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Impact of inhomogeneities on optical and transport properties of molecular aggregates

Kunsel, Tenzin

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Impact of Inhomogeneities on Optical and Transport Properties of Molecular Aggregates

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Impact of Inhomogeneities on Optical and Transport Properties of Molecular Aggregates

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university of
 groningen

Impact of Inhomogeneities on Optical and Transport Properties of Molecular Aggregates

PhD thesis

to obtain the degree of PhD at the
University of Groningen
on the authority of the
Rector Magnificus Prof. C. Wijmenga
and in accordance with
the decision by the College of Deans.

This thesis will be defended in public on

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Molecular aggregates formed through self-assembly have significance both from fundamental and application perspectives. Understanding the origin of inhomogeneities in the aggregate structure and their impact on the properties form a crucial step in achieving the exact functions we desire from these nanosystems. In this chapter, the motivation behind the research presented in this thesis and the contribution of this thesis to the general goal of understanding the impact of inhomogeneities on properties of molecular aggregates are described. It also provides the outline for the remainder of the thesis.

Image: Sketch of Richard Feynman (based on actual image by Tamiko Thiel, 1984) holding a model of ZnChl tubular molecular aggregate.

1.1 MOTIVATION

Richard P. Feynman, one of the three 1965 Nobel laureate in physics, gave the visionary lecture entitled “There is plenty of room at the bottom: An invitation to enter a new field of physics” in 1959,^[1] which many mark as the advent of the field of nanoscience. The scientific field of nanoscience has ever since witnessed staggering advances, ushering in a spectrum of techniques and technology, that allows for fabrication, control, and manipulation at the nanometer (10^{-9} m) scale. Examples include nanoimprint lithography,^[2] molecular beam epitaxy,^[3–5] electron microscopy,^[6,7] and spintronics.^[8–10] However, what is known, synthesized, and controlled at that scale is still rudimentary and yet to reach the level of functionality that is projected in the notable lecture of Feynman. Making progress and developments in this regard forms the general goal of researchers in the field of nanoscience.

The main challenge of nanoscience is associated with the nature and behavior of the objects at the relevant scale. The realm of nanoscience encompasses unraveling features and behavior of aggregates of atoms and molecules. These systems are neither macroscopic (dimensions $> \mu\text{m}$) nor microscopic (individual atoms and molecules, dimensions $\leq \text{nm}$) but are generally referred to as mesoscopic (literally meaning intermediate between microscopic and macroscopic). Consequently, these systems are subject to effects that cannot be easily understood by using only either simple classical physics or mere direct application of quantum mechanics. The systems are small enough to sustain quantum effects while large enough to exhibit collective properties which differ significantly from individual building blocks (atoms or molecules).^[11–13] This combination renders novel properties to these systems; prominent examples include the quantum hall effect,^[14,15] the quantization of electrical^[16,17] and thermal conductance,^[18] single charge tunneling and the coulomb blockade,^[19,20] quantum transport phenomena,^[21–23] and collective linear and non-linear optical properties such as optical shift of the absorption spectrum,^[11,12,24] exchange narrowing,^[25–27] ultrafast cooperative spontaneous emission,^[28–31] and anomalous and size enhanced non-linear optical responses.^[32–34] These properties can be employed for a myriad of applications such as resonant tunneling diode^[35–37] and single-electron transistor in nano-electronics,^[38,39] spintronic devices,^[40,41] nanoelectromechanical systems as sensors,^[42–44] and opto-electronic devices.^[45–50] To realize the desired applications of the mesoscopic systems, the control over their fabrication should be precise due to the acute sensitivity of their properties to inhomogeneities. For instance, if possible, every constituent building block should be positioned and oriented exactly such that it yields the desired property of the composite system. In contrast, lack of uniformity in different aspects is meaningless in single atoms or molecules (microscopic systems), and in the macroscopic objects, although the magnitude of structural disorder is important, the exact realization of the disorder is

insignificant due to ensemble averaging.

Inhomogeneity in various aspects of the mesoscopic objects viz., differences in their shapes, their sizes, nature of their constituents, and orientation of the composing building blocks etc, is inevitable due to lack of complete control over the fabrication and manipulation at the nanoscale. Inhomogeneity can also be caused by inherent environmental fluctuations due to thermal effects unless there is complete isolation. Effects of inhomogeneity can be a boon or a bane depending on the function or the application we desire and the nature of the imperfection or inhomogeneity. For instance, irregularities in the crystal lattices of conductors (dislocations or impurities) scatter electron waves and reduce their mean free path, which consequently hampers conduction.^[21] On the other hand, adding the right impurities (dopants) to semiconductors can significantly improve their conduction properties.^[51] Another example includes destruction of magnetic properties by introducing heat which randomizes the orientation of the building blocks of the magnetic material,^[51,52] while on the other hand, inhomogeneity in the constituents of natural light-harvesting systems helps in expanding their absorption frequency range.^[53] Therefore, understanding the impact of inhomogeneity on the properties and functions of mesoscopic objects is crucial to guide us in their fabrication as well as to probe their degree of inhomogeneity. Despite significant research efforts, our understanding and control of the impact of inhomogeneities on the properties and functions of mesoscopic objects are still elementary. A particularly interesting class of functional mesoscopic objects are molecular aggregates. These are assemblies of mostly organic dye molecules. Molecular aggregates can absorb light and efficiently transfer the excitation energy, which not only found abundant application as photosensitizers in photographic emulsions,^[54] but has also been extensively utilized as light-harvesting systems in natural photosynthetic systems.^[55] Therefore, gaining further insights on the impact of inhomogeneities on the optical properties and functions of molecular aggregates form the core theme of this thesis.

1.2 THESIS CONTRIBUTION AND OUTLINE

The plenty of room at the bottom can be reached and explored through complementary top-down and bottom-up fabrication techniques.^[2-5,56,57] The top-down approach includes nanofabrication techniques such as electron-beam lithography, whereas bottom-up techniques mainly comprise the self-assembly of atoms or molecules. While the top-down techniques have been dominantly employed by the semiconductor industry for fabricating prevalent nano-devices, there is much that can be learned from nature when it comes to the bottom-up technique of self-assembly, and it presents ample opportunities. This thesis focuses on molecular aggregates

formed through self-assembly. Our main goal is to investigate the influence of inhomogeneities in supramolecular aggregates that are formed through self-assembly.

In this regard, although there are many possible interesting questions, we chose to address four specific questions, which are as follows.

1. How sensitive are the optical properties of self-assembled molecular aggregates to their structural inhomogeneity?
2. Can we probe inhomogeneity within individual molecular aggregates?
3. Are the optical properties susceptible to inhomogeneity in size of supramolecular aggregates?
4. What is the influence of energy inhomogeneity within molecular aggregates on their excitation energy transport properties?

Finding the answers to these four questions forms the main purpose of this thesis. To achieve this goal, we begin with the necessary theoretical background study, which is presented in Chapter 2. It contains key concepts required to understand the content of the following four chapters. The subsequent four chapters present the results of our investigations to answer the above four questions. Chapter 3 focuses on answering the first question, dealing with acute sensitivity of optical properties to minute inhomogeneities in molecular packing of different self-assembled molecular aggregates. Chapter 4 then addresses the possibility to probe structural inhomogeneity within individual molecular aggregates. Subsequently, Chapter 5 presents the investigation of the ability to probe size inhomogeneity in supramolecular aggregates whilst Chapter 6 contains the study on the influence of inhomogeneity in molecular energy on the excitation energy transport properties of the molecular aggregates. Finally, we provide conclusions and the outlook for future studies.

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Chapter 2

Theoretical Background

Unraveling the impact of structural inhomogeneities on optical and transport properties of molecular aggregates requires combined experimental and theoretical efforts. The series of works presented in this thesis represent the theoretical contribution to this endeavor. In particular, we focus on optical spectroscopy which is one of the most powerful and widely used methods to shed light on structure-function relationship of molecular aggregates. This chapter gives an overview of the basic concepts which underlie the contents of subsequent chapters. Further details, necessary for each investigation is provided in the respective chapters. As such, this chapter forms the basis for the following chapters, each of which answers one of the key questions raised in the General Introduction.

2

Image: Representative sketch of optical spectroscopy being employed to investigate the impact that structural inhomogeneities (diverse energy and dipole orientation of constituent molecules as well as varying radius and length of tubular molecular aggregates) have on the optical and transport properties of molecular aggregates.

2.1 MOLECULAR AGGREGATES

Self-organization or self-assembly lies at the heart of the process of forming almost everything we see around and beyond in the universe.^[1] Driven by different interacting forces, it scales from the formation of molecular machinery in living beings to gigantic galaxies. Our focus in this thesis is at the small end of this spectrum, the supramolecular scale, where different non-covalent interactions between molecules lead to self-assembly of individual molecules into molecular aggregates.^[2–5] The general goal of researchers investigating this self-assembly process is to understand, mimic, and emulate the natural self-assembly process to potentially use it as a complementary technique to the top-down approach in synthesizing functional mesoscopic structures.^[4,6–9]

Nature has mastered and employed the self-assembly mechanism to bring about complexity at the mesoscopic level; beginning with individual molecules culminating in molecular aggregates which are essential functional components of living beings.^[4,10–16] Natural light-harvesting systems of photosynthetic organisms such as plants, algae, and bacteria epitomize molecular aggregates formed through self-assembly.^[17,18] Natural light-harvesting systems are composed of molecules that can interact strongly with light, generally referred to as chromophores: Thereby these systems can absorb and transport energy from light.^[7,14] These molecular aggregates come in different shapes, such as linear, circular, and tubular, and different sizes ranging from a few to thousands of chromophores.^[17,18]

The natural light-harvesting system of green sulfur and non-sulfur bacteria, in particular, has attracted considerable attention due to its ability to transport excitation energy from the place of initial excitation to the reaction center with high efficiency (close to unity)^[19,20] and the observation of long-lasting quantum beats in their two-dimensional electronic spectra (2DES).^[21–26] Although the interpretation of the origin of the coherent oscillatory signals in the 2DES and their role in the excitation energy transfer have been highly debated,^[27–30] the high efficiency and the robust nature of the excitation energy transport^[31–34] have been found to be essential for their survival in the optically scarce conditions comparable to only 1% of the light from a full moon.^[35,36] Molecular aggregates found in its light-harvesting antennae (known as chlorosomes) have curved lamellar or tubular shapes and are composed of thousands of chromophores, known as bacteriochlorophylls (BChls).^[16,37–44]

The properties of tubular molecular aggregates found in chlorosomes have inspired the fabrication of artificial tubular molecular aggregates with comparable features.^[14,45–69] Semi-synthetic zinc chlorin (ZnChl)^[58,70,71] molecules mimic the natural BChl molecules in their self-assembly into tubular aggregates. ZnChl tubular molecular aggregates surpass the natural system in its chemical stability and homogeneity. The natural BChl tubular molecular aggregates found in chlorosomes and

the artificial ZnChl tubular molecular aggregates form the systems of study in the subsequent chapters.

2.2 COLLECTIVE PROPERTIES

Self-assembled molecular aggregates, like the ones found in the chlorosomes and its synthetic analogues (such as ZnChl tubular aggregates), have distinct properties compared to molecules (chromophores) that constitute the aggregates. This was first discovered independently by Jelley^[72,73] and Scheibe,^[74,75] almost a century ago, for a solution of pseudoisocyanine (PIC) dye molecules. They observed a significant change in the optical properties of the solution due to the aggregation of the PIC molecules. The absorption spectrum of PIC molecules before aggregation at around 525 nm red-shifts to a band close to 570 nm after aggregation.^[76] The changes in the wavelength (color) of the electromagnetic wave (cf. Fig. 2.1) that is absorbed when

Figure 2.1: *Light spectrum and corresponding wavelength in nanometers.*

the PIC dye molecules form aggregates lead to a physically observable change in the color of the sample. An illustration of such a color change for molecular aggregates of another chromophore (C8S3 molecule) is provided in Fig. 1 of Ref. 77 where the orange color of the solution turns to a pink color due to aggregation of the C8S3 molecules into nanotubes. Besides the more obvious change in the color, the aggregate absorption spectrum is much narrower than that of the individual PIC dye molecules, which is also well-understood and termed exchange narrowing of disorder.^[78–81] The red-shift of the absorption spectrum (change in color) and the exchange narrowing are called collective properties. Other examples of collective properties include cooperative spontaneous emission,^[82–85] and enhanced anomalous non-linear optical response of the molecular aggregates.^[80,84,86] The differences between the collective properties of an aggregate compared to the properties of the

individual chromophores, which constitute the aggregate, can be traced back to differences in their energy eigenstates. For the individual chromophores, the energy eigenstates are localized molecular eigenstates, whereas the energy eigenstates of the molecular aggregates are extended collective excited states, commonly known as excitons.^[87] Excitons are formed as a result of interactions between the chromophores. The crux of the matter is that the collective properties of the molecular aggregates are fundamentally distinct from the sum of properties of its constituent entities.

2.2.1 Frenkel-Davydov exciton formalism

Excitons are distributed molecular electronic excitations of dielectric materials.^[88,89] They can be understood using the physical picture of electron-hole pairs that are formed when a material is excited, for instance by absorbing light, and their static and dynamic properties govern the opto-electronic properties of their host materials. Being a pair of two opposite charges, excitons are electrically neutral. Therefore its transport in a material does not contribute to electrical conduction, however, because it carries excitation energy, it leads to energy transport. Excitons are classified into two types based on the typical separation between electron and hole: 1) Wannier-Mott excitons (also called free excitons) have electron-hole separations much larger than a single repeat unit, molecular or atomic, and 2) Frenkel excitons (also called tightly bound excitons) have electron-hole separation of one repeat unit. The two classes of excitons arise from competition between the electron-hole coupling and the hopping rate of electron and holes between repeat units which differ in different materials. Wannier-Mott excitons are typically found in semiconductors whereas Frenkel excitons are found in insulator crystals and molecular aggregates.

In order to quantitatively understand the collective properties of molecular aggregates, a microscopic description of the Frenkel excitons is necessary. The microscopic theory of Frenkel excitons provided in this thesis is semi-classical i.e., although quantum mechanics is applied to obtain the electronic states of the molecular aggregates, the interaction with light is treated as coupling with a classical electromagnetic wave. In the approach of quantum mechanics, we need to solve the time-dependent Schrödinger equation given by,^[90-93]

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi, \quad (2.1)$$

where Ψ is the wave function and $\hat{H}$ is the Hamiltonian of the system. Note that anything operating on the wave function in quantum mechanics is called an operator and is usually denoted with a hat (^). The wave function Ψ describes the state of the system (molecular aggregate), and all the properties of the system can be extracted from the wave function. The expectation value of the Hamiltonian operator of the

system in state Ψ gives its energy. The Schrödinger equation (Eq. (2.1)) is analogous to Newton's second law in classical mechanics: For a given initial condition, $\Psi(t = 0)$, the Schrödinger equation gives the state of the system for all future times, $\Psi(t > 0)$.^[94] So the essential quantity here is the energy or the Hamiltonian operator ($\hat{H}$) of the system which governs its entire dynamics.

2.2.2 Single molecule excited states

Individual molecules of the aggregates are composed of atoms, each of which are in turn composed of a nucleus and electrons. Therefore, the Hamiltonian of the molecule is the sum of kinetic energy of all the electrons and nuclei, and all the Coulomb interactions between these charged entities, given by,^[95]

$$\hat{H}_{\text{mol}} = \hat{T}_{\text{nuc}} + \hat{V}_{\text{nuc-nuc}} + \hat{T}_{\text{el}} + \hat{V}_{\text{el-nuc}} + \hat{V}_{\text{el-el}}, \quad (2.2)$$

where $\hat{T}$ corresponds to the kinetic energy operator and $\hat{V}$ corresponds to the Coulombic interaction operator. Depending on the basis states we choose, the matrix representing the Hamiltonian operator can vary. In one particular basis, the Hamiltonian matrix will have only diagonal elements and these basis states are referred to as the eigenstates of the molecular Hamiltonian ($\hat{H}_{\text{mol}}$). The diagonal elements of such a Hamiltonian matrix are the energies of the eigenstates, referred to as the eigenenergies. Assuming that these eigenstates are known, these states can be denoted as $|s\rangle$ with energy $\epsilon_s = \hbar\omega_s$ using the neat notation of Dirac.^[96]

When an electromagnetic wave is incident on the molecules, there is primarily interaction between the electric dipole moments of the molecules and the electric component of the electromagnetic wave.^[93,97] In quantum mechanics, the electric dipole moment of a molecule is also an operator and quantifies its charge distribution, given by,

$$\hat{\mu} = \sum_j q_j \hat{r}_j, \quad (2.3)$$

where q_j and $\hat{r}_j$ are the charge and the position operator of the charged entity j , respectively. The charged entities refer to nuclei (positively charged) and electrons (negatively charged) of the atoms constituting the molecule. Associated with each transition, for instance between a state $|i\rangle$ and state $|f\rangle$, is a transition dipole moment given by $\langle f|\hat{\mu}|i\rangle$ where $\langle f|$ is hermitian conjugate (conjugate transpose) of state $|f\rangle$ written in Dirac notation. The transition dipole moment is a quantum phenomenon and has no classical analog. On interaction of the molecule in the ground state with the electric component of the electromagnetic wave, all transitions between the lowest energy state ($|g\rangle$ with energy $\hbar\omega_g$) and the higher energy states may potentially contribute to its optical response. The contribution of each transition is proportional

to the square of its transition dipole moment and the detuning ($\Delta\epsilon_{f,g} - E_\lambda$) where $\Delta\epsilon_{f,g}$ is the energy difference between the excited state $|f\rangle$ and the ground state $|g\rangle$, while E_λ is the energy of the incident electromagnetic wave with wavelength λ . If the contribution of one of these transitions dominates all others, which prevails in many situations, we can neglect all other transitions and the molecule can be represented by the two states: the ground state $|g\rangle$ and the specific excited state $|e\rangle$. Within this two-level approximation of the molecule, the two states can be used as basis and the Hamiltonian operator for the molecule can be neatly shown using the Dirac notation as,

$$\hat{H}_{\text{mol}} = \epsilon_g |g\rangle\langle g| + \epsilon_e |e\rangle\langle e|, \quad (2.4)$$

and the dipole moment operator of the molecule is given by,

$$\hat{\mu} = \boldsymbol{\mu}_g |g\rangle\langle g| + \boldsymbol{\mu}_{g,e} |g\rangle\langle e| + \boldsymbol{\mu}_{e,g} |e\rangle\langle g| + \boldsymbol{\mu}_e |e\rangle\langle e|, \quad (2.5)$$

where $\boldsymbol{\mu}_g = \langle g|\hat{\mu}|g\rangle$ and $\boldsymbol{\mu}_e = \langle e|\hat{\mu}|e\rangle$ are the permanent dipoles in the ground and excited states, respectively, whereas $\boldsymbol{\mu}_{g,e} = \langle g|\hat{\mu}|e\rangle$ and $\boldsymbol{\mu}_{e,g} = \langle e|\hat{\mu}|g\rangle$ are the transition dipole moments between the two states of the molecule. If we assume that the chromophores are centrosymmetric, then the permanent dipoles can be neglected ($\boldsymbol{\mu}_g = \boldsymbol{\mu}_e = 0$).

The absorption spectrum of the molecule can be calculated by employing Fermi's golden rule,^[93,97] which follows from first-order time-dependent perturbation theory in the molecule-field interaction, $\hat{H}_{\text{mol-rad}} = -\hat{\mu} \cdot \mathbf{E}$, where $\mathbf{E}$ is the electric field of the incident electromagnetic wave. Omitting several constant prefactors including a prefactor E_λ (which is considered a constant for sufficiently narrow absorption regions), the absorption spectrum is then given by,

$$A(E_\lambda) = |\langle e|\hat{H}_{\text{mol-rad}}|g\rangle|^2 \delta(\epsilon_e - \epsilon_g - E_\lambda), \quad (2.6)$$

where E_λ is the energy of the incident electromagnetic wave with wavelength λ . Equation (2.6) corresponds to a delta peak (infinitely sharp peak) at energy $E = \epsilon_e - \epsilon_g$, which ensures that the absorption occurs only when the energy of the incident light is resonant with the molecular transition, with total area under the peak given by $|\langle e|\hat{H}_{\text{mol-rad}}|g\rangle|^2$. In practice, however, the absorption peak has a finite width due to homogeneous (finite lifetime of the excited state and dephasing due to interaction with surrounding heat bath) and inhomogeneous (random shift of the energy difference $\epsilon_e - \epsilon_g$ due to varying environment of different molecules in the ensemble) broadening. The strength of the absorption peak, commonly referred to as the oscillator strength, is then given by the square of the transition dipole moment projected along the direction of the polarization of the incident electromagnetic wave.

2.2.3 Dimer excited states

The distinction of the collective properties of the molecular aggregates compared to the features of individual molecules will be illustrated here by considering the example of a dimer, which is the simplest possible molecular aggregate. Under the two-level approximation of the molecules, the dimer basis states are $|g, g\rangle$ where both molecules are in their ground states $|g\rangle$, $|e, g\rangle$ where the first molecule is in its excited state $|e\rangle$ whilst the second molecule is in its ground state $|g\rangle$, $|g, e\rangle$ where the first molecule is in its ground state $|g\rangle$ whilst the second molecule is in its excited state $|e\rangle$, and $|e, e\rangle$ where both molecules are in their excited states $|e\rangle$. In this basis, the Hamiltonian matrix of the dimer will generally have sixteen elements, however, when the coupling between the basis states with the different numbers of excitation(s) is small compared to their energy difference (prevalent in the molecular aggregates we treat in this thesis), we neglect all the coupling terms except the coupling between basis states with the same number of excitation ($|g, e\rangle$ and $|e, g\rangle$ for the dimers). This is known as the Heitler-London approximation.^[98,99] Using the Heitler-London approximation, we will consider only the single excited state manifold. Introducing $|n\rangle$ which represents the state where molecule n in the aggregate is in the excited state $|e\rangle$ and remainder molecules are in their ground state $|g\rangle$, $|1\rangle := |e, g\rangle$ and $|2\rangle := |g, e\rangle$. The Frenkel exciton Hamiltonian of the dimer is then given by,^[98–100]

$$\hat{H}_{\text{Dimer}} = \sum_{n=1}^2 E_n |n\rangle \langle n| + \sum_{n=1, m \neq n}^2 J_{nm} |n\rangle \langle m|, \quad (2.7)$$

where the state $|n\rangle$ is the singly excited state of the dimer with only molecule n in its excited state of the dimer, as described above, and E_n is its energy. Furthermore, J_{nm} is the coupling between the singly excited states, often referred to as the resonant interaction, which describes the transfer of excitation from one molecule to another due to Coulomb interactions between the molecules. For the dipole allowed transitions, this term is dominated by the interaction between the molecular transition dipoles, and in this thesis, the interactions J_{nm} are modeled using the point-dipole approximation,^[101–103]

$$J_{nm} = \frac{1}{4\pi\epsilon_0\epsilon} \frac{(\boldsymbol{\mu}_n \cdot \boldsymbol{\mu}_m) r_{nm}^2 - 3(\boldsymbol{\mu}_n \cdot \mathbf{r}_{nm})(\boldsymbol{\mu}_m \cdot \mathbf{r}_{nm})}{r_{nm}^5}, \quad (2.8)$$

where $\boldsymbol{\mu}_n$ is the transition dipole of molecule n , $\mathbf{r}_{nm}$ is the position vector between molecules n and m , r_{nm} is its magnitude, ϵ_0 is the vacuum permittivity, and ϵ is the dielectric constant which is taken equal to 1. It is important to note that model calculations using interactions between extended dipoles do not change our conclusions; they hardly affect the spectral lineshapes and mostly result in an overall spectral shift. Note that in Eq. (2.7) the energy E_n and the resonant interaction J_{nm}

are taken with respect to the corresponding quantities in the total ground state of the aggregate where all the molecules are in their ground state. Considering only up to singly excited states is sufficient to describe linear responses of the molecular aggregates treated in this thesis; non-linear responses of molecular aggregates are beyond the scope of this thesis and interested readers are directed to more suitable references.^[104,105]

The collective excited states of the dimer (Frenkel exciton states) and their corresponding energies are then obtained by diagonalizing the Frenkel exciton Hamiltonian of the dimer (Eq. (2.7)). The nature of the Frenkel exciton states depend strongly on the homogeneity of the system. Assuming that the molecules in the dimer are identical (homogeneous system) with same molecular excitation energy ($E_1 = E_2 = E_{\text{mol}}$), the Frenkel exciton states are given by,

$$|\pm\rangle = \frac{1}{\sqrt{2}} (|1\rangle \pm |2\rangle), \quad (2.9)$$

with their energies,

$$E_{\pm} = E_{\text{mol}} \pm J_{12}. \quad (2.10)$$

The two states $|\pm\rangle$ are called one-exciton states as these states share a single excitation. As seen from Eq. (2.9), both of these states are delocalized, which means, in either of the states, there is a finite probability to find the excitation on both of the molecules. The exciton states differ in their relative phase of the excitation amplitude. Consequently, the optical response of the two states differ, which can be explained by using their transition dipole moment given by,

$$\langle \pm | \hat{\mu} | 0 \rangle = \frac{1}{\sqrt{2}} (\mu_1 \pm \mu_2), \quad (2.11)$$

where $|0\rangle$ corresponds to the dimer state where both molecules are in their ground states $|g\rangle$. Figure 2.2 shows the dimer with its transition dipoles of the molecules oriented in arbitrary directions that subtend an angle ϑ between the transition dipoles of the two molecules. Since the molecules are assumed to be identical, we can use the same transition dipole moment magnitude for both ($\mu_1 = \mu_2 = \mu$), and obtain the oscillator strengths corresponding to the exciton states equal to,

$$I_{\pm} = |\langle \pm | \hat{\mu} | 0 \rangle|^2 = \mu^2 (1 \pm \cos(\vartheta)). \quad (2.12)$$

This translates into an absorption spectrum of the dimer consisting of two peaks that are separated by an energy $2J_{12}$ with the ratio of their oscillator strengths given by,

$$\frac{I_+}{I_-} = \frac{(1 + \cos(\vartheta))}{(1 - \cos(\vartheta))}. \quad (2.13)$$

Figure 2.2: Two molecules with resonant interaction J_{12} that constitute a dimer with their transition dipoles represented by the green arrows. The relative orientation of the transition dipoles is defined by angle ϑ shown between the transition dipole of the first molecule and an imagined overlay (dot edged transparent molecule figure) of the transition dipole of the second molecule on the first molecule.

In order to shed more light on the mathematical description of the collective properties of the one exciton states ($|\pm\rangle$) given so far, we can consider two special cases. First, let us consider a Head-to-Head arrangement of the transition dipoles of the molecules as shown in Fig. 2.3. The interaction (taking $\frac{1}{4\pi\epsilon_0\epsilon} = 1$) between the transition dipoles of the molecules is then given by,

$$J_{12} = \frac{\mu^2}{r_{12}^3}, \quad (2.14)$$

where r_{12} is the distance between the two molecules in the dimer. J_{12} is therefore positive which leads to $E_+ = E_{\text{mol}} + J_{12}$ being larger than $E_- = E_{\text{mol}} - J_{12}$. The oscillator strengths of the two transitions are then given by $I_+ = |\langle +|\hat{\mu}|0\rangle|^2 = 2\mu^2$ and $I_- = |\langle -|\hat{\mu}|0\rangle|^2 = 0$, respectively. Therefore, in this arrangement of the two molecules in the dimer, the absorption spectrum of the dimer is blue-shifted as compared to the monomer absorption spectrum. This particular dimer falls in the class of aggregates referred to as H-aggregate.^[106–108] H stands for hypsochromic which means blue-shift in Greek. This is not consistent with the behavior observed by Jelley and Scheibe of the aggregation of the PIC dyes.

Considering another special case where the transition dipole of the two molecules are arranged in a Head-to-Tail fashion as shown in Fig. 2.4, then the interaction (taking $\frac{1}{4\pi\epsilon_0\epsilon} = 1$) between the molecules is given by,

$$J_{12} = -2\frac{\mu^2}{r_{12}^3}. \quad (2.15)$$

Since J_{12} has a negative value, $E_+ = E_{\text{mol}} + J_{12}$ is smaller than $E_- = E_{\text{mol}} - J_{12}$. Since the oscillator strengths are still given by $I_+ = |\langle +|\hat{\mu}|0\rangle|^2 = 2\mu^2$ and $I_- = |\langle -|\hat{\mu}|0\rangle|^2 = 0$, in this arrangement, the absorption spectrum of the dimer has red-shifted as compared to the monomer absorption spectrum. This behavior is consistent with the ob-

Figure 2.3: Head-to-Head arrangement of the transition dipole moments (green arrows) of the molecules in a dimer with resonant interaction between the transition dipoles of the molecules given by J_{12} . The molecules have energy $E_1 = E_2 = E_{\text{mol}}$ (homogeneous), and due to the resonant interaction between the two molecules, the one-exciton states of the dimer are given by $|\pm\rangle$. In the homogeneous case, $|+\rangle$ accumulates all the oscillator strength of the system (transition dipole represented by the blue arrow) and the $|-\rangle$ has no oscillator strength (transition dipole represented by the red dashed arrow) resulting in no contribution to the optical response. In this arrangement of the dimer, state $|+\rangle$ is at energy J_{12} above the energy of the individual molecules (E_{mol}) resulting in blue-shift of the dimer spectra compared to the spectra of individual molecules.

servation made by Jelley and Scheibe, although the aggregates of PIC dye molecules investigated by Jelley and Scheibe are actually chain-like one-dimensional aggregates instead of dimers described here. The general description given here also applies to the one-dimensional aggregates albeit with minor changes in the details (refer to Sec. 2.3.1). The dimer with the Head-to-Tail arrangement falls in the class of aggregates referred to as the J-aggregates, where J stands for Jelley.^[72–75] Note that by changing the arrangement of the transition dipoles of the molecules from Head-to-Head arrangement to Head-to-Tail arrangement, the angle Θ between the transition dipole moments and the vector connecting the two molecules in the dimer changes from 90° to 0° . The switch in the sign of J_{12} , which determines if the aggregate falls in the class of H- or J-aggregates, happens when $\Theta = 54.7^\circ$ (the magic angle).^[102,109]

Besides the shift in spectrum, the oscillator strength of the dimer peaks are twice as large as that of the individual molecules. Consequently, the spontaneous emission rate of the dimer is twice the spontaneous emission rate of the individual molecules. This phenomenon is what was referred to as the cooperative spontaneous emission which is also known as exciton superradiance. This feature is another collective

Figure 2.4: Head-to-Tail arrangement of the transition dipole moments (green arrows) of the molecules in a dimer with resonant interaction between the transition dipoles of the molecules given by J_{12} . The molecules have energy $E_1 = E_2 = E_{mol}$, and due to the resonant interaction between the two molecules, the one-exciton states of the dimer are given by $|\pm\rangle$. In the homogeneous case, $|+\rangle$ accumulates all the oscillator strength of the system (transition dipole represented by the red arrow) and the $|-\rangle$ has no oscillator strength (transition dipole represented by the blue dashed arrow) resulting in no contribution to the optical response. In this arrangement of the dimer, state $|+\rangle$ is at energy J_{12} below the energy of the individual molecules (E_{mol}) resulting in red-shift of the dimer spectra compared to the spectra of individual molecules.

property that differs from the property of individual molecules as mentioned earlier. Overall, the microscopic description of the Frenkel excitons given in this section for the dimer shows that the Frenkel exciton formalism can describe the collective property emerging due to aggregation of the molecules, and the description provided here for the dimer can be easily extended to general aggregates without drastic changes.

In the Frenkel exciton description of the collective optical properties of dimers, we can observe that small changes in structure of the dimers can have significant influence on these properties. For instance, the arrangement of the molecules determines if there will be either red- or blue-shift in the absorption spectrum of the aggregate compared to that of the individual molecules. Furthermore, the relative intensity of the peaks of the aggregate depends on the relative orientation of the two molecules, refer to Eq. (2.13). In addition to that, the separation between the peaks of the molecular aggregates ($E_+ - E_- = 2J_{12}$) depends on both the distance between the transition dipole of molecules and their orientation (cf. Eq. (2.8)). It reflects the structure-property relationship of the molecular aggregates. Understanding this relationship forms the essence of research conducted and presented in this thesis.

2.3 THE STRUCTURE-PROPERTY RELATIONSHIP

Understanding structure-property relationships provides a blueprint for the selection and fabrication of molecular aggregates to achieve their desired features and functions. As seen in the dimer example given in Sec. 2.2.3, the structure-property relationship is understood based on the excitonic properties of the molecular aggregates. Variation in structural features changes the energetics of the aggregate, such as the interaction between the molecules and the degree of homogeneity, which, in turn, influences the excitonic properties. The change in excitonic properties then manifests itself in the variation in observable collective optical properties of the aggregates. For illustration, in the dimer example given above, changes in the arrangement of the molecules (structure) influenced the interaction between the molecules, which, in turn, leads to changes in the energy positions of the exciton states (excitonic property), which was manifested in the absorption spectrum of the dimer (collective optical property).

Structural features can be broadly classified into gross-aggregate level features such as the shape and size of an aggregate, and microscopic-molecular level features such as the molecular packing and local environment. The molecular packing is determined by the orientation and proximity of neighboring molecules. All of these features, in different ways, influence the interaction and degree of homogeneity within the aggregate. This, in turn, affects the excitonic properties and consequently the observable collective properties. Without going into many details, examples of impact of each of these structural features on the excitonic properties will be briefly discussed below.

2.3.1 Homogeneous aggregates

For simplicity, we first consider only homogeneous or ordered aggregates. Homogeneous refers to regularity or uniformity in molecular packing and local environment. It means that there is a fixed lattice composed of a repeated unit cell which ensures uniformity in the interactions. Furthermore, uniformity in the local environment leads to identical excitation energies for all the molecules. Consequently, the exciton states are delocalized over the whole aggregate.^[79,104] The dimer example given above is one such example of a homogeneous aggregate, and therefore, the exciton states were delocalized over both molecules in the dimer.

Due to delocalization of the excitons over the whole aggregate, gross aggregate-level structural features become significant. For instance, the size of the aggregates dictate the density of states which determines collective optical properties such as linear absorption and circular dichroism spectra of the aggregates.^[48,65,110] Furthermore, the magnitude of the collective properties are enhanced by the size of the

aggregate.^[79,83,104] The shape of the aggregate can also have significant impact on the collective properties. For instance, a regular aggregate with parallel orientation of the transition dipoles of the molecules at certain finite angle with respect to the inter-molecular distance vector (refer to Fig. 2.5) would have very different oscillator strength distribution of the exciton states in linear chain shape^[79,104] compared to when its end molecules are joined to make a circular ring shape.^[111–113] All the molecules in the linear chain have their transition dipoles lying parallel to the plane of the page and are oriented with angle β with respect to the vertical axis z (cf. Fig. 2.5 (a)). When the end molecules in the linear chain are joined, a circular ring shaped aggregate is obtained (cf. Fig. 2.5 (b)) where the transition dipoles of the molecules subtend angle β with respect to the z -axis perpendicular to the plane of the ring.

Figure 2.5: (a) Linear aggregate of molecules with a parallel orientation of their transition dipoles and (b) circular aggregate obtained by connecting two ends of the linear aggregate. The transition dipoles of the molecules subtend angle β with respect to the z -axis perpendicular to the inter-molecular distance vector in the linear aggregate and to the plane of the ring in the circular aggregate.

These two arrangements lead to very different absorption spectra; the spectrum has one peak for the linear chain shape (Fig. 2.5 (a)) and two peaks for the circular ring shape (Fig. 2.5 (b)). To understand this behaviour we can use the extension of the Frenkel exciton Hamiltonian of the dimer (Eq. (2.7)). Assuming that the linear chain is infinitely long, we can impose periodic boundary conditions for both the

linear chain and the ring. The Frenkel exciton states of the systems are then given by the Bloch states,^[114]

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{i \frac{2\pi}{N} kn} |n\rangle, \quad (2.16)$$

where k denotes the quasi-momentum of the exciton states and takes the values $k = 0, \pm 1, \dots, \pm(N-1)/2$ for N odd (with obvious changes for N even). N is the total number of molecules in the aggregate. The states $|k\rangle$ are analogous to states $|\pm\rangle$ for the dimer, and state $|n\rangle$ is the state with molecule n excited and all other molecules in their ground states as described in Sec. 2.2.3. The energies of the exciton states are given by,

$$E_k = E_{\text{mol}} + \frac{1}{N} \sum_{n=1, m \neq n}^N J_{nm} e^{-i \frac{2\pi}{N} k(n-m)}. \quad (2.17)$$

The oscillator strengths of the exciton states in the linear chain arrangement of the molecules are given by,^[114]

$$I_k = |\langle k | \hat{\mu} | 0 \rangle|^2 = N\mu^2 \delta_{k,0}, \quad (2.18)$$

whereas in the ring arrangement of the molecules, the oscillator strengths are given by,^[115]

$$I_k = |\langle k | \hat{\mu} | 0 \rangle|^2 = N\mu^2 \left[\cos^2(\beta) \delta_{k,0} + \frac{\sin^2(\beta)}{2} (\delta_{k,-1} + \delta_{k,1}) \right]. \quad (2.19)$$

$\delta_{k,n}$ in Eq. (2.18) and Eq. (2.19) are Kronecker delta-functions. The results in Eq. (2.18) and Eq. (2.19) show the variation in the oscillator strength distribution resulting from different selection rules associated with each aggregate shape. It also shows the enhancement of the collective optical properties of the aggregates (factor $N\mu^2$) with size of the system.

The collective properties of aggregates are also sensitive to microscopic molecular-level features such as molecular packing. For instance, a theoretical study^[116] on stacks of terrylene derivatives showed strong dependence of the exciton mobility on sub-Angstrom transverse displacements between neighboring chromophores. Additionally, using model calculations, significantly different absorption spectra of tubular molecular aggregates of C8S3^[117,118] dye molecules prepared through varying synthetic routes were interpreted to possess distinct lattice structures; one with a brick wall lattice structure^[48] and the other with a herring-bone lattice structure.^[57,65]

These examples show the strong dependence of collective properties of molecular aggregates on their structural features. The next question then arises as to how the inhomogeneity in the structure as present in real systems influences the collective properties. The inhomogeneity can be in shape, size, molecular packing, and local

environment. The inhomogeneity can be between aggregates (inter-aggregate) or within an aggregate (intra-aggregate).

2.3.2 Inhomogeneous aggregates

All the descriptions so far are for perfectly ordered or homogeneous aggregates. However, in real systems there is always a certain degree of inhomogeneity or disorder in the molecular aggregates either due to differences in the constituent molecules that self-assemble or due to the different conditions in which the molecular aggregates are formed. For instance, the molecular aggregates found in the natural chlorosomes are composed of different types of bacteriochlorophyll molecules which can further vary in their state of methylation.^[18,36,119,120] The different bacteriochlorophyll molecules have varying molecular excitation energies and lead to different molecular packing as well, which introduces molecular excitation energy disorder as well as interaction disorder within the molecular aggregates.^[17,36,120] Disorder of such a type due to varying participating molecules in the aggregation process can be avoided by synthetically fabricating self-assembled molecular aggregates of single type of molecules.^[58,65] However, even in such a case, inhomogeneities are inescapable. Even when all the molecules are identical, disorder is present since the molecular aggregates are embedded in a medium, like a solvent, and every individual molecule is exposed to a varying environment.^[121] The varying environment impacts the molecular excitation energies of the molecules and inevitably introduces molecular excitation energy disorder in the aggregates. Furthermore, there can be disorder in the systems due to thermal effects. Due to finite thermal energy provided by the environment, the dye molecules can exhibit translational and rotational motion that changes their positions and orientations. Consequently, the symmetry in the interaction between the molecules is broken and inhomogeneity in the intermolecular interactions is introduced. These inhomogeneities can be classified into excitation energy disorder (also called diagonal disorder due to the disorder being in the diagonal elements of the Hamiltonian) and interaction disorder (also called off-diagonal disorder) based on what the variation is in.

Inhomogeneities can also be categorized based on the timescale of the disorder. There can be a static disorder, which may be due to thermal fluctuations in the environment that are slow compared to the timescale of the experiment or due to having different kinds of constituent molecules, and dynamic disorder, due to fluctuations in the environment or vibrations in the constituent molecules that have a timescale of the same order or faster than the experiment. The inhomogeneities described so far are at the local molecular level within individual aggregates (referred to as intra-aggregate disorder), however, the inhomogeneities can prevail at a higher hierarchy of structures, at the aggregate level, between different aggregates (referred to as

inter-aggregate disorder) and can extend up to the macroscopic ensemble level. For instance, at the aggregate level, the aggregates can have varying shapes or sizes due to different constituent molecules or due to varying growth conditions or growth stages.^[36,65] As described in Sec. 2.3.1, the aggregates with different shapes and sizes would have varying collective properties. In addition, the average and standard deviation of intra-aggregate disorders (such as energy disorder) can vary between different molecular aggregates. In this thesis, we consider both intra-aggregate disorder as well as inter-aggregate disorder and investigate their impact on the collective properties of the molecular aggregates. We also investigate how these types of disorders can be distinguished and characterized using experimental spectroscopic techniques.

For a microscopic description of the impact of inhomogeneity, we need to refer to the influence of inhomogeneity on the Frenkel exciton states of the aggregates. The variations in properties caused by the aggregate-level inhomogeneities, such as changes in shapes and sizes of the aggregates are explained in Sec. 2.3.1. Local molecular-level inhomogeneity in structural features introduces disorder in the excitation energy of the molecules (E_n in Eq. (2.7)) and the interaction between the molecules (J_{nm} in Eq. (2.7)). Consequently, the translational symmetry in the system is broken, which induces coupling between the exciton states of the homogeneous system (Bloch states), which were delocalized over the whole system.^[79,114,122–124] This leads to the mixing of the homogeneous aggregate exciton states, which, in turn, results in energy shifts and, more importantly, localization of the exciton states to segments of the aggregate.^[81,111,123,124] The localization size of the exciton states in the presence of the disorder depends on the ratio $\frac{J}{\Delta}$, where J is the typical interaction strength and Δ is the strength of the disorder.^[125,126]

One of the most prominent collective properties of molecular aggregates with excitation energy and/or interaction disorder is the exchange narrowing of the aggregate absorption spectrum compared to the monomer absorption spectrum (one of the characteristic feature of J-aggregates observed by Jelley and Scheibe).^[78,79,81] It is a consequence of the exciton states averaging over the molecular scale disorder within its localization segments, which effectively reduces the fluctuation magnitude of the inhomogeneous quantity.^[77] As a consequence, the linewidth of the aggregate absorption spectrum $W_{\text{agg}} = \frac{W_{\text{mol}}}{\sqrt{N_{\text{loc}}}}$, where W_{mol} is the linewidth of single molecule absorption spectrum and N_{loc} is the localization size of the exciton states in the inhomogeneous aggregate. Other changes due to disorder includes the disorder-induced energy shift of the exciton states and the redistribution of the oscillator strengths of the exciton states,^[81,111,113,127] which leads to changes in shape of the absorption spectrum: The symmetric lineshape in the homogeneous case becomes more asymmetric.^[79,128] Furthermore, as a consequence of the localization of the exciton states, the rate of cooperative spontaneous emission of the molecular aggregates reduces

from $N R_{\text{mol}}$ in the homogeneous case to $N_{\text{loc}} R_{\text{mol}}$ in the inhomogeneous case, where N is the total size of the system and R_{mol} is the spontaneous emission rate of individual molecules.^[82,129,130] Similar changes in the collective optical and excitation energy transport properties of (tubular and linear) molecular aggregates form the subject of Chapters 3 - 6 in this thesis. In Chapters 3 - 5, we show how sensitive collective optical properties of tubular aggregates are to different structural inhomogeneities, and in Chapter 6, we show how energy disorder of molecules caused by inhomogeneity in their local environment influences excitation energy transport properties in linear molecular aggregates.

2.4 PROBING INHOMOGENEITIES AND THEIR IMPACT

For the self-assembled molecular aggregates of chromophores, spectroscopic techniques are powerful tools to shed light on their structural inhomogeneities and their impact through probing static and dynamic properties of their excitons. In this thesis, we model single-molecule (single-object) spectra and compare those to experimental data to unravel structural inhomogeneity in tubular molecular aggregates, and we calculate the exciton diffusion constant in a linear molecular aggregate to investigate the impact of static and dynamic energy disorder on the excitation energy transport.

2.4.1 Single-object spectroscopy

The collective properties of self-assembled molecular aggregates are governed by the complex interplay of their essential structural features such as intermolecular interactions and inhomogeneities in both the excitation energy of the molecules and the interaction between the molecules. Optical spectroscopy is a toolbox that allows to probe and investigate this interplay. Steady-state spectroscopic techniques^[17,89] such as absorption and photoluminescence spectroscopy, linear dichroism, and circular dichroism can shed light on the underlying structure of the systems and interaction of the system with its environment. On the other hand, time-resolved techniques^[131,132] such as time-resolved photoluminescence, transient absorption spectroscopy, and two-dimensional spectroscopy allow us to directly observe the evolution of the system's excited states and unravel the timescales of its essential processes. Although these spectroscopic techniques provide a plethora of information on the systems of interest, these techniques are ensemble spectroscopic techniques where the ensemble averaging of the properties of inhomogeneous systems conceal vital information. Therefore, in our pursuit of understanding the impact of inho-

inhomogeneities on the collective properties of the molecular aggregates and separating intra- and inter-aggregate disorder, these techniques are less powerful. The mentioned challenge is addressed with the aid of single-molecule (single-object) spectroscopy,^[133–136] which allows to determine the complete distribution of properties of systems in an ensemble, rather than the moments (mean and standard deviation) of the distribution of the properties in the ensemble.^[49,120,137] The technique also permits to follow system dynamics which are usually washed out by the lack of ensemble synchronization.^[108,138–140] In Chapters 3 and 4, we model the experimental single-aggregate linear polarization resolved spectra for a specific type of tubular molecular aggregate.^[36,120,141] This particular spectroscopic technique allows to unveil the polarization properties in addition to selection rules of the eigenstates of the system. Therefore it helps to determine structural features such as the orientation of the molecules within individual aggregates as well as shape of the aggregate. Since, circular dichroism is known^[110] to be more sensitive to structural features compared to linearly polarized spectroscopic techniques, in Chapter 5 we perform a model study of single-aggregate circular dichroism.^[142–149] From these studies, we learn how structural inhomogeneity within individual aggregates influences their collective properties manifested through the optical signatures in their respective spectra.

2.4.2 Exciton diffusion

The resonant interactions between the molecules, J_{nm} in Eq. (2.7), drive the excitation energy transport.^[94,99] Typically, upon excitation of a system, such as a molecular aggregate, excitation energy transport takes place as a wavepacket which propagates with certain group velocity.^[94,150,151] The environment and molecular degrees of freedom other than the excitation (which cause static and dynamic energy disorder), such as lattice vibrations, then scatter the wavepacket and leads to a finite exciton mean free path.^[94,114,151] This defines the nature of the excitation energy transport: When the scattering is weak, the mean free path will be large compared to the unit cells (intermolecular distance) and there will be ballistic or coherent transport whereas, in the opposite limit of strong scattering, the exciton loses its phase information even just after moving between nearest-neighbor unit cells, which results in incoherent hopping transport. More specifically, the static energy disorder causes localization of the exciton states which always hinders transport,^[79,124–126,152–154] whereas the dynamic energy disorder leads to dephasing which may enhance or impede transport, depending on the conditions.^[94,105,151,155–157] This complex interplay of the typical resonant interaction, the magnitude of the static energy disorder, and the dephasing rate due to the dynamic energy disorder, and its impact on transport can be most directly probed by studying the diffusion constant which characterizes the diffusive motion of the excitons in the long time limit.^[151,158] Experimentally, the dif-

fusion constant of excitons can be determined in different ways^[159] including by observing the delayed fluorescence resulting from capture of excitons after diffusion by impurities^[99,160,161] or alternatively by using time-resolved spectroscopic techniques, such as picosecond transient grating.^[162] Theoretically, the diffusion constant is typically obtained from the long-time limit of the mean-squared displacement, which in turn may be obtained using a variety of methods, such as generalized master equation or the stochastic Schrödinger equation.^[151] The diffusion constant can be alternatively calculated from linear response theory, leading to the Green-Kubo expression,^[163,164]

$$D = \left\langle \frac{1}{Z_0} \int_0^\infty dt \text{Tr} \left(e^{-\hat{H}/k_B T} \overline{\hat{j}(t) \hat{j}(0)} \right) \right\rangle, \quad (2.20)$$

where Z_0 is the partition function of the exciton system, $\hat{H}$ is the system Hamiltonian, k_B is the Boltzmann constant, and T is the temperature. The flux operator $\hat{j}(t)$ is the time derivative of the exciton position operator (defined as $d \sum_n n |n\rangle \langle n|$ for the linear molecular aggregates, with d the lattice constant), the brackets $\langle \cdots \rangle$ denote the average over the static disorder distribution and the overbar $\overline{(\cdots)}$ denotes the average over the stochastic process. This description is employed in Chapter 6 and an in-depth analysis of the impact of the static and dynamic energy disorder on the exciton diffusion properties of a linear molecular aggregate is given.

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Chapter 3

Spectral and Structural Variations of Biomimetic Light-Harvesting Nanotubes

Bio-inspired, self-assembled nanotubes have been investigated by low-temperature, polarization-resolved single-tube spectroscopy. These assemblies are based on zinc chlorin monomers and are considered as model systems that resemble the secondary structural elements in the natural light-harvesting systems of green (non) sulfur bacteria. Compared to the natural systems, the spectral parameters extracted from the single-nanotube spectra feature distributions with significantly smaller widths, which is ascribed to a tremendous reduction of structural heterogeneity in the artificial systems. Employing quantum chemical molecular modeling, the spectra of individual nanotubes can be explained consistently only for a molecular packing model that is fundamentally different from those considered so far for the natural systems. Subsequent theoretical simulations reveal that the remaining spectral variations between single nanotubes can be traced back to small variations of the mutual orientations of the monomer transition dipole moments that are far beyond the resolving power of high-resolution electron microscopy imaging techniques.

3.1 INTRODUCTION

Self-assembled dye aggregates have attracted considerable attention over the past few years.^[1–4] In such supramolecular structures, the tight packing of the molecular building blocks results in strong intermolecular interactions that lead to the formation of exciton states, i.e., electronically excited states that are delocalized over a range of molecules and which govern essential properties, such as energy and charge transfer.^[5] How and to what extent the photophysical parameters of the aggregate differ from those of the monomers depends crucially on the magnitudes of the intermolecular couplings imposed by the architecture of the supramolecular arrangement of the building blocks.^[6–9]

Hence, inspired by the continuous search for novel optoelectronic materials, molecular aggregates with well-defined composition have been investigated for elucidation of the excitonic interactions in multichromophoric systems and to study their self-assembly.^[3,4,10–17] Further inspiration for this research came also from the antenna complexes from green sulfur and non-sulfur bacteria, so-called chlorosomes. These belong to the most efficient light-harvesting systems in nature,^[18–20] enabling photosynthetic growth by absorbing only a few photons per chromophore per day. Chlorosomes contain self-assembled molecular aggregates that accommodate hundreds of thousands of densely packed bacteriochlorophyll (BChl) c, d, e molecules organized in a curved lamellar or cylindrical geometry,^[18,21,22] for the latter with diameters on the order of 5–10 nm and lengths in the μm range. In contrast to many other photosynthetic antenna systems, where the arrangement of the cofactors is determined by a protein scaffold, the monomers in the molecular aggregates of the chlorosomes are stabilized by metal-ligand coordinative bonds and van der Waals interactions.^[19] Especially this feature has motivated many groups to investigate the design principles of chlorosomes and/or to develop synthetic analogues for next generation solar cells.^[12,23–25]

For the natural chlorosomes, the presence of mixtures of various types of BChl molecules that are involved in the self-assembly process is an important source for heterogeneity, together with variations in size, shape, and the number of aggregates in a single chlorosome. Therefore, a lot of effort has been spent synthesizing artificial bacteriochlorophyll mimics.^[3,12,26] Semisynthetic 3¹-hydroxy zinc chlorin (ZnChl) molecules derived from natural chlorophyll a precursors are considered to be the best matching counterparts to the BChl c, d, e found in chlorosomes^[3,12,24,25,27–30] because they feature a similar tetrapyrrole backbone with 3-hydroxymethyl and 13¹-keto groups as the natural BChls. Applying the concept of dendron wedges,^[31] some of us accomplished the first unambiguous example of a highly defined tubular model system based on ZnChl 1.^[29] Using atomic force microscopy (AFM) and transmission electron microscopy (TEM), it was found that the ZnChl 1 monomers

self-assemble into uniform single-wall tubular structures with a total diameter of 6 nm.^[29] Further, the optical properties of these ZnChl 1 and related dendron-appended ZnChl aggregates^[3,29,32] closely matched those of their natural counterparts.

In order to associate the geometric and the electronic structure of the ZnChl 1 aggregates, in this chapter, we combine low-temperature polarization-resolved single-molecule spectroscopy, quantum chemical structure calculations, and spectral simulations. Because the molecular composition of the monomers in ZnChl 1 aggregates is properly defined, this leads to a significant reduction of the widths of the observed spectral bands compared to those observed for single natural chlorosomes,^[33–44] thereby unmasking further spectral variations between the individual ZnChl 1 aggregates. The spectral heterogeneity can be traced back to reflect subtle variations in the mutual alignment of the monomers, which are far beyond the resolving power of high-resolution imaging techniques. Interestingly, these variations can only be explained consistently if we introduce a new supramolecular stacking model between the ZnChl 1 monomers.

3.2 EXPERIMENTAL STUDY

In Fig. 3.1(a), we display a stack of 160 consecutively recorded fluorescence-excitation spectra from a single aggregate as a function of the polarization of the incident light in a two-dimensional representation. This reveals two subbands, each showing a clear modulation of the detected fluorescence intensity with 180° periodicity, Fig. 3.1(a), top. The variation in intensity is compatible with a $\cos^2$ dependence, as indicated by the dashed lines. Integration over all polarizations yields the spectrum shown by the black line in Fig. 3.1(a), bottom, which features a peak at 13624 cm^{-1} (734.0 nm) with a total width of 190 cm^{-1} (full width at half maximum; FWHM). The blue and red lines in Fig. 3.1(a) (bottom) correspond to examples of individual spectra that have been recorded for the polarizations indicated in the two-dimensional representation by the respective horizontal lines. These are characterized by peak positions of 13604 cm^{-1} (735.1 nm) and 13641 cm^{-1} (733.1 nm) and widths (FWHM) of 204 cm^{-1} and 168 cm^{-1} , respectively. In order to analyze the fluorescence-excitation spectra and the underlying spectral contributions more quantitatively, we used Eq. 3.1 to fit the polarization-resolved spectra.

$$F(E, \theta) = B + \sum_i A_i(E) [\cos(\theta - \phi_i)]^2 \frac{2W_i}{4(E - E_i)^2 + (W_i)^2} \quad (3.1)$$

Here, B accounts for a background, i counts the spectral components associated with the individual aggregate, A_i refers to the corresponding amplitude, θ is the polarization angle of the incident light, and ϕ_i represents the angle of the projection

Figure 3.1: (a) Top: Stack of 160 consecutively recorded low-temperature fluorescence-excitation spectra from an individual aggregate of ZnChl 1. Between two successive spectra, the polarization of the excitation has been rotated by 6.2° . On the right-hand side of the pattern, the measured fluorescence intensity (dots) is compared to a $\cos^2$ function (dashed) as a function of the polarization for excitation energies marked by the vertical solid lines at $13710\text{ cm}^{-1}/729.4\text{ nm}$ (dark green) and $13540\text{ cm}^{-1}/738.6\text{ nm}$ (pink). Bottom: Fluorescence-excitation spectrum averaged over all polarizations (black) and individual spectra at the particular polarizations of 130° (red) and 217° (blue), indicated by the respective horizontal lines in the top pattern. The excitation intensity was 25 W/cm^2 . (b) Global fit of the experimental spectrum according to Eq. 3.1 (see the text). The setup of this part of the figure is similar to that in part (a). (c) Distribution of the relative phase angles between the two subbands from an individual aggregate ($\Delta\phi_{12} = |\phi_1 - \phi_2|$ if the result is less than 90° and $\Delta\phi_{12} = |180^\circ - |\phi_1 - \phi_2||$ otherwise). (d) Distribution of the ratio of the oscillator strengths O_1/O_2 of the two subbands from an individual aggregate. (e) Experimental distribution of the angle β (gray bars) that characterizes the orientation of the transition dipole moments of the monomers with respect to the symmetry axis of a tubular aggregate. The black lines indicate the β values obtained from simulations of the four spectra shown as examples in Fig. 3.4 (vide infra). For more details, see the text. Remark: For one single aggregate, we obtained outliers for the ratio of the oscillator strengths (5.15) and for the value of β (32°). For illustration purposes, these data points are not shown in (d) and (e), respectively.

of the transition dipole vector of the respective spectral component onto the sample plane with respect to the laboratory frame. For the line shape, we assume a Lorentzian form characterized by the energetic center position E_i and a width denoted by W_i (FWHM). (Results for a Gaussian lineshape function and further spectroscopic data are provided in Sec. 1 of the Supporting Information of Ref. 45). During the fitting process, the phases ($\theta - \phi_i$) and the amplitudes (A_i) were treated as global parameters. It turned out that to reasonably reproduce the experimental spectra it was sufficient to restrict the analysis to two spectral components. In the following, the two spectral components, labeled as $i = 1, 2$, will be referred to as the low-energy ($i = 1$) and the high-energy band ($i = 2$), respectively, and the whole fitting procedure will be referred to as a two-component fit.

For the example shown in Fig. 3.1(a), the result of this fitting procedure is shown in Fig. 3.1(b). For the low-energy band (red line), we find a peak at 13602 cm^{-1} (735.2 nm) with a width of 210 cm^{-1} (FWHM), and for the high-energy band (blue line), the parameters are 13646 cm^{-1} (732.8 nm) for the peak position and 162 cm^{-1} for the linewidth. The mutual phase difference between these two bands amounts to $\Delta\phi_{12} = 89.0^\circ$. This global fitting procedure was used to analyze the spectra from 52 individual ZnChl aggregates, from which we extracted the mutual polarization angle, $\Delta\phi_{12}$, and the ratio of the total oscillator strengths, O_1/O_2 , of the two bands. The distributions of these parameters are shown in Figs. 3.1(c) and (d), respectively. Further parameters such as the spectral peak positions and linewidths for the low- and high-energy bands, as well as the energy difference between the peak positions of the two bands, $\Delta E = E_2 - E_1$, are provided in the Appendix (Supplementary Information, Note 1). The relative phase angle features a narrow distribution characterized by $(84 \pm 8)^\circ$ (mean $\pm$ standard deviation), Fig. 3.1(c), reflecting that the optical transitions that underlie the two subbands are polarized nearly perpendicular with respect to each other. For the distribution of the ratio of the oscillator strengths O_1/O_2 , we find (1.23 ± 0.63) , Fig. 3.1(d). The observation of a narrow distribution for the relative phase difference peaking close to 90° provides independent evidence for a tubular arrangement of the ZnChl 1 molecules, in agreement with conclusions from previous AFM and TEM experiments.^[29] There it was found that the ZnChl 1 monomers self-assemble into nanotubes with uniform diameter lying on the substrate with the symmetry axis parallel to the substrate. For such a sample arrangement and under the assumption of a homogeneous tubular aggregate (neither geometric nor energetic disorder), the angle β between the transition dipole moments and the cylinder axis can be calculated, in the limit of long aggregates, from the oscillator strength of the mutually orthogonally polarized bands as^[6]

$$\tan(\beta) = \sqrt{\frac{2O_2}{O_1}}. \quad (3.2)$$

Here, O_1 refers to the oscillator strength of the lower-energy exciton state, which is polarized parallel to the symmetry axis of the tube, whereas O_2 is the oscillator strength of the higher-energy exciton state that is polarized perpendicular to the symmetry axis of the tube; the factor of 2 corrects for the fact that any emission polarized parallel to the optical axis cannot be detected.^[46] The experimentally obtained distribution for the angle β is shown in Fig. 3.1(e) together with the results from simulations for four specific aggregates that will be discussed later. The histogram can be characterized by $(52.7 \pm 4.3)^\circ$.

3.3 THEORETICAL STRUCTURE AND SPECTRA MODELING

The structural information obtained from AFM or TEM is not sufficient to explain the observed variations in the angle β , which suggests differences in the molecular packing between individual aggregates that are beyond the resolving power of the high-resolution microscopies. In order to generate an atomistic model and to theoretically model the spectra of the tubular system, we have utilized the experimental information about the orientation of the transition dipole moments of individual monomers within the tube and the inner and outer tube diameters as determined previously by cryo-TEM.^[29] The latter define a range for the number of ZnChl units within a cyclic/helical arrangement, and the former fix the orientation of the transition dipole moment of each individual subunit with respect to the symmetry axis of the tube. The tubular aggregates are considered as a stack of N_1 rings of radius R , each containing N_2 equidistantly arranged molecules, as illustrated in Fig. 3.2(b). In this representation, the molecules are labeled by coordinates $\mathbf{n} = (n_1, n_2)$, where n_1 runs from 1 to N_1 and labels the ring, whereas n_2 runs from 1 to N_2 and labels the position of the molecule within a particular ring. Neighboring rings are separated along the tubular axis by distance h and rotated relative to each other by the helical angle γ . For $\gamma \neq 0$, the structure of the aggregate can be envisaged as a set of helices wrapped around the same symmetry axis; see Fig. 3.2. Then, n_2 simply numbers the helix on which each molecule lies. Thus, the three-dimensional position of molecule $\mathbf{n}$ reads^[6]

$$\mathbf{r}_{\mathbf{n}} = (R \cos(n_1\gamma + n_2\Phi_2), R \sin(n_1\gamma + n_2\Phi_2), n_1h), \quad (3.3)$$

where $\Phi_2 = \frac{2\pi}{N_2}$. The orientation of the transition dipoles is characterized by the angle α between its projection on the plane of the ring and the local tangent of the ring and the angle β with respect to the cylinder axis; see Figs. 3.2(c) and (d). Then, the three-dimensional orientation of the molecular transition dipoles is given by

$$\boldsymbol{\mu}_{\mathbf{n}} = (-\mu \sin \beta \sin(n_1\gamma + n_2\Phi_2 - \alpha), \mu \sin \beta \cos(n_1\gamma + n_2\Phi_2 - \alpha), \mu \cos \beta), \quad (3.4)$$

Figure 3.2: (a) Left: Chemical structure of the ZnChl 1 monomer. Right: Structure used for the molecular modeling. To optimize the structure, the molecule has been rotated by an angle φ (blue curved arrow) around the fixed Q_y transition dipole moment (magenta arrow). The angle φ has a value of zero when a unit vector lying in the molecular plane and perpendicular to the transition dipole moment vector is parallel to the local normal of the tube. (b) Cylindrical aggregate model composed of N_1 rings of radius R , each accommodating N_2 equidistantly arranged monomer transition dipole moments (magenta arrows). Consecutive rings are separated by distance h . (c) Top view of the cylindrical aggregate model illustrating the angle α . (d) Two consecutive rings illustrating the angles β and γ .

where μ indicates the magnitude of the transition dipole. Any tubular aggregate with one molecule per unit cell can be represented in this way. Then, the following free parameters remain to be determined: (i) the number of monomers per ring N_2 , (ii) the vertical distance, h , between the two consecutive rings, and (iii) the angle of inclination, φ , of each monomer around the direction of the transition dipole moment (see Fig. 3.2(a), right).

For a systematic search of the most stable structure that obeys the given experimental constraints, we have constructed aggregates with different N_2 and systematically scanned the energy of a 2×2 arrangement of monomers as a function of the two undetermined parameters h and φ employing quantum chemical methodology. In this way, “Ramachandran-like” plots have been calculated from which stability regions can be identified and optimal values of the parameters h and φ can be extracted; see Fig. 3.3(a) for $N_2 = 13$. More details and an animated movie of the

Figure 3.3: (a) Energy scan for $N_2 = 13$ as a function of φ and h . (b) Section consisting of four molecules from the optimized structure. The dotted yellow line corresponds to the hydrogen bond between two molecules of adjacent rings. The transition dipole moment vectors of the individual monomers are represented by magenta arrows. (c) Structural model of a tubular aggregate consisting of 10 stacked rings based on extrapolation of the optimized three-ring structure (see the text).

structure are given in Secs. 2 and 3 of the Supporting Information of Ref. 45.

In general, we found that increasing N_2 systematically leads to stable regions at

higher vertical distances h . Our attempts to scan also structures for $N_2 > 16$ were not successful because for reasonable values of h the packing arrangement becomes too dense and the monomers partially overlap. This yielded unphysical structures resulting in convergence failures in the quantum chemical energy calculations. Subsequently, we extracted the structural parameters corresponding to the lowest-energy structures with N_2 ranging from 12 to 16 and constructed a minimalistic model for the tubular aggregate that consisted of two stacked rings. Then, these structures were fully relaxed, allowing us to determine the “binding energy per monomer”, E_{bm} , according to

$$E_{\text{bm}} = \frac{(E_{\text{total}} - 2 \cdot N_2 \cdot E_{\text{mol}})}{2 \cdot N_2} \quad (3.5)$$

where E_{total} refers to the total energy and E_{mol} to the energy of a monomer; see Table 3.1.

Table 3.1: Optimal tube parameters calculated at the PM6-D3H4 levelⁱ

N_2	h_{opt} (nm)	R_{opt} (nm)	E_{bm} (kJ/mol)
12	0.72	1.69	-30.6
13	0.67	1.69	-41.5
14	0.71	1.72	-22.0
15	1.05	1.69	-38.3
16	0.97	1.78	-34.5

As can be seen, the most stable configuration is obtained for the tubular structure with $N_2 = 13$. The corresponding energy map is shown in Fig. 3.3(a). Interestingly, already the unrelaxed structure hints toward a coordinative bond between the carbonyl group in the 13¹ position of one monomer to the Zn(II) ion of the neighboring monomer within the same ring. In the subsequently fully optimized structure, these coordination bonds become even more pronounced because the carbonyl groups bend in the direction of the neighboring metal center with a distance of 2.2 Å. Furthermore, we observe the formation of hydrogen bonds that support stacking of the individual chlorin rings. Thus, the carbonyl oxygen of the ester group coordinates with the hydroxyl group of an adjacent chlorin within the next stack with a bond length of 1.9 Å; see Fig. 3.3(b). In order to further validate the molecular arrangement found, we constructed a tubular aggregate consisting of three stacked rings according to the optimal parameters and subsequently optimized the struc-

ⁱThe parameters h_{opt} and R_{opt} were taken from the optimized structures for a system consisting of two stacked rings with variable N_2 . E_{bm} represents the calculated binding energy per monomer.

ture, proving that in principle a periodic arrangement can be possible. The coordinative motifs are preserved in both optimized structures. In summary, the molecular modeling yields tubular aggregates that can be characterized as 13-mer ring structures held together via a metallosupramolecular $\text{Zn} \cdots \text{O}=\text{}$ coordination interacting with the neighboring rings via hydrogen bonds with an offset of one monomer. In Fig. 3.3(b), a scheme illustrating the interactions between the monomers in the tube is presented. A section from the optimized structure demonstrating the binding motif is given in Fig. 3.3(c), and a comparison of the orientation of the transition dipole moments in the optimized structure with those obtained from modeling the experimentally obtained spectral patterns is given in Fig. S6 in Sec. 4 of the Supporting Information of Ref. 45.

The two-dimensional polarization-resolved fluorescence-excitation spectra from individual aggregates featured pronounced variations in shape; see Fig. 3.4, left column. Yet, all patterns showed clear modulation of the registered intensity with 180° periodicities as a function of the polarization of the excitation light, and all measured spectra could be analyzed using the above-mentioned global fitting procedure. In order to investigate whether the observed spectral variations can be associated with differences in the molecular packing between the individual aggregates that are beyond the resolving power of the high-resolution imaging techniques such as electron microscopy, the spectra of the aggregates were modeled. Therefore, each monomer is represented by the transition dipole moment of the optical Q_y transition, μ , which is the only transition that is relevant for the experiments reported here. For the geometrical arrangement of the transition dipole moments, we used the parameters obtained from the molecular modeling described above as a starting point (see Table 3.2) and simulated the polarization-resolved fluorescence-excitation spectra of

Table 3.2: Summary of the parameters used for simulating the spectra

parameters	values
E_{mol}	13939 cm^{-1} (717.4 nm)
μ	4.5 D
R	1.7 nm
h	0.67 nm
N_2	13
N_1	500

the aggregates (which are assumed to be equal to the absorption spectra) using a standard Frenkel exciton Hamiltonian that takes the excitation transfer interaction into account; see Appendix (Supplementary Information, Notes 2 and 3).

Figure 3.4: Left column: Examples of polarization-resolved fluorescence-excitation spectra from experiment for four different individual ZnChl 1 molecular aggregates in two-dimensional representation. The widths (FWHM) of the two spectral bands obtained from the two-component fit were (1) $W_1 = 255 \text{ cm}^{-1}$; $W_2 = 242 \text{ cm}^{-1}$, (2) $W_1 = 210 \text{ cm}^{-1}$; $W_2 = 162 \text{ cm}^{-1}$, (3) $W_1 = 278 \text{ cm}^{-1}$; $W_2 = 193 \text{ cm}^{-1}$, and (4) $W_1 = 179 \text{ cm}^{-1}$; $W_2 = 158 \text{ cm}^{-1}$. For all spectra, the excitation intensity was 25 W/cm^2 . Middle column: Two-dimensional representation of simulated polarization-resolved fluorescence-excitation spectra using the structural parameters given in Table 3.2. The widths (FWHM) of the two spectral bands obtained from the experiment were also used in the simulated spectra to fit the experimental spectra. Right column: Comparison of cross sections through the two-dimensional representations of the experimental and the simulated spectra, allowing one to judge the quality of the fits.

To fit the experimental spectra of individual nanotubes using simulations, we varied the structural parameters α , β , and γ around the values obtained from molecular modeling. Yet, we note that within each aggregate these three angles were kept fixed, which corresponds to the situation of a totally cylindrically symmetric structure. The best agreement between each of the four experimental spectra considered, Fig. 3.4, left column, and the corresponding modeled spectra, as shown in Fig. 3.4, middle column, was achieved by using the parameters given in Table 3.3. The qual-

Table 3.3: Variation of the three angles α , β , and γ in the simulations for reproducing the experimental spectra of aggregates 1-4 in Fig. 3.4ⁱⁱ and comparison of the results obtained from the two-component fit (fit) and the spectral simulation (sim)

parameters	aggregate 1	aggregate 2	aggregate 3	aggregate 4
α	39.9°	41.5°	40.5°	42.4°
β	54.2°	52.4°	48.4°	51.2°
γ	10°	9°	14°	10.5°
ΔE_{fit}	70 cm ⁻¹	44 cm ⁻¹	57 cm ⁻¹	32 cm ⁻¹
ΔE_{sim}	70 cm ⁻¹	43 cm ⁻¹	57 cm ⁻¹	32 cm ⁻¹
$(O_1/O_2)_{\text{fit}}$	1.000	1.146	1.487	1.270
$(O_1/O_2)_{\text{sim}}$	1.017	1.143	1.485	1.273

ity of the simulation can be judged from the comparison of slices from the 2D spectra from experiment and the model, as shown in Fig. 3.4, right column. This can be further quantified by comparing the energetic separations $\Delta E = E_2 - E_1$ and the ratio of the oscillator strength of the two mutually perpendicular bands O_1/O_2 from the two-component fit and from the simulations; see Table 3.3. The numbers obtained from the fit and the simulations are in excellent agreement. For comparison, the results of the simulations for the angle β are indicated in the experimental histogram, Fig. 3.1(e), by the black lines, confirming the good match between simulation and experiment.

3.4 CONCLUSIONS

For all ZnChl 1 aggregates studied, the fluorescence-excitation spectra can be decomposed into two spectral bands with mutually orthogonal polarization. This is consistent with the organization of the ZnChl 1 monomers in single-wall tubular

ⁱⁱThe linewidths of the two spectral bands that have been used for the simulations, W_1 and W_2 , have been taken from the corresponding experimental spectra.

structures, as found in the AFM and TEM experiments.^[29] However, we find considerable variations between the spectral profiles of individual aggregates. These can be well understood using a tubular homogeneous model with very small variations (a few degrees) in the three angles that define the packing of the molecules within the aggregate. Intuitively, the small variations in the angles ($39.9^\circ \leq \alpha \leq 42.4^\circ$, $48.4^\circ \leq \beta \leq 54.2^\circ$, $9^\circ \leq \gamma \leq 14^\circ$), which cannot be resolved by high-resolution imaging techniques, seem to be acceptable from a chemical point of view to yield aggregates with the same overall morphology, in particular, with the same radius. This is also reflected by the minor variations of the corresponding lattices that underlie the tubular structures (see Fig. 3.6 in the Appendix, Supplementary Information, Note 4) featuring an angle of inclination between the two lattice parameters that ranges from 58.5° to 68.5° . These values are remarkably close to the value of 58° (i.e., $180^\circ - 122^\circ$) that has been proposed for the molecular arrangement of the BChl molecules within the secondary structures of the natural chlorosomes.^[47]

Commonly, details of the molecular packing of the self-assembled aggregates are investigated using molecular modeling. This is a challenging task, not only due to the size of the systems but also due to the need to properly account for weak intermolecular interactions that are responsible for the structural arrangement of the (tubular) assemblies. Furthermore, the potential energy landscapes of supramolecular systems exhibit a high complexity, allowing for kinetic trapping of numerous possible structures. Usually, the modeling of tubular aggregates has been carried out either by a full quantum chemical treatment of relatively small structural models representing cut-outs of the tubular architecture^[48] or by classical force field modeling^[49,50] that allows for the description of substantially larger systems, but it also bears several weaknesses. First of all, standard force fields are often insufficient in the description of metallosupramolecular interactions, in particular, when transition metals are involved.^[51] On the other hand, the outcome of classical modeling is strongly dependent on the parametrization. In this context, the transition metal atoms are particularly challenging for force field parametrization because they may assume different coordination numbers in different environments.

In 1994, an intriguing model based on simple semiempirical AM1 calculations was provided by Holzwarth and Schaffner. In their model, parallel metallosupramolecular stacks were interconnected by hydrogen bonds between the hydroxy and the keto groups, and the tube diameter was a function of the rotational displacement between the individual stacks.^[52] However, this model cannot be reconciled with our data from single-molecule spectroscopy. Therefore, in this work, we employed an efficient quantum chemical methodology based on the semiempirical PM6-D3H4 as well as dispersion-corrected tight-binding density functional theory (DFTB) that has been proven to reliably describe the coordination environment of zinc in biological systems.^[53] Using DFTB, we were able to fully optimize structures of tubular aggre-

gates containing 39 individual ZnChl monomers. This resulted in a structural model that was fundamentally different from those previously considered for the natural counterparts of our ZnChl 1 dyes, i.e., bacteriochlorophyll c, d, e assemblies in the chlorosomes of green (non) sulfur bacteria. Thus, in our model, the dyes are organized in a cyclic array, directed by interactions between the central zinc metal ion and the keto groups (metallo-supramolecular interaction) and dispersion interactions between the tetrapyrrole scaffolds ($\pi - \pi$ interactions). Further, the individual rings are interconnected with each other by hydrogen bonds between the hydroxy and the carbonyl groups of the ester functionalities. In fact, an early infrared study by Krasnovskii and co-workers^[54] indeed considered the ligation of the 13¹ keto group to the central metal ion of the tetrapyrrole ring (there Mg; in our case Zn) but was afterward replaced by models that favored coordination of the hydroxy group to the central metal in either so-called parallel and antiparallel arrangement, as suggested for the first time by Smith and Kerres.^[55]

At the moment, it is not clear whether this newly suggested molecular packing for the ZnChl 1 aggregates is also of relevance for the natural chlorosomes. Yet, it is obvious that for the ZnChl 1 aggregates the distributions of the spectral parameters extracted from the spectra are clearly narrower with respect to the corresponding distributions obtained from the natural chlorosomes.^[43,44] This suggests a more homogeneous supramolecular structure for the synthetic system. Presumably, this reflects that in the synthetic system the type of monomeric building block is perfectly controlled. Thus, it consists of a specific chlorin π -scaffold, a particular solubilizing side chain, and is a single stereoisomer, whereas the various types of BChl c, d, e molecules that are co-self-assembled in the natural chlorosomes are inhomogeneous with regard to the π -core, the side chains, and the stereochemistry at the 3¹ position, giving rise to a more disordered molecular arrangement.^[47] The interpretation that the structural order of the aggregates is closely related to the diversity (or the lack thereof) of the molecular building blocks is supported by data obtained from single chlorosomes from mutated species.^[43,44]

In contrast to what has been found for single natural chlorosomes, the width of the low-energy band exceeds that of the high-energy band for most of the ZnChl 1 aggregates. This cannot be explained by an additional relaxation channel for the higher energetic state, for example, a decay to the low-energy state, because this would yield exactly the opposite result. This finding is a strong indication that the observed bands are still inhomogeneously broadened. Given the soft structure of the assemblies, it is reasonable to consider slight structural variations in the overall arrangement of the ZnChl 1 monomers with respect to the symmetry axis of the overall structure within a single aggregate that are beyond the resolving power of high-resolution imaging microscopies. Further studies will be needed to shed more light on this issue.

Author contributions

A. L., T. K., and M. I. S. R. contributed equally to this work. A. L. conducted single-molecule experiments supervised by J. Köhler, M. I. S. R. performed molecular structure calculations and S. S. performed chemical synthesis supervised by F. Würthner. T. K. performed spectral simulations and theoretical analysis supervised by T. L. C. J. and J. Knoester.

3.5 APPENDIX: SUPPLEMENTARY INFORMATION NOTES

3

3.5.1 Supplementary Note 1: Further distributions of spectral parameters

Figure 3.5: Additional parameters extracted from the polarization-resolved spectra using Lorentzian profiles for fitting the lineshapes: 1) Distributions of the spectral peak positions of the two fitted subbands (red, blue). b) Distributions of the bandwidths (FWHM) of the two subbands (red, blue). c) Distribution of the energetic separations ΔE between the two subbands.

3.5.2 Supplementary Note 2: Spectral simulation method overview

The polarization-resolved spectra were simulated for homogeneous tubular molecular aggregates using as a starting point the orientations of the monomer transition dipole moments as obtained from the molecular modeling. When fitting to the polarization-dependent spectra of individual aggregates, these angles were slightly varied. The eigenstates (exciton states) and energies of the electronic states of the entire aggregates were obtained by diagonalizing a standard Frenkel exciton Hamiltonian using Matlab.^[56] Using the thus obtained exciton energies and corresponding oscillator strengths, a stick spectrum was created based on Fermi's golden rule. For

each single aggregate, the final spectra were then obtained by convolution of the stick spectra with Lorentzian functions with full widths at half maximum (FWHM) that were adjusted manually for best match with the experimental spectra.

3.5.3 Supplementary Note 3: Model Hamiltonian and spectra details

Since we are interested only in the Q_y transition of the ZnChl 1 monomers, each molecule may be represented optically as a two-level system with a ground state and one excited state, separated by an energy $E_{\text{mol}} = \hbar\omega_{\text{mol}}$. The optical transitions of different molecules are coupled by the resonance interactions between their transition dipoles, J_{nm} , leading to the well-known Frenkel exciton Hamiltonian:

$$H = \sum_{\mathbf{n}, \mathbf{m}} H_{\mathbf{nm}} |\mathbf{n}\rangle \langle \mathbf{m}| = \sum_{\mathbf{n}} E_{\text{mol}} |\mathbf{n}\rangle \langle \mathbf{n}| + \sum_{\mathbf{n}, \mathbf{m} \neq \mathbf{n}} J_{\mathbf{nm}} |\mathbf{n}\rangle \langle \mathbf{m}|. \quad (3.6)$$

Here, $|\mathbf{n}\rangle$ is the state with molecule $\mathbf{n}$ excited and all other molecules in their ground state. The dipolar excitation-transfer interaction in point-dipole approximation is expressed as

$$J_{\mathbf{nm}} = \frac{1}{4\pi\epsilon_0\epsilon} \frac{(\boldsymbol{\mu}_{\mathbf{n}} \cdot \boldsymbol{\mu}_{\mathbf{m}}) r_{\mathbf{nm}}^2 - 3(\boldsymbol{\mu}_{\mathbf{n}} \cdot \mathbf{r}_{\mathbf{nm}})(\boldsymbol{\mu}_{\mathbf{m}} \cdot \mathbf{r}_{\mathbf{nm}})}{r_{\mathbf{nm}}^5}, \quad (3.7)$$

where $\boldsymbol{\mu}_{\mathbf{n}(\mathbf{m})}$ is the transition dipole moment of molecule $\mathbf{n}(\mathbf{m})$, $\mathbf{r}_{\mathbf{nm}}$ is the position vector between molecules $\mathbf{n}$ and $\mathbf{m}$, $r_{\mathbf{nm}}$ is its magnitude, ϵ_0 is the vacuum permittivity, and ϵ is the dielectric constant which is taken equal to 1. We restrict ourselves to linear optical properties and consider only one-exciton states, i.e., excited states with in total one excitation quantum. In that case, diagonalization of the $N \times N$ Hamiltonian matrix $H_{\mathbf{nm}}$ (with $N = N_1 N_2$) yields as eigenvalues the exciton energies E_k , while the corresponding eigenvectors $\{a_{k\mathbf{n}}\}$ (normalized to unity) define the exciton wave functions expressed in the site basis:

$$|k\rangle = \sum_{\mathbf{n}} a_{k\mathbf{n}} |\mathbf{n}\rangle. \quad (3.8)$$

The transition dipole from the total ground state (the state in which all molecules are in their ground state) to the exciton state $|k\rangle$ is

$$\boldsymbol{\mu}_k = \sum_{\mathbf{n}} a_{k\mathbf{n}} \boldsymbol{\mu}_{\mathbf{n}}. \quad (3.9)$$

This allows us to express the polarization-resolved fluorescence-excitation spectrum of the aggregate (which is assumed to equal the absorption spectrum) as

$$F(E, \theta) = \frac{1}{\pi} \sum_k |\boldsymbol{\mu}_k \cdot \mathbf{e}|^2 \frac{2W_k}{4(E - E_k)^2 + W_k^2}$$

$$= \sum_k \frac{|\mu_k|^2}{\pi} [\cos(\theta - \phi_k)]^2 \frac{2W_k}{4(E - E_k)^2 + W_k^2} \quad (3.10)$$

where $\mathbf{e}$ is the polarization vector, E is the energy and θ is the polarization of the incident light. ϕ_k is the angle of the projection of the transition dipole vector of the exciton state $|k\rangle$ on to the sample plane relative to the laboratory frame. Given the tubular symmetry of the monomer arrangement, only a few exciton states with their transition dipole moments either parallel or perpendicular to the tubular axis have a finite, non-zero oscillator strength. W_k is the width of the Lorentzian that is used to convolute with the spectral components with parallel and perpendicular polarization.

We connect the results from the simulations with the experimental spectra by assigning all simulated exciton states with their transition dipole moments parallel to the tubular axis to the experimentally observed low-energy band (spectral component 1), and those with their transition dipole moments perpendicular to the tubular axis to the experimental high-energy band (spectral component 2).

3.5.4 Supplementary Note 4: Lattice structures

Upon wrapping onto a cylindrical surface the two-dimensional Bravais lattices shown in Fig. 3.6 yield the tubular structures that reproduce the spectral profiles of aggregates 1-4 analyzed in the main text (Fig. 3.4).

Figure 3.6: Bravais lattices underlying the tubular molecular arrangements that yield the four polarization-resolved fluorescence-excitation spectra shown in Fig. 3.4 of the main text. The magenta arrows represent the molecular transition dipole moments. The lattices have been obtained by unrolling the corresponding tubular arrangement. For each lattice the unit cell parameters are shown next to the grid.

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Chapter 4

Unraveling Intra-Aggregate Structural Disorder using Single-Molecule Spectroscopy

Structural disorder within self-assembled molecular aggregates may have strong effects on their optical functionality. Such disorder, however, is hard to explore using standard ensemble measurements. In this chapter, we report on the characterization of intra-aggregate structural disorder through a linewidth analysis of fluorescence excitation experiments on individual zinc chlorin (ZnChl) nanotubular molecular aggregates. Recent experiments (presented in Chapter 3) suggest an anomaly in the linewidths of the two absorption bands that dominate the spectra: the higher-energy bands on average show a smaller linewidth than the lower-energy bands. This anomaly is explored in this chapter by analyzing and modeling the correlation of the two linewidths for each aggregate. We exploit a Frenkel exciton model to show that the experimentally observed correlation of linewidths and other statistical properties of the single-aggregate spectra can be explained from small variations of the molecular orientations within individual aggregates.

4

4.1 INTRODUCTION

Low-dimensional supramolecular aggregates bridge the gap between single molecules and bulk phases and reveal properties that make them suitable for nanoscale functional materials. Important examples are aggregates formed by dye molecules, which show interesting optical properties, including sharp absorption lines,^[1–3] ultrafast emission,^[4,5] enhanced and anomalous nonlinear optical response,^[6–8] and fast and long-range excitation energy transport.^[9,10] Nature also exploits supramolecular aggregates for specific functions. Well-known biological functions are light-harvesting and transport of electronic excitation energy, performed by photosynthetic antenna systems, which are aggregates of tens to many thousands of biological dye molecules that occur in higher plants, certain bacteria, and algae.^[11–19]

The opto-electronic properties of supramolecular aggregates are highly sensitive to the details of the packing of the molecules because excitation transfer interactions and charge-transfer integrals, which dictate these properties and the underlying collective excited states (excitons), depend sensitively on distances between molecules and their mutual orientations.^[20–23] Consequently, structural disorder in dye aggregates may strongly influence their optical properties and excited state dynamics, such as exciton diffusion. Static disorder in the excitation energies of individual molecules within aggregates (diagonal disorder), imposed by variations in the local environment that are slow compared to the experimentally relevant time scale, has been considered in many studies, both phenomenologically^[24–29] -by comparing spectra of model aggregates with disorder to the experiment- as well as by using more sophisticated methods.^[30–34] This type of disorder leads to localization of the exciton states and affects optical properties such as the optical linewidths, optical nonlinearities, and excitation energy transport.^[7,24,25,35–40] Structural disorder, primarily resulting in variations in the intermolecular interactions, which also ultimately leads to line broadening and altered transport properties, has been studied less frequently.^[25,41]

For functionality, it is of interest to distinguish variation between aggregates (inter-aggregate disorder) and fluctuations within aggregates (intra-aggregate disorder).^[42] For example, in the case of transport properties, static disorder within aggregates is more detrimental than static differences between aggregates. In the extreme case where each individual aggregate is completely homogeneous and only inter-aggregate disorder exists (i.e., certain parameters differ systematically between aggregates), the transport properties within each aggregate will not be hampered by the disorder. In the opposite case where static disorder occurs within aggregates, while on average the aggregates are all the same, the transport properties may be strongly affected by the disorder. Thus, it is important to disentangle what disorder should be attributed to single aggregates (on the time scale relevant to the experi-

ment considered) and what disorder derives from differences between aggregates. For this purpose, the (optical) characterization of individual aggregates is essential.

Fluorescence excitation experiments on individual dye aggregates have been carried out since 1999, both for biological light-harvesting complexes^[12,43] and for synthetic aggregates.^[44] Experiments have revealed strong variations between individual aggregates, even for very large aggregates consisting of many thousands of molecules, where one would expect that optical properties average out over the many internal degrees of freedom.^[44] Recent experiments (presented in Chapter 3) on single semi-synthetic zinc chlorin (ZnChl) aggregates are of particular interest.^[45] These aggregates have a tubular shape with a diameter of a few nm and a length of the order of 100 nm up to several micrometers.^[46] Synthetic tubular molecular aggregates have attracted much attention recently,^[47–59] because they bear an interesting morphological resemblance to the bacteriochlorophyll aggregates that occur in chlorosomes - the highly efficient light-harvesting antennae of green sulfur bacteria.^[43,60–64] In contrast to these natural systems, which consist of mixtures of several types of bacteriochlorophyll molecules and therefore suffer from an inherent large degree of heterogeneity, semi-synthetic ZnChl nanotubes are prepared from chemically identical molecules. Despite this, recent fluorescence excitation experiments on individual ZnChl nanotubes show strong variations between each other. These variations have been explained in terms of relatively small differences in the structure between different aggregates, in particular, from differences of a few degrees in the orientation of the molecules within the aggregate and the helical angle of its structure.^[45] In the analysis reported in Ref. 45 (Chapter 3), based on a Frenkel exciton model, these angles were kept constant within each aggregate and only varied *between* aggregates (inter-aggregate structural disorder). While this analysis yielded good fits of theory to the experiment, it also left questions unanswered: In particular, related to the nature and relative magnitude of the linewidths of the two absorption peaks that occur in these nanotubes. The higher-energy bands on average showed smaller widths than the lower-energy ones, suggesting intra-aggregate inhomogeneity.

In this chapter, we report on a detailed analysis of the linewidth correlation within individual ZnChl aggregates and show that the anomaly can be understood from intra-aggregate disorder, namely, from variation of the molecular orientations *within* individual aggregates. We consider two situations, namely, a segment-like variation of the orientations and a more continuous variation. We show that, in particular, the latter model offers a broad understanding of the statistical properties of the single-aggregate spectra, not only of the linewidth anomaly but also of the distribution of peak positions.

The remainder of this chapter is organized as follows. In Sec. 4.2, we briefly describe the general features of the spectra for single ZnChl nanotubular aggregates, and we present the measured correlation of the widths of both absorption lines

within individual aggregates. Next, in Sec. 4.3, we introduce the Frenkel exciton model used to interpret the experimental data, and we analyze whether or not disorder in each one of the three angles defining the molecular packing can potentially explain the anomaly; moreover, we rule out alternative explanations, such as intra-aggregate diagonal disorder. In Sec. 4.4, we present and discuss our results from spectral simulations for the segment and continuous disorder models and compare them to the experiment. Finally, in Sec. 4.5, we conclude.

4.2 EXPERIMENTAL CORRELATION OF LINEWIDTHS

In Ref. 45 (Chapter 3), polarization dependent fluorescence excitation spectra of individual ZnChl nanotubes were reported. It was found that the spectral properties of individual tubular aggregates varied significantly. A more quantitative analysis revealed that for all nanotubes considered, the spectrum could be interpreted in terms of two dominant optical transitions with mutually perpendicular transition dipoles. This is consistent with having highly delocalized exciton states in tubular aggregates,^[37,38] which have optical selection rules such that there is one superradiant exciton transition with its transition dipole along the tube's axis and two degenerate ones (usually higher in energy than the first transition) with their transition dipoles perpendicular to the axis.^[65] The experiments were further analyzed in terms of a Frenkel exciton model, which revealed that small variations in the molecular orientations between different aggregates could explain the differences in their respective polarization resolved spectra. In this exciton model, the orientation angles were kept identical for all molecules within each tube so that only inter-aggregate disorder was allowed for. This fitting procedure yielded good fits, where the angles had to be varied within small intervals of only a few degrees; the linewidths of the two exciton transitions were used as fit parameters.

Both the two-state fitting procedure (referred to as two-component fit in Chapter 3) and the fits based on a microscopic Frenkel exciton model generally seemed to lead to a smaller linewidth for the higher-energy state than for the lower-energy one, which would be counter-intuitive if one assumes that these widths are homogeneous and lifetime dominated. For lifetime dominated widths, one expects that intraband relaxation leads to larger values for the upper-energy states than the lower-energy ones. We therefore refer to the observation as the linewidth anomaly. The histograms reported in the Supporting Information of Ref. 45 (Supplementary Information, Note 1 in the Appendix of Chapter 3) suggest that indeed this anomaly exists, since the distribution of widths found for the lower-energy exciton states is shifted upward compared to the one for the higher-energy state. A clear proof that

indeed the anomaly is characteristic for nearly all tubes is shown in the correlation plot Fig. 4.1. In Fig. 4.1, each data point represents the linewidths (full width at

Figure 4.1: Correlation between the linewidths of the upper and lower exciton transitions obtained from the two-state fits of the polarization dependent fluorescence excitation spectra on 52 individual nanotubular ZnChl aggregates, as performed in the study reported in Ref. 45 (Chapter 3). Each red dot in the graph specifies the full width at half maximum (FWHM) for the lower (W_-) and higher (W_+) exciton states. The crosses represent the experimental data for the four specific nanotubes analyzed in Ref. 45 (Chapter 3). The black dashed line is the diagonal of the graph, while the red solid line represents the best linear regression of all data points, with a slope of 0.8 and an offset of 21.7 cm^{-1} .

half maximum - FWHM) obtained from the two-state fit for one individual aggregate, with the width of the lower state, W_- , specified along the horizontal axis of the graph and the width of the upper state, W_+ , along the vertical axis. A vast majority of the data points, representing the analysis of the experiments on 52 individual tubes, lie below the diagonal of this graph, clearly establishing the general existence of the anomaly. This implies that homogeneous (lifetime) broadening alone cannot explain the exciton linewidth, leaving us with some source of intra-aggregate disorder. In addition, Fig. 4.1 also reveals a positive correlation between both linewidths, indicated by the red line, which is a least-square regression. The analysis in the remainder of this chapter aims at identifying the source of disorder and quantifying its magnitude.

4.3 EXCITON MODEL AND SOURCE OF DISORDER

4.3.1 Model

The model structure we use for the nanotubular aggregates of ZnChl molecules (monomers) is depicted schematically in Fig. 4.2. It consists of a perpendicular stack

Figure 4.2: (a) Structure of the tubular aggregate, consisting of a perpendicular stack of N_1 rings of radius R , each with N_2 ZnChl molecules, presented by their transition dipoles that are shown as magenta arrows. The distance h between adjacent rings and the helical angle γ over which adjacent rings are rotated relative to each other are indicated, as is the angle β between the molecular transition dipole and the tube's axis. (b) Top view of a single ring, indicating the angle α that further specifies the orientation of the molecular dipole (see text). (c) Structure of the ZnChl monomer with its transition dipole vector represented by the magenta arrow.

of N_1 equidistant rings, on each one of which N_2 equidistant molecules are placed. Each molecule is identified by a position vector $\mathbf{n} = (n_1, n_2)$, where n_1 is the ring on which it resides and n_2 gives the position in the ring. For modeling the optical properties of the nanotube, the relevant molecular optical transition is the Q_y transition, with a transition dipole of magnitude 4.5 Debye pointing diagonally within the porphyrin ring where the optical transition takes place. This transition dipole and the interactions between the dipoles of different molecules govern the collective excited states and optical properties of the nanotube. For this reason, it suffices to represent each molecule by its transition dipole. Hence, for the purpose of modeling its optical properties, the nanotube is characterized by its radius R and the number of molecules per ring, N_2 , by the distance h between two adjacent rings, by the helical angle γ that describes the relative rotation angle between two adjacent rings, and by the orientations of the molecular transition dipoles in the tube. The latter are described by the angle β between the dipole and the tube's axis and the angle α between the projection of the dipole on the plane of the ring relative to the local tangent to the ring (for perfect tubular symmetry, α is the same for all molecules and so is β). All these quantities are indicated in Fig. 4.2. The tube's length $L = N_1 h$ is assumed long enough not to affect its absorption spectrum anymore. This stack of rings representation may be derived from rolling a two-dimensional lattice of molecules on a cylinder of radius R .^[28]

The collective linear optical properties of the aggregate are described by the Frenkel exciton Hamiltonian,

$$H = \sum_{\mathbf{n}, \mathbf{m}} H_{\mathbf{nm}} |\mathbf{n}\rangle \langle \mathbf{m}| = \sum_{\mathbf{n}} E_{\mathbf{n}} |\mathbf{n}\rangle \langle \mathbf{n}| + \sum_{\mathbf{n}, \mathbf{m} \neq \mathbf{n}} J_{\mathbf{nm}} |\mathbf{n}\rangle \langle \mathbf{m}|, \quad (4.1)$$

where $|\mathbf{n}\rangle$ is the state with molecule $\mathbf{n}$ in its Q_y excited state and all other molecules in their ground states, $E_{\mathbf{n}} = \hbar\omega_{\mathbf{n}}$ represents the excitation energy of molecule $\mathbf{n}$, and $J_{\mathbf{nm}}$ is the excitation transfer interaction between the transition dipoles of molecules $\mathbf{n}$ and $\mathbf{m}$. The above Hamiltonian allows for disorder in the transition energies and interactions; possible sources of disorder will be considered below.

The q th eigenvalue (E_q) and eigenvector ($a_{q\mathbf{n}}$) of the matrix $H_{\mathbf{nm}}$ give the energies and site amplitudes, respectively, of the q th exciton state. Assuming that the emission quantum yield does not depend on the emission wavelength, the fluorescence excitation spectrum measured in single-aggregate spectroscopy is identical to the aggregate's absorption spectrum, which reads^[25]

$$I(E) = \sum_q |\boldsymbol{\mu}_q \cdot \mathbf{e}|^2 \frac{\Gamma_q}{(E - E_q)^2 + \Gamma_q^2}, \quad (4.2)$$

where E denotes the photon energy and $\mathbf{e}$ is the polarization direction of the light. Furthermore, $\boldsymbol{\mu}_q = \sum_{\mathbf{n}} a_{q\mathbf{n}} \boldsymbol{\mu}_{\mathbf{n}}$ denotes the transition dipole of the q th exciton state

(μ_n is the transition dipole of molecule n), and Γ_q is its homogeneous linewidth. Note that in this study, we are interested in the spectra of individual aggregates, and hence, in contrast to most other theoretical studies of molecular aggregates, we do not perform an average over disorder realizations.

Before turning to the study of disorder, it is useful to describe the generic shape of the spectrum for the above model. For long tubes, the absorption spectrum shows two bands, one polarized parallel to the axis of the cylinder, deriving from a superradiant state with oscillator strength $N_1 N_2 \cos^2 \beta$ (in units of that of a monomer) and one polarized perpendicular to it, deriving from two degenerate transitions, both with oscillator strength $\frac{1}{2} N_1 N_2 \sin^2 \beta$.^[65] Both bands are redshifted relative to the monomer transition energy (J-bands) and positioned close to the lower-exciton band edge, where (usually) the lowest-energy band is the one polarized parallel to the tube's axis and the higher-energy one is polarized perpendicular to the axis. In the polarization resolved experiments analyzed here, the tubes are lying with their axes parallel to the substrate, and only one of the perpendicular transitions is observed, implying that the ratio of oscillator strengths observed in the perpendicular and parallel direction equals $\frac{1}{2} \tan^2 \beta$. For ZnChl nanotubes, this ratio is of the order of unity^[45] implying an angle β of about 55° (also see Sec. 4.3.2).

4.3.2 Sources of intra-aggregate disorder

As argued in Sec. 4.2, single-aggregate experiments suggest that a certain degree of disorder exists within individual aggregates, in order to explain that the lower-exciton states generally have a larger linewidth than the upper ones. The above model allows for a variety of sources of disorder, for instance, in the molecular transition energies, deriving from random matrix or solvent shifts, and in the interactions, deriving from structural disorder. In this subsection, we investigate what type of disorder, in principle, may explain the linewidth anomaly.

We first consider the possibility of disorder in the molecular transition energies $E_n = \hbar\omega_n$. This is the most commonly considered type of disorder, responsible for exciton localization, a rather weak effect in tubular aggregates.^[37,38] In ensemble spectra, such disorder leads to line broadening, which to some extent is mitigated by exchange narrowing.^[3,25] While probably this type of disorder also plays a role in ZnChl nanotubes, it does not lead to a natural explanation of the linewidth anomaly. The reason is that the upper-energy J band derives from two degenerate transitions, which upon adding disorder would mix and repel each other, leading to stronger line broadening than occurs for the lower-energy J band.^[66] This is the opposite effect of the observed anomaly. For this reason, we do not consider this type of disorder as dominant in the line broadening and will ignore it.

Next, we consider shape variations of the tube. Based on previous results, we

exclude variation of R and N_2 . Electron microscopy and atomic force microscopy images of ZnChl nanotubes reveal that their diameter is very uniform along the tubes,^[46] giving a well-defined radius of $R = 1.68$ nm, and energy minimization of model ZnChl tubes showed that given the radius, N_2 is well-determined at $N_2 = 13$.^[45] We note in passing that, even if variations in N_2 would occur, this would not explain the anomaly because in a tubular aggregate, the position of the transition polarized parallel to its axis generally is much less sensitive to N_2 than the position of the ones polarized perpendicular to it,^[28,55] implying that disorder in N_2 would lead to more broadening of the upper band than the lower band. Another obvious shape variation for tubes is an elliptical deformation. Such deformation would mainly lead to mixing of the two degenerate states contributing to the upper J band,^[67,68] thereby again leading to a stronger broadening for the upper J band than the lower J band, so that it does not explain the anomaly.

Along with fixing N_2 (R), the energy minimization calculations in Ref. 45 (Chapter 3), also set a well-determined value for the inter-ring distance h , namely, $h = 0.67$ nm. However, these calculations did leave a relatively large freedom in the angles α and β that describe the molecular orientations and in the helical angle γ , a freedom that was used in Ref. 45 (Chapter 3) to explain the differences in the polarization resolved spectra between individual tubes, by choosing slightly different sets of angles for each aggregate; within each aggregate, the angles were chosen constant so that in Ref. 45 (Chapter 3), only inter-aggregate disorder was considered. By contrast, here, we will explore the possibility of variation of any of these three angles *within* individual tubes to explain the linewidth anomaly as well as other statistical properties of the spectra of single ZnChl nanotubes. This intra-aggregate orientational disorder will lead to disorder in the interactions J_{nm} . One may also argue that interaction disorder will result in a larger broadening of the higher-energy J band as it also lifts the degeneracy of the two contributing states. However, there is an additional immediate effect on the position of the exciton states because their energies linearly depend on the interactions (e.g., the energy of the totally symmetric exciton state in an ordered aggregate is shifted away from the monomer transition energy by an amount given by the sum of all interactions between one molecule and all the other ones).

In order to assess whether disorder in any one of the parameters α , β , or γ may, in principle, explain the linewidth anomaly, we calculated the dependence of the positions $E_{||}$ and $E_{\perp}$ of the superradiant exciton states polarized parallel and perpendicular, respectively, to the tube's axis for homogeneous aggregates (no disorder) on each one of these parameters individually, while keeping the other two fixed. In this analysis, we used $R = 1.68$ nm, $N_2 = 13$, and $h = 0.67$ nm for the tube's radius, the number of molecules per ring, and the inter-ring distance, respectively, which, as explained above, apply for the ZnChl nanotubes; for the length of the tube, we used

$N_1 = 1000$ rings, which makes the physical length ($N_1 h$) fall inside the typical experimental range^[46] and ensures that the absorption spectrum has reached the long-tube limit. Figure. 4.3 displays the results for aggregates where the base choice for

Figure 4.3: Energies of the superradiant exciton transitions polarized parallel ($E_{\parallel}$, blue solid line) and perpendicular ($E_{\perp}$, red dashed line), respectively, to the tube's axis, calculated for long homogeneous aggregates ($N_1 = 1000$) as a function of the angles α (a), β (b), and γ (c) (see text for details). The other structural parameters were fixed at $R = 1.68 \text{ nm}$, $h = 0.67 \text{ nm}$, and $N_2 = 13$. The transition energy and dipole of a single molecule were taken to be $\hbar\omega_0 = 13939 \text{ cm}^{-1}$, and 4.5 Debye, respectively.^[45]

the parameters is taken identical to their values used to fit the spectra for Aggregate 1 studied in Ref. 45 (Chapter 3), i.e., $\alpha_1 = 39.9^\circ$, $\beta_1 = 54.2^\circ$, and $\gamma_1 = 10.0^\circ$. Thus, in order to study the α dependence of the two exciton positions, β and γ are kept fixed at the values β_1 and γ_1 , respectively, while α is varied over a certain range around α_1 (Fig. 4.3(a)). Similarly, the dependencies on the other two angles are obtained. We found that the effects observed in Fig. 4.3 are generic and are also obtained for other base choices of the three angles, valid for the three other aggregates that were studied in detail in Ref. 45 (Chapter 3).

It is clear from Fig. 4.3 that the dependencies of the optically dominant exciton transitions on both β and γ are roughly equally strong, implying that intra-aggregate disorder in these angles would not lead to more line broadening for the lower-energy transition than for the higher-energy one. By contrast, Fig. 4.3(a) clearly shows that the parallel transitions (which for most parameter values are the lower-energy one) are more sensitive to α than the perpendicular one. As a result, intra-aggregate disorder in α would typically lead to larger broadening for the lower-energy transition and, thus, may explain the linewidth anomaly. In Sec. 4.4, we will present numerical results for the spectra of individual tubular aggregates accounting for intra-aggregate disorder in the molecular orientations and explore to what extent this may explain the magnitude of the anomaly as well as other statistical properties of the

spectra.

4.4 RESULTS

We simulated single-aggregate absorption spectra for two models of disorder in the angle α . In all calculations, we used the following fixed structural parameters, appropriate for ZnChl nanotubes:^[45] $R = 1.68$ nm for the tube's radius, $N_2 = 13$ for the number of molecules per ring, and $h = 0.67$ nm for the inter-ring distance (see also Sec. 4.3.2); furthermore, we set all molecular transition energies equal to $E_n = \hbar\omega_n = \hbar\omega_0 = 13939$ cm⁻¹. The transfer interactions J_{nm} were calculated from the electrostatic interaction between the transition dipoles of the two molecules considered, with magnitudes 4.5 Debye and directions imposed by the molecular positions in the tube and the orientations as given by α and β . The angles α , β , and γ , or their disorder distributions, will be specified below. The tube's length N_1 considered depends on the disorder model, as will be explained below. Finally, the homogeneous linewidth for all exciton transitions was (unless indicated otherwise) taken to be $\Gamma_q = 50$ cm⁻¹; no experimental information is available for this parameter.

4.4.1 Two models of disorder

Two different ways were considered to account for the disorder in the molecular orientations. In the first model, each aggregate is considered as a collection of non-interacting segments of different lengths that only differ in the particular value for α that applies to the entire segment; the values for the angles β and γ are taken equal for all segments within one aggregate, i.e., no intra-aggregate disorder was included in these angles. Each segment is assumed long enough so that their exciton transition energies have saturated, i.e., have tended toward the infinite-tube values. Segment (or domain) models of disorder have been used in various studies.^[69–71] Here, the strength of this model lies in its simplicity and the fact that it allows for direct simulation of the experimental spectra of individual aggregates with relative ease. In the segment model, the disorder realization of each individual aggregate is characterized by a histogram that indicates for each α interval the fraction of rings in the aggregate in which the molecules have an orientation characterized by an α value that falls within this interval (in other words, the histogram counts the added lengths of all segments that have an α value within this interval). For a particular aggregate whose experimental polarization resolved fluorescence excitation spectrum was measured, the specific realization of the disorder histogram that characterizes the aggregate can be obtained by adjusting the heights of the histogram in each α bin such that the calculated spectrum agrees with the experiment. This procedure is

explained in more detail in Sec. 4.4.2 and used to fit the spectra of the four particular aggregates also studied in more detail in Ref. 45 (Chapter 3).

In the second disorder model, we allow for a continuous variation of α along the tube. Particularly, we will assume that α is constant within each ring but varies along the tube with a specific correlation length, by taking the α values for all rings from the correlated multivariate Gaussian distribution,

$$P(\alpha_1, \dots, \alpha_{N_1}) = ((2\pi)^{N_1} \det(C))^{-\frac{1}{2}} \exp \left[-\frac{1}{2} \sum_{n,m=1}^{N_1} (C^{-1})_{nm} (\alpha_n - \langle \alpha \rangle) (\alpha_m - \langle \alpha \rangle) \right]. \quad (4.3)$$

Here, α_n denotes the angle α in the n th ring, $\langle \alpha \rangle$ is the mean α value, which is equal for all rings and all aggregates, and C is the covariance matrix with matrix elements,

$$C_{nm} = \sigma_\alpha^2 \exp(-|n - m|/L_c), \quad (4.4)$$

where σ_α denotes the standard deviation of the disorder and L_c denotes the correlation length of the disorder in units of the number of rings. For this disorder model, rather than trying to fit individual spectra, we analyzed the statistical properties of the simulated spectra of individual disordered aggregates, such as the correlation plots for the two linewidths (see Fig. 4.1) and histograms for the linewidths and peak positions, and compared those to the experiment. We discovered that in order to get good comparison with the experiment, a model including only disorder in α does not suffice (see Sec. 4.4.3) and we also have to include disorder in the second angle that describes the molecular orientations, β . In this extended model, we use a similar correlated distribution as Eq. (4.3) for the angles β_n , with mean $\langle \beta \rangle$ and standard deviation σ_β . The correlation length for this distribution is assumed to be the same L_c as for the α distribution.

4.4.2 Results for segment model

Using the segment disorder model described above, the measured polarization dependent spectra of four individual tubes were fitted. Out of the 52 spectra of single tubes available from the study reported in Ref. 45 (Chapter 3), we selected the four that were also studied in more detail in that publication (Chapter 3), because they span much of the variation of the 52 experimental spectra. We refer to these aggregates as Aggregate 1 up to Aggregate 4, in the same way as was done in Ref. 45 (Chapter 3). All four aggregates exhibit the linewidth anomaly, as is evident from their positions in the linewidth correlation plot of Fig. 4.1, indicated by the crosses. The measured polarization dependent spectra for these aggregates are shown in Fig. 4.4, left column.

Figure 4.4: Left column: Fluorescence excitation spectra of four different ZnChl aggregates as a function of polarization angle of the exciting light on the substrate on which the tubular aggregates lie (tubes' axes lie in the plane of the substrate) reported in Ref. 45 (Chapter 3); the cyan solid line indicates the polarization angle at which the low-energy spectral peak reaches its maximum height; the orange dashed line is shifted over 90° relative to the cyan one. Middle column: Spectra obtained at the cross sections indicated by the cyan and orange lines in the left column, together with the best fits (dashed thin lines) obtained for these two polarization angles using the segment model of disorder in the angle α . Right column: The histograms for the distribution of α that give the spectral fits in the middle column, binned per degree. The parameters used in the calculations are given at the start of Sec. 4.4; the length of the tubes is not fixed in the segment model (see text).

The fit procedure was as follows. We first generated a library of theoretical absorption spectra for light polarized parallel and perpendicular to the tube's axis, $I_{\text{theory}}^{\parallel}(\alpha_i, E)$ and $I_{\text{theory}}^{\perp}(\alpha_i, E)$, respectively, for homogeneous tubes with $\alpha = \alpha_i$ varying in steps of 0.1° between 30° and 50° , a range that widely covers all α values required in Ref. 45 (Chapter 3) to fit the spectra without disorder. Here, as above, E denotes the photon energy of the exciting field. When creating this library, we used a constant length of $N_1 = 1000$ for the homogeneous tube. This value does not indicate the length of individual segments; it is used to ensure that the spectra in the library have reached the long-tube limit, where we assume that individual segments are long enough for this limit to apply. For a single aggregate with a particular realization of segment disorder, the theoretical spectrum in both polarization directions is obtained by averaging the respective spectra for different α_i values weighted by their occurrence c_i^2 in that realization, which is characterized by the histogram for the α disorder realization defined in Sec. 4.4.1 (i.e., c_i^2 is the height of the histogram in the i th bin). We note that in the segment model, the total tube length is not fixed; only the relative weights c_i^2 are.

The optimal set of weights c_i^2 for a particular aggregate studied in the experiment was determined by requiring the best simultaneous fits to its experimental spectrum $I_{\text{experiment}}^{\parallel}(E)$ for the polarization angle at which the lower-energy peak (with parallel polarization) reaches its maximum and to the experimental spectrum $I_{\text{experiment}}^{\perp}(E)$ for a polarization angle that is shifted over 90° relative to the first angle. In the experimental spectra in Fig. 4.4, these two polarization angles are indicated by the cyan and orange lines, respectively. This simultaneous optimization is reached by minimizing the error, defined as

$$\epsilon = \sum_{i,j,s} \left(c_i^2 I_{\text{theory}}^s(\alpha_i, E_j) - I_{\text{experiment}}^s(E_j) \right)^2, \quad (4.5)$$

where j labels the discretized set of energies and s labels the two polarization directions. The minimization of the error was performed using the “fminsearch” command of MATLAB, which is a multidimensional unconstrained nonlinear minimization derivative-free method.^[72] We note that in these calculations, the angles β and γ for each one of the four aggregates considered were taken identical to those that generated the best fits in Ref. 45 (Chapter 3); see Table 4.1.

The results for the fits for the four selected aggregates are displayed in the center column of Fig. 4.4, for both polarization directions. The right column of Fig. 4.4 displays the histogram of the α values that characterizes the disorder realization underlying the best fit, and Table 4.1 presents the mean $\langle \alpha \rangle$ and standard deviation σ_α characterizing this histogram for each one of the four aggregates.

Clearly, the segment model yields excellent fits for all four aggregates considered.

Table 4.1: Mean values of α and the standard deviation σ_α in this angle obtained from the histograms in the right column of Fig. 4.4, together with the values of β and γ used to fit the spectra of Aggregates 1 to 4. In the last column, the fixed value of α is shown that was used to analyze the data for each one of the four aggregates in Ref. 45 (Chapter 3) without intra-aggregate disorder.

Aggregate	$\langle\alpha\rangle$	σ_α	β	γ	α [Ref. 45 (Chapter 3)]
1	40.6°	4.5°	54.2°	10.0°	39.9°
2	41.3°	3.9°	52.4°	9.0°	41.5°
3	39.9°	4.8°	48.4°	14.0°	40.5°
4	41.6°	4.4°	51.2°	10.5°	42.4°

Since these four aggregates were selected to span the variation of most of the 52 experimental spectra observed in Ref. 45 (Chapter 3), we are confident that any of those experimental spectra can be fitted using this model. The histograms show that the α distribution that fits each one of the spectra best has a standard deviation of a few degrees and a mean value that is very close to the α value that gave the best model fits without intra-aggregate disorder (last column in Table 4.1).^[45] The advantage of the current approach over the one in Ref. 45 (Chapter 3), is that it offers an explanation of the linewidth anomaly in terms of a narrow disorder distribution in the molecular orientations, as is evident from the quality of the fits of both absorption lines. The fact that such small amounts of disorder in α may explain the anomaly is rooted in the much stronger α dependence of the lower-exciton energy than the higher-energy one, as depicted in Fig. 4.3(a).

4.4.3 Results for continuous disorder model

Above, we found excellent fits to the single-tube spectra using a segment model of disorder in the angle α . It should be realized that the quality of the fits is made possible not only by the fact that disorder in α gives a larger linewidth to the lower-energy band but also because a large set of parameters (the weights c_i^2) may be varied to obtain the fits. We also note that these fits require many segments to be present in a single tube, implying that they may only be obtained for tubes containing many thousands of rings, which may go beyond the typical aggregate length in the experiment or the area of the (diffraction-limited) focus of the excitation light. Of course, a strictly segmented realization of the disorder, while appealing in its simplicity and facilitating finding disorder realizations that fit individual spectra, is only one limit of the more general way of introducing correlated continuous disorder in the aggregates.^[70] For these reasons, in this section, we explore the more advanced model

with continuous disorder in the molecular orientations, presented in Sec. 4.4.1.

Using the continuous disorder model, we calculated absorption spectra for a large number of individual tubular aggregates, each spectrum separated in polarization directions parallel and perpendicular to the tube's axis, respectively. In these calculations, the parameters N_2 , R , h , $\hbar\omega_0$, and Γ_q were taken as above, as was the magnitude of the molecular transition dipoles (see start of Sec. 4.4). The length of each tube was set to $N_1 = 1000$ rings, which corresponds to 670 nm and falls in the experimental length range of 100 nanometers to several micrometers.^[46] For each aggregate, we generated a realization of the disorder in α by drawing correlated random values from the distribution Eq. (4.3) and similarly for the angles β . For the aggregate length considered and the disorder strengths σ_α and σ_β that turn out to be relevant (see below), the spectra of individual tubes in both polarization directions show a main peak with minor substructure. We characterized the simulated spectra by the positions E_- and E_+ of the lower- and higher-energy main peaks, respectively (polarized along and perpendicular to the tube's axis), as well as the separation ΔE between both peaks. Moreover, we also obtained the linewidths (FWHM) of both peaks as W_- and W_+ .

Rather than trying to find the realizations of continuous disorder that happen to generate theoretical spectra that match observed spectra of single nanotubes (which, as opposed to the segment model, would be a practically impossible job in the current model), we compared the statistical properties of the simulated spectra to the statistics found in the experiment. In particular, we used the mean values $\langle\alpha\rangle$ and $\langle\beta\rangle$, the standard deviations σ_α and σ_β , the correlation length L_c , and the value of the fixed helical angle γ as free parameters to obtain a good match between theory and experiment for the linewidth correlation plot of Fig. 4.1 and for the distributions of W_- , W_+ , E_- , E_+ , and ΔE (the latter five distributions were all reported in Ref. 45 (Chapter 3)). Given the limited experimental statistics, determined by the number (52) of tubes for which the spectra were measured, we have not aimed at minimizing a rigorously defined error in the global comparison between the theoretical and experimental statistical properties but instead have judged by eye and from their mean values and standard deviations to what extent the various distributions match.

From our calculations, we found that the phenomenon of the anomalous linewidth correlation can be qualitatively explained using only continuous disorder in α (i.e., setting the angle β to a fixed value), but the linear regression of the theoretical data points always has a significantly smaller slope than the one for the experimental points in Fig. 4.1, even if we try to tune this plot by using different homogeneous linewidths Γ_q for the lower- and higher-energy exciton transitions. The closest to a good agreement between the theoretical and experimental statistics is shown in Fig. 4.5 and was obtained for parameters quoted in the caption, where we had to adjust Γ_q as indicated in the caption in order to reach this level of agreement. We

Figure 4.5: Comparison between theory (blue) and experiment (red) for the linewidth correlation plot and the distributions for W_- , W_+ , E_- , E_+ , and ΔE including continuous disorder in α only. The experimental data for the latter five distributions are taken from Ref. 45 (Chapter 3). The panel for the correlation plot also gives the best linear regressions through the experimental and theoretical data points, with the corresponding slopes and offsets; the other panels give the mean values and standard deviations for the experimental and theoretical distributions. For the calculations, we used $\langle \alpha \rangle = 41.1^\circ$, $\sigma_\alpha = 2.5^\circ$, and $L_c = 70$ rings. The angles β and γ were set to fixed values of 51.6° and 10.9° , respectively, being the averages of the values for these angles used to fit the spectra for aggregates 1 - 4 in Ref. 45 (Chapter 3). All other parameters were chosen as indicated at the start of Sec. 4.4, except for the homogeneous linewidths, for which we used $\Gamma_- = 80 \text{ cm}^{-1}$ for transitions with polarization parallel to the tube's axis and $\Gamma_+ = 100 \text{ cm}^{-1}$ for the perpendicular transitions. The length of the simulated aggregates was set to $N_1 = 1000$ rings (see text).

observe that most of the histograms in Fig. 4.5 give a reasonable to very good match between theory and experiment, with most discrepancy observed for the W_+ and the ΔE distributions. We clearly see, however, that within this model the linewidth correlation has much too small a slope, which, in fact, implies that the effect of disorder in α is overestimated; thus, σ_α should be reduced, but then, another source of disorder has to be introduced in order to match the standard deviations of the

distributions for the individual linewidths W_- and W_+ to the experiment.

To repair the above deficiencies of the model, we have introduced disorder in β as well, which is physically plausible to occur, as it is the other angle characterizing the molecular dipole orientations. Figure 4.3 demonstrates that this will not affect the linewidth anomaly, as both upper and lower exciton energies depend about equally strong on β . It will add additional width contributions to both spectral peaks, however, which is what we need if we lower σ_α . Figure 4.6 gives the comparison between

Figure 4.6: Comparison between theory (blue) and experiment (red) for the linewidth correlation plot and the distributions for W_- , W_+ , E_- , E_+ , and ΔE , allowing for continuous disorder in α and β . The experimental data for the latter five distributions are taken from Ref. 45 (Chapter 3). The panel for the correlation plot also gives the best linear regressions through the experimental and theoretical data points, with the corresponding slopes and offsets; the other panels give the mean values and standard deviations for the experimental and theoretical distributions. For the calculations, we used $\langle \alpha \rangle = 42.2^\circ$, $\sigma_\alpha = 1.0^\circ$, $\langle \beta \rangle = 52.7^\circ$, $\sigma_\beta = 2.0^\circ$, and $L_c = 40$ rings. The angle γ was set to the fixed value of 7.1° . All other parameters were chosen as indicated at the start of Sec. 4.4; the homogeneous width of all exciton transitions was taken to be $\Gamma_q = 50$ cm $^{-1}$. The length of the simulated aggregates was set to $N_1 = 1000$ rings (see text).

theory and experiment for the system parameters that result in the best agreement.

To achieve this, we had to lower σ_α to 1.0° , while the disorder in β was taken to be $\sigma_\beta = 2.0^\circ$, both with a correlation length of $L_c = 40$ rings. The helical angle was taken $\gamma = 7.1^\circ$ in order to match the average of the theoretical distributions of both peak positions to those obtained from the experiment; the precise choice of γ within margins of up to the order of 10° hardly affects the width of the distributions of the positions and the statistics of the spectral widths.

We observe that with the exception of the distribution of ΔE , all panels in Fig. 4.6 show a good agreement between theory and experiment. In particular, we note that the linewidth anomaly is now not only recovered qualitatively but also quantitatively: The linear regression of the theoretical data points shows a good agreement with that of the experimental data. The theoretical and experimental distributions of the peak positions and linewidths are also in good agreement, as is also clear from their mean values and standard deviations given in the insets. However, the distribution for the energy difference ΔE between both spectra peaks is not correctly recovered in this model; in particular, its width is strongly underestimated. As the separate distributions for both peak positions, E_- and E_+ , are fitted very well, this implies that in the current model the correlation between both peak positions is overestimated. Stronger disorder in the angle α would partially undo this correlation, as is clear from the ΔE distribution in Fig. 4.5, but that generates other disagreements, as we have seen.

It is conceivable that besides the intra-aggregate disorder modeled here, there is also an inter-aggregate disorder component, for instance, the mean value $\langle\alpha\rangle$ may vary between aggregates. This would not change the linewidths for the individual tubes and, hence, not change their distributions and correlation plot, but it would affect the positions (mainly E_-) and, in particular, would broaden the ΔE distribution. Combining the information from Figs. 4.5 and 4.6, it appears that such additional inter-aggregate disorder in α would have to have a standard deviation in the order of 1.0° - 1.5° to recover the experimental ΔE distribution; however, its inclusion would require fine-tuning other parameters again. We have not attempted to carry this idea further by doing actual simulations including inter-aggregate disorder, as it would require finding the optimum in an even wider range of free parameters; if one allows for inter-aggregate disorder in α , there is no reason not to allow for it in β .

We have tested the sensitivity of fitting the experimentally observed statistical properties to the model parameters characterizing the disorder (namely, the mean values $\langle\alpha\rangle$ and $\langle\beta\rangle$, the standard deviations σ_α and σ_β , and the correlation length L_c), by repeating simulations for a variety of combinations of values for these parameters. To give an impression of this sensitivity, we present in the Appendix (Supplementary Information, Note 1) an overview of changes in the statistical properties when changing, in particular, σ_α , σ_β , and L_c around their optimal values that led

to the fits displayed in Fig. 4.6. We note that for several separate quantities, better agreement to experiment is, in fact, possible by changing one of the disorder parameters, but that such a change inevitably deteriorates the quality of the fit of one of the other quantities even more.

To end this section, we note that in the experiment, also an effective distribution for the angle β was also obtained through the ratio of the oscillator strengths in both peaks (see end of Sec. 4.3.1).^[45] The standard deviation of that distribution was found to be 4.3° , which is about twice as big as the one we used to get the fits in Fig. 4.6. This discrepancy could be another effect of inter-aggregate disorder (in β) but could also result from the fact that the tubes in the experiment may be bent,^[46] which affects the ratio of oscillator strengths in both peaks.

4

4.5 CONCLUSIONS

In this chapter, we have studied the occurrence of disorder within nanotubular self-assembled ZnChl aggregates. As experimental markers for disorder, we have used the statistical properties of the two optical bands that characterize these aggregates as obtained from polarization resolved fluorescence excitation experiments on single nanotubes. These experiments reveal that the lower-energy exciton band of single nanotubes typically has a larger width than the upper exciton band, which indicates that this width is not determined by homogeneous (lifetime) broadening only and must be caused at least, in part, by inhomogeneous broadening (disorder) within each aggregate. By modeling the spectra using numerical simulations, we have shown that small disorder (a few degrees) in the orientations of individual molecules within the aggregate may explain the observed correlation between both linewidths quantitatively.

To interpret the experiments, we have used two models of orientational disorder. In the first model, the orientations were assumed constant within finite but long segments of the aggregate. By adjusting the occurrence of segments with particular orientations, we were able to generate excellent fits of the experimental polarization resolved spectra of individual nanotubes. The quality of the fits is, *inter alia*, made possible by the very large amount of freedom to vary parameters in this model. In a more advanced model, we allowed for continuous variation of the molecular orientations within the aggregate, with a certain standard deviation and correlation length. We demonstrated that small orientational disorder (order 2°) correlated over several tens of nm may not only explain the linewidth correlation but also explain other statistical properties of the spectra obtained from the experiment, such as the distributions of peak positions and linewidths. Within the model used, the width of the distribution of energy separations between both peaks is significantly underes-

timated; we have argued that this may result from inter-aggregate disorder, which was not taken into account.

The importance of this work lies in the realization that single-aggregate experiments in combination with systematic exciton modeling may be used to disentangle sources of disorder in and between different aggregates, whose markers would get lost in ensemble spectroscopies,^[73,74] which cannot be resolved by high-resolution imaging techniques such as AFM or electron microscopy. The conclusion that the aggregates studied suffer from disorder in the molecular orientations of the order of a few degrees is physically plausible. Indeed, molecular dynamics simulations of other dye aggregates have revealed that such disorder may easily occur.^[32,34] It is interesting that polarization resolved single-aggregate experiments are sensitive to such small variations, which shows the power of this technique in unraveling the molecular basis for the functional properties of large aggregates.

We express caution, though, that our model results should not be overinterpreted as they still are limited by the sources of disorder considered. For instance, we have not included energy disorder in our model because, as we argued, the linewidth correlation strongly suggests that orientational disorder must be a dominant factor to explain it; at the same time, energy disorder caused by random solvent shifts generally plays a role in molecular aggregates. In addition, as mentioned, we did not include inter-aggregate disorder, for instance, by allowing the mean values of the orientational distributions to differ between aggregates. Of course, including all possible sources of intra- and inter-aggregate disorder would generate more freedom to improve the fits, but would be a formidable job to explore systematically, and its value would be restricted by the fact that the experimentally available data obtained from several tens of aggregates, then, may become a limiting factor to draw solid conclusions. This points out the importance of future experimental and theoretical steps to further improve the perspective of a full molecular-scale understanding of the properties of molecular aggregates. On the theoretical side, also a first-principle type of analysis of molecular packing and disorder could add important input for the phenomenological approach used here.^[34,63]

4.6 APPENDIX: SUPPLEMENTARY INFORMATION NOTES

4.6.1 Supplementary Note 1: Sensitivity of statistical properties to the model parameters

Table 4.2 shows the sensitivity of the statistical properties of the simulated spectra for the model whose results are presented in Fig. 4.6, to the parameters that characterize the intra-aggregate disorder, namely, σ_α , σ_β , and L_c .

Table 4.2: *Presentation of the statistical properties of spectra simulated using the continuous disorder model when varying the three model parameters σ_α , σ_β , and L_c around their optimal values that generated the fits in Fig. 4.6. The first column names the statistical property considered (where μ indicates its mean and σ its standard deviation; Slope_W is the slope of the linear regression of the linewidth correlation plot, and W_+ intercept its intercept), the second column presents the experimental value, the third column shows the value obtained in the optimal fit of Fig. 4.6 (where $\sigma_\alpha = 1^\circ$, $\sigma_\beta = 2^\circ$, and $L_c = 40$ rings), and the remaining columns display the variations when changing the model parameters characterizing the disorder as indicated above each column. In all cases displayed, only one parameter was changed at a time (for instance, in the column where σ_α is varied, the results are quoted keeping σ_β and L_c at their optimal values). The full search for the optimal fit was not restricted to only changing one model parameter at a time.*

Statistical Properties	Experiment	Best Fit	σ_α [degree]		σ_β [degree]		L_c [rings]	
			0.5	1.5	1.5	2.5	20	60
Slope_W	0.8	0.72	0.87	0.62	0.75	0.59	0.63	0.72
W_+ intercept [cm^{-1}]	21.7	39.9	12.3	61.2	22.6	82.1	50.4	38.8
μ_{W_-} [cm^{-1}]	231.7	230.9	197.2	264.6	201	259.4	225.8	237.6
σ_{W_-} [cm^{-1}]	47.5	51.9	38.3	61.9	40.8	61.2	42.1	60.3
μ_{W_+} [cm^{-1}]	206.6	206	183.3	226.2	172.7	236.2	192.5	209
σ_{W_+} [cm^{-1}]	46.1	45.8	39.1	51.8	35.8	55.5	36.7	52.9
μ_{E_-} [cm^{-1}]	13610.8	13614.4	13616.2	13612.7	13618.3	13610	13616.1	13613.4
σ_{E_-} [cm^{-1}]	20.1	26.3	21.6	31	22.1	30.4	18.8	32
μ_{E_+} [cm^{-1}]	13649.5	13661.2	13660.7	13661.7	13660.3	13662.5	13662.7	13660.1
σ_{E_+} [cm^{-1}]	18.4	23.2	20.2	26.1	18.9	27.4	16.6	28.3
$\mu_{\Delta E}$ [cm^{-1}]	38.8	46.8	44.6	49	42.1	52.5	46.6	46.6
$\sigma_{\Delta E}$ [cm^{-1}]	14.9	4.6	3.2	6.2	3.8	5.7	3.2	5.5

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Chapter 5

Probing Size Variations of Molecular Aggregates inside Chlorosomes using Single-Object Spectroscopy

We theoretically investigate the possibility to use single-object spectroscopy to probe size variations of the bacteriochlorophyll aggregates inside chlorosomes. Chlorosomes are the light-harvesting organelles of green sulfur and non-sulfur bacteria. They are known to be the most efficient light-harvesting systems in nature. Key to this efficiency is the organization of bacteriochlorophyll molecules in large self-assembled aggregates that define the secondary structure inside the chlorosomes. Many studies have been reported to elucidate the morphology of these aggregates and the molecular packing inside them. It is widely believed that tubular aggregates play an important role. Because the size (radius and length) of these aggregates affects the optical and excitation energy transport properties, it is of interest to be able to probe these quantities inside chlorosomes. We show that a combination of single-chlorosome linear polarization resolved spectroscopy and single-chlorosome circular dichroism spectroscopy may be used to access the typical size of the tubular aggregates within a chlorosome and, thus, probe possible variations between individual chlorosomes that may result, for instance, from different stages in growth or different growth conditions.

5.1 INTRODUCTION

Photosynthesis is one of the most important processes to sustain life on earth. The biomolecular systems and mechanisms that underlie photosynthesis have been the subject of many studies, which not only serve fundamental interest but also are sources of inspiration for technological applications.^[1–6] Investigations of the initial absorption of sunlight in natural light-harvesting systems and the subsequent excitation energy transport to photosynthetic reaction centers guide the selection and design of synthetic supramolecular materials that mimic these functions.^[7–9] Among the natural light-harvesting systems, the chlorosome, which is the antenna system of green sulfur and non-sulfur bacteria, has attracted particular attention. It owes this interest to the fact that it is the most efficient light-harvesting system known in nature^[10,11] and that in contrast to other light-harvesting systems,^[10,12] it contains molecular aggregates that are self-assemblies of only bacteriochlorophyll (BChl) molecules, i.e., they lack complicated protein scaffolds to position the chromophores.^[13] Self-assembled systems of dye molecules are much easier to mimic in laboratories than structures prepared by careful positioning using proteins.^[4,14,15]

Chlorosomes are elongated organelles that contain several tens of self-assembled supramolecular aggregates, each composed of thousands of BChl c, d, and e molecules.^[16–22] The supramolecular organization of BChl molecules in these aggregates, which is of crucial importance for the light-harvesting efficiency, is still a subject of ongoing debate. Many previous studies have led to the proposal of tubular, lamellar, and rolled lamellar structures for the self-assembled aggregates.^[6,13,22–29] These shapes and the molecular packing in the aggregates have been obtained through the combined use of mutagenesis, solid-state nuclear magnetic resonance (NMR), cryogenic electron microscopy (Cryo-EM), single chlorosome linear polarization resolved fluorescence excitation spectroscopic studies, and molecular modeling.^[6,24–26,30,31] The debates about the exact structure may be explained from the fact that the aggregate formation depends on the bacterial strain used and the precise growth conditions. Moreover, the hierarchical structure is prone to heterogeneity, which complicates finding a unique organization. First, structural disorder occurs inside each aggregate because different BChl molecules (c, d, and e), each of which can further vary in their state of methylation, are randomly used in the aggregation process. Second, variations in size of the aggregates may occur within and between individual chlorosomes.

In this study, we investigate theoretically to what extent size variation of the constituent BChl aggregates in different chlorosomes can be probed using single-chlorosome spectroscopy. We adopt the picture that the dominant secondary structural elements inside the chlorosomes are tubular aggregates, which may differ in radius and length. It is known from previous studies that the optical and energy

transport properties of (tubular) aggregates not only depend on the molecular packing (intermolecular distances and orientations)^[15,32–36] but may also depend on the aggregate radius and the length. In particular, the isotropic absorption and linear dichroism (LD) spectra of tubular aggregates were shown to depend on the radius,^[32,37,38] while it has been suggested that the circular dichroism (CD) spectrum of tubular aggregates is sensitive to their length up to rather long lengths.^[39–41] Furthermore, the exciton diffusion constant is sensitive to the ratio of the exciton delocalization length and the radius,^[42] where the delocalization length itself also shows a dependence on both the radius and the length.^[43] All this makes it of interest to investigate how variations in the radius and length of tubular aggregates in different chlorosomes influence light-harvesting properties and whether such variations may be probed experimentally.

To study variations between chlorosomes, the application of single-molecule spectroscopy is indispensable.^[44–47] Since chlorosomes contain many thousands of molecules, we rather refer to the application of this type of spectroscopy to chlorosomes as single-object spectroscopy. Prior studies have applied single-object linear polarization (SOLP) resolved fluorescence excitation spectroscopy to individual chlorosomes, in which fluorescence excitation spectra for different linear polarization directions of the exciting light are recorded; hereafter, we refer to this as SOLP spectroscopy. SOLP spectroscopy gives much more information than LD spectroscopy, which measures the difference in the absorption spectra for two perpendicular polarization directions on an ensemble of oriented objects (molecules, aggregates, and nanostructures).^[48] The SOLP studies of chlorosomes from the wild-type and two mutant species of *Chlorobaculum tepidum* bacteria were consistent with a tubular geometry of the BChl aggregates for the mutants and the majority of the wild-type chlorosomes.^[30,49] They showed an energy difference between two mutually perpendicular exciton transitions in tubular aggregates, which varied between different chlorosomes. Inspired by earlier work,^[32] these variations were interpreted in terms of variations in the average radii of the tubular aggregates in different chlorosomes.^[49] In these studies, a possible length variation of the aggregates was not considered, as the length generally has a much more limited effect on the linear-polarization dependent spectroscopy of tubular aggregates.^[39,43]

Motivated by previous reports that CD spectroscopy may show an interesting and prolonged dependence on the length of tubular aggregates,^[39–41] this study investigates whether single-object CD spectroscopy (SOCD spectroscopy), in combination with SOLP spectroscopy, may be sensitive to variations in (average) length as well as (average) radius of the constituent tubular aggregates between different chlorosomes. Many CD studies have been reported on ensembles of chlorosomes,^[13,50–55] but thus far only one study has reported CD spectra of single chlorosomes, and in that case, the CD strength was only measured at one frequency.^[56]

More generally, SOCD studies are scarce, although some results have been reported for single molecules^[57–60] and others for individual nano-structures,^[61–63] showing that, in principle, the sensitivity required for SOCD spectroscopy can be achieved. To the best of our knowledge, the theory of SOCD spectroscopy was not developed.

We first study the simplest situation, assuming that the radius of the tubular aggregates is the same for all aggregates in all chlorosomes. For definiteness, we use the average radius derived from SOLP experiments on chlorosomes of the *bchR* mutant of *Chlorobaculum tepidum* bacteria;^[49] in addition, the molecular packing derived in that study is used as the basis for our model calculations. We model SOCD as well as SOLP spectra for this situation. From this, we find that the SOCD spectra may indeed probe differences in aggregate length between individual chlorosomes. Ideally, the experiment should measure these spectra as a function of the angle between the wave vector of the exciting light and the tubular axes; if variation of this angle is not possible, the optimal setup is to use 45° for this angle. We observe that these findings are still valid even when we allow for a distribution of aggregate lengths within individual chlorosomes. In that case, SOCD spectroscopy is able to probe differences in the average aggregate length realized for different chlorosomes because the shape of the spectrum turns out to be sensitive to the average length. We also show that the shape of the SOLP spectra has a much weaker length dependence, making it very hard to retrieve length information from SOLP spectroscopy alone.

In the next step of our study, we allow for variations in length as well as radius of the aggregates between chlorosomes. We find that, generally, it is not possible to retrieve the aggregate radius that applies to a particular chlorosome uniquely from SOLP experiments because the energy difference between the two mutually perpendicular transitions also turns out to depend on the aggregate length. However, our results show that for a given value of this energy separation, the combination of SOLP and SOCD spectroscopy, together with spectral modeling, gives sufficient information to probe what combination of length and radius applies to the aggregates within a particular chlorosome. Like in the first part of our study, we show that this conclusion still holds for the more realistic situation where the length and the radius of ~ 50 aggregates within a chlorosome do not all have the same value but are taken randomly from particular distributions. In that case, the combination of SOLP and SOCD spectroscopies, together with spectral modeling, allows one to extract the average length and average radius of the tubular aggregates within an individual chlorosome.

The outline of the remainder of this chapter is as follows. In Sec. 5.2, we first describe the structural model and the Frenkel exciton model used to calculate the SOLP and SOCD spectra of chlorosomes. Next, in Sec. 5.3, numerical results are presented and discussed, first for the case where we assume the same radius for all tubular aggregates, followed by a detailed study of the case where both lengths and

radii of the aggregates are allowed to vary. Finally, we conclude in Sec. 5.4.

5.2 MODEL

5.2.1 Tubular aggregate structure

The model structure we used for the tubular aggregates in chlorosomes of *Chlorobaculum tepidum* is identical to the one found in Ref. 49 by using SOLP spectroscopy in combination with earlier results.^[26] The model is constructed as depicted in Fig. 5.1. We start from a two-dimensional lattice with two molecules per unit cell (indicated

Figure 5.1: Construction of the model structure of the tubular arrangement of the BChl molecules. The starting point is a planar lattice with two molecules per unit cell (panel (a); the unit cell is indicated in blue), only differing in their orientation relative to the lattice plane (panel (b) for side-view along the a -axis). This lattice is wrapped over the rolling vector C , making an angle δ with the a -axis, onto a cylindrical surface with radius R to define the helical tubular structure (panel (c)), where all molecular positions are uniquely defined in terms of the lattice constants (a , b , and γ), the radius R , and the angle δ . The red and green arrows indicate the dipoles of the relevant optical transition (the Q_y transition) in each molecule. Their projections on the lattice plane make an angle η with the a -axis and an alternating angle of $\pm\alpha = \pm 4^\circ$ with the lattice plane. The parameters we used in our calculations were^[49] $a = 1.25$ nm, $b = 0.98$ nm, $\gamma = 122^\circ$, $\delta = 70^\circ$, and $\eta = 35^\circ$. The radius R can take a discrete set of values, depending on the model situation considered.

by green and red arrows, see below for more detail), as depicted in Figs. 5.1(a) and 5.1(b) (the latter indicating a side-view looking along the a -axis). The lattice con-

stants are given by $a = 1.25$ nm and $b = 0.98$ nm, and the angle between both lattice directions is $\gamma = 122^\circ$. Note that angle γ has a different meaning in Chapters 3 and 4 (the notation used in this chapter is consistent with the existing literature on the structural model of tubular aggregates inside chlorosomes). This lattice is rolled onto a cylindrical surface along the rolling vector $\mathbf{C}$ that connects two lattice points. This vector is determined by its length $|\mathbf{C}| = 2\pi R$ and its angle relative to the a -axis, denoted as δ (see Fig. 5.1(a)). Following Ref. 49, we use $\delta = 70^\circ$. This wrapping results in a tubular aggregate of radius R (taking discrete values only), with two molecules per unit cell (Fig. 5.1(c)). The aggregate has a helical structure due to the angle δ differing from 0° and $(180^\circ - \gamma) = 58^\circ$. It can be seen alternatively as a perpendicular stack of N_1 rings, where each ring contains the centers of N_2 equidistant unit cells.^[32] Neighboring rings are separated by a distance $h = 0.11$ nm (dictated by δ and the lattice constants) and are rotated relative to each other over an angle ζ , which also depends on R (or N_2).

The two molecules in each unit cell are positioned in a symmetric way along the a -axis and only differ in their orientations relative to the lattice plane, ultimately resulting in the farnesyl tails of the BChl molecules pointing alternately in and out of the cylindrical surface: syn-anti stacking.^[26] For the optical properties, it is important to characterize the relevant molecular transition dipoles (see Sec. 5.2.2). In Fig. 5.1, these dipoles are indicated by the green and red arrows, whose projections on the plane of the lattice make an angle of $\eta = 35^\circ$ with the a -axis; their angles with the lattice plane alternate for the syn- and the anti-orientations and take the values $\pm\alpha = \pm 4^\circ$ (Fig. 5.1(b)).

For each choice of R , the above procedure and parameters uniquely specify the positions of all molecules inside the aggregate and the orientations of their dipoles. This, in turn, uniquely defines the exciton Hamiltonian that allows us to calculate the optical properties (Sec. 5.2.2). As explained in the Introduction, in the first part of this study, we will assume that R is the same for all tubular aggregates in all chlorosomes. To be specific, we will use the value $R = 15.42$ nm, which is the discrete value allowed by the lattice parameters that is closest to the average value of about 15 nm found from the analysis of the SOLP studies on the bchR mutant of *Chlorobaculum tepidum* in Ref. 49. This model corresponds to $N_2 = 10$. In the second part of our study, where we allow R to vary, it takes discrete values $R = N_2 \times 1.542$ nm, where we vary N_2 in the range $N_2 = 1, \dots, 35$, which covers the entire distribution of values found in Ref. 49.

5.2.2 Frenkel exciton model and spectra

To calculate the optical properties of the tubular aggregates inside the chlorosomes, we use the Frenkel exciton model that accounts for the Q_y excitation on each BChl

molecule and the excitation transfer interactions between each pair of molecules,

$$H = \sum_{n,m} H_{nm} |n\rangle\langle m| = \sum_n E_{\text{mol}} |n\rangle\langle n| + \sum_{n,m \neq n} J_{nm} |n\rangle\langle m|. \quad (5.1)$$

Here, $|n\rangle$ is the state with molecule n excited and all other molecules in their ground state, E_{mol} indicates the energy of the molecular Q_y excitation, and J_{nm} is the excitation transfer interaction between molecules n and m . We will ignore energy and interaction disorder, focusing totally on the effects of aggregate length and radius on the spectra. This leads to exciton eigenstates of the Hamiltonian that are fully delocalized over the tubular aggregate. Models including disorder in tubular aggregates have shown that localization is rather weak in these systems;^[43,64] moreover, the results of SOLP spectroscopy on chlorosomes indeed reflect strongly delocalized states.^[30,49] For the monomer excitation energy, we use $E_{\text{mol}} = 15931.4 \text{ cm}^{-1}$, which gives a good fit to the experimental ensemble CD spectrum of bchR, shown in Fig. 5.9 in the Appendix, Supplementary Information, Note 1.ⁱ The interactions J_{nm} were modeled using a point-dipole approximation,

$$J_{nm} = \frac{\boldsymbol{\mu}_n \cdot \boldsymbol{\mu}_m}{r_{nm}^3} - 3 \frac{(\boldsymbol{\mu}_n \cdot \mathbf{r}_{nm})(\boldsymbol{\mu}_m \cdot \mathbf{r}_{nm})}{r_{nm}^5}, \quad (5.2)$$

where $\boldsymbol{\mu}_n$ is the transition dipole vector of molecule n , $\mathbf{r}_{nm}$ indicates the position vector between molecules n and m , and r_{nm} is its magnitude. (Model calculations using interactions between extended dipoles do not change our conclusions; they hardly affect the spectral lineshapes and mostly show an overall shift.) Using the structural data in Sec. 5.2.1 together with the value $\mu = 5.5$ Debye for the magnitude of the dipole of the Q_y transition,^[26,30] all interactions can be calculated and the collective eigenstates can be obtained through numerical diagonalization of the matrix H_{nm} as

$$|k\rangle = \sum_n \varphi_{kn} |n\rangle, \quad (5.3)$$

where φ_{kn} denotes the n th component of the k th eigenvector of H_{nm} ; the corresponding eigenenergy is denoted as E_k .

From the exciton states, the SOLP and SOCD spectra for the tubular aggregates can be obtained (see below). We must keep in mind that ultimately we are interested in the spectra for chlorosomes, which consist of several tens of aggregates. When modeling the chlorosome spectra, we will assume that the interactions between individual tubes within a chlorosome are weak enough to be ignored, which implies

ⁱIt should be pointed out that the precise value of E_{mol} does not influence our conclusions, as it mostly sets a reference value for the energy (frequency) axes in the spectra; it has no influence on the absorption lineshapes for linearly polarized light and a very small influence on the CD lineshapes (as those depend on the absolute wavelength).

that the optical properties are determined by the (averaged) optical properties of the individual aggregates that make up a chlorosome. This is corroborated by the fact that previous experiments have been well understood on the basis of this assumption.^[49]

Furthermore, to calculate the various polarization dependent spectra of chlorosomes, we assume that the tubular aggregates within an individual chlorosome are all aligned, which results in a common axis, referred to as the tubular axis of the chlorosome. Cryo-EM micrographs of isolated chlorosomes from *Chlorobaculum tepidum* and its mutants in amorphous ice show striated lines in the side-on view and circular ring structures from the end-on view.^[6,26,27] This suggests that tubular aggregates inside chlorosomes are indeed aligned and are oriented with their axes parallel to the long axis of the chlorosome they reside in. Single-chlorosome experiments are carried out on chlorosomes adsorbed on a substrate. Using atomic force microscope (AFM) and linear dichroism (LD) studies,^[45,65] it has been shown that the long axes of the chlorosomes lie parallel to the plane of the substrate (this orientation can be steered using various methods, such as enclosing the chlorosomes in a gel and squeezing the gel along a particular direction^[50,51,66–69]). We therefore assume that the axes of the tubular aggregates inside the chlorosomes are all parallel to the experimental substrate. This is further supported by the results of SOLP measurements, where experimental spectra also strongly suggest this orientation.^[30,49]

The above allows us to focus on the calculation of spectra of individual tubular aggregates with their long axes mutually aligned and parallel to the experimental substrate. We first turn our attention to SOLP spectroscopy, single-chlorosome fluorescence excitation spectroscopy using linearly polarized light (see Fig. 5.2). In this experiment, light is incident from above, perpendicular to the substrate. The experiment is performed by measuring the dependence of the fluorescence excitation spectrum on the angle ϕ of the polarization direction of the light relative to a reference direction on the substrate, for which we may choose, without loss of generality, the direction of **T**. We remind the reader that the single-object fluorescence excitation spectrum is the emission intensity of the object as a function of the frequency (energy) of the exciting photons. Here, the emission is usually from the relaxed state and assuming that the fluorescence quantum yield does not depend on the excitation frequency, as is commonly done, this spectrum is identical in shape to the absorption spectrum. For this reason, the SOLP and SOCD spectra in this study have all been calculated as absorption spectra.

Thus, in terms of the exciton eigenstates and energies, the SOLP spectrum of a single aggregate may be expressed as

$$A_e(E) = \frac{1}{\pi} \sum_k |\boldsymbol{\mu}_k \cdot \mathbf{e}|^2 \frac{\Gamma_k}{(E - E_k)^2 + \Gamma_k^2}, \quad (5.4)$$

Figure 5.2: Setup for single-chlorosome fluorescence excitation spectroscopy using (a) linearly polarized light (SOLP spectroscopy) and (b) circularly polarized light (SOCD spectroscopy). The chlorosome lies on the substrate with its tubular axis $\mathbf{T}$ (parallel to the tubular axes of its constituent molecular aggregates) oriented parallel to the plane of the substrate. For SOLP spectroscopy, linearly polarized light with wave vector $\mathbf{q}$ (blue arrow) is incident perpendicular to the substrate; its polarization vector $\mathbf{e}$ makes an angle ϕ relative to $\mathbf{T}$. For SOCD spectroscopy, the wave vector $\mathbf{q}$ of circularly polarized light (blue spirals) makes an angle ξ with $\mathbf{T}$.

with E being the photon energy of the exciting light, $\mu_k = \sum_n \varphi_{kn} \mu_n$ being the transition dipole from the aggregate's ground state to the exciton state k , $\mathbf{e}$ being the unit vector indicating the orientation of the polarization of the light, and Γ_k being the dephasing rate of the k th exciton transition. Obviously, the spectra $A_{\parallel}(E)$ and $A_{\perp}(E)$, obtained for $\mathbf{e}$ parallel ($\phi = 0^\circ$) and perpendicular ($\phi = 90^\circ$) to the tubular axis are natural basic spectra, from which the spectra for all other polarizations $\mathbf{e}$ are easily obtained,

$$A_{\mathbf{e}}(E) = A_{\parallel}(E) \cos^2 \phi + A_{\perp}(E) \sin^2 \phi. \quad (5.5)$$

Owing to the cylindrical symmetry, tubular aggregates only have exciton transitions with transition dipole either exactly parallel or exactly perpendicular to the tubular axis.^[39,41] The ratio of the total oscillator strengths in both directions is determined by the angle β between the molecular transition dipoles and the tube's axis, which from the parameters in Sec. 5.2.1 is found to be $\beta = 90^\circ - \delta + \eta = 55^\circ$ (ignoring minor corrections resulting from the small angle $\pm\alpha$). In the situation considered here, with light incident perpendicular to the tube's axis, only half of the perpendicular oscillator strength contributes to the spectrum with $\mathbf{e}$ perpendicular to the cylinder axis: $O_{\parallel}/O_{\perp} = 2 \cot^2 \beta$, with $O_{\parallel}$ ($O_{\perp}$) the integrated spectrum for $\mathbf{e}$ parallel (perpendicular) to the tube's axis. For general reference, we also define the single-chlorosome LD spectrum as

$$LD(E) = A_{\parallel}(E) - A_{\perp}(E). \quad (5.6)$$

Next, we turn our attention to the CD spectrum, which is defined as the difference between the absorption spectrum of left (L) and right (R) circularly polarized light,

$$CD(E) = A_L(E) - A_R(E). \quad (5.7)$$

In conventional CD spectroscopy, the spectra are measured in an isotropic ensemble; previous expressions for the CD spectrum of chlorosomes indeed have been derived taking an isotropic average over all possible orientations of the tubular axis of the chlorosomal molecular aggregates.^[39,40] In the case of single-chlorosome CD spectroscopy, such an average does not apply: The exciting light then has a well-defined, unique direction of incidence relative to the tubular axis and the choice of this direction has a strong influence on the resulting spectrum, as we will see. In contrast to SOLP spectroscopy, where light incident perpendicular to the substrate provides us with all important information, we will see that perpendicular incidence is not optimal for getting most information out of SOCD spectroscopy. For this reason, we start by allowing for the most general situation (owing to the cylindrical symmetry), where the wave vector $\mathbf{q}$ of the circularly polarized light makes an arbitrary angle ξ with the tubular axis of the chlorosome (see Fig. 5.2).

The CD spectrum for a single tubular aggregate may be derived using Fermi's golden rule to account for the interaction between the circularly polarized light and the aggregate, similar to the standard derivation of the ensemble averaged CD.^[1,39,70] The resulting spectrum for light incident with wave vector $\mathbf{q}$ reads

$$CD_{\mathbf{q}}(E) = \frac{1}{\pi} \sum_k R_k^{\mathbf{q}} \frac{\Gamma_k}{(E - E_k)^2 + \Gamma_k^2}, \quad (5.8)$$

where E , E_k , and Γ_k are as defined above and the rotational strength equals^[68,69]

$$R_k^{\mathbf{q}} = \frac{\lambda}{8\pi} \sum_{n,m} \varphi_{kn} \varphi_{km}^* \sin(\mathbf{q} \cdot \mathbf{r}_{nm}) [\mathbf{q} \cdot (\boldsymbol{\mu}_n \times \boldsymbol{\mu}_m)], \quad (5.9)$$

where λ is the wavelength of the incident light and the quantities φ_{kn} , $\mathbf{r}_{nm}$, and $\boldsymbol{\mu}_n$ are as defined above. For aggregate sizes (lengths and radii) small compared to an optical wavelength, the expression $\sin(\mathbf{q} \cdot \mathbf{r}_{nm})$ may be linearized, which allows for a faster numerical implementation. In practice, we have used this linearization in all numerical spectra reported here. We have checked that even for lengths as long as 200 nm, this has a negligible effect on the shape of the SOCD spectra (see Appendix, Supplementary Information, Note 2).

It can be shown (see Appendix, Supplementary Information, Note 3) that like in the case of SOLP spectroscopy, also for SOCD spectroscopy in the long-wavelength limit, where $\sin(\mathbf{q} \cdot \mathbf{r}_{nm})$ in Eq. (5.9) is linearized, a decomposition in two basic spectra is possible,

$$CD_{\mathbf{q}}(E) = CD_{\xi}(E) = CD_{\parallel}(E) \cos^2 \xi + CD_{\perp}(E) \sin^2 \xi, \quad (5.10)$$

where $CD_{\parallel}(E)$ is the spectrum for $\xi = 0^\circ$ (which in experiment cannot be achieved fully due to the substrate) and $CD_{\perp}(E)$ is the spectrum for $\xi = 90^\circ$. The first equality in Eq. (5.10) holds due to the rotational symmetry of the tubular aggregates. Because the long-wavelength limit holds for aggregates as long as 200 nm, which covers the maximum lengths expected in chlorosomes, the decomposition (Eq. (5.10)) holds for chlorosomes. This decomposition could open the way to SOCD spectroscopy where ξ is scanned over a maximum range, improving the signal-to-noise ratio to obtain the two basic spectra in a global fit, similar to applications of SOLP spectroscopy where ϕ is scanned.^[30,35,49] As we will see, however, even the application of SOCD spectroscopy with one well-chosen value of ξ provides much information.

5.2.3 Selection rules and basic spectral features

In this subsection, we address general features of the SOLP and SOCD spectra for tubular aggregates that can be obtained (semi-)analytically. To this end, we consider the limit of long tubular aggregates, where the exciton states can be obtained analytically by imposing periodic boundary conditions along the tube's axis. The exciton states then take the form of Bloch waves in both the axis direction (owing to the boundary conditions) and the ring direction (owing to the cylindrical symmetry), with quasimomenta $2\pi k_1/N_1$ and $2\pi k_2/N_2$, respectively, with k_1 and k_2 integers. This leads to strong optical selection rules on the vector $\mathbf{k} = (k_1, k_2)$, which replaces the scalar label for the exciton eigenstates (k) in Eqs. (5.4) and (5.8): Only states with $\mathbf{k} = (0, 0)$ and $\mathbf{k} = \pm \mathbf{h}$ with $\mathbf{h} = (N_1\zeta/2\pi, 1)$ contribute to the spectra.^[39] These are known as superradiant states with oscillator strengths and rotational strengths that scale proportional to the total number of molecules in the tube. For the case of tubular aggregates with one molecule per unit cell, this leads to three superradiant states, where the totally symmetric one ($\mathbf{k} = \mathbf{0}$) has a transition dipole of magnitude $\sqrt{N_1 N_2} \mu \cos \beta$, directed parallel to the tube's axis, while the two "helical" states $\mathbf{k} = \pm \mathbf{h}$ are degenerate and have dipoles of magnitude $\sqrt{N_1 N_2}/2 \mu \sin \beta$, both perpendicular to the axis and perpendicular to each other.^[39] For the SOLP spectra, this implies that both $A_{\parallel}(E)$ and $A_{\perp}(E)$ have one peak, positioned at the eigenenergies E_0 and $E_{\mathbf{h}}$, respectively (see Appendix, Supplementary Information, Note 4 for more details).

The structure considered here has two molecules per unit cell, which only differ from each other in the small tilt angle $\pm\alpha$ of the dipoles. While the numerical calculations reported in Sec. 5.3 were all done including this dimerization, properly accounting for having a Davydov splitting, this induces only minute corrections in the spectrum to the approximation where we set $\alpha = 0^\circ$. Therefore, the calculated spectra are well understood using a one-molecule per unit cell picture, which for long tubes thus leads to one peak in both $A_{\parallel}(E)$ and $A_{\perp}(E)$. For the structure con-

sidered here, the parallel transition has lower energy than the perpendicular one ($E_0 < E_h$). This allows one to find the orientation of the tube (chlorosome) on the substrate by recording the spectrum as a function of the polarization angle ϕ . For short tubes, finite-size effects will lead to small shifts of both peaks. Moreover, the periodic boundary conditions in the axis direction then are no longer valid, breaking the selection rules on k_1 . This leads to weak satellite peaks, which are blue shifted compared to the main peaks. Details on the effects of dimerization and finite length are analyzed in the Appendix, Supplementary Information, Note 4.

The CD spectrum for an isotropic ensemble of long tubular aggregates with one molecule per unit cell was analyzed in Ref. 39. There, a distinction was made between “ring” and “helical” contributions to this spectrum. Interestingly, for the case of SOCD spectroscopy, $CD_{\parallel}(E)$ is totally determined by helical contributions, while $CD_{\perp}(E)$ only has ring contributions. For the structure considered here (ignoring effects of a Davydov splitting), negative ring contributions occur at $E = E_0$, while positive ring contributions occur at $E = E_h$, leading to an overall dispersive (S-type) spectral shape centered between E_0 and E_h . Two degenerate dispersive helical contributions are centered at $E = E_h$; they are derivatives of Lorentzian lineshapes, i.e., they also give an S-type shape, but in this case with the positive part on the low-energy side and the negative part toward higher energies. All these notions survive if we take into account the dimerization due to the small angle $\pm\alpha$ (see Appendix, Supplementary Information, Note 5): One Davydov component dominates the entire spectrum and the spectral contributions arising from the second (higher-energy) Davydov band can be ignored in practice; a new type of contribution arising from the dimerization, namely, a non-dispersive helical contribution in both Davydov bands, is so small, in practice, that it can also be ignored.

From the above, we see that for general ξ , the sum of two partially overlapping S-type lineshapes of the opposite overall sign determine the SOCD spectrum. This makes the spectrum highly sensitive to ξ , to the precise values of the energies E_0 and E_h of the superradiant exciton states (which depend on the aggregate radius and length), and to the relative magnitude of both dispersive shapes. The latter depends on the length: At small length, both are similar in magnitude, but for increasing length, the helical contributions become more important. It is this sensitivity, which will be confirmed in the numerical results in Sec. 5.3, that allows for probing the radius and length using the combination of SOLP and SOCD spectroscopies.

5.3 NUMERICAL RESULTS AND DISCUSSION

In this section, we present the results of our model calculations for the single-chlorosome spectra as a function of linear polarization of the exciting light (SOLP) and the

single-chlorosome CD spectra. As explained in Sec. 5.2, we calculate the spectra as the average of the spectra of the individual tubular BChl aggregates that make up the chlorosome and assume that all tubular axes inside a chlorosome are aligned and parallel to the experimental substrate (see Fig. 5.2). The model for each tube is constructed as specified in Sec. 5.2.1, with model parameters indicated in Fig. 5.1 and their values specified in its caption. These parameters are fixed for all calculations performed. The lengths L and the radius R of the tubular aggregates, alternatively represented as N_1 ($L = N_1 \times 0.11$ nm) and N_2 ($R = N_2 \times 1.542$ nm) of the cylinders, may differ and will be specified below for the different cases considered. The parameters that further define the Hamiltonian are given in Sec. 5.2.2, specifically, we have $E_{\text{mol}} = 15931.4$ cm⁻¹ for the molecular excitation energy and we use dipole-dipole excitation transfer interactions, with a dipole strength of $\mu = 5.5$ Debye and orientations as given in Fig. 5.1. Finally, we use $\Gamma_k = 50$ cm⁻¹ for the exciton dephasing rate. This parameter is not known experimentally; from two-dimensional spectroscopy at zero waiting time, an upper bound of 180 cm⁻¹ can be deduced.^[71] All numerical calculations were performed with open boundary conditions in the axis direction of the tubes.

5.3.1 Model with fixed tubular radii

As explained in the Introduction and Sec. 5.2.1, we first analyze spectra in case all tubular aggregates in all chlorosomes have the same radius of $R = 15.42$ nm ($N_2 = 10$). In the simplest approach, we will assume that all tubes inside one chlorosomes have equal length L and that this parameter may vary between chlorosomes. In this case, the SOLP and SOCD spectra of a single chlorosome are simply given by the spectra for a single tube of length L .

Figure 5.3 presents as contour plots the calculated SOCD spectra for chlorosomes consisting of tubular aggregates with eight different lengths L (constant within each chlorosome) as a function of the angle ξ . As we argued in Sec. 5.2.2, SOLP spectroscopy allows one to assess the orientation of the tubular axis for a single chlorosome, which, in practice, may serve as reference for determining the angle ξ in an SOCD experiment. It is clearly seen that indeed the SOCD spectrum depends on ξ as well as L ; we have checked numerically that for every angle, the spectrum indeed can be obtained through a linear combination of the spectra for $\xi = 0^\circ$ and $\xi = 90^\circ$ (Eq. (5.10)). These two basic spectra indeed follow the general description given in Sec. 5.2.3. For the longest tubes, the spectrum at $\xi = 0^\circ$ shows a dispersive shape centered at $E = E_h < E_{\text{mol}}$, deriving from the helical exciton state (helical contribution), while the spectrum at $\xi = 90^\circ$ shows a dispersive shape centered at slightly lower energies (namely, in between E_0 and E_h) and with sign swapped relative to the spectrum at $\xi = 0^\circ$ (the ring contribution). When the length gets shorter, we

Figure 5.3: Contour plots that present single-chlorosome CD spectra as a function of excitation energy and angle ξ between the wave vector $\mathbf{q}$ of the incident light and the chlorosome's tubular axis. Each panel corresponds to a chlorosome with different length L of the tubular BChl aggregates it consists of, as specified in the panel. All tubes within one chlorosome have the same length; all aggregates have the same radius of $R = 15.42$ nm. The spectrum in each panel is normalized to its maximum absolute intensity.

indeed observe overall shifts in both features and the separation between positive and negative peaks grows. Moreover, for the shortest lengths (5 and 10 nm), we see additional peaks appearing on the higher-energy side of the main features due to finite size effects. Finally, we note that for the longest tubes, the helical contribution is larger than the ring contribution; for short tubes, they are roughly equally strong.

For angles ξ in between 0° and 90° , the linear combination of both basic spectra gives rise to a richer variation of lineshapes, with the possibility to have more than one sign change as a function of E . As a consequence, at such intermediate angles, the spectrum is more sensitive to L than at $\xi = 0^\circ$ and $\xi = 90^\circ$ and the L dependence persists for larger L values (up to about 50 nm). This is seen more clearly by making cuts through the contour plots, which are shown in Fig. 5.4 for five different angles ξ (0° , 30° , 45° , 60° , and 90°), each for six different values of L . These plots show that, in particular, the structure of the spectrum varies much more as a function of length for $\xi = 45^\circ$ as compared to other angles, which makes this angle of incidence the most sensitive one to probe length variations. We can also conclude that the typical experimental setup used for single-object spectroscopy, where light is incident per-

Figure 5.4: Cross sections through the contour plots of Fig. 5.3. Each panel presents the cross sections for six different values of the aggregate length L , coded as specified next to the first panel, for a specific angle ξ , as indicated inside the panels. Each spectrum is normalized to its maximum absolute intensity.

pendicular to the substrate, is not optimal for using SOCD spectroscopy to measure length variations in chlorosomes. The ideal would be to measure the complete contour plot, as this would give most information, but if the experimental setup dictates that only one angle can be used, clearly $\xi = 45^\circ$ seems the best choice. The crux is that at this angle, there is a large contribution from both the ring and the helical spectra, whose interference depends on the length L due to the fact that the relative magnitude of both spectra depends on L .

Thus far, we considered the situation where the tubular aggregates inside a chlorosome all have the same length. This makes the distinction between different chloro-

Figure 5.5: Left column: histograms for the occurrence of the length of the 50 tubular aggregates in four randomly generated chlorosomes using the Poisson distributions for L with four different averages $\bar{L}$ (10, 20, 30, and 40 nm from top to bottom), with mean $\langle L \rangle$ and standard deviation σ_L of each histogram as indicated. The radii of all tubular aggregates in the chlorosomes are taken equal, $R = 15.42$ nm. Middle column: SOLP spectra calculated for these individual chlorosomes, with light polarized parallel ($A_{\parallel}(E)$, blue solid line) and perpendicular ($A_{\perp}(E)$, red dashed line) to the tubular axis; the black dashed-dotted line shows the single-chlorosome LD spectrum. $A_{\parallel}(E)$ and $A_{\perp}(E)$ are normalized to the largest one of the peak intensities of the two; each LD spectrum is normalized to its maximum absolute intensity. Right column: SOCD spectra $CD_{\xi}(E)$ calculated for these individual chlorosomes for three angles between the direction of incidence of the light and the chlorosome's tubular axis: $\xi = 0^\circ$ (solid blue line), 45° (red dashed line), and 90° (black dashed-dotted line). Each CD spectrum is normalized to its maximum absolute intensity.

somes sharp and enhances the possibility to probe the (typical) length of the aggregates they consist of. To see whether some amount of length variation within individual chlorosomes washes out the spectral details that reflect the typical aggregate length, we extend the previous model by allowing for such variations. Individual chlorosomes are known to contain several tens of molecular aggregates.^[1,2] In our model, we assume that each chlorosome contains 50 tubular molecular aggregates, which are identical in all aspects (also radius), apart from their length. The lengths are chosen randomly from a Poisson distribution with average $\bar{L}$.^[72] The advantage is that this is a simple one-parameter distribution, whose variance is equal to its average; this implies that at later stages of the growth of the aggregates inside a chlorosome, the absolute variation in their sizes also grows, which seems a natural assumption to make. Thus, each individual chlorosome is specified by 50 randomly chosen values of L using as a starting point a specific average $\bar{L}$. This leads to chlorosomes with a random distribution of aggregate lengths; each individual chlorosome may be characterized by the average length of its aggregates $\langle L \rangle$ (not necessarily equal to $\bar{L}$). The SOLP and SOCD spectra for an individual chlorosome are then obtained by adding the corresponding spectra of the 50 constituent tubular aggregates (properly accounting for the fact that longer aggregates have a larger weight in the spectrum).

Figure 5.5 shows the results for four particular chlorosomes generated from Poisson distributions with four different values of $\bar{L}$, namely, 10, 20, 30, and 40 nm, from top to bottom, respectively. The left column presents the histograms for the aggregate lengths found in the chlorosome, together with their means and standard deviations; the middle column shows $A_{\parallel}(E)$ and $A_{\perp}(E)$ (characterizing SOLP spectroscopy) and also gives the single-chlorosome LD spectrum, while the right column presents the SOCD spectra for the four individual chlorosomes for three different values of the angle of incidence: $\xi = 0^\circ$, 45° , and 90° . From this, we see that the spectra for linear polarization have a very weak dependence on the average length of the aggregates inside the chlorosome, even for the smallest lengths. This is also true for CD spectroscopy with $\xi = 0^\circ$ and $\xi = 90^\circ$. By contrast, CD spectroscopy with $\xi = 45^\circ$ gives a clear variation of the spectra with the average aggregate length, despite the considerable variations in this length. This confirms the above conclusion that SOCD spectroscopy on individual chlorosomes may indeed probe differences in average aggregate length between chlorosomes if the angle of incidence is chosen close to $\xi = 45^\circ$.

5.3.2 Model with varying tubular radii

Thus far, we have presented results using one fixed value for the radius of the tubular BChl aggregates inside the chlorosomes. This simplifying assumption was made

because it enabled us to isolate the effects of the aggregate length on the spectra, in particular, on the SOCD spectra. Moreover, it is known that the spectra of tubular aggregates obtained using linearly polarized light (such as SOLP spectra) are quite sensitive to the radius^[32,38] and less so to the length,^[39] suggesting that in an experimental approach, radius information can first be obtained by SOLP spectroscopy, after which SOCD can be used to get information on the length of the aggregates. Indeed, this is exactly how the value for R used above was obtained: by averaging the radii obtained by analyzing SOLP spectra.^[49] The method used to get information about the radius from experiments with linearly polarized light uses the notion that for long tubular aggregates, the energy separation ΔE between the main spectral bands polarized parallel and perpendicular to the tube's axis monotonically decreases with growing radius R .^[32] However, for tubular aggregates with finite length of up to about 50 or 100 nm, it has to be established to what extent the length affects ΔE . To this end, we simulated $A_{\parallel}(E)$ and $A_{\perp}(E)$ for tubular aggregates with the lattice structure fixed to the one used throughout this chapter (Sec. 5.2.1) and varying length L and radius R (characterized by N_2) and obtained ΔE from them. Since some of the spectra, especially for small L and R (N_2), have satellite peaks (see Fig. 5.13 in the Appendix, Supplementary Information, Note 4), we calculated the average energy (weighted by the spectral intensity over the whole band) for both polarizations and took their difference as ΔE . The resulting data are presented in Fig. 5.6.

Figure 5.6 clearly shows that for all lengths considered, ΔE indeed monotonically decreases with the radius but that this relation itself depends on L as well. This implies that ΔE alone does not allow a unique determination of the radius if the length is not known. Rather, measuring ΔE allows for a range of combinations of lengths and radii that might apply. As an illustration, consider the four data points in Fig. 5.6 lying between the dashed black lines, which represent tubular aggregates with (L, R) combinations (11, 10.79), (21, 13.88), (31, 15.42), and (41, 16.96) (all numbers in nm) that all have $\Delta E \approx 56 \text{ cm}^{-1}$. Importantly, however, the R dependencies for different lengths in Fig. 5.6 are seen not to cross each other, which keeps the possibility open that the combination of SOLP (ΔE) measurements and SOCD measurements may still allow one to get information on both the typical length and typical radius of the tubular aggregates in a particular chlorosome. This is confirmed by Fig 5.7, in which we show the SOCD spectra for the four above (L, R) combinations for $\xi = 0^\circ$, $\xi = 45^\circ$, and $\xi = 90^\circ$. This figure shows that indeed the different (L, R) combinations with the same ΔE can be distinguished using SOCD spectroscopy and that, as before, this is best done using $\xi = 45^\circ$.

Similar to what we did in Sec 5.3.1, we checked whether the above conclusion still holds if we allow for variation of L and R within an individual chlorosome or whether such variation washes out the spectral differences. Again, we assume

Figure 5.6: Energy difference ΔE between parallel and perpendicular polarized energy bands as a function of radius (characterized by N_2 on the lower horizontal axis) for tubular aggregates of the structure applicable to chlorosomes, with different lengths, as indicated in the legend. The two dashed lines enclose four data points characterizing different (L, R) combinations with the same ΔE .

that each chlorosome consists of 50 tubular aggregates and that now not only their lengths but also their radii are taken randomly from Poisson distributions with averages $\bar{L}$ and $\bar{R}$, respectively. We used four sets of $(\bar{L}, \bar{R})$ combinations that equal the above four sets, which gave $\Delta E \approx 56 \text{ cm}^{-1}$ in case all aggregates inside an individual chlorosome are identical. The spectra for four chlorosomes randomly generated using these distributions were obtained by adding the spectra of the tubular aggregates within each chlorosome. The results are shown in Fig. 5.8. The left column presents the histograms for the aggregate lengths and radii found in each chlorosome, together with their means and standard deviations; the middle column shows the corresponding $A_{\parallel}(E)$ and $A_{\perp}(E)$ (characterizing SOLP spectroscopy) and also

Figure 5.7: SOCD spectra of tubular aggregates of the structure applicable to chlorosomes, calculated for the four combinations of length and radius, (L, R) , which give $\Delta E \approx 56 \text{ cm}^{-1}$ in Fig. 5.6. From top to bottom, the spectra correspond to the wave vector of the incident light making an angle with the tubular axis of $\xi = 0^\circ$, 45° , and 90° . Each SOCD spectra is normalized to its maximum absolute intensity.

gives the single-chlorosome LD spectrum, while the right column presents the SOCD spectra for the four individual chlorosomes for three different values of the angle of incidence: $\xi = 0^\circ$, 45° , and 90° .

The results in Fig. 5.8 show that the SOLP and LD spectra hardly differ for these four chlorosomes; specifically, analysis shows that they all indeed have a ΔE value

Figure 5.8: Left column: histograms for the occurrences of the length (blue) and the radius (red) of the 50 tubular aggregates in four randomly generated chlorosomes using the Poisson distributions for L and R described in the text, with mean and standard deviation of each histogram as indicated. Middle column: SOLP spectra calculated for these individual chlorosomes, with light polarized parallel to the tubular axis ($A_{\parallel}(E)$, blue solid line) and perpendicular ($A_{\perp}(E)$, red dashed line); the black dashed-dotted line shows the single-chlorosome LD spectrum. $A_{\parallel}(E)$ and $A_{\perp}(E)$ are normalized to the largest one of the peak intensities of the two; each LD spectrum is normalized to its maximum absolute intensity. Right column: SOCD spectra $CD_{\xi}(E)$ calculated for these individual chlorosomes for three angles between the direction of incidence of the light and the chlorosome's tubular axis: $\xi = 0^\circ$ (solid blue line), 45° (red dashed line), and 90° (black dashed-dotted line). Each CD spectrum is normalized to its maximum absolute intensity.

close to 56 cm^{-1} . By contrast, the SOCD spectra are more sensitive to the $(\langle L \rangle, \langle R \rangle)$ combination that applies if we use the setup with $\xi = 45^\circ$, even if the differences for the longer lengths are not as big as in Fig. 5.7. We note that the ability to distinguish different sets of lengths and radii generally increases with smaller dephasing rate and hence with lowering the temperature. The above results show that, in principle, the combination of SOLP and SOCD spectroscopy allows one to obtain estimates of the average length and average radius of the tubular aggregates within individual chlorosomes, even if these quantities vary for the aggregates inside each chlorosome according to Poisson distributions. We stress that our conclusions are not unique for the case presented here and can also be found for sets of chlorosomes with other pre-selected values of ΔE . To illustrate this, we present the results for four chlorosomes with $\Delta E \approx 40\text{ cm}^{-1}$ in the Appendix, Supplementary Information, Note 6.

5.4 CONCLUSIONS

5

In this chapter, we investigated theoretically how polarization dependent fluorescence excitation spectroscopy on single chlorosomes can provide information on the average (typical) size of the tubular aggregates that form the secondary structural elements inside these highly efficient light-harvesting organelles. We have found that a combination of single-chlorosome spectroscopies with linearly and circularly polarized light can be used to probe both the typical radius and the typical length of these aggregates. The ideal protocol scans the fluorescence excitation spectrum as a function of the polarization angle ϕ for linearly polarized light (SOLP spectroscopy), in combination with a scan of the single-chlorosome circular dichroism spectrum as a function of the angle ξ between the wave vector of the exciting light and the long axis of the chlorosome (SOCD spectroscopy). SOLP spectroscopy experiments have been used before to contribute to characterizing the structure of the aggregates, and these experiments were also used to estimate typical radii of the tubular aggregates in different chlorosomes.^[30,49] The SOLP spectra, however, show little dependence on the aggregate length, making this quantity inaccessible with linearly polarized light. We have shown in this chapter that, by contrast, CD spectroscopy on individual chlorosomes is expected to be much more sensitive to the length. Moreover, we found that SOLP spectroscopy alone does not allow to uniquely determine the radius; it is the combination of both spectroscopies that allows probing both the typical radius and the typical length.

Single-object CD spectroscopy has only very rarely been applied, and as far as we know, no SOCD spectra have been taken of chlorosomes. It is to be expected that experimental constraints may make it hard to perform a full scan of the dependence of the spectrum on the angle ξ . Our calculations demonstrate that, in principle,

making the measurement at two different angles provide all information and if also that turns out complicated, using $\xi = 45^\circ$ would be the best option. We have explained how the sensitivity of CD spectroscopy to the tubular length results from the interference between so-called ring contributions and helical contributions to the spectrum, both of which yield dispersive (S-type) lineshapes with opposite overall sign, which partially overlap. The relative weight of both depends on the aggregate length, making the lineshape of the sum of these overlapping dispersive contributions highly sensitive to the length. Moreover, at $\xi = 0^\circ$ ($\xi = 90^\circ$), only helical (ring) contributions occur, while at intermediate angles, their linear combination determines the spectrum. This explains why using $\xi = 45^\circ$ by itself already provides much information.

The ability to resolve length and radius is limited by the width of the spectral contributions. If the width gets too large, it washes out the spectral structure that reflects the radius and especially the length. For aggregates with a short length and (or) a small radius, various spectral peaks are well resolved, leading to specific spectral structures that reflect the size, but for larger sizes, this becomes more challenging. For the homogeneous linewidth we used, this limits the lengths that can be resolved to about 50 nm. Using low-temperature conditions may help to reduce this linewidth and boost the resolution also for larger sizes. At the same time, having minimal inhomogeneous width also enhances the size sensitivity. This implies that for chlorosomes of mutants, which are known to have smaller inhomogeneity, the chances to resolve larger sizes are higher than for the wild-type chlorosomes.^[30,49]

In our model calculations, we adopted the picture that the dominant secondary structural elements inside the chlorosomes are tubular aggregates, all with the same molecular packing. We did this in order to isolate the effects of variations in length and radius of the tubular aggregates between different chlorosomes and hope that our observations and predictions will inspire new experiments on single chlorosomes. Of course, in reality the situation is more complicated: The packing may reveal disorder as well, leading to disorder in the molecular transition energies and the excitation transfer interactions, which, in turn, will affect the spectra. In addition, not all aggregates need to be tubular; other secondary structural elements may occur, such as lamellar and multi-walled tubular structures.^[6] Extending the current study to include such effects and investigate how robust the predicted sensitivity to average length and radius is for various additional sources of heterogeneity is an interesting and important topic for future research. Such extensions, however, are outside the scope of this work.

Finally, we note that the idea of combining ϕ dependent SOLP spectroscopy and ξ dependent SOCD spectroscopy also may be fruitful for other supramolecular structures where information on the variation of their internal structure is hard to obtain through other sources.

5.5 APPENDIX: SUPPLEMENTARY INFORMATION NOTES

5.5.1 Supplementary Note 1: Ensemble CD spectrum

We fitted the experimental ensemble CD (ECD) spectrum of bchR mutant chlorosomes reported in a previous study^[49] to obtain the monomer energy (E_{mol}) of BChl molecules in chlorosomes. We used the structural model and Frenkel exciton model as explained in Secs. 5.2.1 and 5.2.2 of the main text, respectively. The experimental spectrum and the fit are shown in Fig. 5.9; the best fit is obtained using $E_{\text{mol}} = 15931.4 \text{ cm}^{-1}$. The experimental spectrum was obtained for an isotropic

Figure 5.9: Experimental ensemble CD spectrum (blue solid curve) with theoretical fit (red dashed line) for bchR mutant chlorosomes. The experimental spectrum is taken from Ref. 49. The fit uses the same structural and Frenkel exciton model as in the main text, with model parameters: $a = 1.25 \text{ nm}$, $b = 0.98 \text{ nm}$, $\gamma = 122^\circ$, $\delta = 70^\circ$, $R = 15.42 \text{ nm}$, $L = 48 \text{ nm}$, $\Gamma_k = 750.5 \text{ cm}^{-1}$, and the monomer energy $E_{\text{mol}} = 15931.4 \text{ cm}^{-1}$.

sample.^[49] It has an S-shape form, which is usually observed for the CD-spectrum of a single ring aggregate.^[73]

To calculate the ensemble spectrum, we use the long-wavelength approximation

of Eq. (5.9) in the main text as basis and perform an average over all orientations of the chlorosome's tubular axis. This leads to

$$ECD(E) = \frac{1}{\pi} \sum_k R_k^{ECD} \frac{\Gamma_k}{(E - E_k)^2 + \Gamma_k^2}, \quad (5.11)$$

where E denotes the photon energy, k labels the exciton states, E_k is the energy of k th exciton transition and Γ_k represents its width. In contrast to the case of single-chlorosome spectroscopy, here Γ_k also accounts for inhomogeneous broadening, which is why the value $\Gamma_k = 750.5 \text{ cm}^{-1}$ used here, exceeds the value used in the main text. For ECD, the rotational strength R_k^{ECD} equals^[1,39,70]

$$R_k^{ECD} = \frac{\pi}{6\lambda} \sum_{n,m} \varphi_{kn} \varphi_{km}^* [\mathbf{r}_{nm} \cdot (\boldsymbol{\mu}_n \times \boldsymbol{\mu}_m)]. \quad (5.12)$$

All symbols in Eq. (5.12) have the same meaning as in the main text. In terms of the decomposed CD spectra $CD_{\parallel}(E)$ and $CD_{\perp}(E)$, introduced in the main text, one may alternatively write

$$ECD(E) = \frac{1}{3} CD_{\parallel}(E) + \frac{2}{3} CD_{\perp}(E), \quad (5.13)$$

keeping in mind that the ensemble value for the linewidth should be used.

5.5.2 Supplementary Note 2: Quality of linearization in the rotational strength

For aggregate sizes (lengths and radii) small compared to an optical wavelength (λ), the expression $\sin(\mathbf{q} \cdot \mathbf{r}_{nm})$ in the rotational strength (Eq. (5.9) in the main text) may be linearized, which allows for a tremendous gain in the computational implementation. Here, we show that the difference between the full and the linearized results for the CD lineshape is negligible for aggregate lengths as long as 200 nm. Since in all physical cases the radius is much smaller than an optical wavelength, we do not expect that linearization affects the spectrum for light incident perpendicular to the tubular axis ($\xi = 90^\circ$). However for light incident parallel to the tubular axis ($\xi = 0^\circ$), phase differences of the light along the aggregate's length are relevant and here, in principle, one expects to see the strongest differences between the linearized and the exact expression for the rotational strength, especially when the tubes are long.

Figure 5.10 shows the calculated CD spectra for tubular aggregates of lengths $L = 100 \text{ nm}$ and $L = 200 \text{ nm}$, using the structural and energetic parameters for the inner wall of the tubular aggregates in bchR chlorosomes applied in Ref. 30: $a = 1.294 \text{ nm}$, $b = 0.98 \text{ nm}$, $R = 10 \text{ nm}$, $\delta = 72^\circ$, $\eta = 35^\circ$, $\pm\alpha = \pm 4^\circ$, $\mu = 5.5$

Figure 5.10: Comparison of calculated SOCD spectra of tubular aggregates with length $L = 100$ nm and 200 nm found in chlorosomes for $\mathbf{q} \parallel \mathbf{T}$ ($\xi = 0^\circ$), obtained by using the exact rotational strength with $\sin(\mathbf{q} \cdot \mathbf{r}_{nm})$ (red dashed line) and its linearized approximation (blue solid line).

Debye and $E_{\text{mol}} = 15500 \text{ cm}^{-1}$.ⁱⁱ The solid curves represent the spectra using the long-wavelength (linearized) limit of the rotational strength and the dashed spectra were obtained using the exact form. Clearly, even for $L = 200$ nm, hardly any differences can be seen, demonstrating the quality of the long-wavelength limit. As in practice chlorosomes are limited in length to a few hundred nanometers, this implies that using the linearized expression for CD spectroscopy of chlorosomes is justified. The excellent quality of the linearization probably results from the fact that even for the considerable length of 200 nm, the vast majority of intermolecular distances featuring in the rotational strength are much smaller than the wavelength.

We note that the linearization of $\sin(\mathbf{q} \cdot \mathbf{r}_{nm})$ in the rotational strength not only

ⁱⁱThese parameters deviate from the ones used in the main text, but their precise values are not important for demonstrating the quality of the linearization of the rotational strength.

makes the numerical implementation of calculating the SOCD spectra much faster, but also simplifies the analysis of these spectra, as it allows for their exact decomposition for arbitrary wave vector $\mathbf{q}$ into the spectra for $\mathbf{q} \parallel \mathbf{T}$ and $\mathbf{q} \perp \mathbf{T}$ (Eq. (5.10) of the main text), as will be shown below in the Supplementary Note 3.

5.5.3 Supplementary Note 3: SOCD decomposition

In this note, we prove the decomposition of the CD spectrum according to Eq. (5.10) in the main text. The starting point is Eq. (5.8) of the main text, with the long-wavelength expression for the rotational strength:

$$CD_{\mathbf{q}}(E) = \frac{1}{\pi} \sum_k R_k^{\mathbf{q}} \frac{\Gamma_k}{(E - E_k)^2 + \Gamma_k^2}, \quad (5.14)$$

with

$$R_k^{\mathbf{q}} = \frac{\lambda}{8\pi} \sum_{n,m} \varphi_{kn} \varphi_{km}^* (\mathbf{q} \cdot \mathbf{r}_{nm}) [\mathbf{q} \cdot (\boldsymbol{\mu}_n \times \boldsymbol{\mu}_m)]. \quad (5.15)$$

Owing to the cylindrical symmetry of the aggregates, we can restrict to considering for the wave vector of incidence $\mathbf{q} = |\mathbf{q}|(\sin \xi, 0, \cos \xi)$, where ξ is the angle between $\mathbf{q}$ and the tubular axis (see Fig. 5.2(b) in the main text), which is identified with the z -axis; the x -axis is an arbitrary direction perpendicular to the tube's axis. The rotational strength may then be written as

$$R_k^{\mathbf{q}} = R_k^{\parallel} \cos^2 \xi + R_k^{\perp} \sin^2 \xi + R_k^{\text{cr}} \cos \xi \sin \xi, \quad (5.16)$$

with

$$R_k^{\parallel} = \frac{\lambda |\mathbf{q}|^2}{8\pi} \sum_{n,m} \varphi_{kn} \varphi_{km}^* \mathbf{r}_{nm}^z (\boldsymbol{\mu}_n \times \boldsymbol{\mu}_m)^z, \quad (5.17)$$

the rotational strength for light of wavelength λ incident along the tube's axis (the superscript z denotes the z -component of the vector; similar for the superscript x below),

$$R_k^{\perp} = \frac{\lambda |\mathbf{q}|^2}{8\pi} \sum_{n,m} \varphi_{kn} \varphi_{km}^* \mathbf{r}_{nm}^x (\boldsymbol{\mu}_n \times \boldsymbol{\mu}_m)^x, \quad (5.18)$$

the rotational strength for light of wavelength λ incident perpendicular to the tube's axis, and

$$R_k^{\text{cr}} = \frac{\lambda |\mathbf{q}|^2}{8\pi} \sum_{n,m} \varphi_{kn} \varphi_{km}^* [\mathbf{r}_{nm}^x (\boldsymbol{\mu}_n \times \boldsymbol{\mu}_m)^z + \mathbf{r}_{nm}^z (\boldsymbol{\mu}_n \times \boldsymbol{\mu}_m)^x], \quad (5.19)$$

is a cross-term that cannot be identified with a specific direction of incidence. Below, we will show that $R_k^{\text{cr}} = 0$ due to the cylindrical symmetry, which upon substitution of Eq. (5.16) into Eq. (5.14) yields Eq. (5.10) of the main text.

To show that the cross-term vanishes, we use the stack-of-rings picture of the tube's structure, explained in the main text, where the tube is viewed as a perpendicular stack of N_1 rings, with each ring containing the centers of N_2 unit cells. We will consider the most general case, where each unit cell contains an arbitrary number of molecules (for the chlorosomes, there are two molecules in each unit cell). Each molecule n is now labeled by three numbers $(n_1, n_2, j) \equiv (\mathbf{n}, j)$, where $n_1 = 1, \dots, N_1$ labels the rings, $n_2 = 1, \dots, N_2$ labels the unit cells in each ring, and j labels the molecules inside the unit cell. The position and transition dipole moment vectors of molecule $(\mathbf{n}, j)$ are then given by,

$$\mathbf{r}_{\mathbf{n}j} = (R \cos(n_1 \zeta + n_2 \phi_2 + \Delta \phi_j), R \sin(n_1 \zeta + n_2 \phi_2 + \Delta \phi_j), n_1 h + \Delta z_j), \quad (5.20)$$

and

$$\boldsymbol{\mu}_{\mathbf{n}j} = (-\mu \sin \beta_j \sin(n_1 \zeta + n_2 \phi_2 + \Delta \phi_j + \alpha_j), \mu \sin \beta_j \cos(n_1 \zeta + n_2 \phi_2 + \Delta \phi_j + \alpha_j), \mu \cos \beta_j), \quad (5.21)$$

respectively, where ζ is the relative angle of rotation of adjacent rings, as defined in the main text, $\phi_2 = 2\pi/N_2$, $\Delta \phi_j$ is the azimuthal position angle of molecule j relative to the center of the unit cell, and Δz_j is the z -coordinate of this molecule relative to the center of the unit cell. Both quantities are illustrated in Fig. 5.11 and explained in its caption. Furthermore, β_j is the angle between the dipole of the j th molecule in the unit cell and the tube's axis and α_j is the angle between the projection of this dipole on the plane perpendicular to the tube's axis and the tangent to the ring direction at the position of the molecule (for chlorosomes, $\beta_1 = \beta_2 = 55^\circ$, $\alpha_1 = 4^\circ$ and $\alpha_2 = -4^\circ$).

Due to rotational symmetry of the system, the eigenstates have Bloch character in the ring direction, implying that we may write

$$\varphi_{kn} = \frac{1}{\sqrt{N_2}} e^{ik_2 \phi_2 n_2} \varphi_{k_1, n_1 j}(k_2), \quad (5.22)$$

where $k_2 = 0, \pm 1, \pm 2, \dots, \pm(N_2 - 1)/2$ (for N_2 odd; obvious changes apply for N_2 even) labels the quasi-momentum in the ring direction, while $\varphi_{k_1, n_1 j}(k_2)$ describes the $n_1 j$ th component of the k_1 th eigenstate in the Bloch sub-band k_2 .

Using Eq. (5.22) in Eq. (5.19), the summations over n and m turn into summations over (n_1, n_2, j) and (m_1, m_2, j') , where the summations over n_2 and m_2 for every n_1, m_1, j , and j' combination can be carried out due to the Bloch nature of the wave functions in the ring direction. Omitting factors that do not depend on n_2 and m_2 , the remaining summations are

$$S = \sum_{n_2} \sum_{m_2} \frac{e^{ik_2 \phi_2 (n_2 - m_2)}}{N_2} [\mathbf{r}_{nm}^x (\boldsymbol{\mu}_n \times \boldsymbol{\mu}_m)^z + \mathbf{r}_{nm}^z (\boldsymbol{\mu}_n \times \boldsymbol{\mu}_m)^x]. \quad (5.23)$$

Figure 5.11: Illustration of the azimuthal position angle $\Delta\phi_j$ (top view) and the z -coordinate Δz_j (side view) of molecule j relative to the center of the unit cell in the model structure of the tubular arrangement of the BChl molecules shown in Fig. 5.1 (c) in the main text. R and T , denote respectively, the radius and the tubular axis of the tubular structure. Here the position of the first molecule is chosen as the center of the unit cell, i.e., $\Delta\phi_1 = 0^\circ$ and $\Delta z_1 = 0$ nm. Consequently $\Delta\phi_2 = a \sin(90^\circ + \delta)/2R$ and $\Delta z_2 = a \cos(90^\circ + \delta)/2$.

Now substituting Eqs. (5.20) and (5.21) into Eq. (5.23) leads to

$$\begin{aligned}
 S = \frac{N_2 \mu^2 R \sin \beta_j \sin \beta_{j'}}{4i} & \left[(e^{im_1 \zeta} e^{i(\alpha_{j'} - \alpha_j)} e^{i\Delta\phi_{j'}} - e^{-in_1 \zeta} e^{-i(\alpha_j - \alpha_{j'})} e^{-i\Delta\phi_j}) \delta_{k_2,0} \delta_{k_2,1} \right. \\
 & + (e^{i(m_1 - 2n_1) \zeta} e^{i(\alpha_{j'} - \alpha_j)} e^{i(\Delta\phi_{j'} - 2\Delta\phi_j)} - e^{-i(n_1 - 2m_1) \zeta} e^{-i(\alpha_j - \alpha_{j'})} e^{-i(\Delta\phi_j - 2\Delta\phi_{j'})}) \delta_{k_2,1} \delta_{k_2,2} \\
 & - (e^{-i(m_1 - 2n_1) \zeta} e^{-i(\alpha_{j'} - \alpha_j)} e^{-i(\Delta\phi_{j'} - 2\Delta\phi_j)} - e^{i(n_1 - 2m_1) \zeta} e^{i(\alpha_j - \alpha_{j'})} e^{i(\Delta\phi_j - 2\Delta\phi_{j'})}) \delta_{k_2,-2} \delta_{k_2,-1} \\
 & \left. - (e^{-im_1 \zeta} e^{-i(\alpha_{j'} - \alpha_j)} e^{-i\Delta\phi_{j'}} - e^{in_1 \zeta} e^{i(\alpha_j - \alpha_{j'})} e^{i\Delta\phi_j}) \delta_{k_2,-1} \delta_{k_2,0} \right] \\
 & + \frac{N_2 \mu^2 (h(n_1 - m_1) + \Delta z_j - \Delta z_{j'})}{2} \left[\right. \\
 & \sin \beta_j \cos \beta_{j'} (e^{in_1 \zeta} e^{i\alpha_j} e^{i\Delta\phi_j} \delta_{k_2,-1} \delta_{k_2,0} + e^{-in_1 \zeta} e^{-i\alpha_j} e^{-i\Delta\phi_j} \delta_{k_2,0} \delta_{k_2,1}) \\
 & \left. - \sin \beta_{j'} \cos \beta_j (e^{im_1 \zeta} e^{i\alpha_{j'}} e^{i\Delta\phi_{j'}} \delta_{k_2,0} \delta_{k_2,1} + e^{-im_1 \zeta} e^{-i\alpha_{j'}} e^{-i\Delta\phi_{j'}} \delta_{k_2,0} \delta_{k_2,-1}) \right]. \quad (5.24)
 \end{aligned}$$

From this, it is seen that every term in S contains a product of two conflicting Kronecker deltas for k_2 , which means that $S = 0$, which in turn implies that, indeed, $R_k^{\text{cr}} = 0$. This proves the decomposition Eq. (5.10) in the main text.

5.5.4 Supplementary Note 4: Long-tube SOLP spectra

In this note, we address the general features of the SOLP spectra for tubular aggregates. For this purpose, we consider the limit of long tubular aggregates and use the stack-of-rings picture of the tube structure, where the tube is viewed as a perpendicular stack of N_1 rings, with each ring containing the centers of N_2 unit cells. Considering the most general case, where each unit cell contains an arbitrary number of molecules, each molecule n in the tube is labeled by three numbers $(n_1, n_2, j) \equiv (\mathbf{n}, j)$, where $n_1 = 1, \dots, N_1$ labels the rings, $n_2 = 1, \dots, N_2$ labels the unit cells in each ring, and $j = 1, \dots, p$ labels the molecules inside the unit cell.

Tubular aggregates automatically have periodic boundary conditions in the ring direction, implying that the eigenstates as a function of n_2 have Bloch character, see Eq. (5.22). In the long-tube limit, we may also impose periodic boundary conditions along the tubular axis. Then the exciton eigenstates take the form

$$|\mathbf{k}, \sigma\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}, j} e^{ik_1 \phi_1 n_1 + ik_2 \phi_2 n_2} \varphi_{\sigma j}(\mathbf{k}) |\mathbf{n}, j\rangle, \quad (5.25)$$

where $N = N_1 N_2$, $\phi_1 = 2\pi/N_1$, $\phi_2 = 2\pi/N_2$, the transverse wave number k_2 takes integer values as specified below Eq. (5.22), and similar for the longitudinal wave number k_1 (replacing N_2 by N_1). Each eigenstate is labeled by its quasi-momentum $\mathbf{k} = (k_1, k_2)$ and the index σ , which numbers the p separate Davydov bands arising from the fact that we deal with p molecules per unit cell. Finally, $\varphi_{\sigma j}(\mathbf{k})$ is the j th component of σ th eigenvector of the $p \times p$ Hamiltonian matrix for quasi-momentum $\mathbf{k}$:

$$H_{jj'}(\mathbf{k}) = \delta_{j,j'} E_{\text{mol}} + J_{jj'}(\mathbf{k}) \quad (5.26)$$

with

$$J_{jj'}(\mathbf{k}) = \sum_{\mathbf{n}}' J_{\mathbf{n}jj'} e^{ik_1 \phi_1 n_1 + ik_2 \phi_2 n_2}, \quad (5.27)$$

where $J_{\mathbf{n}jj'}$ is the interaction between molecules j and j' in unit cells that are n_1 rings separated from each other and n_2 positions along the ring direction. The prime on the summation excludes terms with $\mathbf{n} = \mathbf{0}$ when $j = j'$. The corresponding eigenvalue $E_{\mathbf{k}\sigma}$ is the energy of the exciton state $|\mathbf{k}, \sigma\rangle$. For every $\mathbf{k}$, finding the eigenstates thus reduces to diagonalizing a $p \times p$ matrix. The great advantage of introducing the Bloch states, however, does not only reside in the numerics (small

diagonalizations for every $\mathbf{k}$), but also in the selection rules: The symmetry dictates that in every Davydov band σ only three states contribute to the SOLP and SOCD spectra, namely, the state with $\mathbf{k} = \mathbf{0}$ (totally symmetric exciton state) and the ones with $\mathbf{k} = \pm \mathbf{h}$ with $\mathbf{h} = (\frac{\zeta}{\phi_1}, 1)$ (helical exciton states) (see Ref. 39 and below).

For linearly polarized light (SOLP spectroscopy), the exciton transition dipoles are crucial quantities, given by

$$\boldsymbol{\mu}_{\mathbf{k}\sigma} = \langle g | \boldsymbol{\mu} | \mathbf{k}, \sigma \rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}, j} \boldsymbol{\mu}_{\mathbf{n}j} e^{ik_1 \phi_1 n_1 + ik_2 \phi_2 n_2} \varphi_{\sigma j}(\mathbf{k}). \quad (5.28)$$

Using $\boldsymbol{\mu}_{\mathbf{n}j}$ as given in Eq. (5.21), the summations over n_1 and n_2 in Eq. (5.28) may easily be carried out, leading to the result that for each σ only three exciton states have a non-zero transition dipole to the ground state. These states are $|\mathbf{k}, \sigma\rangle = |\mathbf{0}, \sigma\rangle$ and $|\mathbf{k}, \sigma\rangle = |\pm \mathbf{h}, \sigma\rangle$. The derivation is analogous to the one in Ref. 39, where tubular aggregates with one molecule per unit cell were considered. Exciton states with $\mathbf{k} = \mathbf{0}$ (for each Davydov band) have a transition dipole oriented parallel to the tubular axis and thus contribute to $A_{\parallel}(E)$. The states with $\mathbf{k} = \pm \mathbf{h}$ within each band are degenerate and have dipoles oriented perpendicular to the tubular axis and perpendicular to each other; hence they contribute to $A_{\perp}(E)$. Properly accounting for the $\varphi_{\sigma j}(\mathbf{k})$, one arrives at

$$A_{\parallel}(E) = \frac{1}{\pi} \sum_{\sigma} M_{\mathbf{0}\sigma} \frac{\Gamma_{\mathbf{0}\sigma}}{(E - E_{\mathbf{0}\sigma})^2 + \Gamma_{\mathbf{0}\sigma}^2}, \quad (5.29)$$

with $M_{\mathbf{0}\sigma}$ the oscillator strength $|\mu_{\mathbf{0}\sigma}|^2$ given explicitly by

$$M_{\mathbf{0}\sigma} = N\mu^2 \left| \sum_j \varphi_{\sigma j}(\mathbf{0}) \cos \beta_j \right|^2. \quad (5.30)$$

Similarly,

$$A_{\perp}(E) = \frac{1}{\pi} \sum_{\sigma} M_{\mathbf{h}\sigma} \frac{\Gamma_{\mathbf{h}\sigma}}{(E - E_{\mathbf{h}\sigma})^2 + \Gamma_{\mathbf{h}\sigma}^2}, \quad (5.31)$$

with $M_{\mathbf{h}\sigma}$ the oscillator strength $|\mu_{\mathbf{h}\sigma}|^2$ given explicitly by

$$M_{\mathbf{h}\sigma} = \frac{N\mu^2}{2} \left| \sum_j \varphi_{\sigma j}(\mathbf{h}) \sin \beta_j e^{-i\Delta\phi_j - i\alpha_j} \right|^2, \quad (5.32)$$

where the factor 1/2 arises from the fact that $A_{\perp}(E)$ only probes half of the oscillator strength perpendicular to the tube's axis. From the above, one easily recovers the results obtained in Ref. 39 for the situation with one molecule per unit cell, where the $\mathbf{k} = \mathbf{0}$ state has oscillator strength $N\mu^2 \cos^2 \beta$ and the states $\mathbf{k} = \pm \mathbf{h}$ both have oscillator strength $N\mu^2 \sin^2 \beta/2$.

As explained in the main text, the tubular aggregates found in chlorosomes have two molecules per unit cell, which only differ from each other in the angle $\pm\alpha = \pm 4^\circ$. This leads to two Davydov components for each $\mathbf{k}$ value, i.e., in total 6 states with non-zero oscillator strength. However, due to the small difference in orientation between both molecules, the lower Davydov component ($\sigma = 1$) totally dominates the SOLP spectrum; the higher-energy Davydov band ($\sigma = 2$) has negligible contribution to the total spectrum, as is shown in Fig. 5.12.

Figure 5.12: Contributions to the SOLP spectra $A_{\parallel}(E)$ and $A_{\perp}(E)$ for tubular aggregates found in chlorosomes in the long-tube limit (periodic boundary conditions). The structural and energetic parameters were taken as specified in the main text, using a radius of $R = 15.42$ nm ($N_2 = 10$) and a length of $L = 500$ nm ($N = N_1 N_2 = 46640$) to obtain the energies $E_{0\sigma}$ and $E_{h\sigma}$, and the corresponding eigenvectors $\varphi_{\sigma j}(\mathbf{0})$ and $\varphi_{\sigma j}(\mathbf{h})$ from Eqs. (5.26) and (5.27). (a) $A_{\parallel}(E)$ and $A_{\perp}(E)$ arising from the lower-energy Davydov band ($\sigma = 1$). (b) and (c) $A_{\parallel}(E)$ and $A_{\perp}(E)$, respectively, arising from the second Davydov band (note the differences in the vertical scale with the first band). (d) Comparison between the spectra for the $\sigma = 1$ Davydov components to the spectrum where we set $\alpha = 0^\circ$, approximating the aggregate by a one molecule per unit cell structure. Clearly, this yields an excellent approximation.

As is clear from Fig. 5.12(d), not surprisingly, the dominant contributions to the spectra can be approximated in an excellent way by approximating the small angle α by $\alpha = 0^\circ$. This approximation implies that we treat the aggregate as having

just one molecule per unit cell (with reduced lattice constant a), in which the second Davydov band is absent. Figure 5.13 demonstrates how for shorter aggregates, the spectra $A_{\parallel}(E)$ and $A_{\perp}(E)$ approach the results obtained in the long-tube limit. As is observed, finite-length effects lead to small blue shifts of the absorption peaks for both polarization directions. Furthermore, the periodic boundary conditions in the axis direction are then no longer valid, breaking the selection rules on k_1 , which consequently leads to satellite peaks that are blue shifted compared to the main peaks. These satellite peaks are visible for the tubes of length $L = 25$ nm and $L = 15$ nm.

5.5.5 Supplementary Note 5: Long-tube SOCD spectra

In this note, we concentrate on the general features of the SOCD spectra for tubular aggregates. Similar to Supplementary Note 4 on the SOLP spectra, we consider the long-tube limit with periodic boundary conditions and use the stack-of-rings picture and corresponding notations of the tubular structure. As in Note 4, the exciton eigenstates stated are indicated as $|\mathbf{k}, \sigma\rangle$, with $\mathbf{k}$ the quasi-momentum and σ labeling the Davydov band.

In Supplementary Note 3, we deduced

$$CD_{\mathbf{Q}}(E) = CD_{\parallel}(E) \cos^2 \xi + CD_{\perp}(E) \sin^2 \xi, \quad (5.33)$$

where the rotational strengths for $CD_{\parallel}(E)$ and $CD_{\perp}(E)$ are given by Eqs. (5.17) and (5.18), respectively. Using Eqs. (5.20) and (5.21), and the exciton states $|\mathbf{k}, \sigma\rangle$ according to Eq. (5.25), one again arrives at strong selection rules, which dictate that only the states $|\mathbf{k} = \pm \mathbf{h}, \sigma\rangle$ contribute to $CD_{\parallel}(E)$, while only the states $|\mathbf{k} = \mathbf{0}, \sigma\rangle$ and $|\mathbf{k} = \pm \mathbf{h}, \sigma\rangle$ contribute to $CD_{\perp}(E)$. Explicitly, one arrives at

$$CD_{\parallel}(E) = \frac{\lambda |\mathbf{q}|^2}{8\pi^2} \sum_{\sigma} \left[\underbrace{(U_{-\mathbf{h}\sigma} + U_{\mathbf{h}\sigma}) \frac{\Gamma_{\mathbf{h}\sigma}}{(E - E_{\mathbf{h}\sigma})^2 + \Gamma_{\mathbf{h}\sigma}^2}}_{\text{non-dispersive}} + \underbrace{(V_{-\mathbf{h}\sigma} + V_{\mathbf{h}\sigma}) \frac{2\Gamma_{\mathbf{h}\sigma}(E_{\mathbf{h}\sigma} - E)}{((E - E_{\mathbf{h}\sigma})^2 + \Gamma_{\mathbf{h}\sigma}^2)^2}}_{\text{dispersive}} \right], \quad (5.34)$$

where we used the degeneracy $E_{-\mathbf{h},\sigma} = E_{\mathbf{h},\sigma}$ and defined the quantities

$$U_{\pm \mathbf{h}\sigma} = \text{Im} \left(\pm N \mu^2 \sum_{j,j'} \varphi_{\sigma j}(\pm \mathbf{h}) \varphi_{\sigma j'}^*(\pm \mathbf{h}) \Delta z_{j'} \sin \beta_j \sin \beta_{j'} e^{\pm i(\alpha_j - \alpha_{j'})} e^{\pm i(\Delta \phi_j - \Delta \phi_{j'})} \right), \quad (5.35)$$

Figure 5.13: Influence of finite-length effects on the SOLP spectra for tubular aggregates using the same structural and energetic parameters as in Fig. 5.12, except that the length was varied, as indicated in the legends. The quasi-analytical result obtained for periodic boundary conditions, pbc, (using $L = 500$ nm to calculate $E_{0\sigma}$ and $E_{h\sigma}$ and the corresponding eigenvectors $\varphi_{\sigma j}(\mathbf{0})$ and $\varphi_{\sigma j}(\mathbf{h})$ from Eqs. (5.26) and (5.27)) are indicated as black curves. For all spectra, the focus here is on the spectral peaks caused by the dominant ($\sigma = 1$) Davydov band (cf. Fig. 5.12(a)). Top panel: $A_{\parallel}(E)$, bottom panel $A_{\perp}(E)$.

and

$$V_{\pm\mathbf{h}\sigma} = \text{Re}\left(\frac{\mp N\mu^2 h}{2} \sum_{j,j'} \varphi_{\sigma j}(\pm\mathbf{h}) \varphi_{\sigma j'}^*(\pm\mathbf{h}) v_{\pm\mathbf{h}} \sin \beta_j \sin \beta_{j'} e^{\pm i(\alpha_j - \alpha_{j'})} e^{\pm i(\Delta\phi_j - \Delta\phi_{j'})}\right), \quad (5.36)$$

with $N = N_1 N_2$, as before, and the group velocities

$$v_{\pm\mathbf{h}} = \left(\frac{dE_{\mathbf{k},\sigma}}{d(k_1 \phi_1)} \right)_{\mathbf{k}=\pm\mathbf{h}}. \quad (5.37)$$

The derivations of these expressions are analogous to those in Ref. 39 for the situation with one molecule per unit cell. Similarly, one obtains

$$CD_{\perp}(E) = \frac{\lambda|\mathbf{q}|^2}{8\pi^2} \sum_{\sigma} \left[S_{0\sigma} \frac{\Gamma_{0\sigma}}{(E - E_{0\sigma})^2 + \Gamma_{0\sigma}^2} - (S_{-\mathbf{h}\sigma} + S_{\mathbf{h}\sigma}) \frac{\Gamma_{\mathbf{h}\sigma}}{(E - E_{\mathbf{h}\sigma})^2 + \Gamma_{\mathbf{h}\sigma}^2} \right], \quad (5.38)$$

with

$$S_{0\sigma} = \text{Re}\left(N\mu^2 R \sum_{j,j'} \varphi_{\sigma j}(\mathbf{0}) \varphi_{\sigma j'}^*(\mathbf{0}) \sin \beta_j \cos \beta_{j'} \cos \alpha_j\right), \quad (5.39)$$

and

$$S_{\pm\mathbf{h}\sigma} = \text{Re}\left(\frac{N\mu^2 R}{2} \sum_{j,j'} \varphi_{\sigma j}(\pm\mathbf{h}) \varphi_{\sigma j'}^*(\pm\mathbf{h}) \sin \beta_j \cos \beta_{j'} e^{\pm i(\Delta\phi_j - \Delta\phi_{j'})} e^{\pm i\alpha_j}\right). \quad (5.40)$$

Note that due to the relation $H_{jj'}(+\mathbf{k}) = H_{jj'}^*(-\mathbf{k})$, the eigenvectors with $-\mathbf{k}$ can be obtained from those with $+\mathbf{k}$ by defining $\varphi_{\sigma j}(-\mathbf{k}) = \varphi_{\sigma j}^*(+\mathbf{k})$. Consequently, $U_{+\mathbf{h}\sigma} = U_{-\mathbf{h}\sigma}$, $V_{+\mathbf{h}\sigma} = V_{-\mathbf{h}\sigma}$, and $S_{+\mathbf{h}\sigma} = S_{-\mathbf{h}\sigma}$.

For one molecule per unit cell, $U_{\pm\mathbf{h}\sigma} = 0$ and the expressions for $V_{\pm\mathbf{h}\sigma}$, $S_{0\sigma}$, and $S_{\pm\mathbf{h}\sigma}$ simplify, to yield

$$\begin{aligned} CD_{\mathbf{q}}^{\text{mol}}(E) &= \frac{\lambda|\mathbf{q}|^2}{8\pi^2} N\mu^2 h v_{\mathbf{h}} \sin^2 \beta \frac{2\Gamma_{\mathbf{h}\sigma}(E_{\mathbf{h}\sigma} - E)}{\left((E - E_{\mathbf{h}\sigma})^2 + \Gamma_{\mathbf{h}\sigma}^2\right)^2} \cos^2 \xi \\ &+ \frac{\lambda|\mathbf{q}|^2}{8\pi^2} \frac{N\mu^2 R \sin 2\beta \cos \alpha}{2} \left[\frac{\Gamma_{\mathbf{0}}}{(E - E_{\mathbf{0}})^2 + \Gamma_{\mathbf{0}}^2} - \frac{\Gamma_{\mathbf{h}}}{(E - E_{\mathbf{h}})^2 + \Gamma_{\mathbf{h}}^2} \right] \sin^2 \xi, \end{aligned} \quad (5.41)$$

which upon averaging over an isotropic distribution of directions of the incoming light relative to the tubular axis, reduces to the same expression as obtained in Ref. 39 for the ensemble CD spectrum of tubular aggregates with one molecule per unit cell. In that analysis, the ensemble CD spectrum was found to be composed of “ring” and “helical” contributions. In the general SOCD spectra derived here,

$CD_{\parallel}(E)$ is found to be totally determined by helical contributions (the terms with $U_{\pm h\sigma}$ (non-dispersive contributions) and those with $V_{\pm h\sigma}$ (dispersive) in Eq. (5.34)), while $CD_{\perp}(E)$ only has ring contributions (terms with $S_{0\sigma}$ and $S_{\pm h\sigma}$ in Eq. (5.38)).

The presence of two molecules per unit cell in the tubular aggregates of chlorosomes leads to the Davydov splitting of the superradiant states; the various contributions to $CD_{\parallel}(E)$ and $CD_{\perp}(E)$ are presented in Fig. 5.14(a)-(e). As in the case of SOLP spectroscopy (Supplementary Note 4), the low-energy Davydov components ($\sigma = 1$) are seen to dominate the entire spectrum, except for the case of the non-dispersive helical contributions deriving from the terms with $U_{\pm h\sigma}$, where both Davydov components have about equal strength. Yet, as is seen in Fig. 5.14, the non-dispersive helical terms contribute two orders of magnitude less than the ring and dispersive helical contributions from the lowest-energy Davydov components ($\sigma = 1$) and therefore can be ignored for chlorosomes, as can be the other contributions from the higher-energy Davydov components ($\sigma = 2$). Consequently, the effects of having a Davydov splitting can be ignored in the analysis of the SOCD spectra of tubular aggregates found in chlorosomes. This is further demonstrated in Fig. 5.14(f), where we compare $CD_{\parallel}(E)$ and $CD_{\perp}(E)$ in the energy region of the lower-energy Davydov band to the results obtained by setting the angle $\alpha = 0^\circ$, thereby creating an effective structure with one molecule per unit cell. Like in the case of SOLP (Fig. 5.12(d)), the effects of this replacement (and thus of the dimerization of the lattice) are indeed seen to be negligible.

An important observation from Fig. 5.14 is that the dominant contributions to $CD_{\parallel}(E)$ and $CD_{\perp}(E)$ both have a dispersive (S-type) shape, of opposite sign, which closely overlap. This feature makes the observed spectrum highly sensitive to the angle of incidence ξ and to small shifts of the various features as well as changes in their relative magnitudes originating from, e.g., length variations. The effects of length variations are shown in Fig. 5.15.

5.5.6 Supplementary Note 6: SOLP and SOCD for four chlorosomes with $\Delta E \approx 40 \text{ cm}^{-1}$

In Sec. 5.3.2 of the main text, we showed that the unique identification of the average length and average radius of tubular molecular aggregates within individual chlorosomes requires the combination of SOLP and SOCD spectroscopy. For illustration, we showed an example where four different chlorosomes containing tubular molecular aggregates with varying length and radius (Fig. 5.8, left column) were found with the same $\Delta E \approx 56 \text{ cm}^{-1}$ (energy separation between $A_{\parallel}(E)$ and $A_{\perp}(E)$) as obtained from SOLP spectroscopy (Fig. 5.8, middle column). SOCD spectroscopy (Fig. 5.8, right column) then helped to identify the average length and radius of the tubular aggregates within each individual chlorosome. To show that this result is

Figure 5.14: Contributions to the SOCD spectra $CD_{\parallel}(E)$ (i.e., $\xi = 0^\circ$) and $CD_{\perp}(E)$ (i.e., $\xi = 90^\circ$) for tubular aggregates found in chlorosomes in the long-tube limit (periodic boundary conditions). The structural and energetic parameters were taken as specified in the main text, using a radius of $R = 15.42 \text{ nm}$ ($N_2 = 10$) and a length of $L = 400 \text{ nm}$ ($N = N_1 N_2 = 37320$) to obtain the energies $E_{0\sigma}$ and $E_{h\sigma}$, and the corresponding eigenvectors $\varphi_{\sigma j}(0)$ and $\varphi_{\sigma j}(h)$ from Eqs. (5.26) and (5.27). Panels (a)-(e) present the various contributions to the two spectra, separated by which superradiant states ($|k, \sigma\rangle$) leads to the contributions shown (see legends); the contributions from $|h, \sigma\rangle$ and $|-h, \sigma\rangle$ have been added, as these transitions are degenerate. Panel (f) shows the comparison between the spectra arising from the $\sigma = 1$ Davydov components to the spectrum where we set $\alpha = 0^\circ$, approximating the aggregate by a one molecule per unit cell structure. Clearly, this yields an excellent approximation.

not unique to the particular case shown in Fig. 5.8 in the main text, we present in Fig. 5.16 a similar analysis for four chlorosomes randomly generated using four sets of $(\bar{L}, \bar{R})$ combinations (12, 15.42), (20, 18.50), (30, 21.59), (42, 24.67) (all numbers in nm) which gave $\Delta E \approx 40 \text{ cm}^{-1}$ in case all aggregates inside an individual chlorosome are identical. The histograms for the lengths and the radii of the aggregates within each chlorosome are displayed in the left column of Fig. 5.16. The SOLP spectra for the four chlorosomes considered here (Fig. 5.16, middle column) do not differ significantly and all give $\Delta E \approx 40 \text{ cm}^{-1}$. The SOCD spectra shown in the right col-

Figure 5.15: Influence of finite-length effects on the SOCD spectra for tubular aggregates using the same structural and energetic parameters as in Fig. 5.14, except that the length was varied, as indicated in the legends. The quasi-analytical result obtained for periodic boundary conditions, pbc, (using $L = 400$ nm to calculate $E_{0\sigma}$ and $E_{h\sigma}$, and the corresponding eigenvectors $\varphi_{\sigma j}(\mathbf{0})$ and $\varphi_{\sigma j}(\mathbf{h})$ from Eqs. (5.26) and (5.27)) are indicated as black curves. For all spectra, the focus here is on the spectral peaks caused by the dominant ($\sigma = 1$) Davydov band (cf. Fig. 5.14(a) and (b)). Top panel: $CD_{\parallel}(E)$, bottom panel $CD_{\perp}(E)$. Changes in the length of tubular aggregates influence the energy positions of the superradiant states ($E_{0\sigma}, E_{\pm h\sigma}$) as well as the relative magnitude of their respective contributions. At small lengths, the ring and helical contributions are of similar magnitude, but as the length increases, the helical contribution becomes more important.

umn of Fig. 5.16 show that for $\xi = 0^\circ$ and $\xi = 90^\circ$, also these spectra do not differ significantly for the four chlorosomes. However, the SOCD spectra for $\xi = 45^\circ$ do show significant differences for the four cases, implying that the combination of SOLP and SOCD spectroscopy for $\xi = 45^\circ$ indeed allows to distinguish the average length and radius of the tubular aggregates within these four individual chlorosomes.

Figure 5.16: Left column: histograms for the occurrences of the length (blue) and the radius (red) of the 50 tubular aggregates in four randomly generated chlorosomes using Poisson distributions for L and R with averages $\bar{L}$ and $\bar{R}$, respectively, specified in the text of this note, with mean and standard deviation of each histogram as indicated. Middle column: SOLP spectra calculated for these individual chlorosomes, with light linearly polarized parallel to the tubular axis ($A_{\parallel}(E)$, blue solid line) and perpendicular ($A_{\perp}(E)$, red dashed line); the black dashed-dotted line shows the single-chlorosome LD spectrum. $A_{\parallel}(E)$ and $A_{\perp}(E)$ are normalized to the largest one of the peak intensities of the two; each LD spectrum is normalized to its maximum absolute intensity. Right column: SOCD spectra $CD_{\xi}(E)$ calculated for these individual chlorosomes for three angles between the direction of incidence of the light and the chlorosome's tubular axis: $\xi = 0^\circ$ (solid blue line), 45° (red dashed line), and 90° (black dashed-dotted line). Each SOCD spectra is normalized to its maximum absolute intensity.

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Scaling Relations of Exciton Diffusion in Linear Aggregates with Static and Dynamic Disorder

Exciton diffusion plays an important role in many opto-electronic processes and phenomena. Understanding the interplay of intermolecular coupling, static energetic disorder, and dephasing caused by environmental fluctuations (dynamic disorder) is crucial to optimize exciton diffusion under various physical conditions. We report on a systematic analysis of the exciton diffusion constant in linear aggregates using the Haken-Strobl-Reineker model to describe this interplay. We numerically investigate the static-disorder scaling of (i) the diffusion constant in the limit of small dephasing rate, (ii) the dephasing rate at which the diffusion is optimized, and (iii) the value of the diffusion constant at the optimal dephasing rate. Three scaling regimes are found, associated with, respectively, fully delocalized exciton states (finite-size effects), weakly localized states, and strongly localized states. The scaling powers agree well with analytically estimated ones. In particular, in the weakly localized regime, the numerical results corroborate the so-called quantum Goldilocks principle to find the optimal dephasing rate and maximum diffusion constant as a function of static disorder, while in the strong-localization regime, these quantities can be derived fully analytically.

6.1 INTRODUCTION

Electronic excitation energy transport (EET) is an important process in many materials and biological systems. Therefore, studies of EET go back many decades already.^[1–3] Examples of systems where EET is of crucial importance are luminescent materials,^[4,5] light emitting diodes,^[6,7] scintillators,^[8,9] photodetectors,^[10,11] photovoltaic systems,^[12,13] and photosynthetic light-harvesting systems.^[14–17] In all these cases, EET has important effects on the efficiency of the system's function. For instance, in photovoltaic systems, the transport of photo-induced electronic excitations to the charge separating interface has to be fast enough to beat radiative and non-radiative decay channels.^[18–22] Similarly, in photosynthetic antennae, the transport time of the excitation to the reaction center has to be small compared to the fluorescence lifetime and other relaxation times.^[14,15,23–28] While many results, both theoretical and experimental, are known, the study of EET remains an intriguing and timely area of research.^[27,29–36] This chapter aims at increasing the quantitative understanding of the complicated interplay between intermolecular interactions, static energy disorder, and dephasing in determining the diffusion constant that characterizes EET in one-dimensional exciton systems.

EET is driven by resonant interactions between nearby molecules (or atoms/ions) that coherently couple the state with one molecule in the excited state and the other in its ground state to the state where the excitation has swapped location.^[2,3,15] Resonant interactions are often caused by the Coulomb interaction between the transition dipoles of the two molecules involved but, especially for forbidden transitions, may also be caused by exchange interactions resulting from weak orbital overlap.^[37] For two molecules with exactly the same transition energy (no static disorder) and in the absence of dephasing of the molecular excitations (no fluctuations or dynamic disorder), EET takes place in a back and forth oscillation of the excitation energy between both molecules. In a system of many molecules without static and dynamic disorder, EET takes place as a wave packet motion, leading to coherent or ballistic transport, with the spread of the excitation covering distances that linearly scale with time.^[3,38,39]

In realistic systems, the environment or molecular degrees of freedom other than the excitation of interest (such as vibrations) will lead to static as well as dynamic disorder. The former leads to localization of the exciton states,^[40–46] which always hinders transport, while the latter leads to dephasing, which may enhance or slow down transport, depending on the conditions.^[3,15,29,39] This already hints at the complex interplay between the typical resonant interaction, the amount of static disorder, and the dephasing rate.^[29,47–53]

A seminal step in the understanding of EET was made by Förster,^[54] who analyzed the energy transfer between two resonant molecules in the limit where the

rate of dephasing (caused by vibrational degrees of freedom) is much larger than the resonant dipole-dipole interaction. This leads to incoherent energy transfer with the exponential decay of the excitation on the initially excited molecule (the donor) with the Förster resonant energy transfer (FRET) rate, which scales inversely proportional to the sixth power of the distance between the donor and acceptor. This EET rate has been used to characterize intermolecular distances (spectroscopic ruler).^[55–57] In the past 20 years, the theory of incoherent energy transfer has been generalized to describe systems where the excitation is initially spread over a collection of closely coupled donor molecules that are weakly coupled to an assembly of molecules forming the acceptor system (multichromophore-FRET or MC-FRET).^[58–63] In the incoherent limit, the interactions between donor and acceptor molecules are treated as weak perturbations relative to the dephasing dynamics.

In extended systems of many identical molecules (no static disorder) coupled to each other through resonant interactions, the ballistic (coherent) transport occurring in the absence of dephasing will at finite dephasing rates change to diffusive exciton transport at long times (large distances), characterized by the diffusion constant.^[29,39] At short times/distances, the transport may still be ballistic, depending on the ratio of the typical (near-neighbor) resonant interaction and the dephasing rate. Adding static disorder in the molecular transition energies makes the situation more realistic as well as complicated.^[29,48–51,64–69] Static disorder will localize the exciton states, which imposes natural boundaries to the extent over which ballistic transport can take place; in the absence of dephasing caused by energy fluctuations, the diffusion constant therefore tends to zero for systems with strong enough static disorder. In one-dimensional chains with finite static disorder, all states are localized, leading to a vanishing diffusion constant for zero dephasing rate (low temperatures).^[40–42,45] Adding (weak) dephasing will allow the excitons to jump between neighboring localization domains, allowing for a finite diffusion constant that grows with the dephasing rate. This is sometimes referred to as “environmentally assisted quantum transport”.^[48–51] At a large dephasing rate, the phase coherence between neighboring molecules within localization domains will be destroyed quickly compared to the time scale associated with the resonant interactions and the diffusion constant will diminish again, inversely proportional to the dephasing rate (classical limit). In between these extremes, an optimal dephasing rate exists where the diffusion constant reaches its maximum value.

While the above qualitative picture is well understood, the detailed analysis of the interplay of resonant interactions, static disorder, and dephasing is complicated. Various approaches are known, which all have the property that they can bridge the gap between the coherent and incoherent limits. These include (i) stochastic models for the evolution of the exciton wave function or the exciton density operator, of which the Haken-Strobl-Reineker (HSR) model^[39,70,71] probably is the best-

known representative, and (ii) methods that integrate out bath degrees of freedom to reach an equation for the exciton density operator, usually in combination with perturbative steps.^[3] Here, well known examples are Redfield theory^[72] and its more limited varieties, namely, the Pauli Master equation^[3,73] as well as the Generalized Master equation^[39,74] for the populations of the exciton states with environmentally induced transfer rates, (iii) wave function methods, such as surface hopping^[75–77] and the numerical integration of the Schrödinger equation (NISE),^[36,78,79] and (iv) the Hierarchy of Equations of Motion (HEOM).^[80,81] All these methods come with their own advantages and disadvantages. In addition, simple analytical approximations have been developed or hypothesized for transport characteristics, based on scaling arguments or interpolations between limiting cases, for instance, for the diffusion constant as a function of static disorder (localization size) and dephasing rate.^[29,64,82,83]

In this chapter, we use the HSR model to conduct a systematic study of the EET diffusion constant in a one-dimensional exciton system with static disorder as well as white-noise dynamic fluctuations. We recover the above-described qualitative behavior of the diffusion constant as a function of dephasing rate and quantitatively study its dependence on the magnitude of the static disorder. In particular, we find the static-disorder scaling of the diffusion constant at small dephasing rate, the optimal dephasing rate, and the maximum diffusion constant and show that three regimes for these scaling relations exist, which may all be understood well and whose scaling powers can be recovered analytically.

The remainder of this chapter is organized as follows. In Sec. 6.2, we introduce the HSR model for the exciton dynamics and the expression for the diffusion constant that can be derived in this model. Subsequently, in Sec. 6.3, we present analytical results for the diffusion constant in the limit of vanishing static disorder (homogeneous system) and the strong-static-disorder limit. Next, in Sec. 6.4, we will present and discuss the results from our numerical analysis of the diffusion constant as a function of static disorder and dephasing rate and we discuss how the numerically obtained scaling relations in the various static disorder regimes compare to the analytical results and estimates. Finally, in Sec. 6.5, we summarize and conclude.

6.2 MODEL AND DIFFUSION CONSTANT

6.2.1 Model

We consider a one-dimensional Frenkel exciton system, i.e., a linear chain of N equidistant molecules that may be considered as two-level systems. The transition energy of each molecule has a static disorder component as well as a dynamic fluc-

tuation (dynamic disorder).

The dynamics of such a system is then described by the corresponding time-dependent Hamiltonian,

$$H(t) = H_0 + V(t), \quad (6.1)$$

with

$$H_0 = \sum_{n,m} H_{nm} |n\rangle\langle m| = \sum_n \epsilon_n |n\rangle\langle n| + \sum_{n,m \neq n} J_{nm} |n\rangle\langle m|, \quad (6.2)$$

the exciton Hamiltonian with static energy disorder ϵ_n and excitation transfer interactions J_{nm} and

$$V(t) = \sum_n \delta\epsilon_n(t) |n\rangle\langle n|, \quad (6.3)$$

the fluctuating part representing the dynamic disorder. Here, $n = 1, \dots, N$ labels the molecules, $|n\rangle$ is the state where molecule n is excited and all other molecules are in the ground state, and ϵ_n is the static disorder offset in the transition energy of molecule n , while $\delta\epsilon_n(t)$ is the dynamic disorder component. The average transition energy is set to zero, i.e., it serves as the reference point for the energy. The static and dynamic disorder components are assumed to be statistically uncorrelated. We use Gaussian static disorder, uncorrelated for different molecules, with zero mean and standard deviation σ : $\langle\epsilon_n\rangle = 0$, $\langle\epsilon_n\epsilon_m\rangle = \sigma^2\delta_{n,m}$. Here and hereafter, $\langle\cdots\rangle$ denotes the average over the static disorder distribution. The symbol $\delta_{n,m}$ denotes the Kronecker delta function.

The dynamic disorder reflects the effect of a fluctuating environment on the electronic transitions. We follow the HSR model and assume that these fluctuations follow a Gaussian white-noise stochastic process, again uncorrelated for different molecules, with zero mean, $\overline{\delta\epsilon_n(t)} = 0$ ($\cdots$ denoting the average over the dynamic stochastic process), and the time-correlation function given by $(\hbar = 1)$ ^[39,70,71]

$$\overline{\delta\epsilon_n(t)\delta\epsilon_m(\tau)} = \Gamma\delta_{n,m}\delta(t-\tau), \quad (6.4)$$

with $\delta(t-\tau)$ being the Dirac delta function. In this model, the fluctuations are fully described by the parameter Γ , which equals the relaxation rate (dephasing rate) of the coherences $\rho_{nm} = \langle n|\hat{\rho}|m\rangle$ between the excited states of different molecules n and m induced by the dynamic environment.^[39,70,71] Here, $\hat{\rho}$ is the density operator of the exciton system, averaged over the fluctuations. Viewed alternatively, Γ also represents twice the dephasing rate of a single-molecule transition, meaning that it also equals the molecular homogeneous linewidth. The white-noise character implies that the spectral density of the fluctuations is broad compared to other frequency scales in the problem (specifically the exciton bandwidth) and turns the HSR into an infinite-temperature model in the sense that it leads to an equilibrium state where all eigenstates of H_0 are equally populated.

Most results in Secs. 6.3 and 6.4 will be shown accounting only for nearest-neighbor interactions (NNIs) J , which simplifies the analytical analysis of the numerical results. The results for long-range dipole-dipole interactions (LRIs) $J/|n-m|^3$ do not show significant changes in the various scaling powers and will be briefly addressed in Sec. 6.4.5. In all cases, three parameters with the dimension of energy (frequency) govern the model: J , σ , and Γ . Depending on the values of these three parameters, the size N of the system may be an important parameter as well. Because the sign of J is not a factor in the high-temperature case considered, we will assume it to be positive and generally display quantities as functions of σ/J and Γ/J .

In the absence of dynamic disorder ($\Gamma = 0$), the system is fully characterized by its exciton eigenstates, which are $|k\rangle = \sum_n \phi_{kn}|n\rangle$, where ϕ_{kn} is the n th element of the k th eigenvector of the matrix H_{nm} . The corresponding eigenvalues E_k denote the exciton energies. In the absence of static disorder ($\sigma = 0$), the eigenstates are completely delocalized over the chain, while at finite σ the states are localized on a number of molecules (N_{loc}) that depends on σ/J (assuming $N > N_{\text{loc}}$). Finite Γ leads to scattering between the exciton states and, as mentioned, dephasing of the coherences ρ_{nm} ($n \neq m$), phenomena that are important for the transport properties.

6.2.2 Diffusion constant: Green-Kubo expression

The exciton dynamics within the HSR model can be obtained in different ways. In the wavefunction description, the stochastic Schrödinger equation for the Hamiltonian Eq. (6.1) may be solved numerically, taking an average of the wavefunction over the realizations of the noise to obtain its time-development.^[29] Alternatively, the density matrix approach can be employed where the average over the white-noise fluctuations can be performed analytically and the equation of motion for the noise-averaged exciton density matrix $\hat{\rho}(t)$ is obtained with the above-mentioned intersite coherence relaxation rate Γ .^[70,71,84] While for non-Gaussian noise, exciton systems may reveal a subdiffusive behavior,^[85] for the Gaussian HSR model, the resulting exciton dynamics was always observed to be diffusive in the long-time limit.^[29] The corresponding EET diffusion constant is then well defined and may be extracted by calculating the mean-squared displacement as

$$D = \lim_{t \rightarrow \infty} \frac{\langle \overline{R^2(t)} \rangle}{2t}, \quad (6.5)$$

with $\langle \overline{R^2(t)} \rangle$ being the squared displacement of an initially point-localized excitation at time t averaged over the dynamic disorder ($\overline{\langle \cdots \rangle}$) and the static disorder ($\langle \langle \cdots \rangle \rangle$).

In the HSR model, instead of explicitly integrating the equations of motion, an expression for D can be derived directly starting from the Green-Kubo^[86] expression for D in terms of the two-time correlation function of the exciton flux operator in the

Heisenberg picture, $\hat{j}(t)$.^[83] In one dimension, this expression reads

$$D = \left\langle \frac{1}{Z_0} \int_0^\infty dt \text{Tr} \left(e^{-H_0/k_B T} \hat{j}(t) \hat{j}(0) \right) \right\rangle, \quad (6.6)$$

where Z_0 is the partition function of the exciton system, k_B is the Boltzmann constant, and T is the temperature. Due to the high-temperature nature of the HSR model, $\frac{1}{k_B T} \rightarrow 0$ and $Z_0 = N$. We note that for infinite chains, the overall average $\langle \cdots \rangle$ is not needed, as the diffusion constant is expected to self-average for chains that are long enough; we included it here because in the numerical simulations, we necessarily consider finite chains.

The flux operator $\hat{j}(t)$ is the time derivative of the exciton position operator defined as $d \sum_n n |n\rangle \langle n|$, with d being the lattice constant. This yields

$$\hat{j} = id \sum_{n, m \neq n} (n - m) J_{nm} |m\rangle \langle n|. \quad (6.7)$$

Due to the fact that $\hat{j}(t)$ only contains intersite coherences, the effect of averaging over the fluctuations in the HSR model is a simple exponential relaxation of $\hat{j}(t)$ with rate Γ . Moreover, the coherent evolution is simply described by the solution of the Heisenberg equation of motion. Together this yields

$$\hat{j}(t) = e^{iH_0 t} \hat{j}(0) e^{-iH_0 t} e^{-\Gamma t}. \quad (6.8)$$

Substituting Eq. (6.8) into Eq. (6.6) and going to the eigenstate representation of H_0 , one arrives at a closed expression for the diffusion constant,

$$D = \sum_{k,l} D_{k,l} = \frac{1}{N} \left\langle \sum_{k,l} \frac{\Gamma}{\Gamma^2 + E_{kl}^2} |j_{kl}|^2 \right\rangle, \quad (6.9)$$

where $E_{kl} = E_k - E_l$ is the energy difference between the exciton states with labels k and l , respectively, and j_{kl} is the kl th matrix element of the flux operator in the exciton basis given by

$$j_{kl} = id \sum_{n, m \neq n} (n - m) \phi_{km}^* \phi_{ln} J_{nm}. \quad (6.10)$$

Equation (6.10) shows explicitly that $j_{kl} = j_{lk}^*$, i.e., $\hat{j}$ is Hermitian. If we restrict to nearest-neighbor interactions, this reduces to

$$j_{kl} = idJ \sum_{n=1}^{N-1} (\phi_{kn}^* \phi_{l, n+1} - \phi_{k, n+1}^* \phi_{ln}). \quad (6.11)$$

We note that the analytical result (Eq. (6.9)) is obtained as a consequence of the white-noise nature of the dynamic disorder in the HSR model, which allows for the analytical solution (Eq. (6.8)) for the flux operator. Alternatively, it is also possible to obtain the diffusion constant from Eq. (6.6) in the more general situation of colored (or non-Markovian) classical noise applicable to lower temperatures, by numerically propagating the wavefunction^[87] as well as for quantum noise by using Redfield equations.^[83]

All numerical calculations of the diffusion constant D in this study are performed by using Eq. (6.9), where the exciton energies E_k and eigenstates ϕ_{kn} are obtained by diagonalizing H_0 of Eq. (6.2). Before turning to those results, however, we first consider the limits of weak (vanishing) and strong static disorder, for which Eq. (6.9) may be worked out analytically.

6.3 ANALYTICAL RESULTS

6.3.1 Homogeneous model with nearest-neighbor interactions

The diffusion constant for a homogeneous ($\sigma = 0$) infinite chain with only nearest-neighbor interactions in the HSR model can be obtained analytically in several ways, e.g., by directly writing the equation of motion for the mean-squared displacement; the result reads $D_{\text{hom}} = 2d^2 J^2 / \Gamma$.^[29,39,83,88,89] It is useful to see how this result also derives from Eq. (6.9). Restricting to nearest-neighbor interactions J leads to the fully delocalized eigenstates,

$$\phi_{kn} = \sqrt{\frac{2}{N+1}} \sin\left(\frac{\pi kn}{N+1}\right), \quad (6.12)$$

with $k = 1, 2, \dots, N$ and the corresponding exciton energies

$$E_k = 2J \cos\left(\frac{\pi k}{N+1}\right). \quad (6.13)$$

This exciton band is symmetric around zero energy and has width $4J$. By using Eq. (6.12) in Eq. (6.11), we obtain

$$j_{kl} = -\frac{2idJ}{N+1} \left(1 - (-1)^{(k-l)}\right) \frac{\sin\left(\frac{\pi k}{N+1}\right) \sin\left(\frac{\pi l}{N+1}\right)}{\cos\left(\frac{\pi k}{N+1}\right) - \cos\left(\frac{\pi l}{N+1}\right)}, \quad (6.14)$$

which is non-zero only for $k-l$ odd. Because of the denominator, terms with $l = k+p$ with $p = \pm 1, \pm 3, \pm 5, \dots$ and $|p| \ll N$ will dominate the summation over l in Eq. (6.9).

This is enhanced by the fact that for those terms, also the denominator $(\Gamma^2 + E_{kl}^2)$ in Eq. (6.9) is minimized. For these terms, Eq. (6.14) gives

$$j_{k,k+p} = \frac{4idJ}{\pi p} \sin\left(\frac{\pi k}{N+1}\right) \quad (p \text{ odd}, |p| \ll N). \quad (6.15)$$

Keeping only these dominant terms in Eq. (6.9), we obtain

$$D_{\text{hom}} = \frac{1}{N} \sum_k \sum_{p=\pm 1, \pm 3, \dots} \frac{\Gamma}{\Gamma^2 + E_{k,k+p}^2} \left(\frac{4dJ}{\pi p}\right)^2 \sin^2\left(\frac{\pi k}{N+1}\right). \quad (6.16)$$

For $|p| \ll N$, one easily shows that $E_{k,k+p} = (2J\pi p \sin(\frac{\pi k}{N+1})) / (N+1)$. Thus, in the limit of very large N , such that $2\pi J/N \ll \Gamma$, Eq. (6.16) reduces to

$$D_{\text{hom}} = \frac{1}{N} \sum_k \sin^2\left(\frac{\pi k}{N+1}\right) \sum_{p=\pm 1, \pm 3, \dots} \frac{1}{\Gamma} \left(\frac{4dJ}{\pi p}\right)^2 = 2d^2 \frac{J^2}{\Gamma}, \quad (6.17)$$

which correctly reproduces the result for the infinite homogeneous chain quoted at the beginning of this section.

This result for D_{hom} has a monotonous dependence on Γ , which tends to infinity for $\Gamma \rightarrow 0$ and does not show an optimum at finite Γ . In the strict $\Gamma = 0$ limit, the homogeneous system, even for infinite size, will never reach diffusive motion. Therefore, the singularity at $\Gamma = 0$ is unphysical, as the diffusion constant at this point is not well defined. We note that in the incoherent limit ($\Gamma \gg J$), the above diffusion constant can also be obtained in a simple way from the Förster EET rate J^2/Γ between two resonant neighboring molecules;^[29,33,39,89] for long chains, the results hold for arbitrary ratio Γ/J , as long as the coherence length set by this ratio is small compared to the system size N .

For finite system size N , Eq. (6.17) for D_{hom} is still expected to hold and be physically meaningful as long as the coherence size is small compared to N , i.e., under the condition $2\pi J/N \ll \Gamma$ used to derive Eq. (6.17). In the other limit where $2\pi J/N \gg \Gamma$, Γ^2 in the denominator of Eq. (6.16) can be ignored and one eventually obtains

$$D_{\text{hom}} = \frac{(N+1)^2}{12} d^2 \Gamma \quad (\text{finite } N, \text{ small } \Gamma), \quad (6.18)$$

which is seen to scale linearly in Γ so that $D \rightarrow 0$ as $\Gamma \rightarrow 0$. Consequently, there is an optimal dephasing rate $\Gamma_{\text{opt}} \approx 2\pi J/N$ where the thus calculated diffusion constant for the finite system reaches a maximum. While, indeed, we will recover this behavior in our numerical calculations, it should be realized that both the diffusion constant (Eq. (6.18)) and the associated Γ_{opt} are finite-size artifacts that lack a physical basis; in the real homogeneous system, one does not expect to see a diffusive behavior for $2\pi J/N \gg \Gamma$ because the motion will be coherent over the entire chain.

6.3.2 Limit of strong localization with nearest-neighbor interactions

We now turn to the opposite limit, where we assume the strong static disorder, $\sigma \gg J$, implying that $N_{\text{loc}} \approx 1$. Also, in this limit, an analytical expression can be derived for D . The simplest approach would be to assume that all eigenstates are localized by the static disorder on a single molecule (monomer), which means that the state labels k and l in Eq. (6.9) are simply replaced by site labels n and m , and $E_n = \omega_n$. Using nearest-neighbor interactions, one then easily arrives at

$$D_{\text{mon}} = \frac{2J^2 d^2}{N} \left\langle \sum_n \frac{\Gamma}{\Gamma^2 + \omega_{n+1,n}^2} \right\rangle = 2J^2 d^2 \left\langle \frac{\Gamma}{\Gamma^2 + \omega_{n+1,n}^2} \right\rangle, \quad (6.19)$$

where $\omega_{n+1,n} = \omega_{n+1} - \omega_n$, the difference of the transition energies of two neighboring molecules, which is a Gaussian random variable with mean zero and standard deviation $\sqrt{2}\sigma$. The second step in Eq. (6.19) is valid because the static disorder average of $\frac{\Gamma}{\Gamma^2 + \omega_{n+1,n}^2}$ is independent of n (actually, one sees here explicitly that even if the average over static disorder is not included in the definition of D (see discussion following Eq. (6.6)); for long enough chains, it still appears in the second step of Eq. (6.19) due to the automatic averaging that arises from $N^{-1} \sum_n$). Carrying out the integral over the Gaussian distribution leads to

$$D_{\text{mon}} = J^2 d^2 \frac{\sqrt{\pi}}{\sigma} \exp\left(-\frac{\Gamma^2}{4\sigma^2}\right) \text{Erfc}\left(\frac{\Gamma}{2\sigma}\right), \quad (6.20)$$

where Erfc is the complementary error function. Using the limiting behaviors of the latter for large and small arguments, this result correctly recovers the expression $2J^2 d^2 / \Gamma$ for $\Gamma \gg \sigma$, while for $\Gamma \ll \sigma$, it leads to

$$D_{\text{mon}} = \sqrt{\pi} \frac{J^2 d^2}{\sigma} \left(1 - \frac{\Gamma}{\sqrt{\pi}\sigma} + \dots\right). \quad (6.21)$$

The latter result does not properly recover the physical expectation that for localized states, the diffusion constant should tend to zero for $\Gamma \rightarrow 0$, owing to the fact that fluctuations are necessary to overcome the energy barriers between localized states.

Apparently, the above monomer approximation is too crude. The reason is that in a long chain there will be occasional instances where nearest-neighbor transition energies will be closer to each other than Γ , even for Γ very small, in which case the associated term in Eq. (6.19) gets too large. In fact, if nearest neighbors happen to have exactly the same transition energy, the associated term will tend to infinity for $\Gamma \rightarrow 0$. Obviously, this is an artifact because two (nearly) resonant molecules, with $|\omega_{n+1,n}| \ll J$, will form dimerized states, delocalized over both molecules and with

an energy separation $> 2J$. This finite energy difference properly makes the diffusion constant vanish for $\Gamma \rightarrow 0$. In order to describe this accurately, instead of assuming states that always are completely localized on individual molecules, we account for the possibility that even for large static disorder ($\sigma \gg J$), states on neighboring molecules may in fact still delocalize over them due to an accidental resonance. We will assume, however, that the probability for a trimer (three neighboring molecules with energy differences all in the order of J or smaller) is too small to occur due to the large static disorder we consider.

We thus consider the contributions of a dimer of neighboring molecules n and $n + 1$ to the diffusion constant (Eq. (6.9)). Following the above assumptions, this dimer defines two eigenstates, labeled $+$ and $-$, on the long chain, with energy difference $E_{+,-}$ obeying $E_{+,-}^2 = \omega_{n+1,n}^2 + 4J^2$. The corresponding eigenvectors on the basis $(|n\rangle, |n + 1\rangle)$ read $(\cos \frac{\theta}{2}, \sin \frac{\theta}{2})$ and $(-\sin \frac{\theta}{2}, \cos \frac{\theta}{2})$, respectively, with $\tan \theta = 2J/\omega_{n+1,n}$. Substituting these eigenstates into Eq. (6.11) yields $|j_{+,-}|^2 = |j_{-,+}|^2 = J^2 d^2$. As a result, the contributions from the dimer states to the diffusion constant (Eq. (6.9)) read

$$D_{+,-} = D_{-,+} = \frac{J^2 d^2}{N} \frac{\Gamma}{\Gamma^2 + 4J^2 + \omega_{n+1,n}^2}. \quad (6.22)$$

We note that for $|\omega_{n+1,n}| \gg J$, this result correctly reduces to the contributions from molecules n and $n + 1$ in the above monomer approximation.

Now, let us consider the contributions to the diffusion constant deriving from the two dimer states $+$ and $-$ for a pair of nearly resonant molecules n and $n + 1$ and a localized state on the neighboring molecule $n + 2$. One easily derives that

$$D_{+,n+2} = D_{n+2,+} = \frac{J^2 d^2}{N} \frac{\Gamma}{\Gamma^2 + (E_+ - \omega_{n+2})^2} \sin^2 \frac{\theta}{2} \quad (6.23)$$

and

$$D_{-,n+2} = D_{n+2,-} = \frac{J^2 d^2}{N} \frac{\Gamma}{\Gamma^2 + (E_- - \omega_{n+2})^2} \cos^2 \frac{\theta}{2}. \quad (6.24)$$

Since we assumed that there are no (close to) resonant trimers in the chain, we have $|\omega_{n+2} - E_+| \gg J$ and $|\omega_{n+2} - E_-| \gg J$. If the dimer molecules indeed are nearly resonant (i.e., $|\omega_{n+1,n}| \lesssim J$), we may replace both $(E_+ - \omega_{n+2})^2$ and $(E_- - \omega_{n+2})^2$ by $\omega_{n+1,n+2}^2 + 4J^2$, which introduces errors of the order of J^2 in the denominators, which is small compared to the original energy differences. This allows us to add the two types of terms in Eqs. (6.23) and (6.24) to obtain

$$D_{+,n+2} + D_{-,n+2} = D_{n+2,+} + D_{n+2,-} = \frac{J^2 d^2}{N} \frac{\Gamma}{\Gamma^2 + 4J^2 + \omega_{n+1,n+2}^2}, \quad (6.25)$$

which effectively again looks like the dimer expression of Eq. (6.22).

From the above, it follows that in the strong-static-disorder limit, we may write the total diffusion constant as the sum over dimer expressions for the pairs of molecules $(n, n+1)$, $(n+1, n+2)$, $(n+2, n+3)$, etc., or

$$D_{\text{dim}} = \frac{2J^2 d^2}{N} \left\langle \sum_n \frac{\Gamma}{\Gamma^2 + 4J^2 + \omega_{n+1,n}^2} \right\rangle = 2J^2 d^2 \left\langle \frac{\Gamma}{\Gamma^2 + 4J^2 + \omega_{n+1,n}^2} \right\rangle. \quad (6.26)$$

We refer to this as the dimer approximation, which is seen to differ from the monomer approximation of Eq. (6.19) through the term $4J^2$ in the denominator. This term indeed takes care of the unphysical behavior of the monomer approximation at small Γ values, as is immediately clear: For $\Gamma \ll J$, we may neglect the Γ^2 term in the denominator and the entire expression will be proportional to Γ , with a finite proportionality constant. In fact, similar to the monomer approximation, also the dimer approximation can be solved analytically, by using the fact that $\omega_{n,n+1}$ obeys a Gaussian distribution with mean 0 and standard deviation $\sqrt{2}\sigma$. This allows us to perform the static disorder average to obtain

$$D_{\text{dim}} = \frac{\sqrt{\pi} d^2 J^2 \Gamma}{\sigma \sqrt{\Gamma^2 + 4J^2}} \exp\left(-\frac{\Gamma^2 + 4J^2}{4\sigma^2}\right) \text{Erfc}\left(\frac{\sqrt{\Gamma^2 + 4J^2}}{2\sigma}\right). \quad (6.27)$$

6

In Sec. 6.4, through comparison to numerically exact calculations of D for a variety of parameters, we will find that this analytical result indeed yields an excellent approximation for $\sigma \gg J$.

For $\Gamma \gg \sigma$ (and thus also $\Gamma \gg |J|$), Eq. (6.27) reduces to $D_{\text{dim}} = 2J^2 d^2 / \Gamma$, which is the familiar result in the classical (strong-noise) limit. In the opposite case of $\Gamma \ll \sigma$ and $\Gamma \ll |J|$, Eq. (6.27) leads to

$$D_{\text{dim}} = \frac{\sqrt{\pi}}{2} \frac{\Gamma}{\sigma} d^2 J, \quad (6.28)$$

i.e., in this limit, the diffusion constant indeed scales proportional to Γ , the physically expected behavior.

6.4 NUMERICAL RESULTS AND DISCUSSION

In this section, we numerically calculate the diffusion constant according to Eq. (6.9) as a function of σ/J and Γ/J and analyze the results in terms of three scaling regimes distinguished by the amount of static disorder: weak static disorder ($N_{\text{loc}} > N$, delocalized states), intermediate static disorder ($1 \ll N_{\text{loc}} \ll N$, weakly localized states), and strong static disorder ($N_{\text{loc}} \approx 1$, strongly localized states). As before, N_{loc} denotes the exciton localization size determined by the static disorder. In all simulations, we use $N = 10000$ for the number of molecules on the chain, and for each σ

value, the results are averaged over 100 random realizations of the static disorder on the chain. Except for Sec. 6.4.5, all results are obtained considering nearest-neighbor interactions J only.

6.4.1 Diffusion constant as a function of static disorder and dephasing rate

In Fig. 6.1, we present a log-log plot of the numerically obtained diffusion constant D as a function of Γ for static disorder values ranging from $\sigma = 0.01J$ to $\sigma = 100J$. For reference, we also display the result $D = 2d^2 J^2 / \Gamma$ for the infinite homogeneous chain. The general features of $D(\Gamma)$ observed in Fig. 6.1 are similar for all values of σ . For small Γ , the diffusion constant grows proportional to Γ (with $D \rightarrow 0$ for $\Gamma \rightarrow 0$), characteristic for the quantum regime, where fluctuations (noise) are needed to promote jumps from one localization domain to another; the proportionality constant depends on the static disorder strength (see Sec. 6.4.2). For large Γ , D decreases again and for all static disorder values approaches the classical result $2d^2 J^2 / \Gamma$. In between these two regimes, D reaches a maximum value at $\Gamma = \Gamma_{\text{opt}}$ that depends on σ (see Sec. 6.4.3); the maximum value D_{max} depends on σ as well (see Sec. 6.4.4).

Figure 6.1: Numerically obtained diffusion constant (D) as a function of dephasing rate (Γ) for a linear chain of $N = 10000$ molecules for various static energy disorder strengths (σ). For reference, the diffusion constant for the infinite homogeneous chain ($\sigma = 0$) is also shown.

It is clear from Fig. 6.1 that for σ small enough, as expected, D increasingly tends

toward the analytical result $2d^2J^2/\Gamma$ obtained for the infinite homogeneous chain. However, as necessarily numerical simulations are performed for finite chains, they always display an optimum dephasing rate and a turnover to a regime $D \propto \Gamma$ for Γ small enough (Eq. (6.18)).

Figure 6.2: Numerically obtained diffusion constant D as a function of dephasing rate Γ for a linear chain of $N = 10000$ molecules for three large values of the static energy disorder strength (solid lines). The dashed lines give the analytical strong-static-disorder result according to Eq. (6.27). Notice that in contrast to Fig. 6.1, D is now plotted on a linear scale.

To show how the numerical results compare to the analytical ones obtained in Sec. 6.3.2 for the limit of strong static disorder, we plot in Fig. 6.2 the diffusion constant as a function of Γ/J for three large values of the static disorder: $\sigma = 10^{0.5}J$, $10J$, and $10^{1.5}J$. Clearly, for $\sigma > 10J$, the analytical result obtained via the dimer approach shows good to excellent agreement with the full numerical calculation. We observe that the approximation tends to be of a lesser quality for lower Γ values than for higher ones. The explanation lies in the fact that the approximations made between Eqs. (6.24) and (6.25) generally will become better for larger Γ values. Physically, growing Γ will lower the quantum coherence between different molecules, thereby lessening the effect that accidental near-resonant trimers and larger clusters of molecules may still have. Obviously, it would be interesting to extend the dimer approximation to a trimer approach (and further). However, it seems hard, if not impossible, to get a fully analytical answer for the trimer, as it would involve solving the eigenstates and energies of a general trimer, determining the matrix elements of the flux operator and energy differences, substituting this all in Eq. (6.9) and analytically averaging over all disorder realizations that may occur in the trimer.

6.4.2 Diffusion constant at small dephasing rate

As we have seen in Fig. 6.1, for small dephasing rate, the diffusion constant is proportional to Γ in all cases, except for the special case of an infinite homogeneous chain. In the limits of weak and strong static disorder, this linear behavior was found analytically in Sec. 6.3, Eqs. (6.18) and (6.28). In the intermediate-static-disorder regime, the linear behavior is expected as well at small Γ values because at small dephasing rates, the diffusion is limited by hops between localization domains enabled by the dynamic fluctuations. The corresponding hopping rates are proportional to Γ .

Before turning to estimates of the interdomain hopping rates in more detail, we consider the numerically obtained dependence of D on Γ in the small- Γ regime in more detail. From the above, we expect that in this regime, D/Γ does not depend on Γ , implying that it then is a universal function of σ/J . This is confirmed by Fig. 6.3, where the symbols denote the numerically obtained D/Γ as a function of σ for four different (small) values of Γ . Obviously, all symbols follow one universal dependence. Deviations are only seen in the level of the plateau reached in the small-static-disorder regime, resulting from the fact that for the larger ones of the Γ values considered here, the relation $2\pi J/N \gg \Gamma$ (required to derive Eq. (6.18)) does not really hold for $N = 10000$. The straight lines associated with the analytical solutions (Eqs. (6.18) and (6.28)) indeed show excellent agreement with the numerical results in the weak-static-disorder limit (for the smallest Γ values) and the strong-static-disorder limit, respectively.

We now focus in more detail on the intermediate-static-disorder regime, which is

Figure 6.3: Log-log plot of $D/(\Gamma d^2)$ numerically calculated as a function of σ/J for $\Gamma/J = 10^{-5.0}$ (asterisks), $10^{-4.5}$ (circles), $10^{-4.0}$ (pluses), and $10^{-3.5}$ (squares). Also shown as dashed-dotted lines are the analytical weak- and strong-static-disorder results (Eqs. (6.18) and (6.28)), respectively, and as dashed lines the best power-law fits to the data in the intermediate- and strong-static-disorder regimes. The power-law fit in the strong-static-disorder regime ($\sigma/J \approx 30 - 100$) yielded $D/(\Gamma d^2) = 1.87(\sigma/J)^{-1.14}$. In the simulations, a chain of $N = 10000$ molecules was used.

the most interesting one. Here, the excitons are weakly localized ($1 \ll N_{\text{loc}} \ll N$). In the limit of slow dephasing (small Γ), the transport process may then be viewed as a hopping process between localization domains, where the hops are enabled by the white-noise dynamic disorder $\delta\epsilon_n(t)$, characterized by Γ . Within each localization domain, the transport is ballistic and fast; the hopping process between different domains is the limiting step in the transport. In this situation, one may estimate the diffusion constant as

$$D = \gamma N_{\text{loc}}^2 d^2 \quad (\text{intermediate } \sigma, \text{ weak } \Gamma), \quad (6.29)$$

where γ is the typical hopping rate between localization domains. Using first-order time-dependent perturbation theory, the hopping rate between two exciton states k

and l induced by the white-noise disorder is easily found to be

$$\gamma_{kl} = \Gamma \sum_n |\phi_{kn} \phi_{ln}|^2, \quad (6.30)$$

which is seen to depend on the overlap of the site probabilities of both states (owing to the fact that the dynamic disorder is not correlated for different sites) and not to depend on energy (owing to the white-noise character of the fluctuations).

For states that fully overlap, the above hopping rate γ_{kl} scales like Γ/N_{loc} . Since the total number of states that overlap with a given state is of the order N_{loc} , the total rate away from a given state is thus proportional to Γ . As transport is only possible if hops occur to states that partially overlap with the original one, the relevant effective hopping rate is expected to be of the order of, but numerically smaller than Γ , where we use as estimate $c'\Gamma$, with $c' \approx 1/2$. For the same reason, the step size N_{loc} in Eq. (6.29) should be replaced by a number of the order of but numerically smaller than N_{loc} , where we use as estimate $N_{\text{loc}}/2$. As a result, we reach the estimate

$$D = c\Gamma N_{\text{loc}}^2 d^2 \quad (\text{intermediate } \sigma, \text{ weak } \Gamma), \quad (6.31)$$

where $c \approx 1/8$.

What is left is to translate Eq. (6.31) into a σ dependence. To this end, we use a simple estimate for the localization size, obtained via a self-consistent argument that requires that the static-disorder-induced mixing of two localized states on a domain of size N_{loc} equals the average energy separation between adjacent states in the exciton band for a system of size N_{loc} . Such arguments have been used successfully to obtain the localization size as a function of static disorder in the optically dominant (band-edge) region of J-aggregates, in which case one uses the band-edge state-state separation;^[46,90] here, we use the average separation in the entire band because in the high-temperature situation we consider, all states contribute to the transport. Because the static-disorder-induced mixing scales like $\sigma/\sqrt{N_{\text{loc}}}$ (exchange narrowing of the static disorder) and the average energy separation is $4J/N_{\text{loc}}$ (the total band width divided by the number of molecules in the domain), we arrive at the estimate

$$N_{\text{loc}} = 16 \left(\frac{J}{\sigma} \right)^2, \quad (6.32)$$

which is valid in the intermediate-static-disorder regime. The $(J/\sigma)^2$ scaling has also been found in other studies.^[29,45,83,91]

Combining Eqs. (6.31) and (6.32), we arrive at

$$D = 256c\Gamma d^2 \left(\frac{\sigma}{J} \right)^{-4} \quad (\text{intermediate } \sigma, \text{ weak } \Gamma), \quad (6.33)$$

which agrees very well with the best fit to the numerical data in Fig. 6.3. The scaling relation for D/Γ as a function of σ/J found from that fit has a power of -3.70 , which is in good agreement with our analytical estimate of -4 . The deviation probably results from finite-size effects, which limit the range of the intermediate regime. We have found that with growing system size, the power tends more toward -4 , but it is numerically expensive to go beyond $N = 10000$. We note that also the prefactor of ~ 42 in the numerically obtained scaling relation is well understood from our analytical estimate, which yields a number of about 32.

6.4.3 Optimal dephasing rate

In Fig. 6.1, we have seen that for each value of the static disorder strength σ , the diffusion constant as a function of Γ reaches a maximum value in between the quantum and classical regimes. We will refer to the Γ value at which this maximum is reached as Γ_{opt} , the optimal dephasing rate. From Fig. 6.1, it is clear that Γ_{opt} gets larger for increasing values of σ . In this section, we analyze this dependence in more detail and again will encounter characteristic differences between the three disorder regimes.

The numerically obtained value of Γ_{opt} as a function of σ is displayed in Fig. 6.4, where we show Γ_{opt} for σ ranging from $0.001J$ to $100J$. It is clearly seen that, indeed, three different regimes exist with a totally different scaling behavior. As in Fig. 6.3, the behavior in the weak- and strong-static-disorder limits can be understood from the analytical results derived in Sec. 6.3. As we have argued in that section, in the limit of weak static disorder, where $N_{\text{loc}} > N$ (states fully delocalized over the finite chain), the existence of an optimal value of Γ is a finite-size artifact of the method used to calculate D . The value where D reaches its maximum in this regime is determined by the crossover point between the $\sim \Gamma$ and the $\sim 1/\Gamma$ dependences, which we saw to occur at $\Gamma_{\text{opt}} \approx 2\pi J/N$. Indeed, this agrees well with the behavior seen in Fig. 6.3: For $\sigma \lesssim 0.03J$, Γ_{opt} reaches a plateau at about $6 \cdot 10^{-4}J$. The latter value agrees well with the analytical estimate $2\pi J/N$ for $N = 10^4$. Moreover, substituting $\sigma = 0.03J$ into Eq. (6.32), gives $N_{\text{loc}} \approx 1.6 \cdot 10^4$, indicating that, indeed, the plateau is reached when the localization size exceeds the system size N .

In the limit of strong static disorder, we again resort to the dimer approach of Sec. 6.3.2, from which we found the analytical expression (Eq. (6.27)) for D . Setting the derivative of this expression equal to zero and using that $\sigma \gg J$ and assuming that also $\sigma \gg \Gamma_{\text{opt}}$ (which may be checked afterward), one arrives at the following analytical expression for the optimal dephasing rate:

$$\Gamma_{\text{opt}} = \sqrt{4^{\frac{2}{3}} \pi^{\frac{1}{3}} J^{\frac{4}{3}} \sigma^{\frac{2}{3}} - 4J^2} \quad (\text{strong } \sigma). \quad (6.34)$$

As is shown in Fig. 6.4, this result shows excellent agreement with the numerical

Figure 6.4: Log-log plot of Γ_{opt}/J as a function of σ/J obtained from the numerical simulations, using chains of $N = 10000$ molecules with nearest-neighbor interactions J (symbols). The red dashed-dotted horizontal line at small static disorder σ indicates the value $2\pi J/N$, which is the analytical estimate for the optimal dephasing rate in the weak static disorder regime. The magenta dashed-dotted curve in the strong-static-disorder regime represents the analytical expression Eq. (6.34), valid for strongly localized states. The green dashed line in the intermediate regime is the best power-law fit to the numerical data, specified in the legend, whereas the black dashed line in the strong-static-disorder regime corresponds to the best power-law fit to the numerical data in the range $\sigma/J \approx 30 - 100$, given by $\Gamma_{\text{opt}}/J = 1.54(\sigma/J)^{0.38}$.

data for $\sigma > 5J$, which is not surprising given the quality of the analytical result for D , as displayed in Fig. 6.2 already. It should be noted that Eq. (6.34) may still be simplified further using the fact that the second term in the square root is smaller than the first one (since $\sigma \gg J$). Ignoring the second term yields

$$\Gamma_{\text{opt}} = 4^{\frac{1}{3}}\pi^{\frac{1}{6}}J \left(\frac{\sigma}{J}\right)^{\frac{1}{3}} \approx 1.92J \left(\frac{\sigma}{J}\right)^{\frac{1}{3}} \quad (\text{very strong } \sigma), \quad (6.35)$$

which shows that in the strict strong-static-disorder limit, Γ_{opt} obeys a power-law scaling with σ with a power $1/3$. Indeed, this is also found in the numerical data, but this power is only reproduced if one fits the data from $\sigma \approx 30J$ upward. Starting the fit at lower σ values gives powers that are significantly larger due to the effect of the second term in Eq. (6.34) (e.g., a power of 0.44 is found if one starts fitting from $5J$ upward).

Finally, we turn to the interesting intermediate-static-disorder regime, where the states are weakly localized. In this regime, the numerical data can be fitted well to a power-law scaling relation, as indicated by the green dashed line, with the expression specified in the legend of Fig. 6.4 (power close to 2). The scaling behavior observed is governed by the interplay between the exciton localization size imposed by the static energy disorder (N_{loc}) and the hopping rates between localization domains governed by dynamic disorder. The localization size defines the maximum length over which ballistic (coherent) transport can take place; the time to traverse a localization domain then can be estimated as $\tau_{\text{trav}} = N_{\text{loc}}/2J$. At the edge of the domain, the exciton motion is obstructed, until the dynamic disorder fluctuations aid in incoherent hopping to the neighboring localization domain, where again ballistic transport is possible. Following the discussion just above Eq. (6.31), the incoherent hopping has as characteristic time $\tau_{\text{hop}} = 1/(c'\Gamma)$. Now, the optimal value of Γ is reached if $\tau_{\text{trav}} = \tau_{\text{hop}}$. Namely, if $\tau_{\text{trav}} < \tau_{\text{hop}}$, the exciton has to wait too long to make the jump to the next localization domain after it has traversed the previous one; conversely, if $\tau_{\text{trav}} > \tau_{\text{hop}}$, the time it takes to traverse a single domain takes too long relative to the jump to the next domain. The sweet spot is reached if the hopping rate is just right compared to the localization size, i.e., if Γ is tuned just right to σ . In this situation, the incoherent hopping time between localization domains is synchronized to the coherent transport over a single domain. This argument was made previously^[92] and was referred to as the quantum Goldilocks effect,^[92] inspired by the fairy tale entitled “Goldilocks and the three bears”. Thus, setting $\tau_{\text{trav}} = \tau_{\text{hop}}$ at $\Gamma = \Gamma_{\text{opt}}$ and using Eq. (6.32) for N_{loc} , we arrive at

$$\Gamma_{\text{opt}} = \frac{J}{8c'} \left(\frac{\sigma}{J} \right)^2 \quad (\text{intermediate } \sigma), \quad (6.36)$$

which agrees well with the best fit to the numerical data in Fig. 6.4. The fit gives a scaling relation for Γ_{opt} as a function of σ/J with a power of 1.92, which is in good agreement with our analytical estimate of 2. Similar to the case of the diffusion constant at small dephasing rate, the deviation is probably due to finite-size effects in the numerical simulation for small σ values, which in practice limit the σ range for the intermediate regime. The prefactor 0.29 obtained from the best fit to the numerical result also matches quite well with our analytical estimate of about 0.25 ($c' \approx 1/2$).

6.4.4 Maximum diffusion constant

We now turn to the study of the maximum diffusion constant D_{max} , reached at $\Gamma = \Gamma_{\text{opt}}$. From Fig. 6.1, we observe that D_{max} gets smaller for increasing values of σ , which is the physically intuitive trend: Increasing static disorder will increasingly hinder transport.

Figure 6.5: Log-log plot of $D_{\max}$ as a function of σ obtained from the numerical simulations, using chains of $N = 10000$ molecules with nearest-neighbor interactions J (symbols). The dashed lines in the weak- and intermediate-disorder regimes are the best power-law fits to the numerical data, specified in the legend. The black dashed line in the strong-disorder regime corresponds to the best power-law fit to the numerical data in the range $\sigma/J \approx 30 - 100$, given by $D_{\max}/(d^2 J) = 1.25(\sigma/J)^{-0.94}$. The magenta dashed-dotted line in the strong-disorder regime represents the analytical expression Eq. (6.38), valid for strongly localized states.

The numerical results for $D_{\max}$ as a function of σ are given as symbols in Fig. 6.5 for σ ranging from $0.001J$ to $100J$. Again, we see three distinct static-disorder regimes with a completely different scaling behavior. Similar to Figs. 6.3 and 6.4, the behavior in the weak- and the strong-static-disorder regimes can be understood based on the analytical results derived in Sec. 6.3, in this case augmented by the results for Γ_{opt} obtained for the respective static-disorder regimes in Sec. 6.4.3. In the weak-static-disorder limit, where $N_{\text{loc}} > N$ (states fully delocalized over the finite chain), $D_{\max}$ can be obtained by substituting the analytical estimate $\Gamma_{\text{opt}} \approx 2\pi J/N$ obtained in this static-disorder regime into Eq. (6.18), which gives the σ -independent result,

$$D_{\max} = \frac{\pi}{6} N d^2 J \quad (\text{weak } \sigma). \quad (6.37)$$

This reproduces the behavior observed in Fig. 6.5: For $\sigma \lesssim 0.03J$, $D_{\max}$ saturates to a plateau at about $1.5 \cdot 10^3 d^2 J$. Taking $N = 10^4$, the prefactor obtained from Eq. (6.37) is about $5.2 \cdot 10^3$, which is of the same order of magnitude as the one obtained from the best power-law fit to the small- σ data in Fig. 6.5. The discrepancy in the prefactors

originates from the handwaving nature of Γ_{opt} in the weak-static-disorder limit and the fact that exactly at this value of Γ , the conditions for the derivation of Eq. (6.18) are not fully met. As argued before, the fact that an optimal dephasing rate and a maximum diffusion constant exist in this limit is a finite-size artifact.

In the strong-static-disorder limit, we may again understand the numerical results from the dimer approach of Sec. 6.3.2. In this regime, we found the analytical expression (Eq. (6.27)) for the diffusion constant D . Substituting $\Gamma = \Gamma_{\text{opt}}$ given by Eq. (6.34) into Eq. (6.27) and assuming $\sigma \gg J$ and $\sigma \gg \Gamma_{\text{opt}}$, we arrive at

$$D_{\text{max}} = \sqrt{\pi} \frac{d^2 J^2}{\sigma} = \sqrt{\pi} d^2 J \left(\frac{\sigma}{J} \right)^{-1} \quad (\text{strong } \sigma). \quad (6.38)$$

As can be seen in Fig. 6.5, this result indeed shows very good agreement with the numerical data in the strong-static-disorder regime.

We finally turn to the most complicated regime of intermediate static disorder, where $1 \ll N_{\text{loc}} \ll N$. As shown in Fig. 6.5, the numerical data for D_{max} in this regime can be fitted well to a power-law scaling dependence on σ/J with power close to -2 (represented by the green dashed line, with the expression specified in the legend of Fig. 6.5). In order to obtain an analytical estimate of D_{max} in this regime, we substitute $\Gamma = \Gamma_{\text{opt}}$ according to Eq. (6.36) into Eq. (6.33), which gives

$$D_{\text{max}} = 8d^2 J \left(\frac{\sigma}{J} \right)^{-2} \quad (\text{intermediate } \sigma). \quad (6.39)$$

The power of -2 in this analytical relation agrees very well with the best fit to the numerical results in the intermediate regime shown as a green dashed line in Fig. 6.5. The prefactor in the analytical expression, however, is considerably larger than the one obtained from the numerical data, i.e., Eq. (6.39) overestimates the absolute value of the diffusion constant by a factor of about 6. This overestimation results from the fact that Eq. (6.33) assumes the transport within localization domains to be very fast and unaffected by Γ (i.e., completely coherent), which by definition cannot be the case at $\Gamma = \Gamma_{\text{opt}}$ obtained from the Goldilocks principle used in Sec. 6.4.3; at this Γ value, the motion within localization domains already starts to feel the effects of Γ , which will slow down the transport within the domains. Nevertheless, we conclude that the Goldilocks principle, together with the scaling relation Eq. (6.32) for the localization size, very well captures the scaling power.

6.4.5 Effect of long-range resonant interactions

Thus far, we only considered nearest-neighbor interactions J , which facilitated making analytical derivations and estimates. In this section, we investigate the effect of

including long-range dipole-dipole resonant interactions of the form,

$$J_{nm} = \frac{J}{|n - m|^3}. \quad (6.40)$$

A priori, one expects that the inclusion of the long-range interactions leads to a larger diffusion constant (keeping Γ fixed) because the additional interactions give additional pathways in the transport. In the weak-localization regime, the long-range interactions will increase the localization size,^[44] making for larger effective jumps, which in turn will lead to a larger diffusion constant. At the same time, because the dipole-dipole interactions fall off rapidly with distance, one does not expect that their inclusion has a very strong effect on the diffusion constant, which for most combinations of system parameters ($\Gamma/J, \sigma/J$) is confirmed by our numerical simulations. Figure 6.6 shows the numerical results for both long-range and nearest-neighbor interactions as a function of Γ/J for three values of σ/J (left column) as well as their ratio R_D (right column). First, we observe that, indeed, the long-range interactions always increase the diffusion constant ($R_D > 1$ for all parameters). Second, we observe that in the parameter range where the diffusion constant is of interest (in the peaks in the left column), the relative changes caused by the long-range interactions are small, mostly limited to about 10%. The only considerable effects are visible for large σ in combination with small Γ . The explanation lies in the fact that for large σ the states are strongly localized, in which case the effect of next-nearest-neighbor interactions and beyond may relatively easily change a state delocalized over one or two molecule(s) (monomer and dimer states) to a state where three or even more molecules contribute due to accidental resonances involving second or third neighbors. In the case of strong dephasing, such contributions will be relatively unimportant, as the phase relations between the molecules involved will be destroyed quickly; for weak dephasing (small Γ), this quantum enhancement effect may be larger. We note again, however, that the strongest effects for large σ occur only in the low- Γ tail of the peak of D as a function of Γ , where the diffusion constant is small anyhow.

In the limit of large Γ , the transport becomes entirely incoherent, even at short length and time scales, and the ratio R_D is numerically found not to depend on Γ and σ anymore. In this incoherent limit, R_D can be obtained analytically using the general expression for the diffusion constant in this limit,^[33,93]

$$D = \frac{1}{\Gamma} \sum_{m \neq 0} J_{0m}^2 m^2 d^2, \quad (6.41)$$

where J_{0m} and md are the interaction and distance between the central (reference) molecule on the linear aggregate and molecule m , respectively. In the case of nearest-

Figure 6.6: Left column: Comparison of the diffusion constant D as a function of the dephasing rate Γ calculated using a model including only nearest-neighbor interactions (NNIs, red dashed lines) and a model including long-range dipole-dipole interactions (LRIs, blue solid lines) for three static energy disorder values ($\sigma/J = 0.1, 1$, and 10). The right column shows the corresponding ratio $R_D = D_{\text{LRI}}/D_{\text{NNI}}$.

neighbor interactions, this reduces to Eq. (6.17), while for the long-range dipole-

dipole interactions Eq. (6.41) yields

$$D_{\text{LRIs}} = \frac{2d^2 J^2}{\Gamma} \sum_{s=1}^{\infty} \frac{1}{s^4} = \frac{2d^2 J^2}{\Gamma} \frac{\pi^4}{90} \quad (\text{classical limit}). \quad (6.42)$$

Thus, we arrive at

$$R_D = \frac{D_{\text{LRIs}}}{D_{\text{NNIs}}} = \frac{\pi^4}{90} = 1.08, \quad (6.43)$$

which indeed is independent of Γ and σ and shows excellent agreement with the numerical results in Fig. 6.6 for large Γ .

Due to the absence of significant effects of the long-range interactions on the diffusion constant, one expects that the various scaling relations found for the diffusion constant at small dephasing rate, the optimal dephasing rate (Γ_{opt}), and the maximum diffusion constant (D_{max}) in the case of nearest-neighbor interactions, also do not change much when including long-range dipole-dipole interactions. Detailed numerical simulations indeed confirm this. For all three σ regimes, we performed power-law fits of these quantities as a function of σ/J , both in the case of nearest-neighbor interactions (figures given in Secs. 6.4.2 - 6.4.4) as well as in the case of long-range interactions. The powers (α) and prefactors (a) for all three quantities of interest and all three σ regimes are given in Table 6.1 for both interaction models. Clearly, the vast majority of the fit parameters for both models are very similar, with the biggest deviation occurring for the prefactor in D/Γ at small Γ . The origin of this deviation was addressed above already.

We note that the marginal effect of considering long-range dipole-dipole interactions, instead of nearest-neighbor ones, is specific for one-dimensional systems. For higher-dimensional systems, first of all, the long-range dipole-dipole interactions get a larger weight than in one dimension. Second, in higher-dimensional systems, the exciton energy dispersion (and density of states) has a strong dependence on the orientation of the dipoles, which in turn may strongly affect spectroscopic and diffusion properties and their scaling with disorder.^[94,95]

Table 6.1: Parameters a and α characterizing the best power-law fit of the form $a(\sigma/J)^\alpha$ to the numerical results of D/Γ for small dephasing rate (Γ), Γ_{opt} , and D_{max} in the three distinct σ regimes for the model with only nearest-neighbor interactions (NNIs) and the model that also includes the long-range interactions (LRIs). Several of these best power-law fits for the model including only nearest-neighbor interactions (NNIs) are shown in Figs. 6.3, 6.4, and 6.5.

Fit parameters	Weak σ		Intermediate σ		Strong σ	
	a	α	a	α	a	α
$\frac{D}{\Gamma d^2}$ (NNIs)	$6.62 \cdot 10^{-6}$	0.00	42.3	-3.70	1.87	-1.14
$\frac{D}{\Gamma d^2}$ (LRIs)	$6.82 \cdot 10^{-6}$	0.00	47.5	-3.70	3.18	-0.92
$\frac{\Gamma_{\text{opt}}}{J}$ (NNIs)	$5.90 \cdot 10^{-4}$	0.00	0.29	1.92	1.54	0.38
$\frac{\Gamma_{\text{opt}}}{J}$ (LRIs)	$5.78 \cdot 10^{-4}$	0.00	0.28	1.91	1.54	0.37
$\frac{D_{\text{max}}}{d^2 J}$ (NNIs)	$1.48 \cdot 10^{-3}$	0.00	1.38	-1.87	1.25	-0.94
$\frac{D_{\text{max}}}{d^2 J}$ (LRIs)	$1.57 \cdot 10^{-3}$	0.00	1.53	-1.87	1.36	-0.94

6.5 CONCLUSIONS

We performed a systematic study of the excitation energy diffusion constant D in a one-dimensional exciton system using the Haken-Strobl-Reineker (HSR) model to describe the effects of static and dynamic energy disorder. The interplay between the resonant excitation transfer interactions J , static disorder σ , and dephasing rate Γ caused by the dynamic disorder leads to a rich behavior of the excitation energy transport. At small dephasing rates, quantum diffusion takes place, with the diffusion constant growing linearly with Γ , owing to energy transfer between exciton localization domains assisted by the dynamic fluctuations. At large dephasing rates, the diffusion constant reaches the classical limited $2d^2 J^2/\Gamma$ for all disorder values. In between these two regimes, the diffusion constant reaches a maximum value D_{max} as a function of Γ at $\Gamma = \Gamma_{\text{opt}}$.

We have focused, in particular, on the σ dependencies of the diffusion constant at small Γ values, Γ_{opt} , and D_{max} . We found that these dependencies all are characterized by three different regimes, distinguished by the amount of exciton localization imposed by the static disorder: delocalized states ($N_{\text{loc}} > N$), weak localization

($1 \ll N_{\text{loc}} \ll N$), and strong localization ($N_{\text{loc}} \approx 1$). In the limit of strong localization, the diffusion constant can be derived analytically assuming the exciton states to be delocalized over at most two molecules (dimers). The resulting closed expression for D as a function of Γ and σ yields excellent agreement with numerically calculated results and shows that in this regime $\Gamma_{\text{opt}} \propto J(\sigma/J)^{1/3}$ and $D_{\text{max}} \propto \sigma^{-1}$. Furthermore, at small dephasing rates, the strong-localization regime leads to $D \propto \Gamma J/\sigma$.

In the weak-localization regime, the disorder-dependence of the numerically obtained diffusion constant at small dephasing rates agrees well with the simple scaling argument $D \propto \Gamma N_{\text{loc}}^2 \propto \Gamma(\sigma/J)^{-4}$, which reflects the enhancement of the diffusion constant by the exciton localization size (quantum transport). In the weak-localization regime, the optimal dephasing rate and maximum diffusion constant are of particular interest. The numerical simulations show that both quantities obey a power-law scaling with the static disorder with powers close to 2 and -2, respectively. It turns out that these scaling relations are well-reproduced from the quantum Goldilocks principle, which states that optimal diffusion is reached if the time it takes to ballistically travel over localization domains equals the fluctuation-induced jump time between two adjacent localization domains.^[92] Our numerical results also yield an optimal dephasing rate and maximum diffusion constant for fully delocalized states (very weak static disorder); these results are unphysical, however, and due to finite-size effects that inevitably occur in numerical simulations.

Most results in this chapter were obtained using only nearest-neighbor excitation transfer interactions. Our numerical results show, however, that including long-range dipole-dipole interactions hardly affect the results for the diffusion constant, at least in the range of Γ values where the diffusion constant is non-negligible. Finally, throughout this chapter, we used the HSR model to describe the dynamic disorder. Due to the white-noise nature of the fluctuations in this model, this essentially describes the high-temperature limit. It is of obvious interest to extend the above insights and scaling relations in future studies by including temperature explicitly.^[3,15,30,87]

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Chapter 7

Conclusions and Outlook

This thesis began with the goal to enhance our understanding of the impact of inhomogeneities in supramolecular aggregates by addressing the four key questions raised in Chapter 1. Through thorough investigations presented in Chapters 3 - 6, we obtained answers to the four questions. In this final chapter, I summarize the conclusions drawn in each chapter and highlight what I learned through our research investigations. Furthermore, future studies are also suggested that would add to both the breadth and depth of our current understanding.

7.1 CONCLUSIONS

The aim of this thesis was to push the boundary of our knowledge towards the general goal of understanding the impact of inhomogeneities of structural features on the collective optical properties of self-assembled molecular aggregates. In particular, we focused on four specific questions which formed the content of the four core chapters (Chapters 3-6) of this thesis. In each of the chapters, conclusions and outlook of the respective investigations were presented. The essence of each chapter's answers to our four key questions are as follows.

Chapter 3^[1] addressed the question: **How sensitive are the optical properties of self-assembled molecular aggregates to their structural inhomogeneity?** We found that collective optical property of ZnChl tubular molecular aggregates are highly sensitive to small variations in molecular packing. This result has significance both from fundamental and application perspective. Fundamentally, it shows that despite being composed of thousands of molecules that could wash out any differences in properties between the aggregates through self-averaging, the structural differences at the microscopic level in their molecular packing leaves signatures in their aggregate-level collective properties. From the application perspective, the investigation shows that this phenomenon allows single-aggregate polarization-resolved fluorescence excitation spectroscopy to resolve minute variation in molecular packing, which cannot be achieved even with high-resolution imaging techniques such as atomic force microscopy (AFM) or electron microscopy (EM).^[2]

Further significance of this research relates to the system investigated, ZnChl tubular molecular aggregates. The ZnChl nanotubes serve as a model system for the molecular aggregates found in chlorosomes, which belong to the most efficient light-harvesting antenna system in nature. Due to the presence of mixtures of various types of constituent molecules that are involved in the self-assembly process of the molecular aggregates inside the chlorosomes, and the variations in size, shape, and number of aggregates incorporated into a single chlorosome, it has not been possible to obtain information about the microscopic structure of the molecular aggregates inside chlorosomes with atomic resolution to date. However, the ZnChl tubular aggregates, which feature better defined structural properties owing to their construction from well-defined monomers, allow surmounting the challenge to obtain structural information with atomic resolution. Note that mimicking the processes that govern the highly efficient natural systems has also been achieved with self-assembled molecular dye-aggregates based on cyanine or triarylamine derivatives.^[3,4] In contrast to the natural chlorosomes, which correspond to a small ensemble of molecular aggregates and therefore don't allow for true single-aggregate spectroscopy, the ZnChl tubular molecular aggregates make it possible to perform single-aggregate spectroscopy. The resulting much narrower distribution of the spectral parameters

of the ZnChl tubular molecular aggregates compared to the corresponding distributions from the molecular aggregates found in natural chlorosomes^[5,6] confirms the more homogeneous structure of the ZnChl tubular molecular aggregates. It reflects the better control of the monomer building blocks in the synthetic ZnChl tubes compared to the molecular aggregates found in the natural chlorosomes. The existence of a more inhomogeneous structure of the molecular aggregates found in natural chlorosomes is understood as to widen the range of the electromagnetic spectrum that can be absorbed, which is necessary to survive in the photon scarce conditions where the host organisms (green sulfur and non-sulfur bacteria) exist.^[6-8]

Despite the improvement in control of the monomer building blocks of the ZnChl tubular aggregates compared to the natural chlorosomes (the average linewidth of absorption spectra of natural chlorosomes is ≈ 4 times that of the ZnChl tubular aggregates),^[1,6] the existing distributions of its spectral properties show the difficulty in controlling properties of the molecular aggregates. Even though the aggregates are composed of identical building blocks, the self-assembly process introduces inhomogeneity in their molecular packing, which is beyond our control and has a significant impact on the collective optical properties of the molecular aggregates.

In Chapter 4,^[9] we deal with the question: **Can we probe inhomogeneity within individual molecular aggregates?** We learned that the structural inhomogeneity (disorder in the orientation of individual molecules) within individual tubular molecular aggregates of ZnChl can be probed from signatures in single-aggregate spectroscopy. Specifically, the experimentally observed anomalous correlation of the widths of the dominant optical bands of the ZnChl tubular aggregates, i.e., the higher-energy exciton band observed in a single aggregate has a smaller linewidth compared to the lower-energy one, and their other statistical properties are used as the markers for the intra-aggregate disorder. It shows the possibility to disentangle sources of structural disorder within and between different aggregates by combining experimental single-aggregate spectroscopy and systematic exciton modeling. This is not possible using ensemble spectroscopic techniques. The proposed intra-aggregate disorder in the orientation of the molecules of the order of a few degrees in the ZnChl tubular aggregates is physically plausible based on revelation of similar disorder found in molecular dynamics simulations of other dye aggregates.^[10,11]

Chapter 5^[12] was a theoretical study to approach the question: **Are the optical properties susceptible to size inhomogeneity of supramolecular aggregates?** The findings of Chapter 5 show that polarization-dependent fluorescence-excitation spectroscopy on individual chlorosomes can provide information on the typical size of the tubular aggregates found inside these highly efficient light-harvesting organelles. The relevance of the findings of this investigation relates to the challenges associated with unraveling the internal structure of chlorosomes. Knowing the structural details of molecular aggregates inside chlorosomes has significance for both

fundamental understandings and biomimetic application. The complication originates from the heterogeneity both within and between chlorosomes, resulting from variations in growth conditions and growth stage, as well as having a variety of bacterial strains. Our study demonstrated that the size inhomogeneities of aggregates within the chlorosome can be resolved by combining single-chlorosome linear polarization resolved spectra and single-chlorosome circular dichroism. We emphasize that it is only the combination of the two single-chlorosome spectroscopic techniques that allows to uniquely determine the average size (radius and length) of the tubular aggregates inside individual chlorosomes. The added incentive of unveiling this information lies on the dependence of, *inter alia*, the excitation energy transport efficiencies on the details of the size of the molecular aggregates. The ideal protocol to unveil the size information of the tubular aggregates is to scan the fluorescence-excitation spectrum as a function of the polarization angle ϕ (refer to Chapter 5) for the linearly polarized light (SOLP spectroscopy) and scan the single-chlorosome circular dichroism spectrum as a function of the angle ξ (refer to Chapter 5) between the wave vector of the exciting light and the long axis of the chlorosome (SOC D spectroscopy). However, cognizant of the experimental constraints that may prove to be difficult to perform a full scan of the dependence of SOC D spectrum on the angle ξ , we demonstrated that in principle, making the measurements at two different angles relay all the information, and if also that turns out complicated, using $\xi = 45^\circ$ would be the best option. We also explained that the sensitivity of the CD spectroscopy to the length of the tubular aggregates originate from the interference between so-called ring contributions and helical contributions to the spectrum, which sheds light on the reason why $\xi = 45^\circ$ is the optimal SOC D setup to probe size variations. Based on the importance of the linewidths to resolve the size variation between tubular aggregates found in different chlorosomes, we also drew the conclusion that low-temperature conditions of the SOC D setup can help to resolve up to larger sizes of the tubular aggregates, and the ability to resolve larger sizes improves for structures with less inhomogeneity. For instance, the ability to resolve larger sizes of molecular aggregates is better for chlorosomes of mutants compared to that of wild-type chlorosomes.^[5,6] The results in this chapter also highlight the opportunities that this rarely applied spectroscopic technique opens up; the combination of SOLP spectroscopy and SOC D spectroscopy can be fruitful for other supramolecular structures similar to chlorosomes where information on the variation of their internal structure is hard to obtain through other sources.

In Chapter 6,^[13] we consider the question: **What is the influence of energy inhomogeneity within molecular aggregates on their excitation energy transport properties?** The results in Chapter 6 showed the effects of energy inhomogeneity, static energy disorder resulting from varying constituent building blocks or due to irregularity in the local environment of the chromophores, and dynamic energy disorder.

der mainly due to thermal effects, on the excitation energy transport properties of a generic linear aggregate. The Haken-Strobl-Reineker (HSR) model, which describes exciton dynamics in high-temperature limits, was employed to study the effects of static and dynamic energy disorder on the excitation energy transport. The investigation unveiled a rich behavior of the excitation energy transport as a consequence of the underlying intricate interplay of the three important energy scales: the intermolecular interactions (J), the magnitude of the static disorder (σ), and the dephasing rate (Γ) characterizing the dynamic disorder. In particular, we focused on the σ dependencies of the exciton diffusion constant at small Γ values, the Γ value at which maximum diffusion is obtained (Γ_{opt}), and the maximum diffusion constant (D_{max}). For all these quantities, we found that three different scaling regimes exist as a function of the static energy disorder, characterized by varying magnitude of the exciton localization, classified into complete delocalization ($N_{\text{loc}} > N$, where N_{loc} is the number of molecules over which exciton states are localized, and N is the total number of molecules in the molecular aggregate), weak localization ($1 \ll N_{\text{loc}} \ll N$), and strong localization ($N_{\text{loc}} \approx 1$). All the various scaling relations could be understood fully with physical and analytical arguments. Although most of the results in this chapter were obtained using the model that includes only nearest-neighbor excitation transfer interactions, our numerical results show, however, that including long-range dipole-dipole interactions hardly affects the diffusion constant results, at least in the Γ range where the diffusion constant is significant.

Overall, the essence of the findings from all the chapters lies in the realization that structural inhomogeneities play a significant role in the collective properties of the self-assembled molecular aggregates. It can be a boon or a bane. For instance, having little inhomogeneities in the system allows to achieve sharp absorption lineshapes and enhances excitation energy transport. However, more inhomogeneous systems have larger absorption frequency range which improves absorptivity. Therefore, depending on the desired applications, we need to tune the structural inhomogeneities in the system. Since the properties of self-assembled molecular aggregates are quite sensitive to inhomogeneities, we need to invent or discover fabrication techniques that allow control of the degree of structural inhomogeneity with high precision. Another important aspect of these results relates to the techniques used in these investigations. For instance, the single-aggregate spectroscopic techniques combined with systematic excitonic modeling could probe inter-aggregate as well as intra-aggregate structural inhomogeneities. This combination of methods can be employed on other systems as well, artificial or natural molecular aggregates. In a nutshell, the findings of the investigations allows not only the fundamental understanding of the role of different inhomogeneities in structure on collective properties of the molecular aggregates, but also aids in our pursuit of synthesizing functional mesoscopic objects through application of the achieved insights.

7.2 OUTLOOK

In this thesis, we addressed several interesting questions related to structural inhomogeneity and its effects on the properties of the molecular aggregates. But there are still many issues that need attention. Some are fundamental issues and others are technique or application related.

Several results in this thesis are limited by approximations and assumptions made in the respective investigations, which simplify the problem at hand and isolate the particular effects that we wish to focus on. For instance in Chapter 4, we estimated the magnitude of intra-aggregate orientation disorder of the molecules using a model where we did not include energy disorder within individual aggregates as well as inter-aggregate structural disorder. Similarly, in Chapter 5, we assumed that all the molecular aggregates within and between chlorosomes are identical except for their sizes characterized by their radius and length. Extending these studies to include effects from additional sources of heterogeneity would be a formidable task, but is an interesting and important topic for future research. In Chapter 6, all the diffusion results are from the HSR model, which has an inherent high-temperature approximation. In principle, this limits its application to narrow bandwidth systems. Using methods that treat temperature explicitly^[14–17] and performing a similar systematic analysis of the exciton diffusion properties would expand the scope and applicability of the investigation.

Furthermore, some of the theoretical results should be tested. For instance, our investigation in Chapter 5 showed that there is an optimal SOCD setup to resolve size variation. The setup should be built and tested on artificial individual tubular aggregates, such as ZnChl tubular aggregate, whose size can be measured using cryo-EM, to test if it is indeed optimal. It would be also interesting to test if the scaling behavior of different exciton diffusion properties that were observed numerically and explained analytically in Chapter 6 can be observed in real systems with varying energetic disorder within the aggregates. This can be done systematically, for instance, by changing temperature for linear molecular aggregates with varying energetic disorder strength and measuring diffusion constant for each case.

In addition, it is interesting to check if some of the phenomena we observed and explored can be observed in other systems. For instance, it is interesting to check if the anomalous correlation of the linewidths observed for ZnChl tubular aggregate that allowed to probe intra-aggregate orientation disorder can be observed in other tubular molecular aggregates, both artificial and natural, such as C8S3 tubular molecular aggregate^[3] and tubular molecular aggregates found in chlorosomes.^[5,6] If so, can we use the combination of single polarization resolved fluorescence excitation spectroscopic technique with systematic exciton modeling to estimate the magnitude of intra-aggregate orientation inhomogeneity of the molecules.

Finally, all the optical properties we deal with are linear optical responses of the molecular aggregates. Therefore it would be interesting to study the effect of structural inhomogeneity on non-linear responses of the molecular aggregates. Such studies can be valuable both in terms of fundamental understanding as well as from the application prospects of the molecular aggregates. From a fundamental perspective, non-linear optical responses of molecular aggregates allow probing properties of multi-exciton bands and provide an alternative approach to extract information on the delocalization length (N_{loc}) of the exciton states which shed light on the extent of inhomogeneity in the system and its impact.^[18–20] From the application perspective, strong nonlinear optical responses might be of interest for optical switching applications.^[21]

To this end, returning to where it all began, the vision of Richard Feynman, this thesis is a concrete baby step towards our general goal of understanding the impact of structural inhomogeneities on properties of functional molecular aggregates, which contributes to synthesis and manipulation at the nanoscale. We are still far off the kind of functionality at the nanoscale that Feynman envisioned in his lecture. However, progress made so far has been promising, and the future looks bright in the field of nanoscience and nanotechnology.

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Summary

Nanoscience and Nanotechnology have pervaded pop culture extensively such that almost all of us have at least some inkling about these concepts. It is one of the most popular themes in science fiction movies and books; for instance in the movie “Avengers: Endgame”, the Iron Man suit (Mark L) of Tony Stark is an extremely advanced armour suit based on nanotechnology. For those who haven’t watched the movie, one of the protagonists (Tony Stark), a genius billionaire, possesses a multi-functional suit based on nanotechnology that self-assembles out of a detachable power source. Although having such a technology sometime in the future would be amazing, we have not yet reached such a scientific level. Nevertheless, there has been staggering progress since the visionary lecture entitled “There is plenty of room at the bottom. . .” was given by Richard P. Feynman, which many mark as the advent of the field of nanoscience.

What makes nanoscience exciting but also challenging is that objects investigated in nanoscience are neither macroscopic (dimensions greater than a micrometer) nor microscopic (individual atoms and molecules, dimensions less than a nanometer) but are something intermediate, generally referred to as mesoscopic objects. The intermediate nature of mesoscopic objects renders these systems both quantum mechanical (because they are small enough) and collective (because they are large enough) properties which, can be employed for varied applications. However, to realize these applications, the main challenge is associated with the acute sensitivity of these systems to inhomogeneities in their structure. Inhomogeneity or lack of uniformity of mesoscopic objects can be in their shape, size, nature of their constituents, and orientation of the composing building blocks, etc. Inhomogeneities in these systems are inevitable due to lack of complete control over their fabrication and manipulation techniques; inherent environmental noise or thermal effects introduces disorder in the system. Since inhomogeneities can be a boon or a bane to functions we desire from the functional mesoscopic objects, it is significant to have a good understanding

of the impact of inhomogeneities on the properties of the mesoscopic objects.

Mesoscopic objects can be synthesized by shrinking existing technological designs, generally referred to as the top-down approach, which is the established fabrication method adopted by the electronic industries. Alternatively, mesoscopic objects can be achieved by self-assembly of the constituent building blocks, generally referred to as the bottom-up approach, in which case we have much to learn from the natural world. Natural systems, getting a head start of some billion years of evolution, have employed self-assembly and perfected the designs of their mesoscopic tools for extremely efficient functions. The top-down approach is analogous to sculpting rocks into monuments, whereas the bottom-up approach is similar to building a house brick-by-brick. In this thesis, we focus on the bottom-up approach, and in particular on molecular aggregates, assemblies of organic dye molecules, which form a class of highly interesting mesoscopic objects from both fundamental and application perspectives. Similar to the Iron Man suit of Tony Stark, these systems are formed through self-assembly, but at the nanometer scale. Due to interaction between the constituent building block molecules of the molecular aggregates, their properties are fundamentally different from the addition of the characteristics of the individual molecules composing the molecular aggregate. The properties of the molecular aggregates are generally referred to as their collective properties and are subject of considerable interest and research. From the application perspective, due to the ability of molecular aggregates to absorb light and efficiently transport the excitation energy, these systems have found extensive application in natural photosynthetic organisms as light-harvesting systems, which inspires biomimetic applications in artificial photosynthesis and photovoltaic systems. For these reasons, in this thesis, we focused on extending our understanding of the impact of inhomogeneities on collective properties, such as optical and excitation energy transport properties, of self-assembled molecular aggregates through addressing four key questions:

1. How sensitive are the optical properties of self-assembled molecular aggregates to their structural inhomogeneity?
2. Can we probe inhomogeneity within individual molecular aggregates?
3. Are the optical properties susceptible to inhomogeneity in the size of supramolecular aggregates?
4. What is the influence of energy inhomogeneity within molecular aggregates on their excitation energy transport properties?

To answer these questions, we employed the Frenkel exciton model to describe the electronic excitations of molecular aggregates, generally referred to as excitons. Excitons are delocalized over many molecules of the aggregates due to interactions

between the molecules. Excitons differ from the electronic excitations of individual molecules, which are localized on the molecules. The energetic properties of the system, such as the interactions between the molecules, static energy disorder, and dynamic energy disorder in the system, influence the static and dynamic properties of the excitons, which govern the collective properties of the molecular aggregates.

Our investigations to answer the first question were reported in Chapter 3, in which we learned that small changes in molecular packing between different tubular molecular aggregates of zinc chlorin (ZnChl) molecules can be traced by using single-aggregate spectroscopic techniques. ZnChl tubular molecular aggregate is an interesting system due to its resemblance to the molecular aggregates found in chlorosomes of photosynthetic green sulfur and non-sulfur bacteria, which are known to be the most efficient light-harvesting systems in Nature. Despite being composed of identical ZnChl monomers, there are still variations in molecular packing between individual ZnChl tubular aggregates, which show the difficulty in controlling the properties of the molecular aggregates.

In Chapter 3, although we learned about the impact of variation in molecular packing between different tubular ZnChl molecular aggregates, referred to as inter-aggregate structural disorder, we had no information about the structural disorder within the ZnChl tubular aggregates (intra-aggregate structural disorder). A seemingly unrelated observation of smaller linewidth of the higher-energy exciton band compared to the lower-energy one, which we referred to as the anomalous correlation of the exciton linewidths, allowed to access information on the intra-aggregate orientation disorder of ZnChl tubular aggregates. In Chapter 4, we showed that the anomalous correlation of the linewidths with their statistical properties, combined with systematic exciton modeling, allowed to unveil small orientation disorder within individual ZnChl tubular aggregates, which cannot be achieved, even with high-resolution imaging techniques.

Besides the variations in the molecular packing of the molecular aggregates, it is also interesting to gain insights into the size variation of the molecular aggregates since the excitation energy transport properties are susceptible to size inhomogeneities. In particular, information on size variation of molecular aggregates within chlorosomes is interesting, however, as chlorosomes contain an ensemble of molecular aggregates, they do not allow typical size probing techniques to access the size variation information. In Chapter 5, we proposed a combination of single-aggregate spectroscopic techniques that could shed light on this issue.

In addition to the collective optical properties, the excitation energy transport properties are important features for functionality of molecular aggregates. For instance, in the photosynthetic light-harvesting systems of green sulfur and non-sulfur bacteria, which are found deep within the ocean where there is a scarcity of light, efficient excitation energy transport is crucial for their survival. Similarly, for photo-

voltaic applications of molecular aggregates, their excitation energy transport have to be fast compared to processes that leads to loss of the excitation energy. Therefore, the impact of energy disorder on the excitation energy transport properties in linear molecular aggregates is investigated and reported in Chapter 6. We learned that the intricate interplay of the interaction between the molecules, the static energy disorder, and the dynamic energy disorder leads to a rich behavior of the excitation energy transport in linear molecular aggregates. We observed different scaling behavior of different exciton transport properties, which can be, explained fully with physical and analytical arguments.

In conclusion, from the fundamental perspective we learned about the inevitable presence of inhomogeneities in different aspects of the molecular aggregates and how the collective properties of these aggregates are influenced by the extent of the inhomogeneities. The sensitivity of the collective properties of the molecular aggregates to inhomogeneities allows to access the information about the disorder by using optical spectroscopic techniques combined with systematic exciton modeling. From the application perspective, we learned about the difficulty in the control of self-assembly processes, which results in lack of precision of the properties of the molecular aggregates. It shows, still how far we are from the visions of Richard Feynman, and having better control in this regard should be our focus for the future. But we have also made significant progress, and the field of nanoscience remains a very active research area. At this moment, we constantly learn and mimic design principles used in Nature, where nanotechnologies (self-assembled molecular aggregates) are extensively and efficiently used for purposes such as light-harvesting systems. However, considering the rate of our progress in nanoscience research and applications, we humans might be the next evolutionary step of Nature to emulate existing natural systems and build more complex and functional nanotechnology; maybe even technology like the Iron Man suit of Tony Stark.

Samenvatting

Nanoscience en nanotechnologie hebben dusdanig uitgebreid hun intrede gedaan in de popcultuur dat de meesten van ons wel een vermoeden hebben van deze concepten. Het is een van de meest populaire thema's in sciencefiction films en boeken; zoals in de film "Avengers: Endgame" is het Iron Man pak (Mark L) van Tony Stark een extreem geavanceerd pantser gebaseerd op nanotechnologie. Voor degene die de film niet gezien hebben, een van de hoofdrolspelers (Tony Stark), een geniale miljardair, bezit een multifunctioneel pak gebaseerd op nanotechnologie dat zichzelf opbouwt uit een afneembare energiebron. Ondanks dat het geweldig zou zijn om over dergelijke technologie te beschikken in de toekomst, hebben we dat wetenschappelijke niveau nog niet bereikt. Desalniettemin is er verbluffende vooruitgang geboekt sinds de vooruitstrevende lezing getiteld "There is plenty of room at the bottom. . ." ("Er is genoeg ruimte onderaan. . .") is gegeven door Richard P. Feynman, die door velen wordt aangemerkt als het begin van nanoscience als wetenschapsgebied.

Nanoscience is zowel opwindend als uitdagend omdat de materie in kwestie macroscopisch (dimensies groter dan een micrometer) noch microscopisch (individuele atomen en moleculen, dimensies kleiner dan een nanometer) is maar iets daartussen, over het algemeen mesoscopische materie genoemd. Het gemengde karakter van mesoscopische materie geeft deze systemen zowel kwantummechanische (omdat ze klein genoeg zijn) en collectieve (omdat ze groot genoeg zijn) eigenschappen die verschillende toepassingen hebben. De grootste uitdaging om deze toepassingen te realiseren heeft te maken met de acute sensitiviteit van deze systemen voor inhomogeniteit in hun structuur. Inhomogeniteit, ook wel het gebrek aan uniformiteit van mesoscopische materie, kan voortkomen uit verschillen in vorm, grootte, oorsprong van bestanddelen, oriëntatie van de samengestelde bouwstenen, etc. inhomogeniteit in deze systemen is onvermijdelijk wegens het gebrek aan totale controle over hun fabricatie- en manipulatietechnieken waaronder effecten zoals inherente ruis uit de omgeving of thermische effecten. Omdat inhomogeniteit een ze-

gen of vloek kan zijn voor de functies die we wensen van mesoscopische materialen, is het belangrijk om een goed begrip te hebben van de impact van inhomogeniteit op mesoscopische materialen.

Mesoscopische materialen kunnen gesynthetiseerd worden door miniaturen te maken van bestaande materialen. Deze methode staat bekend als de top-down methode en wordt veel als fabricagemethode toegepast in de elektronische industrie. Als alternatief kunnen mesoscopische materialen gemaakt worden door individuele bouwstenen te assembleren. Deze methode staat algemeen bekend als de bottom-up methode waarbij we nog veel te leren hebben van de natuurlijke wereld. Natuurlijke systemen, die een voorsprong hebben opgebouwd door miljarden jaren van evolutie, hebben de ontwerpen van mesoscopische gereedschappen toegepast en geperfectioneerd voor extreem efficiënte functionaliteiten. De top-down methode is alsof je een monument uit een rots beeldhouwt terwijl de bottom-up methode lijkt op het steen voor steen bouwen van een huis. In dit proefschrift focussen we op de bottom-up methode en in het bijzonder op moleculaire aggregaten, assemblages van organische kleurstof moleculen, een subcategorie van zeer interessante mesoscopische materialen vanuit zowel fundamenteel als applicatie oogpunt. Net als het Iron Man pak van Tony Stark zijn deze systemen allemaal gevormd door middel van zelfassemblage maar dan op de nanometer schaal. Door de interactie tussen moleculaire bouwstenen van de moleculaire aggregaten zijn hun eigenschappen fundamenteel anders dan de som van eigenschappen van de individuele moleculen waaruit het moleculaire aggregaat bestaat. Naar de eigenschappen van moleculaire aggregaten wordt doorgaans gerefereerd als hun collectieve eigenschappen en deze zijn onderhevig aan grote belangstelling en veel onderzoek. Vanuit een applicatie oogpunt hebben deze materialen een weidse applicatie gevonden in natuurlijke fotosynthetische organismen, zoals light-harvesting systems die op hun beurt weer een inspiratie zijn voor biomimetische applicaties in artificiële fotosynthetische en fotovoltatische systemen. Om deze redenen hebben we in dit proefschrift gefocust op het uitbreiden van onze kennis over de impact van inhomogeniteit op de collectieve eigenschappen zoals optische- en excitatie-energietransport eigenschappen van zelfgeassembleerde moleculaire aggregaten door de volgende hoofdvragen te behandelen:

1. Hoe gevoelig zijn de optische eigenschappen van zelfgeassembleerde moleculaire aggregaten voor structurele inhomogeniteit?
2. Kunnen we de inhomogeniteit binnen een individueel moleculair aggregaat meten?
3. Zijn de optische eigenschappen gevoelig voor inhomogeniteit in de grootte van supramoleculaire aggregaten?

4. Wat is de invloed van energetische inhomogeniteit in een moleculair aggregaat op de excitatie-energietransport eigenschappen?

Om deze vragen te beantwoorden hebben we het Frenkel exciton model gebruikt om de elektronische excitaties van moleculaire aggregaten te beschrijven, algemeen bekend als excitonen.

Excitonen zijn gedelokaliseerd over veel moleculen van het aggregaat vanwege interacties tussen moleculen in tegenstelling tot elektronische excitaties van individuele moleculen die gelokaliseerd zijn op de moleculen. De energetische eigenschappen van het systeem, zoals de interacties tussen de moleculen, statische energiewanorde en dynamische energiewanorde in het systeem beïnvloeden de statische en dynamische eigenschappen van de excitonen die de collectieve eigenschappen van het moleculaire aggregaat bepalen.

Ons onderzoek om de eerste vraag te beantwoorden is beschreven in hoofdstuk 3 waarin we hebben geleerd dat kleine veranderingen in de moleculaire ordening tussen verschillende buisvormige moleculaire aggregaten van zinkchlorin (ZnChl) moleculen gevolgd kunnen worden door gebruik te maken van enkel-aggregaat spectroscopie technieken. Buisvormige ZnChl moleculaire aggregaten zijn een interessant systeem vanwege hun overeenkomsten met moleculaire aggregaten die gevonden zijn in chlorosomen van fotosynthetische groene sulfaat en non-sulfaat bacteriën die bekend staan als de meest efficiënte licht absorberende systemen in de natuur. Ondanks dat de buisjes bestaan uit dezelfde ZnChl monomeren is er nog steeds variatie in de moleculaire stapeling tussen individuele buisvormige ZnChl aggregaten. Dit geeft aan hoe moeilijk het is om de eigenschappen van moleculaire aggregaten te controleren.

Ondanks dat we in hoofdstuk 3 geleerd hebben over de rol van variatie van moleculaire configuratie op verschillende buisvormige moleculaire ZnChl aggregaten, ook wel inter-aggregaat structurele wanorde genoemd, hebben we nog geen informatie over de structurele wanorde in de buisvormige ZnChl aggregaten (intra-aggregaat structurele wanorde). Een op het oog ongerelateerde observatie van kleinere lijnbreedte van de hoge-energie excitonband vergeleken met de lage-energie band, wat we aanduiden als abnormale correlatie van de exciton lijnbreedtes, stelt ons in staat om informatie over de intra-aggregaat oriëntatiewanorde van buisvormige ZnChl aggregaten te achterhalen. Kleine oriëntatiewanorde in individuele buisvormige ZnChl aggregaten kan niet direct gedetecteerd worden met de hoogste resolutie afbeeldingstechnieken, zoals electronmicroscopie. Echter laten we in hoofdstuk 4 zien dat abnormale correlatie van de lijnbreedte met de statische eigenschappen, gecombineerd met systematische exciton modellering, ons wel in staat stelt om kleine oriëntatiewanorde binnen individuele buisvormige ZnChl aggregaten te onthullen.

Naast de variaties in moleculaire structuur van de moleculaire aggregaten is het ook interessant om inzicht te krijgen in de variatie van grootte van moleculaire aggregaten omdat de excitatie-energietransport eigenschappen gevoelig zijn voor variaties in grootte. Bijzonder interessant is informatie over de variatie in moleculaire aggregaten binnen chlorosomen, omdat ze een assemblage van moleculaire aggregaten bevatten waarvan variatie van groottes niet te meten is met typische meetmethodes. In hoofdstuk 5 stellen we een combinatie van enkel-aggregaat spectroscopie technieken voor die licht kunnen schijnen op dit probleem.

Als toevoeging op de collectieve optische eigenschappen zijn de excitatie-energietransport eigenschappen belangrijke kenmerken van functionaliteit van moleculaire aggregaten. Bijvoorbeeld voor de fotosynthetische licht opnemende systemen van groene sulfaat en non-sulfaat bacteriën die men diep op de zeebodem vindt is efficiënt excitatie-energietransport cruciaal voor hun overleving, omdat er weinig licht doordringt tot die dieptes. De processen in de bovengenoemde bacteriën zijn vergelijkbaar met fotovoltaische applicaties van moleculaire aggregaten waarvan het excitatie-energietransport snel moet zijn ten opzichte van processen die leiden tot het verlies van excitatie energie. Derhalve wordt de impact van energiewanorde op het excitatie-energietransport in lineaire moleculaire aggregaten onderzocht en beschreven in hoofdstuk 6. We hebben geleerd dat het ingewikkelde samenspel van de interactie tussen moleculen, de statische energiewanorde en de dynamische energiewanorde leiden tot een rijk gedrag van de excitatie-energietransport in lineaire moleculaire aggregaten. We zien verschillende schaalregimes voor verschillende exciton-transporteigenschappen die we volledig kunnen verklaren met natuurkundige en analytische argumenten.

Om samen te vatten hebben we vanuit een fundamenteel perspectief geleerd over de onvermijdelijke aanwezigheid van inhomogeniteit in verschillende aspecten van moleculaire aggregaten en hoe de collectieve eigenschappen van deze aggregaten beïnvloed worden door de reikwijdte van inhomogeniteit. De gevoeligheid van de collectieve eigenschappen van het moleculaire aggregaat voor inhomogeniteit stelt ons in staat de informatie over wanorde te achterhalen door gebruik te maken van optische spectroscopische technieken gecombineerd met systematische exciton modellering. Vanuit een applicatieperspectief hebben we geleerd over de moeilijkheid van het controleren van zelfassemblageprocessen die resulteren in een gebrek aan precisie van eigenschappen van moleculaire eigenschappen. Het laat zien hoever we nog weg staan van de visie van Richard Feynman en dat betere controle in dit opzicht onze focus moet zijn voor de toekomst. Echter hebben we ook significante vooruitgang geboekt en het onderzoeksveld van nanoscience blijft een zeer actief onderzoeksgebied. Op dit moment leren we en kopiëren we principes die gebruikt worden in de natuur die nanotechnologieën (zelfgeassembleerde moleculaire aggregaten) veelvuldig en efficiënt gebruiken in bijvoorbeeld licht-absorberende syste-

men. Desalniettemin, de snelheid van onze progressie in nanoscience onderzoek en haar applicaties in acht nemende, is de mensheid misschien de volgende evolutionaire stap van de natuur om bestaande natuurlijke systemen na te bootsen en om meer complexe- en functionele nanosystemen te bouwen. Misschien zelfs wel de technologie van het Iron Man pak van Tony Stark.

List of publications

1. **Scaling Relations of Exciton Diffusion in Linear Aggregates with Static and Dynamic Disorder [Chapter 6]**
T. Kunsel, T. L. C. Jansen, & J. Knoester
J. Chem. Phys. **155**, 134305 (2021) [doi: 10.1063/5.0065206]
2. **Probing Size Variations of Molecular Aggregates inside Chlorosomes using Single-Object Spectroscopy [Chapter 5]**
T. Kunsel, L. M. Günther, J. Köhler, T. L. C. Jansen, & J. Knoester
J. Chem. Phys. **155**, 124310 (2021) [doi: 10.1063/5.0061529]
3. **Unraveling intra-aggregate structural disorder using single-molecule spectroscopy [Chapter 4]**
T. Kunsel, A. Löhner, J. J. Mayo, J. Köhler, T. L. C. Jansen, & J. Knoester
J. Chem. Phys. **153**, 134304 (2020) [doi: 10.1063/5.0023551]
4. **Interplay between structural hierarchy and exciton diffusion in artificial light-harvesting [Not in this thesis]**
B. Kriete, J. Lüttig, T. Kunsel, P. Malý, T. L. C. Jansen, J. Knoester, T. Brixner, & M. S. Pshenichnikov
Nat. Commun. **10**, 4615 (2019) [doi: 10.1038/s41467-019-12345-9]
5. **Ultrathin molecule-based magnetic conductors: A step towards flexible electronics [Not in this thesis]**
N. Akhtar, M. C. Donker, T. Kunsel, P. H. M. van Loosdrecht, T. T. M. Palstra, & P. Rudolf
MRS Adv. **4**, 3353 (2019) [doi: 10.1557/adv.2019.464]

6. **Spectral and Structural Variations of Biomimetic Light-Harvesting Nanotubes [Chapter 3]**
A. Löhner, T. Kunsel, M. I. S. Röhr, T. L. C. Jansen, S. Sengupta, F. Würthner, J. Knoester, & J. Köhler
J. Phys. Chem. Lett. **10**, 2715 (2019) [doi: 10.1021/acs.jpcllett.9b00303]
7. **Simulating Fluorescence-Detected Two-Dimensional Electronic Spectroscopy of Multichromophoric Systems [Not in this thesis]**
T. Kunsel, V. Tiwari, Y. A. Matutes, A. T. Gardiner, R. J. Cogdell, J. P. Ogilvie, & T. L. C. Jansen
J. Phys. Chem. B **123**, 394 (2019) [doi: 10.1021/acs.jpcc.8b10176]
8. **Structural Variations in Chlorosomes from Wild-Type and a bchQR Mutant of *Chlorobaculum tepidum* Revealed by Single-Molecule Spectroscopy [Not in this thesis]**
L. M. Günther, A. Löhner, C. Reiher, T. Kunsel, T. L. C. Jansen, M. Tank, D. A. Bryant, J. Knoester, & J. Köhler
J. Phys. Chem. B **122**, 6712 (2018) [doi: 10.1021/acs.jpcc.8b02875]

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