DALTON COMMUNICATION

Efficient reduction catalysis of viologen-bound iron porphyrin and its application to six-electron reduction of nitrobenzene to aniline †

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Received 10th January 2000, Accepted 16th February 2000
Published on the Web 9th March 2000

A newly synthesized methylviologen-bound iron porphyrin chloro(5-{4-[3-(1′-methyl-4,4′-bipyridinium)ethylcarboxyamidyl]phenyl}-10,15,20-triphenylporphyrin)iron dichloride, efficiently catalyzes six-electron reduction of nitrobenzene to aniline, a model reaction of NO_2^- conversion to NH_4^+ by nitrite reductase.

Reactions and interactions of NO_x compounds with metalloporphyrins have received a considerable interest, recently.[1] Nitrite reductase is a well-known heme enzyme which efficiently catalyzes six-electron reduction of NO_2^- to NH_4^+ (eqn. (1)).

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

Thus, it is interesting and meaningful to construct a functional model of nitrite reductase with a metalloporphyrin.

The prosthetic group of nitrite reductase is believed to be a $[Fe_4S_4]$-siroheme,[2–6] in which the $[Fe_4S_4]$ cluster works as an electron trapping and storage unit and the siroheme moiety as an active center.[5d] Though several attempts have been made to model its reduction catalysis with metalloporphyrins,[7–11] no electron trapping and storage unit has been introduced into metalloporphyrins to date. Considering the presence of the Fe_4S_4 moiety in nitrite reductase, we can expect to construct its efficient functional model with iron porphyrin by binding a viologen to the porphyrin moiety, since the viologen derivative is a well-known electron trapping and storage compound. A similar idea was recently presented.[12]

In this work, we wish to report the synthesis of the methylviologen-bound iron porphyrin chloro(5-{4-[3-(1′-methyl-4,4′-bipyridinium)ethylcarboxyamidyl]phenyl}-10,15,20-triphenylporphyrin)iron dichloride $[FeCl(mvep\text{-}TPP)]Cl_2$ **1** (see Fig. 1), as a good functional model of nitrite reductase and its application to the six-electron reduction of nitrobenzene to aniline (eqn. (2)) which is a reasonable model of NO_2^- reduction to

$$Ph\text{-}NO_2 + 6H^+ + 6e^- \rightarrow Ph\text{-}NH_2 + 2H_2O \qquad (2)$$

NH_4^+ catalyzed by nitrite reductase (note that both are six-electron reduction reactions). This is the first successful application of viologen-bound metalloporphyrin to a biomimetic catalytic reaction.

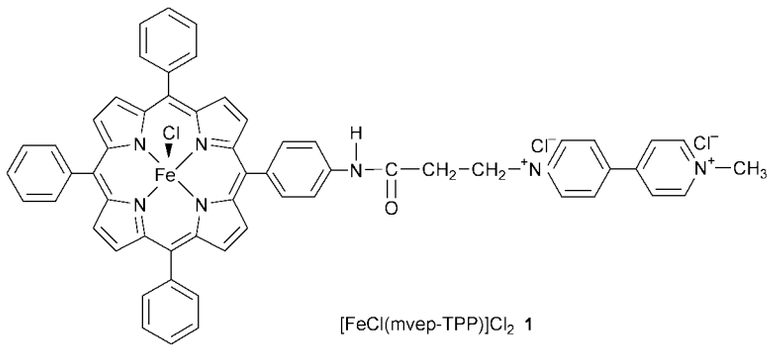
Compound **1** was synthesized by reference to synthetic methods for similar porphyrins.[13,14] ‡ Though an ether group was previously adopted as a bridging linkage in viologen-bound zinc porphyrin,[15] the amide group was employed here. This is because the amide linkage is more amenable than the ether linkage to the introduction of a functional group into the porphyrin moiety.§ In a typical run, reduction of nitrobenzene (1.5×10^{-2} mol dm^{-3}) was carried out with $NaBH_4$ (1.5×10^{-2} mol dm^{-3}) and **1** (or [FeCl(TPP)] **2**) (3.75×10^{-5} mol dm^{-3}) in diglyme–methanol (1 : 1 v/v) under an argon atmosphere. Nitrobenzene and aniline were analyzed by a GC equipped with an FID detector (Ultra ALLOY (8H)5 stainless steel capillary column (30 m), Hitachi G-5000), using 1,2,4,5-tetramethylbenzene as the internal standard.

When **2** is used as a catalyst, the yield and the conversion decrease in the order 1-chloro-4-nitrobenzene > nitrobenzene > *p*-nitroanisole (Table 1). This result is consistent with our expectation since this decreasing order agrees with the decreasing order of the redox potential of the substrate. It is also noted that the yield is much smaller than the conversion in the reduction of 1-chloro-4-nitrobenzene and moderately smaller in the reductions of nitrobenzene and *p*-nitroanisole. However, the situation completely changes when the reaction is catalyzed by **1**, as summarized below; (1) **1** provides a larger conversion and larger yield than does **2** in the reductions of nitrobenzene and *p*-nitroanisole, (2) though the conversion is not sensitive so much to the substrate, the yield unexpectedly increases in the order 1-chloro-4-nitrobenzene < nitrobenzene < *p*-nitroanisole, which is against the expectation from the reduction potential of the substrate, and (3) the yield is almost the same as the conversion in nitrobenzene and *p*-nitroanisole, while **2** gives a smaller yield than conversion in these substrates. A mixture of **2** and methylviologen did not give the above results; the conversion was 60% but the yield was 41%. All these results show that **1** is a much better catalyst for a multi-electron reduction reaction than **2**.

The above results are interpreted in terms of the presence of an intermediate, as follows: after the active species of **2** reduces nitrobenzene to some intermediate, **2** has insufficient electrons to perform further reduction of the intermediate to aniline.¶ This means that the intermediate must react with the other active species to afford aniline. If the intermediate cannot react with the other active species, the intermediate would be either reoxidized to nitrobenzene or converted to a by-product. In the reaction catalyzed by **1**, on the other hand, the intermediate does not need to react with the other active species, as follows; after the active species of **1** reduces nitrobenzene to the intermediate, **1** can receive easily electrons from $NaBH_4$ through the viologen moiety, to successively perform further reduction of the intermediate. This means that both the reoxidation and the side-reaction less easily occur in the reaction catalyzed by **1** than in the reaction catalyzed by **2**, which leads to the larger yield in the former reaction. It was mentioned above that the difference in the yield between reactions catalyzed by **1** and **2** was larger in the reaction of *p*-nitroanisole than in the reaction of 1-chloro-4-nitrobenzene. This is interpreted in terms of reoxidation of the intermediate, as follows: though the intermediate in the reduction of *p*-nitroanisole tends to be more easily reoxidized than that in the reduction of 1-chloro-4-nitrobenzene due to the more negative redox potential of the former intermediate, **1** can suppress the reoxidation of the

† Electronic supplementary information (ESI) available: synthesis and characterisation of complex **1** and details of the oxygen addition technique used. See http://www.rsc.org/suppdata/dt/b0/b000146p/

DOI: 10.1039/b000146p



[FeCl(mvep-TPP)]Cl_2 **1**

Fig. 1

Table 1 Reduction of nitrobenzene derivatives catalyzed by [FeCl(TPP)] and [FeCl(mvep-TPP)]Cl_2 with $NaBH_4$ [a]

	[FeCl(TPP)] **2**		[FeCl(mvep-TPP)]Cl_2 **1**	
	Conversion (%) [b]	Yield (%) [b]	Conversion (%) [b]	Yield (%) [b]
1-Chloro-4-nitrobenzene	75	45	74	46
Nitrobenzene	44	39	60	51
p-Nitroanisole	26	31	65	62

[a] [FeCl(TPP)] = [FeCl(mvep-TPP)]Cl_2 = 3.75×10^{-2} mmol dm^{-3}, [cat] : $NaBH_4$: substrate = 1 : 400 : 400, 3 h at 25 °C. [b] Based on nitrobenzene derivatives used in the reaction.

Table 2 Reduction of *p*-nitroanisole catalyzed by [FeCl(TPP)] and [FeCl(mvep-TPP)]Cl_2 with $NaBH_4$ in the presence of added oxygen [a]

	[FeCl(TPP)] **2**		[FeCl(mvep-TPP)]Cl_2 **1**	
Oxygen	Conversion (%) [b]	Yield (%) [b]	Conversion (%) [b]	Yield (%) [b]
10 eq.	93	89	97	94
50 eq.	67	42	76	58
100 eq.	24	10	56	45

[a] [FeCl(TPP)] = [FeCl(mvep-TPP)]Cl_2 = 3.75×10^{-2} mmol dm^{-3}, [cat] : $NaBH_4$: substrate = 1 : 1200 : 400, 3 h at 15 °C. [b] Based on nitrobenzene derivatives used in the reaction.

intermediate, because the viologen moiety supplies electrons to the iron porphyrin moiety from $NaBH_4$. However, the reoxidation easily occurs in the reaction catalyzed by **2**, because of the absence of the viologen moiety. As a result, the difference between **1** and **2** appears more marked in the reduction of *p*-nitroanisole than in the reduction of 1-chloro-4-nitrobenzene.

A comparison between **1** and **2** was made in the presence of oxygen to present clearer differences between them. When 10 eq. of oxygen molecules are added to the reaction solution,‖ the conversion and the yield are similar between **1** and **2** (see Table 2). However, a large difference appears, when 100 eq. of oxygen molecules are added to the solution; the yield is only 10% in the reduction catalyzed by **2** but still 45% in the reduction catalyzed by **1**. Thus, the viologen-bound iron porphyrin **1** exhibits considerably high catalytic activity even in the presence of oxygen while the non-viologen-bound iron porphyrin **2** gives a very poor yield of aniline. This result is again interpreted in terms of the viologen moiety of **1**; since **1** is easily supplied electrons from $NaBH_4$ through the viologen moiety, **1** can successively perform further reduction of the intermediate to aniline, in competition with reoxidation of the intermediate by oxygen. Thus, a considerable amount of aniline is formed in the reaction catalyzed by **1** even in the presence of oxygen.

In the reduction of nitrobenzene by FeCl(TPP), it was reported that aniline was formed from nitrobenzene through nitrosobenzene and phenylhydroxylamine.[11] To investigate in which reaction step the difference between **1** and **2** appears, we applied **1** and **2** to the reduction of nitrosobenzene to aniline. Though reduction of nitrosobenzene can occur even without **1** and **2**, the yield of aniline is very low in the absence of **1** and **2**, as shown in Table 3. On the other hand, **1** and **2** give large yields of aniline; in particular, it is noted that the yield when **1** is used is significantly large and almost the same as the conversion. It is also noted that differences in the yield and the conversion between **1** and **2** are much larger in the reaction of nitrobenzene than in the reaction of nitrosobenzene. From this result, it should be reasonably concluded that the difference in catalytic activity between **1** and **2** mainly arises from the reduction of nitrobenzene to nitrosobenzene.

Table 3 Reduction of nitrosobenzene with various catalysts

Catalyst	Conversion (%) [b]	Yield (%) [b]
None	96	11
MV^{2+}	97	14
[FeCl(TPP)] **2**	98	55
[FeCl(mvep-TPP)]Cl_2 **1**	100	83

[a] [FeCl(TPP)] = [FeCl(mvep-TPP)]Cl_2 = 3.75×10^{-2} mmol dm^{-3}, [cat] : $NaBH_4$: substrate = 1 : 400 : 400, 3 h at 25 °C. [b] Based on nitrobenzene derivatives used in the reaction.

In conclusion, [FeCl(mvep-TPP)]Cl_2 is presented here as an efficient catalyst for multi-electron reduction reactions. This is because the viologen moiety serves as an electron trapping and storage unit.

Acknowledgements

This work was in part financially supported by Grant-in-Aids from Ministry of Education, Culture, Science, and Sports (No. 09305057, 09044096).

Notes and references

‡ 5-*p*-Nitrophenyl-10,15,20-triphenylporphyrin was synthesized from pyrrole, benzaldehyde, and *p*-nitrobenzaldehyde, and it was converted to 5-*p*-aminophenyl-10,15,20-triphenylporphyrin with $SnCl_2$–HCl. Then, 3-bromopropionic acid was introduced to the above porphyrin by the DCC method (ESI), affording 5-{4-(3-bromoethylcarboxyamidyl)phenyl}-10,15,20-triphenylporphyrin. This porphyrin was reacted with 4-(4′-pyridyl)-*N*-methylpyridinium iodide to yield 5-{3-(1′-methyl-4,4′-bipyridinium)ethylcarboxyamidyl}phenyl-10,15,20-tri-

phenylporphyrin. This porphyrin was metalated with $FeCl_3$ and then washed with 2 M hydrochloric acid, according to the usual procedure.[14] Elemental analysis: H; 4.19 (4.27), C; 67.80 (68.55), N; 9.07 (9.65), where values in parentheses are calc. for $C_{58}H_{43}N_7OFeCl_3$. UV-Vis; λ_{max} = 380 (7.00×10^4), 419 (1.84×10^5), 512 (1.73×10^4), 585 (3650), 649 (3170), 692 (3170), where λ_{max} is in nm and values in parentheses are molar extinction coefficients ($mol^{-1}\,l\,dm^{-1}$). ^1H NMR for metal-free mvep-TPP; δ 10.65 (1H, NH), 9.56 (2H, 4,4′-bpy), 9.30 (2H), 8.83 (12H, pyrrole and 4,4′-bpy), 8.21 (8H, *o*,*o*′-Ph), 8.02 (2H, *m*′-Ph), 7.84 (9H, *m*,*p*-Ph), 5.13 (2H, -CO-CH_2-), 4.45 (3H, 4,4′-bpy), 3.45 (2H, -CH_2-4,4′-bpy), −2.93 (2H, pyrolle NH).

§ If a carboxyl group was connected to the porphyrin ring, the introduction of a viologen unit through the amide linkage failed. The NH_2 group should be connected to the porphyrin ring to utilize the amide group for the bridging linkage.

¶ ESR spectral measurements suggest that both iron porphyrin and viologen moieties are two-electron reduced in THF–MeOH (9 : 1 v/v); *g* = *ca*. 6.0 for **1** without $NaBH_4$ and 2.32 and 1.95 for **1** with $NaBH_4$. In diglyme–MeOH (9 : 1 v/v), these ESR spectra were not observed, while only a very small signal was observed at *g* = 2.02. This very small signal suggests that the iron porphyrin moiety is one-electron reduced and most of the viologen moieties are two-electron reduced but some amount of the viologen is one-electron reduced in this solvent. Thus, the number of electrons that **1** can use for the reduction reaction is less than 4. Since six electrons are necessary for the reduction of nitrobenzene to aniline, one molecule of **1** and **2** cannot reduce nitrobenzene to aniline.

‖ First, the reaction solution was thoroughly degassed through five cycles of freeze–pump–thaw. Then, the appropriate amount of oxygen-saturated methanol was added to the solution (ESI).

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Communication b000146p