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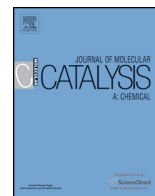


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The first manganese N-confused porphyrins catalyzed oxidation of alkene



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ARTICLE INFO

Article history:

Received 27 March 2014

Received in revised form 2 August 2014

Accepted 5 August 2014

Available online 15 August 2014

Keywords:

N-confused porphyrin

Manganese

Catalytic oxidation

ABSTRACT

A series of *N*-methyl *N*-confused porphyrin manganese complexes (**3a–3f**) were synthesized and characterized by UV–vis, XPS, HR-MS and cyclic voltammetry. These complexes were utilized to catalyze the styrene oxidation. It turned out their catalytic activities were comparable with manganese tetraphenylporphyrin (MnTPP). Among all investigated manganese *N*-confused porphyrins, the most electron deficient **3f** exhibited the best catalytic activity for the alkene oxidation. The proposed mechanism for the catalytic oxidation has also been described.

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1. Introduction

Transition-metal complexes of porphyrins and related macrocycles have attracted increased attention recently due to their promising applications as biomimetic catalysts for cytochrome P450 [1–3]. The most widely studied catalysts in this field are manganese porphyrins, which exhibit very high conversion and good selectivity for alkene oxidation [4]. *N*-confused porphyrin or so-called inverted porphyrin, an isomer of porphyrin having one of the four pyrrole nitrogen atoms lying outside and serving as peripheral nitrogen, was firstly isolated as minor product from the normal porphyrin synthesis by Latos-Grażyński [5] and Furuta [6] independently in 1994. An improved synthesis of *N*-confused porphyrin was achieved by Lindsey et al. in 1999 [7], which significantly accelerated the development of *N*-confused porphyrin chemistry [8]. The presence of an external nitrogen may impart some peculiar characteristics to *N*-confused porphyrin. For example, it may involve in the electrophilic reaction and results in the formation of the alkylation products [9,10]. Unlike *N*-confused porphyrin, its alkylation products do not undergo NH-tautomerism and have only one stable form, which can form manganese(III) *N*-confused porphyrin having a direct carbon–manganese (Mn–C) bond [11]. The metal complexes of *N*-confused porphyrins have been demonstrated to be potent catalysts in cyclopropanation of styrene with high trans-selectivity [12,13] and oxygen atom

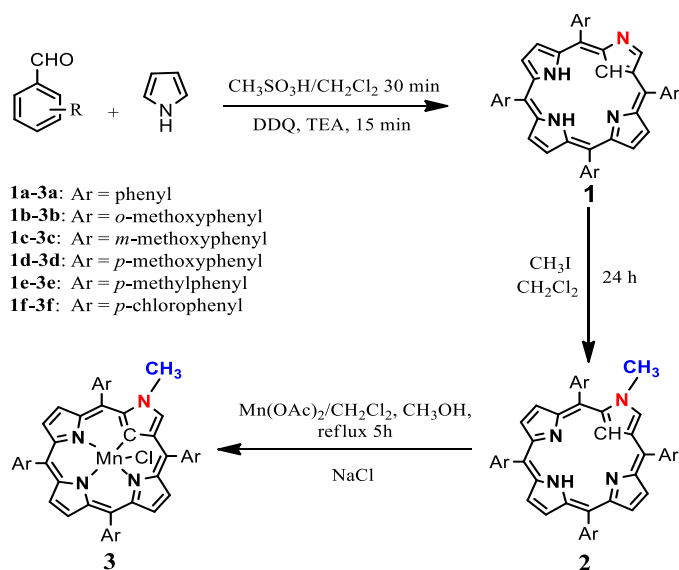
transfer reactions [14]. While numerous manganese complexes of porphyrins [15–18], corroles [19–23], phthalocyanines [24] and related macrocycles [25] have been extensively studied as catalysts in the oxidation of organic substrates, to the best of our knowledge, no report was found for manganese *N*-confused porphyrins catalyzed oxidation of organic substrates so far. Herein, we wish to report the synthesis and spectroscopic characterization of various manganese(III) *N*-methyl *N*-confused tetraarylporphyrins MnNC-TArPs (Scheme 1 **3a–3f**), and their catalytic activity for styrene oxidation.

2. Experimental

2.1. Materials and methods

All reagents and solvents were of analytical grade and obtained commercially. The purity of styrene was checked by GC analysis. UV–vis spectra were obtained with a Hitachi U-2450 spectrophotometer. The ¹H NMR spectra were recorded at room temperature on a Bruker Avance III 400 spectrometer. Mass spectra were taken on Bruker Esquire HCT plus mass spectrometer (ESI/MS) and Bruker maxis impact mass spectrometer with an ESI source (HR-MS). X-ray photoelectron spectroscopy (XPS) was performed using an Axis Ultra DLD spectrometer. All cyclic voltammograms (CV) were performed in acetonitrile solutions containing 0.1 M TBAP (tetrabutylammonium perchlorate) using an Ingens Model 1030 and MnNCTArPs (1 mM) under nitrogen atmosphere at ambient temperature. A three-electrode system consisting of a glassy carbon working electrode, a platinum wire counter

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Scheme 1. Synthesis of manganese N-confused tetraarylporphyrins (**3a-3f**).

electrode and SCE (saturated calomel reference electrode) were employed. The scan rate was 100 mV/s. Half-wave potentials ($E_{1/2}$) for reversible or quasi-reversible redox processes were calculated as $E_{1/2} = (E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} represent the anodic and cathodic peak potentials, respectively. The $E_{1/2}$ value for the ferrocenium/ferrocene couple under these conditions was 0.40 V.

2.2. Synthesis

5,10,15,20-Tetraphenylporphyrin and its manganese (III) complex (MnTPP) were prepared by traditional method [26,27]. All free base N-confused porphyrins were synthesized according to procedure described in references [7,10] and well characterized (Supporting information). Manganese complexes of N-methyl N-confused porphyrin (**3a-3f**) were prepared as follows:

A mixture of N-methyl N-confused 5,10,15,20-tetraarylporphyrin (**2a-2f**) (0.08 mmol) in CH_2Cl_2 (2 mL) and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.4 mmol) in methanol (100 mL) was refluxed for 5 h. After evaporation of the solvent, the residue was dissolved in 100 mL of CH_2Cl_2 and washed with saturated aqueous solution of NaCl. The organic layer was collected and dried over anhydrous Na_2SO_4 . The filtrate was concentrated and the crude product was purified on a silica gel (300–400 mesh) using CH_2Cl_2 /ethyl acetate (8/2, V/V) as eluent. Green colored product was obtained after recrystallization from CH_2Cl_2 /ethyl acetate (1/5).

3a. Yield 49%. UV-vis (CH_2Cl_2 , nm, $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$): 337 (2.734), 393 (3.086), 458 (2.132), 505 (4.831), 580 (0.652), 637 (0.414), 743 (0.424), 809 (0.628). HR-MS (ESI) ($[\text{M}-\text{Cl}]^+$): calcd for $\text{C}_{45}\text{H}_{30}\text{MnN}_4$ 681.1851, found 681.1845, with an isotope distribution pattern the same as the calculated one.

3b. Yield 60%. UV-vis (CH_2Cl_2 , nm, $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$): 338 (3.107), 393 (3.384), 458 (2.785), 505 (4.647), 578 (0.881), 628 (0.627), 743 (0.517), 804 (0.627). HR-MS (ESI) ($[\text{M}-\text{Cl}]^+$): calcd for $\text{C}_{49}\text{H}_{38}\text{MnN}_4\text{O}_4$ 801.2274, found 801.2268, with an isotope distribution pattern the same as the calculated one.

3c. Yield 58%. UV-vis (CH_2Cl_2 , nm, $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$): 338 (2.053), 390 (2.118), 458 (1.721), 505 (2.127), 577 (0.621), 633 (0.451), 733 (0.262), 798 (0.300). HR-MS (ESI) ($[\text{M}-\text{Cl}]^+$): calcd for $\text{C}_{49}\text{H}_{38}\text{MnN}_4\text{O}_4$ 801.2274, found 801.2268, with an isotope distribution pattern the same as the calculated one.

3d. Yield 47%. UV-vis (CH_2Cl_2 , nm, $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$): 334 (2.856), 398 (3.466), 457 (3.472), 506 (3.472), 574 (0.814), 636 (0.592), 727 (0.516), 809 (0.572). HR-MS (ESI) ($[\text{M}-\text{Cl}]^+$): calcd for

$\text{C}_{49}\text{H}_{38}\text{MnN}_4\text{O}_4$ 801.2274, found 801.2268, with an isotope distribution pattern the same as the calculated one.

3e. Yield 52%. UV-vis (CH_2Cl_2 , nm, $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$): 335 (2.359), 392 (2.714), 465 (2.403), 504 (3.191), 577 (0.679), 631 (0.440), 738 (0.398), 802 (0.530). HR-MS (ESI) ($[\text{M}-\text{Cl}]^+$): calcd for $\text{C}_{49}\text{H}_{38}\text{MnN}_4$ 737.2477, found 737.2471, with an isotope distribution pattern the same as the calculated one.

3f. Yield 45%. UV-vis (CH_2Cl_2 , nm, $\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$): 338 (3.202), 392 (3.471), 461 (2.560), 505 (4.797), 579 (0.791), 637 (0.508), 743 (0.465), 807 (0.639). HR-MS (ESI) ($[\text{M}-\text{Cl}-\text{H}]^+$): calcd for $\text{C}_{45}\text{H}_{26}\text{Cl}_4\text{MnN}_4$ 817.0292, found 817.0287, with an isotope distribution pattern the same as the calculated one.

2.3. Catalytic oxidation

A mixture of styrene (1.0 mmol), oxidant (0.1 mmol) and catalyst (**3a-3f**) (1.0 μmol) in 2 mL of solvent was stirred in a 10 mL glass flask at room temperature. After an appropriate reaction time, chlorobenzene (1 μL) was added to this reaction mixture as internal standard. The products were analyzed on an Echrom A90 gas chromatograph equipped with HP-5 capillary column (30.0 m \times 320 μm ID; 0.25 μm film thickness) coupled with FID detector. The carrier gas was nitrogen and the chromatographic conditions were as follows: the oven temperature was increased at a rate of 10 $^\circ\text{C}/\text{min}$ (from 60 to 250 $^\circ\text{C}$); the injector temperature was set 230 $^\circ\text{C}$ while the detector temperature was kept 250 $^\circ\text{C}$. The injection volume of the filtrated reaction mixture was 1.0 μL and the products were confirmed by the retention time using standard samples under the same GC conditions. The yields of products were reported with respect to the amount of oxidant used.

3. Results and discussion

3.1. Synthesis of manganese N-confused tetraarylporphyrins

Manganese complexes of N-confused porphyrin were previously prepared by the direct reaction of free base with MnBr_2 or $\text{Mn}_2(\text{CO})_{10}$ and found to be less stable [28,29]. However, manganese N-alkyl N-confused porphyrins are relatively more stable and can be easily prepared [11,30]. This phenomenon triggered our interest in the synthesis of manganese N-methyl N-confused porphyrins (**3a-3f**). Manganese N-confused porphyrins (**3a-3f**) were prepared by refluxing the corresponding free base (**2a-2f**) and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in dichloromethane/methanol (1/50, V/V) [11].

3.2. UV-vis spectroscopy

UV-vis absorption maxima and molar extinction coefficient of free base N-confused porphyrins (**1a-1f** and **2a-2f**) (Supporting information, Fig S1 and S2) and their manganese complexes **3a-3f** are summarized in Experimental Section. Free base N-confused porphyrins **1a-1f** are characterized by a Soret-band at 437–441 nm and four Q-bands at 532–734 nm. N-methylated freebases **2a-2f** exhibit an extra N-band at 355–377 nm, a Soret-band between 437 and 441 nm and only two Q-bands between 647–722 nm. The maxima of these absorption bands is related to the position and electronic properties of the substituents. In the presence of methoxy or methyl groups, the Soret-band is apparently red shifted. For example, the Soret-band of **1a** and **2a** is located at 437 and 444 nm, respectively, and is red shifted by 4 and 9 nm with respect to the Soret-band of **1d** (441 nm) and **2d** (453 nm). This indicates that substitution by electron-donating groups at the *para*-position of the *meso*-phenyl groups leads to a decrease of the HOMO-LUMO gap as compared to **1a** or **2a** [31]. The difference in the Soret-bands of **1b-1d** and **2b-2d** might be explained by the steric effect of *ortho*-methoxy group, which may result in a red shifted bands [32].

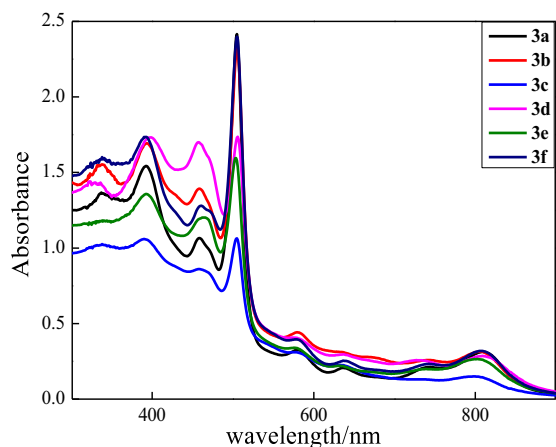


Fig. 1. Absorption spectra of manganese N-confused porphyrins **3a–3f** in dichloromethane.

All manganese N-confused porphyrins **3a–3f** exhibit an N-band (334–338 nm), a split Soret-band (392–398 and 457–465 nm) and four weaker Q-bands (Fig. 1). The absorption at 504–506 nm can be attributed to metal to ligand charge transfer transition (MLCT) band, similar to MnTPP. The relative intensity of this band is usually related with the electron-withdrawing or -donating ability and the steric hindrance of the peripheral substituents on the macrocycle [31].

3.3. X-ray photoelectron spectroscopy (XPS)

XPS was used to directly probe the oxidation state of manganese in all manganese complexes **3a–3f**. Mn 2p region for MnTPP and **3a–3f** are shown in Fig. 2 and the data is given in Table S1 (Supporting information). The peak at 196–203 eV in **3a–3f** is attributed to Cl 2p_{3/2} which indicates that the axial position is occupied by Cl atom [33]. The binding energies of Mn in **3a–3f** is almost similar to MnTPP. Both components of Mn 2p (2p_{3/2}, BE = 641.2–642.4 eV; 2p_{1/2}, BE = 652.4–654.2 eV) are in agreement with the +3 oxidant state of manganese ion [34,35]. As shown in Fig. 2, the binding energy of Mn 2p_{3/2} for **3f** is little higher than that of MnTPP but is lower for **3a–3e**, indicating that **3f** has better stability and is more difficult to be oxidized.

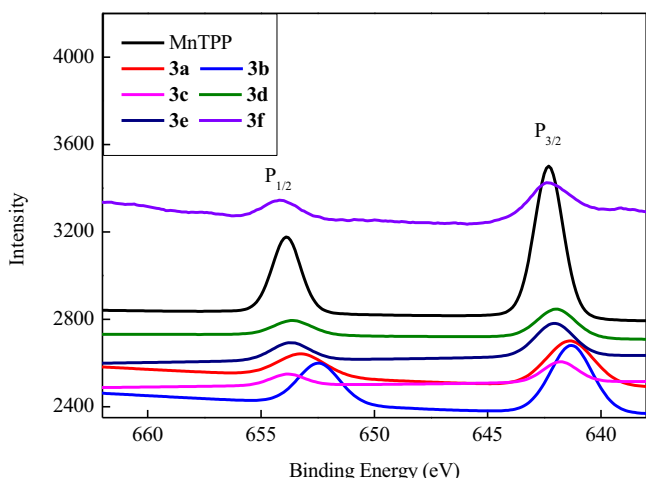


Fig. 2. X-ray photoelectron spectra of MnTPP and **3a–3f**.

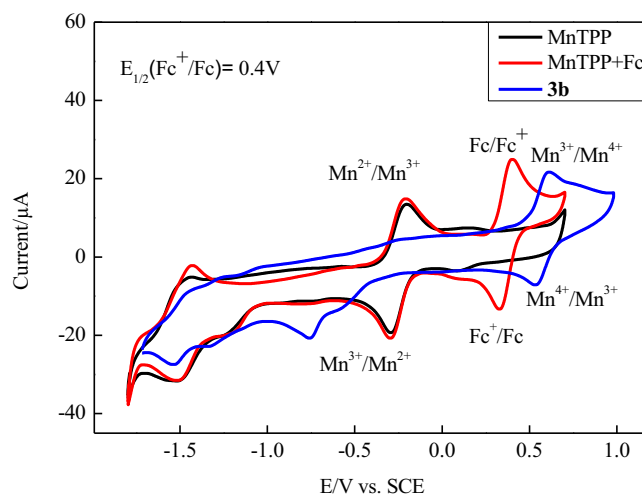


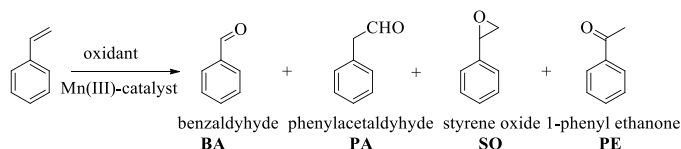
Fig. 3. Cyclic Voltammograms of MnTPP and MnTPP + ferrocene and **3b** in acetonitrile containing 0.1 M TBAP, Scan rate = 0.1 V/s.

3.4. Electrochemistry

The electrochemical characteristics of manganese complexes **3a–3f** were investigated by cyclic voltammetry (CV) in CH₃CN solutions and the data were summarized in Table S2. Fig. 3 represents the cyclic voltammograms of MnTPP, MnTPP + ferrocene and **3b** in acetonitrile containing 0.1 M TBAP. All the manganese N-confused porphyrins show a single one-electron reversible or quasi-reversible oxidation and a series of irreversible reduction within the scan window (−1.8 to 1.0 V). Reference the electrochemistry of other manganese macrocycles [36–40], the first redox process of **3a–3f** may be assigned to manganese oxidation (Mn³⁺/Mn⁴⁺) and the three irreversible reduction process with the potentials in the range of −0.680 to 1.32 V may be attributed to the ligand reduction. The first half wave oxidation potential of **3a–3f** revealed $E_{1/2}$ values in the range of 0.47–1.08 V for Mn⁴⁺/Mn³⁺ analogous to other manganese macrocyclic complexes [36–40]. As expected, the $E_{1/2}$ for the first oxidation of the manganese N-confused porphyrins shifts positively with increase in the electron-withdrawing ability of the substituent, that is, **3f** is 81 mV more difficult to be oxidized than **3a** (Table S2). Compared with the other manganese N-confused porphyrins, **3f** has a greater electron withdrawing ability and is more difficult to lose electron. As a result, **3f** has larger oxidation potential. This trend fits with what would be predicted on the basis of simple substituent's effect. This implies that **3f** has greater ability to stabilize the higher valent oxidation states of metal ions.

3.5. Catalytic activity

PhIO was often used as terminal oxidant in the manganese porphyrin catalyzed oxidation of alkenes [41]. It was found the catalytic oxidation of styrene by manganese N-confused porphyrins using PhIO gave benzaldehyde (**BA**), phenylacetaldehyde (**PA**), styrene epoxide (**SO**) and 1-phenylethanone (**PE**) (Scheme 2). Time-dependent conversion yield for the catalytic oxidation of styrene



Scheme 2. Catalytic oxidation products of styrene by MnNCTArPs.

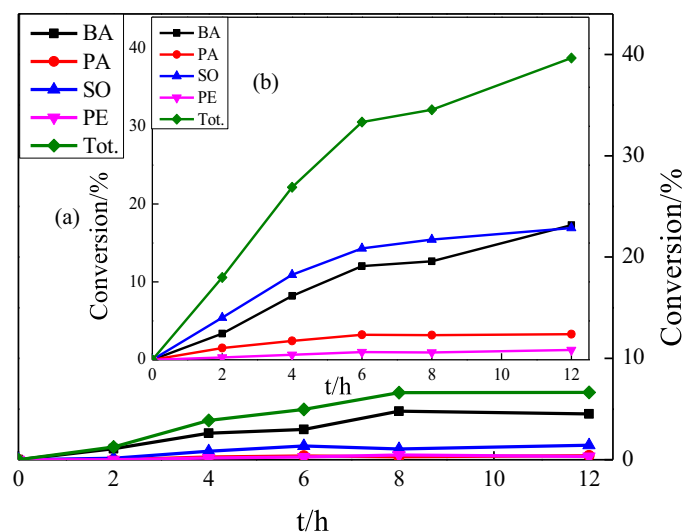


Fig. 4. The effect of reaction time on the catalytic oxidation of styrene by **3a** (b, inset, **3a**/PhIO/styrene = 1/100/1000) and the control experiment without catalyst (a).

by **3a** using PhIO in dichloromethane is depicted in Fig. 4. Without catalyst, only a small amount of benzaldehyde could be detected (less than 5% in 12 h), while the other products were negligible (less than 2%, Fig. 4b). In the presence of manganese *N*-methyl *N*-confused porphyrin **3a**, the conversion yield increased sharply, which indicated that **3a** can catalyze the oxidation reaction significantly. The main oxidation products were styrene oxide and benzaldehyde, while small amounts of phenylacetaldehyde (PA) and 1-phenylethanone (PE) were also detected (less than 4% in 12 h, Fig. 4a). The total conversion yield increased with the increasing of reaction time in the first 6 h, and after that, the increase in the conversion yield was much slower. Therefore, the optimized reaction time was selected to be 6 h.

The effects of catalyst concentration, solvents, oxidants and atmosphere on the catalytic oxidation are summarized in Table 1. The conversion efficiency of styrene and the selectivity of styrene epoxide increase significantly with the increasing concentration of **3a** (Table 1, Entry 1–4), which further confirms that manganese

N-methyl *N*-confused porphyrin **3a** exhibits catalytic activity in styrene oxidation. It should be noted manganese acetate $\text{Mn}(\text{OAc})_2$ has no catalytic oxidation activity under the same conditions (Table 1, Entry 12). When the amount of **3a** was increased from 0.5 μmol to 1.0 μmol , the conversion of styrene increased remarkably and no significant improvement with further increasing the amount of **3a**, so the optimized amount of catalyst was set to 1.0 μmol .

Significant effect of solvent on the catalytic activity of manganese complexes of porphyrins and corroles have been reported recently [18,42]. To determine the effect of solvent on the catalytic oxidation by **3a**, the reaction was carried out in different solvents (Table 1, Entry 5–10). Acetonitrile gave the highest total conversion yield and styrene epoxide selectivity. Under argon atmosphere, the yield and selectivity of styrene epoxide increase slightly (Table 1, Entry 10, 11), while the significant decrease in the yield of benzaldehyde was observed. This evidenced the involvement of oxygen in the catalytic oxidation under aerobic conditions. Similar results were observed for manganese(III) 5,10,15,20-tetraphenylporphyrin (MnTPP) catalyst (Table 1, Entry 13, 14). Whether under aerobic or anaerobic conditions, styrene epoxide was found as the major product. The total yield of oxidation products by **3a** was almost same as that of MnTPP, suggesting that manganese *N*-methyl *N*-confused porphyrins have comparable catalytic activity with manganese porphyrins.

The effect of various oxidants on the styrene oxidation by **3a** and MnTPP was investigated under the same reaction conditions. There was almost no conversion when using air or H_2O_2 as oxidant (Table 1, Entry 17–20). When using tert-Butyl hydroperoxide (TBHP) as oxidant, the main product was benzaldehyde (Table 1, Entry 15–16). This may be attributed to free radical mechanism [43–46]. Two pathways have been envisaged for the formation of metallo-oxo species using TBHP, i.e. the heterolytic and the homolytic cleavage of the O–O bond in the $\text{Mn}^{\text{III}}\text{-O-O-}^t\text{Bu}$ intermediate. Homolytic cleavage results in the formation of $^t\text{BuO}\cdot$ radical along with the formation of poor reactive intermediate $\text{Mn}^{\text{IV}}\text{-OH}$, responsible for the low yield of styrene epoxide [45]. The $^t\text{BuO}\cdot$ radical then initiates a free radical reaction that is propagated by the involvement of oxygen, leading to the formation of benzaldehyde [46]. From Table 1 (Entry 11 and 14), it is clear that **3a** and MnTPP are efficient for the selective epoxidation of styrene in the presence

Table 1
The influence of different factors on the oxidation of styrene.^a

Entry	Catalyst	Catalyst conc. (μmol)	Solvent	Oxidant	Atmosphere	Yield (%) ^b				Tot. Conv. (%)
						BA	PA	SO	PE	
1	3a	0	CH_2Cl_2	PhIO	Air	2.99	0.36	1.35	0.26	4.96
2	3a	0.5	CH_2Cl_2	PhIO	Air	5.52	1.03	5.40	0.38	12.33
3	3a	1.0	CH_2Cl_2	PhIO	Air	12.02	3.21	14.31	0.99	30.53
4	3a	2.0	CH_2Cl_2	PhIO	Air	8.58	4.29	18.68	0.86	32.42
5	3a	1.0	Toluene	PhIO	Air	5.91	1.16	6.20	0.59	13.86
6	3a	1.0	EtOAc	PhIO	Air	4.82	1.94	11.02	0.88	18.66
7	3a	1.0	Acetone	PhIO	Air	5.60	2.10	11.38	0.69	19.77
8	3a	1.0	Methanol	PhIO	Air	9.01	1.08	2.25	0.74	13.08
9	3a	1.0	DMAc	PhIO	Air	5.64	0.45	9.33	0.62	16.04
10	3a	1.0	CH_3CN	PhIO	Air	12.92	5.54	22.05	1.44	41.95
11	3a	1.0	CH_3CN	PhIO	Argon	7.53	8.965	24.93	0.42	41.53
12	$\text{Mn}(\text{OAc})_2$	1.0	CH_3CN	PhIO	Air	1.08	0.19	0.53	0	1.80
13	MnTPP	1.0	CH_3CN	PhIO	Air	3.55	12.79	29.67	0.59	46.60
14	MnTPP	1.0	CH_3CN	PhIO	Argon	2.12	10.69	31.17	0.35	44.33
15	3a	1.0	CH_3CN	TBHP	Argon	23.69	0.32	1.83	3.31	29.15
16	MnTPP	1.0	CH_3CN	TBHP	Argon	32.73	0.65	0.66	10.42	50.46
17	3a	1.0	CH_3CN	H_2O_2	Argon	0.82	0	0	0	0.82
18	MnTPP	1.0	CH_3CN	H_2O_2	Argon	0.84	0	0	0	0.84
19	3a	1.0	CH_3CN	Air	–	–	–	–	–	–
20	MnTPP	1.0	CH_3CN	Air	–	–	–	–	–	–

^a Reaction condition: 1.0 mmol styrene, 0.10 mmol oxidant, 1.0 μmol of catalyst in 2 mL solvent at room temperature. Reaction time: 6 h.

^b Conversion was determined by GC.

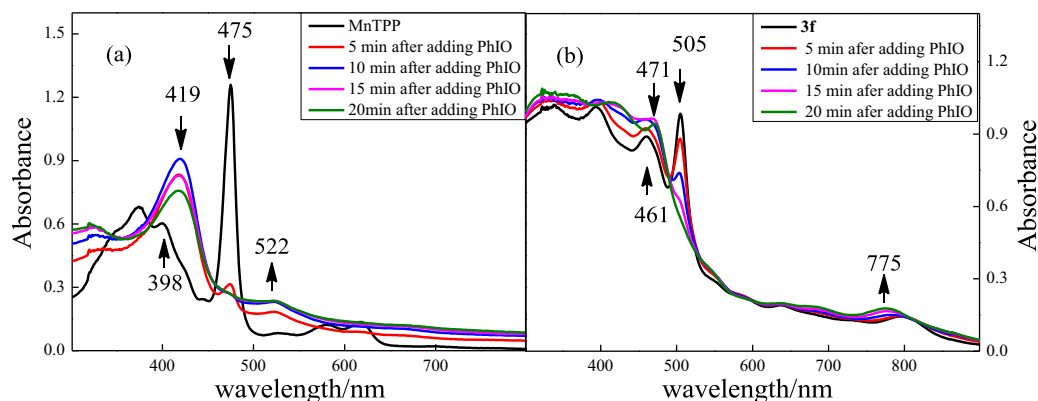


Fig. 5. UV-vis spectra obtained by adding PhIO into the acetonitrile solution of MnTPP (a) and **3f** (b). [MnTPP] = 10 $\mu\text{mol/L}$, [MnTPP]/[PhIO] = 1/10, [**3f**] = 25 $\mu\text{mol/L}$, [**3f**]/[PhIO] = 1/5.

of PhIO. This is because PhIO is a single-oxygen donor and favors the formation of the high-valent (oxo)manganese species $\text{Mn}^{\text{V}}(\text{O})$, which is responsible for oxygen insertion into the carbon–carbon double bond of styrene [47]. As manganese porphyrin (MnTPP) can catalyze the epoxidation of styrene using PhIO oxidant under anaerobic conditions via $\text{Mn}^{\text{V}}(\text{O})$ species, the same mechanism might be expected for manganese N-confused porphyrins.

Catalytic oxidation activities of all synthesized Mn(III) N-methyl N-confused porphyrins (**3a–3f**) under the same conditions were summarized in Table 2. The conversion efficiency of styrene and the selectivity of styrene epoxide for **3f** is obviously higher than **3a** and other Mn-NCTArPs containing phenyl groups substituted with electron-donors (*o*-OMe, *m*-OMe, *p*-OMe, *p*-Me). The total yield of oxidation products by **3f** is also a little higher than that of MnTPP under the same conditions. The improvement of the conversion efficiency of styrene and the selectivity of styrene epoxide for **3f** may be due to its higher first oxidation potential $E_{1/2}$ ($\text{Mn}^{4+}/\text{Mn}^{3+}$) as compared to other Mn-NCTArPs, which favors the formation of more reactive $\text{Mn}^{\text{V}}(\text{O})$ species.

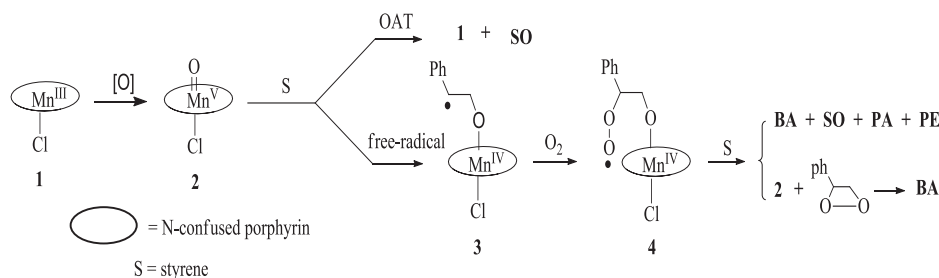
Table 2
The catalytic activities of all synthesized manganese N-confused porphyrins on the oxidation of styrene^a.

Catalyst	Yield (%)				Tot. Conv. (%)
	BA	PA	SO	PE	
MnTPP	1.90	9.99	32.66	0.20	44.75
3a	8.88	8.37	25.50	0.53	43.28
3b	6.00	9.97	25.54	0.77	42.28
3c	6.43	9.81	23.06	0.74	40.04
3d	7.76	11.78	22.10	0.80	42.44
3e	11.69	7.08	17.40	1.16	37.33
3f	4.35	12.80	28.69	0.52	46.36

^a Reaction condition: 1.2 mmol styrene, 0.10 mmol PhIO, 1.0 μmol of catalyst in 2 mL solvent at room temperature under argon. Reaction time: 6 h.

It is well known that manganese porphyrins and related macrocycles possess very high catalytic activity in alkene epoxidation [48–51]. Generally, epoxides are formed via oxygen atom transfer (OAT) from high-valent (oxo)manganese(V) intermediate to carbon–carbon double bond [52,53]. At least three types of active (oxo)manganese intermediates have been postulated for manganese porphyrin catalyzed oxidation reactions: (oxo)manganese(IV)-porphyrin [$\text{PorMn}^{\text{IV}}(\text{O})$], (oxo)manganese(IV)-porphyrin π -radical cation [$\text{PorMn}^{\text{IV}}(\text{O}^{\bullet})$] and the most plausible active intermediate (oxo)manganese(V)-porphyrin [$\text{PorMn}^{\text{V}}(\text{O})$] [54–57]. To explore the active intermediate in the present catalytic system. The direct oxidation of manganese N-confused porphyrin by PhIO in the absence of organic substrates was performed. Fig. 5 shows the UV-vis spectral changes of **3f** and MnTPP upon addition of large excess of PhIO in acetonitrile. For MnTPP, addition of PhIO resulted in the disappearance of the absorption band at 475 nm. At the same time, the bands at 419 and 522 nm were observed (Fig. 5a), consistent with the typical UV-vis spectra of [$\text{PorMn}^{\text{V}}(\text{O})$] species [57]. The reaction between **3f** and PhIO also exhibited a similar spectral changes (Fig. 5b), i.e. disappearance of the band at 505 nm and appearance of the new bands at 471 and 775 nm. Similar spectral changes suggest the existence of $\text{Mn}^{\text{V}}=\text{O}$ intermediate in both cases.

Based on the results described during aforementioned styrene oxidation catalyzed by manganese N-confused porphyrin using PhIO as oxygen source, the suggested mechanism is depicted in Scheme 3. The reaction between PhIO and manganese N-confused porphyrin to form $\text{Mn}^{\text{V}}=\text{O}$ intermediate (**2**), which subsequently transfers its oxygen to the carbon–carbon double bond of styrene to form the products **SO**, **PA** and **PE**. Another pathway is free-radical involved mechanism, the reaction of oxygen and radical species **3** to form the peroxy radical intermediate **4**. Species **3** intermediate can act as radical propagation initiator to generate more alkyl peroxy radicals, which in turn oxidize styrene to benzaldehyde



Scheme 3. Proposed mechanism for the catalytic oxidation of styrene by MnNCTArPs using PhIO oxidant.

and other carbonyl products. The intermediate **4** regenerates the $Mn^V=O$ species **2** along with the formation of other active intermediate dioxetane, which further produce benzaldehyde via cleavage [58,59].

4. Conclusion

We have presented the synthesis of a series of new manganese N-methyl N-confused porphyrins and their characterization by UV–vis, HR-MS and X-ray Photoelectron Spectroscopy as well as by cyclic voltammetry. The first catalytic oxidation of alkene by manganese N-confused porphyrins are also presented. The experimental results showed that manganese N-confused porphyrins **3a–3f** can catalyze the oxidation of styrene in the presence of iodosylbenzene to yield styrene oxide as the major product, which highlights the potential use of manganese N-confused porphyrin complexes for the catalytic epoxidation of various organic substrates. The influence of reaction time, solvents and oxidants on the catalytic reaction were also investigated. A comparable catalytic activity of manganese N-confused porphyrins with the manganese porphyrin suggests their broader catalytic scope in various chemical reactions. The catalytic mechanism was also suggested based on UV–vis spectral changes for the reaction between **3f** and PhIO, as well as the catalytic reaction products under argon atmosphere. Further investigations on the catalytic oxidation by manganese N-confused porphyrins to other organic substrates is going on in our lab

Acknowledgements

This work has been supported by the National Natural Science Foundation of China (Nos. 21171057, 21371059).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2014.08.016>.

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