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A computational study of structural and excitonic properties of chlorosomes

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Citation

Li, X. (2020, May 6). *A computational study of structural and excitonic properties of chlorosomes*. Retrieved from <https://hdl.handle.net/1887/87570>

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Author: Li, X.

Title: A computational study of structural and excitonic properties of chlorosomes

Issue Date: 2020-05-06

A Computational Study of Structural and Excitonic Properties of Chlorosomes

Xinmeng Li

A Computational Study of Structural and Excitonic Properties of Chlorosomes

Ph.D. thesis, Leiden University

X. Li

ISBN: 978 -94 -6380 -812 -5

Keywords: Chlorosome; Exciton Dynamics; Molecular Dynamics; Linear Optical Spectra; Dynamic Disorder; Helical Tube Reconstruction; Light-harvesting.

This research was financed by Leiden University, and co-financed by the VW foundation in the context of an international project on Multiscale hybrid modeling of (bio)membranes. The use of supercomputer facilities was sponsored by NWO Exact and Natural Sciences, with financial support from the Netherlands Organization for Scientific Research (NWO).

A Computational Study of Structural and Excitonic Properties of Chlorosomes

Proefschrift

ter verkrijging van
de graad van Doctor aan de Universiteit Leiden,
op gezag van Rector Magnificus prof.mr. C.J.J.M. Stolker,
volgens besluit van het College voor Promoties
te verdedigen op woensdag 6 mei 2020
klokke 13:45 uur

door

Xinmeng Li

geboren te Shandong, China

in 1990

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For my parents

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A General Introduction

Photosynthesis begins with light-harvesting, where antenna complexes transform sunlight into electronic excitations that are subsequently delivered to reaction centers, where charge separation takes place and chemical energy is stored.^{1,2} The efficiency with which these conversions are performed, and the amount of energy that is dissipated proceeding along the different steps in the conversion pathway, is of utmost significance for the functioning of photosynthetic organisms as a whole.^{3,4} As a result, antenna complexes have developed in response to the environmental conditions that these photosynthetic organisms experience, which translates into specific features that ensure an optimal light-harvesting capability.^{5,6} A very distinctive feature in the chlorosome structural antenna motifs is the amount of pigments that it contains, and their molecular and higher-order packings.^{7,8} This unique type of antenna complexes has evolved at an early stage of evolution and allows photosynthetic green bacteria and some green filamentous anoxygenic phototrophs to survive under extreme low light-intensity conditions.^{9,10} Chlorosomes are antenna assemblies containing hundreds of thousands bacteriochlorophyll (BChl) pigments and a small number of other light-active molecules. They are further distinctive with respect to other antennae in that they form their own responsive matrix without proteins.^{11–16} This finding is intriguing and suggests that the efficiency of both the light-harvesting and exciton transport is *encoded* in the pigment assembly structure, in the absence of proteins. Elucidating the principles behind the efficient excitation energy transfer (EET) that takes place in chlorosomes will contribute to our understanding of photosynthesis^{1,2,6,17–24} and may help to design artificial light-harvesting^{25–28} or other optoelectronic

devices^{29–32} with equivalent efficiency.

The lack of crystalline order in chlorosomes hampered detailed structure elucidation by standard x-ray diffraction techniques.³³ A challenge, particular to natural chlorosomes, is their heterogeneity in size, in overall shape, and in composition, which often strongly depends on the conditions in which they are grown.^{15,34,35} To illustrate these challenges, I cite some comments taken from articles that represented the state-of-the-art at the start of my project in 2015: “the chlorosomes in green bacteria are the last class of light-harvesting complexes to be characterized structurally...” (2009, de Groot),³³ and “Since atomic details of chlorosomal antenna structures are not available (and probably never will)...” (2013, Linnanto and Korppi-Tommola).³⁶

Structural information that did exist at the beginning of my project in 2015 was mainly a model for local pigment packing, the so-called *syn-anti* dimer packing model that will be discussed in more detail further on, that was first published in 2009 and derived from an analysis of solid-state nuclear magnetic resonance (NMR) spectroscopy data.³⁷ It provided a nice unit cell that could be employed for a helical tube model and structure prediction on a larger scale. The considered chlorosomes in this study were isolated from a mutant bacterium that contains significantly less heterogeneity in chemical composition and in overall structure. Additional information came from supramolecular structural level data from cryo-electron microscopy (cryo-EM) and their Fourier transformed counterparts, which provides the diffraction signal, for several types of chlorosomes of a rather homogeneous composition, either rich of BChl *c* or *d*.^{15,37–39} In particular, the diffraction data provided the first clear evidence for the presence of tube chirality within the concentric tubular assemblies, in the form of a (weak) layer line^I, and estimates for the inter-tube stacking distances as well as the intra-tube spacing for different compositions.

This structural information, available at two levels of resolution, was then mapped onto a defect-free packing model for natural and mutant chlorosomes.³⁷ These resulting packing models are used as a basic assembly structure for many studies of chlorosomes.^{35,40–46}

My overarching goal is to study how the coupling of atomistic and electronic

^IThe diffraction pattern of a helical structure is in the form of a series of layers of intensity, so-called layer lines.

degrees of freedom affects the transport efficiency of excitonic energy after sunlight is absorbed. Consequently, existing defect-free and static packing models were no longer sufficient, and we had to introduce irregularity and vibrational dynamics, or static and dynamic disorder, into a tubular molecular assembly that is preferably realistic. As apparent from the content of this thesis, we reached this goal by coupling all-atom molecular dynamics (MD) for the evolution of nuclear coordinates to a quantum mechanical (QM) description for the exciton diffusion. As a first step towards fully understanding functional mechanisms of chlorosomes, we studied the exciton dynamics in a quasi-closed system manner, see Chapter 4. As such, we have constituted an exotic hybrid QM/MM (quantum mechanics/molecular mechanics) approach that is quite general, and thus may find use also in other areas of research. The individual computational approaches are shortly discussed in section 1.3. Before reaching such a goal, we made substantial efforts to obtain realistic tube structures of chlorosomes. We bypassed the sampling limitations of MD for this system.⁴⁷ A reasonable **ansatz** we took is that chlorosomes in different species of bacteria may differ on a higher structural level, *i.e.* in terms of the fingerprint from cryo-EM diffraction and linear optical spectra, but share the same (*syn-anti*) packing unit. A pictorial summary of our strategies or an overview of the whole research content in this thesis is provided in Figure 1.1.

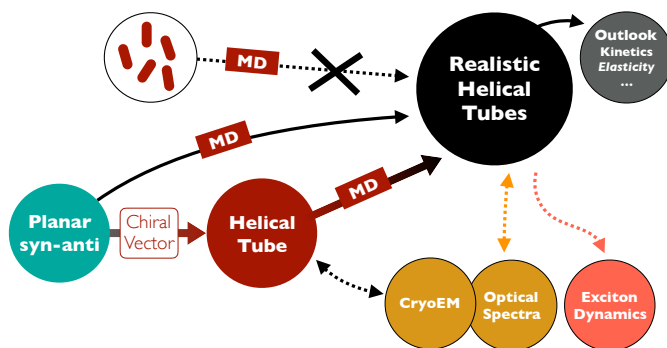


Figure 1.1: An schematic illustration of the strategies adopted in this thesis.

In Chapter 2, we report the results of MD simulations that identify key static and dynamic structural properties. To avoid kinetic trapping, which prevents the spontaneous formation of tube structures from disordered pigment molecules

at time scales that are accessible by all-atom MD simulation, we start from a planar assembly of (*syn-anti*) dimeric units *in vacuo*. We find that curvature spontaneously forms, showing that it is programmed into the local structure, and identify intrinsic dynamic structural heterogeneities involving molecular rotation and hydrogen bonding. In addition, we develop a theoretical analysis that allows us to identify chirality that matches the diffraction information obtained from cryo-EM, noting that this procedure does not provide unique chiral angles. To generate realistic full tubes with customized length, radius, and matching chiral angles, we developed a protocol, see Chapter 5, and an in-house code. This allowed us to verify that the molecular pigment motion that is observed in spontaneously formed curved sheets is the same as in a tube arrangement. In Chapter 3, we calculate linear optical spectra for realistic full tube structures for a direct comparison to experimental linear spectroscopy data, further narrowing down the set of chiral angles that were identified based on the layer line matching in Chapter 2. Our approach differs from a standard Frenkel Hamiltonian treatment in the sense that it includes actual disorder, taken from molecular conformations along the MD trajectory. Moreover, as opposed to the usual uncorrelated variation of the site energy, we incorporate these correlated variations into the electronic coupling between pigments. Although our treatment does not include dynamics on the quantum level, the results are shown to agree with several reported and proposed phenomena for chlorosomes, including exciton localization and level crossing. In particular, it provides the first molecular insight in the intricate mechanisms that underlie efficient energy transfer efficiency. In Chapter 4, we couple ground-state nuclear motion to exciton evolution, by considering a time-dependent Frenkel Hamiltonian, which follows the nuclear coordinates determined by MD, in the Schrödinger equation for exciton evolution. We find that disorder originating from thermal nuclear motions creates a fluctuating landscape for the localized exciton states and, as such, drives efficient transport of excitonic energy throughout the entire chlorosome. We note that our approach, as well as the insights it offers into the structural and excitonic properties of chlorosomes, can also be useful for other artificial tube assemblies.^{48–50} It is recognized as a challenge to obtain realistic atomistic structures of full tubes formed by small organic molecules.⁵¹ Such a difficulty hinders the understanding of such large tube molecular assemblies. For this reason, we shared our protocol for generating such realistic atomistic structures with highly customizable characteristics

in Chapter 5, and systematically analyze the relation between supramolecular chirality and optical response for chlorosome-like tubes. Such a detailed chirality-optical ‘phase diagram’ may be useful as a dictionary for optical spectroscopy characterization. Finally, in Chapter 6, we provide an extension of the current work towards mechanical properties and assembly kinetics in the form of an outlook, by reviewing unpublished results of significance. This may be useful for future research along the same directions.

1.1. Introduction to Chlorosomes

1.1.1. Photosynthesis

The significance of photosynthesis, and of photosynthetic research, for our daily life, in the form of the oxygen that we use, the vegetables we eat, our general well-being as well as the development of artificial devices for a more sustainable form of energy production, can not easily be overestimated.^{17,52} Since my research has only focused on one aspect of photosynthesis, *i.e.* the chlorosome, I restrict myself to reviewing only the bare essentials. Photosynthesis, or more generally phototrophy, is the process in which (autotrophic) organisms convert radiant energy, and especially energy from light, into chemical energy stored in organic compounds.^{52,53} The biological significance of photosynthesis is indisputable as it sustains the bottom of the food chain, and it dominates the global living atmosphere. These two aspects are vital for other (heterotrophic) organisms. Taking as an example plants, *i.e.* the most common photosynthetic organism seen in daily life, one may illustrate their importance by considering the following (from Hall and Coombs⁵⁴): (i) “Each year plant photosynthesis fixes about 2×10^{11} tonnes of carbon with an energy content of 3×10^{21} J; this is about ten times the world’s annual energy use and over two hundred times our food energy consumption”, and (ii) “All the atmospheric CO₂ is cycled through plants every 300 years, all the O₂ every 2,000 years and all the H₂O every 2 million years.”.

Item (ii) is also well demonstrated by considering a time trace of CO₂ concentration data.¹ As shown in Figure 1.2, this time trace shows an intriguing

¹<https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html>

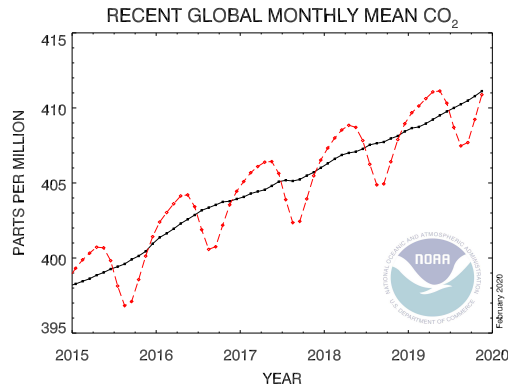


Figure 1.2: Monthly mean carbon dioxide globally averaged over marine surface sites presents seasonal oscillation. The dashed red line represents the monthly mean values. The black line represents the values after correction for the average seasonal cycle. Image provided by NOAA ESRL Global Monitoring Division, Boulder, Colorado, USA (<http://esrl.noaa.gov/gmd/>).

oscillatory behavior that matches the yearly seasonal cycle. It particularly illustrates the significance of natural photosynthesis for the composition of our atmosphere on a global scale.

1.1.2. Green Bacteria

Plants are the best-known photosynthetic organisms (autotrophs), but others exist, including certain types of algae and bacteria.⁵² In particular, different types of organisms possess unique light-harvesting antenna to ensure survival and optimal energy harvesting efficiency in different inhabited environments.⁶ Among these autotrophs, green bacteria, which include green sulfur bacteria *Chlorobi*, the phototrophic Acidobacteria “*Candidatus Chloracidobacterium*”, and the filamentous anoxygenic phototrophs *Chloroflexi* (Figure 1.3),¹⁶ are impressive for their survival ability in harsh environments, for instance in hot springs⁵⁵ and under low light conditions.^{11,56,57} A special species of green sulfur bacteria even does not live off sunlight but from the infrared radiation from thermal vents nearly 2400 meters deep in the ocean.¹² The green sulfur

bacteria form the best-studied group, and especially *Chlorobaculum tepidum* (*C. tepidum*) has become as a model organism for the research of chlorosomes.¹⁵ For this reason, we will also mostly concentrate on this particular group when referring the natural chlorosomes.

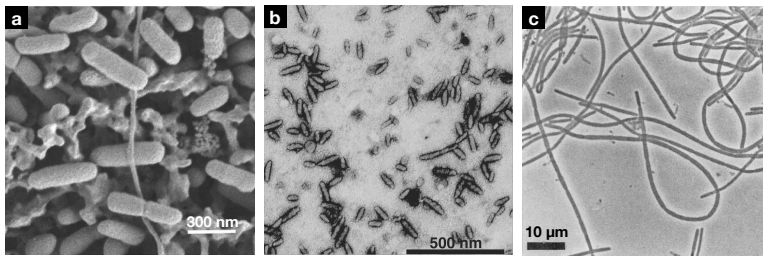


Figure 1.3: Images of different types of bacteria contain with chlorosomes. (a) TEM image of green sulfur bacteria. Figure reproduced with permission from ref [12]. Copyright 2005, National Academy of Sciences of the United States of America. (b) TEM image of *Candidatus Chloracidobacterium thermophilum*. Figure reproduced with permission from ref [58]. Copyright 2007, American Association for the Advancement of Science. (c) Photomicrograph of *Chloroflexus aggregans*. Figure reproduced with permission from ref [55]. Copyright 1995, International Union of Microbiological Societies.

1.1.3. General Information about Chlorosomes

An overall portrait of chlorosomes is given in Figure 1.4. In general, chlorosomes are located on the inside of the cellular membrane (as depicted in Figure 1.4a), and the term chlorosome refers to the organelle as a collection of tubes. Individual tubes are of an ellipsoidal shape, and display a considerable variation of shape and size, but on average they are 100–200 nm in length, and 40–60 nm in diameter.^{15,16} Each chlorosome possesses a unique organization that is regulated by the conditions during formation, which is known to take place via a nucleation and growth mechanism.

An idea of the overall chlorosome shape can be obtained by transmission electron micrograph (TEM), see Figure 1.4a. Isolated tubes or molecular assemblies are composed of different types of molecules, with a total number in the order of 10^5 , and as a whole wrapped by a lipid monolayer.^{52,60} Molecular

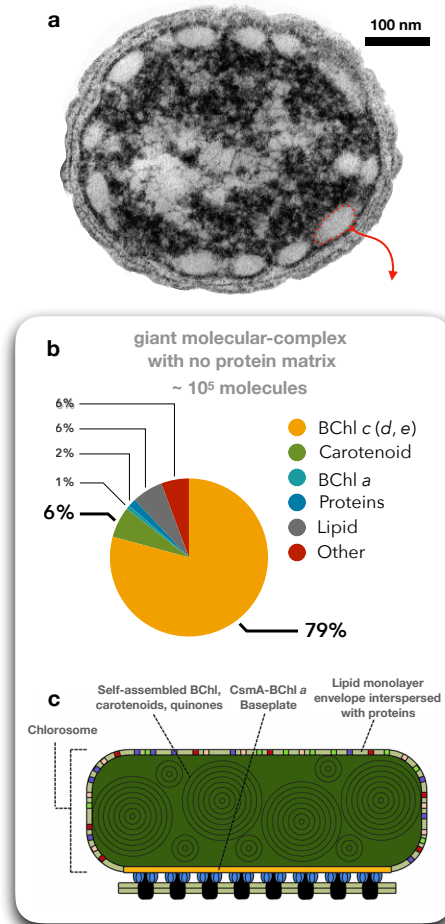


Figure 1.4: (a) TEM image of thin sections of the wild type *C. tepidum*. Figure reproduced with permission from ref [59]. Copyright 2002, American Society for Microbiology. (b) Illustration of typical chemical compositions of an ellipsoid chlorosome complex in green sulfur bacteria. (c) Schematic model of chlorosomes of green sulfur bacteria. Figure reproduced with permission from ref [16]. Copyright 2013, Springer Nature.

ratios in the composition vary with species and growth conditions. The main body, which we refer to as the chlorosome here and further on, is mainly composed of BChl *c/d/e* pigments and contains a small amount of carotenoid molecules, but no proteins, which are only present in the lipid monolayer, see Figure 1.4b. An assembly containing BChl *a* and proteins forms the two-dimensional baseplate that connects the chlorosomes to the next components in the energy transport chain: the Fenna-Matthews-Olson (FMO) complex and the reaction center. Figure 1.4c shows a schematic representation of the chlorosome of green sulfur bacteria. The energy levels for different light-harvesting components in green sulfur bacteria are in a decreasing order, introducing a driving force for energy transfer from chlorosomes to reaction centers.^{61,62}

1.2. The Dawn of Atomistic Tube Structure of Chlorosomes

The *syn-anti* Packing Tube Model. The local structure of the chlorosome, the so-called *syn-anti* model mentioned before, was first determined by matching NMR chemical shifts, which give rise to distance constraints to the molecular structure of a molecule with two neighbors from the stack, and further validation by density functional theory (DFT) calculations.³⁷ A dimeric unit cell was found composed of one molecule in the *syn* and the other in the *anti* conformation, with the electronic dipoles in a staggered parallel orientation, see Figure 1.5. The necessary ingredient for this investigation was the availability of chlorosomes of a reduced structural heterogeneity due to a significantly homogeneous chemical composition, a condition that was satisfied by chlorosomes isolated from *bchQRU* mutant of *C. tepidum*, which are composed of >95% BChl *d* pigments. Next, cryo-EM images taken from this chlorosome first confirmed a concentric tube morphology and allowed for a determination of a 2.1-nm layer spacing between BChl layers. Additionally, the diffraction signal, obtained by Fourier transformation of the cryo-EM images, identified a relevant 0.85 or 1.21 nm periodicity for the mutant type or wild type chlorosome tube structure for a single but weak layer line, confirming that the molecular packing is more irregular or non-crystal-like on a larger scale (Figure 1.5b).

Based on this information, regular tube models that satisfy these two structural constraints were proposed (Figure 1.5c). In the more general framework, these tubes can be obtained by rolling a planar lattice of *syn-anti* unit cells along a rolling vector into a curved lattice on a tube. For more detail on this general procedure and on the correspondence of the resulting helical families and the scattering pattern, we refer to the literature [63]. Consequently, this rolling or chiral vector uniquely defines the resulting tube structure. For instance, the proposed tube model for the mutant type³⁷ means that it is rolled along the *syn-anti* stacks. In this thesis, we develop an approach for more generally relating scattering signals to the direction of rolling, assuming that the chlorosomes from different bacteria species share the same *syn-anti* packing unit. It agrees with the tube models that existed before the project in the sense that we also assume that chlorosomes only differ in their particular chiral vector that sets the chirality of the tube.³⁷

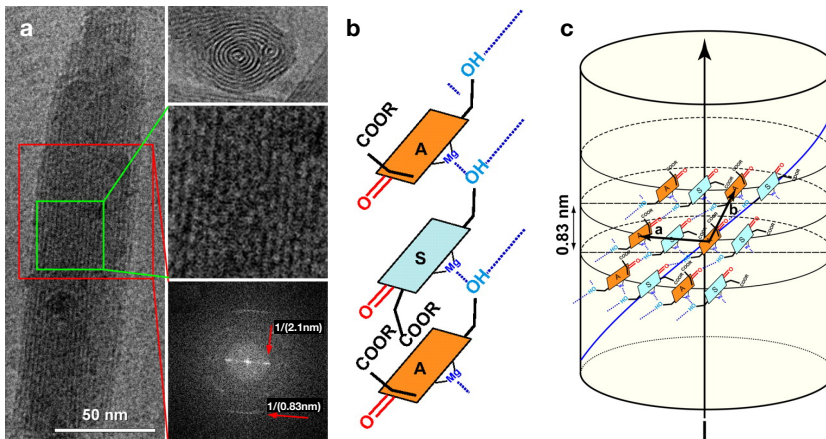


Figure 1.5: The *syn-anti* packing model.³⁷ (a) Cryo-EM images. (b) The *syn-anti* stack structure. (c) A tube model for *bchQRU* mutant *C. tepidum* chlorosomes. Figures reproduced with permission from ref [37]. Copyright 2009, National Academy of Sciences of the United States of America.

The *syn-anti* packing model is visually summarized in Figure 1.6. To better understand the process of building a structure from the *syn-anti* unit cell, I encourage the reader to check the movie showing how to duplicate these

packing units, see the supporting information.¹ Concentrating on an even smaller unit, *i.e.* the molecular building blocks themselves, we note that the BChl *c/d/e* molecules only differ in some side groups, and that we may envision such a molecule composed of a rather rigid head and a flexible farnesyl tail. In the movie, we have represented each molecular head part in a simplified or minimal form as a disc. Similarly, the hydroxyl side group, which determines the molecule's internal chirality (*syn* or *anti*), can be represented as a red sphere, see Figure 1.6, while the red triangle denotes a carbonyl group that can form a hydrogen bond with this hydroxyl group. The *syn-anti* dimeric structure is defined as follows: when the hydroxyl group is at the same side as the wedge bond (green in Figure 1.6), the configuration is denoted as *syn*, while it is denoted as *anti* when they are in the opposite directions. On a larger scale, BChl stacks are stabilized by a network of local interactions: the coordination interaction between Mg and O atoms, hydrogen bonding interactions, and π - π stacking of head parts, see also Figure 1.6. The flexible tails of each molecule cover both sides of the stacks and fill the interstitial space between different layers in the concentric tube topology, as further discussed in Chapter 2. We note that BChl *a* and *f*, which are no natural components of chlorosomes, lack the hydrogen bonding interactions. We also note that the parameters (a, b, γ) corresponding to the underlying (loose) 2D unit cell lattice are not experimentally available and will be estimated from MD simulations.

1.3. Computational Preliminaries

1.3.1. MD Simulation and Its Proper Usage

In classical atomistic simulation by MD, many-body interactions in a system composed of electrons and nuclei are mapped onto effective potentials for a system composed of only nuclei. In such a representation, electrons are assigned as an additional property — charge parameters — to each nucleus. Atomic masses and the atomistic forces that are derived from these effective potentials are then used to evolve the nuclear positions in time, a process that is governed by Newton's classical laws of motion. A typical analytical

¹File `syn-anti-model.mp4` in `chapter_1` folder at https://github.com/xinmeng2015/chlorosome_phd_thesis or <https://doi.org/10.5281/zenodo.3674742>

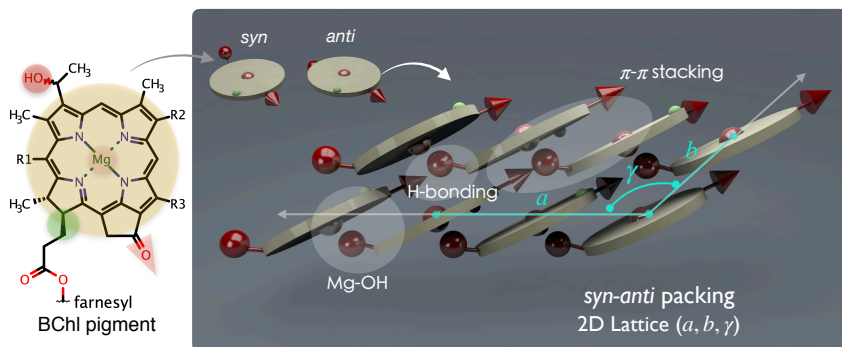


Figure 1.6: A simplified disc model of the *syn-anti* packing model. The macrocycle ring of a BChl is referred to as the head, which is visualized as a disk. The farnesyl chain of a BChl is referred to as the tail, which is omitted in the packing model.

form of the force field is composed of bonded terms, representing chemical bonds, angles and dihedrals, and non-bonded terms, representing van der Waals and electrostatic interactions. There are several popular force fields for organic/biological molecules,^{64,65} e.g. AMBER, OPLS and GROMOS. For further technical details of MD simulations, I refer to a nice book, *The art of molecular dynamics simulation*.⁶⁶

Owing to the optimized and readily available MD simulation packages like GROMACS, NAMD and LAMMPS, and supported by the accessibility of large parallel supercomputers at central high-performance Computing Centers, performing large-scale MD simulations is nowadays relatively straightforward. However, one should not take for granted that simple “brute force” simulations will solve all your molecular puzzles. In particular, one will often experience that, starting from an arbitrary disordered state, the ability of MD to sample all relevant parts of the phase-space is largely insufficient to identify structures or phenomena that can be matched to experimental observations. Especially for large biological or bio-inspired supramolecular systems, simple “brute force” simulation may, and often will fail, as reviewed by the Marrink’s group.⁵¹ There are various reasons for this failing, an important one being that the van der Waals interactions contain an attractive well, which generates numerous local minima that will always hinder the sampling. In particular, when aggregates grow from nucleation, positional adjustment within the aggregates becomes

increasingly difficult and the process of equilibration experiences a critically slowing down phenomenon, with characteristic time scales that become very large. Therefore, computational research of chlorosomes, or similar aggregates with unique mesoscopic/macroscopic order, requires careful consideration of the starting structure, preferably incorporating experimental information. We do not suggest to run MD simulations from totally disordered structures, see the disorganized aggregates we obtained in Figure 1.7. Instead, it is recommended to start from a structure making use of known constraints. For instance, in Chapter 2, we started from a pre-packed planar structure in vacuum. The MD simulation induces spontaneous curvature, a phenomenon that can not be observed by energy minimization methods.⁶⁷ Besides, in Chapter 3, starting from pre-packed full tube structures, the MD simulation will equilibrate the structure and introduce intrinsic structure disorder, and thus generate useful ground-state nuclear motions.

To address the kinetics of chlorosome formation, the system should be simulated on a much longer time scale, possibly even on a macroscopic time scale of minutes and hours. Unique coarse-grained models can be tested to see if this is an option, see a brief discussion in Chapter 6.

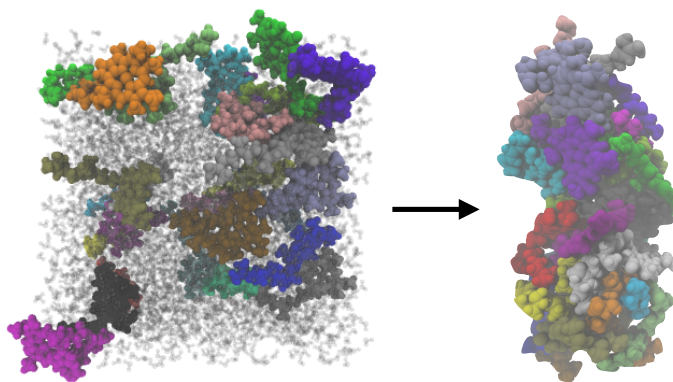


Figure 1.7: Unstructured aggregate of BChl *d* molecules obtained by a 15-ns MD simulation. Initially, the pigments (identified by different colors) are mixed randomly with water molecules (gray). The assembly structure remains stable with elongated simulation time.

1.3.2. Frenkel Exciton and Linear Optical Spectra

Pigments are chemical compounds that can absorb light of an appropriate wavelength. Popular types of pigments found in natural light-harvesting complexes include chlorophylls(Chl), BChl, and carotenoids.²⁶ When a single pigment absorbs light, it goes from a ground state to an excited state. Although such a monomeric case can in principle be described by time-dependent density functional theory (TDDFT), the situation changes when pigments are coupled together by being closely packed into a solid aggregate. In such a situation, they get excited collectively, see Figure 1.8, and the exciton thus becomes delocalized.⁶⁸ The number of pigments, and thus of nuclei and electrons, involved in such a delocalization strongly prohibits the application of "brute force" quantum methods for electronic structure calculation. Instead, the problem can be reformulated in terms of an effective Frenkel exciton Hamiltonian for exciton energy transfer in molecular aggregates, which separates aggregates into Coulomb-coupled monomers, and represents a convenient framework for simulating large-scale electronic excitations.^{69,70} The Frenkel exciton Hamiltonian is widely used to study excitations and exciton evolution in molecular crystals, conjugated polymers, organic photovoltaics, photosensitizers, and light-harvesting complexes in photosynthesis.⁷¹

In a Frenkel exciton treatment, each molecule is represented as a single site, and the interplay/coupling between different molecules is described by a single parameter, the coupling strength. In general, a Frenkel exciton Hamiltonian $\hat{H}$ for a system composed of N molecules is an N by N matrix:

$$\hat{H} = \sum_i \nu_i |i\rangle\langle i| + \sum_{i \neq j} J_{ij} |j\rangle\langle i| \quad i, j \in [1, N]. \quad (1.1)$$

The expression of $\hat{H}$ is adapted slightly in Chapters 3 and 4 where the dependence of the $\hat{H}$ on the nuclear positions or the positions of transition dipoles is emphasized. The diagonal term ν_i represents the monomer excitation energy of the i -th molecule. Off-diagonal terms J_{ij} represent the coupling between excited states of the i -th and j -th molecules, which is also referred to as the electronic (or excitonic) coupling between the i -th and j -th molecules. For a given molecular system of restricted size, *e.g.* for the FMO complex, the site energy ν_i and the coupling strength J_{ij} for each molecule/site can be deter-

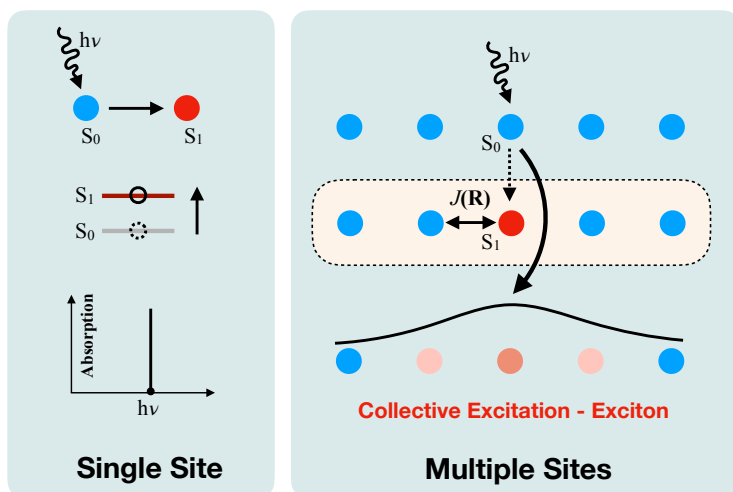


Figure 1.8: From monomeric excitation to collective excitation. The coupling strength $J(\mathbf{R})$ determines whether the excitation energy is blue (or red) shifted compared to the monomeric excitation, which defines the aggregate as an H (or J) type.

mined with good precision using quantum chemical calculations,^{72–77} and used to study the exciton evolution on longer length scales, which is discussed in detail in Chapter 3. Chlorosome-like assemblies of a realistic size, however, are composed of closely packed pigments, meaning that the system size that has to be considered for obtaining reliable parameter values rules out full QM approaches. In consistency with previous chlorosome studies, we therefore consider the experimentally measured site energy and calculate the coupling strength from the standard point-dipole approximation (PDA):

$$J_{ij} = \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{|\mathbf{R}_{ij}|^3} - 3 \frac{(\boldsymbol{\mu}_i \cdot \mathbf{R}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{R}_{ij})}{|\mathbf{R}_{ij}|^5}, \quad (1.2)$$

with $\boldsymbol{\mu}_i$ the effective transition dipole moment vector for the i -th molecule and $\mathbf{R}_{ij}$ the distance vector between the two transition dipoles labeled by i and j . The expression of J is adapted slightly in Chapters 3 and 4 where the dependence of the J on the nuclear positions or the positions of transition dipoles is emphasized.

Diagonalization of the Hamiltonian matrix (1.1) provides N eigenvectors $|\psi_m\rangle$ and eigenvalues ε_m that correspond to stationary exciton states and excitonic transition energies,¹ i.e. $\hat{H}|\psi_m\rangle = \varepsilon_m|\psi_m\rangle$. For a system described by a static $\hat{H}$, the wave functions $|\psi_m\rangle$ are the instantaneously allowed “exciton orbitals” that accommodate the energy of the absorbed photons.

Spectra Calculation. Optical spectra for chlorosomes have been measured experimentally. These spectra, although even not always matching for similar chlorosomes, share several properties: a large red-shift in the absorption (OD) spectra, a dominant positive peak in linear dichroism (LD) spectra and a psi-type shape in circular dichroism (CD) spectra, see Chapter 3. To further narrow down the set of matching chiral angles for chlorosomes, and to understand this experimental variability, we calculated linear spectra for the whole set of candidate chiral angles that were obtained after matching the layer line position. We follow the Frenkel exciton Hamiltonian treatment, and note that each exciton state $|\psi_m\rangle$ corresponds to a (stick) signal amplitude, i.e. d_m for absorption, LD_m for LD and $\mathcal{R}_m$ for CD, computed using Eq. 1.3, for the eigenvalue or energy ε_m on the horizontal axis, with^{36,78–80}

$$\begin{aligned}
 d_m &= \sum_{i,j=1}^N (\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j) c_{mi} c_{mj} \\
 LD_m &= d_m^{\parallel} - d_m^{\perp} = \frac{1}{2} \sum_{i,j=1}^N [3(\boldsymbol{\mu}_i \cdot \mathbf{e})(\boldsymbol{\mu}_j \cdot \mathbf{e}) - \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j] c_{mi} c_{mj} \\
 \mathcal{R}_m &= 1.7 \cdot 10^{-5} \sum_{i,j=1}^N \varepsilon_m [\mathbf{R}_{ij} \cdot (\boldsymbol{\mu}_j \times \boldsymbol{\mu}_i)] c_{mi} c_{mj}
 \end{aligned} \tag{1.3}$$

Here, c_{mi} represents i -th element of $|\psi_m\rangle$ with $c_{mi} = \langle i|\psi_m\rangle$, and $\mathbf{e}$ is a unit vector along the long axis of the tube.

¹One should be careful about how the multidimensional array data are stored. For instance, in the diagonalization function I used, `scipy.linalg.eigh`, the output eigenvectors are stored as column vectors, following the column-major order format in Fortran language.

1.3.3. Quantum Dynamic Simulation of Exciton Evolution

Compared to classical mechanics, where particles move according to Newton's laws of motion, in quantum mechanics, wave functions propagate according to the time-dependent Schrödinger equation⁸¹

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle. \quad (1.4)$$

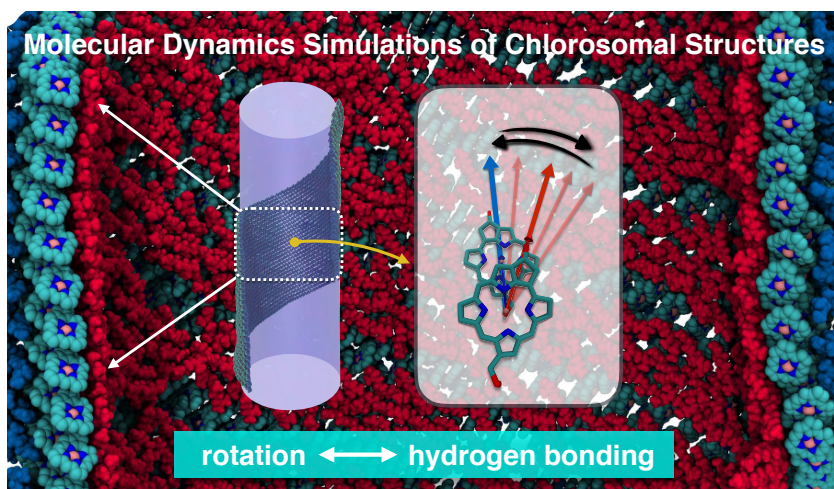
Just as mass is an essential property of particles in the classical domain, energy is a crucial property for wave functions. We only consider closed quantum systems, meaning that the total energy is conserved due to the absence of any form of dissipation. Non-stationary evolution takes place when $|\psi\rangle$ is a mixture of different stationary states $|\phi_i\rangle$ of the Hamiltonian $\hat{H}$, for instance, $|\psi\rangle = c_1 |\phi_1\rangle + c_2 |\phi_2\rangle$. In such a case, the unitary evolution of $|\psi(t)\rangle$ governed by Eq. 1.4 gives rise to a time-dependent density matrix $\rho(t)$

$$\begin{aligned} \rho(t) = |\psi(t)\rangle\langle\psi(t)| &= |c_1|^2 |\phi_1\rangle\langle\phi_1| + |c_2|^2 |\phi_2\rangle\langle\phi_2| \\ &+ c_1 c_2^* e^{-i(E_1 - E_2)t/\hbar} |\phi_1\rangle\langle\phi_2| \\ &+ c_1^* c_2 e^{-i(E_1 - E_2)t/\hbar} |\phi_2\rangle\langle\phi_1|. \end{aligned} \quad (1.5)$$

The first two (diagonal) terms represent populations in the exciton state basis, and the latter two (off-diagonal) terms describe coherences.²³ The phase factors in the coherence terms determine the population variation in the site basis, and give rise to an oscillating exciton evolution in real space. In particular, the frequency of this oscillation depends on the energy difference $\Delta E = E_1 - E_2$ and increases when ΔE increases. If we additionally would concentrate on interactions with the environment, *i.e.* an open quantum system, energy dissipation, and loss of coherence due to decoherence effects will modulate the density matrix $\rho(t)$ in Eq. 1.5. In this thesis, however, such non-stationary effects are not considered. Instead, we study the role of ground-state nuclear motion by using a time-dependent Hamiltonian $\hat{H}(t)$ and solve $i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle$. This Hamiltonian $\hat{H}(t)$ is constructed from a fully in parallel propagating classical molecular description of the same system on which the quantum evolution is considered, which is coupled by exchanging the nuclear information that is required for computing the $J(t)$ contribution to $\hat{H}(t)$ at discrete Δt , *e.g.* 20 fs, intervals. We note that, although $\hat{H}(t)$ has now indeed become time-dependent,

this dependence is in practice rather weak on a short time interval of 20 fs between consecutive updates, owing to the minute variations in intermolecular distances and induced dipole moments that take place on such a time scale. For this reason, we have considered a constant $\hat{H}(t)$ between updates, see also ref [82, 83] and details in Chapter 4, which simplifies the calculation of the wave function evolution by time integration of $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle$. We note that reverse coupling, *i.e.* including the effect of excitation on the nuclear motion, is lacking. This is in line with the usual assumption that molecular reorganizations due to excitation, as signaled by the Stokes shift, are minor and can be neglected, which is particularly the case in the context of our effective Frenkel description.

Contrasting Modes of Self-Assembly and Hydrogen-Bonding Heterogeneity in Chlorosomes of *Chlorobaculum tepidum*



This chapter is based on: Xinneng Li, Francesco Buda, Huub J.M. de Groot, and G. J. Agur Sevink, J. Phys. Chem. C, 2018, 122, 14877-14888 (<https://pubs.acs.org/doi/10.1021/acs.jpcc.8b01790>). Further permissions related to the material excerpted should be directed to the ACS.

Chlorosome antennae form an interesting class of materials for studying the role of structural motifs and dynamics in non-adiabatic energy transfer. They perform robust and highly quantum-efficient transfer of excitonic energy while allowing for compositional variation and completely lacking the usual regulatory proteins. Here, we first cast the geometrical analysis for ideal tubular scaffolding models into a formal framework, in order to relate effective helical properties of the assembly structures to established characterization data for various types of chlorosomes. This analysis shows that helicity is uniquely defined for chlorosomes composed of BChl *d* and that three chiral angles are consistent with the Nuclear Magnetic Resonance (NMR) and Electron Microscope (EM) data for BChl *c*, including two novel ones that are at variance with current interpretations of optical data based on perfect cylindrical symmetry. We use this information as a starting point for investigating dynamic and static heterogeneity at the molecular level by unconstrained molecular dynamics (MD). We first identify a rotational degree of freedom, along the Mg–OH coordination bond, that alternates along the syn-anti stacks and underlies the (flexible) curvature on a larger scale. Since rotation directly relates to the formation or breaking of interstack hydrogen bonds of the O–H $\cdots$ O=C structural motif along the *syn-anti* stacks, we analyzed the relative fractions of hydrogen-bonded and the non-bonded regions, forming stripe domains in otherwise spectroscopically homogeneous curved slabs. The ratios 7:3 for BChl *c* and 9:1 for BChl *d* for the two distinct structural components agree well with the signal intensities determined by NMR. In addition, rotation with curvature-independent formation of stripe domains offers a viable explanation for the localization and dispersion of exciton states over two fractions, as observed in single chlorosome fluorescence decay studies.

2.1. Introduction

The largest light-harvesting antennae found in nature, the chlorosomes, have evolved at an early stage and allow photosynthetic green bacteria to survive under light limiting conditions and at very low light intensity.⁶⁰ In contrast to other photosynthetic light-harvesting antennae, for which a protein scaffold supports the structural order and functionality, the chlorosome antenna function is accomplished by hundreds of thousands bacteriochlorophyll (BChl) *c*, *d*

or *e* molecules that self-assemble into pseudosymmetric *syn-anti* parallel stacks forming curved sheets and concentric tubes.¹⁵ Although every chlorosome has a unique structure, they all share the common feature of long-range transfer of extended excitons over distances of several hundreds of nm.

While high BChl concentrations in solution would result in energy dissipation and loss, owing to a rapid quenching of excitonic energy, nature has managed to avoid this in chlorosomes by a protein-free encoding of distinct, functional BChl packings that display remarkable homogeneity and have gross structural variability at the supramolecular and higher levels. Consequently, there is much interest in obtaining a fundamental understanding of structure-dynamics-function relations in chlorosomes, including how quasi-coherent exciton transfer driven by nuclear motion enables the near-unity yield. This principle can potentially be exploited for more efficient, sustainable and environmentally clean ways of converting solar energy, via the rational design of molecular components for artificial photosynthesis. Currently it is unclear how the hierarchy of structural and dynamical properties enable an amazing quantum efficiency for transfer within and between tubes, and the dominant mechanisms are strongly debated.^{84,85}

Persistent variability in the form of two components that are each well-ordered on a local scale has been concluded from the pronounced splitting of NMR signals for several mutants.³⁹ A recent study of single chlorosomes confirms the NMR finding that the variations in the molecular arrangement and the microscopic disorder over the whole chlorosome assembly are limited.⁴⁵ The optical linewidths of $\sim 100 \text{ cm}^{-1}$ that can be extracted for individual chlorosomes, comprising both static and dynamic disorder, confirm the remarkably homogeneous molecular arrangement in two components observed with MAS NMR. The four peaks in polarization resolved fluorescence-excitation data were attributed to low- and high-energy doublets for separate structure motifs with slightly different characteristics, *i.e.* curvature and molecular arrangement. Their attribution to quantitatively different tubes contrasts with the earlier MAS NMR and TEM investigations, which alternatively attributed the two components to transition regions between domains within the tube. The single layer line and other details of the MAS NMR and TEM diffraction responses for different chlorosome species and mutants³⁹ provide converging evidence that tubes in extended tube structures are quantitatively equivalent.

Our starting point for the current computational study comes from two types of structural information. Information on the short range structure — an elementary *syn-anti* dimer — was previously derived from NMR data³⁷ and later refined by Miloslavina *et al.* (unpublished results), for details see Figure A.7. The arrangement of these elementary dimers, with medium range order extending over several tens of monomers, was revealed by a layer line in the power spectra calculated from cryo-EM images, collected from the more homogeneous mutant chlorosomes,³⁷ and can be used for extracting the overall helicity. The helical nature of the chlorosome is conserved upon variation of the BChl composition and a Bijvoet pair of spots on the equator reveals well-determined inter-tube spacings around 2 nm, depending on the species.¹⁵

In addition, several groups have carried out optical measurements to estimate an angle θ for the effective transition dipole moment relative to the symmetry axis of the tubular aggregates from the dichroic ratio.^{80,86–88} The response to excitation is clearly a collective phenomenon, meaning that this angle does not necessarily translate down to the level of individual molecules.⁸⁰ However, the ratio of the oscillators strengths along the two principal directions was shown to directly relate to the angle β , see Figure 2.1, for monomer transition dipole moments if one assumes a perfect cylindrical lattice model that satisfies special symmetry conditions,^{45,79} which provides an additional geometrical constraint. For *bchR* mutant chlorosomes, the measured ratio translates into $\beta \sim 56.1^\circ$ and $\beta \sim 52.2^\circ$ for the two structural components, values that are well in line with the orientation of the molecular dipoles in the original *bchQRU* model by Ganapathy *et al.*³⁷ and a structure for the wild type (WT) by Miloslavina *et al.* (unpublished results). Nevertheless, since assembly structures can notably deviate from the idealized situation that is at the basis of this explicit relation, we will not regard this information as a strict constraint in this work.

Using unconstrained all atom molecular dynamics (MD) simulations, we first evaluate the stability of the pseudosymmetric *syn-anti* motifs, *i.e.* the principle building block of chlorosomes determined from NMR, and then study the propensity of such *syn-anti* stacks to form concentric chiral tube structures, thereby departing from the ideal tube model. By performing simulations for an initially planar system, containing either BChl *c* or BChl *d*, we resolve the molecular origin of curvature and determine distinct structural variability and global dynamic heterogeneity of the BChls within a curved assembly. Recent computational work based on molecular mechanics (MM) and Density

Functional Theory (DFT) has not been able to reveal these basic properties,⁶⁷ since their phase space exploration capability is too limited.⁸⁹ As the time scale τ for structural rearrangement scales as $\tau \sim \xi^z$, with ξ the correlation length ($\sim$ size) and $z > 0$ a dynamical exponent that depends on the kinetic model, also the starting structure for large-scale MD simulations should be chosen with care to avoid kinetic trapping. We start all simulations from a planar Bravais lattice provided by the most recently proposed triclinic unit cells for BChl *d*.³⁷ In studies of electronically excited states, the molecular structure is usually generated by projecting regular 2D Bravais lattices onto ideal tubes.^{36,40–45,90} As a reference to our MD results, we first refine such idealized models by a geometric analysis that links the position of the layer line for the *syn-anti* stacks to an overall chirality that satisfies all experimental constraints.

The nanosecond MD simulations in this work show that defined curvature develops spontaneously for planar systems, and confirms that symmetry breaking is an inherent property of parallel stacking of the pseudosymmetric *syn-anti* BChl dimer building blocks. According to our simulations, a rotational degree of freedom around the Mg–OH coordination bond enables molecules to resolve frustration at the expense of giving up O–H $\cdots$ O=C interstack hydrogen bonds and assume adaptive curvature of sheets or tubes. The signal ratios for the two fractions determined from the splitting of NMR signals matches the ratio of hydrogen-bonded and non-bonded domains in the simulations of a single tube, which provides a first sound structural basis for the presence of two well-defined structural components, randomly distributed over the curved helical structure. We note that, in a helical structure, a majority phase is likely to percolate, and that the simulated diffraction response for this structure confirms that these diffractions give rise to a single layer line in reciprocal space, in agreement with the cryo-EM diffraction response. We note that the *syn-anti* parallel stacking leads to polar sheets and cylinders with extended dipoles along the central axis, rendering the lowest exciton states strongly delocalized, twisting around the tubes.^{45,86} Since dipoles and transition dipoles of concentric cylinders overlap in space, correlated dynamics will give rise to fluctuations of the cylinder dipoles and time-dependent detuning of energy levels that may give rise to quantum instabilities. Here, we provide the first detailed structural and dynamical information beyond the current, idealized picture of chlorosomes, which is a valuable starting point for future studies of vibrational-excitonic coupling.

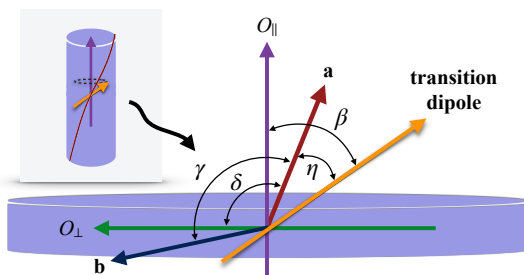


Figure 2.1: Schematic illustration of the angular relations in a tubular structure. The angle between the cylinder axis ($O_{||}$) and the induced molecular transition dipole moment (the so-called monomeric transition) is given by β , its angle with the vector **a** of the Bravais lattice by η and the chiral angle by δ . For δ between 0° and γ , $\beta = |(\delta - 90^\circ + \eta)|$. We note that chiral angle with respect to the parallel symmetry axis, $\delta_{||}$, is obtained as $\delta_{||} = |\delta - 90^\circ|$. Moreover, we selected a Bravais reference frame such that the rolling vector varies between **a** and **b**. Hence, the chiral angle defined in Günther *et al.*⁴⁵ differs from ours and is equal to $|180^\circ - \delta|$, with δ our chiral angle.

2.2. Computational Details

The OPLS-AA force field^{91,92} was used for all simulations. All initial structures of pigment molecules (BChl *c* or *d*) were optimized using DFT calculations (HF/6-31G* or higher level). The equilibrium bond and angle values in the force field were obtained from optimized DFT structures, giving special care to the Mg atom. In order to maintain a ~ 0.21 nm coordination distance between Mg and O, their Lennard-Jones non-bonded interaction parameters were selected based on Roccatano *et al.*⁹³ In addition, four Mg-N bonds were added to keep the Mg atom centered within the ring.

Atomic point charge parameters were obtained by the RESP method⁹⁴ at the HF/6-31g* level using Gaussian03 software.⁹⁵ Charges obtained at the B3LYP/6-31G* level were also considered. In comparing them, we focused on their effect on packing by extracting lattice parameters for a small simulated system (5*5 dimers). We found that lattice parameters vary only very slightly (within 5%) with the chosen method. For larger simulated systems, we expect equivalent variations.

MD simulations with periodic boundary conditions along all dimensions were performed with the Gromacs 5.1.2 software package.^{96,97} A Particle-mesh Ewald method⁹⁸ was used to treat the long-range electrostatic interactions. We performed simulations in a NVT canonical ensemble, maintaining the simulation temperature by a velocity-rescaling thermostat.⁹⁹ Additional details are provided in the Appendix A simulation method section. We simulated the assembly of 17²-farnesyl-(R or S)-[8-ethyl,12-ethyl]BChl *c* or *d* pigments, which have been considered extensively in the experimental and simulation literature.^{37,39,67,100} The ratio between R and S components in the dimer is 1:1 in agreement with Ganapathy *et al.*³⁷

Our initial simulation structures are planar, obtained by prolongating the proposed *syn-anti* dimer structure periodically. The lattice is defined in terms of two principle directors **a** and **b**, with length $a = |\mathbf{a}|$ and $b = |\mathbf{b}|$ relating to the experimental repeat distances, and their mutual angle γ (see Figure A.7c). The whole structure, in terms of the number of periodic repeats of dimers along these two directions, is denoted as (A, B), *e.g.* the structure in Figure A.7c is for (5, 5).

2.3. Results and Discussion

2.3.1. Refinement of the Ideal Tube Model

Since their development in the seventies, Fourier-Bessel reconstruction methods have become a major tool for reconstructing the three-dimensional (3D) structure of naturally occurring helical assemblies like actin, myosin filaments, microtubules, amyloid fibrils and bacterial flagella from 2D electron micrographs. The theory and challenges, associated with indexing and assigning helical symmetry for complicated assemblies like proteins, can be found in a number of review papers,^{63,101–103} and explicit geometrical relations between the layer line position and the chiral BChl packing on a tubular lattice in terms of (variable) unit cell parameters are provided in the Appendix A. For these relations to hold exactly, one only has to assume an ideal tube model for the chlorosome; in the remainder, we will perform unconstrained MD simulations to investigate whether this is justified. We note that this idealized

representation renders the geometrical description of chlorosomes and inorganic single-walled nanotubes (SWNT) equivalent, apart from the particular Bravais lattice.

In mathematical terms, our analysis focuses on finding appropriate solutions for the underdetermined system of equations that relate the four principal unknowns, *i.e.* the parameters (a, b, γ) for the dimeric unit cell and the chiral angle δ , to the layer line position $(1/d)$ determined from TEM. Inspired by the NMR and TEM findings, we consider a δ that is invariant under changes of the tube radius R and conserve the unit cell for chlorosomes that feature different layer line positions. Solutions in previous works were based on selecting chiral angles δ from packing considerations that directly related to unit cell parameters, resulting in the well-known packing models: $\delta = 90^\circ$ for the WT with $d = a = 1.25$ nm and $\delta = 0^\circ$ for *bchQRU* with $d = b \sin(\gamma) = 0.83$ nm.³⁷ Since their publication, these models have been debated and further refined.^{45,104,105} For example, recent optical experiments for single chlorosomes linked $1/d = 1/1.24$ nm⁻¹ for a *bchR* mutant,⁴⁵ equal to the WT value ($1/1.25$ nm⁻¹) within the considered resolution, to two chiral angles $\delta = (71 \pm 2)^\circ$ for two different structural components. This is equivalent to $\delta = (109 \pm 2)^\circ$ in our framework (see caption of Figure 2.1).

On relating the one visible experimental layer line to geometrical properties of the chiral BChl stacks in the Fourier-Bessel framework, our key challenge boils down to selecting the *proper* helical family of the tube,^{63,103} given that each helical family constitutes one layer line in reciprocal space. In particular, the distance to the equator for that layer line relates to the reciprocal value of the axial repeat d for that helical family. As discussed in more detail in the Appendix A information, we concentrate on calculating the d that correspond to the principal $(0, 1)$ and $(1, 0)$ helical families, by a geometrical analysis of the Bravais lattice in real space, since they, together with the $(1, 1)$ helical family, represent the closest packing or most stable spacings in the tube in the considered range of δ . Moreover, it is known that a small tilt of the tube with respect to the plane of imaging can produce a meridian signal,¹⁰¹ and that replacing idealized point scatters by actual vibrating molecules can give rise to an amplification or weakening of the layer line intensity, which explains why only one reflection of these principal helical families is observed in the noisy power spectrum. A power spectrum calculated directly from a 3-tube aggregate with a distinct layer line at $1/d = 1/1.25$ nm⁻¹, Figure A.6, clearly illustrates

this effect. Adopting the nomenclature of Moody *et al.*,¹⁰⁶ the axial repeat d is the repeat distance along the tube axis between adjacent helices (for a n -start helical family, $d = P/n$) and the pitch P is defined as the axial advance after one complete helix turn. Figure 2.2 shows the theoretically predicted axial repeat distance d versus chiral angle δ for three candidate helical families — d_a and d_b , corresponding to assembly along the **a** and **b** direction, respectively, and d_{armchair} , corresponding to an analogue of the armchair conformation in SWNT — rendered for the equilibrium unit cell parameters of the simulated (30, 30) BChl *c* system: $(a, b, \gamma) = (1.48 \text{ nm}, 0.98 \text{ nm}, 124.3^\circ)$ at 300 K. For these unit cell parameters, our geometrical analysis predicts a unique solution $\delta_{0.83} = 13^\circ$ (or, with respect to the tube axis, $\delta_{\parallel} = 77^\circ$) for *bchQRU* and three candidate solutions for the WT. One of these candidates, $\delta_{1.25} = 50^\circ$ ($\delta_{\parallel} = 40^\circ$), implies that chirality varies only gradually with a change of the molecular side groups, since both BChl *c* and *d* stacks wrap along the same **a** direction. The two other candidates for the WT, $\delta_{1.25} = 80^\circ$ (armchair, $\delta_{\parallel} = 10^\circ$) and $\delta_{1.25} = 112^\circ$ ($\delta_{\parallel} = 22^\circ$) (wrapping along **b**), imply that a change of the side groups gives rise to a topological transition.

The predicted chiral angles $\delta_{0.83} = 13^\circ$ for *bchQRU* and $\delta_{1.25} = 112^\circ$ for the WT are consistent with the earlier proposed values in Ganapathy *et al.*³⁷ if one accounts for the different dimension of the unit cell. In particular, the **a**-axis in our larger unit cell needs to be tilted to match the experimentally determined pitch length, hence we find $\delta_{1.25} = 112^\circ$. Following this reasoning, the unprecedented prediction $\delta_{1.25} = 50^\circ$ can be understood in terms of a similar tilt in the opposite direction.

As mentioned in the introduction, a recent study for individual *bchR* mutant chlorosomes, composed of slightly modified BChl *c*, determined an average angle $\beta \approx 55^\circ$ (with respect to the tube axis) for the induced monomer dipoles, from the ratio of parallel and perpendicular oscillator strengths. Yet, angles θ estimated from the dichroic ratio by earlier studies are often smaller ($\theta = 15\text{--}25^\circ$) or distributed over a broader range, which has been interpreted in terms of structural variation between species^{88,107} or in terms of the preparation method.^{86,104} Straightforward analysis of the average angle β between the orientation of the BChl head groups and the symmetry axis in our setup, see Figure A.9, shows that $\delta_{1.25} = 112^\circ$ agrees well with $\beta \approx 55^\circ$. Nevertheless, MD simulations show that pre-packed nested three-tube BChl *c* assemblies are stable for both tested values of $\delta_{1.25}$, *i.e.* $\delta_{1.25} = 50^\circ$ and 112° , and layer line

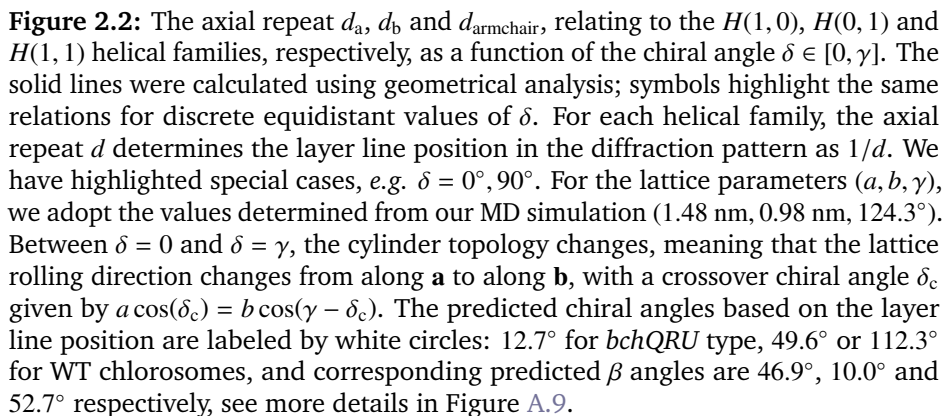
positions determined by FFT are in excellent agreement with predicted values.

We may benefit from the fact that we optimized local structure by MD to extract specific unit cell parameters directly from the simulated (30, 30) BChl *d* system (see Figure A.8 for details). We considered the most cylindrical structure (1 ns at 50 K) to allow for easy extraction of unit cell parameters and δ , giving rise to $(a, b, \gamma) = (1.46 \text{ nm}, 0.93 \text{ nm}, 122.5^\circ)$ and $\delta = 19.1^\circ$. Inserting these unit cell parameters in the general expression for d_a provides the alternative unique solution $\delta = 19.8^\circ$ for $d_a = 0.83 \text{ nm}$. Comparing it to the extracted chiral angle $\delta = 19.1^\circ$, we find that they match very well, so we will consider $\delta_{0.83} = 19.8^\circ$ in the remainder. Thus, although our simulated BChl *d* aggregate is too partial to provide a well-defined layer line by the usual procedure, see discussion in the Appendix A, this equivalence between simulated and theoretical values leads us to conclude that the longer-range structural properties of the simulated BChl *d* aggregate match very well with the ones for the *bchQRU* mutant containing an excess of [E,M]BChl *d*.

As a comment to earlier work,⁴⁵ we find that the experimentally observed sequence of tube radii is fully consistent with two fixed chiral angles, $\delta_{0.83}$ and $\delta_{1.25}$, for nested tubes in the two systems. We considered $\delta_{1.25} = 112^\circ$ in this analysis, but note that it is illustrative for the other two values of $\delta_{1.25}$. Restricting the maximum variation of δ to a tiny $|\Delta\delta| < 0.2^\circ$, lattice periodicity plays a role in determining which radii are commensurate, but we find that commensurate R very consistently match experimental values, see Figure A.4. This analysis also shows that a maximum variation of only 1° is sufficient to produce *any* tube radius R , given that the discrete increment ΔR that stems from lattice restriction is in the order of the experimental resolution. Our simulations thus show that the tube radius is essentially a scale-free parameter, *i.e.* not restricted by any inherent length-scale in the system. This interesting observation agrees well with the nucleation and growth formation kinetics of chlosoromes,^{100,108} since it allows for flexibility to adopt any radius to tightly wrap new layers around an existing (and possibly defected) nucleus.

2.3.2. MD Simulation Results

Unconstrained molecular dynamics simulation allows us to gain fundamental insight in the deviations from the ideal case and the origin of curvature, as



well as relate local structure to global properties of the assembly. Our analysis of MD simulation results focuses on the following complementary aspects: I) Large-scale structure and evolution, as well as properties (radius R , pitch P and chiral/pitch angle δ) of the spontaneously formed tubular structures, including the overall conformation of the farnesyl-tails. II) Local structural details by an *in situ* analysis of the curved aggregates, concentrating on stabilizing factors and interactions, and on the relative rotation between *syn-anti* and *anti-syn* pairs, which provides quantitative insight into the driving factors for curvature formation. III) Since local dynamics changes the detailed network of interactions between BChls, in particular the hydrogen bonding, we also evaluated the dynamics of this rotational degree of freedom and its role in the formation of hydrogen bonded domains. We focused on the angular sampling statistics for an isolated dimer, and consequently evaluated the role of these twisting motion in our simulated structures.

Large-scale structure: intrinsic and flexible curvature

Our MD simulations provide computational evidence that the proposed local *syn-anti* stacking model³⁷ gives rise to a stable aggregate, with initial forces that are well within bounds, and a tendency to spontaneously curve on the scale of the aggregate. Figure A.12 shows MD simulation snapshots for an initially planar sheet, built from (30, 30) BChl *c* *syn-anti* dimer stacks, that wraps quickly as a whole to form a helical tube structure well within 1 ns¹. The obtained curved structure remains stable when further simulated in hexane solvents. To determine the effective tube radius at the end of the simulation, we used a least square algorithm to fit a cylinder to the coordinates of the Mg atoms, see Figure A.12a. Helical features of the BChl packing along the tube can be observed both visually and from the characteristic peaks in the calculated 2D Fourier spectrum for the Mg atoms, see Figure A.12b. The fast kinetics and accompanying jump in the potential energy (Figure A.12c) suggests that the curved structure is thermodynamically much more stable than a planar structure, and that the driving force for this transition is rather large. This argues against a curvature-invariant system, with curvature purely induced by thermal fluctuations, which is usually a very slow process.

¹Full trajectory movie S1-movie.avi in [chapter_2](#) folder at https://github.com/xinmeng2015/chlorosome_phd_thesis or <https://doi.org/10.5281/zenodo.3674742>

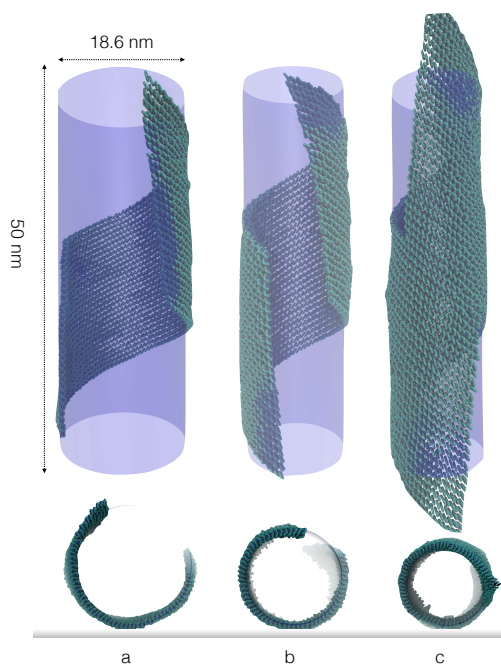


Figure 2.3: Simulation results obtained for different systems: (a) the (30, 30) BChl *c* system at 50 K, (b) the (30, 30) BChl *c* system at 300 K, which started from the final structure obtained at 50 K, and (c) the (40, 30) Me-BChl *c* system at 300 K, *i.e.* in absence of the farnesyl tail. Cylinders are fitted to the coordinates of the Mg atoms using the same procedure as in Figure A.12. All sizes are scaled equivalently, enabling a proper visual analysis of relative sizes. From left to right, the radius of the fitted cylinder is 9.3 nm, 6.8 nm and 6.1 nm respectively. For clarity, side groups of the head part and tails are not shown.

The packing parameters obtained by simulation, (1.48 nm, 0.98 nm, 124.3°) for BChl *c* and (1.46 nm, 0.93 nm, 122.5°) for BChl *d*, see Table A.1, are based on the analysis of the local packing of neighboring dimer units assuming a planar arrangement, which is a valid assumption for large tube radii. Overall, we find that the packing into a curved tubular structure is quite regular, with small static heterogeneity, which is in agreement with the visual observation of regular packing of Mg atoms (Figure A.12b). We have additionally applied a procedure introduced by Connolly¹⁰⁹ on part of the simulated structure, using the standard 1.4 Å Connolly radius, to determine its effective volume and consequently the BChl *c* density as 1.348 g/cm³, which compares well with the density of 1.31 g/cm³ determined by X-ray crystallography for Ethyl Chlorophyllide *a* Dihydrate.¹¹⁰

The tube structure obtained by 50 K NVT simulation remains stable after increasing the temperature to 300 K. The packing parameters show almost no dependence on the simulation temperature, *i.e.* the relative change in the packing parameters is within 2% upon equilibration at 300 K, which is negligible. Yet, globally, the radius of the fitted cylinder can be seen to change significantly, from 9.335 nm to 6.840 nm (Figure 2.3b).¹ This variation of the tube radius, for a structure with very similar local packing features, reveals the sensitivity of our assembly structure to temperature, and the flexibility to adjust the assembly properties on a large scale while conserving the packing on a local scale. We further consider this relation by performing a geometrical analysis.

Large-scale structure: helicity

The simulated assemblies for BChl *c* are defected but clearly tubular and, on a local scale, pigments can be seen to adopt a helical arrangement, so it makes sense to perform a quantitative analysis in terms of large-scale structural properties: the tube radius R , and pitch P and the earlier discussed chiral angle δ of the helix, also known as the pitch angle. For structures obtained after 1 ns simulation, simulated at different temperatures, see Figure 2.4b, we find that both R and P decrease monotonically with increasing temperature. However, the third parameter, δ , adopts a constant value of $\delta \approx 31^\circ$. The only

¹Molecular structure (.pdb) files in `chapter_2` folder at https://github.com/xinmeng2015/chlorosome_phd_thesis or <https://doi.org/10.5281/zenodo.3674742>

exception is $T = 50$ K, where the chiral angle is significantly lower (Figure 2.4c). However, as our simulations are performed sequentially, using the 1 ns result obtained at 50 K as input for a simulation at higher T after (local) equilibration, the deviating chiral angle for 50 K can be explained in terms of the reduced simulation time, if we disregard the alternative explanation of a genuine structural transition in the range 50–100 K.

All simulated curved aggregates are only partial tubes after 1 ns simulation, meaning that the periodicity imposed by the Bravais lattice, which may affect helical properties, does not play a role at that stage. In the absence of the farnesyl tail, see Figure 2.3, the initially flat Me-BChl *c* sheet curves and closes upon itself within 1 ns to form a closed (complete) tube. The extracted chiral angle δ for this system is somewhat larger ($\sim 40^\circ$) than for the partial tubes, but we lack insight in the particular effect of the tail on this property. An axial repeat $d = 1.0$ nm, close to $|\mathbf{b}| = 0.98$ nm, was extracted (see Figure A.5) from the layer line in the simulated electron microscopy images for this full tube. This value agrees with the geometrical prediction for $\delta = 40^\circ$ in Figure 2.2 and the real space observation that the tube symmetry axis is almost parallel to $\mathbf{b}$.

All partial tubular structures appear stable on the 1 ns time scale of the simulation. Continuing the simulation for the highest considered temperature, $T = 300$ K, shows that the partial tube does close up after roughly 2 ns. Closing up stabilizes the structure: the tube diameter is constant and the rugged connection zone does not notably change, either via (local) reorganization of dis-/reconnection, in the following 8 ns of simulation. Apparently, while a flat structure is unstable, the thermodynamic driving force for structural reorganization away from a non-optimal δ and/or radius is tiny and/or the rearrangement kinetics too slow to be captured by MD. Based on these arguments, we conclude that the processing history and/or the environment (e.g. solvent or lipids) is vital for obtaining the appropriate chirality by MD, which agrees well with experimental information on this system.¹¹¹ We may, however, assume that enhanced kinetics will give rise to a chiral structure featuring the predicted $\delta_{1,25} = 50^\circ$ rather than the other two options, $\delta_{1,25} = 80^\circ$ and $\delta_{1,25} = 112^\circ$, which require a topological transition. We also note that partial tube structures that are observed in experiments can be interpreted as a lack of material needed for fully closing up. Overall, these findings are consistent with a templated formation of concentric tubes, in which newly forming layers can easily adapt their curvature to an existing nucleus while reproducing the

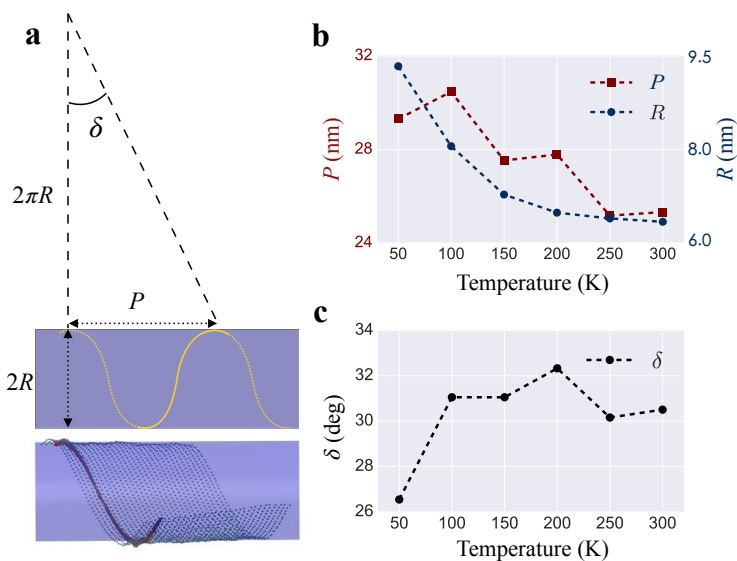


Figure 2.4: (a) Illustration of the principle helical family $H(1,0)$ and its relation to the radius R , pitch P and chiral angle δ . (b–c) Large scale properties (cylinder radius, pitch and chiral angle) for temperatures in the range 50–300 K, as determined for the $H(1,0)$ helical family for the (30, 30) BChl *c* system after 1 ns simulation: (b) Fitted cylinder radii R and pitch P at different simulation temperatures; (c) Fitted chiral angles δ at different simulation temperatures. With increased temperature, both the radius and pitch decrease, while the chiral angle first increases and then assumes a constant value, indicative of a structural transition between 50 K and 100 K. These results show that the chiral angle is the only conserved structural property, with the pitch adapting to a particular radius.

local packing characteristics of that nucleus. Helicity plays a key role in this proposed mechanism, as a helical pigment arrangement is the only option for accommodating a continuously variable tube radius.

Large-scale structure: symmetry breaking

In principle, there are two out-of-plane directions in which the planar symmetry can be broken. Each of them gives rise to a curved structure with different chirality and with different (*syn* or *anti*) tail domains at the concave or convex side of the curved structure. We may distinguish these options in terms of $\pm \mathbf{a} \times \mathbf{b}$, *i.e.* the cross product of two principle directors, see Figure A.7c. In particular, tails distribute to either side of the tube, depending on the head type (*syn* or *anti*) to which they are attached, owing to the mutually parallel orientation of the pigment heads in the elementary *syn-anti* dimer,³⁷ showing that local packing plays a key role in the distribution of tails. This tail distribution is in strong contrast to anti-parallel head-head dimer stacking which would lead to both tails naturally ending up at one side of the stack, see Pandit *et al.*'s work¹¹² for a classification of molecular stacking options for related zinc-chlorins.

Despite limited statistics, only one curving direction ($-\mathbf{a} \times \mathbf{b}$) is consistently found in all simulations. Also without the (farnesyl) tails, *i.e.* when considering Me-BChl *c* instead, the head stacks curve in the same direction. This preferential direction is equivalent to *syn* tails always ending up at the concave side for all curved structures (see Figure 2.5). The appearance of a preferential helical chirality is a feature of chiral asymmetry.

The actual chirality of natural/mutant chlorosomes could be extracted by circular dichroism (CD), which would enable us to validate our finding of chiral asymmetry. In practice, however, CD spectra for such psi-type assemblies show undesired variability.^{15,88,113} Theoretically, the magnitude and sign of these spectra were not only shown sensitive to various particular structural properties,¹¹⁴ but also the same three-band (-, +, -) CD signal was calculated for quite different tubular dipole arrangements by related methods based on point-dipole approximations.^{79,80,105} Nevertheless, for chlorosomes that most closely match the studied systems, *i.e.* the *bchQRU* containing primarily BChl *d*¹¹⁵ and an artificial one composed of only BChl *c*,⁸⁸ the same type I spectrum⁸⁸ was measured, which may be attributed to our type of dipole arrangements based on the available information.⁷⁹

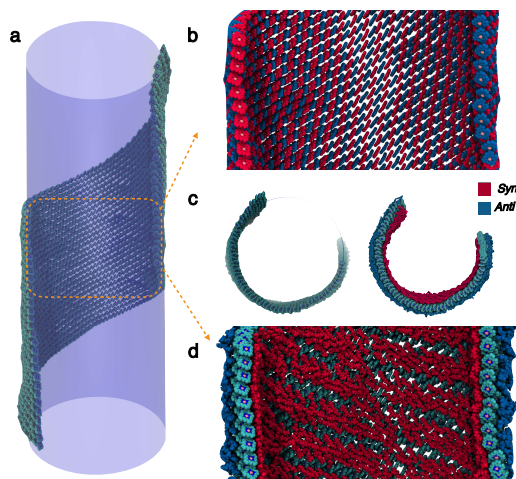


Figure 2.5: Details of the *syn-anti* packing for the curved structure obtained after 1 ns MD simulation of (30, 30) BChl *c* system at 50 K. *Syn* and *anti* BChl *c* molecules are shown in red and blue respectively. (a) Curved structure (repeated from Figure A.12a) and fitted cylinder. For clarity, side groups of head part and tails are not shown; (b) *syn-anti* packing of heads, showing high order of head parts even in curved domain; (c) Projection of the pigment assembly along the cylinder axis with and without tails, displaying the spatial extent of the tails in the curved structure. The concave (convex) side of the curved structure is covered by *syn* (*anti*) tails, respectively; (d) Details of the tail structure, illustrating the groove like nature of the tail phase at the concave side of the curved structure, leaving enough free space for other molecules to occupy, as well as the liquid-crystal like order of the tail phase for this low temperature.

Distributed between the tubular stacks, tails determine the inter-tube structure and spacing. Ideal tube models, *i.e.* single tubes obtained from a lattice of dimers by projection,^{36,40–45,90} usually consider tails to be fully extended orthogonal to the tubular domain, as the experimental data do not provide sufficient information on tail conformations in the assembly. We find that tails adhere to head groups belonging to adjacent dimers, see Figure 2.5d, which explains why simulations for dimers fail to capture these tail configurations. Consequently, the orthogonal projection of the end to end distance ($d_{\perp}$) is quite small ($|d_{\perp}|/|d| \approx 0.2$, see Figure A.10), when compared to the fully extended chains ($|d_{\perp}|/|d| \approx 1.0$) in current projection models.

To analyze whether our tail configurations directly relate to the inter-layer distance $d_{\text{exp}} = 2.0\text{--}2.1$ nm determined from Bijvoet pairs for multi-tubular WT and mutant chlorosomes,³⁷ we determined the thickness of the simulated tail layer. For our aggregates, which comprise a single tube *in vacuo*, we find that the inter-layer distance matches the experimental value 2.1 nm quite well (see Figure A.11). In contrast, fully stretched tails in ideal models would translate into a substantially increased inter-layer distance. This finding gives us confidence to conclude that the tail configurations in our MD simulations are also realistic for a multi-tube system, suggesting that tails from different tubes do not experience notable interpenetration.

From the simulation snapshot shown in Figure 2.5d, tails can be seen to bundle together on a larger scale, leaving sufficient space to accommodate small molecules like the carotenoids that were extracted from natural chlorosomes.^{116,117} Though less ordered than heads, tails adopt a liquid crystal like order at low temperatures when considered locally (Figure 2.5b and 2.5d).

Although tails fill the interstitial space between tube layers, and determine their spatial separation, they are not a key factor in curvature formation. The latter can be concluded from simulation of a (40, 30) Me-BChl *c* sheet at 300 K (Figure 2.3c), where large scale curvature forms spontaneously in the absence of farnesyl tails. Thus, we conclude that curvature formation originates from head-head packing.

In-situ analysis: stabilizing factors

Next, we analyze the interaction network between neighboring BChl *c* by considering the nearest distances distribution of interacting groups in the head domain and their overlap ratio. Two types of pair interactions stand out: (i) The interactions between Magnesium and Oxygen atoms ($\text{Mg} \cdots \text{O}-\text{H}$ in Figure 2.6a) coordinate neighboring pigments along the packing direction **a**. (ii) Hydrogen bonds formed between the hydroxyl group and the carbonyl oxygen, see $\text{O}-\text{H} \cdots \text{O}=\text{}$ in Figure 2.6a, stabilize the molecular assembly along the **b** direction. Since each pigment molecule contains a Donor (hydroxyl group oxygen) and an Acceptor (carbonyl group oxygen), which are both capable of forming hydrogen bonds, three states are needed to describe this bonding: “2-hb”, *i.e.* both Donor and Acceptor form hydrogen bonds, “1-hb”, *i.e.* either Donor or Acceptor forms a hydrogen bond, and “0-hb”, *i.e.* no hydrogen bond is formed.

We find that the distribution of $\text{Mg} \cdots \text{O}-\text{H}$ distances is narrow with an average around 0.21 nm (Figure 2.6b). In contrast to the Mg and O–H groups, which always coordinate to each other, we find that not all neighboring O= and O–H groups always form hydrogen bonds. We quantify this property by considering the ratio between the actual number of hydrogen bonds between Donors and Acceptors and the total number of Donors and Acceptors. For the (30, 30) BChl *c* system at 50 K, this ratio is approximately 0.7, meaning that 70 % of all possible hydrogen bonds is actually formed, see details in Figure A.13. We note that, for a system with a similar packing, modification of groups that are capable of hydrogen bonding did not destabilize the assembly.¹¹⁸ This confirms our finding that the formation of hydrogen bonds along the **b** direction is not vital for the stability of the assembly structure. To conclude this analysis, the ratio extracted from the simulated BChl *d* structures at 50 K is around 0.9, meaning that both simulated values are consistent with the signal splitting ratios in the NMR experiments of chlorosome containing an excess of BChl *c* (7:3) and BChl *d* (9:1).^{37,39}

We attribute the overall stability of the assembly along both **a** and **b** directions to the unique π - π stacking between the head parts along both directions. Earlier static calculations for Zn-chlorins¹¹⁸ confirm this conclusion. The packing distance between head parts for our system is found to be 0.356 nm (Figure 2.6d), as determined from the average line distance, which is a characteristic

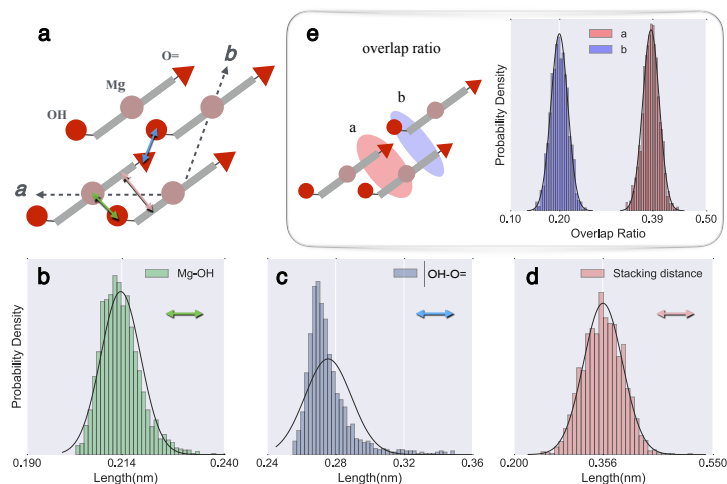


Figure 2.6: Analysis of key interactions in the assembly, as determined from the curved structure obtained by MD simulation of (30, 30) BChl *c* system at 50 K after 1 ns. (a) Schematic representation of the interacting groups that promote pigment assembly along the packing direction *a* and *b*; (b) Distribution of nearest distances between Mg and O atoms, important for coordination between Mg and OH groups; (c) Distribution of nearest distances between OH and O=, important for hydrogen bonds formed between neighboring carbonyl oxygen and hydroxyl group; (d) Distribution of nearest distances between stacking layers, important for π - π interactions. The mean value is 0.356 nm, which is a characteristic value for π - π stacking; (e) Head-head stacking overlap ratio along *a* and *b* directions. The overlap ratio calculation is based on the Van der Waals geometry of carbon atoms in the head part, ignoring substitutes.

value for π - π stacking. The really unique feature in this structure is that along the **a** direction, heads only partially overlap, owing to the $\text{Mg} \cdots \text{O}-\text{H}$ coordination, which is compensated by a partial overlap along the **b** direction: the head-head packing overlap ratios along both **a** and **b** directions were determined as 0.39 and 0.2, respectively, see Figure 2.6e. In this way, π - π stacking plays a role along both directions, strengthening the interaction framework of the assemble structure.

In-situ analysis: curvature-inducing factors

Dimers that satisfy the key stabilizing factors of the larger assembly, *i.e.* coordination and π - π overlap, have only one degree of freedom left: to adjust their rotation relative to their neighbors. In particular, one can anticipate that curvature should originate from consistent adjustment of relative rotation angles throughout the whole structure. For this reason, we extracted the relative rotational angle α between adjacent pigments, which is defined as the angle between $\text{Mg} \cdots \text{O}=\text{}$ and $\text{Mg} \cdots \text{Mg}$ vectors after being projected on one molecule's rigid ring surface (Figure 2.7a), with the aim of providing quantitative molecular insight in the origin of large-scale curvature formation.

It should be understood that, although a *syn-anti* dimer is the structural element, packing in a larger structure gives rise to alternating *syn-anti* (intra-dimer, α_{intra}) and *anti-syn* (inter-dimer, α_{inter}) pairs, see Figure 2.7. The sign of α is determined by the cross product of the two key vectors; for typical pairs, $\alpha_{\text{intra}} > 0$ and $\alpha_{\text{inter}} < 0$. Analyzing all pairs in the curved structure for $T = 50$ K, we find that the signature of alternating positive and negative α is well maintained throughout the large assembly (Figure 2.7b). Analyzing their distributions for a single snapshot of the curved structure, see Figure 2.7c, shows that a broad range of α -values is sampled. This rotational heterogeneity may contribute to the broadening of the optical spectra. Closer examination suggests a slight asymmetry, *i.e.* $\langle \alpha_{\text{intra}} \rangle + \langle \alpha_{\text{inter}} \rangle = -2.78^\circ$. Improving the statistics, however, by adding snapshots of a tubular structure along the simulation trajectory, does not give a unimodal distribution, but clarifies that the sampling of this rotational degree of freedom is broad (see Figure A.14) with a mild preference for specific α -values.

To allow for more firm conclusions about symmetry breaking, we performed additional analysis. In particular, we introduced a simplified representation

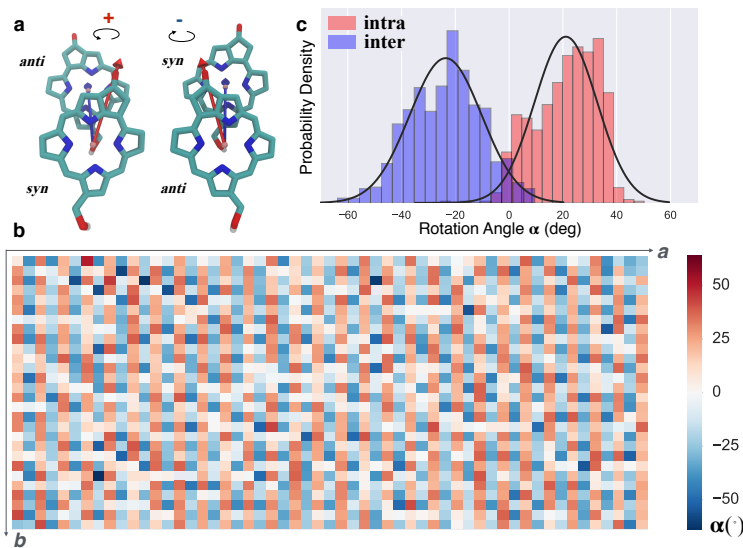


Figure 2.7: Orientational details of head-head stacking, extracted from the curved structure obtained in MD simulation of (30, 30) BChl *c* system at 50 K, after 1 ns. (a) Typical intra-dimer and inter-dimer stacking configurations associated with primarily positive and negative relative rotational angles, respectively. Although the *syn-anti* dimer is the basic structural element, on the level of individual pigment there is an alternating packing of *syn-anti* (intra-dimer) and *anti-syn* (inter-dimer) configurations. The relative rotational angle α is defined by the angle between Mg-O2 and Mg-Mg vectors (labeled as red and blue arrows) after being projected on top molecule's rigid ring surface. The sign is determined by the direction of the cross product of the two vectors; (b) Individual values for the rotational angles along the assembly structure; (c) Distribution of intra-dimer and inter-dimer rotation angles, illustrating the asymmetry in packing.

with handedness and consider $\Delta\beta = \beta_{\text{intra}} - \beta_{\text{inter}}$, with the angles β_{intra} and β_{inter} determined as in the inset of Figure 2.8. Using geometrical arguments, it is easy to show that one obtains a tubular structure with helical ordering for $\overline{\Delta\beta} = c \neq 0$, where the bar represents the average value. Analysis of simulated curved structures along the simulation trajectory at 50 K indeed suggests that such a non-zero $\overline{\Delta\beta}$ exists, as can be seen from the peak position of the $\Delta\beta$ distribution (Figure 2.8). Increasing the temperature (to $T = 300$ K) transforms this bimodal distribution into a unimodal Gaussian-like distribution centered around $\overline{\Delta\beta} \neq 0$. The unimodal nature of this distribution is clearly the result of increased thermal fluctuations (Figure A.15), which helps the system to overcome energy barriers along this rotational coordinate. This finding is consistent with the large-scale analysis of the helical tube structures (see earlier section).

Our detailed analysis illustrates how the pseudo-symmetry of the elementary structure develops into a well-defined asymmetry, via symmetry breaking in the head-head packing, which is the basis for large-scale curvature formation at a molecular level. The global flexibility to adopt varying curvature should also be seen to originate from the local head-head packing. Since the distribution of $\Delta\beta$ is rather broad, the assembly is rather flexible in incorporating various curvatures on a larger, global scale.

In-situ analysis: hydrogen bonding

We consider the curved structure at 50 K to analyze the formation of hydrogen bonds using the three state description introduced earlier. We find that different states are organized into striped domains on the projected 2D structure, see arrows in Figure 2.9, meaning that they form helices on the tube as discussed in the theory section in the Appendix A. Interestingly, almost all “0-hb” states (no hydrogen-bonding) are next to “2-hb” states (fully hydrogen bonded).

With the appearance of “0-hb” and “1-hb” states in Figure 2.9, it is clear that not all residues capable of hydrogen bonding are “saturated”. As mentioned previously, around 70% of these residues do form hydrogen bonds in this curved BChl *c* structure at 50 K. Correlating the two local properties, rotation and hydrogen bonding, via the absolute value of the relative rotation angle distribution $|\alpha|_{\text{no-hbonding}}$ for molecules that are not-hydrogen bonded (the absolute value of the rotation angle is sufficient, since we do not need to

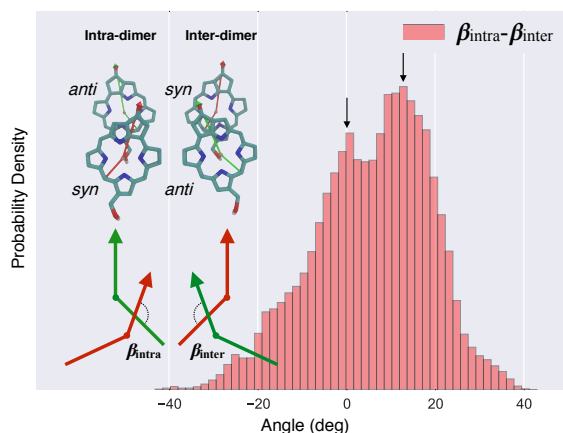


Figure 2.8: Distribution of difference ($\beta_{\text{intra}} - \beta_{\text{inter}}$) between neighboring intra-dimer and inter-dimer rotation angles in the representation that incorporates handedness, as extracted from the curved structures along a MD trajectory for a (30, 30) BChl *c* system at 50 K, between 500 ps to 1 ns. The inset shows the intra-dimer and inter-dimer configurations and the way the corresponding angles β_{intra} and β_{inter} are determined. When the intra-dimer (*anti-syn*) and inter-dimer (*syn-anti*) configurations are (anti-)symmetric, the packing angle difference $\beta_{\text{intra}} - \beta_{\text{inter}}$ is 0° . Nevertheless, a major distribution peak around $12.6^\circ > 0^\circ$ appears, suggesting consistent asymmetry between the chiral intra-dimer and inter-dimer configurations in the curved structure. Such asymmetry is the origin of the transition from the translational symmetry in the initial flat structure to helix symmetry in the simulated curved structure. Moreover, reconstructing structures containing alternating *syn* and *anti* representation with a fixed positive $\beta_{\text{intra}} - \beta_{\text{inter}}$ value gives rise to an anti-clockwise growth and a curved structure. Such a curved structure is consistent with the curved structure obtained in simulation when *syn* tails are located in the concave side of the curved structure.

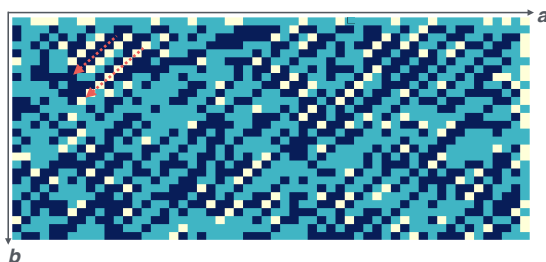


Figure 2.9: Hydrogen bonding states for individual molecules along the curved structure obtained in MD simulation of (30, 30) BChl *c* system at 50 K, after 1 ns. Depending on the number of hydrogen bond formed on a molecule, three states are defined: “2-hb” (dark blue), “1-hb” (light blue) and “0-hb” (white).

distinguish between inter- and intra-dimer pairs), shows that hydrogen bonds are broken when the relative rotations exceed some threshold value, with $|\alpha|_{\text{no-hbonding}}$ distribution peaking around 35° . In particular, hydrogen bonds do not interfere with the interaction between neighboring Mg and carbonyl group oxygen atoms (the $\text{Mg} \cdots \text{O}=\text{C}$ interaction is strongest for $|\alpha| = 0^\circ$, see Figure A.16 for distribution and analysis details.)

Dynamics: rotational sampling distribution

Although the total number of hydrogen bonds can be seen to converge to a constant value with time, see Figure A.13, their distribution over the curved structure varies considerably with time. Hydrogen bonds between molecules in neighboring stacks are formed and broken in a concerted manner to conserve their overall number, but no diffusion of striped “0-hb”, “1-hb” or “2-hb” domains as a whole was observed¹. In combination with the narrow distribution of Donor-Acceptor spacings, see Figure 2.6, these findings clarify the correlation between the relative rotation angle α and hydrogen bonding between BChl stacks, and indicate the role of individual BChl *c* rotations in the curved structure.

We further zoomed in by performing spectral analysis of time traces of the

¹File S2-movie.avi in chapter_2 folder at https://github.com/xinmeng2015/chlorosome_phd_thesis or <https://doi.org/10.5281/zenodo.3674742>

relative rotational angle α for a number of well-chosen dimers, making sure to select combinations of monomers that belong to different states, *i.e.* "0-hb", "1-hb" or "2-hb", at the end of the trajectory. Analysis of individual traces shows that hydrogen bonding does affect this rotational dynamics, by modulating the amplitude of the variations in α . Yet, we find that all calculated spectra in the frequency domain consistently show a band around 125–180 cm⁻¹, see the Appendix A for details. We tentatively assign this band to the 145 cm⁻¹ low frequency mode observed by ultrafast spectroscopy.^{84,85}

Finally, we analyzed the sampling distribution of the relative rotational angle α , see Figure 2.10, for a dimer to obtain a better understanding of the rotational dynamics in the larger aggregate. This reduced dimeric system enabled us to perform a much longer (50 ns) MD simulation, which considerably improves the sampling statistics. Our choice for the Me-BChl *c* dimer means that we neglect the influence of tails and the matrix of surrounding dimers.

The simulated rotational angle distribution for this dimer reveals that several configurations are stable: a higher probability relates to more stable configurations or a lower potential energy via the Boltzmann factor. We identify two dominant rotation angles: $\alpha_I \approx 0^\circ$ and $\alpha_{II} \approx 20^\circ$. Indeed, the Mg and O= groups are in closest contact for α_I , which is associated with the highest probability density. For α_{II} , the probability is only slightly reduced and the intermediate depression is not very pronounced, suggesting that the energetic barrier between states α_I and α_{II} is rather modest. Beyond these two peaks, *i.e.* $\alpha > \alpha_{II}$, the clear drop of probability density hints at the presence of a more pronounced energetic barrier, which is consistent with the probability distribution data extracted for the large assembly in Figure 2.7c.

Four characteristic configurations (labeled by the associated α) were selected for direct potential energy comparison (Figure 2.10): three values for stable states ($\alpha_{I,II,IV}$) along this angular coordinate and an intermediate or transition state (α_{III}). We find that α_I indeed has the lowest potential energy, followed by α_{II} with an increase in the order of 5 kJ/mol. The change of the potential energy for α_{IV} is still modest (see Table 2.1), while the transition state α_{III} is indeed associated with the highest increase. The reduced head-head overlap that accompanies an increasing α clearly gives rise to a destabilization of the structure or an increased potential energy. This is consistent with the larger assembly structure, where the probabilities of these larger α 's are indeed

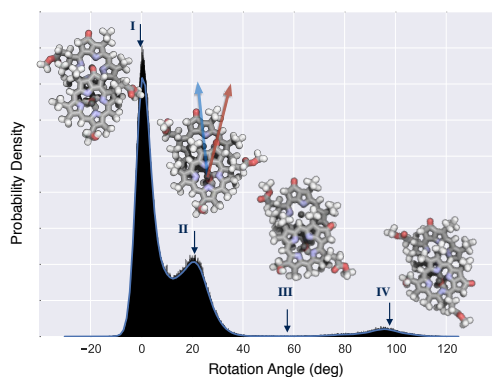


Figure 2.10: The distribution of the relative rotation angle for Me-BChl *c* dimer, obtained by simulating a *syn-anti* dimer at 200 K. The whole 50 ns MD simulation trajectory was considered. Three characteristic configurations are selected for potential energy comparison between fully atomistic and quantum modeling, see Table 2.1, and are denoted by arrows; the fourth, a transition state, is only considered in the context of MD. The simulation temperature was chosen to provide sufficient phase space sampling, while maintaining a chlorosome-like *syn-anti* packing.

considerably reduced, see Figure 2.7. To test the consistency of our MD force-fields, we complemented this analysis by a potential energy calculation by *ab initio* MD (AIMD), using the characteristic configurations from MD as input for AIMD equilibration. AIMD confirms the stability of the three stable MD states (see Appendix A for details of the procedure). Moreover, the potential energy trends are very similar, see Table 2.1, albeit that the potential energy surface for MD is clearly flattened compared to AIMD.

2.3.3. Final Discussion

The heterogeneity in chlorosomes appears due to frustration, as a result of the competition between the stabilizing network of interactions and curvature-driven rotation away from the preferential conformation in a *syn-anti* dimer motif. The aggregation of BChl in sheets and tubular assemblies is apparently not compatible with the formation of an array of hydrogen bonds that is commensurate with the Bravais lattice formed by the BChl. The resulting

Table 2.1: Potential energy comparison of the three stable characteristic configurations. For MD, the potential energy of the transition state is added, to give an idea of the energy barrier. For AIMD, the average energy of the reference state is reported, and reported energies for other configurations are differences.

state	I	II	III	IV
Angle α ($^\circ$)	-0.2	21.5	57.5	98.1
MD (kJ/mol) ^a	0	4.0	15.4	9.0
AIMD (kJ/mol) ^b	0	15.7	-	36.7

^a reference value 2563.9 (kJ/mol); ^b reference value -782.449 (Hartree).

hydrogen-bonding defects form stripes that are randomly distributed over the system, but appear pinned to the underlying lattice. In particular, since the rotational mode is soft, hydrogen bonds can be switched on and off, as we may think of parallels to the folding funnel in proteins. The random distribution of pinned defects over the pseudo-symmetric lattice makes that every chlorosome is unique all the way down to the supramolecular level.

Our computational results provide an alternative explanation for the two sets of super-radiant states that were tentatively attributed to two types of tubes in a single chlorosome:⁴⁵ the FWHM of the frequency spectrum associated with our rotational mode is $30\text{--}40\text{ cm}^{-1}$, *i.e.* well within the residual broadening of $\sim 100\text{ cm}^{-1}$, inferred from fluorescence excitation experiments, that should cover both static and dynamic heterogeneity. In the ground state of the imperfect lattice, several modes are enhanced and contribute to a disordered energy landscape. Since the energy levels of the BChl will depend on its position along the rotational coordinate and the hydrogen bonds, it is tempting to conclude that such modes can give rise to non-adiabatic coupling elements for quasi coherent energy transfer by resonant coupling upon crossing of exciton levels. The relatively strong vibrational band centered around 160 cm^{-1} agrees well with the time scale of 100 fs for rapid exciton transfer in chlorosomes determined by coherent optical spectroscopy.⁸⁴

2.4. Conclusions

Detailed information on the structure and heterogeneity in natural chlorosomes provides necessary insight towards the understanding of the unique excitonic properties of these assemblies, and enables the design of synthetic mimics with similar efficiency. In this study, we have combined a formal geometrical analysis and unconstrained MD to obtain unique insight in the direct relation between molecular detail and structure, curvature formation, symmetry breaking, and stabilizing factors, as well as static and dynamic heterogeneity within a curved structure. An intriguing finding is that out-of-plane rotation and hydrogen bonding compete, which identifies a new type of heterogeneity that is consistent with NMR observations.

From a structural perspective, the overarching question is how and why nature selects particular chiral angles for structuring within the considered chlorosomes. Here, the ‘how’ is clarified: by building in asymmetry at the molecular level, which translates into specific chirality at the macroscale. We find that our MD simulations *in vacuo* properly capture this mechanism for the BChl *d* system, where the $\delta = 19.1^\circ$ extracted from the simulated aggregate agrees very well with the predicted $\delta_{0.83} = 19.8^\circ$ of *bchQRU*. For BChl *c*, our theoretical analysis predicts three chiral angles $\delta_{1.25}$ that match the experimental NMR and cryo-EM information. The tube topology for the chiral angles extracted from simulation, $\delta = 31^\circ$ with farnesyl tail and $\delta = 40^\circ$ without tails, *i.e.* curved along the **a** direction of strongest interactions, agrees with one of these predictions, $\delta_{1.25} = 50^\circ$. Yet, optical measurements for single chlorosomes⁴⁵ were combined with theory to predict an orientation of the monomeric transition dipoles that only agrees with $\delta_{1.25} = 112^\circ$, *i.e.* curved along the **b** direction, albeit that this prediction is uncertified for structures that do not agree with the special symmetry conditions of the theory.⁷⁹ An independent way to ascertain the actual helicity is to numerically calculate optical spectra for our candidates based on a Frenkel Hamiltonian,⁸⁰ which will additionally allow us to evaluate details, such as signals originating from two distinct structural components, that are lost in the averaging procedure. Nanosecond MD simulations of pre-assembled structures (single and multiple tubes) for the alternative $\delta_{1.25}$ confirm their stability.

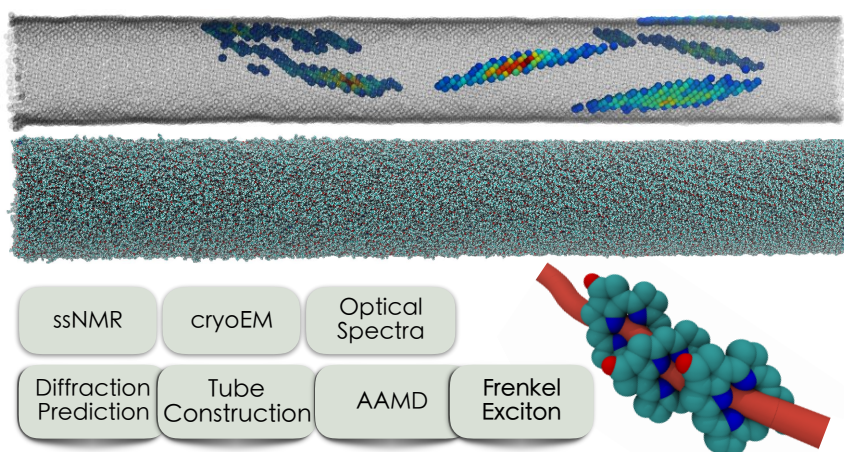
Overall, clearly many factors secure the molecular organization in natural

chlorosomes, such as the formation kinetics, matrix templating and/or nesting, which agrees well with the experimental finding that spectroscopic properties of reconstituted structures crucially depend on processing conditions. The detailed insight provided in this study, into the molecular origin of large-scale curvature and structure, local packing and dynamics within the confines of the curved aggregates, has a general value and validity, and will serve as input and inspiration for more detailed computational investigations of excitonic-vibrational coupling.

2.5. Acknowledgments

We are very grateful to Dr. Yuliya Miloslavina for sharing an unpublished optimized unit cell for BChl *d*. X.L. and G.J.A.S. acknowledge the funding by the VW foundation on the context of an international project Multiscale hybrid modeling of (bio)membranes. The use of supercomputer facilities was sponsored by NWO Physical Sciences, with financial support from the Netherlands Organization for Scientific Research (NWO).

Molecular Insight in the Optical Response of Tubular Chlorosomal Assemblies



This chapter is based on: Xinnmeng Li, Francesco Buda, Huub J.M. de Groot, and G. J. Agur Sevink, *J. Phys. Chem. C*, 2019, 123, 16462-16478 (<https://pubs.acs.org/doi/abs/10.1021/acs.jpcc.9b03913>). Further permissions related to the material excerpted should be directed to the ACS.

A systematic procedure is developed for determining unique stackings of BChl molecules in different types of chlorosomes directly from characterization data, using information about: i) the dimeric unit cell from Nuclear Magnetic Resonance (NMR), ii) local stacking distances from cryo-electron microscopy (cryo-EM), and iii) large-scale chirality from absorption, linear- and circular-dichroism spectra. To enable a comparison with optical data, we have employed a Frenkel Hamiltonian formalism to calculate optical properties of pre-assembled tubes of realistic 120 nm length. Our analysis for the first time explains the variability of optical signals measured for chlorosomes and points at chiral angles $\delta = 105^\circ$ for BChl *c* and $\delta = 19.8^\circ$ for BChl *d* that satisfy all information contained in i)-iii) within experimental and computational accuracy, where the asterisk denotes that the large-scale tube curvature is reversed. We also find that the dynamic disorder is not sensitive to particular chirality. To investigate the effect of disorder on excitonic features, we have represented correlated deviations from a crystalline order due to thermal energy, as extracted from all-atom molecular dynamics (AAMD) calculations, directly in the coupling terms of the Frenkel Hamiltonian, assuming that variations of site energies can be neglected. The use of AAMD snapshot for sampling relevant molecular conformations allows us to study molecular origins of important emergent phenomena in chlorosomes. We find that our model reproduces two mechanisms — exciton localization and level crossing — that have been proposed to play a key role in the transfer of excitonic energy. This highlights the importance of the usually disregarded rotation-related electronic coupling variations in the exciton properties.

3.1. Introduction

Chlorosomes are assemblies of bacteriochlorophylls (BChls) that enable light harvesting at very low light intensities as well as highly efficient transfer of excitonic energy in green sulfur bacteria.¹⁵ They are intriguing examples of how nature manages to secure efficiency and robustness without protein-based encoding and structural frameworks, rendering an improved understanding of their design principles a primary research target for the development of smart nano-devices for light-harvesting. Nuclear magnetic resonance (NMR) and cryo-electron microscopy (cryo-EM) have contributed to a better understanding

of short-range structural properties in chlorosomes of different organisms that each feature a specific composition.³⁷ Limited information on the secondary structural organization for any of the studied chlorosomes or their reconstituted analogues, and incomplete insight how to resolve their secondary structural based on the available experimental information, pose a challenge to a better understanding of chlorosomal function encoding.

The evasiveness of the higher order structural regularity is usually attributed to gross heterogeneity, which encompasses heterogeneity in size, overall shape, and in composition, as well as static and dynamic disorder in the internal organization of molecules on an overall regular lattice.¹⁶ Nevertheless, the widths of spectroscopic signals for individual wild type (WT) chlorosomes provide strong indications that there is considerable regularity in the BChl positioning even at larger scales, and suggest a cylindrical symmetry.⁸⁶ The accepted structural model for chlorosomes is that of a concentric tubular superstructure generated by wrapping curved sheets of stacks of *syn-anti* parallel dimers.³⁷ Within sheets, dimers are thought to be loosely positioned on a 2D Bravais lattice, and held together by an interaction network of π - π overlap, coordination, and hydrogen bonding (Chapter 2).

Combining all-atom molecular dynamics (AAMD) simulations and geometrical analysis, we recently reconsidered the lattice dimensions and we determined a small set of chiral angles δ that agree with the cryo-EM derived power spectra upon 2D lattice-to-cylinder projection (Chapter 2). Moreover, we identified dynamic heterogeneity in terms of a rotational degree of freedom of BChl molecules, which is closely linked to the formation and breakage of hydrogen-bonded domains. This degree of freedom is the hallmark of a plastic crystal, in which weakly interacting molecules possess orientational or conformational degrees of freedom within a regular, crystalline framework. Such intrinsic structural heterogeneity can only be represented at atomic resolution.

The current study has a dual focus. On one hand, we further refine our matching procedure by also including optical data in the matching criteria. The starting point for the comparison of calculated optical spectra are the usual Frenkel Hamiltonian⁸⁰ and pre-assembled 120 nm long tubes with chirality δ determined by our geometrical analysis. Moreover, in contrast to studies that only compare a single spectrum,⁴⁵ we uniquely account for the absorption, linear and circular dichroism spectra simultaneously in our matching procedure.

Our analysis shows that three sources of data — NMR, cryo-EM and optical spectra — suffice to single out chiral angles δ for both wild-type or mutant chlorosomes. Previously, Günther *et al.*⁴⁵ also concluded that combined data is required for unambiguous determination of chirality, but they analyzed the angle-dependent absorption spectrum upon excitation in terms of an idealized lattice model.⁴⁵

Next, we have analyzed the excitonic properties of tubular assemblies along the AAMD trajectory in order to investigate how disorder at a molecular level relates to the unique excitonic properties of chlorosomes.¹¹⁹ We concentrate on both single and three-layered tubes of BChl *c*. In our Frenkel Hamiltonian treatment, we account for explicit disorder only in the coupling between different molecules, *i.e.* the off-diagonal terms of the Hamiltonian, based on our previous finding that molecular rotation is an important dynamical feature. Since exciton delocalization relates to only very weak energetic disorder when compared to coupling,¹⁹ we choose to neglect fluctuations in the diagonal terms. We show that our current treatment is indeed capable of capturing two proposed mechanisms for exciton transfer — localization and level crossing — and thus allows us to rationalize their molecular origins. Our treatment goes well beyond existing computational studies that are based on regular lattices^{36,79,80,105} or investigate disorder in terms of random perturbations of Hamiltonian elements, which ignore correlations in both the small- and large-scale tube dynamics.

The main achievements of this study are (i) the development of a procedure that maps heterogeneous data to unique BChl packings at multiple scales; (ii) the first molecular insight into the effect of disorder on the properties of super-radiant excitonic domains in tubular chlorosomes, extending insight obtained from 2D spectroscopy measurements;¹²⁰ (iii) insight into the sensitivity of the excited state to the dynamic disorder, indicating the key role of correlated molecular motion in the EET of chlorosomes.¹²¹

3.2. Computational Methods

3.2.1. Building and Simulating Molecular Assemblies

For details about our computational approach and unit cell parameters for *syn-anti* dimers of BChl *c* and BChl *d*, we refer to Chapter 2. All AAMD simulations *in vacuo* were performed in a canonical ensemble (NVT), using a velocity-rescaling thermostat⁹⁹ and periodic boundary conditions. To avoid interference with periodic mirrors, the tube structures are centered in a large simulation volume of $30 \times 30 \times 140 \text{ nm}^3$, with at least 7.5 nm distance to any boundary. Tubular superstructures with pre-defined chiral angles are grown through one-by-one addition of dimeric unit cells. The approximate sizes of the resulting optimized tubes are 120 nm (length) and 15 nm (diameter), which are close to the actual dimensions in nature.¹⁵ To alleviate possible molecular frustration and partial overlap of tail parts resulting from the growth algorithm, and to ensure stable AAMD, we first perform standard structure optimization by steepest descent for the complete structure. Structural disorder in the head part after energy minimization is found to be negligible, thus this structure, labeled $T = 0 \text{ K}$, can be seen as ordered. Subsequently, a short (100 ps) MD simulation at 50 K is carried out with the position of atoms in the head part fixed, in order to further relax the configuration of the (farnesyl) tail part of the molecules. After this step, all constraints are relieved and a 1 ns MD simulation is performed at 50 K to introduce mild structural disorder. Finally, the temperature is increased to 300 K and the system is evolved for 1 ns at ambient temperature, which is expected to result in stronger structural disorder.

To investigate the sensitivity of the excited states to the dynamic disorder, we generated MD trajectories for single-tube and concentric-tube with two different time resolutions: one dilute sampling with one configuration every 20 ps, in total 500 ps and one dense sampling with one configuration every 20 fs, in total 1 ps. Since calculating the optical response is computationally intensive, the tube length for both trajectories is 60 nm instead of the usual 120 nm. We have confirmed computationally that the spectra features show very little length dependence in the range from 60 nm to 120 nm (see Appendix B).

3.2.2. Calculating Optical Spectra

We adopt the Frenkel Exciton Hamiltonian^{79,80}

$$\hat{H} = \sum_i v_i(\mathbf{R}) |i\rangle\langle i| + \sum_{i \neq j} J_{ij}(\mathbf{R}) |j\rangle\langle i| \quad i, j \in [1, N] \quad (3.1)$$

to calculate the optical response of chlorosome tube aggregates composed of N molecules. Here, atomistic detail contained in the coordinates $\mathbf{R}$ is explicit in the $v_i(\mathbf{R})$ on the diagonal, representing the monomer excitation energy of the molecule at site i , and in the off-diagonal terms, $J_{ij}(\mathbf{R})$, which represent the electronic coupling between molecules i and j . In the next subsection, we discuss the different options for representing this molecular detail. For ordered helical lattice tube models,^{36,45,79,80,105} i.e. in the homogeneous limit, $v_i(\mathbf{R})$ and $J_{ij}(\mathbf{R})$ are independent of molecular details and $v_i(\mathbf{R}) = v$ is a constant value, while $J_{ij}(\mathbf{R})$ is given by a simple geometrical relation depending on the distance vector $\mathbf{R}$. However, when one includes microscopic molecular detail to account for the disorder that is eminent in most photosynthetic structures,¹⁸ one has to consider the $\mathbf{R}$ -dependence explicitly. For the electronic coupling $J_{ij}(\mathbf{R})$, we consider the standard point dipole approximation (PDA),

$$J_{ij}(\mathbf{R}) = \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{|\mathbf{R}_{ij}|^3} - 3 \frac{(\boldsymbol{\mu}_i \cdot \mathbf{R}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{R}_{ij})}{|\mathbf{R}_{ij}|^5} . \quad (3.2)$$

with $\boldsymbol{\mu}_i = \boldsymbol{\mu}_i(\mathbf{R})$ the effective transition dipole moment vector for molecule i and $\mathbf{R}_{ij}$ the distance vector between the two transition dipoles labeled by i and j .¹²² We note that the PDA stems from the leading term in a multipole expansion of the Coulomb coupling, and is known to overestimate the coupling strengths at distances that are small compared to the spatial dimension of the molecules.⁷⁶ Nevertheless, the PDA is commonly employed for densely-packed BChls in chlorosomes instead of the more elaborate methods that derive couplings from quantum-chemical calculations or efficient transition charges from electrostatic potentials (TrEsp) estimates,⁷⁶ because calculated red shifts based on PDA-coupling and empirical parameters were found to consistently match measured values.^{35,36,40,41,45,79,80} In our case, all off-diagonal coupling terms in the Hamiltonian are calculated using dipoles that are extracted from coordinates $\mathbf{R}$ of our AAMD trajectory. For reasons explained in the next

subsection, we consider a constant site energy in the diagonal terms of $\hat{H}$. The general form of the density matrix describing the excited state manifold for the system at time t after photoexcitation is

$$\rho(t) = \sum_{i=1}^N \sum_{j=1}^N \rho_{ij}(t) |i\rangle\langle j|, \quad (3.3)$$

where $\rho_{ij}(t)$ describes the populations ($i = j$) and coherences ($i \neq j$) in the site basis.¹⁹ In the present study, we do not consider exciton dynamics explicitly.

We select a site energy $\nu = 15390 \text{ cm}^{-1}$ that was derived from the Q_y -transition of isolated BChl *c* in methanol for the monomer excitation energy.⁸⁰ For simplicity, we assign the same monomer excitation energy ν to BChl *d*, as slightly shifted values will only lead to an overall translation of spectra without changing the spectral shapes. The transition dipole moment vector μ_i is taken oriented along the vector connecting two nitrogen atoms (N_I and N_{III})⁴⁰ in agreement with the transition dipole moment determined in a recent theoretical TDDFT study.¹²³ The length $|\mu_i|$ of this vector is 5.48 Debye, which is estimated from experimental data¹²⁴ and used in several studies.^{35,36,40,80} We note that an additional factor 5.04 enters J_{ij} due to a conversion of Debye to units of cm^{-1} .¹²⁵

Diagonalization of the Hamiltonian matrix $\hat{H}$ provides N eigenvectors $|\psi_m\rangle$ and eigenvalues ε_m that correspond to the stationary exciton state and excitonic transition energy, i.e. $\hat{H}|\psi_m\rangle = \varepsilon_m|\psi_m\rangle$. As $\hat{H}$ is both real and symmetric, ε_m are real and the wave functions $|\psi_m\rangle$, providing a state basis for the description of the excited system, can also be chosen to be real.^{36,80} Eigenvectors are usually sorted with respect to the excitonic transition energy, from lowest to highest. A spatial analysis of these state vectors is of vital importance for understanding the excitonic behavior of chlorosomes. For this purpose, a state vector $|\psi_m\rangle$ can be represented on the site basis $|i\rangle$

$$|\psi_m\rangle = \sum_{i=1}^N c_{mi} |i\rangle \quad (3.4)$$

with $|i\rangle$ a state where only the molecule at site i is excited, while all other molecules are in the ground state. In the site basis view, the contribution of a specific site i involved in the state $|\psi_m\rangle$ is given by $p_i^m = |\langle i|\psi_m\rangle|^2 = |c_{mi}|^2$, which

is often called the exciton density of the molecule at site i and can be visualized by color coding. The spatial extent of an excitonic state $|\psi_m\rangle$ is quantified by the inverse participation ratio:^{36,126,127}

$$\text{IPR}_m = \frac{1}{\sum_{i=1}^N |c_{mi}|^4} \quad (3.5)$$

with $\text{IPR} = 1$ for a fully localized state, *i.e.* confined to a single site, and $\text{IPR} = N$ for a state that is fully delocalized over all sites in the tube. In the remainder, we concentrate on the exciton state with the largest oscillator strength, which is often called the absorption state or $\psi_{\max}$ for brevity.³⁶

Each exciton state $|\psi_m\rangle$ corresponds to a wavelength equals to the corresponding eigenvalue ε_m (horizontal position) and a signal strength (vertical axis) d_m for absorption (OD), LD_m for Linear Dichroism (LD) and $\mathcal{R}_m$ for Circular Dichroism (CD), which have been calculated according to the known expressions, see Eq. 1.3.^{78,80}

In order to relate our results to earlier publications, stick spectra calculated using Eq. 1.3 have been convoluted with a normalized Gaussian profile in a post-processing step in a form similar with Linnanto's work.³⁶ This operation mimics the experimental variability that leads to signal broadening, which stems from both the static and dynamic disorder that is present in the studied chlorosomes. Since several estimates have been previously used,⁸⁰ we show spectra plots for range of FWHM values from 10 to 350 cm^{-1} .

3.2.3. Parameters in the Frenkel Hamiltonian

A key limitation in using the Frenkel formalism for large-scale assemblies like chlorosomes is the difficulty to determine all terms in the Hamiltonian $\hat{H}$ microscopically using *ab initio* calculations. Thus, in order to come to a computable $\hat{H}$, several types of approximations have to be made. A common approximation is to account for $\mathbf{R}$ -dependent contributions only in diagonal elements of $\hat{H}$, *i.e.* in structure-dependent variation of the site energy. While this approximation may be warranted for pigment-protein complexes, it ignores the effect of varying electronic coupling $J_{ij}(\mathbf{R})$, *i.e.* the off-diagonal terms, due to the substantial rotational twisting motions of the BChl head groups that has been observed along the AAMD trajectory. Electronic coupling is seen as

a key factor for the fast EET process in photosynthesis complexes.²⁰ We note that, for our simulated structures, the influence of different BChl homologues in the structure, structural defects and variations, and vibrational modes that are slow compared to the exciton life times, is absent or fairly limited. For this reason, the contribution of static disorder to $\nu_i(\mathbf{R})$ is not discussed here.

Several groups have attempted to quantify $\nu_i(\mathbf{R})$. The contribution of changing molecular configurations and/or their environment to a dynamic modulation $\Delta\nu_i(\mathbf{R}) = \nu_i(\mathbf{R}) - \nu_i^0$ can in principle be evaluated using combined quantum chemical/electrostatic methods for a fairly limited number of residues.^{72–76} However, even in such cases, calculating electronic excited states with proper accuracy remains a challenge.⁷³ For example, the accuracy of TDDFT calculations is limited to 0.5–0.4 eV,⁷³ and using the ground state potential surface sampled by MD for TDDFT calculations is known to over-estimate fluctuations of the excitation energy.⁷⁴ For chlorosomes, the task of calculating $\nu_i(\mathbf{R})$ for varying nuclear coordinates $\mathbf{R}$ is computationally intractable even for modern supercomputers, and thus it is always replaced by a more tractable task. The simplest choice is to assume a constant ν_i^0 , which is estimated from experiments, following the argument that the environments of BChls are very similar on average,¹²⁸ and the observation that the HOMO-LUMO gaps in chlorophylls can be quite insensitive to external perturbations, that affect the energy levels, because of correlated instead of anti-correlated variation upon interaction with the environment.¹²⁹ The most notable example of this effect is found in plant photosynthesis, where the chlorophylls in photosystem I and II have the same color despite widely different redox potentials.¹³⁰ On a more fundamental level, delocalized eigenstates like the ones that have been observed in chlorosomes can only exist when transitions are near resonant, meaning that the difference in monomer excitation energies between two molecules must be much smaller than the difference in their electronic coupling.¹⁹ We thus set the monomer excitation energies for all molecules to the same constant value, *i.e.* $\nu_i(\mathbf{R}) = \nu$, meaning that we assume that any fluctuation with respect to this reference energy ν on the diagonal are negligible compared to the fluctuations of the energy in the off-diagonal terms.¹³¹

It is nevertheless common to represent the unknown variations of the internal and external conditions for each pigment molecule in a chlorosome by adding an effective fluctuating contribution to ν_i^0 , usually drawn from a distribution with Gaussian statistics and adjustable width σ .⁸⁰ Although σ could be cho-

sen to match calculated fluctuations of the monomer excitation energy for significantly reduced systems,⁴³ it is usually tweaked to match experimental FWHMs, which are known to reflect both static and dynamic disorder. Furthermore, adding a weak to intermediate correction to the site energy will only results in weak mixing of excitonic wavefunctions and a mild spreading of the peak spectra.⁸⁰ Besides our original arguments, see previous paragraph, we note that adding a Gaussian broadening correction to the monomer excitation energy^{43,80} has the clear disadvantage of blurring or even destroying the effect of cooperativity as included into $J_{ij}(\mathbf{R})$ via the MD simulation.

3.3. Results and Discussion

The first aim of this study is to develop a systematic and rigorous procedure for translating the characterization data, which has been extracted at various levels of resolutions, into a molecular model for chlorosomes. A key challenge in this process is that we can not represent all experimental factors in our computational model. In particular, the structure of natural chlorosomes encompasses heterogeneity in size, overall shape, and in composition; a cryo-EM image of a chlorosome may experience small tilts out of plane of imaging.⁶³ All such factors modulate the signal intensity along layer lines in the diffraction pattern of a cryo-EM image, as can be seen from the single, weak layer lines in the noisy spectra for both WT and *bchQRU* chlorosomes.³⁷ For this reason, we must thus take care in identifying the characteristics that Fourier responses calculated for our pre-assembled tubes should capture beyond the layer line position $1/d$, which is an indicator of a correlation length, in the experimental power spectra. In particular, the geometrical analysis presented here enables further fine tuning if needed, for instance when additional experimental information becomes available in the future. Since the characteristics of dynamic disorder were found conserved under varying tube chirality, the second aim, *i.e.* evaluating the interplay of quantum and classical degrees of freedom, can be considered via a particular case.

An important aspect of this procedure is to generate tubes that are representative for the dynamic disorder that plays a role in actual chlorosomes. We previously (in Chapter 2) found that hydrogen bonding heterogeneity and

head-head rotations are characteristic for the tubular chiral assemblies that are spontaneously formed after a relatively short 1 ns MD simulation at $T = 300$ K. Following our geometrical analysis, tube structures corresponding to matching δ are thus used as input for MD simulations in order to introduce the disorder that is needed for a realistic comparison to experimental diffraction and optical spectra.

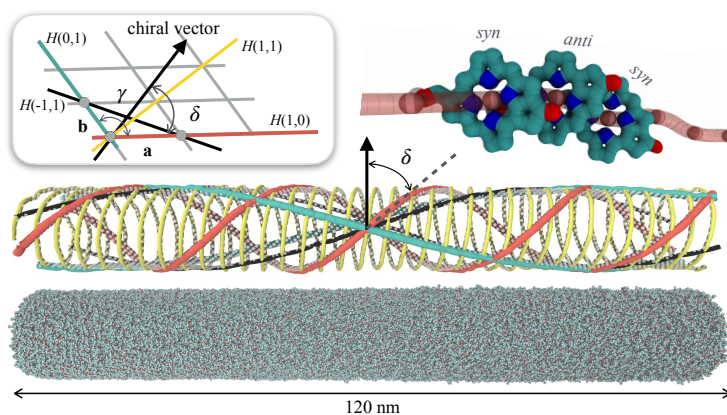


Figure 3.1: Different representations of the pre-assembled tube structure for $\delta = 49.6^\circ$ after 1 ns MD simulation at 300 K. Top, left: Schematic illustration, showing the 2D Bravais lattice and the $H(1,0)$ (red), $H(0,1)$ (green), $H(1,1)$ (yellow) and $H(-1,1)$ (black) helical families as well as the chiral vector. Top, right: Schematic illustration showing the arrangement of alternating *syn* and *anti* molecules along the $H(1,0)$ helical family, which connects the Mg-moieties. Middle: The main helical families in the 3D tube, obtained from connecting Mg-moieties. Two helices for each family are shown, with the same coloring as in the schematic image at top, left. Bottom: Molecular view of the tube. For WT chlorosomes, the lattice parameters are determined as (1.48 nm, 0.98 nm, 124.3°) from MD simulation of BChl *c* pigment aggregates; for *bchQRU* chlorosomes, the lattice parameters are determined as (1.46 nm, 0.93 nm, 122.5°) from MD simulation of BChl *d* pigment aggregates.

3.3.1. Extended Geometrical Analysis

We have extended the geometrical analysis developed in earlier work (Chapter 2) to consider a complete set of candidate helical families and the whole

range of the chiral angle $\delta \in [0^\circ, 180^\circ]$, see Figure B.1-B.2 and details in the Appendix B. As before, we may employ this geometrical framework to link layer line positions $1/d$ in the diffraction pattern, *i.e.* $1/d = 1/1.25 \text{ nm}^{-1}$ for WT and $1/d = 1/0.83 \text{ nm}^{-1}$ for *bchQRU* chlorosomes, to a chirality of the tube. To ensure internal consistency, we selected dimensions of the dimeric unit cell (a, b, γ) that were previously extracted from MD results for assemblies composed of pure BChl *c* and *d* (Chapter 2). It should be noted that, since these unit cell parameters were determined as averages and feature standard deviations in the 0.03–0.05 nm (a or b) and 2–4° (γ) range, see Appendix A, each reported δ is in fact part of a tiny window of appropriate angles associated with that δ . Table 3.1 summarizes the chiral angles δ that exactly match $1/d$ for the considered unit cells of WT or *bchQRU* chlorosomes. In the standard classification, which relates to the orientation of *syn-anti* stacks to the tube long axis,³⁷ *i.e.* perpendicular for $\delta = 0^\circ$ and parallel for $\delta = 90^\circ$, assemblies for $\delta \in \{2.2^\circ, 19.8^\circ, 160.2^\circ\}$ can be seen as primarily perpendicular, while they are primarily parallel for $\delta \in \{80.0^\circ, 94.3^\circ, 108.9^\circ, 112.3^\circ\}$. Intermediate values, *i.e.* for $\delta \in \{27.6^\circ, 42.3^\circ, 49.6^\circ, 130.4^\circ, 136.3^\circ\}$, relate to neither parallel nor perpendicular stacks.

Next, we constructed tube structures for the matching δ in Table 3.1, see Method section for details, and found that they are all stable upon 1 ns MD simulation at $T = 300 \text{ K}$. The pre-assembled structure for one matching chiral angle, *i.e.* $\delta = 49.6^\circ$ is shown in Figure 4.1. Visual inspection shows that it is hard to identify atomic detail, making this representation illustrative for the robustness of such pre-assembled structures to thermal dispersion, in particular when concentrating on the large scale characteristics such as the overall chirality. Later, in section 3.3.3, we will analyze structural properties more quantitatively via the positions of the Mg lattice sites and orientations of the BChl head groups. Consequently, we performed Fourier transforms on these pre-assembled structures, both before and after MD, to determine the power spectra for their EM mimics, see Figure B.3 and Figure B.4 in the Appendix B. Examining these diffraction spectra allows us to validate our geometrical analysis and to qualitatively compare the characteristics of the target layer line signals to experimental data.³⁷ We find that important characteristics of the experimental layer line, *i.e.* signal intensity close to the meridian,³⁷ are reproduced by the target layer line for $\delta \in \{112.3^\circ, 130.4^\circ, 136.3^\circ\}$ for WT and $\delta \in \{19.8^\circ, 160.2^\circ\}$ for *bchQRU* type chlorosomes, see Figure B.3 for all the

diffraction patterns for tube structures after MD simulations.

In the final step of the procedure, optical spectra for all tube structures, after MD simulation ($T = 300$ K), are compared with the optical spectra measured in experiments. We note that the tube size is important for spectral calculations, as optical spectra for tubular assemblies have been reported to be size sensitive;^{35,79,80} especially the shape of the CD spectra, which may change when the tube length crosses a so-called critical value. Tang *et al.*³⁵ particularly focused on the relation of the critical value to the tube diameter and tube length, for an assembly with chiral angle $\delta = 90^\circ$, and determined a critical length of about 90 nm for a tube diameter of 15 nm. Here, we selected a diameter of 15 nm and considered optical signals for tubes up to 120 nm length and all matching δ to evaluate this length dependence. Based on the finding that spectral features show no notable variation in the range from 60 to 120 nm, see Figure B.5–B.6, we further concentrate our analysis on tubes of 120 nm, which is comparable in length to a natural chlorosome. A single tube of this dimension is composed of over one million atoms.

Table 3.1: $\delta \in [0^\circ, 180^\circ]$ for BChl *c* (WT) and BChl *d* (*bchQRU*) assemblies that reproduce layer line positions $1/d = 1.25 \text{ nm}^{-1}$ and $1/d = 0.83 \text{ nm}^{-1}$ for WT or *bchQRU* chlorosomes. The italicized δ value in the table indicates that the tube for that δ displays the experimentally observed meridian signal on the target layer line.

δ (in degrees) wild type								δ (in degrees) <i>bchQRU</i>			
2.2	42.3	49.6	80.0	94.3	<i>112.3</i>	130.4	136.3	19.8	27.6	108.9	160.2

3.3.2. Calculated Optical Spectra

Optical spectroscopy data have been collected from both WT and mutant chlorosomes, including absorption,^{35,86,88,104,107,120,132–136} linear dichroism^{88,104,107,132,135} and circular dichroism.^{35,88,132,134–136} Absorption is most frequently measured and found rather insensitive to the chirality of the assembly, whereas the LD and especially CD spectra are more distinctive of particular chirality and therefore useful for further selection of specific δ .¹¹³ The observed spectral features are summarized in Figure 3.2, which shows that two types of CD spectra have been found for *C. aurantiacus* and *C. tepidum* WT or mutant chlorosomes: type

II (-, +) in the notation of Gribenow *al.*,⁸⁸ and a mixed-type (-/+/-) that can be interpreted as a linear combination of type I (+/-) and type II. Although type I spectra have also been reported for chlorosomes on two occasions,^{88,137} we restrict our matching procedure to the two dominant spectra. Since reversed curving may switch the sign of CD spectra, it has been suggested that mixed-type CD spectra can be assigned to a mixture of tubular complexes with similar BChl packings but opposite curving directions.³⁷ In this section, however, we concentrate on calculating optical properties for single tubes, thereby adopting earlier notions that multiple cylinders can be treated as uncoupled systems for the purpose of modeling optical spectra.^{28,46} Our results will particularly show that a single tube is sufficient to generate a mixed-type CD spectrum. An overview of all simulated spectra is provided in the Appendix B, see Figure B.7 and a comparison of calculated and experimental properties is provided in Figure 3.3.

Absorption spectra are characterized by a shift $\lambda_m - \lambda_0$, with λ_m the absorption peak position of the aggregate and λ_0 of the monomer, which can be either positive (red shift, J-aggregate) or negative (blue shift, H-aggregate).¹³⁸ As mentioned previously, λ_0 is set to 15390 cm^{-1} or 650 nm .⁸⁰ Chlorosomes are J-aggregates associated with a large red-shift, *i.e.* $\lambda_m - \lambda_0 = 60\text{--}80\text{ nm}$,¹⁶ and indeed an equivalent red shift is observed in all calculated absorption spectra for our tube structures, see Figure 3.3. The insensitivity of the shape of the absorption band to tube chirality shows that the Q_y absorption band of chlorosomes is mainly determined by the short-range order of *syn-anti* dimers, and only weakly reflects longer-ranged structural properties like supramolecular chirality. We note that a significantly smaller red shift is produced when switching to the TrEsp treatment for the electronic coupling, although this method was tested more accurate than the PDA.⁷⁶ In particular, calculations with TrEsp for our tubular assemblies ($\delta = 49.6^\circ$ and 112.3°) resulted in a red shift $< 10\text{ nm}$, a finding that is consistent with previous work.⁴¹

Linear dichroism reveals the order of alignment more directly, as strong LD signals are expected only for ordered systems.¹¹³ Indeed, strong signals are observed from the calculated LD spectra for all tube structures, see Figure B.7. The sign of the LD signal is determined by the absorbance of light polarized parallel and perpendicular to the tube axis, $LD = A_{\parallel} - A_{\perp}$, meaning that a negative/positive signal appears when absorption along the tube axis is weaker/stronger than that orthogonal to the tube axis. We introduce the

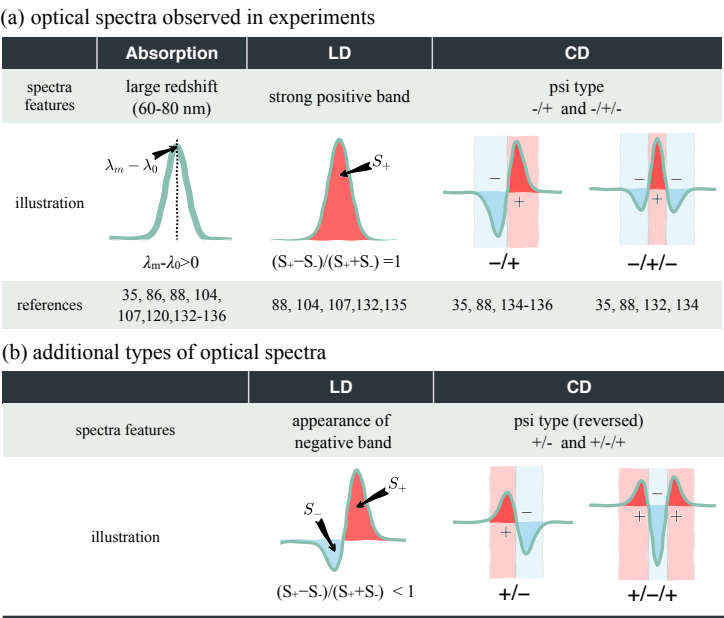


Figure 3.2: (a) Schematic summary of key features of the experimental absorption, linear and circular dichroism spectra measured for chlorosomes. Main features, key properties and the corresponding literature reference are provided. (b) Sketches of additional optical spectra resulting from our calculations, for which no or only few experimental counterparts have been identified.

relative difference $f_{ld} = S_{+} - S_{-} / S_{+} + S_{-}$ to better characterize these LD spectra, with S_{+} and S_{-} the integrated area of the positive and negative parts of the LD signals, respectively. Three types of LD-spectra are observed, see Figure 3.3: i) strictly positive, with $f_{ld} = 1$, as in the experimental LD spectra, ii) signal displaying a small negative peak in the short-wavelength range and $f_{ld} < 1$, and iii) strictly negative signals, with $f_{ld} = -1$. Matching these features to the experimental LD spectra limits the chiral angles to $\delta = 42.3^\circ, 49.6^\circ, 80.0^\circ$ and 94.3° for WT chlorosomes and $\delta = 19.8^\circ$ and 27.6° for *bchQRU*, respectively. We exclude $\delta = 112.3^\circ$ and 108.9° since $f_{ld} < 1$, even though $S_{+} \gg S_{-}$.

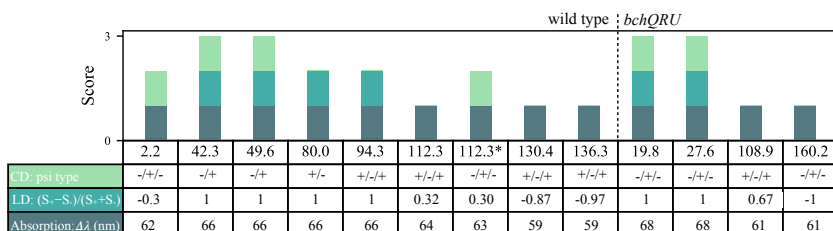


Figure 3.3: Overview of the spectral characteristics for all tube structures with matching chiral angles δ . Stick spectra were calculated for all tubes after 1 ns MD simulation at 300 K, and characteristics determined for the spectra that resulted from convolution of the stick spectra with a Gaussian with FWHM equal to 200 cm^{-1} . Colored scoring bars on top of the table show which characteristics of the simulated spectra agree with the experimentally observed spectral properties.

The circular dichroism (CD) spectrum is most sensitive to the aggregate structure; in particular, a special, psi-type CD spectrum is expected for chiral aggregates.¹¹³ In total four types of psi-type CD spectra are calculated for our pre-assembled tubes: type I ($+/-$, $\delta = 80.0^\circ$), type II ($-/+$, $\delta \in \{42.3^\circ, 49.6^\circ\}$), and two mixed-types, namely ($-/+/-$) for $\delta \in \{2.2^\circ, 19.8^\circ, 27.6^\circ, 160.2^\circ\}$ and ($+/-/+$) for $\delta \in \{94.3^\circ, 108.9^\circ, 112.3^\circ, 130.4^\circ, 136.3^\circ\}$. The results confirm that mixed-type CD spectra are found even for single tubes with well-defined chiralities, and shows that this type can originate from mixing various contributions of the helical families that are present in a tube, see Figure 4.1. Since only types ($-/+$) and ($-/+/-$) are consistently measured for chlorosomes,^{35,88} this further reduces the number of matching δ . Moreover, this is the first time that type II ($-/+$) is calculated for tubular assemblies that approach realistic

chlorosomes dimensions. Extending the tube length for $\delta = 49.6^\circ$ even further, to 300 nm, shows that the type II CD signal is persistent. The novelty of this finding can be explained by the fact that previous computational studies of spectral properties only considered $\delta \in \{0^\circ, 90^\circ\}$.

In combination, our procedure suggests that only a tiny range of the chiral angles in Table 3.1 provide relevant optical spectra: for WT chlorosomes, $\delta = 42.3^\circ$ or 49.6° , and $\delta = 19.8^\circ$ or 27.6° for *bchQRU* chlorosomes, see the score bars in Figure 3.3 for details. We find that the meridian nature of the layer line signal calculated for the tube for $\delta = 19.8^\circ$ agrees well with the experimental layer line characteristics, which provides converging evidence that $\delta = 19.8^\circ$ is a unique solution for *bchQRU* chlorosomes that are rich of BChl *d*. We note that this angle is consistent with the previously extracted $\delta = 19.1^\circ$ for pure BChl *d* aggregates that are formed by spontaneous curvature after 1 ns of MD (Chapter 2), and with the perpendicular-type structural model proposed previously.³⁷ For WT chlorosomes, although the matching δ appear consistent with the angles extracted from MD (Chapter 2), the experimentally observed layer line characteristics, *i.e.* a meridian signal in the diffraction spectrum, is not reproduced. Moreover, for the candidate $\delta = 112.3^\circ$ that does qualitatively agree with these characteristics, both the LD and CD signals are inconsistent. Since our curvature direction and average unit cell dimensions were both adopted from MD simulations in Chapter 2, it makes sense to consider how these factors affect the optical spectra.

If one envisions tubes to be generated by rolling up planar structures, it is easy to understand how reversing the direction of rolling will lead to a reversal of chirality. Current computational studies of spectral behavior^{35,36,41,45,79,80} consider simple dipolar lattices that lack any molecular detail, which clarifies why this subtle issue has never been addressed. So far, our curving direction is selected such that *syn*-tails always direct towards the concave, inner side of the tube (Chapter 2). To investigate the role of the overall curving direction in optical spectra, we have assembled a tubular structure for $\delta = 112.3^\circ$ and a reversed curving direction, *i.e.* with *anti*-tails towards the inside of the tube. This situation is labeled with an asterisk, $\delta = 112.3^*$, to distinguish it from the standard case.

From a 1 ns MD simulation at $T = 300$ K, we find that reversing the curving direction does not notably affect the stability of the molecular and supramolecu-

lar packing. As expected, the CD spectrum can be seen to reverse, from (+/-/+) for $\delta = 112.3^\circ$ to (-/+/-) for $\delta = 112.3^*$, see Figure 3.3, i.e. consistent with the experimental CD spectra, confirming the sensitivity of the CD-spectra to chirality. However, since the OD and LD spectra do not change upon reversing the curving direction, the negative peak that is present in the short-wavelength side of the calculated spectrum for $\delta = 112.3^\circ$, and thus also for $\delta = 112.3^*$, does not agree with the experimental LD spectra. It should be noted, however, that the characteristics of the LD spectrum vary in a range around $\delta = 112.3^\circ$, with f_{ld} changing from $f_{ld} = 1$ for 94.3° to $f_{ld} = -1$ for 136.3° , see Figure B.7. Further testing identified matching OD, LD and CD spectra for $\delta = 105^*$, which is only slightly smaller than $\delta = 112.3^*$ and just within the window of chiral angles around $\delta = 112.3^*$ that are consistent with the earlier identified 0.05 nm margin of the unit cell parameter a . This is converging evidence that $\delta = 105^*$ is the proper chiral angle for WT chlorosomes.

As a final remark, it has always been difficult to explain the uncontrolled variation of measured CD spectra for WT chlorosomes in terms of the underlying structure, with both type II and mixed-types encountered for the same WT chlorosomes in different measurements. The benefit of considering all δ in Table 3.1 is that it allows us to investigate the sensitivity of the LD and CD spectra to the tube chirality. For instance, a transition from a mixed-type to a type II CD spectrum transition is found somewhere between $\delta = 27.6^\circ$ and 42.3° . Such a small variation of the base tube chirality may well be a consequence of BChl compositional heterogeneity or particular growth conditions. Moreover, the highly efficient function of both WT and *bchQRU* chlorosomes is a clear sign that performance is conserved for tubular assemblies that feature different chirality but share important properties on a structural level, something that is confirmed by a detailed comparison of static and dynamic disorder for a number of different δ in the following section 3.3.3. For this reason, in sections 3.3.4–3.3.6 where we investigate the interplay between dynamic disorder and electronic properties, we illustrate a single chiral angle, i.e. $\delta = 49.6^\circ$, for which the optical spectra match the experimental data.

3.3.3. The Origin of Disorder

Next, we focus on the disorder in the tube structures after MD simulation. We do this by considering various structural properties of the pre-assembled tubular assemblies as well as how these properties are affected by the thermal motion. Table B.1 summarizes the structure-average lattice parameters (a, b, γ) and two large-scale structural properties, *i.e.* the chiral angle δ and the tube radius R derived from the best tube fit. When building assemblies following the procedure described in the Method section, lattice parameters are set to $(a, b, \gamma) = (1.48 \text{ nm}, 0.98 \text{ nm}, 124.3^\circ)$. All structural properties are calculated from the Mg positions in the assembly at various steps of the simulation procedure: after preparation and energy minimization at $T = 0 \text{ K}$, after 1 ns MD at $T = 50 \text{ K}$ and $T = 300 \text{ K}$.

We find that lattice parameters are generally conserved within tiny margins, and the same conclusion can be drawn for the input chiral angle δ , even for $T = 300 \text{ K}$. Although the root mean square deviations from the fitted tube, RMSD_{fit} , increase with temperature, the assembly remains cylindrical with $\text{RMSD}_{\text{fit}} \leq 0.3 \text{ nm}$ for all δ of BChl *c*. Apparently the structure does not need to resolve possible frustrations resulting from manual assembly by adapting its unit cell or assuming a non-cylindrical shape. Visual inspection, however, shows that tube assemblies of BChl *c* are slightly more regular than for BChl *d*, which is in agreement with the findings for spontaneously self-assembled structures in Chapter 2 and explains the small increase in RMSD_{fit} for the latter. On basis of this analysis, which mainly considers the central (Mg) position of the BChl molecules, we conclude that the static disorder in all considered assemblies is fairly limited.

As in our previous study for spontaneous assembly (Chapter 2), we identify dynamic disorder in the form of a rotational degree of freedom for BChl head groups, so the tubular assemblies can indeed be seen as a rotor phase.¹³⁹ Whereas the static crystal-like order is quite well conserved, see Table B.1, the distribution of relative intra- and inter-molecular head-head rotation angles, α_{intra} and α_{inter} , is broad, see Figure 3.4 and Figure B.8, and their sampling distributions are comparable to the ones previously observed for spontaneously curving structure. Likewise, the hydrogen bonding heterogeneity that was found to accompany this rotational motion in Chapter 2 is present in all tube considered structures after MD simulation. The previously determined

hydrogen-bonding saturation ratio, *i.e.* the fraction of hydrogen bonds present in the structure that are actually formed, is appropriately reproduced for pre-assembled tubes simulated at $T = 300$ K, namely 0.74 for BChl *c* ($\delta = 49.6^\circ$) and 0.87 for BChl *d* ($\delta = 19.8^\circ$). Since the rotational dynamics is clearly not affected by assembling BChl in a tube structure, it is convincing evidence that they are stable structures. Moreover, it shows that dynamic disorder is much more pronounced in such assemblies than static disorder, in agreement with our choices in the Frenkel Exciton Hamiltonian. The limitation of static disorder is also justified by NMR and optical spectra experiments.^{37,45}

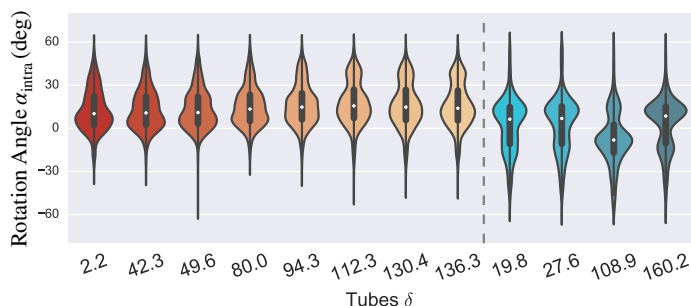


Figure 3.4: Sampling distribution for the relative head-head rotation angle between *syn* and *anti* molecules BChl, α_{intra} , for the tube obtained after 1 ns MD simulation at 300 K. The distribution is calculated for different chiral angles δ on the horizontal axis, and the dashed line separates the matching chiral angles for BChl *c* and *d*. We refer to the Appendix B, figure B.8, for the distribution of α_{inter} .

3.3.4. Localization of Excitonic States by Disorder

In our treatment, disorder that is present in the tubular assemblies, in the form of molecular deformations, vibrating molecular lattices and rotating head parts of BChl, is reflected in the off-diagonal terms J_{ij} of the Frenkel Exciton Hamiltonian matrix. Next, we concentrate on how such disorder affects the spatial distribution of relevant exciton states. Since MD simulations account for correlations within the assembly, it represents a substantial advance compared to previous studies that lack such cooperativity.⁸⁰ We will compare the spatial aspects of exciton states for three degrees of disorder, *i.e.* order at 0 K, mild disorder at 50 K and moderate disorder at 300 K, and for $\delta = 49.6^\circ$ that was

selected for as an illustrative case BChl *c*.

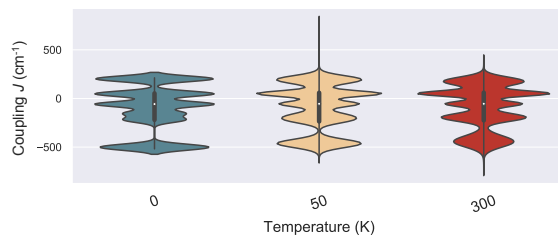


Figure 3.5: Distribution of coupling strengths J_{ij} for $\delta = 49.6^\circ$ and a 120 nm tubular structure at 0 K, *i.e.* pre-packed after energy minimization, 50 K and 300 K after 1 ns MD simulation. The strengths are calculated using a cutoff distance of 1.5 nm.

First, we analyze the distribution of electronic coupling strengths J_{ij} , see Figure 3.5. Since J is a quickly decaying function, we have used a cutoff of 1.5 nm. Five distinct peaks can be observed for all considered T, reflecting the earlier finding that chirality is conserved under thermalization. Distinct bands stem from molecular packing along main helical families in the tube, e.g. the strong coupling peak around -500 cm^{-1} corresponds to *syn-anti* packing along $H(1,0)$, and has a major contribution to the large red-shift of the Q_y band. Due to thermal fluctuations, broadening and smoothing of the coupling strength distributions is observed in the disordered states (50 K and 300 K).

The conservation of the bands in the coupling distribution under thermalization is in line with comparable spectral features for ordered and disordered situations, see spectral plots in Figure B.9, and consistent with the observation of Prokhorenko *et al.*⁸⁰ that the effect of adding off-diagonal noise is equivalent to Gaussian broadening of calculated stick spectra. The insensitivity of the main spectral features to molecular motion justifies the focus on perfect lattice models in previous studies of spectral signals.^{36,45,79,80,105} However, when one is also interested in details like the spatial distribution of exciton states that correspond to stick-signals in optical spectra, it is advantageous to consider structure with realistic disorder from a physical point of view.^{69,119}

Furthermore, profound knowledge of the spatial distribution of an exciton is essential for a fundamental understanding of the energy transfer in chlorosomes. An important feature of Frenkel excitons is that, due to the strong electronic coupling between monomers, exciton states are usually distributed over more than one monomer, which is described as the delocalization of an exciton.^{119,140} Such delocalization is a static property, and should not be confused with exciton transport. In recent years, 2D spectroscopy has identified several cases of intricate dynamic modulation of exciton transport by so-called coherent beatings, and a basic description for the corresponding line shape dynamics for chlorosomes has recently been proposed.^{84,120,141} This model assumes that tubes feature a patchwork of coherent domains in which excitons adopt wave-like behavior, while excitons efficiently hop between coherent domains of very similar energy in an incoherent manner.^{84,120} Yet, existing theoretical and computational studies have not been able to further rationalize this mechanism. In particular, disregarding structural disorder on a molecular level, by considering (semi-)crystalline structures,^{35,36,40,41,43,45,79,80,105} overestimates the delocalization of excitonic states,^{36,79,80} and is therefore

fundamentally unsuited for studying such effects.

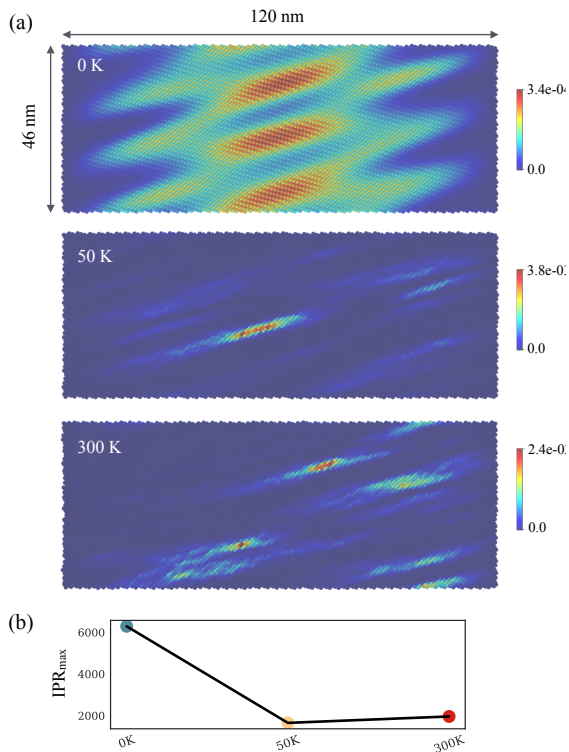


Figure 3.6: Spatial distribution of the exciton states with the highest oscillator strength $\psi_{\max}$ in a 120 nm long tube for $\delta = 49.6^\circ$. (a) From top to bottom: $\psi_{\max}$ for different disorder within the tube: ordered state, labeled as 0 K, and disordered states after 1 ns MD simulation, labeled as 50 K and 300 K. The localization of $\psi_{\max}$ is quantified by the IPR, see (b). Tube structures have been unrolled to planes for the purpose of visualization; see Figure B.10 for corresponding 3D tubes.

Our current treatment enables us to conclude that disorder indeed suppresses the delocalization of excitons. In Figure 3.6, the spatial distribution of the exciton state $\psi_{\max}$, corresponding to the largest oscillator strength in the absorption spectrum, is visualized for different disorder (0 K, 50 K and 300 K) of the tube structure. In the ordered case, see Figure 3.6a, $\psi_{\max}$ can be seen highly delocalized, a finding that is consistent with previous studies for regular structures.^{36,79,80} Introducing disorder due to thermal motion has a localizing effect on the exciton domain size, with the domain of significant exciton density shrinking to $O(10)$ monomers for $T = 300$ K, see Figure 3.6a, as estimated in an experimental investigation.¹²⁴ Most importantly, the spatial distribution of the exciton state can be seen to change from extended striped domains, see Figure 3.6a top for $T = 0$ K, to clusters of tiny domains of high exciton density, see Figure 3.6a bottom for $T = 300$ K.

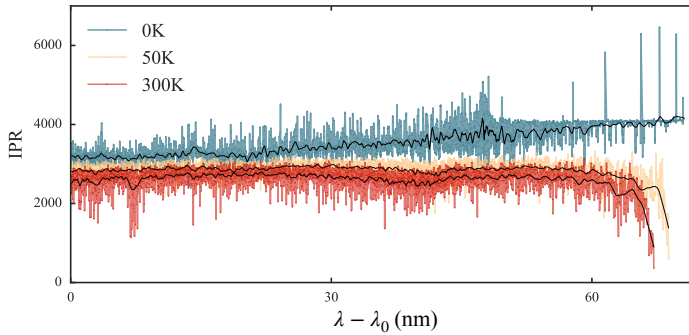


Figure 3.7: The inverse participation ratio (IPR, see Eq. 3.5) for all exciton states with energy lower than the monomer excitation energy 15390 cm^{-1} . In this range, states belong to the red-shift absorption band and satisfy $\lambda - \lambda_0 > 0$. The setup is the same as in Figure 3.6, *i.e.* a 120 nm long tube for $\delta = 49.6^\circ$ and different temperatures.

The (de)localization of states can be quantified by their inverse participation ratio (IPR), see the Methods section for details. Denoting the IPR for the state with the largest oscillator strength as $\text{IPR}_{\max}$,¹²⁷ we find an abrupt decrease from a high value in the ordered state ($\text{IPR}_{\max} = 6289$) to low values for disordered states ($\text{IPR}_{\max} = 1652$ and 1961 in 50 K and 300 K cases, respectively), see Figure 3.6b. Considering all excitonic states, we find that the effect on IPRs belonging to the red-shift Q_y absorption band is very similar around the

peak position ($\lambda - \lambda_0 > 60$), see Figure 3.7, while it is almost absent for exciton states with higher energy, i.e. for $\lambda - \lambda_0 \approx 0$.

In addition to the IPR, we may quantify (de)localization by considering the exciton density distribution of $\psi_{\max}$, i.e. the exciton state with the highest oscillatory strength, for different molecular conformations. By considering conformations that are taken from a MD trajectory, our tubular states reflect correlations that are responsible for the dynamics of BChl molecules within this assembly. In this way, we indirectly investigate the effect of conformational dynamics on the excitonic behavior. We determine, for each MD configuration, the number of molecules $N(f)$ with an exciton density $p_i \geq f \cdot p_{\max}$, where $p_{\max}$, defined as the maximum of the exciton density for $\psi_{\max}$, sets the range of the exciton density for each configuration and $f \in [0, 1]$ is the corresponding fraction. In particular, $N(f)$ can be seen as a measure for the total area of the exciton domains in $\psi_{\max}$ that correspond to exciton densities that are equal or higher than a fraction f . We may now evaluate whether the molecular tube state is significant for $N(f)$ by considering $\langle N(f) \rangle$, where $\langle \cdot \rangle$ denotes the average taken over all considered molecular conformations. Figure 3.8 shows $\langle N(f) \rangle$ versus f for the ordered assembly at $T = 0$ K (one tube state) and for the disordered case, where the averaging is carried out over all snapshots along a 1 ns MD trajectory at 300 K. Since the standard deviation for the latter case is tiny, we may conclude that the localizing effect of the dynamic disorder as illustrated in Figure 3.6 is a general feature shared by all tube states. We may exploit these data further to extract an explicit expression for $\langle N(f) \rangle$, i.e. the effective area of the exciton domains¹⁴² in terms of the threshold fraction f . We extracted a linear relation for the ordered case and an exponentially decreasing relation for the disordered case, see Figure 3.8.

3.3.5. Molecular Origins of Exciton Localization

Next, it is important to identify common structural features that correlate with the localization of exciton density. We thus consider how the dynamic disorder that is present in all tube states along the MD trajectory correlates with high exciton density in $\psi_{\max}$; disorder that was previously evaluated in terms of Mg-Mg distances, the rotational angle between neighboring BChl molecules, which is associated with the dipolar interactions, and hydrogen

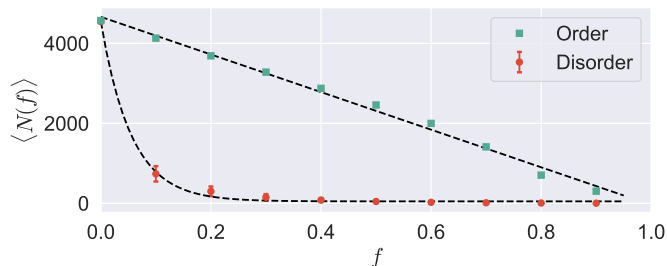


Figure 3.8: Average number of molecules $\langle N(f) \rangle$ versus fraction f for the state with the largest oscillator strength in a 60 nm long tube for $\delta = 49.6^\circ$. Green symbols represent the data for an ordered structure after energy minimization, and red shows averages over 1 ps MD at 300 K. We find that disorder changes linear scaling to exponential scaling: $\langle N(f) \rangle^{\text{order}} = -4703.4f + 4663.7$ and $\langle N(f) \rangle^{\text{disorder}} = 4494.3 \exp(-18.1f) + 48.5$.

bonding. Following a procedure that is very similar to the one used in the previous section, we determined the distributions of Mg-Mg distances $d_{\text{Mg-Mg}}$ and the relative dipolar angles $\alpha_{\text{dipole-dipole}}$ for all molecules in the tubular assembly that satisfy $p_i \geq f \cdot p_{\text{max}}$. Combining distributions for all tube states along the trajectory and normalizing, we obtain the two overall distributions shown in Figure 3.9. From this Figure, it is clear that the highest exciton density is associated with the closest Mg-Mg separation. The distribution of the rotation angles $\alpha_{\text{dipole-dipole}}$ is clearly bimodal when considered over all molecules in all tubes, *i.e.* for $f = 0$, with peaks around 10° and 40° . Concentrating only on very high exciton density, $f = 0.9$, the overall distribution is almost unimodal, and the broad peak around 40° has disappeared in favor of a peak at smaller angles. It suggests that molecules that are associated with very high exciton density do not favor large rotations relative to each other. Relative distances and orientations play a role in PDA coupling, so we conclude that both features can be explained in terms of the coupling strength.

Hydrogen bonding was previously identified as an important source of structural heterogeneity (Chapter 2). While a special role of hydrogen bonding in exciton transfer in chlorosomes has been speculated upon,¹⁴³ our current treatment limits itself only to static properties and correlations. Figure 3.10 shows the ratio of the number of molecules forming 0, 1, and 2 hydrogen bonds versus the fraction f of the exciton density, calculated as an average

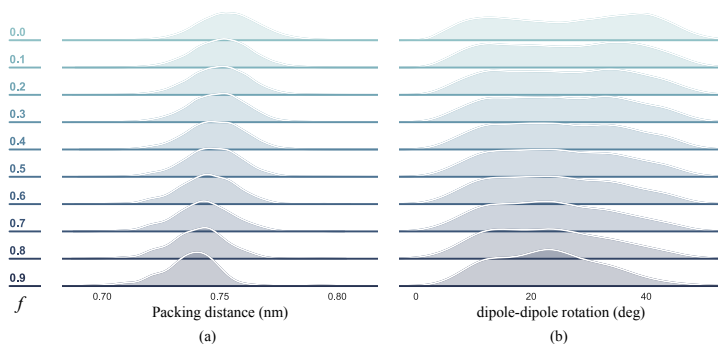


Figure 3.9: Structure analysis of molecules at different exciton density levels satisfying $p_i \geq f \cdot p_{\max}$ in $\psi_{\max}$ for a 60 nm long tube with $\delta = 49.6^\circ$, averaged over a 1 ps MD trajectory at 300 K. (a) distribution of neighboring Mg-Mg distances along the **a** packing direction, and (b) distribution of neighboring dipole-dipole rotation angles along the **a** packing direction .

over all snapshots along a 1 ns MD trajectory at $T = 300$ K; we refer to Figure 3.8 for information about the number of molecules over which this average is taken. Colored regions show that the standard deviations increase with increasing f , which could either be due to variations of these ratios between MD snapshots or the rapidly decreasing number of molecules considered in the averaging procedure. Overall, these data suggest only weak correlation between hydrogen bonding and a high exciton density. Nevertheless, hydrogen bond formation remains a factor in the PDA, albeit only indirectly, through the relation between hydrogen bonding and the relative orientations of induced point dipoles in the molecules.

3.3.6. Interplay between Dynamic Disorder and Exciton States

Finally, we analyze the exciton states in tube assemblies that are extracted from different frames along MD trajectories to evaluate their response to dynamic disorder that is induced by thermal motion. Exciton states are analyzed both in real space and in Hilbert space, and we extended our calculations to three concentric tubes to evaluate inter-tube correlation and delocalization. As mentioned, our current investigations provide no direct information on the role

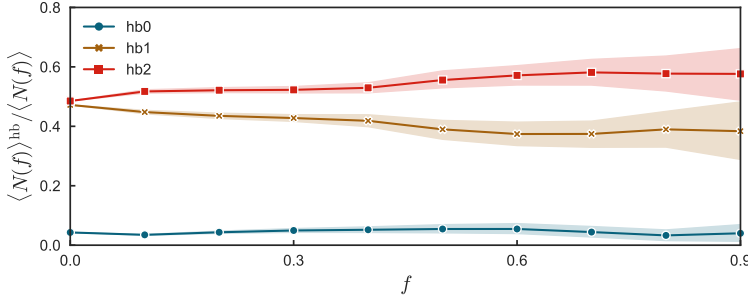


Figure 3.10: Number of molecules $\langle N(f) \rangle^{\text{hb}}$ relative to $\langle N(f) \rangle$ with 0/1/2 hydrogen bonds for varying f (horizontal axis), calculated for ψ_{max} and a 60 nm tube for $\delta = 49.6^\circ$ averaged over a 1 ps MD trajectory simulated at 300 K. Colored bands show the standard derivation.

of temperature¹²¹ or vibrational coherence^{84,120} in exciton migration, since we do not include a propagator at the quantum level. Representing nuclear responses to excitation in a MD force field is currently an open issue¹⁴⁴ and remains challenging,¹⁴⁵ albeit that electronic ground state nuclear dynamics is considered a justified choice for these systems.¹³¹

Exciton migration in chlorosomes is a fast process,^{16,124,146} with an initial energy flow identified to occur in the first 200 fs after excitation.^{84,120,121,141} The two distinct low frequency modes recently identified by ultra-fast 2D spectroscopy for chlorosomes at 80 K relate to coherent beatings with a period of 230/366 fs on a characteristic time scale of ps.⁸⁴ We have thus performed a 1 ps MD simulation and analyzed the resulting trajectory with a time resolution of 20 fs. As the time interval (20 fs) is small, the lattice site (based on Mg atom position) variation between neighboring frames is small, with

$$\text{RMSD}_{\text{lattice}} = \sqrt{\frac{1}{N} \sum_i^N (\mathbf{x}_i(t) - \mathbf{x}_i(t - \Delta t))^2} \quad (3.6)$$

being less than 0.01 nm when calculated over all N positions of the Mg atoms $\mathbf{x}_i$, for both the single tube and concentric tube trajectories.

Single tube

We analyze single tube aggregates by projecting the exciton distribution for the largest oscillator strength $\psi_{\max}$ onto the structure using color coding, see Figure 3.11 and movie S1[†]. We have also plotted the separation distance d_{sep} between molecules that feature the largest occupation probability $p_{\max}$ of $\psi_{\max}$ in consecutive frames. The comparable $\text{RMSD}_{\text{lattice}} = 0.148 \pm 0.018$ nm and d_{sep} behavior for the longer 500 ps trajectory, see Figure B.11 and movie S2[†], show that the short trajectory is representative. While the fluctuating character of d_{sep} suggests equivalent changes to the corresponding exciton distributions, these distributions can be quite similar, see Figure 3.11. Conversely, changes in the exciton distribution in shape, (dis)appearance and shifts along the tube are taking place during the whole 1 ps trajectory, even when the local measure $d_{\text{sep}} \approx 0$. Analyzing the variation of the absorption state $\psi_{\max}$ for different molecular conformations along the MD trajectory using a global measure, *i.e.* the overlap coefficient $|\langle \psi_{\max,t} | \psi_{\max,t-\Delta t} \rangle|^2$ of $\psi_{\max}$ in consecutive frames, see Figure 3.11 (bottom), shows that this absorption state indeed significantly varies with the underlying molecular conformations.

The fluctuating character of the local measure for the response of the exciton distribution to the nuclear dynamics, d_{sep} , suggests that the selection of $\psi_{\max}$ is quite sensitive to small changes in the underlying molecular structure. This agrees well with the earlier suggestion that very fast energy transfer is facilitated by energy crossing within the manifold of exciton states with very similar energies.¹²⁰ Additional analysis of the 30 lowest eigenvalues of our Frenkel Hamiltonians, see Figure 3.12, enables us to study this suggestion. We find that energies fluctuate as a result of dynamic disorder in the underlying molecular assembly that is reflected in the Frenkel Hamiltonian, but the amplitudes of these fluctuations are small in an absolute sense. Note that the time scale in Figure 3.12 is added to provide insight in the evolution of the tube structure along the MD trajectory, whereas our analysis of exciton states remains essentially static. We will nevertheless label eigenstates according to MD time for ease of discussion. Following the eigenstate with the largest contribution to absorption, $\psi_{\max}$, we find that its position shifts within a tiny band of 20 cm^{-1} . Moreover, the energies of all 30 eigenstates lie within a narrow 60 cm^{-1} band

[†]Movie (MPG) file in `chapter_3` folder at https://github.com/xinmeng2015/chlorosome_phd_thesis or <https://doi.org/10.5281/zenodo.3674742>

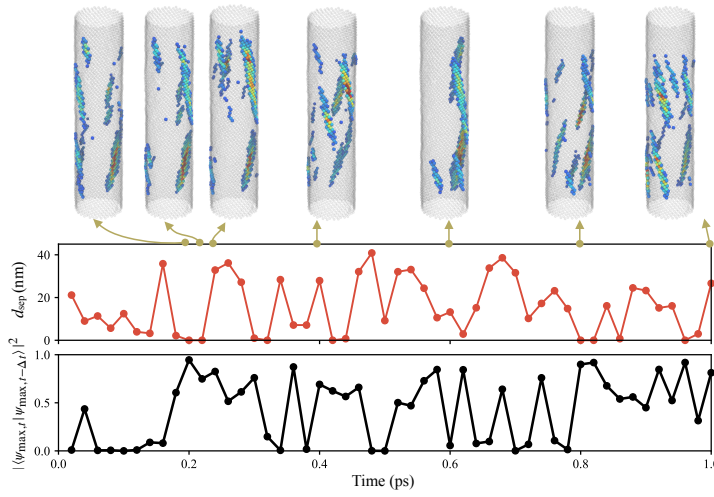


Figure 3.11: Exciton states $\psi_{\max}$ for different molecular conformations along the 1 ps MD trajectory for the $\delta = 49.6^\circ$ tube structure. Top: snapshots of the spatial distribution of $\psi_{\max}$ at different time frames: 0.2 , 0.22, 0.24, 0.4, 0.6, 0.8, 1.0 ps. Molecules are colored according to the exciton density p_i . To also visualize the other side of the tube, we made all molecules i with $p_i < 0.1p_{\max}$, transparent, where $p_{\max} = 0.0066$ is the maximum of the exciton density in all frames. Middle: the distance d_{sep} between molecules with the largest exciton density in $\psi_{\max}$ in consecutive frames. Bottom: the overlap coefficient, $|\langle \psi_{\max,t} | \psi_{\max,t-\Delta t} \rangle|^2$, between $\psi_{\max}$ in consecutive frames.

for all considered molecular conformations. This proximity of energy levels is an indication that non-adiabatic energy transfer is an option, provided that states also have a spatial overlap.

Our choice to rank eigenstates according to their eigenvalues obscures potential crossings, but we note that also the eigenstates change with the considered tube state. The crossing of energy levels can however be anticipated from several anti-correlated kinks that are present in Figure 3.12. Introducing additional overlap coefficients, $|\langle \psi_{k,t} | \psi_{20,0} \rangle|^2$, between $\psi_{k,t}$ for different k and the initial absorption state $\psi_{20,0}$, further quantifies this phenomenon. Focusing on the overlap coefficients for $k = 17, 19$, and 20 , see Figure 3.13, we find that the initial eigenstate for $k = 20$ becomes orthogonal to $\psi_{20,t}$ within 200 fs. As time proceeds, the initial state $\psi_{20,0}$ shows significant overlap with other eigenstates with a different energy rank, $\psi_{19,t}$ and later $\psi_{17,t}$. These results indicate that energy crossing can indeed be facilitated by dynamic disorder.

Concentrating on the projected $\psi_{\max}$ itself, domains can be seen always aligned at an angle with the long cylinder axis, somewhere between the **a** packing direction and the hydrogen-bonding direction, as these two directions accommodate the strongest coupled pairs. In particular, see Figure 3.11 (top), this preferential angle is determined by contributions of all helical families and modulated by factors such as dynamic disorder and the electronic coupling model considered. Our findings reveal the difficulty of relating optical responses directly to properties of the underlying molecular lattices.

Three-layered tubular assembly

In chlorosomes, energy produced by a photon exciting the inner tube needs to migrate within 10 ps (the average annihilation time)⁶¹ to the outer tube to reach the baseplate and subsequently the reaction center. Thus, we performed an analysis for a dense 1 ps MD trajectory (20 fs per frame, 300 K) of a concentric three-tube complex (Figure 3.14a) to explore the relation between dynamic disorder and excitonic properties, and to propose a mechanism that leads to accumulation of excitonic energy in the outer layers. The concentric structure is composed of three pre-packed tubes with radii $R = 5.2, 7.3$ and 9.5 nm, separated by 2.1 nm, as observed in experiments.³⁷ Before collecting the trajectory, the structure was well equilibrated by the standard procedure,

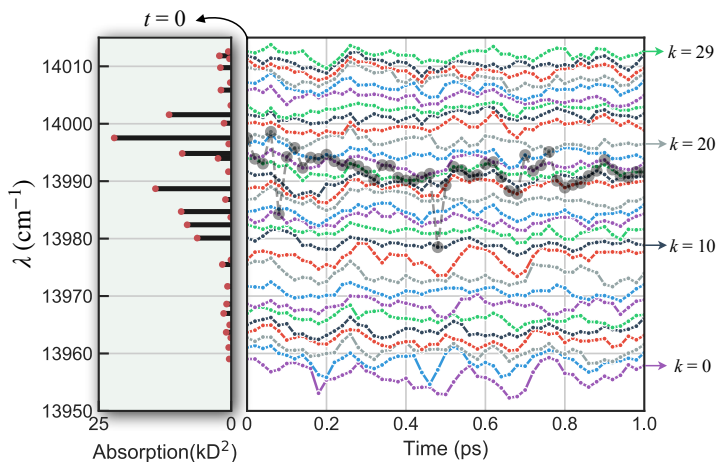


Figure 3.12: Analysis of stick spectra for the absorption calculated for molecular conformations along a 1 ps MD trajectory for $\delta = 49.6^\circ$. Left: Stick absorption spectrum calculated for the assembly at $t = 0$ ps. Right: The values of the 30 lowest energies associated with 30 eigenstates of the Frenkel Hamiltonian. Eigenstates and their energies are calculated for snapshots along the 1 ps MD trajectory. Energies for individual snapshots are ranked from low to high, starting from $k = m - 1 = 0$, see Method section, and colored according to their rank. The energy associated with the largest oscillator strength $\psi_{\max}$ for each snapshot is denoted by a grey sphere.

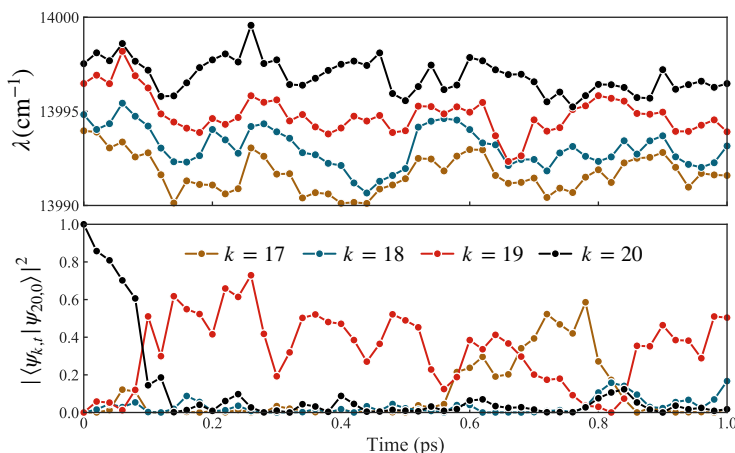


Figure 3.13: The overlap coefficient, $|\langle \psi_{k,t} | \psi_{20,0} \rangle|^2$, between selected states $|\psi_{k,t}\rangle$ and the absorption state $|\psi_{20,0}\rangle$ at $t = 0$ ps, along a 1 ps MD trajectory for $\delta = 49.6^\circ$. In line with this definition, the initial overlap coefficient = 1.0. States $k = 17, 18, 19$ and 20 are labeled by different colors.

see Methods section, and found stable.

Since concentric tubes in a multi-tube structure can be assembled in two distinct relative orientations, either parallel or anti-parallel to each other, we also considered a two-layered assembly and calculated spectral properties for these two different options. Although the stick spectra display tiny differences, the calculated absorption, LD and CD spectra are equivalent after broadening. This finding shows that the current experimental resolution is insufficient to distinguish relative tube orientations. For this reason, we further concentrate on a situation where all tubes are parallel to each other.

Key features identified for a single tube are also found for the concentric tubes: extremely low structure variation ($\text{RMSD}_{\text{lattice}} = 0.009 \pm 0.00003$ nm) and substantial variation of the separation distance d_{sep} (Figure 3.14b). Again, d_{sep} is three orders of magnitude larger than the average $\text{RMSD}_{\text{lattice}}$ for the assembly, and the average value of 24.7 nm is about ten times the gap distance between adjacent layers, suggesting that the position of maximum exciton density in ψ_{max} may well migrate from tube to tube. From the data shown in Figure 3.14b,

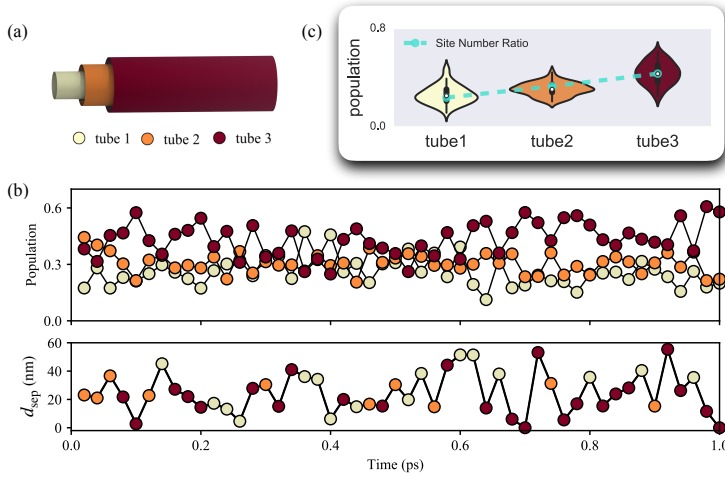


Figure 3.14: Analysis of the exciton states $\psi_{\max}$ in concentric 3-tube structures. (a) Schematic illustration of concentric tube geometry, with radii satisfying tube 3 > tube 2 > tube 1. Colors are used to distinguish between different tubes. (b) Top: the exciton density population in different tubes, denoted by tube color, along a 1 ps trajectory. Bottom: d_{sep} , the distance between molecules associated with the largest exciton density in $\psi_{\max}$ in consecutive frames. Color specify in which tube the molecule with the highest exciton density is situated. (c) The distribution of exciton density population of $\psi_{\max}$ over all frames in the trajectory. The average (white point) agrees well with the trend of the normalized number of molecules (site number ratio, dashed line) in each tube.

we see that this is indeed the case. Since visualization of the exciton distribution for $\psi_{\max}$ in the tubular complex is less straightforward than for a single tube, we determined the fractional population of this state in each of the three tubes, see Figure 3.14b. It shows that $\psi_{\max}$ is indeed delocalized over all three tubes, and that the exciton fraction in each of the tubes fluctuates around the average value with a considerable amplitude. In particular, the fraction present in the outer tube (tube 3) is seen to be the largest for most of the molecular conformations along the MD trajectory. Plotting the distribution of the exciton fractional population in each tube separately, see Figure 3.14c, shows a clear radial dependence, with the population averages (0.26 : 0.31 : 0.43) closely following the molecular ratio (0.24 : 0.33 : 0.43) for each of the three tubes. We thus conclude that the distribution of excitonic energy over each of the tubes does not reflect variations in disorder but directly relates to the number of molecules that is needed to constitute the tube. Since this number increases with increased tube radius R , exciton energy will automatically concentrate in the outer part of the tubular complex. The conclusions obtained from the short and dense trajectory (1 ps) also apply to the long and dilute trajectory (500 ps), see the structure and exciton state analysis shown in the Figure B.12. To further investigate the nature of this coupling, we considered a special case, *i.e.* the electronic couplings $J_{ij} = 0$ when i and j sites belong to tube 1 or tube 3, and $J_{ij} \neq 0$ when one of the sites is located in tube 2. For this J , we find that most of exciton density of $\psi_{\max}$ is confined to tube 2, as expected. In tubes 1 and 3, however, a tiny signal can be observed, indicating that inter-tube coupling is weak but present, even in the case that internal electronic coupling is suppressed.

3.4. Conclusions

Understanding how structural properties of protein-free BChl aggregates like chlorosomes translate into uniquely efficient and robust transfer of excitation energy is a significant but unresolved scientific challenge. In the present work, we have developed a protocol that combines experimental information from NMR, cryo-EM and optical spectroscopy to constitute a unique model of these biological assemblies. Our model is unique in allowing for realistic disorder and for reproducing all available characterization data simultaneously, including

typical features of the absorption, linear (LD) and circular dichroism (CD) spectra.

The developed protocol is general, and can be applied for other helical tube forming molecules. First, our extended geometrical analysis relates the axial repeat distance d of experimentally obtained layer lines³⁷ to chiral angles $\delta \in [0^\circ, 180^\circ]$. Consequently, we employ this set of δ , which is a key structural parameter together with the previously determined *syn-anti* dimer unit cell³⁷ and Bravais lattice parameters (a, b, γ) (Chapter 2), to build tubes for MD simulation of a realistic size, *i.e.* $l = 120$ nm length and $R = 7.5$ nm radius. After confirming stability at $T = 300$ K, a Frenkel exciton Hamiltonian is used to calculate optical spectra of ordered and disordered tubes for a direct comparison to measured spectral types. In this study, we have adopted the point-dipole approximation for the electronic coupling calculation but other descriptions are optional. Our calculations show that CD spectra types change several times along the δ -range, for instance from a type II for $\delta = 42.3^\circ$ to a mixed-type for $\delta = 27.6^\circ$. This finding explains the previously mentioned “uncontrolled” variation of CD signal type,^{35,88} *e.g.* between type II and mixed-type, which is likely due to small modulations of the overall tube chirality due to compositional heterogeneity rather than insufficient tube length or different curving directions in a mixture of tubes.^{35,37,80}

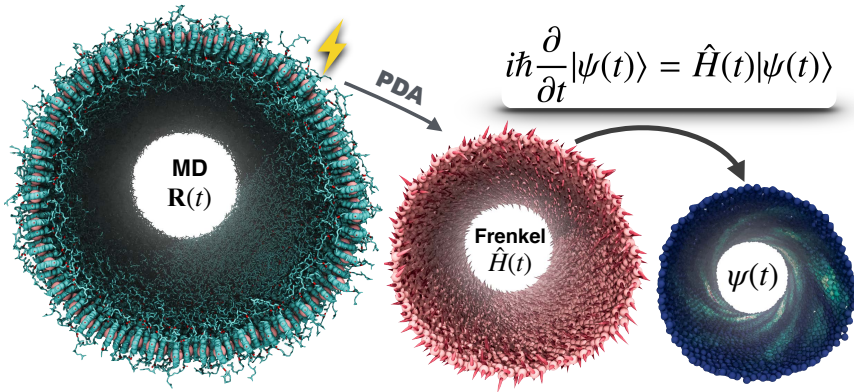
Next, we clarified the intricate effect of disorder on exciton states, with a focus on the state with the largest oscillator strength. We find disorder to induce localization of exciton states, *i.e.* concentration of exciton density in a spatially confined region, to a degree that is consistent with experimental observations.¹²⁴ We quantify this effect by considering distribution profiles of exciton states, their inverse participation ratios and corresponding exciton distributions mapped onto the tubular structure. These mapped distributions for the first time visualize the insight derived from 2D spectroscopy, which described chlorosomes as composed of weakly coupled coherent domains.¹²⁰ The observation that relatively small variations of the underlying molecular structure translate into significant changes in the exciton structure, giving rise to crossings between eigenstates with energies that are part of a tiny band, is in good agreement with earlier suggestion that the presence of many states of comparable energy enhances intra-tube migration of excitons.¹²⁰ Focusing on a concentric tube case, we find the ratio between exciton population in different tubes, when averaged over the MD trajectory, agrees well with their

molar ratio, suggesting the driving force for the migration of exciton energy from inside to outside that is simply the fact that larger tubes contain more molecules, since $N \propto R^2$. We plan to investigate the detailed effect of static and dynamic disorder on actual exciton migration in following chapters.

3.5. Acknowledgments

The authors thank Lina Kan for performing reference simulations of mixed BChl *c*–*d* systems. The authors acknowledge the helpful discussion with Dr. T. L. C. Jansen about the electronic coupling calculation. The use of supercomputer facilities was sponsored by NWO Physical Sciences, with financial support from The Netherlands Organization for Scientific Research (NWO).

Dynamic Disorder Drives Exciton Transfer in Tubular Chlorosomal Assemblies



This chapter was submitted as: Xinmeng Li, Francesco Buda, Huub J.M. de Groot, and G. J. Agur Sevink, Dynamic Disorder Drives Exciton Transfer in Tubular Chlorosomal Assemblies, 2020.

Chlorosomes stand out for their highly efficient excitation energy transfer (EET) in extreme low light conditions. Yet, little is known about the EET when a chlorosome is excited to a pure state that is an eigenstate of the exciton Hamiltonian. In this work, we consider the dynamic disorder in the intermolecular electronic coupling explicitly by calculating the electronic coupling terms in the Hamiltonian using nuclear coordinates that are taken from molecular dynamics simulation trajectories. We show that this dynamic disorder is capable of driving the evolution of the exciton, being a stationary state of the initial Hamiltonian. In particular, long-distance excitation energy transfer between domains of high exciton population and oscillatory behavior of the population in the site basis are observed, in line with two-dimensional electronic spectroscopy studies. We also found that in the high exciton population domains, their population variation is correlated with their overall coupling strength. Analysis in a reference state basis shows that such dynamic disorder, originating from thermal energy, creates a fluctuating landscape for the exciton and promotes the EET process. We propose such dynamic disorder as an important microscopic origin for the high efficient EET widely observed in different types of chlorosomes, bio-inspired tubular aggregates, or other light-harvesting complexes.

4.1. Introduction

The survival of green sulfur bacteria in extreme low-light condition relies on the efficiency of their light-harvesting antenna, chlorosomes, which are assemblies of hundreds or thousands bacteriochlorophylls (BChls) pigments.^{11–16} Elucidating the design principles behind the efficient excitation energy transfer (EET) that takes place in chlorosomes will contribute to our understanding of photosynthesis^{1,2,6,17–24} and may help to develop artificial light-harvesting^{25–28} or other optoelectronic devices.^{29–32} In spite of recent progress in theoretical and experimental understandings of exciton dynamics in chlorosome systems,^{36,40,41,43,44,79,80,84,105,120,121,124,141,146,147} a microscopic origin of efficient EET remains unclear.

Previously in Chapter 2, we identified a rotational degree of freedom that is prominent even though the pigments are densely packed together. This

head-head rotational dynamics between neighboring pigments is expected to affect their electronic couplings (see Chapter 3).¹⁸ Introducing such rotational disorder in the Frenkel Hamiltonian is found to induce delocalization of exciton states. Optically active states near to the bottom of the exciton band are found to be composed of scattered domains of population density that are distributed over the whole tube (Chapter 3). By analyzing the manifold of exciton states along a MD trajectory of molecular conformations, we found level crossings between states and high sensitivity of the exciton state domain patterns to the dynamic disorder. This may induce long-distance exciton transfer between scattered domains involving different exciton states (Chapter 3), in line with 2D electronic spectroscopy (2DES) studies.^{84,120} Beyond our previous treatment, here we conducted quantum dynamics simulations of exciton evolution, investigate the effect of the rotational dynamic disorder on the exciton density matrix, and show that it rapidly converts a pure state generated by optical excitation at the start of the trajectory into a superposition state characterized by many nonzero off-diagonal elements (a.k.a. coherences) in the density matrix. Considering that such dynamic disorder is also shared by artificial tube assemblies^{48–50} with proven efficient exciton transport ability, we propose thermally induced quantum instability by rapid molecular dynamics, faster than the quantum decoherence, and starting from a pure quantum state as a promising microscopic origin of efficient EET beyond the Born-Oppenheimer regime where the electronic motion follows the nuclear dynamics.

Apart from the previous lack of a precise chlorosome structure, the study of exciton evolution in chlorosomes has been hampered by the large dimension of these assemblies, which rule out any full quantum treatment.^{73,75,77,148} In line with previous treatments,^{36,40,41,43,44,71,79,80} we therefore consider an effective model, a Frenkel Exciton Hamiltonian, as a starting point. Fujita *et al.*^{40,43} used such a Hamiltonian to study the exciton dynamics of a stacked-ring structure, adding stochastic fluctuations to the site energies, comparing the exciton diffusion under different types of fluctuations. Márquez *et al.*¹⁰⁵ studied the exciton dynamics for different lattice models of chlorosomes. They introduced site energy variation through exciton-phonon interactions. Upon exciting a single site in the system, these studies all observed exciton diffusion to the whole tube within a ps time. In systems more complicated than a single tube structure, other types of non-stationary initial conditions were also considered.^{41,44}

Based on our recent progress in constructing chlorosome structures that satisfy experimental constraints in terms of microscopic detail (see Chapters 2 and 3), we are capable of studying the exciton dynamics of realistic chlorosomes within the standard Frenkel Exciton treatment. We exploit the nuclear coordinates taken from ground state molecular dynamics trajectories to derive time-dependent electronic coupling terms in the exciton Hamiltonian, thereby including the dynamic disorder explicitly. In line with the low light conditions and in contrast to previous studies,^{40,41,43,44,105} we select the exciton eigenstate of the Hamiltonian with the largest oscillator strength as the initial pure state, *i.e.* at $t = 0$, from which we start our simulation.¹⁴⁹ Since the initial state is stationary, the evolution of the exciton is fully driven by the dynamic disorder. As a first step towards fully understanding functional mechanisms of chlorosomes, we studied the exciton dynamics in a quasi-closed system manner. While the classical trajectories involve coupling to a heat bath with a thermostat, the propagation is performed in a series of closed quantum system simulations, without including energy dissipation or a sink for the exciton. The dynamic disorder parametrically included in $\hat{H}(t)$ is able to introduce both the population variation in the state basis and substantial coherences between exciton states on a time scale < 100 fs, which we consider sufficiently fast to overcome quantum dephasing and contribute to driving long range exciton transport.

4.2. Computational Methods

We conducted all-atom molecular dynamics (MD) simulations to obtain the nuclear coordinates along a trajectory, and used these coordinates to extract time-dependent spatial information of the transition dipole vectors $\mu(t)$ and their positions $\mathbf{R}(t)$ (see Figure C.1 and computational details in Appendix C). Following our previous work (Chapter 3), we considered full tube structures purely composed of BChl *c* molecules, which means that static disorder stemming from chemical compositions and structural defects are not included in our treatment. Given these spatial properties $\{\mu(t), \mathbf{R}(t)\}$, the Frenkel Exciton

Hamiltonian is calculated by

$$\hat{H}(t) = \sum_i \nu |i\rangle\langle i| + \sum_{i \neq j} J_{ij}(\boldsymbol{\mu}_i(t), \boldsymbol{\mu}_j(t), \mathbf{R}_{ij}(t)) |j\rangle\langle i| \quad i, j \in [1, N] \quad (4.1)$$

where diagonal terms ν represent the monomer excitation energy of a BChl *c* pigment molecule, and the off-diagonal terms J_{ij} represent the electronic coupling between molecules *i* and *j*, which is calculated via the standard point-dipole approximation (PDA)

$$J_{ij}(\boldsymbol{\mu}_i(t), \boldsymbol{\mu}_j(t), \mathbf{R}_{ij}(t)) = \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{|\mathbf{R}_{ij}|^3} - 3 \frac{(\boldsymbol{\mu}_i \cdot \mathbf{R}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{R}_{ij})}{|\mathbf{R}_{ij}|^5}. \quad (4.2)$$

Site energies. Although chlorosomes exhibit gross structural heterogeneity at the supramolecular level, they are remarkably homogeneous at the molecular level. First, solid state NMR studies on mutant and WT chlorosomes have consistently revealed two well defined structural fractions.³⁷ Second, fluorescence excitation spectroscopy measurements for individual chlorosomes by Günther *et al* have confirmed the presence of two well-defined components with very little difference in the average site energies of $\Delta E_{12} = 34 \text{ cm}^{-1}$ and limited inhomogeneous broadening.⁴⁵ The energies of the exciton states appear to shift primarily due to variation of the curvature of tubular assemblies.⁴⁵ For a simulated tube of 7.5 nm diameter and with identical site energies for the building blocks, we obtain a total inhomogeneous width of 60 cm^{-1} due to curvature, which is in line with experimental data that also show static optical broadening in the tubes, while the underlying MAS NMR data reveal high, nearly crystalline homogeneity at the molecular level.⁴⁵ Third, in Chapter 2 we found converging evidence that the two components are due to molecules with and without interstack hydrogen bonding. Since the difference in the energies for the lower exciton states are very minor according to the fluorescence excitation data, the direct effect of the environment, including the variation in hydrogen bonding, on the site energies is very small. To simulate these experimentally determined characteristics, the site energies, represented by the diagonal terms in Hamiltonian, were set to a fixed value $\nu_i = \nu = 15390 \text{ cm}^{-1}$ that is the same for all molecules, while the electronic coupling between molecules (off-diagonal terms in Hamiltonian) are parameterized according to conformations and supramolecular structure taken from MD trajectories, which includes both

the molecular rotations and the curvature. More discussions of our choices are available in Chapter 3.

Such a treatment of $\hat{H}(t)$ gives rise to dynamic disorder in the electronic coupling microscopically obtained from the ground state molecular dynamics. Details about the MD simulation setup and Hamiltonian parameterization are available in the Appendix C. The evolution of the exciton wave function is governed by the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle \quad (4.3)$$

For optimal computational efficiency, the time-dependent Hamiltonian $\hat{H}(t)$ is updated discretely every short time interval Δt according to the corresponding nuclear positions and is assumed constant in between updates on the Δt time intervals.^{82,83} A requirement in such a strategy is that Δt is small enough, meaning that each update only introduces a relative small perturbation to the Hamiltonian from the previous interval. Considering the relative motions between molecules are slower than intra-molecule vibrational modes, we select $\Delta t = 20$ fs. In particular, we found that the difference in nuclear positions between structures at $t = 0$ and $t = 20$ fs is quite small (≈ 0.1 Å), see details in later discussions. Furthermore, we take the Hamiltonian $\hat{H}_1 = \hat{H}(t = \Delta t)$ and investigated the exciton dynamics for this constant Hamiltonian, which is referred to as the static case $\hat{H}_1$ in later discussions. As shown later, the exciton evolution in the static case $\hat{H}_1$ is very weak, which confirms that the perturbation to the Hamiltonian $\hat{H}_0$ at $t = 0$ is indeed small. We conclude that the $\Delta t = 20$ fs is small enough in this study. Such an updating strategy is also adopted and discussed in Chapter 3. Since both the Hamiltonian $\hat{H}(t)$ and exciton wave function $|\psi(t)\rangle$ are formulated in the site basis, $|\psi(t)\rangle$ is propagated directly, with a time step of 1 fs, through solving the time-dependent Schrödinger equation (eq 4.3) using the “zvode” ODE solver implemented in the QUTIP package.^{150,151} Due to the discrete nature of $\hat{H}(t)$ in our treatment, $|\psi(t)\rangle$ is propagated step-wise.

The detailed propagation sequence is provided in the Scheme C.1. We take as the initial wave function $|\psi(0)\rangle$, *i.e.* the eigenstate of the Hamiltonian $\hat{H}_0 = \hat{H}(t = 0)$ with the largest oscillator strength. This choice corresponds to a situation in which the chlorosome absorbs one photon in low light conditions.

In contrast to previous studies, we particularly did not choose an initial wave function fully localized at one molecular site, because light excites eigenstates rather than individual molecules.^{149,152} The exciton dynamics trajectory is a collection of $|\psi(t)\rangle$ in the site basis. For any given wave function $|\psi(t)\rangle$, the density matrix $\rho(t)$ in the site basis is obtained as

$$\rho(t) = |\psi(t)\rangle\langle\psi(t)| = \sum_{i=1}^N \sum_{j=1}^N \rho_{ij}(t) |i\rangle\langle j| \quad (4.4)$$

where $\rho_{ij}(t)$ describes the populations ($i = j$) and coherences ($i \neq j$) in the site basis. To clearly characterize the non-stationary nature of the exciton dynamics, we further performed analysis in the state basis $|\phi_k\rangle$, which are the eigenstates of the Hamiltonian at $t = 0$, $\hat{H}_0 |\phi_k\rangle = \varepsilon_k |\phi_k\rangle$. The density matrix ρ^ϕ in the state basis $|\phi_k\rangle$, is calculated from the density matrix in the site basis as

$$\rho^\phi(t) = P^{-1} \rho(t) P \quad (4.5)$$

where P is the projection matrix composed of the column vectors for states in the state basis $|\phi_k\rangle$. The density matrix $\rho_{kl}^\phi(t)$ now describes the populations ($k = l$) and coherences ($k \neq l$) in the reference state basis $|\phi_k\rangle$. In addition, we also projected the density matrix $\rho(t)$ to the state basis of $\hat{H}(t)$ after each update, see more details in Scheme C.1.

4.3. Results and Discussion

We conducted simulations of the exciton dynamics for both single tube and multi-tube structures. Most results consider the single tube system, which we used to investigate how the initial eigenstate evolves, and whether long-distance exciton transfer can take place purely driven by dynamic disorder. The multi-tube system is mainly considered to focus on the effect of hierarchical structure on the inter-tube exciton transfer.

Single Tube Setup. Figure 4.1 illustrates relevant details of the tube structure, together with the initial wave function used in the exciton dynamics simulation. Following our static analysis in Chapter 3, we selected a 60 nm long tube with

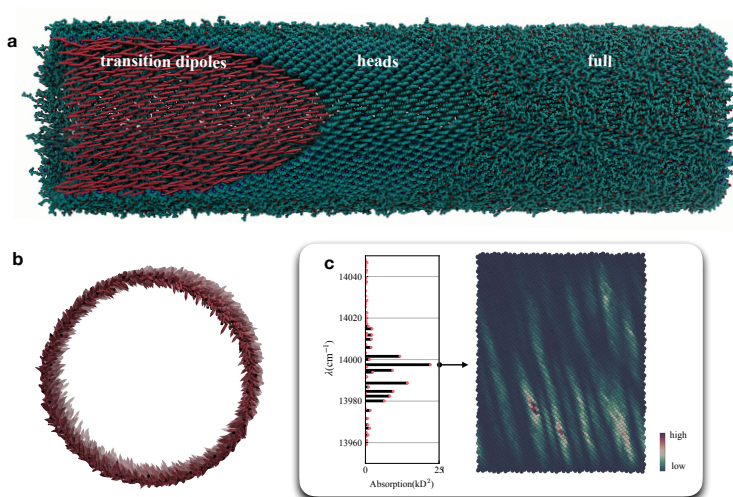


Figure 4.1: Representative images of the tubular structure and the exciton state of largest oscillator strength for a single chlorosomal tube assembly. (a) Atomistic structure. The tube is composed of 4547 BChl *c* molecules, with radius $R = 7.5$ nm and length $L = 60$ nm. Transition dipoles and heads of BChl *c* molecules are highlighted by removing covering atoms. (b) Orthonormal projection of all the transition dipoles in the whole tube, showing considerable disorder in their relative orientations. (c) Absorption spectrum of the tube (left) and spatial distribution the exciton state of largest oscillator strength (right). The wave function is projected on a plane unrolled from the tube structure, see Figure C.2 for other types of visualization.

a chiral angle of 49.6° , which matches optical spectra found in experiments. After equilibration, molecular conformations are collected every $\Delta t = 20$ fs along a 1 ps MD trajectory to determine $\{\boldsymbol{\mu}(t), \mathbf{R}(t)\}$ and consequently the Hamiltonian $\hat{H}(t)$ (Eq.4.1). We refer to Chapter 3 for the details about the variation of exciton states in different molecular conformations along such a MD trajectory. The root mean square displacement RMSD that relates to nuclear coordinates that define the transition dipole, shows that the structural deviation from the initial tube continuously grows on the considered time scale of 1 ps, whereas the RMSD at $t = 20$ fs is quite small (≈ 0.1 Å), indicating that the perturbation $\Delta\hat{H}$ in $\hat{H}_1 = \hat{H}_0 + \Delta\hat{H}$ is indeed quite small, see Figure C.3 for more details. As can be seen from the snapshots in Figure 4.1a–b, varying molecular orientations produce considerable rotational disorder in the transition dipoles. We calculated the absorption spectrum for $\hat{H}_0$, and selected the eigenstate with the largest absorption probability (state number $k = 20$) as the initial exciton wave function $|\psi(0)\rangle$ in the exciton dynamics simulation. As Figure 4.1c shows, disorder in the electronic coupling suppresses exciton delocalization and leads to a few small domains of high exciton population.

Enhancement of Exciton Transport by Dynamic Disorder. In order to quantify transport away from the initial state, we compute the survival probability $P_S(t) = |\langle\psi(0)|\psi(t)\rangle|^2$ of the initial state,⁸² defined as the squared of the overlap integral between the initial wave function and the wave function at time t , see Figure 4.2. For the static case, $\hat{H}_1$, the exciton stays close to the original state as P_S is still significant after 1 ps, with $P_S > 0.9$ along the whole trajectory. For the dynamic case, $\hat{H}(t)$, P_S decreases substantially, with $P_S < 0.3$ at 1 ps. The abrupt changing of the power law behavior of P_S around 200 fs highlights the role of the dynamic disorder in exciton transfer: the original pure state changes into a mixed state due to the changing Hamiltonian.

For the $\hat{H}(t)$ case, a significant variation of the spatial distribution of the wave functions is observed, accompanying the decrease of P_S , as shown in Figure 4.2b (selected snapshots) and Movie S1[†]. Tracing domains of high exciton population, for instance, the domains I – III labeled in Figure 4.2b, we observed the presence of (long-distance) exciton energy transfer between such domains. This observation is in line with experimental studies¹²⁰ and our previous static

[†]Movie S1-S6 (MP4) files in `chapter_4` folder at https://github.com/xinmeng2015/chlorosome_phd_thesis or <https://doi.org/10.5281/zenodo.3674742>

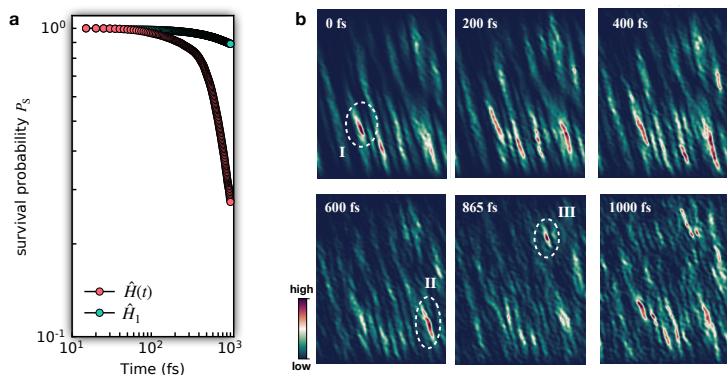


Figure 4.2: Enhancement of exciton dynamics due to dynamic disorder from MD. (a) Comparison of the survival probability P_s of the initial exciton state in case $\hat{H}(t)$ and case $\hat{H}_1$. (b) Spatial distribution of the exciton at selected times in the $\hat{H}(t)$ case. Three domains I–III are labeled to illustrate the long distance migration. See Movie S1 and Movie S2 for the comparison of whole 1 ps exciton dynamics trajectories in the two cases.

analysis in Chapter 3. The substantial variation of the exciton within the short time of 1 ps is also in line with intra-chlorosome exciton transfer time scales (below 1 ps) observed in experimental works.^{84,120,121,124,141,147}

We may relate these observations to photosynthetic bacteria where excitonic energy initially captured in chlorosome antennae needs to migrate to the baseplate within a few ps before exciton annihilation occurs.⁶¹ We note that during the energy transfer process, a spatial barrier may be present, meaning that the initial state, or a low energy state where an exciton might be trapped, is spatially remote from the target state that is localized at the baseplate. We illustrated such a situation in Scheme C.2. In the static case, $\hat{H}_1$, such a spatial barrier will delay or even prohibit the exciton transfer process, as the exciton is trapped in the initial state and the spatial sampling of the exciton is limited (see Movie S2[†]). Introducing dynamic disorder, as shown in the $\hat{H}(t)$ case, renders the exciton capable of dynamically sampling the whole extent of the tube within the characteristic intra-chlorosome transfer timescale of 1 ps.⁶¹ As summarized in Scheme C.2, dynamic disorder may introduce “intermediate” domains that are close to the baseplate and helps the following energy transfer.

From the perspective of energy transfer, the exciton dynamics in our $\hat{H}(t)$ case belongs to a coherent regime, *i.e.* the regime where energy transfer is perceived as fastest, for which the standard Förster and Redfield theories do not apply.²⁰ Such coherent excitation energy transfer is well-recognized in photosynthetic systems. In such a process, the exciton diffusion equation can be described in terms of a coherent part and an incoherent part.^{153–155} Since our initial exciton state is stationary, there is initially no coherence between exciton states. Each update of the Hamiltonian $\hat{H}(t)$ will disturb the coherent evolution in the previous period (incoherent contribution), and at the same time it introduces new coherences (coherent contribution).¹⁵⁵ This illustrates the complexity of energy transfer in such a coherent regime.²⁰

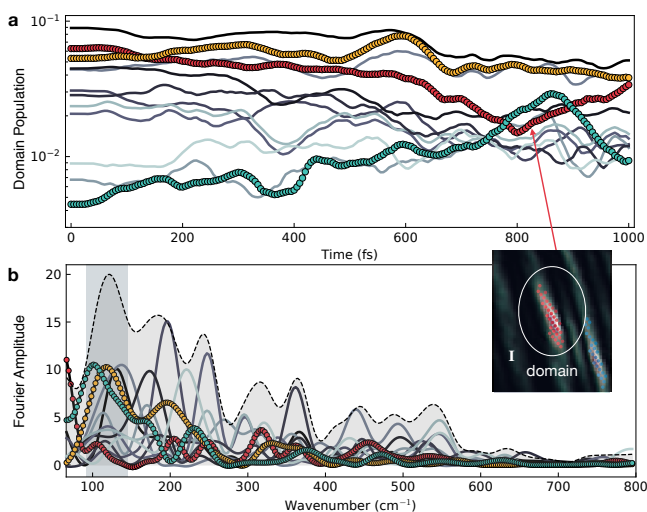


Figure 4.3: Evolution of the domain population $P_{\text{domain}}(t)$, for distinct domains taken from exciton states at 0, 600 and 865 fs for the $\hat{H}(t)$ case, showing a clear oscillatory behavior. (a) Domain population along the 1 ps exciton dynamics trajectory. (b) Fourier spectra (amplitude versus wavenumber) calculated from the time traces of the domain populations. The light gray rectangle highlights the frequencies between 91 cm^{-1} and 145 cm^{-1} . Domain I, II and III are highlighted by red, yellow and green colors. Frequencies corresponding to time scales longer than half of the exciton trajectory of 1 ps are not shown.

Site Basis Population Modulation. As demonstrated in FMO studies,^{22,23} periodic modulation of the population in the site basis along the exciton dynamics trajectory characterizes quantum beatings that have been detected by 2DES. We investigate the population variation to determine periodic modulations that match coherent beatings measured in chlorosomes systems, *e.g.* at 91 and 145 cm⁻¹.⁸⁴ As domains of high exciton population are formed due to strong electronic coupling between pigments in chlorosomes, we determined the population evolution over domains instead of over individual sites, *i.e.* via the total population in a domain, $P_{\text{domain}}(t)$ defined as

$$P_{\text{domain}}(t) = \sum_{\text{site } i \in \text{domain}} \rho_{ii}(t) \quad (4.6)$$

where ρ_{ii} is the population on site i . Figure 4.3 summarizes the $P_{\text{domain}}(t)$ for the considered domains. To capture significant domains at the early and late stages of exciton evolution, we considered domains determined from snapshots at 0, 600 and 865 fs (see Figure 4.2b). For clarity, $P_{\text{domain}}(t)$ for the domains labeled I, II and III in Figure 4.2b are highlighted and more details are provided in the Appendix C (see Figure C.4 for how domains are defined and their $P_{\text{domain}}(t)$ plots).

Oscillatory behavior of the domain population P_{domain} is observed for all domains, see Figure 4.3a, which cannot be explained in terms of monomeric properties but suggest many weak coherences along the exciton dynamics trajectory. In particular, the frequency of these oscillations can be quantified by spectral analysis of the P_{domain} time traces, see Figure 4.3b. Concentrating on the range where quantum beats are experimentally observed, *i.e.* 91 cm⁻¹ and 145 cm⁻¹ (light gray area in Figure 4.3b), we find that the average intensity is maximal, with high-population domains (II and III) showing also a maximum intensity. This match between the periodicity of P_{domain} modulation and experimentally observed coherent beats suggests that quantum beats can also be induced by the ground state nuclear dynamics, in line with the observation in a recent study about FMO.¹⁵⁶ We note that, the P_{domain} variation in the $\hat{H}_1$ case is much weaker, as shown in Figure C.5, and the Fourier spectra are less rich. In particular the maximum intensity is found around 200 cm⁻¹.

Although the exciton evolution is determined by variation of the Hamiltonian of the whole system, we tried to identify microscopic signatures of the dynamic

disorder in the domains that can be correlated to their population oscillations. We first calculated the overall coupling strength J_{domain} , see definition in Appendix C. We observe a clear correlation between J_{domain} and P_{domain} (Figure C.6): higher domain population corresponds to stronger coupling J_{domain} . The calculated cross-correlation values between J_{domain} and P_{domain} for the domain I, II and III are -0.61 , -0.34 , and -0.21 respectively, which shows that they are correlated. This is further supported by the distribution of cross-correlation distribution for all considered domains, see Figure C.7a. To see if there is a direct relation between earlier identified simple structural modes, like rotation (average relative rotation angle α) and lattice vibrations (average distance d between neighboring transition dipoles), and the oscillations of P_{domain} , we analyzed their correlations to P_{domain} as well, see details in Appendix C. We find, see Figure C.7, that their cross-correlations are dispersed, showing that there is no clear direct correlation. Yet, a clear correlation can be identified for J_{domain}^- , the negative part of J_{domain} . This indicates that oscillation of domain population can not be singled out to a particular structural mode, but are rather due to collective motion inside the domains.

Density Matrix in State Basis. Features of the non-stationary propagation, such as the variation in population and coherence in the state basis, can be investigated by visualizing the diagonal and off-diagonal terms in the density matrices $\rho^\phi(t)$ along the exciton trajectory, see Movie S3[†]. In the movie, we only focus on the $k < 350$ part of the density matrix, which covers all the states of significant population: $\rho_{kk}^\phi > 10/N$ ($N = 4547$ which is the total number of sites, see Figure C.8). We refer to Figure C.9 for the snapshot at 200 fs and details of our visualization method. Along the exciton dynamics, the exciton mixes from the initial pure state ($k = 20$) with other states in a close energy range. We note that for states $k < 350$, the energy range is approximately 350 cm^{-1} . As observed in the movie S3, coherences between the initial state and other states are built, especially in the later stages when dynamic disorder introduces more significant variation to the initial Hamiltonian. As discussed in Chapter 3, the eigenstates from $\hat{H}(t = 0)$ to $\hat{H}(t)$ may change. To make sure that the coherences between states in the reference state basis shown in the density matrix $\rho^\phi(t)$ is not due to a simple switch of eigenstates, we also analyzed the density matrix $\rho^*(t)$ in terms of the state basis of the time-dependent Hamiltonian $\hat{H}(t)$, see details in Scheme C.1. As shown in Movie S4[†], consistent with $\rho^\phi(t)$, similar

even stronger population variation and introduction of coherences are observed in $\rho^*(t)$. In particular, we observed substantial coherences $\rho_{ij}^*(t)$ on a time scale < 100 fs, *e.g.* see $\rho^*(t = 20$ fs). This indicates that the dynamic disorder in $\hat{H}(t)$ is sufficient to overcome quantum dephasing and to drive semi-classical exciton transfer.

The enhancement of exciton dynamics by dynamic disorder is further demonstrated in the state basis by the analysis of the mean square displacement $\text{MSD}_k = \sum_k \rho_{kk}^\phi(t)(k - k_0)^2$ in the reference state basis $|\phi_k\rangle$. Using $\text{MSD}_k \propto Dt$, the extracted diffusion coefficient D in the $\hat{H}(t)$ case, $D_t = 21.983 \text{ fs}^{-1}$, is about four orders of magnitude larger than $D_1 = 0.002 \text{ fs}^{-1}$ for $\hat{H}_1$, see Figure 4.4a. Consistent with our analysis of the exciton dynamics trajectories in real space, exciton transport in state basis is limited for the static $\hat{H}_1$ case, where the exciton state is trapped in the initial state. In the dynamic $\hat{H}(t)$ case, however, exciton transport in state basis is facilitated by the dynamic disorder that stems from the thermal energy.

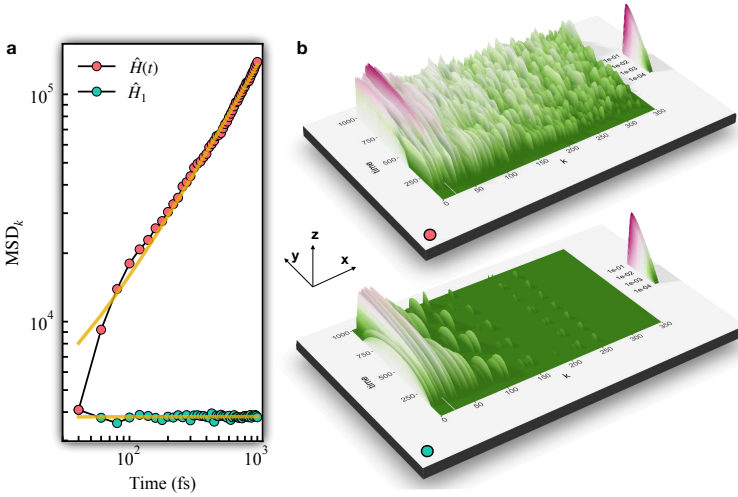


Figure 4.4: Enhancement of exciton dynamics in state basis due to dynamic disorder obtained from MD. (a) Comparison of the MSD_k in the reference state basis for two cases: the dynamic $\hat{H}(t)$ and static $\hat{H}_1$. (b) 3D plots of the population ρ_{kk}^ϕ in the state basis $|\phi_k\rangle$ (z -axis) as a function of state number k (x -axis) and time t (y -axis), top for $\hat{H}(t)$ and bottom for $\hat{H}_1$.

Landscape. We may further analyze these results by considering the time traces of populations in the reference state basis for all states $k < 350$, via the 3D plots in Figure 4.4b. From the $\hat{H}(t)$ case, Figure 4.4b top, it is clear that thermal energy creates a fluctuating (potential) energy landscape for the exciton, which drives migration in the states basis and enhances mixing of exciton states. Without accumulation of perturbations due to thermal fluctuation, in the $\hat{H}_1$ case (Figure 4.4b bottom), the exciton dynamics is much simpler, with well-defined oscillations resulting from fixed phase factors in the coherence terms. Animations for different perspectives of the 3D plots for the two cases are given in Movie S5 and Movie S6.[†]

Multi-tube. As experimental imaging shows that chlorosomes consist of hierarchical tube structures,³⁷ we also conducted exciton dynamics simulations on two types of hierarchical assemblies: concentric tubes (3 nested tubes) and side-by-side aligned tubes (2 tubes). We focused on the question how the inter-tube connectivity affects the exciton transfer. Figure C.10 shows simulation details and our analysis of the initial state survival probability P_S as well as the tube population $P_{\text{tube}}(t) = \sum_{\text{site } i \in \text{tube}} \rho_{ii}(t)$ along the exciton trajectories. As characterized by P_S , the enhancement of exciton transfer by dynamic disorder is also present in both the multi-tube cases. By comparing P_{tube} for both multi-tube topologies, we find stronger inter-tube fluctuations in the concentric tube case and P_{tube} reaches equilibrium faster, reflecting a stronger inter-tube electronic coupling in the concentric tube topology. The inter-tube transfer time scale, *i.e.* the time that P_{tube} reaches equilibrium, is about 4 ps (concentric tube) to 10 ps (aligned tubes), which is longer than the intra-tube transfer time scale of 1 ps. This result suggests that prior to energy annihilation at a timescale of 10 ps,⁶¹ an exciton is able to migrate across different layers in concentric tubes and across separate tubes.

For the different tube radii R in the concentric tube case, the equilibrium P_{tube} increases with increasing radius R , in line with our previous static analysis that there is a biased transfer from inner to outer tube due to the geometric condition that larger tubes contain more molecules with $N \propto R^2$ (Chapter 3). In particular, when *syn-anti* packing units assemble into tubes, their hydrophobic farnesyl tails will cover both the inside and outside of each nested tube, which provides the option of forming tightly packed concentric tubes (Chapter 2). Compared with the side-by-side tube topology, the inter-tube exciton dynamics

is enhanced and biased towards to the outer tube in the concentric tube topology, which is more favored in terms of the efficiency in the whole energy transfer process.

How can we relate our computational results to natural chlorosomes? In nature, chlorosomes are oblong-shaped assemblies of complete and incomplete concentric tubes, with an overall dimension that is generally smaller than the wavelength of the absorbed light.^{34,157} It therefore makes sense to assume that incident light will excite an eigenstate that is delocalized over the entire chlorosome, see the results in this subsection, albeit that high exciton populations will again be confined to small domains that are scattered over the whole structure. In particular, since the total population in each of the concentric tubes is found to scale with the number of constituting pigments at longer times, we may conclude that the intra-tube excitonic features are rather independent of the tube radius. Thus, they are likely to agree with that of a single tube.

The EET, however, can be seen to depend on the inter-tube connectivity, with a more efficient exciton transfer in concentric than in side-by-side tubular assemblies. Yet, since chlorosomes are known to assemble via a nucleation and growth process,¹⁰⁰ it is unlikely that such functional requirements prescribe the actual tube connectivity in natural chlorosomes. It is more likely that energy transfer to a “sink” like the baseplate starts directly after excitation, and that mixing of exciton states due to the dynamic disorder from nuclear motions plays a more dominant role in EET than the actual inter-tube connectivity.

4.4. Conclusion

The essential requirement for utilizing thermal energy to enhance the exciton transfer is that the strength of dynamic disorder, associated with thermal motions, is comparable to the energy gaps between exciton states.²⁰ If the energy gaps are too large or the dynamic disorder too weak, migration in the state basis will be limited, as been illustrated for the static case $\hat{H}_1$. Liquid crystalline materials composed of densely packed pigments, for instance, chlorosomes and carbocyanine dye nanotubes, are suitable for high-efficient long-distance EET since these requirements are easily met: 1) the presence of a large number of pigments expressing structural disorder guarantees a large number of exciton

states of very similar energy; 2) the relative low energetic costs of pigment rotation in the tube due to thermal motion, even in dense packing, gives rise to rotation of transition dipoles or dynamic disorder. This is in contrast to the situation where pigments are confined in a protein matrix, where disorder mainly stems from the environment in which pigments are trapped; 3) the fluctuating nature of the dynamic disorder, at several lengths and time scales, prevents trapping in eigenstates, for instance low energy states, and promotes efficient exciton transfer, in line with a recent 2DES study.¹²¹

By including the pigment assembly dynamics stemming from ground state molecular dynamics at room temperature in the fluctuating electronic coupling terms of our Frenkel Hamiltonian, we have been able to study the role of dynamic disorder in enhancing the exciton transfer. We observed several phenomena that are in line with experimental observations, despite the simplifications considered in our approach. It can be anticipated that methodological improvements within the computational concept,^{73,158} for instance, site-dependent site energy and more precise methods for the electronic coupling, will only strengthen our main conclusions.

In chlorosomes, local molecular motion is a key property. It is a generic property for structures composed of head-head packing unit, and independent of the particular molecular component (or BChl pigment), the hierarchical nature of the structure (close/open tubular or planar), or overall size. Simple but general, dynamic disorder that originates from these local molecular motions is capable of inducing a fluctuating landscape for the excitons, which enhances exciton transfer. Our findings are a key step towards solving the long-lasting puzzle about why efficient exciton transfer is widely observed in different types of chlorosomes and other light-harvesting complexes. Following this principle, we also suggest that the liquid-crystal like aggregates assembled from pigments with some sort of symmetry breaking, for instance, chlorosomes and the carbocyanine dye nanotubes, all rely on the same principle for efficient long-distance energy transfer.

4.5. Acknowledgments

The authors acknowledge Prof. dr. A. R. Holzwarth for helpful discussions. The use of supercomputer facilities was sponsored by NWO Exact and Natural Sciences, with financial support from the Netherlands Organization for Scientific Research (NWO).

Chirality versus Optical Responses of Chlorosomal Tube Aggregates: Highlighting the Role of Sample Preparation

Approaching the end of this thesis, I may become a bit more generic. Therefore, instead of solely considering tubes according to specific chiral angles, I systematically investigate the effect of chirality on the experimentally measurable optical properties. I do so by presenting i) the general protocol for constructing stable atomistic tube structures according to pre-defined chirality, which I apply ii) for the construction of chlorosomal tubes in the range $[0^\circ, 180^\circ)$, with an angular resolution of 5° . I note that the protocol under i) is more generally applicable for the construction of molecular assemblies of a chiral nature. In this short chapter, I employ the Frenkel treatment discussed in Chapter 3 to tube assemblies to determine a ‘phase diagram’ of chirality versus optical spectra, in analogy to known phase diagrams in terms of thermodynamic variables. I considered structures obtained by the protocol substantiated further on, and that the considered range of angles covers all possible chiral tube angles for reasons of symmetry. Such *in silico* experiments allow us to clarify the optical fingerprints of chlorosomal tube aggregates and to obtain an improved understanding of the robustness of circular dichroism (CD) spectra measured in experiments.

This chapter is to be submitted as: *In Silico Prediction of Chirality versus Optical Responses of Chlorosomal Tube Aggregates*, 2020.

5.1. Introduction

Helical structures are particularly prevalent in biology, as exemplified by the helicity in proteins as well as in the molecules that encode proteins and are seen to encode most biological function and thus life itself — deoxyribonucleic acid or DNA — the structure of which was determined in the early 1950s.^{159,160} Beside single helices formed through covalent bonds, like the ones in proteins and DNA, many structures display chiral or helical characteristics as a result of non-covalent interactions,^{101,161} including the cell cytoskeleton,¹⁶² myosin filaments,¹⁶³ bacterial flagella,¹⁶⁴ and filamentous bacteriophage.¹⁶⁵ Yet, since the formation of quasi-2D helical motifs as a result of some sort of symmetry breaking is also frequently observed in synthetic systems and in specific phenomena therein, helicity is of a more universal significance.^{166,167}

As an intriguing and sometimes functionally-relevant property of biological matter and some bio-inspired materials, helicity directly or indirectly relates to distinct and attractive mechanical, optical and other functional properties.^{168–171} An example of particular interest are chlorosomes, *i.e.* tubular aggregates that are solely assembled from pigment molecules, which are recognized as the most efficient light-harvesting antennae found in nature,^{15,16} and are rather unique in the finding that protein-based encoding of their light-harvesting function is essentially lacking. Inspired by chlorosomes, other large tubular molecular aggregates (TMA) formed by small molecules are attracting increasing attention in recent years for electronic and photonic applications.^{28,48,125,172–180} In particular, some TMAs show extraordinary energy transport abilities.^{50,181,182} Such structures are assembled, as noted earlier, from thousands of molecules that have been densely packed into a tubular geometry, having a diameter in the order of 10 nm and a length that may extend to hundreds of nanometers or even several micrometers.²⁸ In general, their structural organization is insufficiently characterized by experiments, owing to structural heterogeneity and the resulting lack of a distinct crystalline organization. More generally, the effect of supramolecular or tube chirality on the optical properties is still poorly understood.

In principle, we are able to reconstruct tube structures systematically and to probe corresponding optical properties by means of theoretical or numerical *in silico* experiments, and also to understand their relation towards extraction

of design parameters. In practice, however, it remains challenging to obtain atomistic structures of tube aggregates with a customized tube chirality, a challenge that seriously hinders such an *in silico* study.⁵¹

Here we demonstrate that, combining a new in-house packing code (CTubeGen)¹ and all-atom molecular dynamics (MD), we can effortlessly produce atomistic chlorosome tube structures with a pre-defined and customized tube chirality. This protocol is described in section 5.2.1. Besides for building the chlorosomes in this work, such a protocol may prove useful for generating other TMA systems. In addition, we use these structures to calculate optical spectra, including absorption, linear dichroism (LD), and circular dichroism (CD), for the full range of chiral vectors. The thus obtained chirality versus spectra ‘phase-diagram’ for the first time elucidates the relation between the overall tube chirality and the optical property of chlorosomes, resolving a long-standing issue how to explain different types of CD spectra observed for very similar chlorosomes. In particular, we show that the mystery of a mixture-type CD signal, which gave rise to explanation in terms of length-dependence, or a mixture of structures with different curving directions,^{35,37,80} can be explained in terms of a single assembly with a particular chirality. We find that the shape of CD spectra changes abruptly when the chiral angle crosses into a different ranges, which may clarify this uncontrollable variation of CD spectra observed in experiments. Hence, it can be attributed to the preparation process: depending on the bacterial species or the chlorosome growth conditions, the chirality is not fully controlled, and even small changes in chirality may cause a distinct change of CD spectra.^{35,88} We add that, besides optical properties, also other properties, *e.g.* mechanical properties, can be studied using these atomistic structures and MD simulation, see the next chapter.

¹A software written in python, available in `chapter_5` folder at https://github.com/xinmeng2015/chlorosome_phd_thesis or <https://doi.org/10.5281/zenodo.3674742>

5.2. Results

5.2.1. The Protocol

Figure 5.1 and the following three steps outline the protocol that we developed for generating chiral structures with atomic resolution. In this study, we applied the protocol for the generation of chlorosome tubes starting from a *syn-anti* dimeric unit cells.

Stage 1, initial preparation. The goal of this stage is to generate a proper local packing, by equilibrating small planar aggregates. The molecular basis or composing unit of a given tube system has to be determined a priori. For chlorosomes, it is a *syn-anti* dimer of BChl pigments determined from a combination of solid-state NMR measurements and DFT calculation.³⁷ Next, one should select parameters in the force field based on the prior knowledge, *i.e.*, the known molecular topology and chemistry. One should take great care of this procedure, since it is important for the accuracy of the MD simulations; we refer to Chapter 2 for details of our force field parameterization for BChl molecules. Next, it is easy to duplicate the composing unit according to the two-dimensional lattice parameters (a, b, γ) and generate small planar aggregates. If the thus formed structure turns out to be stable under MD simulation *in vacuo*, this stage is ready. If not, the lattice parameters (a, b, γ) should be tuned until a stable assembly is formed. Usually, input lattice parameters (a, b, γ) are available from the literature, for instance, from crystal diffraction measurements or DFT calculations. If not, one could perform ‘brute-force’ sampling, considering the limited point groups that are present in two dimensions.

Stage 2, tube packing. The goal of the second stage is to generate customized tube structures by molecular packing, making use of the information from the last stage. The new lattice parameters (a, b, γ) and the unit cell, which are selected from the stable assembly of stage 1, form the primary input to our packing code. This guarantees consistency at the level of the MD force field, which determines the stability of the structure in the following MD simulations, as well as a proper overall mass density. The packing code generates molecular tube structures in a highly customizable fashion. Variable properties include the total length of the tube, its curving direction, the tube radius, and the

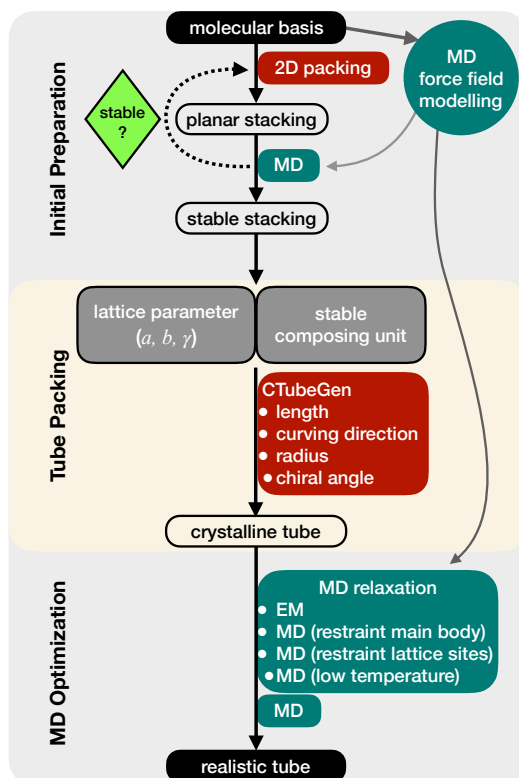


Figure 5.1: A schematic illustration of the protocol developed to obtain atomistic tube structures of chlorosomes.

chiral angle. The last two parameters define the chiral vector, which relates to the chiral indices (n_1, n_2) as $\mathbf{C} = n_1\mathbf{a} + n_2\mathbf{b}$. A key step is to convert the supramolecular chirality to the local twist angle α and rise distance h that is needed for a helical growth of composing units.^{183,184}

By applying rotation (by an angle α) and translation (over a distance h) to a composing unit along both the $\mathbf{a}$ and $\mathbf{b}$ directions, starting from the base of the tube, we obtain a full tube structure. The algorithm details of our code is explained in the following subsection. It makes sense to visually consider the pre-packed tube structure, since distinct molecular overlap should be avoided. In particular, molecules with a ring topology may become interlocked with each other upon placement, an issue that cannot be resolved by simple relaxation.

Stage 3, MD optimization. The final stage aims at resolving stresses that may be present in the pre-packed regular structure,⁵¹ and to introduce structural disorder on the level of classical MD. To this aim, we perform a set of MD simulations in a sequential fashion. First, we perform energy minimization (EM) by steepest descent to remove any distinct structural overlap that may cause numerical instability in MD. Next, we perform MD simulations with changing positional restraints to remove frustrations that may cause unfavorable structural defects. In our case, MD simulations with restraints on the head part (or heads) of all molecules aims at relaxing the conformations of the flexible tails. After removing these head restraints, only the positions of the Mg^{2+} ions, which relate directly to lattice sites, are restrained, allowing all other atoms in the head part to relax while maintaining a unit cell lattice. After this step, all position-restraints are removed, and we perform mild thermal annealing by unconstrained MD simulations at a reduced temperature of 50 K.

Finally, the structure is sufficiently equilibrated to perform unconstrained MD simulations in the target thermodynamic conditions, which, in our case, are at room temperature. We note that it is also possible to include solvent at this stage, in order to obtain a tube structure beyond the *in vacuo* condition. If so, it is also worthwhile to optimize the planar aggregates in the preferred solvent at stage 1.

5.2.2. The Algorithm of CTubeGen

Determination of chiral lattice and helix growth parameters

The pre-requisites:

- Select lattice parameters ($|\mathbf{a}| = a, |\mathbf{b}| = b, \gamma$) for the unit cell. For BChl *c* chlorosomes: $a = 1.48$ nm, $b = 0.98$ nm, $\gamma = 124.3^\circ$ (see Chapter 2).
- A regular lattice on the tube can only be formed if the rolling or chiral vector $\mathbf{C} = n_1 \mathbf{a} + n_2 \mathbf{b}$, with n_1 and n_2 integer numbers that are often referred to as chiral indices.^{185,186} Selecting n_1 and n_2 defines the tube radius $r = |\mathbf{C}|/2\pi$. For the purpose of illustration, we selected $n_1 = 30$ and $n_2 = 10$, equivalent to $r = 6.3$ nm. The corresponding chiral angle $\delta = \arccos(\mathbf{C} \cdot \mathbf{a}/(|\mathbf{C}| \cdot |\mathbf{a}|)) = 11.8^\circ$.
- Align the unit cell by defining the x -axis along the $\mathbf{a}$ -direction and letting the plane spanned by $\mathbf{a}$ and $\mathbf{b}$ coincide with the x - z plane. Subsequently, perform a rotation in this plane to pre-orient $\mathbf{a}$ along the desired direction with a δ angle with the x -axis, as we set the $\mathbf{C}$ along the x -axis. For our case, the desired direction is along $(x, z) = (r \cdot \sin(\alpha_a), -h_a)$, with α_a and h_a given below. Finally, translate the unit cell such that one of the Mg^{2+} ions is centered at $(0, 0, 0)$, and define the set of position vectors for all L atoms: $\mathcal{X}^0 = \{\mathbf{x}_l | l = 1, \dots, L\}$.
- For $0^\circ \leq \delta \leq 180^\circ$, the rotational angle or twist between subsequent molecules growing along the $\mathbf{a}$ and $\mathbf{b}$ directions are given by:

$$\alpha_a = \frac{360^\circ \cdot a \cdot \cos(\delta)}{|\mathbf{C}|}, \quad \alpha_b = \frac{360^\circ \cdot b \cdot \cos(\gamma - \delta)}{|\mathbf{C}|} \quad (5.1)$$

and the translational distance or rise for molecules growing along the $\mathbf{a}$ and $\mathbf{b}$ directions are given by:

$$h_a = a \cdot \sin(\delta), \quad h_b = b \cdot \sin(\gamma - \delta) \quad (5.2)$$

where the subscript relates to the $\mathbf{a}$ or $\mathbf{b}$ direction. Since the signs of these variables depend on the way the tube is built, we will only consider absolute values. For $\delta = 11.8^\circ$, the twists are $\alpha_a = 13.1^\circ$ and $\alpha_b = 3.4^\circ$ and rises $h_a = 0.30$ nm and $h_b = 0.91$ nm.

The corresponding geometrical representations can be found in Figure 5.2.

Tube building through a 2D helix growth

Our chlorosome tube is built starting from the pre-oriented unit cell, by subsequently generating images via translation h and twist rotation α . The matrices used for these transformations are denoted by $T = T^{\mathbf{h}}$ and $R = R^{\alpha}$, where $\mathbf{h}$ the translation vector and α the rotation angle with respect to the z -axis, respectively. The first molecule in the tube is obtained by translation $T \cdot \mathbf{x}$ with $\mathbf{h} = (0, -r, 0)$ to all $\mathbf{x} \in \mathcal{X}^0$. We denote this set as $\mathcal{X}^1$.

1. Growth along the $\mathbf{a}$ -direction: The total number of images generated in this step is n_1 . Taking the image $\mathcal{X}^i$ of the previous step, the next image $\mathcal{X}^{i+1}$ is generated by rotation and translation $T \cdot R \cdot \mathbf{x}$ for all $\mathbf{x} \in \mathcal{X}^i$, with $\alpha = \alpha_a$ and $\mathbf{h} = (0, 0, -h_a)$. This constitutes the basic helix along the $\mathbf{a}$ -direction on the tube.
2. Growth along the $\mathbf{b}$ -direction: Next, this basic helix is copied along the $\mathbf{b}$ -direction. Starting from each of the n_1 images $\mathcal{X}^i$ ($i = 1, \dots, n_1$) that have been grown along the $\mathbf{a}$ -direction, a new image $\mathcal{X}^{i+n_1}$ is generated by rotation and translation, *i.e.* $T \cdot R \cdot \mathbf{x}$, for all $\mathbf{x} \in \mathcal{X}^i$ ($i = 1, \dots, n_1$), for a fixed angle $\alpha = -\alpha_b$ and vector $\mathbf{h} = (0, 0, h_b)$. This process constitutes two helices on the tube. The same procedure is then applied in an iterative fashion to generate new helices by rotation and translation, with $\mathcal{X}^{i+j \cdot n_1}$ being imaged in $\mathcal{X}^{i+(j+1) \cdot n_1}$ for $i = 1, \dots, n_1$ and $j \in \mathbb{N}$. By construction, $\mathcal{X}^1$ and $\mathcal{X}^{n_1 \cdot n_2}$ relate to positions in neighboring unit cells on the lattice, and the total length of the helical assembly can be tuned by the number of helix copies $N_{\text{duplicates}}$ along the $\mathbf{b}$ -direction. Finally, this assembly is truncated at the bottom and top to provide a cylinder of a predefined length.

A geometrical illustration of 2D growth in this algorithm can be found in Figure 5.2 for $n_1 = 30$ and $n_2 = 10$ with $N_{\text{duplicates}} = 12$. Indeed, a closed tube structure is formed.

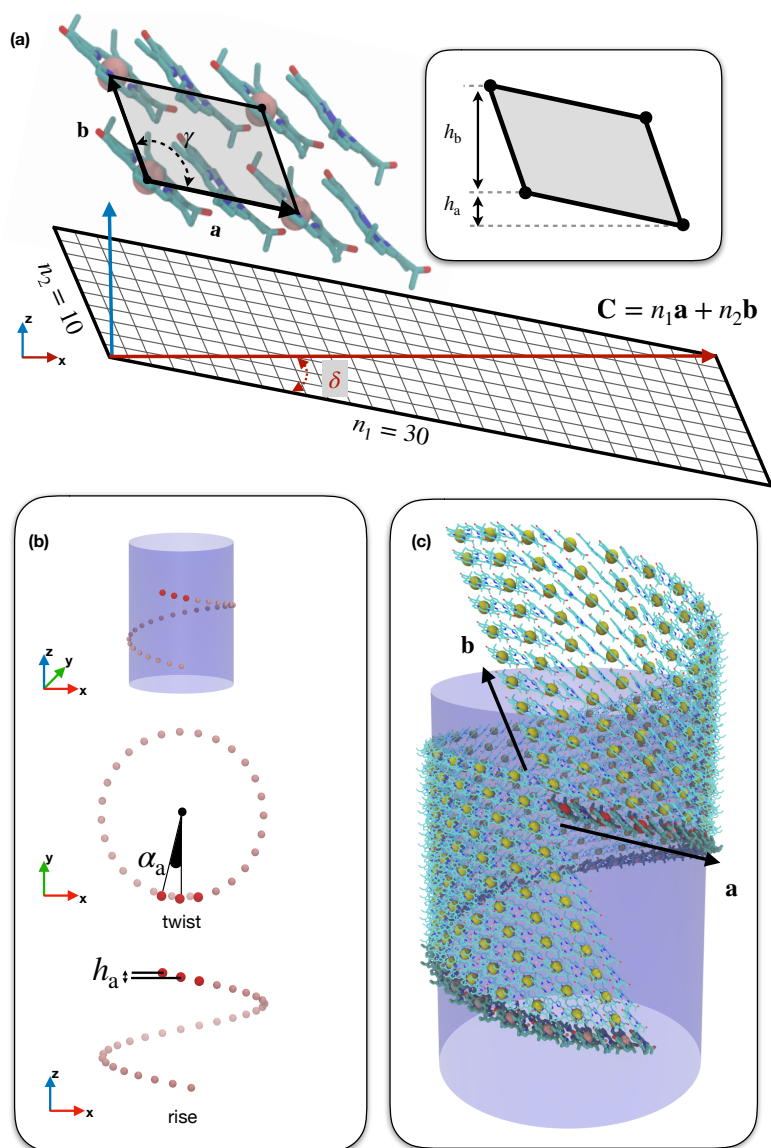


Figure 5.2: Illustration of the tube packing algorithm for the $n_1 = 30, n_2 = 10$ case. (a) The chiral lattice and a properly oriented *syn-anti* dimer packing unit. The inset is a 2D illustration of the rise of helices along $\mathbf{a}$ and $\mathbf{b}$ directions. (b) Illustration of twist and rise for the helix along the $\mathbf{a}$ -direction in 3D. (c) The growth along $\mathbf{a}$ and $\mathbf{b}$ directions in 3D. The molecules belonging to the basis helix along $\mathbf{a}$ -direction are shown by dark colors. The molecules further duplicated along the $\mathbf{b}$ -direction are shown in light colors and their Mg^{2+} are shown in yellow color. The overall structure has 12 basis helices, and it can be treated as a 30-start helix in terms of the helices along $\mathbf{b}$ -direction.

5.2.3. An Entire Family of Chlorosomal Tubes

Besides curving/rolling direction, the tube chirality is determined by the chiral angle δ , which is the angle between the rolling vector and a reference lattice vector, see Figure 5.3a. we note again that the complete range of δ runs between 0 to 180°, and that we assembled tubes spanning this range, with a resolution of 5°, using the protocol described above. In line with the observations for all spontaneously formed curvature, we select a curving direction that relates to *syn* tails that are located in the inner side of the tube, see Chapter 2.

To relate to actual chlorosome dimensions, we pre-assembled long tubes with a diameter of 15 nm. Both theoretical and computational studies have pointed towards a length dependence of the optical spectra, particularly in the signature of the CD spectra for shorter tubes,^{35,80} but we observed no signature change above 60 nm, see Chapter 3, so we also considered 60 nm tubes in our current analysis. For each chiral angle, a tube composed of roughly half a million atoms was positioned in the center of a sufficiently large simulation volume in order to avoid interactions with periodic images. In the stage of unrestrained MD simulations, tube structures were simulated for 5 ns at 50 K and sequentially another 5 ns at 300 K.

Somewhat to our surprise, we found that all our pre-assembled tubes are very stable, see the extracted structural information in the supporting information file.¹ Moreover, as before, we found that rotations of individual molecules previously identified in curved sheets, see Chapter 2, are conserved when they are closely packed into a tube. This led us to the conclusion that both the local structural characteristics are rather indifferent to the overall tube chirality δ .

To more generally discriminate between different types of helical structures, we may consider $|n_1| + |n_2|$ setting the ratio between the size of composing unit and the size of helical structure, as well as its local curvature. As in our chlorosome structures, with large values of $|n_1| + |n_2|$ and small local curvature, the local packing environment for the composing unit is similar to the planar situation; thus, the dependence on chirality is missing. On the contrary, for structures with small values of $|n_1| + |n_2|$, e.g. filaments and protein microtubules, the penalty of changing chirality may be high for the frustrated interactions

¹File `chiral-tubes-structure-summary.csv` in `chapter_5` folder https://github.com/xinmeng2015/chlorosome_phd_thesis or <https://doi.org/10.5281/zenodo.3674742>

between composing units.

5.2.4. Chirality versus Optical Response

Finally, we consider the absorption, LD and CD spectra for all tubes in the full range based on the corresponding Frenkel exciton Hamiltonian, in which electronic couplings between pigments are derived from the molecular transition dipole, see more details in Chapter 3. As usual, calculated (stick) spectra were broadened via a convolution with a Gaussian, which mimics experimental broadening due to heterogeneity. In the spectral plots, we show spectra for a range of Gaussian filters, with FWHM values ranging from 10 to 350 cm^{-1} . The supporting information file ¹ contains all spectral plots. For instance, for the case $\delta = 5^\circ$, spectral plots are named as 5-absorption.pdf, 5-ld.pdf and 5-cd.pdf. To effectively characterize spectra, we have defined and used different measures for the spectral features. $\Delta\lambda = \lambda_m - \lambda_0$ for absorption spectra, where λ_m is the absorption peak position and λ_0 is the monomer excitation energy. $f_{\text{ld}} = (S_+ - S_-)/(S_+ + S_-)$ for LD spectra, where S_+ and S_- are the integrated area of the positive and negative bands of the LD spectrum respectively. Positive/negative f_{ld} indicates that the corresponding structure has a stronger/weaker absorption along the tube axis than that orthogonal to the tube axis. There are four types of psi-shapes for CD spectra: $-/+$, $+/-$, $-/+$ and $+/-$.

Figure 5.3 shows spectral features for all δ , enabling us to group structures into categories with equivalent optical spectra features. Clearly, the variability or sensitivity of the optical spectra to supramolecular chirality follows the order: absorption < LD < CD. From the results for absorption, see Figure 5.3b, an equivalent red-shift $\Delta\lambda \approx 60$ nm can be seen for all δ , which simply demonstrates that they all belong to the class of J-aggregates.¹³⁸ This result indicates that the Q_y absorption band of chlorosomes is mainly determined by the local *syn-anti* packing, with no significant dependence on particular tube chirality. For LD and CD, a clear role of the tube chirality is observed. For LD, see Figure 5.3c, the changing sign of f_{ld} divides the δ range into three separate domains: upon increasing δ from 0° to 175° , f_{ld} changes from

¹File spectra-plots.zip in chapter_5 folder at https://github.com/xinmeng2015/chlorosome_phd_thesis or <https://doi.org/10.5281/zenodo.3674742>

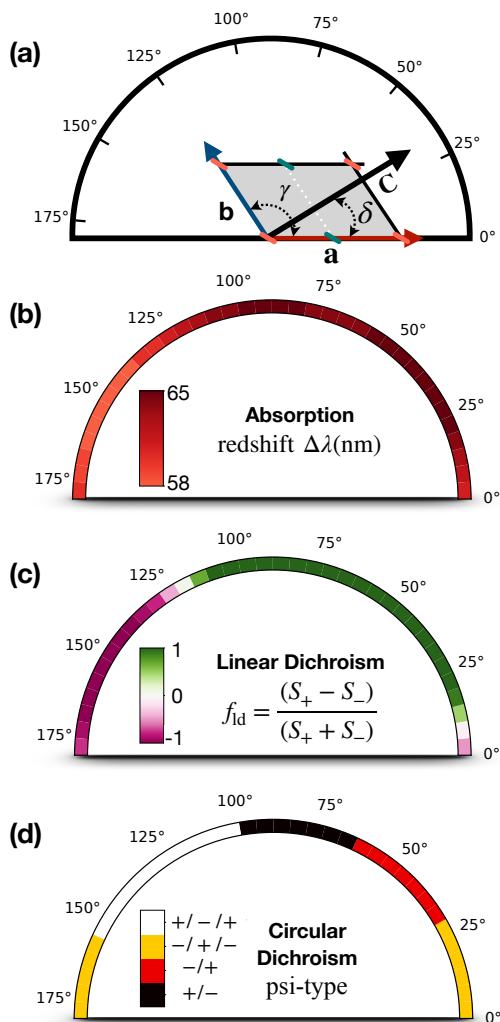


Figure 5.3: (a) Schematics of the 2D helical lattice composed of *syn-anti* packing units and the chiral angle δ . The polar axis is defined according to the δ . (b) A polar plot of spectral features for absorption, LD and CD as a function of δ . The resolution of δ is 5°. For all considered δ tube structures, spectral signatures are identified from spectra that were broadened using a Gaussian kernel with FWHM equal to 200 cm^{-1} , see all the plots in supporting information (spectra-plots.zip).

negative to positive, and then to negative again. Since $f_{ld} \approx 1$ is observed in all experimental LD spectra, it narrows down the possible range to $[15^\circ, 110^\circ]$. As shown in Figure 5.3d, the CD spectrum is much more sensitive to chirality and *five* separate domains can be identified. In particular, our results show that the mixed-type CD spectra, for instance, the $-/+/-$ type frequently identified for chlorosomes, can originate from a single tube with a well-defined chirality, instead of being the result of stemming from separate structures with opposing chirality. As suggested earlier, it is well known that the structure of chlorosomes depends on the species of bacteria and the specific growth condition. Our results can rationalize why different types of CD spectra are observed experimentally.

Our finding elucidates the relation between CD spectra and the underline tube structure characterized by δ quantitatively. It clearly shows that a transition of the CD spectra signature is consistent with a slight variation of δ , which may well be a result of specific growing conditions; for instance, going from 25° to 30° , the psi-type CD signal changes from $-/+/-$ to $-/+$. We note that reversing the curving direction will reverse the tube chirality. As shown in Chapter 3, it will simply switch the sign of CD spectra and has little influence on the absorption and LD spectra.

5.3. Conclusions

Calculated optical spectra for chlorosomes and other inspired large TMA structures systems have been reported before, but only based on idealized structural models and specific chiral angles. Thus far, no attention has been given to deriving a systematic relation between tube chirality and optical properties. One of the challenges involved is to obtain realistic atomistic tube structures with prescribed or customized tube chirality. In the present work, we propose such a protocol, based on an in-house tube packing code and a series of relaxation simulations. We employed this protocol to generate realistic atomistic tube structures with a resolution of 5° in the whole range of $[0, 180)$.

Access to a complete set of chiral tube structures allows us to systematically study their properties by computational means, ranging from diffractive, mechanical, optical, or magnetic. In this work, we focus on the optical properties,

in particular the absorption, LD, and CD spectra. Constituting a direct relation between the signature of the optical spectra and their chirality (as encoded in the chiral angle δ) represents a new step towards compiling a handbook for optical spectra measurements of chlorosomes. Implementing further improvements is straightforward, for instance, in terms of the accuracy of the MD force field and the electronic coupling method used to construct the Frenkel Hamiltonian. This first step proposes a practical way to study the role of supramolecular/tube chirality in the structural and functional properties of chlorosomes, as well as other large size tube molecular aggregates.

Outlook

Thus far, we have considered structural properties of tubular aggregates as simulated by MD at finite temperature, starting from pre-packed (flat and tubular) quasi-2D structures of unit cells that correspond to a *syn-anti* packing model, investigated the excitonic properties of closed and stable (multi)tubes, and eventually gained insights into the microscopic origin of efficient energy transfer in chlorosomes. I hope that both our results and protocols/strategy will help future studies of researchers that focus on chlorosomes or other large tubular molecular aggregates. Of course, to get to this point, other options and properties were considered. In this final chapter, I outline some novel research ideas and initial results that did not make it to the body of my thesis, and that address different aspects of chlorosomes. They deal with the assembly kinetics and mechanical properties of these aggregates, and particularly focus on, and to some extent clarify, the role of the farnesyl tail that are present in all types of BChl pigments.

From Chapter 2, we know that these pigment tails occupy the tiny 2.1 nm space between layers of *syn-anti* stacks and mediate their separation by tight packing. For this reason, we assumed that tails play a vital role in the assembly process and profoundly affect the mechanical properties of chlorosomes. This chapter sheds light on how to validate such an assumption.

6.1. Self-Assembly Kinetics of Chlorosomal Aggregates

One can be easily amazed by chlorosomes found in photosynthetic bacteria. The protein-free strategy that is responsible for the formation of chlorosomes may be utilized for constructing other customized light-harvesting complexes or nanoscale devices. However, attempts to reconstitute tubular aggregates from constituents that were extracted from natural chlorosomes showed a distinct sensitivity to the processing conditions, which illustrates that understanding the precise assembly kinetics of large amounts of BChl molecules into a supramolecular structure is of great significance, albeit that it is fairly limited in practice. Few *in vitro* studies monitored the self-assembly of BChl molecules, or of BChl mimics in different solvent conditions, temperature, or light conditions.^{100,180,187,188} In particular, Balaban *et al.*¹⁰⁰ monitored the self-assembly of BChl *c* molecules into large aggregates, which were shown to be the same as those formed *in vivo*, by tuning the concentration of apolar solvent (in their case, hexane) in water. Based on the time variation of the absorption intensity at the Q_y band, they proposed an auto-catalytic self-assembly mechanism of nucleation and growth.

In principle, an *in silico* method like molecular dynamics (MD) can address any assembly kinetics. In practice, however, ‘brute force’ usage of MD does not work for studying self-assembling of bio-inspired supramolecular systems; for more details, especially for the practical limitations, see a helpful recent review.⁵¹ In particular, the use of all-atom MD for this purpose is restricted by its limited phase-space sampling ability, as discussed in Chapter 1. Considering the actual time and length scales that are needed to address assembly kinetics in a realistic environment, coarse-grained MD may be a solution,^{189,190} as it can speed up the phase space sampling ability by several orders of magnitude. However, incorporating the level of detail that is needed to represent the important interactions on the coarser level requires an additional effort.

Coarse-Graining within the Martini Force Field. The Martini force field constitutes one of the most popular coarse-grained methods for bio-molecules.⁴⁷ It uses a four-to-one (four heavy atoms to one bead) mapping for obtaining a CG representation; for CG beads, plug-and-play CG force fields (FF) have been developed, in analogy to atomistic FF. Following recently reported Martini representation for similar molecules, chlorophyll (Chl) *a* and *b*,^{191,192} we have

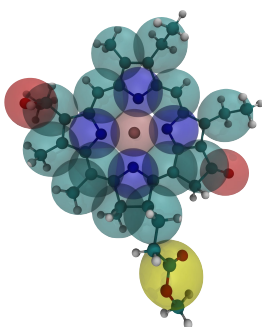


Figure 6.1: Martini CG model for Me-BChl c with a methyl ester termination instead of the farnesyl tail in BChl c. Large transparent spheres represent the CG interaction sites or beads, and are shown overlapping the atomistic representation. The color blue/green/yellow/red/pink corresponds to the SP3/SC3/NO/SNa or SNd/SQa type of martini particles. Equilibrium bond lengths and angle values are extracted from all-atom MD structures; the strengths of bond and angle constraints are mainly taken from de Jong’s work.¹⁹¹ Following their protocol, the Mg atom is mapped 1:1 to an SQda bead, with charge parameter +1.0; each SP3 bead carries a -0.25 charge, which neutralizes the whole molecule. We also apply certain distance restraints and dihedral angle constraints.

focused on the head part of BChl molecules and developed a Martini representation for Me-BChl *c*, *i.e.* BChl *c* without its (farnesyl) tail and with a methyl ester termination. Figure 6.1 shows the CG description.

We found that the thus constituted CG model reproduces the atomic structure of a single molecule quite well. Nevertheless, the intermolecular structure is more problematic; even the basic packing motifs are lost. As shown in Figure 6.2a, we find H-type aggregates after CGMD simulation, rather than the J-aggregates of all-atom MD (AAMD). Careful analysis shows that the Mg-OH coordination interaction is vital for stabilizing J-type aggregate like chlorosomes. In particular, by increasing the strength of this coordination interaction between SQa-SNd by a 100 times, a chlorosomal *syn-anti* stacking structure is indeed formed, see Figure 6.2b. To recover also other structural features, *e.g.* π - π stacking and hydrogen-bonds, much more effort is needed. We note that excessive tuning of the non-bonded interaction parameters is not recommended in general. One key challenge is the isotropic/spherical shape of the CG potentials with an effective isotropic bead radius of 0.47 nm, which is a general issue in Martini and particularly problematic for reproducing correct π - π stacking interactions that give rise to an average spacing of ≈ 0.35 nm. Considering these limitations, it is likely that other types of CG models, for instance based on anisotropic beads such as plate-like particles^{193,194} are more promising for BChl-like systems.

6.2. Mechanical Properties of Chlorosomal Tubes

Mechanical properties of natural complexes are of great importance for sustained biological function.¹⁹⁵ In particular, many of these complexes exhibit extraordinary mechanical characteristics. Although tubular aggregates like chlorosomes have been in the focus of researchers for many years, their mechanical properties have neither been well examined experimentally, especially in relation to their molecular building blocks, nor properly examined by theoretical or experimental means. Here, we share results that for the first time consider mechanical properties of chlorosomes, in the form of an outlook that hopefully may convince other researchers in this field that it is an aspect worth studying. In particular, through a systematic study of their mechanical prop-

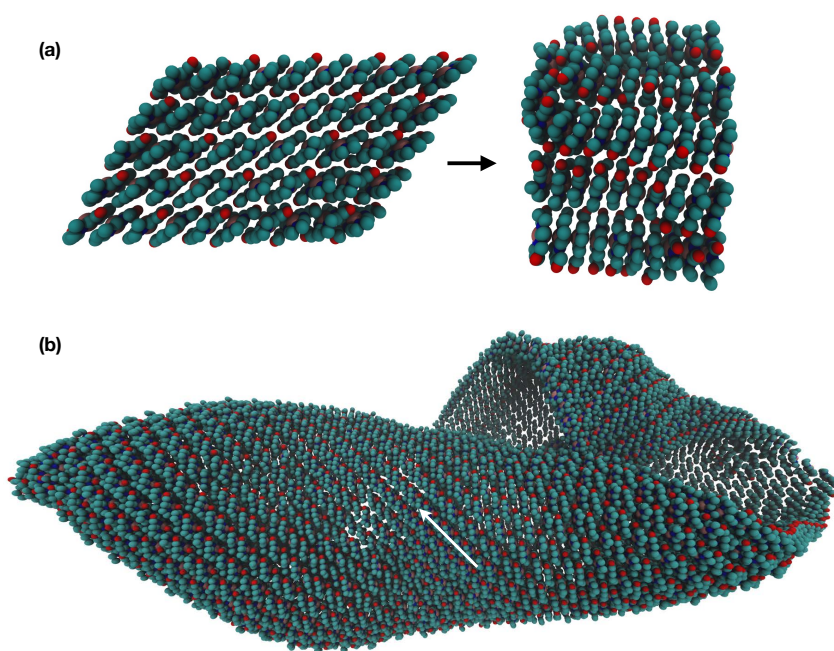


Figure 6.2: Martini CGMD simulation results of structures starting from planar aggregates composed of *syn-anti* dimers. (a) A small aggregate case, snapshots at $t = 0$ (left) and $t = 100$ ps (right) (b) A large aggregate case with stronger interaction mimicking the Mg-OH coordination interaction. This snapshot is at $t = 200$ ps. The white arrow outlines the *syn-anti* stacking direction.

erties for various chiral angles δ , we may begin to understand the effect of supramolecular chirality on mechanical properties.

6.2.1. Elasticity

When a material undergoes an externally applied stress, it may deform by changing its shapes or size, which is described in terms of strain. In the elastic regime, the material is able to recover its original configuration, shape and size, when the applied stress is removed. The elastic modulus measures the resistance of the material to being deformed elastically; its value can be determined from the slope of the stress-strain curve in the elastic deformation region, see Figure 6.3, which is usually the onset of the curve where the deformation is sufficiently small. Depending on how stress and strain are defined, one can determine different types of elastic moduli, including Young's modulus, shear modulus, bulk modulus, and others. For example, Young's modulus, the most common elastic modulus, quantifies to the elastic property of a material that undergoes tension or compression along a uni-axial direction.

Studying the mechanical properties of chlorosomes experimentally is complicated due to their mesoscopic dimensions and known difficulties in sample preparation. Our progress in constructing realistic atomistic tube structures of chlorosomes, however, provides a unique chance to consider their mechanical properties *in silico*, allowing us to make predictions prior to such experimental studies.

Various approaches can be employed to access the elastic properties of tubular assemblies via MD simulations. One approach uses the relation between equilibrium strain fluctuations and elastic constants to determine the elastic modulus from equilibrium MD simulation trajectories.^{196,197} Another approach mimics the protocol in experimental setups, which determines the elastic modulus directly from the measured stress-strain curves. In this approach, one needs to apply an external force to the structure in an equilibrium MD simulation to implement a programmed strain or stress.^{198–205} Wells and Aksimentiev²⁰² illustrated the potential of such a setup for investigating different types of mechanical properties.

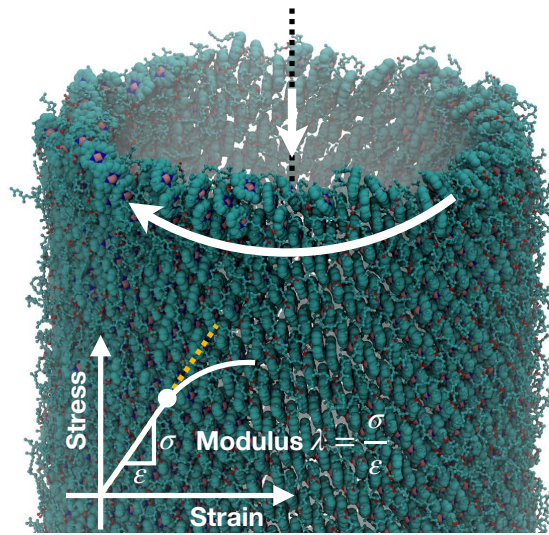


Figure 6.3: Simulation schematics for determining elastic properties based on an all-atom tube structure of chlorosomes. The dashed line represents the tube axis. The elastic modulus is obtained from the relation between strain and stress, as shown in the inset. It is possible to perform different types of deformation to extract different moduli, using a variety of probing methods, for instance by compression or twisting, as labeled by the straight or curved arrows.

6.2.2. Response to Shock Compression

Shock compression plays a role in a material when it is exposed to extreme situations, such as collision, explosion, and explosive welding.²⁰⁶ In such a case, the material is often stressed far beyond its elastic limit, and shock waves occur.²⁰⁷ After this shock wave has passed, atomic positions have been changed irreversibly, which means that the material loses the ability to recover its original state.²⁰⁸ One thus needs to address all detailed microscopic structural deformations in order to understand the consequence of a shock wave on the material.²⁰⁹

Non-equilibrium MD simulations have been widely used to investigate the response of materials to shock compression and to examine the detailed shock-wave propagation, for instance, in metals,^{206,210–212} polymers,^{213–216} small organic molecules,²¹⁷ and lipids.²¹⁸ It is currently unknown how chlorosomes, as well as other tube molecular aggregates, respond to shock compression, so we employed MD simulations to fill this knowledge gap. As an initial test, we considered the simplest setup for shock compression, and we let the tube structure collide with an immobile wall. Such a method was previously employed to study the impinging process of nanodroplets.²¹⁹ In our setup, the tube structure is initially centered in the simulation box *in vacuo*, with its tube axis parallel to the z -direction. An immobile wall is positioned at the bottom of the simulation box, perpendicular to the tube axis. By applying the same, instantaneous velocity v_z to all atoms, in the direction of the wall, the tube structure will eventually collide with the wall and deform, see Figure 6.4 for the consequential compression along the tube axis. This and all other simulations in this section were performed in a NVE ensemble.

Figure 6.4 shows several selected snapshots along an MD trajectory for an initially applied velocity $|v_z| = 500$ m/s, *i.e.* faster than the speed of sound in air. After hitting the wall, the helical tube has to dissipate the additional kinetic energy, and part of the tube close to the wall starts to open outwards (10 ps) into a small deformation zone. Soon after, at 20 ps, modulation of the underlying molecular lattice can be observed along the whole tube. Whether this lattice modulation is the signature of a shock wave, or the onset of structural instability on a larger length scale, we have not considered in detail. However, after 30 ps, the modulations can be seen to decrease, while the size of the outward deformation zone increases. At 130 ps, the deformation

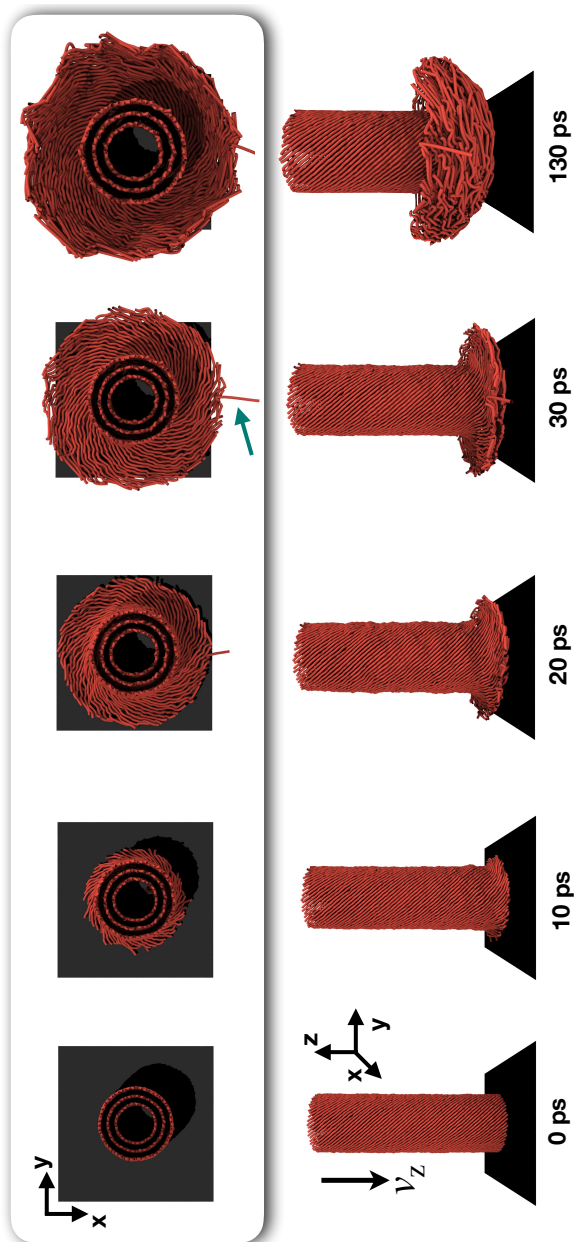


Figure 6.4: Snapshots of an impact compression simulation after an instantaneously applied velocity $|v_z| = 500$ m/s. Snapshots were taken at $t = 0, 10, 20, 30, 130$ ps. The BChl *c* assembly is composed of three concentric tubes. Corresponding orthogonal views along the axis of the tubes are shown on top, since this axis is along the *z*-direction of the applied velocity. The chosen dimension of the assembly is 60 nm in length, and 20 nm in diameter. Since such a structure contains roughly 1.6 million atoms, we only show helices along the *syn-anti* stacks (in red color) for visual clarity. The immobile wall into which the structure collides along the *syn-anti* stacks (in black color) for visual clarity. The immobile wall into which the structure collides is shown in black. As one molecule is detached from its helix, the end of that helix is stretched out in snapshots after 10 ps, as labeled by a green arrow.

zone has even grown larger, and has curled into a half sphere, but the lattice on the remaining part of the tube has completely recovered. At even later stages, the impact of the shock impact fades off, and the evolution of the deformation zone is halted (after 130 ps, not shown). From the orthogonal views in Figure 6.4, it is clear that the helices along the *syn-anti* packing direction are well kept, even though the contact part is substantially distorted. Simulating impact for an increased $|v_z| = 1000$ m/s shows a similar process, with the curling into a spherical shape further progressing into the upper part of the tube. For a smaller value of $|v_z| = 100$ m/s, we only observe a tiny deformation zone, and almost no change of the overall tube structure.

It is intriguing to see that, when the tube structure has to dissipate much energy for higher impact velocities, it responds by forming a unique outward curling deformation at the contact end of the tube, while keeping a memory of the original state of helices along the *syn-anti* packing direction. It is highly likely that the tails parts of the BChl molecules play an important role in this phenomena, and stabilize the structure under deformation. It would be interesting to see whether the tube can recover from a curling deformation, but we leave such computational experiments for the future. We propose that the tube structure of chlorosomes not only has a functional role in light-harvesting, but that it also provides promising resistance to damage and failure under impact and/or high strain rates,²²⁰ and is likely to have a self-repair ability as observed in microtubule systems.²²¹

We realize that, in order to address these mechanical properties of chlorosomes, much more effort is needed. Nevertheless, by providing this general introduction and some of these initial tests, I hope I have aroused the reader's curiosity and drawn more general attention to the unique properties of the *chlorosome*.

Supporting Information for Chapter 2

Relating layer lines to chirality: Fourier-Bessel reconstruction

The usual way of representing a 3D ideal helical/chiral tube assembly⁴⁵ is by unrolling it onto a 2D lattice of unit cells spanned by the two independent vectors $\mathbf{a}$ and $\mathbf{b}$ at an angle γ , see Figure A.1. Any point A on the lattice can be written as $\mathbf{A} = n_1\mathbf{a} + n_2\mathbf{b}$, in short $A(n_1, n_2)$, and the lattice is fully determined by $a = |\mathbf{a}|$, $b = |\mathbf{b}|$ and γ . For single wall carbon nanotube (SWNT), these lattice parameters follow directly from the atomic honeycomb lattice of graphene,¹⁸⁶ but for chlorosomes they are provided by the optimized unit cell. The chiral vector $\mathbf{C}(n_1, n_2)$ (also rolling or circumferential vector) is to be mapped to the tube circumference, and defines both the chirality and the tube radius R via $|\mathbf{C}| = 2\pi R$, while the translation/axial vector $\mathbf{T}$ is parallel to the tube axis, $\mathbf{T} \cdot \mathbf{C} = 0$, see Figure A.1.

In the reconstruction method, helices with the same axial translational symmetry, *i.e.* corresponding to sets of parallel lines in the 2D lattice, are assigned to a helical family $H(h, k; n)$, identified by their Miller index (h, k) and the number of crossings $|n|$ with the chiral vector $\mathbf{C}$. This n defines the chirality of the family ($n < 0$ for a left-handed helical family) and specifies the order of the Bessel functions J_n that describe the distribution of amplitudes along the associated layer line in reciprocal space. Consequently, the measured distribution provides direct information on the helical family; especially for large tube radii

R , it is dense and skewed towards the meridian. Helices in a family are fully described by their pitch P and the tube radius R , with a chiral angle given by $\delta = \arctan(P/2\pi R)$, while the axial repeat (or repeat distance) $d = P/n$ describes the spacing between adjacent helices. Each helical family $H(h, k; n)$ constitutes one layer line in reciprocal space, and its distance to the equator relates to the reciprocal value of the axial repeat d for that family.

Layer lines thus contain a wealth of information that can be exploited for detailed analysis of chiral structures. Yet, concentrating on chlorosomes of a particular type (WT or mutant), all layer lines derived from experimental structures, obtained by averaging FFT responses over a number of these assemblies, are found to be obscured by a low signal-to-noise ratio, and even the simpler question whether a pure meridian signal is observed cannot be firmly answered. From close visual inspection, one could even be tempted to conclude that the FFT data for mutant chlorosomes lacks a pure meridian signal.⁴⁵ Moreover, theoretical analysis for chiral tubular structures shows that the signature of the signal along layer lines is strongly affected by minute ($< 10^\circ$) out-of-plane rotations, which may even produce a pure meridian signal when it is absent for the original (unrotated) case, while the layer line positions are only marginally affected by this rotation. This finding indicates that the signature of the layer line is very sensitive to minute tilts with respect to the plane of imaging that may be introduced in sample preparation prior to cryo-EM,⁶³ and should lead to the conclusion that any particular signature extracted from the noisy data does not have much value if these conditions are unknown. Concentrating on the layer line position, our challenge boils down to relating the single visible layer line to the proper helical family of the tube.^{63,103} Since long-range order is clearly less defined for these systems, the most likely candidates for this basis helical family is when $|h| + |k|$ is minimal, *i.e.* for $H(1, 0)$ or $H(0, 1)$, corresponding to assembly along the **a** or **b** direction, respectively.

Straightforward geometrical analysis of the 2D Bravais lattice provides the axial repeat distances d_a and d_b along these principle directions as a function of the chiral angle δ :

$$d_a = d_{(1,0)}(\gamma, \delta) = \left| \frac{b \sin \gamma}{\cos \delta} \right|, \delta \neq 90^\circ$$

$$d_b = d_{(0,1)}(\gamma, \delta) = \left| \frac{a \sin \gamma}{\cos(\gamma - \delta)} \right|, \delta \neq \gamma - 90^\circ$$

with the chiral angle δ between $\mathbf{a}$ and the chiral vector $\mathbf{C} = (n_2b \sin \gamma, n_1a + n_2b \cos \gamma)^T$ defined as $\cos \delta = (n_1a + n_2b \cos \gamma)/|\mathbf{C}|$. The fact that two axial repeat values are relevant reflects the topological transition taking place between rolling along $\mathbf{a}$ or $\mathbf{b}$, at a cross-over angle δ_c defined by $a \cos(\delta_c) = b \cos(\gamma - \delta_c)$. The additional axial repeat distance, d_{armchair} , is provided for completeness, and corresponds to the chlorosome version of the armchair conformation in SWNT, with

$$d_{\text{armchair}} = d_{(1,1)}(\gamma, \delta) = \left| \frac{ab \sin(\gamma)}{\cos(\gamma_1 - \delta) \sqrt{a^2 + b^2 + 2ab \cos(\gamma)}} \right|$$

and γ_1 the (fixed) angle between the $H(1, 1)$ direction and $\mathbf{a}$.

We note that our expression for the axial repeat along $\mathbf{b}$, d_b , does not match the one provided in Günther *et al.*,⁴⁵ i.e. $d = a \sin \delta$. For completeness, we mention that the different definitions of the chiral angle, our δ and their angle $\delta_{\text{ref}} = 180^\circ - \delta$, are insignificant because of the properties of the sinus.

Variability of the tube radius

The tube radius $R = |\mathbf{C}|/2\pi$ is proportional to the length of the lattice vector $\mathbf{C}(n_1, n_2)$ that defines the rolling direction of the Bravais lattice into a defect-free tubular chiral structure, i.e. with (n_1, n_2) mapping to $(0, 0)$. This means that only closed tubes of a commensurate R can be formed, which restricts the number of commensurate chiral angles δ for a fixed R . The NMR finding that local structure in chlorosomes is well defined suggests that the chiral angle δ , which is closely related to the local BChl packing, is roughly equal for different radii in nested tubes. We are interested in analyzing the inverse problem: we want to determine the vector on the lattice, i.e. $\mathbf{C}(n_1, n_2)$, and the corresponding tube radius $R = |\mathbf{C}|/2\pi$, associated with the smallest variation $\Delta\delta(n_1)$ around a fixed chiral angle δ_0 for all $n_1 \in \mathbb{N}$. This fixed angle δ_0 is the experimental value determined by geometrical analysis: $\delta_0 = 112.3^\circ$ for BChl *c* and $\delta_0 = 19.8^\circ$ for BChl *d*.

Figure A.4 shows $\Delta\delta(n_1)$ and R for varying $n_1 \in \mathbb{N}$, validating that the distribution of radii R is quite dense in $\mathbb{R}$ when a small deviation in δ (up to about 1 %) is acceptable. The left panel shows the data for $\delta_0 = 112^\circ$ for BChl *c*: values that match the commensurability condition $|\Delta\delta(n_1)| < 0.2^\circ$ are marked by dashed line and relate to the lattice vectors $\mathbf{C}(n_1, n_2) = (4,$

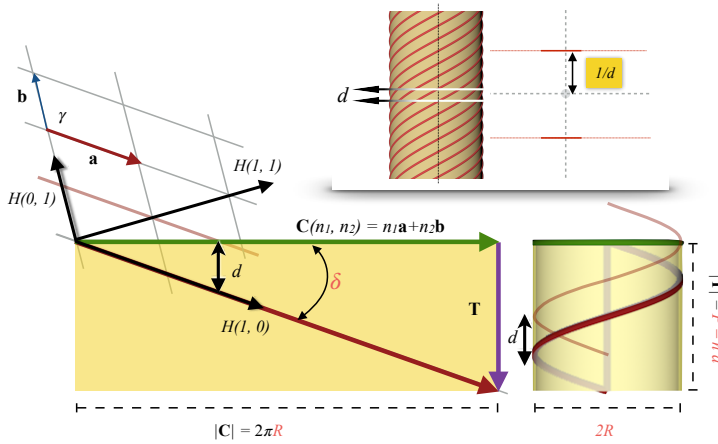


Figure A.1: The 2D Bravais lattice is fully determined by (a, b, γ) . In mapping to 3D, the chiral vector $\mathbf{C}(n_1, n_2)$ maps to the tube circumference, providing the tube radius R as $|\mathbf{C}| = 2\pi R$; the translation/axial vector $\mathbf{T}$ maps parallel to the tube axis. The three key helix families $H(1, 0)$, $H(0, 1)$ and $H(1, 1)$, associated with axial repeat distances d_a , d_b and d_{armchair} , are explicitly shown. The chiral angle δ is defined as the angle between $\mathbf{C}$ and $\mathbf{a}$. The pitch P is defined as the axial advance of a helix after one complete turn. The axial repeat d of the principle helical family relates to the intrinsic repeat distance d of the tube assembly structure along tube axis, which determines the position of the main layer line signal on the diffraction picture. For a n -start helical family, $P = n \cdot d$.

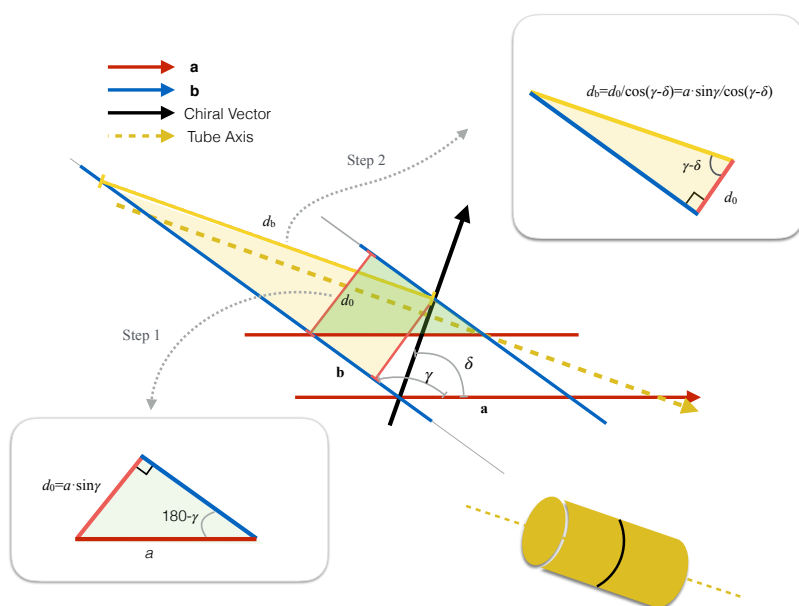


Figure A.2: Geometrical derivation of the axial repeat distance d_b associated with helix family $H(0, 1)$.

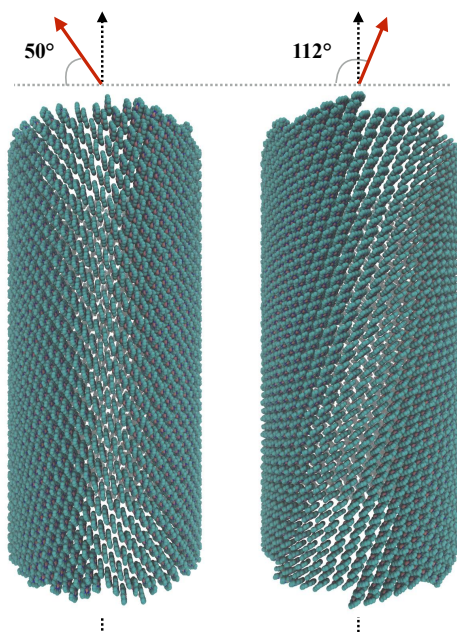


Figure A.3: Snapshots of pre-assembled helical tubes: $\delta = 50^\circ$ (left) and $\delta = 112^\circ$. For clarity, side groups of the head part and tails are not shown. The **a** packing vectors are shown by red arrows.

27), (6, 40), (8, 54), (10, 67), (12, 81), (14, 94), (16, 108) and (18, 121). The corresponding radii $R = 3.8, 5.6, 7.5, 9.3, 11.3, 13.1, 15.1$ and 16.9 nm agree well with the earlier determined experimental values for the *bchR* mutant: $R_{\text{exp}} = 3.7, 5.5, 7.4, 9.2, 11.1, 12.9, 14.7$ and 16.6 nm. The right panel shows data for $\delta_0 = 19^\circ$ for BChl *d*, determined for a slightly different unit cell. In this case, fully commensurate values relate to the lattice vectors $\mathbf{C}(n_1, n_2) = (11, 6), (22, 12), (33, 18), (44, 24), (55, 30), (66, 36)$ and $(75, 41)$. The corresponding radii $R = 2.2, 4.4, 6.6, 8.8, 11.0, 13.2$ and 15.0 are to be compared to experimental values for the *bchQRU* mutant. Estimating these radii by measuring them with a ruler, from the rotationally averaged EM images published in Figure S7 in Ganapathy *et al.*,³⁷ provides: $R_{\text{exp}} = 2.9, 4.9, 6.8, 8.9, 10.8, 13.1$ and 15.2 nm. We again conclude that there is proper agreement between the calculated commensurate tube radii and the experimentally measured radii.

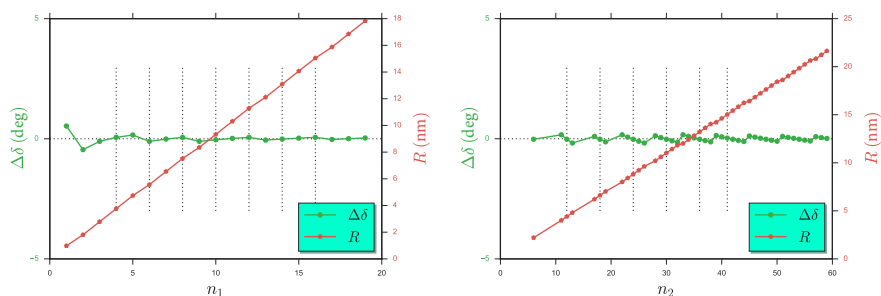


Figure A.4: Radius R of commensurate tubes, associated with chiral vectors $\mathbf{C}(n_1, n_2)$, for which the chiral angle δ is close to the predicted $\delta_0 = 112.3^\circ$ for BChl *c* (left) and $\delta_0 = 19.8^\circ$ for BChl *d* (right). In the calculation for BChl *d*, the different unit cell properties are taken into account. For clarity, only n_1 is shown. For a specific chiral vector (determined by n_1 and n_2), the corresponding deviation $\Delta\delta(n_1)$ from a fixed δ_0 can be found in green on the left vertical axis; the corresponding tube radius R is shown on the right vertical axis (red). Commensurate values, *i.e.* values that satisfying a stringent constraint on the maximum variability of the chiral angle, *i.e.* $|\Delta\delta(n_1)| < 0.2^\circ$, are highlighted by vertical dotted lines.

Determining the layer line position from simulation results

Assemblies obtained by AAMD simulation have been used to generate mimics of electron microscopy (EM) images, by a 2D projection of the electron distri-

bution associated with the atomistic AAMD results. Consequently, just like for experimental EM images, these mimics are passed to a 2D FFT procedure to generate the corresponding power spectra. We employed the EMAN2 software package (<http://blake.bcm.edu/emanwiki/EMAN2>) that is widely used for single particle reconstruction, helical reconstruction, 2D crystallography and whole-cell tomography, and have set the variable resolution of the calculated electron distribution to 6 Å of experimental EM. Experimentally, tomography would be more appropriate than projection techniques aimed at single particle reconstruction, since the overall shapes of chlorosomal tubes vary substantially, see also the discussion about orientation with respect to the imaging plane in the remainder of this section. Unfortunately, in generating the EM mimic from a simulated AAMD structure, standard EMAN2 disregards contributions due to Mg by not assigning electron distributions for these atom types.

An illustrative EM mimic obtained by standard EMAN2, for a tubular Me-BChl *c* assembly after 1 ns of AAMD simulation at 300 K, as well as its 2D Fourier transform can be found in Figure A.5. The position of the clearly visible layer line signal in Figure A.5 is measured as $(1/1.0) \text{ nm}^{-1}$, *i.e.* an axial repeat distance $d = 1.0 \text{ nm}$ close to $|\mathbf{b}| = 0.98 \text{ nm}$. This agrees well with the theoretical prediction for $\delta = 40^\circ$ and the real space finding that the tube symmetry axis is almost parallel to $\mathbf{b}$. For incomplete tubes, like the ones formed by BChl *c* and BChl *d* after 1 ns of AAMD simulation, reduced periodicity gives rise to 2D FFT results with fuzzy and incomplete layer lines, which complicates analysis. An overview of layer line positions extracted from (partial) layer lines for all simulated systems can be found in Table A.3.

We note that estimates for the layer line position can also be extracted directly from the theoretical relation between d and δ , without performing FFT. To illustrate this, we also applied the EMAN2 procedure to a pre-assembled structure consisting of 3 concentric tubes of BChl *c* with $\delta_{1,25} = 112^\circ$. Tubes were built sequentially, *i.e.* by adding BChl *c* molecules one by one to a growing structure, followed by a short constrained AAMD simulation to equilibrate the conformation of the newly added molecule. The stability of the resulting three-tube structure was challenged by another 1 ns of AAMD simulation, and we found that all large-scale structural parameters were conserved. FFT power spectra for this equilibrated structure, obtained via a EMAN2 procedure, are shown in Figure A.6. In particular, the upper left panels show the results of standard EMAN2 (*i.e.* without the Mg contribution, Figure A.6a) and EMAN2

results for Mg only (after replacing Mg by S=Sulphur, an atom that is accounted for in EMAN2, Figure A.6b) based on orthogonal projection.

In experiments, the signal-to-noise ratio is improved by averaging over several spectra calculated for individual chlorosome domains, so we should account for this experimental variability. In particular, when loading chlorosomes to a TEM-grid, individual structures usually experience an (unknown) misalignment or tilt with the grid or imaging plane (and thus with each other) owing to small shape deviations from a perfect tube, in addition to a tiny residual in-plane misalignment after (known) correction for in-plane rotation. For this reason, we introduced a random rotation before projecting the electron distribution to 2D, via `e2project3d -orientgen=eman:delta=2` in EMAN2, and selected six power spectra that closely resemble the spectrum obtained by orthogonal projection. These power spectra, shown in the panels between the upper left and lower right in Figs. A.6a and b, clearly illustrate that a relatively tiny rotation can introduce a diffraction signal on the meridian (meridian signal) without shifting the layer line position. Finally, concentrating on the most distinct signal (stemming from the Mg/S positions, see Figure A.6b), the average over all seven power spectra, shown in the lower right panel, carries a clear layer line signal corresponding to $d = 1.25$ nm, and reproduces several distinct features of the experimental power spectrum.

Details of the computational setup

BChl monomer and *syn-anti* dimer structure

Natural chlorosomes are composed of various BChl homologues that differ in the chemical nature of the side chains R1, R2 and R3 and contain a mixture of R and S stereoisomers at the 3¹ position (Figure A.7a). For BChl c R1 = CH₃, while for BChl d R1 = H. As the main component of natural chlorosomes of *C. tepidum* WT and its *bchQRU* mutant, we simulate the assembly of 17²-farnesyl- (R or S)-[8-ethyl,12-ethyl]BChl c or d pigments, which have been considered extensively in the experimental and simulation literature.^{37,39,67,100} The ratio between R and S components in the dimer is 1:1 (Figure A.7b) in agreement with Ganapathy *et al.*'s study.³⁷ A *syn-anti* dimer was identified as the basic

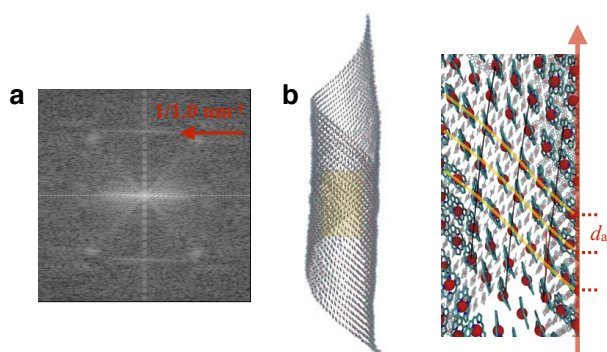


Figure A.5: EM mimic for the closed tubular structure obtained by MD simulation of (40, 30) Me-BChl c system at 300 K after 1 ns, which is shown in Figure 2.3. (a) Power spectrum after 2D Fourier transform. The layer line signal is at $1/d = 1/1.0 \text{ nm}^{-1}$. (b) Full and zoomed orthogonal projections of real space molecular configuration taken from the final simulation snapshots. Helices along the **a** and **b** direction are highlighted with yellow and black lines, respectively, and the tube axis is shown as a red arrow. The $1/1.0 \text{ nm}^{-1}$ layer line position stems from the axial repeat along the **a** direction, *i.e.* d_a .

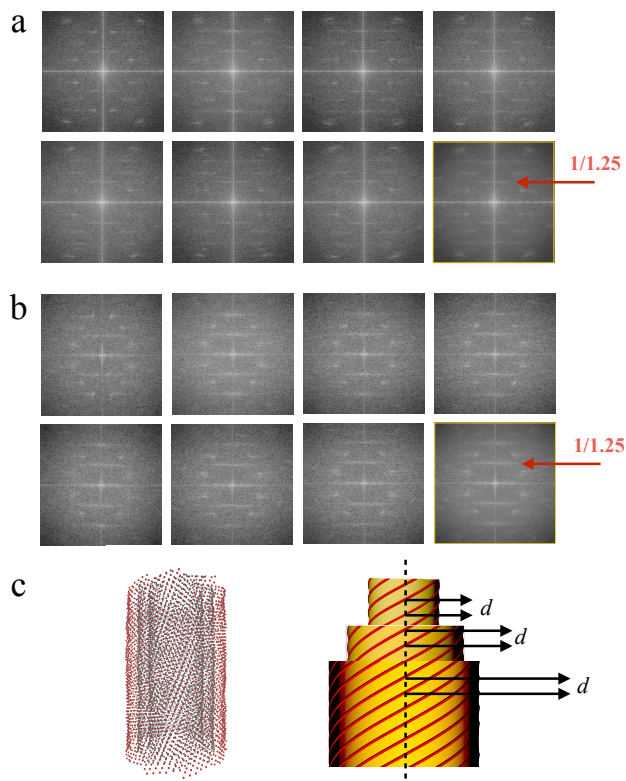


Figure A.6: EM mimics for an equilibrated three-tube BChl *c* structure with $\delta = 112^\circ$: (a) 2D power spectra obtained by the standard EMAN2 procedure that disregards the electron distribution of Mg atoms and (b) 2D power spectra obtained by an EMAN2 procedure that only considers the position of Mg atoms (replacing their electron distribution by that of Sulfur). Different projections were obtained by applying a rotation to the three-tube structure prior to projecting: the upper left result is for an orthogonal projection and lower right the power spectrum after averaging FFT results over all seven considered projections. The layer line signal, labeled by the red arrow, is at $1/d = 1/1.25 \text{ nm}^{-1}$. (c) Projected snapshot showing the positions of Mg atoms in real space, and schematic image of nested tubes carrying the same chiral angle, illustrating how a distinct layer line line can appear for a multi-tube structure.

structural unit from which the BChl *d* chlorosomes of the *bchQRU* mutant are built, and there is ample evidence that such a unit also plays a key role for other BChl pigments in chlorosomes.^{39,118}

The basic motif $\text{Mg}-\text{O}-\text{H}\cdots\text{O}=\text{C}$ for supporting the pigment self-assembly relies on coordination of the magnesium by the 3¹ hydroxyl oxygen functionality of the next BChl within a stack, and hydrogen bonds formed between the hydroxyl hydrogens and the 13 carbonyl oxygens of the BChl in an adjacent stack, see Balaban *et al.*¹⁰⁰ For ease of discussion, we refer to a BChl molecule in terms of a head (ring) and tail (farnesyl) part. When the farnesyl tail is replaced by a methyl group, leaving only a head part, the molecule is denoted as Me-BChl.

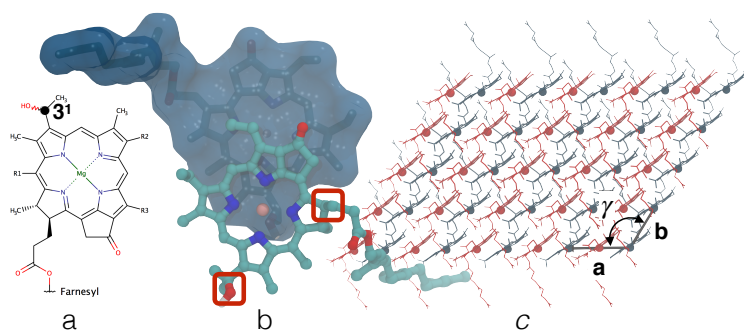


Figure A.7: (a) General structure of BChl molecule. For BChl *c*, R1 = Me, R2 = Et, R3 = Et, while for BChl *d*, R1 = H, R2 = Et, R3 = Me. The hydroxyl group at the 3¹ carbon C atom determines the molecule's chirality, R or S. When the hydroxyl group is at the same side as the wedge bond, the configuration is denoted as *syn*, and *anti* when they are in the opposite directions; (b) The *syn-anti* dimer. Hydrogen bonded with carbon atoms are not shown. The top molecule is in the *syn* configuration with both directions of hydroxyl group and wedge bond out of page (red squares); (c) Initial structure constructed by packing of *syn-anti* dimers in a planar configuration along the principle direction **a** and **b**. This small system is labeled (5, 5); we mainly conducted simulations on a bigger system (30, 30). To distinguish between them, *syn* and *anti* molecules are labeled red and blue respectively, with Mg atoms shown as spheres. Hydrogen atoms are omitted for clarity.

Structure initialization

Since AAMD simulations are generally restricted in terms of attainable time and length scales,²²² the starting structure should be chosen with care to avoid kinetic trapping. Among the models proposed for pigment packing in *bchQRU*, *bchQR* and wild type chlorosomes,^{37,39} the *syn-anti* packing model is conserved and we adopt it to prepare our initial structure prior to MD simulation. In particular, our planar starting structure is obtained by prolongating the proposed *syn-anti* dimer structure periodically, using periodicities determined from cryo-EM data: two principle directors **a** and **b**, with length $a = |\mathbf{a}|$ and $b = |\mathbf{b}|$ relating to the experimental repeat distances, at a mutual angle γ (see Figure A.7c). For simplicity, we denote this set of parameters as (a, b, γ) . The large scale structure, in terms of the number of periodic repeats of dimers along these two directions, is denoted as (A, B) . The structure in Figure A.7c is for $(5, 5)$.

Epimerisation

Chirality at the molecular level can be controlled by cultivation of bacteria under increased photon fluence rates, which in some cases promotes S- over R-epimers at the 3¹-position in BChl c.²²³ Spectroscopic analysis of reconstructed dye aggregates from these organisms led to the proposition that epimers form separate and individually rather homogeneous rod-like structures, indicative of a different role of R- and S-epimers in photosynthesis. One may thus wonder how handedness affects large-scale curvature formation, particularly since the *syn-anti* dimer employed as a basic structural element in our simulations is a 1:1 mixture of S- and R-epimers.³⁷ We considered this factor by generating planar assemblies composed of pure S- or R-epimers, noting that our force field does not impose handedness at the 3¹-position via any torsional constraint. Interestingly, we found that the usual 1 : 1 ratio of S- and R-epimers is quickly restored after the start of simulation, suggesting that our setup is sufficient for studying tube formation.

MD simulation details

We used the OPLS-AA force field^{91,92} in all MD simulations, determined following a protocol developed by Roccatano *et al.*⁹³ Atomic point charge parameters were obtained by the RESP method⁹⁴ at the HF/6-31g* level using Gaussian03 software.⁹⁵ Charges obtained at the B3LYP/6-31g* level were also considered and it was found to have little effect on the assembly structure.

MD simulations with periodic boundary conditions along all dimensions were performed with the Gromacs 5.1.2 software package.^{96,97} A Particle-mesh Ewald method⁹⁸ was used to treat the long-range electrostatic interactions. We performed simulations in a NVT canonical ensemble, maintaining the simulation temperature by a velocity-rescaling thermostat.⁹⁹ We perform all simulations *in vacuo* unless otherwise specified. We note that the considered planar starting structure does not reflect natural conditions, since chlorosomes are assembled in a lipid environment which provides the hydrophobic pocket that is needed for kinetic control of the assembly.^{224,225} In particular, since BChl pigments are hydrophobic, featureless aggregates will form when pigments are mixed with water. To access this effect on the equilibrium structures obtained by simulation, also a few simulations with organic polar solvents were performed. These simulations were pre-equilibrated using the Berendsen²²⁶ and the Parrinello-Rahman^{227,228} barostat.

To accommodate spontaneous curvature formation for the (30, 30) dimer system and to avoid periodicity effects due to boundary conditions, we initially center the planar assembly in a $50 \times 50 \times 50 \text{ nm}^3$ cubic simulation box. This planar structure was generated using the procedure described earlier, based upon the most recently determined unit cells for BChl *c* and BChl *d*.^{37,39} Upon performing an MD simulation, the planar structure for the original set $(a, b, \gamma) = (1.295 \text{ nm}, 0.978 \text{ nm}, 122^\circ)$, with a and b in nm, was found unstable, disintegrating into fragments due to excessive forces at the start of simulation; consequently, all reported simulations start from the parameter set $(1.428 \text{ nm}, 0.987 \text{ nm}, 126^\circ)$, determined from the structure in these stable fragments, instead. For this new set, stable NVT simulations at a reduced temperature of 50 K show a significant decrease of potential energy, within several hundred ps, accompanied by structural rearrangements. A MD trajectory of 1 ns captures global curvature adjustment from the initially planar structure, signaling that the driving force for curving is significant. The resulting stable

structures for 50 K were passed onto simulations for higher temperatures, from 100 K to 300 K (in increments of 50 K). The considered packing parameters, including values extracted from simulation, are summarized in Table A.1.

A 1 ns simulation for a (30, 30) Me-BChl *c* system in vacuum, *i.e.* in the absence of farnesyl tails, confirms that non-bonding interactions between head parts of the pigments are the primary driver for the self-assembly of the dimers to form curved sheets.¹¹⁸ A long trajectory (50 ns) of a *syn-anti* Me-BChl *c* dimer was also simulated, to reveal their structural stability, and to understand the modulation of this property upon their assembly in a large scale structure.

To assess long simulation time stability of the *syn-anti* packing structure, also a much smaller (5, 5) BChl *c* *syn-anti* dimer system was simulated both in vacuum and in hexane solvents, and the resulting 20 ns NVT trajectories and 10 ns NPT trajectories were analyzed. In addition, a (30, 30) BChl *c* curved structure obtained by simulation in vacuum was used as input for a simulation in hexane, to assess the effect of a commonly used co-solvent on the large scale structural stability.¹⁰⁸

Table A.1: Summary of packing parameters. The first two sets of packing parameters are used to generate the initial planar structures. The last two sets of packing parameters are determined by analyzing the simulated curved structures of the (30, 30) BChl *c* system at 50 K and 300 K respectively, 1 ns. The distance and angle values are obtained from the coordinates of the Mg atoms from neighboring dimers

	<i>a</i> (nm)	<i>b</i> (nm)	$\gamma(^{\circ})$
Initial 1	1.295	0.978	122
Initial 2	1.428	0.987	126
(30, 30) BChl <i>c</i> 50 K	1.464 ± 0.027	0.975 ± 0.024	125.1 ± 2.36
(30, 30) BChl <i>c</i> 300 K	1.482 ± 0.033	0.980 ± 0.030	124.3 ± 2.87

AIMD simulations

To increase our understanding of the head part dimer assembly behavior, the potential energy for different characteristic structures of the Me-BChl *c* dimer, obtained from MD simulation, were calculated and compared to the energy obtained via Ab-initio molecular dynamics (AIMD) simulations using the Car-

Parrinello Molecular Dynamics (CPMD) package (see <http://www.cpmd.org/>, Copyright IBM Corp 1990–2019, Copyright MPI für Festkörperforschung Stuttgart 1997–2001.)²²⁹ The PBE exchange-correlation functional was employed and the Kohn-Sham orbitals were expanded in a plane wave basis set with a cut-off energy of 70 Ry. Dispersion-corrected atom-centered pseudopotentials (DCACP) were used for all atomic species.²³⁰ The time-step was set to 4 a.u. The system was evolved at 300 K using a Nose-Hoover thermostat.^{231,232}

The reported AIMD simulations were started from the relevant initial geometries imported from AAMD, and simulated for about 600 fs at 300 K. Although the relative angle were found to oscillate around the initial value, their stability was confirmed by AIMD as they remained on average essentially the same. The DFT potential energy initially decreased, because of readjustment of bond distances, and then oscillated around an average value that is reported in Table 2.1 alongside the AAMD values.

Structure properties in curved structure

Large-scale properties of simulated assemblies

Analysis of the simulated tubular structures is complicated by deviations from the ideal case of a Bravais lattice of unit cells mapped to a perfect cylinder. Yet, our simulation snapshots show that these deviations are fairly limited, which is further quantified by application of a least-squares fitting procedure (LSGE, <http://www.eurometros.org>) to find the corresponding cylinder based on the position of the Mg atoms. Table A.2 shows the radii R of the best fit and standard deviations of the residuals (σ_{res}) for all considered temperatures. This analysis shows that the curved structures obtained after 1 ns of unconstrained AAMD can be sufficiently described by an ideal cylindrical tube for the BChl *c* system considered here. Ideal helical tubular structures are fully quantified by two of the three geometrical parameters defined in the previous section, which are, apart from the tube radius R , two parameters relating to the helical arrangement of pigments: the pitch P , *i.e.* the axial advance of a helix after one complete turn, and the chiral angle δ , *i.e.* the angle between the pitch (a vector with this length along the cylinder symmetry axis) and the plane

of rotation (see Figure 2.4). Such a classification is very common for helical biological structures.⁶³ Since the third parameter can be directly related to the other two via $\delta = \arctan(P/2\pi R)$, we focus on the pitch P , which we determine directly from the simulated structures to avoid ambiguities that may arise when projecting a 3D structure to a 2D (curved) plane.

In agreement with the standard practice in the analysis of helical structures, and also because our aggregates do not feature complete helical turns, the pitch is determined from local properties: the rotational increment ϵ between two neighboring units (here: adjacent Mg atoms along the **a** direction) and the helical rise h , see Table A.2 for their expectation values and standard deviations. Consequently, the pitch is provided by the relation $P = m \cdot h$, with m the (average) number of Mg atoms (equivalent to the number of pigments) in a complete helical turn, *i.e.* $m = 360^\circ/\epsilon$. From this relation, the standard deviation of the pitch P can be formally estimated as

$$\sigma_P = \frac{360^\circ}{\bar{\epsilon}} \sqrt{\bar{h}^2 \left(\frac{\sigma_\epsilon}{\bar{\epsilon}} \right)^2 + \sigma_h^2} \quad (\text{A.1})$$

if we suppose that there are no covariances between the extracted ϵ and h . Comparing the mean value for the pitch at $T = 50$ K, *i.e.* $\bar{P} = \bar{m} \cdot \bar{h} = 28.8$ nm, to the estimated standard deviation $\sigma_P = 3.9$ nm via Eq. (A.1) suggests that there is a considerable variability in the large-scale structural properties of simulated helical assemblies, even at the lowest temperature considered. Yet, this suggestion is inconsistent with direct visual analysis, which shows a very regular structure.

To further study this issue, we have performed analysis at a much longer length scale and determined the mean chiral angle from values that were calculated for the 30 large (partial) helices constituting the aggregate after 1 ns at $T = 50$ K. This alternative method provides $\bar{\delta} = 26.55^\circ$ and a very modest $\sigma_\delta = 0.38$. Since this $\bar{\delta}$ is fully consistent with the chiral angle $\delta = \arctan(\bar{c}/2\pi R) = 26.55^\circ$ calculated from (mean) local properties, we conclude that the variable local structure indeed does not translate into an equivalent variation of structural properties at the relevant length scales. Apparently, in a stable aggregate, local variations average out. For this reason, we have omitted error bars in Figure 2.4 and focused on the fitted R and mean chiral properties determined from local structure: $\bar{c}$ and $\delta = \arctan(\bar{c}/2\pi R)$.

Table A.2: Local structural data extracted from the simulated curved structures of the (30, 30) BChl *c* at different temperatures.

T	$\bar{\epsilon}$ (degrees)	σ_{ϵ} (degrees)	$\bar{h}$ (nm)	σ_h (nm)	R (nm)	σ_{res} (nm)
50	3.99	0.20	0.32	0.04	9.3	0.31
100	4.44	0.23	0.38	0.04	8.1	0.28
150	4.93	0.33	0.38	0.04	7.3	0.35
200	5.06	0.43	0.39	0.04	7.0	0.46
250	5.29	0.39	0.37	0.05	6.9	0.31
300	5.32	0.47	0.37	0.05	6.8	0.38

One nanosecond simulation snapshots of initially planar system that are entirely composed of BChl *d* are shown in Figure A.8, for different temperatures T ($T = 50, 100, 200$ and 300 K). The same procedures as before were applied to extract structural properties of the chiral tube for $T = 50$ K and yielded the following values: $(a, b, \gamma) = (1.4561 \pm 0.042 \text{ nm}, 0.926 \pm 0.030 \text{ nm}, 122.5 \pm 3.42^\circ)$; fitted radius $R = 10.6 \text{ nm}$; mean pitch $\bar{P} = 23.0 \text{ nm}$; chiral angle $\delta = 19.1^\circ$.

Mean values of the induced molecular dipole moment

In practice, it is far from straightforward to calculate the direction of the induced molecular dipole moment of a BChl pigment by quantum simulation, since it will be affected by its structured surroundings. This renders the determination of a mean angle between the induced molecular dipole moment and the symmetry axis of the cylinder an intractable task. However, as the orientation of the ring in the head part of the pigment provides an easy computable and useful estimate of this property, we have instead extracted the instantaneous (1 ns snapshot) mean angle β' of the plane formed by the four nitrogens with the cylinder symmetry axis for the different BChls considered in this study ($T = 300$ K). The results of this exercise are summarized in Table A.3. Since β' is sensitive to out-of-plane macrocycle distortions that are known to affect the planarity of the BChl ring on a short time scale, standard deviations are not reported. Instead, we compare the β' extracted from simulation to the values predicted by the expression introduced in a recent spectroscopic study, which are derived from the unit cell by geometrical considerations.⁴⁵ Figure A.9 shows the predicted β' versus the chiral angle δ in the relevant δ -range.

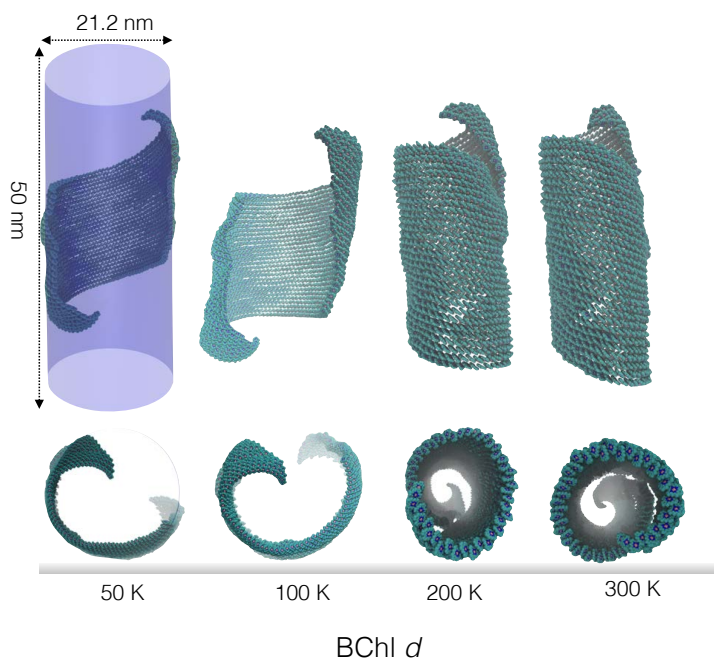


Figure A.8: Simulation results obtained for (30, 30) BChl *d* at 50 K, 100 K, 200 K and 300 K, after 1 ns simulation. For clarity, side groups of the head part and tails are omitted.

The predicted (extracted) values are for the three BChls are (all in degrees): 41 (39) for BChl *d*, 29 (29) for BChl *c* and 19 (18) for Me-BChl *c*, respectively. We conclude that the results of both types of analysis are consistent. A summary of all large-scale chiral tube properties extracted by fitting and *in situ* analysis is presented in Table A.3.

Table A.3: Summary of extracted chiral tube properties for (30, 30) BChl *d* at 50 K, (30, 30) BChl *c* at 300 K and (40, 30) Me-BChl *c* 300 K systems. Snapshots of simulated structures of these systems are shown in Figure 2.3 and Figure A.8. The predicted chiral angles δ based on geometrical analysis of ideal tubes for *bchQRU* ($d = 0.83$ nm) and WT/*bchR* chlorosome ($d = 1.25$ nm) for the relevant unit cell parameters are added in parentheses. $1/d$ determines the layer line position of a simulated EM image. *Since the structures for BChl *c* and *d* are only partial tubes, these values are only estimates.

	(30, 30) BChl <i>d</i> 50 K	(30, 30) BChl <i>c</i> 300 K	(40, 30) Me-BChl <i>c</i> 300 K
R (nm)	10.6	6.8	6.1
δ (deg)	19.1 (19.8)	30.5 (112.3)	40.6
β' (deg)	39.1	29.1	18.2
d (nm)	0.87*	0.95*	1.0

Large-scale tail conformations

We analyzed tail conformations in the curved (30, 30) BChl *c* systems after 1 ns by projecting the 3D curved structure to 2D along the long axis of the fitted cylinder. Using the 2D projection, we determined the radial position, *i.e.* the distance L to the center O of the circle, for a few reference atoms in each of the BChl molecules — Mg, C_1 and C_2 — see Figure A.10c. The end-to-end distance (EED) of the tail part is consequently computed as the difference in the radial position of C_1 and C_2 , *i.e.* $L_{OC_1} - L_{OC_2}$, while the (radial) thickness of the layer formed by the tail is computed as the difference in radial position of Mg and C_2 ($L_{OMg} - L_{OC_2}$). The particular range in the EED distribution for $T = 50$ K can be explained in terms of tail conformations that point towards the center of the cylinder ($EED > 0$), that are parallel to the cylinder axis ($EED = 0$) or directed away from the center, towards neighboring head groups ($EED < 0$). We find that the distribution of the radial thickness can be fitted by a Gaussian, and we used the peak value plus half the radius of the C_2 carbon $\bar{L}$ to estimate the inter-layer distance $d = 2\bar{L}$ between nested cylinders, assuming that there is

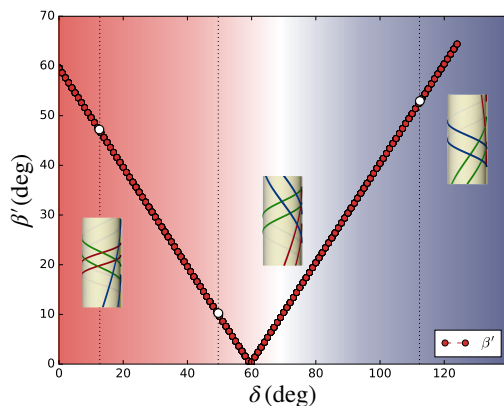


Figure A.9: Predicted β' angles of tubes formed by chiral angles δ between 0° and γ , based on the expression $\beta' = |\delta - 90 + \eta|$ taken from Günther *et al.*⁴⁵ This figure is complementary to Figure 2.2 in the main text. To evaluate this expression, we took $\eta = 30.4^\circ$, which is consistent with the unit cell parameter (1.48 nm, 0.98 nm, 124.3°) used in the Figure 2.2 axial repeat d prediction.

no inter-digitation of tails belonging to BChl molecules in different tubes. The comparison of the estimate d to the consistently found experimental interlayer distance $d_{\text{exp}} = 2.1$ nm, determined from the Bijvoet pair, see Figure A.11, shows that $d \rightarrow d_{\text{exp}}$ with increasing T . We note that the monotonic decrease of d with rising T can also be explained in terms of improved sampling, albeit that the thickness slightly increases for $T = 300$ K. Our finding suggest that there is indeed little or no inter-digitation between tails belonging to neighboring tubes.

Large-scale transition of a planar to a curved aggregate

Details of the transition are shown in Figure A.12, which focuses on the evolution of the total potential energy E (in kJ/mol) with time as well as the stable curved aggregate obtained after 1 ns of simulation (both for $T = 50$ K). The plot of $E - E_0$, *i.e.* E relative to its initial value E_0 , shows a steep decrease that is accompanied by the rapid formation of large-scale curvature (see inset of snapshots along the trajectory). Although the curved structure

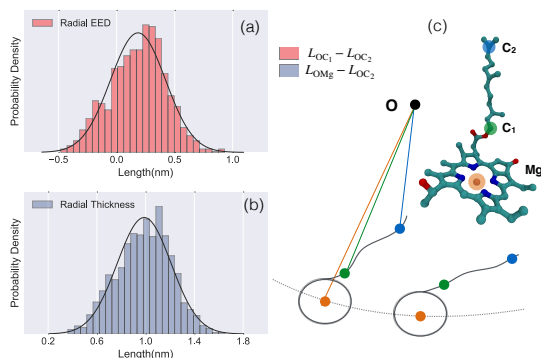


Figure A.10: Spatial analysis of tail configurations in the curved structure, obtained in (30, 30) BChl *c* system at 50 K after 1 ns, projected on fitted cylinder cross-section surface. (a) Distribution of radial end-to-end distance (EED) of tails; (b) Distribution of radial thickness of a single layer pigment molecules; (c) Illustration of how the radial EED ($L_{OC_1} - L_{OC_2}$) and radial thickness ($L_{OMg} - L_{OC_2}$) are determined. O denotes the projected center of the fitted cylinder.

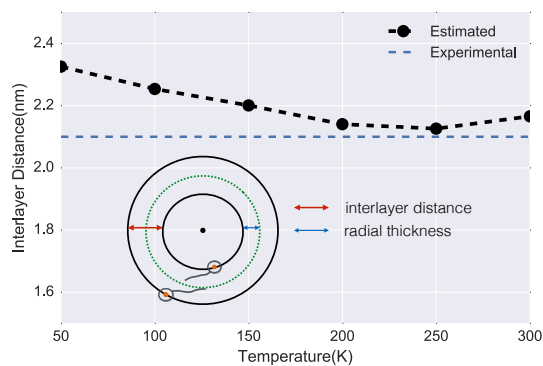


Figure A.11: Inter-layer distances for nested cylinders, as determined from the spatial extent of tails for the simulated curved structures (single cylinder) at different temperatures, from 50 to 300 K (see inset). The inter-layer distances are calculated as two times the radial thickness of a single layer plus one carbon atom van der Waals radius. The experimental inter-layer distance is 2.1 nm.

does not visually change during the last 500 ps of simulation, a non-vanishing driving force for continued curving may be observed from a tiny gradient $\partial E/\partial t$ towards the end of simulation. We note that for a higher temperature, $T = 300$ K, the planar-to-tube transition takes roughly 2 ns. For $T = 50$ K, the curved structure is a very regular on the intermediate scale, with the Mg atoms in the BChl molecules (left side of Figure A.12b; obtained by orthogonal projection of the Mg content in the partial tube) forming a regular lattice. This can be seen from the well-defined layer lines in the power spectrum at the right side of the panel, which shows the 2D Fourier transform of the snapshot at the left.

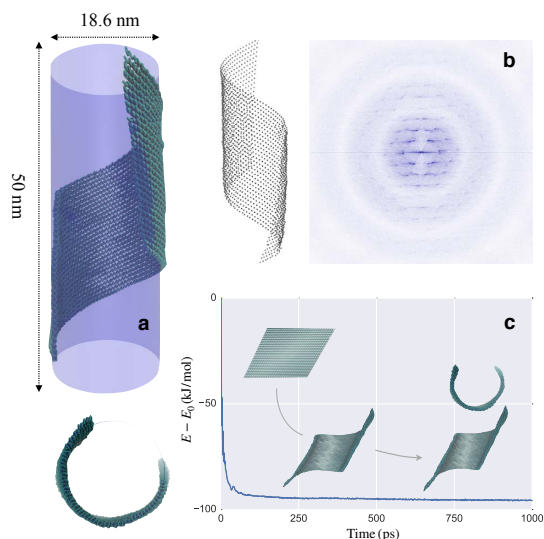


Figure A.12: Simulation results for the (30, 30) BChl *c* system at 50 K: (a) Stable curved structure after 1 ns of simulation and corresponding cylinder, fitted to the Mg atom coordinates using a least-square fitting algorithm (LSGE, <http://www.eurometros.org/>). For clarity, side groups of the head part and tails are not shown; (b) Mg atom configuration snapshot and corresponding scattering pattern, indicative of a helical structure; (c) Evolution of potential energy E along the trajectory, showing the drop in potential energy that accompanies curving. The initial potential energy E_0 is used as a reference value.

Dynamics of the hydrogen bonded network

Each BChl molecule contains two groups that are capable of forming hydrogen bonds: a Donor (hydroxyl group oxygen) and an Acceptor (carbonyl group oxygen). In order to analyze general properties of the hydrogen bonded network, structures should be sufficiently large to rule out strong effects of the BChl molecules at the boundary, which are naturally restricted in candidates for Donor-Acceptor interactions. Figure A.13 shows the evolution of the total number of established hydrogen bonds in large (30, 30) BChl *c* and BChl *d* assemblies during a 1 ns simulation trajectory. Both systems were simulated at 50 K. A geometric criterion implemented in the Gromacs software (default values) was used to determine whether a hydrogen bond is established and to determine their total number within one structure.

Since the Donor/Acceptor groups are shared by BChl *c* and *d* molecules, the maximum number of hydrogen bonds is 1709 for both cases. From Figure A.13, we see that the number of hydrogen bonds in the assembly structure increases quickly from the (planar) start and saturates to a constant value. This saturation value is around 1190 for BChl *c* and 1517 for BChl *d*. In relative terms, we thus find that 70% of the available hydrogen bonds are established for BChl *c* and 90% for BChl *d*.

In situ analysis: time-dependent sampling distribution of head-head stacking angle α

In addition to the instantaneous sampling distribution of the intra- and inter-dimer angle α shown in Figure 2.7, for the (30, 30) BChl *c* system at 1 ns, we also considered the time-dependent sampling distribution for the part of the trajectory where the structure does not visually change, *i.e.* between 500–1000 ps (in steps of 10 ps) for $T = 50$ K. One of the objectives was to evaluate the role of rotations in the dynamics of the structure; the other to see whether there the sampling distributions for α_{inter} and α_{intra} show evidence for a preferred angle and (possibly) symmetry breaking. The result of this exercise can be found in Figure A.14. The multi-modal nature of the distribution confirms that a small number of configurations are preferentially sampled during the 500 ps trajectory. Since this sampling is obtained for $T = 50$ K and a relatively short trajectory, it shows that the underlying potential energy landscape is rather

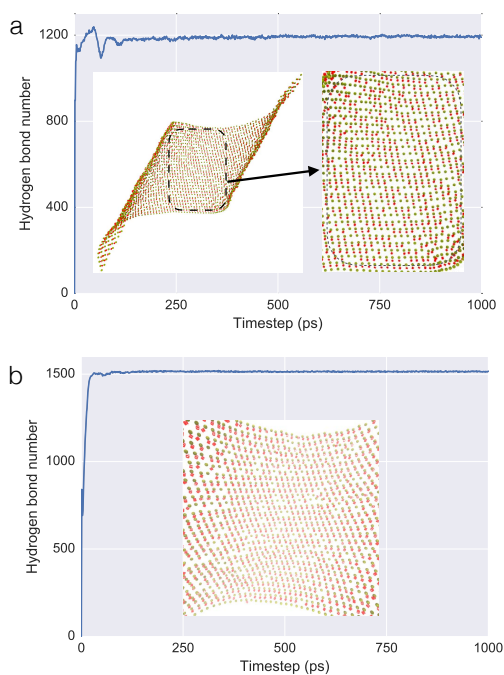


Figure A.13: Evolution of number of hydrogen bonds along the MD simulation trajectory for (a): (30, 30) BChl *c* and (b): (30, 30) BChl *d* system at 50 K. The insets show local details of the hydrogen bonded network in part of the stable curved structures after 1 ns simulation. Green circles indicate Mg atoms; established hydrogen bond are identified by red circles.

flat with rotations taking place on a relatively short time scale. This result, however, does not allow us to draw conclusions about symmetry breaking and the origin of large-scale curvature.

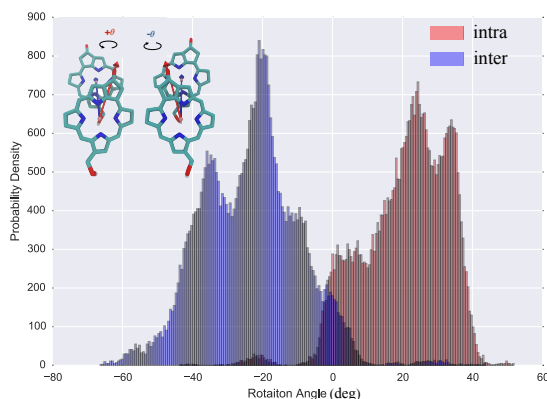


Figure A.14: Distribution of rotation angle α , extracted from the curved structures obtained along trajectory of MD simulation of (30, 30) BChl *c* system at 50 K, from 500 ps to 1 ns.

In situ analysis: sampling distribution of $\Delta\beta$ for a higher temperature

In addition to the relative intra- and inter-molecular rotations α , we also considered a simplified representation that includes handedness. The time-dependent sampling distribution of $\Delta\beta$ for the lowest temperature ($T = 50$ K) considered, see Figure 2.8, sampled between 500–1000 ps (in steps of 5 ps), has a bimodal nature. Although it is clearly skewed towards positive values of $\Delta\beta$, large-scale curvature should result from a pertinent offset in $\Delta\beta$ compared to the fully symmetric case, *i.e.* $\bar{\Delta\beta} = 0^\circ$. For this reason, we additionally evaluated the sampling distribution of $\Delta\beta$ for the highest considered temperature $T = 300$ K using the same procedure, see Figure A.15. We find that the sampling distribution for this higher temperature has a distinct Gaussian shape with a peak position that is small and positive $\bar{\Delta\beta} = 4.6^\circ$. This finding quantifies the symmetry breaking at a local structural level, and clearly identifies the

molecular origin of pertinent curvature at a larger scale.

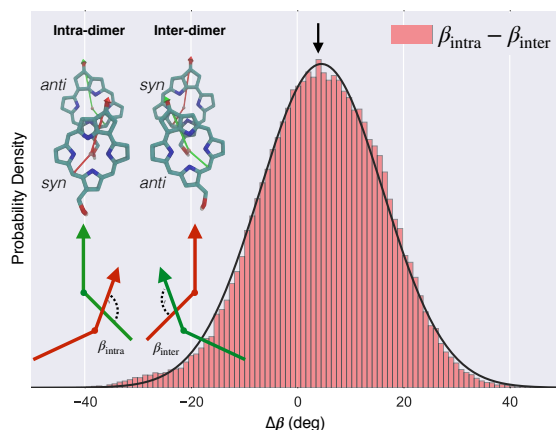


Figure A.15: Distribution of packing angle difference ($\beta_{\text{intra}} - \beta_{\text{inter}}$) between neighboring intra-dimer and inter-dimer rotation angles, extracted from the curved structures in the trajectory obtained in MD simulation of (30, 30) BChl *c* system at 300 K, from 500 ps to 1 ns. The distribution peaks at 4.6°.

In situ analysis: correlating relative rotation and hydrogen bonding

As can already be anticipated from the starting planar configuration in Figure A.7c, out-of-plane rotation of individual BChl molecules, relative to their neighbors, will affect the network of hydrogen bonded interactions along the **b** direction that plays a role in facilitating the structural integrity of the assembly upon curving, see the discussion about stabilizing interactions in the Chapter 2. To quantify how rotation and hydrogen bonding are related, we considered the relative rotational angle $|\alpha|$ for bonded and non-bonded BChl molecules separately, see Figure A.16.

We adopted standard geometric criteria (Donor-Acceptor distance smaller than 0.35 nm and Hydrogen-Donor-Acceptor angle smaller than 30°), as implemented in Gromacs software package, to determine whether a hydrogen bond is formed. The Donor (carbonyl group oxygen) hydrogen bonding situation is used to determine whether a specific site (molecule) is hydrogen bonded.

Then, its absolute relative rotation angle $|\alpha|$ is determined from the angle with the molecule whose hydroxyl oxygen atom is in close contact with its Mg atom, as the pair structure shown in Figure 2.7a (the top molecule is our target molecule for hydrogen bonding state rotation angle analysis). Figure A.16 shows that large relative rotation as expected correlates with the breakage of hydrogen bonds. Yet, the data also confirm that part of the relative rotations are correlated, and that for these cases hydrogen bonds are maintained.

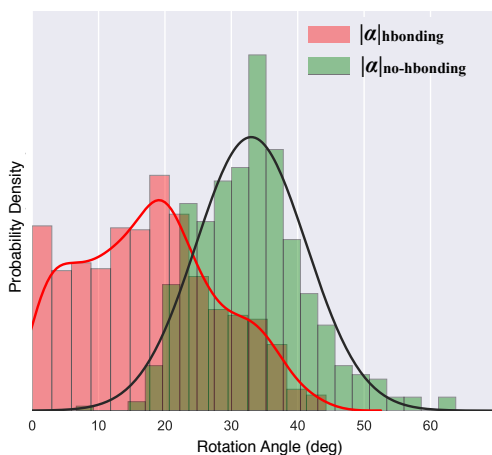


Figure A.16: Relative rotation angle distribution of hydrogen bonded molecules $|\alpha|_{\text{hbonding}}$ and not hydrogen-bonded molecules $|\alpha|_{\text{no-hbonding}}$ for (30, 30) BChl *c* system at 50 K after 1 ns, see Figure 2.7 and 2.9.

Spectral analysis of rotational degree of freedom

To clarify the spectral properties of a particular (local) vibration, *i.e.* the relative rotation between two molecules in a dimer, which is linked to the formation and breakage of hydrogen bonds, we performed spectral analysis on the time traces of the relative angle α for a few selected dimers. These traces were extracted from a densely sampled ($\Delta t = 10$ fs) 25 ps trajectory of the (30, 30) BChl *c* system at 300 K. Since the instantaneous state of a (*syn* or *anti*) monomer in a dimer is either “0-hb”, “1-hb” or “2-hb”, we selected dimers that differ in the number of hydrogen bonds (between 0 to 4) formed between

monomers and their neighbors after 25 ps of simulation. In this analysis, we disregarded whether a hydrogen bond was formed by a molecule in the (*syn* or *anti*) state and also did not explicitly account for changes in the dimeric state along the trajectory.

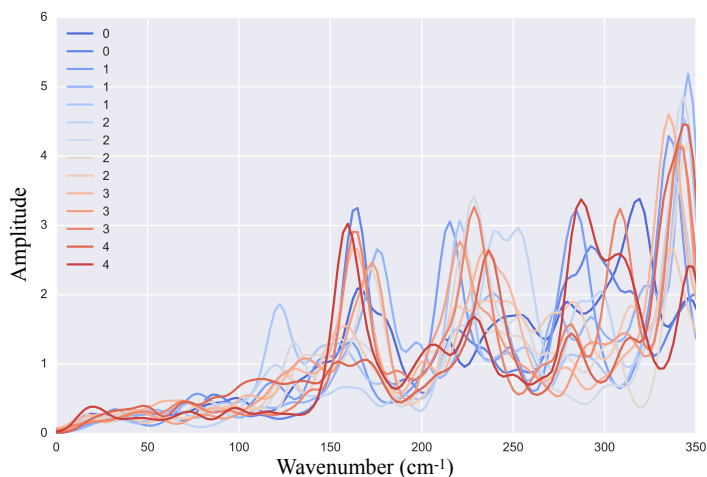


Figure A.17: Fourier spectra (amplitude versus wavenumber) calculated from the time traces of the relative rotational angle α for 14 dimers selected from the large BChl *c* aggregate. The selection criterion was based on a proper representation of the different domains determined by analysis of hydrogen bonding, which is based on individual molecules. Labels indicate the total number of hydrogen bonds formed by the two molecules in the dimers and surrounding molecules at 25 ps.

We considered the effect of a varying number of hydrogen bonds on this spectral analysis by considering a single trace that exhibits a clear change along its short (25 ps) trajectory. We explicitly accounted for this change by performing spectral analysis for the associated partial traces. Although there is an observable difference in the spectra, the position of the first band undergoes only a slightly shift when compared, from around 160 cm^{-1} to 140 cm^{-1} , so we conclude that disregarding the hydrogen bond dynamics will only give rise to a slight peak broadening in the most important range. We will further concentrate on these details in future analysis of molecular vibrations in multi-tube systems.

We employed a central difference scheme to convert each of the extracted time traces of α to a time-dependent velocity of a (fantom) particle. Consequently, we calculated the cosine transform of the normalized velocity autocorrelation function for each particle. A Gaussian filter was applied to the whole time domain to avoid spurious signals in the frequency domain due to the truncation of the time signal at longer times. The resulting spectra for all 14 dimers are plotted in Figure A.17. It shows that all spectra share a number of bands, including one that is close to the experimentally relevant 145 cm^{-1} . We note that applying FFT directly to the time traces gives rise to a very similar band structure, but a much more noisy signal, hence we use the selected procedure via fantom particles.

Supporting Information for Chapter 3

Theoretical prediction of axial repeat distance d

We have extended the geometrical analysis introduced in Chapter 2 to account for a larger range of the chiral angle $\delta \in [0^\circ, 180^\circ]$ and an additional helical family. Using this analysis, the axial repeat distance d determined from the layer line position in the Fourier spectrum that was calculated from cryo-EM images can be related to the four main helical families, $H(1, 0)$, $H(0, 1)$, $H(1, 1)$, $H(-1, 1)$, as:

$$\begin{aligned} d_{H(1,0)} &= \left| \frac{b \sin \gamma}{\cos \delta} \right| \\ d_{H(0,1)} &= \left| \frac{a \sin \gamma}{\cos(\gamma - \delta)} \right| \\ d_{H(1,1)} &= \left| \frac{ab \sin \gamma}{a \cos(\delta) + b \cos(\gamma - \delta)} \right| \\ d_{H(-1,1)} &= \left| \frac{ab \sin \gamma}{a \cos(\delta) - b \cos(\gamma - \delta)} \right| \end{aligned}$$

where the lattice parameters (a, b, γ) relate to unique properties of the dimeric unit cell. In particular, these four helical families can be seen as least sensitive to the disorder that will be present in experimental chlorosomes. When the denominator equals zero, the corresponding helical family constitutes lines parallel to the tube long axis.

The axial repeat distance d cannot be uniquely matched to a value in the

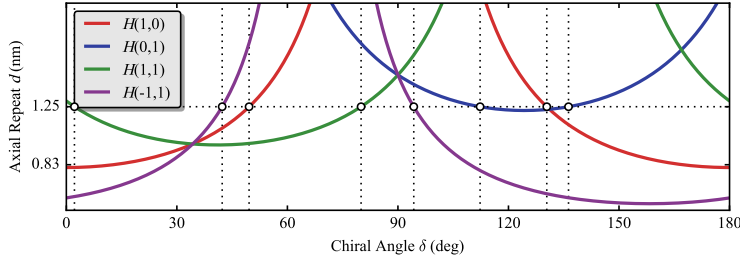


Figure B.1: The axial repeat d as a function of the chiral angle $\delta \in [0^\circ, 180^\circ]$ corresponding to the $H(1, 0)$, $H(0, 1)$, $H(1, 1)$ and $H(-1, 1)$ helical families. Since we are targeting the experimentally determined axial repeat distance $d = 1.25$ nm for WT chlorosomes, lattice parameters are set to (1.48 nm, 0.98 nm, 124.3°) as determined from MD simulations of BChl c tubular assemblies (Chapter 2) to evaluate the geometrical relations. Matching chiral angles are highlighted by white circles.

δ -range, due to the uncertainty which of the main helical families relates to the experimental layer line. Yet, combining these relations and the lattice parameters (a, b, γ) extracted from AAMD simulations (Chapter 2), we can single out a small set of matching chiral δ for each experimentally determined axial repeat d . For wild-type (WT) chlorosomes, that are rich in BChl c , and mutant *bchQRU* chlorosomes rich in BChl d , the axial repeats d have been determined as 1.25 nm and 0.83 nm, respectively.³⁷ In particular, the lattice parameters were determined as (1.48 nm, 0.98 nm, 124.3°) for pure BChl c aggregates and (1.46 nm, 0.93 nm, 122.5°) for BChl d aggregates. Following this procedure, eight candidate chiral angles are found for WT chlorosomes, see Figure B.1: $\delta = 2.2^\circ, 42.3^\circ, 49.6^\circ, 80.0^\circ, 94.3^\circ, 112.3^\circ, 130.4^\circ$ and 136.3° . For the *bchQRU* chlorosomes, only four candidate chiral angles match, see Figure B.2: $\delta = 19.8^\circ, 27.6^\circ, 108.9^\circ$, and 160.2° . For completeness, these values are summarized in Table 3.1.

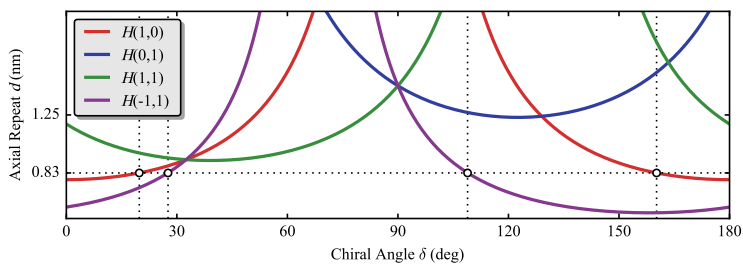


Figure B.2: The axial repeat d as a function of the chiral angle $\delta \in [0^\circ, 180^\circ]$ corresponding to the $H(1, 0)$, $H(0, 1)$, $H(1, 1)$ and $H(-1, 1)$ helical families. Since we are targeting the experimentally-determined axial repeat distance $d = 0.83$ nm for *bchQRU* chlorosomes, lattice parameters are set to (1.46 nm, 0.93 nm, 122.5°) as determined from MD simulation of BChl d tubular assembly (Chapter 2). Matching chiral angles are highlighted by white circles.

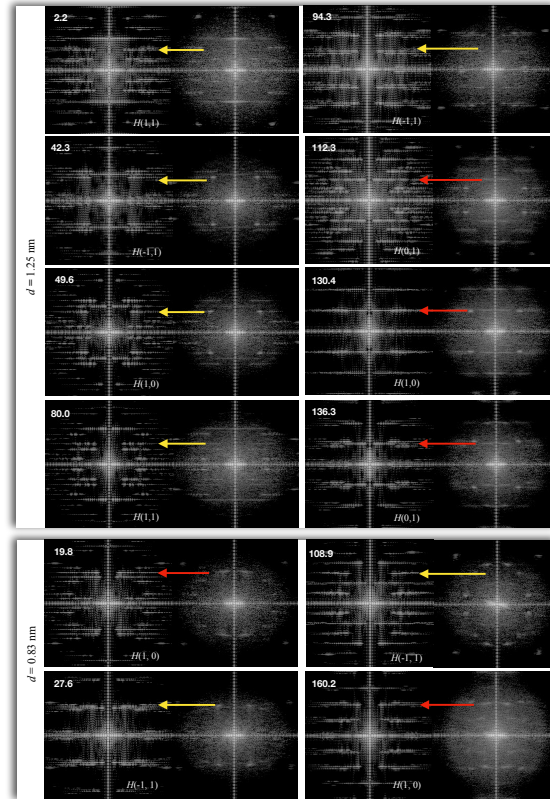


Figure B.3: EM mimics corresponding to tube structures for all δ that are listed in Table 3.1, with layer line positions at $1/d = 1/1.25$ nm⁻¹ for WT or $1/d = 1/0.83$ nm⁻¹ for *bchQRU* chlorosomes. For each δ , we show 2D power spectra for both the ordered structure at $T = 0$ K (left) and the structure after 1 ns MD simulation at ambient temperature, $T = 300$ K (right). The helical family corresponding to the target layer line is given at the right bottom in the 0 K spectrum. Arrows point to the target layer lines from our geometrical analysis: red indicates a meridian signal that is consistent with the diffraction pattern observed in experiments, while yellow indicates a signal further away from the meridian or a missing signal due to structural disorder. The diffraction patterns of the 2D power spectra for the structures after MD simulation at $T = 300$ K are used for a realistic comparison to experimental diffraction data. 2D power spectra are calculated for single tubes of 40 nm length, using a procedure that is described in Chapter 2. For clarity, the contrast of each diffraction pattern is increased by 25%. We note the same diffraction pattern of 112.3° is found for 105°, including the meridian signal characteristics.

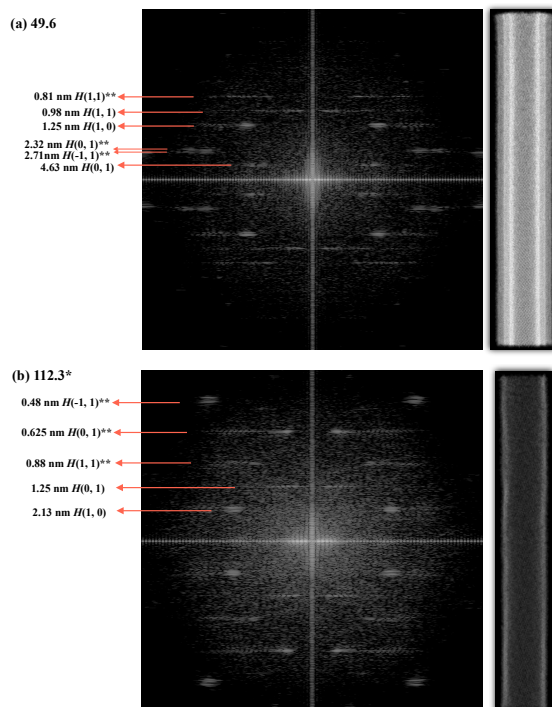


Figure B.4: Left: 2D power spectra for the $\delta = 49.6^\circ$ (a, concentric) and $\delta = 112.3^\circ$ (b, single) tube structures. Layer lines are labeled by the helical family and the corresponding repeat distance. Spectra are calculated for 120 nm long tubes after 1 ns MD simulation at ambient temperature, *i.e.* $T = 300$ K, shown at the right in terms of the 2D projection of the electron density. Layer lines with strong signals denoted by superscript ** originate from a lattice with half the a dimension of the unit cell, which corresponds to the distance between *syn* and *anti*. It shows that *syn* and *anti* cannot always be distinguished in electron diffraction. For clarity, the contrast of each diffraction pattern is increased by 25%.

Table B.1: Small- and large-scale structural properties of pre-assembled structures at different stages of preparation and simulation: after energy minimization (0 K), after 1 ns MD simulation at 50 K and subsequent 1 ns at 300 K. MD simulations were carried out in an NVT ensemble for structures that were pre-assembled for matching δ , following the procedure described in the Method section 3.2. In all cases, only Mg atoms in N molecules are considered for the determination of structural properties, which include local packing parameters (a, b, γ), calculated as an average over the whole structure, and large-scale features like the adopted chiral angle δ and tube radius R which were determined from a best least-square fit. Standard deviations and residuals of this fitting procedure are included.

	$\delta_{\text{ideal}}(^{\circ})$	N	label(K)	$a(\text{nm})$	$b(\text{nm})$	$\gamma(^{\circ})$	$\delta_{\text{fit}}(^{\circ})$	$R_{\text{fit}}(\text{nm})$	$\text{RMSD}_{\text{fit}}(\text{nm})$
wild type $\delta_{1.25}$	2.2	9272	0	1.48 ± 0.0	0.98 ± 0.0	124.0 ± 0.07	2.0 ± 0.0	7.39	0.02
			50	1.49 ± 0.02	0.98 ± 0.03	125.3 ± 1.8	2.3 ± 0.0	7.41	0.15
			300	1.49 ± 0.03	0.99 ± 0.04	123.2 ± 3.19	2.7 ± 0.01	7.36	0.22
	42.3	9397	0	1.48 ± 0.0	0.98 ± 0.0	124.3 ± 0.06	42.2 ± 0.0	7.48	0.01
			50	1.49 ± 0.02	0.98 ± 0.03	125.0 ± 1.96	41.8 ± 0.04	7.39	0.11
			300	1.49 ± 0.03	0.99 ± 0.04	124.0 ± 2.86	42.2 ± 0.08	7.5	0.21
	49.6	9144	0	1.48 ± 0.0	0.98 ± 0.0	124.3 ± 0.06	49.7 ± 0.0	7.28	0.01
			50	1.5 ± 0.02	0.97 ± 0.03	125.0 ± 1.99	48.9 ± 0.05	7.18	0.11
			300	1.5 ± 0.03	0.99 ± 0.04	123.9 ± 2.9	49.4 ± 0.07	7.3	0.17
	80.0	8068	0	1.48 ± 0.0	0.98 ± 0.0	124.3 ± 0.04	80.0 ± 0.0	6.41	0.0
			50	1.49 ± 0.02	0.98 ± 0.03	125.0 ± 2.0	80.3 ± 0.08	6.3	0.11
			300	1.49 ± 0.03	1.0 ± 0.04	123.6 ± 3.0	80.2 ± 0.13	6.48	0.2
	94.3	9253	0	1.48 ± 0.0	0.98 ± 0.0	124.3 ± 0.03	94.2 ± 0.0	7.37	0.0
			50	1.49 ± 0.02	0.98 ± 0.03	125.1 ± 2.0	95.3 ± 0.06	7.28	0.15
			300	1.49 ± 0.03	1.0 ± 0.05	123.3 ± 3.29	94.6 ± 0.16	7.45	0.29
	112.3	9468	0	1.48 ± 0.0	0.98 ± 0.0	124.2 ± 0.04	112.4 ± 0.0	7.53	0.0
			50	1.48 ± 0.02	0.99 ± 0.03	125.1 ± 2.03	113.9 ± 0.07	7.53	0.17
			300	1.48 ± 0.03	1.0 ± 0.05	123.0 ± 3.37	112.2 ± 0.17	7.6	0.29
	130.4	9161	0	1.48 ± 0.0	0.98 ± 0.0	123.9 ± 0.05	130.5 ± 0.0	7.29	0.01
			50	1.48 ± 0.02	0.98 ± 0.03	125.1 ± 1.88	131.8 ± 0.04	7.31	0.13
			300	1.48 ± 0.03	1.0 ± 0.05	122.6 ± 3.51	130.1 ± 0.11	7.31	0.26
	136.3	9392	0	1.48 ± 0.0	0.98 ± 0.0	123.9 ± 0.05	136.4 ± 0.0	7.48	0.01
			50	1.49 ± 0.02	0.98 ± 0.03	125.3 ± 1.91	137.7 ± 0.06	7.52	0.13
			300	1.48 ± 0.03	1.0 ± 0.05	122.6 ± 3.55	136.0 ± 0.17	7.47	0.3
bchQRU $\delta_{0.83}$	19.8	8766	0	1.46 ± 0.0	0.93 ± 0.0	122.4 ± 0.05	19.7 ± 0.0	6.63	0.02
			50	1.48 ± 0.03	0.93 ± 0.03	122.3 ± 2.44	19.3 ± 0.03	6.69	0.22
			300	1.47 ± 0.05	0.94 ± 0.04	120.8 ± 3.71	19.7 ± 0.03	6.65	0.29
	27.6	8844	0	1.46 ± 0.0	0.93 ± 0.0	122.5 ± 0.06	27.6 ± 0.0	6.71	0.02
			50	1.48 ± 0.03	0.92 ± 0.03	122.5 ± 2.47	26.8 ± 0.08	6.76	0.24
			300	1.47 ± 0.05	0.94 ± 0.04	120.7 ± 3.88	27.6 ± 0.07	6.71	0.32
	108.9	8858	0	1.46 ± 0.0	0.93 ± 0.0	122.4 ± 0.04	109.0 ± 0.0	6.71	0.0
			50	1.51 ± 0.02	0.91 ± 0.02	122.3 ± 2.19	108.3 ± 0.11	6.5	0.21
			300	1.48 ± 0.06	0.94 ± 0.05	119.5 ± 4.12	106.6 ± 0.32	6.65	0.6
	160.2	9289	0	1.46 ± 0.0	0.93 ± 0.0	122.0 ± 0.11	160.4 ± 0.0	7.05	0.02
			50	1.47 ± 0.03	0.93 ± 0.02	123.2 ± 2.62	161.0 ± 0.02	7.1	0.19
			300	1.46 ± 0.04	0.94 ± 0.04	120.3 ± 3.99	160.1 ± 0.04	6.91	0.51

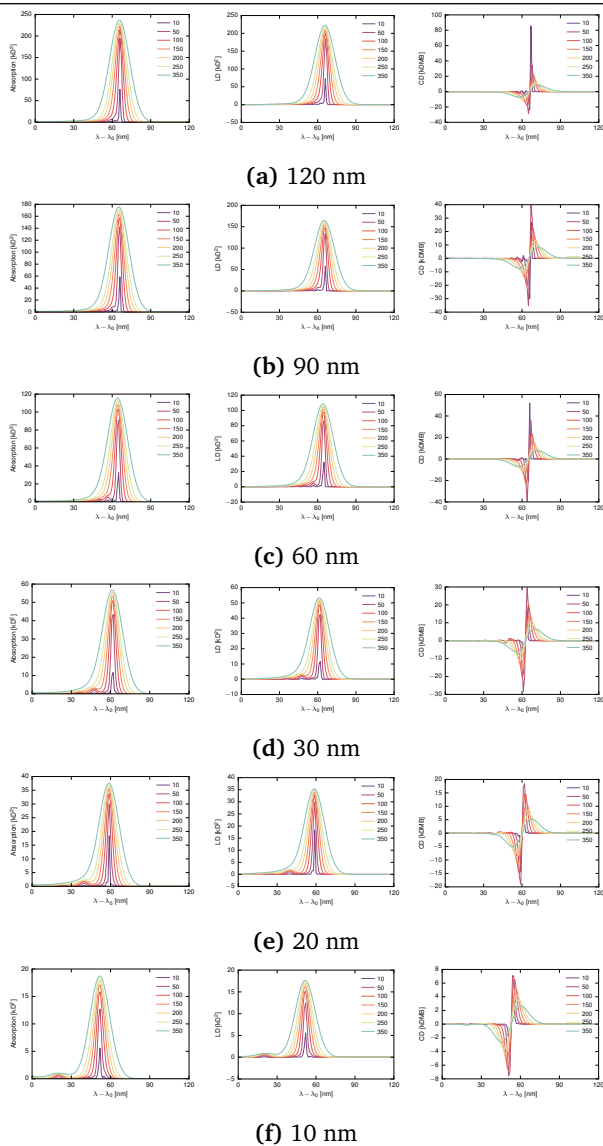


Figure B.5: Spectral plots for the tube at 300 K after 1ns MD simulation for $\delta = 49.6^\circ$, i.e. one of the two matching chiral angles for BChl *c*-rich aggregates like the WT chlorosome. Different tube lengths have been considered, from very short 10 nm tubes to the longest 120 nm. We have convolved stick spectra with Gaussians that feature a range of FWHM values, from 10 to 350 cm^{-1} , to evaluate the broadening effect. In particular, the effect of homogeneous and heterogeneous broadening has been shown to vary in experimental spectra.

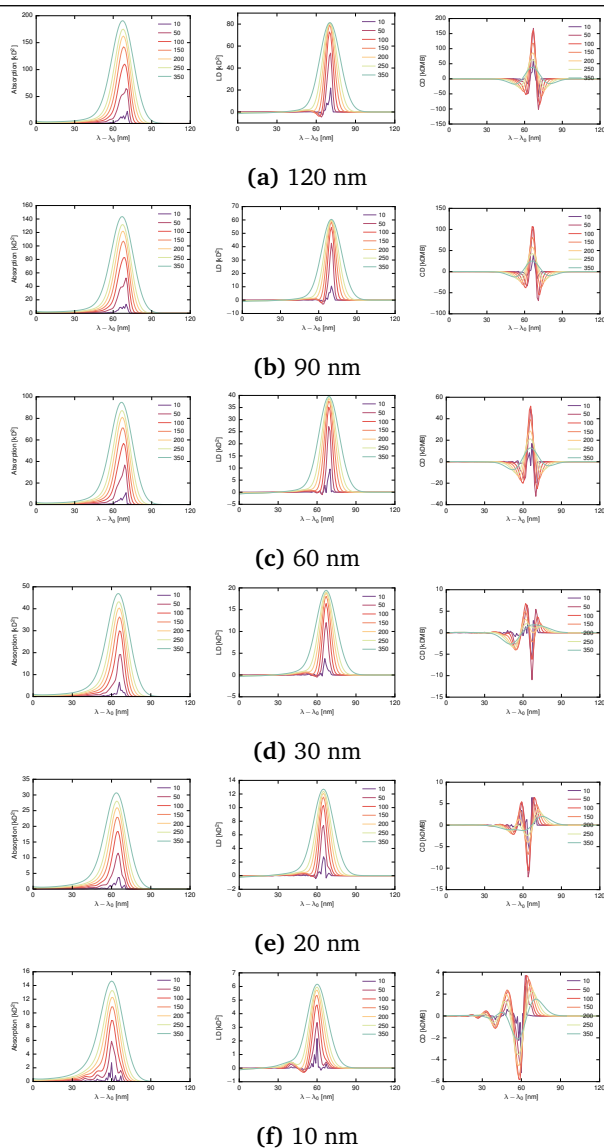
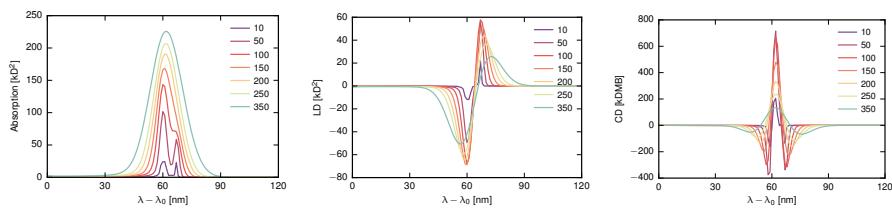
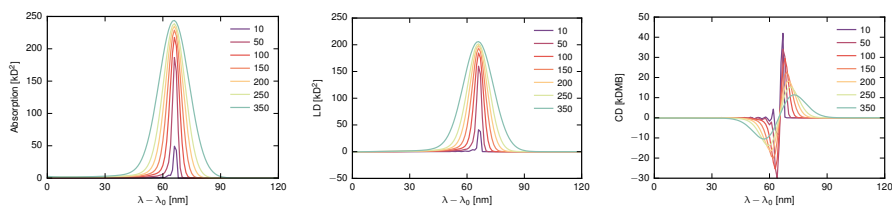


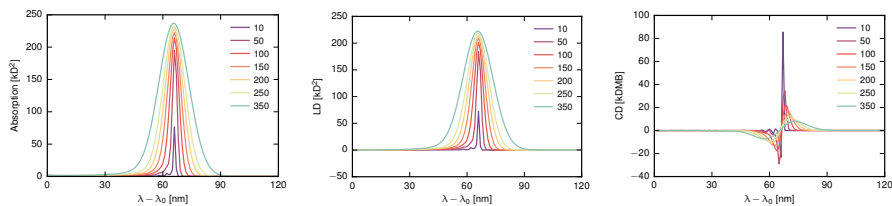
Figure B.6: Spectral plots for the tube at 300 K after 1 ns MD simulation for $\delta = 19.8^\circ$, i.e. one of the two matching chiral angles for BChl *d*-rich assemblies like the mutant *bchQRU* chlorosome. Different tube lengths have been considered, from very short 10 nm tubes to the longest 120 nm. We have convolved stick spectra with Gaussians that feature a range of FWHM values, from 10 to 350 cm^{-1} , to evaluate the broadening effect. In particular, the effect of homogeneous and heterogeneous broadening has been shown to vary in experimental spectra.



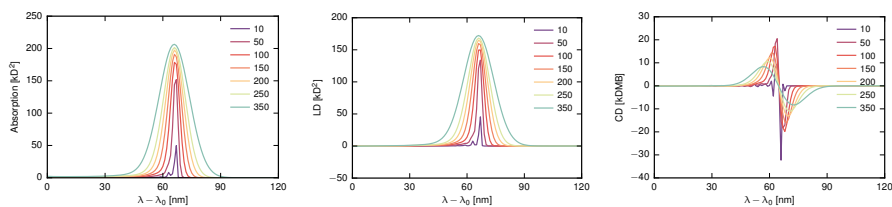
(a) 2.2



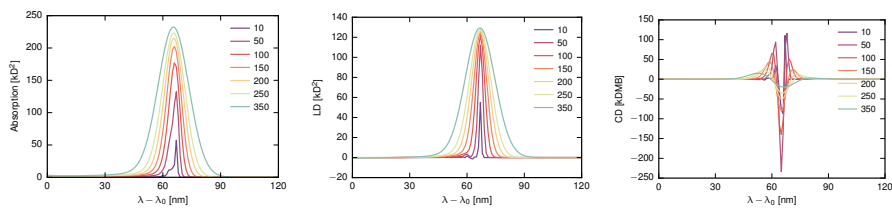
(b) 42.3



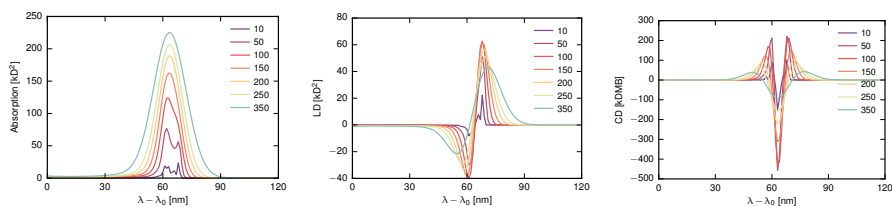
(c) 49.6



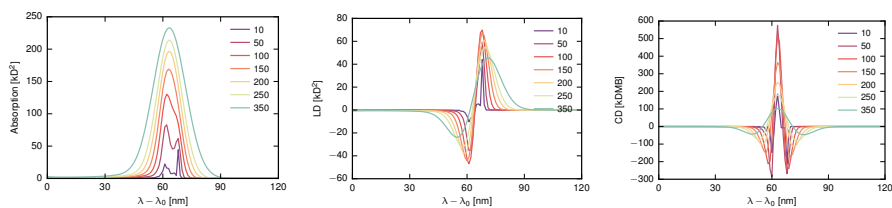
(d) 80.0



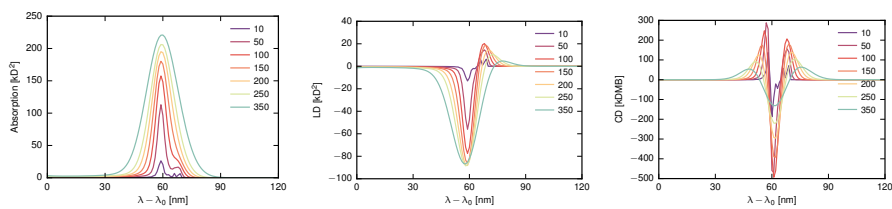
(e) 94.3



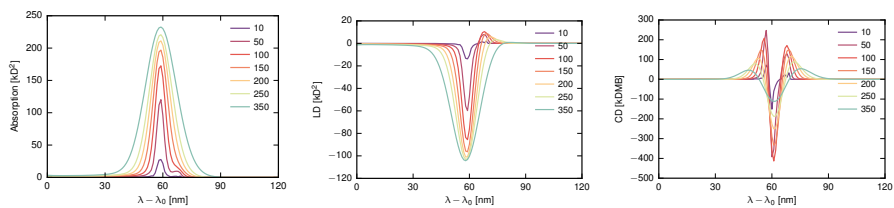
(f) 112.3



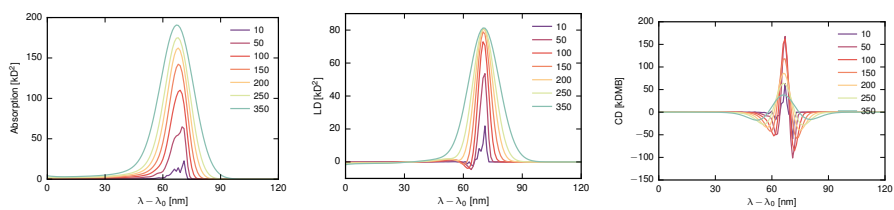
(g) 112.3*



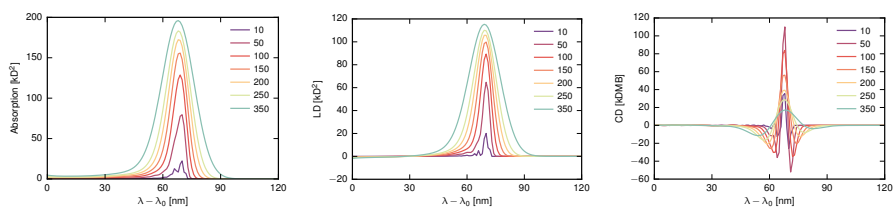
(h) 130.4



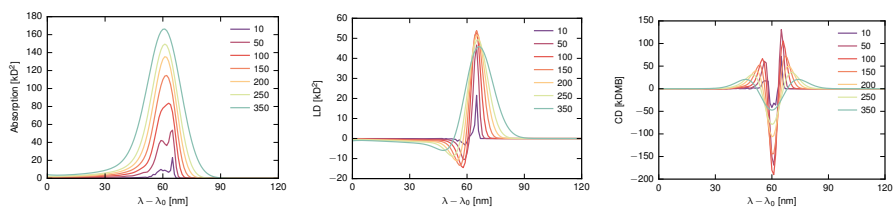
(i) 136.3



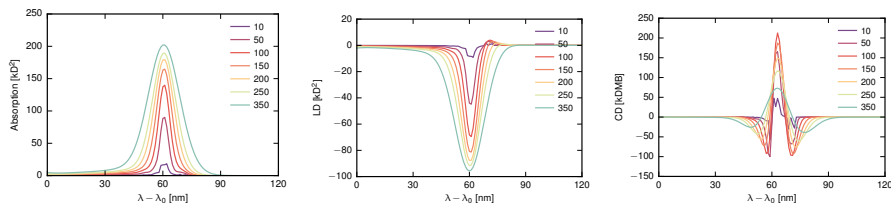
(j) 19.8



(k) 27.6



(l) 108.9



(m) 160.2

Figure B.7: Spectral plots for all tube structures with matching δ at 300 K. We have convolved stick spectra with Gaussians that feature a range of FWHM values, from 10 to 350 cm^{-1} , to evaluate the broadening effect. In particular, the effect of homogeneous and heterogeneous broadening has been shown to vary in experimental spectra.

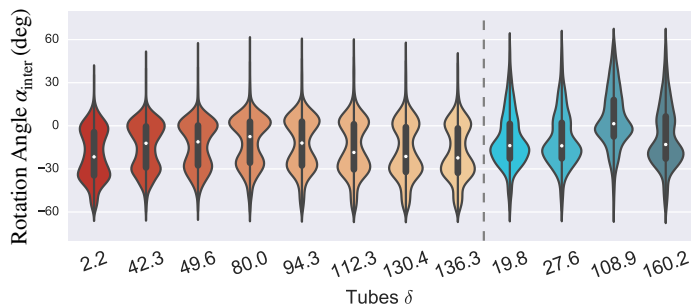


Figure B.8: Sampling distribution for the relative head-head rotation angle between *anti* and *syn* molecules BChl, α_{inter} , for the tube obtained after 1 ns MD simulation at 300 K. The distribution is calculated for different chiral angles δ on the horizontal axis, and the dashed line separates the matching chiral angles for BChl *c* and *d*. We refer to the main text, figure 3.4, for the distribution of α_{intra} .

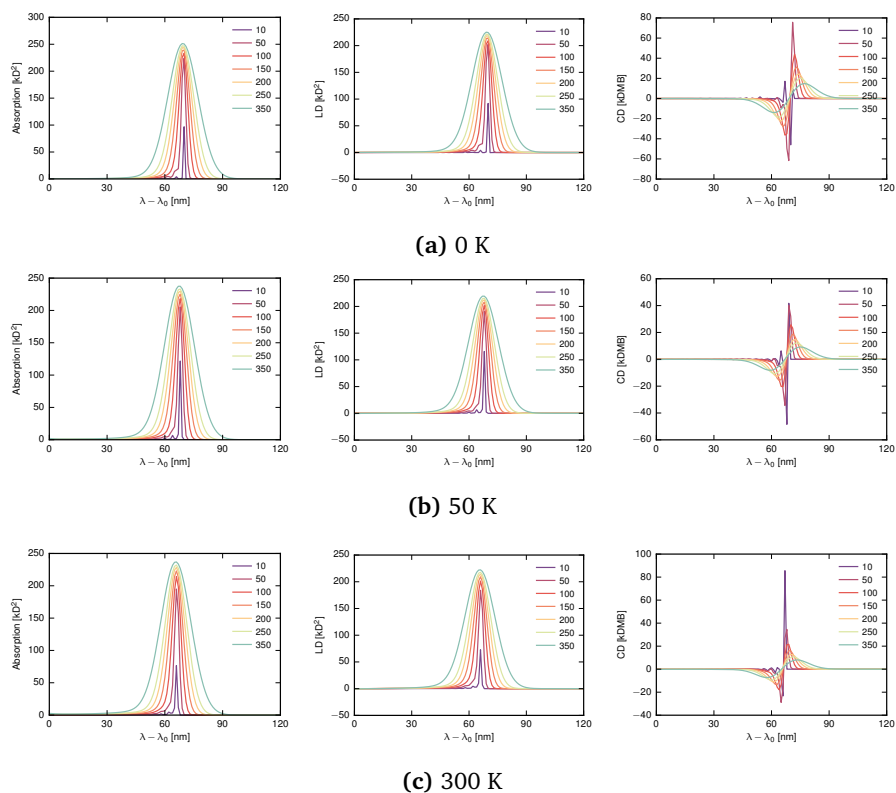


Figure B.9: Spectral plots for the tube that was pre-assembled for $\delta = 49.6^\circ$, at different stages of preparation/simulation: 0 K, 50 K and 300 K. We have convolved stick spectra with Gaussians that feature a range of FWHM values, from 10 to 350 cm^{-1} , to evaluate the broadening effect. In particular, the effect of homogeneous and heterogeneous broadening has been shown to vary in experimental spectra.

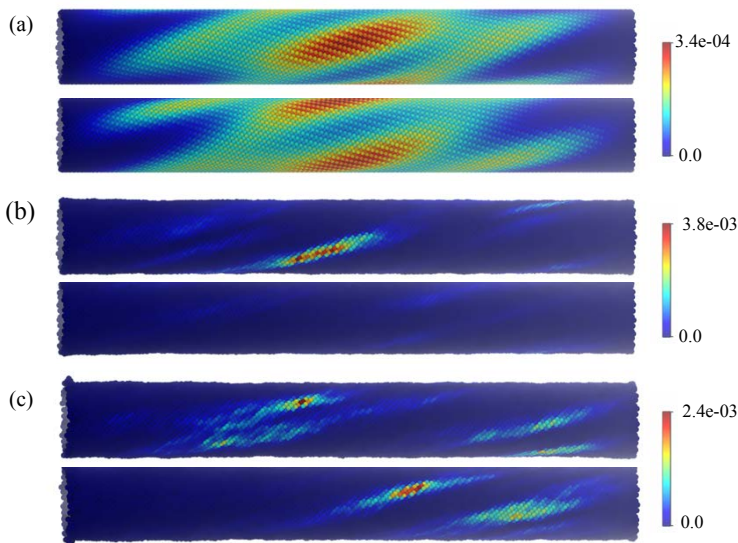


Figure B.10: Spatial distribution of the exciton states with the highest oscillator strength $\psi_{\max}$ in a 120 nm long tube for a matching $\delta = 49.6^\circ$. From top to bottom: $\psi_{\max}$ for different disorder within the tube: ordered state (a), and disordered states after 1 ns MD simulation at 50 K (b) and 300 K (c). In each case, the front and back view of the tube are both shown. Tube structures also have been unrolled to planar ones for the purpose of visualization, see Figure 3.6.

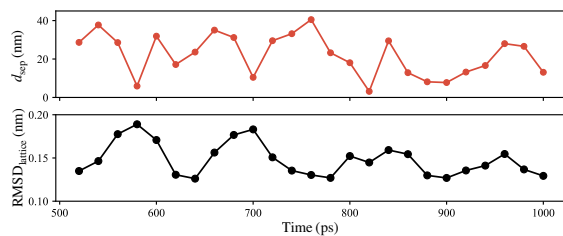


Figure B.11: Analysis of the structural and exciton state variation along a long 500 ps MD trajectory for a tube with $\delta = 49.6^\circ$. Top: Time evolution of d_{sep} , the distance between molecules associated with the largest exciton density in $\psi_{\max}$ in consecutive frames. Bottom: RMSD for the lattice between consecutive frames, calculated from the Mg positions.

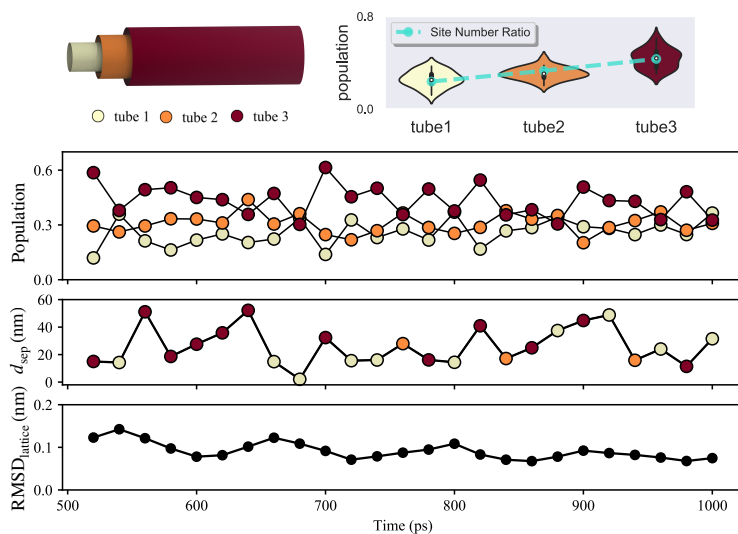


Figure B.12: Analysis of structural and excitons state variation of $\psi_{\max}$ in concentric 3-tube structures along a long 500 ps trajectory. From top to bottom: (left) Schematic illustration of concentric tube geometry, with radii satisfying tube 3 > tube 2 > tube 1. Colors are used to distinguish between different tubes. (right) Distribution of exciton density population of $\psi_{\max}$ over all frames in the trajectory. The average (white point) agrees well with the trend of the normalized number of molecules (site number ratio, dashed line) in each tube. Below: The exciton density population in different tubes, denoted by tube color, along a 1 ps trajectory. Below: d_{sep} , the distance between molecules associated with the largest exciton density in consecutive frames. Color specifies in which tube the molecule with the highest exciton density is situated. Bottom: RMSD for the lattice between consecutive frames, calculated from the Mg positions.

Supporting Information for Chapter 4

Computational Details

AAMD simulation. The tube studied in this work is composed of *syn-anti* dimers of BChl *c* molecules. For MD force field details for the BChl *c* molecule, we refer to Chapter 2. We give a brief summary here. The OPLS-AA force field⁹² was used for all simulations. Charge parameters were refined by the RESP method.⁹⁴ In the pigment head part, four Mg–N bonds were added to keep the Mg atom stable within the ring. Electrostatic interactions were calculated by a particle-mesh Ewald method.⁹⁸ MD simulations with periodic boundary conditions along all dimensions were conducted using the Gromacs software (version 2016.1).⁹⁷ We performed NVT simulations, maintaining the temperature by the velocity-rescaling thermostat.⁹⁹

Helical Tube MD trajectory. We briefly summarize the protocol for obtaining a stable tube structure, and refer to Chapters 3 and 5 for more details. A tube structure for a specific chiral angle was first packed using a in-house code. To alleviate any possible unfavored geometrical overlap, and to ensure stable MD simulation, we first performed steepest descent optimization, then performed constrained MD simulation keeping the head part fixed and sequentially only the Mg atoms, followed by MD simulation without constraints at 50 K (1 ns). After this equilibration, we performed MD simulation at 300 K and collected snapshots of the nuclear coordinates every 20 fs along a 1 ps MD trajectory. These snapshots were used to calculate the Frenkel Hamiltonians.

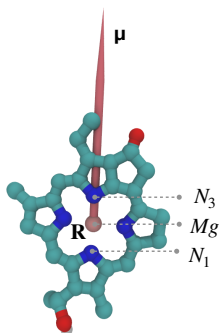


Figure C.1: Molecular detail of the determination of the transition dipole μ from a BChl *c* molecule. The director (shown by a red arrow) is given by the vector connecting the two indicated Nitrogen atoms, with origin given by the coordinates of the Mg atom (shown by a pink sphere). The magnitude $|\mu|$ of this vector is 5.48 D, as estimated from experiments. The tail part of the molecule and most hydrogen atoms are omitted for visual clarity.

Frenkel Hamiltonian Parameterization. We briefly summarize how the Frenkel Hamiltonian is calculated. For more details and discussions, we refer to Chapter 3. As shown in Eq.4.1, the Hamiltonian is a 2D matrix composed of diagonal (site energy) and off-diagonal (electronic coupling) terms. For the site energy, we considered a constant monomer excitation energy of a BChl *c* pigment molecule: $\nu = 15390 \text{ cm}^{-1}$ for the Q_y -transition of isolated BChl *c* in methanol.⁸⁰ The J_{ij} , representing the electronic coupling between molecules i and j , is calculated via the standard point-dipole approximation (PDA),¹²²

$$J_{ij}(\mu_i(t), \mu_j(t), \mathbf{R}_{ij}(t)) = \frac{\mu_i \cdot \mu_j}{|\mathbf{R}_{ij}|^3} - 3 \frac{(\mu_i \cdot \mathbf{R}_{ij})(\mu_j \cdot \mathbf{R}_{ij})}{|\mathbf{R}_{ij}|^5}. \quad (\text{C.1})$$

For a give BChl *c* molecule, the transition dipole moment vector μ is oriented along the vector connecting two Nitrogen atoms, see FigureC.1. The magnitude $|\mu|$ of this vector is 5.48 D, as estimated from experimental data.¹²⁴ The transition dipole moment vector μ is placed at the position of the Mg atom $\mathbf{R}$ in the molecule, see FigureC.1. $\mathbf{R}_{ij}$ is the distance vector between two transition

dipoles at positions $\mathbf{R}_i$ and $\mathbf{R}_j$. Within this PDA treatment, only three atoms in a molecule are relevant for the electronic coupling terms.

Definition of Different Domain Properties. As shown in Figure C.7, we calculated several properties of the domains and checked their correlation with P_{domain} , for instance, the positive (J_{domain}^+) and negative (J_{domain}^-) part of J_{domain} , rotation angle (α) and distance (d) between neighboring transition dipoles.

- J_{domain} is the overall electronic coupling strength in the domain, see Eq. C.1;
- J_{domain}^+ is defined as

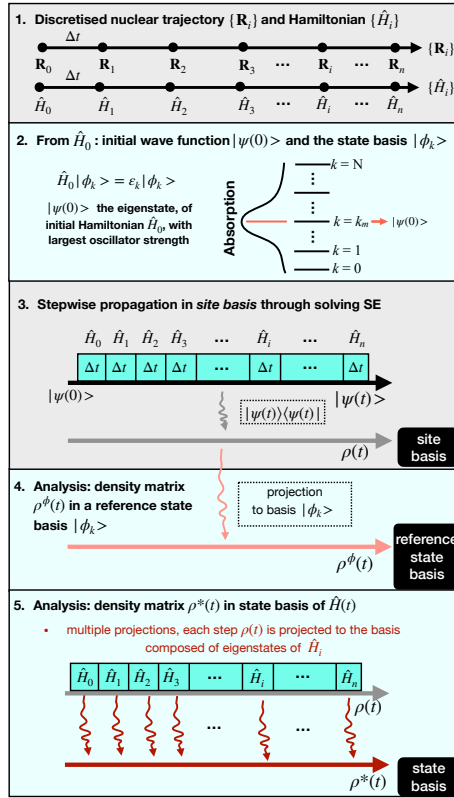
$$J_{\text{domain}}^+ = \sum_{i,j \in \text{domain}, i \neq j} \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{|\mathbf{R}_{ij}|^3}; \quad (\text{C.2})$$

- J_{domain}^- is defined as

$$J_{\text{domain}}^- = - \sum_{i,j \in \text{domain}, i \neq j} 3 \frac{(\boldsymbol{\mu}_i \cdot \mathbf{R}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{R}_{ij})}{|\mathbf{R}_{ij}|^5} \quad (\text{C.3})$$

- α is the average neighboring dipole-dipole rotation angle along the **a** packing direction; d is the average neighboring Mg-Mg distance (equivalent to the dipole-dipole distance) along the **a** packing direction. Such properties were also discussed before in Chapter 3. Neighboring transition dipoles are selected via a distance constraint with a threshold of 0.8 nm. Following such a rule, molecules along the *syn-anti* packing direction, i.e. helices from the (1, 0) helical family (see Chapter 3), are considered.

Exciton dynamics. The details of our exciton dynamics simulations are summarized in Scheme C.1.



Scheme C.1: Schematic representation of the exciton dynamics simulation setup. (1) The time dependent Hamiltonian $\hat{H}(t)$ is updated every $\Delta t = 20 \text{ fs}$ according to the molecular conformations $\mathbf{R}_i$ from MD trajectory that define transition dipoles and origins $\{\mu, \mathbf{R}\}$ (shown in Figure C.1). (2) The initial wave function $|\psi(0)\rangle$ is an eigenstate of the Hamiltonian $\hat{H}_0 = \hat{H}(t = 0)$. We select the eigenstates $|\phi_k\rangle$ as the reference state basis in the following analysis. (3) SE represents the time dependent Schrödinger equation. Within each $\Delta t = 20 \text{ fs}$ time interval, the Hamiltonian is treated as a constant, and the wave function is propagated unitarily with a time step of 1 fs, through solving a SE equation using the “zvode” ODE solver implemented in QUTIP software. (4) Along the exciton dynamics trajectory, we collected the wave function $|\psi(t)\rangle$ and density matrix $\rho(t)$ in the site basis. For analysis, through applying projection from the site basis to a reference state basis of $\hat{H}_0$, we obtained the density matrix $\rho^\phi(t)$ in the state basis $|\phi_k\rangle$. (5) For additional analysis, we also projected the density matrix $\rho^\phi(t)$ to the state basis of $\hat{H}(t)$, through multiple projections. To evaluate our choice of $\Delta t = 20 \text{ fs}$, we considered a static case, where the Hamiltonian $\hat{H}_1$ is constant, computed from the molecule conformation $\mathbf{R}_1$ at $t = 20 \text{ fs}$ taken from the MD trajectory. In such a case, the exciton dynamics is governed by the SE, $i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}_1 |\psi(t)\rangle$.

Extra plots

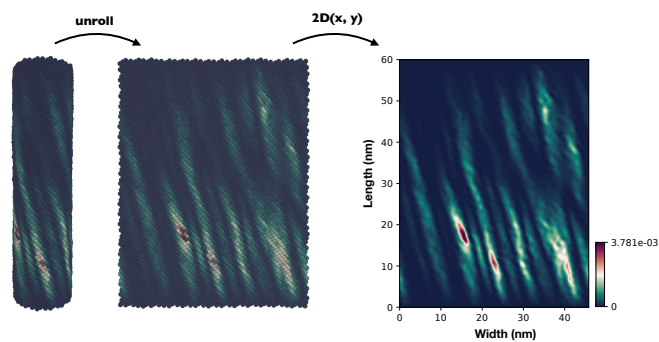


Figure C.2: Spatial distribution of a wave function projected on molecules in tube (left), after unrolling to a planar representation (middle) and subsequent smoothing to a fine 2D grid (right). The resolution of the grid in the smoothed 2D surface is set to $0.5 \text{ \AA}$, interpolated using a multi-quadric radial basis function.

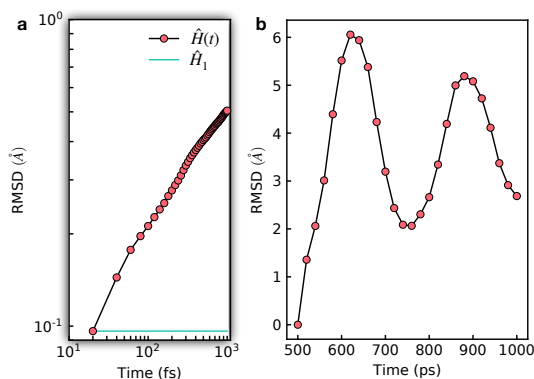
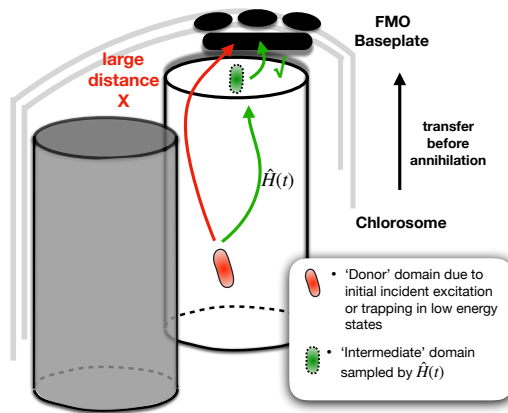


Figure C.3: (a) RMSD of the nuclear coordinates of the two Nitrogen and the Mg atoms that define the transition dipoles in the Hamiltonian for either the $\hat{H}(t)$ and constant $\hat{H}_1$ cases, see Figure C.1. The constant RMSD ≈ 0.1 Å for the nuclear coordinates used in $\hat{H}_1$ are denoted by a horizontal line. Coordinates at $t = 0$ is used as the reference. (b) Plot of the RMSD for a extended 500 ps trajectory, clearly showing that on a longer time scale there is no free diffusion but oscillatory behavior with a periodicity of about 250 ps.



Scheme C.2: Schematic representation of a possible spatial barrier in the energy transfer process from the chlorosome to a sink, *i.e.* baseplate and FMO, in photosynthetic bacteria. When the 'acceptor' in the baseplate/FMO is far away from the 'donor' domain, in the $\hat{H}(t)$ case the dynamic disorder may introduce an 'intermediate' domain that is close enough to the 'acceptor' to enable hopping by a Förster-like mechanism. If consider the Förster mechanism, proximity is key, since its efficiency is inversely proportional to the sixth power of this distance. We note that, if the exciton Hamiltonian also includes the baseplate/FMO, the 'acceptor' domain may be sampled directly.

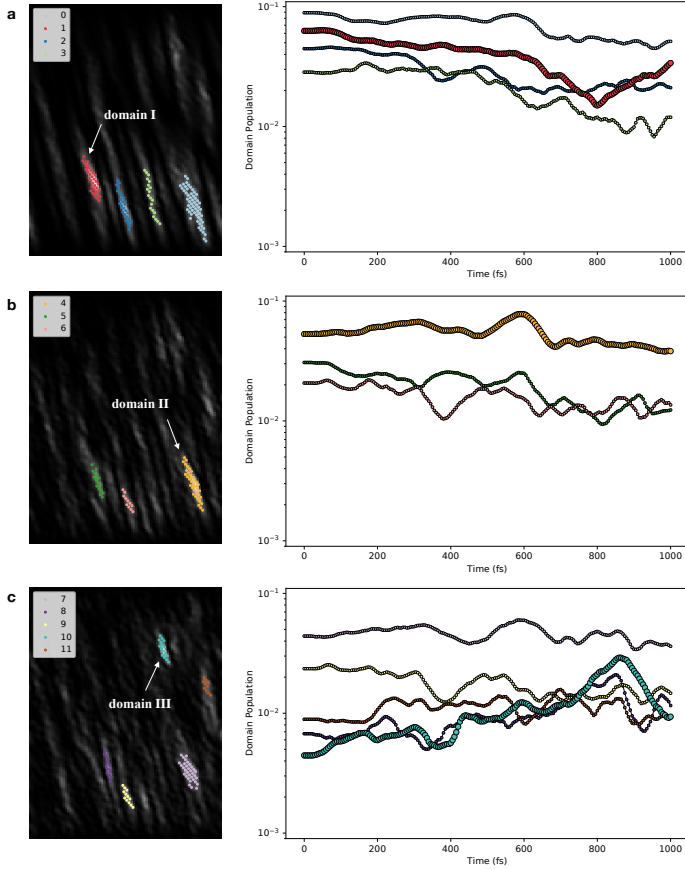


Figure C.4: (left) Tube domains identified from snapshots at 0 (a), 600 (b) and 865 (c) fs, and (right) corresponding domain populations $P_{\text{domain}}(t)$ for the Hamiltonian with dynamic disorder, *i.e.* the $\hat{H}(t)$ case. Domains were obtained via the DBSCAN clustering algorithm.²³³ Each domain is assigned to a specific number and a color.

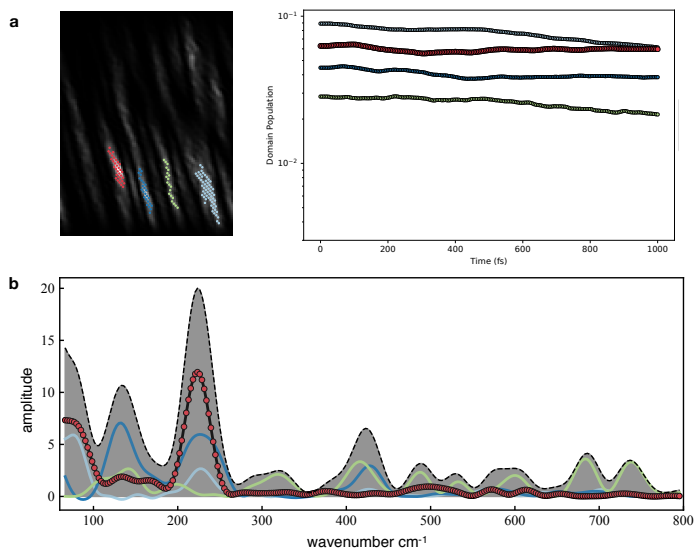


Figure C.5: Analysis for the constant $\hat{H}_1$ case: (a) domains identified at $t = 0$ fs (left) and evolution of the domain population along the 1 ps exciton dynamics trajectory (right). (b) Fourier spectra (amplitude versus wavenumber) calculated from the time traces of the domain populations. Domain I is highlighted by red color. The gray shadow plot shows the average amplitude of different domain cases. For visual clarify, the maximum value in the average amplitude plot is scaled to 20. Frequencies corresponding to time scales longer than half of the exciton trajectory of 1 ps are not shown.

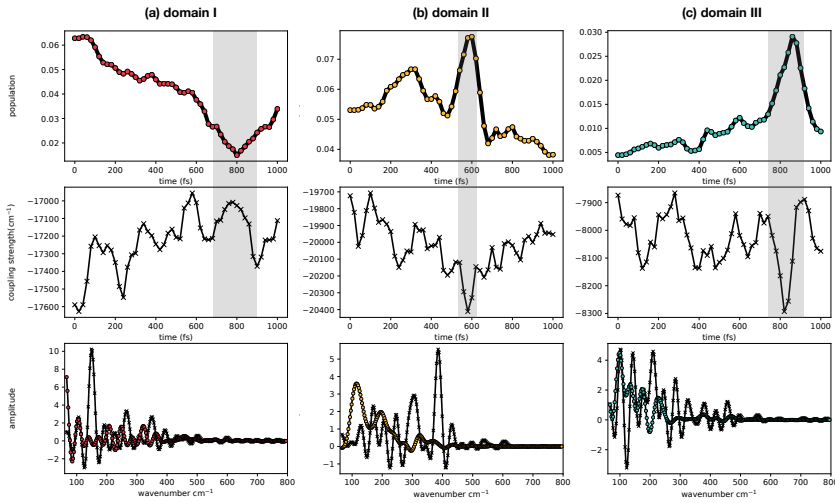


Figure C.6: Comparison of domain properties for the $\hat{H}(t)$ case: domain population P_{domain} (top) and electronic coupling strength J_{domain} (middle) along the exciton trajectory, and the FFT spectral analysis (bottom) of P_{domain} and J_{domain} for domain I (a), II (b) and III (c). The calculated cross-correlations between P_{domain} and J_{domain} (with zero lag) for domain I (a), II (b) and III are -0.61 , -0.34 , and -0.21 respectively. Frequencies corresponding to time scales longer than half of the exciton trajectory of 1 ps are not shown.

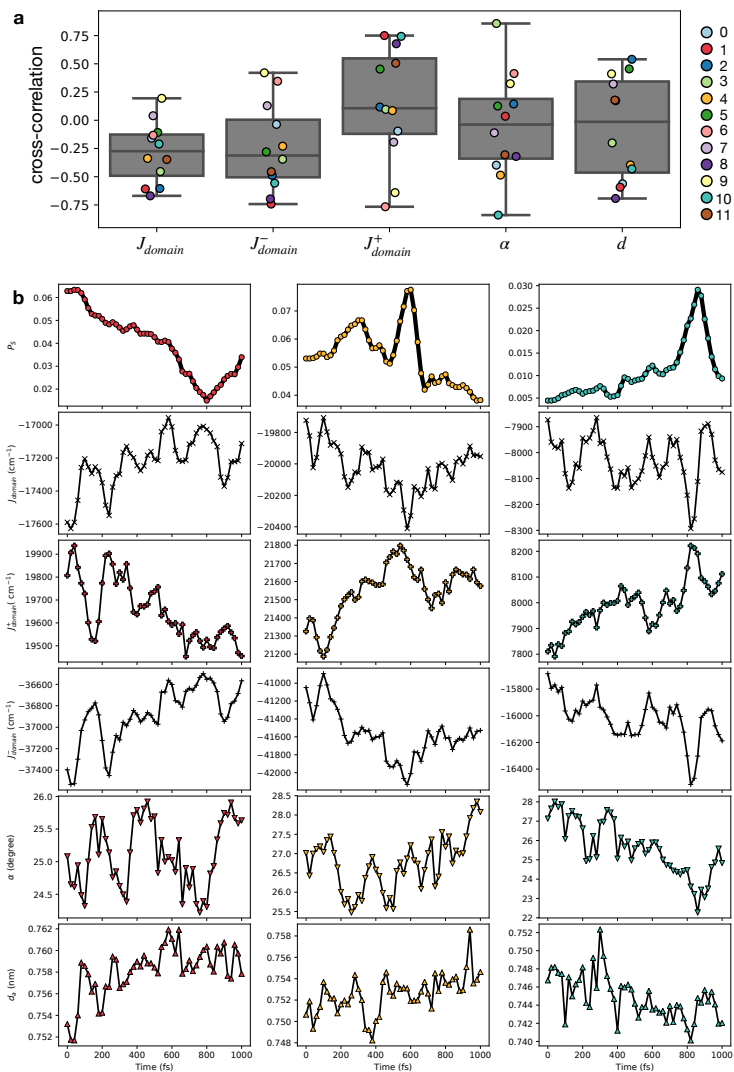


Figure C.7: Domain properties for the $\hat{H}(t)$ case: P_{domain} , J_{domain} , J_{domain}^+ , J_{domain}^- , α and d . (a) Box plot of cross-correlation values between P_{domain} and all other properties for all domains. Domains are labeled by the same color code as in Figure C.4. The domain indices for domain I, II and III are 1, 4 and 10 respectively. (b) Time traces of the examined domain properties for domains I, II and III.

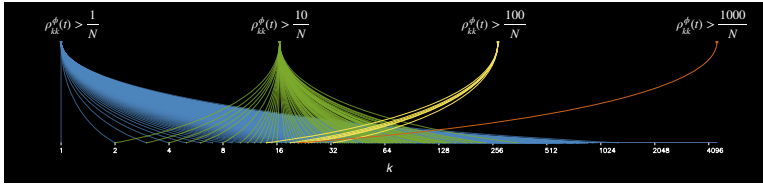


Figure C.8: Collection of states in the reference state basis that satisfy the following population threshold: $\rho_{kk}^\phi(t) > \frac{1}{N}, \frac{10}{N}, \frac{100}{N}$ or $\frac{1000}{N}$. States that satisfy this selection rule are connected.

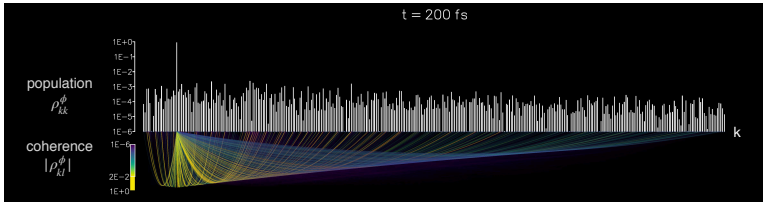


Figure C.9: Visualization of the $k < 350$ part of the density matrix ρ^ϕ in the reference state basis $|\phi_k\rangle$ at $t = 200$ fs. Top part: the magnitude of diagonal elements of the density matrix ρ_{kk}^ϕ are visualized as vertical lines. Bottom part: the relative magnitude of off-diagonal terms $|\rho_{kl}^\phi|$ are visualized via coloring of the arc curve connecting the k and l in the x -axis. On the x -axis, the state number k is arranged from low to high. For clear visualization in the color plot, the transparency (alpha parameter in RGBA color) of an arc curve is set to $20 * |\rho_{kl}^\phi|$, where 0 is completely transparent and 1 not transparent at all. The plots are made using PyCardio package (<https://github.com/obarquero/PyCardio>).

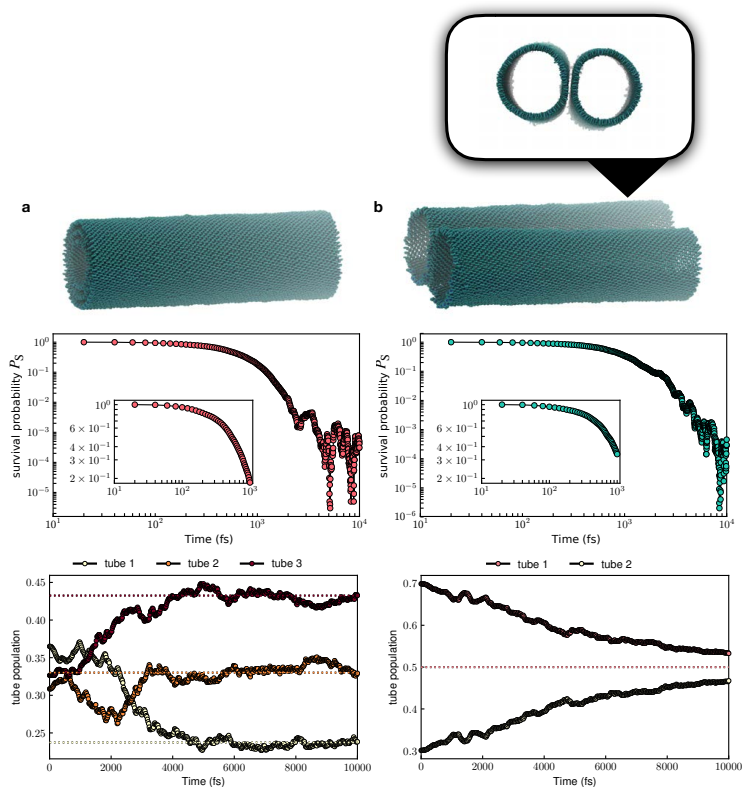


Figure C.10: Analysis of excitonic properties for tubular assemblies with different connectivities: concentric tubes (a) and side-by-side aligned tubes (b). Top: atomistic structures, middle: the initial state survival probability $P_S(t)$, and bottom: the tube population $P_{\text{tube}}(t)$ along the 10 ps exciton dynamics trajectories. As outlined in Scheme C.1, the initial wave function $|\psi(0)\rangle$ is selected as the absorption state of the whole assembly. The orthographic view of the tube assembly in inset of (b) shows that the tubes deform in the contact area.

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Summary

The knowledge of the molecular structures of biological matter has boomed in the last half-century, as a result of enormous advances made in the development and application of intricate techniques for experimental characterization and computation. As a result, the community as a whole has gained confidence and developed an instinct that there should be a molecular basis for most biological functions. In particular, researchers desire to build a connection between structure and function, and to propose molecular mechanisms, following the basic principles of chemistry and physics. The ultimate goal is to utilize such an understanding of molecular mechanisms for a rational design of optimal artificial materials with a desired function. Such type of reverse engineering does not only satisfy our human curiosity, but it also provides potential solutions for topics vital for global human welfare, such as health, energy, and sustainability.

Although substantial progress has been made in this respect, one encounters cases of high complexity that cannot be addressed directly. In such a situation, a tremendous and long-lasting intellectual effort is required to shed light on fundamental, molecular properties. One of such intriguing cases is the chlorosome: a natural light-harvesting antenna that is found in photosynthetic bacteria. On the one hand, we are amazed by the absence of usual regulating factors — proteins — and their high efficiency in capturing energy from light, which enables them to survive in extremely low light conditions at which no other phototrophs can survive. On the other hand, their structure as well as the origin of their efficiency remains mystic at the molecular level. In the thesis, the aim is to fill this knowledge gap, by making use of several computational methods (see Chapter 1 for an overview), and to inspire the community working on the design of artificial mimics.

Considering the structural stability and robustness of chlorosomes, it was found that these bacteria favor only several types of BChl pigments to be included in the antennae assembly. Such pigments carry functional groups that enable

the formation of a 2D linkage network, *i.e.* Mg and hydroxyl groups for Mg-O coordination interactions, and a carbonyl oxygen and hydroxyl group for hydrogen-bonding. In fact, these interactions regulate the third interaction, *i.e.* the π - π stacking interaction between parallel pigment head domains, and in combination they guarantee a unique, densely packed structure: the *syn-anti* packing model first proposed in 2009. In this thesis, we found that the hydrophobic farnesyl tails form dense layers on the outside and inside of tubes, which further strengthens stability and allows for the formation of higher-order structure, in the form of a concentric tube morphology. Although the concentration of pigments (and thus Mg) in chlorosomes reaches an impressive level, *i.e.* it is estimated to be 1–2 mol/L, chlorosomes are able to avoid the concentration quenching effect. Thus, these bacteria have found a remedy for the severely limited exposure to light by allowing for a ‘smart’ and unique increase of their number of pigments. We have thoroughly examined all the structural features of tubular pigment assemblies of chlorosomes by MD simulations (Chapter 2). An eye-catching feature is the Mg-O coordination interaction, which does not only provide the most stable helices in the assembly structure, but also sets the geometrical constraints that define chlorosomes as J-aggregates, giving them an absorption band that is shifted to the near-infrared. As a result, these bacteria can bypass other phototrophs, which is a key piece in the recipe for their survival.

At the supramolecular level, chlorosome assemblies exhibit helical chirality, which has only been partially characterized by experimental methods such as cryo-EM and optical spectroscopy. To relate to general theory, we introduced the concepts of a helical lattice and chiral angle δ , which enabled us to once and for all quantify the supramolecular chirality (Chapter 2 and Appendix A). A systematic, combinatorial procedure was then developed for determining δ , making use of all available experimental pieces of the puzzle (Chapter 3). Consequently, the role of δ in optical spectra of chlorosomes was elucidated in terms of a chirality vs. optical spectra “phase diagram” (Chapter 5), by systematically examining spectra for all possible δ in a resolution of 5° . It became clear that, since δ may vary with the particular pigment aggregate in different species of bacteria and/or the particular growth conditions, the characteristics of the optical signal, especially the circular dichroism spectra, may vary from case to case. The community can benefit from such a “phase-diagram” for a more fundamental dealing with the evasiveness of optical properties for chlorosomes.

We have also explained our protocol for constructing atomistic chlorosomes structures efficiently, which may be useful also for generating other large tube molecular aggregates or bio-inspired supramolecular systems (Chapter 5).

Although pigments are densely packed together in chlorosomes, they retain a prominent rotational degree of freedom around the Mg-O coordination bond. Such molecular motions produce intrinsic dynamic structural disorder, for instance, a distinct range of relative head-head rotation angles along *syn-anti* stacks as well as hydrogen bonding heterogeneity (Chapter 2), and induce considerable disorder in the electronic coupling between molecules (Chapter 3). By simulating the exciton dynamics, the dynamic disorder originating from thermal nuclear motions was found to create a fluctuating landscape for the exciton, which promotes exciton transfer and works against trapping of the exciton (Chapter 4). From these findings, we propose such dynamic disorder as a crucial microscopic origin for the robustness of exciton dynamics that is widely observed in different types of chlorosomes, as well as some bio-inspired tubular aggregates.

I dedicated a final outlook chapter for addressing the importance of farnesyl tails in BChl pigments, which may be vital in the assembly formation process and for the surprising mechanical properties (Chapter 6).

Of course, chlorosomes carry higher complexity than the tube structures considered in our *in silico* studies. We are still a long way from the complete picture. Yet, the ‘minimal’ physical model that we have developed contains atomic detail and captures key signatures of the actual bio-system, and thus represents a promising starting point for further research. Overall, this thesis provides valuable molecular insights in the structural, excitonic, and mechanical properties of chlorosomes, provides a practical way to performed realistic simulations, and makes the chlorosome system less daunting. Extensions of this work in terms of the computational treatment can be readily considered, for instance, to incorporate new MD force fields, other microscopic realizations of the exciton Hamiltonian, and a quantum propagation method for an open system, *i.e.* beyond unitary evolution.

Samenvatting

De enorme toename in de mogelijkheden om microstructuren in biologische materiaal met behulp van experimentele en rekenkundige technieken te bestuderen heeft ertoe geleid dat onze moleculaire kennis van dergelijke materialen de afgelopen vijftig jaar is geëxplodeerd. Het meest in het oog springende gevolg is dat we ons instinctieve vermoeden - dat de meeste biologische functies bepaald worden door eigenschappen van de moleculaire bouwstenen - steeds meer vertrouwen en steeds vaker begrijpen. Hiermee is de langgekoesterde wens van veel bio-wetenschappers - om structuur direct aan functie te koppelen en moleculaire mechanismen vanuit chemische of natuurkundige basisprincipes te verklaren - eindelijk dichterbij gekomen. De belangrijkste doorbraak ligt echter in de toekomst: dat we deze inzichten gebruiken om kunstmatige materialen te *ontwerpen*, door eigenschappen op te leggen die optimaal zijn voor de door ons gewenste toepassing. Dergelijk gebruik van biologische principes bevredigt niet alleen onze wetenschappelijke nieuwsgierigheid, maar biedt ook mogelijke oplossingen voor de vele uitdagingen waar we momenteel voor staan: op het gebied van gezondheid, energie en duurzaamheid.

Ondanks de constante vooruitgang in het onderzoek van fotosynthese komt men ook gevallen tegen die te complex zijn om zomaar op te lossen. Voor dergelijke gevallen is een langdurige intellectuele inspanning vereist om enig licht op de fundamentele, moleculaire eigenschappen te werpen. Een van dergelijke intrigerende gevallen is de chlorosoom: een natuurlijke antenne die voorkomt in specifieke fotosynthetische bacteriën. Deze antenne is uniek vanwege zowel de afwezigheid van de gebruikelijke regulerende factoren - eiwitten - als de efficiëntie waarmee hij fotonen om kan zetten in bruikbare energie, waardoor deze bacteriën kunnen overleven in veel minder licht dan andere fototrofe organismen. De uitdaging is dat zowel de structuur van de chlorosoom als de oorzaak van hun efficiëntie nog steeds niet bekend is op moleculair niveau. Het doel van dit proefschrift is deze leemte in onze kennis op te vullen, door de basiseigenschappen van chlorosomen met behulp van

verschillende rekenmethoden (zie Hoofdstuk 1) te onderzoeken. Zo hopen we een bron van inspiratie te zijn voor zowel de gemeenschap die werkt aan chlorosomen als aan het ontwerp van artificiële zonnencellen.

Wat de structurele stabiliteit en robuustheid van chlorosomen betreft, valt direct op dat deze bacteriën er de voorkeur aan geven om antennes samen te stellen uit slechts enkele soorten bacteriochlorophyll (BChl) pigmenten. De specifieke functionele groepen in deze pigmenten vormen een tweedimensionaal netwerk van coördinatie - magnesium en hydroxyl groepen - en waterstof bruggen - van een carbonyl oxygen en hydroxyl groep - welke, tezamen met een derde - π - π - interactie tussen parallelle ring domeinen, een unieke en zeer dicht gepakte structuur stabiliseert, met als bouwsteen de *syn-anti* eenheidscel die gevonden is in 2009. In dit proefschrift hebben we aannemelijk gemaakt dat de hydrofobe farnesyl staarten een dichte laag aan de buiten- en binnenkant van de individuele cilinders of tubes vormen, die de gelaagde superstructuur van individuele cilinders stabiliseert en versterkt. Bovendien is deze structuur in staat om, ondanks de hoge concentratie van 1–2 mol/L aan pigmenten, de zeer ongewenste uitdoving (quenching) van excitatie energie te vermijden. Deze bacteriën hebben derhalve een manier gevonden om de minieme hoeveelheid beschikbaar licht optimaal te benutten door middel van een ‘slimme’ concentratie van pigmenten in hun antenne. We hebben moleculaire dynamica (MD) simulaties doelmatig gebruikt om de onbekende structuureigenschappen van deze antennes te bepalen (hoofdstuk 2). Een opvallende eigenschap is de Mg-O coördinatie interacties, die zowel de grootschalige heliceit bepalen als de lokale geometrische condities voor de vorming van een zogenaamd J-aggregaat, wat zich direct vertaalt in een absorptieband die verschoven is naar het infra-rood. Tezamen vormen deze regulerende aspecten de sleutel tot het bestaan van deze bacteriën: ze kunnen effectiever omgaan met de condities dan andere fototrofe organismen.

Bestaande experimentele technieken, zoals cryo-EM en optische spectroscopie, zijn ontoereikend om de eerder genoemde heliceit van een aggregaat op supra-moleculair niveau exact te bepalen. In hoofdstuk 2 en appendix A hebben we derhalve een systematische methode ontwikkeld - een combinatie van een roostermodel en de gegevens van de geëquilibreerde eenheidscel uit onze MD simulaties - om de cryo-EM resultaten te relateren aan een klein aantal passende helix/chirale hoeken δ . Gevoegd bij de optische spectra, blijkt het zelfs mogelijk om - uit deze verzameling - een passende δ eenduidig te be-

palen. De lineaire absorptie-, lineaire dichroïsme (LD) en circulaire dichroïsme (CD) spectra die daarvoor zijn berekend, uitgaande van aggregaten die pre-geassembleerd zijn voor alle mogelijke waarden van δ , met een resolutie van 5° , geven vooral uniek inzicht in hoe het optische gedrag verandert als functie van de grootschalige chiraliteit. Omdat optische eigenschappen van chlorosomen in de praktijk gevoelig blijken te zijn voor moeilijk controleerbare experimentele variabelen, waaronder de exacte samenstelling van het pigmentmengsel en de gebruikte groei-condities, welke, volgens ongepubliceerde simulaties, allen invloed kunnen hebben op δ , is dit berekende ‘fase diagram’ een fundamentele stap voorwaarts voor het spectroscopisch onderzoek van chlorosomen. Het protocol waarmee de benodigde cilindrische structuren voor een bepaalde δ molecuul na molecuul werden assembleerd is beschreven in hoofdstuk 5, en kan ook gebruikt worden voor het assembleren van chirale aggregaten uit andere moleculaire bouwstenen.

Ondanks het feit dat individuele pigmenten zijn ingesnoerd in een groot, geconcentreerd aggregaat, behouden ze een belangrijke vrijheidsgraad - rotatie - rondom de Mg-O coördinatiebinding. Deze vrijheidsgraad is verantwoordelijk voor het bestaan van intrinsieke dynamisch wanorde in chlorosomen, wat te zien is in een duidelijke spreiding in de relatieve rotatiehoek tussen ring-domeinen van buurpigmenten in de richting van de *syn-anti* pakking richting, en in de verdeling van pigmenten waartussen waterstofbruggen worden gevormd (hoofdstuk 2). Bovendien veroorzaakt deze rotatie aanzienlijke wanorde in de elektronische koppeling tussen nabijgelegen moleculen (hoofdstuk 3). Door tevens de dynamica van de excitonen te berekenen op basis van de klassieke MD dynamica, zagen we dat de ‘klassieke’ dynamische wanorde een fluctuerend energetisch landschap voor de exciton genereert, waarbij klassieke wanorde slaat op de variërende positie van de nucleï ten gevolge van een eenduidige temperatuur. Deze fluctuaties helpen het exciton zich voort te bewegen en voorkomen dat het exciton gevangen raakt in een bepaalde positie, zie hoofdstuk 4. Derhalve postuleren we de ‘klassieke’ dynamische wanorde als de cruciale microscopische bron van de robuuste excitonen-dynamica, zoals die zowel in chlorosomen als andere bio-geïnspireerde cilindrische aggregaten wordt waargenomen.

Het laatste hoofdstuk concentreert zich op de rol van de farnesyl staarten van BChl pigmenten. Zoals we aannemelijk hebben gemaakt, zie hoofdstuk 6, zijn die zowel in de assemblage als in de verrassende mechanische eigenschappen

van enig belang.

Natuurlijke chlorosomen zijn vanzelfsprekend van een veel hogere complexiteit dan ons beperkte of ‘minimale’ rekenmodel. We hebben nog een lange weg te gaan. Maar het minimale rekenmodel dat we in dit proefschrift hebben ontwikkeld, voldoet aan de belangrijkste voorwaarden voor vervolgonderzoek: het reproduceert basiseigenschappen van het bio-systeem en bezit atomaire resolutie. In dit proefschrift hebben we belangwekkend moleculair inzicht proberen te geven in de structurele, excitonische en mechanische eigenschappen van chlorosomen. We hebben een praktische en realistische manier gezocht, en gevonden, om zo’n complex systeem rekenkundig te onderzoeken; om het ongrijpbare beter grijpbaar te maken. Toekomstige studies die dit werk als uitgangspunt beschouwen, zullen zich concentreren op het gebruik van verbeterde ‘force fields’ voor MD en andere microscopische representaties in de Frenkel Hamiltoniaan, zoals het in acht nemen van fluctuaties in de ‘site energy’ en meer accurate koppeling termen. Daarnaast is het modelleren van quantum propagatie met dissipatie, dus in een open systeem, een interessante manier om energie transport naar de baseplate te onderzoeken.

List of publications

Main Publications

- **Xinmeng Li**, Francesco Buda, Huub J.M. de Groot, and G. J. Agur Sevink, Contrasting Modes of Self-Assembly and Hydrogen-Bonding Heterogeneity in Chlorosomes of *Chlorobaculum tepidum*, *J. Phys. Chem. C*, **2018**, 122, 14877–14888. DOI: 10.1021/acs.jpcc.8b01790 (**Chapter 2**).
 - **Xinmeng Li**, Francesco Buda, Huub J.M. de Groot, and G. J. Agur Sevink, Molecular Insight in the Optical Response of Tubular Chlorosomal Assemblies, *J. Phys. Chem. C*, **2019**, 123, 16462–16478. DOI: 10.1021/acs.jpcc.9b03913 (**Chapter 3**).
 - **Xinmeng Li**, Francesco Buda, Huub J.M. de Groot, and G. J. Agur Sevink, Dynamic Disorder Drives Exciton Transfer in Tubular Chlorosomal Assemblies, **2020**, *submitted* (**Chapter 4**).
 - **Xinmeng Li**, Francesco Buda, Huub J.M. de Groot, and G. J. Agur Sevink, *In Silico* Prediction of Chirality versus Optical Responses of Chlorosomal Tube Aggregates, **2020**, *to be submitted* (**Chapter 5**).
- § **Code**. A software package “CTubeGen” that generates atomistic tube structure of chlorosomes. (<https://doi.org/10.5281/zenodo.3677028>)

The following is a list of additional publications not included in the thesis.

- Xiaonan Kan, Chengyi Xiao, **Xinmeng Li**, Bin Su, Yuchen Wu, Wei Jiang, Zhaohui Wang, Lei Jiang, A Dewetting-Induced Assembly Strategy for Precisely Patterning Organic Single Crystals in OFETs, *ACS Appl. Mater. Interfaces*, **2016**, 8, 18978–18984. DOI: 10.1021/acsami.6b04163
- Xiansha Xiao, Joost Willemse, Patrick Voskamp, **Xinmeng Li**, Meindert Lamers, Jan Pieter Abrahams, Navraj Pannu, Gilles P. van Wezel, Longitudinal cell division is associated with single mutations in the FtsZ-recruiting SsgB in *Streptomyces*, **2019**, bioRxiv 860916. Doi: <https://doi.org/10.1101/860916>

Curriculum Vitae

The author, Xinmeng Li, was born on the 11th of May 1990 in Binzhou, Shandong Province, China. He grew up in a village in Wudi county, belonging to an alluvial plain and near the Bohai Sea, flat everywhere, except around ten kilometers from where he lives, there is a hill, originally named as “giant mountain”, which is 63.4 meters high and covers an area of 0.39 square kilometers.

In 2007, he went to Harbin city in the most northeast province in China, Heilongjiang, and enrolled in the Northeast Forestry University to study polymer material science, developed interests in theoretical/numerical methods, and received a bachelor degree in 2011. Successively, he went to the Institute of Chemistry Chinese Academy of Sciences in Beijing to perform computational research under the supervision of Prof. H. Guo, where he explored multi-scale MD simulation methods, and received a master degree in Polymer Physics and Chemistry in 2015. In September 2015, he moved to Leiden, the Netherlands, and started his PhD research under the supervision of Dr. Agur Sevink and Prof. dr. Huub de Groot at Leiden Institute of Chemistry, Leiden University. During his PhD research about chlorosomes, he extended his research skills to linear optical spectra simulation, diffraction prediction of helical structures and quantum dynamics simulation. He also developed a helical tube reconstruction software. He gave oral presentations of his work at Physics Veldhoven (Jan. 2017), CHAINS (Dec. 2017), Dutch Molecular Dynamics Day (Mar. 2018), Summer School Multi-Scale Modeling at Lorentz Center (Jun. 2019), and Han-sur-Lesse Winter school on Theoretical Chemistry and Spectroscopy (Dec. 2016 and Dec. 2018). He also started to cycle. He cycled with Agur Sevink many times in Netherlands including once around the IJsselmeer (lake) passing the Afsluitdijk, and twice the Dam tot Dam FietsClassic events. He also has cycled along the Pieterpad from Sint-Pietersberg (Maastricht) to Pieterburen (Groningen) in Netherlands (summer 2016), from Han-sur-Lesse to Leuven in Belgium (winter 2018), and along Rhine river from Basel Switzerland to Rotterdam Netherlands (summer 2019).

Afterword

At the end of the thesis, I felt that I have gone through a wonderful adventure. To reach this point, I have made a lot of effort, and I want to emphasize here that some insights originated from daily life activities also contributed. As you may have found, the thesis has a strong focus on one unique degree of freedom, *i.e.* head-head twisting/rotational motions. This focus is largely inspired by the simple idea that a book (plate) spins easily on a finger (stick), after noticing that similarly the heads of BChl pigments in chlorosomes are supported by thin Mg-O coordination bonds (Figure 1.6). It is my luck that I can work it out. Below, I express my gratitude.



The author is spinning a book on his finger.

First, I would like to express my sincere gratitude to Huub de Groot, Francesco Buda, and Agur Sevink for making this happen. The picture of you three during my skype job interview in the summer of 2015 is still vivid. Since then, it has been a wonderful experience for me working with you together in Leiden. Huub, as my promotor, I am grateful for all your input and high scientific standard, which make this research a better one. I didn't become world-famous as you mentioned, but I still feel happy that you enjoy the outcome of this research, and thank you for all your encouragement. Franco, it is great to have you with your kindness, expertise, and wisdom. I always find comfort and benefit each time after a discussion with you. Thank you so much. Agur, as my supervisor, I owe you the most. Actively, you make sure that things went correct; passively, you share the joy (new finding! new figures!) and upsets (not possible! ridiculous, how could they do this!). You have been a great supervisor and a great friend to me;

thank you for always being there and for giving me your invaluable support, guidance, and help. Also, thank you, Soraya, for always treating me well (the beer caddy you gave to me is excellent).

Next, my gratitude to all the members in our BPOC/SSNMR group for being friendly, supportive, and warm-hearted. Especially for my office mates, and for who were visited/bothered by me, as I like to walk around when I solved something. Alia, Anjali, Brijith, Chen, Dario, Dieuwertje, Emanuela, Faezeh, Fatameh, Fons, Jan Paul, Jessica, Karthick, Kiran, Laura, Liesbeth, Lijin, Lina, Lolita, Maithili, Remco, Rianne, Rico, Rubin, Srividya(Vidya), Tirong, Yang, Yuliya, and Zhongwu, as well as other people I met in the university, thank you all. Especially, Liesbeth, thank you for always being there and taking care of all the problems I bring to you. I hope the trick I was walking with a USB mouse pet can bring you some amusement. It is also fantastic for me to meet some Chinese friends in this lovely city. Although we may not be able to meet here anymore, 青山一道同云雨, 明月何曾是两乡.

I am also grateful for the members of the reading committee. Thank you for all your effort and time in the reading and assessment of my thesis. I would like to express my gratitude to all the people giving me understanding, support, and help during my graduation procedure, especially during such a hard time with the outbreak of COVID-19.

My special gratitude goes towards QQ. Thank you for bringing color and sound into my silent film life. The moment you were cooking swimming crab and I was writing on a tissue calculating the distances between helices is one of what I most cherished. Last but not least, my heartfelt gratitude towards my parents and other family members for their patience and support all the time.

Xinmeng
March 2020, Leiden