Coherent dynamics of singlet fission controlled by nonlocal electron-phonon coupling

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Based on the Frenkel-charge transfer (CT) mixing model of singlet fission (SF), we incorporate both the local and nonlocal phonon baths in the Hamiltonian and adopt the algorithm of time-dependent density matrix renormalization group to simulate the fission process in tetracene. The endergonic SF is found to be facilitated by the robust quantum coherence, which concurrently gives rise to a notable quantum beating effect. Controlled by the nonlocal electron-phonon coupling, the density of triplet yield manifests a nonlinear relationship with the singlet density. As a result, the fission rate in tetracene is explicitly obtained, which is in agreement with the experimental measurement.

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Providing rapid advances of power conversion efficiency (PCE), photocells based on organic materials exhibit promising application potential\textsuperscript{1}. From the viewpoint of heat engine model proposed by Shockley and Queisser, however, the excitation energy above the bandgap of the light harvesting material is largely dissipated, lowering the PCE in a considerable manner\textsuperscript{2}. A strategy to overcome this Shockley-Queisser limit of SF is found to be facilitated by the robust quantum coherence, which concurrently gives rise to a notable quantum beating effect. Controlled by the nonlocal electron-phonon coupling, the density of triplet yield manifests a nonlinear relationship with the singlet density. As a result, the fission rate in tetracene is explicitly obtained, which is in agreement with the experimental measurement.

Theoretically, a benchmarking model taking both the Frenkel exciton and the CT state into account has been established, and the density functional theory (DFT) calculations have correspondingly carried out the electron orbital couplings based upon the configuration interaction formalism\textsuperscript{24–27}. Rather, contentions surrounding the appropriate parameters of the model stay active\textsuperscript{24–27}. The key parameters such as the energy of the electronic state and the electron-phonon couplings are yet to be determined solely by DFT\textsuperscript{24}. Obtaining the energy of an electronic state requires the corresponding wavefunction, but the wavefunction of electron in the real materials is greatly delocalized as indicated by experiment\textsuperscript{22}, which can not be handled by DFT\textsuperscript{24} with local functionals. The electron-phonon coupling matters in a dynamical fashion by affecting the decoherence rate and thus the rate of SF\textsuperscript{21}. In this context, one would think of employing

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the full-quantum algorithm to fit the relevant experimental results and then determine the associated microscopic parameters.

Our starting point is based on a recent experiment on the multiphonon relaxation in SF, which sheds light upon the theoretical study on phonons and thereby the quantum coherence. The model Hamiltonian is written as

$$H = H_{el} + H_{ph} + H_{el-ph}.$$  \hfill (1)

Herein, the first term $H_{el}$ represents the Frenkel-CT mixing model for the molecular dimer,\textsuperscript{24,25} that is,

$$H_{el} = \sum_i |i\rangle E_i \langle i| + \sum_{i \neq j} |j\rangle V_{ij} \langle i|,$$  \hfill (2)

where $|i\rangle$ takes five possible states including two singlet states $|1\rangle \equiv |S_1, S_0\rangle$ and $|2\rangle \equiv |S_0, S_1\rangle$, two CT states $|3\rangle \equiv |C, A\rangle$ and $|4\rangle \equiv |A, C\rangle$ (C for cation and A for anion), and one TT state $|5\rangle \equiv |T_1, T_1\rangle$; $E_i$ is the energy level of the state, and $V_{ij}$ is the transition energy from state $i$ to state $j$. As stated, the values of $V_{ij}$ have been obtained by DFT calculations\textsuperscript{24,25}, but $E_i$’s are yet to be determined.

More important are the terms involving phonons. The second and third term of Hamiltonian (1) read ($\hbar = 1$),

$$H_{ph} = \omega L\hat{a}^\dagger\hat{a} + \omega NL\hat{b}^\dagger\hat{b},$$  \hfill (3)

$$H_{ex-ph} = \gamma_L |5\rangle\langle 5|\hat{a}^\dagger + \hat{a} + \gamma_{NL}(|3\rangle\langle 3| + |4\rangle\langle 4|)(\hat{b}^\dagger + \hat{b}),$$  \hfill (4)

where $\hat{a}^\dagger$ and $\hat{b}^\dagger$ are the creation (annihilation) operator of the local and nonlocal phonons with the frequency being $\omega_L$ and $\omega_{NL}$, and $\gamma_L$ and $\gamma_{NL}$ are the coupling strength, respectively. Here, we have two kinds of phonons, local and nonlocal phonons, which have been widely studied in organic crystalline materials.\textsuperscript{28-31} The local phonons couple with the tightly bound excitons in a single molecule. In the current work, we consider the local phonons coupled with the TT state, which is the main concern in the SF process. The nonlocal phonons interact with the CT state, since by definition the CT state is an intermolecular electron-hole pair and the intermolecular vibrational modes take over the relevant couplings.\textsuperscript{28} As stated, the CT state plays an essential role in the SF process, implying the nonlocal phonons would be significant. For simplicity, we assume that both the local and nonlocal phonon baths follow the similar spectral density function, which is usually cut off at the frequency $\omega_c$, i.e., $J_{L(NL)}(\omega) = 2\pi\alpha_{L(NL)}\omega_c^3/\omega_s^4 - \omega^4/\omega_s^4 - \omega/\omega_c$ with $\alpha_{L(NL)}$ being the dimensionless coupling strength for the local (nonlocal) baths and $s$ being the exponent. We mainly consider the sub-Ohmic bath $s = 0.5$ corresponding to the relatively low-frequency vibrational modes, which are the most featured ones in organic molecules.\textsuperscript{28,29} The sub-Ohmic bath holds the non-Markovian feature to induce the long-lived quantum coherence.\textsuperscript{32} It is noticed that, the behavior of the SF process could be quantitatively different if other forms of spectral density were found to be appropriate.

Technically, dealing with two phonon baths in the meantime turns out to be significantly difficult in the framework of the full-quantum simulation. Recently, our effort based on the time-dependent density matrix renormalization group algorithm\textsuperscript{33} within the orthogonal polynomials representation\textsuperscript{34-38} has come up with an ad hoc optimizing method, so-called symmetrically optimized phonon basis,\textsuperscript{39} which allows us to simultaneously study the two phonon baths in a unified framework. In the following, we employ this method to calculate the dynamics of Hamiltonian (1) with the initial state being a singlet excitation $|1\rangle$. The parameters in tetracene are taken as,\textsuperscript{25} $V_{13} = V_{31} = -0.051$ eV, $V_{14} = V_{41} = -0.074$ eV, $V_{23} = V_{32} = -0.118$ eV, $V_{24} = V_{42} = -0.111$ eV, $V_{35} = V_{53} = -0.081$ eV, $V_{45} = V_{54} = 0.056$ eV, and other $V_{ij}$’s are zero. $E_S(= E_1 = E_2)$ is set to be zero, and other parameters are adjustable in the computations.

We first show the population of S1 state ($|1\rangle$ plus $|2\rangle$) and TT state ($|5\rangle$) in Fig. 1 with $E_{CT}(= E_3 = E_4) = 0.6$ eV, $E_{TT}(= E_5) = 0.1$ eV, and $\alpha_L = 0.1$. In the present work, both the local and nonlocal dimensionless couplings $\alpha_{L(NL)}(\sim \gamma_{L(NL)}/2\pi)$ are taken to be around 0.1, since the effective value of Peierls coupling in pentacene is about 0.55 and we estimate it to be similar in tetracene.\textsuperscript{41} It is found that, the singlet population decays from one and the triplet population grows up from zero, implying the singlet is efficiently converted to the triplet, namely SF takes place. At the very initial stage, i.e., the time $t$ is smaller than 1000fs, a quantum beating behavior originated from the quantum coherence emerges for both the singlet and triplet population.\textsuperscript{40} After that, the populations gradually saturate during a long-term evolution. It is worth noting that the quantum beating effect produced by our non-perturbative full-quantum simulation can not be obtained in the framework of incoherent hopping model with Redfield or Förster theory.\textsuperscript{41} The quantum-mechanically treated phonons give rise to
the essential and robust quantum coherence, which is crucial for the endergonic SF as discussed below.

Significantly, we find the conversion from singlet to triplet is accelerated by the nonlocal phonons. We fit the curves of $\alpha_{NL} = 0$ and 0.15 using the exponential function $\exp[-(t/t_0)\nu]$ with $t_0$ being the characteristic fission time for the SF, and $\nu$ the exponent. For the singlet population, two functions $\exp[-(t/2700)^{0.8}]$ and $\exp[-(t/2000)^{0.5}]$ are assigned for the curves of $\alpha_{NL} = 0$ and 0.15, respectively. It is clear that $t_0$ for the large nonlocal coupling case is shorter than that for the small coupling case, indicating the large nonlocal coupling gives rise to a large fission rate. Furthermore, the exponents for the two curves are quite different. When the nonlocal phonon is absent, the decay of singlet population in a robust manner. More importantly, the nonlocal phonon serves as a controller for the coherent SF process, which not only controls the fission rate but also influences the yield of triplet excitons.

To be more elaborate, we draw a schematic in Fig. 2 to show the role of both local and nonlocal phonons. Right after the S1 is transferred to the CT state, the CT state could simultaneously dissipate the energy to the nonlocal phonon bath and recombine to the TT state. The former process could strengthen the latter because the nonlocal phonons act as a sink of the CT state energy, which constantly breaks the detailed balance between the S1 and CT state population and drives the S1-to-CT state conversion, as shown in Fig. 1(a). As the nonlocal phonons mainly refers to the intermolecular vibrational modes, an experimental corroboration for our present viewpoint is the fast charge transfer process in polar solvents. The weak covalent coupling helps form a stable dipolar intermediate and thus enhance the intermolecular couplings, inducing the large fission rate.

In the following, we discuss the endergonic SF process\textsuperscript{16,22}. The energy of both CT and TT state is changed (always above the energy of S1 state, 0eV) as shown in Fig. 3. We first take $E_{CT} = 1.0$eV and $E_{TT} = 0.1$eV, the estimated values obtained by the DFT computations. The curve is fitted by the exponential function with the fission time $t_0$ being 7200fs, in good agreement with the experimental measurement in tetracene. Moreover, when the energy of CT state is reduced, the fission rate is at the initial stage of the evolution enhanced, and finally the yield of triplet is increased by about twice. The energy barrier between S1 and CT state comes on duty in this effect. In addition, when $E_{CT}$ is close to $E_{TT}$ (e.g., $E_{CT} = 0.2$eV), the TT population exhibits a fast decay in the time evolution as it goes back to the CT state. Experimentally, the change of the CT state energy could be implemented by adjusting

![FIG. 2: Schematic for the SF process and the role of local and nonlocal phonons. The CT and TT state are coupled with the nonlocal and local phonon baths, respectively. The baths serve as the sink for the both processes from S1 to CT and from CT to TT.](image)

![FIG. 3: Population evolution of TT state for various sets of energy of CT and TT state with (a) $E_{TT} = 0.1$eV and (b) $E_{CT} = 0.6$eV. The other parameters are: $\alpha_L = 0.1, \alpha_{NL} = 0.1$. The red dashed line in (a) shows the respective fitting curve.](image)
FIG. 4: Triplet population at 4000fs versus the energy of both CT and TT state for $\alpha_L = 0.1$, $\alpha_{NL} = 0.1$. The dash-dot-dot and dash-dot boundary lines indicate the parameter regimes for efficient ($\rho_{TT} > 0.1$) and inefficient SF ($\rho_{TT} < 0.01$), respectively.

The excitation power. Under higher density of excitons, more high-energy CT state could be occupied. In other words, the larger the power, the higher the energy of the highest occupied CT state. It has been observed that under larger power of excitation, the fission of singlet becomes weaker, so the yield of triplets becomes smaller. Obviously, our calculated results match the experiment very well, and the fitting parameters employed here turn out to be approximately the associated parameters of the real material.

The curves for various $E_{TT}$ are shown in Fig. 3(b). The increase of $E_{TT}$ gives rise to the increase of triplet yield for $E_{TT} \leq 0.1$eV, otherwise the TT population decays. The SF is quite efficient as the saturated population of triplet for $E_{TT} = 0.1$eV is larger than 0.5. In Fig. 4 we further show the dependence of the triplet yield and the energetics of electronic states, that is, the population of TT state $\rho_{TT}$ at 4000fs versus the energy of both CT and TT state. To be clearer, we define two parameter regimes of efficient and inefficient SF to be those for $\rho_{TT} > 0.1$ and $\rho_{TT} < 0.01$, respectively. The location of the boundaries are qualitatively different from that calculated by the perturbative master equations approaches. Although the most efficient fission occurs in the regime of small TT energy, but remarkably, the TT energy for efficient SF could be larger than that of S1 state. Based on these results, we thus theoretically prove the hypothesis that, benefitting from the participation of quantum coherence, the superposition of S1 and CT state makes endergonic SF take place in an efficient fashion.

In summary, the local and nonlocal electron-phonon couplings are incorporated into the Frenkel-CT mixing model, and a full-quantum algorithm is adopted to calculate the coherent dynamics of SF process. The quantum beating is obtained at the initial stage of the evolution, manifesting the proper consideration of quantum coherence. By enhancing the nonlocal coupling, both the SF rate and the triplet yield are increased. The nonlinear relationship between the populations of singlets and triplets is rebuilt, and the nonlocal coupling turns out to be the controller for these effects. The energetics of the electronic state is varied to fit the experimental measurement. The SF time of 7200fs in tetracene as well as the endergonic SF phenomenon are obtained by our simulations. In consequence, the present theoretical model has successfully mimicked the coherent SF process in tetracene, and we expect that it could provide some insights for its application on solar energy harvesting.

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The characteristic fission time is sensitive to the choice of experimental technique. The photoemission spectroscopy gives the value 7.2 ps, while the transient photoluminescence gives 110 ps. Theoretically, due to the influence of structural and thermal environment, the electron-phonon coupling is variable. By adjusting the coupling strength in a reasonable extent, it is possible to explicitly fit the measured values.