Langmuir–Blodgett films of \( p \)-terphenyl in different matrices: Evidence of dual excimer

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Abstract

Langmuir–Blodgett (LB) films at different mole fractions of \( p \)-terphenyl have been prepared using two different matrices, viz., stearic acid (SA) and polymethyl methacrylate (PMMA). Multilayered LB films have been formed by changing various LB parameters namely, mole fraction of mixing, changing the number of layers as well as also the different surface pressure of lifting. The spectroscopic characteristics of mixed LB films, solution and microcrystal have been compared using UV–vis absorption and steady state fluorescence spectroscopy. Change of planarity of TP molecules are occurred while going from solution to solid states/films. Fluorescence spectra of the mixed LB films reveal intense excimeric emission in the mixed LB films with \( D_1 \) excimer peak at 397 nm and \( D_2 \) excimer peak at 412 nm. Various LB parameters namely changing the number of layers as well as the different surface pressure of lifting played important roles in the formation of dual excimeric sites in the mixed LB films.

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1. Introduction

The photophysical characteristics of polyphenyls have been extensively studied and continue to be an interesting area of research owing to the many subtle aspects exhibited by them. The extensive applications of polyphenyls as laser dyes and of their derivatives as excellent liquid crystalline materials\(^1\) make them potentially important for various technological applications. The electronic states of polyphenyls are the functions of the dihedral angles between the benzene rings. Parameters like temperature, pressure, electric and magnetic fields, which affect the dihedral angles between the benzene rings, also affect their luminescence spectra. The electronic states of the molecules are also likely to be affected by the microenvironment of the restricted geometry. Incorporation of these molecules into the well-known restricted geometry of Langmuir–Blodgett (LB) films may reveal some new information about the molecular organizations and may yield some interesting results, suitable for various technical applications.

In this paper, we report the detailed investigations of the Langmuir–Blodgett films of a well-known non-amphiphilic polyphenyl molecule, viz., \( p \)-terphenyl (TP), a highly fluorescent laser dye. A preliminary work of the Langmuir–Blodgett films of TP mixed with stearic acid (SA) has been reported\(^2\). The miscibility characteristics of TP mixed with some liquid crystalline material have also been reported\(^3\). However, various interesting properties of the molecules, viz., liquid crystalline\(^1\), non-linear optical properties\(^4\), etc. and their applications to industry and various optoelectronic devices make TP an attractive material and compel us to study in detail the photophysical characteristics of TP molecules in LB films by changing parameters and matrices. The most interesting feature of our observation is that at very low mole fractions of TP in mixed LB films of both stearic acid (SA) and polymethyl methacrylate (PMMA) matrices, an intense longer wavelength band system is generated in fluorescence spectra which is neither observed in solution spectrum nor in microcrystal spectrum.

2. Experimental

\( p \)-Terphenyl (98% pure) purchased from Aldrich Chemical Co., USA was purified under vacuum sublimation followed by repeated re-crystallization before use. SA (purity > 99%)

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Purchased from Sigma Chemical Company and isotactic PMMA from Polyscience were used as received. Spectroscopic grade Chloroform (SRL, India) was used as solvent and its purity was checked by fluorescence spectroscopy before use. Langmuir–Blodgett (LB) film deposition instrument (Apex-2000C, India) was used for the study of isotherm characteristics as well as for multilayer film deposition. Surface pressure at the air–water interface was monitored using a Wilhelmy plate attached to a microbalance, whose output was interfaced to a microcomputer, which controlled the movement of the barrier. Triple distilled deionised water was used as subphase and the temperature was maintained at 24°C. Solutions of TP, PMMA, SA as well as TP-PMMA and TP–SA mixtures at different mole fractions were prepared in chloroform solvent and were spread on the water surface.

After a delay of 15 min, to evaporate the solvent, the film at the air water interface was compressed slowly at the rate of $2 \times 10^{-3} \text{nm}^2 \text{mol}^{-1} \text{s}^{-1}$ to record the surface pressure versus area per molecule ($\pi–A$) isotherm. 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 TP mixed with PMMA as well as SA have been obtained at a 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 standard surface pressure for lifting the LB film in both the matrices. A drying time of 15 min was allowed after each lift. All the LB films were transferred onto quartz slides. For each mole fraction of TP, 10 bilayers (that is 10 layers on each side of the substrate) of the LB films were deposited. We have also studied the characteristics of LB films of TP lifted at different pressures and varying the number of layers.

The transfer ratio of the mixed layer was found to be 0.97 ± 0.02. Fluorescence spectra and UV–vis absorption spectra of the LB films were studied by a Perkin-Elmer LS-55 spectrophotometer and Perkin-Elmer Lambda 25 spectrophotometer, respectively.

3. Results and discussion

3.1. Spectroscopic characterizations

Fig. 1(a) and (b) show UV–vis absorption and steady state fluorescence spectra of mixed LB films of TP in PMMA and SA matrices at different mole fractions of TP along with their respective solution and microcrystal spectra.

It is observed that the solution absorption spectrum in the 200–325 nm region has a distinct broad and structureless band with peak at around 280 nm and is in agreement with the literature reported elsewhere [5]. This band has been assigned to $1_{\text{La}}$ state [5]. Also a weak hump is observed at about 240 nm in the solution absorption spectrum. The microcrystal absorption spectrum shows an overall broadening of the band system with respect to the solution spectrum having its high-energy band at 229 nm along with a broad low intense band in the longer wavelength region with diffused vibrational peaks at 261, 275 and 285 nm, respectively, which are almost indistinguishable in absorption spectra of LB films. The absorption spectra of

![Fig. 1. (a) UV–vis absorption and steady state fluorescence spectra of TP in chloroform solution (CHCl₃), in microcrystal (MC) and in TP/PMMA mixed LB films. The numbers denote the corresponding mole fractions of TP in PMMA matrix. (b) UV–vis absorption and steady state fluorescence spectra of TP in chloroform solution (CHCl₃), in microcrystal (MC) and in TP–SA mixed LB films. The numbers denote the corresponding mole fractions of TP in SA matrix.](image-url)
mixed LB films for both matrices show almost similar band profile and have distinct similarity with the microcrystal absorption spectrum with high-energy band at around 233 nm and a broad low intense band in the longer wavelength region with peak at around 290 nm. The weak hump at 240 nm in solution absorption spectrum give rise to the intense prominent high-energy band at around 233 nm in the LB films. Moreover, all the absorption bands in the LB films are overall broadened. This may be due to the change of planarity of TP molecules due to the organization in the mixed LB films when goes from solution to films/solid states.

It may be mentioned in this context that the absorption spectra of TP in γ-CD is red shifted and broadened and has been discussed as due to the formation of interacting couples of TP molecules in the ground state [6], this leads to the formation of excimer [7] in the γ-CD cavity.

Steady state fluorescence spectrum in chloroform solution is shown in Fig. 1(a) and (b). The striking wavelength is 275 nm. This spectrum shows distinct vibrational bands in 325–400 nm region with 0–0 band at 329 nm and another prominent peak at 341 nm along with a weak hump at around 357 nm and can be analyzed in terms of ring stretching vibration of TP [8,9]. The deviation from the mirror symmetry between the emission and absorption spectra, as well as the large gap between their origins, have been explained by several authors [9–11] considering the non-planar ground state S0 and rigid planar first excited state S1.

The high-energy band at 329 nm in solution spectrum is totally absent in the fluorescence spectra of mixed LB films and in the microcrystal also. The disappearance of this high-energy band may result from a change of planarity of TP molecules from solution to solid phase as suggested by Xie et. al. [12]. It is interesting to note that the quenching of high-energy band with increasing temperature has also been observed and explained by several authors in terms of phase transition [13], due to change of planarity. It has been confirmed that TP molecules are twisted in solution phase but are planar in crystal/solid state at room temperature [2]. The crystal structure of TP at room temperature is monoclinic and the molecule is planar. At low temperature the central phenyl ring is twisted by 20° from the plane of the molecule and the molecule becomes non-planar. As a result, the high-energy region of fluorescence spectrum is eliminated while going from solution to solid states.

The microcrystal fluorescence spectrum has intense bands at 351 and 366 nm and weak humps at 386 and 407 nm. The fluorescence spectra of mixed LB films in PMMA and SA matrices are also shown in Fig. 1(a) and (b). The most interesting thing observed in the fluorescence spectra of mixed LB films is that at very low mole fractions of 0.1–0.4 M in PMMA matrix and 0.1 M in SA matrix, longer wavelength intense bands with peaks at 397 and 412 nm are observed along with the higher-energy bands. The higher-energy bands are prominent in SA matrix with two intense peaks at 352 and 368 nm along with a weak hump at 337 nm. This higher-energy band system is somewhat diffused at very low mole fractions of TP in PMMA matrix. With increasing mole fractions, the longer wavelength bands become gradually reduced in intensity and higher-energy bands become prominent and at higher mole fraction of 8 M the mixed LB films fluorescence spectra have distinct similarity with the microcrystal spectrum. The presence of intense longer wavelength bands at low mole fractions in the mixed LB films in both the matrices can be readily expressed as due to the deformation produced in the electronic states of TP molecules when incorporated into LB films.

It should be mentioned in this context that TP in the presence of γ-CD solution gives structureless broad excimer like emission and by time-resolved spectroscopic study it has been confirmed that this broad structureless band consists of dual excimeric emission namely D1 excimer occurs with peak at 390 nm and D2 excimer with peak at 408 nm [7].

The most interesting thing in our observation is that these two excimer bands have been distinctly observed at the lower mole fraction of TP in the mixed LB films. However, at higher mole fraction these two bands overlap and specially at and above 0.6 M of TP in PMMA matrix this two bands overlap and give broad excimer pattern as has been observed in the γ-CD solution by Pistolis [7].

The dual excimer emission of various fluorophores has been frequently observed not only in organized media in dilute solutions [6,14] but also in the crystalline state [15,16]. Without exceptions, the low energy component has been assigned to a ‘normal’ excimer with a sandwich-type arrangement of aromatic moieties, whereas the higher-energy component has been attributed to a partially overlapped pair of fluorophores.

In the mixed LB films, in both the matrices, at lower mole fractions of TP, due to the presence of large number of matrix molecules, repulsive interaction predominates between unlike components, as a result, the TP molecules are sandwiched among SA chains or PMMA molecules and partial or total overlapping of the aromatic moieties of TP molecules occur.

However, with increasing concentration of TP molecules, attracting interaction between the like components increases which resulted in the formation of stacking of TP molecules and this order of stacking of TP molecules does not favour the partial or total overlapping of aromatic moieties. This resulted in the decrease of excimer intensity. This is evidenced, as at higher mole fractions of TP, in the mixed LB films, higher-energy bands increase in intensity.

3.2. Layer effect

By increasing number of layers, multilayered thick LB films can be made. These thick films are required for various technical applications. Therefore, investigations on the change in photophysical characteristics of LB films with thickness are immensely necessary. Here we have studied the photophysical characteristics of different multilayered LB films in both PMMA and SA matrices at two different mole fractions of 0.1 and 0.5 M.

Figs. 2(a) and (b) and 3(a) and (b) show the UV–vis absorption and steady state fluorescence spectra of mixed LB films at two different mole fractions of 0.1 and 0.5 M in two different matrices PMMA and SA, respectively. From the figures, no appreciable change in the UV–vis absorption spectra is observed in all the mixed LB films. However, interesting change is observed in the fluorescence spectra. At very low mole
Fig. 2. (a) UV–vis absorption and steady state fluorescence spectra of different layered mixed LB films of TP in PMMA matrix at MF = 0.1 of TP. The numbers denote the corresponding layers. (b) UV–vis absorption and steady state fluorescence spectra of different layered mixed LB films of TP in PMMA matrix at MF = 0.5 of TP. The numbers denote the corresponding layers.

Fig. 3. (a) UV–vis absorption and steady state fluorescence spectra of different layered mixed LB films of TP in SA matrix at MF = 0.1 of TP. The numbers denote the corresponding layers. (b) UV–vis absorption and steady state fluorescence spectra of different layered mixed LB films of TP in SA matrix at MF = 0.5 of TP. The numbers denote the corresponding layers.
fraction of 0.1 M of TP in both PMMA and SA matrices (Figs. 2(a) and 3(a)), when the number of layer is small namely 05 and 10 layers, two distinct band systems in the longer wavelength region are observed. Longer wavelength band system has intense and prominent peaks at 397 and 412 nm. The higher-energy band system is somewhat diffused in PMMA matrix but have prominent and distinct high-energy peaks at 352 and 369 nm along with a weak hump at around 336 nm. Moreover, at these lower number of layers, the longer wavelength band system is more intense than that of higher-energy band system. With increasing number of layers in both the matrices, the higher-energy band system becomes gradually increase in intensity than that of longer wavelength band system. At large number of layers of 20 and 25 bilayers, longer wavelength band system becomes sufficiently reduced to weak humps and higher-energy band systems become prominent.

When the mixed LB films have TP concentration of 0.5 M, then in PMMA matrix [Fig. 2(b)] same thing is happened with intense longer wavelength band system and reduced higher-energy band system at lower number of layers and at higher number of layers longer wavelength band system reduced almost to weak humps. However, at 0.5 M of TP in SA matrix, longer wavelength band system always appears as weak hump even at very thin five layers (that is five monolayers on each side of the substrate) LB film [Fig. 3(b)].

It has been discussed earlier that the longer wavelength band with peaks at 397 and 412 nm originate due to the formation of D1 and D2 types of excimer. At lower number of layers due to the presence of smaller amount of TP molecules in the mixed LB films, they may get favourable condition for formation of excimeric sites. However, with increasing number of layers TP molecules may diffuse through the SA matrix and may get stacked to form microcrystalline aggregates. As a result at large number of layers fluorescence spectra of the mixed LB films is the reminiscent of microcrystal fluorescence spectrum.

3.3. Pressure effect

Photophysical characteristics of organized molecular assemblies in LB films can be manipulated with ease by changing various parameters. Here, we present our observations of the change in the spectral characteristics of 10-layered mixed LB films lifted at various surface pressures. We used only SA matrix since PMMA matrix is not suitable at higher surface pressure [8]. Fig. 4(a) and (b) shows the UV–vis absorption and steady state fluorescence spectra of mixed LB films of TP at two different mole fractions of 0.1 and 0.5 M, respectively. All the films are 10-bilayered and lifted at 15, 20, 25 and 30 mN/m surface pressures. No appreciable change is observed in the UV–vis absorption spectra of all the LB films lifted at various surface pressures, however, fluorescence spectra of TP–SA mixed LB films at 0.1 M of TP shows interesting change with increasing pressure [Fig. 4(a)]. In the films lifted at lower surface pressure of 15 mN/m, two distinct band systems with almost equal intensities and prominent peaks are observed. With increasing surface pressure, the longer wavelength excimeric band system becomes gradually reduced in intensity and ultimately reduces to weak humps.

Fig. 4. (a) UV–vis absorption and steady state fluorescence spectra of TP–SA mixed LB films at different surface pressure of lifting at MF = 0.1 of TP. The numbers denote the corresponding surface pressure of lifting. (b) UV–vis absorption and steady state fluorescence spectra of TP–SA mixed LB films at different surface pressure of lifting at MF = 0.5 of TP. The numbers denote the corresponding surface pressure of lifting.
However, at 0.5 M of TP–SA mixed LB films, no appreciable change is observed in the band system with increasing pressure [Fig. 4(b)]. In this case, longer wavelength excimeric band system always gives sufficiently reduced spectral profile with weak humps.

As already mentioned earlier that at lower concentration of TP molecules in the mixed LB films, excimer sites predominates, with increasing surface pressure, concentration of TP molecules increases as a result stacking of microcrystalline TP occurs resulted in the lowering of excimeric sites.

Therefore, we may definitely conclude that the excimeric sites in the mixed LB films mainly predominate at the lower mole fraction of TP and also at lower surface pressure.

4. Conclusion

In conclusion, LB films of non-amphiphilic TP molecules mixed with SA as well as PMMA at different mole fraction of TP have been successfully transferred onto quartz substrate.

Change of planarity of TP molecules are occurred while going from solution to films/solid states. Fluorescence spectra of mixed LB films of TP in both the matrices of SA and PMMA at different mole fractions reveal the formation of dual excimeric sites with $D_1$ excimer at 397 nm and $D_2$ excimer at 412 nm. Changing the number of layers as well as the pressure of lifting play important role in the formation of excimer species of TP molecules in the mixed LB films in both PMMA and SA matrices.

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