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Hiroshi Hachisako^a; Hiroataka Ihara^b; Chuichi Hirayama^b; Kimiho Yamada^a

^a Department of Industrial Chemistry, Kumamoto Institute of Technology, Kumamoto, Japan ^b

Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto, Japan

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Chirally arranged monomeric dyes on helical bilayer membranes

by HIROSHI HACHISAKO*, HIROTAKA IHARA†, CHUICHI HIRAYAMA† and KIMIHO YAMADA

Department of Industrial Chemistry, Kumamoto Institute of Technology, Kumamoto 860, Japan

†Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860, Japan

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Strong exciton coupling around the absorption band of monomeric dyes was induced by helical bilayer membranes formed from various L-glutamic acid-derived amphiphiles which contain three amides per molecule. The mirror-image of the circular dichroism spectra was observed by the corresponding D-isomers. No similar induction was observed by the corresponding ester-type amphiphiles which could not produce helices. It is assumed that dyes are helically arranged on helical bilayer membranes, resulting in an induction of chirality even in monomeric dyes.

Some ionic dyes bind to chiral polyions to produce specific dispersion states. For example, Hatano *et al.* and Yamamoto *et al.* have studied the chiral dimer formation of methyl orange (MO) bound to poly(L-lysine) [1, 2] and poly(L-ornithine) [2]. Similarly, acridine orange binds to poly(L-glutamic acid) to form chiral dimers [3, 4]. On the other hand, Nakashima *et al.* [5] have investigated the binding mode of various dyes on chiral synthetic bilayer membranes. In these cases, induced circular dichroism (ICD) in the dyes is limited only to aggregated species which follows from the coupling of the dipole transition moments between dye molecules.

On the other hand, we have briefly reported that the ICD of monomeric dyes was observed in the case of MO bound to the L-glutamic acid-derived lipid (2) with a β -alanyl head group [6]. However, the mechanism of the ICD of the monomeric dye has not been clarified yet. In this communication, we would like to report that strong exciton couplings around the absorption bands of monomeric methylene blue (MB) and congo red (CR) could be observed in various helical bilayer aggregates from L-glutamic acid-derived amphiphiles 1-4.

Amphiphiles 1-8 were prepared as reported previously [6-9]. It was previously confirmed by electron microscopy and differential scanning calorimetry (DSC) that all the amphiphiles could form bilayer membranes in water. Typical aggregation morphologies of representative amphiphiles are shown in figure 1.

The λ_{\max} of the cationic dye, MB, alone in water are located at 600 and 660 nm which are assigned to dimeric and monomeric species, respectively [5(c)]. This MB solution provided no exciton coupling around their absorption bands in the CD spectra. When anionic 1 was added to the MB solution, the monomer to dimer

* Author for correspondence.

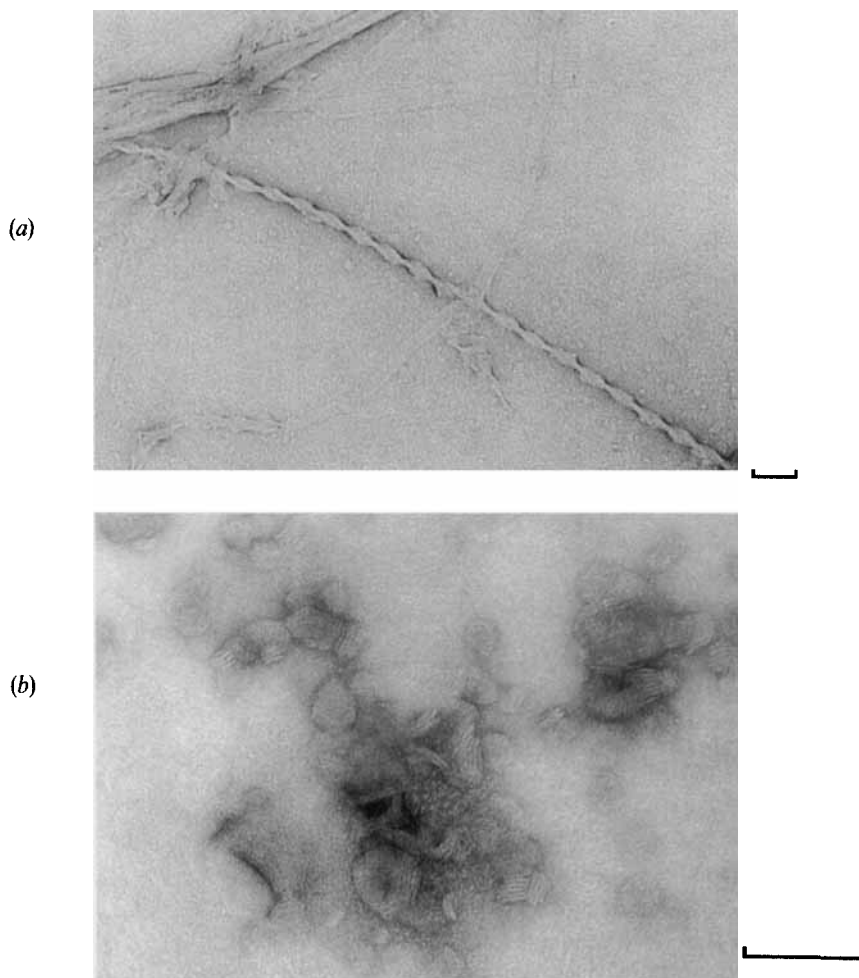


Figure 1. Electron micrographs of an aqueous solution of **2** (a) and **6** (b) negatively stained by uranyl acetate. Scale bars represent 100 nm, respectively.

To obtain the gel to liquid crystalline phase transition temperature, the DSC measurement of **1** [9] was carried out using a 20 mmol l^{-1} aqueous solution in a sealed Ag cell. It was shown that aqueous aggregates of **1** underwent the gel to liquid crystalline phase transition in the temperature range of 20 to 48°C (peak top temperature (T_c); 34°C). In general, induced optical activity of guest dye molecules disappears at a temperature above T_c of the chiral bilayer matrix [5]. However, induced optical activities of MB are maintained exceptionally even in liquid crystalline states of aggregates **1** in our experiments.

Similar induction of chirality was observed in an anionic dye, congo red (CR), in the presence of cationic bilayer aggregates formed from **2**. The λ_{max} of CR alone in water is located at 498 nm. This solution showed no exciton coupling. When **2** was added to the solution, a new λ_{max} appeared at 534 nm in addition to that at 498 nm. The CD spectra of the solution at 20°C showed that both the aggregated and monomeric CR provided

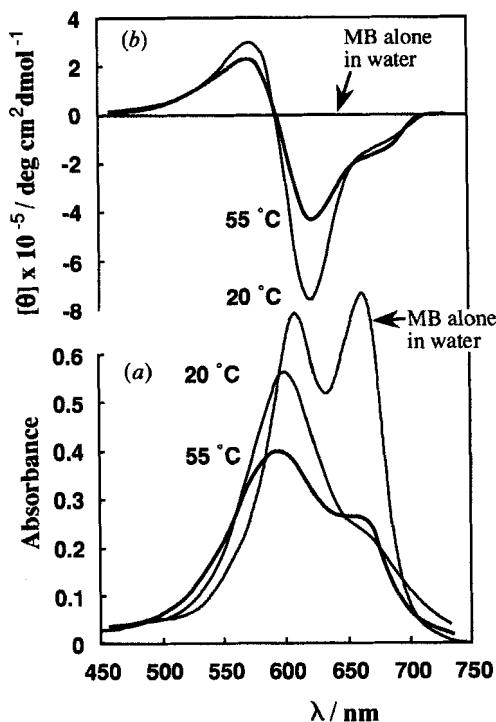


Figure 2. Visible (a) and CD (b) spectra of MB in the presence of aqueous aggregates of **1**. $[1] = 1.2 \times 10^{-3} \text{ mol l}^{-1}$, $[MB] = 1.5 \times 10^{-4} \text{ mol l}^{-1}$, pH 9.0.

strong exciton couplings around their absorption bands. These ICD bands were maintained even at temperatures above T_c (T_c : 33°C and 42°C [6, 7]). However, such an extraordinary maintenance of ICD in the liquid crystalline state of **2** was revealed to depend on the chemical structure of the dyes, as the ICD of MO [6], ethyl orange and tropaeolin O bound to **2** disappeared at temperatures above T_c . The only way not to induce CD in CR in the presence of **2** is to dissolve **2** and CR in water simultaneously at a temperature above T_c . This solution in the liquid crystalline state does not produce ICD in CR. However, once the solution is cooled to a temperature below T_c , ICD emerged and did not disappear upon heating again above T_c . This indicates that CR molecules are excluded outside the membrane surface of **2** stabilized by intermolecular hydrogen bonding and are chirally arranged [6, 9]. Thus, the obtained spectra are attributed to the ICD of CR, depending on the dispersion state of CR.

It is unusual that optical activity is induced in monomeric dyes bound to chiral bilayer membranes. For example, cyanine dyes and MO combine to chiral bilayer aggregates to produce their chirally stacked dimers and achiral monomers at temperatures below T_c [5]. However, no ICD was observed even at temperatures below T_c in the ester-type lipids **5** and **6** corresponding to amide-type lipids **1** and **2**, respectively. For example, the MB molecules bound to aggregates **5** formed their dimers below T_c (T_c : 14°C). However, the dimer showed no chirality. The aggregates **6** showed neither the dimer formation of CR nor the induction of chirality regardless of the phase transition.

To understand the above mentioned, remarkable difference of the binding states of dyes on amide- and ester-type lipids, the morphology of lipid aggregates was

Relationships between the morphologies of bilayer membranes and ICD of dyes.

Amphiphile +	Dye	Morphology†	ICD (below T_c)		ICD (above T_c)	
			Aggregated	Monomeric	Aggregated	Monomeric
1 + MB	Helices		S-chiral	Negative	S-chiral	Negative
2 + CR	Helices		R-chiral	Negative	R-chiral	Negative
3 + MB	Helices‡		S-chiral	Negative	S-chiral	Negative
4 + CR	Helices		R-chiral	Negative	None	None
5 + MB	Ribbons		None	None	None	None
6 + CR	Vesicles		None	None	None	None
7 + MB	Vesicles, Rods		None	None	None	None
8 + MB	Vesicles		None	None	None	None

† Determined by electron microscopy.

‡ No endothermic peak was observed by DSC (temperature range 5–100°C).

investigated. The table shows the relationship between aggregation morphologies of bilayer matrices and ICD of bound dyes. It is noticeable that the extraordinary ICD in the monomeric dyes was observed only in the case of using helical bilayer aggregates formed from amide-type amphiphiles 1–4. The corresponding ester-type lipids could not form helices. On the basis of these results, we assume that the dyes (monomers, and maybe dimers) are helically arranged on helical bilayer membranes, as if the residual chromophores such as pyrene, naphthalene and anthracene were helically arranged along the α -helical main chain of polypeptides [10–12], or as if acridine orange were helically arranged by binding electrostatically to α -helical poly (L-glutamic acid) [4].

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