Exciton mobility control through sub-Å packing modifications in molecular crystals

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Exciton mobility in π stacks of organic chromophores is shown to be highly sensitive to the interference between long-range Coulombic coupling and a short-range coupling due to wave function overlap. A destructive interference, which leads to a compromised exciton bandwidth, can be converted to constructive interference (and an enhanced bandwidth) upon sub-Angstrom transverse displacements between neighboring chromophores. The feasibility of the control scheme is demonstrated theoretically on a derivative of terrylene, where the exciton is essentially immobile despite strong Coulombic coupling. A transverse slip of only 0.5 Å along either the short or the long molecular axis boosts the exciton velocity to $2 \times 10^4$ m/s. Changes in the mobility are correlated to changes in the absorption spectrum, allowing the latter to be used as a screen for high mobility aggregates.

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I. INTRODUCTION

Optimizing energy and charge transport is a crucial element in the design of efficient organic-based photovoltaic and light-emitting devices. Transport in such devices is usually attributed to incoherent hopping [1], although there is increasing evidence of a subpicosecond coherent contribution [2–5]. The mobility of singlet excitons is derived mainly from the Coulombic coupling between chromophores, consistent with the fundamental excitations being Frenkel-type excitons where the electron and hole remain bound to the parent molecule. However, in tightly packed π-stacked organic crystals, such as those corresponding to a multitude of perylene-based dyes [6–8], the proximity of neighboring molecules leads to significant charge transfer (CT) between chromophores through the spatial overlap of their frontier molecular orbitals. It is well known that the electron and hole bandwidths, as well as the optical bandgap in perylene dyes, are sensitive to sub-Angstrom shifts (“slips”) in the relative orientations of neighboring molecules, leading to the remarkable range of colors displayed by such dyes in the crystalline phase. This effect, known as crystallochromy [9–13], is attributed to the changing registry of the frontier molecular orbitals of nearest-neighbor (NN) molecules. Small changes in the slip-stacking distance are also thought to play a strong role in the efficiency of singlet exciton fission [14–16].

In a recent paper [17], the unusual photophysical properties of 7,8,15,16-tetraazaterrylene (TAT) nanopillars grown on silica substrates (see Fig. 1) [18] were explored, showing that the two-band nature of its crystal-phase absorption spectrum [18,19] can be understood as an interference between Coulombic coupling, which promotes H-aggregate behavior (blueshifted features), and CT-mediated coupling, which promotes J-aggregate behavior [20] (redshifted features). The interference was also shown to lead to a significant reduction in the exciton bandwidth, suggesting a coincident reduction in the exciton mobility. Interestingly, the TAT nanopillars show structured exciton emission [19] so that exciton mobility is not inhibited by excimer trap formation, as it is in similarly packed perylene crystals [8,21]. Even more recently, the same interference effect was employed to explain dynamic fluctuations in the net excitonic coupling induced by thermal motions of the nuclei in anthracene and polyaromatic hydrocarbons [22]. In the present paper, we investigate exciton dynamics in TAT stacks and find a dramatic dependence of the exciton velocity on small (sub-Angstrom) slips of one TAT molecule relative to its neighbor. Hence, it should be possible to exploit this dynamic crystallochromy-like effect to control the rate of energy transfer in organic materials.

II. THEORY

The nature of interference between the long-range Coulombic and the short-range CT-mediated couplings can be appreciated within the framework of the electronic Hamiltonian:

$$\hat{H}_{el} = \sum_{m,n} (J_{m,n} - U_{d_m,n}^c)B_m^cB_n + \sum_n [t_n c_n^\dagger e_{n+1} + t_n d_n^\dagger d_{n+1} + \text{H.c.}] - \sum_{n,s \neq 0} V_{CT}(s) c_n^\dagger e_n d_{n+s}$$

(1)

where we assume a subspace consisting of a single electron and a single hole. For the nth chromophore, $c_n^\dagger (c_n)$ creates (annihilates) an electron in the lowest unoccupied molecular orbital (LUMO), $d_n^\dagger (d_n)$ creates (annihilates) a hole in the highest occupied molecular orbital (HOMO), and $B_m^c (= c_m^\dagger d_n)$ and $B_n$ create and annihilate a local Frenkel excitation, respectively. The first term in $\hat{H}$ accounts for energy transfer between the nth and the mth chromophores, occurring directly via the Coulombic coupling $J_{m,n}$. The term also includes the local exciton binding energy $U$. The CT is mediated by the electron ($t_n$) and hole ($t_n$) transfer integrals appearing in the second summation. Such terms also couple the locally excited Frenkel excitons to CT excitons. The latter consist of anion-cation pairs; for charges separated by $|s|d$, where $d$ is the distance between NN chromophores, the Coulombic binding energy is, $V_{CT}(s) = e^2 / (4\pi \varepsilon_0 \varepsilon_R |s|d)$. 

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In order to obtain quantitative agreement for the TAT absorption spectrum, one needs to include vibronic coupling involving the prominent 1200 cm\(^{-1}\) intramolecular stretching mode that is responsible for the pronounced vibronic progressions observed in the absorption and photoluminescence (PL) spectra [18,19]. We use a Holstein-style Hamiltonian to account for the exciton-vibrational coupling involving this mode so that the complete Hamiltonian is written as [23]:

\[
\hat{H} = \hat{H}_{el} + \hbar \omega_{vib} \sum_n b_n^\dagger b_n + \hbar \omega_{vib} \sum_n (\lambda (-b_n^\dagger + b_n) + \lambda^2) B_n^\dagger B_n + \hbar \omega_{vib} \sum_{n,s=\pm 0} \lambda_- (b_n^\dagger + b_n + \lambda_+ (b_{n+s}^\dagger + b_{n+s}) + \lambda^2 n_{\sigma}^\dagger n_{\sigma} + U + \omega_{0-0} + \Delta_{0-0})
\]

In Eq. (2), \(b_n^\dagger(b_n)\) creates (annihilates) a vibrational quantum on molecule \(n\) with the energy \(\hbar \omega_{vib} (=1200\text{ cm}^{-1})\) corresponding to the intramolecular stretching mode. The nuclear potential well of this mode is assumed to be harmonic and characterized by a shifted equilibrium geometry when the molecule is in an excited or ionic state. The corresponding relaxation energy of an exciton is given by \(\hbar \omega_{vib} \lambda^2\), where \(\lambda^2\) defines the dimensionless Huang-Rhys (HR) parameter. For the anionic and cationic states, the respective relaxation energies are \(\hbar \omega_{vib} \lambda_-^2\) and \(\hbar \omega_{vib} \lambda_+^2\), with the associated HR factors given by \(\lambda_-^2\) and \(\lambda_+^2\). The final three terms of the Hamiltonian in Eq. (2) collectively define the molecular transition energy between the ground and the excited state; \(\omega_{0-0}\) is the excitation energy of a monomer in solution, and \(\Delta_{0-0}\) is the solution-to-crystal energetic shift. The addition of \(U\) ensures that the transition energy is equal to \(\omega_{0-0} + \Delta_{0-0}\) in the limit of noninteracting chromophores.

In addition to Coulombic coupling, energy transfer can be accomplished via CT-mediated transfer of a single electron and a single hole; in the limit that the diabatic Frenkel band is energetically well separated from the CT band (by \(\gg |t_e|, |t_h|, \hbar \omega_{vib}\)), application of second-order perturbation theory yields an effective Frenkel exciton Hamiltonian, which replaces the electronic part in Eq. (1) [20]:

\[
\hat{H}_{eff} = \sum_n (\Delta_{SR} - U) B_n^\dagger B_n + \sum_{m,n} (J_{m,n} + J_{SR} \delta_{m,n+\pm 1}) B_m^\dagger B_n
\]

where

\[
J_{SR} = -\frac{2(t_e + t_h)}{U - V_{CT}(1)}
\]

is the effective short-range coupling mediated by a virtual CT state [20] and

\[
\Delta_{SR} = -\frac{2(t_e^2 + t_h^2)}{U - V_{CT}(1)}
\]

is the second-order energy level shift. The effective Hamiltonian shows that the short-range coupling \(J_{SR}\) interferes directly with the NN Coulombic coupling [24–26]. For TAT, our calculations reveal a screened NN Coulombic coupling of \(\sim 300-400\text{ cm}^{-1}\), which is compensated by a short-range coupling of comparable magnitude but opposite sign [17]. Such aggregates were referred to as HJ aggregates because the positive Coulombic coupling promotes H-like photophysical behavior, while the negative CT-mediated coupling promotes J-like behavior. Although the concept of competing short-range \((J_{SR})\) and long-range \((J_{nm})\) coupling is rigorous only for the (second-order) electronic Hamiltonian, it remains a valid qualitative description for the behavior derived from the more complex vibronic Hamiltonian parameterized for TAT in Eq. (2); when the full Hamiltonian was analyzed, it was shown that the exciton bandwidth is narrowed by a factor of three when CT coupling is activated. The question naturally arises as to the sensitivity of the bandwidth reduction to sub-Angstrom slips between neighboring chromophores: Is it possible that such slips can induce a sign change in \(J_{SR}\) but not in the long-range Coulombic couplings? If so, then the resulting constructive interference between short- and long-range couplings may create an enhanced excitation transfer rate with desirable properties for photovoltaic devices.

III. SPATIAL DEPENDENCE OF THE COUPLINGS

Figure 2(a) shows how sensitive \(J_{SR}\), evaluated from Eq. (4), is to a transverse displacement between NN chromophores in a cofacial TAT dimer, with \(t_e\) and \(t_h\) computed using density functional theory (DFT) with the Becke, three-parameter, Lee-Yang-Parr (B3LYP) functional. The origin corresponds to a perfectly eclipsed orientation with cofacial separation, \(d = 3.3\text{ Å}\), while the X and Y dimensions refer to displacements between neighboring molecules along the long and the short molecular axes, respectively (Fig. 1). The green dot indicates the relative orientation for neighboring molecules in a TAT π stack as determined from x-ray analysis [18]. Its placement in the red region indicates short-range J-like behavior, i.e., \(J_{SR} < 0\) (since \(U - V_{CT}(1) > 0\) [27]). The figure shows that sub-Angstrom slips can result in a dramatic change in both the sign and the magnitude of the product \(t_e t_h\). The two yellow dots separated from the green dot by less than 0.5 Å indicate orientations in which the sign of \(J_{SR}\) becomes positive but with a magnitude unchanged from that of

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**FIG. 1.** (Color online) The crystal structure of TAT nanopillars, viewed down the stacking axis, is shown on the left. Here, X and Y denote the long and short molecular axes, respectively. The chemical structure of TAT is shown on the right.
We next considered how the exciton dynamics responds to a change in the sign of \( t_e \). To accomplish this we chose an initial condition in which the first chromophore in a \( \pi \) stack containing 10 chromophores is vibronically excited to the \( S_1 \) state with no vibrational quanta in the shifted (\( S_1 \)) nuclear potential. The subsequent time evolution was determined by solving the \( \text{Schrödinger} \) equation using the complete vibronic Hamiltonian in Eq. (2) with the electronic Hamiltonian in Eq. (1). Figure 3(c) shows how the expectation value of the \( n \)-dependent probability density \( \langle B_n B_n^\dagger \rangle \) evolves with time for a TAT \( \pi \) stack using the same parameters which best reproduced the HJ absorption spectrum in Fig. 3(a). As is immediately obvious, the exciton remains practically pinned on the first chromophore for the better part of a picosecond, a result of the aforementioned destructive interference between short- and long-range couplings.

Figure 3(d) shows the impact of changing just the sign of \( t_e \) on the exciton’s motion, an effect accomplished by a slip of less than 0.5 Å from the green to the yellow dot in Fig. 2. The corresponding change in exciton mobility is quite dramatic—the exciton is now able to traverse the length of the stack in less than 200 fs, which amounts to a velocity of approximately \( 2 \times 10^4 \) m/s. The enhanced mobility is essentially due to the constructive interference between short- and long-range coupling. We have further shown that if the short-range coupling in the TAT HJ aggregate was simply excluded from the system Hamiltonian, this site was traversed the length of the chain at a specific time. Upon propagation of the quantum wave function, this site was excluded from the system Hamiltonian; instead, population
at site 9 \((B_9^\dagger B_9)\) was transferred to the trap site at a rate of 0.15\((B_9^\dagger B_9)\) fs\(^{-1}\), a reasonable value to compare the transfer efficiencies for the HJ and HH aggregates. Figure 3(b) shows how the trap population builds up over time for the two aggregate types. Again, a sign change in the short-range coupling has a dramatic impact on the exciton transfer rate; after 1 ps the HH aggregate is found to transport approximately 10 times more population than the HJ variant.

In order to appreciate the robustness of the destructive interference in the HJ aggregates, we evaluated the evolution of the exciton trap population over a range of \(J_{SR}\) values (leaving the Coulombic coupling unchanged). The results, shown in the contour plot of Fig. 4(a), cover a range of \(J_{SR}\) values from 5\(J_{TAT}^{SR}\) to \(-J_{TAT}^{SR}\), where \(J_{TAT}^{SR}\) \((-290\text{ cm}^{-1}\)) is the short-range coupling corresponding to the (TAT) HJ-aggregate simulations of Fig. 3. Figure 4(b) shows representative absorption spectra. When \(J_{SR} = -J_{TAT}^{SR}\), the (positive) short-range coupling reinforces the positive Coulombic couplings, leading to high exciton mobility and a small 0-0/0-1 peak ratio, indicative of \(H\) aggregation. As \(J_{SR}\) decreases through zero and becomes increasingly more negative, the absorption spectrum displays more \(J\)-like character: The absorption origin increasingly redshifts and the 0-0/0-1 intensity ratio increases. At the same time the exciton becomes increasingly less mobile, reflective of a more efficient destructive interference between the long- and short-range couplings. At the TAT point \(J_{SR} = J_{TAT}^{SR}\), the cancellation of the two coupling sources is quite efficient, as evidenced by a 0-0/0-1 ratio, which is about equal to the monomer value (≈1, [17]). Interestingly, making \(J_{SR}\) even more negative has little effect on the mobility when \(J_{SR}^{TAT} > J_{SR} > 2J_{SR}^{TAT}\). However, once outside this range the mobility begins to recover, being driven by the dominating influence of the short-range coupling. Overall, Fig. 4(a) shows that the low mobility region of efficient destructive interference extends over a wide range of short-range couplings; for \(J_{SR}\) in the range \(J_{SR}^{TAT} > J_{SR} > 2J_{SR}^{TAT}\), the exciton is practically immobile.

V. EFFECTS OF BATH FLUCTUATIONS

The analyses presented so far were based on TAT aggregates free from any impurities, where the excitation was allowed to perform ballistic motion while perfectly maintaining its phase. However, the line broadening observed in absorption spectroscopy of TAT is considerable, suggesting the presence
FIG. 4. (Color online) (a) Contour plot of the trap population as a function of time over a range of $J_{SR}$ values using the Hamiltonian in Eq. (2) with $H_0$, from Eq. (1). The parameters for the Hamiltonian are identical to those corresponding to a TAT HJ aggregate in Fig. 3, with the exception of $t_e$ and $t_h$. The latter were taken to be the TAT values (respectively, 435 and 402 cm$^{-1}$) multiplied by a scaling factor $\sqrt{q}$ so that the corresponding short-range coupling in Eq. (4) is scaled by $q$, i.e., $J_{SR} = q J_{SR}^{TAT}$, where $J_{SR}^{TAT} = -290$ cm$^{-1}$. To obtain the negative scaling $J_{SR} = -q J_{SR}^{TAT}$, $t_e$ was additionally multiplied by $-1$. (b) Calculated absorption spectra for a $\pi$ stack containing 20 chromophores.

FIG. 5. (Color online) (a) The temperature dependent broadening of the 0-0 absorption peak is used to determine the relative contributions of static and dynamic disorder in TAT. (b) The population of the trapping site for the disordered HJ and HH aggregate, showing that the contrasting behaviors of constructive and destructive couplings are robust against disorder and dephasing and may even be enhanced by such effects.
VI. CONCLUSION

The results presented here offer a design strategy for improving energy transport in organic materials by engineering the crystal packing structure so that the short- and long-range couplings constructively interfere. Unlike the long-range Coulombic coupling, the CT-mediated short-range coupling is hypersensitive to sub-Angstrom slips between neighboring molecules within a π stack. Such displacements are tunable through chemical modification; for example, a recent report shows that slip distances along the long molecular axis correlate to the bulkiness of the terminally substituted groups in a series of perylene derivatives [36]. Sub-Angstrom displacements may also be induced through lattice strain. Using a solution-shearing technique, Giri et al. [37] reduced the π-stacking distance in 6,13-Bis(Triisopropylsilylethynyl) (TIPS) pentacene by approximately 0.2 Å, creating an almost sixfold increase in the hole mobility due to enhanced HOMO-HOMO overlap.

We have also shown a strong correlation between the absorption spectral line shape and the exciton mobility (Fig. 4), allowing one to potentially use the absorption spectrum to screen for high mobility aggregates. For example, if the 0-0/0-1 ratio of vibronic oscillator strengths in the solid phase is roughly equal to the ratio observed from unaggregated (i.e., solution phase) molecules, then the short- and long-range couplings are effectively canceled, yielding a low mobility exciton. Such is the case for TAT, where the 0-0/0-1 ratio is practically unchanged upon aggregation [17]. According to Fig. 4, aggregates in which the 0-0/0-1 ratio strongly deviates from the monomer value have the highest mobilities.

Furthermore, we have shown that the concept of interfering couplings remains robust even when diagonal disorder is present in the aggregate (Fig. 5), so interference effects should persist in real systems. In a recent paper, Aragó and Troisi [22] showed that thermal fluctuations in the exciton couplings in polyacene crystals, fueled mainly by the relative twisting motions between edge-to-face neighbors in a herringbone lattice, can be comparable to the mean exciton couplings. In the π stacks of interest here, the excitonic couplings would be most sensitive to fluctuations along the slip and stacking directions induced by longitudinal and optical phonons. We speculate that there is less resistance to twisting a molecule about its long axis within a herringbone lattice than to shearing one molecule against its neighbor within a π stack, so the relative fluctuations in the excitonic couplings would be smaller in π stacks than in herringbone lattices. Although the calculations presented so far do not explicitly include off-diagonal disorder, we can gauge its impact by consulting Fig. 4(a). As stated earlier, the exciton (in TAT stacks) remains immobile, reflective of efficient destructive interference between the charge-mediated interactions and the Coulombic interactions, for a wide range of J_π values. Hence, fluctuations in J_π should be reasonably well tolerated for observing either destructive or constructive interference, even when the standard deviation approaches the mean. The remarkable resiliency of the interference effect to disorder, as well as its hypersensitivity to slip stacking, offers a thrilling prospect for optimizing excitation transport in disordered materials.

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[27] In TAT, one cannot reproduce the vibronic features in the measured absorption spectrum if the diabatic CT states lie energetically below the Frenkel states. If the latter were true, the short-range coupling would change sign, yielding an HH aggregate with different spectral signatures than those of the HH aggregate [Fig. 2(a)].


[33] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.91.195315 for a list of parameters used for the TAT calculations, a detailed description of the methods used to propagate the wave function, a discussion of the disorder model used, and a demonstration of the time development of a system having no short-range coupling.


