

MIXED LANGMUIR-BLODGETT FILMS OF CU-3,5-BISTETRABUTYL PHENYLPORPHYRIN, ARACHIDATE ACID AND HEXATRIACONTANE IN ORDINARY ENVIRONMENT: A UV VISIBLE STUDY

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Abstract. The study of mixed Langmuir-Blodgett Films multilayer was conducted in ordinary experiment conditions by using metallo-porphyrin derivative (3,5-bistetra-butyl-phenylporphyrin with Cu as central metal) and arachidate acid with and without trigger molecule, hexatriacontane. We demonstrated that the mixed multilayer which consist of 4, 20 and 40 layers for each mixed solution (molar ratio porphyrin : arachidic acid : hexatriacontane, 1,5 : 10 : r, where r is 0, 0.5) successfully transfers into glass plates as Langmuir-Blodgett Films and characterized the transferred films using UV visible spectroscopy. The area per monolayer porphyrin molecule is approximately 15-21 Å². The first mixed solution (porphyrin : arachidic acid) produced good multilayer while the second mixed solution (porphyrin : arachidic acid : trigger molecule, hexatriacontane) did not produce 20 and 40 layers as it was expected. Some possible problems such as cleanliness, isotherms condition and compression speed of forming multilayer will be discussed.

Key words: Langmuir-Blodgett Films, multilayer, Cu-3,5-bistetra-butyl phenylporphyrin

Abstrak. Telah dilakukan studi terhadap multilapis film Langmuir-Blodgett pada kondisi eksperimen sehari-hari menggunakan campuran Cu-3,5-bistetra-butyl fenilporpirin, asam arakidat dengan dan atau tanpa inisiator, heksatriakantone. Campuran multilapis film (perbandingan molar porpirin : asam arachidic : heksatriakantone, 1,5 : 10, r, dimana r = 0, 0,5) terdiri dari 4, 20 dan 40 lapis berhasil di transfer ke atas kaca preparat sebagai Langmuir-Blodgett film dan dilakukan karakterisasi dengan spektroskopi sinar tampak (*UV-visible spectroscopy*). Luas daerah per molekul porpirin adalah 15-21 Å². Campuran pertama (porpirin : asam arakidat) memberikan multilapis yang baik, sedangkan campuran dengan adanya inisiator tidak menghasilkan 20 dan 40 lapisan seperti prediksi. Beberapa kemungkinan penyebab hasil tidak optimum seperti tingkat kebersihan (*cleanliness*), kondisi isothermal dan kecepatan kompresi saat pembentukan multilapis film akan di bahas.

Kata-kata kunci: Langmuir-Blodgett Films, multilapis, Cu-3,5-bistetra-butyl-phenylporphyrin

1. Introduction

Porphyrin derivatives, especially metallo-porphyrin thin films prepared by Langmuir Blodgett Films and other methods (e.g. spin coating and vapor deposition) have very interesting properties which attract many scientists to work further in the films. These interesting properties are include electrical properties (organic conduction), optical properties (e.g. nonlinear optical and photoconduction) and chemical properties. Recently, some of these interesting properties have been explored as a series of potential application such as gas sensor and photocatalysts [1,2], photovoltaic cell [3] and some molecular electronic devices [4,5]. Another reason why metallo-porphyrin derivatives get high attention is that they are relatively easy to synthesize with several different well-defined substituted groups [6]. These groups may lead to difference molecular orientation when metallo-porphyrin derivatives were deposited in thin Films. The arrangement of molecules in the thin films or molecular orientations of Langmuir Blodgett Films have been reported

can change the film properties, exemplified by the changes of the photovoltaic effects as molecular orientation varied [7].

Several spectroscopic techniques have been mainly used to investigate the structures of porphyrin molecules in thin films: X-ray absorption fine structure (NEXAFS) spectroscopy [8], electron spin resonance spectroscopy [9], FTIR, Raman spectroscopies and UV-visible [10,11]. Various reports have also been published to explain the structure of metallo-porphyrin derivatives in thin films based on several techniques above. Bulkowski and co-worker [12] have investigated tetraphenylporphyrin (Fig. 1.A) and its derivatives ($R_1 = H$; $R_2 = H$ and $M = Co$ or Zn) using absorption and fluorescence spectroscopy. They found that the stability of the films or the collapse pressure is 40 mNm⁻¹ after the materials form multilayer and the isotherms give an extrapolated area of only 13-17 Å² per molecule. This area was contrast with the expected value of 160 Å² if the molecules lay flat on the surface (in plane) and 70 Å² for

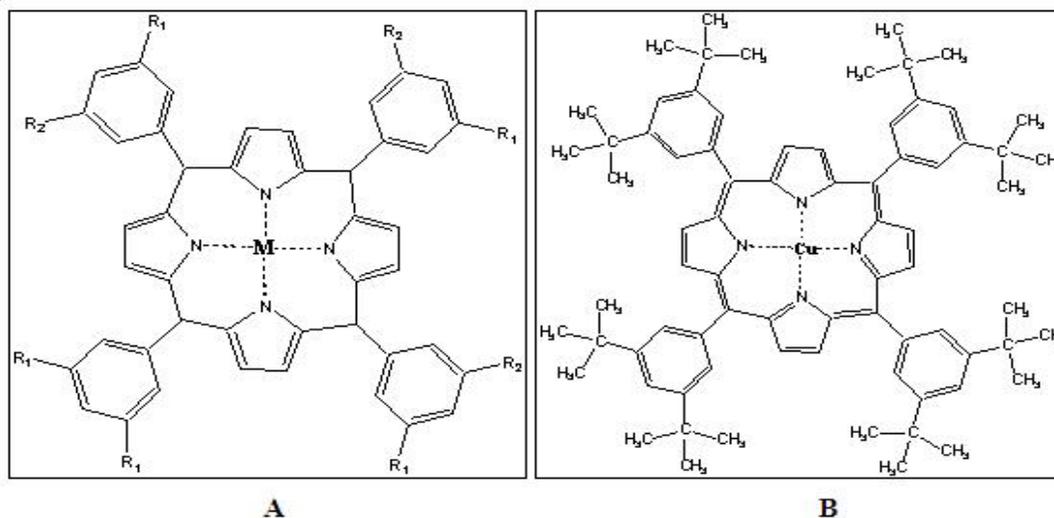


Fig. 1. (A) Structure of tetraphenylporphyrin derivatives [6] (B) structure of Cu-3,5-bistetra-butyl phenylporphyrin.

vertical array (out plane) of the molecules. Another group, Whitten *et al* [13], using the same material as Bulkowski's group but with $M = \text{Mg}$. This material gives surface area of 66 \AA^2 per molecule, which is almost similar with value of a monolayer of vertical molecules. However, the collapse pressure decreases 15 mNm^{-1} .

The present work describes the use of UV visible spectroscopy to investigate the structures of multilayer LB films of Cu-3,5-bistetra-butyl phenylporphyrin (Fig. 1B) mixed with arachidate acid with and without trigger material (molar ratio porphyrin : arachidic acid : hexatriacontane, 1,5 : 10 : r, where r is 0, 0.5). The results show that the area per porphyrin molecule relatively small comparing to some references.

2. Experimental Details

Materials. The synthesis of the porphyrin, Cu-3,5-di-tetra butyl phenyl porphyrin, has been described elsewhere [14], arachidic acid (99+ %) and hexatriacontane (Sigma). For spreading, the monolayer materials were dissolved in chloroform (Merck, spectroscopy grade) and each spread is $30 \frac{1}{4} \text{ L}$. The subphase was a solution of $4 \times 10^{-4} \text{ M CdCl}_2$ (Sigma, A.R) and $0.5 \times 10^{-4} \text{ KHCO}_3$ (Aldrich, A.R) in water. Glass plates were used as substrates for LB deposition. After cleaning by salination procedure, all plates were kept in an environment of 1 % 3-aminopropyltrimethoxy-silane (APTMS) for 10 minutes to create hydrophobic surfaces [15].

Film Formation. Monolayers were spread on subphase solution in the LB instrument and compressed. Surface pressure-molecular area ($-\text{\AA}^2$) isotherms and LB films were obtained at $22.0 \text{ }^\circ\text{C}$. LB films of Cu-3,5-di-tetra butyl phenylporphyrin, arachidic acid and hexatriacontane were prepared on the hydrophobic plates at a surface pressure control of -14.56 mNm^{-1} and a dipping rate of 0.1 mm s^{-1} . The transfer ratio on upstrokes was 10 mm/min and downstrokes was approximately 15 mm/min . After the first two layers have been deposited, the deposition speed was

increased to 25 mm/min . Four, twenty and forty layers were deposited for each solution of the LB films.

UV visible spectroscopy. The UV-vis spectrums were recorded on a Shimadzu UV spectrophotometer. The instrument conditions: Dual Beam Mode, UV-Vis Scan Rate = 9600.00 nm/min , UV-Vis Data Interval = 2.00 nm and UV-Vis Average Time = 0.0125 sec .

3. Result and Discussion

3.1. Pressure-area isotherms of monolayer

The isotherms (fig. 2) displayed the characteristic features of solid, liquid and gas phases during the formation of monolayer. At the surface area $\pm 15\text{-}17 \text{ \AA}^2$ there is an increasing of slope which clearly due to a phase change to an ordered of solidlike arrangement of two dimensional array of molecules. When the Cu-3,5-di-tetra-butyl phenylporphyrin molecules start to form good monolayer, extrapolation the linear portion of the line to zero surface pressure in which the intercept gives the area per Cu-3,5-di-tetra-butyl phenylporphyrin molecule. The isotherms data

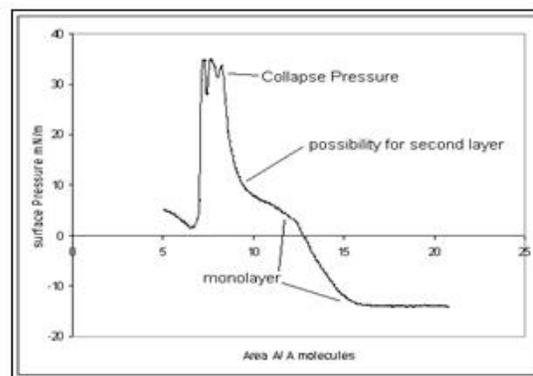


Fig.2. Isotherm for a Langmuir monolayer of Cu-3,5-bistetra-butyl phenylporphyrin

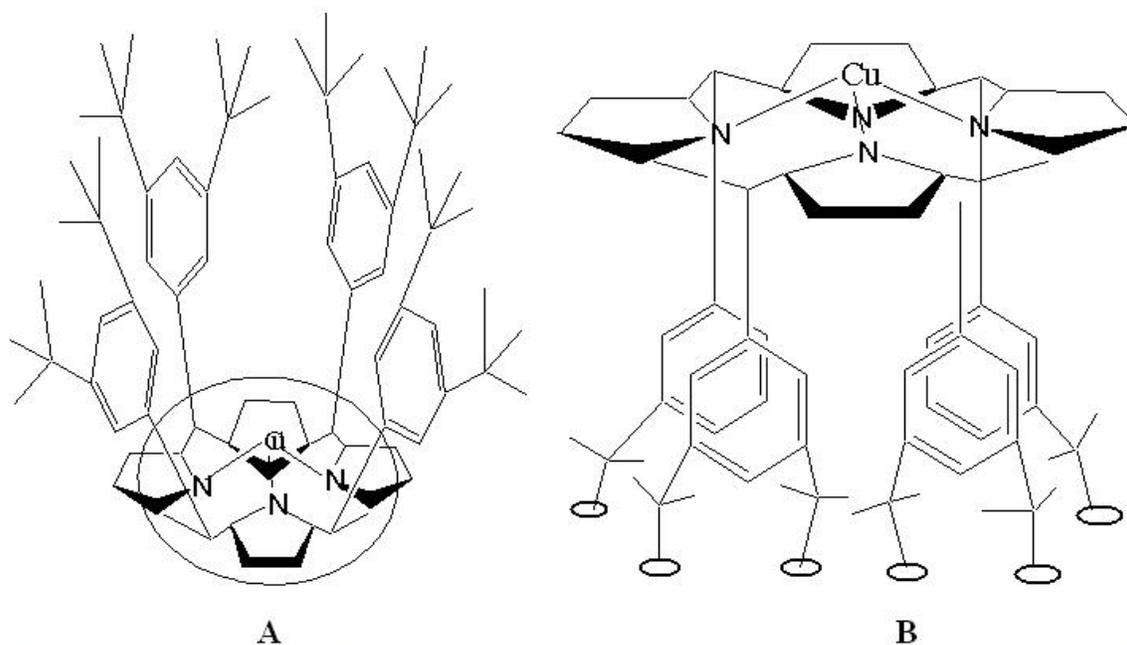


Fig.3. Schematic illustrations of in-plane (A) and out-of-plane (B) configuration of Cu-3,5-bistetra butyl phenylporphyrin moiety. The circular black line is the area of a single molecule of Cu-3,5-bistetra butyl phenylporphyrin when its stick to the surface. (This illustrations ignoring the possibility of steric effect)

was taken at starting point (constant pressure control) equal to -14.56 mNm^{-1} so that the line extrapolation to zero surface pressure is relatively difficult to achieve.

The area occupied by porphyrin molecule is calculated $\pm 15\text{-}21 \text{ \AA}^2$. From this small area obtained, it is predicted that

porphyrin molecule orientation is not lay flat on the surface (in plane orientation) but perform out plane orientation (Fig. 3.B). The reason for this estimation is that several references reported that the area of a porphyrin molecule is 225 \AA^2 ($15\text{\AA} \times 15\text{\AA}$) if this molecule lay flat on the surface. Moreover,

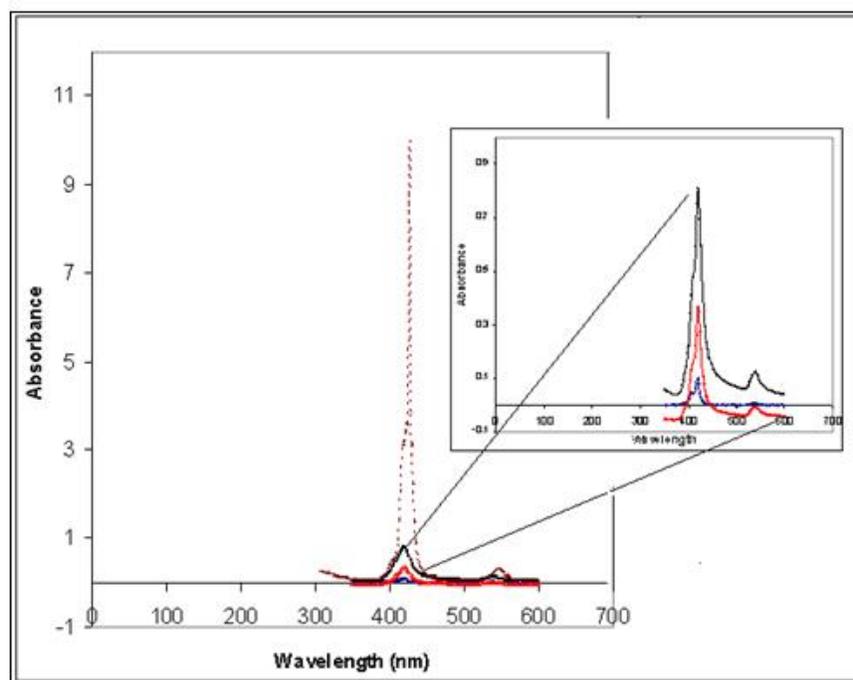


Fig. 4. UV-vis spectrum of four (shift 1), twenty (shift 2), forty-layer (shift 3) LB films of Cu-3,5-bistetra butyl phenylporphyrin without hexatriocontane on hydrophobic plates. For comparison purpose, a UV-vis spectrum of Cu-3,5-bistetra butyl phenylporphyrin in chloroform solution (bulk solution) is also plotted (shift 4).

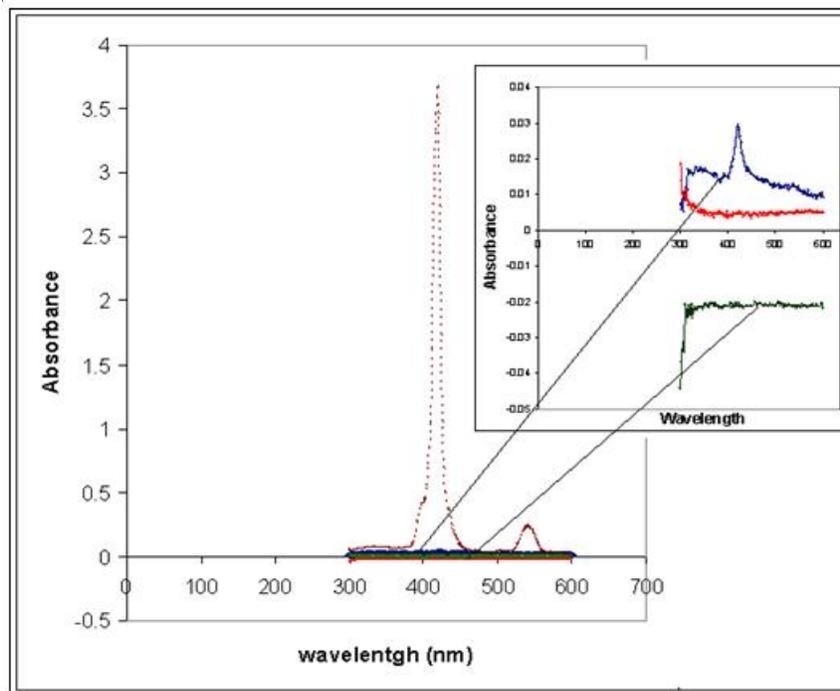


Fig. 5. UV-vis spectrum of four (shift 1), twenty (shift 2), forty-layer (shift 3) LB films of Cu-3,5-bistetra-butyl phenylporphyrin the present of hexatriocontane on hydrophobic plates. For comparison purpose, a UV-vis spectrum of Cu-3,5-bistetra-butyl phenylporphyrin chloroform solution (bulk solution) is also plotted (shift 4).

the out plane orientation leading to porphyrin molecules form Y type deposition. A collapse-point of approximately 30-35 mN m⁻¹ was observed for these films.

Comparing the experiment results with another reference which was conducted in ultra clean environment, there are

3.2. UV-Vis Characterization

Figures 4 and 5 show UV Vis absorption of four, twenty and forty layer LB Films of Cu-3,5-bistetra-butyl phenylporphyrin with and without trigger molecule,

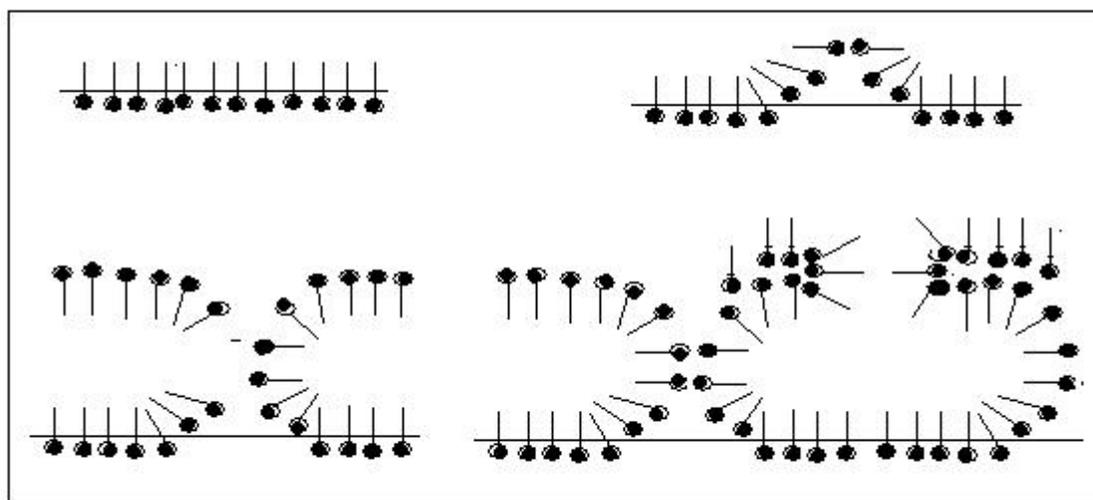


Fig. 6. Collapse of a monolayer [6].

significant differences. Gentle and co-worker¹⁴ reported that the area of per Cu-porphyrin derivatives molecule is 124 Å² when the material perform out plane orientation, consistent with the value obtained from surface pressure-area measurements on the floating monolayer. This condition will be discussed after UV-Vis Characterization

hexatriocontane on highly hydrophobic glass plates. For comparison purpose, a UV-vis spectrum of each bulk solution of Cu-3,5-bistetra-butyl phenylporphyrin in chloroform is also plotted. All absorbance peaks are produced at 419.9 nm which indicate a specific absorbance of porphyrin molecules (approximately 410-430 nm).

Furthermore, the color change of plate substrates appeared when the multilayer was formed (into pink color), the original color of porphyrin molecules. The peaks and the color change demonstrate that four, twenty and forty layer LB films are successfully produced.

As a number of layer increase, the absorbance are also increase. From figure 5, it can be seen that the absorbance of four layers is 0.101 and continuous to increase for twenty and forty layers (0.368 and 0.809). The bulk solution has the highest value of absorbance (10.19) which shows a significant difference with each layer absorbance in LB films. The concentrations of porphyrin molecules are responsible for this absorbance behavior. The bulk solution of porphyrin has the highest concentration of porphyrin molecules so that it will absorb more UV visible light comparing with the four, twenty and forty layers of porphyrin molecules at LB films. However, figure 6 shows that there is no shift or peak for twenty and forty layer which demonstrate that no layers are formed.

3.3. Ordinary environment experiment

Generally, in order to get optimum results, the LB films experiment was held at the ultra-clean environment where all conditions were controlled perfectly. However, this experiment was conducted in ordinary environment where many things such as ambient temperature, pressure and particles (e.g dust) may disturb the experiment conditions. When floating on the subphase, dust produce different result of surface pressure (change the isotherms condition) and also destroy the monolayer structure or lead to monolayer collapse.

Compression speed also play important role for achieving good layer on subphase and plate substrates [6]. If the compression speed was to fast, the layer would overlap to each other or riding on top of each other and formed disordered multilayer, leads to layer collapse. In this experiment, the compression speed was 25 mm/min. Some references use a constant speed while forming multilayer, approximately 10-15 mm/min. This is probably another reason optimum results were not obtained. Fig. 6 shows a monolayer collapse due to inappropriate compression time or speed.

The present of trigger molecule, hexatriocontane (long alkyl chain) seem disturbed the film formation. Figure 6 clearly shows that twenty and forty layers were not formed when hexatriocontane presents in the solution. It suspected hexatriocontane with long alkyl chain and less steric effect ("slimmer" molecule than Cu-3,5-di-tetra butyl phenyl porphyrin molecule) stacked first into the hydrophobic plate substrates and formed layer. As a result, the formation of twenty and forty layer was not performed. However, Gentle and co-worker [14] reported that addition of a trigger (such as hexatriocontane) to the mixed films only disturbed the orientation of the domains in the direction normal to the surface of the LB film and did not stop the films formation. It means that it is still not clear for us whether trigger molecule responsible for zero formation of multilayer or others in this experiment. It clearly needs further experiments.

4. Conclusion.

The mixed Langmuir-Blodgett Films consists of Cu-3,5-di-tetra-butyl phenylporphyrin and arachidate acid with and without hexatriocontane have successfully produced on the hydrophobic plate substrates in ordinary environment. We calculated the area of per molecule porphyrin was small, approximately $\pm 15-21 \text{ \AA}^2$. It predicted that this small area was due to porphyrin molecules were deposited by out plane orientation and it leads to Y type deposition. Moreover, it only produced four layers when hexatriocontane present in the mixed solution while twenty and forty layers of LB films were not formed. The possible reasons for these conditions: 1. the experiment was not conducted at ultra-clean environment so that particle may disturb the formation of multilayer, 2. the possibility of inappropriate speed of compression, 3. there is possibility the trigger molecule, hexatriocontane, disturbed the film formation but further study is needed to get the answer.

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REFERENCES

- [1]. Arnold, D. P.; Manno, D.; Micocci, G.; Serra, A.; Tepore, A.; Valli, L. *Thin Solid Films* 1998, 327-328, 341.
- [2]. Liu, Y. Q.; Liang, Q.; Xu, Y.; Chen, F. S.; Zhu, D. B. *Solid State Commun.* 1996, 99, 167.
- [3]. Harima, Y.; Yamashita, K. *J. Phys. Chem.* 1985, 89, 5325.
- [4]. Honeybourne, C. L.; Hill, C. A. S.; Ewen, R. J.; Collings, M. S.; Clarke, W. C. *J. Phys. Chem. Solids* 1988, 49, 1003.
- [5]. Leray, I.; Vernieres, M. C.; Loucif-Saibi, R.; Bied-Charreton, C.; Faure, J. *Sens. Actuators B* 1996, 37, 67; Harima, Y.; Furusho, S.; Okazaki, K.; Kunugi, Y.; Yamashita, K. *Thin Solid Films* 1997, 300, 213.
- [6]. Gareth Roberts, *Langmuir Blodgett Films*, Platinum Press, 1990
- [7]. Yanagi, H.; Ashida, M.; Harima, Y.; Yamashita, K. *Chem. Lett.* 1990, 385.
- [8]. Narioka, S.; Ishii, H.; Ouchi, Y.; Yokoyama, T.; Ohta, T.; Seki, K. *J. Phys. Chem.* 1995, 99, 1332.
- [9]. Azumi, R.; Matsumoto, M.; Kuroda, S.; King, L. G.; Crossley, M. J. *Langmuir* 1995, 11, 4056.
- [10]. Gryczynski, Z.; Paolesse, R.; Smith, K. M.; Bucci, E. J. *Phys. Chem.* 1994, 98, 8813.
- [11]. Chou, H.; Chen, C.-T.; Stork, K. F.; Bohn, P. W.; Suslick, K. S. *J. Phys. Chem.* 1994, 98, 383.
- [12]. Bull, R. A and Bulkowski, J. E. *J. Colloid Interface Sci.*, 1983, 92, 1-12
- [13]. Schmehl, R. H.; Shaw, J. L and Whitten, D. G. *J. Am. Chem. Soc.* 1976, 98, 1584-1586
- [14]. Azumi, R. Ph.D. Thesis, Kyoto University, Kyoto, Japan, 1995
- [15]. Gentle, I. R, *Langmuir* 2000, 16, 607-611