Singlet fission in lycopene aggregates: the ultrafast consequences of red tomatoes

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Lycopene, a carotenoid with eleven conjugated double bonds, is commonly found in ripe red fruits, such as tomato, red bell pepper and water melon. Although the fruit color is red, lycopene solutions in different solvents are yellow to orange, depending on the polarizability of the environment. In ripe tomato chromoplasts it undergoes a large absorption red-shift. This effect is proposed to arise from the aggregation of lycopene in the chromoplast.

Our recent ultrafast measurements on aggregated lycopene revealed dynamics that is significantly different from monomeric or protein-bound carotenoids. The main discovery was the formation of the sates that decay on µs-ms time scales and are found both in *in vitro* aggregates and intact chromoplasts of tomatoes.[3] We ascribed those states to triplet states formed via singlet fission in closely packed aggregates. Currently, the precise pathway of formation of these triplet states and remains under debate.[2,3]

In this contribution, we present an attempt to address this issue by the combination of UV-VIS pump-probe fs-µs spectroscopy, Raman spectroscopy supported by global and target analysis of the data. The observed transient absorption dynamics shown in Figure 1 present significant challeneges due to apparent rise/fall dynamics and blue-red shifting of induced absorption bands.

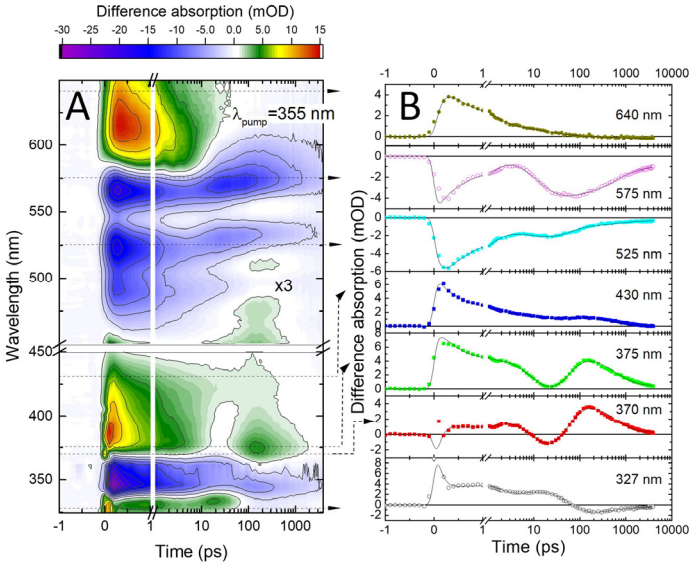

Figure 1: Femtosecond-to-nanosecond transient absorption data of lycopene aggregates upon excitation at 355 nm. A: contour plot of the dataset. B: kinetic traces measured at different wavelengths (indicated on the graphs) along with the results of the global fit.

Target analysis revealed the presence of at least 6 different components in the data. The observed shifting and apparently complicated dynamics seen in Figure 1 is apparently due to both J and H aggregates with large degree of disorder simultaneously present in the preparations and undergoing different relaxation pathways.

References

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