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Dynamics of Exciplex Formation in Cholesteric Liquid Crystals Containing Carbazolyl and Terephthaloyl Group

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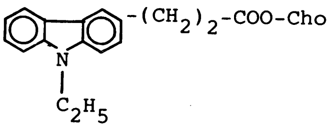
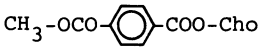
Dynamics of exciplex formation was studied on cholesteric liquid crystals consisting of cholesteryl 3-(9-ethyl-3-carbazolyl)propanoate (3Cz-2), cholesteryl 5-phenylpentanoate (Ph-4), and cholesteryl methyl terephthalate (CMT) with different amounts of CMT. Transient fluorescence spectrum and the analysis of fluorescence rise and decay curves of the exciplex emission indicated that two types of exciplex are present at low temperatures. Rate constants of exciplex formation were obtained at different temperatures in the cholesteric and isotropic phases. The activation energy for the rate constant was nearly zero in the cholesteric phase, but it was positive (3—6 kcal mol^{-1}) in the isotropic phase. The difference was interpreted in terms of different mechanisms of exciplex formation in the two phases.

Photophysical processes, such as excimer formation and exciplex formation in liquid crystalline mesophases have been studied.[1–8] A primary goal of these studies is to clarify the effect of liquid crystalline order on the photophysical processes, which should depend on the interchromophore distances and orientations. In our previous reports, syntheses of cholesteryl ω-arylalkanoates carrying 1- and 2-naphthyl, 1-pyrenyl, 9-anthryl, and 3- and 9-carbazolyl groups were described.[1–5] The orientations of the aromatic groups in cholesteric liquid crystalline (CLC) phases were determined by circular dichroic (CD) spectroscopy in the ground state and by circularly polarized fluorescence (CPF) spectroscopy in the excited state.[2] Studies on the dynamics of excimer formation of CLC mixtures containing cholesteryl 3-(1-pyrenyl)propanoate (Py-2)[5] revealed that the activation energy of the rate constant for excimer formation was slightly higher in the isotropic phase than in the CLC phase. The activation energy for the excimer dissociation was found to be considerably higher in the isotropic phase than in the CLC mesophase. These data were interpreted in terms of a reduced entropy of the ground state by the cholesteric order and efficient energy migrations before the excimer formation. Weiss and co-workers[7] reported an excimer formation between free pyrene molecules dispersed in a cholesteric mixture. They observed a higher activation energy for the excimer formation in the CLC phase than in the isotropic phase and explained the difference in terms of a higher viscosity of the cholesteric phase. They also observed a higher activation energy in the CLC phase on the exciplex formation in other cholesteric mixtures. The different behaviors of our systems and the Weiss's systems may be ascribed to the differences in the order of chromophore arrangement and their mobility in the CLC phases. In Py-2, the pyrenyl groups are covalently linked to the cholesteryl group and their orientation is highly ordered in the CLC phase. Also their translational diffusion may be highly restricted. Therefore the energy migration process may become more important than the diffusion in CLC phase of our system, for which less activation energy will be needed. One of the purpose of this study is to examine the activation energy for exciplex formation in the CLC mixture and in the isotropic phase containing chromophores covalently linked to cholesteryl groups.

In the present work, a cholesteryl ester carrying covalently linked carbazolyl group, i.e., cholesteryl 3-(9-ethyl-3-carbazolyl)propanoate (3Cz-2, **1**) was used as electron donor and cholesteryl methyl terephthalate (CMT, **2**) was used as an acceptor. Other cholesteryl ω-arylalkanoates carrying phenyl and naphthyl group (Ph-2, **3**; Ph-4, **4**) were used as liquid-crystalline solvents.



(**1**)



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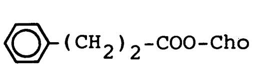

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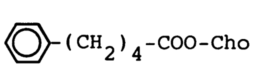

(**4**)

A static structure of the exciplex between cholesteryl 3-(9-carbazolyl)propanoate (9Cz-2) and CMT has been studied.[4] Fluorescence spectra showed a presence of a high-energy exciplex in the CLC phase at low temperatures. Thus, it was shown that the orientational constraints by the CLC order can alter the configuration of the exciplex. However, the high-energy exciplex was not detected in the 3Cz-2/CMT system in the stationary-state fluorescence spectrum.

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The second purpose of this study is to reexamine the exciplex spectra of 3Cz-2/CMT system by using the time-resolved spectroscopy.

Experimental

Preparation of the cholesteryl ω-arylalkanoates has been described.[3] The mixture was placed in an optical cell specially designed to measure surface fluorescence of the liquid crystalline sample under vacuum.[3] Before the fluorescence measurements, the liquid crystalline mixture was mechanically tilted to align the helix axis of the cholesteric texture perpendicular to the cell surface. The perpendicular alignment was confirmed by the appearance of a bright color (blue to red) of the selective reflection.

Fluorescence rise and decay curves were measured on a home-built time-correlated single-photon counting machine, using an air-discharge lamp (half width is about 2.5 ns) as an excitation source. For the measurement of fast processes, a single-photon counting instrument using a picosecond laser pulse was used. The excitation beam was a frequency-doubled laser pulse (314 nm, 13 picosecond, 4 nJ) generated from a synchronously pumped, cavity-dumped dye laser (Spectra Physics 375B dye and Spectra Physics 3000 1W mode-locked YAG lasers). An XP 2020/Q photomultiplier tube was used as a detector. The system was controlled and the data was processed with a PDP-11 minicomputer. The time-resolved fluorescence spectra were obtained by adjusting the time-to-amplitude converter to collect only stop pulses which appeared after a specified time period.

Results and Discussion

Stationary and Transient Spectra. The stationary and the transient fluorescence spectra were measured on a CLC and isotropic mixture of 3Cz-2/Ph-2/CMT (molar ratio: 18/73/9). The mixture of 3Cz-2/Ph-2 (20/80) in the absence of CMT showed little excimer emission in the stationary spectrum, although a weak excimer emission has been observed in a 3Cz-2/Ph-2 (50/50) mixture.[3] Figure 1 compares stationary and transient spectra of the CLC mixture of 3Cz-2/Ph-2/CMT (18/73/9). The transient spectra were measured using a 13 picosecond excitation pulse. The transient spectrum 0.5—1.5 ns after the excitation shows only monomer emission of carbazolyl group. The spectrum around 350 nm is distorted by a self-absorption of carbazolyl groups. The absence of exciplex emission at the early stage indicates the absence of any preformed exciplex site in the CLC mixture. The spectrum 13—18 ns after the excitation shows an exciplex emission centered at 450 nm. (An effect of the selective reflection of the CLC appears as a small trough at 480 nm.) The spectrum profile of the transient exciplex emission is sharper than that of the stationary spectrum and the transient peak locates at shorter wavelength than the stationary one by about 20 nm.

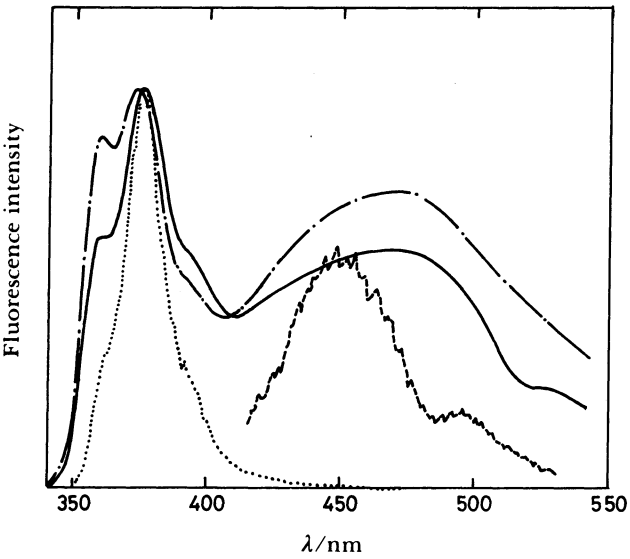


Fig. 1. Stationary and transient fluorescence spectra of 3Cz-2/Ph-4/CMT mixture (molar ratio=18/73/9). Stationary spectra: (——): 70 °C in cholesteric mesophase; (—·—): 130 °C in isotropic phase. λ_{ex}= 333 nm. Transient spectra in cholesteric phase at 76 °C, (--------): 0.5—1.5 ns after excitation; (-----): 13—18 ns after excitation. λ=314 nm. Both the stationary and the transient spectra are uncorrected.

The different profile of the transient spectrum indicates that the configuration of the exciplex at the early stage is different from that of the stationary one.

Rise and Decay Curves of the Exciplex Emission. The rise and decay curves were measured for CLC mixtures of 3Cz-2/Ph-4/CMT having four different molar ratios: (19.5/78/2.4), (19/76.2/4.8), (18.6/74.4/7.0), and (18.1/72.7/9.1). The emissions at longer wavelengths than 500 nm were collected. The curves obtained at lower temperatures than 120 °C were fitted to three component exponential functions (Eq. 1), one for the rise and two for the decay.

$$F(t) = G_1\exp(-t/T_1) + G_2\exp(-t/T_2) + G_3\exp(-t/T_3) \quad (1)$$

The χ^2 values were in most cases less than 1.2. A typical rise and decay curve is shown in Fig. 2. The rise and decay curves at higher temperatures than 120 °C were reasonably fitted to two exponential functions, one for the rise and one for the decay. The rise and decay times (T_1 for rise, T_2 and T_3 for decay) and the ratio of the preexponential factors for the two decay functions (G_2/G_3) are shown in Figs. 3—6.

The longer decay time of the exciplex emission (T_3) shown in Fig. 3 do not depend on the concentration of the acceptor (CMT). As will be discussed later, the longer decay time corresponds to the inverse of the deactivation rate of the exciplex. Therefore, the insensitiveness of the T_3 values to the acceptor concentration can be understood by the independence of the monomolecular process to the acceptor concentration. The activation energy for the deactivation process in cholesteric phase seems to differ slightly

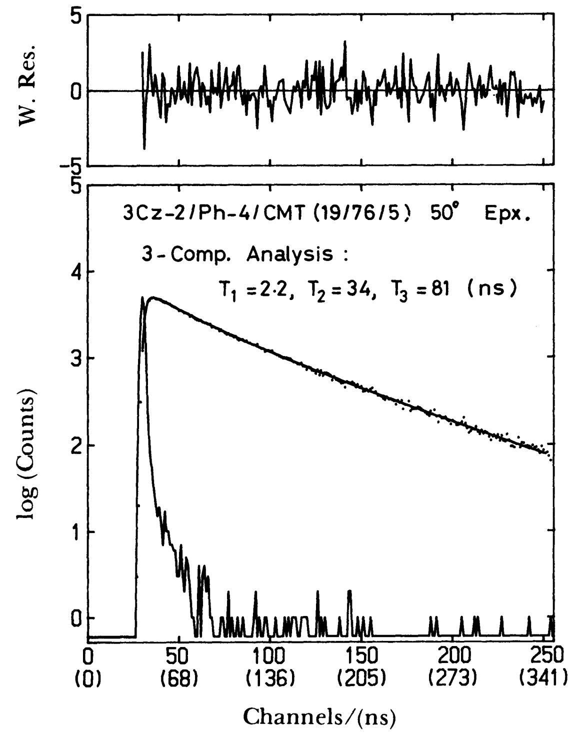


Fig. 2. Rise and decay curve for the exciplex emission from 3Cz-2/Ph-4/CMT (19/76.2/4.8) mixture. $\lambda_{em}>500$ nm. The curve fitting was made with a three-exponential function (Eq. 1), $T_1=2.2$, $T_2=34$, $T_3=81$ (nsec), $G_1=-0.38$, $G_2=-0.23$, $G_3=0.23$, $\chi^2=1.2$.

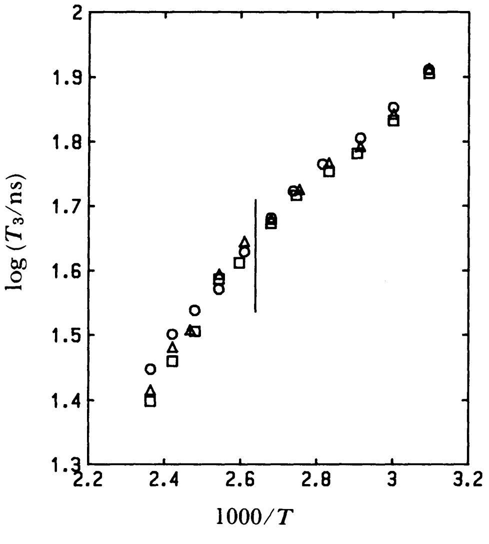


Fig. 3. Temperature dependence of the longer lifetime of the exciplex emission from 3Cz-2/Ph-4/CMT mixtures. Molar ratios are: 19.5/78.0/2.4 (○); 19.0/76.2/4.8 (□); 18.6/74.4/7.0 (△). The vertical bar indicates the cholesteric-isotropic transition point.

from that in isotropic phase.

The shorter decay time of the exciplex (T_2) (Fig. 4) and the G_2/G_3 ratio (Fig. 5) were also insensitive to the acceptor concentration, although the data points scatter to somewhat larger extent.

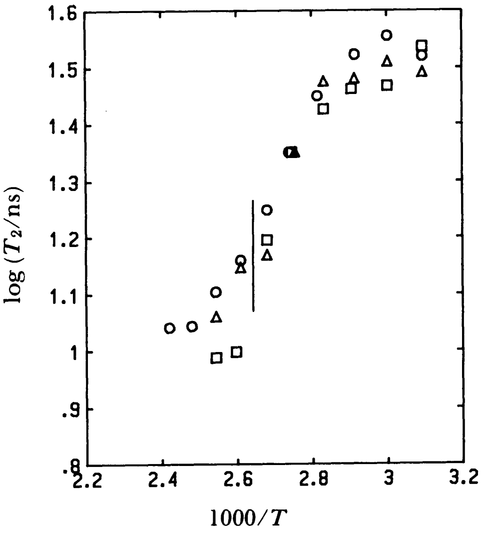


Fig. 4. Temperature dependence of the shorter lifetime of the exciplex emission from 3Cz-2/Ph-4/CMT mixtures. Notations are the same as in Fig. 3.

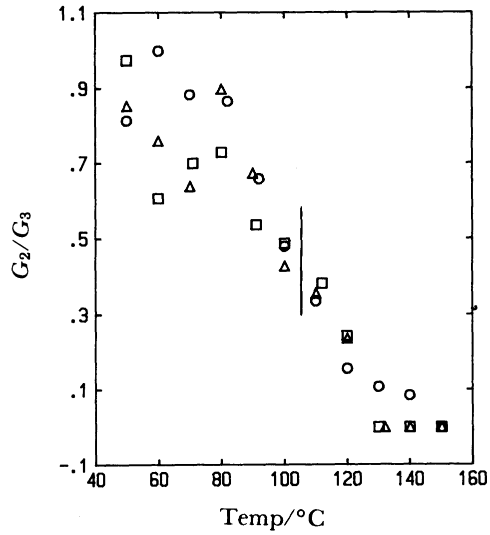


Fig. 5. Temperature dependence of the ratio of preexponential factors for the shorter and the longer lifetime components of the exciplex emission from 3Cz-2/Ph-4/CMT mixtures. Other notations are the same as in Fig. 3.

Contrary to other parameters, the rise time of the exciplex (T_1) becomes shorter with the increase of the CMT concentration (Fig. 6). Furthermore, the Arrhenius plot shows a turning point at the cholesteric-isotropic transition point which is shown by vertical bars in the figure.

The decay curves of the monomer emission were also measured. The decay curves consisted of essentially a single fast component with a small contribution of the slow component, which may be ascribed to the exciplex emission overlapped to the monomer emission. The decay times of monomer

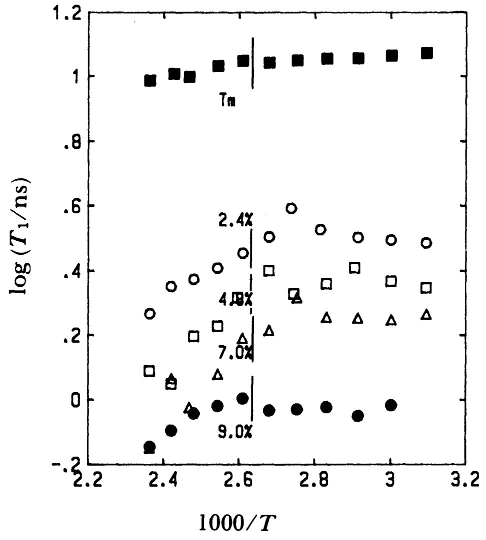
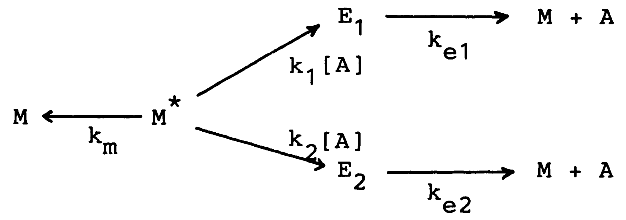


Fig. 6. Temperature dependence of the rise time of the exciplex emission from 3Cz-2/Ph-4/CMT mixtures. Molar ratios of the mixtures are: 19.5/78.0/2.4 (○); 19.0/76.2/4.8 (□); 18.6/74.4/7.0 (△); 18.1/ 72.7/ 9.1 (●). The vertical bars indicate the cholesteric-isotropic transition temperature. The monomer lifetimes observed in the 3Cz-2/Ph-4 (20/80) are also plotted (■).

emission were about the same as the corresponding rise times of the exciplex emission. However, since the former data scattered more than the latter, the latter were used in the following discussion. The decay curves of the monomer fluorescence in the absence of CMT [3Cz-2/Ph-4 (20/80)] at different temperatures were fitted to single exponential functions with a typical lifetime of 11.3 ns (80 °C, CLC) or 9.9 ns (132 °C). The lifetimes T_m are plotted in Fig. 6.

Kinetics of Exciplex Formation in the CLC Mixture. The experimental results described above are summarized as follows. (1) There are two types of exciplex, one decaying faster (typically, 30 ns at 80 °C) than the other (60 ns at 80 °C). The faster component disappears at higher temperatures than about 120 °C. (2) The decay times of the two types of exciplex are independent of the concentration of the acceptor, indicating that the decay times are determined only by monomolecular processes of the types of exciplex. (3) The rise time of the exciplex emission is shortened at higher acceptor concentrations, indicating that the rise time is determined by a bimolecular process of the exciplex formation. The rise time is also sensitive to the phase (cholesteric or isotropic) of the mixture. (4) No preformed exciplex site was detected in the in the transient spectrum.

The above results fit the following kinetic scheme which takes two types of exciplex into account. The exciplex formation process was assumed irreversible, since the monomer decay curve showed only marginal



contribution of the decay component of the exciplex emission, which may be ascribed to the insufficient spectral separation. Since only a single rise time was observed in the exciplex emission, the possibility for the successive formation of two types of exciplex, i.e., $M \rightarrow E_1 \rightarrow E_2$, can be excluded. It is not possible to decide only from the kinetic results whether an interconversion between the two types of exciplex is occurring or not. However, since the two types of exciplex can be distinguished in the time scale of a few ten nanosecond, the interconversion, if it exists, should be slower than the time scale.

The relations between the decay times and the rate constants are:

$$k_{e1} = T_2(e)^{-1},\ k_{e2} = T_3(e)^{-1}. \qquad (2)$$

The rise time of the exciplex is related to the rate constants for the two exciplex formation processes. Since virtually a single rise time was observed in the exciplex emission, the two rate constants should not be very different to each other. In the following discussion, the apparent rate constant of exciplex formation k_{ap}, calculated using Eq. 3 will be discussed.

$$k_{ap} = T_1(e)^{-1}/[A]. \qquad (3)$$

Figure 7 shows the k_{ap} values obtained for the four different concentrations of the acceptor. It is seen that the activation energy in the cholesteric phase is nearly zero, whereas that in the isotropic phase is positive (3—6 kcal mol^{-1}).

Activation Energy for Exciplex Formation. Exciplex formation processes in highly concentrated molecular assemblies are generally governed by the following factors: (1) Diffusion of the donor groups to the acceptor. (2) Energy migration among the donor groups. (3) Population of exciplex-forming sites. (4) Molecular reorientation required for the exciplex formation in the exciplex-forming site. (5) Quenching of the excited state by bimolecular processes, such as an excimer formation, between the excited and the ground-state donor molecules. In the present case, item (5) may be neglected, since only very weak excimer emission was detected in the fluorescence spectrum of 3Cz-2/Ph-4 (20/80) mixture and the decay time of the (20/80) mixture is almost equal to that of the 3Cz-2/Ph-4/Ph-2 (1/33/66) mixture.

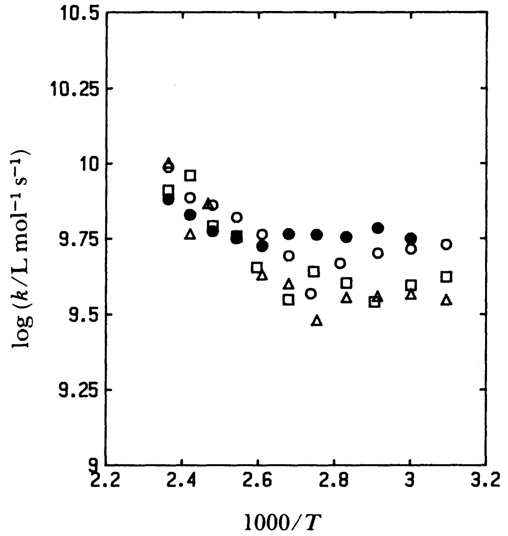


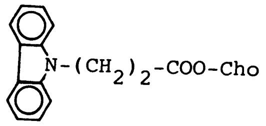
Fig. 7. Arrhenius plot of apparent rate constants for exciplex formation in 3Cz-2/Ph-4/CMT mixtures. Notations are the same as in Fig. 6.

Since cholesteric phase is known to be more viscous than isotropic phase, a higher activation energy for the exciplex formation is expected in the former phase. Actually, Weiss and co-workers reported a higher activation energy of exciplex formation between free pyrene molecules and *N*,*N*-dimethyl-5α-cholestan-3β-ylamine (CA) in the CLC phase (9.9—11.8 kcal mol^{-1}) than in the isotropic phase (5.3—5.4 kcal mol^{-1}). They observed higher activation energy in the CLC phase also in the excimer formation between pyrene molecules dispersed in the cholesteric mixtures. The Arrhenius plots in Fig. 7 contrast the above expectation and experimental results. The very small activation energy in the CLC phase is remarkable, but the activation energy in the isotropic phase is not mush different from that observed by Weiss and co-workers. Therefore, the low activation energy in the CLC phase cannot be interpreted only by the high concentration of carbazolyl groups in the present system. A possible reason is that the cholesteric order may align the carbazolyl groups in a manner which enhances the energy migration among carbazolyl groups and/or facilitates the exciplex formation in the exciplex-forming site. The lower activation energy in the CLC phase has been observed also in the excimer formation in cholesteric mixtures containing 3—25% of Py-2,5) although the difference between CLC and isotropic phase is much smaller than the present case.

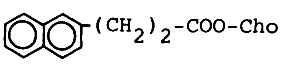
It was concluded that the exciplex or the excimer formation of Ar-2-type molecules requires less activation energy in the CLC phase than in the isotropic phase. This may be accounted for in terms of the high orientational order in the CLC phase which facilitates the photophysical processes, such as the energy migration and the exciplex formation.

Assignment of the Two Types of Exciplex. Two types of exciplex were suggested from the decay curves of exciplex emission. Furthermore, the exciplex at the early stage after excitation showed a shorter peak wavelength than the stationary spectrum. The early stage component should correspond to the first exciplex component with a shorter decay time. This first component (G_2) disappeared at higher temperatures than about 120 °C (Fig. 5). The second component decays more slowly and, therefore, is a major component in the stationary spectrum. A possible explanation for the first component is that the exciplex in the CLC mesophase cannot take the most stable structure due to constraints by the CLC order. The fact that the first component is still present above the transition point (Fig. 5) can be explained by a local CLC order, which is known to be remaining above the transition temperature.11)

Similar finding has been observed in a stationary fluorescence spectra of a mixture of cholesteryl 3-(9-carbazolyl)propanoate (9Cz-2, **5**), cholesteryl 3-(2-naphthyl)propanoate (2N-2, **6**), and CMT (9Cz-2/2N-2/CMT=47.6/47.6/4.8).



(**5**)



(**6**)

In the cholesteric phase, the mixture showed a high-energy exciplex emission located around 425 nm. At elevated temperatures, the exciplex peak shifted to a longer wavelength. The presence of the high-energy exciplex in the CLC phase has been interpreted in terms of an metastable exciplex structure due to the constraints by the CLC order. The high-energy exciplex could not be found in the stationary spectra of a 3Cz-2/Ph-2/CMT mixture. The present study showed the presence of the metastable exciplex also in the latter mixture at an early stage after excitation. Therefore, it may be commonly stated for these types of CLC mixtures that a CLC order imposes constraints on the structure of exciplex.

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