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Systematic Selection of Metalloporphyrin-Based Catalysts for Oxygen Reduction by Modulation of the Donor–Acceptor Intermolecular Hardness

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Abstract: Incisive modulation of the intermolecular hardness between metalloporphyrins and O_2 can lead to the identification of promising catalysts for oxygen reduction. The dependency of the electrocatalytic reduction of O_2 by metalloporphyrins on the nature of the central metal yields a volcano-type curve, which is rationalized to be in accordance with the Sabatier principle by using an approximation of the electro-

Introduction

The search for clean and sustainable energy systems, from their exploitation at the source, through their use and eventual disposal is one of the grand challenges of the 21st century.^[1] Direct electrochemical conversion of chemical energy into useful electric and thermal energy by using fuel cells offers one of the most appealing possibilities for providing clean energy.^[2] The cost of platinum, the premium catalyst at both the anode and cathode of fuel cells, is inhibitive, its natural supply limited, and geographical distribution so inequitable. This combination of inopportune factors jeopardizes the large-scale commercialization of fuel cells if they are to be primarily reliant on platinum as the main catalyst. Whereas improvements in the mass and area specific activities of platinum have been very impressive,^[3] the grim reality of its scarcity cannot be dispelled.^[4] Therefore, too much dependence on such a resource that is so scarce and geo-inequitably distributed is bound to negate any potential benefits that could accrue from ingenious technological progress. To this end, alternative catalysts that can be obtained inexpensively from abundant sources, and whose supply is capable to sustain the demand driven by large-scale commercialization of fuel cells have to be sought to replace platinum.

N₄-Macrocyclic complexes, including metalloporphyrins, metallophthalocyanines, metallocorroles and metallotetra-

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philicity of the complexes. By using electrochemical and UV/Vis data, the influence of a selection of *meso*-substituents on the change in the energy for the $\pi \rightarrow \pi^*$ excitation of manganese

Keywords: electrophilicity • intermolecular hardness • manganese porphyrins • metalloporphyrins • oxygen reduction porphyrins was evaluated allowing one to quantitatively correlate the influence of the various ligands on the electrocatalysis of O_2 reduction by the complexes. A manganese porphyrin was identified that electrocatalyzes the reduction of oxygen at low overpotentials without generating hydrogen peroxide. The activity of the complex became remarkably enhanced upon its pyrolysis at 650 °C.

azaanulenes, among others, have been intensively investigated as potential alternatives to platinum-based catalysts for technological applications involving the oxygen reduction reaction (ORR).^[5] Although it is well recognized that the electrocatalysis of oxygen reduction by these complexes depends on the type of the central metal ion and the nature of substituents on the macrocyclic ring,^[6] no rigorous guiding criteria exist for selection of better catalysts. Given the vast assortment of substituents, and metal combinations that are possible,^[7] it is desirable to develop insightful and systematic selection criteria for the guided development of improved N₄-metallomacrocyclic catalysts for ORR. In this work, an in-depth analysis of the effect of the central metal ion of metalloporphyrins on their electrocatalysis of oxygen reduction was undertaken, covering metalloporphyrins of the first row transition metals except scandium. By synchronizing some critical empirical observations of our studies with existing thermodynamic data, we observed that the dependency of the electrocatalysis of oxygen reduction by metalloporphyrins on the nature of the central metal ion yields a volcano-like curve, which was rationalized using the electrophilicity of the complexes to be in accordance with the Sabatier principle.^[8] The Sabatier principle requires that for optimal catalysis, substrates and their intermediates or products should neither bind too weakly nor too strongly on a catalyst surface.^[8,9] The strength by which oxygen is bound on metalloporphyrins,^[10] the overriding factor for ORR activity, can be modulated by attachment of suitable groups on the macrocyclic ring. Generally, highly electronegative groups strengthen this binding whereas electron-donating groups weaken it. To demonstrate the realism of modulating the intermolecular hardness between oxygen and metalloporphyrins as a means for insightful prediction of improved catalysts for ORR, quantitative structure-activity relationships (QSAR) for a selection of manganese porphyrins with different meso-substituents were investigated by using UV/Vis data, Hammett constants, and electrochemical data. By correlating the relative energy for the $\pi \rightarrow \pi^*$ excitation of the respective metalloporphyrins with electrochemical data, it was possible to get a quantitative picture of the influence of ligand properties on the ORR activity of manganese porphyrins. Previous studies on the electrocatalysis of oxygen reduction by N₄-macrocyclic complexes have mostly offered only a qualitative explanation of the influence of the properties of the ligand on ORR activity. Some studies have correlated the ORR activity of metallophthalocyanines with the formal potential of the transition from the M^{III} to the M^{II} oxidation state of the central metal ion (M). This is the first time that the influence of *meso*-substituents on the energy changes in the frontier orbitals of metalloporphyrins and their ultimate effect on the ORR activity of the respective complexes has been expressed quantitatively. This knowledge was exploited to identify a manganese porphyrin, meso-tetrakis(4-pyridyl)porphyrinato manganese (MnTPyP) with very promising activity for oxygen reduction. The activity of the catalyst was remarkably enhanced upon its pyrolysis at 650 °C in the presence of helium. This study therefore describes a systematic criterion that can be used for rational selection of metalloporphyrin-based catalysts with improved oxygen reduction activity.

Results and Discussion

Metallation of porphyrins was carried out by treatment of the free bases (3 mM) in DMF with the corresponding stoichiometric quantity of the desired metal dichloride $(MCl_2)^{[11]}$ at 100 °C for 6 h in a tightly closed reaction tube with continuous magnetic stirring. A simplified outline of the synthesis is shown in Figure 1.



Figure 1. Reaction outline for the metalation of porphyrins. R^1 , R^2 , R^3 and R^4 represent various *meso*-substituents on the macrocyclic ring.

The resulting metalloporphyrins were purified by column chromatography using neutral aluminum oxide as the stationary phase and dichloromethane as the eluent.^[12] The purified products were characterized by using UV/Vis spectrophotometry and electrochemistry.

As an example, the soret peak was redshifted by approximately 230 Å (Figure 2a) when tetra(4-aminophenyl)porphyrin (TAPhP; in which $R^1 = R^2 = R^3 = R^4 = 4$ -aminophenyl) was successfully metalated with Cr. Similar shifts were observed for the Q-bands.^[13] The Q-bands (Figure 2a, inset) have been enlarged for clarity. Characteristic redox waves of

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Figure 2. a) UV/Vis spectrum of metal-free tetraaminophenyl porphyrin (TAPhP; \bullet) and after its metalation with Cr (\checkmark). b) Cyclic voltammogram of a graphite electrode modified with Mn-TCPhP recorded at a scan rate of 100 mV s⁻¹ in KOH (0.1 M).

Mn^{III}/Mn^{II}, Fe^{III}/Fe^{II}, Co^{III}/Co^{II}, and Cr^{III/(II)} for electrodes modified with Mn, Fe, Co, and Cr complexes were discernible by cyclic voltammetry.

Figure 2b shows a cyclic voltammogram of a graphite electrode modified with a film of manganese tetracarboxyphenyl porphyrin (MnTCPhP) recorded in KOH (0.1 M) at a scan rate of 100 mV s⁻¹. The redox peak at about -0.125 V corresponds to the reversible reduction and oxidation of the porphyrin ring, whereas the one at about 0.243 V, which shows typical features of a surface adsorbed species, is due to the Mn³⁺/Mn²⁺ redox couple. The several oxidation and reduction processes that can be seen in Figure 2b are typical of most manganese porphyrins and are due to the existence of manganese in multiple oxidation states.

Electrocatalysis of oxygen reduction (ORR) by metalloporphyrins depends on the nature of the central metal ion and the type of porphyrin ligand. Tetraaminophenyl porphyrin (TAPhP) was metalated with the first row transition metals (Ti–Zn) according to the reaction outline shown in Figure 1. To investigate the influence of the central metal of the complexes on ORR, specific volumes of the resulting complexes (M-TAPhP), typically equivalent to a surface concentration of 1.06×10^{-7} mol cm⁻², were adsorbed on polished graphite electrodes by drop coating. After being left to dry in air, the films were investigated for ORR in KOH (0.1 M) by using linear sweep voltammetry (LSV).

Figure 3a shows the background-corrected oxygen reduction currents of the M-TAPhP complexes recorded at a scan



Figure 3. a) Linear sweep voltammograms recorded in oxygen-saturated KOH (0.1 M) at a scan rate of 5 mVs⁻¹. b) Activity of metalloporphyrins (average \pm SD; n=5) of the first row transition metals (Cr–Zn) as a function of the number of electrons in the metal d orbitals.

rate of 5 mV s^{-1} . Although Ti-TAPhP and V-TAPhP were synthesized under exclusion of oxygen by using a glovebox, their investigation for ORR was omitted because the complexes were converted to stable oxo-complexes upon their exposure to oxygen or water. Oxo-complexes are not useful for oxygen reduction since all the potential sites on the central metal ion that would bind oxygen and facilitate its reduction are occupied.

In Figure 3b, the potentials corresponding to a current density of $-20 \,\mu\text{A}$ extracted from Figure 3a were plotted against the number of d electrons of the central metal. This current density was chosen because the ORR reaction was under kinetic control for all the investigated metalloporphyrins at this current density. Plotting an intrinsic electroactivity parameter of the metalloporphyrins against the number of electrons in their d orbitals is justified because occupancy of electrons in the d orbitals is the main determinant of their electrocatalytic activity.^[14] Actually, electrocatalysis by metalloporphyrins depends on their ability to generate an empty coordination site so that the substrate can bind to the metal center.^[15]

The importance of filled d_{xz} and d_{yz} and empty d_{z^2} in promoting the ORR was pointed out earlier.^[16] If the data point for Zn is omitted on the basis of its unavailability of empty d orbitals, the remaining data points conform to a volcano-shaped curve to a very good approximation. For a given electrocatalyst to achieve a high thermodynamic efficiency, it is desirable that a specific current density is delivered at a low overpotential. Co-TAPhP, which is at the zenith of the volcano, therefore exhibited the highest activi-

ty. This trend had very good reproducibility for five replicate measurements. We point out here that since the electrocatalytic activity of metalloporphyrins also depends on the nature of the ligand, a different metal may assume the zenith of the volcano for a particular porphyrin ligand. It is also important to mention that the trend of the volcano curve may also change with the type of electrolyte. For example, CoP is the most active catalyst in acidic electrolytes compared with FeP, MnP, CrP, NiP, and ZnP, whereas it performs very poorly in alkaline electrolytes compared with FeP. In a related study, iron phthalocyanine was found to be at the zenith of the volcano when Cr, Mn, Fe, Co, Ni, Cu, and Zn phthalocyanines were investigated as electrocatalysts for ORR in alkaline electrolytes.^[17] We therefore conclude that the points assumed by the various metalloporphyrins on the volcano curve are dynamic and dependent on the type of macrocyclic ligand and pH of the electrolyte among other possible factors.

The active site of N₄-macrocyclic complexes for ORR is the central metal ion, and an inner-sphere electron-transfer mechanism is involved.^[18] The first elementary step in the electrocatalytic reduction of O₂ by these complexes is widely considered to be adsorption of molecular oxygen on the metal ion.^[18] This step is believed to precede the redox transition of the metal ion from a higher oxidation state to a lower oxidation state, which is typically from Fe^{III} to Fe^{II}, and from Co^{III} to Co^{II} for iron and Co complexes, respectively. This has also been suggested to apply for the case of Cr and Mn complexes since they undergo multiple redox transitions, including the M^{III}/M^{II} transition. For Ni, Cu, and Zn metalloporphyrins, which essentially do not undergo a M^{III}/^(II)-type redox transition, a different, but unknown, initial step is believed to be involved. The strength of adsorption of oxygen on the central metal ion is thus a vital factor in the electrocatalytic cycle of oxygen reduction by these complexes. The observed electrocatalytic activity differences in Figure 3b could therefore directly or indirectly be related to the strength and/or mode of interaction of oxygen with the complexes. At least four different modes of interaction of oxygen with metallomacrocyclic complexes namely endon, side-on, bridge-cis, and bridge-trans interactions have been proposed, the operational type of interaction being influenced by structural and steric factors.^[17] Wang et al. reported that the mode of interaction of oxygen with a given macrocyclic complex influences its eventual mechanism for ORR and whether the reduction follows a two- or four-electron-transfer pathway.[19]

According to the Sabatier principle, optimal catalysis requires that the strength of interaction of reactants, their intermediates, and products with the catalyst surface be neither too weak nor too strong.^[9] Low valence metalloporphyrin complexes of the early first row transition metals (Sc–V) are readily oxidized in the presence of oxygen or oxygen-containing groups to form thermodynamically stable oxo-porphyrin complexes.^[20] The lability of metalloporphyrin complexes to form oxo-porphyrin complexes decreases in moving across the period.^[20] This weakening of the binding

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strength of oxygen on the central metal ion in moving across the period may also be understood from inter-metal oxygen atom-transfer reactions.^[21] For example, studies by Watanabe et al., Woo et al., and others have reported that whereas Ti complexes support complete oxygen atom-transfer reactions, complexes of Cr only afford incomplete oxygen atom-transfer reactions.^[22] The groups of van Veen and Zagal reported that despite Mn and Cr exhibiting redox behaviors similar to Fe and Co, the relatively lower ORR activity of their macrocyclic complexes were attributed to their low redox potentials, meaning that they are easily oxidized by oxygen.^[23] The strength of adsorption of O₂ and its reduction intermediates on metalloporphyrins is therefore the overriding factor of its electrocatalytic reduction, and the volcano-type dependence observed in Figure 3b is therefore justified and in direct conformity with the Sabatier principle. This can be rationalized semi-empirically on the premise of the electrophilicity of the metalloporphyrins, and their intermolecular hardness in interacting with molecular oxygen.

The electrophilicity (ω) of a molecule is a measure of its electrophilic power and is expressed by Equation (1), as formulated by Parr et al.^[24]

$$\omega = \frac{\chi^2}{2\eta} \tag{1}$$

in which η and χ are the chemical hardness and the electronegativity of the molecule, respectively. Since the interaction between oxygen and metalloporphyrins essentially takes place at the metal center, it is reasonable to approximate the electronegativity of the metalloporphyrins with that of the central metal atom. Actually, linear correlations have been obtained by plotting electrophilicity against electronegativity or electron affinity.^[25] Moreover, the electrophilicity of first row transition metals has been reported as a good quantitative estimate of their redox potentials.^[26] Figure 4 shows the plots for the intrinsic activity of the metalloporphyrins (Figure 2b) juxtaposed with that for the electronegativity of the central metals, both plotted against the number of d electrons of the metals. The Pauling scale of



Co

Figure 4. Graphs of the ORR activity of meso-tetraaminophenyl metalloporphyrins (O) and electronegativity of the respective first row transition metals (**•**) against the number of d electrons of the transition metals.

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electronegativity was used and the values were rounded to two decimal places. In moving from Cr to Co, the electronegativity difference between the metals and oxygen ($\chi_0 =$ 3.44) generally decreases with only Mn showing an anomaly, which would imply a weakening affinity for electron transfer between the complex and oxygen.

The electronegativity difference is at a minimum for Ni and Cu. Non-coincidentally, the activity of the complexes for ORR was the lowest for the least electronegativity difference between oxygen and the central metal. This shows that the strength of interaction of the central metal ions (Ni and Cu) with oxygen has weakened beyond the optimal interaction required for the reduction of oxygen. Since the electronegativity difference between a Lewis acid (in this case the metalloporphyrin) and a Lewis base (in this case oxygen; due to back-donation), measures the propensity for electron transfer, and thus the degree of interaction between them, the trends observed in Figure 3b confirm that the strength of interaction between oxygen and the catalyst indeed directly influences the activity of the catalyst.

The properties of metalloporphyrins can dramatically change by their modification with particular groups. Because of the numerous possibilities available for their modification, identifying a suitable porphyrin for a given application can be a difficult challenge. There are two options for modulating the strength of interaction, hereafter referred to as "intermolecular hardness" between oxygen and metalloporphyrins. The first one involves changing the central metal, and the second one, which is more versatile, involves variation of the structure of the porphyrin ligands by means of suitable groups. Since the options for variation of the structure of the porphyrin ligand are inexhaustible, we focused our attention on substituents at the meso-position of the porphyrin system.

Intermolecular hardness is a measure of the strength of interaction between two chemical species, and is expressed by Equation (2).

$$\eta_{\rm AD} = \frac{1}{2} (I_{\rm D} - E_{\rm A}) \tag{2}$$

The term η_{AD} is the intermolecular hardness between the electron donor (D) and the electron acceptor (A), whereas $I_{\rm D}$ and $E_{\rm A}$ are the vertical ionization potential and electron affinity of the electron donor and electron acceptor, respectively. In accordance with Koopman's theorem, when A and D interact to form an adduct, η_{AD} is equivalent to half the energy difference between the energy of the highest occupied molecular orbital of D ($\varepsilon_{HOMOdonor}$) and the energy of the lowest unoccupied molecular orbital of A ($\varepsilon_{LUMOacceptor}$) as expressed in Equation (3).^[27]

$$\eta_{\rm AD} = -\frac{1}{2} (\varepsilon_{\rm LUMO(acceptor)} - \varepsilon_{\rm HOMO(donor)}) \tag{3}$$

The nature of groups attached to the porphyrin ring may either deplete or increase the electron density around the

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0.7

0.70

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1.9



Figure 5. a) Absorption spectra of MnP (1), MnTPhP (2) and MnTrMPhPyP (3). b) Absorption spectra of Mn-4-HPhTrTP (1), MnTCPhP (2) and MnTPhP (3). c) Representative cyclic voltammograms of graphite electrodes modified with different Mn porphyrins recorded at a scan rate of 100 mV s^{-1} in deaerated KOH (0.1 M).

metal ion. Assuming that other factors do not change, it is possible to change $\varepsilon_{\text{HOMO}}$, the energy of the frontier orbitals in the porphyrin complex, by means of suitable substituents.

Energy changes in the frontier orbitals of metalloporphyrins can be directly measured by using UV/Vis spectrophotometry, particularly by monitoring the shift in the energy required for the $\pi \rightarrow \pi^*$ excitation, which gives rise to the characteristic soret band of porphyrins.^[27(d)] To illustrate this fact, the influence of some *meso*-substituents on the excitation energy of the $\pi \rightarrow \pi^*$ transition of different metalloporphyrins is shown in Figure 5 together with their influence on the redox properties of the complexes (Figure 5c). Detailed

UV/Vis data of all the complexes is presented in Table 1. The UV/Vis spectra of Mn porphyrins characteristically display two soret peaks in the wavelength region between 350 and 500 nm in addition to the four Q-bands that appear between 500 and 700 nm. The soret peaks may significantly differ in intensity depending on the nature of the ligand, counter ion, and axial ligand. The notation soret band 1 and soret band 2 will be used to refer to the soret peaks at the lower and higher wavelengths, respectively. Mn^{II} and Mn^{III} porphyrins display different UV/Vis spectra. It is therefore highly probable that the soret peaks and their relative intensities relate to the existence of both $Mn^{\rm II}$ and $Mn^{\rm III}$ in the complexes. As discussed earlier, many Mn porphyrins are oxophilic and will have oxygen groups either chemisorbed or physisorbed. It is therefore also possible that the relative intensities of the soret bands depends on the degree and strength of adsorption of oxygen or oxygen groups on Mn^{II} or Mn^{III} porphyrins.

From here on, shifts in the soret peaks will be discussed relative to the soret peaks for the $\pi \rightarrow \pi^*$ excitation in Mn tetraphenyl porphyrin (MnTPhP), which was arbitrarily chosen as a reference to enable the quantification of the energy shifts.

It can be seen in Figure 5a that a remarkable decrease in the energy required for the $\pi \rightarrow \pi^*$ excitation is observed when H (MnP) is replaced by phenyl (MnTPhP). Similarly, the soret peaks were significantly redshifted when the porphine ligand was modified with electron-donating groups such as methoxyphenyl (Figure 5a) and aminophenyl groups among others, or groups with a positive inductive effect as in the case of the tolyl group. The energy shifts were less striking when the phenyl group was replaced by its derivatives (Figure 5b). It is also evident (Figure 5c) that the meso-substituents exert a pronounced effect on the electrochemical properties of the complexes as manifested by the shifts in the redox peaks. Electron-donating groups are generally expected to induce cathodic shifts on the reduction potentials whereas electron-withdrawing substituents exert the opposite effect. Electron-donating groups increase the electron density on the central metal ion making the metal ion easy to oxidize, whereas electron-withdrawing groups deplete this electron density making it easier for the metal ion to accept electrons.

To obtain useful quantitative information concerning the influence of the *meso*-substituents on the energy required for the $\pi \rightarrow \pi^*$ excitation, MnTPhP was chosen as a reference system and the energies of all the other complexes were calculated relative to this arbitrary reference by using Equation (4), in which λ_o is the wavelength at maximum absorption of the reference system, λ is the wavelength at maximum absorption of a given metalloporphyrin, *h* is the Planck's constant (6.63×10^{-34} Js), and c_m is the speed of light through the solution under investigation.

$$\Delta E = hc_{\rm m} \left\{ \frac{1}{\lambda_0} - \frac{1}{\lambda} \right\} \tag{4}$$

Table 1. Effect of the nature of *meso*-substituents on some physical-chemical properties of Mn porphyrins.

meso-substituents	Soret peaks, λ_{max} [nm]		$E_{\mathrm{Mn}^{2+/\mathrm{Mn}^{3+}}}$	Hammett	ORR,
			$[V_{RHE}]$	constant	$E_{1/2}$
	1	2		[σ]	$[V_{RHE}]$
$R^1 = R^2 = R^3 = R^4 = H$	391.99	451.98	0.129	-	0.6169
$R^1 = R^2 = R^3 = R^4 = Ph$	416.98	468.01	-0.006	0.00	0.7398
$R^1 = R^2 = R^3 = R^4 = T$	436.99	465.98	-0.064	-0.68	0.7203
$R^1 = R^2 = R^3 = R^4 = APh$	439.98	482.00	0.009	-2.64	0.7691
$R^1 = R^2 = R^3 = R^4 = CPh$	420.99	469.00	0.282	1.80	0.6885
$R^1 = R^2 = R^3 = T; R^4 = HPh$	419.99	468.01	0.228	-0.88	0.6983
$R^1 = R^2 = R^3 = T; R^4 = APh$	440.98	468.01	0.124	-1.17	0.7276
$R^1 = R^2 = R^3 = T; R^4 = CPh$	438.98	469.00	0.238	-0.21	0.6959
$R^1 = R^2 = R^3 = MPh; R^4 = Py$	437.99	468.01	0.107	-0.81	0.7593
$R^1 = R^2 = R^3 = T; R^4 = Py$	-	469.99	0.250	-0.51	0.7129
$R^1 = R^2 = R^3 = R^4 = Py$	_	465.98	-0.031	_	0.7813
$R^1 = R^2 = R^3 = R^4 = Ph$	416.98	468.01	-0.006	0.00	0.7398

 $\label{eq:abbreviations: Ph=phenyl, Py=pyridyl, T=tolyl, MPh=methoxyphenyl, CPh=carboxyphenyl, APh=aminophenyl, HPh=hydroxylphenyl.$



Figure 6. Energy required for the $\pi \rightarrow \pi^*$ transition by various manganic porphyrins with different *meso*-substituents relative to that required for the same transition in the reference complex MnTPhP.

The concentration of all the solutions for UV/Vis measurements was 1 μ M with an average refractive index (RI) of 1.43. By using this RI value, the speed of light through the solutions was estimated to be $2.1 \times 10^8 \text{ ms}^{-1}$. The calculated relative energies ΔE (eV) of the different Mn porphyrins with various *meso*-substituents are summarized in Figure 6. Since two soret peaks were present, the energy shifts for the lower energy soret peak (soret 2) and higher energy soret peak (soret 1) are presented separately. If no value is reported it means that the soret peak could not be unambiguously identified. In general, it was more straightforward to identify soret band 2 than soret band 1.

Positive values of ΔE in Figure 6 indicate that the energy required for the $\pi \rightarrow \pi^*$ transition was lower than for the reference complex, MnTPhP, whereas negative values indicate that the energy required for the same transition was higher than that for the reference complex. Visualization of the possible energy transitions in the UV/Vis range was deemed useful in interpreting the energy shifts by the various ligands (Figure 7).

Within the UV/Vis range, only $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitations are feasible, as illustrated in Figure 7. The $\sigma \rightarrow \sigma^*$ exci-

tation requires absorption of photons with a wavelength outside of the UV/Vis range. Here, discussion will be confined to the $\pi \rightarrow \pi^*$ excitation (soret band), since calculation of the relative energy transitions of the different ligands was based on this transition. Regardless of the relative energy levels of the π and π^* orbitals, positive values of ΔE imply that the energy separation of the π and π^* orbitals of the given ligand was less than that for the reference compound and vice versa. Therefore, with reference to soret band 2, except for MnP, MnTTP, and MnTPyP, whose $\pi \rightarrow \pi^*$ orbital energy separation was larger than that of MnTPhP, the $\pi \rightarrow$ π^* orbital energy separation of all the other complexes was smaller than that for MnTPhP.

To illustrate the possibility of modulating the intermolecular hardness between metalloporphyrins



Figure 7. Possible electronic transitions in the UV/Vis range.

and oxygen, we opted for Mn porphyrins. Unlike Co and Fe porphyrins, Mn porphyrins have seldom been reported in the electrocatalysis of oxygen reduction. Many Mn^{II} and Mn^{III} porphyrins are known to form kinetically stable oxocomplexes, which render them suitable to facilitate intermetal oxygen atom-transfer reactions.^[21] The strength of the Mn-O₂ bond is increased when the porphyrin ligand is modified with electron-deficient groups, whereas it is weakened when the ligand is modified with electron-rich groups. Indeed, some Mn porphyrins cannot facilitate inter-metal oxygen atom-transfer reactions because either the Mn-O₂ bond is not kinetically stable for the required timescale of the reaction, or it is too strong for the oxygen to be exchanged for another atom or group. This implies that by using the appropriate ligand system, the strength of interaction of oxygen with Mn can be varied from very strong to very weak. In line with the Sabatier principle, this means that there exists a particular ligand system for which the energetics between Mn and O2 would be suitable for the complex to catalyze the electroreduction of oxygen. With this hypothesis in mind, a selection of Mn porphyrins with various meso-substituents were synthesized and investigated for ORR. Specific volumes of the complexes were pipetted onto polished graphite electrodes to form films with a cata-

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Figure 8. a) Representative linear sweep voltammograms showing the influence of various substituents on the electrocatalysis of oxygen reduction by Mn porphyrins. b) Dependency of the activity of Mn porphyrins on their relative energy for $\pi \rightarrow \pi^*$ excitation.

lyst loading of 1.06×10^{-7} mol cm⁻². The films were left to dry in air before electrochemical characterization. Figure 8 shows linear sweep voltammograms of some of the Mn porphyrins. They exhibited a wide variation in the ORR activity with respect to the potential at half-maximum electrocatalytic oxygen reduction current as well as the onset potential of oxygen reduction. Additionally, differences were observed in the electrocatalytic currents. Since the loading of the catalysts was the same, it was reasonable to compare the catalysts by using the observed catalytic currents and also in terms of their overpotential for ORR. It is particularly of interest to examine the properties of MnTrMPyP, MnTAPhP, and MnTPyP since they exhibited the highest activity, both in terms of the observed catalytic currents and in terms of the overpotential for ORR. The π -electron density of the pyridine ring is not evenly distributed due to the negative inductive effect imposed by the nitrogen atom. The lone pair of electrons on the nitrogen atom in pyridine is not part of the aromatic ring thus making pyridine behave like a base, with chemical properties similar to those of tertiary amines. The low overpotential at which MnTPyP reduces oxygen can therefore be accounted for by its relative electron deficiency. This is in perfect agreement with the rationale of increasing the thermodynamic efficiency of the reaction, or its driving force by modifying the ligand with electron-deficient groups. Interestingly, the catalytic current is also comparatively high and is indicative of the selectivity of the reaction towards a direct four-electron-transfer pathway. The lone pair of electrons on the nitrogen atom in aniline is

partially delocalized into the π -electron system of the phenyl ring due to the electron-withdrawing effect of the phenyl group. This enhances the electron-donating ability of the ring compared with pyridine. This reasonably explains the observed minor cathodic shift (Figure 8a) of the onset potential of ORR for MnTAPhP compared with MnTPyP. However, the discrepancy in the catalytic current is difficult to account for. Owing to the instability of films of most complexes formed by drop coating, it is possible that some of the discrepancies observed in the catalytic currents could be caused by partial dissolution of the catalyst films.

Due to the inductive effect of the methoxy group, 4-methoxyphenyl substituents exert a net positive inductive effect on the π -electron system of the ring, thus enriching the π -electron density of the aromatic ring. It is therefore expected that the inductive effect of methoxyphenyl groups in MnTrMPhPyP increases the π -electron density of the central metal ion. This effect should lead to a decrease of the driving force of the complex for ORR, which is in perfect agreement with what was observed. The fact that the ORR catalytic current of MnTrMPhPyP at high overpotentials was higher than that observed for MnTPyP can be explained on the basis of the intermolecular hardness between the complexes and oxygen bearing in mind the fact that electron-donating groups weaken the intermolecular hardness (η_{AD}) between oxygen and the complexes, accompanied by a decrease of the driving force of the complex to reduce oxygen and vice versa. It is therefore reasonable to argue that the reduced $\eta_{\rm AD}$ in the case of MnTrMPhPyP relative to MnTPyP is more optimal for attaining a high catalytic current.

It was necessary to choose a suitable reference system to investigate if any quantitative correlations existed between the electrochemical properties of the complexes and their spectroscopic properties. Figure 8b shows a plot of the logarithm of the catalytic current at 0.75 V against the relative energies for a selection of Mn complexes. Although it is premature to make resolute conclusions, the somewhat linear dependence between the ORR activity and the relative energy of the frontier orbitals are suggestive of an apparent correlation. The graph has a slope of $-8.5065 \text{ dec eV}^{-1}$, which would be interpreted that a tenfold increase in activity is achieved if the porphyrin is modified with a ligand that increases the energy for the $\pi \rightarrow \pi^*$ excitation by one eV relative to that required for the same excitation in MnTPhP. However, this is not absolutely true since the activity of MnP was a lot worse than that of the reference complex although its energy for the $\pi \rightarrow \pi^*$ excitation was 0.066 eV higher than that for the same excitation in MnTPhP. On the other hand, MnTPyP whose $\pi \rightarrow \pi^*$ excitation energy was only 0.008 eV higher than that for MnTPhP, exhibited the highest activity.

By plotting the ORR activity against the formal potential of the M^{III}/M^{II} redox transition of metallophthalocyanines with different substituents, Zagal et al. observed two different slopes, one inclining and the other declining. The straight lines of the graphs would apparently meet at some

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hypothetical formal potential of the M^{III}/M^{II} redox system, where it is imagined that a complex with such a formal potential would serve as the best ORR catalyst for that the particular category of complexes. If this is taken to be true, the same analogy may be used to partially explain the linear correlation observed in Figure 8b. The ORR activity of MnP was so low that a comparison of the current at a given potential was not possible. By plotting the potential at maximum peak current against the relative energy for the $\pi \rightarrow \pi^*$ excitation of the respective complexes (Figure 9a), it is reasonable to imagine a straight line connecting MnP to MnTPy. The ORR activity within this region should increase as the complexes are modified with groups which decrease the energy for the $\pi \rightarrow \pi^*$ excitation.



Figure 9. a) Plot of ORR activity measured as the potential at half-maximum oxygen reduction current against the relative energy required for the $\pi \rightarrow \pi^*$ excitation of the respective Mn porphyrins as indicated in the Figure. b) Plot of ORR activity measured as the potential at half-maximum oxygen reduction current against the formal potential for the Mn^{II}/Mn^{III} transition.

Alternatively, a plot of the ORR activity of the complexes against the formal potential of a suitable redox couple may be considered. Plots of this nature have been reported.^[28,29] Such a plot yielded the graph shown in Figure 9b, when the potential at half-maximum peak current for oxygen reduction is plotted against the formal potential of the Mn^{2+}/Mn^{3+} redox couple. Since formal potentials are sensitive to the pH in which they are measured and on if they are measured with the complex in solution or adsorbed on an electrode, the formal potentials reported in Figure 9b for the Mn^{2+}/Mn^{3+} transition were measured in the same electro-

lyte in which ORR was investigated with the complexes adsorbed on graphite surfaces.

It is interesting to note that a volcano-like curve is obtained, which is in good agreement with the work reported by Zagal et al. for the reduction of O_2 and oxidation of hydrazine by metallophthalocyanines with different substituents attached on the macrocyclic ligand.^[29] It is imperative to caution here that the formal potential for the M^{2+}/M^{3+} transition was considered by Zagal et al. as the driving force with the assumption that adsorption of oxygen at the active site is preceded by a redox transition of the central metal ion from a higher oxidation state to a lower oxidation state.^[29] Therefore, whereas the results obtained in here are in good agreement with those reported for metallophthalocyanines, the fact that the oxygen reduction commences at much higher potentials than the formal potential for the Mn³⁺/Mn²⁺ transition implies that the formal potential of this transition cannot, in a strict sense, be taken as the driving force of the reaction. The accurate determination of the potentials at which high valence redox transitions of the Mn porphyrins take place was difficult using conventional voltammetry techniques.

Hammett constants are commonly used to relate the reactivities of aromatic compounds that only differ in the position of their substituents with either meta or para substituents. For a reaction whose rate or equilibrium constant depends exclusively on the type of *meta* and *para* substituents, a plot of the logarithm of a reactivity quantity against their respective Hammett constants should yield a straight line with either a negative $(-\rho)$ or positive $(+\rho)$ slope, in which ρ is a reaction specific constant. A plot of the logarithm of current at 0.75 V against the Hammett constants yielded a scatter instead of a linear relationship as shown in Figure S1 in the Supporting Information. The Hammett constants were calculated from the compilation reported by Hansch et al.^[30] The non-linearity of the Hammett plot indicates that the rate and mechanism of oxygen reduction are not exclusively dependent on the nature of the substituents. The present data does not however enable us to explain the exact reasons for such a scatter.

MnTPyP, which was the most active catalyst identified in this study on the basis of exhibiting the least overpotential and reasonably high catalytic current, is soluble in aqueous electrolytes and therefore gradually dissolves from the electrode. It was particularly difficult to carry out detailed kinetic studies of the catalysts by using methods of forced convection since the adsorbed films were not tolerably stable on the electrode. Heat treatment of metalloporphyrins is a well-established approach for improving not only their stability but also their activity, although the structural merit of the complexes is often lost.^[31] To enhance the stability of MnTPyP, the complex (1% wt.) was mixed with carbon black (Vulcan) and subjected to heat treatment at 650 °C in the presence of helium. For heat treatment, an impregnation of the catalyst with Vulcan was placed in a quartz boat and inserted into a tubular reactor of a furnace. A catalyst ink was prepared from the resulting catalyst powder as descri-



Figure 10. a) Cyclic voltammograms of a graphite electrode modified with heat-treated MnTPyP in the presence and absence of oxygen at a scan rate of 10 mV s^{-1} in KOH (0.1 M). b) Rotating ring-disk electrode (RRDE) measurements recorded at 10 mV s^{-1} and at a rotation speed of 900 rpm in oxygen-saturated KOH (0.1 M) with the ring polarized at 1.2 V.

bed previously^[32] and an aliquot of this ink was pipetted onto a pre-polished disk of the rotating ring-disk electrode (RRDE; disk = 0.2475 cm^2 , area of Pt ring = 0.1866 cm^2). The loading of the catalyst on the electrode was 0.2 mg cm^{-2} . After being left to dry in air for 20 min, the resulting catalyst film was investigated for ORR. Figure 10a shows cyclic voltammograms recorded in the absence and presence of oxygen. Two reduction peaks at 0.8145 and 0.7413 V can be seen in the voltammogram recorded under Ar, and a broad oxidation wave, which is apparently a convolution of at least two independent oxidation processes, appears between 0.769 and 0.995 V. The reduction and oxidation peaks are very similar to those observed for the non-pyrolyzed complex (Supporting Information, Figure S2), the difference being that the peaks for the pyrolyzed complex were substantially shifted anodically. For example, the reduction peak at 0.8145 is 300 mV more positive than that observed in the non-pyrolyzed complex. The reduction of oxygen by the pyrolyzed complex appears to be closely associated with the reduction process with the peak at 0.8145 V (Figure 10a). As proposed by Beck et al.^[33] for oxygen reduction on metallomacrocyclic complexes, oxygen adsorption and its subsequent reduction on the central metal ion only takes place when the metal ion is in a particular oxidation state. The reduction process with a peak at 0.8145 therefore seems to generate such a site as Mn is reduced to a lower oxidation state. Zagal et al. have suggested that the higher the formal potential for the $M^{n+/m+}$ transition of a given metallomacrocyclic complex, in which n and m are oxidation states of a metal M and *n* is an integer higher than *m*, the higher value is the driving force of the complex for oxygen reduction.^[29] Hence, a plausible means to increase the ORR activity of metallomacrocyclic complexes is to increase the formal potential for the $M^{n+/m+}$ transition.^[29] Upon pyrolysis of MnTPyP at mild temperatures, the reduction of oxygen was achieved at a phenomenally low overpotential for a non-noble metal catalyst. The oxygen reduction current decreased at higher overpotentials after a peak was observed at 0.806 V.

The decrease in the oxygen-reduction current seems to be closely associated with the onset of the second reduction process of Mn. Most probably, a second less-active site is generated. RRDE experiments support the postulate that a more active site is involved at low overpotentials, whereas a less-active site(s) take command at a higher overpotential (Figure 10b). No H_2O_2 peroxide was detected at low overpotentials in the region of potential were the reaction was expected to be controlled by the more active site. Emergence of the second, apparently less active site commences at about 0.785 V.

The percentage of generated H_2O_2 was calculated by using Equation (5) and was found to be less than 0.5% at all potential. The number of electrons transferred was calculated by using Equation (6) and was found to be close to 4.

$$X_{\rm H_2O_2} = \frac{200I_{\rm R}/N}{I_{\rm D} + I_{\rm R}/N} \tag{5}$$

$$n = \frac{4I_{\rm R}}{I_{\rm D} + (I_{\rm R}/N)} \tag{6}$$

 $I_{\rm R}$ and $I_{\rm D}$ denote the currents measured at the ring and at the disk, respectively, whereas N is the collection efficiency. We independently used Ru³⁺/Ru²⁺ as a redox probe and verified that the collection efficiency of the ring was 24.3 % for our type of film and not 37 % as reported by the supplier. Evidently, fragments of the Mn porphyrin that remain after pyrolysis participate actively in the reduction of oxygen.

Conclusion

Manipulation of the properties of metalloporphyrins by careful selection of substitution groups on the porphyrin ligand shows great potential for tailoring their reactivity. Mn porphyrins inherently form stronger bonds with oxygen than corresponding Fe and Co porphyrins, which makes them less attractive as catalysts for oxygen reduction. It was illustrated in this study that the intermolecular hardness between Mn porphyrins and oxygen can be systematically weakened by modifying the porphyrin ligands with electron-donating groups. The effect of various *meso*-substituents of the porphyrin ligands on the energy required for the $\pi \rightarrow \pi^*$ transition was measured using UV/Vis spectroscopy and correlated with the ORR activity of the respective complexes. A de-

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crease in activity was observed when the porphyrin ring was modified with meso-substituents, which decrease the energy required for the $\pi \rightarrow \pi^*$ excitation of the porphyrin ring compared with the energy required to effect the same excitation in MnTPhP. On the other hand, modification of the porphyrin ring with substituents, which slightly increase the energy required for its $\pi \rightarrow \pi^*$ excitation compared with that required for the same excitation in MnTPhP, led to improved ORR activity. However, the ORR activity was observed to fall drastically for Mn porphyrins whose $\pi \rightarrow \pi^*$ excitation energy was substantially higher than that for MnTPhP, whereas the ORR activity of MnTAPhP, which had the least $\pi \rightarrow \pi^*$ excitation energy compared with MnTPhP, exhibited one of the best activities. Therefore, whereas a positive correlation between ORR activity and the relative energy separation of the frontier orbitals may indeed exist, additional factors apparently contribute to the overall reactivity of metalloporphyrins with oxygen. Such factors may include the properties of the electrolyte, the influence of axial ligation, and interaction of the surface groups on the electrode with the complexes. Instability of metalloporphyrins due to their dissolution from the electrode is a major drawback that undermines their potential for any application in which long term stability is required. It was shown that heat treatment of MnTPyP at mild temperatures (650°C) leads to a remarkable increase of its ORR activity.

Experimental Section

Chemicals: Anhydrous chloride salts of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, were from Sigma Aldrich (D) and used as received. The *meso*-tetrakis(4-pyridyl) porphyrin (TPyP), *meso*-tetrakis(4-aminophenyl)porphyrin (TAPhP), *meso*-tetrakis(4-carboxyphenyl)porphyrin (TCPhP), *meso*-tetrakis(phenyl)porphyrin and porphine were purchased from Porphyrin Systems (D). Dimethylformamide (DMF) and KOH were from J.T. Baker, Deventer (The Netherlands), tetrabutylammonium tetrafluoroborate (TBABF₄, >98% purum) was from Fluka Chemie (D) and was used as received. Some of the porphyrin free bases used in this work were synthesized following the procedure reported in the literature.^[34] All aqueous solutions were prepared using Milli-Q water (SG Water, D). The products were purified by column chromatography using neutral aluminum oxide (Riedel-de Haën, D) as the stationary phase and dichloromethane (CH₂Cl₂) as the eluent.

Synthesis and characterization of metalloporphyrins: Metalation of porphyrin free-bases was carried out by direct reaction of a given porphyrin (3 mM) in DMF with the corresponding stoichiometric quantity of anhydrous metal dichloride $(MCl_2)^{[11]}$ in a tightly closed reaction tube at 100 °C for 6 h with continuous magnetic stirring. A simplified scheme of the synthesis is shown in Figure 1. The purified products were characterized using UV/Vis spectroscopy (Cary 60 UV/Vis; Agilent Technologies, D).

Electrochemical measurements: All electrochemical measurements were carried out in a glass cell using a Pt wire as the counter electrode, a graphite electrode modified with metalloporphyrins as the working electrode and a reversible hydrogen electrode (RHE) as the reference electrode. An Autolab potentiostat/galvanostat (PGSTAT 12, Eco Chemie, Utrecht, The Netherlands) controlled with the NOVA 1.6 software was used for the measurements. Rotating ring-disk electrode (RRDE) measurements were carried out using a Gamry Reference 600 potentiostat/galvanostat equipped with accessories for RRDE. The area of the disk electrode was 0.2475 cm², whereas that of the ring was 0.1866 cm² with a sep-

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aration of 320 μ m between them. The electrolyte was first purged with Ar for at least 20 min to record background current. Afterwards, it was purged with O₂ for at least 20 min to record the oxygen reduction current. The currents recorded under Ar were subtracted from those recorded in the presence of oxygen to get the catalytic current. During the measurements under both Ar and oxygen, a gentle stream of the gases was maintained above the surface of the electrolyte. All the measurements were carried out at room temperature.

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