

Interplay between electronic properties and supramolecular arrangements at metal-organic interfaces

Giovanni Costantini

Department of Chemistry, University of Warwick, Gibbet Hill Rd, CV4 7AL, Coventry, UK

Surface engineering through molecular adsorption is emerging as one of the most powerful technologies for the fabrication of advanced nanostructured materials. With the almost unlimited capabilities of modern synthetic chemistry, the real limiting factor for the development and practical use of this technology is the restricted ability to characterise and, in particular, to control molecular adsorption and organisation. In particular, control over molecular assembly must be extended to length scales where it can be integrated with traditional “top down” nanofabrication techniques

In this talk the use of long-range interactions generated by charge transfer at metal-organic interfaces will be demonstrated as a novel method for regulating 2D molecular assembly. Specifically designed donor molecules are deposited at various converges on different metal substrates and characterised by low temperature scanning tunnelling microscopy. The resulting supramolecular assemblies are analysed by comparing the experimental data with density functional theory calculations. Energy level alignment at the metal-organic interface and substrate polarisability appear to regulate the interfacial charge transfer and therefore the development of induced dipoles. These have a profound influence on the supramolecular assembly which is further rationalised by kinetic Monte Carlo simulations taking into account the competition between Van der Waals attraction and electrostatic repulsion among the adsorbed molecules. A coherent picture emerges where long-range forces between charged molecules drive the spontaneous formation of a novel classes of supramolecular structures. Conversely, these can be used to obtain crucial information on the electronic properties of metal-organic interfaces.