

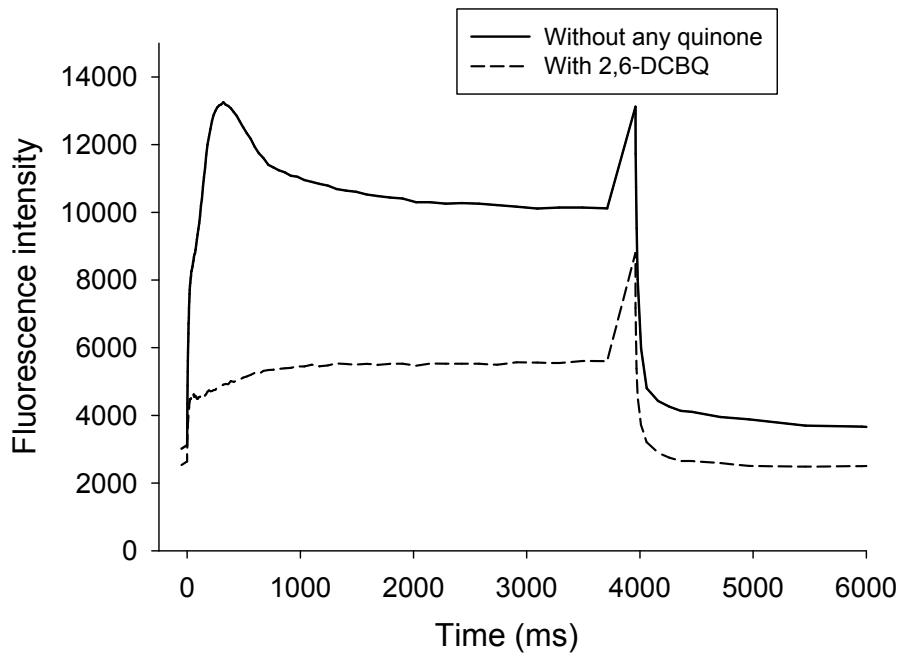
*Supporting Information*

**Mechanism and Analyses for Extracting Photosynthetic Electrons using Exogenous  
Quinones – What Makes a Good Extraction Pathway?**

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### 1. Typical experiment with wild type algae

While experiments of photosynthetic electrons are performed with mutant algae, the same kind of analyses can be achieved on wild-type algae, i.e. with  $b_6f$  complex. In this case, due to a higher endogenous flow if compared to mutant algae, the light intensities used have to be larger to observe a significant variation of the open centers ratio in presence of quinone. Therefore, three light intensities were investigated (340, 800 and 1500  $\mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ). An example of fluorescence measurements is depicted in **Figure S1**.



**Figure S1.** A typical fluorescence experiment demonstrating the photosynthetic electron extraction on wild-type algae by exogenous quinones at  $I^\circ = 800 \mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  without any exogenous quinone (— solid line) or in presence of 2,6-DCBQ (50  $\mu\text{M}$ , --- dashed line).

It has to be emphasized that the whole shapes of the fluorescence curves are quite similar to those obtained with mutant algae. However, without any quinone addition, a transient increase of the fluorescence level is observed before reaching the usual steady-state value. Such behaviour may be related to the fast reduction of the PSII acceptor (that leads to the fluorescence increase) before its subsequent oxidation by downstream electron acceptors in the photosynthetic chain (that decreases the number of closed centers and thus the fluorescence level) until reaching a steady state. The decrease from the initial maximum is likely not observed in the mutant due to the very low endogenous flow. The presence of exogenous quinones as electrons acceptors prevents the initial fluorescence increase.

2. *Supplementary data for the extraction mechanism with 2,6-DCBQ*

a) Reduction of equations 4-7 to Equation 8

The equations to consider are :

$$F(I)[Q_A] + k_{-Q}[QQ_A^-] = (k_{endo} + C_Q k_Q)[Q_A^-] \quad (S1)$$

$$k_{-e}[Q^- Q_A] + k_Q C_Q [Q_A^-] = (k_e + k_{-Q})[QQ_A^-] \quad (S2)$$

$$k_e[QQ_A^-] = (k_{-e} + k_{dQ})[Q^- Q_A] \quad (S3)$$

$$[Q_A] + [Q_A^-] + [QQ_A^-] + [Q^- Q_A] = 1 \quad (S4)$$

(S3) gives to

$$[Q^- Q_A] = \frac{k_e}{(k_{-e} + k_{dQ})} [QQ_A^-] \quad (S5)$$

By inserting (S5) in (S2) one has :

$$\begin{aligned} k_{-e} \frac{k_e}{(k_{-e} + k_{dQ})} [QQ_A^-] + k_Q C_Q [Q_A^-] &= (k_e + k_{-Q}) [QQ_A^-] \\ k_Q C_Q [Q_A^-] &= \left( (k_e + k_{-Q}) - k_{-e} \frac{k_e}{(k_{-e} + k_{dQ})} \right) [QQ_A^-] \\ [QQ_A^-] &= [Q_A^-] \frac{k_Q C_Q (k_{-e} + k_{dQ})}{(k_e + k_{-Q})(k_{-e} + k_{dQ}) - k_e k_{-e}} \\ [QQ_A^-] &= [Q_A^-] \frac{k_Q C_Q (k_{-e} + k_{dQ})}{k_{-Q}(k_{-e} + k_{dQ}) + k_e k_{dQ}} \end{aligned} \quad (S6)$$

By inserting (S6) in (S1) one obtains :

$$\begin{aligned} F(I)[Q_A] + k_{-Q} \frac{k_Q C_Q (k_{-e} + k_{dQ})}{k_{-Q}(k_{-e} + k_{dQ}) + k_e k_{dQ}} [Q_A^-] &= (k_{endo} + C_Q k_Q)[Q_A^-] \\ [Q_A^-] &= F(I) \frac{k_{-Q}(k_{-e} + k_{dQ}) + k_e k_{dQ}}{(k_{endo} + C_Q k_Q)(k_{-Q}(k_{-e} + k_{dQ}) + k_e k_{dQ}) - k_{-Q} k_Q C_Q (k_{-e} + k_{dQ})} [Q_A] \\ [Q_A^-] &= F(I) \frac{k_{-Q}(k_{-e} + k_{dQ}) + k_e k_{dQ}}{k_{endo}(k_{-Q}(k_{-e} + k_{dQ}) + k_e k_{dQ}) + C_Q k_Q k_e k_{dQ}} [Q_A] \end{aligned} \quad (S7)$$

Combining (S7) to (S6) gives :

$$[QQ_A^-] = F(I) \frac{k_Q C_Q (k_{-e} + k_{dQ})}{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_e k_{dQ}) + C_Q k_Q k_e k_{dQ}} [Q_A] \quad (S8)$$

Combining (S8) to (S5) gives :

$$[Q^- Q_A] = F(I) \frac{k_e k_Q C_Q}{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_e k_{dQ}) + C_Q k_Q k_e k_{dQ}} [Q_A] \quad (S9)$$

Inserting (S7), (S8) and (S9) to (S4) gives:

$$\begin{aligned} & [Q_A] + F(I) \frac{k_{-Q} (k_{-e} + k_{dQ}) + k_e k_{dQ}}{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_e k_{dQ}) + C_Q k_Q k_e k_{dQ}} [Q_A] \\ & + F(I) \frac{k_Q C_Q (k_{-e} + k_{dQ})}{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_e k_{dQ}) + C_Q k_Q k_e k_{dQ}} [Q_A] \\ & + F(I) \frac{k_e k_Q C_Q}{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_e k_{dQ}) + C_Q k_Q k_e k_{dQ}} [Q_A] = 1 \\ & \frac{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_e k_{dQ}) + C_Q k_Q k_e k_{dQ}}{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_e k_{dQ}) + C_Q k_Q k_e k_{dQ}} + \\ & \frac{F(I) (k_{-Q} (k_{-e} + k_{dQ}) + k_e k_{dQ}) + F(I) k_Q C_Q (k_{-e} + k_{dQ}) + F(I) k_e k_Q C_Q}{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_e k_{dQ}) + C_Q k_Q k_e k_{dQ}} = \frac{1}{[Q_A]} \\ & \frac{(k_{endo} + F(I)) (k_{-Q} (k_{-e} + k_{dQ}) + k_e k_{dQ}) + C_Q k_Q (k_e k_{dQ} + F(I) (k_{-e} + k_{dQ} + k_e))}{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_e k_{dQ}) + C_Q k_Q k_e k_{dQ}} = \frac{1}{[Q_A]} \quad (S10) \end{aligned}$$

One finally has :

$$\Phi = [Q_A] = \frac{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_{dQ} k_e) + k_Q k_{dQ} k_e C_Q}{(k_{endo} + F(I)) (k_{-Q} (k_{-e} + k_{dQ}) + k_{dQ} k_e) + k_Q C_Q (F(I) (k_e + k_{-e} + k_{dQ}) + k_{dQ} k_e)} \quad (S11)$$

This equation well corresponds to equation (8) in the text.

b) Additional validation of the mechanism

As demonstrated in the article, the open centers ratio  $\Phi$  can be defined according to two equations. Equation (S12) is deduced from the experimental data :

$$\Phi = \frac{\Phi_0 \frac{\Phi_\infty}{\rho_0} + \Phi_\infty C_Q}{\frac{\Phi_\infty}{\rho_0} + C_Q} \quad (\text{S12})$$

Equation (S11) results from the extraction mechanism considered and demonstrated above:

$$\Phi = \frac{k_{endo}(k_{-Q}(k_{-e} + k_{dQ}) + k_{dQ}k_e) + k_Q k_{dQ} k_e C_Q}{(k_{endo} + F(I))(k_{-Q}(k_{-e} + k_{dQ}) + k_{dQ}k_e) + k_Q C_Q (F(I)(k_e + k_{-e} + k_{dQ}) + k_{dQ}k_e)} \quad (\text{S11})$$

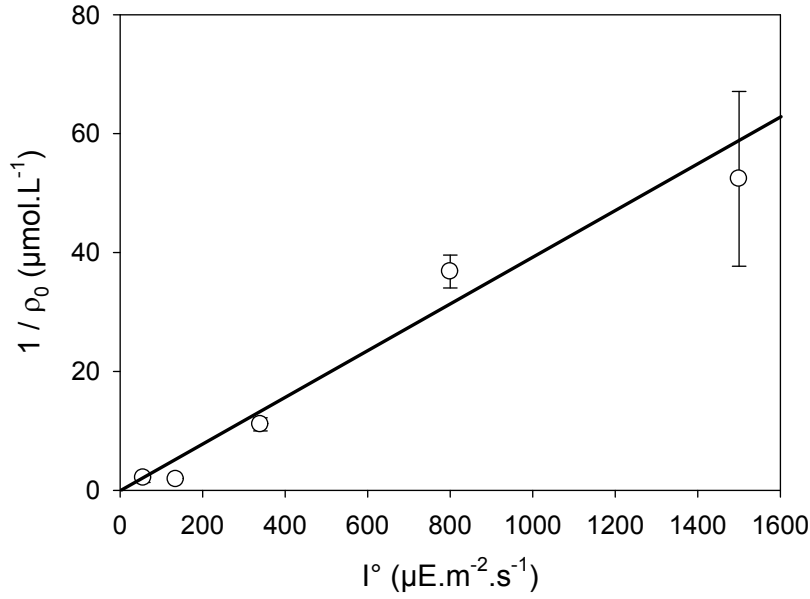
It thus helps to extract peculiar quantities as the initial slope of the exogenous flow part of the  $\Phi = f(C_Q)$  curve ( $\rho_0$ ).

$$\rho_0 = \frac{k_Q k_{dQ} k_e}{(k_{endo} + F(I))(k_{-Q}(k_{-e} + k_{dQ}) + k_{dQ}k_e)} \quad (\text{S13})$$

Thus, it leads to:

$$\frac{1}{\rho_0} = \frac{k_{endo}(k_{-Q}(k_{-e} + k_{dQ}) + k_{dQ}k_e)}{k_Q k_{dQ} k_e} + \frac{(k_{-Q}(k_{-e} + k_{dQ}) + k_{dQ}k_e)}{k_Q k_{dQ} k_e} F(I) \quad (\text{S14})$$

**Figure S2** thus shows a linear dependence between  $1/\rho_0$  and  $I^\circ$  values and consequently strengthening the mechanism considered in the present work.



**Figure S2.** Inverse of  $\rho_0$  (initial slope of the  $\Phi = f(C_Q)$  curves described in **Figure 4**) as a function of the incident light intensity for mutant algae.

### 3. Zone diagrams : derivation of equations (15), (16) and (17)

Equation (2) in the article (or (S12) in the supporting information) gives access to the open centers ratio and can be written as according to :

$$\Phi = \frac{\Phi_0 \frac{\Phi_\infty}{\rho_0} + \Phi_\infty C_Q}{\frac{\Phi_\infty}{\rho_0} + C_Q} = \frac{\Phi_0 + \rho_0 C_Q}{1 + \frac{\rho_0}{\Phi_\infty} C_Q} \quad (\text{S12})$$

Therefore the left part of the numerator is related to the endogenous flux ( $\Phi_0$ ) and the right part to the  $C_Q$ -dependent extraction by the exogenous flux ( $\rho_0 C_Q$ ). The ratio between the right and left parts of the numerator thus corresponds to the ratio (named  $\alpha$ ) between exogenous and endogenous fluxes. Due to the extraction mechanism considered, equation (2) corresponds to equation (8) in the article (or (S11) in the supporting information):

$$\Phi = \frac{k_{endo}(k_{-Q}(k_{-e} + k_{dQ}) + k_{dQ}k_e) + k_Q k_{dQ} k_e C_Q}{(k_{endo} + F(I))(k_{-Q}(k_{-e} + k_{dQ}) + k_{dQ}k_e) + k_Q C_Q (F(I)(k_e + k_{-e} + k_{dQ}) + k_{dQ}k_e)} \quad (\text{S11})$$

Therefore, one obtains the following equation (numbered 15 in the article):

$$\alpha = \frac{k_Q k_{dQ} k_e C_Q}{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_{dQ} k_e)} \quad (\text{S15})$$

Moreover, if considering equation (S11), one has:

$$\Phi = \frac{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_{dQ} k_e) \left( 1 + \frac{k_Q k_{dQ} k_e C_Q}{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_{dQ} k_e)} \right)}{(k_{-Q} (k_{-e} + k_{dQ}) + k_{dQ} k_e) \left( (k_{endo} + F(I)) + \frac{k_Q C_Q (F(I) (k_e + k_{-e} + k_{dQ}) + k_{dQ} k_e)}{(k_{-Q} (k_{-e} + k_{dQ}) + k_{dQ} k_e)} \right)} \quad (\text{S16})$$

By inserting equation (S15) in (S16), one gets :

$$\Phi = \frac{k_{endo} (1 + \alpha)}{\left( (k_{endo} + F(I)) + \frac{k_Q C_Q (F(I) (k_e + k_{-e} + k_{dQ}) + k_{dQ} k_e)}{(k_{-Q} (k_{-e} + k_{dQ}) + k_{dQ} k_e)} \right)} \quad (\text{S17})$$

Furthermore, equation (S17) becomes :

$$\Phi = \frac{k_{endo} (1 + \alpha)}{\left( (k_{endo} + F(I)) + \frac{k_Q k_{dQ} k_e C_Q}{k_{endo} (k_{-Q} (k_{-e} + k_{dQ}) + k_{dQ} k_e)} k_{endo} \left( \frac{F(I) (k_e + k_{-e} + k_{dQ})}{k_{dQ} k_e} + 1 \right) \right)} \quad (\text{S18})$$

By inserting equation (S15) in (S18), one gets equation (S19) that corresponds to equation (16) in the manuscript:

$$\Phi = \frac{k_{endo} (1 + \alpha)}{(k_{endo} + F(I)) + \alpha k_{endo} \left( \frac{F(I) (k_e + k_{-e} + k_{dQ})}{k_{dQ} k_e} + 1 \right)} \quad (\text{S19})$$

The exogenous flux is due to the extraction by the exogenous quinone Q and can be rate-determined by the exogenous quinone Q insertion within the Q<sub>B</sub> pocket or the subsequent electron transfer between Q and Q<sub>A</sub> (the free quinone concentration term of the denominator). The prevalence of each is expected to play a role on the denominator of equation (S11). Indeed, according to the model, if exogenous flow prevails, a mass transfer controlled process should be quinone concentration dependent while it will be not the case if the process is rate-

determined by the electron transfer step. According to equation (S11), if exogenous flow prevails, one has :

$$\Phi = \frac{k_Q k_{dQ} k_e C_Q}{(k_{endo} + F(I))(k_{-Q}(k_{-e} + k_{dQ}) + k_{dQ} k_e) + k_Q C_Q (F(I)(k_e + k_{-e} + k_{dQ}) + k_{dQ} k_e)} \quad (S20)$$

Therefore, the  $C_Q$  dependence of  $\Phi$  within the exogenous flow expression will be related to the comparison between  $k_Q C_Q (F(I)(k_e + k_{-e} + k_{dQ}) + k_{dQ} k_e)$  and  $(k_{endo} + F(I))(k_{-Q}(k_{-e} + k_{dQ}) + k_{dQ} k_e)$ . This consists in fact to compare  $\alpha k_{endo} (\frac{F(I)(k_e + k_{-e} + k_{dQ})}{k_{dQ} k_e} + 1)$  and  $k_{endo} + F(I)$  in equation (S19). This is why a new parameter (named  $\beta$ ) can be defined :

$$\beta = \frac{k_{endo} + F(I)}{k_{endo} (\frac{F(I)(k_e + k_{-e} + k_{dQ})}{k_{dQ} k_e} + 1)} \quad (S21)$$

$\beta$  is thus a specific  $\alpha$  value corresponding to the equality between quinone insertion and electron transfer rates. Therefore, the electron transfer rate will be higher than the insertion if  $\alpha \ll \beta$ .

Moreover, equation (S19) can be written as:

$$\Phi = \frac{k_{endo} (1 + \alpha)}{(k_{endo} + F(I)) \left( 1 + \frac{\alpha k_{endo}}{(k_{endo} + F(I))} \left( \frac{F(I)(k_e + k_{-e} + k_{dQ})}{k_{dQ} k_e} + 1 \right) \right)} \quad (S22)$$

Inserting equation (S21) in equation (S22) gives:

$$\Phi = \frac{k_{endo} (1 + \alpha)}{(k_{endo} + F(I)) \left( 1 + \frac{\alpha}{\beta} \right)} = \frac{k_{endo} \beta (1 + \alpha)}{(k_{endo} + F(I)) (\beta + \alpha)} \quad (S23)$$

Finally, by inserting the  $\Phi_0$  expression (equation (9) in the text) in equation (S23), one obtains:

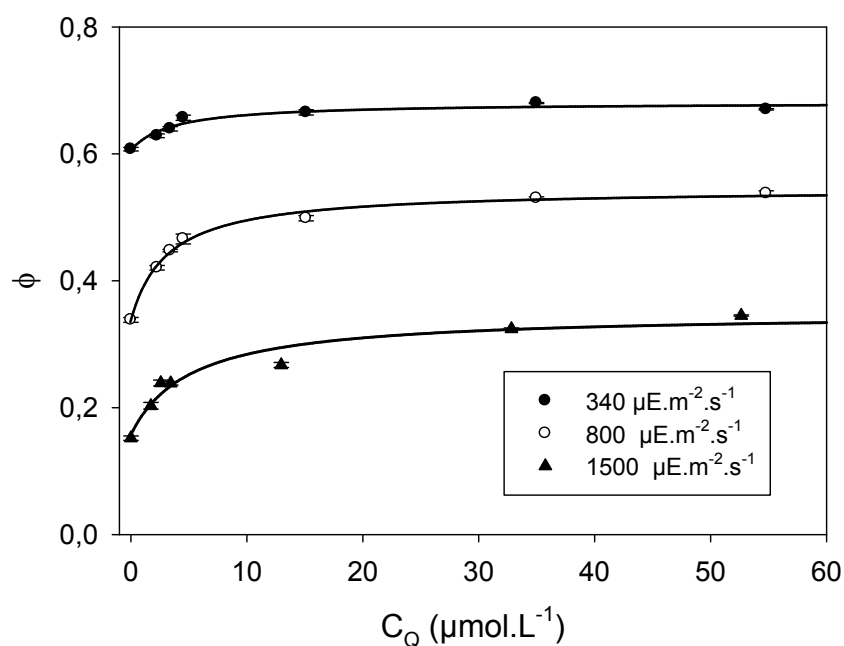
$$\Phi = \Phi_0 \frac{(1 + \alpha) \beta}{\alpha + \beta} \quad (S24)$$

Equation (S24) corresponds to equation (18) in the manuscript.



4. Data treatment and analysis of the electron extraction on wild-type algae with exogenous quinones

Experiments concerning the effect of 2,6-DCBQ concentration were achieved with wild-type algae. As mentioned above, three light incident flows were considered. The results are depicted in **Figure S3**.



**Figure S3.** Open centers ratio  $\Phi$  of a wild-type algae population as a function of the available 2,6-DCBQ concentration  $C_Q$  for three light intensities (340, 800 and 1500  $\mu\text{E.m}^{-2}.\text{s}^{-1}$ ).

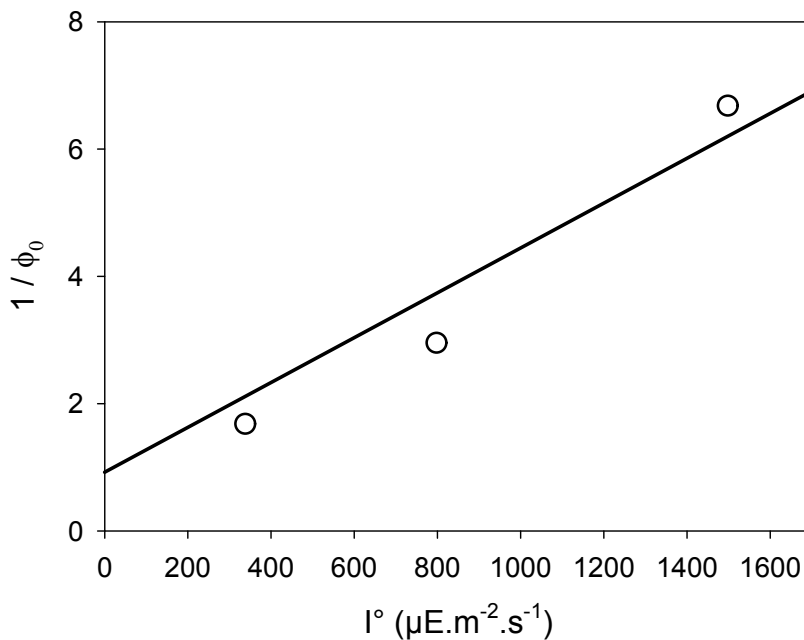
Hence, the  $\Phi_0$ ,  $\Phi_\infty$  and  $\rho_0$  values can be extracted and are summarized in **Table T1**.

$I^\circ$ ( $\mu\text{E.m}^{-2}.\text{s}^{-1}$ )	$\Phi_\infty$	$\rho_0$ ( $\mu\text{mol}^{-1}.\text{L}$ )	$\Phi_0$
1500	$0.37 \pm 0.01$	$(5.2 \pm 2.0).10^{-2}$	$0.15 \pm 0.01$
800	$0.52 \pm 0.01$	$(17 \pm 2).10^{-2}$	$0.34 \pm 0.01$
340	$0.68 \pm 0.01$	$(21 \pm 15).10^{-2}$	$0.60 \pm 0.02$

**Table T1.** Effect of the light intensity  $I^\circ$  on the extracted values reflecting the electron extraction induced by the exogenous 2,6-DCBQ addition ( $\Phi_\infty$  and  $\rho_0$ ) and the open centers ratio in absence of exogenous quinones ( $\Phi_0$ ) for wild-type algae.

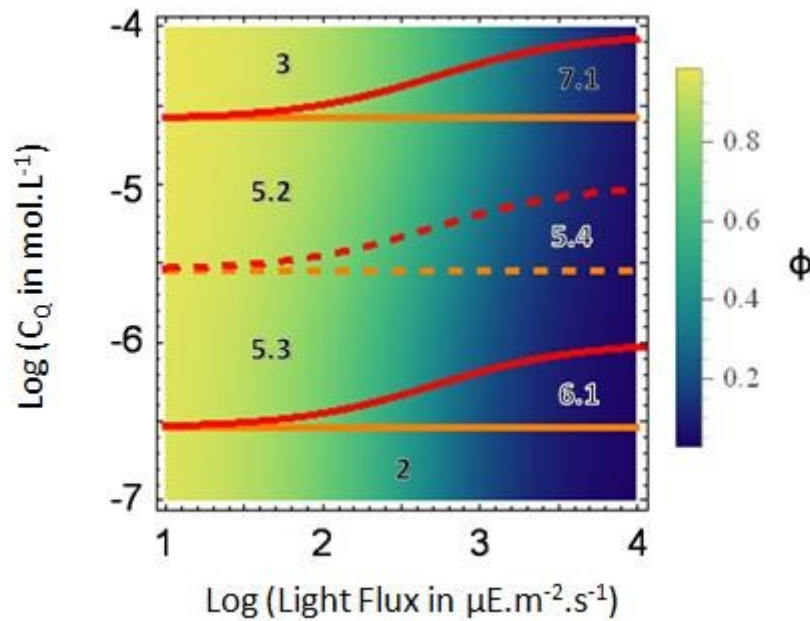
It is worth mentioning that the same trends for  $\Phi_0$ ,  $\Phi_\infty$  and  $\rho_0$  are observed in the case of wild-type algae in presence of exogenous 2,6-DCBQ if compared to mutant algae. It thus means that the inverted region can not be reached in this case although the endogenous flow is larger in wild-type algae. Particularly, it has to be emphasized that the  $\Phi_0$  values are significantly higher for wild-type algae in accordance with a significant endogenous flow that already acts like an electron extraction pathway from the reduced state of PSII. It also supports outstandingly the mechanism suggested in the text because Equation (S7) is experimentally verified (see **Figure S4**):

$$\frac{1}{\Phi_0} = 1 + \frac{F(I)}{k_{endo}} \quad (\text{S25})$$



**Figure S4.** Inverse of the open reaction centers ratio in absence of exogenous quinones ( $1/\Phi_0$ ) as a function of the incident light intensity for wild-type algae ( $1/\Phi_0 = 1 + 0.00364I^\circ$ ;  $R^2 = 0.99$ ).

The knowledge of these values as an incident light function let us to draw the same kind of zone diagram than for the mutant (see **Figure S5**).



**Figure S5.** Zone diagram of the open center ratio as a function of quinone concentration  $C_Q$  and incident light  $I^0$ . Orange solid lines correspond to frontiers from which one of the fluxes can be neglected (within 10%). Red solid lines correspond to frontiers from which fluxes or kinetics can be simplified (by neglecting one of the fluxes or one of the kinetics). Dashed lines allow one to define sub-zones. The dashed orange line corresponds to equal endogenous and exogenous fluxes. The red dashed line is related to conditions for which the exogenous flux is both rate-determined by electron transfer and the quinone arrival.

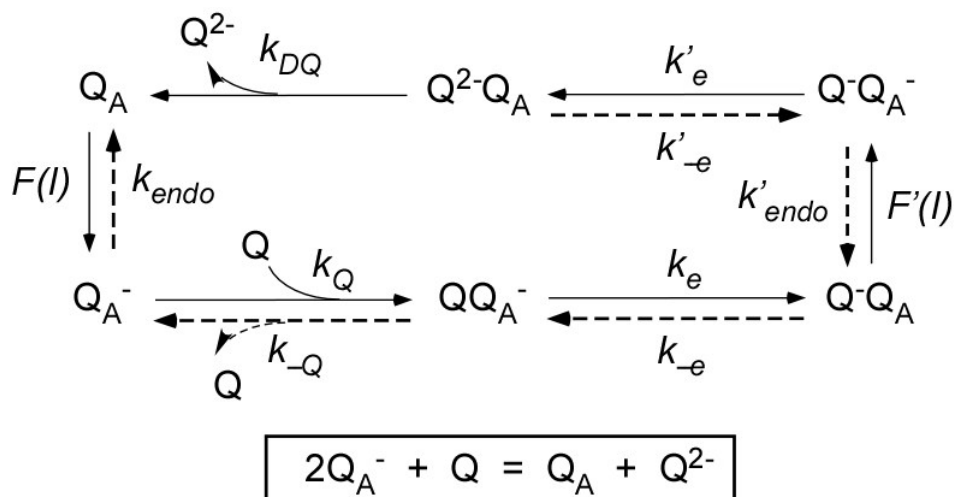
Remarkably all zones of open site ratio control described with the mutant in the article are still obtained for the wild type (2, 3, 5, 6, 7). However, this is not the case for all the expected sub-zones in which both flows (cf zones 6.1 and 6.2) or both kinetics (cf zones 7.1 and 7.2) have to be considered together. Indeed, in the wild-type case, the zones 6.2 and 7.2 disappeared due to the increase of the endogenous flow. The fact that zone 6.2 lacks means that when the electron transfer kinetics limitation can be neglected due to a very low quinone concentration, endogenous flow is always (with this quinone/algae system) higher than exogenous one, while the latter can remain significant. Similarly, the fact that zone 7.2 lacks means that, when quinone concentration is so high that endogenous flow can be neglected, electron extraction is always more limited by electron transfer kinetics than by quinone insertion, while the latter cannot always be considered as infinitely fast. Therefore, such a zone diagram shows that it will be difficult to drastically increase the open site ratio without

decreasing the endogenous flow with the 2,6-DCBQ-WT system. Hence, using wild type algae under conditions corresponding to zones 6.2 or 7.2 (in particular to work without organic matter in solution) and by assuming a term can be neglected in a sum if weighing lower than 10% of the other term, the appropriate exogenous quinone should lead to a  $(QQ_A^-)$  state able to release its charge at least 10 times faster than  $(Q_A^-)$  with endogenous flow. It means that  $\beta$  must be  $>10$  in order to observe this zone. In this case of the 2,6-DCBQ on wild type, a  $\beta$  value of 3 is obtained. This is why the zones 6.2 and 7.2 are not observed here. Despite its high electron transfer rate compare to other quinones previously studied, using 2,6-DCBQ with a wild type favors conditions too close to the inverted region.

### 5. Two electrons mechanism for the extraction by exogenous quinones

#### a. Description of the mechanism – Extraction of $(\Phi; \Phi_\infty; \Phi_0; \rho_0)$ parameters

The fact that quinones correspond to a bi-electronic system may lead to envision a two electrons mechanism for the extraction considered in the text. Because chloroquinones are known to have more affinity for the  $Q_B$  pocket than for the plastoquinone pool the following mechanism can be suggested.



Briefly, the first steps of this mechanism can be compared to those of the simple one described in the text. Firstly, the exogenous quinone  $Q$  binds into  $Q_B$  pocket and is followed by a first electron transfer step. However, the  $Q^-Q_A$  state formation is now followed by a second irradiation step which will reduce  $Q_A$  and eventually lead to the full reduction of the exogenous quinone.

Applying the quasi steady state approximation to intermediate states and summing all states in which  $Q_A$  is oxidized will lead to open centers ratio according to :

$$\Phi = \frac{k_{endo}B + Ak_Q C_Q}{(k_{endo} + F(I))B + k_Q(C_1 + C_2)C_Q} \quad (S26)$$

With :

$$B = k'_{-e} k_{-e} k'_{endo} k_{-Q} + k_{DQ} F'(I) k'_e (k_{-Q} + k_e) + k_{-Q} k_{-e} (k'_{endo} + k'_e)$$

$$A = k_e (k_{DQ} F'(I) k'_e + F(I) (F'(I) k'_e + k'_{endo} (k'_{-e} + k_{DQ}) + k'_e k_{DQ}))$$

$$C_1 = F(I) (F'(I) (k_e (k'_e + k_{DQ} + k'_{-e}) + k'_e k_{DQ}))$$

$$C_2 = F(I) (k_{-e} + k_e) (k'_{endo} (k'_{-e} + k_{DQ}) + k'_e k_{DQ}) + k_e F'(I) k'_e k_{DQ}$$

In comparison with the simple one electron mechanism, a similar dependence of  $\Phi$  with the quinone concentration is obtained.

Moreover the three parameters extracted from the experiments can be calculated from equation (S11) :

$$\Phi_0 = \frac{k_{endo}}{k_{endo} + F(I)} \quad (S27)$$

$$\Phi_\infty = \frac{A}{C_1 + C_2} \quad (S28)$$

$$\rho_0 = \frac{Ak_Q}{(k_{endo} + F(I))B} \quad (S29)$$

Expectedly the initial open centers ratio value (equation (S3)) is the same regardless of the applied mechanism (one electron or two electrons). The comparison for the  $\Phi_\infty$  and  $\rho_0$  parameters is more complicated and will be detailed below.

#### b. Analysis of the $\Phi_\infty$ parameter

According to equation (S28), one has:

$$\frac{1}{\Phi_\infty} = 1 + \frac{F'(I) (k_e (k_{DQ} + k'_{-e}) + k'_e k_{DQ}) + k_{-e} (k'_{endo} (k'_{-e} + k_{DQ}) + k'_e k_{DQ})}{k_e F'(I) k'_e + k'_{endo} k_e (k'_{-e} + k_{DQ}) + k_e k'_e k_{DQ} (1 + \frac{F'(I)}{F(I)})} \quad (S30)$$

Experimental results (see **Figure 7**) showed that the  $1/\Phi_\infty = f(I^\circ)$  correspond to a linear relationship with an intercept value of 1.

Assuming that both  $F(I)$  and  $F'(I)$  are proportional to incident light flow  $I^\circ$ , the experimental relationship between  $1/\Phi_\infty$  and  $I^\circ$  means that the backward first electron transfer step can be neglected and that :

$$F'(I) \ll k_{DQ} \left(1 + \frac{F'(I)}{F(I)} + \frac{k'_{endo}}{k'_e}\right) + \frac{k'_{endo} k'_{-e}}{k'_e}$$

Therefore one obtains:

$$\frac{1}{\Phi_\infty} = 1 + \frac{F'(I)(k_e(k_{DQ} + k'_{-e}) + k'_e k_{DQ})}{k'_{endo} k_e (k'_{-e} + k_{DQ}) + k_e k'_e k_{DQ} \left(1 + \frac{F'(I)}{F(I)}\right)} \quad (\text{S31})$$

The observed dependence of  $1/\Phi_\infty$  with quinone midpoint potential (see **Figure 8**) suggests it should be controlled by electron transfer rate kinetics. Indeed, assuming  $k_{DQ} \gg k'_{-e}$  (according to the plastoquinone mechanism) and  $k'_{endo} \ll k'_e$  (due to a  $Q_B$  pocket filled by the exogenous quinone, all possible endogenous flows -plastoquinones, PETOX- are thus prevented except by charge recombination),  $1/\Phi_\infty$  can be rewritten as :

$$\frac{1}{\Phi_\infty} = 1 + \frac{F'(I)F(I)}{F'(I) + F(I)} \frac{k_e + k'_{-e}}{k_e k'_{-e}} \quad (\text{S32})$$

Equation (S32) evidenced that  $1/\Phi_\infty$  depends on the ratio of a global rate constant of two irradiation steps by a global rate constant of two electron transfer steps. From a mathematical point of view, it is worth to mention that the one electron mechanism globally gave a similar dependence between  $1/\Phi_\infty$  and the global incident light flow.

### c. Analysis of the $\rho_0$ parameter

Using the same hypotheses than described above,  $\rho_0$  can be expressed as :

$$\rho_0 = \frac{\Phi_0 F(I)}{k_{endo} F'(I)} \frac{k_e k_Q (k_{DQ} k'_e \left(1 + \frac{F'(I)}{F(I)}\right) + k'_{endo} (k'_{-e} + k_{dQ}))}{k'_e k_{DQ} (k_{-Q} + k_e)} \quad (\text{S33})$$

As in the one electron mechanism, the relation of proportionality between  $\rho_0$  and  $\Phi_0$  is still deduced.

d. One electron vs two electron mechanism ?

The two electrons mechanism also allows one to rationalize the experimental results and the dependence of the ( $\Phi$ ;  $\Phi_\infty$ ;  $\Phi_0$ ;  $\rho_0$ ) parameters with the quinone concentration or the incident light flow. However, it has to be emphasized that, despite a more simple formalism, the one electron mechanism is also consistent with experimental results. It therefore means that the expected complications resulting from the two electrons mechanism cannot be detected in the range of experimental conditions and sensitivity reported in this work.

It should be pointed out that the simple mechanism also allowed us to determine conditions in which the extraction was controlled by the quinone insertion (rate proportional to quinone concentration) or some electron transfer steps (whose rate does not depend on quinone concentration). Regardless of the mechanism, the similar dependence means that, in the range of the experimental conditions envisioned here, the built zone diagrams are not affected. The general zone diagram and its further conclusions remain not altered, even if the  $\alpha$  and  $\beta$  expressions obviously differ (see equations (S34) and (S35)).

$$\alpha = \frac{C_Q k_Q A}{k_{endo} B} \quad (S34)$$

$$\beta = \frac{k_{endo} + F(I)}{k_{endo} + k_{endo} \frac{C_1}{A}} \quad (S35)$$

The transition between normal and inverted zones still occurs for a  $\beta$  value equal to 1. In this case, the following parameter P is defined as :

$$P = \frac{k_{endo} (k_e (k'_e + k_{DQ} + k'_{-e}) + (k'_e k_{DQ}))}{k_e k'_e k_{DQ} (1 + \frac{F(I)}{F'(I)}) + \frac{F(I)}{F'(I)} k_e k'_{endo} (k'_{-e} + k_{DQ})} = 1 \quad (S36)$$

Assuming that  $k'_{endo} \ll k'_e$  (see above) and  $k_{DQ} \gg k'_e + k'_{-e}$  (according to the plastoquinone reduction), equation (S36) becomes :

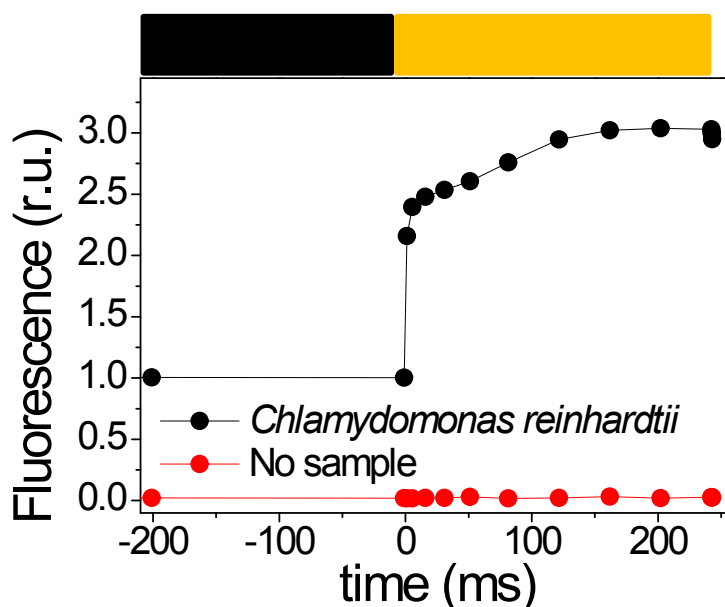
$$P = k_{endo} \frac{k_e + k'_e}{k_e k'_e} \frac{F'(I)}{F(I) + F'(I)} = 1 \quad (\text{S37})$$

As in the simple mechanism, this P parameter still helps to compare endogenous flow and electron transfer. In the general case, it corresponds to the ratio between the  $Q_A^-$  and  $QQ_A^-$  oxidation rate constants. As an example, a P value less than 1 corresponds to  $\beta > 1$ ). Therefore,  $QQ_A^-$  release its charge faster than  $Q_A^-$  that corresponds to a system work in a normal region in accordance with  $\beta > 1$ .

#### 6. Two electrons mechanism for the extraction by exogenous quinones

As mentioned in the article, the saturation pulse method is used to calculate the open centers ratio that is further modeled by an appropriate mechanism.

Such a pulse ( $\sim$  a few thousand  $\mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$  during 250 ms) corresponds to saturation conditions required to fully close the centers (and lead to the fluorescence value  $F_{\text{max}}$ ). In our case (**Figure S6**), the following experiment (in which the fluorescence is monitored during the pulse) shows that saturation readily occurs owing to the pulse. Indeed, the light intensity and pulse time course are appropriate since a fluorescence saturated level is already reached at around 180 ms after the pulse was triggered.



**Figure S6.** Real time fluorescence monitoring during the saturated pulse application ( $5000 \mu\text{E}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ; 250 ms). The saturation is reached before the end of the pulse (that arbitrary starts at 0 in the graph).