Oxygenic Photosynthesis

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Photosystems

- The photosynthetic apparatus of modern cyanobacteria, algae, and vascular plants is more complex than the one center bacterial systems, and it appears to have evolved through the combination of two simpler bacterial photocenters.
- The thylakoid membranes of chloroplasts have two different kinds of photosystems, each with its own type of photochemical reaction center and set of antenna molecules.
- Unlike heterotrophic prokaryotes, **cyanobacteria** have internal membranes. These are flattened sacs called thylakoids or photosynthetic lamellae where **photosynthesis** is performed.
- Photosystem I **absorbs longer wavelength light (700 nm) and** funnels the energy to a special chlorophyll a molecule called P700 (RC_{700}).
- The term P700 signifies that this molecule most effectively absorbs light at a wavelength of 700 nm.
- **Photosystem II traps** light at shorter wavelengths (680 nm) and transfers its energy to the special chlorophyll P680 (RC_{680}).

Cyclic photophosphorylation

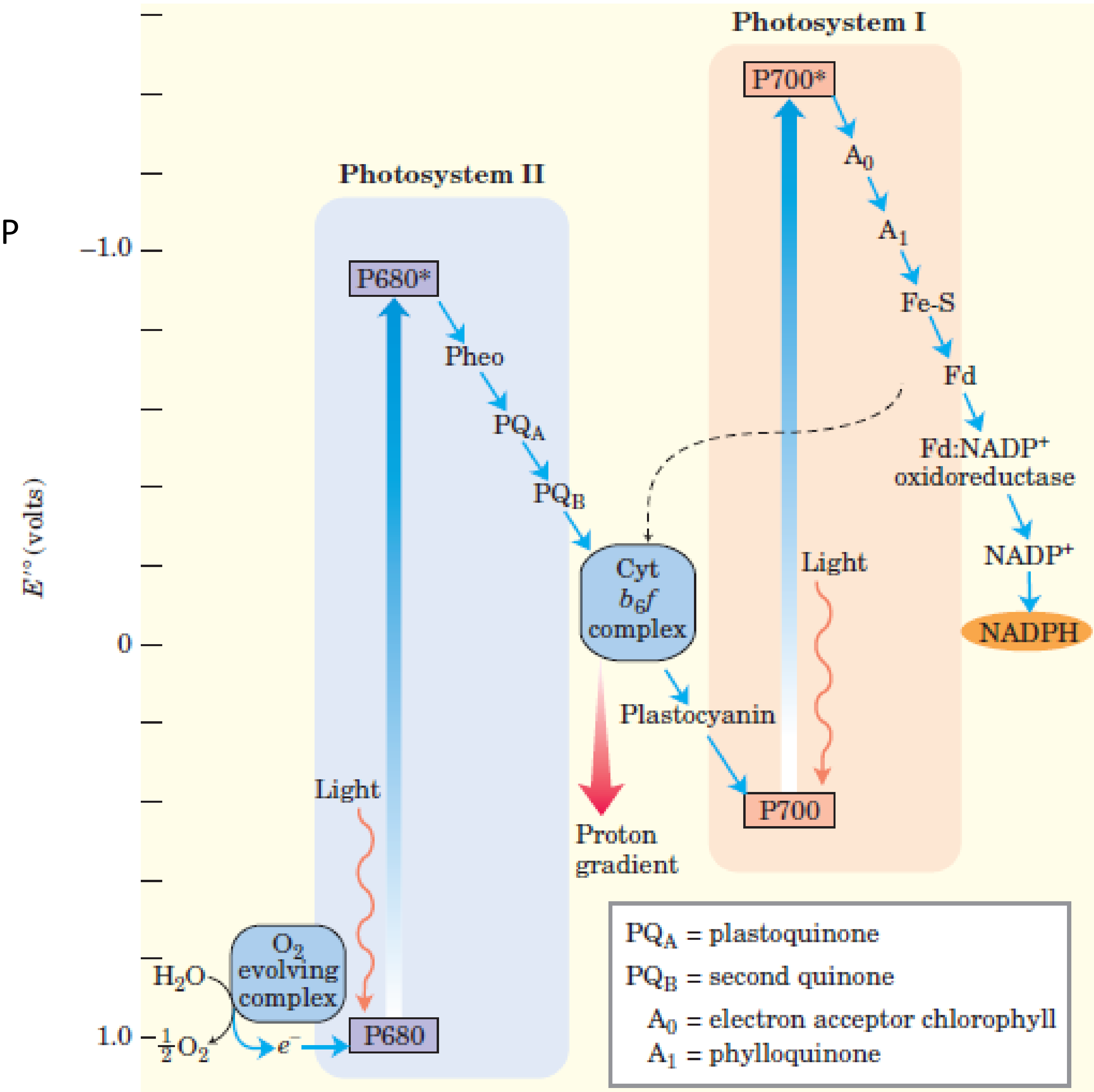
- When the photosystem I antenna transfers light energy to the reaction-center P700 chlorophyll, it absorbs the energy and is excited; its reduction potential becomes very negative.
- It then donates its high-energy electron to a specific acceptor, probably a special chlorophyll *a* molecule (A) or an iron-sulfur protein (**figure 1).**
- **The electron is eventually transferred to** ferredoxin and can then travel in either of two directions.
- In the cyclic pathway (the dashed lines in fig. 1), the electron moves in a cyclic route through a series of elec. carriers and back to the oxidized P700.
- The pathway is termed cyclic because the electron from P700 returns to P700 after travelling through the photosynthetic electron transport chain.
- Proton motive force is formed during cyclic electron transport in the region of cytochrome *b6* and used to synthesize ATP.
- This process is called **cyclic photophosphorylation** because electrons travel in a cyclic pathway and ATP is formed.
- Only photosystem I participates.

Noncyclic photophosphorylation

- Electrons also can travel in a noncyclic pathway involving both photosystems.
- P700 is excited and donates electrons to ferredoxin as before.
- In the noncyclic route, reduced ferredoxin reduces NADP to NADPH (Fig. 1).
- Because the electrons contributed to NADP cannot be used to reduce oxidized P700, photosystem II participation is required.
- It donates electrons to oxidized P700 and generates ATP in the process.
- The photosystem II antenna absorbs light energy and excites P680.
- P680 then reduces pheophytin *a.* Pheophytin a is chlorophyll a in which two hydrogen atoms have replaced the central magnesium.
- Electrons subsequently travel to Q (probably a plastoquinone) and down the electron transport chain to P700.
- Oxidized P680 then obtains an electron from the oxidation of water to O_2.
- Thus electrons flow from water all the way to NADP with the aid of energy from two photosystems, and ATP is synthesized by **noncyclic photophosphorylation.**
- It appears that one ATP and one NADPH are formed when two electrons travel through the noncyclic pathway.

Figure 1. "Z scheme" shows the pathway of electron transfer from H_2O (lower left) to NADP (far right) in noncyclic photosynthesis.

The dashed arrow is the path of cyclic Electron transfer, Which involves only PSI; electrons return via the cyclic pathway to PSI, instead of reducing NADP to NADPH.



Z-Scheme

- The diagram in Figure 1, often called the **Z scheme** because of its overall form, outlines the pathway of electron flow between the two photosystems and the energy relationships in the light reactions.
- The Z scheme thus describes the complete route by which electrons flow from H_2O to NADP, according to the equation:

$$2H_2O + 2NADP^+ + 8\text{ photons} \longrightarrow O_2 + 2NADPH + 2H^+$$

- For every two photons absorbed (one by each photosystem), one electron is transferred from H_2O to NADP.
- To form one molecule of O_2, which requires transfer of four electrons from two H_2O to two NADP, a total of eight photons must be absorbed, four by each photosystem.

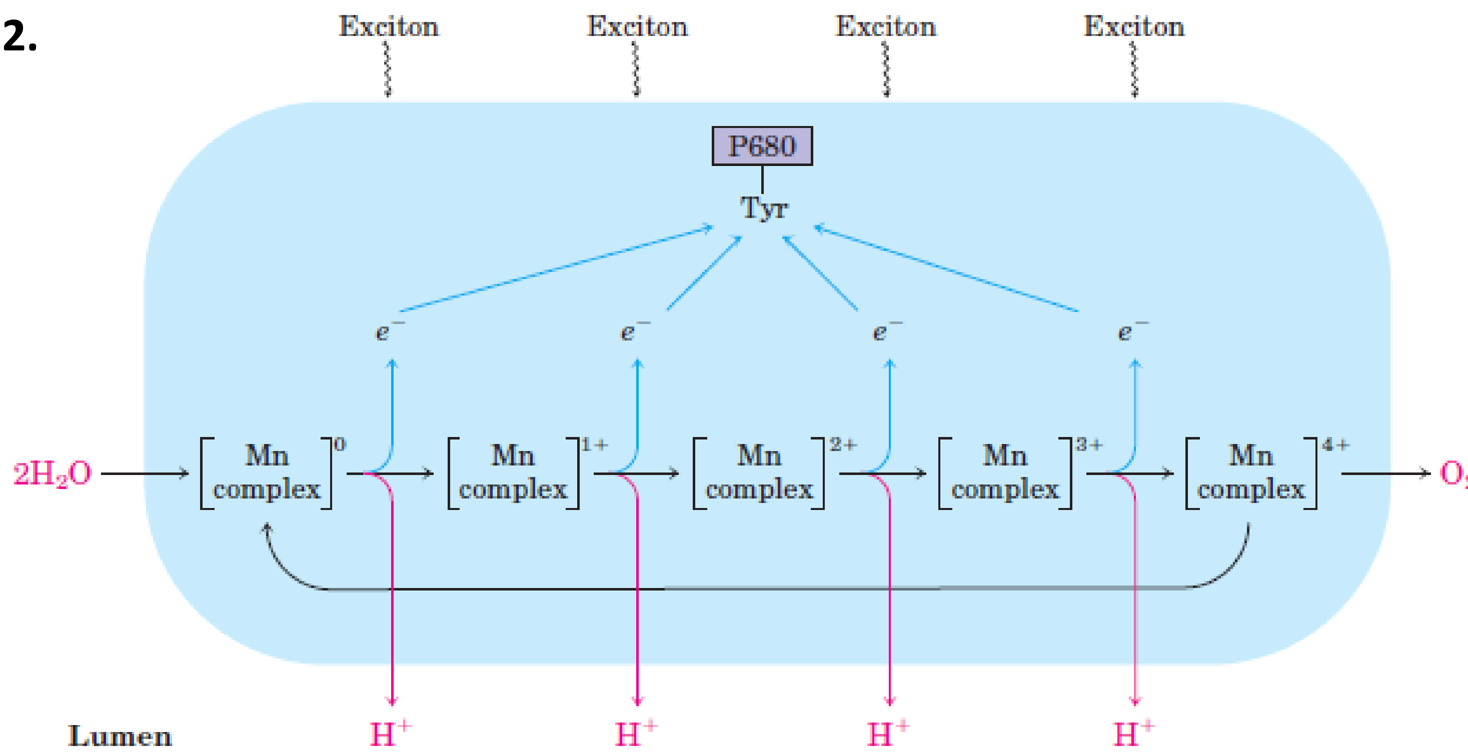
Oxygen-Evolving Complex

- The ultimate source of the electrons passed to NADPH in oxygenic photosynthesis is water.
- Having given up an electron to pheophytin, P680 (of PSII) must acquire an electron to return to its ground state in preparation for capture of another photon.
- In principle, the required electron might come from any number of organic or inorganic compounds.
- Two water molecules are split, yielding four electrons, four protons, and molecular oxygen:

$$2H_2O \longrightarrow 4H^+ + 4e^- + O_2$$

- A single photon of visible light does not have enough energy to break the bonds in water; four photons are required in this photolytic cleavage reaction.
- The four electrons abstracted from water do not pass directly to P680, which can accept only one electron at a time.
- Instead, a remarkable molecular device, the oxygen-evolving complex (also called the water splitting complex), passes four electrons one at a time to P680 (Fig. 2).

Figure 2.



- Oxygen evolving complex believed to be a multinuclear center with several Mn ions—in the water-splitting complex of PSII.
- The sequential absorption of four photons (excitons), each absorption causing the loss of one electron from the Mn center, produces an oxidizing agent that can remove four electrons from two molecules of water, producing O_2.
- The electrons lost from the Mn center pass one at a time to an oxidized Tyr residue in a PSII protein, then to $P680^+$.

Proton and electron circuits in thylakoids

- It is believed that stromal lamellae possess only photosystem I and are involved in cyclic photophosphorylation alone.
- In cyanobacteria, photosynthetic light reactions are also located in membranes.
- **Figure 3 shows a thylakoid membrane carrying out noncyclic photophosphorylation by the chemiosmotic mechanism (autotrophic generation of ATP).**
- An illustration of the thylakoid membrane showing photosynthetic electron transport chain function and noncyclic photophosphorylation.
- The chain is composed of three complexes:
  - PS I
  - Cytochrome bf complex
  - PS II
- Two diffusible electron carriers connect the three complexes.
  - Plastoquinone (PQ) connects PS I with the cytochrome *bf* complex, and
  - Plastocyanin (PC) connects the cytochrome *bf* complex with PS II.
- The light-driven electron flow pumps protons across the thylakoid membrane and generates an electrochemical gradient, which can then be used to make ATP.
- Water is the source of electrons and the oxygen-evolving complex produces oxygen.

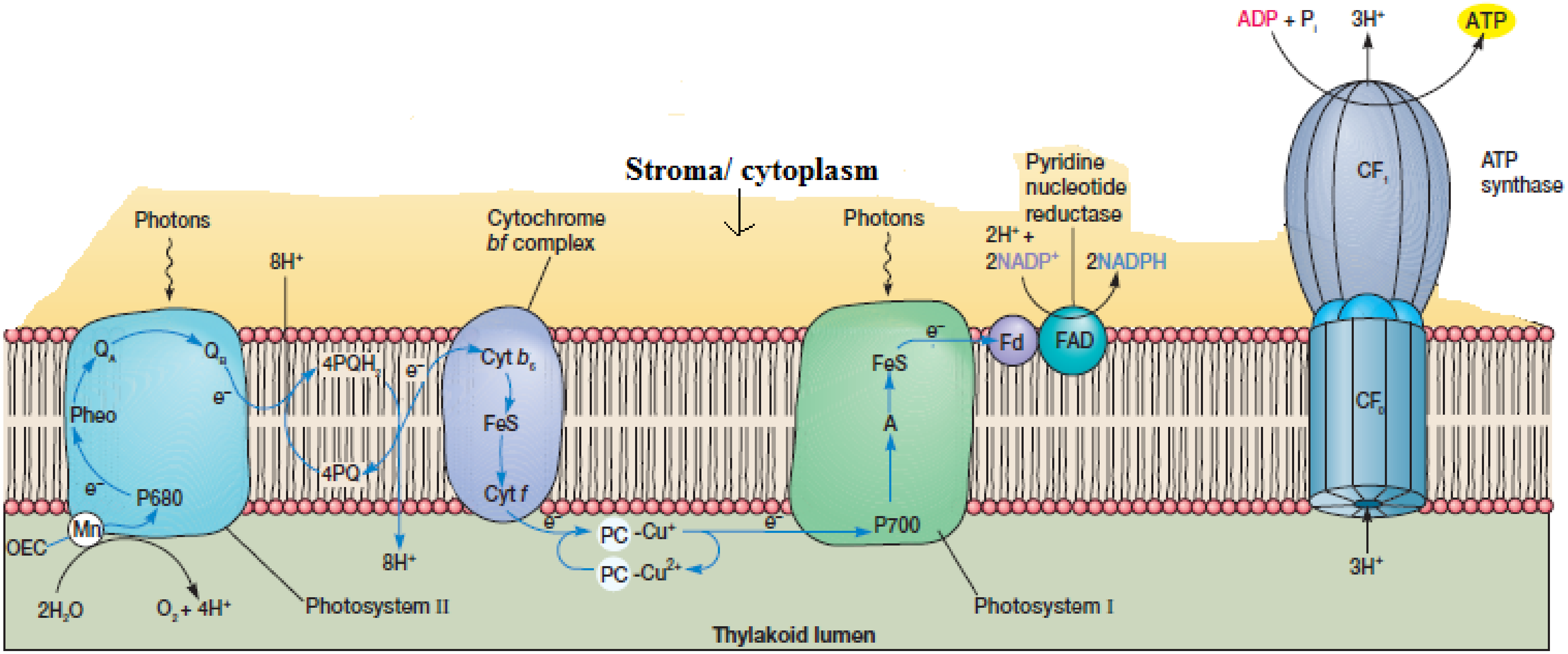
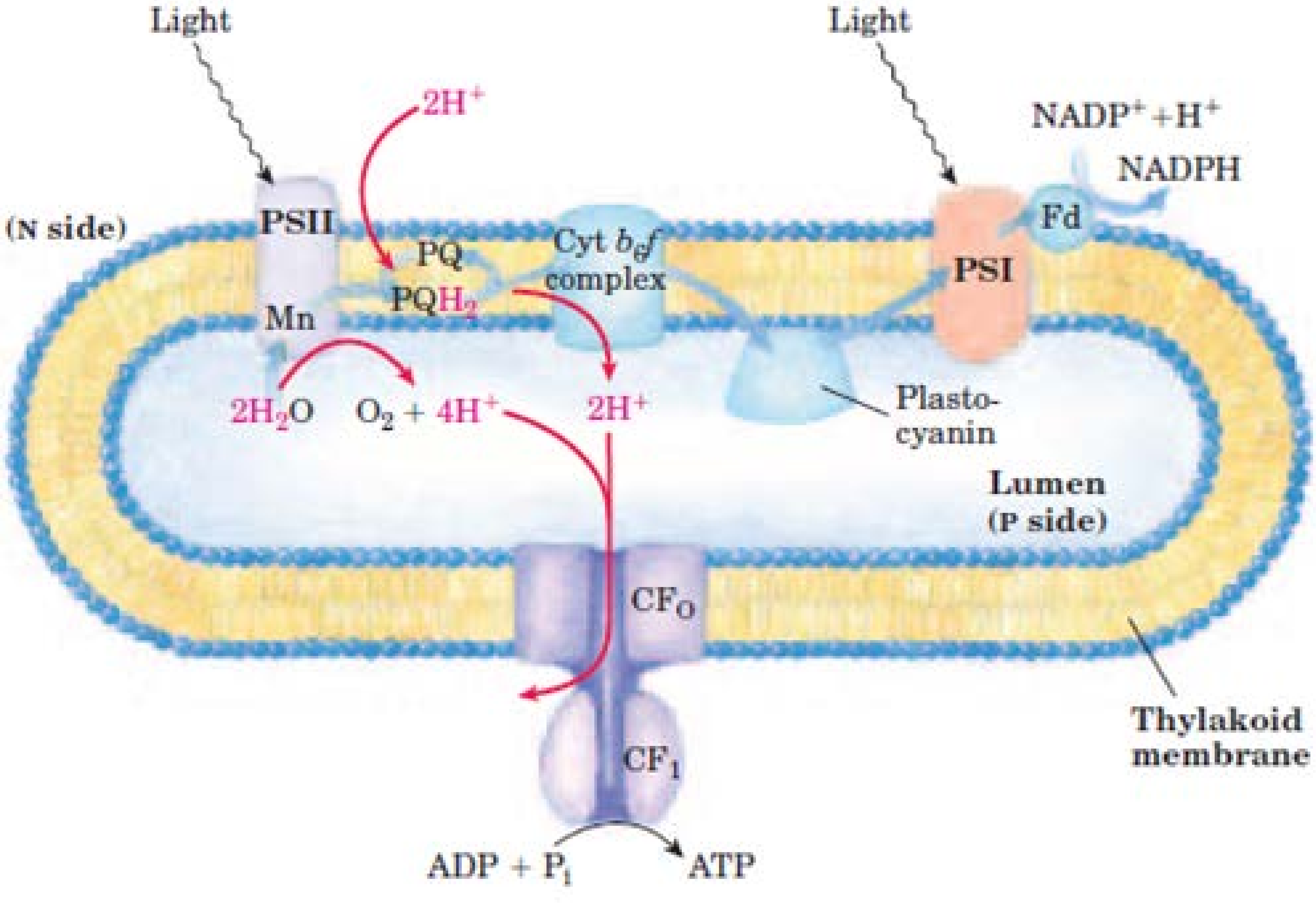

Stroma/ cytoplasm
Photons
8H+
Cytochrome bf complex
Photons
Pyridine nucleotide reductase
2H+ +
2NADP+
2NADPH
ADP + Pi
3H+
ATP
CF1
ATP synthase
QA
QB
Pheo
e−
4PQH2
e−
4PQ
Cyt b6
FeS
Cyt f
e−
FeS
A
Fd
FAD
CF0
P680
Mn
OEC
2H2O
O2 + 4H+
8H+
PC -Cu+
PC -Cu2+
e−
P700
3H+
Photosystem II
Photosystem I
Thylakoid lumen

Figure 3.

Questions

- Explain in detail the Z-scheme of oxygenic photosynthesis found in cyanobacteria.
- What is photophosphoryation? Explain autotrophic generation of ATP.
- Differentiate between cyclic and non-cyclic photophosphoryation.
- Explain in detail the function of oxygen evolving complex.


Light
Light
$2H^+$
$NADP^+ + H^+$
NADPH
(N side)
PSII
Fd
PQ
Cyt b_6f complex
PSI
PQH_2
Mn
$2H_2O$
$O_2 + 4H^+$
$2H^+$
Plasto-
cyanin
Lumen
(P side)
CF_O
CF_1
Thylakoid
membrane
$ADP + P_i$
ATP