

Photophysical and photoconductive properties of a carbazolyl derivative with a mesogen group of alkoxy cyanobiphenyl in mesophases

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Abstract

4-Cyano-4'-(1-(*N*-carbazolyl)-*n*-octyloxy)biphenyl (8OCBCz), where the hydrogen atom of a well-known mesogen 4-cyano-4'-(*n*-octyloxy)biphenyl (8OCB) is substituted with one carbazolyl (Cz) chromophore, was synthesized, and the photophysical and photoconductive properties of its neat form and its binary mixtures with 4-cyano-4'-(*n*-decyloxy)biphenyl (10OCB) were investigated. The 8OCBCz exhibited intermolecular exciplex fluorescence in concentrated solutions. When 8OCBCz was quenched from its molten state, it formed an amorphous state, which exhibited exciplex fluorescence and transient photocurrent signals of both the positive and negative charge carriers. However, their mobilities could not be determined because of the strongly dispersive signals. The mixtures exhibited smectic A (Sm A) and nematic (N) mesophases. These mesophases and the isotropic phase exhibited exciplex as well as monomer fluorescence. The exciplex formation mechanism in the Sm A mesophase differed from those in the N and isotropic phases. The transient photocurrent signals for both the positive and negative charge carriers were also observed for the binary mixtures. Ionic conduction was suggested for the N and isotropic phases, whereas electronic conduction was suggested for the Sm A mesophase. The ionic carrier species were proposed.

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1. Introduction

Liquid crystals (LCs) are one of the important organic materials that have been extensively investigated because of their electro-optical characteristics and their application to display devices. Recently, the photoconductive properties of LCs have attracted attention [1,2] because it was found that columnar discotic LCs and the smectic mesophase of calamitic LCs exhibit a rapid electronic transport. The fluorescence properties of mesogens have attracted considerable attention with respect to the relationship among the photophysical property, phase transition, and molecular ordering in various mesophases. In particular, the fluorescence properties of alkyl- and alkoxy-cyanobiphenyls (abbreviated as *n*CB and *n*OCB, respectively), which are widely known as representative mesogens and have been extensively investigated for technical applications as electro-optical LC

devices, were effectively examined in solution as well as in bulk neat forms [3–5]. In addition, to reveal the photophysics in ordered molecular assemblies, excimer and exciplex formations were investigated in cholesteric mesophases, where the fluorescent chromophore itself was either a cholesteric mesophase-forming substance or not [6–10]. Recently, to apply luminescent mesogens and LC materials to display and electroluminescent (EL) devices, photo-emission and EL properties of mesogens doped with fluorescent chromophores, mesogens having electron- and/or hole-transporting segments, and so on have been investigated [11].

Poly(*N*-vinylcarbazole) (PVCz) is widely known as one of the amorphous polymeric materials possessing highly photoconductive properties; further, amorphous neat films of its dimeric model compounds exhibit high photoconductivity as well [12,13]. In addition to their photoconductive properties, the photophysical properties of these polymeric and dimeric compounds have also been investigated in their amorphous solid state, including luminescence [14–17] and transient absorption measurements [18–21]. Furthermore, PVCz and its related

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polymeric and monomeric compounds were also investigated from the viewpoint of their application to organic EL devices [22]. Therefore, compounds containing Cz chromophores are interesting materials for physicists, chemists, and material scientists.

By combining the recent studies of LCs on their photoconductive and fluorescence properties with the unique characteristics of Cz compounds with respect to their photo-physical and hole transport properties, mesogens comprising Cz chromophores are an interesting class of materials for material chemists. We synthesized a mesogen including one Cz chromophore, 4'-*n*-octylphenyl carbazole-2-carboxylate, and reported its absorption and fluorescence spectra, FT-IR spectra, and picosecond transient absorption spectra [23]. However, the temperature range of the LC phase of this mesogen was remarkably high. Sisido and co-workers synthesized Cz chromophores that were covalently linked to a cholesteric group [10]. These cholesteric Cz compounds did not exhibit a cholesteric mesophase by themselves; however, this mesophase was observed in their 1:1 mixture with other cholesteric mesogens. The fluorescence properties of these mixtures were investigated with regard to their cholesteric and isotropic phases. In addition, cholesteryl methyl terephthalate (CMT) was synthesized and the exciplex formation was investigated in the cholesteric mesophases comprising the cholesteric Cz compounds as a donor and CMT as an acceptor [9]. It was concluded that a constraint on the orientation of these chromophores in the cholesteric mesophase plays an important role in the exciplex formation.

In the present study, we focused on the smectic (Sm) and nematic (N) mesophases containing Cz chromophores and synthesized 4-cyano-4'-(1-(*N*-carbazolyl)-*n*-octyloxy)biphenyl (8OCBCz), where one Cz chromophore is covalently linked to the well-known mesogen, 4-cyano-4'-(*n*-octyloxy)biphenyl (8OCB). This was performed in order to enable the doping of the net concentration of Cz chromophores such that it was more than that in the case of a mixture of free Cz molecules with mesogens. We now investigate the fluorescence and photoconductive properties of both 8OCBCz amorphous neat films and a binary system of 8OCBCz/10OCB (4-cyano-4'-(*n*-decyloxy)biphenyl) in Sm, N, and isotropic (I) phases. The characteristic of the present system is that a mesogen acts as an acceptor by itself, which differs from the cholesteric system proposed by Sisido et al. [9].

2. Experimental

First, carbazole was synthesized from 1,2,3,4-tetrahydrocarbazole. The 8OCBCz was synthesized from the carbazole and 4-cyano-4'-(1-bromo-*n*-octyloxy)biphenyl, which was synthesized from 4-cyano-4'-hydroxybiphenyl and 1,8-dibromooctane. Further, *N*-ethylcarbazole (ECz) was synthesized from the carbazole and iodoethane. The 8OCB was synthesized from 4-cyano-4'-hydroxybiphenyl and 1-iodooctane. These compounds were identified by means of their IR and NMR spectra. The 10OCB (BDH chemicals) was used as received. Tetrahydrofuran (THF) (Dotite, Spectrosol) and dichloromethane (Dotite, Spectrosol) were used without fur-

ther 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. For the time-of-flight (TOF) measurement, the sample was sandwiched between two ITO glass plates with a polyimide or Teflon spacer (thickness, 12.5 or 25 μm , respectively). The surfaces on the quartz and ITO glass plates were not rubbed mechanically to establish self-organized sample structures.

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 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 N₂ 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.

In the TOF measurements, a N₂ laser pulse light (FWHM, *ca.* 8 ns) was irradiated on the cell set in a cryostat with a vacuum or N₂ gas purge. An induced transient current was amplified by a preamplifier (NF corporation 5307) and recorded using a digital oscilloscope (LeCroy 9362C).

3. Results and discussion

3.1. Absorption and fluorescence spectra of 8OCBCz in solution

Fig. 1 shows the absorption and fluorescence spectra of 8OCBCz, ECz, 8OCB, and an equimolar mixture of ECz and 8OCB in a dilute THF solution. The absorption spectrum of 8OCBCz is very similar to that of the mixture of ECz and 8OCB, which indicates no interaction between Cz 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 8OCBCz. However, the fluorescence spectrum of 8OCBCz excited at 292 nm is similar to that of ECz, whereas the fluorescence spectrum of the mixture excited at 292 nm is similar to that of 8OCB. These results indicate the occurrence of intramolecular energy transfer from the CB to Cz chromophores in 8OCBCz.

The fluorescence spectra of 8OCBCz in a dichloromethane solution were examined as a function of the concentration (Fig. 2(a)). With an increase in the concentration of 8OCBCz, a new fluorescence appears in longer wavelengths and its relative intensity to the Cz monomer fluorescence increases. This phenomenon is also observed for the solution of equimolar mixtures of ECz and 10OCB (Fig. 2(b)). This new fluorescence is attributed to an exciplex formed between the Cz and CB chromophores. Further, a similar concentration dependence was observed for the fluorescence spectra with the excitation of the Cz chromophore at 337 nm. These results indicate that 8OCBCz

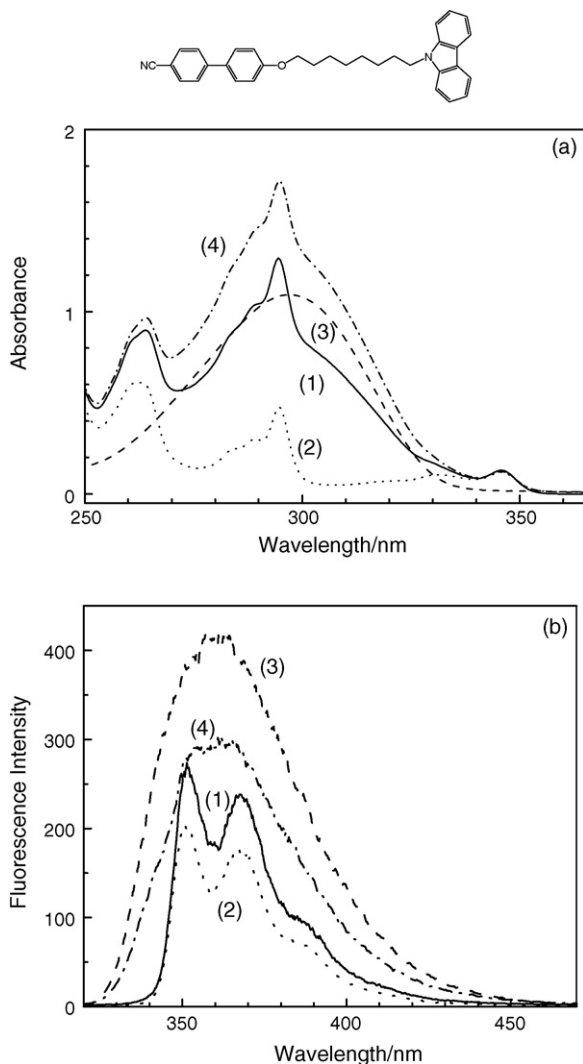


Fig. 1. Chemical structure of 8OCBCz and (a) absorption and (b) fluorescence spectra of (1) 8OCBCz, (2) ECz, (3) 8OCB, and (4) mixture with the same content of ECz and 8OCB in a dilute THF solution. Excitation wavelength, 292 nm.

forms an intermolecular exciplex between the Cz and CB groups 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 THF solutions of 8OCBCz and 10OCB (1×10^{-5} M) were 13.7 and 1.5 ns, respectively. The former lifetime is almost identical to the fluorescence lifetime of ECz. The lifetime of the exciplex fluorescence in a concentrated dichloromethane solution of 8OCBCz (2×10^{-1} M) was determined to be 31 ns.

3.2. Fluorescence spectra of 8OCBCz in its neat form as a function of temperature

8OCBCz transformed into an amorphous state after it was cooled from an isotropic molten state. The results of both the DSC measurement of the neat solid state and its polarizing optical microscope observation revealed the presence of two

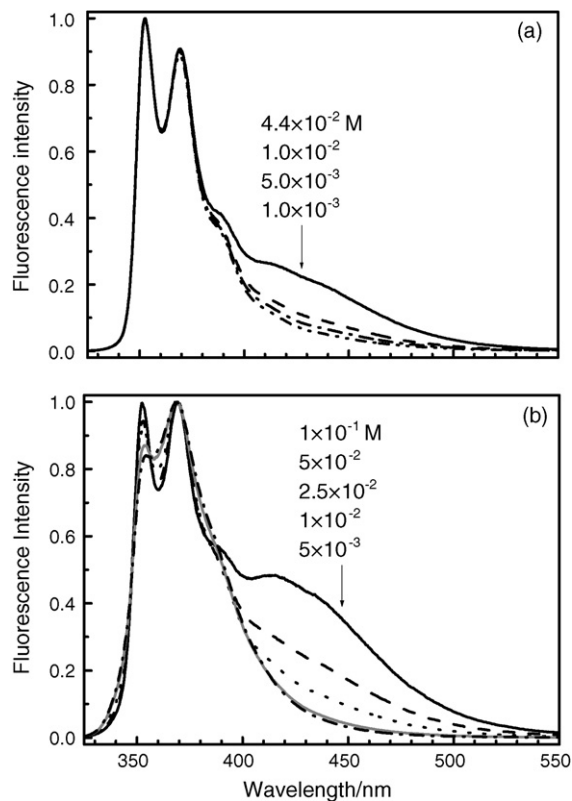


Fig. 2. Normalized fluorescence spectra of: (a) 8OCBCz and (b) mixtures of ECz and 10OCB with various concentrations in dichloromethane solution. Excitation wavelength, 292 nm.

types of crystalline states in addition to the isotropic amorphous state. Fig. 3 shows the temperature dependence of the fluorescence spectra of neat 8OCBCz films. The spectra were measured through a heating process from the amorphous state. The broad fluorescence of the amorphous form with a peak at around 405 nm is attributed to the exciplex formed between the

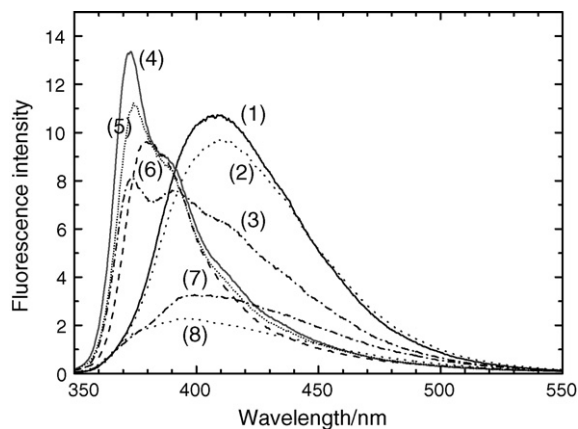


Fig. 3. Temperature dependence of the fluorescence spectra of neat 8OCBCz films. (1) 298, (2) 311, (3) 318, (4) 326, (5) 343, (6) 378, (7) 394, and (8) 427 K. The excitation wavelength is 337 nm, which implies an excitation of Cz chromophores. The spectra were measured by means of a heating process from the amorphous state. The spectra in the figure were obtained from many measured spectra.

Cz and CB chromophores, although the peak position is located at slightly shorter wavelengths than that of the exciplex fluorescence in dichloromethane solution. In neat amorphous films, the excitation energy effectively migrates among the Cz chromophores, is trapped at the exciplex-forming sites, and emits an exciplex fluorescence. Hence, even if the concentration of the exciplex-forming sites is small, almost the entire fluorescence of the neat amorphous form is due to the exciplex.

During heating, the broad exciplex fluorescence abruptly changes to a structured fluorescence (311 → 318 → 326 K). The structured fluorescence is ascribed to the Cz monomer according to its spectral shape and position. This spectral change corresponds to the phase transition from the amorphous to crystalline states. Further, the fluorescence changes to a new non-structured one with a peak at around 380 nm and a shoulder at around 395 nm (378 K). This spectral change corresponds to the transition between two crystalline states. As mentioned earlier, the presence of this transition was indicated by both the DSC measurement and a distinct change in the crystalline morphology observed for this temperature range under the crossed nicols of a polarizing optical microscope. Although the assignment of this new non-structured fluorescence is difficult, this fluorescence is probably due to the Cz monomer perturbed by the surrounding CB chromophores. At the phase transition from the crystalline to isotropic molten states, the fluorescence abruptly changes to a broad fluorescence with a peak at around 400 nm and a shoulder at 378 nm (378 → 394 K). This fluorescence is most probably assigned to the exciplex fluorescence together with a small portion of monomer fluorescence. The formation of the exciplex is most probably because of a dynamic process because the samples are in the liquid state and an iso-emissive point is observed.

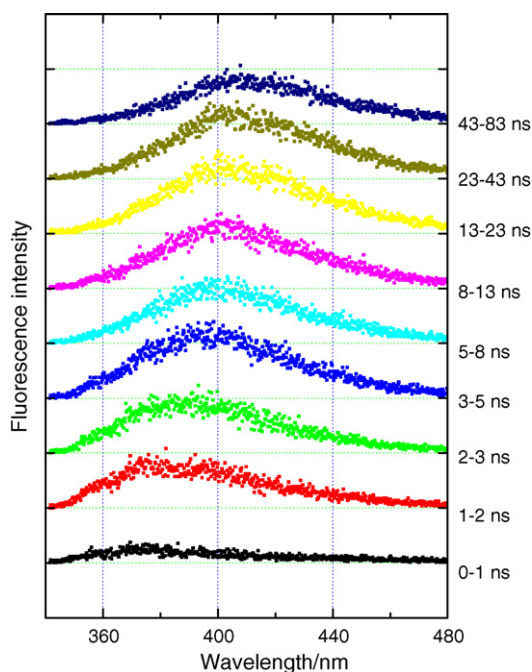


Fig. 4. Time-resolved fluorescence spectra of the amorphous state of neat 8OCBCz films at 295 K. The time window is indicated in the figure.

Fig. 4 shows the time-resolved fluorescence spectra observed for the amorphous state of neat 8OCBCz films at 295 K. In the early-gated spectrum, the fluorescence is mainly observed at short wavelengths. The peak of the fluorescence spectra continuously shifts to longer wavelengths with time. At the latest gated time, the peak is located at around 410 nm. The early- and late-gated spectra are safely assigned to the monomer and exciplex fluorescence, respectively. These results support the exciplex formation mechanism mentioned earlier. The lifetime of the exciplex fluorescence obtained by analysis of the decay curve monitored at 400–415 nm was 29 ns.

3.3. Photoconductive properties of neat amorphous 8OCBCz films

The exciplex formation leads to an increase in the photo-carrier generation efficiency, resulting in high photoconduction. The 1,3-di(*N*-carbazolyl)propane (DCzP), which is one of the dimeric model compounds of PVCz, forms an amorphous state as well as 8OCBCz, and the amorphous state exhibits the hole-transporting property with a high mobility as compared to PVCz films [13]. We examined the photoconductive properties of amorphous 8OCBCz films using the TOF method. Typical transient photocurrent signals are shown in Fig. 5. Both the positive and negative charge carriers are observed, and the time profiles of their signals are strongly dispersive, which are very different from those in amorphous DCzP. That is, for the amorphous DCzP, only the positive charge carrier was observed and the signal was non-dispersive. Since the pulse light at a wavelength of 337 nm is absorbed by Cz chromophores, the original photo-carriers are most likely to be a cation radical of Cz and an anion radical of CB. Since the amorphous 8OCBCz state is rigid, the carrier transport is not considered to be of an ionic nature, but of an electronic one. The carriers, however, are trapped immediately after they begin hopping from the carrier generation sites, resulting in the present dispersive signals. Although Cz compounds have generally been known as

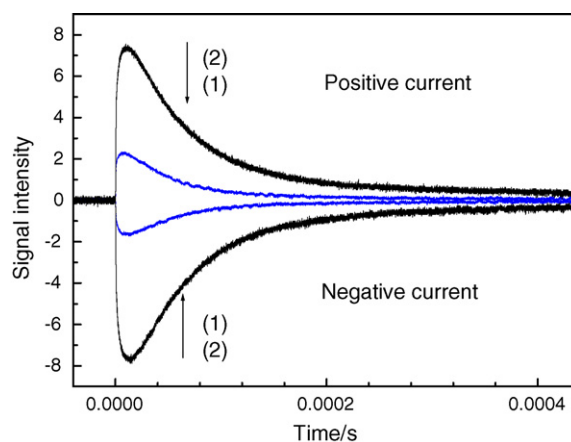


Fig. 5. Transient photocurrent signals of amorphous 8OCBCz films. Electric field: (1) 78.4 and (2) 235.6 kV/cm. Film thickness, 12.5 μm . Positive and negative current signals were obtained for the positive and negative electrode illumination, respectively.

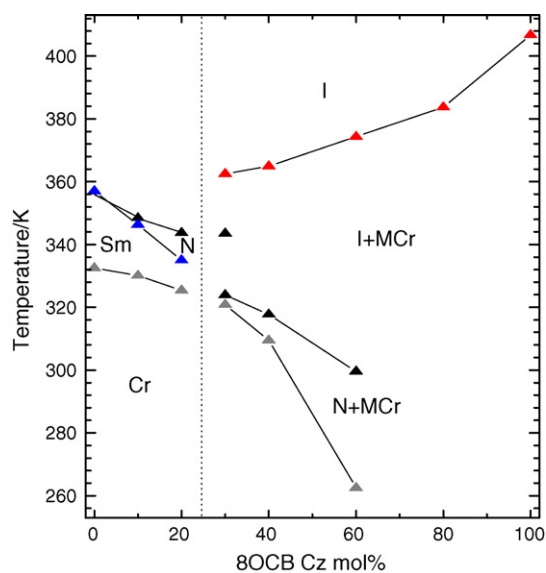


Fig. 6. Binary phase diagram for 8OCBCz/10OCB. MCr denotes mixed crystals.

hole-transporting materials, it has recently been reported that 4,4'-bis(*N*-carbazolyl)-2,2'-biphenyl films exhibit slightly dispersive electron and hole transient signals [24]. The present 8OCBCz is a novel compound that transports both electrons and holes. However, the mobility values were not determined because of the strongly dispersive signals.

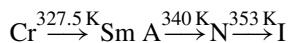
3.4. Binary phase diagram of a 8OCBCz/10OCB system

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



Fig. 6 shows a binary phase diagram of 8OCBCz/10OCB, which was revealed for a heating process using the DSC measurements and polarizing optical microscope observations. For samples doped with >30 mol% 8OCBCz, new melting points different from those of 10OCB and 8OCBCz (406.7 K) were found. The melting points increase with the 8OCBCz content of the mixture. This indicates the appearance of mixed crystals (MCr) formed between these two compounds, which was also confirmed by the polarizing optical microscope observation. As shown in Fig. 6, samples doped with <20 mol% 8OCBCz exhibit a homogeneous N mesophase in addition to the Sm mesophase. Recently, it has been reported that 10OCB exhibits an N mesophase induced by the doping of 8OCB [25].

We doped 8OCBCz into 8OCB, which exhibited the following phase transition:



The doping of >15 mol% 8OCBCz resulted in the formation of mixed crystals, as observed for the 8OCBCz/10OCB mixtures, and the disappearance of the Sm mesophase. Therefore, we used 8OCBCz (20 mol%)/10OCB as the mixed sample. For a cool-

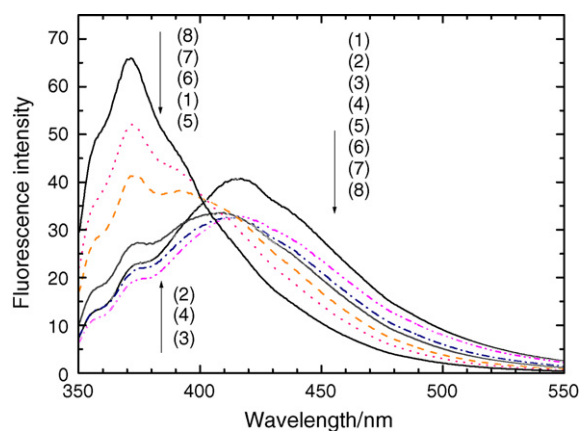
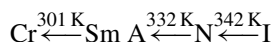


Fig. 7. Temperature dependence of the fluorescence spectra of 8OCBCz (20 mol%)/10OCB. (1) 303, (2) 312, (3) 323, (4) 335, (5) 349, (6) 369, (7) 385, and (8) 410 K. The excitation wavelength is 337 nm, which implies an excitation of Cz chromophores. The spectra were measured by means of a cooling process from the isotropic phase. The spectra in the figure were obtained from many measured spectra.

ing process, this mixed sample exhibited the following phase transition:



3.5. Fluorescence spectra of 8OCBCz (20 mol%)/10OCB mixed samples as a function of temperature

As shown in Fig. 7, the fluorescence spectra of 8OCBCz (20 mol%)/10OCB were measured as a function of temperature during a cooling process from the isotropic phase. The spectra are safely assigned to the monomer and exciplex fluorescence. Thus far, the excimer fluorescence of mesogens themselves and the inter- and intramolecular excimer fluorescence of dopants were investigated in relation with their phase transitions. In addition, although exciplex systems between the donors and acceptors covalently linked to cholesterol groups and the intermolecular exciplex systems of dopants were examined in cholesteric mesophases [9], the present exciplex system where a donor is covalently linked to a mesogen and an acceptor itself is the mesogen is novel.

The spectra were divided into the monomer and exciplex fluorescences, and the intensity ratios of the monomer to the exciplex fluorescence (I_M/I_E) and the peak wavelengths of the exciplex fluorescence were plotted as a function of temperature in Fig. 8. These are apparent values because these spectra are not corrected for detector sensitivity. The intensity ratio decreases linearly against the reciprocal temperature during the I and N phases without exhibiting an abrupt change at the I → N phase transition. The ratio also changes continuously around the N → Sm phase transition and maintains a constant value during the Sm phase. The peak wavelength shifts to longer wavelengths with a decrease in temperature and changes almost smoothly around the I → N phase transition. It shows an abrupt change at the N → Sm phase transition and does not change during the Sm phase. The smooth change in both the intensity ratio and peak wavelength at the I → N phase transition suggests that the effect

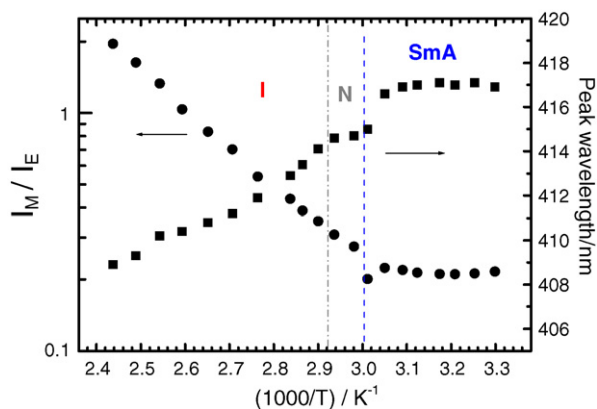


Fig. 8. Temperature dependence of the intensity ratio of the monomer to the exciplex fluorescence and the peak wavelength of the exciplex fluorescence. The intensities and the peak wavelengths were obtained after dividing the spectra into the monomer and exciplex fluorescences shown in Fig. 7.

of the N mesophase on the exciplex formation is not important in the present system. This point is significantly different from the excimer formation between mesogens and between dopants in mesophases. That is, for the excimer formation, an abrupt change was usually observed when the intensity ratio was between the excimer and monomer fluorescences. Thus, the exciplex formation in the present system would be characterized by an indistinct effect of the N mesophase. The reason for this unexpected result may be the following: excited donors are surrounded by acceptors of mesogens and the relative geometrical structures of the donor and acceptor in exciplex are permitted to be loose as compared to those in the excimer.

The different behaviors between the I and N phases and the Sm mesophase in Fig. 8 suggest that the exciplex formation mechanism is different between these phases. A dynamic exciplex formation due to a collision between an excited Cz chromophore and ground-state CB chromophore is suggested in the N and I phases. The binding energy was calculated to be 0.32 eV/mol from the slope of the intensity ratio for the N and I

phase regions, as shown in Fig. 8. This value is reasonable for typical dynamic exciplex formations.

Since the Sm mesophase is rigid as compared to the N and I phases and it restricts molecular motion, the exciplex formation in the mesophase would be attributed to the excitation energy migration among Cz chromophores and the subsequent trapping at the exciplex-forming sites with Cz and CB chromophores as neighbors.

The time-resolved fluorescence spectra were measured at 353, 341, and 319 K, which correspond to I, N, and Sm phases, respectively. As shown in Fig. 9, for the I and N phases, the monomer fluorescence is observed in a late time window of 23–43 ns. In addition, the decay time in the late time region was almost identical between the monomer and exciplex fluorescences (51 ns for I phase and 56 ns for N mesophase), suggesting the presence of an equilibrium between the monomer and exciplex in the late time region. That is, these results support the dynamic exciplex formation mechanism in the N and I phases. The behavior of the spectral change with time for the Sm mesophase is similar to that observed for the 8OCBCz amorphous state shown in Fig. 4. That is, the monomer fluorescence is mainly observed in the early-gated spectrum and the spectra continuously change to the exciplex fluorescence at the late-gated time. This observation also supports the fact that the exciplex formation in the Sm mesophase would be attributed to the excitation energy migration among Cz chromophores and the subsequent trapping at the exciplex-forming sites.

Sisido et al. reported that a constraint on the orientation of Cz and terephthaloyl chromophores covalently linked to cholesteric mesogens results in the formation of a high-energy exciplex (unstable exciplex) in the cholesteric mesophase [7]. However, in the present system, both low- and high-energy exciplex fluorescences are not observed; usually, only exciplex fluorescence is observed. This is most probably because the Cz donor chromophores are surrounded by the acceptor molecules of 10OCB mesogens, which do not induce such a constraint in the mesophases.

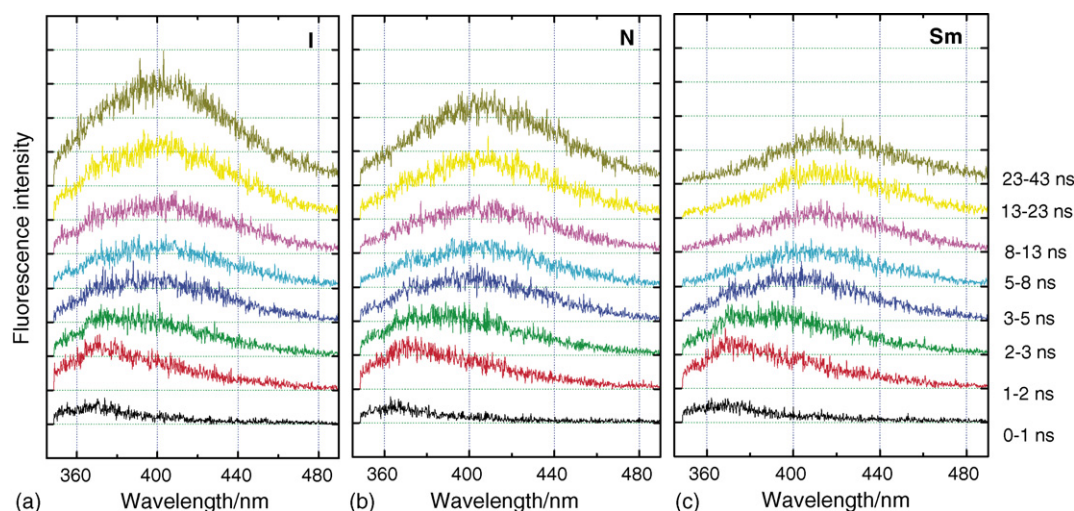


Fig. 9. Time-resolved fluorescence spectra of 8OCBCz (20 mol%)/10OCB. (a) I (353 K), (b) N (341 K), and (c) Sm (319 K) phases. The time window is indicated in the figure.

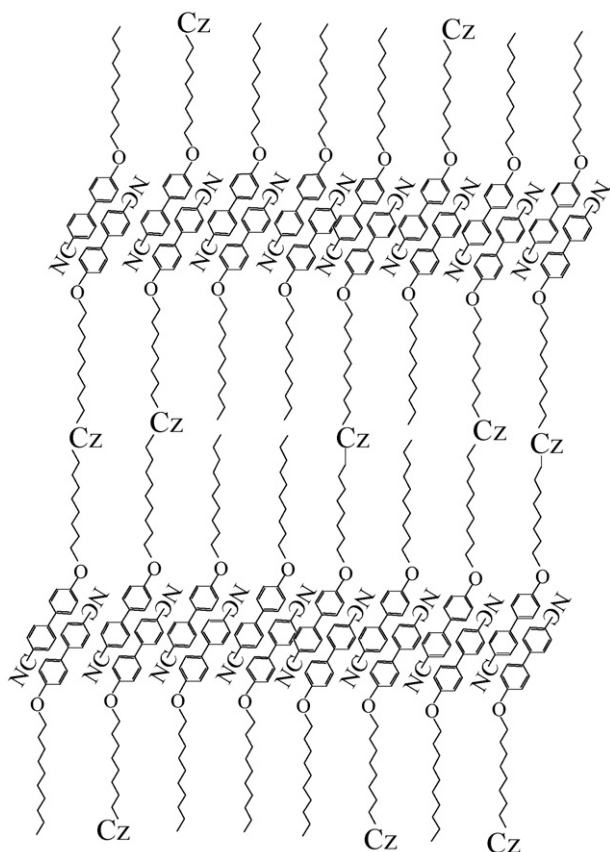


Fig. 10. Possible bilayer molecular alignment in the Sm mesophase of 8OCBCz(20 mol%)/10OCB. The size of the CB groups is emphasized, and carbazolyl chromophores are denoted as Cz.

Here, we consider the alignment of 8OCBCz molecules in the Sm mesophase of 8OCBCz (20 mol%)/10OCB. Fig. 10 shows the molecular alignment of 8OCBCz and 10OCB mesogens in a domain of the Sm mesophase. The 10OCB mesogens form a Sm A mesophase, which is termed as 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 8OCBCz is the same as that of the *n*-decyloxybiphenyl of 10OCB, almost all the Cz chromophores of 8OCBCz are located in the vicinity of a space between the bilayers in the Sm mesophase of this mixed system. However, there would be a small amount of structural defect in such an arrangement (not shown in Fig. 10). In such defect sites, the Cz chromophores are located near the CB chromophores of 10OCB mesogens; thus, the exciplex-forming sites are produced. In addition, this mesophase consists of polydomains, resulting in the formation of exciplex-forming sites at the domain boundary. Although the distance between the different layers of Cz chromophores localized near the space is large, the distance among the Cz chromophores in the same layers is small. Even if energy migration among the Cz chromophores does not occur between the different layers, it easily occurs among the Cz chromophores in the same layers. Hence, it is suggested that the exciplex formation in

the Sm mesophase is attributed to the excitation-energy migration among the Cz chromophores and the subsequent trapping at the exciplex-forming sites in the structural defects and at the domain boundary.

3.6. Photoconductive properties of mixed 8OCBCz/10OCB samples

Fig. 11 shows the typical transient photocurrent signals of 8OCBCz (20 mol%)/10OCB. Similar to the neat 8OCBCz

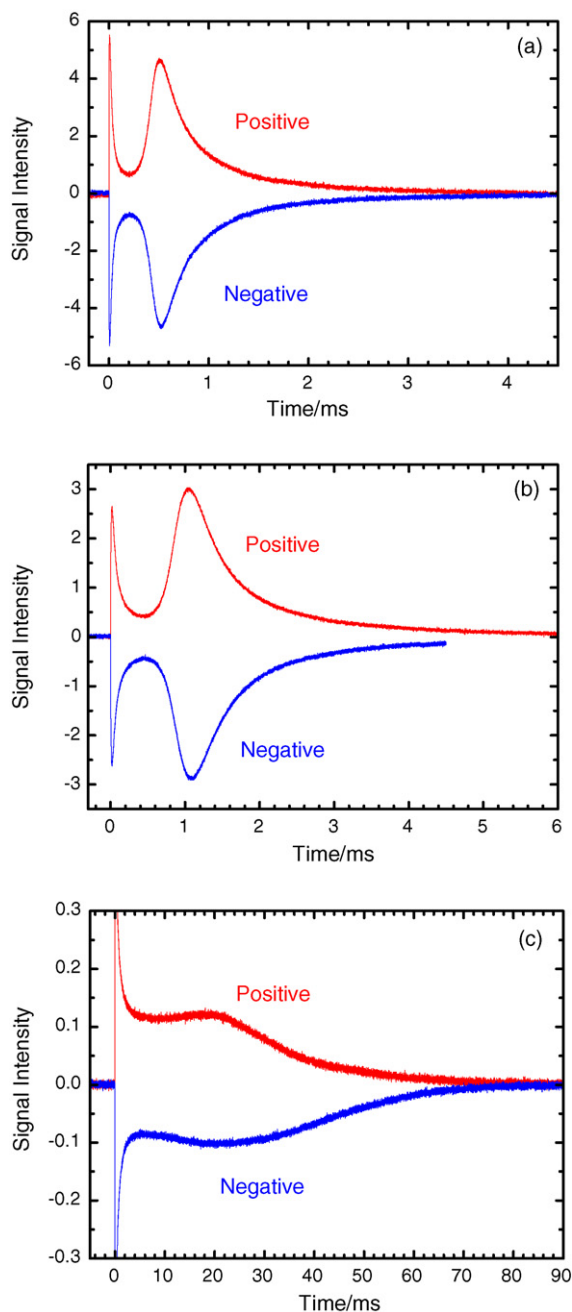


Fig. 11. Transient photocurrent signals of 8OCBCz(20 mol%)/10OCB in various phases. (a) I phase at 352 K, (b) N phase at 335.5 K, and (c) Sm phase at 323 K. Sample thickness, 25 μm . Electric fields, 78.5 kV/cm. Positive and negative current signals were obtained for positive and negative electrode illumination, respectively.

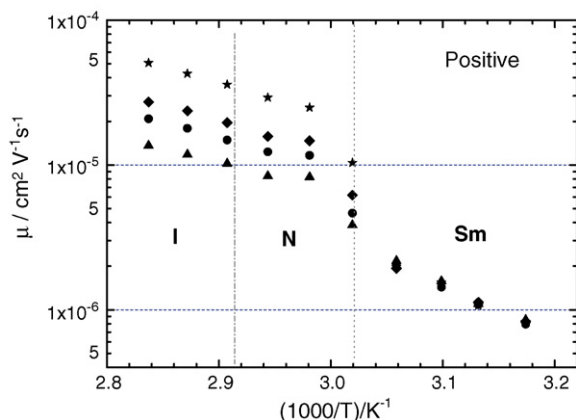


Fig. 12. Temperature dependence of drift mobilities of the positive carriers for 8OCBCz(20 mol%)/10OCB. Electric field: (▲) 19.5 kV/cm, (●) 29.1 kV/cm, (◆) 39.2 kV/cm, and (★) 78.5 kV/cm. As seen in Fig. 10, the negative carriers exhibited the same temperature dependence.

samples, both positive and negative charge carriers are observed. The transient photocurrent exhibits a peak in the I and N phases and a typical TOF signal in the Sm mesophase, which suggests that the photoconduction mechanism is different between the I and N phases and the Sm mesophase. The former transient signals with the peak seem to be due to a typical space-charge-limited current. For these signals, the drift mobility μ was calculated from the peak time t_p according to $\mu = 0.79d^2/t_p V$, where d is the sample thickness and V is the applied voltage. For the latter typical signal, the transit time t_r was determined from the shoulder of the transient photocurrent signal and μ was calculated from the t_r according to $\mu = d^2/t_r V$.

Fig. 12 shows the temperature dependence of the mobilities of positive carriers under various electric fields. In the I and N phases, the mobilities of the positive and negative charge carriers were almost similar, while the mobilities of the positive carriers in the Sm mesophase were slightly greater than those of the negative carriers, as shown in Fig. 11. The mobilities exhibit a discrete change at the N \rightarrow Sm phase transition, whereas they exhibit a continuous change at the phase transition from the I to N phase.

Since the carrier transport in the liquid state is generally proposed to be ionic in nature, the carrier transport in the I phase is attributed to ionic conduction. The continuous change in the mobility between the I and N phases suggests that the ionic conduction is also present in the N mesophase. That is, in the present system, the carrier transport in both the I and N phases are most probably attributable to ionic charge carriers. Here, we note that both the mobilities of the positive and negative charge carriers and their activation energies are almost similar. These facts imply that the effective radii of the positive and negative ionic carriers are the same. If the charges of the original photocarriers, which are ascribed to be the cation radical of the Cz chromophore of 8OCBCz and the anion radical of 10OCB, are transported to the electron-donating and electron-accepting impurities and these positively and negatively charged impurities move in the I and N phases, the effective radii of these two impurities should be the same. However, this idea appears

improbable because it is very difficult to consider that impurities with both the same size and different electronic properties can exist simultaneously.

We observed the polarizing microscopic image of the N mesophase of this sample sandwiched between two ITO glasses under a crossed nicol condition. A typical schlieren texture for the N phase was observed without an electric field, whereas a dark image was observed even under a small electric field; this suggests that a homeotropic alignment in the N mesophase was induced by the applied electric field. The dark image was maintained for several tens of seconds under the electric field. These results strongly suggest that the long molecular axes of both the 10OCB and 8OCBCz molecules are oriented perpendicularly to the two glass electrodes under the TOF measurement condition. Assuming that the original photocarriers are transporting materials in the present experiment, the positive charge carrier seems to be the cation radical of the Cz chromophore in 8OCBCz and the negative carrier is the anion radical of 10OCB. Although these molecular sizes are different, the effective diameters are likely to be almost similar when these radicals drift toward the opposite electrodes through 10OCB mesogens oriented perpendicularly to the electrodes because the longitudinal axes of these radicals are in agreement with the direction of the migration.

One of the authors (AI) investigated the charge-carrier transport in the mesophases of 2-(*p*-decyloxybenzylideneamino)-9-fluorenone (DBAF) [26]. The nature of the carrier transport of photoconduction was not electronic, but ionic. The cation radicals of DBAF and O_2^- were proposed as the ionic carrier species for the N mesophase of DBAF. The latter was the O_2 molecule that accepted an electron from the original negative photocarrier or a DBAF anion radical. In this case, the sizes of the positive and negative carriers are different and the mobility of the negative carrier was ten times greater than that of the positive carrier. In the present case, as mentioned earlier, the mobilities of both the negative and positive carriers are the same and the cation radical of 8OCBCz and the anion radical of 10OCB were proposed to be the ionic carrier species. The gaseous electron affinity of O_2 may be insufficient to accept an electron from the 10OCB anion radical.

The molecular motion of mesogens in the Sm mesophase is strongly restricted as compared to that in the I and N phases. In addition, the profiles of the transient photocurrent signals suggest that the nature of the carrier transport in the Sm phase is electronic, and the transport is regarded as a hopping process in which the hole hops from a localized site to another in the direction of the electric field and the electron hops in the opposite direction. Although the ionic transport is found to depend on the electric field for mobility in the I and N phases, such dependence is not found for the hopping transport in the Sm phase (Fig. 12). It was reported that the mobility in the Sm mesophase of calamitic mesogens is independent of an applied electric field [2(b),27]. The present result is in agreement with these studies. In the present doped system, however, the mobilities of both the holes and electrons are very small as compared to those of the neat calamitic mesogens reported by Hanna and co-workers [2(a and b),27].

The hopping transport is regulated by an overlap of electronic wave functions (so-called localized radius) between corresponding chromophores. The hole and electron carriers in the present system are likely to be the Cz radical cation and CB radical anion, respectively. Since the dopant 8OCBCz concentration is small (20 mol%), the very small hole mobility is attributed to the long distance between the Cz chromophores, even if the localized radius is large. Although the distance between CB chromophores is small because of the large CB concentration, the electron mobility is very small. This is most probably because the localized radius of CB is small.

Here, we consider the alignment of 8OCBCz molecules in the Sm mesophase. As shown in Fig. 10, almost all the Cz chromophores of 8OCBCz are placed in the vicinity of a space between the bilayers in the Sm mesophase. That is, a large distance exists between the Cz chromophore layers that are localized near this space. We observed a polarizing microscopic image of the Sm mesophase of this sample sandwiched between two ITO glasses under a crossed nicol condition. A bright image was observed without an electric field, while the image was slightly dark under an electric field. The degree of darkness was greater under a high electric field than under a low one. These phenomena suggest that a homeotropic alignment of some domains in the Sm mesophase was induced by the applied electric field. Under an electric field, such an alignment results in an increase in the average hopping distance of holes *via* Cz chromophores in the direction of the field. This is also likely to be one of the reasons for the marginal mobility of holes.

Double layers of CB chromophores in the anti-parallel alignment of 10OCB are separated *via* two layers of *n*-decyloxy groups. The homeotropic alignment of some domains induced by the electric field results in an increase in the average hopping distance of electrons *via* CB chromophores in the direction opposite to the electric field. Similar to the case of holes, this is also likely to be one of the factors for the marginal mobility of electrons.

4. Concluding remarks

To dope a large amount of Cz chromophore to mesophases, 8OCBCz was synthesized. However, attempt to dope it with a large amount to cyanobiphenyl mesogens were unsuccessful and the homogeneous doping concentration of 8OCBCz to 10OCB was below 20 mol%. The 8OCBCz formed an amorphous state. The photophysical and photoconductive properties of its neat form and its binary mixtures with 10OCB were investigated.

8OCBCz exhibited intermolecular exciplex fluorescence in a solution. The neat amorphous film exhibited exciplex fluorescence and transient photocurrent signals of both positive and negative charge carriers. The temperature dependence of the fluorescence spectra suggested the presence of two types of crystalline states of 8OCBCz. The mobilities of the charge carriers were not determined because of the strongly dispersive signals.

The mixtures exhibited Sm A and N mesophases. These mesophases and the I phase exhibited exciplex as well as monomer fluorescence. The exciplex formation in the Sm mesophase was resulted from the excitation energy migration

among the Cz chromophores and the subsequent trapping at the exciplex-forming sites, which differed from the dynamic exciplex formation in the N and I phases. The transient photocurrent signals of both the positive and negative charge carriers were also observed for the binary mixtures. Ionic conduction was suggested for the N and I phases, while electronic conduction was suggested for the Sm A mesophase. The charge carriers for positive and negative ionic conduction were suggested to be 8OCBCz and 10OCB, respectively. The reasons for the marginal mobilities of the electronic conduction in the Sm A mesophase observed for the positive and negative carriers was discussed on the basis of the concentration of hopping sites, the localized chromophore radii, and the molecular orientation in the mesophase under an electric field.

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