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# Observation of Oriented Organic Semiconductor using Photo-Electron Emission Microscope (PEEM) with Polarized Synchrotron

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*We have developed photoelectron emission microscope (PEEM) system with excitation of linearly polarized synchrotron X-rays at 30° incidence angle arrangement. The morphology, electronic structure, orientation for P3HT:PCBM hybrid films have been investigated using the PEEM instrument. The sulphur 1s near-edge X-ray-absorption fine structure (NEXAFS) spectra at micro-domains were obtained, where sulphur atoms of thiophene ring were detected. The nature and symmetry in the S 1s excitations of P3HT model cluster were elucidated by DFT calculations that we performed to assign resonant peaks in absorption spectra. We demonstrate that the orientation at micro-domains can be deduced from photon-energy dependencies of PEEM images.*

**Keywords** photo-electron emission microscope (PEEM); near-edge x-ray absorption fine structure (NEXAFS); orientation; organic semiconductor; poly(3-hexylthiophene) (P3HT); [6; 6]-phenyl-C61-butyric acid methyl ester (PCBM)

## 1. Introduction

High degrees of molecular orientation play a crucial role in the improvement of electronic properties in organic semiconductors [1]. For example, the electron mobility has been reported to differ by more than a factor of 100 between two different orientations – parallel and normal to the substrate – for self-organized poly(3-hexylthiophene), P3HT, a semiconducting conjugated polymer [2]. Moreover, self-organization in many solution processed results in complex microstructures, in which ordered microcrystalline domains are embedded in an amorphous matrix. Thus, the development of techniques that can directly prove non-crystalline orientational organization is indispensable [3]. Photo-Electron Emission Microscopy (PEEM) using polarized synchrotron X-rays is one such spectro-microscopic technique [4] that can be used to measure Near-Edge X-ray Absorption Fine Structure

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(NEXAFS) [5] spectra at microscopic regions. Orientation at microscopic scales can be deduced from the spectral data [6].

In this study, we have investigated the effect of orientation in P3HT:PCBM hybrid films containing sulfur atoms using the PEEM combined with linearly polarized synchrotron at the S 1s NEXAFS region. In addition, to assign peaks observed in NEXAFS spectra, we calculated the oscillator strengths of the S 1s inner-shell electronic transitions for a model hexylthiophene oligomer using the discrete variational (DV)  $X\alpha$  method [7], which is based on the density functional theory (DFT). To determine the direction of molecular orientation from X-ray absorption data, we calculated the transition moment projected along the x, y, or z molecular axis.

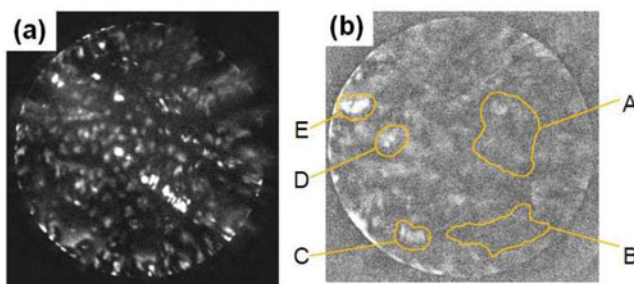
## 2. Method

### 2.1. Experimental

Microscopic images were recorded using the STAIB PEEM 350-10R system installed in bending magnet beamline BL27A of the Photon Factory, KEK. An InSb(111) double crystal monochromator was used to obtain an energy resolution of  $\approx 1.1$  eV at the S K-edge. X-ray incidence angle ( $\theta$ ) with the substrate was  $30^\circ$ , which is smaller than intermediate incidence angle, i.e., magic angle  $54.7^\circ$  producing the same spectrum as that for randomly oriented samples [5]. In  $\theta = 30^\circ$ , the electric field vector ( $\vec{E}$ ) of the X-rays is directed closer to the surface normal, compared with the intermediate direction. Total electrons emitted from the surface were transferred to the entrance grid ( $\sim 10$  kV) of the PEEM and magnified by objective lenses (typically  $\sim 1$  kV). The electron images were projected ( $\sim 0.7$  kV) to a micro-channel plate (MCP) and phosphor screen. The images were accumulated in a charge-coupled device (CCD) as a function of the X-ray photon energies. All intensities were normalized by values at the pre-edge region ( $< 2470$  eV) and then divided by the edge-jump value at  $\sim 2479.5$  eV. We used regioregular (RR)-P3HT and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) powders (both Sigma-Aldrich) without further purification, which were dissolved in p-xylene (both 1 mg/g) thoroughly stirred by ultrasonic agitation to form the P3HT:PCBM (1:1 weight ratio) blend solution. Micrometer-order thick films were prepared on silicon wafers by drop-casting [10].

### 2.2. Computational

The regio-regular planar structure in the ground state of the model cluster (see Fig. 3(b)) was optimized using B3LYP hybrid functional DFT method with a 3-21G\* basis-set using the *ab initio* molecular orbital (MO) program Gaussian98 [8]. Ground and core-hole excited states for the optimized geometry were calculated using the DV $X\alpha$  method with the SCAT code [7]. Minimal basis-sets of 1s, 2s, and 2p for carbon atoms and 1s, 2s, 2p, 3p, and 3d for sulphur atoms were used. Relaxation due to the existence of a core-hole is taken into account in terms of Slater's transition state theory; i.e. half of the electrons in a core orbital are removed and half of them occupy unoccupied molecular orbitals; Here, a hole is created in the 1s-orbital for the third sulphur atom from the left in the cluster. Relative oscillator strengths ( $\Delta E |< i|r|f >|^2$ ), which are proportional to the X-ray absorption cross sections, were calculated and convoluted with a Gaussian-function of width 0.8 eV full width at half maximum (FWHM) for all electronic transitions. MOs were visualized using the VESTA program [9].

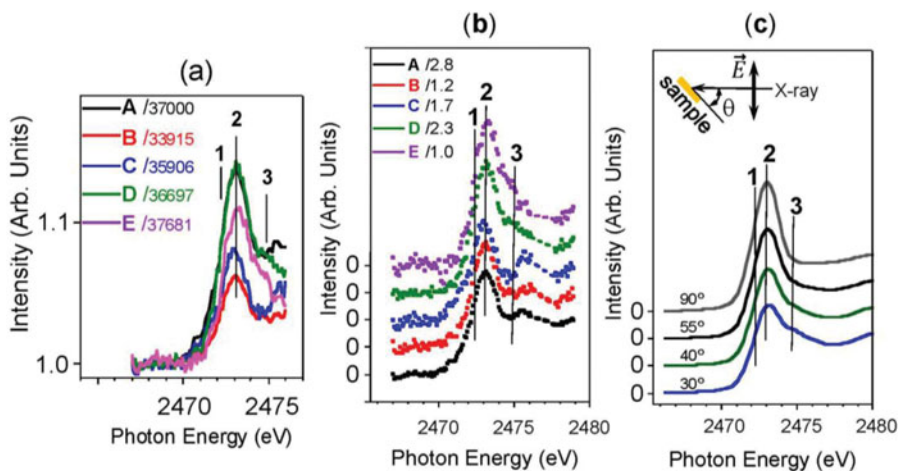


**Figure 1.** (a) PEEM image for a P3HT:PCBM blended film measured with the mercury lamp excitation. Field of view (F.O.V.):  $\sim 120\ \mu\text{m}$ . (b) Image measured with S 1s excitation. F.O.V.:  $\sim 60\ \mu\text{m}$ .

### 3. Results and Discussion

#### 3.1. PEEM Images for the P3HT : PCBM Hybrid Film

Figure 1(a) shows a PEEM image for the blended films measured by the mercury lamp excitation with fixed photon-energy ( $h\nu = 4.9\ \text{eV}$ ). The spherical aggregates have been reported to be attributable to PCBM. Figure 1(b) shows an image measured with the S 1s excitation ( $\sim 2473.1\ \text{eV}$ ). Five representative regions-of-interest (ROI) from A to E are depicted. The regions of A and C are selected as bright part. Zone B is selected as a dark one. The positions D and E are brilliant spots.



**Figure 2.** (a) Photon-energy dependence of intensities for regions A to E. All intensities are normalized by the pre-edge values. (b) Photon energy dependence of intensities normalized by the pre-edge, followed by normalization at high energy regions. (c) The S 1s - NEXAFS spectra of the P3HT large area films measured at  $\theta = 30^\circ, 40^\circ, 55^\circ$ , and  $90^\circ$  [10].

### 3.2. Photon Energy Dependence of Microscopic Regions for the P3HT:PCBM Film

Figure 2(a) shows the integrated intensities for the five regions as a function of X-ray photon energy in the S 1s edge regime, i.e., NEXAFS. The intensities are divided by the areas of the respective five zones and pre-edge intensities averaged over 2467.3–2470.0 eV, as indicated in Fig. 2(a). The steep increase in intensities observed for all zones at around from 2471 to 2473 eV is based on X-ray absorption at the sulphur 1s edge. In the next section, the characteristics of the three resonant features tentatively labelled as **1** (~2472.2 eV), **2** (~2473.1 eV), and **3** (~2474.8 eV) are described on the basis of DFT calculations. The curves for zones **A** and **D** show high intensities, suggesting the higher abundance of sulphur atom at **A** and **D** than those at other areas. On the other hand, zone **C** does not show such high sulphur quantities, although the area **C** shown in Fig. 1(b) appears to be rather bright.

To evaluate the orientation effect accurately, the intensities shown in Fig. 2(a) were normalized by the values at the high energy side, which are less dependent on polarization angles [5]. Figure 2(b) illustrates the normalized intensities of the five selected regions as a function of X-ray photon energies at the S 1s edge.

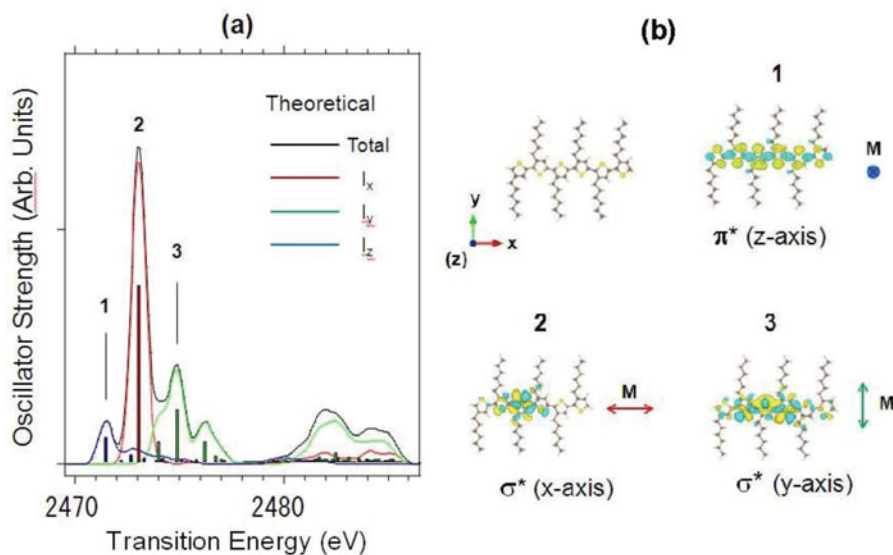
For comparison, Fig. 2(c) shows the S 1s NEXAFS spectra of large area samples for P3HT films measured in several X-ray incidence angles ( $\theta$ ) [10]. Note that the intensities of the spectra shown in Fig. 2(b) can be compared with those shown in Fig. 2(c). In the next section, we describe the electronic states and excitation symmetry of S 1s absorption of P3HT with the help of theoretical calculations.

### 3.3. Theoretical Analysis of S 1s NEXAFS Spectra for the P3HT Model Cluster

Figure 3(a) and (b) depict theoretical calculations for the P3HT model cluster. Figure 3(b) shows the distributions of unoccupied MOs for the final states of S 1s core excitations. Figure 3(a) shows theoretical S 1s absorption spectra for the P3HT model cluster. Components of the oscillator strengths projected along the x (red), y (green), and z (blue) -axes and their convolution curves together with a total one (black) =  $I_x + I_y + I_z$  are shown. The features **1**, **2**, and **3** are assigned to electronic transitions from the sulphur 1s core-orbitals to the  $\pi^*$  (z axis),  $\sigma^*$  (x), and  $\sigma^*$  (y) unoccupied orbitals, respectively. Here, x, y, and z are the molecular axes that are defined to be along the main chain direction of the polymer link, the orthogonal direction to the polymer chain, and the perpendicular direction to the five-membered thiophene-ring plane, respectively.

### 3.4. Comparison of the Normalized X-ray Energy Dependence Between Microscopic Regions and Large Areas

It is worthy to note that intensities of peak **2** shown in Fig. 2(b) observed for the **D** and **E** zones were larger than that for the P3HT film measured at  $\theta = 55^\circ$  shown in Fig. 2(c). A comparison between the NEXAFS spectrum measured at the incidence angle  $\theta = 30^\circ$  corresponding to our PEEM experimental set-up and those measured at the magic incidence angle ( $\theta = 55^\circ$ ) for the oriented sample [10] sheds light on a net molecular orientation, if they differ from each other [6]. On the other hand, it has also been known that such two spectra resemble each other when molecules are randomly oriented or when the averaged tilt angle happens to be just near magic angle ( $54.7^\circ$ ) even if molecules are essentially oriented [5], for example, due to wider distributions of tilt angles in the amorphous region. In the present case, the spectra ( $\theta = 30^\circ$ ) for **D** and **E** in Fig. 2(b) differ from that measured



**Figure 3.** (a) Theoretical S 1s-edge X-ray absorption spectra for the P3HT model cluster. Convolved oscillator strengths for the x (red), y (green), z (blue) -axes, and total (black) =  $I_x + I_y + I_z$  are shown. (b) Cluster model structure and isosurface views of representative unoccupied orbitals in the S 1s inner-shell excitation for features of **1**, **2** and **3**, where a core-hole at 1s orbital is considered for the third sulphur atom from the left. The final states that have strong contributions are as follows; **1**: 272th MO (LUMO), **2**: 275th MO (LUMO+3), **3**: 278th MO (LUMO+6).

at  $\theta = 55^\circ$  in Fig. 2(c). Therefore, we conclude that molecules for the regions **D** and **E** are oriented to some degree.

In addition, this observation can be interpreted in terms of the photoabsorption selection rule. For the K-shell excitation by linearly polarized X-rays, the angular dependence of the dipole transition intensity ( $I$ ) can be expressed as a function of the angle ( $\delta$ ) between the direction of the electric field vector ( $\vec{E}$ ) of the light and that of the transition moment ( $\vec{M}$ ), i.e.,  $I \propto \cos^2 \delta$ . [5] Thus, when  $\vec{M}$  and  $\vec{E}$  are pointing in the same direction, the intensity becomes maximum. In the PEEM experiment, the incidence angle ( $\theta$ ) was  $30^\circ$ , implying that  $\vec{E}$  is directed closer to the surface normal in comparison with the intermediate direction. Thus, if intensities for a surface domain in PEEM images are larger than that at  $\theta = 54.7^\circ$ ,  $\vec{M}$  in the domain is directed closer to the surface normal than the intermediate direction, i.e.,  $54.7^\circ$  from the normal. Therefore, enhanced intensities for the **D** and **E** zones indicate that the polymer chain direction (along the x axis) prefer perpendicular orientation to the substrate plane. In contrast, inspection indicates that the intensities of peak **2** for zones **A**, **B**, and **C** shown in Fig. 2(b) were slightly smaller than those in the  $\theta = 55^\circ$  measurement for the P3HT film shown in Fig. 2(c). This suggests that the polymer chain (x axis) prefers parallel orientation in the regions **A**, **B**, and **C**.

In summary, in some areas, the peak intensities of the PEEM brightness images for P3HT:PCBM films were found to be enhanced or suppressed in X-ray photon-energy dependences. Information on the orientation was deduced from the spectroscopic data. PEEM analysis with polarized synchrotron can be a powerful tool that gives information about not only the concentration of specific elements, but also molecular orientation in microscopic domains.

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