

Surface plasmon excitation of a porphyrin covalently linked to a gold surface

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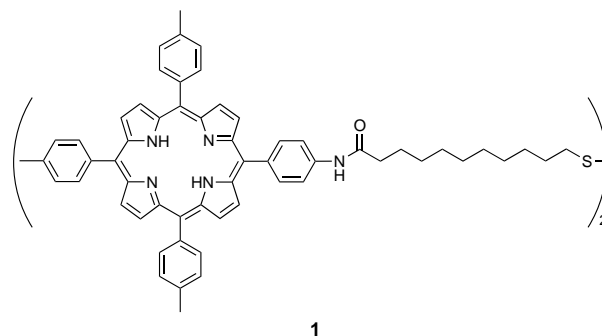
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Fluorescence of a porphyrin covalently linked to a gold surface is observed with surface plasmon excitation using p-polarized light to show higher excitation efficiency for the Q-bands than the Soret band.

Surface plasmon resonance (SPR) is a near-field phenomenon, in which the plasma oscillation of a metal is coupled with the incident light at the resonance angle resulting in strong polarization on the metal surface.¹ SPR has been mainly used as an excellent sensing method for biological purposes.^{2,3} Since surface plasmon (SP) has field enhancement effects,¹ photochemical reactions at the surface are expected to be assisted by SPR similar to the surface enhanced spectroscopy. Here, we have studied electronic excitation of a porphyrin chromophore covalently linked to a gold surface by SPR.

SPs were generated on a gold surface with an attenuated total reflection (ATR) method using a Kretschmann–Raether configuration⁴ [Fig. 1(a)]. The reflectivity was recorded as a function of the incident angle (θ). At the ATR minimum denoted as a SPR angle (θ_R), SPs were created on the opposite side of the gold film. A disulfide derivative of porphyrin **1** was used as a modification reagent to effectively introduce porphyrin chromophores $\{-S(CH_2)_{10}CONH-Por, Por = p\text{-[tris}(p\text{-tolyl)porphyrinyl]phenyl}\}$ on the gold surface. The Au–S covalent bond has been confirmed by X-ray photoelectron spectroscopy by one of us (Y. S.).⁵ All the measurements were performed at room temperature.

A $15 \times 15 \times 15$ mm BK-7 right-angle prism was rigorously cleaned by ultrapure water, spectroscopic grade methanol, acetone and 1,2-dichloroethane. A 50 nm gold film was evaporated on the hypotenuse face from a 99.9995% Au source at a pressure $< 6 \times 10^{-4}$ Pa, rinsed with spectroscopic grade 1,2-dichloroethane, dried in class-100 air, and used as a control bare film. The θ_R was measured with p-polarized 632.8 nm light



from a He–Ne laser. The bare film showed θ_R of 43.6° (Fig. 2) which is consistent with the reported values.⁶

Modification of the gold surface by **1** was performed as follows. The bare film was immersed in a 0.5 mmol dm^{-3} 1,2-dichloroethane solution of **1** for 2 min, washed with a sufficient amount of 1,2-dichloroethane 10 times, and dried in air. After modification, the θ_R shifted to 43.9° (Fig. 2). The shift is attributable to the change in the refractive index for the gold surface covered with $-S(CH_2)_{10}CONH-Por$. The shift required immersion for 2 min for saturation. Therefore, the gold surface was virtually covered with the porphyrin layer after 2 min immersion.

A transmission absorption spectrum of $-S(CH_2)_{10}CONH-Por$ was measured using two gold films prepared on BK-7 flat plates as the sample and reference films. The sample film was modified by $-S(CH_2)_{10}CONH-Por$ similarly to the prism. As shown in Fig. 3, the difference absorption spectrum showed the characteristic bands of tetraarylporphyrin and is quite similar to that of the film of tetraphenylporphyrin evaporated under vacuum on a glass.⁷ Assuming the refractive index of $-S(CH_2)_{10}CONH-Por$ film as 1.5, similar to those of usual organic thin films such as protein⁶ and poly(methyl methacrylate),⁸ the thickness was estimated to be *ca.* 2 nm. This suggests that the $-S(CH_2)_{10}CONH-Por$ moiety adopts a linear conformation perpendicular to the gold surface.⁹ In other words, the gold

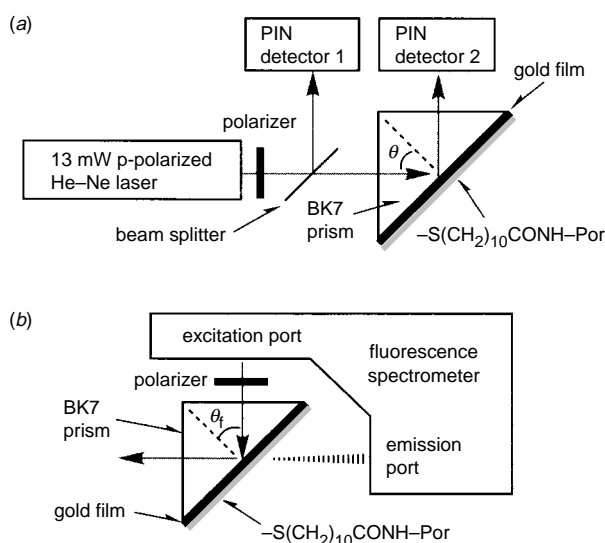


Fig. 1 Experimental configurations of ATR minimum (a) and fluorescence (b) measurements

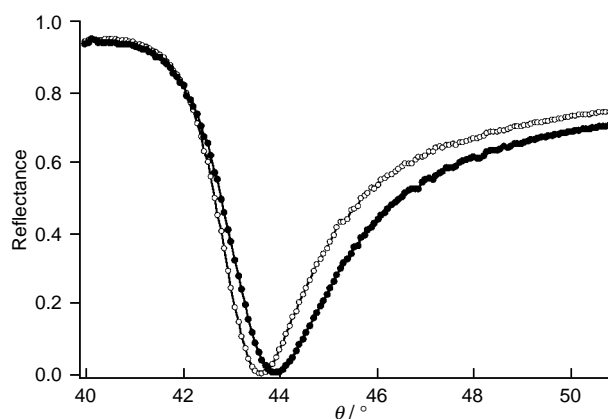


Fig. 2 SPR reflectivity curves for the gold film on a BK-7 right-angle prism (○) and that modified by $-S(CH_2)_{10}CONH-Por$ (●)

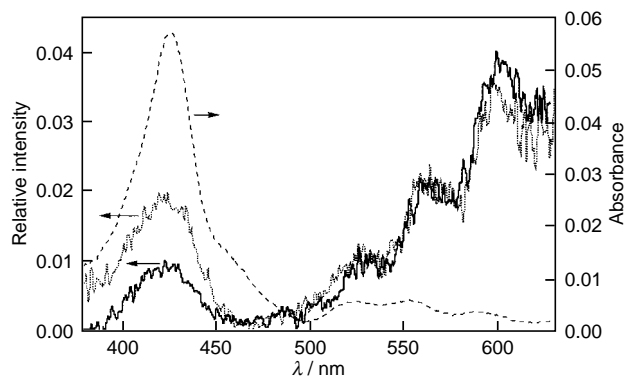


Fig. 3 The excitation spectra of the 655 nm fluorescence band in $-\text{S}(\text{CH}_2)_{10}\text{CONH-Por}$ film on a gold surface with the SPR excitation at the incident angles of $\theta = 45^\circ$ (—) and 75° (---), and a transmission absorption spectrum of the film (· · ·)

surface is covered with the monolayer of linearly ordered $-\text{S}(\text{CH}_2)_{10}\text{CONH-Por}$.

The electromagnetic field of SP shows a maximum on the surface and decays exponentially into the space along the axis perpendicular to the surface.⁸ Since the porphyrin chromophore is bonded to the gold surface at the distance < 2 nm, it can obtain effectively the energy of SP for the electronic excitation. The emission from the gold surface covered with $-\text{S}(\text{CH}_2)_{10}\text{CONH-Por}$ was measured using a fluorescence spectrometer, in which the p-polarized visible light illuminated the gold film through a prism at the incident angle (θ_i) of 45° [Fig. 1(b)]. The characteristic fluorescence spectrum of tetra-arylporphyrin was observed with maxima at 655 and 720 nm, while the fluorescence excitation spectrum using SPR was different from the absorption spectrum (Fig. 3). The intensity ratio between the $Q_y(1,0)$ -band and Soret band, $I_Q/I_S = 4.0$ was significantly larger than that of the absorption spectrum (0.06).[†]

Because of the dispersion of SP, θ_R varies depending on the wavelength of the incident light. Therefore, we should consider an appropriate θ for the excitation wavelength. The excitation spectrum was measured at θ_i of 75° in order to confirm the θ dependence on the excitation wavelength. The Soret band at $\theta_i = 75^\circ$ was certainly increased compared to that at $\theta_i = 45^\circ$, while the I_Q/I_S was still large, 1.8 (Fig. 3).

Since the amplitude of the electromagnetic field of SP exceeds that of the incident field, the evanescent field of SP is expected to enhance inelastic emission such as fluorescence and Raman scattering from molecules adjacent to the metal film.¹⁰ The field enhancement effect of SP is larger in the longer wavelength region. For example, the electric field of SP on the gold surface created by 650 nm light is approximately 50 times larger than that of the incident light.⁸ This is consistent with the preferable excitation at the longer wavelength light in the SPR excitation of the $-\text{S}(\text{CH}_2)_{10}\text{CONH-Por}$ film.

The fluorescence lifetime with the SPR excitation was measured by a single photon counting method. The obtained decay profile was analysed by two components with 500 ps (65%) and 3.5 ns (35%),[‡] both of which were longer than that (310 ps) of a film of tetraphenylporphyrin evaporated under vacuum on Pt surface with the direct photoirradiation.⁷ The long lifetimes seem to be due to weak electronic interaction between the porphyrin chromophore and the gold surface through the $-\text{S}(\text{CH}_2)_{10}\text{CONH-}$ group. Recently, a $-\text{S}(\text{CH}_2)_{10-}$ spacer between a fluorophore and a gold surface has been reported to suppress energy transfer quenching by the gold surface giving high fluorescence yield.¹¹ Similarly, it is suggested that the $-\text{S}(\text{CH}_2)_{10}\text{CONH-}$ group interrupts the energy transfer from the porphyrin excited state to the gold surface.

The present study demonstrates that SP is an effective and specific excitation source of a porphyrin covalently linked to a gold surface. We are currently studying the effects of the spacer length and the nature of metals upon the fluorescence properties.

Dr Hiroshi Imahori and Tsuyoshi Akiyama are acknowledged for their synthetic advice. This work is partly supported by a Grant-in Aid for Scientific Research (No. 08650979 and 09279224 to A. I.; No. 09238234, 09226223 and 09875209 to T. M.) from the Ministry of Education, Science, Sports and Culture of Japan, and by Research Area of 'Fields and Reactions', Precursory Research for Embryonic Science and Technology, Japan Science and Technology Corporation, and NEDO (A. I.).

Footnotes and References

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[†] The characteristic fluorescence spectrum was also observed in the direct photoirradiation of the $-\text{S}(\text{CH}_2)_{10}\text{CONH-Por}$ film, while the value I_Q/I_S was smaller (0.44) than that in the SPR excitation and larger than that of the absorption spectrum.

[‡] Although the fluorescence decay profile showed multi-exponential components, it was analysed by the sum of two components with $\chi^2 = 1.40$. This suggests that the porphyrin chromophores are in different structural and electronic environments.

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Received in Exeter, UK, 11th September 1997; 7/06623F