Synthesis and Properties of Amphiphilic Phthalocyanine Derivatives Substituted by Polyethyleneoxide

Midori Kobayashi

Division of Fundamental Science
Graduate School of Science and Technology
Niigata University

March 2012

# Synthesis and Properties of Amphiphilic Phthalocyanine Derivatives Substituted by Polyethyleneoxide 

Midori Kobayashi

A dissertation submitted in partial fulfillment of the requirements for the Degree of Doctor of Science

Division of Fundamental Science Graduate School of Science and Technology<br>Niigata University<br>Niigata, Japan

March 2012


#### Abstract

Phthalocyanines (Pcs) of functional dye have peculiar optical, magnetic and electronic properties. Pcs have been widely used for dyes, pigments, liquid crystals, sensors, optical limiters, solar cells, and photosensitizer for photodynamic therapy of cancer.

Pcs form aggregates in solution by stacking of Pc rings due to the $\pi-\pi$ interaction between planar rings. The formation of higher aggregates results in lowering the solubility of Pcs. Thus, these are poorly-soluble or insoluble in most solvents. The substituted Pcs are synthesized to improve their solubility. It has been reported that these Pcs form aggregates which are dependent on concentrations, solvents and central metal ions of Pc ring. The understanding of aggregation equilibria of Pcs is very important because the properties of Pcs are significantly changed by the aggregation. The solvent effect on aggregation equilibria of Pcs by using one given Pc have scarecely been studied because of the limit owing to their solubility.

In this research, amphiphilic phthalocyanine derivatives having linear polyethyleneoxide $\left(-\mathrm{O}-\left(\mathrm{CH}_{2} \mathrm{CH}_{2}\right)_{n}-\mathrm{C}_{m} \mathrm{H}_{2 m+1}\right)$ (Fig. 1) were synthesized and solvent effect on their aggregation equilibria and structure of the aggregates were elucidated. Complex formation of Pc ring and polyethyleneoxide side chains with alkali metal ions 


Fig. 1. Structure of amphiphilic phthalocyanine derivatives substituted by polyethyleneoxide.

$$
\left(\mathrm{M}=2 \mathrm{H}^{+} \text {or } \mathrm{Cu}^{2+}, \mathrm{R}=-\mathrm{C}_{12} \mathrm{H}_{25} \text { or }-\mathrm{CH}_{3}\right)
$$

and structures of these complexes were also elucidated.
The Pcs form aggregates successively as given by the following equation. The aggregates are stacked face to face between the Pc rings and their slippage between the Pcs in very small.

$$
\mathrm{Pc}+\mathrm{Pc}_{n} \rightleftharpoons \mathrm{Pc}_{n+1}
$$

In the coordinating solvents, the aggregation of Pcs is promoted by the increase in $D N$ of solvent. $D N$ is the indication of coordination ability of the solvent molecule to cationic moiety of solute such as the metal ion. Thus, if the coordination of solvent to the central cation of $\mathrm{Pcs}, \mathrm{Cu}^{2+}$ or $2 \mathrm{H}^{+}$, is the dominant factor of the solvation of Pcs, the solvent of lager $D N$ must promote the cleavage of aggregate to monomer. But the opposite tendency of the experimental results is explained by the decreases in accepting property of solvent by the increase in $D N$.

In the non-coordinating solvents, the monomerization of Pcs is promoted by the increase in $E_{\mathrm{T}}(30)$ value of solvent. This parameter is an indicator of the interaction of the solvent molecule to an anionic or electron donating part of solute, i.e., the index of the electron pair accepting property of the solvent. Thus, the increase in $E_{\mathrm{T}}(30)$ value of solvent results in the strengthening of the salvation to the ethylene oxide moiety, and enhances the cleavage of the aggregates.

The Pc ring moiety and ethylene oxide chain moiety of Pc derivatives form different structures of complexes depending on the ionic radii of alkali metal ions $\left(\mathrm{Li}^{+}, \mathrm{Na}^{+}\right.$and $\mathrm{K}^{+}$). The ethylene oxide chain coordinates the alkali metal ion by surrounding it (Fig. 2). Complexation ability of ethylene oxide chain increases in the following order, $\mathrm{Li}^{+}<\mathrm{Na}^{+}$ $<\mathrm{K}^{+}$, because of the size fitting of ionic radius of metal ion with the cavity size of helical ethylene oxide chain. On the other hand, Pc ring coordinates alkali metal ion and the structures of them are different depending on the suitability of cavity size of Pc ring and ionic radius. In case of the smaller $\mathrm{Li}^{+}$ion, Pc forms a monolithiumphthalocyanine. $\mathrm{Li}^{+}$ion coordinates into the Pc ring cavity because ionic radius of $\mathrm{Li}^{+}$ion fits to the cavity size of Pc ring (Fig. 3(a)). In the case of larger $\mathrm{Na}^{+}$and $\mathrm{K}^{+}$ions, Pc form disodium and dipotassium phthalocyanines and these ions are located on the top and bottom of the Pc ring, i.e., so called sitting a top (SAT) complex.


Fig. 2. Structure of $\mathrm{M}^{+}$-polyethyleneoxide chain complex ( $\mathrm{M}^{+}$; alkali metal ion).
(a)

(b)


Fig. 3. Structures of alkali-metallated phthalocyanine. (a) Monolithium phthalocyanine and (b) disodium and dipotassium phthalocyanine.

## Table of contents

Abstract ..... ii
Table of contents ..... v
General interoduction ..... 1
Chapter 1. Solvent effect on the dimerization of amphiphilic phthalocyanines substituted by polyethyleneoxide ..... 6

1. Introduction ..... 6
2. Materials and methodology ..... 7
2.1. Reagents ..... 7
2.2. Synthesis ..... 7
2.3. Instrumentation ..... 9
2.4. Procedure ..... 9
3. Results and Discussion ..... 10
3.1. Spectral change by Pc concentration ..... 10
3.2. Monomer/dimer equilibrium ..... 11
3.3. Spectral change by the solvents ..... 14
3.4. Solvent effect on aggregation ..... 15
3.5. Fluorescence spectra in various solvents ..... 17
4. Conclusion ..... 18
Tables and figures ..... 20
Chapter 2. Aggregation equilibria of amphiphilic phthalocyanines substituted by ..... 41
polyethyleneoxide in dichloromethane
5. Introduction ..... 41
6. Materials and methodology ..... 42
2.1. Reagents ..... 42
2.2. Instrumentation ..... 43
2.3. Procedure ..... 43
7. Results and Discussion ..... 43
3.1. ${ }^{1} \mathrm{H}$ NMR spectra of TDEO6-MPc ..... 43
3.2. ${ }^{1} \mathrm{H}$ NMR spectral change by Pc concentration ..... 44
3.3. Aggregation equilibria ..... 46
3.4. Structure of monomer ..... 48
3.5. Structure of dimer ..... 50
3.6. Structure of higher aggregate ..... 51
8. Conclusion ..... 52
Tables and figures ..... 54
Chapter 3. Complexation equilibria of polyethyleneoxide substituted phthalocyanine derivatives with alkali metal ions in methanol ..... 67
9. Introduction ..... 67
10. Materials and methodology ..... 68
2.1. Reagents ..... 68
2.2. Synthesis ..... 68
2.3. Instrumentation ..... 70
2.4. Procedure ..... 70
11. Results and Discussion ..... 71
3.1. Dimerization equilibria of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ in various alcohols ..... 71
3.2. Reaction of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ with lithium ion ..... 73
3.3. Reaction of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ with sodium ion ..... 78
3.4. Reaction of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ with potassium ion. ..... 79
3.5. Complex formation of EO-CuPc with alkali metal ion ..... 81
12. General feature of reaction with alkali metal hydroxides ..... 83
Tables and figures ..... 85
General conclusion ..... 109
Reference ..... 111
Acknowledgement ..... 119
Appendix A ..... 120
Appendix B ..... 133
Appendix C ..... 136

## General introduction

Phthalocyanines (Pcs) are the compound in which the four isoindole molecules are cross-linked by nitrogen atoms $(-\mathrm{N}=)$ and the structure of them are similar with those of porphyrins (Fig. 1). The various elements can be incorporated into the center of Pc ring and form the stable complexes which are called metallophthalocyanine (MPc). Various kinds of phthalocyanine derivatives have been synthesized and used ${ }^{1-12}$.


Phthalocyanine (Pc)


Porphyrin

Figure 1. Structure of phthalocyanine and porphyrin.

Phthalocyanines are around blue to green pigments which have a strong absorption in the region from ultraviolet to visible. They have great heat- and light-resistance, hence they have been used for the permanent paints such as bullet trains and road signs ${ }^{\mathbf{5}, 6,11}$. On the other hand, they have a unique and wide variety of photochemical characteristics such as photoelectric effect, oxidation-reduction property, photosensitization etc. In the recent years, hence, they have been applied for liquid crystals ${ }^{\mathbf{2 , 5 , 6 , 1 3 , 1 4}}$, recording medium for $\mathrm{CD}^{\mathbf{5 , 6 , 1 5 , 1 6}}$, solar cells ${ }^{\mathbf{5 , 6 , 1 7}}$, sensors ${ }^{\mathbf{5 , 6 , 1 8 , 1 9}}$, optical limiters ${ }^{4-6,9,11,20,21}$, catalyst ${ }^{1,2,4-6,9,11,22,23}$ and photosensitizer for photodynamic therapy of cancer ${ }^{4-6,11,24,25}$ as the functional dyes.

As a result of formation of higher aggregates, Pcs which have not substituents are gererally hardly soluble in any solvent except for special solvents such as sulfuric
$\operatorname{acid}^{5,6,11}$. They form aggregates by stacking of Pc ring due to the strong $\pi-\pi$ interaction between the Pc rings which have developed $\pi$-conjugated systems and are highly planar ${ }^{5,6,9}$. The low solubility of Pcs is the disadvantage for processing and application for functional material above listed. Thus, the solubilization of Pcs and the improving their solubility are necessary for these processes.

The two common methods are used to improve the solubility of Pcs. The first method is 'the introduction of axial ligands to the central element of Pc ring' and the second method is 'the introduction of substituents into the phenyl group of Pc ring'.

In case of the first method, the introduction of the axial ligands to the central metal of Pc ring is achieved by using the metals which can form the octahedral six-coordination structure. This leads to the inhibition of the stacking between Pc rings and causes the solubilization of Pcs. Metallophthalocyanines with a metal such as $\mathrm{Si}^{\mathbf{2 6 - 3 0}}$ and $\mathrm{Ge}^{31,32}$ are synthesized and their aggregation are effectively prevented by introducing two axial ligands. In the case of metallophthalocyanines of $\mathrm{Al}^{33,34}, \mathrm{~V}^{35,36}$ and $\mathrm{Ti}^{\mathbf{3 7 , 3 8}}$ in which only one axial position is coordinated by a ligand, effect of ligation on the inhibition of aggregation of Pcs is less than that of above complexes. Although the first method is useful for improving solubility of Pcs, the metals which are applicable for this method are limited. If the central metal of the metallophthalocyanine is the active center of functional property such as catalyst or oxidation-reduction reactions ${ }^{39,40}$, the introduction of inactive axial ligands to central metal of Pc results in the inhibition of these reactions.

On the other hand, the second method, derivatization of Pc ring, can solubilize the Pcs with the activity of the central metal. Various phthalocyanine derivatives substituted at $\alpha$ and/or $\beta$ positions of phenyl group of Pc ring have been synthesized. The introduction of water-soluble substituents such as the ionic or strongly hydrophilic substituents leads to the improving solubility of Pcs in polar solvents such as water. The solubility of phthalocyanines having strongly acidic substituents ${ }^{\mathbf{4 2}}$ is not hardly depend
on the pH of solution. On the other hand, the solubility of carboxyl-substituted phthalocyanines ${ }^{43,44}$ depends on pH and these are dissolved in alkaline aqueous solution as an unprotonated anionic form. Phthalocyanines having neutral and strongly hydrophilic substituents such as carbohydrate ${ }^{45}$ and polyethylene glycol ${ }^{46}$ are also water-soluble.

The introduction of lipophilic bulky substituents to Pc ring leads to the improving solubility of Pcs in non-polar organic solvents. The solubilities of bulky tert-butyl ${ }^{47,48}$ and long linear alkyl ${ }^{49,50}$ substituted phthalocyanines are improved by inhibition of stacking of Pc rings caused by the steric hindrance of these substituents.

As mentioned above, various kinds of phthalocyanine derivatives soluble in solvents have been developed. These phthalocyanines, however are only soluble in either polar or non-polar solvent, thus applicable solvents for the treatment of Pcs are limited on one side solvents. In order to overcome the weakness, in our laboratory the amphiphilic pthalocyanine derivatives soluble in a wide variety of solvents have been developed by the introduction of polyethylene oxide (REOn) to Pc ring where REOn has linear alkyl group (R) at the end of EOn.
$\beta$-Polyethylene oxide-substituted phthalocyanine, REOn-MPc, is the amphiphilic compound which has terminal linear alkyl group ( R ) as a lipophilic moiety and linear polyethylene oxide chain (EOn) as a hydrophilic moiety in a molecule. The lipophilic-hydrophilic balance of REOn-MPc can be controlled by changing the length of terminal linear alkyl group, the number ( $n$ ) of repeating unit of ethylene oxide (EO) and the number $(\mathrm{X})$ of introduced REOn chain.

Even if the solubility of Pc is improved by the inhibition of formation of higher aggregates, the aggregation of Pc generally occurs in solution. Degree of aggregation depends on the concentration ${ }^{51,52}$, solvents ${ }^{53}$, central metal of Pc ring ${ }^{54,55}$, substituents ${ }^{56}$, temperature ${ }^{57}$, etc. The various functional properties of Pc are owing to its $18 \pi$-conjugated electron system ${ }^{1-4}$. Thus, the aggregation of Pcs changes the electronic
state of Pc and significantly changes the chemical and optical properties of Pcs ${ }^{4}$. The control of the aggregation of Pcs and understanding of dominant factors manipulating the aggregation are very important because the different aggregation states are needed for different intended purpose. The solvent effect on aggregation of Pcs has been investigated in one category of solvent, either polar ${ }^{58}$ or non-polar ${ }^{59}$, due to the limitation of the solubility of Pcs. Thus, the contribution of solvent properties to aggregation of Pcs by using one given Pc derivative has been rarely studied for integrated solvents.

Polyethylene oxide derivatives are a kind of non-ionic surfactants and they are soluble in water and organic solvents. The ethylene oxide can coordinate to metal ion to form the cationic complex. This complex is easily extracted into organic solvents by forming the ion-pair with appropriate counter anion. Particularly, polyethylene oxide derivatives can extract the alkali metal ions. On the basis of the property of polyethylene oxide derivatives are applied for the separation and determination ${ }^{60-65}$, ion-selective electrode ${ }^{66-68}$ and chromatography ${ }^{69-71}$ of the metal ions.

Amphiphilic REOn-MPcs synthesized in our laboratory have two coordination sites, Pc ring and EOn chains. Pc ring can react with various metal ions to form metallophthalocyanies and polyethylene oxide chains (EOn) are flexible multidentate ligand. Crown ether substituted phthalocyanine derivatives have been synthesized and the complex formation and the ion-pair extraction of these cationic complexes. Many results have been reported for the complex formation of crown ether moiety with metal ions with respect to the cavity size and radius of metal ions, i.e. size fitting ${ }^{72-74}$. On the other hand, linear polyethylene oxide substituted phthalocyanine derivatives have been a little investigated. And the effect of flexibility of the linear polyethylene oxide introduced to Pc ring on its complex formation is very interesting.

In our laboratory, the properties of octa- $\beta$-polyethylene oxide-phthalocyanine derivatives, where all the $\beta$ positions of Pc are substituted by EO, have been
investigated ${ }^{75-77}$.
In this research, the properties of tetra- $\beta$-polyethylene oxide-substituted phthalocyanine derivatives in which one side of $\beta$ position of phenyl group of Pc is substituted by EO were investigated. Although the octasubstituted phthalocyanine consists of single chemical species, tetrasubstituted phthalocyanine is the mixture of four regioisomers. In addition to the change in the number of EO, the study of tetrasubstituted phthalocyanine is interesting on the viewpoint of the effect of regioisomers on the properties of phthalocyanine derivatives.

The purpose of the present study is to clarify the basic properties of Pcs through the elucidation of the solvent effect on aggregation of Pcs and the complex formation of phthalocyanine derivatives with metal ions in solution. This dissertation consists of the following contents.

In the chapter 1 , solvent effect on the dimerization of phthalocyanine derivatives is investigated. The effect of solvent property on the dimerization of phthalocyanine derivatives has been studied by means of UV-vis absorption and emission spectroscopies. Firstly the dimerization of Pcs is quantitatively studied in some non-coordinating solvents then it is studied semiquantitatively in a wide variety of solvents.

In the chapter 2, aggregation equilibria of phthalocyanines in dichloromethane are investigated by means of ${ }^{1} \mathrm{H}$ NMR spectroscopy. By the analysis of their ${ }^{1} \mathrm{H}$ NMR spectra in wide concentration range, the detailed aggregation equilibria were elucidated. The structures of monomer and aggregates in solution are also estimated.

In the chapter 3, complex formation of phthalocyanines with alkali metal ions in methanol are investigated by means of UV-vis absorption, emission and excitation spectroscopies. The effect of ionic radii of alkali metal ions on the selective coordination of rigid Pc ring and flexible polyethylene oxide side chains are discussed.

## Chapter 1

## Solvent effect on the dimerization of amphiphilic phthalocyanines substituted by polyethyleneoxide

## 1. Introduction

Phthalocyanines (Pcs) generally form aggregates in solution by stacking of Pc rings due to the $\pi-\pi$ interaction between planar rings ${ }^{3,5,6,9}$. The formation of higher aggregates results in lowering the solubility of Pcs. Thus, these are poorly-soluble or insoluble in most solvents and used as pigments ${ }^{5,6,11,78}$. Furthermore, phthalocyanines (Pcs) and their metal complexes have peculiar optical, magnetic and electronic properties ${ }^{1-4}$. So the insolubility is the disadvantage of Pcs for purification, processing and application of the compounds. In recent years, Pcs and their metal complexes are applied for various fields ${ }^{1,2,4-6,9,11,13-25}$. Most of these Pcs have substituents to improve their solubility and these substituents are selected according to the purpose of application.

The solubilization of Pcs depends on the over all lipophilic-hydrophilic balance of Pc derivatives and the degree of aggregation in the solvent. The amphiphilic phthalocyanine derivatives have great merits because of the broadly-applicable solvents.

Phthalocyanines substituted by linear polyethylene oxide, the terminal groups of which are hydrogen or methyl group, have been synthesized. Although these are soluble in water, they form higher aggregates ${ }^{79,80}$. The linear polyethylene oxides become amphiphilic by substituting the terminal proton by the alkyl group. Thus, phthalocyanines, REOn-MPc, substituted by polyethylene oxide (EOn) with terminal alkyl group (R), are expected to be amphiphilic and its amphiphilic property is be controlled by changing the chain lengths of polyethylene oxides and terminal alkyl group (R).

This compound, REOn-MPc, is not only used for practical applications but also suitable for the study of solvent effect on aggregation of Pcs. Most studies of solvent effect on aggregation of Pc have been investigated in either polar ${ }^{58}$ or non-polar ${ }^{59}$ solvents because of the limitation of solubility of Pcs. Various properties of Pc are significantly affected by aggregation of Pcs because it changes the electronic state of Pcs. For these reason, solvent effect on aggregation of Pcs in whole range of solvents by using one given Pc derivatives is very important.

In this study, metal-free and copper (II) phthalocyanines tetra- $\beta$-substituted with hexaethyleneglycolmonododecylether, TDEO6-MPc (Scheme 1-1(a)), were synthesized. The solvent effect on dimerization equilibria were investigated by means of UV-vis absorption and fluorescence spectroscopies.

## 2. Materials and methodology

### 2.1. Reagents

All organic solvents were of reagent grade (Wako Pure Chemicals and Nacalai Tesque), and were used as received without further purification. Mono dispersed hexaethyleneglycolmonododecylether, DEO6 ( $>98 \%$ ee) was purchased from Nikko Chemicals. All other chemicals were of reagent grade (Wako Pure Chemicals).

### 2.2. Synthesis

### 2.2.1.

2(3),9(10),16(17),23(24)-Tetra(1,4,7,10,13,16,19-heptaoxahentriacontyl)phthalocyani ne (TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ )

Hexaethyleneglycolmonododecylether (DEO6) ( $7.00 \mathrm{~g}, 15.5 \mathrm{mmol}$ ) was tosylated with $p$-toluenesulfonylchloride $(3.26 \mathrm{~g}, 17.1 \mathrm{mmol})$ in THF $(5.2 \mathrm{ml})$ at $0{ }^{\circ} \mathrm{C}$ for 4 h .

Excess amounts of sodium hydroxide aqueous solution was added and stirred at $0^{\circ} \mathrm{C}$ for 30 min . After addition of cool water, tosylated DEO6 was extracted into chloroform. The chloroform phase was washed by distilled water twice and saturated sodium chloride solution once. After the addition of anhydrous magnesium sulfate, the chloroform phase was left for 12 h . After filtering out magnesium sulfate, chloroform was removed in vacuo. 4.27 g sample of tosylated DEO6 was obtained as a colorless oily product in $46 \%$ yield.

Tosylated DEO6 ( $1.25 \mathrm{~g}, 2.2 \mathrm{mmol}$ ), 4-hydroxyphthalonitrile ( $0.51 \mathrm{~g}, 3.5 \mathrm{mmol}$ ) and anhydrous potassium carbonate $(0.99 \mathrm{~g}, 7.1 \mathrm{mmol})$ were added in dry acetone $(25 \mathrm{ml})$ and stirred at $56^{\circ} \mathrm{C}$ for 48 hrs under a nitrogen atmosphere. After filtration, reaction mixture was evaporated to dryness. The product was extracted by benzene. By the evaporation of benzene under vacuum, 0.88 g sample of 4-DEO6-phthalonitrile was obtained as light orange oil in $69 \%$ yield.

4-DEO6-phthalonitrile ( $0.38 \mathrm{~g}, 0.66 \mathrm{mmol}$ ) and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) $(0.15 \mathrm{~g}, 0.97 \mathrm{mmol})$ in 1-pentanol $(10 \mathrm{ml})$ were refluxed at $140^{\circ} \mathrm{C}$ for 24 h . After the evaporation of the solvent, the dark blue product was washed with methanol and purified by column chromatography on silica gel (methanol/dichloromethane $=$ 85:15 (v/v) as eluent). Deep blue-green TDEO6- $\mathrm{H}_{2} \mathrm{Pc}(0.13 \mathrm{~g})$ was obtained in $34 \%$ yield. Overall yield is $11 \%$. Anal. calcd. for $\mathrm{C}_{128} \mathrm{H}_{210} \mathrm{~N}_{8} \mathrm{O}_{28}$ : C, 66.58; H, 9.17; N, $4.85 \%$. Found: C, $66.57 ; \mathrm{H}, 9.21 ; \mathrm{N}, 4.84 .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz} ; \mathrm{CD}_{2} \mathrm{Cl}_{2} ; \mathrm{Me}_{4} \mathrm{Si}$ ): $\delta_{\mathrm{H}}$, ppm $9.07(4 \mathrm{H}, \mathrm{m}, \mathrm{Ph}), 8.60(4 \mathrm{H}, \mathrm{m}, \mathrm{Ph}), 7.72(4 \mathrm{H}, \mathrm{m}, \mathrm{Ph}), 4.70-3.48(96 \mathrm{H}, \mathrm{m}$, $\left.-\mathrm{O}-\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{O}-\right)_{6}-\right), \quad 3.34\left(8 \mathrm{H}, \quad \mathrm{m}, \quad-\mathrm{O}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\left(\mathrm{CH}_{2}\right)_{9}-\mathrm{CH}_{3}\right), \quad 1.48 \quad(8 \mathrm{H}, \quad \mathrm{m}$, $\left.-\mathrm{O}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\left(\mathrm{CH}_{2}\right)_{9}-\mathrm{CH}_{3}\right), 1.20\left(72 \mathrm{H}, \mathrm{m},-\mathrm{O}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\left(\mathrm{CH}_{2}\right)_{9}-\mathrm{CH}_{3}\right), 0.84(12 \mathrm{H}, \mathrm{t}$, $\left.-\mathrm{O}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\left(\mathrm{CH}_{2}\right)_{9}-\mathrm{CH}_{3}\right) . \mathrm{MS}(\mathrm{FAB}): m / z 2308.5$ (calcd. for $[\mathrm{M}+\mathrm{H}]^{+} 2308.5$ ).

### 2.2.2.

[2(3),9(10),16(17),23(24)-Tetra(1,4,7,10,13,16,19-heptaoxahentriacontyl)phthalocyan atolcopper(II) (TDEO6-CuPc)

TDEO6-CuPc was synthesized by a similar synthetic procedure as TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$. 4-DEO6-phthalonitrile ( $0.39 \mathrm{~g}, 0.67 \mathrm{mmol}$ ) and $\operatorname{DBU}(0.14 \mathrm{~g}, 0.94 \mathrm{mmol})$ was added in the 1-pentanol solution containing anhydrous copper chloride ( $0.04 \mathrm{~g}, 0.29 \mathrm{mmol}$ ) and refluxed at $140{ }^{\circ} \mathrm{C}$ for 24 h . After evaporating the solvent, TDEO6-CuPc thus obtained was washed by methanol and purified by a silica gel column $($ methanol/dichloromethane $=60: 40(\mathrm{v} / \mathrm{v})$ as eluent). Deep blue-green TDEO6-CuPc $(0.25 \mathrm{~g})$ was obtained in $63 \%$ yield. Overall yield is $20 \%$. Anal. calcd. for $\mathrm{C}_{128} \mathrm{H}_{208} \mathrm{~N}_{8} \mathrm{O}_{28} \mathrm{Cu}: \mathrm{C}, 64.85 ; \mathrm{H}, 8.84 ; \mathrm{N}, 4.73$ \%. Found: C, 64.27; H, 8.72; N, 4.86. Contents of copper in TDEO6-CuPc was determined by ICP-MS. Molar ratio found: TDEO6-CuPc : $\mathrm{Cu}=1: 0.97 .{ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz} ; \mathrm{CD}_{2} \mathrm{Cl}_{2} ; \mathrm{Me}_{4} \mathrm{Si}\right): \delta_{\mathrm{H}}, \mathrm{ppm} 4.10-3.50$ $\left(96 \mathrm{H}, \mathrm{m},-\mathrm{O}-\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{O}-\right)_{6}-\right), 3.37\left(8 \mathrm{H}, \mathrm{m},-\mathrm{O}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\left(\mathrm{CH}_{2}\right)_{9}-\mathrm{CH}_{3}\right), 1.50(8 \mathrm{H}, \mathrm{m}$, $\left.-\mathrm{O}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\left(\mathrm{CH}_{2}\right)_{9}-\mathrm{CH}_{3}\right), 1.22\left(72 \mathrm{H}, \mathrm{m},-\mathrm{O}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\left(\mathrm{CH}_{2}\right)_{9}-\mathrm{CH}_{3}\right), 0.85(12 \mathrm{H}, \mathrm{t}$, $\left.-\mathrm{O}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\left(\mathrm{CH}_{2}\right)_{9}-\mathrm{CH}_{3}\right) . \mathrm{MS}(\mathrm{FAB}): m / z 2369.5$ (calcd. for $[\mathrm{M}+\mathrm{H}]^{+} 2369.5$ ).

### 2.3. Instrumentation

The absorption spectra were measured by UV-visible Spectrometer UV-3400 (Hitachi). The fluorescence spectra were measured JASCO FP-6200 spectrofluorometer.

### 2.4. Procedure

### 2.4.1. UV-vis absorption spectroscopy

The absorption spectra were measured at $25.0^{\circ} \mathrm{C}$ by UV-visible Spectrometer. Absorption spectra of TDEO6-MPc in various solvents were measured over a concentration range of compounds, $C_{\mathrm{Pc}}=10^{-6}$ to $10^{-3} \mathrm{M}\left(\mathrm{M} \equiv \mathrm{mol} . \mathrm{dm}^{-3}\right)$ in quarts cells.

Pure solvent was used as reference. Sample solutions were prepared by the following procedure: $1 \times 10^{-4} \mathrm{M}$ TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ and TDEO6-CuPc benzene stock solutions were prepared. Proper amounts of stock solutions were taken in vials and dried. The sample solutions were prepared just before the measurement by adding suitable amounts of solvent. The spectra of high concentration samples were measured by using knockdown cell ( $1-0.01 \mathrm{~cm}$ ), the light path length of which was calibrated by phenol red aqueous solution.

### 2.4.2. Fluorescence spectroscopy

The fluorescence spectra were measured at $25.0^{\circ} \mathrm{C}$ by spectrofluorometer. The spectra of TDEO6-MPc in various solvents were measured in the region of 370-730 nm at $C_{\mathrm{Pc}}=3.10 \times 10^{-6} \mathrm{M}$ by the excitation at $\lambda_{\mathrm{ex}}=370 \mathrm{~nm}$.

## 3. Results and Discussion

### 3.1. Spectral change by Pc concentration

The absorption spectra of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in benzene at various concentration $\left(C_{\mathrm{Pc}}=\right.$ $10^{-6}$ to $10^{-3} \mathrm{M}$ ) are depicted in Fig. 1-4, where the molar extinction coefficient $\varepsilon$ refers to apparent molar extinction coefficient (absorbance of 1 cm light pass/total concentration of Pc ). These spectra consist of two absorption bands, broad and relatively weak band in the range of 300 to 370 nm (Soret band) and sharp and strong band split to two peaks at 667 nm and 704 nm (Q-band). The strong peaks of Q-band are characteristic of monomeric form of Pcs and splitting into two peaks is characteristic of monomeric form of $\mathrm{H}_{2} \mathrm{Pcs}^{5,6,9}$. Thus, very high molar extinction coefficient $\left(\varepsilon=1.2 \times 10^{5} \mathrm{M}^{-1} . \mathrm{cm}^{-1}\right)$ at low Pc concentration suggests that the predominant species of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ at $C_{\mathrm{Pc}}=$ $10^{-6} \mathrm{M}$ is monomer in benzene.

By increasing the total concentration of Pc, the molar extinction coefficient ( $\varepsilon$ ) of

Q-band decreases. Generally, the absorption of Q-band of aggregates of Pc is much weaker compared with that of monomer and the peak position is around $620 \mathrm{~nm}^{\mathbf{5 , 6 , 9 , 7 2}}$. Thus, decrease in $\varepsilon$ by the increase in concentration of Pc is attributed to the decrease in the proportion of monomeric form. As can be seen from Fig. 1-4, there are isosbestic points at 654 and 723 nm for Q-band region and at 339 nm for the Soret band region. The existence of isosbestic points suggests that the two chemical species are equilibrated in the investigated concentration range. The variation of the Soret band is much smaller than that of the Q-band, although the peak maximum slightly shifts to lower wavelength and the molar extinction coefficient decreases a little. The spectral change of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ by the concentration were also measured for other solvents; carbon tetrachloride, chloroform, dichloromethane and 1,2-dichloroethane (Figs 1-5, 1, 2 and 3). Similar spectral change has been obtained for any solvents, although the magnitude of effect of concentration is different by the solvents. The isosbestic points are observed for any solvent systems expect for the high concentration region of carbon tetrachloride solution.

The change in the absorption spectra of TDEO6-CuPc by the concentration was measured in the same manner as that of $\mathrm{TDEO} 6-\mathrm{H}_{2} \mathrm{Pc}$ systems. The results of benzene solution are shown in Fig. 1-9. The spectra of TDEO6-CuPc consist of Soret band around 340 nm and strong single peak of Q-band at 681 nm . The strong single Q-band peak is characteristic of monomeric form of metal complexes of phthalocyanine. The coalescence to single peak of Q-band of metal phthalocyanine monomer is ascribed to its higher symmetry of MPc compared with that of $\mathrm{H}_{2} \mathrm{Pc}^{5,6,9}$. As seen from Fig. 1-9, TDEO6-CuPc shows the similar spectral change as that of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$. That is, the Q-band peak at 681 nm decreases by the increase in the concentration of TDEO6-CuPc accompanying the isosbestic points at 337,663 and 703 nm . Thus, a single equilibrium between monomer and one polymeric species is suggested for the TDEO6-CuPc system, too. Similar results were obtained for other solvents (Figs. 1-6, 7, 8 and 10).

### 3.2. Monomer-dimer equilibrium

The molar extinction coefficients of Q-band peak of TDEO6-MPc in various solvents are plotted as a function of the logarithmic concentration ( $\log C_{\text {Pc }}$ ) in Fig. 1-11 for TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ and in Fig. 1-12 for TDEO6-CuPc. Generally, the dimer is formed as the first step of aggregation ${ }^{52,56,82,83}$, thus the aggregation equilibrium is given by

$$
\begin{equation*}
\mathrm{Pc}+\mathrm{Pc} \stackrel{K_{2}}{\rightleftharpoons} \mathrm{Pc}_{2} \tag{1.1}
\end{equation*}
$$

Where Pc and $\mathrm{Pc}_{2}$ refer to monomeric and dimeric species of TDEO6-MPc, respectively. The presence of isosbestic points in the spectra indicates that only dimer is formed as an aggregate under the present concentration range $\left(C_{\mathrm{Pc}}=10^{-6}-10^{-3} \mathrm{M}\right)$. The formation constant of dimer $\left(K_{2}\right)$ is defined as

$$
\begin{equation*}
K_{2}=\frac{\left[\mathrm{Pc}_{2}\right]}{[\mathrm{Pc}]^{2}} \tag{1.2}
\end{equation*}
$$

The total concentration of TDEO6-MPc $\left(C_{\mathrm{Pc}}\right)$ is given by

$$
\begin{equation*}
C_{\mathrm{Pc}}=[\mathrm{Pc}]+2\left[\mathrm{Pc}_{2}\right]=[\mathrm{Pc}]+2 K_{2}[\mathrm{Pc}]^{2} \tag{1.3}
\end{equation*}
$$

The calculated molar extinction coefficient ( $\varepsilon_{\text {calc }}$ ) is expressed as follows:

$$
\begin{equation*}
\varepsilon_{\mathrm{calc}}=\frac{\varepsilon_{1}[\mathrm{Pc}]+2 \varepsilon_{2}\left[\mathrm{Pc}_{2}\right]}{C_{\mathrm{Pc}}}=\frac{\varepsilon_{1}[\mathrm{Pc}]+2 \varepsilon_{2} K_{2}[\mathrm{Pc}]^{2}}{C_{\mathrm{Pc}}} \tag{1.4}
\end{equation*}
$$

Where $\varepsilon_{1}$ and $\varepsilon_{2}$ are the molar extinction coefficient per one TDEO6-MPc molecule of monomer and dimer, respectively. By solving quadratic equation of [ Pc ], equation 1.3, the concentration of monomer $\mathrm{Pc}[\mathrm{Pc}]$ is given by

$$
\begin{equation*}
[\mathrm{Pc}]=\frac{-1+\left(1+8 K_{2} C_{\mathrm{Pc}}\right)^{1 / 2}}{4 K_{2}} \tag{1.5}
\end{equation*}
$$

Substitution of equation 1.5 into equation 1.4 leads to equation 1.6

$$
\begin{equation*}
\varepsilon_{\mathrm{calc}}=\varepsilon_{2}+\left(\varepsilon_{1}-\varepsilon_{2}\right) \frac{-1+\left(1+8 K_{2} C_{\mathrm{Pc}}\right)^{1 / 2}}{4 K_{2} C_{\mathrm{Pc}}} \tag{1.6}
\end{equation*}
$$

The plot of experimental results of $\varepsilon$ as a function of $C_{\mathrm{Pc}}$ was fitted with calculated molar extinction coefficient, equation 1.5 , by the least-square method. The values of $\varepsilon_{1}$, $\varepsilon_{2}$ and $K_{2}$ giving a minimum of error square sum, $\Sigma\left(\varepsilon-\varepsilon_{\text {calc }}\right)^{2}$ were evaluated. The formation constants of dimer $K_{2}$ thus obtained are listed in Table 1-1. The calculated curves ( $\varepsilon_{\text {calc }}$ ) using these values are shown in Fig. 1-11 and 12 by solid lines. The calculated curves show good agreements with the experimental results. The values of $\varepsilon_{\text {calc }}$ of asymptotes at low $C_{\mathrm{Pc}}$ and high $C_{\mathrm{Pc}}$ are correspond to the molar extinction coefficients of monomer $\left(\varepsilon_{1}\right)$ and dimer $\left(\varepsilon_{2}\right)$, respectively. As can be seen from Figs. 1-3 and 1-4, molar extinction coefficient of monomer $\left(\varepsilon_{1}\right)$ and dimer $\left(\varepsilon_{2}\right)$ of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ at 704 nm are obtained as $(1.3 \pm 0.1) \times 10^{5} \mathrm{M}^{-1} . \mathrm{cm}^{-1}$ and $(2.6 \pm 0.1) \times 10^{4} \mathrm{M}^{-1} . \mathrm{cm}^{-1}$, respectively. And $\varepsilon_{1}$ and $\varepsilon_{2}$ of TDEO6-CuPc at 681 nm are $(1.2 \pm 0.2) \times 10^{5} \mathrm{M}^{-1} \cdot \mathrm{~cm}^{-1}$ and $(3.2 \pm 0.7) \times 10^{4} \mathrm{M}^{-1} . \mathrm{cm}^{-1}$, respectively. Thus, the value of $\varepsilon_{1}$ and of $\varepsilon_{2}$ of TDEO6-MPc does not differ so much among the solvents. These results indicate that the spectra of Pc hardly differ by the solvent. In the case of carbon tetrachloride solution, $\varepsilon$ deviate to lower value from the calculated at higher $C_{\mathrm{Pc}}$, indicating the formation of trimer $\mathrm{Pc}_{3}$.

Dimerization constants of Pc derivatives in non-coordinating solvent were reported as in the range of $\log K_{2}=3-6$. For example, tetra- $\beta$-cumylphenoxyphthalocyanine in chloroform $(3.85)^{56}$, octadodecoxymethylphthalocyanine in dichloroethane, benzene and $n$-hexane $(3-5)^{82}$, tetra- $\beta$-octadecylsulfonamidophthalocyanine copper(II) (4.20) in benzene ${ }^{83}$ and octa(3,7-dimethyloctoxy)phthalocyanine in dodecane (6.18) ${ }^{52}$. Although it is difficult to compare these constants with the present results because the types of derivatives of Pc are different, these results roughly coincide with present data. The dimerization constant, $\log K_{2}$, of $\beta$-substituted Pc is generally lager than that of
$\alpha$-substituted Pc. The $\alpha$-substituent is more crowded than $\alpha$-substituent and distort the Pc ring, thus the $\alpha$-substituent hiders the formation of aggregate ${ }^{56,84}$.

As can be seen from Table 1-1, dimerization constant, $\log K_{2}$, of copper complex, TDEO6-CuPc, are larger than that of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ about 0.5 unit for the given solvent. This tendency agrees with reported results that CuPc are easy to aggregate compared with $\mathrm{H}_{2} \mathrm{Pc}^{85,86}$. In the case of the metal complexes of Pc such as cobalt and zinc complexes, the metal ion in which can be coordinated by Lewis base, however, the aggregates of MPc is easier to dissociate compared with $\mathrm{H}_{2} \mathrm{Pc}$. That is, in coordinating solvents the aggregates are easy to cleaved by the coordination of solvent on the central metal ion ${ }^{87,88}$.

### 3.3. Spectral change by the solvents

Absorption spectra of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ at $6.18 \times 10^{-6} \mathrm{M}$ in various solvents are shown in Fig. 1-13. The absorption peaks at 667 nm and 704 nm in Q-band region, which is characteristic of monomeric form of $\mathrm{H}_{2} \mathrm{Pcs}$, were observed for every solvent except for $n$-hexane. The absorption intensities of these peaks are significantly altered by the solvent. For example, these are very sharp and intense in chloroform and benzene, whereas these appreciably decrease in 1-pentanol. These peaks completely disappear in $n$-hexane, and the Q-band shows a characteristic peak of aggregate, i.e., a broad and weak peak around $620 \mathrm{~nm}^{5,6,9,72}$. Molar extinction coefficients $(\varepsilon)$ at the maximum of monomer peak around 704 and 667 nm are listed in Table 1-2.

The absorption spectra of TDEO6-CuPc at $4.68 \times 10^{-6} \mathrm{M}$ in various solvents are depicted in Fig. 1-14. The absorption peak of Q-band at around 681 nm , which is the characteristic of the monomeric form of metal complex is observed for any solvent, where the spectrum in hexane is not obtained because of low solubility of TDEO6-CuPc. The intensity of the peak is different by the solvent and the order of intensity by the solvent is almost the same as that of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$. Molar extinction coefficients $(\varepsilon)$ at
the peak maximum around 681 nm are listed in Table 1-2. As can be seen from Figs. 1-13 and 14, the shape of Soret band is not significantly changed by solvent except for $n$-hexane. Higher aggregates are formed in $n$-hexane and Soret band are a little decreased and shifted toward shorter wavelength. In any cases, change in Soret band by the solvents is much smaller than that of Q -band.

### 3.4. Solvent effect on aggregation

Although many kinds of lipophilic or hydrophilic phthalocyanines have been synthesized, these are hardly soluble in another type of solvents. Consequently, the solvent effect covering the both type solvents has not been studied by using a fixed one Pc. The solvents used in the present study are listed in Table 1-2. As seen from this table, TDEO6-MPc, in which the amphiphilic linear polyethylene oxide derivatives (PEO) is introduced on the phthalocyanine ring, are soluble in almost all kinds of solvents except for water. These amphiphilic phthalocyanine derivatives enable to study the effect of wide range of solvents on the optical properties and aggregation behavior of the phthalocyanines.

As mentioned above, the decrease in the Q-band absorption is attributed to the formation of aggregates of TDEO6-MPc ${ }^{52,56,82,83}$. The molar ratio monomer TDEO6-MPc was estimated from the apparent molar extinction coefficient given in Table 1-2. For the solvents listed in Table 1-1, the monomer ratio was calculated by using the values of molar extinction coefficient of monomer ( $\varepsilon_{1}$ ) and dimer ( $\varepsilon_{2}$ ) determined by the analysis. On the other hand, the average values, $1.3 \times 10^{5} \mathrm{M}^{-1} . \mathrm{cm}^{-1}$ $\left(\mathrm{H}_{2} \mathrm{Pc}\right)$ and $1.2 \times 10^{5} \mathrm{M}^{-1} . \mathrm{cm}^{-1}(\mathrm{CuPc})$ for $\varepsilon_{1}$ and $2.6 \times 10^{5} \mathrm{M}^{-1} \cdot \mathrm{~cm}^{-1}\left(\mathrm{H}_{2} \mathrm{Pc}\right)$ and $3.2 \times 10^{5}$ $\mathrm{M}^{-1} \cdot \mathrm{~cm}^{-1}(\mathrm{CuPc})$ for $\varepsilon_{2}$, were used for other solvents. In order to examine the correlation of the aggregation with solvent property, the monomer ratio was plotted against the various solvent parameters such as solubility parameter ${ }^{89}$, dielectric permittivity ${ }^{90}$,
dipole moment ${ }^{\mathbf{9 0}}$, Mayer-Gutmann acceptor number $(A N)^{91}$, Gutmann donor number $(D N)^{92,93}$, Richardt's macroscopic solvent parameter $\left(E_{\mathrm{T}}(30)\right)^{94}$. Simple correlation was not obtained for any solvent parameters. The agreeable correlation was obtained by the combination of two parameters, $D N$ and $E_{\mathrm{T}}(30)$ value.

The plot of the monomer ratio as a function of $D N$ is shown in Fig. 1-15(a). The results of ODEO6-MPc ${ }^{75}$ and OMeEO3-MPc ${ }^{76,77}$ are also depicted, where ODEO6-MPc and OMeEO3-MPc are the Pc derivatives in which all the 8 positions of $\beta$-protons of Pc are substituted by DEO6 $\left(-\mathrm{O}-\left(-\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}-\right)_{6}-\mathrm{C}_{12} \mathrm{H}_{25}\right)$ or MeEO 3 (triethyleneglycolmonomethyl, $-\mathrm{O}-\left(-\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}-\right)_{3}-\mathrm{CH}_{3}$ ) groups, respectively. The $D N$ of solvents are listed in Table 1-2. As the $D N$ of solvent increases, the monomer ratio tends to decrease, i.e., phthalocyanine derivatives tend to form aggregates. $D N$ is the indication of coordination ability of the solvent molecule to cationic moiety of solute such as the metal ion. Thus, if the coordination of solvent to the central cation of Pc, $\mathrm{Cu}^{2+}$ or $\left(\mathrm{H}^{+}\right)_{2}$, is the dominant factor of the salvation of Pc , the solvent of lager $D N$ must promote the cleavage of dimer to monomer. As will be shown below, the opposite tendency of the experimental results is explained by the decreases in acceptor nature of solvent by the increase in $D N$.

The monomer ratios in non-coordinating solvents $(D N=0)$ spread over wide range (Fig. 1-15(a)). The monomer ratio in the non-coordinating solvent is plotted as a function of $E_{\mathrm{T}}(30)$ value of the solvent in Fig. 1-15(b). The $E_{\mathrm{T}}(30)$ values are listed in Table 1-2. The monomer ratio increases as $E_{\mathrm{T}}(30)$ value increases for every Pc derivatives. This parameter is an indicator of the interaction of the solvent molecule to an anionic or electron donating part of solute, i.e., the index of the electron pair accepting property of the solvent ${ }^{95}$. The oxygen atoms of ethylene oxide of side chain have lone pair electrons. Consequently, the increase in $E_{\mathrm{T}}(30)$ value of solvent results in the strengthening of the salvation to the ethylene oxide moiety, and enhances the cleavage of the aggregates. The decrease in the monomer ratio by the increase in $D N$
(Fig. 1-15(a)) might be also explained by this effect. That is, the increase in donor property causes the decrease in the acceptor property by the self interaction of solvent, then the aggregation of Pc is promoted.

As can be seen from Fig. 1-15, aggregation of Pc is strongly correlated to the solvent property, particularly aggregation is promoted in coordinating solvents. The aggregation equilibria have been studied in a limited solvent for the given Pc derivatives because of the restriction of solubility of Pcs. The tendency to form the aggregates in coordinating solvent has been reported ${ }^{79,96}$ and agree with that shown in Fig. 1-15(a). Solvent effect on aggregation of Pc derivatives have been studied in non-coordinating ${ }^{53,97}$ by UV-vis absorption spectroscopy. Aggregation of amphiphilic Pc derivatives such as crown ether substituted Pcs has been studied in various solvents including the aqueous solution ${ }^{73,98,99}$. Although the dimerization constants have estimated in some papers, the role of solvent property for the aggregation has scarcely been discussed.

### 3.5. Fluorescence spectra in various solvents

Fluorescence spectra of TDEO6-MPc at $3.10 \times 10^{-6} \mathrm{M}$ were measured in the range of 370 to 730 nm in various solvents. Excitation light at 370 nm was chosen to minimize the effect of the overtone of excitation light and the absorption of excitation light by the sample solution. These emission spectra consist of Raman scattering of the solvent (near 417 nm ), emission in the visible region (425-620 nm) and near infrared (around 710 nm ) and overtone of the excitation light ( 740 nm ). After subtracting the emissions extraneous to the fluorescence of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$, the emission intensity was collected for the sensitivity of a detector as a function of wavelength. In addition to correction of the absorption of the excitation light, the absorption of the fluorescence by TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ was corrected.

Fluorescence spectra of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in various solvents thus obtained are shown in Fig. 1-16. The emission peak which is characteristic of phthalocyanine is observed around 710 nm . Although emission band in the visible region is observed in the uncorrected spectra, it is diminished to negligibly small by the sensitivity correction of the detector. Intensity of the fluorescence peak strongly depends on the solvent, whereas the maximum wavelength does not change so much. The order of decrease in intensity by solvent almost corresponds with that of the Q-band absorption intensity of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$. The intensity at fluorescence peak maximum is plotted against the molar absorption coefficient of Q-band in Fig. 1-17. The fluorescence intensity shows a good linear correlation with absorption intensity. This fact indicates that only the monomeric species of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ fluoresces and its spectrum is similar each other among any solvents in the same manner as the absorption spectra ${ }^{\mathbf{1 0 0}}$. Thus, UV-vis absorption and fluorescence spectra are effective measure to estimate the monomer ratio of phthalocyanine derivatives in solution. On the other hand, TDEO6-CuPc does not fluoresce in any solvents. The fluorescence quenching of the paramagnetic metal complexes are explained by the acceleration of intersystem crossing of the exited state ${ }^{101}$.

## 4. Conclusion

Phthalocyanines substituted by hexaetyleneglycolmonododecylether (TDEO6-MPc; $\mathrm{M}=\left(\mathrm{H}^{+}\right)_{2}$ or $\left.\mathrm{Cu}^{2+}\right)$ were synthesized. By taking advantage of their amphiphilic property, the solvent effect on the aggregation has been studied for the solvents of wide range properties.

Aggregation of TDEO6-MPc in non-coordinating solvents was studied by means of UV-vis absorption spectroscopy. The dimerization constants were determined by the analysis of concentration dependence of absorption spectra.

Aggregation of TDEO6-MPc is suppressed by the increase in the acceptor property of solvents in non-coordinating solvents, whereas it is promoted by the increase in donor property of solvent in coordinating solvents.

The fluorescence intensity is linearly correlated with the absorption intensity, indicating the fluorescence spectra of monomeric species are hardly different in any solvents in the same manner as the absorption spectra.

Table 1-1. Logarithmic dimerization constant (log $K_{2}$ ) of TDEO6-MPc in non-coordinating solvents.

|  | $\log K_{2}$ |  |
| :--- | :---: | :---: |
|  | TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ | TDEO6-CuPc |
| Benzene | 4.21 | 4.26 |
| Carbon tetrachloride | 4.56 | 5.10 |
| Chloroform | 3.10 | 3.75 |
| Dichloromethane | 3.32 | 4.00 |
| 1,2-Dichloroethane | 3.77 | 4.09 |

Table 1-2. Molar extinction coefficient of Q-band of TDEO6-MPc in various solvents and solvent parameters.

|  | Molar extinction coefficient ( $\varepsilon$ ) $/ 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |  |  | Solvent parameter |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ |  | TDEO6-CuPc | $E_{\mathrm{T}}(30)$ | DN |
|  | 704 nm | 667 nm | 681 nm | $/ \mathrm{kcal} \mathrm{mol}^{-1}$ | $/ \mathrm{kcal} \mathrm{~mol}^{-1}$ |
| $n$-Hexane | 1.47 | 2.23 | 1.16 | 31.0 | 0 |
| Xylene | 11.0 | 9.08 | 11.3 | 33.1 | 0 |
| Toluene | 12.0 | 10.1 | 10.9 | 33.9 | 0 |
| Benzene | 10.5 | 8.91 | 9.51 | 34.3 | 0 |
| Chlorobenzene | 11.4 | 9.55 | 11.1 | 36.8 | 0 |
| Carbon tetrachloride | 10.9 | 9.02 | 7.44 | 32.4 | 0 |
| Chloroform | 12.7 | 10.5 | 12.3 | 39.1 | 0 |
| Dichloromethane | 11.7 | 10.1 | 9.61 | 40.7 | 0 |
| 1,2-Dichloroethane | 12.1 | 10.4 | 9.40 | 41.3 | 0 |
| Ethyl acetate | 8.78 | 8.26 | 6.39 | 38.1 | 17.1 |
| Diethyl ether | 4.05 | 4.61 | 3.08 | 34.5 | 19.2 |
| 4-Methyl-2-pentanone | 6.58 | 6.46 | 5.05 | 39.4 | 20 |
| 1-Pentanol | 4.19 | 4.99 | 3.59 | 49.1 | 25 |

(a)

(b)

(c)


Scheme 1-1. Structures of TDEO6-MPc (a), ODEO6-MPc (b) and OMeEO3-MPc (c). T ; tetra-substituted Pc, O; octa-substituted Pc. D; dodecyl group, Me; methyl group. EOn; number of EO. $\mathrm{M}=\left(\mathrm{H}^{+}\right)_{2}$ or $\mathrm{Cu}^{2+}$.


Figure 1-1. Absorption spectra of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in chloroform. $C_{\mathrm{Pc}}: 10^{-5.80}-10^{-3.81} \mathrm{M}$.


Figure 1-2. Absorption spectra of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in dichloromethane. $C_{\mathrm{Pc}}: 10^{-5.40}-10^{-3.81} \mathrm{M}$.


Figure 1-3. Absorption spectra of $\mathrm{TDEO} 6-\mathrm{H}_{2} \mathrm{Pc}$ at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in 1,2-dichloroethane. $C_{\text {Pc }}: 10^{-5.73}-10^{-3.81} \mathrm{M}$.


Figure 1-4. Absorption spectra of $\mathrm{TDEO}-\mathrm{H}_{2} \mathrm{Pc}$ at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in benzene. $C_{\mathrm{Pc}}: 10^{-5.21}-10^{-3.51} \mathrm{M}$.


Figure 1-5. Absorption spectra of $\mathrm{TDEO}-\mathrm{H}_{2} \mathrm{Pc}$ at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in carbon tetrachloride. $C_{\mathrm{Pc}}: 10^{-5.40}-10^{-4.09} \mathrm{M}$.


Figure 1-6. Absorption spectra of TDEO6-CuPc at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in chloroform. $C_{\mathrm{Pc}}: 10^{-5.68}-10^{-3.78} \mathrm{M}$.


Figure 1-7. Absorption spectra of TDEO6-CuPc at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in dichloromethane. $C_{\mathrm{Pc}}: 10^{-5.68}-10^{-3.74} \mathrm{M}$.


Figure 1-8. Absorption spectra of TDEO6-CuPc at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in 1,2-dichloroethane. $C_{\text {Pc }}: 10^{-5.58}-10^{-3.50} \mathrm{M}$.


Figure 1-9. Absorption spectra of TDEO6-CuPc at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in benzene. $C_{\text {Pc }}: 10^{-5.68}-10^{-3.50} \mathrm{M}$.


Figure 1-10. Absorption spectra of TDEO6-CuPc at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in carbon tetrachloride. $C_{\mathrm{Pc}}: 10^{-5.76}-10^{-3.50} \mathrm{M}$.


Figure 1-11. Concentration dependence of molar extinction coefficient of Q-band peak of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in non-coordinating solvents. $\square$; chloroform, O ; dichloromethane, $\triangle$; 1,2-dichloroethane, $\diamond$; benzene, $\nabla$; carbon tetrachloride.


Figure 1-12. Concentration dependence of molar extinction coefficient of Q-band peak of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in non-coordinating solvents. $\square$; chloroform, $\bigcirc$; dichloromethane, $\triangle$; 1,2-dichloroethane, $\diamond$; benzene, $\nabla$; carbon tetrachloride.


Figure 1-13. Absorption spectra of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ at $6.18 \times 10^{-6} \mathrm{M}$ in various solvents. 1; chloroform, 2; dichloromethane, 3; benzene, 4; ethyl acetate, 5; 1-pentanol, 6; $n$-hexane.


Figure 1-14. Absorption spectra of TDEO6-CuPc at $4.68 \times 10^{-6} \mathrm{M}$ in various solvents. 1; chloroform, 2; dichloromethane, 3; benzene, 4; ethyl acetate, 5; 1 -pentanol, 6; $n$-hexane.


Figure 1-15(a). Monomer ratio of Pc derivatives as a function of donor number ( $D N$ ) of solvent. - ; TDEO6- $\mathrm{H}_{2} \mathrm{Pc}, \mathrm{O}$; TDEO6-CuPc, ■; ODEO6- $\mathrm{H}_{2} \mathrm{Pc}, ~ \square ;$ ODEO6-CuPc, $\boldsymbol{\Delta}$; OMeEO3- $\mathrm{H}_{2} \mathrm{Pc}, \triangle$; OMeEO3-CuPc.


Figure 1-15(b). Monomer ratio of Pc derivatives as a function of $E_{\mathrm{T}}(30)$ value of non-coordinating solvent. - ; TDEO6- $\mathrm{H}_{2} \mathrm{Pc}, \mathrm{O}$; TDEO6-CuPc, $\boldsymbol{\square}$; ODEO6- $\mathrm{H}_{2} \mathrm{Pc}, \quad \square$; ODEO6-CuPc, $\mathbf{\Delta}$; OMeEO3- $\mathrm{H}_{2} \mathrm{Pc}, \quad \triangle$; OMeEO3-CuPc.


Figure 1-16. Corrected fluorescence spectra $\left(\lambda_{\mathrm{ex}}=370 \mathrm{~nm}\right)$ of TDEO6-H2Pc at $3.10 \times$ 10-6 M in various solvents. 1 ; chloroform, 2 ; dichloromethane, 3 ; benzene, 4; ethyl acetate, 5; 1-pentanol, 6; $n$-hexane.


Figure 1-17. Correlation of fluorescence intensity of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ with the molar extinction coefficient in various solvents.

## Chapter 2

## Aggregation equilibria of amphiphilic phthalocyanines substituted by polyethyleneoxide in dichloromethane

## 1. Introduction

Aggregation is a well known phenomenon in phthalocyanine (Pc) chemistry ${ }^{5,6,9,103-105}$. Various chemical and optical properties of Pc are related to its electronic state. Those are significantly changed by aggregation because aggregation causes a substantial change of electronic state of $\mathrm{Pc}^{1-4,9}$. Thus, the elucidation of aggregation equilibria is important for both of the formation constant and application of Pcs.

Various techniques are available for analysis of aggregation equilibria in solution. UV-vis and NMR spectroscopies are the most popular methods. Because of very high molar extinction coefficient of Pcs, UV-vis spectroscopy is effective method for the study in low concentration range of Pcs. The lower aggregation equilibria such as monomer-dimer equilibrium have been studied by this method ${ }^{52,56,82,106}$. The UV-vis spectra contain the structural information about aggregates, however this method is not suitable for the detailed structural analysis ${ }^{107}$.

On the other hand, NMR spectroscopy can be applied for the wide dynamic range of concentration. Thus it is suitable for the study of the aggregation in higher concentration region. By increasing the concentration of $\mathrm{Pc},{ }^{1} \mathrm{H}$ NMR chemical shifts of Pc are changed by the formation of aggregates ${ }^{108,109}$. The chemical shift change by the formation of aggregates provides the structural information about aggregates. For example, oxo(2,3,4,10,16,17,23,24- or 1,2,8,11,15,18,22,25-octasubstitutedphthalocyanato)titanium(IV) ${ }^{110}$ and
methyl(1,4,8,11,15,18,22,25-octa- $n$-phenylphthalocyanato)rhodium(III) ${ }^{111}$ synthesized and their aggregation equilibria were studied by ${ }^{1} \mathrm{H}$ NMR spectroscopy. The detailed analysis of NMR spectral change is limited to monomer-dimer equilibrium because ${ }^{1} \mathrm{H}$ NMR signals of higher aggregates are extremely complicated. Thus, Pcs in these study are designed to allow the formation of dimer but to inhibit the formation of higher aggregates by the steric hindrance of an axial substituent of Pc. ${ }^{1} \mathrm{H}$ NMR analysis of aggregation equilibria higher than dimer has been rarely reported.

Relatively higher concentration of sample solution is required for the NMR measurements. Thus, the solvent in which the formation of aggregates is inhibited is required for this study. The dimerization of polyethylene oxide-substituted phthalocyanines is suppressed in non-coordinating solvents such as chloroform and dichloromethane as shown in chapter 1. Thus, dichloromethane is suitable for the study of aggregation equilibria. The tetrasubstituted phthalocyanine consists of the mixture of four regioisomer, whereas the octasubstituted phthalocyanine has only the single chemical species ${ }^{75-77}$.

In chapter 2, the aggregation equilibria of metal-free (TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ ) and copper complex (TDEO6-CuPc) of phthalocyanine having linear polyethylene oxide (TDEO6-MPc) was investigated by means of ${ }^{1} \mathrm{H}$ NMR spectroscopy in dichloromethane. By the analysis of concentration dependence of ${ }^{1} \mathrm{H}$ NMR signals, successive formation constants of aggregates were determined and structure of monomer and aggregates of TDEO6-MPc were estimated.

## 2. Materials and methodology

### 2.1. Reagents

Deuterated dichloromethane was obtained from Taiyo Sanso. Monodispersed hexaethyleneglycolmonododecylether, DEO6-H ( $>98 \%$ ee), was purchased from

Nikko Chemicals. All other chemicals were of reagent grade (Wako Pure Chemicals). Metal-free (TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ ) and copper complexes (TDEO6-CuPc) of 2(3),9(10),16(17),23(24)-tetra(1,4,7,10,13,16,19-heptaoxahentriacontyl)phthalocyanine (Scheme 1) were synthesized according to the method in chapter 1.

### 2.2. Instrumentation

The ${ }^{1} \mathrm{H}$ NMR spectra were recorded on a Varian Unity- 500 FT NMR spectrometer.

### 2.3. Procedure

The ${ }^{1} \mathrm{H}$ NMR spectra were measured by a $5 \mathrm{~mm} \varnothing$ sample tube at $25^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR spectra of TDEO6-MPc in deuterated dichloromethane (dichloromethane- $d_{2}$ ) were measured over a concentration range of compounds, $C_{\mathrm{Pc}}=10^{-5.5}$ to $10^{-1.5} \mathrm{M}$. Tetramethylsilane was used as internal reference. Sample solutions were prepared by the following procedure: $1 \times 10^{-2}$ and $1 \times 10^{-4} \mathrm{M}$ TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ and TDEO6-CuPc benzene stock solutions were prepared. Proper amounts of stock solutions were taken in vials and dried. The sample solutions were prepared just before the measurement by adding suitable amounts of dichloromethane- $d_{2}$.

## 3. Results and Discussion

## 3.1. ${ }^{1}$ H NMR spectra of TDEO6-MPc

The
structure
of
$2(3), 9(10), 16(17), 23(24)$-tetra- $\beta-(1,4,7,10,13,16,19$-heptaoxahentriacontyl)phthalocyani ne is given in Scheme 2-1 and this will be abbreviated as TDEO6-MPc. In the compound TDEO6-MPc, four protons at $\beta$-positions ( 2 or 3,9 or 10,16 or 17 , and 23 or
24) of Pc are substituted by DEO6 $\left(-\mathrm{O}-\left(-\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}-\right)_{6}-\mathrm{C}_{12} \mathrm{H}_{25}\right)$ groups. Their central metal ion of Pc ring are two hydrogen ions or a copper(II) ion, here these are abbreviated as TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ and TDEO6-CuPc, respectively. ${ }^{1} \mathrm{H}$ NMR spectra of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ at 2.42 $\times 10^{-4} \mathrm{M}\left(\mathrm{M} \equiv \mathrm{mol} \cdot \mathrm{dm}^{-3}\right)$ and TDEO6-CuPc at $3.85 \times 10^{-4} \mathrm{M}$ in deuterated dichloromethane (dichloromethane- $d_{2}$ ) are shown in Fig. 2-1(b) and (a), respectively. All the proton signals were assigned with a help of ${ }^{1} \mathrm{H}_{-}{ }^{1} \mathrm{H}$ COSY measurements and spin analysis ${ }^{65}$. Alphabetical symbols given on the peaks correspond to the symbols of the protons shown in Scheme 2-2. The signals around 5.32 ppm are ascribed to the undeuterated solvent $\mathrm{CHDCl}_{2}$.

The spectrum of the metal-free TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ (Fig. 2-1(b)) consists of the signals of aromatic protons $\mathrm{x}, \mathrm{y}$ and z of the phthalocyanine ring ( 9.0 to 7.3 ppm ), methylene protons $\mathrm{b}-\mathrm{j}$ of ethylene oxide ( 4.8 to 3.3 ppm ) and the terminal alkyl protons $\mathrm{k}-\mathrm{m}$ of the DEO6 side chains ( 1.6 to 0.7 ppm ). In the case of copper complexes TDEO6-CuPc (Fig. 2-1(a)), all the signals are broadened by the effect of the paramagnetic divalent copper ion coordinated in the cavity of the phthalocyanine ring. Particularly, the signals of aromatic protons $\mathrm{x}, \mathrm{y}, \mathrm{z}$ and proton b of DEO6 side chain can not be recognized because of significant broadening of the peaks. The chemical shift of each proton of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ is not significantly changed by the formation of copper complex TDEO6-CuPc.

## 3.2. ${ }^{1}$ H NMR spectral change by Pc concentration

UV-vis absorption ${ }^{52,56,82,106}$ and NMR $^{108,109,110,111}$ spectroscopies are the most commonly used methods for the study of aggregation equilibria in solution. In chapter 1 , we reported the dimerization constants of TDEO6-MPc in various solvents determined by UV-vis spectroscopy. Although UV-vis spectroscopy is suitable for low concentration solution, it is difficult for the measurement in the high concentration
solution because of very large molar extinction coefficient of Pcs. On the other hand, the dynamic range of NMR method is very wide, so it can be applied to the high concentration solution.
${ }^{1} \mathrm{H}$ NMR spectra of TDEO6-MPc were measured at various concentrations $\left(C_{\mathrm{Pc}}=\right.$ $10^{-5.5}$ to $10^{-1.5} \mathrm{M}$ ) in dichloromethane- $d_{2}$. Some examples of spectra of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in the regions of ethylene oxide protons $\mathrm{b}-\mathrm{j}$ and aromatic protons $\mathrm{x}, \mathrm{y}$ and z are depicted in Figs. 2-2(a) and 2-2(b), respectively. All the signals clearly show the concentration dependence for the chemical shift and line broadening. In particular, the signals of the protons $b$ and c are broadened with increasing the concentration, and finally split to two peaks at higher concentration. Direction and magnitude of the chemical shifts change depend on the position of protons in the TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$.

The changes in the chemical shift $(\Delta \delta)$ of each proton by the increase in the concentration were evaluated. The value of $\Delta \delta$ of ethylene oxide protons and the phthalocyanine ring protons of TDEO6 $-\mathrm{H}_{2} \mathrm{Pc}$ are plotted as a function of logarithmic concentration ( $\log C_{\mathrm{Pc}}$ ) in Figs. 2-3(a) and 2-3(b), respectively. Where $\Delta \delta$ is defined by the difference of chemical shift at a given concentration from that at lowest concentration $\left(C_{\mathrm{Pc}}=2.99 \times 10^{-6} \mathrm{M}\right)$. As can be seen from Fig. 2-3(a), the signal of methylene proton $b$, which is the closest methylene proton to the phthalocyanine ring, shows the upfield shift by the increase in the TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ concentration. On the other hand, although the signal of proton c shows the downfield shift at low concentration, the direction is altered to the upfield shift at the high concentration. The signals of protons d - g3 show the downfield shift and the magnitude of their chemical shift change decreases with increasing the distance of protons from phthalocyanine ring. All the signals of aromatic protons $\mathrm{x}, \mathrm{y}$, and z of phthalocyanine ring show the large upfield shift by the increase in concentration (Fig. 2-3(b)) and the extent of upfield shift change of them are much larger than those of protons of DEO6 side chain. Although the peak width of aromatic protons at low concentration is narrower than that of ethylene oxide
protons, the signals become broader and are divided into many complex peaks as the concentration increases.

Some examples of spectra of copper complex TDEO6-CuPc in the regions of ethylene oxide protons are depicted in Fig. 2-4. The chemical shift change $(\Delta \delta)$ is plotted as a function of logarithmic concentration ( $\log C_{\mathrm{Pc}}$ ) in Fig. 2-5. $\Delta \delta$ of TDEO6-CuPc changes by almost the same manner as that of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$, although the signals of protons c and d show the maximum.

### 3.3. Aggregation equilibria

The chemical shift change shown in Figs. 2-3 and 2-5 are generally observed for phthalocyanines in any solvents and this change is attributed to the formation of aggregates by the increase in the concentration ${ }^{108-116}$. The plots of $\Delta \delta$ vs. $\log C_{\mathrm{Pc}}$ of some protons show the maximum, that is, the direction of chemical shift change by Pc concentration alters at higher $C_{\mathrm{Pc}}$. These results indicate the formation of higher aggregates than the dimer at high $C_{\mathrm{Pc}}$.

The successive formation of $n$th aggregate, $\mathrm{Pc}_{n}$, where $n$ is a number of aggregated Pc molecules, and the successive formation constant of $\mathrm{Pc}_{n}, K_{n}$, are given by

$$
\begin{align*}
& \mathrm{Pc}+\mathrm{Pc}_{n-1} \xlongequal{K_{n}} \mathrm{Pc}_{n}  \tag{2.1}\\
& K_{n}=\frac{\left[\mathrm{Pc}_{n}\right]}{[\mathrm{Pc}]\left[\mathrm{Pc}_{n-1}\right]} \tag{2.2}
\end{align*}
$$

In any concentration of Pc the signal of each proton is not separated to corresponding peaks of aggregates, but changes the chemical shift. This fact suggests the aggregation equilibria are fast with respect to the NMR time scale. Consequently, the chemical shifts at various concentrations of Pc are given by the weighted average of the chemical shifts of each aggregate $\left(\delta_{n}\right)$, i.e., the calculated chemical shift, $\delta_{\text {calc }}$, is
given by

$$
\begin{align*}
\delta_{\text {calc }} & =\frac{\delta_{1}[\mathrm{Pc}]+\sum n \delta_{n}\left[\mathrm{Pc}_{n}\right]}{C_{\mathrm{Pc}}} \\
& =\frac{\delta_{1}[\mathrm{Pc}]+2 \delta_{2} K_{2}[\mathrm{Pc}]^{2}+3 \delta_{3} K_{2} K_{3}[\mathrm{Pc}]^{3}+\cdots}{C_{\mathrm{Pc}}} \tag{2.3}
\end{align*}
$$

Where $\delta_{n}$ are the chemical shifts of $n$th aggregates, $\mathrm{Pc}_{n}$.
The successive formation constant of aggregates $\left(K_{n}\right)$ and the chemical shifts of monomer $\left(\delta_{1}\right)$ and each aggregate $\left(\delta_{n}\right)$ giving the minimum error square sum of chemical shift between the observed and calculated, $\Sigma\left(\delta-\delta_{\text {calc }}\right)^{2}$, were evaluated by using the non-linear least-square method. It is required for this analysis to take into consideration the successive formation of aggregates up to the trimer for TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ and to the tetramer for TDEO6-CuPc under the present concentration range of TDEO6-MPc. The chemical shifts of monomer $\left(\delta_{1}\right)$ and each aggregate $\left(\delta_{n}\right)$ thus obtained are listed in Table 2-1 and the successive formation constant of aggregates $\left(K_{n}\right)$ are listed in Table 2-2. As the error of the constant $K_{4}$ for TDEO6-CuPc is very large, it is not listed in Table 2-2. The calculated curves by using these parameters are shown in Figs. 2-3 and 2-5 by solid lines. These curves show good fitting with the experimental results for any signals of protons. The dimerization constants $\left(K_{2}\right)$ obtained by UV-vis absorption spectroscopy in chapter 1 are also listed in parentheses (Table 2-2). The dimerization constants obtained by NMR method are reasonably agreed with those obtained by UV-vis absorption spectroscopy.

Dimerization constant of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ is higher than that of TDEO6-CuPc in any solvents in chapter 1. In the same manner as the dimerization constant, the successive formation constant of trimer, $K_{3}$, of TDEO6-CuPc is higher than that of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$. Although the formation of tetramer is not observed for TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in the concentration range of present experimental conditions, TDEO6-CuPc forms tetramer at higher $C_{\mathrm{Pc}}$. These results agree with the tendency of $K_{2}$ and $K_{3}$ between TDEO6- CuPc
and TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$.

### 3.4. Structure of monomer

In order to estimate the structure of TDEO6-MPc, the chemical shifts of protons of DEO6 moiety were compared with those of DEO6-H and DEO6-ph, where the Pc of TDEO6-MPc is substituted by hydrogen (DEO6-H) or phthalonitrile (DEO6-ph). The structures and alphabetical symbols of protons of these compounds are depicted in Scheme 2-2. ${ }^{1} \mathrm{H}$ NMR spectra of DEO6-H and DEO6-ph are depicted in Fig. 2-1 together with those of TDEO6-MPc. The chemical shifts of each proton of DEO6-H and DEO6-ph determined by the spin analysis ${ }^{65}$ are listed in Table 2-3. These spectra are not changed by the concentration, thus the formation of aggregates is negligible. In case of the TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ the chemical shifts of monomeric form obtained by the analysis of concentration dependence (Table 2-1) are listed. Differences of chemical shifts of each proton $(\Delta \delta)$ of DEO6 moiety of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ and DEO6-ph from DEO6-H, i.e., chemical shift change by the substitution of H of terminal OH by phenyl group (phthalonitrile) or Pc (phthalocyanine), are plotted as a function of proton symbol in Fig. 2-6.

As can be seen from Table 2-3, the chemical shift of methylene protons of ethylene oxide (protons $\mathrm{b}-\mathrm{j}$ ) of DEO6-H are $3.54 \pm 0.13 \mathrm{ppm}$ and not significantly different among them. The substitution of terminal H by the phenyl group or phthlocyanine causes a large chemical shift change $\Delta \delta$ for these protons and the extent of change of Pc is much larger than that of phthalonitrile. Although the extent of $\Delta \delta$ of methylene proton decreases by receding from the Pc ring, the effect of Pc reaches up to protong2. Such a strong influence reached to long distance suggests that the chemical shift change is attributed to the ring current effect of Pc. The downfield shift of the protons $b-\mathrm{g}$ 2 indicates that these methylene protons are located in the equatorial region of the Pc ring.

Contrary to these signals, the signals of proton $\mathfrak{f 3}-\mathrm{m}$ of TDEO6 $-\mathrm{H}_{2} \mathrm{Pc}$ are shifted to upfield than those of DEO6-H. This upfield shift indicates that the alkyl end of DEO6 side chain can be located in the axial region of Pc ring. That is, DEO6 side chain is not fixed straight or helically to the equatorial plane of the Pc ring, but is flexible and moves freely. The signals of the protons $\mathrm{h}-\mathrm{j}$ of TDEO6-CuPc, which are separated by a large number of bonding from Pc ring, also show the line broadening by the effect of paramagnetic copper(II) ion in the center of Pc ring (Fig. 2-4). This fact indicates that the end part of DEO6 chain can spacially come closer to Pc ring. Thus, this fact also supports the flexible structure of DEO6 side chains. In the case of DEO6-ph, because of very small effect of ring current of benzene group compared with that of Pc group, the downfield shift is observed only up to proton fl and the upfield shift of terminal methylene protons was not observed (Fig. 2-6).

In case of present compound TDEO6-MPc, $2(3), 9(10), 16(17), 23(24)$-tetrasubstituted phthalocyanine, one of two $\beta$-positions is substituted at random by the DEO6 side chain, thus this compound is the mixture of four regioisomers. As can be seen from the ${ }^{1} \mathrm{H}$ NMR spectra of Fig. 2-3(b), the signals of any protons show the broadening even at the lowest concentration, where more than $97 \%$ of TDEO6 $-\mathrm{H}_{2} \mathrm{Pc}$ is monomer. The half-height width $(0.03-0.05 \mathrm{ppm})$ of the peaks is larger than the separation of signal caused by the coupling with neighboring protons of phthalonitrile (Fig. 2-1). Thus, these broadening can be attributed to the overlap of the signals of the regioisomers. Because of low resolution of spectrum at very low concentration, the signal is not separated to each regioisomer's signal. 2(3),9(10),16(17),23(24)-Tetra((1S)-endo-(-)-bornyloxy)phthalocyanine was synthesized and each regioisomer was separated ${ }^{117}$. The half-height width of Pc ring protons of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ is almost the same as the chemical shift difference between each regioisomer ( $\sim 0.05 \mathrm{ppm}$ ).

### 3.5. Structure of dimer

The difference of chemical shift of each proton of TDEO6-MPc between dimer $\left(\delta_{2}\right)$ and monomer $\left(\delta_{1}\right)$, i.e., change in chemical shift $\left(\delta_{2}-\delta_{1}\right)$ by the formation of dimer is listed in Table 1. As can be seen from Table 1, the dimerization of Pc causes the upfield shift of the signals of proton $x, y$ and $z$. On the other hand, the protons of DEO6 side chain except for the proton $b$ shift to downfield. These chemical shift changes are attributed to the effect of ring current of another phthalocyanine adjoined by the formation of dimer. The molecular models of the TDEO6-MPc are depicted in Fig. 2-7, where the top view of monomer and the side view of dimer are shown in (a) and (b), respectively. Where only one DEO6 side chain is depicted and all other DEO6 chains are omitted for simplicity. As discussed above, the DEO6 moiety of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ must be actually helical and flexible, although it is described by straight bar model.

Very large upfield shift of Pc protons, x , y and z , indicate that the Pc locates above another Pc ring of dimer. On the other hand, the downfield shifts of the signals of protons of DEO6 moiety indicate that the DEO6 protons locate in the equatorial region of another Pc. The alteration in the direction of chemical shift change by the formation of dimer $\left(\delta_{2}-\delta_{1}\right)$, i.e., upfield to downfield change, occurs near the proton b and upfield shift of proton b is very small. These may indicate that the edge of Pc ring is located above the proton b, i.e., the two Pc rings are stacked in a manner of somewhat slip-stacked face to face as shown in Fig. 2-7(b). The blue shift of the Q-band by the formation of dimer of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ (chapter 1) supports the small slippage of dimer ${ }^{118}$. The distance $3.4 \AA$ reported ${ }^{118-120}$ is used for the spacing between Pc rings of the dimer in Fig. 2-7(b). As the compound TDEO6 $-\mathrm{H}_{2} \mathrm{Pc}$ is the mixture of four regioisomers ${ }^{117}$, many kinds of configurational isomers of dimer are formed by the various combinations of two TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$. The chemical shifts of Pc protons are a little different among these isomers. As the peaks of the protons $\mathrm{x}, \mathrm{y}$ and x consist of these signals, the line width of dimer (Fig. 2-2(b), spectra 2 and 3 ) is broadened by the mixing of the peaks
having small difference.
In case of TDEO6-CuPc, the chemical shift changes $\left(\delta_{2}-\delta_{1}\right)$ of DEO6 moiety are almost the same as those of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$, although the signals of Pc ring protons and proton b were not observed because of broadening. Thus the structure of dimer of TDEO6-CuPc is estimated to be similar to that of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in Fig. 2-7(b).

### 3.6. Structure of higher aggregate

At higher TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ concentration, the higher aggregates such as trimer are formed. Quite a many kinds of configurational isomers are formed for trimer by the combination of three isomers of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$. Thus the signals of Pc protons of trimer are very complicated (Fig. 2-2(b)). The signal of each Pc proton $x, y$ and $z$ splits into three component peaks at high concentration, i.e., $x_{1}, x_{2}$ and $x_{3}$ for $x, y_{1}, y_{2}$ and $y_{3}$ for $y$ and $z_{1}, z_{2}$ and $z_{3}$ for $z$ (Fig. 2-8). These component peaks furthermore split into double ( $\mathrm{x}_{n}, \mathrm{y}_{n}$ ) or multiple $\left(\mathrm{z}_{n}\right)$ peaks. Furthermore, these signals must consist of plural signals and chemical shifts may be similar each other. Thus these signals are not separated and appear one peak. ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY spectra were measured to exam the correlation among these peaks. Two dimensional spectrum of Pc proton region is depicted in Fig. 2-8, where the additional lines are drown to specify the correlated peaks. As shown by the additional lines, there is no correlation between three component peaks of a given proton, e.g., between $x_{1}, x_{2}$ and $x_{3}$. On the other hand, each component peak of $y$ correlates with the corresponding component peaks of other protons x and z , e.g., between $\mathrm{y}_{1}-\mathrm{x}_{1}$ and $\mathrm{y}_{1}-\mathrm{z}_{1}$. These results indicate that the signals of Pc protons consist of three sets of x , y and z peaks, i.e., $\left(\mathrm{x}_{1}, \mathrm{y}_{1}, \mathrm{z}_{1}\right),\left(\mathrm{x}_{2}, \mathrm{y}_{2}, \mathrm{z}_{2}\right)$ and $\left(\mathrm{x}_{3}, \mathrm{y}_{3}, \mathrm{z}_{3}\right)$, that is, at least three different chemical species correspond to the signals are present under this Pc concentration. As the dominant species of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ is trimer under this condition, the trimer has at least three different configurational isomers. The ratio of peak area
between three component signals is $1: 2: 1$ for every protons $\mathrm{x}, \mathrm{y}$ and x might indicate the middle peaks consist of two degenerate isomers.

The fact that the signal of each proton shifts by the concentration indicates that the aggregation equilibria are fast with respect to NMR time scale. On the other hand, the signal of each isomer does not coalesce but is split into component peaks. That is, the conformational change is slow. These results might be interpreted by following mechanism. Pcs form the aggregate by the $\pi-\pi$ interaction of the Pc rings, thus the dissociation and recombination of aggregates are relatively fast. However, even if one Pc dissociates from the aggregate, the large and bulky substituent, DEO6, may prevent the rotation to make another combination of isomers. Consequently, the TDEO6-MPc dissociated from the aggregate recombines to the original conformational combination, i.e., the conformational change will be virtually prevented.

## 4. Conclusion

${ }^{1} \mathrm{H}$ NMR spectra of phthalocyanines substituted by hexaethyleneglycolmonododecylether (TDEO6-MPc; $\mathrm{M}=\left(\mathrm{H}^{+}\right)_{2}$ or $\mathrm{Cu}^{2+}$ ) were measured at various concentrations of TDEO6-MPc $\left(10^{-5.5}-10^{-1.5} \mathrm{M}\right)$ in dichloromethane- $d_{2}$.

Successive formation of aggregates up to trimer $\left(\mathrm{TDEO} 6-\mathrm{H}_{2} \mathrm{Pc}\right)$ and to tetramer (TDEO6-CuPc) under the present experimental conditions of concentration was estimated. The aggregation constants and chemical shifts of monomer and each aggregate were determined by the quantitative analysis of the chemical shift change by the concentration. Comparison of chemical shift of each proton with unsubstituted DEO6, i.e., DEO6-H, reveals that the DEO6 side chains are flexible and move freely. It was estimated that TDEO6-MPc is successively stacked face to face in the aggregates and their slippage between the Pcs is very small. The formation of aggregates of

TDEO6-CuPc is easier than that of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$.

Table 2-1. ${ }^{1} \mathrm{H}$ NMR chemical shifts of monomer $\left(\delta_{1}\right)$, dimer $\left(\delta_{2}\right)$ and trimer $\left(\delta_{3}\right)$ of TDEO6-MPc in dichloromethane- $d_{2}$.

| Signal | TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ |  |  |  | TDEO6-CuPc |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\begin{gathered} \delta_{1} \\ / \mathrm{ppm} \\ \hline \end{gathered}$ | $\begin{gathered} \delta_{2} \\ / \mathrm{ppm} \\ \hline \end{gathered}$ | $\begin{gathered} \delta_{3} \\ / \mathrm{ppm} \\ \hline \end{gathered}$ | $\begin{gathered} \left(\delta_{2}-\delta_{1}\right) \\ / \mathrm{ppm} \\ \hline \end{gathered}$ | $\begin{gathered} \delta_{1} \\ / \mathrm{ppm} \\ \hline \end{gathered}$ | $\begin{gathered} \delta_{2} \\ / \mathrm{ppm} \\ \hline \end{gathered}$ | $\begin{gathered} \delta_{3} \\ / \mathrm{ppm} \end{gathered}$ | $\begin{gathered} \left(\delta_{2}-\delta_{1}\right) \\ / \mathrm{ppm} \\ \hline \end{gathered}$ |
| x | 9.022 | 8.027 | 6.533 | -0.815 | - | - | - | - |
| z | 9.421 | 8.756 | 7.243 | -0.665 | - | - | - | - |
| y | 7.868 | 7.591 | 6.673 | -0.277 | - | - | - | - |
| b | 4.747 | 4.671 | 4.041 | -0.076 | - | - | - | - |
| c | 4.154 | 4.253 | 4.126 | 0.099 | 4.081 | 4.118 | 3.844 | 0.037 |
| d | 3.878 | 3.984 | 4.038 | 0.106 | 3.820 | 3.897 | 3.828 | 0.076 |
| e | 3.766 | 3.857 | 3.962 | 0.091 | 3.725 | 3.799 | 3.788 | 0.074 |
| f1 | 3.708 | 3.759 | 3.881 | 0.051 | 3.666 | 3.722 | 3.760 | 0.056 |
| g1 | 3.654 | 3.705 | 3.805 | 0.051 | 3.643 | 3.678 | 3.735 | 0.035 |

Table 2-2. Logarithmic successive formation constants of aggregates $\left(K_{n}\right)$ in dichloromethane- $d_{2}$.

|  | TDEO6-H2 Pc | TDEO6-CuPc |
| :--- | :--- | :--- |
| $\log K_{2}$ | $3.6(3.32)^{\mathrm{a}}$ | $4.2(4.00)^{\mathrm{a}}$ |
| $\log K_{3}$ | 2.1 | 2.5 |

${ }^{a}$ Values in parentheses are obtained by UV-vis spectroscopy in chapter 1 .


Scheme 2-1. Structure of TDEO6-MPc. $\mathrm{M}=\left(\mathrm{H}^{+}\right)_{2}$ or $\mathrm{Cu}^{2+}$.

DEO6-H:


DEO6-ph:


TDEO6-MPc:


Scheme 2-2. Alphabetical symbols of protons of DEO6-H, DEO6-ph and TDEO6-MPc.


Figure 2-1. ${ }^{1} \mathrm{H}$ NMR spectra of TDEO6-CuPc at $3.85 \times 10^{-4} \mathrm{M}(\mathrm{a})$, TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ at $2.42 \times 10^{-4} \mathrm{M}(\mathrm{b})$, DEO6-ph (c) and DEO6-H (d) in dichloromethane- $d_{2}$. Signals with asterisk * are of impurities.
(a)
(5) b $M^{c}$ $\qquad$
(4)

(3)

(2)

(1)

Figure 2-2(a). $\quad{ }^{1} \mathrm{H}$ NMR spectra of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in dichloromethane $-d_{2}$ in the region of ethylene oxide proton of side chains. $C_{\mathrm{Pc}}$ : (1) $2.99 \times 10^{-6} \mathrm{M}$, (2) 2.69 $\times 10^{-5} \mathrm{M}$, (3) $2.42 \times 10^{-4} \mathrm{M}$, (4) $2.18 \times 10^{-3} \mathrm{M}$, (5) $1.71 \times 10^{-2} \mathrm{M}$. Signals with asterisk * are of impurities.


Figure 2-2(b). ${ }^{1} \mathrm{H}$ NMR spectra of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in dichloromethane- $d_{2}$ in the region of aromatic protons of phthalocyanine. $C_{\text {Pc }}$ : (1) $2.99 \times 10^{-6} \mathrm{M}$, (2) $2.69 \times$ $10^{-5} \mathrm{M}$, (3) $2.42 \times 10^{-4} \mathrm{M}$, (4) $2.18 \times 10^{-3} \mathrm{M}$, (5) $1.71 \times 10^{-2} \mathrm{M}$. Signals with asterisk * are of impurities.


Figure 2-3. Change in chemical shifts $(\Delta \delta)$ of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ as a function of concentration $\left(\log C_{\mathrm{Pc}}\right.$ ). (a) Methylene proton and (b) aromatic proton. $\square$; proton $\mathrm{b}, \mathrm{O}$; proton $\mathrm{c}, \diamond$; proton $\mathrm{d}, \triangle$; proton $\mathrm{e}, \nabla$; proton fl , を; proton g1, ; proton $\mathrm{x}, \Delta$; proton y , ® $_{\text {© }}$; proton z .


Figure 2-4. $\quad{ }^{1} \mathrm{H}$ NMR spectra of TDEO6-CuPc in dichloromethane- $d_{2}$ in the region of ethylene oxide proton of side chain. $C_{\mathrm{Pc}}$ : (1) $4.76 \times 10^{-6} \mathrm{M}$, (2) $4.28 \times$ $10^{-5} \mathrm{M}$, (3) $3.85 \times 10^{-4} \mathrm{M}$, (4) $3.47 \times 10^{-3} \mathrm{M}$, (5) $3.05 \times 10^{-2} \mathrm{M}$. Signals with asterisk * are of impurities.


Figure 2-5. Change in chemical shifts ( $\Delta \delta$ ) of methylene protons of TDEO6-CuPc as a function of concentration $\left(\log C_{\mathrm{Pc}}\right)$. O ; proton $\mathrm{c}, \diamond$; proton $\mathrm{d}, \triangle$; proton e, $\nabla$; proton f1, そ; proton g1.


Figure 2-6. Differences in chemical shifts of methylene protons of DEO6-ph $(\diamond)$ and TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ monomer ( $\square$ ) from DEO6-H in dichloromethane- $d_{2}$.


Fig. 2-7. Top view of TDEO6-MPc monomer (a) and side view of TDEO6-MPc dimer (b). Only one side chain DEO6 is depicted and others are omitted. Although the DEO6 chain is shown by straight rod for simplicity, it is actually helically coiled and is flexible.


Figure 2-8. ${ }^{1} \mathrm{H}-{ }^{1} \mathrm{H}$ COSY spectrum of the aromatic region of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ at $C_{\mathrm{Pc}}=$ $6.55 \times 10^{-3} \mathrm{M}$ in dichloromethane- $d_{2}$.

## Chapter 3

## Complexation equilibria of polyethyleneoxide substituted phthalocyanine derivatives with alkali metal ions in methanol

## 1. Introduction

Phthalocyanines (Pcs) consist of macrocyclic molecules which indicate potentials for technical applications with robust chemical and thermal stability ${ }^{1-6}$. In the inner macrocycle there are two NH groups, the protons of which can be substituted by a metal ion ${ }^{4-6}$.

Polyethylene oxide derivatives (PEO) are amphiphilic functional compound, which can form the complexes even for alkali metal ions. This cationic complex of PEO can be extracted from aqueous phase to organic phase by forming an electrically neutral ion pair with hydrophobic anions. These extraction processes have been applied for the separation and determination of metal ions ${ }^{60-71}$. In case of cyclic polyethylene oxides, i.e., crown ether, stability of complex with metal ion is significantly affected by the size fitting of cavity size of crown ether with ionic radii of cations ${ }^{61,62,67-69}$. On the other hand, linear polyethylene oxide is much more flexible than crown ether. Thus, the effect of flexibility of linear polyethylene oxides on complex formation and the composition and structure of its cationic complexes is interesting subject.

In this study, tetra- $\beta$-substituted phthalocyanine derivatives, EO-MPc, with hexaethyleneglycolmonomethylether (MeEO6) as shown in Scheme 3-1 were synthesized. This compound is amphiphilic and more hydrophilic compared with the DEO6 derivatives (chapter 2). In the present chapter, the complex formation of EO-MPc with lithium, sodium and potassium hydroxide were investigated in methanol by means of UV-vis absorption, emission and excitation spectroscopies. By the analysis
of spectral change, composition and structures of alkali metal complexes of EO-MPc were investigated semiquantitatively. The role of each complexation site, Pc ring and EO chain, on the complex formation with respect to the rigid-flexible property and size matching.

## 2. Materials and methodology

### 2.1. Reagents

Monodispersed hexaethyleneglycolmonomethylether, (EO) (> $98 \%$ ee), was purchased from Nikko Chemicals. All organic solvents were of reagent grade (Wako Pure Chemicals and Nacalai Tesque), and were used as received without further purification.

### 2.2. Synthesis

### 2.2.1. 2(3),9(10),16(17),23(24)-Tetra(1,4,7,10,13,16,19-heptaoxaicosyl)phthalocyanine (EO-H2 $\mathrm{H}_{2}$ )

Hexaethyleneglycolmonomethylether (EO) ( $10.0 \mathrm{~g}, 33.7 \mathrm{mmol}$ ) was tosylated with p-toluenesulfonylchloride ( $7.44 \mathrm{~g}, 39.0 \mathrm{mmol}$ ) in THF $(19 \mathrm{ml})$ at $0^{\circ} \mathrm{C}$ for 4 h . Excess amount of sodium hydroxide aqueous solution was added and stirred at $0^{\circ} \mathrm{C}$ for 30 min . After addition of cool water, tosylated EO was extracted into chloroform. The chloroform phase was washed by distilled water twice and saturated sodium chloride solution once. Anhydrous magnesium sulfate was added and left for 12 h . After filtering out magnesium sulfate, chloroform was removed in vacuo. 8.64 g sample of tosylated EO was obtained as a colorless oily product in $57 \%$ yield.

Tosylated EO ( $8.11 \mathrm{~g}, 18.1 \mathrm{mmol}$ ), 4-hydroxyphthalonitrile ( $4.01 \mathrm{~g}, 27.8 \mathrm{mmol}$ ) and anhydrous potassium carbonate ( $5.29 \mathrm{~g}, 38.3 \mathrm{mmol}$ ) were added in dry acetone ( 150 ml )
and stirred at $56^{\circ} \mathrm{C}$ for 48 h under a nitrogen atmosphere. After filtration, reaction mixture was evaporated to dryness. The product was extracted by benzene. By the evaporation of benzene under vacuum, 6.22 g sample of 4-EO-phthalonitrile was obtained as light orange oil in $53 \%$ yield.

4-EO-phthalonitrile ( $0.97 \mathrm{~g}, 2.30 \mathrm{mmol}$ ) and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) $(0.40 \mathrm{~g}, 2.63 \mathrm{mmol})$ in 1-pentanol $(20 \mathrm{ml})$ were refluxed at $140^{\circ} \mathrm{C}$ for 24 h . After the evaporation of the solvent, the dark blue product was purified by column chromatography on silica gel (methanol and methanol/dichloromethane $=80: 20(\mathrm{v} / \mathrm{v})$ were used as eluent in this order). Deep blue-green EO- $\mathrm{H}_{2} \mathrm{Pc}(0.34 \mathrm{~g})$ was obtained in $35 \%$ yield. Overall yield is $11 \%$. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz} ; \mathrm{CD}_{2} \mathrm{Cl}_{2} ; \mathrm{Me}_{4} \mathrm{Si}$ ): $\delta_{\mathrm{H}}, \mathrm{ppm} 8.89$ $(4 \mathrm{H}, \mathrm{m}, \mathrm{Ph}), 8.41(4 \mathrm{H}, \mathrm{m}, \mathrm{Ph}), 7.64(4 \mathrm{H}, \mathrm{m}, \mathrm{Ph}), 4.76-3.44\left(96 \mathrm{H}, \mathrm{m},-\mathrm{O}-\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{O}-\right)_{6}-\right)$, $3.29\left(12 \mathrm{H}, \mathrm{m},-\mathrm{CH}_{3}\right)$.

### 2.2.2.

[2(3),9(10),16(17),23(24)-Tetra(1,4,7,10,13,16,19-heptaoxaicosyl)phthalocyanatoJcop per(II) (EO-CuPc)

EO-CuPc was synthesized by a similar synthetic procedure as $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$. 4-EO-phthalonitrile ( $0.46 \mathrm{~g}, 1.08 \mathrm{mmol}$ ) and $\operatorname{DBU}(0.18 \mathrm{~g}, 1.18 \mathrm{mmol})$ was added in the 1-pentanol solution containing anhydrous copper chloride ( $0.04 \mathrm{~g}, 0.30 \mathrm{mmol}$ ) and refluxed at $140^{\circ} \mathrm{C}$ for 24 h . After evaporating the solvent, EO-CuPc thus obtained was purified by a silica gel column (methanol and methanol/dichloromethane $=75: 25(\mathrm{v} / \mathrm{v})$ were used as eluent in this order). Deep blue-green EO-CuPc ( 0.34 g ) was obtained in $71 \%$ yield. Overall yield is $21 \%$ yield. ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz} ; \mathrm{CD}_{2} \mathrm{Cl}_{2} ; \mathrm{Me}_{4} \mathrm{Si}$ ): $\delta_{\mathrm{H}}, \mathrm{ppm}$ 4.20-3.44 (96H, m, -O-( $\left.\left.\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{O}-\right)_{6}-\right), 3.32\left(12 \mathrm{H}, \mathrm{m},-\mathrm{CH}_{3}\right)$.

### 2.3. Instrumentation

UV-vis absorption spectra were recorded on a Shimadzu UV-1600 spectrophotometer. Emission and excitation spectra were recorded on a JASCO FP-6200. The concentration of water in methanol solution was measured by Karl Fischer moisture titrator of Kyoto electronics manufacturing Co, Ltd. MKC-210 and adjusted to 0.1 M .

### 2.4. Procedure

### 2.4.1. UV-vis absorption spectroscopy

0.1 M water methanol solution of $\mathrm{LiOH}, \mathrm{NaOH}$ or KOH containing $4.96 \times 10^{-6} \mathrm{M}$ $\left(\mathrm{M} \equiv \mathrm{mol} \mathrm{dm}^{-3}\right)$ EO-MPc was prepared. Suitable amount of each solution were added to 2.5 ml of $4.96 \times 10^{-6} \mathrm{M}$ EO-MPc of methanol solution in a 10 mm quartz cell. The absorption spectra of these solutions were measured at $25.0{ }^{\circ} \mathrm{C}$ by UV-visible Spectrometer. In case of LiOH system, the spectra of the solutions containing $5.00 \times$ $10^{-2} \mathrm{M}$ lithium chloride were also measured. Where the solution was prepared to keep the total concentration of $\mathrm{Li}^{+}$ion $\left(5.00 \times 10^{-2} \mathrm{M}\right)$. The concentration of water in methanol solution was measured at $25.0^{\circ} \mathrm{C}$ by Karl Fischer moisture titrator.

### 2.4.2. Emission and excitation spectroscopy

The change in emission spectra of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of $\mathrm{LiOH}, \mathrm{NaOH}$ or KOH was measured in the region of $370-720 \mathrm{~nm}$ at $25.0^{\circ} \mathrm{C}$ by the excitation at $\lambda_{\mathrm{ex}}=$ 370 nm . The change in excitation spectra of these samples at 679 and 705 nm were also measured in the same region of emission spectral measurement. The UV-vis absorption spectra of the solutions prepared for the emission spectra were also measured.

## 3. Results and Discussion

### 3.1. Dimerization equilibria of $\mathbf{E O}-\mathbf{H}_{2} \mathbf{P c}$ in various alcohols

### 3.1.1. Concentration dependence of $U V$-vis spectra

The UV-vis absorption spectra of EO- $\mathrm{H}_{2} \mathrm{Pc}$ were measured at various concentrations $\left(C_{\mathrm{Pc}}=10^{-6.1}-10^{-4.8} \mathrm{M}\right)$ in a series of alcohols. As the examples of spectral change, the results in 1-decanol, 1-hexanol and methanol are depicted in Figs. 3-1~3-3, where the molar extinction coefficient ( $\varepsilon$ ) refers to apparent molar extinction coefficient (absorbance of 1 cm light pass/total concentration of Pc). For example in 1-decanol (Fig. 3-1), these spectra consist of two absorption bands, broad and relatively weak band in the range of 300 to 370 nm (Soret band) and sharp and strong band split to two peaks at 666 nm and 705 nm (Q-band). The strong peaks of Q-band are characteristic of monomeric form of Pcs and splitting into two peaks is characteristic of monomeric form of $\mathrm{H}_{2} \mathrm{Pcs}^{5,6,9}$. Thus, very high molar extinction coefficient ( $\varepsilon$ ) at low Pc concentration suggests that the predominant species of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ is monomer at this concentration (Fig. 3-1).

By increasing the total concentration of Pc , the molar extinction coefficient $(\varepsilon)$ of Q-band decreases. Generally, the absorption of Q-band of aggregates of Pc is much weaker compared with that of monomer and the peak position is around $620 \mathrm{~nm}^{5,6,9,72}$. Thus, decrease in $\varepsilon$ by the increase in concentration of Pc is attributed to the decrease in the proportion of monomeric form of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$. These spectra have isosbestic point at 723 nm for Q -band region. The existence of isosbestic point suggests that the two chemical species are equilibrated in the concentration range studied. The spectral change of the Soret band is much smaller than that of the Q -band. The peak maximum slightly shifts to lower wavelength and shows small decrease in the molar extinction coefficient. Similar spectral change has been obtained for any solvents, although the magnitude of effect of concentration is different by the solvents. The isosbestic point is
observed for any solvent system.

### 3.1.2. Monomer-dimer equilibrium

The molar extinction coefficients of Q-band peak of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ at 705 nm in various alcohols are plotted as a function of the logarithmic concentration $\left(\log C_{\text {Pc }}\right)$ in Fig. 3-4. Generally, the dimer is formed as the first step of aggregation ${ }^{52,56,82,83}$, thus the aggregation equilibrium is given by

$$
\begin{equation*}
2 \mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc} \stackrel{K_{2}}{\rightleftharpoons}\left(\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}\right)_{2} \tag{3.1}
\end{equation*}
$$

The formation constant of dimer $\left(K_{2}\right)$ is defined as

$$
\begin{equation*}
K_{2}=\frac{\left[\left(\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}\right)_{2}\right]}{\left[\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}\right]^{2}} \tag{3.2}
\end{equation*}
$$

The plot of experimental results of $\varepsilon$ as a function of $\log C_{\mathrm{Pc}}$ in Fig. 3-4 was fitted with calculated molar extinction coefficient $\left(\varepsilon_{\text {calc }}\right)$ by following the same procedure for chapter 1 . The values of $\varepsilon_{1}, \varepsilon_{2}$ and $K_{2}$ giving a minimum of error square sum, $\Sigma\left(\varepsilon-\varepsilon_{\text {calc }}\right)^{2}$ were evaluated. The formation constants of dimer $K_{2}$ thus obtained are listed in Table 3-1. The calculated curves ( $\varepsilon_{\text {calc }}$ ) by using these values are shown in Fig. 3-4 by solid lines. The calculated curves show good agreements with the experimental results. The values of $\varepsilon_{\text {calc }}$ of asymptotes at low $C_{\mathrm{Pc}}$ and high $C_{\mathrm{Pc}}$ correspond to the molar extinction coefficients of monomer, $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc},\left(\varepsilon_{1}\right)$ and dimer, $\left(\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}\right)_{2}$, per one $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ molecule ( $\varepsilon_{2}$ ), respectively. As can be seen from Fig. 3-4, molar extinction coefficient of monomer $\left(\varepsilon_{1}\right)$ and dimer $\left(\varepsilon_{2}\right)$ of EO- $\mathrm{H}_{2} \mathrm{Pc}$ at 705 nm are obtained as $(1.3 \pm 0.1) \times 10^{5}$ $\mathrm{M}^{-1} \mathrm{~cm}^{-1}$ and $(2.2 \pm 0.3) \times 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$, respectively, for any alcohol. Thus, the value of $\varepsilon_{1}$ and of $\varepsilon_{2}$ of EO- $\mathrm{H}_{2} \mathrm{Pc}$ does not differ so much at any wavelength among the alcohols. Thus, the spectra of monomer and dimer of EO- $\mathrm{H}_{2} \mathrm{Pc}$ hardly differ among the alcohols.

The dimerization constant, $\log K_{2}$, of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ increases with the decrease in the
chain length of alkyl group of alcohol. This means that the increase in the balance of hydrophilic to hydrophobic property of alcohol makes the Pcs easy to form the aggregates. In this chapter methanol was used as a solvent to investigate the complexation reactivity of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ dimer with alkali metal ion.

### 3.2. Reaction of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ with lithium ion

### 3.2.1. Spectral change by the formation of lithium phthalocyanine

The UV-vis absorption spectra of EO- $\mathrm{H}_{2} \mathrm{Pc}$ in methanol at $4.96 \times 10^{-6} \mathrm{M}(\mathrm{M} \equiv \mathrm{mol}$ $\mathrm{dm}^{-3}$ ) at various concentration of lithium hydroxide ( $C_{\text {LiOH }} ; 0-10^{-1.87} \mathrm{M}$ ) are depicted in Fig. 3-5. The molar extinction coefficients ( $\varepsilon$ ) at 348 nm (Soret band) and around 674 nm (Q-band) increase by increasing the total concentration of LiOH and there are isosbestic points at 643 and 700 nm for Q-band region and at 328 and 389 nm for the Soret band region. Generally, the absorption of Q-band of monomeric metal-free phthalocyanine $\left(\mathrm{H}_{2} \mathrm{Pc}\right)$ and metallophthalocyanine (MPc) indicate strong split peaks and strong single peak, respectively ${ }^{5,6,9}$. Thus, increase in $\varepsilon$ at 674 nm by the increase in concentration of LiOH is attributed to the increase in the proportion of the monomer of lithium phthalocyanine. The change in the molar extinction coefficient $(\varepsilon)$ is plotted as a function of logarithmic concentration of $\mathrm{LiOH}\left(\log C_{\mathrm{LiOH}}\right)$ by curve 2 of Fig. 3-8.

The spectra of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ at various concentration of lithium hydroxide $\left(C_{\mathrm{LiOH}} ; 0-\right.$ $10^{-1.85} \mathrm{M}$ ) are also measured in the presence of lithium chloride, where the total concentration of lithium $\left(C_{\mathrm{Li}}\right)$ is kept constant at $C_{\mathrm{Li}}=5.00 \times 10^{-2} \mathrm{M}$. These solutions also show the same spectral change as those without LiCl . The changes in the molar extinction coefficient $(\varepsilon)$ at 674 nm are plotted as a function of $\log C_{\text {LiOH }}$ by curve 1 of Fig. 3-8. As seen from Fig. 3-8, the spectral change of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ under the conditions of constant $C_{\mathrm{Li}}$ occurs at lower concentration than that in absence of LiCl .

### 3.2.2. Chemical form of lithium phthalocyanine

The increase in the single peak of Q-band suggests the formation of monomeric complex in which the Pc ring is coordinating to the lithium ion (Fig. 3-5). The existence of isosbestic points suggest that the two chemical species are equilibrated. The lithium complex is formed by the substitution of protons of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$. Thus, the complex formed is given by EO-Li $\mathrm{H}_{2-n} \mathrm{Pc}$ as general form. The complexation equilibrium is given by equation 3.3.

$$
\begin{equation*}
\left(\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}\right)_{2}+2 m \mathrm{Li}^{+}+2 n \mathrm{OH}^{-} \stackrel{K}{=} 2 \mathrm{EO}^{-} \mathrm{Li}_{m} \mathrm{H}_{2-n} \mathrm{Pc}+2 n \mathrm{H}_{2} \mathrm{O} \tag{3.3}
\end{equation*}
$$

Where charge of complex is omitted for simplicity. The formation constant of lithium phthalocyanine $(K)$ is defined as

$$
\begin{equation*}
K=\frac{\left[\mathrm{EO}-\mathrm{Li}_{m} \mathrm{H}_{2-n} \mathrm{Pc}\right]^{2}}{\left[\left(\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}\right)_{2}\right]\left[\mathrm{Li}^{-n}\right]^{2 m}\left[\mathrm{OH}^{-}\right]^{2 n}} \tag{3.4}
\end{equation*}
$$

The total concentration of $\mathrm{Pc}\left(C_{\mathrm{Pc}}\right)$ is given by

$$
\begin{equation*}
C_{\mathrm{Pc}}=2\left[\left(\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}\right)_{2}\right]+\left[\mathrm{EO}-\mathrm{Li}_{m} \mathrm{H}_{2-n} \mathrm{Pc}\right] \tag{3.5}
\end{equation*}
$$

The observed extinction coefficient $(\varepsilon)$ is expressed as follows

$$
\begin{equation*}
\varepsilon=\frac{2 \varepsilon_{\mathrm{dim}}\left[\left(\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}\right)_{2}\right]+\varepsilon_{\mathrm{LiPc}}\left[\mathrm{EO}-\mathrm{Li}_{m} \mathrm{H}_{2-n} \mathrm{Pc}\right]}{C_{\mathrm{Pc}}} \tag{3.6}
\end{equation*}
$$

Where $\varepsilon_{\mathrm{dim}}$ and $\varepsilon_{\mathrm{LiPc}}$ are the molar extinction coefficient per one phthalocyanine molecule of the protonated Pc and lithium complex, respectively. The value of $\varepsilon_{\text {LiPc }}$ is estimated from asymptote at high concentration of LiOH .

Substitution of equation 3.5 into equation 3.6 leads to equations 3.7 and 3.8 , i.e., the concentration of monomeric species of lithium phthalocyanine and dimeric species of EO- $\mathrm{H}_{2} \mathrm{Pc}$ is given by

$$
\begin{equation*}
\left[\mathrm{EO}-\mathrm{Li}_{m} \mathrm{H}_{2-n} \mathrm{Pc}\right]=\frac{\varepsilon-\varepsilon_{\mathrm{dim}}}{\varepsilon_{\mathrm{LiPc}}-\varepsilon_{\mathrm{dim}}} C_{\mathrm{Pc}} \tag{3.7}
\end{equation*}
$$

$$
\begin{equation*}
\left[\left(\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}\right)_{2}\right]=\left(\frac{\varepsilon_{\mathrm{LiPc}}-\varepsilon}{\varepsilon_{\mathrm{LiPc}}-\varepsilon_{\mathrm{dim}}}\right) \frac{C_{\mathrm{Pc}}}{2} \tag{3.8}
\end{equation*}
$$

The total concentration of lithium ion $\left(C_{\mathrm{Li}}\right)$ is given by

$$
\begin{equation*}
C_{\mathrm{Li}}=\left[\mathrm{Li}^{+}\right]+m\left[\mathrm{EO}_{\left.-\mathrm{Li}_{m} \mathrm{H}_{2-n} \mathrm{Pc}\right]}\right. \tag{3.9}
\end{equation*}
$$

The concentration of lithium phthalocyanine is negligible compared with the concentration of lithium ion. Thus, the total concentration of lithium ion $\left(C_{\mathrm{Li}}\right)$ is approximated as

$$
\begin{equation*}
C_{\mathrm{Li}}=\left[\mathrm{Li}^{+}\right] \tag{3.10}
\end{equation*}
$$

The total concentration of hydroxide ion $\left(C_{\mathrm{LiOH}}\right)$ is given by

$$
\begin{equation*}
C_{\mathrm{LiOH}}=\left[\mathrm{OH}^{-}\right]+n\left[{\left.\mathrm{EO}-\mathrm{Li}_{m} \mathrm{H}_{2-n} \mathrm{Pc}\right]}\right. \tag{3.11}
\end{equation*}
$$

The concentration of hydroxide ion reacted with dimeric $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ is negligible compared with the concentration of hydroxide ion. Thus, the total concentration of hydroxide ion $\left(C_{\text {LiOH }}\right)$ is approximated as follows

$$
\begin{equation*}
C_{\mathrm{LiOH}}=\left[\mathrm{OH}^{-}\right] \tag{3.12}
\end{equation*}
$$

Substitution of equation 3.7, 3.8, 3.10 and 3.12 into equation 3.4 leads to equation 3.13.

$$
\begin{equation*}
K=\frac{2 C_{\mathrm{Pc}}\left(\varepsilon-\varepsilon_{\mathrm{dim}}\right)^{2}}{\left(\varepsilon_{\mathrm{LiPc}}-\varepsilon_{\mathrm{dim}}\right)\left(\varepsilon_{\mathrm{LiPc}}-\varepsilon\right) C_{\mathrm{Li}}^{2 m} C_{\mathrm{LiOH}}{ }^{2 n}} \tag{3.13}
\end{equation*}
$$

Rearrangement of equation 3.13 leads to equation 3.14.

$$
\begin{equation*}
\frac{2\left(\varepsilon-\varepsilon_{\mathrm{dim}}\right)^{2}}{\left(\varepsilon_{\mathrm{LiPc}}-\varepsilon_{\mathrm{dim}}\right)\left(\varepsilon_{\mathrm{LiPc}}-\varepsilon\right)}=K C_{\mathrm{Li}}^{2 m} C_{\mathrm{LiOH}}{ }^{2 n} C_{\mathrm{Pc}}{ }^{-1} \tag{3.14}
\end{equation*}
$$

By defining the left-hand side of equation 3.14 as $F$,

$$
F \equiv \frac{2\left(\varepsilon-\varepsilon_{\mathrm{dim}}\right)^{2}}{\left(\varepsilon_{\mathrm{LiPc}}-\varepsilon_{\mathrm{dim}}\right)\left(\varepsilon_{\mathrm{LiPc}}-\varepsilon\right)}
$$

The logarithmic form of equation 3.14 is given by

$$
\begin{equation*}
\log F=2 n \log C_{\mathrm{LiOH}}+2 m \log C_{\mathrm{Li}}+\log K-\log C_{\mathrm{Pc}} \tag{3.15}
\end{equation*}
$$

The value of $\log F$, which is obtained experimentally, is plotted as a function of $\log$ $C_{\text {LiOH }}$ in Fig. 3-9. The results in the presence of $\mathrm{LiCl}\left(C_{\mathrm{Li}}=5.00 \times 10^{-2} \mathrm{M}\right)$ is given by curve $1(\odot)$. Under these experimental conditions, the values of $C_{\mathrm{Li}}$ and $C_{\mathrm{Pc}}$ are constant. Thus, the slope of the plot of $\log C_{\mathrm{LiOH}}$ correspond to $2 n$. As seen from Fig. 3-9, curve 1, the slope of the plot is obtained as four, that is, $n=2$. Thus, the number of proton $(2-n)$ in the lithium complex is 0 , i.e. the lithium complex is entirely deprotonated, $\mathrm{EO}-\mathrm{Li}_{m} \mathrm{Pc}$.

Under the conditions that the lithium chloride is not added to the solution, that is, $C_{\mathrm{Li}}=C_{\mathrm{LiOH}}$. Thus, the equation 3.15 leads to equation 3.16.

$$
\begin{equation*}
\log F=2(m+n) \log C_{\mathrm{LiOH}}+\log K-\log C_{\mathrm{Pc}} \tag{3.16}
\end{equation*}
$$

The plot of $\log F$ as a function of $\log C_{\mathrm{LiOH}}$ is given in Fig. 3-9, curve $2(\mathrm{O})$. The slope of the plot, which corresponds to $2(m+n)$, is six. Thus the number of $\mathrm{Li}^{+}$ion with complex is determined as one. In conclusion, the chemical form of the lithium complex is estimated as an anionic complex, EO-LiPc‥ Thus,

$$
\begin{equation*}
\left(\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}\right)_{2}+2 \mathrm{Li}^{+}+4 \mathrm{OH}^{-} \stackrel{K}{=} 2 \mathrm{EO}^{-} \mathrm{LiPc}^{-}+4 \mathrm{H}_{2} \mathrm{O} \tag{3.17}
\end{equation*}
$$

The value of $\log K$ for the lithium phthalocyanine is evaluated as 11.3.

### 3.2.2. Structure of lithium phthalocyanine

The cavity size of Pc ring is reported as $1.8 \AA^{5,6}$. If the ionic radius of metal ion is smaller than the half cavity size of Pc ring, the metal ion is incorporated into the cavity
of Pc ring. The small size metal ions such as lithium (I) ( $0.90 \AA^{121}$ ), nickel(II) ( 0.83 $\AA^{121}$ ), copper(II) ( $0.87 \AA^{121}$ ) and zinc(II) ( $0.88 \AA^{121}$ ) form stable complexes with phthalocyanines by incorporating into the cavity of the Pc ring ${ }^{122,123}$.

In the case of lithium phthalocyanines, the crystal structures of dilithium phthalocyanine ${ }^{124}$ and anionic monolithium phthalocyanine ${ }^{125,126}$ have been reported. In the case of porphyrin which has the same cavity size ${ }^{127}$, both complexes have also been reported in solution. That is, one $\mathrm{Li}^{+}$ion $\left(0.90 \AA^{121}\right)$ can be bound to all four nitrogens in the porphyrin core (in polar solvents) and two $\mathrm{Li}^{+}$ions interact with the porphyrin nitrogens and these are located on the top and bottom of the center of porphyrin ring (in non-polar solvents) ${ }^{128}$. The formation of anionic monolithium porphyrin, where one $\mathrm{Li}^{+}$ ion is incorporated into the porphyrin ring, has been reported in highly-polar solvent such as water ${ }^{129,130}$. Therefore, one $\mathrm{Li}^{+}$ion is coordinated to all four nitrogens into the center of Pc ring core in methanol. Consequently, the formation of anionic species may be reasonable in the polar solvent methanol.

### 3.2.3. Fluorescence of lithium phthalocyanine

Emission spectra of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ in various concentration of lithium hydroxide $\left(C_{\mathrm{LiOH}}\right.$; $0-10^{-1.85} \mathrm{M}$ ) were measured in the range of $370-720 \mathrm{~nm}$. Results are depicted in Fig. 3-10 where the spectra were corrected in the same manner as chapter 1 . Emission of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ solution in the absence of LiOH totally is quenched because of the formation of dimer ${ }^{101}$. The emission peak at 680 nm is growing by increasing the concentration of LiOH . The changes in the emission intensity at 680 nm are plotted as a function of logarithmic concentration of $\mathrm{LiOH}\left(\log C_{\mathrm{LiOH}}\right)$ in Fig. 3-13 together with the change in molar extinction coefficient ( $\varepsilon$ ) of Q-band at 674 nm . The change in the emission intensity agrees with the change in $\varepsilon$. This fact suggests that monomeric lithium phthalocyanine is fluorescence complex.

### 3.3. Reaction of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ with sodium ion

### 3.3.1. Spectral change by the formation of sodium phthalocyanine

The UV-vis absorption spectra of EO- $\mathrm{H}_{2} \mathrm{Pc}$ in methanol at $4.96 \times 10^{-6} \mathrm{M}$ containing various concentrations of sodium hydroxide ( $C_{\mathrm{NaOH}} ; 0-10^{-0.24} \mathrm{M}$ ) are depicted in Fig. 3-6. By increasing the concentration of NaOH , the molar extinction coefficient ( $\varepsilon$ ) of Soret band at 348 nm and that of Q-band at 677 nm increase (Fig. 3-6). The increase of strong single peak of Q-band at 677 nm suggests the increase in the proportion of monomeric sodium phthalocyanine. The isosbestic points are not observed under these experimental conditions.

Emission spectra of EO- $\mathrm{H}_{2} \mathrm{Pc}$ at $4.96 \times 10^{-6} \mathrm{M}$ in various concentration of sodium hydroxide ( $C_{\mathrm{NaOH}} ; 0-10^{-0.82} \mathrm{M}$ ) are depicted in Fig. 3-11. By increasing the total concentration of NaOH , emission peak which is characteristic of monomeric sodium phthalocyanine is observed at 680 nm .

### 3.3.2. Chemical form of sodium phthalocyanine

The emission intensity at 680 nm of sodium phthalocyanine (Fig. 3-11) is plotted as a function of the logarithmic concentration of $\mathrm{NaOH}\left(\log C_{\mathrm{NaOH}}\right)$ in Fig. 3-14 together with the change in $\varepsilon$ of Q -band at 677 nm (Fig. 3-6).

As can be seen from Fig. 3-14, $\varepsilon$ of Q-band of sodium phthalocyanine at 677 nm shows a one step sigmoid curve. On the other hand, the emission intensity of sodium phthalocyanine shows a two step sigmoid curve. That is, a result indicates that the two kinds of sodium phthalocyanine complexes are formed in this concentration range of NaOH .

The excitation spectra at 680 nm of the concentration of NaOH at $10^{-1.90}$ and $10^{-0.24}$ $M$ are shown in Fig. 3-15(a) and 3-15(b), respectively, to estimate the absorption spectra of chemical species formed in each step. Although the excitation spectra of the solution of lower NaOH (Fig. 3-15(a)) is similar to that of higher NaOH (Fig. 3-15(b)), the line
width of peak at 675 nm become apparently narrower at higher concentration. These results indicate that Pc ring coordinates to $\mathrm{Na}^{+}$ion in case of the intermediate as it is for final chemical species. It is expected that the intermediate is monosodium phthalocyanine ( $\mathrm{EO}-\mathrm{NaPc}^{-}$) and the final chemical species is disodium phthalocyanine $\left(\mathrm{EO}-\mathrm{Na}_{2} \mathrm{Pc}\right)$. Thus, these spectral results indicate the following stepwise complex formation.

$$
\begin{align*}
& \left(\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}\right)_{2}+2 \mathrm{Na}^{+}+4 \mathrm{OH}^{-} \rightleftharpoons 2 \mathrm{EO}-\mathrm{NaPc}^{-}+4 \mathrm{H}_{2} \mathrm{O}  \tag{3.18}\\
& \mathrm{EO}-\mathrm{NaPc}^{-}+\mathrm{Na}^{+} \rightleftharpoons \mathrm{EO}-\mathrm{Na}_{2} \mathrm{Pc} \tag{3.19}
\end{align*}
$$

### 3.3.3. Structure of sodium phthalocyanine

In case of large metal ion such as lead(II) ion ( $1.33 \AA^{121}$ ), Pc ring forms the sitting a top (SAT) complex ${ }^{132}$, i.e., a metal ion is located on the top of the Pc ring plane. The ionic radius of $\mathrm{Na}^{+}$ion $\left(1.16 \AA^{121}\right)$ is close to lead(II) ion, i.e., $\mathrm{Na}^{+}$ion is too large to incorporate into the cavity of Pc ring cavity $\left(1.8 \AA^{127}\right)$. The symmetry of Pc ring moiety of monosodium phthalocyanine is high because the line width of single Q-band of its excitation spectrum in Fig. 3-15(a) is narrow and is almost the same value as that of monomeric $\mathrm{CuPc}^{5,6,9}$. Thus, the possibility of the formation of protonated Na complex must be excluded because of its low symmetry. By the same reason, the structure of disodium complex is also estimated as the SAT type, i.e., two $\mathrm{Na}^{+}$ions are located on the top and bottom of the center of Pc ring is reported for the crystal structure of disodium phthalocyanine ${ }^{12,131}$.

### 3.4. Reaction of $\mathbf{E O}-\mathrm{H}_{2} \mathrm{Pc}$ with potassium ion

### 3.4.1. Spectral change by the formation of potassium complex

The UV-vis absorption spectra of EO- $\mathrm{H}_{2} \mathrm{Pc}$ in methanol at $4.96 \times 10^{-6} \mathrm{M}$ in various
concentration of potassium hydroxide ( $C_{\mathrm{KOH}} ; 0-10^{-0.88} \mathrm{M}$ ) are depicted in Fig. 3-7. By increasing the total concentration of KOH , the molar extinction coefficient ( $\varepsilon$ ) of Soret band at 348 nm and that of Q-band at 675 nm increase. In the concentration range of KOH from $0-10^{-0.88} \mathrm{M}$, split peaks of Q-band at 665 and 697 nm increase. This spectral change indicates the formation of monomeric $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ without coordination of Pc ring with metal ion. That is, EO chain is coordinating to metal ion ${ }^{63-65}$. Thus, the formation of (KEO) ${ }^{+}-\mathrm{H}_{2} \mathrm{Pc}$ complex is estimated in this KOH concentration range. In the concentration of KOH higher than $10^{-0.92} \mathrm{M}$, strong single peak of Q-band at 675 nm increases. This indicates that the complex formation of Pc ring with $\mathrm{K}^{+}$ion.

The emission spectra of EO- $\mathrm{H}_{2} \mathrm{Pc}$ at $4.96 \times 10^{-6} \mathrm{M}$ in various concentration of KOH from $0-10^{-0.88} \mathrm{M}$ is depicted in Fig. 3-12. The emission peak at 708 nm increases at low concentration of $\mathrm{KOH}\left(0-10^{-0.92} \mathrm{M}\right)$, followed peak decreases at the higher concentration than $10^{-0.92} \mathrm{M}$. On the other hand, the emission peak at 679 nm continuously increases even in the higher KOH concentration region.

The emission intensities of peaks at 708 and 679 nm are plotted as a function of the logarithmic concentration of $\mathrm{KOH}\left(\log C_{\mathrm{KOH}}\right)$ in Fig. 3-16 together with the change in $\varepsilon$ at 675 nm .

### 3.4.2. Chemical form of potassium complex

As can be seen from $\varepsilon$ of Q-band at 675 nm plotted in Fig. 3-16, $\varepsilon$ consists of two sigmoid curve. The first and second step corresponds to the formation of these chemical species which have the emission peak at 708 and 680 nm , respectively. The excitation spectra of emission at 705 nm of the solution at $C_{\mathrm{KOH}}=10^{-1.20} \mathrm{M}$ and emission at 679 nm of the solution at $C_{\mathrm{KOH}}=10^{-0.88} \mathrm{M}$ are shown in Fig. 3-17(a) and (b), respectively. These spectra correspond to the absorption spectra of chemical species formed in each step.

In the first step, the excitation spectrum (Fig. 3-17(a)) shows the split peaks of

Q-band at 663 and 705 nm which is characteristic of monomeric EO- $\mathrm{H}_{2} \mathrm{Pc}$. That is, coordination of Pc ring with $\mathrm{K}^{+}$ion is not occurs in this concentration range of KOH and EO chain coordinates alkali metal ion ${ }^{63-65}$. Thus, the dimer of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ disaggregates to monomer by the complex formation of EO chains with $\mathrm{K}^{+}$ions:

$$
\begin{equation*}
\left(\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}\right)_{2}+2 \mathrm{~K}^{+} \rightleftharpoons 2(\mathrm{KEO})^{+}-\mathrm{H}_{2} \mathrm{Pc} \tag{3.20}
\end{equation*}
$$

The excitation spectrum at 679 nm at the second step (Fig. 3-17(b)) shows the strong single peak of Q-band at 673 nm which is characteristic of metallated phthalocyanine. In this concentration range of $\mathrm{KOH}, \mathrm{NaOH}$ forms disodium phthalocyanine. Thus, the composition of potassium phthalocyanine is also considered to be dipotassium phthalocyanine. The metallation equilibrium of monomeric EO- $\mathrm{H}_{2} \mathrm{Pc}$ with $\mathrm{K}^{+}$ions is given by

$$
\begin{equation*}
(\mathrm{KEO})^{+}-\mathrm{H}_{2} \mathrm{Pc}+2 \mathrm{~K}^{+}+2 \mathrm{OH}^{-} \rightleftharpoons(\mathrm{KEO})^{+}-\mathrm{K}_{2} \mathrm{Pc}+2 \mathrm{H}_{2} \mathrm{O} \tag{3.21}
\end{equation*}
$$

### 3.4.3. Structure of potassium phthalocyanine

The ionic radius of $\mathrm{K}^{+}$ion $\left(1.52 \AA^{121}\right)$ is larger than the half radius of Pc ring cavity $\left(0.9 \AA^{127}\right)$. The very narrow line width of single Q -band of its excitation spectrum (Fig. 3-17(b)) indicates that the symmetry of Pc ring moiety of dipotassium phthalocyanine is high, and the two $\mathrm{K}^{+}$ions are located on the top and bottom of the center of Pc ring. The similar structure are reported in water ${ }^{133}$ and crystal ${ }^{134}$. The same coordination manner has been reported for the porphyrin ${ }^{128}$.

### 3.5. Complex formation of EO-CuPc with alkali metal ion

### 3.5.1. Spectral change by the formation of alkali metal complex

In the case of EO-CuPc, the cavity of Pc ring is already occupied by the copper (II) ion. Thus, alkali metal ions only react with EO chains.

The UV-vis absorption spectra of EO-CuPc in methanol at various concentrations of lithium, sodium and potassium hydroxides are depicted in Figs. 3-18, 19 and 20, respectively. In the absence of alkali metal hydroxide, the spectrum shows a broad and weak peak of Q-band which is characteristic of dimeric form of Pcs ${ }^{5,6,9,72}$. Thus, very low molar extinction coefficient $(\varepsilon)$ suggests that predominant species of EO-CuPc at $4.97 \times 10^{-6} \mathrm{M}$ is dimer. UV-vis absorption spectra of EO-CuPc are scarcely changed by the addition of LiOH (Fig. 3-18). In the case of NaOH and KOH system, the increase in the concentration of MOH causes the increase in the absorbance of Q-band (Figs. 3-19 and 3-20). The molar extinction coefficients of Q-band peak at 675 nm are plotted as a function of the logarithmic concentration of alkali metal hydroxide ( $\log C_{\mathrm{MOH}}$ ) in Fig. 3-21.

### 3.5.2. Coordinating ability of EO-CuPc with alkali metal ions

Polyethylene oxide derivatives (EO) can form the complex with alkali metal ion by surrounding $\mathrm{it}^{63-65}$. That is, the EO chain of EO-CuPc can form the complex with alkali metal ion. The growing the strong single peak of Q-band (Figs. 3-18, 19 and 20) suggests that the dimer of $\mathrm{EO}-\mathrm{CuPc}$ is dissociated into monomer by the complex formation. Thus, the complexation equilibrium of EO-CuPc with alkali metal ion is given by

$$
\begin{equation*}
(\mathrm{EO}-\mathrm{CuPc})_{2}+2 \mathrm{M}^{+} \rightleftharpoons 2(\mathrm{MEO})^{+}-\mathrm{CuPc} \tag{3.22}
\end{equation*}
$$

Where $(\mathrm{EO}-\mathrm{CuPc})_{2}, \mathrm{M}^{+}$and $(\mathrm{MEO})^{+}-\mathrm{CuPc}$ are the dimer of $\mathrm{EO}-\mathrm{CuPc}$, the alkali metal ion and the alkali metal complex of monomeric EO-CuPc, respectively. By increasing the concentration of alkali metal ion, the remaining EO chains of monomeric $(\mathrm{MEO})^{+}-\mathrm{CuPc}$ react with alkali metal ions and formed cationic complex step by step. The alkali metal ion is coordinated to EO chain moiety of EO-CuPc, hence the copper (II) ion incorporated into Pc ring is not substituted by alkali metal ion.

As shown in Fig. 3-21, the monomerization of dimeric EO-CuPc due to the complexation of EO chains with alkali metal ions is easy to occur in the following order, $\mathrm{Li}^{+} \ll \mathrm{Na}^{+}<\mathrm{K}^{+}$ion. This result indicates the same tendency as the coordinating ability of linear EO chain. The EO chain coordinates to metal ion by surrounding it, and the cavity size of helical EO chain is most fit to the $\mathrm{K}^{+}$ion ${ }^{63-65}$. Thus, coordinating ability of EO-CuPc with alkali metal ion agrees with that of linear EO. These results suggest that the alkali metal ion is coordinated to EO chain moiety of EO-CuPc.

## 4. General feature of reaction with alkali metal hydroxides

General feature of complexation reactions of dimeric EO- $\mathrm{H}_{2} \mathrm{Pc}$ with alkali metal hydroxides in methanol are summarized in Fig. 3-22. Where only one EO side chain is depicted and all other EO chains are omitted for simplicity.

In the presence of base, $\mathrm{H}_{2} \mathrm{Pc}$ ring moiety having a rigid planar ligand reacts with alkali metal ions in the order, $\mathrm{Li}^{+} \gg \mathrm{Na}^{+}>\mathrm{K}^{+}$. This order is related by the fitness of cavity size of Pc ring with ionic radii of these cations. As the ion size of $\mathrm{Li}^{+}$is smaller than the cavity size of Pc ring, $\mathrm{Li}^{+}$ion is incorporated into the center of Pc ring. Thus, it forms stable complex of monovalent anionic lithium phthalocyaine. In case of larger $\mathrm{Na}^{+}$and $\mathrm{K}^{+}$ion, two cations are located on the top and bottom of the center of Pc ring. Therefore, the fitness of the ionic radii of alkali metal ions having same charge to the cavity size of Pc ring is the main factor of the coordinating ability of rigid Pc ring.

EO- $\mathrm{H}_{2} \mathrm{Pc}$ is easy to form dimer, however, its alkali phthalocyanine is easy to form monomer in methanol. Dimerization of monovalent monolithium phthalocyanine is suppressed by the electrostatic repulsion between anionic Pc rings. On the other hand, that of neutral disodium and dipotassium phthalocyanine is sterically-hindered by two cations located on the top and bottom of the center of Pc ring.

The coordinating ability of EO chain moiety of EO-CuPc with alkali metal ions
increases in the following order, $\mathrm{Li}^{+} \ll \mathrm{Na}^{+}<\mathrm{K}^{+}$. This order is agree with that of linear EO chain. The linear EO chain reacts with alkali metal ion and forms $1: 1$ complex by surrounding it. The cavity size of helical EO chain is similar with that of 18 -crown 6-ether, thus that of helical EO chain is most fit to the $\mathrm{K}^{+}$ion ${ }^{61-65}$.

In case of Pc ring having rigid planar cavity, the composition and structure of alkali phthalocyanine is highly dependent on the ionic radii of alkali metal ion. Although the coordinating ability of EO chain is dependent on the ionic radii of alkali metal ion, the composition and structure of alkali metal complex of EO chain are similar and the versatility of EO chain is higher than that of Pc ring because of the flexibility of EO chain.

Table 3-1. Logarithmic dimerization constant $\left(\log K_{2}\right)$ of EO- $\mathrm{H}_{2} \mathrm{Pc}$ in various alcohols.

|  | EO-H2Pc |
| :---: | :---: |
| Methanol | 7.30 |
| 1-Hexanol | 5.90 |
| 1-Decanol | 5.37 |



Scheme 3-1. Structure of EO-MPc. $\mathrm{M}=\left(\mathrm{H}^{+}\right)_{2}$ or $\mathrm{Cu}^{2+}$.


Figure 3-1. Absorption spectra of $\mathrm{EO} 6-\mathrm{H}_{2} \mathrm{Pc}$ at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in 1-decanol. $C_{\mathrm{Pc}}: 10^{-5.74}-10^{-4.84} \mathrm{M}$.


Figure 3-2. Absorption spectra of $\mathrm{EO} 6-\mathrm{H}_{2} \mathrm{Pc}$ at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in 1-hexanol. $C_{\mathrm{Pc}}: 10^{-6.34}-10^{-4.52} \mathrm{M}$.


Figure 3-3. Absorption spectra of $\mathrm{EO} 6-\mathrm{H}_{2} \mathrm{Pc}$ at various concentrations $\left(C_{\mathrm{Pc}}\right)$ in methanol. $C_{\mathrm{Pc}}: 10^{-6.05}-10^{-4.84} \mathrm{M}$.


Figure 3-4. Concentration dependence of molar extinction coefficient of Q-band peak of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ in various alcohols. $\square$; 1-Decanol, $\triangle$; 1-Hexanol, $O$; Methanol.


Figure 3-5. Change of UV-vis absorption spectra of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of lithium hydroxide $(\mathrm{LiOH})$ in methanol. $C_{\mathrm{Pc}}=4.96 \times 10^{-6} \mathrm{M} . C_{\mathrm{LiOH}}=0-$ $10^{-1.87} \mathrm{M}$.


Figure 3-6. Change of UV-vis absorption spectra of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of sodium hydroxide $(\mathrm{NaOH})$ in methanol. $C_{\mathrm{Pc}}=4.96 \times 10^{-6} \mathrm{M} . C_{\mathrm{NaOH}}=0-$ $10^{-0.24} \mathrm{M}$.


Figure 3-7. Change of UV-vis absorption spectra of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of potassium hydroxide $(\mathrm{KOH})$ in methanol. $C_{\mathrm{Pc}}=4.96 \times 10^{-6} \mathrm{M} . C_{\mathrm{KOH}}=0-$ $10^{-0.88} \mathrm{M}$.


Figure 3-8. Change in molar extinction coefficient ( $\varepsilon$ ) of Q-band as a function of concentration of alkali metal hydroxide $\left(\log C_{\mathrm{MOH}}\right)$. Curve $1 ; \mathrm{LiOH}$ in the presence of 0.05 M LiCl , Curve 2; LiOH , Curve 3; NaOH , Curve 4 ; KOH.


Figure 3-9. Plots of $\log F$ as a function of $\log C_{\mathrm{LiOH}}$ in the presence of 0.05 M LiCl $(\odot)$ and in the absence of $\mathrm{LiCl}(\bigcirc)$.


Figure 3-10. Change of emission spectra of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of lithium hydroxide $(\mathrm{LiOH})$ in methanol. $C_{\mathrm{Pc}}=4.96 \times 10^{-6} \mathrm{M} . C_{\mathrm{LiOH}}=0-10^{-1.85}$ M in the presence of 0.05 M LiCl .


Figure 3-11. Change of emission spectra of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of sodium hydroxide $(\mathrm{NaOH})$ in methanol. $C_{\mathrm{Pc}}=4.96 \times 10^{-6} \mathrm{M} . C_{\mathrm{NaOH}}=0-10^{-0.82}$ M.


Figure 3-12. Change of emission spectra of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of potassium hydroxide $(\mathrm{KOH})$ in methanol. $C_{\mathrm{Pc}}=4.96 \times 10^{-6} \mathrm{M} . C_{\mathrm{KOH}}=0-10^{-0.88}$ M.


Figure 3-13. Change in emission intensity at $680 \mathrm{~nm}(\odot)$ and molar extinction coefficient $(\varepsilon)$ of Q -band at $674 \mathrm{~nm}(\odot)$ as a function of concentration of lithium hydroxide $\left(\log C_{\mathrm{LiOH}}\right)$ in the presence of 0.05 M LiCl .


Figure 3-14. Change in emission intensity at 679 nm ( $\mathbf{\Delta}$ ) and molar extinction coefficient $(\varepsilon)$ of Q-band at $677 \mathrm{~nm}(\triangle)$ as a function of concentration of sodium hydroxide $\left(\log C_{\mathrm{NaOH}}\right)$.


Figure 3-15. Excitation spectra of EO- $\mathrm{H}_{2} \mathrm{Pc}$ at $4.96 \times 10^{-6} \mathrm{M}$ in various concentration of sodium hydroxide ( $C_{\mathrm{NaOH}}$ ) in 0.1 M water-containing methanol. (a) Excitation intensity at $679 \mathrm{~nm}, C_{\mathrm{NaOH}}=10^{-1.90} \mathrm{M}$, (b) excitation intensity at $679 \mathrm{~nm}, C_{\mathrm{NaOH}}=10^{-0.24} \mathrm{M}$.


Figure 3-16. Change in emission intensity at $679 \mathrm{~nm}(\square)$ and $708 \mathrm{~nm}(\checkmark)$ and molar extinction coefficient $(\varepsilon)$ of Q -band at $675 \mathrm{~nm}(\square)$ as a function of concentration of potassium hydroxide $\left(\log C_{\mathrm{KOH}}\right)$.


Figure 3-17. Excitation spectra of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ at $4.96 \times 10^{-6} \mathrm{M}$ in various concentration of potassium hydroxide $\left(C_{\mathrm{KOH}}\right)$ in 0.1 M water-containing methanol. (a) Excitatio intensity at $705 \mathrm{~nm}, C_{\mathrm{KOH}}=10^{-1.20} \mathrm{M}$, (b) excitation intensity at $679 \mathrm{~nm}, C_{\mathrm{KOH}}=10^{-0.88} \mathrm{M}$.


Figure 3-18. Change of UV-vis absorption spectra of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of lithium hydroxide $(\mathrm{LiOH})$ in methanol. $C_{\mathrm{Pc}}=4.97 \times 10^{-6} \mathrm{M} . C_{\mathrm{LiOH}}=0-$ $10^{-1.75} \mathrm{M}$.


Figure 3-19. Change of UV-vis absorption spectra of EO- $\mathrm{H}_{2} \mathrm{Pc}$ by the addition of sodium hydroxide $(\mathrm{NaOH})$ in methanol. $C_{\mathrm{Pc}}=4.97 \times 10^{-6} \mathrm{M} . C_{\mathrm{NaOH}}=0-$ $10^{-0.11} \mathrm{M}$.


Figure 3-20. Change of UV-vis absorption spectra of EO- $\mathrm{H}_{2} \mathrm{Pc}$ by the addition of potassium hydroxide $(\mathrm{KOH})$ in methanol. $C_{\mathrm{Pc}}=4.97 \times 10^{-6} \mathrm{M} . C_{\mathrm{KOH}}=0$ $-10^{-0.40} \mathrm{M}$.


Figure 3-21. Change in molar extinction coefficient ( $\varepsilon$ ) of Q-band at 675 nm as a function of concentration of alkali metal hydroxide $\left(\log C_{\mathrm{MOH}}\right)$. $\bigcirc$; Lithium hydroxide, $\triangle$; Sodium hydroxide, $\square$; Potassium hydroxide.


Figure 3-22. Summary of complexation reaction of EO- $\mathrm{H}_{2} \mathrm{Pc}$ with alkali metal hydroxide (MOH) in methanol.

## General conclusion

Metal-free and copper(II) tetra- $\beta$-polyethylene oxide-substituted phthalocyanine derivatives, TDEO6-MPc and TMeEO6-MPc, where polyethylene oxide derivative are hexaetyleneglycolmonododecylether (DEO6) and hexaethyleneglycolmonomethylether (MeEO6), respectively, were synthesized. Their yields are about $11-20 \%$ and those are higher than those of octasubstituted phthalocyanines (ca. $1 \%$ ). This leads to the ease of the investigation of properties of phthalocyanines. These phthalocyanine compounds (Pcs) are soluble in both of lipophlic and hydrophilic solvents. By taking advantage of this amphiphilic property and high molar extinction coefficient and fluorescence intensity of monomeric Pcs, solvent effect on the dimerization of the phthalocyanine was studied by means of UV-vis absorption and fluorescence spectroscopies.

In non-coordinating solvents, dimerization is suppressed by the increase in the acceptor property. This is attributed to the solvation to oxygen atoms of polyethylene oxide moiety. Thus, the solvation to EO chains is a dominant factor to inhibit the dimerization of Pcs. On the other hand, the dimerization in coordinating solvents is promoted by the increase in donor property of solvent.

Successive aggregation of Pcs in dichloromethane was studied by means of ${ }^{1} \mathrm{H}$ NMR spectroscopy. Because of a very wide dynamic range for solute concentration and high accuracy, ${ }^{1} \mathrm{H}$ NMR spectroscopy is one of most useful method for the study of aggregation. The NMR method requires relatively high concentration of sample solute. Thus in order to study the aggregation equilibria from monomer, dichloromethane was selected as a solvent in which the aggregation is suppressed.

The formation constants of each aggregate up to tetramer were determined. The constants higher than dimer have been scarcely reported. Successive formation
constants of each aggregate $\left(K_{n}\right)$ is decreased in this order $K_{2}>K_{3}>K_{4}$ and $K_{n}$ of metal-free phthalocyanine is smaller than that of copper(II) phthalocyanine. The structures of aggregates are estimated as slip-stacked face-to-face with the small slippage between Pc rings. It was estimated that the polyethylene oxide chains introduced into Pc ring are flexible and moves freely.

TMeEO6-MPc is soluble in polar solvents such as water and methanol according to the increasing of hydrophilic property. By taking advantage of this property, the effect of ionic radii of alkali metal ions on the selective coordination of rigid Pc ring and flexible polyethylene oxide side chains are studied in methanol by UV-vis absorption, emission and excitation spectroscopies. The complex formation with any metal ion, Pc and EO chain, with alkali metal ion causes the monomerization of TMeEO6-MPc dimer.

The coordination ability of Pc ring of $\mathrm{TMeEO}-\mathrm{H}_{2} \mathrm{Pc}$ to the alkali metal ion increases in the order $\mathrm{K}^{+}<\mathrm{Na}^{+} \ll \mathrm{Li}^{+}$, indicating the fitness of cavity size of Pc ring with the ionic radius of alkali metal ion. In case of smallest ion $\mathrm{Li}^{+}, \mathrm{Li}^{+}$ion is incorporated into the center of Pc ring, thus shows the highest stability. In case of larger $\mathrm{Na}^{+}$and $\mathrm{K}^{+}$ion, two cations are located on the top and bottom of the center of Pc ring. Therefore, the coordinating ability of Pc ring which has rigid cavity size and the structure of its complex are greatly affected by the ionic radius of alkali metal ion.

The coordinating ability of MeEO6 side chain of TMeEO6-MPc with alkali metal ion increases in the order $\mathrm{Li}^{+} \ll \mathrm{Na}^{+}<\mathrm{K}^{+}$depending on the fitness of the cavity size of the helical MeEO6 chain with the ionic radius of alkali metal ion. The composition and the structure of its complex are similar among alkali metal ions because of the flexibility of MeEO6 chain.

## Reference

1. Leznoff, C. C.; Lever, A. B. P. Phthalocyanines: Properties and Applications, Volume 1. VCH, New York, 1989.
2. Leznoff, C. C.; Lever, A. B. P. Phthalocyanines: Properties and Applications, Volume 2. VCH, New York, 1989.
3. Leznoff, C. C.; Lever, A. B. P. Phthalocyanines: Properties and Applications, Volume 3. VCH, New York, 1989.
4. Leznoff, C. C.; Lever, A. B. P. Phthalocyanines: Properties and Applications, Volume 4. VCH, New York, 1989.
5. Shirai, H.; Kobayashi, N. Phthalocyanines: Chemistry and Applications, IPC, Tokyo, 1997.
6. Hirohashi, R.; Sakamoto, K.; Okumura, E. Phthalocyanines as Functional Dyes: Basics and Applications, IPC, Tokyo, 2004.
7. Kadish, K. M.; Smith, K. M.; Guilard, R. The Porphyrin Handbook, Volume 15. AP, New York, 2003.
8. Kadish, K. M.; Smith, K. M.; Guilard, R. The Porphyrin Handbook, Volume 16. AP, New York, 2003.
9. Kadish, K. M.; Smith, K. M.; Guilard, R. The Porphyrin Handbook, Volume 17. AP, New York, 2003.
10. Kadish, K. M.; Smith, K. M.; Guilard, R. The Porphyrin Handbook, Volume 18. AP, New York, 2003.
11. Kadish, K. M.; Smith, K. M.; Guilard, R. The Porphyrin Handbook, Volume 19. AP, New York, 2003.
12. Kadish, K. M.; Smith, K. M.; Guilard, R. The Porphyrin Handbook, Volume 20. AP, New York, 2003.
13. Cook, M. J.; Heeney, M. J. Chem. Commun. 2000, 969-970.
14. Hayashi, H.; Nihashi, W.; Umeyama, T.; Matano, Y.; Seki, S.; Shimizu, Y.; Imahori, H. J. Am. Chem. Soc. 2011, 133, 10736-10739.
15. Hurditch, R. Adv. Col. Sci. Tech. 2001, 4, 33-40.
16. Nakagawa, K.; Kim, J.; Itoh, A. J. Appl. Phys. 2006, 99.
17. Martinez-Diaz, M. V.; de la Torre, G.; Torres, T. Chem. Commun. 2010, 46, 7090-7108.
18. Öeztuerk, Z. Z.; Necmettin, K.; Devrim, A.; Güerek, A. G.; Ahsen, V. J. Porphyrins Phthalocyanines 2009, 13, 1179-1187.
19. Cook, M. J.; Chambrier, I. J. Porphyrins Phthalocyanines 2011, 15, 149-173.
20. O'Flaherty, S. M; Hold, S. V.; Cook, M. J.; Torres, T.; Chen, Y.; Hanack, M.; Blau, W. J. Adv. Mater. 2003, 15, 19-32.
21. García-Frutos, E. M.; O’Flaherty, S. M.; Maya, E. M.; de la Torre, G.; Blau, W.; Vázqueza, P.; Torres, T. J. Mater. Chem. 2003, 13, 749-753.
22. Zolomaeva, O. V.; Ivanchikova, I. D.; Kholdeeva, O. A.; Sorokin, A. B. New J. Chem. 2009, 33, 1031-1037.
23. Mugadza, T.; Nyokong, T. Synth. Met. 2010, 160, 2089-2098.
24. Mitzel, F.; FitzGerald, S.; Beeby, A.; Faust, R. Chem. Eur. J. 2003, 9, 1233-1241.
25. Tuncel, S.; Dumoulin, F.; Gailer, J.; Sooriyaarachchi, M.; Atilla, D.; Durmuş, M.; Bouchu, D.; Savoie, H.; Boyle, RW.; Ahsen, V. Dalton Trans. 2011, 40, 4067-4079.
26. Sinha, A. K.; Mandal, B. K. Polym. J. 1995, 20, 1079-1084.
27. Brewis, M.; Clarkson, G. J.; Helliwell, M.; Holder, A. M.; McKeown, N. B. Chem. Eur. J. 2000, 6, 4630-4636.
28. Cheng, G.; Peng, X.; Hao, G.; Kennedy, V. O.; Ivanov, I. N.; Knappenberger, K.; Hill, T. J.; Rodgers, A. J.; Kenney, M. E. J. Phys. Chem. A 2003, 107, 3503-3514.
29. Anula, H. M.; Berlin, J. C.; Wu, H.; Li, Y.-S.; Peng, X.; Kenney, M. E.; Rodgers, M. A. J. Phys. Chem. A 2006, 110, 5215-5223.
30. Lau, J. T. F.; Lo, P.-C.; Fong, W.-P.; Ng, D. K. P. Chem. Eur. J. 2011, 17, 7569-7577.
31. Soncin, M.; Polo, L.; Reddi, E.; Kenney, M. E.; Cheng. G.; Rodgers, M. A. J. Br. J. Cancer 1995, 71, 727-732.
32. Slodek, A.; Wöhrle, D.; Doyle, J. J.; Blau, W. Macromol. Symp. 2006, 235, 9-18.
33. Allen, C. M.; Langlois, R.; Sharman, W. M.; La Madeleine, C.; van Lier, J. E. Photochem. Photobiol. 2002, 76, 208-216.
34. Peng, Y.; Lin, P.; Lin, J.; Xu, G.; Zhang, H.; Shi, J. Mater. Lett. 2009, 63, 914-916.
35. Kobayashi, N.; Narita, F.; Ishii, K.; Muranaka, A. Chem. Eur. J. 2009, 15, 10173-10181.
36. Özçeşmeci, İ.; Yerli, Y.; Okur, A. İ.; Gül, A. Inorg. Chem. Commun. 2009, 12, 625-627.
37. Chauke, V. P.; Arslanoglu, Y.; Nyokong, T. Polyhedron 2011, 30, 2132-2139.
38. Lyubimtsev, A.; Misir, M. N.; Calvete, M.; Hanack, M. Eur. J. Org. Chem. 2008, 18, 3209-3214.
39. Koca, A. J. Electroanal. Chem. 2011, 655, 128-139.
40. Sorokin, A. B.; Kudrik, E. V. Catalysis Today, 2011; 159, 37-46.
41. Bressan, M.; Celli, N.; d'Alessandro, N.; Liberatore, L.; Morvillo, A.; Tonucci, L. J. Organomet. Chem. 2000, 593-594, 416-420.
42. Fukushima, K.; Tabata, K.; Okura, I. J. Porphyrins Phthalocyanines 1998, 2, 219-222.
43. Liu, W.; Jensen, T. J.; Fronczek, F. R.; Hammer, R. P.; Smith, K. M.; Vicente, M. G. H. J. Med. Chem. 2005, 48, 1033-1041.
44. Opris, D. M.; Nuesch, F.; Lowe, C.; Molberg, M.; Nagel, M. Chem. Mater. 2008, 20, 6889-6896.
45. Soares, A. R. M.; Tomé, J. P. C.; Neves, M. G. P. M. S.; Tomé, A. C.; Cavaleiro, J. A. S.; Torres, T. Carbohydr. Res. 2009, 344, 507-510.
46. Karabork, M.; Serin, S. Synth. React. Inorg. Met.-Org. Chem. 2002, 32, 1635-1647.
47. Morisue, M.; Kameyama, K.; Kobuke, Y. Bull. Chem. Soc. Jpn. 2009, 82, 574-581.
48. Ağırtaş, M. S. Dyes Pigments 2008, 79, 247-251.
49. Ogunbayo, T.; Nyokong, T. J. Mol. Struct. 2010, 973, 96-103.
50. Kalkan, A.; Koca, A.; Bayir, Z. A. Polyhedron 2004, 23, 3155-3162.
51. Lyubimtsev, A.; Iqbal, Z.; Crucius, G.; Syrbu, S.; Taraymovich, E. S.; Ziegler, T.; Hanack, M. J. Porphyrins Phthalocyanines 2011, 15, 39-46.
52. Schutte, W. J.; Sluyters-Rehbach, M.; Sluyters, J. H. J. Phys. Chem. 1993, 97, 6069-6073.
53. Odabaş, Z.; Altindal, A.; Bulut, M. Synth. Met. 2011, 161, 1742-1752.
54. Snow, A. W.; Jarvis, N. L. J. Am. Chem. Soc. 1984, 106, 4706.
55. Krogmann, K. Angew. Chem., Int. Ed., 1969, 8, 35.
56. George, R. D.; Snow, A. W.; Shirk, J. S.; Barger, W. R. J. Porphyrins Phthalocyanines 1998, 2, 1-7.
57. Ward, J. R.; Seiders, R. P. Report 1983, 39.
58. Hadasch, A.; Sorokin, A.; Rabion, A.; Meunier, B. New J. Chem. 1998, 45-51.
59. Vacus. J.; Dopplet. P.; Simon, J.; Memetzidis, G. J. Mater. Chem. 1992, 2, 1065-1068.
60. Toei, K.; Motomizu, S.; Umato, T. Talanta 1982, 29, 103-106.
61. Mohite, B. S.; Khopkar, S. M. Anal. Chem. 1987, 59, 1200-1203.
62. Favretto, L.; Tunis, F. Analyst 1987, 101, 198-202.
63. Sawada, K.; Chigira, F.; Satoh, K.; Komatsuzaki, T. J. Chem. Soc., Faraday Trans. 1997, 93, 1903-1908.
64. Sawada, K.; Satoh, K.; Haruta, C.; Kikuchi, Y. Phys. Chem. Chem. Phys. 1999, 1, 2737-2741.
65. Sawada K, Imai A, Satoh K, Kikuchi Y. J. Phys. Chem. B. 2007, 111, 4361-4367.
66. Kimura, K.; Kumami, K.; Kitazawa, S.; Shono, T. Anal. Chem. 1984, 56, 2369-2372.
67. Samec, Z.; Papoff, P. Anal. Chem. 1990, 62, 1010-1015.
68. Nakamura, T.; Ueda, T.; Fujimori, K. Bull. Chem. Soc. Jpn. 1992, 65, 19-22.
69. Nakagawa, T.; Murata, H.; Shibukawa, A.; Murakami, K.; Tanaka, H. J. Chromatogr. 1985, 330, 43-53.
70. Fujita, H.; Yanagida, S.; Okahara, M. Anal. Chem. 1980, 52, 869-875.
71. Okada, T. J. Chromatogr. 1991, 586, 277-281.
72. Kobayashi, N.; Lever, A. B. P. J. Am. Chem. Soc. 1987, 109, 7433-7441.
73. Gürol, I.; Ahsen, V. J. Porphyrins Phthalocyanines 2000, 4, 620-625.
74. Ahsen, V.; Yilmazer, E.; Ertas, M.; Bekâroğlu, Ö. J. Chem. Soc., Dalton Trans. 1988, 401-406.
75. Kawahata, Y. Master's thesis 2005.
76. Sekitani, K. Master's thesis 2003.
77. Sawada, K.; Duan, W.; Sekitani, K.; Satoh, K. J. Mol. Liq. 2005, 119, 171-176.
78. Horn, D.; Honigmann, B. XIIth Fatipec Congress Book 1974, 181.
79. Kobayashi, N.; Higashi, R.; Ishii, K.; Hatsusaka, K.; Ohta, K. Bull. Chem. Soc. Jpn. 1999, 72, 1263-1271.
80. Hofman, J.-W.; van Zeeland, F.; Turker, S.; Talsma, H.; Lambrechts, S. A. G.; Sakharov, D. V.; Hennink, W. E.; van Nostrum, C. F. J. Med. Chem. 2007, 50, 1485-1494.
81. George, R. D.; Snow, A. W.; Shirk, J. S.; Barger, W. R. J. Porphyrins Phthalocyanines 1998, 2, 1-7.
82. Piechocki, C.; Simon, J. Nouv. J. Chim. 1985, 9, 159-166.
83. Monahan, A. R.; Brado, J. A.; Deluca, A. F. J. Chem. Phys. 1973, 58, 2281-2287.
84. Cook, M. J.; McMurdo, J.; Powell, A. K. Chem. Commun. 1993, 903-904.
85. Bernauer, K.; Fallab, S. Helv. Chim. Acta. 1961, 44, 1287-1292.
86. Snow, A. W.; Jarvis, N. L. J. Am. Chem. Soc. 1984; 106, 4706-4711.
87. Negri, R. M.; Zalts, A.; San Román, E. A.; Aramendía, P. F.; Braslavsky, S. E. Photochem. Photobiol. 1991, 53, 317-322.
88. Alemdar, A.; Özkaya, A. R.; Bulut, M. Synth. Met. 2010, 160, 1536-1565.
89. Hildebrand, J. H.; Scott, R. L. The Solubility of Nonelectrolytes (3rd edn), Reinhold Pub. Corp., New York, 1950.
90. Riddick, J. A.; Bunger, W. B.; Sakano, T. K. Organic Solvents (4th edn), Wiley Interscience, New York, 1986.
91. Mayer, U. Pure Appl. Chem. 1979; 51, 1697-1712.
92. Gutmann, V. Coord. Chem. Rev. 1967, 2, 239-256.
93. Gutmann, V. Coordination Chemistry in Non-Aqueous Solutions, Springer: Viena and New York, 1968.
94. Reichardt, C. Solvents and Solvent Effects in Organic Chemistry (2nd edn), WILEY-VCH, Weinheim, 1988.
95. Burger, K. Solvation, Ionic and Complex Formation Reactions in Non-Aqueous Solvents, Elsevier, Amsterdam, 1983.
96. Dumoulin, F.; Durmuş, M.; Ahsen, V.; Nyokong, T. Coord. Chem. Rev. 2010, 254, 2792-2847.
97. Vacus, J.; Dopplet, P.; Simon, J.; Memetzidis, G. J. Mater. Chem. 1992, 2, 1065-1068.
98. Sielcken, O. E.; van Tilborg, M. M.; Roks, M. F. M.; Hendriks, R.; Drenth, W.; Nolte, R. J. M. J. Am. Chem. Soc. 1987, 109, 4261-4265.
99. Atilla D, Durmuş M, Yılmaz Ö, Gürek AG, Ahsen V. Eur. J. Inorg. Chem. 2007, 3573-3581.
100. Darwent, J. R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M. C. Coord. Chem. Rev. 1982, 44, 83-126.
101. Dhami, S.; Phillips, D. J. Photochem. Photobiol. A 1996, 100, 77-84.
102. Matsuura, T. Organic Photochemistry: Chemical monograph series 20, Kagaku-Dojin, Kyoto, 1971.
103. Abkowits, M.; Monahan, A. R. J. Chem. Phys. 1973, 58, 2281.
104. Abel, E. W.; Pratt, J. M.; Whelan, E. J. J. Chem. Soc., Dalton Trans. 1976, 509.
105. Farina, R. D.; Halko, D. J.; Swinehart, J. H. J. Phys. Chem. 1972, 76, 2343.
106. Domingues, D. D.; Snow, A. W.; Shirk, J. S.; Pong, R. G. S. J. Porphyrins Phthalocyanines 2001, 5, 582-592.
107. Ishikawa, N.; Ohno, O.; Kaizu, Y.; Kobayashi, H. J. Phys. Chem. 1992, 96, 8832.
108. Marcussio, S. M.; Svirskaya, P. I.; Greenberg, S.; Lever, A. B. P.; Leznoff, C. C.; Tomer, K. B. Can. J. Chem. 1985, 63, 3057-3069.
109. Cook, M. J.; Cracknell, S. J. Moore, G. R.; Osborne, M. J.; Williamson, D. J. Magn. Reson. Chem. 1991, 29, 1053-1060.
110. Law, W.-F.; Lui, K. M.; Ng, D. K. P. J. Mater. Chem. 1997, 7, 2063-2067.
111. Chen, M. J.; Rathke, J. W. J. Porphyrins Phthalocyanines 2001, 5, 528-536.
112. Terekhov, D. S.; Nolan, K. J. M.; McArthur, C. R.; Leznoff, C. C. J. Org. Chem. 1996, 61, 3034-3040.
113. Isago, H.; Terekhov, D. S.; Leznoff, C. C. J. Porphyrins Phthalocyanines 1997, 1, 135-140.
114. Larchenko, V. E.; Lapkina, L. A.; Tolkacheva, E. O.; Tsivadze, A. Y. Russ. J. Coord. Chem. 1997, 23, 362-366.
115. Chambrier, I.; Cook, M. J.; Mayes, D. A.; MacDonald, C. J. Porphyrins Phthalocyanines 2003, 7, 426-438.
116. Sergeyev, S.; Pouzet, E.; Debever, O.; Levin, J.; Gierschner, J.; Cornil, J.; Aspec, R. G.; Geerts, Y. H. J. Mater. Chem. 2007, 17, 1777-1784.
117. Sommerauer, M.; Rager, C.; Hanack, M. J. Am. Chem. Soc. 1996, 118, 10085-10093.
118. Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. Pure Appl. Chem. 1965, 11, 371-392.
119. Robertson, J. M. J. Chem. Soc. 1936, 1195-1209.
120. Brown, C. J. J. Chem. Soc. A 1968, 2488-2493.
121. Shannon, R. D. Acta Crystallogr., Sect. A 1969, 32, 751-767.
122. Robertson, J. M. J. Chem. Soc. 1935, 1935, 615-621.
123. Scheidt, W. R.; Dow, W. J. Am. Chem. Soc. 1976, 99, 1101-1104.
124. Dolphin, D.; Sams, J. R.; Tsin, T. B. Inorg. Synth. 1980, 20, 159-160.
125. Grossie,D. G.; Feld, W. A.; Kelley, J. Acta Cryst. E65, 2009, m72.
126. Latte, B.; Kienast, A.; Bruhn, C.; Loidl, A.; Homborg, H. J. Porphyrins Phthalocyanines 1997, 1, 267-273.
127. Kadish, K. M.; Smith, K. M.; Guilard, R. The Porphyrin Handbook, Volume 10. AP, New York, 2003.
128. Arnold, J.; Dawson, D. Y.; Hoffman, C. G. J. Am. Chem. Soc. 1993, 115, 2707-2713.
129. Richards, R. A.; Hammons, K.; Joe, M.; Miskelly, G. M. Inorg. Chem. 1996, 35, 1940-1944.
130. Shimomura, T.; Tabata, M.; Nishimoto, J. J. Porphyrins Phthalocyanines 2009, 13, 849-853.
131. Barret, P. A.; Dent, C. E.; Linsted, R. P. J. Chem. Soc. 1936, 1719-1738.
132. Zhong, A.; Bian, Y.; Zhang, Y. J. Phys. Chem. C 2010, 114, 3248-3255.
133. Pietrangeli, D.; Rosa, A.; Pepe, A.; Ricciardi, G. Inorg. Chem. 2011, 50, 4680-4682.
134. Cissell, J. A.; Vaid, T. P. Inorg. Chem. 2007, 46, 4360-4361.

## Acknowledgements

The author is particularly indebted to Professor K. Sawada and Professor K. Satoh for their encouragement and very important discussions throughout the course of this work.

Thanks are due to Professor H. Kudo, Professor E. Hasegawa, Professor H. Iwamoto and Professor Y. Yukawa for reading the manuscript and making a number of helpful suggestions.

The author would like to thank Mr. Y. Kigawa, Ms. M. Minegishi, Ms. M. Saitoh and Mr. K. Inoue for their co-operation in carrying out the experiments.

The author thanks her parents who satisfied her wish to study for a degree of doctoral.

Appendix A

Table A-1. Concentration dependence of molar extinction coefficient of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in chloroform.

| $C_{\text {TDEO6-H } \mathrm{Pc}} / \mathrm{M}$ | $\log \left(C_{\text {TDEO6 }-\mathrm{HoPc}} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $1.58 \times 10^{-6}$ | -5.80 | 12.58 |
| $3.97 \times 10^{-6}$ | -5.40 | 12.61 |
| $4.63 \times 10^{-6}$ | -5.33 | 12.74 |
| $2.10 \times 10^{-5}$ | -4.68 | 12.33 |
| $3.94 \times 10^{-5}$ | -4.40 | 12.33 |
| $7.64 \times 10^{-5}$ | -4.12 | 11.25 |
| $1.56 \times 10^{-4}$ | -3.81 | 10.33 |

${ }^{\text {a }}$ Molar extinction coefficient at 704 nm .

Table A-2. Concentration dependence of molar extinction coefficient of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in dichloromethane.

| $C_{\text {TDEOG-H }{ }^{\text {Pc }}} / \mathrm{M}$ | $\log \left(C_{\text {TDEO6-H } \text { Pc }} / \mathrm{M}\right)$ | Molar extinction coefficient $/ 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $3.97 \times 10^{-6}$ | -5.40 | 11.63 |
| $2.10 \times 10^{-5}$ | -4.68 | 11.33 |
| $4.20 \times 10^{-5}$ | -4.38 | 10.90 |
| $7.64 \times 10^{-5}$ | -4.12 | 9.87 |
| $1.56 \times 10^{-4}$ | -3.81 | 8.73 |

${ }^{\mathrm{a}}$ Molar extinction coefficient at 702 nm .

Table A-3. Concentration dependence of molar extinction coefficient of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in 1,2-dichloroethane.

| $C_{\text {TDEO6-H PPc }} / \mathrm{M}$ | $\log \left(C_{\text {TDEO6-H } \mathrm{Pc}} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $1.85 \times 10^{-6}$ | -5.73 | 11.88 |
| $4.63 \times 10^{-6}$ | -5.33 | 12.10 |
| $1.20 \times 10^{-5}$ | -4.92 | 11.32 |
| $2.10 \times 10^{-5}$ | -4.68 | 11.02 |
| $4.20 \times 10^{-5}$ | -4.38 | 10.00 |
| $7.64 \times 10^{-5}$ | -4.12 | 8.73 |
| $1.56 \times 10^{-4}$ | -3.81 | 7.49 |

${ }^{\mathrm{a}}$ Molar extinction coefficient at 703 nm .

Table A-4. Concentration dependence of molar extinction coefficient of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in benzene.

| $C_{\text {TDEO6 }-\mathrm{H}_{2} \text { Pc }} / \mathrm{M}$ | $\log \left(C_{\text {TDEO6 }-\mathrm{H} \text { Pc }} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $1.69 \times 10^{-6}$ | -5.77 | 13.02 |
| $4.63 \times 10^{-6}$ | -5.33 | 12.29 |
| $6.11 \times 10^{-6}$ | -5.21 | 12.11 |
| $7.78 \times 10^{-6}$ | -5.11 | 11.81 |
| $2.10 \times 10^{-5}$ | -4.68 | 10.05 |
| $4.20 \times 10^{-5}$ | -4.38 | 8.99 |
| $1.56 \times 10^{-4}$ | -3.81 | 6.29 |
| $3.12 \times 10^{-4}$ | -3.51 | 5.32 |

${ }^{\mathrm{a}}$ Molar extinction coefficient at 704 nm .

Table A-5. Concentration dependence of molar extinction coefficient of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in carbon tetrachloride.

| $C_{\text {TDEO6 }-\mathrm{H}) \mathrm{Pc}} / \mathrm{M}$ | $\log \left(C_{\text {TDEO6-H }}\right.$ Pc $\left./ \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{2} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $1.56 \times 10^{-6}$ | -5.81 | 12.62 |
| $3.97 \times 10^{-6}$ | -5.40 | 11.91 |
| $7.93 \times 10^{-6}$ | -5.10 | 10.35 |
| $2.10 \times 10^{-5}$ | -4.68 | 8.82 |
| $4.20 \times 10^{-5}$ | -4.38 | 7.44 |
| $8.11 \times 10^{-5}$ | -4.09 | 6.20 |

${ }^{\mathrm{a}}$ Molar extinction coefficient at 704 nm .

Table A-6. Concentration dependence of molar extinction coefficient of TDEO6-CuPc in chloroform.

| $C_{\text {TDEO6-CuPc }} / \mathrm{M}$ | $\log \left(C_{\text {TDEO6-CUPc }} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{2} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $2.08 \times 10^{-6}$ | -5.68 | 12.98 |
| $4.15 \times 10^{-6}$ | -5.38 | 12.55 |
| $6.31 \times 10^{-6}$ | -5.20 | 12.43 |
| $1.04 \times 10^{-5}$ | -4.98 | 11.77 |
| $2.08 \times 10^{-5}$ | -4.68 | 11.46 |
| $4.15 \times 10^{-5}$ | -4.38 | 10.52 |
| $8.30 \times 10^{-5}$ | -4.08 | 9.46 |
| $1.65 \times 10^{-4}$ | -3.78 | 8.31 |

${ }^{a}$ Molar extinction coefficient at 682 nm .

Table A-7. Concentration dependence of molar extinction coefficient of TDEO6-CuPc in dichloromethane.

| $C_{\text {TDEO6 } 6 \text { CCP }} / \mathrm{M}$ | $\log \left(C_{\text {TDEO6 } 6 \text { CuPc }} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{2} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $2.08 \times 10^{-6}$ | -5.68 | 11.41 |
| $6.31 \times 10^{-6}$ | -5.20 | 11.10 |
| $1.04 \times 10^{-5}$ | -4.98 | 10.83 |
| $2.08 \times 10^{-5}$ | -4.68 | 10.14 |
| $4.15 \times 10^{-5}$ | -4.38 | 9.06 |
| $8.30 \times 10^{-5}$ | -4.08 | 8.40 |
| $1.81 \times 10^{-4}$ | -3.74 | 7.32 |

${ }^{\mathrm{a}}$ Molar extinction coefficient at 680 nm .

Table A-8. Concentration dependence of molar extinction coefficient of TDEO6-CuPc in 1,2-dichloroethane.

| $C_{\text {TDEO6-Cupc }} / \mathrm{M}$ | $\log \left(C_{\text {TDEO6 Cupc }} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $2.63 \times 10^{-6}$ | -5.58 | 10.21 |
| $1.05 \times 10^{-5}$ | -4.98 | 9.42 |
| $2.09 \times 10^{-5}$ | -4.68 | 8.81 |
| $4.17 \times 10^{-5}$ | -4.38 | 7.88 |
| $8.32 \times 10^{-5}$ | -4.08 | 6.93 |
| $1.62 \times 10^{-4}$ | -3.79 | 6.05 |
| $3.16 \times 10^{-4}$ | -3.50 | 5.43 |

${ }^{\mathrm{a}}$ Molar extinction coefficient at 681 nm .

Table A-9. Concentration dependence of molar extinction coefficient of TDEO6-CuPc in benzene.

| $C_{\text {TDEO6-CuPc }} / \mathrm{M}$ | $\log \left(C_{\text {TDEO6-CuPc }} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $2.08 \times 10^{-6}$ | -5.68 | 11.64 |
| $2.66 \times 10^{-6}$ | -5.58 | 11.50 |
| $4.15 \times 10^{-6}$ | -5.38 | 11.32 |
| $6.31 \times 10^{-6}$ | -5.20 | 11.08 |
| $1.04 \times 10^{-5}$ | -4.98 | 10.35 |
| $2.08 \times 10^{-5}$ | -4.68 | 9.50 |
| $4.15 \times 10^{-5}$ | -4.38 | 8.23 |
| $8.30 \times 10^{-5}$ | -4.08 | 6.97 |
| $1.63 \times 10^{-4}$ | -3.79 | 6.03 |
| $3.16 \times 10^{-4}$ | -3.50 | 5.23 |

${ }^{\mathrm{a}}$ Molar extinction coefficient at 681 nm .

Table A-10. Concentration dependence of molar extinction coefficient of TDEO6-CuPc in carbon tetrachloride.

| $C_{\text {TDEO6-CUPc }} / \mathrm{M}$ | $\log \left(C_{\text {TDEO6-CuPc }} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{2} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $1.72 \mathrm{E}-06$ | -5.76 | 9.25 |
| $2.66 \mathrm{E}-06$ | -5.58 | 8.16 |
| $4.15 \mathrm{E}-06$ | -5.38 | 8.00 |
| $6.31 \mathrm{E}-06$ | -5.20 | 7.29 |
| $1.04 \mathrm{E}-05$ | -4.98 | 6.53 |
| $2.08 \mathrm{E}-05$ | -4.68 | 5.70 |
| $4.15 \mathrm{E}-05$ | -4.38 | 4.95 |
| $8.30 \mathrm{E}-05$ | -4.08 | 4.45 |
| $1.63 \mathrm{E}-04$ | -3.79 | 3.92 |
| $3.16 \mathrm{E}-04$ | -3.50 | 3.65 |

${ }^{a}$ Molar extinction coefficient at 680 nm .

Table A-11. Monomer ratio of Pc derivatives as a function of donor number ( $D N$ ) of solvent and $E_{\mathrm{T}}(30)$ value of non-coordinating solvent.

|  | DN | $E_{\mathrm{T}}(30)$ | Monomer ratio / \% |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | TDEO6-MPc |  | ODEO6-MPc |  | OMeO3-MPc |  |
|  |  |  | $\mathrm{H}_{2}$ | Cu | $\mathrm{H}_{2}$ | Cu | $\mathrm{H}_{2}$ | Cu |
| $n$-Hexane | 0 | 31.0 | 1.4 |  | 0 | 4.0 |  |  |
| Carbon tetrachloride | 0 | 32.4 | 74.7 | 57.9 | 59.4 | 54.2 | 17.3 | 17.9 |
| Xylene | 0 | 33.1 | 76.9 | 90.2 | 62.7 | 79.5 | 17.4 | 30.7 |
| Toluene | 0 | 33.9 | 84.6 | 86.0 | 70.7 | 81.2 | 23.8 | 31.7 |
| Benzene | 0 | 34.3 | 85.3 | 87.2 | 80.5 | 85.7 | 31.0 | 39.5 |
| Chlorobenzene | 0 | 36.8 | 80.8 | 88.8 | 95.4 | 91.5 | 55.8 | 66.8 |
| Chloroform | 0 | 39.1 | 98.5 | 95.3 | 100 | 100 | 100 | 100 |
| Dichloromethane | 0 | 40.7 | 97.2 | 92.1 | 99.4 | 100 | 77.5 | 95.2 |
| 1,2-Dichloroethane | 0 | 41.3 | 93.6 | 90.5 |  |  |  |  |
| Diethyl ether | 19 |  | 20.0 | 13.1 | 10.0 | 17.9 |  |  |
| Ethyl acetate | 17.1 |  | 58.4 | 45.8 | 33.4 | 39.3 | 3.3 | 9.7 |
| 4-Methyl-2-pentanone | 20 |  | 40.8 | 32.6 | 16.1 | 25.6 | 7.4 | 0 |
| 1-Pentanol | 25 |  | 21.6 | 18.7 | 6.2 | 18.5 |  |  |
| Methanol | 25 |  |  |  |  |  | 1.4 | 4.8 |
| Water | 32 |  |  |  |  |  | 0 | 0 |

Table A-12. Fluorescence intensity and molar extinction coefficient of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in various solvents at $3.10 \times 10^{-6} \mathrm{M}$.

|  | Molar extinction coefficient $/ 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ | Fluorescence intensity / a.u. |
| :--- | :---: | :---: |
| Chloroform | 12.74 | 6.44 |
| Dichloromethane | 11.73 | 5.24 |
| Benzene | 10.49 | 5.15 |
| Ethyl acetate | 8.78 | 4.26 |
| 1-Pentanol | 4.19 | 1.25 |
| $n$-Hexane | 1.47 | 0.00 |

Appendix B

Table B-1. Concentration dependence of chemical shifts ( $\delta$ ) of aromatic and methylene protons of TDEO6- $\mathrm{H}_{2} \mathrm{Pc}$ in dichloromethane- $d_{2}$.

| chemical shifts ( $\delta$ ) / ppm |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\log \left(C_{\text {Pc }} / \mathrm{M}\right)$ | z | x | y | b | c | d | e | f1 | g1 |
| -5.52 | 9.400 | 8.996 | 7.858 | 4.743 | 4.156 | 3.881 | 3.767 | 3.711 | 3.652 |
| -5.05 | 9.376 | 8.966 | 7.849 | 4.743 | 4.161 | 3.885 | 3.772 | 3.715 | 3.658 |
| -4.57 | 9.313 | 8.891 | 7.824 | 4.735 | 4.170 | 3.895 | 3.781 | 3.715 | 3.663 |
| -4.09 | 9.218 | 8.775 | 7.783 | 4.723 | 4.184 | 3.910 | 3.794 | 3.721 | 3.671 |
| -3.62 | 9.074 | 8.598 | 7.720 | 4.703 | 4.203 | 3.932 | 3.813 | 3.735 | 3.681 |
| -3.14 | 8.929 | 8.423 | 7.654 | 4.678 | 4.217 | 3.951 | 3.831 | 3.746 | 3.691 |
| -2.66 | 8.784 | 8.252 | 7.583 | 4.645 | 4.225 | 3.966 | 3.845 | 3.759 | 3.701 |
| -2.18 | 8.641 | 8.100 | 7.514 | 4.608 | 4.227 | 3.977 | 3.857 | 3.769 | 3.709 |
| -1.77 | 8.518 | 7.956 | 7.440 | 4.566 | 4.223 | 3.985 | 3.869 | 3.778 | 3.719 |
| -1.54 | 8.442 | 7.869 | 7.397 | 4.537 | 4.220 | 3.990 | 3.875 | 3.784 | 3.725 |

Table B-2. Concentration dependence of chemical shifts ( $\delta$ ) of methylene protons of TDEO6-CuPc in dichloromethane- $d_{2}$.

| chemical shifts ( $\delta$ / / ppm |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\log \left(C_{\text {Pc }} / \mathrm{M}\right)$ | z | x | y | b | c | d | e | f1 | g1 |
| -5.32 | - | - | - | - | 4.085 | 3.829 | 3.732 | 3.671 | 3.646 |
| -4.85 | - | - | - | - | 4.088 | 3.839 | 3.743 | 3.680 | 3.653 |
| -4.37 | - | - | - | - | 4.095 | 3.852 | 3.756 | 3.690 | 3.657 |
| -3.89 | - | - | - | - | 4.100 | 3.866 | 3.769 | 3.701 | 3.665 |
| -3.41 | - | - | - | - | 4.098 | 3.874 | 3.778 | 3.709 | 3.670 |
| -2.94 | - | - | - | - | 4.090 | 3.880 | 3.786 | 3.715 | 3.676 |
| -2.46 | - | - | - | - | 4.082 | 3.884 | 3.790 | 3.721 | 3.682 |
| -1.98 | - | - | - | - | 4.061 | 3.880 | 3.794 | 3.727 | 3.687 |
| -1.52 | - | - | - | - | 4.019 | 3.873 | 3.792 | 3.730 | 3.692 |

Appendix C

Table C-1(a). Concentration dependence of molar extinction coefficient of EO- $\mathrm{H}_{2} \mathrm{Pc}$ in 1-decanol.

| $C_{\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}} / \mathrm{M}$ | $\log \left(C_{\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $1.82 \times 10^{-6}$ | -5.74 | 9.25 |
| $3.63 \times 10^{-6}$ | -5.44 | 8.20 |
| $7.24 \times 10^{-6}$ | -5.14 | 6.35 |
| $1.45 \times 10^{-5}$ | -4.84 | 4.77 |
| ${ }^{\mathrm{a}} \varepsilon$ at 704 nm. |  |  |

Table C-1(b). Concentration dependence of molar extinction coefficient of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ in 1-hexanol.

| $C_{\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}} / \mathrm{M}$ | $\log \left(C_{\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{2} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $4.48 \times 10^{-7}$ | -6.35 | 8.26 |
| $8.96 \times 10^{-7}$ | -6.05 | 7.25 |
| $1.79 \times 10^{-6}$ | -5.75 | 6.07 |
| $3.58 \times 10^{-6}$ | -5.45 | 4.92 |
| $3.77 \times 10^{-6}$ | -5.42 | 4.00 |
| $7.17 \times 10^{-6}$ | -5.14 | 3.48 |
| $7.55 \times 10^{-6}$ | -5.12 | 3.36 |
| $1.43 \times 10^{-5}$ | -4.84 | 2.95 |
| $1.51 \times 10^{-5}$ | -4.82 | 2.67 |
| $3.02 \times 10^{-5}$ | -4.52 | 2.06 |
| ${ }^{\mathrm{a}} \varepsilon$ at 704 nm. |  |  |

Table C-1(c). Concentration dependence of molar extinction coefficient of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ in methanol.

| $C_{\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}} / \mathrm{M}$ | $\log \left(C_{\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| $8.96 \times 10^{-7}$ | -6.05 | 2.77 |
| $1.79 \times 10^{-6}$ | -5.75 | 2.19 |
| $3.58 \times 10^{-6}$ | -5.45 | 1.84 |
| $7.17 \times 10^{-6}$ | -5.14 | 1.72 |
| $1.43 \times 10^{-5}$ | -4.84 | 1.52 |

${ }^{\mathrm{a}} \varepsilon$ at 704 nm .

Table C-2(a). Change of molar extinction coefficient of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of lithium hydroxide $(\mathrm{LiOH})$ in methanol in the presence of $5.00 \times 10^{-2} \mathrm{M}$ lithium chloride. $C_{\mathrm{Pc}}=4.96 \times 10^{-6} \mathrm{M}$.

| $C_{\text {LiOH }} / \mathrm{M}$ | $\log \left(C_{\text {LiOH }} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| 0.00 | - | 2.350 |
| $4.01 \times 10^{-5}$ | -4.40 | 2.350 |
| $8.00 \times 10^{-5}$ | -4.10 | 2.358 |
| $1.40 \times 10^{-4}$ | -3.85 | 2.570 |
| $2.00 \times 10^{-4}$ | -3.70 | 3.219 |
| $2.79 \times 10^{-4}$ | -3.55 | 4.833 |
| $3.58 \times 10^{-4}$ | -3.45 | 7.054 |
| $4.37 \times 10^{-4}$ | -3.36 | 9.567 |
| $5.16 \times 10^{-4}$ | -3.29 | 11.40 |
| $5.94 \times 10^{-4}$ | -3.23 | 12.91 |
| $6.72 \times 10^{-4}$ | -3.17 | 14.17 |
| $7.70 \times 10^{-4}$ | -3.11 | 15.14 |
| $9.05 \times 10^{-4}$ | -3.04 | 15.82 |
| $1.19 \times 10^{-3}$ | -2.92 | 16.45 |
| $1.83 \times 10^{-3}$ | -2.74 | 16.87 |
| $3.21 \times 10^{-3}$ | -2.49 | 17.08 |
| $6.35 \times 10^{-3}$ | -2.20 | 17.21 |
| $1.41 \times 10^{-2}$ | -1.85 | 17.30 |

[^0]Table C-2(b). Change of molar extinction coefficient of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of lithium hydroxide $(\mathrm{LiOH})$ in methanol. $C_{\mathrm{Pc}}=4.96 \times 10^{-6} \mathrm{M}$.

| $C_{\text {LiOH }} / \mathrm{M}$ | $\log \left(C_{\text {LiOH }} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| 0.00 | - | 2.490 |
| $1.38 \times 10^{-4}$ | -3.86 | 2.492 |
| $2.47 \times 10^{-4}$ | -3.61 | 2.531 |
| $3.56 \times 10^{-4}$ | -3.45 | 2.620 |
| $4.92 \times 10^{-4}$ | -3.31 | 2.830 |
| $6.01 \times 10^{-4}$ | -3.22 | 3.156 |
| $7.09 \times 10^{-4}$ | -3.15 | 3.688 |
| $8.17 \times 10^{-4}$ | -3.09 | 4.376 |
| $9.24 \times 10^{-4}$ | -3.03 | 5.188 |
| $1.03 \times 10^{-3}$ | -2.99 | 6.010 |
| $1.14 \times 10^{-3}$ | -2.94 | 7.045 |
| $1.22 \times 10^{-3}$ | -2.91 | 8.189 |
| $1.30 \times 10^{-3}$ | -2.89 | 8.932 |
| $1.38 \times 10^{-3}$ | -2.86 | 9.876 |
| $1.46 \times 10^{-3}$ | -2.84 | 10.56 |
| $1.54 \times 10^{-3}$ | -2.81 | 11.54 |
| $1.61 \times 10^{-3}$ | -2.79 | 12.15 |
| $1.69 \times 10^{-3}$ | -2.77 | 12.72 |
| $1.80 \times 10^{-3}$ | -2.75 | 13.47 |
| $1.88 \times 10^{-3}$ | -2.73 | 13.97 |
| $1.98 \times 10^{-3}$ | -2.70 | 14.53 |
| $2.11 \times 10^{-3}$ | -2.68 | 14.94 |
| $2.24 \times 10^{-3}$ | -2.65 | 15.40 |
| $2.55 \times 10^{-3}$ | -2.59 | 16.03 |
| $3.26 \times 10^{-3}$ | -2.49 | 16.61 |
| $3.88 \times 10^{-3}$ | -2.41 | 16.81 |
| $4.68 \times 10^{-3}$ | -2.33 | 16.90 |
| $5.85 \times 10^{-3}$ | -2.23 | 17.02 |
| $7.64 \times 10^{-3}$ | -2.12 | 17.06 |
| $9.75 \times 10^{-3}$ | -2.01 | 17.08 |
| $1.35 \times 10^{-2}$ | -1.87 | 17.02 |

[^1]Table C-2(c). Change of molar extinction coefficient of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of sodium hydroxide $(\mathrm{NaOH})$ in methanol. $C_{\mathrm{Pc}}=4.96 \times 10^{-6} \mathrm{M}$.

| $C_{\text {NaOH }} / \mathrm{M}$ | $\log \left(C_{\text {NaOH }} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| 0.00 | - | 2.314 |
| $3.46 \times 10^{-4}$ | -3.46 | 2.332 |
| $9.66 \times 10^{-4}$ | -3.01 | 2.340 |
| $3.20 \times 10^{-3}$ | -2.49 | 2.380 |
| $1.27 \times 10^{-2}$ | -1.90 | 2.493 |
| $2.07 \times 10^{-2}$ | -1.68 | 2.614 |
| $2.87 \times 10^{-2}$ | -1.54 | 2.773 |
| $3.98 \times 10^{-2}$ | -1.40 | 3.118 |
| $5.08 \times 10^{-2}$ | -1.29 | 3.680 |
| $6.17 \times 10^{-2}$ | -1.21 | 4.605 |
| $6.93 \times 10^{-2}$ | -1.16 | 5.494 |
| $7.68 \times 10^{-2}$ | -1.11 | 6.601 |
| $8.48 \times 10^{-2}$ | -1.07 | 8.124 |
| $9.22 \times 10^{-2}$ | -1.04 | 9.595 |
| $1.01 \times 10^{-1}$ | -0.99 | 11.24 |
| $1.12 \times 10^{-1}$ | -0.95 | 12.83 |
| $1.28 \times 10^{-1}$ | -0.89 | 14.46 |
| $1.51 \times 10^{-1}$ | -0.82 | 15.38 |
| $2.27 \times 10^{-1}$ | -0.64 | 16.17 |
| $3.19 \times 10^{-1}$ | -0.50 | 16.44 |
| $4.43 \times 10^{-1}$ | -0.35 | 16.65 |
| $5.78 \times 10^{-1}$ | -0.24 | 16.58 |

${ }^{\mathrm{a}} \varepsilon$ at 677 nm .

Table C-2(d). Change of molar extinction coefficient of EO- $\mathrm{H}_{2} \mathrm{Pc}$ by the addition of potassium hydroxide $(\mathrm{KOH})$ in methanol. $C_{\mathrm{Pc}}=4.96 \times 10^{-6} \mathrm{M}$.

| $C_{\mathrm{KOH}} / \mathrm{M}$ | $\log \left(C_{\mathrm{KOH}} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| 0.00 | - | 2.348 |
| $3.52 \times 10^{-4}$ | -3.45 | 2.356 |
| $1.14 \times 10^{-3}$ | -2.94 | 2.388 |
| $2.01 \times 10^{-3}$ | -2.70 | 2.445 |
| $3.65 \times 10^{-3}$ | -2.44 | 2.572 |
| $6.26 \times 10^{-3}$ | -2.20 | 2.727 |
| $1.09 \times 10^{-2}$ | -1.96 | 3.009 |
| $1.67 \times 10^{-2}$ | -1.78 | 3.366 |
| $2.82 \times 10^{-2}$ | -1.55 | 4.162 |
| $4.54 \times 10^{-2}$ | -1.34 | 5.317 |
| $6.26 \times 10^{-2}$ | -1.20 | 6.266 |
| $8.53 \times 10^{-2}$ | -1.07 | 7.102 |
| $1.19 \times 10^{-1}$ | -0.92 | 7.782 |
| $1.72 \times 10^{-1}$ | -0.76 | 8.326 |
| $2.62 \times 10^{-1}$ | -0.58 | 8.842 |
| $3.95 \times 10^{-1}$ | -0.40 | 9.299 |
| $5.73 \times 10^{-1}$ | -0.24 | 10.02 |
| $7.42 \times 10^{-1}$ | -0.13 | 10.83 |
| $9.03 \times 10^{-1}$ | -0.04 | 11.81 |
| 1.08 | 0.03 | 12.85 |
| 1.31 | 0.12 | 13.90 |
| 1.75 | 0.24 | 14.86 |
| 2.63 | 0.88 | 15.94 |

[^2]Table C-3(a). Plots of $\log F$ as a function of $\log C_{\mathrm{LiOH}}$ in the presence of 0.05 M LiCl .

| $\log \left(C_{\text {LiOH }} / \mathrm{M}\right)$ | $\log F$ |
| :---: | :---: |
| -3.36 | -0.0555 |
| -3.29 | 0.2557 |
| -3.23 | 0.5157 |
| -3.17 | 0.7557 |
| -3.11 | 0.9794 |
| -3.04 | 1.1768 |

Table C-3(b). Plots of $\log F$ as a function of $\log C_{\mathrm{LiOH}}$ in the absence of LiCl .

| $\log \left(C_{\text {LiOH }} / \mathrm{M}\right)$ | $\log F$ |
| :---: | :---: |
| -2.99 | -0.8149 |
| -2.94 | -0.5481 |
| -2.91 | -0.3008 |
| -2.89 | -0.1565 |
| -2.86 | 0.0157 |
| -2.84 | 0.1354 |
| -2.81 | 0.3061 |
| -2.79 | 0.4130 |
| -2.77 | 0.5168 |
| -2.75 | 0.6598 |
| -2.73 | 0.7646 |

Table C-4(a). Change of emission intensity of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of lithium hydroxide $(\mathrm{LiOH})$ in methanol in the presence of $0.05 \mathrm{M} \mathrm{LiCl} . C_{\mathrm{Pc}}=$ $4.96 \times 10^{-6} \mathrm{M}$.

| $C_{\text {LiOH }} / \mathrm{M}$ | $\log \left(C_{\text {LiOH }} / \mathrm{M}\right)$ | Emission intensity at $680 \mathrm{~nm} /$ a.u. |
| :---: | :---: | :---: |
| 0.00 | - | 0.50 |
| $4.01 \times 10^{-5}$ | -4.40 | 0.49 |
| $8.00 \times 10^{-5}$ | -4.10 | 0.60 |
| $1.40 \times 10^{-4}$ | -3.85 | 2.77 |
| $2.00 \times 10^{-4}$ | -3.70 | 8.67 |
| $2.79 \times 10^{-4}$ | -3.55 | 20.73 |
| $3.58 \times 10^{-4}$ | -3.45 | 36.34 |
| $4.37 \times 10^{-4}$ | -3.36 | 50.62 |
| $5.16 \times 10^{-4}$ | -3.29 | 62.18 |
| $5.94 \times 10^{-4}$ | -3.23 | 71.55 |
| $6.72 \times 10^{-4}$ | -3.17 | 78.48 |
| $7.70 \times 10^{-4}$ | -3.11 | 84.34 |
| $9.05 \times 10^{-4}$ | -3.04 | 89.12 |
| $1.19 \times 10^{-3}$ | -2.92 | 93.95 |
| $1.83 \times 10^{-3}$ | -2.74 | 96.50 |
| $3.21 \times 10^{-3}$ | -2.49 | 98.04 |
| $6.35 \times 10^{-3}$ | -2.20 | 99.13 |
| $1.41 \times 10^{-2}$ | -1.85 | 97.13 |

Table C-4(b). Change of emission intensity of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of sodium hydroxide $(\mathrm{NaOH})$ in methanol. $C_{\mathrm{Pc}}=4.96 \times 10^{-6} \mathrm{M}$.

| $C_{\mathrm{NaOH}} / \mathrm{M}$ | $\log \left(C_{\mathrm{NaOH}} / \mathrm{M}\right)$ | Emission intensity at $681 \mathrm{~nm} /$ a.u. |
| :---: | :---: | :---: |
| 0.00 | - | 0.54 |
| $3.46 \times 10^{-4}$ | -3.46 | 0.56 |
| $9.66 \times 10^{-4}$ | -3.01 | 0.65 |
| $3.20 \times 10^{-3}$ | -2.49 | 1.59 |
| $1.27 \times 10^{-2}$ | -1.90 | 15.00 |
| $2.07 \times 10^{-2}$ | -1.68 | 29.13 |
| $2.87 \times 10^{-2}$ | -1.54 | 33.63 |
| $3.98 \times 10^{-2}$ | -1.40 | 37.19 |
| $5.08 \times 10^{-2}$ | -1.29 | 39.70 |
| $6.17 \times 10^{-2}$ | -1.21 | 42.23 |
| $6.93 \times 10^{-2}$ | -1.16 | 44.67 |
| $7.68 \times 10^{-2}$ | -1.11 | 48.65 |
| $8.48 \times 10^{-2}$ | -1.07 | 53.66 |
| $9.22 \times 10^{-2}$ | -1.04 | 58.56 |
| $1.01 \times 10^{-1}$ | -0.99 | 64.52 |
| $1.12 \times 10^{-1}$ | -0.95 | 71.27 |
| $1.28 \times 10^{-1}$ | -0.89 | 77.62 |
| $1.51 \times 10^{-1}$ | -0.82 | 81.27 |

Table C-4(c). Change of emission intensity of $\mathrm{EO}-\mathrm{H}_{2} \mathrm{Pc}$ by the addition of potassium hydroxide $(\mathrm{KOH})$ in methanol. $C_{\mathrm{Pc}}=4.96 \times 10^{-6} \mathrm{M}$.

|  |  | Emission intensity $/$ a.u. |  |
| :---: | :---: | :---: | :---: |
| $C_{\text {KOН }} / \mathrm{M}$ | $\log \left(C_{\text {KOН }} / \mathrm{M}\right)$ | 679 nm | 708 nm |
| 0.00 | - | 3.50 | 0.48 |
| $3.52 \times 10^{-4}$ | -3.45 | 3.62 | 0.47 |
| $1.14 \times 10^{-3}$ | -2.94 | 4.01 | 0.55 |
| $3.65 \times 10^{-3}$ | -2.44 | 5.15 | 0.71 |
| $6.26 \times 10^{-3}$ | -2.44 | 6.40 | 1.05 |
| $1.09 \times 10^{-2}$ | -2.20 | 8.75 | 1.77 |
| $1.67 \times 10^{-2}$ | -1.96 | 11.80 | 2.46 |
| $2.82 \times 10^{-2}$ | -1.78 | 17.51 | 3.41 |
| $4.54 \times 10^{-2}$ | -1.55 | 23.66 | 4.51 |
| $6.26 \times 10^{-2}$ | -1.34 | 27.00 | 5.26 |
| $8.53 \times 10^{-2}$ | -1.20 | 28.11 | 5.90 |
| $1.19 \times 10^{-1}$ | -1.07 | 28.11 | 5.90 |
| $1.72 \times 10^{-1}$ | -0.92 | 25.65 | 7.13 |
| $2.62 \times 10^{-1}$ | -0.76 | 23.80 | 7.71 |
| $3.95 \times 10^{-1}$ | -0.58 | 19.90 | 8.37 |
| $5.73 \times 10^{-1}$ | -0.40 | 16.55 | 9.12 |
| $7.42 \times 10^{-1}$ | -0.24 | 14.21 | 10.16 |
| $9.03 \times 10^{-1}$ | -0.13 | 12.05 | 11.46 |
| 1.08 | -0.04 | 10.39 | 13.01 |
| 1.31 | 0.03 | 9.19 | 15.27 |
| 1.75 | 0.12 | 8.43 | 17.84 |
| 7.61 | 0.24 |  | 40.08 |

Table C-5(a). Change of molar extinction coefficient of EO-CuPc by the addition of lithium hydroxide $(\mathrm{LiOH})$ in methanol. $C_{\mathrm{Pc}}=4.97 \times 10^{-6} \mathrm{M}$.

| $C_{\text {LiOH }} / \mathrm{M}$ | $\log \left(C_{\text {LiOH }} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} /{10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}}^{0.00}$ |
| :---: | :---: | :---: |
|  | 2.540 |  |
| $1.33 \times 10^{-4}$ | -3.88 | 2.543 |
| $2.39 \times 10^{-4}$ | -3.62 | 2.567 |
| $3.45 \times 10^{-4}$ | -3.46 | 2.561 |
| $4.77 \times 10^{-4}$ | -3.32 | 2.564 |
| $6.87 \times 10^{-4}$ | -3.16 | 2.568 |
| $8.96 \times 10^{-4}$ | -3.05 | 2.582 |
| $1.10 \times 10^{-3}$ | -2.96 | 2.580 |
| $1.33 \times 10^{-3}$ | -2.87 | 2.589 |
| $1.56 \times 10^{-3}$ | -2.81 | 2.597 |
| $1.82 \times 10^{-3}$ | -2.74 | 2.594 |
| $2.17 \times 10^{-3}$ | -2.66 | 2.606 |
| $2.52 \times 10^{-3}$ | -2.60 | 2.602 |
| $3.13 \times 10^{-3}$ | -2.50 | 2.616 |
| $3.76 \times 10^{-3}$ | -2.43 | 2.616 |
| $4.53 \times 10^{-3}$ | -2.34 | 2.623 |
| $5.67 \times 10^{-3}$ | -2.25 | 2.628 |
| $7.41 \times 10^{-3}$ | -2.13 | 2.646 |
| $9.45 \times 10^{-3}$ | -2.02 | 2.658 |
| $1.31 \times 10^{-2}$ | -1.88 | 2.666 |
| $1.78 \times 10^{-2}$ | -1.75 | 2.692 |

${ }^{\mathrm{a}} \varepsilon$ at 675 nm .

Table C-5(b). Change of molar extinction coefficient of EO-CuPc by the addition of sodium hydroxide $(\mathrm{NaOH})$ in methanol. $C_{\mathrm{Pc}}=4.97 \times 10^{-6} \mathrm{M}$.

| $C_{\text {NaOH }} / \mathrm{M}$ | $\log \left(C_{\mathrm{NaOH}} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{2} / 10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| 0.00 | - | 2.540 |
| $3.65 \times 10^{-4}$ | -3.44 | 2.543 |
| $1.02 \times 10^{-3}$ | -2.99 | 2.567 |
| $2.17 \times 10^{-3}$ | -2.66 | 2.561 |
| $3.37 \times 10^{-3}$ | -2.47 | 2.564 |
| $8.38 \times 10^{-3}$ | -2.08 | 2.568 |
| $1.55 \times 10^{-2}$ | -1.81 | 2.582 |
| $3.02 \times 10^{-2}$ | -1.52 | 2.580 |
| $4.47 \times 10^{-2}$ | -1.35 | 2.589 |
| $6.17 \times 10^{-2}$ | -1.21 | 2.597 |
| $8.09 \times 10^{-2}$ | -1.09 | 2.594 |
| $8.88 \times 10^{-2}$ | -1.05 | 2.606 |
| $1.00 \times 10^{-1}$ | -1.00 | 2.602 |
| $1.19 \times 10^{-1}$ | -0.92 | 2.616 |
| $1.38 \times 10^{-1}$ | -0.86 | 2.616 |
| $1.71 \times 10^{-1}$ | -0.77 | 2.623 |
| $2.55 \times 10^{-1}$ | -0.59 | 2.628 |
| $3.46 \times 10^{-1}$ | -0.46 | 2.646 |
| $4.75 \times 10^{-1}$ | -0.32 | 2.658 |
| $6.47 \times 10^{-1}$ | -0.19 | 2.666 |
| $7.80 \times 10^{-1}$ | -0.11 | 2.692 |

${ }^{\mathrm{a}} \varepsilon$ at 675 nm .

Table C-5(c). Change of molar extinction coefficient of EO-CuPc by the addition of potassium hydroxide $(\mathrm{KOH})$ in methanol. $C_{\mathrm{Pc}}=4.97 \times 10^{-6} \mathrm{M}$.

| $C_{\text {NaOH }} / \mathrm{M}$ | $\log \left(C_{\text {NaOH }} / \mathrm{M}\right)$ | Molar extinction coefficient ${ }^{\mathrm{a}} / \mathrm{l}^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ |
| :---: | :---: | :---: |
| 0.00 | - | 2.548 |
| $3.15 \times 10^{-4}$ | -3.50 | 2.433 |
| $1.02 \times 10^{-3}$ | -2.99 | 2.525 |
| $1.80 \times 10^{-3}$ | -2.75 | 2.614 |
| $3.26 \times 10^{-3}$ | -2.49 | 2.793 |
| $5.59 \times 10^{-3}$ | -2.25 | 3.090 |
| $9.74 \times 10^{-3}$ | -2.01 | 3.486 |
| $2.52 \times 10^{-2}$ | -1.60 | 4.843 |
| $4.06 \times 10^{-2}$ | -1.39 | 6.087 |
| $5.59 \times 10^{-2}$ | -1.25 | 7.078 |
| $7.11 \times 10^{-2}$ | -1.15 | 7.847 |
| $9.13 \times 10^{-2}$ | -1.04 | 8.719 |
| $1.11 \times 10^{-1}$ | -0.95 | 9.355 |
| $1.36 \times 10^{-1}$ | -0.87 | 9.985 |
| $1.61 \times 10^{-1}$ | -0.79 | 10.470 |
| $1.91 \times 10^{-1}$ | -0.72 | 10.764 |
| $2.20 \times 10^{-1}$ | -0.66 | 10.945 |
| $2.68 \times 10^{-1}$ | -0.57 | 11.156 |
| $3.29 \times 10^{-1}$ | -0.48 | 11.266 |
| $3.99 \times 10^{-1}$ | -0.40 | 11.303 |

${ }^{\mathrm{a}} \varepsilon$ at 675 nm .


[^0]:    ${ }^{\mathrm{a}} \varepsilon$ at 674 nm .

[^1]:    ${ }^{\mathrm{a}} \varepsilon$ at 674 nm .

[^2]:    ${ }^{\mathrm{a}} \varepsilon$ at 675 nm .

