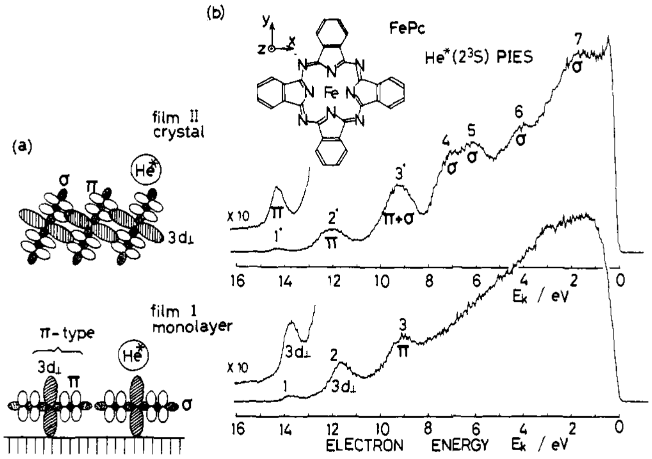

Figure 1. (a) Orientations of surface molecules in monolayer film I and crystalline film II interacting with metastables. (b) He* (2 ^{3}S, 19.82 eV) Penning ionization electron spectra of films I and II. Each band is labeled with the character of MO's mainly responsible for it.

The PIES of the FePc films are shown in Figure 1b. He* (2 ^{3}S, 19.82 eV) metastable beams were used to obtain the spectra. Bands 4–7, which are clearly observed in the tilted orientation (film II), are absent in the flat one (film I). Therefore, these bands are assigned to σ MO's. The π-type bands, which are selectively observed in the film I (bands 1–3), are also found in the film II (bands 1′–3′). However, the origins of these three bands in the both films are different. Bands 1′ and 2′ correspond to the first and second bands in the UPS of the both films.[5] In the UPS of FePc, the first band is due to π MO's distributed on the inner porphine-like ring,[6,7] and the second one is mainly ascribable to π MO's with a large contribution from the benzene ring.[6,8,9] Accordingly, π MO's are selectively probed to form bands 1′ and 2′ in film II. On the other hand, bands 1 and 2 correspond to the 3d-like bands observed in the XPS of an FePc film.[10] Hence, the $3d_\perp$-like MO's are predominantly detected to form these bands in film I. Thus it is confirmed experimentally that the $3d_\perp$-like MO's have a more diffuse distribution to the direction normal to the molecular plane than the π MO's. It is worthwhile to note that the $3d_\perp$-like MO's are detected only when metastables can approach the center of FePc molecules (compare the two orientations in Figure 1a), which is achieved by arranging molecules flat on the substrate. Though both bands 3 and 3′ correspond to the third band in the UPS,[5] which is related to the second UPS band (σ and π) of solid benzene,[8,11] band 3′ is more enhanced than band 3. In this case the π MO's are selectively probed in film I, but the σ MO's as well as the π are detected in film II.

In conclusion, the wave function tails of the $3d_\perp$-like, π, and σ MO's at two different parts of FePc molecules have been probed by PIES. In general, the selections among various substrates, film preparation methods (vacuum deposition, adsorption, Langmuir–Blodgett technique[12] etc.), deposition conditions (depending on the substrate temperature and deposition speed), and film treatments (e.g., annealing) enable us to obtain various films exposing different parts of molecules outside. Studying the PIES of such films, we can probe the local distributions of individual MO's in more detail and approach their whole picture.

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Selective Observation of Molecular Ends Exposed outside Langmuir–Blodgett Monolayer Films by Penning Ionization Electron Spectroscopy

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Langmuir–Blodgett (LB) films[1] have attracted recently particular interest as ultrathin films, because the thickness together with the ordered structure can be controlled at the molecular level and, therefore, unique functions are anticipated to be developed.[2] For such studies, it is of fundamental importance to elucidate the molecular arrangement in the films. However, we have no means for obtaining direct evidence as to which end of the molecule (either head or tail) is exposed to the film surface; it has only been presumed by such an indirect method as contact angle observation.[3] The knowledge of the molecular end exposed outside is not only useful to determine the types (X, Y, or Z) of LB film[4] but is also indispensable in designing LB films containing functional parts at the film surface. We demonstrate here that the molecular end exposed to the outside of an LB film can be selectively probed by Penning ionization electron spectroscopy.

In Penning ionization electron spectroscopy, the kinetic energy of electrons ejected by collisions between targets T and metastable atoms A* is analyzed:[5]

$$T + A^* \rightarrow T^+ + A + e^-, \quad e^- \text{ for energy analysis}$$

Since metastables do not penetrate into the solid, this technique provides information on the outermost surface layer selectively.[6-11] Furthermore, an orbital of T spreading outside the surface interacts with a metastable atom more effectively than an inner orbital and hence gives a stronger band in the Penning ionization electron spectrum (PIES).[7,9-11] These characteristics of PIES enable us

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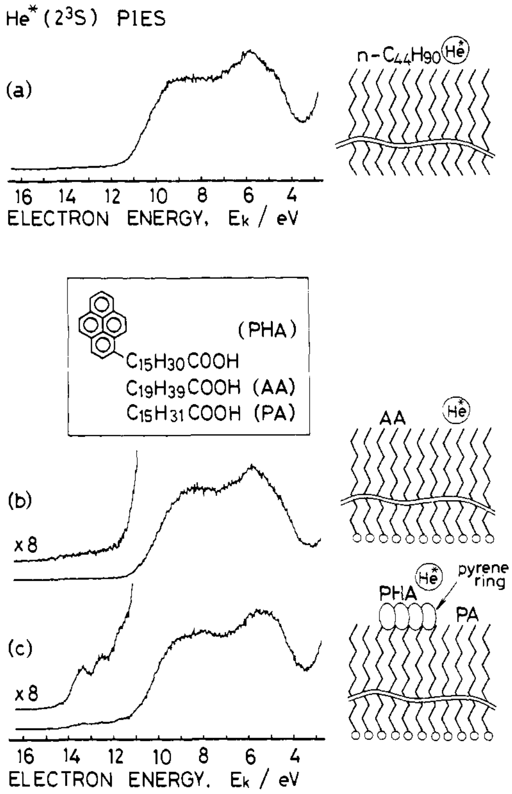

Figure 1. He* (2 ^{3}S, 19.82 eV) PIES of three films: (a) an evaporated film of tetratetracontane (n-$C_{44}H_{90}$); (b) an LB monolayer film of arachidic acid (AA); (c) a mixed LB monolayer film of palmitic acid (PA) and 16-(1-pyrenyl)hexadecanoic acid (PHA) (33 mol % PHA). The schematic diagram of surface molecules in each film is also shown on the right of the corresponding spectrum.

to study the orientation of molecules in the outermost surface layer.[9-11] We have already shown that films prepared with the same molecules but having different orientations provide completely different PIES.[10] We intend in this paper, however, to indicate that films prepared with different molecules but exposing the same part outside the surface give almost the same PIES.

Figure 1a shows He* (2 ^{3}S, 19.82 eV) PIES of a n-alkane (n-$C_{44}H_{90}$, tetratetracontane) film prepared in situ by vacuum deposition onto a copper substrate at room temperature. This film was studied as a model for an alkyl end surface of the LB film. The PIES of monolayer LB films are shown in Figure 1b,c. Curve b is for a film of arachidic acid (AA; eicosanoic acid) and curve c for a mixed film of palmitic acid (PA; hexadecanoic acid) and 16-(1-pyrenyl)hexadecanoic acid (PHA) (33 mol % PHA). AA was spread on an aqueous subphase[12] and transferred onto a stainless steel substrate[13] at 35 mN/m by the Langmuir–Blodgett technique. The mixed monolayer was prepared under the same conditions, except that the surface pressure for deposition was 25 mN/m. All the spectra in Figure 1 were measured with an ultrahigh vacuum electron spectrometer.[11]

The PIES of the AA monolayer has a very similar appearance to that of the n-alkane evaporated film in spite of the lack of the hydrophilic group in the n-alkane and also the different length of the hydrocarbon chain between the two compounds. Upon evaporation, long-chain n-alkanes form polycrystalline films with the c axis, which is parallel to the chain direction, perpendicular to the substrate surface[14] (see the right of Figure 1a). Since a methyl end of the molecule is exposed to the film surface, σ orbitals with large distribution at the methyl end are predominantly attacked by metastables to form the features of the PIES in Figure 1a. Therefore, the close resemblance between the PIES of the n-alkane film and that of the AA monolayer indicates that AA is oriented with its *methyl* end toward the outside (see the right of Figure 1b.[15] Thus, molecules having different structures as a whole but common parts exposed outside give almost the same PIES, which leads to the identification of the molecular end at the film surface.

In the PIES of the mixed-monolayer LB film (Figure 1c), three bands are observed in the high electron energy region. The corresponding bands are not found in Figure 1b. With the ultraviolet photoelectron spectrum (UPS) of pyrene[16] as a reference, these bands are assigned to four π orbitals of the pyrene ring (two orbitals are responsible for the third band). This observation clearly indicates that PHA is oriented with its pyrene ring exposed to the film surface (see the right of Figure 1c). In addition, since the pyrene ring can be regarded as a model for the functional part of the amphiphile, the above results demonstrate the usefulness of PIES in the study of functionalized film surfaces.

In conclusion, PIES provides direct information about the end of molecules exposed outside the LB film surface. It should be noted that the analysis of the PIES is straightforward; we can determine the exposed molecular end of an LB film, comparing its PIES with that of a model compound having the same molecular end. In addition to the study of functionalized film surfaces, the observation of the change in PIES dependent on the number of layers enables us to discriminate among the types (X, Y, or Z) of the LB films. Furthermore, the rearrangement of molecules during film preparation as well as the character of the inhomogeneity at the film surface[17] can be sensitively detected by PIES.

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[12] The subphase contains 0.3 mM $CaCl_2$ and 0.05 mM $NaHCO_3$. Therefore, it may be more appropriate to consider this film as a calcium arachidate film.

[13] The substrate was smoothed with alumina to obtain a mirror surface and cleaned ultrasonically with organic solvents.

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[15] We have also obtained n-alkane films in which surface molecules lie exposing their "sides" (methylene groups) outside. Though the surfaces are hydrophobic in these cases as well, their PIES are entirely different from those of the "methyl surfaces" shown in Figure 1 (Ozaki, H.; Harada, Y., unpublished results).

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(E)-Selective Olefination of Aldehydes by means of *gem*-Dichromium Reagents Derived by Reduction of *gem*-Diiodoalkanes with Chromium(II) Chloride

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The geminal dimetallic reagent **1** is expected to add to a carbonyl carbon to form a β-oxymetal-substituted organometallic compound **2** which can then eliminate to give an olefin (Scheme I).[1] This approach provides useful methods for the methylenation (**1**, R^2 = H) of aldehydes or ketones by means of CH_2I_2–Zn–Me_3Al[2] or CH_2X_2 (X = I, Br)–Zn–$TiCl_4$.[2,3] These methods have some advantages compared to the Wittig reaction.

However, the geminal dimetallic reagents have not been widely utilized for the preparation of a 1,2-disubstituted olefin[4] from an

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