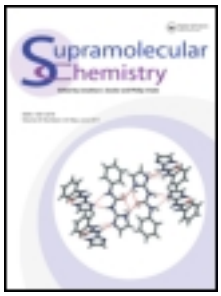

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Novel aroylhydrazine-amide derivatives bearing pyridine core: synthesis, characterisations and selective colorimetric recognition properties

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Four aroylhydrazine-amides receptors AR1-4 with a hydrazine spacer have been designed, synthesised and characterised as novel colorimetric chemosensors by typical spectroscopic techniques. The receptors AR1–3 exhibited certainly selectivity and sensitivity towards F^- and AcO^-, forming 1:1 stoichiometry complex by hydrogen-bond interaction. Furthermore, AR4 has especially shown obvious colour change in the presence of these two important biologically anions.

Keywords: aroylhydrazine-amide; anion recognition; colorimetric sensor; naked-eye

Introduction

Anion recognition with artificial receptors is a focus research area currently in supramolecular chemistry because of the important effects that anions play in different disciplines, such as environmental science, catalysis, biology and medicine (*1–3*). Much effort has been done on this challenge work to synthesis an efficient artificial receptor for various anions sensing (*4*). As we know, most neutral artificial receptors interact with anions by hydrogen-bonding, therefore two influential norms should be followed for the design of a better receptor, that is the charge density and geometry of anions (*5*), as well as the conformation and substituent of host (*6*, *7*). Based on this, the ureido —NHs and thiuoreido —NHs have got considerable interests to design various high sensitivity colorimetric artificial receptors because they can easily provide two efficient hydrogen-bonds (*8*).

Nowadays, the most general and classical methods to strengthen the sensing ability of (thio)urea receptors are to enhance the acidity of ureido —NHs and thioureido —NHs by modifying the *N*,*N*′-substituent, because the more acidity the receptor, the more stronger the hydrogen-bond donor ability by deprotonating of their —NHs group. Recently, *N*-benzamidothioureas, a kind of receptor with lower acidity, was also found to provide a stronger hydrogen-bond donor ability by means of a new hydrogen-bond network induced by the conformation change of single N—N bond (*9–14*). It opens a new way to synthesis urea- and thiourea-based anion receptors, and the variety of this kind of efficient luminescent and colorimetric anion receptors exhibited extraordinary sensing ability with anions (*15–24*).

Based on the aforementioned and our former researches (*25*), the extensive anion recognition urged us to design and synthesise novel anion receptors with high efficient recognition properties. In order to further increase the hydrogen-bond interaction between anions and receptors, we wish to replace the acylthiourea bridge (···CONHCSNH···) by hydrazine unit (···CONH-NHCX···) as described in Figure 1. Therefore, four novel salicylic acid-oriented semicarbazide and thiosemicarbazide anion receptors AR1–4 have been designed and synthesised, and all sensing abilities have been investigated by typical spectroscopic titration techniques. The experimental results indicate that the receptor AR4 can selectively recognise fluoride and acetate anions through naked-eye visible colour changes.

Experimental section

Reagents and general methods

All the anions were purchased from Sigma-Aldrich Chemical Co. (Shanghai, China) or Sinopharm Chemical Reagent Co., (Shanghai, China) were added in the form of tetrabutylammonium salts and stored in the vacuum desiccators containing self-indicating silica. Absorption spectra were recorded on a Shimadzu UV-2450 Spectrophotometer (Shimadzu, Japan) at room temperature by using a 1 cm quartz cell. IR spectra were recorded on a Thermo Nicolet FT-IR Avatar 330 (Thermo Electron Corporation, Waltham, Mass) instrument in potassium bromide (KBr). ^{1}H NMR spectra were recorded on a Brucker spectrometer (Bruker, Fallanden, Switzerland) at 400 MHz using DMSO-d_6 as a solvent and the internal

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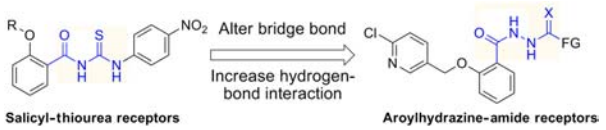


Figure 1. Design strategy of aroylhydrazine-amide derivatives as anion receptors.

standard was TMS, δ (parts per million) values were reported as chemical shifts. Mass spectra were recorded on a MicroMass Quattro micro™ API instrument. All solvents and reagents were analytical reagent and used directly without further purification.

Syntheses of target molecules AR1–4

General synthetic procedure for 2-((6-chloropyridin-3-yl)methoxy)benzohydrazide 4

To a solution of newly prepared methyl 2-((6-chloropyridin-3-yl)methoxy)benzoate (5.55 g, 20 mmol) in EtOH (5 mL), hydrazine hydrate (80%, 3.0 eq.) was added. The resulting mixture was stirred at 60–70 °C for 5–7 h, and TLC was used to monitor the reaction until the end. After cooling the mixture to room temperature, the precipitates were collected by filtration, washed with water and recrystallised by ethanol. The compound 2-((6-chloropyridin-3-yl)methoxy)benzohydrazide was obtained as a white powder, yield 88%, m.p. 116–118°C, MS: 278.4 ($C_{13}H_{13}ClN_3O_2^+$, $[M + 1]^+$).

General synthetic procedure for the target compounds AR1–3

The typical synthetic process of novel aroylhydrazinecarboxamide derivatives AR1–3 is shown as following: the solution of appropriately substituted benzoylisocyanate or isothiocyanate (2 mmol) in dry acetonitrile (5 mL) was added dropwise to a stirred solution of 2-((6-chloropyridin-3-yl)methoxy)benzohydrazide 4 (1.5 mmol) in dry acetonitrile (15 mL). Then the reaction mixture was stirred at 40–50°C for 0.5–2 h, and was monitored by TLC till the disappearance of compound **4**. Finally, the reaction solution was cooled to ambient temperature and the precipitates were collected by filtration, washed with acetonitrile and recrystallised by ethanol. Their physicochemical properties and the spectra data are as follows:

1-(2-((6-Chloropyridin-3-yl)methoxy)benzoyl)-4-(4-chlorophenyl)semicarbazide AR1. This compound was obtained through methods referred above as white powder, yield 92%, m.p. 207–209°C; IR (ν_{max}, KBr, cm^{-1}): 3335.51 (NH), 1712.15, 1658.88 (NHC = O); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta_H = 9.89$ (s, 1H), 8.86 (s, 1H), 8.59 (s, 1H), 8.39 (s, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.67 (d, $J = 7.6$ Hz, 1H), 7.53–7.23 (m, 7H), 7.09 (t, $J = 7.6$ Hz, 1H), 5.31 (s, 2H); MS *m/z* 431.7 $(M + H)^+$, calcd for $C_{20}H_{16}Cl_2N_4O_3$ *m/z* = 430.1.

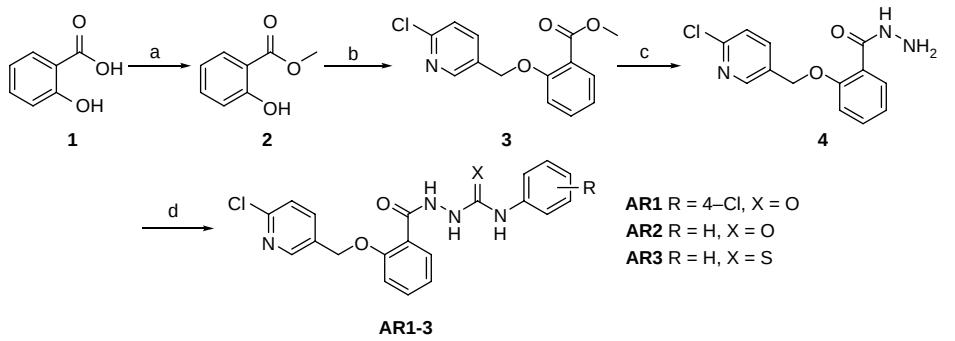
1-(2-((6-Chloropyridin-3-yl)methoxy)benzoyl)-4-phenylsemicarbazide AR2. This compound was obtained through methods referred above as white powder, yield 88%, m.p. 219–221°C; IR (ν_{max}, KBr, cm^{-1}): 3324.30 (NH), 1706.54, 1625.23 (NHC = O); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta_H = 9.90$ (s, 1H), 8.70 (s, 1H), 8.59 (d, $^4J = 2$ Hz, 1H), 8.31 (s, 1H), 8.06 (q, $J = 8$ Hz, 1H), 7.67 (d, $J = 6$ Hz, 1H), 7.53–7.41 (m, 4H), 7.26 (t, $J = 8$ Hz, 3H), 7.07 (t, $J = 7.6$ Hz, 1H), 6.96 (t, $J = 7.2$ Hz, 1H), 5.32 (s, 2H); MS m/z 397.8 $(M + H)^+$, calcd for $C_{20}H_{17}ClN_4O_3$ *m/z* = 396.1.

1-(2-((6-Chloropyridin-3-yl)methoxy)benzoyl)-4-phenylthiosemicarbazide AR3. This compound was obtained through methods referred above as white powder, yield 94%, m.p. 197–198°C; IR (ν_{max}, KBr, cm^{-1}): 3304.47 (NH), 1636.45 (NHC = O), 1241.12 (C = S); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta_H = 10.19$ (s, 1H), 9.91 (s, 1H), 9.39 (s, 1H), 8.60 (s, 1H), 8.03 (d, $J = 8$ Hz, 1H), 7.86 (s, 1H), 7.58–7.28 (m, 7H), 7.17–7.08 (m, 2H), 5.35 (s, 2H); MS *m/z* 413.7 $(M + H)^+$, calcd for $C_{20}H_{17}ClN_4O_2S$ *m/z* = 412.1.

General synthetic procedure for the target compounds AR4

The typical synthetic process of novel aroylhydrazine-oxoacetamide derivative AR4 is shown as following: The mixture of 4-nitroaniline (3 mmol), oxalyl chloride (8 mL) in toluene (5 mL) was heated at 60–70°C for 5 h. Excess oxalyl chloride was removed in vacuo, and the residue oil was directly treated with 2-((6-chloropyridin-3-yl)methoxy)benzohydrazide 4 (1.5 mmol) in dry acetonitrile (15 mL). Then the reaction mixture was stirred at 30–40°C for about 1.5 h. TLC was used to monitor the process of reaction until compound 4 disappear. The ultimate mixture was cooled to ambient temperature and the precipitates were collected by filtration, washed with acetonitrile and recrystallised by ethanol. Their physicochemical properties and the spectra data are as follows:

2-(2-(2-((6-Chloropyridin-3-yl)methoxy)benzoyl)hydrazinyl)-N-(4-nitrophenyl)-2-oxoacetamide AR4. This compound was obtained through methods referred above as white powder, yield 87%, m.p. 242–244°C; IR (ν_{max}, KBr,



Scheme 1. General synthetic route for compounds AR1–3. Reagents and conditions: a. MeOH, Conc. H_2SO_4; b. 2-Chloro-5-(chloromethyl)pyridine, K_2CO_3, MeCN, r.t. to reflux for 10–12 h; c. 3 equiv. Hydrazine hydrate, EtOH, rt to 50–60 °C for 5–7 h; d. Isocyanate or isothiocyanate, MeCN, 40–50 °C for 0.5–2 h.

cm^{-1}): 3285.05 (NH), 1698.13, 1658.88 (NHC = O); ^1H NMR (400 MHz, DMSO-d_6): $\delta_H = 11.40$ (s, 1H), 11.12 (s, 1H), 10.22 (s, 1H), 8.60 (s, 1H), 8.30 (d, $J = 4.8$ Hz, 2H), 8.14 (t, $J = 8.4$ Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 1H), 7.63 (d, $J = 7.6$ Hz, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 1H), 7.27 (d, $J = 8.4$ Hz, 1H), 7.09 (t, $J = 7.2$ Hz, 1H), 5.33 (s, 2H); MS m/z 470.1 $(M + H)^+$, calcd for $C_{21}H_{16}ClN_5O_6$ m/z = 469.1.

Adsorption titration studies

The solution of receptors AR1–4 was prepared at 4.0×10^{-3} M in dry DMSO, while the selected anions, in the form of tetrabutylammonium salt, were prepared at 1.0×10^{-2} M in dried and distilled DMSO, the adsorption ability of these receptors for anions was investigated by UV–Vis spectra with a specific concentration of receptor (4.0×10^{-5} M) and different equivalents of anions.

Results and discussion

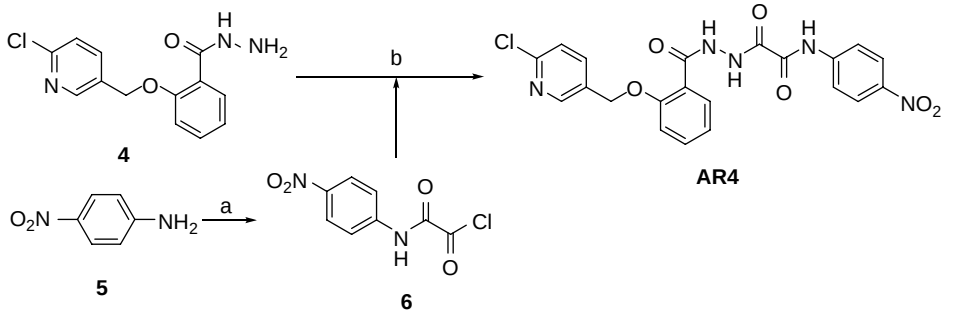
Synthesis of aroylhydrazine-carboxamide derivatives AR1–3

In this study, a series of novel aroylhydrazine-carboxamide derivatives were designed and synthesised as anion receptors. The general methods for the preparation of salicylic acid-oriented *N*-(substituted)benazmido(thio)urea derivatives AR1-3 are outlined in Scheme 1.

First, salicylic acid was conveniently converted to methyl salicylate by esterification reaction, then 2-chloro-5-(chloromethyl)pyridine was treated with methyl salicylate in acetonitrile to obtain intermediate 3 in the participation of potassium carbonate. Hereafter, the colourless crystal 3 was reacted with excess hydrazine hydrate in ethanol to form the important intermediate 2-((6-chloropyridin-3-yl)methoxy)benzohydrazide 4. Finally, the intermediate 4 reacted with various iso(thio)cyanate to obtain receptors AR1-3 through nucleophilic addition reaction. All the synthesised compounds AR1–3 gave satisfactory chemical analyses, and all the IR, ^1H NMR and MS spectra were consistent with the assigned structures.

Synthesis of aroylhydrazine-oxoacetamide derivative AR4

For the purpose of finding a kind of novel anion receptor by naked-eye recognition, compound AR4 with α-ketoamide scaffold has further been designed and synthesised according to the method presented in Scheme



Scheme 2. General synthetic route for compound AR4. Reagents and conditions: a. Oxalyl dichloride, toluene at 60–70 °C; b. MeCN, 30–40 °C.

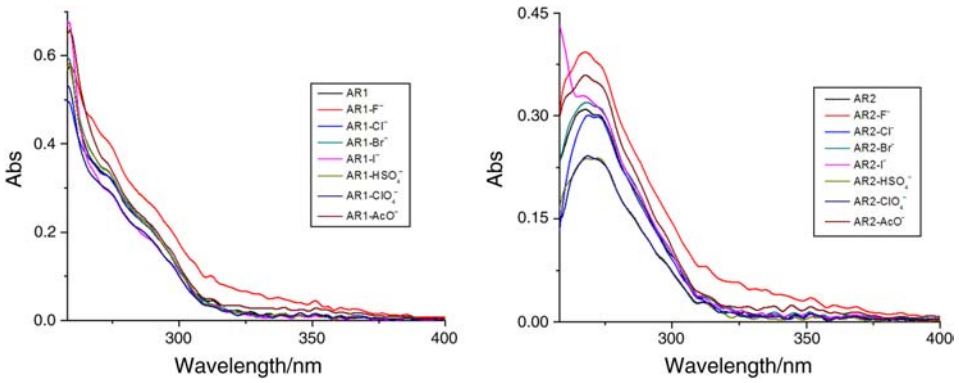


Figure 2. Changes in the UV–Vis absorption spectra of AR1 (4.0×10^{-5} M, Left) and AR2 (4.0×10^{-5} M, Right) with addition of 10.0 equiv. of different anions (4.0×10^{-4} M) in DMSO.

2. The intermediate 4 was synthesised with the method similar to that described in Scheme 1, while the other intermediate 6 was obtained via a simple acylation reaction and was directly treated with compound 4 in solution of dry acetonitrile to get the target molecule AR4. The IR, ^{1}H NMR and MS spectra in the experimental part were consistent with the assigned structure.

Spectroscopic studies on receptors

The anion recognition abilities of AR1-4 were investigated by monitoring the spectra changes of UV–Vis in the presence of different equivalents of anions separately, such as AcO^-, F^-, Cl^-, Br^-, I^-, HSO_4^- and ClO_4^- (as tetrabutylammonium salt) in DMSO.

An initial test of complex AR1 and AR2 was studied first in DMSO with seven anions showed above, while no obviously spectra changes as well as colour changes were observed. From the UV–Vis absorption spectra, we can know that combined with these anions separately, the only change of this host–guest complexation was that the absorbance was strengthen a little after F^- was added in (Figure 2).

We conjecture there were two reasons for this bad communication effect of AR1 and AR2 with anions, one is the rigidity of —NHNH— component, which makes it a little difficult for AR1 and AR2 to form a stable configuration to induce efficient electron transfer when communicate with anions (*9*, *26*, *27*). The other more important reason is that both of the receptor AR1 and AR2 are not acidic enough. Since the stronger interaction established between the more basic anions and the more acidic receptors (*5*), a few studies have verified that the binding efficiency of thiourea-based receptors is better than urea-based receptors in DMSO (*28–30*), mainly because of the acidity of NH proton of thiourea ($pK_a = 21.1$) is higher than that of urea ($pK_a = 26.9$) (*2*, *8*), although O atom is a better hydrogen-bonding acceptor than S atom [13], it is also the reason for why thiourea subunits are widely used for synthesising neutral anion-bonding receptors (*31*). Taking these into account, for the purpose to improve the sensing properties of AR1 and AR2, we designed and synthesised the thiourea receptor AR3 with a same configuration as that of AR1 and AR2, and it was also studied with anions using UV–Vis by the same methods showed above.

From the test result, we found that when anions were added to the solution of AR3 in DMSO separately, the absorption spectra changed in the presence of F^- and AcO^- at ca. 360 nm, while the characteristic absorption peak for AR3 is at ca. 272 nm, and no changes were observed with other anions (Figure 3).

Compared with AR1 and AR2, AR3 is more sensitive with anions with a relatively obvious absorption change, although the absorption intensity is still weak. In order to further explore their sensing ability, ultrasonic means was

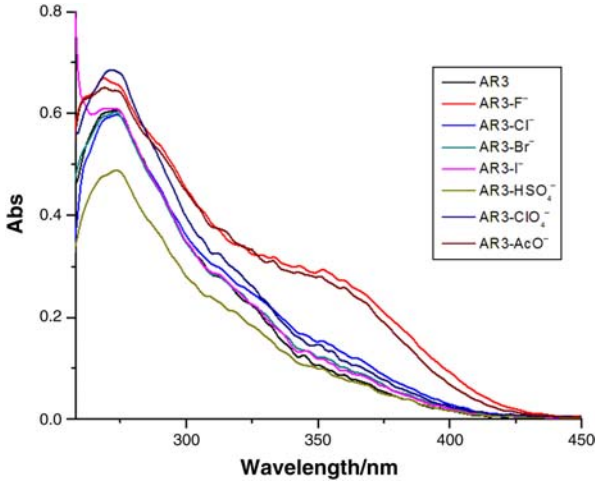


Figure 3. Changes in the UV–Vis absorption spectra of AR3 (4.0×10^{-5} M) with addition of 10.0 equiv. of different anions (4.0×10^{-4} M) in DMSO.

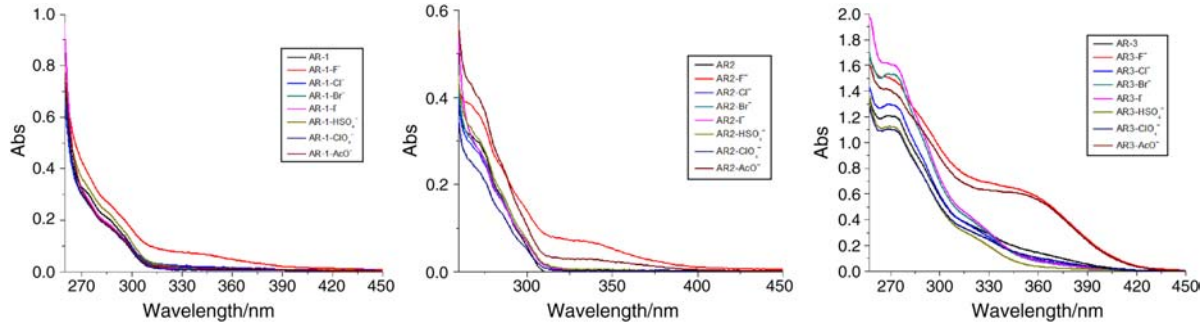


Figure 4. Changes in the UV–Vis absorption spectra of AR1 (4.0×10^{-5} M, Left), AR2 (4.0×10^{-5} M, Middle) and AR3 (4.0×10^{-5} M, Right) with the addition of 10.0 equiv. of different anions (4.0×10^{-4} M) in DMSO after sonicating.

used in UV–Vis for these three receptors with anions. In the solution of AR1, AR2 and AR3 in DMSO, AcO^-, F^-, Cl^-, Br^-, I^-, HSO_4^- and ClO_4^- (10.0 equiv) were added in separately, and then all of these complexation were put into the ultrasonic cleaning equipment and sonicated for 30 min at room temperature, the results were showed in Figure 4. It can be seen that no more absorption changes for these three receptors after sonicating, which can be compared with the result shown in Figure 1. This may indicate that receptors AR1 and AR2 have lower recognition abilities with anions due to its lower —NH acidity induced by the substituent of lower electron-withdrawing groups, while AR3 is good enough as an artificial anion receptor.

Further, receptor AR3 was also studied by successively titrating with different equivalents of anions separately through monitoring the absorption spectra of UV–Vis. The selective titrating process with F^- was set as an example, we found that with the increasing concentration of F^-, the absorption peak at ca. 339 nm was enhanced (Figure 5), but the absorption intensity was not enhanced endless, it was constant at a range of values at a specific proportion of host and anion. This may indicate that a stable configuration was formed between AR3 and F^- at that proportion, which induced no more enhancing of absorption intensity with the constant increasing concentration of F^-.

Through the research on absorption changes of UV–Vis spectra of AR1, AR2 and AR3 with different anions showed above, we know that none of these three receptors can attribute to colorimetric artificial receptors in a sense, since none of them can recognise anions by naked-eye, which does not meet our expectation described in the introduction to find a novel colorimetric receptor to recognise anions by naked-eye. So the novel receptor AR4 was further designed and synthesised for the purpose of sensing of anions by 'naked-eye' in the presence of α-ketoamide scaffold.

In the test of UV–Vis, an immediate and obviously colour change from colourless to bright yellow was shown when F^- and AcO^- were added in the solution of AR4 in DMSO separately (Figure 6). while, no detectable colour changes were observed with the addition of other anions such as Cl^-, Br^-, I^-, HSO_4^- and ClO_4^-, even in large equivalent (anion: host). These results suggested that AR4 has a special bonding ability with AcO^- and F^-, better than any other five tested anions.

Colorimetric sensing behaviour of AR4 (4.0×10^{-5} M) upon the addition of AcO^-, F^-, Cl^-, Br^-, I^-,

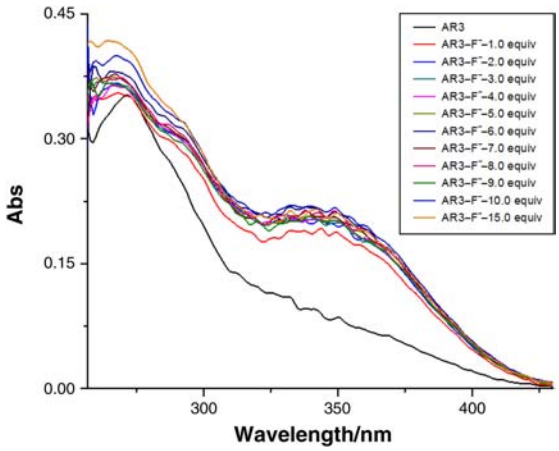


Figure 5. Changes in UV–Vis absorption spectra complex AR3 (4.0×10^{-5} M) upon addition of F^- (equiv = 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 15.0) in DMSO.

Figure 6. Colour changes of receptor AR4 in DMSO solution (4.0×10^{-5} M) in presence of 10.0 equiv. of different anions. From left to right: AR4, AR4 + F^-, AR4 + Cl^-, AR4 + Br^-, AR4 + I^-, AR4 + HSO_4^-, AR4 + ClO_4^-, AR4 + AcO^-.

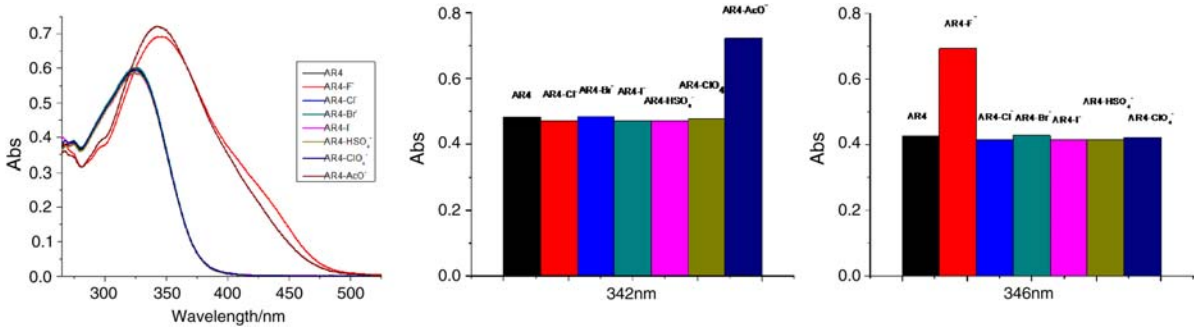


Figure 7. Left: Changes in the UV–Vis absorption spectra of AR4 (4.0×10^{-5} M) with addition of 10.0 equiv. of different anions (4.0×10^{-4} M) in DMSO. Middle: Absorbance of AR4 (4.0×10^{-5} M) with addition of anions (4.0×10^{-4} M) in DMSO at 342 nm. Right: Absorbance of AR4 (4.0×10^{-5} M) with addition of anions (4.0×10^{-4}M) in DMSO at 346 nm.

HSO_4^- and ClO_4^- (10.0 equiv) in DMSO was further studied by absorption test of UV–Vis, and the spectra result was showed in Figure 7. We found that AR4 exhibited two characteristic absorption bands at $\lambda = 274$ nm ($\zeta = 0.96 \times 104\ M^{-1}\,cm^{-1}$) and 326 nm ($\zeta = 1.50 \times 104\ M^{-1}\,cm^{-1}$), as described above addition of anions, respectively, demonstrated that the absorption spectrum of AR4 was obviously redshift not only in the presence of AcO^- but also F^-. According to Figure 7 (Left), after the addition of AcO^-, a new ICT band was formed at 342 nm, while in the presence of F^-, the band was formed at 346 nm. Meanwhile, no significant absorption changes were observed in the presence of Cl^-, Br^-, I^-, HSO_4^- and ClO_4^-. The Figure 7 (Middle) and Figure 7 (Right) showed the absorbance of AR4 (4.0×10^{-5} M) in addition of that seven anions (4.0×10^{-4} M) at 342 and 346 nm in DMSO separately.

The colorimetric properties of AR4 were further evaluated by successively titrating with different equivalents of anions separately, as shown in Figure 8. It can be seen that the intensity of the absorption band at 342 nm increased with the increasing concentration of AcO^- up to 15.0 equiv. (Figure 8 Left). In the presence of increasing concentration of F^-, the absorption band at 346 nm increased too (Figure 8 Right), while the absorption band at 274 nm was gradually reduced. On the other hand, this may reveal that a stable binding state may be not formed between AR4 and this two anions in the present concentration ratio, since the absorption intensity still increased at the ratio of 15.0 equiv ([anion]: [host]).

To find the largest ratio of stable binding state, a further test was studied, with the increasing concentration of F^-, the solution of AR4 changed from pale-yellow to red-yellow which can be observed by naked-eye, and the colour was no more changed when the ratio was 28.0 ($[F^-]$:[AR4]), while no more colour changes was observed with increasing equivalent of AcO^- (Figure 9). No such spectra changes were found in the presence of other five anions. The appearance of the distinctive isosbestic point suggests that two ionic species was emerged which induced a well-defined binding complex of AR4 with these two anions. In this titration experiment, the new absorption band of AR4 located at ca. 342 nm with AcO^- and F^- could be similarly attributed to ground-state charge transfer (*10*).

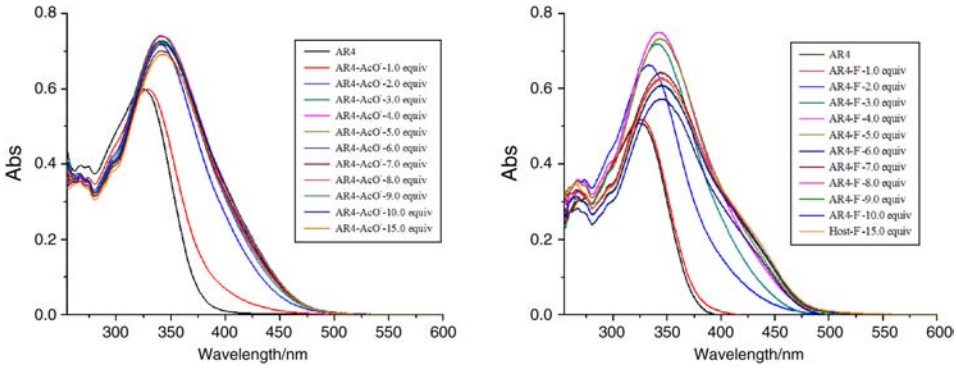


Figure 8. Left: Changes in UV–Vis absorption spectra complex AR4 (4.0×10^{-5} M) upon addition of AcO^- (equiv = 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 15.0) in DMSO. Right: Changes in UV–Vis absorption spectra complex AR4 (4.0×10^{-5} M) upon addition of F^- (equiv = 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 15.0) in DMSO.

Figure 9. Colour changes of AR4 with increasing equivalent of F^- (Left: AR4; Middle: AR4 + F^-, 10.0 equiv; Right: AR4 + F^-, 28.0 equiv).

Binding mechanism and stoichiometry

A further test was studied to explain the combination mode and recognition mechanism between AR4 and AcO^-/F^-, it can be seen that the absorption bond at 342 nm was enhanced with the increasing concentration of AcO^-, while the absorption curve was weaker at 281 nm with one isosbestic point at 321 nm. The similar phenomena were obtained of AR4 and F^- anion. The following job-plots indicate a stable 1:1 stoichiometry formed in the binding complex of AR4 and AcO^-/F^- (Figure 10) in DMSO, and the association constants between the receptors AR4 and AcO^- or F^- are 6.63×10^3 L·mol^{-1} ($r = 0.964$) and 2.26×10^3 L·mol^{-1} ($r = 0.924$), respectively.

Furthermore, when the competitive hydrogen-bonding solvent, such as methanol, was added to the mixed solution of AR4 and AcO^-, the colour of the mixed solution turned to colourless quickly (Figure 11 Right), which indicated that hydrogen bond was formed between host and guest (*32*). In this recognition process, it is difficult for urea to be a recognition moiety because of the configuration rigidity of —NHHN— component induced by the *Z*-confirmation of secondary amine (*33*) and the non-paired electron on neighbouring nitrogen atoms (*34*), but the receptor AR4 can still form a stable intramolecular bonds with AcO^- and F^-, we consider that because of the strong electron-withdrawing $—NO_2$ group as well as the other C═O group of the urea bridge, which made the single —N—N— bond less twisted through a conformation change (*18*, *35*), thus induced an enhanced substituent ($—NO_2$) effect by charge transfer (*14*, *17*, *36*), which result in the enhancement of the N—H acidity by a planar network of hydrogen-bond (*11*), thus made it easy to form a efficient sensing effect with anions by the strong intramolecular hydrogen bond. The other reason for the good sensing ability with AcO^-, we consider it that there are two reasons, one is because that AcO^- has a higher basicity than other anions, the more negative the anion is, the more easier to interact with receptor (*34*, *37*); the other is that AcO^- is a Y-shape anion and the angle of the O—C—O is 120°, the two oxygen atoms of the trigonal planar are suitable to form a stronger hydrogen bond with α-ketoamide receptors by enhancing the receptor's affinity (*38–40*). The receptor AR4 also exhibits similar binding properties with F^- anion, and the detail results for studies on the interaction of AR4 and F^- may seen in the supplementary data provided (Detailed experimental results for the synthesised receptors of the Supplementary Information, available online).

Conclusion

In summary, four novel salicylic acid-oriented aroylhydrazine-amide derivatives bearing pyridine core AR1-4 have been designed, synthesised and characterised as anion receptors. To our knowledge, this is the first study about the salicylic acid-oriented aroylhydrazine-amides receptors, especially the receptor AR4 with α-ketoamide scaffold exhibited obvious naked-eye recognition

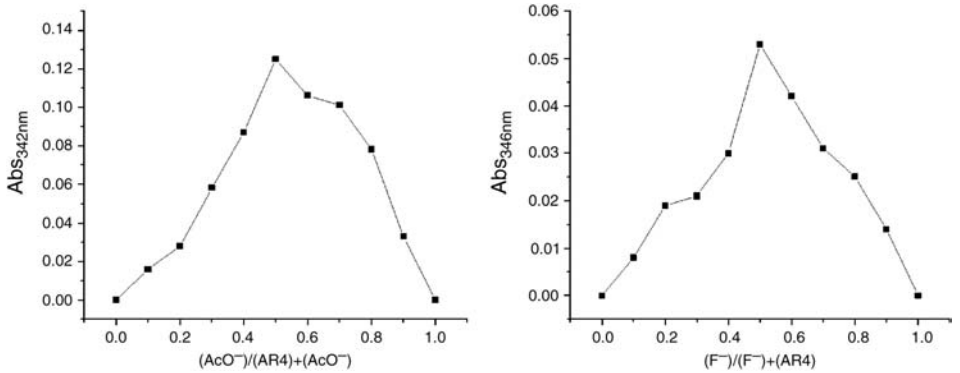


Figure 10. Job's plot between AR4 and AcO^- (Left), AR4 and F^- (Right) in DMSO at 25°C.

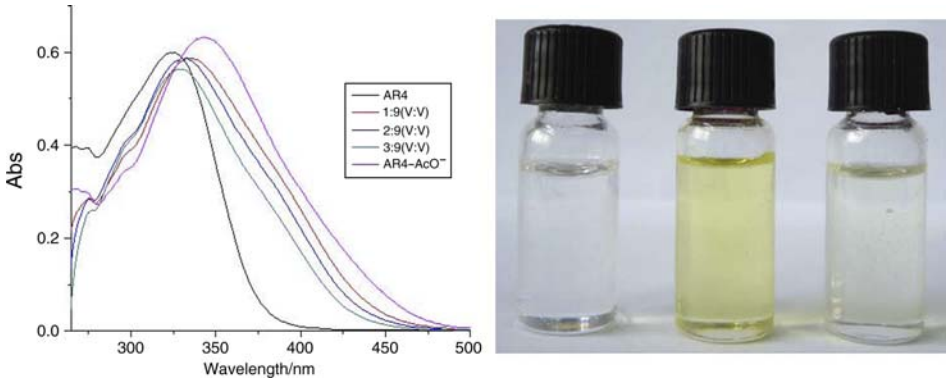


Figure 11. Left: The spectrum changes in UV–Vis of AR4 (4×10^{-5} M) and AcO^- (4×10^{-4} M) in the presence of protonic solvent such as methanol (V_{MeOH}:$V_{AR4+AcO}^{-}$ = 1:9, 2:9, 3:9). The colour of the mixed solution was fade when methanol was dropped in at the proportion of 1:9 (V_{MeOH}:$V_{AR4+AcO}^{-}$), but the colour will recovery when DMSO was dropped in again. However, with the increasing volume of MeOH, the colour of the complexation will be never recover when V_{MeOH}:$V_{AR4+AcO}^{-}$ = 3:9, no matter how much DMSO was dropped in again. Right: colour changes of AR4 and AcO^- in presence of MeOH. From left to right: AR4, AR4 + AcO^-, AR4 + AcO^- + MeOH.

properties, which may provide a new train of thought to developing novel colorimetric chemosensors for the detection of biologically important anions by naked-eye.

Supplementary data

Supplementary data associated with this article can be found online.

Acknowledgements

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Note

1. These two authors contributed equally to this work.

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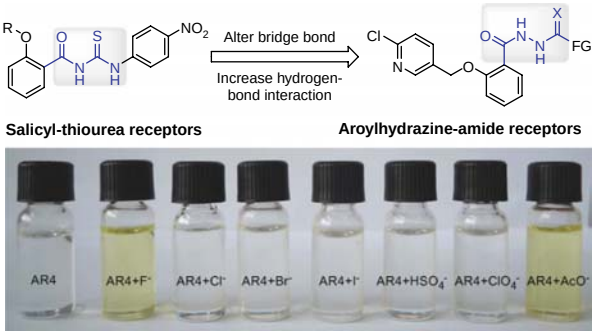

Shaowei Li, Huangyong Li, Changshui Chen, Xiali Yue, Xiufang Cao and Shaoyong Ke

Novel aroylhydrazine-amide derivatives bearing pyridine core: synthesis, characterisations and selective colorimetric recognition properties

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