Poster Presentations

[MS5-P39] Structure of the ADP●AlF3-Stabilized Dark- Operative Protochlorophyllide Oxidoreductase Complex.

Joern Krausze[a], Christiane Lange[b], Dirk W. Heinz[a], Jürgen Moser[b].

[a]*Helmholtz Centre for Infection Research, Inhoffenstr. 7, 38124 Braunschweig, Germany and*
[b]*Institut für Mikrobiologie, Technische Universität Braunschweig, Spielmannstr. 7, 38106 Braunschweig, Germany.*
E-mail: jkr09@helmholtz-hzi.de

Photosynthesis utilises chlorophyll for the conversion of light into chemical energy, which is the driving force of life on Earth. The second-last step in chlorophyll bio-synthesis is the chemically challenging two- electron reduction of the fully conjugated ring system of protochlorophyllide *a*. The reduction of the C-17=C- 18 double bond results in the characteristic ring architecture of all chlorophylls, thereby altering the absorption properties of the molecule and providing the basis for light-capturing and energy-transduction processes of photosynthesis. Two unrelated enzymes have evolved to catalyse this reaction: the light- dependent protochlorophyllide oxidoreductase (LPOR) [1] and the dark-operative protochlorophyllide oxidoreductase (DPOR) [2]. DPOR is found in cyanobacteria, green algae, and gymnosperms but is absent in angiosperms. In its active form, DPOR is an octameric complex of the form $(L_2[NB]_2)_2$, which carries a total of four [4Fe-4S] clusters. The polypeptides L, N, and B are homologous to NifH, NifB, and NifD of nitrogenase, respectively [3,4]. We crystallised the DPOR complex consisting of the subunits L_2 and $(NB)_2$ from the marine cyanobacterium *Prochlorococcus marinus* in the presence of Mg●ADP and protochlorophyllide *a* [5]. We trapped the DPOR in transition state of ATP hydrolysis through addition of $AlCl_3$ and NaI, which, in conjunction with Mg●ADP, formed a transition state mimic of ATP hydrolysis. We report the X-ray crystallographic structure of the DPOR holoenzyme at 2.5 Å resolution. The thorough investigation of the structure revealed the dynamic interplay between L_2 and $(NB)_2$. Upon complex formation, substantial ATP-dependent conformational rearrangements of L_2 trigger the protein-protein interactions with $(NB)_2$ as well as the electron transduction via two redox-active [4Fe-4S] clusters. This 'dynamic switch' mechanism is very similar to that of nitrogenase, which was previously thought to be unique. Further, we identified artificial small-molecule substrates of DPOR that correlate to the ones known of nitrogenase. The catalytic differences and similarities between DPOR and nitrogenase have broad implications for the understanding of energy transduction mechanisms of related multi-protein complexes that are involved in the reduction of chemically stable double- and/or triple-bonds.

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