atures about 375 °C and no emission is observed after thermal treatment. The mordenite samples change emission characteristics after thermal treatment and should be regarded as different materials after thermal activation. On dehydration, cations must bind to framework oxygen atoms. Channel blocking is also known to occur in mordenite and it has been suggested that cations on channel walls hinder or restrict diffusion.[43] After dehydration, these channels open up, and this may explain the new type of emission for sodium mordenite after thermal treatment. These uranyl-exchanged zeolites are stable to ion beams.[25] High-energy electron bombardment[44] can cause loss of crystallinity and mass.

Luminescence Lifetime Measurements. Luminescence lifetime experiments are important in the determination of the number of active sites. The correlation of high activity with a short-lifetime component is also an important observation. Further inspection of the lifetime data reveals several other conclusions. Figure 4 shows that dehydration at 375 °C in a 1×10^{-5} atm vacuum does significantly alter the lifetime. The lifetime can be used as a tracer of the microenvironment in the same way as emission experiments and other spectroscopic measurements. On rehydration of the dehydrated uranyl-exchanged X, Y, and ZSM-5 zeolites the lifetimes return to the same values of the as-prepared hydrated materials. Such information regarding the effects of thermal treatment of ions in zeolites is not always easily obtained.

The luminescence lifetime decay of 1% by weight of UO_2^{2+} in phosphate glass[28a,41] shows a two-component exponential which has been resolved into two lifetimes, one short of 115 μs and one long of 367 μs. Reisfeld and Jorgenson[41] attribute the short-lifetime process to a small concentration of uranyl pairs with a characteristic short U–U distance. Marcantonatos[42] has suggested that these species are excimers and has detected then in aqueous solution at a pH of 2. The uranyl-exchanged mordenite samples have lifetimes that are close to the excimer values. Excimers of uranyl ions could form more easily in a poor system like mordenite that is one dimensional. The emission spectrum of sodium mordenite has bands at 487 and 545 nm which compare well to that of the reported U_2O_2H[41] exciplex which emits at 488 and 544 nm. In any event, ground-state association of some sort should decrease the ability of excited uranyl ions to bind and oxidize isopropyl alcohol and other organic substrates. On dehydration of the mordenite, the channels open up[43] and the emission characteristics are different. Excited-state dimer formation is lowered because of new steric conditions.

Concluding Remarks

We have shown here that one can expect ion-exchanged zeolite molecular sieves to show a general ability to participate in photoassisted catalytic conversions and appear to remain stable for extended periods of time. It is clear that in applications involving zeolites there must be some way to increase the yield of these reactions either by decreasing scattering[21a] of the irradiation or by finding more efficient systems. Such developments would further support the use of zeolites in, for instance, solar conversion schemes. Our experiments suggest that these uranyl-exchanged zeolites are chemically and physically stable photocatalysts and could provide valuable hints concerning the selection of materials for efficient photochemical conversions.

Acknowledgment. We acknowledge support of this work from the Atlantic Richfield Foundation of the Research Corporation. The University of Connecticut Research Foundation also provided support for this work. One of the authors (S.L.S.) acknowledges the support of this work in the form of a University of Connecticut Faculty Fellowship. We especially acknowledge Dr. Gary Holtom, Dr. Michael Topp, and Thomas Felder of the NSF Regional Laser Laboratory in Philadelphia, PA, for help in collecting the liquid helium luminescence data. The generous support of the National Science Foundation under Grant NSF CHE-8204417 is gratefully acknowledged.

Registry No. Uranyl, 16637-16-4; isopropyl alcohol, 67-63-0; acetone, 67-64-1.

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Fluorescence Quenching Processes of Rhodamine B on Oxide Semiconductors and Light-Harvesting Action of Its Dimers

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Abstract: Fluorescence spectra, lifetime, and intensity of Rhodamine B (RhB) adsorbed onto SnO_2, TiO_2, and glass substrates were examined as a function of surface dye concentration. On the basis of the results, fluorescence quenching by RhB dimers and electron injection from the monomers and from the dimers are discussed. The relation with the electrochemical spectral sensitization is also discussed.

Introduction

The photophysical and photochemical behavior of dyes adsorbed on semiconductors are widely attracting recent interest. The spectral-sensitizing action of those dyes have had been playing an extremely important role in the photographic industry.[1] In recent investigations their functions are correlated to light-energy conversion[2] and a model of the primary processes of photosynthetic systems in vivo.[3] The amount of the dyes at interfaces is quite small in contrast to the importance of their functions, and this

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fact makes the characterization as well as the photophysical and photochemical analyses of them difficult. Thus, detailed studies on primary photochemical processes of surface dyes still have great importance for the understanding of their functions.

Fluorescence measurements[4-6] and photocurrent measurements by electrochemical techniques[7-10] have been employed as sensitive methods for the investigation of spectral sensitization of surface dyes. These techniques provide information about different deactivation processes succeeding to electronic excitation of surface dyes induced by light absorption. Namely, electron injection from excited dyes into semiconductors can be monitored by electrochemical means and photon emission from excited dyes by the fluorescence measurements. Although data obtained by these techniques are strongly correlated and complementary to each other, there have been little studies in which this point had been stressed.[11] The most basic information fluorescence measurements can provide is the rate of electron injection from the excited dye into the semiconductor. Furthermore, fluorescence measurements will give us more definite information about the interaction between the surface dyes than photocurrent measurements. Nakashima et al. analyzed the fluorescence intensity decay of RhB adsorbed on crystals of aromatic hydrocarbons, and estimated the rate of hole injection from the excited RhB into the anthracene crystal as 10^{10} s^{-1}.[12] They have pointed out the fluorescence quenching by the contact pairs of the dye under the condition of 0.4 surface dye coverage. Muenter measured the lifetimes of some cyanine dyes on AgCl and estimated the electron injection rate.[5] The surface dye coverage in her measurement was 0.04,[5] and fluorescence quenching processes by dimers and/or other aggregated dyes were neglected. The concentration quenching processes of surface dyes have been examined especially for the chlorophyll monolayer systems from the viewpoint concerned with the photosynthesis in vivo.[13-18] Porter simulated the quenching mechanism by the use of the Monte-Carlo method.[18]

In the present study, the characteristics of the fluorescence of dyes on oxide solids including semiconductors were investigated. Especially, the dependence of the fluorescence characteristics on the concentration of surface dye was examined. It was shown that information about the interaction between dyes on solid surfaces as well as that between dyes and solids can be obtained from these data. Furthermore, the photocurrent due to dyes on the surface of semiconductors was explained in terms of the light-harvesting action of dimers.

Experimental Section

Rhodamine B (RhB) and eosin were purchased from Tokyo Kasei Co. and were used without further purifications. Solid samples used are SnO_2-coated glass plates, 500-Å SnO_2 thickness, purchased from Matsuzaki Shinku Co., and TiO_2-coated glass plates made by a vacuum evaporation method in our laboratory.

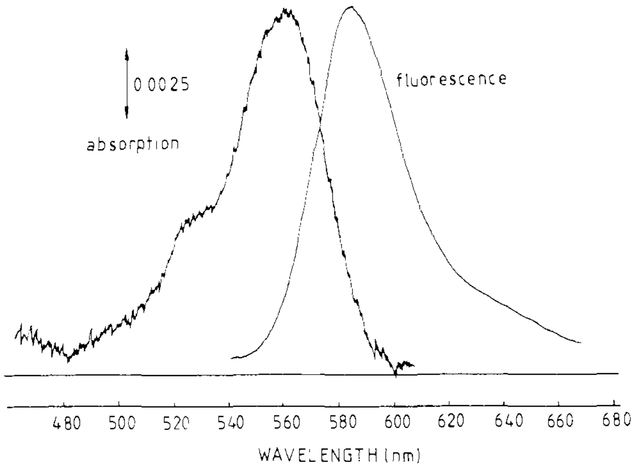

Figure 1. Absorption and fluorescence spectra of RhB adsorbed onto glass substrates.

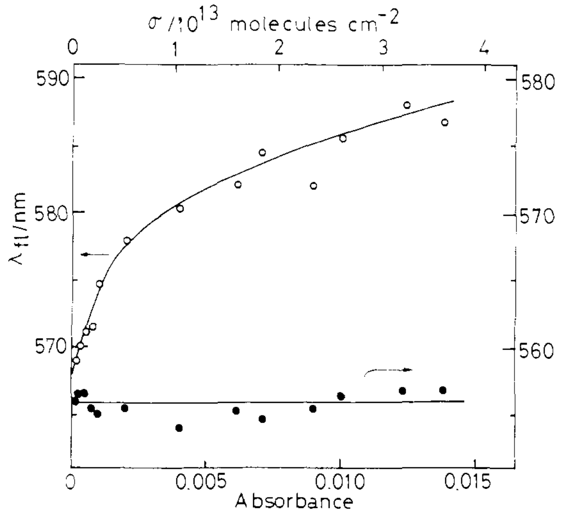

Figure 2. Surface dye concentration dependence of peak wavelengths of fluorescence (λ_{fl}) and excitation (λ_{ex}) spectra of RhB on glass. RhB on SnO_2 showed about the same dependence of λ_{fl} and λ_{ex} as those on glass.

Adsorbed dye samples were prepared as follows. An aqueous solution of dye (different concentrations) was dropped onto the surface of the solid plate and allowed to stand for a minute; then the plate was inclined to remove the solution. The small amount of the solution left on the plate was lightly wiped off with a piece of tissue paper.[12] The absorption spectra and fluorescence spectra of the samples with adsorbed dyes were measured with a Shimazu spectrophotometer MPS-5000 and a Hitachi fluorescence spectrophotometer MPF-4, respectively. Sample plates were covered with a mask having a narrow slit to measure the absorption as well as the fluorescence spectra of dyes at the same area of the sample. In the fluorescence measurements, plate samples were set at 45° against the incident light as well as the out-going light pass, such that the incident light is reflected in the opposite direction to the collector lense of the fluorescence spectrometer. Dyes were adsorbed on the collector-lense side of the sample plates. All the measurements were carried out in air.

A PRA (Photochemical Research Association) single-photon-counting system owned by Sieko Instruments & Electronics Ltd. was used for the fluorescence lifetime measurements. Powdered samples were prepared by adsorption of dyes in aqueous solution. After adsorption the samples were centrifuged and dried.

Results and Discussions

Adsorption Characteristics. Figure 1 shows the absorption and fluorescence spectra of RhB adsorbed on glass surfaces from a 10^{-3} M aqueous solution. The S/N ratio of the fluorescence spectrum is much better than that of the absorption spectrum. It was difficult to determine the absorbance (Abs) and the peak wavelength from the absorption spectrum data when Abs < 10^{-4} and Abs < 10^{-3}, respectively. On the other hand, the fluorescence

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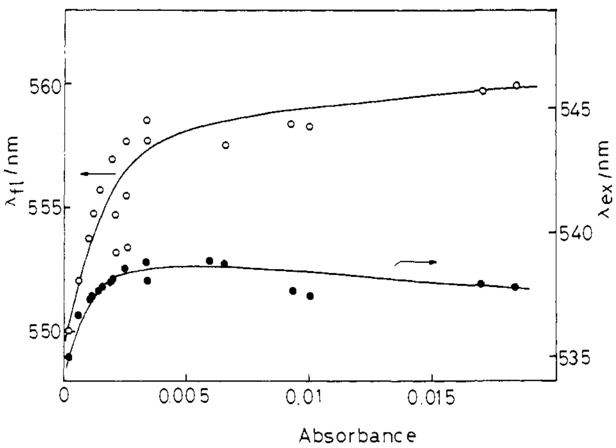

Figure 3. Surface dye concentration dependence of λ_{fl} and λ_{ex} for eosin Y adsorbed onto glass.

peak wavelength (λ_{fl}) could be determined for an Abs greater than 10^{-4}.

Adsorption of RhB onto SnO_2 as well as onto glass was nearly of Langmuir type. Saturation adsorption occurred at Abs = 0.0142 both on SnO_2 and on glass. Abs = 0.0142 gives the apparent surface concentration as 7.4×10^{13} molecules·cm^{-2} when $\epsilon = 1.15 \times 10^5$ was employed as the molecular extinction coefficient. The calculated surface concentration (σ) corresponding to the saturation adsorption is 3.9×10^{13} molecules·cm^{-2} when 8 Å is assumed for the average molecular radius of RhB.[12] Therefore, the roughness factor (RF) is calculated as 1.9. At a certain value of Abs, σ can be obtained as follows:

$$\sigma = \text{Abs} \times 6.02 \times 10^{23}/\epsilon \times 10^3 \times \text{RF} = \text{Abs} \times 2.76 \times 10^{15} \text{ molecules·cm}^{-2} \quad (1)$$

A deviation from a simple Langmuir plot appeared when Abs > 0.01. This is probably because adsorbed RhB molecules are partly multilayered in large σ regions.

Fluorescence Spectra and Excitation Spectra. Figure 2 shows the dependence on σ and Abs of the fluorescence peak wavelength (λ_{fl}) and the excitation peak wavelength (λ_{ex}) on glass surfaces. RhB on SnO_2 surfaces showed nearly the same behavior of λ_{fl} and λ_{ex} as glass (Figure 2). λ_{fl} showed a relatively large change especially in small Abs regions while λ_{ex} remained nearly constant. Figure 3 shows a similar plot for eosin Y; the change in λ_{fl} is larger than that in λ_{ex} as in the case of RhB although λ_{ex} also changes. The independence of λ_{ex} on Abs and/or σ indicates that the fluorescence is based primarily on the light absorption by RhB monomers on the surface. There can be some possible explanation for the large change in λ_{fl} shown in Figure 2. One is a mixing of dimer fluorescence, and the other is a fluorescence spectral change induced by an interaction between an excited dye monomer and neighboring monomers. The former explanation seems implausible since the dimer of RhB is reportedly nonfluorescent.[12] In addition, we can exclude this explanation since λ_{fl} changes even in the region where dimers scarcely exist; dimers cannot easily be formed on the SnO_2 as well as on glass surfaces as stated below. Therefore, the change in λ_{fl} can be interpreted only by the latter process, i.e., the interaction between the excited monomer and neighboring monomers. We also discuss this problem in the section on fluorescence lifetimes in this paper. Figure 4 shows the dependence of λ_{fl} on the mean molecular distance (d). The λ_{fl} change is large in a small d region although Figure 2 shows an apparent large λ_{fl} change in the small Abs (large d) region. The λ_{fl} change is steep at $d \sim 16$ Å where the adsorption is nearly saturated.

The value $\lambda_{fl} \sim 569$ nm, corresponding to λ_{fl} at infinite dilution ($d \rightarrow \infty$) on SnO_2 and on glass, is fairly different from the λ_{fl} of RhB in aqueous solution. This suggests a change in the electronic state of the dye due to adsorption; the magnitude of the energy change is ca. 0.03 eV. The interaction energy between the excited molecules and the monomers is relatively large, e.g., ca. 0.1 eV at $d = 16$ Å.

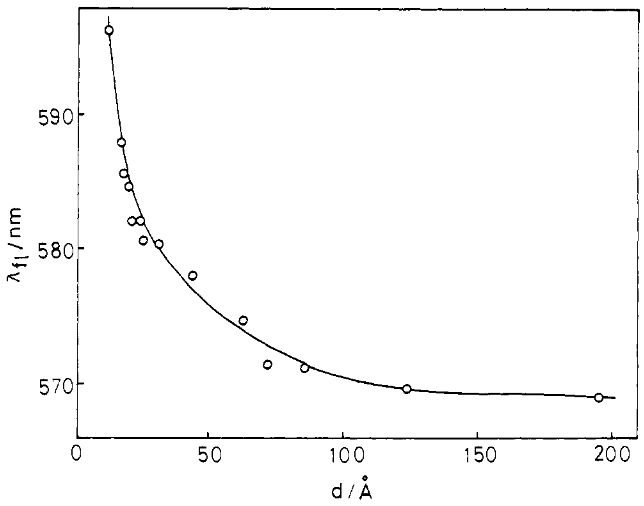

Figure 4. The dependence of fluorescence peak wavelength of RhB adsorbed onto glass (and SnO_2) on the mean intermolecular distance.

The spectral bandwidth of fluorescence also changed a little for Abs > 0.01. The shoulder of the excitation spectrum showed a small increase with increasing Abs, but the magnitude of the change was much smaller than that of the fluorescence spectrum. In addition, the excitation spectrum showed no dependence on the monitoring fluorescence wavelength at any Abs. These facts suggest that the fluorescence of the surface RhB does not contain a dimer component and that the λ_{fl} change comes from the interaction between the excited monomer and monomers around it.

Fluorescence Lifetime of RhB. Fluorescence lifetimes of RhB adsorbed onto solid surfaces were measured only for powdered samples since the fluorescence of plate samples was extremely weak. The fluorescence of RhB on powdered SnO_2 and TiO_2 changed quite fast by irradiation because of a photoinduced deethylation reaction with residual water.[19] This made the fluorescence lifetime measurement difficult. Al_2O_3 powder (no. 2000) was employed as a powdered support since an appropriate glass powder was not available. The samples were excited at 420 nm and emission longer than 520 nm was detected; optimum conditions came from restriction of the equipment, i.e., the spectral response of the photomultiplier and the spectral distribution of the light source (a H_2 lamp).

Figure 5 shows an example of fluorescence decay curves. Here RhB was adsorbed from a 5×10^{-7} M aqueous solution. A lifetimes analysis was made for two exponential components (T_1 = 3.035 ns, T_2 = 6.707 ns, in Figure 5) although longer lifetime components were also found in the decay curves. The lifetime of the T_1 component decreased with increasing dye concentration; e.g., T_1 = 2.3 ns for adsorption from a 10^{-6} M aqueous solution. This decrease of the fluorescence lifetime may be attributed to the quenching by dimers or by contact pairs as stated below. However, nonuniformity of the surface dye concentration which arose from the difficulty in controlling σ experimentally made quantitative analyses difficult. The fluorescence of the sample adsorbed from 10^{-7} M solution contains a T_1 = 3.48 ns component to the extent of 98% of the total fluorescence. Therefore, the value of 3.5 ns was employed in the discussion below as the fluorescence lifetime (τ_{fl}) of RhB monomers adsorbed onto the surface of Al_2O_3. The value of τ_{fl} on solid surfaces significantly increased compared with those in water (1.55 ns) and in methanol (2.38 ns). The natural lifetime (τ^0_{fl}) of RhB was calculated from the literature values of τ_{fl} and of the fluorescence quantum yield (φ_{fl})[20] to give 5.2 ns. The value of τ_{fl} of RhB on Al_2O_3 can be estimated as 0.67 assuming that adsorption onto the solid surfaces does not affect

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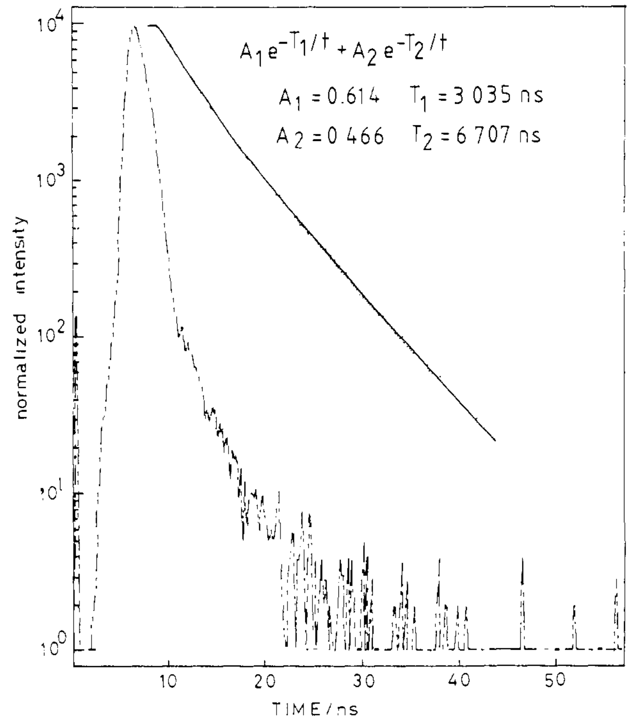

Figure 5. Fluorescence decay curve of RhB adsorbed onto alumina powder. Two exponential analyses were carried out. The pulse width of the H_2 lamp was 2 ns.

τ^0_{fl}. An increase in τ_{fl} (and hence φ_{fl}) can be attributed to the suppression of the $S_1 \rightarrow S_0$ internal conversion rate due to an inhibition of intramolecular rotation modes as a result of adsorption on the solid surfaces. Intramolecular rotation modes reportedly can affect the lifetime of excited states of molecules.[21]

Fluorescence components having longer lifetimes than τ^0_{fl} (it reached more than 10 ns for larger σ's) may correspond with the emission from "loose excimers" formed through an interaction between an excited monomer and monomers around it. Here we employed the term "loose excimer" since there have been reported no excimer emission of RhB in solution. This term means, here, that the electronic interactions is strong enough to affect τ_{fl}. Strong adsorption of RhB onto oxide solid surfaces would make excited monomers interact with neighboring monomers at fixed configuration and form such "loose excimers". We neglected the emission of "loose excimer" in the theoretical calculations below, since its emission intensity may become important only for large σ's.

Fluorescence Intensity of RhB on Glass Surface. Fluorescence Quenching by Dimers. Figure 6 shows an Abs dependence of fluorescence intensity (I_{fl}) of RhB on glass surfaces. Employment of the fluorescence maximum and of the integrated fluorescence intensity as I_{fl} gave the same results within error for the surface concentration employed in Figure 6. Solid lines in Figure 6 are theoretical curves calculated as stated below. I_{fl} increased linearly with Abs and/or σ in small Abs regions, and decreased for Abs > 0.005 having a peak at 0.005. This I_{fl} dependence on Abs could be explained considering a monomer-quencher (Q) equilibrium (eq 2) on the solid surface.

$$2M \overset{K}{\rightleftharpoons} Q \qquad (2)$$

Here, Q means a dimer or a contact pair.[12,18] We did not consider higher aggregates, e.g., trimers, since even the amount of dimers is small when Abs < 0.01 as shown in the treatment below. The main quenching process, eq 3, considered here is a Förster-type energy transfer which causes quenching of monomer fluorescence by quenchers formed according to eq 2. Dimers and contact pairs are assumed to be nonfluorescent:[12,18]

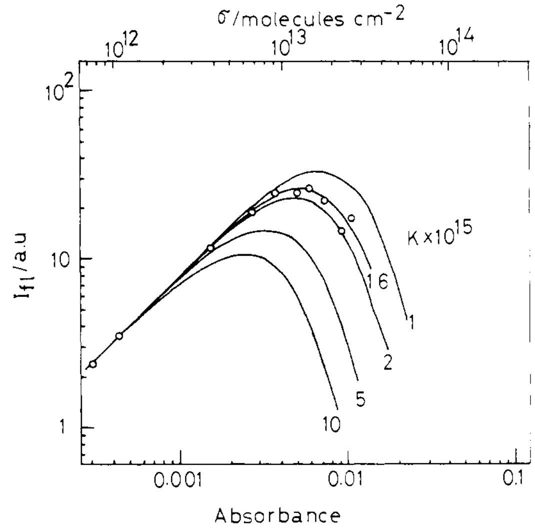

Figure 6. Surface dye concentration dependence of fluorescence intensity of RhB on glass: (○), experimental values; —, theoretical curves. K in eq 2 was changed from 1×10^{-15} to 10×10^{-15} molecule^{-1} cm^{-2}.

$$M \xrightarrow{h\nu} M^* \rightarrow M \qquad (3)$$

Then eq 4 holds for the surface concentration of excited monomer[22,23] $[M^*]$:

$$-\frac{d[M^*]}{dt} = [1/\tau_M + (1/\tau_M)\sum_i^N (R_0/R_i)^6][M^*] \qquad (4)$$

Here, τ_M denotes the fluorescence lifetime of monomers, R_i is the distance between a quencher i and a monomer subject to quenching, N is the number of quenchers, and R_0 is a critical distance for energy transfer,[22,23] we let $R_0 = 50$ Å in the following calculation.[24] Equation 4 is solved to give eq 5 according to Förster[22] when two-dimensional random distribution for quenchers is assumed.[12]

$$[M^*] = [M^*]_0 \exp(-t/\tau_M) \exp[-\Gamma(2/3)(\delta/\delta_0)(t/\tau_M)^{1/3}] \qquad (5)$$

Here, Γ means a gamma function, δ is the concentration of quenchers, $[M^*]_0$ denotes $[M^*]$ at $t = 0$, and $\delta_0 = 1/\pi R_0^2$. A time integral form of eq 5 should be used for the fluorescence intensity under the stationary irradiation condition. Thus eq 6 is derived. A is a constant.

$$I_{fl} = A[M^*]_0 \int_0^\infty \exp(-t/\tau_M) \exp[-\Gamma(2/3)(\delta/\delta_0)(t/\tau_M)^{1/3}]\, dt \qquad (6)$$

This can be rewritten as eq 7 since $[M^*]_0$ is proportional to [M].

$$I_{fl} = A'\tau_M[M]f(\delta/\delta_0) \qquad (7)$$

Here, $f(\delta/\delta_0) = \int_0^\infty \exp(-x) \exp[-\Gamma(2/3)(\delta/\delta_0)x^{1/3}]\, dx$, and A' is a constant. [M] is calculated by the use of eq 8 from the value of surface dye concentration σ (σ = [M] + 2[Q]) and the

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[24] R_0 was taken as 50 Å for energy transfer between RhB monomers. The monomer fluorescence band well overlaps the lower energy side of the dimer band which arises from the monomer band owing to Davidov's splitting,[25] efficient energy transfer can take place. However, the oscillator strength of this dimer band is smaller than that of monomer. We let R_0 = 50 Å for the dimer-monomer energy transfer considering these factors. R_0 is affected by the refractive index n of surroundings of dye molecules as $R_0^6 \propto n^{-4}$.[22,23] This R_0 change should be taken into account to make rigorous comparison between different substrates, i.e., glass and semiconductors, and/or different media, i.e., air, water, and etc., since they have different n's: n = 1 (air), ~2.5 (TiO_2). However, the change in R_0 due to the change in n is not so large since $R_0 \propto n^{-2/3}$, and since n of the interface where dye molecules exist is an "averaged" n of the two phases. Qualitative aspects of our results is not affected by this R_0 change of ~20% at most.

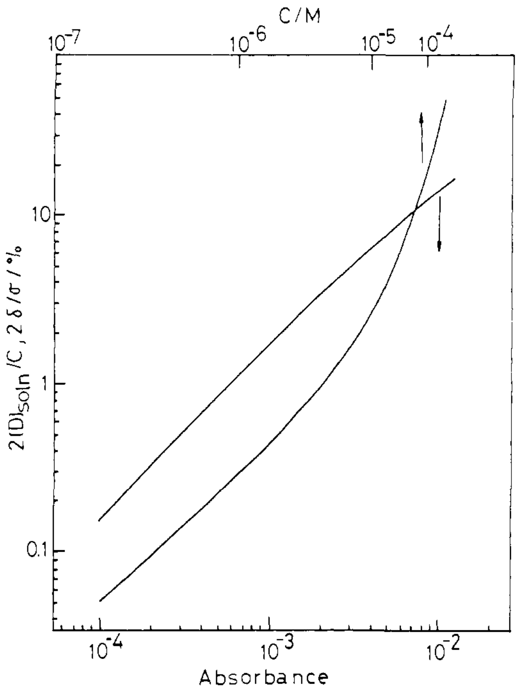

Figure 7. The fraction of dimerized molecules on glass and that in solution. An equilibrium between dyes on the surface and those in solution was assumed.

equilibrium constant K in eq 2, and δ is calculated as $\delta = [Q] = (\sigma - [M])/2$.

$$[M] = (\sqrt{8K + 1} - 1)/4K \tag{8}$$

Finally eq 9 is obtained.

$$I_{fl} = A'[(\sqrt{8K + 1} - 1)/4K]f(\delta/\delta_0) \tag{9}$$

Solid lines in Figure 6 show theoretical curves calculated for different values of K. The value of K was estimated as $K = 1.6 \times 10^{-15}$ molecule^{-1} cm^2 by comparing experimental values of I_{fl} with theoretical curves in Figure 6.

We can discuss the nature of the quenching centers considering the solid surface in contact with solution with RhB concentration C. The fraction of dimerized molecules in solution $2[D]_{soln}/C$ ($[D]_{soln}$: concentration of dimer in aqueous solution) was calculated using the equilibrium constant $K_{soln} = 1.5 \times 10^3$ M^{-1} [12]. σ on the solid surface can be estimated by the use of the experimental $C - \sigma$ relation. The fraction of dimerized molecules or molecules which formed contact pairs is $2\delta/\sigma$; δ can be calculated from K and eq 8. Figure 7 shows the relation between $2[D]_{soln}/C$ and $2\delta/\sigma$ thus obtained. The value of $2\delta/\sigma$ was ca. three times that of $2[D]_{soln}/C$ at lower concentrations and coincided at higher C's. This suggests that the quenching centers are dimers adsorbed onto the solid surface in contact with the solution with the dye concentration C and the dimer concentration $[D]_{soln}$. It should be pointed out that the concentration of dimers on glass surfaces is much less than that in solution when they are compared at the same intermolecular distances; e.g., $2\delta/\sigma \sim 1.6\%$ at Abs = 10^{-2} which corresponds to 7 mM in solution where $2[D]_{soln}/C \sim 80\%$.

Nakashima et al. attributed the quenching of RhB fluorescence to contact pairs of the dye rather than its dimers with aromatic hydrocarbon crystals.[12] Porter assumed a similar mechanism for energy-transfer phenomena in chlorophyll monolayer systems.[18] In these systems, contact pairs are much more numerous than dimers, and consequently the former quench the fluorescence more intensively than the latter.[12] However, the extent of fluorescence quenching in our experiment seems fairly small compared with that in their experiments. Therefore, the quenching center in our experiment would be RhB dimers, and not contact pairs. After all, the mechanism of fluorescence quenching by RhB dimers on solid surfaces is consistent with our experimental results. The difference between our results and those of Nakashima et al. and Porter would come from the difference in adsorption characteristics of dye–solid pairs. In their experiments, the solid–dye interaction is mainly hydrophobic in nature. This condition would make contact pair formation easy. On the other hand, dispersion of RhB molecules is good on the surface of oxide solids employed in our experiments since the adsorption of the dye onto oxide solids is strong and specific, and consequently contact pairs as quenching centers would not be formed. Strong adsorption of dye molecules onto the solids inhibits the contact-pair formation, and therefore the interaction of excited dye with neighboring ground-state dye induces mainly spectral shifts of the fluorescence.

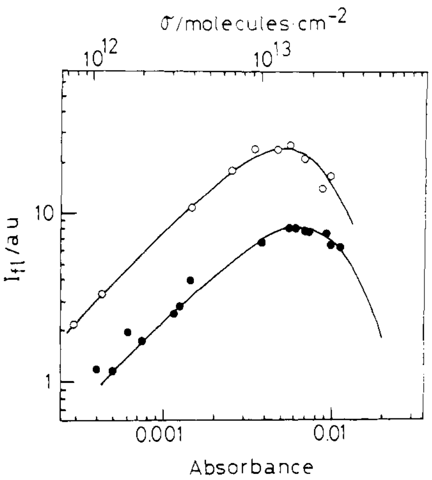

Figure 8. The surface dye concentration dependence of the fluorescence intensity of RhB on SnO_2 (●). That for RhB on glass (○) in Figure 6 is also shown. Solid lines are theoretical curves.

The dimers and the contact pairs are nonfluorescent because of an increasing probability of intersystem crossing.[26] At the same time, there may occur changes in the energy and/or lifetime of their excited states, which largely affect the probability of electron injection into the semiconductor. We discuss this point in the section on electron injection probability.

Fluorescence Intensity of RhB on SnO_2. Electron Transfer Fluorescence Quenching. Electron injection from excited RhB molecules into the conduction bands of semiconductors and resulting fluorescence quenching takes place on the semiconductor surfaces as shown by eq 10. Here, e(SC) represents an electron in the semiconductor and k_e denotes the rate of electron injection.

$$M \xrightarrow{h\nu} M^* \xrightarrow{k_e} M^+ + e(SC) \tag{10}$$

Then the rate equation for [M*], eq 4, is modified to:

$$-\frac{d[M^*]}{dt} = [1/\tau_M + (1/\tau_M)\sum_i^N (R_0/R_i)^6 + k_e][M^*] \tag{11}$$

Equation 13 is obtained by letting

$$1/\tau_M + k_e = 1/\tau \tag{12}$$

and $(\tau/\tau_M)R_0^6 = R'^6_0$.

$$-\frac{d[M^*]}{dt} = [1/\tau + (1/\tau)\sum_i^N (R'_0/R_i)^6][M^*] \tag{13}$$

On integration, eq 13 gives eq 14 for fluorescence intensity (I_{fl}). Here, δ'_0 equals $1/\pi R'^2_0$.

$$I_{fl} = A'[M]\tau f(\delta/\delta'_0) \tag{14}$$

Thus, the electron-transfer quenching process changes fluorescence lifetime τ_M into τ, and critical length R_0 into R'_0. We note that $R'_0 < R_0$ and $\delta'_0 > \delta_0$ since $\tau_M > \tau$. From eq 7 and 14, $I_{fl}^{SnO_2}/I_{fl}^{glass}$

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(25) I. Urrecha and F. Castanõ, *J. Chem. Soc., Faraday Trans. 2*, **74**, 1094 (1978); I. L. Arbeloa and P. Ruiz Ojeda, *Chem. Phys. Lett.*, **87**, 556 (1982).

(26) M. Kasha, H. R. Rawls, and M. A. El-Bayoumi, *Pure Appl. Chem.*, **11**, 371 (1965).

$= \tau/\tau_M$ ($\sigma \rightarrow 0$) is obtained. Here $I_{fl}^{SnO_2}$ denotes I_{fl} on SnO_2 and I_{fl}^{glass} is I_{fl} on glass. Besides, the peak shown in Figure 6 is expected to shift toward large Abs regions. The value of k_e can be estimated by the use of eq 12. Figure 8 shows experimental results and theoretical curves. The values of K and τ/τ_M were obtained as 1.6×10^{-15} molecule^{-1} cm^2 and 0.28, respectively. Note that this K value is substantially the same as that on glass. Agreement between the theoretical and the experimental values is generally good although some scatter exists especially in small Abs regions mainly owing to errors in Abs measurements. $\tau/\tau_M = 0.28$ and $\tau_M = 3.5$ ns give $k_e = 7.4 \times 10^8$ s^{-1} by the use of eq 12, and the electron-transfer quenching ratio, $k_e/(1/\tau_M + k_e) = 1 - \tau/\tau_M$, is calculated as 0.72.

The values of k_e have been reported as 10^9–10^{10} s^{-1} for some dye–semiconductor systems.[5,12] Our result, $k_e = 7.4 \times 10^8$ s^{-1}, is almost consistent with these values. Similar experiments for RhB on TiO_2-coated optically transparent electrodes gave $\tau/\tau_M > 0.9$ and $k_e < 3 \times 10^7$ s^{-1}. This value of k_e is smaller than that on SnO_2 by more than two order of magnitude. The rate of electron injection from excited RhB into the conduction band of TiO_2 is relatively small probably due to the higher energy of the conduction band edge of TiO_2 than that of SnO_2. The characteristics of the electronic interaction between the dye and the solid largely affect the value of k_e. Especially, the condition of dye adsorption, the excited state energy, and the energy and/or the density of electron-accepting levels in the solid are important factors. There have been only few experiments which have determined k_e. Further experimental data are required to understand the nature of the interaction between dye molecules and solid surfaces.

Relation with Electrochemical Systems. Here we compare our results with the data which had been hitherto obtained for electrochemical systems.

a. Dependence of Photocurrent on Dye Concentration in Solution: Light-Harvesting Action of Dimers. Gerischer et al. have reported the steady-state current, I_p, caused by RhB adsorbed onto ZnO, and its dependence on the dye concentration in solution, C.[28] They observed that I_p was nearly linear to C when $C < 10^{-4}$ M, and increased until C reached $\sim 10^{-3}$ M. Kim and Laitinen investigated RhB–SnO_2 systems in aqueous solution, and also reported a monotonical increase of photocurrent with an increase in C up to $C \sim 10^{-4}$ M.[28] We also observed a similar dependence of I_p on C for a SnO_2 electrode in contact with a RhB solution of acetonitrile. The steady-state current, I_p, arises from complicated processes containing not only excitation of the adsorbate followed by electron injection into the semiconductor but also desorption of products of the electron-transfer reaction, readsorption of the dye molecules, reproduction of the original species by reducing reagents, and other processes.[27] However, Fujishima et al. reported that I_p for RhB-containing systems is linear to the amount of dye adsorbed on the semiconductor electrode, except for extremely large C.[10] As revealed in the present experiment, more than 90% of adsorbed dye exists in monomer form when $\theta < 0.7$. Therefore, the photocurrent mostly occurs from the light adsorption due to monomers. The photocurrent i_p (transient and/or steady state) should be linear to I_{fl} as eq 15 shows when i_p is based upon the electron injection from excited monomers into the semiconductor electrodes (the symbol I_p is used only for the steady state here).

$$i_p = B[M][k_e/(1/\tau_M + k_e)]f(\delta/\delta'_0) = B[M]k_e\tau f(\delta/\delta'_0) = B[M]\varphi_{el}^M f(\delta/\delta'_0) \equiv i_p^M \propto I_{fl} = A'[M]\tau f(\delta/\delta'_0) \quad (15)$$

Here, B is a constant, $k_e\tau$ was rewritten as φ_{el}^M, the probability of electron injection from the monomers, and other symbols are the same as those in eq 14. In this case, i_p (and I_p) is expected to have a peak like I_{fl} at $C \sim 5 \times 10^{-5}$ M for RhB systems. In contrast to this, the steady-state current I_p increases up to $C \sim 10^{-3}$ M as stated above. We can explain this discrepancy considering the photocurrent generation due to light absorption by dimers, i_p^D (eq 16), and that due to electron injection into semiconductors from dimers excited by the energy transfer from monomers, $i_p^{M\rightarrow D}$ (eq 17).

$$D \xrightarrow{h\nu} D^* \rightarrow D^+ + e(SC) \quad (16)$$

$$M \xrightarrow{h\nu} M \xrightarrow{D} D \rightarrow D^+ + e(SC) \quad (17)$$

The photocurrent based on eq 16 can be represented as

$$i_p^D = B\alpha[D]\varphi_{el}^D \quad (18)$$

Here, φ_{el}^D represents the electron injection probability of the dimer, and a factor α was introduced to take into account the difference between the absorption spectra as well as molar extinction coefficients of the monomer and the dimer. The photocurrent $i_p^{M\rightarrow D}$ can be represented as

$$i_p^{M\rightarrow D} = B[M][1 - f(\delta/\delta'_0)]\varphi_{el}^D \quad (19)$$

since $B[M][1 - f(\delta/\delta'_0)]$ is the number of excited dimers generated per unit time by energy transfer from excited monomers. Thus the total photocurrent i_p can be represented as follows:

$$i_p = i_p^M + i_p^D + i_p^{M\rightarrow D} = B\{[M]\varphi_{el}^M f(\delta/\delta'_0) + \alpha[D]\varphi_{el}^D + [M]\varphi_{el}^D[1 - f(\delta/\delta'_0)]\} \quad (20)$$

The difference of behavior between i_p (and/or I_p) and I_{fl} can be explained by the use of eq 20. For example, eq 20 gives

$$i_p = B\sigma\varphi_{el}^M \sim B[M]\varphi_{el}^M \quad (21)$$

i.e., photocurrent is proportional to the adsorbed dye amount, when $\varphi_{el}^M = \varphi_{el}^D$, and $[M] >> [D]$ (or $\alpha = 2$). After all, i_p and/or I_p increases with increasing C while I_{fl} decreases according to eq 14 owing to production of nonfluorescent RhB dimers. Therefore, I_p contains a large contribution of the photocurrent of dimers sensitized by monomers especially in large C regions.

The result of Tributsch and Gerischer,[27] that of Fujishima et al.,[10] and that of Kim and Laitinen[28] suggest that eq 21 approximately holds, and hence $\varphi_{el}^M \sim \varphi_{el}^D$ for RhB–ZnO and RhB–SnO_2 systems.

We can calculate how extensively dimers can collect energy from surrounding monomers, in other words, how many monomers, on the average, transferred energy to a certain dimer. This value would be referred to as the light-harvesting factor (LHF). In eq 17 and 20, $[1 - f(\delta/\delta'_0)]$ is a fraction of excited monomers which transferred energy to dimers. Therefore, $[1 - f(\delta/\delta'_0)]([M]/[D])$ corresponds to the number of monomers which are distributed to each dimer with respect to energy transfer, namely, the value LHF.

$$\mathrm{LHF} = [1 - f(\delta/\delta'_0)]([M]/[D]) \quad (22)$$

Equation 17, $i_p^{M\rightarrow D}$, can be rewritten in terms of LHF, by the use of eq 15:

$$i_p^{M\rightarrow D} = B[M]\varphi_{el}^D[1 - f(\delta/\delta'_0)] = i_p^M \frac{1 - f(\delta/\delta'_0)}{f(\delta/\delta'_0)} \frac{\varphi_{el}^D}{\varphi_{el}^M} = i_p^{\dagger}\mathrm{LHF} \frac{\varphi_{el}^D}{\varphi_{el}^M} \frac{[D]}{[M]} \quad (23)$$

Here, $i_p^M(\delta/\delta'_0)$ was rewritten as $i_p^{\dagger} \equiv B[M]\varphi_{el}^M$ by the use of eq 15; $i_p^{\dagger}$ corresponds to i_p with the condition $\varphi_{el}^D = \varphi_{el}^M$. The value of $i_p^{\dagger}$ can be easily estimated by the use of experimental values of $i_p^{\dagger}$ since $i_p^{\dagger}$ is proportional to [M] by definition, and i_p is linear to [M] at small σ regions. LHF finally can be expressed as follows.

$$\mathrm{LHF} = \frac{i_p^{M\rightarrow D}}{i_p} \frac{\varphi_{el}^D}{\varphi_{el}^M} \frac{[D]}{[M]} \quad (24)$$

The value of $i_p^{M\rightarrow D}$ can be estimated as $i_p^{M\rightarrow D} \sim i_p - i_p^M$ since the contribution of i_p^D is negligible at $\theta < 0.7$ where $[D] << [M]$. The values of [D] and [M] were estimated by the use of eq 8. The LHF thus obtained depends on σ as Figure 9 shows. This LHF

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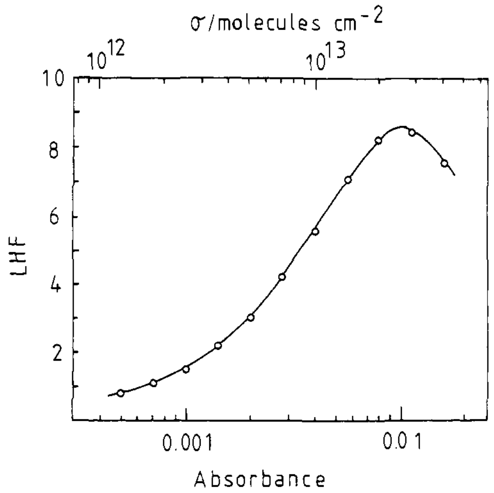

Figure 9. Surface dye concentration dependence of light-harvesting factor of RhB dimer.

characterizes the system as a model of energy-transfer processes realized in photosynthetic systems in vivo., i.e., energy transfer from antenna chlorophylls to reaction center chlorophylls. In the calculation in Figure 9, i_p was assumed to be linear to Abs in the concentration regions employed, that is, $\varphi_{el}^D = \varphi_{el}^M$ for RhB–SnO_2 systems. LHF reached 8.5 at Abs ~ 0.01 as Figure 9 shows. LHF can increase up to 22 since LHF is nearly the same as the number of monomers which exist within a circle with radius R'_0 at smaller Abs's. However, the circles for each dimer tends to overlap each other when the numbers of dimers increase at larger Abs's, and hence LHF takes a maximum value. An extremely highly efficient light-harvesting system is realized in vivo; the number of chlorophyll molecules per one reaction center reportedly reaches 400–500 for PSI particles.[29] The one-step energy-transfer mechanism employed in this treatment would not be applicable to such large number of dyes; a series of continual energy transfer should be considered.[18]

b. Comparison with Chlorophyll Monolayer System. A number of energy-transfer experiments have been carried out employing chlorophyll monolayer deposited on glass substrates.[13-18] All the authors reported a decrease in I_{fl} with increasing surface concentration (σ) of chlorophyll; nonfluorescent dimer and/or contact pair is supposedly formed in the monolayers. In the case of chlorophyll monolayers, fluorescence quantum efficiency reached half of its maximum value (corresponding to an infinitely diluted condition) at $\sigma = 3\text{–}4 \times 10^{12}$ molecules·cm^{-2}.[13,18] In our experiment using RhB, this condition is realized at $\sigma = 1.5 \times 10^{13}$ molecules·cm^{-2}. These facts suggest that the formation of chlorophyll dimers and/or contact pairs which act as fluorescence quenching centers is relatively easy at the surface of glass substrate compared to RhB. This situation for chlorophyll is similar to RhB on aromatic hydrocarbon crystals.[12]

The quantum efficiency of photocurrent (φ_p) of chlorophyll monolayer systems has been shown to decrease with an increase in σ while photocurrent itself increases up to $\sigma \sim 10^{14}$ molecules·cm^{-2}.[30] The relation between I_p and I_{fl} in chlorophyll monolayer systems is almost the same as RhB adsorbed on oxide semiconductors; that is, I_{fl} has a peak at rather small σ values whereas I_p increases with σ. This suggests a large contribution of dimers to the photocurrent (processes eq 16 and 17), also in chlorophyll monolayer systems. The decrease in φ_p with an increase in σ suggests the relation $\varphi_{el}^M > \varphi_{el}^D$ in contrast to RhB ($\varphi_{el}^M \sim \varphi_{el}^D$). The photocurrent at $\sigma = 10^{14}$ molecules·cm^{-2} would thus be wholely attributed to dimers considering that I_{fl} is almost quenched at this σ value.[12,17] Employing the results of Miyasaka et al., $\varphi_{el}^D/\varphi_{el}^M = 0.24$ can be estimated. Killerstreiter has shown that φ_{el}^D is somewhat smaller than φ_{el}^M using cyanine dye monolayers fabricated into solid-state photocells.[31] However, he did not consider process eq 17.

c. Electron Injection Probability φ_{el}^M. The electron injection probability from excited RhB monomers (φ_{el}^M) obtained in this experiment was 0.72; the corresponding value in electrochemical systems is the photocurrent efficiency of spectral sensitization, φ_p. The photocurrent under steady-state conditions generally gives extremely small φ_p's without appropriate reducing reagents. Under the coexistence of hydroquinone, a reducing reagent, chemically modified RhB–SnO_2 systems reportedly gave $\varphi_p \sim 0.2$[32] which is smaller than $\varphi_{el}^M = 0.72$. φ_{el}^M is governed by primary electron-transfer process, although this process as well as succeeding ones determine φ_p. There would be some possible origins which cause $\varphi_{el}^M > \varphi_p$. Our preliminary experiments using SnO_2–RhB chemically modified electrodes showed that the photocurrent rapidly decreases within 10 ms and gives extremely small steady-state values without a reducing reagent; the initial value was approximately equal to that with hydroquinone as a reducing reagent.[30] Pettinger et al. reported similar results in RhB solution–ZnO systems.[33] High values of φ_p as close as φ_{el}^M would be possible within a very short time, e.g., 1 μs, just after the irradiation started.

Electron tunnelling can take place from the conduction band to acceptors in solution when the space charge layer at the semiconductor–solution interface is extremely thin owing to the large carrier density[32,33] as in the case of SnO_2 OTE's. Cationic species yielded by processes 10, 16, and/or 17 as well as the oxidized form of coexisting reducing reagent are candidates for the acceptors. It may happen that the photocurrent does not reach its possible saturation value at the electrode potential employed since oxidation and resulting deactivation of the coexisting reducing reagent often make the photocurrent measurements difficult at highly anodic potentials.[32] This occurs when the semiconductor electrode is highly conductive and has a thin space charge layer.[32]

There would be energy transfer from dyes at semiconductor surfaces to the conduction band electrons;[30] this seemingly increases φ_{el}^M, and would be one reason for the relation, $\varphi_{el}^M > \varphi_p$. The presence of this process can be tested in I_{fl} measurements by changing carrier density of SnO_2 and/or by changing distance between conduction band electrons and the dyes at the interface. An electrochemical cell with an SnO_2 electrode chemically modified by RhB was constructed and was set in the fluorescence spectrometer for this measurement. There was no I_{fl} change over 1 V within the potential range where no electrode reaction such as oxidation of the dye took place. I_{fl} would depend on the electrode potential when the fluorescence quenching due to energy transfer into the conduction band electrons exists since the surface dyes are separated from the conduction band electrons by the space charge layer, and the thickness of it depends upon the electrode potential, e.g., in such a manner that I_{fl} increases with an increase of the space charge layer thickness. The above result, the independence of I_{fl} on the electrode potential, shows that fluorescence quenching by the conduction band electrons is negligible in our experiment.

d. φ_{el}^D. In this paper, based upon eq 20 as well as upon the results of photocurrent measurements reported so far, we showed that $\varphi_{el}^D \sim \varphi_{el}^M$ holds for the RhB–SnO_2 system and $\varphi_{el}^D < \varphi_{el}^M$ for the chlorophyll–SnO_2 system. For other dyes, for example, Tributsch and Gerischer reported C dependence of I_p for rose bengal dye;[27] $\varphi_{el}^D < \varphi_{el}^M$ is expected considering the reported result in which φ_p decreased for larger C's. As seen above, the relation between φ_{el}^D and φ_{el}^M depends on each dye and semiconductor. It is apparent that dimers have a high electron injection probability in certain systems, e.g., RhB–SnO_2 systems; the J aggregate form of cyanine dyes is typical of associated dyes having high electron injection capability.[1]

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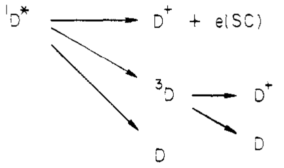
The energy and the lifetime of excited dimers are main determining factors of φ_{el}^{D}. It has been said that an intersystem crossing from the excited singlet state to the triplet state efficiently occurs in the dimers of dyes.[26] Then, it is necessary to taken into account the triplet state of the dimers to deal with the electron injection from the dimers. The process in eq 17 is modified as follows:



(25)

Electron injection following the yield of ^3D would occur when the rate of intersystem crossing $^1D^* \rightarrow {}^3D$ is somewhat larger than the rate of electron injection from $^1D^*$. The presence of this process can be checked through the measurement of transient behavior of the photocurrent and/or through that of the phosphorescence of ^3D on the surfaces. Such experiments are of interest to reveal the basic photochemical processes of dyes at solid surfaces.

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Registry No. RhB, 81-88-9; RhB dimer, 14728-79-1; SnO_2, 18282-10-5; TiO_2, 13463-67-7.

Permeability Characteristics of Polymeric Bilayer Membranes from Methacryloyl and Butadiene Lipids

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Abstract: Four polymerizable lipids were synthesized and used for the formation of synthetic bilayer membranes (vesicles). Two of the lipids were methacryloyl ammonium lipids, one with a methacrylamide at the hydrophilic head group of the lipid (α-MA) and one with a methacrylate group at the hydrophobic tail of the lipid (ω-MA). Thermally initiated polymerization of the monomeric bilayer vesicles gave polymers with retention of vesicle structure. The size distribution of the aqueous suspension was not altered significantly on polymerization, and the membranes continued to entrap [^{3}H]glucose. The permeability of poly(α-MA) and poly(ω-MA) membranes is about half that of the unpolymerized bilayers. Previously we reported that about 500 monomer units were found per average polymer chain of poly(α-MA) and poly(ω-MA), which shows that there are several (20 to 100) polymer chains per vesicle (Dorn, K., et al. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 513). Two butadiene lipids, one based on a phosphatidylcholine (PC) structure, and one with a taurine head group, also formed bilayer membranes, which could be photopolymerized by exposure to ultraviolet light. These lipids have a sorbate unit (λ_{max} 257 nm) in each of the two hydrocarbon chains, which allows the photopolymerization to proceed with the formation of cross-links. Poly(butadiene PC) membranes effectively entrapped [^{3}H]glucose for at least a week and were not disrupted by the use of the surfactant Triton X-100.

Introduction

Synthetic membrane liposomes or vesicles have been a topic of increasingly active research since the early 1960s. These spherical membrane models are composed of a bilayer(s) of lipid that encloses an aqueous volume.[1] In addition to their use as membrane models, vesicles are of interest for their ability to sequester or encapsulate reagents,[2,3] for the separation of charges and charged species in solar energy conversion,[4,5] and for the effect of the lipid bilayer organization on chemical reactions.[6,7] Frequently, vesicles are prepared from phospholipids, either naturally occurring or synthetically accessible lipids. More recently Kunitake and co-workers introduced the concept of a totally synthetic bilayer membrane of dimethyldidodecylammonium bromide.[8] Since 1977, several new bilayer-forming materials have been synthesized, including double-chain cationic, anionic, and zwitterionic amphiphiles and single-chain amphiphiles based on liquid-crystal materials.[9-11]

In 1980 and 1981, several groups reported the synthesis of polymerizable lipids and their incorporation into and polymerization in vesicles. Regen et al.[12] reported a cationic amphiphile with a methacrylate at the terminus of one hydrophobic chain. In short order, several lipid diacetylenes[7,13-15] were described. More recently, butadiene lipids,[6,16] additional methacryloyl lip-

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