

Organic molecular architectures synthesized on Si(001) by means of selective click reactions

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The concept of molecular layer deposition on solid surfaces is promising for the synthesis of layers with well-controlled physical and physicochemical properties. Molecules with two functional groups are suitable building blocks for covalent layer-by-layer synthesis. However, with symmetric bifunctional organic molecules, i.e., with two identical functional groups at one molecule, side reactions which hinder the well-controlled layer-by-layer growth, e.g., by chain termination, may occur.

Here we solve this problem using a combination of two selective and orthogonal click reactions for controlled covalent layer-by-layer growth on Si(001). In order to do so, we combine ultrahigh-vacuum-(UHV)-based functionalization of the Si(001) surface with solution-based click chemistry for the attachment of the further layers. The starting point is the Si(001) substrate which is functionalized via selective adsorption of the bifunctional ethynylcyclopropylcyclooctyne (ECCO) molecule under UHV conditions [1]. This first-layer sample is then transferred into solution [2] in order to perform the subsequent layer-by-layer synthesis using the two orthogonal click chemistry reaction steps in an alternating fashion (Fig. 1): First, a diazide is coupled in acetonitrile via a copper-catalyzed azide-alkyne click reaction; second, a layer of ECCO molecules is coupled via a catalyst-free, strain-promoted azide-alkyne click reaction. Without contact to ambient conditions, the samples are analyzed by means of X-ray photoelectron spectroscopy in UHV after each reaction step in solution; the N 1s spectra clearly indicated in the first step the selective click reaction of the primary azido group of the diazide molecule, whereas the tertiary azido group stayed intact. In the second step, this tertiary azido group was reacted selectively with the strained triple bond of the ECCO molecule in solution, forming a third layer of organic molecules on Si(001) with the terminal triple bond of ECCO available for further reactions according to this cyclic reaction scheme (Fig. 1). Alternating application of the two orthogonal reaction steps then led to a well-controlled layer-by-layer growth up to 11 layers [3]; it opens the possibility for the controlled synthesis of layers with physical or physicochemical properties that alternate on the molecular scale.

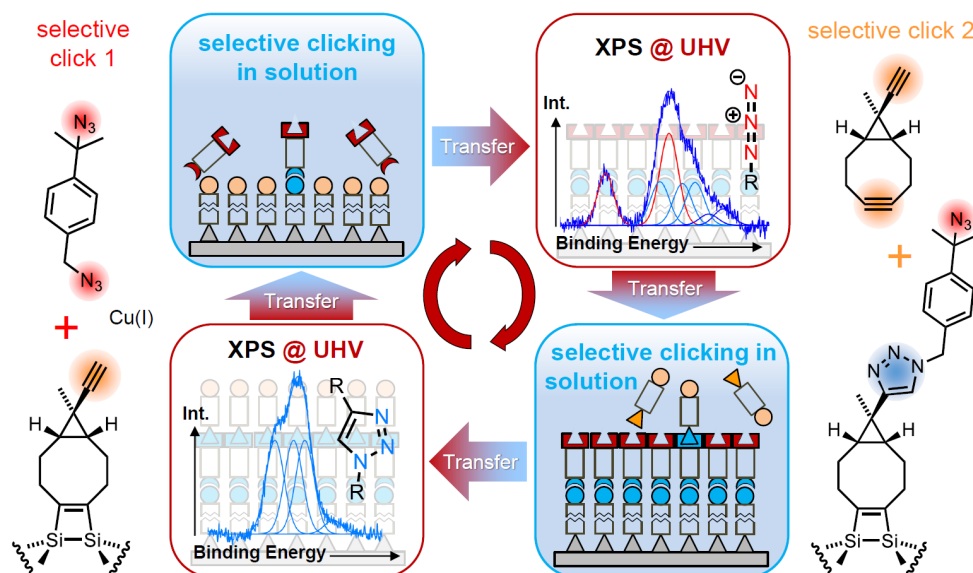


Fig. 1: Two selective click reactions are employed for the controlled layer-by-layer synthesis of organic structures on silicon. Each reaction step is performed in solution and monitored by means of X-ray photoelectron spectroscopy under ultra-high vacuum conditions.

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[2] T. Glaser, J. Meinecke, C. Länger, J. Heep, U. Koert, and M. Dürr, *J. Phys. Chem. C* **125**, 4021 (2021).

[3] T. Glaser, J. A. Peters, D. Scharf, U. Koert, and M. Dürr, *Chem. Mater.* **36**, 561 (2024).