

ISOLATED NANOSCALE PROCHIRAL REACTION ASSEMBLIES ON Pt(111)

Vincent Demers-Carpentier and Peter H. McBreen
 Département de chimie, Université Laval, Québec (Qc), Canada, G1K 7P4

Chiral surfaces can be used to achieve catalytic chirality transfer. The mechanism through which this occurs is one of very precise nanoscale assembly. In particular, it involves a constraint in which the substrate, prochiral, molecule is forced into contact with the catalyst surface uniquely via a specific enantioface. One method to achieve this is to chemisorb a chiral-modifier so as to form molecular chiral sites. Co-adsorption of the substrate then leads to 1:1 prochiral modifier-substrate complexes. We report a combined STM, HREELS and computational study of such 1:1 prochiral assemblies on Pt(111). The study reveals the existence of chemisorption induced strong C-H to O=C intermolecular hydrogen bonding between co-adsorbed ketones and aromatics on Pt(111). It also shows how this unforeseen interaction may be used to sensitively modulate both chemical reactivity at surfaces and nanoscale assembly at surfaces.

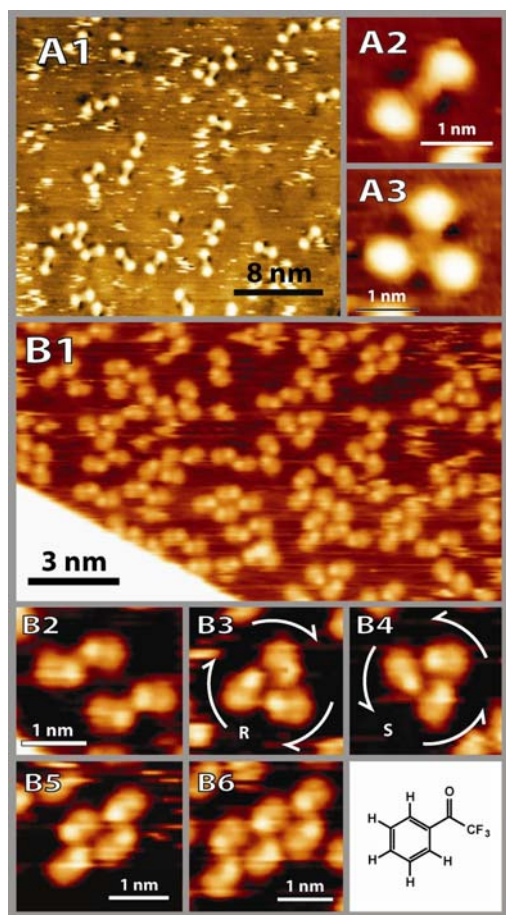


Figure 1. STM images of trifluoroacetophenone (TFAP) adsorbed on Pt(111).¹ Panels A and B show well-defined groups of two (A1,A2,B1,B2), three (A3,B1,B3,B4), four (B1,B5) or six (B6) molecules over the entire surface at room temperature. Only dimers were observed (A1) at low coverages, indicating that they are the basic unit for the larger even-numbered clusters. Left and right-handed trimers are also observed as the coverage is increased. In B1-B6, each molecule is imaged as a lobe composed of a broad protrusion and a smaller bright spot at one end. In A1-A3, each molecule is imaged as a bright protrusion with a smaller dark spot at one end. The high-resolution images show that the dimers are formed from counter-aligned molecules. DFT calculations by Hammer *et al.*¹ show that dimer formation is stabilized by hydrogen bond interactions between the carbonyl group of one molecule and the aromatic CH bonds of the other molecule.

Such C-H \cdots O bonded prochiral dimers, and similar systems formed by enol-enol interactions,² permit the study of surface reaction chemistry in isolated nanoscale assemblies. The combination of STM and electron energy loss spectroscopy is particularly powerful in this respect.

(1) Laliberté, Hammer *et al.* *J. Am. Chem. Soc.* 2008, 130, 5386.

(2) Lavoie, Demers-Carpentier *et al.* *J. Am. Chem. Soc.* 2007, 129, 11668.