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FORMATION OF MONOLAYER AND BILAYER MEMBRANES FROM AMPHIPHILIC ANTHRACENE DERIVATIVES. PECULIAR SPECTROSCOPIC BEHAVIOR AND CHROMOPHORE ORIENTATION[1)]

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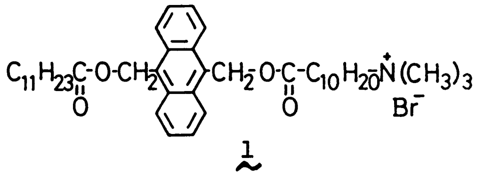
Monolayer and bilayer membranes of anthracene-containing amphiphiles show highly contrasting behaviors in absorption and emission spectroscopies and in energy transfer from biphenyl donors. These peculiarities are ascribed to different chromophore orientations.

Functionalization of molecular assemblies has been the object of a variety of chemical research. Molecular assemblies such as micelles and polymers are currently being studied as model systems of photosynthesis. However, these random assemblies cannot produce highly specified molecular orientations which are the prerequisite of efficient photosynthesis in nature.[2)] Möbius recently discussed the importance of the chromophore orientation in the case of the interfacial monolayer and bilayer systems.[3)]

The anthracene ring is an interesting chromophore from the spectroscopic and photochemical standpoints. Chandross et al. discussed the spectroscopic properties of anthracene dimers.[4)] Tazuke and coworkers performed extensive studies on the spectroscopic and photochemical behaviors of polymer-bound anthracene rings and micellar anthracene derivatives.[5,6)] The effect of molecular orientation may not be fully realized in these systems, since the anthracene ring is not necessarily well oriented. Vincent and Barlow more recently prepared anthracene-containing monolayer films and discussed their spectroscopic characteristics in terms of molecular orientation.[8)]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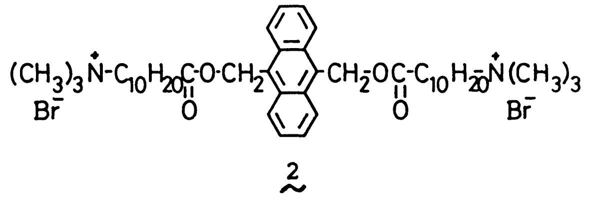
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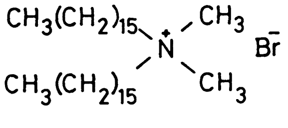
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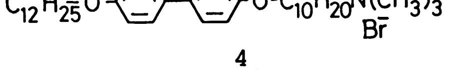
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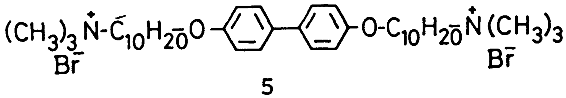
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The chromophore orientation can be improved by using the anthracene ring as a rigid segment in the bilayer and monolayer membrane systems.[9-11] Monocationic and dicationic amphiphiles with the anthracene ring, **1** and **2**,[12] were newly synthesized for this purpose.

Amphiphiles **1** and **2** give clear aqueous solutions upon sonication. The critical concentration for aggregate formation was determined to be 3.0×10^{-5} M for **1** and 1.3×10^{-4} M for **2** by the dye(2,6-dichlorophenolindophenol) probe method,[14] and 5.0×10^{-5} M for **1** and 6.4×10^{-5} M for **2** by the conductivity method.[15] Differential scanning calorimetry(Daini-Seikosha, SSC 560)[16] of 20 mM solutions indicated the presence of the crystal-to-liquid crystal phase transition at 63.5°C for **1** and at 26.5°C for **2**. Figure 1 shows electron micrographs of aqueous dispersions of **1** and **2**. The experimental procedure has been described elsewhere.[9] The disk-like aggregate is formed from **1** with a layer thickness of 50-60 Å and a diameter of 250-300 Å. The top and side views are clearly distinguishable. Amphiphile **2** produces typical lamellar structures with a layer thickness of ca. 30 Å. These morphologies are consistent with the bilayer disk[10] and the monolayer membrane[11] for **1** and **2**, respectively.

Both **1** and **2** contain the same chromophore and they give identical absorption and emission spectra in ethanol as shown in Figure 2. The spectra were the same for aqueous dispersions(monolayer membrane) of **2**.[17] In contrast, absorption and emission spectra of the aqueous bilayer of **1** were different from those of **1** in ethanol. The absorption maximum undergoes a 10-nm red shift (Figure 2c) in water and the emission spectrum is transformed to a broad peak devoid of the characteristic fine structure(Figure 2d). The corresponding excitation spectrum shows a 10-nm shift analogous to that of the absorption spectrum. Similar red shifts in the absorption spectrum have been observed for crystalline,[4] micellar,[7] and multilayer[8] (Langmuir-Blodgett)[8] anthracenes and attributed to the presence of the tilted chromophore(stable dimer).

The absorption and emission spectra of **1** buried in a large excess of the bilayer matrix of dialkylammonium salt **3** are identical to those in ethanol suggesting that **1** can be molecularly dispersed in the matrix without chromophore interaction. However, the situation changes with increase in the content of **1**. Figure 3 describes the variation of the emission spectrum with changing molar ratios of **1** and **3** from 1 : 1 to 1:10. Since the absorption and excitation spectra remain unchanged(identical with those in ethanol), the ground-state interaction of the anthracene chromophore is unlikely under these conditions. A broad emission spectrum with λ_{max} at 480 nm is observed when the molar ratio is 1:1. This new peak is supposedly derived from the anthracene excimer, because the ground-state interaction cannot be detected. As the content of **1** decreases, the excimer emission decreases and the monomer emission with a fine structure appears.

The spectral characteristics of **2** do not change also in the dialkylammonium membrane matrix of **3**. The degree of emission polarization is 0.012 for the aqueous monolayer of **2** and 0.008 when **2** is buried in the dialkylammonium membrane matrix. These values are close to that of **2** found in ethanol(0.013). The observation of the monomer spectrum and the small degree of polarization in the rigid monolayer membrane (below T_C) suggest efficient energy transfer occurring among the anthracene chromophore. The degree of polarization is 0.09 for the "stable dimer" in the single-component bilayer membrane of **1** and 0.03 for the monomeric **1** in the dialkylammonium matrix.

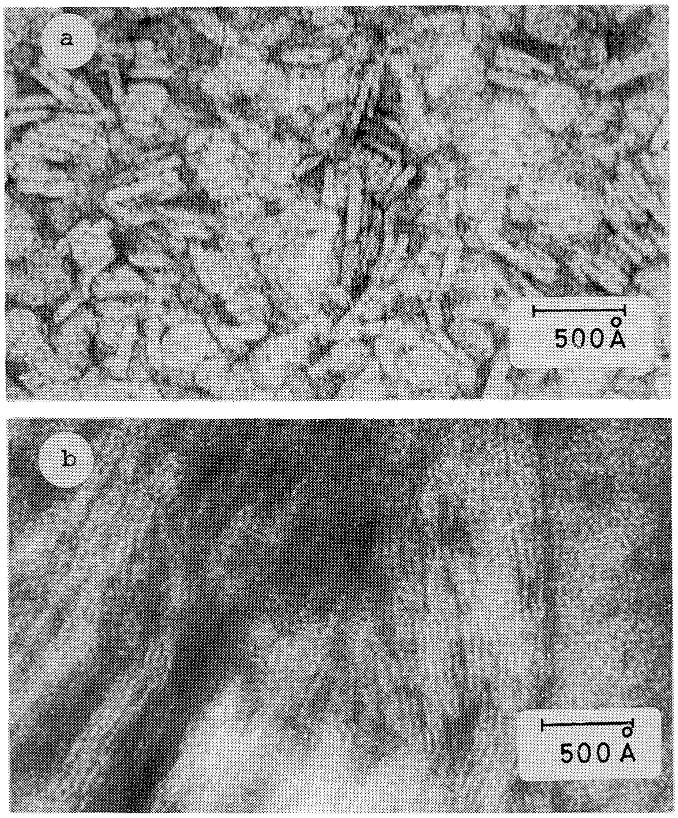

Fig. 1. Electron micrographs of aqueous dispersions of 1 and 2. stained by uranyl acetate.
(a) 1, (b) 2.

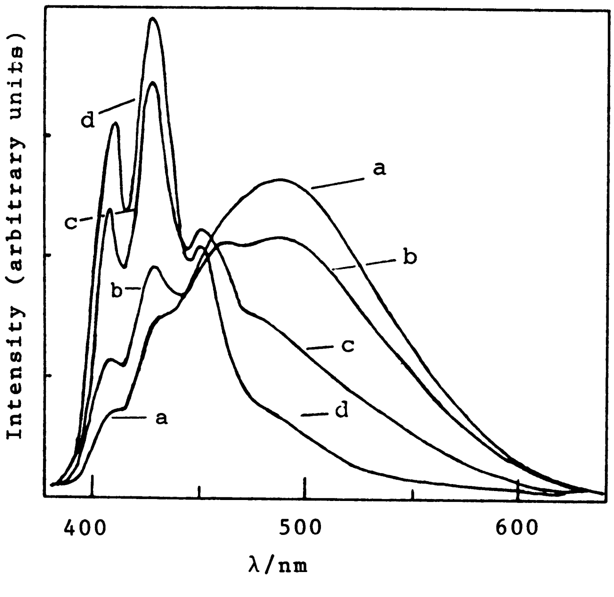

Fig. 3. Fluorescence spectra of 1 in the matrix of 3.
[1] = 1.0 x 10^{-4} M, 20°C, molar ratio of 1 and 3,
(a) 1 : 1, (b) 1 : 2,
(c) 1 : 5, (d) 1 : 10.

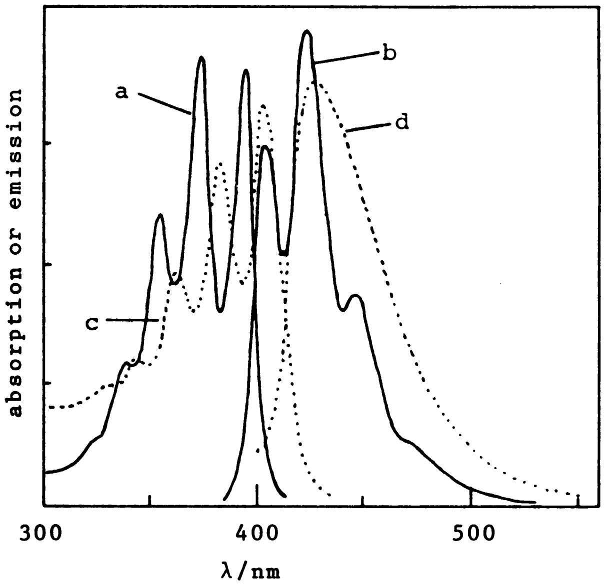

Fig. 2 Fluorescence and absorption spectra of 1.
[1] = 1.0 x 10^{-4} M, 20°C
a: absorption in EtOH
b: emission in EtOH
c: absorption in H_2O
d: emission in H_2O

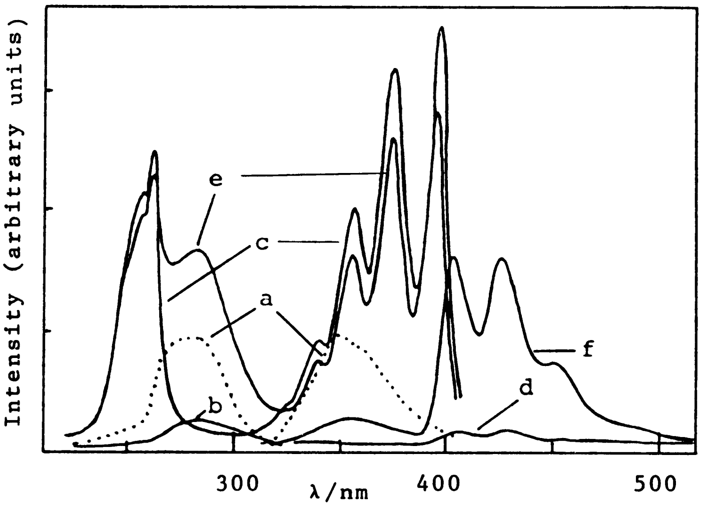

Fig. 4. Energy transfer from 4 to 1 in the matrix of 3.
[1] : [4] : [3] = 1 : 1 : 20, 14°C
a: fluorescence spectra of 4 in the matrix of 3.
b: excitation spectrum of the three component system at an emission of 350 nm.
c: excitation spectrum of 1 in the matrix of 3.
d: emission spectrum of 1 in the matrix of 3 excited at 285 nm.
e: excitation spectrum of the three component system at an emission of 425 nm.
f: emission spectrum of the three component system excited at 285nm

A contrasting behavior is similarly noticed between 1 and 2 in the energy transfer from the biphenyl donor chromophore of 4.[10,18] The biphenyl chromophore possesses an emission maximum at 350 nm which overlaps with the absorption range of the anthracene chromophore. The anthracene emission is not detected when a solution of 1 (1.0×10^{-5} M) and 4 (1.0×10^{-5} M) in ethanol is irradiated at 285 nm. However, the characteristic emission is observed as shown in Figure 4, when the same overall concentrations of 1 and 4 are placed in the bilayer matrix(2×10^{-4} M) of 3. The excitation spectrum detected at the emission maximum of anthracene shows a biphenyl peak at 285 nm, and the excitation spectrum detected at 350 nm produces a much reduced biphenyl peak. These results strongly suggest the occurrence of energy transfer from the biphenyl donor of 4 to the anthracene acceptor of 1 in the membrane matrix. In contrast, the energy transfer cannot be detected when 1 is replaced by 2. When biphenyl amphiphile 5 is used as donor in place of 4, energy transfer is not detected at all without regard to whether the acceptor is 1 or 2.

In conclusion, remarkable contrasts in spectroscopic and energy-transfer behaviors observed between aqueous membranes of 1 and 2 indicate that the molecular(monolayer and bilayer) membranes provide very attractive ways for "fine tuning" of the chromophore orientation and the related photochemical behavior.

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12) Amphiphile 1 was prepared by reaction of 9,10-bis(hydroxymethyl)anthracene (mp 283-288°C)[13] with dodecanoyl chloride and 11-bromoundecanoyl chloride,followed by quaternization with trimethylamine. Amphiphile 2 was similarly obtained from 9,10-bis(hydroxymethyl)anthracene and excess 11-bromoundecanoyl chloride and the subsequent quaternization. The final products were identified by thin-layer chromatography,NMR spectroscopy and elemental analysis. 1 : pale yellow powder; mp 110→150°C(the arrow indicates the liquid crystalline region), Found, C 66.55 H 8.70, N, 1.95%. Calcd for $C_{42}H_{64}O_4NBr \cdot 1.5H_2O$: 66.91, H 8.96,N 1.86%. 2: pale yellow powder, mp 200-206°C, Found: C 59.53, H 8.47, N 3.14%. Calcd for $C_{44}H_{70}O_4N_2Br_2 \cdot 2H_2O$: C 59.59, H 8.41, N 3.16%.
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17) The spectral measurement was performed for aqueous samples of 1×10^{-4} M of 1 and 2 and 2×10^{-4} M of the matarix membrane, if present. The membrane structure is already formed at these concentrations, and the emission spectra do not change up to the concentration of 1×10^{-3} M. Therefore, the unchanged spectra of 2 in water cannot be attributed to de-aggregation.
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