Mechanism and Application of Fluorescent Sensors Containing Ferrocene Groups

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Abstract. Fluorescent chemical sensors have fused many research contents in chemical and physical fields, and attracted widespread attention because of their high sensitivity of fluorescence analysis. Different fluorescence sensing mechanisms are applied to different sensing systems. Among them, ion probes are widely used in biology, food analysis, drug diagnosis and so on, and have broad application prospects. In this paper, the fluorescence sensor containing ferrocene is introduced, and its mechanism and application are discussed.

1. Introduction
Ion recognition often occurs in the fields of chemistry, biological science and metal science. By designing ideal models, we can capture the chemical reaction process into optical signals, which provides strong evidence for the study of reaction process, reaction mechanism and so on. For example, the existence of this process can be determined by applying external stimuli to capture the energy emitted by molecules in the process of transition between two different states. Because of its advantages of simplicity, high selectivity and high sensitivity, ion probes are often widely used in biology, food analysis, drug diagnosis and other fields, and have broad application prospects. [1]

Fluorescent probes are a kind of important sensors in the process of ion recognition. They refer to a set of molecular systems, which can change their physical and chemical properties by reacting with bound chemicals, thus making the fluorescence change. Typical fluorescent probes can be divided into two parts, one is the fluorescent group, which makes the molecule fluorescent by emitting photons; the other is the recognition group, which can generate recognition signals. They usually form a fluorescent group-bridge-recognition group model by bridging. When the recognition group binds to the detected substance, some optical properties of the fluorescent group (such as fluorescence intensity, excitation wavelength, etc.) will be changed through different mechanisms, so that we can detect this process. [2]

2. Recognition mechanism of fluorescent probe

2.1. Photoinduced electron transfer mechanism
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2.2. **Charge transfer mechanism**

Typical photoinduced electron transfer systems consist of receptors containing electron donors, which are connected by spacers such as CH2-interlinked fluorophore. The fluorescent group part is the place where light can be absorbed and fluorescence can be emitted, while the receptor part is used to bind the object. The two parts are separated by spacers and connected by spacers to form a molecule, which constitutes a supramolecular system that selectively recognizes the object and gives the change of light signal. In PET fluorescent molecular probes, photoinduced electron transfer exists between the fluorescent group and the acceptor unit, which has a very strong quenching effect on fluorescence. Usually, the electron is transferred from the donor to the excited fluorescent group. Therefore, the probe molecule does not emit fluorescence or fluorescence is very weak before binding to the guest. Once the receptor binds to the guest, the photoinduced electron transfer is inhibited or even completely blocked, and the fluorescent group emits fluorescence.

3. **Introduction of Fluorescent Sensors Containing Ferrocene Groups**

Based on the electrochemical detection characteristics of ferrocene groups, many research groups have done a lot of related work. Among many efforts, Pedro Molina's team has made the most outstanding contribution. They have synthesized a series of multichannel sensors containing ferrocene groups.

![Figure 1. Ligands of Ferrocene Derivatives.](image)

In 2007-2015, Molina's project combined a variety of benzimidazole ligands containing ferrocene groups 1.14-1.22. These ligands can be chelated with cations to show changes in spectra or colours, and they can form hydrogen bonds with anions in solution through H atoms in the structure, thus recognizing anions. Among them, ligand 1.14 and 1.15 can recognize Pb2+ and Zn2+ ions. Ligand 1.15 optimizes the structure of 1.14, which has lower detection limit and more sensitive recognition...
for Pb$^2+$ ions. Ligand 1.16 can recognize anhydrous HP2O7$^{3-}$, ADP and ATP. When added, the solution will turn orange or pink, and the fluorescence intensity will increase. Ligand 1.17 is formed by ligand 1.16, which coordinates with metal Rh. It can specifically recognize Cl-ions. Ligand 1.17 emits fluorescence at 612 nm, which is 159 nm red-shifted from 453 nm fluorescence at 1.16. For ligand 1.18, besides complexing anions and cations, it was also found that the binding ability of ligands to cations was significantly enhanced after binding with anions. The binding ability of ligands to anions was also enhanced after binding with cations, which was easy to form ion-pair conjugates. The structure of ligand 1.19 is similar to that of ligand 1.18. The bright point is that the recognition ion of ligand can be regulated by adjusting X atom. Ligand 1.20, 1.21 and 1.22 are synthesized by the same method and different substrates. The difference is that ligand 1.20 can recognize HSO4- and Hg2-ions, while ligand 1.21 can recognize AcO- and SO4$^{2-}$-ions, and ligand 1.22 can recognize Cu$^{2+}$, Hg$^{2+}$, H2PO4- and HP2O7$^{3-}$-ions. Among them, the fluorescence of ligand 1.22 is enhanced after binding with anions, and the wavelength is red-shifted, which makes the naked eye effect the most outstanding among the three.

Figure 2. Ferrocene triazole compounds and their applications in detection and ion recognition.

At the same time, Molina's team also synthesized a series of ferrocene triazole compounds, which were used to detect the ion recognition performance [3] - [5]. As shown in the figure above, they are mainly divided into mono-substituted ferrocene triazole compounds and bis-substituted ferrocene triazole compounds. Their main structures are the same, and the recognition performance is changed by connecting different substituent groups. Ligand 1.23 can specifically recognize H2PO4-, while ligand 1.24 can recognize HP2O7$^{3-}$-ion. Because of the pyrene fluorescence group, the fluorescence intensity increases 53 times after binding with ions. Ligand 1.25 has more heteroatoms, which enables it to recognize Hg$^{2+}$, F-, AcO-, H2PO4-, HP2O7$^{3-}$ and other ions. Ligand 1.26-1.28 has pyrene fluorescence group of ligands 1.24, so the multi-channel detection ability is greatly increased. The binding of ligand 1.26 with Pb$^2+$ ions will change the solution from orange to yellow. The binding of
ligand 1.27 with AcO-, H2PO4- and BzO- ions will reduce the absorption peak at 349 nm in the ultraviolet absorption spectrum, while a new absorption peak appears at 400 nm. When ligand 1.28 binds to H2PO4- ions, the fluorescence intensity at 388 nm decreases, while that at 446 nm increases, which results in a strong blue fluorescence.

Among the numerous ferrocene N-containing ligands, Molina's greatest contribution was to introduce acridine structure into ferrocene system and to identify various ions. In 2013, Molina team designed and synthesized ligand 1.29 [6]. By linking two pyrene groups with acrylazine, the ligand can recognize Cu2+, Hg2+ ions, and the naked eye color change is obvious. It can be used as a ligand for visual detection of Cu2+, Hg2+ ions in undergraduate experiments.

![Figure 3. Ligands for visualized detection of Cu2+ and Hg2+ ions.](image)

**4. Conclusion**

Because heavy metal ions such as Cu2+, Hg2+ have fatal harm to human body, and H2S is very important to human body, it is particularly important to have a real-time detection method for these substances. Ferrocene groups are often introduced by scientists as good electrochemical materials because of the good electrochemical response of Fe(II)/Fe(III) redox system, which changes the electrochemical stability of products. Therefore, ferrocene-containing chemical sensor is an important field in the detection of Cu2+, Hg2+ plasma or H2S.

**References**

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