Formation of rod-shaped domains in Langmuir–Blodgett films composed of 7, 8-dimethyl-10-dodecyl isoalloxazine

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A B S T R A C T

7, 8-Dimethyl-10-dodecyl isoalloxazine (DDI) is a derivative of "flavin", which is a good electron donor that is easily found in natural systems. DDI shows high electron transfer efficiency with electron acceptors in artificial electron transport systems made of Langmuir–Blodgett (LB) films. LB films exhibit a variety of morphologies according to the experimental conditions, and the electron transfer efficiency depends strongly on the morphology of the films. In previous studies, the morphology of LB films composed of DDI was not investigated sufficiently. The present study shows that rod-shaped domains are formed in LB films composed of DDI when the DDI monolayer is compressed beyond a specific limiting area. The formation mechanism for rod-shaped domains can be surmised from the surface pressure–mean molecular area isotherm curve and atomic force microscopy data. The fluorescence lifetimes of the rod-shaped domains or nondomains were measured. The data is discussed in terms of the suggested formation mechanism of rod-shaped domains.

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1. Introduction

In biological systems, one-direction long-range electron transfer is extremely efficient [1]. A number of studies have examined methods of increasing the efficiency of electron transfer in artificial systems to reproduce such efficient electron transfer [2–6]. The efficiency of electron transfer is determined by several parameters, such as the difference of reduction-oxidation potential, distance between the electron donors and acceptors, spatial geometry, etc. These parameters have been studied in a range of artificial systems prepared by organic synthesis [2,3], self-assembly [4], and Langmuir–Blodgett (LB) methods [5,6]. Among them, the LB method is the dominant technique to study electron transfer because the distance between the electron donors and acceptors in addition to the spatial geometry in LB films can be easily controlled with sufficient accuracy. In the course of these studies, it was demonstrated that LB films composed of electron donors and acceptors can exhibit molecular photodiode behavior.

Many attempts have been made to produce artificial devices that would simulate highly efficient electron transfer in biological systems. In such devices, isoalloxazine derivatives (flavins) are frequently used as electron donors because flavins are commonly found in biological electron transport systems and have multiple oxidation and reduction steps [7,8]. In several reports, molecular photodiodes prepared using the LB technique were demonstrated, and flavins were used as electron donors [9–13]. These studies reported that the transient photocurrent is increased by charge separation between the electron donor

and acceptor, and investigated the photoinduced electron transfer rate as a function of the distance between electron donors and acceptors.

In the standard LB procedure, amphiphilic molecules spread over water surfaces are compressed to a specific surface pressure and transferred to a substrate in a layer-by-layer procedure. During compression, a variety of domains are formed due to the aggregation of molecules and changes in the monolayer phase [14,15]. Such domains are related to the molecular packing structures that strongly affect the electron transfer processes. Therefore, the morphology of LB films should be examined in great detail to better understand electron transfer processes and increase the electron transfer efficiency in LB films. In the present study, the morphology of LB films composed of 7, 8-dimethyl-10-dodecyl isoalloxazine (DDI) was investigated. The results showed that rod-shaped domains are formed when the DDI monolayer is compressed beyond a specific limiting area. The theoretical molecular area estimated from the DDI molecular dimensions was compared with the experimental molecular area measured from the surface pressure (π)–mean molecular area (A) isotherm curve. Atomic force microscopy (AFM) was used to confirm the formation mechanism of rod-shaped domains. The fluorescence decay was measured on both the rod-shaped domains and nondomains, and the results are discussed in terms of the suggested formation mechanism of rod-shaped domains.

2. Experiment

DDI was synthesized as described elsewhere [9]. LB film deposition was carried out using a commercial LB trough (Type 601D2, NIMA Tech, UK), and a filter-paper type Wilhelmy plate was used to measure the surface pressure. In a typical experiment, DDI was dissolved in

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chloroform to a concentration of approximately 1 mM, and the solution was spread over a deionized water (18.2 MΩcm, 72 mN/m) surface at 20 °C. After the chloroform was evaporated for ~30 min, DDI was compressed at a compression speed of 10 cm² min⁻¹ and transferred to a substrate at a surface pressure of 16 or 22 mN/m by single up-stroke withdrawal at a speed of 2 mm min⁻¹. Deposition ratios for both cases are over ~90%, respectively. The DDI geometry was optimized using semi-empirical calculations at the "PM 3" level using commercial software (Hyperchem). To obtain a fluorescence image of the LB films morphology, a normal optical microscope (BX51, Olympus) was modified to a fluorescence optical microscope, and the LB films were excited with filtered light (375–435 nm) from a Hg lamp. The fluorescence of the LB films was detected at a wavelength longer than 450 nm. Fluorescence micrographs are taken using a common digital camera (Cannon, A60). The height of the rod-shaped domains was measured by AFM (XE-100, Park Systems) in contact mode in air at a scan rate of 1–2 Hz. A home-made confocal scanning optical microscope (CSOM) combined with a time-correlated single photon counting technique (TCSPC) was used to obtain CSOM images of the LB films with the excitation of a He-Cd laser (cw, 442 nm) and the fluorescence lifetime with a femtosecond Ti:sapphire laser frequency doubled using a β-BBO (β-barium borated) crystal. A long pass filter (>520 nm) was used to block the excitation light and detect fluorescence from the LB films at wavelength longer than 450 nm.

3. Results and discussion

The geometry of DDI (Fig. 1a) was optimized by a semi-empirical calculation and the molecular dimensions were obtained, as shown in the space-filling model (Fig. 1b, c.) Because of the lone pair electrons in nitrogen, where the C_{12}-hydrocarbon chain is connected, the C_{12}-hydrocarbon chain is not on the same plane as the isoalloxazine ring plane, and the dihedral angle (θ) can be defined, as shown in the inset of Fig. 1d. The

C_{12}-hydrocarbon chain can rotate around a single C−N bond that connects the hydrocarbon chain with the isoalloxazine ring plane. DDI has three conformations according to the dihedral angle (θ): i) θ = 0° (360°), eclipsed form I (most unstable form), ii) θ = 70° (290°), staggered form (the most stable form), and iii) θ = 180°, eclipsed form II (less unstable form). Fig. 1(d) shows the calculated potential energy of DDI as a function of the dihedral angle. The staggered form is more stable than eclipsed forms I and II by ~42 and ~16 kJ mol⁻¹, respectively. As this energy difference is lower than the thermal energy at room temperature, the hydrocarbon chain can freely rotate around a single C−N bond at room temperature.

During compression of the DDI monolayer on the water surface using movable barriers, the surface pressure remained constant until the mean molecular area reached ~140 Å² and increased slowly to a peak at which the mean molecular area was ~59 Å² (Fig. 2a). Interestingly, the surface pressure decreased beyond this peak when the DDI monolayer was compressed further, and showed a plateau region, where the surface pressure remained almost unchanged despite the continuing compression. Fluorescence optical microscopy revealed rod-shaped domains in the Langmuir–Blodgett (LB) films transferred at 22 mN/m beyond the spike (Fig. 2b). On the other hand, no domains were formed in the LB films (Fig. 2c) transferred at 16 mN/m before the spike. Therefore, relative to the spike, rod-shaped domains are always formed beyond the spike, whereas no domains are formed before it. All domains were rod-shaped, 12 ± 2 μm in length and 5 ± 1 μm in width.

The molecular packing structures of the molecules assembled on the water surface can be estimated from the mean molecular area, which is the mean area obtained experimentally from the π–A isotherm curve. In Fig. 2a, the surface pressure begins to increase slowly from when the mean molecular area is 140 Å². The area highlighted by magenta (rectangle and trapezium) in the right image of the inset in Fig. 2a can be calculated from the molecular dimensions.
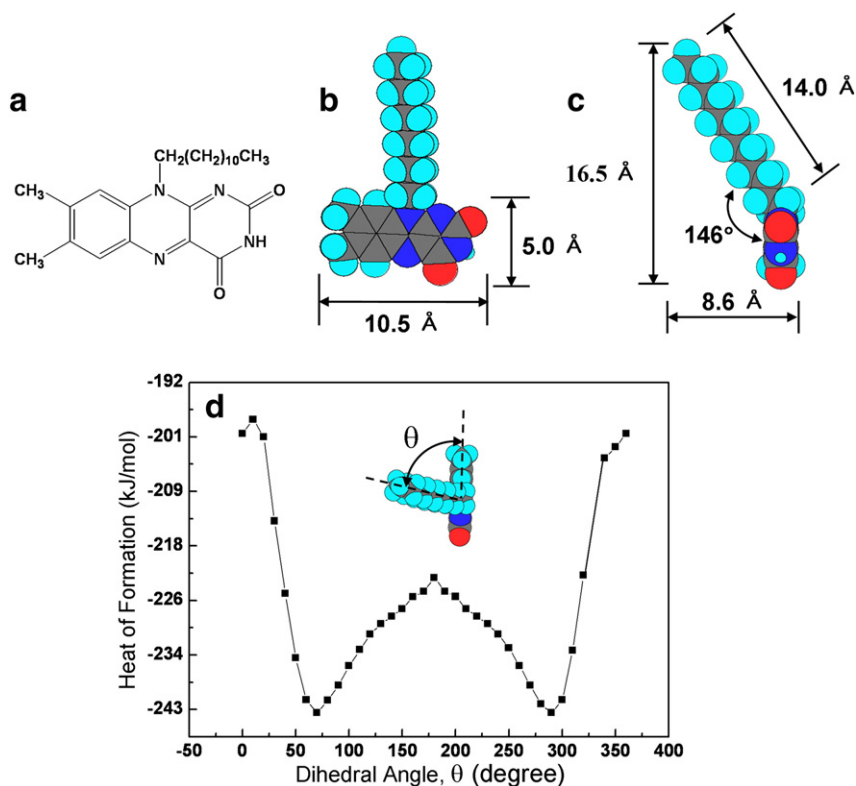

Fig. 1. (a) Molecular structure of DDI, (b, c) Space-filling model of DDI and its dimensions obtained from semi-empirical calculations, (d) energy profile of DDI depending on the dihedral angle between the hydrocarbon chain and isoalloxazine ring plane.