

Dueling dipoles: In search of a new theory of photosynthetic energy transfer

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Chemists of Ludwig-Maximilians-Universitaet in Munich have refuted a basic postulate of Foerster theory, which describes energy transfers between pigment molecules, such as those that underlie photosynthesis. A revised version of the theory could have an impact on the design of optical computers and improve the efficiency of solar cells.

Photosynthesis, the formation of energy-rich [chemical compounds](#) with the aid of sunlight, is fundamental to life on Earth. In [plants](#), sunlight is collected by so-called antennal complexes, consisting of proteins bound to the green pigment chlorophyll. The chlorophyll captures the light energy and relays it, virtually without loss, via several intermediate molecules, to the reaction centers, where it is converted into stable forms of [chemical energy](#). The intermolecular transfer process is described by Förster theory. This postulates that pigments act as oscillating dipoles to electrically excite adjacent molecules, in much the same way as the elements of a dipole antenna pick up and feed radio signals to a receiver.

Measurements carried out in the laboratory of LMU chemist Professor Heinz Langhals, in collaboration with the Department of Physics at LMU Munich, have now refuted this model. "Energy transfer between dipoles depends on their orientation," says Langhals. "When dipoles are orthogonally disposed, no energy transfer should occur. We have now tested this assumption experimentally and, to our surprise, we found that energy is rapidly and very efficiently transferred under these conditions." In collaboration with international partners, the LMU team now wants to establish a firm experimental basis for the formulation of a

new theory of energy transfer. This may well have repercussions for the development of optical computers and might help to enhance the performance of solar cells. (*Journal of the American Chemical Society*, 1 December 2010)

Chlorophylls and other pigment molecules, often in association with specialized proteins, can form complexes which act as efficient antennas that collect light energy and pass it on to the photosynthetic reaction centers or to the conducting layer of a solar cell. The energy is captured and transiently stored in the bonds between specific groups of atoms in the pigments, which are therefore referred to as chromophores. Different chromophores absorb light of different wavelengths, so a complex containing various types can harvest light over a large segment of the spectrum.

Indeed, the original goal of the LMU researchers led by Langhals was to synthesize such a broadband light collector. The first step in designing such a complex involved the use of Förster theory to calculate the efficiency of energy transfer between dyes. This theory posits that intermolecular energy transfer occurs when oscillating dipoles – chemical compounds that carry spatially separated and opposite electric charges – cause adjacent dipoles to oscillate in their turn. Dipole orientation plays a crucial role in the process. Orthogonally oriented dipoles are assumed to be incapable of energy transfer. If molecules are oriented in parallel, energy transfer is allowed.

To everyone's surprise, the measurements actually showed that energy can be transferred between orthogonally arranged chromophores with almost 100% efficiency. As Langhals emphasizes: "The process is extraordinarily efficient. This is reflected in the extremely short reaction time – 9.4 billionths of a second. The findings rule out the idea that energy transfer occurs by a dipole-based mechanism. Instead, our results imply a low-frequency mode of coupling via intramolecular vibrations."

A large-scale collaboration is now being planned to lay the experimental basis for a new version of the theory of energy transfer between dye molecules.

One consequence of the new experimental data is that the so-called "molecular ruler" method may need to be recalibrated. It too is based on an aspect of Förster theory, namely the postulate that rates of energy transfer depend on the distance between the chromophores. This relationship is used to characterize biochemical binding reactions. Chromophores are attached to proteins that are suspected to bind to one another -- antibody and antigen, for example -- and the interaction is monitored by estimating the distance between them from the rate of energy transfer.

The new findings will eventually lead to a new theoretical approach to the whole phenomenon, and this may have important implications for the field of photonics. Optical computers, which process information in the form of light pulses rather than electrical impulses. "This is why energy transfer plays such a central part in molecular optical computers," says Langhals. "Here the dye molecules serve as the basic elements, like the transistors in a conventional computer." Optical computers are the subject of intensive research because they have the potential to deliver extremely high processing power in very small volumes. A replacement for Förster theory could also contribute to the realization of highly efficient dye-based [solar cells](#).

Provided by Ludwig-Maximilians-Universität München

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