

• **Analysis of the excited-state relaxation dynamics of *cis-trans* β -apo-8'-carotenal by femtosecond time-resolved absorption spectroscopy in Vis to Near IR spectral regime**

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Carotenoids are natural pigments that are found all over the world and play important roles of light-harvesting and photoprotection in the primary process of photosynthesis. When carotenoids absorb photons, they are excited up to the second excited singlet (S_2) state from the ground (S_0) state. The optical transition to the first excited singlet (S_1) state is forbidden. The other important excited states are the intramolecular charge transfer (ICT) and S^* excited states. The ICT excited state is very important to improve the efficiency of excitation energy-transfer from carotenoid to chlorophyll [1]. However, there still remains contradictions for the interpretation. It is also controversial that the transient absorption signal around 520 nm wavelength region derives from the S^* excited state or from the hot S_0 state. Thus, although carotenoids have several excited states which are essential for photosynthetic energy transfer, most of their origins are not completely determined yet. In this study, we investigated the excited state dynamics of β -apo-8'-carotenal in terms of the geometric isomers, using femtosecond pump-probe time-resolved absorption spectroscopy.

We measured femtosecond transient absorption spectra of the 13'-, 15-, 13-, 9-, 7-, 9,13'-, 9,13-, and 13,13'-*cis* isomers of β -apo-8'-carotenal dissolved in *n*-hexane, acetone, and methanol. In polar solvents (acetone and methanol), we found that the *cis* isomers of β -apo-8'-carotenal stabilize the ICT excited states as well as the all-*trans* isomer. In the S^* excited state or in the hot S_0 state, however, the *cis* isomers show unique transient absorption spectral characteristics. The intensity of the shoulder signal shown in Figure 1 is in the order, 7-*cis* > 9-*cis* > 13-*cis* > 15-*cis* > 13'-*cis* isomers. This trend corresponds to the order of the position of the *cis*-bend structure from the terminal β -end-ring. This shoulder signal is still controversial whether it originates from the S^* excited state or from the hot S_0 state. However, we found a regularity that leads to the clarification of the shoulder signal, which is unequivocally found in the *cis* isomers.

1) H. Hashimoto, *et al.*, *J. Photochem. Photobiol. C: Photochem. Rev.* **2015**, 25, 46-70.

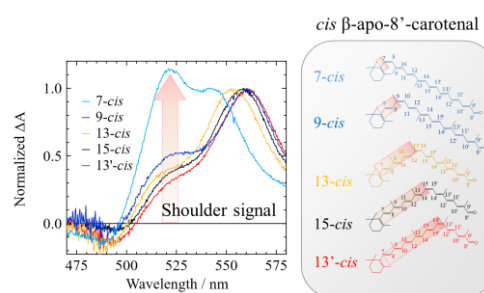


Figure 1. The relationship between the strength of the shoulder transient absorption bands and the mono-*cis* (7-, 9-, 13-, 15-, and 13'-*cis*) isomers of β -apo-8'-carotenal.