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**Density Functional Theory Study of Transitional Metal Macrocyclic Complexes' Dioxygen-Binding Abilities and Their Catalytic Activities toward Oxygen Reduction Reaction**

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# Density Functional Theory Study of Transitional Metal Macrocyclic Complexes' Dioxygen-Binding Abilities and Their Catalytic Activities toward Oxygen Reduction Reaction

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In this paper, density functional theory method is applied to study the dioxygen-binding abilities of transition metal macrocyclic complexes and their electrocatalytic activities toward oxygen reduction reaction. Both end-on and side-on binding modes are examined. Electronic properties, such as ionization potential and Mulliken charge, are evaluated. The effects of central metal, ligand, and substituents on catalyst's dioxygen-binding ability and catalytic activity are investigated. The binding nature of dioxygen adduct is analyzed based on structure property. The general activity trend observed for phthalocyanines and porphyrins is rationalized with the calculated properties. It is illustrated that the catalyst's oxygen reduction activity is related to its ionization potential and dioxygen-binding ability. Cobalt porphyrin derivatives have high ionization potentials, which make them better catalysts than the corresponding iron derivatives, whereas for phthalocyanine systems, iron derivatives have large ionization potential and better dioxygen-binding ability, which make them good catalysts.

## Introduction

Development of new catalysts with low cost, high efficiency and durability is critical to fuel cell technology advancement. Transition metal macrocyclic complex is a promising class of catalyst. They exhibit good catalytic activity for oxygen reduction reaction (ORR). The advantage of transitional metal macrocyclic complexes lies in especially with the material cost. Since the first study by Jasinsky in 1964,[1] numerous studies of oxygen reduction catalyzed by transition metal macrocyclic complexes have been published. Several review papers are available.[2−4] Despite these investigations, our understanding of the mechanisms of oxygen electrocatalysis by transition metal macrocyclic complexes is far from complete. There are a number of proposed mechanisms for transition metal macrocyclic complexes-catalyzed oxygen electroreduction. According to Randin[5] and Beck,[6] M(III)/M(II) redox potential is related to the catalytic activity, and the rate determining step is M(III) + e⁻ → M(II). Savy et al.,[7] on the other hand, suggested that the M(II)/M(I) reversible couple plays a key role in determining catalytic activity. Dong et al. also proposed Co(I) is the active species in catalyzing oxygen reduction.[8]

The adsorption of dioxygen is the first step for oxygen reduction. The interaction between catalyst and oxygen molecule and its effect to dissociation of O−O bond is important in understanding the reaction mechanism. Suggestions have been made that the redox potential of the metal is correlated with the heat of adsorption of $O_2$ on the metal center in the phthalocyanine.[3] Figure 1 shows the structures of transition metal porphyrin and phthalocyanine. Zagal et al.[9,10] have reported ORR activity studies of substituted Co phthalocyanines (Co-Pcs). When the logarithm of the rate constant (Log *k*) is plotted versus the Co(III)/Co(II) redox potential of different substituted phthalocyanines, a straight line is obtained. Log *k*
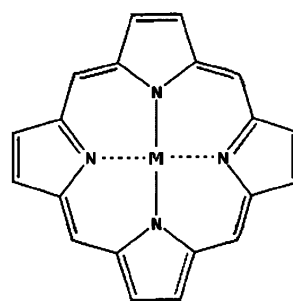


**Metal Porphyrin**
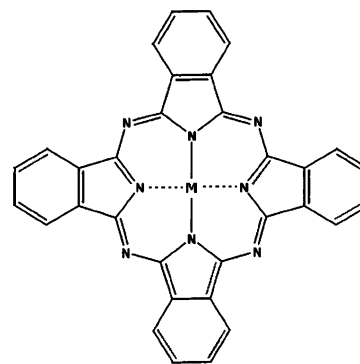


**Metal Phthalocyanine**

**Figure 1.** Structures of metal porphyrin and metal phthalocyanine.

decreased as the driving force (measured by the Co(III)/Co(II) redox potential of the phthalocyanine) increased. So the greater the $O_2$ reducing power of the Co-Pcs is, the less their activity for $O_2$ reduction is. This was explained in terms of the chemical intermolecular hardness of the system (i.e., the larger the energy gap between the frontier orbitals of the donor (Co-Pc) and the acceptor ($O_2$) is, the less the reactivity). In other words, better

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**TABLE 1: Calculated Properties of Transition Metal Macrocyclic Systems**

| | multiplicity | $R_{M-N}$ (Å) | | | IP (eV) | | | Mulliken charge on M |
|---|---|---|---|---|---|---|---|---|
| | | this work | expt | other work | this work | expt | other work | |
| CoPc | 2 | 1.917 | 1.91[a] | 1.92[b,c] | 6.39 | 6.38[d] | 6.00[b],6.47[c] | 0.191 |
| CoMeOPc | 2 | 1.915 | | | 5.61 | | | 0.183 |
| CoTNPPc | 2 | 1.914 | | | 5.83 | | | 0.184 |
| CoF16Pc | 2 | 1.922 | | | 7.07 | | | 0.21 |
| CoTSPc | 2 | 1.919 | | | 7.19 | | | 0.207 |
| CoP | 2 | 1.968 | | 1.98[c],1.987[e] | 6.63 | | 6.98[c] | 0.248 |
| CoTPP | 2 | 1.966 | 1.949[f,g] | | 6.23 | | | 0.236 |
| CoTPFPP | 2 | 1.967 | | | 7.08 | | | 0.255 |
| FePc | 3 | 1.923 | 1.928[h] | 1.92[c] | 6.26 | 6.36[d] | 6.46[c] | 0.384 |
| FeMeOPc | 3 | 1.922 | | | 5.55 | | | 0.309 |
| FeF16Pc | 3 | 1.928 | | 1.922[i] | 7.00 | | 7.84[i] | 0.392 |
| FeTSPc | 3 | 1.923 | | | 7.08 | | | 0.396 |
| FeTPyPz | 3 | 1.925 | | | 7.45 | | | 0.397 |
| FeP | 3 | 1.981 | | 1.984[c,j],1.999[e] | 6.46 | | 6.29[c] | 0.443 |
| FeTPP | 3 | 1.972 | 1.972[k],1.967[l] | | 5.93 | | | 0.429 |
| FeTPFPP | 3 | 1.973 | | | 6.75 | | | 0.45 |

*[a]* Ref 22. *[b]*Ref 23. *[c]*Ref 24. *[d]*Ref 25. *[e]*Ref 14. *[f]*Ref 26. *[g]*Ref 27. *[h]*Ref 28. *[i]*Ref 29. *[j]*Ref 30. *[k]*Ref 31. *[l]* Ref 32.

dioxygen binding of Co-Pcs will result in higher activity. The activity should be associated with dioxygen binding, and the heat of $O_2$ adsorption on the metal center appears to be the origin of the correlation of the activity for $O_2$ reduction with the redox potential.[11]

Theoretical studies of dioxygen binding of heme and some metalloporphyrins (MP, M = Fe, Co, Mn, Ni) have been reported in the literature.[12−17] However, systematic investigation of dioxygen binding for cobalt, iron phthalocyanine, and porphyrin derivatives is not available. To understand the transition metal macrocyclic complexes-catalyzed oxygen reduction mechanisms, we carried out a series of studies. In this paper, we present studies of dioxygen-binding abilities of substituted cobalt, iron phthalocyanine, and porphyrin systems. We also calculated electronic properties such as ionization potential and Mulliken charge of the systems. We intend to explore questions such as how does the oxygen-binding ability of transition metal macrocyclic systems affect their catalytic activity toward ORR? How does central metal and ligand affect their oxygen-binding ability and catalytic activity?
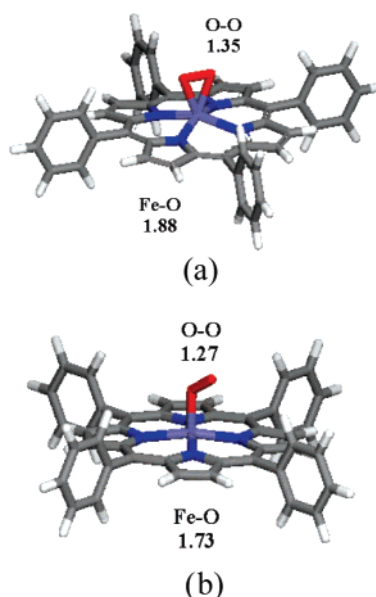
## Computational Method

In this study, we employed Materials Studio DMol3 (version 3.2) program from Accelrys.[18] Density functonal theory (DFT) calculations were carried out with VWN−BP functional.[19−21] An effective potential with relativistic effect-accounted DFT semicore pseudopotential was applied for transition metals. DNP double numerical plus polarization function basis sets were employed for all the calculations. Spin unrestricted method is used for all open shell systems. The structures of catalysts and their corresponding complexes with dioxygen were fully optimized. The vertical ionization potentials were calculated using $\Delta$SCF method. We investigated the following iron and cobalt systems: CoPc (cobalt phthalocyanine), $CoF_{16}Pc$ (cobalt hexadecafluorophthalocyanine), CoMeOPc (cobalt octamethoxyphthalocyanine), CoTSPc (cobalt tetrasulfophthalocyanine), CoTNPPc (cobalt tetraneopentoxyphthalocyanine), CoP (cobalt porphyrin), CoTPP (cobalt tetraphenylporphyrin), CoTPFPP (cobalt tetrakis(pentafluorophenyl)porphyrin), FePc, $FeF_{16}Pc$, FeMeOPc, FeTSPc, FeTPyPz (iron-2,3-pyridinoporphyrazine) FeP, FeTPP, and FeTPFPP.

## Results and Discussions

**A. Structures, Binding Energies, and Bonding Nature of Dioxygen Adducts.** Optimized structures and electronic proper-



**Figure 2.** Optimized structures for (a) side-on dioxygen adsorption on FeTPP and (b) end-on dioxygen adsorption on FeTPP.

ties of metal porphyrin and phthalocyanine systems are listed in Table 1. To verify our computational method, literature available data are presented in the table as well. In general, our optimized structures agree very well with experimental observations and other theoretical works. Our calculated first ionization potentials agree well with experimental photoelectron measurements and calculations from other groups.

There are four possible modes of oxygen binding with transition metal macrocyclic complex (M-L). They are side-on, end-on, bridge, and trans modes. Previous studies have indicated that preference for side-on or end-on adsorption depends on the central metal atom and ring structure.[3,33] We studied both side-on and end-on binding for CoP, CoPc, CoTPP, FeP, FePc, and FeTPP systems. For CoP, CoPc, and CoTPP, we could not locate side-on adduct for Co−O distance within 3.5 Å. For iron systems, only FeTPP could form stable side-on adduct with a binding energy of 0.15 eV; however, its end-on adduct is more stable with a binding energy of 0.78 eV. The optimized side-on and end-on dioxygen adducts for FeTPP are illustrated in Figure 2. For side-on adsorption, the central metal Fe is raised 0.39 Å higher above the porphyrin plane (defined by four nitrogen atoms) while in end-on adduct, the distance is

**TABLE 2: Calculated Dioxygen Adducts Properties**

| | multiplicity | $R_{O-O}$ (Å) | $R_{M-O}$ (Å) | $E_{bO_2}$ (eV) | other work |
|---|---|---|---|---|---|
| CoPc | 2 | 1.261 | 1.894 | 0.43 | |
| CoMeOPc | 2 | 1.265 | 1.883 | 0.47 | |
| CoTNPPc | 2 | 1.262 | 1.889 | 0.41 | |
| CoF16Pc | 2 | 1.258 | 1.896 | 0.27 | |
| CoTSPc | 2 | 1.257 | 1.896 | 0.32 | |
| CoP | 2 | 1.264 | 1.876 | 0.47 | 1.263[a,c] |
| CoTPP | 2 | 1.266 | 1.873 | 0.43 | 1278 (cm$^{-1}$)[b,d] |
| CoTPFPP | 2 | 1.26 | 1.882 | 0.34 | |
| FePc | 1 | 1.269 | 1.748 | 0.75 | |
| FeMeOPc | 1 | 1.273 | 1.748 | 0.65 | |
| FeF16Pc | 1 | 1.266 | 1.753 | 0.63 | |
| FeTSPc | 1 | 1.264 | 1.751 | 0.72 | |
| FeTPyPz | 1 | 1.265 | 1.744 | 0.66 | |
| FeP | 1 | 1.267 | 1.733 | 0.58 | 1.28[a,e], 1.315[a,c] |
| FeTPP | 1 | 1.27 | 1.732 | 0.78 | 1195 (cm$^{-1}$)[b,f] |
| FeTPFPP | 1 | 1.263 | 1.733 | 0.67 | |

$^a$ $R_{O-O}$ (Å). $^b$ $\nu$(O−O). $^c$Ref 14. $^d$Ref 35. $^e$Ref 12. $^f$Ref 34.

0.23 Å. The O−O bond length is stretched further (1.349 Å with vibration frequency of 1066 cm$^{-1}$) in side-on adsorption than that in end-on adsorption (1.270 Å with vibration frequency of 1258 cm$^{-1}$). This is consistent with experimental observation that two types of dioxygen adducts were formed with FeTPP, corresponding to side-on with low vibration frequency (1105 cm$^{-1}$) and end-on with high frequency (1195 cm$^{-1}$) and that side-on binding is not stable and converts to end-on binding at 100 K.[34] Our calculation showed that for FeP and FePc, side-on bindings are not stable with binding energies of −0.06 and −0.05 eV, respectively. This is consistent with reported theoretical calculations for FeP.[12] For the rest of the systems, only end-on bindings were investigated. The optimized structure parameters and dioxygen-binding energies for end-on adducts are listed in Table 2. The oxygen-binding energies for transition metal macrocyclic complexes are evaluated through eq 1

$$E_{bO_2} = (E_{O_2} + E_{ML}) - E_{ML-O_2} \quad (1)$$

where $E_{bO_2}$ is the oxygen-binding energy, $E_{ML-O_2}$ is the total energy of the oxygen adduct, $E_{O_2}$ is the energy of the isolated oxygen molecule, and $E_{ML}$ is the energy of transition metal macrocyclic complex.

The results illustrate that for the end-on adducts reported, iron systems form more stable dioxygen adducts than the corresponding cobalt systems and for cobalt phthalocyanines, the electron-donating substituent (MeO) facilitates the oxygen adsorption process, and the dioxygen-binding energy is increased. The reverse is true for electron-withdrawing substituents (HSO$_3$ and F).

To understand the dioxygen-binding difference between phthalocyanine and porphyrin, and cobalt and iron systems, examinations of electronic structures of these systems are required. First we examined calculated Mulliken charges on central atoms of metal macrocyclic complexes (Table 1). Electron-withdrawing substituents (HSO$_3$, F) of M−X−Pc increase the positive charge on both central metal atoms (Co and Fe), and electron-donating substituents (MeO, neopentoxy, phenyl) decrease the charge on central metal atoms (Co and Fe). In phthalocyanine systems, the central metal has less charge than in porphyrin systems. This is due to better electron-donating ability of the phthalocyanine ligand compared to the porphyrin ligand, which has a lower highest occupied molecular orbital (HOMO) energy and higher ionization potential than that of phthalocyanine.[36] For cobalt, the charges on Co in phthalocya-

nine and porphyrin systems are in the range of 0.18−0.21 and 0.24−0.26, respectively. For iron, they are in the range of 0.31−0.40 and 0.43−0.45, respectively. Cobalt atom generally has a small Mulliken charge than the corresponding iron atom. This is due to lower d orbital energies of cobalt, which make them easier to gain electrons than the corresponding iron orbitals. The calculated HOMO energies of cobalt phthalocyanine systems are in general lower than that of O$_2$ (except for CoMeOPc, which has a higher HOMO energy). For Co-Pcs, the HOMO is the ring orbital.[24] Therefore, the 3d orbital energies of Co in Co-Pcs are even lower. Electron-donating substituent raises the Co 3d orbital energy; hence, the energy gap between the interaction orbitals of Co and O$_2$ decreases, so the binding energy increases. This is in contrast to the rational explanation proposed in the literature[9] that stated that the electronic coupling between the donor (Co-Pcs) and the acceptor (O$_2$) decreases as the electron-donating capability of the substituents increases.

For FePc, HOMO is 3d Fe orbital, which lies very close to the HOMO of O$_2$ and both electron-donating and withdrawing groups increase the energy gap, so the binding energies decrease.

As a result of the high lying ring orbital in cobalt phthalocyanine system, the first ionization results in the loss of an electron from the ring orbital.[24] Photoelectron spectroscopy studies[25] have demonstrated that for metallophthalocyanines (M = Mg, Fe, Co, Ni, Cu, and Zn), the first ionization potential are almost same (6.35−6.38 eV). This is attributed to the electron loss from ring orbitals. Thus for phthalocyanine systems, the difference in ionization potential for the corresponding cobalt and iron complex is small and in the range of 0.06−0.13 eV, while that for porphyrin systems is in the range of 0.18−0.34 eV. This might explain the observed different activities for phthalocyanine and porphyrin derivatives that will be discussed later.

The redox potential of a particular redox pair can be calculated from its gas-phase vertical ionization potential (IP) using eq 2[37]

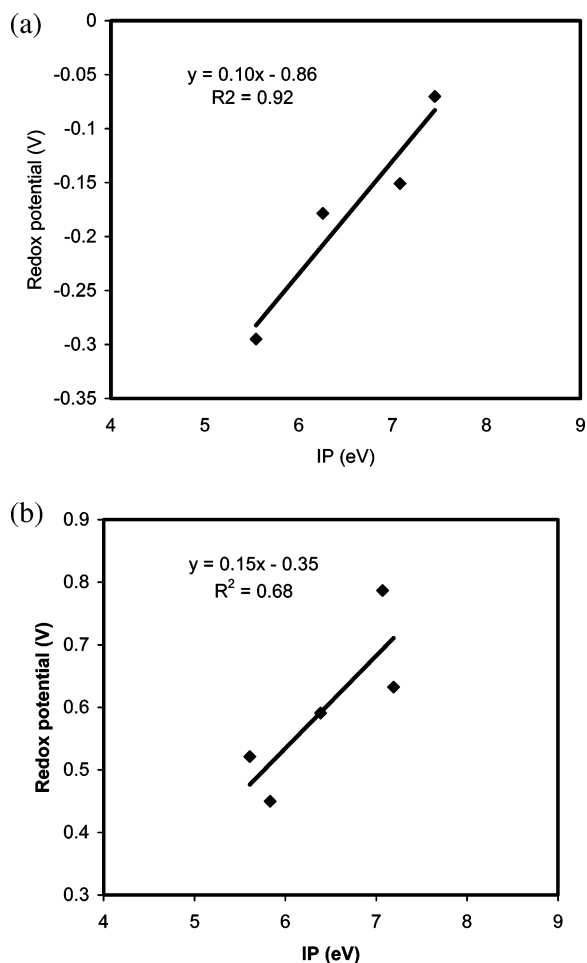$$E^0[O/R] = IP - 4.44 + (1/F)[\Delta G_s^{0O} - \Delta G_s^{0R} - \chi_i] \quad (2)$$

where $\Delta G_s^{0R}$ and $\Delta G_s^{0O}$ are the Gibbs free energies of solvation of the reduced, R, and oxidized, O, species, $\chi_i$ is the inner sphere reorganization energy, $F$ is the Faraday constant, and the constant 4.44 relates the vacuum scale electrostatic zero potential energy to the normal hydrogen electrode (NHE) scale.

It has been demonstrated that for closely related systems that do not involve much of the nuclear change in the redox pair, the last term in eq 2 can be considered as a constant and that there is a linear relationship between the calculated IP and redox potential. For the system reported, we compared our calculated IP with experimental redox potential[9,38] in Figure 3. For iron phthalocyanine systems, the correlation between calculated IP and experimentally measured redox potential is excellent. This indicates that the last term in eq 2 can be considered as a constant as reported for some other systems.[37] For cobalt complexes, however, there is a general correlation that the correlation is not as good as that for iron complexes.

We further explore the relationship between calculated Mulliken charges on central metals and the first ionization potentials of the systems (Figure 4). For cobalt phthalocyanine systems, a small change of charge on the cobalt atom is associated with the largest change in ionization potential. With this relationship, one can estimate ionization potential and redox potential from calculated Mulliken charge.

The bonding nature between O$_2$ and Fe in the porphyrin system has been the subject of dispute for many years. Because

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(a)



(b)

**Figure 3.** Plot of calculated IPs versus experimental redox potentials for: (a) iron phthalocyanine derivatives (ref 38); (b) cobalt phthalocyanine derivatives (ref 9).
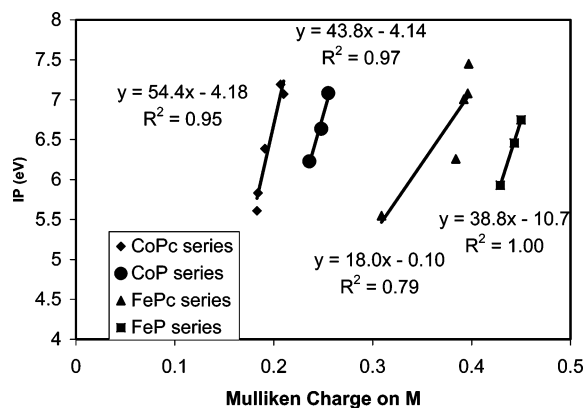


**Figure 4.** Relationship between calculated Mulliken charges on central metal and the first IPs of the systems.

the bonding nature in this system is important in our understanding of the ORR mechanism, we would like to discuss it further here. Weiss[39] proposed that $Fe-O_2$ binding in oxyhamoglobin is better described as $Fe(III)-O_2^-$. Pauling suggested a closed shell $Fe(II)-O_2$ description.[40] Goddard and Hall[41−43] also discussed the bonding nature of the $MP-O_2$ system. More recently, Jensen et al. published multiconfiguration second-order perturbation study of $O_2$-binding to heme.[44] Their results indicated that the electronic structure of oxyheme is a strong multiconfigurational mixture of many different valence-bond states. However, it is dominated by the double occupied orbital of the $Fe(II)-O_2$ (70%). (The O−O bond length is 1.288 Å).[45]

**TABLE 3: Calculated O−O Bond Lengths in Some Systems**

|  | $R_{O-O}$ (Å) |
| --- | --- |
| $O_2$ | 1.216 |
| $O_2H$ | 1.333 |
| $O_2^-$ | 1.360 |
| $FeP-O_2$ | 1.267 |

To elucidate the nature of the bond in the $Fe-O_2$ system, we relied on geometry information. As proposed by Silaghi-Dumitrescu,[46] DFT method provides reliable structure information of the system and this information can be employed to understand the electronic structure of the system. On the basis of the calculated O−O bond length, one can deduce the interaction between oxygen atoms and their bonding to Fe. First, we examined the O−O distance. For the free oxygen molecule, our calculated O−O bond length is 1.216 Å (Table 3) (expt. 1.208 Å). Our calculated O−O bond length for isolated OOH is 1.332 Å (expt. 1.333 Å), and calculated O−O bond length of $O_2^-$ is 1.360 Å (expt. 1.350 Å). It is interesting to note the theoretical study of the electrochemical reduction of the $O_2$ to $O_2^-$ by Ignaczak et al.[47] According to the study, the potential energy surface of $O_2$ and $O_2^-$ crosses over at about 1.284 Å. For O−O distance smaller than 1.284 Å, $O_2$ state dominates while for O−O distance larger than 1.284 Å, $O_2^-$ state dominates. For heme dioxygen adduct, the calculated O−O distance is 1.288 Å and the $Fe(II)-O_2$ configuration is dominative with 70% contribution. We expect that for $Fe(III)-O_2^-$ configuration to be dominative, the O−O bond length in the adduct has to be >1.3 Å. On the basis of this argument and the calculated geometry information from Table 3, for $FeP-O_2$ systems the dominant contribution is $Fe(II)-O_2$. Thus, in the dioxygen adsorption process, partial electron is transferred to dioxygen antibonding $\pi$-orbitals, which weakens and elongates the O−O bond; however, to get to a superoxide state, a solvent is required to stabilize the species.

**B. Dioxygen-Binding Abilities and Activities.** The hardness parameter $\eta$ can be calculated with IP and EA (electron affinity) through eq 3

$$\eta = \frac{1}{2}(IP + EA) \qquad (3)$$

Studies have shown that the calculated intermolecular hardness parameters (defined by eq 4) of substituted cobalt phthalocyanines are related to their ORR catalytic activity[9]

$$\eta_{DA} = \frac{1}{2}(\epsilon_{SOMO/D} - \epsilon_{SOMO/A}) \qquad (4)$$

where $\epsilon_{SOMO/D}$ is the singly occupied molecular orbital of donor Co-Pcs and $\epsilon_{SOMO/A}$ is the singly occupied molecular orbital of acceptor $O_2$. This was attributed to the catalyst's ability to interact with $O_2$. The catalyst that has stronger interaction with dioxygen has better activity. Using the same experimental data,[9] we tried to explore the relationship between the oxygen-binding ability of substituted cobalt phthalocyanines with their oxygen reduction activity directly. We added another set of data with substituted iron phthalocyanines and FeTPyPz.[38] We plotted experimentally measured ORR catalytic activities with our calculated dioxygen-binding abilities. Figure 5 illustrates the result. For substituted cobalt phthalocyanines, there is a trend that the oxygen reduction catalytic activities are inversely related to their dioxygen-binding abilities. Thus, for these catalysts better ORR catalytic activity is associated with smaller dioxygen-binding energy. However, for substituted iron phthalocya-
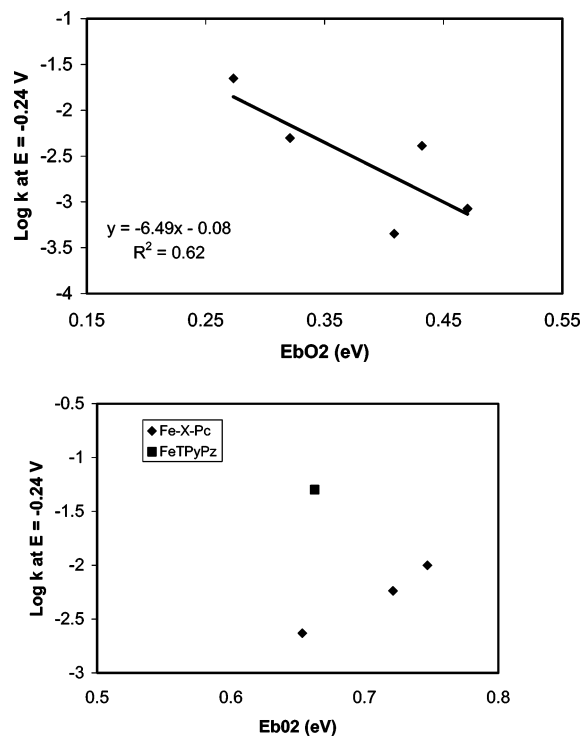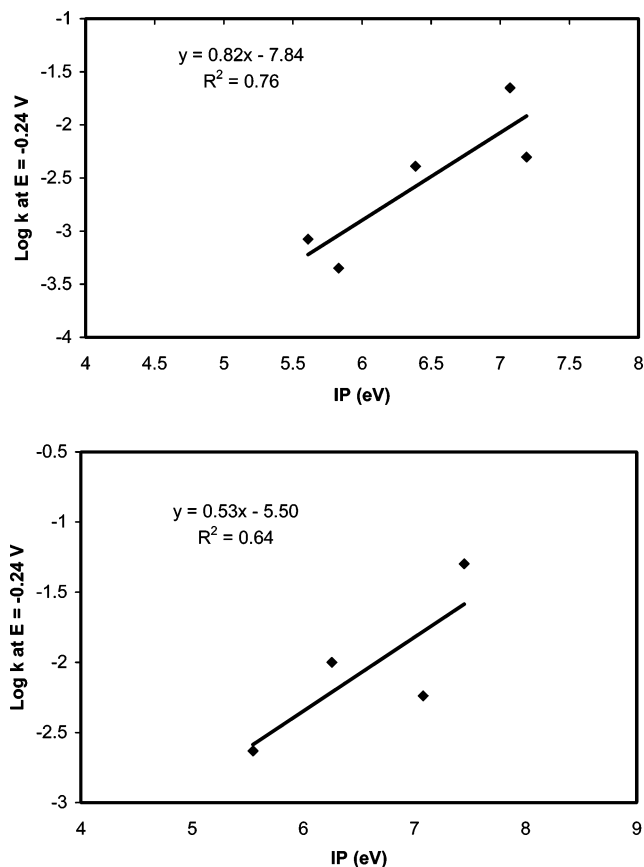
**Figure 5.** Plot of calculated oxygen-binding energies versus experimental oxygen electroreduction catalytic activities: (a) Co−X−Pc, X = H, F, MeO, TS, and TNP (ref 9); (b) Fe−X−Pc system with X = H, MeO, TS, and FeTPyPz (ref 38).

**Figure 6.** Plot of calculated IPs versus experimental oxygen electroreduction catalytic activities: (a) Co−X−Pc, X = H, F, MeO, TS, and TNP (from ref 9); (b) Fe−X−Pc system with X = H, MeO, TS, and FeTPyPz (ref 38).

nine systems, it seems the reverse is true (i.e., increasing dioxygen-binding energy increases the catalytic activity). FeT-PyPz dioxygen binding does not fall into the same line as that of Fe−X−Pc systems. Figure 6 illustrates the relationship between the catalyst's ORR activity and their IP. Good correlation is observed. Thus, the relationship observed between calculated hardness parameters and catalyst's ORR activities for substituted cobalt phthalocyanine[4,9] is actually the correlation between the IP of the catalyst and its ORR activity. In other words, the catalyst's ORR activity is related to its ionization potential or redox potential. This is in support of Randin and Becks' mechanism.[5,6] The larger the catalyst's ionization potential is, the faster the catalyst will be reduced following the first electron transfer to dioxygen and the larger its catalytic activity will be.

For porphyrin systems, it is known that cobalt derivatives are more active than iron derivatives, whereas with phthalocyanines, the reverse is true in most cases.[3,48] We intend to discuss this observed activity trend in light of catalyst's oxygen-binding ability and ionization potential.

In terms of ionization potential, we mentioned earlier that for porphyrin derivatives, the central atom affects its ionization potential greatly; in other words, the electron can be considered extracted from an orbital that has major contribution from central metal d orbital. Thus, cobalt porphyrin derivatives usually have higher IP values than the corresponding iron porphyrin derivatives. For phthalocyanine systems, the central metal has no significant effect on IP because the electron is extracted from an orbital that is mainly a ring orbital. Therefore, the difference in ionization potential between cobalt and iron phthalocyanine systems is usually small within 0.13 eV for the reported systems. Because the ionization potential of the transition metal macrocyclic complex is related to its catalytic activity, high IP is associated with high ORR catalytic activity. Thus for porphyrin derivatives, cobalt systems have much higher IP and, hence,

**TABLE 4: Calculated Activity Parameters of Transition Metal Macrocyclic Complexes**

|  | IP + $E_{bO_2}$ (eV) | | |
| --- | --- | --- | --- |
|  | Co | Fe | $\Delta$(IP + $E_{bO_2}$) (eV)[a] |
| MPc | 6.82 | 7.00 | -0.18 |
| MMeOPc | 6.08 | 6.20 | -0.12 |
| MF16Pc | 7.34 | 7.63 | -0.29 |
| MTSPc | 7.51 | 7.80 | -0.29 |
| MP | 7.11 | 7.03 | 0.08 |
| MTTP | 6.66 | 6.71 | -0.05 |
| MTPFPP | 7.42 | 7.38 | 0.04 |

[a] $\Delta$(IP + $E_{bO_2}$) = (IP + $E_{bO_2}$)$_{Co\ system}$ − (IP + $E_{bO_2}$)$_{Fe\ system}$

higher activity than the corresponding iron systems. For phthalocyanine systems, the difference between IP for cobalt and iron systems is small, so some other factors, such as dioxygen-binding capability contribute. It is interesting to consider the catalyst activity being measured by the sum of its IP and dioxygen-binding energy and compare the difference between cobalt and iron systems (see Table 4). For porphyrin systems, cobalt derivatives generally have a slightly larger sum value than that of iron. For phthalocyanine systems, cobalt derivatives have a much smaller value than that of iron. This simple exercise illustrates quantitatively the merit of the above argument. Therefore, for porphyrin systems, cobalt derivatives are more active than iron derivatives because they have high IPs. For phthalocyanine systems, iron derivatives are more active than cobalt phthalocyanine derivatives because they have better dioxygen-binding ability and similar IP.

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## Summary

In this paper, dioxygen-binding ability, ionization potential, and charge of transition metal macrocyclic systems are presented. These calculations demonstrated that dioxygen-binding abilities of the transition metal macrocyclic complexes are determined by central metal, ligand and substituents. For cobalt phthalocyanine systems electron-donating substituents increase its dioxygen-binding ability and electron-withdrawing substituents decrease the dioxygen-binding ability of the systems.

In general, the transition metal macrocyclic systems' ORR catalytic activity is related to its ionization potential and dioxygen-binding ability. Higher ionization potential and larger dioxygen-binding energy are associated with better catalytic activity. This is consistent with Randin and Becks' redox mechanism.[5,6] The activity trend observed for phthalocyanine and porphyrin systems can be rationalized with ionization potential and oxygen-binding ability. For porphyrin systems, cobalt derivatives have higher ionization potential and higher reactivity. For phthalocyanine systems, iron derivatives have good ionization potential and large oxygen-binding energy.

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