$Ge(CH_2I)_4$ on Si(100): Generating a tip-facing carbon radical for non-planar chemistry

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Scanning probe microscopy (SPM) investigations of on-surface synthesis have garnered significant attention, enabling the formation of synthetically inaccessible off-surface products. However, such studies have largely been confined to high-surface-mobility substrates such as metals or passivated silicon. Here, we expand this paradigm to include reactive silicon surfaces through the development of silicon-specific molecular "tools." These surface-bound molecules, following a post-deposition activation step, present a tip-facing carbon-centered radical with future applications as either an acceptor of functional molecular units or a donor of small molecular "building" blocks. These tools offer potential for both macroscale and nanoscale applications, including use as a silicon–carbon base with a customizable top layer, or as a carbon fragment donor for tip-mediated mechanosynthesis. To guide the creation of a broader class of such molecular tools, we define six molecular design criteria that enable reproducibility, surface specificity, and experimental verifiability. These are experimentally demonstrated using a highly symmetric model compound: tetrakis(iodomethyl)germane ($Ge(CH_2I)_4$; TIMe-Ge). TIMe-Ge consists of four iodomethyl (CH_2I) "legs" attached to a germanium core and was found—under temperature-controlled conditions—to bind to Si(100) 91% of the time with three legs covalently attached and the fourth oriented normal to the surface. Dehalogenation of the tip-facing CH_2I to form a carbon-centered radical was induced via photochemical and tip-mediated processes. Experimental results were supported by scanning tunneling microscopy (STM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations. With this framework, a broad and diverse range of new capabilities for molecular engineering are enabled on silicon.

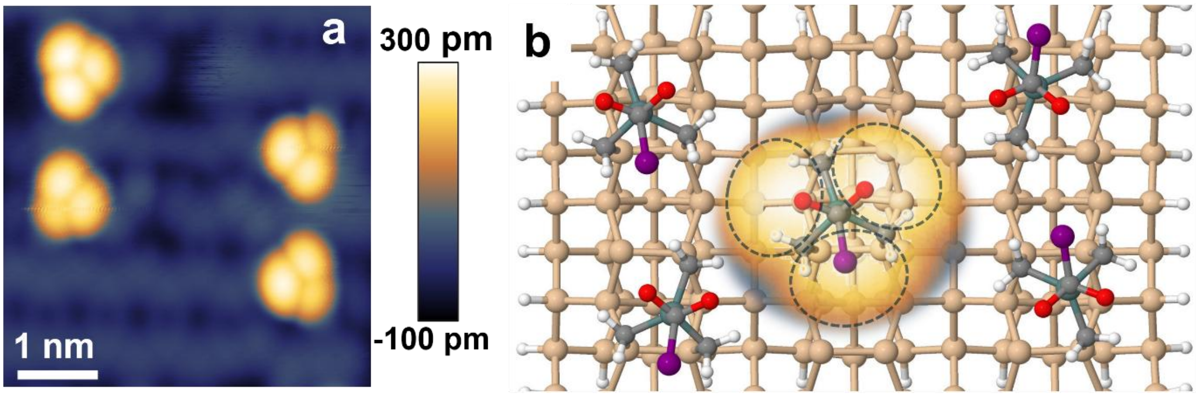

Figure 1. TIMe-Ge molecules on the Si(100) surface at 77 K. (a) Constant current filled states STM image of four TIMe-Ge molecules on Si(100)-(2x1) (I = 50 pA, V = -2V). **(b)** The four expected on-dimer leg rotational configurations of surface-bound TIMe-Ge, predicted by DFT. An experimental tri-lobe is overlaid on a ball-and-stick model in the center, highlighting bright lobes (dashed ellipses) that correlate with the iodine steric minima and the dark lines between lobes correspond to the C-Ge bonds of the underlying 3D scaffold of the molecule.