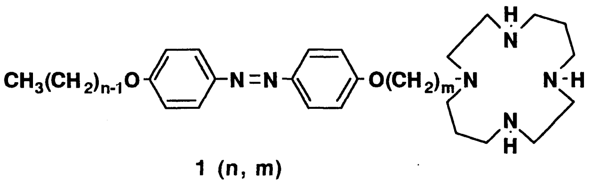
CHEMISTRY LETTERS, pp. 331-334, 1994.

Alternating Molecular Arrangements in Paired Bilayers of Oppositely Charged Amphiphiles [1)]

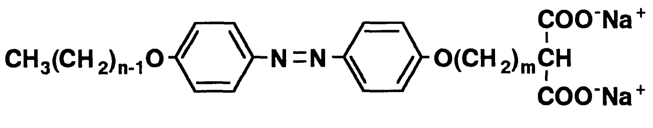
Taisei NISHIMI, Masami TACHIKAWA, Tadashi MAEDA, Yuichi ISHIKAWA, and Toyoki KUNITAKE*
Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, Fukuoka 812

Equimolar mixtures of cyclam amphiphiles and malonate amphiphiles produced uniformly paired bilayers. Absorption spectra and X-ray diffraction measurements showed that molecular alignments were determined by combinations of the alkyl chain length of paired bilayer components as in the respective single-component bilayers.

Formation of specific molecular patterns is one of the most important targets in supramolecular chemistry [2)] and in artificial self-assembling systems. [3)] As an approach toward this target, we have investigated molecular arrangements in mixed bilayer systems. For example, mixed bilayer membranes composed of hydrocarbon and fluorocarbon components showed phase separation, which could be suppressed by addition of a hybrid bilayer component. [4,5)] In the case of azobenzene-containing amphiphiles, phase separation was readily detected by UV absorption shifts,[6)] and was applied to reactivity control in aqueous bilayers.[7)] These conventional phase separations produce only statistical distributions of domains. Spontaneous formation of well-defined molecular patterns should become possible solely via specific interactions of neighboring bilayer components. In this paper, we report alternatingly arranged bilayer structures composed of oppositely charged azobenzene amphiphiles **1** and **2**.



1 (n, m)



2 (n, m)

Bilayer properties and complexation behavior of cyclam amphiphiles **1** are reported elsewhere.[8)] Azobenzene amphiphiles with the malonate head group **2** were synthesized from the reaction of the bromide precursors with sodium salt of diethylmalonate accompanied by hydrolysis in aqueous NaOH.[9)] Formation of aqueous micelles from other malonate amphiphiles has been reported. [10,11)] Brackman and Engberts [12)] recently studied the interaction of malonate micelles with water-soluble polymers. However, no report has been published on bilayer formation by malonate amphiphiles.

Clear aqueous dispersions (10 mM) of malonate amphiphiles, **2**(12,5), **2**(12,10), and **2**(8,10) are obtainable upon sonication. These dispersions are, however, not stable, and tend to precipitate after a few hours at room temperature. Thus, morphologies of these dispersions were studied immediately after the sonication using a transmission electron microscope(Hitachi H-600).[13)] Rod-like aggregates(for **2**(12,5)) and fibers (for **2**(8,10) and **2**(12,10)) were observed. The diameters of these aggregates were approximately 60 Å, and corresponded to two molecular lengths. DSC measurements were difficult because of limited stabilities of the aqueous dispersions.

UV-vis absorption spectra of these three dispersions are shown in Fig. 1. Absorption maxima are located at 315, 325, and 300 nm (with a shoulder at 330 nm) for **2**(12,5), **2**(12,10), and **2**(8,10), respectively, and display blue shifts relative to that of the monomeric dispersion (355 nm). These spectral data suggest parallel stacking of the azobenzene chromophores(so-called H-aggregates) within the bilayer aggregates.[14)]

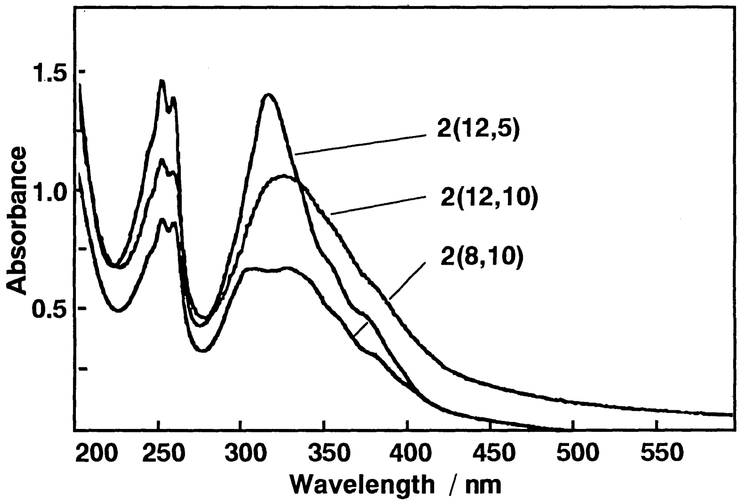


Fig. 1. Absorption spectra of malonate amphiphiles **2** 5×10^{-5} M, 20 °C, pH 8.3(borate buffer), μ=0.01(KCl).

The aqueous dispersions are readily converted to regular multilayer films by casting on Teflon sheets at room temperature, as reported for other aqueous bilayers.[15)] Reflection X-ray diffraction(Rigaku RAD-R-32) of these cast films gave unit layer thicknesses of 44.1 Å and 48.8 Å for **2**(12,5) and **2**(12,10), respectively. Molecular lengths of these two amphiphiles are estimated from CPK models as 36 Å and 43 Å, respectively. Therefore, the observed layer thicknesses are in between one and two molecular lengths, and suggest the formation of tilted bilayer structures. In the case of **2**(8,10), the layer thickness was 39.4 Å and was close to one molecular length. This indicates the presence of the interdigitated structure.[16,17)]

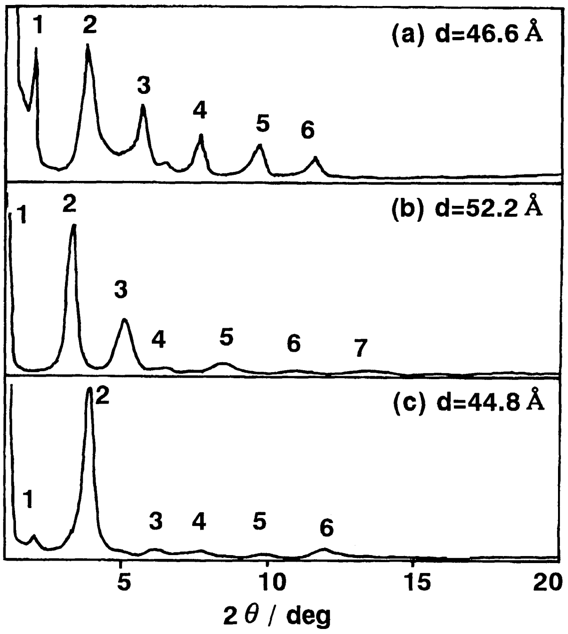


Fig. 2. Reflection X-ray diffraction of cast films of equimolar mixtures. (a) **1**(12,3)+**2**(8,10), (b) **1**(12,10)+**2**(12,10), (c) **1**(8,10)+**2**(8,10). The number indicates the order of diffraction.

Protonation constants (pK_b) of the four amino groups of cyclam were reported as 11.5, 10.2, 1.6, and 0.6.[18)] Amphiphiles **1** would exist as di-cationic species in the neutral pH region and form equimolar ion pairs with di-

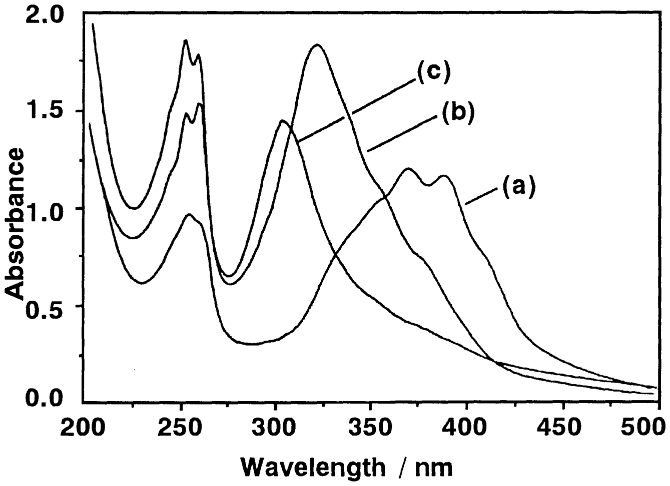


Fig. 3. Absorption spectra of equimolar dispersions of **1** and **2** in water. 20 °C, 2.5×10^{-5} M each. (a) **1**(12,3)+**2**(8,10), (b) **1**(12,10)+**2**(12,10), (c) **1**(8,10)+**2**(8,10).

anionic malonate amphiphiles **2**. Aqueous dispersions of equimolar **1** and **2** are stable. Figure 2 displays X-ray diffraction patterns of cast films of three equimolar mixtures. These XRD patterns are derived from single spacings. Single-spacing patterns were invariably found for other equimolar mixtures. Thus, we conclude that the mixed bilayers are made of uniform ion-paired units that are stabilized by electrostatic and hydrogen bonding interactions. The observed long spacings are close to those of individual bilayer components when alkyl chain lengths are identical; e. g., d=39.4 Å for **1**(8,10). Absorption spectra of these mixtures are shown in Fig. 3. The equimolar mixtures show absorption patterns that are different from the molecularly dispersed species. They must contain bilayer aggregates, like individual dispersions. In the case of **1**(12,3) plus **2**(8,10), the individual absorption maxima (335 nm and 303 nm, respectively) disappear and new peaks appear at 370 nm and 390 nm. The new peaks are typical of the tilted chromophore stacking (so-called J-aggregate).[14] On the other hand, an equimolar mixture of **1**(12,10) and **2**(12,10) shows λ_{max} at 320 nm, in close agreement with those of the individual bilayers. These λ_{max} values are characteristic of the parallelly stacked chromophores (H-aggregate). The mixed bilayer of **1**(8,10) and **2**(8,10) gives λ_{max} at 303 nm, which is unchanged from those of the individual dispersions and is typical of the interdigitated structure.

Absorption maxima of single-component and mixed bilayers are summarized in Table 1. It is notable that λ_{max} values of the mixed bilayers of identical alkyl chain lengths are essentially unaltered from those of the individual bilayers, although λ_{max} of the **1**(12,5)/**2**(12,5) mixture is not red-shifted as much as those of the individual bilayers. Therefore, considering the long spacing data, molecular packing in the individual bilayers must be basically maintained in the paired bilayers of identical alkyl chains. On the other hand, pairing of oppositely charged amphiphiles with different alkyl chain lengths gives rise to red shifts relative to λ_{max}'s of the unpaired component bilayers.

Table 1. Absorption maxima of single-component bilayers and paired bilayers in water, 5×10^{-5}M, 20 ℃

	2(8,10) 303nm	**2**(12,10) 315 nm	**2**(12,5) 325 nm
1(8,10) 303 nm	**1**(8,10) + **2**(8,10) 303 nm	**1**(8,10) + **2**(12,10) 315 nm	**1**(8,10) + **2**(8,10) 367nm, 385 nm
1(12,10) 325 nm	**1**(12,10) + **2**(8,10) 350 nm, 360 nm	**1**(12,10) + **2**(12,10) 320 nm	**1**(12,10) + **2**(12,5) 365 nm, 385 nm
1(12,5) 335 nm	**1**(12,5) + **2**(8,10) 363 nm, 382 nm	**1**(12,5) + **2**(12,10) 350 nm, 380 nm	**1**(12,5) + **2**(12,5) 350 nm
1(12,3) 335 nm	**1**(12,3) + **2**(8,10) 370 nm, 390 nm	**1**(12,3) + **2**(12,10) 363 nm, 382 nm	**1**(12,3) + **2**(12,5) 363 nm

The preceding results are explained by the formation of bilayer assemblies that are schematically illustrated in Fig. 4. The type 1 bilayer assembly is derived by pairing of component amphiphiles with different alkyl chain lengths. XRD data given in Fig. 2a indicate that the paired bilayer of **1**(12,3) and **2**(8,10) possesses a single long spacing. Single long spacings were similarly found for pairing of **1**(12,5) and **2**(8,10), **1**(12,5) and **2**(12,10), **1**(12,3) and **2**(12,10). Then, the neighboring azobenzene chromophore will be located in a tilted arrangement even without molecular tilting(red shift). Similar situations are conceivable for other mismatched (with different chain lengths) pairs because of their common red shifts, although molecular orientation and alignment need to be adjusted according to individual molecular structures. In the case of amphiphile pairs with the identical alkyl chain length, the molecular organizations characteristic of the respective component are maintained as inferred from spectroscopic and XRD data. Thus, the double layer structures(type 2) are most appropriate for the **1**(12,10)/**2**(12,10) pair and the **1**(12,5)/**2**(12,5) pair. The **1**(8,10)/**2**(8,10) pair will assume an interdigitated arrangement(type 3) similar to those of the single-component bilayer, on the basis of the large blue shift.

In conclusion, the present results establish the formation of uniform bilayer membranes of alternating surface structures. The alternating arrangement will be useful for construction of novel supramolecular architectures, since the paired structural unit is known to be essential in many functional materials(charge transfer complexes [19]) and molecular ferromagnet [20,21]).

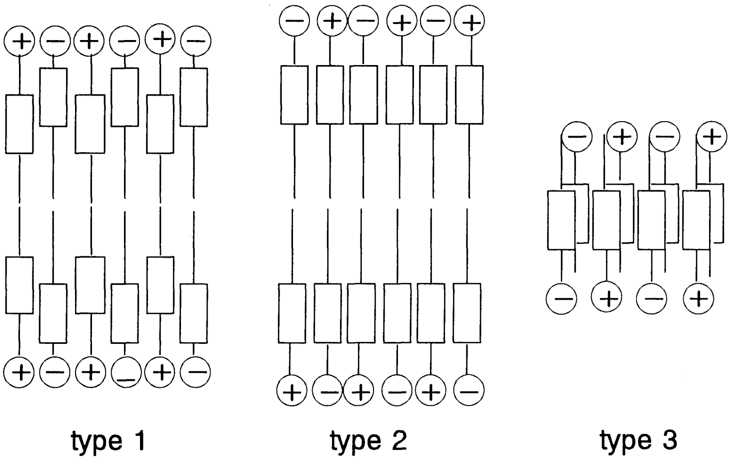


Fig. 4. Patterns of molecular arrangements in paired bilayers. The charges are divalent in the actual bilayer.

References
1) Contribution No. 992 from Department of Chemical Science and Technology(Molecular Systems Engineering).
2) J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.,* **29**, 1304(1990).
3) T. Kunitake, *Angew. Chem., Int. Ed. Engl.*, **31**, 709(1992).
4) T. Kunitake and N. Higashi, *J. Am. Chem. Soc*., **107**, 692(1985).
5) N. Higashi, T. Kunitake, and T. Kajiyama, *Macromolecules*, **19**, 1362(1986).
6) M. Shimomura and T. Kunitake, *Chem. Lett*., **1981**, 1001.
7) T. Kunitake, H. Ihara, and Y. Okahata, *J. Am. Chem. Soc*., **105**, 6070(1983).
8) T. Nishimi, M. Tsukamoto, Y. Ishikawa, and T. Kunitake, Abstracts of the 55th Annual Meeting of the Chemical Society of Japan, Fukuoka, Oct. 1987.
9) **2**(8,10), yellow powder, mp above 300 ℃, Found: C, 63.64; H, 7.53; N, 4.49%. Calcd for $C_{33}H_{46}N_2O_4Na_2$: C, 63.45; H, 7.42; N, 4.48%. **2**(12,10), yellow powder, mp above 300 ℃, Found: C, 65.33; H, 8.06; N, 4.19%. Calcd for $C_{37}H_{54}N_2O_6Na_2$: C, 65.27; H, 7.99; N, 4.11%. **2**(12,5), yellow powder, mp above 300 ℃, Found: C, 63.77; H, 7.44; N, 4.66%. Calcd for $C_{32}H_{44}N_2O_6Na_2$: C, 64.20; H, 7.41; N, 4.68% .
10) K. Shinoda, *J. Phys. Chem*., **59**, 432(1955).
11) Vikingstad and H. Saetersdal, *J. Colloid Interface Sci*., **77**, 407(1980).
12) J. C. Blackman, and J. B. F. N. Engberts, *Langmuir,* **7**, 46(1991).
13) In order to avoid morphology changes by complexation, aqueous malonate bilayers were applied to carbon- coated Cu grids, and then stained by 2% uranyl acetate.
14) M. Shimomura, R. Ando, and T. Kunitake, *Ber. Bunsengesel. Phys. Chem*., **87**, 1134(1984).
15) N. Nakashima, R. Ando, and T. Kunitake, *Chem. Lett*., **1983**, 1577.
16) T. Kunitake, M. Shimomura, T. Kajiyama, A. Honda, K. Okuyama, and M.Takayanagi, *Thin Solid Films,* **121**, L89(1984).
17) T. Nishimi, Y. Ishikawa, T. Kunitake, M. Sekita, G. Xu, and K. Okuyama, *Chem. Lett*., **1993**, 295.
18) M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans*., **1976**, 116.
19) J. D. Wright, "Molecular Crystals," Cambridge Univ. Press (1987), Chap. 3.
20) O. Kahn, Y. Pei, M. Verdaguer, J. P. Renard, and J. Stetten, *J. Am. Chem. Soc*., **110**, 782(1988).
21) H. Tamaki, Z. J. Zhong, N. Matsumoto, S. kida, M. Koikawa, A. Achiwa, Y. Hashimoto, and H. Okawa, *J. Am. Chem. Soc*., **114**, 6974(1992).

(Received November 5, 1993)