Spectroscopic characterizations of non-amphiphilic 2-(4-biphenylyl)-6-phenyl benzoxazole molecules at the air–water interface and in Langmuir–Blodgett films

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Abstract

This communication reports about the successful incorporation of a well-known non-amphiphilic derivative of oxazole chromophore 2-(4-biphenylyl)-6-phenyl benzoxazole abbreviated as PBBO, in Langmuir–Blodgett films when mixed with stearic acid (SA) as well as also an inert polymer matrix polymethylmethacrylate (PMMA). The surface pressure versus area per molecule isotherms of the Langmuir films of PBBO mixed with PMMA or SA at different mole fractions reveal that the area per molecule decreases consistently with increasing mole fractions of PBBO. Area per molecule versus mole fraction curve shows that the experimental data points coincide with the ideality curve predicted by the additivity rule, which leads to the conclusion of either ideal mixing or complete demixing of the binary components. The UV-vis absorption and fluorescence spectroscopic studies of mixed LB films of PBBO reveal the nature of complete demixing of the binary components of the sample molecules (PBBO) and PMMA or SA molecules. This complete demixing leads to the formation of clusters and aggregates of PBBO molecules in Langmuir and Langmuir–Blodgett films. J-type aggregates of PBBO molecules in LB films have been confirmed by UV-vis absorption spectroscopic study. Aggregation of PBBO molecules in LB films giving rise to excimeric emission has been demonstrated by fluorescence spectroscopic study. Excitation spectroscopic study clearly confirmed the presence of excimeric sites.

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1. Introduction

The films obtained by successive transfer [1,2] of insoluble monolayers from a liquid onto a solid surface upon application of an external force (constant deposition pressure and substrate
dipping speed) have been referred to as Langmuir–Blodgett (LB) films [3,4]. Recently these ultrathin Langmuir–Blodgett (LB) films of organized molecular assemblies containing specific photofunctional groups or chromophores are considered to be extremely important for nanotechnology-based optoelectronic and photonic devices and have been the subject of active research in recent years [5–14]. Perhaps, the most interesting feature associated with LB films which makes them attractive for these photonic devices is the ability to control the spatial distribution and orientation of molecules assembled in these films, to bring about desired changes [15,16] in their optical and electronic properties. Interestingly, LB supramolecular assemblies closely resemble natural biomembranes and provide a unique platform for mimicking energy and electron transfer reactions in real energy-harvesting photosynthetic reaction centers [17–20]. Advantages of both charged and neutral lipid mixed LB films of micro-heterogeneous media for control of photophysical processes, chemical reactions and tailoring of charged transfer complexes or π electron arrays [21–23], are their well-defined composition, flexibility, anisotropic nature and possibility of polarity modulation. Lipid based supramolecular assemblies may be organized as multilamellar or tubular micro-structure [24,25] as well as in non-lamellar inverted hexagonal or cubic packings. As host structures, lipid/water phases possess a high capacity to encapsulate various water soluble species among which fluorescent and chemiluminescent dyes have been studied [26,27]. Moreover, the photophysical properties of molecules incorporated in these supramolecular assemblies show enormous changes, which reflect the interaction of the molecules with their microenvironment providing an insight into the structure–property co-relationship in these systems. Non-amphiphilic molecules are not ideally suited for thin film deposition by this technique. However recent studies [28–31] suggest that high quality LB films of these materials can be formed, when a long chain fatty acid or some suitable inert polymer matrix is used as a supporting medium. The spectroscopic properties of such films are quite similar to their amphiphilic counterparts, especially with regard to their spectroscopic and aggregating properties. These similarities justify the study of non-amphiphilic compounds in mixed LB films since they may be readily put to large scale applications that are cost effective, compared to their amphiphilic counterparts.

The current study is focused on a well-known oxazole derivative 2-(4-biphenyl)-6-phenyl benzoxazole abbreviated as PBBO. Molecular structure of PBBO is shown in Fig. 1. The dimension of this molecule, while considering this as a linear chain is about 1 nm. However, in the actual structure as shown in the Aldrich catalog there is slight bending of the molecule and hence the dimension of the actual molecular structure should be less than 1 nm. Generally the five-member ring oxazole chromophore does not emit fluorescence however when oxazole chromophore is attached to one or more phenyl rings, strong fluorescence emission occurs [32]. Oxazole derivatives are characterized by their intense fluorescence and are used in light emitting diodes, solar energy concentrators and in thin film electro-luminescent devices [33,34]. They are also used as ultra fast optical amplitude limit material and UV-laser dye due to their non-linear transmission property [35]. Despite such interesting properties, photophysical characterization of non-amphiphilic PBBO molecules mixed with SA and PMMA have never been studied in Langmuir–Blodgett films.

Here we have studied the monolayer characteristics of PBBO mixed with stearic acid (SA) as well as with isotactic polymethylmethacrylate (PMMA) at the air–water interface. Properties of mixed LB films have been discussed in the light of UV-vis absorption and fluorescence spectroscopy and

![Molecular structure of 2-(4-biphenyl)-6-phenyl benzoxazole (PBBO).](image-url)
compared with the results in solution and microcrystalline phase. The two different supporting matrices, namely fatty acid and polymer, are used because they possess different dielectric constant giving various polar environments for the subject molecules. Another reason for using two different matrices is that these are predicted to have different inner spacing, which may change the conformation of the chromophore.

2. Experimental

PBBO purchased from Aldrich chemical company, USA and vacuumed sublimed followed by repeated recrystallization before use. SA (purity > 99%) from Sigma, USA and isotactic PMMA from Polyscience were used as received. The solvents chloroform (SRL, India) and ethanol (E. Merck, Germany) are of spectral grade and their fluorescence spectra were checked before use. A commercially available Langmuir–Blodgett film deposition instrument (Apex, 2000C, India) was used for isotherm measurements and for multilayer film deposition. The subphase used was triple distilled deionised water. The pH of the sub-phase was 6.5 and the temperature was 24°C. Solutions of PBBO, PMMA, SA as well as PBBO–PMMA and PBBO–SA mixtures at different mole fractions are prepared in chloroform solvent and were spread on the sub-phase. After a delay of 15 min to allow the solvent to evaporate the film was slowly compressed for the measurement of isotherm at ambient temperature. The barrier compression rate was $2 \times 10^{-3}$ nm$^2$ mole$^{-1}$ s$^{-1}$. Surface pressure measurement was recorded using Wilhelmy plate arrangement as described elsewhere [28]. All isotherms were run several times with freshly prepared solutions. Deposition of multilayers was achieved by allowing the substrate to dip with a speed of 5 mm/min with a drying time of 15 min after each lift. Fluorescence grade quartz slides were used for spectroscopic measurement. For each mole fraction of PBBO, 10 bi-layer (both sides of quartz plate) LB films were deposited. We have chosen 15 mN/m as the standard surface pressure for lifting the LB films for both matrices.

The transfer ratio was found to be $0.98 \pm 0.02$. Fluorescence spectra and UV-vis absorption spectra were recorded by a Perkin Elmer LS 55 spectrophotometer and Perkin Elmer Lambda 25 spectrophotometer, respectively. All the measurements were performed at room temperature (24°C).

3. Results and discussions

3.1. Behaviour of Langmuir monolayer at the air–water interface

When dilute solution of PBBO in chloroform was spread onto a pure water surface and compressed very slowly, the surface pressure did not rise above 20 mN/m and no distinct steep region was observed in the isotherm curve. Addition of large amount of solution resulted in the formation of crystalline domains at the air-water interface, which were visible to the naked eye. Moreover, the islets once formed as a result of barrier compression did not degenerate at the molecular level but remained as smaller islets upon relaxation of surface pressure. Repeated attempt to transfer the floating layer onto solid substrate was failed. However, when PBBO was mixed with a supporting matrix of either SA or PMMA, the floating layer was found to be highly stable and could be transferred onto quartz substrate.

The surface pressure versus area per molecule ($\pi$–$A$) isotherm characteristics of pure PBBO, PMMA or SA as well as of PBBO–PMMA and PBBO–SA mixed monolayers at the air–water interface are shown in Fig. 2(a) and (b), respectively. The area per molecule of pure PBBO is found to be negligibly small in comparison to the actual planar area for the molecule as predicted by the space-filling-model. This indicates that pure PBBO molecules do not form monolayer at the air–water interface but form multilayers or aggregates of pure PBBO.

However on mixing PBBO with the supporting matrix PMMA or SA, in different mole fractions, a stable, floating compressible monolayer is obtained.

In pure PMMA isotherm, there exists certain distinct parts [36]. The ‘transition’ observed at
about 8 mN/m is characteristic for the isotherm of PMMA. The isotherm of PMMA also shows an inflection point at about 20 mN/m, but above this surface pressure, the monolayer remains no longer stable. From the isotherms of the mixed monolayer, it is also observed that with increasing mole fraction of PBBO, the inflection portion gradually loses their distinction and at 0.6 and above mole fractions of PBBO, the mixed isotherms show steep rising up to 30 mN/m surface pressure without any transition point.

It is also interesting to note that at higher surface pressure, in PMMA matrix, the isotherms of all molefractions of PBBO almost coincide. It happens because at higher surface pressure the monolayer, which consists of PMMA matrix, no longer remain stable [36] and actually collapsing of monolayer occurs and multilayer and three-dimensional crystalline aggregates are formed at the air–water interface. Thus at higher surface pressure all the isotherms of mixed monolayers in PMMA matrix lose their distinguishability and overlap on each other.

The isotherm characteristics of pure SA as well as the mixed SA–PBBO films are shown in Fig. 2(b). The areas per molecule are 0.23 and 0.21 nm² for pure SA at the surface pressure 15 and 25 mN/m, respectively. With increasing mole fractions of PBBO, the area per molecule of the mixed isotherms of SA–PBBO decrease systematically and even at higher mole fraction, they do not coincide.

It may be mentioned in this context that the thermodynamic nature of the mixing of various

Fig. 2. (a) Surface pressure (π) versus area per molecule (A) isotherms of PBBO in PMMA matrix at different mole fractions of PBBO. The numbers denote corresponding mole fractions of PBBO in PMMA matrix. PM and BO are the pure PMMA and PBBO isotherms, respectively. The inset shows area per molecule versus mole fraction plot at surface pressure 15 mN/m (solid line indicates ideality: data taken from isotherm value). (b) Surface pressure (π) versus area per molecule (A) isotherms of PBBO in SA matrix at different mole fractions of PBBO. The numbers denote corresponding mole fractions of PBBO in SA matrix. SA and BO are the pure SA and PBBO isotherms, respectively. The inset shows area per molecule versus mole fraction plot at surface pressure 15 mN/m (solid line indicates ideality: data taken from isotherm value).
two component systems was established by analyzing the \( \pi - A \) isotherm of the pure components as well as the binary mixtures [37]. The excess areas of mixing \( A^E \), which provides a measure of non-ideality, were calculated as a function of surface pressure, mixture of composition and the molecular weight using the additivity rule [38–40]

\[
A^E = A_{12} - A_{av},
\]

\[
A_{av} = N_1 A_1 + N_2 A_2,
\]

where \( A_{12} \) is the actual area per molecule of mixed monolayer, \( A_{av} \) is the calculated average area per molecule of mixture, assuming molefraction additivity, \( A_1 \) and \( A_2 \) are the area per molecule (or monomer) of each of the single component at a specific surface pressure, \( N_1 \) and \( N_2 \) are their corresponding molefractions.

The insets of Fig. 2(a) and (b) show the plot of the data of the actual area \( (A_{12}) \) per molecule versus molefraction of PBBO in the mixed monolayer with PMMA and SA respectively, at the air–water interface and at a surface pressure of 15 mN/m. The solid lines in the figures represent the ideality curve that corresponds to the plot of average area per molecule \( (A_{av}) \) of the mixture versus molefraction, assuming molefraction additivity.

The experimental data in case of both PMMA and SA matrices almost coincide with the ideality curve. That is from Eqs. (1) and (2) we may say that \( A^E = 0 \) and

\[
A_{12} = A_{av} = N_1 A_1 + N_2 A_2.
\]

It should be mentioned in this context that for binary mixture of molecules exhibiting either ideal miscibility or complete immiscibility, \( A^E = 0 \), which is our case. It is important to note that in bulk binary miscible mixtures if two liquids are ideally miscible, it usually means that they are physically and chemically similar, so that the intermolecular forces of these two components are identical and the presence of the solute does not affect the solvent molecules. However, complete immiscibility means strong attractive interactions among like molecules and almost no interaction between the unlike molecules [37]. The existence of strong attractive interaction among PBBO molecules may lead to the formation of clusters and aggregates.

Although from this additivity characteristics study, we cannot say definitely whether complete mixing or demixing occurs in the monolayer, however our later studies of UV-vis absorption and fluorescence spectroscopic characteristics definitely conclude that complete demixing of molecules occur which lead to the formation of aggregates of PBBO molecules.

3.2. Absorption spectroscopic study

The absorption spectra of the mixed LB films of PBBO in two different matrices PMMA and SA at different mole fractions of PBBO, together with the spectra in ethanol solution and PBBO microcrystal are shown in Fig. 3a and b, respectively. The solution absorption spectrum in the 200–400 nm region shows distinct (0–0) band at 328 nm, a broad and weak hump which extends from 250–290 nm and an intense, prominent high energy band with a peak at 205 nm. The microcrystal absorption spectrum shows an overall broadening of the band system having a broad and weak band at around 287 nm and another high energy band at around 241 nm. The LB film absorption spectra at various mole fractions of PBBO in both matrices are almost similar to microcrystal spectra having identical peak position and broadened spectral profile with respect to the solution spectrum. However it is also observed that there is an extremely weak hump at around 365 nm, which is somehow observable in case of 0.5–0.7 molefractions of PBBO–PMMA mixed LB films and existence of this band has been confirmed by excitation spectroscopic study. In comparison with the solution spectrum, it is evident that the 328 nm intense band in solution spectrum is red shifted to 365 nm and becomes extremely weak, which is somehow visible in certain mole fractions of PBBO–PMMA mixed LB films. The weak and broadened hump in 250–290 nm region and the high energy intense band with peak at around 205 nm in solution spectrum are red shifted to give intense prominent bands with peak at around 287 and 241 nm, respectively, in the LB films and microcrystal
spectra. Moreover all the absorption bands in LB films are overall broadened. Although only the broadening in the spectra cannot be assigned solely to aggregation of molecules in general, the red shift and broadening observed in the mixed LB films are likely to originate due to aggregate.

It is relevant to mention in this context that according to the intermediate strength exciton coupling theory [41,42], dipole–dipole interaction results in the raising or lowering of the exciton band to a position either energetically higher or lower than the monomer band. Such a change in energy is given by

$$\Delta E = \frac{2M^2(1 - 3 \cos^2 \theta)(1 - 1/N)}{r^3},$$

where $M$ is the dipole moment vector, $N$ is the number of monomers in the aggregate, $\theta$ is the angle between the dipole moment of the molecule and $r$, the vector joining the centers of two dipoles. When $0^\circ < \theta < 54.7^\circ$, the exciton band is energetically located below the monomeric band that causes a red shift and the corresponding aggregates are referred to as the J-aggregates [43], while for $54.7^\circ < \theta < 90^\circ$, the exciton band is located energetically above the monomeric band that causes a blue shift and the corresponding aggregates are referred to as H-aggregate [43]. Corresponding to the magic angle $\theta = 54.7^\circ$, no shift in the absorption spectrum is observed and corresponding aggregates are referred to as I-aggregate.

The broadening of the absorption bands accompanied with a red shift in the LB film of PBBO, seems to be due to the formation of J-aggregates.

It may be mentioned in this context that certain rigid nearly planar plate like molecular structure as pyrene [44] or rod like molecule as anthracene [45] form aggregate in the mixed LB films. These molecules are actually sandwiched among the matrix molecules (stearic acid) to form aggregates.

Fig. 3. (a) UV-vis absorption spectra of PBBO in ethanol solution (EtOH), in microcrystal (MC) and in PBBO–PMMA mixed LB films. The numbers denote corresponding mole fractions of PBBO in PMMA matrix. (b) UV-vis absorption spectra of PBBO in ethanol solution (EtOH), in microcrystal (MC) and in PBBO–SA mixed LB films. The numbers denote corresponding mole fractions of PBBO in SA matrix.
in the LB films and actually partial or total binary demixing is occurred in the LB films. In the present work the oxazole derivative PBBO has almost linear rod like structure. For aggregation to be occurred in the mixed LB films of PBBO molecules, the most possibility is the sandwich of PBBO molecules within SA or PMMA molecules in the LB films. A schematic representation of molecular organization is shown in Fig. 4.

3.3. Fluorescence spectroscopic study

In Fig. 5a and b, we have plotted the fluorescence spectra of PBBO in PMMA and SA matrices at different mole fractions of PBBO together with the fluorescence spectra in ethanol solution and of PBBO microcrystal. The fluorescence spectrum of PBBO in ethanol solution (1 × 10⁻⁵ M) shows a broad band in the 350–550 nm region having intense peak (0–0 band) at around 398 nm and an overlapping hump at around 380 nm. The fluorescence spectrum of PBBO microcrystal is somewhat different from the solution spectrum. The high energy hump at 380 nm is totally absent in the microcrystal spectrum having its (0–0) band at about 411 nm and an overall broadened spectral profile is observed.

Fig. 5a shows also the fluorescence spectra of the mixed LB films at different mole fractions of
PBBO (0.1–0.7 M of PBBO) in PMMA matrix. Up to 0.6 mole fraction of PBBO in PMMA matrix, the LB films spectra have weak but prominent high energy band at about 380 nm. The intensity of this high energy band is considerably reduced above 0.6 mole fraction of mixed LB films in PMMA matrix and also in PBBO microcrystal spectra. Moreover the intense band in the solution spectrum (peak at 398 nm) is well resolved into two vibrational peaks at about 398 and 419 nm. With increasing mole fractions, the vibrational bands are gradually diffused and at 0.7 mole fraction of PBBO in mixed LB films of PBBO–PMMA, an overall broadened band is observed. However still at that mole fraction, the high energy band at 380 nm is prominent. In microcrystal spectrum, no high energy band at 380 nm is observed. Moreover a broad spectrum profile is observed.

Fig. 5b shows the fluorescence spectra of the mixed LB films of PBBO-SA at different mole fractions of PBBO (0.1–0.7 M of PBBO).

Here also it is observed that the high energy band at 380 nm is present in all the LB films. Another interesting thing is that unlike that of PMMA mixed LB films, here the broad band profile does not consist of any prominent vibrational structure. In this case the fluorescence spectra have distinct similarity with the microcrystal spectrum.

3.4. Excitation spectra

The excitation spectrum of PBBO in ethanol solution, monitored at its emission maximum (380 nm) gives rise to broad spectrum (Figs. 6 and 7) and is in good agreement with the absorption spectrum. Microcrystal excitation spectra monitoring at two different wavelengths at 380 and 415 nm, show almost the same spectral profile, however these spectra are somewhat different from their absorption counterpart. The existence of
longer wavelength band at around 365 nm has been confirmed in the microcrystal excitation spectra. The other bands are somewhat different.

The excitation spectra of the mixed LB films of PBBO–PMMA in different mole fractions, and monitoring at two different wavelengths of 380 and 415 nm, are shown in Fig. 6a and b, respectively. The excitation spectra are almost similar irrespective of the monitoring wavelength, indicating that both bands originate from the same kind of species of PBBO molecules. In these cases, the 365 nm band is prominent unlike that of absorption spectra. Moreover the excitation spectra give broadened band profile and there may be some difference in the relative intensity distribution among various bands. However the excitation spectra support the various band positions of the absorption spectra. For all these spectra, we observe broadening and change in intensity pattern in comparison to dilute solution spectrum that might be due to the closer association of the molecules. The excitation spectra resemble the same while monitoring at the high energy band and longer wavelength position. This certainly gives the conclusion that the broadband spectral profile of the emission spectrum originates due to the formation of excimer.

It may be mentioned in this context that excimeric emission from short oxazole derivatives have also been observed when they are incorporated into constrained media such as cyclodextrines [46]. Well-known oxadiazole derivative Bu-PBD was also observed to emit excimeric emission when organized in LB films [47]. LB films of some other molecules as pyrene [44] anthracene [45] chromophores and their derivatives [48,29] etc. also give rise to excimeric emission in the longer wavelength region and is an indication of aggregation for such molecules in the LB films.

4. Conclusion

In summary, non-amphiphilic PBBO mixed with PMMA or SA form excellent monolayers at the air–water interface. Isotherm studies as well as area per molecule versus mole fraction study of PBBO indicate either ideal mixing or complete

![Excitation spectra of PBBO](image_url)
demixing of the binary components. The UV-vis absorption study of the mixed LB films of PBBO reveal the nature of complete demixing of the binary components of the sample molecules PBBO and PMMA or SA which leads to the formation of clusters or aggregates. Fluorescence spectroscopic studies show that excimer emission occurs from the microcrystalline aggregates of PBBO. Excitation spectroscopic study confirms the formation of only excimeric sites.

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