Extraordinary exciton conductance induced by strong coupling

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We demonstrate that exciton conductance in organic materials can be enhanced by several orders of magnitude when the molecules are strongly coupled to an electromagnetic mode. Using a 1D model system, we show how the formation of a collective polaritonic mode allows excitons to bypass the disordered array of molecules and jump directly from one end of the structure to the other. This finding could have important implications in the fields of exciton transistors, heat transport, photosynthesis, and biological systems in which exciton transport plays a key role.

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The transport of excitons (bound electron-hole pairs) is a fundamental process that plays a crucial role both in natural phenomena such as photosynthesis, where energy has to be transported to a reaction center [1–3], and in artificial devices such as excitonic transistors [4, 5] or organic solar cells, whose power conversion efficiency can be improved significantly when the exciton diffusion length is increased [6]. Similarly, understanding and manipulating the role of excitons in heat transport has become an active field of research, with possible applications ranging from thermo-electric effects to heat-voltage converters, to nanoscale refrigerators, and even thermal logic gates (cf. [7] and references therein). The exciton transport efficiency depends on a wide range of factors with such surprising features as the occurrence of noise-assisted transport [8–10]. Pioneering works have even suggested that coherent transport can play an important role in biological systems [2, 3, 11]. However, most systems composed of organic molecules are disordered and possess relatively large dissipation and dephasing rates, such that exciton transport typically becomes diffusive over long distances [12].

An intriguing possibility to modify exciton properties is by strong coupling to an electromagnetic (EM) mode, forming so-called polaritons (hybrid light-matter states). This is achieved when the Rabi frequency, i.e., the energy exchange rate between exciton and EM modes, becomes faster than the decay and/or decoherence rates of either constituent. Polaritons combine the properties of their constituents, in particular, mutual interactions and low effective masses, enabling new applications such as polariton condensation in semiconductors [13] and organic materials [14], the modification of molecular chemistry [15] and work functions [16], or the transfer of excitation between different molecular species [17]. Due to the large dipole moments and high densities, organic materials support large Rabi splittings [18–20], and can also be strongly coupled to surface plasmon polaritons [19, 21–24]. The dispersion relation can then be tuned to achieve a further reduction of the effective mass [25].

FIG. 1. Sketch of the model system. A 1D chain of (possibly disordered) quantum emitters with dipole moments $d_i$ inside a cavity with cavity mode $\vec{E}_c(\vec{r})$. Excitons are pumped into the system from the left reservoir with rate $\gamma_p$. The exciton current is measured by the excitons reaching the sink reservoir on the right, coupled through incoherent decay of the last emitter with rate $\gamma_d$.

Very recently, an increase of the electrical conductance of an organic material was shown under strong coupling of the excitons to a cavity mode [26]. Inspired by this result, we demonstrate in this Letter that through strong coupling to an electromagnetic mode, i.e., the creation of polaritonic states, the exciton transport efficiency can be improved by many orders of magnitude. The strong coupling allows the excitons to bypass the disordered organic system, preventing localization and leading to dramatically improved energy transport properties. We note that while we focus on organic molecules in the following, the results can readily be generalized to other systems such as quantum dots and Rydberg atoms, or even chains of trapped ions, which offer a high degree of controllability [27, 28].

We focus on a model system that captures the essential physics: A 1D chain of two-level emitters inside a cavity (see Fig. 1). The emitter dipole transition is coupled to the single cavity mode, and additionally induces Coulombic dipole-dipole interaction between the emitters. The effect of internal (e.g., rovibrational or phononic) and external environment modes is taken into account through effective dephasing and nonradiative decay rates modeled using a master equation of Lindblad form. The system Hamiltonian $H$ in the rotating wave approximation (setting $\hbar = 1$ here...
where $a$ is the bosonic annihilation operator of the cavity mode with energy $\omega_c$ and electric field $\vec{E}_c(\vec{r})$. The molecular excitons of energy $\omega_m$ are created and destroyed by the fermionic operators $\sigma_i^+$ and $\sigma_i^-$. Molecule $i$ is characterized by its position $\vec{r}_i$ and dipole moment $\vec{d}_i$, giving the cavity-molecule interaction $g_i = -\vec{d}_i \cdot \vec{E}_c(\vec{r}_i)$. The dipole-dipole interaction (in the quasi-static limit) is

$$V_{ij}^{dd} = \frac{\vec{d}_i \cdot \vec{d}_j - 3 \vec{d}_i \cdot \vec{R}_{ij} \times \vec{d}_j \cdot \vec{R}_{ij}}{4 \pi \epsilon_0 R_{ij}^3},$$

(2)

with $R_{ij} = |\vec{r}_i - \vec{r}_j|$ and $\vec{R}_{ij} = (\vec{r}_i - \vec{r}_j)/R_{ij}$.

The system dynamics is described by a Lindblad master equation for the density matrix

$$\dot{\rho} = -i[H, \rho] + \sum_{\alpha = i, c} \mathcal{L}_\alpha[\rho],$$

(3)

where $\alpha$ runs over all molecules as well as the cavity mode. The superoperators $\mathcal{L}_\alpha$ describe decay and dephasing:

$$\mathcal{L}_i = \gamma_d \mathcal{L}_{\sigma_i^-} + \gamma_\phi \mathcal{L}_{\sigma_i^+ \sigma_i^-},$$

$$\mathcal{L}_c = \kappa \mathcal{L}_n,$$

(4)

(5)

where $\mathcal{L}_n[\rho] = \frac{1}{2} (2c_p c^\dagger - \{c^\dagger c, \rho\})$ is the standard form for Lindblad superoperators. The total molecule decay rate $\gamma_d$ is given by $\gamma_d = \gamma_r + \gamma_{nr}$, with $\gamma_r$ and $\gamma_{nr}$ the radiative and nonradiative decay rates, while $\gamma_\phi$ is the dephasing rate. The decay rate $\kappa$ of the cavity photons is dominated by leakage through the mirrors. For later reference, we also define the total molecular decoherence rate $\gamma = \gamma_d + \gamma_\phi$.

As mentioned above, we only include one cavity mode and describe the molecules by a linear 1D chain along the longitudinal cavity direction ($z$ axis), with positions $\vec{r}_i = x_i \hat{z}$, such that the cavity electric field is identical for all molecules. It is polarized along the (out-of-plane) $z$ axis, leading to $\vec{E}_c(\vec{r}_i) = E_c \hat{z}$. The total coupling between molecules and the cavity mode can be characterized by the collective Rabi frequency $\Omega_R = 2 \sqrt{\sum_i g_i^2}$. For zero detuning $\omega_m = \omega_c$, strong coupling is entered for $\Omega_R > |\gamma - \kappa|/2$ and leads to the formation of upper and lower polaritons at energies $\omega_m \pm \frac{1}{2} \sqrt{\Omega_R^2 - |\gamma - \kappa|^2}/4$. The Rabi splitting (energy difference between upper and lower polariton) can approach 1 eV in experiments $\omega_m \approx 2.11$ eV, $\gamma_{nr}^{-1} = 500$ ps, $\gamma_\sigma^{-1} = 600$ fs, and $\gamma_\phi^{-1} = 25$ fs. The cavity lifetime $\kappa^{-1} = 66$ fs is typical for experiments using cavities made of thin metal mirrors $\omega_m$.

We choose the quantum emitter parameters to approximately correspond to TDBC J-aggregates at room temperature $\omega_m = 2.11$ eV, $\gamma_{nr}^{-1} = 500$ ps, $\gamma_\sigma^{-1} = 600$ fs, and $\gamma_\phi^{-1} = 25$ fs. The cavity lifetime $\kappa^{-1} = 66$ fs is typical for experiments using cavities made of thin metal mirrors $\omega_m$. The molecule parameters also determine the dipole moment through $\gamma_r = \omega_m^3 d^2/(3 \pi \epsilon_0 \hbar \gamma_\sigma^2)$, giving $d \approx 36$ Debye. The average intermolecular spacing is taken as $\delta x = 3$ nm. Note that while the coupling to the cavity mode is taken into account explicitly, the radiative decay rate into all other electromagnetic modes can also be modified by the presence of a cavity. Since $\gamma_r$ is much smaller than the other rates, this modification can safely be neglected here. While we only show results for the parameters given above, we checked that the main conclusions
drawn in the following apply for a wide range of parameters and do not depend on the specific values chosen here.

Fig. 2 shows the exciton conductance $\sigma_e$ zero cavity-molecule detuning $\omega_c = \omega_m$, as a function of the collective Rabi frequency $\Omega_R$. Here, we keep the number of molecules fixed and change the electric field strength, going through the transition from weak to strong coupling. This can be achieved in an experiment by, e.g., putting the molecules at different positions inside the cavity [34]. We compare regular and random molecule arrangements for chains of 40 and 60 molecules. For the regular distribution, the strong dipole-dipole interaction leads to an additional small energy shift $\Delta$ of the molecular bright state coupling to the cavity; zero detuning thus corresponds to $\omega_c = \omega_m + \Delta$.

For all of the cases shown in Fig. 2, the conductance is approximately constant in the weak coupling limit $\delta \omega \ll \gamma, \kappa$, where the cavity mode does not play a role. Unsurprisingly, the conductance in this limit strongly depends on the molecular configuration—it is almost completely suppressed for the random case, for which 1D systems always show Anderson localization. The conductance in the random case is calculated as the logarithmic mean of 100 random configurations as appropriate for localized systems, i.e., $\sigma_e = \exp(\log \sigma^t_e)$ [35]. Note that even in the regular case, transport is quite inefficient due to the relatively large decay and dephasing rates of the molecular excitons, leading to diffusive transport [10, 12]. Strikingly, when the coupling to the cavity mode is increased, an extraordinary increase of the conductance is observed in all cases. Once strong coupling is reached ($\Omega_R \gg \gamma, \kappa$), the conductance again becomes almost independent of $\Omega_R$, indicating that the fully formed polariton channel dominates exciton conductance. In this limit, the conductance also becomes almost independent of the configuration and only depends on the number of molecules, i.e., length of the 1D chain. While randomness can suppress conduction almost completely in the weak-coupling limit, the polariton modes are barely affected by it. As a consequence of their delocalized nature induced by the collective exciton-cavity coupling, the excitation can efficiently bypass the disordered chain of emitters.

This also provides a possible indication for the mechanism behind the enhanced electrical conduction observed under strong coupling in the experiments by Orgiu et al. [26]. However, the connection between exciton transport through polaritons and electrical conduction is currently unclear, as polaritons are in principle neutral quasiparticles.

We also note that while we focus on incoherent driving for simplicity in this work, we have found that under coherent driving/incoupling at frequency $\omega$, the same general behavior is observed. The main difference is an additional resonant enhancement when $\omega$ coincides with the eigenfrequencies of the system (see details in the supplemental material [36]). An interesting aspect is that even when hopping is completely suppressed, resonant transport occurs not only when driving at the polariton eigenfrequencies, but also at the unmodified molecule frequency—a clear signature that the dark states (which are not coupled to the cavity EM field) are still affected by the existence of strong coupling.

We next focus on the case where the cavity mode is detuned from the molecular excitations by an energy $\delta \omega = \omega_m - \omega_c$. As shown in Fig. 3, the onset of the extraordinary conductance is then shifted to larger coupling strengths for increasing detuning $|\delta \omega|$. However, the final conductance in the strong-coupling limit is independent of the detuning. This again indicates that the conductance proceeds through the polariton modes, which are only fully formed when the Rabi frequency $\Omega_R$ becomes large enough to not only overcome decoherence processes, but also the detuning. Once this is fulfilled, their character does not strongly depend on...
where we have defined the total decoherence rate $\Gamma = \gamma + \kappa$. More details and the full expression for arbitrary detuning are given in the supplemental material [36].

As expected, the analytical solution (Eq. 8) perfectly matches the numerics (cf. Fig. 4). For small Rabi frequency, the conductance through the polariton modes grows with $\Omega_R^2$, while it saturates to a constant value for $\Omega_R \to \infty$. For large $N$, this constant value is given by $\frac{\gamma \gamma_d (\gamma + \Gamma) \omega_m \Omega_R^2}{(2 \gamma_d \Gamma N + (2 \gamma_{\phi} + \gamma_d N) \Omega_R^2)} \left( \frac{\kappa \gamma_d \Gamma N + (\kappa \gamma_{\phi} + \gamma_d \Gamma N) \Omega_R^2}{\Omega_R^2} \right)$

$\sigma_e = \frac{\gamma \gamma_d (\gamma + \Gamma) \omega_m \Omega_R^2}{(2 \gamma_d \Gamma N + (2 \gamma_{\phi} + \gamma_d N) \Omega_R^2)} \left( \frac{\kappa \gamma_d \Gamma N + (\kappa \gamma_{\phi} + \gamma_d \Gamma N) \Omega_R^2}{\Omega_R^2} \right)$

where $\sigma_e$ is the exciton conductance, $\Omega_R$ is the Rabi frequency, $\gamma$ and $\kappa$ are the spontaneous and cavity decay rates, $\gamma_d$ is the dipole decay rate, $\omega_m$ is the molecular exciton frequency, and $N$ is the number of molecules.

The fourth power of $\Omega_R$ in the weak-coupling limit is explained by the rate obtained from two quantum jumps, to the cavity mode and back, with coupling $\propto \Omega_R$. Interestingly, Eq. 8 shows that the conductance, at least in the simplified model without disorder or direct hopping, is not directly related to the conventional criterion for the onset of strong coupling where the vacuum Rabi splitting becomes real ($\Omega_R > |\gamma - \kappa|/2$). Indeed, the difference $\gamma - \kappa$ does not occur in Eq. 8. Instead, the exciton conductance becomes constant when $\Omega_R \gg 2 \gamma$ (for large $N$). This is related to large values of the cooperativity $C = \Omega_R^2 / \gamma \kappa$, which can occur even if strong coupling is not fully reached.

To conclude, we have demonstrated that the formation of polariton modes, i.e., strong coupling, can dramatically enhance exciton transport. When the coupling is strong...
enough and the polaritons are fully formed, the excitons can almost completely bypass the chain of quantum emitters and “jump” directly from one end to the other, leading to large exciton conductance. This robust effect persists almost independently of the exact parameters of the system, and most notably occurs efficiently even when the underlying excitonic system is strongly disordered and its transport is completely suppressed due to localization. Through a simple model, we have furthermore shown that transport through direct hopping and through the polariton modes constitute two effectively independent channels, which helps to explain why the polariton conductance is almost independent of the disorder in the system. These results demonstrate a possible pathway for improving the efficiency of excitonic devices, where the EM mode could be provided by plasmonic structures to enable fully integrated nanometer-scale devices. We note that related results have simultaneously been obtained by Schachenmayer et al. [37].

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SUPPLEMENTAL MATERIAL

COHERENT DRIVING

In this section, we show some results for coherent driving of the system (as opposed to the incoherent driving used in the main text). As mentioned in the main text and shown below, the main conclusions are similar to those obtained under incoherent driving. The main difference is that under coherent driving at frequency \( \omega \), a resonant enhancement of the conductance is observed when \( \omega \) corresponds to one of the eigenmodes of the system. We use the same model as in the main text, but instead of an incoherent pumping term described by \( \mathcal{L}_p \), we add a coherent driving term \( \mathcal{H}_p(t) = \Omega_p \sigma_i^+ e^{i \omega t} + c.c. \) (within the rotating wave approximation) to the Hamiltonian. Here, \( \Omega_p \) and \( \omega \) are the driving amplitude and frequency, respectively. The steady state can then be calculated by going to the rotating frame, in which \( \mathcal{H}_p \) is time-independent, but the system frequencies are shifted by \( \omega \). The exciton conductance is calculated analogously to the incoherent case, using \( \sigma_{\text{coh}} = \hbar J / \Omega_p^2 \), where the factor \( \hbar \) is added to make \( \sigma_{\text{coh}} \) unitless.

We focus again on the case without dipole-dipole interaction, which allows to calculate only the polariton contribution to exciton conductivity even when relatively short chains are used (\( N = 20 \) in the following). For simplicity, we also choose zero cavity-molecule detuning, \( \omega_c = \omega_m \). Fig. 5 demonstrates that the polariton-mediated exciton conductance under coherent driving displays a polynomial increase with \( \Omega_R \), which saturates to a constant value once strong coupling is fully entered. This is identical to the behavior under incoherent pumping. In addition, the conductance is resonantly enhanced when the driving frequency coincides with an eigenfrequency of the system. The system eigenfrequencies correspond to the upper and lower polariton states (\( \omega_{m} \pm \Omega_R/2 \)), as well as the dark states at \( \omega_m \), which are not directly coupled to the cavity. Interestingly, and somewhat surprisingly, the largest conductance is found when driving the dark modes (\( \omega = \omega_m \)), not the polariton modes (cmp. the violet and dashed orange lines in Fig. 5b). This effect persists even when dephasing (which couples between dark and bright states) is turned off, and demonstrates that even the eigenstates that are not themselves strongly coupled to the cavity mode become delocalized when the system enters strong coupling.

SIMPLIFIED MODEL

In this section, we provide more details on the simplified model and its solution described in the text. The starting point is the Hamiltonian given in Eq. 1 in the main text:

\[
H = \omega_c a^\dagger a + \sum_i \omega_m \sigma_i^+ \sigma_i^- + \sum_i g_i (a^\dagger \sigma_i^- + a \sigma_i^+) + \sum_{i,j} V^{dd}_{ij} (\sigma_i^+ \sigma_j^- + \sigma_j^+ \sigma_i^-),
\]

from which we remove the direct dipole-dipole interaction responsible for hopping by setting \( V^{dd}_{ij} = 0 \). We next assume that all molecules are oriented identically, such that the \( g_i \) are constant and given by \( g_i = \Omega_R / \sqrt{4N} \). As explained in the

![FIG. 5.](image)

FIG. 5. Exciton conductance as a function of Rabi splitting and driving frequency for a chain of 20 molecules, where the dipole-dipole interaction has been suppressed to only show the polariton contribution to conductance. Panel (a) shows a map of the conductance as a function of total Rabi frequency \( \Omega_R \) and driving frequency \( \omega \), while the other two panels show cuts of the data at different driving frequencies (b) and at two Rabi frequencies (c). The positions of the cuts are indicated by the dashed grey lines in (a).
Due to the structure and symmetries of the system, we can write the steady-state density matrix within the zero- and single-excitation subspace as

\[ \rho_{ss} = \begin{pmatrix} \rho_{00} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \rho_{cc} & \rho_{c1} & \rho_{c2} & \ldots & \rho_{c2} \\ 0 & \rho_{c1} & \rho_{11} & \rho_{12} & \ldots & \rho_{12} \\ 0 & \rho_{c2} & \rho_{12} & \rho_{22} & \rho_{23} & \ldots & \rho_{23} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \rho_{c3} & \rho_{23} & \rho_{23} & \ldots & \rho_{23} \\ \end{pmatrix}, \]

(11)

where \( \rho_{00} \) is the probability to be in the ground state (no photons or excitons), \( \rho_{cc} \) is the cavity excitation probability, \( \rho_{ii} \) is the excitation probability of molecule \( i \), and \( \rho_{ab} \) is the coherence matrix element between constituent \( a \) and \( b \). Since all but the first molecule behave identically, the density matrix elements involving molecule \( i \) with \( i > 1 \) are all identical and given with \( i = 2 \). Additionally, \( \rho_{23} \) denotes the coherence element between any pair of molecules not involving the first.

The steady state density matrix can then be obtained from \( \dot{\rho}_{ss} = 0 \), which for the specific form of the density matrix corresponds to a set of linear equations for the 4 real probabilities \( \{ \rho_{00}, \rho_{cc}, \rho_{11}, \rho_{22} \} \) and the 4 complex coherence elements \( \{ \rho_{c1}, \rho_{c2}, \rho_{12}, \rho_{23} \} \), giving 12 independent real variables. Note that there are actually \((N + 1)^2 + 1\) linear equations for \( N \) molecules. However, due to the symmetry, only 11 of them are linearly independent. The steady-state density matrix is then obtained by solving for the null space of the coefficient matrix of the linear equations, and subsequently normalized to \( \text{Tr} \rho_{ss} = 1 \).

Having obtained the steady state density matrix, the exciton conductivity is calculated using Eq. 7 in the main text, which explicitly gives

\[ \sigma_e = \frac{\gamma d \Omega R}{\gamma_p} \left( \frac{\Omega}{2} \text{Re}(\rho_{c2}) + \omega_m \rho_{22} \right). \]

(12)

Inserting the solution \( \rho_{ss} \) into this expression and taking the linear-response limit \( \gamma_p \to 0 \) gives the general solution for \( \sigma_e \), which we give here for completeness:

\[ \sigma_e = \frac{\gamma d \Omega R (4N\gamma((\gamma^2 + 2\gamma + N\gamma^2 + \Delta^2) + \gamma^3)\omega_m - \gamma d \Gamma \delta \omega) + ((2\gamma m + N\gamma d)\kappa \delta \omega + N(\gamma + \Gamma)\Gamma \omega_m)\Omega R}{N(16N\gamma^2 \gamma d \Delta^2 + 4(\gamma m + N\gamma d)\gamma \Omega R + (2\gamma m + N\gamma d)\Omega R)(4N\kappa \gamma d \Delta^2 + (\kappa \gamma m + N\Gamma \gamma d)\Gamma \Omega R)}, \]

(13)

where in addition to the definitions in the main text, we use \( \Delta^2 = \delta \omega^2 + \Gamma^2 / 4 \). Finally, we note that the same approach works equally well under coherent driving (not shown here).