

Enhanced activity of manganese(III) porphyrin epoxidation catalysts through supramolecular complexation

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Abstract

Several manganese(III) porphyrins showed significantly increased turnover-numbers for the catalytic epoxidation of styrene upon addition of bulky Lewis acids such as ZnTPP and MgTPP (TPP = tetraphenylporphyrin). Catalytic enhancement of two- to four-fold, depending on the additive, was observed with a manganese porphyrin bearing *bis*-pyridyl groups. The enhancement is primarily attributed to the formation of a coordination trimer, which provides steric protection of the catalyst from bimolecular decomposition. In the absence of coordinating pyridyl moieties on the ligand framework, less significant enhancement is observed; the residual enhancement is speculatively ascribed to the protection of the active manganese-oxo intermediate through direct catalytic site coordination. Finally, in several cases, the addition of Lewis acids also led to the regeneration of deactivated catalysts and full recovery of the original catalytic activity. © 2000 Elsevier Science B.V. All rights reserved.

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The use of synthetic metalloporphyrins as catalysts for olefin epoxidation has been an enormously active research area over the last two decades, in part because the synthetic catalysts mimic the active centers of certain biological oxidation enzymes. To date, however, the utility of these metalloporphyrin catalysts in synthesis has been limited by facile catalyst deactivation, which is thought to occur primar-

ily by two pathways: irreversible ligand oxidation [1] and μ -oxo dimer formation [2]. Both modes of decomposition are bimolecular in the catalyst species and both are circumvented in the natural enzyme via spatial isolation of the active center by the surrounding protein. It is thus conceivable that similar site isolation in synthetic systems would also promote catalyst stability. Efforts in this regard have included incorporation of sterically bulky groups on the porphyrin ligand [3], porphyrin isolation on a polymer backbone [4,5], and design of strapped [6,7], or picnic-basket-type porphyrins [8], to name a few. We present here a novel supra-

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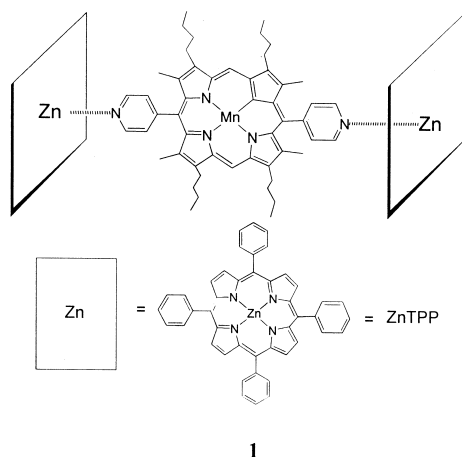


Fig. 1. ZnTPP–MnDPyP–ZnTPP supramolecular complex.

molecular² catalytic epoxidation system, where the synthetic chemistry is based on modular assembly. Such a system can be easily tuned or modified by the alteration of individual components to enhance catalyst stability and induce selectivity. This paper describes our efforts on the first generation of these catalysts where supramolecular complexation is used simply to enhance catalyst stability; subsequent reports with more elaborate assemblies will describe selectivity enhancement.

It has been observed that pyridines bind to zinc porphyrins with binding constants on the order of $3 \times 10^3 \text{ M}^{-1}$ [9–11]. Indeed, coordination oligomers and polymers of zinc [12] and other pyridine-functionalized transition-metal porphyrins such as osmium [13] and ruthenium [14] have already been characterized in both solution and solid states. Binding of pyridine to magnesium porphyrins ($K_b \approx 2 \times 10^3 \text{ M}^{-1}$) has also been observed [9,15,16]. We reasoned that a simple combination of manganese dipyr-dipyrin and Lewis acidic Zn or Mg por-

phyrins would form a structure such as **1**, and this would enhance the stability of the Mn (porphyrin) catalyst. A similar trimeric structure consisting of *meso*-tetra(4-pyridyl)porphyrin and 2 equiv of zinc tetraphenylporphyrin (ZnTPP) has recently been isolated and crystallographically characterized [17]. The formation of a coordination trimer in our system is also indicated by solution ¹H NMR studies. The combination of 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-*bis*(4-pyridyl)porphyrin (DPyP) and ZnTPP showed upfield shifts of 6.0 and 1.8 ppm for the pyridyl protons upon coordination to ZnTPP, which is in excellent agreement with an earlier work [12].

We have observed the significantly enhanced activity of 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-*bis*(4-pyridyl)porphyrinato manganese(III) chloride (MnDPyP) in the catalytic epoxidation of styrene, where the enhancement occurs under conditions where coordination of the pyridyl moieties to zinc(II) or magnesium(II) tetraphenylporphyrin is strongly thermodynamically favored. Epoxidation reactions were carried out at [mM] concentration of the catalyst in methylene chloride using iodosylbenzene as the oxidant. The products, styrene oxide and phenylacetaldehyde, were quantified by GC and GC-MS using calibration curves that were established with pure standards, and the resulting data are listed in Table 1.

In a typical epoxidation procedure, styrene (156 mg, 500 equiv) and octane (14.6 μl) as an internal GC standard were added to a stirred solution of MnDPyP (2.5 mg) and ZnTPP (4.1 mg, 2 equiv) in methylene chloride (3 ml). No effort was made to exclude water or air. Solid iodosylbenzene (0.066 g, 100 equiv) was added at 0, 30, and 60 min for the slow reactions, or every 15 min for the fast reactions. Samples (20 μl) were taken periodically over 3 h and filtered through a silica plug (60 mg) to remove the catalyst. The plug was then washed with methylene chloride ($2 \times 1 \text{ ml}$). The filtrates were combined and analyzed by quantitative GC analysis (HP-1 column, 5°/min temperature

² In some contexts the term “supramolecular” has been reserved for structures generated via weak intermolecular interactions, i.e., hydrogen bonding and van der Waals interactions. Here, we use “supramolecular” in a broader sense to encompass multi-entity structures formed by weak coordination bonds as well.

Table 1

Epoxidation activity of Mn(III) porphyrin catalysts (under benchtop, ambient conditions^a unless otherwise noted)

Entry	Catalyst	Additive (# equiv)	TON ^b	Aldehyde (%)	Time at catalyst deactivation (min) ^c
1	MnDPyP	None	59	19	10
2	MnDPyP	1 ZnTPP	136	19	35
3	MnDPyP	2 ZnTPP	140	19	45
4	MnDPyP	3 ZnTPP	153	23	60
5	MnDPyP ^d	None	44	13	15
6	MnDPyP ^d	2 ZnTPP	141	14	45
7	MnDPyP	1 MgTPP	80	12	20
8	MnDPyP	2 MgTPP	109	10	25
9	MnDPyP	3 MgTPP	119	6	30
10	MnDPP	None	46	9	15
11	MnDPP	2 ZnTPP	83	10	50
12	MnDPyP	2 Zn(phthalocyanine)	103	9	25
13	MnDPyP	2 Zn(2-ethylhexanoate) ₂	222	32	70
14	MnDPyP	None	59		
		+ (2 ZnTPP)	+ 31		
		+ (2 ZnTPP)	+ 33		
		+ (2 ZnTPP) ^e	+ 33		
15	MnDPP	None	46		
		+ (2 ZnTPP)	+ 27		
		+ (2 ZnTPP)	+ 19		
		+ (2 ZnTPP) ^e	+ 9		

^aGeneral experimental conditions: styrene (500 equiv); catalyst (3 μ mol, 1 equiv); CH₂Cl₂ (3 ml); PhIO (100 equiv) added at 0, 30, and 60 min. The reaction was monitored for 3 h.

^bTotal turnover number is determined as the total concentration of oxidation products (styrene oxide and phenylacetaldehyde) divided by the initial catalyst concentration.

^cPoint of catalyst deactivation is taken to be the time when a significant decrease in catalyst turnover rate is observed.

^dStyrene oxide (80 equiv), phenylacetaldehyde (20 equiv), and styrene (400 equiv) added as substrate.

^eZnTPP (2 equiv) was added at 180, 210, and 240 min. The catalyst was deactivated after 20 min.

ramp, 50°C initial oven temperature, 100°C final temperature). The reaction was stopped after 3 h.

For MnDPyP, a significant increase in the total turnover number (TON) upon addition of just 1 equiv of ZnTPP (Table 1, entry 2) was apparent, and the TON improved slightly with larger concentrations of ZnTPP. This TON increase is consistent with an increase in the proportion of bound species **1** in solution based on the binding constants and concentrations (Table 1, entries 2–4). With one equivalent of the coordinating additive, nearly all of the additives will be sequestered in the coordination complex **1**. However, with more equivalents, the proportion of unbound additive in solution, which is available for oxidative degradation, has significantly increased. Assuming that the bound complex is responsible for the TON enhance-

ment, the largest TON increase *per equivalent* of additive occurs with just 1 equiv. In addition, comparable results were obtained for the MgTPP system; however, the stabilization was slightly less (Table 1, entries 7–9), consistent with a smaller binding constant of pyridine to magnesium.

Control experiments using a mixture of styrene, styrene oxide, and phenylacetaldehyde as the substrate have demonstrated that ZnTPP stabilizes the MnDPyP catalyst through a mechanism that is much more important than the exclusion of product inhibition (Table 1, entries 5 and 6). Reactions of ZnTPP, MgTPP, or the free base DPyP ligand with styrene and iodosylbenzene gave no epoxidation products, precluding direct reaction of a Lewis-acid-activated iodosylbenzene complex with the olefin as a significant source of epoxide [18]. Additionally,

consistent turnover-number enhancements for MnDPyP in the presence of 2 equiv ZnTPP were obtained using a buffered commercial bleach solution in place of PhIO as the oxidant. This further indicates a mode of enhancement beyond simple PhIO activation, but consistent with the coordination-induced catalyst stabilization (i.e., **1** formation). Interestingly, however, the addition of 2 equiv of ZnTPP apparently enhances slightly the epoxidation activity of 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrinato manganese(III) chloride (MnDPP) an assembly that lacks the requisite peripheral functionalities for Zn(II) or Mg(II) ligation (Fig. 1) (Table 1, entries 10 and 11).

Under normal reaction conditions, with MnDPyP as the catalyst, neither ZnTPP nor MgTPP could be detected spectrophotometrically in the reaction mixture after ~ 20 min, and thus the decomposition of both additives is suspected.³ Consistent with this notion, we found that the subsequent addition of 2 equiv of ZnTPP at 30 min and again at 60 min further increased the TON to 217 (or 157 for MgTPP addition). Addition of ZnTPP (2 equiv) every 10 min resulted in continuous linear pseudo-first-order catalyst activity that persisted as long as ZnTPP was present in the solution (120 turnovers/h). Even more remarkable is the ability of ZnTPP and MgTPP to reactivate a deactivated catalyst: addition of 2 equiv of either ZnTPP or MgTPP to a reaction containing only MnDPyP 3 h after the catalyst had stopped turning over restored catalytic activity to initial levels (Fig. 2). The restoration process could be repeated at least three times with no loss of

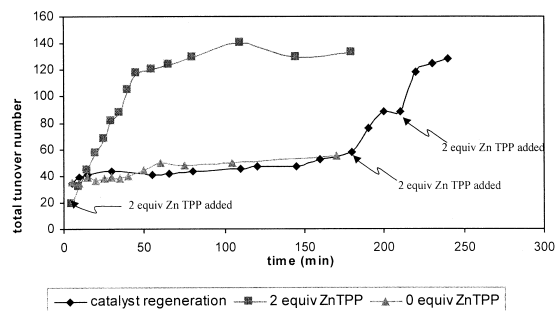


Fig. 2. Plot showing the enhancement of catalyst activity (in terms of TON) and the reactivation of deactivated catalyst by ZnTPP addition.

activity (Table 1, entry 14). Attempts to regenerate deactivated MnDPyP catalyst after 24 h of catalyst inactivity, however, were only partially successful: renewed activity was detected, but only at $\sim 25\%$ of the original level. This is attributed to the almost complete oxidative decomposition of the porphyrin ligand, which was evident by the loss of the characteristic deep red color of the reaction solution.

The use of Zn(phthalocyanine) as an additive under bench-top conditions leads to a two-fold enhancement of catalyst activity (Table 1, entry 12). However, the use of the organic-soluble, sterically bulky zinc(2-ethylhexanoate)₂ additive leads to a greater than four-fold enhancement (Table 1, entry 13)! Notably, for the available series of Lewis acid additives, the degree of stabilization of the catalyst parallels the difficulty of the oxidation of the additive (Table 2), suggesting that oxidative degradation ultimately limits the effectiveness of the first three additives. Thus, the marked increase in TON using the oxidation-resistant zinc *bis*-(2-ethylhexanoate), and the apparent regeneration of deactivated Mn catalyst, provides compelling evidence against an enhancement effect based on additives as sacrificial substrates. Further evidence for a more significant mechanism of enhancement is provided by the non-proportional TON increase with the addition of more equivalents of Lewis acid at the start of the reaction (Table 1, entries 2–4, 7–9).

³ Although the fully aromatic porphyrin species could no longer be spectroscopically observed in solution, its partially oxidized products are expected to remain coordinated to the MnDPyP providing partial steric protection/stability enhancement until complete oxidative decomposition of the additive occurs. This proposal is supported by continuous catalytic stability enhancement of MnDPyP for 50 min after the initial addition of 2 equiv of ZnTPP (Fig. 2).

Table 2
Oxidation potentials of Lewis acid additives

Entry	Additive	First oxidation potential (vs. SCE) ^a (V)	Total TON increase with addition of 2 equiv
1	Zn(phthalocyanine)	0.49	44
2	MgTPP	0.69	60
3	ZnTPP	0.89	81
4	Zn(2-ethylhexanoate) ₂	> 2.20	163

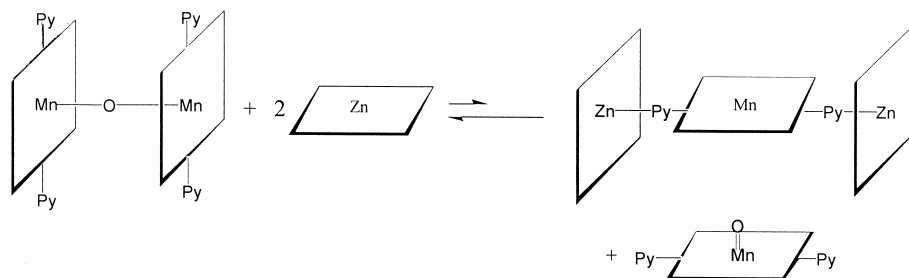
^aData was determined using a glassy carbon electrode in CH₂Cl₂ with 0.1 M Bu₄NPF₆ as the supporting electrolyte.

The enhancement of the catalytic epoxidation activity of MnDPyP is attributed to the formation of the supramolecular Lewis Acid–Lewis Base (LA–LB) complex **1**. The steric bulkiness of the “wings” of the complex should protect the MnDPyP catalyst from both ligand oxidation and metal-based dimerization. Steric interactions between the coordinated “wings” (or electronic effects imposed at the manganese centers) might also force some of the low activity μ -oxo dimer to break up and the highly active monomeric catalyst to be regenerated (Scheme 1). Regeneration of a previously deactivated catalyst by zinc(2-ethylhexanoate)₂, however, was minimal and is presumed to be a consequence of its limited ability to force apart the preformed μ -oxo dimers. This makes sense considering the reduced rigidity and steric bulk of zinc(2-ethylhexanoate)₂ compared to that of ZnTPP.

The infrared and electronic absorption spectra of the catalyst species in our system shortly after it appeared to be deactivated agree quite

well with the data reported for previously characterized dimeric μ -oxo Mn(IV) porphyrin species [19]. Notable features include the appearance of a broad absorption band centered at 416 nm, indicative of a high-valent manganese(IV) porphyrin species, and an intense broad IR absorption band centered at 830 cm⁻¹. This latter absorption, assigned to the Mn–O–Mn moiety, decreases significantly when ¹⁸O-labelled PhIO is used as the oxidant. The analogous Mn–¹⁸O–Mn absorption was not definitively observed in our experiment, presumably because it overlaps with other peaks in the same region. Unfortunately, our attempts to spectroscopically observe the separation of the μ -oxo dimer have so far been unsuccessful due to the difficulty of observing the highly active and short-lived Mn(V) oxo intermediate [20] and because only very little of the monomeric catalyst need be present at any time, even during periods of high activity.

The more modest enhancement of MnDPP activity in the presence of ZnTPP is speculatively ascribed to an additive mechanism, whereby the Lewis acidic ZnTPP forms a weak dative bond with the oxygen lone pairs of the Mn=O intermediate and thereby protects this intermediate from dimerizing. If this were the case, in the presence of additives, one would expect the initial reaction rate to be slower due to the competition between Lewis acid binding and olefin epoxidation; but the catalyst would remain active longer. This is indeed consistent with our findings. In all cases, at $t = 5$ min, the TON of systems with no additive is nearly twice that of additive containing systems. This latter



Scheme 1. Possible modes of catalyst reactivation.

mode of activity enhancement, however, is probably not as significant as the LA–LB mode: attempts to regenerate a deactivated solution of MnDPP by ZnTPP after 3 h of deactivation led only to a partial recovery of the initial activity (Table 1, entry 15), in contrast to the full recovery obtained for MnDPyP (Table 1, entry 14).

These combined findings demonstrate the feasibility of significant catalyst activity enhancement of Mn porphyrin epoxidation catalysts via supramolecular complex formation. Specifically, our work shows that a synthetically simple catalytic epoxidation system based on a LA–LB supramolecular assembly can be used to significantly enhance the total turnover number of Mn–porphyrin catalysts. Finally, we emphasize that this study is meant to be complementary to other works on the stabilization of Mn-based porphyrin epoxidation catalysts. Although higher TON have been achieved using systems based on Mn–porphyrins bearing electronegative halogen substituents [3], various solid-supported Mn–porphyrin catalysts [5,21] and other synthetic sterically protected porphyrins [8,22], the modular approach to catalyst design presented here offers a simplicity and ease of modification that was previously unattainable. The ability to improve or tune the catalyst properties by simple alteration or replacement of one component of a larger supramolecular system clearly warrants further investigation and, indeed, is a focus of our own ongoing studies of epoxidation chemistry with much more highly substrate-selective second-generation catalyst assemblies.

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