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A colorimetric and fluorescence enhancement anion probe based on coumarin compounds

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ABSTRACT

In this paper, anion probe **1** was designed and synthesized by using phenprocoumon containing acyl hydrazine with *p*-nitro azo salicylaldehyde reaction Dickson et al. (2008) Dickson et al. (2008) [1]. In the anion probe **1**, the nitro moiety is a signaling group and the phenolic hydroxyl moiety is anion binding site. Then the anion probe **1** was characterized by mass spectra (MS) and infrared spectra (IR). The binding properties of the anion probe **1** for anions such as F^-, AcO^-, $H_2PO_4^-$, OH^-, Cl^-, Br^- and I^- were investigated by ultraviolet-visible (UV–Vis) spectra and fluorescence spectra Shao et al. (2008) Shao et al. (2008) [2]. Furthermore, the color of anion probe **1** after addition of F^-, AcO^-, $H_2PO_4^-$ and OH^- in DMSO changed from yellow to blue, while no obvious color changes were observed by addition of other tested anions. Accordingly, the anion probe **1** could sense visually F^-, AcO^-, $H_2PO_4^-$ and OH^- without resorting to any spectroscopic instrumentation Amendola et al. (2010) Amendola et al. (2010) [3].

1. Introduction

In the recent years, the colorimetric and fluorescent sensing of anions have played an important role in catalytic chemistry, biological systems, environmental sciences and clinical diagnosis [4]. Therefore, the research on the anionic detection and selective recognition has become the hot spot of research [5,6]. In particular, more and more importance is attached to colorimetric anion sensors which has become a simple and convenient way to detect anions, it can be attributed to the colorimetric anion sensing system would allow the so-called 'naked-eye' detection of anions without resorting to any spectroscopic instrumentation [7]. Consequently, a great number of anion sensors have been synthesized by conventional methods [8]. However, conventional synthetic methods are often very complex and the products are difficult to separate for the synthesis of structurally complicated anion sensors [9]. Therefore, there still is an urgent need for design of novel, simple colorimetric and fluorescent anion sensors [10].

An ideal colorimetric and fluorescent anion sensors may be affected by many factors, such as chemical stability, light stability, selectivity, fluorescence detection sensitivity and so on [11,12]. But most of the fluorescent anion sensors reported cannot meet these requirements. After years of research and exploration, we found that coumarin compounds have not only strong chemical stability and fluorescence, but also high fluorescence quantum yield, which can achieve the changes of continuously wavelength in the visible region by chemical modification for its precursors [13,14]. Therefore, the fluorophore of fluorescent molecules have often been designed and used in ionic detection of certain biomolecules [15]. However, it is easy to generate fluorescence quenching for coumarin derived fluorescent chemosensors, which will seriously affect the signal output [16–18]. How to develop the fluorescence enhancement anion probes which have stable fluorescence properties will be our focus [19].

In this study, an anion probe **1** of fluorescence enhancement was designed and synthesized by using phenprocoumon containing acyl hydrazine with *p*-nitro azo salicylaldehyde reaction [20]. We used UV–Vis spectra and fluorescence spectra to research the relationship between anion probe **1** and anions [21–23]. The results showed that the addition of anions such as F^-, AcO^- and $H_2PO_4^-$ elicited a visible decrease in the fluorescence emission intensity of anion probe **1** owing to a quenching PET process from the —OH or —NH group to the —NO_2 group. As expected, the anion probe **1** was sensitive to anions and showed a unique color change from yellow to blue in the presence of F^-, AcO^-, $H_2PO_4^-$ and OH^-, while there were hardly color changes in the presence of other tested anions [24–27].

2. Experimental procedure

2.1. Materials and reagents

In the titration experiments, all the anions were added in the form of tetrabutylammonium (TBA) salts, which were purchased from Alfa

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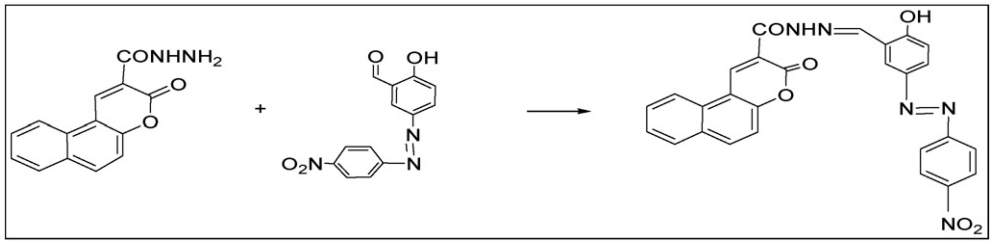
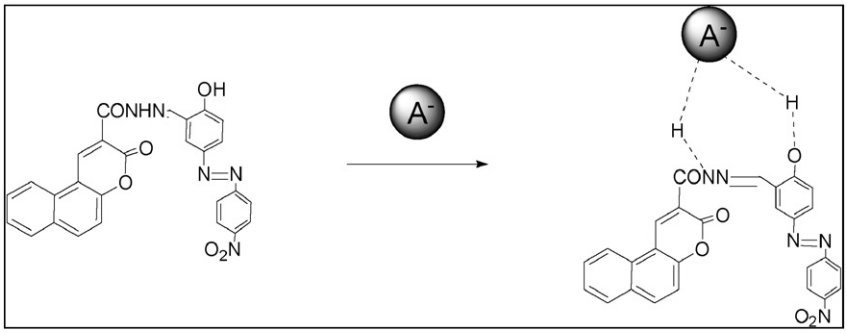


Scheme 1. Synthetic routes for the anion probe **1**.



Scheme 2. The proposed binding mode of probe **1** and A^- (A^- denotes anions such as AcO^-, F^-, $H_2PO_4^-$).

Aesar Chemical, stored in a vacuum desiccator containing self-indicating silica and dried fully before using. DMSO was dried with CaH_2 and the distilled in reduced pressure. All reagents for synthesis were used without further purification.

2.2. Synthesis of anion probe *1*

The synthetic route of anion probe **1** was shown in Scheme 1. Phenprocoumon-3-formylhydrazine (0.1265 g, 0.5 mmol) in ethanol (20.0 ml) was added dropwise a solution of *p*-nitro azo salicylaldehyde (0.1355 g, 0.5 mmol) in ethanol (20.0 ml). Then the mixture was heated to reflux under magnetic stirring for 3.0 h. During the reaction a yellow precipitate appeared which was collected after filtration and lavation with ethanol. Finally, the pure anion probe **1** (0.1465 g) was obtained, yield = 57.8%. (See Scheme 2.)

2.3. Analytical method

UV–Vis spectra was recorded on a TU-1810 Spectrophotometer made by Beijing Puxi Tongyong apparatus company with quartz cuvette (path length = 1 cm) and fluorescence spectra was recorded on a F96 Spectrophotometer made by Shanghai Lengguang Technology Co., LTD. The width of the slits is 10 nm. The synthetic anion probe **1** was characterized by infrared spectrometer made by Thermo Fisher Scientific and Mass Spectrometer made by Micromass UK Limited.

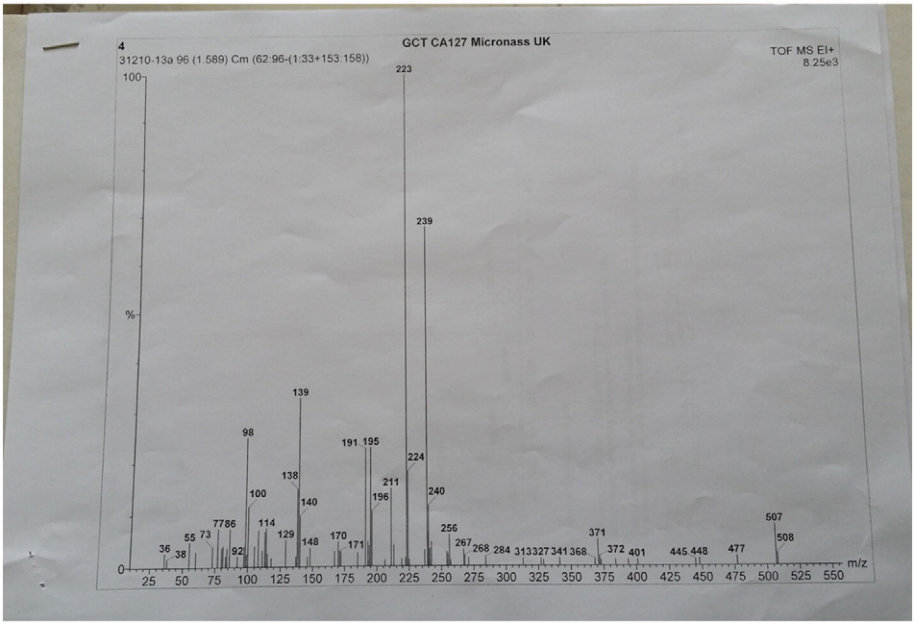


Fig. 1. Mass spectra of anion probe **1**.