

Experimental systems based on bacteria of the genus *Rhodobacter* (*R.*), particularly *R. sphaeroides* and *R. capsulatus*, have produced many insights into the mechanism of light energy transduction in photosynthesis, including the structural basis of light harvesting and photochemical charge separation. Structural and spectroscopic studies have been greatly assisted by the availability of bacterial strains with altered photosystems, such as mutants lacking one or both types of light harvesting complex for example, or with an altered complement of carotenoids (so-called green or blue-green mutants), together with the ability of the bacterium to assemble the photosynthetic apparatus when growing in the dark under conditions of low aeration. The present work involves a systematic study of the structural and functional consequences of (1) expression of structural genes *in trans* in deletion mutants, (2) variation in growth conditions, (3) deletion of one or more light harvesting complexes, (4) changes in the carotenoid composition of the photosystem and (5) removal of the PufX protein. Particular attention is given to the effects of such changes on the composition of the so-called “core complex” formed between the reaction centre and the LH1 antenna protein, and the ability of the bacterium to grow under photosynthetic conditions.

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#### S2/4 The 2-methoxy group of ubiquinone is essential for function of the acceptor quinones in reaction centers from *R. sphaeroides*

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The orientation of a methoxy substituent is known to substantially influence the electron affinity and vibrational spectroscopy of benzoquinones, and has been suggested to be important in determining the function of ubiquinone as a redox cofactor in bioenergetics. Ubiquinone functions as both the primary ( $Q_A$ ) and secondary ( $Q_B$ ) quinone in the reaction centers of many purple photosynthetic bacteria, and is almost unique in its ability to establish the necessary redox free energy gap for 1-electron transfer between them. The role of the methoxy substitution in this requirement was examined using monomethoxy analogues of ubiquinone-4, which were reconstituted into quinone-depleted reaction centers from the purple photosynthetic bacterium, *Rhodobacter sphaeroides*. The analogues used were 2-methoxy-3,5-dimethyl-6-isoprenyl-1,4-benzoquinone (2-MeO-Q) and 3-methoxy-2,5-dimethyl-6-isoprenyl-1,4-benzoquinone (3-MeO-Q) and only 2-MeO-Q was able to simultaneously act as  $Q_A$  and  $Q_B$ . The necessary redox potential tuning was shown to occur in the  $Q_B$  site. In the absence of active  $Q_B$ , the IR spectrum of the monomethoxy quinones was examined *in vitro* and in the  $Q_A$  site, and a novel distinction between the two methoxy groups was tentatively identified, consistent with the unique role of the 2-methoxy group in distinguishing  $Q_A$  and  $Q_B$  functionality.

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#### S2/5 The photosystem I reaction centre of oxygenic photosynthesis

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Photosystem I of oxygenic photosynthesis is a large multi-protein complex binding 100 chlorophylls. At its core are two related polypeptides which each bind symmetrically-related electron transfer chains. We present evidence from studies utilising spectroscopic approaches in combination with site-directed mutagenesis that demonstrate that light-initiated electron transfer occurs on both branches of electron transfer.

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#### S2/6 The unusual configuration of the quinone reduction site of the cytochrome $b_6f$ complex

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Complex cytochrome  $b_6f$  couples electron transfer with proton translocation through the thylakoid membrane in oxygenic photosynthesis. Unlike its counterpart in mitochondria and proteobacteria, it exhibits three additional cofactors whose functions are not understood: a chlorophyll a, whose phytyl chain lies at the entrance of site  $Q_o$ , a  $\beta$ -carotene and an additional haem, called  $c_i$ . X-ray crystal structures in the presence of inhibitors suggest that the putative substrate binding pocket of the  $Q_i$  site is near the iron atom of haem  $c_i$ , providing an unusual site for a quinone involved in an oxidoreduction reaction, where interaction near the edge of the protoporphyrin ring is sufficient for electron transfer. 2-*n*-nonyl-4-hydroxyquinoline N-oxide (NQNO) binds into the  $Q_i$  pocket and is able to coordinate the iron of haem  $c_i$ . Functional implications need to take into account the configuration of the  $Q_i$  site: haem  $c_i$  has no axial ligand contributed by the protein, one side is occupied by a water molecule or hydroxide in interaction with haem  $b_H$ , while the other face of haem  $c_i$  is protected by a phenylalanine, which can be displaced to allow ligand coordination. This raises questions on a mechanism that is thought to be very similar to the Q-cycle of the  $bc_1$  complex.

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#### (S2) Photosystems symposium abstracts (poster and raised abstracts)

##### S2.7 The bacteriochlorophyll $B_A$ is missing in H(L153)Y *Rhodobacter sphaeroides* RC

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The reaction center of *R. sphaeroides* is a membrane-bound pigment-protein complex where the photosynthetic charge separation