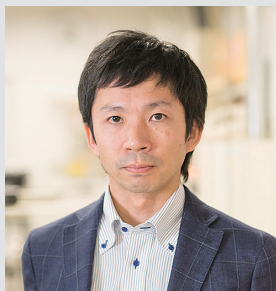


Electronic Property of Functional Organic Materials

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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 the origin of various device characteristics are still under debate. Scientific discussions have been redundant because of long-standing beliefs that the electronic structure of FOM would be conserved as in an isolated molecule even for solid phases due to the weak van der Waals interaction. To reveal characteristics of FOM, it is essential to investigate precisely the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. Recently we realized that the weak electronic interaction manifests itself as small intensity modulations of fine structures in photoelectron spectra, depending on the adsorption and aggregation conditions on the surface. Thanks to recent instrumentation improvements, we can assess hidden fine features in the electronic states, *e.g.* electron–phonon coupling, quasi-particle states, very small densities of gap states, narrow band dispersion, and dynamic electronic polarization. To elucidate what really impacts on the electronic states of the FOM in their assembly as well as at the interface upon weak interaction, an evaluation of the wave-function spread of the

electronic states is very important because the interface states are described as a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization). Observing modifications of electron wave functions upon weak electronic coupling as well as strong electron–phonon coupling is a central issue on our agenda.

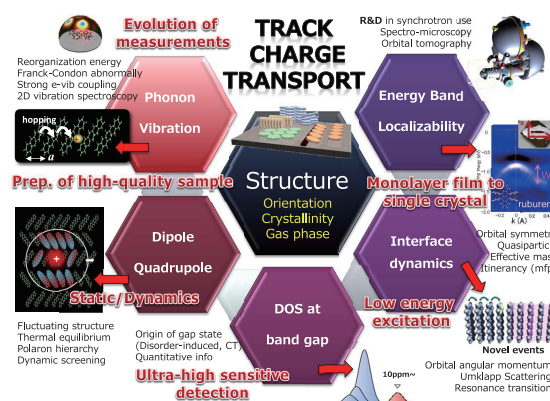


Figure 1. Overview of our agenda. A rich assortment of surface and interface structures of FOM to provide complicated spectral features of ultraviolet photoelectron spectroscopy.

Selected Publications

- Y. Nakayama, S. Kera and N. Ueno, *J. Mater. Chem. C* **8**, 9090–9132 (2020). [review]
- S. Kera, T. Hosokai and S. Duhm, *J. Phys. Soc. Jpn.* **87**, 061008 (7 pages) (2018). [review]
- J.-P. Yang, F. Bussolotti, S. Kera and N. Ueno, *J. Phys. D: Appl. Phys.* **50**, 423002 (45 pages) (2017). [review]
- S. Kera and N. Ueno, *J. Electron Spectrosc. Relat. Phenom.* **204**, 2–11 (2015). [review]

1. Photoemission Tomography of One Dimensional Row Structure of Flat-Lying Picene Multilayer on Ag(110)¹⁾

Photoemission tomography (PT) is a powerful technique for the detailed analysis of the shape and the energy of molecular orbitals from the photoelectron momentum distribution. In the case of planar-conjugated molecules with light atoms, the momentum map of the photoelectrons from frontier orbitals can be seen as the Fourier transform (FT) of the corresponding molecular orbital, by assuming the plane-wave final state in the photoemission process. Thus, PT is able to determine the shape of the molecular orbitals in the sample if the molecular arrangement in the sample is known, while it can also be utilized for the determination of the molecular arrangement in the specimen if the molecular orbital of the sample molecule is known.

We applied PT to a unique one-dimensional row structure of a picene multilayer realized on an anisotropic Ag(110) surface. The clearly deconvoluted experimental momentum maps were compared to the FT simulation of the molecular orbitals of picene in detail, enabling not only the evaluation of the electronic structure of the picene in the multilayer but also the quantitative determination of the molecular orientation in the multilayer within a few degrees. In addition, the PT results indicated the orientation of the molecules in all layers to be flat-lying. The successful demonstration of PT of the multilayer molecular film marks an important step toward the wide-range utilization of the PT technique.

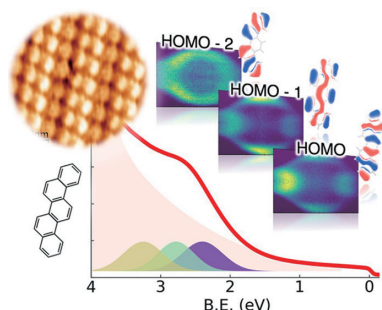


Figure 2. Scheme of photoelectron spectrum of the picene film, STM molecular arrangement, and PT images for top three molecular orbitals. The figure is after ref 1).

2. Sample-Shape Dependent Energy Levels in Organic Semiconductors²⁾

Most of the tuning of the ionization energy and electron affinity was done by changing the constituent molecules in the device. This is because the organic solids consist of organic molecules bound by weak vdW interactions, hence intermolecular interaction is considered to play a minor role. The contribution of the intermolecular interaction to the energy levels of organic solids is represented by the difference in the energy levels between the gas and solid phases.

Recent studies, however, have revealed that the energy levels can be altered as much as 1 eV by the molecular orientation in the film or the molecular mixing ratio in the binary film, owing to the intermolecular electrostatic interaction. Because of the long-range nature of Coulomb interaction, theory predicts that the electrostatic energy should depend on the sample shape. In this study, we examined the coverage-dependent energy levels of zinc phthalocyanine (ZnPc) and per-fluorinated ZnPc (F_{16} ZnPc) in the monolayer region with ultraviolet photoelectron spectroscopy and low-energy inverse photoelectron spectroscopy. Using the procedure we reported previously, we separately evaluated the electronic polarization energy and electrostatic energy as a function of coverage. Unlike the electronic polarization, which contributes only as much as 10 meV, the electrostatic energy contributes as much as 120 meV to the coverage-dependent energy shift. We concluded that the shift in energy levels by changing the coverage is attributed to the sample shape-dependent energy level, owing to the long-range nature of the charge-permanent quadrupole interaction.

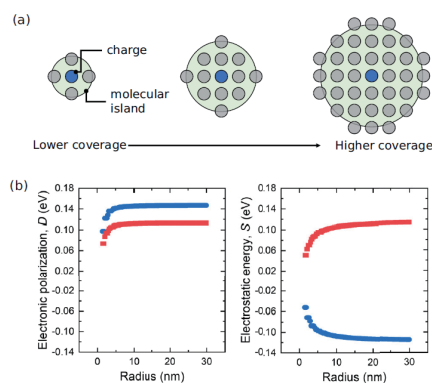


Figure 3. (a) Disk model for the growing island without a changing lattice constant. (b) Calculated polarization energy and electrostatic energy for ZnPc and F_{16} ZnPc are indicated with blue circles and red squares. The figure is after ref 2).

3. Other Activities in UVSOR

We have conducted beamline R&D and user supports in collaboration with other universities. Experiments using photoelectron momentum microscope are developing at BL6U.^{3,4)}

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