

Delocalized vs localized excitations in the photoisomerization of azobenzene-functionalized alkanethiolate SAMs

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Mixed self-assembled monolayers (SAMs) of azobenzene-functionalized and non-functionalized alkanethiolates on Au(111) represent well-defined ensembles enabling reversible bidirectional photoisomerization between the *trans* and *cis* form of the azobenzene. In such SAMs the azobenzene moieties form aggregates with the coupling strength depending on the aggregate size and the density and mutual orientation of the chromophores [1]. It has been under debate in how far the excitonic coupling and thereby the delocalization of the optical excitation influences the photoisomerization. To address this question, we investigated the switching behaviour as a function of excitation wavelength in the range of the excitonically broadened S₂ absorption band. As probe we use differential reflectance spectroscopy and two-photon photoemission spectroscopy (2PPE). The latter technique serves to determine the sample work-function which is a direct measure of the SAM's isomer composition due to the very different static dipole moments of the *cis* and the *trans* isomer [2]. The effective isomerization cross-section is found to increase towards shorter wavelengths while the fraction of *cis* isomers in the photostationary state decreases. This behaviour resembles that of non-interacting molecules in solution, despite the formation of H-aggregates. We thus conclude that strongly excitonically coupled, delocalized states of the aggregate do not contribute significantly to the photoisomerization [3].

References:

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