Optical Properties and Molecular Orientation of Aggregates in Langmuir–Blodgett Films of a Long-Chain Spiropyran

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The aggregate formation was studied for Langmuir–Blodgett films of a spiropyran 5Me-SP1822 (1′-octadecyl-3′,3′-dimethyl-5′-methyl-6-nitro-8-(docosanoyloxymethyl)spiro[2*H*-1-benzopyran-2,2′-indoline]). Both a J-aggregate ($\lambda_{max}=605$ nm) and an H-aggregate ($\lambda_{max}=493$ nm) were formed, depending on the nature of the matrix molecule and the annealing temperature. The compound, having a substituent at the 5′-position, seems to prefer H-aggregation to J-aggregation by heat treatment at elevated temperatures. The molecular orientation in these aggregates was evaluated via analysis of the shifts in the first two absorption bands appearing after formation of the aggregates. Slip angles of 20—30° and 70—80° between the chromophore's transition moment and the center-to-center line of the molecules, were found for the J- and H-aggregates, respectively, and a tilt angle of 20—30° between the chromophore's plane and the film surface were obtained using the transition density model. These are in line with the results of Fourier-transform infrared (FT-IR) analysis.

Spiropyran (SP) molecules are transformed into a colored photomerocyanine (PMC) form when irradiated with UV light.[1] The original SP form is recovered on heating or on irradiation with visible light at wavelengths in the absorption band of the PMC. Since these molecules are applicable to the fabrication of optical memory media, many researchers studied the aggregation properties of these materials in Langmuir–Blodgett (LB) films.[2—13] For example, Ando and his co-workers[6—11] reported red shifted J-aggregates in LB films of a spiropyran SP1822 (1′-octadecyl-3′,3′-dimethyl-6-nitro-8-(decosanoyloxymethyl) spiro[2*H*-1-benzopyran-2,2′-indoline]) which has two long alkyl chains. Another compound MSP1822, having a methoxy group at the 5′-position of SP1822, was found to form J-aggregates and also blue shifted H-aggregates, depending on the preparation conditions.

In this work we studied the aggregation behavior of a new two-long-chain spiropyran, 5Me-SP1822 (1′-octadecyl-3′,3′-dimethyl-5′-methyl-6-nitro-8-(docosanoyloxymethyl)spiro[2*H*-1-benzopyran-2,2′-indoline]). Different aggregates were formed by control of heatment condition. The molecular orientation in the aggregates thus formed was determined by FT–IR transmission and reflection-absorption (RA) spectroscopy and also based on a transition density model.[14]

Experimental

Materials. The spiropyran material 5Me-SP1822 (Fig. 1), with the same molecular structure as SP1822 except for a methyl group in the 5′-position, was purchased from Nippon Kanko-Shikiso Kenkyusho Co. and used without further purification. HPLC analysis showed the purity to be 98%. Anal. Calcd for $C_{40}H_{99}O_5N_2$: C, 77.70; H, 10.65; N, 3.02%. Found: C, 77.78; H, 10.89; N, 3.32%.

Procedure. The material was spread from a chloroform solution of 0.4 μmol dm^{-3} onto a pure water subphase of pH 5.8 at 18 °C, and then a monolayer was prepared on the subphase in a Joyce-Loebl Langmuir trough Model IV. The films were deposited onto quartz substrates (10 mm×30 mm×1 mm) at a surface pressure of 20 mN m^{-1} by the vertical lifting method (dipping speed, 10 mm min^{-1}). The dye was mixed with one of the following three aliphatic compounds: methyl arachidate (MA), octadecane (OD), or dioctadecyldimethylammonium bromide (DDB) at a molar ratio of 1:1, and was incorporated in a Y-type film.

UV-visible absorption spectra of the LB films were measured with a JASCO spectrophotometer Model UVIDEC-610C. IR spectra, averaged over 200 scans, were recorded on a Matson FT-IR spectrophotometer Model 2020) with a resolution of 4 cm^{-1}. RA measurements were done at an incident angle of 80° using p-polarized light passed through a wire grid polarizer. The films for IR measurements were deposited on CaF_2 and Ag coated substrates under equivalent conditions.

Results

Aggregate Formation. Figure 2 shows the absorption spectra of the 5Me-SP1822 LB films doped with MA. On UV irradiation of 365 nm, the material underwent photoisomerization from SP to PMC. A monomeric form gave an absorption peak at 590 nm. Either J- or H-aggregate could be formed by subsequent heat treatment. Heat treatment at 33 °C for 20 min gave in J-aggregates with a λ_{max} at 605 nm; at 37 °C for 10 min both J- and H-aggregates ($\lambda_{max}=493$ nm); and at 40 °C for 5 min H-aggregates alone.

When DDB was used as the matrix, a large absorption band assignable to the H-aggregates ($\lambda_{max}=493$ nm) was observed after heat treatment of PMC at 37 °C for 5 min, as shown in Fig. 3.

When OD was used as the matrix, an intense signal of H-aggregates ($\lambda_{max}=493$ nm) was observed after heat treatment at 37 °C for 5 min. At a lower temperature, 33 °C, both J- and H-aggregates were observed as long as this temperature was maintained for 20 min. We also carried out the same treatment on the LB films of 5Cl-SP1822, with the CH_3 group in 5Me-SP1822 replaced by a chlorine atom. In the DDB matrix, an H-

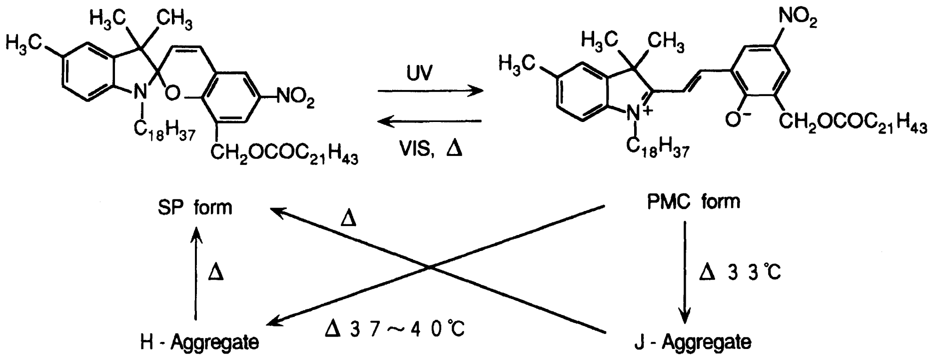

Fig. 1. Chemical structure of spiropyran 5Me-SP1822 and its photochromism.

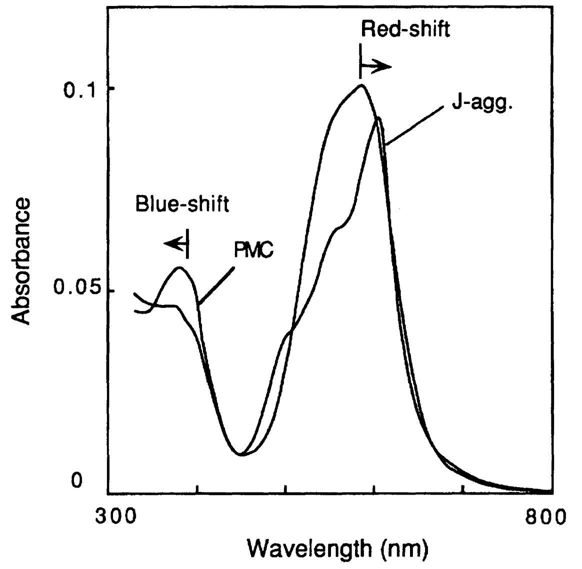

Fig. 2. Absorption spectra for an LB film of 5Me-SP1822 and methyl arachidate (MA). PMC: after UV irradiation; J-agg.: heat treatment at 33 °C after UV irradiation.

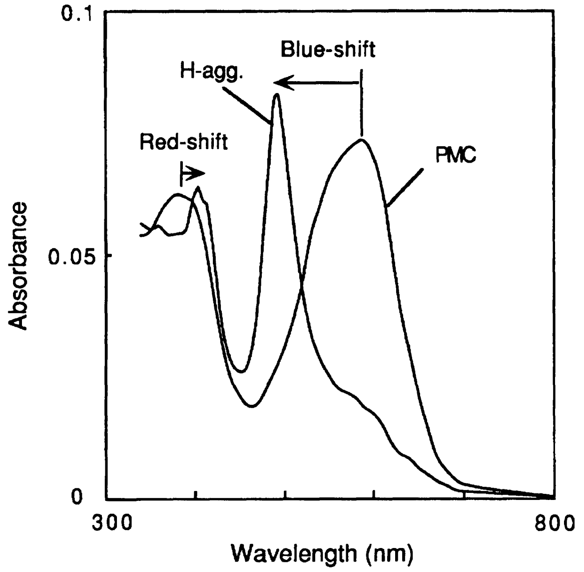

Fig. 3. Absorption spectra for an LB film of 5Me-SP1822 and dioctadecyldimethylammonium bromide (DDB). PMC: after UV irradiation; H-agg.: heat treatment at 37 °C after UV irradiation.

aggregate was exclusively formed ($\lambda_{\max}=498$ nm) when the film was heated to 37 °C, in contrast to the behavior of SP1822. 5Me-SP1822 and 5Cl-SP1822, carring a substituent group at 5′-position, thus seem to prefer H-aggregation to J-aggregation by heat treatment at elevated temperatures.

Molecular Orientation in the Aggregate Film. The first two absorption peaks (590 and 385 nm) of the PMC of 5Me-SP1822 showed red- and blue-shifts, respectively, as depicted in Figs. 2 and 3. A similar tendency has also been noted in other spiropyran J- and H-aggregates. The spectral shifts can be explained using the transition density model proposed by Norland et al.,[14] which considers individual interactions between charged centers in each molecule via summing over all the interacting molecules. This model was extended to estimate not only the slip angle between the chromophore's transition moment and the center-to-center line of the molecules but also the tilt angle between the chromophore's plane and the film surface.

The interaction energy, E, of a molecular aggregate system is given by:

$$E=\sum_{i,j} q(i)q(j)/r(i,j), \tag{1}$$

where $q(i)$ and $q(j)$ are the transition densities of the ith and jth atom in the interacting molecules, respectively, and $r(i,j)$ is the distance between the ith atom in one molecule and the jth atom in the other molecule. The normalizing factor of the total wave function for the aggregate reduces the N aggregate transition dipoles to a monomer basis. N is the number of molecules in an aggregate. In the calculations of the excited state interaction to estimate a spectral shift defined as $2E$, the transition density was split into two equal positions located ±0.84 Å above and below the molecular plane according to the Norland's approximation. The interaction between a point on one molecule and each of 20 pairs of transition density points on the other molecule in the aggregate was calculated. The interaction calculation was then repeated for all the 40 points on the molecule and summed. The transition densities used in our calculations were obtained using the Pariser-Parr-Pople (PPP) molecular orbital method.[15] In this method the electron-excitation energies and transition moments were refined by a limited configuration interaction (CI) treatment where 25 singly excited singlet configurations from five HOMO to five LUMO states. Both the alignment of the transition dipoles and the absorption spectral shifts were predicted. Fig. 4 are schematically illustrated alignment of the transition dipoles of the long and short axes of aggregated chromophores with the slip angle (α) and the tilt angle (β). Figure 5(a) shows the correlation between the experimental absorption spectrum and the line spectra of the PMC form (isolated molecule) generated by our calculations. It is clear that the transition at the longer wavelength is a result of excitation to the first excited state, and that the absorption at the second longest wavelength is contributed by excitations to the second, third, fourth, and fifth excited state. Figure 5-(b) shows the directions of these transition moments relative to the molecular orientation axis (dashed line). The dominant transitions, however, are clearly those to the first excited state which is aligned along the long axis of the molecule, and the fifth excited state which is aligned along the short axis of the molecule. Only these two states are taken into account in the subsequent calculations of dipole interactions within the aggregate.

Figure 6 shows the calculated transition densities for the first and fifth electronic levels on the molecule corresponding to the first two absorption bands. The interaction energies for the long- and short-axis transitions are plotted against the slip angle α for a linear aggregate composed of six molecules. When a J-aggregate of 5Me-SP1822 is formed, the longer and shorter wavelength absorption peaks in the PMC exhibit, respectively, a red shift of $-420\ \mathrm{cm}^{-1}$ and a blue shift of $+340\ \mathrm{cm}^{-1}$, as shown in Fig. 2. By H-aggregation these values are $+3340$ and $-1280\ \mathrm{cm}^{-1}$, respectively (Fig. 3). Correlating these shift values with those calculated using Norland's method, we find that the slip angles for the J- and H-aggregates are 20—30° and 70—80°, respectively, with a common tilt angle of 20—30°. This is for the first case where the tilt angle of molecules was determined in aggregated LB films.

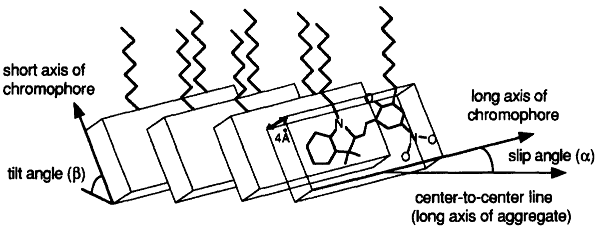

Fig. 4. Schematic representation of the chromophore alignment.

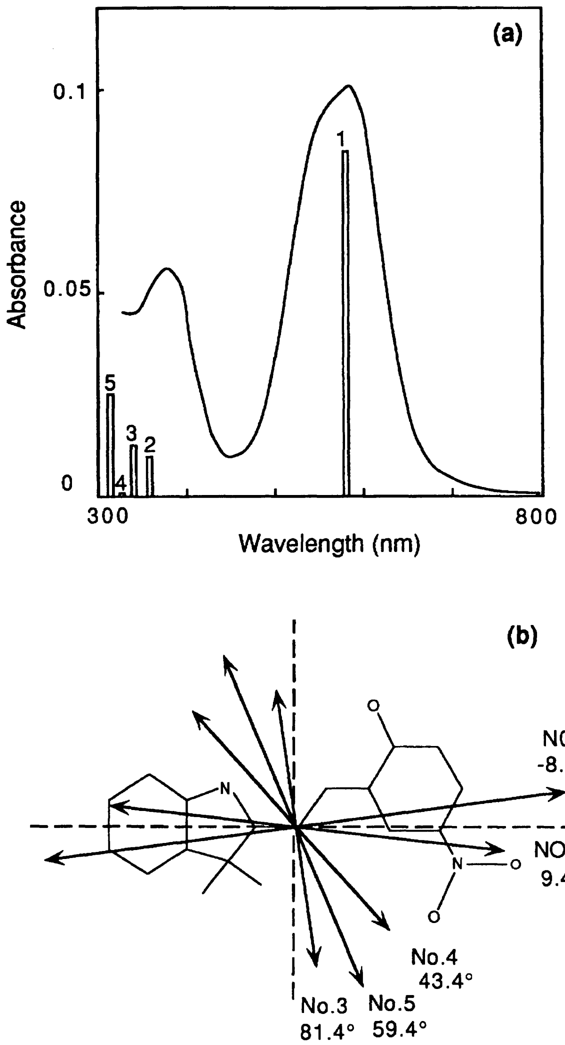

Fig. 5. (a)Line spectra of photomerocyanine (PMC) obtained by PPP calculations with its experimental absorption spectrum (solid curve). ; (b) Calculated transition moment directions.

Infrared Transmission and Reflection-Absorption Spectra. The orientation of the chromophores in the LB films has also been examined by FT-IR transmission and RA spectral measurements. This technique can determine the molecular orientation in aggregates. The angle between the long hydrocarbon chain axis and the normal of the film surface can be determined by analyzing the antisymmetric CH_2 stretching band at 2920 cm^{-1} and the symmetric CH_2 stretching band at 2850 cm^{-1}. Previously, Hibino et al.[11] showed that the angle of the chain axis for SP1822 changed from 30 to 60° when either the monomeric SP form or PMC form changes to the J-aggregate on UV irradiation and heat treatment at 35 °C. Our investigation revealed a similar behavior for the 5Me-SP1822 molecule so that the hydrocarbon chain assumes a large tilt angle on aggregate formation by heating.

Figures 7 and 8 represent the transmission and RA spectra of the 5Me-SP1822 LB films in matrices of meth-

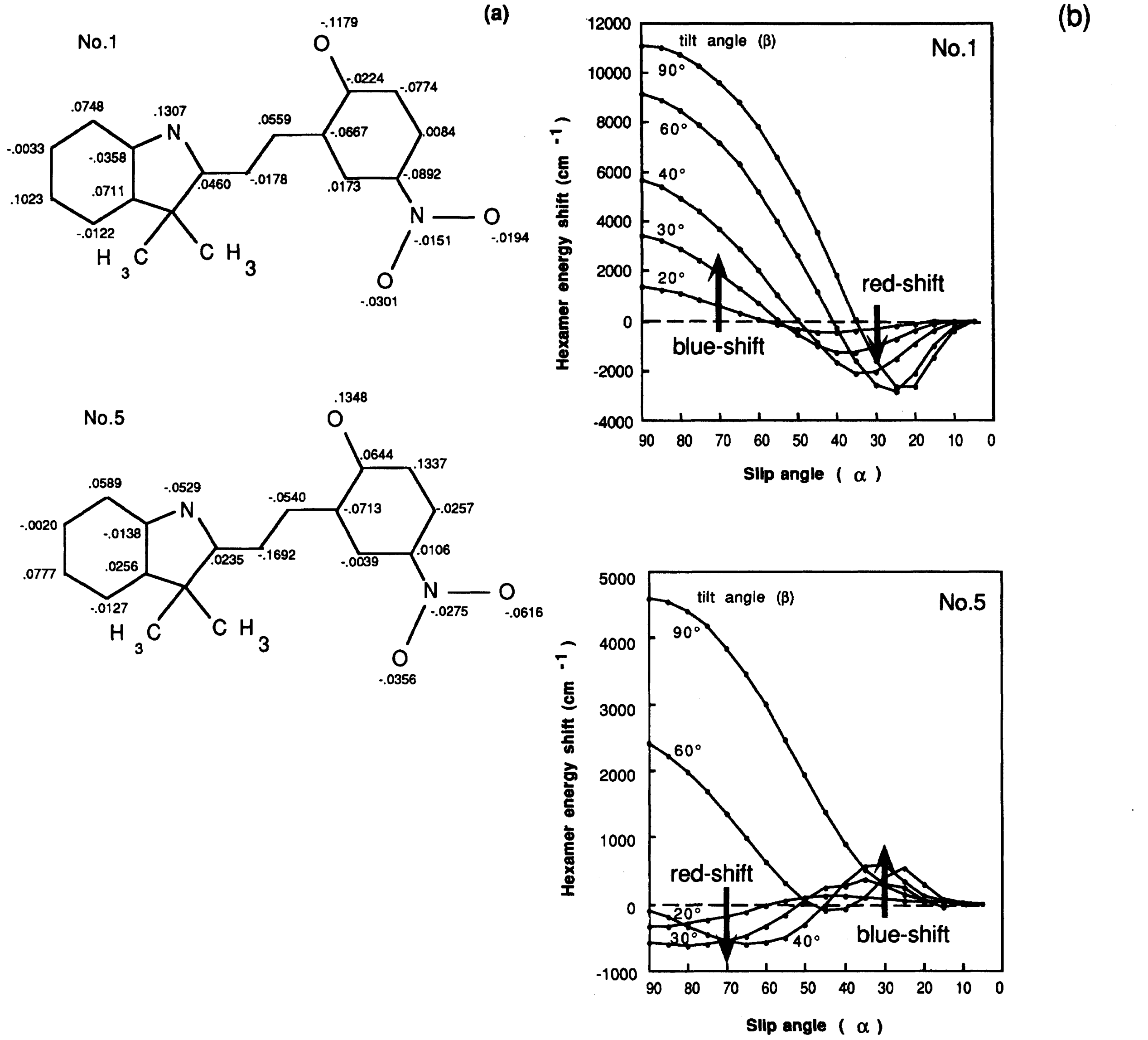

Fig. 6. (a) Transition density maps for the long axis transition moment (No.1) and short axis transition moments (No.5). ; (b) Calculated interaction energy for transition density plotted against slip angle (α) and tilt angle (β).

yl arachidate (MA) and octadecane (OD), respectively. To evaluate the molecular orientation quantitatively, the absorption intensities in the transmission spectra (A_T) and in the RA spectra (A_R) were related using the equation:[11,16)]

$$\tan^2\theta = k(A_T/A_R), \qquad (2)$$

where k is a constant and θ is the angle between the absorption transition moment and the normal of the substrate.

The dichroic ratios of the antisymmetric and symmetric stretching bands of the nitro group, at 1525 cm^{-1} and 1294—1288 cm^{-1}, respectively, for the J- and H-aggregates are summarized in Table 1. In the case of the J-aggregate, the ratio of the antisymmetric stretching absorption is significantly larger than the ratio of the SP or PMC, whereas that of the symmetric stretching is significantly smaller. The reverse holds for the H-aggregates: i.e., ν_sNO_2 of the J-aggregate has a smaller ratio than either the SP or PMC forms, and ν_sNO_2 of the H-aggregate a larger ratio. The orientations of the NO_2 group in the unaggregate states (SP or PMC form) are thus different from the orientation in the J- and H-aggregate states. The angles of direction of the nitro group are schematically illustrated in Fig. 9. The angle (θ_1) of the vibrational transition moments (parallel to the bisector of the O–N–O angle) of symmetric stretching vibrations of the NO_2 group, is smallest for the H-aggregates and largest for the J-aggregates. Our results in the SP and PMC states did not showed that the orientation angle (θ_1) is noticeably influenced by the matrix material.

If the out-of-plane CH bending bands give much stronger intensities in the transmission spectra than in

Table 1. Ratios of the Absorbance Obtained by Transmission Method (A_T) to That Obtained by RAS (A_R)

	$\nu_{as}NO_2$			ν_sNO_2		
	Wavenumber (cm^{-1})	A_T/A_R[a]	A_T/A_R[b]	Wavenumber (cm^{-1})	A_T/A_R[a]	A_T/A_R[b]
SP	1525	0.45	0.52	1340	0.76	0.71
PMC	1518	0.59	0.56	1298	0.50	0.60
J-Agg.	1525	0.86		1288	0.30	
H-Agg.	1524		0.14	1294		1.25

a) 5Me-SP1822/methyl arachidate LB films. b) 5Me-SP1822/octadecane LB films.

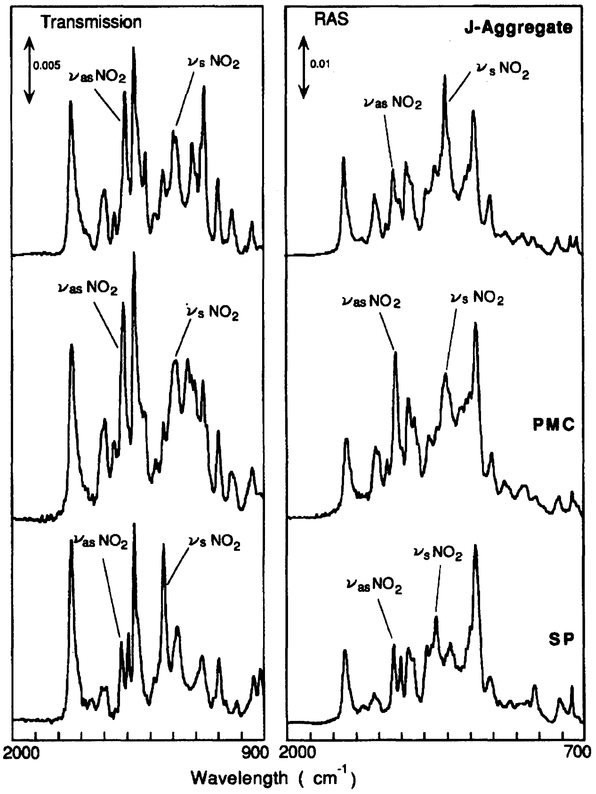

Fig. 7. Transmission and RA spectra of 5Me-SP1822 J-aggregate LB films with MA. Transmission: CaF_2 substrate, 2×20-monolayers (both sides of substrate); RAS: Ag coated substrate, 19-monolayers.

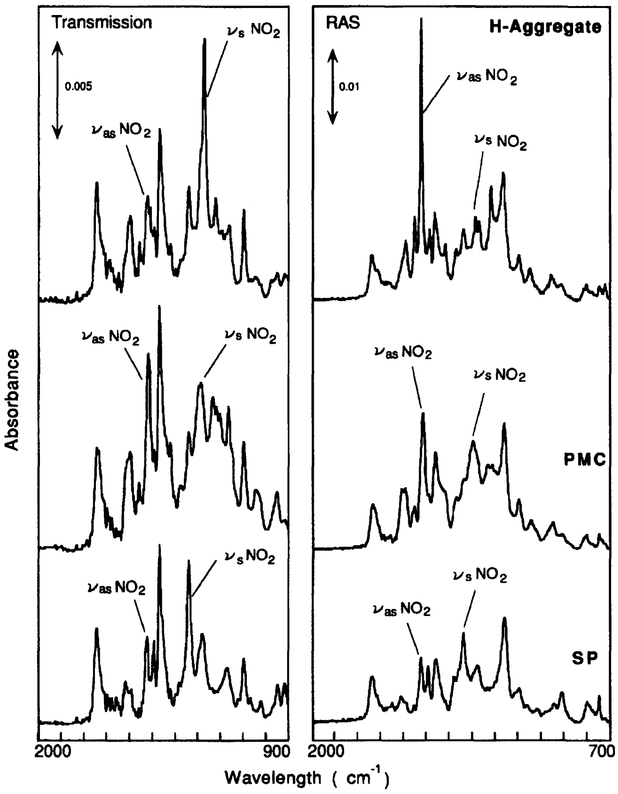

Fig. 8. Transmission and RA spectra of 5Me-SP1822 H-aggregate LB films with OD. Transmission: CaF_2 substrate, 2×20-monolayers (both sides of substrate); RAS: Ag coated substrate, 19-monolayers.

the RA spectra, the molecular plane must be oriented nearly parallel to the film surface. Hibino et al.[11] reported that the tilt angles (β) of the benzene and indoline ring planes were small (20—30°) for the SP, PMC, and J-aggregates of SP1822. The out-of-plane CH bending bands of the benzene and indoline rings at 804 and 748 cm^{-1} can be observed in the RA spectra in Figs. 7 and 8. Our result suggests that the chromophore planes are stacked to orient parallel and with a small tilt angle to the film surface in the aggregates.

Discussion

In order to control the aggregate growth and to prepare novel aggregates with useful properties, it is important to understand the mechanism of aggregate formation in LB films. A correlation between the molecular structure and the ability of aggregate formation shows a dependence on the number, length, and the position of the aliphatic chains and on the hydrophilicity of the substituted functional groups in the chromophore. Previous work[6] showed that SP1822 forms the J-aggregates and that this formation is not influenced by the presence of matrix molecules; MA and OD. Hibino et al.[9] reported that MSP1822 (with CH_3O instead of CH_3) also forms J-aggregates when irradiated with UV light at a temperature above 40 °C and, by use of OD as a matrix, H-aggregates can also be formed. Our results are compatible with these findings and suggest that the size of the molecular group attached to the 5′-position of the SP1822 moiety influences the aggregation mechanism

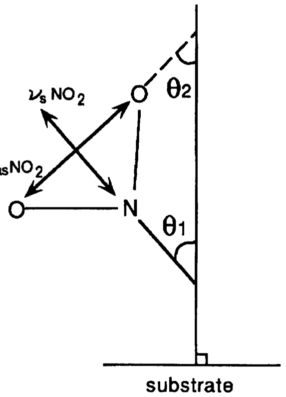

Fig. 9. Schematic illustration of the vibrational orientations of the nitro group in the LB film.

in these films. The 5Me-SP1822 (with CH_3) formed J-aggregates (λ_{max}=605 nm) or H-aggregates (λ_{max}=493 nm). The presence of the bulky group at the 5′-position is thought to hinder the J-aggregation since H-aggregates are formed at elevated temperatures. Combination of heat treatment and matrix species is thus effective to control the mode of aggregates.

Our results show that the tilt angles (β) of the benzene and indoline rings relative to the substrate are similar for all the SP, PMC and aggregate films, with the ring inclined nearly parallel to the substrate. The tilt angle of the hydrocarbon chain axes, however, increases significantly on aggregation. These characteristics are consistent with our assumption that a substituent on the chromophore influences aggregate formation.

In conclusion, we have analyzed the molecular orientation in the J-aggregate and H-aggregate formed in the LB films of 5Me-SP1822 on heat treatment after UV irradiation. Our calculations have accurately predicted the spectral shifts which can be attributed to the interaction between the transition moments along both the long and the short axes. The chromophoric part of the molecule assumed a tilt angle of 20—30° and a slip angle of 20—30° for the J-aggregates and with a slip angle of 70—80° for the H-aggregates.

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