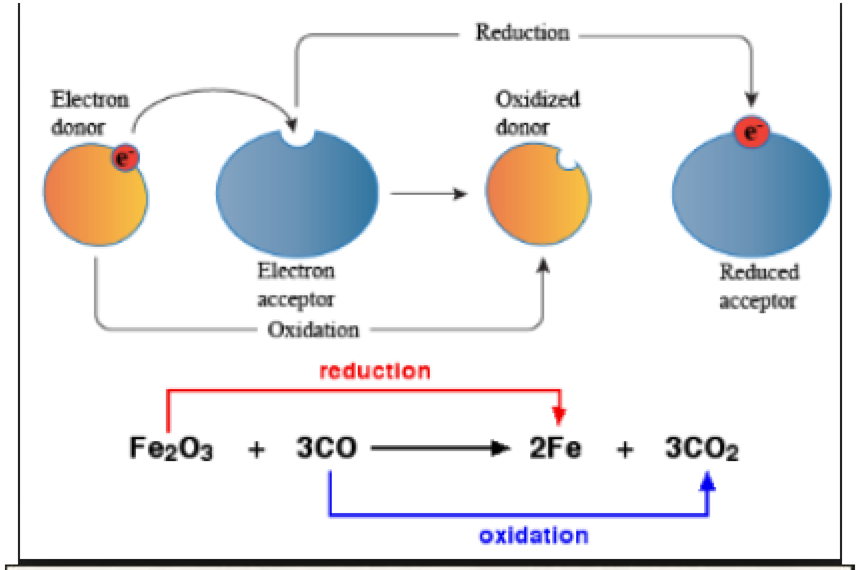
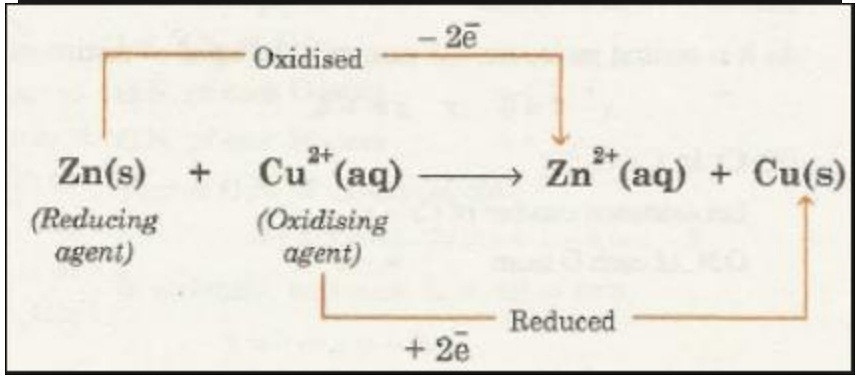
photosynthesis

Part 1

1 Overview of photosynthesis

- 1.1 Photosynthesis is a boilogical oxidation–reduction process





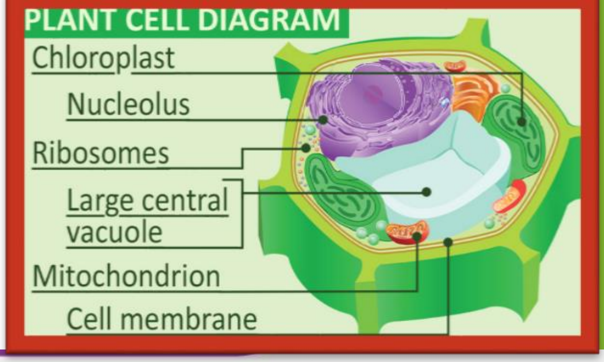
CO_2 is the electron acceptor, and H_2O is reduced compound that can serve as the electron donor.

Many prokaryotes perform **anoxygenic** photosynthetic reactions but utilize electron donors other than water.

- In the case of O2-evolving (**oxygenic**) photosynthesis, water serves as the reductant (Reaction). Water is oxidized, and the electrons released are energized and ultimately transferred to CO2, yielding O2 and carbohydrate.
- Plants, algae, and prokaryotic cyanobacteria are capable of this light-driven, **endergonic** (energy-requiring) reaction, which has a free energy change ($\Delta G^{\circ\prime}$) of +2840 kJ mol^{-1} for the synthesis of hexose.
- Oxygenic photosynthesis was an evolutionary innovation of cyanobacteria that led to the accumulation of O2 in the Earth's atmosphere more than 2 billion years ago.
- **Reaction: Oxygenic photosynthesis**

$$CO_2 + 2H_2O \xrightarrow{h\nu} (CH_2O) + O_2 + H_2O$$

chloroplast, a specialized organelle

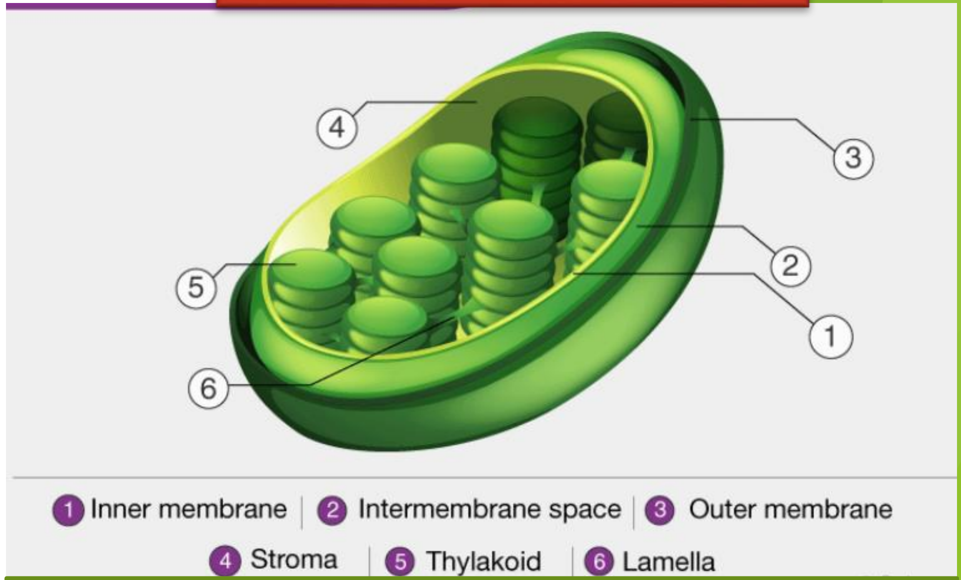


In eukaryotes, photosynthesis occur in a specialized plastid, the **chloroplast**.

All the reactions required for photosynthesis take place in this organelle.

The complex structure of the chloroplast reflects its diverse biochemical functions.

Chloroplasts are surrounded by a double-membrane system consisting of an **outer and inner envelope** and also contain a complex internal membrane system.

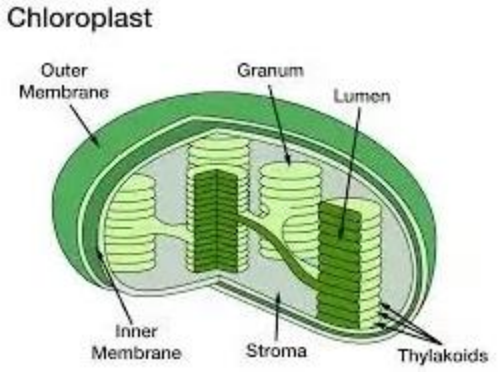


گرانوم ها (grana pl. granum sing): مجموعه های متشکل از کیسه های پهن و مسطح یا تیلاکوئیدها، در داخل کلروپلاست که دارای رنگیزه و انزیم های واکنش های مرحله نوری فتوسنتز هستند.

لاملا: غشای گرانوم ها

تیلاکوئید: کیسه های پهن و مسطح تشکیل دهنده گرانوم ها

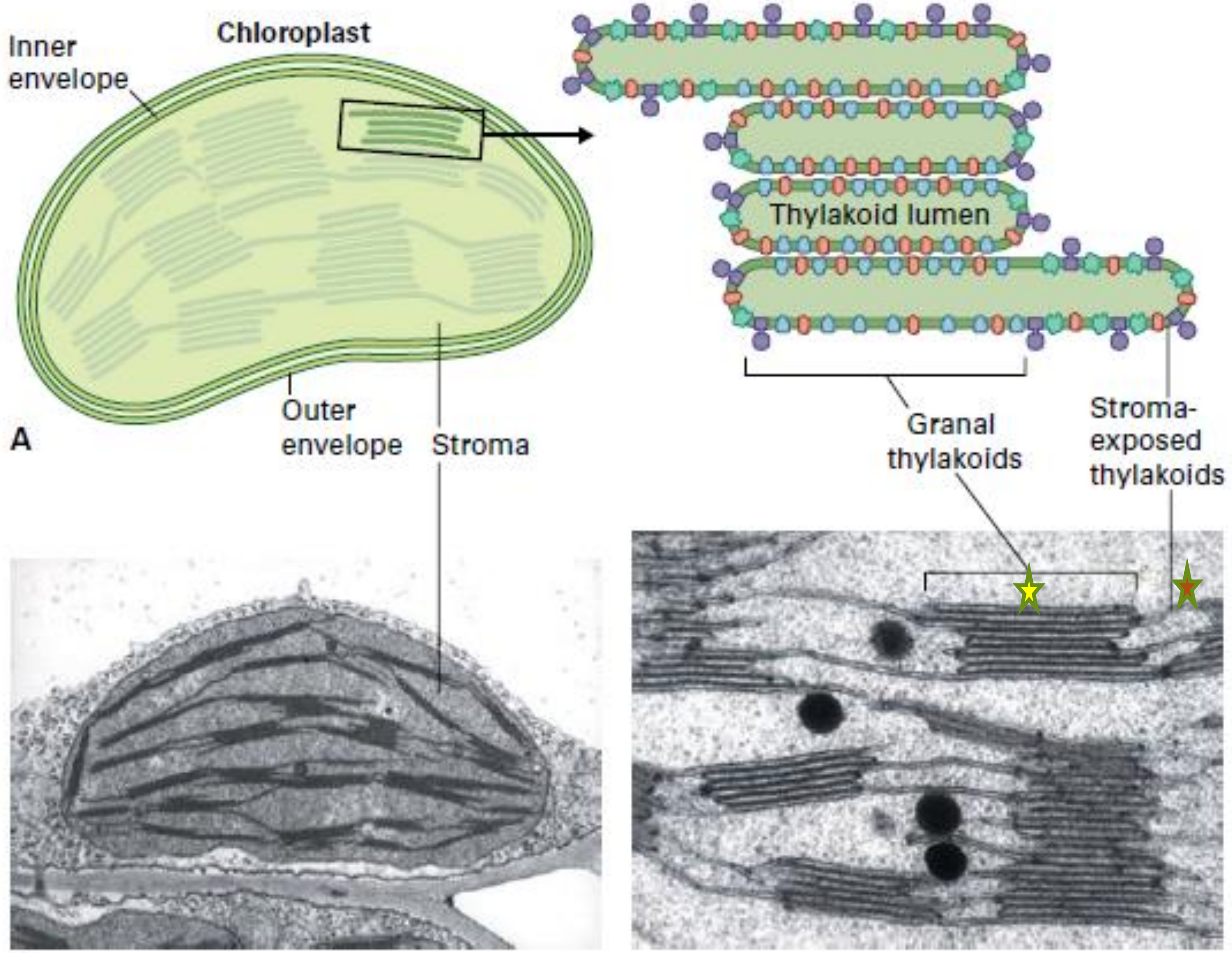
استروما: بخشی از کلروپلاست که در بین گرانوم ها قرار گرفته است.



The internal membrane system, known as the **thylakoid** membrane, contains distinct regions. Some thylakoids (**granal thylakoids**) are organized into **grana**, stacks of appressed membranes, whereas others (**stromal thylakoids**) are unstacked and are thus exposed to the surrounding fluid medium, the chloroplast **stroma**. The thylakoid membranes are interconnected by the **lumen**.

FIGURE 12.1 *Plant chloroplast. (A) Schematic diagram showing compartmentalization of the organelle. In a typical plant chloroplast, the internal membranes (thylakoids) include stacked membrane regions (granal thylakoids) and unstacked membrane regions (stromal thylakoids). (B) Transmission electron micrographs reveal plant chloroplast ultrastructure. The higher magnification emphasizes the membrane stacking and includes electron-dense lipid bodies known as plastoglobuli.*

Source: (B) Staehelin & van der Staay (1996). Structure, composition, functional organization and dynamic properties of thylakoid membranes. In Oxygenic Photosynthesis: The Light Reactions, D. R. Ort and C. F. Yocum, eds. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 11–30.



Photosynthesis consists of light reactions and carbon reactions

photosynthetic process involves two phases:

- the light reactions, which produce O_2, ATP, and NADPH;
- and carbon reactions (the carbon reduction cycle, also called the **Calvin-Benson cycle**, (after its co-discoverers, Melvin Calvin and Andrew Benson), which reduce CO_2 to carbohydrate and consume the ATP and NADPH produced in the light reactions.
- The two phases of photosynthesis occur simultaneously, but they reside in different regions of the chloroplast (Fig).

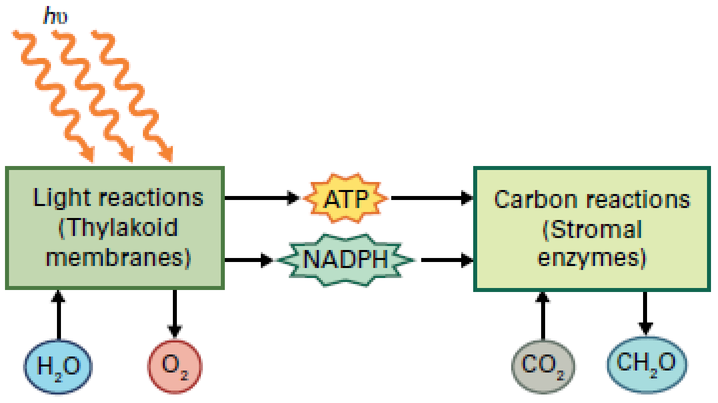
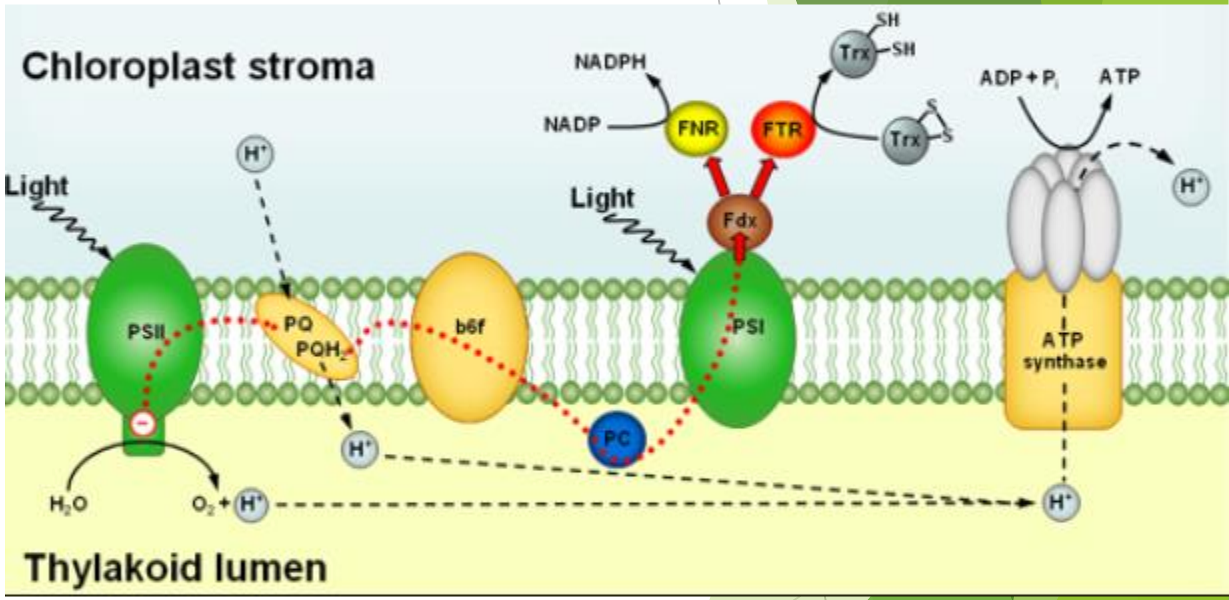
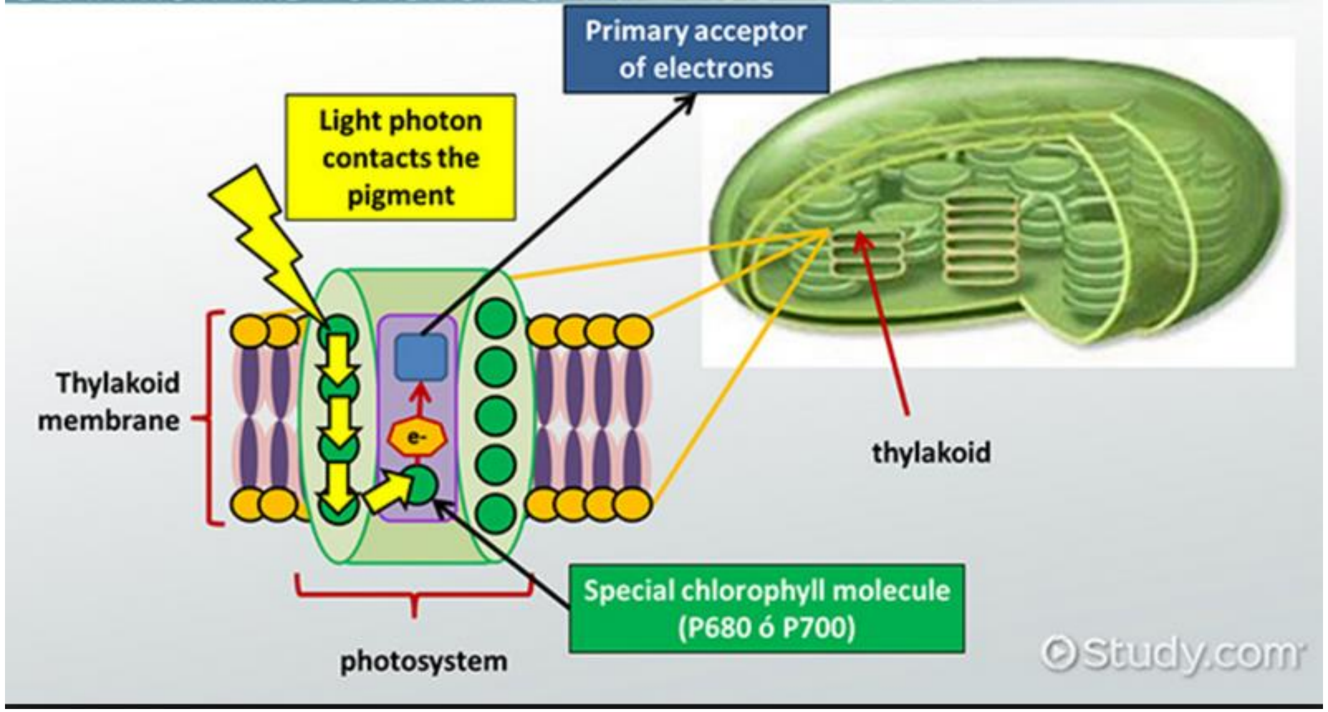
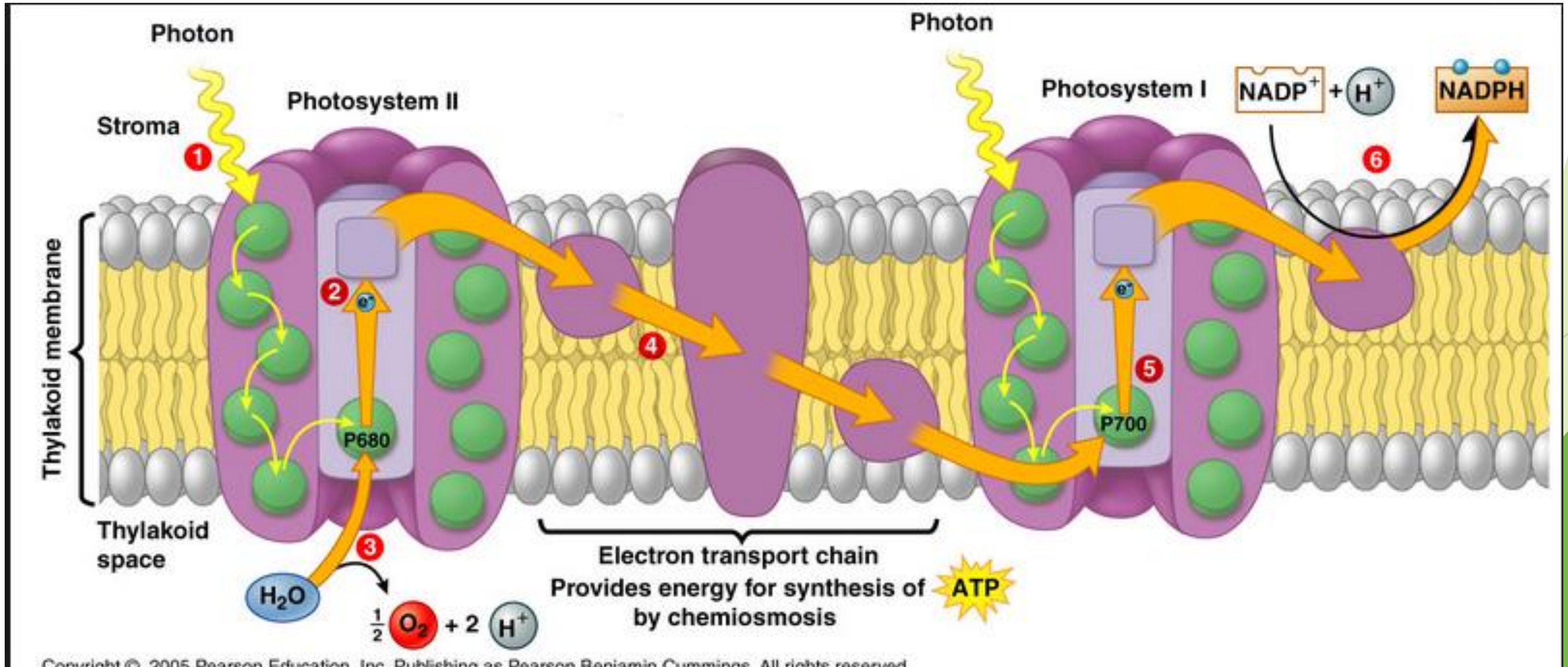


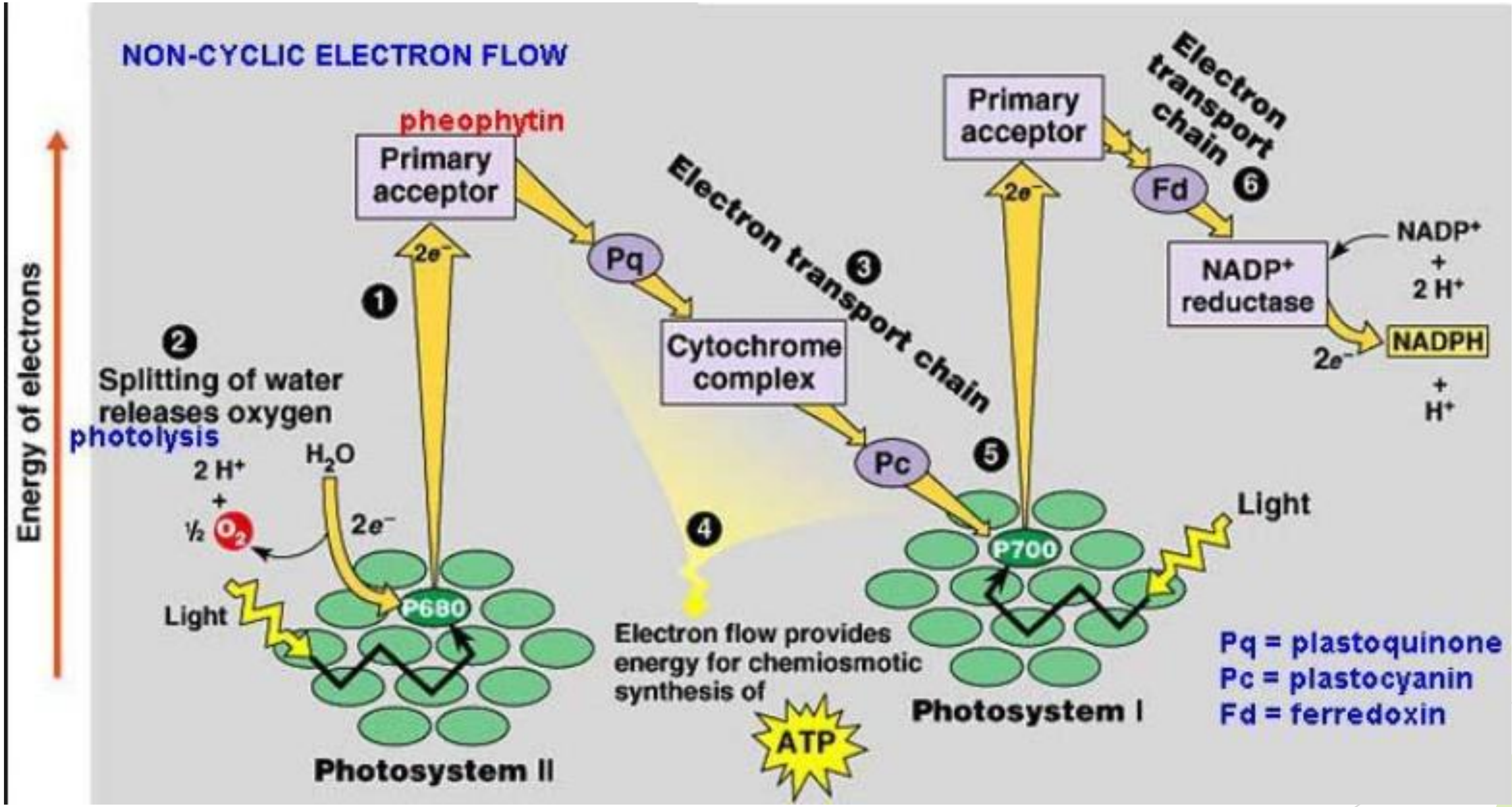
FIGURE 12.2 *The light and carbon (formerly "dark") reactions of photosynthesis occur in separate chloroplast compartments. Light is required for the synthesis of ATP and NADPH substrates in a series of reactions that occur in thylakoid membranes of the chloroplast. These products of the light reactions are then used by a series of stromal enzymes that fix CO_2 into carbohydrates during the carbon reactions.*

- The **thylakoid membranes** contain the multiprotein photosynthetic complexes, photosystems I and II (PSI and PSII), which include the reaction centers responsible for converting light energy into chemical bond energy.
- These reaction centers are part of a photosynthetic electron transfer chain that also contains a transmembrane cytochrome complex (cytochrome *b6f*), a water-soluble copper protein (plastocyanin), and a lipid-soluble quinone (plastoquinone).
- The photosynthetic electron transport chain moves electrons from water in the **thylakoid lumen** to soluble redox-active compounds in the stroma (e.g., NADP+).
- This electron transport is coupled to the phosphorylation of a ADP.



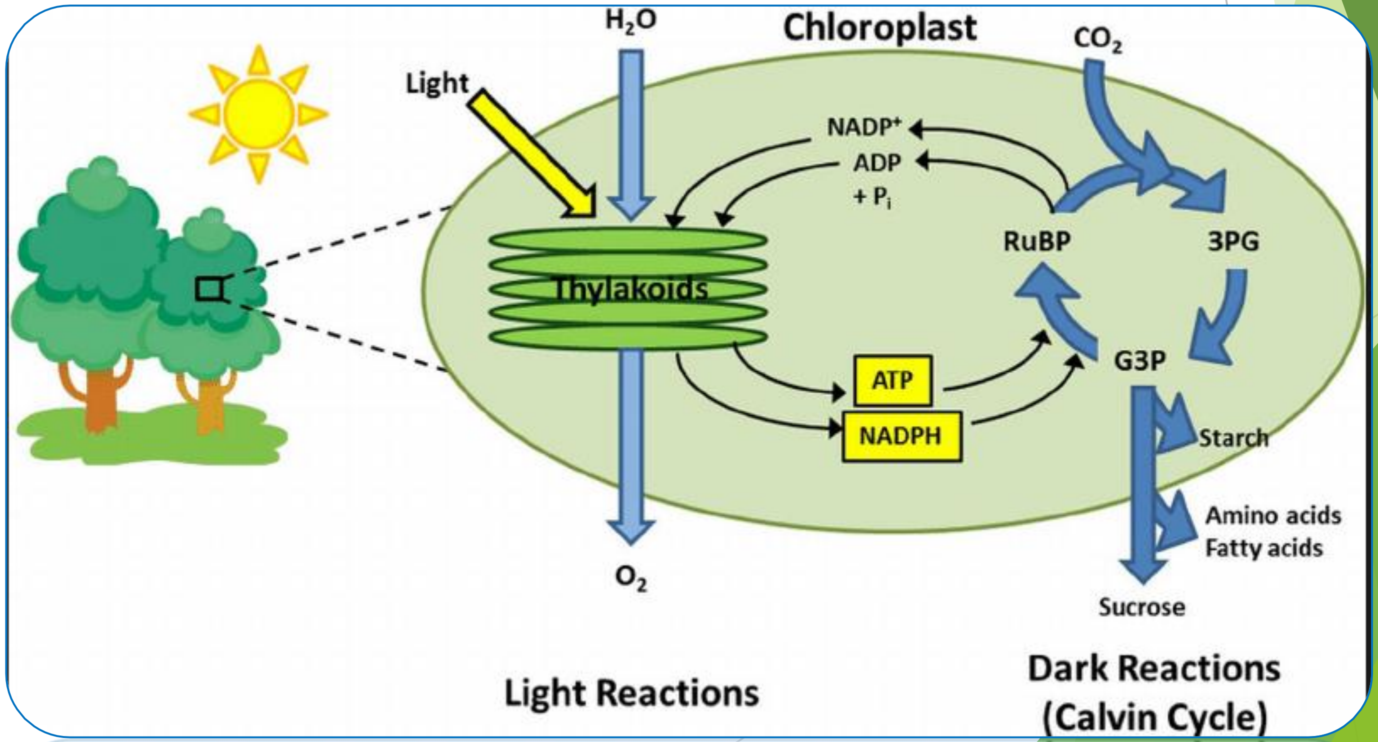

Primary acceptor of electrons
Light photon contacts the pigment
Thylakoid membrane
e-
thylakoid
photosystem
Special chlorophyll molecule (P680 ó P700)
©Study.com


Photon
Photosystem II
Stroma
1
2
e-
P680
3
Thylakoid membrane
Thylakoid space
H_2O
$\frac{1}{2}$ O_2 + 2 H^+
4
Electron transport chain
Provides energy for synthesis of ATP by chemiosmosis
Photon
Photosystem I
$NADP^+$ + H^+
NADPH
6
5
P700
e-



NON-CYCLIC ELECTRON FLOW
pheophytin
Primary acceptor
2e⁻
Pq
Electron transport chain
3
1
2
Splitting of water releases oxygen
photolysis
2 H⁺
+
½ O₂
H₂O
2e⁻
Light
P680
Photosystem II
Cytochrome complex
Pc
4
Electron flow provides energy for chemiosmotic synthesis of
ATP
Primary acceptor
2e⁻
Electron transport chain
Fd
6
NADP⁺
+
2 H⁺
NADP⁺ reductase
2e⁻
NADPH
+
H⁺
5
P700
Light
Photosystem I
Pq = plastoquinone
Pc = plastocyanin
Fd = ferredoxin
Energy of electrons

- In contrast, the Calvin–Benson cycle reactions occur in the stroma.
- In the past, the Calvin–Benson cycle was referred to as the “dark“ reactions of photosynthesis. This terminology may be misleading, because these reactions occur during the day. Furthermore, some of the enzymes involved in CO2 fixation require activation by light.
- It is, therefore, more accurate to say the carbon reactions depend on the light reactions, for both high-energy products and regulatory signals.



- For light energy to be used by any system, the light must first be absorbed. This is a significant problem for photosynthetic organisms, because shading and reflection can result in large losses of available light.

- Molecules that absorb light are called **pigments**.

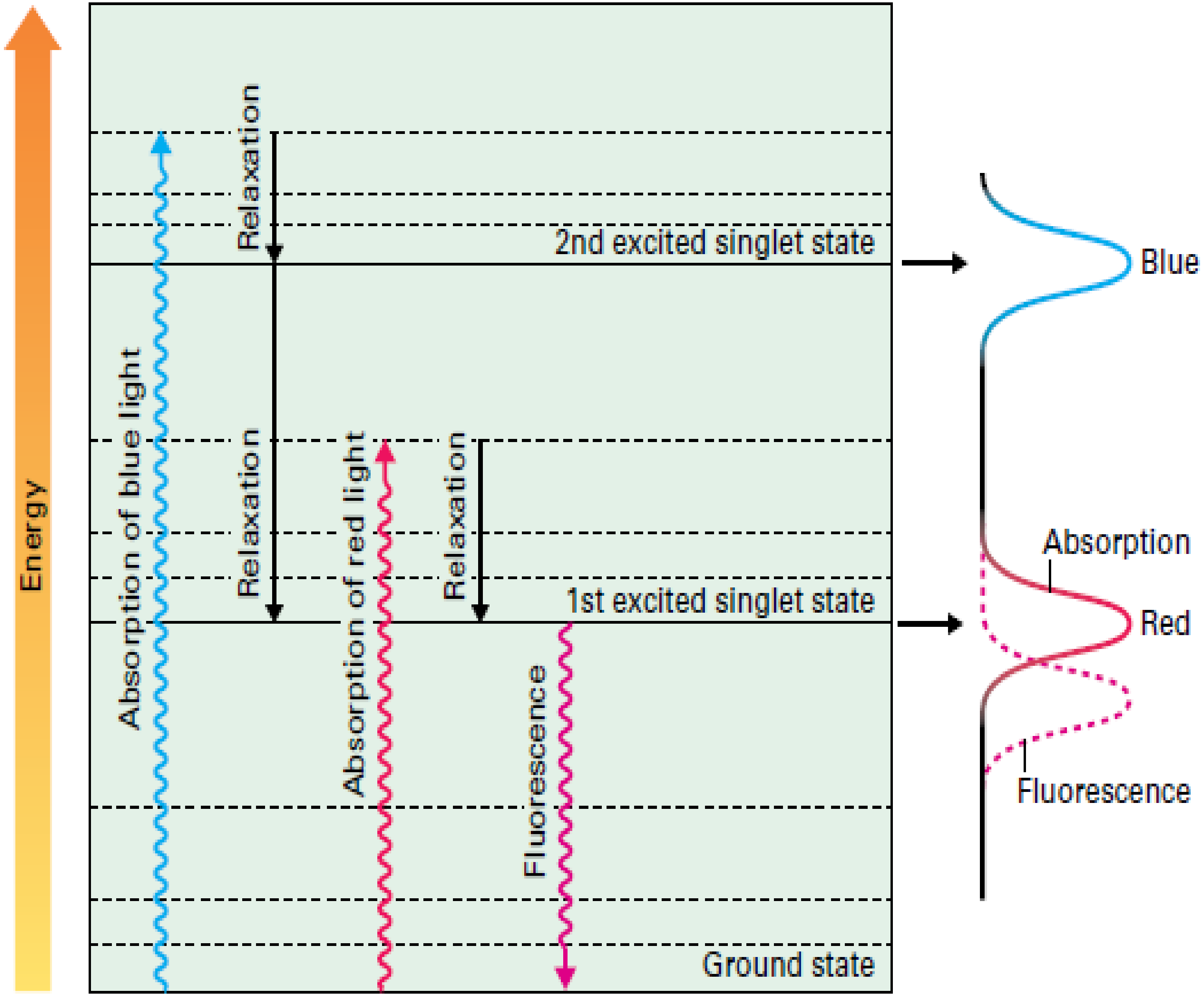
- The absorption of a photon by a pigment molecule converts the pigment from its lowest-energy (ground) state to an excited state (pigment*):

Reaction 12.4: Pigment excitation

$$\text{Pigment} \xrightarrow{h\nu} \text{Pigment}^{*}$$

A pigment molecule becomes excited when absorption of light energy causes one of its electrons to shift from a lower energy molecular orbital, which is closer to the pigment's atomic nuclei, to either of two more-distant, higher-energy orbitals.

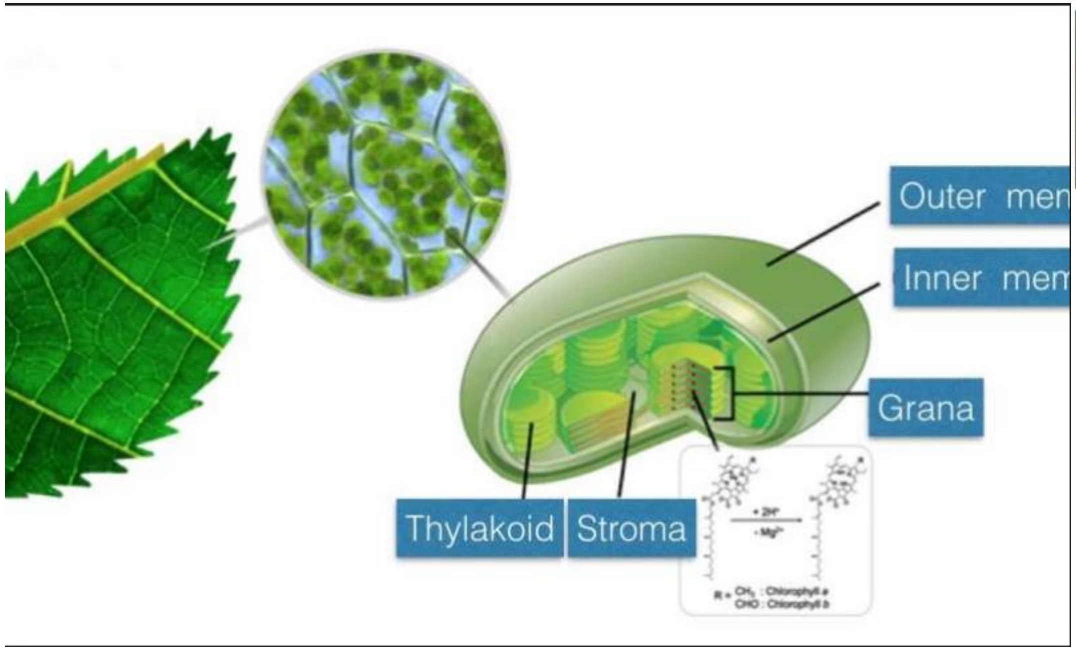
FIGURE 12.3 *Energy levels in the chlorophyll molecule. Absorption of blue or red light causes the chlorophyll molecule to convert into an excited state, with blue light absorption resulting in a higher excited state because of the greater energy of blue light relative to red light. Internal conversions or relaxations convert higher excited states to the lowest excited state, with a concomitant loss of energy as heat. Light may be reemitted from the lowest excited state through fluorescence. The spectra for fluorescence and absorption are shown at the right of the figure. The short-wavelength absorption band corresponds to a transition to the higher excited state, and the long-wavelength absorption band corresponds to a transition to the lower excited state.*

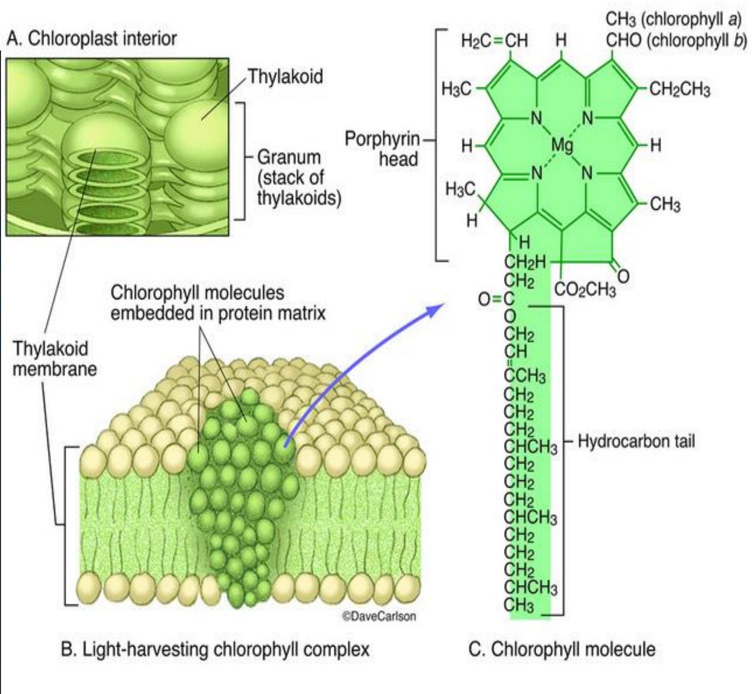


1 mol of photons of 490-nm blue light has an energy of 240 kJ, whereas 1 mol of photons of 700-nm red light has only 170 kJ

All photosynthetic organisms contain chlorophyll or a related pigment

- All photoautotrophic organisms contain some form of the light-absorbing pigment **chlorophyll**.
- Plants, algae, and cyanobacteria synthesize chlorophyll.





Structures of chlorophylls.

- *Chlorophyll molecules have a porphyrin-like ring structure that contains a central magnesium (Mg) atom coordinated to the four modified pyrrole rings. Chlorophylls also contain a long hydrocarbon tail that makes the molecules hydrophobic. Various chlorophylls differ in their substituents around the ring structure. In chlorophyll* a*, a methyl group is present, whereas in chlorophyll* b*, a formyl group is present at the same position.*

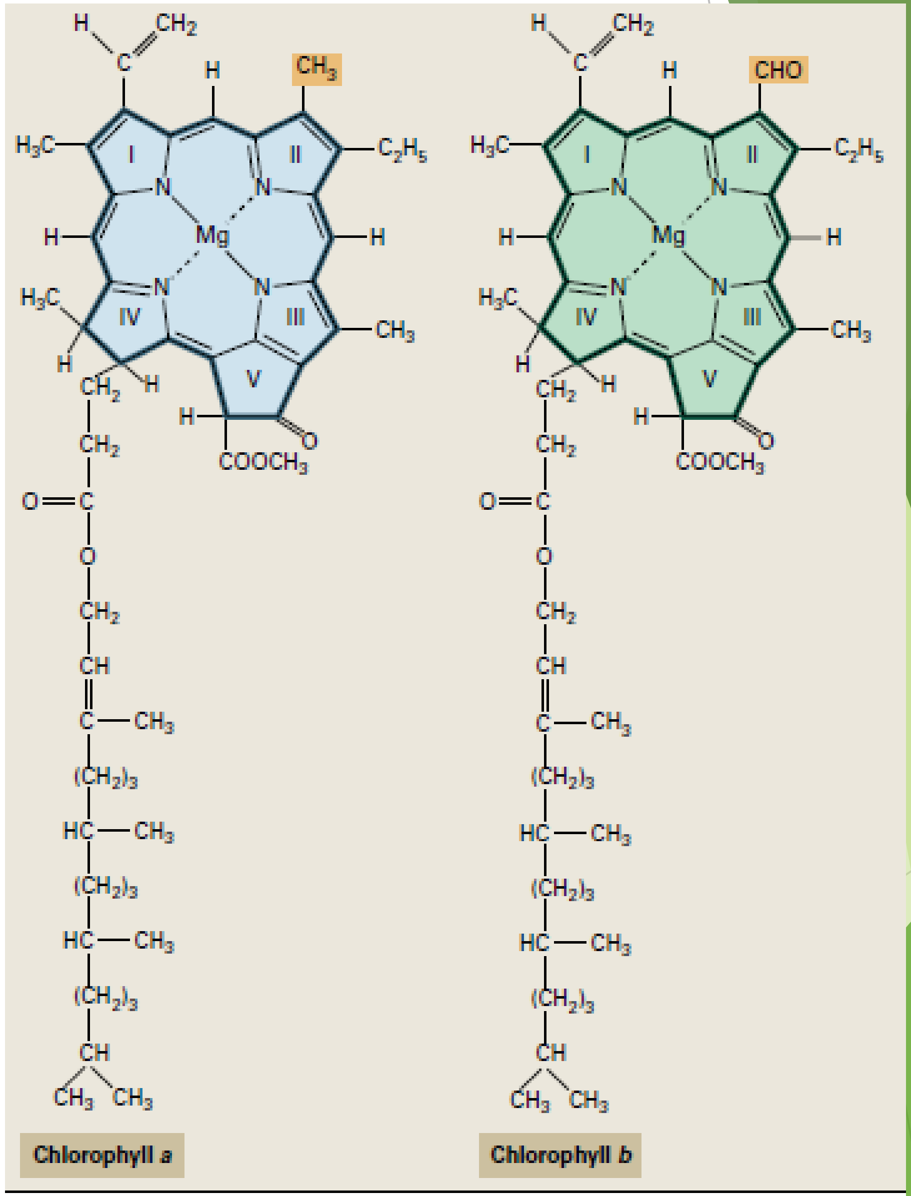
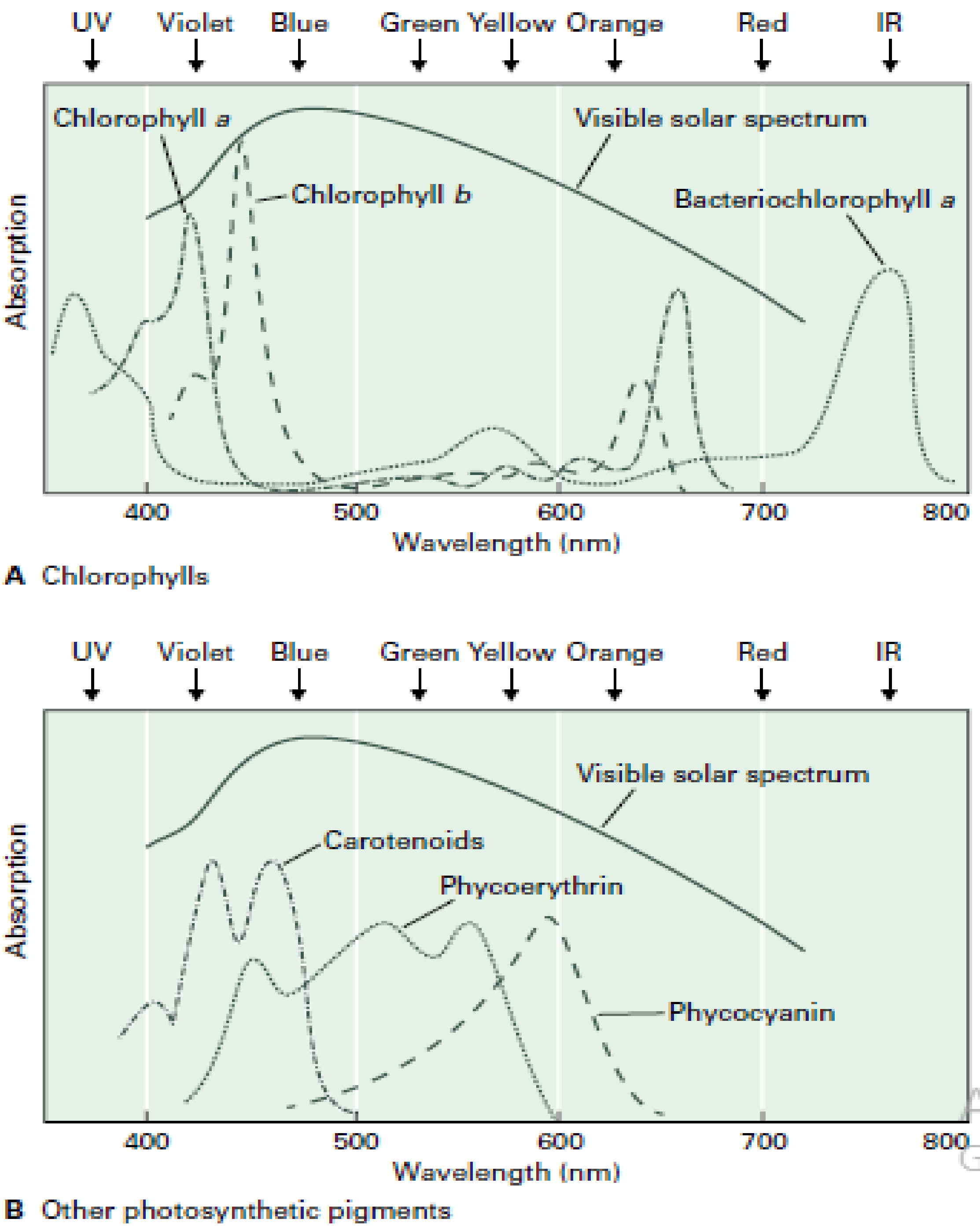


FIGURE 12.6 *(A) Absorption spectra of chlorophylls. The absorbance spectra of pigments dissolved in nonpolar solvents are shown for chlorophylls a and b and bacteriochlorophyll a. The visible region of the solar spectrum is also diagrammed. Note the spectra of these pigments show substantial shifts in absorption in vivo, where they are associated with specific proteins. (B) Absorption spectra of other photosynthetic pigments. The absorption spectrum of the carotenoids is for pigments dissolved in nonpolar solvents; the remaining spectra are for pigments in aqueous solution. UV, ultraviolet; IR, infrared.*



کلروفیل aیا نوع سبز استاندارد که در فتوسنتز کننده ها از جلبکها گرفته تا گیاهان عالی تر یافت می شود. این نوع بیشتر نور آبی را در نواحی ۴۶۵ نانومتر و نور قرمز را در نواحی ۶۶۵ نانومتر جذب می کند(به همین دلیل گیاهان سبز به نظر می رسند). کلروفیل bو cدر موجودات کمتری یافت می شوند. ایندو کلروفیل نور را در گستره ای شبیه به کلروفیل aجذب می نمایند و البته این جذب نور با جابجایی کمی نسبت به کلروفیل aرخ می دهد. کلروفیل dدر گروه خاصی از سیانوباکتریا یافت شده است. بیشترین جذب را در ۶۹۷ نانومتر دارد. طول موج جذب این نوع کلروفیل اندکی کوتاهتر از طول موج جذبی کلروفیل جدید می باشد.

Carotenoids participate in light absorption and photoprotection

- A second group of pigment molecules found in all photosynthetic organisms is the **carotenoids**.

This class of molecules includes:

- the carotenes, which contain a conjugated double-bond system of carbon and hydrogen, and the
- xanthophylls, which in addition contain oxygen atoms in their terminal rings.

- carotenoids play a minor role as accessory light-harvesting pigments, absorbing and transferring light energy to chlorophyll molecules.
- Carotenoids play an important structural role in the assembly of light-harvesting complexes (LHCs).(At least 10 different integral membrane light-harvesting complex (LHC) proteins that bind chlorophylls and xanthophylls have been identified)
- Carotenoids have an indispensable function in protecting the photosynthetic apparatus from photooxidative damage (If carotenoid biosynthesis is blocked by addition of inhibitors or by mutation, and the organism is then exposed to light in the presence of O2, lethal concentrations of singlet oxygen are formed). (p:316)

Photosystem structure and function

- In photosynthesis, light energy is absorbed and converted into relatively stable chemical products by integral membrane pigment-protein complexes called **photosystems**.

All photosystems contain:

- a **reaction center**, where photosynthetic electron transfer begins with a charge separation,
- as well as **an antenna**, array of light-harvesting, or pigments that are bound by proteins.

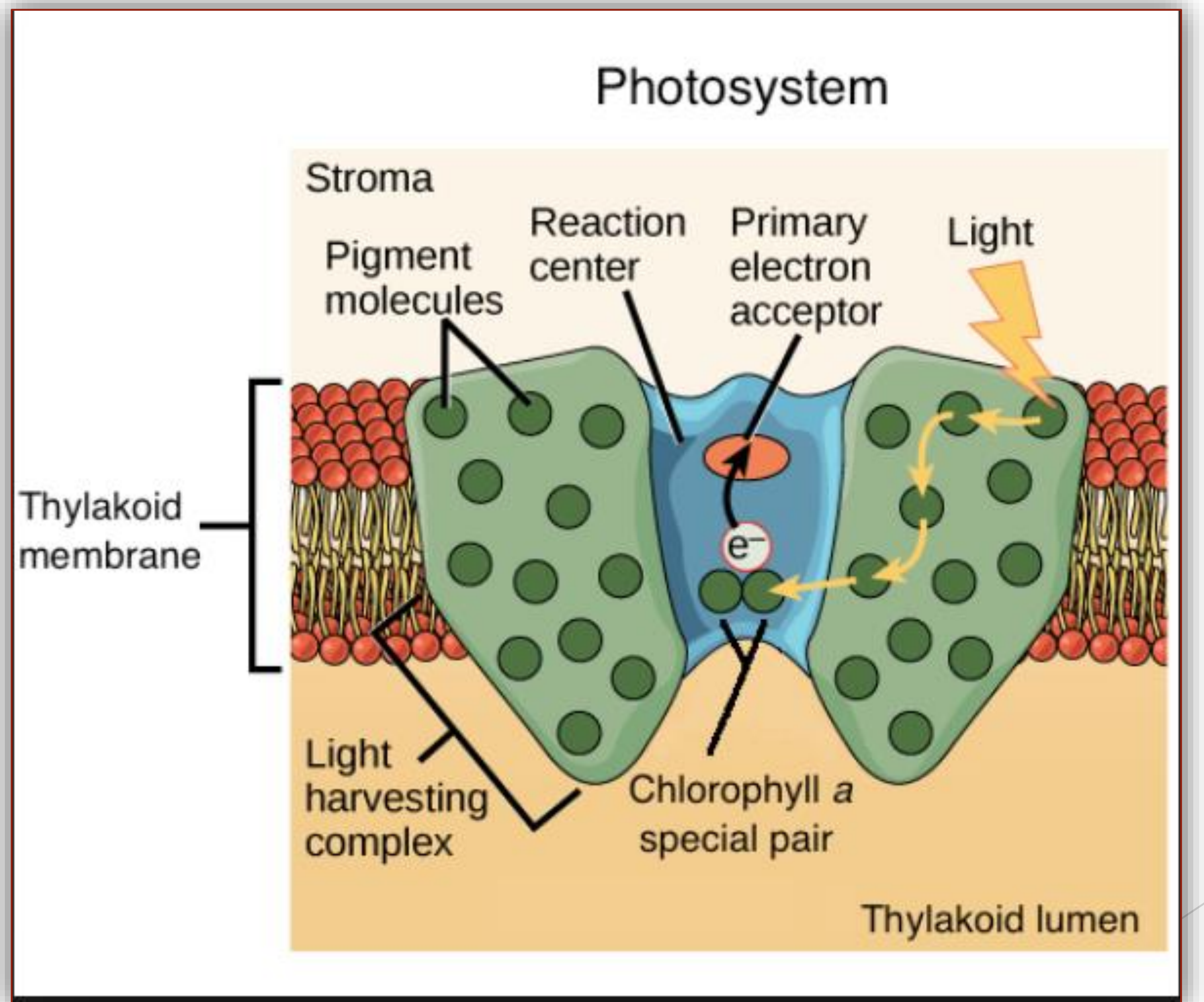
These antennae absorb light energy and transfer it to the reaction center, where excitation of specially bound chlorophyll (Chl) molecules results in transfer of an electron to an acceptor (A), as shown in Reaction.

- This is the primary photochemistry that initiates **conversion of light energy into chemical energy**. (p: 295)

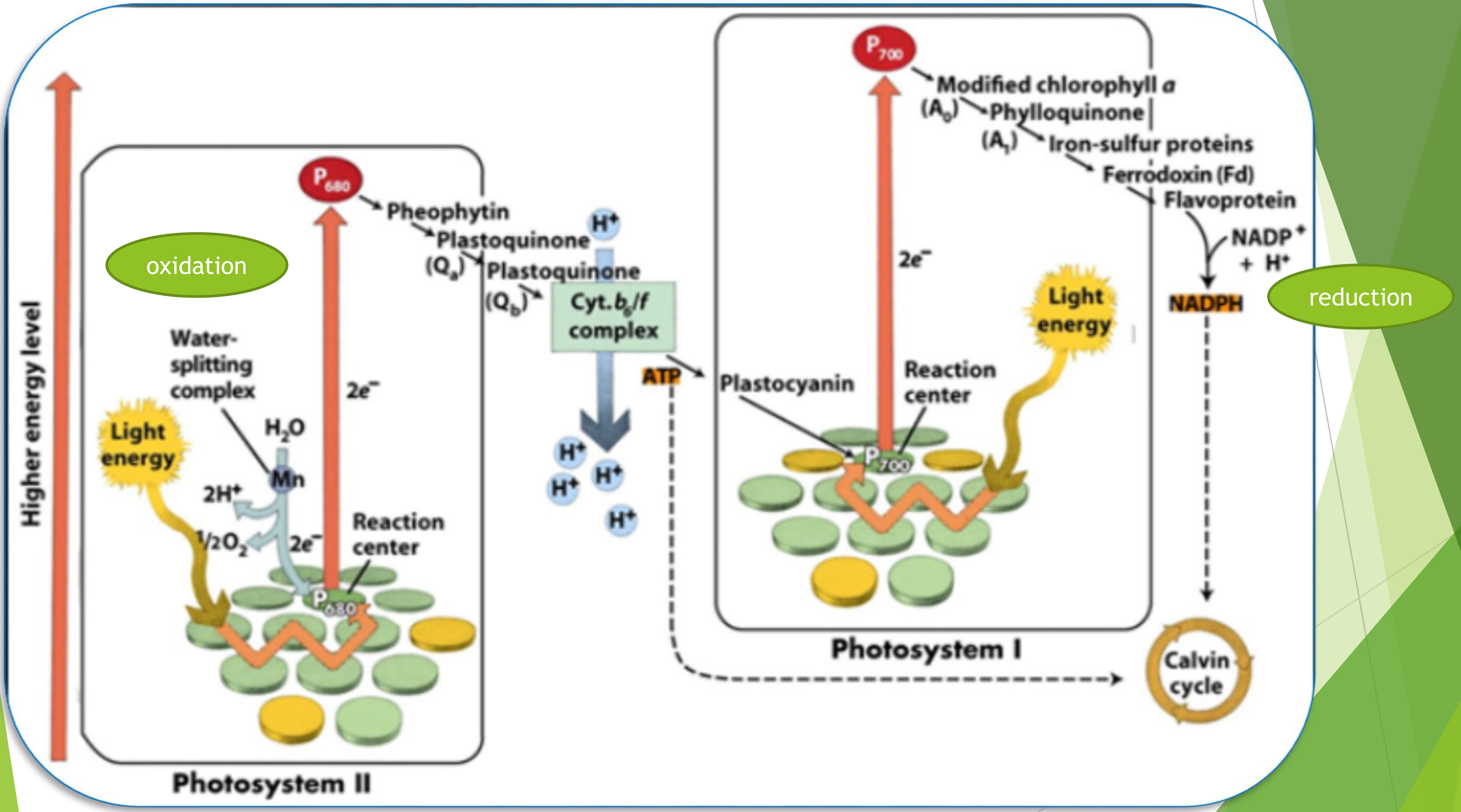
Reaction 12.6: Photochemistry in a reaction center

$$\text{Chl A} \xrightarrow{h\nu} \text{Chl}^{*}\,\text{A} \rightarrow \text{Chl}^{+}\,\text{A}^{-}$$

- The special chlorophyll in the reaction center can be excited directly by absorption of a photon, or it can be excited upon receipt of excitation energy from the antenna. Thus, the antenna, which consists of many pigment molecules, increases the absorption cross-section of the reaction center. (P: 300)



Oxygenic photosynthetic organisms contain two photochemical reaction centers, **PSI** and **PSII**



- Oxidation of water produces O2 and releases electrons required by PSII.
- P680, the reaction center chlorophyll of PSII, undergoes light-induced oxidation to produce the strong oxidant, P680+, which can oxidize water to release O2.
- The oxidation of water is not a direct process, but involves a complex series of reactions on the oxidizing (luminal) side of PSII.
- The oxidation of water involves the transfer of four electrons:

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

- PSI, with its longer-wavelength reaction center P700, is more efficient in far-red light.
- PSII, however, operates more efficiently in red light because of its relatively shorter wavelength reaction center, P680. (p: 326)
- For photosynthesis to occur with optimal efficiency, the two photosystems must cooperate.
- the efficiency of photosynthesis would be expected to diminish if one of the two photosystems were preferentially activated, as would happen under either red or far-red light alone, but not under both combined.
- The red light that activates PSII photochemistry and oxidizes P680 generates reduced compounds, which would reduce subsequent electron carriers in the chain.
- By contrast, the far-red light that activates PSI photochemistry oxidizes the photosystem, which in turn oxidizes electron carriers located between the photosystems (e.g., cytochromes). (p: 304)
- PSI and PSII are in different locations (p: 311)

The chloroplast noncyclic electron transport chain produces O2, NADPH, and ATP and involves cooperation of PSI and PSII

Z-scheme (noncyclic photosynthetic electron transfer), a model of the chloroplast electron transfer chain that takes into account the different pigment and reaction center compositions of the two photosystems.

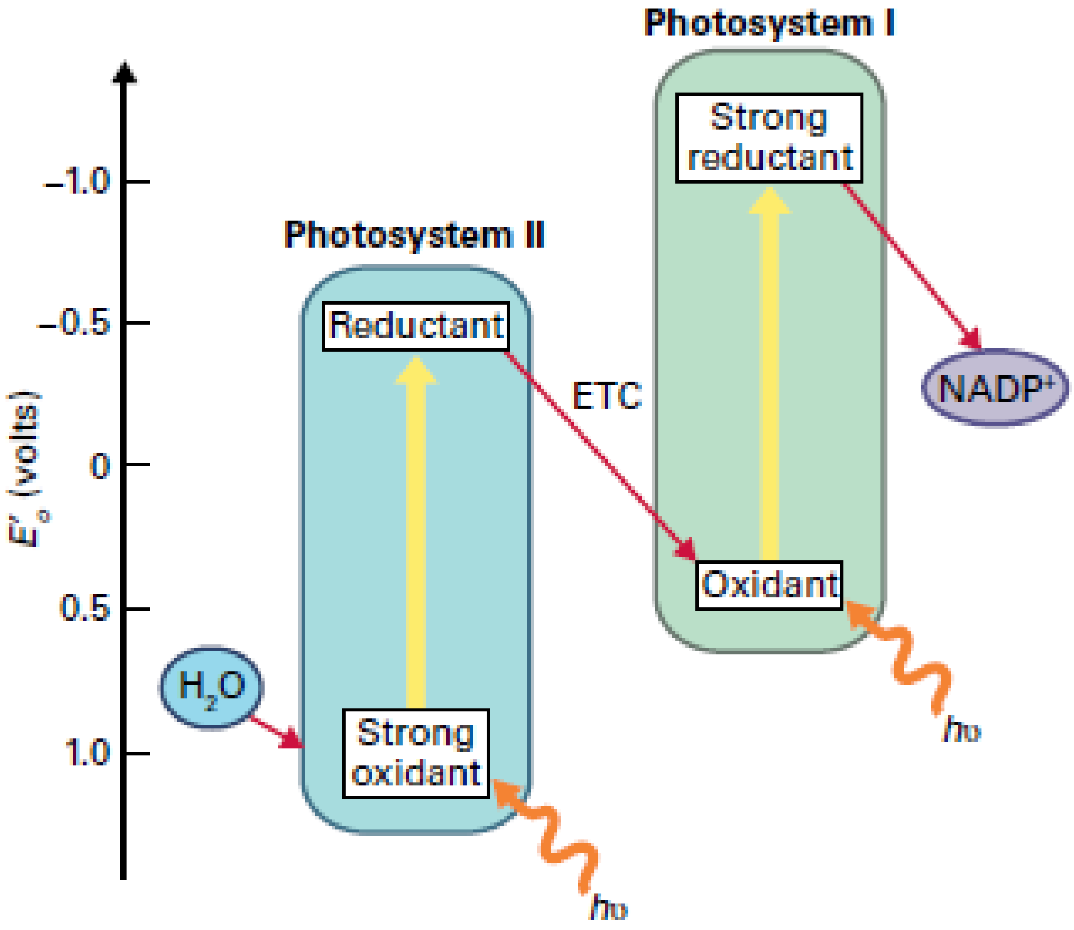


FIGURE 12.21 *Conceptual diagram of the Z-scheme, showing the cooperation of PSII and PSI in the transfer of electrons from water to NADP+. In the light, PSII generates a strong oxidant capable of oxidizing water, and a reductant. Illuminated PSI, in contrast, generates a strong reductant capable of reducing NADP+, and a weak oxidant. The two photosystems are linked by an electron transfer chain (ETC) that allows the PSI oxidant to receive electrons from the PSII reductant.*

This electron transfer pathway generates three principal products: O_2, ATP, and NADPH. The two photosystems are connected by a series of electron carriers that include plastoquinone, the cytochrome *b6f* complex, and plastocyanin. Oxidation of water and exergonic electron transport produce a proton electrochemical gradient that drives synthesis of ATP by the transmembrane ATP synthase.

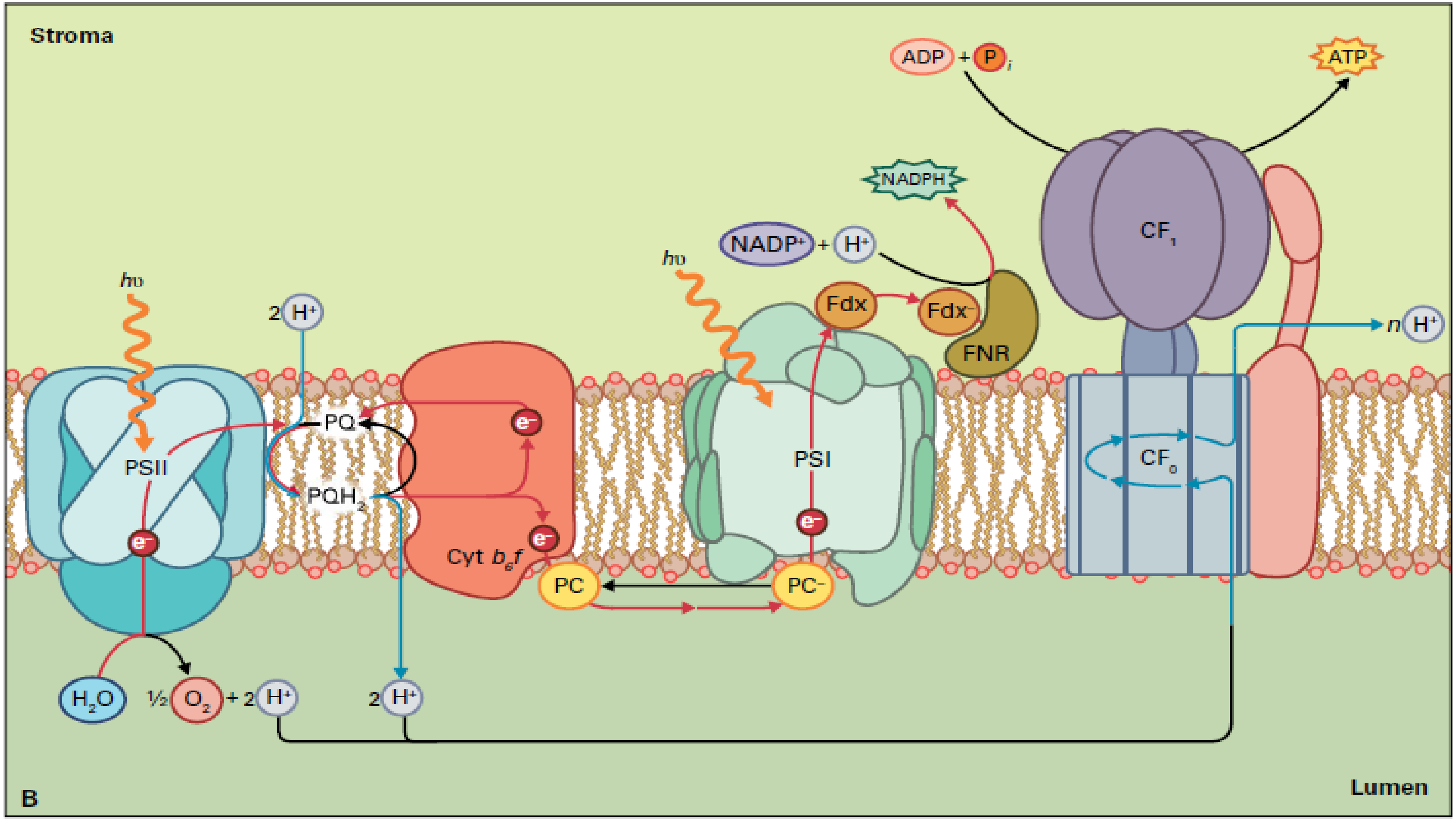


FIGURE 12.22 *(A) The current Z-scheme, showing E_m values of electron carriers. The vertical placement of each electron carrier of the noncyclic electron transfer chain corresponds to the midpoint of its redox potential. These voltage values have been verified experimentally. (B) Membrane organization of the Z-scheme. The components of the chloroplast electron transport chain and the ATP-synthesizing apparatus are illustrated in the thylakoid membrane. Four membrane complexes (PSII, PSI, the cytochrome b_6f complex, and the ATP synthase) are shown. Electrons are transferred from water to $NADP^+$; accompanying this electron transfer, a proton gradient is established across the membrane. This electrochemical gradient is ultimately utilized for the synthesis of ATP by the ATP synthase. Fdx, ferredoxin; FNR, ferredoxin-$NADP^+$ reductase.*

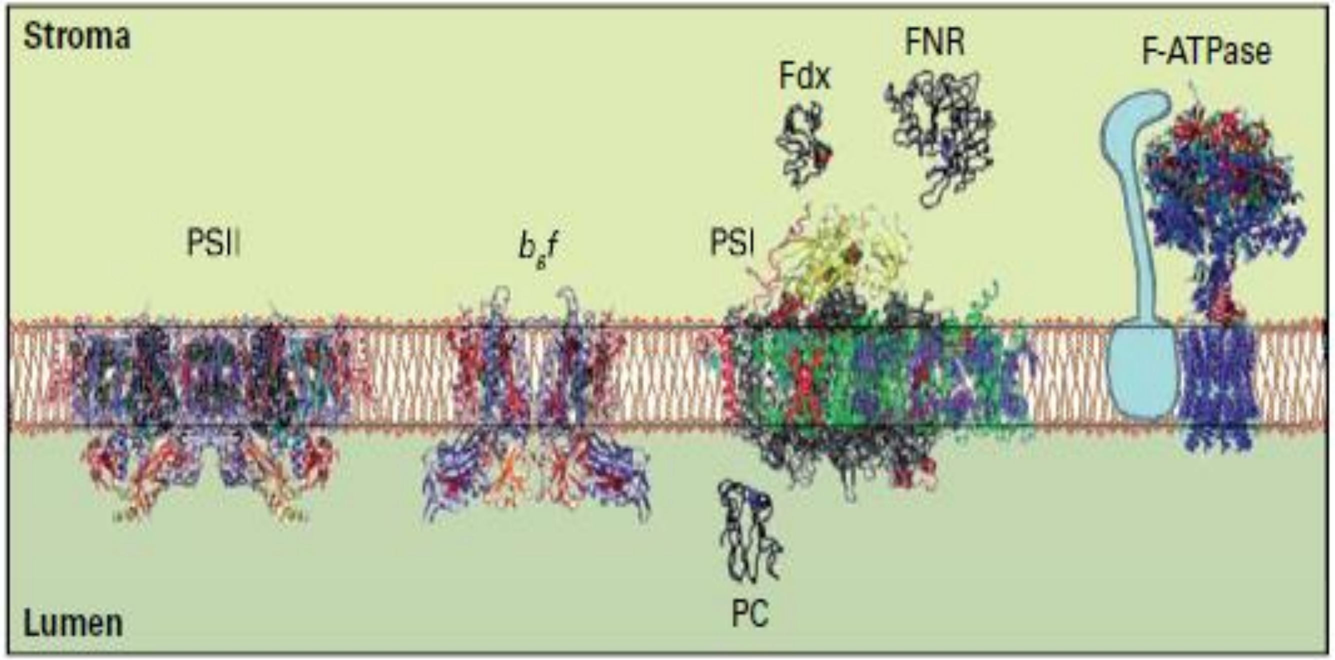


FIGURE 12.23 *A structural view of the Z-scheme showing structures of the major thylakoid membrane complexes (PSII, cytochrome b_6f complex, PSI, and ATP synthase) involved in the light reactions of oxygenic photosynthesis. Also shown are the structures of the soluble proteins Fdx and FNR on the stromal side of PSI, as well as PC in the lumen."*

- Chloroplasts also contain cyclic electron transport chains that involve PSI.
- Cyclic electron transport produces only ATP as a product without net production of NADPH. It seems to be involved in adjusting the ratio of ATP to NADPH production.

Photophosphorylation

- Photophosphorylation refers to the use of light energy from photosynthesis to ultimately provide the energy to convert ADP to ATP, thus replenishing the universal energy currency in living things.
- In eukaryotes, oxidative phosphorylation occurs in mitochondria, while photophosphorylation occurs in chloroplasts to produce ATP.
- Photophosphorylation involves the oxidation of H_2O to O_2, with $NADP^+$ as electron acceptor. Therefore, the oxidation and the phosphorylation of ADP are coupled by a proton gradient across the membrane.
- Energy released by the electron transfer processes pump the protons to the intermembrane region, where they accumulate in a high enough concentration to phosphorylate the ADP to ATP.

- Under the high light intensities found in nature, plants may absorb more light energy than they can use for photosynthesis. This excessive excitation of chlorophylls can increase formation of the triplet state of chlorophyll and the singlet state of oxygen. Damage caused by singlet oxygen and its reactive products can decrease the efficiency of photosynthesis in a process known as **photoinhibition.**
- All oxygenic photoautotrophs regulate light harvesting to protect against photoinhibition when light is in excess. In plants, various **nonphotochemical quenching** (NPQ) processes act as safety valves for photosynthesis that dissipate excess absorbed light energy harmlessly as heat (Fig.).

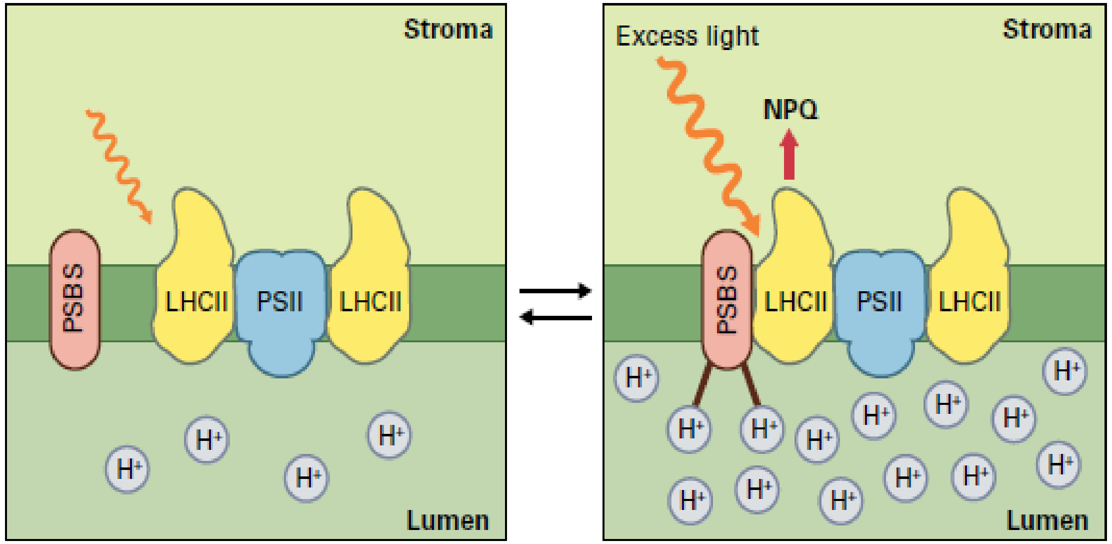


FIGURE 12.33 *Nonphotochemical quenching regulates light harvesting by PSII. In limiting light, LHC proteins efficiently transfer excitation energy to the reaction center of PSII. In excess light, when the rate of photosynthesis is saturated and protons accumulate to a high concentration in the thylakoid lumen, a flexible type of nonradiative dissipation is induced in the PSII antenna on a timescale of seconds to minutes. Proton binding to the PSBS protein and accumulation of zeaxanthin (not shown) causes a conformational change or reorganization of PSII that switches the antenna into a dissipative state that prevents overexcitation of chlorophyll and overreduction of the electron transport chain.*

Carbon reactions:
the Calvin-Benson cycle