Photosynthetic Pigments

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Chlorophylls

- All photosynthetic organisms have pigments for the absorption of light. The most important of these pigments are the **chlorophylls.**
- Chlorophylls are polycyclic, large planar rings composed of four substituted pyrrole rings with a magnesium atom coordinated to the four central nitrogen atoms (**figure 1).**
- All chlorophylls have a long **phytol side chain, esterified to a carboxyl-group substituent** in ring IV, and chlorophylls also have a fifth five membered ring.
- The heterocyclic five-ring system that surrounds the Mg^{2+} has an extended polyene structure, with alternating single and double bonds.
- Such polyenes characteristically show strong absorption in the visible region of the spectrum .

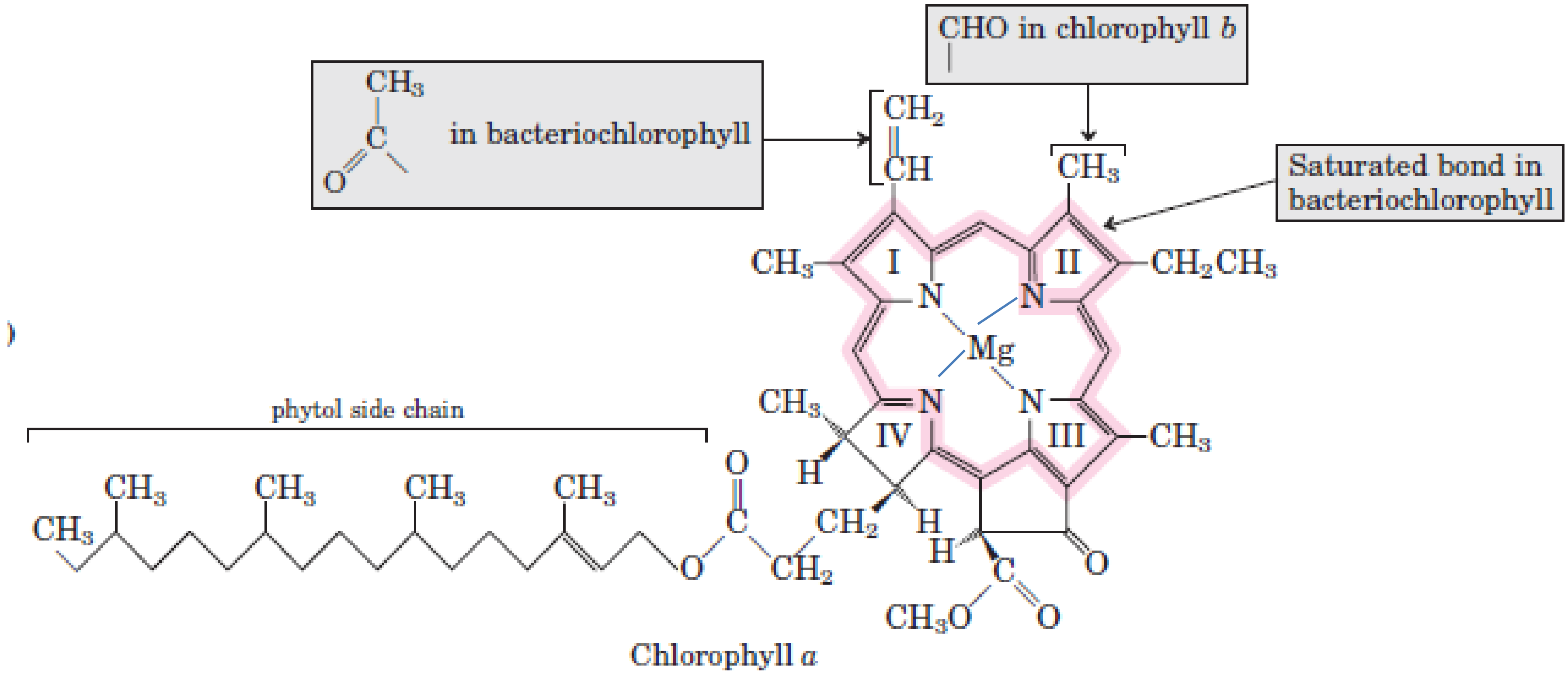

CHO in chlorophyll b
in bacteriochlorophyll
Saturated bond in bacteriochlorophyll
phytol side chain
Mg
Chlorophyll a

Figure 1.

...Chlorophylls

- Several chlorophylls are found in eucaryotes, the two most important of which are chlorophyll *a* and chlorophyll *b.*
- These two molecules differ slightly in their structure and spectral properties.
- When dissolved in acetone, absorb red light at
  - chlorophyll *a* has a light absorption peak at 665 nm;
  - chl *b is at 645 nm*
- In addition to absorbing red light, chlorophylls also absorb blue light strongly:
  - Chla the second absorption peak at 430 nm
  - Chl b at 460 nm.
- Because chlorophylls absorb primarily in the red and blue ranges, green light is transmitted.
- Consequently many photosynthetic organisms are green in color.

...Chlorophylls

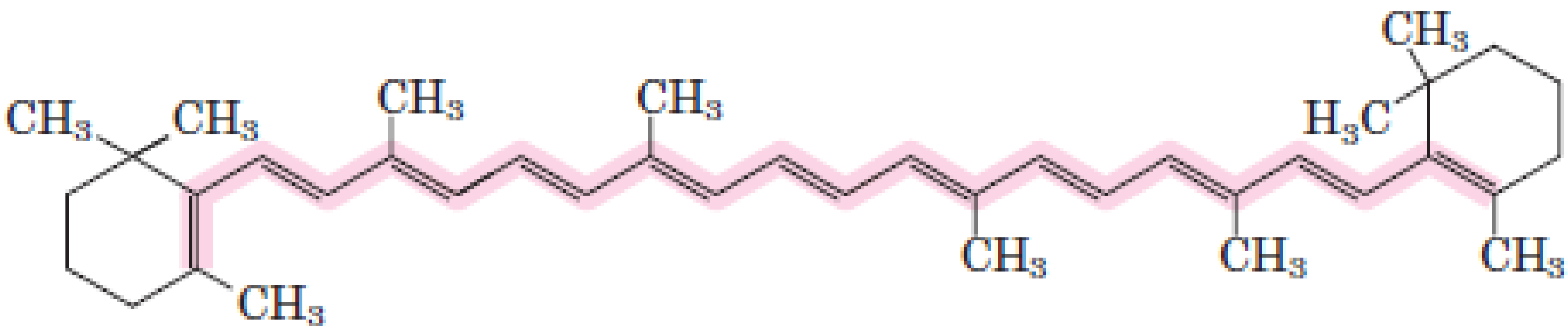
- The long hydrophobic tail attached to the chlorophyll ring aids in its attachment to membranes, the site of the light reactions.
- The pigments in algae and photosynthetic bacteria include chlorophylls that differ only slightly from the plant pigments.
- Chlorophyll is always associated with specific binding proteins, forming **light-harvesting complexes.**
- **(LHCs) in which chlorophyll molecules are** fixed in relation to each other, to other protein complexes, and to the membrane.

Accessory Pigments

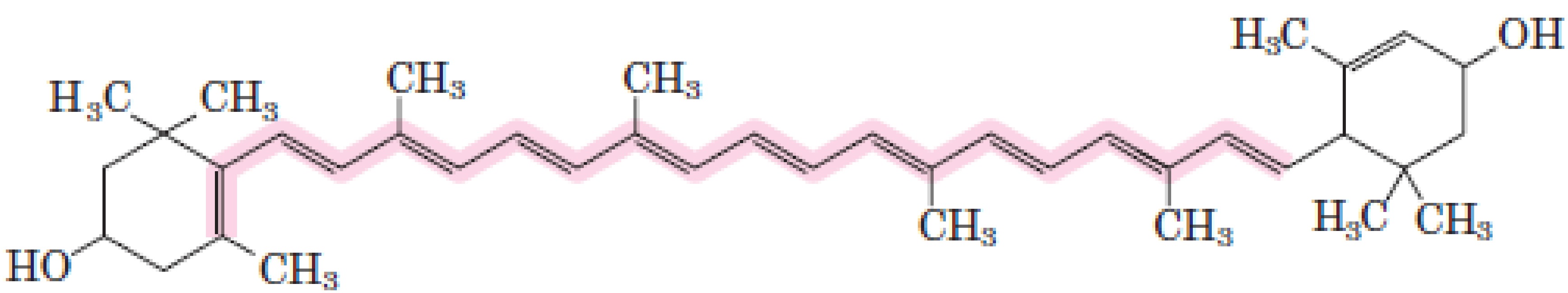
- Other photosynthetic pigments also trap light energy.
- Accessory pigments are therefore essential since they help absorb light of wavelength not absorbed by primary pigment and then pass the energy to a primary pigment, i.e. chlorophyll.
- The most widespread of these are the **carotenoids (eg. Xanthophylls and carotenes) and phycobilins (e.g. Phycoerythrin, phycocyanin etc).**
- By capturing light in a region of the spectrum not used by other organisms, a photosynthetic organism can claim a unique ecological niche.
- For example, the phycobilins in red algae and cyanobacteria absorb light in the range 520 to 630 nm, allowing them to occupy niches where light of lower or higher wavelength has been filtered out by the pigments of other organisms living in the water above them, or by the water itself.

Carotenoids

- Carotenoids may be yellow, red, or purple.
- The most important are β-carotene, which is a red-orange isoprenoid and the yellow carotenoid lutein or xanthophyll (Fig. 2).
- **The carotenoid pigments** absorb light at wavelengths not absorbed by the chlorophylls and thus are supplementary light receptors.
- β-Carotene is present in Prochloron and most divisions of algae.
- Fucoxanthin is found in diatoms, dinoflagellates, and brown algae (Phaeophyta).



β-Carotene



Lutein (xanthophyll)

Figure 2.

Phycobilins

- Cyanobacteria and red algae employ **phycobilins** such as phycoerythrobilin and phycocyanobilin (Fig. 3) as their light-harvesting pigments.
- These open chain tetrapyrroles have the extended polyene system found in chlorophylls, but not their cyclic structure or central Mg^{2+}.
- **Phycoerythrin** is a red pigment with a maximum absorption around 550 nm
- P**hycocyanin** is blue (maximum absorption at 620 to 640 nm).
- Phycobilins are covalently linked to specific binding proteins, forming **phycobiliproteins,** which associate in highly ordered complexes called phycobilisomes.
- Phycobilisomes constitute the primary light-harvesting structures in these microorganisms.

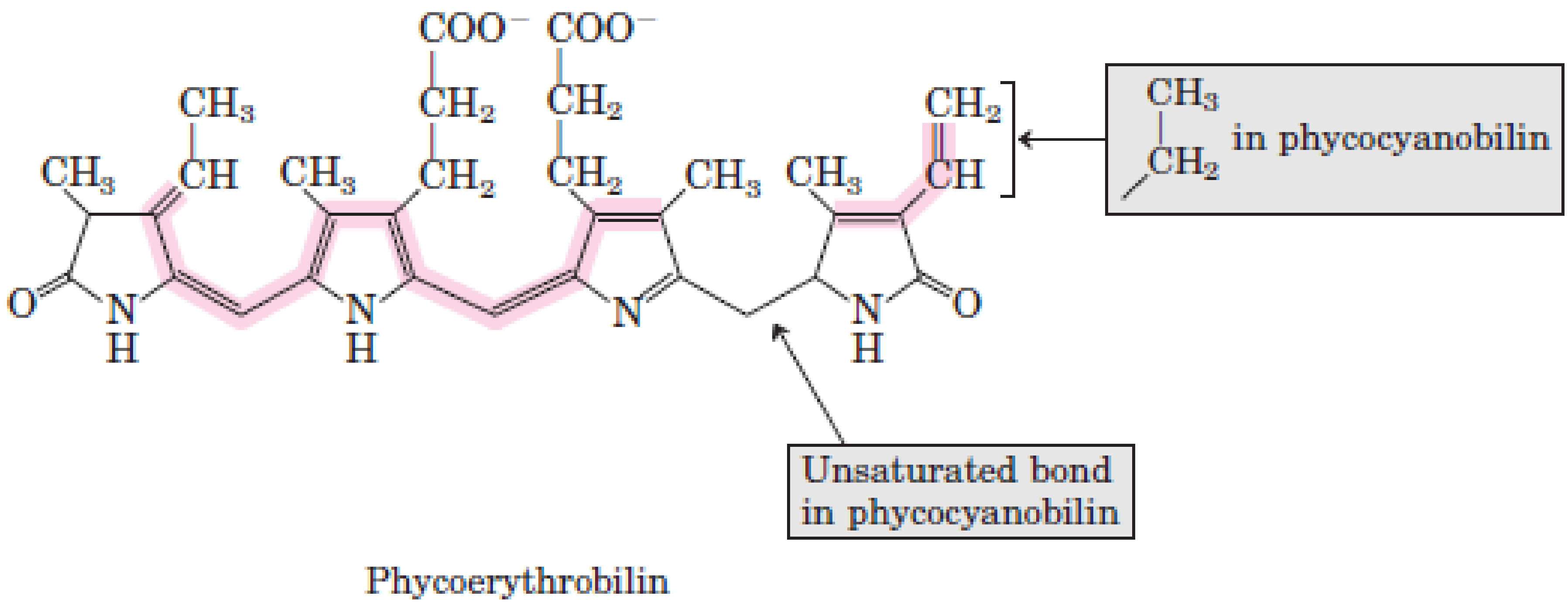

COO⁻ COO⁻
CH₃
CH₂ CH₂
CH₂
CH₃ CH CH₃ CH₂ CH₂ CH₃ CH₃ CH
O N N N N O
H H H
CH₃
CH₂ in phycocyanobilin
Unsaturated bond
in phycocyanobilin
Phycoerythrobilin

Figure 3.

...Phycobilins

- In phycobilisomes, the highly structured assemblies found in cyanobacteria and red algae, phycobilin pigments bound to specific proteins form complexes called phycoerythrin (PE), phycocyanin (PC), and allophycocyanin (AP).
- The energy of photons absorbed by PE or PC is conveyed through AP (a phycocyanobilin binding protein) to chlorophyll *a* of the reaction center by exciton transfer (Fig. 4).

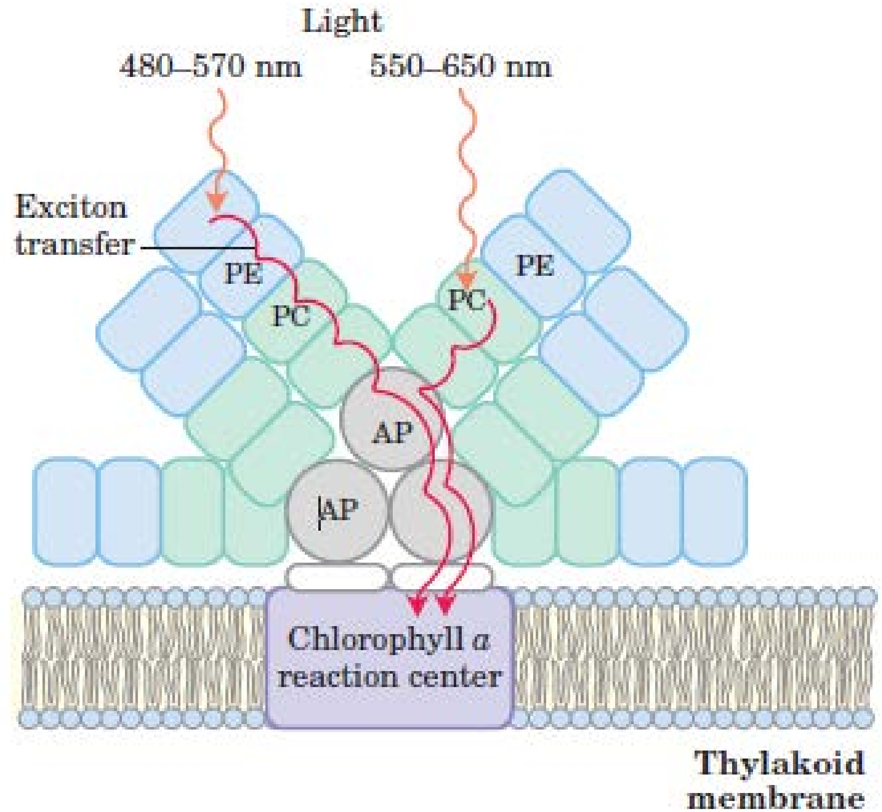


Figure 4.

Functioning of photosynthetic pigments

- The light-absorbing pigments of thylakoid or bacterial membranes are arranged in functional arrays called **photosystems (Fig. 5).**
- Each photosystem contains about 200 chlorophyll and 50 carotenoid molecules.
- All the pigment molecules in a photosystem can absorb photons, but only a few chlorophyll molecules associated with the **photochemical reaction center** are specialized to transduce light into chemical energy.
- The other pigment molecules in a photosystem are called **light-harvesting or antenna molecules.**
- They absorb light energy and transmit it rapidly and efficiently to the reaction center.

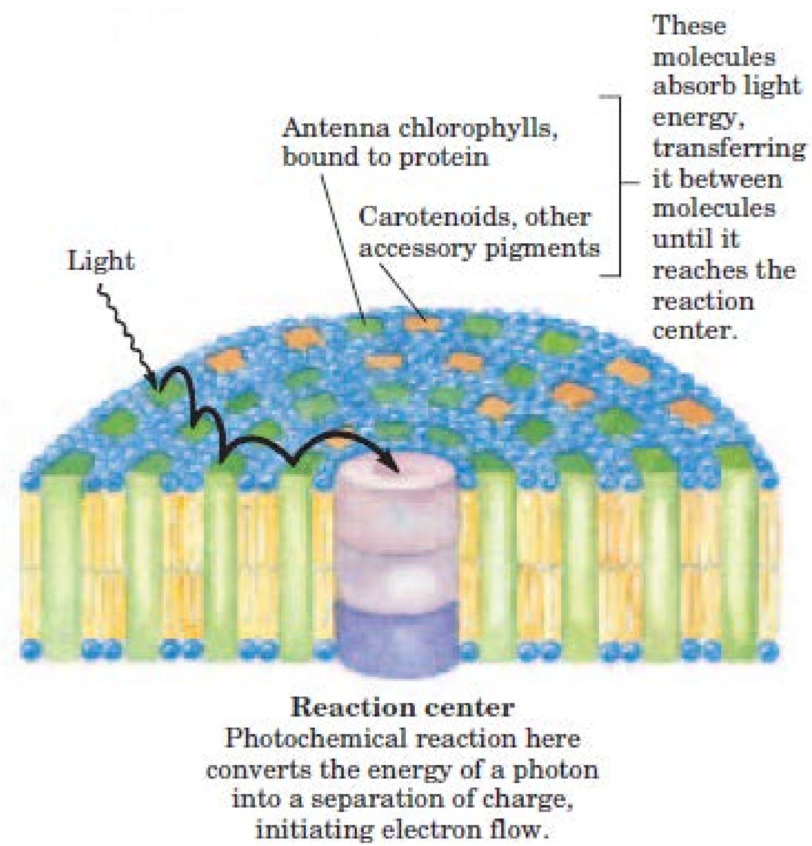


Figure 5.

...Functioning of photosynthetic pigments

- **Step 1** : Chlorophyll molecules are excited by light
- **Step 2:** The excited antenna chlorophyll transfers energy directly to a neighboring chlorophyll molecule, which becomes excited as the first molecule returns to its ground state.
- **Step 3:** This transfer of energy, exciton transfer, extends to a third, fourth, or subsequent neighbor, until one of a special pair of chlorophyll *a* molecules at the photochemical reaction center is excited.
- **Step 4:** In this excited chlorophyll molecule, an electron is promoted to a higher energy orbital.
- This electron then passes to a nearby electron acceptor that is part of the electron-transfer chain, leaving the reaction-center chlorophyll with a missing electron.
- **Step 5:** The electron acceptor acquires a negative charge in this transaction.
- The electron lost by the reaction-center chlorophyll is replaced by an electron from a neighboring electron-donor molecule, which thereby becomes positively charged.
- In this way, excitation by light causes electric charge separation and initiates an oxidation-reduction chain (Fig. 6).

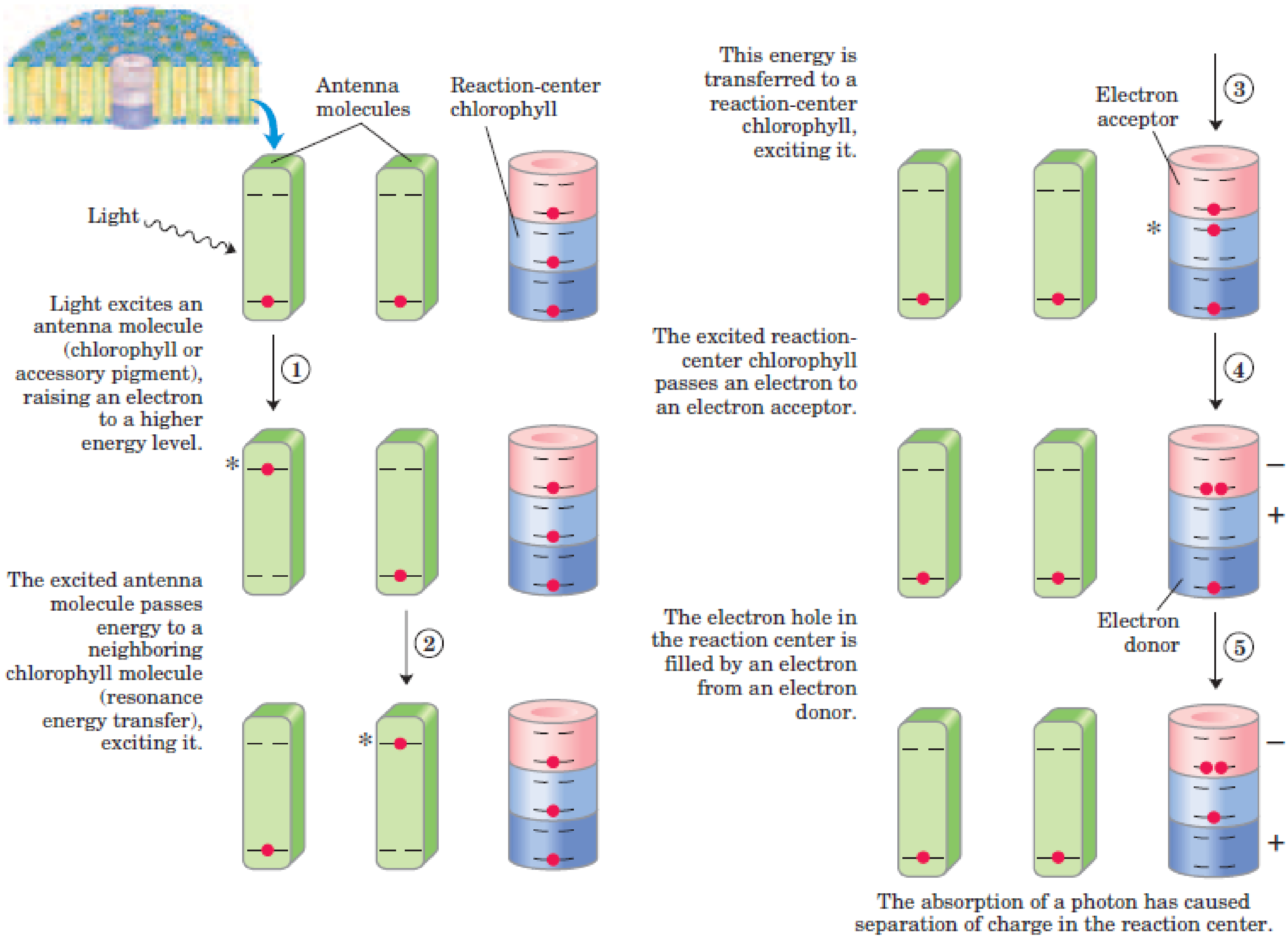

Antenna molecules
Reaction-center chlorophyll
Light
Light excites an antenna molecule (chlorophyll or accessory pigment), raising an electron to a higher energy level.
1
The excited antenna molecule passes energy to a neighboring chlorophyll molecule (resonance energy transfer), exciting it.
2
This energy is transferred to a reaction-center chlorophyll, exciting it.
3
Electron acceptor
The excited reaction-center chlorophyll passes an electron to an electron acceptor.
4
The electron hole in the reaction center is filled by an electron from an electron donor.
Electron donor
5
The absorption of a photon has caused separation of charge in the reaction center.

Figure 6.

Questions

- Write an essay on photosynthetic pigments. How pigments participate in light reaction?
- What are accessory pigments? Discuss the functions of accessory pigments (carotenoids and phycobilins) in phototrophic microorganisms?
- Write short note on bacteriochlorophyll.
- What is the difference between chlorophyll and bacteriochlorophyll.
- What light harvesting complex? How light reaction takes place?