

学校编码: 10384

分类号 \_\_\_\_\_ 密级 \_\_\_\_\_

学号: X200425004

UDC

厦 门 大 学

硕 士 学 位 论 文

萘甲酰肼类荧光受体分子的设计合成  
与分子识别

Design and Synthesis of naphthoylhydrazones  
Fluorescent Receptors for Molecular Recognition

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专业名称: 分析化学

论文提交日期: 2009年08月

论文答辩时间: 2009年12月

学位授予日期: 2009年 月

答辩委员会主席: \_\_\_\_\_

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2009年12月

**Design and Synthesis of naphthoylhydrazone Derivatives  
Fluorescent Receptors for Molecular Recognition**

A Dissertation Submitted for the Degree of  
Master of Science`

By

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August 2009

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## 摘 要

分子识别是超分子化学的核心研究内容之一,包括离子客体和中性分子的识别。荧光检测的高灵敏度、可实时及远程检测等优越性,使其在分子识别与传感的应用得到蓬勃发展。金属离子在环境和生命科学中发挥着重要的作用,设计合成高灵敏、高选择性的荧光化学传感分子近年来备受关注。阴离子在化学、生物、医药、环境等领域的重要作用已为人们所共知。受制于阴离子独特的结构特性,如半径较大、几何构型各异以及对环境 pH 极为敏感的特点,阴离子受体的设计合成以及新的识别体系的建立更具挑战性,已成为超分子化学研究领域活跃的课题之一。

一般地,过渡金属与重金属离子,由于它们多存在空轨道,可发生从荧光团到过渡金属离子的电子转移或能量转移,而重金属离子可诱导自旋轨道的耦合从而猝灭荧光,故早期检测该类金属离子多基于荧光猝灭原理。就检测的灵敏度而言,荧光增强法较荧光猝灭法更为优越。因此,利用荧光增强法识别过渡金属或重金属离子已成为近年的研究热点。

芳香酰基水杨醛脘是良好的金属离子配体,能与多种过渡金属与重金属离子发生配位作用。为此,本论文设计合成了系列酰脘衍生物荧光传感分子,研究了其对金属离子和阴离子的识别与传感。论文共分四章。

第一章,前言。从分子识别原理上概述了荧光传感分子在离子识别方面的近几年研究进展,并在此基础上提出了论文设想。

第二章,实验部分。介绍了研究工作中所涉及到的主要试剂、仪器和受体分子的合成方法与结构鉴定。

第三章,受体分子对金属离子的识别研究。研究了所合成的荧光传感分子(包括邻羟基芳香甲醛缩萘甲酰脘类和邻羟基芳香甲醛缩对二甲氨基苯甲酰脘类)在乙腈或 *N,N*-二甲基甲酰胺或乙醇中的光谱性质及其对金属离子的识别。

首先,研究邻羟基芳香甲醛缩萘甲酰脘类荧光传感分子对金属离子的识别。研究发现,邻羟基芳香甲醛缩萘甲酰脘在基态能与多种金属离子如  $\text{Zn}^{2+}$ 、 $\text{Cu}^{2+}$ 、 $\text{Cd}^{2+}$ 、 $\text{Pb}^{2+}$ 、 $\text{Hg}^{2+}$  和  $\text{Ni}^{2+}$  等发生类似的配位作用,但唯有  $\text{Zn}^{2+}$  引起 2-羟基-1-萘甲酰脘缩 2-萘甲酰脘 ( $\beta\text{-Ar-OH}$ ) 和 2-羟基-1-萘甲酰脘缩对二甲氨基苯甲酰脘

(DM-Ar-OH)的荧光显著增强,乙腈中分别可达101倍和450倍;相同条件下其它离子对 $\beta$ -Ar-OH和DM-Ar-OH的荧光光谱影响较小,故 $\beta$ -Ar-OH和DM-Ar-OH有望成为乙腈中高灵敏、高选择性的 $Zn^{2+}$ 荧光传感分子。荧光的增强主要是由于结构刚性的增大和提高 $n\pi^*$ 激发态能量所致。

其次,研究 $\beta$ -Ar-OH与 $Zn^{2+}$ 的结合模式, $\beta$ -Ar-OH与 $Zn^{2+}$ 以1:1的计量比结合,推测受体分子 $\beta$ -Ar-OH可能通过羰基氧原子、亚氨基氮原子和羟基氧原子与 $Zn^{2+}$ 形成三齿配合物。

第四章,受体分子对阴离子的识别研究。初步研究了多种阴离子如 $F^-$ 、 $H_2PO_4^-$ 、 $AcO^-$ 、 $Cl^-$ 、 $Br^-$ 、 $I^-$ 和 $HSO_4^-$ 等对几种酰脲类受体分子( $\alpha$ -Ar-OH、 $\beta$ -Ar-OH、 $\beta$ -Ph-OH和 $\beta$ -Ph-2OH)的吸收光谱影响。结果表明, $\beta$ -Ar-OH和 $\alpha$ -Ar-OH可选择性识别 $F^-$ ,唯有 $F^-$ 使其溶液由无色转变为淡黄色,所以它们可作为“裸眼”识别 $F^-$ 的阴离子受体。阴离子加入对上述二种受体分子的吸收光谱影响大小为: $F^- > H_2PO_4^- > AcO^-$ ,而其它阴离子对受体分子的吸收光谱几乎不影响。

**关键词:** 分子识别与传感, 荧光增强, 萘甲酰脲, 苯甲酰脲, 锌离子, 氟离子

## Abstract

Molecular recognition is a core research area in supramolecular chemistry which is composed of ionic and neutral species recognition. Due to high sensitivity, intrinsic simplicity and remote sensing capacity, fluorescent sensors have been rapidly developed in molecular recognition and sensing. Heavy and transition metal ions play important roles in many biological and environmental processes. To design and synthesize highly sensitive and highly selective chemosensors for heavy and transition metal ions has drawn much recent interest. To design and synthesize chemosensors for heavy and transition metal ions has drawn much recent interest. With the inherent difficulties of addressing anions characterized by larger sizes (larger than cations in general), a greater varied shapes and pH dependence, design of anion receptors remains a challenging subject.

It is known that heavy and transition metal ions possess mostly empty orbitals and can quench efficiently fluorescence of a fluorophore via enhanced spin-orbit coupling, electron and energy transfer. Therefore, detection of heavy and transition metal ions by fluorescent sensors is operated mainly in fluorescence quenching mode. Due to sensitivity reason, sensors showing fluorescence enhancement as a result of metal-ion binding are to be favored over those exhibiting fluorescence quenching. Fluorescent sensing heavy and transition metal ions based on fluorescence enhancement is a subject of intensive recent interest.

Aromatic series acylhydrazones are known as good ligands for metal ions, including heavy and transition metal ions. Therefore, a series of fluorescent sensors acylhydrazones derivatives were designed and examined in this dissertation, which consists of four chapters.

Chapter 1, briefly summaries the research progresses of fluorescent chemosensors for ions based on molecular recognition. The research to be carried out is presented in the same chapter.

Chapter 2, describes equipments, materials and methods involved in this dissertation. Synthetic details and characterization of sensor molecules are provided.

Chapter 3, absorption and fluorescence spectral properties of the synthesized sensors and their response to metal ions are reported. These sensors involved 2-hydroxy-1-naphthaldehyde naphthoylhydrazones(  $\alpha$ -Ar-OH and  $\beta$ -Ar-OH ), Salicylaldehyde naphthoyl- hydrazones(  $\alpha$ -Ph-OH and  $\beta$ -Ph-OH ), 2,4-dihydroxyphenyl- ethanone naphthoylhydrazones (  $\beta$ -Ph-2OH ), 2-hydroxy -1-naphthaldehyde *p*-Dimethylaminobenzoylhydrazones( **DM-Ar-OH** ) and 2,4-dihydroxyphenyl- ethanone naphthoylhydrazones( **DM-Ph-2OH** ).

First of all, these hydrazones derivatives were examined as sensors for metal ions. It was found that they could bind metal ions such as  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Hg^{2+}$  and  $Ni^{2+}$  in a similar coordination manner in the ground state in acetonitrile or DMF, but only  $Zn^{2+}$  induces dramatic enhancement in the fluorescence of  $\beta$ -Ar-OH and **DM-Ar-OH** while other heavy and transition metal ions have little effect. The fluorescence enhancement factor depend on electron donating ability of substituents at the aromatic ring. With stronger electron donating ability of substituent, the fluorescence enhancement factor is higher. The highest fluorescence enhancement factor was observed in 2-hydroxy-1-naphthaldehyde 1-naphthoylhydrazones( $\beta$ -Ar-OH) with a value of 101 and 2-hydroxy -1-naphthaldehyde *p*-Dimethylaminobenzoyl- hydrazones(**DM-Ar-OH**) with a value of 450 in acetonitrile. It was therefore concluded that  $\beta$ -Ar-OH and **DM-Ar-OH** could be employed as a potential fluorescent chemosensor for  $Zn^{2+}$  with high selectivity and sensitivity. The mechanism of fluorescence enhancement of  $\beta$ -Ar-OH in the presence of  $Zn^{2+}$  was investigated. The fluorescence enhancement due to an enhanced rigidization, conformational restrict and  $n\pi^*$  energy rise resulting from binding  $Zn^{2+}$  was suggested.

Secondly, the binding mode of  $\beta$ -Ar-OH with  $Zn^{2+}$  were examined. Under the experimental conditions, the receptor binds  $Zn^{2+}$  in a 1:1 stoichiometry. Receptor  $\beta$ -Ar-OH binds  $Zn^{2+}$  with oxygen atom of C=O and -OH, nitrogen atom of -NH was presumed.

Chapter 4 , effects of anions on the absorption spectra of receptors in acetonitrile were investigated. The absorption spectra of receptors was found to be sensitive to the presence of anions. Original bands in the absorption spectra of  $\beta$ -Ar-OH and

**DM-Ar-OH** decreased with the appearance a new peak at longer wavelength upon addition of anions. It was found that only  $F^-$  could induce dramatic change in the absorption spectra of  **$\beta$ -Ar-OH** and **DM-Ar-OH** resulting in obvious color change from colorless to yellow. These results suggested that  **$\beta$ -Ar-OH** and **DM-Ar-OH** had higher selectivity for  $F^-$  against other anions and could therefore be employed for naked-eye detection of  $F^-$ . The binding constants varied in general in the order of  $F^- > H_2PO_4^- > AcO^- > Br^-, Cl^-, HSO_4^-$ .

**Key words:** cation sensor, molecular recognition, fluorescence enhancement, naphthoylhydrazones, benzoylhydrazones,  $Zn^{2+}$ ,  $F^-$

## 第一章 分子识别与荧光传感的研究进展

### 第一节 分子识别与荧光传感

#### 1.1.1 分子识别

1987年, J.M. Lehn教授在获诺贝尔化学奖演讲中详细阐述了超分子化学的概念, 给化学家展示了无限宽广的天地。所谓超分子, 是指以非共价键弱相互作用力结合的复杂有序且具有特定功能的分子集合体的化学, 称为“超越分子化学概念的化学”。超分子化学起源于冠醚对碱金属离子的选择性结合, Pedersen于1967年发表的系统性工作标志着超分子化学这一研究领域的诞生<sup>[1]</sup>, 而其发展则是Cram和Lehn的主-客体化学<sup>[2,3]</sup>, 它的诞生与发展极大地激发了化学家的想象力与创造力。超分子化学与经典分子化学有着本质的区别: 经典分子化学是基于原子间的共价键, 而超分子化学则基于分子间的相互作用(如静电力、氢键、范德华力、疏水作用等)。近年来, 超分子化学得到了长足的发展, 主要包含以下内容: 分子识别、离子客体受体和分子客体受体、环糊精、生物有机体系和生物无机体系中的超分子反应性及传输、固态超分子化学、超分子化学中的物理方法、模板和自组装及自组织、超分子技术等。超分子化学是诸多学科的交叉, 涉及无机化学、有机化学、物理化学、分析化学、高分子化学以及材料、信息和生命科学。

分子识别是超分子化学的核心研究内容之一, 早期是由有机化学家和生物化学家在分子水平上研究生物体系中化学问题而提出。分子识别是指不同分子间的一种特殊的、专一的相互作用, 它既满足相互作用的分子间的空间要求, 也满足分子间各种次级键力的匹配。因此, 分子识别本质上是指主体分子(受体)对客体分子(底物)选择性结合并产生某种特定功能的过程。

分子识别包括对中性分子和离子的识别, 本章主要介绍阳离子的识别。早在20世纪60年代末期, Pedersen首次发现了冠醚化合物, 并研究了阳离子与冠醚间高选择性配位作用<sup>[1]</sup>; Lehn开展了穴醚化合物与阳离子配位作用研究<sup>[2]</sup>; Cram提出了“主客体化学”这一概念<sup>[3]</sup>。到20世纪70年代, 碱金属、碱土金属和铵离子的配位化学研究引起了极大的关注, 使阳离子识别迅速成为超分子化学领域的研究热点。

#### 1.1.2 荧光传感



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