Liquid-Crystal Phase Transition Probed by Fluorescent Molecules

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Phase transition of four liquid crystal materials have been studied by measuring the decay times of time-resolved intensity of fluorescence from two kind of dyes, malachite green and cryptocyanine, doped in these materials. It was found that the observed fluorescence lifetimes observed depend strongly on the doped molecules and that they change depending on the phase transition of the liquid-crystal materials. These results show that the fluorescence lifetime measurements are effective molecular probes for estimating the microscopic dynamics in these materials.

KEYWORDS: malachite green, cryptocyanine, fluorescence lifetime, liquid crystal, phase transition

1. Introduction

A group of dye molecules are known to have a fluorescence lifetime and quantum yield very much dependent on the microscopic environment of the molecule. These dyes have been used as probes for the microscopic viscosity of the host materials. In this study, we investigated phase transitions of liquid-crystal (LC) materials using malachite green (perchlorate) and 1,1′-diethyl-4,4′-carbocyanine iodide (cryptocyanine) as microprobes. Fluorescence lifetime of triphenyl methane (TPM) dyes such as malachite green is known to vary by several orders of magnitude depending on the viscosity of the surrounding materials.[1–10] These dyes have been used for studying microscopic dynamics in glass-forming solvents,[1] polymers,[2] organic cells[3] and other systems.[4–10] Internal conversion from the S_1 to the S_0 state through the intramolecular rotational motions of three phenyl groups around the bonds to the central carbon are attributed to be the rate-limiting process of the radiationless relaxation of the excited state. Since the sweep volume of the phenyl group is as small as about 5 Å, malachite green is expected to be sensitive to the dynamics of the hosts on this microscopic scale. Radiationless relaxation of the S_1 state of cryptocyanine, on the other hand, is governed by the dynamics of the trans-cis isomerization of the molecule on the excited-state potential. The sweep volume of cryptocyanine is, therefore, much larger than that of malachite green. The fluorescence lifetime of cryptocyanine has been reported to be tens of picoseconds to a few nanoseconds depending on the viscosity of the solvents.[4,5] The molecular structures of these dyes are shown in the figures given below along with their experimental data. We expect to determine the spatial-scale-dependent microscopic dynamics by measuring the fluorescence lifetime using these two dyes.

We studied the phase transition of LC materials using these dyes. LC materials have several types of phases classified as nematic, smectic and cholesteric phases. We studied four LC materials which exhibit smectic and/or nematic LC phases. We measured fluorescence lifetime of the two dyes in these LC materials by changing the temperature through the transition points from crystal to LC and from LC to isotropic liquid phases.

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2. Experiments

We measured the time-resolved intensity of the fluorescence of malachite green and cryptocyanine doped in the four LC materials, described below, by changing the temperature. The sample was put in a 0.5-mm-thick glass cell and placed in an oven. The temperature of the oven was controlled within ±0.5 K. The sample was excited by light pulses generated by a pulsed laser diode (PicoQuant, PDL800). The wavelength, pulse width, repetition rate and average power of the excitation pulses were 645 nm, 57 ps, 80 MHz, and 100–200 μW, respectively. Malachite green has an absorption peak at 620 nm and cryptocyanine at 700 nm. Both dyes absorb the excitation light at 645 nm very well. Fluorescence emitted by the sample was focused by a lens, dispersed by a monochromator (JASCO, CT-25GDM), and time-resolved by a synchroscan streak camera (Hamamatsu, C3610). The time resolution of the streak camera is about 20 ps. No wavelength dependence of the fluorescence decay was observed, and spectral regions from 690 to 734 nm and 719 to 769 nm were observed for measuring the fluorescence intensity from malachite green and cryptocyanine, respectively.

We used four LC materials in the present study as the samples. The transition temperatures and the types of phases of these materials are summarized in Table I. The first sample was 10-[4-(4-pentylcyclohexyl)phenoxy]-1-decanol (abbreviated as PCH50-10OH). This was newly synthesized for this study. By differential scanning calorimetric (DSC) measurements and by observation through a polarizing microscope, this material was found to show crystal-to-smectic transition at 321 K and smectic-to-isotropic transition at 353 K by increasing temperature. The second sample was a mixture of PCH50-10OH and 3-[4-(4-pentylcyclohexyl)phenoxy]-1-propanol (PCH50-3OH) with the same molar fractions.

Table I. The liquid-crystal samples used in the present study. C, S, N and I represent the crystal, smectic, nematic and isotropic phases. Transition temperatures listed are in K. Phases of PCH50-mOH mixture are assigned tentatively (see text).

LC materials	Phases and transition temperatures
PCH50-10OH	$C \xrightarrow{312} S \xrightarrow{353} I$
PCH50-mOH (mixture)	$C \xrightarrow{313} S \xrightarrow{319} N1 \xrightarrow{322} N2 \xrightarrow{336} I$
7CB	$C \xrightarrow{301.5} N \xrightarrow{315} I$
CP7B	$C \xrightarrow{317} N \xrightarrow{328} I$

PCH50-3OH was also newly synthesized. It is generally known that transition temperatures of mixtures are lower than those of the original compounds. By a DSC measurement, transition temperatures were determined to be at 313, 319, 322, and 336 K by increasing the temperature. By observation through a polarizing microscope, nematic LC phases were observed between 319 and 336 K. The types of phases of this material were tentatively assigned as crystal, smectic, nematic 1, nematic 2, and isotropic phases from the lower to higher temperatures by taking into account these results although the possibility cannot be excluded only from these results that the second phase is another crystal phase. The third sample was 4-cyano-4′-heptylbiphenyl (7CB). This is a well-known cyano-alkylbiphenyl LC material which exhibits crystal-to-nematic transition at 301.5 K and nematic-to-isotropic transition at 315 K. The last sample was 4-cyanophenyl 4-heptylbenzoate (CP7B), which shows crystal-to-nematic transition at 317 K and nematic-to-isotropic transition at 328 K. 7CB and CP7B were used as purchased from Sigma-Aldrich.

The molecular structures of these compounds are shown in the figures given below along with the experimental results. These four LC materials have a similar molecular size. The types of LC phases are different among the four LC samples. The last two have only nematic phases, whereas the first two have smectic phases. Any difference observed in the time-resolved fluorescence study is expected to originate from this fact. Samples were prepared by the following procedure. Malachite green perchlorate or cryptocyanine was first dissolved in dichloromethane. The solution was then added to the LC material. It was mixed well and left in air for more than a day to completely evaporate the solvent. The concentration of the dyes were 1/50,000 by weight ratio for malachite green and 1/12,500 for cryptocyanine in all four LC samples. In the previous study on glass transition of organic solvents using perchlorate and chloride salts of malachite green,[2] no counter anion dependence of the fluorescence decay was observed. In polar solvents such as those used in the previous study and the LC materials used in the present study, it is expected that the dyes and the counter anions are well solvated by the surrouding host molecules and that the effects of the counter anion on the fluorescence dynamics of the dyes are negligible. In the present study, therefore, we used only the perchlorate salt of malachite green.

All the measurements were performed with the temperature increase at a constant rate of about 0.1 K/min. The highest temperature for each sample was limited by the fact that malachite green is bleached at temperatures higher than about 333 K.

3. Results and Discussion

An example of fluorescence decay curve of malachite green is shown in Fig. 1 along with the molecular structure of malachite green. The laser pulse waveform observed by the streak camera is also shown in the figure, which has a shoulder at approximately 300 ps after the peak. The time-resolved fluorescence intensity, $I(t)$, as a function of time was fitted by the convolution of biexponential:

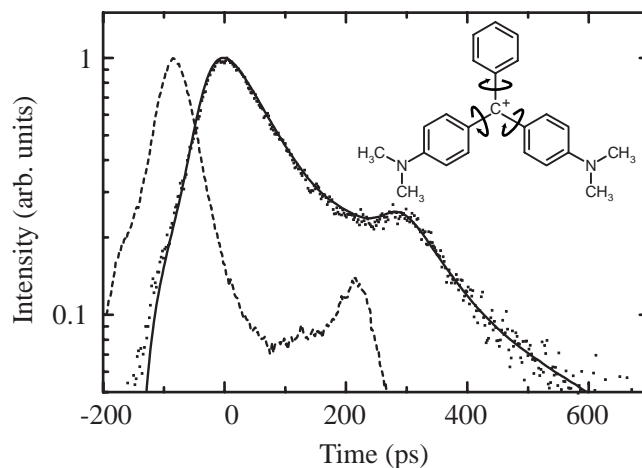$$I(t) = A_{\mathrm{f}}e^{-t/\tau_{\mathrm{f}}} + A_{\mathrm{s}}e^{-t/\tau_{\mathrm{s}}}, \qquad (1)$$

Fig. 1. A plot of time-resolved fluorescence intensity of malachite green. It was obtained from malachite green doped in PCH50-10OH at 310 K. Dots indicate the experimentally observed fluorescence intensity, the dashed line indicates the excitation laser pulse waveform, and the solid line indicates the best-fitted curve of a double exponential convoluted with the laser waveform. The molecular structure of malachite green is shown in the inset. The counter anion (perchlorate) is not shown here.
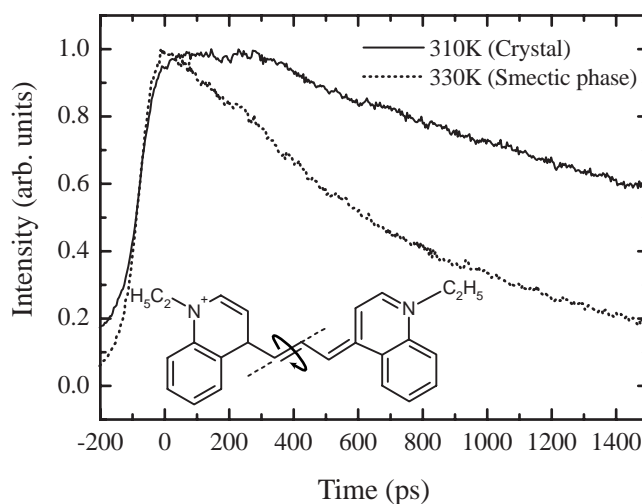

Fig. 2. A plot of time-resolved fluorescence intensity of cryptocyanine. It was obtained from cryptocyanine doped in PCH50-10OH at 310 and 330 K. The molecular structure of cryptocyanine is shown in the inset. The counter anion (iodide) is not shown here.

with the laser waveform. Here, A_{f} and τ_{f} are the amplitude and the decay time of the fast component, and A_{s} and τ_{s} are those of the slow component. The fitting curve is shown in the figure. All the data were fitted well by this procedure.[1,2,6] An example of the fluorescence decay curve of cryptocyanine is shown in Fig. 2 along with the molecular structure of cryptocyanine. Cryptocyanine generally showed longer fluorescence decay than that of malachite green. The decay curve was also fitted by the convolution of the biexponential and the laser waveform. The second peak in the fluorescence decay curve of cryptocyanine is not as clear as that of malachite green shown in Fig. 1. This is due to the longer decay times of cryptocyanine which smear out fine structures in the decay profiles.

The fact that the fluorescence intensity of these dyes decays biexponentially shows that the environment of the dye is dis-
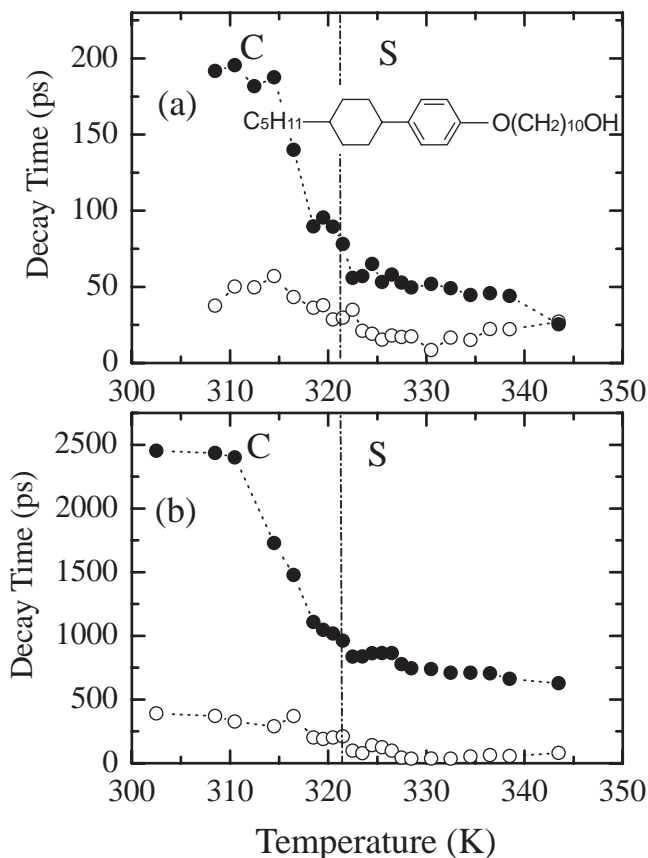
Fig. 3. Temperature dependence of fluorescence decay times of (a) malachite green and (b) cryptocyanine doped in PCH50-10OH. Closed circles indicate the slow decay time, τ_s, and open circles indicate the fast decay time, τ_f. Vertical dotted line at 321 K shows the transition temperature from the crystal to the smectic phase. The molecular structure of PCH50-10H is shown in the inset.
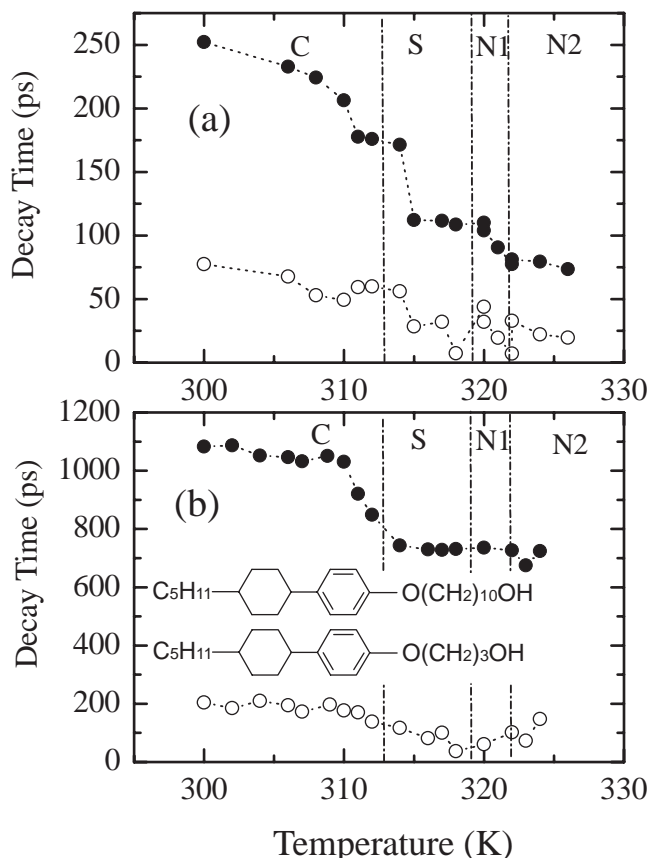

Fig. 4. Temperature dependence of fluorescence decay times of (a) malachite green and (b) cryptocyanine doped in the mixture of PCH50-10OH and PCH50-3OH having the same molar fraction. Closed circles indicate the slow decay time, τ_s, and open circles indicate the fast decay time, τ_f. Vertical dotted lines at 313, 319 and 322 K show the transition temperatures. The phases above 313 K are tentatively assigned to S, N1 and N2 (see text). The molecular structures of PCH50-10H and PCH50-3OH are shown in the inset.

tributed inhomogeneously. Direct observation of the bimodal distribution of another TPM dye has been reported.[11] The fast and slow components have been assigned to fluorescence from dye molecules at sites where the molecules are loosely and tightly bound to the host material, respectively.[6] The dye molecules are more flexible at the loosely bound sites, which leads to the faster nonradiative relaxation due to larger intermolecular motion of the dye.

The decay times of the fast and slow components of the two dyes doped in the four LC samples are plotted as a function of temperature in Figs. 3–6. In each figure, panel (a) shows the fast (open circles) and slow (closed circles) decay times of malachite green, and panel (b) shows those of cryptocyanine. Vertical dashed lines show the transition temperatures, and C, S, N, and I indicate the type of the phase: crystal, smectic, nematic, and isotropic, in each temperature region. The molecular structure of the LC material is also shown in each corresponding figure. Fluorescence of malachite green from 7CB was too weak to be observed with sufficient data quality at temperatures higher than 310 K. At temperatures higher than 302 K, the amplitude of the fast component of the fluorescence decay of cryptocyanine doped in 7CB was very small, and the decay curve fitted well with the single exponential function.

A general trend seen in the data obtained from all the samples is that the decay times of the fast and slow components

of both dyes become shorter by increasing the temperature. According to the Stokes-Einstein-Debye theory,[12] relaxation time, τ, can be expressed as

$$\tau \propto \eta/T. \qquad (2)$$

Here, η is the (microscopic) viscosity of the host medium and T is the temperature. Since experimentally observed change in the decay times is much larger than that expected by only the temperature change from eq. (2), the major cause of the decay time change is due to the change in the microscopic viscosity of the host materials, or, in other words, the change in the mobility of the relevant groups in malachite green or cryptocyanine molecules. Since data quality of the temperature dependence of the decay time of the fast component is more or less limited by the time resolution of the streak camera system, we will focus the discussion on the temperature dependence of the decay time of the slow component in the following.

It is observed from the data obtained of the four LC materials that sudden drops occur at transition temperatures in some cases, and only gradual decrease occurs in other cases.

At transition temperatures from the crystal-to-smectic phase of the PCH50-10OH and PCH50-mOH mixture, decay times of both malachite green and cryptocyanine show a drop. The drop is seen to start at temperatures slightly (5–
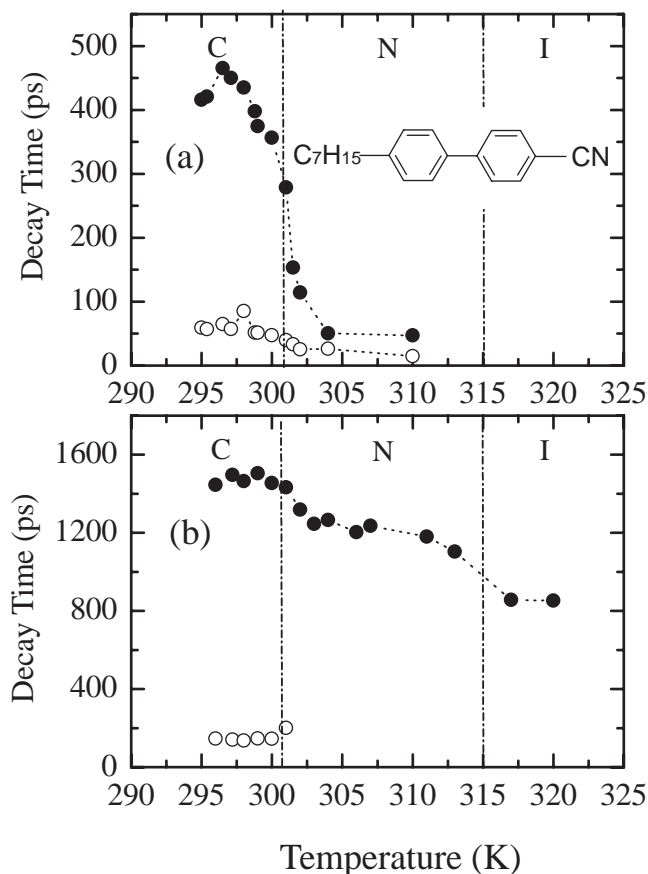
Fig. 5. Temperature dependence of fluorescence decay times of (a) malachite green and (b) cryptocyanine doped in 7CB. Closed circles indicate the slow decay time, τ_s, and open circles indicate the fast decay time, τ_f. Vertical dotted lines at 301.5 and 315 K show the transition temperatures. The molecular structure of 7CB is shown in the inset.
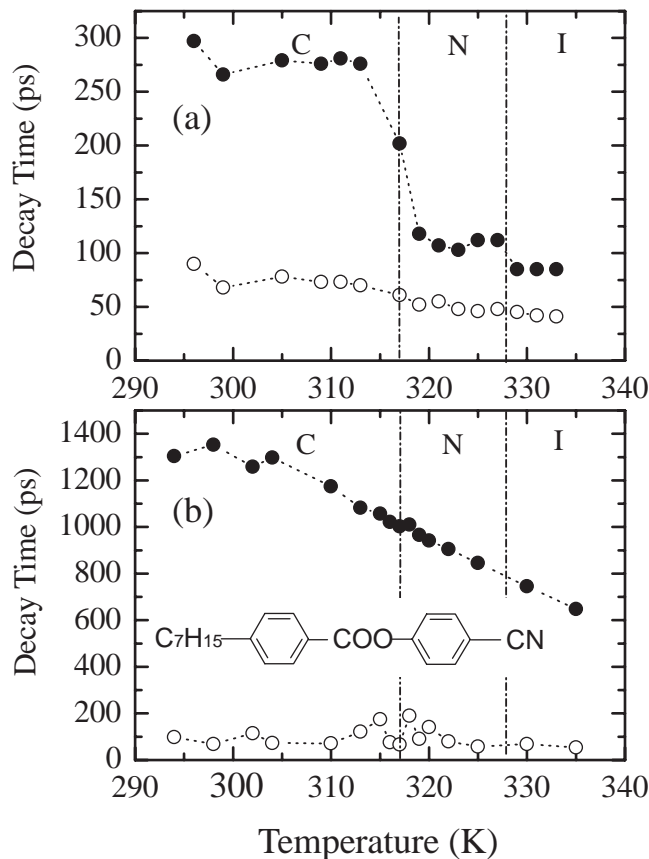
Fig. 6. Temperature dependence of fluorescence decay times of (a) malachite green and (b) cryptocyanine doped in CP7B. Closed circles indicate the slow decay time, τ_s, and open circles indicate the fast decay time, τ_f. Vertical dotted lines at 317 and 328 K show the transition temperatures. The molecular structure of CP7B is shown in the inset.

10 K) lower than the phase transition point. Many experimental results show that sudden changes or kinks of fluorescence lifetime of malachite green as a function of temperature correspond to some kind of phase transition of the host media.[2, 6] In glass-forming solvents, cross-over temperatures which cannot be detected by macroscopic measurements were observed using malachite green as a microscopic probe.[1] Accordingly, the present results suggest that a precursor of the phase transition occurs which was detected by the technique using the microscopic probes. Since the smectic phase is divided into several types depending on the molecular configuration in the molecular layer,[13] there is a possibility that another smectic phase occurs which is not observed by a polarizing microscope but is detected by the present method.

In the case of 7CB and CP7B, behaviors of the temperature dependence of the decay time of malachite green and cryptocyanine are markedly different. The decay time of malachite green shows a sharp drop at the transition temperature from the crystal-to-nematic phase, whereas the change in that of cryptocyanine is smooth around the transition temperature. The decay time of malachite green is almost constant in the nematic phase although that of cryptocyanine decreases gradually. These differences show that the mobility of the molecular probes in this environment depends on the molecular nature of the probe. Since smectic phases have generally much larger macroscopic viscosity than that of nematic phases, it is clear that what is probed in the present measurements is the

microscopic environment of the doped molecules instead of the macroscopic one.

In Fig. 7, the ratios of the amplitude of the fast component to that of the slow component of fluorescence decay of malachite green in the four liquid-crystal samples are shown as a function of temperature. It is seen from the figure that the temperature dependence of the amplitude ratio has a peak around the phase transition point where the slow decay time shows a large change in all four samples. This means that the number of dye molecules relatively loosely bound to the host media is increased around the transition temperature. This shows that the nature of the microscopic environment of malachite green molecules experiences large changes through the phase transition, and that the microscopic structure around the molecule becomes unstable around the transition temperature. The amplitude ratio of the fluorescence decay of cryptocyanine, on the other hand, was below unity in the temperature range observed, and was only weakly dependent on the temperature. This shows that the microscopic environment around cryptocyanine molecules is more stable and its nature is not changed by the phase transition of the LC materials.

These behaviors of the temperature dependence of the decay times of the two dyes are explained as follows. All four molecular species of the LC materials used in the present study have a polar group at one end of the molecule. Since malachite green and cryptocyanine are both ionic dyes, they are expected to be attached to the polar group of these LC
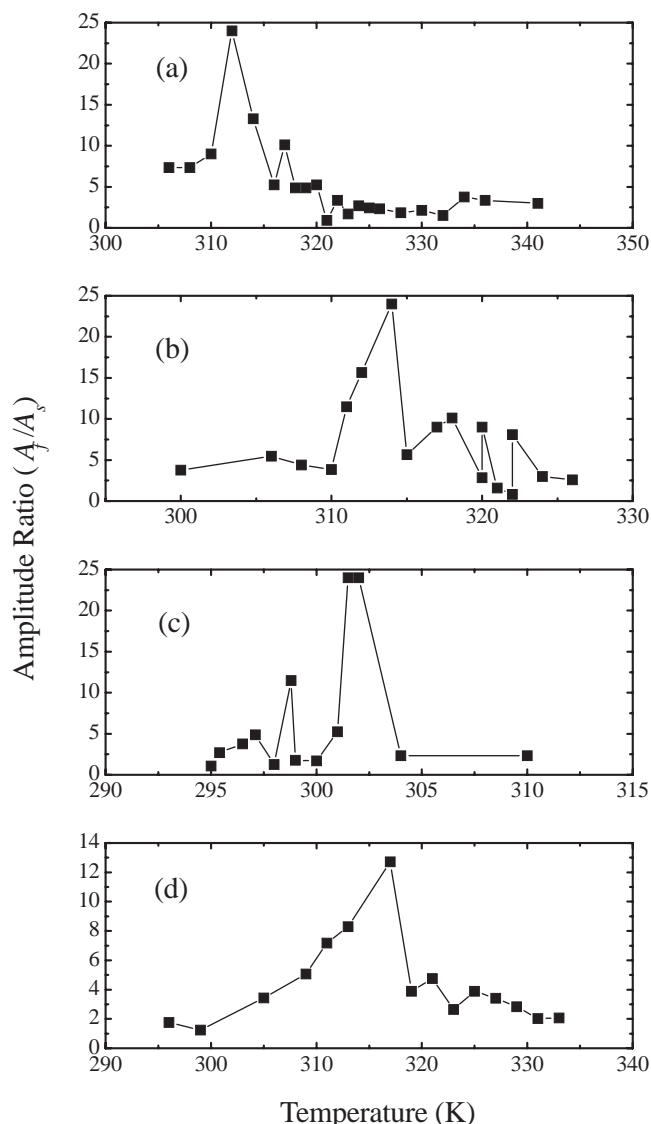
Fig. 7. Temperature dependence of the amplitude ratio of the fast and the slow component (A_f/A_s) of the fluorescence decay of malachite green in (a) PCH50-10OH, (b) PCH50-10OH/PCH50-3OH mixture, (c) 7CB and (d) CP7B.

phase is not sufficiently large to enable the dye to decay nonradiatively through the trans-cis isomerization. Since the sweep volume required for the internal conversion of malachite green is much smaller than that for cryptocyanine, it is conceivable that malachite green is sensitive to the mobility change of the medium due to the crystal-to-nematic transition.

Decay times of malachite green doped in onion cells have been studied previously.[3] Decay times of the fluorescence of the dye emitted from cell walls and from nuclei were found to be approximately 300 and 200 ps, respectively, at room temperature. Based on the results of the present study, it can be concluded that malachite green molecules are actually doped inside the cell walls and that the relatively tight packing of the molecules in the cell walls of biological systems can be probed using the present technique.

4. Conclusions

Fluorescence decay times of malachite green and cryptocyanine doped in four LC materials were measured by increasing the temperature through the phase transition points. The observed behaviors depended on the types of the phases and the doped dyes, reflecting the molecular nature of the LC media and the dyes. The knowledge obtained by the present study should be valuable for future studies on the microscopic dynamics in various materials using molecular probes.

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molecules. It is natural, therefore, to conceive that in smectic phases, which have layered LC structure, the dyes exist in or near the interlayer region. Due to the transition from the crystal to smectic phase, the interlayer restriction becomes loose, although the macroscopic fluidity of the medium remains rather low. The present experimental results suggest the possibility that both malachite green and cryptocyanine molecules detect this microscopic environment change. In nematic phases, on the other hand, the layered structure of the LCs is destroyed, and the dyes are expected to be aligned closely to the LC molecules.[14] Cryptocyanine is almost insensitive to the crystal to nematic transition although the macroscopic fluidity of the medium becomes much higher.[15] This fact shows that the intermolecular space in the nematic