transfers of their operons from bacteria; such transfers would depend on the presence of the archaea-specific systems of fatty synthesis in the respective archaeal genomes [4]. The gradual oxygenation of the atmosphere would have driven further evolution since auto-oxidation of the components of the cytochrome bc complex results in the generation of potentially hazardous reactive oxygen species. The choice of different means of decreasing the extent of autooxidation is proposed to have driven the divergence of the b6f-type complexes of cyanobacteria (ancestors of chloroplasts) and the bc1-type complexes of respiring alpha-proteobacteria (ancestors of mitochondria).

References

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S11.01
Modification of spin coupling between the semiquinone and Rieske cluster in the Qo site of cytochrome bc1
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Usually in electronic bifurcation associated with oxidation of hydroquinone at the Qo site of cytochrome bc1 (mitochondrial complex III) awaits description of its molecular mechanism. Recently, we discovered two distinct populations of semiquinone (SQo) associated with operation of the Qo site: i) SQo coupled to the reduced Rieske cluster (FeS) via spin–spin exchange interaction and ii) a separate, unusually fast-relaxing SQo. Here, using freeze-quench and electron paramagnetic resonance spectroscopy, we examined in detail conditions of formation of these two populations of SQo under a variety of buffer and reaction mixture compositions. The analysis included native cytochrome bc1, and specific mutants that affected the motion of the FeS subunit. The revealed differences in proportions between the SQo signal and the SQo–FeS coupled signal indicated that these signals are inversely correlated with one another. Shifting FeS toward the Qo site increases the amount of SQo–FeS coupled system at the cost of SQo, while shifting the FeS out of the Qo site has the opposite effect—increase in SQo at the cost of SQo–FeS coupled signal. We anticipate that these results will contribute to better understanding of the electron reactions that take place within the Qo site, in particular the formation of SQo intermediates and their relation to superoxide generation by the Qo site.

Reference

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S11.02
A photo-useless chlorophyll: What's for?
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3D structure of the membrane complex cytochrome b6f from the green alga Chlamydomonas reinhardtii was solved in the presence and in the absence of a Qo site inhibitor (TDS) [1]. The analyses of the two structures revealed, besides the reorganisation of the Rieske soluble domain, small conformational changes around the Qo site. Cytochromes b6f and bc1 are structurally and functionally very similar but they have a different sensitivity to inhibitors and in the cytochrome b6f the phytih chain of a chlorophyll molecule stands at the entrance of the Qo site. The presence of this molecule raises the question of its role which is still unknown. In order to gain information on chlorophyll function, its binding to the b6f complex was destabilised by site-directed mutagenesis of the petD gene. Alanine 140 in helix G was replaced by phenylalanine, a bulkier amino acid, this position faces the pigment, but remains away from

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the Qo site. We show that removal of chlorophyll does not impair the overall structure of the b6f complex, but perturbs in vivo and in vitro plastoquinol oxidation in the Qo site, disproving a simple structural role for the chlorophyll. In addition, this compromised activity can be correlated with conformational changes, which comprises the same polypeptide segments that are also subject to conformational changes in the related Qo sites of the bc1 and b6f complexes upon inhibitor binding. This common flexibility might be involved in the gating of the Qo site to avoid short circuits, introducing a double gating.

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S11.P1

Lutein as a mediator of effective yet ‘economic’ regulator of light-harvesting in photosystem II of plants
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The antenna of photosystem II (PSII) in plants possesses an intrinsic photoprotective switch that allows for rapid adaptation to changing light intensity. The essence of this switch is the formation of energy-quenching sites within the antenna that trap and dissipate excess excitation energy, thereby mitigating the photo-inhibitory damage associated with high light [1]. The molecular mechanisms at the heart of this process, known as Non-Photosynthetic Quenching, are still debated and there are several competing models [1]. One such model, based on time-resolved fluorescence measurements, suggests that NPQ occurs via the incoherent transfer of energy from chlorophyll to the xanthophyll lutein 1, followed by rapid (~10 ps) non-radiative decay, in the major PSII antenna complex LHCII [2]. Our recent theoretical model of chlorophyll–xanthophyll energy transfer in LHCII indicates that this mechanism is sufficient to explain the fluorescence quenching in LHCII crystals [3]. Additionally we reported that a combination of solid-state NMR and theoretical modelling implies that aggregation-induced quenching in LHCII may be controlled by fine tuning of chlorophyll–xanthophyll distances [4]. We here present the incorporation of this lutein-mediated quenching mechanism into coarse-grained models of energy transfer in PSII-antenna superstructures and show that lutein is an effective NPQ site in the photosynthetic membrane. Additionally, we show that this model is consistent with our recent fluorescence induction measurements [5]. We show that lutein in the PSII antenna can function as an ‘economic’ quencher, offering protection to closed reaction centres whilst simultaneously preserving photosynthetic productivity in a broad range of light intensities.

References

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S11.P2

Inter-monomer electron transfer in asymmetrically mutated fusion hybrid cytochrome bc1-like complex supports the enzyme function in vivo
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Cytochrome bc\(_1\) is one of the key catalytic complexes involved in the bioenergetic processes. This dimeric enzyme operates according to the Q cycle functionally linking quinone catalytic sites on the opposite sides of the membrane. While recent studies indicate that this link can be achieved by intra- or inter-monomer electron transfer, the physiological relevance of the latter remains unclear. To address this issue we used a system based on a fusion hybrid protein build of cytochrome c subunits from two different species: Rhodobacter capsulatus and Rhodobacter sphaeroides. It assembles into a functional bc\(_1\)-like complex and allows introduction of mutations in an asymmetric manner [1]. We report that the cross-inactivated bc\(_1\) constructs, enforcing the inter-monomer transfer as the only way to electronically connect the opposite catalytic sites, supported the cytochrome bc\(_1\)-dependent phototrophic growth of bacteria. This indicates that inter-monomer route for electrons is able to sustain the function of the enzyme in vivo. Moreover, given the differences in amino acid composition between the fused cytochromes bs, we suggest that the minimal requirement for the enzyme bioenergetic efficiency is to provide the uninterrupted electron connection of the quinone catalytic sites on the opposite sides of the membrane in a manner robustly tolerant to structural alterations.

Reference

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S11.P3

Role of electrostatic and hydrophobic interactions in the encounter complex formation of plastocyanin and cytochrome f
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Cytocchrome f (cyt f) and plastocyanin (pc) are electron transfer proteins forming a transient complex. During complex formation, an initial encounter complex rearranges into an active complex. Both, electrostatic and non-covalent short-range forces have been reported to be important for the complex in Phormidium laminosum or Nostoc [1]. In this work, the association of cyt f and pc were studied using paramagnetic NMR spectroscopy, Monte Carlo simulations [2] and ensemble docking in order to get deeper insights into the dynamics of the electron transfer complexes. For this purpose, spin labels were attached to cyt f, and relaxation enhancements of pc nuclei were measured, demonstrating that a large part of the cyt f surface area is sampled by pc. The distribution of the encounter complex