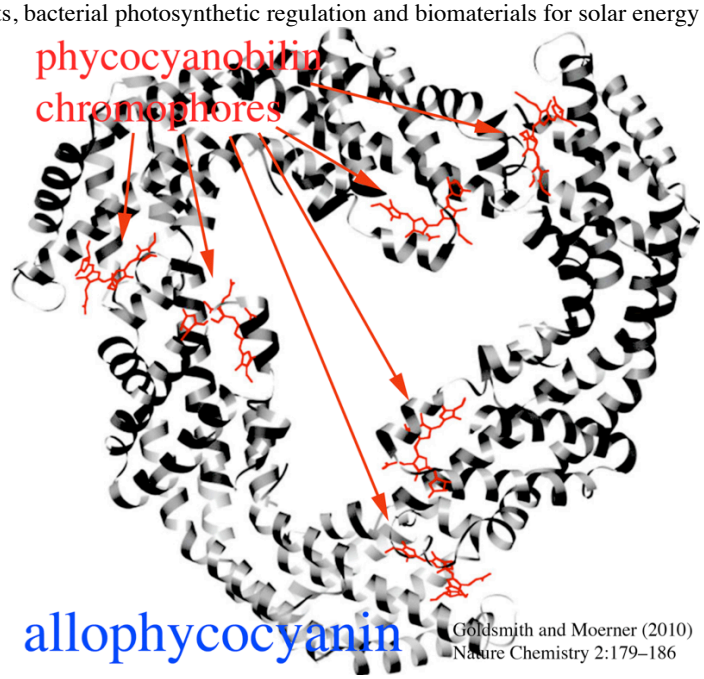
phycocyanobilin
(linear tetrapyrrole)

alternative light-harvesting pigments in photosynthesis

We observe a complex relationship between fluorescence intensity and lifetime that cannot be explained by simple static kinetic models. Light-induced conformational changes are shown to occur and evidence is obtained for fluctuations in the spontaneous emission lifetime, which is typically assumed to be constant. Our methods provide a new window into the dynamics of fluorescent proteins and the observations are relevant for the interpretation of *in vivo* single-molecule imaging experiments, bacterial photosynthetic regulation and biomaterials for solar energy harvesting.

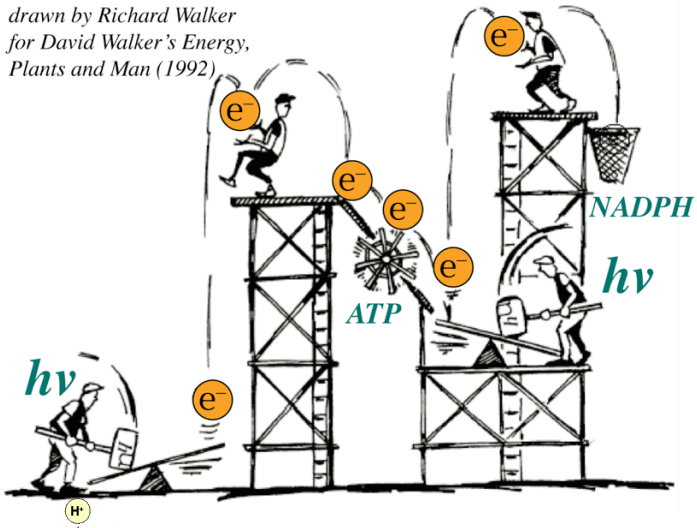
Goldsmith & Moerner (2010) Watching conformational- and photodynamics of single fluorescent proteins in solution. Nature Chemistry2:179–186

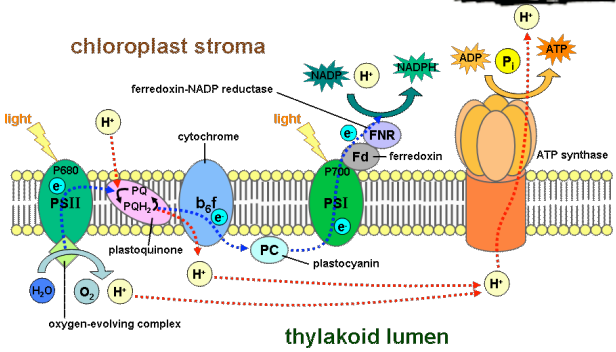
alternative light-harvesting pigments in photosynthesis



Goldsmith and Moerner (2010)
Nature Chemistry 2:179–186

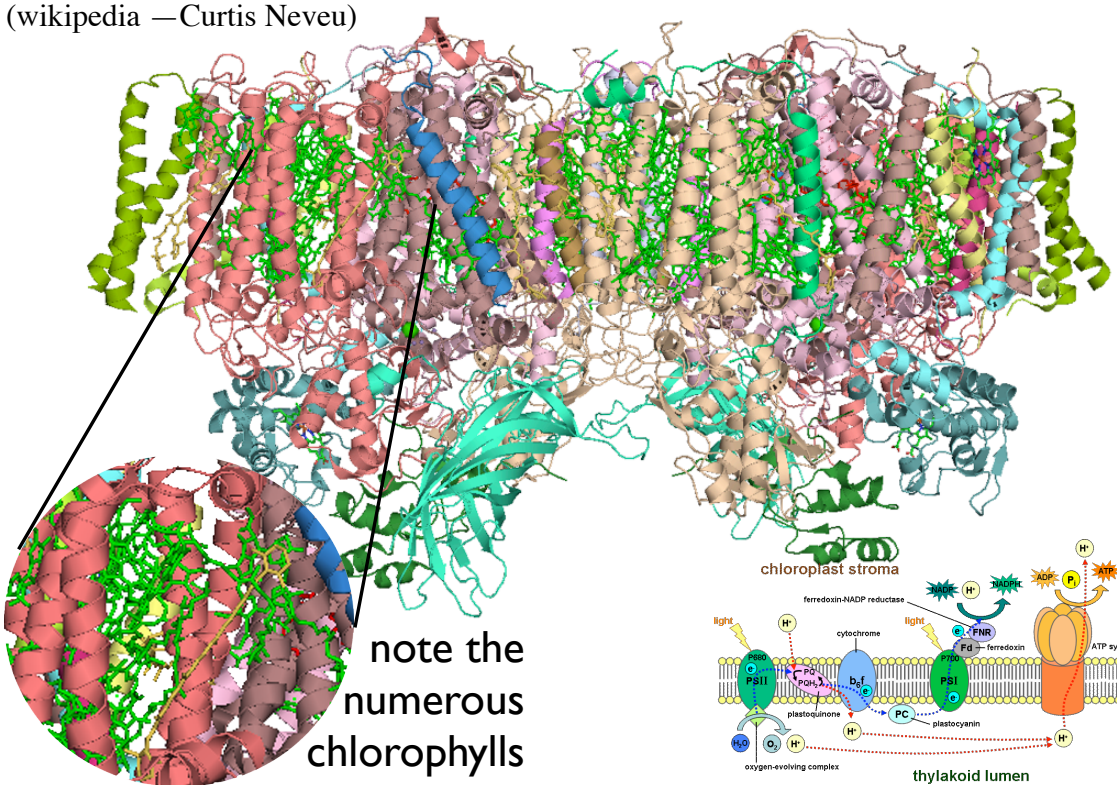
Photosynthesis Overview





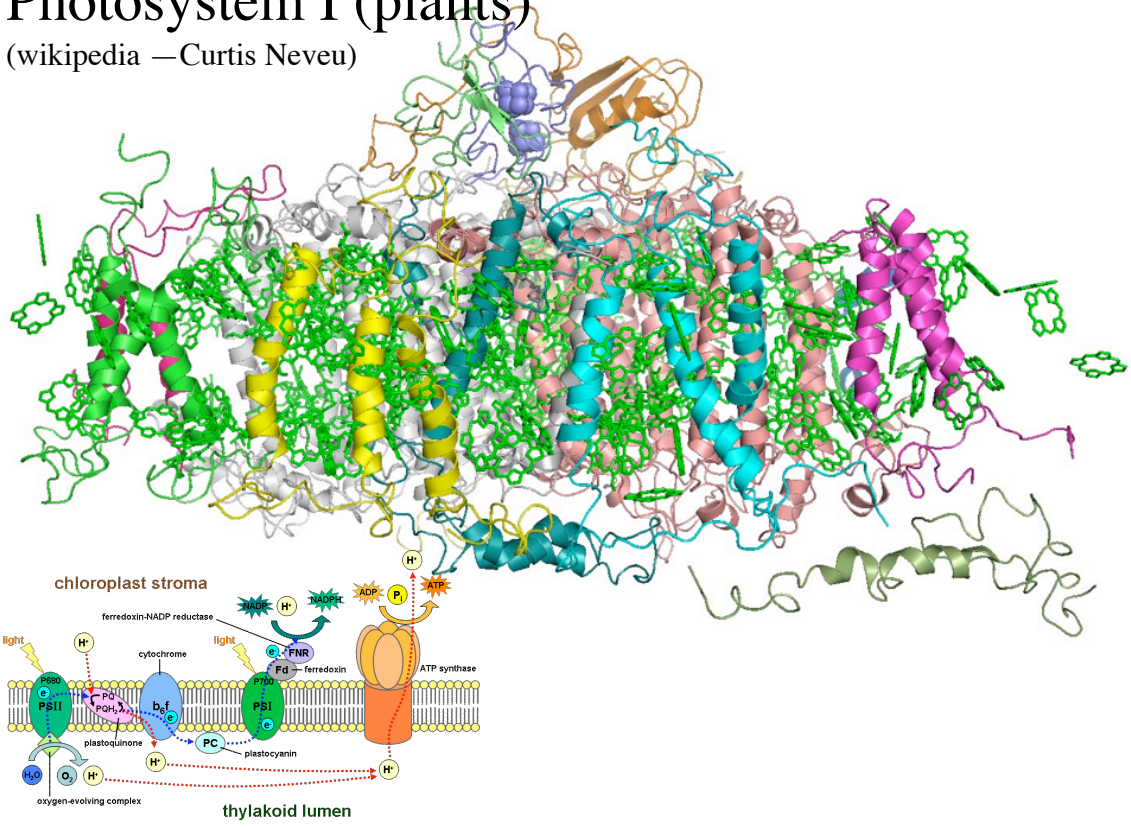
Photosystem II (cyanobacteria)

(wikipedia —Curtis Neveu)



Photosystem I (plants)

(wikipedia —Curtis Neveu)



Cytochrome b_6f (plants)

(PDB 1q90 coordinates)