

Photosynthetic, respiratory and extracellular electron transport pathways in cyanobacteria

David J. Lea-Smith, Paolo Bombelli, Ravendran Vasudevan, Christopher J. Howe δ

Department of Biochemistry, University of Cambridge, Downing Site, Tennis Court Road, Cambridge, CB2 1QW, UK.

δ Corresponding author; E-mail- ch26@cam.ac.uk

Abstract

Cyanobacteria have evolved elaborate electron transport pathways to carry out photosynthesis and respiration, and to dissipate excess energy in order to limit cellular damage. Our understanding of the complexity of these systems and their role in allowing cyanobacteria to cope with varying environmental conditions is rapidly improving, but many questions remain. We summarize current knowledge of cyanobacterial electron transport pathways, including the possible roles of alternative pathways in photoprotection. We describe extracellular electron transport, which is as yet poorly understood. Biological photovoltaic devices, which measure electron output from cells, and which have been proposed as possible means of renewable energy generation, may be valuable tools in understanding cyanobacterial electron transfer pathways, and enhanced understanding of electron transfer may allow improvements in the efficiency of power output.

Keywords:

Terminal oxidase; Flavodiiron; Biophotovoltaic; Photoprotection; Photosynthetic electron transfer; Respiration

Abbreviations:

ARTO alternative respiratory terminal oxidase

BPV biophotovoltaic

CET cyclic electron transport

COX cytochrome *c* oxidase

Cyd cytochrome *bd*-quinol oxidase

HOX bi-directional hydrogenase

PTOX plastid terminal oxidase

1. Introduction.

Cyanobacteria (oxygenic photosynthetic bacteria) are evolutionarily ancient organisms and significant primary producers found in almost every environment on Earth. They are able to conduct both photosynthesis and respiration, and have therefore evolved a diverse range of electron transport pathways. This range is further extended by the requirement to dissipate excess electron flow, essential for many species in order to survive varying light and environmental conditions [1-4]. The majority of cyanobacterial species possess two membrane systems: the cytoplasmic membrane and a series of internal thylakoid membranes. The sole exception is *Gloeobacter violaceus*, which lacks thylakoid membranes and localizes electron transport pathways to specific domains in the cytoplasmic membrane [5]. In all other cyanobacteria, the light reactions occur in the thylakoid membranes, although an additional electron transfer chain localized in the cytoplasmic membrane may be present in some species [6]. The cytoplasmic membrane has also been reported to contain incompletely assembled, nonfunctional Photosystem I (PSI) and Photosystem II (PSII) complexes, perhaps as part of the photosystem biogenesis pathway [7, 8]. Recent experiments using biological photovoltaic (BPV) systems, which contain devices capable of measuring cellular electricity production, have demonstrated that electrons generated via photosynthesis (as well as respiration) can be exported from the cell [9, 10]. This suggests that direct or indirect electron transport routes are present between the thylakoid and cytoplasmic membranes and that these extend beyond the peptidoglycan layer and outer membrane to the cell exterior.

In this review we will discuss electron transport pathways in each of the membrane systems and the role of alternative electron transport pathways in photoprotection. We speculate on possible routes by which electrons can be transferred to the exterior environment and suggest that extracellular electron transport in cyanobacteria may play a significant role in environments such as cyanobacterial mats or biofilms [11, 12]. Much of the work in this field has been conducted in *Synechocystis* sp. PCC 6803 (hereafter referred to as *Synechocystis*) because of the excellent genetic tools available in this species, including well-established protocols to construct mutants with multiple chromosomal deletions and insertions [3], in addition to more precise manipulation, such as the introduction of single point mutations in specific genes [13]. Unless a different species is indicated, this review will focus on electron transport pathways in *Synechocystis*, which is likely to remain the preferred organism for study of electron transport in cyanobacteria in the future

2. Thylakoid membrane linear photosynthetic electron transport.

With the exception of *Candidatus* species, all cyanobacteria generate electrons via water splitting in PSII (Fig. 1A) [14]. *Candidatus atelocyanobacterium thalassa* (previously referred to as cyanobacterium UCYN-A) forms a symbiotic relationship with a single-celled eukaryotic alga, to which it supplies fixed nitrogen in return for fixed carbon [15]. In PSII, for each water molecule split, 2 protons and $1/2$ O₂ are released into the thylakoid lumen, and 2 electrons are generated in the reaction centre [16]. The photosynthetic route of electron transport first involves donation of two electrons to plastoquinone (PQ) within PSII, which is reduced to plastoquinol (PQH₂). In the process PQ accepts two protons from the cytoplasmic side of the thylakoid membrane [16].

Following release from PSII, PQH₂ diffuses through the membrane to the cytochrome *b₆f* complex (cyt *b₆f*) where it is deprotonated and oxidised on the luminal side of the membrane [17]. One electron is transferred by cyt *b₆f* to either plastocyanin (Pc) or cytochrome *c₆* (cyt *c₆*). The other electron is transferred via heme units to the cytoplasmic side where it reduces PQ to PQH[•]. This process is repeated in order to reduce PQH[•] to PQH₂. Overall 2 PQH₂ are oxidized on the luminal side of the membrane, releasing 2 PQ, 2 electrons to Pc or cyt *c₆* and 4 protons into the lumen. On the cytoplasmic side a reduced PQH₂ is regenerated.

In *Synechocystis*, as in many other cyanobacteria, Pc is the dominant redox carrier [18], while cyt *c₆* expression is minimal in the presence of copper [18]. Both proteins reduce PSI with similar kinetics [19]. Following transfer to PSI, the electron substitutes for an excited electron generated in the core of the complex, which is transferred via iron-sulphur clusters to ferredoxin (Fd) [20] and then ferredoxin-NADP⁺ reductase (FNR), leading to conversion of NADP⁺ to NADPH. Two electrons are required for each NADPH produced. Overall to produce one NADPH molecule, 1 water molecule is split and in theory an electrochemical gradient across the thylakoid membrane equivalent to 6 protons could be formed. The proton gradient is used to drive ATP production via ATP synthase. Given that the proton requirement for ATP synthesis in *Synechocystis* could vary between 4.67 H⁺/ATP [21] and 4 H⁺/ATP [22], 1.28 to 1.5 ATPs are produced for each NADPH. In some cyanobacteria the H⁺/ATP ratio may be higher [21]. However, these values may be altered by the occurrence of processes such as cyclic photophosphorylation (see below).

3. Thylakoid membrane respiratory electron transport.

The thylakoid membrane is the main site of respiratory electron transport as well as photosynthetic electron transport in *Synechocystis* (Fig. 1B) [3, 23]. Several components are shared with the photosynthetic electron transport, including PQ, cyt *b₆f* and Pc/cyt *c₆*. In addition to respiration, it is now confirmed that many respiratory complexes play a key role in photoprotection, allowing cyanobacteria to accommodate light fluctuations and preventing over-reduction of the interlinked electron transport chain, with potentially damaging consequences (see below) [1-4].

A range of dehydrogenases, linked to the oxidation of NADPH, NADH or succinate, are potential electron donors to the thylakoid membrane electron transport chain via PQ. Succinate dehydrogenase (SDH) has been suggested to act as the main respiratory donor [24] but is poorly characterized. SDH is a four subunit complex in *E. coli*. Homologues of only two soluble subunits have been identified in *Synechocystis* [25], although a sequence encoding a homologue of one of the membrane subunits (subunit C) has been reported from some strains, such as *Thermosynechococcus elongatus* BP-1 (<http://genome.microbedb.jp/cyanobase/Thermo> accessed 6 July 2015). The other membrane subunit(s) and the mechanism by which SDH reduces PQ have not been determined for cyanobacteria. Four NAD(P)H dehydrogenase type 1 (NDH-1) complexes (reviewed in [26]) and three single subunit NAD(P)H dehydrogenase type 2 (NDH-2) have also been identified [24]. It is still not clear whether NDH-1 complexes can utilize NADH or NADPH directly, due to the absence of subunits involved in NADH binding which have been characterized in the structurally similar *E. coli* complex I [26]. Alternative electron donors facilitating oxidation of NADPH and subsequent electron donation to NDH-1 have not been identified, although Fd has been suggested as a possible candidate [27]. Deletion of any of the NDH-2 proteins results in a small reduction in respiration [28] and, based on analysis of the redox state of the NADPH/NADP⁺ and NADH/NAD⁺ pools, these proteins may bind NADH in preference to NADPH [24]. Recently the NDH-2 protein encoded by *ndbB* has been demonstrated as essential for vitamin K₁ biosynthesis in both *Arabidopsis thaliana* and *Synechocystis* [29], suggesting that this protein may perform multiple functions in the cell. Only NDH-1 builds a membrane electrochemical gradient, potentially pumping 4 protons for every 2 electrons entering the complex [26].

A number of respiratory terminal oxidases have been identified for cyanobacteria (reviewed in [30]). Several terminal oxidases accept electrons directly from PQ. They include cytochrome *bd*-quinol oxidase (Cyd) [31], the alternative respiratory terminal oxidase (ARTO) [32] and plastid terminal oxidase (PTOX) [33]. Different cyanobacterial strains contain different subsets of these. Thylakoids of *Synechocystis* contain only Cyd (although ARTO is likely to be present in the *Synechocystis* cytoplasmic membrane) [3, 31]. Another terminal oxidase, an *aa*₃-type cytochrome-*c* oxidase complex (COX) can accept electrons from Pc/cyt *c*₆ [23], contributing to the membrane electrochemical gradient, and increasing ATP production at the expense of NADPH.

4. Thylakoid membrane cyclic electron transport.

Cyclic electron transport (CET) can occur around PSI, resulting in increased ATP production (Fig. 1C). Several possible routes have been suggested but are poorly characterized. The first involves oxidation of FNR-generated NADPH by either NDH-1 or the unknown NADPH oxidase:NDH-1 reductase protein discussed earlier [26]. A Fd binding site has been identified in the NdhS subunit of chloroplast NDH-1 of *Arabidopsis thaliana* [34]. More recently NdhS from *Thermosynechococcus elongatus* has been shown by surface plasmon resonance and yeast two-hybrid experiments to interact with Fd [27], although this has not been demonstrated *in vivo* in cyanobacteria. If NDH-2 is capable of oxidizing NADPH then this may also be an alternative route. A putative ferredoxin:plastoquinone reductase (FQR), encoded by *ssr2016* in *Synechocystis*, has been suggested to play a role in CET, facilitating electron exchange between Fd and PQ [35]. Little characterization of this protein has been conducted in the decade since this initial publication.

5. Cytoplasmic membrane electron transport.

Early studies suggested the presence of an extensive electron transport pathway containing NDH-1, cyt *b*₆*f*, Pc/cyt *c*₆ and COX in the cytoplasmic membrane [36]. However, recent experiments using purified membrane fractions localized NDH-1, cyt *b*₆*f* and COX specifically to the thylakoid fraction [37-40]. Therefore it is likely that the cytoplasmic membrane pathway consists of electrons donated to PQ by dehydrogenase complexes, SDH and/or NDH-2, followed by direct transfer from PQH₂ to terminal oxidases, ARTO and/or

Cyd (Fig. 1D), although only ARTO has been identified in cytoplasmic membrane fractions [40-42]. ATP synthase is also present [40], suggesting that a membrane potential is formed. ARTO may also have an alternative role in iron reduction [43].

6. Alternative electron transport pathways

It is becoming increasingly clear that a number of alternative electron transport pathways exist. Many of these probably function to protect cells under stress conditions, and are particularly associated with the removal of excess electrons to avoid the production of reactive oxygen species.

6.1 Protective electron sinks in the thylakoid membrane

As a result of the intersection between the respiratory and photosynthetic electron transport chains, the terminal oxidases in the thylakoid membrane apparently have an important role in addition to any function in respiration, namely the transfer of excess electrons generated from PSII to oxygen, preventing over-reduction of the PQ pool. A similar protective role is played by a soluble complex located in the cytoplasm, the flavodiiron 2/4 proteins (Flv2/4) [44, 45]. In a recent study oxygen has been suggested as a possible electron acceptor from Flv2/4 under CO₂ limited conditions [46], although earlier reports had suggested the acceptor was not oxygen [44, 47]. However the nature of the acceptor has not been demonstrated conclusively *in vivo*.

In the absence of these protective electron acceptors, uncontrolled donation of electrons to oxygen can occur at high rates under certain conditions, resulting in production of reactive oxygen species (ROS) [3]. ROS can damage cellular components, notably PSII, leading to reduced photosynthesis and ultimately cell death [3, 4]. Algae and plants, which lack these electron sinks, with the possible exception of PTOX, remove excess electrons via the water-water cycle [48]. This process is the direct reduction of O₂ by PSI resulting in production of singlet oxygen (O₂⁻), followed by conversion to H₂O₂ via superoxide dismutase and subsequent reduction to H₂O by ascorbate peroxidase [48]. The absence of ascorbate peroxidases in cyanobacteria suggests that this process is not a major electron sink, although similar enzymes may be active in removing ROS [49].

The importance of these alternative cyanobacterial electron acceptors has been demonstrated by assaying growth of mutants deficient in these complexes under varying light and carbon conditions, which may be more representative of environmental conditions than growth under constant illumination with provision of CO₂ at higher concentrations than in the atmosphere. When terminal oxidase or Flv2/4 mutants are supplied with sufficient carbon dioxide and cultured under constant illumination, growth is similar to wild-type [3, 23, 45]. However, mutants deficient in thylakoid localized terminal oxidases exhibit slower growth under diurnal conditions and photobleaching and cell death under 12 hour, square wave high light/12 hour dark cycles [3]. Flv2/4 mutants grow poorly under high light and low carbon dioxide conditions [45].

6.2 Alternative electron transport via poorly characterized c-type cytochromes.

Two c-type cytochromes found in most cyanobacteria are presumed to have roles in electron transport, namely cytochrome c_M (originally cytM) [50] and the cyt c_{6B}/c_{6C} family [51], although the details of their roles are not clear. Pc or cyt c_6 are strictly required for thylakoid membrane electron transport [19], so cytochromes c_M and c_{6B}/c_{6C} cannot be simple substitutes for Pc or cyt c_6 . Cytochrome c_M is highly conserved in the majority of sequenced cyanobacterial strains [52] and is expressed under low temperature or high light conditions [53]. Both COX and PSI have been suggested as electron acceptors [52, 54, 55] and Pc or cyt c_6 as potential electron donors [54], although conclusive evidence of this has not been provided. A role in stress conditions has been suggested, given the reaction of cyt c_M with COX [46], but paradoxically, dark respiratory oxygen consumption is increased in cyt c_M mutants [56]. Cytochrome c_{6B}/c_{6C} proteins are distributed in a range of cyanobacteria [51], and were named on the basis of their similarity to the low-potential cytochrome c_6 homologues found in green plants and algae, which had been designated cytochrome c_{6A} [57]. The cyanobacterial proteins have been suggested to transfer electrons to PSI [51, 58], although the *Arabidopsis thaliana* homologue reacts only slowly with PSI *in vitro* [59]. However, the *Arabidopsis* protein can transfer electrons to plastocyanin *in vitro* [60]. The nature of the physiological electron donor to cyt c_{6B}/c_{6C} is also unclear. The redox midpoint potential of cyt c_{6C} from *Synechococcus* sp. PCC 7002 was determined by Bialek et al. to be 148 mV (much lower than the conventional cyt c_6 from the same organism, which was around 319 mV) [51]. As with the plant cyt c_{6A} , the cyt c_{6C} potential would be too low for it

to be an effective electron acceptor from cytochrome *f* with its midpoint potential of approximately 270 mV [51, 61]. The roles of cyt *c*_{6B}/*c*_{6C} under different environmental conditions have not been systematically investigated.

6.3 Ferredoxin electron transfer.

In addition to FNR, Fd is the electron donor required for reduction of a range of metabolites including sulfite [25], nitrate [62], nitrite [62], glutamate [63] and biliverdin [64] and the protein thioredoxin [65] (Fig. 2). Of these only nitrate and nitrite reduction has been demonstrated to be a significant electron sink [62]. More recently the bi-directional hydrogenase complex (HOX), which converts protons to hydrogen, has been demonstrated to undergo reduction preferentially by Fd [66], in contrast to earlier reports which suggested that NADPH was the main electron donor [67]. NADH has also been suggested as another potential electron donor to HOX [68, 69]. HOX limits over-reduction of the thylakoid membrane electron transport chain and mutants deficient in this complex demonstrate reduced growth under both low and high carbon conditions [67]. In addition to Fd, eight other genes encoding putative ferredoxin proteins are present in the *Synechocystis* genome [25, 70]. Four of these are essential for photoautotrophic growth [70]. Other ferredoxins influence tolerance to various environmental stresses, although their exact roles have not been characterized [70].

6.4 NADPH oxidation pathways.

The availability of NADP⁺ is a key factor in preventing over-reduction of the thylakoid membrane electron transport chain. NADPH is crucial for a range of metabolic reactions although the majority is allocated for carbon fixation (Fig. 2). However, under low carbon dioxide concentrations, photorespiratory glycolate metabolism is a significant electron sink [71]. *Synechocystis* mutants deficient in photorespiratory pathways require high CO₂ conditions for survival [71]. In addition, Flavodiiron 1/3 (Flv1/3) proteins play a key role in utilizing excess NADPH. Flv1/3 transfers electrons from NADPH to O₂, generating H₂O, and is a significant electron sink under low carbon conditions [47]. However, Fd may also be a possible electron donor to Flv1/3. Flv1/3 is crucial for cellular viability under rapid fluctuating light conditions [4, 72].

7. Intracellular and extracellular electron transport pathways

So far, we have considered electron transport within individual membranes, namely the thylakoid or the cytoplasmic membrane. Electron transport pathways between the thylakoid and cytoplasmic membranes and to the exterior of the cell are poorly defined in cyanobacteria (Fig. 3), although it is known that electrons initially derived from photosynthesis can be passed to the cell exterior [9-11]. There is some evidence to suggest that thylakoid and cytoplasmic membranes are connected in *Synechocystis* [73], although whether the respective electron transport chains are also directly linked has not been determined. If they are not directly linked then processes localized to the cytoplasm must be involved in any electron exchange that occurs between the two membrane systems. Electron donors from the thylakoid membrane could include Flv2/4 and PQH₂. Based on modelling studies, PQH₂ can be exposed at the membrane surface and therefore possibly interact with cytoplasmic proteins [74]. Specific, unidentified electron carriers localized to the cytoplasm may have the capacity to accept electrons from these components. Possible candidates could include one or more of the eight putative ferredoxin proteins encoded in the *Synechocystis* genome [25, 70] and some of the uncharacterized soluble cytochrome proteins mentioned earlier (depending on their subcellular location). NADPH generated by FNR could potentially be oxidised by cytoplasmic membrane localized NDH-2, as could succinate via SDH, thereby transferring electrons into the cytoplasmic membrane electron transport chain.

In theory, surface exposed PQH₂ could then transfer electrons to electron carriers located in the periplasm, possibly ferredoxin or cytochromes, to give extracellular electron export. Reduction of iron by ARTO in the periplasmic space [43] may also supply a soluble donor for electron export. Other as yet unidentified proteins may directly transport electrons across the cytoplasmic membrane. Electron transport to the exterior could occur via pili, which are long, high tensile strength fibres, up to several micrometres in length and radiating out of the cell from components lodged in the outer and cytoplasmic membranes [75, 76]. Different types of pili may be present in cyanobacteria (reviewed in [76]). *Synechocystis* genes encoding all the subunits required to form functional type IV pili are present in the genome [25]. In cyanobacteria, pili play a role in cell motility, biofilm formation and DNA uptake [75, 76] and in some bacterial species, including *Synechocystis*, have been demonstrated to be highly conductive [77-79]. In *Synechocystis*, production of electrically conductive pili has

been reported to occur under low carbon conditions but not when cells are supplied with sufficient CO₂ [79]. This suggests a possible role in export of excess electrons. The pili conductive mechanism in *Synechocystis* has not been elucidated and further work is required in order to demonstrate conclusively whether these complexes are required for electron export.

8. Biological photovoltaic devices

BPV devices have been recently developed with the main objective of harvesting electrical output from oxygenic photosynthetic organisms (reviewed in [80]). Typically BPVs consist of a transparent chamber containing the photosynthetic organism of interest, which can be exposed to varying light and dark conditions. On one side of the chamber there is an anode, which is often made of indium tin oxide-coated polyethylene terephthalate, although many other materials can be used, including stainless steel and carbon paper [81]. Cells are usually either stirred in suspension, in which case a soluble electron carrier such as ferricyanide is required for electron transport from the cell to the anode (Fig. 4A), or allowed to settle on the anode where a biofilm can form (Fig. 4B). Biofilm formation is dependent on species and growth conditions [11]. In cyanobacteria, conductivity between the biofilm layer and the anode is likely to be dependent on pili formation and connectivity between cells [11]. A cathode, typically consisting of platinum wire or similar material, is wired to the anode by an external circuit. The cathode recombines electrons passing through the external circuit with O₂ and H⁺s generated via water splitting to reform water. The protons pass through a membrane separating the cathode and anode.

8.1 BPVs as a tool to characterize electron transport in cyanobacteria.

BPV systems have been successfully used as diagnostic tools to investigate electron transport in photosynthetic organisms, including cyanobacteria. For example, Bradley et al. analysed the effects of mutations on electron transport from the thylakoid membrane to the exterior of the cell [9]. Mutants lacking the thylakoid membrane-localized COX and Cyd complexes showed increased power output in BPVs, compared to wild-type cells [9]. Further increases in power output were observed when ARTO was also removed, confirming that electron export is dependent on both thylakoid and cytoplasmic membrane electron transport chains.

The requirement for a soluble electron carrier for electron export, such as ferricyanide, which can only accept electrons from donors localized in the periplasm or cytoplasmic membrane [10], showed that *Synechocystis* grown planktonically does not excrete soluble electron carriers, such as quinones [82] or flavins [83]. BPV systems have also been combined with photosynthetic inhibitors, such as DCMU, which blocks electron transfer from PSII to PQ, to study electron transport. Addition of DCMU decreased the light-dependent current output from illuminated *Synechocystis* cells by approximately 65% [10], although photosynthetic oxygen evolution was completely inhibited. This suggests that the light dependent current produced when DCMU is present came from electrons that were initially introduced into the PQ pool from respiratory dehydrogenases and subsequently fed into PSI. Thus, the BPV device allowed estimation of the relative magnitudes of inputs of the respiratory chain and PSII into the PQ pool. Cereda et al. also observed a residual light-stimulation of current output in the presence of DCMU or in Δ PsbB cells [84]. Given the role of terminal oxidases and other electron transport pathways in protecting cells against the effects of excessive reduction of the PQ pool, it will be very interesting to see if the provision of another electron sink, the anode of a BPV, will allow further protection against, for example, excessive light levels.

8.2 Improvement in power output from BPV devices

At present the maximum biological power output density recorded from cyanobacterial cells in a BPV is approximately 100 mW m^{-2} [85], corresponding to an efficiency (defined as power output as a percentage of light energy supplied) of 0.25%. This was in a microfluidic device, which allowed the proton permeable membrane to be dispensed with, and cells to be in close proximity to the anode. This value is already within a factor of 2 or 3 of the average power yield from growing biofuel crops [80]. It has been estimated that a maximum achievable power output from BPV devices working in ambient light in areas of the globe with the highest intensities of sunlight might be around 7 W m^{-2} [80]. This would make the devices comparable with conventional commercial solar photovoltaic farms. Although there is clearly a long way to go before anything like this power density is obtained, it is encouraging that Bradley et al. observed a four-fold increase in power density from a BPV containing *Synechocystis* cells with the three terminal oxidases inactivated by mutation [9], and it will be exciting to see if further increases are possible by combining further mutations.

9. An environmental role for extracellular electron transport?

Many cyanobacteria form biofilms [11] and are key organisms in microbial mats, which consist of multilayered sheets of heterogeneous microbial communities which readily exchange metabolites. Electron exchange between microorganisms in mats containing cyanobacteria has been observed [12]. Furthermore, electron output is light dependent, suggesting that cyanobacteria in these mats may export excess photosynthetic electrons to other organisms [12]. Cyanobacteria could also potentially export electrons under low carbon conditions or sudden light changes, if the various electron sinks and photorespiration were insufficient to prevent over-reduction of the thylakoid membrane electron transport chain. It has also been suggested that electron export could act as a form of extracellular signalling between cells [86], although evidence of this occurring in cyanobacteria has not been demonstrated. Some species of cyanobacteria are believed to be able to use quorum sensing, probably *via* acyl homoserine lactones [87]. It would be very exciting if cyanobacteria were also able to communicate, and perhaps also co-operate and even compete, by extracellular electron transport.

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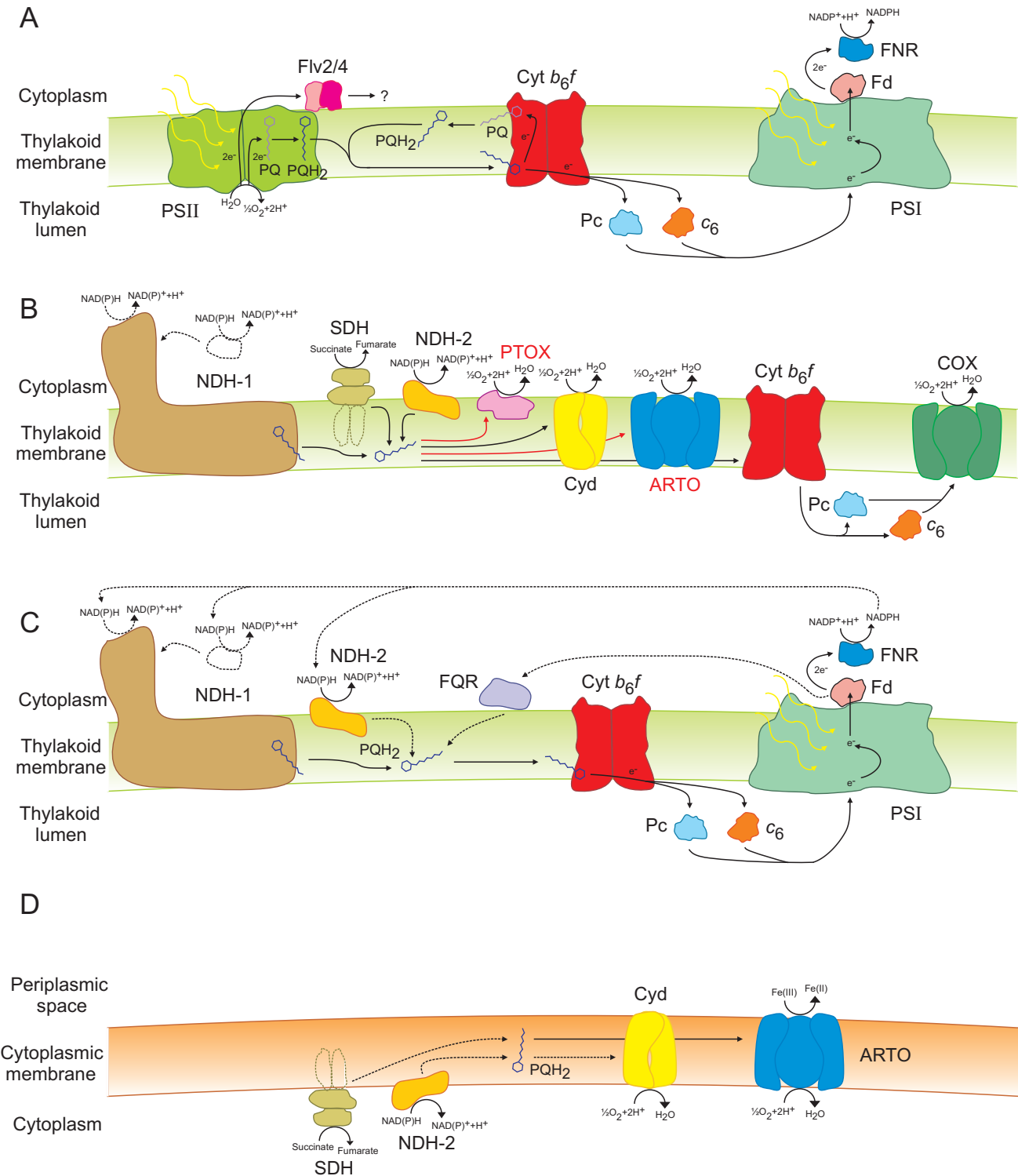


Fig. 1: Schematic diagram of the (A) thylakoid membrane photosynthetic, (B) thylakoid membrane respiratory, (C) thylakoid membrane cyclic and (D) cytoplasmic membrane electron transport chains. Broken lines indicate possible electron transport pathways or proteins not yet verified experimentally. Red lines indicate pathways not present in *Synechocystis*. PSII- Photosystem II, Flv2/4- Flavodiiron 2/4, PQ- plastoquinone, PQH₂- plastoquinol, cyt *b*₆*f*- cytochrome *b*₆*f*, Pc- plastocyanin, Cyt *c*₆- cytochrome *c*₆, PSI- Photosystem I, Fd- ferredoxin, FNR- ferredoxin-NADP⁺-reductase, NDH-1- NAD(P)H dehydrogenase 1, SDH- Succinate dehydrogenase, NDH-2- NAD(P)H dehydrogenase 2, PTOX- Plastid terminal oxidase, Cyd- *bd*-quinol oxidase, ARTO- Alternative respiratory terminal oxidase, COX- cytochrome-*c* oxidase, FQR- Ferredoxin-plastoquinone reductase

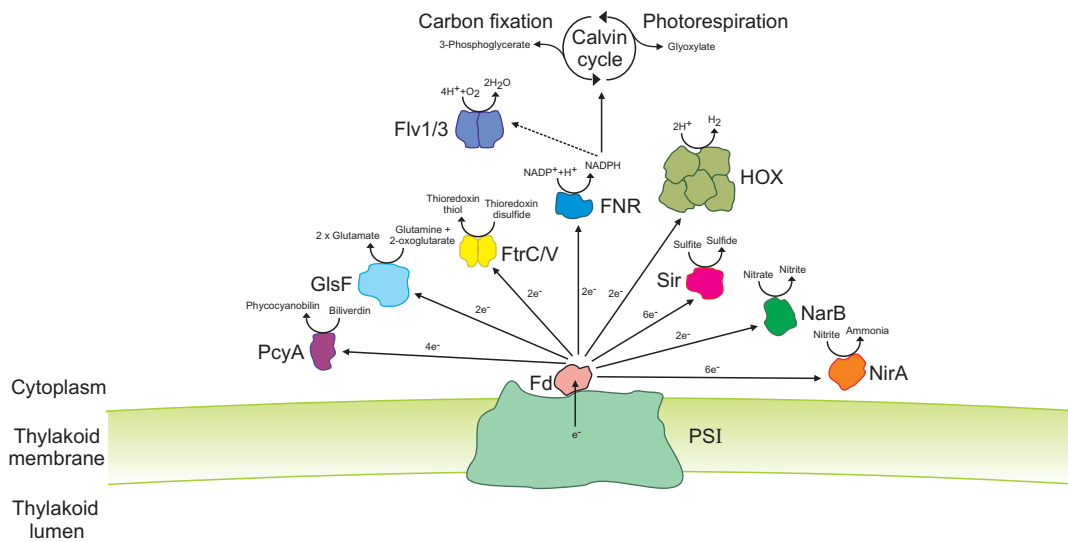


Fig. 2: Schematic diagram of the electron transport chains from ferredoxin and NADPH. PSI- Photosystem I, Fd- ferredoxin, PcyA- Phycocyanobilin:ferredoxin oxidoreductase, GlsF- Ferredoxin-dependent glutamate synthase, FtrC/V- Ferredoxin-thioredoxin reductase, FNR- Ferredoxin-NADP⁺-reductase, Sir- Ferredoxin-sulfite reductase, NarB- Nitrate reductase, NirA- Nitrite reductase, Flv1/3- Flavodiiron 1/3, HOX- bi-directional hydrogenase

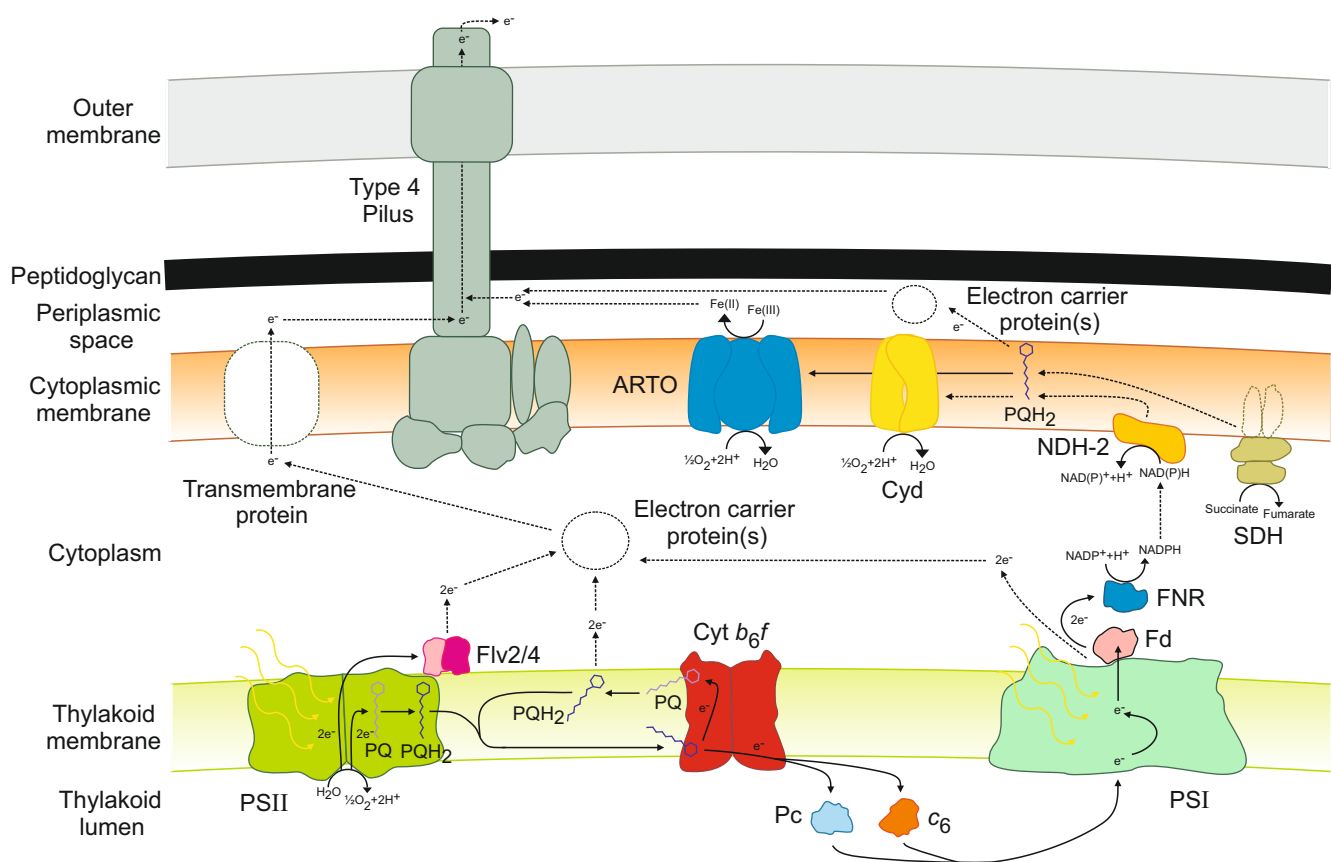


Fig. 3: Schematic diagram of possible electron transport routes between membranes and the exterior. Broken lines indicate possible electron transport pathways or proteins not yet verified experimentally. Red lines indicate pathways not present in *Synechocystis*. PSII- Photosystem II, Flv2/4- Flavodiiron 2/4, PQ- plastoquinone, PQH₂- plastoquinol, cyt b_6f - cytochrome b_6f , Pc- plastocyanin, c_6 - cytochrome c_6 , PSI- Photosystem I, Fd- ferredoxin, FNR- Ferredoxin-NADP⁺-reductase, NDH-1- NAD(P)H dehydrogenase 1, SDH- Succinate dehydrogenase, NDH-2- NAD(P)H dehydrogenase 2, PTOX- Plastid terminal oxidase, Cyd- *bd*-quinol oxidase, ARTO- Alternative respiratory terminal oxidase, COX- cytochrome-*c* oxidase, FQR- Ferredoxin-plastoquinone reductase

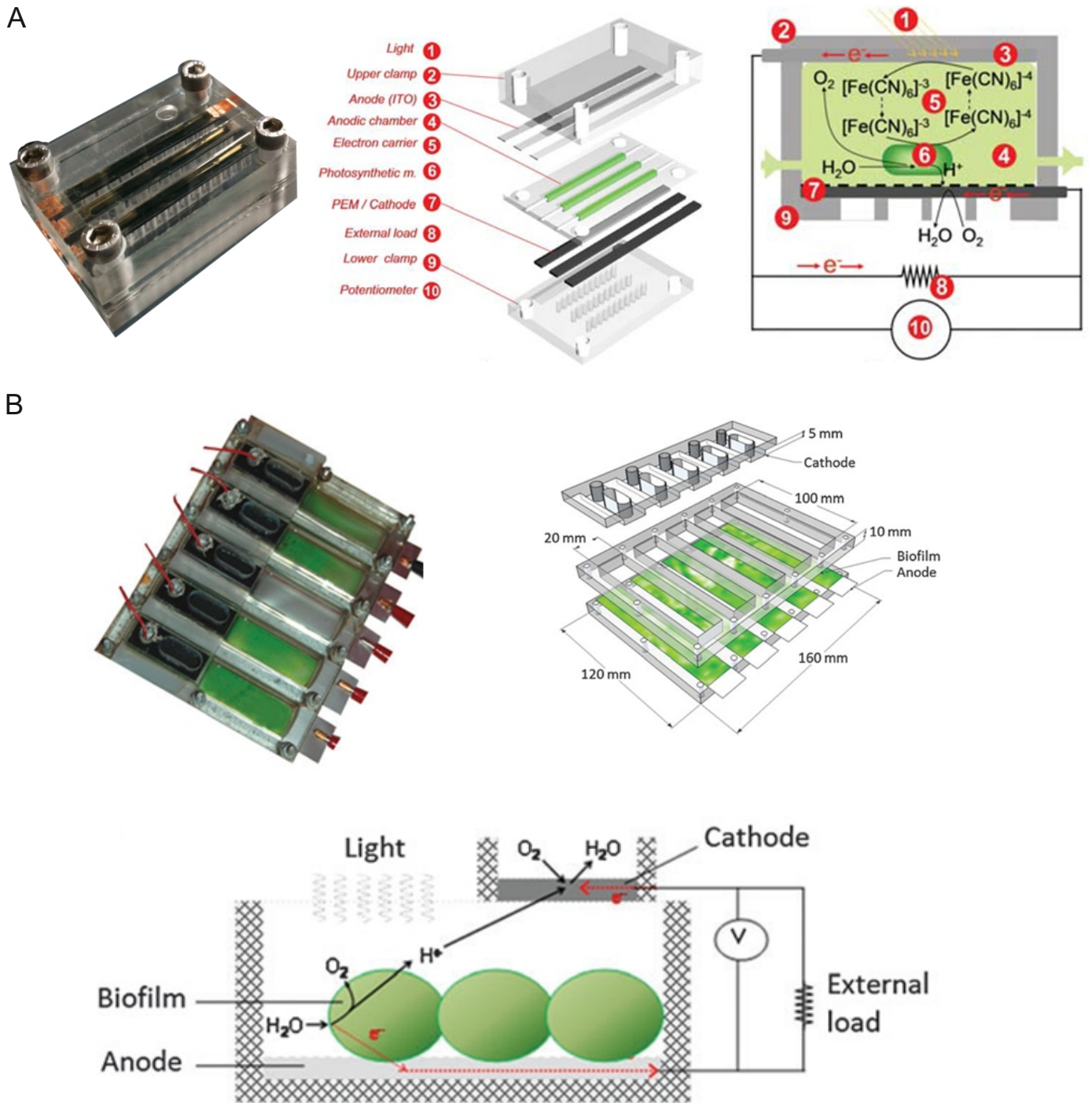


Fig. 4: Biological photovoltaic devices used to generate power from (A) cells in free solution using ferricyanide as an electrode carrier and (B) cells forming a biofilm, which do not require addition of an electron carrier. In both (A) and (B) a photo of a BPV device, a schematic of the various components of the device and a schematic detailing operation of the device, are shown. Adapted from Ref. [9] with permission from The Royal Society of Chemistry.