Chapter 8

Behavior of two Liquid Crystals doped in Langmuir-Blodgett Film of arachidic acid
**Abstract**

Mono and multi-layer films of two liquid crystals namely (4'-fluorophenylazo) phenyl-4-yl 3-[N-(4'-n-hexadecyloxy-2-hydroxy-benzylidene) amino]-2-methyl benzoate (16F) and (4'-cyanophenylazo) phenyl-4-yl 3-[N-(4'-n-hexadecyloxy-2-hydroxy-benzylidene) amino]-2-methyl benzoate (16CN) with and without long chain fatty acid arachidic acid (AA) have been prepared by Langmuir-Blodgett technique. The behavior of Langmuir films of pure 16F and 16CN and their mixtures with AA have been studied with surface pressure-area isotherms. LB films of pure 16F and 16CN and their mixtures with AA were characterized UV-Vis absorption spectroscopy and atomic force microscopy (AFM).
8.1: Introduction:
Organic Light emitting diode (OLED) is a flat light emitting technology, used to make ultra-thin large and small area flat panel flexible self-luminous displays and lighting. As OLEDs emit light they do not require a backlight and so are thinner and more efficient than LCD displays. Generally, OLED are thin film multilayer structures composed of a hole transport layer, an emissive electroluminescent organic thin layer and an electron transport layer [1-3]. In this case the essential requirements for a good organic layer are as follows: (a) Efficient luminescer (b) Good charge transporter (c) Capability of efficient charge transfer to an electrode. The transport of charge carriers in organic compounds will be favored by increasing order of molecules. Liquid crystalline (LC) materials possess the ability to self-organize spontaneously into highly ordered structures thereby help to enhance the mobility of charge carriers significantly. Further, LC materials possessing highly anisotropic flow and curvature elastic properties are ideal for the manufacture of uniform thin films with anisotropic optical properties. All these unique properties of LC materials make them attractive for application as an active material or host material for use in organic LEDs [4-6]. Fabrication of ultrathin monomolecular thick films (layers) by the Langmuir-Blodgett (LB) technique [7-9] is a simple and unique method that provides flexibility in controlling spatial distribution and the orientation of the molecules in these films. Some years ago Stapff et al. proposed to use LB technique in order to obtain active layers in OLEDs [4]. Although there are some reports on the feasibility of the formation of LB films containing liquid crystals [10-13], there is no study on two new fluorescent liquid crystals 16-F and 16-CN.

The aim of this work is the characterization of two liquid crystals 16-F and 16-CN at the air-water and air-solid interfaces. This study also highlights the difference observed in their photochemical/photophysical behavior.

8.2: Experimental:

The molecular structures of 16F, 16CN (are shown in fig.8.1) and AA used in this work. 16F and 16CN were synthesized in the laboratory and AA was purchased from Aldrich Chemical Company (U.S.A.). Teflon-bar-barrier type LB trough (model 2007DC, Apex Instruments Co., India) was used for studying the behavior of the pure monolayer of 16F and
16CN and mixed monolayer of 16F/AA and 16CN/AA at the air-water (A-W) interface. Deposition of the mono- and multi-layers of pure and mixed Langmuir-Blodgett films on quartz slides/silicon wafer was also performed with same LB trough. The subphase used throughout this study was double distilled water. All the measurements were performed at room temperature (24°C). Quartz slides cleaned by leaving them overnight in chromic acid were subsequently boiled in concentrated nitric acid to remove all the traces of organic material and then washed with distilled water, dried and stored in a vacuum oven till use. Surface pressure isotherms of pure monolayer of 16F, 16CN and AA were obtained by spreading 150µl solutions of 16F, 16CN and AA (concentration 0.5mg/ml) in chloroform on the air water interface. Surface pressure isotherms of mixed monolayers of 16F/AA and 16CN/AA were obtained by spreading the chloroform solution of 16F/16CN and AA mixed in a predetermined ratio. After evaporation of the solvent, the film at the (A-W) interface was compressed very slowly at a rate of about $5 \times 10^{-3}$ nm$^2$ mol$^{-1}$ sec$^{-1}$ and a Wilhemy plate was used for measuring the surface pressure at (A-W) interface. Data was acquired by a DELL computer interfaced to Wilhemy balance that also controlled the compressing barrier maintaining the constant pressure of subphase with an accuracy of 0.1mN/m. Y-type deposition of the LB films of 16F/16CN mixed with on quartz slides have been obtained at dipping speed of 5 mm/min at the surface pressure of 15 mN/m. A drying time of 15 minutes were allowed after each lift. For each mole-fraction of 16F/16CN, LB films of 10 bi-layers were deposited. The transfer ratios were found to be 0.96 ± 0.01.

UV-Vis absorption and emission spectra of 16F and 16CN solutions in quartz cell, microcrystal, pure 16F, 16CN and mixed LB films of 16F/AA and 16CN/AA on quartz slides were recorded by a Perkin Elmer Lamda 25 absorption spectrophotometer. Surface morphology of pure AA, pure 16F, 16CN and mixed monolayer films were studied by an AFM (Innova, Bruker Inc., USA). The AFM images were captured in tapping mode under ambient atmosphere.
Figure 8.1: (a) 16-F: (4'-fluorophenylazo) phenyl-4-y1 3-[N-(4'-n-hexadecyloxy-2-hydroxy-benzylidene) amino]-2-methyl benzoate, Mol. Wt : 697.921

8.1(b) 16-CN: (4'-cyanophenylazo) phenyl-4-y1 3-[N-(4'-n-hexadecyloxy-2-hydroxy-benzylidene) amino]-2-methyl benzoate, Mol wt =700.9
8.3: Monolayer characteristics at air-water interface:

Figure 8.2: (a) Surface pressure ($\pi$) versus area per molecule (A) isotherms of 16CN in arachidic acid (AA) matrix at different concentrations of 16CN along with pure 16CN and AA. The numbers 1, 2, 3, 4, 6 & 8 denote the increasing concentrations of 16CN in AA.

8.2(b) Surface pressure ($\pi$) versus area per molecule (A) isotherms of 16F in arachidic acid (AA) matrix at different concentrations of 16F along with pure 16F and AA. The numbers 1, 2, 3, 4, 6 & 8 denote the increasing concentrations of 16F in AA.
Figure 8.2a shows the isotherms for pure AA, pure 16CN and the mixed monolayer systems of AA/16CN with various concentrations. The abscissas of these figures represent the area of Langmuir film divided by the total number of the molecules, \( N = N_{16-CN} + N_{AA} \), where \( N_{16-CN} \) and \( N_{AA} \) are respectively, the numbers of 16CN and AA molecules. The pure 16CN isotherm shows a rise of surface pressure up to 50mN/m. The isotherm of pure AA is consistent with the result reported in the literature [14]. The straight line of pure AA isotherm reveals that surface pressure increases rapidly and a transition point exists at a pressure of about 27 mN/m which indicates the liquid to solid transition point. At this stage molecules are densely packed and the surface is no longer compressible. The pure AA isotherm gives a limiting area of 0.23 nm\(^2\), which is reasonable; since long-chain fatty acid molecules occupy an average molecular area of 0.21 nm\(^2\) when they stand vertically on water. The incorporation of 16CN molecules in the mixed monolayer with AA is confirmed by the changes in the liftoff point. The transition point observed in the pure AA isotherm is found to change with the increase in mole fraction of 16CN and becomes less prominent for higher mole fraction. Such behavior indicates that 16CN is successfully incorporated in mixed monolayer system.

The isotherm of pure 16F shown in the fig.8.2b shows a higher surface pressure (70mN/m) in comparison to 16CN. Although the isotherm of mixed monolayer of AA/16F have similarity with pure AA for lower mole fraction (0.1), the isotherms for other higher mole fractions such as 0.2, 0.3, 0.4, 0.6 and 0.8 show a shape that practically corresponds to the combination of those of the individual components (AA and 16F), even though some difference could be observed. The compressibility coefficients of the both the mixed Langmuir films were calculated using the expression.

\[
C_s = -\frac{1}{A} \left( \frac{\partial A}{\partial \pi} \right)_T
\]
The variation of $|C_s|$ with surface area (A) obtained from the isotherms of AA monolayer, pure 16F monolayer, (AA/16F) mixed monolayer are shown in the fig.8.3. The maximum $|C_s|$ value of AA/16F and AA/16CN mixed monolayers is more than pure AA monolayer indicating a better packing of the 16F/16CN molecules compared to that of pure AA monolayer. Thus the addition of liquid crystals makes the films more rigid.

![Surface pressure versus compressibility plot for pure AA, AA+16F and AA+16CN.](image)

**Figure 8.3:** Surface pressure versus compressibility plot for pure AA, AA+16F and AA+16CN.

### 8.4: Miscibility study:

The miscibility analysis in the Langmuir monolayer is important to know the basic interactions involved among the liquid crystal and fatty acid molecules. To illuminate the mixing behavior of the binary components in the mixed Langmuir monolayer, the average area per molecule is plotted as a function of the film composition at different surface pressures.

For complete miscibility or complete immiscibility, the law of additivity of areas [15] is given by,

$$A_{ideal} = A_1 N_1 + A_2 N_2 \quad \text{-------- (1)}$$

where $A_{ideal}$ is the idea area per molecule, $N_1$ and $N_2$ are the mole fractions of the constituents molecules of the mixed monolayer, $A_1$ and $A_2$ are the area per molecules
(monomer) of single component at a fixed surface pressure. The deviation from the ideal behavior can be found by computing the excess area of mixing $A_E$:

$$A_E = A_{12} - A_{ideal} \quad \text{(2)}.$$ 

Where $A_{12}$ is the experimentally observed area per molecule of the mixed monolayer.

The excess or deficit of area $A_E$ provides information about the nature of interactions that occurs among the constituents molecules of the mixed monolayer. If the components are completely immiscible, then $A_E$ will be zero and therefore a plot between $A_E$ versus $N_1$ will be a straight line. Any deviation from the straight line either positive or negative will indicate miscibility or non-ideality.

![Figure 8.4](image_url) (a) Plot of area/ molecule versus mole fraction for mixed 16CN/AA monolayers on water subphase at various surface pressures.
8.4(b) Plot of area/ molecule versus mole fraction for mixed 16F/AA monolayers on water subphase at various surface pressures.

Figures 8.4a and b show the respective plots of area per molecule versus mole fraction of 16CN/16F in AA matrix, at four different surface pressures, viz., 5, 10, 20 and 30 mN/m. In case of both the mixed systems, positive deviation from the ideality is observed indicating repulsive type of interaction is operative between the constituent components i.e., greater cohesive forces act between the like components. The phase separation triggers the formation of aggregates in the mixed films.

8.5: UV-Vis absorption spectroscopic study of pure 16F /16CN and mixed (16F-AA/16CN-AA) LB films:

The spectroscopic behavior of the pure 16F, mixed AA/16F film and pure 16CN, AA/16CN films are investigated in the light of UV-Vis absorption spectroscopy and the results are shown in the figures 8.5a and b respectively. For comparison we also show the absorption of the solution, microcrystal and LB film of pure 16F and 16CN. The changes of the spectroscopic behavior of mixed films with the increase in mole fraction are presented in the insets.
Figure 8.5: (a) UV-VIS absorption spectra of 16-F in chloroform solution (16F Sol), microcrystal (16F MC), pure 16F film and mixed LB film of 16F in AA matrix at a mole fraction of 0.4.

8.5 (b) UV-VIS absorption spectra of 16-CN in chloroform solution (16CN Sol), microcrystal (16CN MC), pure 16CN film and mixed LB film of 16CN in AA matrix at a mole fraction of 0.4.
16F solution shows prominent peak at about 335nm along with weak hump at 288nm. The absorption spectra of the LB films of pure 16F, 16F/AA mixed film and microcrystal film shows blue shift with expected changes in intensity and broadended spectra in comparison with the pure 16F solution spectrum. In case of fig 8.5(b) The solution absorption spectrum of 16CN shows distinct and intense band systems in the 265 to 395-nm region, with an intense and sharp monomeric band having peak at 340 nm and a weak hump at 284 nm, in addition, in the mixed film of 16CN/AA and pure 16CN film blue shift of about 22 nm is observed with respect to pure 16CN solution (prominent peak at 340 nm). Also, the absorption spectrum of 16CN microcrystal is found to be red-shifted by 25 nm in comparison with pure 16CN solution spectrum. These results clearly indicate the successful of transfer of 16F and 16CN with or without the fatty acid (AA) molecules. The blue shift of absorbance for LB films is probably due to aggregation and the nature of aggregation may be different from microcrystal. Inset 8.5a and 8.5b shows the UV-Vis absorption spectra of 16F/AA and 16CN/AA mixed LB films at different molefractions. It is observed that in both the figure with the increase of molefraction of 16F/16CN in the mixture of 16F-AA/16CN- AA, the intensity of the band profile is found to be increased monotonically.

8.6: Fluorescence study:

![Fluorescence spectrum](image)

Figure 8.6. (a) Emission spectrum of 16-F in microcrystal (16F MC), pure 16F film and mixed LB film of 16F in AA matrix at a mole fraction of 0.4 along with solution spectrum in chloroform (16F Sol) in inset.
(b) Emission spectrum of 16-CN in microcrystal (16CN MC), pure 16CN film and mixed LB film of 16CN in AA matrix at a mole fraction of 0.4 along with solution spectrum in chloroform (16CN Sol) in inset.

Figures 8.6a and b show the fluorescence spectra of 16F microcrystal, pure 16F film, mixed 16F-AA film and 16CN microcrystal, pure 16CN film, mixed 16CN-AA film respectively along with their solution spectra in the insets. The fluorescence spectrum of 16F solution shows two peaks at about 481 and 512 nm. The peak at 481 nm has been shifted to 367 nm in the pure 16F film, microcrystal and mixed AA/16F film. However, two main peaks are observed in the pure 16CN solution spectrum at 466 and 494 nm along with a weak hump at about 536 nm. The two peaks are shifted to 370 nm and 472 nm respectively in the microcrystal, pure 16CN film and mixed AA/16CN film with a slight variation. Such spectral behavior is an indication of special kind of orientation of the two liquid crystals on the solid substrate.
8.7: AFM Study:

Figure.8.7. (a) AFM of bare silicon wafer, (b) one layered pure 16F film (c) one layered mixed 16F-AA film.
The transferred LB monolayer film was observed by high resolution AFM. Figure 8.7 Panel a shows the bare silicon wafer for comparison with the other LB monolayer films. The panel b and d in fig. 8.7 represent the AFM images of the surface morphology of the pure 16F and pure 16CN monolayer film respectively. The aggregated domains of pure 16F pure 16CN molecules are clearly visible in the panel b and d. In case of mixed 16F-AA (shown in panel e) and 16CN-AA (Shown in Panel e) monolayer films, more compact and distinct aggregated domains are formed upon addition of liquid crystals.
8.8: Conclusions:

In summary, our work showed that

i. One can form the Langmuir monolayer of the liquid crystals 16F and 16CN at the air-water interface with or without any fatty acid and these monolayers could be transferred onto solid substrates using Langmuir-Blodgett deposition technique.

ii. The absorbance peak in pure 16F/16CN LB film and mixed films of 16F/16CN with AA is in shifted position in comparison to the pure sample solutions.

iii. Mixed LB monolayer films of AA with 16F/16CN is more compact than pure monolayer films of 16F/16CN.

iv. Aggregated domain structure is formed in the mixed films of 16F/16CN with AA.
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References


Chapter 9