

First Synthesis of Perfluorinated Corrole and Its Mn=O Complex

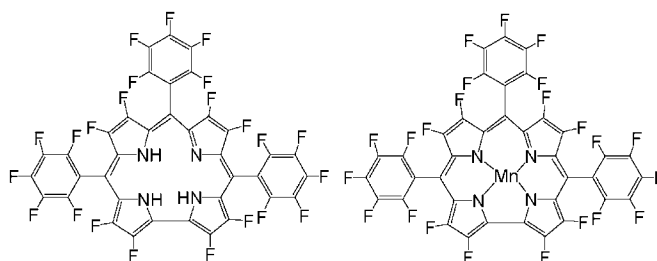
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ABSTRACT



A novel perfluorinated corrole, 2,3,7,8,12,13,17,18-octafluoro-5,10,15-tris(pentafluorophenyl)corrole, and its manganese(III) and oxomanganese(V) derivatives have been synthesized. The perfluorinated manganese corrolate exhibited excellent reactivity and stability in the catalytic oxidation of alkenes with iodosylbenzene.

Corrole is a tetrapyrrolic macrocycle containing a direct linkage between two adjacent pyrrole rings.¹ Being a trianionic ligand, corrole has the capacity to stabilize high oxidation states of transition metal centers such as Cr^V, Mn^{IV}, Fe^{IV}, Co^{IV}, Cu^{III}.² Corrole derivatives have been shown to be promising candidates as chemical sensors,³ catalysts,⁴ cancer therapeutic agents,⁵ and building blocks of supramolecular assemblies.⁶ Thus, the study of corrole compounds

has quickly become one of the most active branches in contemporary porphyrin research.⁷

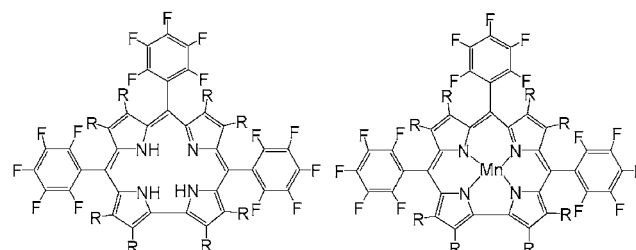
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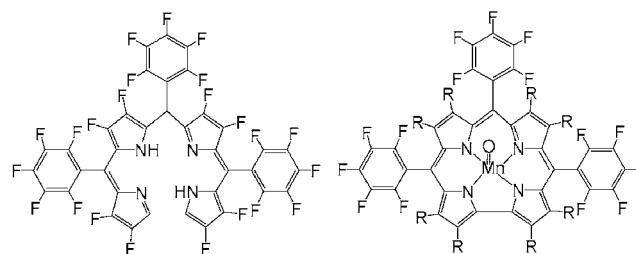
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1a: R=F; 1b: R=H

2a: R=F; 2b: R=H



3

4a: R=F; 4b: R=H

Like the better-known porphyrin macrocycles, coordination and redox properties of corrole should be tunable through adding halogen substituents on the ring by virtue of the electronegativity.^{8–10} β -Halogenation of porphyrin is also known to perturb the relative and absolute d-orbital energy of ligated transition metal via an admixture of σ , π and steric effects.¹¹ While the enhanced reactivity of various halogenated *meso*-tetraarylmetalloporphyrin-oxo (M=O) species in mediating hydrocarbon oxidations has been recognized quite some time ago,^{12,13} the authentic perfluorinated tetraphenylporphyrin was not made until 1997.^{14,15} The electronic effect of the β -fluorination on the reactivity of the oxometalloporphyrin is indeed quite large.¹⁶ Perfluorophthalocyanine complexes have also appeared in the literature.¹⁷ In contrast, study on the β -halogenated corroles is scarce with only β -brominated metalocorrolates being obtained very recently.^{18,19} We herein report the first synthesis and characterization of a perfluorinated corrole: 2,3,7,8,12,13,17,18-octafluoro-5,10,15-tris(pentafluorophenyl)corrole **1a** and its manganese complex **2a**. The oxomanganese(V) derivative has also been isolated, whose smooth reaction with alkenes has allowed a direct measurement of reaction rates.

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Recent advances in the corrole synthesis using a solvent-free condensation of pyrrole and aldehydes have made a previously inaccessible 5,10,15-tris(pentafluorophenyl)corrole **1b** readily available.²⁰ Following the same procedure using 3,4-difluoropyrrole²¹ and pentafluorobenzaldehyde, we initially isolated only small amounts of a purple-colored compound **3** from the reaction mixture, having a molecular ion (m/z 943.0) three mass units above that of the target compound **1a** (m/z 940.0).²² Other evidence led us to suspect that **3** may be a linear bilene that fails to cyclize due to the electron-withdrawing nature of the difluoropyrrole units. Interestingly, irradiation (floodlight) of **3** in CH_2Cl_2 under an ammonia atmosphere (the original procedure of Johnson's synthesis of corrole²³), an intense absorption band at 400 nm developed (Figure 1). Indeed, this product, purified and

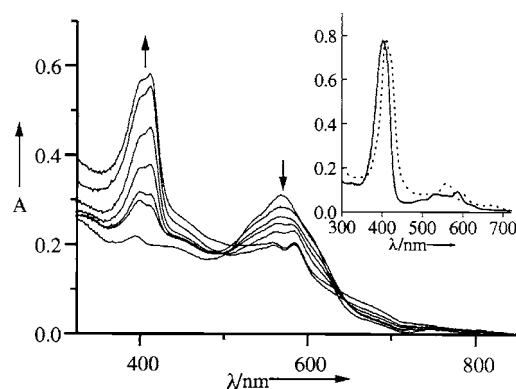


Figure 1. Spectral changes of **3** upon irradiation of light under NH_3 atmosphere in CH_2Cl_2 . Inset: UV/vis spectra of **1a** (—) and **1b** (---) in CH_2Cl_2 .

isolated, was proved to be **1a**. The fact that **3** can be isolated and cyclized to the desired macrocycle is a proof that the formation of corrole in alumina supported solvent-free synthesis still proceeds via a linear tetrapyrrolic intermediate similar to the classical Rothemund synthesis of porphyrin and corrole.¹⁹ The Gross' solvent-free synthesis, in fact, can yield F_{23} -corrole **1a** directly if the reaction condition is altered. For example, using longer heating time, a low but acceptable yield of 5% can be obtained, considering the electron-deficient nature of 3,4-difluoropyrrole.

The ^{19}F NMR peaks of **1a** can be assigned as shown in Figure 2, in a pattern very similar to the F_{15} **1b** with the β -pyrrole fluorine positions at -154.95 , -155.54 , and -161.06 ppm. For the phenyl fluorine peaks near -140 , -153 , and -163 ppm there are small shifts of about 2.6, 0.6, and 1.5 ppm, respectively, going from **1b** to **1a**,

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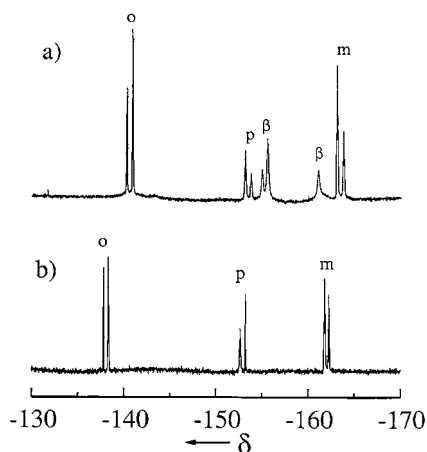
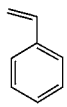
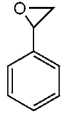
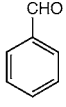


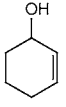
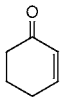


Figure 2. ^{19}F NMR spectra of **1a** (a) and **1b** (b) in CDCl_3 at 22 °C. The broad appearance of the β -signals may be due to NH exchange (see ref 15).

consistent with the assignment of the corresponding signals as *o*-, *p*-, and *m*-fluorine. The perfluorinated corrole **1a** is extremely soluble in both polar and nonpolar organic solvents and does not lend itself to forming crystals suitable for X-ray analysis.

It has been demonstrated that the Mn^{III} F_{15} -corrole **2b** is a good oxidation catalyst,^{2b} and β -pyrrole bromination of **2b** leads to an improvement in its catalytic activity.¹⁸ In our hands, Mn^{III} corrole **2a** and **2b** were synthesized by refluxing a methanol solution of the corresponding free-base corroles with an excess of manganese(II) acetate tetrahydrate. The new Mn^{III} F_{23} -corrole **2a** has been characterized by UV-vis, FAB-MS (m/z 991.9), and ^{19}F NMR. Solubility of **2a** is very high in hexane as well as in methanol. To determine the effect of β -fluoro substituents, we carried out cyclic voltammetric studies on **2a** and **2b** and observed, under identical conditions, a prominent reversible wave assignable to the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ couple at 0.91 and 0.42 V,²⁴ respectively (vs Ag/AgNO_3 reference electrode, in CH_2Cl_2 with 0.1 M TBAPF₆). The remarkable shift of 490 mV going from F_{15} - to F_{23} -system testified the tremendous electron-withdrawing effect brought about by the eight β -fluorine atoms (with each contributing about 61.3 mV positive shift on average). Such a large electronic effect on the metal center suggests that a very electrophilic $\text{Mn}=\text{O}$ moiety could be generated in this unique ligand environment, and as such, the rate of catalytic oxidations should be substantially enhanced. We tested this possibility by using iodossylbenzene (PhIO) as the source of oxygen atom: typically a benzene solution of the Mn^{III} corrole was treated with 100-fold PhIO in the presence of excess alkenes, and the oxidation products were determined by GC. In these cases, we have indeed observed a much higher turnover rate for **2a** when compared with **2b** under

Table 1. Catalytic Oxidation of Styrene and Cyclohexene Using Iodosylbenzene as Oxygen Source

Substrates (catalysts)	Products ^a (yields, %)	TOF ^b (h^{-1})		
				
2a	56	42	588	
2b	2.3	1.3	22	
				
2a	42	27	25	564
2b	1.7	0.3	0.9	17

^a Alkene/PhIO/catalyst = 1000:100:1 in 1 mL of benzene (catalyst, 1.2 μmol) under aerobic conditions at room temperature. Yields were determined by GC after 10 min and based on the PhIO used. ^b Turnover frequency (TOF) was calculated according to the reaction rate of the first 10 min.

identical conditions. The results of some catalytic reactions are summarized in Table 1. **2a** was not bleached at the end of reaction, while significant bleaching of **2b** was observed. Thus, the stability of **2a** against degradation is much enhanced due to perfluorination.²⁵

High-valent oxometal intermediates are commonly regarded as the reactive species in metalloporphyrin-catalyzed oxidations of alkene. We found that $\text{Mn}=\text{O}$ **4a** can be prepared from the reaction of Mn^{III} corrole with PhIO, and it is stable enough to be purified by flash chromatography on silica gel—a convenient method also effective in the preparation of **4b**.²⁶ Both UV-vis and ^{19}F NMR of the oxomanganese(V) **4b** have been reported by Gross.^{2b} In comparison, the UV-vis spectrum of **4a** is similar to that of **4b**, except the former exhibits a broadened peak at 351 nm with a shoulder at about 382 nm while the latter has two peaks at 348 and 410 nm. In ^{19}F NMR, the diamagnetic oxomanganese(V) gave reasonably sharp peaks: four singlets in the ratio of 2:2:2:2 at -145.7 , -147.7 , -148.7 , -152.0

(25) To directly compare the robustness of the two catalysts, we did a comparison in neat cyclohexene: catalyst (1.2 μmol) in cyclohexene (2 mL) at room temperature was added aliquot portions of solid PhIO (0.12 mmol) successively soon after the last portion being consumed in the solution. **2b** was completely bleached after 5 portions of PhIO (giving 450 turnover), while **2a** could still be recovered by more than 50% even after 10 portions of PhIO (near 1000 turnover).

(26) Reaction of PhIO (~20 mg) with **2a**, or **2b** (~10 mg) in CH_2Cl_2 (2 mL) was complete in about 2 min as monitored by UV-vis and color change (**2a**, from red-brown to orange; **2b**, from green to red). The solution was pushed through a short silica gel column to furnish **4a**, or **4b**. **4a**: FAB-MS m/z 1008.9 (6) $[\text{M} + \text{H}]^+$, 991.9 (100) $[\text{M} - \text{O}]^+$; UV-vis (CH_2Cl_2) λ_{max} [nm] = 351, 503; ^{19}F NMR (282.309 MHz, CDCl_3 , -55 °C) δ -138.6 (d, $J = 24.6$ Hz, 2F), -138.8 (d, $J = 24.3$ Hz, 1F), -139.0 (2d, 3F), -145.7 (s, 2F), -147.7 (s, 2F), -148.7 (s, 2F), -149.2 (t, $J = 20.9$ Hz, 2F), -149.7 (t, $J = 20.9$, 1F), -152.0 (s, 2F), -160.5 (m, 6F). **4b**: FAB-MS m/z 864.9 (12) $[\text{M} + \text{H}]^+$, 847.9 (100) $[\text{M} - \text{O}]^+$; UV-vis (CH_2Cl_2) λ_{max} [nm] 348, 410, 520; ^{19}F NMR (282.309 MHz, CDCl_3 , -55 °C) δ -136.5 (d, $J = 22.6$, 2F), -137.0 (d, $J = 26.0$, 1F), -137.2 (d, $J = 20.9$, 2F), -137.6 (d, $J = 24.3$, 1F), -151.1 (2t, 3F), -160.3 (m, 6F).

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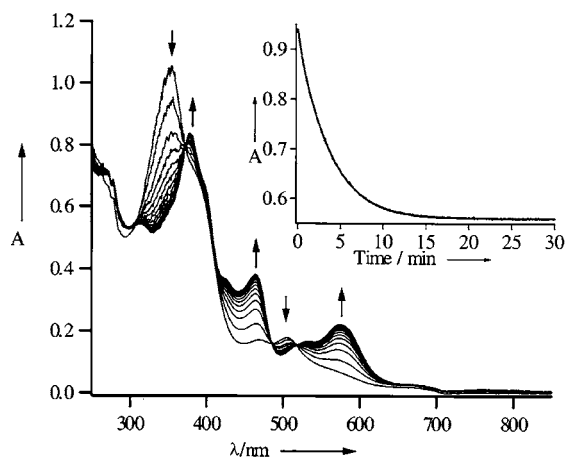


Figure 3. UV-vis spectral changes observed upon mixing **4a** ($\sim 10^{-5}$ M) with cyclooctene (3.9×10^{-2} M) in CH_2Cl_2 at 25°C . Scan interval, 1 min. Inset: The absorbance decay of **4a** monitored at $\lambda = 351$ nm.

ppm were observed for the β -fluoro groups of **4a**. At room temperature, the metal-oxo species **4a** and **4b** decompose gradually, eventually returning to the corresponding Mn^{III} corrole as indicated by UV-Vis.

Half-life of **4a** and **4b** in CH_2Cl_2 at 25°C are ca. 1 and 4 h, respectively. The addition of alkenes could greatly speed up the reduction of both intermediates²⁷ and yield the oxidation products as detected by GC-MS, thus giving unequivocal evidence of **4a** being the reactive oxidant in the system. Figure 3 shows the UV-vis changes of **4a** upon mixing with cyclooctene in CH_2Cl_2 . With excess cyclooctene, the reactions followed pseudo-first-order kinetics (monitored at 351 and 348 nm for **4a** and **4b**, respectively). The rate constant k_{obs} of reactions of oxomanganese(V) corroles with

(27) Despite the earlier conclusion that **4b** is not active (ref 2b), in our study both intermediates reacted with substrates and yielded products, with **4a** being much more active and thus easier to quantify within a given time frame.

Table 2. Pseudo-First-Order Reaction Rate Constants (k_{obs})^a of Oxomanganese(V) Corrole **4a** and **4b** with Cyclooctene in CH_2Cl_2

$T(\pm 0.1^\circ\text{C})$	20.0	25.0	30.0	35.0
4a ; $k_{\text{obs}} \times 10^3$ (s^{-1})	3.78	4.62	7.27	10.8
4b ; $k_{\text{obs}} \times 10^4$ (s^{-1})	1.19	1.66	2.80	5.28

^a [cyclooctene] = 3.9×10^{-2} M; [oxomanganese(V) corrole] = $\sim 1.5 \times 10^{-5}$ M. Pseudo-first-order rate constants (k_{obs}) were determined on the basis of exponential decay fits of absorbance at $\lambda = 351.0$ and 348.0 nm for **4a** and **4b**, respectively. The rates are the average of three runs (± 0.05).

cyclooctene are listed in Table 2. These kinetic data indicate a 28-fold rate increase in the catalytic oxidation of cyclooctene (at 25°C) as a result of the β -fluorination of the corrole ring and is comparable to the rate acceleration estimated for the catalytic oxidation of styrene and cyclohexene in terms of turnover frequency (Table 1).

In conclusion, we have successfully synthesized a perfluorinated triphenylcorrole (**1a**) and demonstrated the high reactivity of its oxomanganese(V) species (**4a**). The eight β -fluorines brought about +490mV shift in the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ redox couple from the nonfluorinated **2b**, as well as a 28-fold increase in the reactivity of the corresponding oxomanganese(V) intermediate at 25°C . The perfluorinated manganese(III) corrole **2a** is extremely robust in terms of ligand stability in catalytic oxidations. The rate acceleration, along with the robustness of the macrocycle has rendered it a superior catalyst in the family of high-valent metal-oxo oxidants.

Acknowledgment. This work was supported by Research Grant Council of Hong Kong under project HKUST6182/99P and Area of Excellence Scheme (AoE/P-10/01).

Supporting Information Available: Experimental and spectroscopic data of **1a**, **2a**, and **4a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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