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双重荧光受体分子的设计合成与分子识别

温 珍 昌

指 导 教 师: 江云宝教授

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Design and Synthesis of Dual Fluorescent Neutral Receptors for Molecular Recognition

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By
Zhen-Chang Wen

Supervisor: Prof. Yun-Bao Jiang

Department of Chemistry, Xiamen University

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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。由于荧光检测的高灵敏度和可实时及远程检测等优越性, 在分子识别与传感中的应用得到蓬勃发展, 设计合成高灵敏、高选择性的荧光化学传感器近年来备受关注。具有分子内电荷转移和激发态质子转移性质的荧光体, 发射大 Stokes 位移的荧光, 可消除基质本底荧光和散射光对化学传感和分子识别的潜在不利影响。为此, 本论文拟以具有分子内电荷转移双重荧光的对二甲氨基苯甲酰胺衍生物和分子内质子转移的水杨醛衍生物为荧光信号报告基团, 耦合阳离子或阴离子识别位点, 设计合成了系列荧光化学传感器。论文共分六章。

第一章: 从分子识别原理上概述了荧光传感器的研究进展, 并提出论文设想。

第二章: 详细介绍论文工作中所涉及的荧光受体的合成方法和结构鉴定。包括对二甲氨基苯甲酰胺、对二甲氨基苯甲酰胺基硫脲、水杨醛缩氨基苯基硫脲、水杨醛缩苯甲酰胺、对二甲氨基苯甲酰胺二苯胍等系列, 共约三十种化合物。

第三章: 将具有分子内电荷转移双重荧光的对二甲氨基苯甲酰胺荧光团与阳离子配体苯甲酰胺衍生物耦合, 合成了三种阳离子荧光受体苯甲醛缩对二甲氨基苯甲酰胺 (**BH-DM**)、邻甲氧基苯甲醛缩对二甲氨基苯甲酰胺 (**MH-DM**) 和水杨醛缩对二甲氨基苯甲酰胺 **SH-DM**。系统研究了合成的荧光受体在乙腈中的光谱性质, 发现 **BH-DM** 和 **MH-DM** 的长波长荧光具有电荷转移特征, 而 **SH-DM** 长波长荧光为电荷转移及分子内质子转移的叠加。过渡金属离子如 Fe^{3+} 、 Co^{2+} 、 Ni^{2+} 、 Cu^{2+} 、 Zn^{2+} 、 Cd^{2+} 和 Hg^{2+} 等均与 **BH-DM**、**MH-DM** 和 **SH-DM** 发生配位作用, 但唯有铜离子使 **BH-DM** 和 **MH-DM** 的荧光显著增强并伴有明显的光谱蓝移, 荧光的增强是由于抑制最低激发态 $n-\pi^*$ 跃迁所致。**BH-DM** 和 **MH-DM** 可作为乙腈中选择性识别铜离子的荧光

传感器；将其拓展到水相，发现在含 10% 水的乙腈溶液中 Cu^{2+} 的加入，可使 **MH-DM** 的荧光光谱蓝移，强度增强 170 倍。**MH-DM** 对 Cu^{2+} 有极高的选择性，相同条件下，除 Fe^{3+} 能猝灭已增强的荧光外，其它金属离子几无影响。由于 **MH-DM** 中邻位甲氧基的引入，可增强荧光受体与铜离子的结合能力，**MH-DM** 识别铜离子的灵敏度较 **BH-DM** 为高，更具应用前景，有望成为水相中高灵敏、高选择性识别铜离子的荧光传感器。

第四章：以胍基为连接臂，将具有双重荧光的对二甲氨基苯甲酰胺荧光团和阴离子识别基团苯基硫脲耦合，合成了系列阴离子荧光受体对二甲氨基苯甲酰胺胍基硫脲衍生物 (**DGTU-Rs**)。系统研究了该类受体分子在乙腈中的光谱性质，发现对二甲氨基苯甲酰胺胍基硫脲衍生物发射双重荧光，长波长荧光发射态具有电荷转移特征，荧光发射峰随苯基硫脲端取代基的拉电子能力增强而红移。胍基是传递取代基电子效应的有效桥梁，苯基硫脲端的取代基效应可通过胍基传递至酰基，并发现苯基硫脲位于电子受体一侧。对二甲氨基苯甲酰胺胍基硫脲衍生物的双重荧光对阴离子极为敏感，阴离子的加入使短波长荧光略有增强，而长波长荧光显著降低且光谱蓝移。阴离子对 **DGTU-Rs** 光谱的影响，可由 ICT 机理解释：阴离子与硫脲结合后，增加了电子受体端的电荷密度，减弱了电子受体的拉电子能力，导致 **DGTU-Rs** 的吸收光谱蓝移，CT 荧光减弱并蓝移，藉此实现 CT 与 LE 荧光强度比值法检测阴离子。苯基硫脲端取代基的引入，既可调控荧光受体的 CT 荧光发射峰位置，又可改变受体与阴离子的结合能力。同一受体与阴离子结合能力依 $\text{F}^- > \text{AcO}^- > \text{H}_2\text{PO}_4^-$, Cl^- , Br^- , HSO_4^- 次序减小；受体与相同阴离子的结合能力按 **DGTU** < **DGTU-p-Cl** < **DGTU-m-Br** < **DGTU-m-CF₃** < **DGTU-p-CN** 次序递增。

第五章：设计合成了具有激发态分子内质子转移特征的新型阴离子受体水杨醛缩氨基苯基硫脲 (**STU-Rs**) 和水杨醛缩苯甲酰胺 (**SH-Rs**) 衍生物。本章分为两节。

第一节：研究了乙腈中阴离子对 **STU-Rs** 吸收和荧光光谱的影响，发现 **STU-Rs** 的吸收和荧光对阴离子极为敏感。阴离子的加入使 **STU-Rs** 的吸收

光谱发生明显改变，且在长波长处出现新的吸收峰；乙腈中 **STU-Rs** 发射双重荧光，长波长荧光随阴离子浓度的增加而显著增强，此系由于 **STU-Rs** 与阴离子结合后，抑制了分子内质子转移所致。核磁共振滴定表明 **STU-Rs** 通过羟基和硫脲氮氢与阴离子以氢键方式结合，ESI-MS 和 Job 作图法表明 **STU-Rs** 与阴离子的结合计量比为 1:1。同一受体与阴离子的结合能力依阴离子碱性 $\text{AcO}^- > \text{F}^- > \text{H}_2\text{PO}_4^- > \text{Cl}^-$, Br^- , HSO_4^- 次序减小；受体与相同阴离子的结合能力按 **STU-*p*-OCH₃** < **STU-*p*-CH₃** < **STU** < **STU-*p*-Cl** < **STU-*m*-CF₃** 次序变化。不含羟基的模型化合物 **MBTU** 和 **BTU** 虽与阴离子的结合能力明显低于 **STU**，但对 F^- 表现出了极高的选择性，表明适当降低受体与阴离子的结合能力，有利于阴离子的选择性识别。

第二节：研究了乙腈中阴离子对 **SH-Rs** 吸收和荧光光谱的影响。发现阴离子中唯有 F^- 使 **SH-Rs** 的吸收光谱发生明显变化，且溶液由无色变为黄色，表明该类分子对 F^- 具有极高的选择性，可直接“裸眼”鉴别和检测 F^- 。Job 作图法证实 **SH-Rs** 与 F^- 的结合计量比为 1:1， F^- 与 **SH-Rs** 的结合能力随苯甲酰端取代基拉电子能力提高而增强，依 **SH-DM** < **SH-OEt** < **SH** < **SH-*p*-Cl** < **SH-*m*-Cl** 次序递增。乙腈中 **SH-Rs** 发射双重荧光，长波长荧光随 F^- 浓度的增加而显著增强且明显蓝移，这是由于 **SH-Rs** 与 F^- 结合后，抑制了分子内质子转移所致。 F^- 导致 **SH-Rs** 荧光增强倍率随 **SH-DM** < **SH-OEt** < **SH** < **SH-*p*-Cl** < **SH-*m*-Cl** 顺序提高，其它阴离子虽使 **SH-Rs** 荧光增强，但荧光增强倍率远低于 F^- ，表明 **SH-Rs** 可作为选择性识别 F^- 的荧光试剂。

第六章：本章分为两节。

第一节：设计合成了具有 ICT 性质的荧光体对二甲氨基苯甲酰二苯胍 (**DG-Rs**)，研究了该类荧光体在系列有机溶剂中的光谱性质，发现 **DG-Rs** 分子中的取代基并不影响其吸收光谱，但荧光光谱随取代基拉电子能力提高而红移，表明 **DG-Rs** 的基态结构与取代基关系甚微，取代基位于 **DG-Rs** 分子的电子受体一侧。乙腈中 **DG-Rs** 的 CT 荧光发射能量与取代基 Hammett 常数间存在良好的线性关系，其线性斜率高于相应的对二甲氨基苯酚酯，表

明胍基传递取代基电子效应的能力强于苯酚酯中的酚氧键。

第二节: 在上节基础上设计合成了具有 ICT 性质的可识别糖分子的荧光受体 **DG-*m*-B(OH)₂**。甲醇-水的混合溶剂中 **DG-*m*-B(OH)₂** 的荧光随溶液 pH 值的提高而增强并伴有光谱蓝移, 这是因为碱性条件下 -B(OH)₂ 转变为 -B(OH)₃⁻, 后者的拉电子能力明显低于 -B(OH)₂ 之故。糖分子的加入, 降低 **DG-*m*-B(OH)₂** 的 pK_a 。因此中性条件下, **DG-*m*-B(OH)₂** 的荧光随糖分子浓度的增加而增强并伴有光谱蓝移, **DG-*m*-B(OH)₂** 与糖的结合能力依果糖 > 葡萄糖 > 半乳糖顺序降低。

关键词

分子识别与传感, 分子内电荷转移, 激发态分子内质子转移, 双重荧光, 对二甲氨基苯甲酰胍基硫脲, 水杨醛缩氨基苯基硫脲, 水杨醛缩苯甲酰脲, 对二甲氨基苯甲酰二苯胍

Abstract

Molecular recognition is an important subject in supramolecular chemistry. Design and synthesis of fluorescent chemosensor have drawn much interests in supramolecular chemistry in recent years due to its intrinsic distinct advantages in terms of high sensitivity, able to monitor substrate concentration in real-time and real-space and remote sensing. Intramolecular charge transfer (ICT) or intramolecular excited-state proton transfer (ESIPT) fluorophores emit large Stokes-shifted fluorescence that will avoid the interference from background auto-fluorescence and light scattering in sensing process. A series of dual fluorescent chemosensors based on *p*-dimethylaminobenzamide or salicylaldehyde derivatives coupled with cation or anion binding site were designed and synthesized in this dissertation. The dissertation consists of six chapters.

In Chapter 1, research progresses of fluorescent chemosensors in terms of recognition mechanisms were briefly reviewed. The research proposal of this dissertation was presented according to the developments of fluorescent chemosensors.

Detailed synthesis procedures and characteristic data of *ca.*30 fluorescent chemosensors were presented in Chapter 2. These sensors include *p*-dimethylaminobenzoylhydrazones, *N*-(*p*-dimethylaminobenzoyliminoyl) thioureas, salicylaldehyde aminophenylthioureas, salicylaldehyde benzoylhydrazones and *p*-dimethylaminobenzoyl diphenyl guanidines.

Three fluorescent sensors **BH-DM**, **MH-DM** and **SH-DM** based on dual fluorescent *p*-dimethylaminobenzamide signal reporter which coupled with benzoylhydrazones containing cation binding site were synthesized in Chapter 3. The spectra of these fluorescent sensors in acetonitrile were investigated in detail. It was found that all the three fluorescent sensors emitted dual fluorescence in acetonitrile. The long-wavelength emission of **BH-DM** and **MH-DM** was assigned to the CT state while that of **SH-DM** to the mixture of the CT and ESIPT states. All of the investigated transition metal ions such as Fe³⁺, Co²⁺, Ni²⁺,

Cu^{2+} , Zn^{2+} , Cd^{2+} and Hg^{2+} can interact with **BH-DM**, **MH-DM** and **SH-DM** in the ground state as shown by the variations of the absorption spectra. However, only Cu^{2+} can lead to dramatic fluorescence enhancement together with obvious blue-shift in the CT emission of **BH-DM** and **MH-DM**. The fluorescence enhancement was ascribed to result from the inhibition of the $n-\pi^*$ transition and conformational restriction. The selectivity of **MH-DM** to Cu^{2+} was found higher than that of **BH-DM** due to the presence of a methoxy group at the ortho-position of benzaldehyde which can enhance the binding affinity with Cu^{2+} . Therefore, **MH-DM** was more favorable in recognition of Cu^{2+} with high selectivity and sensitivity in aqueous solution.

A series of anion sensors (**DGTU-Rs**) in which the *p*-dimethylaminobenzamide moiety is the ICT dual fluorescent signal reporter which is conjugatedly linked to the phenylthiourea anion recognition moiety by an iminoyl group were synthesized in Chapter 4. **DGTU-Rs** exhibited dual fluorescence in acetonitrile and the CT emission was shifted to the red with increasing electron-withdrawing ability of the substituent at the phenylthiourea moiety. This observation indicates that the substituent of phenylthiourea locates in the electron acceptor moiety and the iminoyl group is an efficient bridge that transmit substituent-effect from phenylthiourea to the carbonyl group. The dual fluorescence of **DGTU-Rs** in acetonitrile was sensitive to anions such as F^- , AcO^- and H_2PO_4^- . It was found that addition of F^- resulted in a substantial quenching of the long-wavelength CT emission and an obvious blue shift in its band position, whereas only small changes were observed in the LE emission in both its position and intensity. The spectral response of **DGTU-Rs** to anions can be interpreted under the ICT mechanism. As anion binding to the thiourea moiety, the electron-withdrawing ability of the electron acceptor of **DGTU-Rs** will be reduced that leads to a blue shift in the absorption spectra as well as CT emission and a decrease in the CT to LE fluorescence intensity ratio. The binding constants were found to vary in general in the order of $\text{F}^- > \text{AcO}^- > \text{H}_2\text{PO}_4^-$, HSO_4^- , Br^- , Cl^- with the same receptor. With the same anion, the binding constants varied in

the order of **DGTU** < **DGTU-*p*-Cl** < **DGTU-*m*-Br** < **DGTU-*m*-CF₃** < **DGTU-*p*-CN**, as expected from the increasing acidity of the thioureido –NH protons.

A series of novel anion sensors based on salicylaldehyde aminophenylthioureas (**STU-Rs**) and salicylaldehyde benzoylhydrazones (**SH-Rs**) which possess ESIPT character were synthesized in Chapter 5. This chapter was divided into two sections.

In section 1, influence of various anions on the absorption and fluorescence spectra of **STU-Rs** in acetonitrile were investigated in detail. The spectra of **STU-Rs** was found to be sensitive to the presence of anions. Original bands in the absorption spectra of **STU-Rs** decreased with the appearance a new peak at longer wavelength upon addition of anions, while the long-wavelength emission was enhanced dramatically due to the inhibition of the ESIPT process. ¹H NMR titrations indicated that **STU-Rs** bound anions via –OH and thioureido –NH protons. 1:1 binding mode was confirmed by Job plot and ESI-MS data. The binding constants varied in general in the order of AcO[–] > F[–] > H₂PO₄[–] >> HSO₄[–], Br[–], Cl[–]. With the same anion, the binding constants varied in the order of **STU-*p*-OCH₃** < **STU-*p*-CH₃** < **STU** < **DGTU-*p*-Cl** < **STU-*m*-CF₃**, as expected from the increasing electron-withdrawing ability of the substituent. The control compounds **MBTU** and **BTU** without phenolic –OH showed very high selectivity to fluoride over other anions although the binding constants were much lower than those of **STU-Rs**. This observation indicated that the selectivity to anions can be increased by lowering the binding affinity of the sensors with anions.

In section 2, effects of anions on the absorption and fluorescence spectra of **SH-Rs** in acetonitrile were investigated in detail. It was found that only F[–] could induce dramatic change in the absorption spectra of **SH-Rs** resulting in obvious color change from colorless to yellow. These results suggested that **SH-Rs** had higher selectivity for F[–] against other anions and could therefore be employed for naked-eye detection of fluoride ions. 1:1 binding stoichiometry was confirmed by

Job plot and the binding constants with fluoride varied in the order of **SH-DM** < **SH-OEt** < **SH** < **SH-*p*-Cl** < **SH-*m*-Cl**, as expected from the increasing acidity of the phenolic –OH group. The long-wavelength emission of **SH-Rs** was found enhanced dramatically with a obvious hypochromic shift in the presence of fluoride. These spectral variations were suggested to result from the inhibition of the ESIPT process. The observation that other anions induced much lower enhancement of the **SH-Rs** fluorescence than that of fluoride indicated that **SH-Rs** could be applied as selective fluorescent sensors for fluoride.

Chapter 6 was divided into two sections.

In section 1, a series of ICT fluorophores based on *p*-dimethylaminobenzoyl diphenyl guanidines (**DG-Rs**) were synthesized. The spectra of these derivatives were investigated in detail in a variety of solvents. It was found that the absorption spectra of **DG-Rs** were independent of the substituent at the aniline moiety while the CT emission shifted to the red with increasing electron-withdrawing ability of the substituent. These observations indicated that the substituent located in the electron acceptor and had no influence on the ground state structure of **DG-Rs**. The CT emission energy of **DG-Rs** was found to correlate linearly with the Hammett constant of the substituent and the slope of the linear correlation was higher than that of the corresponding phenol *p*-dimethylaminobenzoates. This observation indicates that iminoyl group is a more efficient bridge in transmission substituent-effect than the –O– bridge in phenol benzoates.

On the basis of the results of section 1, a novel ICT fluorescent chemosensor **DG-*m*-(OH)₂** for saccharide was designed and synthesized. The fluorescence intensity of **DG-*m*-(OH)₂** was enhanced with a hypochromic shift with increasing pH in methanol–water mixtures, due to lowered electron-withdrawing ability of –B(OH)₃[–] than that of –B(OH)₂. An enhanced fluorescence with a hypochromic shift of the emission spectra was observed in **DG-*m*-(OH)₂** solution with increasing of saccharides concentration. The binding constants of **DG-*m*-(OH)₂** with saccharides varied in the order of fructose > glucose > galactose.

Keywords

Molecule recognition, chemosensing, Intramolecular charge transfer, excited-state intramolecular proton transfer, dual fluorescence, *p*-dimethylaminobenzoyliminoyl thiourea, salicylaldehyde aminophenylthiourea, salicylaldehyde benzoylhydrazone, *p*-dimethylaminobenzoyldiphenyl guanidine

厦门大学博硕士论文摘要库

第一章 荧光识别与传感研究进展

第一节 分子识别与传感

由于在超分子化学领域的卓越贡献，C. J. Pedersen、D. J. Cram 和 J. M. Lehn 荣获 1987 年度诺贝尔化学奖。超分子化学始于 Pedersen 对冠醚的发现及其性质的深入研究[1]，发展于 Cram 和 Lehn 的主-客体化学[2-3]。所谓超分子化学，是指以非共价键弱相互作用力结合起来的复杂有序且具有特定功能的分子集合体，称为“超越分子化学概念的化学”。超分子化学与经典分子化学的不同在于：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）。超分子化学是诸多学科的交叉，不仅涉及无机化学、有机化学、物理化学、分析化学和高分子化学，而且涉及材料、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，最初是由有机化学家和生物化学家在分子水平上模拟天然化合物所提出。分子识别是指主体（受体）对客体（底物）选择性结合并产生某种特定功能的过程，维系分子间的作用力是几种弱相互作用力的协同作用，其强度不次于化学键。分子识别可分为离子客体的识别和中性分子的识别。

当客体与受体的识别基团结合时，诱导受体的物理或化学性质发生改变，转换为可检测的宏观信号：如 NMR 中的化学位移变化、光学信号（吸光度或荧光）的变化以及电位的变化等，此过程即为传感。相较其它传感形式而言，由于荧光内在的高灵敏度、可实时检测及可实现远程检测等优越性，其在分子识别与传感中得到蓬勃发展。

与其它化学传感器相似，荧光传感器包含两个亚单元：一是识别基团，另一是荧光团。二者可由联接臂相联或直接相联在同一共轭体系中，如图1所示。

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