**Supporting Information**

The minor component (~1.40 ps) reveled in the isotropic emission kinetics of the purpurin moiety of **1** at wavelengths longer than 699 nm appears as a rise and at wavelengths shorter than 699 nm it is seen as a decay. This observation is highlighted in Figure 1, by plotting the isotropic fluorescence kinetics at 688, 699 and 712 nm in an expanded form after normalization at 4.0 ps. In this case, the isotropic emission points were calculated from the time-dependent fluorescence signals measured with parallel, $I_{\parallel}(t)$, and perpendicular polarized excitation, $I_{\perp}(t)$, using the relationship

$$I_{iso}(t) = [I_{\parallel}(t) + 2I_{\perp}(t)]/3 \qquad (1)$$

Measurements at the same wavelengths were also made with magic angle excitation and it was confirmed that the isotropic kinetics determined by both methods were identical, within experimental error. Furthermore, these measurements establish that the lifetime of the dominant ultrafast rise component in the purpurin emission is also wavelength dependent. At 712 nm, the average rise time is 44 ± 1 fs (SD of 3), which is significantly shorter than that observed between 694 and 703 nm (61 ± 3 fs, SD of 7). Moreover, this purpurin $S_1$ state formation time essentially matches the carotenoid $S_2$ decay time of 40 ± 3 fs. Therefore, if energy transfer from the $S_2$ state of the carotenoid proceeds via an intermediate electronic state, such as the purpurin $Q_x$ ($S_2$) state, internal conversion to the purpurin $Q_y$ ($S_1$) state must occur on a similar, or shorter, timescale.

The emission kinetics at 688 nm, shown in Figure 1, are more complex and two ultrafast components with very similar lifetimes (a rise of 44 ± 5 fs and a decay of 58 ± 25 fs)1 are required to fit this data. The ultrafast decay component at this wavelength could be fluorescence from the $S_2$ state of the carotenoid moiety of **1**, which extends to at least 682 nm, or hot emission from higher vibronic levels of the excited $S_1$ state of the purpurin. Given the uncertainty in this decay lifetime, it is difficult to distinguish between

these possible explanations. Nevertheless, the delayed formation of the purpurin fluorescence in the 694–703 nm region is consistent with a vibronic relaxation process occurring on a slower timescale than energy transfer from the $S_2$ state of the carotenoid. Furthermore, the reappearance of an ultrafast decay component in the 721 and 733 nm kinetics cannot be attributed to overlapping emission from the carotenoid $S_2$ state.[3]

**References and Notes**

(1) The uncertainties were established from fits to different models. A global analysis of the 688–722 nm isotropic kinetics was also performed with four exponential components and lifetimes of 41 fs, 62 fs, 1.4 ps and > 500 ps were obtained.

(2) Macpherson, A. N.; Gillbro, T. In *Ultrafast Phenomena XI*; Elsaesser, T.; Fujimoto, J. G.; Wiersma, D. A.; Zinth, W., Eds.; Springer-Verlag: Berlin, 1998; pp 672–674.

(3) Although not the focus of this study, the observation of an ultrafast decay component in the red-most kinetics is apparently accompanied by an ~3 nm blue-shift in the maximum of the reconstructed time-dependent emission spectra, as well as a similar decrease in the bandwidth, on the < 100 fs timescale.

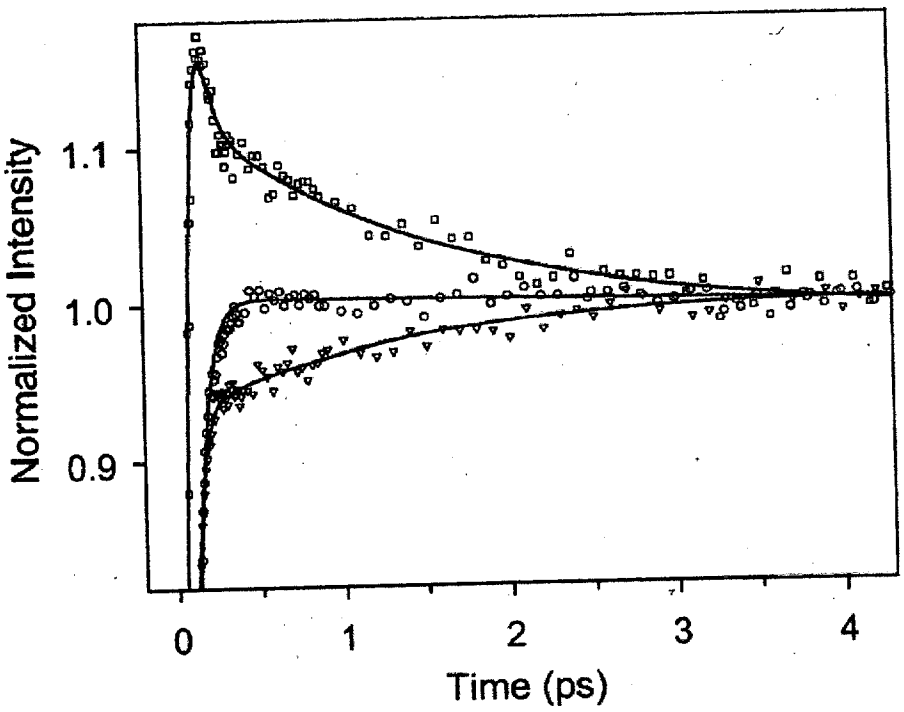


**Figure 1.** Isotropic formation kinetics of the excited $S_1$ state of the purpurin moiety of dyad **1** detected by upconversion of the purpurin fluorescence at 699 nm (O), at 688 nm (□) and at 712 nm (∇) following excitation at 490 nm with magic angle polarization of a ~$1 \times 10^{-4}$ M solution of dyad **1** in toluene.