

学校编码：10384
学号：20520100153685

分类号____密级____
UDC_____

廈門大學

博 士 学 位 论 文

金属卟咯催化与光电性质的理论研究

Computational Characterization of Catalytic and
Photoelectronic Properties of Metal-Corroles

朱 纯

指导教师姓名：曹泽星 教授

申请学位级别：理 学 博 士

专 业 名 称：物 理 化 学

论文提交日期：2013 年 5 月

论文答辩时间：2013 年 5 月

学位授予日期：2013 年 月

答辩委员会主席：_____

评阅人：_____

2013 年 6 月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果,均在文中以适当方式明确标明,并符合法律规范和《厦门大学研究生学术活动规范(试行)》。

另外,该学位论文为()课题(组)的研究成果,获得()课题(组)经费或实验室的资助,在()实验室完成。(请在以上括号内填写课题或课题组负责人或实验室名称,未有此项声明内容的,可以不作特别声明。)

声明人(签名):

年 月 日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

1. 经厦门大学保密委员会审查核定的保密学位论文，
于 年 月 日解密，解密后适用上述授权。

2. 不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

200 年 月 日

目 录

摘 要	I
Abstract.....	III
第一章 绪论	1
1.1 咪咯的结构、性质及应用	1
1.1.1 咪咯的结构及性质.....	1
1.1.2 金属咪咯的应用.....	2
1.1.2.1 催化氧化作用.....	2
1.1.2.2 催化还原作用.....	4
1.1.2.3 催化基团转移反应.....	4
1.1.2.4 咪咯传感器.....	4
1.1.2.5 染料敏化太阳能电池方面的应用.....	5
1.1.2.6 医疗方面的应用.....	5
1.2 金属咪咯的催化机理	5
1.3 染料敏化太阳能电池	7
1.3.1 太阳能电池的发展与分类.....	7
1.3.2 染料敏化太阳能电池的工作原理.....	9
1.3.3 染料敏化太阳能电池性能的主要参数.....	10
1.3.3.1 光电转化效率.....	10
1.3.3.2 短路电流密度.....	11
1.3.3.3 开路电压.....	11
1.3.3.4 填充因子.....	11
1.3.3.5 总的光电能转化效率.....	12
1.3.4 太阳能电池中染料分子的特点与种类.....	12
1.3.4.1 染料分子的特点.....	12
1.3.4.2 染料分子的种类.....	13
1.4 本论文研究的目的	13
参考文献	15

第二章 计算方法	19
2.1 密度泛函理论 (DFT)	19
2.1.1 Thomas-Fermi (T-F) 模型.....	21
2.1.2 Hohenberg-Kohn 定理.....	22
2.1.3 Kohn-Sham 方程	23
2.1.4 近似密度泛函.....	24
2.1.4.1 局域密度近似.....	24
2.1.4.2 含密度梯度校正的泛函.....	25
2.1.4.3 杂化密度泛函.....	27
2.2 含时密度泛函理论	28
2.3 基函数的选择	29
2.3.1 高斯型基组.....	29
2.3.2 Slater 型基组	29
2.3.3 STO-nG 型极小基组.....	30
2.3.4 价分裂基.....	30
2.3.5 扩展基组.....	30
2.3.6 赝势基组.....	31
2.4 过渡态理论	31
2.5 固体能带计算方法	32
2.5.1 投影缀加波方法.....	32
2.6 本论文主要采用的计算软件包	33
参考文献:	35
第三章 锰氧卟啉催化氧原子转移反应中自旋反转效应与多态反应活性的理论研究	37
3.1 前言	37
3.2 计算方法	38
3.2.1 卟啉氧化剂模型.....	38
3.2.2 量子化学计算方法.....	41

3.3 结果和讨论	41
3.3.1 结构和成键	41
3.3.2 氧原子转移反应的机理	46
3.3.2.1 能量和路径	46
3.3.2.2 取代基对氧原子转移反应的影响	49
3.3.2.3 自旋反转对氧原子转移反应的影响	51
3.4 结论	55
参考文献	56
第四章 五价锰氧咪咯活性氧化剂光诱导形成机理的理论研究	60
4.1 前言	60
4.2 计算方法	62
4.3 结果和讨论	62
4.3.1 锰咪咯的几何结构和电子性质	62
4.3.2 五价锰氧咪咯产生的机理	64
4.3.2.1 锰咪咯与氧的反应	64
4.3.2.2 五价锰氧咪咯的产生	67
4.4 结论	68
参考文献	69
第五章 锰氧咪咯催化氧化环己烷成己二醛反应机理的理论研究	71
5.1 前言	71
5.2 计算方法	72
5.2.1 反应过程设计与计算模型	72
5.2.2 量子化学计算方法	72
5.3 结果与讨论	73
5.3.1 第一步羟基化	73
5.3.2 第二步羟基化	75
5.3.3 C-C 键断裂和己二醛生成	77
5.3 结论	80
参考文献	82

第六章 高效金属双咪咯染料的计算设计及其敏化 TiO₂ 半导体复合体系的理论研究	84
6.1 前言	84
6.2 计算方法	85
6.3 结果与讨论	86
6.3.1 自由金属咪咯染料的电学和光学性质.....	86
6.3.1.1 金属单咪咯染料.....	86
6.3.1.2 独特的金属双咪咯染料.....	88
6.3.2 染料-TiO ₂ 体系的电学和光学性质	97
6.3.2.1 染料在 TiO ₂ 表面的吸附	97
6.3.2.2 能带结构和态密度.....	99
6.3.3 电子注入机理.....	100
6.4 结论	101
参考文献	102
发表论文	107
致 谢	108

TABLE OF CONTENTTS

Abstract..... III

Chapter 1 Introduction..... 错误！未定义书签。 1

1.1 The structures, properties and applications of corroles..... 1

 1.1.1 The structures and porperties of corroles 1

 1.1.2 The applications of metal-corroles..... 2

 1.1.2.1 Catalytic oxidation 2

 1.1.2.2 Catalytic rduction..... 4

 1.1.2.3 Catalytic group transfer..... 4

 1.1.2.4 Corrole-based sensors 4

 1.1.2.5 The application in dye sensitized solar cells..... 5

 1.1.2.6 The Medicinal applications..... 5

1.2 The catalytic activity of metal-corroles 5

1.3 Dye sensitized solar cells..... 7

 1.3.1 The development and classification of solar cells 7

 1.3.2 The working principle of dye sensitized solar cells..... 9

 1.3.3 The main parameters of dye sensitized solar cells..... 10

 1.3.3.1 Monochromatic incident photo-to-electron conversion efficiency.. 10

 1.3.3.2 Current Density of Short Circuit..... 11

 1.3.3.3 Voltage of Open Circuit..... 11

 1.3.3.4 Fill Factor..... 11

 1.3.3.5 Total light-to-electric energy conversion efficiency 12

 1.3.4 The features and classification of dye molecules 12

 1.3.4.1 The features of dye molecules 12

 1.3.4.2 The classification of dye molecules..... 13

1.4 Objectives of this paper 13

References 15

Chapter 2 Computational methods.....1919

2. 1 Density functional theory	19
2. 1. 1 Thomas-Fermi model	21
2. 1. 2 Hohenberg-Kohn equation	22
2. 1. 3 Kohn-Sham equation	23
2. 1. 4 Density functional	24
2. 1. 4. 1 Local density approximation	24
2. 1. 4. 2 Generalized gradient approximation	25
2. 1. 4. 3 Hybrid functional	27
2. 2 Time-dependent density functional theory	28
2. 3 Basis function	29
2. 3. 1 Gauss basis function	29
2. 3. 2 Slater function	29
2. 3. 3 STO-nG minimal basis sets	30
2. 3. 4 Split-valence basis sets	30
2. 3. 5 Expensive basis sets	30
2. 3. 6 Pseudo basis sets	31
2. 4 Transition state theory	31
2. 5 Methods of energy bandstructure in solid	32
2. 5.1 Projector Augmented Wave	32
2. 6 Computational package used in this paper	33
References	35
Chaper 3 Significant effect of spin Flip on the oxygen atom transfer reaction from (Oxo)manganese(V) corroles to thioanisole: insight from density functional calculations	37
3.1 Introduction	37
3.2 Computational details	38
3.2.1 Models of the corrole-based oxidants	38
3.2.2 Quantum chemical calculation methods	41
3.3 Results and discussion	41

3.3.1 Structure and bonding	41
3.3.2 Mechanism of the OAT reaction	46
3.3.2.1 Pathway and energetics	46
3.3.2.2 Effect of substitution on OAT	49
3.3.2.3 Effect of spin flip on OAT	51
3.4 Conclutions	55
References	56
Chapter 4 Theoretical investigations on the generation of	
(Oxo)manganese(V) corrole from O₂ and visible Light	60
4.1 Introduction	60
4.2 Computational details	62
4.3 Results and discussion	62
4.3.1 Structure and electronic properties	62
4.3.2 The reaction mechanism	64
4.3.2.1 The reaction of Mn-corrole and O ₂	64
4.3.2.2 The generation of (Oxo)manganese(V) corrole	67
4.4 Conclusion	68
References	69
Chapter 5 Theoretical investigation on Mn-corrole catalyzed	
oxidation of cyclohexane to adipaldehyde	71
5.1 Introduction	71
5.2 Computational details	72
5.2.1 The reaction process	72
5.2.2 Quantum chemical calculation methods	72
5.3 Results and discussion	73
5.3.1 First hydroxylation step	73
5.3.2 Second hydroxylhydroxylation step	75
5.2.3 C-C bond cleavage and adipaldehydeformation	77

5.3 Conclusion	80
References	82
 Chapter 6 Unique metal di-corrole dyes with excellent photoelectronic properties for solar cells: insight from density functional calculations	
6.1 Introduction	84
6.2 Computational details	85
6.3 Results and discussion	86
6.3.1 Electronic and optical properties of free metal-corrole dyes	86
6.3.1.1 Metal-mono-corrole dyes.....	86
6.3.1.2 Unique metal-di-corrole dyes	88
6.3.2 Electronic and optical properties of the dye-TiO ₂ system	97
6.3.2.1 Adsorption of dye on the TiO ₂ surface.....	97
6.3.2.2 Energy band structure and density of states.....	99
6.3.3 Electron injection mechanism.....	100
6.4 Conclusion	101
References	102
List of Publications	107
Acknowledgements	108

摘 要

咪咯是一种新型的类卟啉大环化合物,具有特殊的电子结构和优良的光电性质,在催化、染料敏化太阳能电池、传感器以及医学等研究领域具有广泛的应用前景。和受到广泛关注的金属卟啉相比,金属咪咯的研究相对较少,目前对其特殊性质及其参与的化学、物理过程的微观机制缺乏深入了解。例如,关于咪咯基催化剂活性与催化机理的认识还存在很大的争议;导致咪咯染料敏化太阳能电池(Dye-Sensitized Solar Cells, DSCs)低光电转化效率的关键因素不清楚等。本文通过密度泛函理论计算,对锰氧咪咯催化氧原子转移、分子氧氧化氮杂锰咪咯成活性氧物种的光氧化过程、锰氧咪咯催化环己烷氧化成己二醛等反应进行了深入的研究。此外,为了改进咪咯太阳能电池的光电能转化效率,理论上设计并研究了一类新型的金属双咪咯染料,基于计算结果,讨论了这类新型金属双咪咯染料TiO₂体系的电子注入机制。

本文获得的主要结果如下:

- (1) 通过广泛的密度泛函计算,探明了金属咪咯催化氧原子转移反应的多态活性和显著的旋-轨耦合效应。锰氧咪咯催化底物的氧原子转移反应,在单重态势能面上,反应通常需要克服较高的反应能垒,而三重态的反应从热力学和动力学上来看都容易得多。尽管在咪咯 *meso* 位引入拉电子取代基在某种程度上能提高氧原子转移反应的活性,但最显著的变化来源于氧原子转移反应中的自旋反转。*meso* 位五氟苯取代的锰氧咪咯的 β 位碳原子上的溴代能极大地增大单-叁态势能面交叉点的自旋轨道耦合,从而有效的促进氧原子转移反应通过三态势能面进行,显著增强了 β 位溴代锰氧咪咯催化氧原子转移的活性。
- (2) 计算表明,光诱导制备氮杂五价锰氧咪咯活性氧化剂的反应中,基态的氮杂锰氧咪咯与基态氧分子首先形成弱相互作用的三重态复合物,在光照条件下,该复合物中分子氧和锰咪咯间的强烈相互作用引起前线轨道间电子转移重排,形成分子氧双自由基活性中间体。该自由基可以很容易夺取底物的 H,并通过快速的自由基反应过程生成高价的氮杂锰氧咪咯活性氧化剂。
- (3) 锰氧咪咯催化环己烷氧化成己二醛的反应经历了两步羟基化和一步碳碳

键断裂过程。两步羟基化都是由氢转移开始，形成碳自由基中间体，接着迅速发生的自由基反应形成二醇的中间体。碳-碳键断裂过程由氢转移开始，先形成氧自由基中间体，氧自由基单电子和邻近环 C-C 键存在强烈的相互作用，导致该碳-碳键活化断裂和第二个氢的协同转移。反应的速控步是第二步羟基化过程，因此碳自由基中间体的稳定性决定了该反应的难易，这也解释了实验上观察到叔碳的活性大于仲碳的活性顺序。

- (4) 基于理论计算，设计了一类新型的金属双咪咯染料分子，它们在可见光范围内有很强的光吸收性质，其激发态具有优良的电荷分离性质。通过 π 共轭桥基的引入可以很好地调控它们的光电性质；通过在它的咪咯环的 *meso* 位引入拉电子基团能够调节该染料分子的前线轨道的能级，使其与不同的氧化还原电对的电势很好的匹配。通过对染料/TiO₂ 体系的第一性原理计算研究，详细地讨论了电子直接注入和间接注入机理。

关键词：金属咪咯； 催化活性； 氧原子转移反应； 双自由基； 金属双咪咯染料染料； 敏化太阳能电池； 电子注入机制； 密度泛函理论。

Abstract

Corroles, as the ring-contracted analogues of porphyrins, are also aromatic macrocyclic systems constructed by the four conjugated pyrrole rings. Similar to metal-porphyrins, metal-corroles exhibit novel electronic and photoelectronic properties and they are promising in the fields of catalysis, dye-sensitized solar cell, sensor, medicine, and etc. However, in comparison with the well-studied metal-porphyrins, quite few researches focus on the metal-corroles and their applications, and plausible mechanisms for selected corrole-catalyzed processes and key factors accounting for the low power conversion efficiency (PCE) of corrole-based solar cells are still unclear. In the present work, the catalytic mechanism for the manganese-corrole mediated oxygen atom transfer (OAT) reaction, the formation of the active high-valent Mn(V)-oxo complex under O₂ atmosphere and visible light conditions, Mn-corrole catalyzed oxidation of cyclohexane to adipaldehyde, and the unique metal di-corrole dyes for solar cells have been investigated by extensive density functional calculations.

The main results in the dissertation are summarized as follows:

- (1) The catalytic mechanism for the manganese-corrole mediated OAT reactions has been investigated by density functional calculations. Calculations show that the OAT reactions generally experience relatively high free energy barriers along the singlet PES, whereas the triplet-state pathway is quite favorable, both dynamically and thermodynamically. Although the electronegative *meso*-substituents can increase the OAT reactivity to some extent, the sharp change arises from the spin flip in the OAT reactions. The bromination on β -pyrrole carbon atoms of the pentafluorophenyl *meso*-substituted (oxo)manganese(V) corrole significantly enhances the SOC interactions at the CP between the singlet and triplet PESs, which promotes the OAT reaction to proceed on the triplet PES and dramatically increases its reactivity.
- (2) The generation of the active high-valent Mn(V)-oxo complex under O₂ atmosphere and visible light conditions has been explored by density functional

calculations. Calculations show that a triplet loosely-associated complex of corrolazine with O₂ has been formed initially in reaction. The subsequent strong bonding interactions between dioxygen with metal corrole, triggered by the visible light irradiation, may result in electron rearrangement and charge transfer among frontier orbitals, yielding a dioxygen-containing biradical intermediate, which can easily abstract hydrogen from the substrate. Followed by facile radical processes, the high-valent Mn(V)-oxo active oxidant is generated.

(3) Mn-corrole catalyzed oxidation of cyclohexane to adipaldehyde has been investigated by density functional calculations. Calculations show that the catalytic reaction comprises three processes, i.e. two hydroxylation steps and one C-C bond cleavage step. The consecutive hydroxylations are initiated by the hydrogen-atom transfer (HAT) from substrate to the (oxo)manganese(V) corrole, coupled with a rapid rebounding of the Mn-bound OH group to the carbon radical. Similarly, the C-C bond cleavage was initiated by the hydrogen-atom transfer (HAT) from one of the intermediate with two OH groups to the (oxo)manganese(V) corrole, leading to the oxygen radical. The strong interactions between the oxygen radical and the adjacent C-C bond result in the C-C bond activation remarkably and cleavage, coupled with the HAT from the remaining OH group to the (oxo)manganese(V) corrole. The second hydroxylation is the rate-determining step for the overall reaction, and the stability of the carbon radical intermediate may dominate the reactivity accordingly.

(4) A new type of metal di-corrole dyes has been designed and their optical and electronic properties have been characterized by density functional calculations. Calculations show that the newly-constructed dyes with the unique di-corrole architecture have strong light harvesting ability in broad visible region and their excited states show excellent charge separation features. The electronic and photoelectronic properties of these metal di-corrole dyes can well be modulated by incorporating different bridge groups. Introduction of electron-withdrawing groups onto the *meso*-positions of corrole ring can modulate the energy levels of key molecular orbitals of the metal di-corrole dye to better match various redox

couples. On the basis of extensive first-principles calculations on the dye/TiO₂ system, possible mechanisms for direct and indirect electron injections were proposed. The electron injection may proceed through indirect mechanism under light excitation in relatively short wavelength region. On the contrary, the direct electron injection from dye to TiO₂ occurs under optical excitation in relatively long wavelength region.

Keywords: Metal corroles; Catalytic mechanism; Oxygen atom transfer reaction; Biradical; Dye-sensitized solar cells; Electron injection mechanism; Density functional theory calculations.

Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.

厦门大学博硕士论文摘要库