

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 photoemission 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, 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).

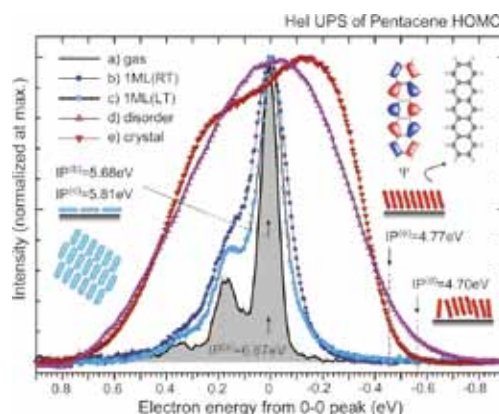


Figure 1. Wide variety in the feature of ultraviolet photoelectron spectra (UPS) for the HOMO band region taken for pentacene molecule in various aggregations (gas-phase, lying monolayers, standing monolayer, and disordered film).

Selected Publications

- Q. Xin, S. Duhm, F. Bussolotti, K. Akaike, Y. Kubozono, H. Aoki, T. Kosugi, S. Kera and N. Ueno, "Accessing Surface Brillouin Zone and Band Structure of Picene Single Crystals," *Phys. Rev. Lett.* **108**, 226401 (5 pages) (2012).
- 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. Impact of Intermolecular Interaction on the Reorganization Energy of Molecules¹⁾

Organic semiconductors are molecular solids with specific charge transport properties due to weak intermolecular interaction. The transport properties of organic single crystals and organic thin films are far from being adequately understood. Important subjects still to be understood are related to molecular and lattice vibrations (phonons) and their coupling to a charge carrier. The electron–phonon interaction depends on the molecular structure and their packing motif and therefore it can impact both molecular site energies and transfer integrals. The overall strength of local electron–phonon coupling observed in highly-resolved UPS is given by the relaxation energy between neutral and ionized states, and the reorganization energy associated.

We investigated the impacts of perfluorination on the electronic structure of pentacene (PEN) monolayer on graphite and hole–vibration coupling, which is specified by the reorganization energy and the binding energy of molecular polaron. We demonstrate that electron-withdrawing property of F atom mediates increase in spatial spread of highest-occupied molecular orbital (HOMO), which contributes significantly to increase in the vibronic-satellite intensity, and then leads to significant increase in reorganization energy. This contribution is much larger than an opposite contribution by lowering of vibration energies by perfluorination of PEN.

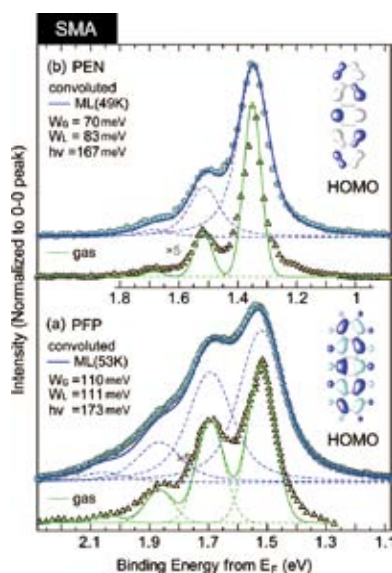


Figure 2. Comparison of HOMO band between gaseous HeI UPS (triangles) and angle-integrated UPS (circles) for the monolayer of perfluoropentacene (PFP) (a) and PEN (b), compared with convoluted curves by the single mode analysis of vibration coupling.

2. Mechanism of Energy-Level Alignment: Gap States Induced by Inert Gas Exposure²⁾

Energy level alignment (ELA) at organic–substrate and organic–organic interfaces is a crucial issue for any organic-based device, given that the interface electronic structure

controls the charge injection process in the organic semiconductor. Despite considerable effort, however, there still remains a mystery why some organic semiconductors, such as PEN, always show p-type charge transport property while some others, such as C₆₀, show n-type property without heavy intentional doping, that is the transport property seems to be determined by molecule itself. Therefore, a consensus on ELA mechanism has yet to be reached.

We examined the energy distribution of density-of-gap state (DOGS) of the order of 10¹⁶ states eV⁻¹cm⁻³, which is comparable to DOGS detected by electrical measurements, in an organic layer by means of ultralow background, high sensitivity UPS technique. We investigate PEN deposited on SiO₂/Si(100) and Au(111) substrates at 295 K. The impact of exposure to 1-atm of inert N₂ atmosphere on the PEN electronic properties is evaluated. Despite the absence of chemical interaction between N₂ and PEN molecules, the DOGS and ELA at the PEN/SiO₂ interface are strongly modified by the exposure to N₂ gas. This effect is ascribed to the structural disorder caused by N₂ molecules penetrating into the PEN film. A similar effect is observed upon exposure to Ar, while in case of O₂ exposure, the DOGS formation is accelerated, presumably because of the difference in the chemical properties of the gas molecules.

The present results demonstrate that structural disorder has a significant impact on the electronic properties and interfacial ELA. This is related to the nature of organic semiconductor crystals, which consists of low-symmetry molecules held together by weak intermolecular forces. The results also have great practical significance, as they show that organic layer processing in inert atmosphere does affect the electronic structure of the organic semiconductor, a point which had not been understood so far.

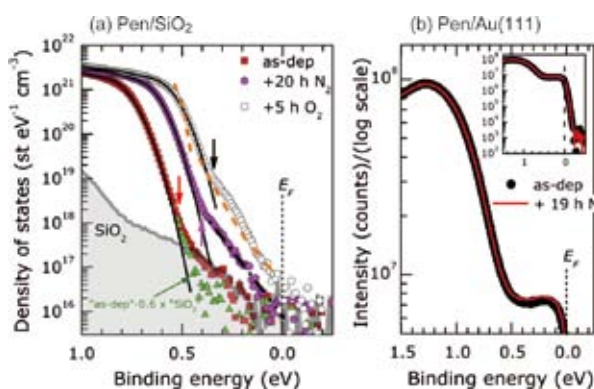


Figure 3. (a) DOS (log scale plot) of as-deposited, N₂-exposed, and O₂-exposed PEN film on SiO₂ by XeI-UPS. (b) XeI-UPS of as-deposited PEN film on Au(111) before and after N₂ exposure.

References

- 1) S. Kera, S. Hosoumi, K. Sato, H. Fukagawa, S. Nagamatsu, Y. Sakamoto, T. Suzuki, H. Huang, W. Chen, A. T. S. Wee, V. Coropceanu and N. Ueno, *J. Phys. Chem. C* **117**, 22428–22437 (2013).
- 2) F. Bussolotti, S. Kera, K. Kudo, A. Kahn and N. Ueno, *Phys. Rev. Lett.* **110**, 267602 (5 pages) (2013).