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Functional organic gels
Chirality induction through formation of highly-oriented structure

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An L-glutamate derivative having one carboxylic and two dodecylamide groups form highly-oriented aggregates in benzene, which interact with a cationic achiral dye to produce extremely strong exciton coupling around the absorption band of the dye.

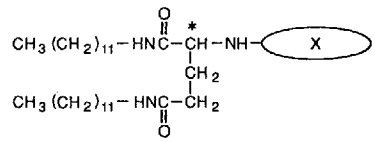
1. Introduction

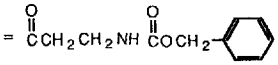
Recently, it has been found that some specific amphiphiles can form highly-oriented aggregates, like those of aqueous lipid bilayer membranes, in organic solvents [1–6]. These observations are very significant for understanding self-assembling behaviour at the molecular level. On the other hand, the aggregates in organic solvents are expected to provide new organic media for organic reaction and selective transportation, for which aqueous lipid membranes have been widely used in biomimetic chemistry. Therefore, we have a great interest in how biomembrane functions can be reproduced in organic solutions.

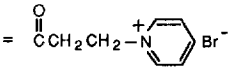
Recently, we have found that double-chain alkyl lipid analogue **1a** (see figure 1) forms gels in benzene and the aggregates show phase separation behaviour, one of the most important phenomena in biomembrane functions. However, functional research of the organic gel is restricted because introduction of functional groups such as ionic ligands into a lipid would lead to lower solubility to organic solvents. In this communication, we report a new lipid analogue **2** which forms gels in organic solvents, which then interact with achiral cationic cyanine dye to produce induced chirality.

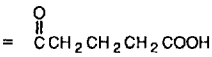
2. Results

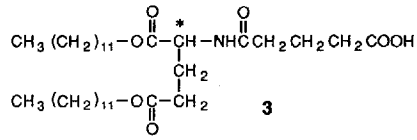
The lipid **2** can be dissolved in benzene (5×10^{-3} mol l^{-1}) and ethanol (20×10^{-3} mol l^{-1}) at 70°C. When the solutions were cooled down to 40°C and



1a X = 

1b X = 

2 X = 



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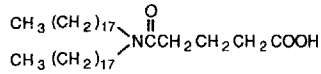

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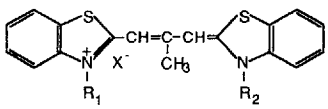

NK-2012

$R_1 = -(CH_2)_3SO_3^-$ $R_2 = -(CH_2)_3SO_3^-H^+$

NK-77

$R_1 = R_2 = -C_2H_5$ X = I

Figure 1. Chemical structures of lipid analogues and cyamine dyes used in this study.

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0°C, respectively, the gelation of the solution was observed. The CD spectrum of the ethanol gel showed extremely large enhancement of CD strength (about 20 times larger at − 20°C than at 20°C in the value of $[\theta]_{217}$), although in the case of the benzene gel the CD spectrum was not determined because of large absorption of benzene. Similar optical activity enhancement has been reported in some chiral lipids in their aqueous solutions [7–10]. These phenomena are explained by a chiral interaction among lipids derived from formation of highly-oriented structures. Therefore, it is estimated that **2** also can form highly-oriented structures in organic solvents and the gelation is due to the remarkable development in aggregate morphology (fibrous aggregates with 20 nm minimum diameters were detected by electron microscopy after casting on a glass plate).

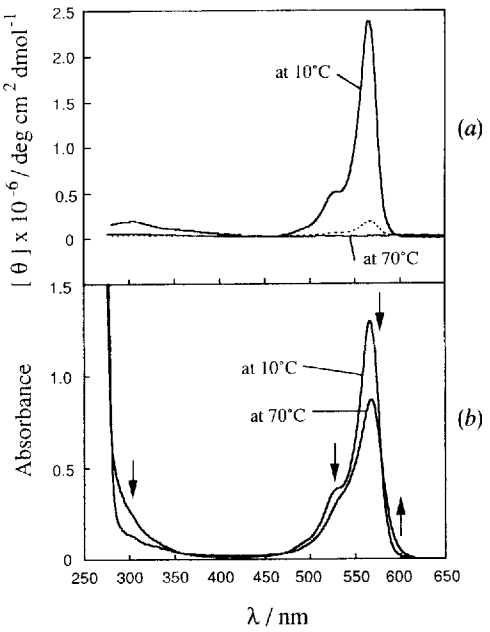

Figure 2. CD (*a*) and UV visible (*b*) spectra of cyanine dyes in the presence of **2** in benzene. (——), NK-77; (·····), NK-2012. [**2**] = $5{\cdot}0 \times 10^{-3}$ mol l^{-1}; [NK-77] = [NK-2012] = $1{\cdot}0 \times 10^{-5}$ mol lk^{-1}.

$[\theta]_{max}$ values for NK-77 in benzene gels.

Lipid†	Additive‡	$[\theta]_{max} \times 10^{-6}$/deg cm^2 dmol^{-1}§	
2	none	2·4	(1·0)
2	triethylamine	9·1	(3·79)
1 a	**2**	3·9	(1·63)
1 a	**3**	2·8	(1·17)
1 a	**4**	2·0	(0·83)
1 a	octadecanoic acid	0·18	(0·075)
1 a	butyl acid	0·16	(0·067)
1 a	acetic acid	0·15	(0·063)

§ The number in parenthesis shows the relative values for that in the **2** benzene gels.
† [**2**] = $5{\cdot}0 \times 10^{-3}$ mol l^{-1}; [**1 a**] = $2{\cdot}5 \times 10^{-3}$ mol l^{-1}.
‡ [additive] = $2{\cdot}5 \times 10^{-3}$ mol l^{-1}, except for triethylamine ($5{\cdot}0 \times 10^{-3}$ mol l^{-1}).

It has been reported that chiral supramolecules such as aqueous lipid bilayer membranes and α-helical poly(α-amino acids) can provide a specific microenvironment for achiral dyes [7, 8, 11–18]. For example, an anionic cyanine dye NK-2012 binds to the **1 b** aggregates [11] and poly(L-lysine) [15, 16] to produce chiral dimers with extremely strong exciton couplings. However, when NK-2012 dyes were added to the **2** benzene gel, relatively small CD strength was induced for dyes compared with that of **1 b** (as shown by the dotted line in figure 2). This indicates that the anionic **2** aggregates in benzene cannot interact electrostatically with anionic NK-2012. On the other hand, when a cationic NK-77 was added to the **2** benzene gel at 10°C instead of NK-2012, extremely strong exciton coupling was observed at the absorption band around the monomeric NK-77 (see figure 2). This induction of chirality was not accompanied by λ_{max} shift in its visible spectrum, although previously reported induced CD in lipid bilayer membranes is closely related to chiral aggregation of dyes with λ_{max} shift [7, 8, 11–14]. In addition, the ellipticity increased four times when an equimolar of triethylamine was present in the **2** benzene gel ($[\theta]_{568} = 9{\cdot}04 \times 10^6$ deg cm^2 dmol^{-1}). These results strongly suggest that NK-77 dye electrostatically interacts with **2** and are chirally arranged on the **2** aggregates.

On the other hand, De Vries and Chandrasekhar hypothesized that positive induced CD like the spectra shown in figure 2 are observed for parallel orientation of dyes along nematic layers in right-handed cholesteric liquid crystalline states [19, 20]. Similar observation has been reported in cholesteric liquid crystals from right-handed α-helical poly(γ-benzyl L-glutamate) by Sisido *et al.* [21]. Therefore, the positive CD pattern in figure 2 indicates parallel orientation of NK-77 on the chiral **2** aggregates.

The following results show a high-orientation of **2** is essentially important to induce chiral perturbation to achiral dyes (also refer to the table):

(1) Induced CD was not observed in the **2** benzene solution at 65°C. At this temperature, **2** cannot form an oriented structure.
(2) An ester type lipid **3** corresponding to **2** cannot form gels in benzene at any temperature; almost no induced CD for NK-77 was observed in the **3** benzene solution.
(3) An achiral and anionic lipid **4** also provided no induced CD for NK-77.
(4) A nonionic and chiral lipid **1 a** provided no induced CD for NK-77, due to the fact that **1 a** has no ionic

functional group. However, when equimolar achiral lipid **4** was mixed with the **1 a** benzene gel, induced CD for NK-77 was observed.

(5) When achiral and monoalkyl carboxylic acids were mixed with the **1 a** benzene gel instead of **4**, their CD strengths were almost 20 times lower than that in **4**.

3. Conclusions

In conclusion, we have shown that lipid membrane analogues which form gels in organic solvents can produce specific microenvironments by introduction of ionic and chiral functions into lipids. This organic system would be not only applicable to new organic media, but would also simplify understanding the specific interaction in supramolecular assemblies because of elimination of hydrophobic effect.

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