Structural Reorientation of Organic Molecules on Surfaces by Alkali Metal Doping

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Organic semiconductors are promising materials for the fabrication of next-generation organic-based electronic devices. In particular, PTCDA molecules are interesting for thin film development due to their rectangular shape and hydrogen bonding. Moreover, the electron properties of the organic thin film can be tuned by alkali metal doping. Here, we study the influence of Cs doping on the structural and electronic properties of the model system PTCDA/Ag(111). Using momentum microscopy and applying the framework of photoemission orbital tomography, we can simultaneously access changes in occupation of the molecular orbitals and determine modifications of the azimuthal orientation of the PTCDA molecules upon Cs doping. We can identify two structural Cs-PTCDA phases depending on the Cs concentration with either 0.5 or 2 Cs atoms per PTCDA molecule. With increasing Cs concentration, we observe a gradual structural reorientation of the molecules that is accompanied by a modification of the population of the molecular states (see constant energy maps in Fig. 1). The intensity maxima in momentum space of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) level indicate that the PTCDA molecules are aligned by 0° and 90° with respect to the [-101] direction of Ag(111) in the case of 0.5 Cs per molecule, while they are all rotated by 90° in the case of 2 Cs per molecule. Our structural findings for Cs-PTCDA are different from the case of bare PTCDA on Ag(111). The structural reorientation of the PTCDA molecules can be attributed to the electrostatic interactions between the partially ionized Cs atoms and the negatively polarized oxygen end groups of PTCDA.

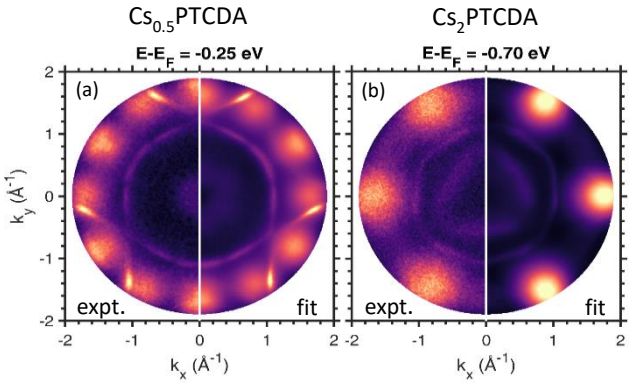

Fig. 1: Constant energy maps of the LUMO for the $Cs_{0.5}$PTCDA (a) and Cs_2PTCDA phase (b). The left parts of the images show the experimental data while the right parts depict our model simulations that are based on density functional theory and photoemission orbital tomography.