

Optical-Cavity Manipulation of Conical Intersections and Singlet Fission in Pentacene Dimers

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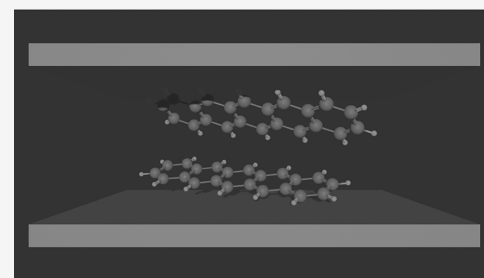


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ABSTRACT: We demonstrate how the singlet fission process in pentacene dimers mediated by a conical intersection is controlled by coupling the molecule to a confined optical cavity photon mode. By following the polariton quantum dynamics of a conical intersection coupled to a cavity mode taking into account vibrational relaxation and cavity loss, we find that the singlet fission can be significantly suppressed because the polaritonic conical intersection is pushed away from the initial Franck–Condon excitation region.



Optical cavities provide a powerful means to manipulate the photophysical and photochemical properties of molecules and materials. Molecules embedded in an optical cavity couple to the vacuum field of the cavity photon mode, forming hybrid light–matter states known as polaritons in the strong coupling regime, where the coupling strength is stronger than the decay rates of the molecule and the cavity mode. The effective coupling strength $g = \mu\sqrt{N\hbar\omega_c/2\epsilon_0V}$ depends on the cavity mode volume V , the transition dipole moment μ , and the number of molecules N . ω_c is the cavity frequency, and ϵ_0 is the electric permittivity of vacuum. Strong coupling and polariton formation have been demonstrated in numerous experiments even for a single molecule.^{1–5} A plethora of chemical processes including photoisomerization, ground state chemical reactions, and energy and electron transfer have been altered in cavities,^{6–12} stimulating intensive theoretical studies.^{13–22}

Singlet fission (SF) is a spin-allowed process whereby a singlet exciton splits into two triplet excitons $S_1 \rightarrow 2T_1$.^{23–30} This carrier multiplication process, whose mechanism is still under debate, has drawn much attention since it can potentially enhance the efficiency of photovoltaic cells. SF can occur either through direct electronic coupling between molecules or via stepwise one-electron processes involving charge-transfer states. Recent experiments suggest that it can also be mediated by conical intersections (CI).^{29,31,32}

Motivated by the capability of optical cavities to alter photochemical processes, it is intriguing to explore their ability to modify the SF process. Based on a kinetic analysis for the Frenkel exciton model of acene aggregates, it was theoretically demonstrated that SF mediated by a direct electronic coupling can be either enhanced or suppressed by the collective strong

coupling.³³ A slower SF rate of amorphous rubrene in a cavity has been reported experimentally.³⁴

Here we investigate the CI-mediated singlet fission dynamics in an optical cavity by employing a dissipative three-electronic-state two-vibrational-mode conical intersection model recently introduced for pentacene dimer.³² Pentacene and its derivatives are promising SF materials for photovoltaics.³⁵ The primary step from the singlet exciton to spin-correlated triplet pair has been experimentally shown to occur at ~ 200 fs.³⁰ Combining the wavepacket dynamics for the nuclear motion, the second-order time-local quantum master equation³⁶ for the vibrational relaxation, and the Lindblad master equation for the cavity loss, we follow the SF quantum dynamics coupled to a single cavity photon mode. We find that the cavity can significantly suppress the SF process while channeling direct relaxation to the ground state. This arises since the polaritonic CI is pushed away from the Franck–Condon region by formation of polaritons. We further explore the influence of cavity quality factor Q on the SF process. Atomic units $\hbar = 1$ are used throughout.

We consider a pentacene dimer, schematically shown in Figure 1a, coupled to a single lossy cavity mode described by the Hamiltonian $H = H_p + H_B + H_{SB}$. The polariton Hamiltonian $H_p = H_M + H_C + H_{CM}$ describes the pentacene dimer³² coupled to a single cavity mode represented by the Hamiltonian $H_C = \omega_c a^\dagger a$, where a and $a^\dagger$ are, respectively, the

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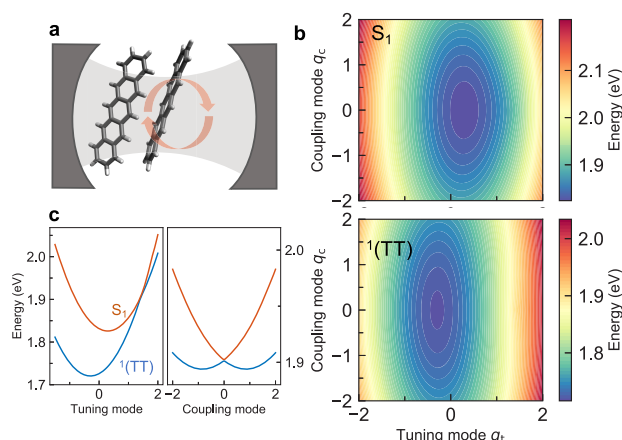


Figure 1. Conical intersection model for the pentacene dimer.³² (a) Geometry of the pentacene dimer embedded in an optical cavity. (b) Singlet and triplet-pair potential energy surfaces. (c) Cuts of the adiabatic surfaces along the tuning mode ($q_c = 0$) and the coupling mode ($q_t = 1.4$) showing the conical intersection.

cavity photon boson annihilation and creation operators that satisfy $[a, a^\dagger] = 1$. The molecular Hamiltonian contains three electronic states (the ground state, an excited singlet S_1 and a correlated triplet pair state $^1(TT)$) and two vibrational modes, a low-frequency intermolecular coupling mode and a high-frequency intramolecular tuning mode, coupled off-diagonally and diagonally to the electronic motion, respectively. Each vibrational mode has a frequency Ω_σ , dimensionless coordinate q_σ and momentum p_σ . The molecular Hamiltonian, in the diabatic representation, is given by

$$H_M = \sum_{k=S_0, S_1, TT} V_k |k\rangle \langle k| + \lambda q_c (|S_1\rangle \langle TT| + \text{H. c.}) \quad (1)$$

where $V_k = V_{S_0} + E_k + \kappa_k q_t$, $V_{S_0} = \frac{1}{2} \sum_{\sigma=t,c} \Omega_\sigma (p_\sigma^2 + q_\sigma^2)$, and H.c. denotes the Hermitian conjugate. Here E_k is the vertical excitation energy at the Franck–Condon point to the k th electronic state, κ_k is the intrastate vibronic coupling constant, and λ is the diabatic coupling constant. We used the following parameters $\Omega_c = 177 \text{ cm}^{-1}$, $\Omega_t = 1013 \text{ cm}^{-1}$, $E_{S_1} = 1.94 \text{ eV}$, $E_{TT} = 1.835 \text{ eV}$, $-\kappa_{S_1} = \kappa_{TT} = 300 \text{ cm}^{-1}$, and $\lambda = 150 \text{ cm}^{-1}$.³² The adiabatic potential energy surfaces (PES), obtained by diagonalizing the electronic (Born–Oppenheimer) Hamiltonian $H_{el}(\mathbf{q}) = H_M - T_N$ with T_N the nuclear kinetic energy operator, are shown in Figure 1b. A cut along the tuning mode in Figure 1c clearly shows the CI. This model was recently constructed by Duan et al. to reproduce the experimental SF time scale and to understand the transient grating and two-dimensional electronic spectra.³²

The cavity-molecule coupling

$$H_{CM} = g(\mathbf{q}) (|S_1\rangle \langle S_0| + \text{H.c.}) (a + a^\dagger) \quad (2)$$

describes the electric dipole coupling between molecular transition $S_0 \leftrightarrow S_1$ and the cavity photon mode. The coupling constant $g(\mathbf{q}) = \sqrt{\frac{a_c}{2\epsilon_0 V}} \boldsymbol{\mu}(\mathbf{q}) \cdot \mathbf{e}_c$, where $\boldsymbol{\mu}(\mathbf{q}) \approx \boldsymbol{\mu}$ is the transition dipole moment between diabatic states, which is assumed to be independent of the nuclear coordinates, and $\mathbf{e}_c$ the cavity polarization.

The bath Hamiltonian contains cavity damping modes responsible for cavity loss and a phonon bath $H_B^{\text{vib}} =$

$\sum_{\sigma=c,t} \int_0^\infty d\omega \omega b_\sigma^\dagger(\omega) b_\sigma(\omega)$ responsible for vibrational relaxation, where $b(\omega)$ ($b^\dagger(\omega)$) annihilates (creates) a environment phonon mode of frequency ω . The system–bath Hamiltonian H_{SB} captures the interaction between the system and the environment. The vibrational modes couple to the environment through $S_\sigma \otimes B_\sigma \equiv q_\sigma \otimes \sum_{\sigma=c,t} \int_0^\infty d\omega \kappa(\omega) (b_\sigma(\omega) + b_\sigma^\dagger(\omega))$. The influence of an equilibrium Gaussian bath to the system is fully encoded in the spectral density $J_\sigma(\omega) \equiv \pi \int d\omega' |\kappa(\omega')|^2 \rho(\omega')$, which is assumed to have the Drude form $J_\sigma(\omega) = 2\lambda_\sigma \Lambda_\sigma \omega / (\omega^2 + \Lambda_\sigma^2)$. Here $\rho(\omega)$ is the bath density of states, λ_σ is the reorganization energy, and Λ_σ is the cutoff frequency.

Due to the presence of vibrational and photon environments, the polaritonic system should be described by a density matrix $\rho(t)$, rather than a wave function. The hybrid second-order time-local and Lindblad quantum master equation for the reduced polariton density matrix reads

$$\frac{d}{dt} \rho(t) = -i[H_p, \rho(t)] + \mathcal{K}(t) \rho(t) + \kappa \mathcal{L}[a] \rho(t) \quad (3)$$

Here

$$\mathcal{K}(t) = \sum_{\sigma=t,c} \int_{t_0}^t d\tau S_\sigma^- (\text{Re } C_\sigma(\tau) S_\sigma^+(-\tau) + i \text{Im } C_\sigma(\tau) S_\sigma^-(-\tau)) \quad (4)$$

is the second-order time-convolutionless generator and $C_\sigma(t) \equiv Z^{-1} \text{Tr}\{\rho_B B_\sigma(t) B_\sigma\}$ is the bath correlation function, $B(t)$ is the operator B in the interaction picture with respect to H_B , and $\mathcal{A}\rho = [A, \rho]$, $\mathcal{A}^+ = \{A, \rho\}$. The first term in the right-hand side of eq 3 describes the unitary polariton dynamics, the second describes the vibrational relaxation induced by the phonon environments, and the third Lindblad superoperator $\mathcal{L}[a]\rho = a\rho a^\dagger - \frac{1}{2}\{a^\dagger a, \rho\}$ describes the cavity damping with rate $\kappa = \omega_c/2Q$. We employ different treatments of the vibrational and photonic environments because the Markovian approximation often holds for the cavity loss whereas a non-Markovian method is required to account for memory effects in vibrational relaxation. In the time-local master equation, memory effects are contained in the time-dependence of $\mathcal{K}(t)$.^{36–38}

For a harmonic environment at thermal equilibrium, the bath correlation function is given by³⁸ $C_\sigma(t) = \frac{1}{\pi} \int_0^\infty (\coth(\beta\hbar\omega/2) \cos(\omega t) - i \sin(\omega t)) J_\sigma(\omega) d\omega$. At high temperatures, $\beta\omega < 1$, $\coth(\beta\omega/2) \approx 2/(\beta\omega)$, and the correlation function reduces to $C_j(t) = \left(\frac{2\lambda_j}{\beta} - i\lambda_j\Lambda_j\right) e^{-\Lambda_j t}$.

The reduced polariton density matrix is represented in a direct product basis $|k\nu_t\nu_n\rangle \equiv |k\rangle \otimes |\nu_t\rangle \otimes |\nu_n\rangle \otimes |n\rangle_{\text{cav}}$, where $|k\rangle$ denotes the k th electronic state, $|\nu_t\rangle$ ($|\nu_n\rangle$) is the number state of the coupling (tuning) mode, and $|n\rangle_{\text{cav}}$ is the number state of the cavity photon mode. Equations 3 and 4 were integrated by the fourth-order Runge–Kutta method with time step 0.2 fs. The sizes of the Fock space used for the coupling, tuning modes, and the cavity mode are respectively 12, 10, and 2. We further assume temperature $T = 300 \text{ K}$, $\lambda_{t/c} = 100 \text{ cm}^{-1}$, and $\Lambda_{t/c} = 200 \text{ cm}^{-1}$.³²

The optical absorption spectra of the polaritonic system for varying the coupling strengths are displayed in Figure 2. The

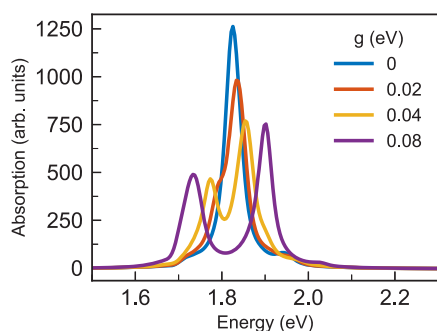


Figure 2. Optical absorption of pentacene dimer in an optical cavity with $\omega_c = 1.8$ eV and $Q = 100$ at various coupling strengths. We note the Rabi splitting at large couplings.

cavity mode is coupled to many vibronic transitions with the transition strength determined by the Franck–Condon factors. Nevertheless, the Rabi splitting is clearly observed, unmasked by the manifold of vibrational states. The absorption spectrum is computed using $A(\omega) = \text{Re} \int_0^\infty dt \langle \mu(t) \mu \rangle$ where $\mu(t) = e^{+iHt} \mu e^{-iHt}$.³⁹ The dipole–dipole correlation function is given by $\langle \mu(t) \mu \rangle = \langle \langle \mu | \mathcal{G}(t, t_0) | \mu \rho_0 \rangle \rangle$, where $\mathcal{G}(t, t_0)$ is the Liouville space Green's function of eq 3 and $|A\rangle$ is the Liouville space vector corresponding to an Hilbert space operator A .³⁹

The SF dynamics is launched by a vertical excitation to S_1 . The initial polariton density matrix is $\rho_0 = |\Psi_0\rangle\langle\Psi_0|$ where

$$|\Psi_0\rangle = |S_1\rangle|X_0\rangle|0\rangle_c \quad (5)$$

$|X_0\rangle$ is the vibrational ground state on the electronic ground surface and $|0\rangle_c$ is the cavity-mode vacuum state.

The simulated population dynamics of $^1(\text{TT})$ state is depicted in Figure 3. The bare dynamics exhibits an ~ 200 fs population transfer to $^1(\text{TT})$, consistent with experiment.³² The population oscillations match the 33 fs tuning mode period. Vibrational relaxation plays an important role in the SF process. Without the vibrational bath, only a small reversible population transfer to the triplet pair state takes place (not

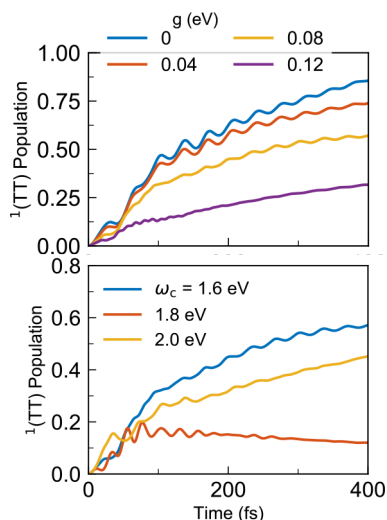


Figure 3. Population dynamics of the correlated triplet pair state for various the coupling strengths g (top) and cavity frequencies ω_c (bottom) as indicated. Here $\omega_c = 1.6$ eV, $Q = 100$ (upper panel) and $g = 0.08$ eV, $Q = 100$ (lower).

shown). Thermal fluctuations are important for the excited molecule to reach the conical intersection region.

With strong coupling to a $Q = 100$ cavity, the SF dynamics is significantly suppressed. The suppression increases at higher coupling strength. The polariton dynamics in high- Q cavities is best described by the polaritonic PES (PPES). These are the eigenstates of the polaritonic Hamiltonian without the nuclear kinetic energy operator $H_p(\mathbf{q}) \equiv H_p - T_N = H_{el}(\mathbf{q}) + H_C + H_{CM}(\mathbf{q})$, which depends parametrically on the nuclear coordinates $\mathbf{q}$. The PPESs control the polariton dynamics by replacing the adiabatic PESs in the bare dynamics. The nonadiabatic coupling between adiabatic PESs is transformed to the PPESs.

The PPESs are displayed in Figure 4, where the line color encodes the photonic fraction of the polariton states $\langle n_c \rangle =$

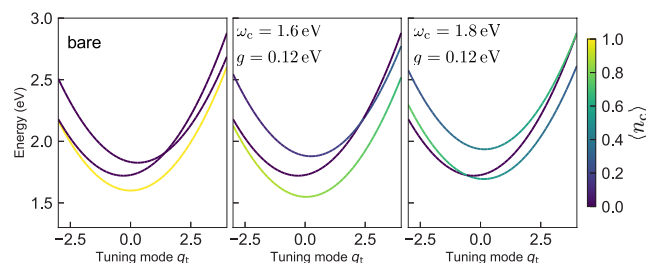


Figure 4. Cut of the (polaritonic) potential energy surfaces along the tuning mode at $q_c = 0$.

$\langle \psi(\mathbf{q}) | a^\dagger a | \psi(\mathbf{q}) \rangle = |\beta(\mathbf{q})|^2$, where $|\psi(\mathbf{q})\rangle = \alpha(\mathbf{q})|S_0\rangle \otimes |1\rangle_c + \beta(\mathbf{q})|S_1\rangle \otimes |0\rangle_c$. The cavity mode alters the conical intersection in the PPESs. As found for pyrazine,¹³ we observe a splitting of the bare CI into two polaritonic CIs. The polaritonic CI between the upper polariton surface and the $^1(\text{TT})$ surface is shifted away from the Franck–Condon point compared to the bare CI, thus reducing the probability to reach the polaritonic CI geometry and suppressing the SF rate. The polaritonic CI location varies with the cavity frequency (Figure 4). The closer the cavity frequency is to the S_0 – S_1 energy gap at the CI geometry, the stronger is its effects on the SF dynamics.

To visualize the polariton effects in the nuclear dynamics, we compare in Figure 5 the nuclear probability density $\langle \mathbf{q} | \sigma(t) | \mathbf{q} \rangle$ of the bare and the polariton dynamics. Here $\sigma(t) = \text{Tr}_{el, cav} \{ \rho(t) \}$ is the reduced density matrix of the molecular vibrations obtained by tracing out the electronic and photonic degrees of freedom.⁴ In the bare dynamics, the distribution first shifts along the tuning mode and spreads along the coupling mode. At $t \sim 80$ fs, we notice a splitting of the distribution corresponding to the relaxation to the $^1(\text{TT})$ state. In contrast, in the polariton dynamics, the motion along the tuning mode is largely suppressed and shows no splitting of the nuclear probability. This can be explained by the PPES displayed in Figure 4; the gradient along the upper polariton surface is much smaller compared to the bare S_1 surface and the nuclear motion tends to be more localized. The nonadiabatic dynamics mainly occurs between the upper and the lower polariton surfaces.

The $^1(\text{TT})$ population dynamics for various cavity Q factors is compared in Figure 6. Population transfer to the $^1(\text{TT})$ state is further reduced in leaky cavities; for $Q \leq 20$, the singlet fission and the cavity-induced oscillations in the population are highly suppressed. The PPES may not be very useful for

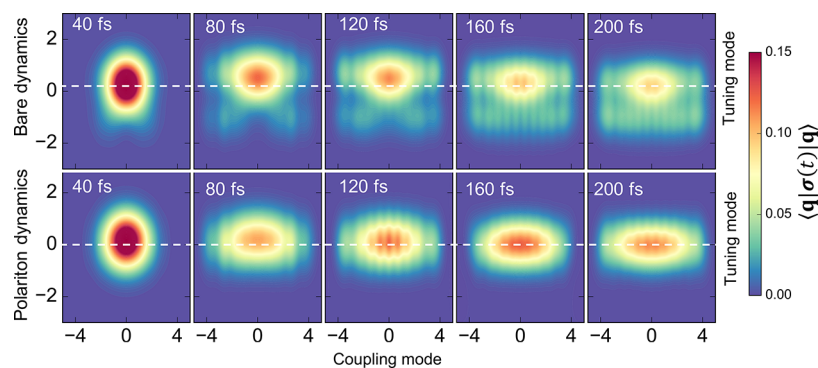


Figure 5. Dynamics of the nuclear distribution for the bare dynamics (upper) and the polariton dynamics (lower). Here $\omega_c = 1.8$ eV, $Q = 100$, and $g = 0.12$ eV are used for the polariton dynamics.

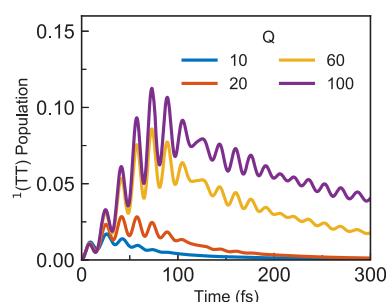


Figure 6. $^1(TT)$ state population dynamics in optical cavities with varying quality factor Q . Here $g = 0.12$ eV and $\omega_c = 1.8$ eV.

interpreting the polariton dynamics in low quality cavities as the hybrid polaritons are not formed. In the time domain, the coherent energy exchange between matter and the cavity mode is not observed for $Q = 10$. Lossy cavities enhance the molecular emission to the cavity mode and the emitted photons rapidly leak out to the cavity damping modes. The cavity mode channels the excitation energy to the extra-cavity modes, depleting the populations of the polariton states and also the $^1(TT)$ populations. For $\kappa \sim g$, the quantum dynamics lies in the middle of coherent polariton dynamics and incoherent emission.

As shown for two pyrazine molecules coupled to a single cavity mode,¹⁴ the shifted polaritonic CIs also occur for $N > 1$ molecules in the bright collective polaritonic surfaces. Nevertheless, collective effects such as polaron decoupling⁴⁰ and collective dark states that may also play important roles in the cooperative polariton dynamics must be then taken into account.^{14,41,42}

To summarize, we have shown how the SF process in the pentacene dimer is affected by an optical cavity in the weak to strong coupling regime. The polaritonic conical intersection is pushed further away from the Franck–Condon region compared to the bare CI, thus suppressing the SF process. Our study suggests that the reverse process of SF, the triplet–triplet annihilation, may be enhanced by strong light–matter coupling. Cavity-suppressed SF has been observed experimentally.³⁴ Future extension to a delocalized excitation in a tetramer model and to the collective strong coupling regime will be of interest.

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Notes

The authors declare no competing financial interest.

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ADDITIONAL NOTE

^aIn practice, this is achieved by a tensor contraction $\sigma_{\mathbf{v},\mathbf{v}'} = \sum_{k,n} \rho_{kvn,kv'n'}$ where $\mathbf{v} = v_c v_q$ is the composite index labeling the vibrational number states.

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■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on February 22, 2021, with Figure 5 absent from the online version. The corrected version was posted March 4, 2021.