Photoexcited State Dynamics and Singlet Fission in Carotenoids

Supporting Information

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1 Parametrization of the UV-Peierls Hamiltonian

Figure S1: Vertical (a) and relaxed (b) singlet excitation energies of UV-Peierls model with $U = 7.25$ eV and $V = 3.25$ eV, found by solving eq (5) of the main paper. $N$ is the number of conjugated carbon atoms of the system. The vertical energy gaps of $\sim 0.1$ eV between $1^1B_u^+$ (magenta) and $2^1A_g^-$ (orange) for $18 \leq N \leq 26$ agree with the corresponding excitation energies reported in ref. 1.
Figure S1 illustrates the diabatic vertical and relaxed excitation energies of the UV-Peierls model parametrized for direct internal conversion from the $1^1B_u^+$ state to the $2^1A_g^-$ state. The parametrization is performed such that the vertical excitation energy gap between the $1^1B_u^+$ to the $2^1A_g^-$ states reproduces the excitation energies reported in Table 2 of ref 1.

2 Parametrization of the symmetry breaking Hamiltonian, $\hat{H}_\epsilon$

As described in ref 2, $\hat{H}_\epsilon$ is optimized under the constraint $|\epsilon_n| < \epsilon_{\text{max}}$ such that the ground state $\pi$-electron density on C-atom $n$ reproduces the Mulliken charge densities of the $\pi$-system found via ab initio density functional theory (DFT) calculations. The optimized $\hat{H}_\epsilon$ is given in Table S1. The cut-off $\epsilon_{\text{max}} = 1.0$ is chosen such that $\Psi(t = 0)$ retains sufficient $1^1B_u^+$ character while accurately reproducing the DFT densities with a coefficient of variation $r^2(\epsilon) = 0.92$. 
Table S1: The π-electron Mulliken charges from the ab-initio DFT calculation, parameters for $H_\epsilon$ found for $\epsilon_{\text{max}} = 1.0$ eV, and the expectation values of number densities calculated from the parametrized $H_\epsilon$. In order to maintain π-electron charge neutrality, each ab-initio charge was increased by 0.05q. The chemical formula of neurosporene is shown in Figure 1 of the main paper.

| Carbon site, n | Mulliken charges (q) | $\epsilon_n$ (eV) | $\langle \hat{N}_n - 1 \rangle$ | $\epsilon_n$ (eV) | $\langle \hat{N}_n - 1 \rangle$ |
|---------------|----------------------|----------------|-------------------------------|----------------|-------------------------------|
| 1             | 0.14                 | -1.00          | 0.17                          | -1.00          | 0.17                          |
| 2             | -0.05                | 0.81           | -0.14                         | 0.56           | -0.14                         |
| 3             | -0.18                | 1.00           | 0.05                          | 1.00           | 0.06                          |
| 4             | -0.07                | 1.00           | -0.10                         | 0.82           | -0.10                         |
| 5             | 0.15                 | -1.00          | 0.15                          | -1.00          | 0.15                          |
| 6             | -0.14                | 0.27           | -0.10                         | 0.02           | -0.10                         |
| 7             | -0.07                | 1.00           | 0.03                          | 1.00           | 0.03                          |
| 8             | -0.16                | 1.00           | -0.09                         | 0.84           | -0.09                         |
| 9             | 0.13                 | -1.00          | 0.12                          | -0.01          | -0.07                         |
| 10            | -0.11                | 1.00           | -0.03                         | 1.00           | -0.04                         |
| 11            | -0.10                | 1.00           | -0.02                         | 1.00           | -0.03                         |
| 12            | -0.11                | 0.32           | -0.09                         | 0.09           | -0.09                         |
| 13            | 0.14                 | -1.00          | 0.13                          | -1.00          | 0.13                          |
| 14            | -0.18                | 1.00           | -0.09                         | 0.92           | -0.10                         |
| 15            | -0.05                | 1.00           | 0.05                          | 1.00           | 0.06                          |
| 16            | -0.19                | 0.90           | -0.14                         | 0.61           | -0.14                         |
| 17            | 0.14                 | -1.00          | 0.18                          | -1.00          | 0.17                          |

3 Probabilities that the adiabatic states, $S_1$, $S_2$ and $S_3$ occupy the diabatic states $2^1A_g^-$, $1^1B_u^+$ and $1^1B_u^-$

Figure S2 illustrates the probabilities that the adiabatic states $S_1$, $S_2$, and $S_3$ occupy the diabatic states $2^1A_g^-$, $1^1B_u^+$, and $1^1B_u^-$. Adiabatic states are $\sim$ 90% occupied by the diabatic states at all times. Using the probabilities that the triplet-pair states, $2^1A_g^-$ and $1^1B_u^-$, occupy the adiabatic states, $S_1$ and $S_2$, the ‘classical’ total triplet-pair yield can be calculated via eq (7) of the main paper.
Figure S2: Probabilities as a function of time that the adiabatic states, $S_1$, $S_2$ and $S_3$, occupies the diabatic states, $2^1A_g^-$, $1^1B_u^+$ and $1^1B_u^-$. Results are for neurosporene ($N = 18$) with $V = 2.75$ eV.

References

(1) Taffet, E. J.; Lee, B. G.; Toa, Z. S. D.; Pace, N.; Rumbles, G.; Southall, J.; Cogdell, R. J.; Scholes, G. D. Carotenoid Nuclear Reorganization and Interplay of Bright and Dark Excited States. *The Journal of Physical Chemistry B* **2019**, *123*, 8628–8643.

(2) Manawadu, D.; Valentine, D. J.; Barford, W. Dynamical Simulations of Carotenoid Photoexcited States using Density Matrix Renormalization Group Techniques. 2022; https://arxiv.org/abs/2211.02022.