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SPECTRAL CHARACTERISTICS AND EFFICIENT ENERGY TRANSFER IN NAPHTHALENE-CONTAINING BILAYER MEMBRANES1)

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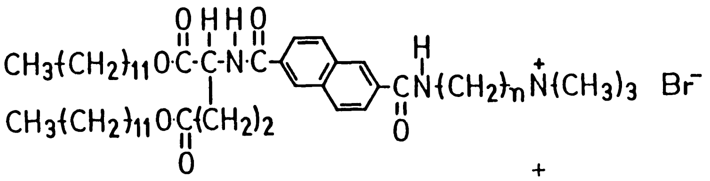
Bilayer membranes of double-chained ammonium amphiphiles which contain the naphthalene unit display characteristic spectral (absorption and emission) behavior and efficient energy transfer to membrane-bound anionic acceptors.

The bilayer membrane is comprised of two-dimensional arrays of amphiphilic molecules and is a convenient vehicle for preparing organized chromophores. We have shown, for example, that the spectral characteristics of azobenzene-containing bilayers are modified by varying orientations of the chromophore.2,3) The orientation and aggregation of cyanine and other dyes bound to ammonium bilayers are affected by the bilayer's physical state and the chemical structure of component amphiphiles.4,5)

In the present paper, we discuss chromophore orientation and energy transfer observed in naphthalene-containing bilayer membranes. The naphthalene chromophore has been frequently used in the energy transfer study in molecular crystals and in polymers,6) and it is interesting to compare its photophysical behavior in different systems.



1 n=3
2 n=6
3 n=10

$2C_{12}$-L-Glu-Naph-C_nN^+

The bilayer components are ammonium amphiphiles which are composed of hydrocarbon tails, glutamate connector, naphthalene, and polymethylene spacer. This particular molecular frame is selected because bilayers derived therefrom produce varied orientations with respect to the benzene chromophore.7)

Amphiphiles $2C_{12}$-L-Glu-Naph-C_nN^+ 8) give transparent aqueous dispersions by sonication (molecular weight, ca. 10^7), and electron microscopy indicates the presence of multi-walled vesicles (diameter, 500 - 2000 Å) for **1** and partly-twisted tape-like aggregates (width, 100 - 300 Å) for **2** and **3**. The crystal-to-liquid crystal phase transition (T_c) determined by differential scanning calorimetry9) is located at 30 °C for **1**, while the transitions are observed at 48 °C and 53 °C for **2**, and at 63 and 88 °C for **3**. Absorption spectra of these bilayer aggregates at 20 °C are different from those of the corresponding isolated molecules. As is apparent from Fig. 1, bilayers of **1** (spacer C_3) show a blue shift and hypochromicity in the ^1B_b band (232 nm) relative to that in ethanol (242 nm). Bilayers of **2** (spacer C_6) and **3** (spacer C_{10}) give the ^1B_b band at 235 nm (cf. 242 nm in ethanol) and show large hyperchromic effects in the ^1L_b band. It is clear that the ground state interaction of the chromophore is affected by the change in the spacer length.

An emission spectrum of **1** (spacer C_3) exhibits a structured band with maxima at 352 and 379 nm and a broad shoulder at 400 - 450 nm (Fig. 2).$^{10)}$ These bands are assigned to the monomer emission and the excimer emission,$^{11)}$ respectively. Bilayers of **2** and **3** give monomer emission alone at 20 °C. The chromophore orientation in the bilayer of **1** is apparently more suitable for producing excimers. The excimer formation is promoted at higher temperatures, as will be discussed in detail elsewhere.

It is known that localized (concentrated) chromophores are prone to excimer formation and concentration quenching that act as energy traps and suppress energy migration.$^{6)}$ The monomer emission observed in Fig. 2, however, suggests that efficient energy migration is possible in the bilayer assembly among the highly oriented naphthalene chromophores. This is proved by the quenching experiment. Figure 3 demonstrates the effect of added perylenetetracarboxylate (Pery,$^{4-}$ Förster type quencher) on the fluorescence emission of aqueous bilayers of **3**. In spite of the limited overlapping between absorption of Pery^{4-} and emission from **3**, a decrease in the emission is recognized even with $1/10^5$ mol/mol of the acceptor.$^{12)}$ With increasing acceptor concentrations, the bilayer emission is lessened and the acceptor emission appears at 486 and 520 nm. Other quenchers(electron exchange type) such as sodium anthraquinone-2-sulfonate (2-AQS) and sodium 1-dimethylamino-naphthalene-5-sulfonate (DANS) are similarly effective. The efficiency of energy migration (quenching factor, Q_H) among the naphthalene chromophore was estimated according to the method of Klöpffer$^{13)}$ by,

$$Q_H=(\eta_{H0}-\eta_H)/\eta_H=n'c \qquad (1)$$

where η_{H0} and η_H are the fluorescence quantum efficiencies (relative fluorescence intensities) of the host chromophore in the absence and the presence of quenchers, respectively, c is the quencher concentration (mol/mol), and n' is the hopping number of the excitation energy within its lifetime. The n' values were determined by extrapolation of the double logarithmic plots given in Fig. 4. The leveling off at higher molar ratios is conceivably attributed to overlapping of quenching domains. In the case of Pery^{4-} acceptor, n' was only ca. 30 for bilayers of **2** and **3**. In contrast, the n' value is 3500 for bilayers of **2** and **3** with 2-AQS quencher, while these values are 2200 (for **2**) and 2500 (for **3**) with DANS quencher. The latter values are much larger than that (n' = 60) obtained for poly (2-vinylnaphthalene) and phenyl vinyl ketone in 2-methyltetrahydrofuran glasses.$^{14)}$ On the other hand, the n' value is small (ca. 12) for bilayer **1** with 2-AQS quencher. The excimer site must act as the energy trap, since excimer emission is observed for this bilayer (Fig. 2).

In conclusion, the spectral characteristics of the naphthalene chromophore is affected conceivably by its orientation in the bilayer, which, in turn, is

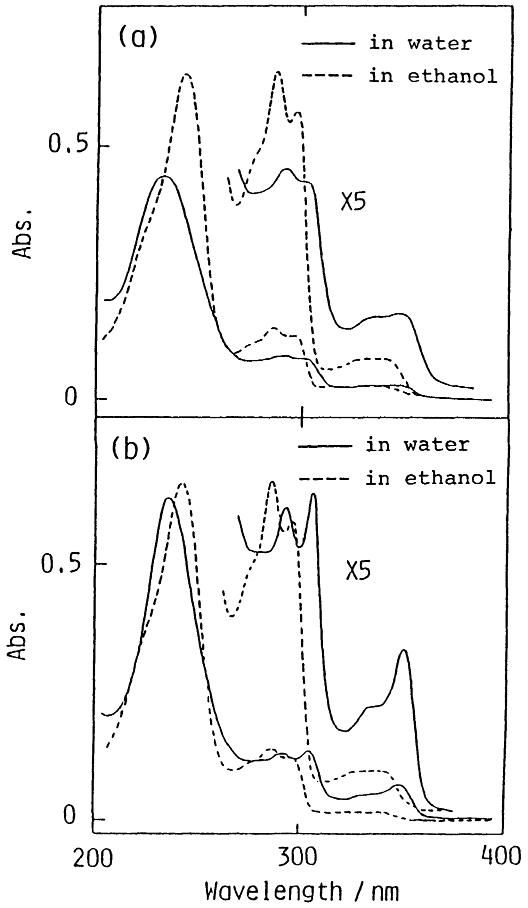


Fig. 1. UV spectra of $\underset{\sim}{1}$ (a) and $\underset{\sim}{2}$ (b); 1.0 X 10^{-4} M, 20 °C.

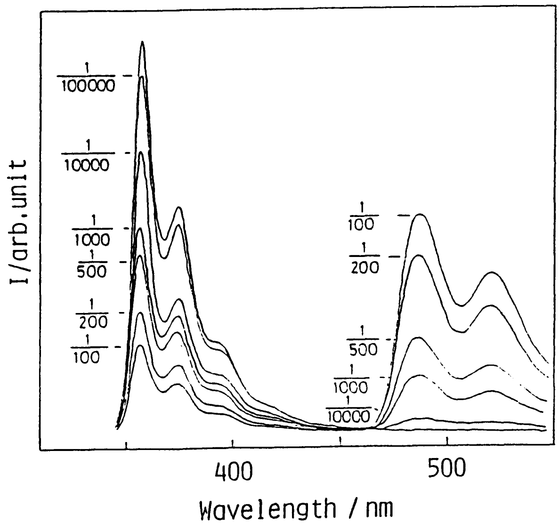


Fig. 3. Energy transfer from naphthalene-containing bilayer $\underset{\sim}{3}$ to Pery^{4-}; $\underset{\sim}{3}$, 1.0 X 10^{-4} M, 20 °C; excitation, 340 nm.

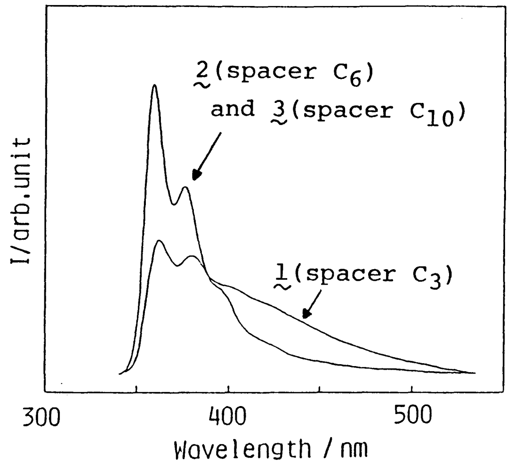


Fig. 2. Fluorescence spectra of aqueous bilayers; 1.0 X 10^{-4} M, 20 °C; excitation, 240 nm ($\underset{\sim}{1}$), 310 nm ($\underset{\sim}{2}$, $\underset{\sim}{3}$)

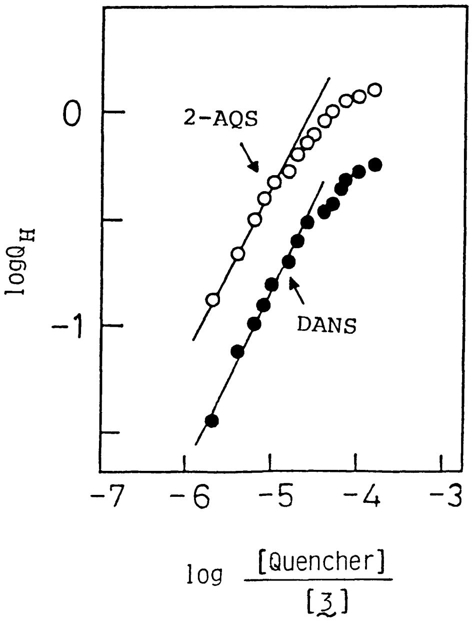


Fig. 4. Quenching factor as a function of the quencher concentration; $\underset{\sim}{3}$, 1.0 X 10^{-4} M, 20 °C.

controlled by the molecular structure of component amphiphiles. Efficient migration of excitaion energy through the naphthalene units establishes, together with similarly efficient energy migration in the anthracene15) and carbazole16) units, that the bilayer assembly provide novel photophysical processes.

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8) The amphiphiles were prepared by application of the reported procedure,4) and were identified by TLC, NMR spectroscopy and elemental analysis. **1**: colorless powder; Mp 115 ⟶ 228 °C(the arrow indicates the liquid crystalline region); Found, C 64.24, H 9.02, N 4.79%. Calcd for $C_{47}H_{78}N_3O_6Br\cdot H_2O$: C 64.22, H 9.17, N 4.78%. **2**: colorless powder; Mp 170 - 171.5 °C; Found, C 64.88, H 9.35, N 4.63%. Calcd for $C_{50}H_{84}N_3O_6Br\cdot 1.5H_2O$: C 64.56, H 9.43, N 4.52%. **3**: colorless powder; Mp 128 - 129 °C; Found, C 66.31, H 9.59, N 4.42%. Calcd for $C_{54}H_{92}N_3O_6Br\cdot H_2O$: C 66.37, H 9.67, N 4.30%.
9) For the detailed procedure: see, Y. Okahata, R. Ando, and T. Kunitake, Ber. Bunsenges. Phys. Chem., 85, 789 (1981).
10) The emission patterns are affected in some cases by the dispersion procedure. Aqueous bilayers of **1** give an emission spectrum of Fig. 2 by thermal dispersion, whereas ultrasonic dispersion gives a broad excimer emission alone. Either dispersion procedure gives the identical emission for bilayer **2**, and an aqueous dispersion of **3** is obtainable only by sonication. In all cases, aqueous dispersions (0.1 mM) were aged in ice water for 1 h prior to the measurement.
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12) Aqueous bilayers (0.1 mM, 200 μl) were placed in a 1-mm quartz cell and kept at 20 °C (below T_c) for 30 - 60 min. Small portions (10 - 20 μl in total) of aqueous quenchers (10^{-6}-10^{-7} M) were added and the cell was shaken for 30 s and allowed to stand for 1 - 2 min. Emission spectra were then recorded.
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