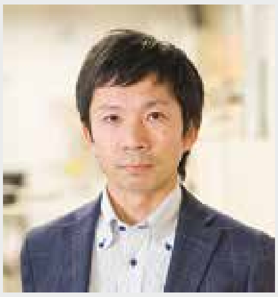
Electronic Property of Functional Organic Materials

Department of Photo-Molecular Science
Division of Photo-Molecular Science III



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Education

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Professional Employment

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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 were sometimes challenging 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 key to precisely investigate the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. In these systems, the weak electronic interaction appears as small intensity modulations of fine features 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, weak band dispersion, and dynamic electronic polarization. To elucidate what really impacts 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 would be 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.

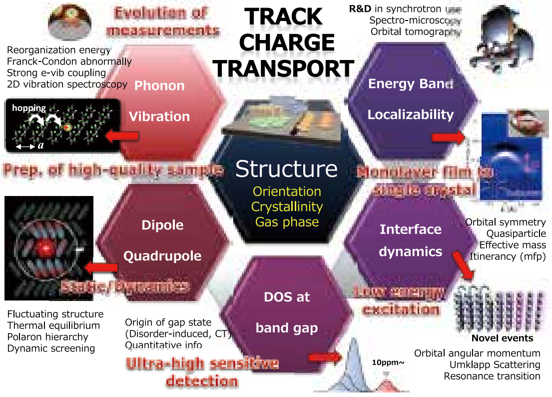

Figure 1. Overview of our agenda. A rich assortment of surface and interface structures of FOM to provide complicated spectral features of ultraviolet photoelectron spectroscopy.

Selected Publications

- 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. Widely Dispersed Intermolecular Valence Bands of Epitaxially Grown Perfluoropentacene on Pentacene Single Crystals[1)]

Strong intermolecular electronic coupling and well-ordered molecular arrangements enable efficient charge transport in semiconducting π-conjugated molecular solids. Molecular heteroepitaxy to form crystallized donor–acceptor molecular interfaces potentially leads to a novel strategy for creating efficient organic optoelectronic devices. In the present study, the crystallographic and electronic structures of a heteroepitaxial molecular interface, perfluoropentacene (PFP, $C_{22}F_{14}$) grown on pentacene single crystals (Pn-SCs, $C_{22}H_{14}$), were determined by means of grazing-incidence X-ray diffraction (GIXD) and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), respectively. GIXD revealed that PFP uniquely aligned its primary axis along the $[1\bar{1}0]$ axis of crystalline pentacene to form well crystallized overlayers. Valence band dispersion (at least 0.49 eV wide) was successfully resolved by ARUPS. This indicated a small hole effective mass and a significant transfer integral between the frontier molecular orbitals of the nearest-neighbor PFP molecules, ensuring the presumable occurrence of efficient band-like transport in the epitaxial PFP crystallites.

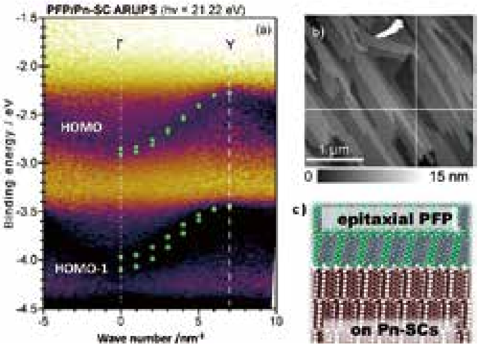

Figure 2. (a) ARUPS intensity map of the 4nm thick PFP overlayer on Pn-SC sample taken in the Γ–Y directions plotted on the $E–K_{||}$ plane. The theoretical band structures predicted by Yoshida *et al.* [*Phys. Rev. B* **92**, 075145 (2015)] are plotted as circles. (b) AFM image of a PFP (5nm)/Pn-SC substrate. The figure is after ref 1) with permission.

2. Molecular Parameters Responsible for Thermally Activated Transport in Doped Organic Semiconductors[2)]

Doped organic semiconductors typically exhibit a thermal activation of their electrical conductivity, whose physical origin is still under scientific debate. We disclose relationships between molecular parameters and the thermal activation energy (E_A) of the conductivity, revealing that charge transport is controlled by the properties of host–dopant integer charge transfer complexes (ICTCs) in efficiently doped organic semiconductors. At low doping concentrations, charge transport is limited by the Coulomb binding energy of ICTCs, which can be minimized by systematic modification of the charge distribution on the individual ions. The investigation of a wide variety of material systems reveals that static energetic disorder induced by ICTC dipole moments sets a general lower limit for E_A at large doping concentrations. The impact of disorder can be reduced by adjusting the ICTC density and the intramolecular relaxation energy of host ions, allowing an increase of conductivity by many orders of magnitude. The observed correlation between E_A and the density of ICTCs indicates that the minimum achievable E_A is generally limited by the electrostatic disorder of ICTCs, which can be reduced by using large molecules or ICTCs with small dipole moments.

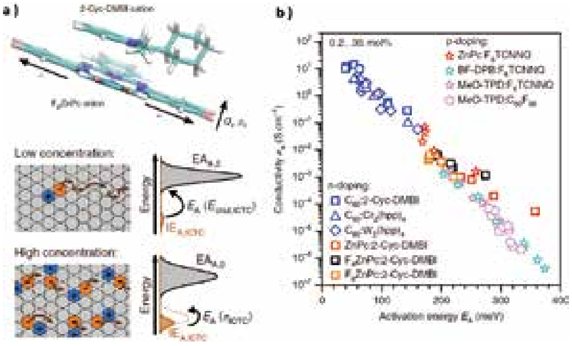

Figure 3. a) Simplified sketch of charge transport in different concentration regimes. At low doping concentrations, electron transport requires a dissociation of ICTCs into separated charges, resulting in an increase of E_A. At large doping concentrations and small distances between ICTCs, transport can be described ideally by electron transport between different ICTC configurations whose local energies change continuously and where multi-electron hops may also play a role. b) The change of conductivity with concentration goes along with a change of E_A. Starting from low doping concentrations, all material combinations investigated show a decrease of E_A with increasing doping concentration, explaining the increase of conductivity. 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. Introduction of novel momentum microscope launched at BL6U is started.

References

1) Y. Nakayama, R. Tsuruta, N. Moriya, M. Hikasa, M. Meissner, T. Yamaguchi, Y. Mizuno, T. Suzuki, T. Koganezawa, T. Hosokai, T. Ueba and S. Kera, *J. Phys. Chem. Lett.* **10**, 1312–1318 (2019). [Selected for Journal Cover]

2) M. Schwarze, C. Gaul, R. Schol, F. Bussolotti, A. Hofacker, K. S. Schellhammer, B. Nell, B. D. Naab, Z. Bao, D. Spoltore, K. Vandewal, J. Widmer, S. Kera, N. Ueno, F. Ortmann and K. Leo, *Nat. Mater.* **18**, 242–248 (2019).

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