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Anomalous excimer formation of a pyrenyl derivative having a mesogen group of alkoxycyanobiphenyl in its smectic mesophase

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ABSTRACT

4-Cyano-4′-(1-(1-pyrenyl)-*n*-octyloxy)biphenyl (8OCBPy), where the hydrogen atom of a well-known mesogen 4-cyano-4′-*n*-octyloxybiphenyl (8OCB) is substituted with one pyrenyl (Py) chromophore, was synthesized. When 8OCBPy was doped in the mesophases of the similar mesogen of 4-cyano-4′-*n*-decyloxybiphenyl (10OCB), the Py chromophores should be oriented by a constraint in the mesophases as compared with free chromophores dispersed in the mesophases. The binary mixture exhibited smectic A (Sm A) and nematic (N) mesophases. The mesophases and isotropic (I) phase of the binary mixture exhibited excimer as well as monomer fluorescence. The intermolecular excimer formation-dissociation kinetics of 8OCBPy in the Sm and I phases of its binary mixture was investigated in comparison with that for a 1-ethylpyrene binary system. Positive enthalpy and entropy changes for the excimer formation were found in the Sm A mesophase, whereas their usual changes were found in the I phase. These anomalous phenomena observed in the Sm A mesophase were interpreted by the entropy-controlled excimer formation associated with the decrease in ordering of the 10OCB-mesogen molecules around the 8OCBPy arranged in the Sm A layers.

1. Introduction

Ordered molecular assemblies are one of the important organic material groups that have been extensively investigated from viewpoints of basic science and practical application. Liquid crystals (LCs) are one of such organic materials, and have been the subject of much research because of their electro-optical, electric, and electronic characteristics and their application to electronic display devices. In LCs, mesogens are oriented along a particular direction. Accordingly, chromophores in the LC media are expected to show photochemical and photophysical behaviors that cannot be observed in an isotropic (I) phase. It should be noted that such behaviors are particularly enhanced for the processes based on the intermolecular interaction.

In such research subjects, there are the following two cases: fluorescent chromophores themselves are mesogens [1–4], and fluorescent chromophores that are not mesogens are dispersed in mesogens [5–10]. One of the typical examples in the former case is alkyl- and alkoxycyanobiphenyls (abbreviated as nCB and nOCB, respectively), which are widely known as representative mesogens and have been extensively investigated for technical applications as electro-optical LC devices, and their photophysical properties were effectively examined in solution as well as in bulk neat forms [2–4]. The first one in the latter case is that usual fluorescent chromophores are dispersed in nematic (N), smectic (Sm), and cholesteric (Ch) mesophases [5]. Recently, photo-emission and electroluminescence (EL) properties of this system have been investigated to apply luminescent mesogens and LC materials to display and EL devices [6]. The second one in the latter is that chromophores are covalently linked with mesogens, and thereby the compounds do not show mesophases [7–11]. When the compounds are dispersed in the mesophases of the same or similar mesogens, the chromophores should be highly oriented by a constraint in the mesophases as compared to free chromophores dispersed in the mesophases. In particular, for calamitic LCs, the Sm mesophases exhibit stronger intermolecular interaction than the N mesophase, resulting in a higher ordering in the molecular arrangement and in a higher viscosity. These should affect effectively the photophysical and carrier-transport processes resulted from interactions between the chromophores. For example, concerning the carrier-transport processes, a fast hole transport, whose mobility is independent of applied electric fields, was reported for Sm mesophases [12].

As for Ch mesophases, Sisido et al. synthesized cholesteric compounds containing pyrenyl (Py) chromophores covalently linked to a cholesteric group [8] and mixed it (3–25 mol%) with cholesteryl phenyl-alkanoates. The fluorescence properties of these mixtures were investigated in their Ch and I phases. It was concluded that the unusual thermodynamic behavior (positive enthalpy

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(+4–6 kcal mol^{-1}) and positive entropy (+0.5 cal K^{-1} mol^{-1})) for the excimer formation in the Ch mesophase was interpreted in terms of an ordered ground-state arrangement of the Py compounds and its local destruction in the excimer state. Recently, we focused on the Sm mesophase of calamitic LCs instead of cholesteric LCs. Thus, we synthesized 4-cyano-4′-(1-(*N*-carbazolyl)-*n*-octyloxy)biphenyl (8OCBCz), where one carbazolyl (Cz) chromophore is covalently linked to the well-known mesogen 4-cyano-4′-*n*-octyloxybiphenyl (8OCB), and mixed it with 4-cyano-4′-*n*-decyloxybiphenyl (10OCB). The fluorescence properties of the exciplex formed between the Cz and environmental OCB chromophores of the mixtures (8OCBCz/10OCB) and the photoconductive properties of these mixtures were reported [10].

In the present study, we focused on the Sm and N mesophases containing Py chromophores and synthesized 4-cyano-4′-(1-(1-pyrenyl)-*n*-octyloxy)biphenyl (8OCBPy), where one Py chromophore is covalently linked to the well-known mesogen 8OCB. We now investigate the fluorescence properties of a binary system of 8OCBPy/10OCB in Sm, N, and I phases in comparison with a 1-ethylpyrene (EPy)/10OCB binary system. Excimer fluorescence was observed in three phases of these binary systems. The thermodynamic parameters of the excimer formation for these mixtures were evaluated from time-resolved fluorescence spectral data and were compared with the case of the cholesteric system reported by Sisido et al. [8]. As the results, larger positive values of enthalpy and entropy for the excimer formation than those observed for the cholesteric system were obtained in the Sm mesophase of the mixture. These large positive values imply the anomalous excimer formation, which was discussed.

2. Experimental

8OCBPy was synthesized from 4-cyano-4′-hydroxybiphenyl and 8-bromo-1-(1-pyrenyl)octane, which was synthesized from the Grignard reaction of 1-bromopyrene and 1,8-dibromooctane. These compounds were identified by means of their IR and NMR spectra. EPy was the same as in the previous experiment [13] and was recrystallized and sublimed *in vacuo*. 10OCB (BDH chemicals) was used as received. Tetrahydrofuran (THF) (Dotite, Spectrosol) and dichloromethane (Dotite, Spectrosol) were used without further purification. For optical measurements, the bulk sample was sandwiched between two quartz plates with a polyimide spacer (thickness: 12.5 μm). The solution samples were contained in a 10-mm quartz cell.

A polarized optical microscope (Olympus, BX50) equipped with a Instec STC200D hot stage was used to observe the phase transitions and textures. A differential scanning calorimeter (Seiko Instruments, DSC220C) was used to determine the phase transition temperatures. The visible and ultraviolet absorption spectra were measured with a JASCO V-550 spectrophotometer. Steady-state fluorescence spectra were measured with a Hitachi F-4500 fluorescence spectrometer. Time-resolved measurements were performed using a two-dimensional streak camera (Hamamatsu Photonics, C4780) as a detector and a N_2 gas laser (Usho KEC-150, 20 Hz, and FWHM of ca. 0.6 ns) as an excitation light source. All of the fluorescence spectra were not corrected for detector sensitivity.

3. Results and discussion

3.1. Absorption and fluorescence spectra of 8OCBPy in solution

Fig. 1 shows the absorption and fluorescence spectra of 8OCBPy, EPy, and 8OCB, and an equimolar mixture of EPy and 8OCB in a dilute THF solution (1.0×10^{-5} M). The absorption spectrum of 8OCBPy is very similar to that of the mixture of EPy and 8OCB, which indicates no interaction between Py and cyanobiphenyl (CB) groups in the ground-state. As shown in Fig. 1(a), an excitation wavelength of 292 nm excites mainly the CB chromophore in 8OCBPy. However, the fluorescence spectrum of 8OCBPy excited at 292 nm (Fig. 1(b-1)) is similar to that of EPy excited at 342 nm (Fig. 1(b-2)), although very weak fluorescence of CB is observed, whereas the fluorescence spectrum of the mixture excited at 292 nm (Fig. 1(b-1)) is very similar to that of 8OCB. These results indicate the occurrence of

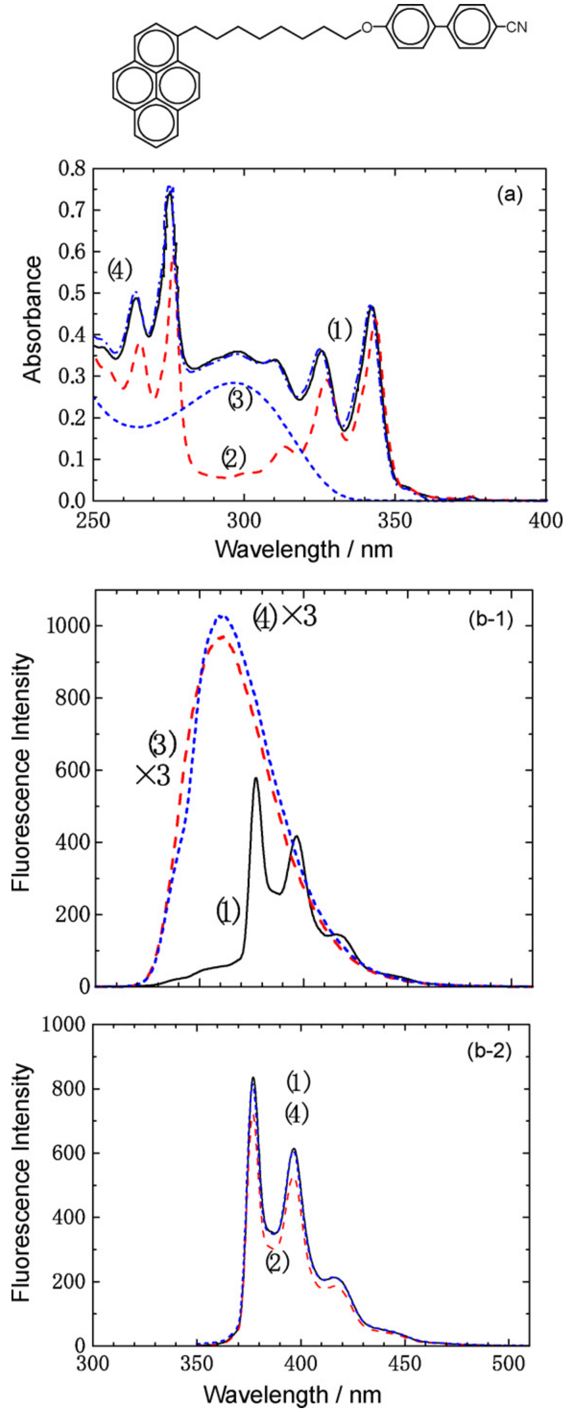


Fig. 1. Chemical structure of 8OCBPy and (a) absorption and (b) fluorescence spectra of (1) 8OCBPy, (2) EPy, (3) 8OCB, and (4) mixture with the same content of EPy and 8OCB in a dilute THF solution (1.0×10^{-5} M). Excitation wavelength: (b-1) 292 nm and (b-2) 342 nm.

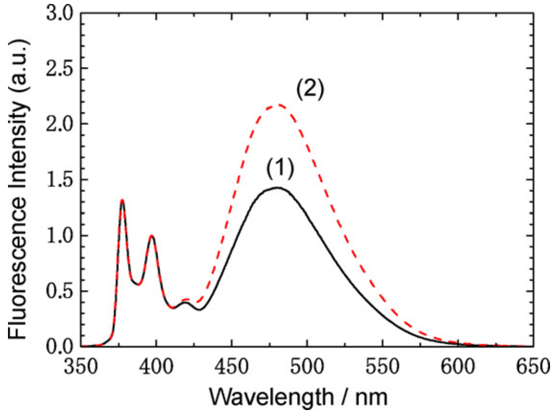


Fig. 2. Normalized fluorescence spectra of (1) 8OCBPy and (2) EPy in degassed dichloromethane solution (1.0×10^{-2} M). Excitation wavelength: 342 nm.

intramolecular energy transfer from the CB to Py chromophores in 8OCBPy.

The fluorescence spectra of 8OCBPy and EPy in a degassed concentrated dichloromethane solution (1.0×10^{-2} M) are shown in Fig. 2. The broad emission in longer wavelengths is safely assigned to excimer fluorescence. That is, 8OCBPy as well as EPy forms an intermolecular excimer in a concentrated solution.

A time-resolved fluorescence measurement with an excitation of 337 nm was performed to obtain their lifetimes. The lifetimes of the dilute dichloromethane solutions of 8OCBPy and EPy (2.0×10^{-5} M) were 76.5 and 77.9 ns, respectively, which also indicates no interaction between the excited Py and ground-state CB chromophores in 8OCBPy. The monomer (λobs = 369–387 nm) and excimer (λobs = 494–512 nm) fluorescence rise and decay curves of the concentrated dichloromethane solution of 8OCBCz and EPy (1.0×10^{-2} M) were fitted to a two-component exponential function according to a usual Birks kinetics.

$$I(t) = G_1 \exp\left(\frac{-t}{T_1}\right) + G_2 \exp\left(\frac{-t}{T_2}\right) \qquad (1)$$

A good agreement was found between the long decay times (T_2) obtained from the monomer and excimer fluorescence of both the samples. These values were ca. 50 ns for both the samples. In addition, a good agreement was also found between the fast decay time (T_1) of the monomer fluorescence and the rise time of the excimer fluorescence of both the samples. These values were ca. 27 and ca. 17 ns for 8OCBPy and EPy samples, respectively. The smaller value for EPy than for 8OCBPy corresponds with the fact that the diffusion coefficient of EPy is larger than that of 8OCBPy, because of the smaller molecular size of EPy than that of 8OCBPy.

3.2. *Mesophases of samples mixed with 10OCB*

As mentioned earlier, 8OCBPy did not exhibit a mesophase by itself. 10OCB is known to exhibit a mesophase with the following phase transitions:

$$\text{crystal (Cr)} \xrightarrow{332.5\,\text{K}} \text{smectic A (Sm A)} \xrightarrow{357\,\text{K}} \text{Isotropic (I)}$$

Miscibility of 8OCBPy with 10OCB was examined using the DSC measurements and polarizing microscope observations. Binary-mixture samples doped with 8OCBPy of 20, 10, 5, and 1 mol% were used. It was confirmed that a nematic (N) mesophase is induced for these binary mixtures. For the 20 mol%-doped binary mixture, mixed crystals formed between these two compounds were found in the N mesophase by the polarizing microscope observation. The appearance of both a N mesophase induced by doping and mixed crystals was reported also for binary mixtures of 8OCBCz/10OCB [11]. For the 10 mol%- and 5 mol%-doped mixtures, when the mixtures were cooled from their isotropic (I) phases, a dark image was partly observed just after finding the N mesophase with a narrow temperature range. To examine the phase exhibiting the dark image, quartz-glass plates that were spin-coated with polyvinylalcohol (PVA) and subsequently treated by rubbing were used as substrates for constructing sandwich-type cells. When the rubbed PVA-film substrates were used, the phase exhibiting the dark image exhibited clearly a Sm mesophase. These results suggest that the phase exhibiting partly the dark image just after the N mesophase during the cooling process is a Sm mesophase with homeotropic arrangement of mesogen molecules. The same homeotropic arrangement was found partly during a cooling process of EPy (10 mol%)/10OCB, although the mixture did not exhibit a N mesophase. On the other hand, the phenomenon was not found for 8OCBCz (<20 mol%)/10OCB [11]. These results suggest that Py groups having an alkyl chain induce partly homeotropic alignment of mesogen molecules at the surface of quartz substrates. The difference between 8OCBPy and 8OCBCz is likely to be attributed to a difference in bulkiness between Py and Cz chromophores.

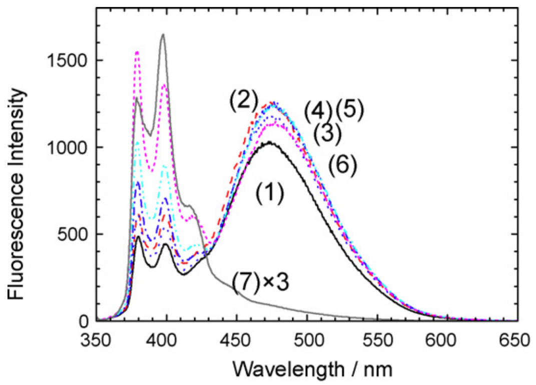


Fig. 3. Temperature dependence of the fluorescence spectra of 8OCBPy (10 mol%)/10OCB. (1) 369 K, (2) 355 K, (3) 350 K, (4) 335 K, (5) 325 K, (6) 311 K, and (7) 306 K. The excitation wavelength is 342 nm, which implies an excitation of Py chromophores. The spectra were measured by means of a cooling process from the isotropic phase. The spectra in the figure were obtained from many measured spectra.

Thus, the following phase transition was found for the 8OCBPy (10 mol%)/10OCB mixture:

$$\text{crystal (Cr)} \xleftrightarrow{305\,\text{K}} \text{smectic A (Sm A)} \xleftrightarrow{350\,\text{K}} \text{nematic (N)} \xleftrightarrow{354\,\text{K}} \text{isotropic (I)}$$

Since a temperature range of the N mesophase is narrow, we will not discuss experimental data in the N mesophase in the followings.

Its reference sample, EPy (10 mol%)/10OCB, exhibited the following transition:

$$\text{crystal (Cr)} \xleftrightarrow{309\,\text{K}} \text{smectic A (Sm A)} \xleftrightarrow{349\,\text{K}} \text{isotropic (I)}$$

3.3. *Steady-state fluorescence spectra of mixed 8OCBPy (10 mol%)/10OCB samples as a function of temperature*

As shown in Fig. 3, the fluorescence spectra of 8OCBPy (10 mol%)/10OCB were measured as a function of temperature during a cooling process from the I phase. The spectrum of the crystal state (306 K) is safely assigned to the monomer fluorescence, and the spectra of the other phases to the monomer and excimer fluorescence. The intensity ratios of the excimer (475 nm) to the monomer (400 nm) fluorescence (I_{475}/I_{400}) were plotted as a function of temperature in Fig. 4, together with those of the EPy

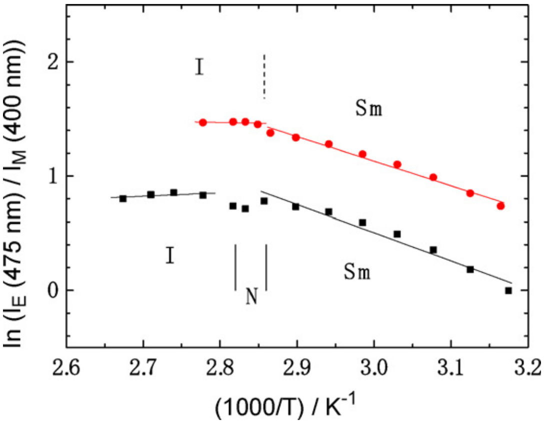


Fig. 4. Temperature dependence of the intensity ratio (I_{475}/I_{400}) of the excimer to the monomer fluorescence. The intensities for the 8OCBPy system were obtained from the spectra shown in Fig. 3. 8OCBPy (10 mol%)/10OCB (■) and EPy (10 mol%)/10OCB (●).

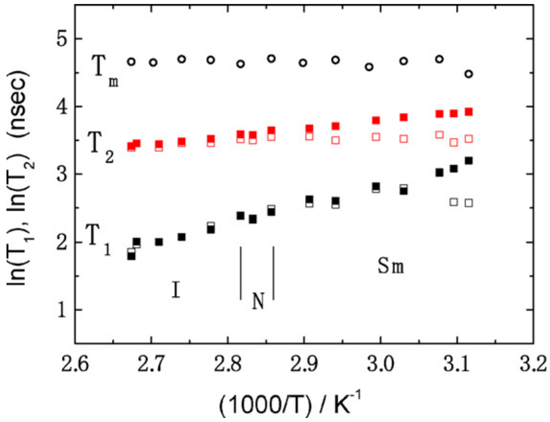


Fig. 6. Decay times T_1 and T_2 obtained from the monomer (□) and excimer (■) fluorescence rise and decay curves of 8OCBPy (10 mol%)/10OCB and the decay time T_m (○) obtained from the monomer fluorescence decay curve of 8OCBPy (0.1 mol%)/10OCB.

(10 mol%)/10OCB sample. These are apparent values because these spectra are not corrected for detector sensitivity and are not divided into the two fluorescence components. The intensity ratio increases with temperature in the Sm mesophase, and its slope exhibits slightly changes at the phase transition temperatures. The former increase with temperature indicates that the increasing temperature induces a larger increase in the excimer formation rate than in the excimer disappearance (= deactivation + dissociation) rate in the Sm mesophase. The smaller ratios for the 8OCBPy system than that for the EPy system suggest that the excimer formation rate for the 8OCBPy system is smaller than that for the EPy system. To reveal a role in the excimer formation and disappearance as environment of mesophases, the following kinetic analysis was performed.

3.4. *Analysis of monomer and excimer fluorescence rise and decay curves*

The typical monomer and excimer fluorescence rise and decay curves in the I and Sm phases of 8OCBPy (10 mol%)/10OCB are shown in Fig. 5 [14]. The observed wavelength regions were 369–387 and 494–512 nm for the monomer and excimer fluorescence, respectively. The rise and decay curves were fitted to a two-component exponential function, (1), as well as in solution. No fast process is detected for the rise curve of the excimer fluorescence, suggesting that there is no preformed excimer site and that excimer is formed *via* the excited monomer state. The present result is the same as the case of the chlolesteric system reported by Sisido et al. [8], where Py compounds covalently linked to the chlolesteric mesogen were doped with a concentration of 3–25 mol%.

Fig. 6 shows the temperature dependence of the time constants T_1 and T_2 obtained from the monomer and excimer fluorescence rise and decay curves of 8OCBPy (10 mol%)/10OCB, together with the monomolecular decay time T_m obtained from the monomer fluorescence decay curve of 8OCBPy (0.1 mol%)/10OCB. The latter dilute sample exhibited only the monomer fluorescence, whose decay curve was fitted to a single-component exponential function. A good agreement is found between the time constants obtained from monomer and excimer fluorescence rise and decay curves except for low temperatures. Because, at low temperatures, the rate of the excimer formation is low and the contribution of the fast decay component (G_1) in the monomer decay curves is small (Fig. 8), the exact determination of T_1 and G_1 values based on the monomer decay curves is very difficult. Hence, we will discuss the experimental data ($<3.05 \times 10^{-3}\,\mathrm{K}^{-1}$) except for those at low temperatures. The monomolecular decay times (T_m) are almost independent of temperature, indicating that the process is not affected by the environment and temperature condition.

In Fig. 7, the decay times T_1 and T_2 obtained for EPy (10 mol%)/10OCB and the monomolecular decay times T_m obtained for the dilute sample of 0.1 mol% are shown. The similar temperature dependence to the 8OCBPy system is observed.

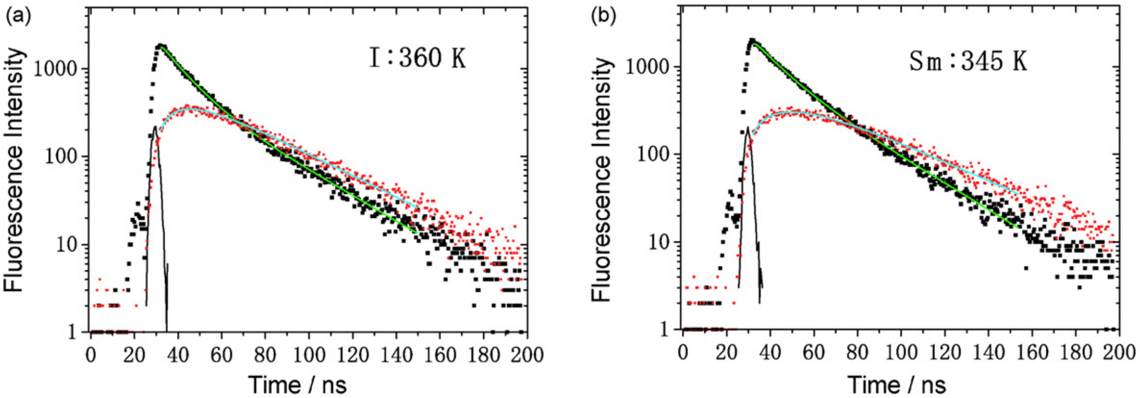


Fig. 5. Rise and decay curves of monomer (λobs = 369–387 nm) and excimer (λobs = 494–512 nm) fluorescence of 8OCBPy (10 mol%)/10OCB. (a) I phase at 360 K and (b) Sm mesophase at 345 K.

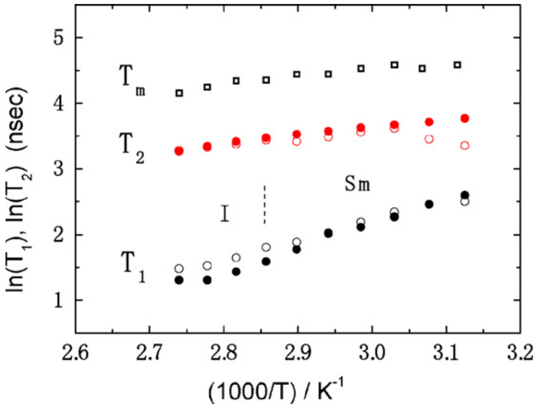


Fig. 7. Decay times T_1 and T_2 obtained from the monomer (○) and excimer (●) fluorescence rise and decay curves of EPy (10 mol%)/10OCB and the decay time T_m (□) obtained from the monomer fluorescence decay curve of EPy (0.1 mol%)/10OCB.

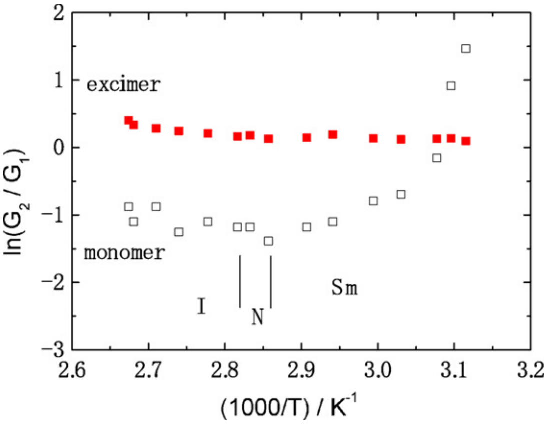
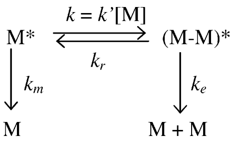


Fig. 8. Ratios of pre-exponential factors ($|G_1/G_2|$) obtained from the analyses of the monomer and excimer fluorescence rise and decay curves of 8OCBPy (10 mol%)/10OCB. Monomer (■) and excimer (▨).

The absolute values $|G_1/G_2|$ of ratios of pre-exponential factors obtained from the monomer and excimer fluorescence rise and decay curves of 8OCBPy (10 mol%)/10OCB are shown in Fig. 8 as a function of temperature. The ratios for the excimer fluorescence rise and decay curves are nearly constant of −1, being irrespective of the temperatures, whereas the ratios for monomer fluorescence decay curves show a slight change at the phase transition. The above results mean that the excimer formation follows to the following Birks scheme:



Assuming that the deactivation rate constant (k_m) of the monomer excited state for the mixtures of 10 mol% is the same as the inverse of the monomolecular decay time T_m for the dilute mixtures, one can evaluate the other three rate constants (k, k_r, and k_e) from three parameters (T_1, T_2, and G_2/G_1) for the monomer fluorescence decay curves according to the following equations connecting between the experimental values and the rate constants:

$$G_\mathrm{m} = \frac{G_1}{G_2} \tag{2}$$

$$k = \frac{(G_\mathrm{m}/T_1 + 1/T_2)}{(G_\mathrm{m} + 1)} - k_\mathrm{m} \tag{3}$$

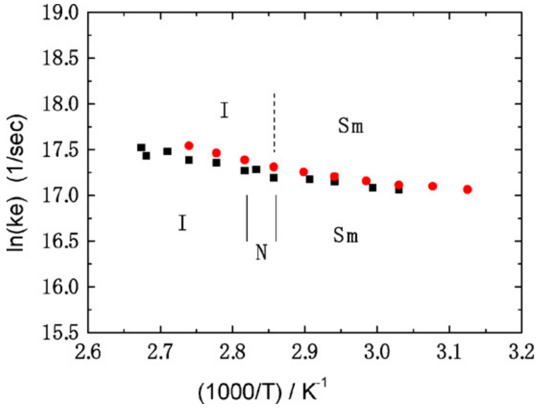


Fig. 9. Rate constants of excimer deactivation, k_e, of 8OCBPy (10 mol%)/10OCB (■) and EPy (10 mol%)/10OCB (●).

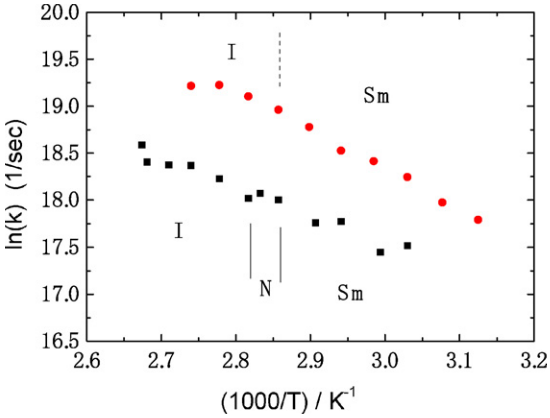


Fig. 10. Rate constants of excimer formation, k, of 8OCBPy (10 mol%)/10OCB (■) and EPy (10 mol%)/10OCB (●).

$$k_\mathrm{r} = \frac{[(k_\mathrm{m} + k)(1/T_1 + 1/T_2 - k_\mathrm{m} - k) - 1/(T_1 T_2)]}{k} \tag{4}$$

$$k_\mathrm{e} = 1/T_1 + 1/T_2 - k_\mathrm{m} - k - k_\mathrm{r} \tag{5}$$

The temperature dependence of the three rate constants for these two systems doped with 10 mol% are shown in Figs. 9–11. As shown in Fig. 9, the rate constants of excimer deactivation (k_e) show no difference between the 8OCBPy and EPy systems and little phase dependence, although the activation energies in the I phase are slightly larger than those in the Sm mesophase. These indicate

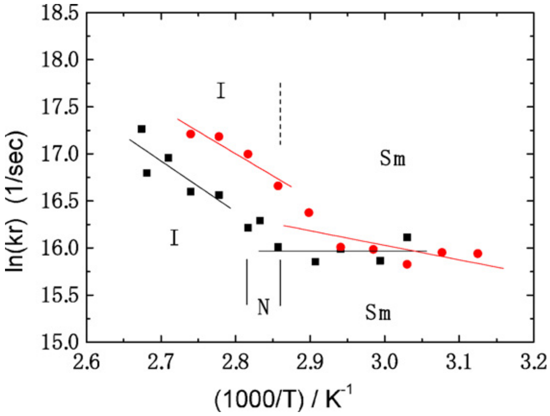


Fig. 11. Rate constants of excimer dissociation, k_r, of 8OCBPy (10 mol%)/10OCB (■) and EPy (10 mol%)/10OCB (●).

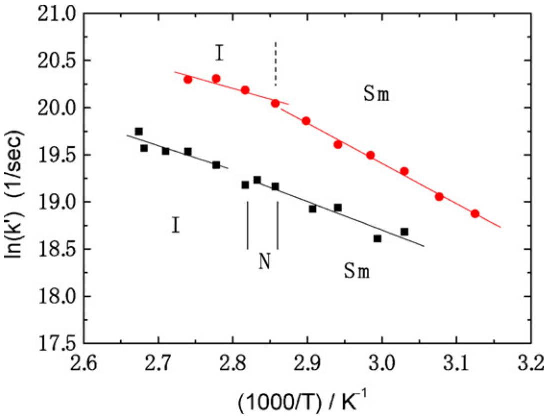


Fig. 12. Bimolecular rate constants of excimer formation, k', of 8OCBPy (10 mol%)/10OCB (■) and EPy (10 mol%)/10OCB (●).

that electronic state of the excimer for the 8OCBPy system is almost the same as that for the EPy system.

The bimolecular rate constants (k') for the excimer formation were evaluated by dividing the rate constants (k) of the excimer formation by the molar concentration of Py compounds, and their temperature dependences are shown in Fig. 12. The bimolecular rate constants for the 8OCBPy system are smaller than that for the EPy system, which corresponds to the result in Fig. 4. Because a diffusion process would not be considered to be important for the excimer formation in the very viscous Sm mesophase of the present systems [15], this difference cannot be interpreted by a slower diffusion of 8OCBPy than EPy. For excimer formation in very viscous systems, the following mechanism would be proposed: the excitation energy migrates among Py chromophores, subsequently is trapped at an excimer-forming site, and a pair of Py chromophores in the excimer-forming site changes both their relative distance and orientation. The presence of the excitation energy migration and trapping processes is not clear. In addition, even if these processes exist, the processes would not be largely thermally activated ones. On the other hand, the reorientation process of Py chromophores in the excimer-forming sites requires some activation energy. The activation energy for the 8OCBPy system evaluated from Fig. 12 is 25 kJ mol^{-1} in the Sm mesophase, and is not much different from that evaluated for the EPy system (36 kJ mol^{-1}). On the other hand, the activation energy in the I phase is 21 and 19 kJ mol^{-1} for the 8OCBPy and EPy systems, respectively, and the value for the 8OCBPy system is only slightly larger than that for the EPy system. Although these values are larger than that reported for pyrene in a cyclohexane solution (13 kJ mol^{-1}) [16], whose value is controlled by the viscosity characteristics of cyclohexane, the excimer formation in the I phase is most probably due to a diffusion-controlled process. This is supported by usual negative values of enthalpy and entropy changes for the excimer formation in the I phase (*vide infra*).

The dependence of the rate constants of the excimer dissociation (k_r) on temperature is shown in Fig. 11. Although the scatter in the data is far large, one can confirm that the activation energies in the Sm mesophase are very smaller than those in the I phase. The activation energies in the Sm mesophase are about 0 and 13 kJ mol^{-1} for the 8OCBPy and EPy systems, respectively. These results indicate that the activation energy of the rate constant of the excimer dissociation is remarkably affected by the environment of the Sm mesophase. Here we consider the binding energy (enthalpy of the excimer formation: $\Delta H = E - E_r$) of the excimer, whose value is obtained by subtracting the activation energy E_r for excimer dissociation from the activation energy E for excimer formation. In addition, the entropy of excimer formation was calculated from the frequency factors, k^0 and k_r^0, of Arrhenius plots for k and k_r shown in Figs. 10 and 11, respectively, according to the following equation:

$$\frac{\Delta S}{R} = \ln\left(\frac{k^0}{k_r^0}\right) \quad (6)$$

Table 1
Enthalpy and entropy for excimer formation in I and Sm phases

	8OCBPy		EPy	
	I	Sm	I	Sm
ΔH (kJ mol^{-1})	−23	25	−21	23
ΔS (J mol^{-1} K^{-1})	−51	90	−39	87
ΔG (kJ mol^{-1})$_{330\,\mathrm{K}}$	−6.7	−4.6	−7.5	−6.3

These values are listed in Table 1.

Fig. 13 shows energy diagrams drawn from the above data. The positive values of the enthalpy in the Sm mesophase indicate that the excimer state has higher energy than the monomer excited state, which situation is anomalous. On the other hand, the negative values in the I phase indicate that the excimer state has lower energy than the monomer excited state, which situation is typically observed in solution. The anomalous situation in the Sm mesophase can be interpreted in the following way. The reorientation of Py chromophores resulting in the excimer formation in the Sm mesophase causes a disorder of the mesogen molecules constructing the Sm mesophase, which results in a strong repulsive force between Py chromophores forming the excimer. The repulsive force will increase the energy of the excimer state, resulting in a decrease of the activation energy for the excimer dissociation. That is, the excimer formation in the Sm mesophase is considered to include the motion of the disordering of mesogen molecules in the Sm mesophase.

The same consideration is also possible from the viewpoint of the entropy for the excimer formation. Usually, ΔS for the excimer formation is negative, because excimer formation is accompanied by the reduction of the degrees of freedom when an excimer having two molecules in a rigid overlap structure is formed from two uncorrelated molecules. Thus, in the present case, the negative values in the I phase are usual for excimer formation, whereas the positive values in the Sm mesophase are unusual (anomalous). The latter unusual values are interpreted by the excimer formation of 8OCBPy including the loss of orientation of the environmental 10OCB-mesogen molecules around 8OCBPy in the Sm

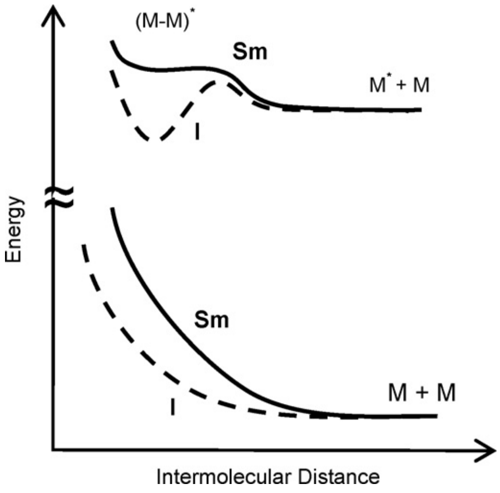


Fig. 13. Energy diagrams for ground and excited states in the Sm and I phases for the 8OCBPy (10 mol%)/10OCB sample.

layer. That is, the excimer formation in the excited state is probably associated with a decrease in ordering of 10OCB-mesogens around 8OCBPy molecules in the Sm layers. This disordering of the 10OCB-molecules around the 8OCBPy molecules overcompensates the increase in order which necessarily occurs in any system upon the excimer formation. Consequently, a free energy change ΔG for the excimer formation becomes negative. That is, in the present systems, the entropy-controlled excimer formation including disordering of the environmental 10OCB-mesogen molecules most probably occurs in the Sm mesophase, where 8OCB-mesogen groups of the 8OCBPy molecules are expected to be buried in the 10OCB layers.

As aforementioned, the anomalous values are observed also for the EPy system. This is most probably correlated with the result of the polarizing microscope observation. As mentioned earlier, the result is that the dark image for the Sm mesophase was partly observed for the EPy system as well as for the 8OCBPy one, which suggests that Py chromophores having an alkyl chain induce partly homeotropic alignment of mesogens. This suggests that EPy molecules are not simply dispersed in the Sm mesophase and that ethyl groups of EPy molecules are also buried in mesogen arrangement in the 10OCB layers.

The negative value of ΔS for the 8OCBPy system is lager than that for the EPy system. The larger degree of the disordering for the 8OCBPy system than that for the EPy system is explained in terms of strong interaction between the 8OCB-mesogen groups of 8OCBPy molecules and 10OCB-mesogen molecules in the layers as compared to the ethyl group of the EPy molecules.

The present results are similar to those for the intermolecular excimer formation of cholesteryl 3-(1-pyrenyl)propanonate in the Ch mesophase of its cholesteric LC mixtures reported by Sisido et al. [8]. The energy diagrams shown in Fig. 13 are also similar to those reported. The present positive ΔS value, however, is larger than that of the chlolesteric system. In Ch mesophases, mesogens are oriented along a particular direction within a quasi-nematic layer. Hence, the degree of the ordering of mesogens in Ch mesophases is smaller than that in Sm A mesophases. The large ordering in Sm A mesophases is most probably responsible for the large positive ΔS value in Sm A mesophases as compared to that in Ch mesophases. The similar positive ΔH and ΔS values to the present results were reported for the intramolecular excimer formation of meso-2,4-di(2-pyrenyl)pentane (meso-2DPP) in methylcyclohexane [17]. The positive values of ΔH (ca. 3 kJ mol^{-1}) and ΔS (ca. 43 J mol^{-1} K^{-1}) for the meso-2DPP system, however, are smaller than those for the present intermolecular excimer formation in the Sm mesophase. Here we consider both the alignment of 8OCBPy molecules in the Sm mesophase of 8OCBPy (10 mol%)/10OCB and a schematic image of the excimer formation in the system. 10OCB-mesogens form a Sm A mesophase, which is named a partial bilayer smectic with an overlapping of core moieties (interdigitated Sm A structure). The molecular motion of the mesogens in the Sm mesophase is strongly restricted as compared to those in the I and N phases. Assuming that the alignment of the *n*-octyloxybiphenyl group of 8OCBPy is the same as that of the *n*-decyloxybiphenyl of 10OCB, almost all of the Py chromophores of 8OCBPy are located in the vicinity of a space between the bilayers in the Sm mesophase of this mixed system. As mentioned earlier, the excimer formation between Py chromophores of 8OCBPy, which are connected to *n*-octyloxybiphenyl groups buried in 10OCB-mesogen layers, will destroy the alignment of the 10OCB-mesogen molecules around the 8OCBPy in the Sm layers. The decrease in ordering resulted from the destruction induces the increase in the entropy for the excimer formation associated with environmental 10OCB-mesogen molecules. Such behavior is likely to induce the large positive ΔH and ΔS values.

4. Concluding remarks

To dope a large amount of Py chromophores to mesophases, 8OCBPy was synthesized. However, attempts to dope it with a large amount to cyanobiphenyl mesogens were unsuccessful and the homogeneous doping concentration of 8OCBPy to 10OCB was below 10 mol%. The photophysical properties of its binary mixtures with 10OCB were investigated in comparison with those of the binary mixture of EPy with 10OCB.

8OCBPy and EPy exhibited intermolecular excimer fluorescence in a highly concentrated solution. The mixture of 8OCBPy exhibited the Sm A and N mesophases, while the mixture of EPy exhibited the Sm A mesophase. The results of their polarizing microscope observations suggested the presence of the Sm A mesophase with homeotropic arrangement of mesogen molecules during the cooling process. The mesophases and I phase of both of the samples exhibited excimer as well as monomer fluorescence. The excimer formation-dissociation kinetics was investigated in the Sm and I phases. Positive enthalpy and entropy changes for the excimer formation were found in the Sm A mesophase, whereas these usual negative changes were found in the I phase. This anomalous phenomenon in the Sm A mesophase was interpreted by the entropy-controlled excimer formation associated with the decrease in ordering of the 10OCB-mesogen molecules around the 8OCBPy arranged in the Sm A layers.

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