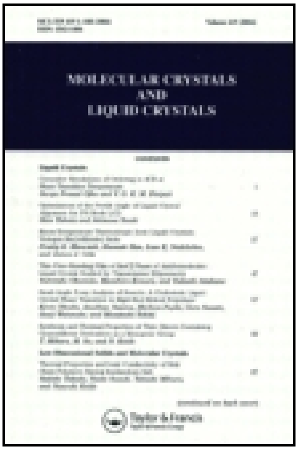

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Time-resolved Study on Unconventional Fluorescence of an Azobenzene Liquid Crystal and its Phase Transition

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Time-resolved Study on Unconventional Fluorescence of an Azobenzene Liquid Crystal and its Phase Transition

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Fluorescence properties of azobenzene liquid crystal, 4.4'-dioctyloxy-azobenzene, were examined by steady-state and picosecond single-photon timing spectroscopy. It was found that the fluorescence from azobenzene aggregate with a peak at ~630 nm was observed in the solid phase in addition to the very weak S_2 fluorescence from azobenzene monomer centered at 420 nm. The fluorescence lifetimes of both aggregate and monomer S_2 state were estimated to be approximately 150 ps and shorter than 2 ps. The relationship between the excited-state dynamics of azobenzene liquid crystal and its phase transition was analyzed on the basis of the temperature dependence of relative fluorescence intensity and fluorescence lifetime of aggregate.

Keywords: azobenzene; liquid crystal; phase transition; fluorescence; single-photon timing

INTRODUCTION

Recently, much attention has been paid for liquid crystals of azobenzene derivatives because of their high potential applications such as image storage, optical memory, and nonlinear optics[1-3]. Unlike stilbene, in which the dynamics of isomerization seems to be well understood[4], the excited-state properties of azobenzene are still unclear even in the solution phase[5].

As far as the luminescence of azobenzene derivatives is concerned, it is well known that the azobenzenes do not show appreciable emission because of the trans-cis isomerization and the nπ* character of the first-excited singlet state[5]. A few time-resolved studies have been done and the presence of S_2 fluorescence of azobenzene with a lifetime shorter than 5 ps was indicated by a picosecond CS_2 Kerr-shutter experiment[6]. Hamai and Hirayama reported the steady-state S_2 fluorescence spectrum of various azobenzene derivatives and their quantum yields ($\Phi_f \sim 10^{-5}$)[7]. The peak wavelength was in the range of 385 nm ~ 435 nm depending on the substituent. Surprisingly, the strong enhancement of fluorescence at ~ 600 nm was observed in the aqueous bilayer aggregates of azobenzene-containing amphiphiles[8]. This was interpreted in terms of relative chromophore orientation of the azobenzene aggregate. In addition, it is also known that fluorescence properties of liquid crystals are strongly dependent on the mesophases as demonstrated by the time-resolved fluorescence spectroscopy of cyanobiphenyl liquid crystals[9,10].

In the present study, we have investigated the fluorescence dynamics of azobenzene liquid crystal, 4.4'-dioctyloxyazobenzene, as a function of temperature by steady-state and picosecond single-photon timing spectroscopy. It was found that fluorescence from the aggregate with a peak at ~ 630 nm was found in addition to the weak S_2 fluorescence of the monomer. The fluorescence lifetime of aggregate and relative fluorescence intensity of aggregate/monomer were found to be strongly dependent on the temperature. From these results, the relationship between the excited-state dynamics of azobenzene and phase transition will be discussed.

EXPERIMENTAL

4.4'-dioctyloxyazobenzene (8AB8) was synthesized and purified as reported previously[11,12]. The phase transition temperature from the solid to nematic and nematic to isotropic phases are 99 °C and 113 °C, respectively[13].

Corrected fluorescence spectra were obtained by a fluorescence spectrophotometer (SPX Fluorolog 2) at the Institute for Molecular Science, Instrument Center. Time-resolved fluorescence spectra and fluorescence decay curves of 8AB8 were measured by a single-photon timing spectroscopy, the details of which was written in elsewhere[14]. The sample was excited by a second harmonics (360 nm) of a synchronously pumped, hybridly mode locked, dispersion compensated femtosecond dye laser (Pyridine 2 as a gain dye, DDI as a saturable absorber). The repetition rate of the dye laser was reduced with an external pulse picker. The response function of the instrument was ~ 30 ps (fwhm). The temperature of the sample was regulated by a temperature-controlled copper block with an accuracy better than 0.1 °C. Fluorescence decay curves were analyzed by a non-linear least-squares iterative convolution method based on Marquardt algorithm.

RESULTS AND DISCUSSION

Fig. 1 illustrates fluorescence spectra of 8AB8 at various temperatures. As clearly shown in the figure, the spectrum with a peak at ~ 630 nm is dominant, whereas the fluorescence spectrum at 420 nm is extremely week in the solid phase at room temperature. With increasing the temperature, the fluorescence intensity at longer wavelength gradually decreases at < 80 °C and suddenly at higher temperature (> 80 °C). In contrast, the fluorescence at 420 nm is almost parallel up to this temperature and increases at higher temperature although the discontinuous change is observed at the phase transition temperature of 99 °C. To make clear the temperature dependence, the fluorescence intensity at 400 nm and the intensity ratio of 600 nm against 400 nm were plotted as a function of temperature as shown in Fig. 2. The ratio discretely changes at the phase transition

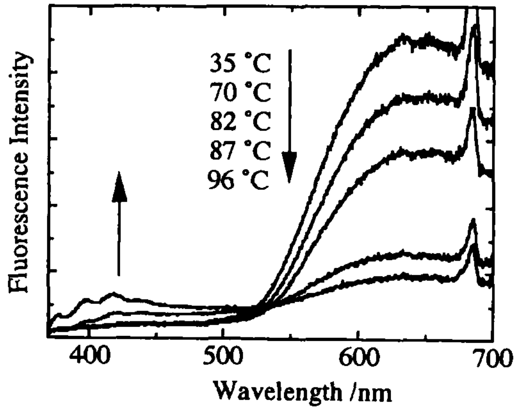

FIGURE 1 Fluorescence spectra of 8AB8 excited at 340 nm at various temperatures.

temperature from the crystal to nematic (99 °C) and the nematic to isotropic (113 °C) phases. In the nematic phase, the ratio is larger than that in the isotropic phase and the crystal just before the phase transition temperature. This indicates the molecular arrangement specific to the nematic phase. In addition, the fluorescence intensity ratio is larger at the temperature lower than 80 °C as compared to that in the nematic phase and suddenly reduces over this temperature even in the solid phase. This result probably suggests that some structural phase transition which cannot be observed by a conventional differential scanning calorimeter is detected by the fluorescence spectroscopic technique.

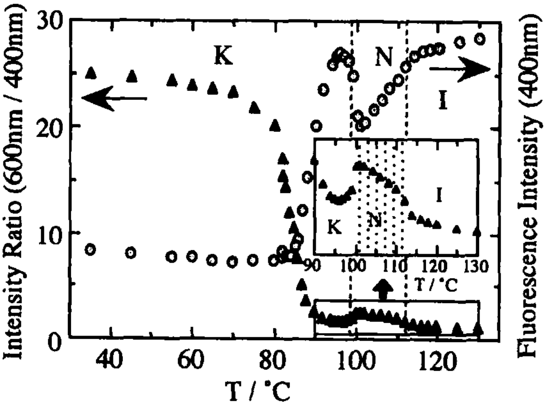

FIGURE 2 Fluorescence intensity at 400 nm and intensity ratio as a function of temperature.

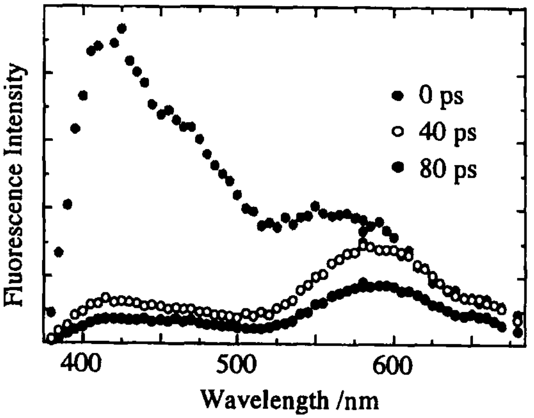

FIGURE 3 Time-resolved fluorescence spectra of 8AB8 observed at 90 °C.

Fig. 3 illustrates time-resolved fluorescence spectra of 8AB8 at various delay times observed at 90 °C. The spectral sensitivity and the effect of system response function (~ 30 ps) are not corrected in this case. The spectrum with a peak at 420 nm is predominant just after the excitation to the S_2 state. The hump also appears at ~ 590 nm which is considered to be the spectrum at 630 nm in the steady-state experiment (Fig. 1). The fluorescence spectrum at 420 nm disappears very rapidly and at a delay time of 40 ps fluorescence is dominated by the spectrum at ~ 590 nm. The fluorescence lifetime of this spectrum is much longer than that at 420 nm.

The fluorescence spectrum at 420 nm is close resemblance to that observed in solution which was assigned to the S_2 fluorescence of azobenzene monomer[7,15], although the spectral width is a little broader than that in the solution. In addition, the decay curve at this wavelength was almost comparable to that of the instrument response function of the system, indicating the fluorescence lifetime shorter than 2 ps. In solution, the lifetime of the S_2 state was estimated to be 250 ~ 300 fs by femtosecond stimulated emission and transient absorption spectroscopy[15]. These results suggest that the spectrum at 420 nm in 8AB8 liquid crystal can be safely assigned to the fluorescence from the S_2 state. On the other hand, the spectrum at 630 nm is probably due to the fluorescence from azobenzene aggregate. This is supported by the excitation spectrum and the temperature dependence of the fluorescence decay curves at 620 nm. The excitation spectrum monitored at 620 nm has a peak at ~ 420 nm and at 525 nm. The excitation peak at 420 nm is very similar to the absorption spectrum of azobenzene J-aggregate (~ 400 nm) in the bilayer membrane system observed by Shimomura and Kunitake[8]. This absorption is originated from the interaction between $\pi\pi^*$ transition of the S_2 state. The J-aggregate emits a fluorescence at ~ 600 nm (no correction of the spectral sensitivity)[8], which may correspond to the fluorescence of 8AB8 liquid crystal centered at 630 nm. The fluorescence spectrum at 630 nm is originated from the J-like structure of 8AB8 in the crystalline phase. The spectrum at 525 nm is probably due to the interaction of $n\pi^*$ state in the aggregate.

Fluorescence decay curves at 620 nm were measured as a function of temperature. In contrast to the decay curve at 420 nm, the fluorescence has relatively long lifetime of 150 ~ 180 ps in the solid phase. The rise time cannot be detected, which indicates the instantaneous formation of 620 nm species. As noted previously, the species with a lifetime of 150 ~ 180 ps is

J-like aggregate of azobenzene. With increasing the temperature, the fast decay component appears being the long lifetime almost constant even in the temperature of > 80 °C, in which the fluorescence intensity at 600 ~ 650 nm suddenly decreases. This result suggests that the some conformational change inducing the decrease in the J-like fluorescence intensity is mainly originated from the amplitude factor but not the fluorescence lifetime. Further analyses of the fluorescence dynamics of azobenzene liquid crystals are now in progress.

Acknowledgments

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References

[1.] T. Ikeda and O. Tsutsumi, *Science*, **268**, 1837 (1995).
[2.] Z. F. Liu, A. Fujishima, and K. Hashimoto, *Nature*, **347**, 658 (1990).
[3.] P. M. Blanchard and G. R. Mitchell, *Appl. Phys. Lett.*, **63**, 2038 (1993).
[4.] R. J. Sension, S. T. Repinec, A. Z. Szarka, and R. M. Hochstrasser, *J. Chem. Phys.*, **98**, 6291 (1993) and references cited therein.
[5.] H. Rau, in *Photochromism - Molecules and Systems -*, eds. H. Durr and H. Bouas-Lauran (Elsevier, Amsterdam, 1990) p.165.
[6.] W. S. Struve, *Chem. Phys. Lett.*, **46**, 15 (9177).
[7.] S. Hamai and F. Hirayama, *Ann. Symp. on Photochem. (Japan)*, 315 (1984).
[8.] M. Shimomura and T. Kunitake, *J. Am. Chem. Soc.*, **109**, 5175 (1987).
[9.] N. Tamai, I. Yamazaki, H. Masuhara, and N. Mataga, *Chem. Phys. Lett.*, **104**, 485 (1984).
[10.] I. Hatta, Y. Nagai, N. Tamai, and I. Yamazaki, *Mol. Cryst. Liquid Cryst.*, **123**, 295 (1985).
[11.] S. Tazuke, S. Kurihara, and T. Ikeda, *Chem. Lett.*, 911 (1987).
[12.] C. Weygand and R. Gabler, *J. Prakt. Chem.*, **155**, 322 (1940).
[13.] A. Shishido, O. Tsutsumi, A. Kanazawa, T. Shiono, T. Ikeda, and N. Tamai, *J. Phys. Chem. B*, **101**, 2806 (1997).
[14.] N. Tamai, M. Ishikawa, N. Kitamura, and H. Masuhara, *Chem. Phys. Lett.*, **184**, 398 (1991).
[15.] N. Tamai, J. Azuma, A. Shishido, and T. Ikeda, to be published.