

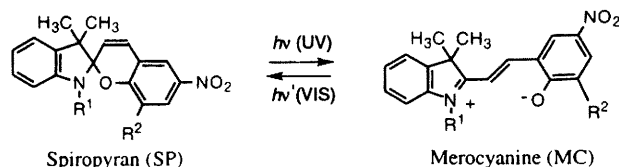
# Photochromic behaviour of surfactant spiro[2*H*-1-benzopyran-2,2'-[2,3]-dihydroindole]s (spiropyrans) adsorbed into clay interlayers

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Spiro[2*H*-1-benzopyran-2,2'-[2,3]-dihydroindole]s (abbreviated as spiropyrans) containing long  $\omega$ -pyridinoalkyl chains have been intercalated into clay interlayers and studied to observe the photochromic characteristics of the resulting molecular assemblies. 1'-Octadecyl-3',3'-dimethyl-6-nitro-8-pyridinomethyl- (SP1801<sup>+</sup>), 1'-(10-pyridinododecyl)-3',3'-dimethyl-6-nitro- (SP10<sup>+</sup>00) and 1'-(10-pyridinododecyl)-3',3'-dimethyl-6-nitro-8-icosylcarbonyloxymethyl-spiropyrans (SP10<sup>+</sup>22) were all quantitatively intercalated into the clay interlayer and exhibit normal photochromism in aqueous clay dispersions. Their thermal decolourations obey simple first-order kinetics and are about one-tenth as slow in clay dispersions and about one-hundredth as slow in clay films as that in bulk solution without clay at 50 °C. However, 1',3',3'-trimethyl-6-nitro-8-pyridinomethylspiropyran (SP0101<sup>+</sup>), a homologue without a long alkyl chain, exhibits inverse photochromism and its thermal decolouration undergoes two kinds of first-order kinetics in aqueous clay dispersions. These results are explicable in terms of the restricted conformational motions of the intercalated spiropyrans.

In the previous paper, the authors reported on the photochromism of 1',3',3'-trimethyl-6-nitro-8-pyridinomethylspiro[2*H*-1-benzopyran-2,2'-[2,3]-dihydroindole]s [abbreviated as 8-pyridinomethylspiropyran (SP0101<sup>+</sup>)] intercalated into montmorillonite clay interlayers.<sup>1</sup> It is well known that in clay interlayers cationic guests are accommodated efficiently by an exchange with, for example, sodium ions and can form a molecular aggregate similar to a mono- or bi-layer assembly.<sup>2,3</sup> Cationic spiropyran SP0101<sup>+</sup> is shown to be accommodated quantitatively into clay interlayers and is equilibrated with the corresponding merocyanine (MC), the ratio SP:MC being 35:65 and hence exhibiting inverse photochromism.



Along with the studies of the photochromic behaviour of molecular assemblies formed in the interlayers of inorganic minerals, the present authors have undertaken a study of a series of surfactant spiropyrans organized in restricted spaces. This is based on the principle that clays can form a mono- or bi-layer in the interlayers. Thus, cationic surfactants such as cetyltrimethylammonium bromide (CTAB) have been reported to form a bilayer film in montmorillonite, similar to the case of Langmuir-Blodgett films.<sup>4,5</sup>

## Experimental

UV-VIS spectra were recorded on a Shimadzu UV-265 spectrophotometer. Fluorescence spectra were obtained with a Hitachi 650-10 fluorescence spectrophotometer. HPLC analyses were carried out with a Jasco HPLC instrument (Model UVIDEC 100 III) detected at 250 nm using a 30 cm SIL column (Jasco) eluting with CH<sub>2</sub>Cl<sub>2</sub> as an eluent. GLC analyses were performed with a Yanagimoto G180 gas chromatograph using 1 or 2 m column of carbowax 300M at 80–260 °C. NMR spectra were recorded on a Varian Gemini-200

NMR spectrometer. Mass spectra were taken with a JEOL high resolution mass spectrometer (Model D-300) employing a direct inlet system; an ionization potential of 20 eV was used. Melting points are corrected.

## Materials

The following cationic spiropyrans were synthesized.

SP0101<sup>+</sup>: 8-Chloromethyl-1',3',3'-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2'-[2,3]-dihydroindole] was prepared by the reaction of 1,3,3-trimethyl-2-methylidene-2,3-dihydroindole with 3-chloromethyl-2-hydroxy-5-nitrobenzaldehyde,<sup>6</sup> mp 133.5–135 °C (lit.,<sup>7</sup> mp 133–134 °C). To the above 2,3-dihydroindole (1 g) dissolved in benzene (60 cm<sup>3</sup>) was added pyridine (10 cm<sup>3</sup>) and the solution was refluxed for a day. The resulting precipitate was filtered off and obtained as a yellow powder;  $\delta$ (CDCl<sub>3</sub>) 9.0 (1 H, d, *J* 2), 8.7 (2 H, m), 8.3 (1 H, m), 8.1 (1 H, d, *J* 2), 7.7 (2 H, m), 7.3 (1 H, m), 7.1 (1 H, m), 7.0 (2 H, m), 6.5 (1 H, d, *J* 7), 6.0 (2 H, d, *J* 12), 5.9 (1 H, d, *J* 7), 2.49 (3 H, s, Me), 1.2 (3 H, s, Me) and 1.0 (3 H, s, Me).

SP1801<sup>+</sup>: 3,3-Dimethyl-1-octadecyl-2,3-dihydroindole was obtained by heating 2,3,3-trimethyl-2,3-dihydroindole (5.2 g, 32 mmol) with a slight excess of octadecylammonium bromide (15.8 g, 48 mmol) followed by dehydrobromination by treatment with conc. aq. NaOH (8 g; 50 cm<sup>3</sup>), yield 4.2 g (84.1%). To a solution of 3-chloromethyl-2-hydroxy-5-nitrobenzaldehyde (1.05 g, 4.87 mmol) in benzene (100 cm<sup>3</sup>) was added the above octadecyldihydroindole (2.0 g, 4.9 mmol) and the mixture was refluxed for 5 h, removing H<sub>2</sub>O in the presence of anhyd. MgSO<sub>4</sub> powder. The mixture was reduced in volume and purified by passing through a SiO<sub>2</sub> column with a mixed solvent (benzene-ethyl acetate, 8:2); mp 159.0–161.0 °C (lit.,<sup>8</sup> 160–162 °C), yield 1.03 g (34.8%). Its pyridinium salt, SP1801<sup>+</sup>, was obtained by heating with a large excess of pyridine (20 cm<sup>3</sup>) for 72 h in chloroform (20 cm<sup>3</sup>).

SP10<sup>+</sup>00: 1'-(10-Bromodecyl)-3',3'-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2'-[2,3]-dihydroindole] was synthesized by the coupling, for 5 h in butan-2-one of 5-nitro-2-hydroxybenzaldehyde (1.55 g, 9.3 mmol) with 1'-(10-bromodecyl)-3',3'-dimethyl-2-methylidene-2,3-dihydroindole (3.52 g, 9.3 mmol) which was prepared from the reaction of 1,10-dibromodecane with 2,3,3-trimethyl-2,3-dihydroindole. After

the reaction, the mixture was condensed under reduced pressure and purified by passing through a  $\text{SiO}_2$  column with a mixed solvent (benzene–hexane, 8:2) yield 1.48 g, (30%). Its pyridinium salt,  $\text{SP10}^+\text{00}$ , was obtained by refluxing for 72 h with a large excess of pyridine ( $20\text{ cm}^3$ ) in chloroform ( $20\text{ cm}^3$ ); yield 0.82 g (48%).

$\text{SP10}^+\text{22}$ : 1'-(10-Bromodecyl)-8-docosanoyloxymethyl-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-[2,3]-dihydroindole] was similarly synthesized by the reaction of 1'-(10-bromodecyl)-3',3'-dimethyl-2-methylidene-2,3-dihydroindole (1.82 g, 4.81 mmol) with 3-docosanoyloxymethyl-2-hydroxy-5-nitrobenzaldehyde (2.52 g, 4.78 mmol); yield 1.63 g (38.4%). Its pyridinium salt,  $\text{SP10}^+\text{22}$ , was obtained by the reaction of the above 2,3-dihydroindole (1.63 g, 1.84 mmol) with a large excess of pyridine ( $20\text{ cm}^3$ ) in chloroform ( $20\text{ cm}^3$ ). After reducing the volume, the reaction mixture was chromatographed on a  $\text{SiO}_2$  column. Eluting with a mixed solvent of benzene and hexane (8:2) gave unchanged starting materials. The target material remaining in the column was eluted with methanol and purified with GPC employing a polystyrene bead column (30 cm length) (Japan Analytical Ind., JAIGEL-2H), yield 0.85 g (48.2%).

#### Intercalation of surfactant spiropyrans in montmorillonite clays

The clay mineral employed in this study, Kunipia F (a purified montmorillonite) was a kind gift from Kunimine Ind. (Japan);  $\text{Na}_x(\text{Al}_{2-x})(\text{SiO}_4\text{O}_{10})(\text{OH})_2 \cdot m\text{H}_2\text{O}$ ,  $x = 0.33$  and its anion exchange capacity is 119 mequiv./100 g. An aqueous dispersion of Kunipia F (1 mequiv./ $1000\text{ cm}^3$ ) was essentially transparent above 300 nm. The degree of intercalation of SP was estimated by measuring the filtrate solution by a membrane filter. The concentration of dissolved SP in the filtrate was measured by the absorbance at 340 nm ( $\epsilon = 9500\text{ m}^2\text{ mol}^{-1}$ ). The degree of intercalation of CTAB onto the clay interlayers was estimated by employing Orange II as a probe.<sup>9</sup>

**In water.** To an aqueous clay dispersion (5.0 mequiv./ $1000\text{ cm}^3$ ) was added an appropriate amount of aqueous surfactant spiropyran ( $1.0 \times 10^{-4}\text{ mol dm}^{-3}$ ), mixed with a homogenizer and then stirred magnetically at ca.  $20^\circ\text{C}$  to yield SP intercalated clay dispersion.

**In organic solvents. Method (A).**—To an aqueous clay dispersion (5.0 mequiv./ $1000\text{ cm}^3$ ) was added aqueous surfactant spiropyran ( $2 \times 10^{-4}\text{ mol dm}^{-3}$ ) and surfactant (DSDAB or CTAB) ( $8 \times 10^{-4}\text{ mol dm}^{-3}$ ). These were mixed with a homogenizer and then stirred magnetically at ca.  $20^\circ\text{C}$ . The resulting SP intercalated clay precipitate was filtered off with a membrane filter (Toyo Roshi Kaisha, Ltd., pore size  $0.45\text{ }\mu\text{m}$ ) and dried overnight *in vacuo*, and then dispersed in hydrophobic solvents such as benzene and decanol and diluted to any necessary concentrations by the same solvents.

**Method (B).**—To a  $500\text{ cm}^3$  round flask was added a chloroform solution of a mixture of surfactant spiropyrans ( $2 \times 10^{-4}\text{ mol dm}^{-3}$ ) and DSDAB ( $8 \times 10^{-4}\text{ mol dm}^{-3}$ ), and then the solvent was evaporated *in vacuo* to make a thin film inside the wall. To an essentially transparent dispersion of the thin film in water (dispersed by a supersonic homogenizer) was added an aqueous clay suspension (5.0 mequiv./ $1000\text{ cm}^3$ ) during warming at  $70^\circ\text{C}$ . The resulting precipitate was filtered off and dried overnight *in vacuo*.

#### Measurement of quantum yields

A 150 W xenon lamp (Hitachi fluorescence spectrophotometer, Model 650-10) was used as a light source in combination with a monochromator, emitting  $520 \pm 10\text{ nm}$ . To an optical quartz cell (10 mm length) was added  $3.0\text{ cm}^3$  of an appropriate solution including  $10^{-4}\text{ mol dm}^{-3}$  surfactant spiropyran intercalated into the interlayers of montmorillonite clay and irradiated with the above visible light after bubbling with argon gas for 10 min. Consumption of the starting SP was monitored

by measuring its absorbance maximum at one minute intervals during irradiation. The quantum yields for the decolouration of the sample spiropyrans were calculated by means of relative reactivities based on that of 1',3',3'-trimethyl-6-nitrospiropyran in methanol, 0.10.<sup>10</sup>

#### Measurement of rate constants of thermal isomerizations between SP and MC

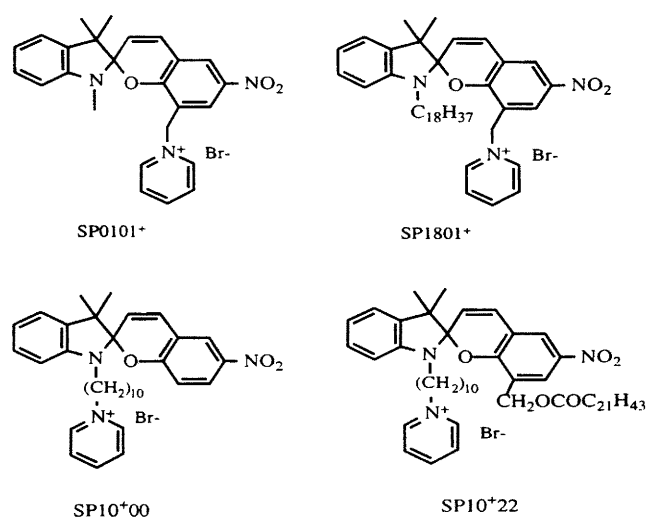
The concentrations of MC were measured by a UV spectrophotometer (Shimadzu, Model UV-265), which was thermostatted at  $50 \pm 0.5^\circ\text{C}$ . A  $3.0\text{ cm}^3$  sample of surfactant spiropyran was put into an optical quartz cell and purged by an argon stream for 10 min. After irradiation with either UV ( $>300\text{ nm}$ ) or visible light (150 W halogen lamp) in order to shift the equilibrium state between SP and MC, retrieval processes from MC to SP or SP to MC were followed by measuring the absorbance of MC monitoring at the  $\lambda_{\text{max}}$ .

A simple first-order rate constant was obtained by means of computer fitting utilizing a least squares method, where the absorption coefficient of MC is assumed to be 30 000.

## Results and discussion

#### Adsorption of surfactant spiropyrans

The cationic spiropyrans,  $\text{SP0101}^+$ ,  $\text{SP1801}^+$ ,  $\text{SP10}^+\text{00}$  and  $\text{SP10}^+\text{22}$  were prepared by the reaction of appropriate indolium



ions with substituted 5-nitrosalicylaldehydes followed by quaternization with pyridine. Each of these spiropyrans were adsorbed onto purified montmorillonite, Kunipia F, and all exhibited photochromism.

Their adsorption efficiencies on the clay were quite high as shown in Table 1. The thermal equilibrated ratios of MC:SP at ambient temperature vary depending on the substituents and dispersing solvents. The ratios of MC:SP for the surfactant spiropyrans in aqueous dispersions increase with the increasing hydrophobicity of the substituents in the order  $\text{SP0101}^+ < \text{SP1801}^+ < \text{SP10}^+\text{22}$ . In the case of  $\text{SP10}^+\text{00}$ , the ratio could not be estimated on account of further decomposition of the corresponding merocyanine (MC).

The absorption maximum of MCs may be an index of the local polarity of their surroundings. Table 1 includes the ratios and absorption maxima of MC intercalated in the presence and absence of co-adsorbed DSDAB (distearyldimethylammonium bromide). Added DSDAB occupies 80% of the available adsorption sites in the interlayers and the remaining 20% of the adsorption sites were occupied by surfactant spiropyrans. Here, DSDAB, a self-assembled surfactant in water, was employed in

**Table 1** Physical properties of surfactant spiropyran intercalated in montmorillonite

Spiropyran (SP)	Adsorption degree (%) <sup>a</sup>	In water <sup>b</sup>		In decanol <sup>c</sup>	
		MC:SP	$\lambda_{\max}$ of MC/nm	MC:SP	$\lambda_{\max}$ of MC/nm
SP0101 <sup>+</sup>	90	65:35	510	8:92	540
SP1801 <sup>+</sup>	97	49:52	530	4:96	540
SP10 <sup>+</sup> 00	95			9:91	575
SP10 <sup>+</sup> 22	91	25:75	561	36:64	575
				(43:57)	565) <sup>d</sup>

<sup>a</sup> Aqueous clay colloid (5.0 mequiv./1000 cm<sup>3</sup>) was sonicated at ca. 20 °C with an equivalent amount of spiropyran ( $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>) based on CEC in aqueous suspension. <sup>b</sup> SP0101<sup>+</sup>, SP1801<sup>+</sup> and SP10<sup>+</sup>22 were intercalated 20%, 5% and 4%, respectively, based on available amounts of adsorption sites of clay. <sup>c</sup> SP0101<sup>+</sup>, SP1801<sup>+</sup>, SP10<sup>+</sup>01 and SP10<sup>+</sup>22 were intercalated 15%, 20%, 20% and 20%, respectively, based on available amounts of adsorption sites of clay modified by adsorption of DSDAB (degree of intercalation: 80%). <sup>d</sup> In film obtained from filtration of the above suspension with a membrane filter *in vacuo*.

**Table 2** Effect of reaction media on first-order rate constants of mutual isomerizations between surfactant spiropyran and merocyanines intercalated in montmorillonite<sup>a</sup>

Spiropyran (SP)	Intercalation of SP (%) <sup>b</sup>	Co-intercalant (%)	K <sup>c</sup>	Rate constant/s <sup>-1</sup>	
				10 <sup>5</sup> k <sub>SP→MC</sub>	10 <sup>5</sup> k <sub>MC→SP</sub>
(a) Dispersed in water					
SP0101 <sup>+</sup>	5	—	26/74	53, 50	d
	10	—	32/68	75, 12	d
	20	—	35/65	91, 19	d
SP1801 <sup>+</sup>	2.5	—	54/46	44	52
	5	—	52/48	72	78
SP10 <sup>+</sup> 22	4	—	75/25	130	390
(b) Dispersed in decanol					
SP0101 <sup>+</sup>	10	CTAB (80)	92/8	4.6	52
	15	DSDAB (80)	92/8	6.0	69
SP1801 <sup>+</sup>	20	DSDAB (80)	96/4	2.7	64
SP10 <sup>+</sup> 00	20	DSDAB (80)	91/9	6.3	67
SP10 <sup>+</sup> 22	20	DSDAB (80)	64/36	170	310
	20 (film) <sup>e</sup>	DSDAB (80)	57/43	30	39
(c) In homogeneous solution without clay					
SP0101 <sup>+</sup>	—	H <sub>2</sub> O	53/47	13	15
	—	CH <sub>3</sub> CN	66/34	65	130
	—	CHCl <sub>3</sub>	90/10	93	840
SP1801 <sup>+</sup>	—	H <sub>2</sub> O	50/50	46	46
	—	CH <sub>3</sub> CN	52/48	92	100
	—	CHCl <sub>3</sub>	80/20	130	520
SP10 <sup>+</sup> 00	—	CH <sub>3</sub> CN	98/2	6.5	400
	—	CHCl <sub>3</sub>	99/1	6.3	690
SP10 <sup>+</sup> 22	—	CH <sub>3</sub> CN	92/8	190	2200
	—	CHCl <sub>3</sub>	95/5	240	4500

<sup>a</sup> Measured at  $50 \pm 0.5$  °C. <sup>b</sup> Aqueous clay colloid (5.0 mequiv./1000 cm<sup>3</sup>) was sonicated at around 20 °C with an equivalent amount of spiropyran ( $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>) based on CEC in aqueous suspension. <sup>c</sup>  $k_{MC \rightarrow SP}/k_{SP \rightarrow MC}$ . <sup>d</sup> Too slow to be measured. <sup>e</sup> Film samples held by two sheets of optical quartz plates.

order to increase the hydrophobicity in the interlayer. The Table shows that except for SP10<sup>+</sup>22 the absorption maxima shift to longer wavelength as the ratio of MC to SP decreases. This fact is understood in terms of the instability of the corresponding ionic MC form. In the case of SP10<sup>+</sup>22, in spite of shifts of its absorption maximum to longer wavelength (*i.e.*, 575 nm), the MC content in an equilibrium mixture is relatively high, which implies that the spiropyran resides in a rather poor hydrophilic environment. These differences might be attributed to the structural difference between non-planar SP and planar MC. MC might prefer to be seated in molecular assemblies owing to the parallel-orientation of the two long alkyl chains attached to the indolium and salicyl rings, while the perpendicular orientation of the two long alkyl chains of the spiro ring of SP10<sup>+</sup>22 does not fit such an assembly.

This is not the case with spiropyran bearing only one long alkyl chain such as SP0101<sup>+</sup> and SP1801<sup>+</sup>.

#### Thermal isomerization between MC and SP

The rates of thermal isomerizations between SPs (SP0101<sup>+</sup>, SP1801<sup>+</sup>, SP10<sup>+</sup>00 and SP10<sup>+</sup>22) and their MCs were analysed at  $50 \pm 0.5$  °C in montmorillonite clay dispersions. As shown in Table 1, all the spiropyran exist as equilibrium mixtures between MC and SP in the clay dispersions. Hence, the colouration process (SP  $\rightarrow$  MC) was followed by employing unequilibrated samples irradiated at an absorption maximum of the MC. On the other hand, the decolouration rate was monitored by using a MC enriched sample which was produced by irradiation at  $340 \pm 10$  nm. The apparent rate constant,  $k_{\text{obsd}}$ , is expressed by the sum of the forward,  $k_{SP \rightarrow MC}$  and

**Table 3** Quantum yields for the conversion of merocyanines into spiropyrans intercalated in montmorillonite<sup>a</sup>

Spiropyran (SP)	Intercalation of SP (%)	Co-intercalant (%)	$\lambda_{\text{max}}$ of merocyanine	Quantum yield ( $\Phi_{\text{MC} \rightarrow \text{SP}}$ )
(a) Dispersed in water				
SP0101 <sup>+</sup>	10	—	510	0.011
	20	—	510	0.016
SP1801 <sup>+</sup>	2.5	—	530	0.066
	5	—	530	0.060
(b) Dispersed in decanol				
SP0101 <sup>+</sup>	20	DSDAB (80)	540	0.11
SP1801 <sup>+</sup>	20	DSDAB (80)	540	0.10
(c) In solution without clay				
SP0101 <sup>+</sup>	—	CH <sub>3</sub> OH	522	0.34
	—	C <sub>10</sub> H <sub>21</sub> OH	560	0.28
SP1801 <sup>+</sup>	—	CH <sub>3</sub> OH	528	0.34
	—	C <sub>10</sub> H <sub>21</sub> OH	566	0.37

<sup>a</sup> A 150 W Xenon lamp was used as a light source with a monochromator, emitting 520 ± 10 nm.

backward rate constants,  $k_{\text{MC} \rightarrow \text{SP}}$ , as mutual isomerizations between SP and MC should occur thermally as shown in eqn. (2).



$$k_{\text{obsd}} = k_{\text{SP} \rightarrow \text{MC}} + k_{\text{MC} \rightarrow \text{SP}} \quad (3)$$

Rate constants,  $k_{\text{SP} \rightarrow \text{MC}}$  and  $k_{\text{MC} \rightarrow \text{SP}}$  for the isomerization of SP to MC and MC to SP are expressed as eqns. (4) and (5),

$$k_{\text{SP} \rightarrow \text{MC}} = \frac{1}{1 + K} k_{\text{obsd}} \quad (4)$$

$$k_{\text{MC} \rightarrow \text{SP}} = \frac{K}{1 + K} k_{\text{obsd}} \quad (5)$$

$$(K = k_{\text{MC} \rightarrow \text{SP}}/k_{\text{SP} \rightarrow \text{MC}})$$

respectively, when an equilibrium constant for eqn. (2) is written as  $K$ . Both processes were clearly subject to simple first-order kinetics except for the case of SP0101<sup>+</sup>. The results are compiled in Table 2.

An analysis of the kinetics of a thermal isomerization sometimes provides information about the molecular level heterogeneity of the reaction. Thus, as reported in the preceding paper,<sup>1</sup> SP0101<sup>+</sup> exhibits two-component first-order kinetics with faster ( $k_1$ ) and slower rate constants ( $k_1'$ ), the ratios of which changed linearly with degree of adsorption in the interlayers.

$$A_{\infty} - A_0 = C_1 \exp(-k_1 t) + C_2 \exp(-k_1' t) \quad (6)$$

Here,  $A_{\infty}$  and  $A_0$  are the absorbance at time  $t$  and at infinite time, respectively;  $C_1$  and  $C_2$  denote fractions of faster and slower components, respectively.

We have proposed that SP0101<sup>+</sup> molecules are heterogeneously accommodated in the interlayers. In the interlayer space, some of the SP0101<sup>+</sup> molecules aggregate, whilst some of them are isolated. It is naturally expected that the fraction of the aggregated form increases at the expense of isolated ones which go to increase the degree of intercalation. This has been

observed in the intercalation of SP0101<sup>+</sup> into clay from water. However, such a phenomenon was not observed with the surfactant spiropyran even with a low degree of intercalation (*ca.* 5%). For example, SP1801<sup>+</sup> and SP10<sup>+</sup>22 in aqueous or organic solvents–clay suspensions exhibit simple first-order kinetics (Table 2), suggesting that these surfactant spiropyran are quite easy to self-assemble. A similar tendency has been observed in the photochemical cyclodimerization of hydrophobic stilbazolium ions organized in saponite clay interlayers, where the olefin molecules are found to self-assemble under very low degrees of intercalation (*ca.* 0.1%).<sup>11</sup>

SP0101<sup>+</sup> exists preferentially as the MC form in aqueous solution, but changes to SP as a major form in hydrophobic solvents, *e.g.*, chloroform. In contrast, SP1801<sup>+</sup>, SP10<sup>+</sup>00 and SP10<sup>+</sup>22 always form SP, irrespective of the change of solvent from hydroxylic to non-hydroxylic. These surfactant spiropyran, themselves hydrophobic, are difficult to dissolve in water and always exist as SP. Table 2 summarizes the rate constants for mutual thermal isomerizations of clay intercalated surfactant spiropyran and compares them with those without clay. For SP0101<sup>+</sup>, the inverse photochromism in an aqueous clay dispersion changed to the normal one in 80% DSDAB co-adsorbed clay dispersion in decanol, implying a hydrophilic to hydrophobic change of the local environments. Most importantly, the isomerizations are greatly suppressed by intercalation in the clay interlayer when compared with those of the corresponding homogeneous solutions. The suppression is largely due to the steric restriction of molecular isomerization. Similar tendencies are also observed in the cases of SP10<sup>+</sup>00, SP1801<sup>+</sup> and SP10<sup>+</sup>22. Such suppressing effects have occasionally been reported in local heterogeneous systems.<sup>12</sup> For example, the thermal isomerization of anionic spiropyran was, when dissolved in an AOT reversed micelle, found to be 10 to 20 times slower than those in homogeneous solutions.<sup>13</sup> A similar effect was noted with spiropyran included in a bilayer film formed by dipalmitoylphosphatidylcholine.<sup>14</sup> A variation of aggregation morphology in liquid crystals of potassium laurate or sodium decylsulfate caused a discontinuous change of the thermal isomerization of spiropyran included in the system.<sup>15</sup>

Ando *et al.* have reported that a Langmuir–Blodgett film of SP with two long alkyl chains (SP1822) forms a quite stable J-aggregated MC.<sup>16</sup> The structure of SP18<sup>+</sup>22 is similar to that of SP1822 except for having a pyridinium substituent at the terminal carbon atom of the octadecyl group. Nonetheless, no intense absorption was observed in the visible region with the



SP18<sup>+</sup>22 aggregate in the clay interlayer, although an organized form was implied by the significant retardation of MC  $\rightarrow$  SP isomerization. The cation-adsorbing sites of the clay are scattered on both sides of the interlayer surfaces, with average intervals of *ca.* 10 Å as estimated by the lattice constant and molecular composition.<sup>17</sup> The disposition of SP18<sup>+</sup>22 at 10 Å intervals might be somewhat too far to form a stable J-aggregate, compared to the reported bilayer system.

#### Photochemical decolouration of surfactant spiropyrans

Quantum yields for the photochemical isomerization of MC to SP were measured in clay dispersed solutions. As shown in Table 3, the MC to SP isomerizations are suppressed on intercalation into the clay interlayers. An extreme example is SP0101<sup>+</sup> which is isomerized *ca.* 30 times less efficiently in clay dispersed solution than without clay in water. This is presumably because indolium ions of MC are electrostatically trapped by anionic sites at the interlayer surfaces, hence retarding the ring closure to SP. In fact, when the remaining anionic sites are buried by cationic DSDAB, the quantum yield is significantly improved and is as high as 0.11. On the other hand, surfactant spiropyrans undergo more smooth photochemical decolouration in a clay dispersion. These spiropyrans tend to assemble to form molecular clusters, which make indolium nitrogen cations free from clay anionic sites, resulting in the smooth photochemical isomerization.

#### Conclusions

Spiro[2H-1-benzopyran-2',2'-[2,3]-dihydroindoles] containing long alkyl chains and  $\omega$ -pyridinium ions, SP1801<sup>+</sup>, SP10<sup>+</sup>00 and SP10<sup>+</sup>22, were all quantitatively intercalated into the clay interlayer, and exhibit normal photochromism in clay dispersed aqueous solutions. Their thermal decolourations obey simple first-order kinetics and are about one-tenth as slow in clay dispersed solution and about one-hundredth as slow in a clay film as that in bulk solution without clay.

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