Organized Photodimerization of Unsaturated Carboxylates. Selectivity Control by Normal and Reversed Micelles

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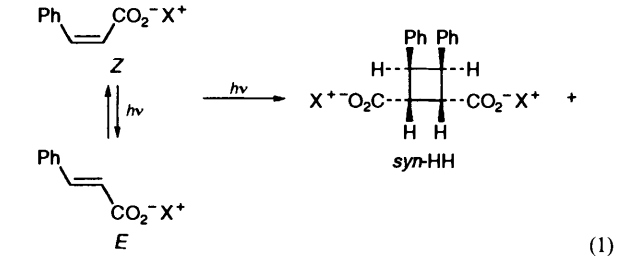
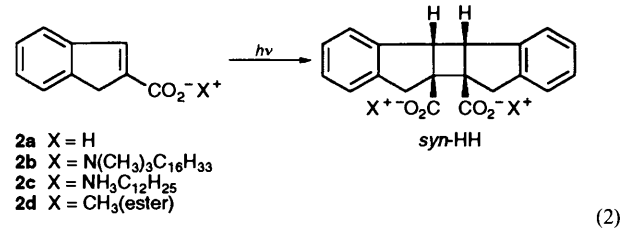
Aromatic unsaturated carboxylates such as cinnamate and 2-indenecarboxylate form, in the presence of long-chain alkylammonium ion, short rod-like micelles with an aggregation number of an order of 10^3 in water and premicelle aggregates including 2–3 surfactant molecules in carbon tetrachloride. It was found that these aggregates undergo efficient and stereoselective photodimerizations. Photoreactions in aqueous rod-like micellar solutions resulted in the predominant formation of *anti*-head-to-head dimers (*anti*-HH), while the reaction in small aggregated premicelles yielded thermodynamically least stable *syn*-head-to-head dimers (*syn*-HH). The addition of a small amount of methanol to the premicelle aggregate shifted the major product from *syn*-HH to *anti*-HH. Control experiments showed that the photoreaction of the corresponding methyl ester afforded mixtures of four isomeric dimers, *syn*- and *anti*-HH and HT (head-to-tail), of statistical distribution. These stereochemical selectivities are discussed in terms of the organized olefin orientation and correlated to the results of light scattering and NMR probe techniques.

Anisotropy or organization are characteristic of self-assembled molecular aggregates of amphiphilic substances. Such organized systems may provide potentially favourable reaction media for selective phototransformations, due to the preorientation of incorporated guest molecules,[1] and increasing attention has been focussed on the control of stereochemistry of chemical reactions by organizing substrates in heterogeneous circumstances.[2,3,4] The purpose of organized photochemistry is not only to establish a basic methodology for catalytic photochemical reactions,[5] but also to develop photochemical or photophysical molecular devices.[6]

It has been established that preorientation of guest olefins in organized circumstances is crucial for stereoselective photocycloadditions in solid crystals,[7] liquid crystals,[8] micelles,[9] bilayer membranes[10] and inclusion or intercalation complexes of host molecules.[11] Previous work has concentrated on controlling the photocycloaddition of ionic olefins in electrostatic fields such as micelles[12] and layered minerals.[13] The utilization of normal micellar systems for synthetic purposes has rather been neglected, because product isolations are extremely tedious or difficult. As shown in the present paper, however, the reversed micellar systems have convenient work-up procedures, allowing isolation of the photoproducts. The paper summarizes the data on photocycloaddition of unsaturated carboxylates in the presence of long-chain alkylammonium ions forming aqueous micelles or reversed premicelle solutions.





Results and Discussion

Irradiation of Hexadecyltrimethylammonium Cinnamate (**1b**) *and 2-Indenecarboxylate* (**2b**) *in Water*.—Cinnamic (**1a**) and 2-indenecarboxylic (**2a**) acids form 1 : 1 ion-pairs with hexadecyltrimethylammonium hydroxide (CTAOH) (*i.e.*, **1b** and **2b**, respectively), which are fairly, but not freely soluble in water (at most *ca.* 7 mmol dm^{-3}). The irradiation of a 5.0 mmol dm^{-3} aq. solution of **1b** at >290 nm under Ar resulted in rapid *E*–*Z* photoisomerization and a photostationary state of a mixture of *E*- (18%) and *Z*-isomers (82%) was attained within 30 min. On successive irradiation for 9 h, the formation of *anti*-head-to-head dimer (*anti*-HH, 2% based on **1b** consumed) among the four expected isomeric dimers (*syn*-HH, *anti*-HH, *syn*-HT and *anti*-HT) was detected [eqn. (1)].[7] Similar irradiation of a 5.0 mmol dm^{-3} aq. solution of hexadecyltrimethylammonium 2-indenecarboxylate (**2b**) resulted in quite efficient photocyclodimerization, giving *syn*-HH and *anti*-HH dimers in 12 and 50% yields, respectively on irradiation for 3 h [eqn. (2)]. Lack of *E*–*Z* photoisomerization for indenecarboxylate **2** is the major reason for the highly efficient cycloaddition. Product characterization was performed by means of MS and NMR

Table 1 Quantum yields for the photochemical reactions of unsaturated carboxylic acids[a]

Entry	Unsaturated Carboxylate	Solvent	Quantum yields (%)[b]				
			Z	*syn*-HH	*anti*-HH	*syn*-HT	*anti*-HT
(A) reaction in aqueous micelle solutions:							
1	**1b**	H_2O	33	—[c]	0.7	—[c]	—[c]
2	**2b**	H_2O		4.1	18	—[c]	—[c]
(B) reaction in reversed micelle solutions:							
3	**1c**	CCl_4	38	0.5	0.1	—[c]	—[c]
4	**2c**	CCl_4		13	1.8	—[c]	3.0
(C) reaction in homogeneous solutions:							
5	**1d**	CH_3OH	32	—[c]	—[c]	—[c]	—[c]
6	**2d**	CCl_4		0.7	0.8	0.5	1.0

[a] Carboxylates (5.0 mmol dm^{-3} concentration) were irradiated with a 300 W Hg lamp through a Pyrex filter under argon at room temperature. [b] Quantum yields (%) for the formation of *cis*-cinnamate (*Z*), head-to-head (HH) and head-to-tail dimers (HT). [c] Not detected by GLC and/or HPLC (*i.e.* < 0.03%).

spectroscopy, by comparison with independently synthesized authentic samples[14] and parent indene dimers[15] (see Experimental).

The 1:4 ratio of *syn*-HH to *anti*-HH dimers formed was independent of irradiation times and concentrations from 0.04–2.5 mmol dm^{-3}. However, the rate of dimer formation was dependent on the concentration of salt **2b**. Thus, dimer yields increased with increasing [**2b**] and levelled off at above *ca.* 0.5 mmol dm^{-3}, which was close to the critical micelle concentration (cmc) of 0.2 mmol dm^{-3} for **2b** as measured independently by a tensiometer (Fig. 1). This fact suggests that the photoaddition of **2b** is accelerated by micelle formation. It is interesting to note that the photodimerization of **2b** is about nine times more efficient than the photoreactivity of sodium 2-indenecarboxylate in the presence of hexadecytrimethylammonium bromide (CTAB) under the same conditions.

Table 1 compiles quantum yields for formation of dimers and/or *Z*-isomers for **1b** and **2b** at the concentration above their cmc (*i.e.*, 5.0 mmol dm^{-3}).

Irradiation of Dodecylammonium Unsaturated Carboxylates in Carbon Tetrachloride.—To a 5.5 mmol dm^{-3} solution of cinnamic acid (**1a**) in methanol was added an equal amount of dodecylamine, the reagents were mixed by a sonicator and the solvent was evaporated *in vacuo*, giving a white powder. The powder was soluble in carbon tetrachloride by forming, as discussed later, a reversed premicelle. UV irradiation of a 7.6 mmol dm^{-3} solution of cinnamate (**1c**) in CCl_4 through a Pyrex-filter with a 300 W Hg lamp attained a photostationary state of *E*- and *Z*-isomers (30:70) within 30 min irradiation. Prolonged irradiation (10 h) yielded *syn*-head-to-head dimer (*syn*-HH, 40%) and *anti*-head-to-head dimer (*anti*-HH, 8.6%). Similarly, 30 min irradiation of a 5.0 mmol dm^{-3} solution of dodecylammonium indene-2-carboxylate (**2c**) in CCl_4 afforded mainly *syn*-HH dimer (44%) accompanied by formation of *anti*-HH (6%) and *anti*-HT dimers (10%).

The most interesting point here is the efficient formation of *syn*-HH dimers from both cinnamate **1c** and indenecarboxylate **2c**, in contrast with the above mentioned aq. micelle systems affording predominantly *anti*-HH dimers. In addition, it should be stressed that the present system has a convenient work-up for isolation of the photoproducts. Product separations from the reaction mixtures were completed by simple extractions with CH_2Cl_2 under weakly alkaline conditions by adding aq. sodium hydroxide.

The effect of concentration of **1c** on the cyclodimer yields was examined. As shown in Fig. 2 the cyclodimer formation

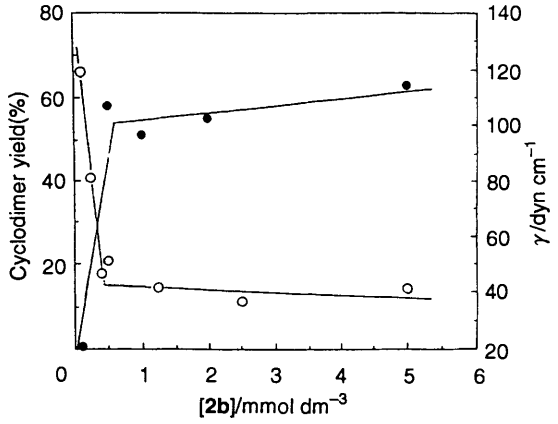


Fig. 1 Dependence of cyclodimer yields (●) from irradiation (30 min) and of aqueous solution surface tensions (○) on **2b** concentration. Yields are based on the reacted **2b**. 1 Dyn = 10^{-5} N.

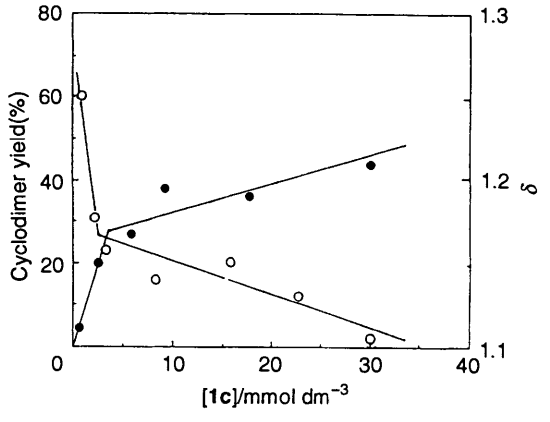


Fig. 2 Concentration dependence of cyclodimer yields (●) from irradiation (10 h) of **1c** solutions and chemical shift of vinyl proton of **1c** (○) in CCl_4. Yields are based on the reacted **1c**.

increased sharply with increasing the concentrations of **1c** up to 2–3 mmol dm^{-3}, but the slope at the higher concentrations levelled off, showing break points at *ca.* 5 mmol dm^{-3}. A similar concentration effect was observed, when the chemical shifts of vinyl proton of **1c** were plotted against the concentration; *i.e.*, a break point appeared at *ca.* 3 mmol dm^{-3}. Similar plots were obtained for indenecarboxylate **2c** (Fig. 3); the break point appeared at *ca.* 0.5 mmol dm^{-3} in CCl_4. The presence of break

Table 2 Solvent effect on isomer distributions from the irradiation of carboxylates **2c** and **2d**[a]

Entry	Unsaturated carboxylate	Solvent	Conversion (%)	Isomeric cyclodimers (%)			
				syn-HH	*anti*-HH	*syn*-HT	*anti*-HT
7	**2c**[b]	CCl_4	60	72	13	—[c]	14
8		C_6H_6	59	74	12	—[c]	14
9		$CHCl_3$	50	54	19	—[c]	28
10		CH_3OH	34	—[c]	85	4	11
11		CH_3CN	30	—[c]	88	—[c]	12
12		CCl_4–1% CH_3OH	42	62	16	—[c]	20
13		CCl_4–2% CH_3OH	39	24	44	—[c]	32
14		CCl_4–5% CH_3OH	14	15	54	—[c]	32
15	**2d**[d]	CCl_4[e]	53	24	16	1	59
16		C_6H_6	20	8	29	26	37
17		CH_3OH	31	27	27	24	22

[a] Carboxylate concentration 5.0 mmol dm^{-3}. Conversion 30–55% unless otherwise noted. [b] Irradiated for 30 min. [c] Not detected by GLC (< 1%). [d] Irradiated for 3 h. [e] 79% of reacted **2d** was converted into by-products, *i.e.*, chlorinated and trichloromethylated methyl 2-indenecarboxylates (detected by GC–MS analyses).

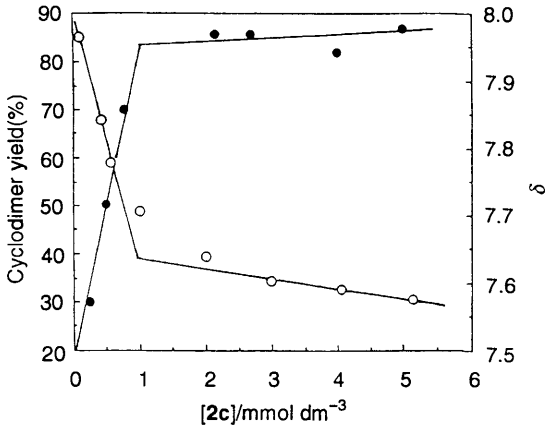


Fig. 3 Concentration dependence of cyclodimer yields (●) from irradiation (30 min) of **2c** and chemical shifts of vinyl proton of **2c** (○) in CCl_4. Yields are based on the reacted **2c**.

points, although not so clear-cut, implies a change in microscopic circumstances of aggregates.

Fendler *et al.*[16] have proposed the formation of small aggregates with aggregation number (n_A) of 2–3 in the solution of dodecylammonium propionate (DAP), a typical ion-pair surfactant, in hydrophobic solvents, and noticed a significant change of the size of the aggregates depending either on the concentration or cosolubilization of water molecules. The present photodimerization results suggest a significant change in molecular aggregation. As discussed later, the cmc of the solution of **1c** or **2c** (3.2 or 0.3 mmol dm^{-3}, respectively) could be estimated from NMR chemical shifts of the surfactants according to the literature method[16] and the values are approximately coincident to the break points (*cf.* Figs. 2 and 3).

The reversed micelle reaction was in contrast to that in homogeneous solution; that is, a control experiment of methyl cinnamate **1d** in methanol or CCl_4 showed a quite inefficient photodimerization under otherwise similar conditions. The observed photoreaction for **1d** was only the *E*–*Z* photoisomerization even after prolonged irradiation (10 h) in methanol. The photodimerization of methyl 2-indenecarboxylate (**2d**, 5.0 mmol dm^{-3}) in CCl_4 was *ca.* 20 times less efficient than that of **2b** in water, and the 9 h irradiation afforded a nonselective mixture of *syn*-HH, *anti*-HH and *anti*-HT dimers (*i.e.*, 14, 10 and 36% yields, respectively).

Quantum yields for dimer formations from **1c**, **1d**, **2c** and **2d** are summarized in Table 1. The quantum efficiencies of dimer formation in micelles are much higher than those in non-organized solutions, and the efficiencies increase in the order homogeneous solution, aq. micelles and reversed micelles.

Effect of Solvents on Photocyclodimerization.—Product distributions for cyclodimerization of indenecarboxylate **2c** were profoundly effected by solvents as shown in Table 2. The *syn*-HH dimer [eqn. (2)] was the major product in CCl_4 and benzene, and the ratio of *syn*- and *anti*-HH was as high as 73 : 12 (entries 7 and 8). In contrast, the major product in methanol and acetonitrile changed from the *syn*-HH dimer to the *anti*-HH one (entries 10 and 11). It is apparent that the predominant product changes from *syn*-HH dimer in non-polar solvents to *anti*-HH dimer in polar solvents; the result in chloroform is of the intermediary case (entry 9). These results are in sharp contrast to the homogeneous reaction of methyl ester **2d** to yield four isomers nonselectively in any solvents (entries 15–17).

It is interesting to note that the product selectivity in CCl_4 changed dramatically by adding a small amount of methanol. For example, the addition of only 2% methanol changed the major product from *syn*-HH to *anti*-HH dimers (*cf.* entries 12–14, Table 2). The dramatic effect of a small amount of methanol is attributable, as discussed below, to a structural change of tight reversed premicelles.

^1H NMR spectra of **2c** in CCl_4 showed that the chemical shift of the signal for the vinyl proton is dependent on concentration; that is, the vinyl proton appeared at δ 7.96 and 7.53 at 0.1 and 45.0 mmol dm^{-3}, respectively. The chemical shift of the vinyl proton of **2c** was estimated to be δ 7.99 and 7.51 at infinite and zero concentrations, respectively. The former may be assigned to aggregated **2c** molecules and the latter to isolated ones in CCl_4. On adding 5% methanol, the vinyl proton signals at δ 7.99 and 7.51 shifted to 7.76 and 7.63 at infinite and zero concentrations, respectively, indicating a significant interaction of methanol with the aggregated and isolated indenecarboxylate **2c**. The dramatic effect of a small amount of methanol on the product selectivity is related to hydrogen bonding or penetration of methanol with ion-pair **2c**. The details are discussed in the following section.

Self-Aggregation of Ion-pairs.—Unsaturated carboxylic acids, **1a** and **2a**, form 1 : 1 ion-pairs either with CTAOH or dodecylamine. Ion-pairs **1b** and **2b** with CTAOH are soluble in water, giving a clear, dispersed solution, but sparingly soluble in CCl_4. In contrast, ion-pairs **1c** and **2c** with dodecylamine as a white powder were freely soluble in CCl_4, hexane, and benzene, but sparingly soluble in water. Hexadecyltrimethylammonium salicylate (CTASal), an analogous surfactant, is reported to form rod-like micelles in the presence of sodium salicylate

Table 3 Critical micelle concentrations and aggregation numbers of micelles from alkylammonium unsaturated carboxylates

Entry	1:1 ion-pair	Solvent	cmc (mmol dm^{-3})	Aggregation number (n_A)	Micelle	Stereochemistry of major dimer
18	**1b**	H_2O	0.2[b]	1000[c]	rod-like[a]	*anti*-HH
19	**2b**	H_2O	0.2[b]	1100[c]	rod-like[a]	*anti*-HH
20	**1c**	CCl_4	3.2[d]	2.3[d]	reversed	*syn*-HH
21	**2c**	CCl_4	0.3[d]	2.8[d]	reversed	*syn*-HH
22	**2c**	5% CH_3OH–CCl_4	1.6[d]	3.1[d]	reversed	*anti*-HH
23	**3c**	CCl_4	4.5[d]	2.8[d]	reversed	

[a] Assumed form on the basis of dynamic light scattering analyses (see Experimental). [b] Measured by a tensiometer at ambient temperature (~25 °C). [c] Values obtained on the basis of light scattering measurements. [d] Measured from NMR probe techniques.

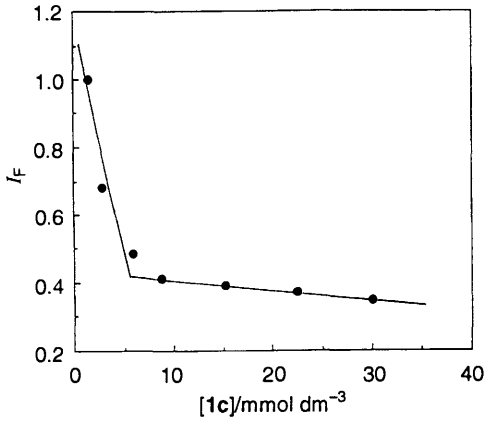


Fig. 4 Concentration dependence of relative intensities of fluorescence maximum at 325 nm from [**1c**] in CCl_4; excited at 280 ± 20 nm

(NaSal) (0.1 mol dm^{-3}) in water, and to form spherical micelles when codissolved by excess NaSal (1 mol dm^{-3}).[17] In contrast, dodecylammonium aliphatic carboxylates are reported to form reversed micelles in hydrophobic solvents.[16] In order to determine the form and nature of the aggregation involved in the present photodimerization, the following examinations were undertaken.

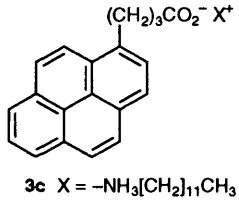
Aqueous solutions of **1b** or **2b** (5.0 mmol dm^{-3}) are clear and viscous (*i.e.*, viscoelastic) at room temp. (~20 °C). These characteristics seem to imply that the ion-pair solutions in water include elongated aggregates. In fact, measurement of dynamic light scattering revealed that these transparent solutions include molecular aggregates with hydrodynamic radius (R_H) of 14.4 and 15.2 nm for **1b** and **2b**, respectively, which are comparable with those of CTASal, a reported, similar surfactant forming rod-like micelles.[17] Since the radii of the aggregates are much larger than those of typical spherical micelles,* it is reasonably assumed that the aggregates are large micelles, *i.e.*, rod-like ones. If the present micelles are assumed to be of rigid rod with contour length of L and cross section radius of r (equal to molecular lengths of **1b** or **2b**, *i.e.*, 2 nm), aggregation numbers (n_A) are estimated to be *ca.* 1×10^3 using eqn. (3) for a

$$R_H = L/\{2 \ln (L/r) - 0.19 - 8.24/\ln (L/r) + 12/[\ln (L/r)]^2\} \quad (3)$$

hydrodynamic radius (R_H) of rod-like particles in fluid medium and the volume occupied by a CTAB molecule in its micelle, 2.44 nm^3.[17b]

Here, L, r and R_H mean rigid rod length (nm), rod diameter (nm) and hydrodynamic radius (nm), respectively. Indeed, static dynamic scattering of an aq. solution of **2b** (5.0 mol dm^{-3}) at 25 °C revealed a similar aggregation number.[19] The estimated values of n_A = *ca.* 1000 is close to 609 from the static dynamic scattering, which verifies the involvement of rod-like micelles.

On the other hand, no dynamic light scattering could be observed at all for solutions of **1c** and **2c** in CCl_4 (5.0 mol dm^{-3}). According to the NMR probe method introduced by Fendler *et al.*[16] **1c** and **2c** in CCl_4 were found to form small molecular aggregates (n_A = 2–4) as reversed premicelles. It is known that alkylammonium propionates form similarly small micelles of reversed type with their polar head groups located in the ionic interior in non-polar solvents.[20]



3c X = $-NH_3[CH_2]_{11}CH_3$

In Table 3 are listed the resulting cmc and n_A values together with those of dodecylammonium 1-pyrenylbutyrate (**3c**). The aggregation numbers show a large difference between the rod-like and reversed premicelles, *i.e.*, 1000 and 2–3, in water and CCl_4, respectively. The addition of 5% methanol to ion-pair **2c** in CCl_4 increased the cmc value from 0.3 to 1.6 mmol dm^{-3}, but did not alter the aggregation number (see entries no. 21 and 22).

Fluorescence Emission Probe for Dodecylammonium Carboxylates.—Fluorescence probe techniques have been widely applied to micelle systems;[21] that is, fluorescence quenchings by a quencher molecule in a micelle are often utilized to determine cmc and n_A values.[22] Typically for micelle systems, the fluorescence intensity is significantly decreased owing to self quenching between probe molecules in the same micelle. This is especially important when surfactants are probe molecules as in the present cases for **1c** and **2c**. Thus, the fluorescence intensity of cinnamate **1c** at 325 nm in CCl_4 decreased with the increasing concentration, and the plots of relative intensity *vs.* [**1c**] shows a break point at 5.0 mmol dm^{-3} (Fig. 4). Similar plots for **2c** afforded a break point at 0.2 mmol dm^{-3}. These cmc values are comparable with those of 3.2 and 0.3 determined by the NMR technique listed in Table 3.

Quite interesting is the observation of excimer fluorescence at 370 nm, in addition to monomer emission at 325 nm, from the reversed premicelle of cinnamate **1c** in hexane. The excimer emission increased with increasing [**1c**] as shown in Fig. 5. At a concentration of 22 mmol dm^{-3} the monomer emission had disappeared almost completely, indicating the absence of monomer or premicelle molecules.

Similarly, 1-pyrenylbutyrate (**3c**), a known fluorescence probe,[16,23] exhibited its excimer emission at 452 nm, in addition to that for the monomer at 385 nm at the intermediate

* Generally, simple micelles are characteristically spherical in shape with a diameter of 2–10 nm.[18]

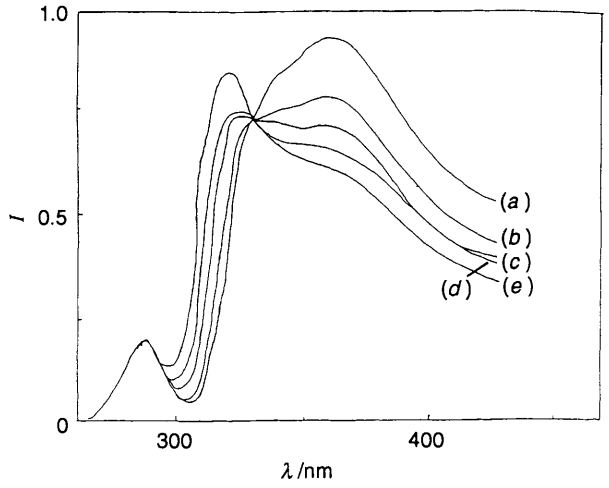


Fig. 5 Concentration dependence of monomer (λ_{max} 325 nm) and excimer emission spectra (λ_{max} 370 nm) from **1c** in hexane. Excitation at 280 ± 20 nm. The concentrations of **1c** were 22.4, 15.0, 9.0, 6.0 and 3.0 mmol dm^{-3} for (*a*), (*b*), (*c*), (*d*) and (*e*), respectively.

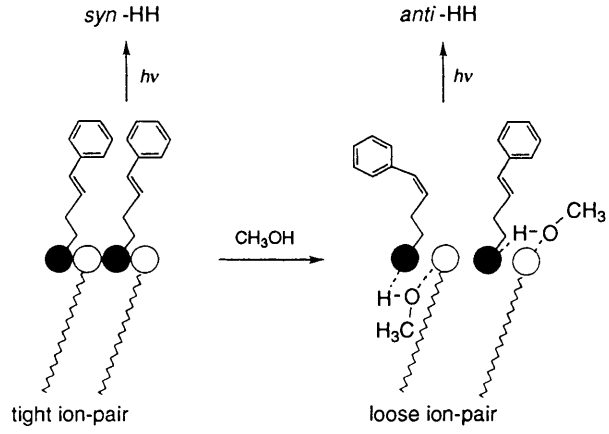


Fig. 6 A simplified picture for the *syn*- and *anti*-selectivity for the photodimerization of cinnamate **1c** in premicelle aggregates: ●, carboxylate ion; ○, ammonium ion

concentration of 0.5 mmol dm^{-3}, below the cmc of 4.5 mmol dm^{-3} in CCl_4. These facts suggest that the aggregate formation starts even at the one-tenth of the cmc. A control experiment showed no observation of excimer emission from 1-pyrenylbutyric acid (**3a**, X = H) in the absence of dodecylamine in methanol.

Divergent syn- *and* anti-*Stereoselectivity of Cyclodimers in Normal and Reversed Micelles.*—The most interesting result for the photocycloaddition of alkylammonium cinnamates and indenecarboxylates is the selective formation of *syn*-HH dimers from small reversed premicelles in non-polar solvents. Addition of methanol to these reversed systems altered the stereochemistry to *anti*-HH dimers, which are also the major product from the reaction in large rod-like micelles in aq. solution. The *syn*-HH dimer is the least stable of the four possible isomers, *syn*-HH, *syn*-HT, *anti*-HH and *anti*-HT. This could be verified by the MM2 calculations for four isomeric dimers from methyl 2-indenecarboxylate; the steric strain energies were 53.6, 51.6, 51.1 and 49.9 kcal mol^{-1} [24] for *syn*-HH, *anti*-HH, *syn*-HT and *anti*-HT, respectively; the *syn*-HH dimer being *ca.* 2 kcal mol^{-1} more unstable reflects the aggregation forms of micelles. The predominant formation of the *syn*-HH dimer in reversed micelles suggests that the ion-pair packing is tight and should be in a *syn*-HH fashion. When a small amount of methanol was added, the tight ion-pair aggregates change into a loose one as depicted in Fig. 6. It is reasonable that in the presence of the polar hydroxylic solvent the loosened ion-pair aggregates yield the more stable *anti*-HH dimer.

Conclusion

Unsaturated carboxylates such as cinnamate and 2-indenecarboxylate, in the presence of long-chain alkylammonium, were found to form rod-like micelles in water and reversed premicelles in carbon tetrachloride. The formation of these micelles was characterized by light scattering measurements, NMR spectroscopy, and fluorescence probe techniques. Photoreactions in aqueous micellar solutions afforded predominantly *anti*-HH dimers, while the reaction of reversed premicelles yielded the least thermodynamically stable *syn*-HH dimers. Addition of a small amount of methanol to the reversed micelle system changed the major product from the *syn*-HH to *anti*-HH dimers. These significant stereochemical selectivities are discussed in terms of organized orientation of olefin molecules.

It is concluded that the reversed premicelles in CCl_4 are tight ion-pair aggregates with *syn*-HH type packing, which are loosened, by addition of a small amount of methanol, to a more stable *anti*-HH type ion-pair.

Experimental

General.—NMR spectra were recorded on Varian Gemini-200 and/or JEOL DX-400 spectrometers; chemical shifts are reported in δ relative to tetramethylsilane as an internal standard; *J* values are given in Hz. Mass spectra were recorded on a JEOL D-300 mass spectrometer with an ionization potential of 20 eV; peaks are reported as *m/z* (% intensity relative to a base peak). UV spectra were recorded on a Shimadzu UV 265 spectrophotometer. IR spectra were recorded on a Hitachi 260-30 spectrophotometer as a solid sample (KBr disk). Gas chromatography was performed on a Shimadzu G180 gas chromatograph with a 1 m column of carbowax 300W operating at 100–260 °C (10 °C min^{-1}). HPLC was recorded on a Shimadzu LC-6A HPLC chromatograph with a Fine sil C18-10 ODS column; eluting solvent: ethanol–water–acetic acid (200:300:2) for cinnamic acid; ethanol–water–acetic acid (220:280:2) for 2-indenecarboxylic acid; and ethanol–aq. triethylamine (0.2 mol dm^{-3}), adjusted to pH 2 by addition of phosphate buffer solution (45:55), for 9-anthracenecarboxylic acid; detected at 222 nm or 240 nm with flow rate of 1.0 cm^{-3} min^{-1}.

Fluorescence spectra were recorded on a Hitachi 650-10 fluorescence spectrophotometer with a xenon lamp. Surface tension was measured by a Shimadzu DuNuy tensiometer at 22 °C. Static and dynamic light scatterings were recorded on an Otsuka Densi DLS-700 dynamic light scattering spectrophotometer. Irradiation was carried out by means of either a Eikosha PIH-300 medium mercury arc lamp (300 W) through a pyrex vessel or a Hamamatsu photonics xenon lamp (450 W) through $CuSO_4 \cdot 5H_2O$ (5.0 g per 100 cm^3) aq. solution of 100 mm thickness (> 365 nm).

Materials. All solvents and reagents were obtained from commercial sources of guaranteed grade and used without further purification, unless otherwise noted. 2-Indenecarboxylic acid was prepared by the reaction of indene with oxalyl bromide, m.p. 225–228 °C (lit.[25] 232–233 °C).

syn- *and* anti-*Head-to-head Dimers of Methyl 2-Indenecarboxylate.*—A solution of $Ca(OH)_2$ (70 mg) and 2-indenecarboxylic acid (300 mg) in degassed water (300 cm^3) was heated to reflux under Ar to give a white powder of calcium 2-indenecarboxylate. The calcium salt (50 mg) dispersed in benzene (100 cm^3) was irradiated for 24 h, acidified with conc.

HCl (10 cm^3) and treated with CH_2N_2. Extraction with CH_2Cl_2 gave the *syn*-head-to-head dimer as a white solid (45 mg).[14] δ_H(200 MHz, $CDCl_3$) 3.2 (d, 2 H, *J* 15), 3.35 (d, 2 H, *J* 15), 3.73 (s, 6 H, 2 CH_3), 4.5 (s, 2 H) and 6.8–6.95 (m, 8 H);* *m/z* 348 (M^+, trace), 317 (M^+ – OMe, 20.1%), 303 (14.3), 289 (M^+ – CO_2Me, 6.9), 288 (9.1), 274 (6.9), 256 (73.2), 229 (18.9), 174 ($M^+/2$, 100), 143 ($M^+/2$ – OMe, 56.6), 129 (27.1) and 115 ($M^+/2$ – CO_2Me, 54.3).

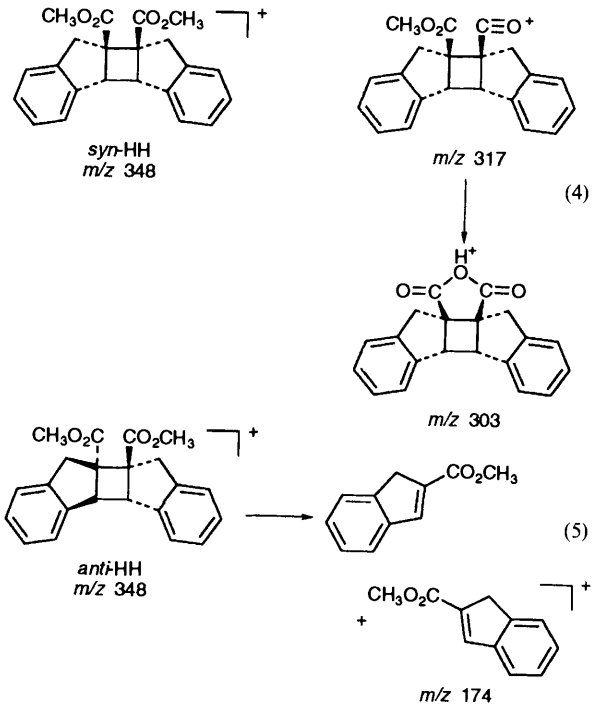
An aq. solution of sodium 2-indenecarboxylate (3.5 g) in water (400 cm^3) was irradiated for 15 h, acidified by addition of excess conc. HCl, and the solution extracted with CH_2Cl_2 affording a white solid. The solid was dissolved in methanol and treated with CH_2N_2 in the presence of H_2SO_4 catalyst. The resulting esters were separated on a SiO_2 column using an eluent of hexane–ethyl acetate (8 : 2 v/v), eluting two components (A) and (B) in addition to the recovered starting olefin (1.0 g). The major component A was found to be the *anti*-HH dimer;[14] (A) (R_f 0.35), 2.5 g (70% yield) and (B) (R_f 0.54). δ_H(200 MHz, $CDCl_3$) 2.95 (d, 2 H, *J* 15), 3.2 (d, 2 H, *J* 15), 3.8 (s, 6 H, 2 CH_3), 4.6 (s, 2 H) and 6.8–7.2 (m, 8 H);[27] *m/z* 348 (M^+, trace), 317 (trace), 289 (M^+ – CO_2Me, 0.4%), 256 (0.4), 229 (1.8), 174 ($M^+/2$, 100), 143 ($M^+/2$ – OMe, 16.2), 129 (13.0) and 115 ($M^+/2$ – CO_2Me, 17.8).

The *syn*- and *anti*-dimers of methyl 2-indenecarboxylate exhibited characteristic fragment sequences: Electron bombardment at 20 eV for the *syn*-HH dimer yields a meta-stable ion at *m/z* 303 by cyclization of the parallel oriented methoxycarbonyl groups *via* the deoxymethylated ion at *m/z* 317 in addition to a monomer base peak at 174 by fragmentation [eqn.(4)]. In contrast, the *anti*-HH dimer was subject only to fragmentation into monomer ion [eqn. (5)] because the cyclization to anhydride is impossible for the anti-parallel oriented methoxycarbonyl groups.

Salts of Unsaturated Carboxylic Acids and Cetyltrimethylammonium Hydroxide.—To a methanol solution of cetyltrimethylammonium hydroxide (0.74 mol dm^{-3}; 7.45 cm^3) was added cinnamic (**1a**) or 2-indenecarboxylic (**2a**) acid (5.54 mmol) in methanol (50 cm^3) and the mixture was sonicated for 10 min, then the solvent removed *in vacuo* to give a white powder (**1b** or **2b**). The IR spectra of **1b** showed the carbonyl stretching vibration bands at 1540 and 1400 cm^{-1} which are characteristic of carboxylate anions.

Salts of Unsaturated Carboxylic Acids and Dodecylamine.—To a solution of dodecylamine (1.03 g) in methanol (50 cm^3) was added a methanol solution of cinnamic acid (**1a**), 2-indenecarboxylic acid (**2a**), or 1-pyrenylbutylic acid (**3a**) (5.54 mmol), the solution was sonicated for 10 min, then the solvent removed by evaporation *in vacuo* to give a white or pale yellow powder (**1c**, **2c** or **3c**). The IR spectra of **2c** showed the disappearance of carbonyl stretching vibration band of free acid at 1660 cm^{-1}. The corresponding C=O absorption for the salt was overlapped with those of the coexisting NH_3^+ and carboxylate ion.

Irradiation of **1b** *in water.* An aq. solution of **1b** (5.0 mmol dm^{-3}; 25 cm^3) was irradiated with a medium Hg lamp for 9 h at ambient temp., then an excess of conc. HCl (10 cm^3) was added and the reaction mixture extracted with diethyl ether (4 × 50 cm^3), the extracts combined and evaporated to give a yellowish viscous semisolid. The reaction mixture was analysed by HPLC; R_t/min, **1b**, 12.7; *cis*-isomer of **1b**, 9.2; *syn*-HH dimer, 17.9; *anti*-HH dimer, 20.9.



Irradiation of **2b** *in water.* An aq. solution of **2b** (5.0 mmol dm^{-3}; 25 cm^3) was irradiated with a medium Hg lamp for 45 min then an excess of conc. HCl (10 cm^3) was added and the reaction mixture extracted with diethyl ether (4 × 50 cm^3), the extracts combined and evaporated to give a yellowish viscous semisolid. The reaction mixture was analysed by HPLC; R_t/min, **2b**, 10.6; *syn*-HH dimer, 14.4; *anti*-HH dimer, 17.2.

Irradiation of **1c** *in* CCl_4. A solution of **1c** in CCl_4 (5.0 mmol dm^{-3}; 25 cm^3) was flushed with an argon stream for 10 min and irradiated with a medium Hg lamp for 10 h, then the reaction mixture was extracted with 1 mol dm^{-3} aq. NaOH (3 × 25 cm^3). The extracts were acidified with conc. HCl (10 cm^3) and the solution extracted with CH_2Cl_2 (3 × 50 cm^3), the extracts combined and evaporated to give yellowish viscous solid. The mixture, having been dried (Na_2SO_4), was treated with diazomethane and the resulting methyl esters were analysed by GLC; R_t/min, **1c**, 6.5; *cis*-isomer of **1c**, 5.0; *syn*-HH dimer, 17.0; *anti*-HH dimer, 17.5.

Irradiation of **2c** *in* CCl_4. A solution of **2c** in CCl_4 (5.0 mmol dm^{-3}; 25 cm^3) was flushed with an argon stream for 10 min and irradiated by a medium Hg lamp for 30 min, then the reaction mixture was extracted with 1 mol dm^{-3} aq. NaOH (3 × 25 cm^3). The extracts were acidified with conc. HCl (10 cm^3), and the solution extracted with CH_2Cl_2 (3 × 50 cm^3), the extracts combined and evaporated to give a yellowish viscous solid. The mixture, having been dried (Na_2SO_4) was treated with CH_2N_2 and the resulting methyl esters were analysed by GLC; R_t/min, **2c**, 7.3; *syn*-HH dimer, 15.7; *anti*-HH dimer, 14.9.

Quantum Yields.—Aq. solutions of **1b** and **2b**, and solutions of **1c** or **2c** in CCl_4 (5.0 mmol dm^{-3}) in quartz optical cells (4.0 cm^3 volume), were flushed with a gentle argon stream for 10 min. Each sample was then irradiated at 313 ± 10 nm through a monochromator with a 150 W xenon lamp. Aliquots (0.5 cm^3) were taken at appropriate time intervals and analysed by HPLC with C18-10 ODS column using aq. ethanol containing *ca.* 0.04% of acetic acid as an eluent. Light quanta absorbed by the sample solutions of **1b** and **2b** in H_2O, and **1c** and **2c** in CCl_4

* On addition of the shift reagent $Eu(tfc)_3$ (Aldrich Co.) to cyclodimers of methyl 2-indenecarboxylate (6.09 mg) in CCl_4–$CDCl_3$ mixed solvent (1 : 1 in v/v) in 0–1.35 ratios of [$Eu(tfc)_3$] : [dimer], the methine protons shifted the most significantly, and methylene and methyl protons shifted slightly in the *anti*-HH dimer. In contrast, these three kinds of protons for the *syn*-HH dimer were all slightly affected by the shift reagent in the same order.

were 7.2×10^{18}, 3.6×10^{18}, 7.2×10^{18} and 1.8×10^{18} quanta per min and transformed 10–20% of the substrates. The results are summarized in Table 1.

Fluorescence Measurements.—Fluorescence spectra of **1c**, **2c** and **3c** in hexane and/or CCl_4 was recorded out on a Hitachi 650-10 spectrophotometer. Fluorescence intensities of **1c** were recorded in a concentration range of 3.0–30.0 mmol dm^{-3} by exciting at 280 ± 2 nm (Fig. 4). For **2c**, relative fluorescence intensities were determined on excitation at 310 ± 2 nm with [**2c**] = 0.006–6.0 mmol dm^{-3} with a break point at around 0.3 mmol dm^{-3}. As for **3c**, the sample solution was excited at 342 ± 2 nm and fluorescence emission was observed at 385 and 452 nm as monomer and excimer maxima, respectively.

NMR Measurements of cmc and Aggregation Numbers.—Solutions of **1c**, **2c** and **3c** in CCl_4 (0.10–44.97 mmol dm^{-3}) were placed in 5 mm NMR tubes with a capillary including 0.03% TMS–$CDCl_3$, and measured at 20 °C with a JEOL DX-400 NMR spectrometer. Chemical shifts of aromatic protons, δ, varied on changing concentration of substrates. According to eqn. (6) derived by Fendler *et al.*,[17] aggregation numbers (n_A)

$$\log (C_D - [s]) = \log n_A K + n_A \log [s] \qquad (6)$$

and cmc were estimated from slopes of plots of log [s] against log (C_D − [s]). Here, C_D, [s], n_A and K are concentration of surfactant, concentrations of dissociated surfactant, aggregation numbers and equilibrium constant of aggregation of surfactant.

Light Scattering Measurements.—Static and dynamic light scatterings were recorded on an Otsuka Densi DLS-700 dynamic light scattering spectrophotometer. Light of 488 nm wavelength from an argon ion laser was used, and the scattering angles were changed from 20–150°. The cell housing was filled with di-n-butyl phthalate and maintained at 25 °C. Solvent and solutions were filtered 5 times through a membrane filter (Advantec; pore size, 0.45 μm). Measurement of specific diffractive index increment was carried out at 25 °C on an Otsuka Densi Differential Refractometer RM-102 by using light of 488 nm wavelength. The apparatus was calibrated with aq. solutions of sucrose. Measurement of dynamic light scattering was performed in the homodyne mode according to the literature.[16]

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References

1 (*a*) K. Kalyanasundaram, *Photochemistry in Microheterogeneous Systems*, Academic Press, Orland, Florida, 1987; (*b*) V. Ramamurthy, *Tetrahedron*, 1986, **42**, 5753; (*c*) M. A. Fox, *Organic Phototransformations in Non-homogeneous Media*, American Chemical Society, Washington D.C., 1985; (*d*) J. K. Thomas, *The Chemistry of Excitation at Interfaces, ACS Monograph 181*; The American Chemical Society, Washington, D.C., 1984.

2 N. J. Turro, M. Gratzel and A. M. Braun, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 675.

3 (*a*) M. Anpo, T. Wada and Y. Kubokawa, *Bull. Chem. Soc. Japan*, 1977, **50**, 31; (*b*) L. Horner and J. Klaus, *Liebigs Ann. Chem.*, 1981, 782; (*c*) R. K. Bauer, R. Borenstein, P. deMayo, K. Okada, M. Rafalska, W. R. Ware and K. C. Wu, *J. Am. Chem. Soc.*, 1982, **104**, 4635; (*d*) R. Farwara, P. deMayo, J. H. Schaulbe and Y. C. Toong, *J. Org. Chem.*, 1985, **50**, 245; (*e*) D. Avnir, E. Wellner and M. Ottolenghi, *J. Am. Chem. Soc.*, 1989, **111**, 2001; (*f*) N. J. Turro, M. B. Zimmt, I. R. Gould and W. Mahle, *J. Am. Chem. Soc.*, 1985, **107**, 5826.

4 (*a*) R. A. DellaGuardla and J. K. Thomas, *J. Phys. Chem.*, 1983, **87**, 990; (*b*) G. Villemure, C. Detellier and A. G. Szabo, *J. Am. Chem. Soc.*, 1985, **107**, 5826; (*c*) G. Villemure, H. Kodama and C. Detellier, *Can. J. Chem.*, 1985, **63**, 1139; (*d*) P. K. Ghosch and A. J. Bard, *J. Phys. Chem.*, 1984, **88**, 5519; (*e*) A. Habti, D. Keravis, P. Levitz and H. van Damme, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 67; (*f*) H. Nijs, H. van Damme, F. Bergaya, A. Habti and J. J. Fripiat, *J. Mol. Catal.*, 1983, **21**, 223.

5 (*a*) I. Tabushi, S. Kugimiya and T. Mizutani, *J. Am. Chem. Soc.*, 1983, **105**, 1658; (*b*) K. Takagi, N. Miyake, E. Nakamura, H. Usami and Y. Sawaki, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 3475.

6 (*a*) H. Eckhardt, A. Bose and V. A. Krongauz, *Polymer*, 1987, 1959; (*b*) V. A. Krongauz, *Isr. J. Chem.*, 1979, **18**, 304; (*c*) V. A. Krongauz and E. S. Goldburt, *Macromolecules*, 1981, **14**, 1382; (*d*) E. Ando, J. Hibino, T. Hashida and T. Morimoto, *Thin Solid Films*, 1988, **160**, 279.

7 (*a*) M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 1996; (*b*) G. M. J. Schmidt, *J. Pure Appl. Chem.*, 1971, **27**, 647; (*c*) M. D. Cohen, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 386; (*d*) M. D. Cohen, G. M. J. Schmidt and F. I. Sonntag, *J. Chem. Soc.*, 1964, 2000; (*e*) G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2014.

8 (*a*) T. Nakano and H. Hirata, *Bull. Chem. Soc. Japan*, 1982, **55**, 947; (*b*) J. M. Nerbonne and R. G. Weiss, *J. Am. Chem. Soc.*, 1978, **100**, 2571; (*c*) J. M. Nerbonne and R. G. Weiss, *J. Am. Chem. Soc.*, 1979, **101**, 402; (*d*) T. Kuneida, T. Takahashi and M. Hirobe, *Tetrahedron Lett.*, 1983, **24**, 5107; (*e*) G. Aviv, J. Sagiv and A. Yogev, *Mol. Cryst. Liq. Cryst.*, 1976, **36**, 349; (*f*) Y. Tanaka, H. Tuchiya, M. Suzuki and K. Tsuda, *Mol. Cryst. Liq. Cryst.*, 1981, **68**, 113.

9 (*a*) T. Wolff, *J. Photochem.*, 1981, **16**, 343; (*b*) T. Wolff and N. Muller, *J. Photochem.*, 1983, **23**, 131; (*c*) T. Wolff and N. Muller, *J. Photochem.*, 1983, **22**, 61.

10 (*a*) F. H. Quina, D. Mobius, F. A. Carroll, F. R. Hopf and D. G. Whitten, *Z. Phys. Chem. N. F.*, 1976, **101**, 151; (*b*) F. H. Quina and D. G. Whitten, *J. Am. Chem. Soc.*, 1977, **99**, 877.

11 (*a*) A. Ueno, F. Moriwaki, A. Azuma and T. Osa, *J. Org. Chem.*, 1989, **54**, 295; (*b*) A. Ueno, F. Moriwaki, Y. Iwama, I. Suzuki, T. Osa and T. Ohta, S. Nozoe, *J. Am. Chem. Soc.*, 1991, **113**, 7034.

12 (*a*) K. Takagi, B. R. Suddaby, S. L. Vadas, C. A. Backer and D. G. Whitten, *J. Am. Chem. Soc.*, 1986, **108**, 7865; (*b*) K. Takagi, H. Fukaya, N. Miyake and Y. Sawaki, *Chem. Lett.*, 1988, 1053; (*c*) K. Takagi, E. Nambara, H. Usami, M. Itoh and Y. Sawaki, *J. Chem. Soc., Perkin Trans. 1*, 1991, 655.

13 (*a*) K. Takagi, H. Usami, H. Fukaya and Y. Sawaki, *J. Chem. Soc., Chem. Commun.*, 1989, 1174; (*b*) H. Usami, K. Takagi and Y. Sawaki, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1723; (*c*) H. Usami, K. Takagi and Y. Sawaki, *Bull. Chem. Soc. Japan*, 1991, **64**, 3395; (*d*) H. Usami, K. Takagi and Y. Sawaki, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 77; (*e*) H. Usami, K. Takagi and Y. Sawaki, *Chem. Lett.*, 1992, 1405.

14 F. D. Lewis, S. L. Qillen, P. D. Hale and J. L. Oxman, *J. Am. Chem. Soc.*, 1988, **110**, 1261.

15 (*a*) T. Majima, C. Pac and H. Sakurai, *J. Am. Chem. Soc.*, 1980, **102**, 5265; (*b*) W. Mettzner and D. Wendisch, *Justus Liebigs Ann. Chem.*, 1969, **730**, 111.

16 (*a*) E. J. Fendler, J. H. Fendler, R. T. Medary and O. A. El Seoud, *J. Phys. Chem.*, 1973, **77**, 1432; (*b*) J. H. Fendler, E. J. Fendler, R. T. Medary and O. A. El Seoud, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 280.

17 (*a*) T. Imae, *J. Phys. Chem.*, 1990, **94**, 5953; (*b*) T. Imae, K. Hashimoto and S. Ikeda, *Colloid Polym. Sci.*, 1990, **268**, 460.

18 J. H. Fendler, *Membrane Mimetic Chemistry*, Wiley-Interscience, New York, 1982.

19 T. Imae, O. Mori, K. Takagi, M. Itoh and Y. Yawaki, Unpublished results.

20 A. Kitahara, *Cationic Surfactants*, ed. E. Jungerman, Marcel Dekker, New York, 1970.

21 M. Grätzel and J. K. Thomas, *Modern Fluorescence Spectroscopy*, ed. E. L. Wehry, vol. 2, Plenum Press, New York, 1976, p. 169.

22 (*a*) N. J. Turro and A. Yekta, *J. Am. Chem. Soc.*, 1978, **100**, 5951; (*b*) P. P. Infelta, *Chem. Phys. Lett.*, 1979, **61**, 88.

23 S. S. Atik and L. A. Singer, *J. Am. Chem. Soc.*, 1979, **101**, 6759.

24 (*a*) N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127; (*b*) A. Allinger, Y. Yuh, *QCPE*, 1980, **12**, 395.

25 W. H. Perkin and G. Revay, *J. Chem. Soc.*, 1893, **65**, 228.

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