As electronic properties of organic semiconductors are predominated by their electronic structures around the energy gap, examining those of unoccupied states as well as valence states is essentially important; Photoemission spectroscopy (PES), particularly ultraviolet photoemission spectroscopy (UPS), has widely been applied to observe valence electronic structures, however, the direct observation of unoccupied electronic structures using inverse photoemission spectroscopy (IPES) has so far been carried out only for a few organic materials because of difficulties in the experimental method chiefly caused by a very low efficiency of the inverse photoemission process.

Recently we designed and installed an apparatus of IPES in the mode of Bremsstrahlung Isochromat Spectroscopy (BIS), with aiming at the measurements of organic samples in particular [1]. In this work we have studied the charge carrier injection into an organic semiconductor by direct examination of electron transfer into unoccupied electronic states in perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) thin films due to alkali metal. By the analysis of the observed results the amount of injected electrons per PTCDA molecule was evaluated with relation to the dopant concentration. The derived relationship has been explained with the aid of DV-Xα calculations of energy levels concerned.

Keywords: Inverse photoemission/ Unoccupied electronic state/ Organic semiconductor/ Alkali metal doping /Electron injection

Inverse photoemission spectroscopy (IPES) in the vacuum ultraviolet region was applied to directly observe behaviors of electron injection into unoccupied electronic states in perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) thin films due to alkali metal. By the analysis of the observed results the amount of injected electrons per PTCDA molecule was evaluated with relation to the dopant concentration. The derived relationship has been explained with the aid of DV-Xα calculations of energy levels concerned.

PTCDA purchased from BASF were purified by repeated sublimation. Its thin films in the thickness of 6 nm were vacuum-deposited onto gold substrates under the pressure lower than 5 × 10⁻⁸ Pa. IPES measurements of these specimen films were carried out in situ as follows: mono-energetic electrons in the range of 4-12 eV were irradiated onto a sample film and vacuum ultraviolet light emitted from the film was detected by a band-pass detector with sensitivity maximum at 9.8 eV (1 eV ≈ 0.1602 aJ) and the full width at half maximum (FWHM) of 0.65 eV. The detected photocurrent normalized by the

**Keywords:** Inverse photoemission/ Unoccupied electronic state/ Organic semiconductor/ Alkali metal doping /Electron injection

As electronic properties of organic semiconductors are predominated by their electronic structures around the energy gap, examining those of unoccupied states as well as valence states is essentially important; Photoemission spectroscopy (PES), particularly ultraviolet photoemission spectroscopy (UPS), has widely been applied to observe valence electronic structures, however, the direct observation of unoccupied electronic structures using inverse photoemission spectroscopy (IPES) has so far been carried out only for a few organic materials because of difficulties in the experimental method chiefly caused by a very low efficiency of the inverse photoemission process.

Recently we designed and installed an apparatus of IPES in the mode of Bremsstrahlung Isochromat Spectroscopy (BIS), with aiming at the measurements of organic samples in particular [1]. In this work we have studied the charge carrier injection into an organic semiconductor by direct examination of electron transfer into unoccupied electronic states in perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) thin films due to alkali metal. By the analysis of the observed results the amount of injected electrons per PTCDA molecule was evaluated with relation to the dopant concentration. The derived relationship has been explained with the aid of DV-Xα calculations of energy levels concerned.

PTCDA purchased from BASF were purified by repeated sublimation. Its thin films in the thickness of 6 nm were vacuum-deposited onto gold substrates under the pressure lower than 5 × 10⁻⁸ Pa. IPES measurements of these specimen films were carried out in situ as follows: mono-energetic electrons in the range of 4-12 eV were irradiated onto a sample film and vacuum ultraviolet light emitted from the film was detected by a band-pass detector with sensitivity maximum at 9.8 eV (1 eV ≈ 0.1602 aJ) and the full width at half maximum (FWHM) of 0.65 eV. The detected photocurrent normalized by the
incidence electron-beam current was recorded to give an IPE spectrum, with the overall energy resolution of about 0.80 eV. Alkali metal doping into a PTCDA film was carried out using a SAES Getters alkali metal dispenser, followed by aging. The dopant concentration was determined by a quartz oscillator monitor and also by X-ray photoemission spectroscopy in C1s and K2p regions. All the experiments were performed at room temperature.

Fig. 1 depicts IPE spectra (drawn in dotted lines) observed for potassium-doped PTCDA thin films, i.e., K_{PTCDA}, where n is potassium concentration defined as the mole fraction of potassium atoms against PTCDA molecules. The abscissa is energy of the state relative to the Fermi level. The decrease in intensity of the first or lowest-energy feature among three ones with increasing n is most notable. To make a close study of this phenomenon we tried to deconvolute each spectrum using three Gaussians; the spectrum fitted by these Gaussians indicated by a solid line reproduces the observed one well. By such a procedure it is demonstrated that the intensity of the first feature decreases with increasing n while those of the second and third ones almost unchanged. This can be explained by a decrease in density of the lowest unoccupied states in PTCDA caused by electron injection from potassium atoms.

The first feature of IPE spectrum is derived only from LUMO of PTCDA which can accommodate maximal two electrons and a decrease of its intensity is proportional to the number of electrons transferred to LUMO, so that the number δ of electrons injected to a PTCDA molecule in the film can be expressed as follows:

\[
δ = 2 \left( 1 - \frac{I_i}{I_0} \right)
\]

where I₀ and I are intensities of the first feature before and after potassium doping, respectively. In order to explain the obtained result that the δ values calculated from I using eq (1) are much less than the corresponding n especially at large n values, the following simple electron-transfer equilibrium is considered:

\[
P_{\text{PTCDA} - nK} + nK = P_{\text{PTCDA} - δK} + nK^{+δn} \quad (2)
\]

At the initial stage the highest occupied atomic orbital (HOAO) of a potassium atom is located energetically higher than LUMO of PTCDA. On the one hand, the increase of electron density on an atom or a molecule will raise its one-electron levels. With taking this into account, electrons pre-distributed at HOAOs of potassium atoms to a PTCDA molecule are possible to transfer to LUMO of the PTCDA molecule so far as the energies between LUMO of PTCDA, E_{LUMO}^{+δ}, and HOAO of the potassium, E_{HOAO}^{+δn}, coincide with each other.

To consider this, orbital energies of LUMO in a PTCDA molecule and HOAO in a potassium atom, i.e., E_{LUMO}^{+δ} and E_{HOAO}^{+δn}, respectively, were calculated as functions of nominal charge qε by the DV-Xα method, where q is a real number not restricted to the integer and ε is the elementary charge. From the results of such density functional calculations it is clarified that both E_{LUMO}^{+δ} and E_{HOAO}^{+δn} are expressed by linear functions of q as follows: E_{LUMO}^{+δ} = A_q + qB_q, where A_q and B_q are constants determined for PTCDA and A_q and B_q are for potassium. With bearing in mind eq (2), the electron transfer reaction will reach equilibrium when the energy-level matching, E_{LUMO}^{+δ} = E_{HOAO}^{+δn}, is established. By combining this relation with the linear functions above, the number δ of electrons injected from n potassium atoms to a PTCDA molecule can therefore be evaluated by the following equation:

\[
δ = δ(n) = (A_q - A_q) / (B_q + B_q/n) \quad (3)
\]

Thus-obtained result of δ(n) turned out to be in good agreement with the experimental one for δ vs. n. This conformity leads us to conclude that the number of electrons transferred from potassium atoms to a PTCDA molecule in the thin film is predominantly regulated by the electronic recirculation between LUMO of the molecule and HOAO of a potassium atom with electron correlations involving Coulombic screening and repulsion in those atoms and molecules.

![Figure 1 IPE spectra of a PTCDA evaporated thin film at different levels of potassium doping, K_{PTCDA}.](image)

References