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INFLUENCE OF AGGREGATION AND LINKER PROTEINS ON CHROMOPHORE STRUCTURE IN ALLOPHYCOCYANIN (MASTIGOCLADUS LAMINOSUS)

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In cyanobacteria and red algae, the antenna proteins contain several open-chain tetrapyrrole bilin chromophores which are bound covalently to the apoprotein. Chromophore-protein interaction determines the geometry of the chromophores and tunes the spectral properties according to their biological function. The knowledge of the chromophore geometry and/or its changes upon aggregation or under the influence of the so-called linker proteins are therefore essential for the understanding of the energy transfer processes within the antenna complexes (phycobilisomes).

In the cyanobacterium Mastigocladus laminosus, the phycobilisomes contain three different biliproteins, namely phycoerythrocyanin (PEC), phycocyanin (PC) and allophycocyanin (APC). In contrast to PC, the UV-vis absorption spectrum of APC changes dramatically upon going from the monomeric to the trimeric aggregation state and depends also on the presence of linker proteins [1]. In Fig. 1 the CARS-spectra of APC in various states are compared. Each solid line represents the best fit applying the usual expression for the third order suszeptibility $\chi^{(3)}$ (for more details see ref.2). The numbers given in the figures represent the vibrational frequencies as derived from the fit procedure.

The CARS spectrum of the monomers is independent of the presence of linker proteins and very similar to that of PC monomers. This indicates that in the monomeric state the chromophores exhibit similar geometries and experience similar interaction with the apoprotein. Upon aggregation into the trimeric state, one observes only minor but significant changes in relative intensity in the spectral region below 1500 cm^{-1}. The 1644 cm^{-1} band is reduced in intensity (and slightly shifted), and a new strong band shows up at 1618 cm^{-1}; the band at 1592 cm^{-1} splits up into two bands. If one assumes that, like in the case of PC and PEC, the $\alpha 84$ chromophore experiences new interactions with the protein of

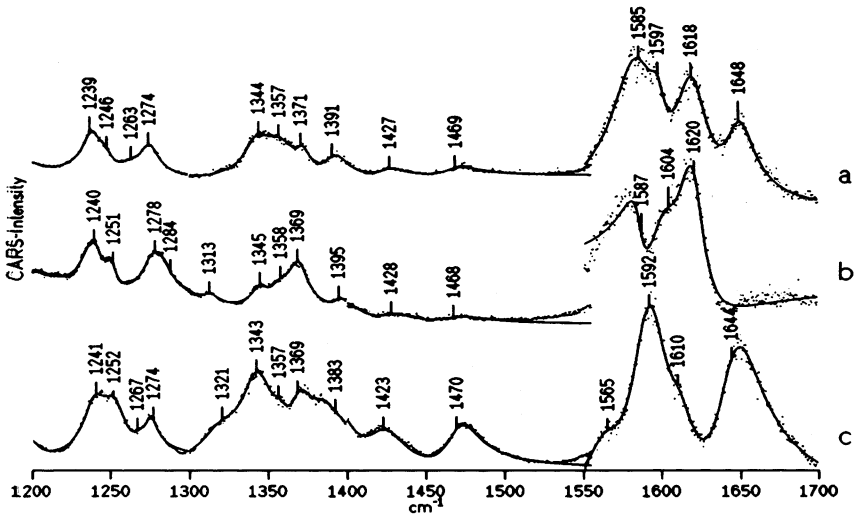

Fig. 1. CARS spectra of APC in H_2O (λ_P = 630 nm). a: trimer without linker, b: trimer with linker, c: monomer.

the neighbouring monomeric unit, then it should be the α-chromophore which undergoes the rearrangement in geometry. Upon introduction of the linker, the most pronounced change is the complete dissappearance of the band around 1648 and the increase of the band around 1620 cm^{-1}. The band at 1597 cm^{-1} is replaced by one at 1604 cm^{-1}. These spectral changes must be related to changes in chromophore-protein arrangement of the ß-chromophore. The described spectral changes are similar to those observed with pump wavelength 645 nm and suggest isomerisation around the double bond between rings C and D combined with a change in the state of hydrogen bonding and/or protonation.

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