ULTRAFAST ELECTRON TRANSFER IN MUTANT PHOTOSYNTHETIC REACTION CENTERS

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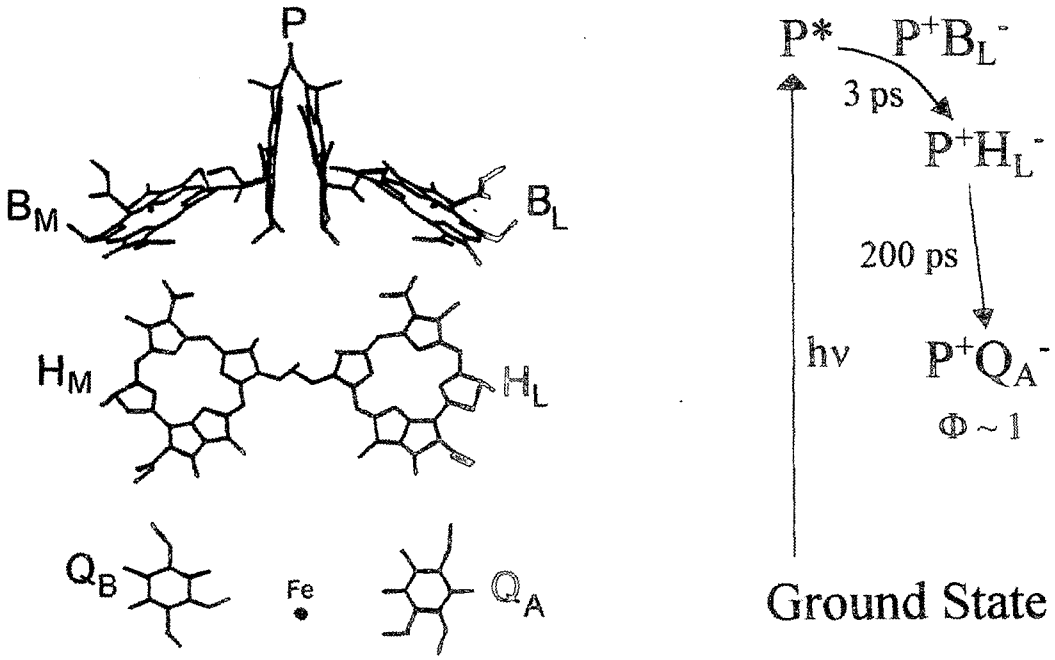
The primary photochemical energy conversion process in photosynthesis occur in pigment-protein complexes called reaction centers (RCs). The process involves a sequence of electron transfers between cofactors that separate charge across a membrane within one nanosecond of photoexcitation and with a near-unity quantum yield (see figure below). We have prepared and investigated a number of mutant bacterial RCs that have given key insights into the mechanisms of the primary events. The issues include the roles of individual cofactors in the electron-transfer sequence, the basis of the high quantum yield of charge separation, and the factors controlling the directionality of charge separation via one of two parallel electron transport chains. Some mutations can have significant effects on the free energies of the transient intermediate states of charge separation via changes in the metallation state, hydrogen bonding, or general environmental interactions (incorporation or polar or ionizable residues) of the cofactors. These changes in turn modulate the rates and yields of charge separation and charge recombination. In certain mutants, electron transfer down the normally photoinactive electron transport chain has been observed. By combining multiple mutations, changes in the primary events at the various stages of charge separation now can be achieved in a predictable manner.



Bacterial RC showing the dimer of bacteriochlorophyll molecules (P), the accessory bacteriochlorophylls (B_L and B_M), the Mg-free bacteriopheophytin analogs (H_L and H_M), the quinones (Q_A and Q_B), and the non-heme iron. The designations L and M refer to the membrane-spanning polypeptide subunits with which the tetrapyrrole cofactors are most closely associated. The primary events in the native RC are summarized at the right.