# Molecular photonics

Lecture 10

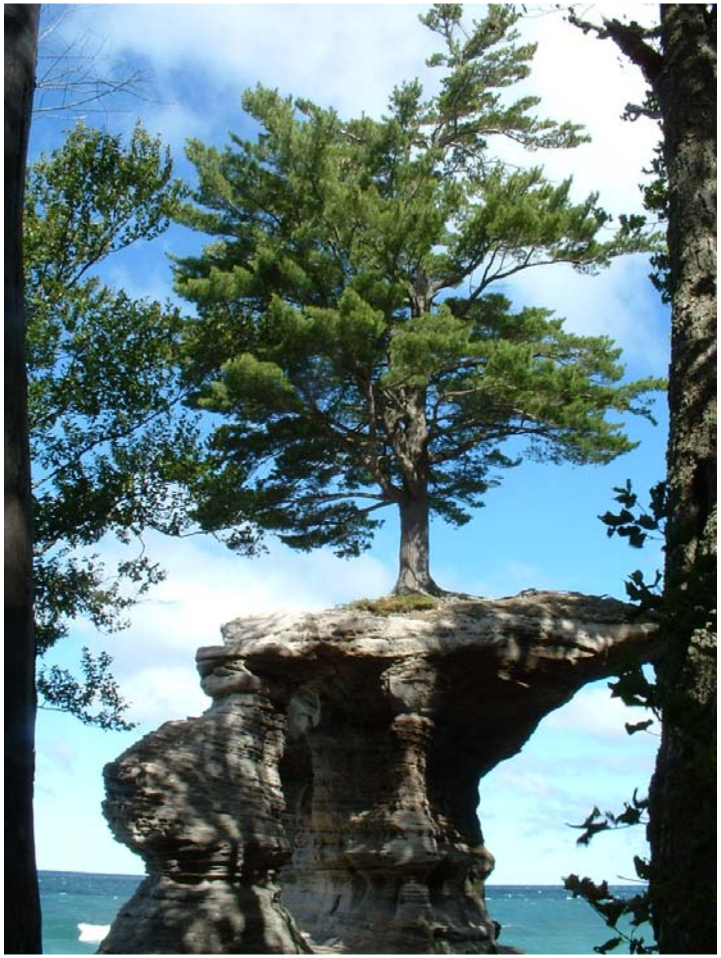
Photosynthesis

http://www.life.uiuc.edu/govindjee/paper/gov.html
http://www.emc.maricopa.edu/faculty/farabee/BIOBK/BioBookPS.html

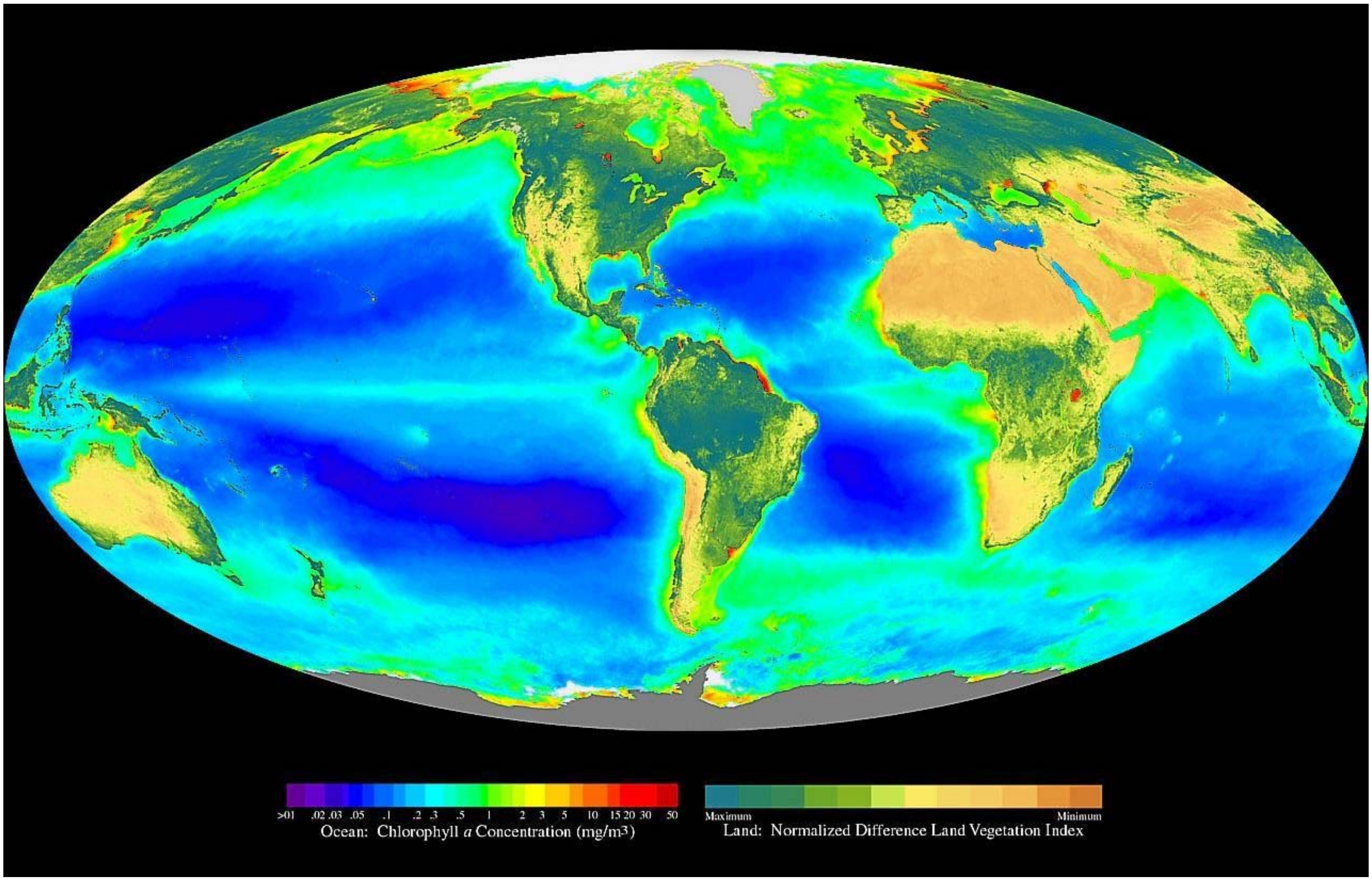
# Why Study Photosynthesis?

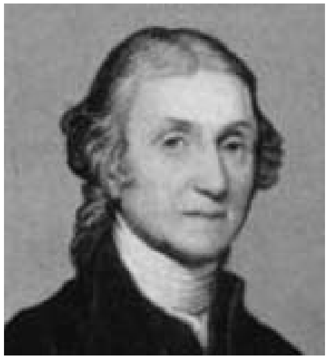
- Photosynthesis is arguably the most important biological process on earth. By liberating oxygen and consuming carbon dioxide, it has transformed the world.
- Directly or indirectly, photosynthesis fills all of our ***food requirements*** and many of our needs for fiber and building materials.
- The energy stored in ***petroleum, natural gas and coal*** all came from the sun via photosynthesis, as does the energy in firewood.
- If we can understand and control the photosynthetic process, we can learn how to increase crop yields of food, fiber, wood, and fuel, and how to better use our lands.
- The energy-harvesting of plants can be adapted to ***man-made systems*** which provide new, efficient ways to collect and use solar energy.
- Because photosynthesis helps control the makeup of the ***atmosphere***.

# Photosynthesis



# Global distribution of photosynthesis, including both oceanic phytoplankton and terrestrial vegetation



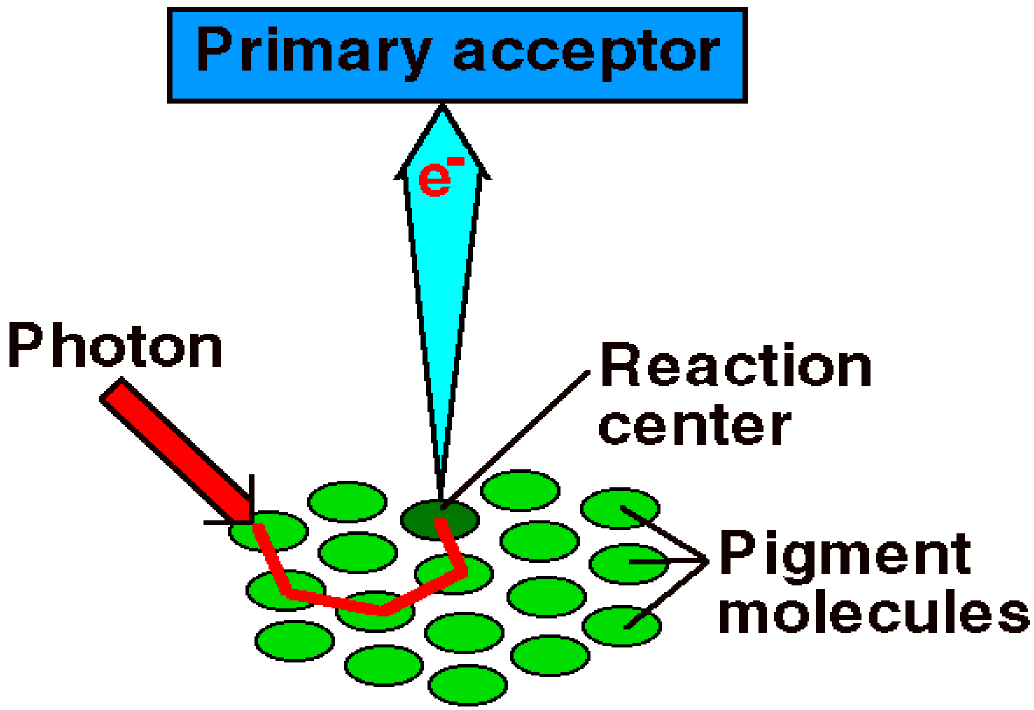


In the 1770s **Joseph Priestley**, an English chemist and clergyman, performed experiments showing that plants release a type of air that allows combustion. He demonstrated this by burning a candle in a closed vessel until the flame went out. He placed a sprig of mint in the chamber and after several days showed that the candle could burn again.

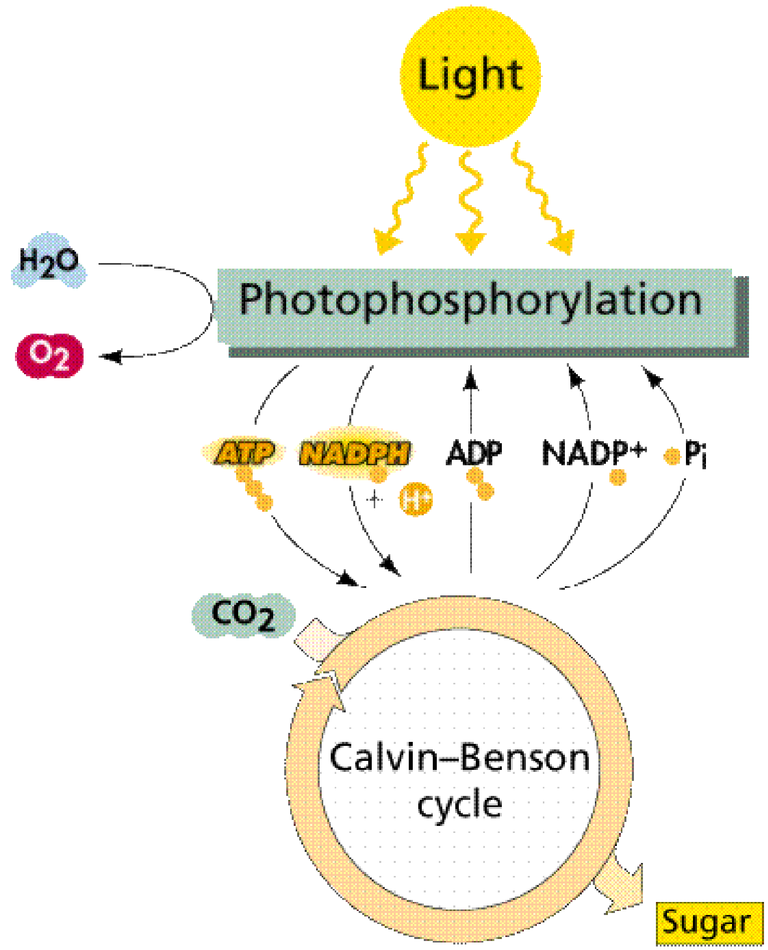
Scientific curiosity led him to dissolve his new gases, or "airs" as he called them, in water. The result with one gas was a carbonated drink, which he called "soda water." In addition to his discovery of several gases and their properties, he was also the first to confirm that graphite could conduct electricity. When others could find no use for a New World substance called "India gum," he did, calling it "rubber" because it could rub out or erase pencil marks.

His book *History of Corruptions of Christianity* (1782) was officially ***burned*** in 1785. Due to his open support of both the American and French Revolutions, his Birmingham home and church were ***burned*** to the ground by an angry mob in 1791. He moved to London, but the **persecution continued**.
Finally, in 1794, Priestley and his family hopped a boat for an eight week voyage and emigrated to the United States.

# PS core principle



# Plant PS



Light
$H_2O$
$O_2$
Photophosphorylation
ATP
NADPH
H+
ADP
NADP+
Pi
$CO_2$
Calvin–Benson cycle
Sugar

# Two types of photosynthesis:

- **Anoxygenic**

  –photosynthetic bacteria

  –Light energy used to create organic compounds, does not release oxygen, does not use water

  $CO_2 + 2H_2A$ + light energy -> $[CH_2O] + 2A + H_2O$

  e.g. A = S

- **Oxygenic**

  –Plants, algae, cyanobacteria

  –uses light energy and $CO_2$ from atmosphere, $CO_2$ is reduced to synthesize carbohydrates and release molecular oxygen

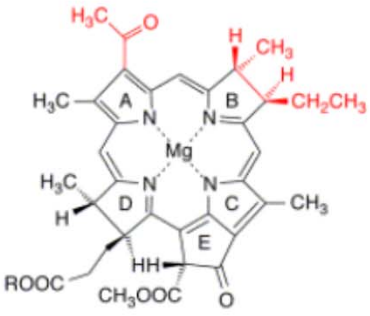
  $CO_2 + 2H_2O$ + light energy -> $[CH_2O]$ (carbohydrate) + $O_2 + H_2O$

# The organisms

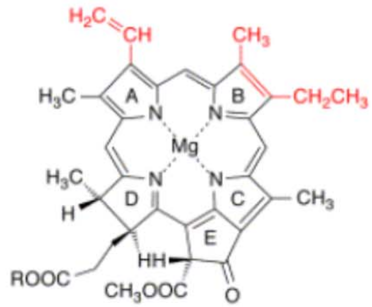
- ***Anoxygenic Photosynthetic Organisms***
  Some **photosynthetic bacteria** can use light energy to extract electrons from molecules other than water. These organisms are of ancient origin, presumed to have evolved before oxygenic photosynthetic organisms. Anoxygenic photosynthetic organisms occur in the domain Bacteria and have representatives in four phyla - Purple Bacteria, Green Sulfur Bacteria, Green Gliding Bacteria, and Gram Positive Bacteria.

- ***Oxygenic***
  The photosynthetic process in **all *plants* and algae as well as in certain types of photosynthetic bacteria** involves the reduction of $CO_2$ to carbohydrate and removal of electrons from $H_2O$, which results in the release of $O_2$. In this process, known as oxygenic photosynthesis, water is oxidized by the photosystem II reaction center, a multisubunit protein located in the photosynthetic membrane. Years of research have shown that the structure and function of photosystem II is similar in plants, algae and certain bacteria, so that knowledge gained in one species can be applied to others.

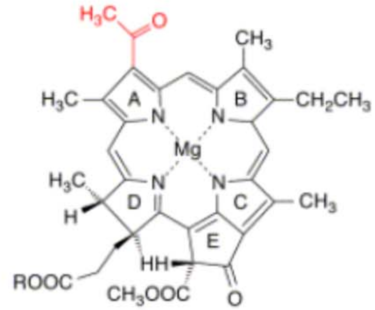
# Photosynthetic pigments: Chlorophylls



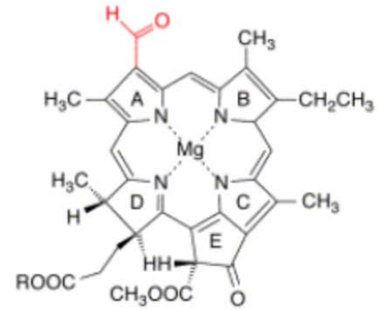
**(a)** Bacteriochlorophyll *a*



**(b)** Chlorophyll *a*

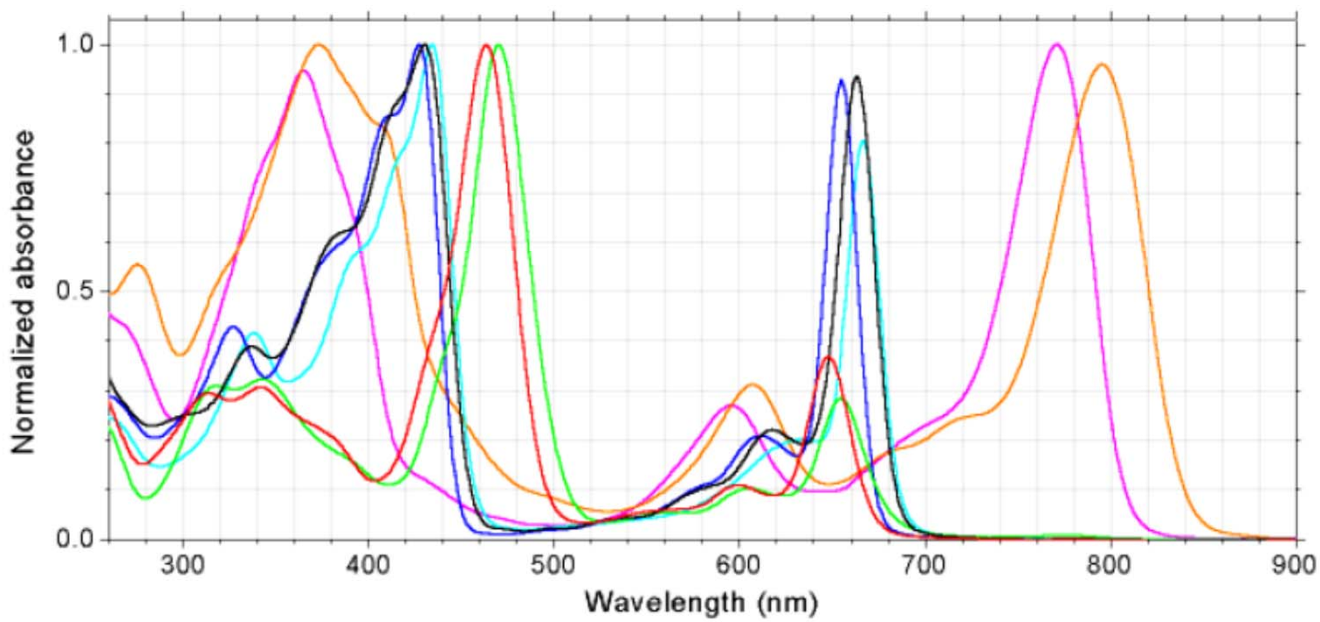


**(c)** 3-Acetyl-chlorophyll *a*



**(d)** Chlorophyll *d*

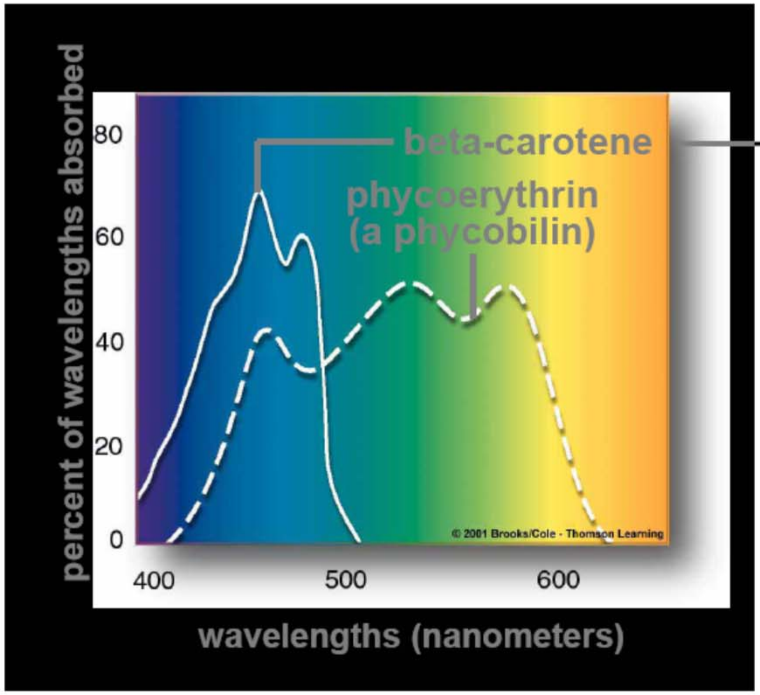
**Chl *a*: black**
**Chl *b*: red**
**BChl *a*: magenta**
**BChl *b*: orange**
**BChl *c*: cyan**
**BChl *d*: bue**
**BChl *e*: green**

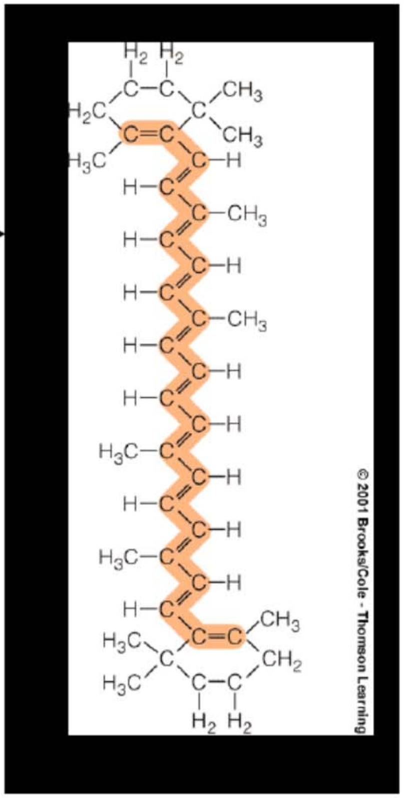



PS in ***all*** organisms is based on the ***same type*** of pigment: chlorophyll

# Accessory pigments

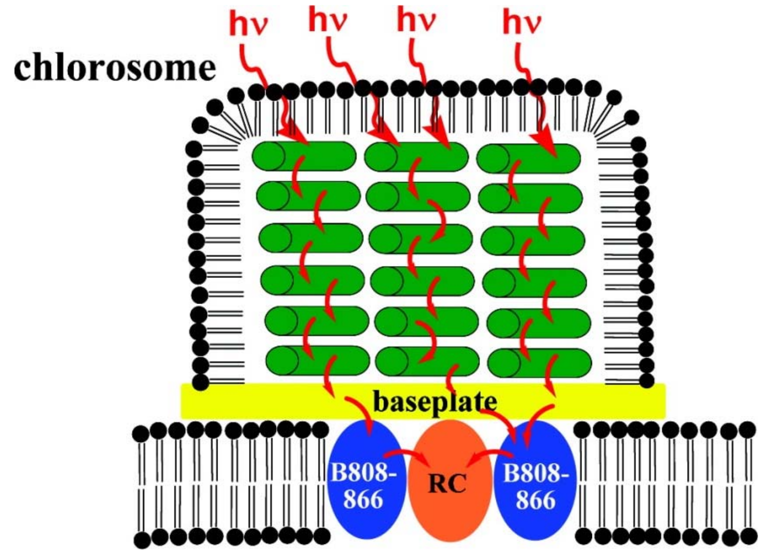
Carotenoids, Phycobilins, Anthocyanins

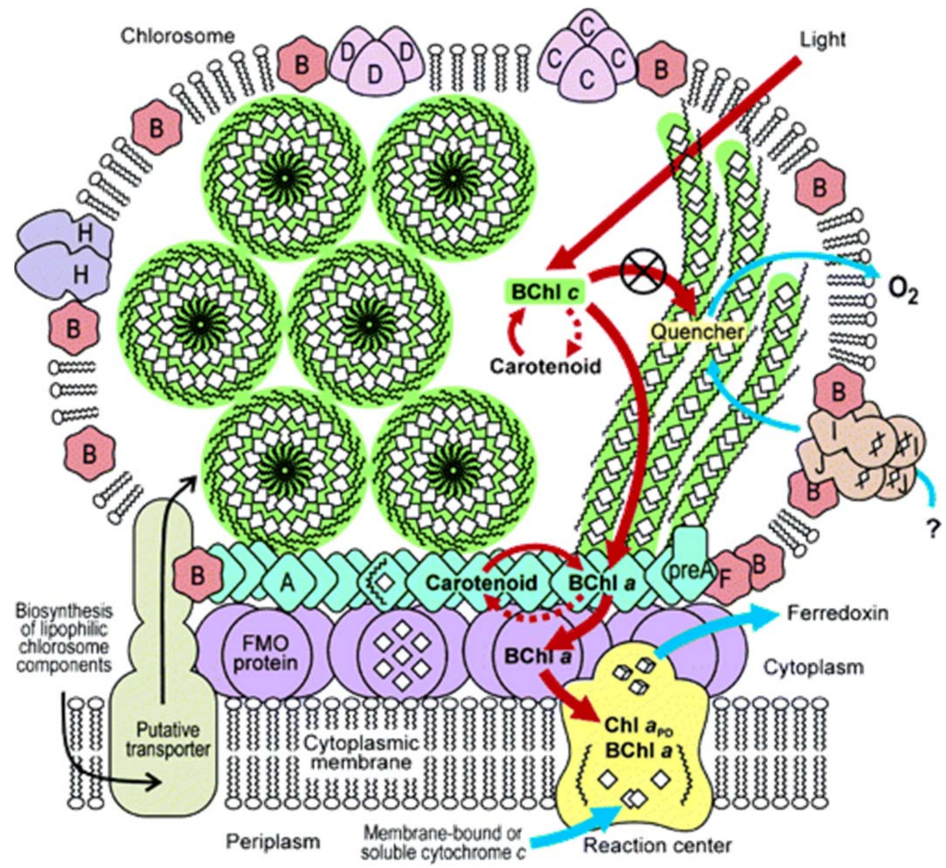


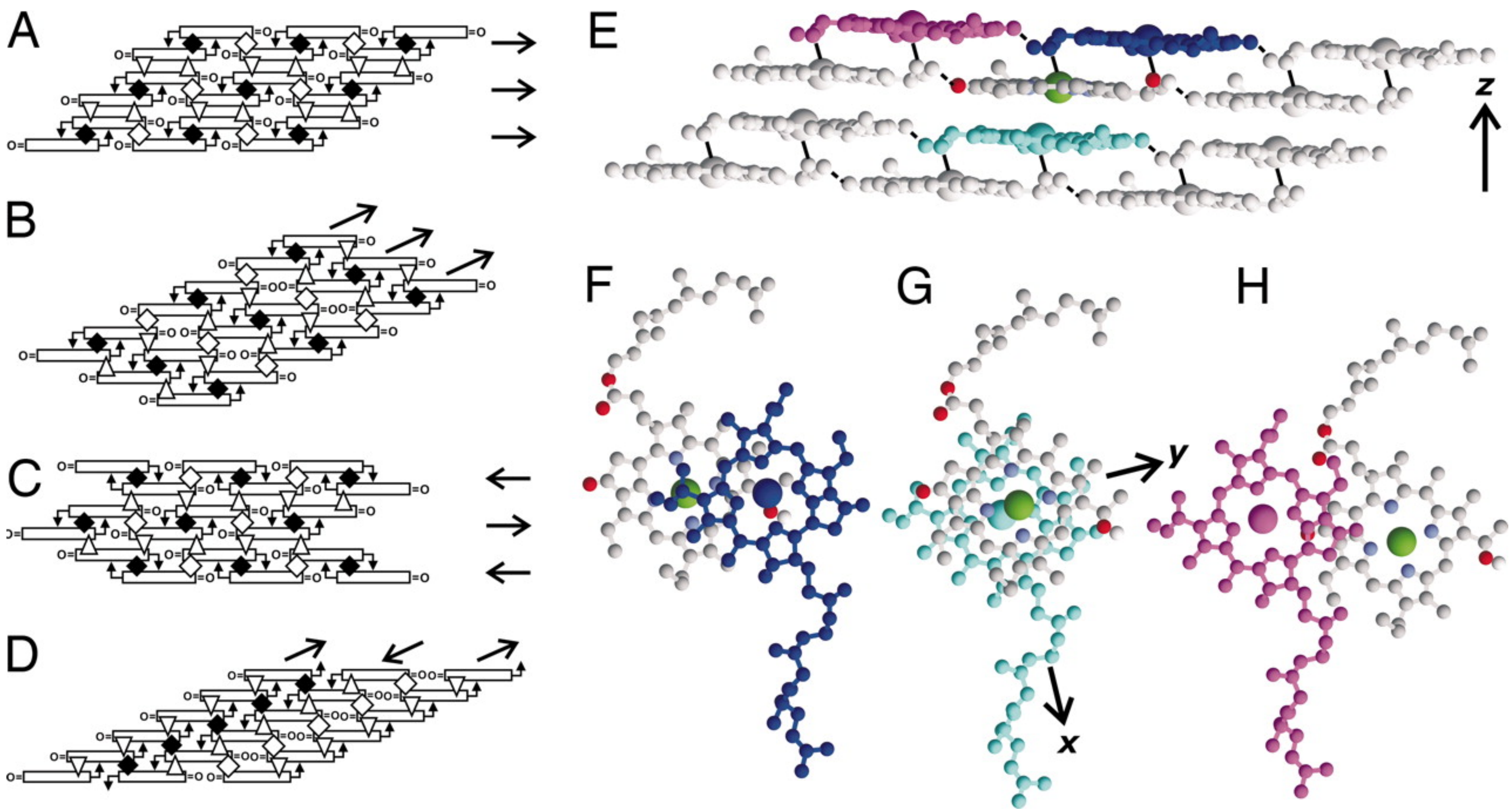
# Chlorosome

A Chlorosome is a photosynthetic antenna complex found in **green sulfur bacteria** (GSB) and some green filamentous anoxygenic phototrophs. They differ from other antenna complexes by their large size and lack of protein matrix supporting the photosynthetic pigments. Green sulfur bacteria are a group of organisms that generally live in extremely low-light environments, such as at depths of 100 meters in the Black Sea. The ability to capture light energy and rapidly deliver it to where it needs to go is essential to these bacteria, some of which see only a few photons of light per chlorophyll per day. To achieve this, the bacteria contain chlorosome structures, which contain up to 250,000 chlorophyll molecules.

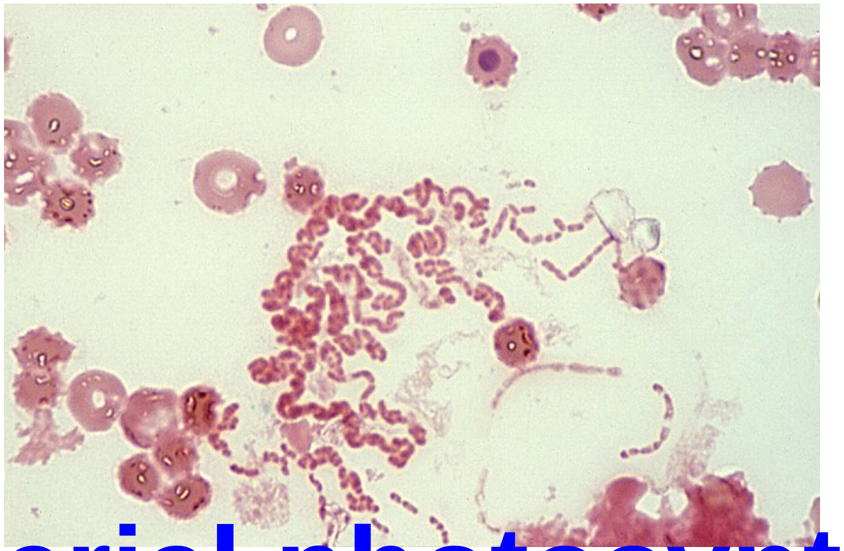


## BChl c assembly models satisfying head–head, head–tail, and tail–tail contacts and the structure of the BChl c assembly determined under 13C13C distance constraints.



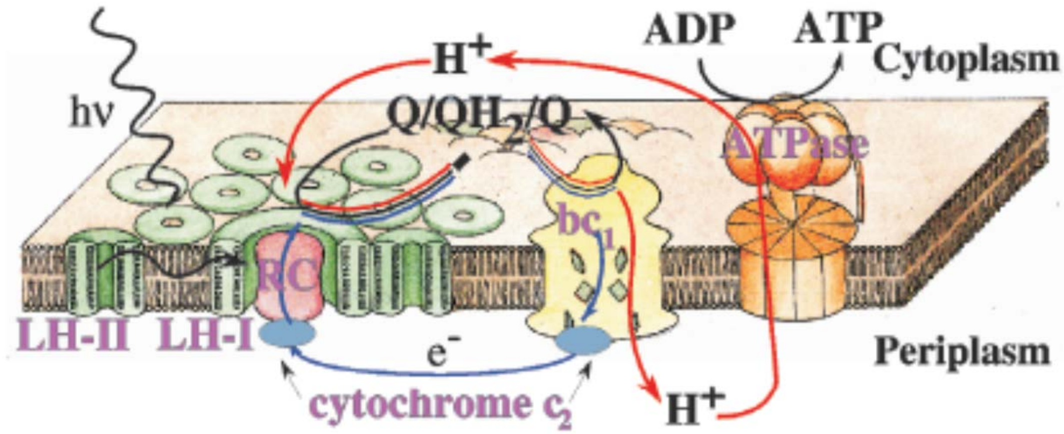

Egawa A et al. PNAS 2007;104:790-795



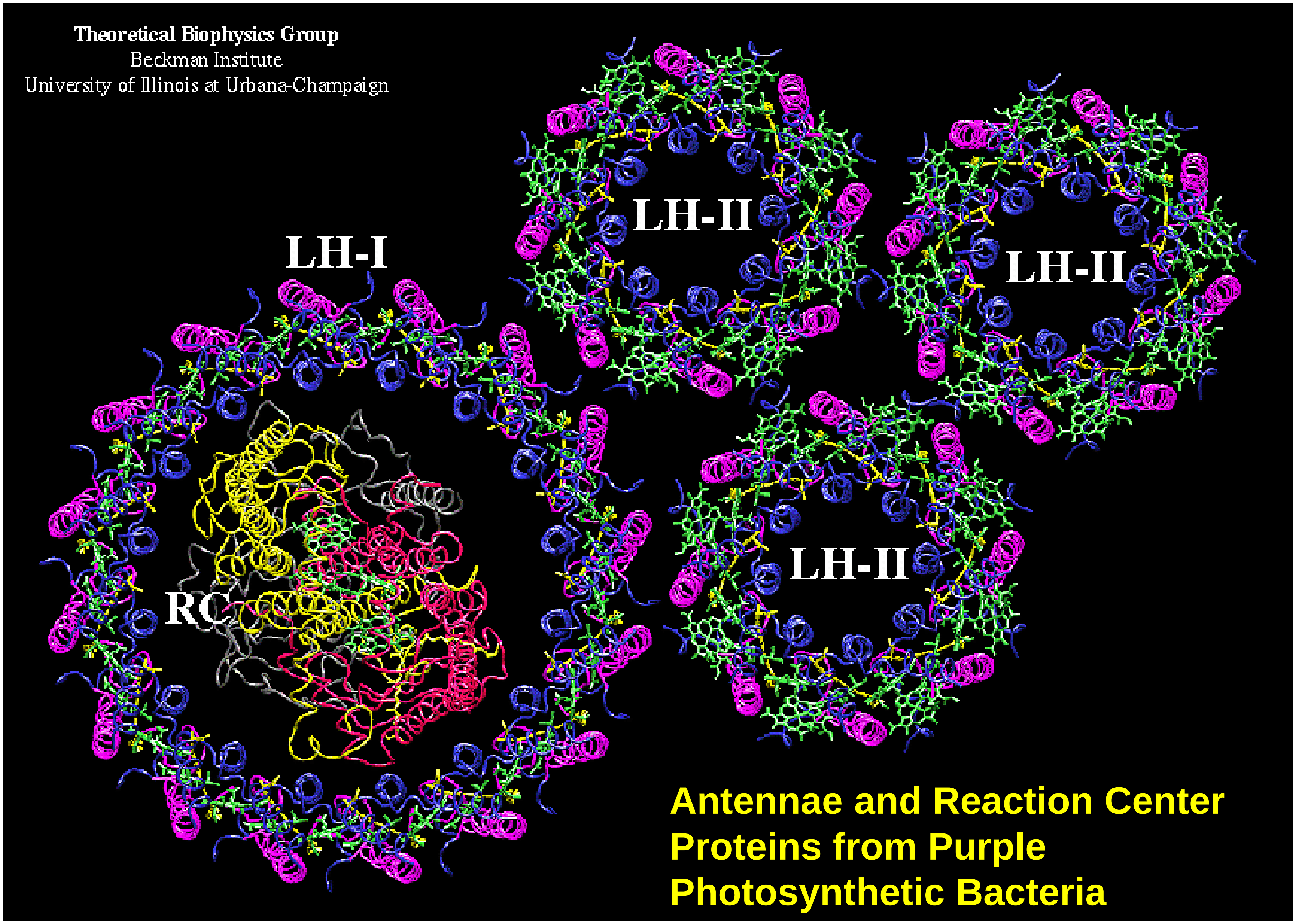
# Bacterial photosynthesis (purple bacteria)

- Structure of PS system is known.
- Relatively well understood
- The simplest PS system
- Important general principles are demonstrated

# Global picture: membrane system with electron and proton flow, ATP synthesis



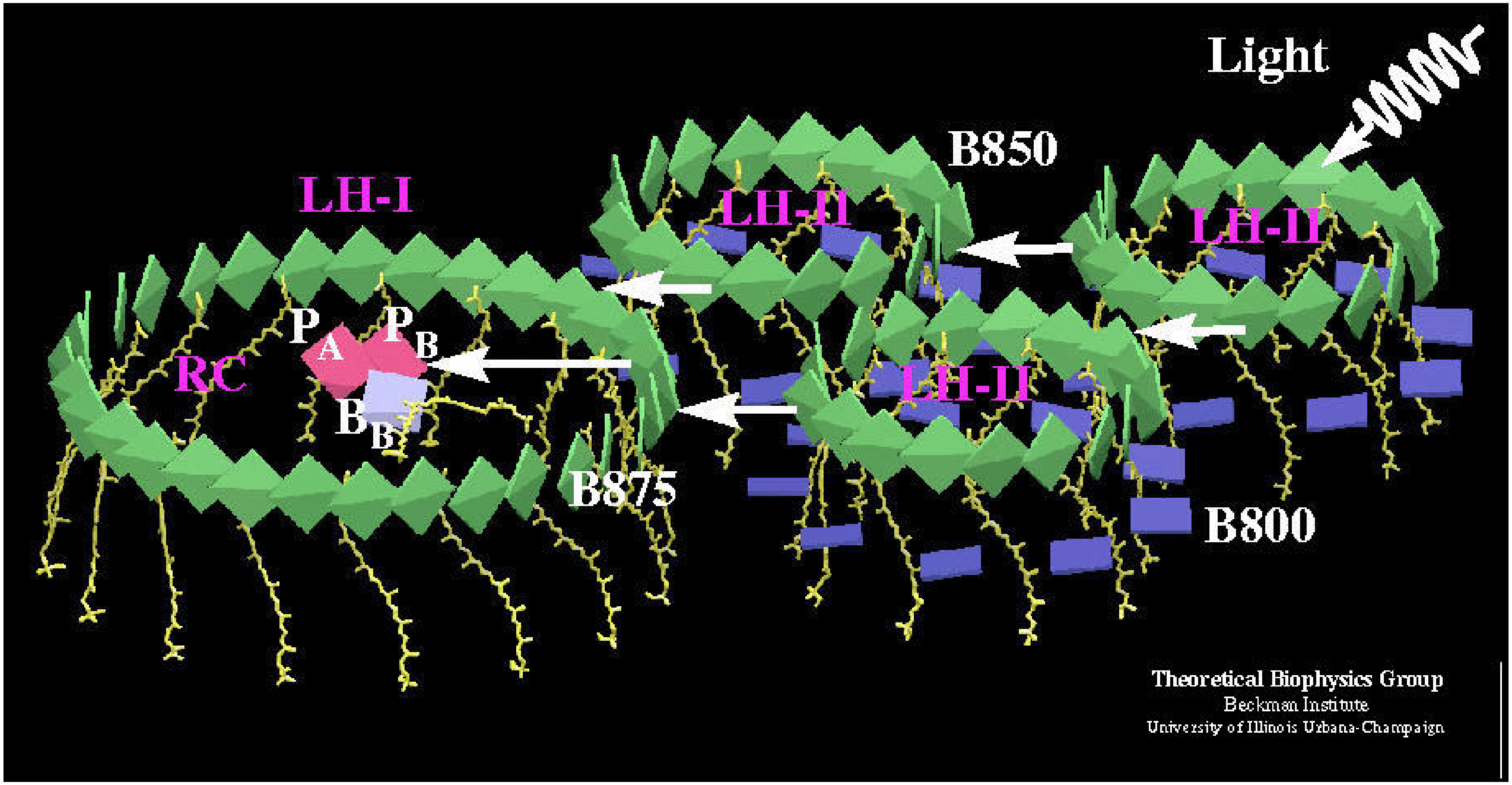

Schematic representation of the photosynthetic apparatus in the intracytoplasmic membrane of purple bacteria. The reaction center (RC, red) is surrounded by the light-harvesting complex I (LH-I, green) to form the LH-I–RC complex, which is surrounded by multiple light-harvesting complexes LH-II (green), forming altogether the photosynthetic unit (PSU). Photons are absorbed by the light-harvesting complexes and excitation is transferred to the RC initiating a charge (electron-hole) separation. The RC binds quinone $Q_B$, reduces it to hydroquinone $Q_BH_2$, and releases the latter. $Q_BH_2$ is oxidized by the bc1 complex, which uses the exothermic reaction to pump protons across the membrane; electrons are shuttled back to the RC by the cytochrome c2 complex (blue) from the ubiquinone-cytochrome $bc_1$ complex (yellow). The electron transfer across the membrane produces a large proton gradient that drives the synthesis of ATP from ADP by the ATPase (orange). Electron flow is represented in blue, proton flow in red, and quinone flow — likely confined to the intramembrane space — in black.


Theoretical Biophysics Group
Beckman Institute
University of Illinois at Urbana-Champaign
LH-I
LH-II
LH-II
LH-II
RC
Antennae and Reaction Center
Proteins from Purple
Photosynthetic Bacteria

The overall process of photosynthesis takes place in four stages.

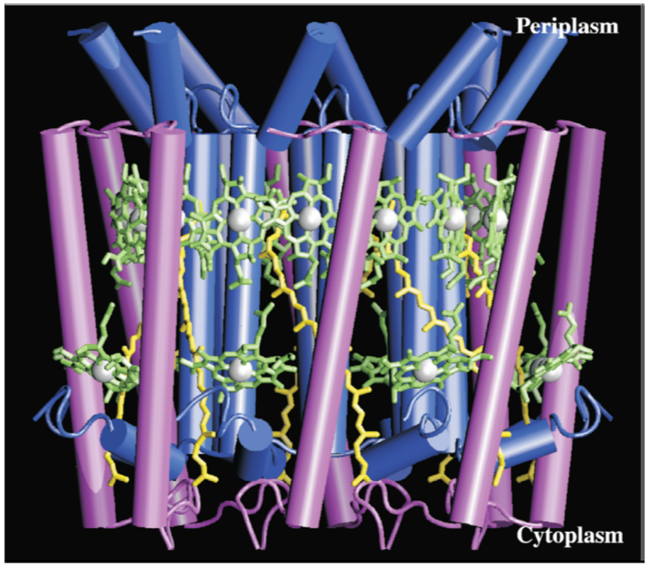
1. Energy transfer in antenna chlorophyll takes place in the femtosecond to picosecond time scale.
2. The transfer of electrons in photochemical reactions, takes place in the picosecond to nanosecond time scale.
3. The electron transport chain and ATP synthesis, takes place on the microsecond time scale.
4. Carbon fixation and export of stable products and takes place in the millisecond to second time scale.

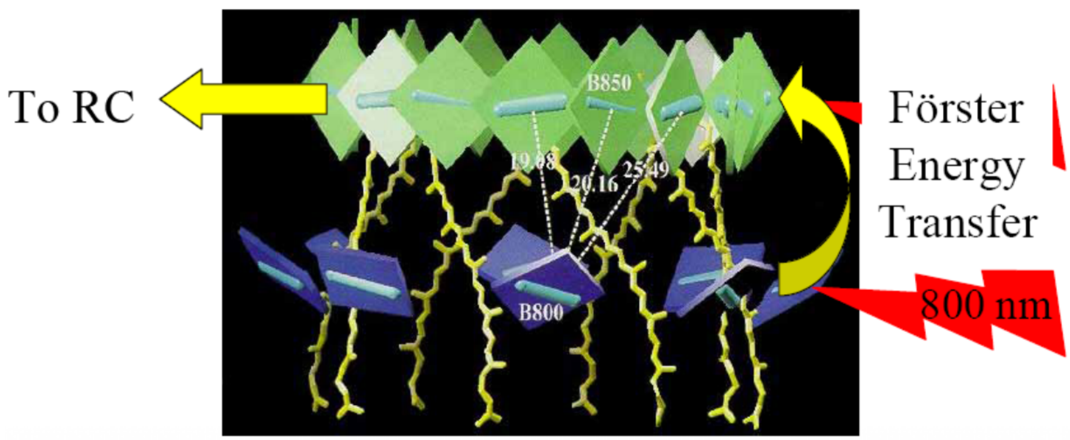
# Light harvesting: big picture

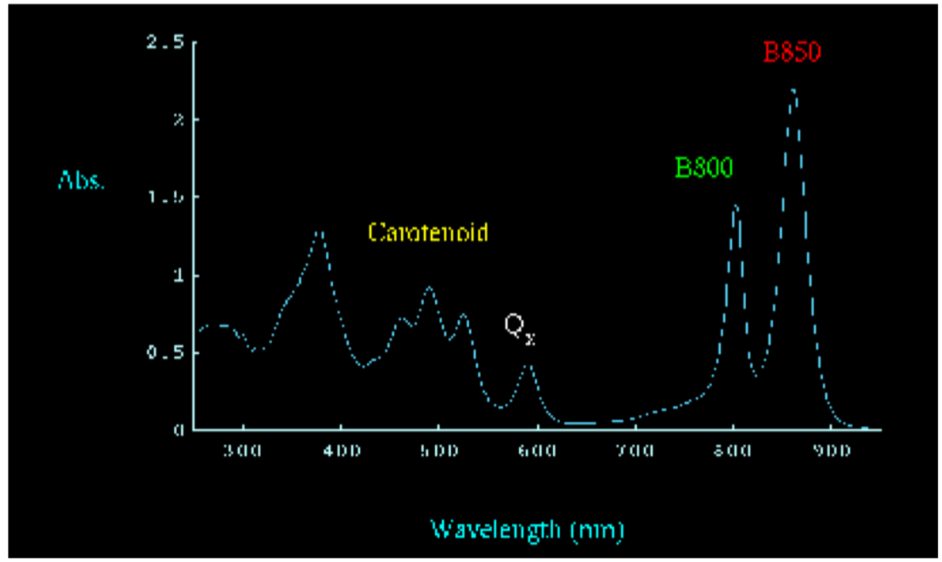



**Noncovalent assembly of *identical* chromophores at specific distances and orientations to provide particular photophysical and redox functions is critical in photosynthetic antennae and reaction centers**

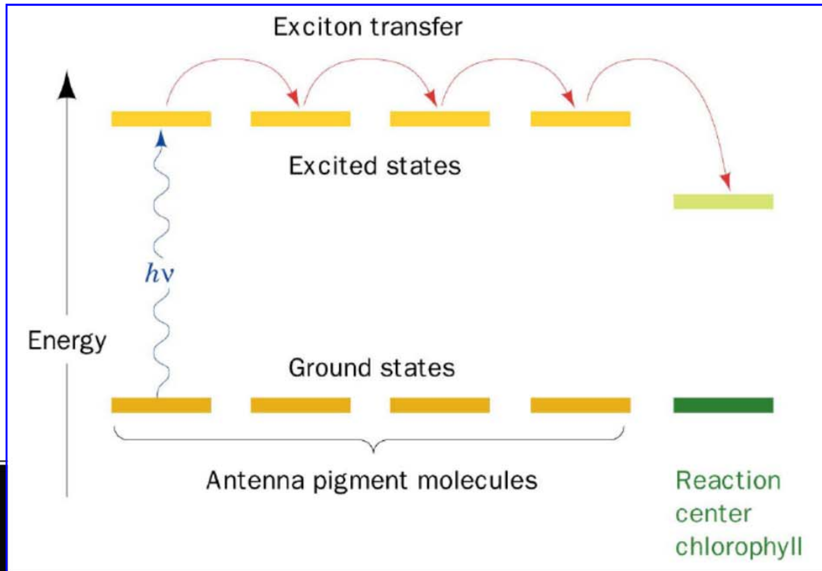
LH-II



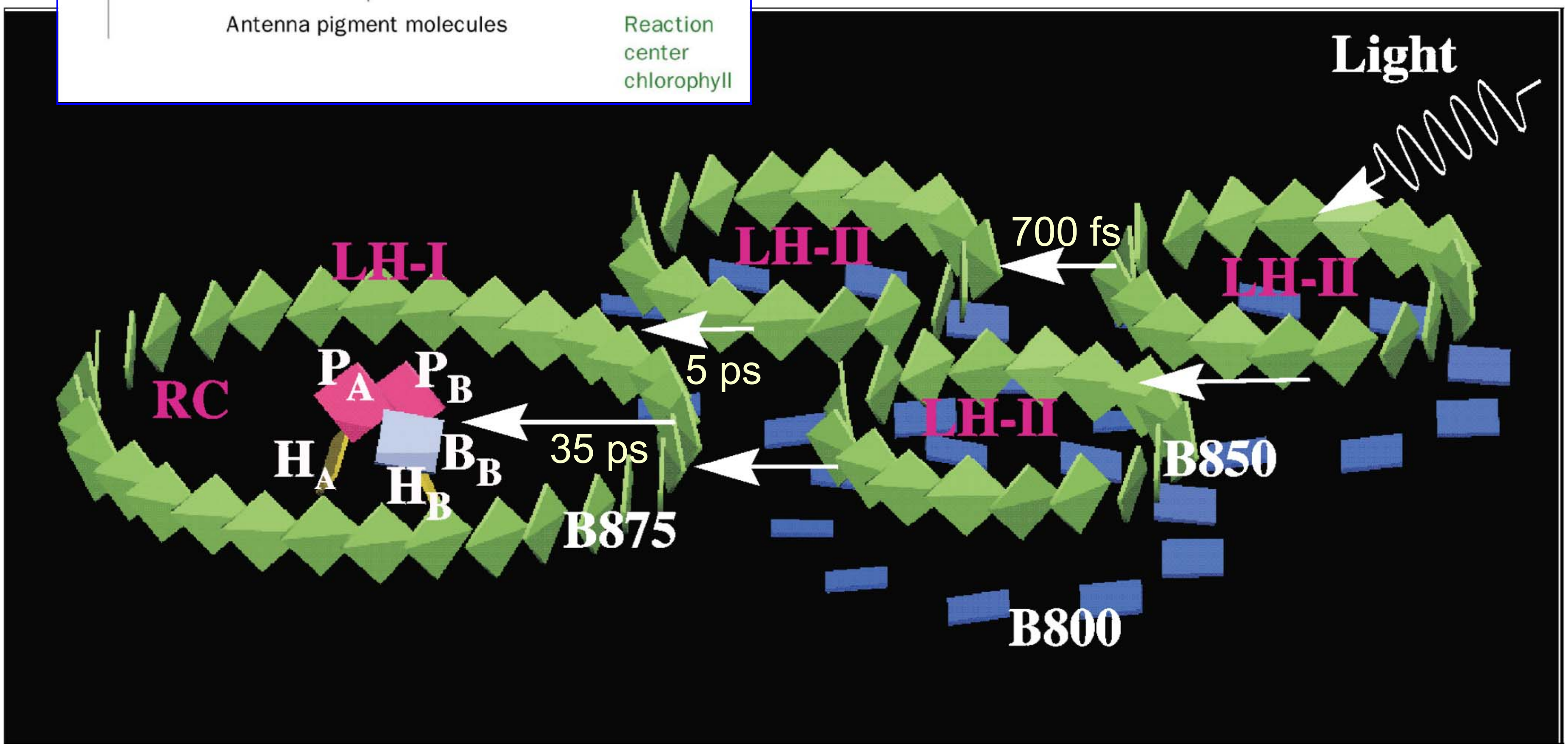



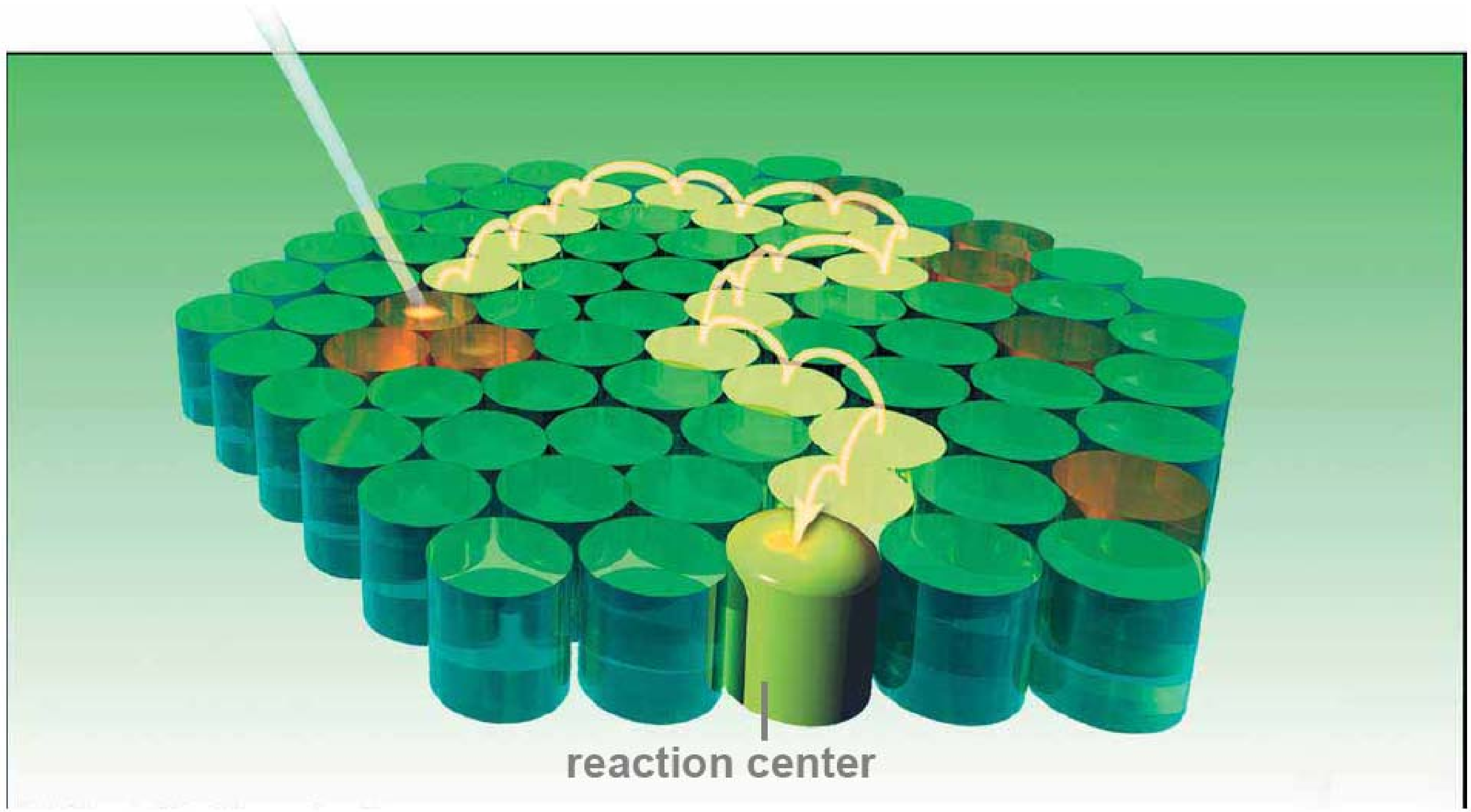

The excitation energy is transferred from B800 to B850 and then to RC



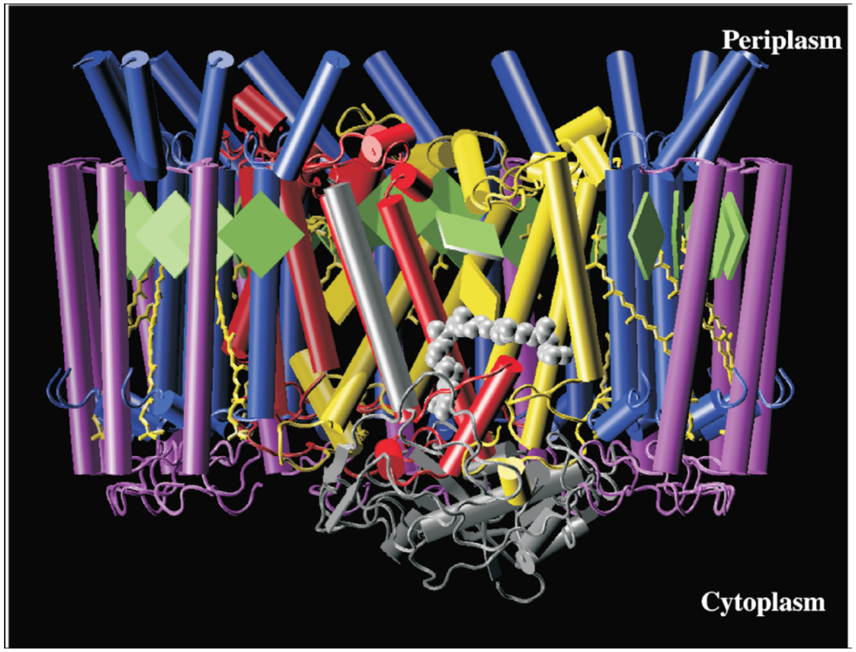

The excitation is trapped by the reaction center chlorophyll because its lowest excited state has a lower energy than those of the antenna pigment (chlorophyll) molecules.

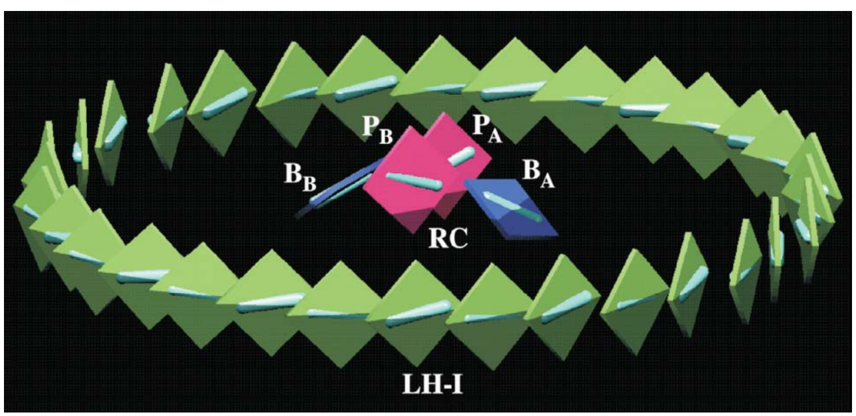


# Exciton migration

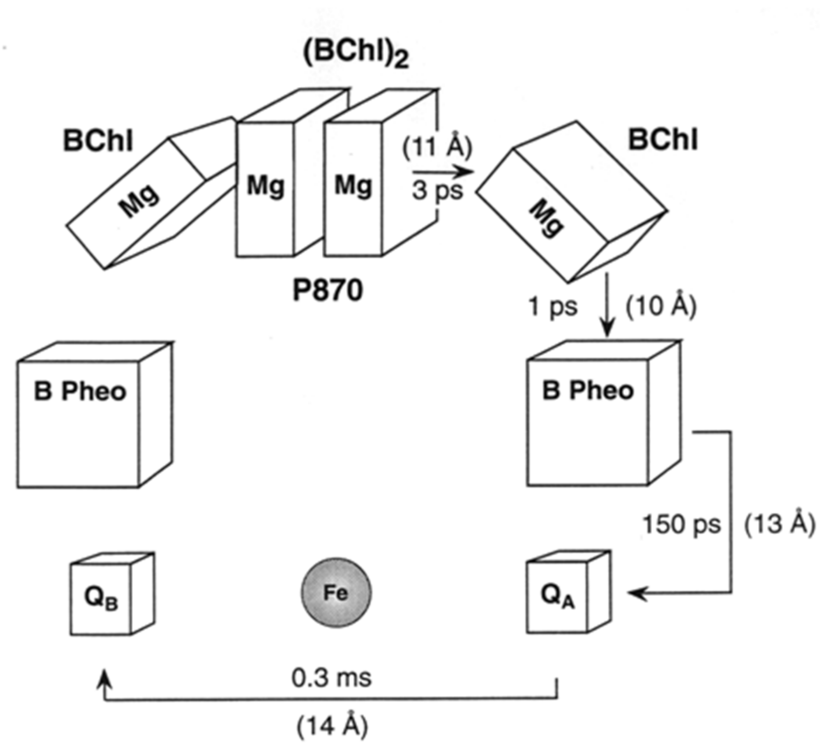


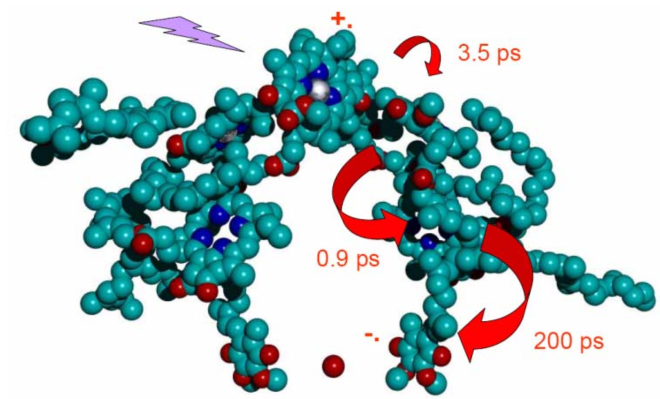
# Reaction center + LHI

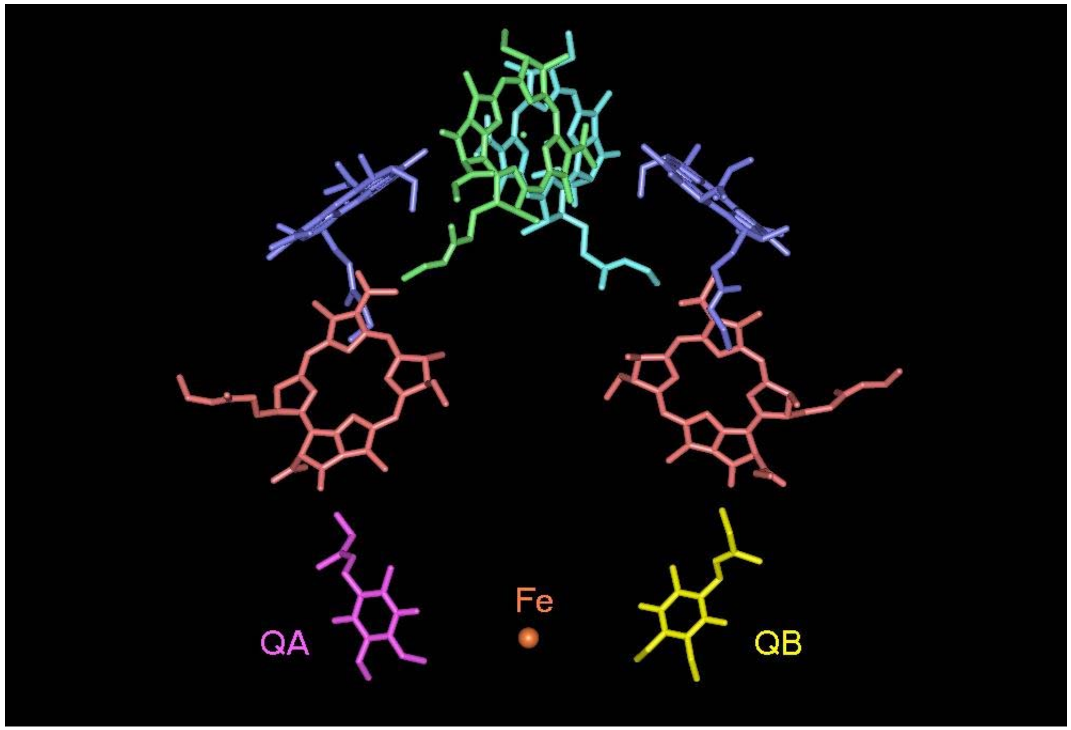


# Reaction center and electron transfer: primary events



# PS highlights

- Complex function is achieved not by chromophore diversity but by their organization
- Charge separation is stepwise – electronic coupling and inverted region play an important role
- Electron transfer is coupled to proton transfer

# Plant photosynthesis

Plant photosynthesis is driven primarily by visible light (wavelengths from 400 to 700 nm) that is absorbed by pigment molecules (mainly chlorophyll a and b and carotenoids). Plants appear green because of chlorophyll.

Plant Cell Chloroplast Structure

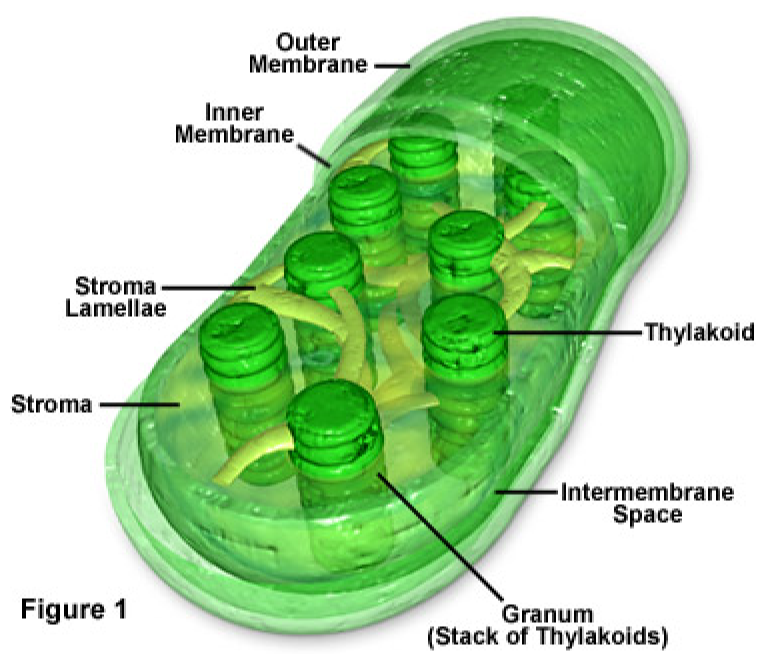
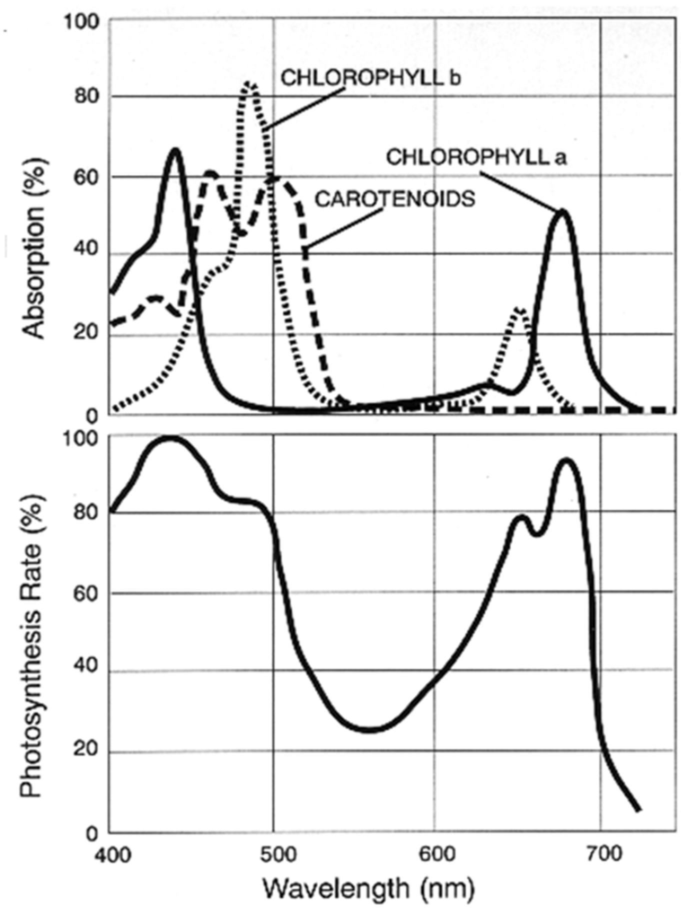
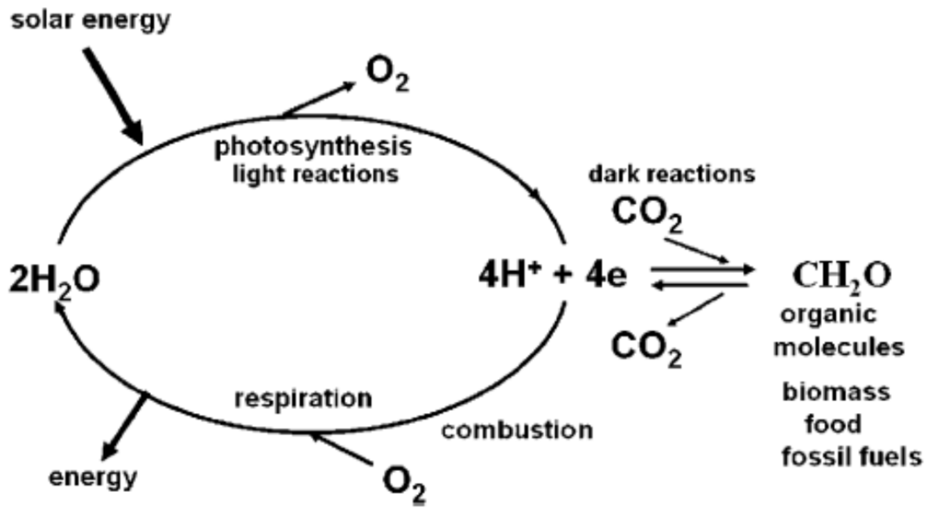



Figure 1




Chloroplasts have many similarities with photosynthetic bacteria




The main source of oxygen in the atmosphere is oxygenic photosynthesis, and its first appearance is sometimes referred to as the oxygen catastrophe.

An average hectare of corn produces enough oxygen per hectare per day in mid summer to meet the respiratory needs of about 325 people. This means that the one million or so hectares of corn grown in Ontario produce enough oxygen for the annual respiratory needs of Ontario's 10 million residents in about 11 summer days!" From: Corn and Photosynthesis

# Overall Chemistry

Carbon Dioxide + Water + Light energy → Glucose + Oxygen + Water

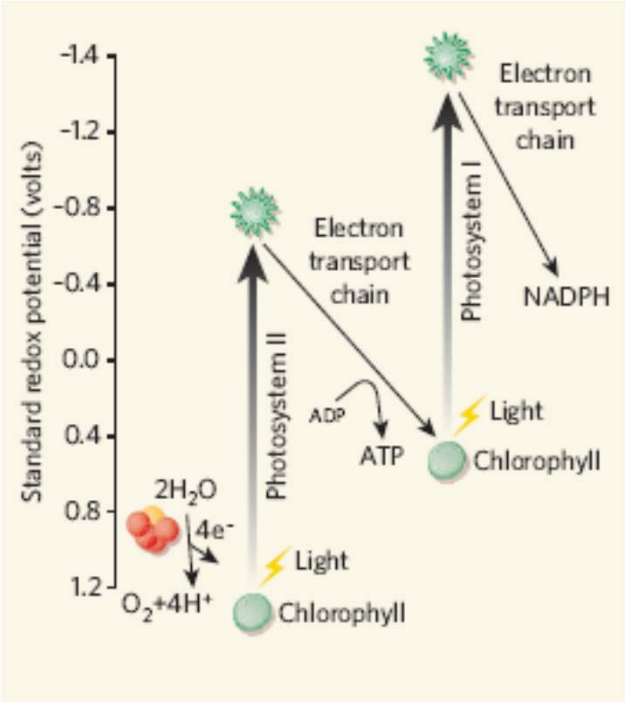
$$6\ CO_2 + 12\ H_2O + ATP + NADPH \rightarrow C_6H_{12}O_6 + 6\ O_2 + 6\ H_2O$$

In the first phase **light-dependent reactions** or **photosynthetic reactions** (also called the *Light reactions*) capture the energy of light and use it to make high-energy molecules. During the second phase, the **light-independent reactions** (or *Dark Reactions*) use the high-energy molecules to capture carbon dioxide and make the precursors of glucose.

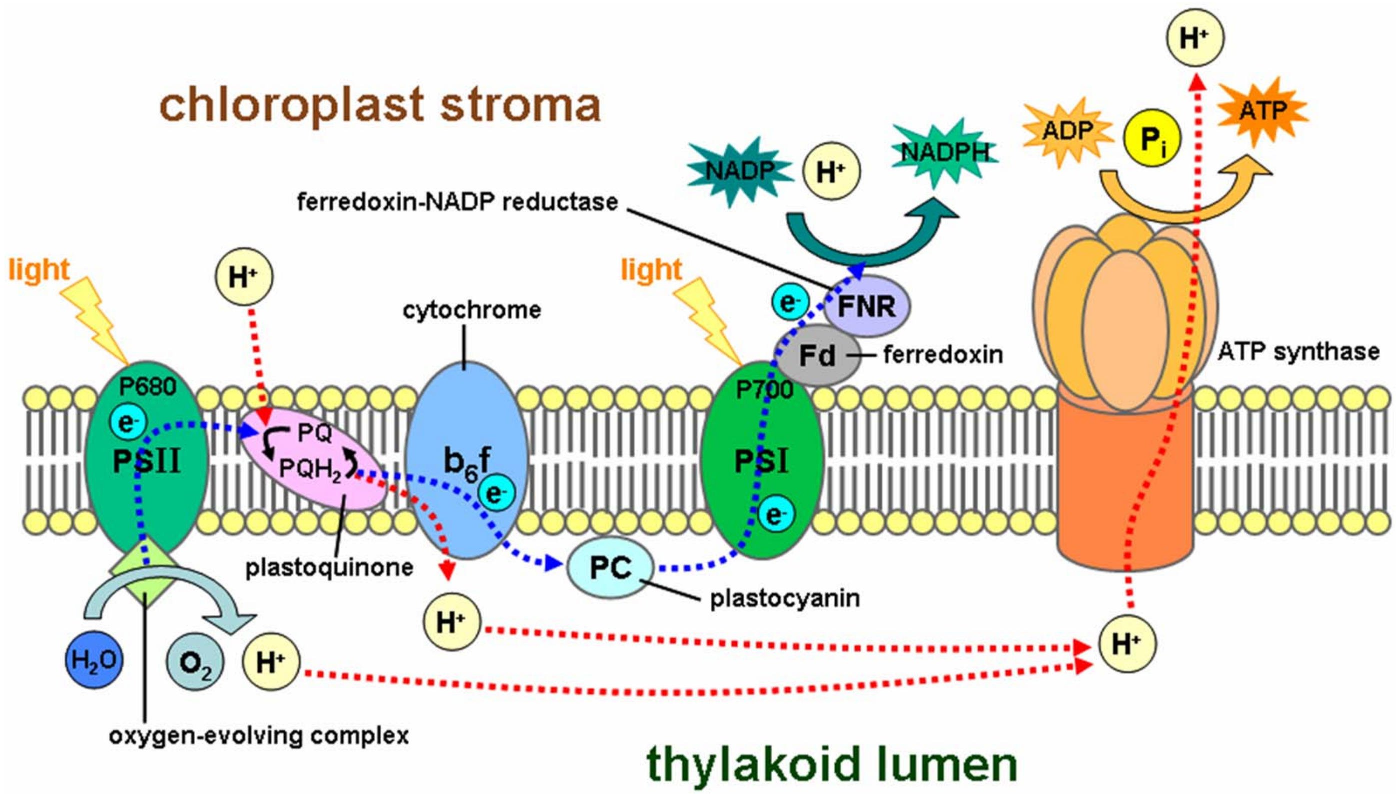
In the *light-dependent reactions* the pigment chlorophyll absorbs light and loses an electron that travels down an electron transport chain producing the high energy molecules NADPH and ATP. The chlorophyll molecule regains its electron by taking one from water, which results in releasing oxygen gas.

In the *Light-independent or dark reactions* the enzyme RuBisCO captures $CO_2$ from the atmosphere and in a complex process called the Calvin-Benson cycle releases 3-carbon sugars which are later combined to form glucose.

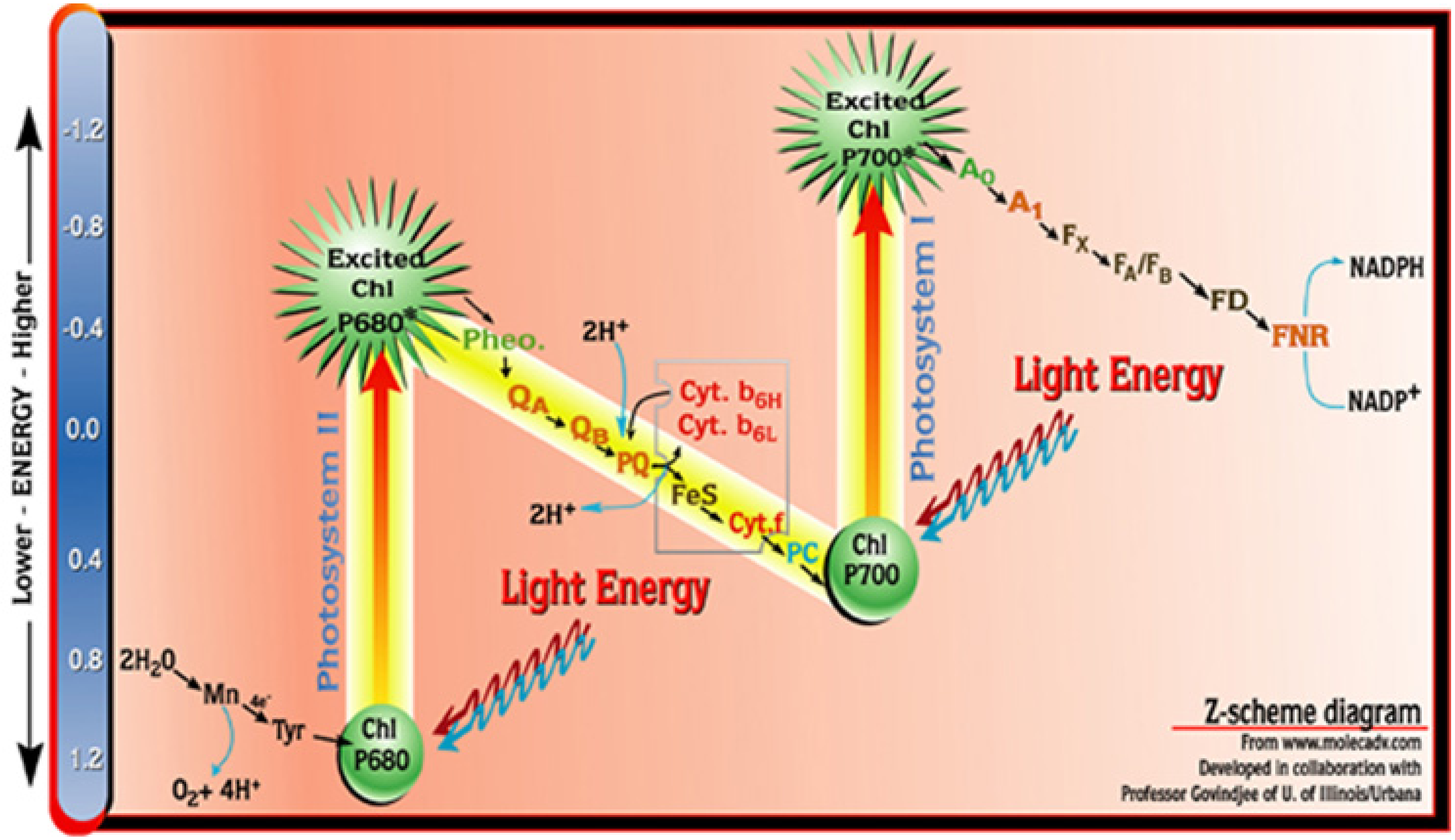
Photosynthesis may simply be defined as the conversion of light energy into chemical energy by living organisms.




The main players are two molecular machines, photosystem I and photosystem II, that act as electrochemical solar cells. They transform sunlight into electrical current. Photosystem II generates an electrochemical potential of 1.1 volts, enough to remove two electrons from each of two water molecules, making a molecule of $O_2$ at a cost of four photons — one for each electron moved. Photosystem II performs this remarkable feat only when photosystem I is present to dispose of the electrons. Photosystem I grabs the four electrons and uses four more photons to deposit them, in two pairs, on an electron carrier called NADP. NADP ultimately transfers the electrons to carbon dioxide, thereby providing the energy to make carbon-based sugars and the other molecules of life: light makes life and oxygen out of water and carbon dioxide.

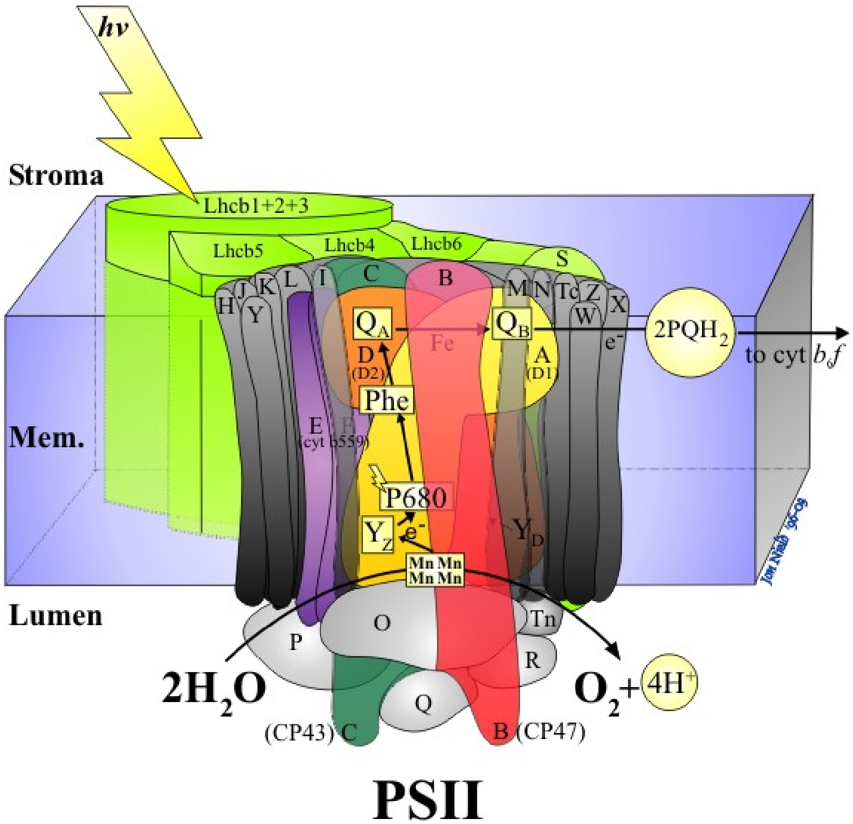


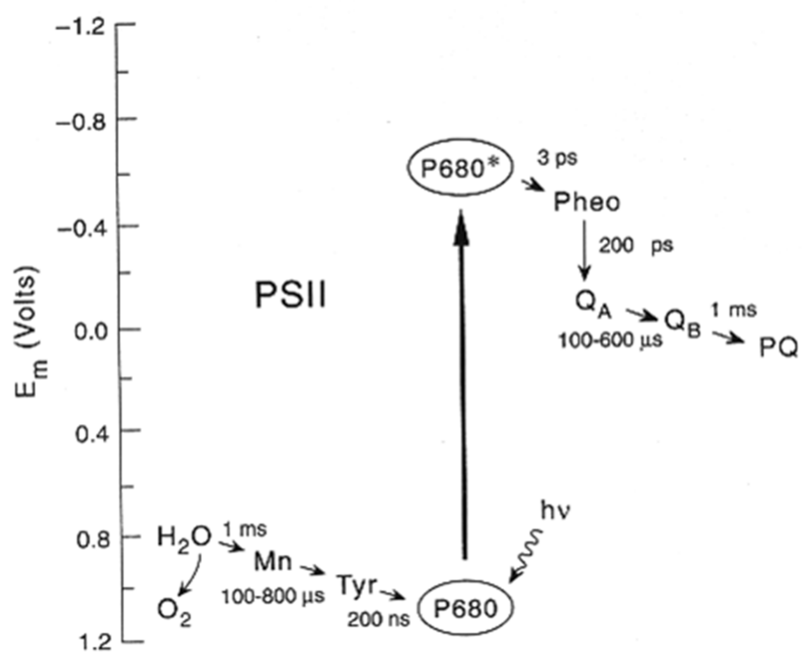

Featuring - efficient exciton, electron and proton transfer, molecular machine, use of water as a source of electrons and $CO_2$ as a reagent, powered by solar light




Photosystem II uses light energy to drive two chemical reactions - the oxidation of water and the reduction of plastoquinone.
The photosystem I complex catalyzes the oxidation of plastocyanin, a small soluble Cu- protein, and the reduction of ferredoxin, a small FeS protein.
***$H_2O$ is just a source of electrons (sacrificial electron donor), and $O_2$ is a side product of water oxidation!***

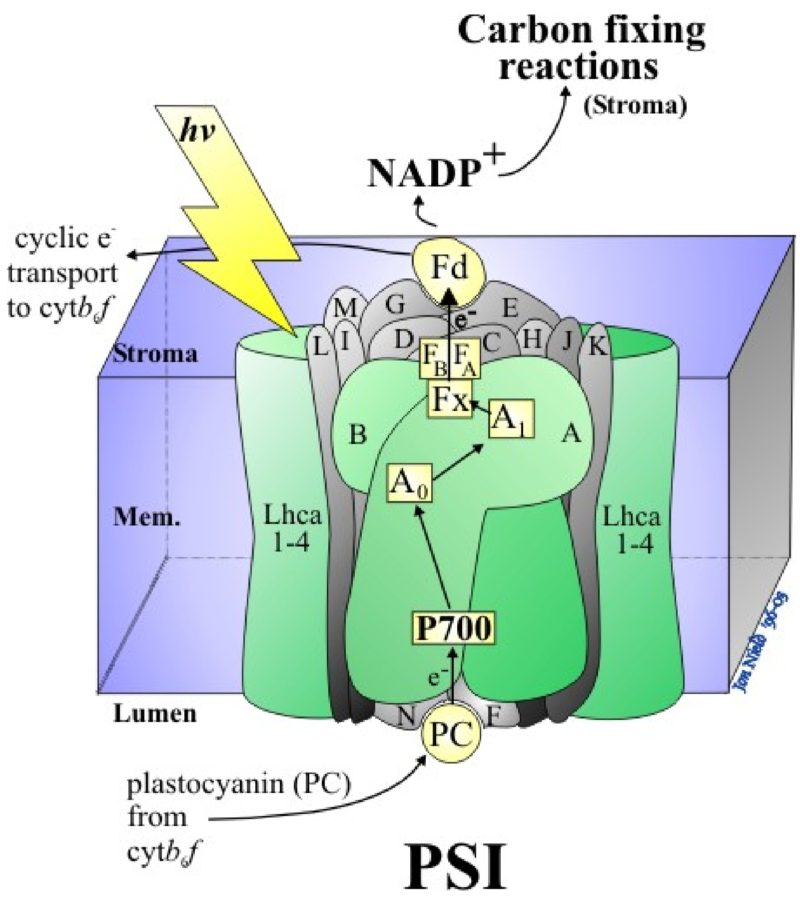
# PSII

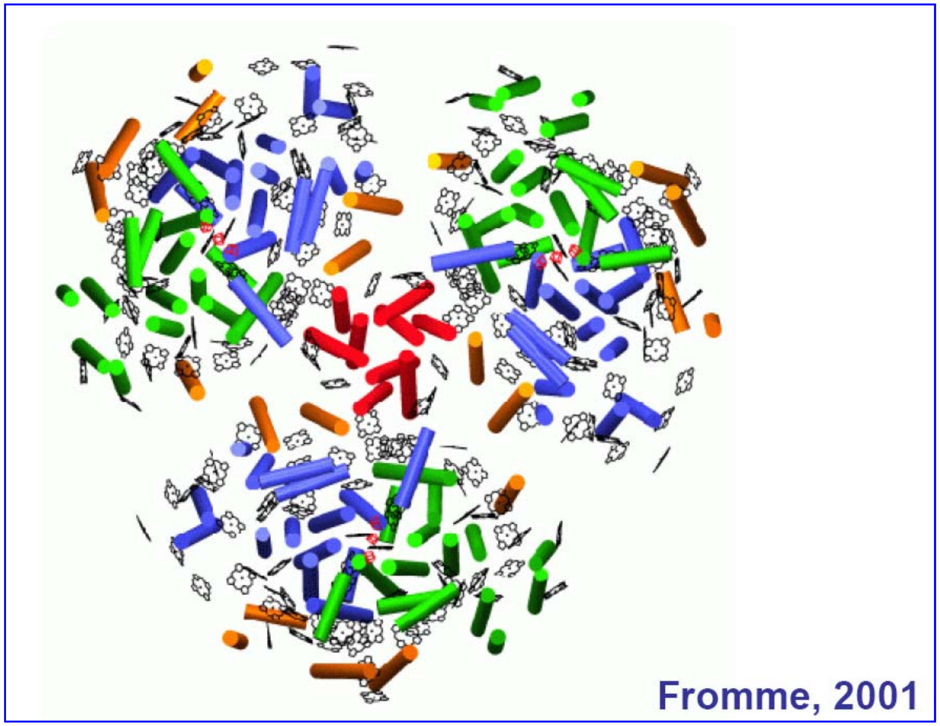


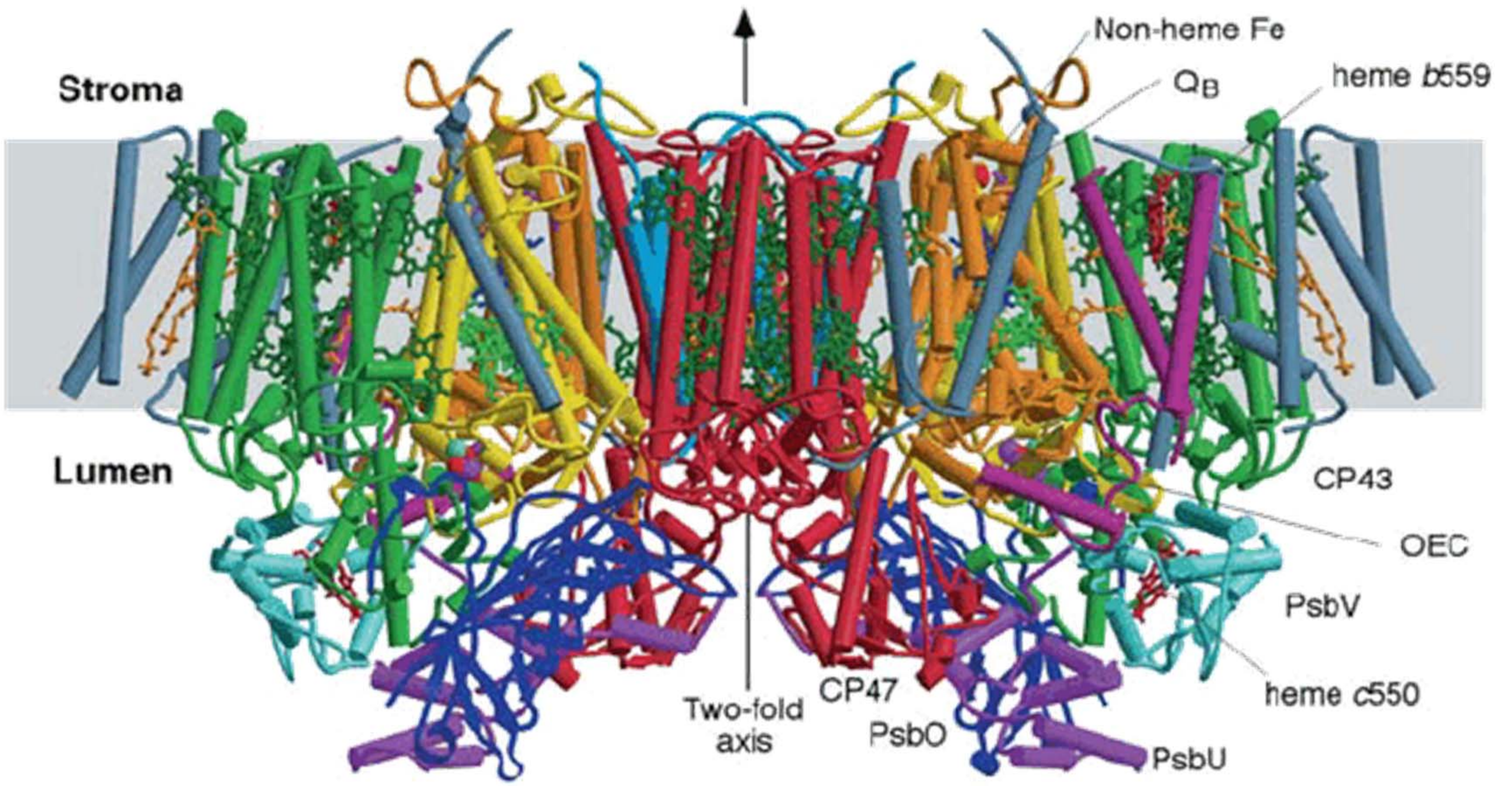

Photochemistry in photosystem II is initiated by charge separation between P680 and pheophytin, creating P680+/Pheo-. Primary charge separation takes about a few picoseconds. Subsequent electron transfer steps have been designed through evolution to prevent the primary charge separation from recombining. This is accomplished by transferring the electron within 200 picoseconds from pheophytin to a plastoquinone molecule (QA) that is permanently bound to photosystem II.

# PSI

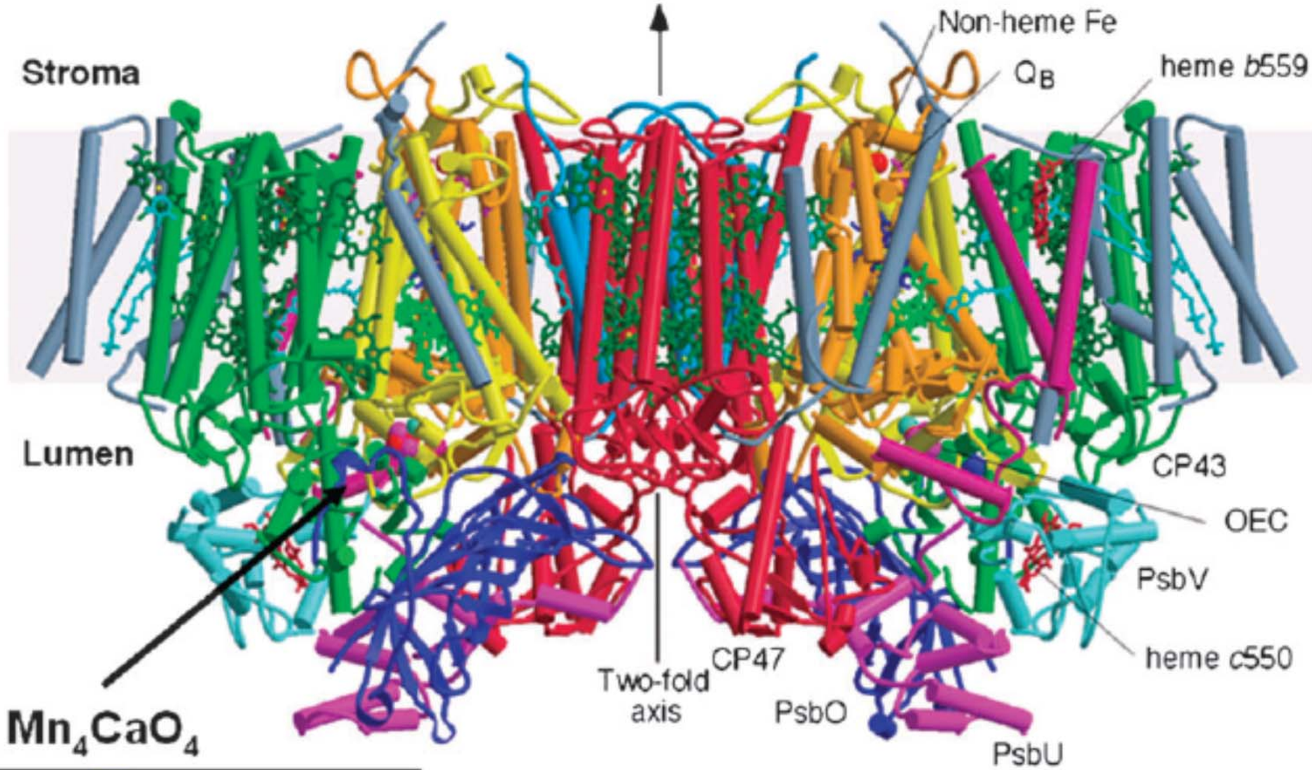

Carbon fixing
reactions
(Stroma)
hν
NADP+
cyclic e-
transport
to cytb6f
Fd
e-
M
G
E
L
I
D
C
H
J
K
Stroma
FB
FA
Fx
A1
B
A
A0
Mem.
Lhca
1-4
Lhca
1-4
P700
e-
Lumen
N
F
PC
plastocyanin (PC)
from
cytb6f
PSI

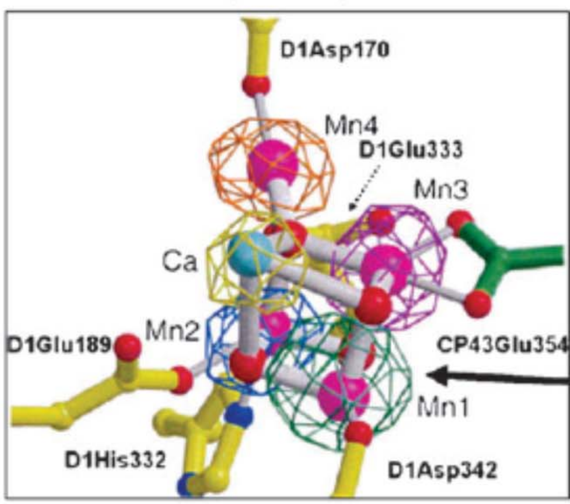

Fromme, 2001

# PSII structure




Barber et al. 2004

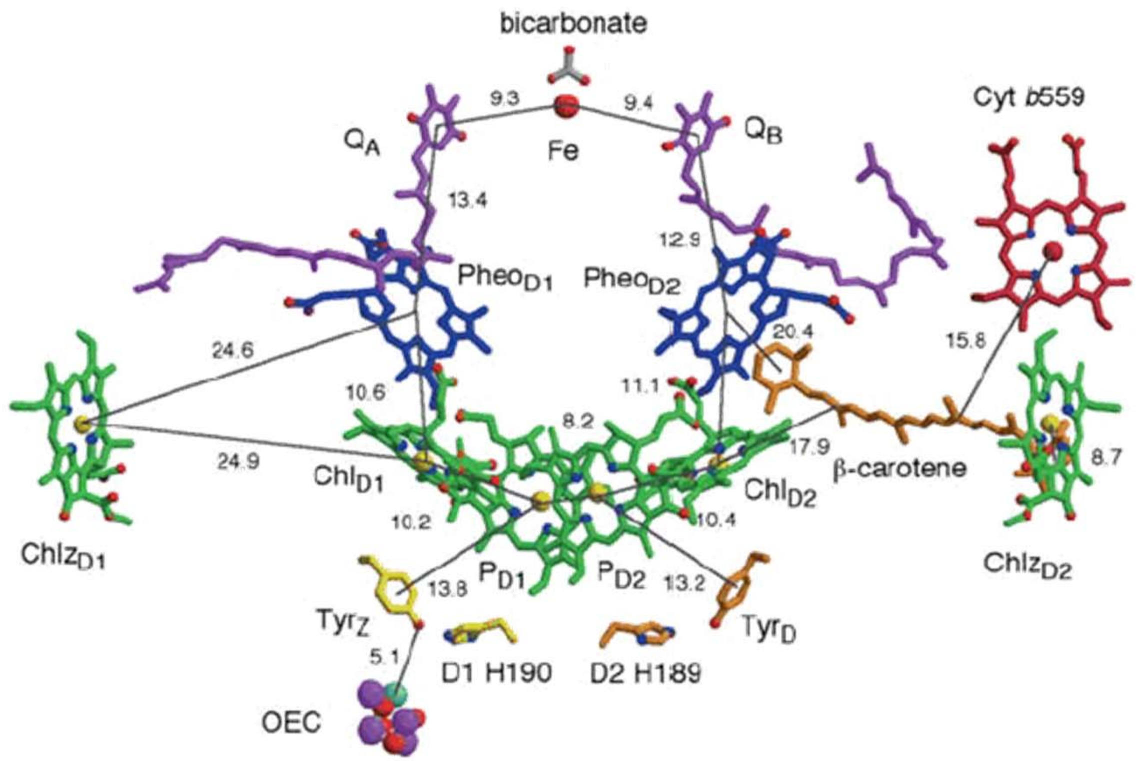


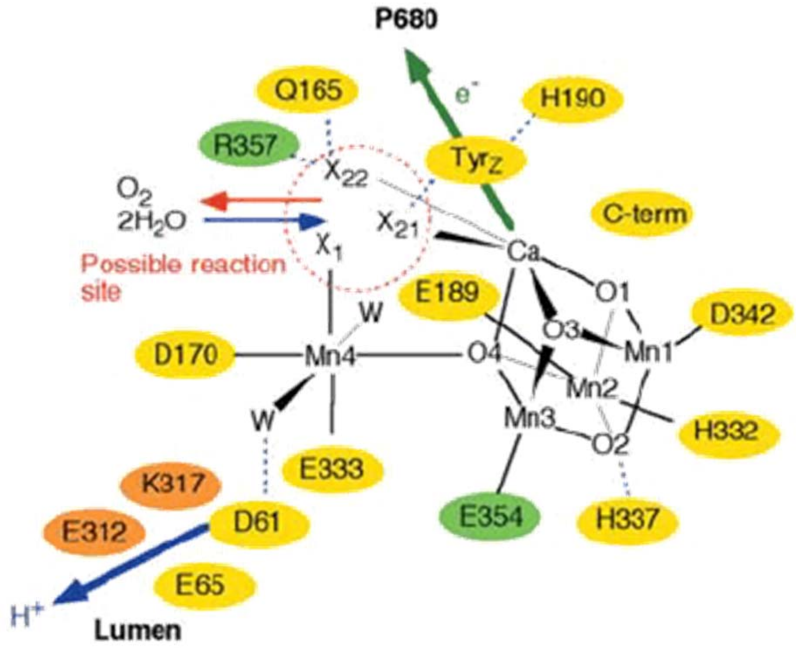

# Photosystem Two

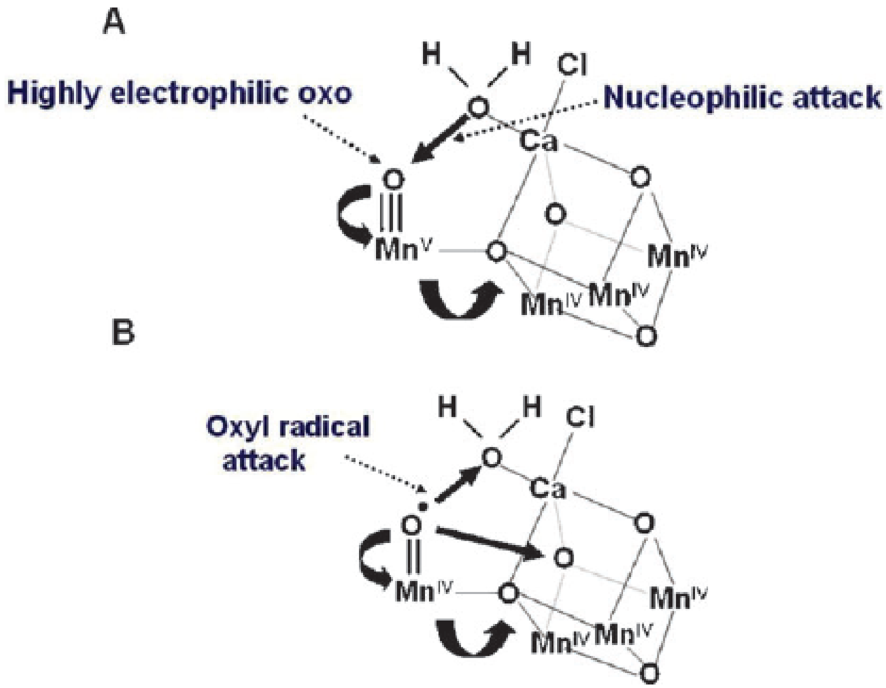
water splitting site

# Primary charge separation cofactors



# Water splitting cluster



# Calvin-Benson cycle