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Electrochemical Investigations of High-Spin (10,20-Diaryletioporphyrinato II) Iron(III) Complexes

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The redox behaviors of high-spin (10,20-diaryletioporphyrinato II) iron(III) complexes were investigated by cyclic voltammetry in both anodic and cathodic regions in dichloromethane. Whether the redox waves are due to a porphyrin-ring-centered reaction or a metal-centered reaction was examined in terms of the spectroelectrochemical results and Hammett reaction constants.

Enormous amounts of electrochemical data concerning 5,10,15,20-tetraarylporphyrins (TAP) have been reported and the redox processes have been established systematically in various metal complexes as well as some metal spin states.[1] However, the redox processes of 2,3,7,8,12,13,17,18-substituted porphyrins (called β-pyrrole porphyrins) are still obscure due to the difficulty in preparing and modifying, compared with those of $TAPH_2$. It is necessary to elaborately compare the redox behavior of β-pyrrole porphyrins with that of TAP in order to utilize the various forms of information concerning TAP.

10,20-Diaryletioporphyrin II ($DAEPH_2$) is symmetrically shaped and is easily prepared and modified.[2] The absorption spectra and redox potentials are typical of a β-pyrrole porphyrin,[3] due to the larger substituent effect of the β-pyrrole position than that of the 5,10,15,20-position (*meso*-position).[1d] An elucidation concerning the redox behavior of metalloporphyrins, especially the iron porphyrins, is not only important biochemically, but also synthetically. The pattern of cyclic voltammogram of $DAEPFe^{III}Cl$ (Fig. 1a) is similar to those of $TAPFe^{III}Cl$[1c] and 2,3,7,8,12,13,17,18-octaethylporphyrinato iron(III) chloride ($OEPFe^{III}Cl$).[4] The anodic oxidation waves of $DAEPFe^{III}Cl$ are symmetrically shaped as well as reversible, meaning that the redox species of DAEPFeCl are stable as well as those of TAPFeCl and OEPFeCl. Preliminary investigations suggest that $DAEPH_2$ is the desired ligand for systematic electrochemical investigations of β-pyrrole porphyrins because of the good stability of the redox species, the electronic state regarded as a β-pyrrole porphyrin, and the good solubility in some organic solvents, such as dichloromethane, *N*,*N*-dimethylformamide, and benzene. In this study, the redox behavior of high-spin porphyrinato iron(III) complexes was systematically investigated in dichloromethane by using diaryletioporphyrin as an equatorial ligand.

Experimental

Measurements. Cyclic voltammetric measurements were carried out with a Hokuto Denko Corporation HA-501 potentiostat/ galvanostat and an HB-107 function generator. A conventional three-electrode system was constructed using a Beckman 39273 S601A platinum inlay electrode as the working electrode, a platinum wire as a counter electrode, and a TOA electronics HC-205C saturated calomel electrode (SCE) as a reference electrode. All current–voltage curves were measured under a static condition at 0.1—0.5 V s^{-1} in dichloromethane (2 mM sample and 0.1 M (1M=1 mol dm^{-3}) tetrabutylammonium perchlorate (TBAP)) under a nitrogen atmosphere at 20 °C. The half-wave potentials ($E_{1/2}$) were determined from the values of the peak potentials (E_{pa} and E_{pc}) recorded by continuous-wave clipping scans of the redox wave. The clipped waves were symmetrically shaped, and the peak potentials were separated by relatively small ΔE_p values within 150 mV.

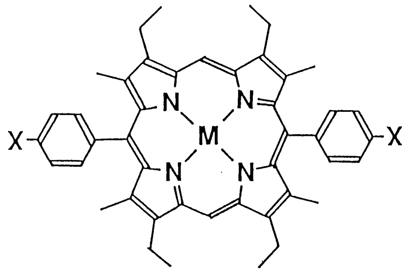
NMR measurements were carried out using a JEOL PMX-60si as well as Varian XL100 and XL300 in order to identify the structure of porphyrin **1**. The IR spectra were recorded using a JASCO FT/IR-5MP (DR-81). The ESR measurements were carried out using a JEOL JES-PE-3X. Absorption spectra were recorded by a JASCO UVIDEC-660. Thin-layer spectroelectrochemical measurements were carried out according to a reported method.[5]

Materials. Tetrabutylammonium perchlorate was purchased from Tokyo Kasei Kogyo Co., Ltd., and was recrystallized from ethyl acetate. The supporting electrolyte was dried before use in electrochemical measurements. Solvents were purified in the usual manner. The other chemicals used in this study were of reagent grade.

Preparations of $DAEPH_2$ (1) and Their Iron(III) Complexes (2, 3, and 4). 10,20-Diaryletioporphyrin II ($DAEPH_2$ **1**) was prepared stepwise according to a reported method.[2] The insertion of iron into $DAEPH_2$ was carried out by an $FeBr_2$ method[6] or by an $FeCl_2$ method[7] to give $DAEPFe^{III}Cl$ (**2**). Phenoxide coordinated $DAEPFe^{III}$ complexes (**3**) were prepared by the reaction of $DAEPFe^{III}ClO_4$ and 4-substituted phenolate (1) or by the reaction of $(DAEPFe^{III})_2O$ **4** prepared by a reported method[7] with phenol (2).

Method (1): $DAEPFeClO_4$ (0.15 g) prepared by the reaction of **2** with $AgClO_4$ in benzene was dissolved in dry benzene (50 ml). To this solution, four-fold moles of 4-substituted phenol and NaH were added. After the reaction for 1 h at room temperature an insoluble material was removed by filtration. To a benzene solution condensed to about 10 ml, petroleum ether (10 ml) was added, which was allowed to stand for 10 h in a refrigerator. The precipitated porphyrin was recrystallized from CH_2Cl_2–petroleum ether to give pure DAEPFeOAr **3**. The metal perchlorates should be carefully handled, since these compounds are potentially explosive.

Method (2): $(DAEPFe)_2O$ **4** (0.2 g) was dissolved in benzene (50 ml). To the benzene solution, seven-fold moles of 4-substituted phenol was added and allowed to react for 12 h at room temperature. The crude porphyrin precipitated by the addition of petroleum ether or hexane was collected by filtration and recrystallized from benzene–hexane. Elemental analysis data of these porphyrins prepared in this work agreed with the calculated values within ±0.4%. $DAEPFe^{III}$ complexes (**2**, **3**, and **4**) showed a typical high-spin iron(III) porphyrin signal around g=6 by ESR measurements in dichloromethane at 77 K, respectively.



DAEPH2			DAEPFeCl		
1a	X=OMe,	M=2H	2a	X=OMe,	M=FeCl
1b	X=Me,	M=2H	2b	X=Me,	M=FeCl
1c	X=H,	M=2H	2c	X=H,	M=FeCl
1d	X=Cl,	M=2H	2d	X=Cl,	M=FeCl
1e	X=COOMe,	M=2H	2e	X=COOMe,	M=FeCl

DAEPFeOAr		
3a	X=OMe,	M=4-MeOCOC$_6$H$_4$O-Fe
3b	X=H,	M=4-MeOCOC$_6$H$_4$O-Fe
3c	X=Cl,	M=4-MeOCOC$_6$H$_4$O-Fe
3d	X=COOMe,	M=4-MeOCOC$_6$H$_4$O-Fe
3e	X=OMe,	M=4-MeOC$_6$H$_4$O-Fe
3f	X=H,	M=4-MeOC$_6$H$_4$O-Fe
3g	X=Cl,	M=4-MeOC$_6$H$_4$O-Fe
3h	X=COOMe,	M=4-MeOC$_6$H$_4$O-Fe
3i	X=CN,	M=4-MeOC$_6$H$_4$O-Fe
3j	X=H,	M=C$_6$H$_5$O-Fe
3k	X=H,	M=4-NO$_2$C$_6$H$_4$O-Fe

(DAEPFe)$_2$O			
4a	X=OMe,	4c	X=Cl,
4b	X=H,	4d	X=COOMe,

Results

Cyclic Voltammetry of 10,20-Diaryletioporphyrinato Iron(III) Complexes. Typical cyclic voltammograms of high-spin iron(III) porphyrins (**2**, **3**, and **4**) are shown in Fig. 1. Two anodic redox couples, one cathodic redox couple, and one cathodic irreversible wave were observed in case of $DAEPFe^{III}Cl$ **2** (Fig. 1a). In the case of iron(III) porphyrins coordinated a phenolate, $DAEPFe^{III}OAr$ **3**, two anodic and one cathodic redox couples were observed (Fig. 1b). Especially, iron(III) porphyrins coordinated a p-methoxyphenolate (**3e**—**i**) have another anodic oxidation wave at around 0.85 V. In the case of iron(III) porphyrin μ-oxo dimers, $(DAEPFe^{III})_2O$ **4**, three anodic and one cathodic redox couples have been observed (Fig. 1c). The cyclic voltammetric data of these high-spin iron(III) porphyrins are summarized in Table 1.

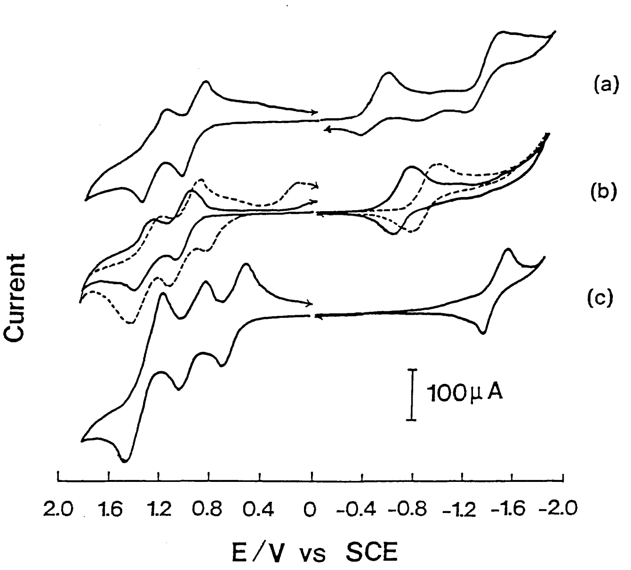


Fig. 1. Cyclic voltammograms of high-spin iron(III) porphyrins: (a) DAEPFeCl **2c**, (b) DAEP-FeOC$_6$H$_4$COOMe **3d** (dotted line represents a cyclic voltammogram of DAEPFeOC$_6$H$_4$OMe **3e**), (c) $(DAEPFe)_2O$ **4b**.

Substituents Effect on Redox Potentials. A linear relationship between the half-wave potentials ($E_{1/2}$) and the sum of the Hammett substituent constants for para substituents has been reported (Eq. 1).[1c,d] Here, ρ_{an} and ρ_{cn} represent a reaction constant due to an anodic n-th redox reaction and a cathodic n-th redox reaction, respectively. The ρ values of the Hammett reaction constants obtained in this work are summarized in Table 2.

$$\Delta E_{1/2} = \rho_{an}\sum\sigma_p \ (\text{or } \rho_{cn}\sum\sigma_p) \qquad (1)$$

The equatorial p-substituents of the *meso*-phenyl group in high-spin iron(III) porphyrins mainly affect the anodic redox potentials, i.e., large ρ values (about 0.1) are obtained in anodic electrode reactions. Contrary to the anodic reactions, small ρ values (almost 0) are obtained in the case of cathodic reactions. Moderate ρ values (about 0.06) are obtained in the case of $DAEPFe^{III}OAr$ (ρ_{a2}) and $(DAEPFe^{III})_2O$ (ρ_{a3}, ρ_{c1}). A different tendency, a large ρ_{a2} value and a small ρ_{c2} value, is observed in the case of $DAEPFe^{III}Cl$ **2** by comparing with the reported ρ values of $TAPFe^{III}Cl$.[8] In addition, the μ-oxo dimer **4** has similar reaction constans to those of $(TAPFe^{III})_2O$ reported before.[9]

Table 1. Cyclic Voltammetric Data of High-Spin DAEPFe^{III} Complexes[a)]

Porphyrin	Anodic wave $E_{1/2}$/V			Cathodic wave $E_{1/2}$/V	
	3rd	2nd	1st	1st	2nd
DAEPFeCl					
2a		1.22	0.92	−0.53[b)]	−1.32
2b		1.26	0.95	−0.54[b)]	−1.32
2c		1.28	0.99	−0.53[b)]	−1.32
2d		1.33	1.03	−0.53[b)]	−1.32
2e		1.35	1.05	−0.53[b)]	−1.34
DAEPFeOC$_6$H$_4$CO$_2$Me					
3a		1.27	0.94	−0.70	
3b		1.29	0.97	−0.70	
3c		1.33	1.03	−0.69	
3d		1.36	1.04	−0.66	
DAEPFeOC$_6$H$_4$OMe					
3e	1.31	1.03	0.85[b)]	−0.84	
3f	1.30	1.02	0.83[b)]	−0.84	
3g	1.40	1.06	0.86[b)]	−0.81	
3h	1.45	1.06	0.89[b)]	−0.84	
3i	1.56	1.15	0.91[b)]	−0.80	
DPEPFeOAr[c)]					
3j		1.31	1.00	−0.81	
3k		1.27	1.00	−0.60	
(DAEPFe)$_2$O					
4a	1.28	0.94	0.61	−1.44	
4b	1.30	0.98	0.64	−1.41	
4c	1.33	1.06	0.72	−1.38	
4d	1.35	1.07	0.74	−1.37	
4e	1.40	1.15	0.85	−1.34	

a) Conditions: 2 mM iron(III) porphyrin in CH$_2$Cl$_2$ (0.1 M tetrabutylammonium perchlorate), at 20 °C, Pt electrode, scan rate; 0.1 V s^{-1}, potentials are referred to SCE. b) A peak potential value. c) *p*-Substituted phenoxide ligated (10,20-diaryletioporphyrinato II) iron(III) complexes.

Table 2. Hammett Reaction Constants for the Electrode Reactions of Equatorial and Axial Substituted Iron(III) Porphyrins[a)]

Porphyrin	Reaction constant ρ					Ref.
	ρ_{a3}	ρ_{a2}	ρ_{a1}	ρ_{c1}	ρ_{c2}	
(A) Equatorial substituted porphyrins						
DAEPFeCl **2**		0.088	0.090	−0.002[b)]	−0.012	
DAEPFeOC$_6$H$_4$CO$_2$Me **3a—d**		0.064	0.074	0.025		
DAEPFeOC$_6$H$_4$OMe **3e—i**	0.138	0.059	0.038[b)]	0.017		
(DAEPFe)$_2$O **4**	0.062	0.110	0.124	0.052		
TAPFeCl		0.048	0.098	0.038	0.068	8
(TAPFe)$_2$O	0.056[c)]	0.141[c)]	0.143[c)]			9
(B) Axial substituted porphyrins						
DPEPFeOAr[d)] **3**		−0.032	−0.025	0.232		
TPPFeOAr			0.003[c)]	0.212[c)]		10
OEPFeOAr			−0.030[c)]	0.269[c)]		10

a) 0.1 M TBAP–CH$_2$Cl$_2$. b) Calculated from the peak potential values. c) An estimated value from the reported data. d) *p*-Substituted phenoxide ligated (10,20-diaryletioporphyrinato II) iron(III) complexes.

Contrary to the effect of equatorial substituents, axial substituents mainly affect the cathodic reaction in the case of high-spin iron(III) porphyrins. A large ρ_{Cl} value and small ρ_{a} values are obtained in the case of phenoxide ligated *meso*-diphenyletioporphyrinato iron(III) complexes (DPEPFe$^{\mathrm{III}}$OAr, **3**). This tendency is good in accord with TPPFe$^{\mathrm{III}}$OAr and OEPFe$^{\mathrm{III}}$OAr.[10]

Spectroelectrochemical Results of High-Spin DAEPFe$^{\mathrm{III}}$. The spectroelectrochemical results of high-spin DAEPFe$^{\mathrm{III}}$Cl **2b** are shown in Fig. 2a. The thin-layer spectrum of one-electron oxidized **2b** shows a typical porphyrin π-cation radical, which is characterized by a decrease in the absorbance at the Soret band (Fig. 2b). On the other hand, when the thin-layer spectra of one-electron and two-electron reduced DAEPFe$^{\mathrm{III}}$Cl **2b** are compared with the porphyrin π-anion radical of 10,20-diphenyletioporphyrin II (DAEPH$_2$, **1c**) (Figs. 2a and 2b), no decrease in the absorbance at the Soret band is observed. These results suggest that the cathodic reductions of **2** are not ligand-centered reactions, but are metal-centered reactions.

Similarly, the thin-layer spectra (Fig. 3a) suggest that the first anodic oxidation of DAEPFe$^{\mathrm{III}}$OC$_6$H$_4$CO$_2$Me **3b** is a porphyrin ligand-centered reaction and that the first cathodic reduction of **3b** is a metal-centered reaction. In the case of DAEPFe$^{\mathrm{III}}$OC$_6$H$_4$OMe **3e**—**i**, another irreversible wave than the three redox couples observed in **3b** was observed (Fig. 1b). The anodic peak at 0.85 V and the cathodic peak at 0.15 V of **3e** was found to be a redox couple by conducting selected continuous scans between 1.0 and −0.2 V. The first anodic one-electron oxidation of **3f** was found not to be a porphyrin-ligand centered reaction by the thin-layer spectrum (Fig. 3b). The absorption spectrum of the one-electron oxidation product is similar to (10,20-diphenyletioporphyrinato II) iron(III) perchlorate (DPEPFe$^{\mathrm{III}}$ClO$_4$),[11]

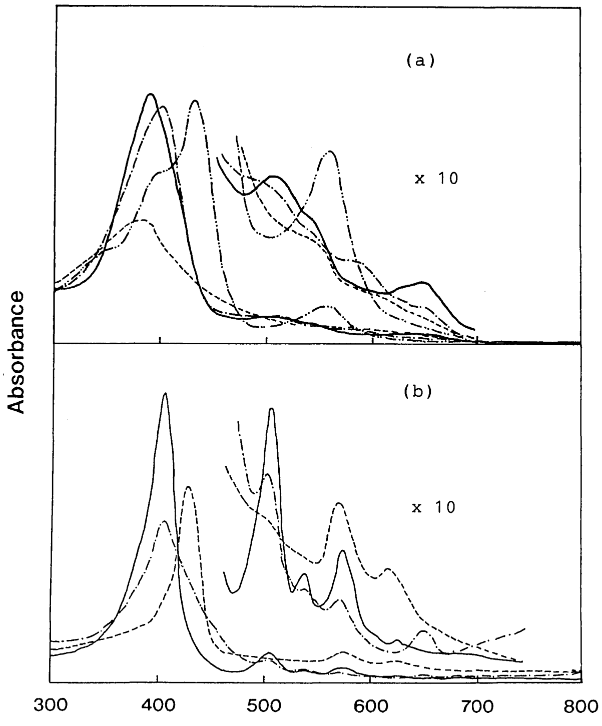


Fig. 2. Thin-layer spectra of DAEPFeCl **2b**, DAEPH$_2$ **1c**, and their electrolyzed products: (a) DAEPFeCl **2b** (——), one-electron oxidation of **2b** at 1.4 V vs. SCE (-----), one-electron reduction of **2b** at −0.6 V (—•—), and two-electron reduction of **2b** at −1.5 V (—••—); (b) DAEPH$_2$ **1c** (——), one-electron oxidation of **1c** at 1.03 V (-----), and one-electron reduction of **1c** at −2.0 V (—•—).

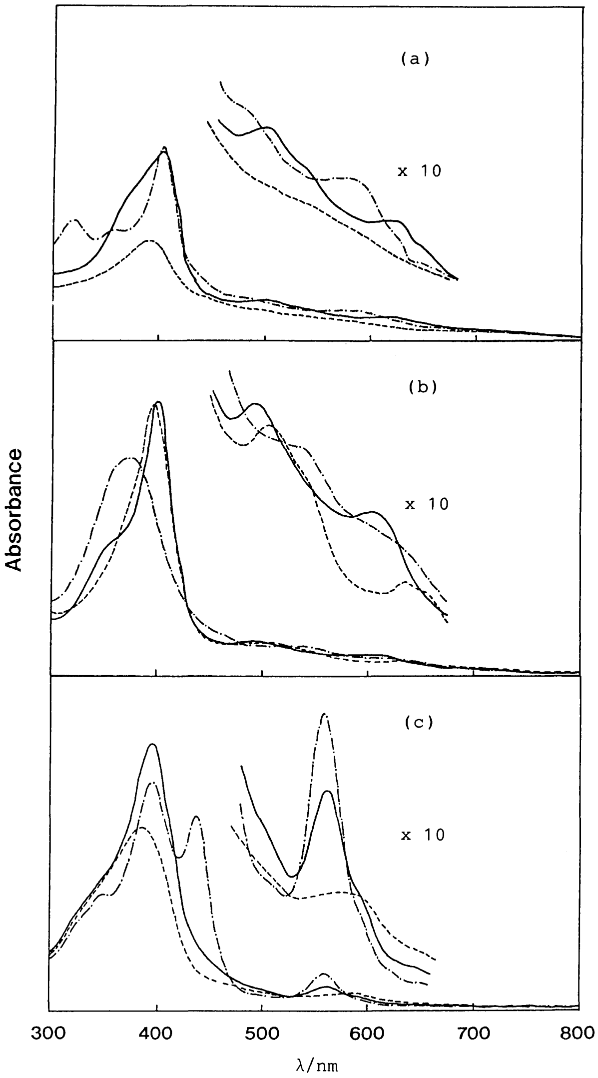


Fig. 3. Thin-layer spectra of DPEPFeOC$_6$H$_4$CO$_2$Me **3b**, DPEPFeOC$_6$H$_4$OMe **3f**, (DPEPFe)$_2$O **4b**, and their electrolyzed products: (a) DPEPFeOC$_6$H$_4$CO$_2$Me **3b** (——), one-electron oxidation of **3b** at 1.06 V (-----), and one-electron reduction of **3b** at −0.92 V (—•—), (b) DPEPFeOC$_6$H$_4$OMe **3f** (——), one-electron oxidation of **3f** at 0.84 V (-----), and two-electron oxidation of **3f** at 1.15 V (—•—), (c) (DPEPFe)$_2$O **4b** (——), one-electron oxidation of **4b** at 0.75 V (-----), and one-electron reduction of **4b** at −1.6 V (—•—).

though the redox potentials ($E_{1/2}$) are different from those of DPEPFe^{III}ClO$_4$.[12] These results suggest that the one-electron oxidation product of **3f** is assumed to be an axial phenolate-ligand oxidized product, which is especially stabilized by the *p*-methoxyl substituent. A phenolate ligand oxidation has suggested before.[10,13] The resemblance of the absorption spectrum of oxidized phenolate coordinated DPEPFe^{III} to that of DPEPFe^{III}ClO$_4$ is assumed to be due to a weak coordination of the fifth ligand. The succesive oxidation of **3f** at 1.15 V shows a typical porphyrin π-cation radical. Further, an oxidized sample is reduced again at -0.1 V to give the spectrum of **3f**.

The thin-layer spectrum of the one-electron oxidation product of (DAEPFe^{III})$_2$O **4b** is suggested to be a ligand-centered oxidation product (Fig. 3c). Although the spectrum of the one-electron reduction product shows a partial decrease of the absorbance, it is difficult to determine whether the reduction process is a metal-centered reaction or a ligand-centered reaction.

Discussion

The effects of substituents on the redox potentials of high-spin iron(III) porphyrins imply important structural information. When an iron porphyrin takes a five-coordinated square-pyramidal structure, the ligands are assumed to be located on the dsp^3 hybrid orbitals, i.e., the axial fifth ligand is located on the *z*-axis of iron, and iron is located out of the porphyrin-ligand plane. The location of the ligands is expected to be reflected in the Hammett reaction constants (ρ). The redox processes of high-spin DAEPFe^{III} are assumed by examining the ρ values as well as spectrophotometric data.

The large ρ_{a1} value supports the idea that the one-electron oxidation process is a ligand-centered reaction for the contribution of *p*-substituents of the *meso*-phenyl group to the porphyrin π-electron system. The spectroelectrochemical method has a limit for examining redox processes. When the first redox process is a porphyrin-ligand-centered reaction, it is hard to determine whether the succesive second redox process is a ligand-centered reaction or a metal-centered reaction. For this reason, the two-electron oxidation product of **2** is still ambiguous by spectrophotometry; however the large ρ_{a2} value strongly suggests that the second oxidation process is also a ligand-centered reaction. If a great structural change does not occur during the first oxidation process, the ρ_{a2} value must be almost identical to ths ρ_{a1} value. In fact, the square-pyramidal structure of [TpPPFe^{III}]$^{+\bullet}$ has been shown by the X-ray crystal structure,[14] and the out-of-plane (Ct–M) has been estimated to be about 0.43 Å from the reported X-ray crystallografic data.

The low ρ_{c1} and ρ_{c2} values of DAEPFe^{III}Cl **2** support the idea that reduction processes are metal-centered reactions, since the iron atom locates out of the porphyrin π-electron system. When the iron porphyrin takes an octahedral structure, ρ_{c1} is larger than the ρ_{c1} of **2**.[15] The small change of the values between ρ_{c1} and ρ_{c2} suggests that little structural change occurs during the first cathodic reaction of **2**. A square-pyramidal structure of high-spin iron(II) porphyrin has also been reported.[16]

The redox processes of DAEPFe^{III}Cl **2** in dichloromethane can be summarized in Eq. 2, involving a small structural change from these examinations. The coordination of chloride to iron[17] during the redox reactions is still ambiguous. The redox processes of high-spin DAEPFe^{III}OAr **3** are essentially identical to those of DAEPFe^{III}Cl **2** from the results of axial and equatorial substituent effects, and from the spectroelectrochemical results.

$$[\mathrm{DAEPFe^{III}Cl}]^{2+} \overset{e}{\rightleftarrows} [\mathrm{DAEPFe^{III}Cl}]^{+\bullet} \overset{e}{\rightleftarrows} \mathrm{DAEPFe^{III}Cl} \overset{e}{\rightleftarrows} [\mathrm{DAEPFe^{II}Cl}]^{-} \overset{e}{\rightleftarrows} [\mathrm{DAEPFe^{I}Cl}]^{2-} \qquad (2)$$

The ρ_{a1} and ρ_{a2} values of (DAEPFe^{III})$_2$O **4** are extremely large compared with those of monomeric high-spin DAEPFe^{III} complexes. This phenomenon is assumed to be due to a specific μ-oxo dimeric structure of iron(III) porphyrins, i.e., the dihedral angle between the mean plane of the porphyrin skeleton and the plane of a *meso*-phenyl group has been reported to be unusually small at 53.3°.[18] If there is only a small structural change of **4** during electrode reactions, the ρ_{a3} and ρ_{c1} values of **4** would be somewhat too small to be due to a ligand-centered reaction and, reversely, too large to be due to a metal-centered reaction. From these electrochemical results, the four redox waves of **4** are assumed to be due to a ligand-centered reaction, although the third anodic two-electron oxidation and the first cathodic one-electron reduction are still doubtful.

On the whole, the equatorial alkyl substituents at the β-pyrrole position of the DAEPFe(III) complexes cause a shift of the redox potentials more cathodically than those of the corresponding TAPFe(III) complexes, about 0.15 V, as expected.[1d] Somewhat smaller ρ-values of the DAEPFe(III) complexes than the corresponding TAPFe(III) in Table 2(A) are assumed to be due to a decreased in the electronic contribution of the *p*-substituted *meso*-phenyl groups to a porphyrin π-electron system caused by an increased in the steric hindrance between the *meso*-phenyl groups and the alkyl substituents at the β-pyrrole position. The axial ligand effect of DPEPFe(III)OAr is analogous to that of OEPFe(III)OAr, rather than that of TPPFe(III)OAr (Table 2(B)). The small difference might be due to a different degree of mobility between the alkyl substituents at the β-pyrrole position and the *meso*-phenyl substituents, which would be reflected by an electronic state or a strain of the porphyrin ring. In conclusion, the redox behaviors of high-spin DAEPFe^{III} complexes are suggested to be substantially identical to those of high-spin TAPFe^{III} complexes from the results obtained in this work. Some ambiguous processes and points need to be investigated by other techniques.

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11) An absorption spectrum data of DPEPFe^{III}ClO$_4$ in CH_2Cl_2: nm (log ε) 628 (3.38), 584 sh(3.48), 533 sh(3.86), 502 (4.00), 398 (5.08).

12) Cyclic voltammetric data of DPEPFe^{III}ClO$_4$ in CH_2Cl_2–0.1 M TBAP with Pt: $E_{1/2}$ (V vs. SCE); 1.20, 0.93, −0.04, −1.48.

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