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## Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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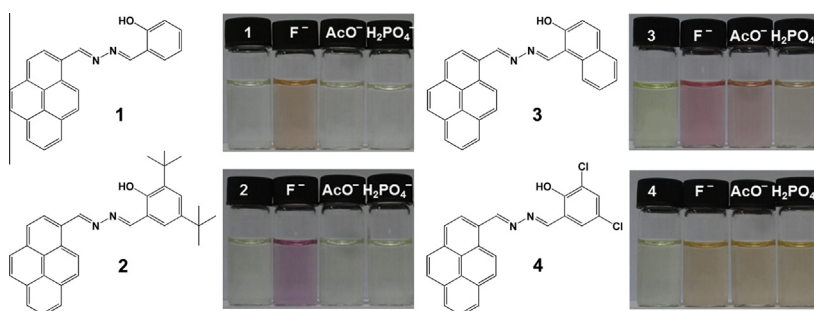
## Substituent effects on anion sensing of salicylidene Schiff base derivatives: Tuning sensitivity and selectivity

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## HIGHLIGHTS

- Synthesis of four novel colorimetric anion sensors based on salicylidene Schiff base.
- Sensitivity and selectivity are interrelated with the substituent of chromophores.
- F<sup>-</sup> sensing through color changes based on deprotonation.
- Sensor **1** can be applied in qualitative detection of F<sup>-</sup> in aqueous medium.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 5 February 2015

Received in revised form 18 May 2015

Accepted 4 June 2015

Available online 17 June 2015

## Keywords:

Salicylidene Schiff base

Anion sensing

Substituent effects

Sensitivity

Selectivity

## ABSTRACT

A series of colorimetric anion sensors using the salicylidene Schiff bases with different substituents, including electron donating group (tert-butyl, in sensor **2**), conjugated group (naphthyl, in sensor **3**) and electron withdrawing group (chlorine, in sensor **4**), respectively, have been developed. The substituents can not only impact chromogenic signal output, but also tune the sensitivity and selectivity of the anion sensing by their specific electron push–pull features. In particular, both **1** (without substituent) and **2** show high selectivity for F<sup>-</sup> over Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, AcO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, but the sensitivity of **2** is poorer than **1** due to the effect of electron donating groups. Sensor **3** exhibits higher sensitivity for F<sup>-</sup> than **1**, but it is disturbed by the weak response to AcO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. Sensor **4** has the highest sensitivity for F<sup>-</sup>, but shows the significant response to AcO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, which also decreases the selectivity for F<sup>-</sup>. Finally, analytical applications of **1** for the detection of F<sup>-</sup> in aqueous medium and toothpaste have been studied.

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## Introduction

Anion binding and sensing is now a major field within supramolecular chemistry with potential applications in pollutant sequestration, biomedical and environmental monitoring, anion exchange, and anion transport [1,2]. Considerable attention has been focused on the design of colorimetric hosts that can

selectively recognize anion species through visible color changes with the advantages that the responses can be conveniently detected by the naked eye [3,4]. A variety of colorimetric sensors containing a number of different types of anion binding group have been designed and tested for anion recognition and sensing over the past years [5–11]. Most of these sensors are developed based on hydrogen bonding interaction [12–14], deprotonation [15–17] or chemical reaction [18–20]. However, many anion sensors are not able to differentiate F<sup>-</sup>, AcO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> because of their similar basicity and surface charge density [21,22]. Among various

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anions,  $F^-$  is attracting a great deal of interest because of the importance of this anion in dental health and its possible toxicity when administered in high doses [23,24]. Thus, there is considerable current interest in sensitive and selective recognition of  $F^-$ . Salicylidene Schiff base derivatives, as an excellent class of anion receptors, have been integrated into a variety of anion sensors to detect  $F^-$  or other specific anionic guests [25,26]. However, it is not sufficient to engage in the act of solving the problem of differentiating  $F^-$ ,  $AcO^-$ , and  $H_2PO_4^-$  [27]. In the literature, several studies have shown that the substituents have a great impact on the selectivity and sensitivity of anion sensors [12,28]. Therefore, changing substituting group of sensors should be an effective way to solve this problem. However, to the best of our knowledge, the substituent effects on anion sensing of salicylidene Schiff base derivatives have not been reported so far.

Herein, four anion chemosensors based on salicylidene Schiff bases bearing pyrene moiety have been designed and synthesized. As depicted in Scheme 1, they are sensor **1** (without substituent), electron donating groups (tert-butyl) substituted sensor **2**, conjugated group (naphthyl) substituted sensor **3**, and electron withdrawing groups (chlorine) substituted sensor **4**. These representative substituent groups will help us understand the substituent effects on anion sensing process, including color change, the sensitivity and the selectivity. Meanwhile, the introduction of pyrene group induces an increase in conjugate level of sensors, and this will provide a good chromogenic signal output in the visible region. All the four sensors exhibit excellent responsive properties but various effects in molecular recognition of anions. The mechanisms controlling the maximum of the absorption shift, as

well as the sensitivity and selectivity of anion recognition have been investigated in detail (see below).

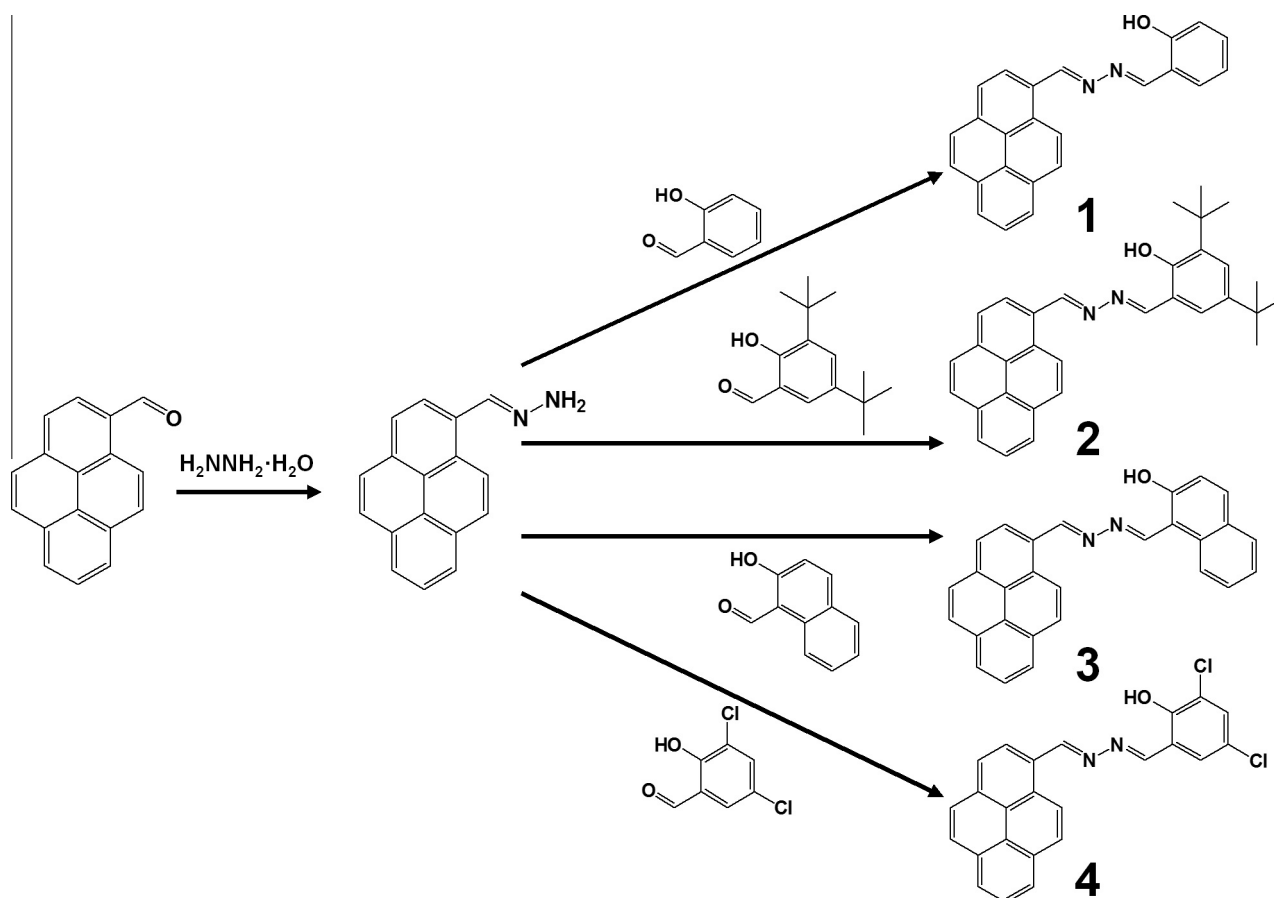
## Experimental

### Materials and methods

All the materials for synthesis and spectra were purchased from commercial suppliers and used without further purification. All solvents and reagents used in the spectroscopic studies were analytical grade. All anions were in the form of tetrabutylammonium (TBA) salts.  $^1H$  NMR (TMS) was recorded on a Bruker UltraShield 500 MHz spectrometer. UV–vis absorption spectra were taken on a Shimadzu 3100 UV–VIS–NIR recording spectrophotometer using a 2 nm slit width in 1 cm quartz cells. The binding abilities of **1**, **2**, **3** and **4** with anions were investigated by UV–vis absorption spectroscopy in  $CH_3CN$  solution using a constant host concentration (10  $\mu M$ ) and increasing concentrations of anions. The equilibrium constants of the sensors and anions were calculated by the method which had been reported previously [29].

### Synthesis

Sensors **1**, **2**, **3** and **4** were prepared from the condensation of pyren-1-ylmethylene-hydrazine [30] with Salicylaldehyde, 3,5-di-tert-butyl-2-hydroxy-benzaldehyde, 2-hydroxy-naphthalene-1-carbaldehyde and 3,5-dichloro-2-hydroxy-benzaldehyde, respectively, as depicted in Scheme 1 and characterized by  $^1H$  NMR (Figs. S1–S5).



Scheme 1. The synthetic routes of **1**, **2**, **3** and **4**.

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