In Situ Fluorescence Observation of the Vacuum-Deposition Process of 1,3-Di-*N*-carbazolylpropane and Morphological Characteristics of the Deposited Film

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The deposition processes of 1,3-di-*N*-carbazolylpropane (DCzP) have been investigated by measuring in situ fluorescence spectra during deposition on hydrophilic and hydrophobic quartz substrates. Excimer fluorescence was observed even at the initial stage of deposition, and its intensity ratio to monomer fluorescence changed with the progress of deposition, depending upon the nature of the substrate and the temperature. The deposition process of DCzP on hydrophilic substrates consisted of four stages, whereas three stages were observed for deposition on hydrophobic substrates. The fluorescence spectrum of the deposited DCzP film consisted of monomer, partial overlap excimer, and sandwich excimer fluorescence and was different from that of an amorphous DCzP film prepared by fast evaporation of the solvent. Fluorescence and optical microscopies of deposited films were performed after taking the films out of the vacuum chamber. The deposited molecules formed aggregates on the substrates which were initially spherical but which changed to a fractal-like shape after having been stored in a desiccator. The initial aggregates were amorphous, but the fractal-like aggregates were crystalline. These behaviors were compared with the results of *meso*-2,4-di-*N*-carbazolylpentane presented in our previous work and discussed in terms of interactions between the substrate and the compound and difference in a conformational distribution between these bichromophoric compounds.

Introduction

Important factors that determine the vacuum-deposition process of organic compounds are both interaction among deposited molecules and interaction between the molecules and the substrate surface. The structure and electronic properties of deposited films are different from those of their crystalline and molten states, and a new aggregate state may be formed. Characterizations of deposited films (molecular arrangement, physical and optical properties, electronic structure, photophysical property, and so on) have generally been performed ex situ with X-ray and electron diffraction measurements, optical and electron microscopic methods, light absorption and emission measurements, and so on.[1] To control the molecular arrangement and orientation in the film, it is necessary to understand the deposition mechanism. Such studies have been performed for several substrate–molecule combinations by characterizing ex situ films deposited under various experimental conditions and considering factors such as a deposition rate and substrate temperature which affect the molecular orientation. To obtain more direct information on the deposition mechanism including molecular aggregation processes, in situ observation of the vacuum-deposition process is essential. Recently an in situ deposition process of phthalocyanine was observed by measuring lateral photocurrent during deposition, and the deposition process was discussed by comparing the result with film morphology observed ex situ by scanning electron microscopy.[2]

An in situ fluorescence spectroscopy is a powerful method for elucidating the formation process of various organic films. For example, for Langmuir–Blodgett films, by measuring fluorescence spectra, its intensities and its lifetimes of monolayer-forming compounds at various stages of compression, the formation process of a monolayer on water subphase is discussed in terms of aggregate formation, molecular interactions, the change of phase transition, and so on.[3] The electropolymerization process on a conducting electrode was also monitored by the fluorescence spectroscopy.[4] Fluorescence spectral changes observed during solvent-casting, dissolution, and annealing processes of polymer films have provided information on drying behavior, solvent concentration profile in polymers, a swelling process of polymer films, and phase transition.[5-7]

For vaccum-deposited films, the number of molecules on a substrate is limited at the initial stage of deposition, and molecular diffusion and interactions which are responsible for the molecular aggregation process on the substrate during film growth are dynamic in nature. Hence, to elucidate the molecular aspects of the vacuum-deposition processes, we consider that fluorescence spectroscopy is one of the most suitable methods for in situ

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observation of the deposition process, because it has high sensitivity, high time resolution, and versatility and does not damage deposited films. Moreover, since the fluorescence is based upon the transition between electronic states, we can obtain information on intermolecular and intramolecular interactions and electronic properties of deposited films.

Examining various possibilities, we have started to probe the excimer-to-monomer fluorescence intensity ratio for elucidating molecular aspects of deposition processes. For example, we observed in situ the deposition process of 10-(1-pyrenyl)decanoic acid by measuring fluorescence spectra during deposition.[8] Pyrene and its derivatives are typical molecules which form an intermolecular excimer in concentrated solution and molecular assemblies and form dimers and/or aggregates in rigid matrices at high concentrations.[9] On the basis of a series of fluorescence spectral data, the formation mechanism of excimer sites and pyrenyl aggregates characteristic of deposited films was revealed.[8] The laser-assisted vacuum deposition process of this compound was investigated also by using in situ fluorescence spectroscopy.[10]

To further discriminate intermolecular and intramolecular excimer formation and elucidate molecular aggregation phenomena during deposition, we selected the carbazolyl chromophore, since it does not form an intermolecular excimer. That is, *N*-ethylcarbazole shows no excimer fluorescence in concentrated solution and even in molten and solid states.[11] On the other hand, a dimeric compound, *meso*-2,4-di-*N*-carbazolylpentane (*meso*-DCzPe), which satisfies the $n = 3$ rule for intramolecular excimer formation,[12] shows intense intramolecular sandwich excimer fluorescence in addition to structured monomer fluorescence in solution.[13,14] We investigated the deposition mechanism of *meso*-DCzPe by means of in situ fluorescence spectroscopy.[15] The fluorescence spectrum of the deposited *meso*-DCzPe film consisted of both sandwich excimer and structured monomer fluorescence and was similar to that of *meso*-DCzPe films which were prepared by fast evaporation of the solvent. On the basis of the observed thickness-dependent fluorescence spectra, which depended upon nature of substrate and temperature, the formation mechanism of *meso*-DCzPe aggregates during film growth was discussed in connection with interactions between the substrate and the compound.

1,3-Di-*N*-carbazolylpropane (DCzP) is another type of dimeric compound with carbazolyl chromophores. This compound shows weak intramolecular sandwich excimer fluorescence in addition to strong monomer fluorescence in solution.[14,16] The DCzP film prepared by fast evaporation of the solvent showed partial overlap excimer fluorescence in addition to both monomer and sandwich excimer fluorescence.[17] The partial overlap excimer, which was proposed to interpret fluorescence spectra of poly(*N*-vinylcarbazole) (PVCz), is formed in the syndiotactic sequence of the polymer.[18] The partial overlap excimer fluorescence is never observed for *meso*-DCzPe, which is the model for the isotactic diad of PVCz chain. The dominant ground-state conformations of DCzP are tt and tg^+ conformations (vide infra), while *meso*-DCzPe has only TG/GT conformation.[14] That is, the conformational distribution of DCzP is wider than that of *meso*-DCzPe. Hence, using DCzP as a deposited molecule, we will be able to obtain more information on deposition processes of dimeric compounds.

In this work, we observed the deposition process of DCzP by measuring in situ fluorescence spectra during deposition and compared with that of *meso*-DCzPe. The fluorescence spectrum of the deposited DCzP film was different from that of the amorphous DCzP film prepared by fast evaporation of the solvent, which in fact was different from the case of *meso*-DCzPe. We also observed an interesting morphological change in the deposited films with time. As mentioned above, these compounds are dimeric models for PVCz. The polymer film is well-known to show a high photoconductivity and interesting photophysical properties.[18-20] Hence, the present study will contribute to the preparation of new carbazolyl films and an understanding of the photophysical properties of carbazolyl films.

Experimental Section

DCzP was the same as used previously.[17] Hydrophilic and hydrophobic quartz plates were used as substrates. The latter was prepared by immersing the plate in a chloroform solution of dichlorodimethylsilane. To suppress contamination by impurities contained in the sample, molecules in the early and late stages of evaporation were not used and only the middle part was deposited on substrates.

Fluorescence spectra were observed during deposition by means of a homemade fluorescence spectrometer attached to the vaccum deposition chamber. The spectrometer was almost the same as described in the previous paper.[8,10] It consists of a 300-W high-pressure Hg lamp, a water filter (7 cm), an interference filter ($\lambda_{max} = 290$ nm, $\Delta\lambda_{1/2} = 10$ nm), a Jobin-Yvon H-10 monochromator, and a Hamamatsu Photonics R212 photomultiplier. The substrate surface deposited was irradiated by the excitation light, and fluorescence was observed from the front of the substrate. The photocurrent from the photomultiplier was measured with a Toadenpa-kogyo PM-18R electrometer, the output of which was monitored on a Graphtec WX1100 *X*–*Y* recorder. The widths of the entrance and exit slits of the monochromator were 1 mm, corresponding to bandwidth of 8 nm. Absorption spectra of deposited films were measured in air after taking the films out of the vacuum chamber.

In situ fluorescence measurements were done using the following cycle: deposition on a substrate, cessation of deposition, measurement, and recommencement of deposition. We confirmed that both interruption of deposition and excitation light

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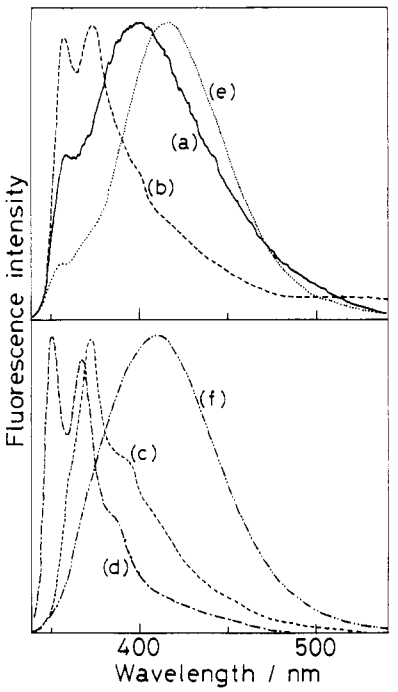

Figure 1. Normalized fluorescence spectra of DCzP: (a) the film deposited on a hydrophilic substrate at 23 °C, (b) the amorphous film (DCzP(a)), (c) the polycrystalline film, (d) an aerated benzene solution of DCzP, (e) reference spectrum of the *meso*-DCzPe film deposited on a hydrophilic substrate a t room temperature, and (f) reference spectrum of the PVCz film.

irradiation for fluorescence measurement did not affect the properties and morphology of the deposited films. The deposition rate was controlled to be constant. However we could not refer to an average film thickness for deposited films, because we observed spherical aggregates of the molecules deposited for the deposited films taken out of the deposition chamber (vide infra). Hence, a relative coverage defined as follows was used instead of an average film thickness: When an absorbance of the 0–0 absorption band of deposited DCzP films was 0.034, a relative coverage was defined as 10. Since a linear relation between an absorbance measured after deposition and an amount of molecules deposited, directly determined by using a calibrated quartz crystal oscillator, was obtained, a value of the relative coverage indicates a relative amount of the molecules deposited on the substrate. The constant deposition rate was equivalent to ca. 0.1 of a relative coverage per minute.

An amorphous DCzP (DCzP(a)) film was prepared by fast evaporation of the solvent (benzene)[17] and studied for comparison.

Results and Discussion

Fluorescence Spectra of Deposited Films. Figure 1 shows fluorescence spectra of a DCzP film deposited on a hydrophilic quartz substrate, a polycrystalline DCzP film, a DCzP(a) film, and DCzP in aerated benzene solution. The spectrum of the solution is known to be composed of monomer and weak intramolecular sandwich excimer fluorescence.[14,16] Spectra of a PVCz film and a *meso*-DCzPe film deposited on a hydrophilic substrate are also shown for comparison. The deposited DCzP film shows broad fluorescence with a peak at ca. 400 nm and weak fluorescence with a peak at 356 nm. The deposited *meso*-DCzPe film is composed of an intense sandwich excimer fluorescence with a peak at 418 nm and a weak monomer fluorescence observed as a peak at 355 nm and a shoulder around 370 nm.[15] The spectrum of PVCz films is well-known to consist of both the sandwich excimer fluorescence with a peak at 420 nm and weak partial overlap excimer fluorescence around 370 nm.[20] The fluorescence spectrum of the DCzP(a) film consists of vibrational band with peaks at 355 and 372 nm, a shoulder at 400 nm, and a descending tail in the longer wavelength region and is thus considered to be composed of three components: monomer, partial overlap excimer, and sandwich excimer fluorescence.[17] We notice that the fluorescence spectrum of the deposited DCzP film is remarkably different from that of these carbazolyl films. Although the position of the weak fluorescence peak at 356 nm of the deposited DCzP film is slightly shifted to longer wavelength compared with that of the first vibrational band of DCzP in aerated benzene solution (ca. 350 nm), it is the same as that of the DCzP(a) film and the deposited *meso*-DCzPe film. Hence, this band is assigned to the first vibrational band of the monomer fluorescence. The main broad fluorescence of the deposited DCzP film is located at a wavelength shorter than that of a deposited *meso*-DCzPe film, and the bandwidth of the farmer fluorescence is slightly broader than that of the latter one. Considering that the fluorescence spectrum of the deposited *meso*-DCzPe film consists of the monomer and the sandwich excimer fluorescence and that the film never shows the partial overlap excimer fluorescence,[15] the main broad fluorescence of the deposited DCzP film is assigned to overlap of both the sandwich and the partial overlap excimer fluorescence.

We have reported that the fluorescence spectrum of the deposited *meso*-DCzPe film was similar to that of an amorphous *meso*-DCzPe film (*meso*-DCzPe(a)) prepared by fast evaporation of the solvent.[15] In the case of the present dimeric compound, the fluorescence spectrum of the deposited film is quite different from that of the DCzP(a) film. The difference in fluorescence spectra of various films between DCzP and *meso*-DCzPe is attributed to a wide conformational distribution of DCzP compared with *meso*-DCzPe. That is, the microstructure of fluorescent sites in DCzP films is liable to be diverse and sensitive to film-preparation methods compared with *meso*-DCzPe.

The absorption spectrum of the deposited DCzP film was quite similar to those of DCzP(a) and deposited *meso*-DCzPe films, although it shifted slightly to longer wavelength compared with that of DCzP in 1,2-dichloroethane solution (Figure 2). Hence, in the ground state, the interaction between carbazolyl chromophores of the deposited DCzP film is similar to those of DCzP(a) and deposited *meso*-DCzPe films.

Figure 3 shows temperature dependence of the fluorescence spectrum of the DCzP film deposited on hydrophilic substrates at 25 °C. The film was cooled immediately after deposition, and the spectra were measured with increasing temperature from −40 to 40 °C. The fluorescence intensity increases with increasing temperature up to 10 °C and then decreases above 10 °C, and the peak of the broad fluorescence shifts to a shorter wavelength with increasing temperature up to 10 °C. The change of the monomer fluorescence is small compared with that of the excimer fluorescence. This fluorescence spectral change of the deposited DCzP film is remarkably different from those of PVCz[21] and deposited *meso*-DCzPe films.[15] That is, the total fluorescence intensity of both PVCz and deposited *meso*-DCzPe films increased monotonically with decreasing temperature. The decrease of

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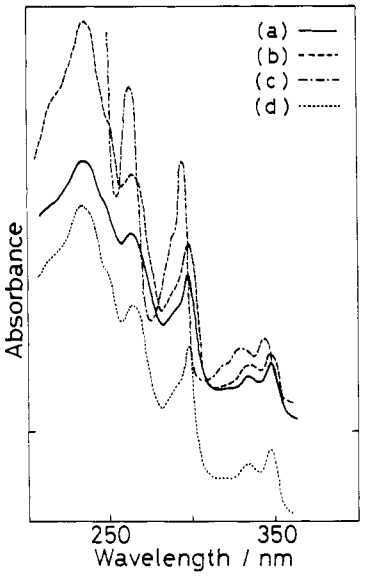


Figure 2. Absorption spectra of DCzP: (a) the film deposited on a hydrophilic substrate at room temperature, (b) the amorphous film (DCzP(a)), (c) a 1,2-dichloroethane solution of DCzP, and (d) reference spectrum of the *meso*-DCzPe film deposited on a hydrophilic substrate.

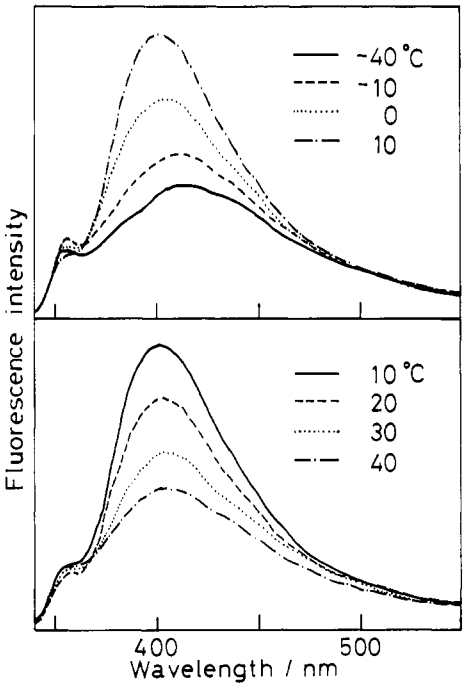


Figure 3. Temperature dependence of the fluorescence spectra of DCzP film deposited on a hydrophilic substrate at 25 °C. Relative coverage: 11.

the fluorescence intensity of the deposited DCzP film with decreasing temperature in the low-temperature region is anomalous for carbazolyl films. This is attributed to a presence of shallow and nonfluorescent trap sites which trap effectively excitation energy at low temperature and/or a low fluorescence yield of DCzP thin films in nature at low temperature.

In Situ Fluorescence Observation of the Deposition Process on Hydrophilic Substrates at Room Temperature. The change in the fluorescence spectrum observed during deposition of DCzP on hydrophilic substrates is shown in Figure 4. Since molecules are deposited singly under the present deposition condition, they are isolated one by one on substrates at the initial

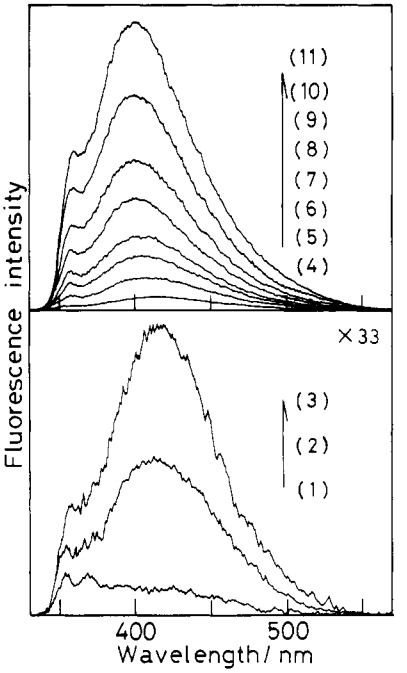
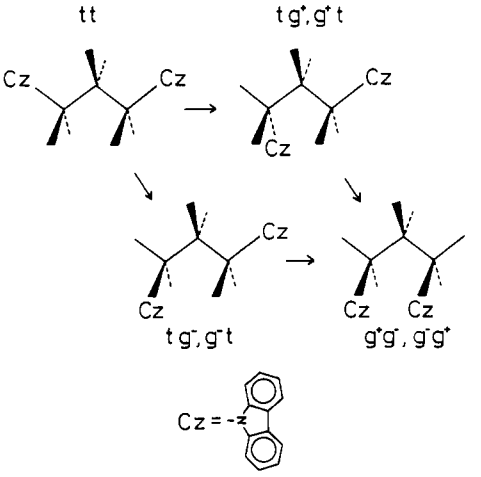


Figure 4. Fluorescence spectral change observed during deposition of DCzP on a hydrophilic substrate at 23 °C. Relative coverage: (1) 0.3, (2) 0.5, (3) 0.8, (4) 1.1, (5) 2.0, (6) 3.3, (7) 4.6, (8) 6.2, (9) 8.4, (10) 11, and (11) 18.

Scheme 1. Excimer Formation in DCzP



stage, and there is no appreciable intermolecular interaction at the stage. Even at this stage, however, a broad excimer fluorescence is observed in addition to the monomer fluorescence with peaks at 355 and 370 nm. The reason for observation of the excimer fluorescence is that DCzP molecules form an intramolecular excimer. This situation is the same as that for deposition of *meso*-DCzPe.[15] Since the dominant ground-state conformations of a 1,3-disubstituted propane are considered to be tt and $tg^{\pm}$ conformations, for DCzP, the intramolecular sandwich excimer fluorescence observed in the initial stages of deposition is due to the formation of the $g^{\pm}g^{\mp}$ conformation (sandwich-excimer conformation) via one ($tg^{\mp} \rightarrow g^{\pm}g^{\mp}$) or two rotations ($tt \rightarrow tg^{\mp} \rightarrow g^{\pm}g^{\mp}$) of the chain backbone of DCzP molecules on substrates, as shown in Scheme 1.

As deposition progresses, both excimer and monomer fluorescence intensities increase, the increase being larger for the excimer fluorescence than for the monomer fluorescence.

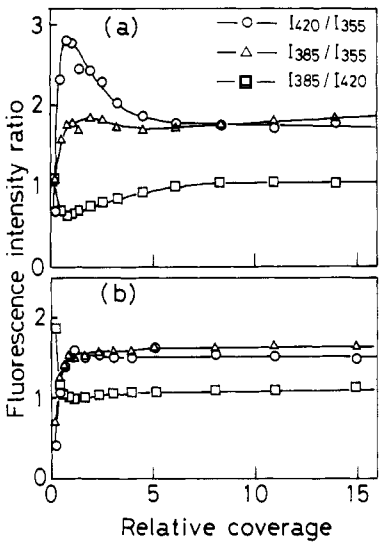


Figure 5. Dependence of the fluorescence intensity ratio I_{420}/I_{355}, I_{385}/I_{355}, and I_{385}/I_{420} on a relative coverage as a measure of the spectral change. Deposition condition: (a) on a hydrophilic substrate at 23 °C and (b) on a hydrophobic substrate at 22 °C.

To clarify the change in the fluorescence spectrum observed during deposition, ratios of the fluorescence intensity observed at 420 (I_{420}) and 385 nm (I_{385}) to that at 355 nm (I_{420}/I_{355} and I_{385}/I_{355}, respectively) and a ratio of I_{385} to I_{420} were plotted against a relative coverage in Figure 5a. The 420-, 385-, and 355-nm bands correspond to a peak wavelength of the sandwich excimer, the partial overlap excimer, and the monomer fluorescence, respectively. This figure shows that the deposition process consists of four stages as follows. At the first stage, which has been described above, deposited molecules are isolated one by one on substrates. As the deposition progresses, both I_{420}/I_{355} and I_{385}/I_{355} increase until a relative coverage of ca. 1, while I_{385}/I_{420} decreases (the second stage). These changes mean that an increase in the intensity of both excimer fluorescence is larger than that in the monomer. *N*-Ethylcarbazole molecules do not form an excimer even in molten and solid states.[11] Hence, although we cannot reject the possibility that DCzP molecules form an intermolecular partial overlap excimer in amorphous states, they are not considered to form an intermolecular sandwich excimer. Consequently, the large increase in the sandwich excimer fluorescence intensity is attributed to excitation energy migration through carbazolyl chormophores to intramolecular sandwich excimer-forming sites of DCzP in aggregates produced by an increase of molecules deposited. The slight decrease in I_{385}/I_{420} is due not to an increase in the partial overlap excimer fluorescence but to both an increase in the sandwich excimer fluorescence intensity and a decrease in the monomer fluorescence intensity, because the monomer fluorescence contributes to the I_{385} and a clear blue shift of the fluorescence is not observed for this stage of deposition (Figure 5).

The third stage of deposition is the region of a relative coverage from ca. 1 to 6. A peak of the main broad fluorescence shifts to the shorter wavelength (blue shift) with increasing a relative coverage in this stage. Such a peak shift was never observed for deposition of *meso*-DCzPe,[15] which does not show the partial overlap excimer fluorescence in solution and in the solid state. This suggests that the blue shift is attributed to partial overlap excimer-forming sites in the deposited DCzP film. The

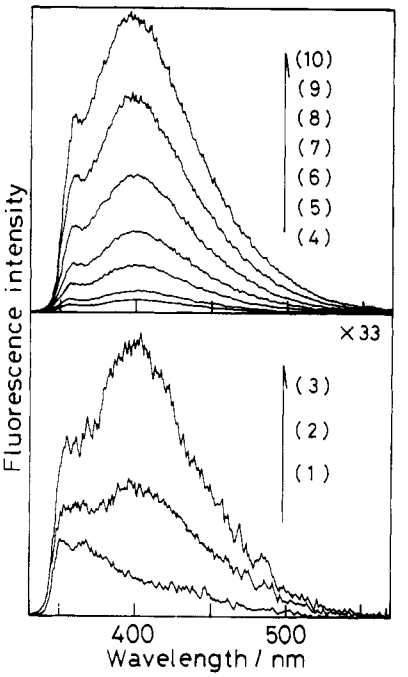


Figure 6. Fluorescence spectral change observed during deposition of DCzP on a hydrophobic substrate at 22 °C. Relative coverage: (1) 0.2, (2) 0.5, (3) 0.7, (4) 1.0, (5) 1.7, (6) 3.1, (7) 5.2, (8) 8.1, (9) 11, and (10) 15.

decrease in both I_{420}/I_{355} and I_{385}/I_{355} means that an increase of the contribution of the monomer fluorescence to the spectrum is large compared with that of both types of excimer fluorescence during this stage. That is, formation of both excimer-forming sites in deposited films is suppressed in this stage compared with the previous stage (second stage). The increase in I_{385}/I_{420} under such a condition indicates that an increase in the concentration of the partial overlap excimer-forming sites is larger than that of sandwich excimer-forming sites. Hence, the blue shift observed during this third stage is attributed not only to an increase in the partial overlap excimer fluorescence but also to an increase in the monomer fluorescence.

In the fourth stage of deposition (relative coverage larger than ca. 6), the three ratios attain a plateau value. This means completion of the change in the fluorescence spectrum, indicating that an amount of deposition which was required to overcome completely the fluorescence intensity of the end of the second stage of deposition (relative coverage of ca. 1) corresponds to ca. 5 of a relative coverage.

In Situ Fluorescence Observation of the Deposition Process on Hydrophobic Substrates at Room Temperature. Figure 6 shows the change in the fluorescence spectrum observed during deposition of DCzP on hydrophobic substrates at 22 °C. Comparing the spectral change with the case of hydrophilic substrates, we notice the following two points: (1) the peak of the excimer fluorescence of films with a relative coverage smaller than 0.1 is observed in the short wavelength compared with deposition on hydrophilic substrates, and (2) the blue shift of the excimer fluorescence is not observed for deposition on hydrophobic substrates.

To examine difference in the deposition process between hydrophilic and hydrophobic substrates, intensity ratios (I_{420}/I_{355}, I_{385}/I_{355}, and I_{385}/I_{420}) were plotted against a relative coverage (Figure 5b). In this case, the deposition

process consists of only three stages, that is, the third stage observed for deposition on hydrophilic substrates does not exist. Both I_{420}/I_{355} and I_{385}/I_{355} increase with an increasing relative coverage up to ca. 1, while I_{385}/I_{420} decreases (second stage). The third stage for deposition on hydrophobic substrates corresponds to the fourth stage for deposition on hydrophilic substrates. Thus the fluorescence spectral change for deposition on hydrophobic substrates is completed during deposition up to ca. 1 of a relative coverage.

The difference in the spectral change observed for deposition betweeen hydrophobic and hydrophilic substrates is interpreted as follows: the microstructure of the fluorescent sites of DCzP molecules in the vicinity of a substrate surface is considered to be affected by the DCzP–substrate interaction. If the hydrophobic interaction among DCzP molecules is similar to the DCzP–hydrophobic substrate interaction, the microstructure of fluorescent sites of DCzP in the vicinity of a hydrophobic substrate surface may be similar to that in aggregates of DCzP molecules. On the other hand, because of the interaction between the nitrogen atom of carbazolyl chromophores and the hydrophilic surface, the DCzP–hydrophilic substrate interaction is different from the DCzP–hydrophobic substrate interaction. Hence, in the case of deposition on hydrophilic substrates, as a relative coverage increases to 1, the hydrophilic property disappears and the hydrophobic interaction among DCzP molecules induces formation of the fluorescent sites similar to those formed by the DCzP–hydrophobic substrate interaction. Such a difference in the DCzP–substrate interaction may result in the difference in the deposition process between hydrophilic and hydrophobic substrates. Judging from the presence of the blue shift observed for deposition on hydrophilic substrates, the DCzP–hydrophilic substrate interaction gives a large amount of sandwich excimer-forming sites compared with partial overlap ones and, on the contrary, the DCzP–hydrophobic substrate interaction is liable to give partial overlap excimer-forming sites.

The deposition process of *meso*-DCzPe on both hydrophilic and hydrophobic substrates consisted of three stages,[15] which situation is not complicated compared with DCzP. This is also attributed to a wide conformational distribution of DCzP compared with *meso*-DCzPe because of a low conformational restriction of DCzP and strongly supports the claim that *meso*-DCzPe does not form the partial overlap excimer even in the amorphous state.[14]

Fluorescence Spectra of DCzP Films Deposited on Hydrophilic Substrates at Various Temperatures. Fluorescence spectra during deposition on hydrophilic substrates at 42, 0, −15, −30, and −45 °C were measured. The deposition process under these conditions consisted of four stages, which is the same as that at 23 °C. However, the behavior of the deposition process strongly depended upon the substrate temperature and were complicated. Hence, we did not discuss the deposition process in detail.

For the DCzP film deposited at 42 °C, a clear shoulder at 375 nm in addition to the first vibrational band of the monomer fluorescence is observed (Figure 7). This shoulder is assigned to the second vibrational band of the monomer fluorescence, judging from its position. This indicates that the monomer fluorescence of the DCzP film deposited at 42 °C is intense compared with that of films deposited at temperatures below 42 °C. Since a crystalline

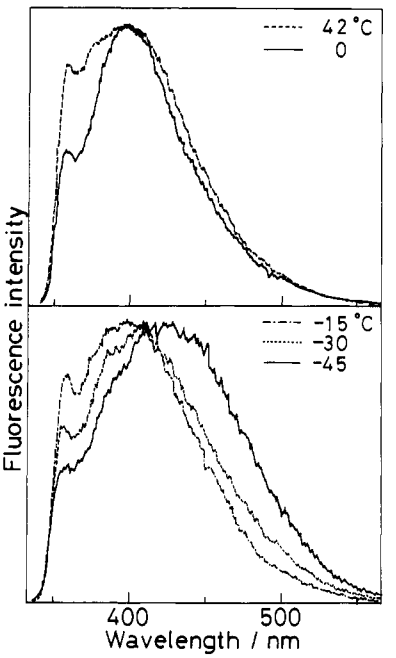


Figure 7. Normalized fluorescence spectra of DCzP films deposited on hydrophilic substrates at (1) 42, (2) 0, (3) −15, (4) −30, and (5) −45 °C. Relative coverage: (1) 19, (2) 14, (3) 18, (4) 12, and (5) 12.

DCzP does not show the excimer fluorescence, but only the monomer fluorescence, the clear observation of the second vibrational band suggests the possibility that deposition of DCzP at 42 °C forms a polycrystalline state of DCzP. By means of a polarizing microscope, however, a dark image was observed for the deposited DCzP film using crossed Nicol prisms, indicating that the film is amorphous. Hence, the size of DCzP microcrystals showing the monomer fluorescence is too small to detect using an optical microscope. That is, deposition at 42 °C forms an amorphous deposited DCzP film which includes microcrystals of DCzP. The formation of microcrystals is due to molecular motion activated thermally on high-temperature substrates.

For deposition at −30 °C, the deposited DCzP film shows fluorescence with peaks at 355 and 408 nm and a clear shoulder at 383 nm. The shoulder, which was also observed for deposition at −15 °C, is attributed to the partial overlap excimer, judging from its position. Observation of the intense partial overlap excimer fluorescence at low temperature is consistent with the fact that partial overlap excimer-forming sites are a shallow trap.[20]

As shown in Figure 7, the excimer fluorescence of the film deposited at −45 °C is broad. Figure 8 shows the dependence of fluorescence intensities on a relative coverage for deposition on substrates at various temperatures. The fluorescence intensities were obtained after correcting for the detector sensitivity. The fluorescence intensity for deposition at low temperature is lower than that at high temperature. That is, characteristics of DCzP films deposited on low-temperature substrates are (1) low fluorescence intensity, (2) a large contribution of the partial overlap excimer component to the spectrum, and (3) the remarkably broad excimer fluorescence. Both the low fluorescence intensity and the broad excimer fluorescence were observed also for *meso*-DCzPe films deposited on low-temperature substrates.[15] These behaviors seem to be characteristics of deposited films of bichromophoric carbazolyl compounds.

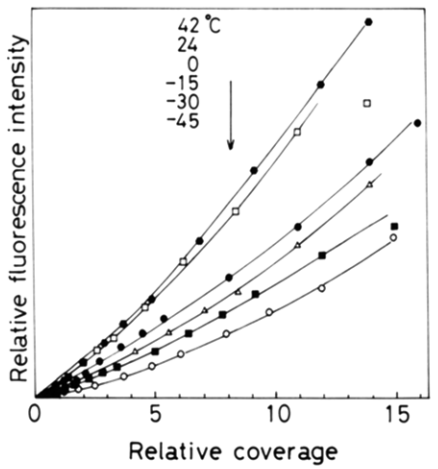


Figure 8. Variation of the fluorescence intensity of deposited DCzP films observed during deposition on hydrophilic substrates at various temperatures.

As for *meso*-DCzPe, the low fluorescence intensity for deposition on low-temperature substrates was explained by assuming that deposition at low temperature results in formation of nonfluorescent sites which are responsible for the decreased fluorescence intensity. For DCzP, however, we notice that, even at the initial stage of deposition, the fluorescence intensity for deposition at low temperature is lower than that at high temperature (Figure 8). This indicates that the fluorescence yield of DCzP molecules deposited on low-temperature substrates is low compared with the high-temperature one. This type of behavior seems to be characteristic of deposited DCzP films. Similar behavior (low fluorescence yield at low temperature compared with high temperature) was reported for thin films with an organized-molecular system (Langmuir–Blodgett films containing pyrene chromophores).[22]

In the case of deposition at low temperature, molecular diffusion and motion on substrates are thermally suppressed, and aggregation of the molecules occurs under unfavorable conditions. On the other hand, since molecular motion and diffusion on high-temperature substrates are fast, the molecules deposited form a more favorable and more stable aggregate structure. The farmer condition results in diverse distribution of the relative geometrical structure of carbazolyl chromophores compared with the latter condition. Thus, the fluorescence spectrum of DCzP films deposited on low-temperature substrates is broad compared with that on high-temperature ones.

Fluorescence spectra of films deposited at various temperatures are different from those measured at −40 to 40 °C for the film deposited at room temperature (Figure 3). This fact indicates that the microstructure of fluorescent sites in deposited films strongly depends upon the substrate temperature during deposition. This situation is reminiscent of polymer films, in which the concentration of excimer-forming sites is determined during film-casting process.

Morphological Change of the Deposited Films. Fluorescence and optical microscopy measurements were performed on films deposited on hydrophilic substrates after taking the films out of the vacuum chamber. As shown in Figure 9a, the molecules deposited form spherical aggregates. The shape of the aggregates change from spherical to fractal-like patterns with time. By using a polarizing microscope, a dark image was observed for the spherical shape and a bright one for the fractal-like one. The spherical aggregates were amorphous, and the aggregates with a fractal-like pattern were crystalline. That is, the deposited DCzP films is initially amorphous, but it crystallizes with time. When crystallization occurs, DCzP molecules diffuse a distance of tens of micrometers on substrates (Figure 9b,c). Similar behavior was observed for films deposited at various temperatures. The change from amorphous to crystalline states correlated with the changes in the fluorescence spectra. The fluorescence spectrum of the stored film in a desiccator for 2 weeks was similar to that of the polycrystalline DCzP film.

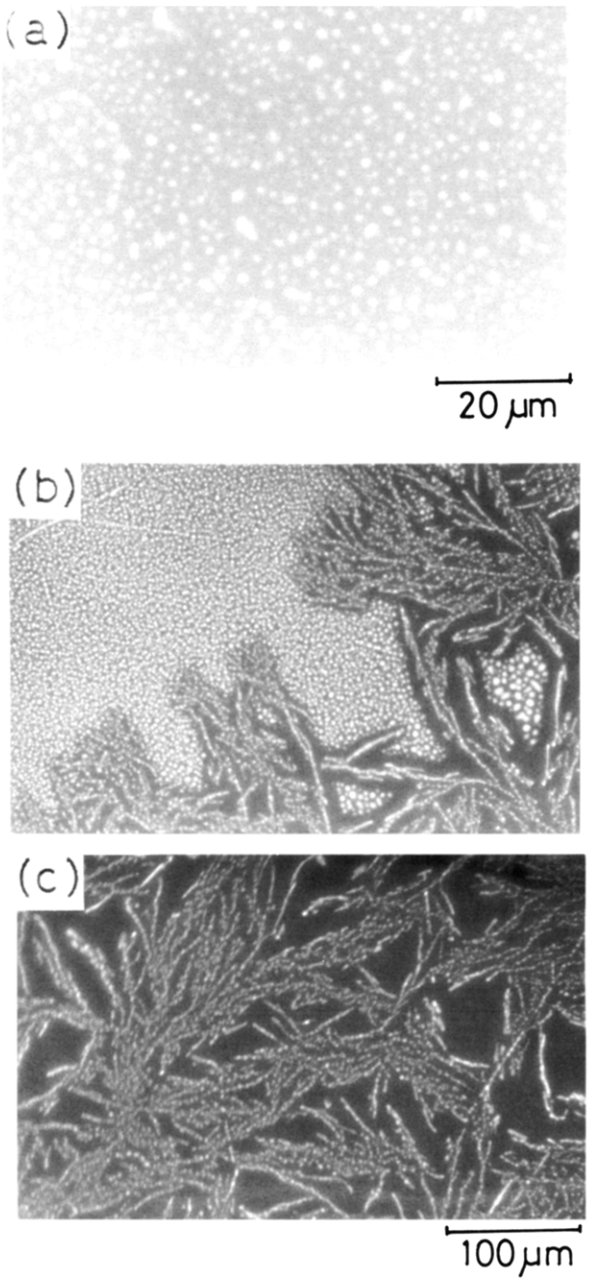


Figure 9. Fluorescence micrograph of the DCzP film deposited on a hydrophilic substrate at −45 °C. Relative coverage: 13. (a) Immediately after deposition; (b) after having been stored in a desiccator for 3 days; (c) after having been stored in a desiccator for 10 days.

(22) Lemmetyinen, H.; Ikonen, M.; Mikkola, J. *Thin Solid Films* **1991**, *204*, 417.

The morphological change from amorphous to crystalline in deposited films was faster for DCzP than for *meso*-DCzPe. This is related to the fact that internal rotation (conformational change) in DCzP is easier than in *meso*-DCzP because of low steric hindrance.

Since the spherical aggregates of the molecules deposited on substrates were observed, we used a relative coverage instead of an average film thickness, as described in the Experimental Section. However, the interpretation proposed for the relative coverage-dependent fluorescence spectra observed during deposition on hydrophilic and hydrophobic substrates suggests a uniform thickness rather than the spherical aggregates of the molecules. That is, these results suggest the possibility that the molecular arrangement of as-deposited films in the vacuum chamber, particularly for thin films, is different from that of the films taken out of the chamber. In other words, the molecular arrangement of the deposited DCzP thin films may change upon exposure to the atmosphere. Under these circumstances in situ observations of the vacuum deposition process are essential to understand the deposition mechanism. For amorphous vacuum-deposited organic films, in situ fluorescence spectroscopy is a powerful method for investigating the molecular aspects of the vacuum deposition process.

Summary

The deposition processes of DCzP have been investigated by measuring in situ fluorescence spectra during deposition, and the results have been compared with those of *meso*-DCzPe. The experimental results are summarized as follows.

(1) The fluorescence spectrum of the deposited DCzP film consisted of monomer, partial overlap excimer, and sandwich excimer fluorescence, while the spectrum of the deposited *meso*-DCzPe film consisted of monomer and sandwich excimer fluorescence. The fluorescence spectrum of the deposited DCzP film was different from that of an amorphous DCzP film prepared by fast evaporation of the solvent, while *meso*-DCzPe films prepared by both methods showed a similar fluorescence spectrum. The difference in fluorescence spectra of various films between DCzP and *meso*-DCzPe was attributed to a wide conformational distribution of DCzP compared with *meso*-DCzPe. The temperature dependence of the fluorescence spectrum of the deposited DCzP film was remarkably different from those of PVCz and deposited *meso*-DCzPe films.

(2) For both compounds, excimer fluorescence was observed even at the initial stage of deposition, and its intensity ratio of the monomer fluorescence changed with the progress of deposition, depending on the nature of the substrate and the temperature. The deposition process of DCzP on hydrophilic substrates consisted of four stages, whereas three stages were observed for deposition of DCzP on hydrophobic substrates and deposition of *meso*-DCzPe on both substrates. These complicated behavior for deposition of DCzP compared with *meso*-DCzPe were explained by the facts that the conformational distribution of DCzP is wider than that of *meso*-DCzPe and that *meso*-DCzPe does not form the partial overlap excimer.

(3) The difference in deposition of DCzP between both substrates suggested that the DCzP–hydrophilic and the DCzP–hydrophobic substrate interaction are liable to give sandwich and partial overlap excimer-forming sites, respectively.

(4) The microstructure of fluorescent sites in deposited films depended upon the substrate temperature during deposition. Deposition at 42 °C formed an amorphous DCzP film which included small microcrystals of DCzP. Characteristics of DCzP and *meso*-DCzPe films deposited on low-temperature substrates were the low fluorescence intensity and the broad excimer fluorescence.

(5) The deposited molecules on substrates taken out of the vacuum chamber formed amorphous aggregates with a spherical shape. The spherical aggregates changed to crystals with a fractal-like pattern with time.