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Angle-Resolved X-Ray Photoelectron Spectroscopic Study on a Self-Assembled Monolayer of a Porphyrin–Ferrocene–Thiol Linked Molecule on Gold: Evidence for a Highly Ordered Arrangement for Efficient Photoinduced Electron Transfer

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The orientation of a self-assembled monolayer (SAM) of the 5-(4-{8-[(11-mercaptoundecanoyl)ferrocenyl]octyloxy}phenyl)-10,15,20-triphenylporphyrin ($PC_8FcC_{11}SH$) molecule on a gold substrate, at which a photoinduced up-hill electron transfer with the highest quantum efficiency (>10%) ever reported was achieved, was investigated using angle-resolved X-ray photoelectron spectroscopy (ARXPS) combined with an electrochemical coverage determination. The total thickness and the distance between the Fe and the outermost part of the SAM of the $PC_8FcC_{11}SH$ molecule was determined to be 44 and 29 Å, respectively, showing that while alkyl chains in the ferrocenecarbonylundecanethiol ($FcC_{11}SH$) part of the $PC_8FcC_{11}SH$ SAM should be oriented with a tilt angle of ca. 30° normal to the gold surface, the plane of the porphyrin ring should be almost surface-normal. This result suggests that one of the most important reasons for the very high photoconversion efficiency is the large separation between gold and the porphyrin ring, leading to a reduction in the reverse electron transfer and energy transfer quenching of the excited porphyrin state by gold.

In natural photosynthetic systems, various functional moieties, such as a photon absorber and electron donors and acceptors, are organized with molecular dimensions so that a very efficient photoinduced charge separation is achieved with minimum reverse electron transfer.[1,2] In order to construct a very efficient artificial photosynthetic device, it is essential to arrange the functional moieties in order. A self-assembled monolayer (SAM) of an alkanethiol on gold has been very widely investigated as an ordered molecular layer at the molecular level.[3,4] We have demonstrated that photoinduced up-hill electron transfer can be achieved at gold electrodes modified with the SAMs of molecules containing porphyrin and electron relay groups, such as quinone and ferrocene.[5—7] The highest quantum efficiency (>10%) ever reported at metal electrodes modified with organic thin films was achieved at a gold electrode modified with a SAM of the 5-(4-{8-[(11-mercaptoundecanoyl)ferrocenyl]octyloxy}phenyl)-10,15,20-triphenylporphyrin ($PC_8FcC_{11}SH$: Fig. 1(a)) molecule in an electrolyte solution containing methylviologen as the electron acceptor.[7,8] An important factor that controls the efficiency of photoinduced electron transfer includes the molecular orientation of the SAM and the distance between the functional groups.

Angle-resolved X-ray photoelectron spectroscopy (ARXPS) is one of the useful techniques to investigate the molecular orientation of thin-layer materials on solid substrates.[9—14] For example, Nakayama et al. determined the molecular orientation of azobenzene-containing ammonium amphiphiles in a vesicle by ARXPS.[11] We also employed this technique to investigate the orientation of the ferrocenylalkanethiol molecule in a SAM[12] and the layer-by-layer structure of composite thin films of cadmium sulfide nanoparticles and alkanedithiol.[13] Recently, we have proposed a novel method to determine the absolute thickness of a SAM by ARXPS combined with an electrochemical coverage determination.[14]

In this study, this method was applied to evaluate the molecular orientation and distance between the functional moieties of the $PC_8FcC_{11}SH$ SAM. The total thickness and the distance between the Fe and the outermost part of the SAM of $PC_8FcC_{11}SH$ were found to be 44 and 29 Å, respectively, showing that while alkyl chains in the ferrocenecarbonylundecanethiol ($FcC_{11}SH$) part in the $PC_8FcC_{11}SH$ SAM should be oriented with a tilt angle of ca. 30° normal to the gold surface, the plane of the porphyrin ring should be almost surface-normal. This result suggests that one of the most important reasons for the very high photoconversion efficiency is the large separation between gold and the porphyrin ring, leading to a reduction in the reverse electron transfer and energy transfer quenching of the excited porphyrin state by gold.

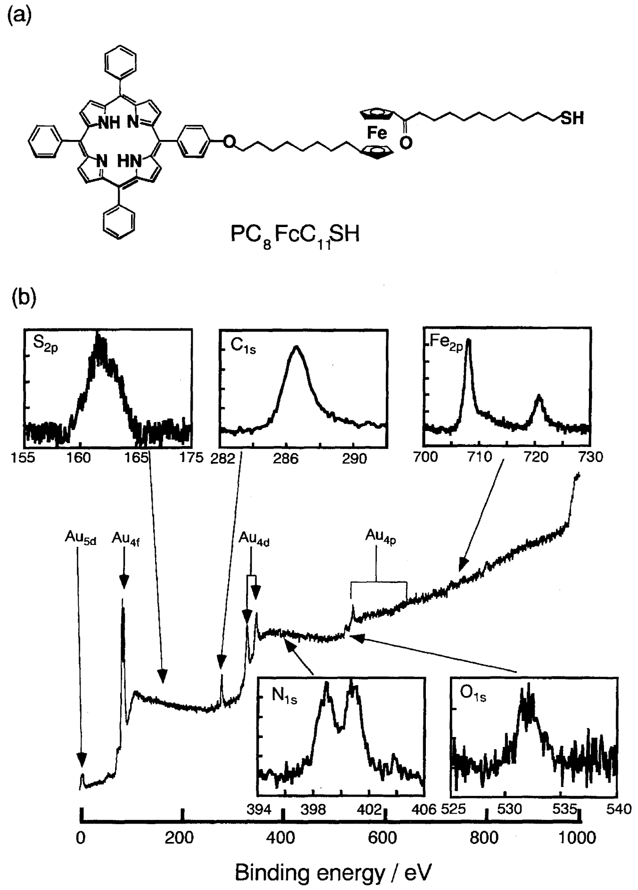

Fig. 1. (a) Molecular structure of $PC_8FcC_{11}SH$. (b) X-ray photoelectron (XP) spectrum of the $PC_8FcC_{11}SH$ SAM on Au(111) measured at θ of 90°. Insets: Narrow scan in the region of S_{2p}, C_{1s}, N_{1s}, O_{1s}, and Fe_{2p}.

Experimental

$PC_8FcC_{11}SH$ was synthesized using previously reported procedures.[7] A Au(111)-oriented gold substrate was prepared by vacuum evaporation on polycrystalline gold.[15] The surface modification of Au(111) was carried out by dipping the substrate in a dichloromethane solution containing 1 mM $PC_8FcC_{11}SH$ at 20 °C for 15 h under a N_2 atmosphere. After the modification, the sample was sequentially washed with dichloromethane, ethanol, and pure water. The XP spectra were obtained using an X-ray spectrometer (Rigaku, XPS7000) with Mg $K\alpha$ radiation (1253.6 eV) for excitation. The detector was placed normal to the direction of the incident and reflection X-rays. The sample holder was rotated at the line intersecting the sample surface and the plane of the X-ray incidence and reflection. The XP spectra were measured at take-off angles (θ) of 25°, 30°, 40°, 50°, 70°, and 90° by rotating the sample holder. Au_{4f}, Fe_{2p}, S_{2p}, C_{1s}, N_{1s}, and O_{1s} signals were acquired for 4, 16, 256, 8, 128, and 8 scans, respectively. All of the core levels were referenced to $Au_{4f7/2}$ (83.8 eV). The experimental conditions were the same as those previously reported.[14] The adsorbed amount of $PC_8FcC_{11}SH$ was electrochemically determined by measuring the charge for the redox of the ferrocene moiety in 0.1 M $HClO_4$ (1 M = 1 mol dm^{-3}).

Results and Discussion

Figure 1(b) shows a typical XP spectrum of the $PC_8FcC_{11}SH$ SAM on Au(111). Peaks corresponding to Au_{4f}, S_{2p}, C_{1s}, N_{1s}, O_{1s}, and Fe_{2p} were observed, and are shown in the inset. Damage of the SAM by the X-rays was negligible during the present XPS measurements, since the amount of the electrochemically determined adsorbed molecules, 1.4×10^{14} molecules cm^{-2}, was not changed before and after the XPS measurement. Two peaks due to $Au_{4f5/2}$ and $Au_{4f7/2}$ were observed at 87.5 and 83.8 eV, respectively.[16] The peaks in the S_{2p} region were observed at 163.0 eV for $S_{2p1/2}$ and at 161.8 eV for $S_{2p3/2}$, indicating that $PC_8FcC_{11}SH$ molecules adsorb on Au(111) through the Au–S bond.[12,17] In the N_{1s} region, two peaks were observed at 397.8 and 399.8 eV, corresponding to the –NH– and –N= groups, respectively, in the porphyrin ring.[18] The O_{1s} signal around 532 eV indicates the existence of carbonyl and ether groups.[16] In the Fe_{2p} XP spectrum, two peaks were observed at 720.8 and 708.0 eV for $Fe_{2p1/2}$ and $Fe_{2p3/2}$, respectively, confirming the presence of the ferrocene group.[19—21]

Figure 2 shows (a) Au_{4f} and (b) Fe_{2p} XP spectra of the $PC_8FcC_{11}SH$ SAM on Au(111) measured at various θs. The intensities of both the Au_{4f} and Fe_{2p} peaks decreased along with a decrease in θ. The intensity of the photoelectrons from a thin-film-covered substrate is known to vary with θ as[9,10)]

$$\ln(I) = -d/(\lambda \sin\theta) + \ln(I_0), \tag{1}$$

where I_0 and I are the intensities of the photoelectrons from a

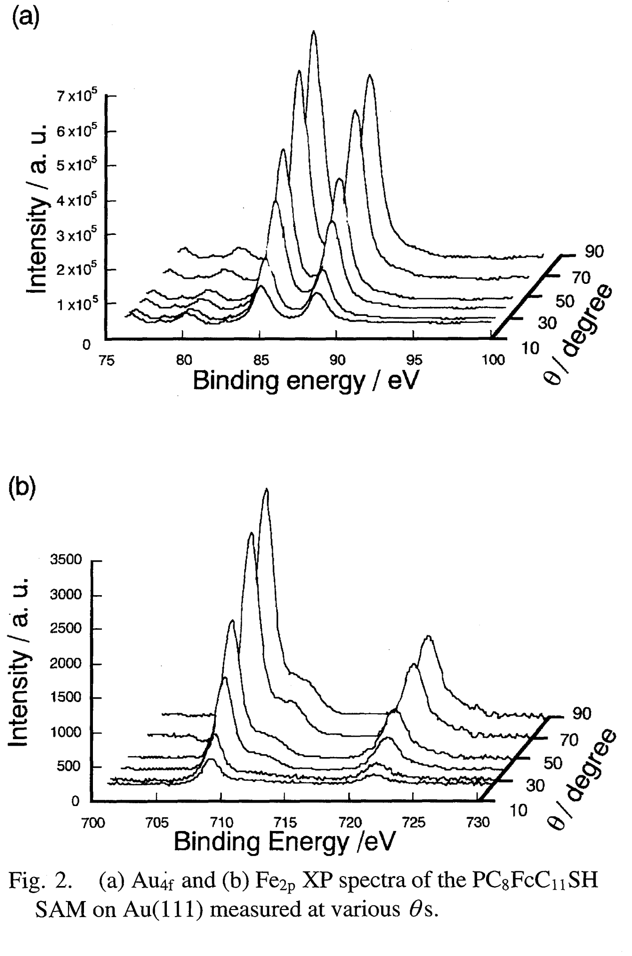

Fig. 2. (a) Au_{4f} and (b) Fe_{2p} XP spectra of the $PC_8FcC_{11}SH$ SAM on Au(111) measured at various θs.

clean substrate and from a substrate covered with a thin film of thickness d, respectively, and λ is the photoelectron mean-free path, which is defined as the thickness of the material where the flux of the emitted photoelectron is reduced to $1/e$ of the original flux. Equation 1 shows that $\ln(I)$ should be linearly related to $1/(\sin\theta)$ with a slope of $-(d/\lambda)$. Figure 3 shows that the logarithm of the integrated peak intensities of both the (a) Au_{4f} and (b) Fe_{2p} peaks are linearly related to $1/(\sin\theta)$ presented in Fig. 2, as expected from Eq. 1 with slopes of -1.3 ± 0.1 and -1.6 ± 0.1, respectively.

We have already demonstrated that the thickness of an alkanethiol SAM can be calculated using the values of $-(d/\lambda)$ determined from ARXPS measurements and the surface coverage (Γ/molecules cm^{-2}) determined from the reductive desorption using the following equation:[14)]

$$-\frac{d}{\lambda}=\frac{d\left[E_{\mathrm{p}}^{2}\left\{\beta\ln\left(0.191E_{\mathrm{k}}\left(\frac{\Gamma M}{N_{\mathrm{A}}d}\right)^{-0.5}\right)-\frac{1634-0.91E_{\mathrm{p}}}{829.4E_{\mathrm{k}}}+\frac{4429-20.8E_{\mathrm{p}}}{829.4E_{\mathrm{k}}^{2}}\right\}\right]}{E_{\mathrm{k}}}, \tag{2}$$

where E_{k} (eV) is the kinetic energy of the photoelectron, E_{p} (eV) is the free electron plasmon energy, M the molecular weight of the molecules on the gold substrate, N_{A} Avogadro's number, and β an empirical parameter. E_{p} and β are given by the following two equations:

$$E_{\mathrm{p}}=28.8\left(\frac{N_{\mathrm{v}}\Gamma}{N_{\mathrm{A}}d}\right)^{0.5}, \tag{3}$$

$$\beta=-0.10+0.944(E_{\mathrm{p}}^{2}+E_{\mathrm{g}}^{2})^{-0.5}+0.069\left(\frac{M\Gamma}{N_{\mathrm{A}}d}\right)^{0.1}, \tag{4}$$

where N_{v} and E_{g} (eV) are the number of valence electrons and the edge energy of the optical absorption,[22—25)] respectively, of the overlayer molecule.

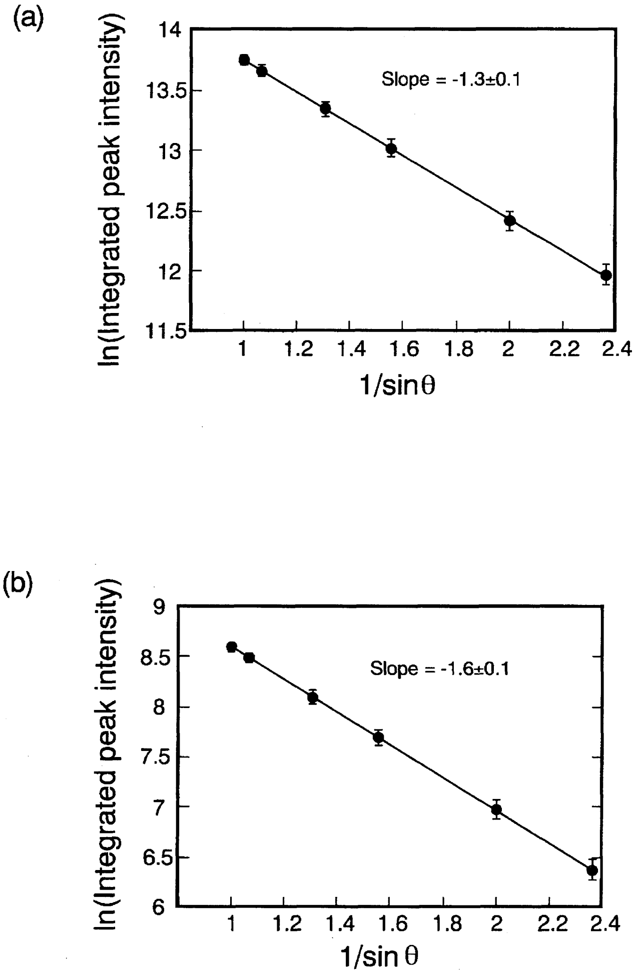

Fig. 3. Relation between $1/(\sin\theta)$ and logarithm of integrated peak intensity of (a) $Au_{4f7/2}$ and (b) $Fe_{2p3/2}$ in the XP spectrum of the $PC_8FcC_{11}SH$ SAM on Au(111).

By applying Eqs. 2, 3, and 4 to the Au_{4f} spectra, we determined the total thickness of the $PC_8FcC_{11}SH$ SAM on Au(111). The values used for the calculation were as follows: $-d/\lambda=-1.3\pm0.1$, obtained as the slope in Fig. 3(a); $\Gamma=1.4\times10^{14}$ molecules cm^{-2}, electrochemically determined from the charge of the redox of the ferrocene moiety; $E_{\mathrm{k}}=1169.8$ eV, calculated by subtracting the binding energy of the $Au_{4f7/2}$ electron from the incident X-ray energy ($=1253.6-83.8$), $M=1126$ ($C_{73}H_{73}N_4O_2SFe$), $N_{\mathrm{v}}=411$ (C = 4, H = 1, N = 5, O = 6, S = 6, and Fe = 8);[22,23)] and $E_{\mathrm{g}}=1.9$ eV, which is the edge energy in the absorption spectrum of $PC_8FcC_{11}SH$.[7)] One may suggest that the use of $E_{\mathrm{g}}=1.9$ eV, which is due to absorption by the porphyrin moiety in the SAM, may lead to some error, since the surface layer consists not only of the porphyrin group. However, the error must be small. The variation in E_{g} does not significantly affect the value of β, since the value of E_{p} (ca. 14 eV) is much larger than E_{g} (see Eq. 4). The values of d and λ are 44±3 and 34±3 Å, respectively. The value of d shows that the adsorbed $PC_8FcC_{11}SH$ molecules stand almost perpendicular and that the value of λ is in good agreement with those for the SAM of alkanethiols on gold reported by Bain et al. of 34 Å,[26,27)] and for the dodecanethiol SAM on Au(111) determined by us, 36 Å.[14)]

By applying the above procedure to the Fe_{2p} spectra, we can also determine the thickness of the layer over Fe in the SAM. We used the values of $-d/\lambda=-1.6\pm0.1$ (slope in Fig. 3(b)), $\Gamma=1.4\times10^{14}$ molecules cm^{-2}, $E_{\mathrm{k}}=545.6$ ($=1253.6-708$) eV, $M=806$ ($C_{57}H_{49}N_4O$), $N_{\mathrm{v}}=303$, and $E_{\mathrm{g}}=1.9$ eV. Here, we used $M=806$ ($C_{57}H_{49}N_4O$) and $N_{\mathrm{v}}=303$, since one pentadienyl ring of ferrocene and the PC_8 portion of $PC_8FcC_{11}SH$ (see Fig. 1(a)) should exist over Fe in the SAM. The values of d, i.e., the distance between Fe and the outer-most part of the SAM, and λ of this part were determined to be 29±2 and 18±2 Å, respectively. The value of λ (22 Å) is similar to that the reported for the Fe_{2p} photoelectron within 26-n-paraffin.[23)]

From the values of the total thickness and the distance between Fe and the outermost part of the SAM, the thickness of the ferrocenecarbonylundecanethiol ($FC_{11}SH$) part in the SAM was calculated to be 18±3 Å. Alkyl chains in the closed-packed SAM are known to be extended due to their hydrophobic interactions.[3)] If the alkyl chains are extended so as to be all trans, the length of the $FcC_{11}SH$ part is estimated to be 21.6 Å. Thus, alkyl chains in the $FcC_{11}SH$ part of the $PC_8FcC_{11}SH$ SAM should be oriented with a tilt angle of ca. 30° normal to the gold surface. This result is in good agreement with that of the alkanethiol SAM previously reported.[28] Although the porphyrin part of the $PC_8FcC_{11}SH$ molecule can be rotated around the ether bond, the plane of the porphyrin ring should be almost surface-normal in this case to satisfy the conditions that the alkyl chain of the $FcC_{11}SH$ part is oriented with a tilt angle of 30° and the total thickness of $PC_8FcC_{11}SH$ SAM is 44 Å. The orientation of $PC_8FcC_{11}SH$ in the SAM is schematically shown in Fig. 4. The size of the porphyrin ring, 86 $Å^2$ $molecule^{-1}$, when the porphyrin ring orients as shown in Fig. 4, agrees well with the molecular area of $PC_8FcC_{11}SH$ estimated from the adsorbed amount of $PC_8FcC_{11}SH$ molecules on Au(111) of 1.4×10^{14} molecules cm^{-2}, ca. 83 $Å^2$ $molecule^{-1}$.

In our previous report,[7] we proposed two reasons why this system showed such a very high efficiency. One is the high electron transfer rate between the ferrocene moiety and the gold. The other is the effective inhibitation of reverse electron transfer and energy transfer from excited porphyrin to the gold. According to the present study, the distances between the center of porphyrin and the gold, the centers of porphyrin and ferrocene, and the center of ferrocene and the gold were estimated to be ca. 35, 20, and 15 Å, respectively. While forward electron transfer from gold to ferrocene and ferrocene to porphyrin should take place at a reasonable rate as estimated distances between the centers of porphyrin and ferrocene and between the center of ferrocene and the gold are 20 and 15 Å, respectively, reverse electron transfer and energy transfer quenching of the excited porphyrin state by gold should not be significant, because the distance between the center of porphyrin and the gold is 35 Å. Thus, we can conclude that this is one of the most important reasons for the highly efficient visible-light-induced photocurrent generation at the gold electrode modified with the SAM of $PC_8FcC_{11}SH$.[7]

Conclusions

The orientation of the self-assembled monolayer (SAM) of the 5-(4-{8-[(11-mercaptoundecanoyl)ferrocenyl]octyloxy}phenyl)-10, 15, 20-triphenylporphyrin ($PC_8FcC_{11}SH$) molecule on the Au(111) substrate was investigated using angle-resolved X-ray photoelectron spectroscopy (ARXPS) combined with an electrochemical coverage determination. The thickness of the $PC_8FcC_{11}SH$ SAM and of the ferrocenecarbonylundecanethiol part in the SAM were determined to be 44±3 and 18±3 Å, respectively, showing that while alkyl chains in the $FcC_{11}SH$ part in the $PC_8FcC_{11}SH$ SAM should be oriented with a tilt angle of ca. 30° normal to the gold surface, the plane of the porphyrin ring should be almost surface-normal. This result suggests that one of the most important reasons for the very high photoconversion efficiency is the large separation between gold and the porphyrin ring of 35 Å, leading to a reduction of reverse electron transfer and energy transfer quenching of the excited porphyrin state by gold.

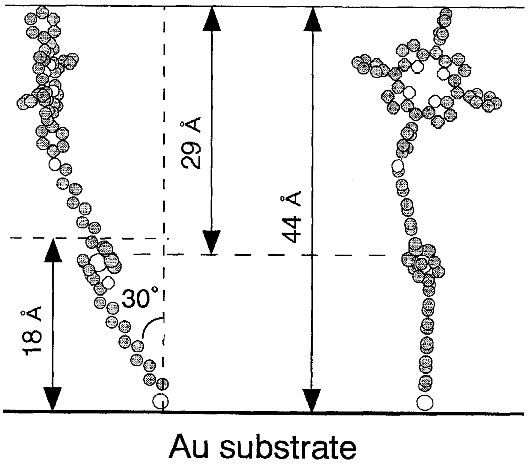

Fig. 4. Schematic models of orientation of $PC_8FcC_{11}SH$ molecule.

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