Two-photon Spectra of Chlorophylls and Carotenoid-Tetrapyrrole Dyads

Daniel A. Gacek [a], Ana L. Moore [b], Thomas A. Moore [b], Peter Jomo Walla [a,*]

[a] Technische Universität Braunschweig, Institute for Physical and Theoretical Chemistry, Department of Biophysical Chemistry, Gaußstraße. 17, 38106 Braunschweig, Germany

[b] School of Molecular Sciences and Center for Bioenergy and Photosynthesis, Arizona State University, Tempe, Arizona 85287-1604, United States

* Author for correspondence, e-mail: pwalla@gwdg.de, Tel: +49-531-3915328, Fax: +49-531-3915352

Supporting Information

Influence of direct chlorophyll/tetrapyrolle two-photon excitation on the parameter $\Phi^{\text{Car S}_1\text{-Chl}}_{\text{Coupling}}$

Remember that the parameter $\Phi^{\text{Car S}_1\text{-Chl}}_{\text{Coupling}}$ describing energy transfer between optically forbidden Car states and Chlorophyll/Tetrapyrroles is calculated from

$$F^{OPE} = \Phi^{Chl-Fl} \tag{1}$$

$$F^{TPE} = \Phi^{Car\,S_1-Chl}_{Coupling} \cdot \Phi^{Chl-Fl} \tag{2}$$

$$\rightarrow$$

$$\Phi^{Car\,S_1-Chl}_{Coupling} = \frac{F^{TPE}}{F^{OPE}} \tag{3}$$

Here, $\Phi^{\text{Chl-Fl}}$ is the fluorescence quantum yield of the corresponding chlorophyll or tetrapyrrole. For both types of excitation, TPE and OPE, only the chlorophyll/tetrapyrrole fluorescence is observed. Therefore, additional direct chlorophyll TPE excitation would have been to be considered by

$$F^{OPE} = \Phi^{Chl-Fl} \tag{4}$$

$$F^{TPE} = (\Phi_{Coupling}^{Car\,S_1-Chl} + \Phi_{direct}^{Chl\,TPE}) \cdot \Phi^{Chl-Fl} \tag{5}$$

→

$$\left(\Phi_{Coupling}^{Car\,S_1-Chl} + \Phi_{direct}^{Chl\,TPE}\right) = \frac{F^{TPE}}{F^{OPE}} \tag{6}$$

Here, $\Phi_{\mathrm{direct}}^{\mathrm{Chl\,TPE}}$ is the amount of direct chlorophyll two-photon excitation for a distinct wavelength in comparison to direct carotenoid two-photon excitation. From eq. 6 it is obvious, that this factor only leads to a constant offset when comparing two different values of $\Phi_{\mathrm{Coupling}}^{\mathrm{Car\,S_1\text{-}Chl}}$. For example, when there was initially 50 % direct chlorophyll two-photon excitation and 0% carotenoid to chlorophyll energy transfer then the initially observed value of

$$\frac{F^{TPE}}{F^{OPE}} = \left(\Phi_{Coupling}^{Car\,S_1-Chl} + \Phi_{direct}^{Chl\,TPE}\right) = 0 + 0.5 = 0.5$$

will increase to

$$\frac{F^{TPE}}{F^{OPE}} = \left(\Phi_{Coupling}^{Car\,S_1-Chl} + \Phi_{direct}^{Chl\,TPE}\right) = 0.5 + 0.5 = 1.0$$

for a rise of carotenoid to chlorophyll energy transfer to 50 % and to

$$\frac{F^{TPE}}{F^{OPE}} = \left(\Phi_{Coupling}^{Car\,S_1-Chl} + \Phi_{direct}^{Chl\,TPE}\right) = 1.0 + 0.5 = 1.5$$

for a rise of carotenoid to chlorophyll energy transfer to 100 %.

Without any direct chlorophyll two-photon excitation the following three values

$$\frac{F^{TPE}}{F^{OPE}} = \Phi_{Coupling}^{Car\,S_1-Chl} = 0.0$$

$$\frac{F^{TPE}}{F^{OPE}} = \Phi_{Coupling}^{Car\,S_1-Chl} = 0.5$$

$$\frac{F^{TPE}}{F^{OPE}} = \Phi_{Coupling}^{Car\,S_1-Chl} = 1.0$$

would be observed experimentally.

Thus, any direct chlorophyll or tetrapyrrole two-photon excitation will only lead to a constant offset when comparing different samples or changing carotenoid to chlorophyll/tetrapyrrole energy transfer efficiencies under otherwise identical conditions. (see also supplementary Figure S1)

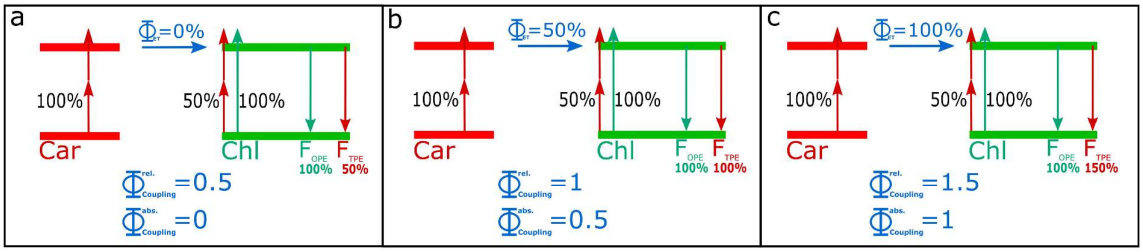

Figure S1. Direct chlorophyll two-photon excitation only leads to a constant offset in $\Phi_{\mathrm{Coupling}}^{\mathrm{Car\,S_1\text{-}Chl}}$ but does not alter the general observation that increasing or decreasing $\Phi_{\mathrm{Coupling}}^{\mathrm{Car\,S_1\text{-}Chl}}$ reflects increasing or decreasing Car to Chl energy transfer, respectively.