In situ Fluorescence Observation of the Vacuum Deposition Process of Cyanooctyloxybiphenyl. Fluorescence Behavior Related to Structural Transformation during Deposition

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Fluorescence spectra of 4–cyano–4'–n–octyloxybiphenyl were measured during vacuum deposition on various substrates. A discontinuous change was found in the series of the fluorescence spectra observed during deposition. The change was ascribed to structural transformation from an amorphous state to a crystalline one. The average film thickness where the deposited film showed the transformation depended upon the property of substrate surfaces. These phenomena were discussed in terms of interactions between the substrate and the compound.

It is well–known that liquid crystals (LCs) are oriented by rubbing treatment and chemical modification of substrate surfaces. Orienting mechanisms of LC molecules on the surfaces, however, have not been well revealed on a molecular level yet. To reveal it, information on the interaction between LC compounds and the substrate surface is indispensable.

We consider that fluorescence spectroscopy is one of the most suitable methods for elucidating intermolecular interaction in organic thin films, because it has high sensitivity, high time resolution, and versatility, and does not damage thin films. Moreover, fluorescence is sensitive to micro–environment and molecular aggregation. For example, for Langmuir–Blodgett films, the formation process of a monolayer on water subphase has been investigated by the fluorescence spectroscopy.[1] We observed *in situ* the deposition process of 10–(1–pyrenyl)decanoic acid and carbazolyl dimeric compounds by measuring fluorescence spectra during deposition and discussed the formation mechanism of excimer sites and pyrenyl aggregates in terms of the interaction between substrates and the compounds.[2,3] For the former compound, pyrene monomer fluorescence was observed at the initial stage of deposition, indicating that the deposited molecules are isolated each other on substrates.[2] It is difficult to observe such an initial stage of deposition by using other *in situ* observation methods. Thus, this method makes it possible to obtain information on the formation process of molecular aggregates on substrates.

Alkylcyanobiphenyls are well–known as LC compounds, and their fluorescence properties have been investigated extensively compared with other LC molecules.[4–8] By measuring *in situ* fluorescence spectra during deposition of 4–cyano–4'–n–octyloxybiphenyl (8OCB) on various substrates, we have tried to obtain information on interactions of the molecule with substrates and formation processes of 8OCB–deposited films.

8OCB (BDH Chemicals) was used as received. *In situ* fluorescence spectra were observed by means of a home–made fluorescence spectrometer attached to the vacuum chamber.[3] Quartz plates used as hydrophilic substrates were cleaned with chromic acid mixture. Hydrophobic plates were prepared by immersing quartz plates in a chloroform solution of dichlorodimethylsilane (Hydrophobic 1) or by adsorbing octyltrichlorosilane onto quartz plates from hexadecane solution (Hydrophobic 2).[9]

Figure 1 shows the fluorescence spectra of 8OCB. The peak of the fluorescence spectra of 8OCB in solution depends upon solvent polarity, indicating that the fluorescence is ascribed to an intramolecular charge transfer state. The fluorescence spectra of nematic and isotropic states measured in sandwich type cells were almost the same. Tamai *et al.* reported that their fluorescence are ascribed to an excimer–like state and that the crystalline state emits only monomer–like fluorescence.[5]

Figure 2 shows the change in the fluorescence spectrum observed during deposition of 8OCB on hydrophilic substrates. To clarify the change, ratios of the fluorescence intensity observed at 380 to that at 360 nm (I_{380}/I_{360}) are plotted against the average film thickness in Figure 3. At the initial stage of deposition, monomer–like fluorescence is observed. With deposition, the fluorescence shifts to longer wavelengths and its intensity increases. Afterwards, the fluorescence with a peak of

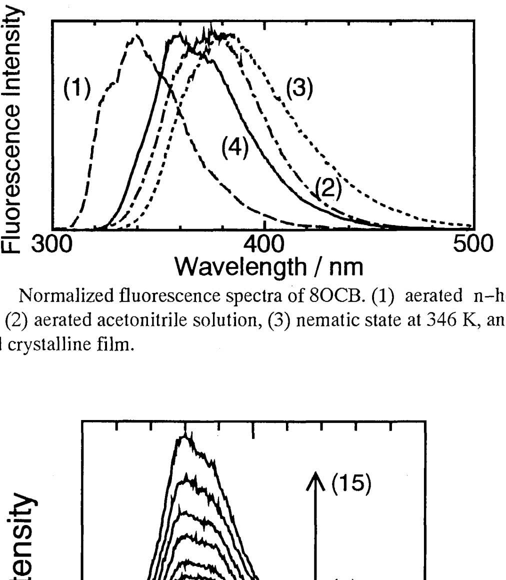

Figure 1. Normalized fluorescence spectra of 8OCB. (1) aerated n–hexane solution, (2) aerated acetonitrile solution, (3) nematic state at 346 K, and (4) deposited crystalline film.

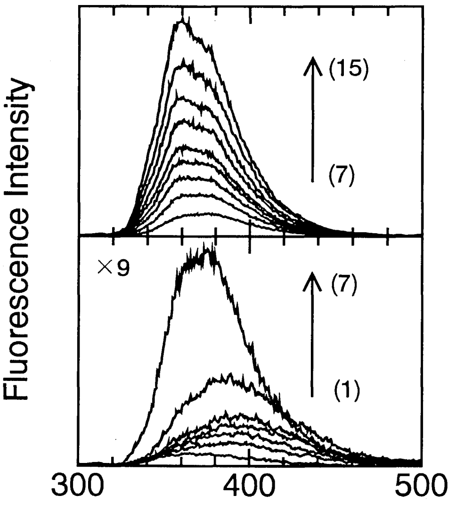

Figure 2. Fluorescence spectral change observed during deposition of 8OCB on a hydrophilic substrate at 293 K. Average film thickness increases from (1) (0.25 nm) to (15) (37.2 nm).

ca. 390 nm increases monotonically. Judging from the spectral shape and the peak position, this broad spectrum can be assigned to excimer-like fluorescence. With further deposition, the spectrum shows a discontinuous change (a sudden peak shift to shorter wavelengths and a sudden increase in the intensity), which corresponds to a sudden decrease in the I_{380}/I_{360} with an increase in the average film thickness from 3.7 to 5.0 nm (Figure 3). Then, the shoulder at the short wavelength in the spectrum becomes more intense, and finally the peak of the fluorescence is located at 360 nm.

Such a discontinuous spectral change in the evolution of fluorescence spectra during deposition has never been observed for *in situ* fluorescence observation of deposition process of fluorescent molecules examined until now.[2,3] The change was also observed for deposition on other substrates, while both average film thicknesses where deposited films showed the spectral change and fluorescence spectra at the initial stage depended upon the property of substrate surfaces (*vide infra* and Figure 3, respectively), although the latter dependence was small. To make the origin of the change clear, we performed optical microscopy and absorption measurements after taking out samples from the chamber. By means of a polarizing microscope with crossed Nicol prisms, a dark image was observed for the films which were taken out before the spectral change was observed, while a bright image for the films after the spectral change was observed. The absorption spectrum of the films before the change differs from that after the change and is similar to that of 8OCB in solution (Figure 4), while the spectrum of the films after the change was quite similar to that of the crystalline state of 8OCB. These results indicate that the discontinuous fluorescence spectral change corresponds to the structural transformation from an amorphous state to a crystalline one during film growth.

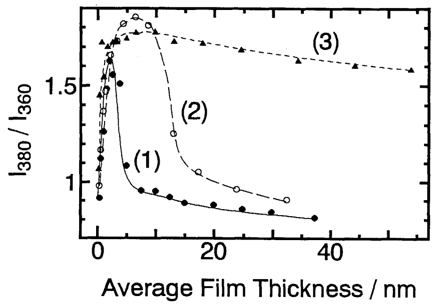

Figure 3. Dependence of the fluorescence intensity ratio I_{380}/I_{360} on an average film thickness. Deposition condition: on (1) hydrophilic, (2) Hydrophobic 1, and (3) Hydrophobic 2 substrates.

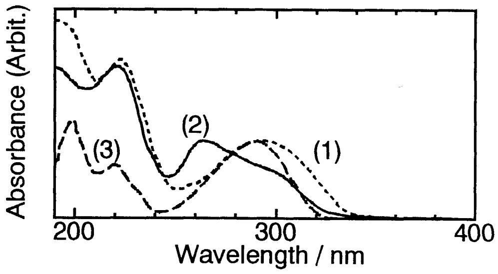

Figure 4. Absorption spectra of deposited 8OCB films before (1) and after (2) the fluorescence spectral change was observed. (1) and (2) correspond to amorphous and crystalline films, respectively. (3) in n-hexane solution.

The average film thicknesses where the deposited films showed the transformation were 3.7–5.0 and 8.6–12.9 nm for hydrophilic and Hydrophobic 1 substrates, respectively (Figure 3). For Hydrophobic 2 substrates, the transformation was not observed upto the average film thickness of 53.9 nm. These results indicate that 8OCB on hydrophilic substrates undergoes the structural transformation even with a quite small amount of 8OCB molecules and that 8OCB on hydrophobic substrates forms thick amorphous films. The difference in fluorescence behavior among these substrates is interpreted by the following way. Since both biphenyl skeleton and octyl group of 8OCB molecules are hydrophobic, interaction of these groups with Hydrophobic 2 substrates with octyl groups is strong compared with hydrophilic ones, and as a consequence, the strong interaction disturbs the transformation to crystalline state of 8OCB on substrates upto a large amount of 8OCB molecules. For Hydrophobic 1 substrates with methyl groups, the interaction between 8OCB and the substrate is not strong compared with Hydrophobic 2, and consequently, the transformation occurs even if an amount of 8OCB molecules is small. Since the interaction of 8OCB with hydrophilic substrates is weaker than that with Hydrophilic 1 substrates, the transformation occurs even with the smaller amount of 8OCB molecules. These interpretations seem to be supported by the difference in the fluorescence spectra observed at the initial stage of deposition among substrates, as mentioned above. That is, the difference indicates that micro-environment around 8OCB molecules on substrates depends upon substrates. This suggests a possibility that the strength of the interaction of 8OCB with substrates responsible for the transformation is different among these substrates.

In the present study the amorphous state of 8OCB was found for the first time, and this state emits excimer-like fluorescence. *In situ* fluorescence observation of deposition process of fluorescent organic compounds makes it possible to observe the structural transformation of very thin films during deposition. The present method gives fruitful information for understanding interactions between substrates and LC compounds.

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References and Notes

1 See, for example: M. Bohorguez and L. K. Patterson, *J. Phys. Chem.,* 92, 1835 (1988); M. Matsumoto, R. C. Ahuja, and D. Möbius, *J. Phys. Chem.,* 96, 5939 (1992).
2 A. Itaya, S. Takada, H. Masuhara, and Y. Taniguchi, *Thin Solid Films*, 197, 357 (1991).
3 N. Tai, A. Itaya, and H. Masuhara, *J. Mater. Chem.*, 2, 897 (1992); A. Itaya, N. Tai, and H. Masuhara, *Chem. Mater.*, 6, 174 (1994).
4 R. Subramanian, L. K. Patterson, and H. Levanon, *Chem. Phys. Lett.,* 93, 578 (1982).
5 N. Tamai, I. Yamazaki, H. Masuhara, and N. Mataga, *Chem. Phys. Lett.*, 104, 485 (1984).
6 T. Ikeda, S. Kuriyama, and S. Tazuke, *Liq. Cryst.*, 7, 749 (1990).
7 T. Ikeda, S. Kuriyama, and S. Tazuke, *J. Phys. Chem.*, 94, 6550 (1990).
8 R. A. Hall, P. J. Thistlethwaite, and F. Grieser, *Langmuir*, 9, 2128 (1993).
9 K. Mathauer and C. W. Frank, *Langmuir*, 9, 3002 (1993).