



Application of metalloporphyrins and methylviologen-pendent iron porphyrin to reduction of diphenylsulfoxide

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Abstract

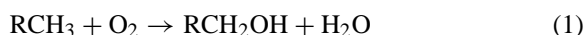
In the two-electron reduction of diphenylsulfoxide to diphenylsulfide, which is considered a model reaction of sulfite reduction catalyzed by sulfite reductase, methylviologen-pendent iron(III) porphyrin exhibits much higher catalytic activity than usual iron(III) and manganese(III) tetraphenylporphyrins, while cobalt(II) tetraphenylporphyrin exhibits much less catalytic activity than the others. Discussion about the active species and the reason of the acceleration by methylviologen-pendent is presented.

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Keywords: Model of sulfite reductase; Methylviologen-pendent; Metalloporphyrin; Diphenylsulfoxide; Two-electron reduction

1. Introduction

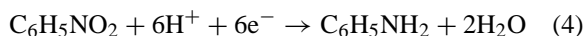
Heme enzymes play biologically important roles, as well known. For instance, cytochrome P-450 catalyzes oxidative hydroxylation of alkane (see Eq. (1)) [1].



Also, nitrite reductase and sulfite reductase, which are typical heme enzymes, too, catalyze six-electron reductions of nitrite (NO_2^-) and sulfite (SO_3^{2-}) (see Eqs. (2) and (3)), respectively [2,3].



The active site of these enzymes is iron hydroporphyrin to which an iron–sulfur cluster is connected through a sulfide bridge [3c,4]. Though a lot of efforts have been made so far to mimic the oxidation catalysis of heme enzyme with synthesized iron porphyrins, only a few attempts have been made to perform the nitrite reduction with a model compound, as follows: Rhodes et al. [5] carried out electrochemical reduction of nitrite with iron(III) porphyrin and EDTA complexes. Also, Arai et al. [6] succeeded reduction of nitrobenzene to aniline (Eq. (4)) with iron(III) porphyrin. This reduction is considered a model reaction of nitrite reduction catalyzed by nitrite reductase, since this reaction involves six-electron reduction like the reduction of nitrite. However, six-electron reduction



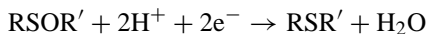
of sulfite with metalloporphyrin has not been investigated yet to our best knowledge except for only one

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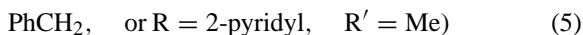
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work in which two-electron reduction of organic sulfoxide (Eq. (5))

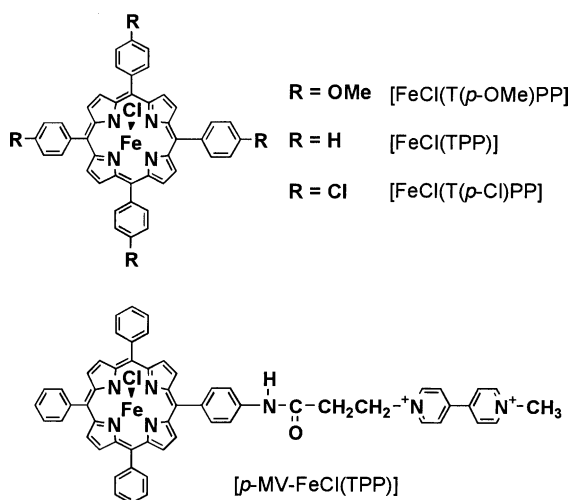


(R = R' = Ph,



was performed with iron(III) porphyrin [7]. However, this reaction was not carried out under mild conditions. Moreover, the yield reported was not very large in spite of very long reaction time. It is of considerable interest to find a good metalloporphyrin catalyst for the reductions of sulfite and organic sulfoxide, since such metalloporphyrin is considered a model of sulfite reductase and also the reduction of SO_x is an important subject of research from the point of view of environmental chemistry.

In the present work, we investigated two-electron reduction of diphenylsulfoxide with manganese(III), cobalt(II), and iron(III) tetraphenylporphyrins and methylviologen-pendent iron(III) porphyrin to find a good metalloporphyrin catalyst for this reduction (see Scheme 1 for these metalloporphyrins). Our intention here is to show that though usual manganese(III), iron(III), and cobalt(II) tetraphenylporphyrins do not catalyze well the reduction of organic sulfoxide the methylviologen-pendent iron(III) porphyrin efficiently catalyzes the reduction of organic sulfoxide and exhibits higher catalytic activity than that reported previously [7].



Scheme 1.

2. Experiments

All the reagents (guaranteed grade) were purchased from Nakarai Chemical Co. Ltd. They were used without further purification unless otherwise indicated. Methanol, tetrahydrofuran (THF), and diethyleneglicol dimethylether (diglyme) were purified through distillation.

2.1. Synthesis

5-{4-(1'-methyl-4,4'-bipyridinium)ethylamido}phenyl-10,15,20-triphenylporphyrin iron trichloride (*p*-MV-FeCl(TPP)): 5-*p*-Nitrophenyl-10,15,20-triphenylporphyrin was synthesized from pyrrole, benzaldehyde, and *p*-nitrobenzaldehyde in acetic acid. It was converted to 5-*p*-aminophenyl-10,15,20-triphenylporphyrin with $\text{SnCl}_2\text{-HCl}$ [8]. Then, 3-bromopropionic acid was introduced to the above porphyrin with dicyclohexylcarbodiimide, to afford 5-(4-bromoethylamido)phenyl-10,15,20-triphenylporphyrin. This porphyrin was combined with 1-methyl-4,4'-bipyridinium iodide to yield 5-{4-(1'-methyl-4,4'-bipyridinium)ethylamido}phenyl-10,15,20-triphenylporphyrin. The resultant porphyrin was metalated with FeCl_3 to afford *p*-MV-FeCl(TPP), according to the usual procedure [9]. Re-crystallization was carried out by dissolving crude crystals to minimum amount of chloroform followed by addition of hexane. Anal. Calcd. for $\text{C}_{58}\text{H}_{43}\text{N}_7\text{OFeCl}_3$: C, 68.55; H, 4.27; N, 9.65%. Found: C, 69.65; H, 4.14; N, 8.84. ^1H NMR for metal-free MV- H_2 (TPP) (400 MHz, DMSO) δ 10.67 (1H, s, -NHCO-), 9.56 (1H, d, 4,4'-bpy), 9.29 (1H, d, 4,4'-bpy) 8.83 (12H, m, pyrrole, 4,4'-bpy), 8.22 (8H, m, Ph-*o,o'*) 8.02 (2H d, Ph-*m'*), 7.85(9H, m, Ph-*m,p*), 5.13(2H, t, -CO-CH₂-), 4.45(3H, s, 4,4'-bpy-CH₃), 3.45 (2H, t, 4,4'-bpy), -2.93 (2H, s, pyrrole-NH).

Other metalloporphyrins were synthesized in usual method [9,10]. [FeCl(T(*p*-OMe)PP)]: Anal. Calcd. for $\text{C}_{48}\text{H}_{38}\text{N}_4\text{O}_4\text{FeCl}$: C, 69.95; H, 4.40; N, 6.80%. Found: C, 70.06; H, 4.39; N, 6.82. [Fe(T(*p*-Cl)PP)]: Anal. Calcd. for $\text{C}_{48}\text{H}_{38}\text{N}_4\text{O}_4\text{FeCl}$: C, 78.68; H, 4.20; N, 8.34%. Found: C, 79.05; H, 4.41; N, 8.31. [FeCl(TPP)]: Anal. Calcd. for $\text{C}_{44}\text{H}_{28}\text{N}_4\text{FeCl}$: C, 75.06; H, 4.01; N, 7.96%. Found: C, 75.17; H, 4.03; N, 8.02. [MnCl(TPP)]: Anal. Calcd. for $\text{C}_{44}\text{H}_{28}\text{N}_4\text{MnCl}$: C, 75.16; H, 4.01; N, 7.96%. Found: C, 75.18; H, 4.12; N, 7.87. [Co(TPP)]: Anal. Calcd. for $\text{C}_{44}\text{H}_{28}\text{N}_4\text{Co}$:

C, 78.68; H, 4.20; N, 8.34%. Found: C, 79.05; H, 4.41; N, 8.31.

2.2. Reduction of diphenylsulfoxide

The reduction of diphenylsulfoxide was carried out at 50 °C in either THF/methanol or diglyme/methanol (3.0 ml) involving metalloporphyrin (0.0113 mmol (3.75 mmol dm⁻³)), diphenylsulfoxide (0.113 mmol) and NaBH₄ (2.7 mmol) under N₂ atmosphere. Small aliquots were withdrawn at appropriate time intervals to analyze the product by a GC equipped with an FID detector (Hitachi G-5000, Ultra Alloy-(8H)5 EX stainless steel capillary column (30 m)),¹ where 1,2,4,5-tetramethylbenzene was used as an internal standard.

3. Results and discussion

3.1. Catalytic activity of usual metalloporphyrins

Iron(III), manganese(III), and cobalt(II) tetraphenylporphyrins catalyze the reduction of diphenylsulfoxide with NaBH₄ to afford diphenylsulfide, as shown in Fig. 1. This reaction does not proceed in the absence of metalloporphyrin. The catalytic activity increases in the order Co(TPP) < FeCl(T(*p*-Cl)PP) < MnCl(TPP) < FeCl(TPP) < FeCl(T(*p*-OMe)PP). This result clearly indicates that iron(III) porphyrin is a better catalyst for the reduction of organic sulfoxide than the other metalloporphyrins.

Interestingly, addition of methanol to THF significantly accelerates this catalytic reduction, as shown in Fig. 2; though the yield of diphenylsulfide (after 6 h) is only 6% in THF/methanol (9:1 v/v), it increases to 27% in THF/methanol (7:3 v/v), where FeCl(T(*p*-OMe)PP) is used as a catalyst. The yield of diphenylsulfide in THF/methanol (5:5 v/v) is similar to that in THF/methanol (7:3 v/v), but the reaction more rapidly proceeds in THF/methanol (5:5 v/v) than that in THF/methanol (7:3 v/v). Though the similar acceleration by methanol was previously reported in the six-electron reduction of nitrobenzene catalyzed

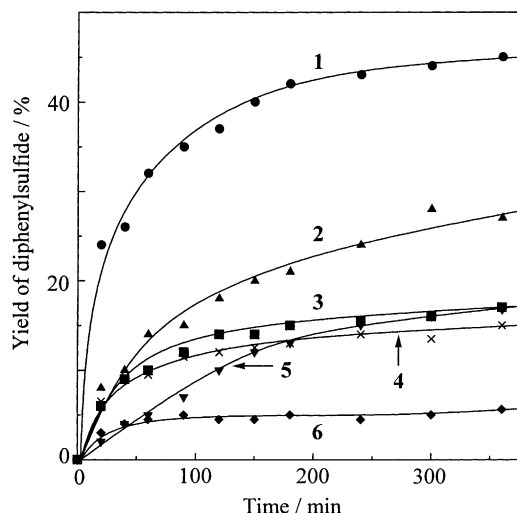


Fig. 1. The reduction of diphenylsulfoxide catalyzed by metalloporphyrins with NaBH₄; *p*-MV-FeCl(TPP) (1), FeCl(T(*p*-OMe)PP) (2), FeCl(TPP) (3), MnCl(TPP) (4), FeCl(T(*p*-Cl)PP) (5), and Co(TPP) (6) in THF/methanol (7:3 v/v) at 50 °C. [Metalloporphyrin] = 3.75 mmol dm⁻³, and metalloporphyrin/NaBH₄/diphenylsulfoxide = 1/240/10 in mole ratio.

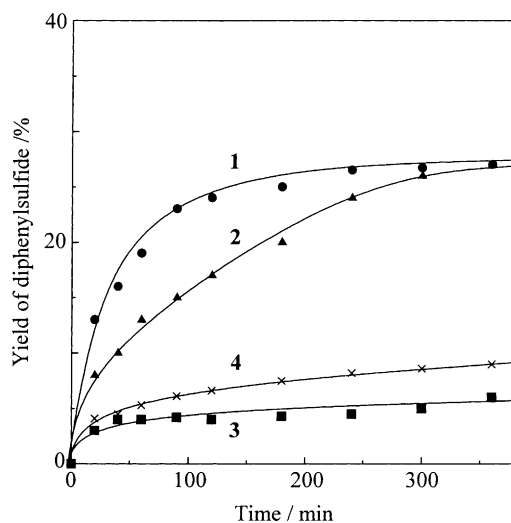


Fig. 2. Reduction of diphenylsulfoxide catalyzed by FeCl(T(*p*-OMe)PP) with NaBH₄ in THF/methanol (5/5 v/v) (1), THF/methanol (7:3 v/v) (2), THF/methanol (9:1 v/v) (3), and diglyme/methanol (7:3 v/v) (4) at 50 °C. [Iron porphyrin] = 3.75 mmol dm⁻³, iron porphyrin/NaBH₄/diphenylsulfoxide = 1/240/10 in mole ratio.

¹ Diphenylsulfoxide could not be analyzed with this GC like that in the previous work [7]. We could not find a good system to analyze both reactant and product.

by FeCl(TPP) [11], the acceleration by methanol has not been noticed yet in the reduction of organic sulfoxide. In the study of the reduction of nitrobenzene [11], one of the present authors (SS) clearly revealed that methanol played a role of proton donor to accelerate the reaction because the reduction of nitrobenzene needs six protons, as shown in Eq. (4). Similarly, the reduction of diphenylsulfoxide needs two protons, as shown in Eq. (5). Thus, it is reasonably proposed here that methanol accelerates the reaction by providing two protons to the substrate. The other interesting solvent effect is that the use of diglyme instead of THF significantly suppresses the reaction, as shown in Fig. 2. The reason will be discussed later in detail.

3.2. Catalytic activity of methylviologen-pendent iron porphyrin

Since iron(III) tetraphenylporphyrin exhibits higher catalytic activity than manganese(III) and cobalt(II) tetraphenylporphyrins, modification of iron(III) tetraphenylporphyrin is one of the reasonable ways to find a good catalyst for the reduction of sulfoxide. One way is to introduce either electron-releasing or electron-withdrawing substituent. Certainly, the introduction of the methoxy group to tetraphenylporphyrin increases the yield, as shown above (see the yield by FeCl(T(*p*-OMe)PP) in Table 1 and Fig. 1). However, the improvement was not significantly large. Here, we adopted the different way, in which we attempted to introduce an electron-trapping and storage unit to

iron(III) tetraphenylporphyrin. One can expect that the catalytic activity for multi-electron reduction is enhanced by the introduction of the electron-trapping and storage unit since sulfite reductase consists of iron hydroporphyrin and iron–sulfur cluster which was proposed not only to be an active site [12] but also to be an electron-trapping and storage unit [13]. Here, we adopted methylviologen as the electron-trapping and storage unit and synthesized methylviologen-pendent iron(III) porphyrin, *p*-MV-FeCl(TPP). Expectedly, *p*-MV-FeCl(TPP) exhibits much higher catalytic activity than usual iron(III) tetraphenylporphyrin, as shown in Table 1 and Fig. 2. The yield of 45% is considerably larger than the previously reported value (38%), since the reaction temperature (50 °C) in this work is much lower and the reaction time (3 h) is much shorter than those (80 °C and 40 h) of the previous work [7]. These results strongly suggest that the introduction of electron-trapping and storage unit is powerful means to improve the catalytic activity of the iron(III) porphyrin for multi-electron reduction. The reason that the methylviologen-pendent accelerates the reduction of diphenylsulfoxide will be discussed later.

3.3. Active species and reaction mechanism

p-MV-FeCl(TPP) shows the broad signal at the *g* value of about 6 in diglyme/methanol (9/1 v/v) in the absence of NaBH₄, as shown in Fig. 3. This is a typical ESR signal of iron(III) porphyrin [14]. Upon addition of NaBH₄ to the solution, this signal disappears and the small signal newly appears at *g* = 2.02. These results indicate that both methylviologen and iron(III) porphyrin moieties undergo one-electron reduction to afford ESR-active one-electron reduced methylviologen and ESR-silent one-electron reduced iron(II) porphyrin [15], respectively. In THF/methanol, ESR signals change in a different manner from that observed in diglyme/methanol, as follows: Though the signal at *g* = 6.0 disappears upon addition of NaBH₄, too, new signals appear at *g* = 2.34 and 1.92 besides the small signal at *g* = 2.02. These new signals agree well with those of two-electron reduced iron(I) porphyrin, [FeCl(TPP)][−] [11,16]. From these results, it is reasonably concluded that the iron(III) porphyrin undergoes two-electron reduction in THF/methanol but one-electron reduction in diglyme/methanol. Since

Table 1
Reduction of diphenylsulfoxide catalyzed by metalloporphyrins with NaBH₄^a

Catalyst	THF/methanol	Yield (%)
No catalyst	7/3	0
Co(TPP)	7/3	6
MnCl(TPP)	7/3	17
FeCl(T(<i>p</i> -Cl)PP)	7/3	15
FeCl(TPP)	7/3	17
FeCl(T(<i>p</i> -Ome)PP)	9/1	6
	7/3	27
	5/5	27
	7/3	8 ^b
<i>p</i> -MV-FeCl(TPP)	7/3	45

^a [Metalloporphyrin] = 3.75 mmol dm^{−3}, [cat.]: NaBH₄: substrate = 1: 240: 10, 6 h at 50 °C.

^b Solvent is diglyme/methanol (7/3 v/v).

the iron(III) porphyrin exhibits much higher catalytic activity in THF/methanol than in diglyme/methanol (vide supra), the above results of ESR study suggest that the iron(I) porphyrin is an active species for the reduction of organic sulfoxide.

The $\text{Fe}^{(\text{I}/\text{II})}$ and $\text{Fe}^{(\text{II}/\text{III})}$ redox potentials of *p*-MV-FeCl(TPP) are -1.09 V and -0.05 V (versus Ag/AgCl), respectively, while the reduction potential of diphenylsulfoxide is -2.17 V (versus Ag/AgCl).² Thus, the simple electron transfer from the iron(I) porphyrin to diphenylsulfoxide can not occur. One of the most conceivable processes is that the reduction of diphenylsulfoxide occurs via its coordination with the iron center. The similar coordination of organic sulfoxide with the iron center was proposed by Nagata et al. [7].³ Since the redox potentials of $\text{MV}^{0/+}$ and $\text{MV}^{+/2+}$ in *p*-MV-FeCl(TPP) are -0.85 V and -0.37 V (versus Ag/AgCl), respectively, one- or two-electron reduced methylviologen moiety can supply one-electron to the iron(III) porphyrin moiety which is formed through two-electron transfer to organic sulfoxide from the iron(I) porphyrin moiety. If the methylviologen-pendent was not bound with the iron(III) porphyrin, the reverse electron transfer from the intermediate to the iron(III) porphyrin moiety would occur. This reverse electron transfer retards the reduction of diphenylsulfoxide. Thus, it is reasonably concluded that the methylviologen-pendent suppresses this reverse reaction, to enhance the catalytic activity.

In conclusion, methylviologen-pendent iron porphyrin exhibits much higher catalytic activity for the reduction of organic sulfoxide than the usual metalloporphyrin, in which the methylviologen-pendent is considered to play a role of electron-trapping and storage unit. This porphyrin is expected to be an efficient catalyst for various multi-electron reduction reactions.

² All redox potentials were measured with PS-06 (Toho Technical Research Co. Ltd.) in THF/methanol (1/1 v/v) under Ar atmosphere, where glassy carbon and Pt wire were used as a working electrode and a counter electrode, respectively. Ag/AgCl was employed as a reference electrode. *n*-Tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) was used as a supporting electrolyte.

³ Though iron(II) porphyrin was proposed to be an active species by Nagata et al. [7], iron(I) porphyrin is proposed here to be an active species from the ESR study. This difference is not unreasonable, since the polar solvent used here stabilizes the two-electron reduced iron(I) porphyrin species compared to less polar toluene and the similar solvents used in the previous work [7].

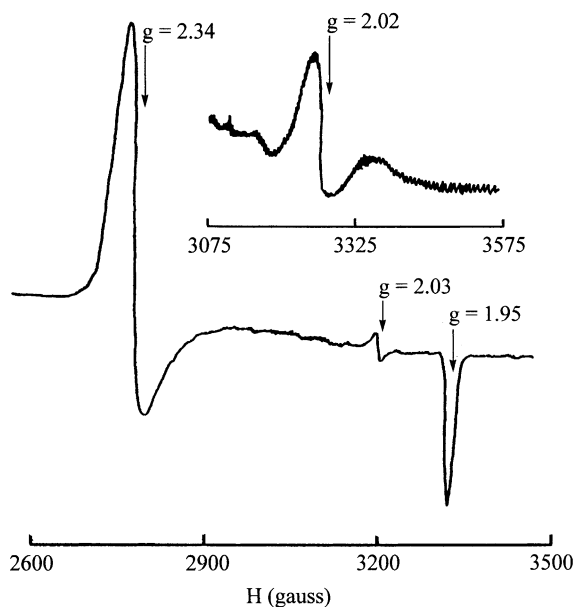


Fig. 3. ESR spectra of *p*-MV-FeCl(TPP) with NaBH_4 in THF/methanol at 77 K. Inset is *p*-MV-FeCl(TPP) with NaBH_4 in diglyme/methanol.

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