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Theoretical study of stability of metal-N₄ macrocyclic compounds in acidic media

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ABSTRACT

Fe and Co porphyrins and phthalocyanines are excellent catalysts for the oxygen reduction reaction (ORR) and are promising alternatives to Pt in fuel cells. However, the stability of these molecular catalysts in acidic media is poor. This study explores whether demetalation through proton exchange causes these metal macrocyclic catalysts to be unstable in acidic media. We first present a theoretical scheme for investigating exchange reactions of metal ions in metal macrocyclic compounds with protons in acidic media. The equilibrium concentrations of metal ions in solution when various metalloporphyrins (MPs) and metallophthalocyanines (MPcs) are brought into contact with a strongly acidic solution (pH = 1) were then estimated using density functional theory calculations; these values were used to evaluate the stability of these metal macrocyclic compounds against demetalation in acidic media. The results show that Fe, Co, Ni, and Cu phthalocyanines and porphyrins have considerable resistance to exchange with protons, whereas Cr, Mn, and Zn phthalocyanines and porphyrins easily undergo demetalation through ion exchange with protons. This suggests that the degradation in the ORR activity of Fe and Co macrocyclic molecular catalysts and of carbon materials doped with Fe(Co) and nitrogen, which are believed to have metal-nitrogen coordination structures similar to those of macrocyclic molecules as ORR catalytic centers, is not the result of replacement of metal ions by protons. The calculation results show that electron-donating substituents could enhance the stability of Fe and Co phthalocyanines.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are environmentally benign power generation devices that can effectively convert chemical energy to electricity, and therefore have potential application in electric vehicles and stationary power stations [1,2]. However, various technical and economic challenges hinder the widespread use of PEMFCs [3,4]; for example, because of the sluggish kinetics of the oxygen reduction reaction (ORR), a highly active cathode catalyst is needed [5,6]. At present, Pt and its alloys are still the most effective catalysts for

the ORR [7], but the limited supply and high cost of Pt are the main obstacles to the commercialization of PEMFCs [8,9]. Non-noble-metal catalysts with high activity in the ORR have therefore attracted much attention.

Various materials have been explored as non-noble-metal catalysts for the ORR, including heteroatom (N, B, S)-doped carbons [10–14], transition-metal- and nitrogen-codoped carbons [15–17], transition-metal chalcogenides [18,19], and transition-metal oxides [20]. Among these materials, metal- and nitrogen-codoped carbons, i.e., M-N-C materials (M is usually Fe or Co), have shown great promise [21–24], with ORR

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activity approaching those of Pt-based catalysts. However, these materials are generally poorly stable in acidic media.

It is generally accepted that metal-nitrogen coordination structures (e.g., M-N₄) are the main catalytic sites in Fe-N-C materials for the ORR [25,26]. The poor stability of this class of materials is caused by exchange of the metal ions in the M-N₄ structures with protons and/or oxidative attack by the peroxide intermediates formed in the ORR [27]. Metalloporphyrins and metallophthalocyanines are the two main types of metal macrocyclic compounds containing M-N₄ coordination structures. And they are excellent molecular catalysts for various reactions, especially ORRs in alkaline media [28–32]. But they have poor activity and stability in acidic solutions [33–40].

We used density functional theory (DFT) calculations to investigate possible ion-exchange reactions between metal ions in various metalloporphyrins and metallophthalocyanines and protons in strongly acidic solutions (pH = 1) to determine whether the replacement of metal ions by protons degrades the performances of M-N-C materials and metal macrocyclic compounds in acidic media. The results show that ORR-active Fe and Co macrocyclic molecular catalysts are stable against ion-exchange with protons; this suggests that the performance degradation of these molecular catalysts and the corresponding M-N-C catalysts is not caused by replacement of metal ions by protons.

2. Computational details

Spin-polarized DFT calculations implemented with the DMol³ module [41] in the BIOVIA Accelrys Materials Studio program were used. The exchange-correlation functionals were based on the Perdew-Burke-Ernzerhof functional within the generalized gradient approximation. Core treatment was adopted for all electron relativistic methods to obtain metal relativistic effects. Double numerical plus polarization function basis sets were used in the calculations. A smearing of 0.005 Ha (1 Ha = 27.21 eV) was applied to the orbital occupation. Geometric optimizations were performed using the Broyden-Fletcher-Goldfarb-Shanno algorithm and the geometric convergence tolerance for the energy change, maximum force, and maximum displacement were 1×10^{-5} Ha, 0.002 Ha/Å (1 Å = 0.1 nm), and 0.005 Å, respectively. Self-consistent-field procedures were performed with a convergence criterion of 1×10^{-6} Ha on the total energy to achieve accurate electronic convergence. The total energy (E) of all electrons involved in the system was obtained from geometric optimization of the molecular structure, and the zero-point energy (E_{ZPE}) and entropy (S) corrections (at 0.1 MPa, 298.15 K) were calculated using frequency analysis.

3. Results and discussion

3.1. Thermodynamic scheme for investigating stability of metal macrocyclic molecules against ion exchange with protons

Ion exchange between metal ions and protons was investigated in a thermodynamic scheme by calculating the free en-

ergy of the following reaction:

where M = Cr, Mn, Fe, Co, Ni, Cu, or Zn, and P = phthalocyanine (Pc) or porphyrin (P). The free energy of reaction (1) can be obtained from the chemical potentials (μ) of the species involved:

$$\Delta G = \mu_{\text{H}_2\text{P}} + \mu_{\text{M}^{2+}} - \mu_{\text{MP}} - 2\mu_{\text{H}^+} \quad (2)$$

The chemical potentials of the metal-coordinated and protonated macrocyclic molecules, i.e., μ_{MP} and $\mu_{\text{H}_2\text{P}}$, can be estimated from the DFT-calculated total energy (E), zero-point energy (E_{ZPE}), and entropy (S) of the corresponding molecules, i.e., $\mu_{\text{H}_2\text{Pc}} = E_{\text{H}_2\text{Pc-total}} + E_{\text{H}_2\text{Pc-ZPVE}} - TS_{\text{H}_2\text{Pc}}$. The chemical potential of M^{2+} in solution, $\mu_{\text{M}^{2+}}$, can be estimated from

$$\mu_{\text{M}^{2+}} = \mu_{\text{M}} + 2eU_{\text{M}^{2+}/\text{M}}^0 + RT\ln c_{\text{M}^{2+}} \quad (3)$$

where $c_{\text{M}^{2+}}$ is the concentration of M^{2+} in the medium, $U_{\text{M}^{2+}/\text{M}}^0$ is the standard equilibrium electrode potential of $\text{M}^{2+} + 2\text{e}^- = \text{M}$ (these can be found in Ref. [42]), and μ_{M} is the chemical potential of metal atom M and can be estimated from the DFT-calculated cohesive energy (E_{M}), zero-point energy ($E_{\text{M-ZPE}}$), and vibrational entropy (S_{M}) of metal M, i.e., $\mu_{\text{M}} = E_{\text{M}} + E_{\text{M-ZPE}} - TS_{\text{M}}$.

The chemical potential of a proton in the solution [43] can be calculated as

$$\mu_{\text{H}^+} = 1/2\mu_{\text{H}_2} + RT\ln c_{\text{H}^+} \quad (4)$$

where c_{H^+} is the proton concentration, which is 0.1 mol/L for pH = 1, and μ_{H_2} is the chemical potential of H_2 gas at 0.1 MPa. Here, $1/2\mu_{\text{H}_2}$ is used as a substitute for the standard chemical potential of H^+ in solution (μ_{H^+}); they have the same value because the zero reference potential is set at the potential of the standard hydrogen electrode. The chemical potential of H_2 can be estimated from the DFT-calculated total energy (E), zero-point energy (E_{ZPVE}), and entropy (S), i.e., $\mu_{\text{H}_2} = E_{\text{H}_2\text{-total}} + E_{\text{H}_2\text{-ZPVE}} - TS_{\text{H}_2}$. In the above equations, T is the experimental temperature, i.e., 298.15 K.

Eqs. (2)–(4) can be used to calculate the equilibrium concentration of M^{2+} in the solution by setting $\Delta G = 0$, at which exchange equilibrium is reached between MP molecules and protons. The amount of MP molecules that undergo degradation through demetalation is then $Vc_{\text{M}^{2+}}\bar{M}_{\text{M}}$, where V is the volume of the solution used in the measurement, which is assumed to be 50 mL here, and $\bar{M}_{\text{MP}}$ is the molar mass of the corresponding MP. The percentage of degraded MPs can be estimated as

$$x\% = 100Vc_{\text{M}^{2+}}\bar{M}_{\text{MP}}/m_{\text{t}} \quad (5)$$

where m_{t} is the total mass of MP loaded on the electrode, which is usually from a few tens to hundreds of micrograms per square centimeter.

3.2. Effects of metal ions on stability of metal macrocyclic compounds

Table 1 gives the equilibrium concentrations of M^{2+} and the demetalation percentages for various MPs and MPcs on an electrode of diameter 5 mm, estimated according to the procedure described in section 3.1 (assuming that the loading of MPs

on electrode is $150 \mu\text{g}/\text{cm}^2$). The data show that MPs with Cr, Mn, and Zn metal centers are less stable than other MPs under strongly acidic conditions; for example, the equilibrium concentrations of Cr^{2+} , Mn^{2+} , and Zn^{2+} are greater than 0.07 mol/L when the corresponding MPs are in contact with a solution of $\text{pH} = 1$. This corresponds to a demetalation amount of about $2.0 \times 10^6 \mu\text{g}$, and is several orders of magnitude higher than the total mass of MPs normally loaded on the electrode for electrocatalysis. The MPs with Fe^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} metal centers are fairly stable under strongly acidic conditions, with ion equilibrium concentrations less than $3.2 \times 10^{-15} \text{ mol/L}$, which are negligibly low and below the possible detection limit. Fe- and Co-based metal macrocyclic molecules are usually used as ORR electrocatalysts, therefore we can conclude that the exchange of metal ions with protons is not the main cause of performance degradation for these molecular catalysts. Similar conclusions can be drawn for carbon materials doped with Fe (Co) and nitrogen, which are believed to contain similar metal-nitrogen coordination structures to those in macrocyclic molecules as ORR catalytic centers.

A possible reason for the poor stability of MPs with central Cr, Mn, and Zn atoms is that the $3d$ orbitals of these three metals are half filled ($3d^5$) or fully filled ($3d^{10}$), which reduces the ability of the $3d$ orbitals to coordinate with nitrogen and other atoms. For a given metal, MPc is more stable than MP in strongly acidic solutions. This is because π -conjugation is greater for phthalocyanines than for porphyrins, which results in shorter and stronger M–N bond. The MP stability order is $\text{CoPc} > \text{NiPc} > \text{FePc} > \text{CuPc}$ and $\text{CoP} > \text{NiP} > \text{CuP} > \text{FeP}$, which is approximately consistent with the Lewis acidity with the bivalent cations: $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Fe}^{2+} > \text{Cu}^{2+}$ [44].

3.3. Effects of substituents on stability of metal macrocyclic compounds

The electronic structures of metal macrocyclic molecules can be altered by introducing substituents. We therefore investigated the effects of various substituents on the stability of Fe and Co phthalocyanines in acidic media. Fe and Co phthalocyanines with halogen (F-, Cl-), nitro (NO_2 -), methyl (Me-), tertiary

Table 1

Equilibrium concentrations of exchanged metal ions, mass of demetalated MPs (m), and demetalation percentages on 5-mm electrode in solution of $\text{pH} = 1$ (assuming $m_t = 150 \mu\text{g}/\text{cm}^2$).

MPs/MPcs	$c_{\text{M}^{2+}}/(\text{mol/L})$	$m/\mu\text{g}$	$x/\%$
CrPc	$\sim 7 \times 10^{-2}$	$\sim 1 \times 10^6$	$\sim 7 \times 10^4$
MnPc	$\sim 5 \times 10^{-1}$	$\sim 1 \times 10^7$	$\sim 5 \times 10^5$
FePc	$\sim 1 \times 10^{-23}$	$\sim 4 \times 10^{-16}$	$\sim 1 \times 10^{-17}$
CoPc	$\sim 4 \times 10^{-30}$	$\sim 1 \times 10^{-22}$	$\sim 4 \times 10^{-24}$
NiPc	$\sim 4 \times 10^{-29}$	$\sim 1 \times 10^{-21}$	$\sim 4 \times 10^{-23}$
CuPc	$\sim 4 \times 10^{-22}$	$\sim 1 \times 10^{-14}$	$\sim 4 \times 10^{-16}$
ZnPc	$\sim 2 \times 10$	$\sim 5 \times 10^8$	$\sim 1 \times 10^7$
CrP	$\sim 2 \times 10^{-4}$	$\sim 3 \times 10^3$	$\sim 1 \times 10^2$
MnP	$\sim 1 \times 10^8$	$\sim 3 \times 10^{15}$	$\sim 9 \times 10^{13}$
FeP	$\sim 3 \times 10^{-15}$	$\sim 6 \times 10^{-8}$	$\sim 2 \times 10^{-9}$
CoP	$\sim 3 \times 10^{-22}$	$\sim 6 \times 10^{-15}$	$\sim 2 \times 10^{-16}$
NiP	$\sim 1 \times 10^{-21}$	$\sim 2 \times 10^{-14}$	$\sim 6 \times 10^{-16}$
CuP	$\sim 4 \times 10^{-18}$	$\sim 8 \times 10^{-11}$	$\sim 3 \times 10^{-12}$
ZnP	$\sim 2 \times 10^3$	$\sim 4 \times 10^{10}$	$\sim 1 \times 10^9$

butyl ($t\text{Bu}$ -), and amino (NH_2 -) substituents were considered (Fig. 1), respectively. The structures are denoted by 16F-MPc, 16Cl-MPc, 4 NO_2 -MPc, 4F-MPc, 4Cl-MPc, 4 NH_2 -MPc, 4Me-MPc, and 4 $t\text{Bu}$ -MPc ($\text{M} = \text{Fe}$ or Co), based on the type and number of substituents. Our DFT geometric optimization showed that 16Cl-FePc has a distorted structure, different to those of the other substituted FePcs.

Table 2 gives the equilibrium concentrations of M^{2+} and the demetalation percentages for various substituted metallophthalocyanines on electrodes of diameter 5 mm, estimated using the procedure described in section 3.1 (assuming that the MP loading on the electrode is $150 \mu\text{g}/\text{cm}^2$). A comparison of the results shown in Tables 1 and 2 shows that the demetalation percentages of FePc and CoPc with electron-donating substituents (Me-, NH_2 -, $t\text{Bu}$ -) are lower than those of the parent compounds, which indicates that the stability of FePc and CoPc can be enhanced by introducing electron-donating substituents into the macrocycles.

Electron-withdrawing substituents, i.e., 4Cl-, 4F-, and 16Cl-, enhance the stability of FePc to some extent; however, strongly electron-withdrawing groups such as 4 NO_2 - and 16F- decrease the stability of FePc. Electron-withdrawing substituents all decrease the stability of CoPc, and the destabilization increases with increasing electron-withdrawing ability. However, regardless of whether the substituents were electron-withdrawing or electron-donating, the equilibrium concentrations of Fe^{2+} and Co^{2+} were lower than $4.4 \times 10^{-14} \text{ mol/L}$ when the corresponding MPs were in contact with a solution of $\text{pH} = 1$. This corresponds to negligible demetalation of the corresponding MPs for electrodes under normal electrocatalytic conditions.

3.4. Further discussion

As already stated in the introduction, demetalation via exchange of metal ions with protons during the ORR is a possible cause of degradation of metal- N_4 compounds in acidic media. Our calculations show that ORR-active metal- N_4 macrocyclic compounds have considerable resistance to exchange with protons. Although our results cannot confirm whether such molecular catalysts are stable in ORRs in acidic media, they show that the replacement of metal ions by protons is not the reason for the performance degradation of ORR-active Fe and Co macrocyclic molecular catalysts and carbon materials doped

Fig. 1. Molecular structures of substituted metal phthalocyanines: $\text{M} = \text{Fe}$ or Co ; $\text{R} = \text{F}$ or Cl ; $\text{R}_1 = \text{NH}_2$, Me, $t\text{Bu}$, NO_2 , or Cl, F.

Table 2

Equilibrium concentrations of exchanged metal ions, mass of demetallated MPs (m), and demetalation percentages on 5-mm electrode in solution of pH = 1 (assuming $m_t = 150 \mu\text{g}/\text{cm}^2$).

MPs	$c_{M^{2+}}/(\text{mol/L})$	$m/\mu\text{g}$	$x/\%$
4Me-FePc	$\sim 1 \times 10^{-26}$	$\sim 4 \times 10^{-19}$	$\sim 1 \times 10^{-20}$
4NH ₂ -FePc	$\sim 5 \times 10^{-26}$	$\sim 2 \times 10^{-18}$	$\sim 5 \times 10^{-20}$
4tBu-FePc	$\sim 5 \times 10^{-28}$	$\sim 2 \times 10^{-20}$	$\sim 6 \times 10^{-22}$
4Cl-FePc	$\sim 7 \times 10^{-25}$	$\sim 2 \times 10^{-17}$	$\sim 8 \times 10^{-19}$
4F-FePc	$\sim 5 \times 10^{-25}$	$\sim 2 \times 10^{-17}$	$\sim 6 \times 10^{-19}$
4NO ₂ -FePc	$\sim 7 \times 10^{-21}$	$\sim 3 \times 10^{-13}$	$\sim 9 \times 10^{-15}$
16Cl-FePc	$\sim 5 \times 10^{-25}$	$\sim 3 \times 10^{-17}$	$\sim 9 \times 10^{-19}$
16F-FePc	$\sim 4 \times 10^{-14}$	$\sim 2 \times 10^{-6}$	$\sim 6 \times 10^{-8}$
4Me-CoPc	$\sim 5 \times 10^{-33}$	$\sim 2 \times 10^{-25}$	$\sim 6 \times 10^{-27}$
4NH ₂ -CoPc	$\sim 3 \times 10^{-33}$	$\sim 9 \times 10^{-26}$	$\sim 3 \times 10^{-27}$
4tBu-CoPc	$\sim 3 \times 10^{-33}$	$\sim 1 \times 10^{-25}$	$\sim 4 \times 10^{-27}$
4Cl-CoPc	$\sim 4 \times 10^{-30}$	$\sim 2 \times 10^{-22}$	$\sim 5 \times 10^{-24}$
4F-CoPc	$\sim 3 \times 10^{-30}$	$\sim 1 \times 10^{-22}$	$\sim 3 \times 10^{-24}$
4NO ₂ -CoPc	$\sim 1 \times 10^{-32}$	$\sim 4 \times 10^{-25}$	$\sim 1 \times 10^{-26}$
16Cl-CoPc	$\sim 9 \times 10^{-30}$	$\sim 5 \times 10^{-22}$	$\sim 2 \times 10^{-23}$
16F-CoPc	$\sim 1 \times 10^{-21}$	$\sim 6 \times 10^{-14}$	$\sim 2 \times 10^{-15}$

with Fe (Co) and nitrogen, which are believed to contain similar metal-nitrogen coordination structures to those of macrocyclic molecules as ORR catalytic centers.

The oxygenated species produced during the ORR, e.g., peroxide intermediates, could also cause degradation of metal-N₄ macrocyclic compounds. The ORR mechanism needs to be investigated to fully understand the stability of macrocyclic molecular catalysts for ORRs in acidic media; and this is a complicated and challenging task. It is difficult for us to cover this in the present paper, but our calculation results suggest that the degradation of these molecular catalysts may be caused by attack by peroxide intermediates formed during the ORR.

Hydrogen peroxide can destroy materials by forming hydroxyl radicals in the presence of metal ions through the Fenton reaction [45,46]:

The negligible demetalation of ORR-active Me-N₄ molecules shown by the present calculations suggests that peroxide attack on these Me-N₄ compounds would not be strong, as is generally believed, unless the medium is contaminated by metal ions.

4. Conclusions

A theoretical scheme was established to investigate exchange between metal ions of metallophthalocyanines and metalloporphyrins with protons in acidic media. The equilibrium concentrations of metal ions in solution were obtained, using DFT calculations, for various transition-metal phthalocyanines and porphyrins in contact with a strongly acidic solution, i.e., pH = 1. The results show that Fe, Co, Ni, and Cu phthalocyanines and porphyrins are stable against ion exchange with protons in acidic media, but Cr, Mn, and Zn ions in phthalocyanines and porphyrins are easily replaced by protons. In addition, it was found that electron-donating substituents enhance the stability of metal phthalocyanines. These results suggest that the exchange of metal ions with protons is not the main cause of performance degradation of Fe/Co-based macrocyclic molecules and Fe/Co-N-C materials, which are being widely investigated as non-noble-metal electrocatalysts for the ORR to replace Pt in fuel cells.

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Graphical Abstract

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Theoretical study of stability of metal-N₄ macrocyclic compounds in acidic media

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Demetalation through exchange with protons is not the main cause of performance degradation of Fe/Co-N₄-based electrocatalysts in acidic media, because these materials are stable against exchange with protons.

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密度泛函理论计算研究金属-N₄大环化合物在酸性介质中的稳定性

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摘要: 质子交换膜燃料电池 (PEMFCs) 是一种能够有效地将化学能转换成电能的装置, 其具有较高的效率及功率密度, 还兼具环境友好的优点, 因而在电动车和分布式电站等领域有广泛应用前景。然而, 昂贵的价格及较差的耐久性阻碍了 PEMFCs 的广泛应用。阴极氧还原反应 (ORR) 缓慢的动力学是限制 PEMFCs 性能的主要因素。目前, Pt 及其合金仍然是最有效的 ORR 催化剂。有限的 Pt 供应量是 PEMFC 商业化的主要障碍之一。因此, 具有较高 ORR 活性的非贵金属催化剂越来越多的引起了人们的关注。在众多非贵金属 ORR 催化剂中, Fe, Co 等金属与氮共掺杂的碳材料最有望取代 Pt。一般认为, 这类材料中起催化作用的活性中心是与金属酞菁 (MPc) 和卟啉 (MP) 等大环分子类似的金属-N₄ 配位结构。无论是 MPc 和 MP, 还是掺杂碳材料催化剂, 在酸性介质中的耐久性都不够好。具体原因至今仍未有定论。一些研究者认为中心金属离子与酸性介质中的质子交换引起的去金属中心是原因之一。我们通过密度泛函理论计算和热力学分析研究酸性介质 (pH=1) 中金属大环分子中金属离子和溶液中质子的交换反应, 探讨去金属中心是否是造成金属大环类分子催化剂和金属与氮共掺杂碳基催化剂在酸性介质中不稳定的原因。

我们建立了研究金属大环化合物中心金属离子与溶液中质子的交换反应的热力学分析方法。在此基础上借助密度泛函理论计算获得各种金属酞菁和卟啉在强酸性介质中的金属离子平衡浓度, 以确定相应金属大环分子的稳定性。研究结果表明, 在酸性介质中铬、锰、锌类酞菁和卟啉分子很容易被质子化而形成相应的非金属酞菁和卟啉, 原因可能是这三类金属的二价阳离子的 3d 轨道均为半充满或者全充满状态, 使得它们与氮的配位能力下降; 而铁、钴、镍、铜类酞菁和卟啉在酸性介质中金属化离子的平衡浓度几乎为零, 表明它们基本上不发生金属离子与质子的交换反应, 且稳定性趋势为 CoPc > NiPc > FePc > CuPc 和 CoP > NiP > CuP > FeP, 同时, 相应的金属酞菁比金属卟啉更稳定。这表明具有氧化还原活性的铁、钴类大环分子催化剂及铁、钴与氮共掺杂的碳材料在酸性溶液中的活性衰减并不是由于金属离子与质子的交换引起的。

我们还考察了取代基对大环分子中金属离子与质子交换反应的影响, 结果发现, 给电子取代基 (甲基, 氨基, 叔丁基) 会极大地增强酞菁铁和酞菁钴在酸性介质中的稳定性。对于酞菁铁而言, 具有中等强度吸电子效应的四氯、四氟和十六氯取

代后, 其在酸性中稳定性有一定程度的增强, 而具有强烈吸电子效应的四硝基及十六氟取代后, 稳定性则降低. 对于酞菁钴而言, 上面提到的所有吸电子取代基都会使得其在酸性介质中变得更加不稳定, 并且其不稳定程度随着取代基吸电子能力的增强而上升.

关键词: 金属卟啉; 金属酞菁; 去金属化; 金属离子-质子交换反应; 密度泛函理论计算; 取代基

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