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Effect of Electric Field on J-aggregate in Ultrathin Films

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Abstract

In the present paper we have demonstrated the application of electric field towards the reconstruction of J-aggregate of an indocarbocyanine dye onto LB film. Similar approach can also be applied for the improvement of J-aggregate using other molecules.

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1. Introduction

Recently molecular aggregates of organic dyes have attracted considerable attention due to their potential application in various fields such as energy transfer in photosynthesis [1], optical memory [2], light harvesting [3], organic light emitting diodes [4], organic solar cells [5], photodynamic therapy [6], photographic process [7] etc. Demand for the development of smaller and smaller sized devices with different functionality stimulates the importance to study the molecular aggregation property in ultrathin films. Aggregates are basically assemblies of molecules held in place together. Based on the molecular orientation, various kinds of aggregated species developed...
such as J-aggregate, H-aggregate, excimer, exciplex etc. Langmuir – Blodgett (LB) technique is one of the best techniques for the preparation of ultrathin film with controlled structure.

J-aggregates are the end to end or head to tail arrangement of molecules in an aggregate and is spectroscopically defined as the narrow absorption band appeared at longer wavelength region of absorption spectra with a very small stoke shift. Numerous devices have been proposed using the properties of dye J-aggregates. For example J-aggregates are used in light harvesting system for solar cell [8], sensor devices [9], components for non linear optical devices [10], optical recording system [11], OLED [12], storage of photo electrons in nanoparticles [13]. On the other hand excimer is a pair of identical molecule, one at ground state and another in the excited state. This is unstable and rapidly dissociates with emission of radiation.

Cyanine dyes are the best known self associating dyes for the formation of different types of aggregates in ultrathin film. Due to the high polarizability of the $\pi$ electrons along with the polymethine group, the dispersion forces between the cyanine molecules are very strong [14]. These dispersion forces plays a vital role for the formation of extend aggregates of cyanine dye molecules in ultrathin films [15]. Most of the works on cyanine derivatives concentrated on the formation of single type of aggregating species. For example, some derivatives are found to form H-aggregate [16 – 18] some form J-aggregates, [10, 19, 20] some while other form excimer in the ultrathin films [21]. Extent of such aggregation may be controlled by varying the environmental as well as electrical parameters [22] which may result in the formation of dye aggregates with different functionality. Studies on aggregate reveal that electric field may change the properties of aggregates in ultrathin films. Thus emphasis must be given on the efforts to quantify the optimized condition to fabricate different types of technologically friendly aggregated species and their stability. Otha et al. studied the effects of electric field on absorption and fluorescence spectra of a cyanine dye in LB films [23].

DiI forms excimer in LB and also it forms J-aggregate when mixed with a long chain fatty acid SA [24]. Investigation on the stability of DiI J-aggregate reveals the formation of stable J-aggregate at higher surface pressure [25]. Here we report the variation of J-aggregation of an indocarbocyanine dye – fatty acid in LB films due to electric field. Considering the wide application of nanoscale aggregates, this result is very important from application point of view.

2. Experimental

DiI and Stearic Acid (SA) purity >99%, were purchased from Sigma-Aldrich chemical company and were used as received. Working solutions were prepared by dissolving them in spectroscopic grade chloroform (SRL). The clay mineral used in the present work was synthetic Laponite, obtained from Laponite Inorganics, UK and used as received.

A commercially available Langmuir-Blodgett (LB) film deposition instrument (Apex 2000C, Apex Instruments Co., India) was used for surface pressure–area isotherm measurements as well as for mono and multilayer film preparation. Ultra pure Milli-Q water of resistivity 18.2 M$\Omega$-cm was used as subphase. The concentration of the stock solutions for both SA and DiI was 0.5 mg/ml. DiI and SA were mixed at molar ratio of 0.4M using the stock solutions. In order to measure the isotherm and film preparation, 60 micro liters of either pure or mixed solutions were spread onto the subphase with a micro syringe. After complete evaporation of volatile solvent, barrier was compressed at a rate of 5 mm/minute to record the surface pressure–area per molecule isotherms. The surface pressure ($\pi$) versus average area available for one molecule (A) was measured by a Wilhelmy plate arrangement [24]. Each isotherm was repeated a number of times and data for surface pressure – area per molecules isotherms were obtained by a computer interfaced with the LB instrument. Smooth fluorescence grade quartz plates (for spectroscopy) and Si-wafer (for AFM studies) were used as solid substrate. Y-type deposition at a particular surface pressure was followed to transfer Langmuir films at a deposition speed of 5 mm/minute. For AFM measurement, a single layer was deposited. The transfer ratio was estimated by calculating the ratio of decrease in subphase area to actual area on the substrate coated by the layer and was found to be 0.98±0.02.

UV-Vis absorption and fluorescence of pure solutions as well as those of mixed LB films were recorded using absorption spectrophotometer (Perkin Elmer, Lambda 25) and fluorescence spectrophotometer (Perkin Elmer, LS 55) respectively. The absorption spectra were recorded at 90° incidence and using a clean quartz slide as reference. For electrical measurement we have used Keithley source meter.
Results and Discussion

3.1. Monolayer characteristics at air – water interface:

Surface pressure vs molecular area (π - A) isotherm gives an idea about the thermodynamic behavior of mixed monolayer at the air-water interface and also the nature of interactions amongst the constituent components. Fig. 1 shows the surface pressure-area per molecule isotherms of pure DiI, SA and DiI – SA mixed monolayer at X_{DiI}=0.4. We had spread 60 μl of solution over the water subphase. Each isotherm collected from a compilation of three compressions of three different sets of experiments.

![Fig. 1 Surface pressure vs area per molecule isotherm of pure DiI, SA and DiI – SA mixed monolayer at X_{DiI} = 0.4. Inset shows the molecular structure of DiI](image)

A smooth rise in surface pressure was observed for all the monolayers. The shape of the SA isotherm is steeper than DiI isotherm in nature. The lift off area of SA and DiI were found to be 0.27 nm² and 1.9 nm² respectively, determined by the method described by Ras et al [26]. The lift off areas of SA and DiI isotherm are in well agreement with the reported results (24). The DiI isotherm showed a sharp phase transition near about π = 32 mN/m. In one of our previous paper we had shown that DiI forms ideal monolayer with SA at X_{DiI}=0.4 (25). For the DiI – SA mixed isotherm, the lift off area was in between pure SA and DiI which are in well agreement with our previous report. Also the nature of the mixed isotherm possesses characteristics of both the pure components indicating interaction as well as certain amount of miscibility between SA and DiI molecules in the mixed monolayer.

3.2. Stability of Langmuir monolayer

![Fig. 2 Stability of Langmuir monolayer taken at different molefractions of DiI in DiI – SA mixed monolayer](image)
To have an idea about the stability of Langmuir monolayer at air water interface we have studied the stability behaviour (recording the change in surface pressure time) with the passage of time keeping surface pressure fixed at 25 mN/m. It is clear from the figure 2 that mixed monolayer at $X_{\text{DII}} = 0.4$ is very stable with respect to the other mixed monolayers. This is well in agreement with our previous result (24) that DII mixed film at $X_{\text{DII}} = 0.4$ the interaction between DII and SA balance out and found to be most suitable for the formation of maximum J-aggregate.

### 3.3. Formation of DII J-aggregate

Absorption spectrum of DII solution possesses prominent band system within 450 – 600 nm regions with distinct monomer peak at around 562 nm and the vibronic component of the monomer at around 524 nm (figure not shown) [24]. Solution fluorescence spectrum possesses prominent monomer band at around 570 nm. It has been observed that DII forms excimer in LB film resulting a broad and structureless band appeared at around 704 nm in the fluorescence spectrum of DII LB films (figure not shown) [24]. However, DII forms J-aggregate in the LB films when DII is mixed with a long chain fatty acid SA [24].

![UV – Vis absorption spectra and (b) deconvolution of absorption spectra of DII – SA mixed LB film at $X_{\text{DII}} = 0.4$](image.png)

It has been observed that DII – SA mixed LB films at DII molefraction of 0.4 ($X_{\text{DII}}=0.4$) is ideal for the formation of DII J-aggregates in LB monolayer films [24]. In our previous communication we have seen that DII forms J-aggregate in LB film at different subphase temperatures viz. 10$^\circ$C, 15$^\circ$C, 20$^\circ$C, 30$^\circ$C and 35$^\circ$C [25]. But 15$^\circ$C subphase temperature is best suitable for the formation of maximum J-aggregate in LB films [25]. Thus we have fabricated all the J-aggregated film at 15$^\circ$C temperature for further study. Figure 3a shows the UV-Vis absorption spectra of DII - SA mixed LB film at $X_{\text{DII}}=0.4$. A narrow and sharp band at 597 nm having a small stokes shift in fluorescence spectra reveals the formation of J-aggregate in LB film (figure not shown).

The process of deconvolution of spectra into several Gaussian curves allows the adequate determination of different species present in the spectra. Deconvolution of DII J-aggregate possesses two bands (figure 2b), on at around 597 nm which is assigned due to the formation of J-aggregate and another at 525 nm for the vibronic band [24].
3.4. Effect of electric field on J-aggregate

J-aggregates are basically the head to tail arrangement of molecules. According to exciton coupling theorem a molecule may be regarded as a point dipole and the orientation or the conformational change of this dipole may occur due to the change in film forming parameter, environmental parameter etc. Orientation of this molecular dipole may also change due to the change in electric field, magnetic field etc. Thus to have an idea about the effect of electric field on DiI J-aggregate we have exposed the DiI J-aggregate film in an electric field.

![Fig. 4 (a) UV – Vis absorption spectra and (b) fluorescence spectra of DiI – SA mixed LB film before and after exposing the film to an electric field](image)

Our previous study revealed that J-aggregate of DiI degrades with aging (25). We demonstrated the enhancement of J-aggregate through humidity treatment (25). Also the stability was improved by incorporating clay particle laponite onto LB films (19).

In the present case we applied a potential of 3V across freshly prepared DiI J-aggregate in LB films. However no significant change was observed. But when bias across aged film was applied, significant improvement in J-aggregate band intensity with respect to the same decreased due to aging was observed. Corresponding UV – Vis absorption and fluorescence spectrum is shown in figure 4a and 4b. It has also been observed that the coherence size or spectroscopic aggregation number also increase after application of electrical field which was absent before application of electric field.

Application of electric field caused change in conformation of molecule in the aggregated film resulting favourable condition of J-aggregate. Conformational change due to passage of current through LB film has already been reported (22)

4. Conclusion:

The application of electric field for the reconstruction of J-aggregate of an indocarbocyanine dye onto LB film has been successfully demonstrated. This is very important keeping in mind about the enormous application potential of J-aggregate in LB films. This approach may also be employed to the reconstruction of J-aggregate using other molecules in thin films.
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