Unique fluorescence spectra of a disubstituted pyrene surfactant in Langmuir-Blodgett films

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Abstract

We first observed an unique pyrene (Py) emission from
10-(1-(6-hexyl)pyrenyl)decanoic acid (1,6-HPDA) Langmuir-Blodgett (LB) films. In
the fluorescence spectra of the 1,6-HPDA LB films, the normal bands of monomer and
excimer emission of Py were absent but the new structured emission band with peaks at

422, 448, and 473 nm was observed. Besides the intensity, the shape of the characteristic structured emission band at shorter wavelengths than normal excimers did not changed essentially on lowering the Py concentration in the LB monolayer from 100 mol% to 1mol%. The spectroscopic studies on HPDA LB films of a variety of Py concentrations suggested that a novel excimer responsible for the structured new emission would be efficiently formed by photo-excitation of a Py-Py pre-associated dimer in different manners than those of normal excimer formations.

Key words: disubstituted pyrene; pre-associate dimer; static excimer; Langmuir-Blodgett film

1. Introduction

In biophysical studies on conjugated molecular systems, fluorescence probe analysis is a powerful technique to investigate the structural and dynamic properties of biological molecules. As such a photophysical probe, pyrene (Py) has been widely used due to the features which make it suitable for use as an effective probe, notably the long lifetime, the medium sensitivity of the emission, and a great tendency to form excimer.

In biomembrane model systems, such as lipid bilayers, Langmuir-Blodgett (LB) monolayers, and so on, Py labeled phospholipids and Py terminated fatty acids are frequently used as excimer probes. As classically defined by Birks [1], an excimer formation and dissociation include diffusive processes. But, in addition to the dynamic formation of excimer, there are also instances where the excimer states are statically formed from pre-associated Py in the LB films [2, 3]. The static excimer emissions usually resemble the dynamic excimer emissions.

In the present study, we report very unique fluorescence emission spectra observed on LB films including a newly synthesized Py fatty acid, 10-(1-(6-hexyl)pyrene)decanoic acid (1,6-HPDA) (Fig. 1). The total length of the two substituents on Py ring of 1,6-HPDA corresponds to the length of the long chain fatty acid group of a reference compound, 16-(1-pyrenyl)hexadecanoic acid (PHA) (Fig. 1). Spectroscopic studies of PHA have been extensively performed in the form of LB films by Yamazaki et al. [2, 4]. The emission spectra observed on PHA LB films consist of a structured monomer band and a broad excimer band. On the other hand, in the unique emission spectra of 1,6-HPDA LB films, both monomer-like and excimer-like emission bands were almost absent but a novel structured emission band at shorter wavelengths than excimers was appeared. The novel emission should be attributed to a new aggregation of Py different

from normal Py dimers. In order to control the formation of this new aggregation, we diluted the lateral concentration of Py by adding arachidic acid (AA) as a spacer molecule to the 1,6-HPDA LB film. We studied spectroscopic behavior of the mixed 1,6-HPDA monolayers with AA at the Py concentrations of 100, 50, 10, 1, 0.5, 0.25, 0.05, and 0.025 mol%.

2. Experimental details

2.1 Materials

In most of the Py surfactants which have ever studied in the form of LB films, the chromophore have been introduced as a terminal group of a hydrocarbon chain. As a typical compound of such "termination-type", we synthesized PHA by following similar procedures reported by Sunamoto et al. [5]. In this study we newly synthesized 1,6-HPDA as an "insertion-type" in which the Py chromophore is inserted between two alkyl chains as shown in Fig. 1. The two substituents on the Py ring were introduced by repeating Friedel-Crafts acylation reaction twice, which afforded a mixture of three regioisomers (1,3-, 1,6-, and 1,8-disubstituted Py compounds). In our previous studies [6-9], we had used the regioisomeric mixture to fabricate LB films because of difficulties in purification. The emissions from the LB monolayers of the regioisomeric

mixture consisted of normal monomer and excimer emissions, which is probably due to the homogeneous dispersion of each regioisomer. In this study, we separated pure 1,6-HPDA from the regioisomeric mixture by column chromatography. The purity of the compound and the positions of the two substituents were confirmed by 270 MHz ^1H NMR. The detailed synthetic procedures of 1,6-HPDA will be described elsewhere. All other chemicals were of reagent grade and used as received. Quartz plates from Fujiwara Scientific Company were used for the substrates on which LB films were deposited.

2.2 Procedures

The monolayer LB films were formed with a Langmuir trough equipped with an electronic microbalance and a glass Wilhelmy plate (Kyowa Kaimenkagaku, HBM-AP). The quartz substrates were cleaned with chromic acid mixture. The subphase was pure water from a milli-Q system (Millipore Ltd.). The temperature of the subphase was maintained at 15 °C. The monolayers were spread from chloroform solutions containing 1,6-HPDA, and AA in the μM molar concentrations of 100, 50, 10, 1, 0.5, 0.25, 0.05, and 0.025 mol%. The compression speed of the monolayer was 14 $\text{cm}^2 \text{min}^{-1}$. The monolayers were deposited as Y-type films on both sides of the quartz substrates at the

constant surface pressure of 20 mN m⁻¹. The UV-vis absorption and the fluorescence spectra were taken with a Shimadzu UV-265FW recording spectrophotometer and a Jasco FP-777 recording fluorescence spectrophotometer, respectively. To protect compounds against photo-oxidation and decomposition, an entirely closed fluorescence cell equipped with quartz windows was employed. The oxygen free atmosphere can be easily obtained by flowing N₂ gas into the cell.

3. Results and discussion

Fig. 2 shows the surface pressure-area (π - A) isotherms of the 1,6-HPDA (solid curve *a*) and the PHA (solid curve *b*) pure monolayers. The π - A isotherms of the 10 mol% monolayers of 1,6-HPDA and PHA diluted are also represented by dashed curves *c* and *d*, respectively. The both solid curves of the pure monolayers show similar take-off area of ca. 0.4 nm² but the steep rise of surface pressure in the condensed phase was observed only with the 1,6-HPDA monolayer. PHA cannot give a stable pure monolayer so that the stabilization of the PHA monolayer by mixing with other inert surfactants such as AA is necessary for LB depositions at high surface pressures. On the other hand, the pure monolayer of 1,6-HPDA gave a high collapse pressure (ca. 30 mNm⁻¹) and could be easily transferred onto solid substrates. It is remarkable that the structural

change from termination-type to insertion-type significantly improve the monolayer stability.

The limiting area of the 1,6-HPDA pure monolayer estimated to be $0.36 \text{ nm}^2 \cdot \text{molecule}^{-1}$ is much larger than the size of the hydrophilic group, therefore the area of the 1,6-HPDA monolayer would be determined by the lateral size of the Py chromophore group arranged on the surface. The cross-sectional area of the chromophore in a side-on arrangement (Fig. 3), with which the chromophores lie with the molecular planes parallel to the monolayer plane is ca. 0.67 nm^2 , whereas in a edge-on arrangement, with which the chromophores stick with their molecular planes perpendicular to the monolayer plane, the cross-sectional area is ca. $0.23 \sim 0.30 \text{ nm}^2$. Considering the limiting area deduced from the π - A isotherms, the chromophore arrangement in the 1,6-HPDA monolayer is close to the side-on arrangement.

The UV-vis absorption spectra of the 10 mol% LB films of 1,6-HPDA and PHA (solid and dashed curves, respectively) deposited on quartz substrates (35 layers on both sides) are shown in Fig. 4. In the wavelength region in this figure, ${}^1\text{L}_b$, ${}^1\text{L}_a$, and ${}^1\text{B}_b$ bands of Py absorption appear in the order from higher to lower wavelength [10]. The red-shift of the solid curve, which is obvious at the ${}^1\text{L}_b$ and ${}^1\text{B}_b$ bands around 380 and 285 nm, respectively, was also observed with solution systems where PHA and

1,6-HPDA are molecularly dissolved, therefore it should be due to the addition of the second alkyl group in Py ring. The broad absorption band around 320 ~ 370 nm of each curve corresponds to the 1L_a band. Small but significant peaks at 331 and 347 nm in the 1L_a band observed on the PHA LB film correspond to monomer absorption of Py, whereas they are almost disappeared in the 1L_a band observed on the 1,6-HPDA LB film. The remarkable broadening of the 1L_a band observed on the 1,6-HPDA LB film clearly indicates the existence of ground state association of the Py group.

With regard to absorption coefficients, large hyperchromic effects of the 1L_b and 1B_b bands are observable on the 1,6-HPDA LB film. In the absorption measurements of these spectra, the incident lights were directed perpendicularly to the film planes. The transition dipoles of the 1L_b and 1B_b bands are polarized across the long axis of Py chromophore, on the contrary, that of the 1L_a band is polarized along it. Considering the hyperchromic effects and the direction of the incident light, we can expect that an edge-on like arrangement where the long axis of the pyrenyl chromophore is near perpendicular to the film surface are achieved in the 1,6-HPDA LB film more regularly than in the PHA LB film. Although not shown, the absorption profile of the 10 mol% 1,6-HPDA LB films shown in Fig. 4 did not change essentially even at the Py concentration of 1 mol%. This indicates that the arrangement and the pre-association

state of Py chromophore should be kept at such lower concentration.

In Fig. 5, fluorescence spectra of 1,6-HPDA LB films at a variety of chromophore concentrations (100, 50, 10, 1, 0.5, 0.25, 0.05, and 0.025 mol%) are summarized. As a reference, fluorescence spectrum of the 10 mol% PHA LB film is also shown. The spectral feature of the excimer emission in the fluorescence spectra of the PHA LB film characterized by a structureless band centered around 470 nm have been normally observed on many LB films of Py fatty acids [2, 11]. At the lower wavelength region, a structured monomer emission band with peaks at 381 and 401 nm is also observed with the PHA LB film. On the other hand, the fluorescence spectra of 1,6-HPDA LB films at higher concentrations are quite unusual. A conspicuous structured emission band with peaks at 422, 448, and 473 nm is observed, whereas the normal bands of monomer and excimer are almost disappeared. It suggests that the most of the Py chromophores in the 1,6-HPDA LB films form pre-associated Py dimers or higher aggregates in different manners than those of excimer formations. At the wavelength region around 420 nm, a broad structureless emission band had been observed by time-resolved fluorescence spectra of stearic acid LB films doped with PHA [2] and of an aqueous solution of Py-labeled hydroxypropyl cellulose [12]. But the blue shifted excimer band vanishes in longer time domain, so that there was no contribution to the steady state fluorescence

spectra. The structureless emission band at 420 nm observed on these studies was assigned to a higher energy excimer species with only partial overlap of the Py moieties [2]. The partial excimer-like emission was also observed in steady state fluorescence spectra of stearic acid LB films doped with nonamphiphilic Py [13], but the much broadened structureless fluorescence band had substantial intensities even at the longer wavelength range of the normal sandwiched excimer emission. There were still instances where a structured emission band at longer wavelength than 420 nm was reported [14]. In that study a structured emission band with peaks around 450, 480, and 510 nm, was observed on vacuum-deposited films of Py terminated fatty acids. In the emission spectra, monomer and excimer bands were still remained and the structure around 450 ~510 nm was not so fine as that we observed here. According to our best knowledge, a structured emission band of Py around 420 ~ 470 nm have never reported before. The novel association of Py responsible for the structured emission band around 420 ~ 470 nm is remarkable for its efficient formation even at 0.5 mol% Py concentration. But further dilution of the 1,6-HPDA LB film from 0.5 to 0.025 mol% caused dramatic fluorescence changes as shown in Fig. 5. At the beginning concentration of 0.5 mol%, the monomer peaks at 382 and 402 nm are only slight. Then they immediately grow with the dilutions. Considering the trade-off between the

decrease of the structured emission band around 420 ~ 470 nm and the increase of the monomer emission band with the further dilutions to such low concentrations, no higher aggregate than a pre-associated dimer of Py is likely to responsible for the structured emission band around 420 ~ 470 nm. The structured emission of the pre-associated Py-Py dimer suggests that the deactivated Py-Py dimer can complete a vibrational cycle without its dissociation [15]. Although much remains to be elucidated about the dimer structure, it must be stabilized enough for the static deactivation in the LB films.

4. Conclusions

In this study, we synthesized and isolated 1,6-HPDA. The 1,6-HPDA monolayer was much stable than the PHA monolayer on a water surface. The fluorescence spectra observed on 1,6-HPDA LB films were strikingly different from those observed on PHA and other conventional pyrenyl surfactants. The unique fluorescence spectrum consisted of a fine structured emission band with peaks at 422, 448, and 473 nm. Besides the intensity, the shape of the emission spectrum did not change over a wide Py concentrations from 1 to 100 mol%. The spectroscopic studies suggested that some static Py excimer responsible for the new emission band is efficiently formed within the 1,6-HPDA LB films even at the low Py concentration of 0.5 mol%. The π -A isotherm of

the 1,6-HPDA monolayer indicated that the Py chromophores are arranged in the edge-on like manner. Efforts are underway to investigate the molecular configuration of the static Py excimer.

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Figure captions

Figure 1. Structural formulae of 1,6-HPDA, PHA, and AA..

Figure 2. Surface pressure-area (π -A) isotherms for (a) 1,6-HPDA and (b) PHA pure monolayers, and for (c) 1,6-HPDA and (d) PHA mixed monolayers with AA (10 mol%).

Figure 3. Side-on and edge-on arrangements of 1,6-HPDA on monolayer surfaces.

Figure 4. Absorption spectra of 1,6-HPDA and PHA (solid and dashed curve, respectively) in mixed LB films with AA (10 mol%)..

Figure 5. Fluorescence spectra of 1,6-HPDA LB films at the concentrations of 100, 50, 10, 1, 0.5, 0.25, 0.05, and 0.025 mol% and of 10 mol% PHA LB film.

Figure(1)

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Figure(2)

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Figure(5)

Fig. 5 Fluorescence spectra of 1,6-HPDA LB films at the concentrations of 100, 50, 10, 1, 0.5, 0.25, 0.05, and 0.025 mol% and of 10 mol% PHA LB film...