

# Disentangling energy transport in photosynthetic proteins using action spectroscopy on fast ions beams

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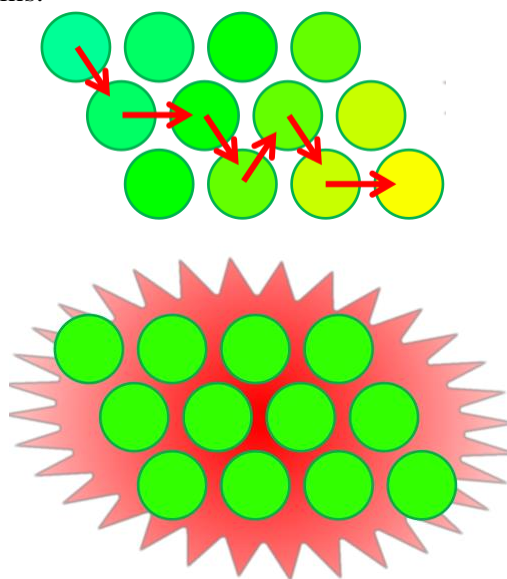
**Synopsis** We use action spectroscopy experiments and Density Functional Theory to study interactions between chlorophyll pigments and other molecules in small ionic complexes *in vacuo*. Such micro-environmental effects finely adjust the transition energies of Chls and govern the energy transport in photosynthetic proteins.

In photosynthesis, the solar energy harvested by chlorophyll (Chl) pigments is transported to the reaction centers of photosystem I and II proteins, where charge separation occurs. The efficiency of this light-to-charge conversion exceeds 95%, far higher than that in man-made photovoltaic devices. Although the interactions between the Chls clearly govern the energy transport, the exact mechanism is hotly debated. According to the traditional weak-coupling view, energy funneling (analogous to climbing down a ladder) occurs via non-radiative transfer between localized excitation sites on a potential energy landscape, where the local protein environment finely adjusts the excited-state energies of each Chl. A competing interpretation is that all of the pigments are strongly electronically coupled via delocalized exciton states to allow for so-called supertransfer.

To distinguish between the weak and strong coupling scenarios, it is necessary to quantify perturbations to excitation energies caused by the protein microenvironment as well as the strength of exciton couplings.

We have taken a bottom-up experimental approach, in which perturbations are isolated one at a time by studying small model systems *in vacuo*. Performing photo-induced dissociation action spectroscopy on fast ions beams, in connection with Density Functional Theory calculations, we have measured the intrinsic absorption spectra of Chl *a* and *b*, the variants present in green plants [1,2]. Using these data as a baseline, we have proceeded to measure the strength of exciton coupling in Chl dimers [3] and the impact of protein binding to Chl (axial ligation) [4]. This method definitively establish-

es the impact of individual perturbations, providing vital data needed to fully explain the energy-transport processes in photosynthetic proteins.



**Figure 1.** Two models of energy transfer: climbing down the ladder (top) and strong coupling (bottom).

## References

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