

Photosynthesis

March 7, 2003

Bryant Miles

The vast majority of energy consumed by living organisms stems from solar energy captured by phototrophic organisms. 1.5×10^{22} kJ of energy produced by the sun reaches the earth every day. Photosynthetic organisms convert 1 % of the solar energy into chemical energy. This chemical energy is stored in the form of biomolecules, which are harvested by the organisms that eat them forming food chains. The basic equation of photosynthesis is deceptively simple. Water and carbon dioxide combine to form carbohydrates and molecular oxygen.

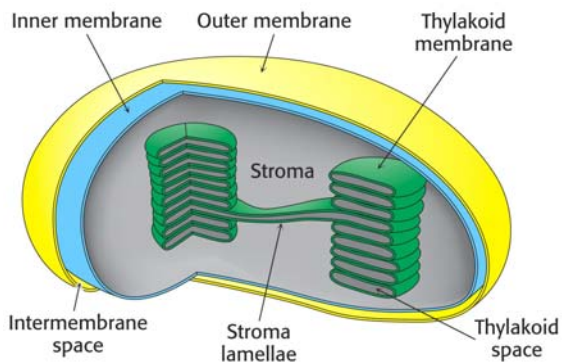


$$\Delta G^{\circ} = 2,798 \text{ kJ/mol}$$

Of course the process of photosynthesis is a complex process involving photoreceptors, reaction centers, protein complexes, electron carriers, ect. By this complex process 10^{11} tons of carbon dioxide are fixed globally every year.

A diverse group of organisms are capable of photosynthesis. From bacteria to the tallest trees, photosynthesis occurs in membranes. In photosynthetic bacteria the plasma membrane fills up the cells interior. In eukaryotes, the photosynthetic membranes are contained within an organelle called a chloroplast.

The Chloroplast



The chloroplast has many similarities to the mitochondrion.

It has a porous outer membrane, an intermembrane space and an inner membrane that is impermeable to most molecules.

The inner membrane encloses the stroma which is analogous to the matrix of the mitochondria.

In the stroma are the soluble enzymes that utilize NADPH and ATP to convert CO_2 into carbohydrates.

Also contained in the stroma is the DNA of the chloroplast and the machinery for replication,

transcription and translation. Chloroplasts are not autonomous they require many proteins encoded by the nuclear DNA.

Within the stroma are membraneous structures called thylakoids which are flatten discs stacked to form granum. Different grana are linked together by stroma lamellae. The thylakoid membranes are impermeable to most ions and molecules. The chloroplasts have three distinct membranes, outer, inner and thylakoid membranes, which enclose three separate spaces, intermembrane space, stroma, and the thylakoid space (also called the thylakoid lumen). The thylakoid membrane is the site of oxidation-reduction reactions that generate a proton motive force analogous to the cristae in the mitochondrion. The thylakoid membrane also contains the energy-transducing machinery that harvests the energy of the sun. The pigments that absorb light, the reaction centers, electron transport chains and ATP synthase are all contained within the thylakoid membrane.

Light and Dark Reactions

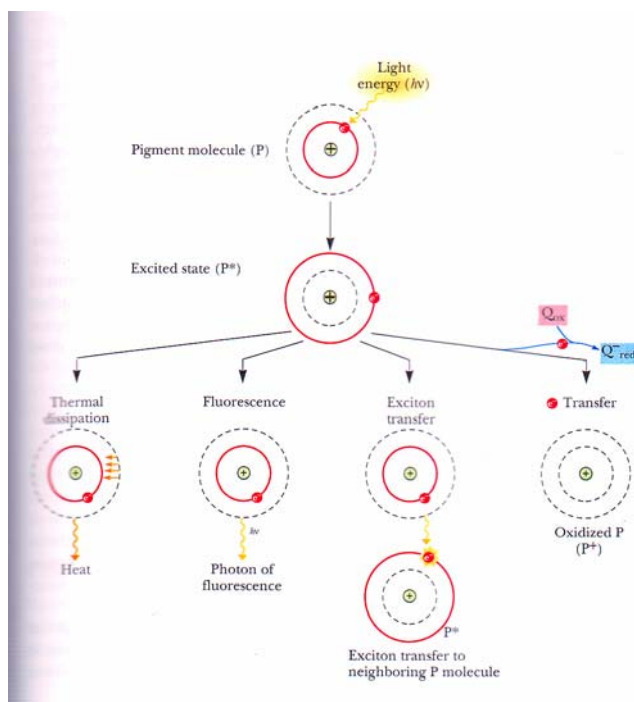
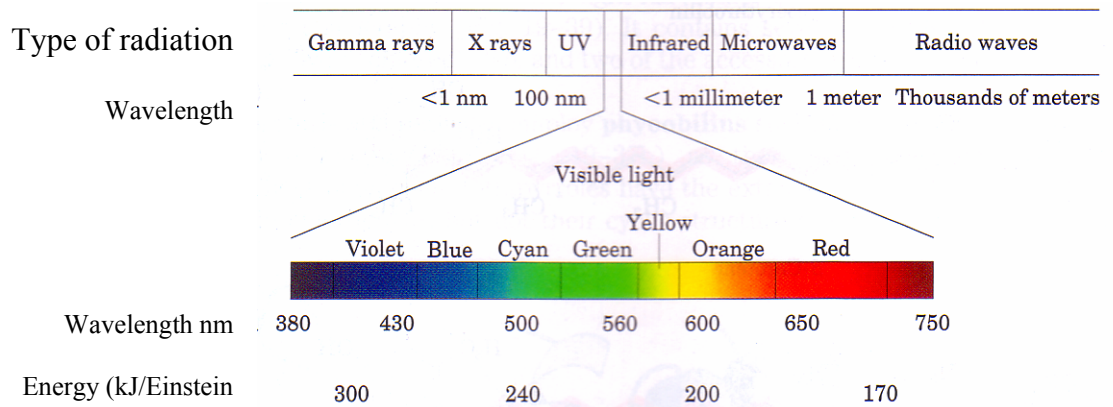
The light reactions are reactions that couple the energy produced by the absorption of a photon of light with redox reactions. These light reactions occur within the thylakoid membrane. The dark reactions are the chemical reactions involved in fixing CO₂ for the synthesis of carbohydrates. These reactions occur in the stroma. Dark reactions can occur in the dark or in the light. They are called dark reactions because they are driven by the energy provided by ATP and NADPH, not by photons of light.

Light Absorption.

Visible light is electromagnetic radiation of wavelengths between 400 – 700 nm which is a very small part of the electromagnetic spectrum. Because the speed of light is constant, $c = 2.9979 \times 10^8$ m/s, and the energy $E = hc/\lambda$ where h is Planck's constant (6.626×10^{-34} J·s), c is the speed of light and λ is the wavelength, the shorter the wavelength the higher the energy.

A mole of photons is called an Einstein = 6.22×10^{23} photons.

The energy range of visible light is 170 to 300 kJ/Einstein which is ten time more energy than we need to synthesize ATP from ADP and Pi.

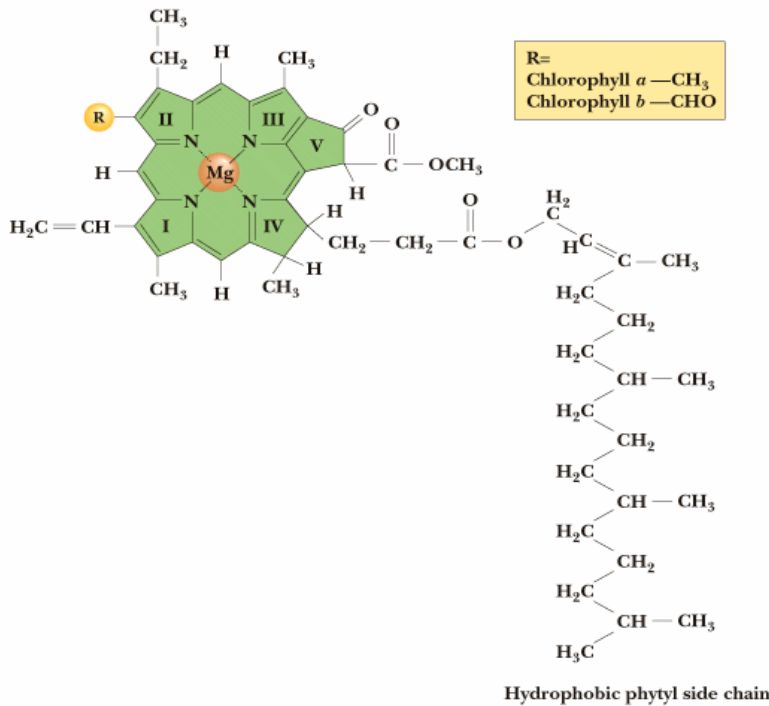


When a photon of light is absorbed, an electron in the absorbing molecule is lifted to a higher energy level. Due to the principles of quantum mechanics, this is an all or nothing event. This requires that the energy of the photon be exactly equal to the energy of the electronic transition. A molecule that has absorbed a photon is in an excited state. The excited molecule will eventually return to the ground state giving up the energy as either heat, electron transfer, exciton transfer or as emission of a photon of light at a longer wavelength (Fluorescence).

Exciton transfer is the transfer of excitation energy, by a radiationless process to a neighboring molecule. This resonance energy transfer is called exciton transfer.

The electron in the excited state has a significantly higher energy than the ground state. The excited state dramatically changes the standard reduction potential of the pigment that absorbs the photon. The excited electron has a much higher transfer potential than the ground state electron. The absorption of a photon generates a potent electron donor. This transduction of light energy into chemical energy, this photochemical event, is the essence of photosynthesis.

Chlorophylls



Chlorophylls are magnesium containing substitute tetrapyrroles whose basic structure is similar to heme porphyrins.

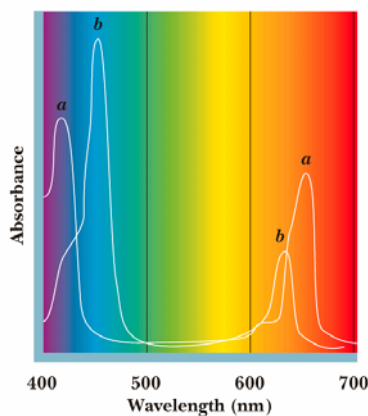
Chlorophylls have magnesium coordinated to the planar center of the conjugated ring.

Chlorophylls contain a long chain alcohol called phytyl which is attached to the tetrapyrrole ring by an ester linkage.

Chlorophylls are excellent light absorbers because of their aromaticity. When a chlorophyll molecule absorbs a photon of light, the excited electron has an enhanced potential for transfer to a suitable electron acceptor. The

loss of this high energy electron is an oxidation-reduction reaction. The net result is the conversion of light energy into chemical energy driving a redox reaction.

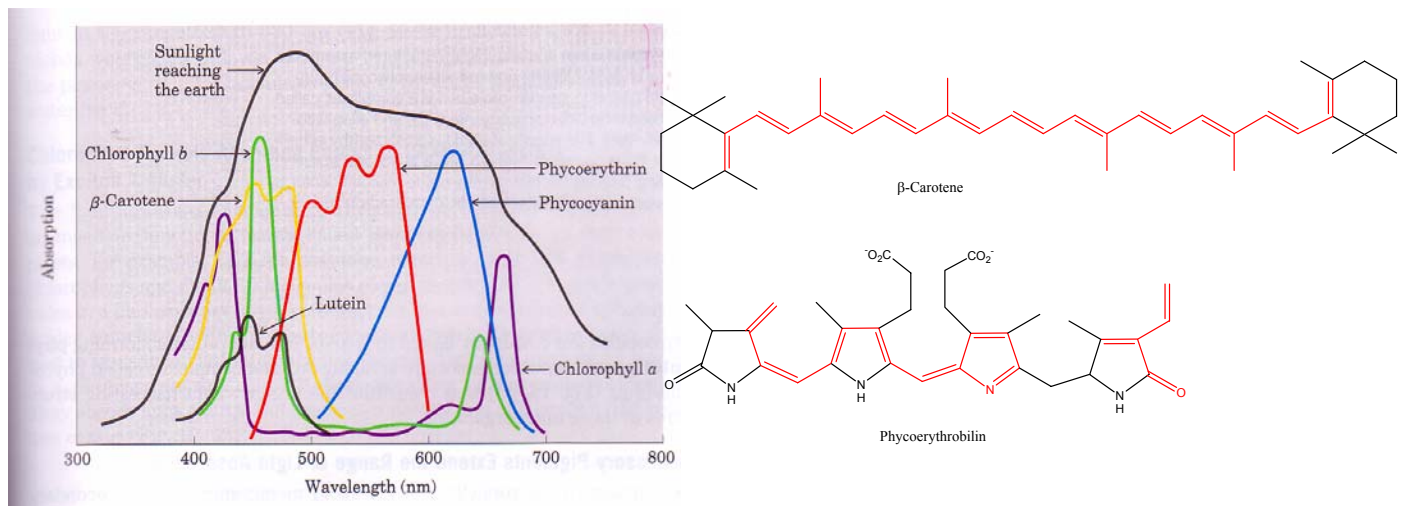
The absorption spectra of chlorophylls *a* and *b* is shown below.



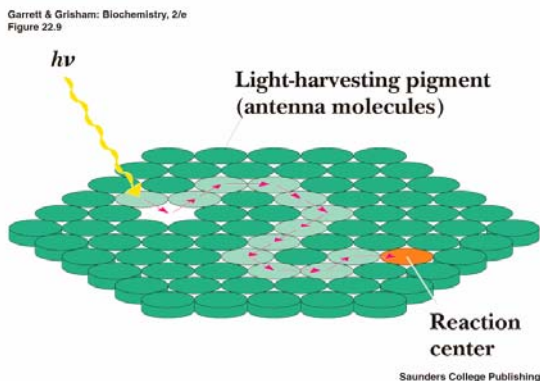
Chloroplasts of plants always contain both chlorophyll *a* and chlorophyll *b*. Both chlorophylls have a green color, but their absorption spectra are slightly different allowing them to complement each other's range of light absorption in the visible region. Typically plants contain twice as much chlorophyll *a* than chlorophyll *b*.

Note there is a big gap in the middle of visible spectrum. There are other pigments in photosynthetic organisms that increase the probability of absorption of visible light within this gap. These pigments are called accessory light harvesting pigments which absorb wavelengths of light not absorbed by the chlorophylls. These accessory pigments such as carotenoids and phycobilins are responsible for the beautiful colors of autumn because these accessory

pigments last a lot longer than chlorophyll. Like chlorophyll these pigments have conjugated double bonds and absorb visible light.



Exciton Transfer



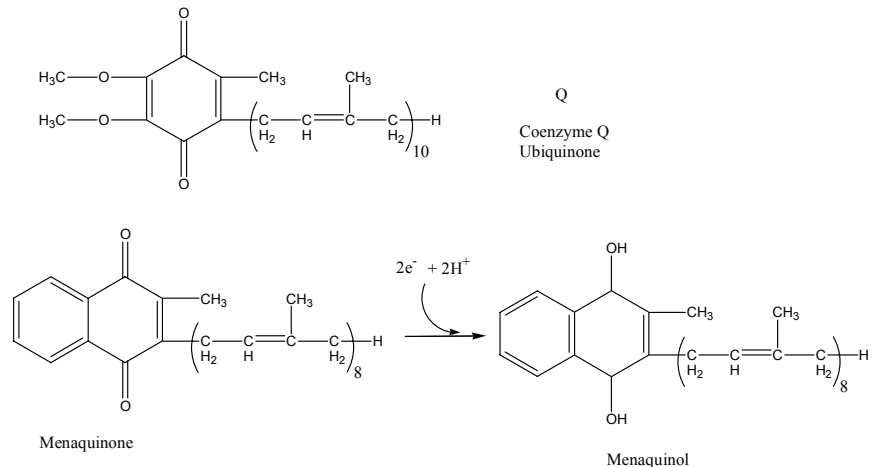
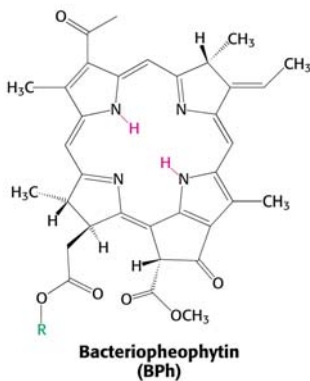
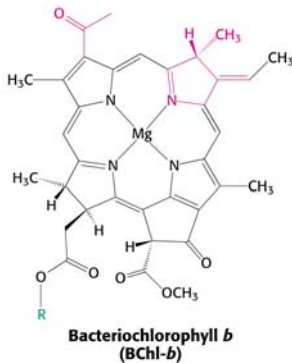
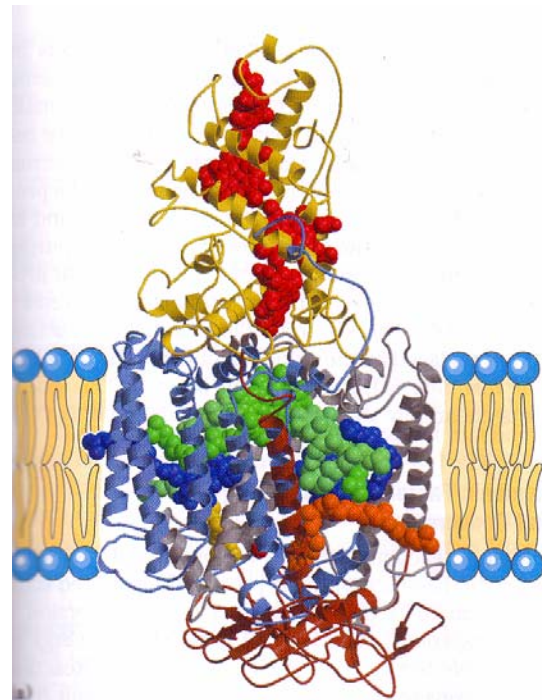
The light absorbing pigments and chlorophylls of the thylakoid membranes are arranged into functional arrays called **photosystems**. Each chloroplast contains approximately 200 molecules of chlorophylls and about 50 molecules of carotenoids. Only a few of the chlorophylls are associated with a photochemical **reaction center** where the energy of the absorbed light is transduced into chemical energy. All of the other chlorophyll and pigment molecules are light harvesting or antenna molecules. They absorb photons of light energy and transfer the energy by exciton transfer to the reaction centers.

Purple Photosynthetic Bacteria, *Rhodospseudomonas viridis*

Photosynthetic bacteria do not contain chloroplasts. They contain a relatively simple photosynthetic center which contains 4 polypeptides designated L (31 kD), M (36 kD), H (28 kD) and C, a c type cytochrome. The bacterial photosynthetic center is found in the plasma membrane. The primary sequence of the bacterial photosynthetic center is homologous to the two types of photocenters found in plants. The structure of this bacterial photocenter is similar to the photocenters found in plants as well.

The L and M subunits form the structural and functional core of the bacterial photosynthetic center. The two subunits are homologous with each containing 5 transmembrane α -helices. The H subunit has one transmembrane α -helix and lies on the cytoplasmic side of the membrane. The C subunit contains 4 c-type cytochromes and is found on the opposite periplasmic side of the membrane. Associated with the L and M subunits are 4 bacteriochlorophyll b molecules, 2 bacteriopheophytin molecules, two types of quinones and a ferrous ion.

In crystal structure on the right, **H (Brown)**, **M (Blue)**, **L (Gray)** and **C (Yellow)**. Shown as ball and sticks are the prosthetic groups that participate in photochemical events. Bound to the L and M subunits are the two pairs of bacterialchlorophylls shown in **green**. One of the pairs of bacteriochlorophylls is the special pair that absorbs the initial photon. There is also a pair of bacteriopheophytin (**light blue**) and two quinones, **menaquinone A (Q_A)** and **ubiquinone (Q_B)**

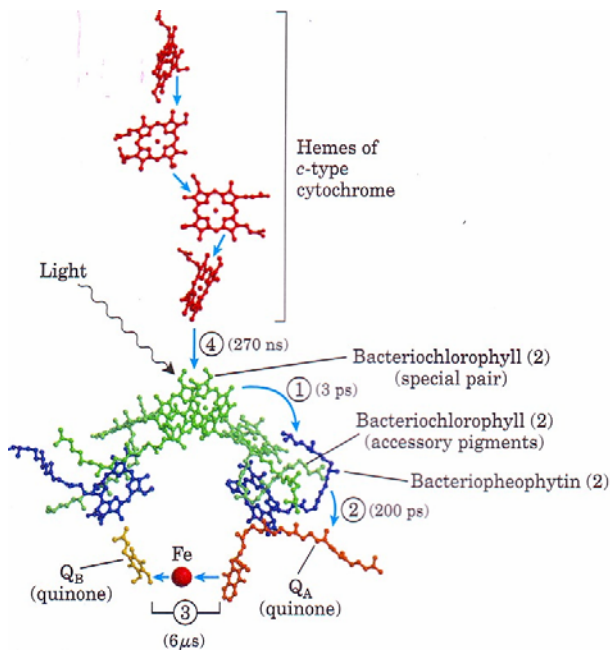


The bacteriochlorophylls are similar to plant chlorophylls except for the reduction of one of the pyrrole rings and other minor differences that shift the absorption maxima to the near infrared ≈ 1000 nm. This is important because these purple bacteria live in stagnant murky waters which visible light does not penetrate. Near-infrared light does penetrate, so these bacteria are equipped with bacteriochlorophylls that absorb the near-infrared light.

Bacteriopheophytin is a bacteriochlorophyll that has two protons instead of coordinating a magnesium ion.

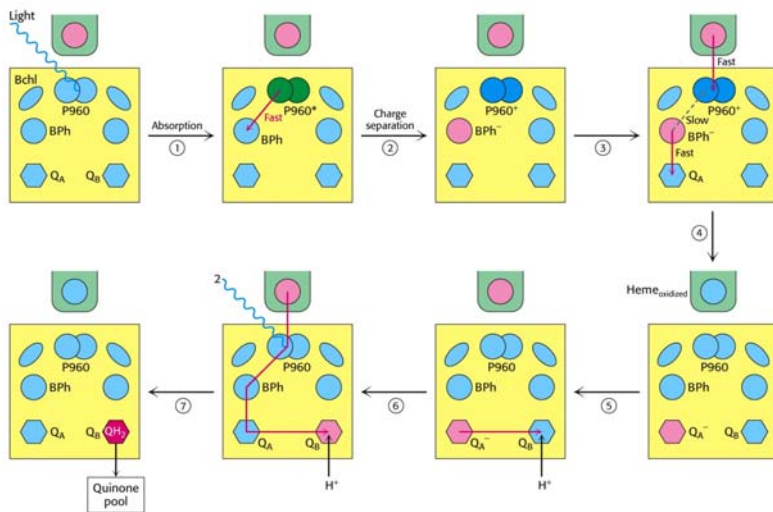
Energy from a photon of light is absorbed by one of the many photoreceptors surrounding the reaction center. This energy is transmitted via exciton transfer to the reaction center. Within the reaction center is a dimer of bacteriochlorophylls that lie near the periplasmic side of the membrane (opposite to the cytosolic side of the membrane). This dimer is called the **special pair**. The two Mg^{2+} ions are closely associated separated by a mere 7 \AA . The special pair can directly absorb a photon of light, the maximum

absorption is P960. When the special pair absorbs a photon of light or absorbs an exciton, the special pair gives up the high energy electron to a neighboring bacteriochlorophyll of the L subunit which in turn passes the electron to bacteriopheophytin. The special pair having lost the electron now is a positive radical. This cation radical is a powerful oxidizing agent. The ferrous iron of a near by cytochrome c of the C subunit transfers its electron to the cation radical. The bacteriopheophytin is a negative radical. This photo induced charge separation is a crucial part of photosynthesis. The pheophytin passes its electron to a loosely bound menaquinone (Q_A). This electron is then transferred via the non heme Fe^{2+} to ubiquinone (Q_B).



The sequence of events is shown to the left.

- (1) The excited electron located in the special pair is transferred to a bacteriochlorophyll which takes 270×10^{-9} seconds. The electron is then quickly transferred to a bacteriopheophytin (3×10^{-12} seconds).
- (2) The electron is then transferred to Q_A (200×10^{-12} seconds).
- (3) The electron is then slowly (6×10^{-6} seconds) to Q_B via the nonheme ferrous iron.
- (4) The electron hole in the special pair is filled by an electron from the heme of the cytochrome c.
- (5) A second exciton is transferred to the special pair. The electron is transferred via the same route to the semiquinone to form ubiquinol which is free to diffuse within the membrane.



The ubiquinol formed carries its electrons to an electron transport complex Cytochrome bc_1 which is similar to the complex III, that we studied in electron transport and oxidative phosphorylation.

The electrons are transferred by the Q cycle to generate a proton gradient to drive ATP synthesis.

In Cytochrome bc_1 , the electrons are transferred from ubiquinol to a special water soluble periplasmic cytochrome c_2 , which carries the electrons back to the C-subunit of the photosynthetic reaction center and transfers the electrons back to the same cytochrome

c that donated its electron to reduce the radical cation of the special pair formed in step 4. The flow of electrons is cyclic. The net result is that for every two electrons transferred from ubiquinol to cyt c_2 . Four protons are released into the periplasmic space (the space between the cell wall and the plasmamembrane). This helps generate a proton gradient that drives ATP synthesis. Similar to oxidative phosphorylation, this light dependent process is called photophosphorylation.