



Universiteit
Leiden
The Netherlands

Bridging the gap between natural & artificial light-harvesting : a structure-function investigation with MAS NMR

Ganapathy, S.

Citation

Ganapathy, S. (2008, November 26). *Bridging the gap between natural & artificial light-harvesting : a structure-function investigation with MAS NMR*. Retrieved from <https://hdl.handle.net/1887/13282>

Version: Corrected Publisher's Version

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/13282>

Note: To cite this publication please use the final published version (if applicable).

Summary

Photosynthesis is a process in which the light-energy from the sun is captured and converted into biochemical energy. The process of photosynthesis contains multiple steps, the first of which involves the capture of light by the photosynthetic antenna systems and subsequent transfer of excitation energy to the RC. The role of these antenna systems as solar energy collectors makes their extensive characterization a starting point towards the construction of artificial devices mimicking photosynthesis to collect, direct, and apply solar radiation to produce environmentally clean fuel. In this thesis it is demonstrated how MAS NMR, in combination with ring current shifts calculations, can be adapted and exploited for the structural characterization of light-harvesting antennae comprising of supramolecular assemblies of pigments having biological origin or those that are chemically synthesized. **Chapter 1** presents a general introduction to the biological and artificial antenna systems that are studied during the course of this thesis.

Chapter 2 provides a brief theoretical overview of the solid-state NMR methods that have been utilized for the work presented in this thesis. An introduction to MAS NMR and CP has been given. The methods used for ^{13}C and ^1H chemical shift assignment are briefly discussed. The CHHC experiment that has been used to obtain structure-defining through-space distance constraints is also described in this chapter.

The LH2 complex is an α -helical membrane protein complex with BChl cofactors. In **Chapter 3** the CHHC experiment has been successfully applied on this protein for the detection of through-space intermolecular distance constraints on uniformly ^{13}C labeled and pattern labeled preparations. It has been possible to detect correlations between nearby amino-acid residues within a helical segment and also between segments. Additional contacts between amino-acid residues and the BChl cofactors could also be resolved. These experiments were done primarily to ascertain the effectiveness of the experiment as well as to get a first hand estimate of the polarization transfer range.

Chlorosomes are a class of BChl light-harvesting antenna found in phototrophic bacteria. Chlorosomes from the *bchQRU* mutant are studied in **Chapter 4**, which is a BChl biosynthesis mutant of *C. tepidum* that comprises of self-organized 17²-farnesyl-*R*-[E,M] BChl *d* molecules. The advantage of studying chlorosomes from this mutant is based on cryo-EM data that has shown these mutant chlorosomes to possess a high degree of structural order. This translates into well resolved MAS NMR datasets, which allow the detection of distance constraints from measurements on uniformly ¹³C-enriched chlorosome preparations. These constraints have shown that alternating BChls form *syn-anti* monomer stacks. Together with structural constraints obtained from cryo-electron microscopy, it has been shown that chlorosomes are assembled from a basic unit of two BChl molecules into helical tubes with tails on both sides of the layers. A comparison of experimentally determined proton aggregation shifts with those derived from DFT modeling validated *syn-anti* monomer stacking as the fundamental unit.

This model has been adapted to describe the suprastructural assembly of another mutant of *C. tepidum* in **Chapter 5**, which is the 17²-farnesyl-*R*-[E,M] BChl *c* producing *bchQR* mutant. A preliminary comparative assessment of the structure of this mutant with respect to the WT has been made in this chapter. Distance constraints resolved also suggest *syn-anti* stacking of the BChl *c* molecules. Pronounced doubling (1:1) of selective ¹³C and ¹H resonances is observed revealing the presence of two distinct and nonequivalent BChl *c* components. The presence of a methyl group at the 20-meso position in BChl *c* results in varying ring distortion between *syn* and *anti* ligated molecules in a stack of the saddling, ruffling, and doming types. Chemical shift calculations performed on *syn* and *anti* coordinated monomers of BChl *c* suggest that the different ring deformations that arise from the steric hindrance of the methyl group present at the 20-meso position upon rotation of the 3¹ methyl group going from a *syn* to an *anti* coordinated molecule within a stack is in part responsible for the doubling observed in the NMR spectra.

Finally in **Chapter 6** the transition from the natural pigment aggregates of the chlorosomes to artificial pigment aggregates is made. Aggregates of

two semi-synthetic zinc chlorin compounds, differing only in their 3¹ substituents with one having a hydroxy group and the other a methoxy group are investigated in the solid-state. Using the ¹H-¹³C heteronuclear dipolar correlation MAS NMR experiment on natural abundance samples, a ¹H chemical shift assignment of the chlorin ring of the hydroxy-chlorin and methoxy-chlorin has been made and corresponding aggregation shifts relative to their monomer shifts in solution are determined. Ring-current shift calculations reveal unambiguously that out of two possible types of well-ordered π -stacked arrangements of the aggregates that have been observed for the methoxy-chlorin in solution, *i.e.* the parallel stack and the antiparallel stack, in the solid-state both zinc chlorins self-assemble in antiparallel stacks. As a result even without isotopic enrichment, access to the proton chemical shifts of aggregated zinc chlorins allows accurate probing of ring-currents and can be related to the stacking of macrocycles.

