Photoreactivity and emission properties of liquid-crystalline twin dimers containing cinnamic acid moieties at both ends of ethylene glycol spacers. II. Emission properties

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Emission properties of liquid-crystalline twin dimers containing 4-methoxy-cinnamic acid moieties at both ends of various ethylene glycol derivatives (nEGMC), where n denotes the number of the ethylene glycol units in the spacers, have been explored by steady-state and time resolved fluorescence spectroscopy in relation to the morphology of the system. Characteristic emissions were observed in the twin dimers, particularly in 2EGMC and 5EGMC, which were ascribed to excimer emission, and the energy gap between the locally excited state (monomer emission) and the excimer state and could be correlated to the difference in the spatial orientation of the mesogenic 4-methoxycinnamate groups adopted in nEGMC in the ground state. The picosecond time resolved fluorescence spectroscopy revealed no observed rise in the excimer emission in any sample at any temperature, indicating that the excimer is most probably formed by direct excitation of the pair wise arrangement of the 4-methoxycinnamate moieties in the ground state; thus, the excimer formation behaviour reflects well the ground state morphology of the twin dimers.

1. Introduction

Emission spectroscopy is a powerful tool to investigate the microscopic environment of fluorophores incorporated into the system. This is mainly due to the rich information associated with photons which possess a number of characteristic features such as energy, polarization and coherency [1,2]. Further, the fluorescence is extraordinarily sensitive to the microenvironment around the fluorophore, which is another reason for the high use of fluorescence spectroscopy. However, this method has apparent shortcomings. When a probe molecule is incorporated into the system by doping or covalent attachment, it is not easy to control the location site, since the location of the probe is determined by the affinity of the probe to the microsite of the system [3]. It is evident that the location site of the probe molecule is of primary importance because the information we can obtain concerns exactly that of the vicinity of the location site of the probe molecule. Another problem of the fluorescence probe method is the disturbance of the organization of the system by the introduction of the probe molecule, which is a serious problem encountered when we use an extrinsic probe since this is just a foreign molecule to the system. To prevent the disturbance by the

probe molecule, it would be best to use an intrinsic probe, but few molecules or groups are available that fulfil the requirements of fluorescence probes, such as the high fluorescence quantum yield and clear photophysical properties [1–3].

In previous papers, we reported the characterization of the phase behaviour of liquid crystals by the fluorescence spectroscopic method by the use of steady-state as well as time resolved measurements of fluorescence, in which cyanobiphenyls were employed as mesogens [4, 5]. The choice of cyanobiphenyls was based on the fact that (1) cyanobiphenyls are popularly used as active media in display devices; (2) since they exhibit clear fluorescent behaviour, they can act as the intrinsic probes; (3) the cyanobiphenyls were found to form excimer, which could provide additional information on the orientational ordering of the relevant mesogens. In fact, excimer formation in liquid crystal systems is a current topic of interest with regards to how the morphology of the chromophores in the ground state affects the excimer formation [6–8].

In this paper, we report the emission properties of liquid-crystalline twin dimers which possess 4-methoxycinnamic acid moieties at both ends of various ethylene glycol derivatives as studied by steady-state and picosecond time resolved fluorescence spectroscopy. We observed characteristic emission in these twin dimers which could be ascribed to excimer emission and we discuss the properties of the excimer emission in relation to the spatial orientation of the mesogens in these twin dimers.

2. Experimental

The structure of the twin dimers containing 4-methoxycinnamic acid moieties at both ends of various ethylene glycol derivatives (nEGMC) used in this study is shown in figure 1. Their synthesis and thermotropic properties were described in full detail in Part 1 of this series of papers [9]. Liquid-crystalline behaviour and phase transition behaviour were examined on an Olympus model BHSP polarizing microscope equipped with a Mettler hot stage, model FP 80 and FP 82.

Steady-state fluorescence spectra (corrected) were measured on an Hitachi F-4000 fluorescence spectrometer. The time resolved fluorescence measurements were performed with a picosecond time correlated single photon counting system, details of which have been reported elsewhere [5, 10]. A synchronously pumped, cavity-dumped dye laser (Spectra Physics 375B and 344S) operated with a mode-locked Nd:YAG laser (Spectra Physics 3460 and 3240) was used as an excitation pulse source with a pulse width of 4 ps (FWHM). We obtained a frequency doubled pulse for the excitation of the samples through a KDP crystal (Inrad 531). Fluorescence from the samples was detected at right angles to the excitation pulse through a monochromator (JASCO CT-25C) with a microchannel plate photomultiplier (Hamamatsu R1564U-01). Signals from the photo-multiplier were amplified (HP 8447D), discriminated (Ortec 583) and used as a stop pulse for a time to amplitude converter (Ortec 457). A start pulse was provided from a fast photodiode (Antel AR-S2) monitoring a laser pulse through a discriminator (Ortec 436). Data were stored in a multichannel analyser (Canberra 35

$$CH_3O\text{—}\bigcirc\text{—}CH\text{=}CH\text{-}COO(C_2H_4O)_nCO\text{-}CH\text{=}CH\text{—}\bigcirc\text{—}OCH_3$$
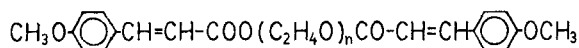
$$n=2\ ,\ 2EGMC\ ;\quad n=3\ ,\ 3EGMC\ ;\quad n=4\ ,\ 4EGMC\ ;\quad n=5\ ,\ 5EGMC$$

Figure 1.   The structure of nEGMC used in this study.

Plus) and then transferred to a microcomputer (NEC 9801) where decay analysis was performed. The instrument response function of the whole system was 60 ps FWHM.

Fluorescence spectra of liquid crystals in neat or in concentrated solution were measured under front face excitation and front face measurement of emission with 1 mm quartz cells in the presence of air. The temperature of the samples was controlled by means of a JASCO HTV cell coupled with a temperature controlling unit, which was well calibrated.

3. Results and discussion

Figure 2 shows the fluorescence spectra of 4-methoxycinnamic acid (MC) and ethyl-4-methoxycinnamate (MCE) in chloroform solution (10^{-5} molar). The fluorescence quantum yield of MC was high while MCE showed only weak emission. The emission maximum of MCE was red shifted in comparison with that of MC. Figure 2 also includes the fluorescence spectra of nEGMC in dilute chloroform solutions. These spectra were similar to that of MCE in both shape and quantum yield and showed no difference between homologues with different spacer length. These results are in good
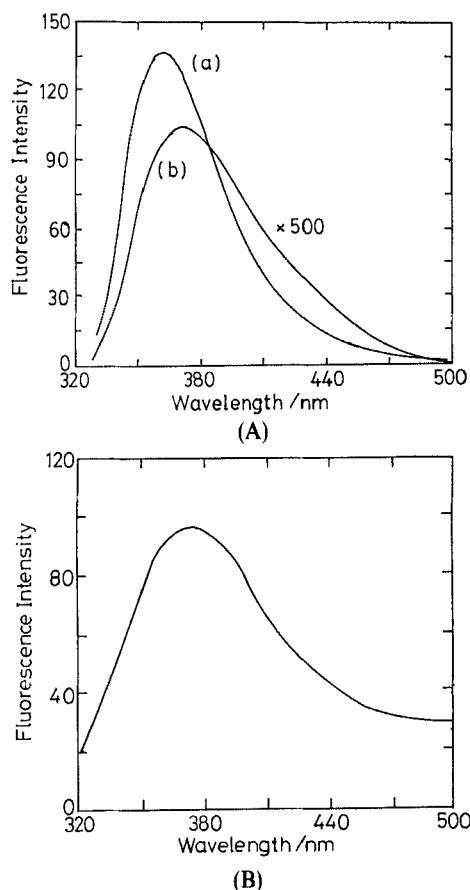

Figure 2. Fluorescence spectra of nEGMC and their model compounds in dilute chloroform solution. (A): (*a*) MC; (*b*) MCE. (B): nEGMC. Since nEGMC showed almost identical spectra, each spectrum is not shown separately.

agreement with the previous studies on the emission behaviour of cinnamic acid derivatives [11, 12], which demonstrated that although the fluorescence quantum yield of cinnamic acid was high, ethyl cinnamate showed a very low quantum yield ($< 10^{-3}$).

In order to explore the fluorescence behaviour of nEGMC in relation to the morphology of the system, the fluorescence spectra of the twin dimers were measured in neat solution at various temperatures. Figures 3, 4 and 5 show the fluorescence spectra of 2EGMC, 4EGMC and 5EGMC at various temperatures, respectively. All compounds exhibited an emission maximum at ≈ 390 nm and a broad peak was observed at longer wavelength for 2EGMC and 5EGMC. Further, the spectra were found to be very sensitive to temperature and the emission intensity decreased monotonically with temperature. Although the intensity itself was dependent on temperature, the shape of the spectrum can be visualized clearly in the normalized spectra ((b) in each figure).

In the course of the fluorescence measurements, we realized that the fluorescence spectra of nEGMC were sensitively dependent on the annealing condition of the samples. This seems to imply that the microscopic environment of mesogens is affected by annealing. For 2EGMC, 4EGMC and 5EGMC, we observed reproducible spectra on annealing under the same condition, however, reproducibility for 3EGMC was very poor. Therefore, we will not mention the emission behaviour of 3EGMC here.

Previous studies have shown that p-phenylene diacrylic acid diethyl ester (Et$_2$PDA), a cinnamic acid derivative, exhibits a structured fluorescence with maximum at 370 nm in a dilute solution of 1,2-dichloroethane [8, 13]. On increasing the concentration of Et$_2$PDA, the fluorescence intensity at 370 nm decreased and a new peak which was broad and structureless appeared at 470 nm. These peaks have been assigned to monomer emission (370 nm) and excimer emission (470 nm), respectively [8, 13]. The liquid-crystalline polyesters composed of PDA and EG showed both monomer and excimer emissions, but the latter was predominant [8]. Further, the excimer emission was found to depend strongly on the phase of the liquid crystal polyesters [8]. Namely, excimer is formed with high efficiency in the liquid-crystalline state, which is explicable in terms of spatial orientation adopted by the PDA chromophores in the polymer liquid crystals. In the liquid-crystalline state, the PDA chromophores are aligned parallel to each other, and the face to face configuration, essential for excimer formation, is easily attained.

On the basis of the emission behaviour of Et$_2$PDA and the liquid crystal polyesters, the broad peak observed at longer wavelength on 2EGMC and 5EGMC may be assigned to excimer emission. Of particular interest is the difference in the peak maxima at longer wavelength between 2EGMC and 5EGMC. Since the monomer emission showed a maximum at a similar wavelength in all compounds, it is reasonable to assume that the nature of the locally excited state is similar among the three compounds. The energy gap in the excimer state between 2EGMC and 5EGMC is therefore most probably ascribed to the different structure of the relevant excimer states. It can be assumed, therefore, that the two 4-methoxycinnamate mesogens involved in the excimer formation exhibit different spatial orientations between 2EGMC and 5EGMC, sensitively reflecting the ground state morphology of the system (see figures 3, 4 and 5)).

Figure 6 shows the fluorescence decay profile of 5EGMC monitored at 370 nm ((a) monomer emission) and 470 nm (b) excimer emission) as a typical example of time resolved fluorescence decay analysis. 5EGMC showed the liquid crystal phase at a temperature of 22°C. It is evident that the decay of monomer fluorescence was fast and showed a profile similar to the instrument response function (≈ 60 ps FWHM). Because

Figure 3. Fluorescence spectra of 2EGMC in neat solution at various temperatures. (*a*), absolute spectra; (*b*), normalized spectra at maxima. $\lambda_{ex} = 300$ nm. (See figure 3 of Part I for phase behaviour at each temperature.)
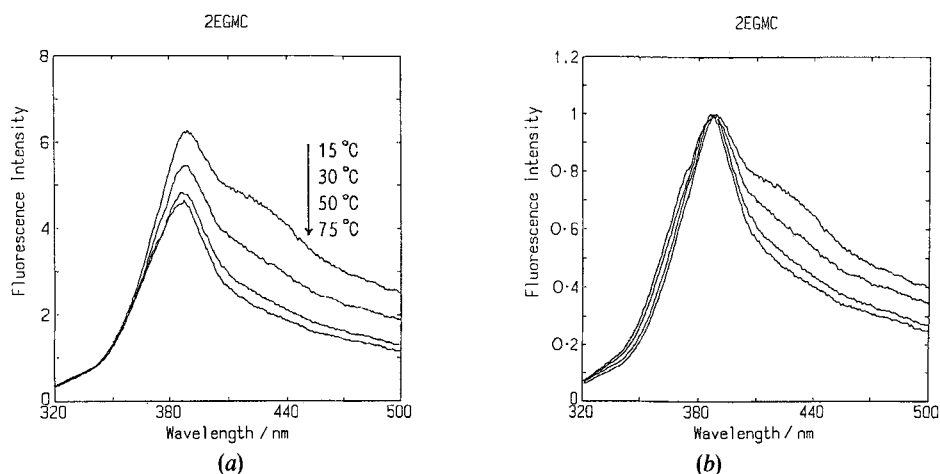
Figure 4. Fluorescence spectra of 4EGMC in neat solution at various temperatures. (*a*), absolute spectra; (*b*), normalized spectra at maxima. $\lambda_{ex} = 300$ nm. (See figure 3 of Part I for phase behaviour at each temperature.)
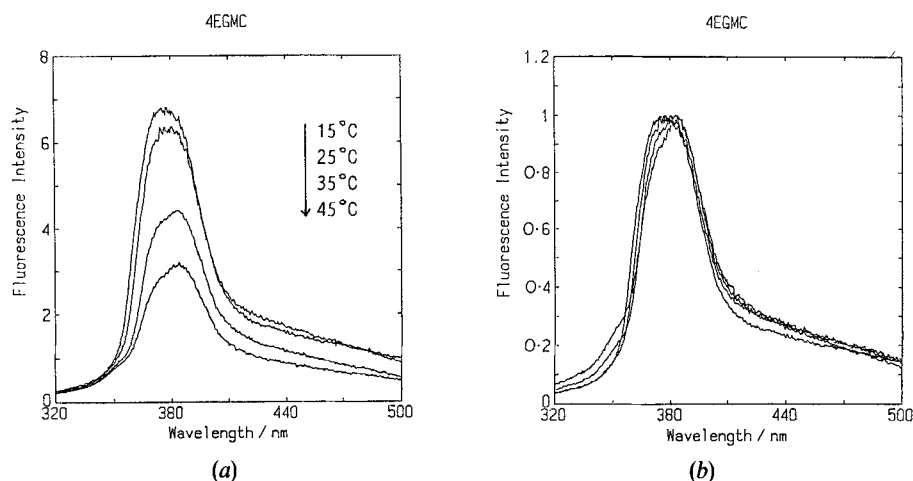
of the fast decay of monomer emission, fitting the decay curves with a function in the form of $\Sigma A_i \exp(-t/\tau_i)$ was difficult, giving unreliable values of the lifetimes as judged by χ^2 and Durbin–Watson (DW) parameters. Although the absolute values of the lifetimes of the monomer emission could not be obtained reliably, it is clear that the decay of the monomer emission is very fast. Unlike the monomer emission, the excimer emission could be analysed satisfactorily with a triple exponential function irrespective of phases ($0.9 < \chi^2 < 1.2$; DW > 1.85). Fitting of the decay curve shown in figure 6 (*b*), for example, gave the results of $A_1 = 0.44$, $\tau_1 = 41$ ps, $A_2 = 0.13$, $\tau_2 = 320$ ps, $A_3 = 0.031$, $\tau_3 = 1.9$ ns with $\chi^2 = 1.07$ and DW $= 1.90$. In the following, therefore, we limit our discussion to the decay profiles of the excimer emissions.
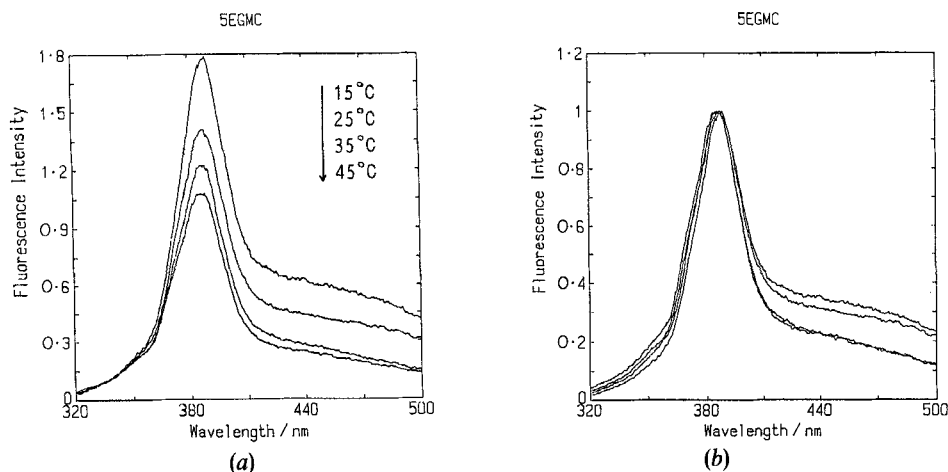
Figure 5. Fluorescence spectra of 5EGMC in neat solution at various temperatures. (*a*), absolute spectra; (*b*), normalized spectra at maxima. $\lambda_{ex} = 300$ nm. (See figure 3 of Part I for phase behaviour at each temperature.)

Figure 7 shows the lifetimes of the excimer emission as a function of temperature. It is of particular note that no rise component was observed at any temperature for any samples. This means that the excimer formation is so fast that it could not be detected with our apparatus or the excimer is formed directly by the excitation of paired chromophores. As a result, Reiser *et al.* and ourselves investigated the emission properties of polyesters composed of PDA and flexible spacers [8, 13]. In these polyesters, the excimer was not formed by the usual diffusion process but by the excitation of paired chromophores. Even in solution, the PDA chromophores have a strong tendency to aggregate in the ground state [13]. Thus, it is reasonable to assume that the 4-methoxycinnamate chromophores exist almost exclusively as a pair in the present system, leading to excimer formation through the excitation of the preformed chromophore pairs. This view is well supported by the absence of the rise component in the excimer emission.

Although the quantitative discussion on the basis of the results of the lifetime analysis is impossible, the results can be discussed qualitatively in relation to the morphology of the system. Since the short components (τ_1) and the medium components (τ_2) seem to be associated with a relatively large error because of the time resolution of our apparatus, the long components (τ_3) are considered here. The values of τ_3 were larger in the liquid-crystalline state than in the isotropic state and a discrete change was observed at the temperature close to the liquid crystal–isotropic phase transition temperature $(T_C; T_C$ is indicated in figure 7 by an arrow). The random structure of the isotropic state may lead to the high mobility of the mesogenic chromophores, although the paired structure, as expected, remains above T_C; thus, a bimolecular quenching process which leads to a shorter lifetime may be facilitated in the isotropic phase. On the other hand, the mobility of the mesogenic chromophores in the liquid crystal phases is expected to be restricted because of the ordered structure. This would result in a slow nonradiative decay of the excited state and a longer lifetime. The discrete change in the lifetimes can be explained in this way.

There have been many studies on excimers with identical chromophores but different structure. Johnson reported that in the fluorescence of poly(*N*-vinylcarbazole)
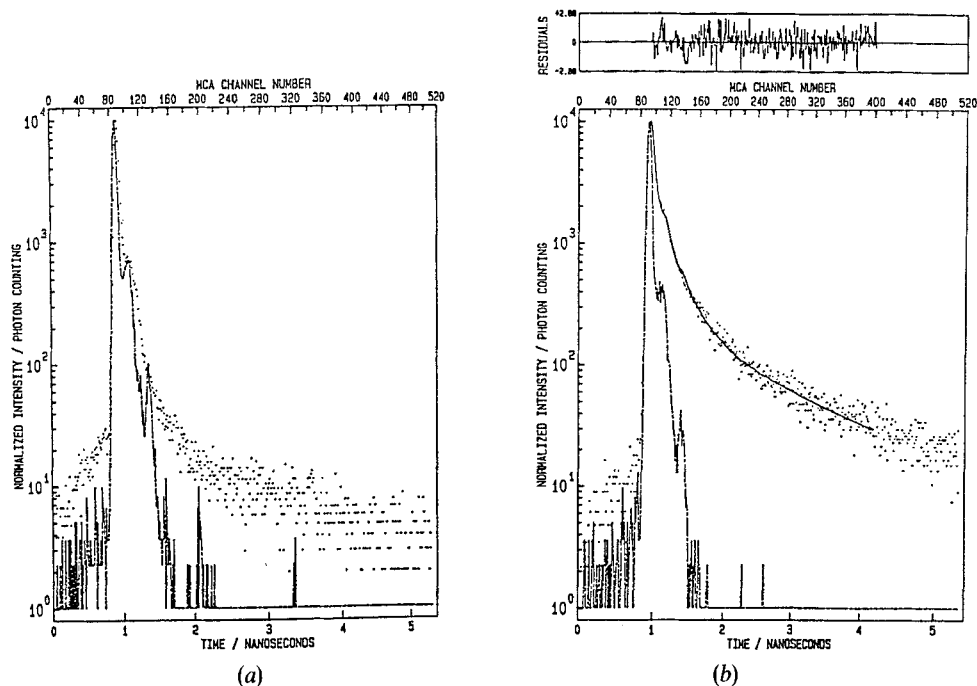
Figure 6. Fluorescence decay profiles of 5EGMC monitored at (a) 370 nm and (b) 470 nm. The instrument response function (FWHM 60 ps) is also shown in both figures and a fitting curve based on the triple exponential function is included in (b). $\lambda_{ex} = 300$ nm.
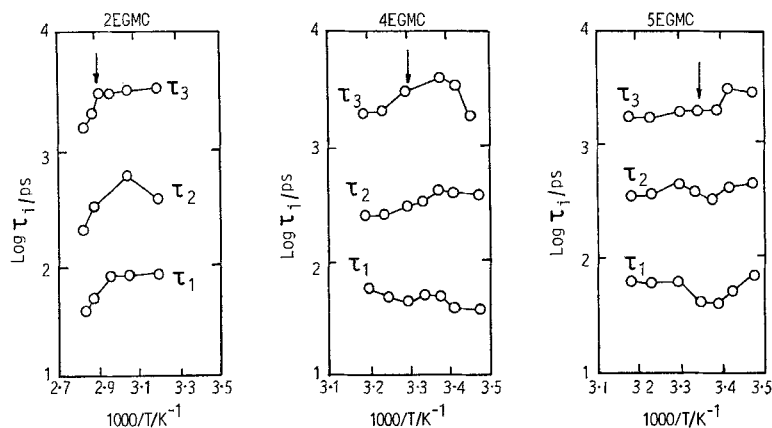

Figure 7. Lifetimes of excimer emission of 2EGMC, 4EGMC and 5EGMC as a function of temperature. $\tau_1 < \tau_2 < \tau_3$; $\lambda_{ex} = 300$ nm; $\lambda_{em} = 470$ nm. Arrows in the figures indicated T_C.

negligible emission due to monomer (locally excited state) was observed while two kinds of excimers were clearly recognized: one possesses a face to face arrangement (sandwich excimer) of the chromophores, the emission maximum of which lies at longer wavelength, and the other arises from partial overlap of the relevant chromophores, showing its emission maximum at shorter wavelength, and called second excimer or high energy excimer [14]. Many examples of the two types of excimer states have so far been reported for naphthalene [15], anthracene [16] and carbazole [17] derivatives.

On the basis of these previous results, it is not unreasonable to ascribe the excimers with different energy observed in 2EGMC and 5EGMC to those with different mutual orientation of the 4-methoxycinnamate chromophores. In other words, the emission properties of the excimer reflect sensitively the orientation of the relevant two mesogens. From the standpoint of the stability of the excimer, the antiparallel configuration of the two chromophores (figure 8 B) is preferred, giving a low energy excimer (longer wavelength). The excimer emission of 2EGMC and 5EGMC observed at longer wavelengths implies the existence of the interdigitated structure as schematically illustrated in figure 8 D, where the mesogens of different molecules are interleaved. The energy gap in the excimer emission observed for 2EGMC and 5EGMC is most probably ascribed to the different ways of overlapping two chromophores involved in the excimer formation. This type of interdigitated structure of liquid crystal dimers has already been proposed by Luckhurst *et al.* [18]. In Part I, it was shown that the photodimer of 4EGMC has the head to head structure which is expected to arise from the parallel arrangement of the 4-methoxycinnamate mesogens in the ground state (figure 8 A) [9]. Absence of emission at longer wavelengths in 4EGMC may indicate that the parallel arrangement of the mesogens is predominant in this compound, which is well correlated with the fact that in 4EGMC the yield of the photo-dimer formation was quite high [9].
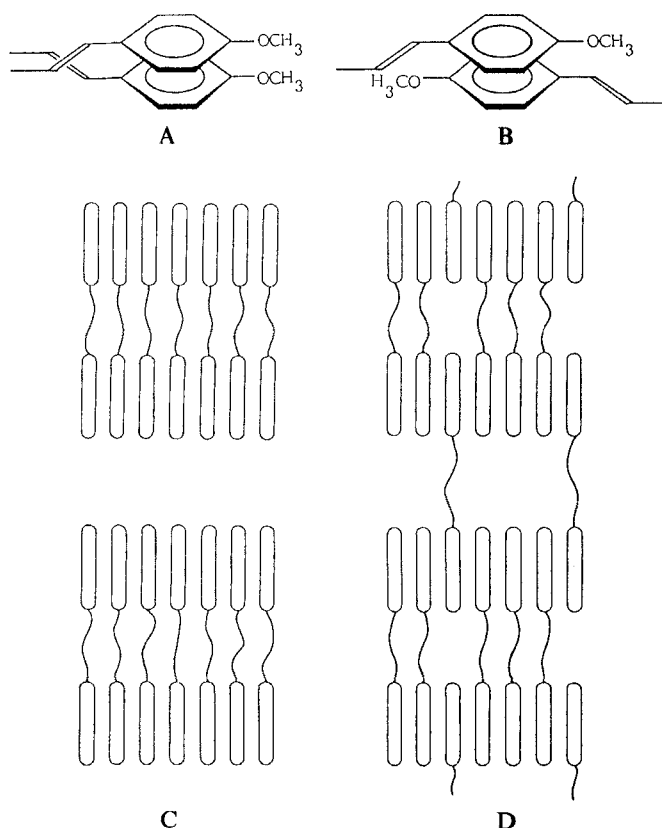

Figure 8. Schematic illustration of the configuration of mesogens (A and B) and expected structure of liquid-crystalline phase (C and D).

4. Conclusion

The present study has clearly demonstrated the validity of fluorescence spectroscopy to explore the microscopic structure of liquid crystal systems, if the mesogen is emissive. Excimer as well as monomer emissions were observed in nEGMC and the structure of the excimer was assumed to be different in the homologues, which in turn was expected to provide an insight into the microscopic structure of liquid-crystalline phases. There are so many methods to characterize the macroscopic structure of liquid crystals like differential scanning calorimetry and polarizing microscopy, however, very few are available to investigate the microscopic ordering of mesogens in liquid crystal systems: only X-ray diffraction has been employed exclusively. Since for the excimer formation the ground state morphology of the relevant chromophores plays an important roll, the investigation of the intrinsic excimer in liquid crystals will enable us to explore in detail the microscopic ordering of mesogens, which is difficult to study by other methods.

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