

# Oxygen atom transfer reactions from sterically encumbered brominated (oxo)manganese(V) corroles to styrene

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Received 7 August 2015 Accepted 16 November 2015

**ABSTRACT:** Seven  $A_{3^-}$  and *trans*- $A_2B$  manganese(III) corroles (1–7-Mn) differing widely in their electronic and steric features were synthesized and transformed to their corresponding  $\beta$ -brominated manganese(III) corroles derivatives (1a–7a-Mn). Their corresponding (oxo)manganese(V) corroles 1–7-Mn(oxo) and 1a–7a-Mn(oxo) were further prepapred by treating with iodosylbenzene (PhIO). The reactivity for the oxygen atom transfer from 1–7-Mn(oxo) to styrene followed the order of 1-Mn(oxo) > 2-Mn(oxo) > 7-Mn(oxo) > 4-Mn(oxo) > 3-Mn(oxo) > 6-Mn(oxo) ≈ 5-Mn(oxo). The same pattern was observed for their  $\beta$ -brominated analogs 1a–7a-Mn(oxo), albeit their reactivity was remarkably higher. The steric protection of Mn<sup>V</sup>=O moiety by *ortho–ortho*'-dibromophenyl substituents was found to enhance the stability of (oxo)manganese(V) corroles significantly.

**KEYWORDS:** corrole, manganese, manganese-oxo, bromination, oxygen atom transfer reaction.

# INTRODUCTION

Biomolecules having manganese such as catalase, superoxide dismutase (Mn-SOD), and manganeseperoxidase have considerably contributed to the understanding of manganese chemistry in many synthetic models with reference to structural, electrochemical and photophysical properties. This understanding has facilitated the development of manganese complexes having real applications in catalysis and biomedicines [1–4]. Manganese-oxo species have long been postulated as the active intermediate in manganese-mediated oxidation of hydrocarbons [5-7]. Study on high-valent manganese-oxo species still presents considerable challenge because they are generally too reactive to be isolated [8]. Identification of different porphyrin manganese-oxo species has provided great insights into the catalytic oxidation by manganese porphyrins [9-11]. Since corrole stabilizes high oxidation state

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metal better than porphyrin, it is expected that some of its metal-oxo complexes might be stable enough to be isolated and be useful probe in oxygen atom transfer (OAT) reactions. Manganese corroles are proved efficient in catalytic oxidation of various organic substrates [1].  $\beta$ -halogenation on corrole macrocycle may also remarkably increase the catalytic oxidation activity of manganese corroles [12, 13]. Multiple active intermediates have been suggested for the catalytic oxidation reaction of manganese corroles, depending on various factors such as electronic structure of corrole macrocycle [14-17], steric hinderance [18], and the solvent [19, 20]. (Oxo) manganese(V) corrole has been demostrated to be active in the OAT reaction, and  $\beta$ -halogenated (oxo) manganese(V) corroles exhibit higher OAT reactivity towords alkenes [12] and sulfides [21].  $\beta$ -bromination of the tetrapyrrolic macrocycle is a convenient method to increase the catalytic oxidation activity of metallocorroles [13] and metalloporphyrins [22]. The higher reactivity of  $\beta$ -brominated (oxo)manganese(V) corrole has been interpreted as the spin-flipping effect related to the spin-obital interaction by DFT calculations [23, 24]. To further investigate the bromination effect on the OAT reactivity of (oxo)manganese(V) corroles towards

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Scheme 1. Structures of synthesized corroles and their manganese complexes

alkene, we here wish to report the synthesis of a series of  $A_3$ - and *trans*- $A_2B$ -type sterically encumbered corroles starting from 2,6-dibromobenzaldehyde, and their manganese complexes, as well as the OAT reaction from corresponding (oxo)manganese(V) corroles to styrene.

# **RESULTS AND DISCUSSION**

#### Synthesis

Except for hexabrominated free base  $A_3$ -type aryl corrole (5, 6; Scheme 1) from *ortho–ortho*'-dibromobenzaldehyde, all other  $A_3$ - and *trans*- $A_2B$  free base corroles could be prepared smoothly by conventional methods [25–31]. The optimization of synthesis of  $A_3$ -type aryl corrole from *ortho–ortho*'-dibromobenzaldehyde was finally achieved by using BF<sub>3</sub>·Et<sub>2</sub>O catalyst in the condensation of 2,6-dibromobenzaldehyde and the target corroles were obtained in a satisfactory yields of ~12% [32–35]. Manganese insertion was made by reacting free base corroles with manganese acetate in methanol dichloromethane mixture [12, 13, 18].

## EPR spectroscopic characterization of manganese(III) corroles

An EPR spectrum of manganese(III) corrole is particularly useful to get information about the oxidation



Fig. 1. EPR spectrum of 1a-Mn

state of central manganese [36]. Manganese(III) corroles having high-spin d<sup>4</sup> configuration (S = 2) are EPR silent at room temperature [37, 38]. However, by decreasing the temperature, EPR signals are observable for manganese(III) corroles. The X-band EPR spectra of a frozen solution of all manganese complexes 1–7-Mn and 1a–7a-Mn (Scheme 1) in CH<sub>2</sub>Cl<sub>2</sub> at 88 K showed a single line centered at  $g_{\rm eff} = 2.0$ . A typical EPR spectrum for 1a-Mn is shown in Fig. 1, and the data for all other

manganese corroles is given in Supporting information (Table S1, Supporting information). This may be attributed to the presence of high-spin mononuclear Mn(III) (S = 2) center in all these manganese(III) corroles. The value of g = 2 for Mn(III) corrole has been assigned as Mn(II)  $\pi$ -cation radical, which is EPR silent at room temperature due to the enhanced electron spin relaxation rate by spin-spin magnetic interactions between metal ion and the ligand radical [38].

#### Cyclic voltammetry of manganese(III) corroles

Metallocorroles are generally harder to reduce but easier to oxidize compared with their metalloporphyrin analogs owing to the different formal charge on both the macrocycles, which is -2 in porphyrins and -3 in corroles [39]. This feature is consistent with the ability of corrole to stabilize high-valent transition metal ions more than the corresponding porphyrins. The electrochemistry of manganese corroles having various  $\beta$ -alkyl and mesoaryl substituents has been widely studied [37, 40, 41]. Although manganese(III) corroles are sufficiently stable in air, they can be oxidized at relatively low potential to the corresponding manganese(IV) corrole derivatives. Various manganese(IV) corrole derivatives containing OPPh<sub>3</sub> and halide ions (Br-, Cl- and I) as fifth axial ligand have been structurally characterized, indicating that corrole macrocycle can stabilize Mn(IV) in the core [42-44]. Electronic and steric features of corroles show remarkable influence on the oxidation potentials of manganese(III) corroles [17, 37, 40, 41, 45]. For example, highly electron-rich octaethylcorrole (OEC) manganese(III), devoiding mesoaryl substituents, is much easily oxidized as compared to tris(pentafluorophenyl) manganese(III) corrole or its  $\beta$ -fluoro and  $\beta$ -bromo analogs. The electron-poor nature

of these manganese(III) corrole macrocycle renders them resistant to ring oxidations or reductions.

The cyclic voltammograms of all manganese(III) corroles were meassured in acetonitrile solvent using glassy carbon as working electrode, platinum wire as counter electrode and Ag/AgCl as reference electrode. TBAP was used as supporting electrolyte. Figure 2 shows the typical CV of Mn(III) corroles 1-Mn and **1a-Mn**, while all others are shown in Figs S1 and S2. The half wave potentials of Mn(IV)/Mn(III) couple are summarized in Table 1.  $E_{1/2}$  of Mn(IV)/Mn(III) couple of manganese(III) corroles 1-7-Mn lie in the range of 490-850 mV depending on the nature of attached substituents (Table 1). While the first oxidation potential values of 1–7-Mn are significantly higher than manganese OEC by 130-480 mV [40, 46], but still lower than manganese(III) tetraarylporphyrins by more than 300 mV [39, 47]. The first oxidation potential of highly electron-rich mesotriphenylcorrole manganese(III) 3-Mn is still higher than Mn(III)-OEC by about 130 mV, indicating the stabilizing effect of *meso*-substitution [40]. The first oxidation potential of ortho-sterically hindered hexabrominated manganese(III) corroles 5-Mn and 6-Mn are remarkably lower than electron-poor corroles 1-Mn, 2-Mn and 7-Mn containing three, two and one electron-withdrawing meso-pentafluorophenyl groups, respectively. However, these values are still higher than 3-Mn and 4-Mn having meso-phenyl and meso-cyanophenyl groups, respectively. Transformation of manganese(III) corroles to their fully  $\beta$ -brominated analogs **1a–7a-**Mn leads to an increase in the first oxidation potential by about 160-540 mV. Variations in the first oxidation potentials of 1-7-Mn and **1a–7a-Mn** as a function of  $\beta$ -pyrrole and *meso*substituents further indicate that a metal-centered redox process is involved in all these manganese(III) corroles. Interestingly, the increase in the first oxidation potential



Fig. 2. CV spectra of 1-Mn and 1a-Mn in acetonitrile containing TBAP as supporting electrolyte. Scan rate 100 mV/s

**Table 1.** Oxidation potentials (*vs.* Ag/AgCl) of manganese(III) corroles in acetonitrile containing TBAP as supporting electrolyte<sup>a</sup>

Corrole	$E_{1/2}$ Mn <sup>IV</sup> /Mn <sup>III</sup>	Corrole	$E_{1/2}$ Mn <sup>IV</sup> /Mn <sup>III</sup>	$\Delta E^{\rm b}$
1-Mn	0.845	1a-Mn	1.249	0.405
<b>2-</b> Mn	0.736	2a-Mn	1.106	0.370
3-Mn	0.496	3a-Mn	0.908	0.412
4-Mn	0.627	4a-Mn	1.169	0.542
5-Mn	0.685	5a-Mn	0.884	0.199
6-Mn	0.682	6a-Mn	0.923	0.250
7-Mn	0.740	7a-Mn	0.907	0.167

<sup>a</sup>Fc/Fc<sup>+</sup> couple were measured as 0.47 V under identical conditions. <sup>b</sup> $E_{1/2}$  of brominated corroles —  $E_{1/2}$  of nonbrominated corroles.

values upon  $\beta$ -pyrrole bromination is less significant in **5a–7a-M**n than in **1a–4a-M**n, which indicates that bromine atoms at 2,6-dibromophenyls will reduce the effect of  $\beta$ -bromination on the redox potential of central Mn atom.

#### **UV-vis spectroscopy**

The electronic spectra of all manganese(III) and (oxo) manganese(V) corroles resemble with the previously reported manganese complexes of various peripherally substituted corroles [12, 17, 21]. Typically, all manganese(III) corroles **1–7-M**n (Fig. 3) display sharp Soret band around 400 nm, metal-ligand charge transfer band around 490 nm and a broad Q-band in the range of 580–660 nm. The exact position of these bands is,

however, sensitive to the electronic and steric features of the substituents attached to the *meso*-phenyl groups. The electronic spectra of octabrominated manganese(III) corroles **1a–7a-**Mn (Fig. 4) are much more similar to their corresponding non-brominated derivatives, except that their Soret and Q-bands are significantly red-shifted owing to the inductive electron-withdrawing effect of  $\beta$ -bromo-substituents [21].

The electronic spectra of (oxo)manganese(V) corroles show significant difference from their corresponding manganese(III) corroles owing to the change in oxidation state of manganese accompanied with the oxygen coordination. All (oxo)manganese(V) corroles 1–7-Mn(oxo) display characteristic split Soret band in the range of 351–413 nm and a broad Q-band around 520 nm (Fig. 5). The corresponding  $\beta$ -brominated (oxo)manganese(V) corroles 1a–7a-Mn(oxo) also exhibit the same pattern (Fig. 6), but significant red-shift was observed for Soret and Q-bands [21].

#### Kinetic studies for oxygen atom transfer reaction

(Oxo)manganese(V) corroles are legitimate oxygen atom transfer agents [12, 18, 21]. For studying the kinetics of OAT reactions of various  $\beta$ -brominated and -nonbrominated (oxo)manganese(V) corroles **1–7-**Mn (oxo) and **1a–7a-**Mn(oxo) to organic substrates, styrene was chosen as substrate and toluene as the solvent [19, 20]. The green colored toluene solutions of manganese(III) corroles precursors **1–7-**Mn and **1a–7a-**Mn were treated with freshly prepared iodosylbenzene (PhIO). The initial green colored manganese(III) corroles were converted to red pink colored (oxo)manganese(V) corroles, indicating the transformation of Mn(III) to Mn(V) accompanied with the oxygenation of manganese center. The excess



Fig. 3. UV-vis spectra of manganese(III) corroles 1–7-Mn in toluene at  $20.0 \pm 0.1$  °C



Fig. 4. UV-vis spectra of manganese(III) corroles 1a–7a-Mn in toluene at  $20.0 \pm 0.1$  °C



Fig. 5. UV-vis spectra of (oxo)manganese(V) corroles 1–7-Mn(oxo) in toluene at  $20.0 \pm 0.1$  °C



Fig. 6. UV-vis spectra of (oxo)manganese(V) corroles 1a-7a-Mn(oxo) in toluene at  $20.0 \pm 0.1$  °C

PhIO was then removed by flash chromotograpgy on a short column of basic alumina to afford (oxo)manganese(V) corrole solution. The stability of these (oxo)manganese(V) corroles varied significantly depending on the combined electronic and steric factors. More electron-poor manganese(III) corroles in both  $\beta$ -brominated and  $\beta$ -nonbrominated series produced much more reactive (oxo)manganese(V) corroles. Similarly,  $\beta$ -brominated (oxo)manganese(V) corroles **1a–7a-**Mn(oxo) were observed more reactive than corresponding  $\beta$ -nonbrominated (oxo)manganese(V) corroles **1–7-**Mn(oxo).

The self-decay process of (oxo)manganese(V) corroles can easily be monitored by UV-vis spectroscopy. From UV-vis spectral changes of 1-7-Mn<sup>V</sup>(oxo) (Fig. 7), it is clear that all (oxo)manganese(V) corroles decayed with the passage of time. This can be observed by the disappearance of typical absorption peak corresponding to Mn<sup>V</sup>≡O moiety in the range between 350 to 360 nm along with the disappearance of O-band at about 500 nm, as well as the appearance of absorption peaks at about 480 nm corresponding to metal-ligand charge transition (MLCT) band and the appearance of broad Q-band at about 600 nm typical of manganese(III) corroles complexes. Exceptions to this are 3-Mn(oxo) and 4-Mn(oxo) which decayed to their corresponding manganese(IV) corroles, rather than manganese(III) corroles as indicated by their UV-vis spectral changes. In contrast to other corroles in the series, corrole macrocycle in 3-Mn(oxo) and 4-Mn(oxo) is relatively less electronpoor. Almost similar phenomenon was observed for 1a-7a-Mn(oxo) whose UV-vis spectral changes are shown in Fig. 8. Corresponding changes for the transformation of (oxo)manganese(V) corroles to manganese(III) corroles can be seen, except for **3a-**Mn(oxo) and **4a-**Mn(oxo). (Oxo)manganese(V) corroles 3a-Mn(oxo) and 4a-Mn(oxo) did not display distinct split Soret band, however, the characteristic peak for Mn<sup>V</sup>≡O moiety at about 385 nm can be clearly observed whose intensity decreased with the passage of time. A blue-shift of about 10-20 nm during the transformation of 3a-Mn and 4a-Mn to 3a-Mn(oxo) and 4a-Mn(oxo) also testifies the formation of their corresponding (oxo)manganese(V) corroles. The kinetics of the self-decay of (oxo)manganese(V) corroles was monitored by the absorption at left arm of the Soret band (Figs S3 and S4, Supporting information). The self-decay rate constants were computed from the exponential fit of the kinetic curves, and are summarized in Table 2.

After confirming that all (oxo)manganese(V) corroles 1-7-Mn(oxo) and 1a-7a-Mn(oxo) are reasonably stable, their reactivity with reference to oxygen atom transfer (OAT) to styrene at 20 °C in toluene was investigated. The addition of 1000



Fig. 7. UV-vis spectral changes for 1–7-Mn(oxo) in toluene at  $20.0 \pm 0.1$  °C. Inset shows the self-decay kinetic curve



Fig. 8. UV-vis spectral changes for 1a-7a-Mn(oxo) in toluene  $20.0 \pm 0.1$  °C. Inset shows the self-decay kinetic curve

**Table 2.** Self-decay rate constant (*k*) and pseudo-first-order rate constants ( $k_{obs}$ ) for various (oxo)manganese(V) corroles in toluene at  $20.0 \pm 0.1 \,^{\circ}C^{a,b}$ 

Corrole	$k/k_{\rm obs} (10^{-4}  {\rm S}^{-1})$		Corrole	$k/k_{\rm obs} \ (10^{-4} \ { m S}^{-1})$	
	Self-decay	Styrene		Self-decay	Styrene
1-Mn(oxo)	3.669	12.467	1a-Mn(oxo)	5.781	39.078
2-Mn(oxo)	2.972	9.502	2a-Mn(oxo)	3.406	27.669
3-Mn(oxo)	1.638	4.537	3a-Mn(oxo)	1.874	13.633
4-Mn(oxo)	2.072	6.811	4a-Mn(oxo)	2.908	20.007
5-Mn(oxo)	1.051	2.944	5a-Mn(oxo)	1.220	8.947
6-Mn(oxo)	1.252	3.019	6a-Mn(oxo)	1.738	9.122
7-Mn(oxo)	2.432	7.589	7a-Mn(oxo)	3.152	22.513

<sup>a</sup>The reaction was monitored by the absorption at left arm of the Soret band. <sup>b</sup>The decay rate constants were obtained from the exponential fit of the kinetic curve.

equivalents of styrene to the toluene solutions of 1–7-Mn(oxo) resulted in the color change of solution from pink to green, indicating the transformation of (oxo)manganese(V) corroles 1-7-Mn(oxo) back to manganese(III) corroles 1–7-Mn via oxygen atom transfer [19, 21]. The decay was remarkably accelerated in the presence of styrene as compared with their corresponding self-decays, consistent with the kinetics of oxygen atom transference from (oxo)manganese(V) corroles to styrene resulting in the formation of styrene epoxide. Furthermore,  $\beta$ -brominated (oxo)manganese(V) corroles **1a–7a**-Mn(oxo) exhibited higher reactivity in terms of oxygen atom transfer to styrene than their  $\beta$ -nonbrominated analogs, as might be expected on the basis of reactivity induced by  $\beta$ -bromination [21, 23]. The *pseudo*-first-order rate constants were measured for all (oxo)manganese(V) corroles 1-7-Mn(oxo) and 1a-7a-Mn(oxo) for at least three times, and the average of these data for each (oxo) manganese(V) corrole is depicted in Table 2. It must be noted that the orders of self-decay and *pseudo*-first-order reaction rate constants are the same in both the series.

The rate constants for the stochiometric oxidation of styrene to styrene epoxide by various  $\beta$ -nonbrominated  $(\infty)$ manganese(V) corroles 1–7-Mn<sup>V</sup> $(\infty)$  revealed the following reactivity order: 1-Mn(oxo) > 2-Mn(oxo)> 7-Mn(oxo) > 4-Mn(oxo) > 3-Mn(oxo) > 6-Mn(oxo)  $\approx$ 5-Mn(oxo). This pattern is consistent with two main factors: the electron-poor or electron-rich meso-substituents, and the presence or absence of steric protection by these mesophenyl groups. The first three members of the series differ by the number of pentafluorophenyl groups (3, 2 and 1, respectively) in their skeleton. The pentafluorophenyl group is the most highly electron-poor among various mesosubstituents in the above manganese corroles complexes, and the reactivity may be related with the number of meso-pentafluorophenyl groups attached to the corrole ring. While the remaining (oxo)manganese(V) corroles 4-Mn(oxo) to 7-Mn(oxo) lack any meso-pentafluorophenyl groups, their reactivity order can be justified by either electron-rich or ortho sterically hindered meso-phenyl groups. (Oxo)manganese(V) corroles 4-Mn(oxo) and 3-Mn(oxo) represent the examples of corroles having fairly "bare" Mn<sup>V</sup>≡O moiety as compared with the other corroles in the series by keeping in mind the following order of steric hindrance Br > F > H. Both differs by the presence of only one substituent attached at the meso-paraphenyl, *i.e.* a H in **3**-Mn(oxo) is replaced with a CN group in 4-Mn(oxo). The observed difference in the reactivity of 4-Mn(oxo) and 3-Mn(oxo) can safely be attributed to the presence of electron-withdrawing CN group in 4-Mn(oxo), although the reactivity of both 4-Mn(oxo) and 3-Mn(oxo) is still lower than those containing mesopentafluorophenyl groups. (Oxo)manganese(V) corroles 6-Mn(oxo) and 5-Mn(oxo) represent the most sterically hindered  $\beta$ -nonbrominated (oxo)manganese(V) corroles in the series. Both 6-Mn(oxo) and 5-Mn(oxo) contain meso-2,6-dibromophenyl groups, with the former containing an additional F-substituent at the para-position. Steric protection by 2,6-dihalophenyl groups (2,6-dichloroand 2,6-difluorophenyls) in various (oxo)manganese(V) corroles has been responsible for the lower reactivity of (oxo)manganese(V) corroles towards oxygen atom transference to thioanisoles [21]. The observed reactivity of 6-Mn(oxo) and 5-Mn(oxo) can thus be attributed to the steric protection by the *meso*-2,6-dibromophenyl substituents. Their Mn<sup>V</sup>≡O is the most protected and hence the most stable amongst the investigated series of **1–7-M** $n^{V}(xx)$  corroles. From the above, it is evident that the observed reactivity of (oxo)manganese(V) corroles can be correlated with two aspects: Firstly, the presence and number of *meso*-pentafluorophenyl groups in the (oxo)manganese(V) corroles, and Secondly, the extent of steric protection by the bulky meso-2,6-dibromophenyl substituents. This steric protection is present but less efficient in 7-Mn(oxo) (due to only two meso-2,6dibromophenyl substituents), totally lacking in case of 3-Mn(oxo) and 4-Mn(oxo), and present up to maximum in 5-Mn(oxo) and 6-Mn(oxo) corroles.

The pseudo-first-order rate constants for the stochiometric oxidation of styrene by various  $\beta$ -brominated (oxo)manganese(V) corroles, 1a-7a-Mn(oxo), indicated the following order of reactivity: 1a-Mn(oxo) >2a-Mn(oxo) > 7a-Mn(oxo) > 4a-Mn(oxo) > 3a-Mn(oxo) >6a-Mn(oxo)  $\approx$  5a-Mn(oxo). While the reactivity order of  $\beta$ -brominated (oxo)manganese(V) corroles followed the same pattern as that of corresponding  $\beta$ -nonbrominated (oxo)manganese(V) corroles, a noteworthy observation is the difference in their rate constants. The rate constant for the oxygen atom transference from **1a-7a-Mn**(oxo) to styrene increased dramatically as compared to 1–7-Mn(oxo). The difference in the reactivity of 1a–7a-Mn(oxo) as compared to 1-7-Mn(oxo) is correlated with the differences in the electrochemistry of their corresponding manganese(III) corroles 1a-7a-Mn and 1-7-Mn, respectively, and has been identified in case of sulfides [21].  $\beta$ -bromination induced enhancement of oxygen atom transfer from (oxo)manganese(V) corroles to organic substrates is also supported from theoretical studies [23, 24]. DFT calculations have indicated that, while (oxo)manganese(V) corroles generally exists in singlet states, there is only a slight difference of about 12 kcal/mol between their singlet and triplet states. As oxygen atom transfer is more favorable in triplet state pathway,  $\beta$ -bromination provides a convenient way of spin flipping (change of singlet state to triplet state) in (oxo)manganese(V) corroles for efficient OAT. DFT calculations have also indicated that electron-withdrawing meso-substituents can also increase the rate of OAT, but the effect of  $\beta$ -bromination is more profound and can sharply increase the rate of OAT via spin flipping.

Variations in the rate constants with changing electronic and steric effects suggest that oxygen atom transference proceeds through direct pathway in all cases [23]. All electron-poor (oxo)manganese(V) corroles containing highly electron-withdrawing pentafluorophenyl groups (whether  $\beta$ -brominated or -nonbrominated) are more reactive, and undergo direct oxygen atom transfer on reaction with styrene and form styrene epoxide. Comparatively electron-rich and sterically protected (oxo)manganese(V) corroles are less efficient for oxygen atom transfer to styrene. While (oxo)manganese(V) corroles **3–6-**Mn(oxo) are comparatively electron-rich, the least reactivity of **6-**Mn(oxo) and **5-**Mn(oxo) may be attributed to the enhanced steric protection of Mn<sup>V</sup>=O by *ortho*-dibromophenyl substituents.

## **EXPERIMENTAL**

#### General

All chemicals and solvents were purchased from Sinopharm Chemical Reagents Co. Ltd. and used without further purification unless otherwise mentioned. Pyrrole was redistilled prior to use. Commercial analytical grade styrene (Aladdin) was passed through short column of basic alumina prior to use. Iodosylbenzene (PhIO) was synthesized by a reported method [48]. The supporting electrolyte in CV experiments, tetrabutylammonium perchlorate, was purchased from Fluka and recrystallized from ethanol at least three times. EPR spectra were measured on an X-band Bruker A300 spectrometer equipped with an Oxford Instruments liquid helium cryostat. Mass spectra were taken on ESI/MS (Bruker Esquire HCT plus mass spectrometer with an ESI source) and MALDI-TOF spectra were measured on a Bruker auto flex III smart beam instrument, using 4-chloro- $\alpha$ -cyanocinnamic acid (CCA) as the matrix. All experiments, unless specified otherwise, were carried out at room temperature.

All cyclic voltammograms (CV) were performed in acetonitrile solutions containing 0.1 M TBAP (tetrabutylammonium perchlorate) using an Ingens Model 1030 and manganese corroles  $(1 \times 10^{-3} \text{ M})$  under nitrogen atmosphere at ambient temperature. A threeelectrode system consisting of a glassy carbon working electrode, a platinum wire counter electrode and Ag/AgCl 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 0.47 V.

Kinetic studies were carried out using a Blue Star B UV-vis spectrophotometer connected with a thermostat at 20.0  $\pm$  0.1 °C in quartz cuvette with PTFE septa. The freshly synthesized Mn(V)-oxo corrole solution (~3 × 10<sup>-3</sup> M) was taken in the cuvette and placed immediately in a thermostat cell holder in a UV-Vis spectrophotometer. The absorbance data was collected over the range of 300–800 nm at 5-sec interval. Each measurement was repeated three times at 20.0  $\pm$  0.1 °C [19].

#### Synthesis of manganese corroles

Synthesis of  $\beta$ -nonbrominated manganese(III) corroles. All manganese corroles were prepared by reacting free base corroles with manganese acetate in methanol dichloromethane mixture [12, 13, 18, 49]. The detail procedure is given below.

Typical procedure for the synthesis of β-nonbrominated manganese(III) corroles. 25 mg of corrole was dissolved in 10 mL of dichloromethane in 100 mL round bottom flask. Subsequently, 50 mL of methanol and 15–20 folds excess of  $Mn(OAC)_2 \cdot 4H_2O$  were further added into the flask. The green colored reaction mixture was refluxed for about 2 h and the progress of the reaction was monitored by TLC and UV-visible spectroscopy. After the completion of reaction, the reaction mixture was transferred to a separating funnel. Manganese corrole was extracted in dichloromethane, washed with saturated brine several times and dried over anhydrous  $Na_2SO_4$ . After evaporation of the solvent, the crude product was purified over silica gel using dichloromethane as eluent. The yield of manganese corroles in all cases were 80–90%.

**5,10,15-Tris(pentafluorophenyl)corrolato** manga **nese(III), 1-Mn.** Yield 90%. 22.5 mg (2.652 × 10<sup>-5</sup> moles). UV-vis (toluene):  $\lambda_{max}$ , nm (ε, × 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 411 (1.056), 478 (0.574), 599 (0.351). MS (HRMS): *m/z* found [M + H]<sup>+</sup> 848.9963; calcd. for C<sub>37</sub>H<sub>9</sub>F<sub>15</sub>MnN<sub>4</sub><sup>+</sup> 848.9968.

**5,15-Bis(pentafluorophenyl)-10-(4-bromophenyl) corrolato manganese(III), 2-Mn.** Yield 90%. 22.5 mg (2.687 × 10<sup>-5</sup> moles). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 409 (1.211), 480 (0.423), 584 (0.380), 630 (0.385). MS (MALDI-TOF): *m/z* found [M]<sup>+</sup> 837.905; calcd. for C<sub>37</sub>H<sub>12</sub>BrF<sub>10</sub>MnN<sub>4</sub><sup>+</sup> 837.945.

**5,10,15-Triphenylcorrolato manganese(III), 3-Mn.** Yield 85%. 21.25 mg (3.673 × 10<sup>-5</sup> moles). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 408 (1.041), 426 (0.921), 497 (0.343), 650 (0.284). MS (ESI): *m/z* found [M]<sup>+</sup> 578.9; calcd. for C<sub>37</sub>H<sub>23</sub>MnN<sub>4</sub><sup>+</sup> 578.1.

**5,10,15-Tris(4-cyanophenyl)corrolato manganese** (**III**), **4-Mn.** Yield 88%. 22.0 mg (3.366 × 10<sup>-5</sup> moles). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 413 (1.304), 443 (1.048), 496 (0.423), 648 (0.404). MS (MALDI-TOF): m/z found [M]<sup>+</sup> 653.062; calcd. for C<sub>40</sub>H<sub>20</sub>MnN<sub>7</sub><sup>+</sup> 653.116.

**5,10,15-Tris(2,6-dibromophenyl)corrolato manganese(III), 5-Mn.** Yield 90%. 22.5 mg (2.139 × 10<sup>-5</sup> moles). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 411 (0.783), 489 (0.391), 606 (0.264). MS (ESI): *m/z* found [M]<sup>+</sup> 1051.9; calcd. for C<sub>37</sub>H<sub>17</sub>Br<sub>6</sub>MnN<sub>4</sub><sup>+</sup> 1051.6.

**5,10,15-Tris(2,6-dibromo-4-fluorophenyl)corrolato manganese(III), 6-Mn.** Yield 90%. 22.5 mg  $(2.034 \times 10^{-5} \text{ moles})$ . UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ ,  $\times 10^{3} \text{ M}^{-1} \text{ cm}^{-1}$ ) 411 (0.911), 480 (0.501), 605 (0.245). MS (MALDI-TOF): m/z found [M]<sup>+</sup> 1105.447; calcd. for  $C_{37}H_{14}Br_{6}F_{3}MnN_{4}^{+}$  1105.559.

**5,15-Bis(2,6-dibromo-4-fluorophenyl)-10-(pentafluorophenyl)corrolato manganese(III), 7-Mn.** Yield 90%. 22.5 mg (2.206 × 10<sup>-5</sup> moles). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 411 (1.068), 480 (0.523), 607 (0.287). MS (MALDI-TOF): *m/z* found [M]<sup>+</sup> 1019.661; calcd. for C<sub>37</sub>H<sub>12</sub>Br<sub>4</sub>F<sub>7</sub>MnN<sub>4</sub><sup>+</sup> 1019.702.

#### Synthesis of $\beta$ -brominated manganese(III) corroles

All manganese corroles were converted into their corresponding  $\beta$ -brominated analogs by reacting with molecular bromine [21] according to the following procedure.

**Typical procedure for the synthesis of**  $\beta$ **-brominated manganese(III) corroles.** 10 mg of manganese corrole was dissolved in 5 mL of methanol in 50 mL round bottom flask and was stirred for about 10 min. Bromine (0.3 mL) diluted in 10 mL of methanol was added through funnel drop wise into the flask, while the stirring was continued overnight at room temperature. After the completion of reaction, the excess bromine was evaporated by a stream

of nitrogen gas. The green solution was evaporated to dryness and chromatographed over silica gel using dichloromethane as eluent. The yield of manganese corroles in all cases were between 60–85%.

**2,3,7,8,12,13,17,18-Octabromo-5,10,15-tris** (**pentafluorophenyl)corrolato manganese(III), 1a-Mn.** Yield 85%. 8.5 mg (5.744 × 10<sup>-6</sup> moles). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 402 (1.182), 423 (1.653), 493 (0.725), 614 (0.399). MS (MALDI-TOF): *m/z* found [M + H]<sup>+</sup> 1480.54; calcd. for C<sub>37</sub>HBr<sub>8</sub>F<sub>15</sub>MnN<sub>4</sub><sup>+</sup> 1480.273.

**2,3,7,8,12,13,17,18-Octabromo-5,15-bis(penta-fluorophenyl)-10-(4-bromophenyl)corrolato manganese(III), 2a-Mn.** Yield 85%. 8.5 mg (5.788 × 10<sup>-6</sup> moles). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 402 (0.692), 430 (0.587), 503 (0.477), 620 (0.220). MS (MALDI-TOF): *m/z* found [M]<sup>+</sup> 1467.171, [M – Br]<sup>+</sup> 1307.365; calcd. for C<sub>37</sub>H<sub>4</sub>Br<sub>9</sub>F<sub>10</sub>MnN<sub>4</sub><sup>+</sup> 1467.223.

**2,3,7,8,12,13,17,18-Octabromo-5,10,15triphenylcorrolato manganese(III), 3a-Mn.** Yield 60%. 6.0 mg (4.959 × 10<sup>-6</sup> moles). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 400 (0.909), 499 (0.411), 586 (0.376), 656 (0.349). MS (MALDI-TOF): *m/z* found [M]<sup>+</sup> 1209.378; calcd. for C<sub>37</sub>H<sub>15</sub>Br<sub>8</sub>MnN<sub>4</sub><sup>+</sup> 1209.406.

**2,3,7,8,12,13,17,18-Octabromo-5,10,15-tris(4cyanophenyl)corrolato manganese(III), 4a-Mn.** Yield 65%. 6.5 mg (5.059 × 10<sup>-6</sup> moles). UV-vis (toluene):  $\lambda_{\text{max}}$ , nm ( $\epsilon$ , × 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 404 (1.988), 444 (1.976), 506 (0.673), 656 (0.375). MS (HRMS): *m/z* found [M + H]<sup>+</sup> 1285.4002; calcd. for C<sub>40</sub>H<sub>13</sub>Br<sub>8</sub>MnN<sub>7</sub><sup>+</sup> 1285.3998.

**2,3,7,8,12,13,17,18-Octabromo-5,10,15-tris(2,6-dibromophenyl)corrolato** manganese(III), **5a-Mn.** Yield 60%. 6.0 mg ( $3.564 \times 10^{-6}$  moles). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ ,  $\times 10^3$  M<sup>-1</sup>.cm<sup>-1</sup>) 408 (0.863), 445 (0.822), 508 (0.612), 655 (0.233). MS (HRMS): *m/z* found [M + H]<sup>+</sup> 1683.8648; calcd. for C<sub>37</sub>H<sub>10</sub>Br<sub>14</sub>MnN<sub>4</sub><sup>+</sup> 1683.8710.

**2,3,7,8,12,13,17,18-Octabromo-5,10,15-tris(2,6dibromo-4-fluorophenyl)corrolato** manganese(III), **6a-Mn.** Yield 60%. 6.0 mg ( $3.454 \times 10^{-6}$  moles). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ ,  $\times 10^{3}$  M<sup>-1</sup>.cm<sup>-1</sup>) 403 (1.193), 502 (0.624), 622 (0.378). MS (HRMS): *m/z* found [M]<sup>+</sup> 1736.8304; calcd. for C<sub>37</sub>H<sub>6</sub>Br<sub>14</sub>F<sub>3</sub>MnN<sub>4</sub><sup>+</sup> 1734.8370.

**2,3,7,8,12,13,17,18-Octabromo-5,15-bis(2,6-dibromo-4-fluorophenyl)-10-(pentafluorophenyl) corrolato manganese(III), 7a-Mn.** Yield 65%. 6.5 mg (3.936 × 10<sup>-6</sup> moles). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>3</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 407 (1.255), 428 (1.044), 502 (0.731), 618 (0.344). MS (HRMS): *m/z* found [M]<sup>+</sup> 1650.9791; calcd. for C<sub>37</sub>H<sub>4</sub>Br<sub>12</sub>F<sub>7</sub>MnN<sub>4</sub><sup>+</sup> 1650.9782.

#### Synthesis of (oxo)manganese(V) corroles

All manganese(III) corroles were transformed into their corresponding (oxo)manganese(V) corroles according to reported procedure [12, 18]. A typical procedure is described below:

Typical procedure for the synthesis of (oxo) manganese(V) corroles. Stock solutions  $(3 \times 10^{-3} \text{ M})$  of

manganese(III) corroles (1-Mn to 7-Mn and 1a-Mn to 7a-Mn) were prepared in volumetric flask. 3 mL aliquots of each manganese solution was treated with an appropriate amount of PhIO in a small glass tube until the green colored manganese(III) corrole turned to the corresponding (oxo) manganese(V) corrole. The solution was passed through a short column of basic alumina to filter the excess of PhIO. The filtered solution was used for characterization and kinetic studies.

**5,10,15-Tris(pentafluorophenyl)corrolato manganese(V)-oxo, 1-Mn(oxo).** UV-vis (toluene):  $\lambda_{max}$ , nm (ε, × 10<sup>2</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 352 (4.46), 409 (4.76), 524 (1.18). MS (ESI): *m/z* found [M]<sup>+</sup> 864.03, [M – O]<sup>+</sup> 848.84; calcd. for C<sub>37</sub>H<sub>8</sub>F<sub>15</sub>MnN<sub>4</sub>O<sup>+</sup> 863.98.

**5,15-Bis(pentafluorophenyl)-10-(4-bromophenyl) corrolato manganese(V)-oxo, 2-Mn(oxo).** UV-vis (toluene):  $\lambda_{max}$ , nm (ε, × 10<sup>2</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 353 (4.70), 408 (4.87), 528 (1.27). MS (ESI): *m/z* found [M + H]<sup>+</sup> 852.93, [M - O]<sup>+</sup> 836.98; calcd. for C<sub>37</sub>H<sub>12</sub>BrF<sub>10</sub>MnN<sub>4</sub>O<sup>+</sup> 852.95.

**5,10,15-Triphenylcorrolato** manganese(V)-oxo, **3-Mn(oxo).** UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>2</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 354 (4.26), 409 (4.35), 515 (1.21). MS (ESI): m/zfound [M + H]<sup>+</sup> 595.48, [M – O]<sup>+</sup> 580.72; calcd. for C<sub>37</sub>H<sub>23</sub>MnN<sub>4</sub>O<sup>+</sup> 595.13.

**5,10,15-Tris(4-cyanophenyl)corrolatomanganese(V)oxo, 4-Mn(oxo).** UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>2</sup> M<sup>-1</sup>. cm<sup>-1</sup>) 357 (4.26), 412 (4.63), 520 (1.36). MS (HRMS): *m/z* found [M]<sup>+</sup> 669.1100; calcd. for C<sub>40</sub>H<sub>20</sub>MnN<sub>7</sub>O<sup>+</sup> 669.1110.

**5,10,15-Tris(2,6-dibromophenyl)corrolato manganese(V)-oxo, 5-Mn(oxo).** UV-vis (toluene):  $\lambda_{max}$ , nm (ε, × 10<sup>2</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 355 (3.04), 412 (3.24), 527 (0.96). MS (HRMS): *m/z* found [M]<sup>+</sup> 1067.5811; calcd. for C<sub>37</sub>H<sub>17</sub>Br<sub>6</sub>MnN<sub>4</sub>O<sup>+</sup> 1067.5822.

**5,10,15-Tris(2,6-dibromo-4-fluorophenyl)corrolato manganese(V)-oxo, 6-Mn(oxo).** UV-vis (toluene):  $\lambda_{max}$ , nm (ε, × 10<sup>2</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 354 (4.40), 413 (4.01), 525 (1.25). MS (HRMS): *m/z* found [M]<sup>+</sup> 1121.5521; calcd. for C<sub>37</sub>H<sub>14</sub>Br<sub>6</sub>F<sub>3</sub>MnN<sub>4</sub>O<sup>+</sup> 1121.5539.

**5,15-Bis(2,6-dibromo-4-fluorophenyl)-10-(penta-fluorophenyl)corrolato manganese(V)-oxo, 7-Mn(oxo).** UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>2</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 354 (3.80), 411 (4.26), 522 (2.34). MS (HRMS): *m/z* found [M]<sup>+</sup> 1035.6957; calcd. for C<sub>37</sub>H<sub>12</sub>Br<sub>4</sub>F<sub>7</sub>MnN<sub>4</sub>O<sup>+</sup> 1035.6972.

**2,3,7,8,12,13,17,18-Octabromo-5,10,15-tris(penta-fluorophenyl)corrolato manganese(V)-oxo, 1a-Mn(oxo).** UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>2</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 392 (5.37), 423 (5.51), 540 (2.34). MS (HRMS): *m/z* found [M]<sup>+</sup> 1495.2589; calcd. for C<sub>37</sub>Br<sub>8</sub>F<sub>15</sub>MnN<sub>4</sub>O<sup>+</sup> 1495.2598.

**2,3,7,8,12,13,17,18-Octabromo-5,15-bis(pentafluorophenyl)-10-(4-bromophenyl)corrolato manganese-(V)-oxo, 2a-Mn(oxo).** UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>2</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 388 (4.76), 423 (4.66), 544 (1.99). MS (HRMS): *m*/*z* found [M]<sup>+</sup> 1485.2121; calcd. for C<sub>37</sub>H<sub>4</sub>Br<sub>9</sub>F<sub>10</sub>MnN<sub>4</sub>O<sup>+</sup> 1485.2154.

2,3,7,8,12,13,17,18-Octabromo-5,10,15-triphenylcorrolato manganese(V)-oxo, 3a-Mn(oxo). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>2</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 384 (3.63), 541 (1.26). MS (HRMS): m/z found [M]<sup>+</sup> 1225.4009; calcd. for  $C_{37}H_{15}Br_8MnN_4O^+$  1225.4012.

**2,3,7,8,12,13,17,18-Octabromo-5,10,15-tris**(4cyanophenyl)corrolato manganese(V)-oxo, 4a-Mn (oxo). UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>2</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 384 (4.16), 545 (0.70). MS (HRMS): *m/z* calcd. found [M + H]<sup>+</sup> 1301.3964; calcd. for C<sub>40</sub>H<sub>13</sub>Br<sub>8</sub>MnN<sub>7</sub>O<sup>+</sup> 1301.3947.

**2,3,7,8,12,13,17,18-Octabromo-5,10,15-tris**(**2,6-dibromophenyl)corrolato manganese**(**V**)**-oxo, 5a-Mn-(oxo).** UV-vis (toluene):  $\lambda_{max}$ , nm ( $\epsilon$ , × 10<sup>2</sup> M<sup>-1</sup>.cm<sup>-1</sup>) 379 (4.69), 421 (5.10), 542 (1.95). MS (HRMS): *m/z* found [M]<sup>+</sup> 1698.8603; calcd. for C<sub>37</sub>H<sub>9</sub>Br<sub>14</sub>MnN<sub>4</sub>O<sup>+</sup> 1698.8581.

 $\begin{array}{l} \textbf{2,3,7,8,12,13,17,18-Octabromo-5,10,15-tris(2,6-dibromo-4-fluorophenyl)corrolato manganese(V)-oxo, \\ \textbf{6a-Mn(oxo).} UV-vis (toluene): $\lambda_{max}$, nm ($\epsilon$, $\times$ 10^2 M^{-1}$, cm^{-1}$) 392 (4.62), 424 (4.77), 547 (1.51). MS (HRMS): $m/z$ found [M]^+ 1752.8332; calcd. for $C_{37}H_6Br_{14}F_3MnN_4O^+$ 1752.8298. \end{array}$ 

 $\begin{array}{l} \textbf{2,3,7,8,12,13,17,18-Octabromo-5,15-bis(2,6-dibromo-4-fluorophenyl)-10(pentafluorophenyl)corrolato \\ \textbf{manganese(V)-oxo, 7a-Mn(oxo). UV-vis (toluene): $$\lambda_{max}$, nm ($\epsilon$, $$\times 10^2 M^{-1}.cm^{-1}$) 392 (4.62), 424 (4.64), 540 (1.58). \\ \textbf{MS (HRMS): $$m/z$ found [M]^+ 1666.9721; calcd. for $$C_{37}H_4Br_{12}F_7MnN_4O^+$ 1666.9732. \\ \end{array}$ 

# CONCLUSION

In conclusion, we report the synthesis of several novel  $\beta$ -brominated and  $\beta$ -nonbrominated manganese(III) corroles differing in their electronic and steric properties based on meso-substitution. The transformation of manganese(III) corroles into their corresponding (oxo)manganese(V) corroles on treating with PhIO, and subsequent kinetics studies for their oxygen atom transfer to styrene in toluene revealed significant dependence of pseudo-first-order rate constants on the electronic and steric properties of manganese corroles. The following order of reactivity was observed for  $\beta$ -nonbrominated  $(\infty)$ manganese(V) corroles: 1-Mn $(\infty) > 2$ -Mn $(\infty)$ > 7-Mn(oxo) > 4-Mn(oxo) > 3-Mn(oxo) > 6-Mn(oxo)  $\approx$ **5-**Mn(oxo). The rate constants for  $\beta$ -pyrrole-brominated analogs followed the same pattern but significantly larger in all cases, indicating the effect of  $\beta$ -bromination. This reactivity order is in accordance with the followings: Firstly, electron-poor (oxo)manganese(V) corroles are more reactive for oxygen atom transfer to styrene, and their reactivity is directly correlated with the number of mesopentaflurophenyl groups attached to corrole. Secondly, electron-rich and sterically unhindered (oxo)manganese(V) corroles are less reactive t han highly electron-poor (oxo)manganese(V) corroles but still more reactive than sterically hindered (oxo)manganese(V) corroles. Thirdly, highly sterically protected (oxo)manganese(V) corroles containing 2,6-dibromophenyl substituents are the least reactive (oxo)manganese(V) corroles, and conversely have the most stable Mn<sup>V</sup>≡O moiety.

### Acknowledgements

The financial support from the National Natural Science Foundation of China (21171057, 21371059) is gratefully acknowledged.

#### **Supporting information**

Figures S1–S4 and Table S1 are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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