A computational study of structural and excitonic properties of chlorosomes

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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.