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Evaluation of photosynthetic electrons derivation by exogenous redox mediators

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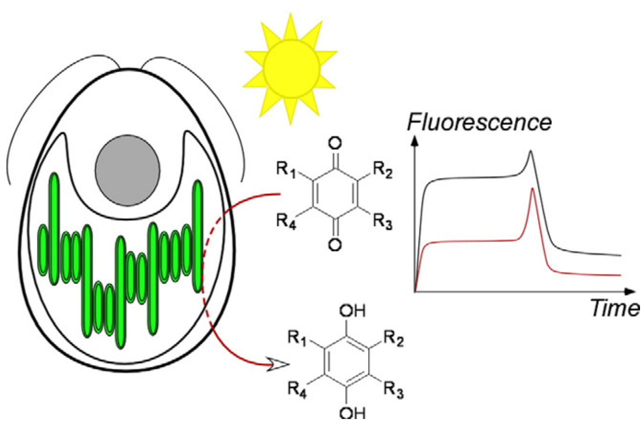
HIGHLIGHTS

- Photosynthetic electrons derivation by exogenous quinones was investigated.
- Fluorescence measurements were achieved with unicellular green algae lacking b_6f complex.
- Data allowed defining and measuring a global parameter characterizing the derivation efficiency.
- The quinone concentration involved in electrons derivation differs from that effectively added.

GRAPHICAL ABSTRACT



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ABSTRACT

Oxygenic photosynthesis is the complex process that occurs in plants or algae by which the energy from the sun is converted into an electrochemical potential that drives the assimilation of carbon dioxide and the synthesis of carbohydrates. Quinones belong to a family of species commonly found in key processes of the Living, like photosynthesis or respiration, in which they act as electron transporters. This makes this class of molecules a popular candidate for biofuel cell and bioenergy applications insofar as they can be used as cargo to ship electrons to an electrode immersed in the cellular suspension. Nevertheless, such electron carriers are mostly selected empirically. This is why we report on a method involving fluorescence measurements to estimate the ability of seven different quinones to accept photosynthetic electrons downstream of photosystem II, the first protein complex in the light-dependent reactions of oxygenic photosynthesis. To this aim we use a mutant of *Chlamydomonas reinhardtii*, a unicellular green alga, impaired in electron downstream of photosystem II and assess the ability of quinones to restore electron flow by fluorescence. In this work, we defined and extracted a “derivation parameter” D that indicates the derivation efficiency of the exogenous quinones investigated. D then allows electing 2,6-dichlorobenzoquinone, 2,5-dichlorobenzoquinone and p-phenylbenzoquinone as good candidates. More particularly, our investigations suggested that other key parameters like the partition of quinones between different cellular compartments and

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their propensity to saturate these various compartments should also be taken into account in the process of selecting exogenous quinones for the purpose of deriving photoelectrons from intact algae.

1. Introduction

Quinones constitute a family of ubiquitous molecules playing a key role in fundamental biological processes. In particular, they act as electron carriers in key mechanisms of Life such as anaerobic or aerobic respiration (menaquinone or ubiquinone) or photosynthesis (plastoquinone) [1]. Indeed, in both cases, the oxidized form Q can act as an electron acceptor readily converted into its doubly-reduced and protonated-form QH_2, which, being neutral and soluble in the membrane can shuttle electrons along the respiratory and photosynthetic chains. This is probably one of the main reasons why quinones are preferably used as exogenous redox mediators in biofuel cells to partially short-circuit the electron transfer involved during photosynthesis [2] (in cyanobacteria [3,4], protoplasts [5], isolated thylakoid membranes [6,7] or isolated photosystem II complexes [8,9]) or microbial metabolism [10,11] and to subsequently shuttle electrons from the biological chain to the man-made electrode surface.

This applies in particular to the extraction of photosynthetic electrons since some quinones appear among electron acceptors of the photosystem II. Along these lines, recent works took benefits of such properties to derive electrons from photosynthesis and thereby obtained promising oxidation current densities [6,8]. Yet, there are many different types of quinones whose structure and physico-chemical properties differ. Until now, the quinones used in experiments aimed at coupling the photosynthetic electron transfer chain to an electrode have been selected empirically. Yet, beyond basic requirements such as appropriate standard potentials of the QH_2/Q couple with respect to the different steps involved during the electron transfer, several other parameters such as solubility, partition between the different phases, reactivity at the electrode surface, to mention a few, are expected to matter as well in determining the overall efficiency of the derivation methodology.

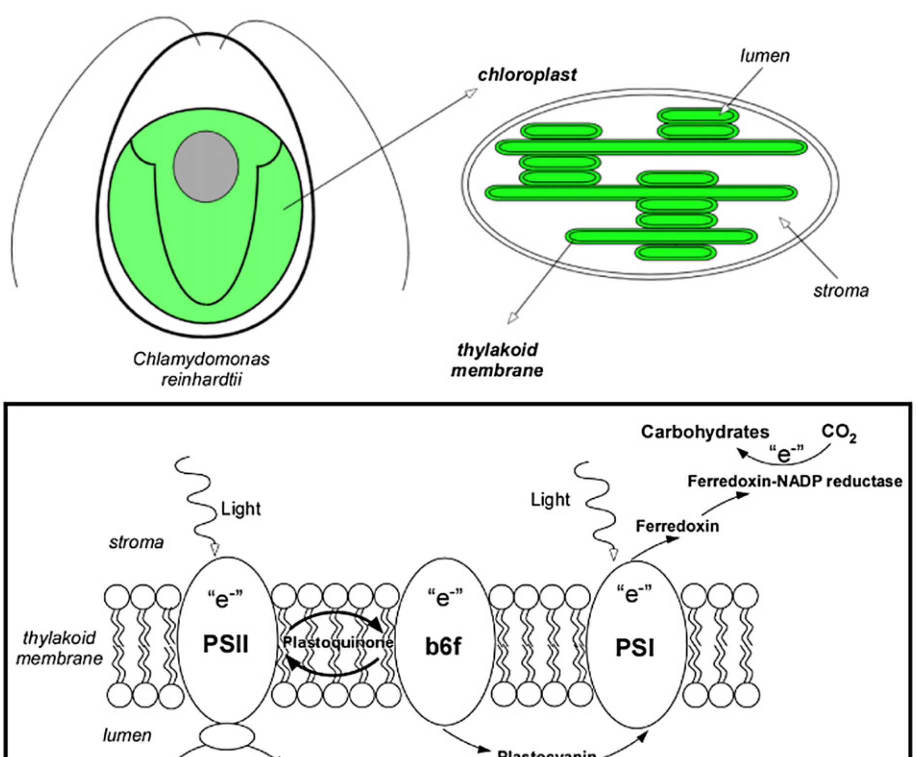
In this work we thus describe a systematic approach based on fluorescence measurements through which we have analyzed the ability of several quinones to extract photosynthetic electrons from chloroplasts and particularly from photosystem II. To do so, an intact biological system (algae containing chloroplasts instead of isolated thylakoid membranes, see Scheme 1) was considered in order to preserve as much as possible the integrity and the physiology of the system.

In this work, a related "derivation parameter" D was determined for estimating the derivation efficiency of the exogenous quinones investigated. Additionally, this work established that other aspects than the redox properties of quinones have to be taken into account, notably the partition of quinones between membranes and other aqueous compartments that could alter the quinone concentration available for the derivation.

2. Experimental section

2.1. Cell culture and preparation

Chlamydomonas reinhardtii Δ*petA* mutant [12] that corresponds to cells lacking cytochrome b_6f was used in this work. The cytochrome b_6f complex is a quinol:plastocyanin oxidoreductase in the absence of which the plastoquinol generated by the light-induced turnovers of



Scheme 1. Representative schemes of the system investigated in this work : from the unicellular alga to the photosynthetic chain within the thylakoid.