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硕 士 学 位 论 文

富勒烯吡咯金属配合物的合成、表征
及其光电性能研究

Synthesis, Characterization and Photoelectric Property
of Pyrrolidine Ring-fused Metallofullerenes

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摘 要

富勒烯金属配合物在催化、超导、非线性光学性质、生物活性及光电转换性能等方面都有潜在的应用价值，但是其在大多数有机溶剂中溶解性很小，限制了富勒烯金属配合物在很多领域的应用。本论文合成的富勒烯吡咯金属配合物在传统金属配合物的基础上键合了水溶性的吡咯羧酸酯基团，较大的提高了其在有机溶剂中的溶解度。由于产物为 D-A-A 体系的配合物，具有较好的电荷转移能力，因而在非线性光学和光电转换性能方面将有更好的应用。

本文首先通过光化学反应（自由基加成反应）制备出一系列富勒烯吡咯衍生物，然后以其为原料，在氮气氛下用配体取代法合成了一系列富勒烯吡咯金属配合物。采用元素分析、紫外-可见吸收光谱、红外光谱、质谱、X 射线光电子能谱和 ^{31}P NMR 等多种方法对中间物及产物进行了表征；并结合理论计算结果分析了反应机理、预测了产物的可能结构。

测定了该系列化合物与 GaAs 电极组成的 n+n 型异质结复合光电极在光化学电池中的光伏效应。此外，研究了介质电对、配合物薄膜厚度、中间物等因素对光电转换性能的影响，并对这些规律进行了理论分析。结果显示：n+n 型的 $\text{C}_{60}\text{Pyr-ML}_n/\text{GaAs}$ 光电极在 I_2/I_3^- 和 $\text{O}_2/\text{H}_2\text{O}$ 介质电对中，尤其是在 $\text{O}_2/\text{H}_2\text{O}$ 中，当镀层厚度在 $1\mu\text{m}\sim 2\mu\text{m}$ 时，具有较好的光电性能；若为相同的 ML_n ，则 $\text{C}_{60}\text{Pyr}_2$ 金属配合物的光电转换性能较好。

关键词： 富勒烯；吡咯；金属

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Abstract

Recently, η^2 -fashion metallofullerenes have been paid much attention because of their promising properties in photoelectric, catalytic, optical nonlinearity aspects, etc. However, the low solubility in organic solvent limit their applications in many aspects. An effective way to circumvent such a hindrance is to introduce some hydrophilic substituting groups into the fullerenes. The products that we synthesized in this dissertation have high solubility in organic solvent because a hydrophilic pyrrolidine was added to the conditional metallofullerene. Moreover, the products are D-A-A compounds and have excellent charge-transfer ability.

In this thesis, we prepared pyrrolidine ring-fused fullerene derivatives ($C_{60}\text{Pyr}$) under photolysis and we chose Pd as the central metal coordinated *TPP*、*dppm* and *dppe* reported. The products $C_{60}\text{Pyr-ML}_n$ ($M=\text{Pd}$; $L=\text{TPP}$, *dppm*, *dppe*; $n=1,2$) were gained by the method of ligand substitution via the reaction of $C_{60}\text{Pyr}$ with ML_n under the condition of a nitrogen atmosphere and the room temperature. And all products were characterized by methods of elemental analysis, infrared spectra, UV-Vis electronic spectra, X-ray photoelectron spectra, ESI-MS, ^{31}P NMR etc. The reasonable structures of $C_{60}\text{Pyr-ML}_n$ were predicted through the anlysis of experiment datas and computational calculation results .

The photovoltaic effect (PVE) for $C_{60}\text{Pyr-ML}_n$ complexes on GaAs single crystal electrode forming n+n heterojunction in the photo electrochemical cell were studied. Influences of various redox couples on the photovoltaic effect were observed. The results showed that the photovoltaic effect of (n+n) heterojunction electrode formed by $C_{60}\text{Pyr-ML}_n/\text{GaAs}$ was effective, especially in the $\text{O}_2/\text{H}_2\text{O}$, I_2/I_3^- redox couple. The photoelectric effect was related with the thickness of the complex film, the media and the substituting groups etc. The photovoltaic performance of $C_{60}\text{Pyr}_2\text{-Pd(dppm)/GaAs}$ electrode in the $\text{O}_2/\text{H}_2\text{O}$ redox couple was the best, and the maximum of photovoltaic potential was up to 356mV at the $1\mu\text{m}$

for thickness of C₆₀Pyr2-Pd(dppm) film.

In conclusion, we synthesized, characterized the C₆₀Pyr-ML_n complexes by the reaction of C₆₀Pyr and low-valent transition metal compounds and studied the photoelectric effect, which can provide much convenience for further research of the analogs and promote the development of chemistry of the pyrrolidine ring-fused metallofullerene.

Keywords: Fullerene; Pyrrolidine ; Metal

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