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Convenient synthesis and anion recognition property of acylhydrazone-based molecular tweezer receptors

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Three acylhydrazone-based compounds were designed as novel neutral sensors for anions, and synthesized by simple steps in good yields. Their anion recognition properties were studied by UV-vis and ^{1}H-NMR spectroscopy. The results showed that the receptors **1**, **2**, and **3** all had a better selectivity for F^- and CH_3COO^-, but no evident binding with Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, or HSO_4^-. The results indicated that anion recognition was achieved via convergent hydrogen bond interactions from acylhydrazone functionality on the side arms. The UV-vis data indicated that a 1:1 stoichiometry complex was formed between compounds **1**, **2**, or **3** and anions. The binding and selectivity were also tuned by the change of the place of the nitro group attached to the phenyl. Moreover, receptor 3 can act as the colorimetric sensor for such anions as F^- and CH_3COO^-, and the recognition mechanism and binding mode were discussed.

Key Words: Anion recognition; molecular tweezer; acylhydrazone

Introduction

The selective recognition of biologically and/or chemically important anions by means of artificial molecular receptors represents as an active field of research with applications spanning from analytical chemistry to environmental science, toxicology, and biology.[1] A variety of artificial receptors for anions have been reported, including polyammonium macrocycles,[2] guanidinium,[3] amides,[4] urea/thiourea,[5] and calixarenes.[6] However, acylhydrazone-based receptors have not been reported. Furthermore, to encapsulate the particular guest more efficiently, the calixarenes (and their derivatives) have been used as large macrocyclic organic building blocks,[7] on the other hand, molecular 'tweezers' for anion recognition has also received considerable attention in recent

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times.[8] Continuing our efforts to develop a highly selective anion receptor,[9−11] here we report the synthesis, characterization, and anion recognition nature of a series of acylhydrazone-based tweezer receptors for the first time. The properties of the anion recognition have been investigated by UV-vis in DMSO and ^{1}H-NMR spectroscopy in DMSO-d_6. The results show that receptor 3 can be used as anion sensors in the solution of DMSO. Furthermore, the anion binding is accompanied by a visually striking color change, giving naked eye anion sensing.

Experimental

Materials and methods

The substituent aryloxyacetyl hydrazones have been prepared using the published literature.[12] DMSO was dried and distilled before using according to standard practice. All other commercially available reagents were used without further purification. The tetrabutylammonium salts were used as anionic substrates. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). The infrared spectra were obtained on a Digilab FTS-3000 FT-IR spectrophotometer. Elemental analyses were determined with a PE-2400 CHN elemental autoanalyzer. ^{1}H-NMR spectra and ^{13}C-NMR spectra were recorded on a Varian Mercury plus-400 MHz spectrometer. UV-Vis spectra were obtained on a Lab Tech UV-2100 spectrometer. Mass spectra were recorded on a HP-5988 spectrometer.

Synthesis of receptors

The synthesis of receptors was carried out by condensation of substituent aryloxyacetyl hydrazide with isophthalic aldehyde using HCl as the catalyst. The reaction mixture was filtered. The solid obtained was washed with ethanol 3 times to give a pure product.

Information of receptors

1: Yield: 70%; mp: 246-247 ° ° C; ^{1}H-NMR(CD_3SOCD_3, ppm): 5.4 (4H, O-CH_2), 4.868 (2H, N=C-H), 11.79 (2H, -NH), 7.1-8.8 (12H, Ar); IR (cm^{-1}, KBr): 3190.57 (N-H), 2977.49 (N=C-H), 1681.90 (C=O), 1608.17 (C=N); Anal. Calcd. for $C_{24}H_{20}N_6O_8$ (%): C: 55.39, H: 3.87, N: 16.15, O: 24.59; Found: C: 55.4, H: 3.89, N: 16.13, O: 24.54; MS(FAB): m/z: 180, 131.

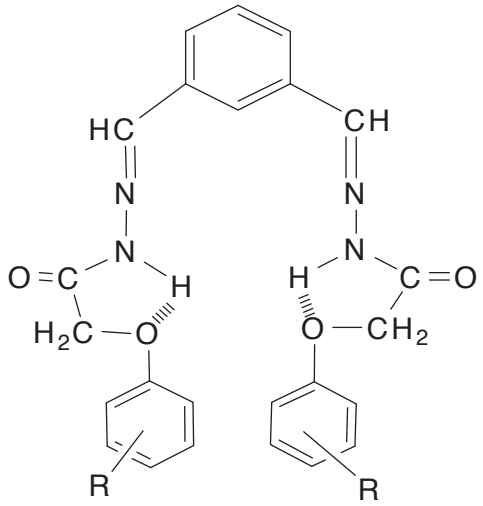
2: Yield: 72%; mp: 249-251 ° ° C; ^{1}H-NMR (CD_3SOCD_3, ppm): 4.88-5.37 (4H, O-CH_2), 3.358 (2H, N=C-H), 11.75-11.78 (2H, -NH), 7.43-8.4 (12H, Ar); ^{13}C-NMR (CD_3SOCD_3, ppm): 168.05, 179.15, 163.73, 115.63-148.6, 65.3-66.7; IR (cm^{-1}, KBr): 3185.24 (N-H), 2974.24 (N=C-H), 1685.78 (C=O), 1527.55 (C=N); Anal. Calcd. for $C_{24}H_{20}N_6O_8$ (%): C: 55.39, H: 3.87, N: 16.15, O: 24.59; Found: C: 55.42, H: 3.87, N: 16.15, O: 24.52; MS(FAB): m/z: 180, 131.

3: Yield: 77%; mp: 277-280 ° ° C; ^{1}H-NMR (CD_3SOCD_3, ppm): 4.89-5.38 (4H, O-CH_2), 3.372 (2H, N=C-H), 11.76-11.8 (2H, -NH), 7.14-8.37 (12H, Ar); ^{13}C-NMR (CD_3SOCD_3, ppm): 168.2, 163.5, 115.14-147.39, 65.4-66.6; IR (cm^{-1}, KBr): 3263.28 (N-H), 2926.73 (N=C-H), 1702.64 (C=O), 1593.12 (C=N); Anal.

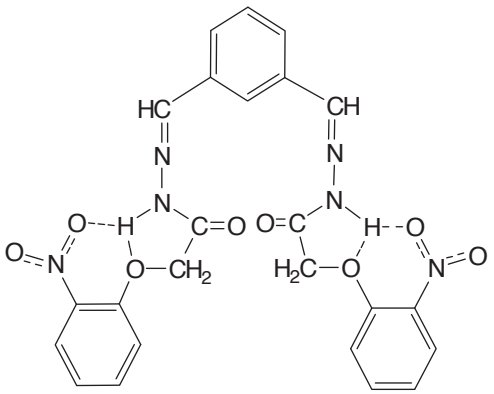
Calcd. for $C_{24}H_{20}N_6O_8$ (%): C: 55.39, H: 3.87, N: 16.15, O: 24.59; Found: C: 55.38, H: 3.91, N: 16.15, O: 24.52; MS(FAB): m/z: 180, 131.

Results and discussion

The resulting ^{1}H-NMR data displayed peaks shifts of the amide NH toward downfield (1, 2, and 3 peaked at 11.79, 11.77, and 11.76 (ppm), respectively). This implies the formation of intramolecular hydrogen-bonding interactions. The IR spectra of **1**, **2**, and **3** (**1**, **2**, and **3** peaked at 3190.57, 3185.24, and 3263.28 (cm^{-1}) respectively) also illustrated this note. The peaks downshift more than 100 wavenumbers. The UV-Vis spectra show the characteristic absorption band of **1, 2**, and **3** centered at 287.50 nm, 285.50 nm, and 292.00 nm, respectively, which illustrated that a better conjugated system was formed in the receptor **3**. The possible structures of the receptors are shown in Figure 1.



2: R=*m*-NO_2; **3:** R=*p*-NO_2



Receptor **1**

Figure 1. The possible structures of the receptors.

The sensing ability of the receptors **1**, **2**, and **3** with anions in dimethyl sulfoxide was monitored by using UV-Vis absorption. The receptors exhibited selective recognition for CH_3COO^- and F^- over other anions, such as Cl^-, Br^-, I^-, HSO_4^-, and NO_3^- in DMSO. Sensor **2** (2×10^{-5} mol/L) showed a broad absorption band centered at 286 nm. Upon addition of F^- anion (as their tetrabutylammonium salts), the band at 334 nm increased in intensity at the expense of the 286 nm transition. Meanwhile, a clear isosbestic point was observed at 313 nm. Upon addition of CH_3COO^- anion, the band at 320 nm increased in intensity at the expense of the 286 nm transition. Meanwhile, a clear isosbestic point was observed at 308 nm. The change of **2** from colorless to light yellow is observed in the presence of F^- or CH_3COO^-. Figure 2 showed the spectra of **2** obtained during the titration with F^- (**a**) and CH_3COO^- (**b**). Absorbance values at 286 nm were taken for nonlinear least-squares treatment to obtain the binding constants (Ka) of the host **2** with guests (F^-, CH_3COO^-). The insets (Figure 2) represent the change in absorbance of **2** at 286 nm with varying molar equivalents of anions.

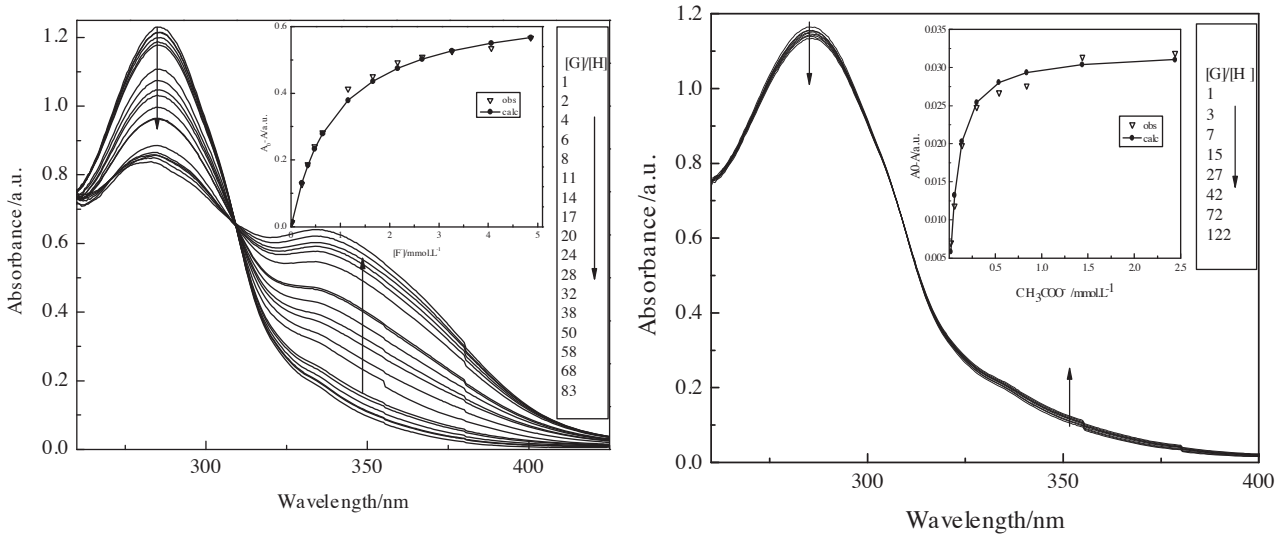


Figure 2. The UV-Vis titration spectra of receptor **2** with F^- (**a**) and CH_3COO^- (**b**) in DMSO (298 K). [**2**]=2×10^{-5} mol/L.

In addition, a more sensitive response of **2** toward F^- in the titration spectra was also observed than CH_3COO^- from Figure 2, which may be due to different complexation states of the host **2** and guests.

Sensor **1** exhibited similar recognition for F^- or CH_3COO^- as Sensor **2.** Sensor **3** (2×10^{-5} mol/L) showed a broad absorption band centered at 292 nm. Upon addition of F^- anion, the band at 355.5 nm increased in intensity at the expense of the 292 nm transition. Meanwhile, a clear isosbestic point was observed at 315 nm. The change of **3** from colorless to dark red is clearly evident to the naked eye. Upon addition of CH_3COO^- anion, the band at 323 nm increased in intensity at the expense of the 292 nm transition. Meanwhile, a clear isosbestic point was observed at 316 nm. The change of **3** from colorless to dark yellow is clearly evident to the naked eye.

We propose that these changes are consistent with the anions binding to the hydrazone moiety through hydrogen bonding. These combined binding modes give rise to an enhanced ICT character with concomitant color changes. The more obvious color change in receptor **3** than **1** and **2** in the presence of F^- or CH_3COO^-

will be explained by the fact that only when the nitro-group was in the para position of the phenyl group was internal charge transfer (ICT) the easiest.

Continuous variation methods were used to determine the stoichiometric ratios of the complexes formed between the receptors and the anion guests. The total concentration of the host and the guest was kept constant (4×10^{-5} mol/L) in DMSO, while the molar fraction of the guest {[G] / ([G] + [H])} was continuously varied. Figure 3 shows the Job plot for **2** with F^- in DMSO. When the molar fraction of the guest is 0.5, the absorption reaches a maximum, demonstrating that receptor **2** formed a 1:1 complex with F^-.

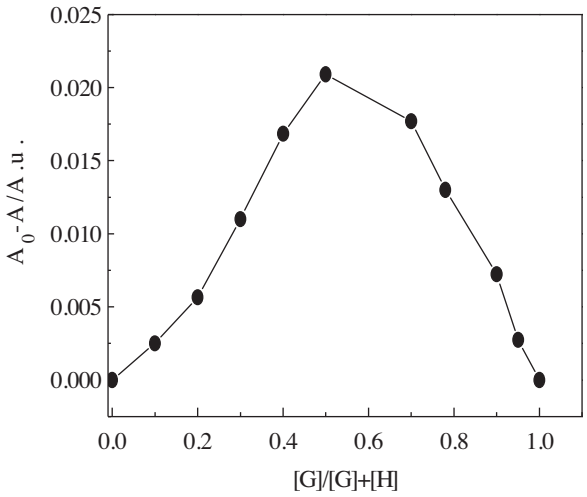


Figure 3. Job plot of **2** and F^- at a total concentration of 4×10^{-5} mol/L. [G] and [H] represent the concentration of the guest anion and the host, respectively.

Table. Binding constants (Ka) for the 1:1 complexes between these hosts (**1-3**) with guests (F^-, CH_3COO^-) in DMSO at 298 K.

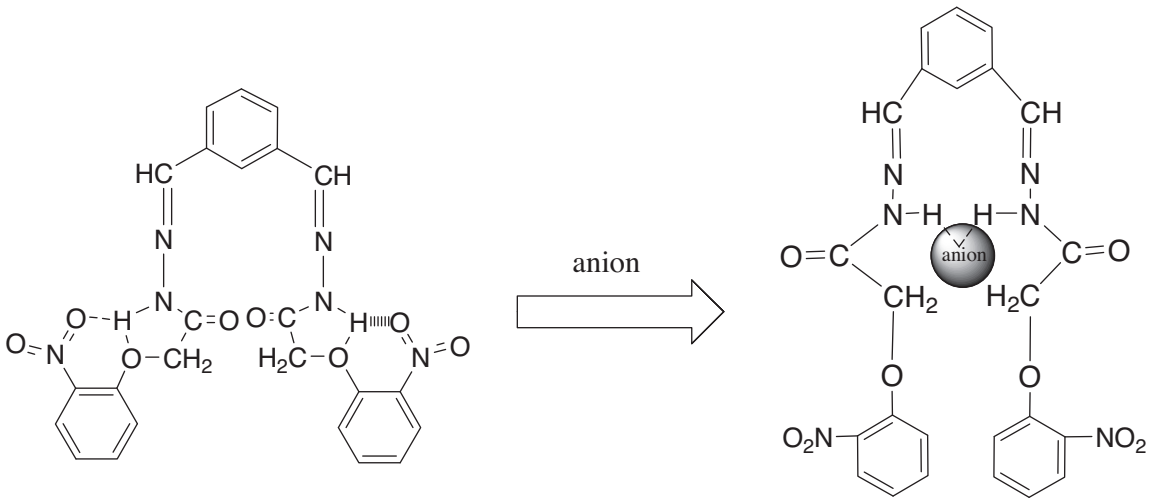
Host	Guest[a]	Ka (dm^3 mol^{-1})[b]	R
1	CH_3COO^-	7450	0.991
	F^-	1930	0.9938
2	CH_3COO^-	13700	0.9918
	F^-	1127	0.9976
3	CH_3COO^-	18100	0.994
	F^-	3080	0.9926

a, Tetrabutylammonium salts were used as anion sources.

b, Binding constants were represented as the average of 2-3 runs. Experiments errors were estimated to be $<10\%$.

Experimental results showed that F^- was sensed effectively by receptors **1-3** with binding constants of 1930, 1127, and 3080 dm^3 mol^{-1}, respectively; For CH_3COO^-, higher Ka values are observed from Table 1. That illustrated that the receptors had a stronger affinity towards CH_3COO^- than F^-, which supported

the notion that complementary structure played an important role in anion recognition. As an example, the binding mode of **1** for the anions is illustrated in Scheme.



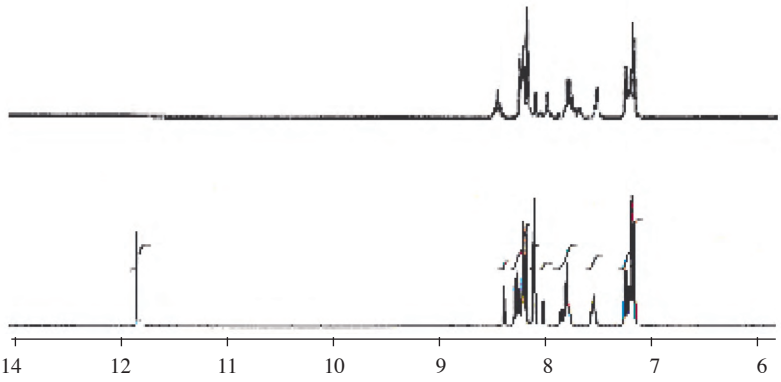
Scheme. The binding mode of the receptor **1** for the anions.

At the beginning of the titration with the tested anions, no obvious change was observed in the spectra of the receptors, which was because at the beginning the anions were too scarce to compete with the solvent molecular for the hydrogen-bonding sites.

It was immediately apparent from Table 1 that receptor **3** had a strong ability to complex with the tested anions in comparison with **1** and **2**, which was explained by the nature of hydrogen-bonding. The substituent of NO_2 attached to phenyl, as an electron-withdrawing and meta directing group, resulted in the order **2** < **1, 3** in the case of the acidity of N-H of amide unit; in addition, considering that **1** has a greater steric hindrance caused by intramolecular hydrogen bonding (Figure 1) particularly for the bigger CH_3COO^-, it was not surprising that **3** took on the strongest hydrogen-bond ability for the tested anions. Selectivity depends both on energy terms (related to the intensity of the receptor–substrate interaction) and on geometrical factors (size and shape matching between receptor and substrate). For F^-, it has a small volume, and the former play an important role; while for the bigger CH_3COO^- anion, the latter is more important. The fact resulted in the order 2 < 1 < 3 in the case of binding ability of the receptors for F^-, and the order 1 < 2 < 3 for CH_3COO^-.

Introduction of protic solvents such as methanol into the dimethyl sulfoxide solution of **2** plus F^- led to a gradual recovery of the absorption spectrum of **2** itself, which supported the hydrogen-bonding nature of the anion-receptor interaction, likely at the amide NH sites.

To confirm this assumption, ^{1}H-NMR titration in DMSO-d_6 was carried out. Addition of equivalent tetrabutylammonium fluoride to the DMSO-d_6 solution of **3** resulted in a disappearance of the N-H resonance. A similar observation was reported earlier and was presumably due to strong hydrogen bonding with the fluoride ion.



a) receptor **3** in the presence of F^-; b) receptor **3**.

Figure 4. ^{1}H-NMR spectra of receptor **3** in DMSO-d_6.

Conclusions

In summary, we reported 3 receptors that were synthesized by a simple method. Their properties of anion recognition were studied by UV-vis spectroscopy. The results showed that receptors **1**, **2**, and **3** can form 1:1 complex with anions such as F^-, CH_3COO^- by multiple hydrogen bonding interactions, and the 3 receptors had a strong binding to F^-, CH_3COO^-. The results described in this paper lead us to suggest a new approach to a receptor for selective recognition of acetate anion in polar solvent. Most notably, the selectivity of receptors to anions could be efficiently tuned by changing the place of the chlorine substituent group at the N-phenyl moiety. Of course, other cooperative or allosteric systems could be developed by further modifying these receptors. Extensive efforts are being directed toward this end.

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