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Monitoring excited-state relaxation in a molecular marker in live cells-a case study on astaxanthin

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Small molecules are frequently used as dyes, labels and markers to visualize and probe biophysical processes withing cells. Though the optical properties and excited-state relaxation pathways of these molecules have been studied intensively, [1, 2] very little is generally known about the light-driven excited-state reactivity of such systems when placed in live cells. In this work, we introduce an experimental approach to study ps time-resolved excited state dynamics of a benchmark molecular marker, AXT (astaxanthin), in live human cancer cells. AXT stains lipids in cells rendering lipid-containing structures easily detectable by resonance Raman microscopy. Based on shifts in the C=C stretching band of the Raman spectrum [3] it was suggested that AXT undergoes confirmational changes in the cellular organelles as compared to isolated AXT in solution. In contrast, the photoinduced excited-state dynamics in AXT recorded in cellulo

appears to be unchanged compared to the dynamics detected in solution. That indicates that the absence of AXT aggregation in the cells, and the structural distortion of the AXT molecules do not alter the excited-state properties. [4]

In a methodological context we show that our approach to in cellulo transient absorption spectroscopy offers a valuable path to study the impact of the local environment on the photoinduced dynamics in stains, markers and beyond this in light-activated drugs, e.g. for photodynamic therapy, [5] and interactions between phototherapy agents and live cells.

[1] Fuciman, M., et al., Chemical Physics Letters, 2013, 568, 21-25. https://doi.org/10.1016/j.cplett.2013.03.009

[2] Kaczor, A. and Baranska, M. Anal Chem, 2011, 20,7763-7770. https://doi.org/10.1021/ac201302f

[3] Czamara, K., et al., Cell Mol Life Sci, 2021, 7, 3477 - 3484. https://doi.org/10.1007/s00018-020-03718-1

[4] Yang, T., et al., Chem Commun, 2021, 57, 6392-6395. https://doi.org/10.1039/D1CC01907D

[5] Monro, S., et al., Chemical Reviews, 2018, 119, 797-828. https://doi.org/10.1021/acs.chemrev.8b00211

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