# Synthesis and Coordination Behaviors of New Double-Sided Porphyrinatoiron(II) Complexes: Effect of the Pocket-Size for Imidazole on Dioxygen Binding

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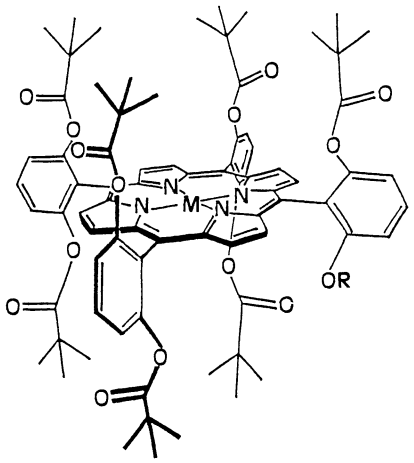
The synthesis and characteristic ligation behaviors of new "double-sided porphyrinatoiron(II) complexes" having two pockets of different spacing-size on each side of a ring plane and a larger sized one on both sides of a macrocycle, are described. The equilibrium constants for the imidazole derivatives to the four-coordinated porphyrinatoiron(II)s were increased in proportion to the size of the pocket-space, which is reflected by the $\Delta H$ term. The five-coordinated complexes of the porphyrinatoirons, obtained by the addition of 1,2-dimethylimidazole (1,2-dmin) in a toluene solution, formed stable and reversible dioxygen adducts at 25 °C. The oxygen affinities for the iron(II) complexes increased as the steric bulk on the rear side of the porphyrin plane was relieved. These changes in the oxygen affinity are attributed to the strength of the $\pi$-electron donation from the imidazole to the central iron ion.

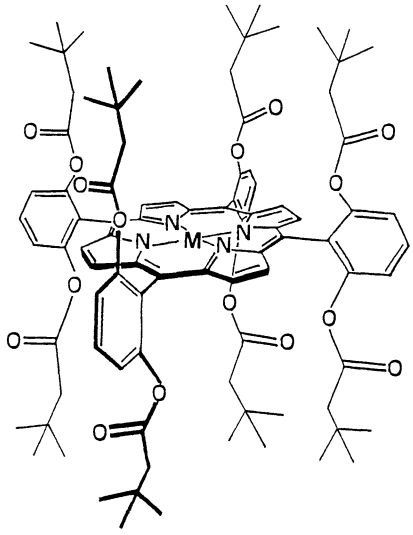
Simple porphyrinatoiron(II)s are well known to react rapidly with dioxygen to form irreversible $\mu$-oxo-iron(III) dimers. A number of synthetic analogs of oxygen-carrying hemoproteins have been synthesized to inhibit such undesirable bimolecular reactions and have demonstrated a dramatic variation in $O_2$ affinities due to the nature of the pocket structure and/or the effect of the proximal base.[1-9]

Single-face highly modified porphyrinatoiron(II)s (picket-fence, capped, and pocket porphyrins) having an appropriate cavity on the ring plane, bind dioxygen reversibly in aprotic organic solvents containing an excess of axial base; their dioxygen adducts are stable against irreversible oxidation.[1-5] However, these iron(II) complexes have a very short lifetime under conditions in which the axial base concentration is very low, since the $\mu$-oxo dimer can be formed through the unprotected side of a heme.

It is therefore necessary to modify the rear side of the porphyrin plane; the proximal imidazole binding site. Both-faces hindered porphyrinatoiron(II) (bis-pocket and basket-handle porphyrin) have been synthesized in order to sterically prevent irreversible oxidation and to perform a unique feature for dioxygen binding.[3,4] The preparation of such derivatives, however, is generally not easy and the yield is rather low.




| R; | | -H | -C(=O)C(CH3)3 |
|---|---|---|---|
| M; | H | 1a | 3a |
| | Fe(III) | 1b′ | 3b′ |
| | Fe(II) | 1b | 3b |



| M; | H | 2a |
|---|---|---|
| | Fe(III) | 2b′ |
| | Fe(II) | 2b |

On the other hand, in recent years many of the dioxygen-carrier model derived from 5,10,15,20-tetrakis(*o*-aminophenyl)porphyrin have amide residues, which have been suggested to interact with bound dioxygen (hydrogen bonding, local polarity effect, etc.) and to contribute to the stability of oxygen-adduct formation.[1-3,7] In some cases, the oxygen-binding affinity of the porphyrinatoiron complex is surely affected by the polarity of the environment around the binding site.[2-4]

We recently reported a new methodology for the synthesis of both-faces hindered and highly symmetric porphyrin, 5,10,15,20-tetrakis[2,6-bis(pivaloyloxy)phenyl]porphyrinatoiron (**3b**), which is much simpler and gives higher yields in comparison with the previous models.[10] Our results have shown that an ester-fenced porphyrin without amide groups can form a stable, reversible dioxygen adduct at 25 °C in toluene, suggesting that an electrostatic interaction between the fence residues and the bound dioxygen is not essential for the formation of a dioxygen adduct. However, the double-sided porphyrinatoiron(II) and porphyrinatocobalt(II) complexes quantitatively showed a steric hindrance of the bulky ester fences on both sides of the porphyrin plane when axial ligands bind. Generally, $\pi$-electron donation from the axial base to the metal can be varied with the binding character of the base ligand, making it possible for the oxygen-affinities of metalloporphyrins to be controlled by changes in the strength of the metal-base bonding.[3,5,8,9] It is therefore considered that the low oxygen affinity of the **3b** complex can be attributed to a decrease in the $\pi$-electron flow from the axial base to the bound dioxygen due to a steric interaction between the axial base and the bulky ester groups. In order to increase the oxygen affinity of this porphyrin, we designed and synthesized new "double-sided porphyrins", 5,10,15-tris[2,6-bis(pivaloyloxy)phenyl]-20-[(2-hydroxy-6-pivaloyloxy)phenyl]porphyrinatoiron (**1b**) and 5,10,15,20-tetrakis[2,6-bis(3,3-dimethylbutyryloxy)phenyl]porphyrinatoiron (**2b**), each having a larger cavity for axial base binding on the ring plane. Their characteristic ligation properties with imidazole derivatives or dioxygen have been clarified by spectroscopic measurements. We now wish to report on the effects of a steric change in the fences on the rear side of the ring plane, both on the binding of the axial base and on the oxygen affinities for the double-sided porphyrinatoirons.

## Experimental

**General.** A Shimadzu UV-2100 highly-sensitive spectrophotometer equipped with a thermostatted cell holder and bath (±0.2 °C) was used for spectroscopic measurements. Infrared spectra (IR) were taken with a JASCO IR-810 spectrometer. $^1$H NMR and $^{13}$C NMR spectra were recorded on a JEOL GSX-400 instrument. Chemical shifts are expressed in parts per million downfied from $Me_4Si$ as an internal standard. FAB MS spectra were measured with a JEOL DX-303 spectrometer. Elemental analyses were performed on a Yanagimoto MT3 CHN corder. Thin-layer chromatography (TLC) was carried out on 0.2 mm precoated plates of silica gel 60 F-254 (Merck). Products purification was performed by silica gel 60 (Merck) column chromatography. Solvents were evaporated with a type-N2 Tokyo Rikakikai rotary evaporator.

**Materials and Solvents.** 1-Methylimidazole (1-mim) and 1,2-dimethylimidazole (1,2-dmim) were purified before use by distillation in vacuo under reduced pressure. Pivaloyl chloride, 4-(dimethylamino)pyridine, 3,3-dimethylbutyric acid, and thionyl chloride are commercially available as special grade and were used without further purification. Tetrahydrofuran (thf) and toluene were purified immediately before use by distillation from sodium and benzophenone uder argon.

The synthetic routes for the complexes (**1b′**) and (**2b′**) are as follows.

**5,10,15,-Tris[2,6-bis(pivaloyloxy)phenyl]-20-[(2-hydroxy-6-pivaloyloxy)phenyl]porphyrin (1a).** 5,10,15,20-Tetrakis(2,6-dihydroxyphenyl)porphyrin ($H_2T_{(OH)_2}PP$)[10] (1.0 g, 1.35 mmol) and 4-(dimethylamino)pyridine (1.18 g, 9.69 mmol) were dissolved in dry thf (200 ml). To this ice-cooled solution pivaloyl chloride (1.19 cm$^3$, 9.69 mmol) was added dropwise with stirring under an argon atmosphere; the reaction mixture was stirred for 1 h at room temperature. The solution was further stirred for 12 h at 60 °C, then brought to dryness on a rotary evaporator and extracted with $CHCl_3$. The organic layer was washed, first with dilute hydrochloric acid and then with aqueous ammonia. The organic phase dried over anhydrous $Na_2SO_4$ was concentrated and the residue was chromatographed on a silica-gel column using $CHCl_3$–diethyl ether, 10:1 (v/v), as the eluent. The second elution band was collected and reduced to a small volume on a rotary evaporator. The residue was then dried at room temperature for several hours in vacuo to give a purple crystalline product (**1a**) (0.17 g, 9.3%). $R_f$ 0.45 $CHCl_3$–diethyl ether, 10:1 (v/v). Anal. Found: C, 70.45; H, 6.77; N, 4.03%. Calcd for $C_{79}H_{86}N_4O_{15}\cdot H_2O$: C, 70.35; H, 6.58; N, 4.15%. FAB MS $[M]^+$ 1331. IR (KBr); 3450 cm$^{-1}$ ($\nu_{OH}$), 1760 cm$^{-1}$ ($\nu_{CO}$(ester)). $^1$H NMR ($CDCl_3$) $\delta$=−2.9 (2H, s, inner H), −0.5—−1.0 (63H, m, pivaloyl), 7.4—8.0 (12H, m, phenyl H), 8.8 (8H, d, pyrrole $\beta$-H). VIS. ($CHCl_3$) 636, 583, 538, 506, and 412 nm.

**5,10,15-Tris[2,6-bis(pivaloyloxy)phenyl]-20-[(2-hydroxy-6-pivaloyloxy)phenyl]porphyrinatoiron(III) Bromide (1b′).** The synthetic procedure for complex **1b′** was similar to that used for **1a**, except for using 5,10,15,20-tetrakis(2,6-dihyroxyphenyl)porphyrinatoiron bromide ($FeT_{(OH)_2}PP$)[10] (1.0 g). Finally, dark-purple crystalline products **1b′** (83.6 mg, 5.0%) were obtained. $R_f$ 0.25 ($CHCl_3$–$CH_3OH$, 100:1 (v/v)). Anal. Found: C, 65.22; H, 6.30; N, 3.83%. Calcd for $C_{79}H_{84}N_4O_{15}FeBr\cdot 0.5C_6H_6$: C, 65.47; H, 5.83; N, 3.72%. FAB MS $[M-Br]^+$ 1385. IR (KBr); 3450 cm$^{-1}$ ($\nu_{OH}$), 1760 cm$^{-1}$ ($\nu_{CO}$(ester)). VIS. ($CHCl_3$) 680, 649, 586, 507, and 411 nm.

**5,10,15,20-Tetrakis[2,6-bis(3,3-dimethylbutyryloxy)phenyl]-porphyrin (2a).** 3,3-Dimethylbutyric acid (15 cm$^3$, 0.12 mol) was suspended in thionyl chloride (10.0 cm$^3$, 0.11 mol); the mixture was refluxed for 2.5 h and distilled in vacuo: colorless oil, yield 12.1 g (76.2%), bp 58 °C/69 mmHg

(1 mmHg=133.322 Pa). The acid chloride (3.62 g, 26.9 mmol) was added dropwise with stirring to an ice-cooled mixture of $H_2T_{(OH)_2}$ PP (1.0 g, 1.35 mmol) and 4-(dimethylamino)pyridine (3.29 g, 26.9 mmol) in dry thf (200 $cm^3$) under argon. The mixture was stirred further at room temperature for 1 h and at 50 °C for 12 h. The solution was brought to dryness on a rotary evaporator and extracted with $CHCl_3$. The organic layer was washed, first with dilute hydrochloric acid and then with aqueous ammonia. The organic phase dried over anhydrous $Na_2SO_4$ was concentrated and the residue chromatographed on a silica gel column using $CHCl_3$–diethyl ether, 30:1 (v/v), as the eluent. The eluent was collected and reduced to small volume on a rotary evaporator. The residue was then dried at room temperature for several hours in vacuo, to give a purple crystalline product (**2a**) (0.69 g, 33.6%). $R_f$ 0.34 ($CHCl_3$–diethyl ether, 30:1 (v/v)). Anal. Found: C, 70.59; H, 7.33; N, 3.37%. Calcd for $C_{92}H_{110}N_4O_{16}\cdot 0.3CHCl_3$: C, 70.90; H, 7.11; N, 3.58%. FAB MS $[M]^+$ 1526. IR (KBr); 1760 $cm^{-1}$ ($\nu_{CO}$(ester)). $^1H$ NMR ($CDCl_3$) $\delta$=−3.0 (2H, s, inner H), −0.2 (72H, s, $C(C\underline{H}_3)_3$), 1.2 (16H, s, $C(=O)C\underline{H}_2$–), 7.4—7.9 (12H, m, phenyl H), 8.8 (8H, s, pyrrole $\beta$-H). $^{13}C$ NMR ($CDCl_3$) $\delta$=28.6 (methyl), 29.9 (quaternary carbon), 46.0 (methylene), 109.1 (5,10,15,20-C), 130.8 (pyrrole $\beta$-carbon), 146.9 (pyrrole $\alpha$-carbon), 120.2, 128.5, 129.6, 152.0 (phenyl), 169.6 (carbonyl). VIS. ($CHCl_3$) 653, 583, 534, 506, and 413 nm.

**5,10,15,20-Tetrakis[2,6-bis(3,3-dimethylbutyryloxy)phenyl]-porphyrinatoiron(III) Bromide (2b′).** The synthetic procedure for complex **2b′** was similar to that used for **2a**, except for using $FeT_{(OH)_2}$ PP (1.0 g). Finally, dark-purple crystalline products **2b′** (0.22 g, 11.5%) were obtained. $R_f$ 0.61 ($CHCl_3$–diethyl ether, 30:1 (v/v)). Anal. Found: C, 66.73; H, 6.84; N, 3.59%. Calcd for $C_{92}H_{108}N_4O_{16}FeBr$: C, 66.50; H, 6.55; N, 3.37%. FAB MS $[M]^+$ 1661, $[M-Br]^+$ 1580. IR (KBr); 1760 $cm^{-1}$ ($\nu_{CO}$(ester)). VIS. ($CHCl_3$) 675, 644, 577, 506, and 412 nm.

**Iron(II) Complex.** An iron(III) complex (0.1 μmol) was dissolved in toluene (8 $cm^3$) and the solution bubbled with argon to removed any oxygen. Then, a deoxygenated aqueous $Na_2S_2O_4$ solution (8 $cm^3$) was added. The mixture vigorously stirred for 1 h and the red-orange organic layer was collected and dried over anhydrous $Na_2SO_4$. After filtration from $Na_2SO_4$ under argon, a toluene solution of a four-coordinated porphyrinatoiron(II) (20 μmol $dm^{-3}$) was obtained.

**Base Equilibrium Measurement.** The equilibrium constants of the bases were determined at 25 °C under argon by titration of the four-coordinated porphyrinatoiron(II)s with aliqouts of an imidazole derivative in deoxygenated toluene. For the bases there are two possible equilibria, (1) and (2).

$$P + B \overset{K^B}{\rightleftharpoons} P(B) \quad (1)$$

$$P(B) + B \overset{K_B{}^B}{\rightleftharpoons} P(B)_2 \quad (2)$$

When $K_B{}^B$=0, the titration shows isosbestic points. However, no isosbestic ones were observed when the three species (P, P(B), and $P(B)_2$) were simultaneously present. The corresponding thermodynamic parameters ($\Delta H$, $\Delta S$) were calculated using the equilibrium constants at various temperatures and van't Hoff plots. The temperature of the solution was maintained to a precision of ±0.2 °C. In general, porphyrinatoiron(II) concentrations of 20 μmol $dm^{-3}$ were used, and the spectra were recoorded within the range of 650—360 nm.

**Dioxygenation of Porphyrinatoiron(II).** Dioxygenation of porphyrinatoiron(II) complexes can be expressed by equation (3).

$$P(B) + O_2 \overset{K_B{}^{O_2}}{\rightleftharpoons} P(B)O_2 \quad (3)$$

The oxygen-binding affinity (oxygen pressure at half oxygen binding for the porphyrinatoiron(II), ($P_{1/2}(O_2)=1/K_B{}^{O_2}$) was determined from the spectral changes at various partial pressures of dioxygen, using an equation employed by Collman et al.[11] The thermodynamic parameters ($\Delta H$, $\Delta S$) of dioxygenation were calculated by the oxygen-binding affinity at various temperatures, using van't Hoff plots of $\ln(760/P_{1/2}(O_2))$ vs. $1/T$. The temperature of the solution was maintained to a precision of ±0.2 °C. In general porphyrinatoiron(II) concentrations of 20 μmol $dm^{-3}$ were used; the spectra were recorded within the range of 650—360 nm.

## Results and Discussion

In this study, we designed and synthesized new double-sided porphyrinatoiron complexes (**1b** and **2b**), having large pockets for axial base binding on the rear side of the ring plane, respectively. The **1b′** complex, which has four and three pivaloyloxy groups on each side of a macrocycle, was synthesized by the reaction of $FeT_{(OH)_2}PP$ with a 7.2-times molar quantity of pivaloyl chloride. During purification on a silica-gel column, the first band, which was the least polar porphinatoiron, was identified as **3b′**. The **1b′** complex corresponded to the second band. The **2b′** complex was obtained by the coupling of $FeT_{(OH)_2}$ PP with 3,3-dimethylbutyryl chloride. Kyuno et al. reported that picket-fence type porphyrinatocobalt, having only one cavity comprising four 3,3-dimethylbutyryl amides on one side of the ring plane, was easily dissolved in organic solvents and had a higher oxygen affinity than did the picket-fence porphyrinatocobalt.[12]

The identification and structural assignments of these complexs were based on some physicochemical analyses.

The both-faces protected structure must have a similar effect as that of the protein in natural dioxygen carriers (hemoglobin and myoglobin), which forms a hydrophobic pocket around the heme, and inhibits the contact necessary for oxidation reactions. However, axial base binding to porphyrinatoiron is depressed with an increase in the steric bulk of the fences appended to the ring plane. In both planes of highly modified complexes, the effect of a steric hindrance on the protected distal face can be investigated using external nitrogenous ligands bound to the protected face of the porphyrins.[4]

The equilibrium constants were measured for the ligation of the double-sided porphyrinatoirons. Large changes in the absorption spectra occur upon titration of a toluene solution of iron(II) four-coordinate species with imidazole derivatives under an argon atmosphere. For the less-hindered base, 1-mim, these iron(II) complexes bind to a second base more strongly than does the first one due to the accompanying electron-spin changes in going from five- to six-coordinate iron(II) ($K_B^B > K^B$). In the addition of 2-substituted imidazole, 1,2-dmim, to **1b** or **2b**, however, gives only five-coordinate high-spin species cleanly ($K_B^B \ll K^B$); well defined isosbestic points are observed in the visible absorption spectra during titration (Figure 1). In order to study the oxygenation equilibrium [equation (3)], the condition must be chosen so as to ensure that the dominant species is the five-coordinate P(B). The values for the equilibrium constants for base additions to complexes **1b** and **2b** are given in Table 1.

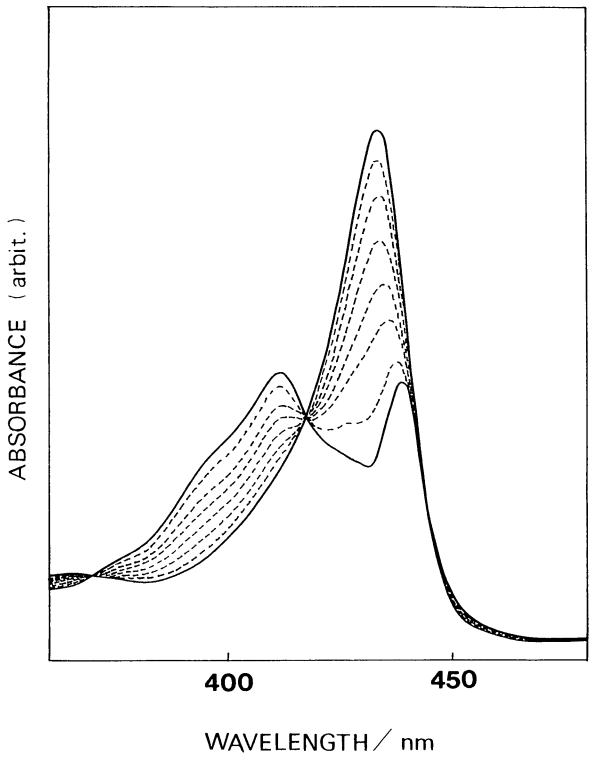



Fig. 1. Visible absorption spectral changes occurring upon titration of a 20 μmol dm$^{-3}$ toluene solution of **2b** with 1,2-dmim (the final base concentration=12.8 mmol dm$^{-3}$) at 25 °C.

In a previous study we reported that the **3b** complex, having two highly modulated cavities on both sides of the porphyrin plane, showed significantly decreased values of $K_B$, due to their great steric hindrance afforded by the 2,6-bis(pivaloyl ester) groups held rigidly around the coordination cavities.[10] These results indicated that **3b** binds nitrogenous bases more weakly than do other unhindered porphyrin complexes.

Table 1 shows that the values of $K^B$ for the binding of 1,2-dmim to each of the three complexes (**1b**, **2b**, and **3b**), having different pocket-space for axial base binding, are increased in the order of pocket-size, **2b**≫**1b**>**3b**. Since the $K^B$ of complex, **1b** is slightly larger than that of **3b**, it can be said that 1,2-dmim distinguishes the two different pockets regarding size and micropolarity on each side of the ring plane in **1b**. The discriminative ligation of 1,2-dmim to this complex must be attributed to a reduction of the steric hindrance by substituting one pivaloyl group by hydrogen and to the polar nature of the rear side. The value of $K^B$ for **2b**, having a large or flexible pocket constructed by 3,3-dimethylbutyryloxy groups is 1.3×10$^3$ (M$^{-1}$) (1 M=1 mol dm$^{-3}$), which is one order of magnitude lower than that for single-face hindered porphyrin (picket-fence porphyrin, etc.) or flat-open TPP. This large $K^B$ value indicates that the unfavorable steric factor on the rear side of **2b** is appreciably weakened.

It is therefore concluded that the coordination of double-sided porphyrin to an axial base can be presumed to be controlled by the nature and structure of the rear side pocket.

Table 1 also gives thermodynamic parameters for

Table 1. Equilibrium Constants and Thermodynamic Parameters for the Binding of Axial Base to Fe(II) Porphyrin Complexes in Toluene at 25 °C

| Porphyrin | Ligand | $K^B$ / dm$^3$ mol$^{-1}$ | $\Delta H$ / kcal mol$^{-1}$[a] | $\Delta S$ / cal K$^{-1}$ mol$^{-1}$ | Ref |
|---|---|---|---|---|---|
| **1b** | 1,2-dmim | 60 | −8.5 | −21 | This work |
| **2b** | 1,2-dmim | 1.3×10$^3$ | −9.8 | −18 | This work |
| **3b** | 1,2-dmim | 36 | −6.9 | −16 | This work |
| TPP | 2-mim[b] | 2.4×10$^4$ | — | — | 11 |
| $T_{piv}PP$[c] | 1,2-dmim | 3.2×10$^4$ | — | — | d) |
| $T_{bp}PP$[e] | 1,2-dmim | 2.7×10$^4$ | — | — | 4 |
| $T_{cap}PP$[f] | 1,2-dmim | 7.9×10$^2$ | −6.1 | −7 | g) |

a) cal=4.184 J. b) 2-mim; 2-methylimidazole. c) $T_{piv}PP$: picked-fence porphyrinatoiron(II). d) Collman et al., *J. Am. Chem. Soc.*, **105**, 3038 (1983). e) $T_{bp}PP$: bis-pocket porphyrinatoiron(II). f) $T_{cap}PP$: capped porphyrinatoiron(II). g) Basolo et al., *J. Am. Chem. Soc.*, **102**, 1889 (1980).

base binding, derived from the van't Hoff plots of $\log K^B$ vs. $1/T$ (15—30 °C). The order of enthalpy changes for 1,2-dmim binding is **3b>1b>2b**, indicating the enthalpy dependence of the free energy changes in this system.

Kyuno et al. discussed the thermodynamic parameters for base and dioxygen binding to four atropisomers of the picket-fence porphyrinatocobalt(II).[12] The higher base affinities of the *trans*-$\alpha^2$ complex, compared with the $\alpha^4$ complex, were due to an increase in the binding energies of the bases, although a substantial decrease in entropy change also occurs. They concluded that the stabilization of the base binding by the pickets was attributed to an intermolecular interaction between the ligated base and the *t*-butyl groups.

Indeed, entropy changes of double-sided porphyrins are small because the orientation of the 1,2-dmim plane is regulated by the fence through the process of binding to porphyrinatoiron. However, the existence of four and three bulky ester residues around the base binding site might overcome, or even cancel out, the advantageous intermolecular stabilization effect of the pocket.

The new double-sided porphinatoiron complexes (**1b** and **2b**) with 1-mim or 1,2-dmim gave stable and reversible dioxygen adducts in toluene at 25 °C. Spectrophotomeric dioxygen titrations of **1b**/1,2-dmim and **2b**/1,2-dmim were carried out under conditions of excess base. The isosbestic points were maintained in all titrations. The dioxygen complex changed to the corresponding CO adduct upon bubbling carbon monoxide gas through the solution. The electron-absorption spectral data are listed in Table 2. The values for $P_{1/2}(O_2)$ were found to be independent of the wavelength used to determined the extent of dioxygenation, and are shown in Table 3 (Figure 2).

For complexes **1b** and **2b**, the bulky ester groups on both sides of the porphyrin plane impede the formation of an intermolecular $\mu$-dioxo dimer, as did **3b**. The $P_{1/2}(O_2)$ values of the double-sided type porphyrins were large compared to those of the corresponding adducts having intermolecular polar amido groups. Our previous study, with regard to **3b** complex, suggested that the unfavorable steric repulsions from bulky fences with imidazole must play a major role in the reduced oxygen-binding affinity.[10]

It is well known that the dioxygen affinities of porphyrinatoiron increase with increasing $\sigma$- and $\pi$-electron donation of an axial ligand.[1-3,8,9] Walker et al. reported that the rotation of 1-mim in *trans*-$\alpha^2$ picket-fence porphyrinatoiron(III)(1-mim)$_2$ was restricted by pivaloyl groups, and that the dihedral angle of the bound 1-mim plane with respect to the Np–Fe–Np

Table 2. Electron-Absorption Spectra of Fe(II) Porphyrin Complexes in Toluene at 25 °C

| Porphyrin | Ligand | $\lambda_{max}$/nm | | |
|---|---|---|---|---|
| | | Deoxy | Oxy | Carbonyl |
| **1b** | None | 565, 532, 438, 410 | — | — |
| | 1-mim | 562, 536, 430 | 546, 423 | 542, 423 |
| | 1,2-dmim | 557, 535, 434 | 543, 423 | 541, 421 |
| **2b** | None | 565, 532, 438, 411 | — | — |
| | 1-mim | 557, 530, 423 | 542, 419 | 538, 419 |
| | 1,2-dmim | 554, 532, 433 | 545, 419 | 535, 419 |
| **3b** | None | 565, 535, 440, 411 | — | — |
| | 1-mim | 561, 535, 429 | 544, 423 | 542, 424 |
| | 1,2-dmim | 558, 535, 436 | 545, 422[a] | 542, 422 |
| $T_{piv}PP$[b] | None | 565, 535, 435, 415 | — | — |
| | 1-mim | 562, 537, 432 | 548, 429 | 542, 427 |
| | 1,2-dmin | 562, 535, 439 | 544, 421 | 542, 424 |

a) At −20 °C. b) See c) of Table 1. Ref. 1.

Table 3. Oxygen-affinity and Thermodynamic Parameters for Oxygenation of Fe(II) Porphyrin Complexes in Toluene at 25 °C

| Porphyrin | Ligand | $P_{1/2}(O_2)$ | $\Delta H$ | $\Delta S$ | Ref |
|---|---|---|---|---|---|
| | | mmHg[a] | kcal mol$^{-1}$[b] | cal K$^{-1}$ mol$^{-1}$ | |
| **1b** | 1,2-dmim | 503 | −13.0 | −43 | This work |
| **2b** | 1,2-dmim | 229 | −14.1 | −45 | This work |
| **3b** | 1,2-dmim | 866 | −9.3 | −31 | 10 |
| $T_{piv}PP$[c] | 1,2-dmim | 38 | −14.3 | −42 | 1 |
| $T_{bp}PP$[d] | 1,2-dmim | 508 | −14.4 | −47 | 4 |
| $T_{cap}PP$[e] | 1,2-dmim | $4.0\times10^3$ | −9.7 | −49 | 5 |

a) mmHg=133 Pa. b) cal=4.184 J. c), d), e) See c), e), f) of Table 1.

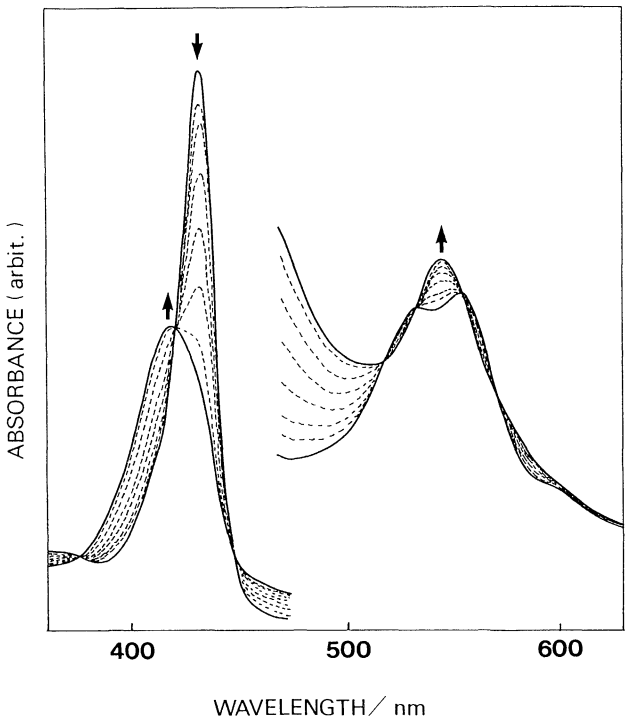



Fig. 2. Visible absorption spectral changes in the dioxygen binding to **2b**/1,2-dmim complex in toluene at 25 °C. Arrows indicate the changes with increasing dioxygen pressures.

direction is equal to 45°.[13] The lobe of the Fe dπ ($d_{xz}$ or $d_{yz}$) orbitals therefore point to the pyrrole nitrogen and the lobe of pπ ($p_x$ or $p_y$) orbitals on the nitrogen of 1-mim point of 135°.

Kyuno et al. suggested that the decreased oxygen affinities of "jellyfish type porphyrinatocobalt(II) complexes" can be attributed to the regulated orientation of 1-mim plane ($\phi$=45°), in which π–π interaction between metal and 1-mim reaches a minimum due to the steric repulsions with appended fence groups.[14] However, the oxygen and carbon monoxide affinities for the corresponding porphyrinatoiron(II) complexes did not exhibit a similar trend to that observed for the oxygen affinities for the Co(II) complexes. They suggested that conformational changes in the cavity, constructed strapped methylene chain, were concerned with reduced oxygen and carbon monoxide affinities.

In the case of the **3b** complex, since the dihedral angle may be equal to 0°, the π-electron donation of 1,2-dmim is expected to be at the maximum because of the maximum π-overlap with the Fe dπ orbitals. Although the favorable orientation of the axial base, accelerating π–π interaction between Fe and the axial base, the $P_{1/2}(O_2)$ values were low in comparison to those of other models.

In order to quantitatively clarify the correlation $P_{1/2}(O_2)$ with the pocket-space on the rear side of the macrocycle for imidazole binding, the oxygen affinities of **1b**, **2b**, and **3b** complexes were compared.

The oxygen-binding affinities of the double-sided porphyrinatoirons were of the order **2b**>**1b**>**3b**, in proportion to the spacing-size of the rear pocket space. This result indicates that oxygen affinities for the iron(II) complexes increased as the unfavorable steric bulk on rear side of the porphyrin plane was relieved. That is, in spite of the orientation of the axial base plane to π-orbital, great steric hindrance of ester fences reduced their π-bond character in the Fe(II)-base. The oxygen affinities decrease in the order of the repulsion of the substituents, and can be controlled by the pocket-size for axial base binding.

On the other hand, the oxygen affinity is surely attributed to the nature of the hydrophobic pocket for dioxygen binding ((1) steric effect, (2) solvation effect, and (3) local polarity).[1–5,15] (1) The steric hindrance significantly influences the $P_{1/2}(O_2)$ of the protected porphyrin. But the "central" and "peripheral" effects, proposed by Basolo, might not be found in the pivaloyloxy type.[5] (2) Among the "protected" heme, a small difference in the solvation effect has no significant meaning on $P_{1/2}(O_2)$. In double-sided porphyrinatoiron complexes, the solvation effects were considered to be almost the same for the other protected models. (3) The polarity of the dioxygen binding site considerably influences the oxygen affinity. From structural studies and $^{17}O$ NMR spectroscopic data of picket-fence porphyrin, though there is no hydrogen-bonding between the amido proton and bound dioxygen, these amide groups can be expected to increase the polarity at the binding site.[7,16] Bis-pocket and ether hanging-base porphyrin which had a nonpolar pocket, showed a low oxygen affinity in comparison to the amide handle derivatives.[3,4] Therefore, the low oxygen affinity of the double-sided porphyrins systems might be the result of a smaller polar pocket effect around the oxygen-binding site. However, from the quantitative results for a series of this type of porphyrins, it is concluded that the oxygen affinity can be controlled by the pocket-size for imidazole binding.

Chang et al. have determined the individual contribution of dipole–dipole interactions in stabilizing the Fe–$O_2$ cmplex.[17] A disadvantageous dipole–dipole orientation may exist between $FeO_2$ and the ester moieties of the double-sided porphyrin.

Table 3 also shows the enthalpy and entropy changes of the dioxygenation equilibrium of the **1b**/1,2-dmim and **2b**/1,2-dmim complex determined from van't Hoff plots (15—30 °C). The thermodynamic values given in Table 3 show that a major difference in dioxygen binding is manifested in the enthalpy terms. Among the double-sided porphyrins, the order of $P_{1/2}(O_2)$ was **3b**>**1b**>**2b**. A similar tendency was also found for the $\Delta H$, indicating the enthalpy dependence of the free energy changes in this

system.

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