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Methylviologen-pendant iron porphyrins as models of a reduction enzyme: six-electron reduction of nitrobenzene to aniline †

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Methylviologen-pendant iron porphyrins, in which methylviologen was introduced to the *meso*-phenyl group through an amido-bridge at either the *p*- or *m*-position, were newly synthesized, in expectation that these methylviologen-pendant iron porphyrins would be good functional models of a multi-electron reductase such as nitrite reductase since the methylviologen-pendant can play the role of an electron-trapping and storage unit like the iron–sulfur cluster of the nitrite reductase. These iron porphyrins were successfully applied to the six-electron reduction of nitrobenzene to aniline, which is a model reaction of nitrite reduction to ammonia catalyzed by nitrite reductase. Both *p*- and *m*-methylviologen-pendant iron porphyrins give somewhat larger yields of aniline in the reduction of nitrobenzene and much larger yields of *p*-methoxyaniline in the reduction of *p*-nitroanisole than does normal iron tetraphenylporphyrin. Though normal iron tetraphenylporphyrin can not catalyze well the reduction of *p*-nitroanisole in the presence of the dioxygen molecule, these methylviologen-pendant iron porphyrins can catalyze well the reduction of *p*-nitroanisole and give a considerably larger yield of *p*-methoxyaniline even in the presence of the dioxygen molecule. These methylviologen-pendant iron porphyrins give a much larger yield of aniline in the reduction of nitrosobenzene and somewhat larger yield of aniline in the reduction of phenylhydroxylamine than does iron tetraphenylporphyrin. *m*-Methylviologen-pendant iron porphyrin exhibits higher catalytic activity than does the *p*-pendant one. The role of methylviologen moiety is discussed, based on cyclic voltammograms and UV-VIS spectra of these iron porphyrins.

Metalloporphyrins play biologically important roles in many metalloenzymes, as well known. In many cases, their biological reactions take place with electron injection and/or electron ejection. One of the interesting features to be noted is that some of heme enzymes efficiently catalyze multi-electron reduction reactions in which many electrons are successively supplied to substrate. For instance, oxianions such as NO_3^-, NO_2^-, SO_3^-, *etc.* undergo multi-electron reduction by heme enzymes,[1–5] as shown by eqn. (1) and (2).

$$NO_2^- + 8H^+ + 6e^- \longrightarrow NH_4^+ + 2H_2O \quad (1)$$

$$SO_3^{2-} + 7H^+ + 6e^- \longrightarrow HS^- + 3H_2O \quad (2)$$

$$\text{1,2-dibromocyclohexane} + 2e^- \longrightarrow \text{cyclohexene} + 2Br^- \quad (3)$$

Though a lot of efforts have been made so far to mimic oxidation catalysis of such heme enzyme as cytochrome P-450,[6] only limited attempts have been made to mimic the multi-electron reduction catalysis of metalloenzymes.[7–11] Since such multi-electron reduction is one of the important biological functions of enzymes, it is interesting and worthwhile to synthesize a model compound of a metalloenzyme that can perform multi-electron reduction. Pioneering work was reported by Meyer and his collaborators.[7] They succeeded electrochemical six-electron reduction of nitrite anion (NO_2^-) to ammonia with $[Fe(H_2O)(TPPS)]^{3-}$ (TPPS = *meso*-tetrakis(*p*-sulfonato-phenyl)porphyrinate). Watson and his collaborator also carried out photoreduction of nitrate anion (NO_3^-) to NO_2^- with MnCl(TPP) and FeCl(TPP) (TPP = tetraphenylporphyrinate).[8] Savéant and his collaborators electrochemically performed two-electron reduction of organic dibromide with M(OEP) (M = Zn, Cu, Ni, or Fe; OEP = octaethylporphyrinate), as shown by eqn. (3).[9] Oae *et al.* reported reduction of sulfoxide [eqn. (4)] with FeCl(TPP), where $NaBH_4$ and 1-benzylnicotinamide were used as a reductant.[10]

$$RSOR' + 2H^+ + 2e^- \longrightarrow RSR' + H_2O \quad (4)$$

One of the present authors (SS) also reported six-electron reduction of nitrobenzene to aniline [eqn. (5)] with FeCl(TPP), where $NaBH_4$ was used as a reductant.[11] This reaction is considered a good model of eqn. (1) which is carried out by nitrite reductase, since both reactions involve six-electron reduction.

$$Ph–NO_2 + 6H^+ + 6e^- \longrightarrow Ph–NH_2 + 2H_2O \quad (5)$$

Electrochemical reductions of dioxygen molecule and carbon dioxide were carried out with metalloporphyrins as a catalyst, too.[12–18] Not only metalloporphyrins but also similar transition-metal complexes such as edta complexes,[19,20] macrocyclic complexes,[21] and iron–sulfur cluster complexes[22–24] have been applied to multi-electron reductions of oxianions and organic halides.

Though metalloporphyrins have been applied to multi-electron reduction as a catalyst in the above mentioned reports, the electron-trapping and storage moiety has not been taken into consideration in constructing the metalloporphyrin catalysts. Considering that typical multi-electron reduction enzymes such as nitrite reductase and sulfite reductase consist of heme and iron–sulfur cluster[25–29] and that the iron–sulfur

† Electronic supplementary information (ESI) available: time-courses of reduction, UV-VIS spectral changes, cyclic voltammograms, EPR spectra, conversion and yield percentages for the reduction of *p*-nitroanisole. See http://www.rsc.org/suppdata/dt/b2/b211125j/

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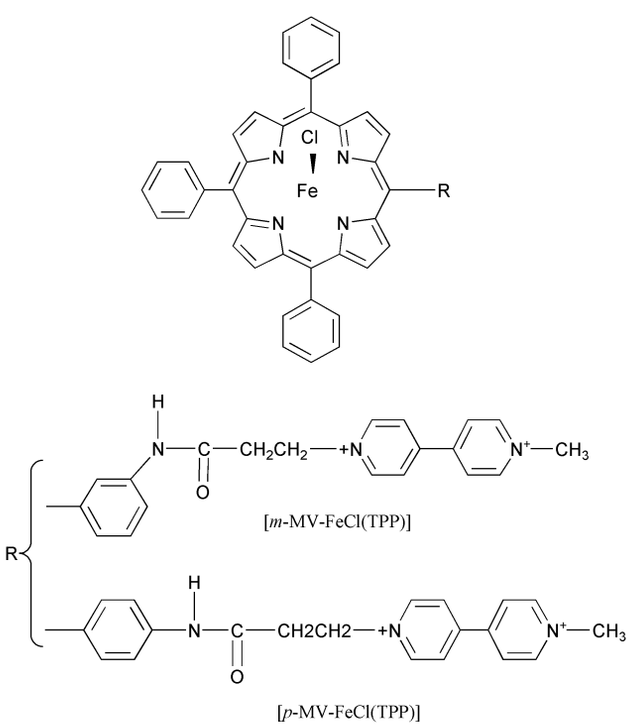
cluster was proposed to play not only the role of an active site[30] but also the role of an electron-trapping and storage unit,[5] we can expect that an excellent catalyst for multi-electron reduction is formed by introducing an electron-trapping and storage moiety to the metalloporphyrin. Recently, many metalloporphyrins which were introduced electron donor and/or electron acceptor were synthesized to achieve the long-lived charge-separation state.[31,32] However, those metalloporphyrins have not been applied to multi-electron reduction, to the best of our knowledge.

In our preliminary work,[33] we synthesized a methylviologen-pendant iron porphyrin, since the methylviologen-pendant was expected to play the role of an electron-trapping and storage moiety, and successfully applied it to six-electron reduction of nitrobenzene to aniline [eqn. (5)]. In that porphyrin, the methylviologen moiety was introduced at the *p*-position of *meso*-phenyl group. In the present work, we wish to present detailed report of the six-electron reduction of nitrobenzene by the methylviologen-pendant iron porphyrins in which the methylviologen moiety is introduced at either the *p*- or *m*-position of the *meso*-phenyl group (see Scheme 1). Our purposes here are to show whether or not the reduction catalysis of metalloporphyrin is enhanced by introduction of methylviologen moiety to the porphyrin, to clarify what is an active species, to investigate the dependence of the catalytic activity on the pendant position and to elucidate what role the methylviologen-pendant plays in the catalytic reaction. It is our intention here to present an efficient functional model of nitrite reductase which catalyzes multi-electron reduction.



Scheme 1

Experimental

Materials

All the reagents (guaranteed grade) were purchased from Nakarai Chemical Co. Ltd. and used without further purification unless otherwise indicated. Methanol, diethylene glycol dimethylether (diglyme) and nitrobenzene were purified through distillation. *p*-Nitroanisole was purified through recrystallization. Phenylhydroxylamine was synthesized from nitrobenzene with activated zinc metal.[34]

Synthesis

5-*m*-Aminophenyl-10,15,20-triphenylporphyrin (*m*-NH_2-TPP). 5-*m*-Nitrophenyl-10,15,20-triphenylporphyrin (*m*-NO_2-TPP) was synthesized from pyrrole (35 ml; 0.5 mmol), benzaldehyde (38.2 g; 0.375 mmol) and *m*-nitrobenzaldehyde (19 g; 0.125 mmol) in acetic acid, according to the previous report.[35] Purple crystals were obtained through filtration followed by washing with methanol. Purification was carried out with silica gel column chromatography, where chloroform/hexane (7/3 v/v) was employed as eluent. Yield was 490 mg (1.1%). Found: C, 76.39; H, 4.80; N, 9.49. Calc. for $C_{44}H_{29}N_5O_2$ $2H_2O$: C, 75.96; H, 4.78; N, 10.07%. NMR chemical shift: δ_H (400 MHz; $CDCl_3$; $SiMe_4$) 9.13 (1H, s, Ph-*o*″), 8.88 (8H, m, pyrrole), 8.73 (1H, d, Ph-*o*′), 8.60 (1H, d, Ph-*p*′), 8.24 (6H, m, Ph-*o*), 7.96 (1H, t, Ph-*m*′), 7.75 (9H, m, Ph-*m*,*p*), −2.81 (2H, s, pyrrole-NH).

The *p*-nitro analogue was synthesized in a similar way. Found: C, 80.17; H, 4.40; N, 10.35. Calc. for $C_{44}H_{29}N_5O_2$: C, 80.10; H, 4.43; N, 10.62%. NMR chemical shift: δ_H (400 MHz; $CDCl_3$; $SiMe_4$) 8.86 (8H, m, pyrrole), 8.66 (2H, d, Ph-*m*′), 8.41 (2H, d, Ph-*o*′), 8.22 (6H, d, Ph-*o*), 7.79 (9H, m, Ph-*m*,*p*), and −2.80 (2H, s, pyrrole-NH).

m-NO_2-TPP (150 mg; 0.68 mmol) was converted to *m*-NH_2-TPP with $SnCl_2$ (350 mg; 1.53 mmol) at 70 °C for 1 h in conc. HCl (6.5 ml).[35] After the solution was cooled to 5 °C, its pH was adjusted to 10.0 by adding conc. ammonia aqueous solution (10 ml). Then, chloroform (40 ml) was added to the solution, which was washed with water and dried with sodium sulfate. Finally, the purple crystals were obtained through silica gel column chromatography [eluent = chloroform/hexane (7/3 v/v)]. Re-crystallization was carried out by dissolving the crystals to minimum amount of chloroform followed by addition of hexane. Yield was 113 mg (78%). Found: C, 82.45; H, 5.17; N, 10.36. Calc. for $C_{44}H_{31}N_5$: C, 83.91; H, 4.96; N, 11.12%. NMR chemical shift: δ_H (400 MHz; $CDCl_3$; $SiMe_4$) 8.85 (8H, m, pyrrole), 8.20 (6H, m, Ph-*o*), 7.76 (9H, m, Ph-*m, p*), 7.62 (1H, t, Ph-*m*′), 7.50 (1H, d, Ph-*o*′), 7.41 (1H, d, Ph-*p*′), 7.13 (1H, s, Ph-*o*″), 4.11 (2H, s, NH_2), −2.82 (2H, s, pyrrole-NH).

The *p*-amino analogue was synthesized in a similar way. Found: C, 84.44; H, 5.11; N, 11.03. Calc. for $C_{44}H_{31}N_5$: C, 83.91; H, 4.96; N, 11.12%. NMR chemical shift: δ_H (400 MHz; $CDCl_3$; $SiMe_4$) 9.02 (8H, m, pyrrole), 8.39 (6H, d, Ph-*o*), 8.15 (2H, d, Ph-*o*′), 7.93 (9H, m, Ph-*m*,*p*), 4.37 (2H, s, –NH_2), 7.20 (2H, d, Ph-*m*′), −2.58 (2H, s, pyrrole-NH).

5-{3-(3-Bromoethylcarboxyamidyl)phenyl}-10,15,20-triphenylporphyrin (*m*-Br-TPP). Chloroform solution of *m*-NH_2-TPP (144 mg; 0.23 mmol), 3-bromopropionic acid (58.5 mg; 0.38 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (81 mg; 0.39 mmol) was stirred at 5 °C for 4 h and then at 25 °C for 24 h. The crude crystals were obtained by removing solvent with evaporator under reduced pressure. They were dissolved into ethylacetate, and then urea was removed by filtration. From the filtrate, the purple crystals were obtained through silica gel column chromatography [eluent = chloroform/dichloromethane (8/2 v/v)]. Re-crystallization was carried out by dissolving the crystals to minimum amount of chloroform followed by addition of hexane. Yield was 150 mg (85%). Found: C, 73.45; H, 4.87; N, 8.45. Calc. for $C_{47}H_{34}N_5OBr$: C, 73.82; H, 4.46; N, 9.16%. NMR chemical shift: δ_H (400 MHz; $CDCl_3$; $SiMe_4$) 8.91 (8H, m, pyrrole), 8.55 (1H, t, Ph-*m*′), 8.24 (6H, m, Ph-*o*), 8.09 (1H, d, Ph-*o*′), 7.95 (1H, d, Ph-*p*′), 7.75 (9H, m, Ph-*m*,*p*), 7.68 (1H, s, Ph-*o*″), 7.42 (2H, s, NH_2), 3.72 (2H, t, –CH_2–Br), 3.05 (2H, t, –CO–CH_2–), −2.83 (2H, s, pyrrole-NH).

The *p*-bromo analogue was synthesized in a similar way. Found: C, 73.64; H, 4.61; N, 8.66; Calc. for $C_{47}H_{34}N_5OBr$: C, 73.82; H, 4.46; N, 9.16%. NMR chemical shift: δ_H (400 MHz; $CDCl_3$; $SiMe_4$) 8.84 (8H, m, pyrrole), 8.21 (8H, m, Ph-*o*,*m*′), 7.91 (2H, d, Ph-*o*′), 7.78 (9H, m, Ph-*m*,*p*), 7.60 (H, s, –NHCO–),

Table 1 Reduction of nitrobenzene and *p*-nitroanisole catalyzed by iron porphyrin with $NaBH_4$

Catalyst	Reduction of nitrobenzene[a]		Reduction of *p*-nitroanisole[a]	
	Conversion (%)[b]	Yield (%)[b]	Conversion (%)[b]	Yield (%)[b]
[*m*-MV-FeCl(TPP)]	74	67	72	68
[*p*-MV-FeCl(TPP)]	71	61	65	62
FeCl(TPP)/MV^{2+}[c]	63	41		
FeCl(TPP)	44	39	32	30

[a] [Iron porphyrin] = 3.57×10^{-2} mmol dm^{-3}. [cat.] : $NaBH_4$: substrate = 1 : 400 : 400, 3 h at 25 °C. [b] Based on nitrobenzene or *p*-nitroanisole. [c] [MV^{2+}] = 3.75×10^{-2} mmol dm^{-3}.

3.85 (2H, t, $–CH_2–Br$), 3.12 (2H, t, $–CO–CH_2–$), −2.78 (2H, s, pyrrole-NH).

5-{3-(1′-Methyl-4,4′-bipyridinium)ethylcarboxyamidyl}phenyl-10,15,20-triphenylporphyrin (*m*-MV-TPP). DMF solution of *m*-Br-TPP (135 mg; 0.16 mmol) and monomethyl-4,4′-bipyridinium iodide (1 g; 3.36 mmol) was stirred at 110 °C for 34 h under N_2 atmosphere.[36] After DMF was removed with evaporator under reduced pressure, the crude crystals were washed with water to remove remaining 1-methyl-4,4′-bipyridinium iodide, and then washed with chloroform to remove remaining *m*-Br-TPP. Re-crystallization was carried out by dissolving the crystals to minimum amount of methanol followed by addition of chloroform. Yield was 45 mg (31%). Found: C, 63.16; H, 4.23; N, 8.94. Calc. for $C_{58}H_{43}N_7OI_2$: C, 62.76; H, 4.08; N, 8.84%. NMR chemical shift: δ_H (400 MHz; DMSO; $SiMe_4$) 10.55 (1H, s, –NHCO–), 9.40 (2H, d, 4,4′-bpy), 9.19 (2H, d, 4,4′-bpy), 8.83 (10H, m, pyrrole and 4,4′-bpy), 8.55 (2H, d, 4,4′-bpy), 8.49 (1H, s, Ph-*p*′), 8.22 (7H, m, Ph-*o*,*o*′), 7.94 (2H, t, $–CH_2–$ 4,4′-bpy), 7.85 (10H, m, Ph-*m*,*p*,*o*″), 7.74 (1H, t, Ph-*m*′), 4.98 (2H, t, $–CO–CH_2–$), 4.37 (3H, s, 4,4′–bpy–CH_3), −2.94 (2H, s, pyrrole-NH).

The *p*-analogue was synthesized in a similar way. Found: C, 62.17; H, 4.22; N, 8.61. Calc. for $C_{58}H_{43}N_7OI_2$: C, 62.76; H, 4.08; N, 8.84%. NMR chemical shift: δ_H (400 MHz; DMSO; $SiMe_4$) 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, $–CO–CH_2–$), 4.45 (3H, s, 4,4′-bpy–CH_3), 3.45 (2H, t, 4,4′-bpy), −2.93 (2H, s, pyrrole-NH).

5-{3-(1′-Methyl-4,4′-bipyridinium)ethylcarboxyamidyl}-phenyl-10,15,20-triphenylporphyrin iron trichloride [*m*-MV-FeCl(TPP)]. *m*-MV-TPP (100 mg; 0.09 mmol) was metalated with $FeCl_2 \cdot nH_2O$ (27 mg; 0.135 mmol) at room temperature for 0.5 h and then at 140 °C for 10 h in DMF (30 ml) under N_2 atmosphere.[37] After removing DMF with evaporator under reduced pressure, the crystals were washed with water and then dissolved into chloroform. Remaining *m*-MV-TPP was removed with filtration, and then chloroform was removed with evaporator under reduced pressure to afford crude crystals. The crystals (70 mg) were dissolved into chloroform (15 ml) and the solution was treated with 1 M HCl (30 ml) in a separatory funnel to substitute iodide for chloride. The crude crystals were obtained by removing chloroform with evaporator under reduced pressure. Re-crystallization was carried out by dissolving the crystals to minimum amount of chloroform followed by addition of hexane, to afford the purple crystals. Yield was 59 mg (64%). Found: C, 67.61; H, 4.44; N, 9.06. Calc. for $C_{58}H_{43}N_7OFeCl_3$: C, 68.55; H, 4.27; N, 9.65%.

The *p*-analogue was synthesized in the same way. Found: C, 69.65; H, 4.14; N, 8.84. Calc. for $C_{58}H_{43}N_7OFeCl_3$: C, 68.55; H, 4.27; N, 9.65%.

Reduction of aromatic nitro compounds and nitrosobenzene

The reduction reaction was carried out at 25 °C in diglyme/MeOH mixed solvent (4.0 ml; 1/1 v/v) involving iron porphyrin [*m*-MV-FeCl(TPP), *p*-MV-FeCl(TPP), or FeCl(TPP); 0.15 mmol (3.75×10^{-2} mmol dm^{-3})], nitro compound (0.06 mol) and $NaBH_4$ (60 mmol) under N_2 atmosphere. Small aliquots were withdrawn at appropriate time intervals to analyze the reactant and the product by a GC equipped with an FID detector [Hitachi G-5000, Ultra Alloy-(8H)5 EX stainless steel capillary column (30 m)], where 1,2,4,5-tetramethylbenzene was used as an internal standard.

Reduction of phenylhydroxylamine

The reduction of phenylhydroxylamine was carried out under the same reaction conditions as those of nitrobenzene reduction, while the reactant and the product were analyzed by HPLC (Hitachi L-4000H with UV-detector) equipped with CrestPac-C18T column. Napthalene was employed as an internal standard.

Measurements

All UV-VIS spectra were measured under Ar atmosphere, where the sample solutions were prepared under Ar atmosphere, too. Cyclic voltammograms were recorded with PS-06 (Toho Technical Research, Co. Ltd.) in diglyme/MeOH (1/1 v/v) solution under Ar atmosphere, where the glassy carbon and the Pt wire were used as a working electrode and a counter electrode, respectively. Ag/AgCl was employed as a reference electrode. *n*-Tetrabuthylammonium hexafluorophosphate (0.1 mol dm^{-3}) was used as supporting electrolyte.

Results and discussion

Reduction of aromatic nitro compounds

Reduction of nitrobenzene is efficiently catalyzed by FeCl(TPP), *p*-MV-FeCl(TPP) and *m*-MV-FeCl(TPP), as shown in Table 1 and ESI Fig. S1.† Methylviologen-pendant iron porphyrins provide somewhat larger yield of aniline and somewhat larger conversion of nitrobenzene than does normal FeCl(TPP). It is noted that the yield is slightly smaller than the conversion in the reactions by *p*-MV-FeCl(TPP) and *m*-MV-FeCl(TPP) but much smaller than the conversion in the reaction by FeCl(TPP). Addition of methylviologen (MV^{2+}) to FeCl(TPP) somewhat increases the conversion but little increases the yield. Thus, not the presence of free MV^{2+} but the introduction of methylviologen to porphyrin is indispensable for efficient catalysis. The reduction of *p*-nitroanisole shows much larger differences in catalysis between normal FeCl(TPP) and the methylviologen-pendant iron porphyrins than does the reduction of nitrobenzene (see Table 1 and ESI Fig. S2†). In this reduction reaction, these methylviologen-pendant iron porphyrins give much larger conversion and yield than does FeCl(TPP). Since the reduction potential of nitrobenzene (−1140 mV (*vs.* Ag/AgCl) in diglyme) is less negative than that of *p*-nitroanisole (−1250 mV (*vs.* Ag/AgCl) in diglyme), *p*-nitroanisole is less reactive for reduction than nitrobenzene. Thus, it is clearly concluded that methylviologen-pendant iron porphyrins exhibit efficient catalysis even for reduction of

Table 2 Reduction of *p*-nitroanisole catalyzed by iron porphyrin with $NaBH_4$ in the presence of the dioxygen molecule[a]

Catalyst	Conversion (%)[b]	Yield (%)[b]
[*m*-MV-FeCl(TPP)]	54	50
[*p*-MV-FeCl(TPP)]	56	45
FeCl(TPP)	24	10

[a] [Iron porphyrin] = 3.57×10^{-2} mmol dm^{-3}, [cat.] : $NaBH_4$: substrate : $[O_2] = 1 : 1200 : 400 : 100$, 3 h at 15 °C. [b] Based on *p*-nitroanisole.

less reactive substrate. It is also noted here that the reaction by *m*-MV-FeCl(TPP) more rapidly takes place than that by *p*-MV-FeCl(TPP) (see Fig. 1). This result clearly shows that the *meta*-position is better for the introduction of an electron-trapping and storage moiety than the *para*-one.

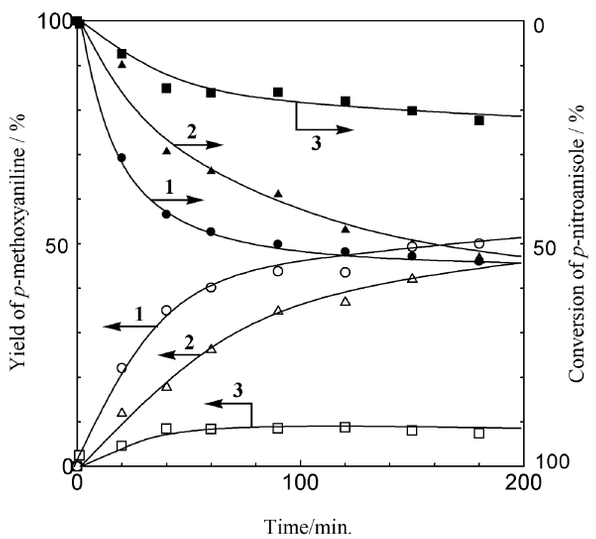


Fig. 1 Time-courses of reduction of *p*-nitroanisole catalyzed by iron porphyrins with $NaBH_4$ in the presence of the dioxygen molecule. In diglyme/MeOH (1/1 v/v) at 25 °C. [Iron porphyrin] = 3.75×10^{-2} mmol dm^{-3}. Iron porphyrin : substrate : $NaBH_4$: $O_2 = 1 : 400 : 1200 : 100$ (molar ratios). **1**; *m*-MV-FeCl(TPP), **2**; *p*-MV-FeCl(TPP), **3**; FeCl(TPP).

The reduction of *p*-nitroanisole under dioxygen atmosphere also shows significantly large differences between FeCl(TPP) and methylviologen-pendant iron porphyrins, as shown in Fig. 1 and Table 2, where the concentration of the dioxygen molecule is 3.75 mol dm^{-3} (100 eq. to the catalyst).‡ In the reaction by FeCl(TPP), the dioxygen molecule substantially suppresses the reaction and decreases very much both the conversion and the yield, as expected.§ In the reactions by *p*-MV-FeCl(TPP) and *m*-MV-FeCl(TPP), on the other hand, the dioxygen molecule moderately decreases the conversion and the yield; as a result, the yield and the conversion by *p*-MV-FeCl(TPP) and *m*-MV-FeCl(TPP) are much larger than those by FeCl(TPP). From these results, it should be concluded that methylviologen-pendant iron porphyrins can catalyze the reduction of nitrobenzene and its derivatives even in the presence of the dioxygen molecule. We will discuss the reason below in more detail.

‡ Methanol saturated with the dioxygen molecule was added to the reaction solution. The concentration of the dioxygen molecule in the methanol is 0.012 mol dm^{-3} at 25 °C.[40] The differences in catalysis between normal FeCl(TPP) and methylviologen-pendant iron porphyrins become larger as the concentration of the dioxygen molecule increases (see ESI Table S1 †).

§ There are several possible reasons that the dioxygen molecule suppresses the reaction; one is the re-oxidation of the intermediate by the dioxygen molecule and the other is the conversion of the iron porphyrin to unreactive μ-oxo diiron species by the dioxygen molecule.

Table 3 Reduction of nitrosobenzene catalyzed by iron porphyrin with $NaBH_4$[a]

	Conversion (%)[b]	Yield (%)[b]
[*m*-MV-FeCl(TPP)]	98[c]	88[c]
[*p*-MV-FeCl(TPP)]	99	84[d]
FeCl(TPP)	98	56[d]
MV^{2+}	97	0[c]
No catalyst	96	0[c]

[a] [Iron porphyrin] = [MV^{2+}] 3.57×10^{-2} mmol dm^{-3}, [cat.] : $NaBH_4$: substrate = 1 : 400 : 400, 3 h at 25 °C. [b] Based on nitrosobenzene. [c] This works. [d] Ref. 33.

Table 4 Reduction of phenylhydroxylamine catalyzed by iron porphyrin with $NaBH_4$[a]

	Conversion (%)[b]	Yield (%)[b]
[*m*-MV-FeCl(TPP)]	100	98
[*p*-MV-FeCl(TPP)]	100	98
FeCl(TPP)	96	88
MV^{2+}	28	0
No catalyst	28	0

[a] [Iron porphyrin] = 3.57×10^{-2} mmol dm^{-3}, [cat.] : $NaBH_4$: substrate = 1 : 400 : 400, after 3 h at 25 °C [b] Based on phenylhydroxylamine.

Reduction of nitrosobenzene and phenylhydroxylamine

We found in our previous work[11b] that nitrobenzene was reduced to aniline through nitrosobenzene and phenylhydroxylamine in catalytic reduction by FeCl(TPP); in other words, nitrobenzene undergoes two-electron reduction to afford nitrosobenzene, nitrosobenzene undergoes two-electron reduction to afford phenylhydroxylamine and finally phenylhydroxylamine undergoes two-electron reduction to afford aniline. It is interesting to clarify which step the methylviologen-pendant accelerates. We applied FeCl(TPP), *p*-MV-FeCl(TPP) and *m*-MV-FeCl(TPP) to reductions of nitrosobenzene and phenylhydroxylamine. Though all these iron porphyrins give the conversion near to 100% in the reduction of nitrosobenzene, FeCl(TPP) gives a much smaller yield of aniline than do *p*-MV-FeCl(TPP) and *m*-MV-FeCl(TPP), as shown in Table 3.¶

In the reduction of phenylhydroxylamine, the methylviologen-pendant iron porphyrins give somewhat larger yield of aniline than does normal FeCl(TPP), as shown in Table 4. This step does not take place at all in the absence of iron porphyrin. These results lead us to the conclusions that the iron porphyrin is indispensable for the reduction of phenylhydroxylamine to aniline and that the methylviologen-pendant accelerates the reduction of nitrosobenzene to phenylhydroxylamine and that of phenylhydroxylamine to aniline. Since both the reduction step of nitrosobenzene to phenylhydroxylamine and that of phenylhydroxylamine to aniline need two electrons, electrons must be successively supplied to the substrate by the catalyst in these steps. If one-electron reduced intermediate can not be successively supplied one more electron, it would easily return to the substrate. In particular, such re-oxidation easily occurs in the presence of the dioxygen molecule. The methylviologen moiety efficiently accepts an electron and transfers it to the substrate and/or to the iron porphyrin moiety which is considered the active site. Thus, the methylviologen-pendant suppresses the re-oxidation of intermediate and accelerates the multi-electron reduction even in the presence of the dioxygen molecule. All these results clearly show that the

¶ In the reduction of nitrosobenzene by FeCl(TPP), the yield of aniline is much smaller than the conversion of nitrosobenzene. Moreover, nitrosobenzene is almost consumed but no aniline is yielded in the absence of iron porphyrins. We tried to find by-product, but we failed to detect it.

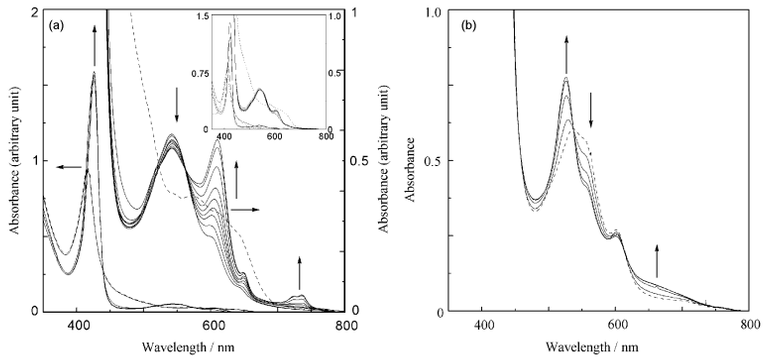


Fig. 2 UV-VIS spectral changes of *p*-MV-FeCl(TPP) by addition of $NaBH_4$ in the presence of nitrobenzene and those of *p*-MV-FeCl(TPP) by addition of aniline in the presence of $NaBH_4$. In diglyme/MeOH (1/1 v/v) at 25 °C. [*p*-MV-FeCl(TPP)] = 3.75×10^{-2} mmol dm^{-3}. *p*-MV-FeCl(TPP)/$NaBH_4$/(nitrobenzene or aniline) = 1 : 400 : 400 (molar ratios). Broken line represents the spectra of *p*-MV-FeCl(TPP) in the absence of $NaBH_4$. Solid lines represent spectra of *p*-MV-FeCl(TPP) in the presence of $NaBH_4$. The inset shows the spectral changes of FeCl(TPP) by addition of $NaBH_4$ under the same conditions as those of *p*-MV-FeCl(TPP) (A). Broken line represents the spectrum of *p*-MV-FeCl(TPP) in the absence of aniline. Solid lines represent spectral changes of *p*-MV-FeCl(TPP) upon addition of aniline (B).

methylviologen-pendant is necessary to a catalyst for multi-electron reduction and it plays the role of an electron-trapping and storage unit.

UV-VIS spectra

It is interesting to clarify what is an active species and how the methylviologen moiety accelerates the reaction. There are several possibilities in the reduction state of iron porphyrin and methylviologen; iron porphyrin can take one-electron and two-electron reduced states and methylviologen can take one-electron and two-electron reduced states, too. To investigate which state the iron porphyrin and methylviologen moieties take under the reaction conditions employed, we recorded UV-VIS spectra of FeCl(TPP), *p*-MV-FeCl(TPP) and *m*-MV-FeCl(TPP). As shown in Fig. 2, addition of $NaBH_4$ to *p*-MV-FeCl(TPP) immediately changes absorption spectra from the dotted line to the solid lines. Then, the absorptions at 600 and 420 nm gradually increase, while the absorption at 530 nm gradually decreases. Isosbestic points are observed during these gradual changes, while no isosbestic point is observed between the dotted line and the solid lines. One-electron reduced methylviologen exhibits a large absorption at 606 nm (molar extinction coefficient (ε) = 1.38×10^4 mol^{-1} dm^3 cm^{-1}),[38] and one-electron reduced iron tetraphenylporphyrin exhibits large absorptions at 426 nm ($\varepsilon = 3.15 \times 10^5$ mol^{-1} dm^3 cm^{-1}) and 535 nm ($\varepsilon = 2.26 \times 10^4$ mol^{-1} dm^3 cm^{-1}) and a very small absorption at 600 nm (see inset of Fig. 2).[39] Since the absorption at 600 nm is very small in the one-electron reduced iron porphyrin, the considerably large absorption at 600 nm in *p*-MV-FeCl(TPP) is assigned to one-electron reduced MV^+ moiety. This assignment is consistent with the fact that the absorption at 600 nm increases more slowly than that at 420 nm; that is, the species exhibiting the absorption at 600 nm is different from the species exhibiting the absorption at 420 nm. Essentially the same spectral changes are observed in *m*-MV-FeCl(TPP). These spectral changes clearly show that methylviologen-pendant iron porphyrin involves one-electron reduced iron tetraphenylporphyrin and one-electron reduced methylviologen moieties under the reaction conditions employed.

At the end of this section, we mention the possibility that aniline also coordinates to the iron center. The UV-VIS spectra of *p*-MV-FeCl(TPP) and FeCl(TPP) in the presence of $NaBH_4$ show that a new absorption appears at 526 nm upon addition of aniline, as shown in Fig. 2B and ESI Fig. S3. † In the catalytic reaction solution, a small shoulder is observed at around 526 nm, too (Fig. 2A). From these results, it is concluded that aniline coordinates to the iron center in the catalytic reaction. The coordination of aniline would suppress the reaction.

Table 5 Redox potentials of iron porphyrin, MV^{2+}, nitrobenzene, nitrosobenzene, and phenylhydroxylamine[a]

	$Fe^{I/II}$ [b]	$MV^{0/+}$ [b]	$MV^{+/2+}$ [b]	$Fe^{II/III}$ [b]
[*m*-MV-FeCl(TPP)]	−1090	−810	−550	−90
[*p*-MV-FeCl(TPP)]	−1090	−850	−365	−50
FeCl(TPP)	−1100			−70
MV^{2+}		−840	−370	

Ph–NO_2 [b,c]	Ph–NO [b,c]	Ph–NHOH [b,c]
−1040	−600	+50

[a] The redox potentials were measured in Ar satulated diglyme/MeOH (1/1 v/v) solution using *n*-Bu_4NPF_6 (0.1 mol dm^{-3}) as a supporting electrolyte with a scan rate of 50 mV s^{-1}. [b] In mV (*vs.* Ag/AgCl). [c] These potentials correspond to the peak of the reduction-wave.

Redox potentials of these iron porphyrins

Since the reduction of nitrobenzene to aniline needs six-electrons [see eqn. (5)], the reduction catalysis is deeply related to the reduction potentials of iron porphyrin and methylviologen moieties. We recorded cyclic voltammograms of methylviologen-pendant iron porphyrins, as shown in Fig. 3 and Table 5. Apparently, methylviologen-pendant iron porphyrins exhibit sum of redox potentials of iron porphyrin and methylviologen, while the redox potentials of the methylviologen moiety somewhat shift in methylviologen-pendant iron porphyrins; in particular, the $MV^{+/2+}$ redox potential moves to more negative value in the *p*-MV-FeCl(TPP) than that of free methylviologen, of which reason is ambiguous (see Table 5 and ESI Fig. S4 for cyclic voltammograms of iron tetraphenylporphyrin). †

Nitrobenzene is electrochemically reduced at −1014 mV (*vs.* Ag/AgCl) in diglyme/MeOH (see Table 5 and ESI Fig. S5), † while nitrosobenzene is electrochemically reduced at −600 mV (Table 5 and Fig. 3B). The reduction of phenylhydroxylamine occurs at 50 mV, being much more positive than the $Fe^{II/III}$ redox potential of the iron porphyrin moiety (see Table 5 and ESI Fig. S6). † It is noted that the reduction potential of nitrobenzene is very negative and only the $Fe^{I/II}$ redox of the iron porphyrin moiety occurs around this reduction potential. These results indicate that only two-electron reduced iron porphyrin can reduce nitrobenzene; in other words, the two-electron reduced iron porphyrin is an active species for the reduction of nitrobenzene to nitrosobenzene. It is noted that the $Fe^{I/II}$ redox potential is much more negative than the $MV^{0/+}$ redox potential of the methylviologen moiety. This means that the two-electron reduced methylviologen moiety can not supply electron to the

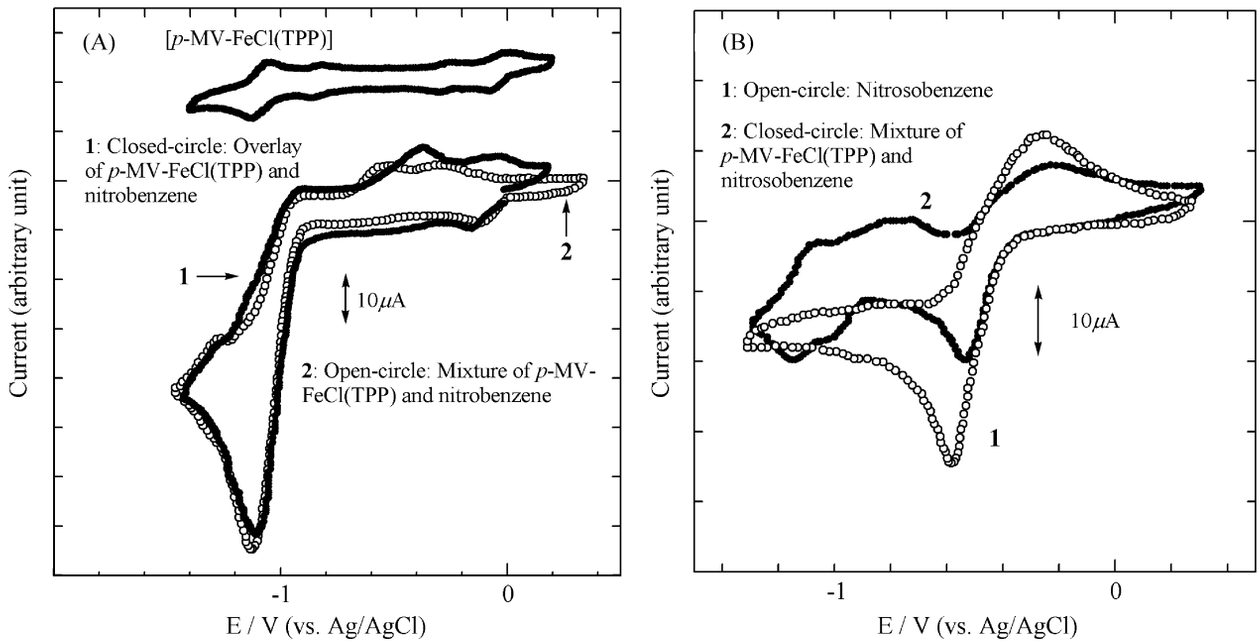


Fig. 3 Cyclic voltammograms of *p*-MV-FeCl(TPP), nitrobenzene, and *p*-MV-FeCl(TPP) with nitrobenzene (A), nitrosobenzene and its mixture with *p*-MV-FeCl(TPP) (B). In diglyme/MeOH (1/1 v/v) at room temperature. [*p*-MV-FeCl(TPP)] = [nitrobenzene] = [nitrosobenzene] = 1.0 mmol dm^{-3}. Scans were carried out between +0.4 to −1.4 V (A), and +0.3 to −1.3 V (B) (*vs.* Ag/AgCl), where scan rate was 50 mV s^{-1}.

one-electron reduced iron porphyrin, which will be discussed below in more detail.

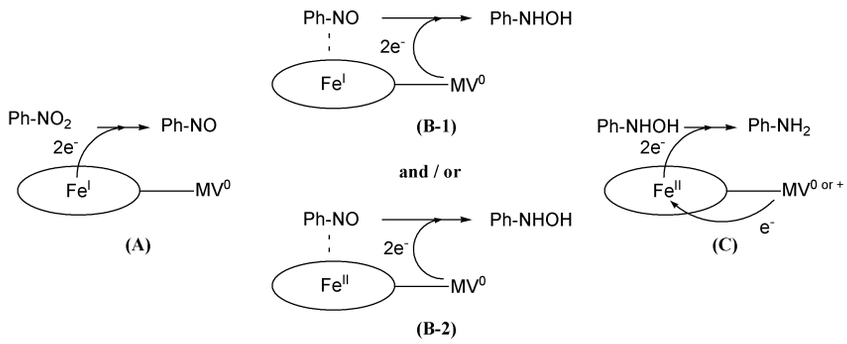
The cyclic voltammogram of nitrosobenzene exhibits the reduction current at −600 mV in the absence of iron porphyrin, as shown in Fig. 3B. This reduction occurs at slightly less negative potential in the presence of *p*-MV-FeCl(TPP) and FeCl(TPP), where the cyclic voltammogram in the presence of FeCl(TPP) is omitted for brevity because it is essentially the same as that of nitrosobenzene in the presence of *p*-MV-FeCl(TPP). It should be noted that no reduction wave is observed around −80 mV in the cyclic voltammogram of iron porphyrin in the presence of nitrosobenzene; that is, the $Fe^{II/III}$ redox of the iron porphyrin moiety at −80 mV disappears upon addition of nitrosobenzene. One plausible explanation is that nitrosobenzene coordinates with the iron porphyrin moiety and restrains the iron porphyrin moiety from interaction with the electrode to suppress the electrochemical reduction. This explanation is consistent with the fact that the reduction wave of nitrosobenzene shifts to a slightly less negative value in the presence of iron porphyrin (Fig. 3B).

The other point to be noted is that two oxidation waves are observed around −360 and −30 mV (*vs.* Ag/AgCl) in the cyclic voltammogram of nitrobenzene and these oxidation waves shift to more negative potentials (−520 and −260 mV (*vs.* Ag/AgCl), respectively) in the presence of methylviologen-pendant iron porphyrin and FeCl(TPP) (see Fig. 3A), where the cyclic voltammogram of nitrobenzene with FeCl(TPP) is omitted for brevity because it is essentially the same as that of nitrobenzene in the presence of *p*-MV-FeCl(TPP). These results suggest that the oxidation waves result from the oxidation of some intermediates which are formed by electrochemical reduction of nitrobenzene and that the intermediates interact with iron porphyrin. To present information of the intermediates, we inspected cyclic voltammogram of nitrosobenzene. It is noted that the oxidation wave is observed at −280 mV (*vs.* Ag/AgCl) in the absence of iron porphyrin and −240 mV in the presence of iron porphyrin (Fig. 3B). In the cyclic voltammograms of phenylhydroxylamine with and without iron porphyrin, no oxidation wave is observed in −520 to −360 and −260 to −30 mV (*vs.* Ag/AgCl), as shown in ESI Fig. S6 and S7.† From these results, we propose the following suggestions. (1) There is a possibility that the intermediate with the oxidation wave at −260 mV in the presence of iron porphyrin is the one-electron reduced nitrosobenzene that coordinates with the iron center, since this oxidation potential is similar to that of nitrosobenzene in the presence of iron porphyrin. And, (2) the intermediate with the oxidation wave at −520 mV in the presence of iron porphyrin is different from one-electron reduced nitrosobenzene and one-electron reduced phenylhydroxylamine. One of the plausible candidates is one-electron reduced nitrobenzene that coordinates with the iron center. Further investigation is, however, necessary to present more detailed information.

Role of methylviologen-pendant

Summarizing the above results, we wish to discuss what role the methylviologen-pendant plays in this reaction. Since the $Fe^{I/II}$ redox occurs at more negative potential than the $MV^{0/+}$ redox (*vide supra*), the two-electron reduced methylviologen moiety can not reduce the one-electron reduced iron porphyrin to the two-electron reduced iron porphyrin which is an active species for the reduction of nitrobenzene. This means that the methylviologen moiety can not accelerate the reduction of nitrobenzene to nitrosobenzene.

Since the reduction of nitrosobenzene occurs at a less negative potential (−600 mV) than the $MV^{0/+}$ and $Fe^{I/II}$ redoxes but a more negative potential than the $Fe^{II/III}$ and $MV^{+/2+}$ redoxes, nitrosobenzene can be reduced by a two-electron reduced iron porphyrin moiety and two-electron reduced methylviologen-pendant. It would be mistaken to conclude that only the two-electron reduced iron porphyrin moiety is an active species for the reduction of nitrosobenzene, for the following reason. If so, the methylviologen-pendant can not accelerate the reduction of nitrosobenzene, because the two-electron reduced methylviologen can not supply one electron to the one-electron reduced iron porphyrin moiety (*vide supra*). This contradicts the fact that the methylviologen-pendant does accelerate the reduction of nitrosobenzene. One plausible explanation is that the two-electron reduced methylviologen-pendant directly participates in the reduction of nitrosobenzene. In the reduction by methylviologen-pendant iron porphyrin, some intermediate would exist near to the methylviologen-pendant because the intermediate interacts with the iron porphyrin moiety. Actually, the



Scheme 2

cyclic voltammograms of nitrobenzene and nitrosobenzene suggest that some intermediates interact with the iron porphyrin, as discussed above. As a result, the two-electron reduced methylviologen can easily reduce the intermediates. The free methylviologen, on the other hand, can not reduce nitrosobenzene to aniline, as described above. This result is not inconsistent with the above explanation, as follows: the free methylviologen must make diffusional movement to collide with the intermediate because of the lack of an interacting site. This situation is less favorable for the reaction, since the intermediate tends to undergo re-oxidation or side reaction before the collision with methylviologen.

In the reduction of phenylhydroxylamine, the iron porphyrin moiety is necessary, as shown above. Since the $Fe^{II/III}$ redox of the iron porphyrin moiety occurs at more negative potential than the reduction potential of phenylhydroxylamine, the one-electron reduced iron porphyrin moiety is considered an active species for the reduction of phenylhydroxylamine. This $Fe^{II/III}$ redox potential is less negative than the $MV^{+/2+}$ redox potential. Thus, the methylviologen moiety can supply successively electrons to the iron porphyrin moiety to accelerate two-electron reduction of phenylhydroxylamine to aniline.

From the above discussion, we reach a reasonable picture of this catalytic reduction, as follows. Two-electron reduction of nitrobenzene is performed by two-electron reduced iron porphyrin to afford nitrosobenzene, as shown in Scheme 2(A). The two-electron reduced methylviologen, as well as the two-electron reduced iron porphyrin, is an active species for reduction of nitrosobenzene to phenylhydroxylamine, as shown in Scheme 2(B). If the catalyst did not possess the methylviologen moiety, only two-electron reduced iron porphyrin participated in the reduction of nitrosobenzene. Since the two-electron reduced iron porphyrin is not sufficiently formed in the reaction solution (*vide infra*), the re-oxidation of intermediate to nitrosobenzene and/or some side-reaction would take place easily in the normal iron porphyrin without the methylviologen-pendant. In the methylviologen-pendant iron porphyrin, on the other hand, the methylviologen-pendant accelerates the successive reduction of nitrosobenzene to phenylhydroxylamine, to suppress the re-oxidation. Phenylhydroxylamine is reduced to aniline by one-electron reduced iron porphyrin. In this step, the one-electron or two-electron reduced methylviologen moiety can successively supply electrons to the iron porphyrin moiety, to complete two-electron reduction of phenylhydroxylamine to aniline, as shown in Scheme 2(C).

Here, we mention the fact that two-electron reduced iron porphyrin is not observed in UV-VIS and EPR spectra.‖ This is not unreasonable because the two-electron reduced iron porphyrin is not formed sufficiently in diglyme/MeOH, as reported.[11b] Though methylviologen-pendant iron porphyrin including one-electron reduced iron porphyrin and one-electron reduced methylviologen moieties are spectroscopically observed, it is considered to be a resting state of catalyst.

Conclusions

In this study, iron porphyrin was introduced methylviologen to the *meso*-phenyl group through amido-bridge at either the *p*- or *m*-position, to present a functional model of such multi-electron reductase as nitrite reductase. One can expect that methylviologen-pendant iron porphyrin is a good model catalyst of nitrite reductase since the methylviologen moiety can play the role of an electron-trapping and storage unit. Actually, these methylviologen-pendant iron porphyrins efficiently catalyze six-electron reduction of nitrobenzene to aniline, which is a model reaction of six-electron reduction of nitrite to ammonia by nitrite reductase.

Though the yield of aniline by these methylviologen-pendant iron porphyrins is somewhat larger than the yield by the normal iron tetraphenylporphyrin in the reduction of nitrobenzene, the yield of *p*-methoxyaniline by these methylviologen-pendant iron porphyrins is two times as large as that of iron tetraphenylporphyrin in the reduction of *p*-nitroanisole. The *m*-pendant porphyrin provides a somewhat larger yield of aniline than does the *p*-pendant one. The investigation of this interesting difference between the *p*- and *m*-pendant positions is under progress now. The significantly large differences between normal iron tetraphenylporphyrin and methylviologen-pendant iron porphyrins are found in the reduction of *p*-nitroanisole in the presence of the dioxygen molecule, too; though the iron tetraphenylporphyrin can not catalyze well the reduction of *p*-nitroanisole in the presence of the dioxygen molecule, these methylviologen-pendant iron porphyrins do catalyze well this reduction and give considerably larger yield of *p*-methoxyaniline even in the presence of the dioxygen molecule. These results clearly indicate that methylviologen-pendant iron porphyrins exhibit excellent catalytic activity in the reduction of a less reactive substrate and under unfavorable reaction conditions.

The electrochemical reduction of nitrobenzene occurs at −1040 mV (*vs.* Ag/AgCl) in the absence of iron porphyrin. Since the redox potential of $Fe^{I/II}$ of these iron porphyrins is −1090 to −1100 mV (*vs.* Ag/AgCl), it should be concluded that the active species for the reduction of nitrobenzene to nitrosobenzene is the two-electron reduced iron porphyrin. The two-electron reduced methylviologen, as well as the two-electron reduced iron porphyrin, catalyzes the reduction of nitrosobenzene to phenylhydroxylamine. The methylviologen-pendant also accelerates the reduction of phenylhydroxylamine to aniline by supplying one electron to the iron porphyrin moiety which plays the role of active species for the reduction of phenylhydroxylamine to aniline.

From these results, we wish to conclude that the methylviologen-pendant iron porphyrin exhibits efficient catalysis for multi-electron reduction.

‖ Though two-electron reduced iron porphyrin was not detected with EPR measurement in diglyme/MeOH, the characteristic EPR signal of the two-electron reduced iron porphyrin was observed in the similar solvent mixture, THF/MeOH (ESI Fig. S8).

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