The photosynthetic unit of oxygenic photosynthesis is organized as two large multimolecular membrane complexes, photosystem II (PSII) that extracts low-energy electrons from water and photosystem I (PSI) that raises the energy level of such electrons using light energy to produce a strong reductant, NADPH. The two photosystems operate in a series linked by a third multiprotein complex called the cytochrome $b_6f$ complex (Fig. 1). The cytochrome $b_6f$ complex is a membrane-spanning protein complex embedded in the thylakoid membrane of photosynthetic organisms. The molecular weight of the complex is 220,000 as a dimer with 26 transmembrane helices. The $b_6f$ complex controls the electron transfer between the plastocyanin reduced by PSII and the electron carrier protein plastocyanin that associate with PSI. Coupled with the electron transfer, the $b_6f$ complex also generates a transmembrane proton gradient for ATP synthesis. The crystal structures of the cytochrome $b_6f$ complex [1,2] complete the description of the architecture of the oxygenic photosynthetic electron transport chain, since three-dimensional structures have been provided for PSI and PSII [3-5].

The structure of the $b_6f$ complex from cyanobacterium *M. laminosus* was determined by the isomorphous replacement method using Pb and Pt derivatives and multiwavelength anomalous diffraction from native iron atoms. X-ray diffraction data from native crystals and the pigment molecules, chlorophyll $a$ and $\beta$-carotene. Heme $x$ occupies the binding site of the $n$-side bound quinone in the $bc_1$ complex. The presence of heme $x$ in contact with heme $b_6$ and a plastocarbinone in the cavity suggests the mechanism of ferredoxin-mediated cyclic electron transfer (dotted line in Fig. 1) that uses classical elements of the Q-cycle mechanism [1,2].

The quinone-mediated redox connection between the $(p)$ and $(n)$ sides of the complex can be visualized through (a) a plastocarbinone molecule close to heme $x$ on the $n$-side, and (b) a quinone analogue inhibitor, TDS, on the $p$-side of the other monomer that surrounds the cavity (Fig. 3). The position of TDS in the $b_6f$ complex is similar to that of the $p$-side inhibitor myxothiazol in the $bc_1$ complex. Another $p$-side inhibitor, DBMIB, is bound near Glu in the conserved sequence in the $p$-side peripheral loop. Both of these inhibitors are >10 Å from the closest histidine ligand of the [2Fe-2S] cluster of Rieske ISP.

**Fig. 1.** Integral membrane protein complexes and electron carrier proteins responsible for electron transport and proton translocation in oxygenic photosynthesis.
and cannot form an H-bond with the histidine ligand as does stigmatelline in the bc₁ complex.

The [2Fe-2S] cluster is 29 Å from the heme Fe of its electron acceptor, cyt f. In the case of the bc₁ complex, the positional change of the [2Fe-2S] cluster to a more c₁-proximal position in different crystal forms suggests that Rieske ISP mediates the electron transfer between the membrane-bound quinol and cyt c₁ by shuttling between the membrane-proximal and c₁-proximal states. However, only a single membrane-proximal position for the Rieske ISP has been observed in the b₆f complex. Together with the different positions of cytochrome f and its heme relative to cyt c₁, this implies the difference in trajectory between Rieske ISP and cyt f.

Fig. 2. Side view of eight-subunit dimeric cytochrome b₆f complex. Hemes bn, hp and f (grey), heme x (dark brown), chlorophyll a (dark green), β-carotene (orange), cyt b₄ (blue), subunit IV (red), cyt f (purple), iron-sulfur protein (orange), and small subunits (light green).

Fig. 3. Molecular surface of the complex mapping the electrostatic potential. Plastoquinone (PQ) and Q-analogue inhibitor (TDS) are drawn in the cavity as a cpk model, and the chemical formulas of inhibitors are shown on the right.

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References