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ORIGINAL ARTICLE

Simple urea/thiourea sensors for the biologically important ions

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Abstract Two anion receptors **1** and **2** with a nitrophenyl group as a signaling group and urea/thiourea as a binding group were synthesized and their anion binding abilities were examined. The receptor **1** formed the hydrogen-bonded complex with various anions except fluoride. However, the receptor **2** immediately formed deprotonated receptor with various anions. Therefore, they operated based on a hydrogen bonding and an acid–base equilibrium. In addition, the receptor **1** proved to be an efficient and selective naked-eye detector for the fluoride ion.

Keywords Anion receptor · Urea/thiourea · Colorimetric receptor · Anion recognition

Introduction

Considerable interest has been, in the recent past, paid to the development of simple receptors capable of recognizing biologically relevant anions such as fluoride, chloride, phosphate, and carboxylate [1–12]. Among them, urea or thiourea derivatives connected with a series of chromogenic and fluorogenic substituents proved to be very efficient for the anion sensors [13–30]. In addition, they can be often easily synthesized from commercially available reagents even by a single step procedure [31–33]. Therefore, a variety of receptors containing one or more urea/thiourea subunits have been designed and tested for anion recognition and sensing over the past years. In the design of urea/thiourea receptors, nitrophenyl groups have been frequently used [14–16]. Nitrophenyl groups not only help hydrogen bonding of anion by increasing the acidity of urea/thiourea hydrogen but also serve as a single chromophore independently or dual chromophores with other chromogenic substituents.

Previously, we have reported on novel colorimetric receptors containing a nitrophenyl group and a benzophenone group as dual chromogenic signaling subunits and urea/thiourea as binding sites, which were selective for fluoride or acetate ion [34, 35]. As an effort of trying to find out simpler and more efficient naked eye anion receptor and to examine a role of the benzophenone group as a chromogenic signaling subunit, we have designed very simple urea/thiourea receptors with only a nitrophenyl group as a chromogenic signaling subunit. We have attached a single *p*-nitrophenylurea group or *p*-nitrophenylthiourea group to a simple 1,2-diaminobenzene ring to produce the receptors **1**[36, 37] and **2** (Scheme 1). Although the structures of the receptor **1** and **2** were simpler than the receptors **3** and **4** which had been previously reported [35], they were found to be more efficient detectors for fluoride and acetate. We report herein on the synthesis, characterization and anion recognition of the urea/thiourea receptors **1** and **2**. The anion recognition via hydrogen-bonding interactions could be easily monitored by anion-complexation induced

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Scheme 1 The synthetic procedure for the anion receptors **1** and **2**

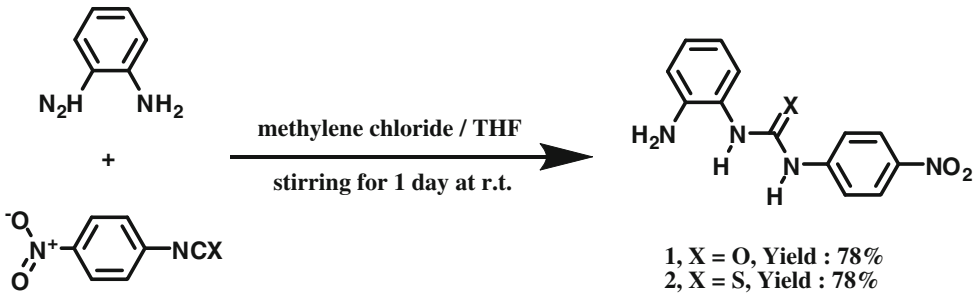
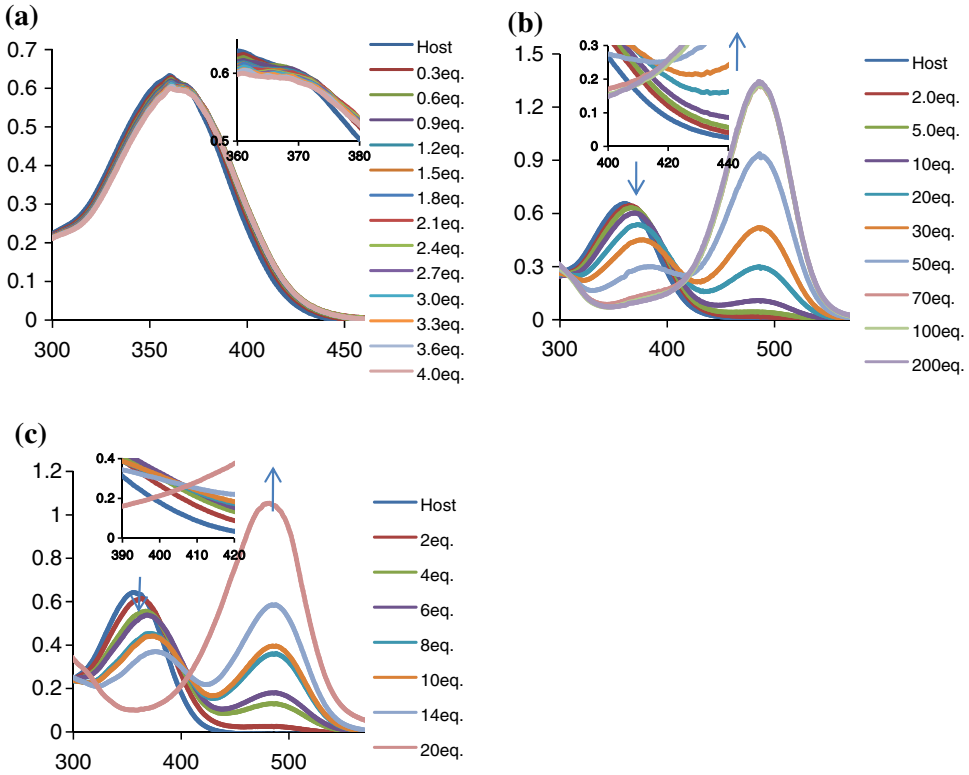


Fig. 1 Family of spectra recorded over the course of titration of 40 μM DMSO solution of the receptor **1** with the standard solution tetrabutylammonium anions (**a**) 0 to 4 equivalents of tetrabutylammonium fluoride added (**b**) 0 to 200 equivalents of tetrabutylammonium fluoride added (**c**) 0 to 20 equivalents of tetrabutylammonium hydroxide added



changes in UV–vis absorption spectra and with the naked eye.

Experimental section

General

All reagents were purchased from Aldrich and used without further purification. ^{1}H-NMR spectra were recorded on a JEOL JNM-AL400 spectrometer, operating at 9.39 T. UV–Vis spectra were obtained using a Cary 3 spectrophotometer with a quartz cuvette (path length = 1 cm). IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets. Elemental analysis was carried out by using an EA1108 (Carlo Erba Instrument, Italy) in the Organic Chemistry Research Center of Sogang University, Korea.

Synthesis of compound **1**

To increase the yield of **1**,[1][36, 37] a modified method was used. To a solution of 4-nitrophenyl isocyanate (0.17 g, 1.0 mmol) in a mixture of methylene chloride/THF (9:1; 10 mL), 1,2-phenylenediamine (0.11 g, 1.0 mmol) in methylene chloride (5 mL) was added slowly while being stirred vigorously. Orange solids were precipitated after stirring for 1 day at room temperature, filtered and dried. (0.21 g, 78.0% yield). Anal. Calcd for C13H12N4O3 (272.26): C, 57.35; H, 4.44; N, 20.58. Found: C, 57.40; H, 4.27; N, 20.58%. ^{1}H NMR (DMSO-*d*6) δ 9.56 (s, 1H), 8.18 (d, 2H, J = 9.6 Hz), 7.96 (s,1H), 7.68 (d, 2H, J = 9.2 Hz), 7.31 (d, 1H, J = 7.6 Hz), 6.88 (t, 1H, J = 7.6 Hz), 6.75 (d, 1H, J = 8.0 Hz), 6.58 (t, 1H, J = 7.6 Hz), 4.85 (s, 2H). IR (KBr): 3412 (N–H), 3337 (N–H), 3215 (N–H), 1674 (C=O),

[1] Synthetic method of compound **1** was reported in the literature.

1333 (NO2) cm^{-1}. FAB MS *m/z* (M^+): Calcd, 272.26, Found, 272.09.

Synthesis of compound **2**

To a solution of 4-nitrophenyl isothiocyanate (0.93 g, 5.0 mmol) in a mixture of methylene chloride/THF (9:1; 10 mL), 1,2-phenylenediamine (0.55 g, 5.1 mmol) in methylene chloride (10 mL) was added slowly while being stirred vigorously. Pale yellow solids were precipitated after stirring for 1 day at room temperature, filtered and dried. (1.12 g, 78.0% yield). Anal. Calcd for C13H12N4O2S (288.32): C, 54.15; H, 4.20; N, 19.43; S, 11.12. Found: C, 54.13; H, 4.13; N, 19.32; S, 11.29%. Mp : 148 °C. ^{1}H NMR (DMSO-*d*6) δ 9.46 (s, 2H), 8.19 (d, 2H, $J = 9.2$ Hz), 7.90(d, 2H, $J = 9.2$ Hz), 7.09 (d, 1H, $J = 8.0$ Hz), 6.98 (t, 1H, $J = 8.0$ Hz), 6.76 (d, 1H, $J = 8.0$ Hz), 6.57 (t, 1H, $J = 7.6$ Hz), 5.02 (s, 2H). ^{13}C NMR (DMSO-*d*6) δ 180.544, 147.22, 144.63, 142.76, 128.80, 128.11, 124.99, 124.11, 122.01, 116.84, 116.53. IR(KBr): 3370 (N–H), 3316 (N–H), 3221 (N–H), 1336 (NO2), 1113 (C=S) cm^{-1}. FAB MS *m/z* (M^+): Calcd, 288.32, Found, 288.30.

Results and discussion

We have previously reported two new urea/thiourea receptors **3** and **4** (see Fig. 7 for the molecular structures) with both a benzophenone group and a nitrophenyl group as dual chromogenic signaling subunits that were synthesized using the one step reaction of 3,4-diaminobenzophenone and 4-nitrophenyl isocyanate or 4-nitrophenyl isothiocyanate. It was found that the receptors, effectively and selectively, recognized fluoride and carboxylate anions from other anions such as chloride, bromide, iodide, perchlorate, hydrogensulfate, and nitrate in DMSO. In this study, we have synthesized two receptors **1** and **2** with only a nitrophenyl group in order to examine a role of the benzophenone group as a chromogenic signaling subunit, and tested their sensing ability for various anions.

The receptor **1** displayed strong absorption bands at 360 nm in DMSO. Figure 1a shows the family of spectra obtained over the course of the titration of solution **1** with tetrabutylammonium fluoride in DMSO. Until 4 equivalents of fluoride were added to the 40 μM solution of **1**, λ_{max} of **1** is moved to the longer wavelength slightly and spectra showed the clear isosbestic point at 372 nm. This result suggests that a typical hydrogen bonding complex forms between the receptor and the anion. However, when an excess of fluoride ion was added, a new intense absorption band developed at 486 nm, which is attributed to the deprotonated receptor [38]. In addition, spectra showed a new isosbestic point at 412 nm (Fig. 1b) and the color of the receptor **1** changed from yellow to orange. The new isosbestic point indicates that only two chemical species exist at equilibrium. Therefore, fluoride ion initially forms the hydrogen bonded complex, but with high excess of added anions, the deprotonation occurs with formation of the hydrogen bonded anion dimer F_2H^- (Fig. 2) [39].

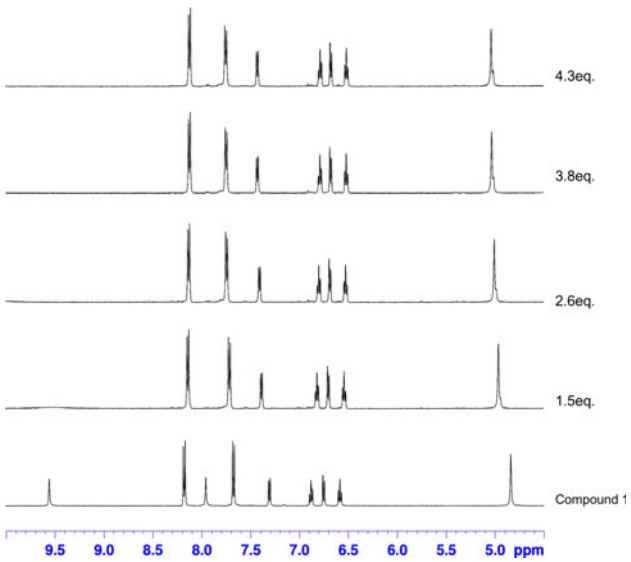
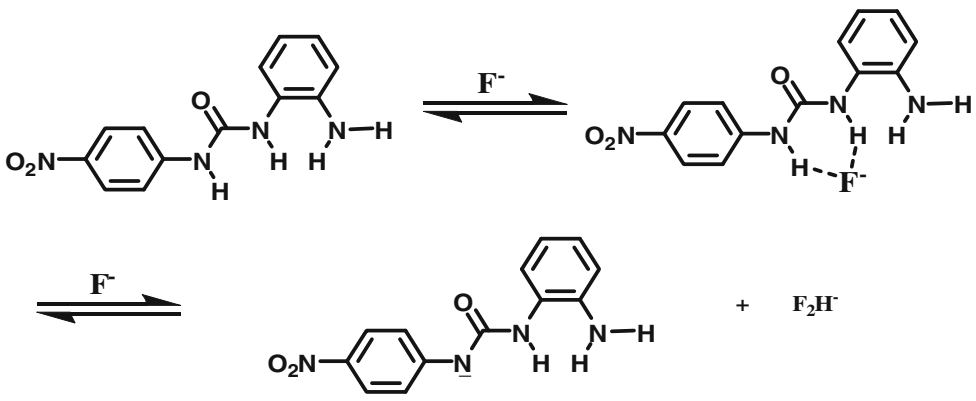


Fig. 3 ^{1}H NMR spectra of 2 mM **1** with increased amounts of tetrabutylammonium fluoride in DMSO-d_6

Fig. 2 The interaction of receptor **1** and fluoride



The deprotonation of the receptor **1** can be seen clearly when the solution of the receptor **1** is titrated with tetrabutylammonium hydroxide (Fig. 1c). As hydroxide ions were added absorption band at 486 nm developed again, which pertains to the deprotonated receptor **1.** Assuming 1:1 stoichiometry, a Benesi–Hildebrand plot [40] by use of absorption intensity change in the 360 nm and 486 nm gave association constant and equilibrium constant. From the experiments, the association constant and equilibrium constant for fluoride were calculated as 1.5×10^4 and 4.2×10^2, respectively.

This phenomenon could be confirmed by a ^{1}H NMR titration (Fig. 3). In DMSO-d_6, the urea N–H hydrogen peak of receptor **1** became invisible upon addition of fluoride ion. Therefore, one of the aromatic signals was used for titration. In the case of receptor **1**, the signal at 7.68 ppm was used. This aromatic signal moved from 7.68 ppm to 7.75 ppm until 4 equivalents of fluoride ion was added and then, no more shift was observed. In fact, two effects are expected as a result of hydrogen bond formation between the urea subunit and the anion; (i) a through-bond propagation, which causes a shielding effect and promotes an upfield shift, and (ii) a through-space effect, which causes deshielding and promotes a downfield shift. In this case, through-space effect dominates, and a downfield shift is observed. Analysis of chemical shift utilizing EQNMR [41] gave association constant 2.0×10^4, which is similar to the value obtained from UV–vis titration.

With acetate, both UV–vis titration spectrum and ^{1}H NMR spectrum showed evidence for the formation of a discrete hydrogen-bonded complex. In case of the UV–vis titration, as tetrabutylammonium acetate was added to the 40 μM solution of **1** in DMSO, the intensity of absorption spectrum decreased at 360 nm and increased at 367 nm. The clear isosbestic point appeared at 363 nm as well (Fig. 4). In case of the ^{1}H NMR titration, as tetrabutylammonium acetate was added, two urea peaks moved to downfield (from 7.95 and 9.53 ppm to 10.97 and 12.68 ppm). In addition, the adjacent NH_2 signal shifted from 4.82 to 5.05 ppm (Fig. 5). This suggests that the typical hydrogen bonding complex forms between the receptor and the anion, and that not only urea but also the adjacent NH_2 group participate in hydrogen bonding. The association constants obtained from UV–vis spectrum and ^{1}H NMR titration were 1.1×10^4 and 1.7×10^4, respectively.

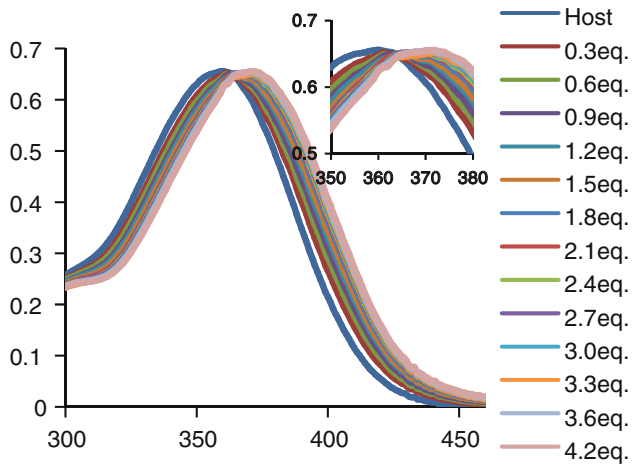


Fig. 4 Family of spectra recorded over the course of titration of 40 μM DMSO solution of the receptor **1** with a standard solution tetrabutylammonium acetate

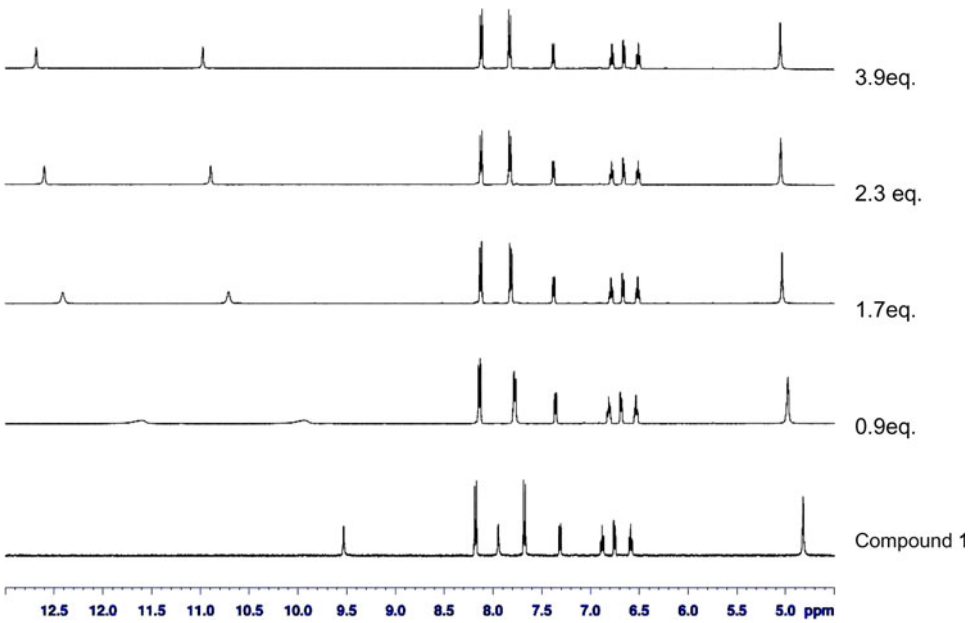


Fig. 5 ^{1}H NMR spectra of 2 mM **1** with increased amounts of tetrabutylammonium acetate in DMSO-d_6

Table 1 The association constants (K_a) or equilibrium constants (K_{eq}) of the receptors **1** and **2** with various anions in DMSO

Anion	1		2
	UV(K_a)	NMR(K_a)	UV(K_{eq})
F^-	1.5×10^4	2.0×10^4	1.5×10^5
$CH_3CO_2^-$	1.1×10^4	1.7×10^4	2.1×10^5
$C_6H_5CO_2^-$	5.8×10^3	–	1.7×10^4
$H_2PO_4^-$	2.8×10^3	–	1.0×10^4

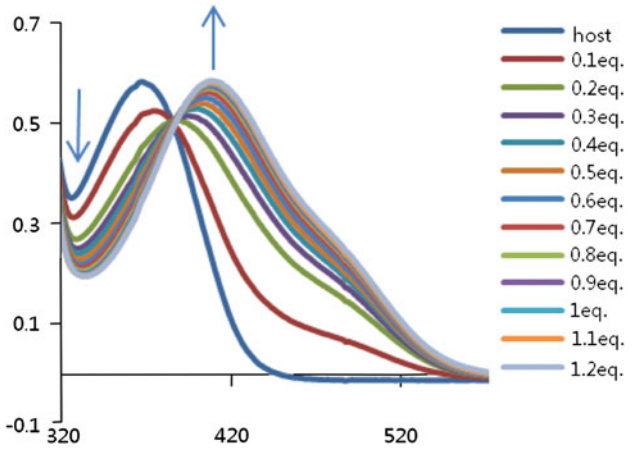


Fig. 6 Family of spectra recorded over the course of titration of 40 μM DMSO solution of the receptor **2** with a standard solution tetrabutylammonium fluoride

With other anions such as benzoate and dihydrogenphosphate, the receptor **1** also showed a typical spectrum pattern for the formation of hydrogen bonded complex. The association constants from the experiment were summarized in Table 1. Other anions such as chloride, bromide, iodide, perchlorate, hydrogensulfate, nitrate did not bind to the receptor **1** in DMSO at all.

The more acidic thiourea fragment ($pK_a = 21.1$ in DMSO) typically interacts more strongly with anions than urea ($pK_a = 26.9$ in DMSO) [42]. Therefore, addition of fluoride to more acidic thiourea derivative **2** induced immediate deprotonation in DMSO. Spectroscopic titration of the receptor **2** by tetrabutylammonium fluoride in DMSO showed the appearance of the new band at 405 nm characteristic of deprotonation of receptor (Fig. 6). Also, the presence of the sharp isosbestic point at 385 nm indicates that only two species were present at equilibrium. The equilibrium constant for the deprotonation was calculated as 1.5×10^5 for fluoride. Acetate showed a similar behavior and its equilibrium constant for the deprotonation was calculated as 2.1×10^5. With other anions such as benzoate and dihydrogenphosphate, the recepror **2** also showed a typical spectrum of immediate deprotonation. The equilibrium constants from the experiment were summarized in Table 1.

The solution color of receptor **1** changed upon additions of fluoride, acetate and benzoate in DMSO. It can be seen that that the color changed from colorless to orange with

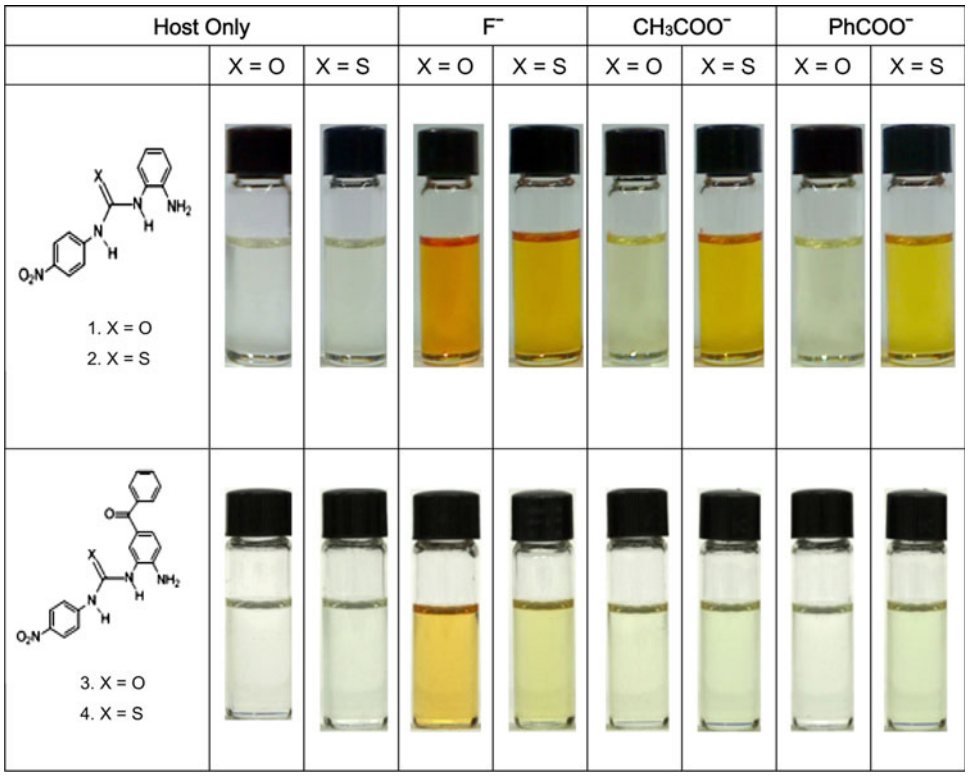


Fig. 7 The color changes of the receptors when 100 μM solutions of four receptors were treated with 20 equivalents of various anions

naked eye depending on the concentration of the solution. The solution of receptor **2** showed more intense color change than the receptor **1** for the most of the anions investigated. In addition, despite of simpler structures than the receptors **3** and **4** with a benzophenone group as a chromogenic signaling subunit [34, 35], the receptors **1** and **2** showed more intense color change at the same concentration of host and anions. This result suggests that the benzophenone moiety may not act as a chromogenic signaling subunit, unlikely we have proposed in the previous study [34, 35]. In this case, single nitrophenyl group is better than dual chromophore.

The changes of solution color on additions of anion were shown in Fig. 7 with structures of hosts.

In summary, we developed new chromogenic anion receptors **1** and **2** with a nitrophenyl group as a signaling group. The receptor **1** formed the hydrogen-bonded complex with various anions except fluoride. However, the receptor **2** formed deprotonated receptor immediately with various anions. Therefore, they operated based on a hydrogen bonding and an acid–base equilibrium. In addition, the receptors **1** and **2** proved to be efficient naked-eye detectors despite of their simple structures.

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