

University of Groningen

Modeling of excitonic properties in tubular molecular aggregates

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DOI:
[10.33612/diss.98528598](https://doi.org/10.33612/diss.98528598)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Bondarenko, A. (2019). *Modeling of excitonic properties in tubular molecular aggregates*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen. <https://doi.org/10.33612/diss.98528598>

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General introduction

Supramolecular aggregates of synthetic dye molecules offer great possibilities to develop nanoscale functional materials for optoelectronic applications. The functionality of such systems is defined by the efficiency of absorbing light and excitation energy transport. To study the optical properties of such systems, theoretical modeling of absorption spectra and excitation energy transfer is essential. This chapter introduces general concepts of the exciton theory in molecular aggregates. In essence, it forms the basis for the later chapters of this thesis.

1.1. Supramolecular systems

Manipulating matter at the nanoscale offers great opportunities for solving large-scale societal problems.^{1,2} The hallmark of nanoscience and nanotechnology is the exploitation of the unique phenomena that occur when matter is organized at the nanoscale, affecting its optical, electrical and magnetic behavior.³ One of the strategies to achieve functional nanoscale materials is the possibility of bottom-up engineering, i.e., arranging molecules and atoms in a particular fashion.⁴⁻⁷ This includes self-assembly of molecules into supramolecular structures. Almost unlimited opportunities are offered by using organic molecules as building blocks, as they allow for tuning of the size and properties of materials with high precision.

An important and fascinating feature of assemblies of organic dye molecules, or

molecular aggregates, is their ability to absorb light and efficiently transport it in the form of excitation energy.^{8–11} Molecular aggregates can be found in Nature; a notable example is constituted by light-harvesting complexes of plants and bacteria. There, the process of photosynthesis starts with the absorption of solar energy by assemblies of chromophores. Such systems can also be produced artificially. Depending on the intermolecular forces guiding the self-assembly process, molecular aggregates can be obtained in a variety of shapes, such as linear chains,^{12,13} rings,¹⁴ films,^{15–18} or tubes.^{19–21}

Molecules within supramolecular structures are held together via non-covalent forces (van der Waals, electrostatic, hydrogen bonding, etc.), therefore, they keep their chemical identity. However, high order and close packing within molecular aggregates give rise to strong Coulomb interactions which lead to collective excited states. These collective excited states, or *Frenkel excitons*, are coherently shared by many molecules and are responsible for intriguing optical properties of these aggregates. This phenomena of molecular aggregates was first discovered more than 80 years ago by Jelley^{22,23} and Scheibe.²⁴ They independently observed that the aggregation of pseudo-isocyanine (PIC) dye molecules is accompanied by a dramatic change in the absorption spectrum: a typical broad band corresponding to the monomer optical response disappears and a characteristic red-shifted narrow band attributed to the collective optical response appears. Today, this red-shifted narrow band is known as J-band after Jelley, and the aggregates exhibiting it are referred to as J-aggregates. There is another type of aggregates, with blue-shifted absorption band, which are called H-aggregates, where H stands for “hypsochromic” meaning a change of the spectral band position to a higher frequency.

1.2. Collective excited states in molecular aggregates

Frenkel exciton model. The nature of the collective excited states of molecular aggregates can be understood on the basis of the Frenkel exciton model.^{25–28} Although a molecule usually possesses many excited states, it is often sufficient to consider only one that optically dominates all others. Hence, each molecule can typically be modeled as an effective two-level system—a ground state and a single excited state. The one-quantum states of the molecular aggregate are then described by the Frenkel exciton Hamiltonian:

$$H = \sum_{n=1}^N \epsilon_n |n\rangle \langle n| + \sum_{n \neq m}^N J_{nm} |n\rangle \langle m|, \quad (1.1)$$

where $|n\rangle$ denotes the state where only molecule n ($n = 1, 2, \dots, N$) is excited while all other molecules are in their ground state, ϵ_n is the transition energy of the molecule n , and J_{nm} is the excitonic coupling between molecules n and m . When the molecular orbitals of the chromophores do not overlap, J_{nm} is dominated by Coulomb interactions

between the transition dipoles of the molecules.

The eigenstates of the Hamiltonian in eq. (1.1) are one-exciton states $|k\rangle$, i.e., one excitation quantum is shared by the molecules. The state $|k\rangle$ is a linear combination of the molecular excitations $|n\rangle$:

$$|k\rangle = \sum_{n=1}^N c_{kn} |n\rangle, \quad (1.2)$$

where the coefficient c_{kn} , obtained by diagonalization of the Hamiltonian in eq. (1.1), reflects the participation of molecule n in the k th exciton state. The one-exciton manifold is the energetically lowest exciton band consisting of N states. The next higher manifold consists of $N(N-1)/2$ two-exciton states in which the molecules share two excitation quanta, etc. For the description of the linear response, like the absorption spectrum, it is sufficient to consider only the one-exciton band, while higher exciton-states are relevant to the nonlinear response.

Ring aggregates. To understand the (linear) optical properties of molecular aggregates, it is instructive to consider a simple model of circular one-dimensional geometry, for which many properties can be found analytically.²⁹ We consider a homogeneous ring aggregate consisting of N equidistant molecules with equal monomer energies, i.e., $\epsilon_n = \epsilon$, and equal magnitude of the transition dipole, μ . All transition dipoles are arranged in such a way that they have an angle $\pi/2 - \beta$ with the plane of the ring, while their projections on the same plane are tangent to the ring (see Figure 1.1). For the sake of simplicity, we restrict ourselves to nearest-neighbor interactions only, denoted as J .

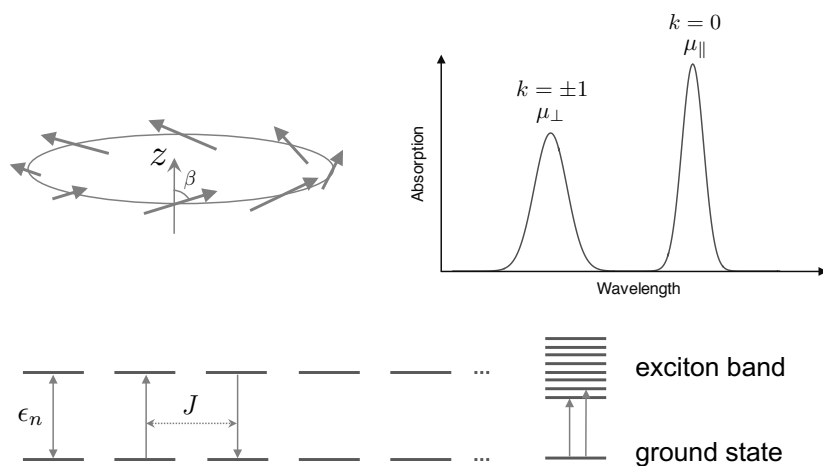


Figure 1.1 | Schematic illustration of the Frenkel exciton model for a circular aggregate. The molecules are placed equidistantly along the ring with equal magnitude of the transition dipoles. All transition dipoles make an angle $\pi/2 - \beta$ with the plane of the ring, while their projections on the same plane are tangent to the ring. Each molecule is a two-level system, i.e., it has a ground state and one excited state, with equal excitation energy ϵ . The excited states of the aggregate resulting from the excitation transfer interactions J between the molecules are coherently shared between the molecules and are called Frenkel exciton states. Such exciton states can be classified in bands according to the number of shared excitation quanta.

Due to translational symmetry, the exciton eigenstates are Bloch states or “exciton waves” along the ring with wave number k :

1

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{ik\phi n} |n\rangle, \quad \phi = 2\pi/N, \quad (1.3)$$

with corresponding energies

$$E_k = \epsilon + 2J \cos(k\phi), \quad (1.4)$$

where k takes integer values, $k = 0, \pm 1, \pm 2, \dots, \pm(N-1)/2$, assuming N is odd (for N even, k takes the values $k = 0, \pm 1, \pm 2, \dots, \pm(N/2 - 1), N/2$).

From eq. (1.4), it follows that the intermolecular interaction J lifts the degeneracy of the energy levels of the monomers ϵ and creates an exciton band of delocalized exciton states. These exciton states are distributed in the exciton band centered around ϵ and the band width is equal to $4|J|$ for $N \gg 1$.

The oscillator strength between the ground state $|g\rangle$ and the exciton state $|k\rangle$ is given by³⁰

$$\mu_k^2 = |\langle k | \hat{M} | g \rangle|^2 = N\mu^2 \left(\cos^2 \beta \delta_{k,0} + \frac{1}{2} \sin^2 \beta \delta_{k,\pm 1} \right), \quad (1.5)$$

where $\hat{M} = \sum_n \hat{\mu}_n$ is the total transition dipole operator given by the sum of the molecular dipole operators and μ is the magnitude of the transition dipole moment of a monomer. Eq. (1.5) marks an important result: only three states are optically allowed, namely the $k = 0$ state, which is polarized perpendicular to the plane of the ring, and two degenerate $k = \pm 1$ states, that are polarized within the plane of the ring, perpendicular to each other. These three states collect all the oscillator strength of the individual molecules and all the other states are dark. Due to the giant oscillator strength (proportional to N) collected by these states, they are often referred to as *superradiant* states. Therefore, the absorption spectrum of the aggregate is dominated by two optical bands.

The $k = 0$ exciton state is the only completely symmetric state, meaning that the oscillations of the transition dipoles of the individual molecules are maximally in phase resulting in a constructive interference of molecular states. For a J-aggregate, as a result of the negative dipole-dipole interactions ($J < 0$), the $k = 0$ exciton state lies at the bottom of the exciton band at energy $E_{k=0} = \epsilon - 2|J|$. Hence, the absorption spectrum of the J-aggregate is red-shifted compared to the monomer absorption spectrum. For an H-aggregate, the opposite is true: positive dipole-dipole interactions ($J > 0$) result in the $k = 0$ state lying at the top of the exciton band at energy $E_{k=0} = \epsilon + 2|J|$. Accordingly, the absorption spectrum of the H-aggregate is blue-shifted compared to the monomer spectrum. The effect of including long-range dipole-dipole interactions slightly modifies these numbers, however, it does not significantly change the essential

features of the model. The sign of the dipole-dipole interaction J is defined by the angle Θ between the transition dipole moment and the vector connecting the two molecules.^{31–33} The angle $\Theta < 54.7^\circ$ results in $J < 0$, i.e., the system is a J-aggregate, while for an H-aggregate, $\Theta > 54.7^\circ$ resulting in $J > 0$. The distinction between J- and H-aggregates is schematically depicted in Figure 1.2 using dimers for simplicity. It should be noted, that identification of J and H aggregates based on spectroscopic changes can be misleading, as short-range, non-Coulombic interactions may contribute significantly to the overall shift. A notable example includes aggregates or thin films of poly(3-hexyl thiophene) or P3HT.^{34,35}

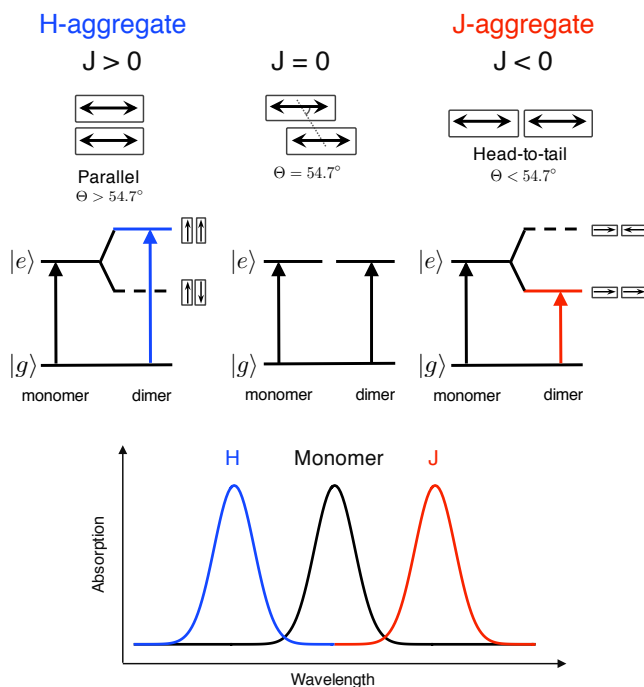


Figure 1.2 | A schematic exciton energy diagram for a molecular dimer with parallel transition dipoles. Molecular profiles with the transition dipole moments are depicted by rectangles with the double arrows (\uparrow). The dipole-dipole interaction J between monomers lifts the degeneracy of the molecular energy level. The selection rule for light absorption dictates that only *in-phase* arrangement of the transition dipoles give a dipole allowed state. In the J-aggregate, as a result of a negative dipole-dipole interaction ($J < 0$), this state is located at the bottom of the exciton band, therefore, the absorption spectrum is red-shifted compared to the monomer spectrum. In the H-aggregate, due to a positive dipole-dipole interaction ($J > 0$), the *in-phase* exciton state is located at the top of the exciton band, resulting in the blue-shifted absorption spectrum. The sign of the dipole-dipole interaction J is defined by the angle Θ between the transition dipole moment and the vector connecting the two molecules.

Tubular aggregates. The analysis of the ring aggregate discussed above can be extended to a tubular aggregate. The simplest cylindrical aggregate considered here is composed of N_1 equidistant rings that are stacked on top of each other, with each ring

consisting of N_2 equidistant molecules. The orientation of the transition dipoles on each ring is the same as for the single ring considered above. Each molecule is labeled by a two-dimensional vector $\mathbf{n} = (n_1, n_2)$, where $n_1 = 1, 2, \dots, N_1$ denotes the ring number and $n_2 = 1, 2, \dots, N_2$ denotes the position of the molecule in the ring (denoted N in the previous section).

In the absence of disorder, the cylindrical symmetry of the aggregate governs the Bloch nature of the exciton eigenstates in the ring direction (n_2 coordinate). In the longitudinal direction of the cylinder (n_1 coordinate) with open boundary conditions, the exciton eigenstates are those of a linear chain. The exciton eigenstates of the tubular aggregate are then given by the direct product of the linear chain and the ring wave functions. Restricting to the interactions between neighboring rings, the corresponding expression for the exciton eigenstate has the following form:

$$|\mathbf{k}\rangle = |k_1, k_2\rangle = \sqrt{\frac{2}{(N_1 + 1)N_2}} \sum_{\mathbf{n}} \sin(k_1 \phi_1 n_1) e^{ik_2 \phi_2 n_2} |\mathbf{n}\rangle, \quad (1.6)$$

where $\phi_1 = \pi/(N_1 + 1)$ and $\phi_2 = 2\pi/N_2$. The wave numbers are defined as $k_1 = 1, 2, \dots, N_1$ and $k_2 = 0, \pm 1, \pm 2, \dots, \pm(N_2 - 1)/2$ (if N_2 is odd).

In the subspace describing the ring direction, the oscillator strength is concentrated in three Bloch states with $k_2 = 0$ and $k_2 = \pm 1$, as described before. In the subspace describing the linear chain direction, the oscillator strength is mostly concentrated in the non-degenerate state with $k_1 = 1$.³⁶ Therefore, like in the case of the ring, the cylindrical aggregate has three superradiant states: ($k_1 = 1, k_2 = 0$), polarized along the axis of the cylinder, and two degenerate states ($k_1 = 1, k_2 = \pm 1$), polarized perpendicular to the axis.

The selection rules obtained above are exact only for homogeneous rings and cylindrical aggregates. Clearly, these homogeneous models are an oversimplification of the reality. In the presence of disorder, the exciton states will be localized^{37,38} on segments of the aggregate, the selection rules will be broken to some extent, and the states will mix.³⁹ Disorder can arise from inhomogeneity in the molecular transition energies, the position and orientation of the transition dipoles, or deformation of the tube. In the following section disorder will be discussed in more detail.

1.3. Disorder and localization

In perfectly ordered aggregates, like the homogeneous rings and tubes considered in the previous section, collective excited states are delocalized over the entire aggregate. In reality, however, aggregates are embedded in a medium, for example, a solvent or a protein scaffold, where each molecule of the aggregate “feels” a slightly different environment that fluctuates both spatially and temporally. This results in position- and time-dependent inhomogeneities in individual molecular transition energies

and intermolecular couplings, referred to as *static* and *dynamic disorder*, respectively. Both types of disorder may severely affect the delocalized nature of the excitons and, consequently, the observed optical properties. When the coupling to the fast dynamic degrees of freedom, such as vibrations or phonons, is rather small, the effect of static disorder dominates over the dynamic disorder in the environment, and the latter can be omitted. This is usually a good approximation at low temperature or for molecular aggregates where the Stokes shift is small, suggesting a weak coupling to the dynamic environment.

Static disorder. The usual way to treat static disorder is to impose randomness on the individual molecular excitation energies as a consequence of slightly different molecular surroundings. This can be modeled as:

$$\epsilon_n = \epsilon_0 + \delta\epsilon_n, \quad (1.7)$$

where ϵ_0 is an average molecular excitation energy and $\delta\epsilon_n$ is taken randomly from a Gaussian distribution with width of σ . This is referred to as static *diagonal* or *energy disorder* and the parameter σ is the measure of the amount of this disorder. Often, it is assumed that each molecule sees “its own” local environment and, therefore, the energy shifts $\delta\epsilon_n$ are uncorrelated on neighboring molecules. Moreover, physical irregularities of the molecular aggregate, such as changes in positions and orientations of the molecules, cause inhomogeneities in intermolecular interactions. This is referred to as *off-diagonal*, or *interaction disorder*. Off-diagonal disorder is in general rarely included, though it was shown to be important for optical properties.^{40,41}

In excitonic systems, disorder breaks the translational symmetry and mixes the homogeneous exciton states. As a result, dark exciton states close to the superradiant state will borrow its oscillator strength. This may lead to a considerable change of the aggregate’s optical properties. For example, a typical characteristic of one-dimensional J-aggregates—*asymmetric line shape* at low temperatures—arises from the mixing of the superradiant state, lying at the bottom of exciton band, with higher energy states.⁴² A disorder-induced red-shift also originates from mixing of the J-band with higher energy states that push it to lower energy.⁴²

Disorder also causes broadening of the absorption band. However, the width of the absorption band of a J-aggregate is typically still much smaller than that of an ensemble of monomers. This commonly observed characteristic of J-aggregates is referred to as *exchange narrowing*.^{40,43–45} This phenomenon originates from the fact that the exciton states delocalized over a delocalization length N^* effectively average over N^* uncorrelated Gaussian variables. This reduces the fluctuations in their excitation energy by a factor $\sqrt{N^*}$ as compared to the single molecule. This means that the J-band width is narrowed by a factor $\sqrt{N^*}$ as compared to the monomer absorption spectrum.

The extent of delocalization of the exciton wave function is determined by an interplay between the intermolecular coupling that delocalizes exciton states and the

disorder that tries to localize them.^{37,38} A common way to quantify the degree of localization is to estimate the number of molecules that coherently share a given exciton state, the so-called *participation number*.^{40,46,47} Another particularly useful measure is the *autocorrelation function* of the exciton wave function^{48,49} that estimates not only the size but gives also the directionality of the localization for aggregates with dimension larger than one.

Dynamic disorder. When coupling to the dynamic environmental degree of freedom that causes the disorder is large, and the timescale of the fluctuations of the molecular excitation energies or the intermolecular couplings are fast compared to the exciton processes, the effect of dynamic disorder dominates static frequency disorder. Dynamic disorder may lead to considerable changes in the absorption spectrum as well. One of such changes, for example, is a result of *motional narrowing*, i.e., with the decrease of the time-scale of the environment fluctuations, the process of averaging over stochastic processes becomes more effective, thus reducing the width of the absorption band.

It is often a good approximation to account for interactions of the excitons with dynamic degrees of freedom classically. A simple stochastic model is constituted by the overdamped Brownian oscillator.⁵⁰ This model assumes that the classical heat bath randomly pushes the system. This affects the molecular transition energies and this can be expressed by adding a fluctuating term $\delta\epsilon_n(t)$ to the average value:

$$\epsilon_n(t) = \epsilon_0 + \delta\epsilon_n(t), \quad (1.8)$$

It should be noted that if the coupling to these bath degrees of freedom is large, the latter should be included explicitly as quantum degrees of freedom.⁵¹

1.4. Excitation energy transfer

Static and dynamic disorder affect the nature of exciton states and as a result excitation energy transfer (EET). Understanding the mechanisms of EET in molecular systems is not only a matter of fundamental scientific interest, but also of relevance for technological applications. EET is one of the key processes regulating the efficiency of photosynthetic light-harvesting systems, and organic electronic devices, such as solar cells.^{52–57}

Coherent vs incoherent dynamics. The nature of the EET in molecular systems is dictated by a complex interplay of various parameters such as the molecular transition energy, excitonic coupling J , strength of the disorder σ , and coupling to the thermal fluctuations of the surrounding Γ . In the limit of strong excitonic coupling, i.e., when the excitation transfer interaction between the donor and acceptor molecules, is much larger than their coupling to the vibrational degrees of freedom, and the strength of the disorder, $J/(\Gamma, \sigma) \gg 1$, exciton states are a coherent superposition of the molecular

(localized) states and, therefore, are delocalized over the donor and acceptor. In this regime, the exciton motion is characterized by a wave-like transfer of energy between molecules, referred to as *coherent*. Coupling to the vibrations of the environment is responsible for the loss of coherences and, consequently, the wave-like transfer is disturbed. In the limit of weak excitonic coupling, i.e., when $J/(\Gamma, \sigma) \ll 1$, the exciton motion is described as a diffusive hopping from site to site, named as *incoherent*.

To visualize these two limiting types of exciton motion, it is convenient to consider a site basis representation, in particular to look at the population of the donor and acceptor site as a function of time, as shown in Figure 1.3. Coherent energy transfer is described by the forth and back oscillations in populations of the donor and acceptor. Incoherent energy transfer is characterized by the exponential decay of the population of the donor and a complementary increase of the acceptor's population till the equilibrium—in the example, where the energy difference between the donor and acceptor is assumed vanishing, this means till equal population. An intermediate regime of exciton motion is characterized by damped oscillations, as shown in the middle panel.

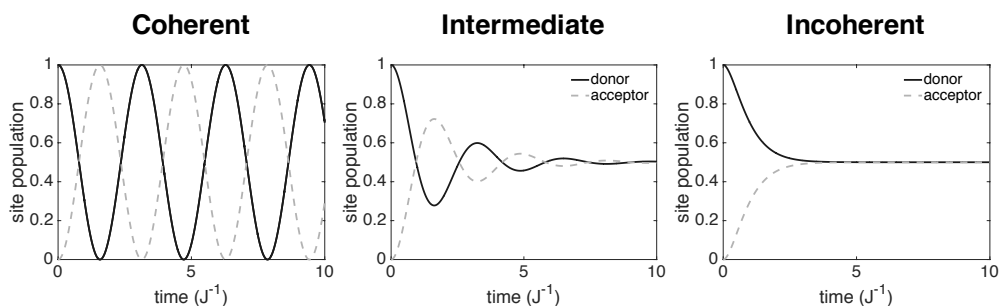


Figure 1.3 | Types of exciton motion between a donor and an acceptor molecule. Coherent motion is characterized by the forth and back oscillations in populations of the donor and acceptor states. Incoherent motion is characterized by the exponential decay of the population of the donor state and exponential increase on the acceptor state till equilibrium is reached. The intermediate regime of exciton motion is characterized by damped oscillations.

Theoretical models used for treating exciton dynamics are commonly based on perturbative approaches. In the regime of strong excitonic coupling, the EET can be described by the Redfield theory.^{51,52} This is a second-order perturbation theory with respect to the coupling to the bath. In the regime of strong system-bath coupling, the EET is described by the well-known Förster theory.⁵⁸ This is also based on a second-order perturbation theory, but this time with respect to excitonic coupling.

Non-perturbative methods treating both coherent and incoherent energy transfer are available.^{59–61} However, they are numerically costly, an issue of particular importance when dealing with multichromophoric systems as molecular aggregates.

1.5. Multiscale modeling

1

Delicate structure-property relationships. So far we used the Frenkel exciton model to explain optical and transport properties of molecular aggregates assuming that we know the molecular arrangement, and as a result the couplings between the molecules and their transition energies. However, typically this molecular arrangement is not known. In the best case, the overall morphology can be resolved by imaging techniques such as cryo-TEM. However, the resolution of this technique is not enough to reach the molecular level.

A long-established way to model optical properties is to combine experimental measurements with phenomenological modeling. Although such approach has proven to be immensely helpful,⁸ the high sensitivity of the optical properties to the details of the molecular packing requires a more accurate and explicit modeling procedure. In this regard, multiscale approaches that combine different levels of modeling show great potential to help reveal the molecular structure.

Multiscale approaches. A wide range of multiscale approaches exist to couple computational models ranging from coarse-grained to highly accurate quantum mechanical calculations. Classical molecular dynamics (MD) simulations can address questions regarding the plausibility of the overall morphology of the molecular aggregate as well as the underlying molecular packing. Assuming that we know the ‘exact’ force field, MD simulations can predict the intermolecular interaction between the dye molecules and with the solvent at atomistic level of detail. MD trajectories give also access to the level of the structural disorder, i.e., variations in the position and orientation of the molecules. Such structural variations, that give rise to the fluctuations of the intermolecular excitonic couplings—the off-diagonal disorder—can be directly translated into the parameters that determine the Frenkel exciton Hamiltonian. This is particularly interesting, because off-diagonal disorder, being important for the excitonic states and thus the optical properties, is usually not easy to model and, therefore, typically neglected. This arises from the fact that even if the fluctuations of the positions and orientations of the neighboring molecules are uncorrelated, the fluctuations of the arising couplings are correlated.⁴¹

Furthermore, the fluctuations of the molecular transition energies can be estimated from microelectrostatic calculations,⁶² that is atomistic calculations which take into account electrostatic and polarization interactions between the chromophores and the environment. In such calculations, the interaction between a molecule and the environment around it can introduce an energy shift to the gas-phase molecular transition energy. Calculating energy shifts for a large number of molecules results in a distribution. The mean value and the width of this distribution can then be used to construct a Frenkel exciton model with diagonal disorder obtained from calculations rather than from fitting to experiment.

Challenges in multiscale modeling. While multiscale approaches promise an enormous progress in understanding complex molecular systems, there are still many challenges which hinder their full adoption. Accurate MD simulations require large-scale calculations of big aggregates made of dye molecule. This is a problematic task since current standard MD force fields are mainly designed to simulate biomolecules, such as proteins, carbohydrates, lipids, and nucleic acids, and are therefore not fitted well to simulate molecules having extended aromatic systems such as dye molecules, fullerenes, or conjugated polymers. The aggregate structure can potentially be obtained from self-assembly simulations. However, the timescale of the self-assembly process is still beyond the reach of current MD tools.⁶³ An alternative approach is to start from a guessed structure, for example a phenomenological model fulfilling the boundary condition set by, for instance, the morphology obtained through cryo-TEM imaging.

Ultimately, the success of the multiscale approach is defined by a trade-off between the precision of the computational methods and computational costs. Complicated large-scale molecular systems require complicated modeling. Still, arguably, a simple modeling that gives a clear picture and deep understanding should not be necessarily left behind.

1.6. Tubular cyanine dye aggregates

Aggregation of cyanine dyes is an outstanding example of self-organization of organic molecules. The basic structure of cyanine dyes allows to achieve highly ordered molecular aggregates of various structures and morphologies.⁶⁴ The extended π -conjugated electronic system in the dye's structure is responsible for the high efficiency of light absorption. In fact, the uniqueness of cyanine dyes as spectral sensitizers in silver halide photography was recognized already in the late 19th century.^{16,65} The discovery of distinguished optical properties of J-aggregates made it possible to achieve higher levels of photosensitivity.⁶⁶ Since then, cyanine J-aggregates have dominated the field of photography in the past century.

In the last decades, it was discovered that the principles governing cyanine aggregates are very similar to those of the antennae complexes in natural photosynthetic systems. In this respect, particularly captivating examples are the double-walled tubular dye aggregates composed of amphiphilic dyes 3,3'-bis(2-sulfopropyl)-5,5',6,6'-tetra-chloro-1,1'-dioctylbenzimidacarbocyanine (C8S3).⁶⁷ These tubular aggregates resemble the light-harvesting complex of green sulfur bacteria^{68,69}—the most efficient photosynthetic organisms known. Like natural photosynthetic antennae, these synthetic nanotubes are formed by thousands of closely packed molecules organized in a tubular geometry. The remarkably uniform supramolecular structure of double-walled C8S3 aggregates provides an excellent model system for studying how intermolecular interactions tailor the excitation energy landscape to control and direct energy transfer.

1.7. Aim and outline of this thesis

1

The development of functional nanoscale materials for photonic and optoelectronic applications will be boosted from establishing structure–optical property relationships for biomimetic light-harvesting aggregates. The challenges in establishing these relationships are related to the current lack of information on the microscopic details of the molecular packing within aggregates. Ordering and arrangement of the molecules determine the delicate balance of the excitonic interactions that dictate the optics and exciton dynamics. The details of the molecular packing can be elucidated by a powerful tool—the modeling of the optical spectra combined with comparison to measured spectra.

This thesis is focused on studying the optical properties of large double-walled tubular aggregates of the cyanine dye C8S3, which is an excellent model system for studying optics and energy transfer in biomimetic systems. We establish how structure and molecular packing affect optical signatures. Moreover, we examine the methods applicable to study exciton dynamics in such large multichromophoric systems.

It was shown experimentally that a slight chemical modification in the original C8S3 dye results in the increase of the diameter of the double-walled tubular system in a well-defined fashion. This change of size is accompanied with a change of the optical spectrum. Understanding the origin of the observed changes in the absorption spectra forms the main motivation of **Chapter 2**. In order to decipher whether the changes in the optical properties arise from the changes in diameter or whether they result from a different molecular packing, we use phenomenological modeling to reproduce the linear absorption and the linear dichroism spectra. An extended herringbone model is used in combination with a Frenkel exciton model to calculate the absorption spectra. Our findings reveal that the observed spectral changes originate purely from the radial growth of the aggregate. This affects the collective optical properties of the supramolecular structure.

The findings of Chapter 2 demonstrate that the physical size of the tubular aggregates affects the exciton states, in turn resulting in changes of their optical signatures. It is also known, as explained in Section 1.3, that energetic disorder destroys the exciton delocalization by breaking the translational symmetry (Section 1.2). Therefore, the following question arises: is it size or is it disorder that matters most in these systems? Answering this question forms the scope of **Chapter 3**. A systematic study of the size effects on the localization properties in disordered tubes is performed using numerical simulations of the exciton states. Specifically, the radius and length dependencies of the localized properties are studied for small and large values of static disorder. The extent of the exciton delocalization is characterized numerically by calculating the participation ratio and the autocorrelation function of the exciton wave function. It is demonstrated that the effects of the tube's radius on

the localization properties in the range of parameters relevant to experiment is strong.

Despite the enormous utility of the phenomenological modeling discussed so far, it is limited in its predictive power, which is at the heart of the design of new functional materials, as explained in Section 1.5. The need to improve the available phenomenological modeling formed the basis of **Chapter 4**. It is demonstrated that accurate insights into the packing of thousands of dye molecules in the complex C8S3 double-walled tubular structure can be obtained by an iterative multiscale approach that combines molecular dynamics and quantum mechanical exciton modeling. It is shown that a thorough understanding of what to use as a starting point and how to validate the structure is required. Both are acquired by modeling of the optical spectra of the obtained structure and comparing it to experimental data. The optical spectra of the thus obtained optimized structure compare very well with experiment. The microscopic model developed opens the route to accurate predictions of energy transport and other dynamic properties.

Theoretical methods designed to describe energy transfer in extended systems consisting of closely packed chromophores, such as C8S3 aggregates, should provide reliable results and be computationally tractable in order to be useful. Such methods are still not well established, despite a number of available promising methods. A systematic study of the validity, efficiency, and performance of several popular methods to study energy transfer in multichromophoric molecular systems is carried out in **Chapter 5**. We compare the multichromophoric Förster resonance energy transfer (MC-FRET) method, the numerical integration of the Schrödinger equation (NISE) method, and the Haken-Strobl-Reineker (HSR) model, validating them against the numerically exact Hierarchy of Equations of Motion (HEOM) method. A model system of a monomeric donor coupled to a multichromophoric acceptor ring of varying size is considered in two limiting configurations and for a variety of system and bath parameters, including the regime relevant to biological light-harvesting systems. The NISE method gives the most reasonable results throughout the parameter regimes tested, while still being computationally tractable, showing promise in studying exciton dynamics in large systems, such as C8S3 aggregates.

