

Site- and Energy-Selective Intramolecular Manipulation of Polychlorinated Biphenyl (PCB) Molecules

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 Supporting Information

ABSTRACT: We demonstrate the conversion of an adsorbed precursor state of polychlorinated biphenyl (PCB) molecules on the Si(111)-7 × 7 surface at room temperature into a more stable configuration via site- and energy-selective atomic manipulation in the scanning tunneling microscope (STM). Whereas molecular desorption is maximized by electron injection into the chemisorbed molecular ring at low voltage, injection into the physisorbed molecular ring above a threshold voltage (2.5 V) favors the reconfiguration of the bonding. The results clearly demonstrate both intramolecular charge localization and intramolecular charge transportation as key ingredients in the atomic manipulation of individual polyatomic molecules.

Single molecule manipulation through the injection of electrons from the tip of the scanning tunneling microscope (STM) unlocks the quantum dynamics of the target molecule.^{1,2} The outcome of the process depends upon the coupling of the excited electronic state to the nuclear degrees of freedom of the molecule,³ but the majority of studies to date focus on a single dynamical outcome, whether it is desorption,^{4–8} bonding site switching,^{9,10} tautomerization,¹¹ dehydrogenation,¹² isomerization,¹³ or bond dissociation.^{15–17} Here we demonstrate that the branching ratio between two competing dynamical channels of polychlorinated biphenyl (PCB) molecules on the Si(111)-7 × 7 surface can be controlled by appropriate selection of the energy of the injected electrons (voltage) and by the precise injection site chosen within the molecule. PCB molecules are of considerable environmental importance.¹⁸ In this work these molecules are chemically bonded to the Si(111)-7 × 7 surface through (only) one of the phenyl rings, while the second phenyl ring interacts only weakly with the surface (initially). The two decay channels are molecular desorption and, intriguingly, a chemisorbed state in which both rings interact strongly with the surface. Thus the latter channel corresponds to the stimulated conversion of a molecular precursor state into a strongly bound state at the single molecule level via atomic manipulation.

The experiments were conducted with a Beetle-type STM (RHK-400) in an ultrahigh vacuum chamber with a base pressure of 8×10^{-11} Torr. The silicon samples were cut from a phosphorus-doped n-type (1–30 Ω cm) Si(111) wafer. The recipes for achieving a near defect-free (<0.97%) Si(111)-7 × 7 surface and sharp tungsten tip were described previously.⁵ The PCB

molecule used was 4,4'-dichlorobiphenyl (PCB No. 15, from Sigma-Aldrich). A near ambient-temperature effusion cell (NATC) heated to 50 °C was used to deposit the high molecular weight (222.8 amu) and high melting point (142–145 °C) PCB molecules. The sample surface was exposed to the cell in direct line-of-sight for 2 to 3 s with a background pressure of 5×10^{-9} Torr. This produced a coverage of less than 0.8 PCB molecules per Si(111)-7 × 7 unit cell. Variable gap *I*–*V* spectra were recorded over 100 different PCB molecules to produce the scanning tunneling spectrum (STS), $(dI/dV)/(I/V)$ following ref 5 (with $\kappa = 1 \text{ \AA}^{-1}$). The electron injection experiments were performed at voltages from +1.5 V to +3.6 V at a tunnel current of 20 pA for 2 s. Bias voltages given are always those on the sample. To remove tip effects⁸ as much as possible, we used a pulsing technique to ensure the STM imaging characteristics of the PCB molecule and Si(111)-7 × 7 surface at +1.5 V were always similar to those presented in Figure 1. The drift tracking feature of the RHK XPMPro software was used to 'lock on' to the molecule during the experiments, allowing site-specific intramolecular charge injection with atomic precision. The injections sites were within 1.6 Å of the center of the underlying silicon adatom, and the reported experimental manipulation yields are an average over this spatial range. By comparing passive STM images (1.5 V, 20 pA) before and after injection, we could determine if a manipulation event had occurred and its type. A total of 410 PCB molecules were manipulated.

Figure 1 demonstrate the two main dynamical outcomes of PCB manipulation. PCB presents in various configurations on the Si(111)-7 × 7 surface,¹⁹ but for our purposes the most interesting species is circled in the STM images of Figure 1a, c, obtained at +1.5 V. We associate the bright spot with the phenyl ring that interacts weakly with the surface and the dark spot as the adatom where the chemisorbed ring sits. This bright-dark configuration is observed at all voltages from +1 V to +2.6 V. For comparison, the chlorobenzene molecule presents as a single dark adatom when chemisorbed to the surface (a di-σ bond is formed with one adatom and an adjacent rest atom).^{2,20} Furthermore, our proposed bonding configuration implies a weaker interaction between the PCB and the "bright-spot" adatom; this is reflected in the silicon adatom having only a slightly perturbed STS signature relative to a clean adatom. This is different from the case of strong bonding (e.g., Cl²¹ or Pb adatoms²²), where the silicon adatom's electronic structure appears markedly altered by

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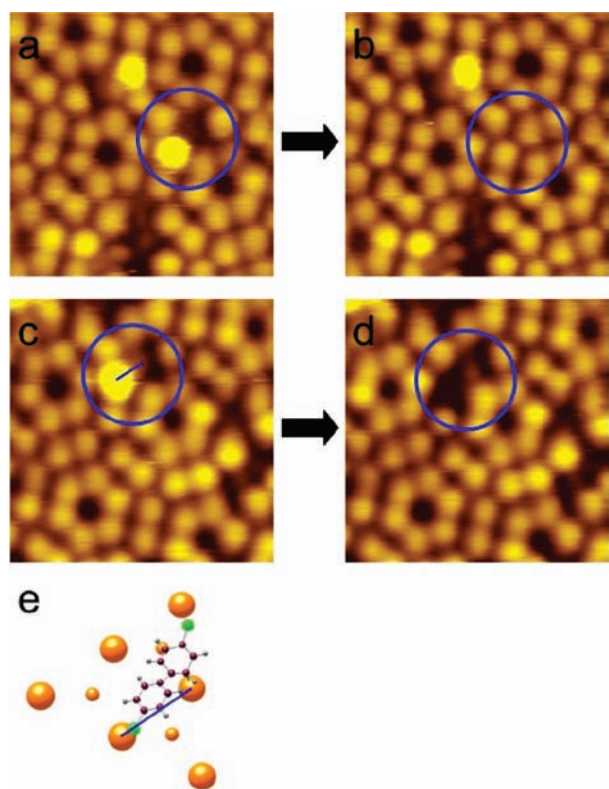


Figure 1. STM images (1.5 V, 20 pA, 6 nm \times 6 nm) obtained before (a, c) and after (b, d) the site-specific intramolecular injection of electrons into PCB molecules (circled) on the Si(111)-7 \times 7 surface at room temperature.

the adsorbate. The injection of electrons into the adsorbed PCB molecules at elevated voltage leads to a range of manipulation outcomes. Figure 1b shows complete desorption of the molecule from the surface and thus the recovery of the clean silicon surface. This also demonstrates that the bright-dark feature of Figure 1a is due to one single PCB molecule. Figure 1c illustrates a process in which the original bright ring is transformed into a dark feature, suggesting that the ‘physisorbed’ ring has changed its bonding configuration. In some cases, as in Figure 1d, the new dark feature is distinctly visible, in some cases not. But on rare occasions the bright feature reappears in subsequent images, confirming the proposal that the disappearance of the bright spot is due to a change in the adsorption configuration. A third outcome of STM charge injection, in which the bright-dark feature switches to a dark-bright feature, will be treated elsewhere.¹⁹

Figure 2 presents the dependence of the competing manipulation outcomes on the bias voltage and the intramolecular electron injection site in the STM manipulation experiments. From the total reaction yield (sum of all channels including the bright-dark to dark-bright switching process), Figure 2a, we can identify two energy regimes. Below +2.5 V, manipulation is, on average, more probable for injection into the dark side of the PCB molecule, whereas, above +2.5 V, the yield is much increased and higher for injection into the bright ring. Figure 2b shows the probability for the molecular desorption channel, again as a function of bias voltage and electron injection site (bright or dark); Figure 2c similarly for the disappearance of the bright ring (enhanced interaction with surface). We see that in the low energy regime (<2.5 V) only molecular desorption is observed and that this channel is

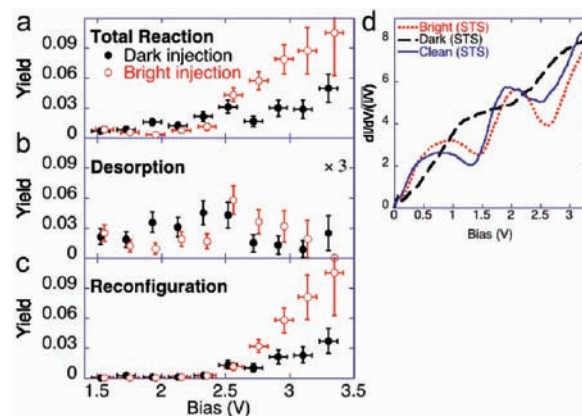


Figure 2. Probability of atomic manipulation of PCB/Si(111)-7 \times 7 as a function of voltage and intramolecular injection site. (a) Total reaction yield, (b) desorption yield, and (c) adsorption reconfiguration yield as a function of the bias voltage for injection into the bright (red) and dark (black) sides of the molecule (labeled). (d) Comparison of the STS curves taken at different sites. The red circles are displaced by 0.05 V for clarity. Yield means the probability that a reaction happens averaged over all (2 s injection) experiments. The data are binned in 0.2 V intervals.

more efficient for charge injection on the dark side of the molecule. Since the dark site corresponds to the phenyl ring chemisorbed to the surface, we conclude that localization of the injected charge on this site leads to the most efficient cleavage of the molecule—surface bond. Presumably the desorption process is similar to that for single organic rings, such as chlorobenzene,^{1,2,5–8} from the Si(111)-7 \times 7 surface. Above a surface bias voltage of +2.5 V, the desorption probability, Figure 2b, decreases as the other two channels (full chemisorption, Figure 2c, and switching) open. In particular, the enhanced chemisorption channel dominates all other outcomes and its probability is much enhanced for injection into the bright side of the PCB molecule. The electric field between tip and molecule, though large, should remain relatively constant (or at least the same order of magnitude), since (with feedback on) the tip withdraws almost linearly²³ as a function of increasing injection pulse voltage within the range we probe. We conclude that localization of the injected charge on the physisorbed ring is what leads to its enhanced interaction with the surface. Moreover, it appears that electrons injected into the dark side above the +2.5 V threshold appear to escape from the dark side to the bright side, leading to enhanced adsorption rather than molecular desorption. There must be a channel for charge injected into the physisorbed ring, whether from the tip or from the chemisorbed ring, which opens at the threshold voltage (+2.5 V).

The notion of a molecular state on the physisorbed ring above the threshold voltage can be tested by STS measurement obtained at the bright and dark sides of the PCB molecule, Figure 2d. At the dark side of the molecule, the adatom state of the clean surface at \sim 0.5 V is lost and a new broad shoulder appears between +1.0 V and +2.2 V, which is not present in the STS spectrum of the bright ring. This broad feature, most probably a remnant of the π^* state of the “dark” ring, accounts for the energy and spatial dependence of the STM-induced molecular desorption channel. On the bright side of the molecule, we see a state which appears at \sim +2.5 V and rapidly increases thereafter. Although this behavior is to some degree mirrored in the clean STS curves, the rise above +2.5 V is steeper for the molecular bright site. Since it seems unlikely that excitation of a substrate surface state would lead to

the molecular manipulation outcomes observed in this work, we suggest that there is a molecular orbit on the bright side of the PCB molecule above $\sim +2.5$ V whose transient occupation by the injected electrons drives a reconfiguration of the molecule into a geometry that interacts more strongly with the surface.

In summary, we have discovered competing dynamical channels in atomic manipulation of PCB molecules whose probability is controlled by the intramolecular electron injection site and energy on the Si(111)- 7×7 surface. Below +2.5 V desorption is favored and is maximized upon injection into the dark (chemisorbed) ring of the molecule, while above +2.5 V a reconfiguration of the molecular adsorption dominates (leading to an enhanced molecule–surface interaction) especially for injection into the bright (physisorbed) ring of the molecule. The manipulation results are consistent with the local density of state on the two rings measured by STS. In future, given the desirability of removing chlorine from a PCB molecule,¹ it would be interesting to probe the C–Cl dissociation channel and whether they mimic the behaviors of the single-ring analogue chlorobenzene, including thermal enhancement and the nonlocal effect.^{5,6} More generally, our work is a demonstration of the chemical conversion of a molecular precursor state into a more stable adsorbed species by atomic manipulation at the single molecule level.

■ ASSOCIATED CONTENT

S **Supporting Information.** 1. Bonding configurations of PCB on the Si(111)- 7×7 surface. 2. The three reaction outcomes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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