

Electronic Property of Functional Organic Materials

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Functional organic materials (FOM) have recently attracted considerable attention both for fundamental research and device applications because of peculiar properties not found in inorganics and small molecules. However the mechanisms and its origin of various device characteristics are still under debate. Scientific mysteries would be raised because people have believed that electronic structure of FOM would be conserved as in an isolated molecule for solid phases due to van der Waals interaction. To reveal characteristics of FOM the key investigation would be on precise experiments on the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. In these systems, the impacts of weak interaction on the electronic structure would be appeared as small intensity modulation of photoelectron-emission fine features depending on adsorption and aggregation on the surface. By recent development in the instrumental we can assess hidden fine structures in the electronic states, *e.g.* electron–phonon coupling, quasi-particle states, very small gap-state DOS, weak band dispersion and dynamic electronic polarization. To elucidate what really happens for the FOM at the interface upon weak interaction, an evaluation on the wave-function

spread of the electronic states would be very important because the interface states for the physisorbed systems are described to be a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization). Seeing a modification of electron wave function upon weak electronic coupling as well as strong electron–phonon coupling is central issue on our agenda.

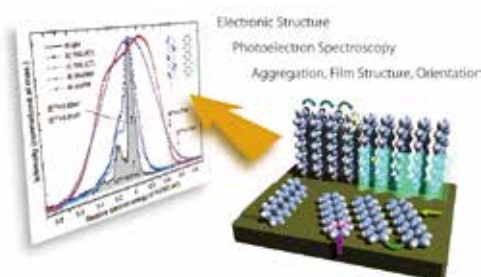


Figure 1. Scheme of a rich assortment in the structure of functional molecular materials and variety in the spectral feature of ultraviolet photoelectron spectrum (UPS) for the HOMO band taken for various structural phases (gas-phase, lying monolayers, standing monolayer, and disordered film).

Selected Publications

- F. Busolotti, S. Kera, K. Kudo, A. Kahn and N. Ueno, “Gap States in Pentacene Thin Film Induced by Inert Gas Exposure,” *Phys. Rev. Lett.* **110**, 267602 (5 pages) (2013).
- S. Duhm, Q. Xin, S. Hosoumi, H. Fukagawa, K. Sato, N. Ueno and S. Kera, “Charge Reorganization Energy and Small Polaron Binding Energy of Rubrene Thin Films by Ultraviolet Photoelectron

Spectroscopy,” *Adv. Mater.* **24**, 901–905 (2012).

- S. Kera, H. Yamane and N. Ueno, “First Principles Measurements of Charge Mobility in Organic Semiconductors: Valence Hole-Vibration Coupling in Organic Ultrathin Films,” *Prog. Surf. Sci.* **84**, 135–154 (2009).

1. Charge Transfer States Appear in the π -Conjugated Pure Hydrocarbon Molecule on Cu(111)¹

Understanding the metal and adsorbed molecule interaction is required to discuss the mechanism of charge transfer in functional molecular solids. We report on the results of experimental and theoretical studies on the electronic structure of gas-phase diindenoperylene (DIP) and DIP-monolayer (ML) on Cu(111). Vapor-phase ultraviolet photoelectron spectroscopy (UPS) was realized for 11.3 mg of DIP, giving reference orbital energies of isolated DIP, and UPS and inverse photoemission spectroscopy of DIP-ML/graphite were performed to obtain DIP-ML electronic states at a weak interfacial interaction. Furthermore, first-principles calculation clearly demonstrates the interfacial rearrangement. These results provide evidence that the rearrangement of orbital energies, which is realized in HOMO–LUMO and HOMO–HOMO-1 gaps, brings partially occupied LUMO through the surface-induced aromatic stabilization (SIAS) of DIP, a pure hydrocarbon molecule, on Cu(111) surface. It has been considered in SIAS, that a site-specific interaction between the heteroatoms in adsorbate molecules and the substrate plays a key role, while the present results demonstrated that the heteroatoms are not necessarily required for the formation of the charge transfer states through SIAS. In passing, it was reported that no charge transfer states are formed at the interface of perylene on Ag(111) and Cu(111), suggesting that the perylene core alone does not play a role in the CT state formation. We therefore conclude that a combination of a specific chemical structure and functional groups leading to the flexibility of the molecular skeleton is a key requirement of SIAS on metal substrates, even if the functional groups do not involve heteroatoms such as indeno-groups in DIP.

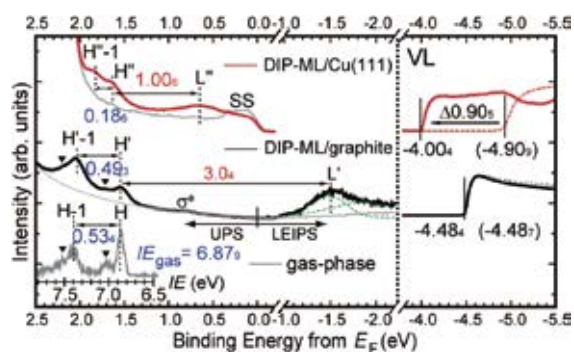


Figure 2. Comparison of He I UPS of DIP-ML on Cu(111) (red), Xe I UPS and LEIPS of DIP-ML on graphite (black), and gas-phase UPS (gray). The right panel shows vacuum levels before (dashed curves) and after (solid curves) DIP deposition. Spectra of clean surfaces of Cu(111) and graphite are also shown (pale gray). SS indicates the surface states of clean Cu(111). The gas-phase spectrum is shown in ionization energy for comparison with DIP MLs. Vibration satellites in the gas phase and DIP-ML-graphite spectra are indicated by

inverted triangles. Weak features marked by σ^* in UPSs of DIP-ML-graphite and the graphite substrate are the conduction band features of graphite.

2. Mechanism for Doping Induced p Type C₆₀ Using Thermally Evaporated Molybdenum Trioxide (MoO₃) as a Dopant²

Thermally evaporated molybdenum trioxide (MoO₃) doped C₆₀ films, which could change n type features of pristine C₆₀ to form a p type mixed C₆₀ layer, are investigated by x-ray and ultraviolet photoelectron spectroscopy. It is found that C₆₀ HOMO progressively shifts closer to the Fermi level after increased MoO₃ doping concentration, and final onset of C₆₀ HOMO is pinned at binding energy of 0.20 eV, indicating the formation of p type C₆₀ films. It is proposed that in charge transfer induced p type C₆₀ formation, due to large electron affinity of MoO₃ (6.37 eV), electrons from HOMO of C₆₀ could easily transfer to MoO₃ to form cations and therefore increase hole concentration, which could gradually push C₆₀ HOMO to the Fermi level and finally form p type C₆₀ films. Moreover, clear different types of C₆₀ species have been confirmed from UPS spectra in highly doped films.

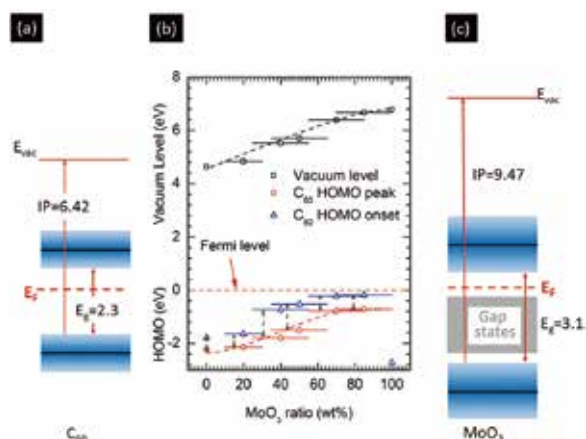


Figure 3. Evolution of energy level of MoO₃-doped C₆₀ film with MoO₃ ratios. (a) and (c) Energy level diagram for pristine C₆₀ and MoO₃ films respectively; (b) summarized HOMO peak of C₆₀, HOMO onset of C₆₀ and vacuum level as a function of different MoO₃ doping ratios are shown according to the Fermi level position.

References

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- 2) J.-P. Yang, W.-Q. Wang, L.-W. Cheng, Y.-Q. Li, J.-X. Tang, S. Kera, N. Ueno and X.-H. Zeng, *J. Phys.: Condens. Matter* **28**, 185502 (6 pages) (2016).