

# Chapter XXXIV

## Photosynthesis: How Proteins Control Excitation Energy Transfer

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### **ABSTRACT**

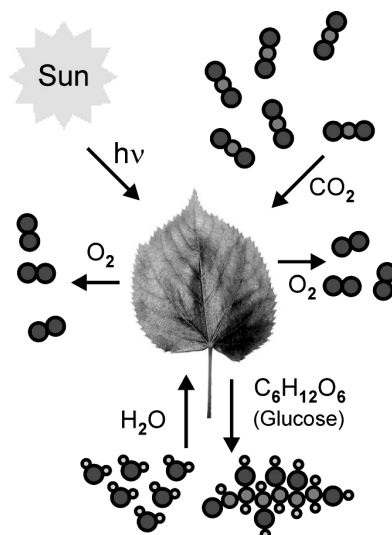
*This chapter introduces the theory of optical spectra and excitation energy transfer of light harvesting complexes in photosynthesis. The light energy absorbed by protein bound pigments in these complexes is transferred via an exciton mechanism to the photosynthetic reaction center where it drives the photochemical reactions. The protein holds the pigments in optimal orientation for excitation energy transfer and creates an energy sink by shifting the local transition energies of the pigments. In this way, the excitation energy is directed with high efficiency (close to 100 %) to the reaction center. In the present chapter, this energy transfer is studied theoretically. Based on crystal structure data, the excitonic couplings are calculated taking into account also the polarizability of the protein. The local transition energies are obtained by two independent methods and are used to predict the orientation of the FMO protein relative to the reaction center.*

### **INTRODUCTION**

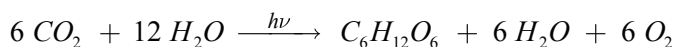
In photosynthesis energy from the sunlight is converted to chemical energy (Figure 1). The photons of the sunlight are absorbed by so-called antenna pigments (chlorophylls, bacteriochlorophylls and carotenoids) and the excitation energy is transferred to the photosynthetic reaction centre (RC), where transmembrane charge transfer reactions are driven.

In the oxygenic photosynthesis water is used as an electron source and the electron transfer is accompanied by proton gradients, which drive the production of ATP (Adenosine triphosphate), the universal energy currency, from ADP (Adenosine diphosphate). In this way light energy is converted to chemical energy. As a by-product of the water-fission, oxygen is released, which forms a basis of our life.

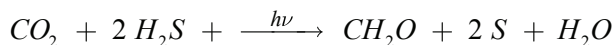
Figure 1. Cartoon of the photosynthesis



The oxygenic photosynthesis is performed by higher plants, algae and cyanobacteria. The water splitting of oxygenic photosynthesis requires a relatively high redox potential, which can only be achieved with two RCs connected in series. These two RCs are called photosystem (PS) I and II. Both PSs receive energy from antenna pigments or in principal from direct optical excitation. PS II is the first one in the serial connection and it is the water splitting part while PS I is the second part and the one where the proton gradient drives the ADP to ATP synthesis. The well known overall equation for the oxygenic photosynthesis reads:



where  $h\nu$  is the energy of a photon with frequency  $\nu$  and  $h$  is Planck's constant and  $\text{C}_6\text{H}_{12}\text{O}_6$  is the chemical formula for glucose. Another, in the sense of evolution older process<sup>1</sup>, is the anoxygenic photosynthesis, performed by anaerobic bacteria, such as green sulfur bacteria. In contrast to the organisms performing oxygenic photosynthesis, they have only one RC. It is called bacterial reaction centre (bRC) and is structurally similar to PS I. It is able to oxidize  $\text{H}_2\text{S}$  and similar compounds. Its reaction is described in simplified form by:



where  $\text{CH}_2\text{O}$  is the chemical formula of formaldehyde. Although the scheme of the primary photosynthetic reaction is in the main well understood, the molecular mechanisms are still unclear in many cases. A combined approach by high-resolution structure determination, optical spectroscopy and theory is necessary to understand the building principles of photosynthetic systems and how function and structure of these nano-machines are related. This progress was initiated by the first high-resolution x-ray structure (2.8 Angstrom) determination of a photosynthetic pigment-protein complex (PPC)

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