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Electronic state observation of inner organic thin films beneath electrodes: Fluorescence-yield X-ray absorption spectra of pentacene derivative films

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ABSTRACT

The electronic states of inner organic thin films have been investigated by X-ray absorption spectroscopy (XAS) in a bulk-sensitive fluorescence-yield (FY) mode with theoretical analysis. The thin films of the synthesized pentacene derivative, i.e., 6,13-dihydrodiazapentacence ($C_{20}N_2H_{14}$), on SiO_2-covered Si substrates were fabricated and their morphology and crystallinity were characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD) analysis, respectively. The observed N K-edge FY-XAS spectra were different from the surface-sensitive XAS spectra measured in a partial-electron-yield (PEY) mode. The peaks on the FY-XAS spectra were well reproduced by the theoretical calculation of the unoccupied states of an HAPn molecule. In addition, the incident angle dependence of the FY-XAS spectra was consistent with the expected molecular orientation in the thin films. As a result, we successfully obtained the N and C K-edge FY-XAS spectra of the inner HAPn thin films even beneath Au electrodes.

1. Introduction

In order to develop elaborately designed molecular devices, it is desired to observe *in situ* electronic states in operating devices under applied bias. Organic molecular devices have recently been intensively investigated to respond to various requirements for future electronic devices [1–4]. One of the typical molecular devices desired is an organic field effect transistor (OFET) that controls conductivity by injecting carriers into the organic thin film under an applied electric field. The conduction mechanism has generally been understood in terms of band bending of electronic states, based on the knowledge of inorganic semiconductor transistors. However, the energy diagram might not be exactly the same between organic and inorganic materials, because orbitals are more localized in organics. Furthermore, it is important to focus on the differences in their electronic structures for development of future advanced devices utilizing the novel functionality of organic materials. Therefore, the direct observation of electronic states in organic layers under operation conditions has been required.

Conventional photoelectron spectroscopy, such as X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS), are not suitable for electronic state observations of operating molecular devices, because organic layers are located between or beneath electrodes formed with substantial thickness, while the mean free path of emitted electrons in those methods is typically 1 nm. In addition, the bias applied to the operating devices should perturb the kinetic energy of emitted electrons. Thus, photodetection spectroscopy is required, since light (or X-ray) signals generally have a longer escape depth than electrons and are not perturbed by electric field.

So far, the direct characterization of organic layers under OFET operating conditions has been performed by infrared (IR) spectroscopy [5–7] and sum frequency generation (SFG) spectroscopy [8], by which the vibrational spectrum change of the thin organic layers depending on the gate bias is observed. The direct observation of electronic states near the Fermi level has been reported by a limited number of groups using voltage-modulated UV–vis–NIR transmission spectroscopy [9–11]. Since optical transmission implies electronic transitions from occupied to unoccupied electronic states of the materials, the spectral change depending

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on the bias reflects the change of both electronic states exactly but intricately. Methods of independently observing either occupied or unoccupied states under operating conditions are more informative; fluorescence-yield X-ray absorption spectroscopy (FY-XAS) can be one such method for molecular device investigations.

The XAS measurements for solid samples are usually performed in an electron-yield detection mode, in which the total electron yield (TEY) or partial-electron-yield (PEY) is measured, because most of the inner-shell excited states are nonradiatively de-excited by emitting electrons through Auger or Auger-like decay processes and other secondary processes. However, the mean free path of the emitted electrons might be too short to observe electronic states of inner organic thin films, as above mentioned. Therefore, bulk-sensitive FY detection is promising in the present work.

Since organic materials consist mostly of light elements, e.g., H, C, N, and O, soft X-ray excitation provides the near K-edge absorption spectra in which site-selective unoccupied states in the organic devices can be clearly observed. Although the relative yield of fluorescence from a K-shell core hole has been expected to be very small for light elements, i.e., less than 1% at $Z \leq 8$ [12], many successful FY-XAS studies have already been reported for various samples: for instance, molecules adsorbed on single-crystal surfaces within and without reactive gases [13–17], solutions [18–20], organic materials [21–25], and inorganic materials [26–34]. However, there has been no attempt to study molecular devices consisting of not only target materials but also electrodes to realize the operating device conditions, so far, to our knowledge.

In this study, therefore, we aim to establish FY-XAS for the investigation of *in situ* electronic states of operating molecular devices. 6,13-Dihydrodiazapentacence ($C_{20}N_2H_{14}$; HAPn) thin films fabricated on the SiO_2-covered Si substrates were utilized. The morphology and crystallinity of the thin film was evaluated by atomic force microscopy (AFM) and X-ray diffraction (XRD) analysis, respectively, in comparison with those of pentacene ($C_{22}H_{14}$; Pn) thin films. Since no nitrogen impurity on the substrates was confirmed (see Supplementary data; Fig. S1), we first focused on the N K-edge XAS spectra to neglect contributions from hydrocarbon impurities. The N K-edge XAS spectra of the HAPn thin films were measured in both PEY and FY detection modes. Then, clear differences in those spectra were observed and their origin was experimentally attributed to the difference in the depth of observed regions in the films. The results clearly show that, in the obtained FY-XAS spectra, the main components of the signals come from the inside of the thin film and the signals from the surface are in the minority. Since the present FY-XAS setup had sufficient potential to observe the inner electronic states of the films, we successfully obtained both N and C K-edge FY-XAS spectra of the HAPn thin films even beneath Au electrodes (35 nm thick). The peaks on the FY-XAS spectra in the N and C K-edge range were consistently reproduced by ab initio molecular orbital (MO) calculations.

2. Experimental and theoretical

In accordance with the previous report [35], the HAPn molecules were synthesized and purified by filtration with acetone rinse and by sublimation of the remaining chemicals before thin film deposition. The final purity was estimated to be 99.5% by ^{1}H NMR (JEOL: JNM-EX270). The HAPn molecules were deposited on the SiO_2-covered Si substrate at 40 °C from a K-cell in a high-vacuum chamber at the deposition rate of 0.025 nm/s. The deposited thin films were reproducible and macroscopically uniform over the whole area of the substrate (10 mm × 10 mm). The quality of the microscopic morphology and crystallinity of the films was evaluated by AFM (JEOL: JSPM-4200) and XRD analysis (MAC Science: M21X), respectively. In addition, the time evolution of the thin film surface composition during storage in a conventional desiccator was characterized by XPS (Omicron: MULTIPROBE S). The performance of the fabricated HAPn thin films on OFET was also confirmed with the additional deposition of Au electrodes on the films [36]; the electric property was in good agreement with that in the previous report [35]. By the same procedure, Au electrodes were prepared on the HAPn thin films for FY-XAS measurements to reproduce the operating conditions of OFET.

The FY-XAS measurements were performed at the BL3U beamline of the UVSOR facility in IMS. The samples were set in a BL3U end station through the sample-entry system. Both partial-electrons and fluorescence signals were detected using a retarding-field detector consisting of micro-channel plates (MCPs) in the counting mode to obtain a better signal-to-noise ratio and stability. At the detection of the N and C K-edge PEY-XAS spectra, the retarding bias was −300 and −260 V, respectively; hence the spectra mainly consisted of KLL Auger electrons of each element. In the case of FY-XAS measurements, the applied retarding bias exceeded −1 kV to shut out the photoelectrons excited by not only the fundamental X-rays but also the false second-order X-rays generated from gratings. For the measurements of incident angle dependence,

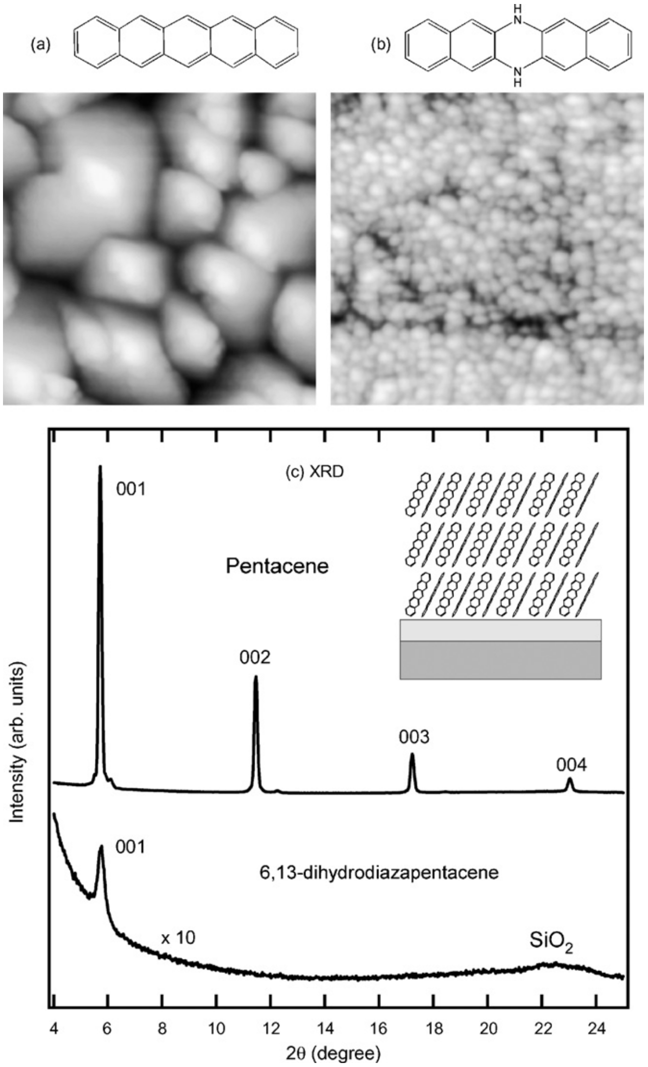

Fig. 1. AFM images of (a) pentacene, (b) 6,13-dihydrodiazapentacene thin films deposited on the oxidized Si substrates at 40 °C, and (c) their XRD distributions. The thickness of all the thin films shown in the figure is 100 nm. The AFM images were observed in the tapping mode with the scan area of 2 μm × 2 μm. The X-rays in XRD measurements were generated using a revolving Cu anode.