

FIRST-PRINCIPLES INVESTIGATION OF ELECTRON-INDUCED CROSS-LINKING OF AROMATIC SELF-ASSEMBLED MONOLAYERS ON Au(111)

Pepa Cabrera-Sanfeli¹, Daniel Sánchez-Portal² and Andrés Arnau^{2,3}

¹ Donostia International Physics Center (DIPC), Manuel de Lardizabal 4, San Sebastian, Spain.

² Unidad de Física de Materiales, Centro Mixto CSIC-UPV, Manuel de Lardizabal 4, San Sebastian 20018, Spain.

³ Departamento de Física de Materiales UPV/EHU, Facultad de Química, Apartado 1072, San Sebastián 20080, Spain.

swbcasam@sc.ehu.es

Experimental techniques, such as X-ray photoelectron, infrared and near edge X-ray absorption fine structure spectroscopy show that self-assembled monolayers (SAMs) of 1,1'-biphenyl-4-thiol (BPT) adsorbed on Au(111) arrange well ordered. Upon electron irradiation these films undergo strong structural modifications that have been investigated recently. After irradiation with 50 eV electrons, important changes appear in the corresponding X-ray photoemission (XP) and infrared (IR) spectra.^{1,2} These changes are believed to be mainly due to the dehydrogenation of BPTs and the cross-link between neighbouring phenyl groups. Through chemical treatments, cross-linked regions can be removed from the substrate and form free-standing sheets of ~15Å thickness. We present here a first theoretical approach to this complex problem. We use Density Functional Theory (DFT) calculation to study the adsorption of one layer of BPT molecules on Au(111) surface, as well as several plausible cross-linked structures that dehydrogenated BPT and biphenyl (Bph) molecules can adopt depending on different input conditions. The possible role of the gold substrate is examined in detail.

(1) Eck, W.; Stadler, V.; Geyer, W.; Zharnikov, M.; Golzhauser, A.; Grunze, M. *Advanced Materials* **2000**, *12*, 805-808.

(2) Geyer, W.; Stadler, V.; Eck, W.; Zharnikov, M.; Golzhauser, A.; Grunze, M. *Applied Physics Letters* **1999**, *75*, 2401-2403.