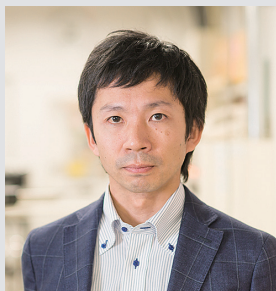


Electronic Property of Functional Organic Materials

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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.

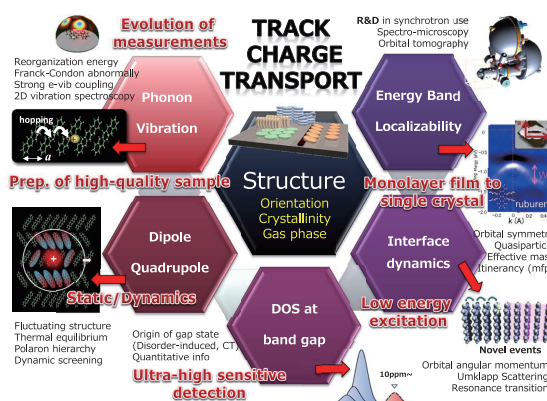


Figure 1. Overview of our agenda. A rich assortment of surface and interface structures of FOM to provide complicated spectral features of ultraviolet photoelectron spectroscopy.

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. Experimental Observation of Anisotropic of Valence Band Dispersion in the Organic Semiconductor Crystal (DNTT)¹⁾

Organic semiconductors based on the aromatic compounds having wide π -conjugation are attracting the attention of researchers because of their applications in various electronic devices. One of the central interests of these materials considering their physicochemical properties is their charge transport mechanism. In general, the conduction of charge carriers in most of the organic semiconductor solids is happening through the intermolecular hopping processes among the discrete molecular orbitals. However, some organic semiconductors with high charge-carrier mobility such as pentacene and rubrene exhibit continuous energy dispersion of valence bands, and the characteristics of the so-called “band transport” have been proposed.

The molecule focused on in this study is dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT). Although it has been proposed that the transport mechanism of DNTT is a band transport, the valence band dispersion has not yet been observed experimentally. In this study, we elucidate the valence band structure of DNTT single crystals using angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) along three inequivalent crystallographic directions in the surface Brillouin zone. The valence band maximum is verified to be positioned at the Γ point, and the ionization energy of a DNTT single crystal is determined to be 5.02 eV at the VBM. The effective mass of hole is derived from the curvature of the experimental valence band at the Γ point in all three directions, where the lowest value of $2.6m_0$ is measured along the Γ -S direction.

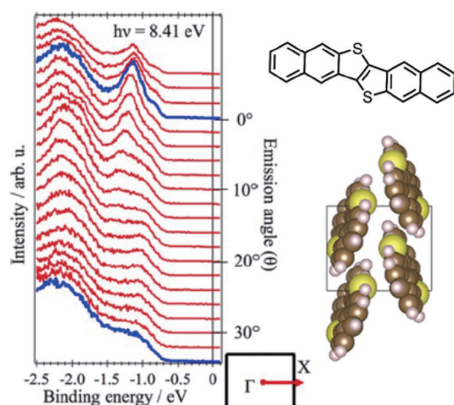


Figure 2. Xel-ARUPS spectra of the DNTT single crystal taken along Γ -X direction. The figure is after ref 1).

2. Accessing the Conduction Band Dispersion in $\text{CH}_3\text{NH}_3\text{PbI}_3$ Single Crystal²⁾

The conduction band dispersion in methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$), which is a potential candidate for photovoltaic absorbers due to its high-light absorption coeffi-

cient, long carrier lifetime and diffusion length, low exciton binding energy, and easy fabrication, was studied both by angle-resolved two photon photoelectron spectroscopy (AR-2PPE) with low photon intensity (~ 0.0125 nJ/pulse) and angle-resolved low-energy inverse photoelectron spectroscopy (AR-LEIPS). Clear energy dispersions of the conduction band along Γ -M direction are observed by these independent methods under different temperatures for the first time, and the dispersion is found to be consistent with band calculation under a cubic phase. The effective mass of the electrons at Γ point is estimated to be $(0.20 \pm 0.05)m_0$ at 90 K. The observed energy position is significantly different between the AR-LEIPS and AR-2PPE, which is ascribed to the electronic-correlation effects depending on the difference of initial/final state probing processes. The present results also indicate that the surface structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is given by a $\text{CH}_3\text{NH}_3 + \text{I}$ plane, which provides the cubic dominated electronic property even at lower temperatures.

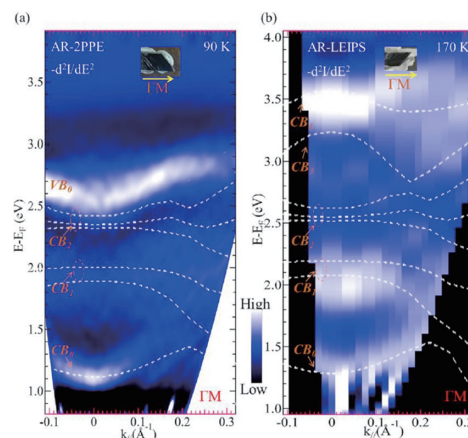


Figure 3. Second-derivative intensity maps of (a) AR-2PPE spectra and (b) AR-LEIPS spectra of $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystal. The figure is after ref 2).

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⁾

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