Supporting Information

Role of Missing Carotenoid in Reducing the Fluorescence of Single Monomeric Photosystem II Core Complexes

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S1

This algorithm is used to determine the wavelength position of the most intense fluorescence emission and its full width at half-maximum (fwhm). In each data set, a constant offset due to the CCD camera is subtracted, and the wavelength position of the most intense contribution is determined. Starting from the maximum position, the width is determined where the intensity reaches half of the maximum value. The results are shown as 2D scattering plot in Figure 2b in the main text.

S2

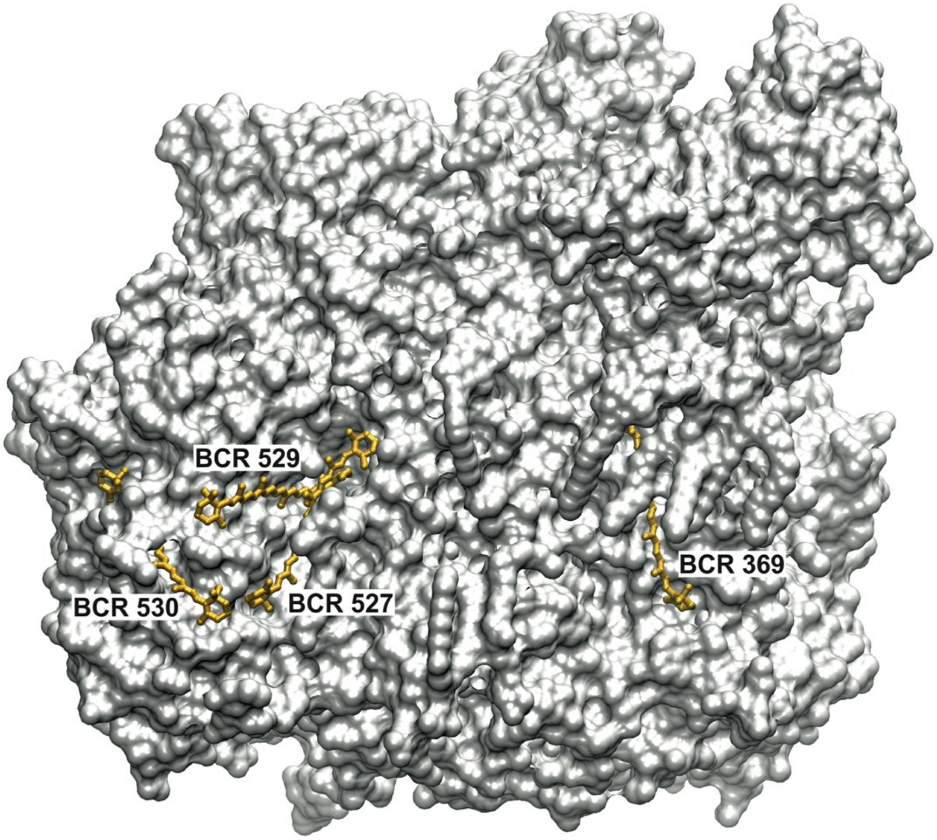

Figure 5: Molecular surface of mPSIIcc (PDB 3KZI). The view is on the dimerization surface [1], which is in contact with the second monomer in dPSIIcc and thus part of the monomer-monomer interface. The β-Car pigments (yellow) located at this interface are surface-exposed in mPSIIcc (i.e., exposed to the detergent phase) and despite being located in binding niches may detach from the complex. Figure made with VMD [2].

S3

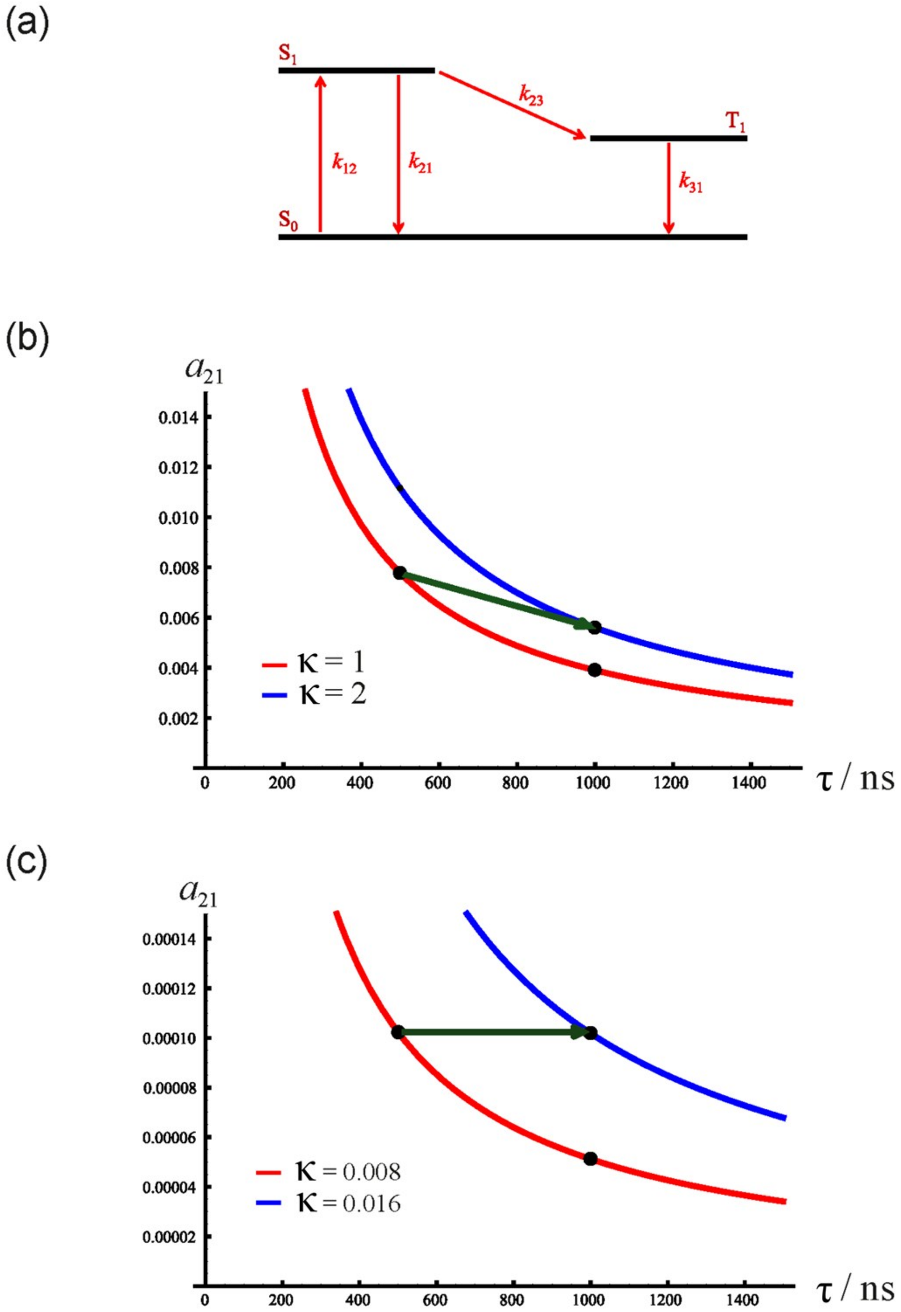

Figure 6: (a) Energy level diagram illustrating the kinetic model. k_{12}: excitation rate; k_{21}: fluorescence rate; k_{23}: intersystem crossing rate; $k_{31} = 1/\tau$: inverse triplet lifetime. (b) Steady-state population of the singlet state S_1 of the emitter (a_{21}) as a function of the triplet lifetime τ for two different values of the ratio $\kappa = k_{12}/k_{31} = \tau\, k_{12}$ ($\gamma := k_{23}/k_{21} = 1.8$, $1/k_{21} = 18$ ns). Both rates are in the same order of magnitude (i.e., κ is close to 1). The green arrow indicates the change in a_{21}, when τ is doubled from 500 to 1000 ns while keeping k_{12} constant (i.e., κ has to be doubled as well). (c) Same as in Figure 6b, but with a significantly lower excitation rate (i.e., significantly smaller κ for the same triplet lifetimes).

Kinetic model

To find the populations of the three states S_0 (singlet ground state), S_1 (first singlet excited state of the emitter) and T_1 (lowest triplet state of the emitter), we have to solve the set of differential equations related to the kinetic scheme depicted in Figure 6a. With the abbreviations

$$u_1 \equiv [S_0] \quad ; \quad u_2 \equiv [S_1] \quad ; \quad u_3 \equiv [T_1] \quad ; \quad \mathbf{u} = \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} \tag{1}$$

we have to solve $\dot{\mathbf{u}} = \mathbf{Au}$ with

$$\mathbf{A} = \begin{pmatrix} -k_{12} & k_{21} & k_{31} \\ k_{12} & -(k_{21}+k_{23}) & 0 \\ 0 & k_{23} & -k_{31} \end{pmatrix} \tag{2}$$

Determination of the roots from the condition

$$|\mathbf{A} - \lambda\mathbf{I}| = 0 \tag{3}$$

yields $\lambda_1 = 0$ and

$$\lambda_{2,3} = \frac{1}{2}\left(-p \pm \sqrt{p^2 - 4q}\right) \tag{4}$$

with

$$\begin{aligned} p &= k_{12} + k_{21} + k_{23} + k_{31} = -\lambda_2 - \lambda_3 \\ q &= k_{21}k_{31} + k_{23}k_{31} + k_{12}k_{23} + k_{12}k_{31} = \lambda_2\lambda_3 \end{aligned} \tag{5}$$

With the reasonable assumption $k_{21} > k_{31}$, it follows that $p^2 - 4q > 0$, so that all roots are real and we have:

$$u_i(t) = \sum_{k=1}^{3} a_{ik} e^{\lambda_k t} \qquad (i = 1,2,3) \tag{6}$$

Insertion of (6) into the system of differential equations yields for each k

$$\begin{aligned} a_{2k} &= a_{3k} \frac{(\lambda_k + k_{31})}{k_{23}} \\ a_{1k} &= a_{2k} \frac{(\lambda_k + k_{21} + k_{23})}{k_{12}} \end{aligned} \tag{7}$$

We assume that the system is in the S_0 state at $t = 0$. Then $u_1(0) = 1$, $u_2(0) = u_3(0) = 0$, and it follows from (6) that

$$\begin{aligned} a_{11} + a_{12} + a_{13} &= 1 \\ a_{21} + a_{22} + a_{23} &= 0 \\ a_{31} + a_{32} + a_{33} &= 0 \end{aligned} \tag{8}$$

Inserting (7) into (8) and taking into account that $\lambda_1 = 0$, yields three equations for the three quantities a_{3k} ($k = 1,2,3$), from which it follows that

$$
\begin{aligned}
a_{31} &= -a_{32} - a_{33} \\
a_{32} &= -a_{33} \frac{\lambda_3}{\lambda_2} \\
a_{33} &= \frac{k_{12} k_{23}}{\lambda_3^2 - \lambda_2 \lambda_3} = \frac{k_{12} k_{23}}{\lambda_3^2 - q}
\end{aligned}
\tag{9}
$$

In the following, we use units of ns^{-1} for the rates and assume $\gamma := k_{23}/k_{21} = 1.8$ (corresponding to a triplet yield of 64% for Chl *a* in ether solution and neglecting internal conversion [3]) as well as $1/k_{21} = 18$ ns [4]. Furthermore, we introduce the ratio $\kappa := k_{12}/k_{31}$ and the triplet lifetime $\tau = 1/k_{31}$. We then have:

$$
\begin{aligned}
p &= \frac{1+\kappa}{\tau} + \frac{1+\gamma}{18} \\
q &= \frac{1}{\tau}\left(\frac{1}{18} + \frac{1+\kappa}{10} + \frac{\kappa}{\tau}\right) \\
a_{2k} &= a_{3k}\, 10 \left(\lambda_k + \frac{1}{\tau}\right) \\
a_{1k} &= a_{2k} \frac{\tau}{\kappa}\left(\lambda_k + \frac{14}{90}\right) \\
a_{33} &= \frac{\kappa}{10\, \tau\, (\lambda_3^2 - q)}
\end{aligned}
\tag{10}
$$

Of particular interest is the steady-state population (i.e., for $t \to \infty$) of S_1, which is given by

$$
a_{21} = \frac{\kappa}{\tau^2\, (\lambda_3^2 - q)}\left(\frac{\lambda_3}{\lambda_2} - 1\right) \tag{11}
$$

We note that a similar model was used by Avarmaa [5] that also includes the excited triplet state T_2. The present three-state model does not consider triplet-triplet absorption, but can be solved exactly.

References

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[3] P. G. Bowers, G. Porter, Quantum Yields of Triplet Formation in Solutions of Chlorophyll, *Proc. Roy. Soc. Lond. A*, **1967**, 296, 435-441.

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