Supporting information to

Dual singlet excited-state quenching mechanisms in an artificial caroteno-phthalocyanine light harvesting antenna

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Figure S1: Structure of reference Zn-phthalocyanine (Pc-ref).
Figure S2. Time traces of Pc-ref in toluene upon 670 nm excitation at the probe wavelengths indicated, with raw data in black and the fits according to Fig. 2 in red. Note that the time axis is linear up to 1 ps and logarithmic thereafter.
Figure S3. Time traces of the dyad in toluene upon 670 nm excitation at the probe wavelengths indicated, with raw data in black and the fits according to Fig. 4 in red. Note that the time axis is linear up to 1 ps and logarithmic thereafter.
Fig. S4. Red line: Spectrum obtained by subtracting the unsolvated excited state of the \textit{Pc-ref} model compound (192 fs EADS) from the unsolvated excited state spectrum of the dyad excited at 670 nm (348 fs EADS). Black line: Decay-Associated Difference Spectrum (DADS) with associated time constant of 7.3 ps of the dyad with 530 nm excitation. Blue line: Decay-Associated Difference Spectrum (DADS) with associated time constant of 7.8 ps of the model carotenoid, reproduced from ref. \textsuperscript{1}. The latter two spectra exclusively result from internal conversion of the carotenoid \textit{S\textsubscript{1}} state to the ground state.
Figure S5. ΔA spectra (raw data) of Pc-ref (A) and dyad (B) upon 670 nm excitation around time zero, at the time delays indicated.

ΔA spectra are given with an interval of 30 fs. The spectra show an early rise at the short wavelength side and a late rise on the long wavelength side due to group velocity dispersion of the probe pulse. It can be seen that the Car S1 features are already present during the rise of signal and are not imposed on a later timescale.
Figure S6. Selected raw time-resolved ΔA spectra on the dyad dissolved in toluene upon excitation at 670 nm at the time delays indicated. (A): raw ΔA spectra on the sub-ps and ps timescale in the region 450 – 650 nm; (B) raw ΔA spectra on the sub-ps and ps timescale in the region 650 – 725 nm; (C) raw ΔA spectra on the 10s of ps – ns timescale in the region 450 – 650 nm; (D) raw ΔA spectra on the 10s of ps – ns timescale in the region 650 – 725 nm.
Figure S7: global analysis with one less component with respect to that shown in Fig. 4, with the 3.6 ps component omitted and the other components fixed to the values of Fig. 4. (A) Evolution-Associated Difference Spectra (EADS); (B) Decay-Associated Difference Spectra (DADS); (C) experimental kinetic traces (black lines) along with the fit (red lines) (top) and residuals (bottom). Note that the time axis is linear up to 1 ps and logarithmic thereafter. The clear structure in the residuals indicate a significant misfit.
Figure S8: global analysis with one less component with respect to that shown in Fig. 4, with the first two components running free. (A) Evolution-Associated Difference Spectra (EADS); (B) Decay-Associated Difference Spectra (DADS); (C) experimental kinetic traces (black lines) along with the fit (red lines) (top) and residuals (bottom). Note that the time axis is linear up to 1 ps and logarithmic thereafter. The clear structure in the residuals indicate a significant misfit.
Figure S9: EADS (top) and DADS (bottom) resulting from global analysis of the dyad in toluene upon 530 nm excitation.

Upon 530 nm excitation the dyad is excited to the carotenoid S2 state. In global analysis, seven components are needed for a sufficient fit of the data. The first EADS (black, 83 fs) shows the typical carotenoid S2 spectrum, mixed with artifact features. The decay time of this EADS is on the edge of our time resolution and cannot be determined accurately. The second EADS (red, 339 fs) has a negative band at 690 nm, assigned to phthalocyanine bleach and stimulated emission, indicating that energy transfer from the Car S2 state to Pc has occurred. The second EADS displays a positive ΔA signal between 520 and 665 nm and above 710 nm. The ESA around
550 nm is assigned to carotenoid S*, around 600 nm to carotenoid S₁ and around 650 and above 710 to phthalocyanine excited state absorption. Like in the 670 nm excitation case, the kinetic processes discussed below provide evidence for the presence of both the excitonically coupled excited state and weakly coupled carotenoid and phthalocyanine states. We therefore postulate that in the conformation with coupled excited states S₂ evolves into this coupled excited state, while in the uncoupled conformation the S₂ is quenched by energy transfer to phthalocyanine and by internal conversion to S₁ and S*.

The second DADS (red, 339 fs) shows a loss of signal around 540 nm and a growth around 610 nm. This is interpreted as internal conversion from the Car S* state to the S₁ state. This phenomenon was observed before by Berera et al. in a carotenoid-phthalocyanine dyad with an amide linkage.² The second DADS also contains the loss of phthalocyanine bleach around 682 nm.

Subsequently, the third DADS (blue 7.3 ps) shows the decay of the typical carotenoid S₁ spectrum together with a band-shift pattern at the phthalocyanine Q-band position. It is assigned to decay of carotenoid S₁ of dyads in the weak-coupling conformation; the timescale agrees well with the lifetime of carotenoid reported by Berera et al.¹ The band-shift at the phthalocyanine Q-band can be explained by a change of the local environment of the phthalocyanine upon Car relaxation.

In the EADS the 54 ps (green) and 148 ps (magenta) processes a large decay of the Q-band bleach occurs. The spectral evolution is very similar to the 77 ps and 213 ps processes found upon phthalocyanine excitation (Fig. 2) and are assigned to relaxation of the excitonically coupled excited state and energy transfer from phthalocyanine to carotenoid, respectively.

The 3.4 ns component (cyan) is assigned to phthalocyanine decay in the dyad conformations without excited state coupling or energy transfer. This phthalocyanine Q-state must originate from energy transfer from the carotenoid S₂ state, confirming that there is a fraction of intact dyad in which the phthalocyanine Q to carotenoid S₁ energy transfer does not occur. The non-decaying component (gray) is assigned to triplet formation.
Figure S10. Time traces of dyad in toluene upon 530 nm excitation at the probe wavelengths indicated, with raw data in black and the fits according to Fig. S9 in red. Note that the time axis is linear up to 1 ps and logarithmic thereafter.
Figure S11. Results from quantum mechanical calculations on the dyad structure. 
Top panel: two of the calculated structural conformers. Conformation 1: dihedral angle \( \alpha = 40^\circ \), dihedral angle \( \beta = 5.6^\circ \). Conformation 2: dihedral angle \( \alpha = 145^\circ \), dihedral angle \( \beta = 2.5^\circ \). Conformation 1 is 0.1 kcal/mol higher in energy than Conformation 2. Bottom panel: abundance of conformers vs dihedral angle \( \alpha \), according to the expression given above the plot.
References

1. Berera, R.; Moore, G. F.; Stokkum, I. H. M. v.; Kodis, G.; Liddell, P. A.; Gervaldo, M.; Grondelle, R. v.; Kennis, J. T. M.; Gust, D.; Moore, T. A.; Moore, A. L., Charge separation and energy transfer in a caroten–C60 dyad: photoinduced electron transfer from the carotenoid excited states. Photochem. Photobiol. Sci. 2006, 5 (12), 1142-1149.

2. Berera, R.; van Stokkum, I. H. M.; Kodis, G.; Keirstead, A. E.; Pillai, S.; Herrero, C.; Palacios, R. E.; Vengris, M.; van Grondelle, R.; Gust, D.; Moore, T. A.; Moore, A. L.; Kennis, J. T. M., Energy Transfer, Excited-State Deactivation, and Exciplex Formation in Artificial Caroteno-Phthalocyanine Light-Harvesting Antennas†. The Journal of Physical Chemistry B 2007, 111 (24), 6868-6877.