Division of Multidisciplinary Chemistry
– Molecular Aggregation Analysis –

http://www.kuicr.kyoto-u.ac.jp/labos/is2/scope.html

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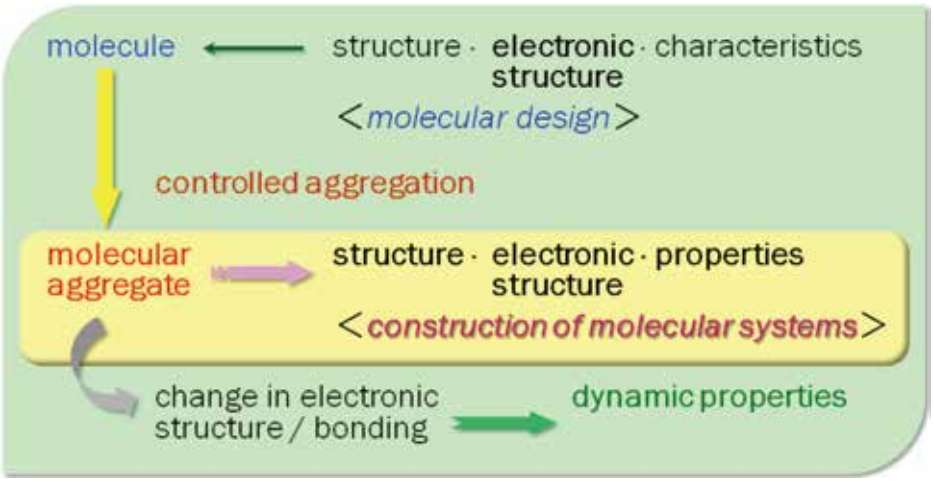
Scope of Research

The research of this subdivision is devoted to correlation studies on structures and properties of molecular aggregates, in particular, organic semiconductor solids and thin films, from two main standpoints: photoelectric and electric properties. The electronic structure of organic thin films is studied using photoemission and inverse photoemission spectroscopies in connection with the former, and its results are applied to create novel molecular systems with characteristic electronic functions. The latter is concerned with fabrication of organic electronic devices; elucidation of charge carrier generation and transport, examination of trapping states, understanding of interface electronic behaviors, and so on.

KEYWORDS
Charge Carrier Transport
Electronic Structure
Frontier Electronic State
Organic Semiconductor
Thin Film



Selected Publications

Murdey, R.; Sato, N., Photocurrent Action Spectra of Organic Semiconductors, *In "Advances in Organic Crystal Chemistry, Comprehensive Reviews 2015", Tamura. R.; Miyata, M. Eds., Springer, Tokyo*, 627-652 (2015).

Yoshida, H.; Yamada, K.; Tsutsumi, J.; Sato, N., Complete Description of Ionization Energy and Electron Affinity in Organic Solids: Determining Contributions from Electronic Polarization, Energy Band Dispersion and Molecular Orientation, *Phys. Rev. B*, **92,** 075145 (2015).

Photocurrent Action Spectra of Organic Semiconductor Thin Films

Photocurrent action spectra were measured for vacuum-deposited pentacene thin films 20 nm to 100 nm in thickness, as functions of incident photon energy, applied bias, photon flux, film thickness, and measurement temperature, in order to better understand the mechanisms underpinning photo-induced charge carrier generation, injection, and transport in molecular semiconductors. A strong dependence on the electrode material was found, and, for aluminum electrodes, the measured photocurrent was determined to originate from an intrinsic mechanism, where photogenerated electron-hole geminate pairs are created in the bulk film. For gold or titanium electrodes, a substantial contribution to the photocurrent from extrinsic, or injected, photocurrents was observed. The intrinsic photocurrent spectrum of pentacene thin film resembled the previous measurements obtained for thick films and single crystals (Figure 1). The onset of the intrinsic photocurrent, taken to indicate the transport energy gap, E_G, was determined to be 2.25 eV, the same value as in previous studies. Aluminum electrodes form blocking contacts that substantially reduce extrinsic photocurrents attributed to exciton-enhanced charge injection and transport, enhancing the visibility of the intrinsic processes. The dependence of the intrinsic photocurrent on temperature, photon flux, and applied field is consistent with a mechanism in which optical generation of a charge transfer state is followed by the thermally assisted dissociation of the geminate electron–hole pair into independent charge carriers.

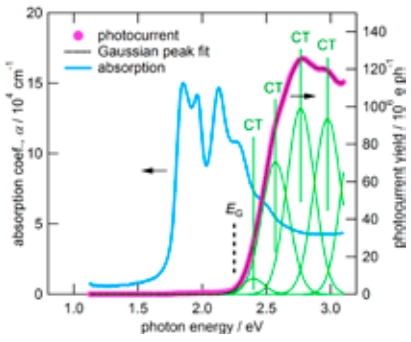


Figure 1. Photocurrent action spectra and absorption coefficient obtained for the 100 nm pentacene film / aluminum electrode device. Photocurrents are normalized to the incident photon flux. The transport energy gap is E_G = 2.25 eV, estimated from the threshold onset of the photocurrent yield.

Complete Description of Ionization Energy and Electron Affinity in Organic Solids: Determining Contributions from Electronic Polarization, Energy Band Dispersion, and Molecular Orientation

Ionization energy and electron affinity in organic solids are understood in terms of electronic energy levels of a single molecule perturbed by solid-state effects such as polarization energy, band dispersion, and molecular orientation as primary factors. We have precisely determined the electron affinities of pentacene (PEN) and perfluoropentacene (PFP) thin films with different molecular orientations (lying on HOPG and standing on SiO_2) to a precision of 0.1 eV using low-energy inverse photoemission spectroscopy (LEIPS) to confirm their molecular orientation dependence (Figure 2). On the basis of the determined electron affinities and the corresponding data of ionization energies in the solid state, and other relevant energy parameters, we evaluate the individual contribution of these effects quantitatively, with the aid of theoretical calculations. It turns out that the bandwidth ($2w_+$ and $2w_-$ for HOMO- and LUMO-derived bands, respectively) as well as the polarization energy (P_+ and P_- for a hole and an electron, respectively), in particular, the polarization energy of the thin film (P_+^{film} and P_-^{film}), which depends on the molecular orientation, contributes to the ionization energy (I_s) and electron affinity (A_s) in the solid state, while the effect of the surface dipole d is a few tenths of an eV at most and does not vary with the molecular orientation (Figure 3). As a result, we conclude that the I_s and A_s values of an organic thin film—key energy parameters characterizing the electronic structure of its frontier electronic states—are determined by corresponding values of component molecules under polarization energy and the energy dispersion, and that the molecular orientation dependence of the ionization energy and electron affinity of organic solids originates from the orientation-dependent polarization energy in the film.

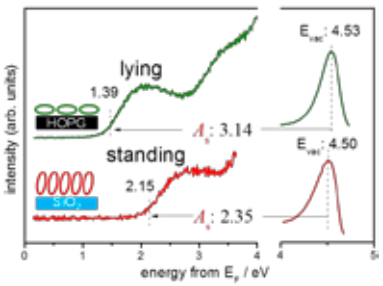


Figure 2. LEIPS spectra of pentacene thin films on HOPG and SiO_2 substrates together with the first derivatives of the sample current spectra to determine the vacuum level E_{vac}.

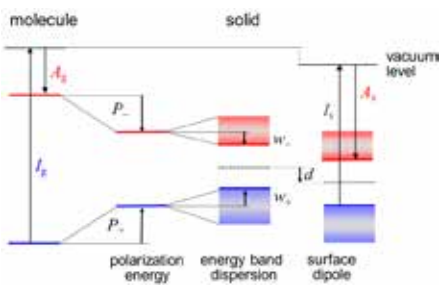


Figure 3. Schematic energy-level correlation diagram showing ionization energy and electron affinity in gaseous and solid states.