Vacuum-deposited Films of *meso*-2,4-Di(*N*-carbazolyl)pentane

In situ Fluorescence Observation of the Deposition Process and Fluorescence and Morphological Characteristics of the Films

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The deposition processes of *meso*-2,4-di(*N*-carbazolyl)pentane have been investigated by measuring *in situ* fluorescence spectra during deposition on hydrophilic and hydrophobic quartz substrates. Excimer fluorescence was observed 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. Polarizing, optical and fluorescence microscopies of deposited films were carried out after taking the samples out of the deposition 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 for 1 month. The initial aggregates were amorphous, but the fractal aggregates were crystalline. This behaviour is discussed in terms of interactions between the substrate and the compound.

Keywords: *Fluorescence spectroscopy; Vacuum deposition; meso-2,4-Di(N-carbazolyl)pentane; Excimer*

The structures and electronic properties of organic films are different from those of their crystalline and molten states, and the formation of a new aggregate state is expected. For vacuum-deposited films, molecular arrangements, crystallinity, physical and optical properties and electronic structures have generally been elucidated *ex situ* by X-ray diffraction, electron diffraction, optical and electron microscopies, light absorption *etc.*[1] By understanding the deposition mechanism, it will be possible to control the molecular arrangement and orientation in the film. Such studies have been performed for several substrate–molecule combinations by examining various experimental conditions such as deposition rate and substrate temperature.[1] To gain more direct information on the deposition mechanism, including molecular aggregation processes during film growth, *in situ* observation of the vacuum deposition process is essential; a recent representative study was of *in situ* measurement of the lateral photocurrent.[2] During vacuum deposition, the photocurrent of phthalocyanine was measured, molecular aggregation processes were elucidated and a relation between the photocurrent and film morphology observed *ex situ* by scanning electron microscopy was discussed.[2]

The number of molecules on the 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 are dynamic in nature. Accordingly, we consider that fluorescence spectroscopy is one of the most suitable methods for *in situ* 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 started to probe monomer–excimer kinetics of aromatic molecules for elucidating molecular aspects of vacuum deposition processes. For example, we recently observed *in situ* the deposition process of 10-(1-pyrenyl)decanoic acid (PyC$_{10}$).[3] Pyrene and its derivatives are typical of molecules that form an intermolecular excimer in concentrated solution and molecular assemblies and form dimers and/or aggregates in rigid matrices at high concentrations,[4,5] *i.e.* they are liable to form aggregates themselves. On the basis of a series of fluorescence spectral data, the formation mechanism of pyrenyl aggregates characteristic of deposited films was discussed.[3] Furthermore, the laser-assisted vacuum deposition process of PyC$_{10}$ was investigated also by using *in situ* fluorescence spectroscopy.[6]

N-Ethylcarbazole is another representative molecule which does not form an intermolecular excimer.[7] On the other hand, a dimeric compound with carbazolyl chromophores, *meso*-2,4-di(*N*-carbazolyl)pentane (*meso*-DCzPe), which satisfies the $n = 3$ rule for intramolecular excimer formation,[8] shows intense intramolecular excimer fluorescence in addition to structured monomer fluorescence in solution.[9] Hence *in situ* fluorescence observation of the deposition process of this molecule makes it possible to discriminate between intermolecular and intramolecular interactions and elucidate molecular aggregation phenomena during deposition.

In this work, we observed the deposition process of *meso*-DCzPe by measuring *in situ* fluorescence spectra during deposition. The fluorescence spectrum of the deposited *meso*-DCzPe film was unique among amorphous films of carbazolyl derivatives. We also observed an interesting morphological change in the deposited films with time and furthermore found that laser irradiation has an effect on deposition itself. Since this compound is one of the dimeric model compounds of poly(*N*-vinylcarbazole) (PVCz), a polymer which has received considerable attention owing to its high photoconductivity and its interesting photophysical behaviour,[10,11] the present study will contribute to the preparation of new carbazolyl films with new structure and new functionality.

Experimental

meso-DCzPe (supplied by Professor M. Yokoyama, Osaka University[12]) was purified by column chromatography and subsequent recrystallization. Hydrophilic and hydrophobic quartz plates were used as substrates. The hydrophobic substrate was prepared by immersing the plate in a chloroform solution of dichlorodimethylsilane.

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Vacuum deposition and fluorescence spectral measurements were performed in a newly constructed vacuum-deposition chamber, similar to that reported previously.[3,6] Fluorescence spectra were measured with a homemade fluorescence spectrometer attached to the chamber. Spectra were not corrected for the detector sensitivity.

The average thickness of films was estimated, and fluorescence spectra were measured in the same way as reported elsewhere.[3] The deposition rate was kept constant (*ca.* 0.1 nm min^{-1}) by adjusting the temperature of the sample boat.

For comparison, an amorphous *meso*-DCzPe [*meso*-DCzPe(a)] film was prepared by fast evaporation of the solvent (benzene). This is the same method as for preparation of an amorphous 1,3-di(*N*-carbazolyl)propane.[13]

Laser irradiation was performed using a Lambda-Physik EMG 101-MSC excimer laser with XeF (351 nm, FWHM = 15 ns).

Results and Discussion

Fluorescence Properties of Deposited Films

Fig. 1 shows the fluorescence spectrum of a *meso*-DCzPe film deposited on a hydrophilic quartz substrate compared with that of an amorphous PVCz film, a *meso*-DCzPe(a) film and a polycrystalline *meso*-DCzPe film. The spectrum of *meso*-DCzPe in aerated benzene solution, which is composed of monomer and intramolecular sandwich excimer fluorescence,[9] is also shown for comparison. PVCz films show one broad fluorescence, which is mainly composed of a sandwich excimer component with a peak at 420 nm, although weak partial overlap excimer fluorescence with a peak at *ca.* 370 nm is also observed.[11] The fluorescence spectrum of the deposited *meso*-DCzPe film is composed of a broad and intense fluorescence band with a peak at 418 nm and a weak fluorescence band with both a peak at 355 nm and a shoulder around 370 nm. The former broad fluorescence is assigned to the sandwich excimer fluorescence, judging from the peak position and the spectral shape. The latter fluorescence band with both a peak and a shoulder is due to the monomer. The *meso*-DCzPe(a) film shows similar fluorescence to the deposited *meso*-DCzPe, although the main broad fluorescence is slightly shifted to longer wavelengths. Hence the fluorescence spectrum of the *meso*-DCzPe(a) film is also composed of both the monomer fluorescence and the sandwich excimer fluorescence.

After having stored the deposited *meso*-DCzPe film in a desiccator, a change in the fluorescence spectrum was observed. The stored film showed structured fluorescence with a peak at 370 nm and weak shoulders at 355 and 392 nm.
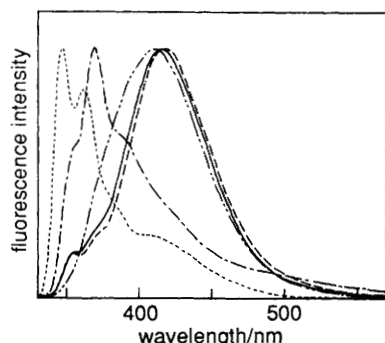
This fluorescence spectrum was similar to that of the polycrystalline *meso*-DCzPe film. By means of a polarizing microscope, a dark image was observed for the freshly deposited *meso*-DCzPe film using crossed Nicol prisms. With time, bright crystallites, the size of which increased with time, were found in the dark background. Therefore the deposited *meso*-DCzPe film is initially amorphous but it crystallizes with time.

The absorption spectrum gives information on the major components, namely, aggregates of chromophores, while the fluorescence spectrum reveals minor fluorescent sites of chromophores because of excitation energy migration through chromophores. The absorption spectrum of the deposited *meso*-DCzPe film was measured in air after taking the film out of the vacuum chamber. The spectrum was similar to those of *meso*-DCzPe(a), PVCz films and the *meso*-DCzPe in iso-octane solution, although it was slightly shifted to longer wavelength compared with that of the compound in solution. Therefore in the ground state the interaction between the carbazolyl chromophores of the deposited *meso*-DCzPe film is similar to that of *meso*-DCzPe(a) and PVCz films. Assuming that the efficiency of singlet excitation energy migration is the same for these films, the difference in the fluorescence spectrum between PVCz and *meso*-DCzPe films suggests that the concentration of the sandwich excimer forming site in *meso*-DCzPe films is lower than that in PVCz films.

Fig. 2(*a*) shows the temperature dependence of the fluorescence spectrum of the *meso*-DCzPe film deposited on hydrophilic substrates at room temperature. The film was cooled immediately after deposition and the spectra were measured with increasing temperature from −50 to 40 °C. The intensity of the broad excimer fluorescence decreases with increasing temperature, whereas the intensity of the monomer fluorescence increases with an isoemissive point. The ratio of intensity of the excimer fluorescence peak (415 nm) to the
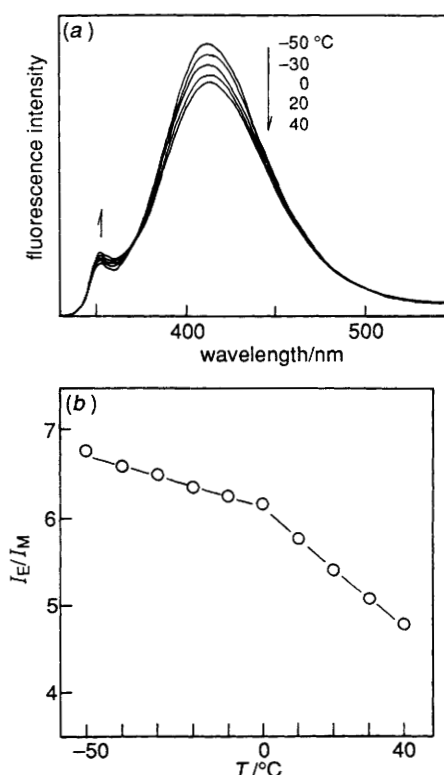

Fig. 1 Fluorescence spectra of *meso*-DCzPe: (—) film deposited on a hydrophilic substrate at room temperature (average film thickness *ca.* 30 nm), (− − −) amorphous film prepared by fast evaporation of the solvent [*meso*-DCzPe(a)], (− · −) polycrystalline film, (− − − −) reference spectrum of the PVCz film, and (· · ·) reference spectrum of a benzene solution of *meso*-DCzPe

Fig. 2 (*a*) Temperature dependence of the fluorescence spectra of *meso*-DCzPe film deposited on a hydrophilic substrate at room temperature. (*b*) Dependence of I_E/I_M on the temperature of measurement. Average film thickness 25 nm

fluorescence observed at 355 nm (monomer band) (I_E/I_M) decreases with increasing temperature, as shown in Fig. 2(b). In solution, where excimer formation is due to a dynamic process such as one rotation of a chain backbone, the intensity ratio increases with temperature up to 40 °C and then decreases.[9] The different temperature dependence suggests that the excimer formation in the deposited film is not due to a dynamic process. It is reasonable to suggest that the concentration of excimer-forming sites in the film is determined during deposition. Note that the concentration of excimer-forming sites in aromatic vinyl polymer films is determined during the film-casting process. Hence the present temperature dependence could be attributed to an increase in monomer excited states that are re-activated (detrapped) from the sandwich excimer. Such a reverse process, from the sandwich excimer to the monomer excited state, has been observed for PVCz in solution and in a polymer matrix.[14]

In situ Fluorescence Observation of the Deposition Process on Hydrophilic and Hydrophobic Substrates at Room Temperature

Fig. 3 shows the change in the fluorescence spectrum observed during deposition of *meso*-DCzPe on hydrophilic substrates. Even during the initial stages of deposition the broad sandwich excimer fluorescence is observed. As deposition progresses, an increase in the intensity of both the excimer and the monomer fluorescence was observed, the increase being larger for the excimer fluorescence than for the monomer fluorescence.

The change in the fluorescence spectrum observed during deposition on hydrophobic substrates was similar to that on hydrophilic substrates; however, the intensity ratio I_E/I_M was different. The values measured during deposition are plotted against the average film thickness in Fig. 4. Independent of the substrate, the ratio increased sharply during the initial stages of deposition and attained a plateau value. A saturated value corresponds to completion of the fluorescence spectral change. Since molecules are deposited singly under the present deposition conditions, they are isolated one by one on the substrates and there is no appreciable intermolecular interaction at the initial stages of deposition. It is proposed on the basis of NMR measurements and steric consideration that
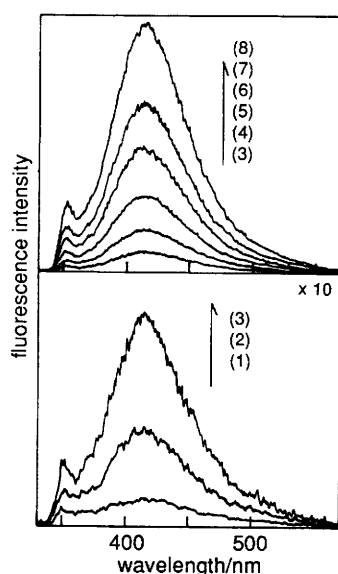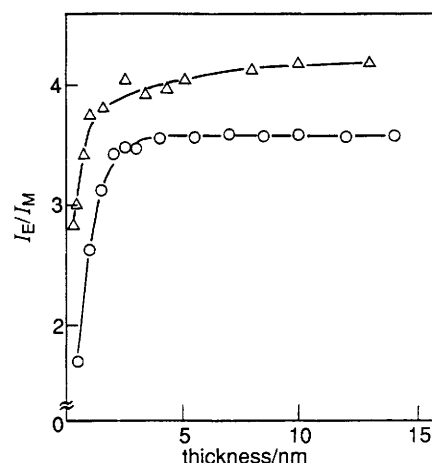

Fig. 4 Dependence of I_E/I_M on the average film thickness. Deposition conditions: (○) on a hydrophilic substrate at 15 °C; (△) on a hydrophobic substrate at 15 °C

the *TG/GT* conformation of *meso*-DCzPe molecules is the most stable in the temperature range 180–350 K.[9] Therefore it is difficult to conceive that many molecules are deposited on substrates in the *TT*-conformation (sandwich-excimer conformation) with total overlap of the two carbazolyl chromophores of *meso*-DCzPe. Hence observation of the intramolecular excimer fluorescence in the initial stages of deposition means that the excimer is formed *via* one rotation of the chain backbone of *meso*-DCzPe molecules on the substrate.

A large increase is observed in the intensity of excimer fluorescence compared with the intensity of monomer fluorescence as deposition proceeds. One explanation for this is singlet excitation energy migration due to the occurrence of an intermolecular interaction between *meso*-DCzPe molecules. That is, an increase in the amount of deposition results in the formation of aggregates. Since *meso*-DCzPe molecules do not form an intermolecular excimer, the increase in the excimer fluorescence intensity is attributed to excitation energy migration through carbazolyl chromophores to intramolecular sandwich excimer-forming sites in aggregates. The saturation of I_E/I_M takes place when the size of aggregates is comparable to the energy migration length. Thus the deposition process consists of three stages: the first stage where molecules are isolated one by one on substrates, the second stage where I_E/I_M increases, and the third stage where the ratio is constant.

I_E/I_M is larger for deposition on hydrophobic substrates than for deposition on hydrophilic substrates during these deposition stages. As mentioned above, the intramolecular excimer at the first stage of deposition is formed *via* one rotation of the chain backbone from the *TG/GT* conformation to the *TT* conformation. Hence the difference in I_E/I_M at this stage suggests that the rotation of the chain backbone of *meso*-DCzPe molecules on hydrophobic substrates is easier than that on hydrophilic substrates.

The difference in I_E/I_M between substrates observed during the second stage is interpreted by the following consideration. As mentioned above, the rotation of the chain backbone of *meso*-DCzPe molecules is easier on hydrophobic substrates than on hydrophilic ones. This suggests that the interaction between *meso*-DCzPe molecules and hydrophilic substrates is strong compared with the case of hydrophobic substrates. This is due to interaction between the nitrogen atom of the carbazolyl chromophores and the hydrophilic surface. Consequently, molecular diffusion of the compound on hydrophobic

Fig. 3 Fluorescence spectral change of *meso*-DCzPe film deposited observed during deposition on a hydrophilic substrate at 15 °C. Average film thickness: (1) 0.5, (2) 1.0, (3) 1.5, (4) 2.5, (5) 4.3, (6) 7.0, (7) 10, and (8) 14 nm

substrates is easier than that on hydrophilic substrates, and aggregates of *meso*-DCzPe molecules are formed easily on hydrophobic substrates compared with hydrophilic ones. In aggregates, observation of excimer fluorescence due to the excitation energy migration to excimer-forming sites is possible. Hence during the second stage, I_E/I_M for deposition on hydrophobic substrates is larger than that on hydrophilic ones. Furthermore, the microstructure of *meso*-DCzPe molecules in aggregates may be different between hydrophilic and hydrophobic substrates, resulting in a difference in the efficiency of excitation energy migration and concentration of the sandwich excimer-forming sites. Consequently a difference in I_E/I_M is observed between hydrophilic and hydrophobic substrates.

The plateau value of the intensity ratio for deposition on hydrophobic substrates is larger than that on hydrophilic ones (Fig. 4). The molecules on hydrophilic substrates, where the interaction between the substrate and the molecule is large compared with the case of hydrophobic ones, are liable to form aggregates that are more spread out and flattened than those on hydrophobic substrates. This phenomenon is observed (*vide infra*). These results suggest that, even in layers far from a substrate surface, the structure of aggregates is different for hydrophilic and hydrophobic substrates, *i.e.* the influence of substrates on molecules is transmitted far from the substrate during deposition.

Dependence of Substrate Temperature on Deposition on Hydrophilic Substrates

The spectral change observed during deposition on hydrophilic substrates at $-50\,°C$ was similar to that at room temperature except for broadening of the excimer fluorescence. Fig. 5 shows I_E/I_M of the fluorescence spectra observed during deposition at various temperatures plotted against the average film thickness. The film thickness at which the ratio attains 90% of the saturation value decreases with increasing temperature (insert in Fig. 5), *i.e.* for deposition at high temperature, the fluorescence spectrum of the thin film resembles that of a thick film. This observation is explained by the fact that the molecular diffusion of compounds on substrates is accelerated with an increase in the substrate temperature. Hence, even if the deposited molecules are limited in number (thin film), the compounds on high-temperature substrates form large aggregates compared with low-temperature substrates.

Fig. 6 shows normalized fluorescence spectra of films deposited at various substrate temperatures. The film thick-
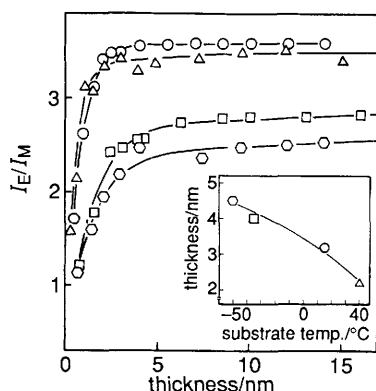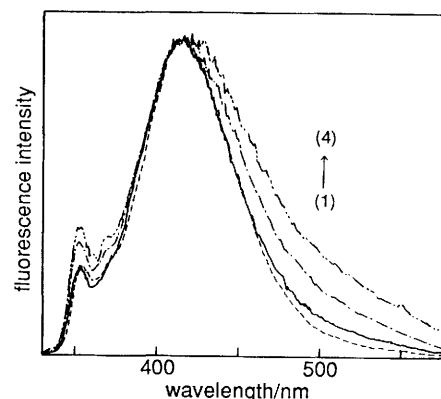

Fig. 6 Normalized fluorescence spectra of the *meso*-DCzPe film deposited on hydrophilic substrates at (1) 40, (2) 15, (3) -30 and (4) $-50\,°C$. The average film thickness is *ca.* 15 nm

ness is *ca.* 15 nm, where I_E/I_M shows the plateau value. The contribution of the long-wavelength component to the spectrum is large for deposition on high-temperature substrates and the bandwidth of the excimer fluorescence decreases with increasing substrate temperature. On the other hand, as shown in Fig. 2, the spectral shape of the excimer fluorescence of the film deposited at room temperature was almost the same regardless of the temperature, and I_E/I_M measured at low temperature was larger than that at high temperature. These results are in disagreement with the result in Fig. 6, suggesting that the difference in the fluorescence spectra observed in Fig. 6 cannot be attributed to the difference in temperature of measurement, but to the difference in the substrate temperature during deposition. This indicates that the geometrical structure of fluorescent sites in deposited films depends upon the substrate temperature.

The fluorescence yield at low temperature is usually larger than that at high temperature. The deposition rate on low-temperature substrates should be higher than that on high-temperature substrates. However, the fluorescence intensity measured during deposition on low-temperature substrates was lower than that on high-temperature substrates. This anomalous behaviour can be explained by assuming that deposition on low-temperature substrates results in formation of non-fluorescent sites which are responsible for fluorescence quenching.

In the case of deposition on high-temperature substrates, the molecular motion and diffusion on substrates are fast and, consequently, the deposited molecules form stable and more favourable aggregate structures for themselves, resulting in the formation of excimer-forming sites whose geometrical structure is relatively limited. For deposition on low-temperature substrates, on the other hand, the molecular diffusion and motion are slower, and aggregation of the molecules occurs under unfavourable conditions compared with the former. Thereby, both excimer-forming sites, whose relative geometrical structure of carbazolyl chromophores takes diverse distributions, and non-fluorescent sites are formed.

Morphological Change of the Deposited Films

Fluorescence and optical microscopies of films deposited at room temperature on hydrophilic and hydrophobic substrates were carried out after taking the sample out of the vacuum chamber (Fig. 7). These clearly show that deposited molecules form spherical aggregates. The spherical shape of the aggregates is clearer for the film on hydrophobic substrates than for that on hydrophilic substrates. This corresponds to the
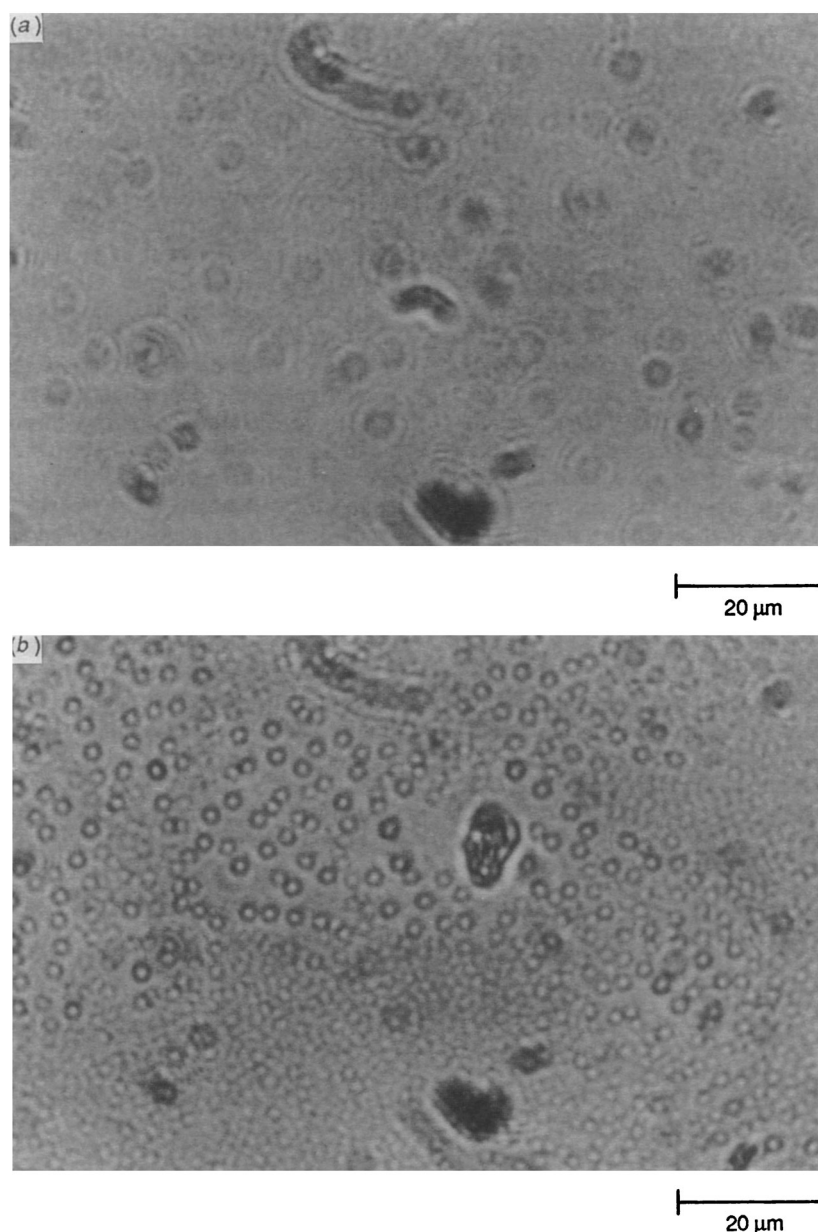

Fig. 5 Dependence of I_E/I_M on the average film thickness. Deposition conditions: on hydrophilic substrate at ($\triangle$) 40, ($\bigcirc$) 15, ($\square$) -30 and ($\mathbf{O}$) $-50\,°C$. The insert shows the temperature dependence of the average film thickness which corresponds to 90% of the saturated value of I_E/I_M

Fig. 7 Optical micrographs of the *meso*-DCzPe film deposited on (*a*) a hydrophilic substrate and (*b*) a hydrophobic substrate

description that aggregates on hydrophilic substrates are spread out and flattened compared with those on hydrophobic substrates.

After deposited films had been stored in a desiccator, the shape of the aggregates changed from spherical to fractal-like patterns, as shown in Fig. 8. By using a polarizing microscope, a dark image was observed for a region where the spherical shape in the film was observed and a bright one for the fractal-like one. That is, the film for which we observed the spherical aggregates is amorphous and the film for which we observed the fractal-like pattern is crystalline. As mentioned above, this change in the film from amorphous to crystalline correlates with the change in the fluorescence spectrum.

As can be seen in Fig. 8, *meso*-DCzPe molecules move through a distance of tens of micrometres on substrates to form crystals with fractal-like patterns. This change from amorphous to crystalline state was faster on hydrophobic substrates than on hydrophilic ones. Since a distinct particle shape and a fast morphological change are observed for the film deposited on hydrophobic substrates compared with
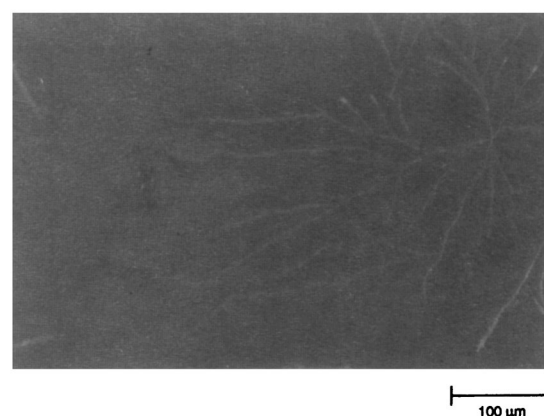

Fig. 8 Fluorescence micrograph of the deposited *meso*-DCzPe film stored in a desiccator for 12 days after deposition on a hydrophobic substrate

hydrophilic ones, interactions between *meso*-DCzPe molecules and the substrate surface are larger for hydrophilic substrates than for hydrophobic ones. This is consistent with the change in I_E/I_M observed during the first and second stages of deposition.

Effect of Laser Irradiation on the Deposited Film during and after Deposition

We have investigated the effect of laser irradiation on the deposited film (irradiation after deposition) and on the deposition process (irradiation during deposition). Fig. 9 shows the fluorescence spectral change of the deposited film induced by excimer laser irradiation (351 nm XeCl excimer laser, laser fluence 0.62 mJ cm^{-2}, repetition rate 1 Hz) in the vacuum-deposition chamber. Both the monomer and the excimer fluorescence intensities decrease with an increase in the number of laser shots. However, the absorption spectrum of the irradiated film was the same as that of non-irradiated films. This indicates that laser irradiation after deposition does not induce structural change in the carbazolyl aggregates that are responsible for the absorption spectrum and that the decrease in the fluorescence intensity cannot be attributed to desorption of *meso*-DCzPe molecules from the deposited film. Hence the decrease in the fluorescence intensity is due to the formation of non-fluorescent sites which are responsible for fluorescence quenching. That is, laser-irradiation on the deposited film induces the non-fluorescent sites. These sites trap the exci-

tation energy which migrates through carbazolyl chromophores and consequently cause the decrease in the fluorescence intensity.

The effect of laser irradiation on the deposition process on hydrophilic substrates was investigated by measuring *in situ* fluorescence spectra during deposition. For the laser fluorescence from 0.07 to 0.7 mJ cm^{-2}, I_E/I_M is plotted against the deposition time (the number of laser shots) in Fig. 10. I_E/I_M for irradiation with high laser fluence was larger than that with low laser fluence. On the other hand, the absorption spectrum of deposited films prepared with laser irradiation was similar to that for films deposited without laser irradiation during deposition. These results indicate that laser irradiation during deposition results in deposited films with a high concentration of excimer-forming sites compared with the deposited film without laser irradiation. As reported, the laser irradiation during deposition of PyC$_{10}$ caused a new aggregate structure of pyrenyl chromophores.[6] Laser irradiation during deposition of *meso*-DCzPe did not result in a change in the main aggregate structure, but in an increase in the concentration of excimer-forming sites. This difference between PyC$_{10}$ and *meso*-DCzPe is likely to be due to the property that pyrenyl chromophores are liable to form aggregates and carbazolyl ones are not. Laser irradiation during deposition (laser-assisted vacuum deposition) opens the possibility of preparing new films with new structures and new functionality.
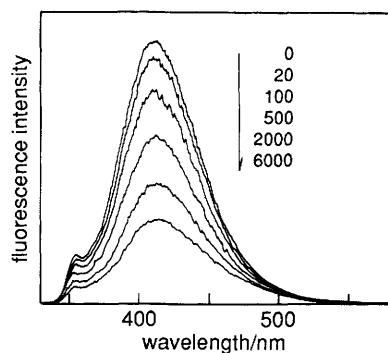
Fig. 9 Fluorescence spectral change of the deposited film of *meso*-DCzPe induced by excimer laser irradiation in a vacuum deposition chamber. The irradiated laser fluence per pulse is 0.62 mJ cm^{-2}, the laser repetition rate is 1 Hz. The number of shots is shown against the curves
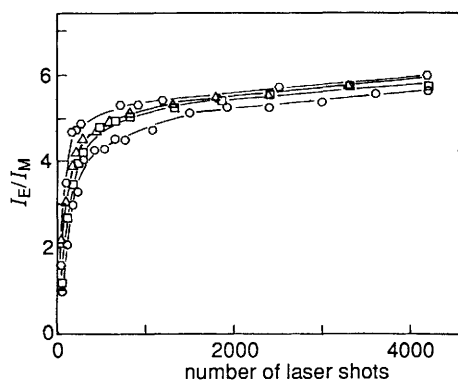
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Fig. 10 Dependence of I_E/I_M on the number of laser shots during deposition. The irradiation laser fluence per pulse is 0.07 (○), 0.15 (□), 0.23 (△) and 0.7 (⬡) mJ cm^{-2}. The laser repetition rate is 1 Hz