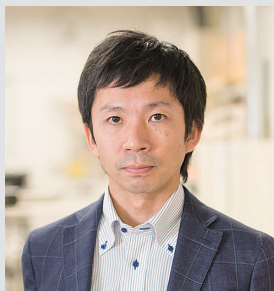


# Electronic Property of Functional Organic Materials

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2009 Visiting Associate Professor, Institute for Molecular Science  
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2013 Visiting Associate Professor, Soochow University  
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Professor, The Graduate University for Advanced Studies  
Visiting Professor, Chiba University  
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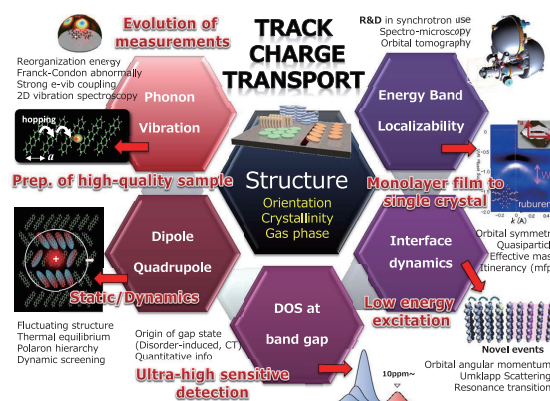
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## Keywords

Photoelectron Spectroscopy, Molecular Assemble, Electronic State

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.

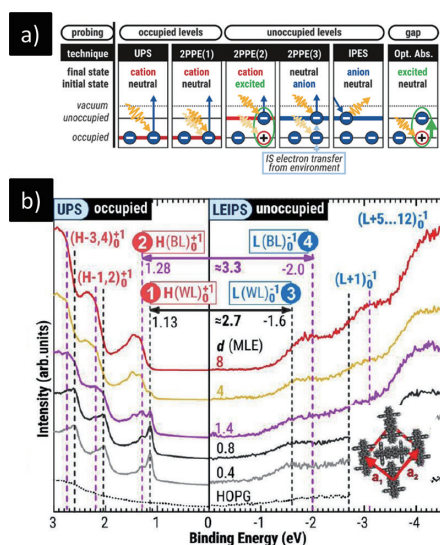
## Selected Publications

- 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. The Role of Initial and Final States in Molecular Spectroscopies: A Case Study of DBP<sup>1,2)</sup>

Interpreting experimental spectra of organic semiconductor films is challenging, and understanding the relationship between experimental data obtained by different spectroscopic techniques, UPS, IPES, 2PPE and optical absorption requires a careful consideration of the initial and final states for each process. We present a coherent framework that is capable of treating on equal footing most spectroscopies. We develop a simple model for the expected energy level positions by the spectroscopies and relate them to the energies of molecular states. Molecular charging energies in photoionization processes, as well as adsorption energies and the screening of molecular charges due to environmental polarization, are taken into account as the main causes for shifts of the measured spectroscopic features. We explain the relationship between these quantities, as well as with the transport gap, the optical gap and the exciton binding energy.<sup>1)</sup>

Our considerations serve as a model for weakly interacting systems where wave function hybridizations between adjacent molecules are negligible as demonstrated for DBP films on graphite.<sup>2)</sup>

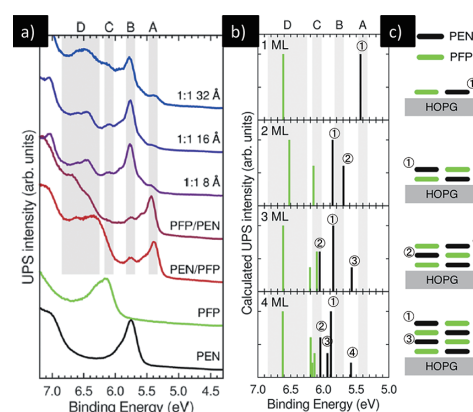


**Figure 2.** a) Scheme of the typical spectroscopic processes in UPS, 2PPE, IPES, and optical absorption in relation to the initial and final states. b) Thickness dependences of Xel-UPS and IPES (LEIPS) of DBP films on graphite. The energy positions of bilayer (BL) are shifted from wetting layer (WL) of monolayer. The figure is after ref 1,2).

## 2. Impacts of Electrostatic Interactions on the Energy Levels of Organic Semiconductor Blends<sup>3)</sup>

Halogenation of conjugated molecules represents a powerful approach to tune the electronic structure of molecular thin

films through inductive effects and long-range intermolecular electrostatic interactions. We provide a comprehensive experimental and theoretical analysis of the prototypical blend formed by pentacene (PEN) and perfluoropentacene (PFP) to relate structure with electronic properties. We find a mixed-stack structural motif in standing and lying orientations depending on the substrate nature. In the standing orientation, the ionization potential lies in between the values of the pure components, in line with the established picture of averaged molecular quadrupole moments. For the lying orientation, however, we experimentally observe an ionization potential lower than both pristine values, which seems at odds with this simple rationale. Electrostatic simulations based on the knowledge of the atomistic structure of the films capture the complex experimental scenario for both orientations. In particular, the ultralow ionization potential of films formed by lying molecules is identified as a signature of the monolayer structure, where quadrupolar interactions are responsible for a difference of *ca.* 0.4 eV in the highest occupied molecular orbital energy as compared to thicker films with the same molecular orientation.



**Figure 3.** (a) UPS of blends PEN/PFP films of lying orientation on graphite. The spectra of PEN and PFP monolayers are shown as reference. b) Calculated energy levels of PEN:PFP layers; black and green bars correspond to the IPs of PEN and PFP, respectively. The calculated intensity (bar height) depends on the depth  $z$  of the ionized layer from the surface in Figure 3c). The figure is after ref 3).

## 3. Other Activities in UVSOR

We have conducted beamline R&D and user supports in collaboration with other universities. Experiments using photoelectron momentum microscope is started at BL6U.<sup>4)</sup>

### References

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- 4) F. Matsui *et al.*, *Jpn. J. Appl. Phys.* **59**, 067001 (2020).

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