



**Figure 4.1** The “Z-scheme” for photosynthetic electron transport. In this schematic representation, the photosynthetic electron carriers are placed in series on a scale of midpoint potentials. The  $E_{m7}$  for the oxidation of water by a one-electron reaction is +0.82 V. Thus, to photo-oxidize water, a redox potential must be minimally of that value. The oxidation of the primary electron donor in PSII,  $P_{680}$ , leads to a charge separation of about 1.7 V. This charge separation occurs within about 1 ps, and the formation of a reduced phaeophytin anion intermediate follows within about 3 ps. The electron hole in  $P_{680}^+$  is filled by the oxidation of the amino acid tyrosine,  $Y_Z$ , which obtains electrons in turn from Mn atoms. The timescale for the reduction of  $Y_Z$  varies, depending on the “S” state (see text). The Mn atoms obtain electrons from water. Hence, like a front-wheel drive in a car, electrons are “pulled” from water via the photochemical oxidation of  $P_{680}$ . The reactions leading to the re-reduction of  $P_{680}^+$  from water are designated to be on the “donor side” of PSII. The phaeophytin anion reduces the “primary” acceptor,  $Q_{A^-}$ , which is a quinone bound to a protein. This reaction leads to a change in the midpoint potential of about +0.2 V, which helps to stabilize the electron and reduces the probability of a useless backreaction between the phaeophytin anion and  $P_{680}^+$  (note that it takes five orders of magnitude longer to reduce  $P_{680}^+$  from  $Y_Z$  than it takes to reduce phaeophytin; hence in the absence of the electron transfer to  $Q_{A^-}$  the probability of a backreaction is very high). Two electrons are sequentially transferred from  $Q_A$  to the secondary acceptor,  $Q_B$ ; the time constants for these electron transfers are dependent on the level of reduction of  $Q_B$ . Upon receiving two electrons,  $Q_B$ , which, like  $Q_{A^-}$  is a plastoquinone (PQ) molecule, dissociates from its “binding pocket” and diffuses within the thylakoid membrane until it reaches the cytochrome  $b_6/f$  complex. Reduced plastoquinone is oxidized by cytochrome  $b_6$ , which is in turn oxidized by cytochrome  $f$ . The oxidation of plastoquinol is typically the slowest reaction overall in the photosynthetic electron transport pathway. Cytochrome  $f$  delivers electrons to either a copper-containing protein, plastocyanin (PC), in the case of the chlorophyte algae, or an iron-containing protein, cytochrome  $c_{553}$ , in the case of chromophytes. In either case, this electron carrier ferries electrons to the reaction center of PSI,  $P_{700}$ , by diffusion in the thylakoid lumen. All the reactions between phaeophytin and  $P_{700}$  are on the “acceptor side” of PSII or the “donor side” of PSI, depending on the reaction center of reference. In the PSI reaction center, the absorption of a second photon leads to the generation of a second photochemical charge separation, with a midpoint potential difference of about 1.6 V. The electron is rapidly passed through a series of electron carriers,  $A_0$ , a chlorophyll monomer,  $A_1$ , phyloquinone (also called vitamin K),  $F_X$ , an iron sulfur cluster,  $F_B$  and/or  $F_B$ , which are iron-containing proteins, and then to  $F_d$ , a molecule of ferredoxin (Chitnis 2001). The reactions from  $P_{700}^+$  to ferredoxin are on the “acceptor side” of PSI.

