  Bull. Chem. Soc. Jpn., 65, 1915—1919 (1992)

Bis(1-methylimidazole)iron(II) Complexes of Porphyrins Substituted with Highly Electron-Withdrawing CF_3 Groups: Electronic Spectra with Split Q-Bands and MCD Spectra with Unusual Features

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(Received February 12, 1992)

The bis(1-methylimidazole)iron(II) complexes of porphyrins substituted with one, two, or four CF_3 groups at pyrrole β-positions of a porphyrin have been studied by electronic absorption and magnetic circular dichroism (MCD) spectroscopies. The splittings of Q-bands observed in the electronic spectra of the complexes may arise from asymmetrical electronic effects of the highly electron-withdrawing CF_3 group on the porphyrin periphery. The ratio of absorption intensity $(\varepsilon(\alpha)/(\varepsilon(\beta))$ decreased with an increase of the number of CF_3 group, suggesting the decrease of a splitting in HOMOs. The MCD spectra of the bis(1-methylimidazole)iron(II) porphyrin complexes were markedly sensitive to the porphyrin peripheral substituents. The MCD spectra in Soret region successively changed in shape with the number of CF_3 group on porphyrin periphery and consequently were apparently inverted in sign, which can be explained by the shift of maximal wavelength accompanied by a change in intensity.

The splitting of visible Q-bands has been frequently observed in the electronic spectrum of hemoproteins in the reduced state.[1] Various *c*-type cytochromes such as cytochrome *c*-557 (551) from *Alcaligenes faecalis*,[2] cytochrome *c* peroxidase from *Pseudomonas aeruginosa*,[3] and cytochrome *c*-553 (550) from *Chromatium vinosum*[4] exhibit a splitting or asymmetry of the α band [Q(0,0) transitions] and a broadening or splitting of the β band [Q(1,0) transitions] at room temperature. The α and β bands of cytochromes *b* and *c* are generally further resolved into several components at lower temperature.[5,6] Recently, Cowan and Gray demonstrated that metalloporphyrin-reconstituted myoglobins exhibit Q-band splitting and the splitting would be due to the superposition of spectra arising from orientational isomerism of the porphyrin in the heme pocket.[1d] On the other hand, DiFeo and Addison emphasized that the Q-band splitting in iron hemoproteins can be ascribed not from the presence of different heme orientational isomerism but from the nature of the distal ligand.[1e] However, at present, there are insufficient interpretations to permit detailed evaluation of the origin of Q-band splittings in the electronic spectra of various hemoproteins.

In the course of the spectral study on the iron complexes of porphyrins substituted with highly electron withdrawing CF_3 groups,[7] it has been found that the iron(II) complexes with bis 1-methylimidazoles exhibit Q-band splittings in the electronic spectra and unusual features in Soret MCD spectra[8] which vary with the number of CF_3 groups at the porphyrin periphery. In this study we describe the electronic absorption and MCD spectral properties of the iron(II) complexes of electron-deficient porphyrins with one, two, or four CF_3 groups at pyrrole β-positions of a porphyrin (the dianion of the porphyrins; mtfp, btfp, and ttfp, respectively); and compare their spectral properties with those of (etioporphyrin I) iron(II) complexes (the dianion of etioporphyrin I, etpI). The Q-band splittings and the MCD were discussed in relation to the electron-withdrawing ability of peripheral substituents.

Experimental

Fe(etpI)Cl was obtained commercially and Fe(mtfp)Cl, Fe(btfp)Cl, and Fe(ttfp)Cl were synthesized as described before.[7] 1-Methylimidazole (*N*-MeIm) was distilled at reduced pressure under nitrogen atmosphere. All other chemicals used were obtained as the bast available grade and were used without further purification. All of the iron(II) complexes were prepared by reduction of the iron(III) complexes in CH_2Cl_2 with sodium dithionite, using a bilayer technique, in a Thunberg-type tube with optical cuvette (path length, 1 cm), after the solutions were deoxygenated by flushing with argon saturated with CH_2Cl_2 on a vacuum line.[9]

The electronic absorption spectra were recorded on a Hitachi U-3210 spectrometer at 23±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.

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Results and Discussion

The electronic absorption spectrum of Fe(etpI)(*N*-MeIm)$_2$ (Figure 1a) resembles, in spectral pattern, those of low-spin bis(N-base)iron(II) complexes of the other *meso*-unsubstituted porphyrins such as protoporphyrin IX dimethyl ester and octaethylporphyrin.[10]

Introduction of electron-withdrawing groups at the periphery of a porphyrin results in the shift to positive side of the redox potentials of the porphyrin and the corresponding metalloporphyrins.[11,12] As shown in Table 1, the first redox potential of free base porphyrins becomes more positive with an increase in the number of

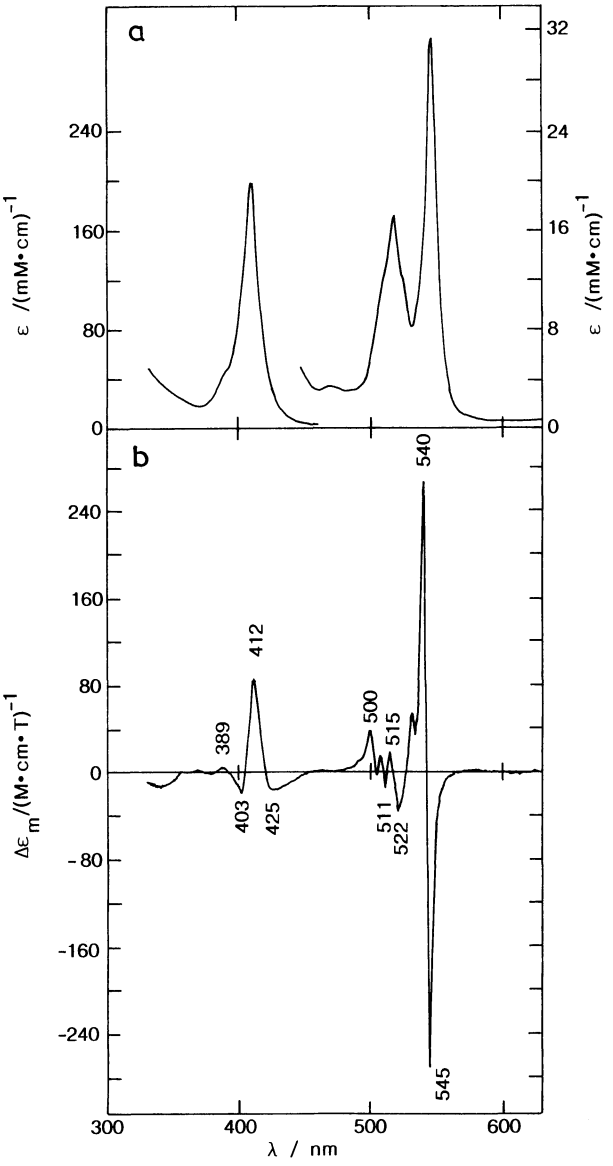

Fig. 1. Electronic (a) and MCD spectra (b) of Fe(etpI)-(*N*-MeIm)$_2$ in CH_2Cl_2 at room temperature. [Fe(etpI)(*N*-MeIm)$_2$]=0.0096 mM.

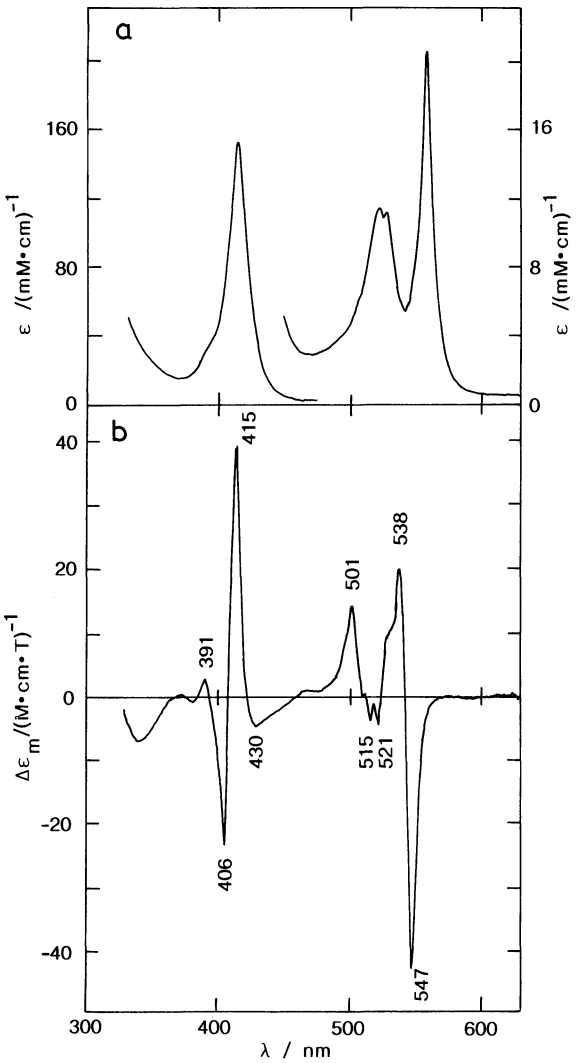

Fig. 2. Electronic (a) and MCD spectra (b) of Fe(mtfp)-(*N*-MeIm)$_2$ in CH_2Cl_2 at room temperature. [Fe(mtfp)(*N*-MeIm)$_2$]=0.0186 mM.

Table 1. Electronic Spectral Data of Fe(Porph)(*N*-MeIm)$_2$ at Room Temperature[a]

Porph	$E_{1/2}$(I)[b]	Absorption maxima/nm (ε, mM^{-1} cm^{-1})				
	V	Soret	β		α	
etpI	−1.39	410.8(198)	519.2(17.1)		548.4(31.4)	
mtfp	−1.22	414.0(153)	520.0(10.9)	527.2(10.2)	556.8(20.0)	
btfp	−1.08	418.0(210)	522.0(16.1)	527.2(17.3)	548.4(10.0)	557.6(21.8)
ttfp	−0.81	420.8(224)	527.6(16.6)		555.2(11.8)	

a) Solvent, CH_2Cl_2; [Fe(Porph)(*N*-MeIm)$_2$]=0.01—0.015 mM. b) The first redox potentials of free base porphyrins. Ref. 7.

CF_3 groups on porphyrin periphery. In the following description, we use the first redox potential of the free base porphyrins as a measure of the electron-withdrawing power of the substituents.

Table 1 lists the electronic absorption spectral data of four complexes and Figs. 1—4 illustrate the electronic and MCD spectra.

The electronic absorption spectra in Figs. 1a—4a exhibit complicating features in the visible Q-band region. The β band of Fe(mtfp)(*N*-MeIm)$_2$ and both of the α and β bands of Fe(btfp)(*N*-MeIm)$_2$ are distinctly split. These iron(II) porphyrin complexes represent a novel instance having a markedly split peak of the β band at room temperature.

Since heme orientational isomerism and any interactions with amino-acid residues[1d] are not present in the protein-free iron(II) porphyrin complexes studied here, the Q-band splitting thus observed is an inherent feature of the complexes. The mtfp and btfp complexes with split Q-bands are lower in symmetry than the etpI and ttfp complexes without them. The π electron density distribution on porphyrinato core would be markedly asymmetric in the mtfp and btfp complexes because their porphyrins are asymmetrically substituted for CF_3 groups with a highly electron-withdrawing ability. This remakable asymmetry can lead to the splitting of Q-bands in the electronic spectra of the mtfp and btfp complexes, because the Q-bands correspond to degenerate π–π^* transitions.

The ratio of absorption intensity, Q(0,0)/Q(1,0) for metalloporphyrins and $[Q_x(0,0)+Q_y(0,0)]/[Q_x(1,0)+Q_y(1,0)]$ for free base porphyrins, provides a useful measure of the splitting in the HOMOs (a_{1u} and a_{2u}), as suggested by

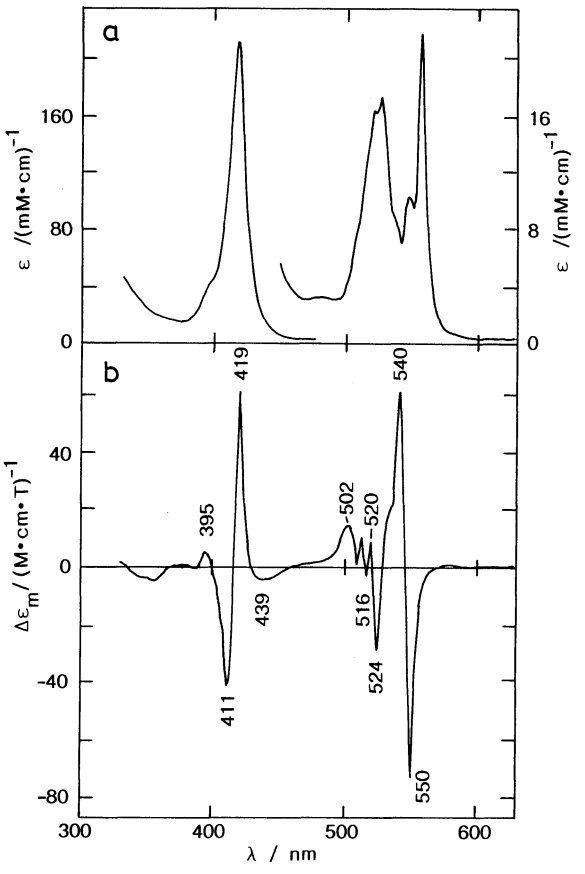

Fig. 3. Electronic (a) and MCD spectra (b) of Fe(btfp)-(*N*-MeIm)$_2$ in CH_2Cl_2 at room temperature. [Fe(btfp)(*N*-MeIm)$_2$]=0.0118 mM.

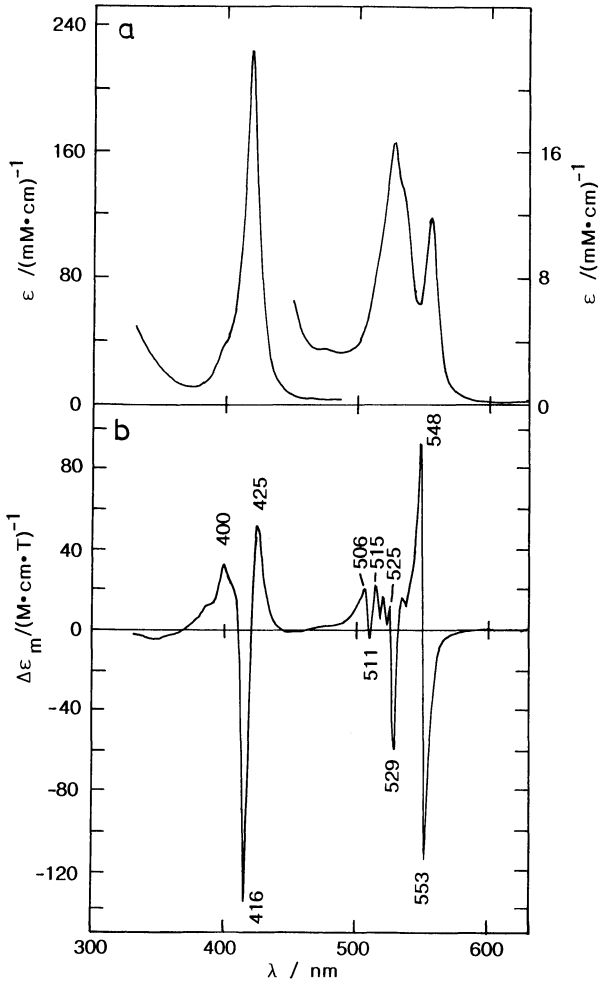

Fig. 4. Electronic (a) and MCD spectra (b) of Fe(ttfp)-(*N*-MeIm)$_2$ in CH_2Cl_2 at room temperature. [Fe(btfp)(*N*-MeIm)$_2$]=0.0118 mM.

Table 2. Ratios of Visible Absorption Band Intensity of Free Base Porphyrins and Fe(Porph)(*N*-MeIm)$_2$

Porph	$E_{1/2}$(I)[b]	$\varepsilon(\alpha)/\varepsilon(\beta)$[a]	
	V	Porph	Fe(Porph)(*N*-MeIm)$_2$
etpI	−1.39	0.76	1.8
mtfp	−1.22	0.79	1.8
btfp	−1.08	0.62	1.3
ttfp	−0.81	0.41	0.71

a) Q(0,0)/Q(1,0) for Fe(II) complexes; $[Q_x(0,0)+Q_y(0,0)]/[Q_x(1,0)+Q_y(1,0)]$ for free base porphyrins. b) The first redox potentials of free base porphyrins. Ref. 7.

Spellane et al.[13] These ratios are given in Table 2 for the free base porphyrins and the iron(II) porphyrin complexes, together with the first redox potentials of the free base porphyrins. As shown in Table 2, the ratio of absorption intensity almost linearly decreases from mtfp to btfp and ttfp and also in their iron(II) complexes, as the redox potential becomes positive. This suggests the splitting in the HOMOs (ΔHOMO) decreases with an increase of the number of CF_3 group. This result can explain from the electron density distribution in a_{1u} and a_{2u} orbitals. Pyrrole β positions of octaalkylporphyrins such as etpI and oep are occupied by the alkyl groups with an electron-donating ability. In these porphyrins, the a_{1u} orbital should be higher in energy than the a_{2u} orbital, because the a_{1u} has appreciable electron density and the a_{2u} has negligible density at the pyrrole β positions.[14] Consequently, the introduction of CF_3 group with a highly electron-withdrawing ability to the pyrrole β position of an octaalkylporphyrin should result in the lowering the orbital energy of a_{1u} toward that of a_{2u} or in the decrese of ΔHOMO.

The absorption intensity ratio of mtfp can be expected to be lower than that of etpI. However, Table 2 shows that the ratios of etpI and mtfp and their iron(II) complexes are similar. This may be explained as follows. The lowering of a symmetry arising from the asymmetrical substitution on porphyrin periphery can result in a broadening of the β band[1], and concomitant decrease in the peak height, which increases the absorption intensity ratios of mtfp and btfp. As a result, the ratio of mtfp appears to be similar to that of etpI.

The overall MCD spectral pattern of Fe(etpI)(*N*-MeIm)$_2$ (Figure 1b) is similar to those of low-spin bis(1-methylimidazole)iron(II) complexes of protoporphyrin IX dimethyl ester, octaethylporphyrin, and iron(II) cytochrome b_5.[15,16] The positive extremum (at 412 nm) and the negative one (at 425 nm) of Fe(etpI)(*N*-MeIm)$_2$ in the Soret region are much more intense than those of the latter complexes and are comparable to those of ferrous cytochrome *c*.[17] The difference in intensity in the Soret region of the bis(1-methylimidazole)iron(II) porphyrin complexes would arise from a difference of porphyrinato ligand.

It has been demonstrated that the MCD spectra of cytochrome *c* and b_5 in the reduced state are composed of apparent Faraday A term coupled with B term in the Soret band region and of A term in the α band.[17] As shown in Figures 1b—4b, the α band of four complexes has a derivative shape characteristic of A term MCD band, while the shape of Soret band appears to differ for each complexes.

All the MCD bands shift to longer wavelength side with an increase in the number of CF_3 group on porphyrin periphery in analogy with the electronic spectral bands. The α band in intensity and the β band in splitting pattern remakably varies depending on the porphyrinato ligand. Thus, MCD spectral features corresponding to the Q-band splittings in electronic spectra are not differentiated. In the Soret region, the 389 nm peak and 403 nm trough of Fe(etpI)(*N*-MeIm)$_2$ shift, respectively, to 391 and 406 nm of mtfp complex, to 395 and 411 nm of btfp complex, and to 400 and 416 nm of ttfp complex, accompanying the increase in intensity. Concomitantly, the 412 nm peak of Fe(etpI)(*N*-MeIm)$_2$ shifts to 415 nm, to 419 nm, and to 425 nm; and the 425 nm trough of the etpI complex is profoundly weakened with an increase in CF_3 number and it is appeared at 430, 439, and 447 nm in mtfp, btfp, and ttfp complex, respectively. Consequently, the minus-plus-minus band pattern with decreasing wavelength in the Soret MCD spectrum of etpI complex is apparently inverted in the sign of the spectrum of ttfp complex if weak 389 nm peak in etpI complex and weak 447 nm trough in ttfp complex are ignored.

The sign variation in the MCD spectra of free base porphyrins and metalloporphyrin complexes has been extensively investigated by Keegan et al.[18] and it has been interpreted in terms of the Michl's perimeter model.[19] According to their studies, the sign of the MCD is determined by the relative magnitudes of the orbital splittings, ΔHOMO and ΔLUMO; if ΔHOMO is larger than ΔLUMO, normal MCD sign pattern (Q band, $-+$ and Soret band, $-+$, with increasing energy) is expected and if ΔLUMO is larger, inverted MCD sign pattern ($+--+$ or $+-+-$) is expected. It has not been reported that the sign is normal in Q band and is inverted in Soret band or that the sign pattern is $-++-$.[20] As shown in Figs. 1b—4b, both α and β band exhibit normal sign pattern. Then, Soret band would have the normal sign. Accordingly, the 389 nm peak in the etpI complex and the 447 nm trough in the ttfp complex should not be ignored. It is concluded that this 'apparent' spectral investion in the Soret region as observed in this study results from both the shifts of peak and trough in wavelength and the change in intensity. As described before, although the ΔHOMO in the ttfp complex with four CF_3 groups on the periphery is the smallest in the complexes studied here, the ΔHOMO can be rather larger than the ΔLUMO.

Svastits and Dawson have demonstrated that the sign of MCD spectra of Fe(tpp)(ImH)$_2$ in the Soret region is inverted as compared to that of spectra of the ppixdme and oep complexes[16] which is assigned to be normal. Since the MCD sign of Q band in Fe(tpp)(*N*-MeIm)$_2$ is normal ($-+$),[21] this inversion in the Soret region appears to be 'apparent' as described above.

In summary, the bis(1-methylimidazole)iron(II) complexes of porphyrins substituted with CF_3 groups exhibit the splittings of Q-bands in the electronic spectra. The splittings may arise from asymmetrical electronic effects of the highly electron-withdrawing CF_3 group on the porphyrin periphery. In the similar manner, *cis*-effects arising from the hydrophobic interaction of heme periphery with amino acid residues of the protein,[22] as

well as well-established *trans* effects,[1d,e] possibly contribute to the splitting and broadening of Q-bands in the electronic spectra of ferrous hemoproteins. The MCD spectra of the bis(1-methylimidazole)iron(II) porphyrin complexes are markedly sensitive to the porphyrin peripheral substituents. The MCD spectra in Soret region successively changes in shape with the number of CF_3 group on porphyrin periphery and consequently are inverted in sign. This apparent sign inversion can be explained by the shift of maximal wavelength accompanied by a change in intensity.

We wish to thank Dr. S. Suzuki of the College of General Education, Osaka University for measurement of MCD spectra and for interesting and helpful discussions. The research was supported in part by a grant from the Yamagata Technopolis Foundation.

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8) Abbreviations: MCD, magnetic circular dichroism; mtfp, dianion of 1-trifluoromethyl-2,3,4,5,6,7,8-heptaethyl porphyrin; btfp, dianion of 1,8-bis(trifluoromethyl)-2,3,4,5,6,7-hexaethyl porphyrin; ttfp, dianion of 1,3,5,7-tetrakis(trifluoromethyl)-2,4,6,8-tetraethyl porphyrin; etpI, dianion of etioporphyrin I or 1,3,5,7-tetramethyl-2,4,6,8-tetraethyl porphyrin; oep, dianion of octaethylporphyrin; ppixdme, dianion of protoporphyrin IX dimethyl ester; tpp, dianion of *meso*-tetraphenylporphyrin; ImH, imidazole; *N*-MeIm, 1-methylimidazole.

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