Charge transfer at metal/oxide/organic interfaces revealed by photoemission orbital tomography and scanning tunneling microscopy

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Charge transfer processes through ultrathin, supported oxide films have received increasing attention in recent years because of the possibility to control the charge state of adsorbates or the direction of catalytic reactions. The main driving force for the occurrence of charge transfer in these systems is the reduction of the substrate work function induced by deposition of the oxide film in combination with an adsorbate of relatively high electron affinity. While previous studies have focused on the charging of metal atoms (e.g. Au) or small molecules (e.g. O_2, NO_2), we have recently extended these investigations to charge transfer processes into organic molecules. In this contribution, we present results on the adsorption and charging of model organic semiconductors (e.g. pentacene (5A), 2H-tetraphenylporphyrin (2H-TPP) and others) on ultrathin MgO(001) films supported on Ag(001). By combing scanning tunneling microscopy and photoemission spectroscopy and tomography, we identify and quantify charge transfer into the organic monolayer film. In addition, we show that by tuning the work function and/or the MgO thickness it is possible to control: the ratio of charged and neutral species, the number of electrons transferred and, concomitantly, the conformation of the adsorbates. In the case of 2H-TPP, charge transfer also appears to strongly influence the self-metalation of 2H-TPP to Mg-TPP. Thus, our investigations lay the basis for the ultimate control of charge transfer, and the related chemistry, on ultrathin oxide film systems [1-5].

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