Carotenoids to bacteriochlorophyll c energy transfer in self-assembled aggregates

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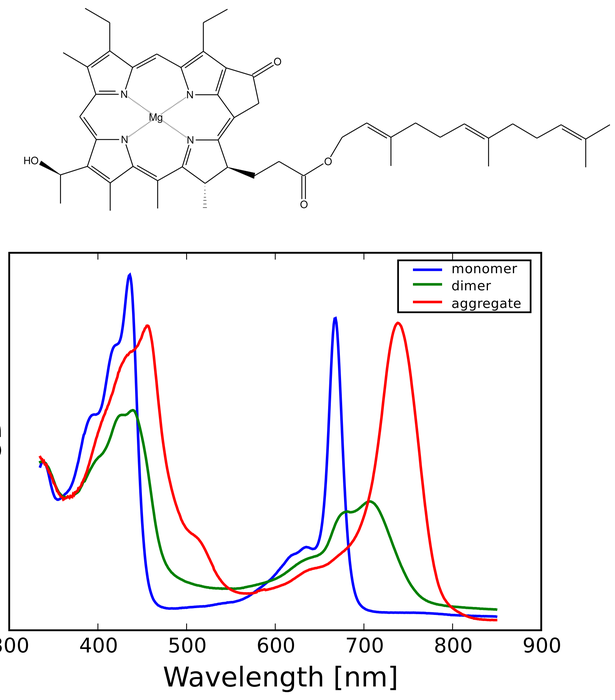
MOTIVATION

Carotenoids are together with bacteriochlorophyll (BChl) c, d or e important constituents of chlorosomes, the unique light-harvesting antennae of green photosynthetic bacteria. The chlorosomes also contain quinones and, in the envelope and baseplate connecting the chlorosome to the cell membrane, lipids and proteins.

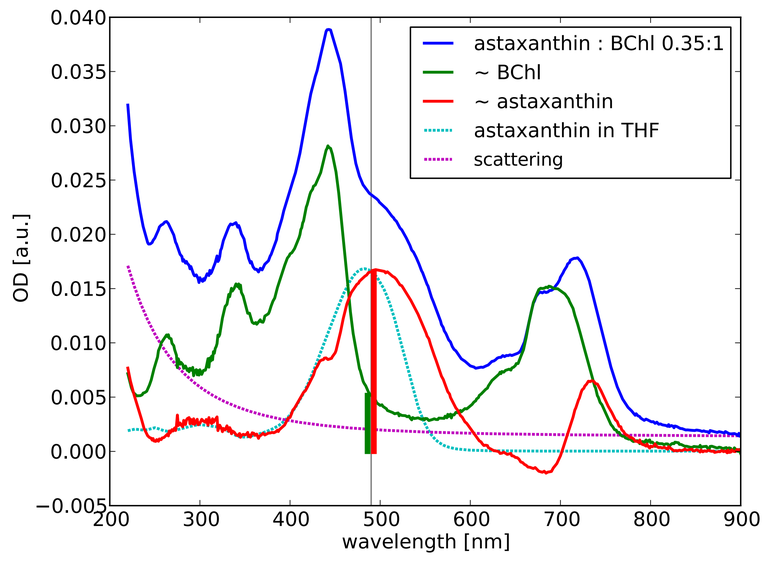
Aggregates of BChl c with spectroscopic properties similar to those of chlorosomes can be prepared in vitro by injecting BChl mixed with a suitable non-polar molecule into a polar environment. In this study we used carotenoids astaxanthin and β-carotene as aggregation inducing agents.

Aggregation of BChl c was evaluated on the basis of the red shift of its Qy absorption band. This shift is caused by excitonic interactions between BChl c molecules and depends on mutual orientation of their transient dipole.



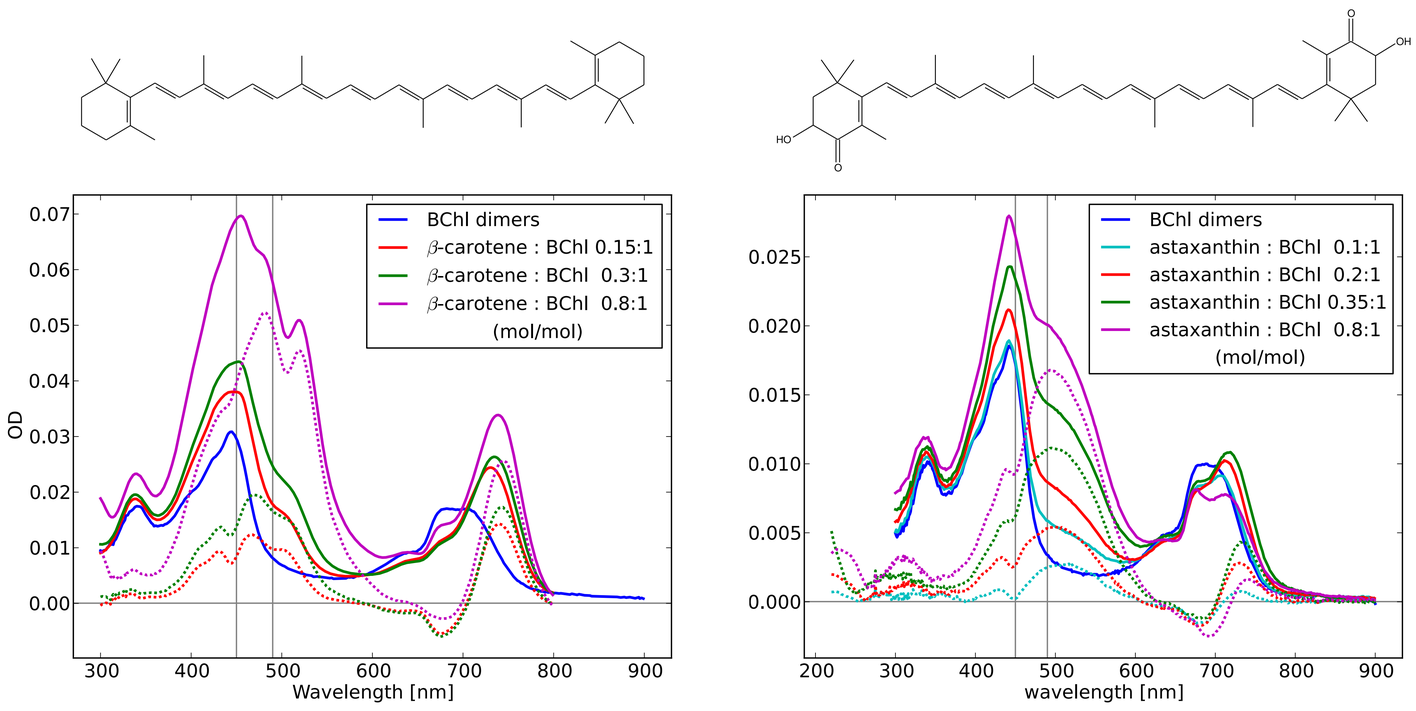
The red shift of Q_Y absorption band of BChl c (structure on top) depends on the aggregation state.

SPECTRA DECOMPOSITION



Absorption spectra of the BChl:carotenoid aggregates can be decomposed to BChl and carotenoid contributions. Relative amount of respective molecules in the sample (molar ratio) and relative amount of excited molecules for a given excitation wavelength can be estimated from the decomposition.

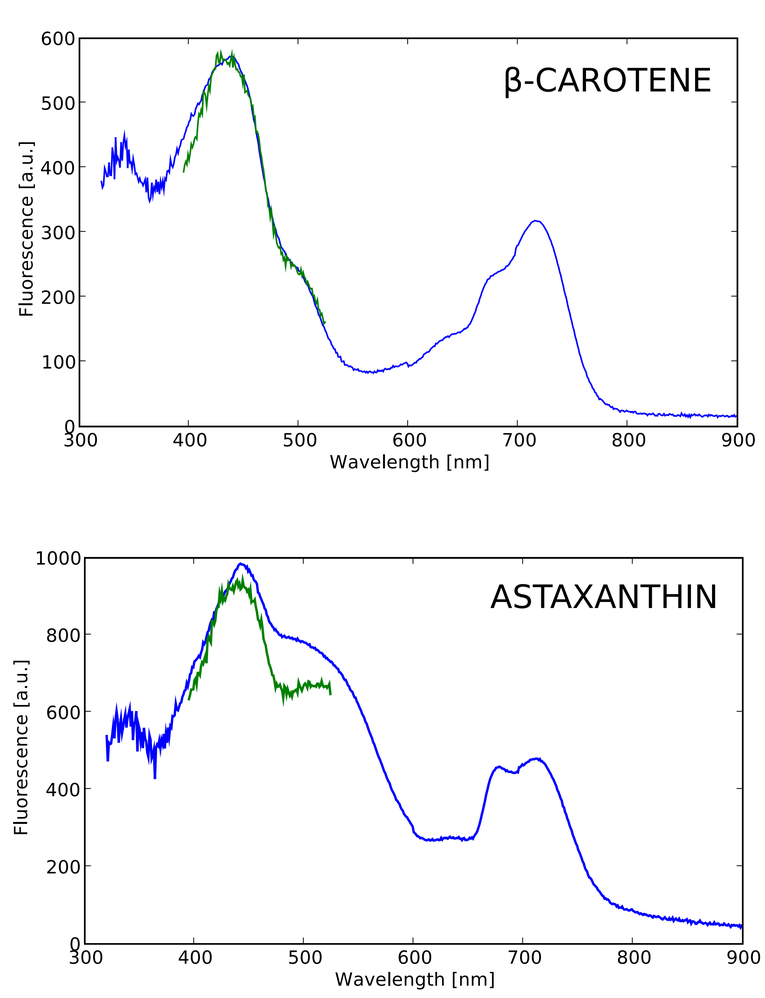
ABSORPTION SPECTRA OF BCHL AGGREGATES



Absorption spectra of BChl aggregates with β-carotene (left) or astaxanthin (right) as aggregation inducing agent. Carotenid contributions are depicted as dotted lines (of corresponding colour). Carotenoid structures are shown on top of the figures.

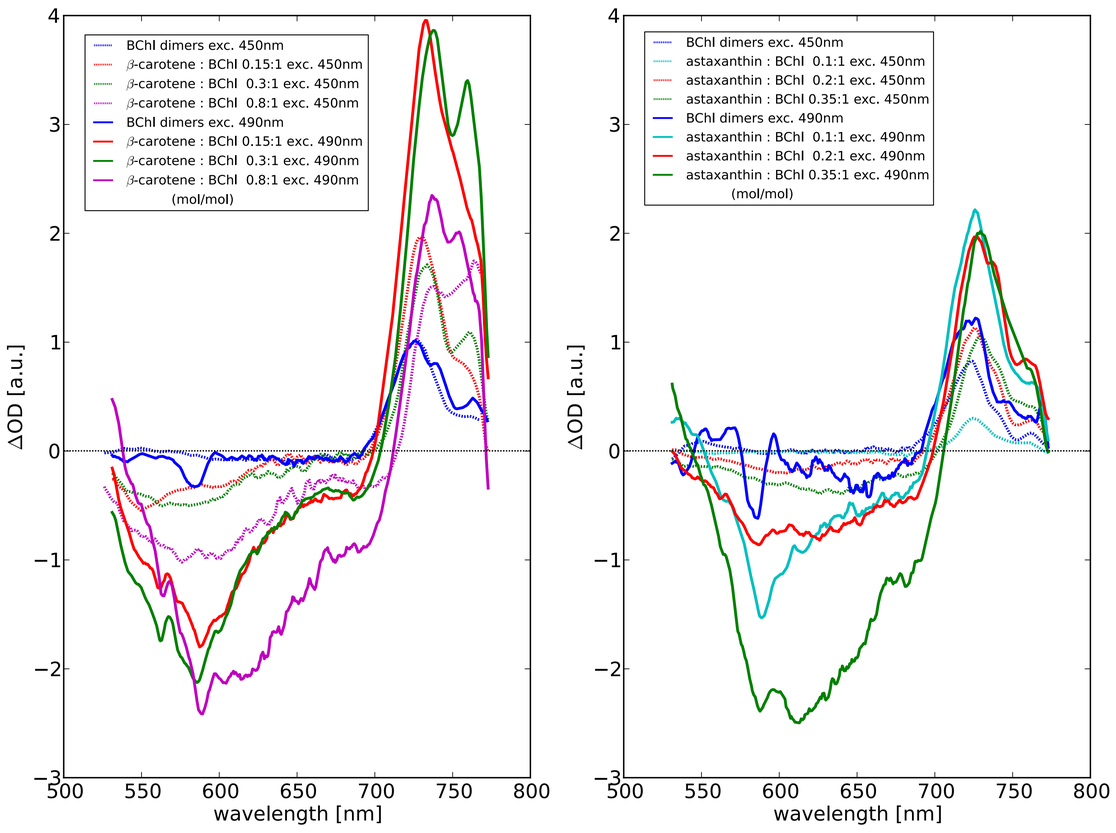
- β-carotene is more effective than astaxanthin in inducing BChl c aggregation.
- Astaxanthin promotes formation of a monomer-like form of BChl c, presumably because hydroxy and keto groups of astaxanthin compete with respective groups of BChl c for bonding sites stabilizing BChl aggregate.
- Contribution of β-carotene to the sample absorption changes for higher concentrations, probably due to β-carotene aggregation.

EXCITATION SPECTRA



Excitation spectra (green line) and corresponding (1-Transmittance) spectra (scaled to fit, blue line).

TRANSIENT ABSORPTION - DECAY ASSOCIATED SPECTRA



Transient absorption spectra were measured after excitation at 450nm and 490nm. Data were fitted with a multi-exponential model. Figures to the left show comparison of decay associated spectra (normalized to the same amount of excited BChl molecules) of a ~100fs component determined for samples with different carotenoid concentrations. This component corresponds to the energy transfer from higher excited states to the S1 state of BChl c.

The negative band corresponds to stimulated emission from the S2 state of carotenoids. The positive band corresponds to photo-bleaching and stimulated emission of S1 state of BChl c; it has a positive sign because the S1 state is receiving energy.

Theoretical analysis shows that the amplitude of carotenoid band should be proportional to the ratio of directly excited carotenoid and BChl molecules. This is indeed true within 22% error. BChl c band should consist of contribution due to energy transfer from the S2 state of BChl c (dark blue lines) and, possiby, an additional contribution due to energy transfer from the S2 state of carotenoids. The second contribution is expected to be proportional to the ratio of excited molecules and to the energy transfer rate constant.

- Energy transfer occurs from the S2 state of β-carotene and astaxanthin to the S1 state of BChl c.
- Energy transfer from β-carotene is more efficient than from astaxanthin as manifested by both transient absorption and fluorescence excitation spectra.
- Energy transfer efficiency is decreasing for higher concentrations of carotenoids.

Acknowledgements
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