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Research

Lipid functions in cytochrome *bc* complexes: an odd evolutionary transition in a membrane protein structure

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Lipid-binding sites and properties were compared in the hetero-oligomeric cytochrome (cyt) b_6f and the yeast bc_1 complexes that function, respectively, in photosynthetic and respiratory electron transport. Seven lipid-binding sites in the monomeric unit of the dimeric cyanobacterial b_6f complex overlap four sites in the *Chlamydomonas reinhardtii* algal b_6f complex and four in the yeast bc_1 complex. The proposed lipid functions include: (i) interfacial–interhelix mediation between (a) the two 8-subunit monomers of the dimeric complex, (b) between the core domain (cyt *b*, subunit IV) and the six trans membrane helices of the peripheral domain (cyt *f*, iron–sulphur protein (ISP), and four small subunits in the boundary 'picket fence'); (ii) stabilization of the ISP domain-swapped transmembrane helix; (iii) neutralization of basic residues in the single helix of cyt *f* and of the ISP; (iv) a 'latch' to photosystem I provided by the β-carotene chain protruding through the 'picket fence'; (v) presence of a lipid and chlorophyll *a* chlorin ring in b_6f in place of the eighth helix in the bc_1 cyt *b* polypeptide. The question is posed of the function of the lipid substitution in relation to the evolutionary change between the eight and seven helix structures of the cyt *b* polypeptide. On the basis of the known n-side activation of light harvesting complex II (LHCII) kinase by the p-side level of plastoquinol, one possibility is that the change was directed by the selective advantage of p- to n-side trans membrane signalling functions in b_6f, with the lipid either mediating this function or substituting for the trans membrane helix of a signalling protein lost in crystallization.

Keywords: assembly; cytochrome complex; LHCII kinase; quinol/quinone; super-complex; trans membrane signalling

1. INTRODUCTION

The crystal structure of the 230 kDa (including prosthetic groups) symmetrically dimeric cytochrome (cyt) b_6f complex of oxygenic photosynthesis has been determined for the filamentous cyanobacteria *Mastigocladus laminosus* [1–4] and *Nostoc* PCC 7120 [5], and the green alga *Chlamydomonas reinhardtii* [6]. The Protein Data Bank (PDB) accession numbers are, respectively, (i) *M. laminosus*: 2E74 (native), 2E75 (with bound electrochemically negative (n)-side inhibitor, 2-nonyl-4-hydroxyquinoline N-oxide, NQNO), 1VF5 and 2E76 (with tridecyl-stigmatellin, usually considered an electrochemically positive (p)-side inhibitor, but found at both n- and p-side quinone-binding sites), 2D2C (with p-side inhibitor, DBMIB)]; (ii) *Nostoc*: 2ZT9 (native); (iii) *C. reinhardtii*: 1Q90 (with tridecyl-stigmatellin). The crystal structures are consistent in describing eight polypeptide subunits, 13 trans membrane helices (TMHs) per monomer and seven prosthetic groups (four haems (haem *f* on the p-side luminal phase, two *b*-type haems, b_p and b_n, on the p- and n-sides of the complex, covalently bound haem c_n whose central Fe atom is within 4 Å of the propionate of haem b_n), one [2Fe–2S] cluster at the p-side interface, one chlorophyll *a*, and one β-carotene]. Four of the five redox prosthetic groups, with the exception of haem c_n, have the corresponding functional groups haems c_1, b_p and b_n, and the [2Fe–2S] cluster, in the cyt bc_1 complex.

The core of the cyt b_6f complex consists of: (i) the four TMHs of the cyt *b* subunit containing two trans membrane haems, which is structurally and functionally equivalent to the N-terminal trans membrane helical (helices A–D) haem-binding domain of the eight TMH cyt *b* subunits in the bc_1 complex (reviewed recently in [7]); (ii) subunit IV, with three TMHs that are structurally homologous to TMHs E–G of the bc_1 complex. The peripheral domain of the b_6f complex consists of six single TMH subunits, cyt *f* [8], the Rieske iron–sulphur protein (ISP) [9] and the small photosynthetic electron transport (Pet) subunits G, N, L and M that have been described as 'hydrophobic sticks' [10]. A ribbon diagram of the structure derived from PDB 2E74 is shown in figure 1*a*.

A dependence of the membrane protein crystal structures on the presence of specific lipids has been demonstrated for a number of membrane proteins and protein complexes. These include the photosynthetic light-harvesting chlorophyll protein [11], the bacterial

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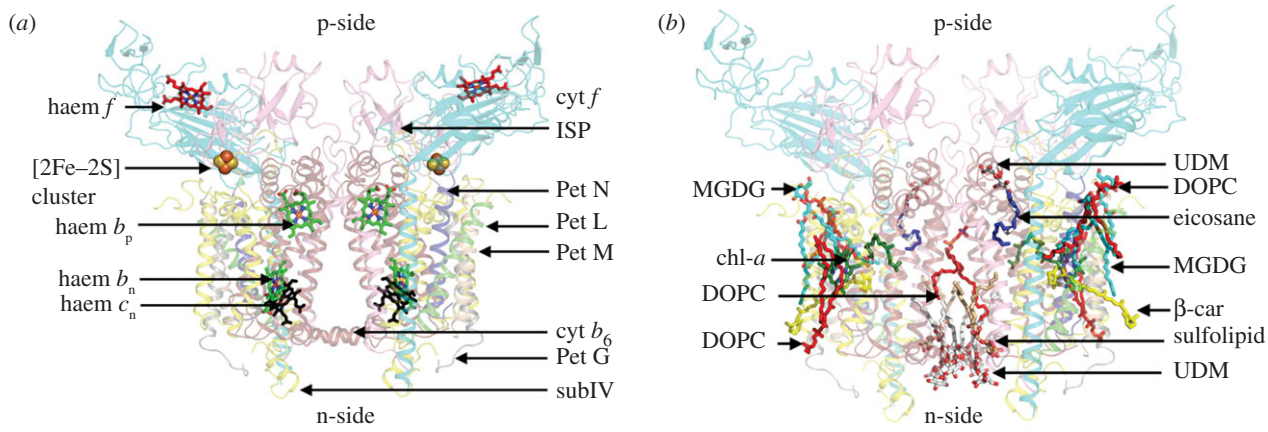

Figure 1. Cytochrome b_6f complex of *Mastigocladus laminosus* (PDB 2E74). (*a*) Redox groups in the cyt b_6f complex. The trans membrane *b*-haems (b_p and b_n) are shown in green, and haem c_n in black. Haem of cyt *f* soluble domain is shown in red; [2Fe–2S] cluster of the ISP is shown as brown and yellow spheres (brown, Fe; yellow, S). The eight polypeptides in cyt b_6f monomer are shown as ribbons (cyt *f*, cyan; cyt b_6, light brown; ISP, pink; subIV, yellow; Pet G, gray; Pet L, green; Pet M, wheat; Pet N, dark blue). (*b*) Lipid-, detergent- and pigment-binding sites in cyt b_6f. Natural acidic sulfolipid is shown in wheat. Natural galactolipid, monogalactosyl-diacylglycerol (MGDG), in *C. reinhardtii* b_6f structure (PDB 1Q90) are in cyan and red. The synthetic lipid, dioleoylphosphatidylcholine (DOPC), used for crystallization of b_6f from *M. laminosus* and *Nostoc* PCC 7120 is shown in red. Ordered molecules of the detergent *n*-undecyl-β-D-maltopyranoside (UDM) found in the cyanobacterial b_6f structures are shown as, white and red sticks. Native chlorophyll *a* (chl-*a*), β-carotene (β-car) and eicosane (from *C. reinhardtii* b_6f) are shown as green, yellow and dark blue sticks. Figure was generated by superposition of *C. reinhardtii* (PDB 1Q90) and *M. laminosus* b_6f (PDB 1VF5, 2E74).

photosynthetic reaction centre [12–16], photosynthetic reaction centres II [17–19] and I [18,20], bovine [21] and bacterial cyt oxidase [22,23] and the cyt bc_1 complex [24].

2. DISCUSSION

Lipid functions in the b_6f complex, described in figure 1*b*, include [25]: first, n-side and p-side stabilization of the dimer structure, the former analogous to function of the second cardiolipin in the bc_1 complex (yeast; 3CX5 [26]); and secondly, n-side stabilization of the domain-swapped trans membrane helices of the high potential Rieske ISP by anionic sulpholipid [25,27], and by phosphatidic acid in the yeast bc_1 complex [26]. Thirdly, lipids also mediate the division between a bipartite intra-membrane structure of the b_6f complex, in which each monomer of the dimer consists of: (i) the conserved core consisting of the cyt *b* and subunit IV polypeptides, with four and three TMHs, respectively; (ii) the peripheral domain containing the single TMH of cyt *f* and the domain-swapped TMH of the ISP and the four small peripheral hydrophobic peptides, Pet G, L, M and N, the latter a set of single closely packed TMHs that define a unique 'picket fence' around each monomer. The spatial distribution of the subunit polypeptides and their B-factors are consistent with the concept of a two-tiered structure: (a) the polytopic core of the cyt b_6 and suIV subunits with four and three TMHs, respectively, the only polytopic subunits in the complex; and (b) a peripheral domain containing the single TMH of cyt *f*, ISP, Pet G, L, M and N. The function of the lipids in mediating interactions between the core and peripheral domain, and thus stabilizing the complex, is a consequence of the binding sites of the p-side lipids residing on residues from both the cyt b_6 and 'subunit IV' subunits of the core, and on the four single TMH subunits, Pet G, L, M and N, in the total set of six single TMH subunits in the peripheral domain [18,25].

(a) *Two unique lipid functions*

(i) *Formation of a super-complex of the b_6f complex with the photosystem I reaction centre*

A curious situation exists for the function of the lipid-like β-carotene molecule. Carotenoids serve a universal role in photosynthesis as a quencher of the deleterious chlorophyll triplet state whose decay to the ground state can be coupled to the generation of excited state singlet oxygen, which is deleterious to plant and human tissue. Thus, on the one hand, the b_6f complex contains a β-carotene whose function is ostensibly to carry out a triplet–triplet transfer and thus to quench the chlorophyll triplet state and thereby prevent the formation of singlet oxygen. However, crystal structures of the b_6f complex from both the cyanobacteria and from a green alga are in agreement with a distance of closest approach of the single chlorophyll *a* in the structure and the one β-carotene of 14 Å [1,6,28]. Theoretically, this separation is much too large for efficient triplet–triplet transfer [29]. However, a significant extent of such energy transfer, measured on a rapid time scale, less than 8 ns, has been determined [28]. It is noted, however, that if the only function of the β-carotene would be to carry out triplet–triplet transfer, it should be in a position much closer to the chlorophyll *a* in the structure. Therefore, it is inferred that it has at least one additional function in the complex.

Considering its position in the structure, in which the β-carotene protrudes through the 'picket fence', between the Pet G and Pet M single TMHs by approximately 11 Å (figure 2), it is suggested that it could function as a 'latch' that connects to another structure in the photosynthetic membrane.

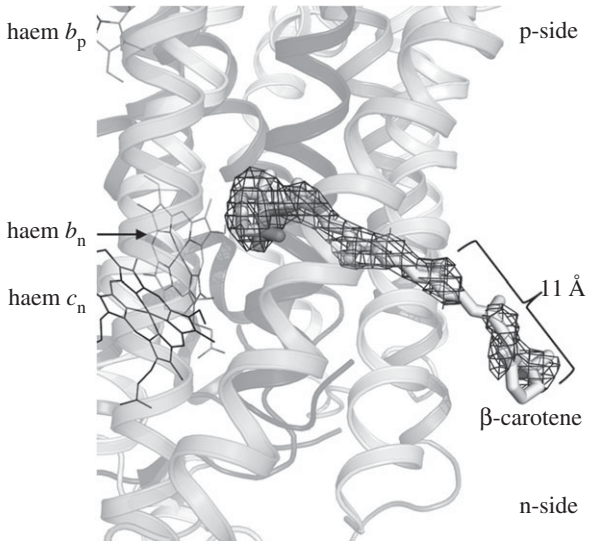

Figure 2. The exposed (11 Å) chain of β-carotene that is proposed to be a 'latch' to photosystem I, mediating the formation of a super-complex [30]. The b_6f complex has a peripheral β-carotene inserted into the trans membrane core of the complex (PDB 2E74). This pigment overlaps with the position of a peripheral cardiolipin of the yeast respiratory cyt bc_1 complex (PDB 3CX5) that mediates the formation of a bc_1–cyt *c* oxidase super-complex. The extension of the b_6f β-carotene into the lipid bilayers is proposed to allow it to act as a structural antenna for the formation of b_6f–photosystem I super-complex. 2Fo-Fc map, 1.0σ (approx. 0.1 $e^-/Å^3$).

Examination of superimposed b_6f and bc_1 structures indicates that the enigmatic β-carotene in the b_6f complex is in a position similar to that of a cardiolipin [31], which is positioned at the interface of a super-complex of the bc_1 complex formed with cyt oxidase in the bovine respiratory chain [32,33]. It had previously been suggested that formation of a cyt b_6f—photosystem I (PSI) reaction centre 'super-complex' could be mediated by the β-carotene [6,34]. The b_6f complex in the green alga *C. reinhardtii* has been isolated in a large ('super') complex that includes the PSI reaction centre [30]. Thus, it is proposed that the surface-exposed and significantly protruding β-carotene in the peripheral domain of the b_6f complex is involved in mediating the formation of a super-complex with the PSI reaction centre complex.

(ii) *Lipid replacement of a trans membrane helix: transmembrane signalling in the* b_6f *complex; an unusual transition in evolution*

It has long been known [35,36] that the eight TMHs of the cyt *b* subunit of the cyt bc_1 complex are split into two subunits in the b_6f complex: firstly, the four TMH cyt b_6 subunit, which corresponds to the N-terminal haem-binding four TMHs of the bc_1 complex, and secondly subunit IV, consisting of three TMHs, the fourth largest subunit in the b_6f complex. Thus, the eight TMHs (A–H) in the cyt *b* subunit of the cyt bc_1 complex are replaced by seven TMHs (A–G) in the b_6f complex. However, with no material in this niche formed by the eighth TMH in bc_1, a vacuum would result at this position in the structure of the b_6f complex. Presumably, membrane protein structures abhor a vacuum (see discussion in [37]). It has recently been found that this space in the b_6f complex can largely be filled by a lipid and the bound chlorophyll *a* [25] (figure 3). The eight versus seven TMH problem in the cyt *b* polypeptide in energy-transducing membranes has previously been discussed in the evolutionary context of the residence of the split (four + three) seven TMHs of b_6f-like complexes in the 'green clade' [38]. In addition to the questions posed in [38] in the context of the finding that a lipid molecule in the b_6f complex occupies much of the space filled by the eighth TMH in the bc_1 complex, one may ask: (i) which cyt *bc* complex appeared first in evolution, the respiratory or photosynthetic cyt *bc* complex? (ii) Thus, was the eighth TMH (the 'H' helix) replaced by two subunits consisting of seven TMHs, with a space in the structure for a lipid or another TMH from another subunit? (iii) Alternatively, was the sequence of events *vice versa*, i.e. the two subunits with seven TMHs replaced by a single cyt *b* subunit with eight TMHs? (iv) What was the 'driving-force' or 'evolutionary pressure for one direction of the change or the other? A hypothesis for the answer to question (iv) is provided below.

Briefly summarizing available dating information and directions in the relevant branches of the evolutionary tree [38,39]: (i) carbon signatures implying established life in the absence of evidence for the presence of molecular oxygen have been found in Greenland rocks that have been dated to 3.8 Ga [40], implying the presence of bacteria containing chemo-lithotrophic respiratory chains; (ii) the presence of these bacteria substantially precedes that of the molecular oxygen (2.8–2.4 Ga [40]) that is associated with the existence of primitive oxygenic photosynthetic bacteria (i.e. cyanobacteria); (iii) the subunit structure of the b_6f complex from the cyanobacteria, with eight subunits, five redox prosthetic groups and seven prosthetic groups in total, has a greater degree of complexity than that of the proteobacterial bc_1 complex that possesses three protein subunits and a total of four prosthetic groups [41]. Therefore, although not certain, it does not seem unlikely that the transition of the cyt *bc* complex in evolution was from the proto-bc_1 complex with an eight TMH cyt *b* polypeptide to the seven TMH b_6f complex present in the 'green clade', consistent with a 'respiration-early' hypothesis [42].

(b) *The evolutionary force in the cytochrome* b *transition: a hypothesis*

It is proposed that an evolutionary selection for this transition is trans membrane signalling in the b_6f complex in which the level of plastoquinol or quinol oxidation by the Rieske protein on the p-side of the complex can activate an enzyme bound on the n-side of the complex, studied mostly for the light harvesting complex II (LHCII) kinase [43–45] that regulates state transitions of light-harvesting chlorophyll proteins. The p-side site of the quinol oxidation by the [2Fe–2S] complex is proximal to the trans membrane F and G α-helices, as seen in the structure of the b_6f

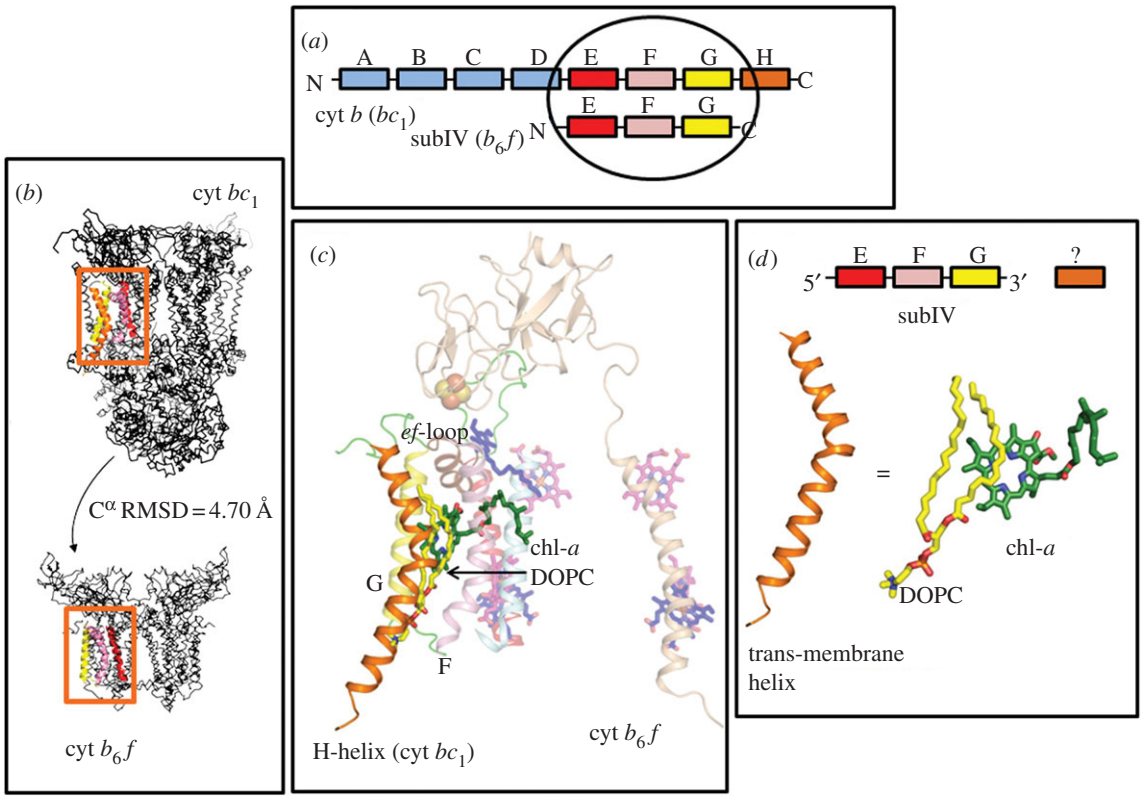

Figure 3. The missing helix; trans membrane signalling. Substitution of the eighth helix in the bc_1 complex with a lipid in b_6f. Trans membrane signalling by cyt b_6f; p-side niche between the 'F' and 'C' TMHs defines a portal for passage of lipophilic quinol/quinone. (*a*) The eight TMHs of the respiratory bc_1 complex and the seven (four + three) TMHs in b_6f; (*b*) Domain containing F, G and H TMHs in the yeast bc_1 complex and the F and G TMHs in b_6f. (*b*) binding niche of quinone analogue inhibitor, tridecyl-stigmatellin. (*c*) Ribbon diagram showing superposition of bc_1 H-helix (orange) and, in b_6f, DOPC lipid (yellow) and the chlorophyll *a* chlorin ring and phytyl tail (green). Binding site of p-side quinone analogue inhibitor, tridecyl-stigmatellin (blue). (*d*) Inferred structure–function equivalence of bc_1 TMH 'H' and (lipid together with chlorophyll *a*) in b_6f complex.

complex. The niche unoccupied by the H-helix that is lost from the bc_1 complex also spans the complex and the membrane at this site. This niche could be occupied by a trans membrane helical domain documented for the LHCII kinase (stt7) of *C. reinhardtii* (J.-D. Rochaix 2012, personal communication). However, along with four other proteins that have been found in isolated b_6f complex [7] before crystallization, the stt7 LHCII protein kinase is not present in the crystals of the complex. It is presumed that such proteins are peripherally or loosely bound, which should not be the case for a subunit with a TMH. Alternatively, conformational changes associated with trans membrane signalling could be mediated by the intercalated lipid observed in the structure of the b_6f complex (PDB 2E74 [4,25]), perhaps coupled to the conformational flexibility of the chlorophyll *a* phytyl chain that is inferred from the different positions of this chain in the structures of the complex from the cyanobacteria (PDB 2E74) and *C. reinhardtii* (PDB 1Q90).

A caveat for the inference of a first appearance of an LHC kinase in cyanobacteria during the course of evolution is that cyanobacteria do not display the state transitions characteristic of algae and higher plants that are associated with the function of the light-harvesting chlorophyll proteins in regulating the distribution of light energy to the two photosystems. However, a functionally similar regulatory mechanism has been proposed for cyanobacteria [46,47], in which phosphorylation of the phycobiliproteins has been implicated [46]. Other redox-linked functions that have been proposed to be coupled to the redox state of the plastoquinone pool, and thereby quinol oxidation by the [2Fe–2S] Rieske protein, are chloroplast [48] and nuclear [49] gene expression, and other sensing functions [49].

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