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Orientation and Distribution of the Carbazole Unit in Monolayers and Their Fluorescence Characteristics[1]

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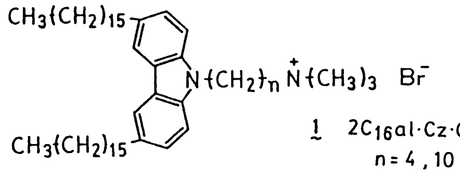
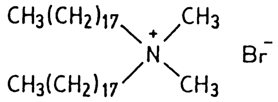
Double-chain ammonium amphiphiles that contain the carbazole ring formed stable monolayers on water. Their fluorescence patterns indicated different packing modes of the chromophore which depended on chemical structure and component distribution.

Controlled assembly of chromophores is crucial for producing effective photophysical functions. Carbazoles in polymers and in molecular aggregates have been studied particularly well in this respect, in relation to their photoconductivity.[2)] Regular polymer structures were used in order to promote energy migration by suppressing formation of excimers which act as energy trap.[3,4)] Bulky substituents were introduced to avoid undesirable carbazole association.[5)] On the other hand, Langmuir-Blodgett films of 11-carbazolylundecanoic acid and palmitic acid[6,7)] and of poly(vinylcarbazole) and stearic acid[8)] were prepared and their spectroscopic and energy transfer properties were examined. However, the mode of chromophore assembly is not sufficiently controlled in these studies.

We reported that double-chain ammonium amphiphiles which contain the carbazole unit form stable bilayer membranes when dispersed in water. These membranes display characteristic absorption and emission spectra and efficient transfer of excitation energy.[9)] Photoinduced electron transfer and the consequent formation of stable positive holes were also observed.[10,11)] Monolayers at the air-water interface are more convenient than aqueous bilayer dispersions for studying the relation between molecular assemblage and photophysical property. Therefore, we examined the monolayer formation and the fluorescence characteristics of carbazole-containing, self-assembling amphiphiles.



1 $2C_{16}al{\cdot}Cz{\cdot}C_n\overset{+}{N}$
$n = 4, 10$



2 $2C_{18}N^+2C_1$

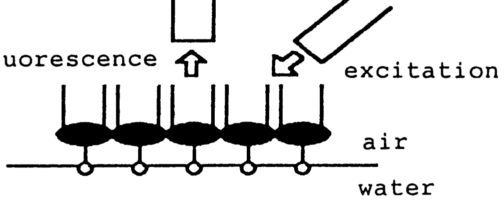


Fig. 1. Fluorescence spectral measurement of monolayers.

The amphiphiles were prepared as described elsewhere.[9,12] The surface pressure-area isotherms (π-A curve) were obtained with a computer-controlled film balance (San-esu Keisoku Co., Japan, model FSD-20). The experimental details were given before.[13]

Fluorescence spectra were measured with an intensified multi-channel photodetector system (Otsuka Electronics, Japan, model IMUC 7000). A Xenon lamp with a band-pass filter (λ_{max} 278 nm, half-band width 14 nm) was used as light source. The incident light through an optical fiber was directed at an angle of 45° against water surface, and emission was detected by a vertically-positioned optical fiber (Fig. 1). The sampling time for a single spectrum was 10 s.

Figure 2 shows π-A curves of carbazole amphiphiles **1** (n = 4 and 10) on pure water (Milli-Q II system, Millipore Co.). Both compounds form stable monolayers. The amphiphile with a longer spacer (n = 10) produces a more expanded monolayer. The molecular areas (as extrapolated to zero pressure from solid-like regions) are approximately 63 $Å^2$ for n = 4 and 66 $Å^2$ for n = 10. These values are much larger than the cross section (ca. 45 $Å^2$) estimated from the CPK molecular model, and suggest that the component molecules are tilted in monolayers or that dense packing is not achieved.

Figure 3 contains fluorescence spectra of these monolayers. In the case of **1** (n = 10), an emission accompanied by the vibrational structure (λ_{max} 365-385 nm) is observed even at very low surface pressures and the emission pattern does not change with increasing pressures. This spectral pattern is identical with that of the aqueous dispersion. Monomer-like emissions are found in both systems in spite of the chromophore stacking. In contrast, a monolayer of **1** (n = 4) gives a broad excimer emission centered at 410 nm in addition to the monomer-like emission. The excimer emission is intensified relative to the latter emission by compression. That the two types of emission coexist implies that the chromophore orientation is not uniform. The length of the spacer methylene in the monolayer compound produces a distinct difference in the emission behavior. In contrast, such tendency was not observed in the absorption spectra. In ethanol, absorption λ_{max} s of ^1B_b and ^1L_a band of the carbazole chromophore are located at 265 nm and 299 nm, respectively. Monolayer **1**(n=10) gave these bands at 269 nm and 302 nm throughout the compression process, and those bands of **1**(n=4) were located at 268 nm and 302 nm at relatively higher surface pressures($\approx$40 mN m^{-1}).

Subsequently, the monolayer behavior and fluorescence characteristics were studied for mixtures of **1** (n = 4) and $2C_{18}N^+2C_1$, in order to see the effect of the chromophore distribution in monolayer. As can be seen from Fig. 4, the collapse pressure of the 1:1 mixed monolayer is higher than either of the single-component monolayers, indicating increased stability of mixed monolayers. This mixture also gives more condensed monolayers in the high surface pressure region. The transition characteristics of this π-A curve is analogous to that of the $2C_{18}N^+2C_1$ monolayer rather than to that of the other component. The mean molecular area is minimal at the 1:1 mixing ratio at 10, 20 and 40 mN m^{-1}, as shown in Fig. 5. This is consistent with the inference from Fig. 1 that **1** alone

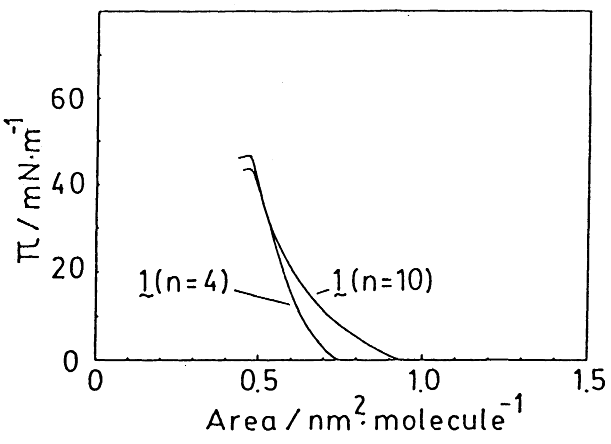


Fig. 2. π-A curves of 1 at 20 ℃.

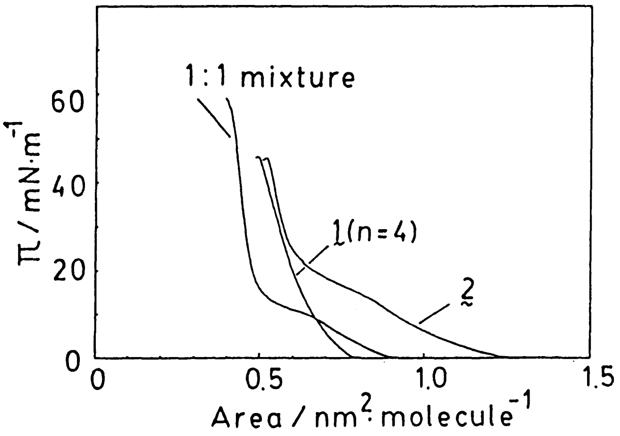


Fig. 4. π-A curves of 1(n=4), 2 and the mixed monolayer.

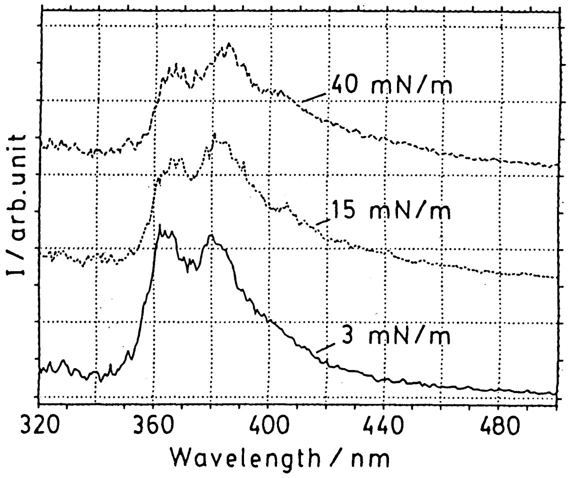


Fig. 6. Fluorescence spectra of the 1:1 mixed monolayer of 1(n=4) and 2 at 20 ℃.

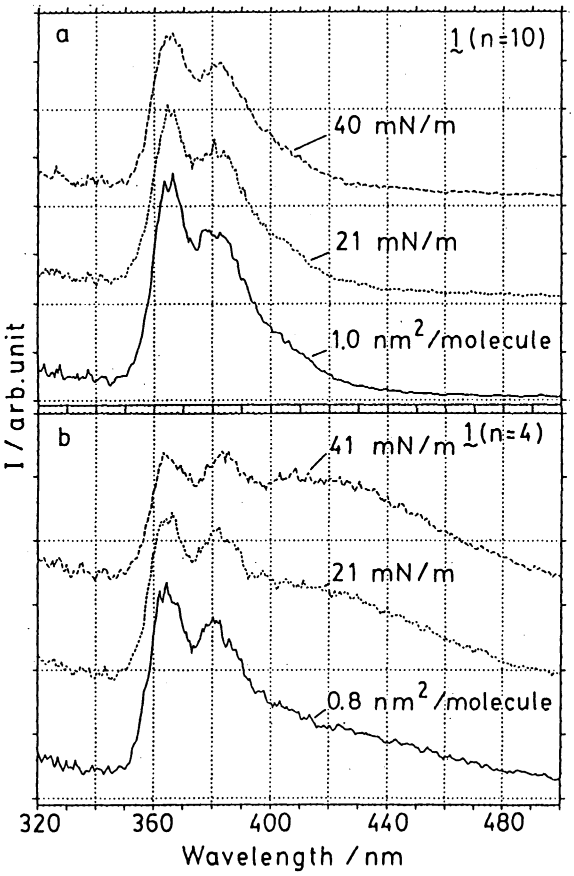


Fig. 3. Fluorescence spectra of surface monolayers of 1 at 20 ℃.

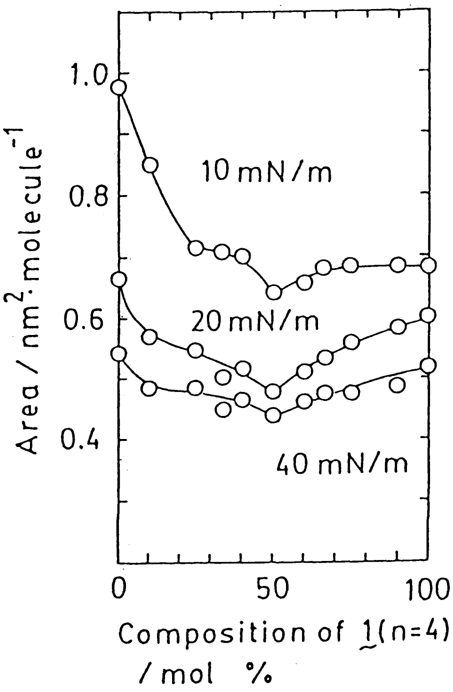


Fig. 5. Mean molecular area as a function of the composition of 1(n=4).

cannot form densely-packed monolayers. A regular structure seems to exist in the 1:1 mixed monolayer. The smallest mean molecular area observed is 0.49 nm^2 molecule^{-1} in close agreement with that estimated for the vertically-aligned mixed monolayer.

Fluorescence spectra of the 1:1 mixed monolayer are shown in Fig. 6. An excimer emission observed for the single-component monolayer (see Fig. 3b) is absent in the mixed monolayer. There are observed small red shifts in the emission maxima with increasing surface pressures: from 364 and 380 nm to 366 and 384 nm. The relative intensity at 380 nm and the shoulder intensity at 400 nm are also enhanced upon compression. Yamamoto and coworkers observed a small red shift in fluorescence of a bulky poly(vinylcarbazole) due to formation of a excimer with slight chromophore stacking.[15] The emission spectral change of Fig.6 and red shifts of absorption bands of the mixed monolayer as discussed above indicate formation of insufficiently stacked carbazole rings.

In conclusion, fluorescence property of the organized carbazole unit in monolayer can be modified by changing the chemical structure of components and the mode of monolayer assemblage. The macroscopic data in the form of π-A curves are consistent with fluorescence data which reflect the microscopic chromophore interaction. Although fluorescence spectra of a monolayer[16] or in inert monolayer matrices[17,18] have been reported, the present finding provides the first example of the relation between the chromophore orientation and the fluorescence characteristics.

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