May, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **60**, *1667—1672 (1987)*

# Electrochemical and Spectroelectrochemical Speciation of [5-phenyl-10,15,20-tris(4-sulfonatophenyl)porphinato]iron in Aqueous Solution

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The equilibria among the species of [5-phenyl-10,15,20-tris(4-sulfonatophenyl)porphinato]iron (Fe-TPPS$_3$) ion in aqueous solution and the redox reactions of the central metal were investigated by electrochemical and spectro-electrochemical methods. In the range of pH 3—12.5, the species formed by the reduction of Fe(III)–TPPS$_3$ in solution was identified as the monomeric Fe(II)–TPPS$_3$, while Fe(III)–TPPS$_3$ exists in both monomeric and dimeric species in equilibrium. The monomeric Fe(III)–TPPS$_3$ was demetallated at pH below 3 in the course of reduction of the Fe(III)–TPPS$_3$ solution. The $\mu$-oxo-dimer of Fe(III)–TPPS$_3$ in highly basic solution was reversibly reduced to Fe(II)–TPPS$_3$ and subsequently the monomeric Fe(I)–TPPS$_3$. The formation of the stacking-type dimer of Fe(III)–TPPS$_3$, significantly depending on the concentration of Fe(III)–TPPS$_3$, was presumed to have a pH below 6.

Metalloporphyrin complexes are well-known to play important roles in various biological systems.[1,2] These complexes are essential for the carriers and storage of oxygen and as enzymatic cofactors. Recently, noteworthy reports on an electrocatalytic reduction of molecular oxygen by metalloporphyrins, together with metallophthalocyanines, have been reported.[3,4]

Some of these functions of metalloporphyrins must depend on the addition or replacement of axial ligands of the central metals.[5] In order to elucidate the specificity of such macrocyclic compounds, it is important to clarify their solute species and redox properties. Therefore, we have been interested in studying the properties of some water-soluble iron-porphyrin complexes.[6–8]

The characteristics of a monomer and a $\mu$-oxo-dimer of [tetrakis(*p*-sulfonatophenyl)porphinato]iron(III) (abbreviated as Fe(III)–TPPS$_4$) in aqueous solution was investigated in detail.[9,10] We found, by spectrophotometric and magnetochemical methods, that the solute species in a $1.00\times10^{-5}$ mol dm$^{-3}$ [5-phenyl-10,15,20-tris(4-sulfonatophenyl)porphinato]iron(III) (abbreviated as Fe(III)–TPPS$_3$) solution were similar to that in a Fe(III)–TPPS$_4$ solution.[11] However, the solute species of the reduced form has not been established. The purpose of the present study is to determine the redox characteristics of Fe(III)–TPPS$_3$ in aqueous solution on the glassy carbon electrode and to identify the solute species of the reduced complex using electrochemical and spectro-electrochemical methods.

## Experimental

**Materials and Sample Solutions.** Fe(III)–TPPS$_3$ was prepared by metal insertion of tetraphenylporphinetrisulfonic acid (Dojindo Laboratories, abbreviated as TPPS$_3$) with $FeSO_4\cdot7H_2O$ according to the method of Fleischer et al.[9] All other chemicals of guaranteed reagent grade (Wako Pure Chemical Industries) were used without further purification. The pH of the sample solution was adjusted with a sulfuric acid and/or sodium hydroxide solution. The ionic strength was adjusted to 0.1 mol dm$^{-3}$ with a sodium sulfate solution except for solutions of pH below 1 or above 13. Where buffered solutions were required, the following buffers were used: acetate buffer at pH 4—6, phosphate-borate buffer at pH 6—9, and carbonate buffer at pH 9—11. Measurements of the pH were made on a Toa HM-5B pH meter.

**Spectrophotometric, Electrochemical, and Spectroelectrochemical Measurements.** A Hitachi 228A spectrophotometer was used for the spectrophotometric investigation.

The cyclic voltammograms of Fe(III)–TPPS$_3$ in solutions of various pH were obtained by means of Dual Potentiogalvanostat DPGS-1, Potential Sweeper NPS-2 (Nikko Keisoku) and X-Y recorder WX4403 (Watanabe, Inc.) equipped with a conventional three-electrode system. A glassy carbon rod (GC-30, Tokai Carbon) plugged into a Teflon tube was used as the working electrode. The carbon surface exposed to a solution was a circle 0.196 cm$^2$ in area. The exposed disc surface of a GC-30 electrode was polished with an abrasive paper followed with suspensions of alumina powders (Marumoto, Inc.) of decreasing size, down to 0.06 µm in diameter, until a mirror-like finish was obtained. To completely remove the alumina particles adhering on the polished electrode surfaces,[12,13] the electrodes were thoroughly washed by ultrasonication for 20 s in 0.05 mol dm$^{-3}$ sulfuric acid.[14]

The spectroelectrochemical experiments were achieved with an optically transparent thin-layer electrode (OTTLE)[6,15] constructed with a gold minigrid (500 wires per inch, Backbee Mears) which was sandwiched between two micro-slide glasses. The distance between the two plates was controlled with Teflon spacers (Delectrix DF-1200). While the Soret and Q band spectra of Fe(III)–TPPS$_3$ and its reduced-form complexes were measured with a Hitachi 228A spectrophotometer, the potential at the gold minigrid as the working electrode was controlled by a Potentiostat NPOT-2501 (Nikko Keisoku).

Prior to both the electrochemical and spectro-electrochemical measurements, the sample solution was deoxygenated by bubbling nitrogen gas through the solution for about 20 min, and the measurements were carried out under an atmosphere of nitrogen. A saturated calomel electrode (SCE) was employed as a reference electrode. All the measurements were performed at 25 °C.

## Results and Discussion

**Electrochemistry.** Figures 1 and 2 illustrate typical cyclic voltammograms of $5.00\times10^{-4}$ mol dm$^{-3}$ Fe(III)-TPPS$_3$ aqueous solutions at different pH values. The dashed line in Fig. 1 shows the 1st cyclic voltammetric curve observed in Fe(III)-TPPS$_3$ solution of pH 2.04. The catalytic reduction of oxygen, which was not removed from the solution, via the reduction of Fe(III)-TPPS$_3$ was observed at ca. −0.1 V. In addition to this reduction peak, two redox peak couples were clearly observed at the more cathodic potential. The solid line in Fig. 1 shows the stationary cyclic voltammogram (9th cycle) and indicates that the reduction wave at ca. −0.1 V virtually disappeared and the two redox peak couples remained. This disappearance of the 1st current peak must be attributed to a demetallation of Fe(III)-TPPS$_3$ in addition to a consumption of oxygen in an electrical double layer. The 1st current peak at ca. −0.1 V corresponds to the peaks at ca. −0.1 V in Fig. 3 and at ca. −0.07 V in Fig. 4. The redox couple at ca. −0.3 V was observed only in solutions of pH<6 (cf. Fig. 4); the peak current of this redox couple decreased with a decrease in the concentration of the porphyrin complex and the peak couple was then no longer detectable in the solution of $1.00\times10^{-5}$ mol dm$^{-3}$ Fe(III)-TPPS$_3$.

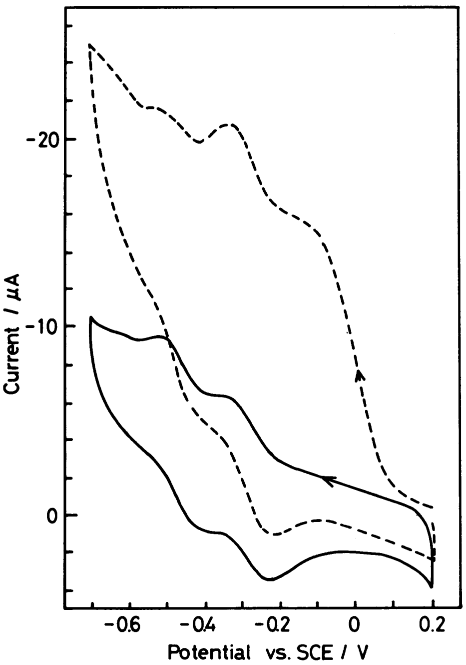


Fig. 1. Cyclic voltammograms of $5.00\times10^{-4}$ mol dm$^{-3}$ Fe(III)-TPPS$_3$ aqueous solution (pH 2.04). ------: 1st cycle, ——: 9th cycle. Scan rate: 0.05 V s$^{-1}$.

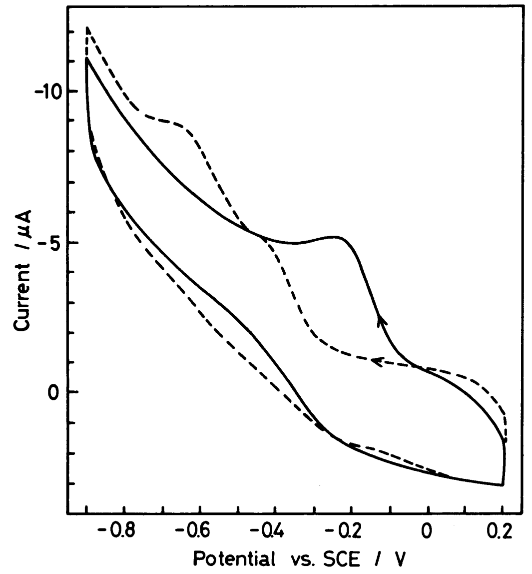


Fig. 2. Cyclic voltammograms of $5.00\times10^{-4}$ mol dm$^{-3}$ Fe(III)-TPPS$_3$ aqueous solutions. ——: pH 7.16, ------: pH 12.81. Scan rate: 0.05 V s$^{-1}$.

Figure 2 shows the stationary cyclic voltammograms observed in the Fe(III)-TPPS$_3$ solution at pH 7.16 and 12.81. At these pH, the 1st peak attributable to the reduction of Fe(III)-TPPS$_3$ remained intact even after multicycles. The value of

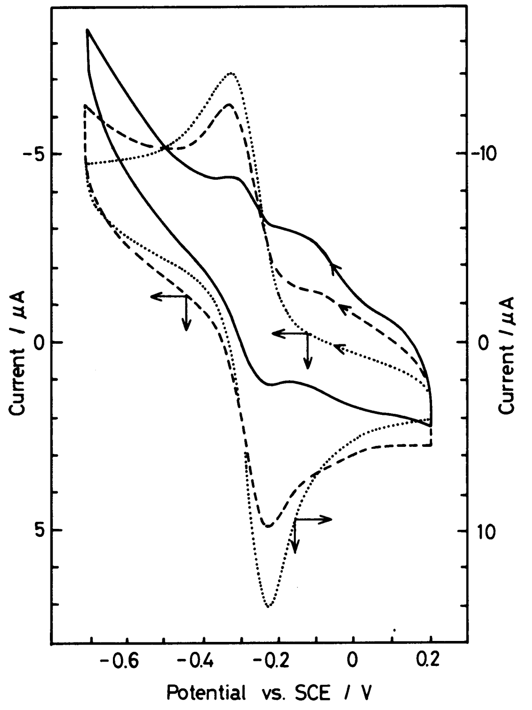


Fig. 3. Cyclic voltammograms of Fe(III)-TPPS$_3$ aqueous solutions (pH 4.21). ——: $1.00\times10^{-4}$ mol dm$^{-3}$, ------: $3.00\times10^{-4}$ mol dm$^{-3}$, ······: $9.00\times10^{-4}$ mol dm$^{-3}$. Scan rate: 0.05 V s$^{-1}$.

the reduction current of Fe(III)-TPPS$_3$ at pH 7.16 is almost the same as that of each of two reduction peaks at pH 12.81, respectively. That is to say, the total quantity of electron transfered to Fe(III)-TPPS$_3$ in the two-step reduction at pH 12.81 is twice that at pH 7.16 in the potential range from −0.2 to −0.9 V.

Figure 3 shows the stationary cyclic voltammograms obtained in the Fe(III)-TPPS$_3$ solutions of three different concentrations at pH 4.21, where a well defined redox peak couple appeared around −0.3 V. The reduction wave at ca. −0.1 V, which was observed clearly in $1.00\times10^{-4}$ mol dm$^{-3}$ Fe(III)-TPPS$_3$ solution, diminished with increase in the concentration of Fe(III)-TPPS$_3$ and was scarcely observed in the solution of $9.00\times10^{-4}$ mol dm$^{-3}$. On the other hand, the reversible redox peak couple around −0.3 V became sharp and well-behaved with increasing concentration of Fe(III)-TPPS$_3$. This phenomenon suggests that a certain species, transformed from Fe(III)-TPPS$_3$ monomer, accumulated in the electrical double layer. However, no significant difference in near-UV and visible absorption spectra obtained in $1.00\times10^{-5}$ and $1.00\times10^{-3}$ mol dm$^{-3}$ Fe(III)-TPPS$_3$ solutions was observed. Furthermore, the excellent linearity between the absorbance at the Soret band peak and the concentration of the solutions at pH 3.9 was obtained over a wide range of concentration.[11]

Figure 4 shows the plot of the reduction peak potential $(E_p)_R$ of the 1st cyclic voltammograms obtained in $1.00\times10^{-3}$ mol dm$^{-3}$ Fe(III)-TPPS$_3$ against pH of the solutions. The potential of the 1st reduction peak at pH<6 was measured by observing the catalytic peak of dissolved oxygen. The peak potential of the 1st and 2nd reduction peaks in the low pH range were −0.07 V (pH<4) and −0.32 V (pH<5), respectively, and no potential shift was observed except for the point at pH 0.6. The 2nd reduction peak was observed at pH<6 and was shifted by ca. −60 mV/pH in the pH range of 5—6. The peak potential ca. −0.5 V of the 3rd reduction peak at low pH is approximately in agreement with that of metal-free TPPS$_3$. The $(E_p)_R$ of the 1st reduction peak shifted by ca. −60 mV/pH in the pH range 4—11. At pH>11, a pH-independent reduction peak was observed at −0.47 V followed by a pH-dependent reduction peak by ca. −60 mV/pH.

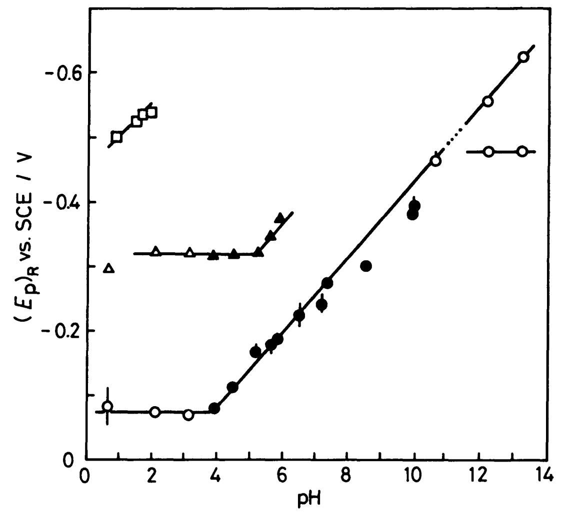


Fig. 4. Plot of $(E_p)_R$ vs. pH for $1.00\times10^{-3}$ mol dm$^{-3}$ Fe(III)-TPPS$_3$ solution. ○, △, □: in nonbuffered solution. ●, ▲: in buffered solution. $(E_p)_R$: see text.

**Spectroelectrochemistry.** Figures 5—7 show the typical absorption spectra of the reduced sample solutions, which are prepared by reducing $1.00\times10^{-4}$ mol dm$^{-3}$ Fe(III)-TPPS$_3$ solutions potentiostatically

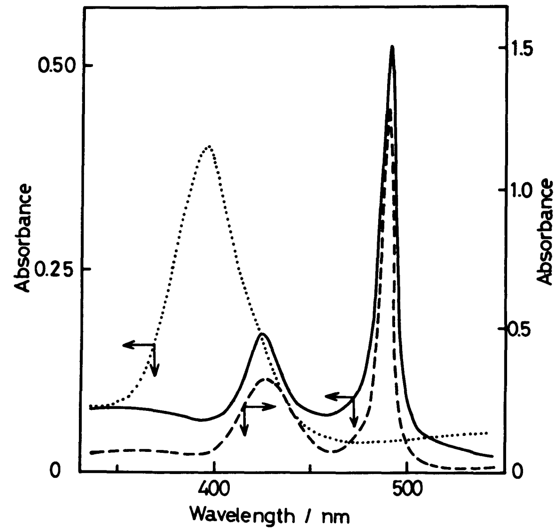


Fig. 5. Soret band spectra of Fe(III)-TPPS$_3$ and its reduced form in aqueous solutions at pH 1.54. ——: $1.00\times10^{-3}$ mol dm$^{-3}$ reduced Fe(III)-TPPS$_3$ at −0.5 V for 3.5 h in OTTLE, ······: $1.00\times10^{-5}$ mol dm$^{-3}$ Fe(III)-TPPS$_3$ in quartz cell, ------: $1.00\times10^{-4}$ mol dm$^{-3}$ TPPS$_3$ in OTTLE cell.

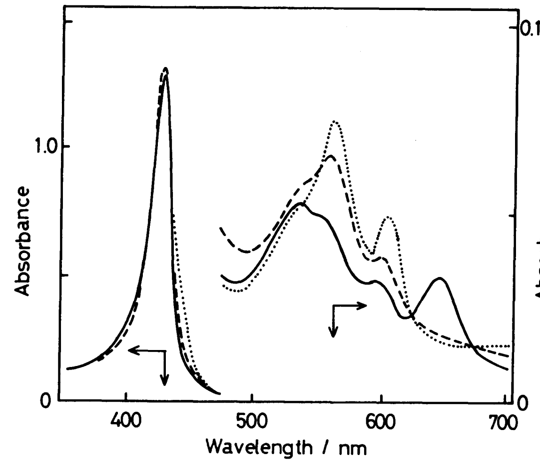


Fig. 6. Absorption spectra of $2.00\times10^{-4}$ mol dm$^{-3}$ Fe(II)-TPPS$_3$ solution. ——: pH 3.05, ------: pH 7.24, ······: pH 12.00.

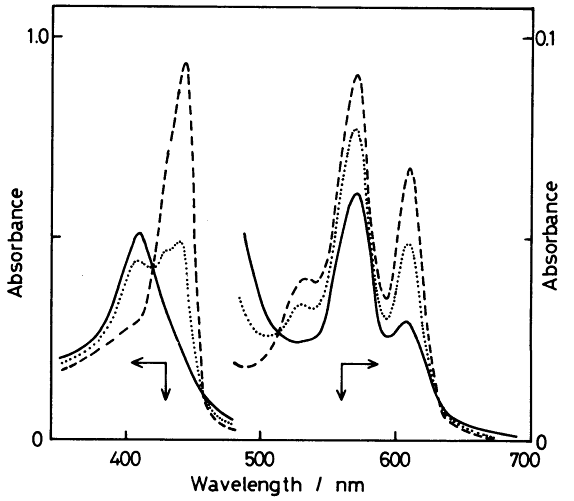


Fig. 7. Absorption spectra of $2.00\times10^{-4}$ mol dm$^{-3}$ Fe(III)-TPPS$_3$ solution during reduction at constant potential of $-0.8$ V at pH 12.72. Reduction time: ——0 min, ······10 min, ------40 min.

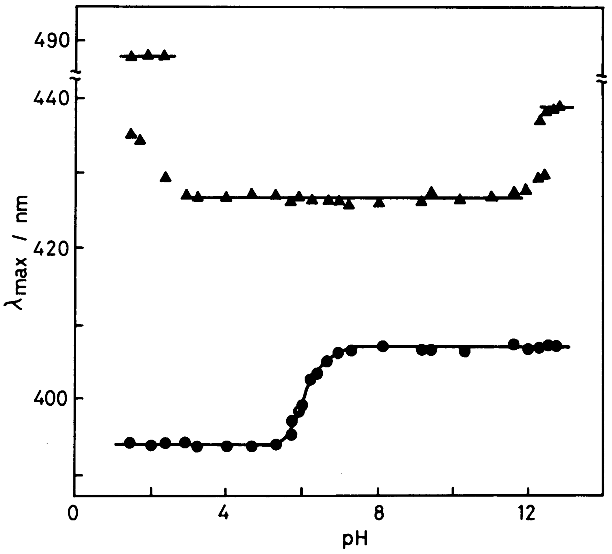


Fig. 8. Wavelength of Soret-band maxima ($\lambda_{max}$) vs. pH of $2.00\times10^{-4}$ mol dm$^{-3}$ Fe(III)-TPPS$_3$ solution before (●) and after (▲) the reduction on OTTLE.

in the OTTLE cell at various pH. At pH 1.54 (Fig. 5), the Soret band shifted from 394 to 488 nm, leaving a weak absorption band at 424 nm in the course of the reduction of Fe(III)-TPPS$_3$. The Soret band at 488 nm was also observed in the solutions containing metal-free TPPS$_3$ in contact with an Au-minigrid electrode. Therefore, the appearance of the Soret band at 488 nm suggests the occurrence of a demetallation[16] from the reduced species of Fe(III)-TPPS$_3$ in highly acidic solution of pH<2.5. This phenomena is supported also by the electrochemical results described in the preceding section.

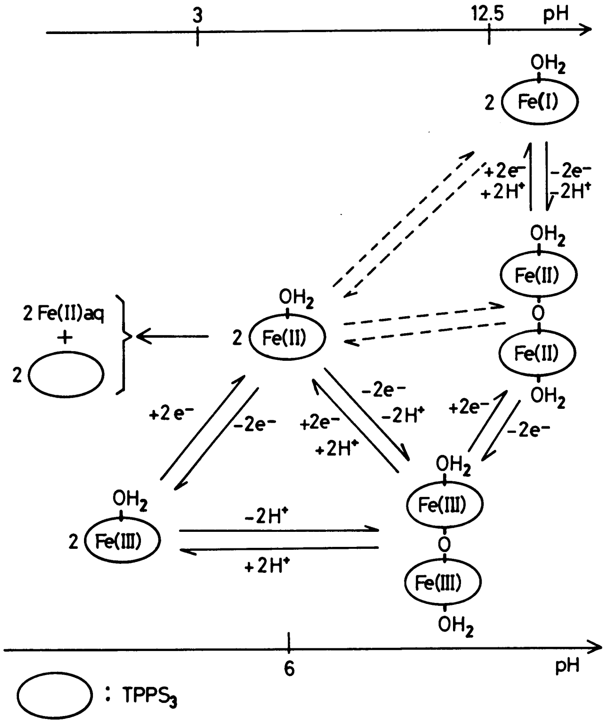
The Soret band and visible absorption spectra in the pH range of 3—12 are represented in Fig. 6. The Soret band shifted from 394 (pH<5.5) or 406 nm (pH>7) to 427 nm by the reduction of Fe(III)-TPPS$_3$ (see Fig. 8 also). The visible absorption of the reduced species changes from a four-band toward a two-band spectrum with an increase of pH. Such a change in the visible absorption spectrum suggests that the unsymmetric structure of the complex species changes with pH toward the more symmetric one in highly basic solutions.

Figure 7 shows the change of the absorption spectrum in the course of reduction at pH>12.5. The Soret band shifted from 406 to 439 nm via 427 nm transiently at pH>12.5. The change in the shape of the visible spectra suggests that a symmetric structure of Fe(III)-TPPS$_3$ with a six-coordination was transformed to an unsymmetric structure of the reduced species with five-coordination. When the reduction potential was put off, the reduced species of Fe(III)-TPPS$_3$ in the solution of pH>3 was rapidly reoxidized to give the initial Fe(III)-species without degradation of the porphyrin ring system.

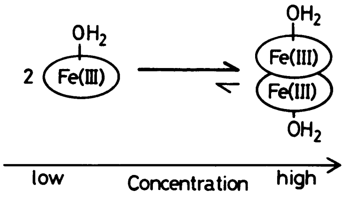
The relationship between the pH of the sample solution and the wavelength of the Soret band maximum of Fe(III)-TPPS$_3$ or its reduced species is summarized in Fig. 8. No change in the structure of the reduced species was observed at 4<pH<11, while the structure of the Fe(III)-species transformed clearly at around pH 7.

**Electrochemical Characteristic and Speciation of Fe(III)-TPPS$_3$ and Its Reduced Fe-TPPS$_3$.** The solute species of Fe(III)-TPPS$_3$ and its reduced form in the aqueous solution at the concentration of $1.00\times10^{-5}$ mol dm$^{-3}$ are assigned to those in Scheme 1 from the results of the spectrophotometric experiment[11] and the electrochemical and spectro-electrochemical experiments presented above. Scheme 1 also presents the numbers of protons and electrons transferred in each redox reaction, which were observed from the data in Fings. 2 and 4.

The results of the spectro-electrochemical experiment indicate the reduced complex in aqueous solutions to be a single ionic species over the pH range of 3—12.5. The pattern of the visible absorption spectrum in Fig. 6 together with the numbers of proton and electron added to the Fe(III)-TPPS$_3$ suggest that the species is in the low symmetric structure similar to the five-coordinated Fe(III)-TPPS$_3$(H$_2$O). In the solution of pH<3, the release of iron ion easily occur in the course of reduction of Fe(III)-TPPS$_3$ because of the enlargement of the electron cloud of the central ion. In the solution of pH>12.5, the data in Fig. 4 suggest that the $\mu$-oxo-dimer of Fe(III)-TPPS$_3$ is first reduced to that of Fe(II)-TPPS$_3$ by the two-electron transfer per dimer, and then the second reduction rapidly follows to give



Scheme 1.



Scheme 2.

Table 1. pH Values of the Inflection Point on the Spectroscopic pH Titration Curves of Fe(III)-TPPS$_3$ Aqueous Solutions

| Concentration<br>mol dm$^{-3}$ | Monitoring Wavelength<br>nm | Inflection Point<br>pH |
|---|---|---|
| $5.60 \times 10^{-6}$ | 394 | 6.7 |
| $8.20 \times 10^{-5}$ | 529 | 6.3 |
| $1.00 \times 10^{-3}$ | 394 | 5.6 |
| $1.00 \times 10^{-3}$ | 529 | 5.6 |

two Fe(I)–TPPS3 monomers by the two-proton and two-electron transfer per dimer. The iron(I) monomer is suggested to be a species of low symmetry, such as Fe(I)–TPPS3 ($H_2O$), by the shape of visible spectrum in Fig. 7 (dashed line).

In accordance with the inference from Fig. 3, it may be presumed that the Fe(III)–TPPS3($H_2O$) monomer, in the acidic and relatively concentrated solution (more than $10^{-4}$ mol dm$^{-3}$), could make a stacking-type dimer, as suggested for the metal-free TPPS4.[17] The stacking -type dimer, as is shown in Scheme 2, is made up possibly of the two five-coordinated porphyrin complexes, which have an unoccupied axial site and stack each other with the dispersion force such as van der Waals force. The formation of the stacking-type dimer is supported by the data of the pH titration in Table 1. If the stacking-type dimer is formed, the $\pi$-electron energy level of the dimer is lowered comparing to the monomer and hence the donation of electron from the axial ligand to the central $Fe^{3+}$ will be increased. The lowering the electron density of the axial ligand will facilitate the deprotonation from the axial ligand of the complex; consequently, the formation of $\mu$-oxo-dimer occur more easily from the two stacking-type dimers compared to the formation from two monomeric species. That is to say, the pH value of the inflection point of the spectrophotometric pH titration curves decreases with the increase in the amount of stacking-type dimer in the solution, as is shown in Table 1.

No difference in near-UV and visible absorption spectra between the monomer and the stacking-type dimer was observed because of the limitation of the resolution of the spectrophotometer used, since the magnitude of the dispersion force corresponded to the order of $10^2$ cm$^{-1}$.

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