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Spectroscopic study of non-amphiphilic 9-phenyl fluorene assembled in Langmuir–Blodgett films in two different matrices: dimer and excimer formation

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Abstract

Multilayered Langmuir–Blodgett (LB) films at different mole fractions of 9-phenyl fluorene (9PF) have been prepared using two different matrices viz. stearic acid (SA) and polymethyl methacrylate (PMMA). The spectroscopic properties of the mixed LB films, solution and microcrystal have been compared using absorption, steady-state fluorescence, and excitation spectroscopy. The spectroscopic studies give evidence of formation of excimeric sites in 9PF–SA LB films, while formation of dimeric species along with the excimeric sites have been evidenced in case of 9PF–PMMA LB films.
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1. Introduction

The potential applications of the ultrathin films by the Langmuir–Blodgett (LB) technology have stimulated research with a wide variety of materials. Non-amphiphilic molecules are not ideally suited for thin film deposition by this technique. However, recent studies [1–15] suggest that high quality LB films of these materials can be formed, when a long chain fatty acid or some polymer matrix is used as supporting medium. The spectroscopic properties of such films are quite similar to their amphiphilic counterparts. In LB film, it is expected to observe new aspects of photophysical process of electronically excited molecules. Because of multilayers and by mixing with such molecules, it might show configurational behavior quite different from those of homogeneous solutions or from the bulk.

Fluorene and its derivatives are well known as highly fluorescent compounds [16–18]. These molecules contain a rigidly planer biphenyl structure in the fluorene monomer unit with facile functionalization at the C-9 position offering the prospect of controlling physical properties [19]. Moreover, the remote substitution at C-9 position does not induce steric effects with the adjacent

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aromatic rings [20]. We have chosen the 9PF molecule because (a) fluorene molecule is known to form excimers in concentrated solutions [21,22], (b) a model for the excimer configuration has been proposed [22] and (c) transformation of the ground-state dimer to excimer takes place upon excitation of the origin band of the dimer [23].

In the present work, our goal is to investigate the spectroscopic behaviors of LB films of 9PF incorporated into two different types of matrices, and to compare them with the results in the solution and the microcrystalline phase. The matrices used in this work are polymethyl methacrylate (PMMA) polymer and stearic acid (SA). Those are chosen because they possess different dielectric constants giving various polar environments for the subject molecule and have been used by several researchers as supporting medium for making non-amphiphilic organic molecules LB compatible. Another reason for using two different matrices is that, those are predicted to have different inner spacing, which may change the conformation of the chromophores. Properties of the mixed LB films have been discussed in the light of UV–vis absorption, steady-state fluorescence, and excitation spectroscopic studies. These studies reveal that in the SA matrix, 9PF forms excimeric species along with the monomeric species, however, in the PMMA matrix, dimeric species is also formed along with the monomeric and excimeric species at certain mole fractions of 9PF.

2. Experimental

9PF purchased from Aldrich Chemical Company, USA (>99%) was used after sublimation followed by repeated recrystallization. SA (>99%), a Sigma product, USA, was used as received. Isotactic PMMA from Polyscience was used as received. The solvents ethanol (Merck, Germany) and chloroform (SRL, India) used are of spectral grade. The purity of the sample was checked by absorption and emission spectroscopy before use. For PMMA, the molecular weight of one monomer unit was taken as standard. A commercially available alternate layer LB trough (Joyce–Loebl, Model 4, UK) was used for isotherm measurements and film depositions. After a delay of 15 min, to allow the solvent to evaporate, the film at the air–water interface was slowly compressed for the measurements of isotherms at room temperature (23 °C). The barrier compression rate was 2×10^{-3} molecule^{-1} s^{-1}. The accuracy of the system under the conditions in which the measurements were performed, was 0.5 mN/m for surface pressure. Y-type deposition of the LB films of 9PF mixed with SA as well as PMMA have been obtained at dipping speed of 5 mm/min at the surface pressure of 15 mN/m. Since PMMA monolayer is no longer stable at higher surface pressure, we have chosen 15 mN/m as slandered surface pressure for lifting the LB film in both matrices. A drying time of 15 min was allowed after each lift. All the LB films were transferred onto the quartz slides. For each mole fraction of 9PF, 10 bilayer of the LB films were deposited. The transfer ratio was found to be 0.95 ± 0.02. Details of the experimental procedure and the instruments used were discussed elsewhere [13]. All the measurements were performed at room temperature (23 °C).

3. Results and discussion

3.1. Absorption spectra

Fig. 1a shows the absorption spectra at room temperature of the mixed LB films at different mole fractions of 9PF (0.2–0.7 M) in SA matrix along with the spectra in ethanol solution and in microcrystal for comparison. The absorption spectrum of 9PF in ethanol solution shows distinct and intense band systems in 200–315 nm region having 0–0 band at about 305 nm, which is in excellent agreement with the reported data [24]. The origin of 0–0 band is attributed to the $^1A_1 \rightarrow {}^1B_2$ transition according to mother fluorene molecule [25]. The microcrystal absorption spectrum shows fairly quenched and broadened band system in comparison to the solution spectrum. Moreover, the intense band that appears at ~260 nm in solution spectra is almost disappeared in the microcrystal spectrum.

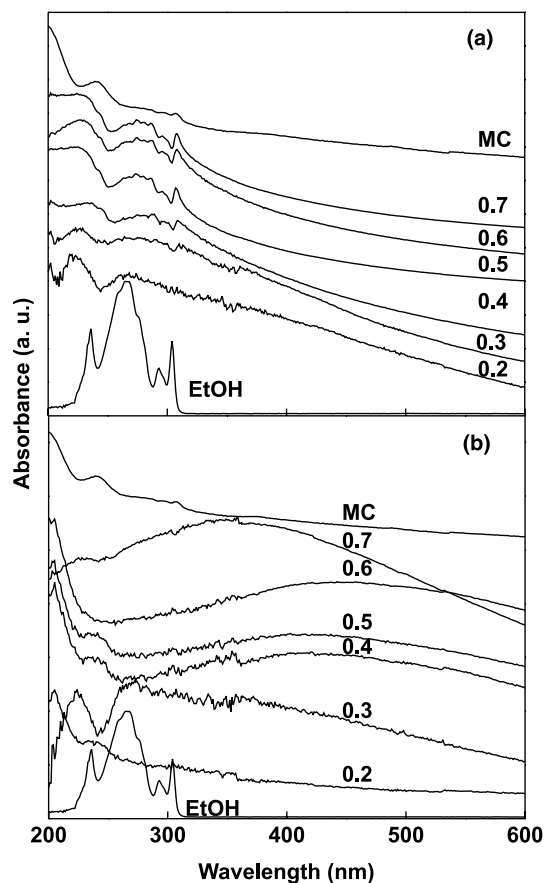The absorption spectra of the mixed LB films at various mole fractions of 9PF (0.2–0.7 M) in SA

Fig. 1. Steady-state absorption spectra of 9PF in ethanol solution (EtOH), microcrystal (MC), and mixed LB films with (a) SA and (b) PMMA. The numbers denote the corresponding mole fractions of 9PF in SA/PMMA matrix LB films.

matrix are also shown in Fig. 1a. At all concentrations of the mixed LB films, the bands are broadened and quenched. Moreover, the broad and intense band at ∼260 nm is sufficiently quenched.

Fig. 1b shows the absorption spectra of the mixed LB films at various mole fractions of 9PF (0.2–0.7 M) in PMMA matrix along with the ethanol solution and microcrystal spectra. The most interesting feature is that in the mixed LB film spectra in PMMA matrix, unlike that in the SA matrix, a broad low intense band is developed in 350–550 nm region. Dissolving the mixed film in the ethanol solution reproduces the solution spectrum, confirms that the broad band is not due

to the formation of any exciplex or impurities. The other possibility is that this broad band may originate due to the formation of dimeric sites in the LB films. The formation of the dimeric sites has been confirmed in the discussion of excitation spectra later.

3.2. Fluorescence spectra

Fig. 2a shows the steady-state fluorescence spectra of mixed LB films of 9PF (0.2–0.7 M) mixed with SA along with the spectra in the ethanol solution and microcrystal for comparison. The solution spectrum shows an intense band
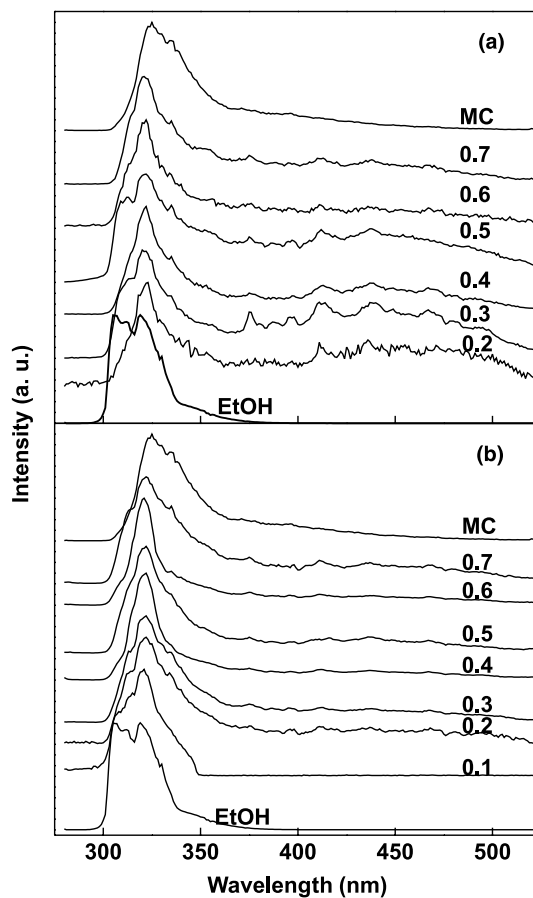

Fig. 2. Emission spectra of 9PF in ethanol solution (EtOH), microcrystal (MC), and mixed LB films with (a) SA and (b) PMMA. The numbers denote the corresponding mole fractions of 9PF in SA/PMMA matrix LB films.

system in 300–350 nm region with the 0–0 band at ~306 nm and the other band at ~320 nm, respectively. The spectrum is in good agreement with that published by Berlman [26]. The fluorescence spectrum of 9PF microcrystal shows that the high-energy band at ~306 nm of the solution spectrum is completely absent and a broad band at ~320 nm increases considerably.

The spectra of mixed LB films of 9PF (0.2–0.7 M) in SA matrix also have distinct similarity with the microcrystal spectrum. However, for all mole fractions of 9PF, the high-energy band is not totally absent, although the intensity is considerably reduced. The high-energy band is appeared as a hump in the LB film spectra of 9PF mixed with SA. The absence of high-energy band in microcrystal and the quenching of high-energy band in mixed LB films has been observed in some other molecules and has been explained in terms of aggregation induced reabsorption effect [11]. However, with the simultaneous quenching of the high energy band, a new structureless emission band appears in the 350–525 nm region to the red side of the monomer fluorescence spectrum. This broad featureless low intense band was not observed in case of microcrystal or in solution spectrum. In this context, it is relevant to mention that this phenomenon was first observed in pyrene solution by Förster [27] and was explained as due to transitory complex formation between the ground and the excited state molecules. With the increase of mole fraction of 9PF in SA matrix, the gradual transition to such excimer band is not observed in LB films in our case. In order to verify whether the broad band is due to the formation of excimer or due to aggregate, we have checked the excitation spectrum when monitoring emission at positions 320 and 450 nm, respectively. In both cases, the excitation spectra are identical and closely resemble the absorption spectrum of the monomer. This suggests that the broad band emission in the lower energy side of the spectrum is not due to aggregate but of excimeric origin. In fact, the excimer formation of fluorene molecule with increasing the concentration has been observed [28]. A model of formation of excimeric aggregates using semi-empirical molecular orbital method has been proposed [22], in which two fluorene molecules are in

parallel and displaced configuration, being atop one another but displaced from perfect superposition. The calculated near-zero oscillator strength ($f < 10^{-2}$) predicts that the excimer emission should be weak. This may be the reason for the low intense excimeric emission in case of 9PF–SA LB films. Excimeric emission of 9PF in SA matrix, incorporated in well-known restricted geometry of LB film, is quite possible since it may favor the formation of excimeric sites in the 9PF–SA LB films.

Fig. 2b shows the fluorescence spectra of LB films of 9PF (0.1–0.7 M) in PMMA matrix along with the solution spectra in ethanol and microcrystal. The observed fluorescence spectra of the LB films of 9PF in PMMA matrix exhibit all the spectral features of fluorescence originated from 9PF–SA LB films and the broad band profile in the higher wavelength region is evident. However, the intensity of the low-energy broadband profile is quite low in comparison to the SA matrix. This suggests that the energy of the monomer level of 9PF in both the matrices, are similar. However, the low energy band in 9PF–PMMA LB film cannot be assigned to excimeric origin as discussed in Section 3.3.

3.3. Excitation spectra

The excitation spectra of 9PF in ethanol solution monitored at its emission maxima give rise to structured spectrum (Fig. 3) and is in good agreement with the absorption spectrum. 9PF microcrystal excitation spectrum monitoring at its emission maxima also has distinct similarity with the microcrystal absorption spectrum. The excitation spectra taken for different mole fractions (0.2–0.7 M) of 9PF in SA matrix LB films are also shown in Fig. 3. The excitation spectra have been recorded by monitoring the emission at 320 nm (Fig. 3a) and 450 nm (Fig. 3b), respectively. These spectra are found to be identical irrespective of the monitoring wavelength. It may be concluded that, the low intense broad profile in the lower energy region at around 450 nm in the fluorescence spectrum of the mixed LB films of 9PF–SA, is due to excimeric emission as the excitation spectra of the mixed LB films, monitoring at the two different
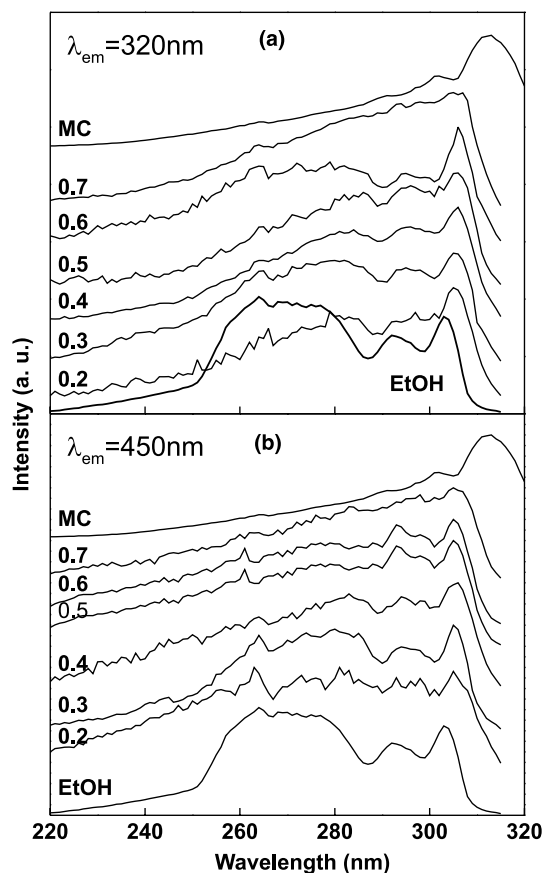
Fig. 3. Excitation spectra of 9PF in ethanol solution (EtOH) (λ_{em} = 320 nm), microcrystal (MC), and mixed LB films with SA. The numbers denote the corresponding mole fractions of 9PF in SA matrix LB film. (a) Emission monitored at 320 nm. (b) Emission monitored at 450 nm.

Fig. 4. Excitation spectra of 9PF in ethanol solution (EtOH) (λ_{em} = 320 nm), microcrystal (MC) and mixed LB films with PMMA. The numbers denote the corresponding mole fractions of 9PF in PMMA matrix LB film. (a) Emission monitored at 320 nm. (b) Emission monitored at 450 nm.

wave lengths (320 and 450 nm) give the same excitation pattern. This excimeric emission may originate due to the closer association of 9PF molecules in the microcrystalline sites in the mixed LB films in SA matrix.

Fig. 4 show the excitation spectra of 9PF–PMMA mixed LB films at different mole fractions of 9PF (0.1–0.7 M) along with the spectra in ethanol solution and 9PF microcrystal. The monitoring wavelengths for the PMMA mixed LB films (320 nm (Fig. 4a); 450 nm (Fig. 4b)) are same as SA mixed LB films, respectively. The most interesting feature in case of the excitation spectra in PMMA matrix is that, unlike that in 9PF–SA LB
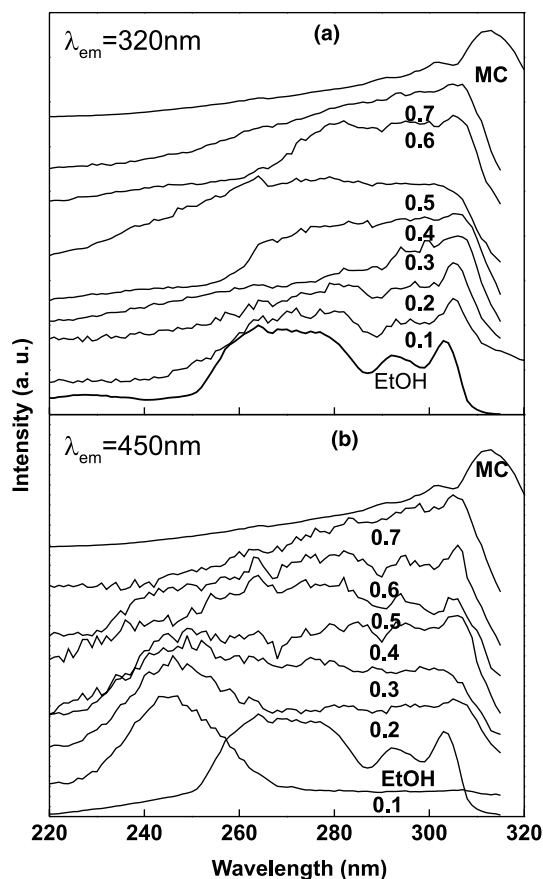
films, the excitation spectra at low mole fraction of 9PF are different when monitoring at the two different positions at 320 and 450 nm. However, at higher mole fractions of 0.6 M and above, the excitation spectra monitoring at different wavelengths are almost same. It may be mentioned in this context that the absorption spectra of 9PF–PMMA mixed LB films were different from 9PF–SA absorption spectra. The absorption spectra of 9PF–PMMA mixed LB films have broad band profile at the longer wavelength side of the spectrum. The most plausible explanation about this difference in the excitation spectra is that the low intense broad band in the longer wavelength side

of the fluorescence spectra of the mixed LB films in PMMA matrix is not only due to the formation of excimeric sites, rather some dimeric sites are also formed. At low mole fraction of 9PF, dimeric sites dominate over excimeric sites, which results in the difference of excitation spectra monitoring at two different wavelengths. At higher mole fractions of 9PF, formation of excimeric sites predominates over dimeric sites. It may be mentioned that in case of fluorene [29], the dimers have the structure of a parallel-displaced sandwich type and closely packed. Such structures, held together by weak van der Walls (vdW) interactions [30]. However, the corresponding vdW geometry may vary from dimer to dimer and photoexcited vdW dimers exhibit excimer formation through structural rearrangement. Therefore, it may be concluded from the combined results that, in SA matrix, 9PF form excimeric site only along with the monomeric site whereas, in PMMA matrix, along with the monomeric site, there is a mixture of excimeric and dimeric species. This may be due to different inner spacings and different polar environment of two different matrices, which may change the conformation of 9PF in the mixed LB films. Depending on the mole fraction of 9PF, the ratio of dimeric and excimeric species varies in PMMA matrix.

4. Conclusion

In conclusion, LB films of non-amphiphilic 9PF molecules mixed with SA as well as also PMMA at different mole fractions of 9PF have been successfully transferred onto quartz substrate. The absorption spectra of the mixed LB films of 9PF–SA have distinct similarity with the microcrystal spectra. Whereas the absorption spectroscopic study shows anomalous result in the mixed LB films of 9PF in PMMA matrix. Steady-state fluorescence and excitation spectroscopic study gives evidence of formation of excimeric sites in the mixed LB films of 9PF–SA while formation of dimeric species along with the excimeric sites have been evidenced in case of PMMA matrix. The combined result suggests that beside the polarity effect there may exist environmental effects of the different matrices by their confined inner spaces

that could change significantly the conformational changes of 9PF molecules.

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