Supplementary Materials for

Intermolecular vibrations mediate ultrafast singlet fission

Hong-Guang Duan, Ajay Jha, Xin Li, Vandana Tiwari, Hanyang Ye, Pabitra K. Nayak, Xiao-Lei Zhu, Zheng Li*, Todd J. Martinez, Michael Thorwart*, R. J. Dwayne Miller*

*Corresponding author. Email: dmiller@lphys.chem.utoronto.ca (R.J.D.M.); michael.thorwart@physik.uni-hamburg.de (M.T.); zheng.li@pku.edu.cn (Z.L.)

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Supplementary Materials

In these Supplementary Materials, we first show the measured X-ray diffraction data of polycrystalline pentacene. Then, we describe the details of the global fitting approach and the obtained two-dimensional (2D) decay-associated map. We further explain the details of the difference of the frequency resolution between the transient grating (TG) and the 2D measurements. In addition, we show the differences of the vibrational frequencies and their Huang-Rhys factors between the singlet excited state and triplet-pair state. Finally, we describe the two-state two-mode model and its parameters. The calculated dynamics along the coupling mode is presented.

I. X-RAY DIFFRACTION DATA

First, we show the measured X-ray diffraction data in Fig. S1.

II. GLOBAL FITTING AND TIMESCALE OF PRIMARY SINGLET FISSION

Multidimensional global fits of both experimental arrays of 2D spectra were performed in accordance with the available algorithm developed earlier (59). A detailed description of the technique can be found in the Supplementary Information of Ref. (60). In this method, a sequence of 2D spectra taken at different $T$ values are collected to form a three-dimensional array $S(\omega, \tau, T)$. This 3D array is then decomposed into a sum of two-dimensional decay-associated spectra $A_i(\omega, \tau)$ with individual exponential decays of correspondingly associated lifetimes $\tau_i$ according to

$$S(\omega, \tau, T) = \sum_i A_i(\omega, \tau) \exp(-T/\tau_i). \quad (S1)$$

We apply the global fitting to the 2D spectra of pentacene. The decay-associated spectrum $A_i(\omega, \tau)$ for the retrieved lifetime of 100 fs is shown in Fig. S2. Based on the fitting, we observe one positive peak whose center is located at $(\omega, \tau) = (14600, 14600)\text{cm}^{-1}$ and one negative peak at $(\omega, \tau) = (14600, 14000)\text{cm}^{-1}$, respectively. Accordingly, a positive peak indicates the decay of magnitude of the center peak which is associated to the GSB. In addition, the negative peak manifests the increase of the amplitude of the ESA process, which shows the generation of the triplet-pair state. Based on our fitting analysis, we observe that the primary step of singlet fission occurs in about 100 fs.
FIG. S1. X-ray diffraction pattern of polycrystalline pentacene.

FIG. S2. Retrieved decay-associated spectrum for the lifetime of 100 fs. It shows the generation of the triplet-pair state during the primary step of singlet fission. The red peak indicates that the magnitude of the GSB decreases rapidly and the blue peak manifests the increase of magnitude of the ESA peak.
III. 2D CORRELATION ANALYSIS IN 2D ELECTRONIC SPECTRA

In this brief overview, we summarize the details of the 2D correlation analysis of measured 2D electronic spectra. As described in the previous section, the 2D residuals are obtained after applying the global fitting to the time series of the measured 2D electronic spectra. Then, the correlation analysis can be described by

$$C(\omega_t, \omega_\tau) = \text{corr} [R(\omega_t, \omega_\tau, T), R(\omega_\tau, \omega_t, T)],$$  \hspace{1cm} (S2)

where corr evaluates the correlation with respect to the waiting time $T$.

IV. FREQUENCY RESOLUTION IN THE TG AND 2D MEASUREMENTS

In this section, we discuss the difference of the frequency resolution in the TG and 2D spectroscopic measurements. In the TG spectrum, we probe the signal up to 2 ps with a time step of 2 fs. Thus, the obtained resolution of the vibrational frequency is $d\omega = 16.5 \text{ cm}^{-1}$. In our 2D spectroscopic measurement, the 2D spectra are recorded up to 2.1 ps with equally distributed time steps of 10 fs. That is, the frequency resolution is $d\omega = 15.7 \text{ cm}^{-1}$. This gives rise to a slight difference of the resolved vibrations in TG and 2D spectroscopic measurements.

V. WAVELET TRANSFORM

In this section, we describe the technical principles of the wavelet transform. The details have been presented in Refs. (61, 62). We start from the definition of a zero-mean and short-time oscillating function $\psi$, called a “mother” wavelet, which is used to decompose a one- or multi-dimensional real signal into different frequency bands. This mother wavelet function is translated in time by $t$ and stretched by the scale of $\omega^{-1}$, giving the wavelet “atom” function

$$\psi_{t, \omega}(t') = \sqrt{\omega} \psi([t' - t]/\omega).$$ \hspace{1cm} (S3)

It provides the effective basis for the transformation. The two most common transforms are the discrete wavelet transform and the continuous wavelet transform (63). The discrete one decomposes the signal into several frequency bands and is frequently used for data and image compression. The continuous one, which is used in this paper, is based on an expansion of a temporal signal $f(t)$ via the inner product of the function with a wavelet atom,

$$\text{CWT}_f(t, \omega) = \int_{-\infty}^{+\infty} dt' f(t') \sqrt{\omega} \psi^*([t' - t]/\omega).$$ \hspace{1cm} (S4)

The parameter $t$ indicates where the wavelet atom is centered, while the scale parameter $\omega^{-1}$ controls the relative width of the wavelet atom compared to the mother wavelet function. This nonlinear integral transform provides a high time resolution of high-frequency components, while for the slowly varying components of the signal, the frequency resolution is high. It projects the signal onto basis functions with a varying “center” frequency and a varying range fixed by the scaling factor.

VI. QM/MM SIMULATION

The pentacene crystal is modeled as a finite system of the size $76 \times 33 \times 26 \text{Å}^3$ without periodic boundary condition. The choice of QM and MM regions are illustrated in Fig. S3. The structure of the QM region is optimized while the MM regions remains intact.

VII. CALCULATED VIBRATIONAL MODES AND ASSOCIATED HUANG-RHYS FACTORS

In this section, we present the calculated vibrational modes in the frequency range between 260 and 900 cm$^{-1}$ in Fig. S4. The calculated vibrational motions of the pronounced high-frequency modes at 1196 and 1517 cm$^{-1}$ are shown in Fig. S5.
VIII. CORRELATION ANALYSIS OF LOW-FREQUENCY MODES OF 177 CM$^{-1}$ AND 150 CM$^{-1}$

In this section, we describe the correlations of the low-frequency modes of 177 cm$^{-1}$ and 150 cm$^{-1}$ on the singlet excited and triplet-pair state, which is calculated from the overlap between the eigenvectors of the vibrational modes in the $S_1$ and $T_1T_1$ states. In the TG and 2D spectroscopic measurements, our results strongly suggest that the low-frequency mode of 177 cm$^{-1}$ is coherently transferred to the lower excited state $T_1T_1$ with the frequency shifted to 150 cm$^{-1}$. This coherent process has been confirmed by our advanced quantum chemistry calculations. Here, we perform the correlation analysis of the vibrations on both electronic excited states. The results are shown in Fig. S6. Based on the observation, we find a strong magnitude of an off-diagonal peak located at (177 cm$^{-1}$, 148 cm$^{-1}$). Clearly, the newly generated mode of 150 cm$^{-1}$ on the $T_1T_1$ state emerges due to the transfer of the vibrational motion at 177 cm$^{-1}$ and to the change in frequency on the $T_1T_1$ state.
FIG. S5. The calculated vibrational motion of the high-frequency modes at 1196 and 1517 cm$^{-1}$.

FIG. S6. The correlation analysis of the low-frequency modes in the $S_1$ and $T_1T_1$ states. It shows a strong correlation (0.52) between the 177 cm$^{-1}$ mode in the $S_1$ state and the 148 cm$^{-1}$ mode in the triplet-pair state. The frequencies listed on the axes are not evenly spaced.

IX. CHANGE OF THE ELECTRONIC COUPLING BY INTERMOLECULAR ROCKING MODE

To assign the origin of the intermolecular rocking mode, we examine the change of the electronic coupling between the electronic singlet excited state $S_1$ and the triple-pair state $T_1T_1$ by modulating the displacement of rocking motion of pentacene. Based on the calculation in Fig. S7, the electronic coupling between $S_1$ and $T_1T_1$ is dramatically
modulated by intermolecular rocking mode. For this reason, we consider this mode as the coupling mode between the singlet and the triplet-pair states in our model.

![Graph](image.png)

**FIG. S7.** The fluctuation of electronic coupling modulated by intermolecular rocking mode (177 cm\(^{-1}\)).

### X. TWO-STATE TWO-MODE MODEL

To illustrate the role of the intermolecular rocking mode, we construct the standard two-state two-mode model based on the parameters from quantum chemistry calculations. In order to simplify the calculation, we only select one high-frequency (tuning) mode which is the intermolecular rocking mode at 177 cm\(^{-1}\) in order to construct the PESs. Thus, on the basis of these two modes, a minimal model of a conical intersection can be constructed with the proper parameters.

The total Hamiltonian can be written as

\[
H = H_{\text{mol}} + H_{\text{env}},
H_{\text{mol}} = H_e + H_{TT},
H_e = |e\rangle (h_1 - \epsilon/2) \langle e|,
H_{TT} = |TT\rangle (h_2 + \epsilon/2) \langle TT| + (|TT\rangle V \langle e| + \text{h.c.}).
\]

Here, \(\epsilon\) is the electronic energy difference between singlet excited state \(S_1\) and triplet-pair state \(T_1T_1\). The vibrational part of the Hamiltonians \(h_1\) and \(h_2\) are associated with the \(S_1\) and \(T_1T_1\) state, respectively. They include two vibrational modes, the tuning \((Q_t)\) and coupling mode \((Q_c)\). They are given by \(h_g = \sum \Omega_i (P_i^2 + Q_i^2)\) and \(h_1 = h_g - \kappa Q_i\) and \(h_2 = h_g + \kappa Q_i\), where \(\Omega_i\) denotes the vibrational frequencies of the tuning and coupling modes, respectively. In addition, \(\kappa\) is the vibronic coupling strength. The electronic coupling between two electronic excited states is assumed to be linearly related to the coupling mode \(Q_c\), such that \(V = \Lambda Q_c\) with the electronic coupling strength \(\Lambda\). Furthermore, we assume that all relevant interactions between the two electronic PESs are captured by the coupling mode, which is explicitly included. Thus, the bath only couples vibrational states within the same electronic PES, and we assume that the two vibrational modes are coupled to their own linear bath according to the Hamiltonian

\[
H_{\text{env}} = \sum_{\alpha} \left[ \frac{p_{\alpha}^2}{2m_{\alpha}} + \frac{m_{\alpha}\omega_{\alpha}^2}{2} \left( x_{\alpha} + \frac{c_{\alpha}Q_{1\alpha}}{m_{\alpha}\omega_{\alpha}^2} \right)^2 + \frac{q_{\alpha}^2}{2M_{\alpha}} + \frac{M_{\alpha}\nu_{\alpha}^2}{2} \left( y_{\alpha} + \frac{d_{\alpha}Q_{2\alpha}}{M_{\alpha}\nu_{\alpha}^2} \right)^2 \right].
\]

Here, the momenta of the bath oscillators are denoted as \(p_{\alpha}\) and \(q_{\alpha}\), while their coordinates, masses, and frequencies are denoted by \(x_{\alpha}, m_{\alpha}, \omega_{\alpha}\) and \(y_{\alpha}, M_{\alpha}, \nu_{\alpha}\). The respective coupling constants are \(c_{\alpha}\) and \(d_{\alpha}\). The baths are
characterized by the spectral densities. Throughout this work, we assume that both the tuning and coupling mode experience fluctuations with an Ohmic spectral distribution according to $J_{c/t}(\omega) = \eta_{c/t} \omega e^{-\omega/\omega_c}$. Here, $\eta_{c/t}$ are the damping strengths for the coupling and tuning mode, respectively, and $\omega_c$ is the cutoff frequency. We assume that the two baths have the same cutoff frequencies.

Based on the results for the parameters obtained from the quantum chemistry calculations, we assume for the tuning and coupling modes $\Omega_t = 1013 \text{ cm}^{-1}$ and $\Omega_c = 177 \text{ cm}^{-1}$, respectively. Moreover, the values of the vibronic coupling strength of the tuning and the coupling modes are obtained from the Huang-Rhys factors and we have $\kappa = 300 \text{ cm}^{-1}$ and $\Lambda = 150 \text{ cm}^{-1}$. In addition, to mimic the dissipation induced by the phonons in the environment, we assume the damping strength $\eta_c = \eta_t = \eta = 2.0$ and the cutoff frequency $\omega_c = 200 \text{ cm}^{-1}$. With these parameters, the population dynamics of the wave-packet along the coupling mode has been calculated up to 1 ps. The dynamics along coupling and tuning modes are shown in main text. It clearly shows the wave-packet transfer from the upper state to the lower state within an ultrafast timescale. To quantify the time scale of the population transfer, the wave packet has been summed along the reaction coordinates and the obtained kinetics are shown in Fig. S8. Based on the exponential fitting, we find the transfer time of 180 fs, which is actually slightly larger than the experimental observation of 100 fs. However, this simple two-state two-mode model solely takes into account one high-frequency vibrational mode with strong vibronic coupling. In our measurements, more vibrations are retrieved with strong vibronic couplings, which further reduce the barrier between the singlet excited state and the triplet-pair states. They speed up the transition of the wave packet through the conical intersection. In addition, we show the population transfer at $Q_c = 0$ from $S_1$ to $T_1T_1$ in Fig. S9. We observe clear oscillations of the population of the electronic state $T_1T_1$ with a period of 32 fs, which indicates the vibrational coherence of the tuning mode. Based on our calculation, we demonstrate that the vibrational coherence of the coupling mode can not be transferred through the conical intersection, but is determined by the target PES.

![FIG. S8. Population transfer of the wave packet from the higher excited state (red solid line) to the lower excited state (blue solid line) with a time scale of 180 fs.](image-url)
FIG. S9. Population dynamics of the wave packet at $Q_c = 0$ from $S_1$ to $T_1 T_1$. 
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