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New Quantum Secrets of Photosynthesis

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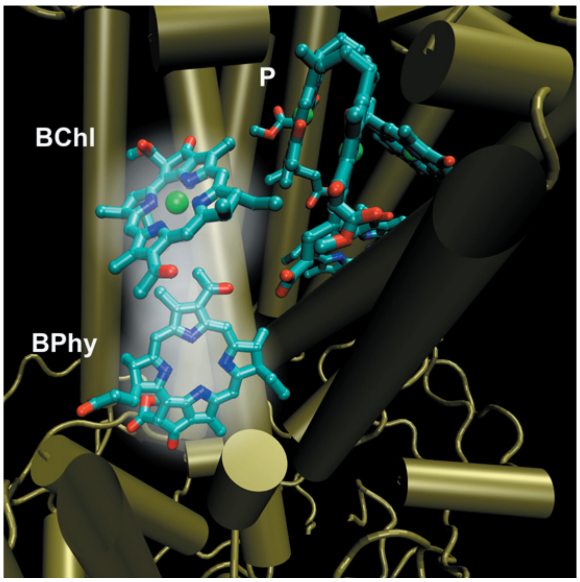

In this depiction of a pigment-protein complex in a reaction center from the purple photosynthetic bacteria Rhodobacter sphaeroides, the white fog indicates quantum coherence between the excitations of two pigment molecules, accessory bateriochlorophyll (BChl) and bacteriopheophytin (Bphy), which promotes efficient energy transfer to the protein (P).

Like the peeling of an onion, the secrets of photosynthesis are being revealed layer by layer. Early in 2007 a team of Berkeley Lab and UC Berkeley researchers identified quantum mechanical effects as the key to the astonishing ability of photosynthesis to utilize nearly all the photons absorbed by the leaves of green plants. Now a different team has found new evidence that points to a closely packed pigment-protein complex of the photosystem as the key to those quantum mechanical effects.

Green plants and certain bacteria are able to transfer solar energy almost instantaneously from light-capturing pigment molecules—for plants, the main photosynthetic pigment is chlorophyll—into reaction centers where solar energy is converted into chemical energy. The energy transfer happens so fast and is so efficient that less than five percent is lost as heat.

How nature manages to pull off this stunt was a long-standing mystery until the spring of 2007, when a study led by Graham Fleming, Deputy Director of Berkeley Lab and a UC Berkeley chemistry professor, found the first direct evidence of what he calls a "remarkably long-lived wavelike electronic quantum coherence." Quantum-mechanical effects enable a plant's photosystem to simultaneously sample all the potential energy pathways from pigment molecules to reaction centers and choose the most efficient one.

However, as is so often the case in science, solving one mystery led to another. What is the source of this remarkably long-lived quantum coherence? A second team, again led by Fleming, believes it has found the answer.

Preserving quantum coherence

"From our investigation, we conclude that the protein environment in the reaction center works collectively to keep the fluctuations of excited electronics states of pigment molecules in phase, and therefore protects quantum coherence," says Hohjai Lee, a member of Fleming's research group and co-author a recent paper in Science describing their work. "This is a brand-new function of the protein in the reaction center."

The quantum effects in photosynthesis were originally revealed through "quantum beating" signals: coherent electronic oscillations generated in both donor and acceptor molecules by light-induced energy excitations. Like the famous final piano chord in the Beatles' "A Day in the Life," these quantum beating signals seem to go on and on—though in this case, "on and on" means a few hundred femtoseconds. (A femtosecond, a guadrillionth of a second, is to a second what a second is to about 30 million years.)

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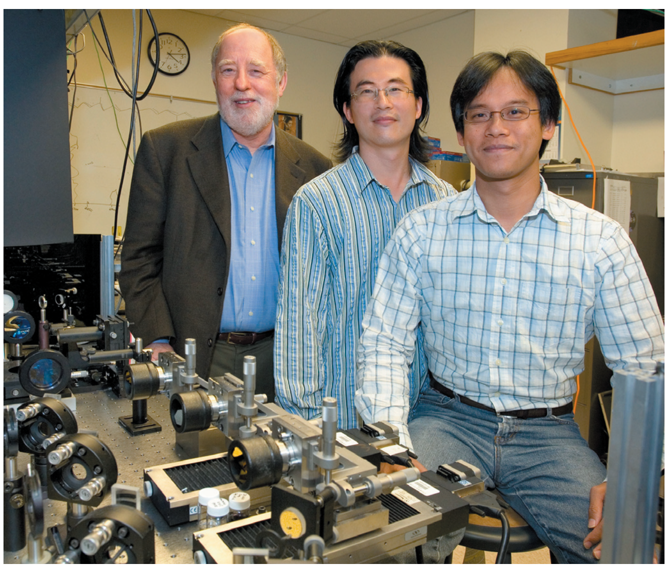
In the latest results, Fleming and his group have found that in the tightly packed complex formed by pigments and proteins, the light-induced energy excitations in the pigment molecules also set off the vibrational modes of the proteins. This creates a resonance that enhances energy transfer efficiency and is responsible for the long lifetime of the electronic coherence.

“Our results suggest that correlated protein environments preserve electronic coherence in photosynthetic complexes and allow the excitation to move coherently in space, enabling highly efficient energy harvesting and trapping in photosynthesis,” says Fleming. “Rather than simply serving as a static structure that holds the pigments in the proper geometry for efficient energy transfer to the reaction centers, as was anticipated, we find that the protein environment in the reaction centers plays a dynamic role in optimizing the efficiency of the energy transfer.”

The astonishing efficiency by which photosynthesis can transfer solar energy has made the process a prime target for scientists who would like to emulate it to help meet human energy needs. If we could effectively harness even a tiny fraction of the total solar energy available each year, we would have a clean, sustainable, and carbon-neutral source of energy to meet all our needs. Artificial photosynthesis, however, has been an elusive dream because, until recently, researchers lacked the tools to follow its lightning-fast events.

Fleming is an internationally acclaimed leader in spectroscopic studies of events that take place on the femtosecond time-scale. In discovering the signal that fingered quantum mechanics as the secret to the speed of photosynthetic energy transfer, he and his group used a technique they developed called two-dimensional electronic spectroscopy (2DES), which enabled them to follow the flow of light-induced excitation energy through molecular complexes with femtosecond temporal resolution. For their new discovery, they used another technique of their own development, called two-color electronic coherence photon echo (2CECPE), which allows electronic coherences between a pair of pigment molecules in an excited state to be directly probed.



Graham Fleming, Hohjai Lee and Yuan-Chung used two-color electronic coherence photon echo (2CECPE), a technique they developed to show that protein environments surrounding the pigment molecules in a photosystem act to preserve quantum mechanical effects, which enhance the efficiency of energy transfer.

“Because the signal from our 2CECPE technique is free of contamination by signals from other quantum-coherence pathways, we can selectively follow one specific electronic coherence pathway,” said Lee. “This enables us to focus on the electronic coherence between a selected pair of excited states, and quantify the coherence dynamics.”

Photon echoes from coherent states

In this study, Fleming, Lee and Cheng worked with the pigment-protein complexes of a purple photosynthetic bacteria, Rhodobacter sphaeroides. They zapped these complexes with three pulses of laser light, each lasting about 40 femtoseconds, whose delay times between pulses were controlled. The first pulse was blue (750-nanometer wavelength), and it created a coherence between the ground state and one pigment-molecule excitation state. The second pulse was red (800-nanometer wavelength), and it created a coherence between the first excitation state and a second pigment-molecule excitation state. The third pulse, again blue, generated a photon-echo signal only if the two excitation states were mixed -- evidence of electronic coherence. Fleming and his group were able to obtain a photon echo even when the delay between the second and third pulses of light was as much as 400 femtoseconds, indicating that electronic coherence was retained for at least this length of time.

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“The vibrational motions of the protein environments had correlated effects on the transition energies of the pigment molecules, which allowed electronic coherence to be preserved,” says Lee. “Given that closely packed pigment-protein complexes are a ubiquitous configuration for efficient energy harvesting and trapping in photosynthetic organisms, the long-range correlated fluctuations indicated by our results are unlikely to be unique.”

Fleming adds, “We suggest that the overall effect of the protection of electronic coherence is to substantially enhance the energy-transfer efficiency for a given set of electronic couplings over that obtainable when electronic dephasing is fast compared with transfer times.”

In the past, scientists seeking to mimic photosynthesis based their efforts on the idea that excitation energy is transferred from pigment molecules to reaction-center molecules by hopping down the molecular energy ladder one excitation step at a time.

“Our works provide a breakthrough in this field by showing that the quantum coherence effect is crucial for the energy transfer, and that the protein environments surrounding the pigments contributes to this quantum coherence,” says Lee. “In order to design efficient artificial light-harvesting devices, the protein surroundings of the pigments will need to be optimized so that quantum coherence can be preserved.”

Additional information

“Coherence dynamics in photosynthesis: protein protection of excitonic coherence,” by Hohjai Lee, Yuan-Chung Cheng, and Graham R. Fleming, appears in the 8 June 2007 issue of Science and is available online to subscribers http://www.sciencemag.org/cgi/content/abstract/316/5830/1462

More about the discovery of quantum mechanical effects in photosynthesis is at http://www.lbl.gov/Science-Articles/Archive/PBD-quantum-secrets.html

More about Graham Fleming’s research is at http://www.cchem.berkeley.edu/~grfgrp/