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Novel salicylic acid-oriented thiourea-type receptors as colorimetric chemosensor: Synthesis, characterizations and selective naked-eye recognition properties

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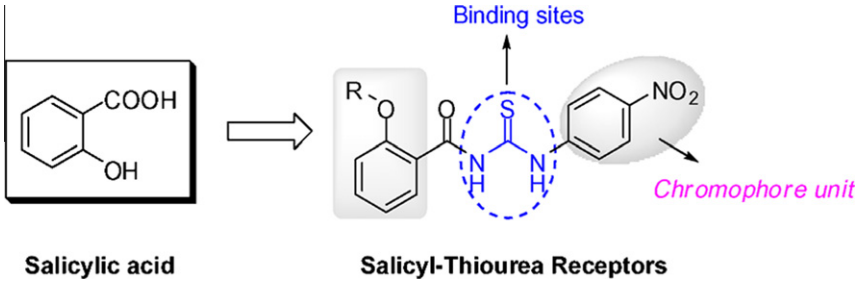
HIGHLIGHTS

- Receptors AR1–3 can be utilized as a colorimetric chemosensor for detection of F^- anion.
- Receptors AR1–3 are novel salicylic acid-oriented thiourea-type receptors.
- Receptors AR1–3 showed excellent selectivity toward F^- over the other competitive anions.

GRAPHICAL ABSTRACT



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ABSTRACT

Based on the salicylic acid backbone, three highly sensitive and selective colorimetric chemosensors with an acylthiourea binding unit have been designed, synthesized and characterized. These chemosensors have been utilized for selective recognition of fluoride anions in dry DMSO solution by typical spectroscopic titration techniques. Furthermore, the obtained chemosensors **AR1–3** have shown naked-eye sensitivity for detection of biologically important fluoride ion over other anions in solution.

Introduction

In recent years, anions recognition has attracted considerable attentions due to the increasing importance of anions in extension areas such as the biology, environment and industry [1,2]. So the development of novel anion receptors is of great interest and significance in the field of host–guest chemistry [3]. Anion recognition by artificial receptors has represented a unique bioanalytical application in anion sensor, membrane transmit carrier and simulation, enzyme catalyst synthesis, etc. [4]. Up to now, there are several structural types of synthetic receptors (Fig. 1) have been developed mainly included urea/thiourea-based receptors (compounds **1**–**3**) [5–7], amide-based receptors (compounds **4**–**6**) [8–10], and other neotype receptors (compounds **7**–**9**) [11–13], etc. In particular, colorimetric-based sensing is especially attractive in these years, as it may allow naked-eye detection of the analyte without resorting to any expensive equipment [7,9,14].

Meanwhile, as we know, salicylic acid is one of a wide variety of phenolic compounds distributed in many organisms, and which plays an important role in biochemical process [15–17] and coordination chemistry [18,19]. Thus, keeping these perspectives in mind, a novel series of salicylic acid-oriented thiourea-based

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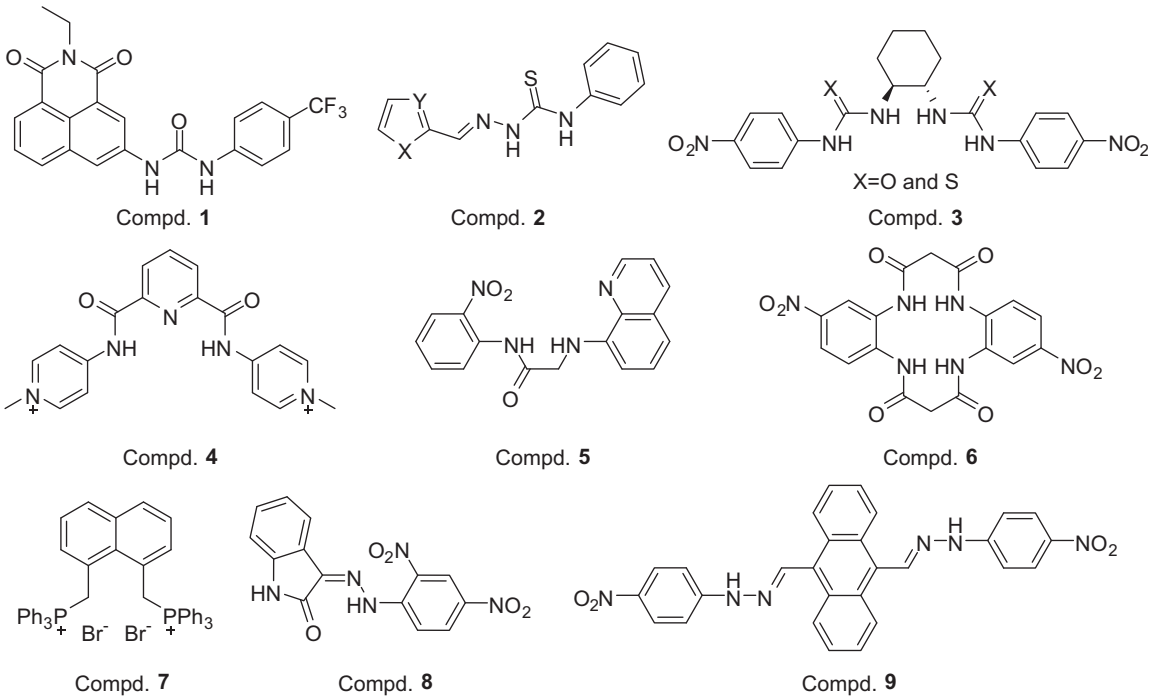

Fig. 1. Representative structural types of various anion receptors.

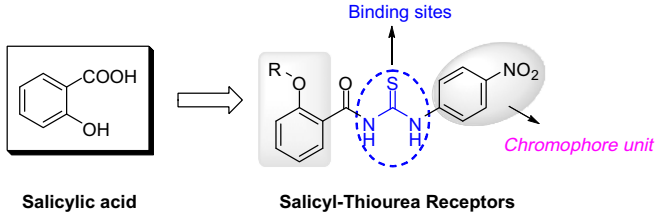

Fig. 2. Design strategy of salicylic acid-oriented thioureas as anion receptors.

colorimetric anion receptors (Fig. 2) have been designed and synthesized, and which have been elucidated to selectively recognize for fluoride anions through naked-eye visible color changes. The thiourea subunit in these receptors, speculated to be a hydrogen bond-donor and suitable to interact with the anions, has been appended in between substituted-salicyl and 4-nitrophenylamine units. The covalently linked 4-nitrophenylamine moiety intends to act as a chromophore unit. The experimental results indicate that these receptors are highly selective and sensitive to recognize fluoride anion in dry DMSO and the processes of sensing can be obviously seen through the visible color changes for naked-eye recognition.

Experimental section

Materials and general methods

All melting points (m.p.) were obtained using a digital model X-5 apparatus and are uncorrected. Infrared (IR) spectra in potassium bromide (KBr) were recorded on a Thermo Nicolet FT-IR Avatar 330 instrument. ^{1}H NMR spectra were recorded on a Brucker spectrometer at 400 MHz with DMSO-d_6 as the solvent and TMS as the internal standard. Chemical shifts are reported in δ (parts per million) values. Coupling constants ^nJ are reported in Hz. Mass spectra were performed on a MicroMass Quattro *micro*™ API instrument. Elemental analyses were performed on a Vario EL III elemental analysis instrument. Analytical thin-layer chromatography (TLC) was carried out on precoated plates, and spots were visualized with ultraviolet light. The UV–vis spectra were recorded on a Shimadzu UV-2450 Spectrophotometer (Shimadzu 2.1 Apparatus Corp., Kyoto, Japan) using a quartz cuvette (path length = 1 cm) at 298.0 ± 0.1 K. All the anions in the form of tetrabutylammonium salts were purchased from Sigma–Aldrich Chemical Co. or Sinopharm Chemical Reagent Co., and stored in a vacuum desiccator containing self-indicating silica. Anhydrous solvents like dimethylsulphoxide (DMSO) and acetonitrile (CH_3CN) were dried according to standard methods [20]. All other solvents and reagents were analytical reagent and used directly without purification.

Syntheses of target receptors AR1–3

General synthetic procedure for the key intermediates ***3***

The key intermediates **3** can be obtained *via* three steps including esterification, alkylation and saponification reactions. The general procedures are as follows: (1) To a solution of prepared methyl 2-hydroxybenzoate (4.56 g, 30 mmol) and halides (30 mmol) in MeCN (40 mL) was added K_2CO_3 (4.55 g, 33 mmol). The resultant mixture was stirred at room temperature for 1.5 h and another about 6–8 h at 50–60 °C, which was detected by TLC. The mixture was cooled to ambient temperature, after filtration and concentration *in vacuo*, the residue was recrystallized from ethanol. (2) To a solution of the newly prepared compound **2** (20 mmol) in MeOH (5 mL) was added aqueous NaOH (20%, 1.5 eq.). The resulting mixture was stirred at 45–50 °C for 4–6 h. After cooling the mixture to room temperature, it was acidified with aqueous HCl (5.0 M) to pH 2–3 and the precipitates were filtered off by filter paper. After washing (H_2O and hexanes) and drying *in vacuo*, the intermediates **3** were obtained as a white powder. **3a** (R^1 = 2-chloro-5-methylpyridine), yield 94%, m.p. 151–152 °C, ESI–MS: 264.5 ($C_{13}H_{11}ClNO_3^+$, $[M+H]^+$); **3b** (R^1 = 4-fluorobenzyl), yield 96%, m.p. 85–86 °C, ESI–MS: 229.4 ($C_{14}H_{11}FO_3$, $[M\text{-}OH]^+$).