Supporting information:

The excitonic nature of Carotenoid-Phthalocyanine Dyads and its role in the transient absorption spectra

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We tested three different DFT functionals (B3LYP, CAM-B3LYP and ωB97X-D) to determine which one provides the best description of the geometrical properties and vibrational modes for both Car and ZnPc. Because the experimental vibrational IR and Raman spectra for the Car used in these dyads are not available, we compared vibrational spectra for the structurally similar β-carotene,\(^1\) which has also 10 double bonds (DB) in the conjugation chain. The best agreement for both IR and Raman spectra for the β-carotene is obtained for the B3LYP functional, Figure S1. The same is true also for the ZnPc. The intensities of some IR peaks for the ZnPc are slightly different from the experimental spectra, but their frequencies are well described. The computed Raman spectra for both molecules show very nice agreement with the experimental one. Based on this analysis we decided to use the B3LYP functional for the structure optimization and vibrational analysis.

Figure S1: Comparison of the IR and Raman spectra computed with different DFT functionals. The experimental spectra for the β-carotene were obtained from Ref. 1 and for the ZnPc from Ref. 2.
S2 Exciton model and spectra

S2.1 Exciton vibronic model

Within the exciton model, the excited states of the whole system are determined by the excitation energies of the individual molecules and the couplings between them. Given the significant vibronic coupling of the Car states, we resorted to using a vibronic basis for the exciton model. The vibrational modes with the highest coupling to electronic transitions are included into the exciton Hamiltonian and treated on equal footing as the electronic states.

To obtain the coupling $V_{ij\nu\eta,kl\kappa\xi}$ between vibronic states $|ij\nu\eta\rangle$ and $|kl\kappa\xi\rangle$, the purely electronic coupling is multiplied by the corresponding Franck-Condon integrals,\(^3\) namely

\[
V_{ij\nu\eta,kl\kappa\xi} = V_{ij,kl} \langle \nu^{(j)} | \kappa^{(l)} \rangle \langle \eta^{(j)} | \xi^{(l)} \rangle
\]

\[
V_{ij,kl} = \int dr_1 \int dr_2 \rho_{i\rightarrow k}(r_1) \frac{1}{|r_1 - r_2|} \rho_{j\rightarrow l}(r_2), \tag{S1}
\]

where $V_{ij,kl}$ is the purely electronic coupling between state $|i^{(ZnPc)}, j^{(Car)}\rangle$ and state $|k^{(ZnPc)}, l^{(Car)}\rangle$, and $\nu\eta$ and $\kappa\xi$ correspond to the vibrational quantum numbers for the two considered Car modes. Here in fact, we explicitly consider different vibrational states only for Car. $\rho_{i\rightarrow k}(r_1)$ is the transition density from electronic state $i$ to electronic state $k$, and the $|\nu^{(j)}\rangle$ is a wavefunction of the $\nu$-th vibrational state for electronic state $j$.

The exciton coupling between doubly and singly excited electronic states can be obtained from the coupling between singly excited states as
\[ V_{0,kl} = \langle i \rangle^{(ZnPc)} \left\langle 0 \right| V \left| k^{(ZnPc)}, l^{(Car)} \right\rangle \]

\[ = \int dr_1 \int dr_2 \cdots \int dr_N \int d\bar{r}_1 \int d\bar{r}_2 \cdots \int d\bar{r}_M \psi_i^{(ZnPc)}(r_1, r_2, \ldots, r_N)\psi_0^{(Car)}(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_M) \times \]

\[ \times \sum_{i=1, j=1}^{N,M} \frac{1}{|r_i - \bar{r}_j|} \psi_k^{(ZnPc)}(r_1, r_2, \ldots, r_N)\psi_l^{(Car)}(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_M) \]

\[ = \int dr \int d\bar{r} \rho_{i \rightarrow k}^{(ZnPc)}(r) \frac{1}{|r - \bar{r}|} \rho_{0 \rightarrow l}^{(Car)}(\bar{r}) \]  

\[ (S2) \]

where \( r \) and \( \bar{r} \) represent the position vector of the ZnPc and Car electrons, respectively, with \( N \) and \( M \) being number of electrons on each molecule. Eq. S2 corresponds to the interaction of the transition density between higher excited states on the ZnPc and transition density of the Car representing the excitation from the ground state.

The exciton states \( |M\rangle \) obtained from diagonalization of the Hamiltonian (eq. 1 in the main text) can be written as a linear combination of the site vibronic basis \( |ij_{\nu\eta}\rangle \) as

\[ |M\rangle = \sum_{\nu\eta} \sum_{i,j} c^M_{ij_{\nu\eta}} |ij_{\nu\eta}\rangle, \]  

\[ (S3) \]

where \( c^M_{ij_{\nu\eta}} \) is the coefficient of the state \( |ij_{\nu\eta}\rangle \) in the wavefunction of the exciton state \( M \), where ZnPc is in the electronic state \( i \) and Car in the electronic state \( j \) and vibrational state \( \nu \) and \( \eta \) for the first and second vibrational mode, respectively.

The transition dipole between two singly excited states \( \mu_{mn} = \langle m | \mu | n \rangle \) can be obtained from the transition density matrix \( \rho^{(mn)}(r) \), eq. (S5), as

\[ \mu_{ik} = \int \mu \rho^{(mn)}(r) dr \]  

\[ (S4) \]
The transition density matrix between the two singly excited states $\rho^{(mn)}(r)$ (where $i \neq k \neq 0$) can be written in the molecular orbital basis as

$$ \rho^{(mn)}(r) = \sum_{i \in \text{occ}} \sum_{a \in \text{virt}} X_{ia}^{(m)} X_{ib}^{(n)} \varphi_a(r) \varphi_b(r) - \sum_{ij \in \text{occ}} \sum_{a \in \text{virt}} X_{ia}^{(m)} X_{ja}^{(n)} \varphi_i(r) \varphi_j(r) $$

where $X_{ia}^{(m)}$ are the CIS/TDA coefficients of excited state $m$ in the molecular orbital basis, $\varphi$ are the molecular orbitals, indices $i, j$ run on the occupied orbitals, and indices $a, b$ run on the virtual orbitals.  

The intensity of the TA spectra is proportional to the transition dipole moment between two exciton states. The transition dipole $\mu_{MN}$ between two vibronic exciton states $M$ and $N$ can be obtained from the transition dipoles between singly excited states as

$$ \mu_{MN} = \sum_{\nu \eta \kappa \zeta} \sum_{ijkl} c_{k\nu \zeta} c_{i\eta \kappa} \left( \langle i \mid \mu_{ZnPc} \mid k \rangle + \langle j \mid \mu_{Car} \mid l \rangle \langle \nu \mid \kappa \rangle \langle \eta \mid \zeta \rangle \right). $$

### S2.2 Spectral densities

The effects of the coupling of the electronic transitions to the nuclear motion are included through the spectral density formalism. The spectral density $J_i(\omega)$ for transition $i$ is divided into two contributions $J_i(\omega) = J_i^{(UBO)}(\omega) + J_i^{(OBO)}(\omega)$ from the intra-molecular vibrations described by the underdamped Brownian oscillator $J_i^{(UBO)}(\omega)$ and from the environmental fluctuations described by the overdamped Brownian oscillator $J_i^{(OBO)}(\omega)$. The individual contributions read

$$ J_i^{(OBO)}(\omega) = \frac{2 \lambda_i \omega}{\tau_i (\omega^2 + 1/\tau_i^2)} $$

$$ J_i^{(UBO)}(\omega) = \sum_{\zeta} 2 \lambda_i \gamma_i \omega_{\zeta}^2 \frac{\omega}{\left(\omega^2 - \omega_{\zeta}^2\right)^2 + \omega^2 \gamma_{\zeta}^2} $$

Where $\lambda_i$ is the environmental reorganization energy for electronic state $i$, $\tau_i$ is the correlation lifetime, $\lambda_i \gamma_{\zeta}$ is reorganization energy for the vibrational mode $\zeta$ for electronic state $i$, $\gamma_{\zeta}$ is the inverse correlation lifetime of the vibrational mode and $\omega_{\zeta}$ is frequency of the vibrational mode.
The vibrational normal mode frequencies $\omega_\zeta$ were obtained from the normal mode analysis of the ZnPc in the ground state. The reorganization energies $\lambda_{i\zeta}$ for each normal mode $\zeta$ and electronic state $i$ were obtained from the gradients in the Cartesian coordinates $f_a^{(i)} = \partial V_i / \partial x_a$ of the excited state potential surface in ground state optimal geometry, where $V_i$ corresponds to the potential of the electronic state $i$ and $x_a$ is Cartesian displacement. The reorganization energy reads as

$$\lambda_{i\zeta} = \frac{\left( \sum_{a=1}^{3N} f_a^{(i)} A_{a\zeta} \right)^2}{2k_\zeta}$$  \hspace{1cm} (S8)

where $A$ is the transformation matrix between Cartesian and normal mode coordinates and $k_\zeta$ is a “spring constant” of the normal mode $\zeta$.

More generally, the reorganization energy $\lambda_{MN}$ of the $N$-th exciton state in the $M$-th exciton state equilibrium geometry can be computed within the harmonic approximation from the excited state gradients at the ground state geometry as

$$\lambda_{MN} = \sum_{\zeta} \lambda_{MN,\zeta}$$

$$\lambda_{MN,\zeta} = \frac{\left( \sum_{a=1}^{3N} \left( f_a^{(N)} - f_a^{(M)} \right) A_{a\zeta} \right)^2}{2k_\zeta}$$

$$f_a^{(N)} = \sum_k \left( c_{kl,a \zeta}^{N} \right)^2 f_a^{(k)}$$  \hspace{1cm} (S9)

where $c_{kl,a \zeta}^{N}$ are expansion coefficients of the $N$-th exciton state in the site vibronic basis.

For the calculation of the gradients $f_i^{(N)}$ of the exciton state $N$, the contribution from the Car is not included, because the vibrational contribution of the Car is included within the two normal modes which are treated together with the electronic levels as exciton basis states.

The spectral densities were computed at B3LYP ground state geometry. The same functional was used for computing the vibrational normal modes in the ground state: frequencies
\( \omega_\zeta \), transformation matrix \( A_{\alpha \zeta} \) and spring constant \( k_\zeta \). On the other hand, the gradients \( f^{(k)}_\alpha \) were computed with CAM-B3LYP functional because it describes better the excited state properties. The correction for computing the spectral density with different functional for the ground state properties and gradients is described in the Section S4.

### S2.3 Linear absorption spectra

Optical spectra were simulated employing the exciton model and the cumulant expansion formalism.\(^6\) This method is widely employed in the modeling of light-harvesting complexes and assumes small off-diagonal exciton vibrational coupling in the exciton basis. This assumption is reasonable for our system, given that we treat the most vibronically coupled modes exactly (See Section S2.1). Within this approximation, the absorption \( \alpha (\omega) \) and fluorescence \( I (\omega) \) spectra are obtained as a sum over exciton states:

\[
\alpha (\omega) \propto \omega \sum_M |\mu_{0M}|^2 D_M (\omega),
\]

\[
I (\omega) \propto \omega^2 \sum_M p_M |\mu_{0M}|^2 \tilde{D}_M (\omega), \tag{S10}
\]

where \( p_M \) correspond to the Boltzmann factor and \( \mu_{0M} \) is the transition dipole between the ground and the \( M \)-th exciton state.

The homogeneous lineshape \( D_M (\omega) \) is obtained in the cumulant expansion formalism as:

\[
D_M (\omega) = \int_{-\infty}^{\infty} e^{-i(\omega_M - \omega)t - g_M(t) - t/\tau_M} dt, \tag{S11}
\]

where \( \tau_M \) represents the lifetime of the exciton state \( M \), and \( g_M(t) \) is the lineshape function of the exciton \( M \).

The fluorescence lineshape \( \tilde{D}_M (\omega) \) is similarly calculated as

\[
\tilde{D}_M (\omega) = \int_{-\infty}^{\infty} e^{-i(\omega_M - \omega)t + 2i\lambda_M - g_M^*(t) - t/\tau_M} dt, \tag{S12}
\]
where $\lambda_M$ is the corresponding reorganization energy.

Assuming that the individual sites are uncorrelated and neglecting the effect of coupling fluctuations on the homogeneous lineshape, we can write

$$g_M(t) = \sum_{\nu\eta} \sum_{i,j} |c_{ij\nu\eta}^M|^4 \left( g_{i}^{(ZnPc)}(t) + g_{j}^{(Car)}(t) \right), \quad (S13)$$

where $g_i(t)$ is the lineshape function of the electronic state $i$, which is zero for the ground state and for the excited state it is obtained from the corresponding spectral density $J_i(\omega)$:

$$g_i(t) = -\int_0^\infty d\omega J_i(\omega) \frac{\coth(\beta\hbar \omega/2)}{\pi \omega^2} \left[ \cos(\omega t) - 1 \right] - i \left[ \sin(\omega t) - \omega t \right]. \quad (S14)$$

### S2.4 Transient absorption spectra

The transient absorption spectra can be separated into three contributions: ground-state bleaching (GSB), stimulated emission (SE) and excited-state absorption (ESA). The optical signal from each contribution at the thermal equilibrium reads as

$$I_{GSB}(\omega) \propto -\omega \sum_M |\mu_{0M}|^2 D_M(\omega)$$

$$I_{SE}(\omega) \propto -\omega \sum_M p_M |\mu_{0M}|^2 \tilde{D}_M(\omega)$$

$$I_{ESA}(\omega) \propto \omega \sum_M \sum_N p_M |\mu_{MN}|^2 D_{MN}(\omega) \quad (S15)$$

where the $\mu_{MN}$ is the transition dipole from the exciton state $M$ to the exciton state $N$.

The homogeneous lineshape $D_{MN}(\omega)$ for the excited-state absorption from the state $M$ to the state $N$ is obtained similarly to the ground state absorption lineshape:

$$D_{MN}(\omega) = \int_{-\infty}^{\infty} e^{-i(\omega - \omega^0_M + \lambda_{MN} - \omega) t - g_{MN}(t) - t/\tau_N} dt \quad (S16)$$
where $\omega^0_N - \omega^0 = \omega_N - \lambda_N$ is the zero phonon transition energy between the ground and $N$-th exciton state. $\lambda_{MN}$ correspond to the reorganization energy of the $N$-th exciton state in the $M$-th exciton state equilibrium geometry.

The lineshape function $g_{MN}(t)$ for the transition from the exciton state $M$ to the exciton state $N$ is computed applying eq. (S14) with the reorganization energies $\lambda_{MN,\zeta}$ (eq. S9). The environmental part of the spectral density is modeled by the OBO same as for the transitions from the ground state.

The Förster energy transfer

The Förster rate $^{7,8} k_{M \rightarrow N}$ of the excitation transfer from the state $M$ to the state $N$ can be then written as

$$k_{M \rightarrow N} = 2 \frac{V_{MN}^2}{\hbar^2} \Re \left\{ \int_0^\infty dt \ e^{-g_{M}(t)-g_{N}(t)+i(\omega_{NM}-2\lambda_{M})t} \right\}. \tag{S17}$$

where the integral represents the spectral overlap of the fluorescence from state $M$ and the absorption of state $N$, and $V_{MN}$ is the full electronic coupling between the two states. The $\omega_{NM} = \varepsilon_M - \varepsilon_N$ corresponds to the difference between vertical excitation energies of the states.

Figure S2: Schematic representation of the transient absorption signals. The ESA and SE signals are calculated at the excited potential minima.

S3 Förster energy transfer

The Förster rate $^{7,8} k_{M \rightarrow N}$ of the excitation transfer from the state $M$ to the state $N$ can be then written as

$$k_{M \rightarrow N} = 2 \frac{V_{MN}^2}{\hbar^2} \Re \left\{ \int_0^\infty dt \ e^{-g_{M}(t)-g_{N}(t)+i(\omega_{NM}-2\lambda_{M})t} \right\}. \tag{S17}$$

where the integral represents the spectral overlap of the fluorescence from state $M$ and the absorption of state $N$, and $V_{MN}$ is the full electronic coupling between the two states. The $\omega_{NM} = \varepsilon_M - \varepsilon_N$ corresponds to the difference between vertical excitation energies of the states.
and $N$, which are assumed to be localized on different fragments. The lineshape functions $g_{M/N}(t)$ are computed as detailed in equation S14 and describe the vibronic coupling for the two transitions. Within this model, all the effects of the intramolecular vibrations were included into the spectral density, and the vertical excitation energy $\varepsilon^{S_1} = \varepsilon^{S_1}_{0-0} + \lambda^{S_1}_{vib}$ has to be used instead of the 0-0 transition energy $\varepsilon^{S_1}_{0-0}$.

### S4 Correction for the different GS and ES method

The best agreement between the simulated and the experimental optical spectra was obtained for the geometry of the dyad optimized with B3LYP functional and the excited state properties calculated with the CAM-B3LYP functional at the TD-DFT level. This, however, leads to non-zero gradients in the ground state, but zero ground state gradients are required for computing the spectral densities and the reorganization energies. Within the approximation of the shifted harmonic potential surfaces in different electronic states, discussed above, the nonzero gradients can be corrected. The spectral density for the excitations from the ground state is then calculated from the difference of the gradients in the excited and the ground state in the B3LYP ground state geometry $R_{0}^{B3LYP}$ as

$$f_a^{(i)} = f_a^{(i)} (R_{0}^{B3LYP}) - f_a^{(g)} (R_{0}^{B3LYP})$$

(S18)

In the harmonic approximation the definition (S18) of the gradient $f_a^{(i)}$ is independent on the geometry $R_0$ for which the gradient is calculated. This approach for the calculation of the excited state gradients provide correct spectral densities and reorganization energies, but also indirectly affect the excitation energies. In this case the vertical excitation energy should be also computed at optimal ground state geometry for the cam-B3LYP functional. The corresponding vertical excitation energy $\omega_i$ can be obtained within the harmonic approximation from the excited state quantities at B3LYP optimal ground state geometry $R_0^{B3LYP}$ as $0 - 0$ transition energy plus reorganization energy $\lambda_i$ calculated from the difference of the
gradients, Figure S3. The transition energy then reads

\[ \omega_i = \omega_i \left( R_0^{\text{B3LYP}} \right) + \lambda_g \left( R_0^{\text{B3LYP}} \right) - \lambda_i \left( R_0^{\text{B3LYP}} \right) + \lambda_i \]  

(S19)

where \( \lambda_g \left( R_0^{\text{B3LYP}} \right) \) and \( \lambda_i \left( R_0^{\text{B3LYP}} \right) \) are reorganization energies of the ground and excited state, respectively, calculated from the gradients at \( R_0^{\text{B3LYP}} \) ground state geometry and \( \omega_i \left( R_0^{\text{B3LYP}} \right) \) corresponds to the vertical excitation energy at the \( R_0^{\text{B3LYP}} \) ground state geometry. The same approach was applied for the calculation of the transition densities from the excited states, where the quantities at the excited state optimal geometry were obtained from the ones computed at the B3LYP ground state optimal geometry.

Figure S3: Schematic representation of the quantities at B3LYP ground state optimal geometry \( R_0^{\text{B3LYP}} \) and cam-B3LYP optimal ground state geometry \( R_0^{\text{cam-B3LYP}} \). The potential surfaces represent cam-B3LYP vibrational potential surface.
S5  Optical model of the dyads and individual monomers

S5.1  ZnPc

All the investigated TA experiments were performed by excitation of the system into the ZnPc $Q$ states. Because the $Q$ band is excited by the pump pulse, there is ESA from the $Q$ band to the higher excited states. In order to cover the spectral region of interest (14000-21000 cm$^{-1}$), 24 excited states were included to properly describe the transient spectra of the ZnPc and the exciton dyad. The reorganization energy for the environmental part of the spectral density $\lambda_i = 35$ cm$^{-1}$ was obtained by fitting the difference between absorption and fluorescence spectra of the isolated ZnPc. The correlation lifetime was set to $\tau_i = 170$ fs, which is commonly used for simulation of the optical spectra of the other tetrapyrroles e.g. chlorophylls. The intramolecular part of the spectral density was obtained within the vertical gradient approximation as described in Section S2.2.

The lifetime $\tau_N$ of the higher excited states $S_n$ of the ZnPc is set to 3 fs to account for the fast relaxation to the $Q_x$ and $Q_y$ electronic states. This value was set by fitting the width of the ZnPc soret band around 29000 cm$^{-1}$.

S5.2  Carotenoid

In the dyads, after the excitation to the ZnPc $Q$ band, the population is directly transferred to the Car $S_1$ state and the Car $S_2$ state is thus never populated, because it is energetically much higher than the ZnPc $Q$ band (Table S4). Therefore, the $S_2 \rightarrow S_N$ ESA signal is not observed in the spectra. In addition, when the $S_1$ state is not included, there is no ESA from the Car. Therefore the Car spectral properties in the dyad can be described by a single electronic state $S_2$.

The Car was described within the vibronic model to correctly include the mixing between Car $S_2$ states and ZnPc higher excited states, which have significant effect on the transient spectra. For the vibronic model, two normal modes with the strongest coupling to the elec-
tronic degrees of freedom were included into the exciton system. The reorganization energies and frequencies of the individual vibrational modes were obtained from the vertical gradient approach where the gradients for the excited and ground state were computed with the CAM-B3LYP functional whereas the frequencies were computed with the B3LYP functional (see Section S1 and S2.2). For the vibronic model only the two most intense normal modes were included: C-C stretch mode with frequency 1150 cm\(^{-1}\) and reorganization energy 566 cm\(^{-1}\) and the C=C stretch mode with frequency 1510 cm\(^{-1}\) and reorganization energy 1327 cm\(^{-1}\). The computed frequencies are consistent with the experimental frequencies of a wide range of Cars.\(^{10}\) For the environmental part of the Car spectral density the reorganization energy \(\lambda_{S_2} = 800\) cm\(^{-1}\) was obtained by fitting the width of the Car experimental vibronic transitions and the correlation lifetime \(\tau_{S_2}\) was used the same as for the ZnPc. The intramolecular spectral density \(J^{(UBO)}(\omega)\) was not used for the Car because the intramolecular vibrations were included into the exciton system.

The Car transition energy \(\varepsilon_{S_2}^{(0-0)} = 18850\) cm\(^{-1}\) as well as the transition dipole \(|\mu_{S_2}| = 8.584\) a.u. was obtained from TD-DFT CAM-B3LYP/6-31G(d) excited-state calculations. The lifetime of the Car \(S_2\) state \(\tau_{S_2}^{(Car)} = 100\) fs is the experimentally determined lifetime from time-resolved spectroscopy.\(^{11-13}\)

### S6 Comparison between full QM and exciton models

We report in Table S3 the comparison of energies and transition dipoles between the full-QM dyad and the exciton dyad for Dyad-Ph. All calculations were done at the TD-CAM-B3LYP/6-31G(d) level at the dyad B3LYP ground state geometry. Full-QM refers to a QM calculation on the entire dyad. The diabatic basis was obtained by using the multistate FED-FCD scheme (See Methods section in the main text), and then truncated to the first three states of the dyad \((S_2, Q_y, Q_x)\). The same states were computed from the exciton model with ZnPc-Ph and Car-Ph fragments.
Table S4 compares the diabatic states of the dyad with the excited states of the fragments (ZnPc or ZnPc-Ph, Car or Car-Ph).

Table S1: Excitation energies and transition moments of Dyad-Ph calculated with different schemes (see text). The numbers in the parentheses correspond to the energy difference from the $Q_x$ state.

|                      | $E$ [cm$^{-1}$] | $|\vec{\mu}|$ [AU] |
|----------------------|-----------------|---------------------|
| **Full-QM Dyad**     |                 |                     |
| $Q_x$                | 16090           | 4.94                |
| $Q_y$                | 16421 (+331)    | 3.08                |
| $S_2$                | 20225 (+4135)   | 8.40                |
| **Exciton system (reduced diabatic basis with $S_2,Q_y,Q_x$)** |                 |                     |
| $Q_x$                | 16280           | 4.55                |
| $Q_y$                | 16500 (+220)    | 3.09                |
| $S_2$                | 20414 (+4134)   | 8.42                |
| **Exciton system (ZnPc-Ph and Car-Ph fragments)** |                 |                     |
| $Q_x$                | 16200           | 4.35                |
| $Q_y$                | 16444 (+244)    | 3.08                |
| $S_2$                | 20711 (+4511)   | 7.80                |

Table S2: Comparison of diabatic states either obtained from the Full-QM calculation followed by diabatization or from calculation on the single fragments. The numbers in the parentheses correspond to the energy difference from the $Q_x$ state.

|                      | $E$ [cm$^{-1}$] | $|\vec{\mu}|$ [AU] |
|----------------------|-----------------|---------------------|
| **$Q_x$**            |                 |                     |
| **Full-QM Diabatic** |                 |                     |
|                       | 16341           | 3.51                |
| ZnPc                  | 16443           | 3.10                |
| ZnPc-Ph               | 16265           | 3.40                |
| **$Q_y$**            |                 |                     |
| **Full-QM Diabatic** |                 |                     |
|                       | 16502 (+161)    | 3.10                |
| ZnPc                  | 16501 (+58)     | 3.09                |
| ZnPc-Ph               | 16450 (+185)    | 3.08                |
| **Car $S_2$**        |                 |                     |
| **Full-QM Diabatic** |                 |                     |
|                       | 20350 (+4009)   | 8.90                |
| Car                   | 21601 (+5158)   | 7.63                |
| Car-Ph                | 20641 (+4376)   | 8.26                |
Table S3: Excitation energies and transition moments of Dyad-Ph calculated with different schemes (see text) with the ωB97X-D functional. The numbers in the parentheses correspond to the energy difference from the $Q_x$ state.

|        | $E [cm^{-1}]$ | $|\vec{\mu}| [AU]$ |
|--------|---------------|------------------|
| $Q_x$  | 15813         | 4.67             |
| $Q_y$  | 16111 (+298)  | 3.10             |
| $S_2$  | 20714 (+4901) | 8.53             |

Exciton system (reduced diabatic basis with $S_2,Q_y,Q_x$)

|        | $E [cm^{-1}]$ | $|\vec{\mu}| [AU]$ |
|--------|---------------|------------------|
| $Q_x$  | 15894         | 4.50             |
| $Q_y$  | 16145 (+251)  | 3.12             |
| $S_2$  | 20818 (+4924) | 8.46             |

Exciton system (ZnPc-Ph and Car-Ph fragments)

|        | $E [cm^{-1}]$ | $|\vec{\mu}| [AU]$ |
|--------|---------------|------------------|
| $Q_x$  | 15905         | 4.11             |
| $Q_y$  | 16127 (+222)  | 3.10             |
| $S_2$  | 21095 (+5190) | 7.90             |

Table S4: Comparison of diabatic states either obtained from the Full-QM calculation followed by diabatization or from calculation on the single fragments. All quantities are computed with the ωB97X-D functional. The numbers in the parentheses correspond to the energy difference from the $Q_x$ state.

|        | $E [cm^{-1}]$ | $|\vec{\mu}| [AU]$ |
|--------|---------------|------------------|
| $Q_x$  |               |                  |
| Full-QM Diabatic | 15957 | 3.53             |
| ZnPc   | 16113         | 3.13             |
| ZnPc-Ph| 15946 (+4794) | 8.99             |

|        | $E [cm^{-1}]$ | $|\vec{\mu}| [AU]$ |
|--------|---------------|------------------|
| $Q_y$  |               |                  |
| Full-QM Diabatic | 16148 (+191) | 3.11             |
| ZnPc   | 16171 (+58)   | 3.11             |
| ZnPc-Ph| 16130 (+184)  | 3.10             |

|        | $E [cm^{-1}]$ | $|\vec{\mu}| [AU]$ |
|--------|---------------|------------------|
| $S_2$  |               |                  |
| Car    | 21946 (+5833) | 7.62             |
| Car-Ph | 21046 (+5100) | 8.22             |
Figure S4: Comparison of the simulated absorption spectra of the dyads based on the exciton model with overlapping monomers as presented in the main text (blue) and the full QM dyad, where the excited states were computed at QM level for the full dyad molecule (orange). The full QM dyad leads to larger splitting of the ZnPc \( Q \) states and therefore broader \( Q \) band \( \sim 14500 \) in agreement with the experiment. On the other hand the full QM dyad spectra is too blue-shifted compared to the experimental spectra, which is probably caused by overestimation of the electron delocalization with TD-DFT approach. The experimental spectra for the Dyad-Ph were obtained from Ref. 14 and for Dyad-PhA from Ref. 15.

S7 Origin of the signals in TA difference spectra

The effect of the interaction between ZnPc higher excited states and the doubly excited state of the dyad can be again demonstrated on a simplified system consisting only two interacting states \( |S_n^{ZnPc}0\rangle \) and \( |Q_x^{ZnPc}S_2\rangle \). The resulting exciton states are then:

\[
|1\rangle = c_1 |S_n^{ZnPc}0\rangle + c_2 |Q_x^{ZnPc}S_2\rangle
\]

\[
|2\rangle = \tilde{c}_1 |S_n^{ZnPc}0\rangle + \tilde{c}_2 |Q_x^{ZnPc}S_2\rangle
\]
The ESA from the ZnPc $Q_{x}^{ZnPc}$ to the higher excited state $S_{n}^{ZnPc}$ is for the interacting system proportional to

$$\left|\mu_{ESA}^{Q_{x} \rightarrow 1}\right|^2 \propto |\langle Q_{x}, 0 | \mu | 1 \rangle|^2 = c_1^2 \left|\mu_{S_n}^{Q_{x} \rightarrow S_n}\right|^2 + c_2^2 \left|\mu_{Car}^{S_2}\right|^2 + 2c_2c_1\mu_{ESA}^{Q_{x} \rightarrow S_n}\mu_{Car}^{S_2}$$

and the ESA to the doubly excited state which corresponds to the signal in the Car $S_2$ region reads as:

$$\left|\mu_{ESA}^{Q_{x} \rightarrow 2}\right|^2 \propto |\langle Q_{x}, 0 | \mu | 2 \rangle|^2 = c_1^2 \left|\mu_{S_n}^{Q_{x} \rightarrow S_n}\right|^2 + c_2^2 \left|\mu_{Car}^{S_2}\right|^2 + 2c_2c_1\mu_{ESA}^{Q_{x} \rightarrow S_n}\mu_{Car}^{S_2}$$

For our J-type orientation of the dyad $c_1c_2 > 0$ while $\mu_{ESA}^{Q_{x} \rightarrow S_n}$, $\mu_{Car}^{S_2}$ > 0 for the strongest interacting states, which leads to the enhancement of the $Q_{x}^{ZnPc} \rightarrow S_{n}^{ZnPc}$ ESA and decrease of the $Q_{x} \rightarrow Q_{x}^{ZnPc}S_{2}^{Car}$ ESA. For the noninteracting system the later excitation has exactly the Car $S_2$ state transition dipole, therefore the ESA has exactly the same intensity as the Car GSB and no signal is observed in the difference spectra in the Car $S_2$ spectral region $> 18000cm^{-1}$.
S7.1 Effect of the geometry and Ph linker

Figure S5: TA difference spectra for the dyads with the phenyl (a) and phenyl-amino linker (b) for the 10 double-bond carotenoid. The experimental (black) difference spectra is compared to the simulated ZnPc-Ph(A) in the dyad geometry (orange) difference spectra. The simulated difference signal corresponds to the dyad spectra with no coupling between ZnPc and Car. For the Dyad-Ph the plotted spectra correspond to the difference from the optimized ZnPc, whereas for the Dyad-PhA to the difference from the optimized ZnPc-PhA. The experimental spectra for the Dyad-Ph were obtained from Ref. 14 and for Dyad-PhA from Ref. 15.
From the absorption spectra in Figure 5 of the main text, it can be seen that the energy gap between ZnPc Q state Car $S_2$ is underestimated by the TD-DFT approach with CAM-B3LYP functional. This also affects the TA spectra because the GSB signal is red-shifted. To investigate this effect, the excitation energy of the Car $S_2$ state was shifted to match the experimental one. This system was then used to compute the TA and difference spectra (Figure S6). The overall shape of the TA spectra is very similar to the case without the shift of the Car excitation energy (Figure 6), as is the difference spectra between Dyad and the ZnPc monomer. However, in Figure S6 the experimental zero-energy crossing in the difference spectra is now precisely reproduced.

Figure S6: TA spectra for the dyads with the phenyl (upper part) and phenyl-amino linker (lower part) for the 10 double-bond carotenoid with shifted excitation energy to match the experimental one. The left panels show the full spectra, where the solid lines correspond to the experimental results whereas the dashed ones to the simulated spectra. The spectrum of the ZnPc-PhA was shifted to have the same energy of the main ZnPc GSB peak as the Dyad-PhA as was done for the experimental spectra in Ref. 15. The right panels show the difference spectra between the dyad and the ZnPc (or ZnPc-PhA for the case of the the dyad with the phenylamine linker). The experimental spectra for the Dyad-Ph were obtained from Ref. 14 and for Dyad-PhA from Ref. 15.
S7.2 TA spectra for the two conformations

There are two possible conformations of the dyads with different population at thermal equilibrium. To assess the contribution of the less populated conformation 1 on the final spectra of the dyad, we simulated the TA spectra for the conformation 1 of both Dyad-Ph and Dyad-PhA. The final equilibrium spectra is obtained by combination of the TA spectra for the conformation 2 weighted by 0.65 (0.68) and TA spectra for conformation 1 weighted by 0.35 (0.32) for the Dyad-Ph and Dyad-PhA (values in the brackets), respectively. The final spectra together with the difference spectra is plotted in Figure S7.

Figure S7: TA spectra for the dyads with the phenyl (upper part) and phenyl-amino linker (lower part) for the 10 double-bond carotenoid. Thermal equilibrium occupation of the dyad conformations was used to simulate the spectra. The left panels show the full spectra, where the solid lines correspond to the experimental results whereas the dashed ones to the simulated spectra. The spectrum of the ZnPc-PhA was shifted to have the same energy of the main ZnPc GSB peak as the Dyad-PhA as was done for the experimental spectra in Ref. 15. The right panels show the difference spectra between the dyad and the ZnPc (or ZnPc-PhA for the case of the dyad with the phenylamine linker). The experimental spectra for the Dyad-Ph were obtained from Ref. 14 and for Dyad-PhA from Ref. 15.
S8 Carotenoid $S_1$ state effect

S8.1 Fitting of the reorganization and excitation energy.

The carotenoid $S_1$ optical properties were estimated from fitting of the two photon absorption and fluorescence spectra. The experimental TPA results identify three peaks which can be related to the $S_1$ transition and additional peaks with a possible TPA contribution from the bright $S_2$ state, Table S5. All of these states are separated by 1400 cm$^{-1}$, which also corresponds to the effective normal mode frequency of the Car $S_2$ transition. The description of the vibronic progression by a single effective mode instead of the two modes (C-C and C=C modes) was successfully used in several spectroscopic studies of the Cars and excitation transfer between Chlorophylls and Cars. These results suggest that the individual peaks could correspond to the vibrational states of the $S_1$ electronic state.

The lowest resolved peak in the TPA study was at 15600 cm$^{-1}$ which is energetically much higher than the ZnPc $Q$ transitions. This would not favor either the exciton mixing or the excitation transfer from the ZnPc to the Car $S_1$ state. The fluorescence experiments available are on the structurally similar $\beta$-carotene, which also has 10 double bonds in the conjugation chain. They suggest that the 0-0 excitation energy for the $S_1$ state is 14500 cm$^{-1}$. Because the Car used in the dyad has a phenyl head, we can assume that the effective conjugation length of the studied Car is even larger, leading to a lower $S_1$ excitation energy than for $\beta$-carotene. In particular, the 0-0 transition of the Car in the dyad should be much lower than 15600 cm$^{-1}$. The lower boundary for the 0-0 transition energy is set by lycopene, which has 11 double bonds in the conjugation chain and an $S_1$ the excitation energy of 13200 cm$^{-1}$. Based on these results, we infer that there is one more state below the lowest state determined in the TPA with too small intensity to be resolved in the TPA experiment. We set the energy of this state to 14200 cm$^{-1}$ from our assumption that the individual peaks in the TPA spectra correspond to a vibronic progression with frequency 1400 cm$^{-1}$.
The Huang-Rhys factor of the GS $\rightarrow$ S$_1$ transition was obtained by fitting the ratio of the intensities $I_i/I_3$ of the i-th vibrational state $I_i$ and the third (second resolved) vibrational state, with the restriction of not having higher intensity for the higher vibrational states. The higher peaks might include possible TPA contributions from the Car S$_2$ state and therefore they were not included in the fitting but serve only as the upper limit for the peak intensity. The best fit was obtained for a reorganization energy $\lambda_{S1}^{10DB} = 8970 \text{cm}^{-1}$. All the data used for the description of the effect of the Car S$_1$ state are reported in Table S5.

The reorganization energy of the single vibrational mode for the 8 DB Car was obtained the same way as explained above for the 10 DB Car, from the fitting of the experimental TPA spectra as $\lambda_{S1}^{8DB} = 6216 \text{cm}^{-1}$, Table S5. In the TPA experiments for the 8DB Car the lowest resolved peak was at 15600 cm$^{-1}$, which is exactly the same as for the Car with 10DB. However, the S$_1$ excitation energy should be larger for the 8 DB Car than for the 10 DB Car. Therefore, we assume that for the Car with 8 DB the lowest observed band does correspond to the 0-0 excitation energy. This is also consistent with the S$_2$ state energy, which is $\sim 1400 \text{cm}^{-1}$ above the S$_2$ state of the 10 DB Car.$^{15}$

For the Car with 11 DB, no experimental data are available. The energy of the 0-0 transition of the S$_1$ state was linearly extrapolated as a half of the difference between 8 DB and 10 DB Cars to 13500 cm$^{-1}$ which is close to the excitation energy of lycopene (which has 11 DB in the conjugation chain). The reorganization energy was kept the same as for the Car with 10 DB.

![Figure S8: Transition density of the Car 3-rd singly excited state which corresponds to the single excitation contribution of the S$_1$ state with the A$_g$ symmetry.](image-url)
Table S5: The experimental and estimated parameters of the Car $S_1$ transition. The vibronic spectra was estimated using shifted harmonic potential surfaces with single effective vibrational mode $1400\text{cm}^{-1}$ and reorganization energy $\lambda_{10DB} = 8970\text{cm}^{-1}$ and $\lambda_{8DB} = 6216\text{cm}^{-1}$ for the 10DB and 8DB in the conjugation chain of the Car. For the fitting the ratio between the peak at $18600\text{cm}^{-1}$ and the lower ones was used.

| Car 10 DB | Car 8DB |
|-----------|---------|
| frequency $[\text{cm}^{-1}]$ | TPA intensity $I$ | estimated intensity $\langle 0 | i' \rangle$ | frequency $[\text{cm}^{-1}]$ | TPA intensity $I$ | estimated intensity $\langle 0 | i' \rangle$ |
| 14200 | 4.75 | 1.0 | 0.041 | 15600 | 3.57 | 3.55 | 0.109 |
| 15600 | 9.2 | 6.37 | 0.103 | 17000 | 10.7 | 15.8 | 0.229 |
| 17000 | 43.6$^a$ | 20.4 | 0.184 | 18200 | 35.0$^a$ | 35.0$^a$ | 0.341 |
| 18600 | 69.9$^b$ | 69.9 | 0.340 | 19600 | 61.9 | 51.8 | 0.415 |
| 20000 | 89.2$^b$ | 89.5 | 0.385 | 21000 | 95$^b$ | 57.8 | 0.437 |

$^a$ The estimated intensity was normalized to this experimental peak.
$^b$ Peaks with possible contribution of the TPA from the Car $S_2$ state. These states were not included into the fitting.

S8.2 Förster transfer rates

Figure S9: $Q_x$ lifetimes for three dyads with carotenoids of different conjugation lengths. The simulated lifetimes (solid lines) were computed from the Förster rates as a function of the Car $S_1$ excitation energy. The filled areas around the lines correspond to the range of the lifetimes for the reorganization energies $\pm 1000\text{cm}^{-1}$ from the fitted value. The arrows at the computed lifetimes represent the uncertainty of the experimental Car $S_1$ excitation energy. The simulated lifetimes are compared with the experimental ones (dashed lines) obtained from transient absorption experiments combined with EADS analysis.\textsuperscript{15}
S8.3 TA difference spectra

The intensity of the Car $S_1$ signal (ESA $S_{1^{Car}} \rightarrow S_{n^{Car}}$) from the excitonically mixed state is proportional to the transition dipole from the mixed state $|1\rangle$ to the Car $S_n$ states

$$ESA \left(1 \rightarrow S_{n^{Car}} \right) \propto \left| \left( c_1 \langle Q_x^{ZnPc}, 0^{Car} | + c_2 \langle 0^{ZnPc}, S_1^{Car} | \right) \mu |0, S_{n^{Car}} \rangle \right|^2 = c_2^2 \left| \mu_{ESA}^{S_{1^{Car}} \rightarrow S_{n^{Car}}} \right|^2.$$  

(S20)

This signal is therefore proportional to the contribution of the Car $S_1$ state to the exciton eigenstate.

The Car $S_1$ TA signal multiplied by a factor of 0.1 or 0.2 is shown alongside with the difference TA spectra in Figure S10. From this comparison it is clearly visible that $\sim 10\%$ contribution of the Car $S_1$ state to the lowest bright state of the dyad would be needed to explain the simulated signal originating from interaction of the ZnPc higher excited states with the doubly excited state, and $\sim 20\%$ contribution of the Car $S_1$ is needed to explain the experimental signal. The 10\% contribution would correspond to a coupling of $\sim 100\, cm^{-1}$ between 0-0 transitions, which is unrealistically high. The 20\% contribution needed for explanation of the experimental spectra would correspond to an even larger coupling of $\sim 190\, cm^{-1}$. Taking into account the Franck-Condon factors (Table S5), this would imply a bare electronic coupling $> 2000 \, cm^{-1}$. 

S24
Figure S10: TA difference spectra for the dyad with with phenyl-amino linker. The computed (blue) and experimental\textsuperscript{15} (black) difference spectra for the Dyad-PhA are compared with experimental $S_1$ signal\textsuperscript{11} (green) obtained after excitation of isolated Car with 10DB. The Car $S_1$ signal is scaled by factor 0.1 and 0.2 to have the same intensity as a simulated dyad difference signal and experimental dyad difference signal, respectively.

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