フタロシアニン超薄膜と超分子構造に関する研究
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ULTRATHIN FILMS AND SUPRAMOLECULAR ARCHITECTURE OF PHTHALOCYANINE DERIVATIVES

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CHAPTER 1
OVERVIEWS

§1-1. Material Designs of Functional Molecules and Thin Film Preparation Techniques

§1-1-1. Functional Organic Materials for Practical Use in Electronics and Photonics

A number of organic substances have attracted special interests for application in the field of electronics and photonics, since they possess a variety of unique properties and functions that cannot be seen among inorganic materials. Until now, several organic compounds have actually been available as bulk or thin films because of many advantages involving plasticity, flexibility, non-toxicity, chemical reactivity, lightweight, processability, and productivity, in spite of some disadvantages compared to corresponding inorganic materials.

Table 1-1 summarizes the merits and demerits of such functional organic materials compared with alternative inorganic materials. Polyethylene is invariably used as an insulator for coaxial metal wires and cables, due to its flexibility and light-weight. Various polymeric resists for microlithography, which exhibit degradation properties under irradiation of ultraviolet (UV) light, electron beam, or X-ray, are indispensable for making fine circuit patterns with micron or sub-micron scales in the large-scale integrate circuits (LSI) technology. Poly(vinylidene fluoride) (PVDF) is utilized as an acoustic-electric transducing material, which is applied for headphones, microphones, and hydrophone for use of the computer tomography. Poly(methyl methacrylate) (PMMA) exhibiting optical transparency in visible and near infrared (IR) regions is applied to a core material of low-loss optical plastic fibers (OPF) because of an easy handling and low price. A family of liquid crystals serves flat, light-weight, and color displays operated at low electric power. Organometallic compounds employed in the chemical vapor deposition (MOCVD) process are inevitably necessary to fabricate large-area "superlattice" semiconductors that are artificial periodic ultra thin films consisting of GaAs/AlGaAS, ZnS/ZnSe, Si/SiGe, and so on. Organic photoconductors (OPC) exhibiting electrophotographic properties, such as poly(vinylcarbazole) and organic pigments, are commercialized as plain paper copiers (PPC) because of non-toxicity and have now over 50% shares in a market of electrophotographics.

Recently, many π-conjugative organic and polymeric solids possessing mobile electrons and higher polarizability have been of particular interest since these have prospect of developing a variety of applications with excellent performances: non-linear
either heat or photon mode, rechargeable battery, 36,37 and static charge dissipating materials.38

At a practical device level, several requirements must be considered on a molecular level. O

- Photoconductivity
- Decomposition
- Transparency in UV, visible, or near IR
- Pyroelectricity
- Photocopying
- Opaque or near IR optical information processing devices,26-29 conducting materials,30-32 electrooptical copiers using near IR laser-diodes,22-24 optical information storages with either heat or photon mode,1,2,22,23 gas sensors,33 electrochromic displays,18,34,35 rechargeable battery,36,37 and static charge dissipating materials.38

§1-1.2 Fundamental Concept of Molecular Design for Application

In order to advance functional potential of the π-conjugating organic compounds at a practical device level, several requirements must be considered on a molecular level.

Table 1-1. Merits and Demerits of Functional Organic Materials and Alternative Inorganic Materials.

<table>
<thead>
<tr>
<th>Function</th>
<th>Organic Material (Organic Materials)</th>
<th>Merits</th>
<th>Demerits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical insulator</td>
<td>Polyethylene</td>
<td>Light weight</td>
<td>Flammability</td>
</tr>
<tr>
<td></td>
<td>Polystyrene</td>
<td>Olefinic character</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polymethylmethacrylate</td>
<td>Transparency in UV</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CNTs</td>
<td>Large-area film</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Poly(vinylidene fluoride) (PVDF)</td>
<td>Transparency in UV</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polyacetylene (PA)</td>
<td>Transparency in UV</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Poly(vinylcarbazole)</td>
<td>Transparency in UV</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Poly(3-octylthiophene)</td>
<td>Transparency in UV</td>
<td></td>
</tr>
</tbody>
</table>

§1-1.3 Thin Film Preparation Techniques

Many preparation techniques of organic thin film have been presented. They can be classified into two categories: the wet and dry processes. Table 1-2 gives the advantages and disadvantages of those methodologies.

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Type</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir-Blodgett (LB)</td>
<td>Wet</td>
<td>Ultra thin film</td>
<td>Slow productivity</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Solute water subphase</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Preparation of surface active material</td>
</tr>
<tr>
<td>Casting</td>
<td>Wet</td>
<td>Film thickness</td>
<td>Control of film orientation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical adsorption</td>
<td>Wet</td>
<td>Oily process</td>
<td>Preparation of surface active material</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrochemical deposition</td>
<td>Wet</td>
<td>Oily process</td>
<td>Preparation of surface active material</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor deposition</td>
<td>Dry</td>
<td>Oily process</td>
<td>Preparation of surface active material</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion cluster beam (ICB)</td>
<td>Dry</td>
<td>Oily process</td>
<td>Preparation of surface active material</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical vapor deposition (CVD)</td>
<td>Dry</td>
<td>Oily process</td>
<td>Preparation of surface active material</td>
</tr>
</tbody>
</table>

First, choice of an organic framework exhibiting high chemical and thermal stabilities is of the primary importance. Second, the organic framework must possess a film forming ability, while maintaining its function. Almost all of the functional materials are usually employed as thin films. Third, the materials must be made up in a desired packing structure and morphology. Organic compounds often exhibit polymorphisms in solid and/or in solution. The morphology of the materials, which is affected strongly by chemical and physical treatments, is related significantly to their chemical and physical properties. Next, defect-deficient thin films of functional organic materials should be formed with a desired thickness and preferential orientation on a suitable substrate. Finally, the intended devices consisting of thin films of the functionalized organic materials will be evaluated and judged by customers, in comparison with the alternative inorganic devices.
Techniques are commonly used in the fabrication process of polymer films in electrophotography and LSI technology, since the high-quality and large area films with high-throughput can easily be prepared at an ambient condition. The chemical adsorption technique is frequently used to control the wettability of surfaces by silane coupling agents. The electrochemical polymerization is applicable to electrochemically active molecules but lacks controllability and regularity of the polymers deposited.

On the other hand, the dry techniques basically consist both of evaporation and deposition processes of molecules in an evacuated chamber. All the dry techniques need large-scale equipments consisting of chamber, vacuum pumps, heating boat, and in-situ monitors, unlike the wet techniques. The vapor deposition technique is frequently used for preparation of thin films for thermally stable and evaporable organic materials. The ion cluster beam (ICB) technique, which is a modification of the vapor deposition method, is useful to obtain densely packed and oriented films. The chemical vapor deposition (CVD) technique, which involves an introduction of gaseous molecules and high energy such as UV light or plasma, is especially important for preparation of inorganic semiconducting thin films with large area, high-quality, and regulation of the deposition processes of molecules in an evacuated chamber. All the dry techniques need large-scale equipments consisting of chamber, vacuum pumps, heating boat, and in-situ monitors, unlike the wet techniques. The vapor deposition technique is frequently used for preparation of thin films for thermally stable and evaporable organic materials. The ion cluster beam (ICB) technique, which is a modification of the vapor deposition method, is useful to obtain densely packed and oriented films. The chemical vapor deposition (CVD) technique, which involves an introduction of gaseous molecules and the subsequent chemical reaction stimulated by thermal treatment and/or irradiations of high energy such as UV light or plasma, is especially important for preparation of inorganic semiconducting thin films with large area, high-quality, and regulation of the composition.

§1-1-4. Molecular Assemblage

Self-assembling phenomena are recognized to be one of the most essential natures in the living and inanimate worlds. Nevertheless, understanding and control of self-assembling nature on a molecular level are still at a rudimentary stage, except for a few successful studies.

Wegner et al. found that substituted diacetylene derivatives polymerized in solid state and gave a single crystal of the p-conjugative polymer. Schmidt et al. elucidated a relation between solid-state photoreaction and crystal structure by means of X-ray analysis based on the assumption of topochemical hypothesis in 1964. Since a few systematic studies for forced control of molecular packing arrangement had been established, in 1971 Schmidt proposed a crystal engineering concept that manipulate organic crystals and control its chemical reactivity in the solid state by an introduction of specific substituents to the molecules. From their continuing studies, it was demonstrated that the presence of hydrogen-bonding groups such as primary amides and urethane, dichlorophenyl groups, unsaturated carbonyl, or charge-transfer interaction are the most important factors in the solid-state photochemical reactivity.

Kuntake et al. demonstrated for the first time that some simplified synthetic dialkyl ammonium salts in water for bilayer membranes with vesicle and lamella structures in analogy with the living cells in 1977. Since the finding, a relation between the morphology of the membrane and the molecular structure of the amphiphiles was intensively studied. The synthetic lipids, which usually contain both of two hydrophobic long alkyl chains and hydrophilic moiety, form aggregates with bilayer thickness in aqueous media and spontaneously develop higher-order morphological structures: globules, vesicles, rods, tubes, disks, and helical superstructures. They concluded that these morphologies are primarily related to the surface curvatures of the lipid molecules.

§1-2. Historical View of Phthalocyanines and Langmuir-Blodgett Films

§1-2-1. Choice of Phthalocyanine and the Langmuir-Blodgett Technique for Application

Phthalocyanine and metallophthalocyanine are the p-conjugating, planar and robust macrocyclic dyes like porphyrins. The phthalocyanine structures are exceptionally stable to alkalies, acids, heat, UV light, and electron beam among organic compounds. In addition, the compounds have been of particular interest in many basic and applied researches because of their versatile chemical and physical properties. The frameworks can fulfill the first requirement as the functional molecule as mentioned in §1-1-2.

The LB technique provides tailored ultra thin organic films with a molecular size thickness and with a certain orientation on substrates under the conditions of ambient temperature and pressure. The technique can fulfill the fourth requirement on the functional molecule as mentioned in §1-1-2.

§1-2-2. Phthalocyanines

Figure 1-1 shows the chemical structure of metallophthalocyanine. Compared with porphyrins, phthalocyanines had received relatively little interest, because researchers other than the phthalocyanine chemists had believed for a long time that phthalocyanines are insoluble in water as well as in organic solvents and are hard to modify their chemical structures. However, recent progresses on chemical modification of the phthalocyanine framework have been remarkable, because many applied chemists and physicists intend to exploit thin films of robust molecules including phthalocyanine, anthracene, and tetracyanoquinodimethane.

Metal-free phthalocyanine was for the first time obtained in 1907 accidentally by Braun and Tcherniac, as a by-product of the preparation of ortho-cyanobenzamide from phthalaldehyde and acetic anhydride. Linsead et al. determined the chemical structure of metal-free phthalocyanine and several metallophthalocyanines in 1933. Robertson et al. confirmed their planarity and dimensions by means of X-ray analysis in 1935.
During the 1930s to 1950s, understanding of versatile chemical and physical properties, such as catalytic properties, oxidation and reduction, photoconductivity, X-ray diffraction, absorption and emission spectra and polymorphism were elucidated. Soluble phthalocyanine was first appeared as sulfonate in the UK patent in 1929. Since then, several water and organic solvent soluble phthalocyanines have been demonstrated and patented in the form of quaternary and ternary ammonium salts of pyridyl derivatives of phthalocyanine, sulfur dyes, azo dyes, and leuco dyes.

In the 1960s to 1980s, further studies on the physical and chemical properties of phthalocyanine solids focused on applications to photoconductor, conductor, gas sensor, multi-colored electrochromic materials, rechargeable battery, negative-type patterning materials using electron beam, photochemical hole burning memory, data storage media using a near laser diode (0.78, 0.85 μm region). Marks et al. reported high electrical conductivity of phthalocyanine that is oxidized with iodine in 1975. Since their finding, several conducting phthalocyanines and related polymeric solids appeared.

Novel phthalocyanine derivatives and their chemical reactivities are recently characterized. Naphthalocyanine as an extended π-electron system of phthalocyanine skeleton was first reported by Mikhalenko et al. in 1969. Unusual ring contractive reaction of metalloid phthalocyanines by reducing regents which give rise to new tetrapyrrolic macrocycles, triazatetrazenocorrole, was identified by Fujiki et al. in 1986. "A super phthalocyanine" consisting five phthalonitril units was isolated and determined by Marks et al. in 1975. Self-assembling phthalocyanines containing crown-ether moieties have appeared in connection with ionic transport and recognition of ions by Turkish and Netherlands researchers respectively in 1987.

§1-2-3. The Langmuir-Blodgett Films

Historically speaking, the LB film studies are devided into three important phases of development. In the first stage, pioneering works by Blodgett and Langmuir were published in the 1930s. They demonstrated that a wide range of materials, e.g., long alkyl carboxylic acid, alcohol, and ester, could be deposited as monolayers at the air-water interface onto solid substrates, although the technique still involved some difficulties concerning control of the deposition process. In the second phase, elegant works were achieved by Kuhn et al. in the 1960s. Elucidated energy transfer phenomena in the interlayer and the intralayer of built-up films using amphiphilic chromophores with proper monolayer manipulation. The third development started in the 1980s. New potential applications of built-up films were opened in the field of microolithography, integrated and nonlinear optics, information storage using photochromism and thermochromism, gas sensors, low-dimensional conductors, and insulator. Such applied researches were stimulated by the concept on "Molecular electronic devices" proposed by Carter in 1982.

Figure 1-2 illustrates a typical surface pressure-area isotherm of fatty acid on water subphase. When a solution containing fatty acid is spread and the resulting monolayer is compressed, the isotherm normally contains four stages: gas-like, expanded (liquid-like), condensed, and collapsed phases. In the gas-like phase I, fatty acid molecules float on the water as an isolated molecules or as small-size islands. In the expanded or liquid-like phase II, the small islands coalesce to larger islands. In the condensed phase III, the islands are completely joined in the form of multi-crystals including several boundaries with monolayer thickness. The multi-crystals eventually collapse via Tc.

There are two typical techniques of obtaining built-up films. One is the conventional vertical dipping technique invented by Blodgett and the other is the horizontal lifting method demonstrated by Fukuda et al.

The former is basically composed of three stages and is illustrated in Figure 1-3: (a) a solution containing materials is first spread on a water surface, (b) a mobile monolayer on water is compressed to eliminate voids, (c) a solid multilayer film is then built up by repeated immersion of a substrate into the water.

In the conventional technique, if a monolayer is deposited on a substrate only in a downstroke of the substrate, the built-up film is called as a "z-type" film. If a monolayer is deposited only in an upstroke, a "x-type" film is obtained. When a monolayer is deposited in both of the upstroke and downstroke processes, the built-up film is named as a "y-type" film. Figure 1-4 illustrates the three patterns of the deposition processed and the built-up films.
IV. COLLAPSED PHASE

III. CONDENSED PHASE

II. EXPANDED (LIQUID-LIKE) PHASE

I. GAS-LIKE PHASE

Figure 1-2. Typical force-area isotherm of fatty acid on water subphase.

Figure 1-3. Schematic view of the vertical dipping technique of obtaining Langmuir-Blodgett built-up film.

Figure 1-4. Three patterns of the Langmuir-Blodgett built-up films through immersion of a substrate. (a) x-type films; (b) y-type films; (c) z-type films.

Figure 1-5. Schematic view of the horizontal lifting technique of obtaining Langmuir-Blodgett built-up film.
In contrast, the latter technique requires some tricky procedures to obtain a good quality film. Figure 1-5 displays a schematic view of the horizontal lifting technique.

(a) a compressed monolayer on water is prepared.

(b) one face of a substrate is kept parallel to the water surface and comes into contact with the monolayer under a constant film pressure.

(c) a new barrier is put on the monolayer at the left side closely adjoining the substrate and then a right-side barrier of the substrate is removed.

(d) the substrate is slowly lifted up from the water surface.

By repeating these procedures, the multilayers which correspond to "x-type" films by the conventional LB method are prepared.

§1-2.4. Phthalocyanine Langmuir-Blodgett Films

Studies on the LB films consisting of phthalocyanines have been less active than those on other functional materials. This may be attributed to a preconception that the phthalocyanines cannot produce built-up films, since the phthalocyanines are immiscible in all common organic solvents and the molecular shape is quite different from the conventional fatty acids.

Alexander conducted a pioneering study on force-area isotherms of unsubstituted metal phthalocyanines in 1937. In 1983, Roberts et al. examined the possibility of the built-up films and the electrical properties for both unsubstituted metal-free phthalocyanine and soluble copper tetra(tert-butyl)phthalocyanine, in which metal-free phthalocyanine was produced by hydrolysis of di lithium phthalocyanine at the water-air interface. Snow et al. demonstrated in 1984 the surface isotherms and self-assembling properties of several soluble metal phthalocyanines with phenox substituents. Their successful studies in the early 1980s invoked many researches on the LB films consisting of a variety of soluble phthalocyanines. Until now, over 30 papers on the phthalocyanine LB films have appeared.

§1-3. Purpose and Contents of the Present Thesis

A variety of molecular approaches have been attempted for a construction of one-dimensional phthalocyanine conductors so far. The phthalocyanines containing metalloids, first-row transition metals, and rare-earth metals can provide one-dimensional conductors, whose stacking structures are controlled by covalent linkage (O, F, S, and organic ligands) by the out-of-plane structure of the central metals, and by long chain alkyl peripheral substituents. Unfortunately, these phthalocyanines seem not to form LB films because of extremely low solubilities and the lack of hydrophilic moieties.

Among the one-dimensional phthalocyanine assemblies mentioned above, Marks et al. systematically examined the relationship between electrical conductivity and interplaner separation for a series of O-linked, one-dimensionally stacked cofacial phthalocyanine assemblies that are oxidized with iodine. They concluded that phthalocyanine molecules must be arranged in close spatial proximity as possible to obtain higher conductive state. They polymers are obtained by dehydration of dihydroxy metalloid phthalocyanine (metalloid = Si, Ge, and Sn) in solid state, and are quite immiscible in organic solvents, except for in concentrated sulfuric acid, and lack the LB film forming ability.

Main subjects of the present thesis are to construct one-dimensional phthalocyanine assembly and to control its conductivity in the LB film.

In Chapter 2, self-assembling features of the alkylamide substituted nickel(II) phthalocyanines in cast film, in solid, and even in solution are discussed using a modified molecular exciton theory. New phthalocyanines were designed based on the following ideas. If four secondary amides are symmetrically substituted on each of the peripheral position of phthalocyanine ring, the most favorable structure is expected to form one-dimensionally stacked arrays resulting from directional hydrogen-bonding forces of the amide units and strong van der Waals' stacking forces of phthalocyanine rings. Also, introduction of the flexible and hydrophilic o-octadecylamine moieties leads to increased solubility and afford the capability to form the LB film.

In Chapter 3, characterization of the LB films of soluble nickel phthalocyanines is discussed. The phthalocyanines gave built-up films with one-dimensional stacking structures, while maintaining their assembling structures in chloroform solution. In-plane dichroisms were also invariably observed in the UV-visible and infrared regions. The origin of the dichroisms is discussed. Molecular arrangement and orientation of the phthalocyanine assemblies are proposed.

In Chapter 4, applications of thin films consisting of the soluble nickel phthalocyanines are demonstrated in terms of fine patterning and electrical properties. The film conductivity increases by 2 to 4 orders of magnitudes upon exposure to iodine vapor. The films exhibited negative patterning features to electron beam dose and excellent resistance to plasma-assisted etching.

In Chapter 5, facile synthesis of soluble metal phthalocyanines including short and compact alkyls and/or cyano moieties is reported. Metal-free and metal tetra(tert-butyl)phthalocyanines were obtained in only two to three steps from alkylbenzene starting materials, whereas a previous procedure required seven steps. The phthalocyanines including four alkyl groups and four cyano groups are newly prepared for the purpose of controlling both highest occupied and lowest unoccupied energy levels in solid films.
In Chapter 6, characterization of the LB films of lightly substituted phthalocyanines is presented. The phthalocyanines can be dissolved in organic solvents as monomeric dispersion and the one-dimensional phthalocyanine assemblies are formed in the LB films and in powders. Molecular arrangement and orientation of the phthalocyanine assemblies are discussed.

In Chapter 7, the electrical properties of the LB films of the lightly substituted phthalocyanines are examined. In-plane electrical conductivities of undoped LB films of the phthalocyanine containing both alkyl and cyano groups are highly sensitive and reversible. The film conductivity increases steeply by five orders of magnitude, when the film is exposed to active gases such as iodine, triethylamine and n-butane thiol. Conductivity responses of the phthalocyanine LB films to these gases are explainable in terms of ionization potentials and electron affinities of the films.

In Chapter 8, a new tetrapyrrolic macrocycle: α,β,γ-triazatetrazenecorrole is described. It was characterized by means of elemental analysis, spectral measurements (mass, UV-visible, IR, and 1H NMR), chemical reactivity, and oxidative titration results. This compound was reported previously as a divalent germanium phthalocyanine (Ge11Pc). The finding was initiated based on the idea that the divalent germanium phthalocyanines is presented.

In Chapter 9, summary and some concluding remarks are included.

§1-4. References
CHAPTER 2
SELF-ASSEMBLING PHENOMENA OF NICKEL PHTHALOCYANINES SUBSTITUTED WITH ALKYLAMIDES

SYNOPSIS
Two new types of highly soluble nickel phthalocyanines containing four octadecylamides (AmPc1 and AmPc2) have been prepared. Both the AmPc1 and AmPc2 derivatives are predicted to form one-dimensional, self-assembled structures with van der Waals' thickness. This results from the hydrogen-bonding force of the secondary amides in solid, in cast film, and in solution and is evident from visible and emission spectra and the X-ray diffraction data. The assembling numbers in AmPc1 and AmPc2, which strongly depend on the condition of the solution, are evaluated as 5-18 for AmPc1 and 2-5 for AmPc2 using a modified molecular exciton theory.

§2-1. Introduction
Phthalocyanines (Pc's), which exhibit high chemical and thermal stabilities among organic compounds, have been of particular interest in many fields of basic and applied research concerning catalysts, solar cells, photosensitizers, low-dimensional metals, gas sensors, electrochromism, lithium batteries, electron beam negative resists, photochemical hole burning memories and molecular electronic devices. However, unsubstituted Pc's generally have some limitations in arranging and organizing the Pc moieties in a desired crystal structure and thickness on solid substrates, because the Pc's usually exhibit polymorphism in the solid state and extremely poor solubilities in common organic solvents.

One of our main interests involves how to control the lattice architecture and electronic delocalization of films prepared by spin cast and Langmuir-Blodgett (LB) techniques for microelectronic devices based on organic substances. For this purpose, several requirements will exist. First of all, the Pc's should be soluble in a suitable solvent. A second important requirement is that the Pc's should be arranged in a one-dimensional (1-D) linear stack with van der Waals' thickness and arrayed in a preferential orientation on a suitable solid substrate.

A variety of molecular approaches has been attempted for the construction of 1-D Pc conductors. The Pc's containing group 13 and 14 metalloids, first-row transition metals and rare-earth metals can provide 1-D conductors, whose stacking structures are linearly controlled by covalent linkage (O, F, S, and organic ligands) and by the out-of-
Unfortunately, these PC's seem not to form spin cast and LB film because of their extremely low solubilities.

As our first attempt to obtain highly soluble 1-D PC self-assemblies having spin cast and LB film forming ability, two new nickelphthalocyanines with four octadecylamide substituents (See Figure 2-1, abbreviated as AmPc1 and AmPc2, respectively) have been synthesized based on the following ideas: If four secondary amides are symmetrically substituted to each of the peripheral position of Pc ring, the most favorable structure is expected to be in 1-D stacked arrays resulting from directional hydrogen-bonding forces of the amide units and intense van der Waals' stacking forces of Pc rings. In addition, introduction of the flexible and hydrophilic n-octadecylamide moieties will help to increase solubility and afford the ability to form LB films of the PC's assemblies. In biological systems, the secondary amides are well known to play an important role in fixing the functional moieties into a specific conformation through the directional hydrogen bonding forces, such as α-helix and β-sheet in proteins and base-pairings in nucleic acids.

In this chapter, we discuss self-assembling features of AmPc1 and AmPc2 in the solid, in the cast films, and in the solutions using a modified molecular exciton theory.

§2-2. Chemical Structure of Phthalocyanines with Alkylamide Substituents

Both the AmPc1 and AmPc2 molecules possess the so-called degenerate Q-bands originating from π-π∗ transitions. These bands are comprised of M and L transitions with the same energies and oscillator strengths along the Pc ring, as shown in Figure 2-1. Accordingly, the characteristic Q-bands are considered as a sensitive probe for discussing the self-assembling features and for characterization of AmPc1 and AmPc2 in solution and in cast films from their electronic absorption spectra.

§2-3. Electronic Absorption Spectra of the Phthalocyanine Assemblies

Figures 2-2 and 2-3 illustrate electronic absorption spectra and their second derivative spectra for AmPc1 and AmPc2 in chlorobenzene solution and in cast films from CHCl3 solution. Figure 2-4 shows electronic absorption and emission spectra of the monomeric state of highly soluble tetraterry-butylPCNi (Ni(TBP)) in CHCl3 solution.

For the respective AmPc1 and AmPc2 derivatives, the shape of the Q-bands in solution resembles the Q-bands in the films. This indicates that the basic assembling structures for AmPc1 and AmPc2 in solution are similar to those in the films.

The Ni(TBP) monomer in solution has a sharp Q(0'-0") band at 670 nm with a width of 450 cm⁻¹ at half height. In contrast, the Q-bands of both AmPc1 and AmPc2 are strongly blue-shifted by ca. 70 nm and broadened by 1770 cm⁻¹ for AmPc1 and by 2680 cm⁻¹ for AmPc2, when compared to the Q(0'-0") of the Ni(TBP) monomer Q-band. The absorption maxima (λmax) values in the main Q-bands are blue-shifted by ca. 4 nm for AmPc1 and by 20 nm for AmPc2, and the satellite Q-bands intensities decrease for both.

Such broadening and blue-shifts in the Q-band spectra for both AmPc1 and AmPc2 seem to be characteristic of the Q-band spectra of 1-D linearly stacked Pc polymers with van der Waals' thickness, such as O-linked tetraterry-butylPcM polymer (TBPOMO)n, O-linked PcM polymer (PcMO)n, and F-linked PcM' polymer (PcMF)n (M = Si, Ge and M' = Al, Ga). In these Pc polymers, the Q-bands are strongly blue-shifted by ca. 30 - 70 nm (600 - 700 cm⁻¹) and exhibit broadening when compared with the corresponding monomer Q-bands. The Q-band spectra of well-defined Pc oligomers have also been reported. The (PcSi)20 and (PcGe)20, which are linearly assembled Pc dimers having van der Waals' thickness, are blue-shifted by 840 and 870 cm⁻¹ from the corresponding PcSi and PcGe monomer Q-bands, respectively. In a series of the O-linked PcSi 1-D oligomers ((PcSiO)n, n means the association number) the Q-band spectra, with increasing n from 1 to 4, have been reported to be blue-shifted, decreased in extinction coefficient, and broadened markedly. In contrast, β-PcCu and β-PcH2 thin films existing in obliquely
Figure 2-2. Electronic absorption (solid line) and its second derivative (dotted line) spectra of AmPc1 (a; 10^{-5} M in chlorobenzene at 80 °C, b; 10^{-3} M in chlorobenzene at room temperature, c; cast film from CHCl₃ solution. Spectrum b is almost identical to spectrum c.)

Figure 2-3. Electronic absorption (solid line) and its second derivative (dotted line) spectra of AmPc2 in CHCl₃ solution (a; 10^{-5} M in chlorobenzene at 80 °C, b; 10^{-3} M in chlorobenzene at room temperature, c; cast film from CHCl₃ solution).

Figure 2-4. Electronic absorption (solid line) and emission (dotted line) spectra of Ni(TBP) (a; absorption spectra for 10^{-5} M in CHCl₃, b; emission spectra for 10^{-5} M in CHCl₃ under excitation at 610 nm).

Figure 2-5. Schematic pictures of one-dimensional phthalocyanine stack array. (M, r, α, and β mean the transition dipole, interplaner spacing, torsion angle, and tilt angle, respectively.)
Figure 2-6. Assembling structures of eclipsed (left), staggered (center), and slipped (β-polymorph) (right) stacks of nickel(II) phthalocyanine.

Stacked structures have two red-shifted Q-bands compared to the monomer Q-bands. Unfortunately, AmPcI and AmPc2 could not be completely dissociated into their monomeric states, even in hot dilute solution due to extremely strong association. The satellite bands are considered to be assigned to the monomeric species, since the $\lambda_{\text{max}}$ values of these are close to that of the TBPNi monomer. These results strongly suggest that both AmPcI and AmPc2 take 1-D assembling structures in solution and in films.

2-4. Calculation of Q-band Spectral Shift Using Molecular Exciton Theory

In Figure 2-5, one-dimensional phthalocyanine stacking array is pictured schematically. According to the molecular exciton approximation, the energy shift ($\Delta E$) between the exciton band for a 1-D infinite chain stack of dyes and its monomer, when the end effects are neglected, is given as follows:

$$\Delta E = E_A - E_m = 2 \left[ \left[ \frac{N!}{N} \right] \left[ \frac{M!}{2} \right] \cos \alpha \cdot \cos \beta \right]$$  \hspace{1cm} (2-1)

where $E_A$ and $E_m$ are the respective assemblies and monomer transition energies, $N$ the association number of the stacks, $M$ the transition dipole strength, $\alpha$ the closest ring spacing between the moments, $\beta$ the torsion angle between the moments, and $\beta$ the tilt angle. The theory has also predicted that from the selection rule, when $0^\circ < \beta < 54.7^\circ$, the absorption band of assemblies will be red-shifted and when $54.7^\circ < \beta < 90^\circ$, the band will be blue-shifted.

The value of $M$ is given as:

$$M = \frac{3h e^2 f}{8\pi^2 m_e c g_0 F_m} \text{erg cm}^3$$  \hspace{1cm} (2-2)

where $h$ is the Planck constant, $e$ the electronic charge, $m_e$ the electron mass, $c$ the velocity of light in vacuum, $g_0$ the degeneracy of the excited state, and $f$ the oscillator strength.

The value of $f$ is calculated by:

$$f = 4.32 \times 10^{-9} \int_{v_1}^{v_2} \epsilon \, dv \text{erg cm}$$  \hspace{1cm} (2-3)

where $\epsilon$ is the molar absorption coefficient in M$^{-1}$ cm$^{-1}$ and $v_1$ and $v_2$ are the initial and final frequencies of the monomer absorption band in cm$^{-1}$. From the integral of the main and satellite Q-bands in Figures 2-2 and 2-3 the $f$ values are evaluated as $f = 3.84 \times 10^{-4}$ erg cm$^{-1}$ for AmPcI and $f = 3.37 \times 10^{-4}$ erg cm$^{-1}$ for AmPc2, assuming that the $f$ value in the assemblies are close to the $f$ in the monomer, based on the sum rule of $f$.

The $M$ values are calculated by substituting the above computed $f$ values and experimentally determined $E_m$ values (14790 and 14950 cm$^{-1}$ for the respective AmPcI and AmPc2 monomeric transitions in the films) into equation 2-2. Accordingly, $M = 2.78 \times 10^{-35}$ erg cm$^3$ for AmPcI and $M = 2.41 \times 10^{-35}$ erg cm$^3$ for AmPc2. Therefore, the value of $\Delta E$ can be evaluated, assuming that $r = 3.36 \AA$, $\beta = 90^\circ$, $\alpha = 0^\circ$ and $45^\circ$ for the AmPcI 1-D linear stacks and $r = 3.36 \AA$, $\beta = 90^\circ$, $\alpha = 0^\circ$ and $45^\circ$ for the AmPc2 1-D linear stacks. The $r$ values are adopted from the X-ray diffraction data as discussed later. The $\alpha = 0^\circ$ and $45^\circ$ values, which are two limiting cases for 1-D Pc systems, mean that the Pc molecules stack in an eclipsed and a staggered form, respectively.

Table 2-1 gives the evaluated and observed exciton shift values for the AmPcI and AmPc2 assemblies in the films, assuming that the assemblies are in infinite stacks. Evidently, the evaluated exciton shift values using eqs 2-1 - 2-3 overestimate the observed ones by a magnitude of three to four times. Since the molecular exciton theory is recognized as a rough approximation in determining exciton shift, only a sufficiently large $r$ value is useful in comparing the distance between the positive and negative charges in excited states (R)$^{44-48}$. In the present Pc assembly systems, the $r$ value (ca. 3.4 Å) is much smaller than the R value (ca. 10 Å). Although eq 2-1 is not suitable to evaluate an actual assembling number of the Pc stacks, the theory should be useful to predict the trend of the exciton shift of the assemblies qualitatively.
§ 2-5 Evaluation of Q-band Spectral Shift Using a Modified Molecular Exciton Theory

In order to evaluate the assembling number in the 1-D Pc stacks briefly and semieperimentally, eq 2-1 reduces as follows:

\[ N = \frac{\Delta E(N \rightarrow \infty)}{\Delta E(N \rightarrow \infty) - \Delta E(N)} \]  

(2-4)

where \( \Delta E(N) \) is the exciton shift for the 1-D Pc stacked with assembling number of \( N \) and \( \Delta E(N \rightarrow \infty) \) the exciton shift for the infinite 1-D Pc stacks. Equation 2-1 or 2-4 indicates that the exciton shift value for the dimer is half that for the infinite chain. If the transition energies in both the dimer and monomer or in both the infinite stacks and monomer are obtained experimentally, the assembling number could be evaluated.

Table 2-2 summarizes the observed exciton shift values and calculated assembling numbers for the AmPc1 and AmPc2 assemblies and the previously reported 1-D Pc polymers and oligomers in their solutions. In the \( (\text{PcSiO}_n) \) oligomers, the calculated assembling numbers for the trimer and tetramer are in good agreement with the actual number, substituting the observed exciton shift value for the dimer and \( (\text{PcSiO}_n) \) polymer into eq 2-4. Both the Pc dimers, \((\text{PcSiO})_2\) and \((\text{PcGeO})_2\), seem to possess similar exciton shift values (840 - 870 cm\(^{-1}\)). Also for \((\text{TBPSiO}_n)\), \(40 \) O-linked tetra(trimethylsilyl)PcGe polymer \((\text{TMSPcGeO}_n)\), AmPc1, and AmPc2, the exciton shift values have approximately

![Graph of Powder X-ray diffraction patterns of two nickel phthalocyanine derivatives with four alkylamide substituents (CuK\(_\alpha\)).](image)

Figure 2-7. Powder X-ray diffraction patterns of two nickel phthalocyanine derivatives with four alkylamide substituents (CuK\(_\alpha\)). (a; AmPc1, b; AmPc2).

### Table 2-1. Observed and Calculated Exciton Shift Values of the Q Bands and AmPc1 and AmPc2 in Cast Films.

<table>
<thead>
<tr>
<th>Pc</th>
<th>( E_\text{cr}^a )</th>
<th>( E_\text{m}^a )</th>
<th>( \Delta E )</th>
<th>( \Delta E )</th>
<th>( \text{error}^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AmPc1</td>
<td>16230</td>
<td>14710</td>
<td>1520</td>
<td>6800</td>
<td>4550</td>
</tr>
<tr>
<td>AmPc2</td>
<td>16400</td>
<td>14710</td>
<td>1740</td>
<td>7000</td>
<td>4550</td>
</tr>
</tbody>
</table>

\( ^a \) Calculated values based on the observed values of oscillator strengths, transition energies, and interplaner spacings for the infinite stacks \( (N \rightarrow \infty) \) using eqs 2-1 - 2-3. \( \alpha = (0^\circ \text{ and } 45^\circ) \) correspond to eclipsed and staggered stacks, respectively (see Figure 2-6). \( \Delta E_{\text{cr}} \) is the observed transition energies for assemblies and monomer in the cast films, respectively.

### Table 2-2. Results for the \( \lambda_{\text{max}} \) Values in the Main Q Bands and Assembling Numbers for One-Dimensional Phthalocyanine Assemblies.

<table>
<thead>
<tr>
<th>Pc</th>
<th>( \eta^a )</th>
<th>( \alpha = 0^\circ )</th>
<th>( \alpha = 45^\circ )</th>
<th>( \text{error}^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (\text{PcSiO})_n )</td>
<td>1</td>
<td>15040</td>
<td>14970</td>
<td>15080</td>
</tr>
<tr>
<td>2</td>
<td>15400</td>
<td>15300</td>
<td>15420</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15850</td>
<td>15760</td>
<td>15880</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>16150</td>
<td>16070</td>
<td>16180</td>
<td></td>
</tr>
<tr>
<td>( (\text{PcGeO})_n )</td>
<td>1</td>
<td>14970</td>
<td>14930</td>
<td>15030</td>
</tr>
<tr>
<td>2</td>
<td>15350</td>
<td>15300</td>
<td>15400</td>
<td></td>
</tr>
<tr>
<td>( (\text{TBPSiO})_n )</td>
<td>1</td>
<td>14710</td>
<td>14790</td>
<td>14870</td>
</tr>
<tr>
<td>2</td>
<td>15040</td>
<td>15080</td>
<td>15120</td>
<td></td>
</tr>
<tr>
<td>( \text{TMSPcGeO}_n )</td>
<td>1</td>
<td>14660</td>
<td>14650</td>
<td>14690</td>
</tr>
<tr>
<td>2</td>
<td>14950</td>
<td>14930</td>
<td>14970</td>
<td></td>
</tr>
<tr>
<td>AmPc1 ((10^{-3}\text{M at rt})^d )</td>
<td>1</td>
<td>14130</td>
<td>14110</td>
<td>14170</td>
</tr>
<tr>
<td>AmPc2 ((10^{-3}\text{M at rt})^d )</td>
<td>1</td>
<td>14300</td>
<td>14300</td>
<td>14350</td>
</tr>
</tbody>
</table>

\( ^a \) in cyclohexane. \( ^b \) in n-hexane. \( ^c \) in benzene. TBP and TMSPc represent \( \text{tetra}(\text{tert-butyl})\text{phthalocyanine} \) and \( \text{tetrakis}(\text{trimethylsilyl})\text{phthalocyanine} \), respectively. \( ^d \) in chlorobenzene; \( rt \) means room temperature. \( ^e \) Actual assembling number. \( ^f \) \( \Delta E_\text{cr} \) and \( \Delta E_\text{m} \) mean the transition energies for the assembly and monomer, respectively. \( ^g \) Observed exciton shift values between the assembly and monomer. \( ^h \) Estimated assembling number based on the observed exciton shift value for the dimer or infinite stacks using eq 2-2 - 2-4.

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constant values, ranging between 1630 - 1770 cm⁻¹, except for the (TBPGeO)₆ polymer. (i(TBPGeO)₈ is expected to be present as an oligomer with n = 4.) These results indicate that eq 2-4, based on the observed exciton shift values of the Pc dimers or infinite assemblies, is applicable in evaluating the association number of the finite 1-D linear Pc stack systems.

Since the observed exciton shift value of AmPc2 in a hot dilute solution of chlorobenzene is similar to those in the above-mentioned O-linked Pc dimers, AmPc2 in solution is presumed to be a dimer. The assembling number of AmPc1 and AmPc2 in solution are also evaluated based on the observed exciton shift value listed in Table 2-2, using equation 2-4. When the solutions were changed from the concentrated ones to a hot dilute states, the assembling numbers of AmPc1 and AmPc2 decrease from 18.7 to 14.4 and markedly from 5.1 to 2.0, respectively. AmPc1 has a higher assembling number than AmPc2. This may be attributed to the difference in hydrogen-bonding forces of the amides of AmPc1 and AmPc2. Although GPC measurements were attempted in order to determine the assembling number directly, both AmPc1 and AmPc2 were strongly absorbed into the column and were not eluted.

§2-6. Further Evidence of One-Dimensional Self-Assembling Feature

Both the AmPc1 and AmPc2 assemblies correspond to the so-called 'H-aggregates' with β = 90°. The exciton theory also predicts that the H-aggregates will quench fluorescence and stimulate phosphorescence. Indeed no emissions from AmPc1 and AmPc2, even in very dilute CHCl₃ solution, were detected in the 600 - 800 nm region by 585 nm-excitation (Stokes shift is 773 cm⁻¹). This also supports the idea that the AmPc1 and AmPc2 assemblies are in the 1-D association state with β = 90°. To estimate the distance of ring separation in the Pc assemblies, X-ray diffraction patterns of the AmPc1 and AmPc2 powders were measured. The Q-band spectra of the powders in nujols are identical to that of the corresponding cast films. Figure 2-5 displays X-ray diffraction patterns of AmPc1 and AmPc2 powders. The AmPc1 pattern shows several sharp peaks, while the AmPc2 pattern has a few broad peaks. This suggests that AmPc1 has a highly crystalline structure due to the strong hydrogen-bonding force of amides, while AmPc2 is less crystalline. Peaks appear at 2θ = 26.0° and 26.5° in the AmPc1 and AmPc2 powders, respectively. These reflections would be associated with closest ring spacings of the Pc assemblies. Similar reflections were already reported for the (PCSO)₆ and (PCGeO)₈ polymers, and seem to be independent of the eclipsed or staggered 1-D structures. If these reflections correspond to the ring separation, the separations are calculated as 3.43 Å for AmPc1 and 3.36 Å for AmPc2, respectively. This suggests that both the AmPc1 and AmPc2 molecules cofacially assemble with van der Waals' thickness, due to the directional hydrogen-bonding force of the secondary amide attached to the Pc peripheral ring. Accordingly, it is concluded that the basic assembling structure of both AmPc1 and AmPc2 in solution and in the cast films are close to that of the corresponding powder crystals.

§2-7. Preparation of Phthalocyanines with Alkylamide Substituents

Soluble nickel phthalocyanines, AmPc1 and AmPc2, were prepared according to the schemes 2-1 and 2-2. Electronic absorption spectra and their second derivative spectra were recorded with a Hitachi 330 UV/visible/near IR spectrophotometer. IR absorption spectra were recorded with a Perkin-Elmer 1800 FT IR spectrometer. ¹H and ¹³C NMR spectra were obtained with both Varian XL-200 and XL-400 FT NMR spectrometers. Elemental analyses for C, H, and N were carried out using a Heraeus CHN-2600 rapid automatic elemental analyser equipment. X-ray diffraction patterns were measured with a Rigaku X-ray diffractometer. Emission spectra were obtained with a Hitachi F-4000 fluorescence spectrophotometer at band path widths of 5 nm for excitation and emission.

(a)Nickel[II] 4,4',4",4"'-Tetrakis(octadecylamino)carbonyl]phthalocyanine (AmPc1)

This was obtained in four steps based on the literature procedure. First of all, nickel 4,4',4",4"'-tetracarbamoylphthalocyanine (I) was obtained by the conventional Wyler method from 4-carboxyphthalic acid anhydride, urea, NiCl₂ and ammonium molybdate tetrahydrate in 1,2-trichloroethane. Hydrolysis of I in aqueous NaOH and HCl gave nickel 4,4',4",4"'-tetracarbamoylphthalocyanine (2). Nickel 4,4',4",4"'-tetrakis(chlorocarbonyl)phthalocyanine (3) was converted to 2 by SOCl₂. A mixture of 3 (0.70 g, 0.85 mmol) and octadecylamine (1.0 g, 3.7 mmol) was heated in 50 mL of dry pyridine at 125 °C for 24 h. The solvent was removed under reduced pressure and the residual solid was redisolved in CHCl₃. The solution was repeatedly washed with dilute HCl and water. After drying over Na₂SO₄ for a day, the solution was concentrated under reduced pressure. The crude product was isolated by column chromatography on silica gel (Woelm Pharm TSC Activity Ill, CHCl₃/EtOH = 98/2) as a first blue fraction. After removal the solvent, the solid was dried in vacuo at 100 °C overnight. A dark blue solid was obtained and the yield was 0.45 g (29 %). Anal. Found: C, 71.07; H, 8.84; N, 9.86. C₁₀₀H₁₆₄N₁₂₀₄Ni-4H₂O: C, 71.10; H, 9.50; N, 9.20. IR (cm⁻¹ )KBr, (v(C-NHCO) amidic I) 1635 br s; (v(C=N amidic II) 1536 br s. ¹H NMR (CDCl₃, (CH₃)₂Si, 200 MHz, 1024 scans) 0.92 (CH₃, 12H), 1.3 br s (CH₃, 12H), 3.5 br s (CH₂-NHCO), 8H); 13C NMR (CDCl₃, (CH₃)₂Si, 100 MHz, 10,000 scans), 14.0 (CH₃), 22.6 (CH₂-CH₃), 29.3-29.7 (CH₂) 31.9 (CH₂-NHCO), 124 (br Pc unit). AmPc1 was dissolved in CHCl₃ at a concentration of about 10⁻¹ M and in hot pyridine or hot decalin up to about 10⁻² M.
(b) NickelII 4,4',4'',4'''-Tetrakis(n-nonadecanoylamino)phthalocyanine (AmPc2).

This was prepared in three steps by the following procedure. First, nickel 4,4',4'',4'''-tetranitrophthalocyanine (4) was obtained by the Wyler method using 4-nitrophthalimide, urea, NiCl2, and ammonium molybdate tetrahydrate in o-dichlorobenzene as starting materials. Nickel 4,4',4'',4'''-tetraaminophthalocyanine (5) was prepared by reduction of 4 with SnCl2 in a mixed solvent of concentrated HCl and EtOH. Compound 5 (0.7 g, 0.9 mmol) was dried over 5.0 g of molecular sieves 4A in 30 mL of dry pyridine at room temperature for 4 h and then allowed to cool. N-Nonadecanoyl chloride (4.0 g, 12.6 mmol) was added to the solution and was allowed to react at room temperature for 1 h and at 100 °C for 2 days. The hot reaction mixture was filtered off and the solvent was removed under reduced pressure. The resulting solid was redissolved in CHCl3 and washed extensively with dilute Na2CO3 and water. After it was dried over molecular sieve 4A for 1 day, the solid was removed under reduced pressure. The solid was dissolved in a small quantity of CHCl3 and the solution was reg precipitated with hot EtOH. The powder was filtered and the solvent was removed under reduced pressure and then dissolved with CHCl3. The final product was isolated by column chromatography on silica gel (Woelm Pharm, TSC Activity III, CHCl3/EtOH = 98/2) as a first green fraction. A dark green product was obtained and the yield was 0.48 g (29%). Anal. Found: C, 72.34; H, 9.23; N, 8.78. Calecd for C4nH4nNiO4N2H2·4H2O: C, 72.07; H, 9.50; N, 9.20. IR (cm⁻1) (KBr): (νC=O, amide I) 1656 br s; (νN-H +νC-N, amide II) 1531 br s; ν(CH) (1-10⁻3 M) λmax (nm) (ε, M⁻1·cm⁻1) 603 (3.05·10⁴), 330 (1.95·10⁴), 1H NMR ((CH₃)₄Si, CDCl₃, 400 MHz, J/CH₃) 0.92 t (CH₃, 12 H), 1.3 br s (CH₂, 12 8H), 3.3-3.8 br m (CH₂-CONH), 6.1 10 none; 13C NMR ((CH₃)₄Si, CDCl₃, 100 MHz FT, 16 100,000 scans). 14.0 (CH₃), 22.6 (CH₂-CH₃), 31.8 (CH₂-CONH), 124 br (Pc ring). AmPc2 could be dissolved in CHCl3 at concentration over about 10⁻¹ M and in hot pyridine and hot decalin up to about 10⁻² M.

(c) NickelII 4,4',4'',4'''-Tetrabutylyphthalocyanine (Ni(TBP)).

This was prepared in three steps using tert-butylbenzene as a starting material by the modified short step procedure of the literature and will be described in Chapter 5 in detail. Anal. Calecd for C₄₄H₄₄Ni: C, 72.46; H, 6.08; N, 14.08. Found: C, 72.26; H, 5.99; N, 13.94. The four possible geometrical isomers of AmPc1 and AmPc2 derivatives could not be characterized by 1H and 13C NMR even in dilute solution, due to strong association.

§2.8 Conclusion

Two new types of highly soluble nickelphthalocyanines with four octadecylamide substituents (AmPc1 and AmPc2) were prepared. Both AmPc1 and AmPc2 are concluded to have one-dimensional, self-assembled structures with van der Waals' thickness. This arises from the directional hydrogen-bonding force of the secondary amides in the solid, in the cast films, and even in dilute solution, as is evident from the visible and emission spectra and the X-ray diffraction data. The assembling numbers of AmPc1 and AmPc2, which strongly depend on the condition of the solution, are evaluated as 5-18 for AmPc1 and 2-5 for AmPc2 using a semimechanistic modified molecular exciton theory.

Other self-assembling phenomena of related Pc compounds have also been reported so far. For example, the PCs involving cumylphenoxy groups have been demonstrated to form tetramers in concentrated solutions (10⁻³ M) and have a interplaner spacing of 3.4 Å in the
solid. The Pc's containing long chain alkyl sulfamides, which have much weaker hydrogen bonding forces than carbamide, dimerize in dilute solutions. PeCu, with eight substituted dodecoxymethyl moieties, has been reported to form dimers or higher aggregates even in very dilute solution.

§2-9. References
CHAPTER 3
IN-PLANE DICHROISMS OF PHTHALOCYANINE LANGMUIR-BLODGETT FILMS

SYNOPSIS
Spectroscopic properties of Langmuir-Blodgett (LB) films of two new highly soluble nickel phthalocyanines (AmPc1 and AmPc2) have been studied. The films have been prepared by vertical dipping as well as by horizontal lifting. The assembling numbers of AmPc1 and AmPc2 strongly depend on the preparation condition of the LB films, and are evaluated as ca. 5 - 14 for the AmPc1 and 5 for the AmPc2 using a modified molecular exciton theory. In-plane dichroisms of the LB films prepared by either the vertical dipping or horizontal lifting technique are invariably seen in UV-visible and IR regions. The dichroic ratios are sensitive to the condition of the film preparation (film pressures, deposition rates, additives, and transfer techniques). Molecular arrangement and orientation in the AmPc1 LB film prepared by the vertical dipping method are characterized by means of the polarized UV-visible and IR spectra, and force-area isothermn.

§3-1. Introduction
Phthalocyanines (Pc's) have received much attention both in basic and applied research,1-3 in connection with solar cells,4,5 photosensitizers,6-8 molecular metals,9-11 gas sensors,12,13 electrochromism,14,15 rechargeable batteries,16,17 electron beam resists,18-20 photochemical hole burning,21 and molecular electronic devices.22 Nevertheless, there are generally limitations in arrangement and organization of unsubstituted Pc moieties in desired crystal structures and thickness onto solid substrates, because Pc’s usually exhibit polymorphisms in the solid state and extremely poor solubilities in common organic solvents.

In recent years, the Langmuir-Blodgett (LB) technique has been noted as a useful means of obtaining tailored thin films of molecular size thickness for a variety of potential applications, such as electron beam resists, non-linear optics, Josephson tunnel junctions, electroluminescences and field effect transistors.22-24 Various surface active molecules can form high quality LB films, which are characterized by new physical and spectral methods. Preparations, characterizations, and photonic and electrical properties of LB films have been studied, using soluble Pc’s which contain various substituents such as tert-butyl, isopropylaminoethyl, dodecoxymethyl, octadecoxy, methoxy-octyloxy, and cumyl-phenox,25-39 Spectral dichroisms has been studied only for five Pc systems.35-39

The control of molecular orientation, assembling structure, and electronic delocalization in Pc LB films in order to apply them to gas-sensitive and photoactive devices
is a primary subject in this thesis. This purpose has several requirements. First, the Pc's should be soluble in spreading solvents. Second, the Pc's should be arranged in the one-dimensional (1-D) linear stack of van der Waals' thickness and arrayed in a preferred orientation on a suitable solid substrate.

In the previous chapter, self-assembling 1-D features of AmPc1 and AmPc2 in the solid, in the cast film, and in the solutions are discussed using a modified molecular exciton theory. This chapter deals with intense in-plane dichroisms observed in both UV-visible and IR regions of AmPc1 and AmPc2 LB films.

§3-2. Evaluation of the Phthalocyanine Assemblage in Langmuir-Blodgett Film

In order to evaluate the assembling number of 1-D Pc stacks simply, the modified molecular exciton theory, as mentioned in chapter 2, is applied to the present Pc LB films:

\[ N = \frac{\Delta E(N \rightarrow \infty)}{\Delta E(N \rightarrow \infty) - \Delta E(N)} \]  

(3-1)

where \( \Delta E(N) \) is the exciton shift for the the 1-D Pc stacks with an assembling number of \( N \) and \( \Delta E(N \rightarrow \infty) \) is the exciton shift for the infinite 1-D Pc stacks. In eq 3-1, the \( \lambda_{max} \) value of the Q-band in the Pc assemblies relates directly to the assembling number.

For evaluation of the orientation of the Pc ring in AmPc1 and AmPc2 LB films using polarized UV-visible and IR spectroscopies, space coordinates used in the present study are shown in Figure 3-1. \( X, Y, \) and \( Z \) are the optical axes, \( Y \) lies in the transfer direction of the substrate in the vertical dipping technique, \( X \) is parallel to the meniscus, \( \omega \) is the angle between the molecular axis of the Pc plate (\( Z^* \)) and \( OZ \), \( \theta \) is the angle between the incident polarized light plane (\( X^* \)) and \( X \), and \( \phi \) is the angle between the mean molecular axis and \( X \). \( A(\theta) \) is the absorbance at \( \theta \). The dichroic ratio (D) is defined as \( A(90^\circ)/A(0^\circ) \). A rather simple expression of biaxial orientation parameters for the degenerate transition molecular system on a substrate is given as follows:

\[ D = \frac{\cos^2 \phi}{\sin^2 \theta} \]  

(3-2)

This equation is based on the assumption that the Pc ring is a flat circular plate with a uniformly distributed transition dipole, although a Pc ring has \( D_4h \) molecular symmetry. If a Pc ring is oriented perpendicularly to the substrate (\( \omega = 90^\circ \)), eq 3-2 can be reduced as follows:

\[ D = \frac{\cos^2 \phi}{\sin^2 \theta} \]  

(3-3)

§3-3. Force-Area Isotherms of the Phthalocyanine Assemblies

Force-area isotherms of AmPc1 and AmPc2 on pure water at 18°C are shown in Figure 3-2. Both AmPc1 and AmPc2 form fairly stable and reproducible films at the air-water interface. The observed occupied area per molecule is 120 and 112Å² for AmPc1 and AmPc2, respectively. Collapsed film pressures are obtained as 30 mN·m⁻¹ for the AmPc1 and 20 mN·m⁻¹ for the AmPc2. The AmPc1 film at the air-water interface can be transferred onto hydrophobic solid substrates by both of the vertical dipping LB technique (abbreviated VDLB, y-type) and the horizontal lifting LB technique (abbreviated HLLB, x-type). The AmPc2 film can be transferred only by the HLLB technique.
Figure 3-2. Force-area isotherms of AmPc1 and AmPc2 on pure water at 18 °C: a, AmPc1; b, AmPc2.

Two typical arrangement models for AmPc1 and AmPc2 molecules at the air-water interface are illustrated in Figure 3-3. Assuming that a Pc square plane has an edge of 12 Å and a ring spacing of 3.4 Å and that the long alkyl moiety has a cross section of 20 Å², the occupied area per molecule is evaluated as 121 Å² for model A and 224 Å² for model B. If the alkyl chain axes are vertical to the air-water interface, the film thickness per layer is calculated as 37 Å for model A and 28 Å for model B. The previously reported 1-D self-assembling character of AmPc1 and AmPc2 is consistent with either of models A and B. If the Pc assemblies develop as in model A, the Pc ring planes are vertically oriented to the air-water interface with a monolayer thickness. If the Pc assemblies develop as in model B, the Pc planes are parallel to the air-water interface with bimolecular thickness. This involves comparison between the observed and calculated limiting area values. Further polarized spectroscopic analysis is required.

Figure 3-3. Two probable models (A and B) for molecular arrangements of AmPc1 and AmPc2 at the air-water interface (square and cylinder represent a Pc ring and octadecyl amide moiety).

§3-4. Dichroism of the Phthalocyanine Langmuir-Blodgett Films by Polarized UV-Visible Absorption Spectroscopy

Typical polarized electronic absorption spectra for AmPc1 VDLB, AmPc1 HLLB, and AmPc2 HLLB films are illustrated in Figures 3-4a to 3-4c. The angular dependence of the main Q-bands at \( \lambda_{\text{max}} = 611 \) nm for the AmPc1 VDLB film sample are shown in Figure 3-5. All these VDLB and HLLB films show dichroism in which the main Q-bands show maxima at \( \theta = \pm 90° \) and a minimum at \( \theta = 0° \) in the angular dependence of the main Q-band intensity. The electronic absorption spectra of AmPc1 VDLB film are almost identical with that of AmPc1 spin cast film. In contrast, the electronic absorption spectra of AmPc1 and AmPc2 HLLB films have a much stronger satellite band at 680 nm than the corresponding spectra of the spin cast film. Also, the main Q-bands of LB films are red-shifted by 11 and 12 nm, respectively. Since the Q-band intensity maximizes at \( \theta = \pm 90° \), the Pc ring planes must be arrayed perpendicularly to the substrate plane. This is because the degenerate M and L transitions of the Q-bands lie in the Pc ring plane. If the Pc ring planes are parallel to the substrate plane, dichroism does not occur. In addition, Pc planes of AmPc1 and AmPc2 seem to take an edge-on configuration at the air-water interface, because of their inherent 1-D self assembling nature even in hot dilute solution. The observed film thickness of AmPc1 (36 Å/layer) is consistent with the estimated value for model A. These results support the idea that AmPc1 and AmPc2 take model A as the molecular arrangement at the air-water interface. This is
Figure 3-4a

Figure 3-4b

Figure 3-4c

Figure 3-4. Polarized electronic absorption spectra of AmPc1 and AmPc2 LB films on quartz substrates. (Figure 3-4a) AmPc1 LB film prepared by the vertical dipping method (80 layers, film pressure 15 mN·m⁻¹, deposition rate; 7 mm·min⁻¹, substrate is parallel to the moving barrier). (Figure 3-4b) AmPc1 LB film prepared by the horizontal lifting method (8 layers, film pressure 18 mN·m⁻¹, substrate is perpendicular to moving barrier). (Figure 3-4c) AmPc2 LB film prepared by the horizontal lifting method (10 layers, film pressure 18 mN·m⁻¹, substrate is perpendicular to moving barrier).

also consistent with the assumption that, in eq 3-3, a Pc ring is oriented perpendicularly to the substrate with \( \omega = 90^\circ \).

There has been little research on dichroism in Pc LB film. To date, there are such studies with two monomeric and one oligomeric Pc systems. The monomeric Pc compounds includes eight docooxymethyl and three isopropylaminomethyl groups.35,36 The oligomeric system is 1-D linear stack PcSi substituted with tetramethoxy-tetraoctyloxy groups (assembling number is 15).37 In the monomeric Pc systems, the dichroic ratios of the Q-band are 2.1 for the Pc substituted with eight long alkyl chains and 1.4 for the Pc substituted with three iso-propylaminomethyl groups. In the oligomeric Pc system, the dichroic ratio of the Q-band is 2.7 for an as-prepared film and becomes 5.8 after thermal annealing. In the present Pc systems, dichroism can consistently be seen for AmPc1 and AmPc2 LB films in both the
Figure 3-5. Angular dependence of the main Q-band intensity ($\lambda_{\text{max}} = 608$ nm) for the AmPc1 VDLB film (data are taken from Figure 3-4a).

Figure 3-6. Angular dependence of the characteristic alkyl amide intensities in the AmPc1 VDLB film (dichroic ratio is 2.0 at 611 nm).

Figure 3-7. Molecular Arrangement Models of the AmPc1 VDLB film on the Substrate (square stands for phthalocyanine ring and rod means long alkyl amide).

UV-visible and IR regions. In particular, the dichroic ratio of AmPc1 (N=14.4) is 2.4 at 608 nm. Except for the Pc with three isopropylamino groups, the other four Pc systems, which are symmetrically substituted with flexible alkyl moieties, are fixed into a 1-D assembled structure by the Si-O-Si covalent linkage or the hydrogen bonding of the secondary amide. We suppose that the coexistence of such flexible alkyl moieties and strongly immobilized Pc ring arrays is very important to achieve a preferential orientation of Pc molecules on substrates.

From Figure 3-4a, the dichroic ratio of AmPc1 is determined to be 2.4. This could correspond to $\phi = 33^\circ$. This suggests that the mean stacking axis of AmPc1 assemblies is tilted by $33^\circ$ to the meniscus (X-axis). Similarly, $\phi = 41^\circ$ could be obtained for AmPc HLLB film by using $D = 1.35$ at 620 nm.

§3-5. Dichroisms of the Phthalocyanine Langmuir-Blodgett Films by Polarized IR Absorption Spectroscopy

Dichroisms in a typical AmPc1 VDLB film can also be seen in the IR region of the alkyl amide moieties. The angular dependence on the intensities of the characteristic alkyl amide bands is shown in Figure 3-6. The amide II band at 1536 cm$^{-1}$, which is a...
The arrangement of the amide moiety, however, is rather difficult, because of the unresolved geometric isomers present in AmPc1 and AmPc2.38 Dichroisms in the IR region closely relate to the Pc ring arrangement. Further discussion on a combination band of \( \text{Abs}(\theta_{\max}) \) maximizes at \( \epsilon = 0^\circ \). The band due to \( \nu_{\text{C-H}} \) maximizes at \( \epsilon = \pm 90^\circ \) and has \( D = 1.6 \). The amide III band due to \( \nu_{\text{C-O}} \) at 1635 cm\(^{-1}\) shows a weak dichroism of \( D = 0.93 \) that maximizes at \( \epsilon = 0^\circ \). The band due to \( \nu_{\text{C-N}} \) at 2922 cm\(^{-1}\) has no dichroism. Such dichroisms in the IR region closely relate to the Pc ring arrangement. Further discussion on the arrangement of the amide moiety, however, is rather difficult, because of the unresolved geometric isomers present in AmPc1 and AmPc2.38

### Table 3-1. Characteristic Parameters in AmPc1 and AmPc2 Langmuir-Blodgett Films Prepared by the Vertical Dipping and Horizontal Lifting Techniques.

<table>
<thead>
<tr>
<th>Pc</th>
<th>method ( b )</th>
<th>( \text{Im} ) (^{a} )</th>
<th>( f ) (^{c} )</th>
<th>( T_{\text{d}} ) (^{d} )</th>
<th>( D ) (^{e} )</th>
<th>( \lambda_{\max} ) (^{f} )</th>
<th>direction of substrate (^{g} )</th>
<th>( N ) (^{h} )</th>
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<tr>
<td>AmPc1</td>
<td>VD 1/0/0</td>
<td>15</td>
<td>1.8</td>
<td>2.4</td>
<td>608</td>
<td>( \perp )</td>
<td>//</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>VD 1/0/0</td>
<td>15</td>
<td>7</td>
<td>2.4</td>
<td>608</td>
<td>( \perp )</td>
<td>//</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>VD 1/0/0</td>
<td>15</td>
<td>7</td>
<td>2.4</td>
<td>608</td>
<td>( \perp )</td>
<td>//</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>VD 1/0/0</td>
<td>15</td>
<td>28</td>
<td>2.1</td>
<td>608</td>
<td>( \perp )</td>
<td>//</td>
<td>14.4</td>
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<td>7</td>
<td>2.0</td>
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<tr>
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<td>1.2</td>
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<td>( \perp )</td>
<td>//</td>
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<tr>
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<td>7</td>
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<td>VD 1/4/0</td>
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<td>1.7</td>
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<tr>
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<tr>
<td>AmPc2</td>
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<td>18</td>
<td>1.1</td>
<td>614</td>
<td>( \perp )</td>
<td>//</td>
<td>6.4</td>
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</tr>
<tr>
<td></td>
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<td>1.1</td>
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<td>( \perp )</td>
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<td>620</td>
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<td>620</td>
<td>( \perp )</td>
<td>//</td>
<td>5.2</td>
<td></td>
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</table>

\( \text{Im} \) and \( f \) represent the molar composition ratio for the phthalocyanine, \( n \)-nonadecanoic acid, and \( n \)-hexadecane, respectively. \(^{a} \) Film pressure. \(^{b} \) Deposition rates of a substrate in the VD method. \(^{c} \) Dichroic ratio for the main Q-bands, defined as \( \text{Abs}(\theta_{\max}) = \text{Abs}(\theta_{90^\circ}) \). \(^{d} \) \( f \) and \( T_{\text{d}} \) mean that a meniscus is parallel and perpendicular to the moving barrier, respectively. \(^{e} \) Values based on the observed \( \lambda_{\max} \) and eq \( \text{eq} 3-1 \). \(^{f} \) Collapse pressure 35 mmN/m. \(^{g} \) Collapse pressure 22 mmN/m. \(^{h} \) No transfer.

§3-6. Effect of Deposition Conditions on the Phthalocyanine Assemblies

The dichroic ratios and absorption maxima of the main Q-bands are sensitive to film pressure, deposition rate, additives, and film deposition methods. For AmPc1 and AmPc2 LB films prepared by the VDLB and HLLB methods, the value of dichroic ratios, \( \lambda_{\max} \), and the evaluated assembling number based on the \( \lambda_{\max} \) value and eq \( 3-1 \) are summarized in Table 3-1.

In AmPc1 single component VDLB systems (\( \text{Im} = 1/0/0 \), where \( l \), \( m \), and \( n \) represent the molar ratios for AmPc1, \( n \)-nonadecanoic acid, and \( n \)-hexadecane, respectively), the dichroic ratio value decreases markedly from 2.4 to 1.2 with increasing film pressures from 15 to 30 mmN/m.\(^{1} \). Also, the \( \lambda_{\max} \) values tend to be red-shifted with increasing film pressures and deposition rate. The red-shift of the main Q-bands indicates that the assembling number of AmPc1 in LB films decreases from 14.4 to 7.8.

Although in AmPc1 composite VDLB systems (\( \text{Im} = 1/4/0 \)) the dichroic ratio increases with increasing deposition rate, the \( \lambda_{\max} \) values of the main Q-bands are red-shifted by 7 - 9 nm compared to those the single component system. This suggests that the assembling number in the composite system markedly decreases, when compared with the single component systems.

Even in the HLLB films, weak dichroisms can be seen. AmPc2 HLLB films have larger dichroic ratios smaller than AmPc1 HLLB films. For AmPc2, the main Q-bands in HLLB films are red-shifted by 13 nm and have intense satellite Q-bands compared to cast films.\(^{38} \) For AmPc1, the main Q-bands in HLLB films are also red-shifted by 3 - 11 nm more than those in cast and VDLB films. This indicates that assembling numbers decrease to 6.4 for AmPc1 and 5.4 for AmPc2.

§3-7. Orientation Mechanism of the Phthalocyanine Assemblies

The molecular arrangement and orientational models of the AmPc1 VDLB film on the substrate are illustrated in Figure 3-7. AmPc1 showing \( \lambda_{\max} = 611 \) nm corresponds to 1-D assemblies with \( N = 8.9 \) from the modified exciton theory.\(^{38} \) The Pc rings of the assemblies are perpendicularly oriented to the substrate. The mean stack axis of the assemblies and the mean direction of the hydrogen bonding band are oriented to the direction of the meniscus.

There are two possible steps in producing orientation of Pc assemblies in LB films. One is the transfer step at the meniscus and the other is the compression step by the moving barrier. If the former process is the cause of the orientation, the dichroic ratio and its phase are independent of the relative direction between the moving barrier and the meniscus in the dipping process. In contrast, the latter leads to a phase shift of the dichroic ratio: though the dichroic ratio is independent of the relative direction between the meniscus and substrate, the Q-bands maximize at \( \epsilon = \pm 90^\circ \) when the meniscus is parallel to the moving barrier, and...


the Q-bands maximize at $\theta = 0^\circ$ when the meniscus is perpendicular to the barrier. Actually, in all AmPc1 VDLB and AmPc2 HLLB films, the respective Q-bands, in which the dichroic ratios in the parallel direction are equal to those in the perpendicular direction, are independent of the relative positions and show maxima at only $\theta = 90^\circ$. This strongly indicates that orientation of Pc assemblies occurs during the transfer step of the meniscus but not during the compression process by the barrier.

The $\lambda_{\text{max}}$ values of the main Q-bands in LB films, which tend to be blue-shifted with increasing dichroic ratios, can be closely related to the assembling number, as discussed previously. From observation of dichroisms in VDLB film and even in HLLB films, both transfer steps of the meniscus and reorganization of AmPc1 and AmPc2 assemblies seem to be important during the up and down strokes of the meniscus in generating a preferential orientation. In this situation, an intense shear stress is applied to the meniscus during deposition of the monolayer. The increase in stress leads to decomposition of Pc assemblies and prevents their reorganization at the meniscus. This also restricts a preferential orientation of 1-D Pc stacks. Stress seems much stronger in the HLLB technique than in the VDLB technique, since dichroic ratios in the HLLB process are smaller than those in the VDLB process under the same film pressure. Increase in film pressure might repress the reorganization of assemblies at the meniscus. Also, addition of hydrogen-bonding oleophilic molecules, which may strongly interact with amide moieties of Pc assemblies, markedly decreases the dichroic ratio and assembling number. Such information may control a preferential orientation of desired molecules on suitable substrates.

§3-8. Preparation of Langmuir-Blodgett Films

A Kyowa Kaimen Kagaku film balance (model HBP-AP) was used, which consists of a Teflon-coated trough, a Wilhelmy type glass float, and vertical dipping and horizontal lifting units. Subphase temperature was regulated at 18 °C by using a Lauda RCS20 thermostat. Doubly distilled pure water was used as the subphase. Optically polished fused quartz and CaF$_2$ were used as solid substrates. Hydrophobic quartz was obtained by treatment with octadecyltrimethylsilane.

A CHCl$_3$ solution containing either AmPc1 or AmPc2 and/or other additives was passed through a Millipore 0.45 μm filter and spread on water. Two techniques were employed for building up films at a desired constant film pressure. One is the conventional LB technique in which only y-type multilayers are deposited by the vertical dipping technique. The other is a modified LB technique in which only x-type multilayers can be formed by the horizontal lifting technique with a small tilt angle. The transfer ratio of AmPc1 by the vertical dipping LB method was equal to unity. Electronic absorption intensities of the built-up films were proportional to the number of the deposition cycles. An LB film thickness per layer was evaluated by using a mechanical stylus method (Sloan: dektak 3030, stylus force: 1 mg, stylus radius: 12.5 μm) to obtain the film thickness of a multilayer.

Electronic absorption spectra and their second derivative spectra were recorded by using a Hitachi 330 UV/visible/near IR spectrophotometer. IR absorption Spectra were recorded with a Perkin-Elmer 1800 FT IR spectrometer. Polarized electronic and IR absorption spectra, in which the incident angle of the light beam is normal, were recorded by using a Glan prism, a gold wire grid polarizer, and a goniometer.

§3-9. Conclusion

LB films of two new types of highly soluble nickel phthalocyanines with four octadecyl amide substituents (AmPc1 and AmPc2) were prepared by using the vertical dipping and horizontal lifting techniques. The assembling numbers of AmPc1 and AmPc2, which depend on the preparation condition of LB films, are evaluated by using a modified molecular exciton theory as ca. 5 - 14 for AmPc1 and ca. 5 for AmPc2. LB film dichroism prepared by either the vertical dipping or horizontal lifting can be consistently seen in UV-visible and/or IR regions. Dichroic ratios and $\lambda_{\text{max}}$ values of Q-bands that correlate to the assembling number are sensitive to the preparation conditions, such as film pressures, deposition rate, additives, and film transfer techniques. Molecular arrangement and orientation models of AmPc1 LB film prepared by the vertical dipping are proposed, on the basis of polarized UV-visible and IR spectra, and force-area isotherms. The transfer steps at the meniscus, which are involved in the vertical dipping and horizontal lifting techniques, strongly suggest the cause of the in-plane dichroism of AmPc1 and AmPc2 LB films. They suggest that dichroic ratios and their phases are independent of the relative direction between the moving barrier and meniscus.

§3-10. References

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