ior of heat release or thermalization of photofragments. This kind of quantum interference effects are to be found even in the cell experiment,[16] where the different dissociation channels can be investigated by detection of photoacoustic or photothermal signals.

Summary

We have shown that the acoustic wave generated by multiphoton dissociation of chlorine molecules in argon can be detected by PBD. Since PBD is a noncontact technique, this detection method can be used in the corrosive environment where the diaphragm of microphone can be easily destroyed. Detection of acoustic wave or heat release by PBD can be an alternative choice of studying photodissociation of molecules with high sensitivity and even quantum interference effect in the cell may have good reason to be studied by PBD.

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Effect of Electrolyte and Solvent in Axial Ligation of Tetrakis(2,6-dichlorophenyl)porphyrinato Manganese(III) and -(II) Complexes

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Manganese porphyrins have several interesting aspects of physical, chemical, and biological properties which distinguish them from other metalloporphyrins.[1-3] Manganese porphyrins are of interest as catalysts for the epoxidation of olefins and for hydrocarbon oxygenation,[4-8] as models for the behavior of cytochrome P-450,[9] photosystem II,[10] and superoxide dismutase.[11] Particularly axial ligation of manganese porphyrins coupled with their redox chemistry is very crucial in diverse biological functions.[12-17] Recently we investigated the redox chemistry and autoreduction of $Mn^{III}(Cl_8TPP)Cl$ by hydroxide ion.[18] Electrochemistry, spectrophotometry, and conductometry were used for determining the state of axial ligation of $Mn^{III}(TPP)Cl$ in solutions, they reveal that the axial Cl^- ligand is bound to Mn^{III} and Mn^{II} oxidation states in non-ligating solvents, but Cl^- is dissociated from $Mn^{III}(TPP)Cl$ in stronger ligating solvents.[19-23] In this study, thin-layer spectroelectrochemistry has been used to probe the effect of electrolyte and solvent on axial ligation of manganese substituted tetra-phenyl porphyrins [$Mn^{III}(Cl_8TPP)Cl$ and $Mn^{III}(Me_{12}TPP)Cl$].

Experimental

Reagents. $Mn^{III}(Cl_8TPP)Cl$ and $Mn^{III}(Me_{12}TPP)Cl$ were synthesized by literature procedures.[16,24] Anhydrous acetonitrile (MeCN), methylene chloride (CH_2Cl_2), tetrahydrofuran (THF), dimethyl formamide (DMF), and dimethylsulfoxide (DMSO) were used as received from Aldrich. As supporting electrolytes, tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6) and tetrabutyl ammonium tetrafluoroborate (Bu_4NBF_4) were used as received from Aldrich, and tetrabutyl ammonium perchlorate (Bu_4NClO_4) and tetraethyl ammonium chloride (Et_4NCl) were purchased from Tokyo Chemical Inc. and vacuum desiccated before use.

Equipment and Procedures. Spectroelectrochemical experiments were carried out in an optically transparent thin-layer cell containing a Pt mesh working electrode *via* controlled potential electrolysis using three electrode potentiostat (Bioanalytical Systems, Model CV-27). A platinum-wire electrode separated from the analyte compartment by a medium porosity glass frit was used as an auxiliary elec-

trode. A Ag/AgCl reference electrode (filled with aqueous tetramethylammonium chloride solution and adjusted to 0.00 V vs SCE)[25] with a solution junction *via* a Pyrex-glass tube closed with a cracked-glass bead (soft glass). Absorption spectra were recorded on a Jasco V-530 spectrophotometer equipped with a HMC-358 constant temperature cell holder, and an optical path length is 0.2 mm. All experiments are carried out under anaerobic conditions and at room temperature.

Results and Discussion

Spectroelectrochemical studies for $Mn^{III}(Cl_8TPP)Cl$ in CH_2Cl_2. The electronic absorption spectra of Mn^{III} and Mn^{II} porphyrins were measured over the range of 340-800 nm. Figure 1 illustrates the absorption spectra of $Mn^{III}(Cl_8TPP)Cl$ and its spectroelectrochemical reduction product in CH_2Cl_2 containing 0.1 M Et_4NCl. The spectrum of $Mn^{III}(Cl_8TPP)Cl$ exhibits a Soret band maximum at 478 nm and Q band at 580 nm. The spectrum of reduced Mn^{II} complex is obtained by holding the potential of the working electrode at −0.3 V *vs* SCE. When Et_4NCl or Bu_4NClO_4 is used as a supporting electrolyte, the optical spectra of the reduced Mn^{II} form reveals that the Soret maximum shifts slightly in energy to 448 nm and intensifies relative to that of $Mn^{III}(Cl_8TPP)Cl$, and Q band shows at 589 nm. The result suggests the formation of $[Mn^{II}(TPP)Cl]^-$ as Mn^{II} form by electrochemical reduction of $Mn^{III}(TPP)Cl$ in CH_2Cl_2 containing 0.1 M Et_4NCl or Bu_4NClO_4 as an electrolyte. It was recently reported that the axial Cl ligand is bound to the metal in both oxidation states of $Mn^{III}(TPP)Cl$ and $[Mn^{II}(TPP)Cl]$ in non-ligating solvents such as CH_2Cl_2 and $ClCH_2CH_2Cl$ containing 0.1 M Bu_4NBF_4. This result described the direct formation of $[Mn^{II}(TPP)Cl]^-$ by reduction of $Mn^{III}(TPP)Cl$ without any exchange at axial position.[19]

Spectroelectrochemical studies for the reduction of $Mn^{III}(Cl_8TPP)Cl$ is executed in non-ligating solvents containing 0.1 M Bu_4NBF_4 or Bu_4NPF_6 as a supporting electrolyte. The electronic spectra of $Mn^{III}(Cl_8TPP)Cl$ obtained from a series of supporting electrolytes (Et_4NCl, Bu_4NClO_4, Bu_4NBF_4, and Bu_4NPF_6) are almost identical in CH_2Cl_2. Visible spectral changes observed for the spectroelectrochemical reduction of $Mn^{III}(Cl_8TPP)Cl$ in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 is shown in Figure 2 over the range of 400-500 nm. The similar result is obtained when Bu_4NBF_4 is used as a supporting electrolyte. Examination of Figure 2 describes that the absorption band gives initially rise to 434 and 446 nm during thin-layer electrolysis, and then the band at 434 nm slowly disappears, and 446 nm shifts to 448 nm and intensifies relative to that of $Mn^{III}(Cl_8TPP)Cl$. The Q bands have at 577 and 621 nm. There are seen isosbestic points (417, 439, 463 and 495 nm) which demonstrate the absence of any long-lived intermediates. On the basis of its Soret band, the absorbance at 434 nm may be assigned to $Mn^{II}(Cl_8TPP)$ as a dissociation form of chloride ion, and the Soret band at 448 nm may be assigned to $[Mn^{II}(Cl_8TPP)Cl]^-$. These assignments are comparable to the results reported from the literature.[16,26] Although the direct formation of $[Mn^{II}(TPP)Cl]^-$ by electrochemical reduction of $Mn^{III}(TPP)Cl$ in CH_2Cl_2 containing 0.1 M Et_4NCl or Bu_4NClO_4 is apparently dominant, it has been demonstrated that Cl is lost in the reduction process to $Mn^{II}(Cl_8TPP)$, and then $Mn^{II}(Cl_8TPP)$ may slowly recombine with the Cl in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 or Bu_4NBF_4. Effect of supporting electrolytes for $Mn^{III}(Me_{12}TPP)Cl$ is not observed in CH_2Cl_2 containing any electrolytes, and the result is similar to that of $Mn^{III}(TPP)Cl$ solution. Spectroelectrochemical reduction of $Mn^{III}(TPP)Cl$ in CH_2Cl_2 gives the direct formation of $[Mn^{II}(TPP)Cl]$ without any intermediates. These

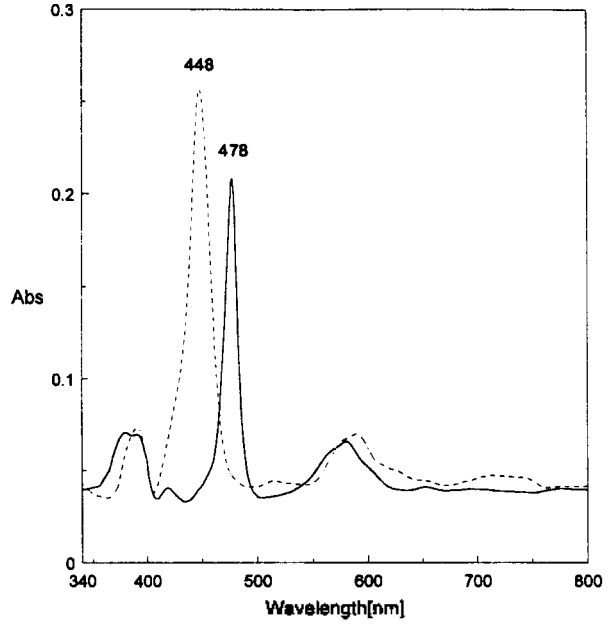

Figure 1. Spectroelectrochemical reduction of $Mn^{III}(Cl_8TPP)Cl$ in CH_2Cl_2 containing 0.1 M Et_4NCl. $Mn^{III}(Cl_8TPP)Cl$ (—) and Mn^{II} form (---).

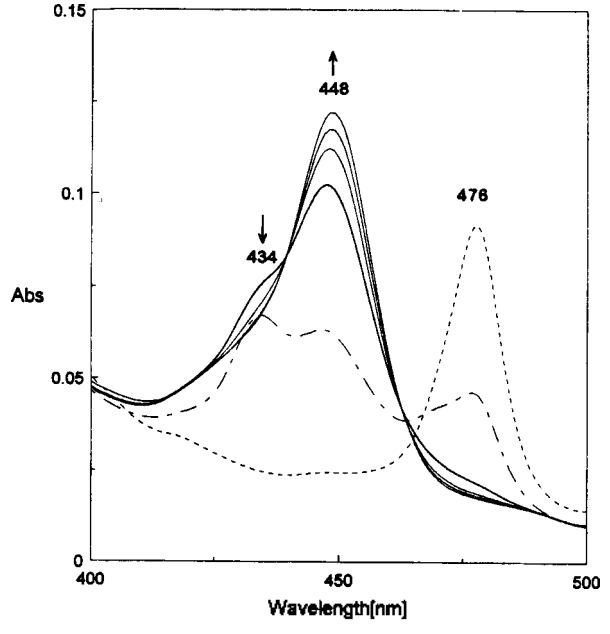

Figure 2. Visible spectral changes observed for the spectroelectrochemical reduction of $Mn^{III}(Cl_8TPP)Cl$ in CH_2Cl_2 containing 0.1 M Bu_4NPF_6.

results indicate that the reduced $Mn^{II}(Cl_8TPP)$ of $Mn^{III}(Cl_8TPP)Cl$ having electron withdrawing substituted phenyl group bonded to *meso*-position of porphyrin ring may be somewhat metastable under conditions which are not contained chloride or perchlorate ion, that can be easily coordinated to manganese center.

Spectroelectrochemical studies for $Mn^{III}(Cl_8TPP)Cl$ in ligating solvents. Figure 3 illustrates the spectroelectrochemical reduction of $Mn^{III}(Cl_8TPP)Cl$ in MeCN containing 0.1 M Bu_4NPF_6 and 0.1 M Et_4NCl, respectively. The spectrum of $Mn^{III}(Cl_8TPP)Cl$ exhibits a Soret band maximum at 476 nm and Q band maxima at 581 nm, and is similar in solutions containing Bu_4NClO_4 or Bu_4NBF_4. From the results of spectroscopic and conductometric methods, there is no evidence that $Mn^{III}(Cl_8TPP)Cl$ dissociates the chloride ion in MeCN as a weekly ligating solvent. On the basis of its Soret band, presumably $Mn^{III}(Cl_8TPP)Cl$ retains the chloride ion as five coordinate, or the chloride ion and MeCN as mixed-ligand six coordinate. The dissociation of chloride ion from $Mn^{III}(Me_{12}TPP)Cl$ was observed,[16] but does not occur for $Mn^{III}(TPP)Cl$ in MeCN.[19]

Examination of Figure 3 suggests that the optical spectra of reduced Mn^{II} complex are different in the electrolyte solutions. The spectrum of reduced Mn^{II} complex shows a Soret maximum at 434 nm and Q band at 575 nm in 0.1 M Bu_4NPF_6 solution, whereas a Soret band at 446 nm and Q band at 580 nm in 0.1 M Bu_4NCl solution. According to the position of Soret band the formation by reduction of $Mn^{III}(Cl_8TPP)Cl$ is apparently $[Mn^{II}(Cl_8TPP)Cl]^-$ as five-coordinate in 0.1 M Bu_4NCl solution. A band at 434 nm is probably ascribed to $Mn^{II}(Cl_8TPP)$ or $Mn^{II}(Cl_8TPP)(MeCN)n$ (n=1 to 2) as ligation of solvent in 0.1 M Bu_4NPF_6 or Bu_4NBF_4 solution. In CH_2Cl_2 containing 0.1 M Bu_4NPF_6, the absorption band at 434 nm observed from the reduction of $Mn^{III}(Cl_8TPP)Cl$ is assigned to $Mn^{II}(Cl_8TPP)$, but it is unstable and slowly converts to $[Mn^{II}(Cl_8TPP)Cl]^-$. However in MeCN, $Mn^{II}(Cl_8TPP)$ seems to be stable and it may be ligated with ligating solvent to form $Mn^{II}(Cl_8TPP)(MeCN)_n$. The product assigned as $Mn^{II}(Cl_8TPP)(MeCN)_n$ is not observed in MeCN solutions having Bu_4NClO_4 or Bu_4NCl, whereas $[Mn^{II}(Cl_8TPP)Cl]$ is predominant product.

The spectrum of $Mn^{III}(Cl_8TPP)Cl$ exhibits a Soret band maximum at 464 nm and Q bands at 566 and 605 nm in DMF containing 0.1 M Bu_4NPF_6. The spectrum of reduced Mn^{II} complex shows a Soret band at 438 nm and intensifies relative to that of $Mn^{III}(Cl_8TPP)Cl$. Table 1 summarizes Soret bands measured from spectroelectrochemical method as a function of solvents for $Mn^{III}(Cl_8TPP)Cl$ and its Mn^{II} form in the solution containing 0.1 M Bu_4NPF_6 as a supporting electrolyte. To infer the identity of the axial ligands of manganese complexes in solvent employed, the shift of Soret band may be used under these conditions. The Soret band in ligating solvents gives blue shift relative to that in non-ligating solvents. Considering the relationship between the donor number of solvent and the extent of blue shift of Soret band for Mn^{III} and Mn^{II} complexes, the shift extent for Mn^{III} complex is presumably proportional to the donor number of solvent. This result indicates that the Mn^{III} complex can be strongly ligated with solvent having higher value of donor number, and makes larger blue shift of Soret band. Adding ligating solvent to Mn^{III} complex may give

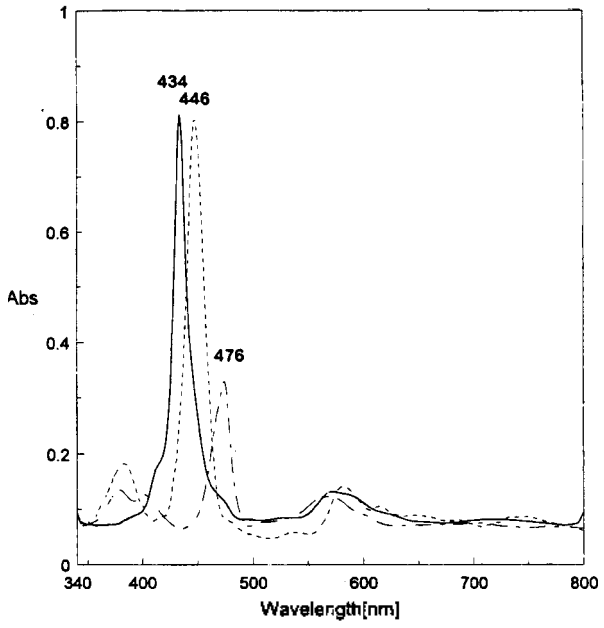

Figure 3. Spectroelectrochemical reduction of $Mn^{III}(Cl_8TPP)Cl$ in MeCN containing 0.1 M Bu_4NPF_6 and 0.1 M Bu_4NCl. $Mn^{III}(Cl_8TPP)Cl$ ( ), Mn^{II} form in Et_4NCl (---), and Mn^{II} form in Bu_4NPF_6 (—).

Table 1. Absorption Soret bands measured from spectroelectrochemical method as a function of solvents for $Mn^{III}(Cl_8TPP)Cl$ and its Mn^{II} form (0.1 M Bu_4NPF_6)

Solvent	DN[a]	$\lambda_{max[Mn(III)]}$(nm)	$\lambda_{max[Mn(II)]}$(nm)
CH_2Cl_2		478	448
$ClCH_2CH_2Cl$		478	448
MeCN	14.1	476	434
THF	20.0	469	436
DMF	26.6	464	438
DMSO	29.8	464	438

[a] DN: Donor Number, from ref. 27.

mixed six-coordinate $\{Mn^{III}(Cl_8TPP)(L)Cl\}$ or bisligated six-coordinate $\{Mn^{III}(Cl_8TPP)(L)_2^+\}$ structure. The red shift extent of Soret band for Mn^{II} form seems to be proportional to the donor number of solvent based on the chloride dissociated form $[Mn^{II}(Cl_8TPP)]$ which is shown Soret band at 434 nm in CH_2Cl_2. The suggestion on the red shift of Soret band in the Mn^{II} form may also be donation effect of solvent, and the coordination of chloride ion to $Mn^{II}(Cl_8TPP)$ to produce $[Mn^{II}(Cl_8TPP)Cl]$ shifts to 448 nm from 434 nm as Soret band of $Mn^{II}(Cl_8TPP)$. Finally, we conclude that the dissociation of chloride ion is dependent on solvent as well as electrolyte used for the spectroelectrochemical studies, and the dissociation of chloride ion from $Mn^{III}(Cl_8TPP)Cl$ is more difficult than from $[Mn^{II}(Cl_8TPP)Cl]^-$.

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Thermal Generation of 2-Silanaphthalene Intermediates

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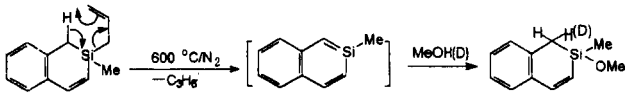
There have been many reports of the generation and reaction of silabenzene intermediate, an attractive molecule in silicon chemistry, from the readily available chloro or allyl precursors.[1] The first generation of silatoluene intermediate formed *via* a thermally induced retro-ene extrusion of propene from 1-methyl-1-allyl-1-silacyclohexa-2,4-diene was reported by the Barton group,[2] and the existence was confirmed by matrix isolation method at low temperature.[3] Thermal fragmentation of 1-methyl-2,3,4,5-tetraphenylsilacyclopentadienyl-diazomethane to give silatoluene was reported by Ando and Sekiguchi.[4] West and Rich reported evidence for the existence of hexamethyl-1,4-disilabenzene intermediate produced by photochemical or thermal extrusions of anthracene from the precursor.[5] The attempted generation of 9-silaanthracene from the suitable precursors has been reported.[6,7a] However, in solution, the necessary elimination for formation of 9-silaanthracene from the chloro precursors fails to occur and reaction proceeds *via* intermolecular substitution leading to dimeric or polymeric products.[6a,b] No evidence for the generation of 9-silaanthracene intermediate from photolysis of 10-diazo-9,9-dimethyl-9,10-dihydro-9-silaanthracene in methanol[7a] and flash vacuum thermolysis of 9,10-dibenzyl-9,10-diphenyl-9,10-dihydro-9-silaanthracene[6c] was observed. There is a precedent for the unsuccessful approach to generate 2-silanaphthalene intermediate from the thermolysis or photolysis of diazo-2,2-diphenyl-4-bromo-1,2-dihydro-2-silanaphthalene (**4**) in the presence of methanol.[7]

Recently, we reported the results of a thermolytic reaction of 2-allyl-2-methyl-1,2-dihydro-2-silanaphthalene (**1**) with methanol or methanol-d_1 in which apperared to involve generation of, an aromatic silicon-containing analogue of naphthalene, 2-methyl-2-silanaphthalene intermediate (**2**).[8]



1 **2** **3**

We now wish to report the generation and trapping of 2-allyl- (**9**) and 2-methoxy-2-silanaphthalene (**11**) intermediates which could arise from the thermolytic reaction of 2,2-diallyl-1,2-dihydro-2-silanaphthalene (**7**) with methanol or methanol-d_1.