

Benzoic acids on calcite: From templated assembly to on-surface synthesis

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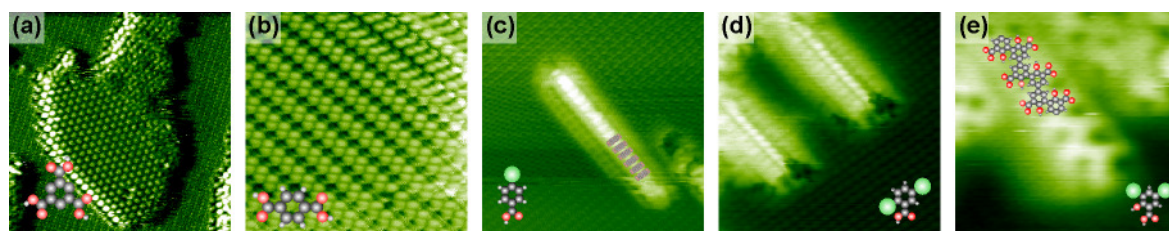
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Fundamental surface-supported processes such as chemical transformations and reactivity of organic molecules are of utmost importance for a large number of daily-life applications [1]. Benefiting from a detailed understanding of molecule-metal interactions, pivotal experiments have very recently demonstrated the potential of the on-surface synthesis concept. By the thermal activation of precursor molecules, stable molecular structures with tailored properties have been achieved, however, these studies have been limited to metallic substrates [2-4]. Nevertheless, for many applications such as molecular (opto-) electronic devices, it would be exceedingly attractive to transfer the assembly and reaction principles to bulk insulator substrates where an electronic coupling and leakage to the underlying conductor is avoided.

The calcite (10 $\bar{1}$ 4) surface has very recently been introduced as one of the most promising substrates for molecular adsorption at room temperature [5]. First, by using non-contact atomic force microscopy we will here present the structure formation of small benzoic acid molecules on this surface. Most notably, the resulting structures are templated by the underlying calcite substrate [6].

In a second step, we demonstrate the covalent linking of different halide substituted benzoic acids on calcite. The presence of the carboxylate group is expected to weaken the phenyl-halide bond and, therefore, favour homolytic cleavage of this bond leading to reactive phenyl radicals after heating to moderate temperatures. By varying the number and position of the halide substitutions, we rationally design the resulting structures revealing dimers, straight lines as well as zig-zag structures and, thus, provide clear evidence for the covalent linking step [7].



High-resolution NC-AFM images of various benzoic acid molecules presenting surface templating (a, b) and covalent linking (c-e).

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