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Inhomogeneous Aggregation of a Merocyanine Dye at the Solid/Liquid Interface Layer. A Picosecond Time-Resolved Total Internal Reflection Fluorescence Study

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Fluorescence spectra and their rise and decay dynamics of a merocyanine dye in the interface layer have been studied as a function of penetration depth of the evanescent wave intensity by total internal reflection fluorescence spectroscopy. The aggregation of the dye was enhanced in the interface layer of up to ≈ 100 nm thickness compared to the bulk solution.

Investigation of interfaces such as solid/liquid has attracted much attention because of incontinuous natures of interfaces. At a solid/liquid interface layer, physical and chemical properties of the liquid are anticipated to be different from those in the bulk liquid. Molecular interactions and dynamics at the solid/liquid interface layer can be examined using total internal reflection (TIR) fluorescence spectroscopy in which fluorescent molecules in the liquid are excited by an evanescent wave of the laser pulse penetrating from the solid substrate. [1-4]

Recently, we have demonstrated that the rates of solvent reorientational relaxations around excited coumarin 460 and a proton transfer from excited 1-naphthol to water are decreased in the sapphire/1-butanol and sapphire/water interface layers, respectively. [5,6] The results were interpreted in terms of the longitudinal relaxation effects caused by hydrogen bonding interactions between the surface and liquids.

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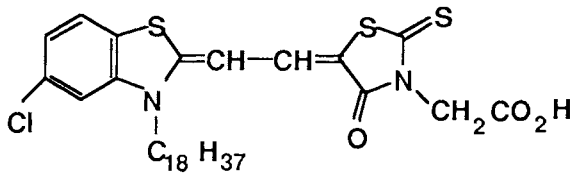
In this letter, we report an inhomogeneous aggregation of a merocyanine dye in the sapphire/1-butanol interface layer on the basis of time-resolved TIR fluorescence spectroscopic measurements.

Time-resolved fluorescence decays at 560 nm were measured by a picosecond single-photon timing technique equipped with a TIR fluorescence assembly. [3,7] The second harmonic (527 nm) of a mode-locked Nd: YLF laser (Quantronix 4217ML) was used as an excitation light. In TIR fluorescence spectroscopy, the penetration depth of the evanescent wave intensity changes depending on the incidence angle of an excitation light: the more the incidence angle enlarges, the more the penetration depth becomes shallow. A merocyanine dye (Nippon Kankou Shikiso) was used as received. Sample solutions were deaerated by bubbling Ar followed by attaching an Ar balloon to a sample cell.



Merocyanine dye
(MCD-18)

Figure 1 shows fluorescence spectra of MCD-18 (4.6×10^{-5} mol dm^{-3}) in 1-butanol under normal and TIR excitation conditions. The maximum of the MCD-18 fluorescence observed under TIR excitation condition is slightly shifted to longer wavelengths (≈ 558 nm) compared to that (556 nm) for the bulk solution. At the same time, the fluorescence intensity of a shoulder at ≈ 580 nm is reduced as the penetration depth is decreased. Figure 2 illustrates the concentration effect of MCD-18 in bulk 1-butanol on its fluorescence spectrum.

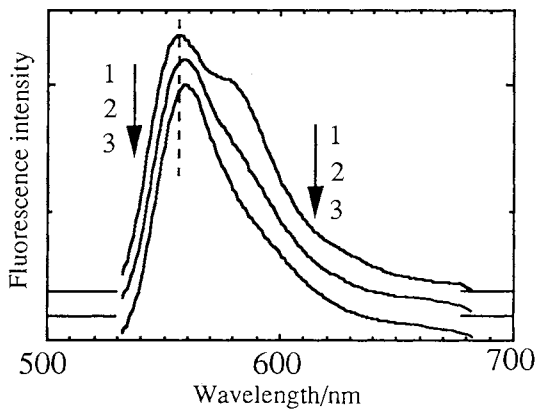


Fig. 1. Normalized fluorescence spectra of MCD-18 (4.6×10^{-5} mol dm^{-3}) in bulk 1-butanol (1) and in the sapphire/ 1-butanol interface layers. Penetration depth: 2) 112 ± 13; 3) 53 ± 2 nm.

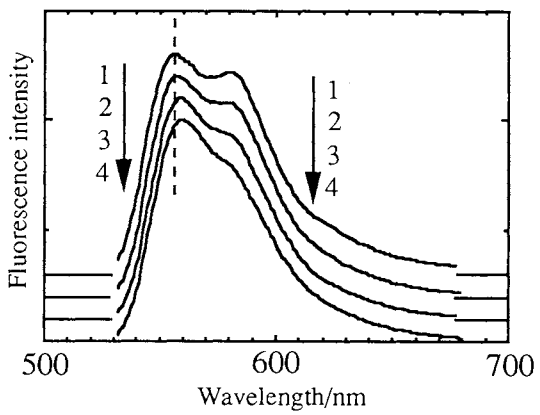


Fig. 2. Concentration dependence of the normalized MCD-18 fluorescence in bulk 1-butanol. Concentration of MCD-18: 1) 2.4×10^{-6}; 2) 1.1×10^{-5}; 3) 4.6×10^{-5}; 4) 1.0×10^{-4} mol dm^{-3}.

When the concentration increases, the fluorescence maximum is shifted to longer wavelengths accompanied by an intensity reduction of the shoulder at ≈ 580 nm. The spectral changes in Fig. 2 are safely attributable to the aggregation of MCD-18. As the fluorescence spectral changes in Fig. 1 resemble those in Fig. 2, it is considered that the aggregation of MCD-18 occurs more efficiently in the interface layer compared to the bulk 1-butanol.

A fluorescence decay curve of MCD-18 (4.6×10^{-5} mol dm^{-3}) in bulk 1-butanol could be analyzed by a bi-exponential function. The lifetimes of fast and slow decay components were 16 and 150 ps, respectively. The former amplitude A_1 (97.9%) is much greater than the latter A_2 (2.1%). These amplitude values indicate that the fast and slow decay components are due to a monomer and an aggregate of MCD-18, respectively. In the TIR mode, the fluorescence decay curves of MCD-18 were measured by varying the incidence angle of the excitation beam. These decay curves were analyzed by three exponentials; an additional component of a few hundreds ps was observed. The shortest lifetime was attributed to the monomer because, at a penetration depth of about 100 nm, it was nearly the same as the shorter lifetime for a bulk solution. All the lifetimes became larger as the penetration depth was decreased from about 100 nm. As the penetration depth was decreased, the amplitude of the monomer component, A_1, was decreased in contrast to those (A_2 and A_3) of the aggregates. The amplitude ratio of aggregates to the monomer, $(A_2 + A_3)/A_1$, is plotted as a function of penetration depth (Fig. 3). In Fig. 3, also shown is the A_2/A_1 value for a bulk solution as a dashed line.

With a decrease in the penetration depth, $(A_2 + A_3)/A_1$ is increased, indicating that the aggregation is significantly promoted in the interface layer. Such an inhomogeneous aggregation is probably due to an enhancement of equilibrium constants for the aggregation at the interface relative to a bulk solution; water adsorbed on the surface may be responsible for the enhanced equilibrium constants.

For a concentrated MCD-18 solution (5.5×10^{-4} mol dm^{-3}), the lifetimes and $(A_2 + A_3)/A_1$ increased similarly but in the range of the shallower penetration depth.

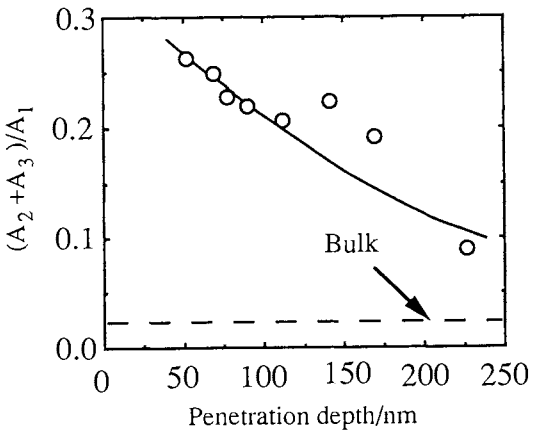


Fig. 3. Penetration-depth dependence of $(A_2 + A_3)/A_1$ for MCD-18 (4.6×10^{-5} mol dm^{-3}) in 1-butanol (See text). A dashed line represents A_2/A_1 for the bulk solution.

This finding suggests that the aggregation exerted by the interface effect becomes prominent in the region nearer to the surface relative to a dilute MCD-18 solution since MCD-18 associates to some extent in the bulk solution of high concentration.

Another possible explanation is that the aggregated species is adsorbed MCD-18 on the sapphire surface and, in addition, the fluorescence contribution is extremely higher than that of the bulk. Thus, we examined the fluorescence of MCD-18 adsorbed on sapphire under the atmosphere. A sample of adsorbed MCD-18 was prepared by dropping an aliquot of the 1-butanol solution on a sapphire prism and then drying it with an Ar stream. The fluorescence of the adsorbed MCD-18 on sapphire has a peak at ≈ 562 nm, and is most likely to be attributed to aggregates because of a disappearance of the shoulder at ≈ 580 nm. It is worth noting that the fluorescence of the adsorbed MCD-18 is slightly red-shifted (≈ 4 nm) relative to that in the interface layer. When the adsorbed MCD-18 is hemispherically surrounded by solvent 1-butanol molecules posessing a large dielectric constant, the fluorescence peak of the adsorbed MCD-18 is expected to be shifted to much longer wavelengths compared to that of adsorbed one surrounded by atmosphere. The present result is inconsistent with this expectation, so that it is concluded that the fluorescence in the interface layer shown in Fig. 1 are not due to MCD-18 aggregates adsorbed on sapphire but due to those at the interface layer.

Our results on the excitation energy relaxation of the merocyanine dye strongly suggest that the sapphire surface affects some physical and/or chemical properties of liquids to a great extent. The changes in the liquid property is related with an abnormaly of the longitudinal relaxation of 1-butanol in the interface layer.[5)]

References

1) H. Masuhara, N, Mataga, S. Tazuke, T. Murao, and I. Yamazaki, *Chem. Phys. Lett.*, **100**, 415 (1983).

2) M. Yanagimachi, M. Toriumi, and H. Masuhara, *Chem. Mater.*, **3**, 413 (1991).

3) M. Toriumi, M. Yanagimachi, and H. Masuhara, *Advances in Resist Technology and Processing VIII*, SPIE **1466**, 458 (1991).

4) G. Rumles, A. J. Brown, and D. Phillips, *J. Chem. Soc., Faraday Trans.*, **87**, 825 (1991).

5) M. Yanagimachi, N. Tamai, and H. Masuhara, *Chem. Phys. Lett.*, **200**, 469 (1992).

6) M. Yanagimachi, N. Tamai, and H. Masuhara, *Chem. Phys. Lett.*, **201**, 115 (1993).

7) M. Toriumi and H. Masuhara, *Spectrochim. Acta Rev.*, **14**, 353 (1991).

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