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REVIEW

Progress on Optical Probes for Hydrogen Sulfate Anion Sensing

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Abstract: The hydrogen sulfate anion (HSO_4^-) plays an important role in biological and environmental areas, which could contaminate the environment and cause harm to human body. Thus a highly selective and sensitive detection of HSO_4^- is of significant importance. Among various methods for detection of hydrogen sulfate anion, optical chemosensors based on molecular recognition is desirable with unique advantages. Anions optical sensing systems are predominantly attractive due to their simplicity, high specificity, low detection limits, easy on-line analysis and especially colorimetric recognition and in-situ detection. Herein, the progresses during the last decades on optical chemosensors and probes for HSO_4^- based on the recognizing mechanism were summarized. The further research orientations were also prospected.

Key Words: Hydrogen sulfate; Molecular recognition; Colorimetric recognition; Fluorescent probe; Review

1 Introduction

Anion recognition and sensing is an important and active research topic in the field of supramolecular chemistry, and the design of receptors for anions has also caused great attention[1-4]. Amide, amine, thiourea, urea, guanidine, pyrrole/indole and phenolic hydroxyl groups with hydrogen bonding groups as anions binding units have been widely used in receptor design and anion recognition, and the receptors would have good photochemical sensing properties by introducing reporting groups with fluorescence/absorption signal. The optical sensing molecules (probes) based on the concept of molecular recognition have unique advantages[5–8]. The anion sensing systems have caused great attention due to the advantages including good selectivity, high sensitivity, easy on-line analysis, especially visual colorimetric identification and in-situ detection. Among various important anions, the hydrogen sulfate anion (HSO_4^-) is especially important in biological, environmental and catalytic areas. Firstly, SO_4^{2-} and HSO_4^- are very important macronutrients in cells and are the fourth most abundant anion in human plasma, which are also required for development of organism and cell growth and involved in a variety of important biological processes, including biosynthesis and detoxification via sulfation of many endogenous and exogenous compounds. Secondly, HSO_4^- could be found in agricultural fertilizer and nuclear fuel waste, which enter into the environment and eventually dissociate under high pH conditions and generate toxic sulfate ion, causing irritation of skin and eyes, and even respiratory paralysis. Thirdly, sodium bisulfate has been widely concerned as a very important catalyst, especially effective for catalytic condensation and dehydration reaction. Therefore, the detection of HSO_4^- is of great significance. The commonly used methods for detection of anions include inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectroscopy

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(ICP-AES), ion chromatography and ion electrode methods. These techniques suffer from the use of expensive instruments, hazardous sample preparation and require highly trained operators. The photochemical probe method using UV spectrophotometer and fluorescence spectrophotometer which are relatively cheap has the virtues of simple operation, good selectivity and high sensitivity[9–16]. However, HSO_4^- is an amphiphilic ion with hydrogen bond donor/acceptor properties and has a tetrahedral structure. The receptor's selective recognition for substrate could be described as "lock and key" spatial matching, resulting in the quite complex design of receptor for HSO_4^-. So, there are relatively few studies on the photochemical probe for HSO_4^-. The recognition of HSO_4^- by photochemical probe is mainly through hydrogen bonding, metal-ligand coordination and chemical reactions. Based on its identification mechanism, the progresses on photochemical probes for HSO_4^- over the past decade were reviewed in this paper.

2 Hydrogen bonding/protonation based optical probes for hydrogen sulfate anions

2.1 Receptors containing pyrrole/indole moiety

A new diamidodipyrromethane macrocycle based anions receptor **1** (Fig.1) was synthesized by Sessler *et al*[17], which was linked by a pyridine-diamide group and a dipyrromethane group via C=N group. Receptor **1** showed a high selectivity for dihydrogen phosphate and hydrogen sulfate relative to nitrate in acetonitrile solution, which might be used to the selective removal of HSO_4^- from nitrate-rich waste mixtures. However, the photochemical signal of pyrrroles-based receptor is quite weak, which limits the application in photochemical sensing.

The indole compounds can not only provide NH groups as hydrogen bonding donors, but also act as photochemical signal reporting units, which has attracted much attention in the design of photochemical sensing. The anions recognition and sensing properties of Norharmane-based receptor **2**[18] was studied by Mallick *et al*. Receptor **2** contains an acidic hydrogen bond donor NH and a basic hydrogen bond acceptor unit N atom, which could easily form hydrogen bonds with a strong base and protonated by the relatively strong acidic substance. The receptors allowed the ratiometric selective detection of F^- and HSO_4^- ions with high selectivity through the absorption and emission spectroscopic method.

An new and simple oxidized bis(indolyl)methane-based chromogenic receptor **3** containing an acidic H-bond donor moiety and a basic H-bond acceptor moiety was developed by our group[19]. This receptor could act as a selective colorimetric sensor either for F^- in aprotic solvent or for HSO_4^- in water-containing solution. The deprotonation/ protonation of receptor **3** is responsible for the dramatic color change.

Anion recognition and sensitivity of anthracene-substituted bis(indolyl)methane **4** and tris(indolyl)methane **5** was studied by Sain *et al*[20]. Receptor **4** could selectively recognize HSO_4^- through colorimetric and fluorescent methods. Receptor **5** could detect and discriminate cyanide and HSO_4^- according to the color change. The recognizing and sensing mechanism of receptors **4** and **5** were studied by UV-vis absorption spectra, fluorescence spectra, ^1H NMR and quantum chemical DFT calculations, which proposed that a hydrogen-bonded complex formed between receptors and HSO_4^-.

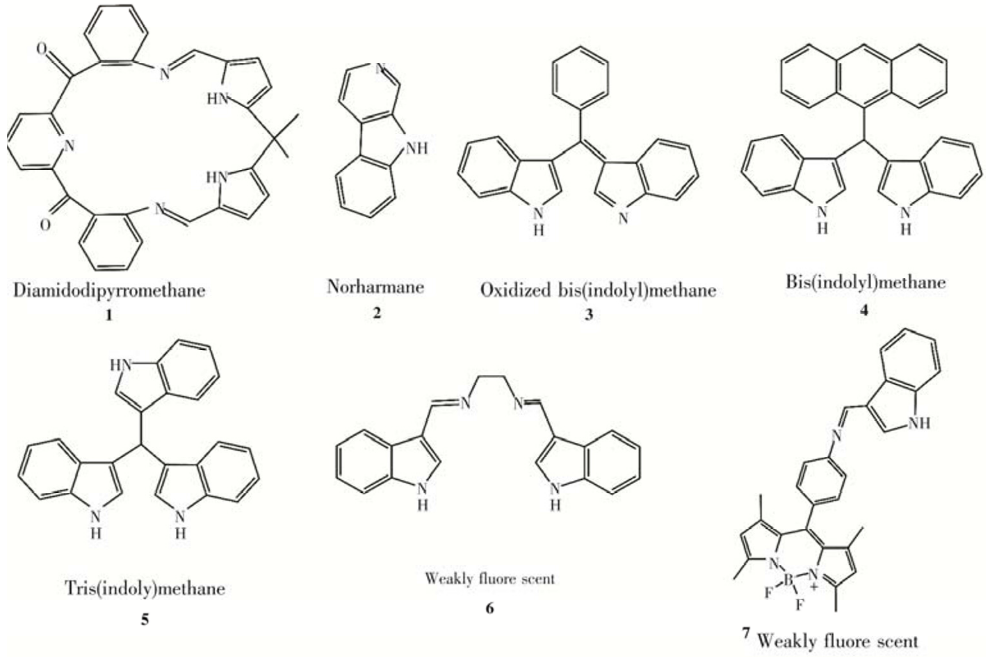

Fig.1 Pyrrole and indole-based optical receptors for anions