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QE

Quantum Efficiency Seminar und Colloquium

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Evolutionary fine-tuning of biological electron transfer reactions for energy conversion

The production of the vast majority of ATP, the biological universal energy currency, is coupled with electron transfer reactions. The electron transfer reactions are either driven by light as in photosynthesis or by the oxidation of chemical compounds such as glucose in oxidative phosphorylation. Independent of the energy source, the electron transfer reactions are used to constitute an ion gradient across a membrane. This gradient is used by a membrane bound nano-rotor, the ATP-synthase, to produce ATP.
The energy-converting NADH:ubiquinone oxidoreductase, respiratory complex I, is the main entry point of electrons in oxidative phosphorylation. It couples the electron transfer from NADH to ubiquinone with a translocation of protons across the membrane. The enzyme complex has an L-shaped structure consisting of a peripheral arm catalyzing the redox reaction and a membrane arm performing the proton translocation. In humans a dysfunction of the complex is associated with numerous neurodegenerative diseases. However, the human complex consists of about 44 different proteins adding to a molecular mass of 1 MDa complicating its analysis. We are using the homologous complex from the bacterium Escherichia coli as a model. It consists of 14 different subunits giving rise to a molecular mass of 0.5 MDa but contains the same cofactors, namely 1 flavin mononucleotide and 9 iron-sulfur (Fe/S) clusters.
We investigated the electron transfer steps in the complex by microsecond freeze-quench experiments analyzed by Electron Paramagnetic Resonance and UV-vis spectroscopy. Our data show that the rate of electron transfer from FMN to the most distal centre is limited by the longest electron tunnelling distance and the overall driving force. With the most distal cluster reduced, the second electron travels the same trajectory with a six-fold lower rate owing to a lower driving force. This uniquely allowed the direct determination of the reorganization energy. In addition, it is most likely that aromatic amino acids are involved in the electron transfer step bridging the longest electron tunneling distance. By fine-tuning the midpoint potentials of the redox centres electron tunnelling rates are decreased to milliseconds, the time scale for conformational changes required for proton pumping. Synchronization of electron tunnelling and proton pumping rates enables efficient energy conversion by complex I. Adjustment of electron and proton transfer rates by redox tuning is proposed as a general mechanism to enhance the catalytic efficiency in enzymes.

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