Exciton transport in thin-film cyanine dye J-aggregates

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We present a theoretical model for the study of exciton dynamics in J-aggregated monolayers of fluorescent dyes. The excitonic evolution is described by a Monte-Carlo wave function approach which allows for a unified description of the quantum (ballistic) and classical (diffusive) propagation of an exciton on a lattice in different parameter regimes. The transition between the ballistic and diffusive regime is controlled by static and dynamic disorder. As an example, the model is applied to three cyanine dye J-aggregates: TC, TDBC, and U3. Each of the molecule-specific structure and excitation parameters are estimated using time-dependent density functional theory. The exciton diffusion coefficients are calculated and analyzed for different degrees of film disorder and are correlated to the physical properties and the structural arrangement of molecules in the aggregates. Further, exciton transport is anisotropic and dependent on the initial exciton energy. The upper-bound estimation of the exciton diffusion length in the TDBC thin-film J-aggregate is of the order of hundreds of nanometers, which is in good qualitative agreement with the diffusion length estimated from experiments.

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I. INTRODUCTION

In organic materials, excitons, quasiparticles of bound electron-hole pairs, act as the intermediates between light (photons) and charge (electrons and hole). Understanding which physical properties make certain molecular aggregates optimal for exciton transfer is one of the main current technological goals in organic materials research. In this article, we develop a computational model and employ it to explore excitonic energy transport in a particular class of organic materials: cyanine dye J-aggregates.

Discovered over 50 years ago,1, 2 J-aggregates are typically formed by organic fluorescent dye molecules and can be identified spectroscopically by the narrowing and bathochromic shift (J-band) of the lowest electronic excitation relative to the monomer band.3, 4 These structures are characterized by the unique properties associated with their J-band: a large absorption cross section, short radiative lifetimes, a small Stokes shift of the fluorescence line, and efficient energy transfer within the aggregate.3

The applications of J-aggregates range from their use as “reporter molecules” in mitochondrial membrane potentials in living cells5 to photosensitizing silver halides in photography.6 Moreover, J-aggregates are employed in dye-sensitized organic solar cells which provide several advantages over inorganic solar cells.7, 8 Recently, cyanine dye J-aggregates have been combined with optical cavities9–11 or coupled to quantum dots12 to form hybrid systems. However, the current understanding of exciton transport properties, even for the most ordered J-aggregates, is rather limited. This limitation arises from the challenges encountered in the experimental characterization of their structure3 and from the lack of information on the dissipation processes involved. In an effort to overcome these difficulties, the aim of our study is to provide a theoretical model, with a minimal number of phenomenological parameters, which is useful for the determination of the J-aggregate structure and able to describe the exciton dynamics in hybrid excitonic-photonic and excitonic-electronic devices.

J-aggregates can be found in various structural arrangements including one-dimensional, planar and cylindrical5 aggregates each exhibiting different optical and exciton energy transfer properties.13–15 The structure of liquid-crystal cyanine dyes was initially studied using absorption and fluorescence spectroscopy by Scheibe and Kandler,16 and more recently using x-ray diffraction and NMR by Harrison et al.17 Nonetheless, the packing structure of J-aggregates remains unknown.3 Different theoretical packing models for two-dimensional (2D) arrays of these pseudo-cyanine dye aggregates have been proposed by Nakahara and Kuhn.18 In this study, we focus on modeling the exciton transport properties of 2D thin-films using cyanine dye J-aggregates such as those realized experimentally in Ref. 19. These highly efficient light absorbing thin-films are employed in various optoelectronic systems for applications such as lasers and optical switches.20, 21 Exciton dynamics in these films, in general, possesses both ballistic (quantum) and diffusive (classical) regimes and can be analyzed at different levels of approximation.

Experimentally, transport properties, such as exciton diffusion coefficients in organic materials, have been obtained using indirect methods only. These include exciton-exciton annihilation,11, 22, 23 photoluminescence quenching,24, 25 transient grating,26 and photocurrent response.27, 28 In a recent study by Akselrod et al.,11 the singlet exciton diffusion length in a 2D cyanine dye film was estimated to be of the order of 50 nm at room temperature which is more than twice larger than the diffusion length measured in standard organic semiconductor films25 and is comparable to the spatial

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resolution of the recently developed coherent nanoscopy technique.\textsuperscript{29}

Theoretically, exciton transport has been studied using a classical hopping model.\textsuperscript{30} However, this approach is applicable only in the weak Förster coupling regime,\textsuperscript{31} where the exciton mobility is low. Beyond this regime, the tight-binding Hamiltonian with classical noise model, proposed in the 70’s by Haken, Strobl, and Reineker\textsuperscript{32,33} allows for a unified description of ballistic and diffusive exciton dynamics. For perfect structures with translational symmetry this model can provide analytic solutions for the moments of the exciton wave function\textsuperscript{34} that characterize exciton transport. Variations of this type of analysis have been provided by others.\textsuperscript{35–37}

In this paper, we introduce a multi-scale computational model to study exciton transport properties in J-aggregates. Within the model the diffusion coefficients are extracted from the finite-time stochastic propagation of the exciton wave function. The molecular properties are computed using density functional theory (DFT), and the coupling to the environment is simulated by adding stochastic noise to the molecular electronic transition frequencies. To illustrate its applicability, we present a detailed study of exciton diffusion in three types of cyanine-dye J-aggregates, namely, TC (5,5′-dichloro-3,3′-disulfopropyl thiacyanine), TDBC (5,6-dichloro-2 [3-[5,6-dichloro-1-ethyl-3-(3-sulfopropyl)-2(3H)-benzimidazolidene]-1-propanyl]-1-ethyl-3-(3-sulfopropyl) benzimidazolium hydroxide), and U3 (3-[(2Z)-5-chloro-2-((3E)-3-chloro-3,3′-disulfopropyl thiacyanine)], TDBC (5,6-dichloro-2 [3-[5,6-dichloro-1-ethyl-3-(3-sulfopropyl)-2(3H)-benzimidazolidene]-1-propanyl]-1-ethyl-3-(3-sulfopropyl) benzimidazolium hydroxide), and U3 (3-[(2Z)-5-chloro-2-((3E)-3-chloro-3,3′-disulfopropyl thiacyanine)]. While the model doesn’t explicitly include the molecular vibronic structure, and fluctuations in the molecule-molecule interaction were not presently accounted for, the computed diffusion coefficient for a TDBC J-aggregate agrees qualitatively with the value measured from exciton-exciton annihilation experiments.\textsuperscript{11} The model is flexible and different sources of noise as well as different aggregate geometries or even coupling to optical cavities\textsuperscript{9–11} can be incorporated. Our findings indicate anisotropy in the exciton diffusion, the presence of coherent dynamics at times shorter than tens of femtoseconds and finally a dependence of transport on the specific molecular excitation parameters.

The paper is organized as follows. In Sec. II, we describe the theoretical model for the exciton dynamics. In particular, we introduce the Hamiltonian of the system and the associated Langevin equation. Then, the static and dynamic noises, which represent different types of disorder present in J-aggregate films, are discussed, and the description of the model is completed with a derivation of the diffusion equation. Section III includes details of the calculation of the Hamiltonian’s parameters and also gives an overview of the Monte-Carlo wave function method employed in the study of the exciton propagation. In Sec. IV we analyze exciton transport in thin-film J-aggregates of three different cyanine dyes: TC, TDBC, and U3 (structures are shown in Fig. 1). We conclude the study by summarizing our results in Sec. V.

II. THE MODEL

A. Hamiltonian and single exciton dynamics

We apply the general exciton theory developed previously for molecular crystals and molecular aggregates\textsuperscript{38} to a specific system – a 2D monolayer J-aggregate of fluorescent dye molecules. The Hamiltonian for a single exciton in a molecular aggregate can be written as

\[
\hat{H} = \hat{H}^{el} + \hat{V}^{el-bath} + \hat{H}^{bath},
\]

where \(\hat{H}^{el}\) is the system Hamiltonian which includes the electronic degrees of freedom, \(\hat{V}^{el-bath}\) is the system-bath interaction Hamiltonian, and \(\hat{H}^{bath}\) is the bath Hamiltonian which models environmental degrees of freedom. In the site basis, the electronic Hamiltonian of an aggregate consisting of \(N\) monomers can be expressed as

\[
\hat{H}^{el} = \sum_{n=1}^{N} \epsilon_n \ket{n}\bra{n} + \frac{1}{2} \sum_{n,m=1}^{N} J_{nm} \ket{n}\bra{m},
\]

where \(\epsilon_n\) are the energies of the electronic excitations at each site \(n\) and \(J_{nm}\) are the couplings between electronic transitions of monomers at sites \(n\) and \(m\). In Eq. (2), \(\ket{n} = \ket{0...1_n...0}\) corresponds to the state where an exciton is localized at the

FIG. 1. Structure of the monomer dye molecules TC, TDBC, and U3 which form the aggregates, The full International Union of Pure and Applied Chemists names of the molecules are given in the text.
nth molecule and all other molecules are in their ground electronic state. In the aggregate, each monomer is modeled as a two level system and the environment is assumed to be a harmonic bath formed by the intra and intermolecular vibrations

$$\hat{H}^{\text{bath}} = \sum_n \sum_q \omega_q \hat{b}^\dagger_{qn} \hat{b}_{qn},$$

where \( q \) runs over all vibrational modes and \( \omega_q \) is the vibrational frequency of mode \( q \), while \( \hat{b}^\dagger_{qn} \) and \( \hat{b}_{qn} \) are the (bosonic) creation and annihilation operators for the bath modes at site \( n \). The system-bath interaction term in the linear coupling limit is

$$\mathcal{V}^{\text{el-bath}} = \sum_n |n\rangle \langle n| \sum_q \kappa_q (\hat{b}^\dagger_{qn} + \hat{b}_{qn}),$$

where \( \kappa_q \) is the coupling constant between the \( q \)th vibrational mode and the electronic system, assumed to be equal for all sites.

For singlet exciton transport the major contribution to the \( J_{nm} \) coupling terms in Eq. (2) is due to Förster interaction.\(^{31}\) In practice, numerical calculations of the Förster term can be computationally heavy, especially for large structures. For J-aggregates, where the distance between stacked molecules is comparable to the spatial extent of each molecule, it is possible to use the extended dipole model.\(^{39}\) Within this model, the Förster interaction between two particular electronic transitions is parametrized by a transition charge, \( q \), and a transition dipole length \( l \). The interaction term can therefore be simplified and written as a sum of Coulomb interactions between the transition charges located on different molecules

$$J_{nm}^F = \frac{q^2}{4\pi \varepsilon_0 \varepsilon} \left( \frac{1}{r_{nn}} + \frac{1}{r_{nm}} - \frac{1}{r_{nm}} - \frac{1}{r_{nn}} \right),$$

where \( r_{nn} \) is the distance between the charge \(+q\) located on the \( n \)th molecule and the charge \(-q\) located on the \( m \)th molecule.

Fluorescent dyes may self-aggregate in a number of different structures. When dealing with two-dimensional films of cyanine dye aggregates, the brickstone model is one of most commonly employed models which can account for the experimentally observed optical properties of these aggregates. Therefore, in our work, the molecular arrangement within the 2D layer is modeled as a brickstone lattice,\(^{40}\) as shown schematically in Fig. 2. In this model, the dye molecules are stacked parallel to each other and subsequent rows are displaced by an angle \( \theta \). The lattice is characterized by two lattice vectors \( \mathbf{L}_x \) and \( \mathbf{L}_y \).

Given the Hamiltonian of the system, we proceed to derive an equation for the quantum evolution of the system’s wave function on this lattice. We define a quantum stochastic equation following the Langevin procedure, as described in Ref. \(^{41}\) as

$$\frac{\partial}{\partial t} |\psi(t)\rangle = \left( -\frac{i}{\hbar} \hat{H}^{\text{eff}} + \sum_{m,\mu} \eta_m^\mu(t) \hat{C}_m^\mu \right) |\psi(t)\rangle,$$

where the effective Hamiltonian \( \hat{H}^{\text{eff}} = \hat{H}^{\text{el}} - \frac{\hbar}{2} \sum_{m,\mu} (\hat{C}_m^\mu)^\dagger \hat{C}_m^\mu \) includes a decay term and a stochastic fluctuation term \( \eta_m^\mu(t) \) for site \( m \) and channel \( \mu \) which represents a dynamic force and is introduced to conserve the norm of the wave function. The \( \hat{C}_m^\mu \) are Lindblad operators for two channels \( \mu \in \{\cdot, \phi\} \) (relaxation or dephasing) for each site \( m \). These channels allow the initially excited exciton state to eventually decay back to the ground state due to interaction with the environment. These terms can be expressed as

$$\hat{C}_m = \sqrt{\Gamma_m} |0\rangle \langle m|,$$

$$\hat{C}_m^\phi = \sqrt{\Gamma_m^\phi} \sum_k \langle k| - |m\rangle \langle m|,$$

where \( \hat{C}_m \) describes single exciton relaxation and \( \hat{C}_m^\phi \) is introduced for dephasing processes while \( \Gamma_m \) and \( \Gamma_m^\phi \) are the corresponding relaxation and dephasing rates. The states \( |m\rangle \) span over the single exciton manifold, and the state \( |0\rangle \) denotes the ground state, where no exciton is present. The relaxation and dephasing rates are taken to be equal for all sites \( \Gamma = \Gamma_m \) and \( \Gamma^\phi = \Gamma_m^\phi \), because the aggregate is constructed of identical molecules which are assumed to be in identical local environments. It is easy to see that with the noise operators written in the site basis this model is equivalent to the Haken, Strobl and Reineker model.\(^{32}\)

### B. Static and dynamic noise

The environmental noise can be introduced into this J-aggregate model as fluctuations of site energies and of the site-to-site couplings as well as a term which induces exciton relaxation. When studying transport properties within the single exciton manifold, one is mostly interested in the dynamics occurring on a timescale sufficiently shorter than the exciton relaxation time, this corresponds to saying that over the time scale of the dynamics, in Eq. (10), \( \hat{C}_m \sim 0 \). Moreover, in the provided examples we do not consider fluctuations of intermolecular interactions. These fluctuations can give a noticeable contribution to the transport properties\(^{35}\) and can easily be included in the model. However we have chosen to neglect them since no experimental data is currently available to estimate relative contributions of site energy fluctuations and fluctuations in the couplings. A detailed atomistic \textit{ab initio} study of the system could answer these questions.\(^{42}\) However,
this type of analysis can be time consuming and is beyond the scope of the present work.

We introduce the standard distinction between static and dynamic noise based on the correlation time characterizing the fluctuations as compared to the exciton propagation time. Static noise is associated with fluctuations in site energies which are correlated for a long time respect to the lifetime of the exciton, while dynamic noise is associated to instantaneous fluctuations in the site energies respect to the exciton lifetime.

Static noise can be accounted for in the Hamiltonian, Eq. (2), by extracting random shifts in the site energies. In our model, we extract the random shifts from a Gaussian distribution

$$f(\epsilon_a - \epsilon_0) = \frac{1}{\sqrt{2\pi}\sigma^2}e^{-(\epsilon_a-\epsilon_0)^2/2\sigma^2},$$  

where $\sigma$ is the variance, and $\epsilon_0$ is the transition energy of each isolated molecule. The static noise distribution is assumed to be identical for all monomers. Other choices of static disorder models are possible. For instance, a more general Levy distribution can be used, which results in different static distributions and optical properties.\textsuperscript{43}

Dynamic noise directly enters the Schrödinger-Langevin equation, Eq. (6), described in Sec. II A, through a stochastic force $\xi(t)$, which is a result of multiple uncorrelated microscopic movements of the molecules constituting the aggregate lattice and does not have memory, i.e., $(\xi(t)\xi(t')) \propto \Gamma^\phi \delta(t - t')$. This corresponds to the Markov approximation, in the sense that the system-bath interaction is assumed to be quasi instantaneous and successive interaction events are not correlated. In general, the Markov approximation holds, as long as the bath correlation time is much smaller than the time over which one extracts properties of the system. Therefore it is only necessary that the bath correlator be sharply peaked.\textsuperscript{41}

Within this argumentation, the dynamic noise can be characterized by a single parameter $\Gamma^\phi$, which describes both the bath dynamics and the system-bath coupling. While avoiding a detailed description of the specific environment of a J-aggregate we can make a rather qualitative assumption that $\Gamma^\phi$ is of the order of $k_B T$. This assumption is not strictly justified but can be intuitively explained as following.

If we assume that the bath modes can be modeled as a set of harmonic oscillators, we can define, within linear response theory, a system bath interaction term linear in the displacement of the bath modes. It follows that the bath correlator can be expressed as\textsuperscript{44}

$$\langle \eta(\tau)\eta(0) \rangle = \sum_q |q|\gamma_q^2 \left[ (\hat{b}_q(\tau) + \hat{b}_q(0))(\hat{b}_q^\dagger(\tau) + \hat{b}_q^\dagger(0)) \right]$$

$$= \int d\omega J(\omega) \left[ \coth \left( \frac{\hbar \omega - \lambda}{2k_B T} \right) \cos(\omega \tau) - i \sin(\omega \tau) \right],$$  

where the bath operators are given in the interaction picture and we have assumed that the noise correlator is the same for all sites and that each bath is uncorrelated from that of other sites. The second line corresponds to the approximation of a continuous bath spectrum with a spectral density $J(\omega)$.

This approximation provides a qualitative correspondence between the temperature and the dynamic noise in the system. In general, a more quantitative analysis should explicitly include the bath vibrational modes. By using the continuous limit of the spectral density we intentionally simplified the model making it independent of the specific molecular vibrational modes. Several forms of bath spectral densities are used for modeling dissipative quantum dynamics in molecular aggregates.\textsuperscript{45, 46} We choose to employ the Ohmic exponentially cutoff spectral density $J(\omega) = \frac{\lambda}{\hbar\omega} e^{-\frac{\hbar \omega}{\lambda}}$ where $\lambda$ is the reorganization energy and $\hbar\omega_c$ is the cutoff frequency. In our model, the correlator in Eq. (9) can only be used in the limit where the time-dependent characteristics of exciton dynamics remain steady on timescales sufficiently longer than the bath correlation time. In this case, the temperature-dependent dephasing rate can be defined as\textsuperscript{47, 48}

$$\Gamma^\phi = 2\pi \frac{k_B T}{\hbar} \frac{\lambda}{\hbar\omega_c},$$  

where physical properties of the bath and the system-bath coupling are introduced through the slope of the spectral density at zero frequency $\frac{d J(\omega)}{d\omega} |_{\omega=0} = \frac{\lambda}{\hbar\omega_c}$ (Ref. 46). Equation (10) is strictly valid for $T \gg \frac{\hbar \omega_c}{k_B}$ (Ref. 49). If we use values of $\omega_c = 150 \text{ cm}^{-1}$ and $\lambda = 35 \text{ cm}^{-1}$, typical for the analysis of quantum dynamics in photosynthetic systems,\textsuperscript{45, 50} the dephasing rate $\Gamma^\phi \approx 1.4 k_B T$. The reorganization energy of J-aggregates is comparable to this value, for instance, $\lambda_{\text{TDBC}} = 29 \text{ cm}^{-1}$ (Ref. 51). By setting $\Gamma^\phi = k_B T$ we choose a lower bound for the exciton dephasing rates. For room temperature we thus have $\Gamma^\phi \approx 26 \text{ meV}$. In reality, there may be more sources of dissipation, and different estimates for the bath spectral density\textsuperscript{46, 52} can give values of the dephasing rate, $\Gamma^\phi$ which are several times larger than the value we use.

C. Diffusion model

In this section, we consider methods for calculating the diffusion constant $D$ from the transport properties of the excitonic system. For classical Brownian motion, it is well-known that the diffusion constant is related to the long-time limit of the second moment $\langle (r(t) - r_0)^2 \rangle$ evaluated for the initial condition where the particle is localized at a single point $r_0$ in space. Explicitly, it is given by

$$D = \lim_{t \to \infty} \frac{1}{2 d t} \langle (r(t) - r_0)^2 \rangle,$$  

where $d$ is the dimension of the space. For excitonic systems, in the first place, we will not assume that exciton motion can be described as the motion of classical Brownian particles. Here, our goal is to show that the above relationship (Eq. (11)) holds even for excitonic systems where a fully quantum mechanical treatment is assumed.

To get started, we consider a dilute system of excitons where their reciprocal interaction can be ignored. We will trace the motion of a “tagged” exciton. The probability $P(r(t), t)$ of finding that exciton at location $r$ and time $t$ is given by $P(r(t), t) = \text{Tr}[\rho(t) \hat{r}^n(t)]$, where $\rho(t)$ is the density matrix of the total system (i.e., exciton plus the bath) at time $t$. Using
the following identity

$$|\mathbf{r}\rangle \langle \mathbf{r}| = \frac{1}{(2\pi)^d} \int_{-\infty}^{\infty} dke^{-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')} \langle \mathbf{r}'| \langle \mathbf{r}'|$$

(12)

where $d$ is the dimension, and $\mathbf{r} \equiv \sum_{\mathbf{r}'} \mathbf{r}'|\langle \mathbf{r}'| \mathbf{r}\rangle$ is the position operator for the exciton, we write the probability of finding the exciton as

$$P(\mathbf{r}, t) = \frac{1}{(2\pi)^d} \int_{-\infty}^{\infty} dke^{i\mathbf{k} \cdot \mathbf{r}} \tilde{P}_k(t),$$

(13)

where $\tilde{P}_k(t) \equiv \text{Tr}[e^{-i\mathbf{k} \cdot \mathbf{r}(t)} \hat{\rho}(0)]$, $\hat{\mathbf{r}}(t) \equiv \hat{U}(t)\hat{\mathbf{r}}\hat{U}^\dagger(t)$, where $\hat{U}(t) = e^{-i\hat{H}t}$ and $\hat{H}$ is defined in Eq. (1).

Since we are considering the fluctuations of the exciton in some steady-state (long-time $t \rightarrow \infty$) limit, measurable physical quantities, including the diffusion constant, should not depend on the initial condition. We can therefore choose the following initial state $\hat{\rho}(0) = I_S \otimes \hat{\rho}_B/\text{Tr}(I_S)$, where $I_S$ is the identity matrix for the system, i.e., the exciton, and $\hat{\rho}_B = e^{-\beta \hat{H}_\text{bath}}/\text{Tr}(e^{-\beta \hat{H}_\text{bath}})$ is the density matrix of the bath, which is assumed to be in thermal equilibrium. Now, inserting the resolution of the identity, $I_S = \sum_{\mathbf{r}_0} |\mathbf{r}_0\rangle \langle \mathbf{r}_0|$, we can write $\tilde{P}_k(t) = (1/\text{Tr}(I_S)) \sum_{\mathbf{r}_0} e^{-i\mathbf{k} \cdot \mathbf{r}_0} \text{Tr}[e^{-i\Delta \hat{r}(t)} |\mathbf{r}_0\rangle \langle \mathbf{r}_0| \otimes \hat{\rho}_B]$, where $\Delta \hat{r}(t) \equiv \hat{\mathbf{r}}(t) - \mathbf{r}_0$. Performing the cumulant expansion and keeping terms up to the second-order, we obtain

$$\tilde{P}_k(t) \approx \frac{1}{\text{Tr}(I_S)} \sum_{\mathbf{r}_0} e^{-i\mathbf{k} \cdot \mathbf{r}_0} e^{-(1/2)|\langle \mathbf{k} \Delta \hat{r}(t)^2 \rangle_0|},$$

(14)

where $\langle \mathbf{k} \cdot \Delta \hat{r}(t)^2 \rangle_0 \equiv \text{Tr}[(\mathbf{k} \cdot \Delta \hat{r}(t)^2) |\mathbf{r}_0\rangle \langle \mathbf{r}_0| \otimes \rho_B]$. Then, we arrive at the diffusion equation

$$\frac{\partial}{\partial t} P(\mathbf{r}, t) \approx \sum_{i,j} D_{ij}(t) \frac{\partial^2}{\partial r_i \partial r_j} P(\mathbf{r}, t),$$

(15)

where

$$D_{ij}(t) \equiv \frac{1}{2} \frac{d}{dt} \langle \Delta \hat{r}_i(t) \Delta \hat{r}_j(t) \rangle = \frac{1}{2} \frac{d}{dt} M_{ij}^{(2)}(t)$$

(16)

is the time-dependent tensor of the diffusion coefficients. Here, we have defined the second moments $M_{ij}^{(2)}(t) \equiv \langle \Delta \hat{r}_i(t) \Delta \hat{r}_j(t) \rangle$. In order for the diffusion coefficients $D_{ij}(t)$ to converge in the long time limit ($t \rightarrow \infty$), the right-hand side of Eq. (16) should scale at most linearly in $t$. This result coincides with that in Eq. (11), which is a special case of isotropic diffusion.

III. COMPUTATIONAL DETAILS

A. Monomer properties

Density-functional calculations of the molecular structure and electronic excitation spectra were performed with the quantum-chemistry package Turbomole, version 5.10. (Ref. 53). Triple-ζ valence-polarization basis sets (def2-TZVP84) were used together with the hybrid functional of Perdew, Burke, and Ernzerhof (PBE0).55 Dielectric properties of the medium accounted for by using COSMO56 as implemented in Turbomole.

To calculate the extended dipole parameters of the fluorescent dyes, the HOMO and LUMO orbitals of the molecules were computed on a homogeneous spatial grid. The grid steps are $dx = 0.5$ Å, $dz = 0.5$ Å in the plane of the molecular backbone, and $dy = 0.25$ Å in the direction orthogonal to the backbone. The Förster,31 and the Dexter57 interactions between pairs of molecules were calculated for center-to-center displacements scanned over $x = [-60, 60]$ Å and $y = [-10, 10]$ Å with step size $\Delta x = \Delta y = 0.5$ Å.

B. Monte-Carlo wave function propagation

Equation (6) is a Markovian stochastic open quantum system equation, which is equivalent to a Lindblad master equation for the density matrix.41 As such one can evolve single stochastic eigenfunction trajectories instead of the full density matrix, using the Markov Monte-Carlo wave function method.38

The initial wave function $|\psi(0)\rangle = |00\ldots1\ldots0\rangle$ is defined as an exciton localized at the center of the lattice (i.e., in the position $\left(\frac{2}{3}, \frac{2}{3}\right)$). At time $t + \delta t$, $|\psi(t + \delta t)\rangle$ can be obtained from $|\psi(t)\rangle$ according to the stochastic scheme depicted in the second block of Fig. 3. This figure shows the overall computational algorithm employed to obtain the density matrix and the moments. In particular, at each time step, if the stochastic variable extracted, $\epsilon$, is larger than the quantum dephasing jump probability $\Omega_\varphi$ the wave function will propagate freely under the non-Hermitian effective Hamiltonian $\hat{H}^{\text{eff}}$ introduced in Eq. (6)

$$|\psi(t + \delta t)\rangle = \frac{1}{\sqrt{N}} \left(1 - \frac{i\hat{H}^{\text{eff}}\delta t}{\hbar}\right) |\psi(t)\rangle,$$

(17)

where $N = \sqrt{|\langle \psi(t + \delta t)|\psi(t + \delta t)\rangle|}$ is the normalization constant. However, if $\epsilon$ is smaller than $\Omega_\varphi$, a quantum dephasing jump will occur. The quantum dephasing jump, a specific type of quantum jump, is described as a flip of the sign of wave function’s coefficient corresponding to a site $m$ and corresponds to applying the dephasing jump operator $\hat{C}_m^\varphi$, Eq. (7), to the wave function.38 The phase jump occurs in position $N = \text{round}(\frac{\epsilon}{\Omega_\varphi\delta t\sqrt{n}})$, where $\Omega_\varphi$ is defined as $\Omega_\varphi = \frac{\Gamma^\varphi_{\text{norm}}}{\sqrt{n}}$, and where $\Gamma^\varphi_{\text{norm}}$ was given in Eq. (10), while $\delta t$ is the time step which is assumed to be small enough so that $\Omega_\varphi \ll 1$. For the trajectories controlled by exciton dephasing only, the effective Hamiltonian $\hat{H}^{\text{eff}}$ is the same as $\hat{H}_0$, thus the norm of the wave function in Eq. (17) is conserved.

To analyze the exciton transport properties of TC, TDBC, and U3 aggregates the exciton wave function was propagated on a lattice of 2601 monomers ($n_x = n_y = 51$) for a total time of $t = 100$ fs. The quantum trajectories were averaged over 1000 different realizations of static disorder (convergence on the populations was reached with 1000 realizations within an error $\leq 4\%$). The averaging over static disorder and realizations of quantum jumps were combined in such a way that for each quantum trajectory $|\psi(t)\rangle$ we introduced a unique realization of the static disorder $\sigma_i$ and a unique sequence of quantum jumps $\Gamma^\varphi_{\text{norm}}$. This procedure is applicable as long as both disorders are not correlated and could be considered in analogy with the Monte-Carlo integration of a multi-dimensional function. It should be noticed that the obtained results characterize an inhomogeneous ensemble
of quantum systems averaged over multiple disorder realizations. The time step in the propagation was set to $\delta t = 0.6$ as thus the probability of the quantum jump within the step is sufficiently smaller than 1, and the wave function was collected at each femtosecond. The long range interaction between the molecules was accounted for within the cutoff distance $l_{\text{cutoff}} = 6 \cdot L_x$, more details about this cutoff can be found in Sec. IV A. At the initial time the exciton was localized on the central site (26,26) of the lattice. The energy of this site can be varied to study the dependence of the exciton dynamics on the initial conditions. The results were obtained in general over the range $\Gamma_{\phi} = [20 - 110] \text{ meV}$ and $\sigma = [0 - 110] \text{ meV}$. Exciton diffusion coefficients where estimated from a linear fit of the second moments of the exciton distribution functions $M^{(2)}_{I\phi}$, as per Eq. (16).

**A. Model parameters**

**1. Monomer calculations and absorption spectra**

The structures of the TC, TDBC, and U3 cyanine dye molecules have been optimized using DFT. In the computation, we considered single-charged anions and assumed that the Na$^+$ ions were dissociated. For each molecule, although the conjugated part of the structures remain almost planar, there are many conformations which differ slightly by the orientations of the sulphonated group side chains and are all closely spaced in energy. Examples of such conformations for the cis-isomers are shown in Fig. 1. It should be noted that the computed spectra reflect pure electronic transitions and do not include vibronic components. The difference between the ground-state energies of cis- and trans-isomers of the molecules is of the order of hundreds of meV. We have chosen cis-isomers as our reference structure because it is most likely that in this conformation, with the sulphonate groups pointing towards the surface and binding chemically or physically to it, that one would obtain the observed 2D monolayers.\(^{10}\) For each optimized molecular structure, we have computed the 100 lowest electronic excitations which fall in the energy range 2–7 eV. The computed spectra of the molecules shown in Fig. 1 are provided in Fig. 4. The strong lowest excitation can be accounted for by the HOMO to LUMO transition for more than 98%. Such transition is generally assigned to the lowest absorption peak observed in the monomer spectra of fluorescent dyes. The second electronic transition is separated from the lowest one by about 0.7 eV, 1.0 eV, and 1.4 eV for TC, TDBC, and U3, respectively. Moreover, the oscillator strengths of these subsequent transitions are about two orders of magnitude smaller than that of the lowest one. These results support the two-level model provided that the static energy disorder is of the order of at most about 100 meV. The computed frequencies of the lowest electronic transitions are systematically blue-shifted by about several hundreds of meV as compared to the experimental values. This shift typically occurs in DFT calculations with the PBE0 functional.\(^{59}\) Similarly to what was found for the ground state energies, the lowest electron transition frequencies for trans- and cis-isomers differ by hundreds of meV. The high frequency part of the computed spectrum shows multiple electronic states with
about double the exciton energy. These states may be involved in the exciton-exciton annihilation process.\textsuperscript{11}

2. Couplings

The extended dipole parameters for the lowest electronic excitation are calculated within the frontier orbital approximation,\textsuperscript{60} in which one assumes that only the HOMO-LUMO transition gives a significant contribution. To obtain the $l$ and $q$ parameters in the extended dipole coupling formula Eq. (5), we assume that the only type of interaction involved is Förster interaction\textsuperscript{31} and fit the interaction between two molecules on the $x - y$ plane to the Förster results. An example of the calculated interaction contour plot for a pair of TDBC molecules is shown in Fig. 5. For intermolecular distances larger than 2 Å, the profile reproduces the interaction of two dipoles and can easily be fitted with the extended dipole formula. The largest positive shift of the electronic transition is obtained when the molecules are displaced along the $y$ axis (direction orthogonal to the backbone of the molecules). The largest negative shift of the electronic transition corresponds to the case when molecules are displaced along the $x$ axis approximately by half of their length. These results are consistent with the extended dipole model. The computed properties of TC, TDBC, and U3 monomers are summarized in Table I. We also computed Dexter couplings and these were much smaller than the corresponding Förster terms for distances of the order of the physical spacing between molecules and were therefore neglected.

3. Lattice parameters and absorption spectra

The brickstone lattice parameters where determined as following. The horizontal distance between monomers $L_x = |L_x|$ was chosen to be the optimized length of the molecule in the cis-geometry $L_{0}^{cis}$ plus twice the van der Waals radius of the chlorine atom. In particular we chose the longitudinal van der Waals radius determined for a C–Cl type bond $r_{Cl} = 1.58$ Å, as reported in Table 11 of Ref. 61. The angle between monomers was set to $\theta = \tan^{-1}\left(\frac{2L_y}{L_x}\right)$. Having fixed $\theta$ and $L_y$ we then determined the vertical distance between layers of monomers $L_y \cdot \sin \theta$ by fitting the theoretical position of the J-band in the absorption spectra to the experimental result. All of these parameters are reported in Table II.

The measured energies of the lowest electronic transitions for TC, TDBC, and U3 dyes in solution and also in the aggregated form are collected in Table III.

To estimate the shifts of the J-band due to the molecular aggregation the excitonic spectra of the aggregates have been computed by diagonalizing the Hamiltonian, Eq. (2), for all three dyes. The oscillator strength of a particular transition is proportional to the square of the corresponding transition dipole. To account for the static disorder the transition frequencies of the monomers were taken from a Gaussian distribution of width 70 meV. In Fig. 6 the calculated spectra of J-aggregates are shown as compared to the energies of single molecule excitations. The peak positions where fitted to the experimental results. To obtain the correct shift within 5% of error, we determined that the cutoff distance for the molecule-molecule interaction is $L_{\text{cutoff}} = 6 \cdot L_x$. We observe the typical band narrowing of the J-band whereas the exact vibrational structure of the monomer and the J-band cannot be captured with this simple analysis and is beyond the scope of the present paper. Moreover, the present analysis doesn’t account for the line shift due to non-resonant (van der Waals) interactions.

B. Quantum exciton dynamics

The developed model accounts for both coherent and incoherent properties of exciton dynamics. In view of the recent interest in the presence of long lived coherences in photosynthetic aggregates\textsuperscript{65,66} and in polymers\textsuperscript{67} this type of analysis is useful to identify the time over which one should truncate

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\omega$ [eV]</th>
<th>$\mu$ [D]</th>
<th>$\mu_H$ [D]</th>
<th>$l$ [Å]</th>
<th>$q$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC</td>
<td>3.3</td>
<td>8.9</td>
<td>8.3</td>
<td>9.1</td>
<td>0.20</td>
</tr>
<tr>
<td>TDBC</td>
<td>2.9</td>
<td>13.1</td>
<td>11.0</td>
<td>10.5</td>
<td>0.22</td>
</tr>
<tr>
<td>U3</td>
<td>2.4</td>
<td>14.6</td>
<td>12.5</td>
<td>11.1</td>
<td>0.24</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dye</th>
<th>$L_{0}^{cis}$ [Å]</th>
<th>$L_x$ [Å]</th>
<th>$L_y \cdot \sin \theta$ [Å]</th>
<th>$\theta$ [rad]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC</td>
<td>15.01</td>
<td>18.17</td>
<td>3.815</td>
<td>0.421</td>
</tr>
<tr>
<td>TDBC</td>
<td>17.36</td>
<td>20.52</td>
<td>4.600</td>
<td>0.404</td>
</tr>
<tr>
<td>U3</td>
<td>19.72</td>
<td>22.88</td>
<td>5.120</td>
<td>0.427</td>
</tr>
</tbody>
</table>
TABLE III. Experimental data for electronic excitations in monomer and J-aggregated dyes as well as the energy shift $\Delta$ between monomer and J-band.

<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>TC</td>
<td>2.900</td>
<td>2.613</td>
<td>0.287</td>
<td>62</td>
</tr>
<tr>
<td>TDBC</td>
<td>2.396</td>
<td>2.115</td>
<td>0.281</td>
<td>63</td>
</tr>
<tr>
<td>U3</td>
<td>1.864</td>
<td>1.571</td>
<td>0.293</td>
<td>64</td>
</tr>
</tbody>
</table>

the dynamics and extract with sufficient accuracy the diffusion constant. In the long time limit, the contribution to the dynamics is mostly incoherent and this is when one enters the diffusive regime. These properties can be monitored by following the spatial distribution of the exciton population

$$P_{ij}(t) = (\langle ij \mid \psi(t) \rangle \langle \psi(t) | ij \rangle),$$

where $(i, j)$ is the pair of cartesian indices for a particular molecule on the 2D lattice and the bar above the expression indicates the ensemble average over quantum trajectories. In addition, to characterize specifically the role of coherences in the exciton transport we analyze the two-point one-time correlations between the central site (the point of the exciton injection) and the current site $(i, j)$

$$C_{ij}(t) = \langle \langle ij \mid \psi(t) \rangle \langle \psi(t) | 0 \rangle \rangle.$$  

A similar quantity was used previously in Refs. 68 and 69 to estimate the exciton delocalization length in natural molecular aggregates. If the exciton transport is completely incoherent and represented by the hopping of exciton population between sites, the correlation function, Eq. (19), should remain zero for all times provided that no initial site-site correlations were created. This is consistent with the conventional Bloch equations, where the coherence dynamics and the population dynamics are separated.

In Figs. 7 and 8 we show an example of the population and coherence dynamics in TDBC J-aggregate when the dynamic disorder is $\Gamma^d = 30$ meV and static disorder is $\sigma = 70$ meV. Based on the discussion in Sec. II B, this value of dynamic disorder represents a lower bound to the exciton dephasing rate (upper bound to the exciton diffusion length) at room temperature. One can see that exciton transport is anisotropic and the population spreads in time following approximately an elliptic shape with major axis $x$ and minor axis $y$ (such directions are indicated in Fig. 2). The population spreads about 2 to 3 times faster in the $x$ direction than it does in the $y$ direction. This can be explained by analyzing the direction of maximum coupling between nearest neighbors. In fact, looking at the lattice in Fig. 2 and considering the molecule placed at the origin of the purple lattice vectors, we see that it has four first nearest neighbors, one of which is indicated by the $L_y$ vector. The sum of the nearest neighbors coupling vectors taken in pairs along the $x$ axis is greater than that along the $y$ axis. The fact that the exciton is transported in the direction of maximum coupling is also seen in Fig. 9 where the population is more rapidly transferred to site $(26,27)$ along the principle $x$ direction respect to site $(24,27)$ which is along the $y$ axis.

By comparing Figs. 7 and 8, we notice that coherences spread and are suppressed much more rapidly than populations. However, the principal transport axis remains the same, i.e., it is the major axis of the ellipse. This is true for all examined values of static and dynamic disorder. At times shorter than about 30 fs the dynamics is coherent and interesting shapes such as a four leafed clover at 2 fs appear in the coherence plot. At longer timescales incoherent diffusion prevails and these features mostly disappear. The peaks of these correspond to beats in coherences between second to fourth nearest neighbors but such beats die off rapidly over a couple of tens of femtoseconds. At 40 fs only a small fraction of sites populated by the exciton are correlated with the injection site. This timescale also corresponds to the decay of coherent beatings in the population of sites near the injection point, Fig. 9. Thus, within the approximations of our model the exciton diffusion properties can be extracted from 100 fs dynamics. While quantitative differences are observed between the molecules, the general trend is qualitatively similar to the one shown in the example. As a possible extension of this initial study of coherent dynamics it would be interesting to explore the phase directed exciton transport in these two-dimensional aggregates as has been done for the one-dimensional case.70

While the initial condition (a localized exciton) determines a rather large population of the central site even at relatively long times, this does not globally affect the exciton diffusion properties of the aggregate. Furthermore, the localized excitation can be viewed as exciton injection from a donor.

C. Diffusion coefficient and diffusion length

The computed wave function provides the most complete source of information about the exciton dynamics. Its second moment can capture the main diffusive and ballistic features of the transport. For a homogeneous system with stochastic dephasing noise and translational invariance, the moments of the wave function in Eq. (6) can be written analytically.

If the exciton is initially localized on a particular molecule one should expect a ballistic exciton propagation (the second moment scales quadratically in time, $M^{(2)} \propto t^2$) followed by the diffusive motion (the second moment is linear in time, $M^{(2)} \propto t$). For systems with static disorder similar transport regimes should be observed provided that the dynamic noise.
is strong enough to overcome exciton localization. To verify this the second moments of each trajectory were computed over an interval of 100 fs with a time step of 1 fs and averaged over a thousand trajectories. In Fig. 10 an example of $M^{(2)}(t)$ for the TDBC J-aggregate with static disorder $\sigma = 70$ meV and dynamic disorder $\Gamma^\phi = 30$ meV is shown. On timescales shorter than about 30 fs the scaling of $M^{(2)}$ is approximately quadratic, while the longer time dynamics reflects the diffusive transport. A similar tendency is observed for other molecules within the whole spectrum of $\sigma$ and $\Gamma^\phi$ we studied with the free exciton propagation time shrinking down to below 20 fs for large values of $\Gamma^\phi$.

The exciton transport properties depend on the energy of the central lattice site where the exciton is localized at time zero – the initial injection energy $E_{in}$ – relative to the J-band. This reflects which eigenstates are populated at the initial time. If the injection energy is close to the monomer transition, almost all eigenstates are populated. In contrast, if this energy is far below the J-band the exciton remains localized. Results showing the second moment as a function of $E_{in}$ together with the exciton density of states (DOS) are reported in Fig. 11. We see that there is a maximum in the moments somewhere between the J-band ($E_{in} = -281$ meV) and the monomer band ($E_{in} = 0$ meV). This is true at all times and the position of the maximum is different for the $xx$ component than it is for the $yy$ component. This can be correlated to the large density of states in that energy interval (Fig. 11 top panel). The high density of states is not sufficient to explain the exact position of the maximum, in fact, while the density of states has a maximum at about $-72$ meV, the second moment is peaked at about $-170$ meV for the $xx$ component. The same trend in the second moments is observed for TC, and the only apparent difference is that the values of the second moment are smaller. One aspect to keep into consideration is that although there is a large density of states around 60–80 meV, these states mostly have small oscillator...
are observed and the transition is always at about 20–30 fs. To estimate the exciton diffusion coefficients the linear fit was taken over the time interval $\Delta t_1 = 30–100$ fs to exclude the initial ballistic propagation of the exciton. The injection energy was set equal to the J-band frequency. For most values of static and dynamic disorder, the boundary effects associated with the finite size of the simulated lattice are negligible on the timescale of 100 fs. However, for weak dynamic noise the exciton wave function reaches the boundary of the simulated lattice along the y-axis at about 70 fs. In such cases the yy component of the diffusion coefficient $D$ was fitted on the time range 30–70 fs. With the initial condition of injection into the J-band, the diffusion coefficients components were calculated using

$$M_{ii}^{(2)}(t) = 2 D_{ii} t \quad (20)$$

for each type of aggregate. The results are shown in Fig. 12. Two distinct characteristics emerge from this plot. First of all, we notice that diffusion is greater for U3 than it is for TDBC which in turn is greater than that of the TC aggregate. This can be explained by looking at the physical characteristics of the molecules (Table I). U3 has the largest transition dipole, this leads to stronger coupling between the monomers and thus to more rapid exciton density transfer. The diffusion coefficients normalized with respect to the square of the corresponding transition dipole (not shown in the figures) are similar for two molecules, TDBC and U3, while the normalized diffusion for TC is still higher. We attribute this difference to the closer packing of TC molecules. This trend is robust to both static and dynamic disorder, so long as both are finite and not so large as to lead to localization. This implies that independently of temperature, within the studied interval, the transport efficiency is dictated by the specific physical properties of the molecules. Of course, the geometric arrangement is a criteria which can alter this trend since it will explicitly

FIG. 10. Second moment of the exciton wave function in time for TDBC aggregate with static disorder $\sigma = 70$ meV and dynamic disorder $\Gamma^D = 30$ meV. Both $xx$ and $yy$ components are included with their respective error bars. A transition from the ballistic regime to the diffusive regime is observed at about 30 fs. For all studied values of static and dynamic disorder these two regimes are observed and the transition is always at about 20–30 fs.

FIG. 11. Top panel: Density of exciton states as a function of energy of states computed for an aggregate of 51 x 51 TDBC molecules and averaged over 1000 realizations of static disorder $\sigma = 70$ meV. The zero of energy corresponds to the electronic transition of a single molecule. The energy of the central site (injection point) in the lattice is assumed to be zero. Bottom panel: Plot of second moments of the wave function at time $t = 100$ fs as a function of the initial injection energy for TDBC with static disorder $\sigma = 70$ meV and $\Gamma^D = 30$ meV.

FIG. 12. Comparison of diffusion constants as a function of dynamic disorder $\Gamma^D$ for TC, TDBC, and U3 with static disorder $\sigma = 70$ meV. As dynamic disorder is increased, the diffusion constants decrease. Further, $xx$ diffusion constants components are larger than $yy$ components for all values of dynamic disorder. Finally, diffusion is larger for U3 than it is for TDBC and TC. This can be explained by the molecular coupling parameters as described in the text.
modify the couplings. Then second, as noticed from the wave function propagation, diffusion is faster along the x axis than it is along the y axis. This difference is largest for small values of disorder (about a 3-fold difference) where the propagation is fastest, in the quasi-ballistic regime. Going to larger disorder, the wave function spreads much slower and propagation is reduced in both directions.

Finally, we investigated the transport as a function of static disorder as well. The three-dimensional surface plots for TC and TDBC are shown in Fig. 13. We notice that diffusion is strongly dependent on $\Gamma^\phi$ and much less dependent on $\sigma$. For each fixed value of $\Gamma^\phi$, the largest variation of $D_{ii}$ over the $\sigma$ interval is of about 30% of the largest values. On the other hand, the largest variation of $D_{ii}$ at fixed $\sigma$ and varying $\Gamma^\phi$ is of the order of 80% of the largest value. Due to the presence of static disorder the dependence of the diffusion coefficient on the dephasing rate $\Gamma^\phi$ deviates from the conventional $D \propto 1/\Gamma^\phi$ derived within the Haken-Strobl-Reineker model for homogeneous systems.\textsuperscript{34}

Recently, Akselrod \textit{et al.},\textsuperscript{11} have estimated the exciton diffusion length in thin-film J-aggregates of TDBC molecules based on an exciton-exciton annihilation experiment at room temperature. In that study, the exciton lifetime obtained from time-dependent photoluminescence was determined to be $\tau_{\exp} = 45$ ps, and an expression for three-dimensional exciton diffusion was used to determine the annihilation rate. However, the sulphonated group side chains are about 6 Å long and in addition, in the growth process a layer of polymer molecules is introduced between the J-aggregate layers. As a result the spacing between the monolayers of fluorescent dyes is several times larger than the distance between nearest neighbor molecules in a layer. Therefore we can assume

![FIG. 13. Diffusion coefficients of singlet excitons in 2D J-aggregates of TC (panel a) and TDBC (panel b) as functions of static $\sigma$ and dynamic disorders $\Gamma^\phi$. The initial condition for propagation was injection at $E_{in} = -281$ meV for TDBC and $E_{in} = -287$ meV for TC. The red color corresponds to smaller diffusion while the yellow indicates larger diffusion coefficients.](image-url)
that diffusion in these aggregates is two-dimensional rather than three-dimensional. Using a 2D model, we find that the experimental exciton diffusion length is about $\ell_{\text{exp}} \approx 60$ nm. We can estimate the exciton diffusion length along the $i$th direction using the measured lifetime and a computed diffusion coefficient as

$$\ell_i = \sqrt{2D_{ii} \tau_{\text{exp}}}.$$ (21)

For the value of the dynamic disorder $\Gamma^\phi = 30 \text{ meV}$, which should approximately correspond to room temperature, as discussed in Sec. II B, and the static disorder $\sigma = 70 \text{ meV}$ we find $\ell_x \approx 200 \text{ nm}$ and $\ell_y \approx 100 \text{ nm}$. These values are in a good qualitative agreement with the measured one. However, the quantitative discrepancy can be due to a number of factors such as different lattice constants of the aggregate, additional exciton dephasing and relaxation channels, and also domain boundaries in the experimental structures. All of these aspects can be incorporated into the model provided that one can extract the actual parameters from experiments.

V. CONCLUSIONS

In this article, a mixed model combining an open quantum systems approach to ab initio calculations has been employed to gain insight on the exciton dynamics of thin-film J-aggregates. This model can capture both coherent and incoherent transport and allows for a detailed study of transport parameters such as diffusion coefficients and diffusion length. The role of the initial state of the system on transport can also be captured. Further one can investigate all these aspects as a function of the structure of the aggregates through the lattice parameters.

As an example the model was applied to three different cyanine dye aggregates. Within this model we conclude that transport depends explicitly on the molecular properties of the monomers which compose the aggregate. In particular, for molecules packed in a brickstone arrangement, transport increases with the monomers’ transition dipoles and hence with the coupling between monomers. Furthermore, the coupling induces a preferential direction for transport which leads to an anisotropic spread of populations and coherences. Such directionality is robust to both static and dynamic disorder within the investigated ranges and does not change for different molecules. This model has permitted the identification of timescales for the different transport regimes. A ballistic regime is present for all values of disorder at times smaller than 20 fs while afterwards a diffusive regime is observed. The transport is also determined by the choice of the initial condition, at a specific value of injection energy a maximum in diffusion is observed. Investigations on the origin of the exact position of this maximum are planned but qualitatively it can be explained by the large DOS located between the J-band and the monomer transition.

The obtained diffusion length is in good agreement with experimental results, however a more accurate comparison to experiment would only be possible after including relaxation in the excited state manifold and fluctuations in the off-diagonal elements of the Hamiltonian. The model also does not account for exciton domains which would reduce diffusion, and further it cannot be applied straightforwardly in the low temperature regime. Work in these directions is currently in progress in our research group.

The efficient exciton transport observed in these thin-film aggregates and the possibility of tuning this transport by the choice of monomers or by selecting the initial condition makes these aggregates good candidates for devices where large exciton diffusion lengths are sought. In particular coupling them to optical micro-cavities opens the road to a range of control possibilities which we plan to study in future work. Finally, coupling these large-exciton diffusion length materials to high-hole mobility materials might also provide some advantages for technological applications such as all-organic photon detectors.

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