Interfacial Electronic Structure of Copper Phthalocyanine on a Gold Surface Studied by Synchrotron Radiation Photoemission

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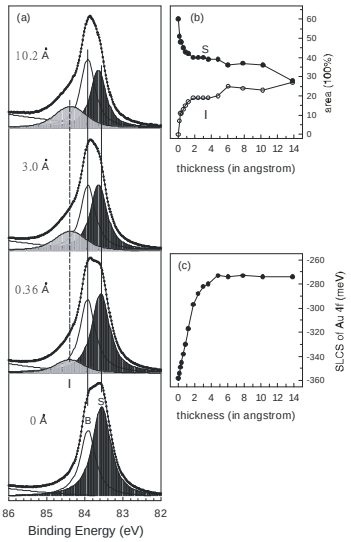
We have studied copper phthalocyanine (CuPc) molecules deposited on a clean gold surface via synchrotron radiation photoemission. The persistent appearance of Au4f surface core-level emission in a series of depositions suggests columnar growth of the adsorbed molecules covering only one-fifth of the surface. Molecular adsorption reduced the line intensity of emission from the Au surface slightly and also produced a shortened core-level shift, which demonstrates weakened s-d hybridization of the surface band. Moreover, manifestation of excess charge in the C1s core, along with an induced component in the Au4f core, indicates that charge polarization occurred at the organic/metal contact. The interface introduces an electronic state 1.09 eV below the Fermi level. Further analysis reveals that only the carbon atoms in the benzene rings are affected upon adsorption, suggesting that the molecular plane lies flat on the surface without changing the nominal bent configuration.

The fitted results for the $Au4f_{7/2}$ core peaks are shown in the figure. In it, B (open curves), S (black curves), and I (gray curves) components are clearly shown. We plot the areal change of components S and I with respect to the film thickness. The I component increases in intensity at the expense of the S component until about 2 Å. According to the percentage change of the intensity of the S component, we can show that the CuPc molecules cover only one-fifth of the Au surface. Not plotted in this figure is the area of the bulk curve, which maintains a constant value of 43±2%. The constancy makes it clear that CuPc affects only the surface atoms without disturbing the underlying subsurface layers.

As the figure shows, the surface core-level shift (SCLS) of the molecule-free spectrum black-shaded curve is –360 meV. In the CuPc-exposed surface, the magnitude of the SCLS becomes small and reduces gradually to –273 meV at 4.8 Å, remaining constant thereafter [see Fig. 4(c)]. The induced feature (I) (gray-shaded curves) shows a +470 meV positive shift from the bulk. The decrease in SCLS with CuPc coverage reveals significant physics. It is known that the origin of an SCLS in a noble metal is attributed to enhanced s-d hybridization at the surface layer. The hybridization narrows the surface bandwidth, thereby shifting its centroid away from the bulk reference. The greater the hybridization, the greater the shift toward the Fermi level in the case of a noble metal. In the present organic/metal case, a smaller SCLS thus manifests a reduction of surface s-d hybridization due to molecular adsorption. The s charge no longer hybridizes with the d states, but in turn hybridizes with the π orbital of the carbon atoms in the benzene rings



A representative fit to $Au4f_{7/2}$ core-level spectra (a). Areal change of surface (S, solid circles) and induced (I, open circles) emission (b). Changes of surface core-level shift with CuPc thicknesses (c).