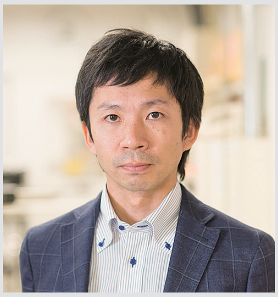
Electronic Property of Functional Organic Materials

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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2001	Research Associate, Chiba University
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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.

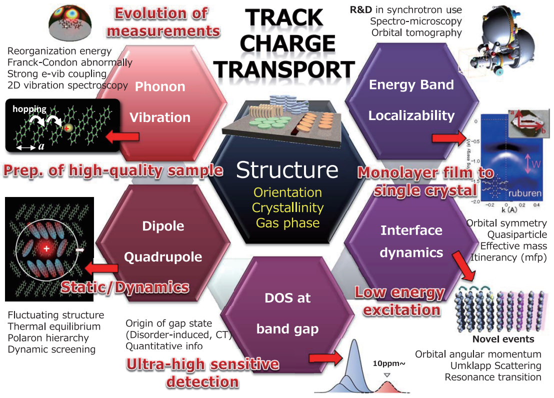

Figure 1. Overview of our agenda. A rich assortment of surface and interface structures of FOM to provide complicated spectral features of ultraviolet photoelectron spectroscopy.

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. Surface Characterization of Covalent Organic Frameworks[1)]

Covalent organic frameworks (COFs), as a large class of porous organic materials, have attracted intense research in the past few decades due to the great potential for applications. Substituting carbon with silicon in organic molecules and materials has been an attractive way to modify their electronic structure and properties. Silicon-doped graphene-based materials are known to exhibit exotic properties, yet conjugated organic materials with atomically precise Si substitution have remained difficult to prepare. We present the on-surface synthesis of one- and two-dimensional covalent organic frameworks whose backbones contain 1,4-disilabenzene (C_4Si_2) linkers. Silicon atoms were first deposited on a Au(111) surface, forming a $AuSi_x$ film on annealing. The subsequent deposition and annealing of a bromo-substituted polyaromatic hydrocarbon precursor on this surface led to the formation of the C_4Si_2-bridged networks, which were characterized by a combination of high-resolution scanning tunnelling microscopy and X-ray photoelectron spectroscopy taken at BL2B of UVSOR supported by density functional theory (DFT) calculations. Each Si in a hexagonal C_4Si_2 ring was found to be covalently linked to one terminal Br atom. For the linear structure obtained with the pyrene-based precursor, the C_4Si_2 rings were converted into C_4Si pentagonal siloles by further annealing.

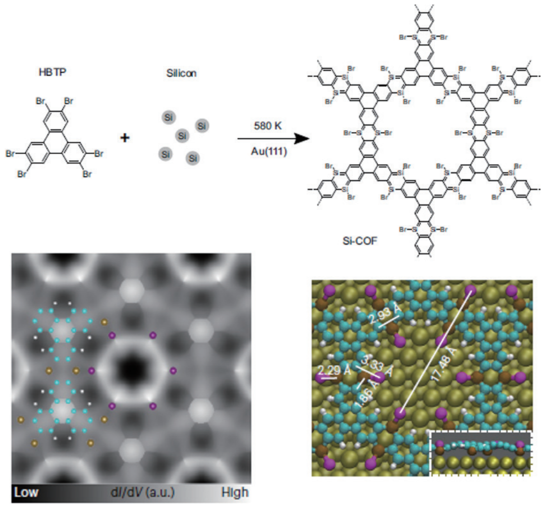

Figure 2. Top: Scheme of on-surface reaction for the aryl–Si coupling reaction on Au(111). Bottom: High-resolution constant height *dI*/*dV* map of the COF taken with a CO tip and the top and side views of DFT simulation. The figure is after ref 1).

2. Photoemission Tomography of Br-Doped Perylene Monolayer[2)]

Energy level alignment at the organic–metal interface is an important issue in the field of organic electronics to understand the efficiency of charge injection and fundamental conduction mechanisms. The spectroscopic data of organic cations seem slightly insufficient, comparing to that of organic anions using strong molecular acceptor and alkali metal doping. Halogens are fundamental elements and have been widely used as hole dopants for organic electronics since the very early stages of research. Perylene doped with bromine exhibit a dramatic increase in conductivity. In this study, we observed the geometric and electronic structures of a monolayer of perylene molecules on the surfaces of Au(110) and Au(111). The effect of bromine doping was studied using C-K NEXAFS, angle-resolved photoemission spectroscopy (ARPES), and X-ray photoelectron spectroscopy (XPS). C-K NEXAFS can be used to observe vacant states, particularly a hole state, which is essential for p-type organic semiconductors. Moreover, the inclined molecular orientation is analyzed by measuring the polarization dependence. ARPES and 2D momentum map using a photoelectron momentum microscope at BL6U of UVSOR is a powerful technique for discussing the changes in the molecular orbital character upon the doping.

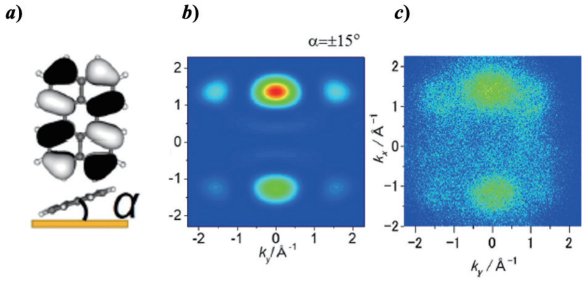

Figure 3. (a) HOMO distribution of a perylene molecule. (b) Simulated photoemission momentum maps of HOMO. (c) Experimental momentum map at binding energy of 1.5 eV. The figure is after ref 2).

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.[2,3)] The perspectives required for future light-source facility have been discussed with communities.[4)]

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2) O. Endo, F. Matsui, S. Kera, W.-J. Chun, M. Nakamura, K. Amemiya and H. Ozaki, *J. Phys. Chem. C* **126**, 15971–15979 (2022).
3) Y. Hasegawa, F. Matsui and S. Kera, *e-J. Surf. Sci. Nanotechnol.* **20**, 174–179 (2022).
4) H. Ota *et al.*, *J. Phys: Conf. Ser.* **2380**, 012003 (5 pages) (2022).

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