Supporting Information

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SI Text

Error Analysis and Treatment. There are four main considerations related to uncertainties involved in determining the angles between transition dipole moments of chlorophyll EET pairs in CP29. First, the error in the relative angle, θ, between transition dipole moments determined for each of two chlorophyll pairs may in turn be determined as a function of the root mean squared fluctuations in the according cross-peak signals from the polarized spectra that are employed. We demonstrate below the method used to calculate an error estimate of $\pm 3°$ for each cross-peak. Second, there is uncertainty associated with the degree of isolation of the cross-peaks from other signals. Third, the error introduced in the fit that is used to obtain the complex normalization of the polarized spectra may be compared to the noise in the spectra. Furthermore, errors introduced by the phasing of the conventional, parallel-polarized, spectrum via fitting to spectrally resolved pump-probe data could also contribute to the overall error, though we show below that the fitting routine employed for the polarization-phasing is insensitive to these phasing errors for variations of $\pm 25°$. All of these sources will potentially contribute to the overall error of the angle determination. In the following, we address the four sources of error specifically.

Uncertainty Due to Noise in Cross-Peaks. The angle between transition dipole moments of chlorophyll pigment energy transfer pairs may be determined as described in the manuscript to be

$$\theta = \arccos\sqrt{\frac{4r+1}{2r+3}},$$

where $r = \overline{ZYZY}/\overline{ZZYY}$ is the ratio of properly normalized spectra at the cross-peak location. The differential of θ is given by

$$\begin{aligned} d\theta &= \sqrt{\left(\frac{\partial\theta}{\partial\overline{ZYZY}}\right)^2 d\overline{ZYZY}^2 + \left(\frac{\partial\theta}{\partial\overline{ZZYY}}\right)^2 d\overline{ZZYY}^2} \\ &= 5\Big[(\overline{ZYZY}^2 d\overline{ZZYY}^2 \\ &\quad + \overline{ZZYY}^2 d\overline{ZYZY}^2)/(2(\overline{ZZYY} - \overline{ZYZY})(4\overline{ZYZY} \\ &\quad + \overline{ZZYY})(2\overline{ZYZY} + 3\overline{ZZYY})^2)\Big]^{1/2}. \end{aligned}$$

To calculate the uncertainty in θ, the average amplitude of the according cross-peak regions of interest, boxed in Fig. 3 of the manuscript, are inserted above for $\overline{ZYZY}$ and $\overline{ZZYY}$. The standard deviation about these averages for the same regions of interest are inserted for $d\overline{ZYZY}$ and $d\overline{ZZYY}$. In arbitrary units, the average and standard deviation values obtained for the A_5–B_5 cross-peak are $\overline{ZYZY} = 0.6 \pm 0.2$ and $\overline{ZZYY} = 2.7 \pm 0.7$. Likewise, the values obtained for the A_3–B_3 cross-peak are $\overline{ZYZY} = 0.14 \pm 0.19$ and $\overline{ZZYY} = 4.0 \pm 0.8$.

Thus $d\theta$ provides an estimated error of $\pm 3°$ for each of the cross-peaks considered in the manuscript. This estimate is the uncertainty in the relative transition dipole moment angle associated with the noise in the polarization-phased spectra.

Uncertainty in the Amplitude Offset of the Cross-Peaks. The use of our methods for determining the relative transition dipole angles, θ, is predicated on being able to isolate the cross-peaks that are being studied. The cross-peaks that we have chosen are very well isolated, however in the $\overline{ZZYY}$ spectrum, we fit a cut along the cross-peaks at $\omega_t = 14{,}750$ cm^{-1} to ensure that it was possible to remove any background in the cross-peak amplitudes due to the overlap of other peak's tails. The A_3–B_3 cross-peak is dominant in the Chl *b* to Chl *a* EET region of this spectrum, and thus the amplitude of the signal at its position is due entirely to this EET. However, the A_3–B_3 cross-peak's tail and the tail arising from Chl *a* to Chl *a* EET contribute to the spectrum's amplitude at the position of the A_5–B_5 cross-peak. Therefore, the actual value that we used in our angle determination for the latter was 70% of the total signal amplitude.

This adjustment is predicated on the quality of the fitting of the trace to a series of spectral forms. We estimate an upper bound of $\pm 4°$ in angle determination uncertainty due to uncertainty in peak amplitude offsets, as the difference in the angle that would be determined from the A_5–B_5 cross-peak representing 70% or 100% of the total signal is 4°.

Together with the above-mentioned $\pm 3°$ due to amplitude noise, these calculations yield a total estimated uncertainty in the angles of $\pm 5°$.

Uncertainty in Polarization-Phasing. In order to assess the uncertainty in the polarization-phasing procedure, the least squares deviation per pixel between the measured *ZZZZ* spectrum and the spectrum constructed out of the normalized polarized spectra, $\overline{ZZYY} + \overline{ZYZY} + \overline{ZYYZ}$, must be compared to the noise floor of the signal in the *ZZZZ* spectrum. To do so, a region of the latter, devoid of signal, was characterized in terms of the root mean squared fluctuations about zero. This procedure provided a value of 0.06 as compared to the fit root mean squared deviation per pixel of 0.01, both in the same arbitrary units used above. Therefore, the metric for the noise floor was found to be six times greater than the minimized root mean squared error in the polarization-phasing procedure. Importantly, the fit itself is accurate to within the noise of the spectrum, and obtaining a fit that agrees even better is no more meaningful because the noise in the spectrum ultimately limits the ability to perform the fit.

Insensitivity of Polarization-Phasing to Initial *ZZZZ* Phase Error. In order to determine the robustness of the transition dipole moment angle determination, the polarization-phasing routine was initiated using measured *ZZZZ* spectra whose overall phases were altered by up to $\pm 25°$ compared to the phase determined by fitting the projection of Re{*ZZZZ*} to spectrally resolved pump-probe data. These tests altered the resulting transition dipole moment angles by at most 1°, and the variances associated with determining these angles did not exceed 4°. Therefore, the initial phase error in the parallel spectrum does not appear to have a strong influence on the measured angles. This comparatively negligible response points to the robustness of the methods employed in our treatment of CP29. Such behavior may result from correlated changes to the two spectra used in the angle determination.