Exploring disordered exciton landscapes in chlorosomes

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Summary

Research is never finished, only abandoned.

All of you patient readers, enthusiasts, and explorers, our quest for spectral signatures is now ending! This journey might have opened more questions than it answered, so I hope you will not resent it but use it as an inspiration for future endeavours.

If we think about photosynthesis, the initial idea that comes to mind might be plants and their elegant way of orienting towards the Sun. The photosynthetic world is substantially larger, full of contradictions and mysteries. For a long time, the existence of tiny organisms called green bacteria that perform photosynthesis in extremely dark conditions, like at the bottom of the sea, was a well-kept secret.

Their discovery made scientists wonder about *how are they doing it?* And ask questions about *the key mechanisms responsible for capturing enough scarcely incoming photons and preventing unnecessary energy loss*. Furthermore, solutions implemented in nature inspire improvements and the development of new artificial systems, which can support the efficiency of our solar energy sources not only during sunny but also on cloudy days.

Years of dedicated research showed the importance of chlorosomes for efficient light harvesting in green sulfur bacteria. Chlorosomes are light-harvesting antennae known for their large size and unusual structure free from a protein scaffold. They capture light and initially transfer the excitation energy in the photosystem of green bacteria. Studies of light harvesting processes in controlled conditions often involve spectroscopy experiments. These experiments utilize light sources like laser pulses to access and characterize properties and dynamical processes in different states of matter. Several spectroscopy experiments were performed on chlorosomes and photosynthetic apparatus of green bacteria, observing different transfer pathways of the absorbed energy, and providing novel insights into key mechanisms that these or-

ganisms rely on for survival.

This thesis presents the results of the theoretical modelling and spectroscopic simulations. It provides a detailed physical understanding of the mechanisms supporting the functional role of chlorosomes. The general question raised in this thesis is: *"Are there (observable) spectroscopic signatures of the molecular effects supporting efficient light-capture and energy transfer in chlorosomes?"* To find answers to this question, I studied the origin of the absorption band broadening, which is relevant for absorbing as many photons of different energy, and mechanisms supporting observed ultrafast energy transfer in chlorosomes. Since chlorosomes are a natural 'messy' system, my work especially focuses on describing the effects of irregularities [I] in the structure and molecular interactions on the collective properties of the whole system. To reveal this intricate structure-signature relationship, I constructed a computational framework which relies on several chemical and physical models to simulate spectroscopic experiments.

Based on the experimental evidence, we chose our models of chlorosome aggregates to be cylindrical structures made of thousands of chromophores (bacteriochlorophyll BChl molecules). The collective electronic excitation (exciton) dynamics dictate the function of these light-harvesting aggregates, which are directly probed in optical spectroscopy experiments. The presence of irregularities and structure fluctuations lead to irregularities (disorder) in exciton dynamics. Even though the presence of heterogeneities appears as a negative feature, studies showed that biological systems utilize fluctuations and disorder for efficient and robust light absorption and energy transfer, critical for initiating the process of photosynthesis. Optical spectroscopy and structure determination provide evidence for a large amount of structural disorder in chlorosomes from green bacteria. The work presented in this thesis uncovered the origin of the molecular disorder leading to changes in excited state landscape and observable effects in optical spectra and spectral dynamics in chlorosomes.

Figure S summarizes the spectral studies of four different properties of chlorosomes explored in this thesis. Here, I combine the interpretation of existing (Chapters 2 and 4) and propose new spectroscopic signatures and experiments (Chapters 3 and 5) to resolve open questions on the connection between structure and spectral dynamics.

The first aim was to identify sources of disorder in molecular interactions and their effect on spectral properties. Bacteriochlorophyll molecules, the building block of chlorosomes, have donor and acceptor hydrogen bond groups, and they can form up to two hydrogen bonds in chlorosomes. Not all possible hydrogen bonds are

[I] Irregularities, heterogeneity, and disorder are used interchangeably in this text.

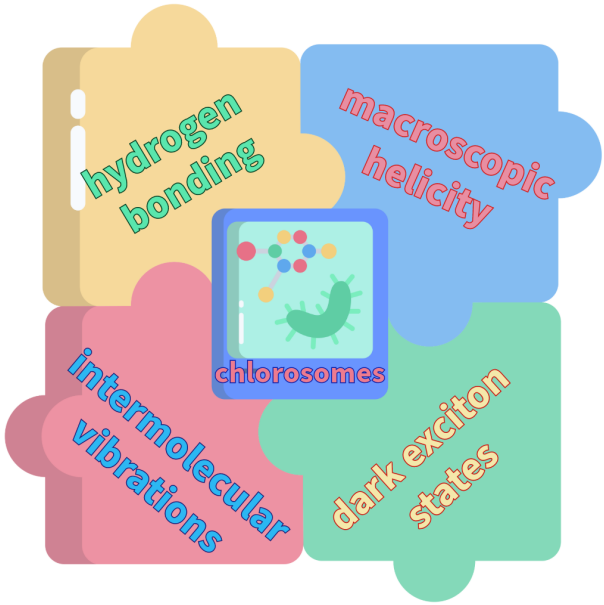

Figure S: *Summary of the research presented in this thesis. We connected hydrogen bonding [Chapter 2], macroscopic helicity [Chapter 3], dark exciton states [Chapter 4], and intermolecular vibrations [Chapter 5] in chlorosomes to their spectral signatures in optical spectroscopy experiments.*

formed in realistic chlorosome aggregates, leading to irregularities in hydrogen bonding networks. Chapter 2 portrays this heterogeneity as a leading cause of the significant spectral broadening of absorption spectra of chlorosomes and proposes a functional role of hydrogen bonds in chlorosomes.

The second aim was to resolve the debate about the molecular organization in chlorosomes. These aggregates can be presented as sets of helices wrapped around cylindrical geometry. Thus, the macroscopic helicity determines molecular arrangement in the aggregate. Two different experiments reported contrasting structures of chromosomal aggregates. Our comparative study identified that the ultrafast anisotropy decay experiment yields contrasting signals for the two chlorosome structures, providing a potential solution to this debate. Furthermore, the connection of our findings with existing literature on chlorosomes from different bacterial species shows that macroscopic chirality highly depends on the light conditions in which bacteria grow, and it can present an adaptation mechanism.

Chapter 4 provides a novel interpretation of experimentally observed ultrafast