Polariton-assisted Singlet Fission in Acene Aggregates

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Singlet fission is an important candidate to increase energy conversion efficiency in organic photovoltaics by providing a pathway to increase the quantum yield of excitons per photon absorbed in select materials. We investigate the dependence of exciton quantum yield for acenes in the strong light-matter interaction (polariton) regime, where the materials are embedded in optical microcavities. Starting from an open-quantum-systems approach, we build a kinetic model for time-evolution of species of interest in the presence of quenchers and show that polaritons can decrease or increase exciton quantum yields compared to the cavity-free case. In particular, we find that hexacene, a typically poor singlet-fission candidate, can feature a higher yield than cavity-free pentacene when assisted by polaritonic effects. Similarly, we show that pentacene yield can be increased when assisted by polariton states. Finally, we address how various relaxation processes between bright and dark states in lossy microcavities affect polariton photochemistry. Our results also provide insights on how to choose microcavities to enhance similarly related chemical processes.

Singlet fission (SF) is a spin-allowed process undergone by select materials that permits the conversion of a singlet exciton into a triplet-triplet (TT) state with an overall singlet character, which later decoheres and forms two triplet excitons. This process has been used to enhance the external quantum efficiency of organic solar cells [1, 2] by allowing a single absorbed photon to produce more than one exciton. In this work we explore the influence of strong light-matter coupling (SC) on the TT yield of acenes. This regime can be achieved at room-temperature, for example, in optical microcavities enclosing densely packed organic dyes [3]. Under these conditions, the energy of interaction between the microcavities and the molecules of the material is larger than their respective linewidths. The hybrid states that arise from this interaction are called polaritons. The latter have preocolored character.

By developing a microscopic model for the relevant processes, we address the effects of SC on the TT yield in aggregates of acene dyes (tetracene, pentacene and hexacene) and determine the important molecular parameters that rule this yield. Our starting point is a kinetic model based on a Pauli master equation formalism that describes the population dynamics of the states that take part in SF [22]. We then use this model to elucidate the circumstances under which polaritons can enhance SF under realistic dissipative conditions.

Theoretical model.— We consider a simplified one-dimensional acene aggregate comprised of \( N \) identical molecules embedded in a microcavity and strongly interacting with a single electromagnetic mode supported by the latter. The Hamiltonian of the model is given by

\[
H = H_{S} + H_{B} + H_{S-B} + H_{p} + H_{p-S} + H_{TT} + H_{TT-B} + H_{TT-S},
\]

where \( H_{S} \) (\( H_{TT} \)) is the electronic singlet (TT) Hamiltonian of the aggregate given by \( (\hbar = 1) \)

\[
H_{S} = \sum_{n} \omega_{e} |n\rangle \langle n|,
\]

\[
H_{TT} = \sum_{n=0}^{N-1} \omega_{TT} |T_{n}T_{n+1}\rangle \langle T_{n}T_{n+1}|,
\]

where \( |n\rangle \) is a localized singlet (Frenkel) exciton \( [23] \) at the \( n \)th site (molecule), and \( |T_{n}T_{n+1}\rangle \) denotes a TT state delocalized over sites \( n \) and \( n+1 \). Here \( \omega_{e} = \omega_{e} + \sum_{i} \omega_{i} \lambda_{S,i}^{2} \) (\( \omega_{TT} = \omega_{TT} + 2 \sum_{i} \omega_{i} \lambda_{TT,i}^{2} \)) is the vertical singlet (TT) excitation frequency, where \( \omega_{e} \) and \( \lambda_{S,i} \) (\( \lambda_{TT,i} \)) are the 0-0 excitation frequency and the square root of the Huang-Rhys factor \( [24] \) for the \( i \)th vibrational mode coupled to the transition \( |G\rangle \rightarrow |n\rangle \) (\( |G\rangle \rightarrow |T_{n}T_{n+1}\rangle \)), respectively, and \( |G\rangle \) is the state corresponding to all molecules in the electronic ground state. \( H_{B} = \sum_{n,i} \omega_{i} b_{n,i}^{\dagger} b_{n,i} \) accounts for the vibrational degrees of freedom of the ensemble, where \( b_{n,i}^{\dagger} \) (\( b_{n,i} \)) is the creation (annihilation) operator of the \( i \)-th harmonic vibrational degree of freedom with frequency \( \omega_{i} \) on site \( n \). The singlet (TT) vibronic couplings are encoded in \( H_{S-B} \) (\( H_{TT-B} \)), given by

\[
H_{S-B} = \sum_{n,i} |n\rangle \langle n| \omega_{i} \lambda_{S,i} (b_{n,i} + \text{h.c.}),
\]

\[
H_{TT-B} = \sum_{n=0}^{N-1} |T_{n}T_{n+1}\rangle \langle T_{n}T_{n+1}|
\]
The singlet-TT electronic coupling is (assuming periodic boundary conditions \(|T_{-1}T_0| = |T_{N-1}T_0|) \): \[ H_{TT-S} = \frac{V_{TT-S}}{2} \sum_{n=0}^{N-1} \left[ (|T_nT_{n+1}| + |T_{n-1}T_n|) (n) + \text{h.c.} \right]. \] (4)

Finally, the photonic degree of freedom is included in \( H_p = \omega_{ph} a^\dagger a \) where \( a^\dagger (a) \) is the creation (annihilation) operator of the cavity photonic mode. Its interaction with the singlet excitons is described by the light-matter Hamiltonian

\[
H_{p-S} = \sum_n g (a^\dagger |G\rangle \langle n| + \text{h.c.}) = \sqrt{N} g (a^\dagger |G\rangle \langle 0| + \text{h.c.}) = \frac{\Omega}{2} (a^\dagger |G\rangle \langle 0| + \text{h.c.})
\] (5)

where in the second line we have introduced a delocalized Fourier basis for the singlet excitons \(|k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i kn} |n\rangle k = \frac{2 \pi n}{N}, m = 0, 1, 2, \ldots, N - 1 \). The \( \sqrt{N} g \) term in (5) is the collective light-matter coupling and \( \Omega \) is the so-called Rabi splitting. Importantly, the singlet excitons are optically bright, in contrast to the dark (TT) state manifold. 

The singlet-TT electronic coupling is (assuming periodic boundary conditions \(|T_{-1}T_0| = |T_{N-1}T_0|) \): \[ \frac{V_{TT-S}}{2} \sum_{n=0}^{N-1} \left[ (|T_nT_{n+1}| + |T_{n-1}T_n|) (n) + \text{h.c.} \right]. \] (4)

In our approach we consider the reduced population dynamics of the manifold of TT states \(|\{ |T_nT_{n+1}\rangle \})\), the two polariton states \(|\{ |\pm\rangle \})\) and the so-called dark states \(|\{ |d\rangle \})\) that emerge from SC (see Fig. and the Supporting Information (SI) for additional details of the method), where

\[
|\pm\rangle = c_{\pm} ph |G\rangle \otimes |1 ph\rangle + c_{\pm} ex |k = 0\rangle \otimes |0 ph\rangle, \quad (6a)
\]

\[
|\mp\rangle = c_{\mp} ph |G\rangle \otimes |1 ph\rangle + c_{\mp} ex |k = 0\rangle \otimes |0 ph\rangle, \quad (6b)
\]

with (zeroth-order) eigenenergies given by

\[
\omega_{\pm} = \bar{\omega}_e + \omega_{ph} \pm \sqrt{\left( \frac{\bar{\omega}_e - \omega_{ph}}{2} \right)^2 + (\sqrt{N} g)^2}, \quad (7)
\]

In Eq. (6), \(|n ph\rangle\) is the state with \( n \) photons in the photonic space and \(|\pm\rangle \) (\(|\mp\rangle \)) is the upper (lower) polariton state. Meanwhile, \( c_{\pm} ph \) and \( c_{\pm} ex \) are the Hopfield coefficients for the photon and exciton components, respectively, of the polariton states. The reduced dynamics is described by means of a Pauli master equation derived using the Redfield formalism under the secular and Markov approximations (see SI). The kinetic model can be summarized by the following equations,

\[
\partial_t P_{\pm} (t) = -|c_{\pm} ex|^2 \frac{\alpha (\omega_{\mp}D)}{N} (N - 1) P_{\pm} + |c_{\pm} ex|^2 \frac{\alpha (\omega_{\mp}D)}{N} P_{\text{total}} \] (8a)

\[
- |c_{\pm} ex|^2 \frac{\gamma (\omega_{TT,\pm})}{N} (N) P_{\pm} + |c_{\pm} ex|^2 \frac{\gamma (\omega_{\pm}, TT)}{N} P_{\text{total}}
\]

\[
\partial_t P_{D} (t) = |c_{\pm} ex|^2 \frac{\alpha (\omega_{\pm}D)}{N} (N - 1) P_{\pm} - |c_{\pm} ex|^2 \frac{\alpha (\omega_{\pm}D)}{N} P_{\text{total}} + |c_{\pm} ex|^2 \frac{\alpha (\omega_{\mp}D)}{N} (N - 1) P_{\mp} - |c_{\pm} ex|^2 \frac{\alpha (\omega_{\mp}D)}{N} P_{\text{total}} + \gamma (\omega_{TT,D}) \] (8b)

\[
\partial_t P_{TT} (t) = |c_{\pm} ex|^2 \frac{\gamma (\omega_{TT,\mp})}{N} P_{\mp} - |c_{\pm} ex|^2 \frac{\gamma (\omega_{TT,\pm})}{N} P_{\mp} - \gamma (\omega_{TT,D}) P_{TT} + \gamma (\omega_{TT,D}) \] (8c)

where \( P_{\pm} (t) (P_{\mp} (t)) \) is the population in the \(|\pm\rangle \) (\(|\mp\rangle \) state and \( P_{\text{total}} \) (\( P_{\text{total}} \)) is the total population in the dark (TT) state manifold. The photon and exciton content of the polaritonic states are given by \(|c_{\pm} ph|^2\) and \(|c_{\pm} ex|^2\) while \( \omega_{D} = \bar{\omega}_e \) and \( \omega_{ab} = \omega_a - \omega_b \). In Eqs. (8a) and (8b), we phenomenologically introduce the rate constant \( k_c (\omega) \) to account for the contribution to the decay rate of the dressed states due to their single exciton fraction. \( k_c \) can account for e.g. radiative or non-radiative relaxation of the singlet to the ground electronic state, or its conversion into charges at the interface with charge acceptors, which is the case in donor-acceptor blends used for organic solar cells. The various cases are treated in more detail below.

The \( \alpha (\omega) \) transfer rates appearing in Eqs. (8a) and (8b) are calculated in terms of a bath spectral density and thermal populations at frequency \( \omega \). The \( \gamma (\omega) \) rates are computed with a Bixon-Jortner-like equation adapted to the SC regime. For sake of simplicity, in the calculation of the latter the vibrational bath is treated by using an effective high (low) frequency \( \bar{\omega}_h (\bar{\omega}_l) \) that satisfies \( \bar{\omega}_h \gg 1/\beta \) (\( \bar{\omega}_l \ll 1/\beta \)), to which we associate a so-called inner (outer) sphere reorganization energy. We refer the reader to the SI for details of the derivation and other relevant parameters employed in the calculation of \( \alpha (\omega) \) and \( \gamma (\omega) \). The parameters \( \Delta G = \omega_{TT} - \omega_e \), and \( V_{TT-S}/2 \) take part in these calculations and are treated as material-dependent; they are taken from Ref. and are summarized in Table (see SI).
Figure 1. a) Bare triplet-triplet (red) and singlet (blue) vibronic energies of the different molecules considered. From left to right: tetracene, pentacene and hexacene. For clarity only the vibrational mode with highest frequency is shown. The SF dynamics is schematically shown for bare case (b) and the SC scenario (c). In (c) the fastest decay constant $\alpha \approx 100$ \text{ps}^{-1} is due to vibrational relaxation. $\gamma$ is the dressed SF rate, $k$ is the cavity-photon leakage rate and $|c_{i\delta}|^2/(|c_{\alpha\delta}|^2)$ is the exciton fraction in the upper (lower) polariton. $k_f$ is the singlet fluorescence decay rate. Continuous arrows denote radiative decay. Thicker lines indicate larger density of states. Approximate SF and relaxation rates for pentacene interacting with a resonant photonic mode are included. The decay timescale for the triplet-triplet state is significantly longer than the timescales considered here.

| Molecule   | $V_{TT-S}/2$ (meV) | $\Delta G$ (meV) | $k_{SF}$ (ps$^{-1}$) | $\epsilon_{TT}$ (%) |
|------------|---------------------|------------------|----------------------|---------------------|
| Tetracene  | 41.5                | 150              | 0.01                 | 0.01                |
| Pentacene  | 42                  | -110             | 17                   | 100                 |
| Hexacene   | 22                  | -630             | 6                    | 48                  |

Table I. Summary of bare material-dependent parameters. The values for $V_{TT-S}$ and $\Delta G = \omega_{TT} - \omega_c$ were taken from Ref. [2]. Based on these, we calculate the bare SF rates $k_{SF}$ and bare TT yields $\epsilon_{TT}$. Importantly, $\epsilon_{TT}$ is calculated assuming that SF competes with the fast singlet decay process (charge production) $k_{CT} = 17$ \text{ps}^{-1}, as discussed in the main text.

rate, and $k_{TF}$ is the bare triplet fusion rate, which corresponds to the reverse process to SF. $k_{SF}$ and $k_{TF}$ are calculated by means of the Bixon-Jortner equation [27], with the parameters in Table I. For all cases we compute $P_S(t)$ and $P_{TT}(t)$ assuming $P_S(0) = 1$, $P_{TT}(0) = 0$ (see Fig. 2). Under these conditions, we define the TT yield

$$\epsilon_{TT}(t^* \gg 0) = 200\% \times P_{TT}(t^*)$$

(10)

as the relevant figure of merit for our subsequent analysis where $t^*$ was chosen to reach a stationary $P_{TT}(t)$ value for pentacene and hexacene. We notice that when $k_i(\omega) = k_f = O(10^{-4})$ \text{ps}^{-1} (singlet fluorescence rate [22]) pentacene and hexacene are expected to exhibit a 200\% TT yield in view of $k_{SF} \gg k_f$ and $k_{TF} = e^{\Delta G} k_{SF} \ll k_{SF}$ (detailed balance, where $\beta$ is the inverse temperature). This contrasts with tetracene, in view of its higher TT energy compared to the singlet, ($\omega_{TT} > \omega_e$) so that $k_{SF} \ll k_{TF}$ and the TT population decays to zero for long $t$. The experimental TT yield of tetracene is well above zero [29, 30], which is in contrast with our findings (see Fig. 2). The reason is that the mechanism that leads to this unexpected yield is related to entropic gain not considered in our model. [31]. We opted to analyze the results that follow from our model, as they should be valid for a similar energetic singlet and TT arrangement in the absence of the aforementioned entropic mechanism.

In organic solar cells TT yield is typically below 200\% because the processes of singlet migration and charge separation are fast enough to compete with $k_{SF}$ [1]. To consider a similar situation, we assume that the singlet state quickly decays to a charge-transfer state. In our model, this would correspond to a scenario where there is a charge-acceptor next to each of the acene molecules of the chain. For simplicity and for the purpose of showing the possibilities of control of TT yield by polaritonic means, we assume $k_i(\omega) = \delta_{\omega_D,\omega} k_{CT}$, ($\delta_{ij}$ being the Kronecker delta function) where $k_{CT}$ is equal to the bare pentacene rate $k_{SF} = 17$ \text{ps}^{-1}. The form introduced for $k_i(\omega)$ is approximately correct as long as the spectral density describing the singlet-charge-transfer state is peaked around $\omega_D$ and decays quickly with $\omega$. The aforementioned $k_{CT}$ value is experimentally reasonable as it has been observed in solar cells with a thin slab of SF material [1].

We use Eq. (10) to compute the $\epsilon_{TT}$ values summarized in Table I in the presence of $k_{CT}$. Our definition of yield is thus different from that obtained in steady-state, but follows the spirit of many experiments that
measure SF using time-domain spectroscopy techniques [32–34].

Turning now to the polariton-assisted SF case, the non-trivial dynamics that emerge are due to differences in the density of states (DOS) between the polariton and exciton manifolds, as well as to the photonic character of each polariton state. These traits are encoded in the prefactors $|c_{ph}^\pm|^2$, $|c_{ex}^\pm|^2$, $N$ and $1/N$ in Eqs. (8a–8c). Notably, in the $N \gg 1$ limit, the transfer rates from $P_D$ and $P_T^{\text{total}}$ to the polariton manifold are largely suppressed. This is a consequence of the large DOS of the former (which act like a population sink) and the small DOS of the latter (which is spectrally isolated). The reverse transfers are fast as they have single-molecule relaxation scalings and correspond to going into the population sink. Similar findings are reported in Ref. [15], in the context of the dynamics of molecular vibrations under the SC regime and in [35–36] for exciton polaritons. Therefore, once population reaches the dark and TT states, it is no longer transferred back to the polariton manifolds, and the subsequent dynamics is determined by transfer rates between dark and TT states. We stress, however, that such asymmetry is approximate, as we are ignoring the polariton bandwidth that emerges from the many photonic modes hosted by the microwater, which yields non-zero transfer rates between to the aforementioned manifolds [39–37].

We performed numerical simulations of the dynamics of the polariton-assisted scenario by assuming two different initial conditions: pumping of the upper polariton (UP) ($P_u(0) = 1, P_{u\neq0}(0)$) and of the lower polariton (LP) ($P_l(0) = 1, P_{l\neq0}(0)$) for mentioned acenes. We denote $\tilde{\epsilon}_{TT}$ as the polariton-assisted TT yields. They were calculated using the same criteria as in Eq. (10). From a comparison of $\tilde{\epsilon}_{TT}$ (Table I) and the values $\epsilon_{TT}(\Delta, \Omega)$ (where $\Delta = \omega_{ph} - \omega_D$ is the detuning between the cavity photon and the singlet) in Fig. 2 we notice an enhancement in the TT yield for hexacene, especially when the LP is pumped. Under these conditions and high $\Delta$ values, the state $|\downarrow\rangle$ is almost purely excitonic ($(c_{ex}^-)^2 \approx 1$), and the rate of the channel associated to photon leakage is suppressed. Moreover, $\omega_-$ becomes closer to resonance with the third vibrational state of the TT manifold (with frequency $\omega_n$) for a given range of $\Omega$. Thus population transfer $|\downarrow\rangle \rightarrow \{T_{n, n+1}\}$ is faster than the bare SF, as the energetic barrier is lower in the former. Finally, there is no competition between the previous transfer process and the decay channel associated to $k_c$, as $k_c(\omega_-) = 0$, under the assumptions of our model. The enhancement considering pumping of the UP for the same molecule (Fig. 3c, upper) is weaker since the fast rate of the transfer $|\uparrow\rangle \rightarrow \{|d\rangle\}$ competes with the rate of $|\downarrow\rangle \rightarrow \{T_{n, n+1}\}$.

Pentacene shows a similar behavior: when $\Delta \approx -3\omega_h$ and the UP is pumped (Fig. 3b, upper), then $|\uparrow\rangle$ is mainly excitonic and population of the TT states is mainly determined by transfer from the dark state manifold, since $\alpha(\omega_{TT,D}) \gg \gamma(\omega_{TT,+})$, i.e. the population from the UP is quickly transferred to dark states before transfer to TT states is carried out. Hence, noting that $\gamma(\omega_{TT,D}) \approx k_{SF}$, we recover (the bare) pentacene yield $\epsilon_{TT}$. Notice however that for large detunings $\tilde{\epsilon}_{TT}(\Delta \approx -3\omega_h, \Omega \approx 1.6\omega_h) > \epsilon_{TT}$ because a phonon blockade prevents fast UP decay into dark states and additionally the charge-transfer decay channel is suppressed ($k_c(\omega_+) = 0$). On the other hand, $\tilde{\epsilon}_{TT}$ values are higher for pumping of the LP (Fig. 3b, lower) as a result of a reduced decay rate $\alpha(\omega_{TT,D})$ to the dark states such that the predominant transfer process is from $|\downarrow\rangle$ to TT states.

Tetracene shows a distinct behavior in view of the bare energetic arrangements of its singlet and TT states (see Fig. 1). More concretely we have $|c_{ex}^\pm|^2, \gamma(\omega_{TT,-}), |c_{ex}^\pm|^2, \gamma(\omega_{TT,+}), \gamma(\omega_{TT,D}) \ll \gamma(\omega_{TT,U})$ for most of the explored ($\Delta, \Omega$) values. This translates into a rapid depletion of the population of the TT manifold during the considered timescale; which is a consequence of the energy of the TT states lying above the dark state energy, in such a way that the rate of population depletion of TT states towards the dark states outcompetes the rate of the inverse process (in view of detailed balance) as well as rates from the polariton manifold to the TT states. The largest $\tilde{\epsilon}_{TT}$ values are reached when the UP is pumped (Fig. 3a, upper) and for parameters ($\Delta, \Omega$) which yield a predominantly excitonic character to $|\uparrow\rangle$, and a sufficiently high rate for the $|\uparrow\rangle \rightarrow \{T_{n, n+1}\}$ process, such that it can better compete with the rates associated to $|\uparrow\rangle \rightarrow \{|d\rangle\}$ and $\{T_{n, n+1}\}$ to $\{|d\rangle\}$. Considering the pumping of the LP (Fig. 3a, lower), the maximal $\epsilon_{TT}$ values are lower in view of $\omega_{TT} - \omega_+ > 0$, which greatly diminishes the rate of the transfer $|\downarrow\rangle \rightarrow \{T_{n, n+1}\}$.

Until now, we have considered SF materials that al-
material with an outer sphere reorganization energy of \(630\) meV. We consider initial conditions with LP population \(P_a(0) = 1, P_{a\neq+}(0) = 0, P_-(0) = 0\).

To summarize, in this letter, we have shown that when SF materials are subjected to SC with a microcavity mode, the photonic leakage of the resulting polariton states constitutes an important decay channel that can decrease TT production, when compared to the bare case. However, the rates associated with this competing decay channel can be tuned by modifying the ratio \(\Delta/\Omega\) (see Fig. 3), in such a way that the dynamics are dictated by the energy differences and the DOS of the dressed states involved in SF. Given the large DOS of the dark state manifold and TT states, the latter must lie lower in energy with respect to the former so as to avoid population leakage towards the dark state manifold and enhance TT yield. Remarkably, while hexacene is a poor SF candidate in the bare case when quenchers are present, it is the material which features the highest enhancement under the proposed polaritonic approach and can even outcompete the bare pentacene TT yield under the conditions considered in this work. Similarly, we notice an increase of the pentacene TT yield, although the improvements are modest in com-
parison with those obtained for hexacene. Finally, we have also considered the putative scenario of a SF material with low TT yield, where the SF rate competes with fluorescence. In this case, our model predicts (for acene-like molecules) that $\Delta G \ll 0$ substantial enhancement of TT yield can be achieved by polariton methods.

**ACKNOWLEDGMENTS**

L.A.M.M is grateful for the support of the UC-Mexus CONACyT scholarship for doctoral studies and with Jorge Campos-González-Angulo for useful discussions. R.F.R., M.D. and J.Y.Z. acknowledge support from the Canada Research Chairs program and NSERC RGPIN-2014-06129. L.A.M.M., R.F.R., M.D. and J.Y.Z. are thankful with UCSD for generous startup funds. L.A.M.M. and J. Y. Z. acknowledge Ming Lee Tang, Michael Tauber, Shane R. Yost and Troy Van Voorhis for helpful comments.

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SI: Polariton-assisted singlet fission in acene aggregates

DESCRIPTION OF THE OPEN-QUANTUM-SYSTEMS MODEL

In this Supporting Information (SI), we provide the theoretical basis for the kinetic model presented in the main text. To begin, consider the explicit form of the Hamiltonian given in Eq (1) of the main text:

\[
H = \left(\omega_c + \sum_i \omega_i \lambda_{S,i}^2\right) \sum_n |n\rangle \langle n| + \sum_{n,i} \omega_i b_{n,i}^\dagger b_{n,i} + \sum_{n,i} |n\rangle \langle n| \omega_i \lambda_{S,i}(b_{n,i} + h.c.) + \omega_{ph} a^\dagger a + \sum_n g(a^\dagger |G\rangle \langle n| + h.c.) + \sum_{n=0}^{N-1} \left(\omega_{TT} + 2 \sum_i \omega_i \lambda_{T,i}^2\right) |T_n T_{n+1}\rangle \langle T_n T_{n+1}| + \sum_{n=0}^{N-1} |T_n T_{n+1}\rangle \langle T_n T_{n+1}| \sum_i \omega_i \lambda_{T,i}(b_{n,i} + b_{n+1,i} + h.c.)
\]

Assuming periodic boundary conditions (|T_{N-1} T_N\rangle = |T_{N-1} T_0\rangle), we introduce delocalized Fourier bases for the singlet excitons |k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i k n} |n\rangle and vibrational degrees of freedom \(b^\dagger_{q,i} = \frac{1}{\sqrt{N}} \sum_n e^{i q n} b^\dagger_{n,i}\), where \(k, q = \frac{2 \pi m}{N}, m = 0, 1, 2, \ldots, N - 1\). We can then rewrite the Hamiltonian above as

\[
H = \sum_k \left(\omega_c + \sum_i \omega_i \lambda_{S,i}^2\right) |k\rangle \langle k| + \sum_{q,i} \omega_i b^\dagger_{q,i} b_{q,i} + \frac{1}{\sqrt{N}} \sum_{q,k} \sum_i \omega_i \lambda_{S,i} \left(|k\rangle \langle k| + q |b_{q,i}^\dagger + h.c.\right) + \omega_{ph} a^\dagger a + \sqrt{N} g \left(a^\dagger |G\rangle \langle k = 0| + h.c.\right) + \sum_{n=0}^{N-1} \left(\omega_{TT} + 2 \sum_i \omega_i \lambda_{T,i}^2\right) |T_n T_{n+1}\rangle \langle T_n T_{n+1}| + \sum_{n=0}^{N-1} |T_n T_{n+1}\rangle \langle T_n T_{n+1}| \sum_i \lambda_{T,i} \omega_i (b_{n,i} + b_{n+1,i} + h.c.)
\]

The introduction of the delocalized basis in the singlet electronic manifold is the starting point to find approximate eigenstates for \(H\) in the strong-coupling (SC) regime, such that the rates of population transfer between these eigenstates can be calculated by a perturbative approach. Along these lines, we introduce a zeroth order Hamiltonian:

\[
H_0 = \sum_k \left(\omega_c + \sum_i \omega_i \lambda_{S,i}^2\right) |k\rangle \langle k| + \sum_{n',i} \omega_i b^\dagger_{n',i} b_{n',i} \left(|G\rangle \langle G| + \sum_k |k\rangle \langle k| + \sum_{n=0}^{N-1} |T_n T_{n+1}\rangle \langle T_n T_{n+1}| \right)
\]

\[
+ \omega_{ph} a^\dagger a + \sqrt{N} g \left(a^\dagger |G\rangle \langle k = 0| + h.c.\right) + \sum_{n=0}^{N-1} \left(\omega_{TT} + 2 \sum_i \omega_i \lambda_{T,i}^2 + \sum_i \lambda_{T,i} \omega_i (b_{n,i} + b^\dagger_{n,i} + b_{n+1,i} + b^\dagger_{n+1,i})\right) |T_n T_{n+1}\rangle \langle T_n T_{n+1}|
\]

\[
= \sum_{n,i} \omega_i b^\dagger_{n,i} b_{n,i} |G\rangle \langle G|
\]

\[
+ \sum_k \left(\omega_c + \sum_i \omega_i b^\dagger_{q=0,i} b_{q=0,i} + \sum_{q \neq 0,i} \omega_i b^\dagger_{q,i} b_{q,i} + \left(1 - \frac{1}{N}\right) \sum_i \omega_i \lambda_{S,i}^2\right) |k\rangle \langle k| + \omega_{ph} a^\dagger a + \sqrt{N} g \left(a^\dagger |G\rangle \langle k = 0| + h.c.\right)
\]

\[
+ \sum_{n=0}^{N-1} \left(\omega_{TT} + \sum_i \lambda_{T,i} \omega_i (b_{n,i} + b^\dagger_{n,i} + b_{n+1,i} + b^\dagger_{n+1,i})\right) |T_n T_{n+1}\rangle \langle T_n T_{n+1}|
\]

\[
+ \sum_{n=0}^{N-1} \left(\omega_{TT} + \sum_i \lambda_{T,i} \omega_i (b_{n,i} + b^\dagger_{n,i} + b_{n+1,i} + b^\dagger_{n+1,i})\right) |T_n T_{n+1}\rangle \langle T_n T_{n+1}|
\]
where we have used, \( \sum_{n,i} \omega_i b_{n,i}^\dagger b_{n,i} = \sum_{q,i} \omega_i b_{q,i}^\dagger b_{q,i} = \sum_{n',i} \omega_i b_{n',i}^\dagger b_{n',i} \) (|G\rangle \langle G| + \sum_k |k\rangle \langle k| + \sum_{n=0}^{N-1} |T_n T_{n+1}\rangle \langle T_n T_{n+1}|), and the definitions \( \delta_i^{q=0,i} = b_{q=0,i}^\dagger + \lambda_{S,i}/\sqrt{N}, \bar{b}_{n,i}^\dagger = b_{n,i}^\dagger + \lambda_{T,i} [|R1,R2]\]). Accordingly, the perturbation is defined as \( V = H - H_0 \) that is

\[
V = \frac{1}{\sqrt{N}} \sum_{q \neq 0,k} \sum_i \omega_i \lambda_{S,i} \left( |k\rangle \langle k + q| + \text{h.c.} \right) \\
+ \frac{V_{TT-S}}{2} \sum_{n=0}^{N-1} \left[ \langle T_n T_{n+1} + |T_n T_{n-1}\rangle \langle n| + \text{h.c.} \right] \\
= \frac{1}{\sqrt{N}} \sum_{q \neq 0,k} \sum_i \omega_i \lambda_{S,i} |k\rangle \langle k + q| + \text{h.c.} \\
+ \frac{V_{TT-S}}{2} \sum_{n=0}^{N-1} \left[ \langle T_n T_{n+1} + |T_n T_{n-1}\rangle \langle n| + \text{h.c.} \right],
\]

which accounts for the scattering of the singlet electronic states due to phonons (Eq. [S6a]) and the coupling of singlet to TT states (Eq. [S6b]). The diagonalization of Eq. [S6a] is carried out as follows: since our rate calculations are performed in the linear response regime with respect to an external pump, we consider only zero- and one-photon-dressed states. In the limit \( N \gg 1 \), \( \delta_i^{q=0,i} \approx b_{q=0,i} [R1] \) for all \( i \) and \( \frac{1}{N} \approx 0 \) which results in the diagonal Hamiltonian

\[
H_0 = \sum_{n,i} \omega_i b_{n,i}^\dagger b_{n,i} |G\rangle \langle G| \\
+ (\omega_+ + \sum_{i,q} \omega_i b_{q,i}^\dagger b_{q,i}) |+\rangle \langle +| + (\omega_- + \sum_{i,q} \omega_i b_{q,i}^\dagger b_{q,i}) |-\rangle \langle -| \\
+ \sum_d (\omega_d + \sum_{i,q} \omega_i b_{q,i}^\dagger b_{q,i} + \omega_i \lambda_{S,i}^2) |d\rangle \langle d| \\
+ \sum_{n=0}^{N-2} \omega_{TT} + \sum_i \left( \delta_i^{q=0,i} \bar{b}_{n,i}^\dagger \bar{b}_{n+1,i} + \bar{b}_{n+1,i}^\dagger \bar{b}_{n,i} \right) + \sum_{n \neq n, n+1} \omega_i b_{n',i}^\dagger b_{n',i} |T_n T_{n+1}\rangle \langle T_n T_{n+1}| \\
= H^{\text{vb}}_S |G; 0\rangle \langle G; 0| \\
+ (\omega_+ + H^{\text{vb}}_S) |+\rangle \langle +| + (\omega_- + H^{\text{vb}}_S) |-\rangle \langle -| \\
+ \sum_d (\omega_D + H^{\text{vb}}_S) |d\rangle \langle d| \\
+ \sum_{n=0}^{N-2} \omega_{TT} + H^{\text{vb}}_{TT} |T_n T_{n+1}\rangle \langle T_n T_{n+1}|,
\]

where \( |G; 0\rangle = |G\rangle \otimes |0_{ph}\rangle \) (|n_{ph}\rangle is the state with \( n \) photons) the vibrational Hamiltonians are \( H^{\text{vb}}_S = \sum_{n,i} \omega_i b_{n,i}^\dagger b_{n,i} \) and \( H^{\text{vb}}_{TT} = \sum_{T_n T_{n+1}} \omega_i \left( \bar{b}_{n,i}^\dagger \bar{b}_{n+1,i} + \bar{b}_{n+1,i}^\dagger \bar{b}_{n,i} \right) + \sum_{n \neq n, n+1} \omega_i b_{n',i}^\dagger b_{n',i} \right|, \) and we have invoked the convenient notation \( |d\rangle = |k \neq 0\rangle, d = \frac{2\pi m}{N} \) for \( m = 1, \cdots, N - 1 \) to denote the dark states. The upper and lower polariton eigenstates are given by

\[
|+\rangle = \cos \theta |G\rangle \otimes |1_{ph}\rangle + \sin \theta |k = 0\rangle \otimes |0_{ph}\rangle, \\
|-\rangle = -\sin \theta |G\rangle \otimes |1_{ph}\rangle + \cos \theta |k = 0\rangle \otimes |0_{ph}\rangle,
\]

with their corresponding eigenenergies given in Eq. (7) of the main text. The factors \( \cos \theta \) and \( \sin \theta \) account for the degree of mixing of the considered photon-dressed electronic states, where \( \tan \theta = \frac{2\sqrt{N} \omega}{\omega + \sum \omega_i \lambda_{S,i}^2 - \omega_{ph}}. \) Notice that the corresponding vibrational Hamiltonians for \( |G\rangle, |+\rangle, |-\rangle \), and \( \{|d\rangle\} \) are all the same \( (H^{\text{vb}}_S) \) in this zeroth-order treatment. Here, we note that the energy offset of the dark states is at \( \omega_D = \omega_c + \sum \omega_i \lambda_{S,i}^2 \).
CALCULATION OF KINETIC RATES

We now describe the reduced dynamics of the polaritonic and excitonic states (namely $|\pm\rangle$, $\{|d\rangle\}$, $\{|T_nT_{n+1}\rangle\}$) due to the perturbation $V$. Since we are only interested in the evolution of populations, we derive a Pauli master equation using the Redfield formalism under the secular and Markov approximations [R3],

$$\frac{dP_a(t)}{dt} = \sum_{b \neq a} \left( k_{b \rightarrow a} P_b - k_{a \rightarrow b} P_a \right),$$

where $P_a(t)$, $a \in \{+, -, d, T_nT_{n+1}\}$, is the population in state $a$. The population-transfer rate from state $b$ to state $a$ is given by [R3],

$$k_{b \rightarrow a} = \int_{-\infty}^{\infty} d\tau \langle V_{ba}(\tau)V_{ab}(0) \rangle,$$

which is Fermi’s golden rule in the form a correlation function Fourier transform; here, $V_{ba}(\tau) = \langle b|e^{iH_0\tau}V e^{-iH_0\tau}|a\rangle = e^{-i\omega_{ab}\tau}\langle b|e^{iH_{\text{vib}}\tau}V e^{-iH_{\text{vib}}\tau}|a\rangle$, where we are using $\omega_D$, $\omega_{T_nT_{n+1}} = \omega_{TT}$ as the bare energies of the dark and TT states respectively, and $\omega_{ab} = \omega_a - \omega_b$. Here, $\langle O \rangle = \text{Tr}_{\text{vib}}\{\rho_{\text{eq}}^{\text{vib}}(\tau)\}$ denotes a vibrational trace over the thermal ensemble of phonons governed by $H_{\text{vib}}^2$ at inverse temperature $\beta$, $\rho_{\text{eq}}^{\text{vib}} = \frac{e^{-\beta H_{\text{vib}}}}{\text{Tr}_\text{vib}(e^{-\beta H_{\text{vib}}})}$.

Upon insertion of Eq. (S6) into Eq. (S10), the population transfer between a state $|a\rangle \in S, S = \{|+, |-, |k \neq 0\rangle\}$ and a state $|b\rangle \in TT, TT \{T_nT_{n+1}\}$ results in a Marcus-type expression [R3]. For instance, the rate from $|+\rangle$ to $|T_0T_1\rangle$ is given by

$$k_{+ \rightarrow T_0T_1} = \int_{-\infty}^{\infty} \frac{V_{TT-S}^2 f_+}{N} \int_{-\infty}^{\infty} d\tau \left\langle \exp \left( iH_{\text{vib}}^{\text{T}_{0}\text{T}_{1}}(\tau) \right) \exp \left( - iH_{\text{vib}}^{\text{T}_{0}\text{T}_{1}}(\tau) \right) \right\rangle e^{-i\omega_{TT}^{+}\tau}$$

$$= \frac{V_{TT-S}^2 f_+}{N} \int_{-\infty}^{\infty} d\tau \left\langle \exp \left[ i \left( \sum_{i,n} \omega_i b_{n,i}^{\dagger} b_{n,i} \right) \right] \exp \left\{ - i \left[ \sum_{i} \sum_{\nu,\mu} \omega_i b_{\nu,i}^{\dagger} b_{\mu,i} + b_{\nu,i}^{\dagger} b_{\mu,i} \right] \right\} e^{-i\omega_{TT}^{+}\tau},$$

where we use the notation $f_+ = \langle i|T_{\text{xc}}^S |i\rangle$ ($T_{\text{xc}}^S \equiv \sum_n |n\rangle\langle n|$) for the singlet-exciton fraction in state $i$; here, $f_+ = \sin \theta^2$. The $1/N$ prefactor accounts for the portion of the delocalized polariton state which is in sites 0 and 1 (see Eq. (S9)) and can thus undergo SF at these positions. To evaluate Eq. (S12), we now introduce the gap Hamiltonian $H_{T_0T_1,S}^{\text{vib}} = H_{T_0T_1}^{\text{vib}} - H_{S}^{\text{vib}}$ [R3],

$$k_{+ \rightarrow T_0T_1} = \int_{-\infty}^{\infty} \frac{V_{TT-S}^2 f_+}{N} \int_{-\infty}^{\infty} d\tau \left\langle \exp \left[ - i \int_0^\tau H_{T_0T_1,S}^{\text{vib}}(t')dt' \right] \right\rangle e^{-i\omega_{TT}^{+}\tau},$$

where $\hat{T}$ is the time-ordering operator and

$$H_{T_0T_1,S}(t') = \exp \left( iH_S^{\text{vib}} t' \right) H_{T_0T_1,S}^{\text{vib}} \exp \left( - iH_S^{\text{vib}} t' \right)$$

$$= 2 \sum_i \lambda_i^2 \omega_i + \sum_i \lambda_i^2 \omega_i |b_{0,i}^{\dagger}e^{i\omega_{i}t'} + b_{0,i}e^{-i\omega_{i}t'} + b_{1,i}^{\dagger}e^{i\omega_{i}t'} + b_{1,i}e^{-i\omega_{i}t'} \rangle.$$
In Eq. (S15), we have assumed a thermalized vibrational bath and independent localized phonon modes, \( \bar{n}_i(\omega_i) = \frac{1}{e^{\beta \omega_i} - 1} \) is the average bosonic occupation number of the \( i \)-th vibrational mode. Using Eqs. (S14) and (S15) altogether yields,

\[
k_{+ \rightarrow T_0 T_1} = \frac{|V_{TT-S}|^2 f_+}{N} \int_{-\infty}^{\infty} d\tau e^{-i(\omega_{TT} - \omega_+)} e^{-G(t)}. \tag{S16}
\]

The integral in Eq. (S16) can be simplified [R4] by introducing a separation of low and high vibrational frequency bath modes \( G(t) \approx G_l(t) + G_h(t) \), where

\[
G_i(t) = -2\lambda_{TT,i}^2 \left[ \coth \left( \frac{\beta \omega_i}{2} \right) \left( \cos \omega_i t - 1 \right) - i \sin \omega_i t \right].
\]

Here, \( \bar{\omega}_h \) (\( \bar{\omega}_l \)) corresponds to an effective high (low) frequency that satisfies \( \bar{\omega}_h \gg 1/\beta \) (\( \bar{\omega}_l \ll 1/\beta \)), while \( 2\lambda_{TT,h}^2 \) (\( 2\lambda_{TT,l}^2 \)) is an effective Huang-Rhys factor for the bath mode with frequency \( \bar{\omega}_h \) (\( \bar{\omega}_l \)). Under this approach we obtain

\[
k_{+ \rightarrow T_0 T_1} = \frac{1}{N} f_+ \gamma_d(\omega_{TT} - \omega_+), \tag{S17a}
\]

\[
\gamma_d(\omega_{TT+}) = \sum_{n=0}^{\infty} \gamma^{(n)}(\omega_{TT} - \omega_+), \tag{S17b}
\]

\[
\gamma^{(n)}(\omega_{TT+}) = |V_{TT-S}|^2 \sqrt{\frac{\pi \beta}{R_l}} e^{-2\pi^2 \lambda_{TT,h}^2} \left( \frac{n!}{\lambda_{TT,h}^2} \right) \exp \left[ -\frac{\beta(\omega_{TT} + n\bar{\omega}_h - \omega_+)^2}{4R_l} \right], \tag{S17c}
\]

where \( R_l = 2\bar{\omega}_l / \lambda_{TT,l}^2 \) is the reorganization energy of the low-frequency vibrational mode and \( \gamma^{(n)}(\omega_{TT}) \) can be interpreted as a single-molecule rate from the lowest-energy vibronic state of \( |a\rangle \) to the vibronic state of \( |b\rangle \) with \( n \) phonons in the high-frequency vibrational mode. Notice that Eq. (S17a) does not feature an energy scale associated to the reorganization energy of the singlet, as a result of polaron decoupling [R1].

The rates \( k_{- \rightarrow T_0 T_1} \), \( k_{d \rightarrow T_0 T_1} \) can be calculated in analogous ways giving

\[
k_{- \rightarrow T_0 T_1} = \frac{1}{N} f_- \gamma_d(\omega_{TT} - \omega_-), \tag{S18}
\]

\[
k_{d \rightarrow T_0 T_1} = \frac{1}{N} f_+ \gamma_d(\omega_{TT} - \omega_+ - \sum_i \omega_i \lambda_{S,i}^2). \tag{S19}
\]

The rates of backward transfer can be calculated by invoking detailed balance, i.e., \( k_{a \rightarrow b} = e^{\beta \omega_{ba}} k_{b \rightarrow a} \). Due to similarity in chemical structure, we assume that the values for \( \bar{\omega}_h = 174 \text{ meV} \) and \( \lambda_{TT,h} = 1.6 \) are independent of the identity of the acene. The latter was estimated as \( \lambda_{TT,h} = \lambda_{S-\rightarrow TT,h} + \lambda_{S,h} \), where \( \lambda_{S-\rightarrow TT,h} \) is the square root of the Huang-Rhys factor for the \( |n\rangle \rightarrow |T_{n+1} T_{n+1}\rangle \) transition [R5] and \( \lambda_{S,h} \) is the analogous quantity for the \( |G\rangle \rightarrow |n\rangle \) transition. Since there is no available data in the literature to estimate \( R_l \), we opted to use the low-frequency reorganization energy of the transition \( |n\rangle \rightarrow |T_{n+1} T_{n+1}\rangle \) for hexacene, and we set \( R_l = 100 \text{ meV} \) [R5] for all the materials considered. On the other hand the parameters \( \Delta G = \omega_{TT} - \omega_e \), and \( V_{TT-S}/2 \) are treated as material dependent; they are taken from Ref. [R6] and are given in the main text.

Marcus rates for the cavity-free case are approximately one order of magnitude larger than the experimental ones when \( V_{TT-S} \) is large, i.e. in the adiabatic limit. In the section below we introduce corrections to these rates to make a connection with the Bixon-Jortner equation [R7] which correctly interpolates between the diabatic and adiabatic limits.

We now consider the calculation of transfer rates between states \( |a\rangle, |b\rangle \in S \). As an example, the transfer rate
between the upper polariton and one dark state $|d\rangle$ is given by

$$k_{+\rightarrow d} = \int_{-\infty}^{\infty} \langle V_d(\tau)V_{d+}(0)\rangle d\tau$$

$$= \frac{1}{N} f^+ \sum_{i,j} \omega_i |\lambda_S,i| \omega_j |\lambda_S,j| \int_{-\infty}^{\infty} \left( e^{iH_{\text{ vib}} \tau} (b_{q=d,i} + b_{q=-d,i}^\dagger) e^{-iH_{\text{ vib}} \tau} (b_{q=d,j}^\dagger + b_{q=-d,j}) \rho_{eq} \right)$$

$$\times e^{-i \left[ \sum_i \omega_i \lambda^2_S,i + \omega_e - \omega_\perp \right] \tau} d\tau$$

$$= \frac{1}{N} f^+ \sum_i |\omega_i |\lambda_S,i|^2 \int_{-\infty}^{\infty} \left( \langle b_{q=d,i} e^{-i\omega_i \tau} + b_{q=-d,i}^\dagger e^{i\omega_i \tau} \rangle \langle b_{q=d,j}^\dagger + b_{q=-d,j} \rangle \right) e^{-i \left( \sum_i \omega_i \lambda^2_S,i + \omega_e - \omega_\perp \right) \tau} d\tau.$$ (S20)

where we used the fact that the phonons are uncorrelated to simplify the double summation. Notice that in our model the energy of the phonon modes is independent of their momentum (in fact, the calculation using a localized phonon basis would render the same answer [R8]). Identifying $\langle b_{d,i} b_{d,i}^\dagger e^{-i\omega_i \tau} + b_{-d,i}^\dagger b_{-d,i} e^{i\omega_i \tau} \rangle = C(\tau,0)$ as a bath correlation function [R3],

$$C(\tau,0) = \int_0^{\infty} J(\omega) \left[ \pi(\omega) + 1 \right] e^{-i\omega \tau} + \pi(\omega) e^{i\omega \tau} d\omega,$$

where $J(\omega) = 2 \sum_i |\omega_i |\lambda_S,i|^2 \delta(\omega - \omega_i)$ is the bath spectral density, we obtain

$$k_{+\rightarrow d} = \frac{f^+}{N} \alpha \left( \omega_e - \sum_i \omega_i \lambda^2_S,i - \omega_\perp \right),$$

where $\alpha(\omega) = \pi J(\omega) \pi(\omega) + 1$ for $\omega \geq 0$ and $\alpha(\omega) = \pi J(\omega) \pi(\omega)$ for $\omega < 0$. In our calculations, we use an Ohmic spectral density with a Lorentzian frequency cutoff: $J(\omega) = 2R\Omega \omega^{-1} \frac{\omega}{\pi}$, with the parameters $R = 50$ meV and $\Omega = 180$ meV taken from Ref. [R9] and are assumed to be the same for the acenes considered. The same approach can be used to compute the rates of relaxation $k_{+\rightarrow -}$, $k_{d\rightarrow -}$, and the backward rates inferred from the detailed balance condition, as explained before. It is noteworthy that our approach predicts rates $k_{+\rightarrow -} = k_{-\rightarrow +} = 0$. This follows from the perturbation (see Eq. (S18)), which does not couple the $|+\rangle$ and $|\rangle$ states.

**Adiabatic corrections to Marcus equations.—** To make a stronger connection with experimental circumstances, we will now consider an *ad-hoc* way to include corrections to the Marcus-type treatment above, so that our predictions remain valid throughout the diabatic (small $V_{TT-S}$) and adiabatic (large $V_{TT-S}$) regimes. To do so, we renormalize the rates in Eq. (S17c) $\gamma^{(n)}(\omega_i) \rightarrow \gamma^{(n)}(\omega_i) e^{-\Gamma^{(n)}}$ [R3] where

$$\Gamma^{(n)} = \frac{2\pi}{v} \frac{|V_{TT-S}|^2}{|F_S - F_T|} \left( \frac{\tau^2_{TT,h}}{n!} \right) \text{FC factor}$$

is a FC-corrected Massey parameter with $v$ being a characteristic velocity of the (slow) low-frequency coordinate; $|F_S - F_T|$ is the corresponding absolute difference in slopes of these potential energy surfaces (PESs) at their crossing point. The factor $e^{-\Gamma^{(n)}}$ accounts for the probability the system will remain in the initial PES after times much longer than $\frac{2\pi}{v}$. Taylor expanding the correction factor, we obtain,

$$\frac{\gamma^{(n)}(\omega_i)}{e^{\Gamma^{(n)}}} \approx \frac{\gamma^{(n)}(\omega_i)}{1 + \Gamma^{(n)}}.$$

To define $\Gamma^{(n)}$ in terms of parameters of our model we have $|F_S - F_T| = 2 \frac{R_l}{\sqrt{\frac{2\pi m\beta}{\hbar^2}}} |\lambda_{TT,l}|$ where $m$ and $R_l$ are the mass and the reorganization energy of the effective low-frequency vibrational mode introduced previously. To obtain an estimate for $v$, we consider the root-mean square of the velocity $<v^2>^{1/2}$ around the minimum of the singlet PES which in the high temperature limit can be calculated as [R7],

$$v = <v^2>^{1/2} \approx \frac{\lambda_{TT,l}}{\tau_d} \sqrt{\frac{2}{m\beta \omega_d^2}} \equiv \frac{\lambda_{TT,l}}{\tau_{nad}},$$

where $\tau_d$ is the decay time of the position autocorrelation function for the low-frequency vibrational mode, and we have accordingly introduced the non-adiabatic timescale $\tau_{nad}$. By using the previous set of approximations, we
heuristically obtain the Bixon-Jortner equation [R7], which has been shown to predict SF rates close to experimental values [R6]. Collecting the results above, Eqs. (S17)–(S19) become:

\[ k_{i \rightarrow j} = \frac{f_i}{N} \sum_{n=0}^{\infty} \frac{\gamma^{(n)}(\omega_{ij})}{1 + 4\pi|V_{nR}|^2 \tau_{nad} e^{-2\pi \frac{q_{nR}^2}{n^2}}} \]

\[ = \frac{f_i}{N} \sum_{n=0}^{\infty} \gamma^{(n)}(\omega_{ij}) \Gamma_{ad}^{(n)} \]

\[ = \frac{f_i}{N} \gamma(\omega_{ij}) \]

assuming \(|i\rangle \in \mathcal{S}\) and \(|j\rangle \in \mathcal{TT}\). Notice that the \(\gamma(\omega)\) rates introduced above are the ones used in the main text.

**FINAL KINETIC EQUATIONS**

With the rates calculated above we construct the following kinetic model for SF in the SC regime:

\[ \partial_t P_{\pm} = -f_\pm \frac{\alpha(\omega_{\pm,D})}{N} (N-1) P_{\pm} + f_\pm \sum_d \frac{\alpha(\omega_{D,D})}{N} P_d - f_\pm \frac{\gamma(\omega_{TT,\pm})}{N} (N) P_{\pm} \]

\[ + f_{\pm} \sum_{n=0}^{N-2} \frac{\gamma(\omega_{\pm,TT})}{N} P_{T_n T_{n+1}} - (f_\pm k_c(\omega_{\pm}) + f_{\pm}^p k_{phot}) P_{\pm} \]

\[ \partial_t P_d = f_+ \frac{\alpha(\omega_{+,D})}{N} P_+ - f_+ \frac{\alpha(\omega_{+,D})}{N} P_d + f_- \frac{\alpha(\omega_{-,D})}{N} P_- - f_- \frac{\alpha(\omega_{-,D})}{N} P_d - \frac{\alpha(0)}{N} (N-2) P_d \]

\[ + \frac{\alpha(0)}{N} \sum_{d \neq d'} P_{d'd'} - \frac{\gamma(\omega_{TT,D})}{N} (N) P_d + \sum_n \frac{\gamma(\omega_{D,TT})}{N} (N) P_{T_n T_{n+1}} - k_c(\omega_{D}) \rho_{dd} \]

\[ \partial_t P_{T_n T_{n+1}} = f_+ \frac{\gamma(\omega_{TT,+,D})}{N} P_+ - f_+ \frac{\gamma(\omega_{TT,+,D})}{N} P_{T_n T_{n+1}} - \frac{\gamma(\omega_{D,TT})}{N} (N) P_{T_n T_{n+1}} + \sum_d \frac{\gamma(\omega_{TT,D})}{N} P_d \]

\[ + f_- \frac{\gamma(\omega_{TT,-,D})}{N} P_- - f_- \frac{\gamma(\omega_{TT,-,D})}{N} P_{T_n T_{n+1}} \]

where \( f_{\pm}^p = |\langle 1_{ph} | \otimes \langle G|\rangle|^2 \) and \( k_{phot} \) is the rate constant that accounts for photon leakage. The latter is only relevant for the polariton states as the photonic component for the dark states is zero. By introducing \( P_{D}^{total} = \sum_d P_d \) and \( P_{TT}^{total} = \sum_n P_{T_n T_{n+1}} \), we arrive at Eqs. (8a)–(8c) of the main text. We have also introduced the rate constant \( k_c(\omega) \) to account for the decay of the singlet due to a process that competes with SF (see main text).

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