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A Green Process for Oxidation of *p*-Nitrotoluene Catalyzed by Metalloporphyrins under Mild Conditions

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Abstract:

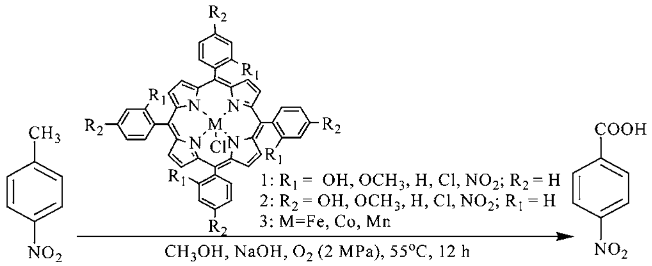
A novel synthetic technology of *p*-nitrobenzoic acid has been investigated with dioxygen by using metalloporphyrins RTPP-M^{III}Cl (M = Fe, Co, Mn) as biomimetic catalysts. Oxidation of *p*-nitrotoluene to *p*-nitrobenzoic acid under 2.0 MPa of O_2 in the presence of a microamount of metalloporphyrins (RTPP-M^{III}Cl) at 55 °C was achieved with the highest (up to 90.4%) yield. Further research results show that the catalytic activities were relative to the nature of the substituted groups and the central metal ions of metalloporphyrins. For the metalloporphyrins with the same center metal ions, the greater the electron-withdrawing degree of groups in the porphyrin ring, the higher the catalytic activities of the metalloporphyrins. The catalytic activities for metalloporphyrins with different center metal ions followed the order RTPPMn ^{III}Cl > RTPP Fe ^{III}Cl > RTPP Co ^{III}Cl.

Introduction

p-Nitrobenzoic acid, an important intermediate of pharmaceutical and organic synthesis, was conventionally manufactured through the oxidation of *p*-nitrotoluene using cobalt bromide and manganese salt as catalysts.[1] In one of our previous works, the oxidation of *p*-nitrotoluene with metal phthalocyanines as catalysts in an alkali−methanol solution had been reported, in which a rather high yield (ca. 88.8%) of *p*-nitrobenzoic acid was achieved.[2]

In the past two decades, the biomimetic catalysis of metalloporphyrins under mild conditions has increasingly attracted considerable attention.[3−5] More processes involved in the catalysis of metalloporphyrins under mild conditions had been developed.[6,7] The selection of O_2 as the oxygen source in alkane and alkene oxidations catalyzed by metalloporphyrins has raised great prospects in the oxidation of hydrocarbons.

Scheme 1



Our team also reported a one-pot oxidation of cyclohexane to adipic acid catalyzed by Fe-porphyrin in the presence of molecular oxygen without any additives with a yield of 21.4%, which was a promising process for production.[8] In this paper, with metallotetraphenylporphyrin chloride complexes (RTPPM^{III}Cl) as biomimetic catalysts for preparation of *p*-nitrobenzoic acid from oxidation *p*-nitrotoluene, the highest (90.4%) yield of *p*-nitrobenzoic acid was obtained. The effect of substituted groups and central metal ions on catalytic activities of metalloporphyrins was further investigated, and so far, this research work has not been reported yet.

Results and Discussions

Catalytic Activities of Metalloporphyrins. The structures of different metalloporphyrin catalysts and the dioxygen oxidation of *p*-nitrotoluene to the *p*-nitrobenzoic acid catalyzed by these metalloporphyrins were shown in Scheme 1.

The oxidation of *p*-nitrotoluene catalyzed by Fe, Co, and Mn porphyrins was investigated in a NaOH−methanol solution under 2.0 MPa of dioxygen at 55 °C for 12 h, and the results were shown in Table 1 and Figure 1.

Note: There will be a potential hazard of explosion when using methanol in a pure oxygen environment, although the explosion limit range of methanol (6.0−36.5 vol %) is relatively narrower and its flash point (9 °C) is relatively higher than those of hydrocarbon solvents (<0 °C). When considering safety, much attention and careful design must be given in industrial practice. So the reaction temperature or O_2 pressure should be selected as low as possible. To solve the above problems, the technologies for preparing *p*-nitrobenzoic acid using ethanol−water at 60% (v/v) instead of methanol as solutions and using air instead of dioxygen are being investigated by our group, and the research work will be reported soon.

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(1) Partenheimer, W. *Catal. Today* **1995**, *23*, 69−158.

(2) Song, X. F.; She, Y. B.; Ji, H. B.; Zhang, Y. H. *Organic Process Research & Development*, **2005**, *9* (3), 297−301.

(3) Meunier, B. *Chem. Rev.* **1992**, *9* (6), 1411−1456.

(4) Groves, J. T.; Bonchio, M.; Carofiglio, T.; Shalyaev, K. *J. Am. Chem. Soc.* **1996**, *118*, 8961−8962.

(5) Zhang, R.; Horner, J. H.; Newcomb, M. *J. Am. Chem. Soc.* **2005**, *127* (18), 6573−6582.

(6) Maldotti, A.; Bartocci, C.; Varani, G.; Molinari, A. *Inorg. Chem.* **1996**, *35*, 1126−1131.

(7) Haber, J.; Matachowski, L.; Pamin, K.; Poltowicz, J. *J. Mol. Catal. A: Chem.* **2003**, *198*, 215−221.

(8) Yuan, Y.; Ji, H. B.; Chen, Y. X.; Han, Y.; Song, X. F.; She, Y. B.; Zhong, R. G. *Org. Process Res. Dev.* **2004**, *8*, 418−420.

10.1021/op060056z CCC: $33.50

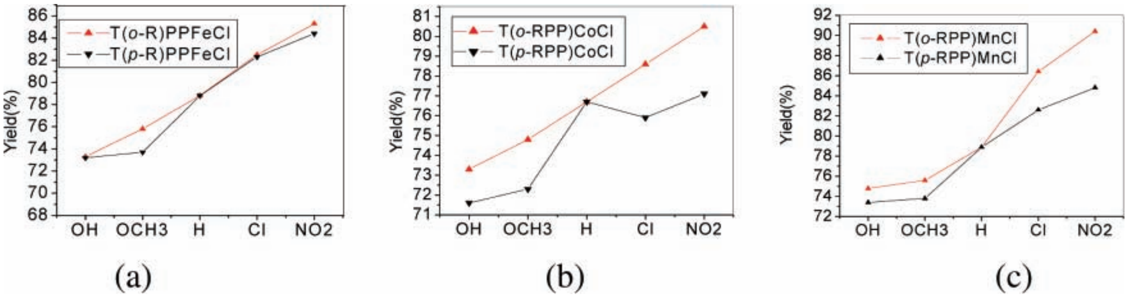

Figure 1. **Comparative catalytic activities of metalloporphyrins with different structures.**

Table 1. **Results of oxidation of *p*-nitrotoluene catalyzed by Fe, Co, and Mn porphyrins**[a]

		yields of *p*-nitrobenzoic acid[b] (%)		
entry	catalyst	Fe	Co	Mn
1	T(*o*-OH)PPMCl (R_1 = OH, R_2 = H)	73.3	72.3	74.8
2	T(*p*-OH)PPMCl (R_1 = H, R_2 = OH)	73.2	71.6	73.4
3	T(*o*-OCH_3)PPMCl (R_1 = OCH_3, R_2 = H)	75.8	74.8	75.6
4	T(*p*-OCH_3)PPMCl (R_1 = H, R_2 = OCH_3)	73.7	72.3	73.8
5	TPPMCl (R_1 = H, R_2 = H)	78.8	76.7	78.9
6	T(*o*-Cl)PPMCl (R_1 = Cl, R_2 = H)	82.5	78.6	86.4
7	T(*p*-Cl)PPMCl (R_1 = H, R_2 = Cl)	82.3	75.9	82.6
8	T(*o*-NO_2)PPMCl (R_1 = NO_2, R_2 = H)	85.3	80.5	90.4
9	T(*p*-NO_2)PPMCl (R_1 = H, R_2 = NO_2)	84.4	77.1	84.8

[a] Reaction conditions: *p*-nitrotoluene (20 mmol); catalysts (1.24×10^{-3} mol %, based on the initial amount of *p*-nitrotoluene); methanol (50 mL); NaOH (120 mmol); oxygen pressure (2.0 MPa); at 55 °C for 12 h. [b] The all yields of *p*-nitrobenzoic acid were the isolated yield.

The results of Table 1 and Figure 1 showed that all the metalloporphyrin catalysts presented excellent activities for the oxidation of *p*-nitrotoluene to *p*-nitrobenzoic acid with the isolated yield of product being more than 71.6%. The yields were much higher than the results obtained from Chandalia and coauthors, who used another type of biomimetic catalyst, i.e., cobalt phthalocyanine catalyst and reported their best yield at less than 40%.[9] Moreover, the yields were comparable to the results with metal phthalocyanines previously reported by our team, with the highest yield reaching up to 88.8%. [2]

From Table 1 and Figure 1, we could find that the structure of metalloporphyrins also affected their catalytic performance to some extent, i.e., the catalytic activities of metalloporphyrins in the oxidation of *p*-nitrotoluene to *p*-nitrobenzoic acid not only change with the variety of metal atom ions in metalloporphyrins but also change with the variety of peripheral substituents on the porphyrin ring in the same pattern of metalloporphyrins. For the chloro-iron tetraphenylporphyrin (RTPPFeCl) catalyst, the different substituents in the phenyl ring of porphyrin ligands exhibited different isolated yields of *p*-nitrobenzoic acid. For example, for TPPFeCl with different *ortho*- substituents from *o*-NO_2 to *o*-OH, yields changed from 85.3% to 73.3%; and for TPPFeCl with different *para*- substituents from *p*-NO_2 to *p*-OH, yields changed from 84.4% to 73.2%. Furthermore, the catalytic activities with different substituents from *o*/*p*-NO_2 to *o*/*p*-OH followed the order T(*o*/*p*-NO_2)PPFeCl > T(*o*/*p*-Cl)PPFeCl > TPPFeCl > T(*o*/*p*-OCH_3)PPFeCl > T(*o*/*p*-OH)PPFeCl. It is obvious that these iron−porphyrin catalysts with an electron-withdrawing group such as *o*/*p*-NO_2 exhibit higher yields than those with an electron-donating group such as *o*/*p*-OH. A similar result was reported by Guo et al.; that is, the existence of electron-withdrawing groups could also accelerate the reaction rate of cyclohexane hydroxylation with the metalloporphyrin catalysts.[10] The reasons might be that the electronic density of Fe ions in metalloporphyrins decreased with the increase of the electron-withdrawing degree of substituents from *o*/*p*-OH to *o*/*p*-NO_2, thus leading to the enhancement of the $Fe^{(III)}/Fe^{(II)}$ reduction potential, and $Fe^{(III)}$ could be easily reduced to $Fe^{(II)}$, and the all catalytic cycle of metalloporphyrins could be easily fulfilled.[11]

Furthermore, Fe porphyrins with *ortho*-position electron-withdrawing substituents, such as T(*o*- NO_2)PPFeCl and T(*o*-Cl)PPFeCl, exhibited higher yields of *p*-nitrobenzoic acid than those with *para*-position electron-withdrawing substituents such as T(*p*- NO_2)PPFeCl and T(*p*-Cl)PPFeCl. It is well-known that self-aggregation of metalloporphyrins could easily occur and the existence of steric hindrance could well prevent self-aggregation.[12] Comparing Fe porphyrins having *ortho*- substituents with those having *para*- substituents, it was clear that the steric hindrance for *ortho*- substituents was greater, and corresponding catalytic activities were higher.

Similarly cobalt porphyrins were also efficient active catalysts for the oxidation of unactivated *p*-nitrotoluene. For example, the chloro-cobalt tetra-(*o*-nitrophenyl)porphyrin T(*o*-NO_2)PPCoCl could catalyze the oxidation of *p*-nitrotoluene smoothly under the same reaction conditions, with a yield of *p*-nitrobenzoic acid of 80.5%. A similar relationship between substituents of the phenyl groups and catalytic activities could also be obtained as shown in Figure 1b.

Inspired by the high yields from Fe and Co porphyrins, Mn was tried in catalyzing the oxidation of *p*-nitrotoluene

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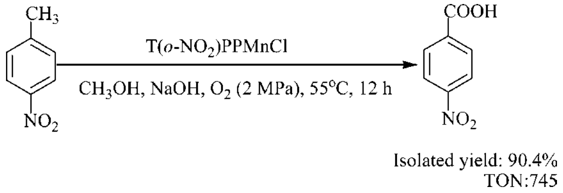
(9) Chandalia, S. B.; Mukhopadhyay, S.; *Org. Process Res. Dev.* **1999**, *3*, 109−113.

(10) Guo, C. C.; Song, J. X.; Chen, X. B.; Jiang, G. F. *J. Mol. Catal.* **2000**, *157*, 31−40.

(11) Lyons, J. E.; Ellis, P. E.; Myers, H. K. *J. Catal.* **1995**, *155*, 59−73.

(12) Guo, C. C.; Liu, X. Q.; Liu, Y.; Liu, Q.; Chu, M. F.; Zhang, X. B. *J. Mol. Catal. A: Chem.* **2003**, *192*, 289−294.

Scheme 2



under the same reaction conditions. In this case, the result of chloro-manganese tetra-(*o*-nitrophenyl)porphyrin T(*o*-NO_2)PPMnCl was shown in Scheme 2.

In this oxidation, the chloro-manganese tetra-(*o*-nitrophenyl)porphyrin T(*o*-NO_2)PPMnCl presented a yield of 90.4% for *p*-nitrobenzoic acid in the presence of molecular oxygen, which was the highest yield reported presently. A similar relationship of chloro-manganese porphyrin complexes could also be found as shown in Figure 1c.

The results of Table 1 also showed that tetra-(*o*-nitrophenyl) porphyrins with Fe, Co, and Mn central metal ions gave different yields such as 85.3%, 80.5%, and 90.4%; that is, the order Mn > Fe > Co could be observed. Haber[13] also reported a similar sequence when performing the oxidation of cyclohexane. The most active catalyst was a manganese tetra-(*o*-nitrophenyl) porphyrin with the highest yield (90.4%) of *p*-nitrobenzoic acid.

The three possible O_2 oxidation paths were fully described in our former work with metal phthalocyanines as catalysts.[2] The catalytic mechanism of metalloporphyrins was reported by Lyons for the oxidation of isobutene and propane using halogenated porphyrin chromium, manganese, and iron complexes as catalysts.[11] During the reaction process, a high valence manganese−oxygen cation radical as an active intermediate was reported to be more stable than the high valence iron−oxygen cation radical, [14] making the reaction easily performed. For Co, the lower stability of trivalent Co might attribute to the lower catalytic activity. This might explain the order Mn > Fe > Co towards the oxidation of *p*-nitrotoluene.

Conclusions

Metalloporphyrins were more active catalysts than metal phthalocyanines for the oxidation of *p*-nitrotoluene to *p*-nitrobenzoic acid. The nature of the porphyrin rings and the central metal ions had a remarkable effect on the activities of metalloporphyrins. Metalloporphyrins with electron-withdrawing groups located in the *ortho*-position of a phenyl ring were more efficient catalysts than those with electron-donating groups located in the *para*-position of a phenyl ring while using the same center metal ions; that is, catalytic activities of metalloporphyrins were in the order T(*o*/*p*-NO_2)PPMCl > T(*o*/*p*-Cl)PPMCl > TPPMCl > T(*o*/*p*-OCH_3)PPMCl > T(*o*/*p*-OH)PPMCl. The catalytic activities of metalloporphyrins with different center metal ions were in the order RTPPMn ^{III}Cl >RTPP Fe ^{III}Cl > RTPP Co ^{III}Cl.

Experimental Section

Materials and Instruments. Pyrrole was redistilled before use. Other reagents such as *p*-nitrotoluene purchased from Aldrich were of high purity and used without further purification.

UV−vis spectra were recorded on a Brucker HITACHI U-3100. Infrared spectra were recorded on a Brucker VERTEX 70. A THERMOQUEST Flash EA 1112 elemental analysis meter was used.

Syntheses of Biomimetic *meso*-Phenyl Substitute Metallotetraphenylporphyrin. The substituted tetraphenylporphyrins ($RTPPH_2$) were synthesized by the direct condensation of pyrrole with the substituted benzaldehydes according to the documented procedures.[15]

Chloro-iron Tetraphenylporphyrin (RTPPFeCl). T(*o*-NO_2)PPFeCl. 200 mg (0.25 mmol) of T(*o*-NO_2)PPH_2 were dissolved in 100 mL of glacial acetic acid. The solution was heated to reflux with magnetic stirring. Upon dissolution of T(*o*-NO_2)PPH_2, 300 mg (1.50 mmol) of $FeCl_2 \cdot 4H_2O$ were added in three portions within 30 min. When thin-layer chromatography (alumina) indicated no free base porphyrin at this point, using methylene chloride as eluant, 50 mL of HOAc were removed from the solution. The solution was cooled to 70 °C, and 40 mL of 6 M HCl were added to it. The solid appeared in the solution and then was filtrated and washed with 3 M HCl until the filtrate no longer appeared green. The resulting solid was vacuum-dried and afforded above 91.9% yield of T(*o*-NO_2)PPFeCl. Mp > 300 °C. Anal. Calcd for $C_{44}H_{24}N_8O_8ClFe$: C, 59.78; H, 2.74; N, 12.68. Found: C, 59.35; H, 2.64; N, 12.61. UV−vis(CH_2Cl_2) λ_{max}: 422.0 nm (Soret band), 509.6 nm, 579.0 nm (Q-band). IR: 999.8 cm^{-1} (δ_{Fe-N}), 367 cm^{-1} (ν_{Fe-Cl}).

T(*o*-Cl)PPFeCl. The solution of T(*o*-ClTPP) 200 mg (0.26 mmol) in dimethylformamide(100 mL) was heated to reflux with magnetic stirring. 300 mg (1.50 mmol) of $FeCl_2 \cdot 4H_2O$ were added in three portions within 30 min. When thin-layer chromatography (alumina) indicated no free base porphyrin, the reaction mixture was cooled to 70 °C, and 40 mL of 6 M HCl were added to it. The solid appeared in the solution and then was filtrated and washed with 3 M HCl until the filtrate no longer appeared green. The resulting solid was vacuum-dried and afforded above 94.7% yield of T(*o*-Cl)PPFeCl. Mp > 300 °C. Anal. Calcd for $C_{44}H_{24}N_4Cl_5Fe$: C, 62.78; H, 2.87; N, 6.66. Found: C, 62.44; H, 3.16; N, 7.01. UV−vis(CH_2Cl_2) λ_{max}: 418.5 nm (Soret band), 505.4 nm, 576.0 nm (Q-band). IR: 998.3 cm^{-1} (δ_{Fe-N}), 369.6 cm^{-1} (ν_{Fe-Cl}).

T(*o*-OCH_3)TPPFeCl was prepared using the same procedure as that described for T(*o*-Cl)PPFeCl, and the final solid was recrystallized from methylene chloride to yield 91.5%. Mp > 300 °C. Anal. Calcd for $C_{48}H_{36}N_4ClFeO_4$: C, 69.96; H, 4.40; N, 6.80. Found: C, 69.36; H, 4.73; N, 6.78. UV−vis(CH_2Cl_2) λ_{max}: 418.9 nm (Soret band), 512.9 nm, 668.9 nm (Q-band). IR: 997.8 cm^{-1} (δ_{Fe-N}), 360.4 cm^{-1} (ν_{Fe-Cl}).

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(13) Haber, J.; Matachowski, L.; Pamin, K.; Poltowicz, J. *J. Mol. Catal.* **2000**, *162*, 105−109.

(14) Guo, C. C.; Huang, G.; Li, Z. P.; Song, J. X. *J. Mol. Catal.* **2001**, *170*, 43−49.

(15) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32* (2), 476−476.

T(*o*-OH)TPPFeCl was prepared using the same procedure as that described for T(*o*-Cl)PPFeCl, and the final solid was recrystallized from methanol to yield 61.5%. Mp > 300 °C. UV−vis(CH_2Cl_2): λ_{max}: 415.6 nm (Soret band), 523.2 nm, 578.6 nm (Q-band). IR: 998.8 cm^{-1} (δ_{Fe-N}), 361.4 cm^{-1} (ν_{Fe-Cl}).

TPPFeCl was prepared using the same procedure as that described for T(*o*-Cl)PPFeCl and recrystallized from CH_2Cl_2/methanol, and the yield was up to 97.4%. Mp > 300 °C. Anal. Calcd for $C_{44}H_{28}N_4ClFe$: C, 75.07; H, 4.01; N, 7.96. Found: C, 74.29; H, 4.07; N, 7.92. UV−vis(CH_2Cl_2): λ_{max}: 418.8 nm (Soret band), 507.2 nm, 572.4 nm (Q-band). IR: 999.6 cm^{-1} (δ_{Fe-N}), 378.9 cm^{-1} (ν_{Fe-Cl}).

T(*p*-NO$_2$)PPFeCl: 200 mg (0.25 mmol) of T(*p*-NO$_2$)PPH$_2$ were dissolved in 100 mL of propionic acid. The solution was heated to reflux with magnetic stirring. Upon dissolution of the T(*p*-NO$_2$)PPH$_2$, 300 mg (1.50 mmol) of $FeCl_2$•$4H_2O$ were added in three portions within 30 min. When thin-layer chromatography (alumina) indicated no free base porphyrin, 50 mL of propionic acid was removed from the solution. The solution was cooled to 70 °C, and 40 mL of 6 M HCl were added to it. The solid appeared in the solution and then was filtrated and washed with 3 M HCl until the filtrate no longer appeared green. The resulting solid was vacuum-dried and afforded above 92% yield of T(*p*-NO$_2$)PPFeCl. Mp > 300 °C. Anal. Calcd for $C_{44}H_{24}N_8O_8ClFe$: C, 59.78; H, 2.74; N, 12.68. Found: C, 59.35; H, 2.74; N, 12.68. UV−vis(CH_2Cl_2) λ_{max}: 422.0 nm (Soret band), 514.4 nm, 583.0 nm (Q-band). IR: 998.8 cm^{-1} (δ_{Fe-N}), 368 cm^{-1} (ν_{Fe-Cl}).

T(*p*-Cl)PPFeCl was prepared using the same procedure as described for T(*o*-Cl)PPFeCl and recrystallized from CH_2Cl_2/methanol. The yield was up to 99.4%. Mp > 300 °C. Anal. Calcd for $C_{44}H_{24}N_4Cl_5Fe$: C, 62.78; H, 2.87; N, 7.04. Found: C, 62.32; H, 3.31; N, 6.66. UV−vis(CH_2Cl_2) λ_{max}: 420.5 nm (Soret band), 509.4 nm, 573.0 nm (Q-band). IR: 998.6 cm^{-1} (δ_{Fe-N}), 359.1 cm^{-1} (ν_{Fe-Cl}).

T(*p*-OCH$_3$)PPFeCl was prepared using the same procedure as that described for T(*o*-Cl)PPFeCl, and the resulting solid was washed twice with water (50 mL) and then recrystallized from CH_2Cl_2/methanol, in a yield of 95.2%. Mp > 300 °C. Anal. Calcd for $C_{48}H_{36}N_4ClFeO_4$: C, 69.96; H, 4.40; N, 6.80. Found: C, 69.30; H, 4.68; N, 6.86. UV−vis(CH_2Cl_2) λ_{max}: 421.5 nm (Soret band), 509.4 nm, 571.0 nm (Q-band). IR: 997.9 cm^{-1} (δ_{Fe-N}), 359.7 cm^{-1} (ν_{Fe-Cl}).

T(*p*-OH)PPFeCl was prepared using the same procedure as that described for T(*o*-Cl)PPFeCl and then recrystallized from methanol, in a yield of 91.6%. Mp > 300 °C. Anal. Calcd for $C_{44}H_{28}N_4ClFeO_4$: C, 68.74; H, 3.60; N, 7.29. Found: C, 67.29; H, 3.95; N, 7.21. UV−vis(CH_2Cl_2) λ_{max}: 418.3 nm (Soret band), 503.2 nm, 575.8 nm (Q-band). IR: 998.4 cm^{-1} (δ_{Fe-N}), 339.7 cm^{-1} (ν_{Fe-Cl}).

Chloro-manganese Tetraphenylporphyrin (RTPP-MnCl). T(*o*-NO$_2$)PPMnCl. 200 mg (0.25 mmol) of T(*o*-NO$_2$)PPH$_2$ were dissolved in 50 mL of dimethylformamide. The solution was heated to reflux with magnetic stirring. Upon dissolution of T(*o*-NO$_2$)PPH$_2$, 300 mg (1.50 mmol) of $MnCl_2$•$4H_2O$ were added in three portions within 30 min. When thin-layer chromatography (alumina) indicated no free base porphyrin, using dimethylformamide as eluant, 30 mL of dimethylformamide were removed from the solution. The solution was cooled to 70 °C, and 40 mL of 6 M HCl were added to it. The solid appeared in the solution and then was filtrated and washed 3 times with 3 M HCl. The resulting solid was vacuum-dried and afforded above 94.9% yield of T(*o*-NO$_2$)PPMnCl. UV−vis(CH_2Cl_2) λ_{max}: 471.0 nm (Soret band), 508.8 nm, 563.2 nm (Q-band). IR: 1009.3 cm^{-1} (δ_{Mn-N}), 322 cm^{-1} (ν_{Mn-Cl}).

T(*o*-Cl)PPMnCl. 200 mg (0.26 mmol) of T(*o*-Cl)PPH$_2$ were dissolved in 50 mL of dimethylformamide. The solution was heated to reflux with magnetic stirring. Upon dissolution of T(*o*-Cl)PPH$_2$, 300 mg (1.50 mmol) of $MnCl_2$•$4H_2O$ were added in three portions within 30 min. When thin-layer chromatography (alumina) indicated no free base porphyrin, using methylene chloride as eluant, the solution was cooled to 70 °C, and 40 mL of 6 M HCl were added to it. The solid appeared in the solution and then was filtrated and washed 3 times with 3 M HCl. The resulting solid was vacuum-dried and afforded above 94.9% yield of T(*o*-Cl)PPMnCl. UV−vis(CH_2Cl_2) λ_{max}: 478.0 nm (Soret band), 583.6 nm, 620.0 nm (Q-band). IR: 1008.5 cm^{-1} (δ_{Mn-N}), 322 cm^{-1} (ν_{Mn-Cl}).

TPPMnCl was prepared using the same procedure as that described for T(*o*-Cl)PPMnCl and recrystallized from CH_2Cl_2/methanol. The yield was up to 88.5%. UV−vis(CH_2Cl_2) λ_{max}: 477.0 nm (Soret band), 534.0 nm, 583.3 nm (Q-band). IR: 1008.0 cm^{-1} (δ_{Mn-N}), 320 cm^{-1} (ν_{Mn-Cl}).

T(*o*-OCH$_3$)PPMnCl was prepared using the same procedure as that described for T(*o*-Cl)PPMnCl and recrystallized from CH_2Cl_2, in a yield of 90%. UV−vis(CH_2Cl_2) λ_{max}: 477.5 nm (Soret band), 513.3 nm, 583.0 nm (Q-band). IR: 1007.0 cm^{-1} (δ_{Mn-N}), 321 cm^{-1} (ν_{Mn-Cl}).

T(*o*-OH)PPMnCl was prepared using the same procedure as that described for T(*o*-Cl)PPMnCl and recrystallized from methanol, in a yield of 90%. UV−vis(CH_2Cl_2): λ_{max}: 472.0 nm (Soret band), 530.3 nm, 583.0 nm (Q-band). IR: 1007.0 cm^{-1} (δ_{Mn-N}), 317 cm^{-1} (ν_{Mn-Cl}).

T(*p*-NO$_2$)PPMnCl was prepared using the same procedure as that described for T(*o*-Cl)PPMnCl and recrystallized from DMF, in a yield of 91.0%. UV−vis(CH_2Cl_2) λ_{max}: 477.8 nm (Soret band), 528.6 nm, 583.6 nm (Q-band). IR: 1008 cm^{-1} (δ_{Mn-N}), 323 cm^{-1} (ν_{Mn-Cl}).

T(*p*-Cl)PPMnCl was prepared using the same procedure as that described for T(*o*-Cl)PPMnCl and recrystallized from methanol, in a yield of 99.5%. UV−vis(CH_2Cl_2) λ_{max}: 477.6 nm (Soret band), 532.0 nm, 585.6 nm (Q-band). IR: 1007.9 cm^{-1} (δ_{Mn-N}), 320 cm^{-1} (ν_{Mn-Cl}).

T(*p*-OCH$_3$)PPMnCl was prepared using the same procedure as that described for T(*o*-Cl)PPMnCl and recrystallized from methanol, in a yield of 97.5%. UV−vis(CH_2Cl_2): λ_{max}: 479.2 nm (Soret band), 535.2 nm, 589.6 nm (Q-band). IR: 1005.1 cm^{-1} (δ_{Mn-N}), 322 cm^{-1} (ν_{Mn-Cl}).

T(*p*-OH)PPMnCl was prepared using the same procedure as that described for T(*o*-Cl)PPMnCl and recrystallized from methanol, in a yield of 81.9%. UV−vis (CH_2Cl_2) λ_{max}: 471.0 nm (Soret band), 535.2 nm, 584.6 nm (Q-band). IR: 1007.9 cm^{-1} (δ_{Mn-N}), 321 cm^{-1} (ν_{Mn-Cl}).

Chloro-cobalt Tetraphenylporphyrin (RTPPCoCl). T(*o*-NO$_2$)PPCoCl. 200 mg (0.25mol) of T(*o*-NO$_2$)PPH$_2$ were dissolved in 100 mL of propionic acid. The solution was heated to reflux with magnetic stirring. Upon dissolution of T(*o*-NO$_2$)PPH$_2$, 300 mg (1.20 mmol) of Co(OAc)•4H$_2$O were added in three portions within 30 min. When thin-layer chromatography (alumina) indicated no free base porphyrin using benzene/ligroin as eluant, 50 mL of propionic acid were removed from the solution. The solution was cooled to 70 °C, and 40 mL of 6 M HCl were added to it. The solid appeared in the solution and then was filtrated and washed with 3 M HCl until the filtrate no longer appeared red. The resulting solid was recrystallized from DMF and then vacuum-dried, and affording above 85% yield of T(*o*-NO$_2$)PPCoCl. UV−vis(CH$_2$Cl$_2$) λ_{max}: 414.3 nm (Soret band), 535.1 nm, 565.2 nm (Q-band). IR: 1000.8 cm^{-1} (δ_{Co-N}), 307 cm^{-1} (ν_{Co-Cl}).

T(*o*-Cl)PPCoCl was prepared using the same procedure as that described for T(*o*-NO$_2$)PPCoCl, and only the reaction solvent was DMF instead of propanoic acid. The resulting solid recrystallized from methanol, in a yield of 99.7%. UV−vis(CH$_2$Cl$_2$) λ_{max}: 419.0 nm (Soret band), 541.4 nm, 559.0 nm (Q-band). IR: 1005.0 cm^{-1} (δ_{Co-N}), 317 cm^{-1} (ν_{Co-Cl}).

TPPCoCl was prepared using the same procedure as that described for T(*o*-Cl)PPCoCl and recrystallized from CH$_2$Cl$_2$/methanol, in a yield of 99.0%. UV−vis (CH$_2$Cl$_2$) λ_{max}: 405.5 nm (Soret band), 544.3 nm, 571.3 nm (Q-band). IR: 1004.0 cm^{-1} (δ_{Co-N}), 301 cm^{-1} (ν_{Co-Cl}).

T(*o*-OCH$_3$)PPCoCl was prepared using the same procedure as that described for T(*o*-Cl)PPCoCl and recrystallized from CH$_2$Cl$_2$/methanol, in a yield of 98%. UV−vis(CH$_2$Cl$_2$) λ_{max}: 411.5 nm (Soret band), 523.6 nm, 562.3 nm (Q-band). IR: 1000.0 cm^{-1} (δ_{Co-N}), 306 cm^{-1} (ν_{Co-Cl}).

T(*o*-OH)PPCoCl was prepared using the same procedure as that described for T(*o*-Cl)PPCoCl and recrystallized from methanol, in a yield of 98%. UV−vis(CH$_2$Cl$_2$) λ_{max}: 406.5 nm (Soret band), 530.6 nm, 562.3 nm (Q-band). IR: 1001.0 cm^{-1} (δ_{Co-N}), 310 cm^{-1} (ν_{Co-Cl}).

T(*p*-NO$_2$)PPCoCl was prepared using the same procedure as that described for T(*o*-NO$_2$)PPCoCl and recrystallized from DMF, in a yield of 63.0%. UV−vis(CH$_2$Cl$_2$) λ_{max}: 414.0 nm (Soret band), 553.0 nm (Q-band). IR: 1003.3 cm^{-1} (δ_{Co-N}), 320 cm^{-1} (ν_{Co-Cl}).

T(*p*-Cl)PPCoCl was prepared using the same procedure as that described for T(*o*-Cl)PPCoCl and recrystallized from CH$_2$Cl$_2$/methanol, in a yield of 98.9%. UV−vis(CH$_2$Cl$_2$) λ_{max}: 410.0 nm (Soret band), 529.0 nm, 653.0 nm (Q-band). IR: 1000.6 cm^{-1} (δ_{Co-N}), 320 cm^{-1} (ν_{Co-Cl}).

T(*p*-OCH$_3$)PPCoCl was prepared using the same procedure as that described for T(*o*-Cl)PPCoCl and recrystallized from CH$_2$Cl$_2$/methanol, in a yield of 98.3%. UV−vis(CH$_2$Cl$_2$) λ_{max}: 414.0 nm (Soret band), 530.0 nm (Q-band). IR: 1001.2 cm^{-1} (δ_{Co-N}), 321 cm^{-1} (ν_{Co-Cl}).

T(*p*-OH)PPCoCl was prepared using the same procedure as described for T(*o*-Cl)PPCoCl and recrystallized from methanol, in a yield of 87.3%. UV−vis(CH$_2$Cl$_2$) λ_{max}: 410.0 nm (Soret band), 546.0 nm, 603.0 nm (Q-band). IR: 1000.1 cm^{-1} (δ_{Co-N}), 323 cm^{-1} (ν_{Co-Cl}).

The above results showed that the synthetic complexes were metalloporphyrins as expected.

Dioxygen Oxidation of *p*-Nitrotoluene with Substitute Metallotetraphenylporphyrin. The catalytic oxidation of *p*-nitrotoluene to *p*-nitrobenzoic acid was carried out using molecular oxygen as an oxidant. For these experiments, a solution of *p*-nitrotoluene and catalyst in methanol was sealed into a 200 mL stainless steel autoclave equipped with a baffled magnetic stirrer. The reactor was pressurized at 2.0 MPa of oxygen and heated to reaction temperature for 12 h. Then, the reactor was cooled to room temperature, and the gas was slowly vented. *p*-Nitrobenzoic acid was obtained via dissolving the reaction mixture with water, filtration, extraction with benzene, acidifying the water phase with concentrated HCl, filtration, and drying.

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