This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Two Thiourea-based Colorimetric Sensors for Anions: Structure and Binding Study

Lan-Hua Wei[a]; Yong-Bing He[a]; Jin-Long Wu[a]; Xiao-Jun Wu[a]; Ling-Zhi Meng[a]; Xi Yang[a]
[a] Department of Chemistry, Wuhan University, Wuhan Hubei, China

Online publication date: 29 October 2010

To cite this Article Wei, Lan-Hua , He, Yong-Bing , Wu, Jin-Long , Wu, Xiao-Jun , Meng, Ling-Zhi and Yang, Xi(2004) 'Two Thiourea-based Colorimetric Sensors for Anions: Structure and Binding Study', Supramolecular Chemistry, 16: 8, 561 — 567

To link to this Article: DOI: 10.1080/10610270412331315226

URL: http://dx.doi.org/10.1080/10610270412331315226

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Supramolecular Chemistry, December 2004 Vol. 16 (8), pp. 561–567

Taylor & Francis
Taylor & Francis Group

Two Thiourea-based Colorimetric Sensors for Anions: Structure and Binding Study

LAN-HUA WEI, YONG-BING HE*, JIN-LONG WU, XIAO-JUN WU, LING-ZHI MENG and XI YANG

Department of Chemistry, Wuhan University, Wuhan, Hubei 430072, China

Received (in Southampton, UK) 26 May 2004; Accepted 10 September 2004

Two colorimetric thiourea-based chemsensors with two relatively rigid arms, 2A and 2B, were synthesized. Their binding abilities with halide anions, AcO^-, $H_2PO_4^-$ were studied by UV-Vis spectroscopy in DMSO. The two sensors showed a notable selective color response to F^- anion from colorless to green–yellow in recognition. The structures of the two sensors and their binding behaviors are discussed. The association constants were calculated by nonlinear fittings of 1:1, 1:2 or 1:1 to 1:2.

Keywords: Colorimetric sensor; Fluoride; Anion recognition; Thiourea; Crystal structure

INTRODUCTION

In recent years, there has been a great development in the design of receptors for recognizing and sensing ions and small molecules. The recognition and sensing of important anionic guest species in biology and the environment by artificial receptors have attracted increasing attention in the field of supramolecular chemistry [1–6]. A variety of artificial receptors have been designed and synthesized, and their binding selectivities toward different anions have been investigated [7–11]. In particularly, the design of colorimetric chemsensors for anions is developing rapidly in this field, because an obvious color change can be observed by the naked eye and has a reliable calibration stability [12–18]. This type of sensor is generally composed of at least two parts: an anion binding site and a signal subunit. Anion binding sites based on various binding groups including Lewis acids, [19,20] protonated polyammonium macrocycles, [21,22] pyrroles, [23–26] guanidiniums, [27,28] metalloreceptors [29,30] *etc.* have been proved effective in anion recognition. Because of its binding strength and direction, hydrogen bonding is one of the most important recognition elements in anion sensing and plays a key role in biological processes [31,32]. Hydrogen bonding for the fluoride ion is especially effective in recognition of halide ions. The signal subunit is often a chromophore that can transform receptor–anion interactions into optical signals. A clear color change from colorless to chromatic for anion recognition is especially attractive because it's relatively more perceivable. Colorimetric sensors of this type for anions are still rare [33] due to the difficulty in the design of them.

In this article, we report the synthesis and binding properties of two thiourea-based colorimetric chemsensors **2A** and **2B** (Scheme 1). The recognizing selectivities of two receptors for different anions have been investigated by UV-Vis spectra. The binding models involving 1:2 and 1:1 to 1:2 are discussed and association constants are calculated by nonlinear least-square curve fittings.

RESULTS AND DISCUSSION

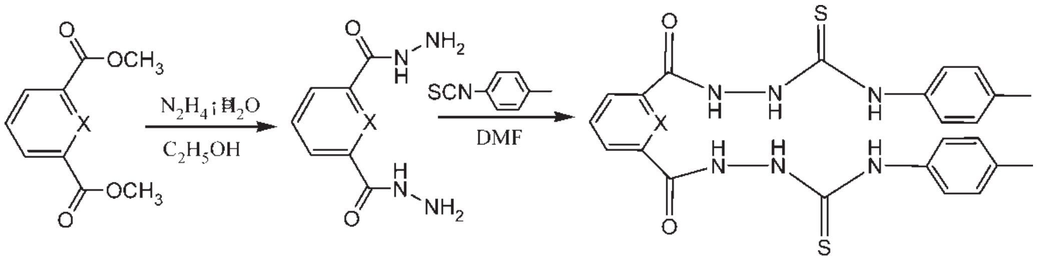
X-ray Structural Analysis of 2A

The single crystal of **2A** consists of **2A**·2CH_3OH. The structure (Fig. 1) features the molecule with three benzene ring planes (the main one and two on the arms) and two thiourea planes. The molecule adopts a zigzag formation such that intermolecular interactions are easy to form. The crystal of **2A**·2CH_3OH is formed mainly by hydrogen bonds and π–π stacking interaction. Fig. 2 shows the intermolecular interactions in the crystal of **2A**·2CH_3OH.

---

*Corresponding author. Fax: +86-27-87647617. E-mail: ybhe@whu.edu.cn

ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/10610270412331315226



1A X = CH
1B X = N

2A X = CH
2B X = N

SCHEME 1 Synthesis of **2A** and **2B**.

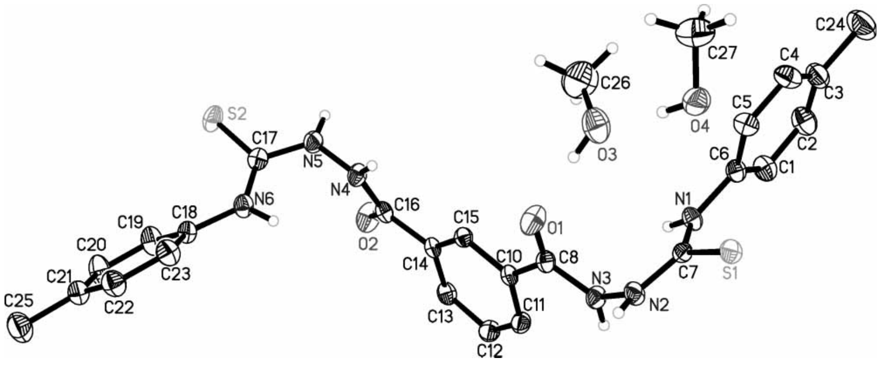


FIGURE 1 Crystallography of **2A**·2CH_3OH (partial hydrogen atoms were removed for clarity).

Selected bonding parameters are listed in Table I and hydrogen bonds are in Table II. There are two type of intermolecular hydrogen bonds: those between C=O or C=S and NH units on the arms of **2A**, and those between NH of **2A** and solvent CH_3OH. The distribution of π−π stacking in the crystal can be seen more clearly in the packing diagram of **2A**·2CH_3OH in Fig. 3. In a symmetric unit of **2A**·2CH_3OH, the main benzene rings of two molecules are π−π stacked. Units are hydrogen bonded to form the layers of the crystal. Between two layers are arms of **2A** and molecules of CH_3OH, which connect two layers. The single crystal of the sensor **2B** cannot be obtained in the same way as **2A**, which may be ascribed to the different hydrogen bonding styles led by the structural difference between **2A** and **2B** [34]. The nitrogen atom in the pyridine ring of **2B** may form hydrogen bonds with

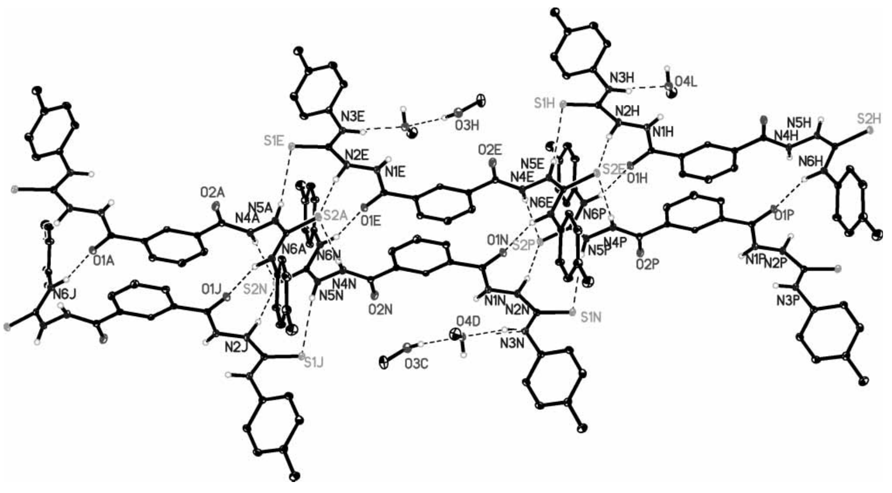


FIGURE 2 Partial structure of intermolecular hydrogen bonds and π−π stacking in **2A**·2CH_3OH. Hydrogen bonds are shown as dashed line. Partial hydrogen atoms are omitted for clarity.

TABLE I Selected bond lengths (Å) and angles (°) for **2A**

S(1)-C(7)	1.698(3)	N(2)-N(3)	1.394(3)
N(1)-C(7)	1.341(3)	N(3)-C(8)	1.362(4)
N(1)-C(6)	1.430(4)	C(8)-C(10)	1.510(4)
N(2)-C(7)	1.345(4)		
O(1)-C(8)-N(3)	121.9(3)	N(1)-C(7)-S(1)	124.4(2)
O(1)-C(8)-C(10)	123.1(2)	N(1)-C(7)-N(2)	117.7(2)
N(3)-C(8)-C(10)	115.0(3)	C(7)-N(1)-C(6)	127.3(2)
C(8)-N(3)-N(2)	121.3(3)	C(1)-C(6)-N(1)	118.5(3)
C(7)-N(2)-N(3)	122.2(2)	C(5)-C(6)-N(1)	121.5(3)
N(2)-C(7)-S(1)	117.8(2)		
C10D..C10H*	3.4257		

*Distances between C10D, C11D, C12D, C13D, C14D, C15D and C10H, C11H, C12H, C13H, C14H, C15H are 3.4257 Å.

the adjacent NH on the two arms, leading to the closing of the two arms and the weakening of intermolecular interactions.

Absorption Spectra

Fig. 4 shows the absorption spectra changes of **2A** in DMSO upon addition of fluoride ion. The characteristic absorption peak of **2A** in DMSO is at about 266 nm. With the addition of F^- to the solution of **2A** in DMSO, the characteristic absorption peak of the host at about 266 nm was increased slightly with a slight red shift, and a new peak at 350 nm is produced. At the same time, the color of the solution of **2A** changes from colorless to green–yellow. The color change can be completely reversed by addition of a small amount of CH_3OH, which demonstrates the hydrogen bonding between **2A** and F^- during recognition. In fact, the solvent molecule of CH_3OH plays an important role in the crystal of **2A**; we obtained only the crystal of **2A**$\cdot 2CH_3OH$ from a mixed solution of equivalent **2A** and AcO^- or F^- in CH_3OH. The inset in Fig. 4 indicates the absorption change of the solution of **2A** upon gradual increase of the concentration of F^- at 350 nm. Fig. 5 shows the Job plot of **2A** with F^- ion (at 350 nm). The receptor–anion complex concentration approaches a maximum when the molar fraction of guest is about 0.66, meaning that receptor **2A** and F^- anion formed a 1:2 complex [35].

TABLE II Selected hydrogen bonds (Å and °) for **2A***

D-H	d(D-H)	d(H..A)	<DHA	d(D·A)	A
O3-H3	0.82	2.263	145.19	2.973	O1
O3-H3	0.82	2.595	123.21	3.12	O1
O4-H4	0.82	1.985	165.68	2.787	O3
N5-H5E	0.858	2.478	177.41	3.336	S1
N2-H2E	0.869	2.582	167.08	3.435	S2
N4-H4E	0.804				
N3-H3E	0.815	2.807	167.04	3.606	S1
N1-H1E	0.876	1.985	155	2.803	O2
N6-H6E	0.913	2.051	158.22	2.918	O4

*Hydrogen bonds with H..A < r(A) + 2.000 Å and ⟨DHA⟩ 110°.

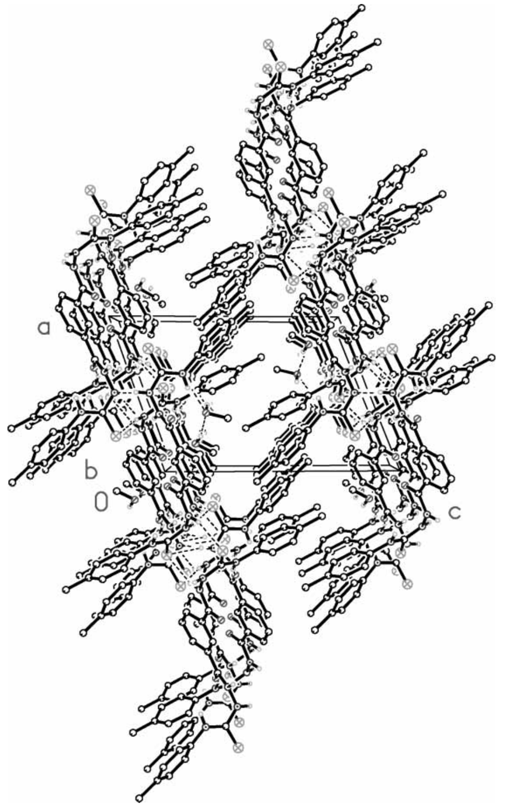


FIGURE 3 Packing diagram of **2A**$\cdot 2CH_3OH$.

Addition of F^- to a solution of receptor **2B** in DMSO leads to a similar color change. Upon addition of F^-, the color of the solution of **2B** in DMSO changes from colorless to green–yellow also. Fig. 6 shows the absorption spectra changes of **2B** in DMSO upon addition of F^-, a new peak at 377 nm was produced and increased gradually with a slight blue shift from 377 to 359 nm. The obvious increase in the absorption spectra in the adjacent visible region at 350 nm (**2A**) or 359 nm (**2B**) results in the color change. The curve of absorption change of **2B** at 359 nm (Fig. 6, inset) is entirely different from that of **2A**, which suggests possibly a different binding style of **2A** or **2B** with F^- due perhaps to the different

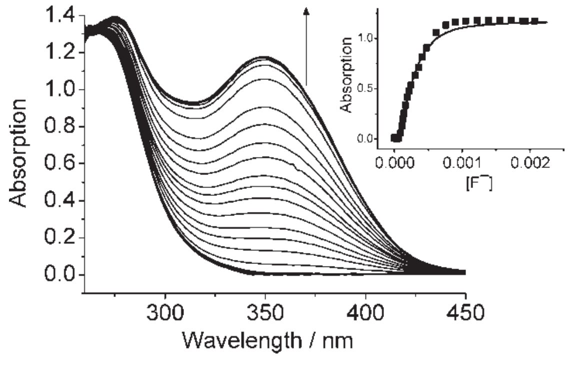


FIGURE 4 Absorption spectra changes of **2A** in DMSO upon addition of F^-. The inset is the nonlinear least-square fitting curve at 350 nm. [**2A**] $= 5 \times 10^{-5}$ M and [F^-] is from 0 to 2.25×10^{-3} M.

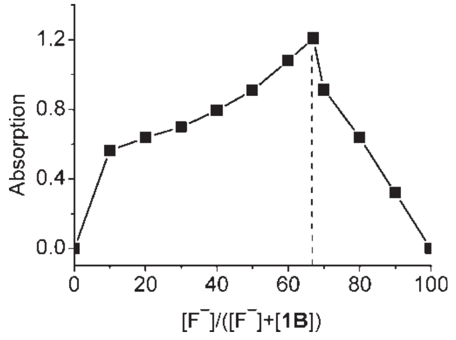


FIGURE 5 Job plot of F^- with **2A**. Total concentration ($[F^-] + [\textbf{2A}]$) is 1.4×10^{-4} M.

inter/intramolecular hydrogen bonds in the complexation between **2A** or **2B** and F^- in DMSO. The binding model between **2B** and F^- can be assumed to form a complex of 1:1 to 1:2. The possible binding style of **2A** or **2B** with F^- is showed in Fig. 7.

The same color changes can be observed upon addition of AcO^-, $H_2PO_4^-$ to the solution of **2A** or **2B** in DMSO. New peaks occur in the absorption spectra at 350 nm (**2A**) or 359 nm (**2B**). Fig. 8 shows the nonlinear fitting curves of the absorption spectra changes of **2A** (at 350 nm) or **2B** (at 359 nm) in DMSO upon addition of AcO^-or $H_2PO_4^-$. Again, slight blue shifts of the peaks can be observed upon addition of these anions to the solution of **2B** in DMSO. The difference in binding of these anions and F^- with two hosts lies in the different stoichiometry between host and guest. Job plots show that the binding stoichiometry of AcO^- or $H_2PO_4^-$ with **2B** is 1:1, which may be due to the larger size of these anions. Nonlinear 1:1 curve fittings [36] on these UV-Vis spectra changes of **2A** or **2B** have perfect results (Table III).

The absorption spectra of **2A** or **2B** in DMSO shows almost no change upon addition of a large excess of the other halide anions including Cl^-, $Br^-$and I^- (*e.g.*, $[Cl^-]$ / $[\textbf{2A}] > 50$), which may be due to their weak hydrogen bonding abilities.

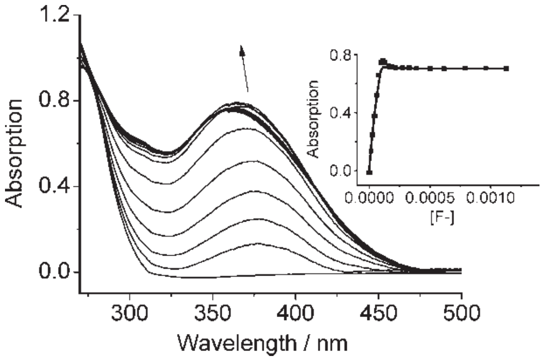


FIGURE 6 Absorption spectra changes of **2B** in DMSO upon addition of F^-. The inset is the 1:1 to 1:2 nonlinear fitting curve at 377 nm. $[\textbf{2B}] = 5 \times 10^{-5}$ M, and $[F^-]$ is from 0 to 1.13×10^{-3} M.

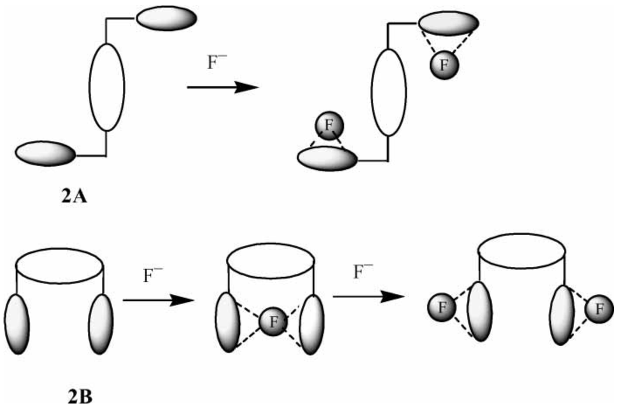


FIGURE 7 Schematic diagram of binding of **2A** or **2B** with F^-.

^{1}H NMR Titration

^{1}H NMR titration of F^- adding to **2A** in DMSO-d_6 ($[\textbf{2A}] = 0.04$ M) was carried out to investigate the chemical shift change of the NH groups led by hydrogen bonding. Before addition of F^-, the ^{1}H NMR chemical shifts of the three active protons on the NH groups of **2A** in DMSO are 10.60, 9.75, 9.65 ppm respectively. When $[F^-]$:$[\textbf{2A}]$ is 0.5, the proton peaks are broadened, one is shifted downfield from 10.60 to 10.65 ppm and the other two are combined (9.70 ppm). When $[F^-]$:$[\textbf{2A}]$ is changed to be 1 or 1.5, the peak at 10.65 ppm is further broadened and shifted downfield to 10.80 or 10.87 ppm, and the peak at 9.70 ppm shows almost no change (9.66, 9.64 ppm). The continuous downfield shifts can be ascribed to the formation of hydrogen bonds between the NH groups of **2A** and F^-. However, the addition of F^- only slightly affects the other two NH groups, which seems to mean that the two NH groups play a minor role in the complexation.

Calculation of Association Constants

For the complex with 1:1 stoichiometry between **2A** or **2B** with AcO^- *etc.*, the association constants can be

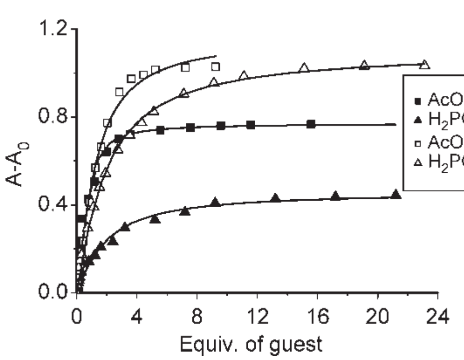


FIGURE 8 Nonlinear fitting curves of **2A** (350 nm) or **2B** (359 nm) in DMSO upon addition of AcO^- or $H_2PO_4^-$. $[\textbf{2A}] = 5 \times 10^{-5}$ M, $[\textbf{2B}] = 5 \times 10^{-5}$ M.

TABLE III Calculated association constants k and correlation coefficients R of **2A** or **2B** with anions*

2A	R	k (M^{-1})	**2B**	R	k (M^{-1})
AcO^-	0.99816	2.62×10^4	AcO^-	0.99192	1.13×10^5
$H_2PO_4^-$	0.99692	1.40×10^4	$H_2PO_4^-$	0.98883	1.46×10^4
$F^{-\dagger}$	0.99577	$3.44 \times 10^{8\ddagger}$	$F^{-\P}$	0.99381	k_1 2.86×10^4 k_2 1.20×10^7
Cl^-, Br^-, $I^{-\S}$	–	–			

* Errors <10%; † The constants are calculated by a 1:2 equilibrium; ‡ (M^{-2}); ¶ The constants are calculated by a 1:1 to 1:2 equilibrium; § No obvious spectra change can be observed even when far excess of these anions are added.

calculated according to the following equation:

$$A = A_0 + 0.5 \times \Delta\varepsilon \times \{C_H + C_G + 1/K_s - [(C_H + C_G + 1/K_s)^2 - 4C_H \times C_G]^{1/2}\}$$

Where A is the absorption intensity; A_0 is the absorption of pure host. C_H and C_G are the overall concentrations of the host and the guest respectively; K_s is the association constant.

In a system of 1:2 binding equilibrium, we can get several equations:

$$\mathrm{H} + 2\mathrm{G} \overset{k}{\rightleftharpoons} \mathrm{HG_2}$$

$$k = \frac{[HG_2]}{[H][G]^2}$$

$$[H] + [HG_2] = H_0$$

$$[G] + 2 \times [HG_2] = x$$

and the absorption equation deduced from Lambert–Beer Law:

$$y = e_0 \times [H] + e_2 \times [HG_2]$$

where $[H]$, $[HG_2]$, $[G]$ are species concentrations in the solution respectively; k is the association constant; x is the total concentration of the guest G; H_0 is the initial concentration of the host H; e_0 and e_2 are molar absorption coefficients of H and HG_2, respectively; y is the absorption value under a given wavelength and a given x value.

Herein we introduce a variable $a : a = [G]/H_0$. Subsequent deduction will give a cubic equation with one variable a:

$$\left(k \times H_0^2\right) \times a^3 + \left(2 \times k \times H_0^2 - k \times H_0 \times x\right) \times a^2 + a - x/H_0 = 0$$

The equation is resolved by the Newton–Rapson formula in the following nonlinear curve fitting, and the values of e_0, e_2, and k are worked out. The equation for a system involving 1:1 to 1:2 binding model can be deduced and resolved in a similar way. The association constants are listed in Table III, which shows that **2A** or **2B** binds to AcO^- more strongly than $H_2PO_4^-$, and **2B** shows high selectivity to bind to AcO^- against $H_2PO_4^-$. Furthermore, **2B** shows a stronger binding ability with AcO^- than **2A** does, which may be due to their different structures in DMSO, because the two arms of **2A** have to be close to each other before forming a 1:1 complex with AcO^-.

CONCLUSION

Two novel thiourea-based compounds, **2A** and **2B**, are found to be good colorimetric sensors for anions. Their binding properties with halide anions, AcO^- and $H_2PO_4^-$ in DMSO have been studied by UV-Vis spectroscopy. Receptors **2A**, **2B** form 1:1 complexes with AcO^- or $H_2PO_4^-$, respectively. Receptor **2A** forms a 1:2 complex with the fluoride ion, whereas **2B** forms a1:1 to 1:2 complex with the fluoride ion. Both **2A** or **2B** have a high selectivity for recognition of the fluoride ion among halide ions with a clear color change from colorless to green–yellow at recognition and show promise to be used as colorimetric chemosensors for fluoride ion.

EXPERIMENTAL

Materials and Methods

Dimethyl isophthalate and dimethyl 2,6-pyridinedicarboxylate were synthesized according to the literature [37,38]. Anions were used as their tetrabutylammonium salts. All other commercially available reagents were used without further purification.

Melting points were measured on a Reichert 7905 melting-point apparatus (uncorrected). Infrared spectra were performed on a Nicolet 670 FT-IR spectrophotometer. FAB mass spectra were recorded on a ZAB-HF-3F spectrometer and the ESI mass spectra were recorded on a Finnigan LCQ advantage spectrometer. Elemental analyses were determined by a Perkin-Elmer 204B elemental autoanalyzer. ^{1}H NMR spectra were recorded on a Varian Mercury VX-300 MHz spectrometer. ^{13}C NMR spectra were recorded on a Varian Inova-600. UV-Vis spectra were taken on a TU-1901 spectrometer.

Synthesis

Compound 1A (isophthalate-dihydrazide). Dimethyl isophthalate (0.97 g, 5 mmol) and hydrazine hydrate (85%, 20 mmol) were added into ethanol (20 ml). After refluxing for 1 h, the solution was concentrated to 1/4, and then was cooled to room temperature. After filtration, the collected precipitate was washed with water and cold ethanol, respectively. The residue was dried to give needle crystals of solid **1A** (0.89 g, yield 92%). mp >220°C; IR (KBr film, ν/cm^{-1}): 3265 (N–H), 3096 (C–H), 1638 (C═O); ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 9.68 (s, 2H, O═C–NH), 8.27(s, 1H, PhH), 7.97 (d, $J = 7.5$ Hz, 2H, PhH), 7.46 (t, $J = 7.5$ Hz, 1H, PhH), 3.93 (s, 4H, NH_2). The solid can be used in further reaction directly.

Compound 2A. **1A** (0.10 g, 0.5 mmol) and DMF (10 ml) were added to a flask; *p*-methylphenyl isothiocyanate (0.16 g) was then added. After stirring at room temperature for 10 min, the solution turned clear. After stirring for 1 h, distilled water (20 ml) was dropped into the solution. The resulting precipitate was filtered and washed slowly with distilled water (5 × 10 ml) and cold diethyl ether (3 × 10 ml), respectively. The crude solid gave a clear ^{1}H NMR spectrum. The solid was recrystallized in methanol and dried *in vacuum* to give **2A** as a white powder (0.18 g, yield 71%), mp 177–179°C: ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 10.60 (s, 2H, NH), 9.75 (s, 2H, NH), 9.65 (s, 2H, NH), 8.46 (s, 1H, PhH), 8.10 (d, 2H, $J = 7.5$ Hz, PhH), 7.59 (t, 1H, $J = 7.5$ Hz, PhH), 7.24 (d, 4H, $J = 8.1$ Hz, PhH), 7.10 (d, 4H, $J = 8.1$ Hz, PhH), 2.27 (s, 6H, CH_3); ^{13}C NMR (600 MHz, DMSO-d_6, δ/ppm): 181.8 (CS), 166.2 (CO), 137.3 (C Ph), 134.9 (C Ph), 133.4(C Ph), 131.6 (C Ph), 129.2–128.4 (C Ph), 126.7 (C Ph), 21.2 (CH_3); IR (KBr film, ν/cm^{-1}): 3250, 3203, 3029, 2918, 2860, 1669, 1644, 1540, 1514, 1244. MS (FAB): m/z 493 ($M^+ + 1$). Anal. Calcd for $C_{24}H_{24}N_6O_2S_2$: C, 58.52; H, 4.91; N, 17.06. Found: C, 58.27; H, 5.01; N, 16.95.

1B (2,6-pyridine-dihydrazide). **1B** was synthesized in the same way as **1A** by the reaction of dimethyl 2,6-pyridinedicarboxylate with hydrazine hydrate (yield 90%), mp >220°C.

Compound 2B: **2B** was synthesized in the same way as **2A** by the reaction of **1B** (0.10 g) with *p*-methylphenyl isothiocyanate (0.16 g) to give an off-white power (0.19 g, 73%), mp 200°C decomp. ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 11.20 (s, 2H, NH), 9.86 (s, 2H, NH), 9.75 (s, 2H, NH), 8.22 (bs, 3H, PyH), 7.26 (d, 4H, $J = 7.8$ Hz, PhH), 7.08 (s, 4H, $J = 7.8$ Hz, PhH), 2.26 (s, 6H, CH_3); ^{13}C NMR (600 MHz, DMSO-d_6, δ/ppm): 181.7 (s, CS), 166.2 (CO), 137.3 (C Ph), 134.9 (C Ph), 133.4(C Ph), 131.6 (C Ph), 129.2–128.4 (C Ph), 126.8 (m, C Ph), 21.2 (s, CH_3); IR (KBr film, ν/cm^{-1}): 3268, 3228, 2963, 2923, 1704, 1675, 1540, 1514, 1274; MS (FAB): m/z 494 ($M^+ + 1$). Anal Calcd for $C_{23}H_{23}N_7O_2S_2$: C, 55.97; H, 4.70; N, 19.86. Found: C, 55.71; H, 4.95, N, 19.67.

Crystal Structure Determination of Compound 2A

Single crystals (colorless blocks) of **2A** were grown from CH_3OH at room temperature. Crystal data was recorded on a R-AXIS-IV single-crystal diffractometer in Zhengzhou Univ. Henan. Crystal data: **2A**·$2CH_3OH$, Empirical formula: $C_{26}H_{32}N_6O_4S_2$, Formula weight = 556.7, crystal size: 0.20 × 0.18 × 0.18 mm; triclinic; space group $P1$ (no. 2), $Z = 2$, μ (Mo-K\a) = 0.230 mm^{-1}; $T = 291$ K, wavelength 0.71073 Å; θ range for data collection: 1.55 to 25.00 deg; completeness to $2\theta = 25.00$: 87.4%; Refinement method: full-matrix least-squares on F^2; goodness-of-fit on F^2: 0.992; 3712 reflections measured, 3721 unique ($R_{int} = 0.000$); $a = 10.707(2)$, $b = 10.708(2)$, $c = 14.186(3)$ Å, $\alpha = 96.91(3)°$, $\beta = 106.83(3)°$, $\gamma = 110.21(3)°$, $V = 1416.3(5)$ Å^3; R, wR (all data): 0.07912, 0.1395, final R, wR [$I > 2\sigma(I)$]: 0.0525, 0.1307. Software for structure solution/refinement: SHELXL-97 – DOS/WIN95/NT VERSION. CCDC number: 249060.

Binding Studies

The studies on binding properties of hosts were carried out in DMSO. UV-Vis spectra study was carried out with a series of solutions of **2A** or **2B** (5.0×10^{-5} M^{-1}) containing different amounts of anions. All of the titrations were carried out two or more times to get average values. Association constants were calculated by means of nonlinear least-square curve fittings with Origin 7.0 (OriginLab Corporation).

Acknowledgements

We thank the National Natural Science Foundation for financial support (Grant No. 20372054) and Mrs Zhuyu in Zhengzhou Univ. for the X-ray structure measurement.

References

[1] Smith, D. K. *Org. Biomol. Chem.* **2003**, *1*, 3874.
[2] Hossain, M. A.; Kang, S. O.; Powell, D.; Bowman-James, K. *Inorg. Chem.* **2003**, *42*, 1397.
[3] Yang, R.-H.; Chan, W.-H. A.; Lee, W. M.; Xia, P.-F.; Zhang, H.-K.; Li, K. *J. Am. Chem. Soc.* **2003**, *125*, 2884.
[4] Yoon, D. W.; Hwang, H.; Lee, C. H. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 1757.
[5] Yuan, Y.; Gao, G.; Jiang, Z.-L.; You, J.-S.; Zhou, Z.-Y.; Yuan, D.-Q.; Xie, R.-G. *Tetrahedron* **2002**, *58*, 8993.
[6] Beer, P. D.; Gale, P. A. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 486.
[7] Zeng, Z.-Y.; He, Y.-B.; Wei, L.-H.; Wu, J.-L.; Huang, Y.-Y.; Meng, L.-Z. *Can. J. Chem.* **2004**, *82*(3), 454.
[8] Zhong, Z.-L.; Anslyn, E. V. *Angew. Chem. Int. Ed.* **2003**, *42*, 3005.
[9] Duff, T.; Grüβing, A.; Thomas, J. L.; Duati, M.; Vos, J. G. *Polyhedron* **2003**, *22*, 775.
[10] Gale, P. A.; Hursthouse, M. B.; Light, M. E.; Sessler, J. L.; N. Warriner, C.; S. Zimmerman, R. *Tetrahedron Lett.* **2001**, *42*, 6759.
[11] Amendola, V.; Fabbrizzi, L.; Mangano, C.; Pallavicini, P.; Poggi, A. *Coord. Chem. Rev.* **2001**, *219–221*, 821.
[12] Palomares, E.; Vilar, R.; R. Durrant, J. *Chem. Commun.* **2004**, 362.
[13] Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*(*11*), 4419.
[14] Piateka, P.; Jurczak, J. *Chem. Commun.* **2002**, 2450.
[15] Tong, H.; Zhou, G.; Wang, L. X.; Jing, X. B.; Wang, F. S.; Zhang, J. P. *Tetrahedron Lett.* **2003**, *44*, 131.

[16] Aït-Haddou, H.; L. Wiskur, S.; M. Lynch, V.; V. Anslyn, E. *J. Am. Chem. Soc.* **2001**, *123*, 11296.

[17] Gunnlaugsson, T.; P. Leonard, J. *J. Chem. Soc., Perkin Trans. 2*, **2002**, 1980.

[18] Perring, L.; Basic-Dvorzak, M.; Andrey, D. *Analyst* **2001**, *126*, 985.

[19] Aldridge, S.; A. Fallis, I.; T. Howard, S. *Chem. Commun.* **2001**, 231.

[20] Yamaguchi, S.; Akiyama, A.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*(*46*), 11372.

[21] Alfonso, I.; Dietrich, B.; Rebolledo, F.; Gotor, V.; Lehn, J.-M. *Helv. Chim. Acta* **2001**, *84*, 280.

[22] Maubert, B. M.; Nelson, J.; McKee, V. *J. Chem. Soc., Dalton Trans.* **2001**, 1395.

[23] Sessler, J. L.; Pantos, G. D.; Katayev, E.; M. Lynch, V. *Org. Lett.* **2003**, *5*(*22*), 4141.

[24] Gale, P. A.; Camiolo, S.; Chapman, C. P.; Light, M. E.; Hursthouse, M. B. *Tetrahedron Lett.* **2001**, *42*(*30*), 5095.

[25] Miyaji, H.; Anzenbacher, P., Jr.; Sessler, J. L.; R. Bleasdale, E.; Gale, P. A. *Chem. Commun.* **1999**, 1723.

[26] Gale, P. A.; Sessler, J. L.; Král, V. *J. Am. Chem. Soc.* **1996**, *118*(*21*), 5140.

[27] Gleich, A.; P. Schmidtchen, F.; Mikulcik, P.; Müler, G. *J. Chem. Soc., Chem. Commun.* **1990**, 55.

[28] Müller, G.; Riede, F. J.; Schmidtchen, P. *Angew. Chem.* **1988**, *100*, 1574.

[29] Kuo, L.-J.; Liao, J.-H.; Chen, C.-T.; Huan, C.-H.; Chen, C-S.; Fang, J.-M. *Org. Lett.* **2003**, *5*(*11*), 1821.

[30] Nicolas, M.; Fabre, B.; Simonet, J. *Electrochim. Acta* **2001**, *46*, 1179.

[31] Wu, J.-L.; He, Y.-B.; Zeng, Z.-Y.; Wei, L.-H.; Meng, L.-Z.; Yang, T.-X. *Tetrahedron* **2004**, *60*(*19*), 4309.

[32] Sun, S.-S.; Lees, A. J.; Zavalij, P. Y. *Inorg. Chem.* **2003**, *42*, 3445.

[33] Iménez, D.; Martúnez-Máñez, R.; Sancenón, F.; Soto, J. *Tetrahedron Lett.* **2002**, *43*, 2823.

[34] Hamuro, Y.; J. Gab, S.; D. Hamilton, A. *J. Am. Chem. Soc.* **1997**, *119*, 10587.

[35] Kim, J. S.; Shon, O. J.; Yang, S. H.; Kim, M. J. *J. Org. Chem.* **2003**, *67*, 6514.

[36] Valeur, B.; Pouget, J.; Bourson, J. *J. Phys. Chem.* **1992**, *96*, 6545.

[37] He, Y.-B., *Master Thesis*, Wuhan University, 1982.

[38] Brooker, S.; Dunbar, G. S.; Jameson, G. B. *Polyhedron* **1999**, *18*, 679.