

Supporting Information

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SI EPR Analysis

At the magnetic field of 366.2 mT, the emissive triplet signals of the carotenoid moiety are dominating, resulting in negative signals. A positive absorption at this field corresponds to presence of the porphyrin triplet. Thus, the fast initial positive rise in dyad-2 (within our time resolution) can be attributed to porphyrin triplet absorption, followed by appearance of the carotenoid triplet signal. For dyad-1, the initial signal after the laser flash is negative with very small intensity that increases with time. These results are in agreement with the optical kinetics, which found faster triplet-triplet energy transfer for dyad-1 than dyad-2. The (slower than optical room temperature data) initial rises of the negative carotenoid triplet signals (negative amplitude) can be explained by difference in the decay rates of the different triplet sublevel. Similar effects have been observed and previously discussed (22). If, as a consequence of T-TET, all carotenoid triplet sublevels are populated equally or almost equally, the intensity of the triplet EPR signal will be zero or very small. The signal will be built up in time due to the difference in the sublevel decay rates.

The simulations of the carotenoid triplet in the two dyads used identical ZFS parameters, $|D| = 355 \times 10^{-4} \text{ cm}^{-1}$ and $|E| = 37 \times 10^{-4} \text{ cm}^{-1}$. These ZFS parameters are in very good agreement with previous triplet EPR studies on similar carotenoids in organic solvents (23–25). Considering the good agreement between dyad-1 and -2 as well as the literature data, we can safely reject delocalization of the triplet excited state over both the carotenoid and the porphyrin moieties.

SI Preliminary Experimental Evidence for an Upshifted ν_{1b} Band in the Carotenoid Triplet State

DFT calculations predict an upshifted ν_{1b} band in the Raman spectra of the carotenoid triplet state, which has not yet been experimentally reported. However, obtaining a pure resonance Raman of a carotenoid in its triplet state is not possible, as the intense signal of carotenoid ground state contributes at the excitations used for probing carotenoid triplet state. As a result, populating carotenoid triplet state induces both the appearance of the signal of this species, together with the bleaching of the carotenoid ground-state signal, including that of the intense ν_1 , which is located close to the ν_{1b} band. The appearance of the ν_{1b}

band will thus depend on how the difference spectra are computed. Proper normalization of resonance Raman difference would ideally require the presence of external standards. However, the very high-resonance cross-section of the resonance Raman of carotenoid (10^7 , actually close to the highest observed) makes it very difficult to introduce in the sample high concentrations of standards that would allow (i) to observe the Raman signal of these standards and (ii) not to perturb the samples under measurement.

We are thus left with artificial normalization of the spectra before calculating differences. Of course, it is easy to cancel the ν_1 from the ground state, so to observe only the shifted ν_{1a} from the triplet state, and measure its frequency. However, upon buildup of the triplet state, part of the ground-state signal should be depleted, which would result in the S-shaped signal with a positive ν_{1a} from the triplet and a negative ν_1 from the ground state. Performing such a difference leads to inaccurate frequency measurement of the ν_{1a} of the triplet state.

It is possible to perform a difference leading to evidence the ν_{1a} and ν_{1b} from the triplet state (see below). However, it is emphasized that this depends on the way we normalize the spectra, and more elaborate measurements are needed to unambiguously confirm the presence of the ν_{1b} of the triplet state.

SI DFT Analysis

Fig. S3 shows the analysis of bond order changes along the carotenoid chain induced by singlet- to triplet-state transition. Defining the change in bond order as the triplet-*minus*-singlet bond orders, a positive change indicates an increase in double-bond character upon excitation to the triplet state. Following the numbering of double bonds as in Fig. 1, there is a gradual increase in bond order of the C–C bonds toward the center of the carotenoid. Additionally, the C=C bonds (8–10) in dyad-1 exhibit a more significant reduction of double-bond character compared with those of dyad-2. This effect is also mirrored in terms of a more significant gain in double-bond character of the CC bonds in the triplet state (7' to 10'). In contrast, bond order changes in dyad-2 are almost identical to those of the unperturbed carotenoid-3.

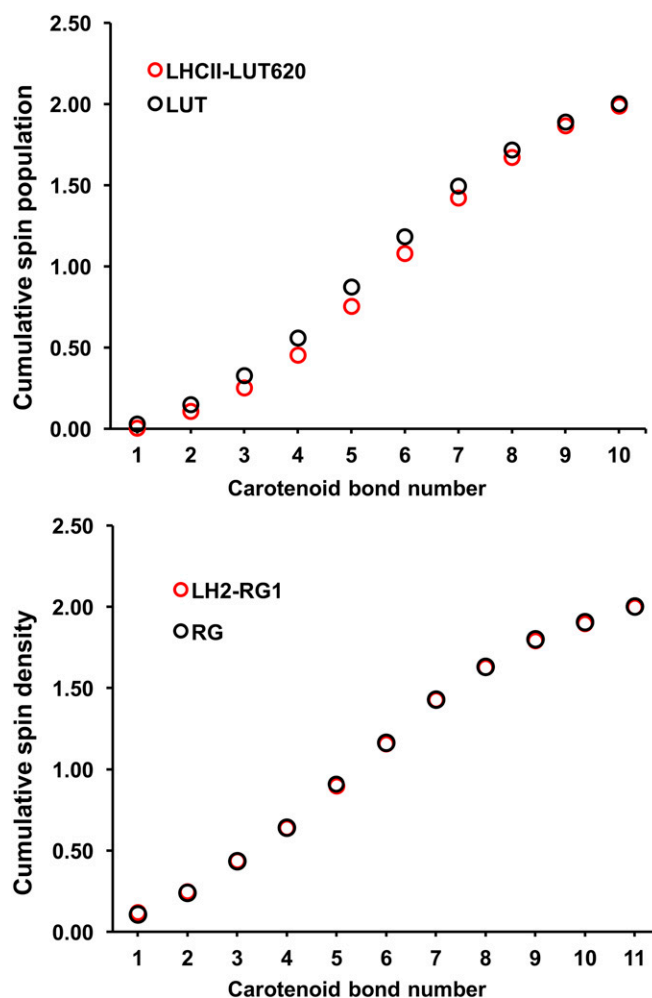


Fig. S6. Cumulative spin density (*Top*) lutein in LHCII and in the gas phase. (*Bottom*) Rhodopsin glucoside in LH2 and in the gas phase.

Table S1. Energy decomposition analysis of the interchromophore interaction in dyad-1

Energy term	ΔE , kJ/mol
Dyad-1 in Por(S0)–Car(S0) state	
Frozen density (FRZ)*	–70.8
Polarization (POL) [†]	–3.2
SCF delocalization (V-DEL)	–32.6
SCF basis set superposition error (V-BSSE)	28.1
SCF charge transfer (V-CT = V-DEL + V-BSSE) [‡]	–4.5
Dyad-1 in Por(S0)–Car(T1) state	
Frozen density (FRZ)*	–75.1
Polarization (POL) [†]	–3.6
SCF delocalization (V-DEL)	–32.8
SCF basis set superposition error (V-BSSE)	27.2
SCF charge transfer (V-CT = V-DEL + V-BSSE) [‡]	–5.6

*The frozen density term is a sum of the Coulomb (electrostatic) term and an exchange-correlation term in the Kohn–Sham theory.

[†]The polarization energy is defined as the energy lowering due to intramolecular relaxation of each fragment's absolutely localized molecular orbitals in the field of all other fragments in the system.

[‡]The charge transfer term corresponds to the remaining portion of the total interaction energy and includes counterpoise correction.

Dataset S1. Optimized geometries of dyad-1 and dyad-2 in THF simulated using the SMD solvation model

[Dataset S1](#)

Note: All species had zero imaginary frequencies, as determined from frequency calculations at the ω B97XD/6-31G(d) level.