Metalation of Water-Soluble Octabromoporphyrin with Lithium(I), Cadmium(II), and Mercury(II)

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A water-soluble porphyrin, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($H_2obtpps^{4-}$; H_2P^{4-}) was synthesized and the equilibrium constants have been determined for the reaction of $H_2obtpps^{4-}$ with lithium(I), cadmium(II), and mercury(II) at 25 °C in $I = 0.1$ mol dm^{-3} ($NaNO_3$). The protonation constants of $H_2obtpps^{4-}$ were found to be $10^{4.83\pm0.04}$ mol^{-1} dm^3, $10^{1.96\pm0.06}$ mol^{-1} dm^3, and $10^{-10.02\pm0.02}$ mol dm^{-3} for $K_1 = [H_3P^{3-}][H^+]^{-1}[H_2P^{4-}]^{-1}$, $K_2 = [H_4P^{2-}][H^+]^{-1}[H_3P^{3-}]^{-1}$, and $K_{-1} = [HP^{5-}][H^+][H_2P^{4-}]^{-1}$, respectively. The porphyrin reacted with lithium(I) in alkaline aqueous solution to form LiP^{5-}, of which formation constant was $10^{-18.81\pm0.02}$ mol dm^{-3} for $K_{LiP} = [LiP^{5-}][H^+]^2[Li^+]^{-1}[H_2P^{4-}]^{-1}$. Sodium and potassium ions did not form their complexes under the same experimental conditions. The equilibrium constants for the formation of cadmium(II) and mercury(II) porphyrins defined by $K_{MP} = [MP^{4-}][H^+]^2[M^{2+}]^{-1}[H_2P^{4-}]^{-1}$, $M = Cd^{2+}; Hg^{2+}$, were $10^{-8.60\pm0.13}$ mol dm^{-3} and $10^{0.12\pm0.06}$ mol dm^{-3} for K_{CdP} and K_{HgP}, respectively. Mercury(II) also forms homodinuclear porphyrin, Hg_2P, and the value was $10^{3.57\pm0.03}$ mol^{-1} dm^3 for $K_{Hg_2P} = [Hg_2P^{2-}][Hg^{2+}]^{-1}[HgP^{4-}]^{-1}$. The octabromo groups lower the basicity of the porphyrin, which results in the formation of lithium(I) porphyrin.

Metalloporphyrins are very stable complexes, but the incorporation rate of metal ions into the porphyrin core is 10^6—10^8 time slower than that of open-chain ligands due to rigidity of the porphyrin plane.[1—4] Planar porphyrins should deform to a greater extent to accept incoming metal ion. Thus some deformed porphyrins have been synthesized by introducing alkyl group or heavy halogen atoms on pyrrole nitrogen (i.e. N-substituted porphyrins) or on pyrrole β-position (i.e. β-substituted pyrrole porphyrin).[5—7] X-Ray analysis of N-substituted porphyrin complexes indicates that the N-substituted pyrrole ring is canted by ca. 40° from the average porphyrin plane.[5,8] The lone-pair electrons on nitrogen atom of the N-substituted porphyrin are readily available to accept incoming metal ion. Similarly, β-substituted pyrrole porphyrins exhibit S_4 distortion of porphyrin ring to a saddle shape with pyrrole rings tilted up and down.[6,7,9] Such a distortion significantly changes a variety of chemical and physical properties of the porphyrins and alters mechanism path ways in the reaction.[10]

A lot of kinetic and equilibrium studies have been done for N-substituted porphyrins and reviewed by Lavallee,[5] but only a few preliminary results on the reactivity have been reported for a β-substituted pyrrole porphyrin in organic medium[9] and there is no investigation on equilibrium and kinetic study in aqueous solution. We synthesized a water-soluble deformed porphyrin, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($H_2obtpps^{4-}$) by bromination at pyrrole β-position of tetraphenylporphyrin (H_2tpp) and by sulfonation at p-position of phenyl group in order to know the reactivity of the deformed porphyrin in aqueous solution. The distorted porphyrins are more easily oxidized and adsorb light at lower energies than planar porphyrins.[6] In addition to the deformation of the porphyrin, the inductive effect of electron-withdrawing octabromo substituents decreases the basicity and increases the oxidation potential of the porphyrin with lowering the energy of the highest occupied molecular level (HOMO).[11—13] It is interesting to know how the deformed structure and the lowered basicity of the porphyrin affect the formation of the metalloporphyrins.

We here report the results of equilibrium investigations of the protonation of $H_2obtpps^{4-}$ and the formation of the metalloporphyrins with lithium(I), cadmium(II), and mercury(II).

Experimental

Synthesis of the Porphyrin. 2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($H_2obtpps^{4-}$, Fig. 1). Tetraphenylporphyrin (H_2tpp) was brominated to afford 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin (H_2obtpp, **1**) by improving the reported method,[6] and followed by sulfonation of p-position of phenyl ring of H_2obtpp to obtain $H_2obtpps^{4-}$, **2**. Tetraphenylporpyrin (1g, 1.62 mmol) was treated with N-bromosuccinimide (NBS, 3 g, 16.8 mmol) in dibromomethane which was sufficiently dried by molecular sieve (4 A) before use. The reaction was carried out at 100 °C for 5 d under protecting the reaction flask from light by covering it with aluminum foil. The reaction product was checked by absorption spectra, i.e., the Soret band shifted to 469 nm by octabromination. The crude product gave three bands on an activated alumina chromatography (300 mesh, Wako, Japan) using chloroform as an eluent and the first band was collected. The purity of the product, compound **1**, was characterized by ^1H NMR and UV-vis. Yield was 53%. Absorption

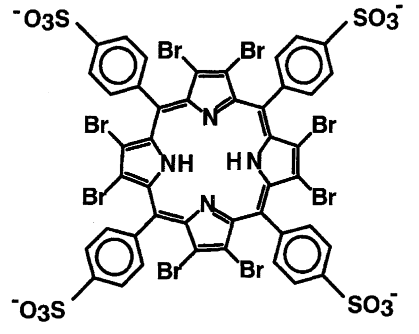

Fig. 1. 2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($H_2obtpps^{4-}$; H_2P^{4-}).

maxima and chemical shifts of ^1H NMR of the compound **1** were observed at 370, 469, 569, 626, and 743 nm in chloroform, and at 7.79 ppm (m, 12H, for *m*- and *p*-H of phenyl) and 8.19 ppm (d, 8H, *o*-H of phenyl) in $CDCl_3$ vs. TMS, respectively. The compound **1** was sulfonated in a concentrated sulfuric acid at 90 °C for 2 d. The product was precipitated by careful addition of small amount of water and separated by centrifugation. The precipitate was washed with acetone three times to completely remove remaining sulfuric acid and water, and followed by recrystallization from methanol–acetone. The product was further purified by a Sephadex column LH-20 which was soaked in a water–methanol (7 : 3) mixed solvent. Absorption maxima ($\log \varepsilon/\text{mol}^{-1}\,\text{dm}^3\,\text{cm}^{-1}$) and ^1H NMR data (δ/ppm) of the final product, $H_6obtpps$, were as follows: 376 (4.54), 478 (5.30), 657 (4.25), and 760 nm (4.07) in aqueous solution at pH 7.0; 8.62 (d, 8H, *o*-H of phenyl) and 8.09 (d, 8H, *m*-H of phenyl) in d_6-dimethylsulfoxide.

Reagents. Sodium nitrate used for adjusting ionic strength was purified by solvent extraction using phenyldiazenecarbothionic acid 2-phenylhydrizide (dithizone) in carbon tetrachloride to remove metal ions (Zn(II), Fe(II), Pb(II), and other heavy metal ions) and recrystallized from hot water. Otherwise these metal ions form their metalloporphyrins in the presence of mercury(II) and cadmium(II). Other metal nitrates were of analytical-reagent grade and were used without further purification. The concentrations of cadmium(II) and mercury(II) in stock solutions were determined by titration with ethylenediaminetetraacetic acid (H_4edta) and the concentration of lithium(I) was determined by a flame spectrophotometry. The buffer solutions were prepared by addition of nitric acid or sodium hydroxide to solutions of sodium acetate for pH 4—6, MES [2-morpholinoethanesulfonic acid] for pH 6—7, HEPES [2-(4-(2-hydroxylethyl)-1-piperazinyl)ethanesulfonic acid] for pH 7—8.5 and sodium borate for pH 8.5—10 (Wako Pure Chemical Industry, Osaka, Japan). All solutions were prepared in water treated by a Mill-Q SP TOC (Nippon Millipore Ltd., Japan).

Apparatus. Absorption spectra were recorded on a Shimadzu UV-2100 and a JASCO Ubest spectrophotometers. The pH values were determined with a radiometer Ion 85 analyzer with a combined electrode (GK2401C). A 1.000×10^{-2} mol dm^{-3} nitric acid solution containing 0.09 mol dm^{-3} sodium nitrate was employed as the standard hydrogen ion concentration ($-\log[H^+]=2.000$). From the pH meter reading in various hydrogen ion concentrations, the pH meter and electrode system was calibrated in terms of $-\log[H^+]$ at an ionic strength of 0.1 mol dm^{-3} (HNO_3–$NaNO_3$). All experiments were carried out at 25 °C.

Results and Discussion

Protonation Constant of $H_2obtpps^{4-}$. Absorption spectra of $H_2obtpps^{4-}$ in aqueous solution were measured in various pH values at ionic strength of 0.1 mol dm^{-3} ($NaNO_3$). The absorption maxima were observed in three pH regions: 490 and 740 nm at pH lower than 2, 475 and 660 at pH 6—8.2 and 505 and 745 nm at pH higher than 11. Absorbance at 720 nm is plotted against $-\log[H^+]$ in Fig. 2. The change in absorbance suggests three steps of proton-equilibria and their equilibrium constants as given in Eqs. 1, 2, and 3:

$$H^+ + H_2P^{4-} \rightleftarrows H_3P^{3-};\quad K_1 = \frac{[H_3P^{3-}]}{[H^+][H_2P^{4-}]} \tag{1}$$

$$H^+ + H_3P^{3-} \rightleftarrows H_4P^{2-};\quad K_2 = \frac{[H_4P^{2-}]}{[H^+][H_3P^{3-}]} \tag{2}$$

$$H_2P^{4-} \rightleftarrows HP^{5-} + H^+;\quad K_{-1} = \frac{[HP^{5-}][H^+]}{[H_2P^{4-}]} \tag{3}$$

where H_2P^{4-} denotes free-base form of the porphyrin which is main chemical species in neutral pH. The observed apparent molar absorptivity ($\bar{\varepsilon}$=absorbance/C_{H2P}) is correlated to the protonation constants and hydrogen ion concentration. The protonation constants were determined by using a nonlinear least-squares minimization program in two pH ranges: one region is 1—8 and other is pH 8—13, since the change in absorbance is constant at around pH 7.5 (see Fig. 2). The protonation and deprotonation constants were found to be 4.83±0.04, 1.96±0.06, and −10.02±0.02 for $\log(K_1/\text{mol}^{-1}\,\text{dm}^3)$, $\log(K_2/\text{mol}^{-1}\,\text{dm}^3)$, and $\log(K_{-1}/\text{mol}\,\text{dm}^{-3})$, respectively, at 25 °C and I=0.1 mol dm^{-3} ($NaNO_3$).

The K_1 and K_2 values are different by an about 3 orders of magnitude, although the protonation constants for non-de-

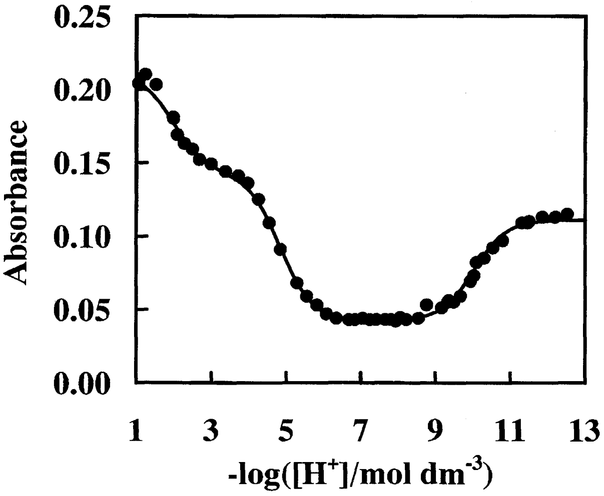

Fig. 2. Change in absorbance of $H_2obtpps^{4-}$ at 720 nm in various $-\log[H^+]$. The solid line was calculated by using K_1, K_2, and K_{-1} values listed in Table 1.

formed porphyrin like H_2tpps^{4-} are very similar each other ($\log(K_1/\mathrm{mol}^{-1}\,\mathrm{dm}^3)$ and $\log(K_2/\mathrm{mol}^{-1}\,\mathrm{dm}^3)$ are 4.99 and 4.76 for H_2tpps^{4-}).[14] Computer calculation (MM+ on the software HyperChem™ program) of $H_2obtpps^{4-}$ indicated the deviation of the pyrrole ring by 23.6° from the mean porphyrin plane. Generally, deformation of porphyrin separates the two protonation constants: The basicity for the first protonation increases, but that for the second protonation decreases due to a decrement in π-conjugation of porphyrin core in deformed structure.[15,16] Another effect of bromination is to lower the basicity of the porphyrin by electron-withdrawing of octabromo groups. Interestingly, the deprotonation of the free-base form, $H_2obtpps^{4-}$, was observed at pH higher than 10. Most of non-deformed free base porphyrins hardly dissociate proton even in a strong alkaline medium, e.g., the dissociation of proton in H_2tpps^{4-} occurs at pH more than 14.

Formation of Lithium(I) Porphyrin. Lithium hydroxide reacted with $H_2obtpps^{4-}$ to sift the absorption spectrum towards shorter wavelength. But sodium hydroxide and potassium hydroxide did not alter the absorption spectra. Typical absorption spectra are given in Fig. 3a, for the reaction $H_2obtpps^{4-}$ with lithium(I) ion at its various concentrations in pH 11.7. The absorption maxima ($\log \varepsilon/\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1}$) of the lithium(I) porphyrin complex are 490.5 nm (5.31) and 734 nm (4.36). Non-brominated

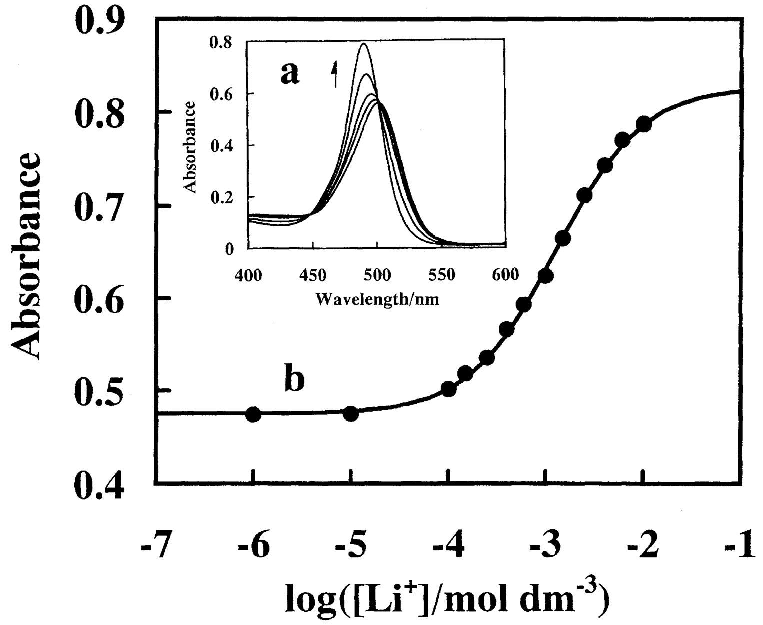

Fig. 3. Typical spectral change of $H_2obtpps^{4-}$ in the presence of various concentrations of lithium(I) nitrate at pH 11.7 (a). An arrow indicates the increase of absorbance with the concentration of lithium(I) ion. The absorbance at 490.5 nm was plotted against the concentration of lithium(I) ion (b). The solid line was calculated by using K_{LiP} given in Table 1.

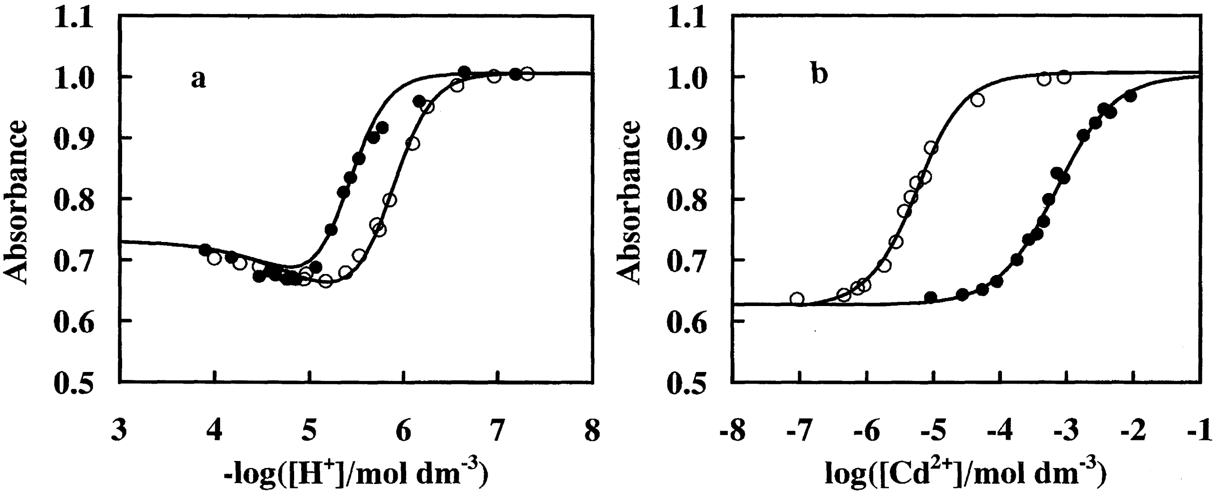

Fig. 4. Change in absorbance at 488 nm and at $10^3[\mathrm{Cd(II)}]/\mathrm{mol\,dm}^{-3}=0.979$ (○) and 9.79 (●) in various $-\log[H^+]$ (a), and at pH 5.96 (●) and 6.99 (○) in the various concentrations of cadmium(II) (b). The solid lines were calculated by using K_{CdP} listed in Table 1.

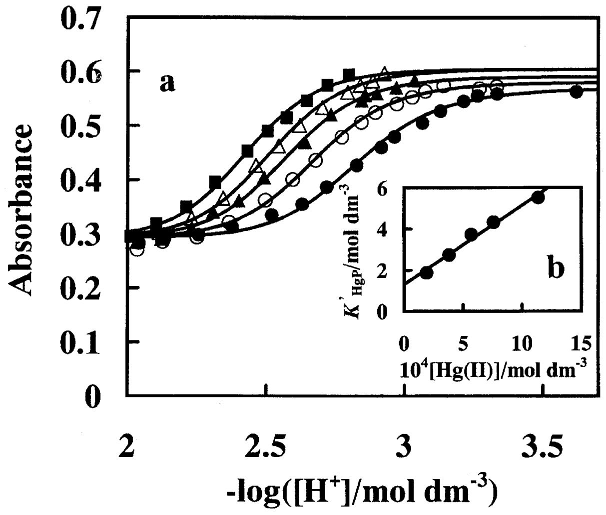

Fig. 5. Change in absorbance at 510 nm with pH at 10^4[Hg(II)]/mol dm^{-3}=1.90 (●), 3.79 (○), 5.69 (▲), 7.58 (△), and 11.4 (■) (a), and the plot of K'_{HgP} vs. [Hg^{2+}] (b). The solid lines in (a) and (b) were calculated by using K_{HgP} and $K_{\mathrm{Hg_2P}}$ listed in Table 1.

porphyrin, i.e., H_2tpps^{4-}, did not give any spectral change even in 0.1 mol dm^{-3} LiOH. This is a unique behavior of $H_2obtpps^{4-}$ and the equilibrium constant of the lithium(I) porphyrin complex was determined as follows. Absorption spectra were measured at different concentrations of lithium ion (10^{-6}—10^{-2} mol dm^{-3}) and sodium hydroxide (pH 11.7—12.3). The change in absorbance is depicted in Fig. 3b, as a function of lithium(I) concentration. The dependence of concentrations of lithium(I) and hydroxide on the change in absorbance is explained by Eq. 4:

$$\mathrm{Li^+ + H_2P^{4-} \rightleftarrows LiP^{5-} + 2H^+};$$
$$K_{\mathrm{LiP}} = \frac{[\mathrm{LiP^{5-}}][\mathrm{H^+}]^2}{[\mathrm{Li^+}][\mathrm{H_2P^{4-}}]} \tag{4}$$

The equilibrium constant was found to be $\log(K_{\mathrm{LiP}}/\mathrm{mol\,dm^{-3}}) = -18.82\pm0.02$ at $I=0.1$ mol dm^{-3} ($NaNO_3$). Since it has been believed that porphyrins form complexes with transition and heavy metal ions and do not form with alkali metal ions, the formation of stable lithium(I) porphyrin is first example.

Formation of Cadmium(II) Porphyrin. Cadmium(II) reacted easily with $H_2obtpps^{4-}$ to form the cadmium(II) porphyrin which has absorption maximum at 488 nm. Absorption spectra were measured to determine the formation constant of the cadmium(II) porphyrin at different concentrations of hydrogen ion (pH 2.5—6.0) and cadmium(II) (10^{-6}—10^{-2} mol dm^{-3}), and typical change in absorbance is shown in Fig. 4(a) and (b), where the cadmium(II) concentration of lower than 10^{-5} mol dm^{-3} was corrected to actual free concentration by considering the extent of formation of cadmium(II) porphyrin. The equilibrium for the formation of $Cd(obtpps)^{4-}$ is given by following equation with definition of the formation constant:

$$\mathrm{Cd^{2+} + H_2P^{4-} \rightleftarrows CdP^{4-} + 2H^+};$$

Table 1. Equilibrium Constants for the Protonation and Metalation of $H_2obtpps^{4-}$ and H_2tpps^{4-} with Lithium(I), Cadmium(II), and Mercury(II)[a)]

Equilibrium constants[b)]	$H_2obtpps^{4-}$	H_2tpps^{4-} [c)]
$\log(K_1/\mathrm{mol^{-1}\,dm^3})$	4.83±0.04	4.99±0.01
$\log(K_2/\mathrm{mol^{-1}\,dm^3})$	1.96±0.06	4.76±0.02
$\log(K_{-1}/\mathrm{mol\,dm^{-3}})$	−10.02±0.02	—
$\log(K_{\mathrm{LiP}}/\mathrm{mol\,dm^{-3}})$	−18.81±0.02	—
$\log(K_{\mathrm{CdP}}/\mathrm{mol\,dm^{-3}})$	−8.60±0.13	−9.94±0.04
$\log(K_{\mathrm{HgP}}/\mathrm{mol\,dm^{-3}})$	0.12±0.06	—
$\log(K_{\mathrm{Hg_2P}}/\mathrm{mol^{-1}\,dm^3})$	3.57±0.03	$\log\beta$[d)]=5.51±0.08

a) At 25 °C and $I=0.1$ ($NaNO_3$). b) The equilibrium constants are defined as $K_1=[\mathrm{H_3P^{3-}}][\mathrm{H^+}]^{-1}[\mathrm{H_2P^{4-}}]^{-1}$, $K_2=[\mathrm{H_4P^{2-}}][\mathrm{H^+}]^{-1}[\mathrm{H_3P^{3-}}]^{-1}$, $K_{-1}=[\mathrm{HP^{5-}}][\mathrm{H^+}][\mathrm{H_2P^{4-}}]^{-1}$, $K_{\mathrm{MP}}=[\mathrm{MP}^{n-6}][\mathrm{H^+}]^2[\mathrm{M}^n]^{-1}[\mathrm{H_2P^{4-}}]^{-1}$ for $\mathrm{M}^{n+}=\mathrm{Li^+}$, Cd^{2+}, and Hg^{2+}, $K_{\mathrm{Hg_2P}}=[\mathrm{Hg_2P^{2-}}][\mathrm{Hg^{2+}}]^{-1}[\mathrm{HgP^{4-}}]^{-1}$. c) 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin and its equilibrium data were cited from Ref. 14. d) $\beta=K_{\mathrm{HgP}}K_{\mathrm{Hg_2P}}$ and the value was cited from Ref. 14.

$$K_{\mathrm{CdP}} = \frac{[\mathrm{CdP^{4-}}][\mathrm{H^+}]^2}{[\mathrm{Cd^{2+}}][\mathrm{H_2P^{4-}}]} \tag{5}$$

Since the main chemical species of the porphyrin are H_3P^{3-} and H_2P^{4-} at pH 3.6, the apparent molar absorptivity, $\bar{\varepsilon}$, at 488 nm is given as follows:

$$\bar{\varepsilon} = \frac{\varepsilon_1[\mathrm{H_2P^{4-}}] + \varepsilon_2[\mathrm{H_3P^{3-}}] + \varepsilon_3[\mathrm{CdP^{4-}}]}{[\mathrm{H_2P^{4-}}] + [\mathrm{H_3P^{3-}}] + [\mathrm{CdP^{4-}}]}$$
$$= \frac{\varepsilon_1 + \varepsilon_2 K_1[\mathrm{H^+}] + \varepsilon_3 K_{\mathrm{CdP}}[\mathrm{Cd^{2+}}][\mathrm{H^+}]^{-2}}{1 + K_1[\mathrm{H^+}] + K_{\mathrm{CdP}}[\mathrm{Cd^{2+}}][\mathrm{H^+}]^{-2}} \tag{6}$$

where ε_1, ε_2, and ε_3 denote the molar absorptivities of H_2P^{4-}, H_3P^{3-}, and CdP^{4-} at 488 nm, respectively. The value of K_{CdP} was determined by the nonlinear least-squares minimization program and was found to be $10^{-8.60\pm0.13}$ mol dm^{-3} at 25 °C. We considered the formation of a homodinuclear complex and protonated species like Cd_2P and CdHP, but their formation constants were very small as negligible.

Formation of Mercury(II) Porphyrin. Absorption spectra were measured at pH 2—3 for different concentrations (2×10^{-4}—1×10^{-2} mol dm^{-3}). Since the absorption spectra of the uncoordinated porphyrin changed with pH and overlapped with the absorption spectrum of the formed mercury(II) porphyrin, we plotted the absorbance at an isosbestic point of the porphyrin, 510 nm, against pH at five different concentrations of mercury(II) (Fig. 5a). Apparent molar absorptivity, $\bar{\varepsilon}$, is correlated to the formation constant of the mercury(II) porphyrin and the concentrations of mercury(II) and hydrogen ion by a similar equation as given by Eq. 6. The formation constant was determined at different pHs in a given concentration of mercury(II). The observed formation constant depended on the concentration of mercury(II) and increased with the concentration of mercury(II). The formation of the mercury(II) porphyrin complex can be expressed by the following equation:

$$\mathrm{Hg^{2+} + H_2P^{4-} \rightleftarrows (HgP^{4-})' + 2H^+};$$
$$K'_{\mathrm{HgP}} = \frac{[(\mathrm{HgP^{4-}})'][\mathrm{H^+}]^2}{[\mathrm{Hg^{2+}}][\mathrm{H_2P^{4-}}]} = K_{\mathrm{HgP}}(1 + K_{\mathrm{Hg_2P}}[\mathrm{Hg^{2+}}]) \tag{7}$$

where K'_{HgP} is conditional formation constant of HgP^{4-} and $[(HgP^{4-})']=[HgP^{4-}]+[Hg_2P^{2-}]$. The determined K'_{HgP} value was linearly correlated to the concentration of mercury(II) with an intercept (Fig. 5b). The incept and the slope gave the values of $K_{HgP}=1.31\pm0.19$ mol dm^{-3} and $K_{Hg_2P}=(3.83\pm0.27)\times10^3$ mol^{-1} dm^3, where K_{HgP} and K_{Hg_2P} are defined as $[HgP^{4-}][H^+]^2[Hg^{2+}]^{-1}[H_2P^{4-}]^{-1}$ and $[Hg_2P^{2-}][Hg^{2+}]^{-1}[HgP^{4-}]^{-1}$, respectively. The results are summarized in Table 1 with the equilibrium constants of Cd(II)- and Hg(II)-porphyrins of H_2tpps^{4-}.

The octabromo groups decrease the basicity of the porphyrin. The lowered basicity of $H_2obtpps^{4-}$ leads to the formation of lithium(I) porphyrin. It is interesting to know how $[LiP]^{5-}$ is stable compared to lithium(I) crown-ether complexes. Although the equilibrium constant for the reaction $Li^+ + P^{6-} \rightleftarrows LiP^{5-}$ was not able to be determined, the conditional formation constant defined by $K'=[LiP^{5-}][Li^+]^{-1}[(P^{6-})']^{-1}$ was calculated as $10^{4.21}$ in 0.1 mol dm^{-3} NaOH from the K_{LiP} and K_{-1} values, where $[(P^{6-})']$ is the total concentration of the porphyrin unbound to lithium(I). The equilibrium constant is much larger than the formation constant of Li with crown-ethers.[17] Since the ionic radius of lithium(I) (73 pm) is comparable to that of zinc(II) (74 pm),[18] the lithium ion may be incorporated well in porphyrin core like tetraphenylporphyrinatozinc(II) (Zn(tpp)).[19] However, sodium and potassium ions did not form stable complexes with H_2P^{4-} under the same experimental conditions because of the large ionic radii of sodium (113 pm) and potassium (151 pm).

It is expected that the deformed $H_2obtpps^{4-}$ may easily accommodate large metal ions. The formation constant of cadmium(II) with $H_2obtpps^{4-}$ is about 20 times as large as that of H_2tpps^{4-},[14] but the formation constant of mercury(II) with $H_2obtpps^{4-}$, $K_{HgP}K_{Hg_2P}$, is smaller 66 times compared to that of H_2tpps^{4-}.[20] Cadmium(II) is stabilized for the reaction with $H_2obtpps^{4-}$, while mercury(II) is not. The binding of two mercury(II) atoms to $H_2obtpps^{4-}$ requires so large deformation of the porphyrin ring as observed in $Hg_2(tpps)^{2-}$ that the octabromo groups in $[Hg_2(obtpps)]^{2-}$ sterically hinder it.[21]

Finally, it should be pointed out that the reactivity of $H_2obtpps^{4-}$ is much altered by electron-withdrawing effect rather than the deformation effect of the octabromo groups. The most significant feature of this study is the demonstration of the formation of lithium(I) porphyrin complex in aqueous solution. The lithium porphyrin can be applied to new and useful separation and spectrophotometric methods for the determination of lithium ion. These studies are in progress in our laboratory and the results will be reported elsewhere.

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