Micellar effect of surfactant on the aggregation pattern of a fluorescent dye in ultra-thin film

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This communication reports the effect of micelles on the molecular organisation of an anionic fluorescent dye, Fluorescein Sodium Salt (FSS), in Langmuir-Blodgett (LB) films. FSS forms non-fluorescent H-aggregates in LB film when interact with Cetyltrimethylammonium Bromide (CTAB) molecules below critical micellar concentration (CMC). While above CMC, LB films of FSS adsorbed on the micellar surface of CTAB, show predominant J-aggregated sites. Complex LB films of FSS are also prepared by allowing it to adsorb onto a preformed Langmuir monolayer of cationic amphiphile octadecylamine (ODA) at the air-water interface and then depositing it onto the solid substrate. Complex ODA-FSS LB films are also investigated and a comparison is made with the SA-CTAB-FSS complex LB films. Unlike SA-CTAB-FSS complex LB films, ODA-FSS LB films can not effectively control the non-fluorescent H-aggregated sites. The films are characterised by UV-vis absorption and fluorescence spectroscopic studies and in-situ Brewster Angle Microscopic (BAM) studies. Thus CTAB micelles play an important role to decrease the H-aggregated sites in the SA-CTAB-FSS complex LB films. This complex LB film can act as efficient fluorescence probe for several biological systems due to the absence of non-fluorescent H-aggregated sites.

1. Introduction

Fluorescein Sodium Salt (FSS), an anionic xanthene dye, has interesting spectral characteristics. It has wide-range of applications as biological stainers [1], fluorescent probes [2], sensitizers [3], laser dyes [4], quantum yield standards [5], nonlinear optics [6] etc. It is non-toxic, readily soluble in water and an organic semiconductor. It is also employed for diagnostic purposes in different branches of medicine [7–10].

Being water soluble, FSS molecules cannot form a stable Langmuir monolayer at the air-water interface. There are several reports [11–15] that water soluble ionic molecules can be electrostatically adsorbed onto a oppositely charged preformed Langmuir monolayer at the air-water interface of the Langmuir trough. Being anionic FSS molecules can be electrostatically adsorbed onto a preformed cationic Langmuir monolayer. Thus a complex Langmuir monolayer is formed. Moreover in the solution state anionic FSS molecules can be adsorbed electrostatically onto a cationic micellar surface. Thus their organisation can be controlled on the micellar surface. This FSS tagged micelle can be further adsorbed onto a preformed Langmuir monolayer to form a complex Langmuir monolayer.

In the present communication the aggregation behaviour of FSS molecules has been studied in aqueous solution, in an aqueous micellar solution and in the well-known solid state restricted geometry of Langmuir-Blodgett (LB) films. Cationic Octadecylamine (ODA) molecules are also used to prepare ODA-FSS complex monolayer without any micellar structure. Further anionic surfactant stearic acid (SA) is used to form a preformed SA monolayer, onto which FSS tagged CTAB micelles are adsorbed from the aqueous sub-phase to form SA-CTAB-FSS complex Langmuir monolayer. The adsorption of FSS molecules on the CTAB micellar surface restricts their organization which can be controlled by changing various parameters. Langmuir monolayer at the air-water interface is characterized by surface pressure vs. time (π-γ) characteristic studies and in-situ Brewster Angle Microscopic (BAM) studies.

Both ODA-FSS and SA-CTAB-FSS Langmuir monolayer are transferred onto solid substrates to form mono- and multilayered Langmuir-Blodgett (LB) films. The films are characterized by UV-vis absorption and fluorescence spectroscopic techniques. A comparison of two different types of films is made to investigate the better control of molecular organization in LB films. Depending on various film forming parameters and molecular
organisation in the LB films, various kinds of dye aggregation become possible, which modify the spectral properties of the dye. It results either a blue shift or a red shift of the absorption band [16]. For J-type aggregates (side by side arrangement of molecules), the absorption band is red shifted relative to monomer. While a blue shifted absorption band is observed for H-aggregates (face to face arrangement of molecules) which reduce the fluorescence intensity [17–19].

In the present work an effort has been given to control the non-fluorescent H-aggregated sites in the LB films to obtain increased fluorescence intensity.

2. Experimental

2.1. Chemicals

Fluorescein Sodium Salt (FSS), Octadecylamine (ODA), Stearic acid (SA) and Cetyltrimethylammonium Bromide (CTAB) are purchased from Sigma Aldrich Chemical Company and used as received. Solvent chloroform (SLR, India) is of spectrophotometric grade and its purity is checked by fluorescence spectroscopy before use.

2.2. Instruments


Ultrapure Milli-Q (18.2 MΩ -cm) water is used for the preparation of the aqueous sub-phase of the Langmuir trough and for the preparation of the aqueous solution of FSS and CTAB.

UV–vis absorption and fluorescence spectra are recorded by UV–vis absorption spectrophotometer (Lambda 25, Perkin Elmer) and fluorescence spectrophotometer (LS-55, Perkin-Elmer) respectively. For recording the fluorescence spectra of aqueous solution of pure FSS and mixed FSS-CTAB, slits used are of 3.5-3.5 nm. In case of LB films 5-5 nm slits are used. For recording the fluorescence spectra 435 nm excitation wavelength is used in all the cases. Computer controlled cut-off filters at 290, 350, 390, 430 and 515 nm are used. LB films deposited onto thoroughly cleaned quartz substrates are mounted in the sample holder and placed at an angle of 45° to the excitation beam in Front Face geometry.

2.3. Methods

Stock solutions of SA (0.5 mg/ml) and ODA (0.5 mg/ml) are prepared using spectroscopic grade chloroform. Stock solution of FSS (1.0 \(\times\) 10\(^{-7}\) M) is prepared using ultra-pure Milli-Q water.

For recording the (\(\pi-t\)) characteristics and BAM images at the air water interface of two different types of complex Langmuir monolayer namely ODA-FSS and SA-CTAB-FSS, the following procedure is followed.

For preparation of ODA-FSS Langmuir monolayer at the air-water interface, first of all FSS is dissolved in the aqueous sub-phase (1.0 \(\times\) 10\(^{-7}\) M) of the Langmuir trough. Then 60 μL chloroform solution of ODA (0.5 mg/ml) is spread gently at the air-water interface by using a micro syringe. After sufficient time is allowed to evaporate the solvent, the film is compressed slowly and reached a position where the surface pressure just started rising from 0 mN/m surface pressure. At that position the barrier is kept fixed and surface pressure vs. time (\(\pi-t\)) characteristic graph is recorded.

Due to electrostatic interaction anionic FSS molecules are adsorbed onto the cationic ODA monolayer. Thus ODA-FSS complex molecules are formed. With the passage of time, pure ODA monolayer at the air-water interface is replaced by ODA-FSS complex Langmuir monolayer. The area per molecule of the complex Langmuir monolayer is greater than that of pure ODA monolayer. Thus the area per molecule started increasing but as the barrier is kept fixed at a particular position, hence the tendency to increase the area per molecule is manifested as the increase in surface pressure with the passage of time.

In-situ BAM images are also taken at different surface pressures with the passage of time that is during the formation of complex Langmuir monolayer at the air-water interface.

Same procedure is applied for the study of SA-CTAB-FSS complex Langmuir monolayer. But in this case the aqueous sub-phase of the Langmuir trough is prepared at two different concentrations of CTAB namely 0.1 mM (below cmc) and 1.0 mM (above cmc) in the two cases. FSS is also mixed in the aqueous sub-phase (1.0 \(\times\) 10\(^{-7}\) M). That is, first of all desired amount of CTAB and FSS are mixed in the aqueous sub-phase so that in the mixed solution CTAB concentrations are remained fixed at 0.1 mM and 1.0 mM respectively in the two cases where as the concentration of FSS is remained fixed at 1.0 \(\times\) 10\(^{-7}\) M in both the cases.

The mixed solution is then sonicated for 10 min prior to use as the sub-phase of the Langmuir trough. Being anionic, FSS molecules are attached electrostatically to the cationic parts of CTAB molecules and form CTAB-FSS complex molecules and remain in the aqueous sub-phase of the Langmuir Trough. Now an anionic SA monolayer is prepared at the air-water interface of the Langmuir trough by the same method as discussed previously for the preparation of ODA monolayer.

CTAB-FSS complex molecules are electrostatically adsorbed on the preformed anionic SA monolayer and thus with the passage of time pure SA monolayer is gradually replaced by SA-CTAB-FSS complex monolayer. (\(\pi-t\)) characteristic studies and in-situ BAM images of this complex Langmuir monolayer are taken by the same procedure as discussed previously in the case of ODA-FSS complex monolayer.

In all the cases BAM images are taken at different surface pressures namely 5 mN/m, 15 mN/m and 20 mN/m during the formation of Langmuir monolayer at the air-water interface.

To study the photophysical characteristics, complex Langmuir monolayer is deposited onto quartz substrate at 20 mN/m surface pressure in both the cases to obtain mono- and multi-layered (1, 3, 5 and 11) Langmuir-Blodgett (LB) films.

3. Results and discussions

3.1. Surface pressure vs. time (\(\pi-t\)) characteristic studies and in-situ Brewster Angle Microscopic (BAM) images of ODA-FSS complex monolayer at the air-water interface

Fig. 1(i) shows the (\(\pi-t\)) characteristic curve of ODA-FSS complex Langmuir monolayer at the air-water interface. The curve exhibits a steep rising and reaches a maximum value of 15 mN/m surface pressure within 150 min. Then it attains a plateau region, which is an indicative of the ending of the reaction. Thus in that point the pure ODA monolayer is totally replaced by the ODA-FSS complex Langmuir monolayer.

With the progress of interactions, BAM images of the Langmuir monolayer at the air-water interface are taken by in-situ BAM instrument. Fig. 1(ii), (iii) and (iv) are the BAM images taken at 5, 10 and 15 mN/m surface pressures. At smaller surface pressure of 5 mN/m, BAM image (Fig. 1(ii)) shows distinct small white circular domains having dimensions of the order of 1–2 microns. These domains are formed by ODA-FSS complex molecules and spread throughout the film in almost uniform distribution. At 10 mN/m surface pressure (Fig. 1(iii)) domains are larger in number and more compact and at 15 mN/m surface pressure, when the stable region is achieved the BAM image (Fig. 1(iv)) shows a compact film structure with closely spaced domains. Some regular patterns in the organization of the domains are also observed. Thus it may be concluded that at 15 mN/m surface pressure, a stable and compact complex Langmuir monolayer is formed.
at the air-water interface. This film is transferred onto solid substrates to form mono- and multi-layered Langmuir Blodgett (LB) films.

3.2. UV-vis absorption and fluorescence spectroscopic studies of aqueous solution of FSS and monolayer complex LB film

Fig. 2(a) shows the UV–vis absorption spectra of (i) aqueous solution of FSS (10⁻⁷ M) along with ODA-FSS monolayer LB films lifted at (ii) 15 mN/m and (iii) 20 mN/m surface pressures respectively. When the stable surface pressure is achieved as observed from the (π–π) curve (Fig. 1(i)), then the barrier is compressed slowly at the rate of 5 mm/min to obtain the desired surface pressure and LB film is lifted at such desired surface pressure. The temperature is maintained at 25 °C throughout the experiment.

In aqueous solution, UV–vis absorption spectrum of FSS shows two distinct absorption bands with maxima at 487 nm and 457 nm. These are the characteristic absorptions of FSS [6] in monomeric form. UV–vis absorption spectra of monolayer ODA-FSS complex LB films lifted at 15 and 20 mN/m surface pressures show almost the same band profile having intense longer wavelength band with maximum at 502 nm and a high energy weak hump at 463 nm. 15 nm red shifting of longer wavelength band with respect to monomeric band cannot be explained readily.

It may be mentioned in this context that the critical interaction distance between the dye molecules to form aggregated species is 0.35 nm. When the intermolecular distance becomes greater than 0.35 nm, then only monomeric species exists [20]. In the solid state restricted geometry of LB films, there is a possibility that the molecules may come closer to each other such that the intermolecular distance becomes less than 0.35 nm. This results in the formation of closer molecular association leading to the formation of molecular aggregates. Depending on the molecular orientation there may be H and J type aggregates. In J-type aggregates absorption band is shifted to longer wavelength and for H-type aggregates it is shifted to shorter wavelength. In the present study the 15 nm red shifting of monomeric absorption band may be due to formation of J-type aggregates in the monolayer LB film. To confirm this proposition, we have taken the Gaussian deconvolution of the UV–vis absorption spectrum of monolayer LB film lifted at 20 mN/m surface pressure that is viewed in the inset of Fig. 2(a). Gaussian deconvolution reveals three bands with maxima at 502 nm, 487 nm and at about 457 nm; this last one located at the higher energy region has a relatively low intensity when compared to the others. The 487 nm and 457 nm bands are also observed in the solution absorption spectrum and have been assigned as due to monomeric form presence. In order to confirm the longer wavelength band at 502 nm the following calculation is performed.

It is important to remark that aggregation of molecules modifies the absorption characteristics resulting in spectral shifts and band splitting. This phenomenon can be explained using the molecular exciton theory developed by Kasha et al. [21].
Two geometrical structures are accepted in ideal case: (i) Perfect sandwiched structure (H-dimer) where the dipole moments of the monomeric units are aligned in parallel planes with $\theta = 90^\circ$ and $\alpha = 0^\circ$ where $\theta$ is the angle between the direction of the dipole moments of the participating chromophores and the line connecting the molecular centers, $\alpha$ is the angle between the transition moments of the monomers in the dimer and sandwiched structure in which the participating chromophores are in parallel planes as shown in the schematic of Fig. 3. Such aggregation forms non-fluorescent H-dimers. (ii) In-Line Head-to-Tail or side by side structure (J-aggregate) in which the dipole moments are coplanar and in-line $\theta = 0^\circ$ and $\alpha = 90^\circ$ and gives intense fluorescence band.

Other than the above two extreme cases, in general dye chromophores can arrange themselves with intermediate values of $\theta$ and $\alpha$. Such aggregation forms non-fluorescent H-dimers. (ii) In-Line Head-to-Tail or side by side structure (J-aggregate) in which the dipole moments are coplanar and in-line $\theta = 0^\circ$ and $\alpha = 90^\circ$ and gives intense fluorescence band.

Where $A_1$ and $A_2$ are the areas of the Gaussian bands of the absorption spectrum corresponding to the longer and shorter wavelengths. In case of H-aggregates, $A_1$ is the area of the monomeric band and $A_2$ is the area of the H-band whereas in case of J-aggregates, $A_1$ is the area of the J-band and $A_2$ is the area of the monomeric band. After calculating the value of $\alpha$, values of $\theta$ for H- and J-aggregates are calculated using the equation $\alpha + 2 \theta = 180^\circ$ (from schematic of Fig. 3). In Fig. 2(a) left inset shows the Gaussian deconvolution of UV–vis absorption spectrum of FSS in monolayer LB film. Gaussian deconvolution shows monomeric band at 487 nm and J-aggregated band at 502 nm. From the deconvoluted spectrum the angle is calculated as $\theta = 49.72$. This value of $\theta$ satisfies the conditions for J-band ($\theta$ less than 54.7). Thus it may be conclude that 502 nm band is the J-band originating due to J-aggregated states of FSS molecules in LB film.

Fig. 3. Schematic representation for the condition of formation of ideal H- and J-aggregates.
intensity of longer wavelength vibrational mode is reduced for film lifted at higher surface pressure (graph (iii)). It may be that at higher surface pressure monolayer film attains more compact structure thus reducing the molecular vibrations to a larger extent.

### 3.3. Effect of surfactant micelle on the organisation of FSS molecules in the Langmuir monolayer and in LB film

The well-known cationic surfactant Cetyltrimethylammonium Bromide (CTAB) forms micelle in the aqueous solution for concentration above 0.92 mM (CMC). Anionic FSS molecules interact electrostatically with the cationic head group of CTAB molecules and form CTAB-FSS complex molecules in aqueous solution. These complex molecules are further adsorbed onto a preformed anionic stearic acid (SA) Langmuir monolayer at the air-water interface. Thus a SA-CTAB-FSS complex monolayer is formed at the air-water interface. In our experiment the films are prepared at two different CTAB concentrations (below and above CMC) in the aqueous sub-phase, namely 0.1 mM and 1.0 mM. Above CMC, CTAB molecules form spherical micelles as shown schematically in Fig. 6. FSS molecules are adsorbed on the surface of the spherical micelles forming oblique orientation among themselves. FSS tagged CTAB micelles are further adsorbed on the preformed anionic SA monolayer to form the SA-CTAB-FSS complex Langmuir monolayer. During the process of formation of Langmuir monolayer at the air-water interface, BAM studies give the visual images of Langmuir monolayer. This has been discussed in the next section.

### 3.4. In situ Brewster Angle Microscopic (BAM) images of SA-CTAB-FSS complex monolayer at the air water interface

In situ BAM images of Langmuir monolayer at the air-water interface at two different sub-phase concentrations of CTAB are shown in Fig. 4(a) and (b). Images are taken at different surface pressures marked in the (π–r) curves during the formation of the complex Langmuir monolayer. BAM images in Fig. 4(a) are taken for Langmuir monolayer at 0.1 mM CTAB sub-phase concentration (below CMC). At 5 mM/m surface pressure BAM image shows large number of small black domains spreading throughout the monolayer (Fig. 4(a) (ii)). These black domains indicate voids or absence of molecules. At such smaller surface pressure molecules form gaseous phase and intermolecular separation is large. Thus large number of voids are observed. The white illuminating background indicates the presence of molecules. At 15 mM/m surface pressure the number of voids decrease (Fig. 4(a) (iii)) and at 20 mM/m surface pressure several voids coalesce to form somewhat larger voids (Fig. 4(a) (iv)). But these voids are smaller in number. The white background increases indicating the presence of larger number of molecules and a compact film structure.

However when the Langmuir monolayer is formed above CTAB CMC, BAM images (Fig. 4(b)) show some interesting features. Fig. 4(b) (i) shows (π–r) curve of the Langmuir monolayer where the plateau region is observed at about 20 mM/m surface pressure. At very small surface pressure of 5 mM/m, BAM image (Fig. 4(b)(ii)) shows distinct white circular flower like domains appeared on a black background. Black background is the pure aqueous surface in the absence of molecules. The white flower like domains are the FSS tagged CTAB micelles adsorbed on SA molecules. The dimensions of these domains are about 5 to 10–5 to 10 micron. Thus it may be concluded that several such micelles are associated to form such flower like domains. At 15 mM/m surface pressure the domains become smaller in dimension but larger in number [Fig. 4(b) (iii)]. At higher surface pressure, these domains coalesce to form large domains and compact film structure as shown in Fig. 4(b) (iv).

The distinct dissimilarities between the BAM images of Langmuir monolayer formed below and above CTAB CMC indicate different types of predominant interactions.

### 3.5. UV-vis absorption and fluorescence spectroscopic studies of aqueous solution of CTAB-FSS complex molecules below and above CTAB CMC

Fig. 5(a) shows the normalised UV–vis absorption spectra of CTAB-FSS aqueous solution at different concentrations of CTAB namely (i) 0.1 mM, (ii) 0.5 mM, (iii) 0.7 mM and (iv) 1 mM. In all the cases, concentration of FSS was kept fixed at 10⁻⁷ M.

At 0.1 mM CTAB concentration, UV–vis absorption spectrum of aqueous solution shows three distinct bands; one longer wavelength intense band with maximum at 506 nm and two small intense bands at 463 nm and a high energy band at 427 nm. 463 nm band is due to monomeric origin as discussed previously. This band is slightly red shifted with respect to pure aqueous solution absorption spectrum. This may be due to changes in polar environment. The origin of longer wavelength 506 nm band is due to J-aggregate as has been confirmed previously in section 3.2. The origin of high energy band at 427 nm is assigned as higher order H-aggregates [25]. With increasing CTAB concentrations in aqueous solution the intensity of 427 nm H-aggregated band decreases and above CMC, this band diminishes totally.

This has been explained schematically in Fig. 6. In situ BAM images of Langmuir monolayer at the air-water interface, BAM studies give the visual images of Langmuir monolayer. The well-known cationic surfactant Cetyltrimethylammonium Bromide (CTAB) forms micelle in the aqueous solution for concentration above 0.92 mM (CMC). Anionic FSS molecules interact electrostatically with the cationic head group of CTAB molecules and form CTAB-FSS complex molecules in aqueous solution. These complex molecules are further adsorbed onto a preformed anionic stearic acid (SA) Langmuir monolayer at the air-water interface. Thus a SA-CTAB-FSS complex monolayer is formed at the air-water interface. In our experiment the films are prepared at two different CTAB concentrations (below and above CMC) in the aqueous sub-phase, namely 0.1 mM and 1.0 mM. Above CMC, CTAB molecules form spherical micelles as shown schematically in Fig. 6. FSS molecules are adsorbed on the surface of the spherical micelles forming oblique orientation among themselves. FSS tagged CTAB micelles are further adsorbed on the preformed anionic SA monolayer to form the SA-CTAB-FSS complex Langmuir monolayer. During the process of formation of Langmuir monolayer at the air-water interface, BAM studies give the visual images of Langmuir monolayer. This has been discussed in the next section.

In situ BAM images of Langmuir monolayer at the air-water interface at two different sub-phase concentrations of CTAB are shown in Fig. 4(a) and (b). Images are taken at different surface pressures marked in the (π–r) curves during the formation of the complex Langmuir monolayer. BAM images in Fig. 4(a) are taken for Langmuir monolayer at 0.1 mM CTAB sub-phase concentration (below CMC). At 5 mM/m surface pressure BAM image shows large number of small black domains spreading throughout the monolayer (Fig. 4(a) (ii)). These black domains indicate voids or absence of molecules. At such smaller surface pressure molecules form gaseous phase and intermolecular separation is large. Thus large number of voids are observed. The white illuminating background indicates the presence of molecules. At 15 mM/m surface pressure the number of voids decrease (Fig. 4(a) (iii)) and at 20 mM/m surface pressure several voids coalesce to form somewhat larger voids (Fig. 4(a) (iv)). But these voids are smaller in number. The white background increases indicating the presence of larger number of molecules and a compact film structure.

However when the Langmuir monolayer is formed above CTAB CMC, BAM images (Fig. 4(b)) show some interesting features. Fig. 4(b) (i) shows (π–r) curve of the Langmuir monolayer where the plateau region is observed at about 20 mM/m surface pressure. At very small surface pressure of 5 mM/m, BAM image (Fig. 4(b)(ii)) shows distinct white circular flower like domains appeared on a black background. Black background is the pure aqueous surface in the absence of molecules. The white flower like domains are the FSS tagged CTAB micelles adsorbed on SA molecules. The dimensions of these domains are about 5 to 10–5 to 10 micron. Thus it may be concluded that several such micelles are associated to form such flower like domains. At 15 mM/m surface pressure the domains become smaller in dimension but larger in number (Fig. 4(b) (iii)). At higher surface pressure, these domains coalesce to form large domains and compact film structure as shown in Fig. 4(b) (iv).

The distinct dissimilarities between the BAM images of Langmuir monolayer formed below and above CTAB CMC indicate different types of predominant interactions.
Fig. 4. a). (i) Surface pressure vs. time ($\pi t$) characteristic curve of SA-CTAB-FSS complex Langmuir monolayer at 0.1 mM CTAB (below CMC) concentration in the aqueous sub-phase. (ii) – (iv) in-situ Brewster Angle Microscopic (BAM) images of the Corresponding SA-CTAB-FSS complex Langmuir monolayer is taken at different surface pressures namely (ii) 5 mN/m, (iii) 15 mN/m and (iv) 20 mN/m. Scale bar represents 20 μm. b). (i) Surface pressure vs. time ($\pi t$) characteristic curve of SA-CTAB-FSS complex Langmuir monolayer at 1.0 mM CTAB (above CMC) concentration in the aqueous sub-phase. (ii) – (iv) in-situ Brewster Angle Microscopic (BAM) images of the Corresponding SA-CTAB-FSS complex Langmuir monolayer is taken at different surface pressures namely (ii) 5 mN/m, (iii) 15 mN/m and (iv) 20 mN/m. Scale bar represents 20 μm.
Fig. 5. (a) Normalised UV–vis absorption spectra of FSS in aqueous solution mixed with different concentrations of CTAB namely (i) 0.1 mM, (ii) 0.5 mM, (iii) 0.7 mM and (iv) 1.0 mM. In all the cases concentration of FSS remain fixed at $10^{-7}$ M. (b) Fluorescence spectra of FSS in aqueous solution mixed with different concentrations of CTAB namely (i) 0.1 mM, (ii) 0.5 mM, (iii) 0.7 mM and (iv) 1.0 mM. In all the cases concentration of FSS remain fixed at $10^{-7}$ M.

Fig. 6. (a) Schematic representation of FSS, (b) Schematic representation of CTAB, (c) Schematic representation of CTAB-FSS complex molecule, (d) Schematic representation of orientation of CTAB-FSS complex with respect to each other before micelle formation, (e) Schematic representation of formation of J-aggregate when FSS molecule adsorb on the surface of CTAB micelle.
Fig. 7. (a) Normalised UV–vis absorption spectra of SA-CTAB-FSS complex monolayer LB films lifted at different subphase concentrations of CTAB namely (i) 0.1 mM, (ii) 0.5 mM, (iii) 0.7 mM and (iv) 1.0 mM; (b) Corresponding Fluorescence spectra.

Fig. 8. (a) UV–vis absorption spectra of different layered (1, 3, 5, 11) SA-CTAB-FSS complex LB films lift at 1.0 mM subphase concentration of CTAB (b) Corresponding Fluorescence spectra. Spectra corresponding to 1, 3, 5 and 11 layered LB films are marked as (i), (ii), (iii) and (iv) respectively.
extent.

3.7. UV–vis absorption and fluorescence spectra of multi-layered LB films lifted above CTAB-CMC in sub-phase

Fig. 8 shows the UV–vis absorption and fluorescence spectra of 1, 3, 5 and 11 layered SA-CTAB-FSS complex LB films lifted above CTAB CMC in sub-phase. UV–vis absorption spectra shows intense J-aggregated band with increasing layer number. H-aggregated band is totally absent. It indicates that with layer number, orientation of FSS molecules in the CTAB micelle remained unaffected. Thus with increasing layer number, number of J aggregated sites in the LB film increase [Fig. 8(a)]. Fig. 8(b) shows the corresponding fluorescence band with increasing layer number. It shows that with increasing layer number, 538 nm fluorescent band increases in intensity while the longer wavelength vibrational mode reduces significantly and diminishes totally at higher layer number. It indicates that with increasing layer number due to overlapping of different layers, molecular vibration becomes restricted to a larger extent.

4. Conclusion

Our investigations show that molecular organisation on the CTAB micellar surface effectively reduces the H-aggregated sites of FSS molecules to a larger extent. H-aggregated sites become predominant when FSS molecules are tagged to the CTAB molecules before micelle formation and incorporated into the LB film. On the other hand non-fluorescent H-aggregated sites become almost absent and J-aggregated sites become predominant in the LB films fabricated above CTAB CMC in the sub-phase of Langmuir trough. In this case FSS molecules are tagged to the micellar surface of CTAB and formed J-aggregated sites. It results in intense fluorescence band. Multilayer complex LB films prepared above CTAB CMC in the sub-phase of the Langmuir trough also retain this characteristic as is observed from the UV–vis absorption spectroscopic studies. Fluorescence intensity also increases remarkably with layer number. In-situ Brewster Angle Microscopic (BAM) images of the complex Langmuir monolayer at the air-water interface prepared below and above CTAB CMC show distinct dissimilarities indicating different nature of organisations. On the other hand ODA-FSS LB film can not effectively control the H-aggregated sites. This micellar tagged FSS films can be used as an efficient fluorescence probe to investigate several biological processes.

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Appendix A. Supplementary data

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References