

Bond-selective single molecule manipulation at room temperature

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Bond-selective molecular manipulation is one of the frontiers of atomic manipulation with the Scanning Tunnelling Microscope (STM). Traditionally such experiments are conducted in the stable, low temperature regime; room temperature manipulation presents new challenges. Here we demonstrate room temperature, bond selective manipulation (“molecular dissection”) in a polyatomic molecule, chlorobenzene (C₆H₅Cl), anchored to the Si(111)-7x7 surface by chemisorption. Recently we showed that electron (or hole) injection from the STM tip into the π^* LUMO (π HOMO) orbitals of the benzene ring leads to controlled molecular desorption beyond a threshold voltage of +2.5V (-1.5V) [1]. Desorption is a one electron process. In this work we explore C-Cl bond dissociation in the chemisorbed chlorobenzene molecule [2]. Detailed STM images identify the azimuthal orientation of the individual chlorobenzene molecules and allow us to correlate the final location of the liberated chlorine “daughter” atoms with their parents. We identify Cl atoms up to 50Å from the parents. We also find that dissociation is a two-electron process and propose a vibrationally-mediated electron attachment mechanism. Finally, the branching ratio between desorption and dissociation is shown to depend on the STM tip configuration [3].

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