Ordered monolayer growth of N-heterocyclic carbenes on silicon surfaces

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N-Heterocyclic carbenes (NHCs) have been shown to be excellent modifiers and anchors for the functionalization of surfaces [1], but the investigation has been limited to metals. Thus a controlled functionalization of silicon surfaces by ordered NHC layers is particularly interesting. Here, we present an extensive scanning tunneling microscopy (STM), density functional theory, and X-ray photoemission spectroscopy study of the growth of NHCs on Si(111) and demonstrate a binding to the surface via a single Si–C bond [2]. We varied the molecule–substrate interaction by using different model NHCs on a Si(111)$\sqrt{3}\times\sqrt{3}$R30°-B surface. This substrate is deactivated by the subsurface incorporation of B atoms and thus particularly suited for the ordered growth of organic films [2,3]. We find that the NHC molecules bind via a single covalent C-Si bond in an upright adsorption geometry and demonstrate the formation of highly ordered monolayers that are thermally stable and show strong work function reductions. The degree of ordering in the monolayers as well as their periodicity depends on the NHC molecule, in particular on the nature of its sidegroups, as well as on the defect density of the substrate.

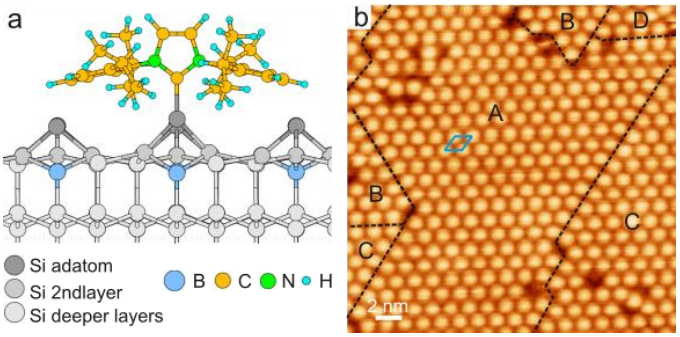

Fig. 1: (a) Adsorption geometry of the NHC molecules on Si(111)-B. (b) STM image of a highly ordered NHC monolayer on Si(111)-B.

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[2] M. Franz, S. Chandola, M. Koy, R. Zielinski, H. Aldahhak, M. Das, M. Freitag, U. Gerstmann, D. Liebig, A. K. Hoffmann, M. Rosin, W. G. Schmidt, C. Hogan, F. Glorius, N. Esser, and M. Dähne, Nat. Chem. **13**, 828 (2021).
[3] H. Aldahhak, C. Hogan, S. Lindner, S. Appelfeller, H. Eisele, W. G. Schmidt, M. Dähne, U. Gerstmann, and M. Franz, Phys. Rev. B **103**, 035303 (2021).