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Short communication

Salicylaldehyde based colorimetric and "turn on" fluorescent sensors for fluoride anion sensing employing hydrogen bonding

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ABSTRACT

Two salicylaldehyde based colorimetric and fluorescent chemosensors **1** and **2** were developed. Both receptors **1** and **2** showed unique selectivity for the fluoride anions over other anions in DMSO solution. [TBA] OH and ^{1}H NMR titration experiments revealed that the F^--induced colorimetric and "turn on" fluorescence response were driven by hydrogen bonding interaction between the OH protons and F^-.

1. Introduction

The design and development of selective and sensitive optical sensors for anions have gained considerable attentions, as anions play major roles in a wide range of chemical and biological processes [1–5]. Recently, much effort has been devoted to developing fluorescent anion sensors, due to their simplicity, high degree of specificity and low detection limit, however, only few of them are "turn on" fluorescent sensors [6–15]. In terms of sensitivity concerns, sensors exhibiting fluorescence enhancement (fluorescence "turn on") in sensing process are favored over those showing fluorescence quenching (fluorescence "turn off"), because fluorescence "turn off" sensors may report false results caused by other quenchers in practical samples [16].

Despite the higher acidity of the hydroxyl group, far less attention has been given to the OH based anions receptors and sensors [17–20]. As part of our ongoing studies on simple and easy-to-make anions receptors and sensors [21–24], here we presented Salicylaldehyde based anions receptors **1** and **2** (Scheme 1), synthesized by one facile step condensation, behaved as a highly selective F^- sensor in both colorimetric and fluorometric analysis. An earlier reported on the possibility of the analogous bisazine-type ligand [25–28] to act as a bischelating ligand toward transition metal ions has led us to synthesize the receptors **1** and **2** for recognition of anions. In the bisazine-type ligand, the electron density are located on the C=N-N=C moiety, the binding of metal ions to the ligand would affect the electron density and thus influence the fluorescence of the ligand. In our paper, the strategy for the design of the receptors was based upon the idea that the binding of anions to the receptors may trigger the conformational switching of C=N and influence the charge distribution of entire conjugate system of the receptors, which would modulate the spectral properties of the receptors.

2. Experimental

2.1. Materials

All reagents for synthesis obtained commercially were used without further purification. In the titration experiments, all the anions were added in the form of tetrabutylammonium (TBA) salts, which were purchased from Sigma–Aldrich Chemical, stored in avacuum desiccator.

2.2. Synthesis of receptor *1*

1.22 g salicylaldehyde was dissolved in ethanol (50 ml) and 0.25 ml of hydrazine hydrate (99%) was added at room temperature. The reaction mixture was stirred at room temperature overnight. After completion of the reaction, the obtained yellow precipitate was filtered and washed several times with cold ethanol to yield the pure **1**. Yield 85%.

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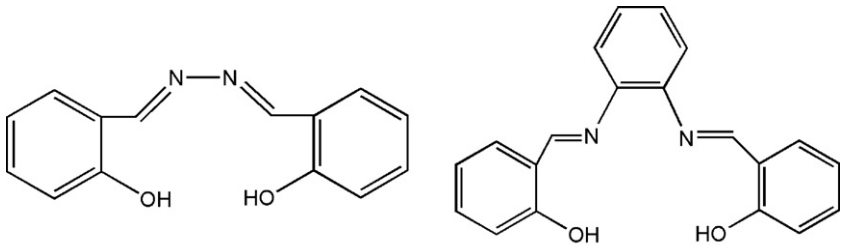

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Scheme 1. Structure of receptor **1** and **2**.

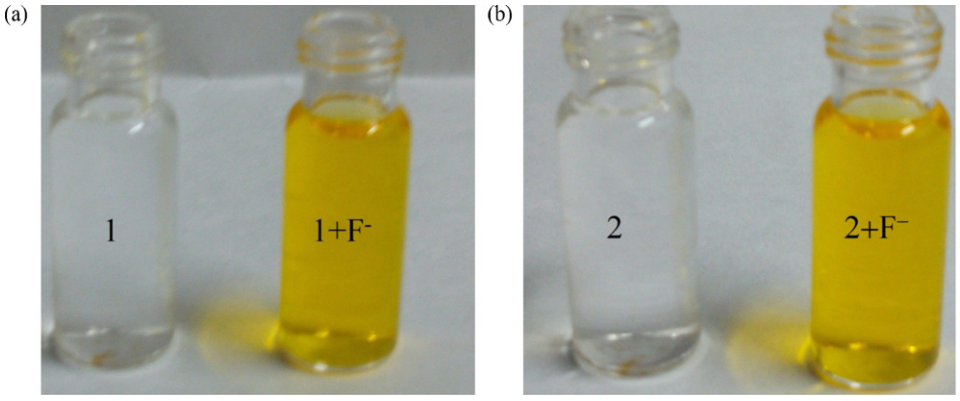

Fig. 1. Color changes of receptor **1** (a) and **2** (b) in DMSO solution with the addition of F^-.

EI-MS: *m*/*z* 241.2 ($M+H^+$).

^1H NMR (400 Hz, DMSO-d_6), δ: 11.122 (s, 2H, OH), 8.999 (s, 2H, N=CH), 7.676–7.699 (m, 2H, Ar–CH), 7.372–7.414 (m, 2H, Ar–CH), 6.943–6.982 (m, 4H, Ar–CH).

Anal. calcd. for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.74; H, 4.86; N, 11.64.

Melting point: 219–220 °C.

2.3. Synthesis of receptor **2**

A solution of salicylaldehyde (1.22 g, 10 mmol) and 1,2-phenylenediamine (0.54 g, 5 mmol) in 50 mL of ethanol was stirred at room temperature overnight. After completion of the reaction, the obtained yellow precipitate was filtered and washed several times with cold ethanol to yield the pure **2**. Yield 82%.

EI-MS: *m*/*z* 317.2 ($M+H^+$).

^1H NMR (400 Hz, DMSO-d_6), δ: 12.937 (s, 2H, OH), 8.932 (s, 2H, N=CH), 7.648–7.671 (m, 2H, Ar–CH), 7.387–7.474 (m, 6H, Ar–CH), 6.944–6.987 (m, 4H, Ar–CH).

Anal. calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.36; H, 4.91; N, 8.78.

Melting point: >300 °C.

3. Results and discussion

The anion binding properties of receptors **1** and **2** were investigated by UV–vis, fluorescence and ^1H NMR spectroscopy.

The result of receptor **1** treated with various anions (F^-, Cl^-, Br^-, I^-, AcO^-, ClO_4^-, HSO_4^-, $H_2PO_4^-$, tetrabutylammonium salts, TBA) in DMSO solvent was shown in Fig. 1(a). The color of the solution changes from colorless to yellow upon addition of F^-. In contrast, no obvious changes in color were observed upon addition of other anions.

The UV–vis spectrum of receptor **1** in DMSO exhibited two absorption bands with maxima at 293 and 354 nm. Titration of receptor **1** with fluoride anions resulted in a bathochromic shift absorption band with a maxima at 461 nm (Fig. 2). Three isosbestic points at 270, 310 and 390 nm were observed during the titration, indicating a single component was produced in response to the interaction between receptor **1** and fluoride anions. No obvious changes in absorption spectrum were observed on the addition of other anions (Supplementary data, Fig. S1). The corresponding fluorescence titrations were carried out in DMSO solution. As shown in Fig. 3, receptor **1** showed very weak fluorescence, with an emission band at 520 nm when excited at 396 nm. Addition of fluoride anions to the solution of receptor **1** induced an increas-

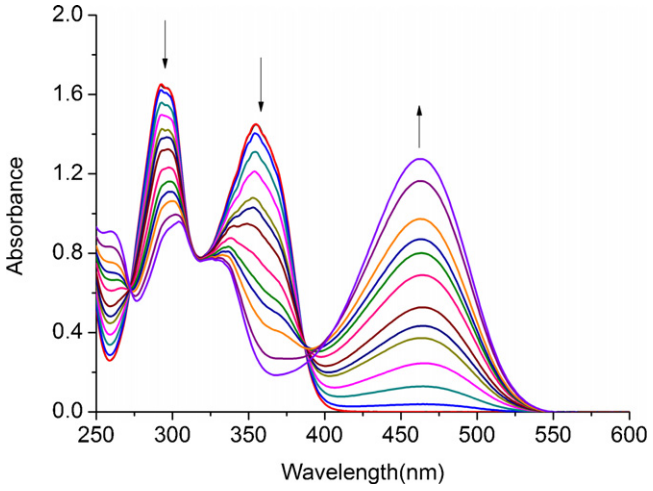

Fig. 2. Changes in the UV–vis absorption spectrum of receptor **1** (1.5×10^{-5} M) in DMSO upon addition of F^- anions in TBA salts form (0–20 equiv.).