



Simple colorimetric sensors with high selectivity for acetate and chloride in aqueous solution

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ABSTRACT

A series of novel colorimetric anion sensors bearing phenol O–H and hydrazone N–H groups were synthesized and their structures were confirmed by X-ray single-crystal diffraction. In DMSO/H₂O (9:1, v/v) solutions, two-arm pincer type sensors **1** and **2** could bind Cl[−] through the collaboration of phenol O–H and hydrazone N–H groups. In DMSO/H₂O (7.5:2.5, v/v) solutions, sensors **1**, **2** and **4** showed colorimetric single selectivity for AcO[−]. When AcO[−] was added to their solutions, dramatic color changes from orange to magenta were observed. Yet other anions such as F[−], Cl[−], Br[−], I[−], HSO₄[−] and H₂PO₄[−] could not cause any color change. Comparison with compound **5** (the analogues of **1–4**, but not containing the O–H groups) indicates that the phenol O–H group plays a critical role in the anion-recognition process.

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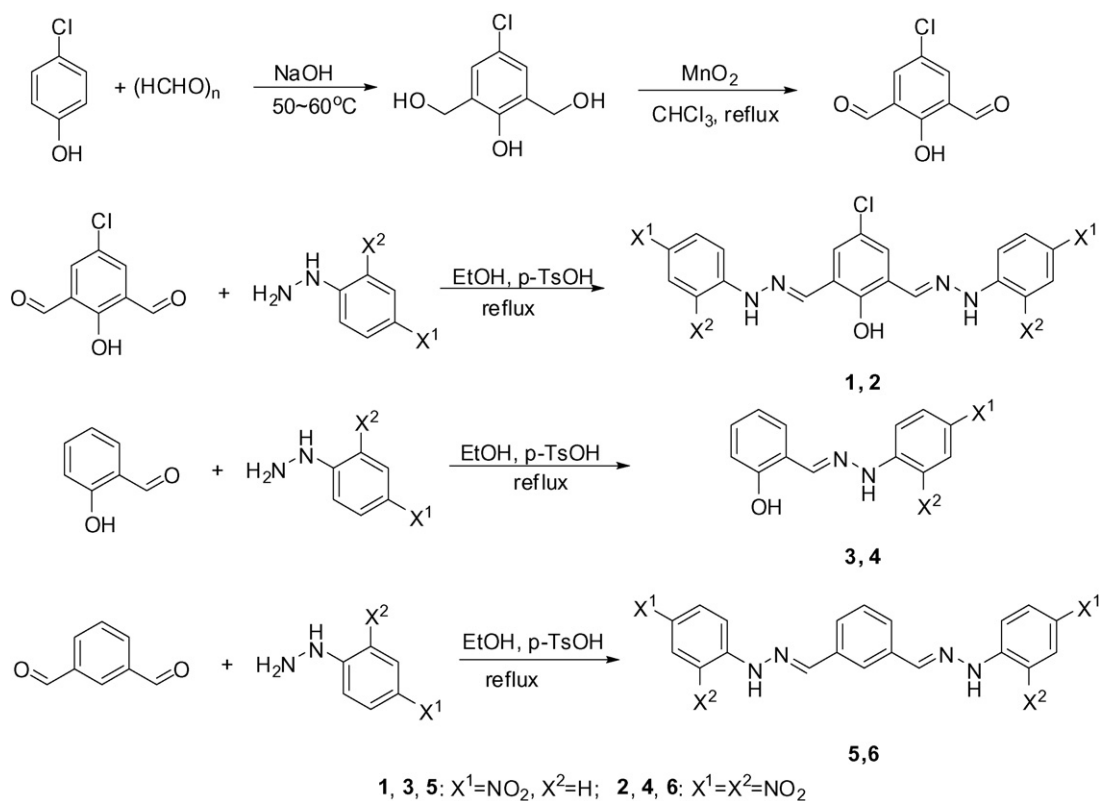
1. Introduction

Anions play a fundamental role in a wide range of chemical, biological and environmental processes. The rational design and synthesis of efficient sensors to selectively recognize anion analytes is an emerging field of supramolecular chemistry. Since the first synthetic sensor for inorganic anions was reported in 1968 [1], great progress has been made [2–8]. While previous work has focused on developing a wide variety of sensors based on electrostatic interactions, hydrogen bond donor groups, Lewis acid groups and hydrophobic interactions, it is still a challenge to design the anion sensors with high selectivity and sensitivity in a competitive media. As a subset of the anion receptor, the chromogenic anion sensors have shown unique merit, because they can reveal the host-anion binding information through a change of color [6,8,9].

With higher concentrations than most other anions in the biological systems, the chloride anion (Cl[−]) is of considerable interest in biology. This has inevitably given rise to an incentive for the development of Cl[−] sensors [10–15]. Due to its spherical structure, weak basicity and relatively large ionic radius, Cl[−] often requires sophisticated sensors. As a matter of fact, very few colorimetric sensors have been able to provide selective binding to Cl[−] [10]. On the other hand, acetate (AcO[−]) is a critical component of numerous

metabolic processes. The rate of AcO[−] production and oxidation has been frequently used as an indicator of organic decomposition in marine sediments [16]. Compared with the F[−] [17–19] and H₂PO₄[−] [20,21] sensors, AcO[−] sensors are limited for most of the AcO[−] sensors usually have a stronger affinity for F[−] [22–24]. In general, the colorimetric anion sensors use N–H containing groups in amide [7,25], urea/thiourea [26–28], pyrrole [11,29] and guanidinium [30] as binding sites. So far, very few colorimetric sensors have been synthesized by using hydrazone N–H as the anion binding site [24,31–36]. Even though O–H groups generally play the role of the anion binding site in biological systems including Cl[−] chloride channels [37], very little effort has been made to develop some anion sensors bearing the O–H group [12,32,33,38,39]. In the present paper, we describe the synthesis and anion-binding properties of a series of novel colorimetric anion sensors **1–4** bearing phenol O–H and hydrazone N–H groups (Scheme 1). Sensors **1**, **2** and **4** showed colorimetric single selectivity for AcO[−] in DMSO/H₂O (7.5:2.5, v/v) solutions. Moreover, sensors **1** and **2** could allow selectively recognition of Cl[−] in DMSO/H₂O (9:1, v/v) solutions. The strategies for design of these sensors are as follows. Firstly, we have introduced O–H and N–H groups into the same sensor molecule. The cooperation of these two groups can increase the anion binding ability of the sensors [39]. Secondly, in order to achieve “naked-eye” recognition, we introduced nitrophenyl groups as the chromophore. Thirdly, the two-arm pincer type structure (for **1** and **2**) was used to firmly chelate anions. Finally, these sensors were designed to be easy to synthesize. In order to figure out the O–H group’s contribution to the anion binding abilities of sensors **1–4**, compounds **5** and **6** of

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Scheme 1. Synthetic procedures for sensors **1–6**.

analogous structure but without containing O–H group were also synthesized.

In biological and environmental systems, anion–sensor interactions commonly occur in aqueous solution, therefore, much attention has been paid to developing anion sensors that work in the aqueous phase [8,18,23,24,36,40]. The challenge is that strong hydration in the aqueous phase stops the sensors from recognizing the anions. So far, only a few sensors have been synthesized that are able to recognize anions in the aqueous phase. For these reasons, we investigated the anion recognition abilities of compounds **1–5** both in DMSO and in DMSO/H₂O binary solutions using UV–vis spectroscopy and ¹H NMR titrations. The anion recognition ability of **6** was not studied because of its poor solubility.

2. Experimental

2.1. Materials and physical methods

¹H NMR spectra were recorded with a Mercury-400BB spectrometer at 400 MHz. ¹H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with the solvent resonances as internal standards). Electrospray ionization mass spectra (ESI-MS) were measured on an Agilent 1100 LC-MSD-Trap-VL system. UV–vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. All reagents used were of analytical grade. Single-crystal intensity data were collected on a Siemens SMART CCD diffractometer.

2.2. Synthesis of 5-chloro-2-hydroxyisophthalaldehyde

5-Chloro-2-hydroxyisophthalaldehyde were synthesized according to literature methods [41,42], yield 30%, m.p. 122–123 °C.

2.3. Synthesis and characterization of **1–6**

5-Chloro-2-hydroxyisophthalaldehyde (369.2 mg, 2 mmol), (4-nitrophenyl)hydrazine (641.5 mg, 4.2 mmol) and catalytic amount

of p-toluenesulfonic acid (p-TsOH) were mixed in hot absolute ethanol (30 mL). An orange precipitate was observed immediately. The solution was stirred under reflux conditions for 6 h, and the precipitate was filtrated, washed with hot absolute ethanol three times, then recrystallized with DMSO to get orange crystal **1** (804.8 mg, 1.66 mmol) in 83% yield. The other compounds **2–6** were prepared through the similar procedures.

2.3.1. 4-Chloro-2,6-bis(2-(4-nitrophenyl)hydrazono)methylphenol **1**

Yield 83%, m.p. >300 °C, ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.57 (s, 2H, NH), 11.20 (s, 1H, OH), 8.34 (s, 1H, HC=N), 8.18 (d, 4H, $J = 9.2$, ArH), 7.76 (s, 2H, ArH), 7.16 (d, 4H, $J = 8.8$, ArH). IR (KBr, cm^{-1}): 3440(mb), 3270(w), 3072(w), 1654(m), 1596(s), 1496(s), 1303(s), 1269(s), 1107(s), 996(w), 930(w), 833(w), 746(w). ESI-MS, m/z : 453.1. Anal. Calcd. for C₂₀H₁₅ClN₆O₅: C, 52.81; H, 3.32; N, 18.48; Found: C, 52.79; H, 3.28; N, 18.52.

2.3.2. 4-Chloro-2,6-bis(2-(2,4-dinitrophenyl)hydrazono)methylphenol **2**

Yield 85%, m.p. >300 °C, ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.80 (s, 2H, NH), 10.72 (s, 1H, OH), 8.94 (s, 2H, ArH), 8.45 (s, 2H, HC=N), 8.40–8.37 (m, 2H, ArH), 8.02–7.86 (m, 4H, $J = 9.2$, ArH). IR (KBr, cm^{-1}): 3437(mb), 3274(w), 3103(w), 1668(w), 1616(s), 1512(m), 1429(w), 1333(s), 1280(m), 1139(m), 1092(m), 926(w), 831(w), 738(w). ESI-MS, m/z : 543.2. Anal. Calcd. for C₂₀H₁₃ClN₈O₉·DMSO: C, 42.42; H, 3.07; N, 17.99; Found: C, 42.31; H, 3.15; N, 17.87.

2.3.3. 2-(2-((4-Nitrophenyl)hydrazono)methyl)phenol **3**

Yield 80%, m.p. 230–231 °C, ¹H NMR (DMSO-*d*₆, 400 MHz) δ 11.31 (s, 1H, NH), 10.16 (s, 1H, OH), 8.36 (s, 1H, HC=N), 8.16–8.13 (m, 2H, ArH), 7.76–7.74 (m, 1H, ArH), 7.24–7.20 (m, 1H, ArH), 7.12–7.10 (m, 2H, ArH), 6.92–6.86 (m, 2H, ArH). ¹³C NMR (DMSO-*d*₆, 100 MHz)

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