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Ionic Manganese Porphyrins with S-containing Counter Anions: Mimicking Cytochrome P450 Activity for Alkene Epoxidation

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Abstract The ionic manganese porphyrins, composed of trimethylbenzylammonium cations and S-containing anions, were designed to mimic cytochrome P450. S-containing anions could function as the stoichiometric axial ligands and counterions dually. Such ionic catalysts showed good catalytic performance in alkene epoxidation as compared with their neutral counterparts, in terms of activity, epoxide selectivity, and recyclability.

Keywords Epoxidation · Ionic catalysts · Manganese porphyrins · Sulfur axial ligands

1 Introduction

Synthetic metalloporphyrins have been used as cytochrome P-450 models and found to be highly efficient catalysts for alkene epoxidation [1–3]. Great efforts have been made to the chemical modification of metalloporphyrin microenvironment for the improvement of the catalytic efficiency as oxidation catalysts. Significant advances have been achieved by the introduction of bulky and/or electron-withdrawing substituents into the porphyrino ring to restrict the formation of unreactive μ-oxo Mn^{IV}-porphyrin dimmer and hence improve the activity/selectivity/stability of metalloporphyrins [4–8]. In addition, the supported-metalloporphyrins such as mesoporous molecular sieve (MCM-41) [9], Merrifield's peptide resin [10], highly crossing-linked polymer [11] are robust catalysts toward oxidative degradation/self aggregation for alkene epoxidations due to efficient porphyrin site-isolation. However, those heterogeneous catalyses showed quite slow reaction rate, probably owing to mass transfer interface. In a metalloporphyrin system, another important influence on the nature of metalloporphyrin catalysts is the axial ligand bound to metal. The use of nitrogenous bases like pyridine/imidazole or their derivatives as axial ligands was originated from biomimetic chemistry as replacements for the axial cysteine thiolate (P-450) or histidine imidazole in the natural metalloproteins (horseradish peroxidase, hemoglobin, myoglobin, cytochrome oxidase) [1–3]. The presence of N-containing bases greatly enhance the product distribution, the rate of the overall reaction, and the stability of the catalyst toward degradation by facilitating the formation of the proposed active Mn(V)=O porphyrin intermediate, and preventing its dimerzation into an unreactive and autodestructive μ-oxo Mn^{IV}-porphyrin dimmer [12]. Nevertheless, the problems coming from this strategy are to form inactive 6-coordinate bis-ligated complex in the presence of excess axial ligands, which may result in retardation in reaction rates, and the sacrifice of axial ligands (pyridine/imidazole or its derivatives) by the oxidants, which is the reason for excess axial ligands required [13]. The way to circumvent such drawback is to attach the oxidation-tolerant axial ligands to metalloporphyrins stoichiometrically [14–17].

Interestingly, unlike many of other metal-containing enzymes, cytochrome P-450 prefers to sulfur ligation to the iron center rather than nitrogen donors, in which the iron is bound to a peptide backbone via a thiolate bridge of a cysteine residue [18]. As a result, cytochrome P-450 shows strong differences in the electronic properties and catalysis compared to other enzymes, particularly in monoxygenation processes [19–23]. In considerations of the sacrifice

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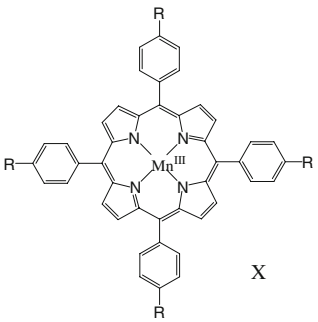
of conventional N-containing axial ligands and the feature of thiolate as the axial ligand of cytochrome P-450, we try to modify the neutral metalloporphyrin into an ionic one, along with the S-containing group as the counter anion to imitate the oxygenation function of cytochrome P-450. The incorporated sulfur donor supposedly could act as the axial ligand at stoichiometric control. Towards this end, the ionic manganeseporphyrins, bearing trimethylbenzylammonium cations and S-containing anions, 5,10,15,20 tetrakis-(4-*N*,*N*,*N*-trimethylammoniumbenzyl)-porphyrinatomanganese (III) mercaptoacetate ($[Mn^{III}TTMAPP]^{5+}[SHCH_2COO^-]_5$, **1**) and 5,10,15,20 tetrakis-(4-*N*,*N*,*N*-trimethylammoniumbenzyl)-porphyrinatomanganese(III) *o*-mercaptobenzoate ($[Mn^{III}TTMAPP]^{5+}[PhSHCOO^-]_5$, **2**) were synthesized. Their applications in the epoxidation of styrene (derivatives) with PhIO as an oxidant were studied from aspects of activity, stability, recyclability, separation work-up, and substrate availability. For comparison, the manganese porphyrins without S-containing anions were also synthesized as 5,10,15,20 tetrakis-(4-*N*,*N*,*N*-trimethylammoniumbenzyl)-porphyrinatomanganese(III) iodide ($[Mn^{III}TTMAPP]^{5+}[I^-]_n[OAc^-]_{5-n}$, $n = 1$–5, **3**) and 5,10,15,20 tetrakis-(4-*N*,*N*-dimethylammonobenzyl)-porphyrinatomanganese(III) ($[Mn^{III}TDMAPP]^+[OAc^-]$, **4**) (Scheme 1).

2 Experimental

2.1 Measurements

^{1}H NMR spectra were recorded on a Bruker DRX-500 (500 MHz) instrument. FT-IR spectra were recorded on a Nicolet Nexus 670 FT-IR spectrometer (KBr disc). GC-MS analyses were recorded on an Agilent 6890 instrument equipped with Agilent 5973 mass selective detector. GC analyses were performed on a SHIMADZU-14B gas chromatography equipped with HP-1 capillary column (30 m × 0.25 mm × 0.25 μm). The UV–Vis spectra were recorded on a Shimadzu UV-2550 UV–Vis spectrophotometer.



Manganese porphyrin	R	X
$[Mn^{III}TTMAPP]^{5+}[SHCH_2COO^-]_5$ (**1**)	$N^+(CH_3)_3$	5 $[SHCH_2COO^-]$
$[Mn^{III}TTMAPP]^{5+}[PhSHCOO^-]_5$ (**2**)	$N^+(CH_3)_3$	5 [*o*-$SHPhCOO^-$]
$[Mn^{III}TTMAPP]^{5+}[I^-]_n[OAc^-]_{5-n}$ (**3**)	$N^+(CH_3)_3$	$[I^-]_n[OAc^-]_{5-n}$, n=0~5
$[Mn^{III}TDMAPP]^+[OAc^-]$ (**4**)	$N(CH_3)_2$	$[OAc]^-$

Scheme 1 Structures of the manganese porphyrins of **1**, **2**, **3**, and **4**

2.2 Materials

All solvents and reagents were analytical grade and used as received. The free bases of 5,10,15,20 tetrakis-(4-*N*,*N*-dimethylammonobenzyl)-porphyrin ($[H_2TDMAPP]$) and 5,10,15,20 tetrakis-(4-*N*,*N*,*N*-trimethylammoniumbenzyl)-porphyrin iodide ($[H_2TTMAPP]^{4+}[I^-]_4$) were synthesized according to the Ref. [24]. $[Mn^{III}TTMAPP]^{5+}[I^-]_n[OAc^-]_{5-n}$ (**3**) and $[Mn^{III}TDMAPP]^+[OAc^-]$ (**4**) were synthesized as previously reported [25].

2.3 Synthesis

*2.3.1 Synthesis of $[Mn^{III}TTMAPP]^{5+}[SHCH_2COO^-]_5$ (**1**)*

A mixture of $[H_2TTMAPP]^{4+}[I^-]_4$ (0.27 g, 0.2 mmol) and excess sodium mercaptoacetate (0.114 g, 1.0 mmol) in water (10 mL) was stirred under N_2 at room temperature for 24 h, and then concentrated in vacuo to remove water. The residue was further purified by f by a silica gel column to give the free base, $[H_2TTMAPP]^{4+}[SHCH_2COO^-]_4$ as a dark brown solid (0.12 g, 49%). ^{1}H NMR (500 MHz, D_2O, ppm): $\delta = 8.80$ (s, 8H, β-porrole), 8.40 (d, 8 Hz, 8H, phenyl-*H*), 8.20 (d, 8 Hz, 8H, phenyl-*H*), 3.90 (s, 36H, N-CH_3), 2.90 (s, 4H, $SHCH_2COO$), 2.75 (s, 4H, $SHCH_2COO$). FT-IR (KBr disc, cm^{-1}): $\nu = 3130$, 3006, 2951, 2500, 1650, 1573, 1400, 1114, 1002. UV–Vis (water): $\lambda_{max} = 412$ (s, Soret band), 514 (w, Q band), 551 (w, Q band), 579 (w, Q band), 634 (w, Q band) nm.

To avoid the ion-exchange of $SHCH_2COO^-$ by OAc^-, $[H_2TTMAPP]^{4+}[SHCH_2COO^-]_4$ was not used to prepare **1** by reacting with $Mn(OAc)_2 \cdot 4H_2O$ directly. A mixture of $[Mn^{III}TTMAPP]^{5+}[I^-]_n[OAc^-]_{5-n}$ (0.28 g) and excess sodium mercaptoacetate (0.114 g, 1.0 mmol) in water (10 mL) was stirred under N_2 at room temperature for 24 h, and then concentrated in vacuo to remove water. The obtained mixture was purified by (silica gel) column chromatography to give the product, $[Mn^{III}TTMAPP]^{5+}[SHCH_2COO^-]_5$ as a dark green solid (0.14 g). Due to influence of ^{55}Mn quadrupolar nucleus and the paramagnetism of Mn^{III} porphyrin, the signals of ^{1}H NMR of **1** were unobservable. UV–Vis (MeCN): $\lambda_{max} = 343$ (w, Q band), 374 (w, Q band), 476 (s, Soret band), 569 (w, Q band), 637 (w, Q band) nm. FT-IR (KBr disc, cm^{-1}): 3033, 2947, 2928, 2501, 1604, 1518, 1398, 1258, 1192, 1002.

2.3.2 Synthesis of $[Mn^{III}TTMAPP]^{5+}[PhSHCOO^-]_5$ (2)

A mixture of $[H_2TTMAPP]^{4+}[I^-]_4$ (0.27 g, 0.2 mmol) and excess sodium *o*-mercaptobenzoate (0.176 g, 1.0 mmol) in water (10 mL) was stirred under N_2 at room temperature for 24 h, and then concentrated in vacuo to remove water. The residue was further purified on a silica gel column to give $[H_2TTMAPP]^{4+}[PhSHCOO^-]_4$ as a dark brown solid (0.19 g, 65%). ^{1}H NMR (500 MHz, D_2O, ppm): $\delta = 8.80$ (s, 8H, β-porrole), 8.45 (d, 7 Hz, 8H, phenyl-*H* in porphyrin), 8.40 (d, 7 Hz, 8H, phenyl-*H* in porphyrin), 7.10–7.60 (m, 16H, Phenyl-*H*), 3.85 (s, 36H, N-CH_3). FT-IR (KBr disc, cm^{-1}): 3114, 2955, 2499, 1584, 1546, 1476, 1392, 1110. UV–Vis (MeCN): $\lambda_{max} = 417$ (s, Soret band), 514 (w, Q band), 549 (w, Q band), 588 (w, Q band), 647(w, Q band) nm.

Similarly, $[H_2TTMAPP]^{4+}[PhSHCOO^-]_4$ was not used to prepare **2** by reacting with $Mn(OAc)_2 \cdot 4H_2O$. A mixture of $[Mn^{III}TTMAPP]^{5+}[I^-]_n[OAc^-]_{5-n}$ (0.28 g) and sodium *o*-mercaptobenzoate (0.176 g, 1.0 mmol) in water (10 mL) was stirred under N_2 at room temperature for 24 h, and concentrated in vacuo to remove water. The obtained mixture was purified by (silica gel) column chromatography to give the product, $[Mn^{III}TTMAPP]^{5+}[PhSHCOO^-]_5$ as a dark green solid (0.16 g). Due to influence of ^{55}Mn quadrupolar nucleus and the paramagnetism of Mn^{III} porphyrin, the signals of ^{1}H NMR of **2** were unobservable. UV–Vis (MeCN): $\lambda_{max} = 350$ (w, Q band), 386 (w, Q band), 474 (s, Soret band), 580 (w, Q band), 618 (w, Q band) nm. FT-IR (KBr disc, cm^{-1}): 3118, 2913, 2920, 2503, 1650, 1604, 1518, 1398, 1401, 1192.

2.4 General Procedures for Epoxidation

To a mixture of styrene or its derivatives (0.5 mmol) and catalyst (2.5 μmol, 0.5 mol%) in MeCN (2 mL) was added PhIO (0.65 mmol) [26]. The resulting mixture was stirred at 30 °C, and then treated with cyclohexane (5 mL) to precipitate the catalyst. The resultant organic solution was analyzed by GC to determine the conversions (1-dodecane as internal standard) and the selectivities (normalization method). The structures of obtained products were further confirmed by GC-Mass.

The precipitated catalyst could be reused directly for the next run without further treatment.

3 Results and Discussion

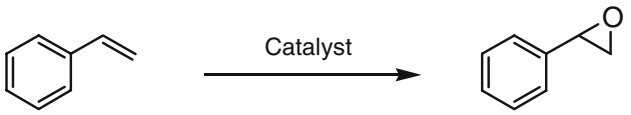
To avoid the ion-exchange of $SHCH_2COO^-$ by OAc^-, **1** and **2** were not prepared by direct insertion of Mn^{3+} into the corresponding free bases of $[H_2TTMAPP]^{4+}[SHCH_2COO^-]_4$ and $[H_2TTMAPP]^{4+}[PhSHCOO^-]_4$. So the ionic $[Mn^{III}TTMAPP]^{5+}[I^-]_n[OAc^-]_{5-n}$ (**3**) was used to exchange with $Na^+[SHCH_2COO^-]$ and Na^+ $[PhSHCOO^-]$, respectively, to yield **1** and **2** in our work. The preparation of free bases $[H_2TTMAPP]^{4+}[SHCH_2COO^-]_4$ and $[H_2TTMAPP]^{4+}[PhSHCOO^-]_4$ was just to confirm the exact canion–anion composition, which could be identified by ^{1}H NMR analysis truly, and to indirectly show that the anions of $SHCH_2COO^-$ and $PhSHCOO^-$ could be incorporated into the manganese porphyrins stoichiometrically.

3.1 Comparison of the Catalytic Performance of Manganese Porphyrins 1, 2, 3, and 4

For the initial studies on the catalytic activity of ionic manganese porphyrins **1** and **2**, the epoxidation of styrene by PhIO oxidant was chosen as a model reaction, which was carried out under mechanical stirring in the absence of any additives. The reaction conditions were optimized in terms of temperature, solvents, catalyst concentration, and ratio of PhIO to styrene. It was found that styrene epoxide was obtained as the major product (≥98% selectivity) with high conversion (≥97%) in MeCN under the optimal conditions (30 °C, 1.5 equiv. PhIO, 0.5 mol% catalyst loading), and that the by-products (benzaldehyde and phenyl acetaldehyde) were formed in very low yields which were identified by GC-MS (Table 1, Entries 1, 5). The blank epoxidation of styrene without catalyst gave no detectable conversion under the same conditions.

It was suggested (Entries 1, 5 of Table 1) that the high conversion with excellent epoxide selectivity be derived from the involvement of S-containing anion in **1** or **2** as the axial ligand. To address this issue, the reactions catalyzed by neutral manganese porphyrin **4** or S-free ionic manganese porphyrin **3** were investigated. Expectantly, the reactions catalyzed by **3** or **4** gave low styrene conversions (73% for **3**, 60% for **4**) under the identical conditions (Entries 9, 13 of Table 1), indicating that sulfur in the counter anion indeed contributed to the improved activity of metalloporphyrins. These results further confirmed that S-containing anion may function as the axial ligand with advantage of stoichiometric usage, avoiding the retarded activity when much excess ligands surrounding the manganese porphyrin center [13]. It is well known that the axial ligands like nitrogenous bases, originated from the applications as the substituents for the axial cysteine thiolate (P-450) or histidine imidazole in the natural metalloproteins, were required basically in metallporphyrins catalyzed epoxidations to enhance the strength of the metal–O bond, consequently with benefits of improvements in the reactivities and selectivities of the catalysts, as well as protection against the formation of unreactive μ-oxo Mn^{IV}-porphyrin dimmers [13, 27]. The sulfur atom as an electron-donor also exhibited a favorable ligation to Mn

Table 1 Epoxidation of styrene catalyzed by the manganese porphyrins[a]



Entry	Catalyst	Time (h)	Conversion (%)[b]	Epoxide selectivity (%)[b]
1	**1** (fresh)	1	97	98
2[c]	**1** (2nd run)	2	82	96
3[c]	**1** (3rd run)	4	65	95
4[c]	**1** (4th run)	4	46	93
5	**2** (fresh)	4	99	99
6[c]	**2** (2nd run)	4	93	97
7[c]	**2** (3rd run)	4	85	96
8[c]	**2** (4th run)	4	68	96
9	**3** (fresh)	4	73	96
10[c]	**3** (2nd run)	4	44	96
11[c]	**3** (3rd run)	4	40	96
12[c]	**3** (4th run)	4	0	–
13	**4** (fresh)	4	60	97
14[c]	**4** (2nd run)	4	38	95
15[c]	**4** (3rd run)	4	0	–

[a] Catalyst 0.5 mol%, styrene 0.5 mmol, PhIO 0.65 mmol, CH_3CN 2 mL, reaction temperature 30 °C

[b] Determined by GC

[c] Reuse of the catalyst

ion owing to the better mixing of its orbital with manganese 3*d* orbital [20].

Moreover, the improved conversion of styrene in the ionic system **3** in comparison with that in the neutral system **4** was attributed to the strong electron-withdrawing nature of quaternary ammonium cations in the porphyrin ring, suppressing the oxidative degradation of **3** [7–10].

Due to high polarity of the ionic manganese porphyrin catalysts (**1**, **2**, **3** and **4**), upon completion of the first run, the catalyst was precipitated with cyclohexane, and the organic substrate/product/MeCN were transferred into cyclohexane simultaneously for GC analysis. So the reuses of the precipitated catalysts could be manipulated simply. The recycling uses of **1**, **2**, **3**, and **4** in Table 1 showed that the stability of the ionic manganese porphyrins of **1**, **2**, and **3** was much better than that of the neutral **4** (Entries 1–12), especially when sulfur was included in the anions as the axial ligands (Entries 1–4, 5–8), though the conversions was decreased gradually due to self-oxidative degradation of the manganese porphyrins. Obviously, the catalyst **2** was the most robust one with favorable activity. It is well known that metalloporphyrins are super-conjugated systems with planar structure at porphyrino rings, susceptible to form μ-oxo Mn^{IV}-porphyrin dimmer due to π–π stacking of porphyrin itself [28, 29]. The formed μ-oxo Mn^{IV}-porphyrin dimmer is an inactive complex in further catalysis, and easily undergoes decomposition (oxidative degradation) through electrophilic attack on the electron-rich *meso*-C of porphyrino ring [2]. This dimerization is commonly prevented by strategies of increasing the steric bulk of the axial ligands [13]. The catalyst **2** is endowed not only with bulky S-containing anion as an axial ligand, but also with the conjugated feature that can counteract the π–π stacking through interaction between the porphyrin and the phenyl group. The accessibility of the porphyrin to the phenyl group can be further intensified by (positive/negative charge) Coulombic forces. In consideration of the oxidation tolerance of S-containing anions, the recovered **2** after the second run and the fresh **2** were analyzed by FT-IR spectroscopy for comparison. A new peak appeared at 582 cm^{-1} (S–S stretching frequency) [30] in the IR spectrum of the recovered **2** indicated that –SH group was oxidized to disulfide with. Fortunately, the formed disulfide was very stable against further oxidation, and could act as the ligand without negative impact on the catalytic activity of **2** as shown in Table 1 (Entry 6, Conv. 93%).

1 and **2** were the highly efficient catalysts. Even the concentrations of **1** and **2** were decreased to 0.005 mol%, the styrene conversions of 32% and 35% were obtained

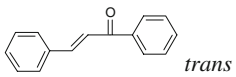
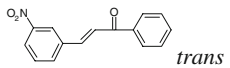
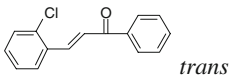
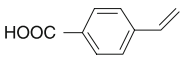
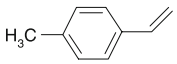
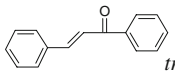
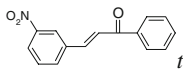
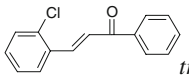
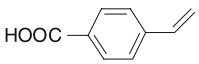
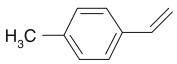
Table 2 Effect of concentration of catalyst on epoxidation of styrene[a]

Entry	Catalyst (mol%)	Time (h)	Conversion (%)[b]	Epoxide selectivity (%)[b]	TON
1	**1** (0.005)	1	32	98	6400
2	**1** (0.01)	1	47	98	4700
3	**1** (0.05)	1	62	97	1240
4	**2** (0.005)	4	35	96	7000
5	**2** (0.01)	4	52	97	5200
6	**2** (0.05)	4	65	100	1300

[a] Styrene 0.5 mmol, PhIO 0.65 mmol, CH_3CN 2 mL, reaction temperature 30 °C

[b] Determined by GC

Table 3 Epoxidation of styrene derivatives catalyzed by **1** and **2**[a]

Entry	Substrate	Catalyst	Time (h)	Conversion (%)[b]	Epoxide selectivity (%)[b]
1	 *trans*	**1**	1	69	100
2	 *trans*	**1**	1	86	100
3	 *trans*	**1**	1	59	100
4		**1**	1	100	99
5		**1**	1	98	26 (68[c])
6	 *trans*	**2**	4	72	100
7	 *trans*	**2**	4	83	100
8	 *trans*	**2**	4	80	100
9		**2**	4	100	100
10		**2**	4	99	89 (10[c])

[a] Substrates 0.5 mmol, catalyst 0.5 mol%, PhIO 0.65 mmol, MeCN 2 mL, temperature 30 °C

[b] Determined by GC and GC-Mass

[c] Selectivity to phenyl acetaldehyde

with turnover number of 8200 and 7000 respectively, as shown in Table 2.

3.2 The Generality of **1** and **2** for Epoxidation of Styrene Derivatives

To examine the generality of **1** or **2** as the catalysts for the epoxidations of different substrates, a wide array of styrene derivatives with different electronic and steric effects was examined under the optimal conditions (Table 3). As to the chalcones (Entries 1–3, 6–8) with the internal C=C bonds, the epoxides were the only products, implicating the facial access of the substrate to oxomanganese(V) porphyrin domain [31]. And due to the bulky hindrance, the conversions of the chalcones were relatively lower due to the unfavorable accessibility of C=C site to the manganese porphrin center. As to the same reactions with electron-rich group ($-CH_3$), the increased electron-density at α-C of C=C bond resulted in the incensement of the rearranged product phenyl acetaldehyde through a radical mechanism (Entries

5, 10) [7]. Compared to the case of electron-deficient *p*-vinyl benzoic acid, the selectivity for epoxide was remarkable (Entries 4, 9). The formation of benzaldehyde via the oxidation of side-chain cleavage (i.e. cleavage at α-C and β-C of styrene/derivatives) could not be observed in any case.

4 Conclusion

Without additional involvement of the axial ligands, the ionic manganese porphyrins of **1** and **2** prove to be the efficient and recyclable catalysts for epoxidations of styrene (derivatives) under the mild conditions. By introduction the S-containing groups stoichiometrically into **1** or **2**, the sulfur ligation to Mn atom fine-tuned the electronic properties of the metalloporphyrin to mimic the thiolate residue axially bounded in P-450 porphyrino site. Additionally, the quaternary ammonium cations with strong electron-withdrawing nature could suppress the oxidation degradation of **1** and **2**, due to the decreased electron density at *meso*-carbons. Especially for the catalyst **2**, the interaction between the conjugated phenyl and prophyrino ring counteracted the π–π stacking of metalloporphyrin itself, leading to its much improved recyclability.

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