Journal of Photochemistry and Photobiology B: Biology 104 (2011) 341–347

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology B: Biology

journal homepage: www.elsevier.com/locate/jphotobiol

Short Review

Enzymatic function of cytochrome b_{559} in photosystem II

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ARTICLE INFO

Article history:
Available online 16 February 2011

Keywords:
Cytochrome b_{559}
Photosystem II
Redox potential
Superoxide anion radical

ABSTRACT

Cytochrome b_{559} (cyt b_{559}) is a heme-bridged protein heterodimer in photosystem II (PSII) of all oxygenic photosynthetic organisms. In spite of the fact that cyt b_{559} is strictly required for proper function of PSII, it is not involved in the linear electron transport chain from water to plastoquinone. Instead of that the participation of cyt b_{559} in the cyclic electron transport around PSII has been proposed mainly based on the ability of the heme iron to accept and donate an electron form the electron acceptor and to the electron donor side of PSII, respectively. In addition to the involvement of cyt b_{559} in the cyclic electron transport around PSII, several lines of evidence have been provided on the enzymatic function of cyt b_{559}. The ability of oxygenic photosynthetic organisms to oxidize water and reduce plastoquinone is connected to the formation of reactive oxygen species (ROS) and thus required to develop an effective antioxidant defense system against ROS. The review attempts to summarize a recent progress on the role of cyt b_{559} as oxygen reductase, superoxide reductase, superoxide oxidase and plastoquinol oxidase. The focus is mainly given on the characterization of redox, redox potential and acid-base properties of the heme iron in the putative enzymatic cycles. The possible oxidase and reductase enzymatic activity of cyt b_{559} in protection from photoinhibition is discussed.

Contents

1. Introduction

1.1. Structure of cyt b_{559}

Cytochrome b_{559} (cyt b_{559}) is an intrinsic component of photosystem II (PSII) in all oxygenic photosynthetic organisms such are cyanobacteria, algae and plants [1–3]. It is heme-bridged heterodimer composed of α- and β-subunits, which are encoded by the psbE and psbF genes, respectively. The α- and β-subunits consist of the membrane-spanning α-helix with the amino terminal end oriented to the stroma and the carboxyl end located in the lumen of thylakoid membrane [4,5]. Two histidine residues of the α- and β-subunits are coordinated to the heme iron as the fifth and sixth axial ligands [6,7]. Polypeptide sequence analysis in various types of prokaryotic and eukaryotic organisms showed that histidine position varies with the organisms [2].

The three-dimensional crystal structure of PSII from thermophilic cyanobacteria *Thermosynechococcus elongatus* and *Thermosynechococcus vulcanus* showed that the heme is located on the stromal side of the thylakoid membrane and oriented perpendicu-

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doi:10.1016/j.jphotobiol.2011.02.013

lar to the membrane plane [8–12]. The heme is distanced at about 50 Å from the Q_A site, 25 Å from the Q_B site, 50 Å and 25 Å from pheophytins of D1 ($Pheo_{D1}$) and D2 ($Pheo_{D1}$) proteins, respectively (edge-to-edge distance) [10,11].

1.2. Redox potential properties of cyt b_{559}

The most important property of cyt b_{559} is its unique variable midpoint redox potential [3,13,14]. In comparison to other *b*-type of cytochromes, which have the midpoint redox potential close to 0 mV, cyt b_{559} covers more broad range of the redox potentials. The high-potential (HP) form of cyt b_{559} exhibits the midpoint redox potential in the range from +310 to +400 mV (pH 7), whereas the intermediate-potential (IP) and low-potential (LP) forms range from +125 to +240 mV (pH 7) and −40 to +80 mV (pH 7), respectively [13,15–20].

Several hypotheses have been proposed to explore the existence and significance of various forms of cyt b_{559} in PSII: (1) orientation of the two histidine imidazole rings [6], (2) different hydrophobicity of the heme environment [18,21,22], (3) variation in the nature of the heme coordination [16], (4) protonation state of the imidazole group of histidine [17,23,24], (5) the presence of molecular oxygen around the heme iron [25–27] and (6) the binding of plastoquinone at the Q_C site [28].

It has been proposed that the protein environment around the heme iron in the HP form of cyt b_{559} is more hydrophobic compared to the IP and LP form of cyt b_{559} [21]. Three-dimensional crystal structure provided the evidence that hydrophobic environment around the heme of cyt b_{559} is maintained by the fatty acids of sulfoquinovosyl-diacylglycerol (SQDG4), monogalactosyl-diacylglycerol (MDGD7) and the isoprenoid chain of plastoquinone in the PQ-PQH_2 exchange cavity [12]. In agreement with these considerations, it has been suggested that the binding of plastoquinone at the Q_C site enhances the hydrophobicity around the heme iron and stabilizes HP form of cyt b_{559} [28].

1.3. Redox properties of cyt b_{559}

The heme iron of cyt b_{559} exists in the both reduced and oxidized forms [1–3]. In the freshly prepared sample, the heme iron of HP form of cyt b_{559} is mainly in the reduced state, whereas the heme iron of LP form of cyt b_{559} is solely in the oxidized state [16,17,23,29]. However, the storage of the sample brings about oxidation of the ferrous heme iron in HP form of cyt b_{559}. It is proposed that the heme iron in HP form of cyt b_{559} temporarily remains in the reduced state mainly because of the fact that ferrous heme iron is unable to be autooxidized by molecular oxygen. As the midpoint redox potential of HP form of cyt b_{559} is in the range from +310 to +400 mV (pH 7), the ferrous heme iron of HP form of cyt b_{559} has no power to reduce molecular oxygen ($E_m(O_2/O_2^-)$ = −160 mV, pH 7). The ability of the heme iron of HP form of cyt b_{559} remains temporarily in the reduced state provides a capability to the ferrous heme iron to donate an electron to the PSII electron donor side. By contrast, the unstability of ferrous heme iron of LP form of cyt b_{559} is caused by the autooxidation of ferrous heme iron by molecular oxygen. As the midpoint redox potential of LP form of cyt b_{559} is in the range from −40 to +80 mV (pH 7), the ferrous heme iron of LP form of cyt b_{559} is easily oxidized by molecular oxygen to ferric heme iron. The ferric heme iron of LP form of cyt b_{559} has a capability to accept an electron from the PSII electron acceptor side.

1.4. Acid-base properties of cyt b_{559}

It has been demonstrated that the redox potential properties of cyt b_{559} are controlled by the formation of hydrogen bond between the imidazole group of histidine and the polypeptide backbone [24]. More recently, the protonation of amino acid and formation of the hydrogen bond between the imidazole group of histidine and carbonyl group of α-subunit were demonstrated as an essential requirement for attaining HP form of cyt b_{559} [17,30,31]. It has been shown that the relative content of HP form of cyt b_{559} decreased, when pH is above 7 [17]. It has been concluded that HP form of cyt b_{559} is converted to LP form of cyt b_{559} due to the deprotonation of nitrogen atom of the imidazole group of histidine in HP form of cyt b_{559}. Based on these considerations, the authors proposed that the heme has a single ionizing group that affects the midpoint redox potential of cyt b_{559} with a higher affinity for protons in the reduced form and a lower affinity in the oxidized form [17]. The authors assumed that nitrogen atom of the imidazole group of histidine in the HP form of cyt b_{559} is in the protonated state with hydrogen bond between the imidazole group of histidine and the α-subunit, whereas in the IP form of cyt b_{559} it is in the protonated state with no hydrogen bond between the imidazole group of histidine and the α-subunit. In the LP form of cyt b_{559}, the nitrogen atom of the imidazole group of histidine has been proposed to be in the unprotonated state [17].

1.5. Function of cyt b_{559}

Even though the function of cyt b_{559} has been deeply studied during the last three decades, the exact function of this heme protein is still unclear. The unique presence of cyt b_{559} in all oxygenic photosynthetic organisms (cyanobacteria, algae and plants) is the main structural difference, when compared to anoxygenic photosynthetic organisms (purple bacteria). The presence of cyt b_{559} in oxygenic photosynthetic organisms suggests that molecular oxygen has some role in cyt b_{559} function.

As a plausible explanation for the role of molecular oxygen in cyt b_{559} function is involvement of cyt b_{559} in the splitting of water to molecular oxygen. The role of cyt b_{559} in the stabilization of water-splitting manganese complex during the photoactivation has been described [32–34]. However, the participation of cyt b_{559} in the splitting of water to molecular oxygen seems to be unlikely due to the fact the heme iron is localized at about 50–60 Å from the water-splitting manganese complex (edge-to-edge distance) [10,11]. An alternative hypothesis proposed that cyt b_{559} serves as an intra-membrane oxygen transporter [35]. The hypothesis is based on the replacement of the histidine ligand by molecular oxygen under high concentration of molecular oxygen formed by PSII.

Cytochrome b_{559} has been demonstrated to play an essential role in the early steps of assembly of the PSII complex [36–42]. The authors proposed that cyt b_{559} acts as a redox-controlled nucleation factor that determines the level of PSII within the thylakoid membrane.

The largest focus has been given on the involvement of cyt b_{559} in the cyclic electron transport around PSII as a protective mechanism during the process of photoinhibition [2,3,43]. Barber and De Las Rivas [44] have proposed a dual model, which describes the mechanism of interconversion between LP and HP form of cyt b_{559} during the acceptor- and donor-side photoinhibition of PSII. The ferric heme iron of LP form of cyt b_{559} was proposed to prevent the over reduction of PSII electron acceptor side by acceptance of an electron from the primary electron acceptor pheophytin (Pheo) [44–46]. Buser et al. [47] demonstrated that plastoquinol, which occupies the Q_B site, reduces ferric heme iron of HP form of cyt b_{559}. The ferrous heme iron of HP form of cyt b_{559} was suggested to prevent PSII against donor-side photoinhibition by an electron donation to highly oxidizing $P680^+$ via sequential or branched pathway with β-carotene and chlorophyll z as an intermediate electron carriers [47–52].

Besides the participation of cyt b_{559} in the cyclic electron transport around PSII, the evidence has been afforded on the enzymatic