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Synthesis and recognition properties of a class of simple colorimetric anion chemosensors containing OH and CONH groups

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ABSTRACT

Two simple colorimetric anion chemosensors **1** and **2** containing OH and CONH groups were synthesized and their recognition properties toward various anions were investigated by naked-eye observation, UV–vis and ^{1}H NMR titration spectra. The experiment results showed that compound **1** was able to selectively recognize F^- and AcO^- through the formation of 1:1 hydrogen bonding complex, concomitant with a detectable color change (from colorless to pale yellow) during the recognition process. For compound **2**, a noticeable color change was seen only in the case of F^-, which was very similar to compound **1** in the molecular structure merely lack of a salicyloyl OH group. Additionally, compound **1** displayed a moderate binding affinity to $H_2PO_4^-$ ($K_a = 5.96 \times 10^3\ M^{-1}$). In contrast, there were no detectable interactions between compound **2** and $H_2PO_4^-$. In a word, the current studies suggested that a subtle change to receptor structure may lead to large and unpredictable differences to recognition behavior of receptor compound.

1. Introduction

The investigations on synthetic anion receptors have attracted growing attentions from chemists due to the key roles played by anions during the chemical, biological and environmental processes [1–6]. The binding units of anion receptors are often composed of amide [7–9], urea [10–13], thiourea [14–16], sulfonamide [17,18], pyrrole [19–21] and indole [22–24] groups. Compared with other H-bonding donors, hydroxyl group was less studied during the past years [25–30]. It is well known that some proteins in biological system can efficiently bind some specific anions cooperatively utilizing OH and CONH groups. For example, a phosphate-binding protein interacts with hydrogen phosphate involving in a total of twelve hydrogen bonds, four with OHs of serine and threonine, five with the backbone CONHs [31,32]. Moreover, there is also the participation of OH and CONH groups for stabilization of Cl^- in the ClC chloride channel [33,34].

Colorimetric sensing possesses huge advantages in practical applications as it can rapidly provide qualitative information about the analyte without any expensive instruments, however, colorimetric anion chemosensors based on OH group have seldom been reported [35–43].

Bearing the above considerations in mind, herein we reported two simple colorimetric anion chemosensors **1** and **2** containing OH and CONH groups (Scheme 1), which can discriminate biologically important F^-, AcO^- and $H_2PO_4^-$ from each other based on different color responses by cooperative utilization of compounds **1** and **2**.

2. Experimental

2.1. General

Dichloromethane and triethylamine were refluxed with CaH_2 and then distilled. Other chemicals were directly utilized as received without further purification. Melting points were determined on a XT-4 binocular microscope (Beijing Tech Instrument Co., China). IR spectra were recorded on a Bruker VECTOR 22 spectrophotometer in KBr disk. ^{1}H and ^{13}C NMR spectra were measured on a JEOL-ECX 500 NMR spectrometer at room temperature using TMS as an internal standard. Mass spectra were recorded on Agilent 5973inter GC/MSD. Elemental analysis was performed on an Elementar Vario-III CHN analyzer. UV–vis spectra were recorded on TU-1901 spectrophotometer (Beijing Pgeneral Instrument Co., China).

2.2. Syntheses

2.2.1. Synthesis of intermediate **4** [44]

Salicylic acid (0.83 g, 6.0 mmol) in $SOCl_2$ (20 mL) was heated to reflux for 2 h in the presence of several drops of DMF. After evapora-

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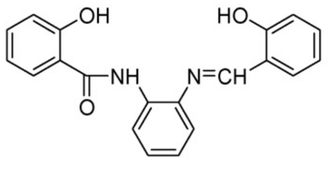
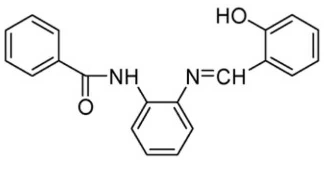
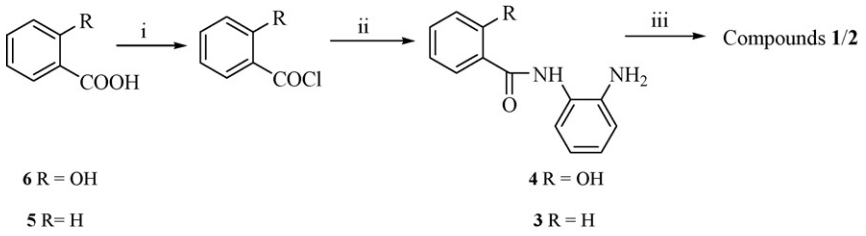


Compound **1**



Compound **2**



Scheme 1. Synthesis of compounds **1** and **2**. Reaction conditions: (i) $SOCl_2$/reflux; (ii) *o*-phenylenediamine/dry CH_2Cl_2/dry Et_3N/rt; (iii) salicylaldehyde/EtOH/reflux.

tion of excess of $SOCl_2$ under reduced pressure, the resultant acid chloride dissolved in dry CH_2Cl_2 (10 mL) was added dropwise to the stirred CH_2Cl_2 solution (20 mL) of *o*-phenylenediamine (0.78 g, 7.2 mmol) and dry Et_3N (1.50 mL, 10.8 mmol) over 0.5 h. The resultant mixed solution was stirred overnight at room temperature and then concentrated in vacuum. The crude product was purified by silica column chromatography (ethyl acetate/petroleum ether, 1/2, v/v) to afford the pure 4 as a white solid. Yield: 0.32 g (23%), Mp: 155–157 °C. ^1H NMR (500 MHz, DMSO-d_6): δ 4.94 (s, 2H), 6.60–6.62 (m, 1H), 6.78–6.80 (m, 1H), 6.93–7.00 (m, 3H), 7.24–7.25 (m, 1H), 7.42–7.45 (m, 1H), 8.02–8.03 (m, 1H), 9.95 (s, 1H), 12.20 (br, 1H). ^{13}C NMR (DMSO-d_6): δ 116.5, 116.9, 117.1, 117.7, 119.3, 123.0, 127.1, 127.2, 129.5, 134.2, 143.6, 159.8, 167.7. FT-IR (KBr): 3385, 3298, 3254, 1634, 1591, 754 cm^{-1}. MS (EI): *m*/*z* 228 (M$^+$). Anal. Calcd for $C_{13}H_{12}N_2O_2$ C 68.41, H 5.30, N 12.27, found C 68.21, H 5.42, N 12.32.

2.2.2. *Synthesis of intermediate **3** [45]*

A similar method was carried out to prepare intermediate **3** using benzoic acid in place of salicylic acid. Yield: 0.69 g (54%), Mp: 150–152 °C. ^1H NMR (500 MHz, DMSO-d_6): δ 4.87 (s, 2H), 6.55–6.58 (m, 1H), 6.74–6.76 (m, 1H), 6.92–6.95 (m, 1H), 7.13 (d, J = 7.5 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.53–7.55 (m, 1H), 7.95 (d, J = 7.5 Hz, 2H), 9.64 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 116.7, 116.8, 123.8, 127.0, 127.2, 128.3, 128.8, 131.9, 135.2, 143.7, 165.9. FT-IR (KBr): 3269, 1641, 748 cm^{-1}. MS (EI): *m*/*z* 212 (M$^+$). Anal. Calcd for $C_{13}H_{12}N_2O$ C 73.56, H 5.70, N 13.20, found C 73.42, H 5.85, N 13.35.

2.2.3. *Synthesis of compound **1***

Intermediate **4** (68 mg, 0.30 mmol), salicylaldehyde (0.05 mL, 0.52 mmol) and several drops of acetic acid were dissolved in anhydrous ethanol (30 mL). The above mixed solution was stirred and heated to reflux for 4 h, and then evaporated to dryness. The obtained solid was subject to silica column chromatography (ethyl acetate/petroleum ether, 1/4, v/v) for purification to give pure 1 as a yellow solid. Yield: 38 mg (38%), Mp: 163–165 °C. ^1H NMR (500 MHz, DMSO-d_6): δ 6.97–7.06 (m, 4H), 7.23–7.26 (m, 1H), 7.31–7.35 (m, 1H), 7.38–7.46 (m, 3H), 7.81–7.83 (m, 1H), 8.03–8.05 (m, 1H), 8.30–8.32 (m, 1H), 8.96 (s, 1H), 10.79 (s, 1H), 11.64 (s, 1H), 11.95 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 117.2, 117.6, 118.6, 119.3, 119.5, 120.1, 120.7, 122.8, 125.6, 127.6, 130.9, 132.2, 133.0, 134.0, 134.1, 141.1, 157.6, 160.2, 163.1, 164.9. FT-IR (KBr): 3371, 1649, 1614, 1531, 755 cm^{-1}. MS (EI): *m*/*z* 332 (M$^+$). Anal. Calcd for $C_{20}H_{16}N_2O_3$ C 72.28, H 4.85, N 8.43, found C 72.59, H 5.03, N 8.37.

2.2.4. *Synthesis of compound **2***

A similar method was conducted to synthesize compound **2** using intermediate **3** in place of intermediate **4**. Yield: 44 mg (46%), Mp: 161–163 °C. ^1H NMR (500 MHz, DMSO-d_6): δ 6.91 (d, J = 8.6 Hz, 1H), 6.96–6.99 (m, 1H), 7.35–7.42 (m, 3H), 7.47–7.49 (m, 1H), 7.53 (t, J = 7.4 Hz, 2H), 7.58–7.61 (m, 1H), 7.66–7.70 (m, 2H), 7.95–7.97 (m, 2H), 8.93 (s, 1H), 10.07 (s, 1H), 12.87 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 117.2, 119.5, 119.6, 120.2, 126.8, 127.2, 127.5, 128.1, 129.0, 132.2, 132.5, 133.0, 133.9, 135.0, 144.0, 160.8, 164.0, 165.8. FT-IR (KBr): 3443, 3403, 1674, 1610, 1521 cm^{-1}. MS (EI): *m*/*z* 316 (M$^+$). Anal. Calcd for $C_{20}H_{16}N_2O_2$ C 75.93, H 5.10, N 8.86, found C 76.20, H 5.14, N 8.74.

2.3. *Titration experiments of compounds **1** and **2***

The UV–vis titration experiments were conducted in 10-mm quartz cuvette at 298 K. Compound (**1** or **2**) was dissolved in DMSO to give a concentration of 5 mM stock solution, which was subsequently diluted with DMSO up to 50 μM. Anions (as tetrabutylammonium salts, 20 mM) in DMSO were added to 50 μM host solution and used for titration experiments.

3. Results and discussion

3.1. *Naked-eye observations and UV–vis titration studies*

The recognition and sensing properties of compound **1** toward various anions were firstly investigated by UV–vis titration spectra. In the absence of anions, compound **1** (5.0×10^{-5} M in DMSO) displayed two obvious absorption peaks at 262 and 304 nm along with a shoulder peak at 353 nm. As shown by Fig. 1, significant spectral changes were seen upon addition of F^- to DMSO solution of compound **1**. While increasing F^- concentration in the mixed solution, the absorption peak at 262 nm was slightly redshifted (*ca.* 2 nm) along with a notable increase in intensity. At the same time, the absorption peak at 304 nm was gradually decreased and a new absorption peak at 355 nm appeared. Two clear isosbestic points at 278 and 323 nm were seen during the titration process, indicating the coexistence of only two species at equilibrium [46]. Noticeably, colorless DMSO solution of compound **1** changed to pale yellow after interaction with F^-, which was attributed to significant development of absorption peak at 355 nm. Interestingly, addition of protic solvent (such as H_2O or MeOH) to the solution of compound **1** bound to F^- made pale yellow solution