Chemoselective Hierarchical Dehalogenation: 4-Bromo-3”-iodo-p-terphenyl on the Cu(111) Surface

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There is over a century of experience how to control reactions in solution, but the course of a transformation on surfaces has only been scarcely addressed. While the inherent reactivity and stability of bonds is universal, the surface substrate can have a crucial role, either acting as catalyst or by stabilizing intermediates. We investigate the selective cleavage of aromatic carbon-halogen bonds, which allow the construction of highly complex polycyclic aromatics. In order to fully understand this elementary step, the selective cleavage of carbon-halogen bonds on a substrate, 4-bromo-3”-iodo-p-terphenyl (BrI-TP) on Cu(111) has been chosen as model compound. The two different halogen atoms have been placed in different positions (bromine in para-position, the iodine in meta-position) for easy differentiation.

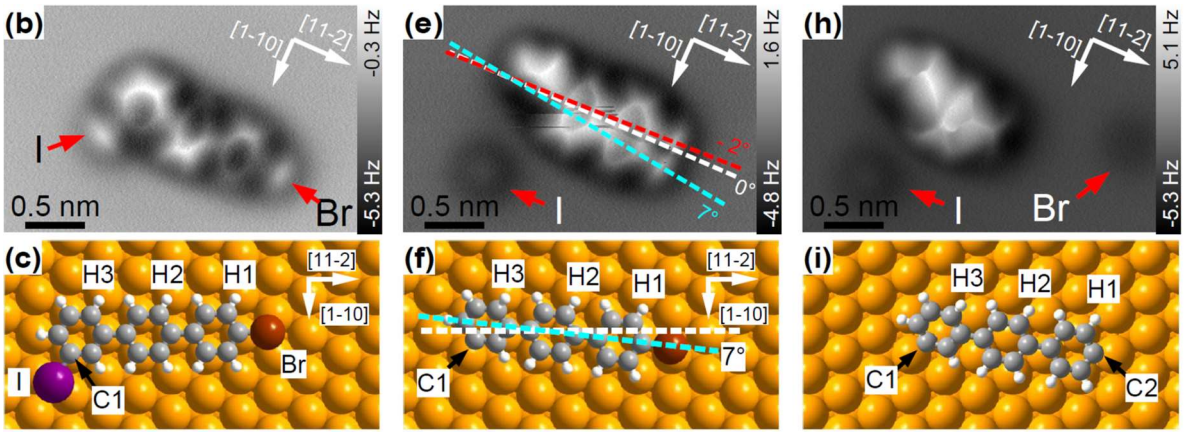

Figure 1. Upper graphs: The initial state, adsorbed monoradical, and biradical of the same BrI-TP molecule. The sequential de-iodination and de-bromination reactions are induced by applying different voltage pulses. Lower graphs: Corresponding ab-initio calculated (PBE-D3/pw(PAW P)) adsorption structures of the three different reaction states

Here we demonstrate the sequential dehalogenation reactions of iodine and bromine from 4-bromo-3”-iodo-p-terphenyl (BrI-TP) on a Cu(111) substrate using scanning tunneling microscopy (STM) and atomic force microscopy (AFM). By utilizing the chemical bond imaging method [1,2] with CO-tip functionalization we were able to image the BrI-TP molecules as well as the adsorbed mono- and biradicals with atomic resolution. In combination with dispersion corrected density functional theory (DFT-D3) calculations we can unambiguously assign the adsorption structures of the pristine molecules, as well as the mono- and biradicals. The mono- and biradicals chemisorb to Cu(111) top sites that are lifted by 16-24 pm from the surface plane. Therefore, the radical sites at corresponding *meta*- and *para*-positions bend strongly towards the Cu surface atoms. The information obtained about the dehalogenation process is crucial for designing uniform functional devices at the atomic level.

References:

[1] Gross, Mohn, Moll, Liljeroth, Meyer, Science **325**, 1110 (2009)
[2] Zint, Ebeling, Schlöder, Ahles, Mollenhauer, Wegner, Schirmeisen, ACS Nano **11**,4183 (2017).