The ^{19}F NMR of the compound at ~10 °C in SO_2ClF shows a single CF_3 peak at −73.42 ppm relative to external $CFCl_3$. As the sample was warmed to 35 °C, successive spectra showed a decrease in the signal for the xenon compound and a subsequent growth of two other singlets, one due to CF_3Cl (−28.27 ppm) and the other at −76.34 ppm. The latter does not correspond to previously observed decomposition products for the compound, and along with the CF_3Cl, this indicates a reaction with the solvent upon decomposition.

Further structural characterization of $Xe[N(SO_2CF_3)_2]_2$ to provide direct physical evidence for the xenon–nitrogen bond is in progress, and extension of this now reaction type to other systems is planned.

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Registry No. $Xe[N(SO_2CF_3)_2]_2$, 82113-64-2; $(CF_3SO_2)_2NH$, 82113-65-3; $Me_3SiN(SO_2CF_3)_2$, 82113-66-4; XeF_2, 13709-36-9.

Drastic Fluorescence Enhancement of Cyanine Dyes Bound to Synthetic Bilayer Membranes. Its High Sensitivity to the Chemical Structure and the Physical State of the Membrane[1]

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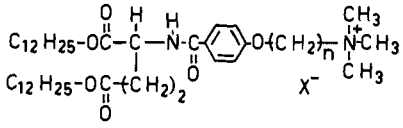
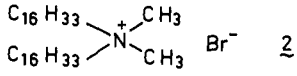
We describe herein that the fluorescence intensity of cyanine dyes is markedly enhanced by binding to synthetic bilayer membranes and that the enhancement is strongly affected by the chemical structure and fluidity of the membrane. Cyanine dyes have been known as sensitizers in the photographic process.[2] Recent attempts to use these dyes as probes for the physical state and the membrane potential of liposomes and interfacial monolayers[3-5] and as chromophores in organic solar cells[6] and dye lasers[7] called for widespread attention to their fluorescence behavior.

Dialkylammonium amphiphiles **1** and **2** produce stable bilayer



1 (n = 2, 4, 6, 10), X = Cl, Br



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aggregates (vesicles and lamellae) upon dispersion in water by sonication.[8-11] These bilayer membranes possess physicochemical characteristics common to those of biolipid bilayers such as the crystal-to-liquid crystal phase transition.[12]

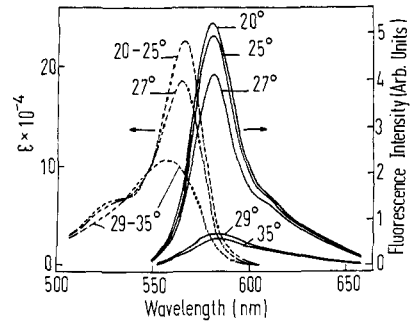


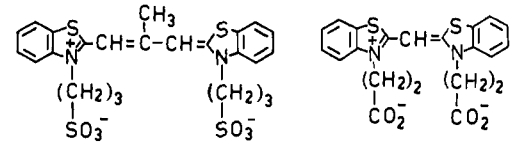
Figure 1. Absorption (dotted line) and fluorescence (solid line) spectra of cyanine dye **3** bound to aqueous bilayer **1**, $n = 4$ (X = Cl; [**1**] = 2×10^{-3} M, [**3**] = 5×10^{-7} M).

Table I. Quantum Yield of Cyanine Dye 3 in Various Media

media	Φ_F 20 °C	Φ_F 35 °C	P, (20 °C)
1, $n = 2$, (X = Br)	0.40		0.47
1, $n = 4$, (X = Cl)[a]	0.64	0.08	0.47
1, $n = 6$, (X = Br)	0.60		0.47
1, $n = 10$, (X = Br)	0.64		0.46
2	0.063	0.047	0.43
CTAC	0.035	0.019	0.39
water	~0.0025	~0.0018	0.40
methanol	~0.0024	~0.0017	0.39
glycerol	0.24		0.47

[a] Φ_F is almost the same when Cl is replaced by Br.

Figure 1 shows absorption and fluorescence spectra of cyanine dye **3** bound to aqueous bilayers of **1** ($n = 4$) (counterion, Cl^-).[13]



3 (NK 2012) **4** (NK 1881)

The molar ratio of the dye and the membrane is 1:4000, and self-quenching of fluorescence is not observed in this range. Both the absorption and fluorescence spectra show remarkable temperature dependence. Although the absorption spectrum is not sensitive to temperature at 20–25 °C with λ_{max} at 565 nm (ϵ_{max} 220000), its intensity diminishes drastically at 27–29 °C, becoming constant again at 30–35 °C (λ_{max} 555 nm, ϵ_{max} 110000). In contrast, the spectrum is virtually invariable in the whole temperature range in methanol (λ_{max} 542 nm), in water (λ_{max} 541 nm), and in aqueous cetyltrimethylammonium chloride (CTAC) micelles (λ_{max} 565 nm). These results are to be discussed elsewhere in terms of organization of dye molecules at the membrane surface.[14]

The fluorescence spectrum shows temperature dependence similar to that of the absorption spectrum in that a drastic intensity change is observed at 27–29 °C. The fluorescence intensity, I_F, in the low-temperature range is ca. 8 times larger than that in

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the high-temperature region, although the location of the emission maximum does not vary. The fluorescence intensities in water and in the CTAC micelle are much smaller and decrease gradually with temperature (20–35 °C); in the CTAC micelle I_F at 20 °C is ca. 2 times larger than that at 35 °C. The crystal-to-liquid crystal phase transition occurs at 31 °C (transition range 27–36 °C) for the aqueous bilayer of **1** (n = 4).[10] Therefore, the drastic spectral changes of Figure 1 are related to the phase transition of the membrane matrix. The I_F value is affected by the phase transition also when the cyanine dye is bound to the bilayer membrane of the simpler dialkylammonium salt **2** (transition temperature (T_c) 28 °C); however, the intensity enhancement is much smaller, I_F at 27 °C being only 20% larger than that at 30 °C.

On the other hand, the fluorescence spectrum of cyanine dye **4** is strongly influenced by the phase transition of both of bilayers **1** and **2**. The I_F value of dye **4** in the bilayer matrix of **1** (n = 4) drastically changes at T_c (I_F at 27 °C is 5 times larger than that at 30 °C), and I_F in the rigid membrane is 23 and 100 times larger than those in the CTAC micelle and in water, respectively. A similar, though less drastic, spectral change of dye **4** is observed at T_c in the bilayer matrix of **2**.

The fluorescence quantum yields (Φ_F) of dye **3**[15] in various media are summarized in Table I. The Φ_F is enhanced by more than 10 times in the CTAC micelle (0.035 at 20 °C) than in water; this increment coincides with that observed by Grätzel et al. for a cationic cyanine dye in the anionic micelle of sodium lauryl sulfate.[17] A much greater Φ_F enhancement is observed for the dye bound to the rigid (below T_c, 20 °C) bilayer membrane of **1** (n = 4, X = Cl). This value (0.64) is 20 times larger than that in the CTAC micelle and 250 times larger than those in water or in methanol. The enhancement is much reduced in the fluid membrane matrix, although Φ_F is still larger than that in the CTAC micelle.

The chemical structure of the membrane surface exerts significant influences on Φ_F. The Φ_F value of the membrane of **1**, n = 6 and 10, is close to that of **1**, n = 4, whereas that for **1**, n = 2, is reduced (0.40). The small difference in the spacer length can be crucial for obtaining high Φ_F values. The Φ_F value obtained in the matrix of the simple dialkylammonium bilayer of **2** is only 2 times larger than that in the CTAC micelle. It is clear that large fluorescence enhancement is rendered possible by dye binding to specific membrane surfaces.

The degree of fluorescence polarization (P)[18] is used as a measure of the rotational motion of the excited state. The P value (Table I) is relatively large even in water, and consequently, the increment in the membrane matrix is small. In general, Φ_F of cyanine dyes is enhanced by the prevention of internal conversion due to suppression of twisting of the polymethine chain, as confirmed by fluorescence measurements of rigidized dyes.[20,21] Our preliminary experiments indicate that the fluorescence lifetime (τ_F) of **3** is lengthened to approximately the same extent in bilayer membranes (**1** and **2**), CTAC micelle, and glycerol. The Φ_F value is still different among these media, and therefore, the Φ_F enhancement cannot be explained by the τ_F term alone. We reported recently that absorption spectra of methyl orange and cyanine dyes were extensively modified in the bilayer matrix, and discussed the results in terms of specific orientation and association of the dye molecules at the membrane surface.[11,14] The absorption spectrum of **3** changes also specifically with the physical state (Figure 1) or chemical structure[22] of the matrix membrane. This indicates that the ground-state electronic configuration is perturbed by the specific interaction and that the Φ_F variation may not be attributed solely to the excited-state characteristics. It is well-known that the fluorescence property changes drastically by dye aggregation.

We have observed similar fluorescence enhancements for other anionic cyanine dyes. In addition, cationic cyanine dyes show enhanced fluorescence in the presence of the anionic bilayer membrane.[23] Therefore, the fluorescence enhancement in the rigid bilayer matrix appears to be a widely observable phenomenon. Recent data by Whitten and co-workers for a stilbene surfactant point to the same conclusion.[24] We are currently examining the effect of the bilayer matrix on the fluorescence property of a large variety of cyanine and merocyanine dyes. These studies would provide unique means to control the flow of the excitation energy of cyanine and related dyes at the membrane surface. Practical applications of this technique in various fields can be readily envisaged.

Acknowledgment. We thank H. Fukushima for his capable experimental assistance and Dr. K. Kano for the lifetime measurement.

Registry No. 1 (n = 2; X = Br), 82135-66-8; **1** (n = 4; X = Cl), 82135-67-9; **1** (n = 6; X = Br), 82135-68-0; **1** (n = 10; X = Br), 82135-69-1; **2**, 70755-47-4; **3**, 82135-70-4; **4**, 82135-71-5; CTAC, 112-02-7; water, 7732-18-5; methanol, 67-56-1; glycerol, 56-81-5.

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(18)

$$P = \frac{I_{\parallel\parallel} - I_{\parallel\perp}(I_{\perp\parallel}/I_{\perp\perp})}{I_{\parallel\parallel} + I_{\parallel\perp}(I_{\perp\parallel}/I_{\perp\perp})}$$

where $I_{\parallel\parallel}$ and $I_{\perp\perp}$ are emission intensities measured with parallel polarizers (veritical and horizontal) and $I_{\parallel\perp}$ and $I_{\perp\parallel}$ are those measured with crossed polarizers.[19]

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Photochemical Transformation of Cephalosporins into Carbapenems

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Thienamycin **1** is the first reported member of a series of recently discovered antibiotics possessing the novel carbapen-2-em ring system.[1,2] Its remarkable antibacterial activity[3] has prompted

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