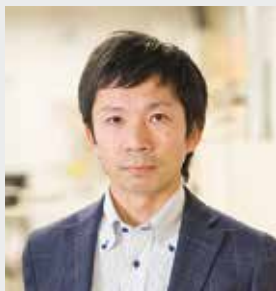# Electronic Property of Functional Organic Materials

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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 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.
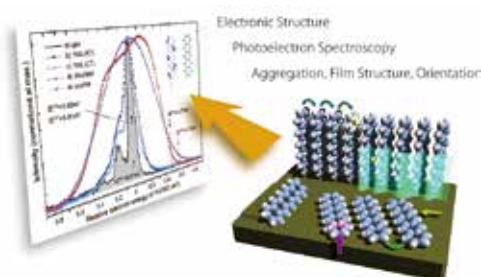

Figure 1. Scheme of a rich assortment of structures of functional molecular materials and spectral features of ultraviolet photoelectron spectroscopy (UPS) for the highest occupied molecular orbital (HOMO), measured for various structural phases (gas-phase, lying monolayers, standing monolayer, and disordered film).

Selected Publications

• S. Kera, T. Hosokai and S. Duhm, "Characteristics of Organic–Metal Interaction: A Perspective from Bonding Distance to Orbital Delocalization," *J. Phys. Soc. Jpn.* **87**, 061008 (7 pages) (2018). [review]

• J.-P. Yang, F. Bussolotti, S. Kera and N. Ueno, "Origin and Role of Gap States in Organic Semiconductor: As the Nature of Organic Molecular Crystals," *J. Phys. D: Appl. Phys.* **50**, 423002 (45 pages) (2017). [review]

• S. Kera and N. Ueno, "Photoelectron Spectroscopy on the Charge Reorganization Energy and Small Polaron Binding Energy of Molecular Film," *J. Electron Spectrosc. Relat. Phenom.* **204**, 2–11 (2015). [review]

1. Evolution of Intermolecular Energy Bands in Organic Thin Films[1]

In organic semiconductors, the hole and electron transport occurs through the intermolecular overlaps of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), respectively. A measure of such intermolecular electronic coupling is the transfer integral (t), which can experimentally be observed as energy level splittings or the width of the respective energy bands. Quantum chemistry textbooks describe how an energy level splits into two levels in molecular dimers, into three levels in trimers and evolves into an energy band in infinite systems, a process that has never been observed for the LUMO or beyond dimers for the HOMO. In this work, our new technique, low-energy inverse photoelectron spectroscopy (LEIPS), was applied to observe the subtle change of the spectral line shape of a LUMO-derived feature while we used ultraviolet photoelectron spectroscopy (UPS) to investigate the occupied states. We show at first that tin-phthalocyanine molecules (SnPc) grow layer-by-layer in quasi one-dimensional stacks on graphite, and then discuss a characteristic and systematic broadening of the spectral line shapes of both HOMO and LUMO. The results are interpreted as energy-level splittings due to the intermolecular electronic couplings. On the basis of the Hückel approximation, we determined the transfer integrals for HOMO−1, HOMO, and LUMO to be ~15 meV, ~100 meV, and ~128 meV, respectively.
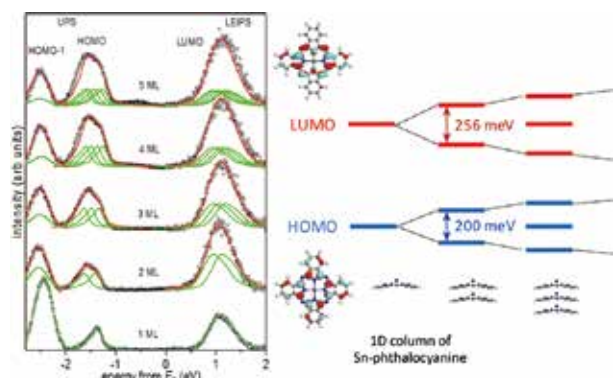

Figure 2. Left: Combined UPS and LEIPS spectra of SnPc films prepared on graphite (HOPG), with the thickness ranging between 1 and 5 monolayer (ML). The experimental data (open circles) are reproduced with the sum (red lines) of several spectral line shapes of the 1 ML peak (green lines) based on the energy levels calculated by Hückel model. Right: Energy splittings of HOMO and LUMO due to intermolecular orbital interaction. Corresponding orbital distributions are schematically shown together with quasi one-dimensional molecular stacking.

2. Efficient Organic Semiconductor Doping[2]

Doping plays a crucial role in semiconductor physics, with n-doping being controlled by the ionization energy of the impurity relative to the conduction band edge. In organic semiconductors, efficient doping is dominated by various effects that are currently not well understood. Here, we simulate and experimentally measure, with direct and inverse photoemission spectroscopies, the density of states and the Fermi level position of the prototypical materials C_{60} and zinc phthalocyanine n-doped with highly efficient benzimidazoline radicals (2-Cyc-DMBI). We simulate the electronic states of nanoclusters with different molecules in the centre surrounded by up to 14 additional C_{60} molecules to describe the near-field dielectric screening of charge distributions, and evaluate various charging states of the molecules in the centre of the clusters and their charging energies (EA and IP), and thereby construct the DOS of the doped system. We study the role of doping-induced gap states, and, in particular, of the difference Δ_1 between the electron affinity of the undoped material and the ionization potential of its doped counterpart. We show that this parameter is critical for the generation of free carriers and influences the conductivity of the doped films. Efficient dopants should be optimized with regard to the molecular doping parameter Δ_1, which is crucial in organic semiconductors but does not exist in traditional inorganic semiconductors because of the strong screening of electrostatic effects in inorganic materials.
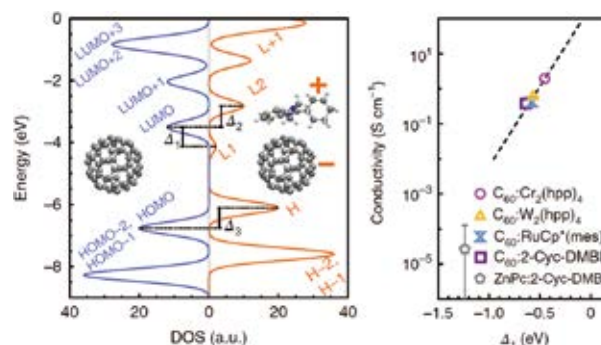
Figure 3. Left: DOS for neutral C_{60} (blue) and charged C_{60} next to a dopant (orange) in neat C_{60} bulk (14 molecules). Energy zero is aligned to vacuum and a Gaussian broadening of 0.2 eV is applied for illustration purposes. The introduction of dopants modifies the DOS of neat C_{60} considerably. While almost all levels of the anion shift upwards, the only one that shifts downwards is the occupied former LUMO of C_{60} (L1). Right: Conductivities in n-doped C_{60} at 2% concentration against Δ_1 for various molecular dopants. Tuning of Δ_1 may provide alternative strategies to optimize the electronic properties of organic semiconductors.

References

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2) C. Gaul, M. Schwarze, S. Schellhammer, F. Bussolotti, S. Kera, Z. Bao, G. Cuniberti, K. Leo and F. Ortmann, *Nat. Mater.* **17**, 439–444 (2018).

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