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Preparation and Electrochemical Behaviors of Phenoxide-coordinated Iron(III) Porphyrins

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A new series of iron(III) porphyrins having various phenoxide anions as the axial ligand, [Fe^{III}(porphyrin)-(4-X-$C_6H_4O^-$)] (porphyrin=octaethylporphyrin and tetraphenylporphyrin; X=OCH_3, CH_3, H, C_6H_5, Cl, Br, $COCH_3$, CN, CHO, and NO_2) were synthesized. All these complexes are five-coordinated high-spin complexes ($S=5/2$). Their electrochemical behaviors were investigated by the cyclic voltammetry and the controlled potential coulometry. The complexes showed significantly negative potentials for the Fe^{II}/Fe^{III} redox couple (−0.4—−0.8 V). A good linear relationship was found between the half-wave potentials of the Fe^{II}/Fe^{III} redox couple and the Hammett σ-values of the substituent X. A new characteristic feature is the appearance of the redox peaks of the coordinated phenoxide anions near the redox couple of the porphyrin ring oxidoreduction. The role of the tyrosine-67 in the enzymatic mechanism for cytochrome c is discussed.

As to the biological functions of cytochrome c such as its electron transferring activities, some hypotheses were presented on the basis of the crystallographic data of its several variant forms.[1,2] All of these hypotheses point out the importance of the interaction between the heme (iron porphyrin) and the tyrosine-67 residue, where the phenol group or its anionic form may act as the one-electron donor to the ferric porphyrin through the ionic interaction $(\text{tyr-67})^-\cdots\cdots(\text{heme})^+$ to give ferrous porphyrin and tyrosine radical.[2] It, therefore, seemed to be considerable interest to evaluate qualitatively the strength of the ionic interaction by use of model complexes.

For this purpose, we systematically prepared a series of iron(III) porphyrin complexes having phenoxide anions substituted at the 4-position (*para*-position), and investigated their basic physicochemical properties, particularly electrochemical behaviors.

Experimental

Syntheses of Complexes, General Procedures. To a dichloromethane solution of (octaethylporphyrinato)iron(III) acetate,[3] [Fe^{III}(oep)(OAc)] or (tetraphenylporphyrinato)iron(III) acetate, [Fe^{III}(tpp)(OAc)] (100 mg) was added a dichloromethane solution of phenol derivatives (100 mg). Due to the low solubility in dichloromethane, *p*-hydroxybenzaldehyde and methyl *p*-hydroxybenzoate were dissolved in methanol, and biphenyl-4-ol was dissolved in acetone. After stirring for about 3—4 h, the solvent was removed to dryness. The residual solid was washed with acetonitrile and recrystallized from dichloromethane–methanol (1:1 vol/vol) or dichloromethane–acetonitrile (1:1 vol/vol) to give purple crystals in about 60—80% yields. The elemental analyses, and the spectral data of UV-VIS and IR are summarized in Tables 1, 2, and 3, respectively.

Cyclic Voltammetry and Controlled Potential Coulometry. Dichloromethane was dried and distilled over CaH_2 before use. As a supporting electrolyte, tetrabutylammonium per-

Table 1. Elemental analyses

	Compound	C (%) Found(Calcd)	H (%) Found(Calcd)	N (%) Found(Calcd)
1	[Fe^{III}(oep)(4-CH_3O-$C_6H_4O^-$)]·$(H_2O)_{1/2}$	71.72(71.65)	7.21(7.27)	8.32(7.77)
2	[Fe^{III}(oep)(4-CH_3-$C_6H_4O^-$)]·$(H_2O)_{1/2}$	73.17(73.28)	7.32(7.43)	8.47(7.95)
3	[Fe^{III}(oep)(4-C_6H_5-$C_6H_4O^-$)]·$(H_2O)_{1/2}$	75.47(75.18)	7.00(7.10)	7.45(7.31)
4	[Fe^{III}(oep)($C_6H_5O^-$)]·$(H_2O)_{1/2}$	72.93(73.03)	7.21(7.30)	8.66(8.11)
5	[Fe^{III}(oep)(4-Cl-$C_6H_4O^-$)]·$(H_2O)_{1/2}$	69.52(69.57)	6.64(6.67)	7.57(7.73)
6	[Fe^{III}(oep)(4-Br-$C_6H_4O^-$)]·(H_2O)	64.97(64.79)	6.21(6.47)	7.09(7.20)
7	[Fe^{III}(oep)(4-CH_3CO-$C_6H_4O^-$)]·$(H_2O)_{1/2}$	71.91(72.12)	7.71(7.65)	7.08(7.15)
8	[Fe^{III}(oep)(4-CN-$C_6H_4O^-$)]·(H_2O)	71.54(71.26)	6.76(6.67)	9.69(9.67)
9	[Fe^{III}(oep)(4-CHO-$C_6H_4O^-$)]·$(H_2O)_{3/2}$	70.38(70.10)	7.92(7.61)	7.04(7.12)
10	[Fe^{III}(oep)(4-NO_2-$C_6H_4O^-$)]·$(H_2O)_{1/2}$	68.80(68.47)	6.66(6.70)	9.61(9.51)
11	[Fe^{III}(tpp)(4-CH_3O-$C_6H_4O^-$)]·(H_2O)	75.55(75.65)	4.38(4.61)	7.17(6.92)
12	[Fe^{III}(tpp)(4-CH_3-$C_6H_4O^-$)]·$(H_2O)_{1/2}$	77.85(78.06)	4.88(4.62)	6.80(7.14)
13	[Fe^{III}(tpp)(4-C_6H_5-$C_6H_4O^-$)]·$(H_2O)_2$	76.38(76.97)	4.32(4.73)	6.29(6.41)
14	[Fe^{III}(tpp)($C_6H_5O^-$)]·$(H_2O)_{1/2}$	77.95(77.92)	4.53(4.45)	7.37(7.27)
15	[Fe^{III}(tpp)(4-Cl-$C_6H_4O^-$)]·(H_2O)	74.15(73.76)	4.07(4.21)	6.84(6.88)
16	[Fe^{III}(tpp)(4-Br-$C_6H_4O^-$)]·(H_2O)	69.52(69.94)	3.86(3.99)	6.35(6.52)
17	[Fe^{III}(tpp)(4-CH_3CO-$C_6H_4O^-$)]·$(H_2O)_{1/2}$	76.72(76.85)	6.94(6.89)	4.42(4.47)
18	[Fe^{III}(tpp)(4-CN-$C_6H_4O^-$)]·$(H_2O)_{1/2}$	73.62(76.98)	3.99(4.05)	8.71(8.80)
19	[Fe^{III}(tpp)(4-CHO-$C_6H_4O^-$)]·(H_2O)	75.62(75.84)	4.16(4.24)	6.96(6.94)
20	[Fe^{III}(tpp)(4-NO_2-$C_6H_4O^-$)]·$(C_6H_6)_{1/2}$	74.95(75.27)	4.30(4.17)	8.14(8.28)

Table 2. UV-VIS spectral data for phenoxide complexes of iron(III) porphyrins in CH_2Cl_2

Compound	λ_{max}/nm (log ε)						
1		392(4.63)	489(3.71)	510 sh(3.66)	600(3.55)		
2		391(4.51)	488(3.56)	513 sh(3.51)	600(3.38)		
3		392(4.87)	491(3.93)	515 sh(3.87)	604(3.75)		
4		391(4.45)	488(3.52)	515 sh(3.47)	602(3.35)		
5		390(4.40)	491(3.49)	515(3.46)	606(3.32)		
6		391(4.57)	491(3.67)	515(3.63)	607(3.49)		
7	370 sh(4.70)	393(4.74)	495(3.87)	520 sh(3.85)	612(3.63)		
8	370 sh(4.72)	393(4.75)	496(3.86)	522(3.84)	615(3.61)		
9	370 sh(4.73)	394(4.75)	496(3.85)	520 sh(3.82)	613(3.57)		
10	365 sh(4.34)	394(4.43)	490(3.81)	522(3.76)	615(3.53)		
[Fe^{III}(oep)(OAc)]		381(5.01)	460(3.88)	508(3.97)	537(3.99)	584(3.46)	640(3.65)
[Fe^{III}(oep)F]		395(4.96)	481(3.95)	514(3.86)	599(3.80)		
[Fe^{III}(oep)Cl]		381(4.93)	461(3.76)	508(3.87)	536(3.89)	584(3.33)	640(3.58)
11		414(4.81)		566 sh(3.57)	620 sh(3.49)		
12		413(4.64)	484 sh(3.75)	540 sh(3.46)	620(3.33)		
13		414(4.99)	487 sh(4.06)	561(3.76)	610 sh(3.64)		
14		415(4.64)		571(3.41)	614 sh(3.31)		
15		414(5.15)	485 sh(4.27)	548 sh(3.97)	629(3.83)		
16		414(5.48)	486 sh(4.60)	550 sh(4.30)	631(4.16)		
17	340(4.40)	415(4.84)	495(3.96)	555 sh(3.66)	632(3.50)	655(3.49)	
18	342(4.55)	415(4.94)	498(4.04)	555 sh(3.70)	636(3.86)	661(3.86)	
19	346(4.42)	415(4.73)	496(3.79)	555 sh(3.46)	636(3.28)	662(3.27)	
20	359(4.54)	405(4.93)	499(4.03)	560 sh(3.66)	640(3.49)	685(3.50)	

sh: Shoulder.

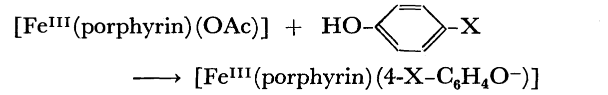
Table 3. Characteristic IR bands for coordinated phenoxide anions of phenoxide compllexes of iron(III) porphyrins

Compound	$\nu_{C\cdots C}/cm^{-1}$	$\nu_{C\cdots C}/cm^{-1}$	ν_{C-O}/cm^{-1}	Others
1		1486	1224	
2		1492	1262, 1254	
3	1590	1477	1253, 1260	
4	1584	1484	1267, 1280	
5	1577	1475	1261	
6	1571	1472	1255	
7	1584	1492	1267	1664 ($\nu_{C=O}$)
8	1588	1498, 1485	1298	2208 ($\nu_{C\equiv N}$)
9	1581	1495	1282	1670 ($\nu_{C=O}$)
10		1482	1276	1575, 1328 (nitro group)
11	1594	1491	1226	
12	1594	1493	1246	
13	1592	1476	1255	
14	1594, 1581	1482, 1474	1257	
15	1594	1475	1262	
16	1594, 1571	1473	1259	
17	1581	1492	1266	1661 ($\nu_{C=O}$)
18	1589	1484	1281	2212 ($\nu_{C\equiv N}$)
19	1581	1490	1273, 1281	1683 ($\nu_{C=O}$)
20		1481	1274	1574, 1328 (nitro group)

chlorate (TBAP) was used after being subjected twice to recrystallization from benzene. Cyclic voltammograms were obtained on a HA-104 potentiostat (Hokuto Denko) in combination with a HB-107A function generator (Hokuto Denko). A three-electrode system was used which consisted of platinum working and counter electrodes and a commercial saturated calomel electrode (SCE) separated from the bulk of solution by a bridge filled with the solvent containing supporting electrolyte. The bridge had its solution changed periodically to avoid aqueous contaminants from entering the cell *via* SCE. All solutions were purged of oxygen by passing purified nitrogen through them for 10 min just before taking cyclic voltammograms. After the degassing a blanket of nitrogen was kept over the solution. The half-wave potential $E_{1/2}$ was taken as that potential lying midway between the oxidation and reduction peaks for a given couple. All experiments were carried out at room temperature (15 °C) and the potentials reported refer to the SCE. The scan rate was constantly 100 mV/s. The controlled potential coulometry was carried out on a HA-104 potentiostat with a HF-201 coulomb-amperehour meter (Hokuto Denko). The number of electron was obtained as the mean value of three experiments.

Results and Discussion

The acetate ion of the starting complexes could be easily replaced by various types of phenoxide anions.



$$[\mathrm{Fe^{III}(porphyrin)(OAc)}] + \mathrm{HO\text{-}C_6H_4\text{-}X} \longrightarrow [\mathrm{Fe^{III}(porphyrin)(4\text{-}X\text{-}C_6H_4O^-)}]$$

The substituents X were varied from the most electron donating OCH_3 to the most electron-withdrawing NO_2.

The coordinated phenoxide anions could be easily confirmed by the characteristic IR bands[4] as summarized in Table 3. These complexes showed UV-VIS spectra (Fig. 1) similar to those of the typical iron(III) high-spin complexes.[5] Compared with the acetate complex, the Soret band of these complexes shifted toward longer wavelength region by about 10 nm, and the so-called charge-transfer band around 600—650 nm shifted toward shorter wavelength region by about 20—30 nm. These absorption maxima are similar to those of fluoro complex, [Fe^{III}(oep)F].

All of these complexes showed magnetic susceptibilities of about 5.9 BM at room temperature, indicating that these phenoxide complexes are of five-coordinated high-spin (S=5/2) type.

Although the absorption maxima of the charge-transfer band were expected to be a good indicator of the strength of the interaction between iron(III) porphyrin-phenoxide anion, the effect of substituent X was found to be small. Since the redox potential of the cobalt(III)[6] or iron(III) porphyrins[7] are also known to be sensitive to the nature of the counter anions, such quantities of the phenoxide complexes were measured by the cyclic voltammetry. The half-wave potentials thus obtained are summarized in Table 4. In order to eliminate the complication by the coordination of polar solvent molecules,[7] the cyclic voltammograms were obtained in dichloromethane. As in the case of usual iron(III) porphyrins,[7] two quasi-reversible redox couples were observed at −0.5—−0.8 V and +1.1—+1.2 V. From the electrospectrochemistry and the controlled potential coulometry, these couples could be assigned to the Fe^{II}/Fe^{III} and Fe^{III}/Fe^{IV} or porphyrin ring oxidoreduction as shown in Fig. 2, reflecting the effect of the substituents on the porphyrin ligand. The values of octaethylporphyrin derivatives were more negative by about 0.1 V than those of tetraphenylporphyrin derivatives. The Fe^{II}/Fe^{III} redox values were found to be significantly dependent on the kind of substituent X in the phenoxide anion and ranged over −0.8—−0.4 V. These values are much negative compared with usual iron(III) complexes,[7] in particular the values of 4-methoxyphenoxide complexes are probably the most negative ones reported so far in iron(III) porphyrins. As shown in Fig. 3, there are good linear correlation between the half-wave potentials and the Hammett σ-values of substituent X.

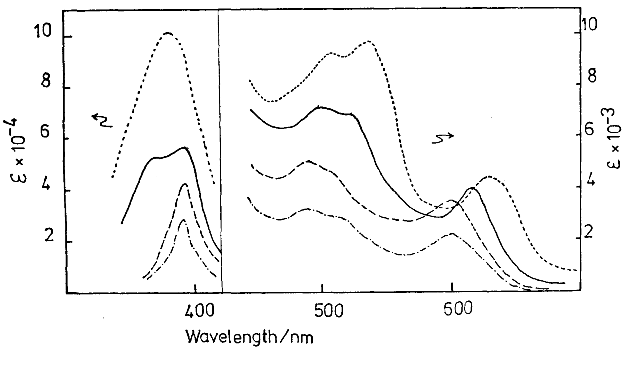


Fig. 1. UV-VIS spectra of (— — —) [Fe^{III}(oep)(4-CH$_3$O-C$_6$H$_4$O$^-$)], (—·—·—) [Fe^{III}(oep)(C$_6$H$_5$O$^-$)], (——) [Fe^{III}(oep)(4-CN-C$_6$H$_4$O$^-$)], and (······) [Fe^{III}(oep)(OAc)] in CH$_2$Cl$_2$.

Table 4. The half-wave potentials of the Fe^{II}/Fe^{III}, porphyrin ring oxidoreduction, and the oxidation peaks of phenoxide anions for phenoxide complexes of iron(III) porphyrins in CH$_2$Cl$_2$

Compound	Fe^{II}/Fe^{III}	Oxidation peak of phenoxide anion	Porphyrin ring oxidation
1	−0.80	+0.92	+1.06
2	−0.83	+0.98	+1.10
3	−0.71	+0.99	+1.10
4	−0.75	+1.05[a]	+1.07
5	−0.66	+1.02[a]	+1.09
6	−0.65	+1.01[a]	+1.09
7	−0.66	b)	+1.04
8	−0.58	b)	+1.06
9	−0.60	b)	+1.11
10	−0.50	b)	+1.06
11	−0.66	+0.98	+1.19
12	−0.65	+1.14	+1.19
13	−0.62	+1.10[a]	+1.16
14	−0.63	b)	+1.18
15	−0.58	b)	+1.18
16	−0.56	b)	+1.12
17	−0.50	b)	+1.17
18	−0.50	b)	+1.19
19	−0.46	b)	+1.16
20	−0.43	b)	+1.19
[Fe^{III}(tpp)ClO$_4$]	+0.22		+1.10[c]
[Fe^{III}(tpp)Br]	−0.21		+1.18[c]
[Fe^{III}(tpp)Cl]	−0.29		+1.14[c]
[Fe^{III}(tpp)N$_3$]	−0.42		+1.08[c]
[Fe^{III}(tpp)F]	−0.50		+1.14[c]

a) Inflection. b) Not observed. c) Ref. 7.

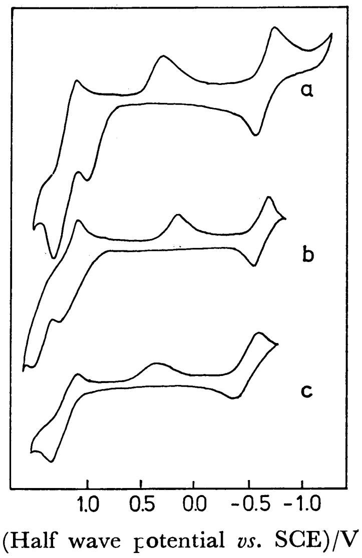


Fig. 2. Cyclic voltammograms of (a) [$\mathrm{Fe^{III}(tpp)(4\text{-}CH_3O\text{-}C_6H_4O^-)}$], (b) [$\mathrm{Fe^{III}(tpp)(4\text{-}C_6H_5\text{-}C_6H_4O^-)}$], and (c) [$\mathrm{Fe^{III}(tpp)(4\text{-}CN\text{-}C_6H_4O^-)}$] in CH_2Cl_2.

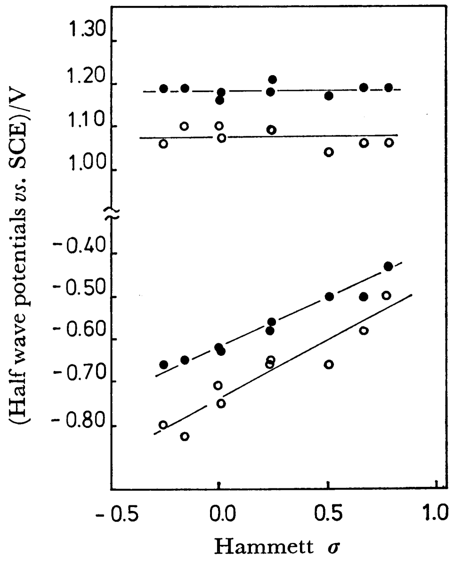


Fig. 3. The correlation between the half-wave potentials of [$\mathrm{Fe^{III}(porphyrin)(4\text{-}X\text{-}C_6H_4O^-)}$] and the Hammett σ-values of substituent X; (○) octaethylporphyrin derivatives and (●) tetraphenylporphyrin derivatives.

The σ-values adopted are follows; X=CH_3O(−0.268), CH_3(−0.170), H(0.00), C_6H_5(−0.01), Cl(+0.227), Br(+0.232), CN(+0.660), CH_3CO(+0.502), NO_2-(+0.778).

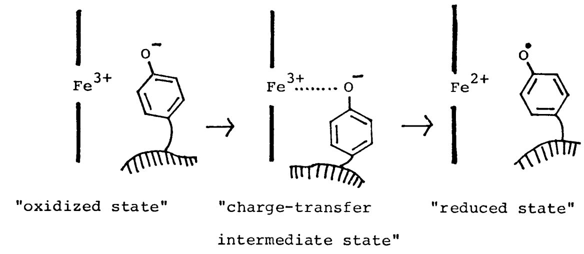
On the other hand, the redox couple at +1.1—+1.2 V showed no correlation with Hammett σ-values of X. This probably means that the redox couple is assignable to the redox process on the porphyrin ring rather than on metal.[7]

A new characteristic feature in these phenoxide complexes is the appearance of an additive oxidation and corresponding reduction peaks near the redox potential of porphyrin ring. These new oxidation peaks are remarkably dependent on the kind of substituent X. In 4-methoxyphenoxide complexes, the peaks could be clearly observed as a separated peak at about +0.9 V (Fig. 2a). These peaks were proved to be a one-electron process by the controlled potential coulometry and could be unambiguously assigned to the oxidation of coordinated phenoxide anions. The peak positions are consistent with those of the corresponding free phenols or phenoxide anions found in the literatures.[8] Such additive peaks have never been observed in iron(III) porphyrins, because the electrochemical studies so far dealt with iron(III) porphyrins with electrochemically inert halide ions or another inorganic anions. Very recently we reported that the catecholate complexes of iron(III) porphyrins had similar oxidoreduction peaks of coordinated catecholate anions.[9] As the electron-donating character of the substituent X decreases, the peak shifted to a more positive region finally to overlap the peak of porphyrin ring oxidation (Fig. 2b) and give a single peak (Fig. 2c). The overlapped peak at about +1.1—+1.2 V had doubled in current.

Very negative values of the $\mathrm{Fe^{II}/Fe^{III}}$ redox couple of these phenoxide complexes suggest that the strong electron donation, *i.e.*, the charge-transfer occurs from the phenoxide anions to iron(III) ion.

$$\mathrm{Fe^{3+} \leftarrow L^- \longleftrightarrow Fe^{2+}\text{----}L^{\cdot}}$$

Moreover, the coordinated phenoxide anions are subjected to the one-electron oxidation at more negative voltage than that of the porphyrin ring oxidation. These facts suggest the important catalytic role of the phenoxide anions (tyrosine-67) as a deliverer of electrons in enzymatic mechanism.[2] It is reasonably supposed that phenoxide group of tyr-67 in the enzyme can be brought so close to the ferric heme moiety probably due to the conformation change of the peptide chain that the electron transfer smoothly proceeds resulting ferrous heme and phenoxide radical as illustrated above.



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