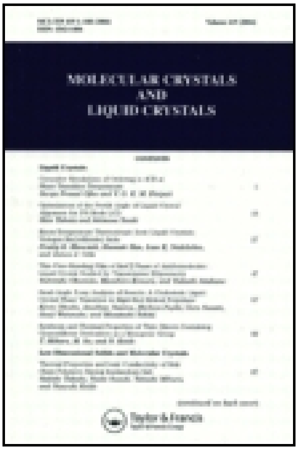

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Preparation of Organic Thin Films of Stearic Acid/Pyrazoline Nanoparticles by Langmuir-Blodgett Technique

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The organic thin films of stearic acid/pyrazoline nanoparticles were prepared by transferring Langmuir monolayer of stearic acid/pyrazoline nanoparticle onto the solid substrate. The Langmuir behavior of stearic acid/pyrazoline nanoparticle complex was studied with pressure-area isotherm at the air/water interface. The prepared Langmuir-Blodgett film was identified with linearly increasing optical absorbance around 370 nm by increasing the number of deposited layers. The surface morphology of the LB film was observed with AFM. The dispersion of pyrazoline nanoparticle in the thin film was studied with TEM.

Keywords: Langmuir monolayer; organic thin film; pyrazoline nanoparticles

INTRODUCTION

Nanoparticles of semiconductors and metals have been an extremely active area of research because of their interesting quantum confinement effect on optical and electronic properties [1]. However, studies of organic nanoparticles have been paid little attention. But it is a tendency to extend the research on nanoparticles into organic material, especially into general organic molecules due to their diversity [2,3]. As far as the application is concerned, organic nanoparticles are expected to hold

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the higher potentials because organic nanoparticles allow much more variability and flexibility in materials synthesis and nanoparticle preparation. Investigations on the organic nanoparticles, however, are only at their very initial stages presently.

Formation of ordered thin films of uniform nanoparticles provides a route to new nanostructured materials. The Langmuir-Boldgett (LB) technology is a suitable technique allowing the manipulation of materials at the molecular level and the fabrication of ultra-thin and highly ordered organic films. In the LB method, a thin molecular layer spread at the air/water interface (Langmuir monolayer) is transferred on to a solid substrate, the process can be repeated several times with the same substrate to form multiplayer films [4,5].

LB films have great scientific value and applications. In addition, new electrical, magnetic, photoelectricity, and chemical properties have been found for some materials prepared in nano-crystalline form. Nano-particle/macro-molecular composite films prepared with the LB technique are expected to possess superior properties.

Organic nanoparticles of 1-phenyl-3-naphthyl-5-((dimethylamino)-phenyl)-2-pyrazoline with sizes ranging from tens to hundreds of nanometers were prepared by the reprecipitation method. Their excitonic transitions responsible for absorption and emission, as compared with those of dilute solution, have been investigated as a function of nanoparticle size. We found that pyrazoline nanoparticles possess a special size dependence in their optical properties [6].

In this study, the thin films of stearic acid/pyrazoline nanoparticles were prepared by the Langmuir-Boldgett technique. The Langmuir behavior of the monolayer at the air/water interface was studied in terms of the equilibrium pressure-area isotherm. The fabrication of the LB films was characterized with FT-IR, UV-vis, TEM and AFM.

EXPERIMENTAL

Materials

4-(Dimethylamino)aldehyde, sodium ethoxide, 2′-acetonaphthone, phenyl-hydrazine and stearic acid were purchased from Aldrich Chemical Co. and used without any further purification. All solvents were obtained from Junsei Chemical Co. and used without further purification. House-distilled water was passed through a four-cartridge Barnstead Nanopure II purification system consisting of macropure pretreatment, organic-free) for removing trace organics, two-ion exchangers and 0.2 mm hollow-fiber final filter for removing particles. Its resistivity was 18.3 MΩ and used in all the experiments.

Preparations of Pyrazoline Nanoparticles

1-Phenyl-3-naphthyl-5-((dimethylamino)phenyl)-2-pyrazoline was synthesized according to the previous report [6] and conformed by NMR and MS. Its molecular structure is shown in Figure 1. The fabrication procedure of pyrazoline nanoparticle was previously reported [6].

Methods

The pressure-area isotherm of stearic acid in pure water and water dispersion of pyrazoline nanoparticles (40 nm) were obtained with a KSV Mini-through operated at room temperature. The preparations of Langmuir-Boldgett films of stearic acid/pyrazoline nanoparticles were carried out by transferring Langmuir layers at a surface pressure of 20 mN/m onto ZnSe and quartz plates for FT-IR and optical absorption spectroscopy studies. The experimental set-up is shown in Figure 2. The optical absorption and FT-IR spectra were recorded with a Varian Carry UV-vis spectrophotometer and a Hitachi model U-3210 spectrometer, respectively. The dispersion of pyrazoline nanoparticle in the thin film was studied with TEM (Hitachi S-2400, Japan). The surface morphology and top view image of the film surface was obtained with AFM (Multimode SPM, Digital Instruments, USA).

RESULTS AND DISCUSSION

Figure 3 shows the surface pressure-area isotherm for stearic acid on the subphase of pure water (a) and water dispersion of pyrazoline

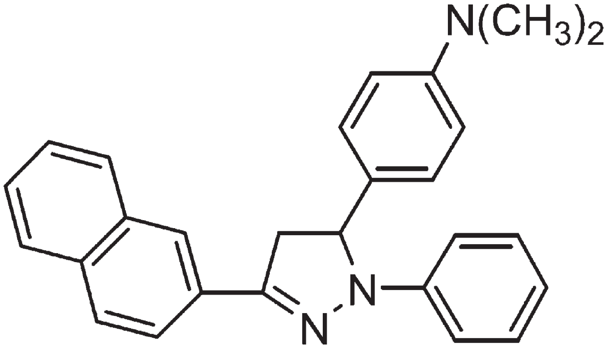


FIGURE 1 The molecular structure of 1-phenyl-3-naphthyl-5-((dimethylamino)phenyl)pyrazoline.

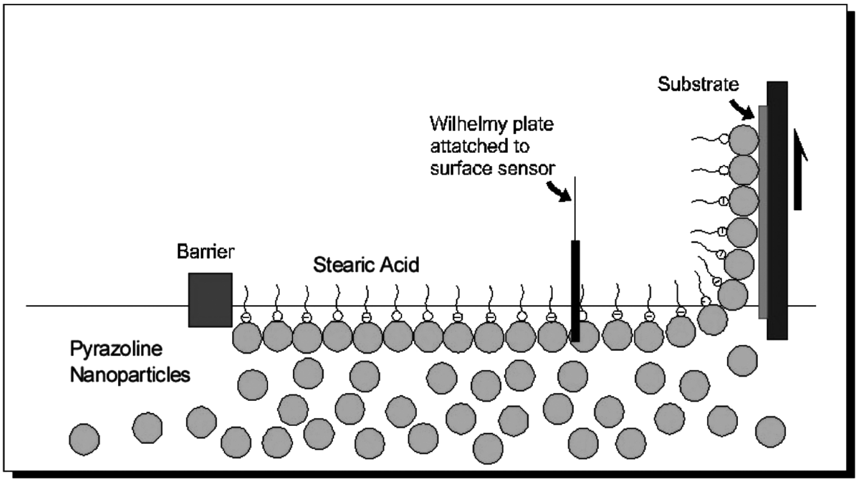


FIGURE 2 Schematic drawing of Langmuir-Blodgett deposition of stearic acid/pyrazoline nanoparticle complex monolayer at the air/water interface.

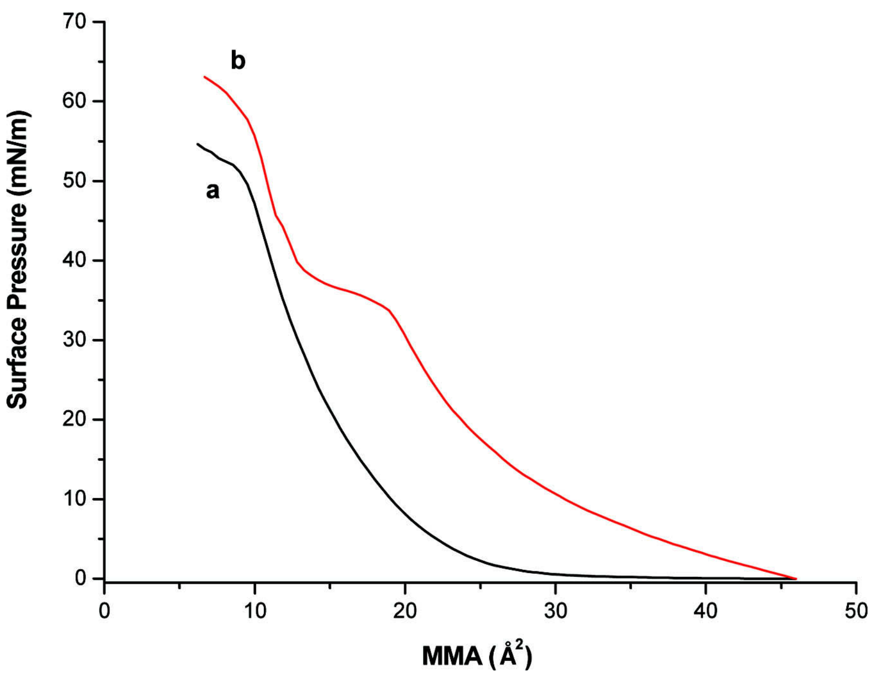


FIGURE 3 (a) Surface pressure-area isotherm for stearic acid on the subphase of pure water (b) and water dispersion of pyrazoline nanoparticles.

nanoparticles (b). The isotherm of stearic acid on the water dispersion of pyrazoline nanoparticles was more expanded than on the pure water. This indicates that the complex of pyrazoline nanoparticle with carboxylate of the stearic acid possibly expands the monolayer at specific mean molecular area compared with the pure water because of large particle size of pyrazoline nanoparticle. The same trend was observed for positively charged γ-Fe_2O_3 nanoparticles interacting with a Langmuir monolayer of a stearic aicd at the air/water interface [7].

Figure 4 shows the FT-IR spectra of Langmuir-Blodgett films of stearic aicd deposited from Langmuir monolayers on the pure water and on the water dispersion of pyrazoline nanoparticles. 100 layers were deposited with transfer ratio of 1.0 at 20 mN/m surface pressure and room temperature. The LB film of stearic acid prepared on a pure water subphase shows an absorption peak around 1700 cm^{-1}. This absorption peak indicates the presence of the carboxylic acid groups

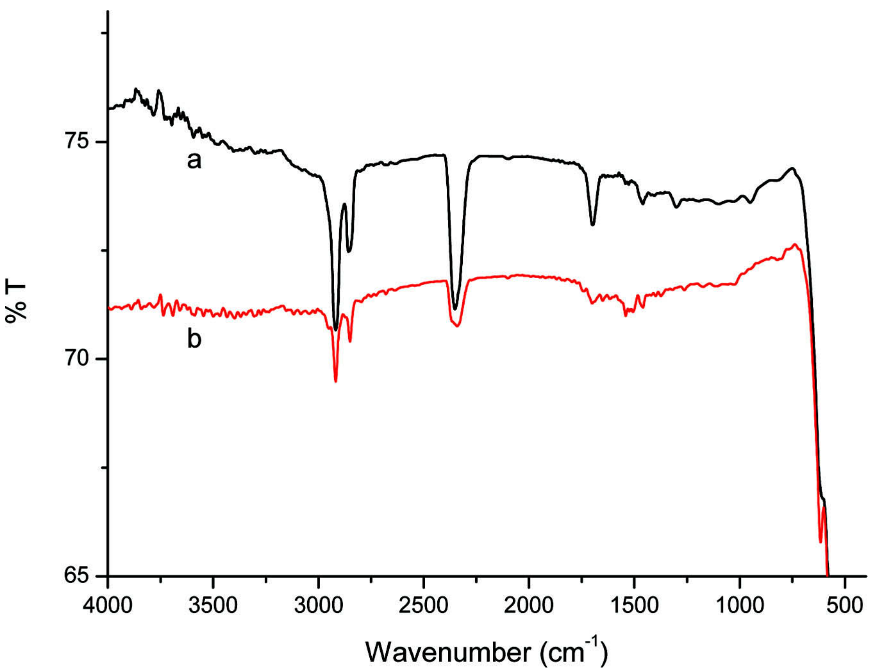


FIGURE 4 FT-IR spectra of LB films of stearic acid (a) and stearic acid/pyrazoline nanoparticle complex (b). The number of monolayers in LB film was 100.

for the LB film of stearic acid. The intensity of the carbonyl stretching vibration was reduced significantly and the peaks of 1540 and $1500\,cm^{-1}$ were appeared in the LB film of stearic acid/pyrazoline nanoparticles. This indicates that most of the COOH groups in the films have been conserved from the monolayer. It is interpreted as the complexation between the carboxylic group and pyrazoline nanoparticle was formed by hydrogen bonding.

The UV-vis spectra for LB films of stearic acid/pyrazoline nanoparticles and the optical absorption density data with the number of monolayers are shown in Figure 5. The UV-vis spectrum of LB films obtained from Lagmuir layers on a pure water subphase did not show any absorption band. The deposition of the Langmuir monolayer to solid quartz plate substrates was carried out with a transfer ratio of 1.0. The spectra show a linear increase of the optical absorption density around 370 nm with an increasing number of layers of stearic acid/pyrazoline nanoparticles.

The dispersion of pyrazoline nanoparticle in the LB film of stearic acid/pyrazoline nanoparticle was studied with TEM image as shown in Figure 6. The TEM image of the LB film deposited one layer onto copper grid shows the almost homogeneous dispersion. This is caused

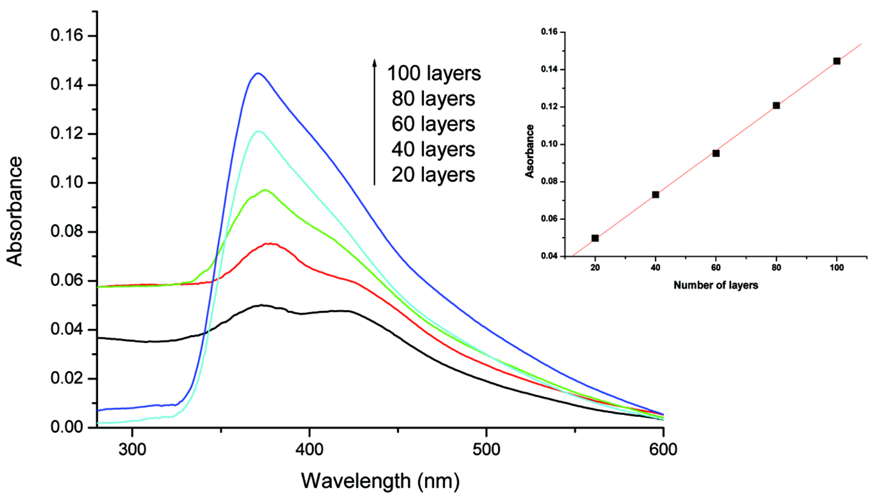


FIGURE 5 UV-vis spectra LB films of stearic acid/pyrazoline nanoparticle complex of 20, 40, 60, 80 and 100 multilayers. The inset shows the optical absorbance versus the deposited number of layers at 370 nm.

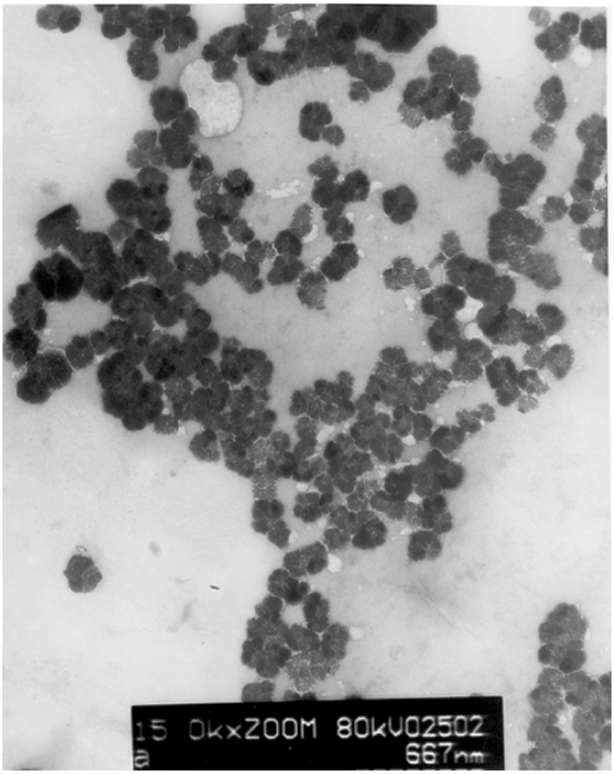
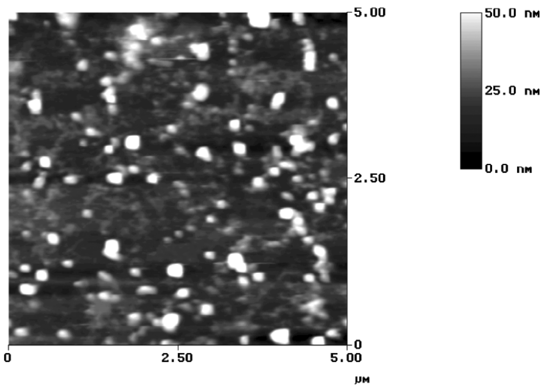


FIGURE 6 TEM image of LB film of stearic acid/pyrazoline nanoparticle complex deposited onto copper grid with one layer.

by the hydrogen bonding between carboxylic group of stearic acid and pyrazoline nanoparticle. The previous study already reported on the homogeneous dispersion of inorganic nanoparticle with stearic acid [8]. The homogeneous dispersion of nanoparticle resulted in a single domain of an isolated particle between stearic acid layers. The stacking of pyrazoline nanoparticle between stearic acid layers by increasing deposition number is consistent with increasing optical absorption of pyrazoline nanoparticle in the LB films.

The surface morphology of the LB film of stearic acid/pyrazoline nanoparticle was characterized with AFM. The surface morphology and top view of the one layer deposited LB film of stearic acid/pyrazo-pyrazoline nanoparticle are shown in Figure 7. The surface morphology shows the peaks corresponding to the pyrazoline nanoparticle coated with stearic acid. The LB film of stearic acid/pyrazoline nanoparticle

(A)



(B)

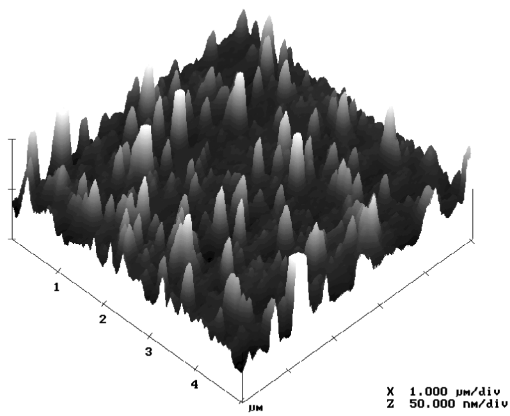


FIGURE 7 Three-dimensional surface morphology (A) and top view on the surface image (B) of LB film of stearic acid/pyrazoline nanoparticle complex deposited onto glass surface with one layer obtained AFM.

with one layer was deposited well on the glass surface homogeneously. The surface covered by pyrazoline nanoparticles with stearic acid in the LB film showed a well-formed surface morphology. The peak size is approximately consistent with diameter of pyrazoline nanoparticle determined with Dynamic Light Scattering (DLS) and TEM image. The DLS and TEM studies were reported in the previous report [7]. Also the top view image of the one layered film shows the distinct single domains of the pyrazoline nanoparticle.

CONCLUSIONS

The organic thin film of stearic acid/pyrazoline nanoparticle was successfully prepared by the Langmuir-Blodgett technique. The hydrogen bonding of pyrazoline nanoparticle with stearic acid resulted in an homogeneous dispersion of pyrazoline nanoparticle in the stearic acid. The dispersion of pyrazoline nanoparticle in the LB film was well investigated with TEM image, AFM morphology and top view image.

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