厦门大学

博　士　学　位　论　文

金属咔咯催化与光电性质的理论研究

Computational Characterization of Catalytic and Photoelectronic Properties of Metal-Corroles

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摘　要

咔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，金属咔咯的研究相对较少，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，关于咔咯基催化剂活性与催化机理的认识还存在很大的争议；导致咔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，对锰氧咔咯催化氧原子转移、分子氧氧化氮杂锰咔咯成活性氧物种的光氧化过程、锰氧咔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，为了改进咔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咔咯染料，基于计算结果，讨论了这类新型金属双咔咯染料TiO$_2$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，探明了金属咔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。锰氧咔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。尽管在咔咯 *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咔咯的 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 位溴代锰氧咔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咔咯活性氧化剂的反应中，基态的氮杂锰氧咔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咔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咔咯活性氧化剂。

（3）锰氧咔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咔咯染料分子，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；通过在它的咔咯环的 *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/TiO$_2$ 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：金属咔咯； 催化活性； 氧原子转移反应；双自由基；金属双咔咯染料染料；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 O_2 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 the its reactivity.

(2) The generation of the active high-valent Mn(V)-oxo complex under O_2 atmosphere and visible light conditions has been explored by density functional

calculations. Calculations show that a triplet loosely-associated complex of corrolazine with O_2 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/TiO$_2$ 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 TiO$_2$ 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.