

## Tetrapyrazinoindoloporphyrazine Langmuir-Blodgett Films

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**Abstract:** We fabricated tetra(5-*n*-nonyl-8-*tert*-butyl-2,3-pyrazino[2,3-*b*]indolo)porphyrinato copper(II) (Cu-Pc-C<sub>8</sub>) Langmuir-Blodgett (LB) films. We further investigated the influence of arachidic acid (AA) as a transfer promoter, as well as the effect of dipping speed, on the deposition of the films on hydrophilic and hydrophobic substrates. In the case of pure Cu-Pc-C<sub>8</sub> LB deposition on a hydrophilic substrate, the transfer ratio was close to one for up-stroke depositions, but the previously deposited film was peeled off and re-spread onto water at down-stroke depositions. Whereas the stability of the Cu-Pc-C<sub>8</sub> LB films was not improved by AA addition on hydrophilic substrates, the deposition of Cu-Pc-C<sub>8</sub> was significantly improved by the presence of AA on a hydrophobic substrate. The AA-assisted deposition had transfer ratio of close to 1 and was essentially stable up to 10-layer depositions. Comparison of the UV-visible spectrum of a Cu-Pc-C<sub>8</sub>/AA LB film with that of Cu-Pc-C<sub>8</sub>/AA solution in dichloroethane revealed that the Soret and Q bands for the Cu-Pc-C<sub>8</sub>/AA LB film were broadened and red-shifted due to the aggregation of phthalocyanines upon assembly in the LB film.

**Keywords:** arachidic acid, Langmuir-Blodgett, tetrapyrazinoindoloporphyrazine, transfer promoter.

### Introduction

Phthalocyanines have remarkable chemical and thermal stability and advantageous optical absorption and emission properties. Owing to these properties, they have found applications in the field of organic light emitting diodes, organic field effect transistors, organic solar cells, photodynamic therapy, chemical sensors, and laser dyes.<sup>1,2</sup> Phthalocyanines also offer tremendous architectural flexibility in their structure, facilitating the tailoring of physical, optoelectronic, and chemical properties. The properties of phthalocyanines can be easily tuned via simple chemical modification either by introducing appropriate substituents into the periphery of the phthalocyanine macrocycle ring or by changing the nature of the central metal ion.<sup>3,4</sup>

Tetrapyrazinoporphyrazine is one of the phthalocyanine derivatives having two nitrogen atoms at equivalent 1,4-positions of the phthalocyanine benzene units.<sup>5-7</sup> Due to the additional nitrogen atoms, tetrapyrazinoporphyrazines are less electron-rich than the corresponding phthalocyanine.<sup>6</sup> Like phthalocyanines, tetrapyrazinoporphyrazines can be substituted in their peripheral 2,3-positions with a variety of functional groups. Lee *et al.* synthesized push-pull type tetrapyrazinoporphyrazines based on 2,3-dicyanopyrazines with an alkoxyphenyl and a nitrophenyl substituents.<sup>7</sup> The alkoxy-

phenyl substituent works as an electron donor group, and the nitrophenyl substituent works as an electron acceptor group. This push-pull intramolecular charge-transfer chromophoric system has been shown to be important for applications in optical communication.<sup>8</sup> Introduction of an indole group at the 2,3-positions of pyrazine leads to tetrapyrazino [2,3-*b*]indoloporphyrazines. J. Y. Jaung *et al.* synthesized this porphyrazine molecule by ring closure reactions of 2,3-dichloro-5,6-dicyano-pyrazine with enamines.<sup>9</sup> This molecule also has push-pull intramolecular charge-transfer chromophoric systems in which the indole ring works as a donor group and the pyrazine ring as an acceptor group.

An important consideration in applications of phthalocyanine molecules is the necessity of forming thin films. Phthalocyanine thin films can be fabricated by several methods such as spin-coating, thermal evaporation and Langmuir-Blodgett (LB) techniques.<sup>2</sup> The spin-coating technique is simple, rapid, and convenient, but the homogeneity of the film structure is inferior to thermally evaporated and LB films. Thermal evaporation is widely used to make phthalocyanine thin films because of its simplicity in the control of the film thickness and crystal structures of the molecules.<sup>10</sup> However, decomposition of the molecules may occur during thermal evaporation.<sup>11</sup> The Langmuir-Blodgett (LB) technique is one of the most popular methods for fabricating molecularly well-oriented and assembled thin films utilizing air-water interfaces.<sup>12-15</sup> It also enables precise control of

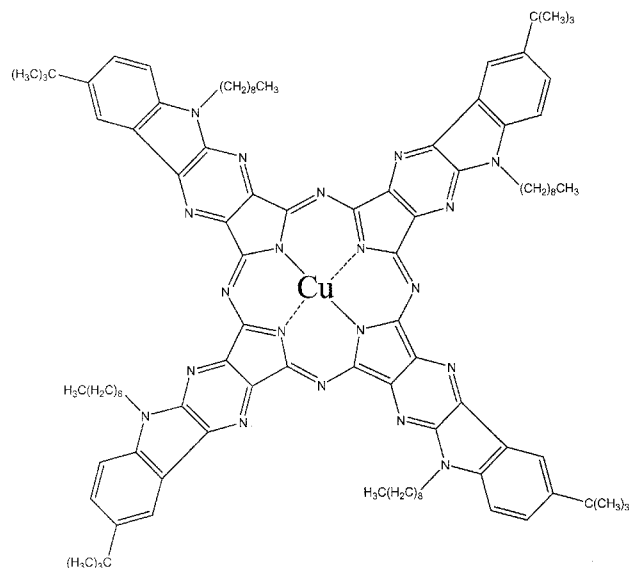
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the monolayer thickness, homogeneous deposition of the monolayer over large areas, and the fabrication of multilayers with varying layer organization. The typical procedure for obtaining the LB film is as follows. Amphiphilic molecules dissolved in an organic solvent are spread at the air-water interface. The solid-like monolayer can be formed by adjusting the surface pressure. Stable monolayers at the air-water interface can be transferred onto hydrophilic or hydrophobic solid substrates by dipping them. However, difficulties have been found in obtaining excellent quality phthalocyanine LB films due to aggregation. In order to improve phthalocyanine LB film quality, various transfer promoters, such as arachidic acid, stearyl alcohol and stearamide, have been used with phthalocyanines.<sup>16,17</sup> Liu *et al.* reported that the most critical factors determining the stability and quality of LB films formed using arachidic acid as a transfer promoter are the pH value of the subphase and the presence of divalent cations such as  $\text{Cd}^{2+}$  and  $\text{Ba}^{2+}$ .<sup>18</sup> The results show that the divalent cations interact with dissociated carboxylic groups of arachidic acids to form a “di-soap”, which apparently enhances the LB film stability. Therefore, when arachidic acid is used as a transfer promoter in LB film preparation, divalent cations are always added in the subphase.<sup>18,19</sup>

In this work, we have fabricated tetra(5-*n*-nonyl-8-*tert*-butyl-2,3-pyrazino[2,3-*b*]indolo)porphyrinato copper(II) (referred to as Cu-Pc-C<sub>8</sub>) films using the Langmuir-Blodgett technique. Note that the thermal evaporation and spin-coating techniques could not be used to fabricate Cu-Pc-C<sub>8</sub> thin films because the molecule decomposes during thermal evaporation and crystallizes during spin-coating.<sup>11</sup> We have also investigated the influence of dipping speed, the use of a transfer promoter, and the nature of the substrate on LB film fabrication by analyzing transfer ratios for the LB deposition. We demonstrate that the Cu-Pc-C<sub>8</sub> LB films are perfectly transferred onto hydrophobic substrates in the presence of arachidic acid as a transfer promoter. In contrast, in the case of LB deposition on hydrophilic substrates, the film is well-transferred onto the substrate during up-stroke depositions. However the deposited film peels off and re-spreads onto the water during the down-stroke depositions due to weak interactions between the molecules and the substrates. Addition of the transfer promoter does not improve the LB film deposition on hydrophilic substrates. UV-vis spectroscopy is performed to measure and compare electronic transitions of the LB films with those in dichloroethane solutions.

## Experimental

**Materials.** Tetra(5-*n*-nonyl-8-*tert*-butyl-2,3-pyrazino[2,3-*b*]indolo)porphyrinato copper(II) (Cu-Pc-C<sub>8</sub>) was synthesized as previously described.<sup>9</sup> Figure 1 shows the chemical structure of this phthalocyanine. As seen in the figure, the equivalent 2,3-positions of pyrazine are substituted with an



**Figure 1.** The chemical structure of tetra(5-*n*-nonyl-8-*tert*-butyl-2,3-pyrazino[2,3-*b*]indolo)porphyrinato copper(II).

indole group containing a nonyl and *tert*-butyl moieties. Owing to the introduction of the nonyl group, this molecule is soluble in common organic solvents. Chloroform (special grade) was purchased from Samchun Pure Chemical Co. and used as received without additional purification. Arachidic acid (AA), potassium hydrogencarbonate and cadmium chloride were purchased from Sigma-Aldrich. Tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane was obtained from Gelest. Double-sided, polished Si(111) wafers and quartz slides were purchased from LG SILTRON, Inc. and DAIHAN Scientific, Inc., respectively.

**Substrate Preparation.** To prepare hydrophilic substrates, Si(111) wafers and quartz slides were cleaned in “piranha” solution (a 30:70 (v/v) mixture of concentrated 30%  $\text{H}_2\text{O}_2$  and 95%  $\text{H}_2\text{SO}_4$ ) for 60 min and then repeatedly ultrasonicated in ultrapure water for 10 min. The cleaned substrates were rinsed with acetone by ultrasonication for 15 min and dried under pure nitrogen. For preparation of hydrophobic substrates, the cleaned hydrophilic quartz slide and silicon wafer substrates were exposed to tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane in vacuum. Quartz slides were used only for UV-visible spectroscopy experiments.

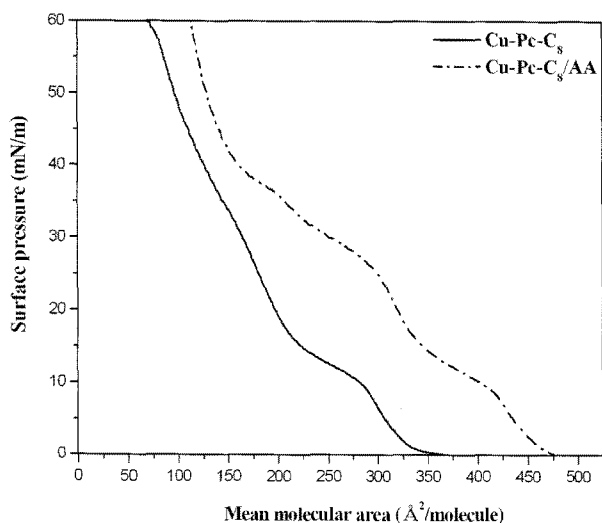
**Langmuir-Blodgett Film Preparation.** The Langmuir-Blodgett films have been fabricated using a computer controlled KSV Minitrough II instrument (KSV instruments Ltd., Finland). Ultra-pure water with a resistivity of ca. 18.2  $\text{M}\Omega$  and a pH value of 5.8, purified by a Milli-Q ultra-pure water system, was used as the subphase for pure Cu-Pc-C<sub>8</sub> LB film deposition. For Cu-Pc-C<sub>8</sub>/AA LB film deposition, the aqueous subphase contained  $3.0 \times 10^{-4}$  M  $\text{CdCl}_2$  buffered with  $1.0 \times 10^{-5}$  M  $\text{KHCO}_3$ . The 1:4 molar mixture of Cu-Pc-C<sub>8</sub> and arachidic acid was dissolved in chloroform as the spreading solvent. The concentrations of Cu-Pc-C<sub>8</sub> and arachidic

acid solutions in chloroform were  $7.5 \times 10^{-5}$  and  $3.1 \times 10^{-4}$  M, respectively. The chloroform solution of Cu-Pc-C<sub>8</sub>/AA (200  $\mu$ L) was spread onto the air-water interface using a glass syringe (Hamilton Co., USA). After complete evaporation of the chloroform, the floating monolayer was compressed at a speed of 20 mm/min. The LB films were transferred onto substrates by dipping them at a surface pressure of 20 mN/m with a dipping speed of 17 mm/min unless otherwise stated.

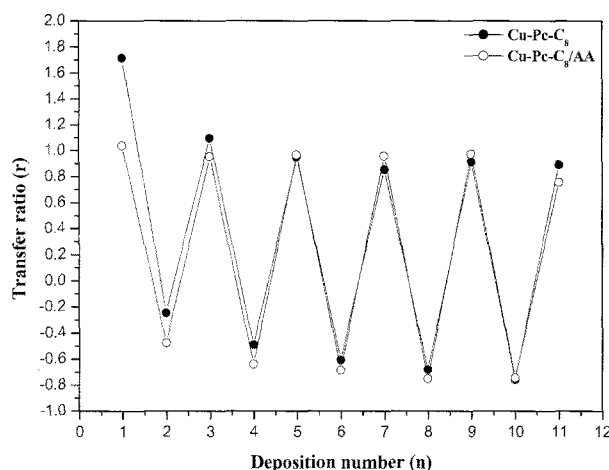
## Results and Discussion

The surface pressure-area isotherms ( $\pi$ -A) of pure Cu-Pc-C<sub>8</sub> and Cu-Pc-C<sub>8</sub>/AA monolayers on the water subphase are shown in Figure 2. In the case of pure Cu-Pc-C<sub>8</sub>, the isotherm shows three regions: an expanded monolayer region at low surface pressure, a transition region starting at about 10 mN/m, and a condensed region above 15 mN/m. The surface pressure of the pure Cu-Pc-C<sub>8</sub> monolayer starts rising at 363  $\text{\AA}^2$ , and the collapse of the monolayer occurs at about 60 mN/m. For Cu-Pc-C<sub>8</sub>/AA, three transitions are observed at about 10, 27, and 36 mN/m. The additional transitions in the isotherm of Cu-Pc-C<sub>8</sub>/AA monolayer may be due to the presence of arachidic acid.<sup>18</sup> The extrapolated area per molecule at 20 mN/m is 275 and 380  $\text{\AA}^2$  for pure Cu-Pc-C<sub>8</sub> and Cu-Pc-C<sub>8</sub>/AA, respectively. These values are analogous to the typical molecular area of phthalocyanines bearing long side chains.<sup>20</sup>

The quality of the deposited monolayer on a substrate may be evaluated by a so-called transfer ratio. This is defined as the ratio between the decrease in monolayer area during a deposition stroke and the area of film deposited on the substrate. Thus, for ideal transfer the transfer ratio is equal to 1. Figure 3 shows the transfer ratio of pure Cu-Pc-C<sub>8</sub> and Cu-Pc-C<sub>8</sub>/AA LB films with respect to the number of layers



**Figure 2.** Surface pressure-mean molecular area ( $\pi$ -A) isotherm of a Cu-Pc-C<sub>8</sub>/AA and Cu-Pc-C<sub>8</sub> monolayer at the air/water interface at 25 °C.

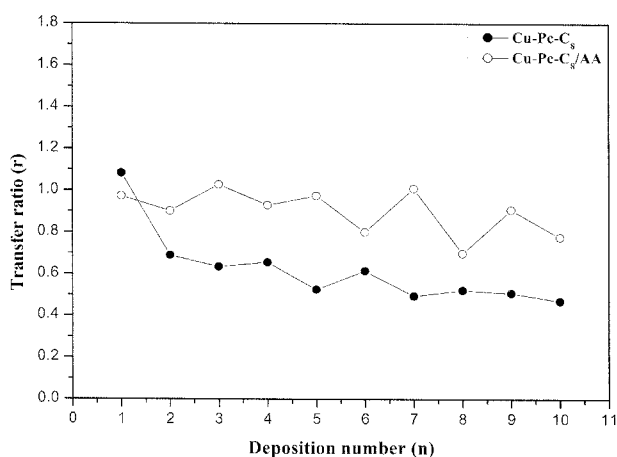


**Figure 3.** The transfer ratio versus the number of deposited layers of pure Cu-Pc-C<sub>8</sub> (●) and Cu-Pc-C<sub>8</sub>/AA (○) LB films on a hydrophilic Si(111) substrate at a surface pressure of 20 mN/m.

transferred onto hydrophilic Si(111) substrates at a constant surface pressure of 20 mN/m. Note that the first deposition is up-stroke and the second one is down-stroke. Thus the transfer ratios for the odd number and even number of depositions are for up-stroke and down-stroke depositions, respectively. As shown in the figure, both Cu-Pc-C<sub>8</sub> and Cu-Pc-C<sub>8</sub>/AA display transfer ratios that are close to 1 for up-stroke depositions. In contrast, the transfer ratios have negative values for even deposition numbers, corresponding to the down-stroke depositions. These results indicate that Cu-Pc-C<sub>8</sub> and Cu-Pc-C<sub>8</sub>/AA LB films are almost perfectly transferred during the up-stroke deposition but that the deposited LB films are stripped off and re-spread onto the water surface during the subsequent down-stroke deposition. During the up-stroke deposition, the aqueous subphase wets the hydrophilic substrate well and, thus, the direction of the movement of the substrate and that of the surface of the subphase near the substrate form an obtuse angle. Subsequently, a monolayer on the subphase can touch and attach to the hydrophilic substrate, resulting in transfer of the LB film. However, during the down-stroke deposition, the direction of the movement of the substrate and that of the subphase near the substrate form an acute angle. Therefore, the monolayer cannot attach to the substrate. In addition, part of the LB film deposited on the previous up-stroke deposition is peeled from the substrate and re-spread onto the air-water interface. For the deposition of LB films, contact angles and contact lines have been recognized to play an important role.<sup>18,21</sup> The role of contact angles in LB film deposition has been discussed.<sup>22,23</sup> Even though the specific contact angle values are slightly different, the general conclusion is that LB film deposition is possible if the dynamic contact angle is greater than 90° during the down-stroke deposition or smaller than 90° during the up-stroke deposition. In the current study, the measured contact angles of the

hydrophilic substrate and Cu-Pc-C<sub>8</sub> LB film are 5 and 32°, respectively. Therefore, in accord with the aforementioned role of contact angle in LB film formation, the Cu-Pc-C<sub>8</sub> cannot form LB films on the hydrophilic substrate during the down-stroke deposition. In addition, the observed negative values of the transfer ratios during down-stroke depositions indicate re-spreading of the LB film from the substrate onto the water surface. This re-spreading of the LB film implies weak or essentially no interaction between the Cu-Pc-C<sub>8</sub> and hydrophilic substrate. Comparison of the transfer ratios between pure Cu-Pc-C<sub>8</sub> and Cu-Pc-C<sub>8</sub>/AA illustrates the effect of the presence of arachidic acid as a transfer promoter for LB film deposition. As shown in Figure 3, in the case of LB deposition on a hydrophilic substrate, arachidic acid does not play a role as a transfer promoter to improve the LB deposition.

Figure 4 shows the transfer ratio of pure Cu-Pc-C<sub>8</sub> and Cu-Pc-C<sub>8</sub>/AA LB films with respect to the number of layers deposited on hydrophobic Si(111) substrates at a constant surface pressure of 20 mN/m. Note that the first deposition on a hydrophobic substrate is a down-stroke deposition. In the case of pure Cu-Pc-C<sub>8</sub>, the transfer ratio for the first down-stroke deposition is about 1.1 mN/m, and it gradually decreases with increasing number of depositions. However, in the case of Cu-Pc-C<sub>8</sub>/AA depositions, the transfer ratio is close to 1 and stable up to 5 multilayer depositions, which indicates improvement in the deposition quality due to the presence of arachidic acid. The transfer ratio slowly decreases for further depositions. It has been reported that incorporation of transfer promoters such as arachidic acid, stearyl alcohol, and stearamide can produce high quality LB multilayers of porphyrins or phthalocyanines.<sup>16,17</sup> Ohigashi *et al.* proposed that the transfer promoter played a role as stiffening poles for the stack of phthalocyanines in LB multilayers.<sup>24</sup> In addition, stabilization of the mixed Cu-Pc-C<sub>8</sub>/AA LB films can be enhanced by the addition of divalent ions in

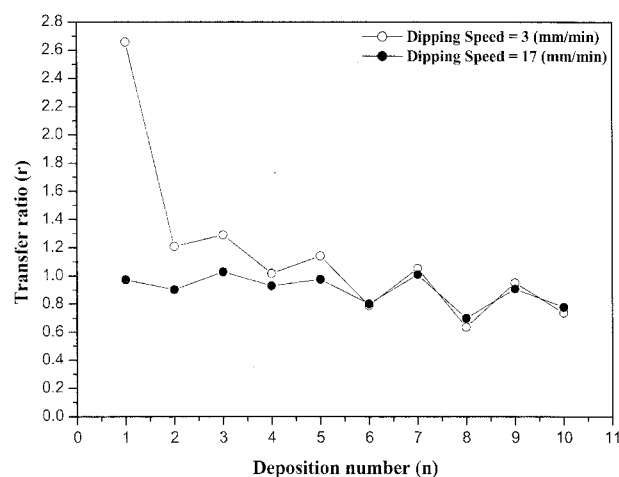


**Figure 4.** The transfer ratio versus the number of deposited layers of pure Cu-Pc-C<sub>8</sub> (●) and Cu-Pc-C<sub>8</sub>/AA (○) LB films on a hydrophobic Si(111) substrate at a surface pressure of 20 mN/m.

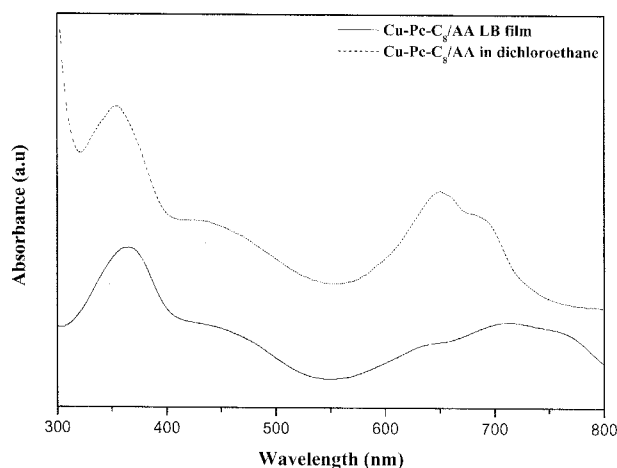
the subphase. It has also been reported that the divalent cations dramatically improve film stability during deposition because they interact with arachidic acid to form a “di-soap”, which enhances the film stability.<sup>18,25,26</sup> Liu *et al.* studied the effects of the addition of cations in AA LB films.<sup>18</sup> It is reported that the addition of Cd<sup>2+</sup> or Ba<sup>2+</sup> improves the AA LB film quality. Therefore, when AA is used as a transfer promoter, divalent cations are suggested to be added with AA. The results of Figure 4 clearly show the effect of the addition of a transfer promoter on the deposition of the Cu-Pc-C<sub>8</sub> LB film. Comparison between Figures 3 and 4 indicates the effect of hydrophobic and hydrophilic substrates on the deposition of the Cu-Pc-C<sub>8</sub>/AA LB film. In the case of the hydrophilic substrate, as shown in Figure 3, the presence of the transfer promoter does not improve the LB film deposition. In contrast, LB deposition of Cu-Pc-C<sub>8</sub> with transfer promoter can be significantly improved when the LB film is deposited on a hydrophobic substrate.

Figure 5 displays the transfer ratio of Cu-Pc-C<sub>8</sub>/AA LB films with respect to the number of layers deposited on hydrophobic Si(111) substrates at a constant surface pressure of 20 mN/m with different dipping speeds of 3 and 17 mm/min. The transfer ratios for both dipping speeds are close to 1 except for the first down-stroke deposition at a dipping speed of 3 mm/min. This may be due to multiple transfers of Cu-Pc-C<sub>8</sub>/AA monolayers onto the substrates at low dipping speeds for the first deposition. In other words, if the dipping speed is too low, multilayer of Cu-Pc-C<sub>8</sub>/AA LB can be formed on a hydrophobic substrate for the first deposition.

The phthalocyanines exhibit absorption spectra with Soret bands at around 350 nm and Q bands at about 650 nm.<sup>27-30</sup> Figure 6 shows UV-vis spectra of Cu-Pc-C<sub>8</sub>/AA dichloroethane solutions and a 10-layered LB film on a hydrophobic



**Figure 5.** The transfer ratio versus the number of deposited layers of Cu-Pc-C<sub>8</sub>/AA LB films on a hydrophobic Si(111) substrate at a surface pressure of 20 mN/m with dipping speeds of 3 and 17 mm/min.



**Figure 6.** UV-visible spectra of Cu-Pc-C<sub>8</sub>/AA solution in dichloroethane and a 10-layered LB film on quartz slide.

quartz substrate. The UV-vis spectrum of a Cu-Pc-C<sub>8</sub>/AA dichloroethane solution shows a strong Soret band at near 360 nm with a slight shoulder at about 440 nm which can be assigned to the  $\pi$ - $\pi^*$  transition in the fused porphyrin ring structure and/or d- $\pi^*$  transitions.<sup>9,31</sup> The Q bands due to the  $\pi$ - $\pi^*$  transitions in the phthalocyanine macrocycle are observed at 650 and 700 nm.<sup>31</sup> In the case of the Cu-Pc-C<sub>8</sub>/AA LB films, the Soret band is slightly broadened and red-shifted compared to that of the dichloroethane solution. The Q bands exhibit substantial broadening and red-shifting with a loss of resolution. These phenomena may be due to aggregation of phthalocyanine rings as the LB films assemble or a conformational change of the phthalocyanine macrocycle in the film.<sup>27,32</sup> Note that the absorption band for the Cu-Pc-C<sub>8</sub>/AA LB film extends beyond 800 nm. Thus, this phthalocyanine LB film could be useful in the field of optical data storage and for security printing, which require absorbance in the near infrared.

## Conclusions

This research investigates the effect of the presence of arachidic acid as a transfer promoter on the deposition quality of a tetra(5-*n*-nonyl-8-*tert*-butyl-2,3-pyrazino[2,3-*b*]indolo)porphyrinato copper(II) (Cu-Pc-C<sub>8</sub>) LB film on hydrophobic and hydrophilic substrates. The transfer ratio for the deposition of pure Cu-Pc-C<sub>8</sub> and Cu-Pc-C<sub>8</sub>/AA on a hydrophilic substrate significantly depends on the relationship between the liquid contact line on the substrate and the direction of movement of the substrate. The transfer of pure Cu-Pc-C<sub>8</sub> on a hydrophilic substrate is almost perfect during the up-stroke depositions. However, for the down-stroke depositions, part of the previously deposited films are peeled off and re-spread onto the water surface. No improvement is found in the deposition quality with the presence of arachidic acid. In the case of LB transfer on hydrophobic substrate,

the transfer ratio of pure Cu-Pc-C<sub>8</sub> is close to 1 for the first up-stroke deposition and decreases as the number of strokes increases, indicating the lack of reproducibility in the deposition process. With the addition of arachidic acid, however, the transfer ratio of Cu-Pc-C<sub>8</sub> is close to 1 and stable for both up and down-stroke depositions. In other words, deposition of Cu-Pc-C<sub>8</sub> on hydrophobic substrates is significantly improved by the presence of arachidic acid. The Soret and Q bands for Cu-Pc-C<sub>8</sub> LB films are broadened and red-shifted compared with those for Cu-Pc-C<sub>8</sub> solutions, which is due to the aggregation of phthalocyanine rings as the Cu-Pc-C<sub>8</sub> LB films assemble.

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