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Super-reaction: The collective enhancement of a reaction rate by molecular polaritons in the presence of energy fluctuations

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ABSTRACT

Recent experiments have demonstrated that molecular polaritons, hybrid states of light and matter formed by the strong coupling between molecular electronic or vibrational excitations and an optical cavity, can substantially modify the physical and chemical properties of molecular systems. Here, we show that by exploiting the collective character of molecular polaritons in conjunction with the effect of polaron decoupling, i.e., the suppression of environmental influence on the polariton, a super-reaction can be realized, involving a collective enhancement of charge or excitation-energy transfer reaction rate in a system of donors all coupled to a common acceptor. This effect is analogous to the phenomenon of super-radiation. Since the polariton is a superposition state of excitations of all the molecules coupled to the cavity, it is vulnerable to the effect of decoherence caused by energy fluctuations in molecular systems. Consequently, in the absence of a strong light–matter interaction, the reaction rate decreases significantly as the number of molecules increases, even if the system starts from the polariton state. By turning on the light–matter interaction, the dynamic behavior of the system changes dramatically, and the reaction rate increases with the number of molecules, as expected for a super-reaction. The underlying mechanism is shown to be the protection of quantum coherence between different donors as the light–matter interaction becomes stronger.

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The last decade has witnessed the emergence of a new field of study around molecular polaritons. Polaritons modify the physical and chemical properties of molecular systems significantly through the strong coupling of electronic or vibrational molecular excitations to an optical cavity. This coupling leads to the formation of a hybrid state of light and matter,[1–5] resulting in various interesting phenomena. Important applications have been proposed and demonstrated, including the manipulation of chemical landscapes,[6–9] the modification of chemical reactivity by molecular-vibration polaritons,[10–17] cavity-enhanced energy transfer, and conductivity in organic media.[18–20] Further applications include polariton lasing and Bose–Einstein condensates[21–24] and nonlinear optical properties with applications in optoelectronic devices.[25,26]

In the absence of interaction with the environment, the molecular polariton has the form of a superposition state in which all the molecules coupled to the cavity are collectively excited. However, recent studies have shown that, in most cases, the collective effect displayed by a molecular polariton does not prominently influence chemical reactivity, except for its contribution to the collective coupling strength between the polariton and the cavity. In some cases, no collective effect is observed;[14,27] the collective coupling can even lead to the suppression of an effect that scales as $1/N$, where N is the number of molecules.[16] Therefore, it is unclear whether the inherent collective excitation in the polariton state can play a key role in chemical reactions or not. On the other hand, the collective coupling reportedly produces dramatic changes in physical system properties. A notable example is the phenomenon of super-radiance,[28,29] where the collective interaction of a group of emitters with a vacuum field causes them to emit a short burst of light radiation with a strong intensity proportional to N^2. This behavior differs drastically from the conventional exponential decay of a group of independent emitters with a rate proportional to N. Super-radiance has been observed in systems ranging from quantum-dot arrays[30] to molecular aggregates.[31–34]

In this study, we exploit the inherent collective character of the molecular polariton state in a system of donors all coupled to a

common acceptor to obtain a super-reaction with a collective enhancement of charge or excitation-energy transfer reaction rate. This effect is analogous to the super-radiance described above. The collective enhancements that occur in super-radiance and super-reaction are purely quantum mechanical effects resulting from the constructive quantum interference between pathways starting from different group members. Thus, quantum coherence between donors is a necessary condition for realizing super-reaction. On the other hand, the energy fluctuations caused by the molecule–environment interactions make the molecular polariton state vulnerable to decoherence. Therefore, a collective enhancement of the reaction rate is not guaranteed even if the system starts from the molecular polariton state. Supertransfers have been proposed in the context of molecular aggregates.[35–38] The effect of energy fluctuations has, however, not been investigated explicitly as they were implicitly assumed to be small compared to the electronic couplings among constituent molecules, which is usually not the case, especially in condensed-phase molecular systems. As shown below, light–matter interaction provides a means to control the effect of energy fluctuations on the molecular polariton state and thus enables super-reactions even in the presence of strong energy fluctuations.

We first numerically simulated molecular quantum dynamics, subject to system–environment interactions, to show that energy fluctuations decrease the reaction rate considerably as the number of molecules increases. Attaining a super-reaction appears to be impossible in a system of molecules in condensed phase, where environmental effects cannot be ignored. However, a sufficiently strong light–matter interaction between molecules and the cavity causes a dramatic change in the system dynamics. In this case, the reaction rate increases with the number of molecules coupled to the cavity, as expected for a super-reaction. We show that the underlying mechanism of this change in behavior is the protection of quantum coherence between donors as the light–matter interaction becomes stronger. The effect of polaron decoupling is thus demonstrated in a dynamic context.[7] This is in contrast to its static manifestation in optical spectroscopy, which was first studied for a molecular aggregate with electronic excitation coupled to a single vibration mode.[39] The effect of polaron decoupling was then generalized to the case where the electronic excitation was coupled to an environment consisting of many vibration modes spanning a wide frequency range.[40] It has been observed experimentally.[41]

As illustrated in Fig. 1, we consider an electron or excitation-energy (exciton) transfer reaction from a system of N identical donors coupled to a common acceptor, modeled by the Hamiltonian $\hat{H}_{tr} = \hat{H}_D^{tr} + \hat{H}_A + \hat{H}_{DA}$ with

$$\hat{H}_D^{tr} = \sum_{j=1}^{N} \hbar\omega_D |e_j\rangle\langle e_j|, \qquad (1)$$

$$\hat{H}_A = \left\{ \hbar\omega_A + \sum_{j=1}^{N}\sum_\xi g_\xi^{DA}\left[\left(\hat{b}_\xi^j\right)^\dagger + \hat{b}_\xi^j \right] \right\} |a\rangle\langle a,| \qquad (2)$$

and

$$\hat{H}_{DA} = -\sum_{j=1}^{N} \hbar V_{DA}\left(|a\rangle\langle e_j| + |e_j\rangle\langle a| \right). \qquad (3)$$
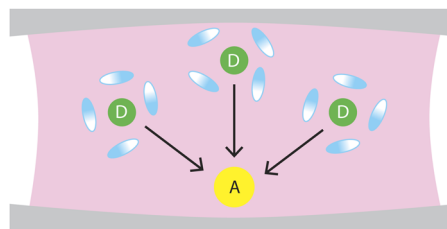

FIG. 1. Schematic illustration of a super-reaction involving the collective enhancement of the electron or exciton transfer reaction rate in a system of donors (green) coupled to a common acceptor (yellow), all located inside an optical cavity. The collective coupling between the molecules and the cavity field (light magenta) produces a molecular polariton, a hybrid state of light and matter. The blue ellipsoids surrounding the donors represent the molecular environments whose thermal dynamics give rise to strong energy fluctuations in the molecular system.

Here, $|e_j\rangle$ denotes the one-exciton state with the jth donor being in its electronic excited state, while the other molecules are in their electronic ground states; $|a\rangle$ is the state where the electron or exciton is transferred to the acceptor (in the case of electron transfer, the resulting positive charge is assumed to be distributed equally among donors); $\hbar\omega_D$ and $\hbar\omega_A$ are the energies of, respectively, a donor in its electronic excited state and the acceptor state; V_{DA} is the coupling strength between the donors and the acceptor. The transfer from each donor to the acceptor is assumed to be accompanied by a configurational change in an independent environment, which is modeled by a collection of harmonic oscillators with the Hamiltonian $\hat{H}_{env}^{tr} = \sum_{j=1}^{N}\sum_\xi \hbar\omega_\xi \left(\hat{b}_\xi^j\right)^\dagger \hat{b}_\xi^j$. The reorganization energy per donor molecule associated with the transfer is given by $\lambda_{DA} = \sum_\xi \left(g_\xi^{DA}\right)^2/(\hbar\omega_\xi)$.

The donor electronic excitations are all coupled to a single cavity mode, as specified by the interaction Hamiltonian

$$\hat{H}_I = -\sum_{j=1}^{N} \hbar\Omega_R\left(|e_j\rangle\langle g|\hat{c} + |g\rangle\langle e_j|\hat{c}^\dagger \right), \qquad (4)$$

where $|g\rangle = \prod_{j=1}^{N} \otimes |g_j\rangle$ is the ground state of the system with all the donors in their electronic ground states, $\hat{c}$ is the annihilation operator of a cavity photon, and Ω_R is the single-emitter Rabi frequency that characterizes the light–matter interaction strength. Here, a rotating-wave approximation is applied, as we do not consider an ultrastrong coupling regime.[16] The Hamiltonian of the cavity photons is given by $\hat{H}_{ph} = \hbar\omega_c\hat{c}^\dagger\hat{c}$, where ω_c is the cavity resonance frequency. Below, we consider resonant excitation, namely, $\omega_c = \omega_D$. The electronic excitation of each donor is assumed to be accompanied by a change in the configuration of an independent environment, as modeled by the coupling Hamiltonian

$$\hat{H}_D^{ex} = \sum_{j=1}^{N}\sum_\chi g_\chi^{ex}\left[\left(\hat{b}_\chi^j\right)^\dagger + \hat{b}_\chi^j \right] |e_j\rangle\langle e_j| \qquad (5)$$

and the environment Hamiltonian $\hat{H}_{env}^{ex} = \sum_{j=1}^{N}\sum_\chi \hbar\omega_\chi\left(\hat{b}_\chi^j\right)^\dagger \hat{b}_\chi^j$. The reorganization energy associated with electronic excitation is given by $\lambda_{ex} = \sum_\chi \left(g_\chi^{ex}\right)^2/(\hbar\omega_\chi)$.

Before performing a full numerical simulation of the transfer dynamics, we first present a qualitative analysis of the N-dependence of the transfer rate in the limit where Fermi's golden rule is valid. Consider a system initially prepared in the molecular polariton state

$$|p\rangle = \frac{1}{\sqrt{2}}\left(|1\rangle \otimes |g\rangle + |0\rangle \otimes \frac{1}{\sqrt{N}}\sum_{j=1}^{N}|e_j\rangle\right), \qquad (6)$$

where $|0\rangle$ and $|1\rangle$ denote the photon-number states with zero and one cavity photon, respectively. We first make the *a priori* assumption that environmental energy fluctuations negligibly affect the polariton state so that the polariton state is maintained throughout the transfer reaction. Physically, it means that the coherence time of the polariton state is assumed to be long compared with the timescale of the transfer. Then, by Fermi's golden rule, the transfer rate in the weak-donor–acceptor-coupling and high-temperature limit is given by

$$k_{P\rightarrow A}^{tr} = \sqrt{\frac{\pi}{\hbar^2 k_B T \lambda_{PA}}}|\langle p|\hat{H}_{DA}|a\rangle|^2 \exp\left[-\frac{(\Delta E_{PA}-\lambda_{PA})^2}{4\lambda_{PA}k_B T}\right], \qquad (7)$$

where ΔE_{PA} denotes the energy difference between the polariton and acceptor states and λ_{PA} is the reorganization energy associated with the transfer from the polariton to the acceptor. If the displacements of the potential energy surfaces associated with the electronic excitations in the system of N donors is small compared with those associated with the transfer from the donors to the acceptor, we have an approximate relation $\lambda_{PA} \simeq N\lambda_{DA}$. On the other hand, Eqs. (3) and (6) give

$$\langle p|\hat{H}_{DA}|a\rangle = -\hbar V_{DA}\sqrt{\frac{N}{2}}. \qquad (8)$$

Therefore, the maximum transfer rate, obtained for $\Delta E_{PA} = \lambda_{PA}$, scales as $N^{1/2}$. On the other hand, if the donor system is independent and one donor is initially excited, the maximum transfer rate scales as $N^{-1/2}$. It can be understood by the fact that when the transfer is accomplished, i.e., when the exciton/electron has been transferred to the common acceptor, there are changes in the environment configurations associated with all the donors such that the total reorganization energy scales as N. It is worth noting that super-reactions cannot be realized if the transfer occurs in independent pairs of donor and acceptor.[7] Physically, the collective enhancement of reaction rates in super-reactions is a result of the constructive interference between different pathways of transfer connecting donors to a common acceptor.

The above analysis suggests that a system initially prepared in the molecular polariton state can produce a super-reaction whose rate is greater than that of a system of independent donors and increases with the number of molecules. This is true, provided that the influence of energy fluctuations from the environment on the polariton state can be ignored. On the other hand, because the molecular polariton is a superposition state involving collective excitation from all molecules coupled to the cavity [as expressed in Eq. (6)], it is conventionally argued that the polariton state is vulnerable to decoherence, namely, the loss of quantum coherence due to energy fluctuations. Therefore, it is highly nontrivial whether a super-reaction can be achieved or not. To examine the prediction of the above analysis, we numerically simulated the dynamics of

the system described by the above set of Hamiltonians. To limit the computational workload (which increases exponentially with the number of independent environments), the environments associated with the electronic excitation of each donor and with the transfer from the donor to the acceptor are described by a common set of harmonic oscillators $\xi = \chi$. We also assumed that the coupling strengths are related by a constant η, that is, $g_\xi^{DA} = \eta g_\xi^{ex} \equiv \eta g_\xi$. The environmental dynamics are characterized by their correlation functions

$$C(t) = \int_0^\infty d\omega\, J(\omega)\left[\coth\left(\frac{\beta\omega}{2}\right)\cos\omega t - i\sin\omega t\right], \qquad (9)$$

where $\beta = 1/(k_B T)$ and $J(\omega) = \sum_\xi g_\xi^2 \delta(\omega - \omega_\xi)$ is the environmental spectral density. Considering the Drude–Lorentz spectral density $J(\omega) = 2\lambda\tau\omega/(\tau^2\omega^2 + 1)$ in the high-temperature limit ($k_B T\tau/\hbar \gg 1$), the correlation function $C(t)$ becomes exponential. Here, $\lambda = \sum_\xi g_\xi^2/(\hbar\omega_\xi)$ is the reorganization energy (per donor molecule), and τ is the relaxation time of the environment. In this case, the dynamics of the reduced system can be obtained by integrating out the environmental degrees of freedom. The resulting hierarchical equation of motion describes the dynamics of open quantum systems for a wide range of coupling strengths in a numerically exact manner.[42] Our numerical simulation sets the following parameter values for the molecular system and environment: $V_{DA} = 10\,\text{cm}^{-1}$, $T = 300\,\text{K}$, $\tau = 250\,\text{fs}$, $\lambda = 10\,\text{cm}^{-1}$, and $\eta = 1$, which correspond to the high-temperature and strong-energy-fluctuation limits ($V_{DA} < \sqrt{\lambda k_B T}$). By varying the molecule–cavity coupling strength, the donor–acceptor energy difference $\Delta\omega_{DA} = \omega_D - \omega_A$ is always set to be equal to the collective Rabi frequency $\Omega_R\sqrt{N}$ such that the acceptor state has the same energy as the lower polariton state. Here, the cavity loss rate κ is assumed to be negligibly small, corresponding to a good optical cavity with a high Q factor, such as the microcavities using distributed Bragg reflector (DBR) mirrors ($Q \sim 10^4$).[43] The effects of radiative and nonradiative population decays of molecules in donor and acceptor states were also ignored as their timescales are typically much longer than the timescale of the transfer. For the initial state, we consider the case in which the system is initially prepared in the molecular polariton state [Eq. (6)] by a vertical excitation under the Condon approximation, that is, the environments are at the equilibrium positions of the potential energy surfaces associated with the donor electronic ground states.

Figure 2 compares the transfer dynamics in the absence and presence of energy fluctuations if the molecules and the cavity are uncoupled, i.e., $\Omega_R = 0$. Here, the time-dependent probability $p_A(t)$ of finding an electron/exciton at the acceptor is calculated for systems with different numbers of donors $1 \leq N \leq 4$. Evidently, despite the initial increase in transfer rate with the number of molecules due to the collective effect of the polariton state, the transfer rate rapidly changes its behavior as a result of energy fluctuations, becoming smaller for systems with many molecules. This change in behavior can be attributed to decoherence.

Figure 3 shows the transfer dynamics for systems with different numbers N of molecules if the coupling between the molecules and the cavity is set to the collective Rabi frequency $\hbar\Omega_R\sqrt{N} = 20\,\text{meV}$. Here, the single-emitter Rabi frequency Ω_R is changed while keeping the collective Rabi frequency fixed to the above value as N is
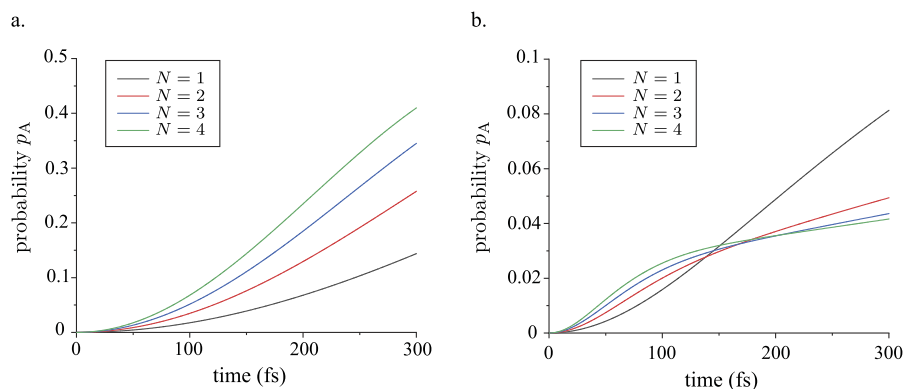
FIG. 2. Comparison of electron/exciton transfer dynamics from a system of donors to an acceptor in the (a) absence and (b) presence of energy fluctuations when there is no coupling between the molecules and the cavity, namely, $\Omega_R = 0$. The probability p_A of finding an electron/exciton at the acceptor is plotted as a function of time for systems with different numbers N of donors. In both cases, the system is initially prepared in the molecular polariton state given by Eq. (6). The reorganization energy per donor molecule is $\lambda = 10$ cm^{-1}. The other parameters of the molecular system and environment are given in the text.

varied. The collective Rabi coupling is strong in the sense that it is greater than the energy fluctuation amplitude characterized by $\sqrt{\lambda k_B T}$. It is clear from the numerical result that the transfer rate increases with N, as expected for a super-reaction. By comparing this result with that in Fig. 2(b) when the light–matter interaction is turned off, it can be inferred that the effect of decoherence is suppressed when the molecular system is strongly coupled to the cavity. This, in turn, leads to an increase in the transfer rate with N. This demonstrates the effect of polaron decoupling in a dynamic context, as opposed to its static manifestation in optical spectroscopy.[39–41] It is also worth noting that the transfer dynamics considered in this study and their timescales depend on the coupling between the system and the environment as the system eventually approaches the
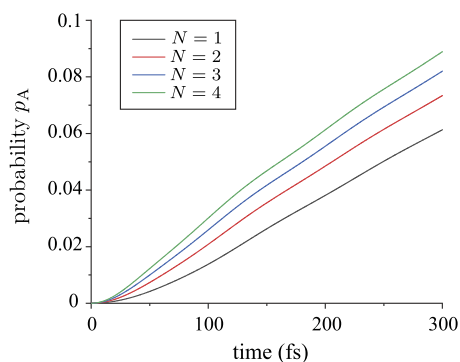

FIG. 3. Transfer dynamics from a system of donors to an acceptor when the coupling between molecules and the cavity is turned on. As in Fig. 2, the probability p_A of finding an electron/exciton at the acceptor is plotted as a function of time for systems with different numbers N of donors. The system is initially prepared in the molecular polariton state, and the dynamics occur in the presence of strong energy fluctuations. Here, the collective Rabi frequency is fixed at $\hbar\Omega_R\sqrt{N} = 20$ meV as the number of molecules is varied. The reorganization energy per donor molecule is $\lambda = 10$ cm^{-1}.

thermal equilibrium state. Therefore, the dependence of the transfer rate with respect to the number N of molecules coupled to the cavity, which is obtained by numerical simulations, should differ from the power scaling law obtained by the Fermi's golden rule analysis.

To justify the above prediction of the polaron decoupling mechanism for realizing a super-reaction, we investigated the dependence on the Rabi coupling strength of the transfer dynamics and quantum coherence between different donors. Figure 4 plots the time-dependent electron/exciton population $p_A(t)$ at the acceptor and the quantum coherence between two different donors $i \neq j$, as quantified by the modulus of the off-diagonal matrix element $|\rho_{ij}(t)|/\sqrt{p_i(t)p_j(t)}$ of the density matrix of the system normalized by the populations, for different light–matter interaction strengths. Evidently, the transfer rate increases with the coupling strength, and the underlying mechanism is the protection of quantum coherence between different donors. This can be understood by noting that the collective enhancement is a purely quantum-mechanical effect for which quantum coherence is an absolutely necessary condition.

The dependences of transfer dynamics on the other different parameters, including the reorganization energy, temperature, and cavity loss rate, are also investigated, and the results are plotted in Figs. S1–S3 in the supplementary material. The reaction rate decreases with increasing reorganization energy and temperature as the energy fluctuations become stronger. However, as shown in Figs. 2(b) and 3, the reaction rate increases with N, provided that the system is in the strong-coupling regime, namely, $\hbar\Omega_R\sqrt{N} > \sqrt{\lambda k_B T}$. The population transfer also depends on the lifetime of the cavity photon. For an optical cavity with a low Q-factor, such as metallic-mirror-based cavities ($Q \sim 10^2$), the transferred population $p_A(t)$ increases rapidly before decaying to zero due to the loss of cavity photon. The time point at which p_A reaches its maximum value is determined by the lifetime of the cavity photon. However, since this lifetime is independent of N, the growth of p_A with increasing N characteristic of the super-reaction can be
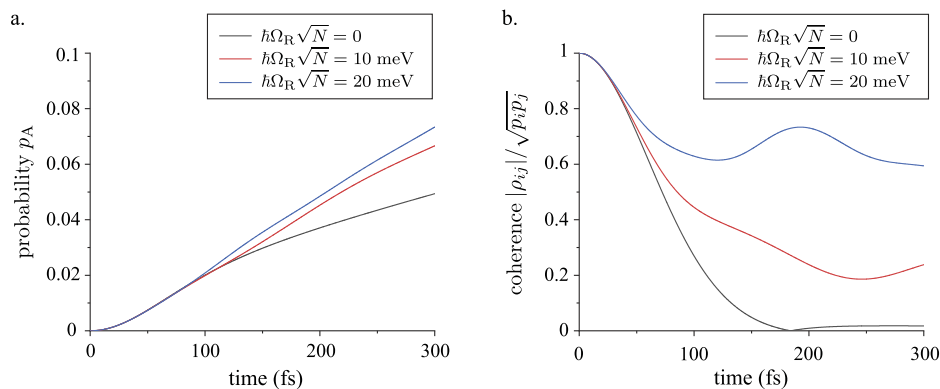
FIG. 4. (a) Electron/exciton transfer dynamics from a system of donors to an acceptor and (b) the quantum coherence between different donors for different values of the collective Rabi coupling strength $\Omega_R\sqrt{N}$. The quantum coherence between donors is quantified by $|\rho_{ij}(t)|/\sqrt{p_i(t)p_j(t)}$, where $\rho_{ij}(i \neq j)$ is the off-diagonal matrix element of the density matrix of the system and p_i, p_j are the probabilities of finding an electron/exciton at the i,jth donors.

observed at any time (Fig. S3). In order to get a large population transfer, of course, an optical cavity with a high Q-factor, such as the microcavities using DBR mirrors ($Q \sim 10^4$), should be employed.[43]

In conclusion, we have shown that by exploiting the collective character of the molecular polariton state, a super-reaction with a collective enhancement of the electron/exciton transfer reaction rate can be obtained in a system of donors coupled to a common acceptor. Such a super-reaction requires the persistence of quantum coherence between different donors in the presence of strong energy fluctuations. This condition can be fulfilled by the effect of polaron decoupling, provided that the light–matter interaction is sufficiently strong. The number of donors coupled to a common acceptor is, however, limited by the finite-range interaction between molecules and the finite density of molecules in the system. As a result, super-reactions do not occur in the thermodynamic limit $N \rightarrow \infty$.[44] Nevertheless, they can be observed in systems with finite N by, for example, measuring the increase in the reaction rate with variable molecular density. Alternatively, by varying the light–matter interaction strength, the system can be moved from the independent to the cooperative transfer regime or vice versa, by which the reaction rates of the normal reaction and the super-reaction can be measured for a comparison. Moreover, since the finite-range super-reaction can be overwhelmed by long-range transfers mediated by the cavity field in large-size systems,[18,19,44] the latter should be avoided for the observation of the former by, for example, using acceptors whose couplings to the cavity are prohibited. An important open question is what kind of molecular arrangements would be optimal for a super-reaction.

See the supplementary material for the dependences of transfer dynamics on different parameters, including the reorganization energy, temperature, and cavity loss rate.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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