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Full Length Article

Stability of J-aggregated species in an indocarbocyanine dye in Langmuir–Blodgett Films

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ABSTRACT

Here, the stability behaviour of J-aggregate of an indocarbocyanine dye 1,1′-Dioctadecyl-3,3,3′,3′-Tetramethylindocarbocynine perchlorate (DiI) in fatty acid mixed ($X_{DiI}=0.4$) Langmuir–Blodgett (LB) films under different condition was reported. Surface pressure–area per molecule (π–A) isotherm measurement suggest that the molecular interaction between the constituent molecules changes with subphase temperature. UV–vis absorption and fluorescence spectroscopy and Atomic Force Microscopy (AFM) were used to study the stability behaviour. It has been observed that prominent J-aggregate of DiI occurred in the mixed films at subphase temperature 15 °C. With the passage of time as well as post heat treatment DiI J-aggregate decayed to excimer in both mono- and multilayer LB films. Total transition from J-aggregate to excimer occurred in monolayer films, whereas, the transition was partial in multilayer films. The stability of DiI J-aggregate in monolayer films was increased by two ways – (i) depositing the DiI-SA mixed LB films at higher surface pressure, (ii) exposing the films at 50 °C for 5 min. It has been observed that after heat treatment the DiI J-aggregate remained almost stable even after 200 days. AFM investigations gave the compelling visual evidences of the same.

1. Introduction

Many dyes possess self-association and self assembling properties leading to the formation of aggregates in solution and in ultrathin films [1–7]. Such aggregation affects on coloristic and photophysical properties of dyes and therefore being of special importance [8]. The aggregation behaviors both in solution and at the solid-liquid interface is a frequently encountered phenomenon owing to strong intermolecular Van der Waals-like attractive forces between the molecules. It is well known that the ionic dyes have a common tendency to aggregate in dilute solutions, leading to formation of dimer, and sometimes even higher order aggregates. Based on the orientation of the dyes in the aggregates, there exist various kinds of aggregating species viz. H-aggregates, J-aggregates, excimer etc. Various parameters like dye concentration, structure, ionic strengths, temperature and presence of organic solvents may strongly influence the extent of aggregation [7]. Dye aggregates are often found to play important roles in both fundamental science and technological applications such as optical memory, organic solar cells and nonlinear optical application etc. [9–12].

Non-covalently coupled molecules (dyes) such as porphyrines, cyanine, squaranine etc form well ordered nano-scale J-aggregates [13–15]. Highly ordered molecular stacking (head to tail alignment of transition dipole moments of the dye molecule) in the J-aggregate results in the appearance of narrow and very sharp absorption band (J-band) red shifted with respect to the monomer band [13–15]. Spectral features of J-aggregates are governed by the exciton delocalization length, which is usually up to tens monomers, rather than the physical size of aggregates [15]. Due to excitonic nature of electronic excitations, J-aggregates reveal a number of unique spectral properties such as for organic molecules very narrow sharp bands (tens of cm^{-1} at liquid helium temperatures), large extinction coefficients (hundreds of thousands of cm^{-1} M^{-1}), very large scale second and third-order optical nonlinearities up to 10^{-5} esu and so on [16]. Such optical properties make the J-aggregates a very promising candidate for many technological applications, e.g. spectral sensitization in photovoltaic cells, optical waveguide,

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nonlinear optical devices, luminescent, optical switch, probes in biology and medicine and so on [9–18].

On the other hand, several dye molecules may also form excimer in solution or bulk, which is a molecular complex of two, usually identical, molecules that is stable only when one of them is in an excited state. It is evidenced by a broad and structureless longer wavelength band in the fluorescence spectrum and is important in excimer laser technologies [19].

Cyanines and their derivatives have attracted gaining interest as building blocks for the construction of new functional nanoscale aggregates for electronics and optoelectronics [20]. In addition, Langmuir–Blodgett (LB) technique has been emerged as one of the best method for preparation of such aggregate in ultrathin films [21–24]. Herein the organization and hence the properties of molecules can be controlled as a function of molar composition, temperature, humidity, surface pressure, layer number etc. [16,21–27].

In these cases, aggregates are formed onto solid surfaces or in monomolecular layers at the air–water interface (Langmuir monolayer), where the chromophore packing can be controlled by changing various LB parameter [21–23]. Due to the strong tendency of self association as well as technology friendly aggregate formation, in our laboratory, we have studied the aggregating behaviour of cyanine and thiacyanine molecules assembled onto LB films [25–28]. It has been observed that J-aggregate of thiacyanine onto LB films can be controlled by incorporating nano-clay laponite [26], irradiation of UV-light decays J-aggregate to H-aggregate and monomers [27], SHG active J-aggregate of a intrinsically SHG inactive NK in LB film has also been studied [28]. It has been observed that stability of J-aggregate increases in presence of nano-clay [28].

In one of our earlier works, we reported the reversible transition between excimer and J-aggregate of an indocarbocyanine dye 1,1′-Dioctadecyl-3,3,3′,3′-Tetramethylindocarbocynine perchlorate (DiI) in mixed LB films [25]. It has been observed that molar composition plays an important role in determining the nature of aggregating species in dye-fatty acid mixed LB monolayer films. As a continuation of that work, here we report the results of our investigation on the stability of J-aggregate in DiI-SA mixed LB films. Stability of specific aggregating species in ultrathin films is an important issue in order to have their practical application. We have demonstrated that the stability of DiI J-aggregate in LB films can be improved either by increasing the surface pressure of lifting during LB film preparation or by post-heat treatment of the LB monolayer for certain time period. Interestingly it was found that the DiI J-aggregate was stable even after 200 days in treated films. This observation is very important for the future application of such aggregates.

2. Experimental

2.1. Materials and methods

DiI, 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).

A commercially available Langmuir–Blodgett (LB) film deposition instrument (Apex 2000C, Apex Instruments Co., India) was used for the measurements of surface pressure–area isotherm as well as for mono and multilayer film preparation. Ultra pure Milli-Q water of resistivity 18.2 MΩ 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 different molar ratios using the stock solutions. In order to measure the isotherm and also for film preparation, 60 µl 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 12.33 mm^2/s to record the surface pressure–area per molecule isotherms. The surface pressure (π) versus average area available for each 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 molecule 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/min. Here we investigated one layer and ten layers of mixed LB films. For monolayer LB film preparation, initially the substrate was kept inside the water and the monolayer was deposited during upward movement of the substrate. Multilayer (10 layers) was deposited by repeatedly moving the substrate upward and downward within the subphase across the floating Langmuir monolayer. All the films were deposited at 15 mN/m surface pressure. A detail about LB technique has been described in our previous work [24]. 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.

2.2. Characterization

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 fluorescence spectra measurement the excitation wavelength (λ_{ex}) was 520 nm for all cases.

A homemade glass chamber was used for the post heat treatment of the J-aggregated thin films, in which the films are placed at the middle of the chamber from a suspension point. UV–visible absorption spectra were recorded immediate after the heat treatment. The temperature dependent UV–visible and fluorescence measurements were started immediate after the preparation of the sample and checked to avoid the aging effects of the mixed films.

The atomic force microscopic (AFM) image of monolayer film was taken with a commercial AFM system, Innova AFM system (Bruker AXS Pte Ltd.) by using silicon cantilevers with a sharp, high apex ratio tip (Veeco Instruments). The AFM images presented here was obtained in intermittent-contact ("tapping") mode. Typical scan areas were 1×1 μm^2.

3. Experimental results

3.1. Effect of subphase temperature on floating monolayer at air–water interface

In LB technique, surface pressure–area per molecule (π–A) isotherms is considered as two dimensional finger prints to have idea about the intermolecular interactions as well as thermodynamic behaviour of the floating monolayer [29]. Thermodynamic behaviour of pure DiI as well as DiI-SA mixed monolayer at air–water interface under ambient condition had already been studied [25]. It has been observed that mixing ratio of DiI and SA in DiI-SA mixed films plays an important role in determining the nature of aggregation of DiI molecule in mixed LB films. DiI molefraction of 0.4 ($X_{DiI}=0.4$) in DiI-SA mixed films was found to