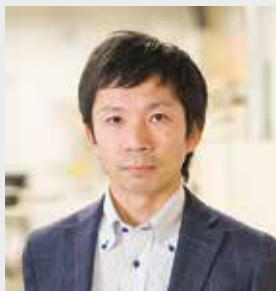


Electronic Property of Functional Organic Materials

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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 even for solid phases due to weak 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 impacts on the electronic states of 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.

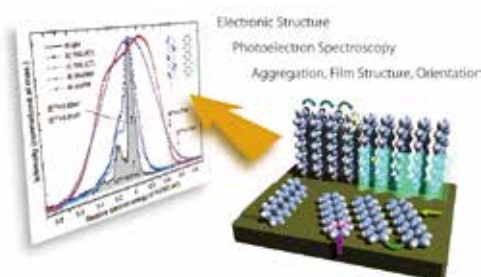


Figure 1. Scheme of a rich assortment in the structure of functional molecular materials and variety in the spectral feature of ultraviolet photoelectron spectrum (UPS) for the HOMO band taken for various structural phases (gas-phase, lying monolayers, standing monolayer, and disordered film).

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. Hole–Phonon Coupling Effect on the Band Dispersion of Organic Molecular Semiconductors¹⁾

Understanding the mechanism of charge transfer in functional molecular solids, the electronic structure measurement, especially of the energy-band dispersion, is requested for molecular materials. However the electronic structure measurement has not been well achieved due to experimental difficulties for the molecular solids. More importantly, the dynamic interaction between the traveling charges and the molecular vibrations is critical for the charge transport in organic semiconductors. However, a direct evidence of the expected impact of the charge–phonon coupling on the band dispersion of organic semiconductors is yet to be provided. We reported on the electronic properties of rubrene single crystal as investigated by angle resolved ultraviolet photoelectron spectroscopy. A gap opening and kink-like features in the rubrene electronic band dispersion are observed. In particular, the latter results in a large enhancement of the hole effective mass, well above the limit of the theoretical estimations. The results are consistent with the expected modifications of the band structures in organic semiconductors as introduced by hole–phonon coupling effects and represent an important experimental step toward the understanding of the charge localization phenomena in organic materials.

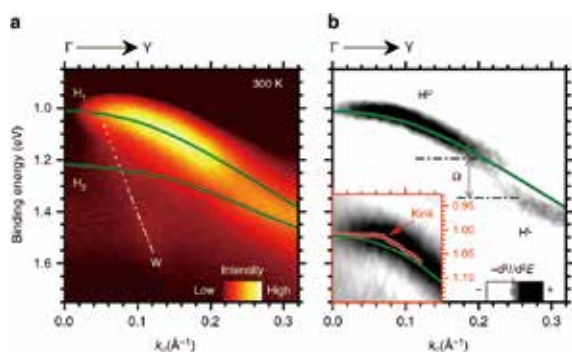


Figure 2. Renormalization of the energy-band dispersion of HOMO band of rubrene single crystal at 300 K. a) The photoelectron-emission intensity map by ARUPS. Binding energy vs. k_{\parallel} along the ΓY direction of the single crystal. Theoretical HOMO band dispersions are plotted as continuous green lines. The secondary-electron emission feature of W is overlapping (dashed line). b) Second derivative of ARUPS intensity map as obtained from data in a). The splitting of the HOMO band in two subband H^U and H^L is evidenced as separated by gap Ω . Inset: Magnification of second derivative map close to Γ point. Experimental H peak positions are also indicated by red circles and compared with theoretical band dispersion (continuous green line) to highlight the kink-like distortion.

2. Metal–Organic Interface Functionalization via Acceptor End Groups²⁾

The presence of functional groups in π -conjugated molecules not only determines the specific electronic and geo-

metrical properties of the molecule, but also impacts the molecule–substrate and the molecule–molecule interactions. We reported a comprehensive study of the complex interface between perylene-3,4,9,10-tetracarboxylic diimide (PTCDI) and the (111) surfaces of the three coinage metals. The specific structural, electronic, and chemical properties of the interface rendered by the different substrate reactivities are monitored with low-energy electron diffraction (LEED), x-ray standing waves (XSW), and ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS). In particular, the balance between molecule–substrate and molecule–molecule interactions is considered when interpreting the core-level spectra of the different interfaces. By presenting additional adsorption distances of the unsubstituted perylene, we show that the molecular functionalization via end groups with acceptor character facilitates the charge transfer from the substrate but it is not directly responsible for the associated short adsorption distances, demonstrating that this frequently assumed correlation is not necessarily correct.

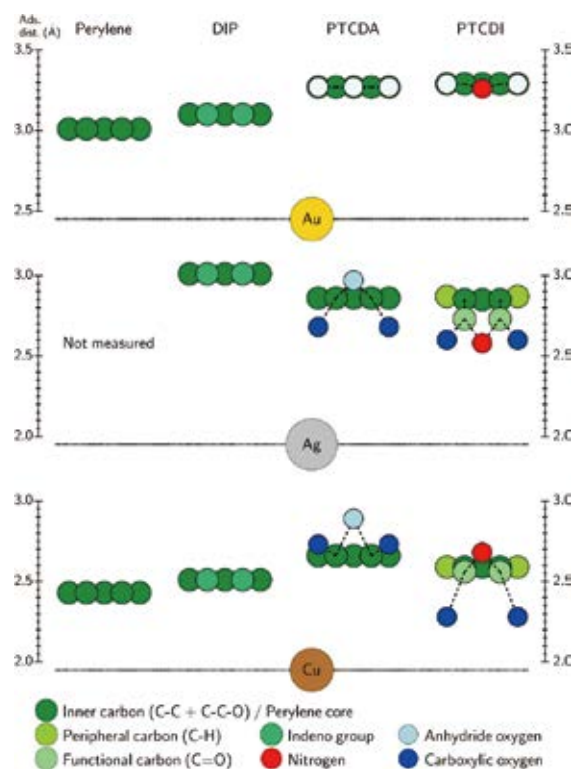


Figure 3. Adsorption distances extracted from XSW measurements for different perylene derivatives. Together with the data for perylene, DIP and PTCDI on Au(111), Ag(111) and on Cu(111). The adsorption distances on Au(111) have been corrected taking into account the surface reconstruction.

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- 1) F. Bussoletti, J. Yang, T. Yamaguchi, Y. Nakayama, M. Matsunami, H. Ishii, N. Ueno and S. Kera, *Nat. Commun.* **8**, 173–179 (2017).
- 2) A. F.-Canellas, Q. Wang, K. Broch, D. A. Duncan, P. Kumar Thakur, L. Liu, S. Kera, A. Gerlach, S. Duhm and F. Schreiber, *Phys. Rev. Mater. (Rapid)* **1**, 013001 (6 pages) (2017).