

Dibenzothiophene *S*-Oxide Molecules investigated on metallic and insulating substrates by LT-SPM

M.Hankache^{1,#}, V.Magné^{2,3}, E.Geagea¹, P.Simón Marqués³, E.Fodeke¹, S.Claire¹, L.Giovanelli¹, S.Mallet-Ladeira⁴, E.Maerten², C.Kammerer³, D.Madec², L.Nony¹, C.Loppacher¹

¹Aix Marseille Univ, Université de Toulon, CNRS, IM2NP, Marseille, France

²LHFA, Université de Toulouse, CNRS, UMR 5069, Toulouse, France

³CEMES, Université de Toulouse, CNRS, Toulouse, France

⁴ICT, Université de Toulouse, UAR 2599, Toulouse, France

#melissa.hankache@im2np.fr

Due to their rich in-solution chemistry, sulfoxide derivatives are promising reagents for the development of new chemical tools for on-surface synthesis. Among them, dibenzothiophene *S*-oxide (DBTO) is known to undergo *S*=O bond cleavage under UV irradiation in the solvent.[1] This following work provides a comprehensive analysis of these compounds on metallic and insulating surfaces.

First the molecules were deposited on Au(111) surface. Non-contact AFM intramolecular imaging of an isolated molecule with a CO-functionalized tip at 9.8 K allows identification of its configuration adsorption (Fig.1a), which is later confirmed by X-ray standing wave photoemission spectroscopy and DFT calculations. A thermal analysis of these molecules' behavior on Au(111) at different temperatures – from the supramolecular regime to the Ullmann polymerization reaction (Fig.1b), passing by the deoxygenation – was also carried out by combining SPM and XPS observations.

The supramolecular phase of molecules was then investigated upon deposition on two mono-layers of NaCl/Au(111) under illumination (UV 280 nm) (Fig.1c). Successful deoxygenation of the molecules was put in evidence by statistical analysis of high-resolution images. The deoxygenation rate increases with time and reaches a plateau after six hours of illumination, at which point approximately 40% of the molecules were deoxygenated. Structural characterization was further completed by bias spectroscopies acquired on a statistical set of pristine/deoxygenated molecules. Deoxygenated molecules exhibit increased contact potential difference (CPD), indicating a more negative charge state at the sulfur atom, consistent with the loss of oxygen.[2]

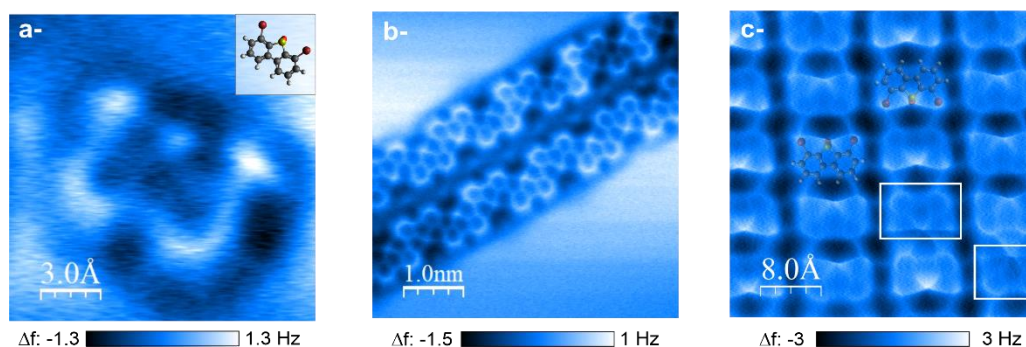


Figure 1. **a**, Δf image of a single (ortho-Br)₂-DBTO molecule on Au(111). **b**, Ullmann polymerization on Au(111). **c**, Supramolecular regime on 2ML-NaCl / Au(111) after UV irradiation. White frames are used to indicate deoxygenated molecules.

Reference

- [1] Mrinmoy Nag and William S. Jenks, *J. Org. Chem.* **70** (9), 3458-3463 (2005).
- [2] Mélissa Hankache *et al.*, *Nature Comm.* **16**, 4841 (2025).