Density-Dependent Reorientation and Rehybridization of Chemisorbed Conjugated Molecules for Controlling Interface Electronic Structure

B. Bröker,1 O. T. Hofmann,2 G. M. Rangger,2 P. Frank,2 R. P. Blum,1 R. Rieger,3 L. Venema,4 A. Vollmer,5 K. Müllen,3 J. P. Rabe,1 A. Winkler,2 P. Rudolf,4 E. Zojer,2 and N. Koch1,*

1Institut für Physik, Humboldt-Universität zu Berlin, Newtonstrasse 15, D-12489 Berlin, Germany
2Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria
3Max Planck Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany
4Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
5Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, BESSY II, D-12489 Berlin, Germany

(Received 21 January 2010; published 18 June 2010)

The adsorption of the molecular acceptor hexaazatriphenylene-hexacarbonitrile on Ag(111) was investigated as function of layer density. We find that the orientation of the first molecular layer changes from a face-on to an edge-on conformation depending on layer density, facilitated through specific interactions of the peripheral molecular cyano groups with the metal. This is accompanied by a rehybridization of molecular and metal electronic states, which significantly modifies the interface and surface electronic properties, as rationalized by theoretical modeling.

Understanding the fundamental mechanisms that determine the properties of interfaces between metals and conjugated organic materials is a key prerequisite for advancing the fields of organic and molecular electronics, where the (opto-)electronic function of devices depends critically on, e.g., charge density distribution [1,2], energy level hybridization and interface state formation [1,3,4], molecular conformation changes [3–6], and energy level alignment [5,7–9]. Additionally, it has been shown recently that the ionization energy of ordered molecular layers depends critically on the surface orientation of molecules, and that the energy levels at interfaces can be manipulated via molecular orientation [10]. However, it is commonly accepted that the orientation of a conjugated molecular monolayer with respect to a metal electrode surface is set for a particular material pair, only depending on the relative strength of metal-molecule and intermolecular interactions. If substrate-molecule interactions prevail, as for clean metal surfaces, at least the first molecular layer is found to be face-on [11–13]. Only multilayers are known to eventually adopt a different orientation [13–15] because the strong interaction with the metal is already screened by the monolayer. Here, we demonstrate the molecular density-dependent reorientation of an entire stable face-on monolayer to a stable edge-on conformation, which is achieved through balancing the surface energy in the two orientations by enabling strong hybridization of molecular and metal electronic states in both orientations through functional terminal groups. Particularly, the chemisorbed molecular state in the edge-on monolayer exhibits extraordinary electronic properties with a potential for huge application relevance, which is not the case for the face-on orientation.

Ultraviolet photoelectron spectroscopy (UPS) spectra were taken at the end station SurICat at BESSY II (Berlin). Kelvin-probe (KP) and thermal desorption spectroscopy (TDS) was done at the Graz University of Technology (Graz), and reflection absorption infrared spectroscopy (RAIRS) at the Zernike Institute for Advanced Materials (Groningen). All sample preparation steps and measurements were performed at room temperature and in ultrahigh vacuum. Metal single crystals were cleaned by repeated cycles of heating and sputtering and molecules were sublimed from pinhole sources. Further details can be found in the supporting information [16], where also details on the density-functional theory (DFT) calculations employed in this study are reported.

Hexaazatriphenylene-hexacarbonitrile (HATCN, chemical structure shown in the inset of Fig. 2) is a strong electron acceptor without an intrinsic dipole moment, which was here chemisorbed on Ag(111). The Ag(111) surface work function (\(\Phi\)) changes due to HATCN deposition as shown in Fig. 1, determined independently by UPS and KP measurements. A pronounced deviation from the expected dependence of sample \(\Phi\) on acceptor coverage (\(\theta\)) is observed, as three regimes instead of two occur: (i) for low \(\theta\), \(\Phi\) is essentially constant (from 4.4 eV to \(\sim\)2.5 eV [17], highlighted in red (dark gray) in Fig. 1), (ii) followed by a strong and almost linear \(\Phi\) increase by \(\sim\)1 eV (from \(\sim\)2.5 eV to \(\sim\)8 Å, highlighted in black); (iii) finally a saturation of \(\Phi\) is reached [beyond \(\sim\)8 Å, highlighted green (light gray)]. The value of \(\Phi\) changes from 4.4 eV [pristine Ag(111)] to 5.4 eV (26 Å HATCN/Ag(111)). Commonly, the deposition of acceptors on metal surfaces involving net metal-to-acceptor electron transfer leads to the observation of regime (ii) from the very beginning, followed by regime (iii) [18]. Such a “delayed” increase of \(\Phi\), i.e., the additional appearance of regime (i), has not been reported before and cannot be rationalized on the basis of the Helmholtz-equation (or the Topping model...