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Efficient azo dye degradation by hydrogen peroxide oxidation with metalloporphyrins as catalysts

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Abstract

Degradation of organic dyes is a matter of great environmental concern. Despite many significant efforts and the numerous systems, which have been exploited, the problem is still unsolved due to intrinsically low activity or use of non-convenient chemical reagents. In this work, we describe the use of an oxidative system based on hydrogen peroxide activated by metalloporphyrins as catalysts to carry out the degradation of methyl orange, a model azo dye, in fairly high concentrations. Some inhibition of the catalytic activity during the reaction was originally observed. Adjustments in the system were made in order to prevent this inhibition and improve the efficiency of the system.

Keywords: Azo dye degradation; Metalloporphyrin; Hydrogen peroxide; Catalysis; Environment

1. Introduction

The presence of dyes in water effluents is a problem of great environmental concern. Particularly significant is the case of azo dyes since the low reactivity of the azo linkage makes this class of compounds resistant to microbiological degradations, thus blocking the process, which can lead to complete mineralization. A survey of the literature shows that the oxidative degradation of these structures seems the most convenient solution and some promising degradative systems have been disclosed [1]. Concerning environment protection, hydrogen peroxide is a desirable oxidant but its activation to generate an efficient oxidant species is still a challenge. Activation with non-porphyrinic manganese complex has shown limited ability to destroy azo dyes [2]. The use of Fenton chemistry seems to be attractive either in the presence or absence of light [3–8]. However, results, so far, are not very significant. Metalloporphyrins have shown very good efficiency for hydrogen peroxide activation, essentially in alkene epoxidations but their use in the catalytic degradation of dyes has not been relevant [9]. We developed an efficient oxidation system with diluted hydrogen peroxide under metalloporphyrin catalysis [10] and now attempt to extend the application of this system to dye degradation.

2. Results and discussion

In this work, the results of the degradation of azo dyes by diluted solutions of hydrogen peroxide activated by manganese complexes of *meso*-tetra-arylporphyrins (**1**–**5**) are presented in Scheme 1.

Metalloporphyrin **1** has proved to be a catalyst with good activity in epoxidation reactions with dilute hydrogen peroxide as oxidant [11,12]. For the oxidations expected to be more difficult than carbon–carbon double bond epoxidation we selected a set of more active catalysts such as **2**–**4**. Catalyst **4** is studied as an oxidation catalyst for the first time. We compared our catalysts to the known low efficiency catalyst **5**.

For alkene oxidations we previously developed a biphasic system using a dilute aqueous solution of hydrogen peroxide as oxidant and a chlorinated solvent for catalyst and substrate

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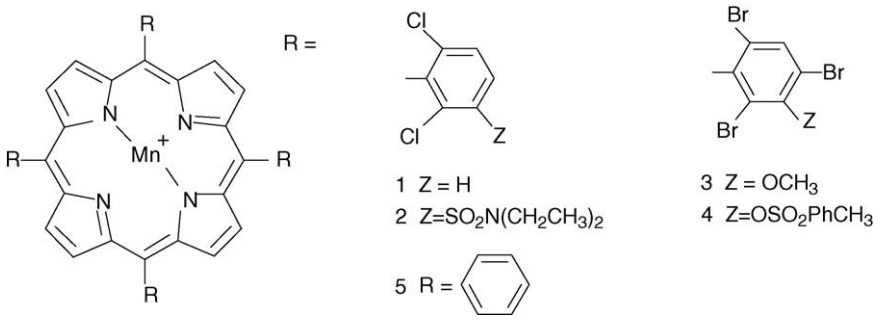


Scheme 1.

[13]. Important additives of this system are benzoic acid as co-catalyst and *tert*-butylpyridine as axial ligand. The use of this biphasic system to degradate azo dyes posed two major problems: the intrinsic lack of reactivity of the azo bond and the solubility of the dyes in the aqueous phase that blocks the interaction with the oxidative species present in the organic phase. In a previous work, we made an exploratory attempt to degradate azo dyes using a micelar medium with promising results [14]. To evaluate the capacity of the biphasic system for the degradation of an azo linkage we began studying the oxidation of sudan IV, an organic soluble azo dye, favouring the interaction with the oxidant species. Starting with a catalyst/substrate ratio of 1 to 25, which corresponds to a concentration of about 1×10^4 mg/L of dye, the results obtained with catalysts **1** and **3** are illustrated in Fig. 1.

It is clear that with both catalysts the great majority of the dye is destroyed after 30 min of reaction, since the value of absorbance is, then, mainly due to the residual metalloporphyrin catalysts. No significant difference of reactivity between the two catalysts is observed. A blank experiment in the absence of catalyst showed no indication of dye degradation.

In a second stage, we changed to methyl orange, a water-soluble dye. In this case we used a volume of 4 mL for the organic phase and 10 mL for the aqueous phase and, since the amount of dye was small, the total amount of hydrogen peroxide solution was reduced using diluted solutions of 2.5%. The dye degradation was followed by measuring the absorbance values for aliquots of 300 μL of the reaction medium, relatively to the initial absorbance value. The results with catalyst **1** and different dye concentrations are shown in Table 1.

Table 1
Bleaching of methyl orange solutions (total volume 10 mL) by hydrogen peroxide (2.5%) catalysed by metalloporphyrin **1**[a]

Initial dye concentration (mg/L) $(CH_3)_2N$–N=N–SO_3Na	Time (min)	Absorbance[b] (%)
70	10	2
	30	1
140	10	12
	30	9
210	10	17
	30	7

[a] Molar ratio of catalyst/axial ligand/organic acid, 1:5:20.
[b] Value relatively to initial absorbance value (100%).

It is clear that our catalytic system is able to destroy the dye despite it being present in the aqueous phase. The final solution is completely bleached as illustrated by the visible spectra at the beginning and end of the reaction in Fig. 2.

A blank experiment in the absence of catalyst shows decrease to 77% of the initial absorbance after 10 min, this value being the same after 2 h standing under the same con-

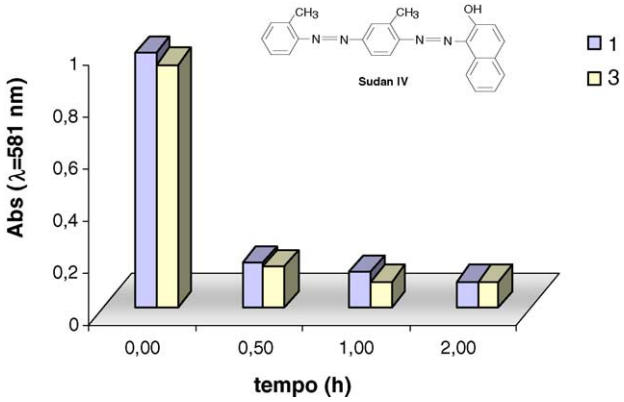


Fig. 1. Bleaching of sudan IV solutions (1×10^4 mg/L) in biphasic medium using hydrogen peroxide (5%) as oxidant and metalloporphyrins **1** and **3** as catalysts.

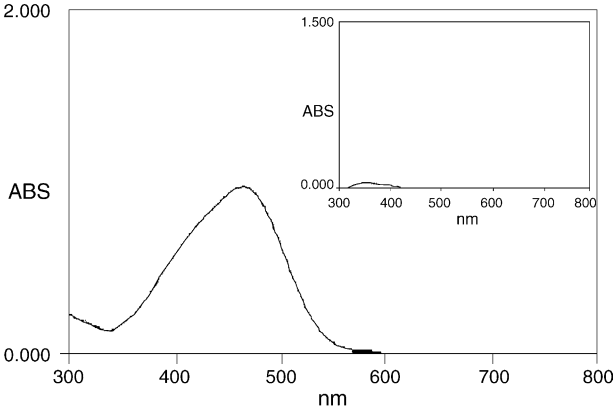
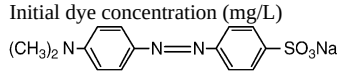


Fig. 2. Visible spectra of the dye solution at the beginning of the reaction. In inset the spectra at the end of the reaction.

Table 2
Bleaching of methyl orange solutions (total volume 20 mL) through oxidation by hydrogen peroxide (2.5%) catalysed by metalloporphyrin **1**[a]

Initial dye concentration (mg/L) 	Time (min)	Absorbance[b] (%)
70	10	19
	30	14
	60	13
140	10	26
	30	17
		14
210	10	41
	30	11

[a] Molar ratio of catalyst/axial ligand/organic acid, 1:5:20.
[b] Value relatively to initial absorbance value (100%).

ditions. The range of dye concentrations which was studied, varied from 0.21 to 0.63 mM, a value substantially higher than those used in other systems for dye degradation and much higher than typical concentrations of this sort of compounds in polluted waters [1].

Concerning the possibility of practical applications, the amount of dye destroyed relatively to the amount of catalyst used is important. Keeping the same dye concentration from previous experiments but doubling the dye molar quantity, which means the use of a double volume dye solution (20 mL), gave the results presented in Table 2.

As expected dye destruction is somewhat slower than conditions corresponding to Fig. 2 due to higher amounts of the dye present in the aqueous phase. However, after 60 min a fairly high degradation of the dye is accomplished even with the more concentrated solution, where the total dye amount is 4.2 mg.

Our next objective was to further improve the catalytic system. In previous work, we showed the advantage of the presence of a radical scavenger like 2,6-di-*tert*-butyl-4-methoxyphenol (BHT) to the catalyst stability and catalytic efficiency [10]. Similarly, in this study, we tried the oxidation of methyl orange at a concentration of 210 mg/L in the presence of the radical scavenger (20 to 1 ratio relatively to the catalyst) observing a significant enhancement in the level of dye degradation (Experiments 1 and 2, Table 3). In order to further approach, the system of more convenient conditions for practical use, we studied the effect of lowering the concentration of hydrogen peroxide to 1% although using an excess relatively to the amount of the dye. The results showed that these conditions are extremely efficient as illustrated in Table 3 (Experiments 3 and 4).

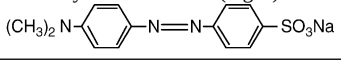
Once our original catalytic conditions were optimized by adding a radical scavenger and using a more diluted hydrogen peroxide solution (1%), a comparison of efficiency of the catalysts **1**–**5** in methyl orange degradation was performed. Experiments were carried out using a dye concentration of 140 mg/L and two different dye molar quantities: one corresponding to 5 mL of the dye stock solution (1.4 mg of dye) and the other to 10 mL of the stock solution (2.8 mg of dye) (Fig. 3).

The experiments with the higher amount of dye (2.8 mg) show a slower rate of degradation but still go to completion after 60 min with catalysts **1**–**4**. As expected catalyst **5** showed poor activity. Similar conclusions were reached in other cases of oxidation catalysis when halogen atoms are present in the *ortho* positions of the phenyl groups of catalysts [15,16]. Catalyst **2**, having sulphonamide groups, is a little more active than others [17,18]. Catalysts **3** and **4** with bromine atoms have similar activities, and are also more active than catalyst **1**. The presence of the *p*-toluenesulphonate groups does not have a large influence on the activity of the catalyst as shown by similar results obtained for catalysts **3** and **4**.

One important characteristic for a catalytic system intended to be used in dye degradation is the ability to perform several cycles of dye destruction. We studied this problem by doing experiments where an organic phase containing the catalyst, co-catalysts and the pyridine was used successively to oxidize new batches of the aqueous phase (every 30 min) containing the dye and the hydrogen peroxide. The results obtained are illustrated in Fig. 4.

Fig. 4 shows that only the first two cycles of dye oxidation are efficient. Cycles 3 and 4 give lower levels of bleaching cor-

Table 3
Results of the influence of BHT presence and hydrogen peroxide concentration in the bleaching of methyl orange solutions catalysed by metalloporphyrin **1**[a]

Experiment	Initial dye concentration (mg/L) 	BHT[b]	Hydrogen peroxide solution (%)	Time (min)	Absorbance[c] (%)
1	210	–	2.5	10	20
				30	8.6
2	210	20/1	2.5	10	13
				30	9.5
3	140	20/1	2.5	10	12
				30	5.1
4	140	20/1	1	10	6.2
				30	3.9

[a] Molar ratio of catalyst/axial ligand/organic acid, 1:5:20.
[b] Molar ratio relatively to the catalyst.
[c] Value relatively to initial absorbance value (100%).

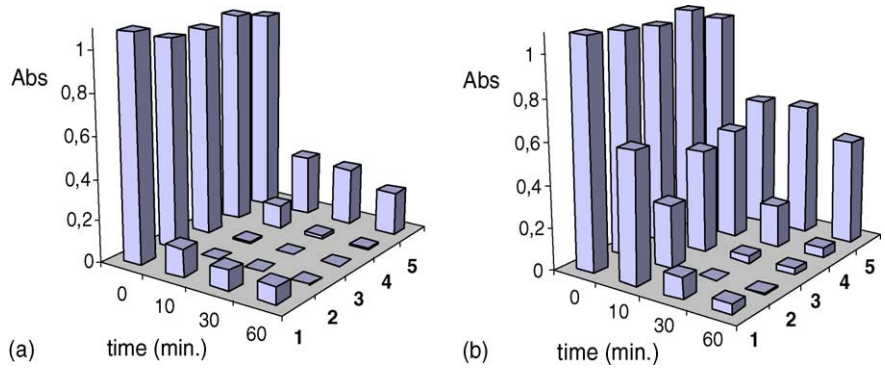


Fig. 3. Bleaching of methyl orange solutions catalysed by metalloporphyrins **1**–**5** with different amounts of methyl orange: (a) 1.4 mg and (b) 2.8 mg.

responding to a slow down of the catalytic process. Checking the amount of catalyst at the end of the last cycle, we found evidence that the amount of catalyst still present should allow for catalytic activity in the system. The reason for the reaction to stop should be the lack of another of the essential components of the catalytic system, *tert*-butylpyridine or benzoic acid. Adding more amounts of benzoic acid between cycles does not change anything. However, adding more pyridine after the second cycle allows recovering of some catalytic activity as shown in Fig. 5.

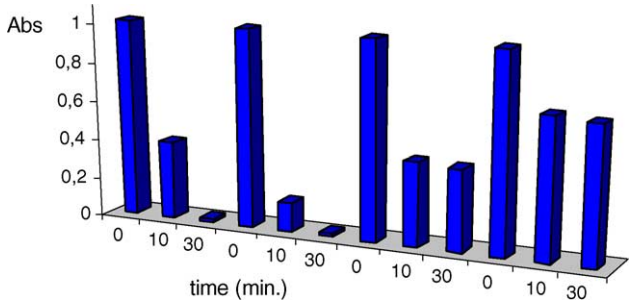


Fig. 4. Sequence of bleaching cycles of oxidation of methyl orange solutions (140 mg/L) performed using metalloporphyrin **1**. Zero values in time scale correspond to the start of a new cycle with the addition of a fresh amount of dye solution.

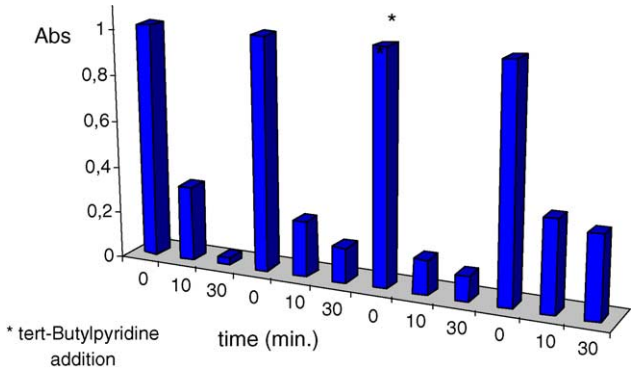


Fig. 5. Sequence of bleaching cycles of methyl orange solutions (140 mg/L) performed using metalloporphyrin **1**. Zero values in time scale correspond to addition of a fresh amount of dye solution. *tert*-Butylpyridine was added after the second cycle.

Under the latter conditions, we also studied the performance of catalysts **3** and **4** that proved to be more active than catalyst **1** in our first experiments (Fig. 6).

Surprisingly, both catalysts had a poorer performance in this sequence of reactions than catalyst **1**. Only the first cycle is efficient. The analytical control of the catalyst at the end of the sequences showed the presence of a significant amount of metalloporphyrin, although with a blue shift of 3–5 nm of the Soret band. When the organic phase from the experiment with catalyst **3** is removed at the end of the sequence, and a *cis*-cyclooctene epoxidation is attempted with it, only 26% of conversion after 30 min of reaction is observed. The same reaction with fresh catalyst in the same catalytic conditions is expected to be complete in 10 min [11]. These results point to some inhibition of the catalyst activity. The poisoning effect is more pronounced with catalysts **3** and **4** than with catalyst **1**. Catalyst stability at the end of the reaction and the Soret shift points to some metalloporphyrin interaction with the inhibition product by the axial position, preventing the essential linkage between catalyst and the pyridine ligand and slowing down the catalytic activity.

The analysis of the first cycles of Fig. 6 shows reactions are fast going to completion in 10 min. The inhibition process most likely occurs after this, when substrate is no longer available. With this rationale we tried the same set of experi-

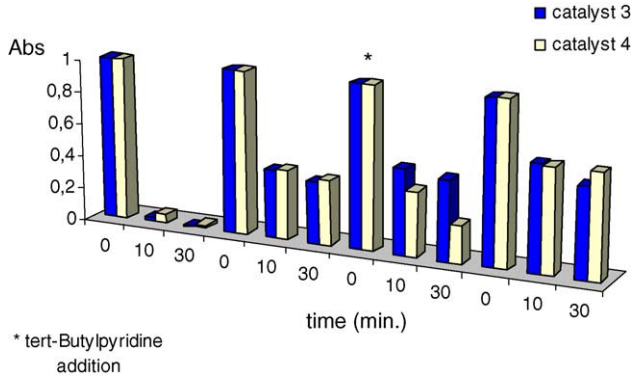


Fig. 6. Sequence of bleaching cycles of methyl orange solutions (140 mg/L) performed using metalloporphyrins **3** and **4**. Zero values in time scale correspond to addition of a fresh amount of dye solution. *tert*-Butylpyridine was added after the second cycle.

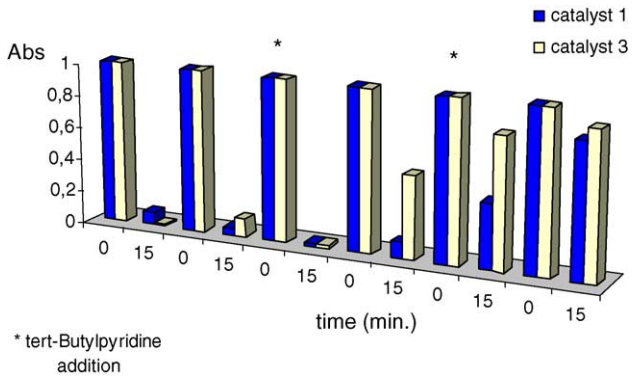


Fig. 7. Sequence of bleaching cycles of methyl orange solutions (140 mg/L) performed using catalysts **1** and **3**. Zero values in time scale correspond to addition of a fresh amount of dye solution. *tert*-Butylpyridine at the end of every two cycles.

ments, shortening the time cycles from 30 to 15 min. Results with catalysts **1** and **3** are presented in Fig. 7.

The decrease of the cycle extent to 15 min allows for a higher number of efficient cycles, five for catalyst **1** and three for catalyst **3**. These last observations seem to demonstrate that the inhibitory event develops mainly when the substrate is consumed pointing to the presence of some product derived from dye degradation. Experiments are under way to better clarify the nature of this inhibitory product and attempts for overcoming its inhibitory action on catalysts.

3. Conclusions

An efficient catalytic system to oxidize methyl orange an azo compound based on metalloporphyrins as catalysts and diluted hydrogen peroxide as oxidant was developed. This system can be an effective approach to dye degradation from aqueous effluents. Studies proved that catalytic efficiency was limited due to inhibition by the product.

4. Experimental

^{1}H NMR spectra were recorded on a 300 MHz Bruker-AMX spectrometer. Mass spectra were obtained on a VG 7070E mass spectrometer or an HP 5977 mass spectrometer detector. Absorption spectra were measured on a Jasco 7800 spectrophotometer. Gas chromatography was carried out on a Hewlett-Packard 5890 A with a flame ionisation detector and equipped with a OV1 (25 m × 0.3 mm, i.d.) capillary column. GC–MS analyses were made on a Agilent 6890 GC system with a Hewlett-Packard 5973 Mass Selective detector equipped with a capillary column HP-5 MS (25 m).

Dichloromethane was distilled from CaH_2 before use. Other solvents used were commercially available and used as received. *cis*-Cyclooctene was obtained from Aldrich and was passed through a short column of alumina before used. Methyl orange, *tert*-butylpiridyne and 2,6-di-*tert*-butyl-4-methylphenol were purchased from Aldrich and used as received. Benzoic acid was purchased from Fluka. Hydrogen peroxide 5% was prepared from a concentrated solution from Riedel titrated by iodometry. The pH of this solution was set to 4.5–5 with hydrogen carbonate. Stock solutions of methyl orange were prepared before experiments.

Stock solutions of benzoic acid in dichloromethane (4.3×10^{-2} mmol/mL) and *tert*-butyl pyridine in dichloromethane (1.08×10^{-1} mmol/mL) were prepared. These solutions were stored in refrigerator.

The following stock solutions of methyl orange in distilled water were prepared immediately before use:

- solution A: 0.14 mg/mL;
- solution B: 0.28 mg/mL;
- solution C: 0.42 mg/mL.

Metalloporphyrins **1**–**3**, and **5** were prepared as described [12,19,20].

Manganese complex of meso-tetrakis (2,4,6-tribromo-3-*p*-toluenesulphonyloxyphenyl) porphyrin **4**.

2,4,6-Tribromo-3-p-toluenesulphonyloxybenzaldehyde. A solution of 3.6 g (10 mmol) of 2,4,6-tribromo-3-hydroxylbenzaldehyde [21] in 25 mL of pyridine was treated with 2.1 g (11 mmol) of tosyl chloride. The solution was left 4 h at 70 °C. The addition of acidified water precipitates a white material that is filtered and recristalized in ethanol/$CHCl_3$ to give 4.0 g of 2,4,6-tribromo-3-*p*-toluenesulphonyloxybenzaldehyde (η = 78%). m.p. = 120–121 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 10.09 (s, 1H, CHO), 7.93 (s, 1H, Ar), 7.91 (d, 2H, J = 8.4 Hz, Ar), 7.41 (d, 2H, J = 8.4 Hz, Ar), 2.49 (s, 3H, CH_3); (M^+) = 514.

meso-Tetrakis(2,4,6-tribromo-3-p-toluenesulphonyloxyphenyl)porphyrin. A solution of 3.1 g (6.0 mmol) of 2,4,6-tribromo-3-*p*-toluenesulphonyloxybenzaldehyde and 0.37 mL (6.0 mmol) of pyrrole in 500 mL of distilled CH_2Cl_2 was purged with N_2 for 10 min, then 0.10 mL of a solution of BF_3.OEt_2 (0.25 mL in 1 mL of CH_2Cl_2) was added at room temperature. The solution was left for 4 h, neutralized with 20 μL of triethylamine and concentrated to 100 mL. This solution was then poured over a solution of acetic acid–acetic anhydride–H_2O_2(30%) (100:5:5) and left for 20 min at 40 °C. The acid was washed with water and the solution neutralized, dried and concentrated in vacuo. The residue was chromatographed on silica-gel (CH_2Cl_2–ethyl acetate, 6:1) giving 118 mg of the porphyrin (η = 4%). ^{1}H NMR (300 MHz, $CDCl_3$ ppm): δ 8.66 (s, 8H, β-H), 8.32 (s, 4H, Ar), 8.0 (d, 8H, J = 8.4 Hz, Ar), 7.33 (d, 8H, J = 8.4 Hz, Ar), 2.34 (s, 12H, CH_3). V/UV λ_{max} (CH_2Cl_2/nm) (relative height) 423 (100%), 516 (5.5%), 597 (3%).

*Manganese(III) complex of meso-tetrakis(2,4,6-tribromo-3-p-toluenesulphonyloxyphenyl) porphyrin (**4**)*. *meso*-Tetrakis(2,4,6-tribromo-3-*p*-toluenesulphonyloxyphenyl)porphyrin (100 mg) was added to a solution of 600 mg of manganese(II) acetate in 40 mL of acetic acid. The mixture

was refluxed for 7 h. After that 300 mL of CH_2Cl_2 were added and the organic phase washed with water and dried (Na_2SO_4). The solution was concentrated and the residue chromatographed on silica-gel (CH_2Cl_2, then CH_2Cl_2–ethyl ether–ethanol, 5:4:1). The fraction with the complex was washed with a concentrated solution of NaCl, dried and evaporated, giving 70 mg of the manganese complex ($\eta = 67\%$). M^+ (FAB^+) 2296; V/UV λ_{max} (CH_2Cl_2/nm) (ε mmol/L) 481.5 (94), 584 (9.3).

Catalytic reactions were carried out at room temperature. They were monitored by removing aliquots of 300 μL of the aqueous phase and measuring the maximum absorbance at 581 nm for sudan IV and 463 nm for methyl orange. All the results correspond to the average of two assays.

- Sudan IV oxidation (Fig. 1)
  Molar ratio of catalyst/axial ligand/organic acid/dye, 1:5:20:25).
  Oxidations were carried out as follows: a 20 mL flask is charged with 2.15×10^{-3} mmol of the metalloporphyrin, 20.4 mg of sudan IV, 1 mL of dichloromethane stock solution of benzoic acid, 0.1 mL of *tert*-butyl pyridine stock solution and the volume adjusted to 2 mL with dichloromethane. Then 2 mL of hydrogen peroxide solution (5%) were added and the mixture stirred at maximum rate.

- Methyl orange oxidations
  (Table 1) Molar ratio of catalyst/axial ligand/organic acid, 1:5:20.
  Oxidations were carried out as follows: a 20 mL flask is charged with 2.15×10^{-3} mmol of the metalloporphyrin, 1 mL of dichloromethane stock solution of benzoic acid, 0.1 mL of *tert*-butyl pyridine stock solution and then adjusted to 4 mL with dichloromethane. Then 5 mL of hydrogen peroxide solution (5%) and 5 mL of the corresponding dye stock solution (to give the desired concentration) were added and the mixture stirred at maximum rate.
  (Fig. 2) Molar ratio of catalyst/axial ligand/organic acid, 1:5:20.
  Oxidations were carried out as follows: a 20 mL flask is charged with 2.15×10^{-3} mmol of the metalloporphyrin, 1 mL of dichloromethane stock solution of benzoic acid acid, 0.1 mL of *tert*-butyl pyridine stock solution and then adjusted to 4 mL with dichloromethane. Then 5 mL of hydrogen peroxide solution (5%) and 5 mL of the dye stock solution B were added and the mixture stirred at maximum rate.
  (Table 2) Molar ratio of catalyst/axial ligand/organic acid, 1:5:20.
  Oxidations were carried out as follows: a 20 mL flask is charged with 2.15×10^{-3} mmol of the metalloporphyrin, 1 mL of dichloromethane stock solution of benzoic acid acid, 0.1 mL of *tert*-butyl pyridine stock solution and then adjusted to 4 mL with dichloromethane. Then 10 mL of hydrogen peroxide solution (5%) and 10 mL of the corresponding dye stock solution (to give the desired concentration) were added and the mixture stirred at maximum rate.
  (Table 3, Experiments 1 and 2) Molar ratio of catalyst/axial ligand/organic acid, 1:5:20.
  Oxidations were carried out as follows: a 20 mL flask is charged with 2.15×10^{-3} mmol of the metalloporphyrin, 4.3×10^{-2} mmol BHT (except for Experiment 1), 1 mL of dichloromethane stock solution of benzoic acid acid, 0.1 mL of *tert*-butyl pyridine stock solution and then adjusted to 4 mL with dichloromethane. Then 5 mL of hydrogen peroxide solution (5%) and 5 mL of dye stock solution C were added and the mixture stirred at maximum rate.
  (Table 3, Experiments 3 and 4) Molar ratio of catalyst/axial ligand/organic acid, 1:5:20.
  Oxidations were carried out as follows: a 20 mL flask is charged with 2.15×10^{-3} mmol of the metalloporphyrin, 4.3×10^{-2} mmol BHT, 1 mL of dichloromethane stock solution of benzoic acid acid, 0.1 mL of *tert*-butyl pyridine stock solution and then adjusted to 4 mL with dichloromethane. Then a solution of 2 mL of hydrogen peroxide solution (5%), 5 mL of dye stock solution B and 3 mL of distilled water were added and the mixture stirred at maximum rate.
  (Fig. 3a) Molar ratio of catalyst/axial ligand/organic acid/BHT, 1:5:20:20
  (Table 3) Oxidations were carried out as described for experiment 4.
  (Fig. 3b) Molar ratio of catalyst/axial ligand/organic acid/BHT, 1:5:20:20.
  Oxidations were carried out as follows: a 20 mL flask is charged with 2.15×10^{-3} mmol of the metalloporphyrin, 4.3×10^{-2} mmol BHT, 1 mL of dichloromethane stock solution of benzoic acid acid, 0.1 mL of *tert*-butyl pyridine stock solution and then adjusted to 4 mL with dichloromethane. Then a solution of 4 mL of hydrogen peroxide solution (5%), 10 mL of dye stock solution B and 6 mL of distilled water were added and the mixture stirred at maximum rate.
  (Fig. 4) Molar ratio of catalyst/axial ligand/organic acid/BHT, 1:5:20:20.
  Oxidations were carried out as follows: a 20 mL flask is charged with 2.15×10^{-3} mmol of the metalloporphyrin, 4.3×10^{-2} mmol BHT, 1 mL of dichloromethane stock solution of benzoic acid acid, 0.1 mL of *tert*-butyl pyridine stock solution and then adjusted to 4 mL with dichloromethane. Then a solution of 2 mL of hydrogen peroxide solution (5%), 5 mL of dye stock solution B and 3 mL of distilled water were added and the mixture stirred at maximum rate. The aqueous phase is carefully removed every 30 min and new aqueous phase is added over the same organic phase.
  (Figs. 5 and 6) Molar ratio of catalyst/axial ligand/organic acid/BHT, 1:5:20:20.

Oxidations were carried out as described for Fig. 4 except that 0.1 mL of *tert*-butyl pyridine stock solution is added at the time indicated.

(Fig. 7) Molar ratio of catalyst/axial ligand/organic acid/BHT, 1:5:20:20.

Oxidations were carried out as follows: a 20 mL flask is charged with 2.15×10^{-3} mmol of the metalloporphyrin, 4.3×10^{-2} mmol BHT, 1 mL of dichloromethane stock solution of benzoic acid acid, 0.1 mL of *tert*-butyl pyridine stock solution and then adjusted to 4 mL with dichloromethane. Then a solution of 2 mL of hydrogen peroxide solution (5%), 5 mL of dye stock solution B and 3 mL of distilled water were added and the mixture stirred at maximum rate. Every 15 min of reaction the aqueous phase is carefully take off and new aqueous phase is added over the same organic phase. At the time indicated 0.1 mL of *tert*-butyl pyridine stock solution is added.

- *cis*-Cyclooctene oxidation

  After a catalytic reaction with methyl orange the organic phase with catalyst **3** is transferred to a 20 mL flask with bromobenzene as internal standard and *cis*-ciclooctene (200 to 1 relatively to the catalyst). A fresh solution of hydrogen peroxide (5%) is added and the mixture stirred at maximum rate. The epoxide of *cis*-cyclooctene was identified by comparison with retention times of an authentic sample and GC–MS experiment. Conversions are reported relatively to bromobenzene as internal standard.

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