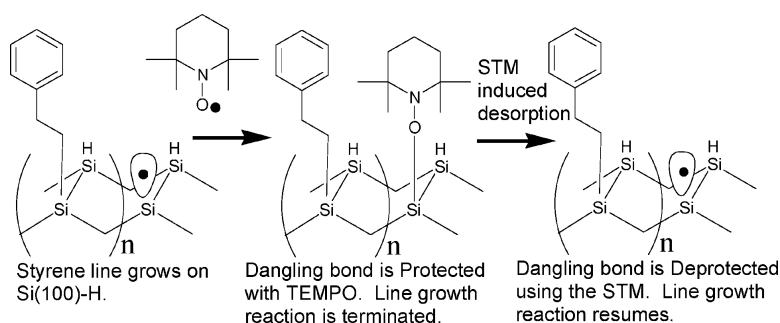


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Protection–Deprotection Chemistry to Control Styrene Self-Directed Line Growth on Hydrogen-Terminated Si(100)

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It has been proposed that well-defined hybrid organic molecular–silicon surfaces will have properties applicable to new sensor and molecular device technologies.^{1,2} To be of sharply defined character, and therefore most useful, such surfaces must be of meticulously controlled composition, configuration, and lateral extent. Moreover, a degree of automatic fabrication, such as exhibited by a recently described “self-directed” nanostructure growth process,^{3–7} is required to have any hope of making harnessable materials. An enhanced ability to control the course of such reactions is described here. Protection–deprotection chemistry that allows reliable customization of individual silicon surface-bound molecular nanostructures is demonstrated.

The mechanism for the self-directed growth of molecules on hydrogen-terminated Si surfaces has been described elsewhere.³ Briefly, an alkene reacts with a dangling bond on the silicon surface with concomitant formation of a carbon-centered radical. The carbon radical then abstracts a hydrogen atom from the silicon surface to create a new silicon dangling bond that can react further with another alkene. The propagation of these reactions leads to multiple additions to form lines of molecules on the surface. The promise of parallel growth of many lines is enticing. Conceivably, variants of the lines studied here could serve to connect commensurately small active entities, or the lines could be active entities in themselves. As lines formed by the self-directed growth procedure also provide a miniature laboratory for detailed study of molecular interactions and intermolecular transport, it is worth extending the methodology to gain better control over the growth process. One problem relates to the reactive dangling bond that remains at the end of a line once the intended reaction has completed. This dangling bond can lead to further undesired reactions, such as uninhibited line growth, desorption of molecules from the line, or unintentional reaction upon exposure to new molecules. Therefore, a mechanism to protect the dangling bonds at the end of molecular lines is needed. It is also desirable to have control over which particular lines are protected and which lines are not. With this enhanced capability, reactions involving multiple steps could be performed to create lines of varying length, structure, and orientation, enabling detailed studies of the physical and electrical properties of the lines.

We have previously shown that TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) can passivate and protect isolated dangling bonds on hydrogen-terminated silicon surfaces through a radical coupling reaction.⁸ Here, we use the silicon dangling bond–TEMPO reaction together with relatively straightforward manipulation with the tip of a scanning tunneling microscope (STM) to gain single molecule-level control over nanostructure growth. Specifically, it is shown that the STM can be used to reform the terminal dangling bond at select molecular lines by removing TEMPO caps with local control.

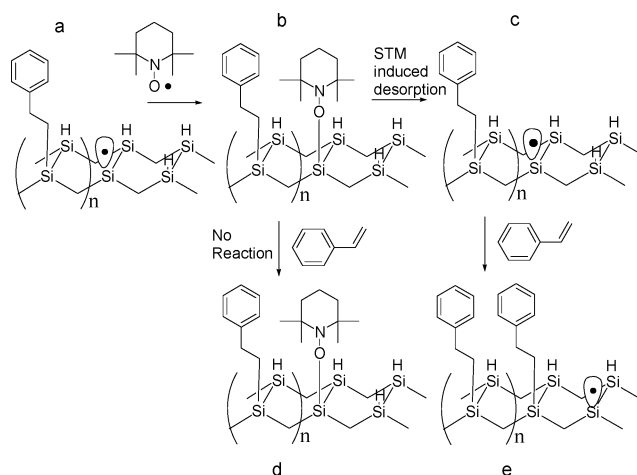


Figure 1. Depicts a scheme where the dangling bond at the end of a line of molecules is protected and deprotected using TEMPO and the STM. (a) A line of molecules grown on Si(100)–H through the reaction of styrene. (b) The dangling bond at the end of the styrene line is reacted with TEMPO and is protected from reaction. (c) TEMPO is removed by scanning at voltages above -3 V with the STM. (d) Exposure of a protected line to styrene does not lead to further growth. (e) Exposure of the deprotected line to styrene leads to continued line growth.

Further exposure to styrene leads to growth of deprotected lines only. The procedure is depicted schematically in Figure 1.

All reactions and STM measurements (Omicron VT AFM/STM) were performed at room temperature in an ultrahigh vacuum (UHV) chamber with a background pressure of 6×10^{-11} Torr. Surfaces (2×1 Si(100)–H) were formed by heating the clean surface to 330 °C during exposure to atomic hydrogen.⁹ N-type (As, 5 m Ω cm) Si(100) crystals were used in all of the experiments. Exposures of the silicon surfaces to reactants were performed by dosing the molecules into the vacuum chamber through a variable leak valve while monitoring the uncorrected pressure gauge readings.

The procedure for protection with TEMPO, deprotection, and selective growth is illustrated in Figure 2. Small differences in the images are due to minor tip changes which can occur during imaging. Figure 2a shows the Si(100)–H surface. Dimer rows are clearly visible as are the dangling bonds. Four dangling bonds of interest are indicated with an arrow, while contaminants and other dangling bonds are labeled “C” and “D”, respectively. The surface was subsequently exposed to styrene at a pressure of 1×10^{-7} Torr for 40 s. Figure 2b shows an image of the same area. It can be seen that each dangling bond has reacted with the styrene resulting in the formation of multimolecular lines. A dangling bond at the terminus of each line is clearly visible as a bright feature. Figure 2c shows the result of exposure of the surface to TEMPO (15 s at 1×10^{-6} Torr). The chosen exposure caused capping of most, but not all, dangling bonds. Three lines indicated by wedges have been passivated with TEMPO, while one line has

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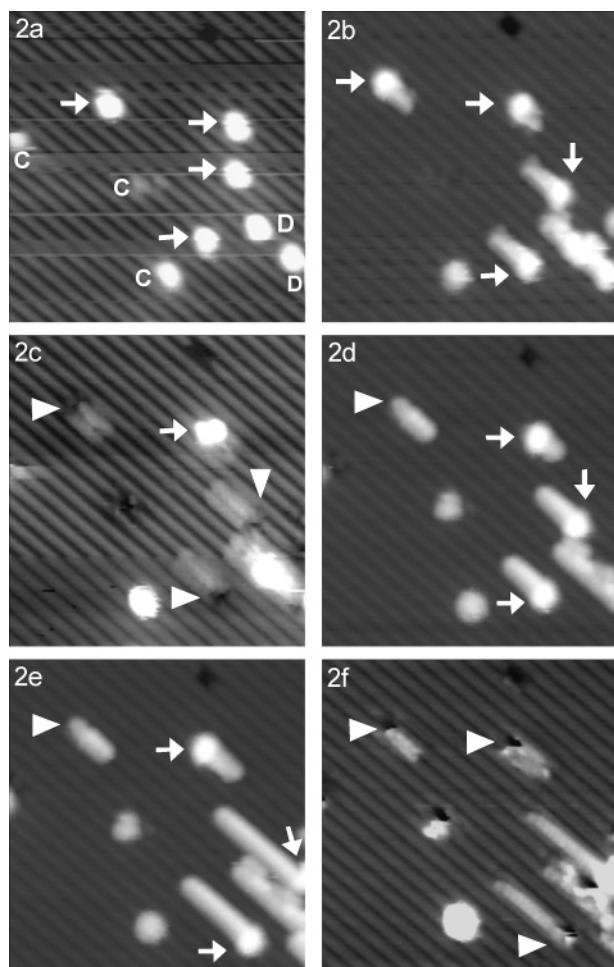


Figure 2. STM images (18×18 nm) of Si(100)-H acquired at -2 V and 50 pA. (a) Four dangling bonds of interest are indicated with arrows. Contaminants are labeled with the letter “C”, and other dangling bonds are labeled “D”. (b) Exposure to 4 langmuirs of styrene leads to the formation of styrene lines. Each line has a dangling bond at its terminus (indicated with arrows). (c) Exposure to 15 langmuirs of TEMPO leads to the capping of the dangling bonds. Three of the four lines have been capped with TEMPO. The capped lines are indicated with wedges. The uncapped line has a dangling bond and is indicated with the arrow. (d) TEMPO was removed from two of the three capped lines by scanning the TEMPO caps at -3.5 V. The dangling bonds are indicated with arrows, and the TEMPO-capped line is indicated with the wedge. (e) Exposure of 5 langmuirs of styrene leads to the continued growth of all lines that have no TEMPO cap (indicated with arrows). The TEMPO-capped line remains unchanged. (f) Exposure of the dangling bonds to a further 20 langmuirs of TEMPO caps all lines (indicated with wedges).

a dangling bond at its terminus, indicated as with arrow. Comparison of the dangling bond and TEMPO-reacted regions shows a clear difference in appearance.

Next, TEMPO molecules were removed from the end of specific molecular lines by scanning those regions at voltages greater than -3 V sample bias. The ease of removal of TEMPO molecules from the surface is related to the weak covalent bond formed between TEMPO and the surface radical. We have calculated the Si–O bond enthalpy for a TEMPO radical attached to a 14-silicon atom cluster to be 63.6 kcal/mol.¹⁰ While the N–O bond dissociation enthalpy is 13.9 kcal/mol lower,¹⁰ the Si–O bond is preferentially cleaved during STM-induced desorption. Cleavage of the N–O bond would

lead to oxidation of the dangling bond and a distinct change in its appearance.¹¹ No such change is observed; dangling bonds before TEMPO adsorption and after TEMPO desorption are indistinguishable, indicating Si–O cleavage. The desorption of TEMPO from dangling bonds on hydrogen-terminated silicon differs from the results on clean silicon reported by Guisinger, where desorption is not observed.^{12,13}

Removal of TEMPO from the surface deprotects the dangling bond and allows for further reaction. Figure 2d shows that TEMPO has been removed from two particular lines to regenerate the dangling bonds. In that image, a single line remains passivated by TEMPO. Again, a clear contrast between the TEMPO-reacted line and lines with dangling bonds is evident. Exposure of the surface to more styrene (5 s at 1×10^{-6} Torr) shows that each line with a dangling bond has increased in length, while the TEMPO-protected line remained unchanged (Figure 2e). It is also important to note that the removal of TEMPO had no effect on the further growth of styrene lines, and there are no apparent differences between lines grown through this protection–deprotection chemistry to those lines grown without. The newly extended lines continue to have a dangling bond associated with the end of the line. Further exposure to TEMPO once again passivated each dangling bond, as shown in Figure 2f.

The ability to reversibly cap styrene lines with TEMPO to selectively halt or enable reaction with spatial resolution at the single molecule level has been demonstrated. Our approach, using relatively easy scanned probe intervention (compared to methods requiring arduous positioning of each atom) together with automatic self-directed growth procedures, creates a new approach for producing nanostructures for study, and possibly even for practical production in cases where single or small numbers of molecular nanostructures will bring unique function to a hybrid silicon–organic device.

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