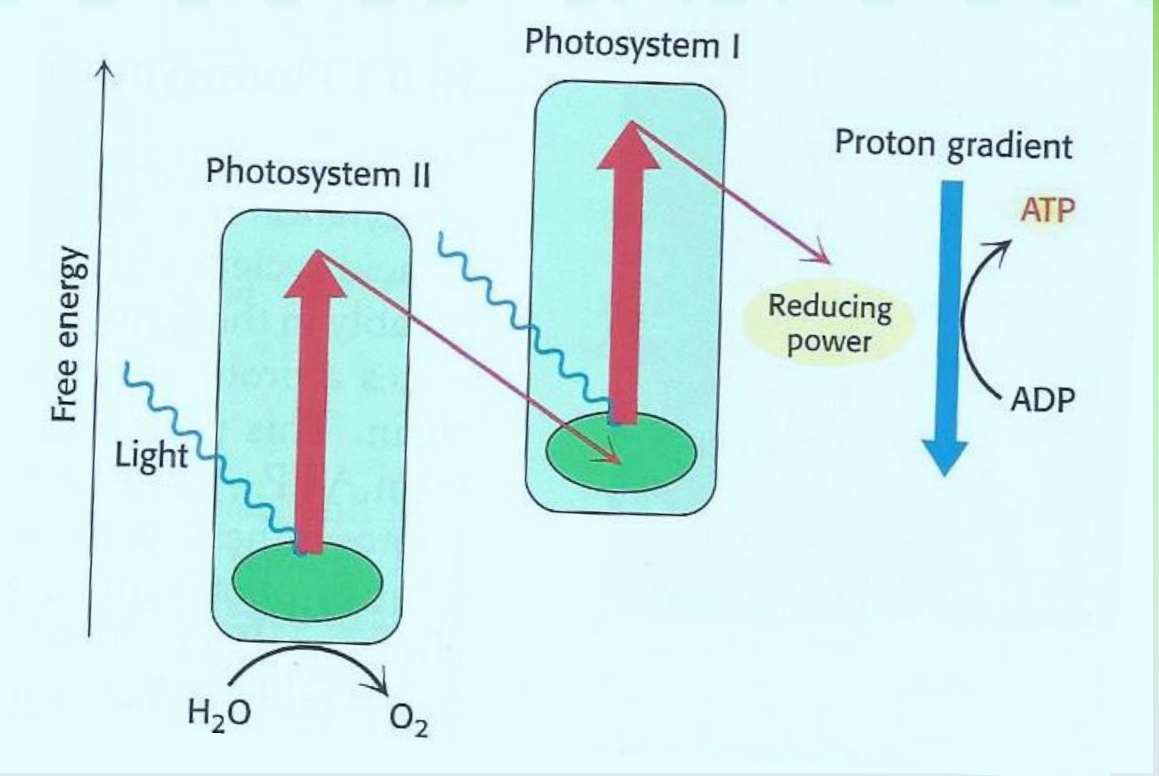
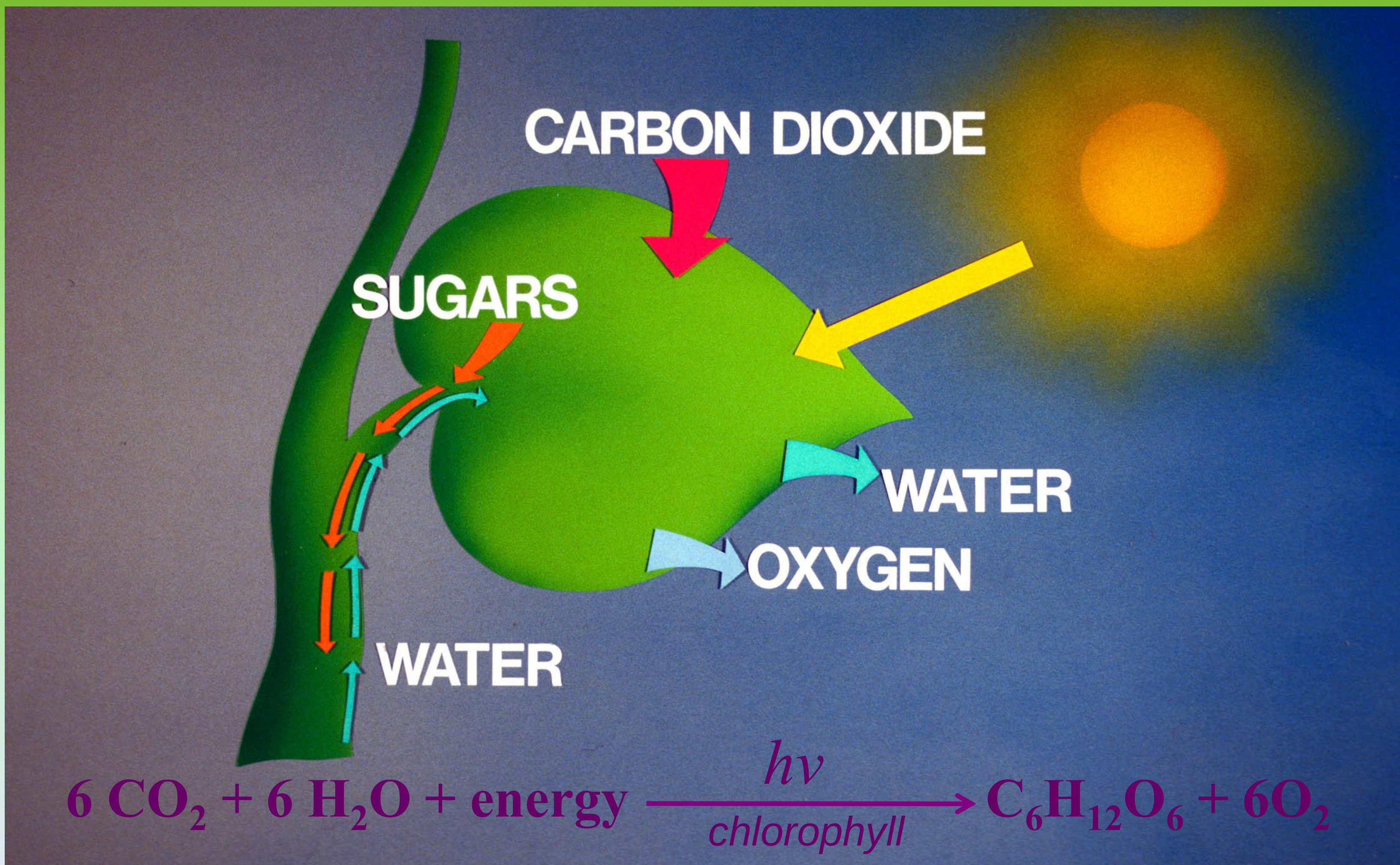
PHOTOSYNTHESIS



- Physico-chemical process which converts ***solar energy*** into ***chemical energy***
- The primary source of all food on earth.
- Responsible for the release of oxygen into the atmosphere
- Plants, some algae and cyanobacteria are photoautotrops

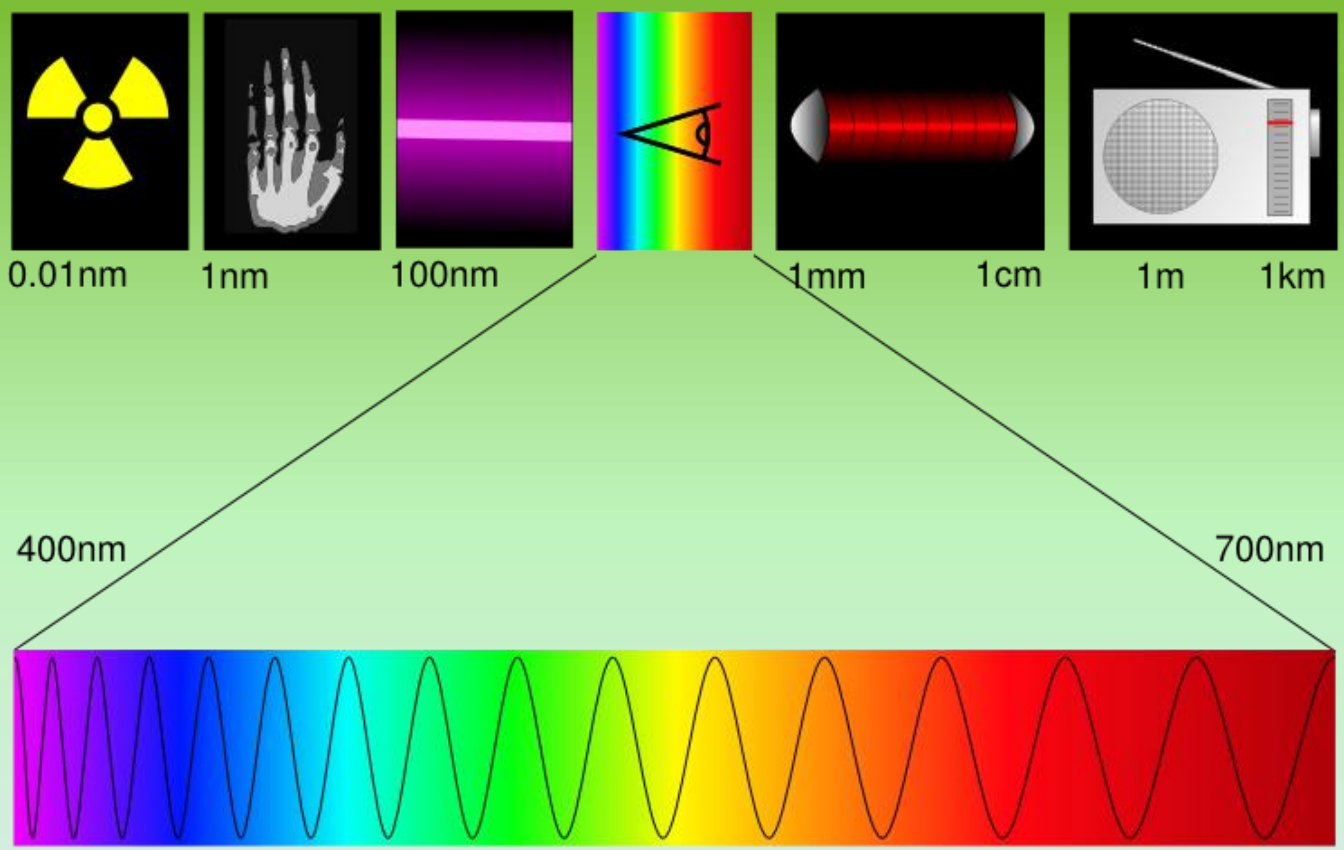


$$6\ CO_2 + 6\ H_2O + \text{energy} \xrightarrow[\text{chlorophyll}]{h\nu} C_6H_{12}O_6 + 6O_2$$

PROPERTIES OF LIGHT

Virtually all life depends on it!

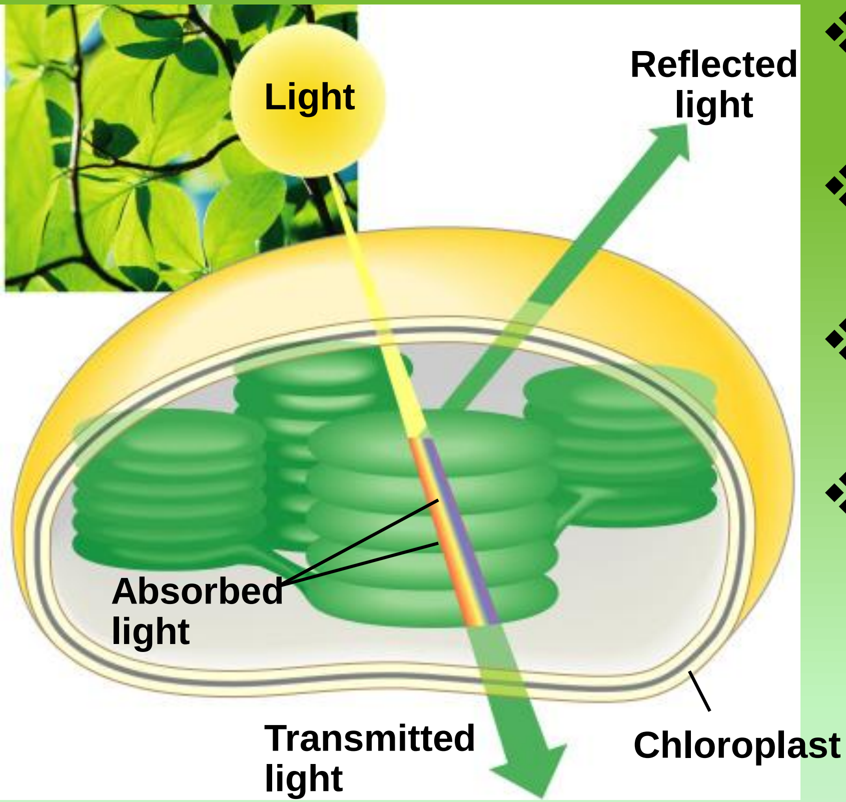
- Light moves in waves, in energy units called PHOTONS
- Energy of a PHOTON inversely proportional to its wavelength



- Visible light occurs in a spectrum of colors. It contains the right amount of energy for biological reactions

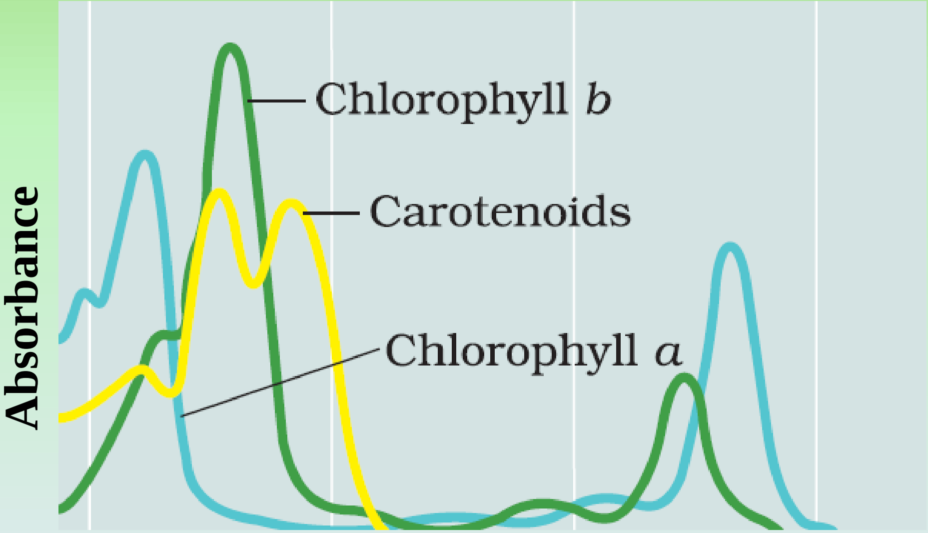
WHY ARE PLANTS GREEN?

Color of light seen is the COLOR NOT ABSORBED (reflected)

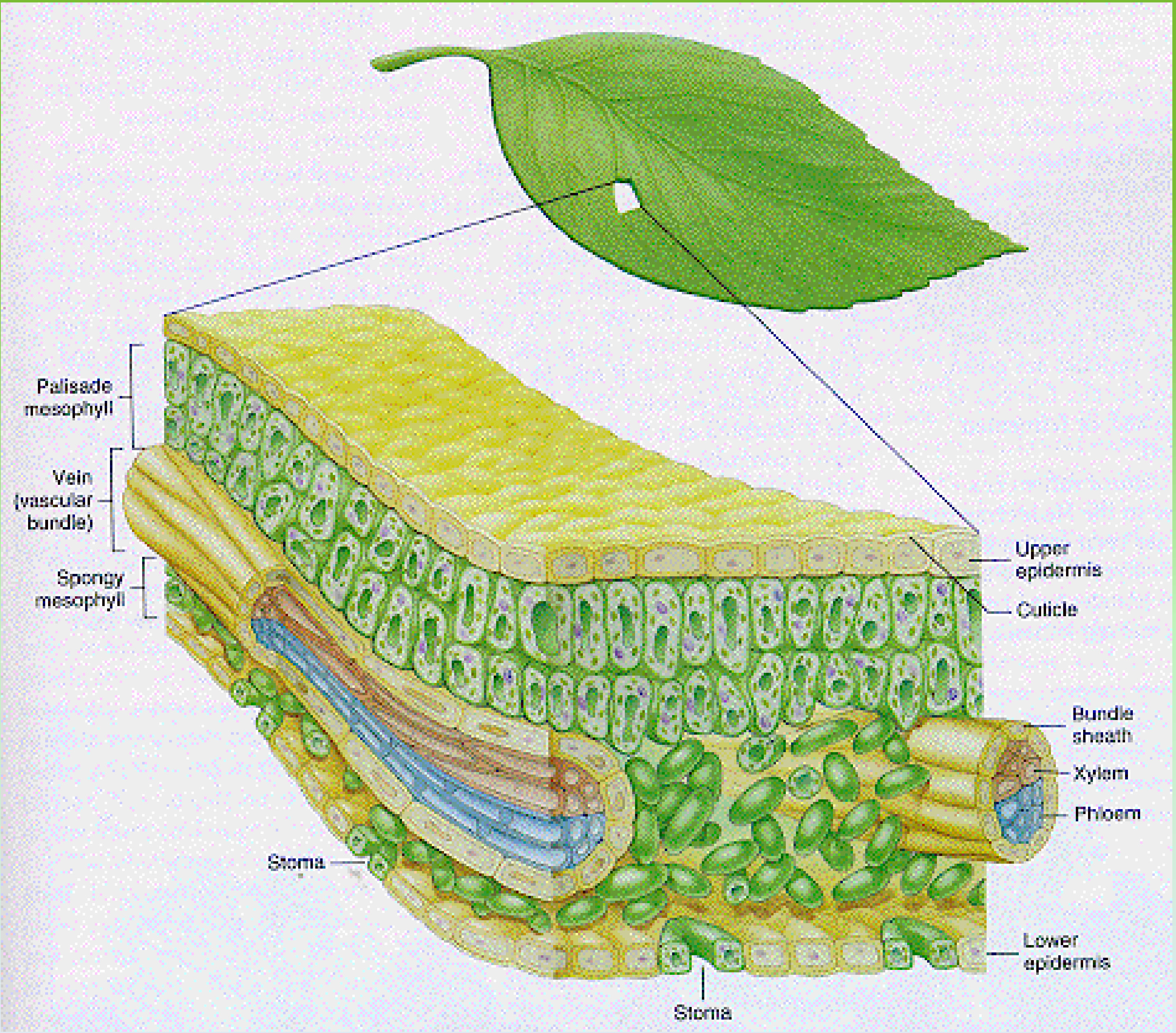


- Auxiliary Pigments: *chlorophyll b, carotenoids*
- Absorb light at different wavelengths, (extending the absorption range)
- Help transfer some energy to *chlorophyll a*
- Protect cell from harmful byproducts

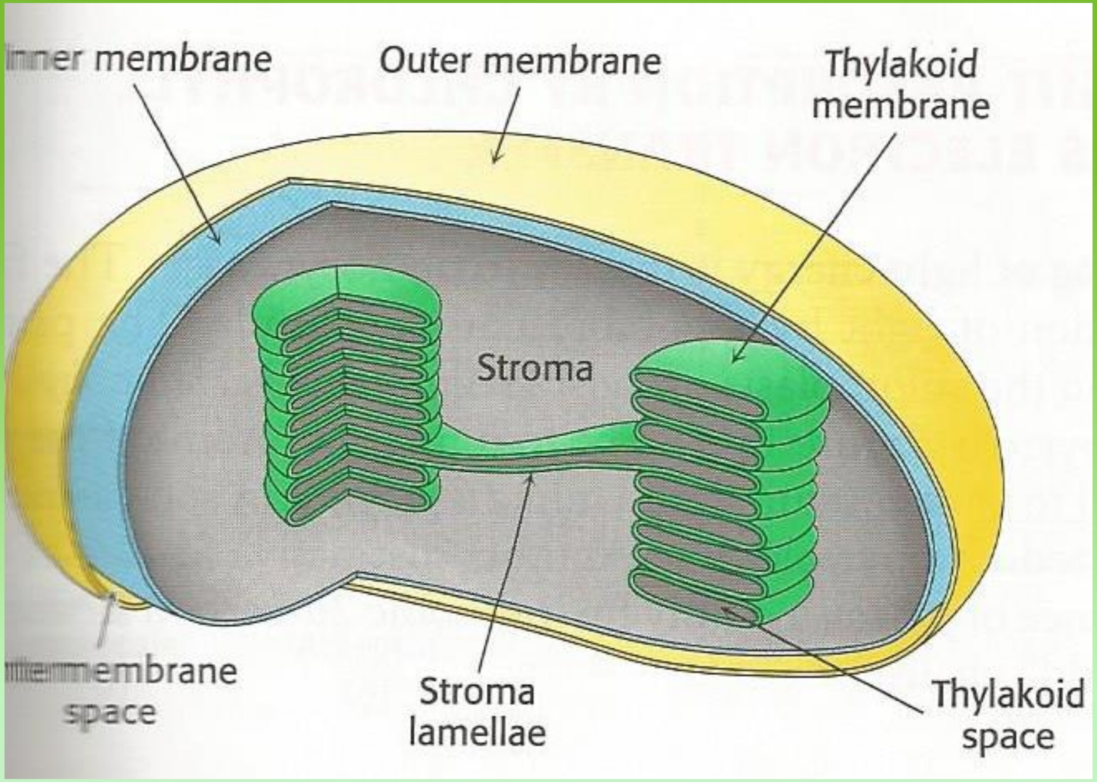
- Light is absorbed by **pigments**
- The primary pigment for photosynthesis is *chlorophyll a*
- It absorbs blue and red light, not green (green light is reflected back!)



Where does photosynthesis occur?

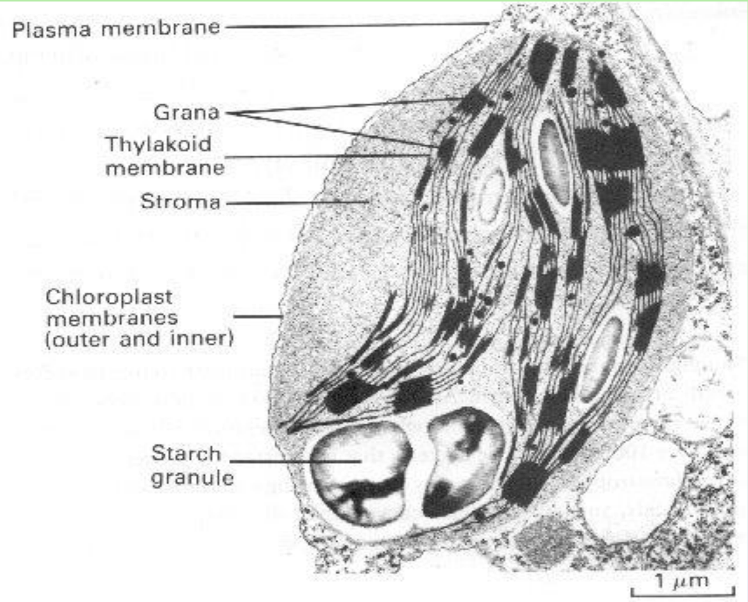


Chloroplasts: Sites of Photosynthesis



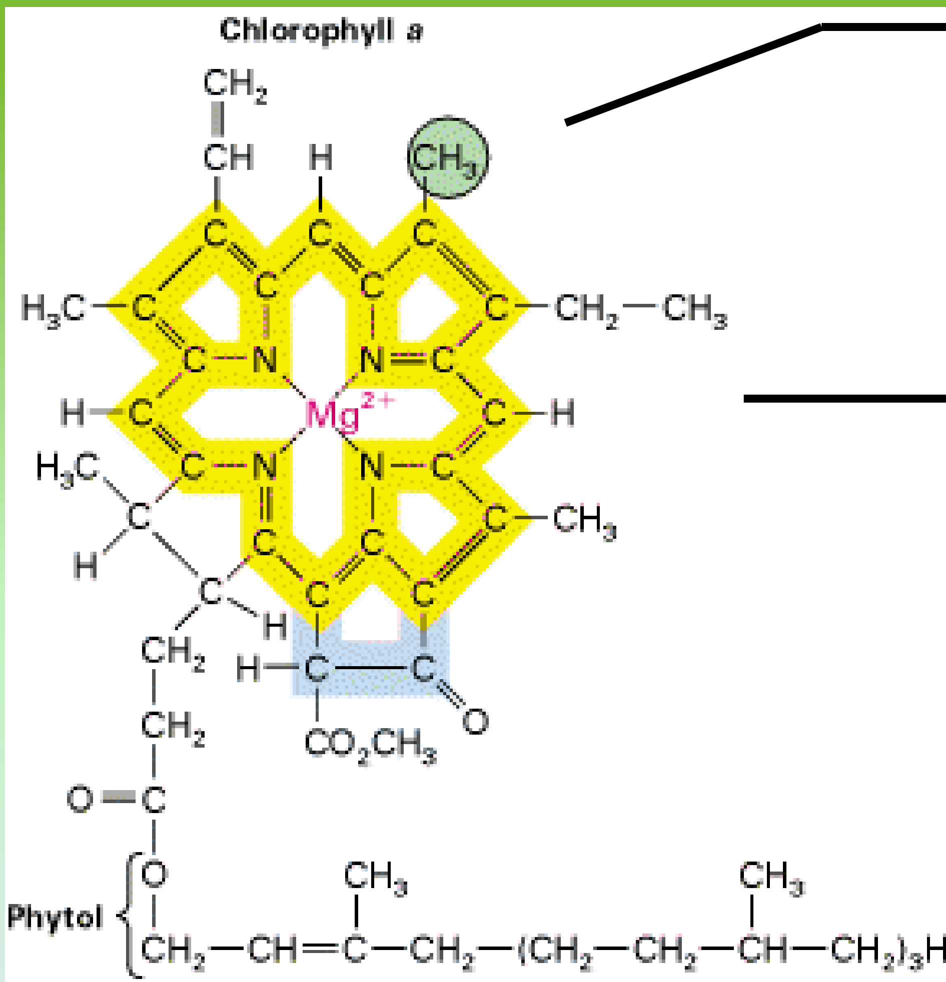
An outer membrane
    High permeability
An inner membrane
    Nearly impermeable
The stroma
    Aqueous; Contains enzymes, DNA, RNA, ribosomes
The "thylakoid"
    A membraneous compartment
    A single highly-folded vesicle
    "Grana" : disk-like sacs
    Grana are connected by "stromal lamellae"

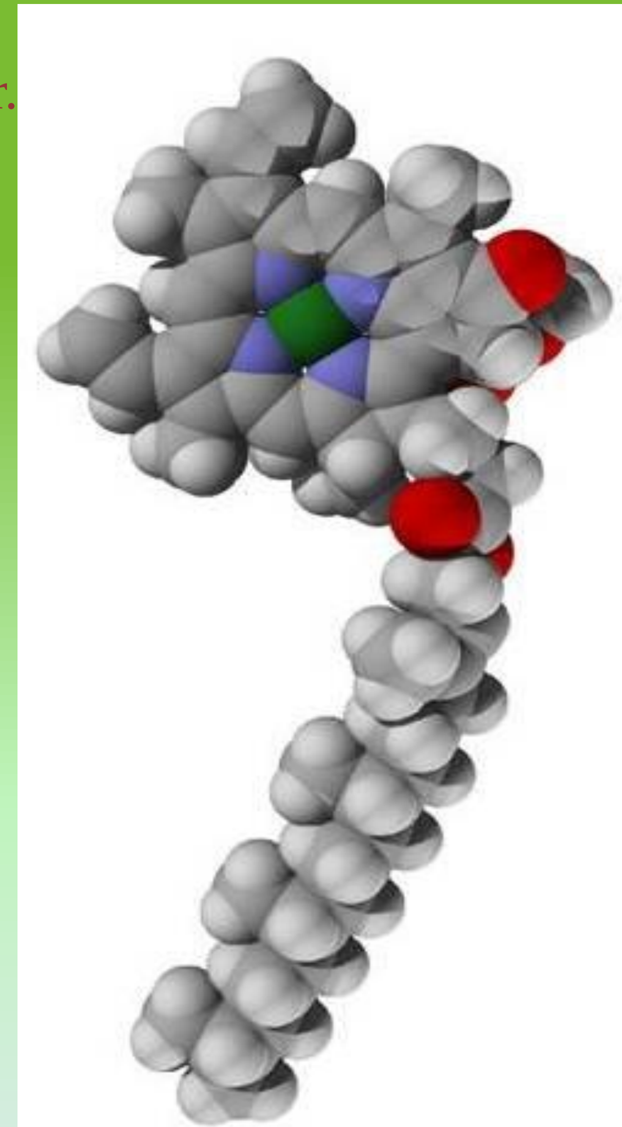
The thylakoid membrane of the chloroplast is impregnated with photosynthetic pigments



Chlorophyll a & b

- Located in the **thylakoid membranes**.
- A cyclic tetrapyrrole, like heme with **Mg**$^{+}$ in the center.
- A cyclopentanone ring is fused to pyrrole ring





Phytol tail

AN OVERVIEW OF PHOTOSYNTHESIS

- The light reactions convert solar energy to chemical energy
  - Produce ATP & NADPH
  - Occurs at Thylakoid

- The Calvin cycle makes sugar from carbon dioxide
  - ATP generated by the light reactions provides the energy for sugar synthesis
  - The NADPH produced by the light reactions provides the electrons for the reduction of carbon dioxide to glucose
  - Occurs in the Stroma

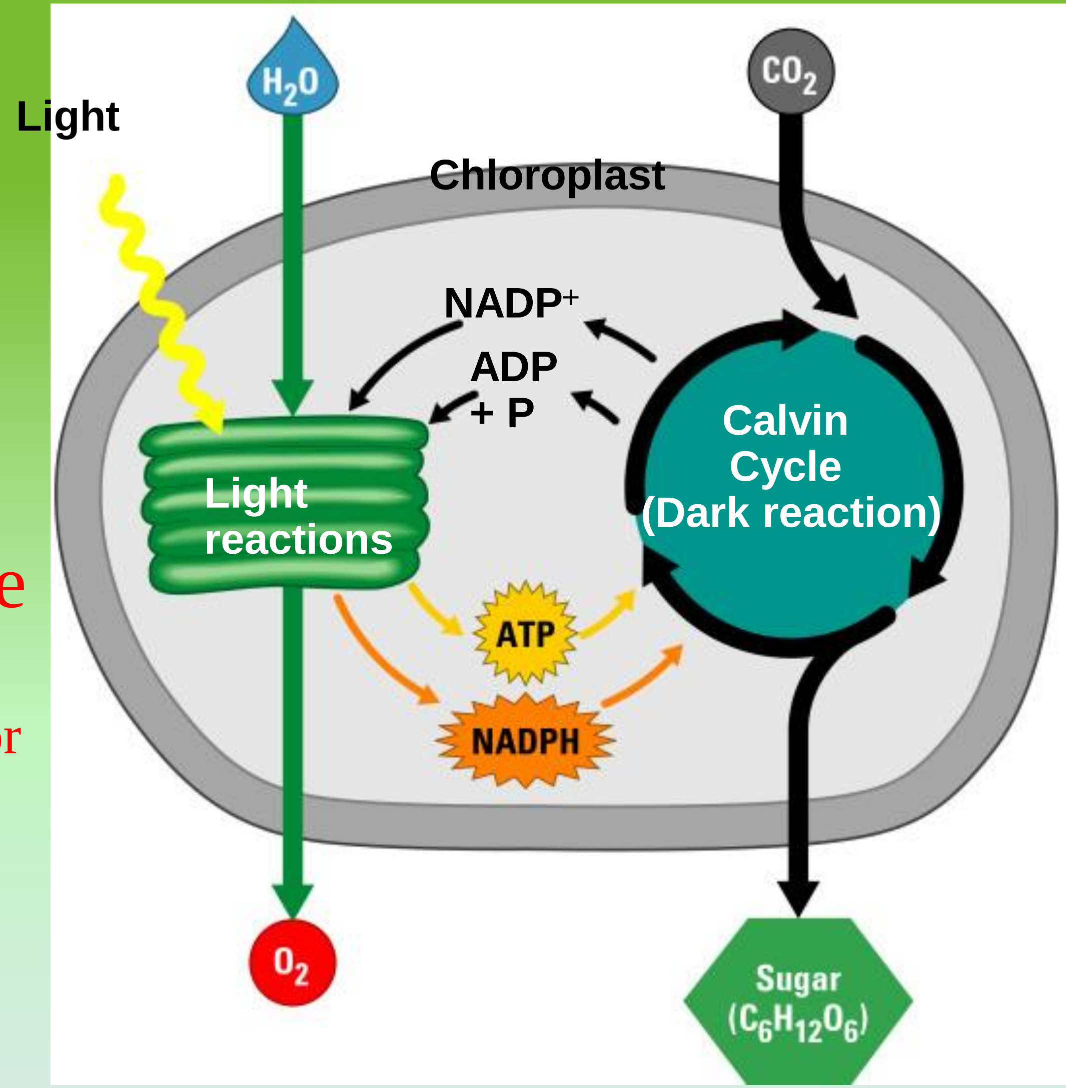
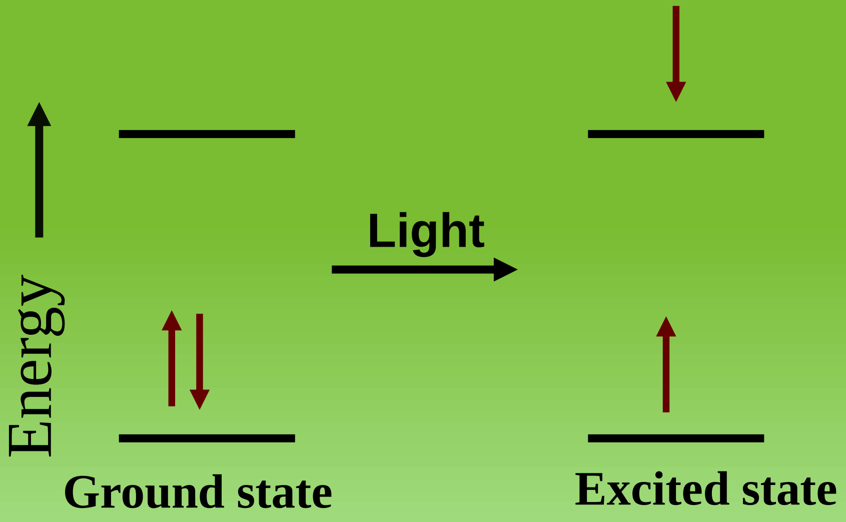


Photo Induced Charge Separation

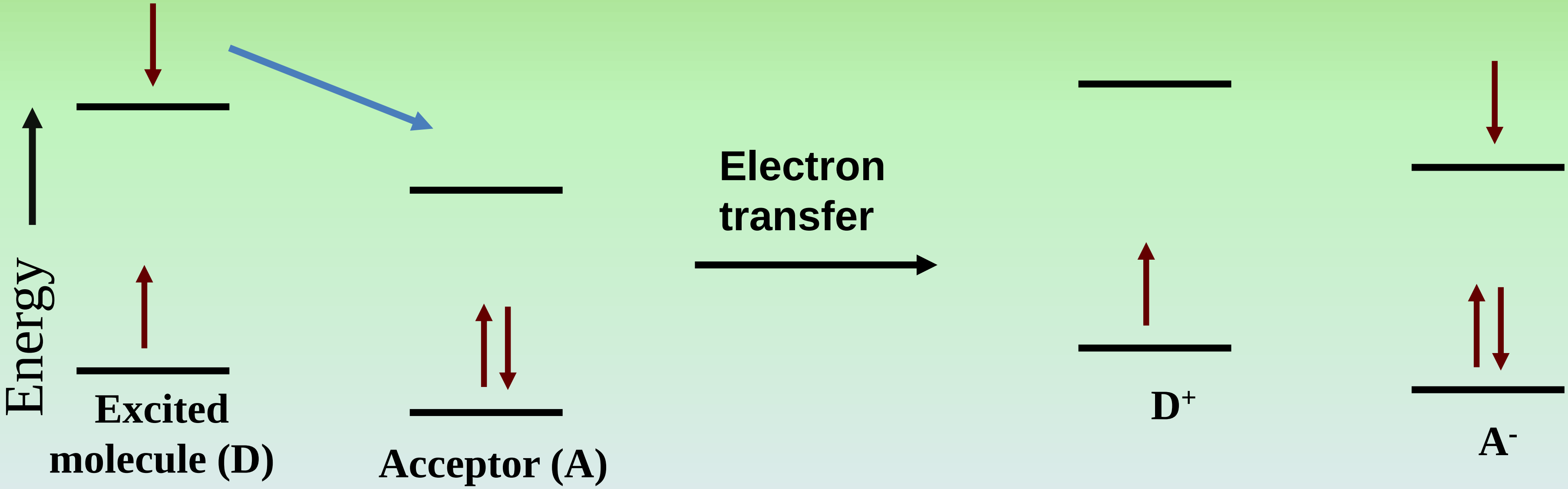


Fate of excited electron:

- ❑ Simply return to the ground state
- ❑ Chemical reactions
- ❑ Fluorescence, Phosphorescence

Fluorescence of isolated chlorophyll in solution

- ❑ **Acceptor molecules can receive the excited electron**



Excited electron reduce the acceptor molecule to store light energy in chemical forms

Light absorption and Electron Flow

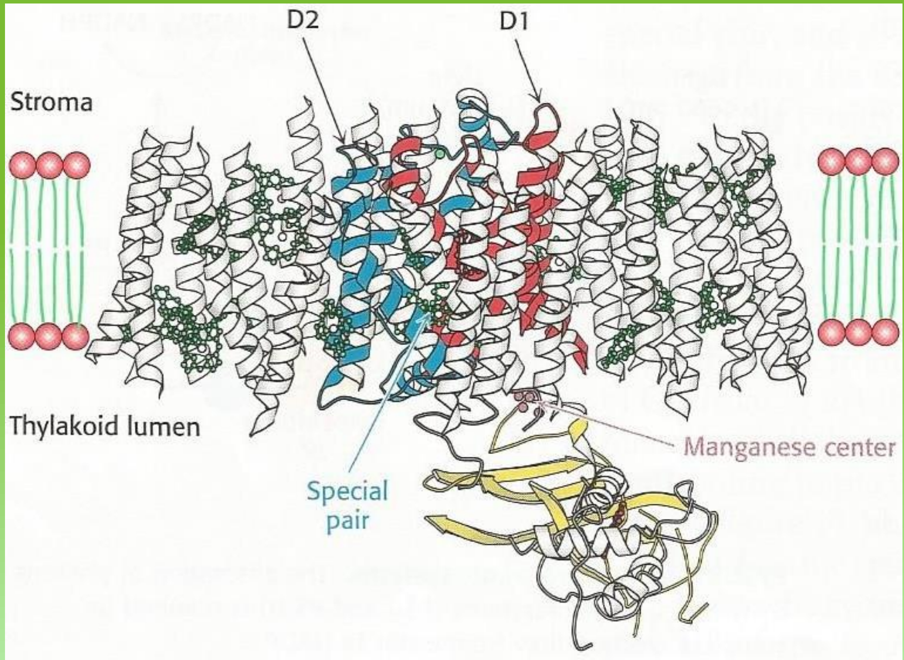
- Interplay of two photosystems linked by common intermediates
  - Photosystem I : > 700 nm *(13 polypeptide chain, more than 60 chlorophyll molecules, a quinone, 4Fe-4Ss clusters)*
  - Photosystem II : > 680 nm *(10 polypeptide chain, more than 30 chlorophyll molecules, a nonheme Iron ion and 4 Manganese ions)*

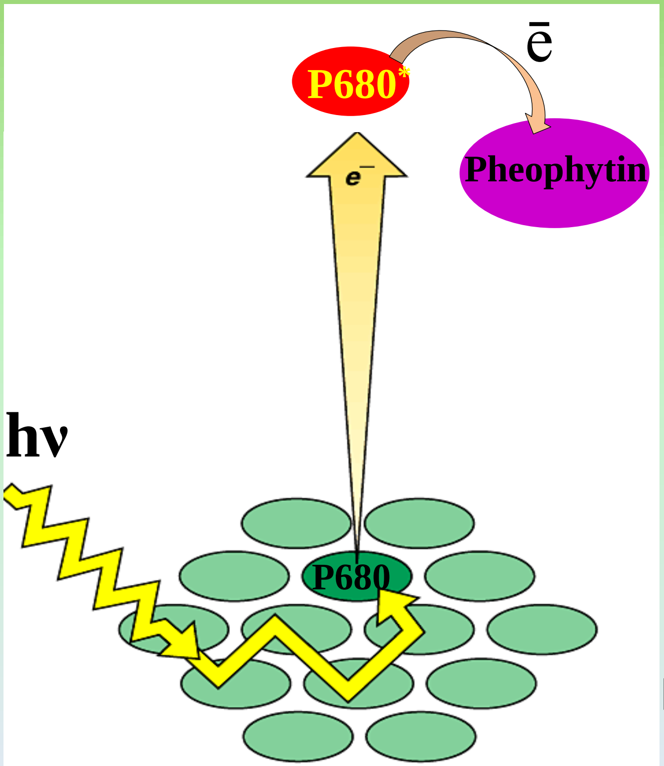
Electron Flow

- Photosystem II ⟶ Cytochrome *bf* ⟶ Photosystem I
- Electrons from water: Two molecules of water are oxidized to a molecule of O_2 for every 4 $\bar{e}$s sent through the electron transport chain
- Electrons reduce $NADP^+$ to NADPH
- Proton gradient generated across the thylakoid membrane drives the formation of ATP

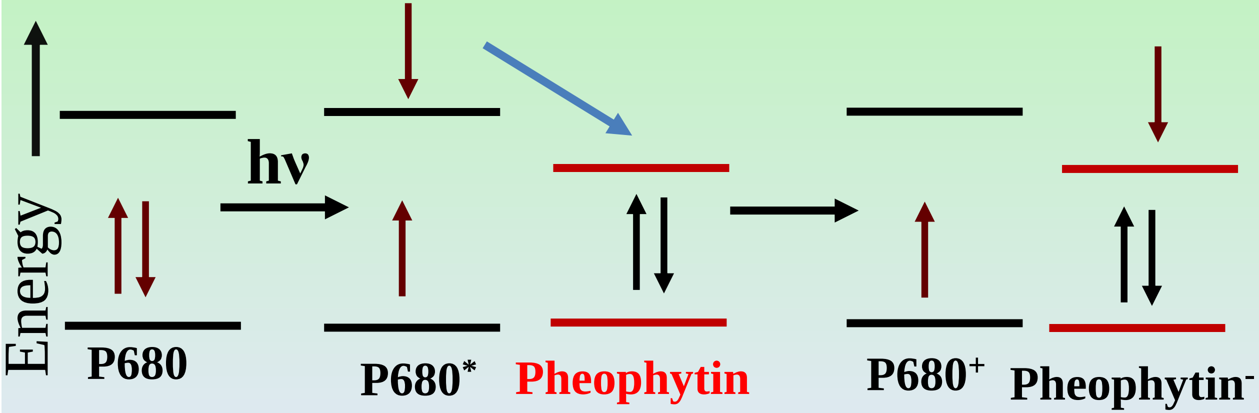
Photosystem I

- The core is formed by D1 and D2, pair of similar 32-kd subunits that span the thylakoid membrane
- Photochemistry begins with the excitation of a special pair (P680) of chlorophyll molecules



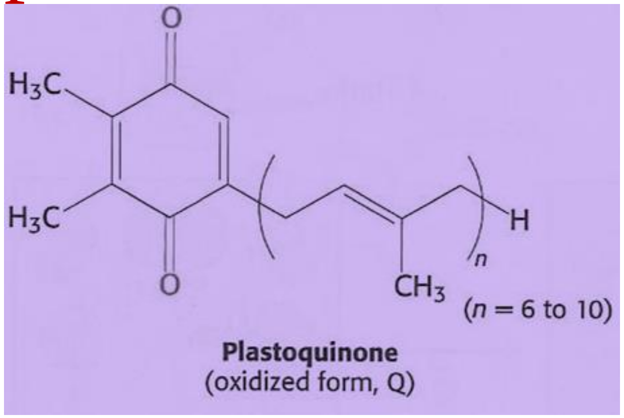


- On excitation P680 rapidly transfers an electron to a nearby pheophytin.

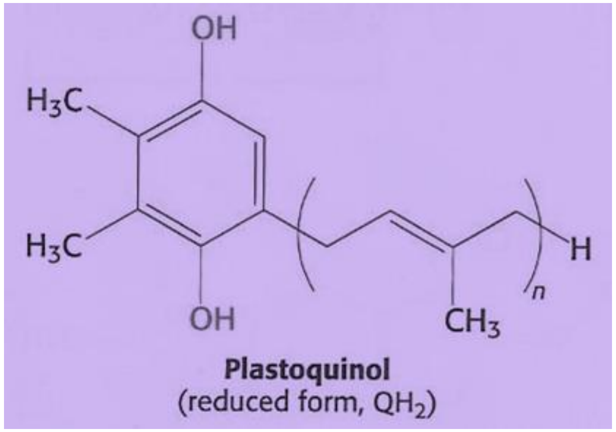


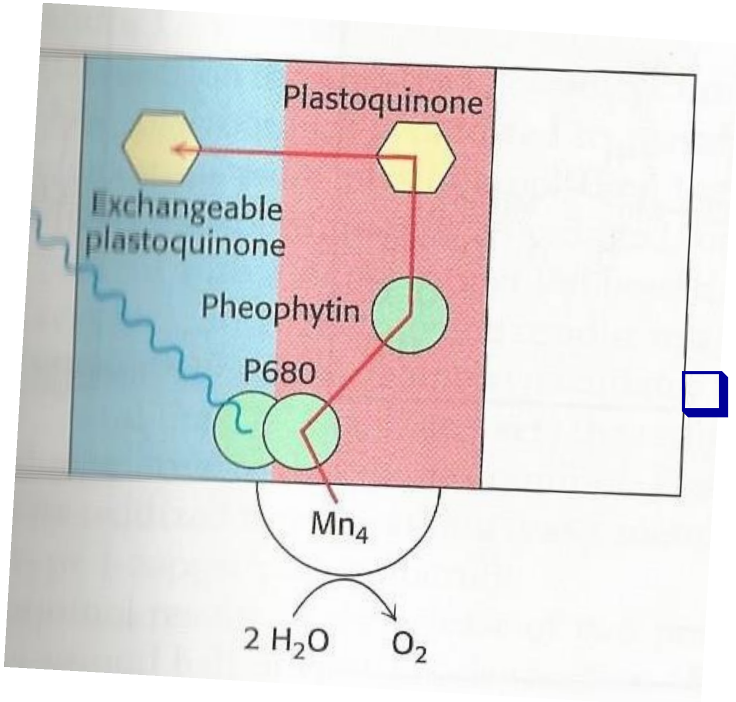
Electron Transport

- From pheophytin ē is transferred first to tightly bound plastoquinone at site Q_A and then to an exchangeable plastoquinone at site Q_B
- With the arrival of a second ē and uptake of two protons the exchangeable plastoquinone reduced to QH_2



$\downarrow 2H^+, 2ē$

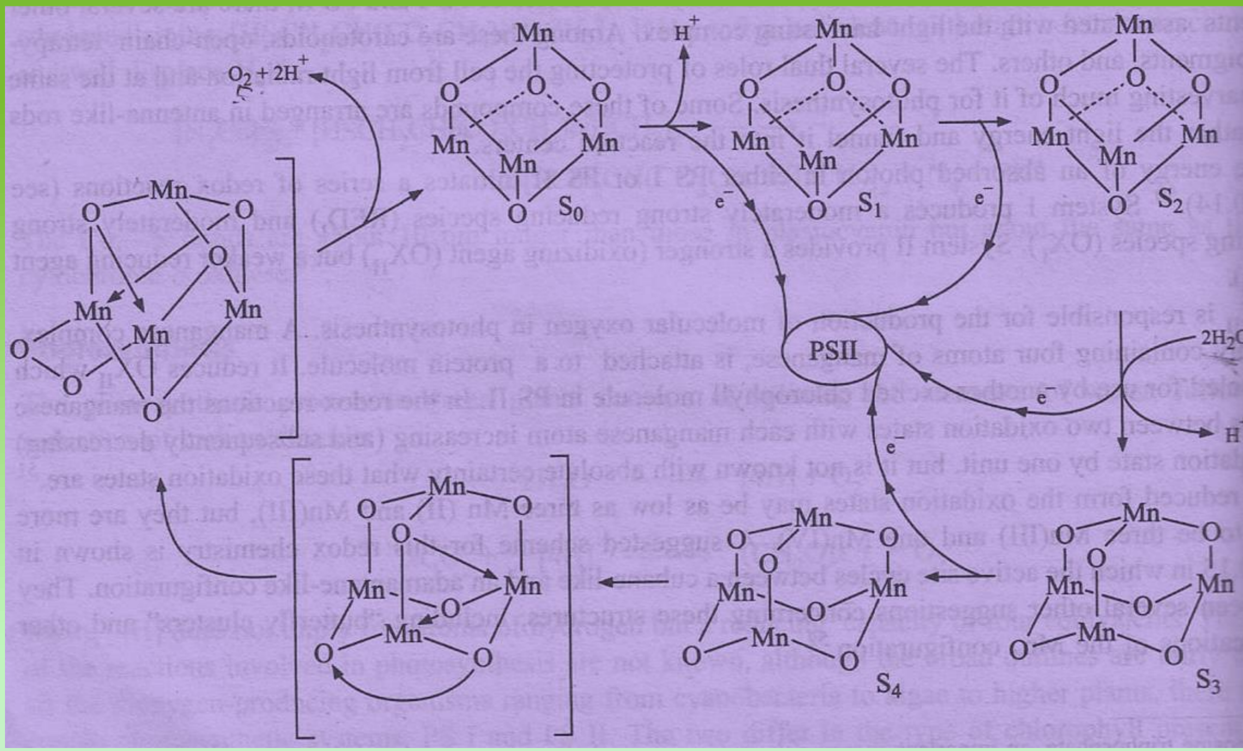




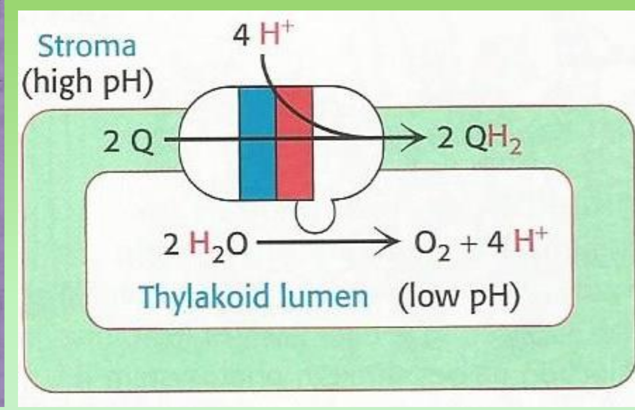
- $P680^+$ extracts ēs from the water molecules bound at Mn center to neutralize the positive charge.

Water splitting system

- Water splitting center includes 4 Mn ions, a Ca ion, a Cl ion and a tyrosine residue that forms a radical



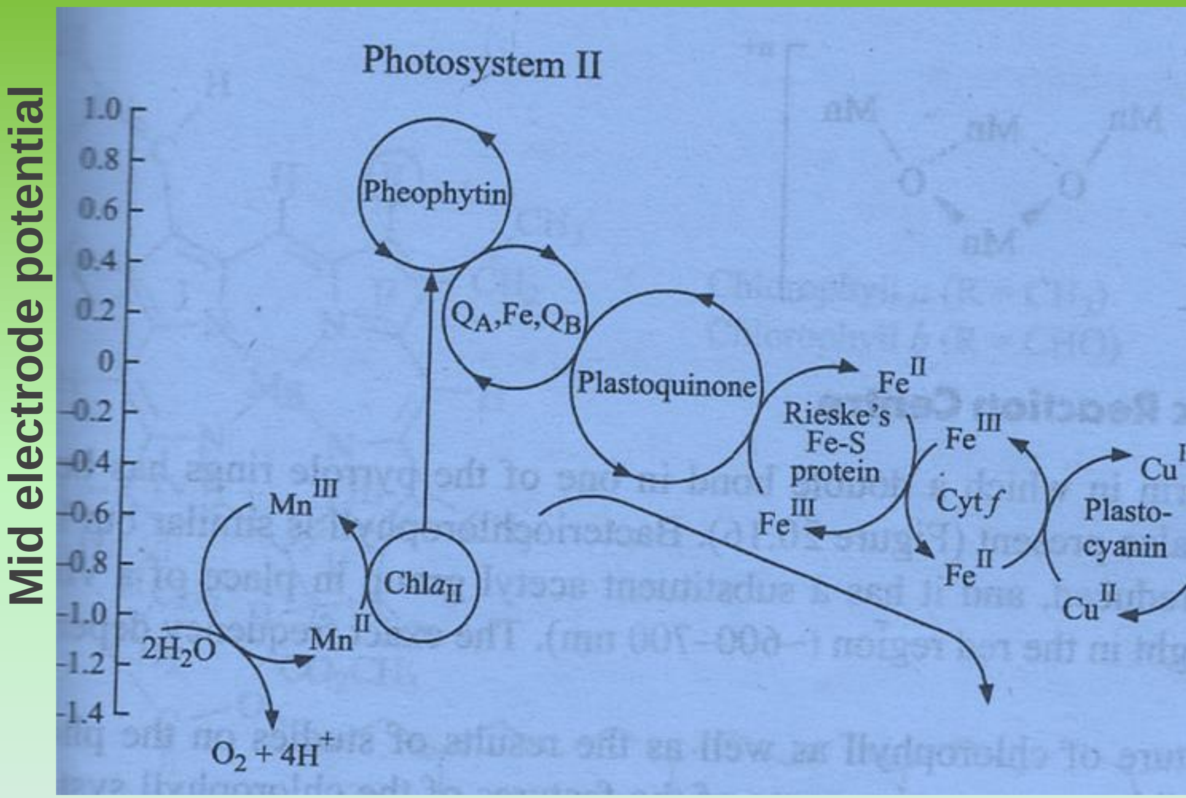
$$2H_2O$$
$$\downarrow$$
$$4H^+ + O_2 + 4\bar{e}$$



- Four ēs harvested from water are used to reduce two molecules of Q to QH_2
- Two H^+ are taken from the stroma for the reduction of plastoquinone and 4 H^+ are liberated into the thylakoid lumen, resulting in a proton gradient

Cytochrome *bf* links PSI and PSII

- ❑ Cytochrome *bf* complex includes 4 subunits: a 23-kd cytochrome with 2 b-type hemes, a 20-kd Reiske-type Fe-S protein, a 33-kd cytochrome f and a 17-kd chain.
- ❑ The complex catalyzes the electron transport through a Q cycle.

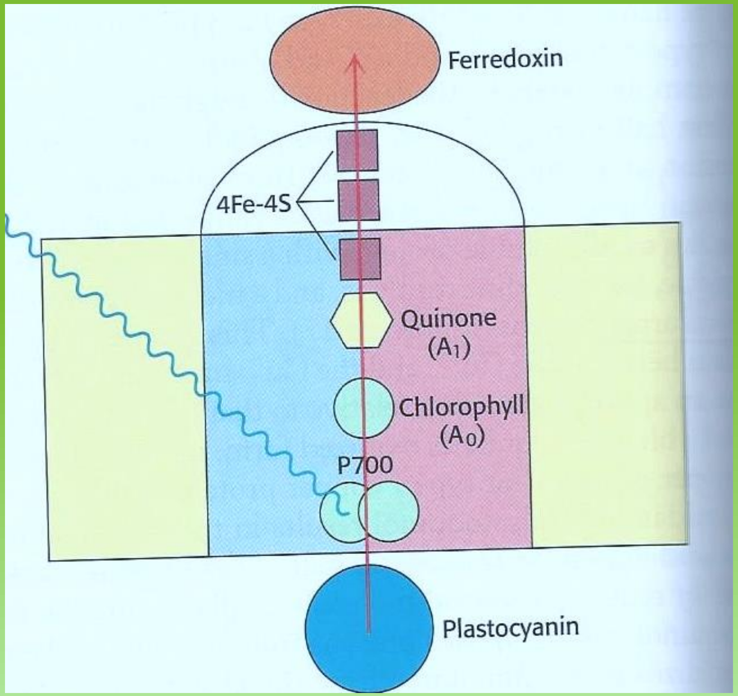


- ❖ Plasoquinol oxidized to plasoquinone
- ❖ ēs flow through Fe-S protein to convert oxidized plastocyanin (P_c) into its reduced form
- ❖ P_c is a Cu protein in thylakoid lumen, with interconvertible oxidation states +2 and +1.

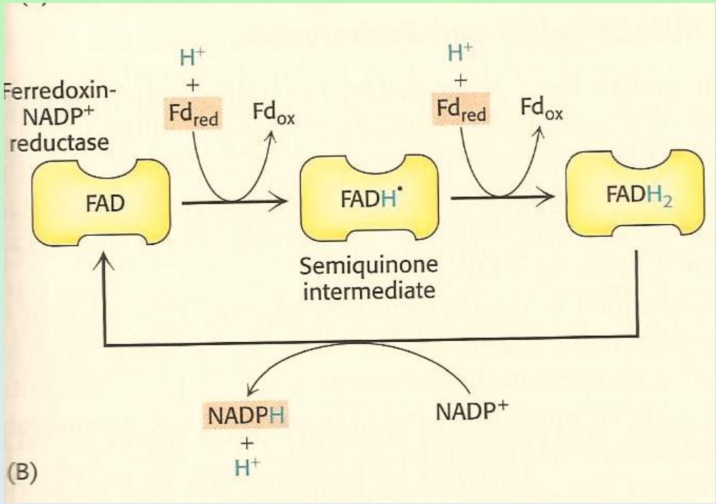
- ❑ Cytochrome *bf* complex oxidizes QH_2 to Q and 4 H^+ are released into thylakoid lumen further increasing the proton gradient.

Photosystem I

- The final stage of light reactions
- The core is a pair of similar subunits psaA (83kd) and psaB (82kd)
- Special pair of chlorophyll at the center, P700 initiates photoinduced charge separation.
- The ē is transferred down a pathway chlorophyll at site A_0 and quinone at site A_1 to a set of 4Fe-4S clusters.
- From there the electron is transferred to ferredoxin (Fd).
- The enzyme ferredoxin-NADP$^+$ reductase accepts 2 ēs from ferredoxin to form NADPH through a semiquinone intermediate.
- The uptake of proton to reduce NADP$^+$ further contributes to proton gradient.

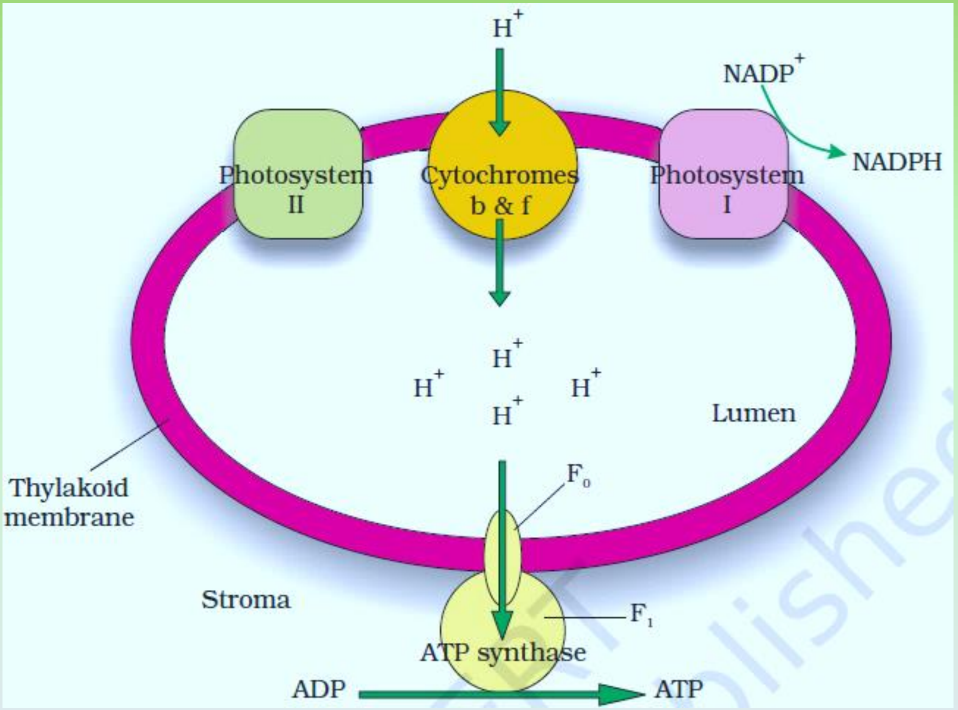


$$Pc(Cu^{+}) + Fd_{ox} \xrightarrow{\text{Light}} Pc(Cu^{2+}) + Fd_{red}$$



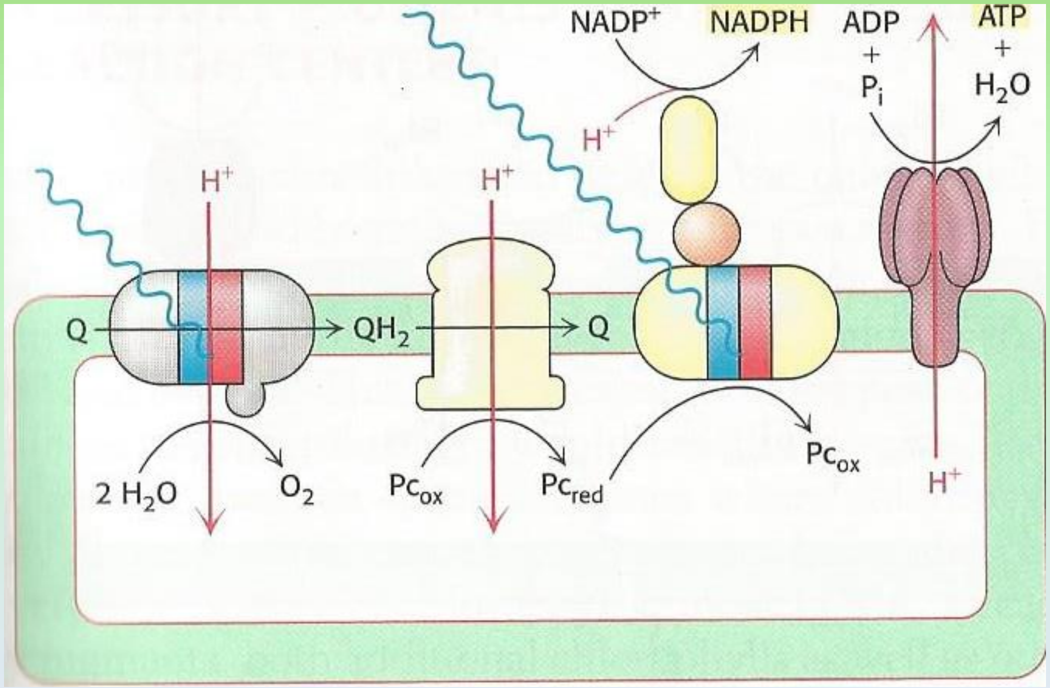
Chemiosmotic hypothesis of ATP synthesis

- Protons in the stroma decrease in number, while in the lumen there is accumulation of protons during the light reaction
- A proton gradient is generated across the thylakoid membrane with measurable decrease of pH in the lumen (about 4).
- The energy inherent in the proton gradient is called the proton motive force.
- The light induced transmembrane proton gradient is about 3.5 pH units which corresponds to a proton motive force of 0.20 V or a ΔG of -20.0 KJ/mol
- The proton motive force is converted into ATP by the *ATP synthase* of chloroplasts.



ATP synthesis

- The *ATP synthase* enzyme (CF_1-CF_0 complex) consists of two parts:
  - F_0: embedded in the membrane and forms a transmembrane channel to conduct protons across the membrane.
  - F_1: Protrudes on the outer surface of the thylakoid membrane on the side that faces the stroma catalyses the formation of ATP.
- The break down of the gradient provides enough energy to cause conformational change in the F_1 particle of the ATPase, activate ATPase enzyme to catalyses the formation of ATP



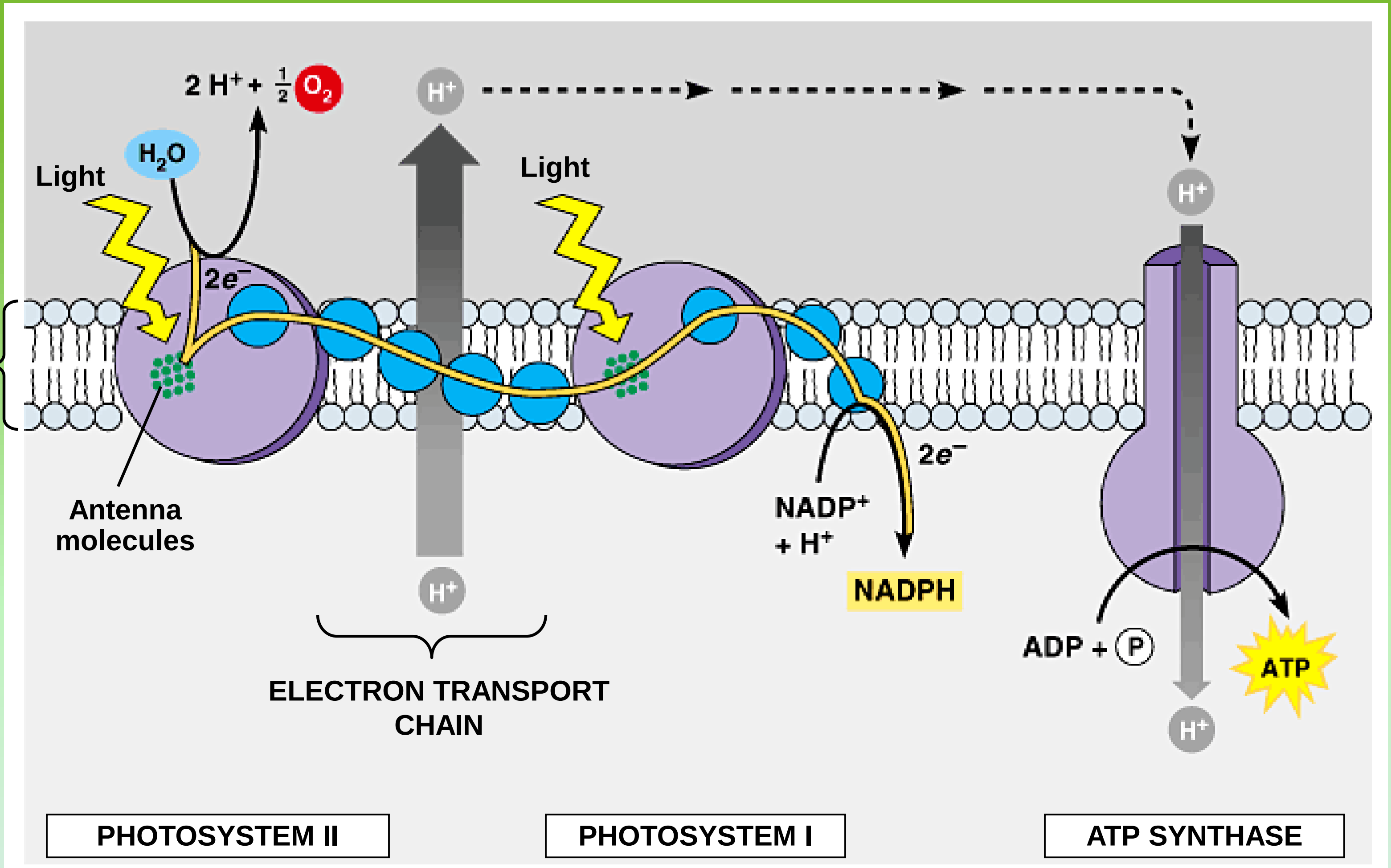
- The products of the light reactions, ATP and NADPH are released into the stromal surface for subsequent dark reaction

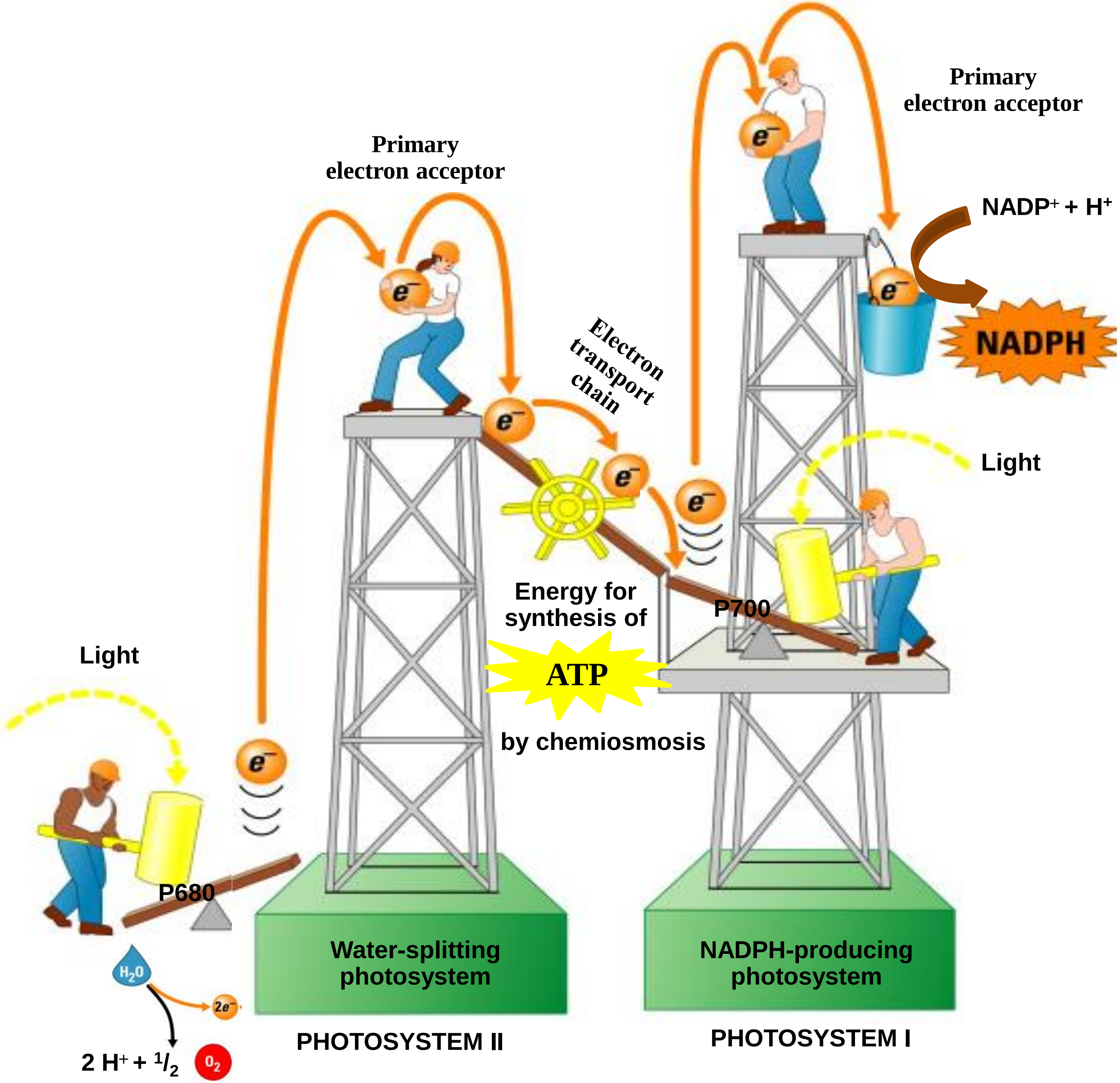
Production of ATP by chemiosmosis

Thylakoid compartment (high H^+)

Thylakoid membrane

Stroma (low H^+)

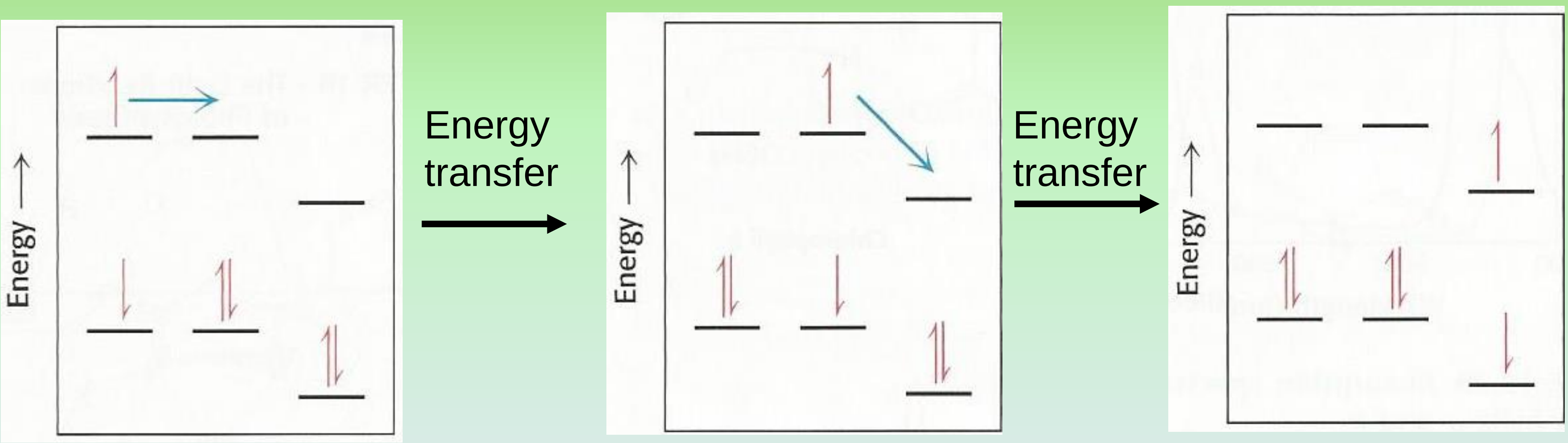




Primary
electron acceptor
Primary
electron acceptor
NADP+ + H+
NADPH
Electron
transport
chain
Light
Energy for
synthesis of
ATP
by chemiosmosis
P700
Light
P680
H2O
2e−
2 H+ + 1/2 O2
Water-splitting
photosystem
NADPH-producing
photosystem
PHOTOSYSTEM II
PHOTOSYSTEM I

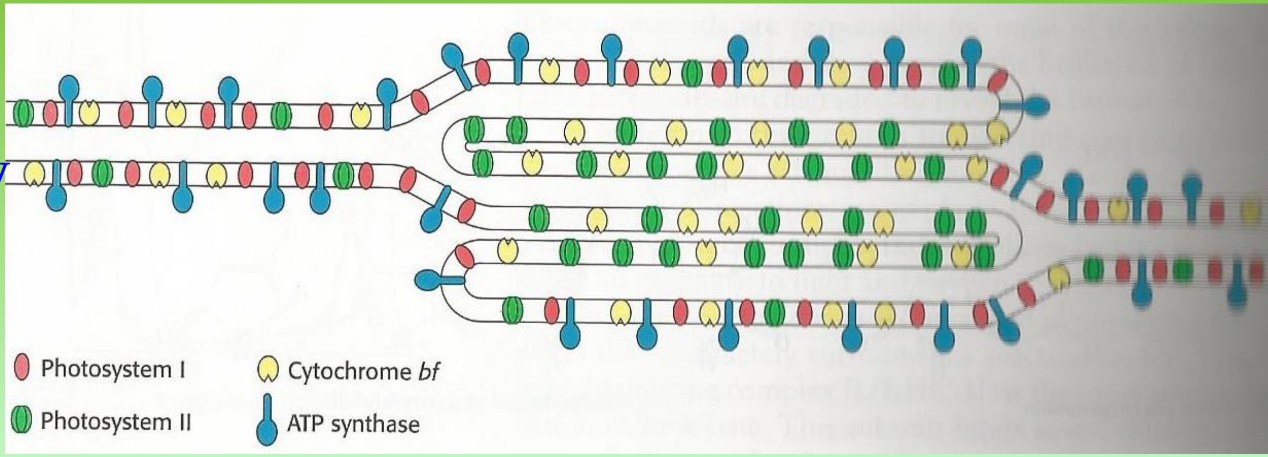
Auxiliary Pigments funnel energy into reaction center

- Energy absorbed by one molecule can be transferred to nearby molecules with excited states of equal or lower energy
- These transfer of energy through electromagnetic interactions in space is called resonance energy transfer
- The excited state of special pair of chlorophyll molecules is lower in energy than for single chlorophyll molecule



Organization of Photosynthetic Components

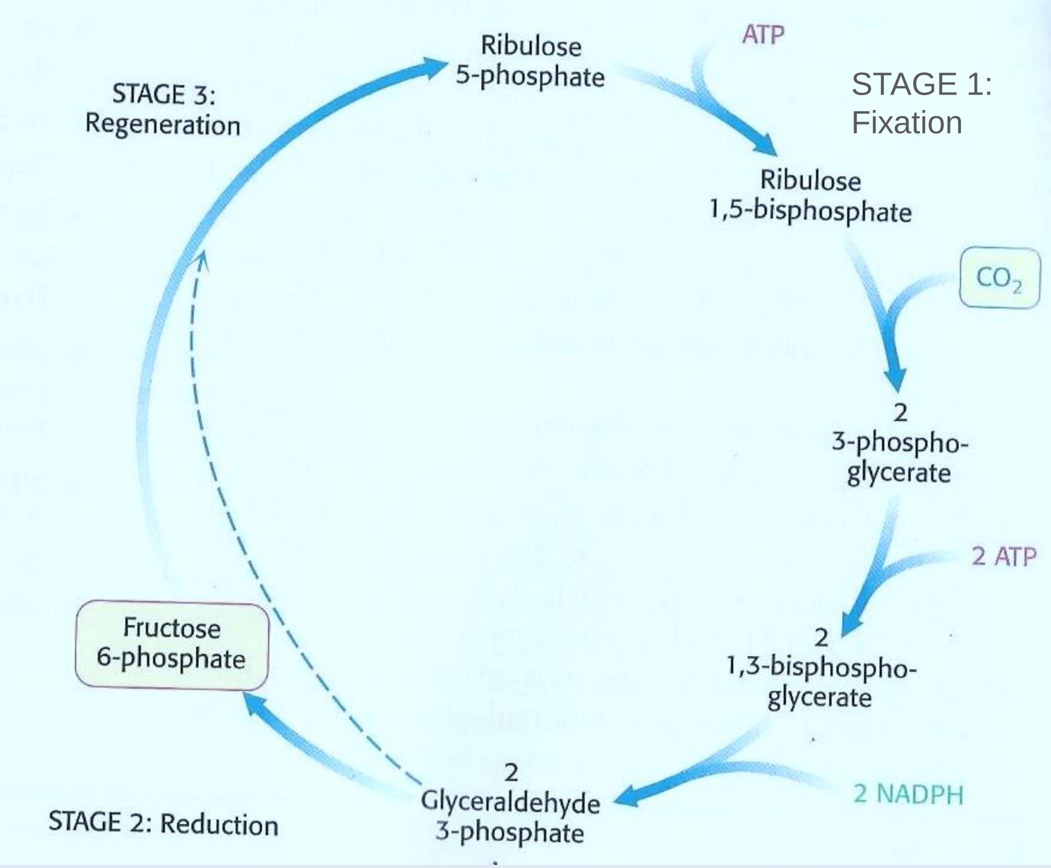
- Thylakoid membranes are differentiated into stacked and unstacked regions.
- Stacking increases the amount of thylakoid membranes in a given chloroplast volume. Only unstacked regions have direct contact with the stromal region.
- PSI and ATP Synthase are located exclusively in unstacked region.
- PSII is present mostly in the stacked region.



- Cytochrome *bf* complex is found in both regions and rapidly moves back and forth between the stacked and unstacked regions.
- Plastoquinone and plastocyanin are mobile carriers of electrons.
- Common internal thylakoid space enables H^+ liberated by PSII in stacked membranes to be utilized by ATP synthase molecule located in unstacked membranes

DARK REACTION: CALVIN CYCLE

- Named after Melvin Calvin, biochemist who elucidated the pathway
- Not a photochemical reaction
- Source of C atom is the simple CO_2 molecule
- Reduce carbon atoms from CO_2 to hexose sugar
- Takes place in the stroma of the chloroplast



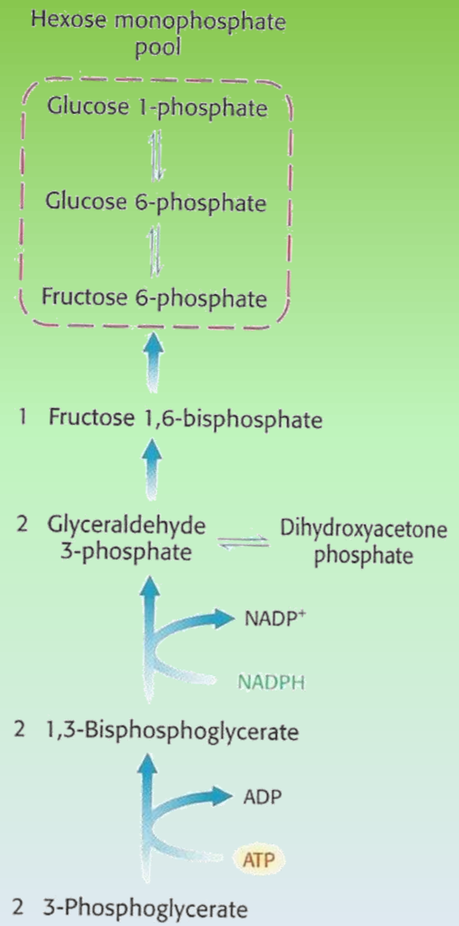
Comprises of three stages

- Fixation of CO_2 by ribulose-1,5-biphosphate to form 3-phosphoglycerate
- Reduction of 3-phosphoglycerate to form hexose sugars
- Regeneration of ribulose-1,5-biphosphate

CALVIN CYCLE

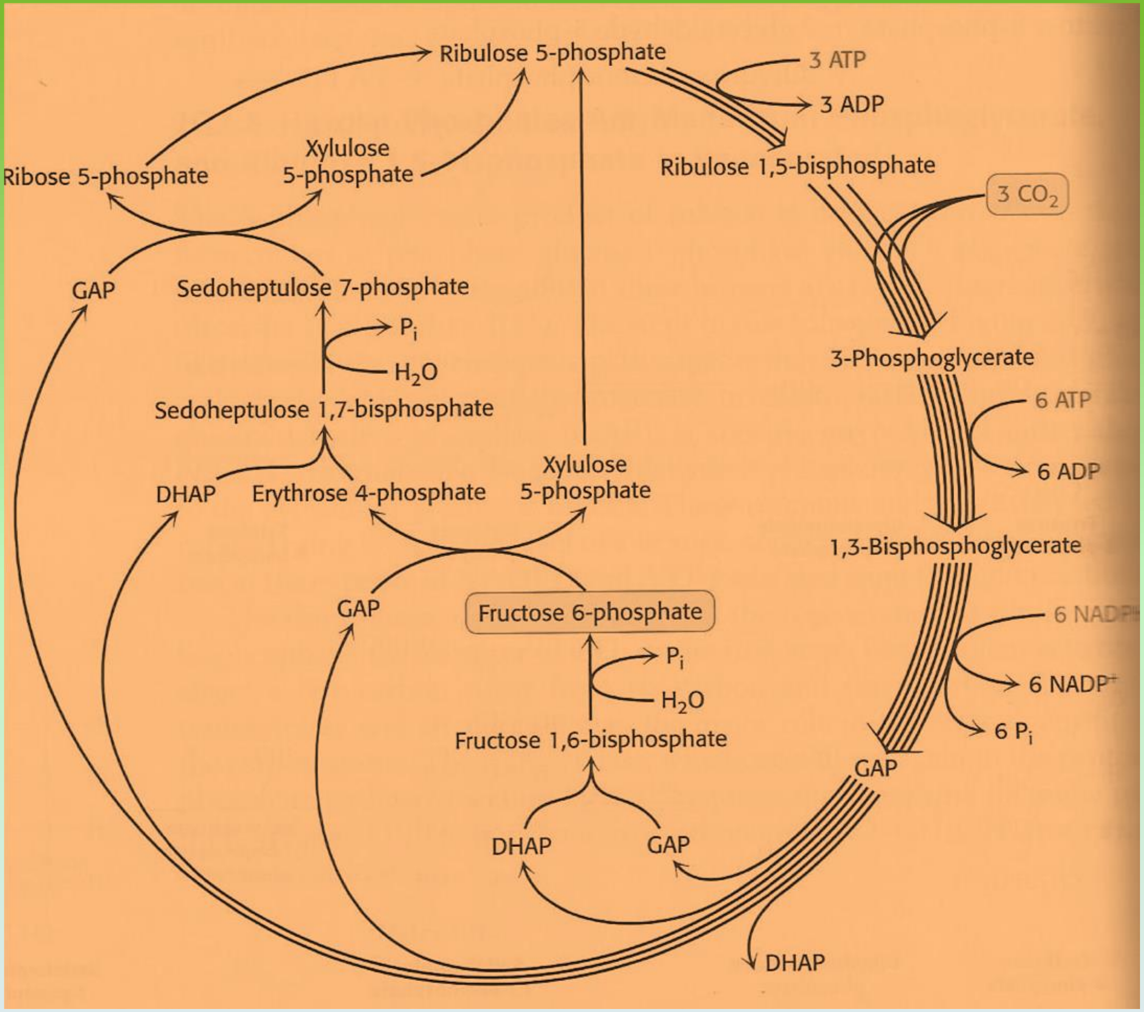
- CO_2 molecule condenses with ribulose-1,5-biphosphate to form 2 molecules of 3-phosphoglycerate. The reaction is catalysed the enzyme Rubisco.
- 3-phosphoglycerate is next converted into three forms of hexose phosphate which are readily interconvertible viz glucose-1-phosphate, glucose-6-phosphate and fructose-6-phosphate.
- Third phase is the regeneration of ribulose-1,5-biphosphate: Construct 5 C sugar from 6 C and 3 C sugars.
- Enzymes transketolase and aldolase catalyse the reaction.
- Ribulose-5-phosphate formed is phosphorylated to regenerate Ribulose-1,5-biphosphate
- The sum of these reactions is:

  Fructose-6-phosphate + glyceraldehyde-3-phosphate + dihydroxyacetone phosphate + 3 ATP ⟶ *3 Ribulose-1,5-phosphate + 3 ADP*



Complete reactions of CALVIN CYCLE

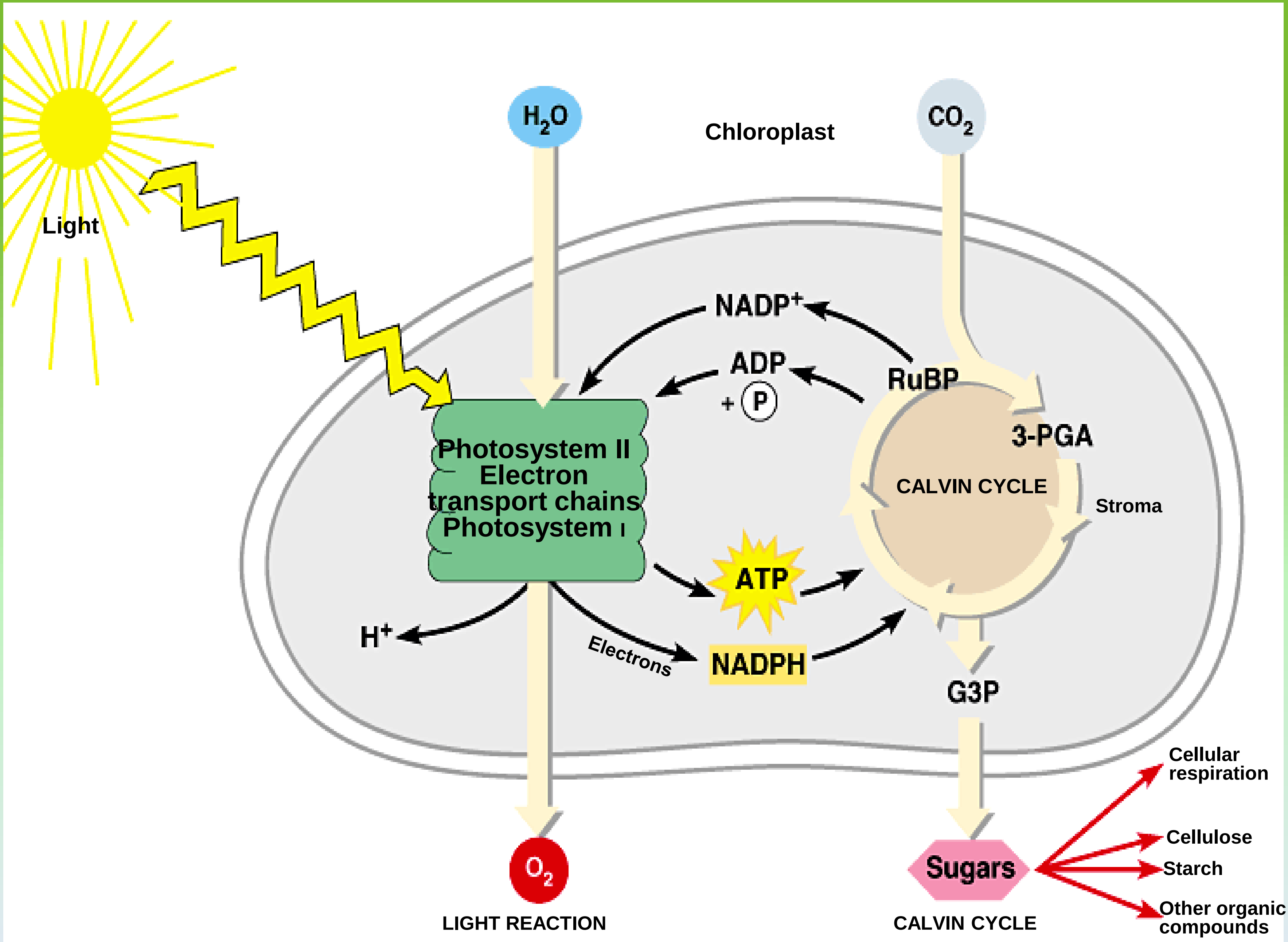
- 6 rounds of Calvin cycle is required to synthesize a hexose
- 12 molecules of ATP are expended in phosphorylating 12 molecules of 3-phosphoglycerate

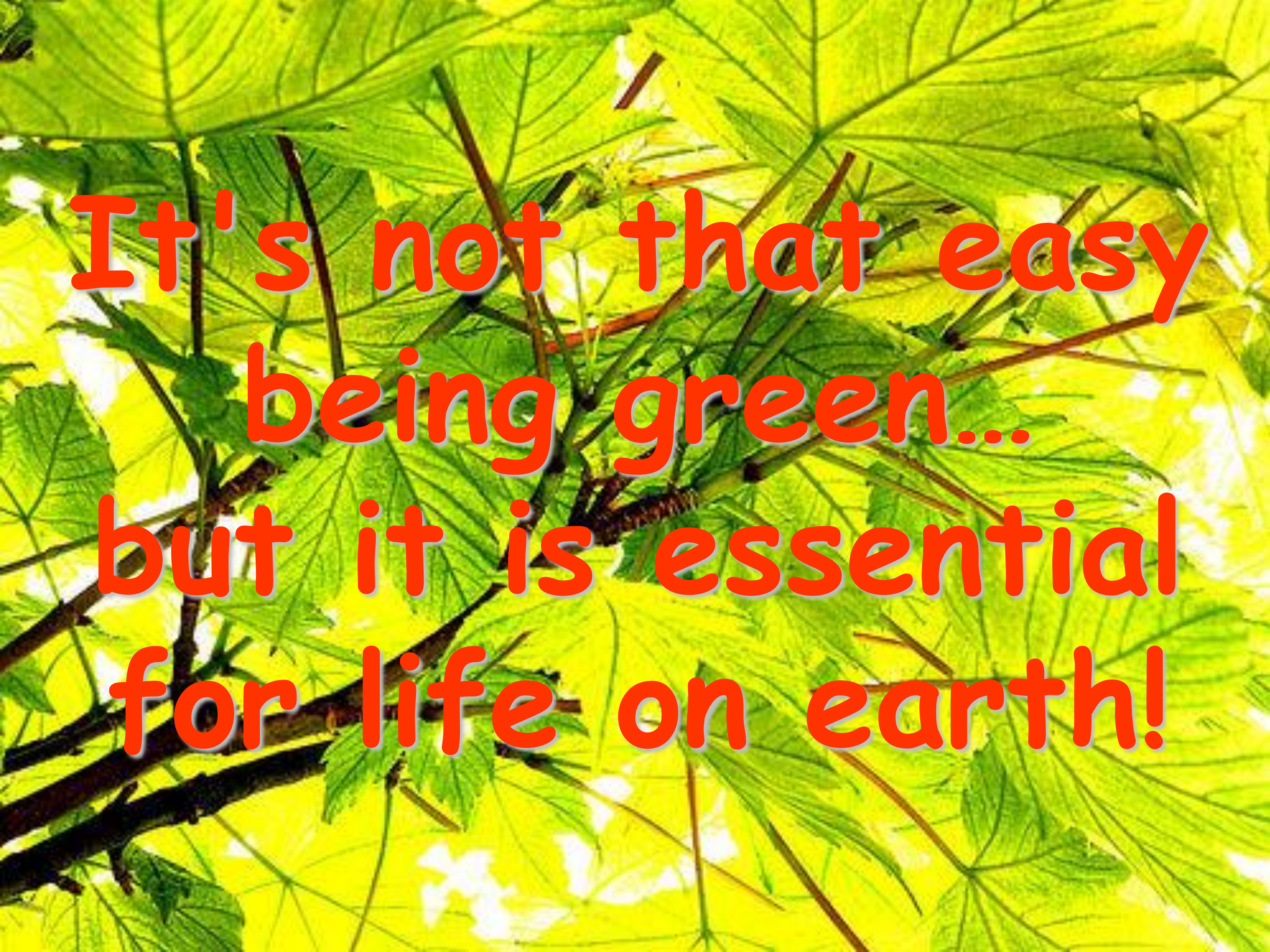


- 12 molecules of NADPH are consumed in reducing 12 molecules of 1.3-biphosphoglycerate
- 6 molecules of ATP to regenerate ribulose 1,5-biphosphate
- The overall reaction:

$6\ CO_2 + 18\ ATP + 12\ NADPH + 12\ H_2O \longrightarrow C_6H_{12}O_6 + 18\ ADP + 18\ P_i + 12\ NADP+ 6H^+$

Summary of Photosynthesis




It's not that easy
being green…
but it is essential
for life on earth!