

Spectroscopic Characterizations of Nonamphiphilic 5-(2-([3-(*Tert*-Butylamino)-2-Hydroxypropyl]Sulfanyl)- 1,3-Thiazol-4-Yl)Thiophene-2-Carboxamide Molecules At The Air-Water Interface And In Langmuir-Blodgett Films

S. Biswas^{*a}, B. Das^b and R. K. Nath^b

^aDepartment of Chemistry, Ramthakur College, Agartala-799003

^bDepartment of Chemistry, Tripura University, Suryamaninagar-799130, Tripura, INDIA

Abstract: The π -A isotherm and spectroscopic characterizations of mixed Langmuir and Langmuir-Blodgett films of a non-amphiphilic thiophene derivative, namely, 5-(2-([3-(*tert*-butylamino)-2-hydroxypropyl]sulfanyl)-1,3-thiazol-4-yl)thiophene-2-carboxamide (BHTC) molecules, mixed with polymethyl methacrylate (PMMA) and stearic acid (SA) has been reports in this communication. The π -A isotherms and molefraction versus area per molecule studies indicate some repulsive interaction between sample (BHTC) and matrix (PMMA or SA) molecules. At higher surface pressure in the SA mixed Langmuir monolayer, a of phase transition occurs, which has been revealed by π -A isotherm studies. UV-Vis absorption and fluorescence spectroscopic studies also reveal this phase transition and closer association of molecules. Spectroscopic studies of LB films lifted at higher surface pressure clearly confirm the presence of dimmers and higher order n-meric sites.

Key words: Nonamphiphilic, Langmuir-Blodgett films, UV-Vis absorption and fluorescence spectroscopy.

I. Introduction

Insoluble monolayer formed at the air-water interface upon application of an external force (surface pressure) is known as Langmuir monolayer. This monolayer can be transferred onto a solid substrate (namely quartz, glass, ITO glass etc.) to form mono and multilayered Langmuir-Blodgett (LB) films [1,2]. In recent years, various organic, polymeric, organometallic, bioactive compounds are being widely investigated for the fabrication of ultrathin films following Langmuir-Blodgett technique. These ultrathin LB films of organized molecular assemblies containing specific photofunctional groups or chromophores are considered to be extremely important in optoelectronic and photonic devices [3-12]. The ability to control the spatial distribution and orientation of molecules assembled in LB films makes them attractive for these photonic devices. Interestingly, LB supramolecular assemblies closely resembled naturally occurring biomembranes and provide a unique platform for mimicking energy and electron transfer reactions in real energy-harvesting photosynthetic reaction centre [13-16]. Lipid based supramolecular assemblies may be organized as multilamellar or tubular micro-structure as well as in non-lamellar inverted hexagonal or cubic packings as host structures [17,18]. Lipid/water phases cause a high capacity to encapsulate various water soluble species among which fluorescent and chemiluminescent dyes have been studied [19,20]. The photophysical characteristics of molecules incorporated in this 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.

Organic molecules which are nonamphiphilic in nature are not ideally suited for thin film deposition by this technique. However, recent studies [21-25] show that high quality LB films of these nonamphiphilic 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 counterpart, especially with regard to their spectroscopic and aggregating properties. These similarities have justified the study of nonamphiphilic materials in the mixed LB films as these compounds are available in bulk quantity and also cost effective compare to their amphiphilic counterparts.

Current work is focused on a thiophene derivative viz. 5-(2-([3-(*tert*-butylamino)-2-hydroxypropyl]sulfanyl)- 1,3-thiazol-4-yl)thiophene-2-carboxamide abbreviated as BHTC. Molecular structure of BHTC is shown in figure 1. BHTC has been widely used in optical electronic devices such as light emitting devices and solar cells [26-29]. Blend films of BHTC has been shown to provide a simple way of improving charge carrier transport into the film [30]. However, detailed photophysical studies of BHTC have never been studied in ultrathin films fabricated by LB technique.

Here we have studied the monolayer characteristics of BHTC mixed with stearic acid (SA) as well as with isotactic polymethyl methacrylate (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 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 constants giving various polar environments for the subject molecules. Another reason for using two different matrices is that they are predicted to have different inner spacing, which may change the conformation of the chromophore.

II. Materials and methods

BHTC purchased from Aldrich Chemical Company, USA and repeatedly recrystallized before use. SA (purity > 99%) from Sigma, USA and isotactic PMMA from Polyscience were used as received. Spectral grade chloroform (SRL, India) was used as solvent. Prior to the use of the solvent, its fluorescence spectrum was checked thoroughly. The Langmuir-Blodgett (LB) film deposition instrument (Apex, 2000C, India) was used for the study of isotherm and also for multilayer LB film deposition onto quartz substrates. Triple distilled deionized, Millipore water (pH 6.5 at 24°C and resistivity 18.2 MΩ cm) was used as subphase. Solutions of BHTC, PMMA, SA as well as BHTC-PMMA and BHTC-SA mixtures at different molefractions were prepared in chloroform solvent and were spread on the subphase. After allowing sufficient time to evaporate the solvent, the film was compressed slowly at the rate of $2 \times 10^{-3} \text{ nm}^2 \text{ mol}^{-1} \text{ s}^{-1}$. Surface pressure of the monolayer was recorded using Wilhelmy plate arrangement as described elsewhere [31]. All the isotherms were run several times with freshly prepared solutions. The deposition of multilayer was done by allowing a quartz substrate to dip with a speed of 5 mm/min with a drying time of 15 min after each lift. For each molefraction of BHTC, 10 bilayers (both sides of quartz plate) LB films were deposited. Mixed LB films of 5, 10, 15, 20 and 25 bilayers were also prepared to study the changes in photophysical characteristics with the change in thickness of the films. Pressure dependent studies were also performed by lifting mixed LB films of SA-BHTC at various surface pressures of 15, 20, 25 and 30 mN/m. However, for molefraction dependent studies, a standard surface pressure of 15 mN/m was chosen. The transfer ratio was found to be 0.98 ± 0.02 . UV-Vis absorption and steady state fluorescence spectra were recorded by a Perkin Elmer Lambda-25 spectrophotometer and Perkin Elmer LS-55 spectrophotometer respectively. All the measurements were performed at room temperature (24°C).

III. Results and discussions

Behaviour of Langmuir monolayer at the air-water interface:

When a dilute solution of pure BHTC in chloroform solvent was spread on the pure water surface of the Langmuir trough and compressed very slowly at the rate of $2 \times 10^{-3} \text{ nm}^2 \text{ mol}^{-1} \text{ s}^{-1}$, the surface pressure rise upto 40 mN/m. However, when this Langmuir monolayer of BHTC was tried to transfer onto a solid substrate to make LB film, a highly inhomogeneous and patchy film was observed. But, when BHTC was mixed with a building matrix of stearic acid (SA) or inert polymer matrix; namely Polymethyl methacrylate (PMMA), the floating monolayer was found to be highly stable and uniform deposition of multilayer LB film could be easily obtained. The surface pressure versus area per molecule (π -A) isotherm characteristics of pure BHTC, PMMA, SA as well as BHTC-PMMA and BHTC-SA mixed monolayers at the air-water interface are shown in figures 2(a) and 2(b) respectively. In pure PMMA isotherm there exists certain distinct parts [32]. The 'transition' observed at about 8 mN/m is characteristic for the isotherm of pure PMMA. PMMA isotherm also shows an inflection point at about 20 mN/m, and above this surface pressure, the monolayer remains no longer stable. The isotherms of the mixed monolayers of BHTC-PMMA at various molefraction of BHTC are also shown in figure 2(a). At very lower molefraction of 0.1 M of BHTC, an inflection point is also observed at about 20 mN/m. However, the inflection portion loses its distinction at and above 0.3 M of BHTC. Isotherm curves of 0.5 M of BHTC and above, give higher area per molecule than pure BHTC and pure PMMA. The inset of figure 2(a) shows the area per molecule versus molefraction curve at a surface pressure of 10 mN/m. From this curve it is observed that area per molecule of the mixed monolayer at all molefractions are much higher than the ideality curve (solid line). It definitely concludes that there are some repulsive interactions between BHTC and PMMA molecules resulting in an increase in area per molecule in the mixed monolayer. Figure 2(b) shows the surface pressure versus area per molecule isotherms of pure SA, BHTC and BHTC-SA mixed monolayer at various molefraction of BHTC. From these isotherm characteristic and also from the inset of figure 2(b), it is also evident that area per molecule increases in the mixed monolayer and definitely confirms that some repulsive interaction plays between BHTC and SA molecules in the mixed monolayer.

Another interesting thing to be observed from figure 2(b) is that, in the SA mixed monolayer at various molefractions of BHTC, there is an inflection point. This inflection point started at about 25 mN/m for higher molefraction of 0.7 M of BHTC and gradually increases to about 30 mN/m at 0.1 M of BHTC mixed monolayer. This inflection point definitely confirms the fact that there is some kind of phase transitions of BHTC molecules in the mixed monolayer at higher surface pressure. The changes in the photophysical characteristic due to this phase transition has been confirmed by UV-Vis absorption spectroscopic studies in the LB films fabricated at higher surface pressure and has been discussed in the later section of pressure effect.

UV-Vis absorption and steady state fluorescence Spectroscopic Study:

Figures 3(a) and 3(b) show the UV-Vis absorption and Steady State fluorescence spectra of the mixed LB films of BHTC (0.1 to 0.8 M) in PMMA and SA matrices respectively along with the spectra in chloroform solution and BHTC microcrystal for comparison. Absorption spectrum of BHTC in chloroform solution shows distinct bands within 225-425 nm region with high energy band having peak at 253 nm and a weak hump at 328 nm and a broad band with peak at 364 nm along with a 0-0 band at 399 nm. The absorption spectrum of BHTC microcrystal also consist of bands in the spectral region 200-425 nm and have distinct similarities with the solution absorption spectrum. However, the high energy bands are diffused and red shifted having a broad low energy overlapping band systems with peak at around 366 nm and a weak 0-0 band at about 415 nm. The LB films absorption spectra at different molefractions of BHTC in both PMMA and SA matrices are somewhat in between solution and microcrystal spectra. However, the interesting point to note is that the weak hump at 329 nm in the solution spectrum is prominent in the LB film spectra. It may be definitely concluded that actually the broad band system in the 300-375 nm spectral region actually consists of two different band systems. It may be noted in this context that in case of both PMMA and SA mixed LB films the broad band system has sharp peak at around 329 nm which actually corresponds to the weak hump in solution absorption spectrum at 329 nm. In microcrystal absorption spectrum, this broad band is shifted to around 360 nm. The overall differences in the intensity distribution of various band systems in the microcrystal, solution and mixed LB films absorption spectra clearly reveal that there are some specific type of organization of BHTC molecules in the LB films which leads to some kind of deformation in the electronic energy level.

The fluorescence spectrum of BHTC in chloroform solution (1×10^{-5} M) shows a structured band system in the 375-500 nm spectral regions with high energy 0-0 band at 410 nm along with 433 nm band and a weak and broad hump at 462 nm. A shift of about 10 nm of the 0-0 band in solution fluorescence spectrum in comparison to the solution absorption spectrum may be due to the little deformation produced in the electronic state of the molecule. In the microcrystal fluorescence spectrum, the high energy band at 410 nm is totally absent. The total quenching of this high energy band is due to the reabsorption effect owing to the formation of microcrystalline aggregates and has been observed in several other molecules [33]. The fluorescence spectra of the mixed LB films of BHTC in PMMA and SA matrices at different molefractions of BHTC have distinct similarities with the solution fluorescence spectrum with all the bands are prominently present. However, certain distinct features are observed in the mixed LB films. In the LB films all the vibrational bands are red shifted and broadened in comparison to the solution fluorescence spectrum. Moreover there are differences in the intensity distribution among various bands. This may be attributed due to reabsorption effect owing to the closer association of the molecule.

IV. Layer effect study

Various technical applications may sometime require thick films. Figures 4a and 4b shows UV-Vis absorption and fluorescence spectra of different layered mixed LB films of BHTC in PMMA and SA matrices respectively at two different molefractions of 0.1 and 0.5 M of BHTC.

The UV-Vis absorption spectra in SA mixed LB films show almost similar band pattern irrespective of layer number and molefraction of BHTC except small changes in intensity distribution. However, in case of PMMA mixed LB films some interesting thing is observed in UV-Vis absorption spectra. At higher number of layers an overlapping broad band is observed in the 300-400 nm region and especially at 25 layer and 0.5 M BHTC-PMMA mixed LB films, this broad band has intense peak at 314 nm. This intense peak may originate due to some changes in intensity distribution among the diffused overlapping band systems in 300-400 nm spectral region. This may occur due to some changes in electronic energy levels of BHTC in the mixed LB films of large number of layers. Another interesting point to note that in the fluorescence spectra of lower number of layer (5 layer) and 0.1 M molefraction of BHTC in the mixed LB films of both the matrices, show weak high energy band at 396 nm which is totally absent at higher number of layer (25 layer) and also at higher molefraction. In case of mixed LB films it may be concluded that with increasing layer number and thickness of LB films, molecular association may occur to a greater extent resulting in the disappearance of high energy band.

Pressure effect study:

The morphology of the crystal parameters of the LB films may be controlled by varying the surface pressure of lifting. Figure 5 shows the UV-Vis absorption and steady state fluorescence spectra of BHTC/SA mixed LB films at different surface pressure of lifting at molefractions 0.1 and 0.5 M of BHTC. Here we have studied the spectroscopic characteristics of the mixed LB films of BHTC in SA matrix at two different molefractions (0.1 and 0.5 M of BHTC) lifted at two different surface pressures of 15 mN/M and 30 mN/m. All the films are 10 bilayered. It is interesting to note that the absorption spectra of mixed LB films in both molefractions lifted at lower surface pressure of 15 mN/m shows the normal spectral profile in the 225-425 nm

region as discussed before. However, the LB films lifted at higher surface pressure of 30 mN/m show some interesting changes. The broad band in the 275-375 nm region becomes broadened having plateau in the peak region. This enormous broadening in the absorption band profile may be the result of certain kind of phase transition in BHTC molecules in the mixed LB films when subjected to higher surface pressure. This thesis of phase transition of BHTC molecules can get its support from the pressure area isotherm characteristics of BHTC molecules in the SA mixed Langmuir films at various molefractions as shown in figure 2b and discussed previously. This kind of phase transition may bring a favourable orientation of BHTC molecules resulting in the formation of closer association which may lead to the formation of dimer or higher order n-mers of BHTC molecules in the mixed LB films lifted at higher surface pressure.

V. Summary

In conclusion our result shows that non-amphiphilic BHTC molecules form an excellent Langmuir monolayer at the air-water interface when mixed with a building matrix of PMMA or SA. This Langmuir films can be easily transferred onto a quartz substrate to form mono and multi layered LB films. Isotherms as well as area per molecule versus molefraction studies of BHTC reveal that a repulsive interaction occurs between BHTC and PMMA/SA mixed monolayer. Moreover, some kind of phase transition of BHTC molecules has been observed in the SA mixed monolayer at higher surface pressure. UV-Vis absorption spectroscopic studies reveal that there are some specific types of organisation of molecules in the LB films. Fluorescence spectroscopic studies reveal that some reabsorption effect occurs due to closer association of molecules in the LB films. Phase transition in BHTC molecules in the SA mixed LB film occurs when the films are lifted at higher surface pressure. This phase transition brings a favourable orientation of BHTC molecules resulting in the formation of closer association and which leads to the formation of dimer and higher order n-mers of BHTC molecules in the SA mixed LB films.

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Figure captions:

Figure 1: Molecular structure of 5-(2-([3-(*tert*-butylamino)-2-hydroxypropyl]sulfanyl)-1,3-thiazol-4-yl)thiophene-2-carboxamide (BHTC).

Figure 2a: Surface pressure (π) versus area per molecule (A) isotherms of BHTC in PMMA matrix at different molefractions of BHTC. The numbers denote corresponding mole fractions of BHTC in PMMA matrix. The inset shows area per molecule versus mole fraction plot at surface pressure 10 mN/m (Solid line indicates ideality; data taken from isotherm value).

Figure 2b: Surface pressure (π) versus area per molecule (A) isotherms of BHTC in SA matrix at different molefractions of BHTC. The numbers denote corresponding mole fractions of BHTC in SA matrix. The inset shows area per molecule versus mole fraction plot at surface pressure 10 mN/m (Solid line indicates ideality; data taken from isotherm value).

Figure 3a: UV-Vis absorption and steady state fluorescence spectra of BHTC in chloroform solution (CHCl_3), in microcrystal (MC) and in BHTC/PMMA mixed LB films. The numbers denote the corresponding mole fractions of BHTC in PMMA matrix.

Figure 3b: UV-Vis absorption and steady state fluorescence spectra of BHTC in chloroform solution (CHCl_3), in microcrystal (MC) and in BHTC/SA mixed LB films. The numbers denote the corresponding mole fractions of BHTC in SA matrix.

Figure 4a: UV-Vis absorption and steady state fluorescence spectra of different layered mixed LB films of BHTC in PMMA matrix at MF=0.1 and 0.5 M of BHTC. The numbers denote the corresponding layers.

Figure 4b: UV-Vis absorption and steady state fluorescence spectra of different layered mixed LB films of BHTC in SA matrix at MF=0.1 and 0.5 M of BHTC. The numbers denote the corresponding layers.

Figure 5: UV-Vis absorption and steady state fluorescence spectra of BHTC/SA mixed LB films at different surface pressure of lifting at MF=0.1 and 0.5 M of BHTC. The numbers denote the corresponding surface pressure of lifting.

Figures:

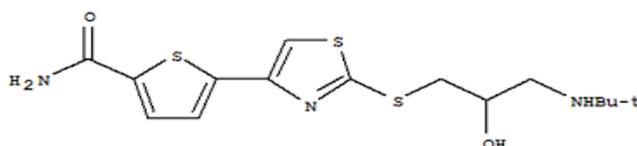


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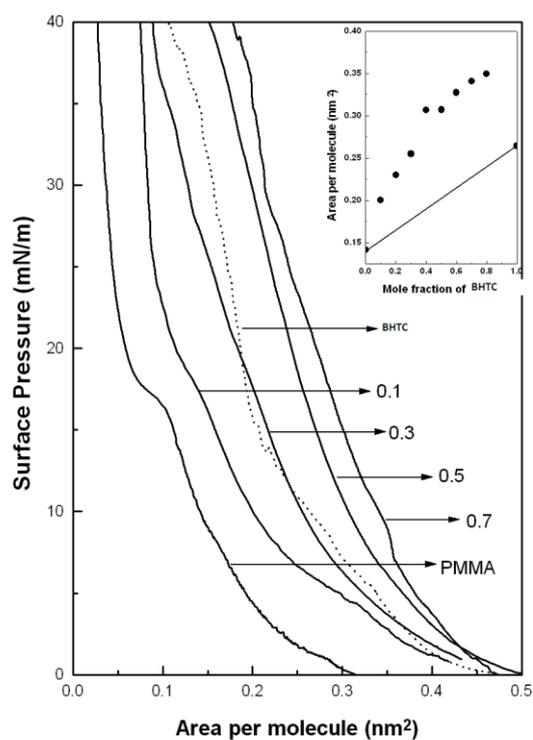


Fig: (2a): S. Biswas et.al

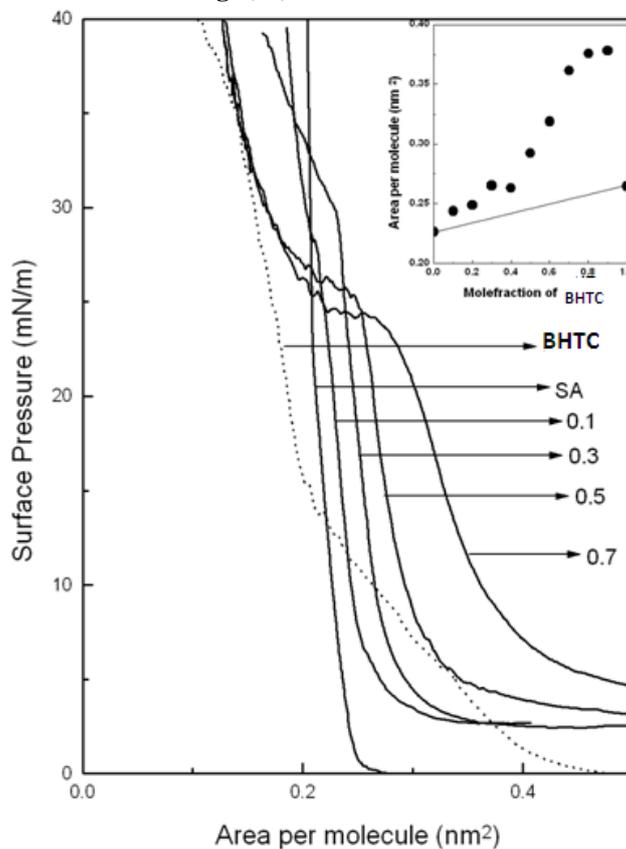


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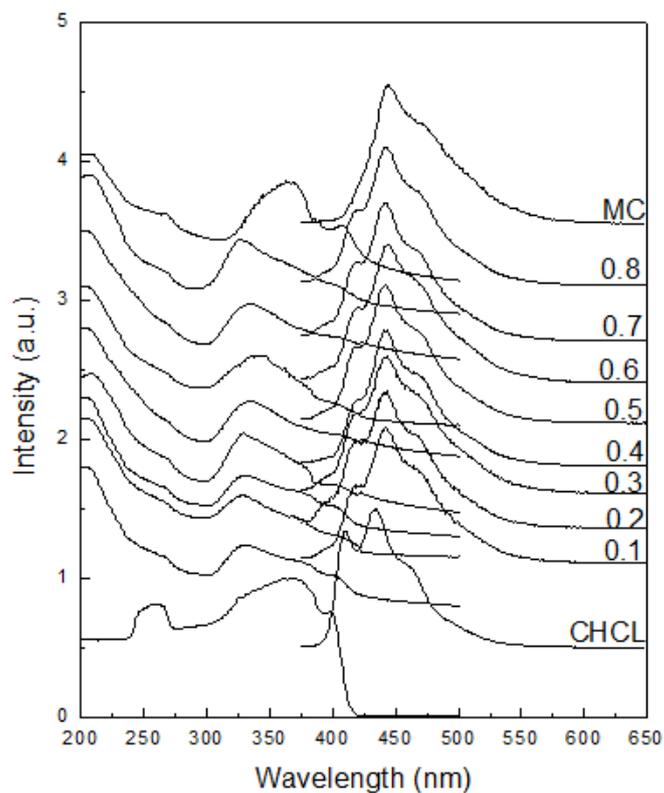


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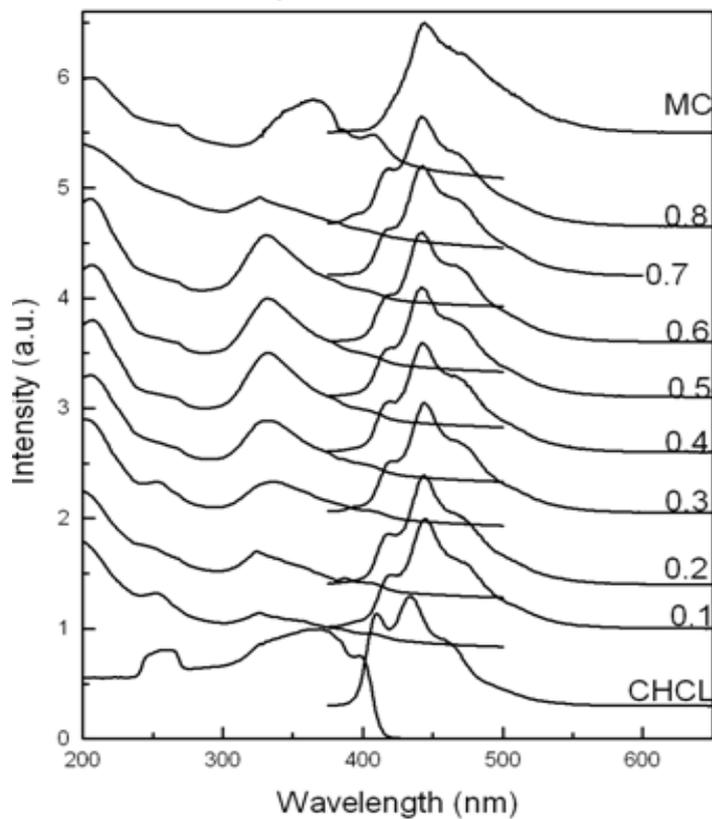


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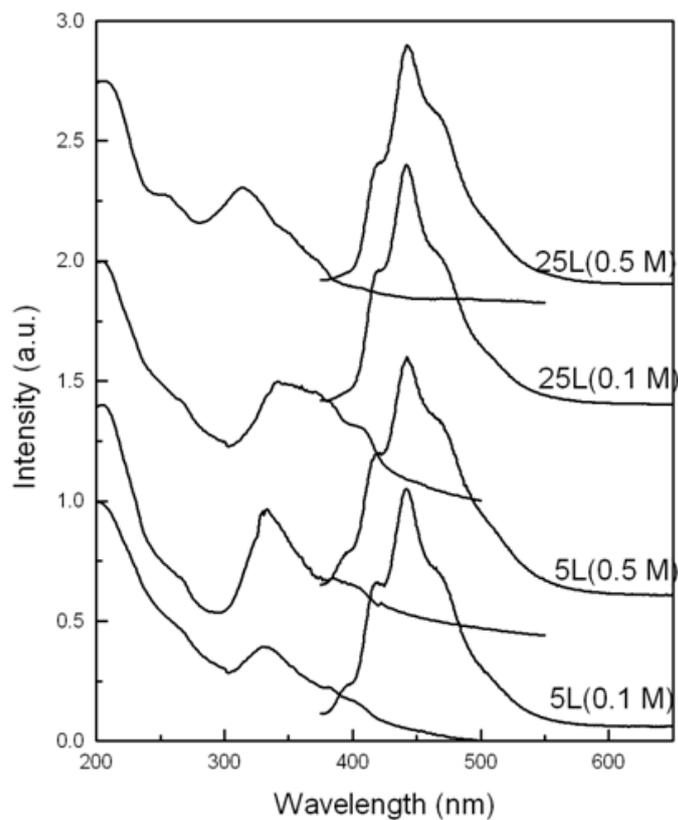


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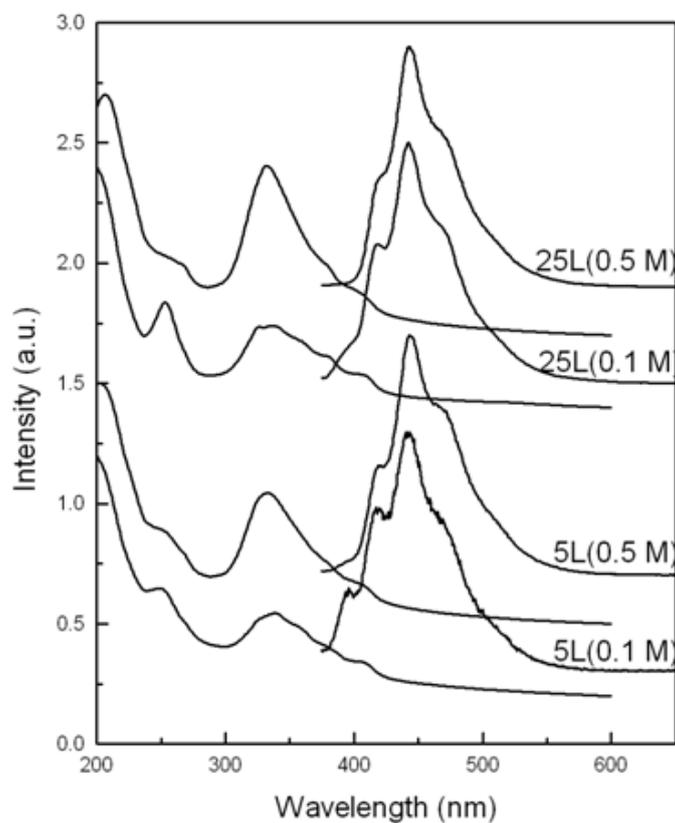


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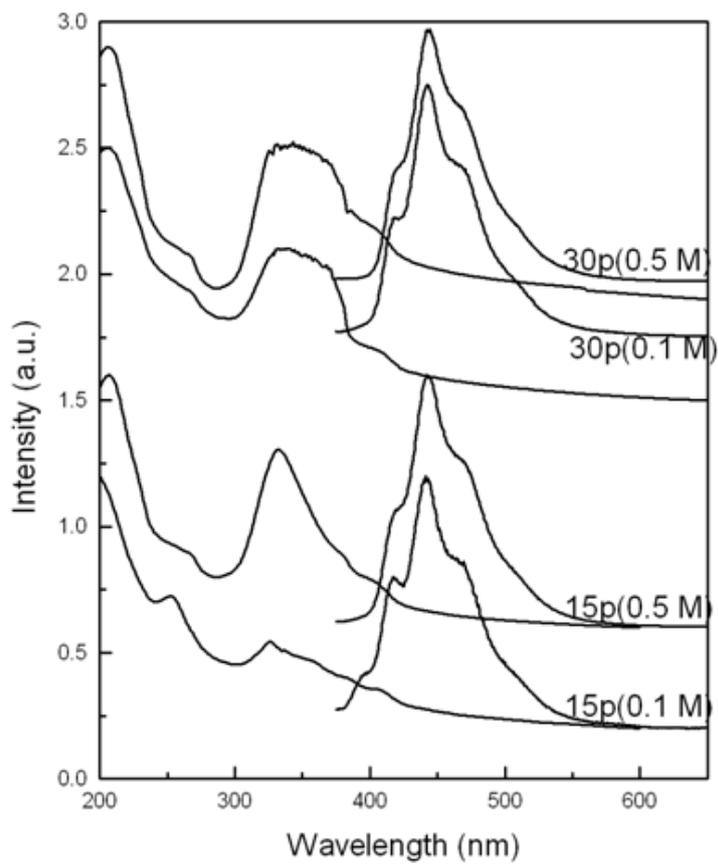


Fig: (5): S. Biswas et.al