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Aggregates in Langmuir-Blodgett Films of Spiropyrans Having Hydroxyl or Hydroxymethyl Group

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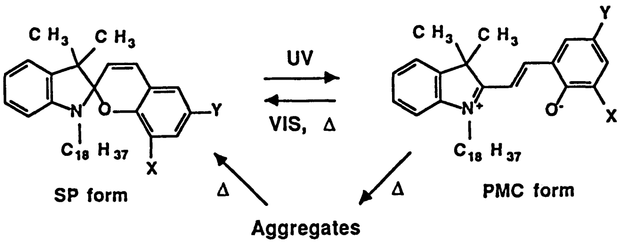
The optical properties of monomolecular layers at an air-water interface and also of Langmuir-Blodgett (LB) films of several photochromic spiropyrans with a single hydrophobic long chain and either a hydroxyl or a hydroxymethyl group have been investigated. Changes in the optical spectra of these films were induced by either UV irradiation or heating. UV-visible, and IR absorption spectra showed that spiropyran SP145 formed J-aggregates and SP147 formed H-aggregates. The half-decay period of the J-aggregate to the spiropyran (SP) form was longer than that of the colored monomeric photomerocyanine (PMC) to the SP form. It was concluded that hydrogen bonding between neighboring colored PMC molecules via hydroxyl, hydroxymethyl, and nitro groups stabilizes the aggregate state.

Spiropyran (SP) molecules are converted into the photomerocyanine (PMC) form on UV irradiation, and a reverse change takes place when the colored product is irradiated with visible light of a specific wavelength. This photochromic reaction can be applied to developing high density optical recording information storage media. In view of this, several workers[1—4] have studied the photochromic reactions of spiropyran monomolecular layers and multilayers prepared by the Langmuir-Blodgett (LB) technique.

The LB technique is useful to prepare a well-ordered molecular aggregation state of spiropyran molecules. Under such conditions these molecules often exhibit spectroscopic changes due to aggregate formation, i.e., red-shifted J-aggregates and blue-shifted H-aggregates. Ando et al.[5] reported that SP1822 (Fig. 1) LB films mixed with hexadecane formed J-aggregates after successive UV irradiation and heat treatment procedures at 35—50 °C. The J-aggregate state is featured by its sharper, more intensely colored band at a longer wavelength (λ_{max}=618 nm) than in the PMC state (λ_{max}=583 nm). A small Stokes shift in the fluorescence peak is another characteristic of the J-aggregate. The SP1801 (Fig. 1) LB films, however, formed a J-like aggregate (λ_{max}=600 nm) when either stearic acid or octadecyl alcohol was used as matrix molecules.[6] These films do not form an aggregate without admixing. This J-like aggregate formation was also noted in alternating LB films of SP1801 and stearic acid.



	X	Y
SP144	H	OH
SP145	CH_2OH	NO_2
SP147	OH	NO_2
SP18	H	NO_2
SP1801	OCH_3	NO_2
SP1822	$CH_2OCOC_{21}H_{43}$	NO_2

Fig. 1. Chemical structures of spiropyran derivatives used.

Only a few studies have been done on the aggregate formation of amphiliphilic spiropyrans, though the characterization of dye aggregate states in general has been performed by many researchers. Their formation of well-ordered J- and H-aggregate states, and examination of a correlation between the structure and aggregate forming ability of spiropyrans are therefore of interest. Molecules in an aggregate interact through various cohesive forces, i.e., hydrogen, ionic, and covalent bonding. In this paper the importance of hydrogen bonding in aggregation is emphasized.

The present work deals with the photochromic behavior of spiropyran derivatives prepared as monolayers at the air-water interface or as LB films. The spiropyrans used here contain a long alkyl chain and a hydroxyl group. These formed an LB film without matrix molecules such as stearic acid or octadecyl alcohol. The colored PMC form and the J- and H-aggregate forms are highly stable, and the results suggest that these aggregates are formed through hydrogen bonding.

Experimental

Materials. The spiropyrans (Fig. 1) were purchased from the Nippon Kankoh-Shikiso Kenkyusho Co., and were used without further purification. The spreading solvent was spectroscopic grade chloroform.

Procedures. Measurements of surface pressure-area (π-A) isotherms and the deposition of monolayers onto quartz slides were performed by means of a conventional Langmuir trough (Joyce Loebl, Langmuir Trough IV, UK) equipped with a Whilhelmy balance. The substrates for visible spectroscopic measurements were rendered hydrophobic by immersion in a 10% chloroform solution of trimethylchlorosilane. The LB films were deposited at a surface pressure of 20 mN m^{-1} and a dipping speed of 15 mm min^{-1}. The subphase was maintained at 20 °C, pH 5.8.

The visible absorption spectra of monolayers were measured with a multichannel spectrophotometer (Otsuka Electronics Co., model MCPD-200), whereas a double-beam UV-visible spectrophotometer (Japan Spectroscopic Co., model UVIDEC-610C) was used for multilayers. Infrared spectra of the LB films were measured with an IR spectrophotometer (Japan Spectroscopic Co., model IR-810), and fluorescence spectra were detected by means of a monochromator (Japan Spectroscopic Co., model CT-25C) combined with photomultiplier (Hamamatsu Corp., model R943-02) by excitation at 550 nm. The monochromator had a spectral band width of ca. 0.1 nm. To make proceed photochromic reactions from the SP to the PMC form on the subphase, the monolayer was irradiated with a UV lamp (366 nm, UVP Inc., model UVL-56, USA).

Results

Surface Pressure-Area (π-A) Isotherms. When monolayers of the spiropyran derivatives were compressed after conversion from the SP to the PMC form by UV irradiation, it was possible to deposit them as an LB film onto the substrate. Figure 2 shows the π-A isotherms for the monolayers of SP144, SP145, and SP147 after UV irradiation. The monolayers were stable up to a surface pressure of 40 mN m^{-1}, and the limiting areas are 0.53 nm^2 (SP144), 0.57 nm^2 (SP147), and 0.58 nm^2 (SP145).

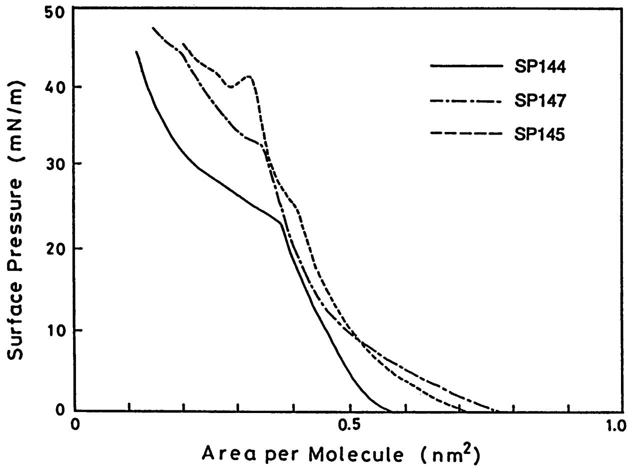


Fig. 2. Surface pressure-area isotherms for monolayers of spiropyran derivatives after UV irradiation.

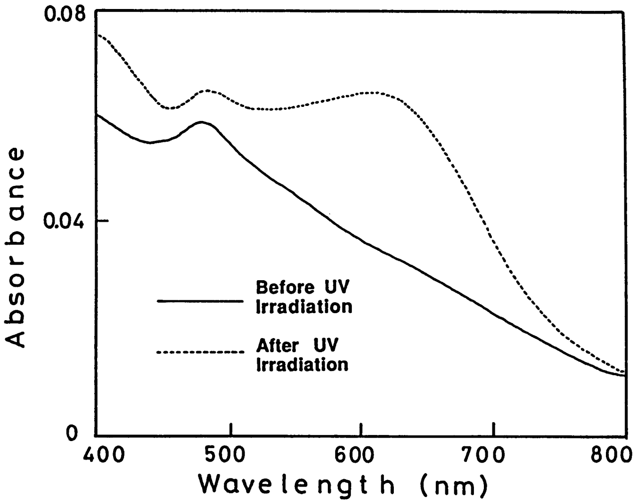


Fig. 3. SP144 LB film absorption spectra.

Photochromic Behavior of SP144. The absorbance of the SP144 monolayer at the air-water interface was negligible because its colored PMC without NO_2 group had a small extinction coefficient. Spectral measurements became possible with ten double multilayers formed on both sides of the substrate. Figure 3 shows the absorption spectra before UV irradiation, where the dye was in the SP form, and after UV irradiation. In the latter case a broad band is seen around 610 nm arising from the PMC form. On visible irradiation, the absorption spectrum returned to the original one, which was obtained also by heating in darkness. This reversible transformation was repeated using UV light and heating, and the change from the PMC to the SP form took place with a half-decay time of 2 min at 25 °C. A small absorption band at 480 nm is probably due to H-aggregates. No further changes were noted in the visible spectrum when the SP144 LB film was irradiated with UV light (366 nm, 1.0 mW cm^{-2}) for more than 10 min. This indicates that new aggregates are not formed after photoisomerization from the SP to the PMC form.

Infrared spectral analysis of the SP144 LB films was performed on a calcium fluoride support. The results

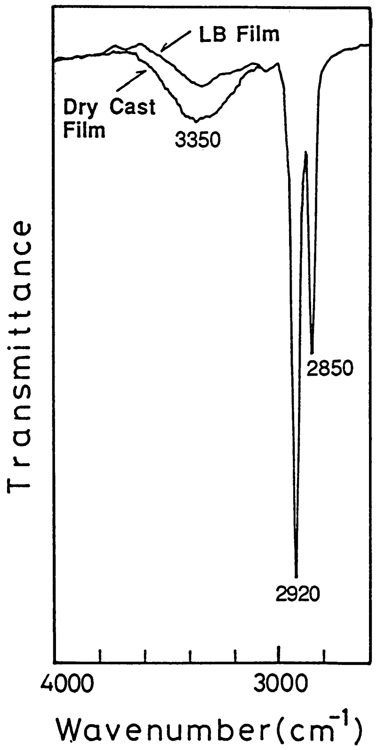


Fig. 4. SP144 IR spectra in the region 4000—2600 cm^{-1}.

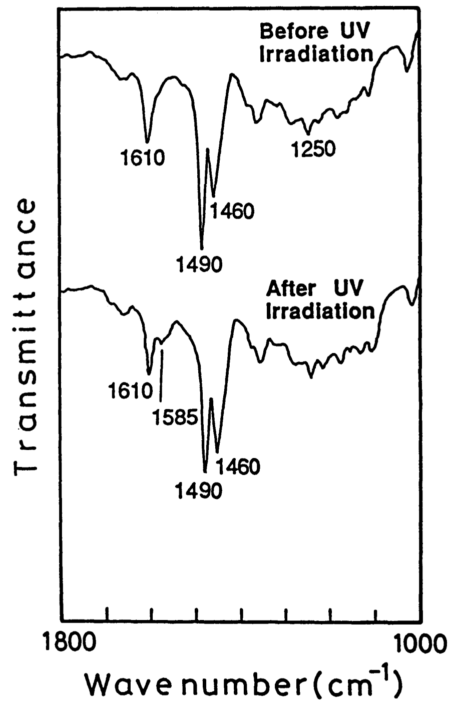


Fig. 5. SP144 LB film IR spectra in the region 1800—1000 cm^{-1}.

are shown in Figs. 4 and 5. In CCl_4 the SP form molecules exhibit a peak at 3620 cm^{-1} reflecting the free O-H stretching. However, in the LB films this free OH-band is absent and instead a broad band peaking at 3350 cm^{-1}, which appeared also in a dry SP144 film cast from a dichloromethane solution, is observed due to the stretching of the hydrogen bonded OH groups (Fig. 4). In the LB films deposited at pH 9.0, the broad band did not exist due possibly to deprotonation of the hydroxyl groups. As seen in Fig. 5, no substantial change took place in the spectral shape over a wavenumber range 1800 to 1000 cm^{-1} in going from the SP to the PMC form in the LB film. The intensity of the 1610 cm^{-1} peak, assignable to the C=C stretching of *trans*-photomerocyanine,[3] did not increase by UV irradiation. Therefore, we conclude that no significant change took place in the molecular skeleton, and the PMC form is an alternatively open form (cisoid) and not a completely open (almost planar) form, or the so called transoid. An IR study by Morinaka et al.[7] demonstrated the occurrence of similar phenomena, namely hydrogen-bond formation and no cisoid-transoid isomerization in vacuum-deposited films of a spiropyran having a hydroxy group but no long alkyl chain. Reportedly they observed a stabilization of the PMC form via intermolecular hydrogen bonding in the vacuum-deposited films, but we were unable to prepare a stable PMC form in the LB films. Presumally the strengths of the hydrogen bonding are different between the two experiments because of a difference in the molecular orientation in the films.

Photochromic Behavior of SP145. A larger extinction coefficient of spiropyrans having nitro groups enabled measurement of their monolayers at the air-water interface. Monolayer absorption spectra after UV irradiation are displayed in Fig. 6. A broad band (555 nm) assigned to the PMC form appeared at a surface pressure of 5 mN m^{-1}, whereas a relatively sharp band (638 nm) reflecting the J-aggregate form appeared at surface pressures of 15—25 mN m^{-1}.

The J-aggregated state was maintained by the transfer of surface monolayers onto the substrate. Figure 7 shows the absorption spectra of the transferred LB films. The J-aggregate (λ_{max}=638 nm) was converted into the colorless SP form with a half-life of 560 min at 25 °C in darkness. Subsequent UV irradiation of the SP form regenerated the PMC form (λ_{max}=585 nm) without J-aggregate formation. The half-decay period for the PMC-to-SP conversion of SP145 is 135 min, being longer than those of the colored PMC forms of SP18 (15 min) and SP1801 (30 min)[6] for which no intermolecular hydrogen bonding was observed by IR

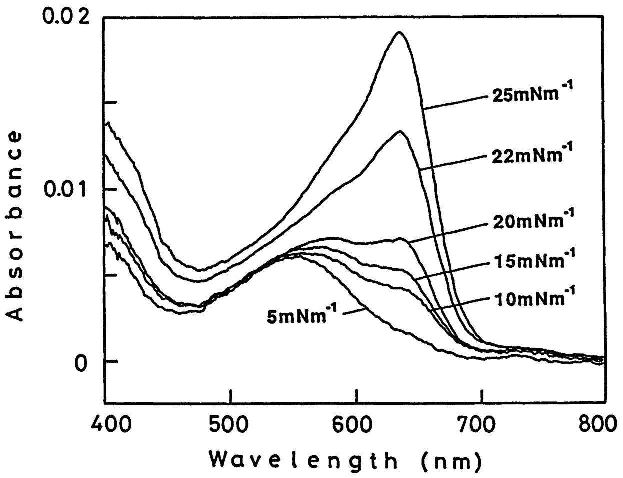


Fig. 6. Absorption spectra of the SP145 monolayer at the air–water interface.

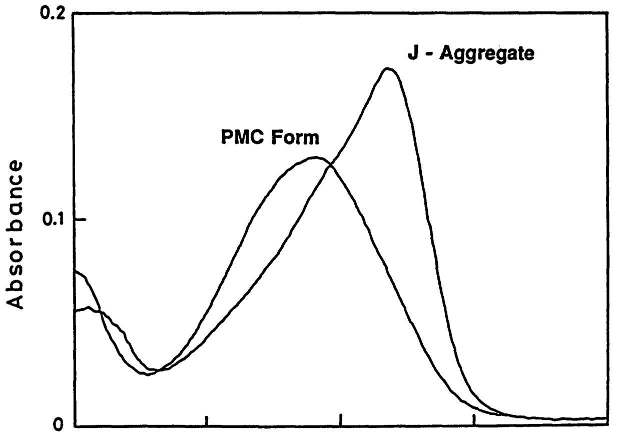


Fig. 7. SP145 LB film absorption spectra.

spectroscopy. A possible reason for the non-reformation of J-aggregates may be that their two-dimensional arrangements were sterically hindered by a molecular structural change during the conversion from the initial J-aggregated state to the SP form. Once such a change has occurred, recovery on the substrate is apparently impossible because an arrangement favorable for the J-aggregate formation may take place only at the air–water interface.

In order to examine whether the absorption band at 638 nm was due to J-aggregates, the fluorescence spectrum of the SP145 LB film was measured. A relatively small Stokes shift (65 nm) suggests that the dye is in a J-aggregated state as shown in Fig. 8. The Stokes shift, however, is larger than that (16 nm) of SP1822 having two long alkyl chains. This may reflect an inhomogeneous arrangement of the SP145 J-aggregate, or suggest that SP1822 J-aggregate is more tightly packed and well-ordered. Figure 9 shows the IR spectra for the J-aggregate, SP, and PMC form of the SP145 LB film. The NO_2 asymmetrical stretching at 1520 cm^{-1} in the SP form is shifted to 1518 cm^{-1} in both the J-aggregate and the PMC form. In contrast, the symmetrical NO_2 stretching mode at 1340 cm^{-1} in the SP form is shifted to 1295 cm^{-1} in the PMC form, and to split peaks at 1280 and 1250 cm^{-1} in the J-aggregate form. Since the colored PMC form has a zwitterion structure, the wavenumber lowering of the symmetrical NO_2 stretching peak may be a result of a resonance effect between the phenoxide ion and *p*-nitro group. The significantly lower frequency and larger intensity of the symmetrical NO_2 stretching bands in J-aggregate may reflect a stronger resonance effect, which promotes an intermolecular charge transfer from the negative oxygen atom of phenoxide ion in the pyran ring to the positive nitrogen atom in the indoline ring of an adjacent PMC molecule. Similarly, in the SP1822 LB film the sysmetrical NO_2 stretching peak was shifted from 1340 cm^{-1} in the SP form to 1290 cm^{-1} in the PMC and J-aggregate form.[8] To examine the state of the OH group, IR spectra were measured in the region 4000—2400 cm^{-1}. The SP form in CCl_4 showed a free OH-band at 3600 cm^{-1}. In the LB films, a weak band at 3220 cm^{-1} reflecting the O–H stretching in a hydrodgen bonded state was observed in both the PMC and the J-aggregate form, but not in the SP form. This demonstrates the formation of intermolecular hydrogen bonding in the PMC and J-aggregate form. The IR spectra for a SP145 cast film onto a CaF_2 substrate is shown in Fig. 10. By the SP-to-PMC conversion, the intensity of a broad peak at 3350 cm^{-1} increased while that of sharp peak at 3550 cm^{-1} decreased to a shoulder of the former peak. The 3550 cm^{-1} band is assigned to free

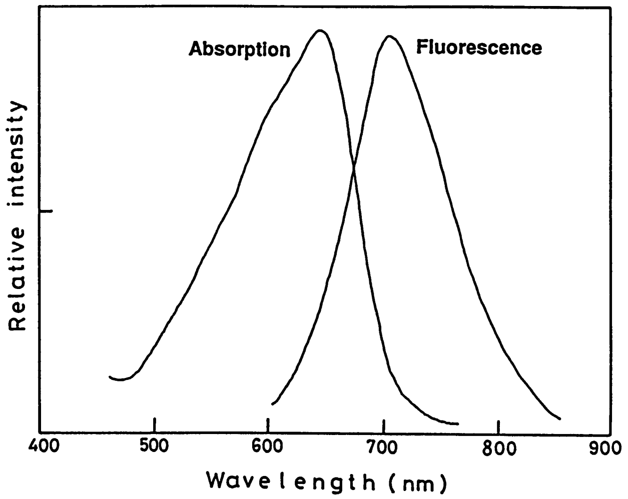


Fig. 8. Absorption and fluorescence spectra of J-aggregates in SP145 LB film.

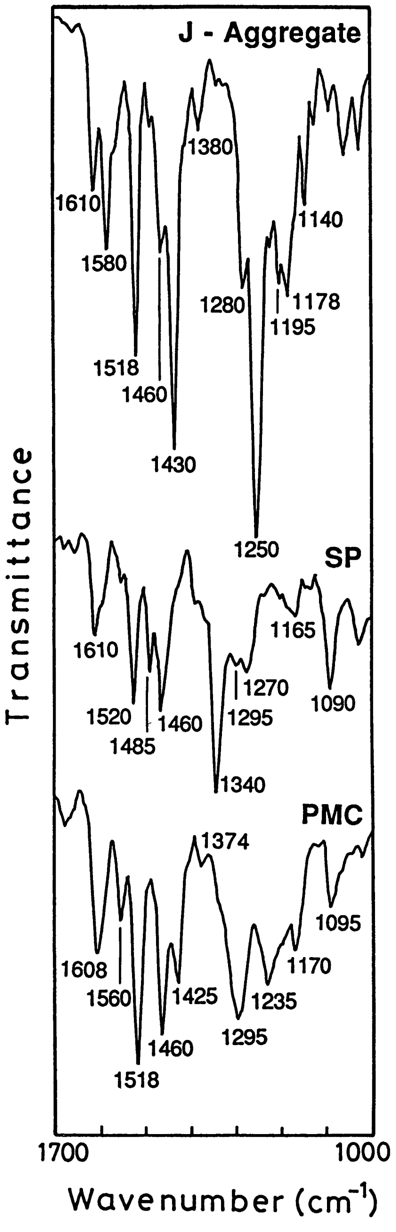


Fig. 9. IR spectra in the region 1700—1000 cm^{-1} for SP145 LB film.

O–H streching. Accompanying the ring closure by 580-nm irradiation and by heating, the intensity of the free OH-band (3550 cm^{-1}) was recovered and that of the hydrogen-bonded OH-band decreased. These spectral changes were well reproducible. The intensity of the hydrogen-bonded OH-band in the dry cast films, however, was much larger than that in the LB films.

Photochromic Behavior of SP147. After spiropyan SP147 was spread on water, the colored PMC form (λ_{max}=590 nm) was observed without UV irradiation. The absorption spectra for the monolayer after UV irradiation are shown in Fig. 11. In the LB film a broad band at 590 nm is transformed into a new absorption band at 560 nm due to aggregate formation by heat treating at 35 °C for 120 min (Fig. 12). This peak shift seems the higher dipole interaction energy increased due to formation of either H-dimer or H-aggregate containing three or four molecules. This H-aggregate was stable and did not decay for more than a month.

The IR spectra of the PMC and the H-aggregate form are depicted in Fig. 13. On heating the LB films, the intensities of the hydrogen-bonded O–H stretching (3220 cm^{-1}) and of the symmetric NO_2 stretching (1290 cm^{-1}) increased. This suggests that hydrogen-bond formation among the NO_2 group, phenoxide ion, and OH group is responsible for the formation of the H-aggregate. By heat treatment, the SP147 dry cast film behaved in essentially the same manner as the LB film with regard to these features. Hydrogen bonding is

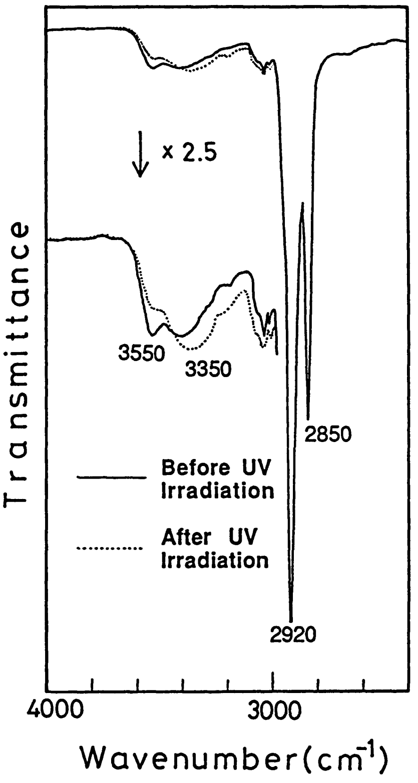


Fig. 10. IR spectra in the region 4000—2400 cm^{-1} for SP145 dry cast film.

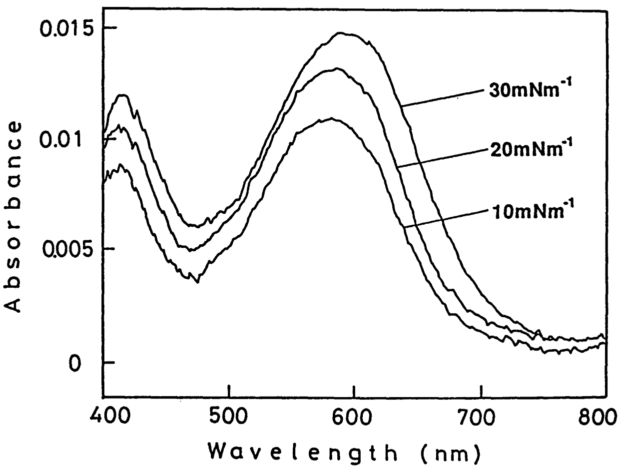


Fig. 11. Absorption spectra for the SP147 monolayer at the air–water interface.

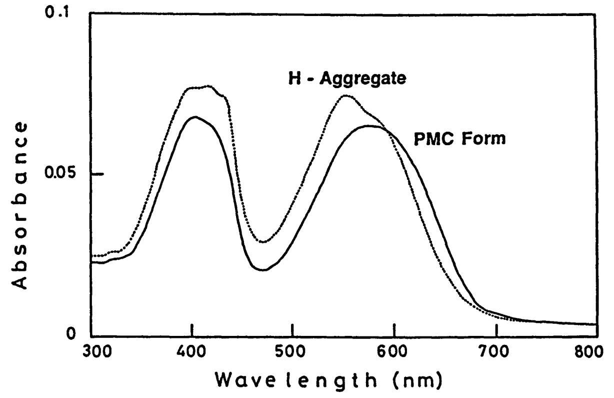


Fig. 12. SP147 LB film absorption spectra.

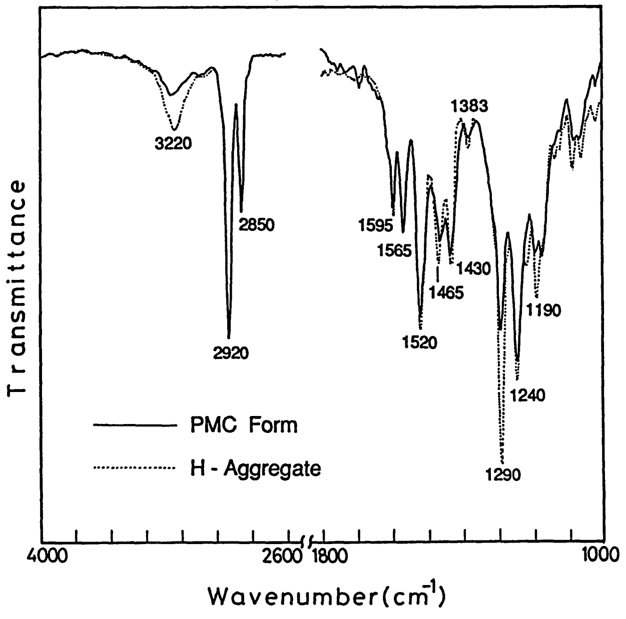


Fig. 13. IR spectra in the region 4000—2600 cm^{-1}, and 1800—1000 cm^{-1} for SP147 LB film.

one of the key driving forces for aggregate formation. An intramolecular hydrogen bonding may also occur in the PMC molecules, but the IR band reflecting this may have been hidden by the asymmetrical and symmetrical $-CH_2-$ stretching peaks (2910 and 2850 cm^{-1}) of the long alkyl chain.

Discussion

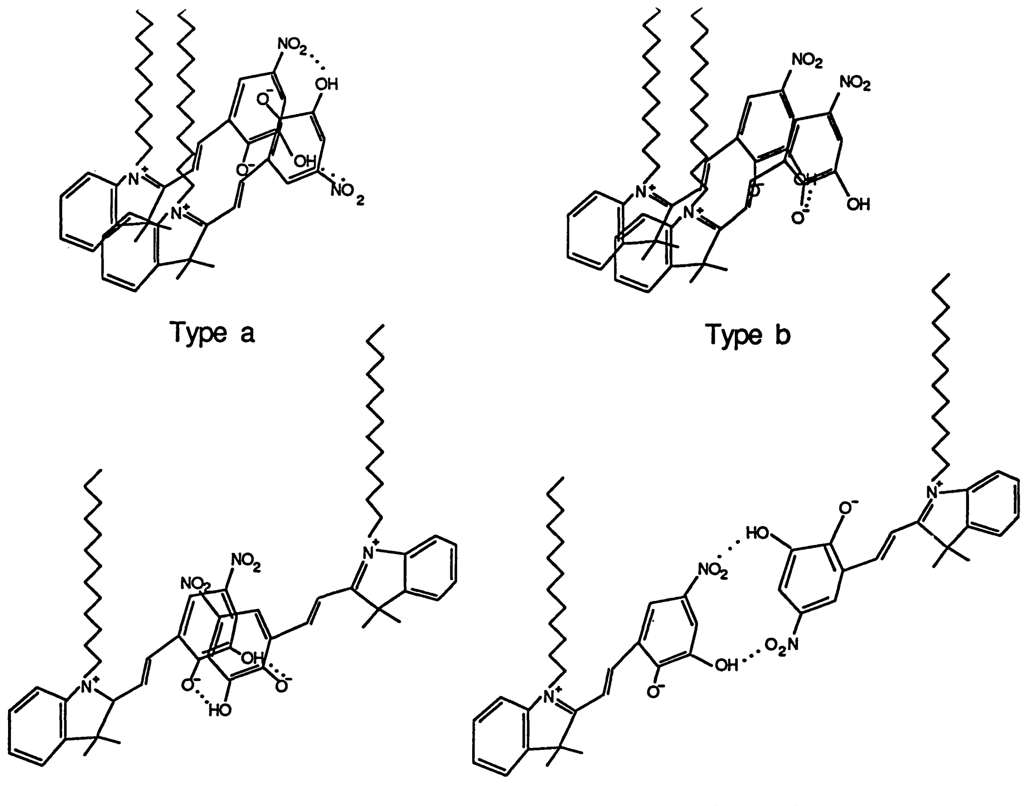
The photochromic behaviors of the spiropyran derivatives studied here are summarized in Table 1. UV-generated PMCs of SP18 (X=H),[9,10] SP145 (X=CH_2OH), and SP1822 (X=$CH_2OCOC_{21}H_{43}$)[11] have a head-to-tail configuration due to dipole–dipole interaction, and form J-aggregates in the monolayer at the air–water interface. Since the PMC form is more polar than the SP form, an electrostatic interaction may occur between neighoring PMCs in the J-aggregate. Previous studies have shown that the SP18 J-aggregate is unstable and readily converted into the PMC form in the LB films.[9,10] As verified in the presented work, the PMC of SP145 formed a J-aggregates which is more stable than the SP18 J-aggregate in the LB films. The stability of J-aggregates is a result of stronger dye–dye interaction and prevents the PMC-to-SP isomerization via formation of microcrystals. In contrast, the UV-generated PMCs of SP1801 (X=OCH_3)[11] and SP147 (X=OH) having the electron donating groups did not form J-aggregate in the monolayer on water. The SP147 PMC form, however, changed to an H-aggregate or an H-dimeric state by heat treatment in the LB film and dry cast film.

Table 1. Aggregate Formation in the Monolayer and LB Film

	Monolayer	LB film
SP144	No Data[a]	PMC (H-aggregate)
SP145	J-aggregate	J-aggregate
SP147	PMC	H-aggregate
SP18	J-aggregate	J-aggregate
SP1801	PMC	PMC
SP1822	J-aggregate	J-aggregate

a) Signal not measurable.

Based on the blue-shifted visible absorption band and intensity increase of IR OH-band, we propose four types of molecular configuration for a hydrogen-bonded SP147 dimer in Fig. 14. It is generally known that H-dimer and H-aggregate assume a side-by-side arrangement.[12] In the type a and b the hydrogen bonding occurs among the OH group, phenoxide ion, and the NO_2 group. The transition dipole moments of the two molecules are in parallel, and this molecular configuration should exhibit a bule-shifted absorption from the monomer band. In type c the hydrogen bond forms between the OH group and the phenoxide ion, and here



Type a Type b Type c Type d

Fig. 14. Molecular configuration models of SP147 dimer.

the two transition moments are oriented anti-parallel. The slip angle between the molecular long axis and the center-to-center line, is small. Thus PMC molecules are essentially in a head-to-head arrangement. In type d, the hydrogen bond forms between the OH group and the NO_2 group. Again, PMC molecules are in a head-to-head arrangement. Both type c and d should hence exhibit a red-shifted absorption. In view of these, type a or b is the most plausible configuration for the reported H-dimer or H-aggregate.

In conclusion, intermolecular hydrogen bonding acts in stabilizing the colored PMC form and in promoting aggregation of spiropyrans having hydrophilic OH and CH_2OH groups, in systems where hydrophilic matrix molecules are absent. Spiropyrans with an NO_2 group and either OH or CH_2OH groups form diffrent types of aggregates depending on the mode of configurations of open-ring PMC molecules in the LB films and the dry cast films.

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