Quantum Sensing of Light-Induced Electron Transfer in Natural Photosynthesis:

A Time-Resolved 130 GHz EPR and ENDOR Study

Oleg Poluektov, Jens Niklas, Lisa Utschig
Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave., Lemont, IL 60439, USA
Oleg@anl.gov

Photosynthetic reaction centers, RCs, are integral membrane proteins which capture and convert sunlight into chemical energy via efficient charge separation achieved following photoinitiated sequential electron transfer (ET) steps. The fast primary electron transfer steps create a so-called spin-correlated radical pair, SCRP, which also referred as an entangled two electron spins qubit pair. This entangled state contains detailed information about weak magnetic interactions, structure, and dynamics of local protein environments involved in the charge separation events. However, extracting this information is still a great challenge. The high spectral resolution of 130 GHz time-resolved EPR and ENDOR, combined with extra resolution afforded by deuterated proteins, allows us to provide new mechanistic insight into the regulation of light-induced electron transfer in type I and type II RCs. Type II RCs like the bacterial RC (bRC) or Photosystem II (PSII) have two asymmetric branches of ET cofactors which fulfill different functions, while in type I RCs such as Photosystem I (PSI) both branches fulfill the same function.

In PSI, the EPR spectra of SCRPs formed in each of the two quasi-symmetric branches of ET cofactors, A or B, exhibit distinctive line shapes.[1,2] Biochemically modified PSI samples were used to analyze the asymmetry of electron transfer as a function of temperature, freezing condition, and temperature cycling.[3] Analysis on the temperature dependency support a dynamic model in which the conformational states of the protein regulate the directionality of electron transfer.

In the bRC, electron transfer is unidirectional proceeding down one branch of cofactors. Using time-resolved ENDOR we were able to probe protons located along the electron transfer pathway between the donor-acceptor SCRP. Spectroscopic analysis reveals hydrogen-bonding interactions involved in regulating the route electrons travel from the primary donor through the RC protein during charge separation.[4,5] This work adds to our understanding of Nature's control of primary electron transfer reaction mechanisms; fundamental insight that provides a basis for developing advanced solar energy conversion systems based on photosynthetic designs.

References

1. O.G. Poluektov *et al., J. Am. Chem. Soc.* **127**, 11910 (2005).
2. O.G. Poluektov *et al., J. Phys. Chem. B*, **119**, 13771 (2015).
3. O.G. Poluektov *et al., J. Phys. Chem. B*, **123**, 7536 (2019).
4. O.G. Poluektov *et al., J. Am. Chem. Soc.* **126**, 1644 (2004).
5. O.G. Poluektov *et al., J. Phys. Chem. B*, **125**, 4025 (2021).