

## Chemoselective Reactivity of Bifunctional Cyclooctynes on Si(001)

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Organic functionalization of semiconductor surfaces and its potential for the miniaturization in semiconductor technology has motivated detailed investigations of the adsorption of organic molecules on semiconductors, especially on silicon. However, controlled organic functionalization of semiconductor substrates under well-defined vacuum conditions has not been achieved so far. The challenge is the chemoselective covalent fixation of bifunctional molecules on these substrates leaving the remaining second functional group available for further building up of complex molecular architectures. The main difficulty in achieving the required chemical selectivity on semiconductor surfaces, especially on the technologically most relevant Si(001) surface, arises from the high reactivity of their dangling bonds; typically, a mixture of molecules adsorbed with different functional groups is observed.

In this contribution, we present STM- and XPS-experiments on the adsorption configurations of bifunctional cyclooctyne derivatives with different functional side groups. These molecules show indeed such a chemoselective fixation: The strained cyclooctyne triple bond adsorbs selectively on-top of a silicon dimer while leaving the other functional groups intact. The achieved chemoselectivity is explained taking the distinctly different adsorption dynamics of the separate functional groups into account: Using molecular beam techniques, we demonstrate a direct adsorption pathway for the strained cyclooctyne triple bond. This is opposed to the majority of most organic functionalities, which generally adsorb on Si(001) via a metastable intermediate state. Thus, even if the cyclooctyne derivative first adsorbs in this metastable intermediate, the reaction of the strained triple bond is still accessible and in fact kinetically more favorable than the further reaction of the other functional group.

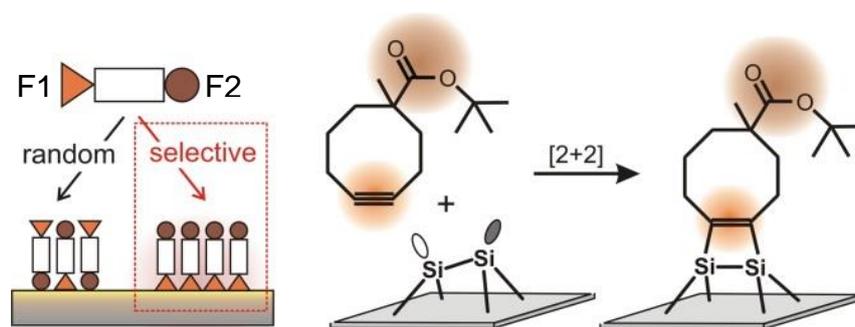


Fig. 1. (left) Schematics of the adsorption process of bifunctional (F1, F2) organic molecules on Si(001). The high reactivity of the surface dangling bonds leads typically to a random adsorption via F1 or F2. (right) In the case of bifunctional cyclooctyne derivatives, a chemoselective adsorption with the strained triple bond is observed; F2 stays intact for further functionalization.

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