Chemical-State Analysis of Organic Semiconductors Using Soft X-ray Absorption Spectroscopy Combined with First-Principles Calculation

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ABSTRACT: The chemical states of organic semiconductors were investigated by total-electron-yield soft X-ray absorption spectroscopy (TEY-XAS) and first-principles calculations. The organic semiconductors, pentacene (C₂₂H₁₄) and pentacenequinone (C₂₂H₁₂O₂), were subjected to TEY-XAS and the experimental spectra obtained were compared with the 1s core-level excited spectra of C and O atoms, calculated by a first-principles planewave pseudopotential method. Excellent agreement between the measured and the calculated spectra were obtained for both materials. Using this methodology, we examined the chemical states of the aged pentacene, and confirmed that both C–OH and C=O chemical bonds are generated by exposure to air. This result implies that not only oxygen but also humidity causes pentacene oxidation.

INTRODUCTION

Over the past decade, the development of organic electronic and optoelectronic devices has seen vigorous efforts, including light-emitting devices, ¹⁻⁴ photovoltaic cells, ⁵⁻⁷ and field-effect transistors. ⁸⁻¹⁰ The electronic properties required for commercial use of such devices have been improved to be competitive with those of amorphous silicon devices. However, the major barrier for practical uses of organic devices is the lack of stability and reliability. Many researchers have studied the degradation mechanism of organic semiconductors, revealing that oxygen, humidity, and light are the principal causes of pentacene oxidation. ¹¹⁻¹⁵

In our previous study, we confirmed that pentacene (C₂₂H₁₄, Mw = 278) thin-film transistors (TFTs) exhibit a threshold-voltage (Vth) shift after long-term storage in air and concluded that the Vth shift is caused by oxidation of pentacene, on the basis of a time-of-flight secondary ion mass spectroscopy (TOF-SIMS). ¹⁴ Mass spectroscopy (MS) is a powerful method to determine impurity compounds and their concentrations; however, information on the chemical structures of impurities has to be presumed from the MS mass numbers. In our aged pentacene thin films, the specific mass peaks at 294 and 309 were determined, and these peaks correspond to mono- and dioxygenated pentacene (C₂₂H₁₃O, C₂₂H₁₃O₂), respectively. In the mass spectrum, the additional H atom is bonded to oxygenated pentacene; therefore, we could not conclude whether the H atom is derived from protonation during the TOF-SIMS analysis or whether the OH bond is originally included in the molecule as hydroxypentacene. Needless to say, there are a variety of well-established methods for analyzing the chemical structure, such as nuclear magnetic resonance (NMR), infrared spectroscopy (IR), and X-ray photoelectron spectroscopy (XPS), and thus one can determine the chemical structure of the impurity in addition to the MS analysis.

X-ray absorption spectroscopy (XAS) using synchrotron radiation (SR) is a very useful method to analyze the chemical states of materials. In particular, for carbon materials, XAS is a powerful tool to elucidate chemical states or electronic structures. ¹⁶ Using this method, it is possible to obtain information on the electronic structure of unoccupied states for the selected element. The C–OH and C=O bonds mentioned above are considered to form different electronic structures; therefore, it is expected to elucidate the origin of the H atom in the TOF-SIMS spectrum. X-ray absorption near-edge structure/near-edge X-ray absorption fine structure (XANES/NEXAFS) and electron energy-loss near-edge structure (ELNES) analyses are well-recognized powerful techniques for studying material properties at the atomic level. Recently, a first-principles calculation for XANES/ELNES spectra has been widely used to interpret the experimental results, using program codes such as FEFF,¹⁷ WIEN2k,¹⁸⁻²⁰ StoBe-deMon,²¹ and CASTEP ²²⁻²³. Excellent agreements between the simulated and experimental spectra have been presented in previous studies. ²⁴⁻³⁶

In this study, we examine chemical-state changes accompanying the oxidation of pentacene in air, using total-electron-yield (TEY) XAS. In the analysis, XANES spectra in the C-K and O-K regions for pentacene-related materials were obtained experimentally and compared with simulated spectra calculated with a plane-wave pseudopotential method within the framework of density functional theory (DFT). We discuss the
chemical state of the oxidized pentacene after storage in air and discuss whether the oxidized pentacene contains the C−OH bond.

**EXPERIMENTAL METHODS**

The TEY-XAS measurements were performed at beamline BL-6.3.2 in the Advanced Light Source (ALS) synchrotron, Lawrence Berkeley National Laboratory (Berkeley, CA).37 The scanning energy region was tuned to 200−600 eV, which includes the C−K (ca. 285 eV) and O−K (ca. 530 eV) absorption edges. The theoretical energy resolution (E/ΔE) of the incident SR beam ranged from 5000 (200 eV) to 2000 (600 eV) using a 1200 mm−1 varied line-spacing grating with a 40 μm slit. Organic compound powder was pressed on an indium sheet pasted on a glass substrate, which was held in the spectrometer chamber; monochromatized SR X-rays were irradiated onto the samples. Photocurrents in the samples, I, and in a clean gold sheet, I₀, regarded as the incident beam intensity, were measured during photoion-energy-scanning of the incident SR X-rays. TEY-XAS spectra were obtained by plotting I/I₀ versus the photon energy. All measurements were performed in a vacuum of ca. 10⁻⁵ Pa, where no change in the spectral profiles was observed during the SR X-ray irradiation.

Pentacene (C₂₂H₁₄, Pen) and pentacenequinone (C₂₂H₁₂O₂, PQ) were obtained from Tokyo Chemical Industry, and the aged pentacene was obtained by keeping the materials in the dark in air for more than 3 months. We confirmed that 3 months are sufficient to oxidize pentacene into pentacenequinone, in our previous study.14

**RESULTS AND DISCUSSION**

Figure 1 shows the crystal structures of Pen and PQ that contain two nonequivalent molecules in the individual unit cells, with both molecules having six nonequivalent C atoms. These six pairs of nonequivalent C atoms over two nonequivalent molecules in the unit cell were almost identical to each other in terms of the simulated XANES spectra. The C−K edge spectra for each C atom were calculated with a core hole in the 1s orbital, followed by a linear combination of each spectrum with weighted coefficients to obtain the total spectrum (Figure 2). In this process, it is important to calculate the theoretical transition energy for each excited atom. The simulated spectrum was constructed by broadening the square modulus of the matrix elements, where a Lorentz broadening function was used for the Brillouin zone spectral integration and was convolved with a Gaussian taking into account the instrumental resolution.28 In the present study, Lorentzian and Gaussian broadening factors of 0.17 eV for the C atom and 0.19 eV for the O atom were used, and 0.2 eV for all atoms in broadening the Gaussian function was used, respectively.

Figure 1. Molecular and crystal structures of organic semiconductors. Indices of the carbon atom represent the nonequivalent atoms, on which the core hole is introduced separately in the XANES calculations.
the O- edge in the C- (measured and calculated). The a-Pen mainly exhibited the Pen each other in the O- PQ, the experimental and simulated spectra corresponded to experimental result were split into several components not thin films, and thus the resulting spectrum was not as fine respectively. The samples for the measurements were powders, pentacene, we measured the O- edge spectra of the a-Pen ranging from the C- Pen (a-Pen) and PQ samples. Figure 3 shows the wide scan vacuum-deposited pentacene thin films were previously reported,\textsuperscript{46} where the two peaks at ca. 285 eV in our two structural models. If the PQ and P- OH models are calculated separately, then one cannot discuss whether a difference in the peak positions of the simulated spectra is correct. Moreover, because the crystal structure of P-OH has not been reported, we have to attempt an alternative method to obtain the O-K edge spectrum for the P-OH and the relative peak positions in the O-K edge spectra compared with PQ. First, to obtain the simulation spectrum of P-OH, it was assumed that the P-OH molecule was included in the unit cell of the Pen. The virtual crystal model containing two molecules of the P-OH and the Pen was generated, followed by geometry optimization. The calculated O-K edge spectrum of the P-OH is shown in Figure 4. Second, in the case of calculating the difference in the transition energy between PQ and P-OH (defined as $\Delta E_{\text{rel}}$) for the O-K edge spectra, a virtual crystal model that contains the PQ and P-OH molecules in the same unit cell based on the pentacene crystal was also assumed. After two C-O bonds and a C-OH bond were introduced to the pentacene molecule in the unit cell (corresponding to the PQ and P-OH, respectively), geometry optimization was carried out. Thereafter, the O-K edge spectra for the PQ and P-OH were separately calculated. In this calculation, the focus was on the energy difference, $\Delta E_{\text{rel}}$ (1.2 eV), between the first peaks for both O-K edge spectra because the respective spectra for the P-OH and PQ have already been obtained in the above calculations. The linear combination of the PQ and P-OH spectra with the transition energy correction is shown in Figure
described in Ref 45

<table>
<thead>
<tr>
<th>atom</th>
<th>pen (eV)</th>
<th>PQ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>286.6</td>
<td>289.7</td>
</tr>
<tr>
<td>C2</td>
<td>287.3</td>
<td>287.7</td>
</tr>
<tr>
<td>C3</td>
<td>286.7</td>
<td>287.5</td>
</tr>
<tr>
<td>C4</td>
<td>287.3</td>
<td>288.0</td>
</tr>
<tr>
<td>C5</td>
<td>287.0</td>
<td>287.6</td>
</tr>
<tr>
<td>C6</td>
<td>287.1</td>
<td>287.6</td>
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= 294 in TOF-SIMS analysis, was observed. The transition energy of the first peak for a-Pen and PQ was 531 eV (\(\pi^*\) transition), which suggested the existence of C=O chemical bonds in a-Pen. This interpretation should be consistent with the TOF-SIMS analysis in our previous work. However, the remaining two peaks at 533 and 539 eV could not be fully explained from the O-K edge spectrum of PQ in terms of the intensity ratio. Another compound, detected as $m/z = 294$ in TOF-SIMS analysis, was observed in the case of a-Pen; therefore, the O-K edge spectrum of the hydroxypentacene (P-OH) was calculated using the first-principles calculation. It is well known that the center-edge carbon atoms (6, 13-C site) of pentacene molecules are most reactive;\textsuperscript{15,44} therefore, we examined only 6-hydroxypentacene here.

In first-principles calculations, the absolute transition energy is not always able to be defined between different simulation models. If the PQ and P-OH models are calculated separately, then one cannot discuss whether a difference in the peak positions of the simulated spectra is correct. Moreover, because the crystal structure of P-OH has not been reported, we have to attempt an alternative method to obtain the O-K edge spectrum for the P-OH and the relative peak positions in the O-K edge spectra compared with PQ. First, to obtain the simulation spectrum of P-OH, it was assumed that the P-OH molecule was included in the unit cell of the Pen. The virtual crystal model containing two molecules of the P-OH and the Pen was generated, followed by geometry optimization. The calculated O-K edge spectrum of the P-OH is shown in Figure 4. Second, in the case of calculating the difference in the transition energy between PQ and P-OH (defined as $\Delta E_{\text{rel}}$) for the O-K edge spectra, a virtual crystal model that contains the PQ and P-OH molecules in the same unit cell based on the pentacene crystal was also assumed. After two C-O bonds and a C-OH bond were introduced to the pentacene molecule in the unit cell (corresponding to the PQ and P-OH, respectively), geometry optimization was carried out. Thereafter, the O-K edge spectra for the PQ and P-OH were separately calculated. In this calculation, the focus was on the energy difference, $\Delta E_{\text{rel}}$ (1.2 eV), between the first peaks for both O-K edge spectra because the respective spectra for the P-OH and PQ have already been obtained in the above calculations. The linear combination of the PQ and P-OH spectra with the transition energy correction is shown in Figure

![Figure 2](Image)

**Figure 2.** Experimental and simulated C-K edge XANES spectra for (a,b) Pen and (c,d) PQ. The total simulation spectra were formed by a linear combination of the respective ones for the nonequivalent C atoms, where the transition energy of the first peak was corrected by the differences from the experimental value.

**Table 1. Transition Energy Values for Each Non-Equivalent C Atom, Calculated with the Formalism Described in Ref 45**

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drespective peaks, the excellent agreement between the measured and calculated spectra was confirmed. It is concluded that the approximation in the calculation is reasonable and that the transition energy shift is also sufficiently valid to discuss the change in the chemical states for the respective atoms within the same structural model. In addition, the XAS spectra for vacuum-deposited pentacene thin films were previously reported,\textsuperscript{46} where the two peaks at ca. 285 eV in our experimental result were split into several components respectively. The samples for the measurements were powders, not thin films, and thus the resulting spectrum was not as fine as that reported in ref 46.

To investigate the chemical structures of the oxidized pentacene, we measured the O-K edge spectra of the aged Pen (a-Pen) and PQ samples. Figure 3 shows the wide scan spectrum of the a-Pen ranging from the C-K to the O-K region and the O-K edge spectra for a-Pen (measured and calculated). The a-Pen mainly exhibited the Pen spectrum in the C-K edge region; however, slight and noisy peaks could be observed in the O-K edge region. In the case of PQ, the experimental and simulated spectra corresponded to each other in the O-K edge spectrum as well, although the energy correction was larger than that in the case of the C-K edge. A significant difference between the a-Pen and PQ spectra was observed. The transition energy of the first peak for a-Pen and PQ was 531 eV (\(\pi^*\) transition), which suggested the existence of C=O chemical bonds in a-Pen. This interpretation should be consistent with the TOF-SIMS analysis in our previous work. However, the remaining two peaks at 533 and 539 eV could not be fully explained from the O-K edge spectrum of PQ in terms of the intensity ratio. Another compound, detected as $m/z = 294$ in TOF-SIMS analysis, was observed in the case of a-Pen; therefore, the O-K edge spectrum of the hydroxypentacene (P-OH) was calculated using the first-principles calculation. It is well known that the center-edge carbon atoms (6, 13-C site) of pentacene molecules are most reactive;\textsuperscript{15,44} therefore, we examined only 6-hydroxypentacene here.

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![Figure 3](Image)

**Figure 3.** XANES spectra for the a-Pen and PQ. (a) Wide scan spectrum for the a-Pen ranging from the C-K to the O-K edge region and (b) experimental and simulated O-K edge spectra for PQ for comparison with the experimental O-K edge spectrum for a-Pen (expansion from panel a).
the O $\pi^*$ peak at ca. 531 eV for the PQ was set to the same experimental value as in Figure 3. The tendency of the a-Pen spectrum was successfully reproduced in the simulated one, whereas the problem with the quantitative accuracy of the peak intensities still remained. Furthermore, O-K edge spectrum for the a-Pen was broader than that of the simulated one for PQ +P−OH; hence it can be assumed that the broadening of the peaks indicates the structural disorder of oxidized pentacene molecules in the a-Pen.

We conclude that the a-Pen includes both PQ and P−OH and that the mass peak at 294 in the TOF-SIMS likely originated from the P−OH. The oxidation mechanism of Pen is confirmed to be related not only to oxygen but also to humidity. Obtaining the standard spectrum of the P−OH will be difficult experimentally. In such a case, first-principles simulation is very powerful to examine the changes in the structures and chemical states.

■ CONCLUSIONS

The chemical states of the organic semiconductors Pen and PQ were investigated using TEY-XAS and first-principles calculations. The first-principles calculation was applied to obtain the XANES standard spectra. It was confirmed that the simulated spectra of the O-K and C-K edges reproduced the experimental ones for Pen and PQ. Using this calculation method, the oxidation mechanism of Pen was examined. We assumed the coexistence of P−OH in the a-Pen sample because of the significant difference in the O-K edge experimental spectra between PQ and a-Pen. The P−OH spectrum was calculated based on the virtual model for simulation, and the simulated spectrum from the linear combination of the PQ and P−OH spectra was revealed to reproduce the O-K edge experimental spectrum for the a-Pen sample. It was concluded that both C=O and C−OH bonds were generated in the oxidation of Pen and that not only oxygen but also humidity causes pentacene oxidation.

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ACKNOWLEDGMENTS

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

REFERENCES


Figure 4. Simulated XANES spectra for PQ and P−OH compared with the experimental one for the a-Pen.