Substituent Effects on the Electronic Absorption and MCD Spectra of Five- and Six-Coordinate Nitrosyl(tetraphenylporphyrinato)iron(II) Complexes

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Synopsis. Electronic absorption and MCD spectra of five- and six-coordinate nitrosyl iron(II) complexes of a series of tetrakis(para-substituted phenyl)porphyrins have been investigated in order to elucidate the cis-effect of para-substituents. The MCD spectroscopy was more sensitive to the substituent effect than the electronic absorption spectroscopy.

A variety of biological functions of various hemoproteins are markedly influenced by the electronic states of heme at the prosthetic group, which are sensitive to the nature of the equatorial porphyrinato and axial ligands. The investigations of cis and trans effects on various properties of metalloporphyrins have been performed for the purpose of obtaining information about the structure-function relationships of the hemoproteins.[1–3]

Studies on the model complex, nitrosyl(porphyrinato)iron(II), under various conditions have given significant clues to understanding the various properties of nitrosylhemoproteins, in which nitrosyl ligand is employed as a useful electronic probe for elucidating the heme environments and the heme group.[4–8] In this study, we have characterized the electronic absorption and magnetic circular dichroism (MCD) spectral properties of five- and six-coordinate nitrosyl iron(II) complexes of a series of tetrakis(para-substituted phenyl)porphyrins and demonstrated the substituent effects on the spectral properties in an attempt to elucidate a cis-effect on axial nitrosyl ligand.

Experimental

Materials and Methods. Tetrakis(*p*-substituted phenyl)-porphyrins and their iron(III) chlorides were purchased and/or synthesized as described previously.[9] 1-Methylimidazole (*N*-MeIm) and pyridine (Py) were distilled by flowing N_2 under reduced pressure. Nitrogen monoxide (99.5% minimum) purchased from Seitetsu Kagaku Co. was passed through a KOH column to remove higher nitrogen oxides. All other chemicals were obtained as the best available grade and were used without further purification.

The electronic absorption spectra were recorded on a Hitachi U-3210 spectrometer at 20±1 °C. The MCD spectra were measured at room temperature with a JASCO J-500A spectropolarimeter attached to an electromagnet (1.3 T) and a JASCO DP-501 data processor for data accumulation and manipulation.

Sample Preparation. The reduction of iron(III) to iron(II) and the reaction with NO were carried out in a Thunberg-type tube with an optical cuvette (path length, 1 cm) on a vacuum line. Five-coordinate nitrosyl(porphyrinato)iron(II) complexes were prepared as follows. Porphyrinatoiron(II) complexes were prepared by the reduction of the porphyrinatoiron(III) chlorides in CH_2Cl_2 with sodium dithionite, using a bilayer technique, after the solutions were deoxygenated by repeated flushing with argon saturated with CH_2Cl_2.[10] Then, the porphyrinatoiron(II) solutions thus obtained were equilibrated with NO gas; tube containing the solution was shaken gently until the solution changed to red, indicating the formation of nitrosyl complex. (Excess NO was consumed by sodium dithionite.) The six-coordinate nitrosyl(porphyrinato)iron(II) complexes were prepared by the reductive nitrosylation with NO. The solution containing Fe(P)Cl (where P is dianion of porphyrin) and nitrogenous base in chloroform was carefully deoxygenated by repeated flushing with argon saturated with chloroform. Then the solution was equilibrated with NO gas at slightly below 1 atm, followed by spectral measurements. The concentrations of Fe(P)(NO), *N*-MeIm, and Py were 0.015—0.02 mM, ca. 0.2—2.4 M, and ca. 4 M, respectively.

Results and Discussion

The inductive electron transfer from the para-substituents on the phenyl ring of 5,10,15,20-tetraphenylporphyrin is predominant in the metalloporphyrins.[3] The electron-withdrawing or -donating para-substituents of the phenyl rings affect the interaction of porphyrin π-system with iron d_π orbital,

Table 1. Electronic Spectral Data of Five-Coordinate Nitrosyl(porphyrinato)iron(II) Complexes in CH_2Cl_2 at Room Temperature[a]

Porph	$E_{1/2}$(I)[b]	Absorption maxima/nm (ε, $mM^{-1}\,cm^{-1}$)				
	Volt	Soret				
(*p*-OCH_3)tpp	−1.593	410.4(103)	473sh(17)	540.0(9.0)		614.4(3.3)
(*p*-H)tpp	−1.557	404.0(111)	470sh(17)	538.0(9.6)		607.6(2.7)
(*p*-F)tpp	−1.520	403.6(105)	470sh(16)	540.0(9.6)		606.0(3.3)
(*p*-CO_2CH_3)tpp	−1.435	406.4(112)	470sh(19)	542.0(8.3)		606.4(3.4)
(*p*-NO_2)tpp[c]	−1.340	404.8		540.0		602.8
(F_5)tpp[d]	−1.205	398.0(130)	470sh(17)	541.2(11.8)	570sh(7.5)	620sh(1.1)

a) Porph, dianion of porphyrin; sh, shoulder. b) The first redox potentials of free base porphyrins. Ref. 11. c) Iron complex of (*p*-NO_2)tpp could not be obtained in pure form[3]; so the extinction coefficients were not be determined. d) (F_5)tpp, dianion of (pentafluorophenyl)porphyrin.

Table 2. Electronic Spectral Data of Six-Coordinate Nitrosyl(porphyrinato)iron(II) Complexes with Nitrogenous Base in $CHCl_3$ at Room Temperature[a]

Porph	$E_{1/2}$(I)[b]	Base	Absorption Maxima/nm (ε, $mM^{-1} cm^{-1}$)		
	Volt		Soret		
(p-OCH_3)tpp	−1.593	N-MeIm	426.4(153)	548.8(9.3)	600sh(4.5)
		Py	424.4(133)	544.4(9.1)	612.4(3.9)
(p-H)tpp	−1.557	N-MeIm	424.0(161)	549.6(9.8)	600sh(3.5)
		Py	421.6(148)	543.6(10.4)	606.4(3.4)
(p-F)tpp	−1.520	N-MeIm	423.6(174)	548.8(10.9)	600sh(4.4)
		Py	420.8(141)	544.0(9.6)	604.0(3.7)
(p-CO_2CH_3)tpp	−1.435	N-MeIm	426.0(167)	551.6(10.1)	589sh(4.7)
		Py	423.6(153)	547.6(9.0)	601sh(3.3)
(p-NO_2)tpp[c]	−1.340	N-MeIm	426.8	552.4	
		Py	426.4	551.6	
(F_5)tpp[d]	−1.205	N-MeIm	418.8(185)	539.6(13.8)	577sh(4.2)
		Py	416.4(196)	540.8(13.0)	573sh(5.3)

a, b, c, d) See the foot note a, b, c, and d of Table 1, respectively.

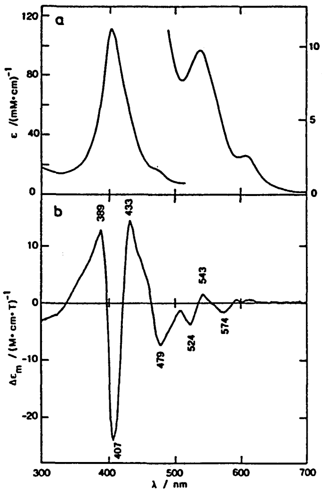

Fig. 1. Electronic (a) and MCD (b) spectra of Fe(tpp)(NO) in CH_2Cl_2 at room temperature.

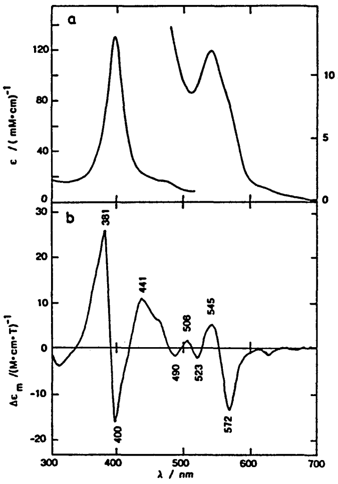

Fig. 2. Electronic (a) and MCD (b) spectra of Fe[(F_5)tpp](NO) in CH_2Cl_2 at room temperature.

followed by a shift to positive or negative side of the redox potentials of porphyrins and iron porphyrins.[1,11] The first redox potentials of the free base porphyrin ($E_{1/2}$(I))[11] are hereinafter used as a measure of the electron-withdrawing or -donating power of the porphyrin peripheral substituents.

Electronic Absorption Spectra. Tables 1 and 2 list the electronic absorption spectral data of five- and six-coordinate nitrosyl(porphyrinato)iron(II) complexes together with the first redox potentials of free base porphyrins and Figs. 1a—4a illustrate the electronic spectra of Fe(tpp)(NO), Fe[(F_5)tpp](NO), Fe(tpp)(NO)(N-MeIm), and Fe[(F_5)tpp](NO)(N-MeIm), respectively, where tpp is dianion of 5,10,15,20-tetraphenylporphyrin. The absorption maxima for five-coordinate nitrosyl(porphyrinato)iron(II) complexes were located at shorter wavelength side than those for six-coordinate complexes with respective porphyrin. Further, the Soret band for the former was markedly weak compared with that for the latter. These differences in spectral features between the five- and six-coordinate complexes of tpp derivatives are similar to those of protoporphyrin IX dimethyl ester.[8d] Perutz et al. explained[12] that an increase from six- to five-coordinate nitrosylheme in the displacement of iron from the porphyrin plane increases the interaction of porphyrin a_{2u} orbital with iron d_{z^2} orbital which lowers the a_{2u} in energy;[13] resulting increase of energy separation between a_{2u} and e_g^* causes the shift to shorter wavelength side of absorption maxima.

As shown in Tables 1 and 2, the Soret-band maxima for both five- and six-coordinate nitrosyl(porphyrinato)iron(II) complexes slightly shift to shorter wavelength side as $E_{1/2}$ becomes more positive, though the visible Q-band maxima were almost insensitive to the variation in $E_{1/2}$. The shift to shorter wavelengths of absorption maxima with increasing electron-withdrawing power of the para-substituents has been observed also in the electronic spectra of tetrakis(p-substituted phenyl)porphyrins[14] and iron (III) complexes of tetrakis(p-substituted phenyl)porphyrins.[3]

Magnetic Circular Dichroism Spectra. MCD spectra for hemoproteins and iron porphyrins are sensitive to oxidation state, spin state, and coordination number of the iron.[15]

The NO has an unpaired electron unlike diamag-

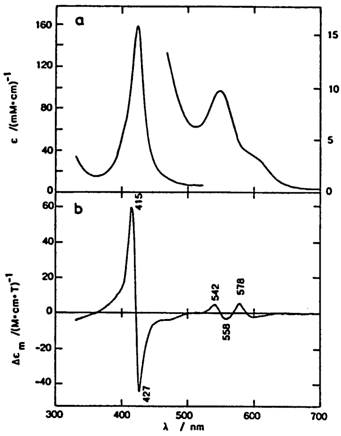

Fig. 3. Electronic (a) and MCD (b) spectra of Fe(tpp)(NO)(N-MeIm) in $CHCl_3$ at room temperature.

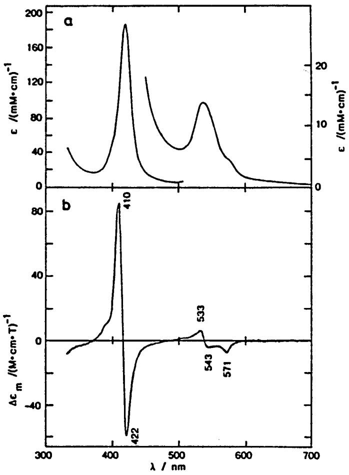

Fig. 4. Electronic (a) and MCD (b) spectra of Fe[(F_5)tpp](NO)(N-MeIm) in $CHCl_3$ at room temperature.

netic CO and the unpaired electron in nitrosyl(porphyrinato)iron(II) complexes has been shown to be considerably delocalized into iron d orbital.[4,5] The MCD spectrum for Fe(tpp)(NO)(N-MeIm) (Fig. 3b) nevertheless quite resembles that for Fe(tpp)(CO)(N-MeIm),[16] in which derivative shaped Soret and Q-bands are composed of Faraday A term. This result indicates that the delocalization of unpaired electron of NO ligand to iron exerts little, if any, effects upon the MCD spectra of low-spin iron(II) porphyrins.

Significant differences in the MCD spectral line shape between five- and six-coordinate nitrosyl(porphyrinato)iron(II) complexes of which iron(II) is in low-spin state were observed, especially in the Soret band region (Fig. 1b—4b). The overall MCD spectral patterns for five- and six-coordinate nitrosyl iron(II) complexes of tpp or (F_5)tpp (Fig. 1b—4b) were markedly different from those of protoporphyrin IX dimethyl ester,[8f] suggesting that the MCD spectra for nitrosyl(porphyrinato)iron(II) complexes are sensitive to differences in the porphyrin peripheral substituents. In the MCD spectra as well as the electronic spectra, the bands for the complexes of (F_5)tpp appeared at shorter wavelengths than those of tpp. Spectral change in line shape accompanied by a change in porphyrinato ligand from tpp to (F_5)tpp was more significant for five-coordinate complexes than for six-coordinate complexes and for Soret band region than for visible Q-band region.

Accordingly, MCD spectroscopy is useful for the elucidation of the cis-effect of porphyrin peripheral substituents in the nitrosyl(porphyrinato)iron(II) complexes.

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