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Short communication

P680: what is it and where is it?

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Abstract

Electron and X-ray crystallography have provided intermediate structural models for photosystem II (PSII), the membrane located multisubunit complex which uses light energy to split water into its elemental constituents. This reaction is thermodynamically demanding and involves the production of redox potentials in excess of 1 V. Structural analyses have now shown that the primary oxidant, P680, is not a 'special pair' of chlorophylls, as in other types of photosynthetic reaction centres, but a tetramer of equally spaced chlorophyll *a* molecules. Its high redox potential, and the involvement of four weakly coupled isoenergetic monomers rather than a strongly excitonically coupled 'special pair', has implications for redox mechanisms which are unique to PSII, and therefore not found in any other photosynthetic system. The importance of these features is discussed. © 2002 Published by Elsevier Science B.V.

Keywords: Photosystem II; Chlorophyll *a*; Photosynthetic reaction centres; Redox potential

1. Organisation of chlorophylls within the PSII reaction centre

The 3D structural map of a photosystem II (PSII) complex of higher plants deduced by electron crystallography [1,2] showing the D1, D2, CP47, and cytochrome b559 subunits, together with the low molecular weight proteins, PsbI, $PsbT_C$, and PsbW [3], was of sufficient resolution (~ 8 Å) to identify densities that could be assigned to the tetrapyrrole head groups of porphorin molecules bound into the protein matrix. In particular, six such densities were identified within the four transmembrane helical clusters composed of the D and E helices of the D1 and D2 reaction centre subunits. These densities were related by a pseudo two-fold axis in a way that is very similar to the porphorins within the L and M subunits of the reaction centre of purple photosynthetic bacteria. Accordingly, two densities towards the stromal surface of the PSII structure were assigned to pheophytin molecules, and four densities close to the lumenal surface of the complex were assumed to be chlorophylls equivalent to the 'special pair' and 'accessory' bacteriochlorophylls of the bacterial reaction centre. However, the two chlorophylls equivalent to the 'special pair' were spaced farther apart than those found in their bacterial counterparts (10 to 11 Å in PSII compared with 7 Å in bacteria based on centre-to-centre). The lack of a special pair in the PSII reaction centre had been predicted by a range of spectroscopic studies [4] and by molecular modelling [5]. Recently, a 3.8-Å structure of the cyanobacterial PSII reaction centre complex has been calculated from X-ray diffraction data [6]. As can be seen in Fig. 1b, this work confirmed the existence of four chlorophyll molecules on the donor side of PSII and that there was no special pair. The better resolution of the X-ray-derived structure, compared with that obtained by electron crystallography, showed that the tetrapyrrole rings of the two chlorophylls equivalent to the special pair were parallel to each other and at right angles to the membrane plane. The two accessory chlorophylls, however, were orientated at about 30° to the membrane plane. As previously shown by electron crystallography [1], all four chlorophylls are about equidistant from each other based on centre-to-centre distances.

2. What is P680?

The notation, P680, has been used to describe the primary electron donor of PSII in the same way that P700 and P870 are designated as the primary donors of photosystem I and the purple bacterial reaction centres. It is derived from P, for pigment, which has an absorption maximum at 680 nm, hence the nomenclature P680. Spectral analysis showed that

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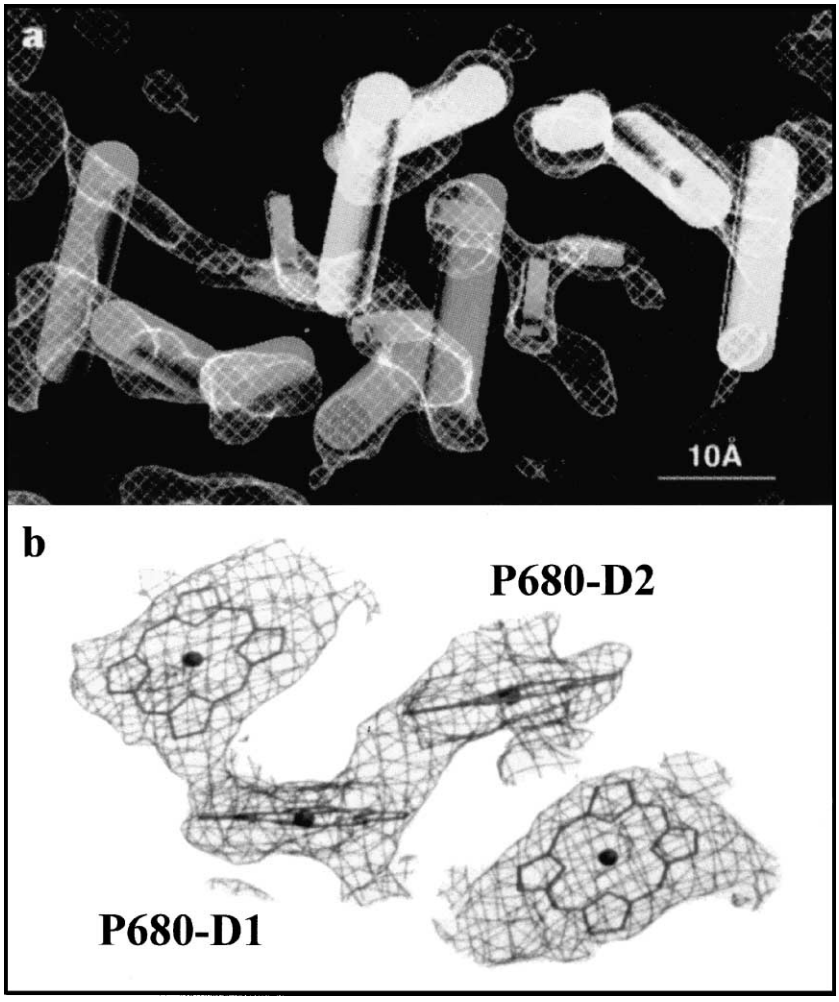

Fig. 1. (a) Positioning of the four 'core' chlorophylls within the D1 and D2 transmembrane helices depicted as rods showing the absence of a special pair. The data was obtained by electron crystallography and published in Rhee et al. [1]. (b) Positioning of the four 'core' chlorophylls of P680 as determined by X-ray crystallography confirming the absence of a special pair in PSII [6].

the pigment is chlorophyll *a* [7]. P680 is unique since it has a redox potential of 1.12 V or more in its oxidised state ($P680^+$). This very high redox potential is required to oxidise water. This is accomplished by the accumulation of four oxidising potentials in a cluster of 4 Mn ions. This charge accumulation requires four successive light-induced oxidations of P680 and electron flow from the $(Mn)_4$ cluster via a redox active tyrosine of the D1 protein (residue 161). In the case of P700 and P870, two chlorophylls form a 'special pair' which gives rise to excitonic interactions between them. As a consequence, the chlorophyll/bacteriochlorophyll absorption bands split to give a lower energy transition state which acts as the pho- tochemical trap. Since PSII contains no special pair, there is no strong excitonic interaction between the four chlorophylls and, therefore, no significant red shift of the absorption spectrum. Therefore, all four chlorophylls have similar absorption spectra suggesting that the excited state P680* is delocalised over all four and perhaps also including the two pheophytin molecules of the reaction centre. This concept is the basis of the multimer model formulated by Durrant et al. [8]. If this is the case, then the question of which chlorophyll acts as the primary donor has to be addressed. It would seem reasonable to consider the chlorophyll molecule closest to the active pheophytin acceptor as the primary oxidant. As in the case of primary charge separation in the purple bacterial reaction centre, the active branch of PSII is confined to one side. Given that the tyrosine residue D1 161 acts as the primary donor to P680 and by analogy with the bacterial reaction centre, the active branch is on the D1 side of the reaction centre. From these considerations, it follows that the chlorophyll molecule within PSII, which is equivalent to the accessory bacteriochlorophyll on the L-branch of the bacterial reaction centre, could act as the primary donor (see Fig. 2). Based on edge-to-edge distances provided by the X-ray structure [6], this chlorophyll is 4.5 Å from pheophytin. In contrast, the chlorophyll that corresponds to the bacterial special pair on the D1 side and ligated to D1 His198 is 8.1 Å from the pheophytin acceptor. On the other hand, the D1 His198 chlorophyll is closer to D1 Tyr161 (8.7 Å) than the accessory

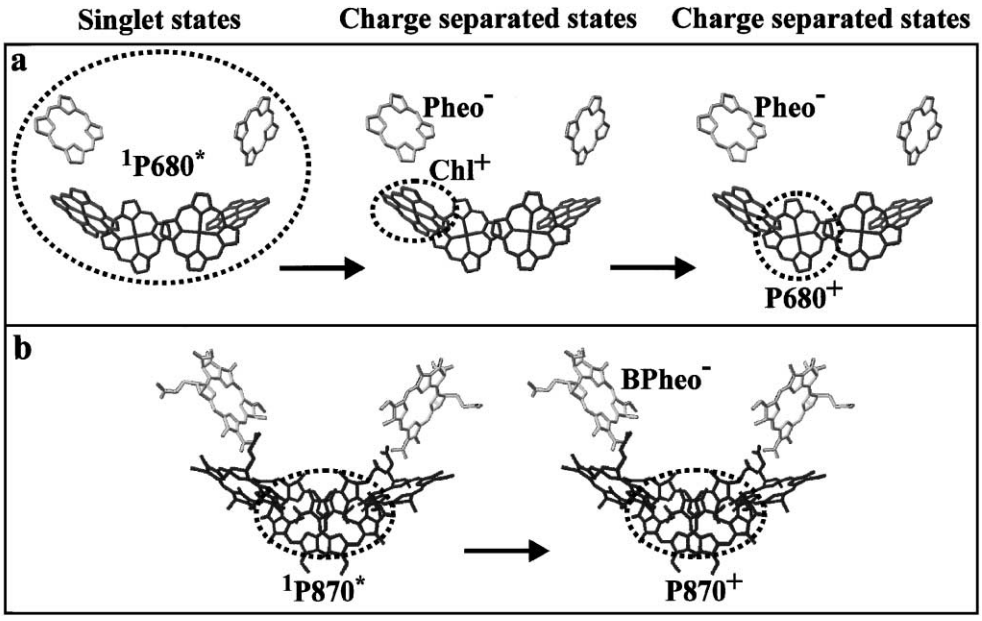

Fig. 2. Schemes for primary charge separation in PSII (panel a) and purple bacteria (panel b), emphasising the distinct differences between the two systems.

chlorophyll (11.8 Å). This could mean that the oxidising equivalent migrates to this chlorophyll as indicated in Fig. 2. There is accumulating evidence that this series of events occurs [9,10] and distinguishes the mechanism of the primary charge separation in PSII from those of other types of reaction centres.

3. Implications

As $P680^+$ has a potential of 1 V or more, it follows that all four chlorophylls in the PSII reaction centre must have high redox potentials when oxidised. If this were not so, then any one of them could be oxidised by $P680^+$ with a loss of redox energy. Why PSII has chosen to have a tetramer of monomeric chlorophylls, which are isoenergetic, rather than a 'special pair' as found in other types of photosynthetic reaction centres is unclear. The possible explanations are given below.

(i) A monomeric form of chlorophyll is required in order to develop a redox potential of 1.12 V or more. However, extensive hydrogen bonding or other 'electron' drawing side chains would also tend to facilitate a high redox potential.

(ii) The lack of a special pair in PSII, and therefore no significant red-shift of the absorption spectrum, means that the maximum free energy can be extracted by P680 from a red quantum. This minimisation of energy loss due to the lack of a deep photochemical trap is required in order to bridge the large redox gap between the oxidation of water and reduction of pheophytin ($\sim$1.6 eV).

(iii) Since P680 is a shallow trap, excess excitations can be readily transferred back into the antenna system and dissipated as fluorescence and heat. Thus, PSII has a relatively high fluorescence yield compared with other types of reaction centre and possesses special mechanisms to quench excess excitations [11]. These mechanisms play a protective role, as PSII is highly vulnerable to photoinduced damage (photoinhibition) which is linked to its unique redox chemistry [12].

Acknowledgements

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