

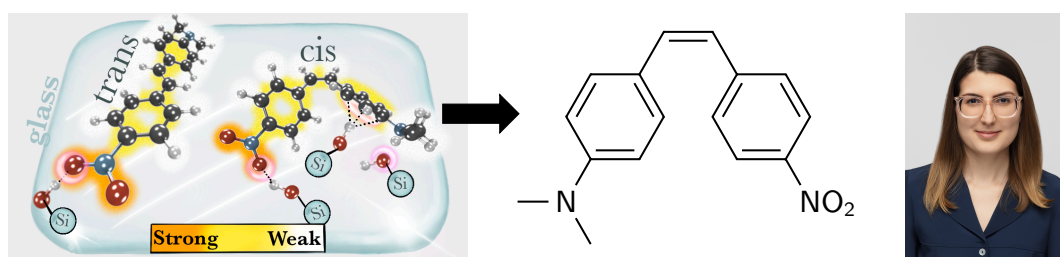
# Adsorption and Absorption of Push-Pull Functionalized Stilbene on an Amorphous Silica Glass

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Photoswitches are molecules that can reversibly change between different isomers when excited by light. One notable example is 4-(N,N-dimethylamino)-4'-nitrostilbene (DANS), which exhibits a strong charge transfer character in its excited state, thereby making it highly sensitive to environmental conditions. While the effects of solvents are well-studied, the impact of heterogeneous environments, such as metal oxide surfaces like alumina and silica, is rather neglected despite their common use in various analytical setups.

In our study, we investigate how an amorphous silica surface influences the photophysics and photochemistry of DANS (i.e. photoisomerization vs. fluorescence decay). To achieve this, we employed density functional theory calculations to determine the preferred adsorption orientations of DANS on silica surfaces.[1] Our findings indicate that O–H···O hydrogen bonds between surface hydroxyl groups and the NO<sub>2</sub> group of DANS makes the most significant contribution to the interaction energy and predominantly dominates the adsorption mode of the molecule. Additionally, weaker dispersion-like interactions contribute promoting a very stable parallel adsorption geometry. To further understand the influence of glass, we computed and analyzed the absorption spectra of DANS both in the gas phase and in various configurations on a silica cluster.[2] Our focus was on how different adsorption modes impact the absorption spectra. The electron-accepting capacity is significantly enhanced by O–H···O hydrogen bonds, which in turn strengthens the "push-pull" properties. Conversely, O–H···N hydrogen bonds to the NMe<sub>2</sub> group reduce its electron-donating capacity.

As a final step towards completing our study on the influence of glass on DANS, we plan to carry out nonadiabatic dynamics simulations of the molecule on the surface. This presents several challenges. Firstly, simulating the photoswitching via the conical intersection between the ground state and the first excited state of DANS requires a multireference method. Secondly, due to the surface environment, we need to decide between using periodic boundary conditions or a cluster approach. Either option necessitates a large unit cell or cluster, which significantly

increases computational costs. The Libra Summer School on Excited States and Nonadiabatic Dynamics in Materials provides an opportunity to address the aforementioned challenges and to gain understanding of the influence of glass on the photophysics and photochemistry of DANS.

## References

- [1] D. Vörös, A. Angeletti, C. Franchini, S. Mai, L. González, “Adsorption of 4-(N, N-Dimethylamino)-4'-nitrostilbene on an Amorphous Silica Glass Surface”, *J. Phys. Chem. C*, 2023, *127*, 22964–22974.
- [2] D. Vörös, F. Proché, S. Mai, L. González, “Hydrogen Bonding to the Electron accepting Group Controls the Absorption Spectrum of a Push–pull Stilbene adsorbed on Amorphous Silica”, submitted, **2024**.