Photosynthesis: The light Reactions

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When Molecules Absorb or Emit Light, They Change Their Electronic State

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\text{Chl} + h\nu \rightarrow \text{Chl}^* \]

- **lowest-energy, or ground state**
- **higher-energy, or excited, state**
- extremely unstable

stable for a maximum of several nano-seconds \((10^{-9} \text{ s})\)
In the lowest excited state, the excited chlorophyll has four alternative pathways for disposing of its available energy.

1. Excited chlorophyll can re-emit a photon and thereby return to its ground state—a process known as **fluorescence**. Chlorophylls fluoresce in the red region of the spectrum.

2. The excited chlorophyll can return to its ground state by directly converting its excitation energy into heat, with no emission of a **photon**.

3. Chlorophyll may participate in **energy transfer**, during which an excited chlorophyll transfers its energy to another molecule.

4. A fourth process is **photochemistry**, in which the energy of the excited state causes chemical reactions to occur. The photochemical reactions of photosynthesis are among the fastest known chemical reactions.
Photosynthesis Takes Place in Complexes Containing Light-Harvesting Antennas and Photochemical Reaction Centers

Many pigments together serve as an antenna, collecting light and transferring its energy to the reaction center, where chemical reactions store some of the energy by transferring electrons from a chlorophyll pigment to an electron acceptor molecule.

An electron donor then reduces the chlorophyll again.

The transfer of energy in the antenna is a purely physical phenomenon and involves no chemical changes.
The integral membrane proteins contain a large proportion of hydrophobic amino acids and are therefore much more stable in a nonaqueous medium such as the hydrocarbon portion of the membrane.

The reaction centers, the antenna pigment–protein complexes, and most of the electron transport enzymes are all integral membrane proteins.

In all known cases, integral membrane proteins of the chloroplast have a unique orientation within the membrane.

Thylakoid membrane proteins have one region pointing toward the stromal side of the membrane and the other oriented toward the interior portion of the thylakoid, known as the lumen.
Thylakoids Contain Integral Membrane Proteins

The chlorophylls and accessory light-gathering pigments in the thylakoid membrane are always associated in a non-covalent but highly specific way with proteins.

Both antenna and reaction center chlorophylls are associated with proteins that are organized within the membrane so as to optimize energy transfer in antenna complexes and electron transfer in reaction centers, while at the same time minimizing wasteful processes.
Photosystems I and II Are Spatially Separated in the Thylakoid Membrane

Photosystem II is located predominantly in the stacked regions of the thylakoid membrane.

Photosystem I and ATP synthase are found in the unstacked regions protruding into the stroma. Cytochrome b₆f complexes are evenly distributed.

This lateral separation of the two photosystems requires that electrons and protons produced by photosystem II be transported a considerable distance before they can be acted on by photosystem I and the ATP-coupling enzyme.

Most commonly, the ratio of PSII to PSI is about 1.5:1, but it can change when plants are grown in different light conditions.
Antenna systems function to deliver energy efficiently to the reaction centers with which they are associated.

The physical mechanism by which excitation energy is conveyed from the chlorophyll that absorbs the light to the reaction center is thought to be **resonance transfer**.

**Resonance transfer** is very efficient: Approximately 95 to 99% of the photons absorbed by the antenna pigments have their energy transferred to the reaction center, where it can be used for photochemistry.

There is an important difference between energy transfer among pigments in the antenna and the electron transfer that occurs in the reaction center:

- energy transfer is a purely physical phenomenon
- electron transfer involves chemical changes in molecules
The Antenna Funnels Energy to the Reaction Center

The excited-state energy of pigments increases with distance from the reaction center; that is, pigments closer to the reaction center are lower in energy than those farther from the reaction center.

This energy gradient ensures that excitation transfer toward the reaction center is energetically favorable and that excitation transfer back out to the peripheral portions of the antenna is energetically unfavorable.

Some energy is lost as heat to the environment by this process, but under optimal conditions almost all the excitations absorbed in the antenna complexes can be delivered to the reaction center.
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Many Antenna Complexes Have a Common Structural Motif

In all eukaryotic photosynthetic organisms that contain both chlorophyll a and chlorophyll b, the most abundant antenna proteins are members of a large family of structurally related proteins.

Some of these proteins are associated primarily with photosystem II and are called light-harvesting complex II (LHCII) proteins;

Others are associated with photosystem I and are called LHCl proteins.

These antenna complexes are also known as chlorophyll a/b antenna proteins.
The antenna complex is a transmembrane pigment protein, with three helical regions that cross the nonpolar part of the membrane.

Approximately 15 chlorophyll a and b molecules are associated with the complex, as well as several carotenoids.

The positions of several of the chlorophylls are shown, and two of the carotenoids form an X in the middle of the complex.

In the membrane, the complex is trimeric and aggregates around the periphery of the PSII reaction center complex.
Many Antenna Complexes Have a Common Structural Motif

When the antenna is excited with light, excitations are transferred to the reaction center within \( \sim 40 \) ps

Smaller “LH2” antenna complexes transfer energy rapidly to LH1

1 ps = \( 10^{-12} \) s

antenna BCHls are green and blue in this figure.
MECHANISMS OF ELECTRON TRANSPORT

Electrons Ejected from Chlorophyll Travel Through a Series of Electron Carriers Organized in the “Z Scheme”
Almost all the chemical processes that make up the light reactions of photosynthesis are carried out by four major protein complexes:

1. Photosystem II
2. Cytochrome b₆f complex,
3. Photosystem I
4. ATP synthase.

These four integral membrane complexes are vectorially oriented in the thylakoid membrane to function as follows:

- Photosystem II oxidizes water to \( \text{O}_2 \) in the thylakoid lumen and in the process releases protons into the lumen.

- Cytochrome b₆f receives electrons from PSII and delivers them to PSI. It also transports additional protons into the lumen from the stroma.

- Photosystem I reduces NADP+ to NADPH in the stroma by the action of ferredoxin (Fd) and the flavoprotein ferredoxin–NADP reductase (FNR).

- ATP synthase produces ATP as protons diffuse back through it from the lumen into the stroma.
The Photosystem II Reaction Center Is a Multisubunit Pigment–Protein Complex

Photosystem II is contained in a multisubunit protein supercomplex.

In higher plants, the multisubunit protein supercomplex has two complete reaction centers and some antenna complexes.

The core of the reaction center consists of two membrane proteins known as D1 and D2, as well as other proteins.

Helical arrangement of the D1 and D2 (red) and CP43 and CP47 (green) core subunits.
The Photosystem II Reaction Center Is a Multisubunit Pigment–Protein Complex

View from the lumenal side of the supercomplex, including additional antenna complexes, LHCII, CP26 and CP29, and extrinsic oxygen-evolving complex, shown as orange and yellow circles. Unassigned helices are shown in gray.

Side view of the complex illustrating the arrangement of the extrinsic proteins of the oxygen-evolving complex.
Water is a very stable molecule.

Oxidation of water to form molecular oxygen is very difficult, and the photosynthetic oxygen-evolving complex is the only known biochemical system that carries out this reaction.

It has been known for many years that manganese (Mn) is an essential cofactor in the water-oxidizing process.
Water Is Oxidized to Oxygen by Photosystem II

Model of the S state cycle of oxygen evolution in PSII.

Successive stages in the oxidation of water via the Mn oxygen-evolving complex are shown.

$Y_z$ is a tyrosine radical that is an intermediate electron carrier between $P_{680}$ and the Mn cluster.

A radical formed from a tyrosine residue in the D1 protein of the PSII reaction center
Pheophytin and Two Quinones Accept Electrons from Photosystem II

Pheophytin is a chlorophyll in which the central magnesium atom has been replaced by two hydrogen atoms.

This chemical change gives pheophytin chemical and spectral properties that are slightly different from those of chlorophyll.

The precise arrangement of the carriers in the electron acceptor complex is not known.

Two plastoquinones ($Q_A$ and $Q_B$) are bound to the reaction center and receive electrons from pheophytin in a sequential fashion.
The plastoquinone consists of a quinoid head and a long non-polar tail that anchors it in the membrane.

Transfer of the two electrons to \( Q_B \) reduces it to \( Q_B^{2-} \), and the reduced \( Q_B^{2-} \) takes two protons from the stroma side of the medium, yielding a fully reduced plastohydroquinone (\( QH_2 \)).

The plastohydroquinone then dissociates from the reaction center complex and enters the hydrocarbon portion of the membrane, where it in turn transfers its electrons to the cytochrome \( b_6f \) complex.

Hydroquinone is a small, nonpolar molecule that diffuses readily in the nonpolar core of the membrane bilayer.
Electron Flow through the Cytochrome b₆f Complex Also Transports Protons (Q cycle)

The cytochrome b₆f complex is a large multisubunit protein with several prosthetic groups

- two b-type cytochromes
- a c-type cytochrome
- a Rieske Fe–S protein (FeS₉)
- two quinone oxidation–reduction sites
Electron Flow through the Cytochrome b₆f Complex Also Transports Protons

The noncyclic or linear processes:

1. A plastohydroquinone (QH₂) molecule produced by the action of PSII is oxidized near the lumenal side of the complex, transferring its two electrons to the Rieske Fe–S protein and one of the b-type cytochromes and simultaneously expelling two protons to the lumen.

2. The electron transferred to FeSₐ is passed to cytochrome f (Cyt f) and then to plastocyanin (blue-colored copper protein; PC), which reduces P700 of PSI.

3. The reduced b-type cytochrome transfers an electron to the other b-type cytochrome, which reduces a quinone (Q) to the semiquinone (Q•) state.

(A) First QH₂ oxidized

STROMA
Thylakoid membrane

PSII

LUMEN

2 H⁺
Electron Flow through the Cytochrome $b_6f$ Complex Also Transports Protons

The cyclic processes:

1. A second $\text{QH}_2$ is oxidized, with one electron going from $\text{FeS}_R$ to PC and finally to P700.

2. The second electron goes through the two b-type cytochromes and reduces the semiquinone to the plastohydroquinone, at the same time picking up two protons from the stroma.

3. Overall, four protons are transported across the membrane for every two electrons delivered to P700.

Gives rise to an electrochemical potential across the membrane, due in part to $\text{H}^+$ concentration differences on the two sides of the membrane.
Plastocyanin Carry Electrons between Cytochrome b₆f and I

Plastocyanin is a small (10.5 kDa), water-soluble, copper-containing protein that transfers electrons between the cytochrome b₆f complex and P700.

This protein is found in the lumenal space.

In certain green algae and cyanobacteria, a c-type cytochrome is sometimes found instead of plastocyanin; which of these two proteins is synthesized depends on the amount of copper available to the organism.
The Photosystem I Reaction Center Reduces NADP⁺

The PSI reaction center complex is a large multisubunit complex.

Components of the PSI reaction center are organized around two major proteins, PsaA and PsaB.

Minor proteins PsaC to PsaN are labelled C to N.

Electrons are transferred from plastocyanin (PC) to P700 and then to a chlorophyll molecule: A₀ to phylloquinone: A₁, to the FeSₓ, FeSᴬ, and FeSᴮ Fe–S centers, and finally to the soluble iron–sulfur protein, ferrodoxin (Fd).

The membrane-associated flavoprotein ferredoxin–NADP reductase (FNR) reduces NADP⁺ to NADPH, thus completing the sequence of non-cyclic electron transport that begins with the oxidation of water.
PROTON TRANSPORT AND ATP SYNTHESIS IN THE CHLOROPLAST

Summary of the experiment carried out by Jagendorf and coworkers.
The ATP is synthesized by a large (400 kDa) enzyme complex known by several names: ATP synthase, ATPase (after the reverse reaction of ATP hydrolysis), and CF<sub>0</sub>–CF<sub>1</sub>

This enzyme consists of two parts: a hydrophobic membrane-bound portion called CF<sub>0</sub> and a portion that sticks out into the stroma called CF<sub>1</sub>

CF<sub>0</sub> appears to form a channel across the membrane through which protons can pass.

CF<sub>1</sub> is made up of several peptides, including three copies of each of the α and β peptides arranged alternately much like the sections of an orange.

Whereas the catalytic sites are located largely on the β polypeptide, many of the other peptides are thought to have primarily regulatory functions.

CF<sub>1</sub> is the portion of the complex that synthesizes ATP.
Similarities of photosynthetic and respiratory electron flow in bacteria, chloroplasts, and mitochondria.

(A) A reaction center (RC) in purple photosynthetic bacteria carries out cyclic electron flow, generating a proton potential by the action of the cytochrome bc\(_1\) complex.

(B) Chloroplasts carry out noncyclic electron flow, oxidizing water and reducing NADP\(^+\). Protons are produced by the oxidation of water and by the oxidation of PQH\(_2\) (Q) by the cytochrome b\(_6\)f complex.

(C) Mitochondria oxidize NADH to NAD\(^+\) and reduce oxygen to water. Protons are pumped by the enzyme NADH dehydrogenase, the cytochrome bc\(_1\) complex, and cytochrome oxidase.

The ATP synthases in the three systems are very similar in structure.
THE END