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Synthesis and Anion Recognition Property of Acylhydrazone-Based Tweezer Receptors

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Three acylhydrazone-based receptors have been synthesized. Their anion recognition properties were studied by UV-visible and ^{1}H NMR spectroscopy. The results showed that the receptors **1**, **2** and **3** all had a stronger complexity with F^-, $H_2PO_4^-$ and CH_3COO^-, but no evident binding with Cl^-, Br^-, I^-, NO_3^- and HSO_4^-. Moreover,upon addition of such anions as F^-, $H_2PO_4^-$ and CH_3COO^-, **1** and **2** produced obvious colour changes. The recognition mechanism and binding mode were discussed.

Keywords: Anion recognition, Colourimetric, Acylhydrazone, Selectivity, UV-Visible.

INTRODUCTION

The development of colourimetric chemosensors for the specific anion has been an emerging area of supramolecular chemistry[1]. The colourimetric receptors attract the attention of many workers as they can detect the specific anion quickly and easily without any instrument[2-6]. Usually, if auxochrome or chromophore acts as the signaling units of the receptors[7,8], the colour change occurs when the receptors complex with the anions. In previous work, we have synthesized a series of colourimetric chemosensors by introducing auxochrome of nitro[9-11]. In order to study the anion recognition difference from the receptors containing auxochrome and chromophore respectively, we have synthesized a series of acylhydrazone-based tweezers receptors for the first time and reported the synthesis, characterization and anion recognition nature. (Fig. 1).

EXPERIMENTAL

Dimethyl sulfoxide 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 a X-4 digital melting-point apparatus (uncorrected). The infrared spectra were performed

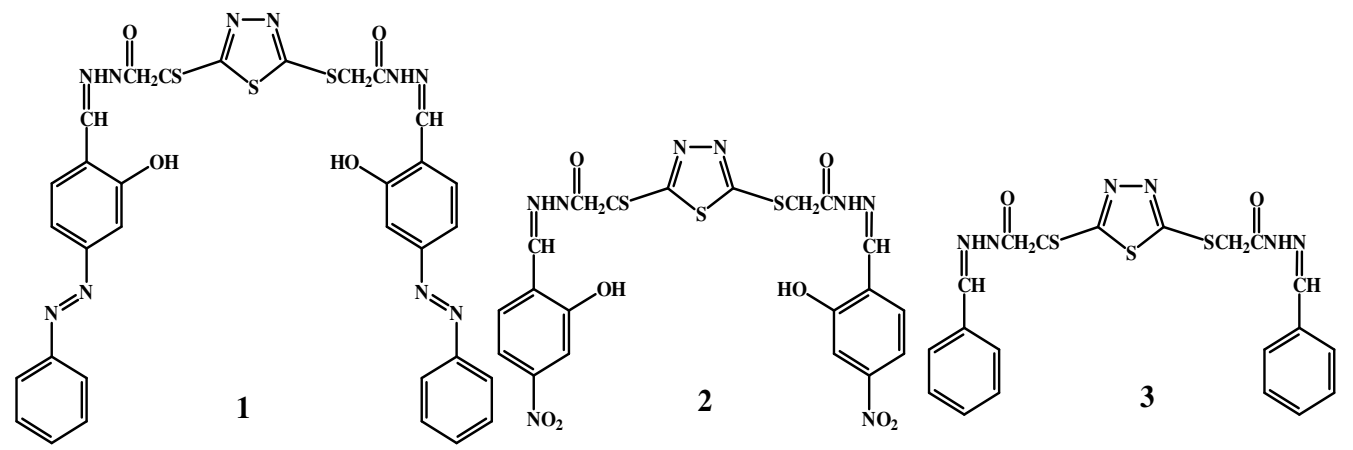
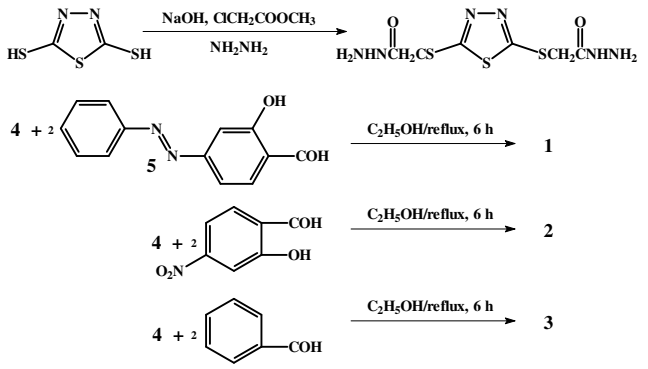


Fig. 1. Anion-binding receptors

on a Digilab FTS- 3000 FT-IR spectrophotometer. Elemental analyses were determined by a PE-2400 CHN elemental autoanalyzer. 1H NMR spectras were recorded on a Varian Mercury plus-400 MHz spectrometer. UV-visible spectra were taken on a Lab Tech UV- 2100 spectrometer.

Synthesis of receptors: The syntheses of **1**, **2** and **3** are outlined in **Scheme-I**. **4** and **5** were obtained by the procedures of the literatures[12,13].



Scheme-I: Syntheses of **1**, **2** and **3**. (Chemical structural formula of the receptors **1**, **2** and **3** are in Fig. 1)

Compound 1: Yield: 67 %; m.p.: 239-241 °C; IR (KBr, ν_{max}, cm^{-1}): 3742 (-OH), 3185.24 (N-H), 2974.24 (N=C-H), 1498 (-N=N-), 1685.78 (C=O), 1527.55 (C=N); ^{1}H NMR (DMSO-d_6): 11.40 (2H,C=O-NH-N), 11.16 (2H, OH), 4.24 (4H, -SCH_2-), 3.358 (2H, N=C-H), 6.2-8.4 (16H, Ar); ^{13}C NMR (DMSO-d_6): 128.51, 127.49 (-N=C-S); 164.84 (CONH), 115.63 (-N=C-) 65.3,66.7 (CH_2),127.37-135.23 (Ar) Anal. calcd. for $C_{32}H_{26}N_{10}O_4S_3$: C, 54.08; H, 3.66; N, 19.72. Found: C, 54.13; H, 3.58; N, 19.67.

Compound 2: Yield: 72 %; m.p.: 218 - 220 °C; IR (KBr, ν_{max}, cm^{-1}): 3738 (-OH), 3183.76 (N-H), 2965.67 (N=C-H), 1683.64 (C=O), 1524.17 (C=N); ^{1}H NMR (DMSO-d_6): 11.28 (2H, C=O-NH-N), 11.13 (2H, OH), 4.13 (4H, -SCH_2-), 3.17 (2H, N=C-H), 7.4-8.45 (6H, Ar); ^{13}C NMR (DMSO-d_6): 128.13, 127.19 (-N=C-S); 164.73 (CONH), 115.52 (-N=C-) 65.1,66.9 (CH_2), 129.57-138. 87 (Ar). Anal. calcd. for $C_{20}H_{16}N_8O_8S_3$: C, 40.54; H, 2.70; N, 18.92. Found: C, 40.24; H, 2.55; N, 18.71.

Compound 3: Yield: 85 %; m.p.: 205-207 °C; IR (KBr, ν_{max}, cm^{-1}): 3180.13 (N-H), 2980.14 (N=C-H), 1683.56 (C=O), 1529.34 (C=N); ^{1}H NMR (DMSO-d_6): 11.43 (2H, C=O-NH-N), 4.18 (4H, -SCH_2-), 3.27 (2H, N=C-H), 7.31-8.24(10H, Ar); ^{13}C NMR (DMSO-d_6): 128.15, 127.87 (-N=C-S); 164.33 (CONH), 115.58 (-N=C-) 64.9,65.7 (CH_2),130.87-135.23 (Ar). Anal. calcd. for $C_{20}H_{18}N_6O_2S_3$: C, 51.06; H, 3.83; N, 17.87. Found: C, 51.13; H, 3.91; N, 17.78.

RESULTS AND DISCUSSION

UV-visible spectral titrations: The sensing abilities of the receptors **1**, **2** and **3** with anions in dimethyl sulfoxide were monitored by using UV-visible absorptions, which were recorded from the solutions of these compounds in the absence or presence of anions such as F^-, Cl^-, Br^-, I^-, CH_3COO^-, $H_2PO_4^-$. Fig. 2 showed that the obvious change in the absorption spectra of receptors (**1**, **2** and **3**) upon addition of F^-, CH_3COO^- and $H_2PO_4^-$ to the solutions of the receptors but no detectable changes upon addition of such anions as Cl^-, Br^-, I^-. Especially, the UV-visible absorption bands of **1**, **2** undergo a red shift respectively when such anions as F^-, CH_3COO^- and $H_2PO_4^-$ are bounded, as a result of auxochrome or chromophore introduced. At the same time, colour changes could be observed from the receptors of **1**, **2** immediately. The same phenomenon was not observed in the receptor **3**.

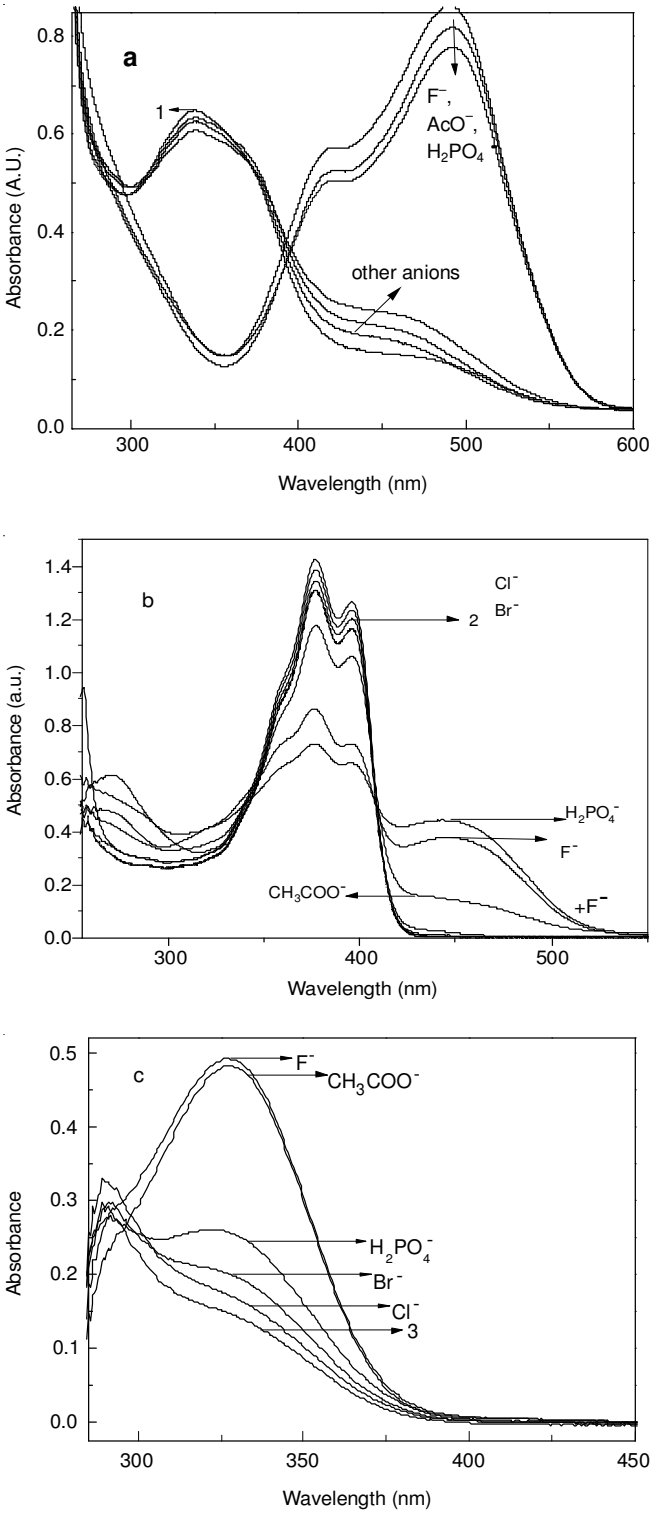


Fig. 2. UV-visible absorption spectras of receptors (**1**, **2**, **3**) in the presence of various anions; a, b and c are corresponding to receptor **1**, **2**, **3**, respectively

Upon the addition of F^-, CH_3COO^- or $H_2PO_4^-$ ions to the solution of **2**, the colour of the solution produced almost the same change from pale yellow to orange. In addition, for the receptor **1**, the colour of its solution changes similarly from pale yellow to dark red when the addition of F^-, CH_3COO^- or $H_2PO_4^-$ to its solution.

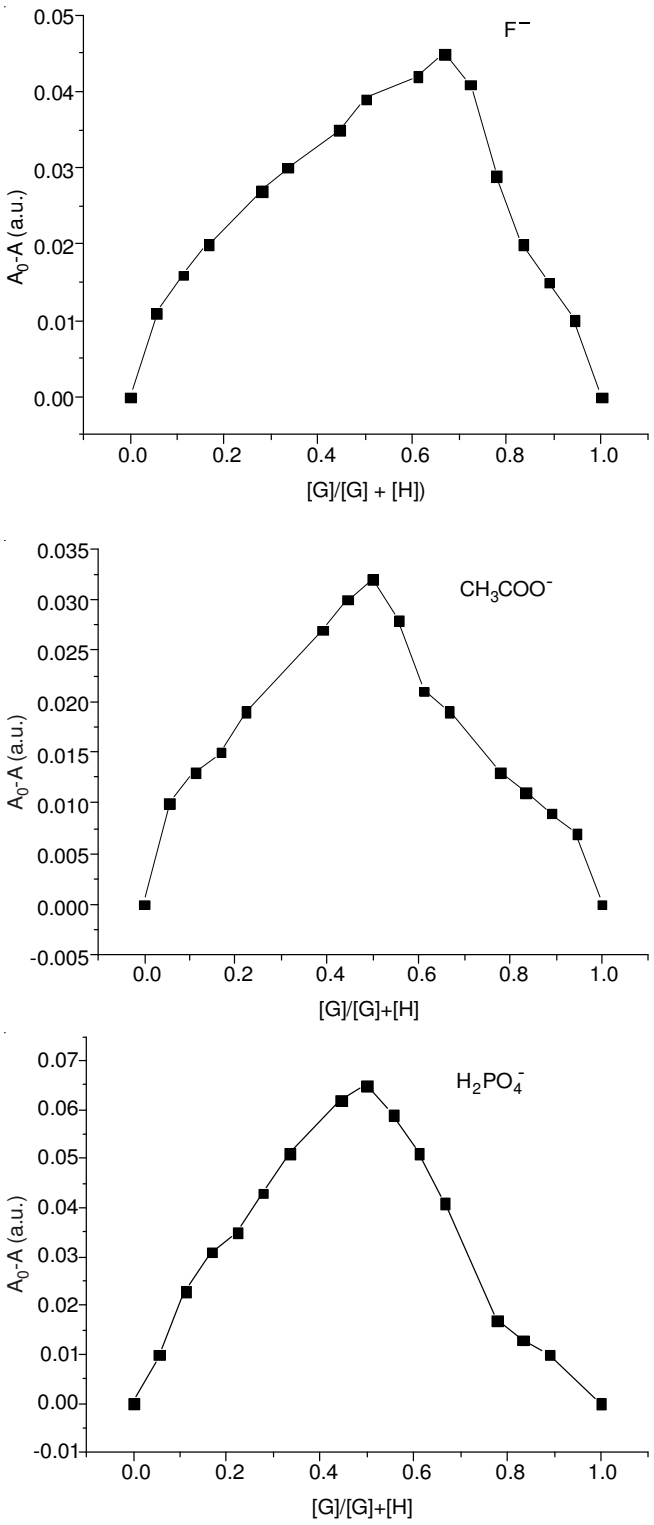


Fig. 3. Job plots for the receptor **2** with F^-, CH_3COO^- and $H_2PO_4^-$ anions at a total concentration of 3×10^{-5} mol L^{-1} in DMSO

The Job plots of the receptor **2** with F^-, CH_3COO^- and $H_2PO_4^-$ were reported in Fig. 3. It conformed 1:2 binding stotichiometry ($2:F^-$) and 1:1 binding stoichiometry ($2:CH_3COO^-$ or H_2PO4^-). The same fact happened to the receptor **1**, which could be interpreted as that F^- is too small in volume to reorganize the hydrogen donor sites of the receptors (**1**, **2**) in comparison with CH_3COO^- and $H_2PO_4^-$.

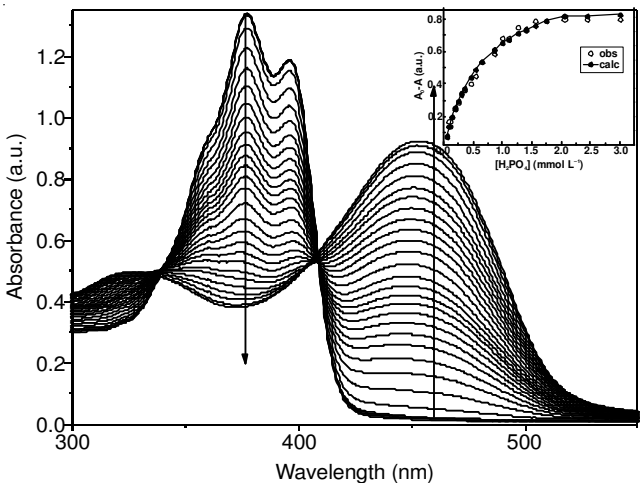


Fig. 4. UV-Visible titration spectra of receptor **2** with $H_2PO_4^-$ in DMSO (298 K). [**2**] = 2×10^{-5} mol L^{-1}. The inset represents the change in absorbance of 2 at 375 nm with varying molar equivalents of anions

Fig. 4 shows the significant UV-visible spectral changes of sensor **2** on addition of $H_2PO_4^-$. As we gradually added the $H_2PO_4^-$ into the solution of the receptor **2**, the absorbance bands centered at 375 nm and 391 nm diminished little by little, accompanied with a new band generated at 452 nm, suggesting the formation of the complex between receptor **2** and $H_2PO_4^-$ ion. Meanwhile, two clear isosbestic points were observed at 348 nm and 402 nm. In the same time, we examined the complexity with $H_2PO_4^-$ of receptors **1** and **3**. The association constants and correlation coefficient can be obtained by the nonlinear least-squares method according to the curve fitting equation[14]. The association constants (Ks) and correlation coefficients (R) are listed in Table-1.

The data indicated that the binding ability of the three receptors with $H_2PO_4^-$ and CH_3COO^- followed the trend: receptor 2 > 1 > 3 (for $H_2PO_4^-$); receptor 1 > 2 > 3 (for CH_3COO^-); Receptors **1** and **2** contain two acylhydrozone NH groups and two phenolic OH groups, which can provide hydrogen donor sites. In comparison, receptor **3** contains no phenolic OH groups. So receptor **3** exhibited the weakest complexity for $H_2PO_4^-$ and CH_3COO^-. In addition, the selectivity of the different receptors for the same anion depends on the geometrical conformation of the receptors. Nitro-group has a smaller volume than azobenzene group, so **2** would have a smaller repulsive interaction than **1** and form a larger cavity to bind the anions; also, $H_2PO_4^-$ with four oxygens makes the strongest complex via multitopic hydrogen-bonding interactions with **2**, which thanks to the conformational complementarity between **2** and $H_2PO_4^-$. The possible binding model of the complex of receptor **2** with $H_2PO_4^-$ is presented in Fig. 5.

Contrary to $H_2PO_4^-$, a larger steric of azobenzene group didnot weaken the complexity between **1** and the planar triangular acetate, also, its stronger conjugation effect leads to that **1** exbits the stronger hydrogen bonding complexity with CH_3COO^- than **2**.

TABLE-1
ASSOCIATION CONSTANTS Ks (mol^{-1} L) AND CORRELATION COEFFICIENTS (R) OF RECEPTORS 1, 2 AND 3 WITH THE ANIONS IN DMSO AT 298 K

Anion	Receptor **1**(Ks/R)		Receptor **2** (Ks/R)		Receptor **3** (Ks/R)	
$H_2PO_4^-$	481410	0.9921	526420	0.9971	278023	0.9957
CH_3COO^-	559707	0.9930	471082	0.9967	122280	0.9941
F^-	–	–	–	–	–	–

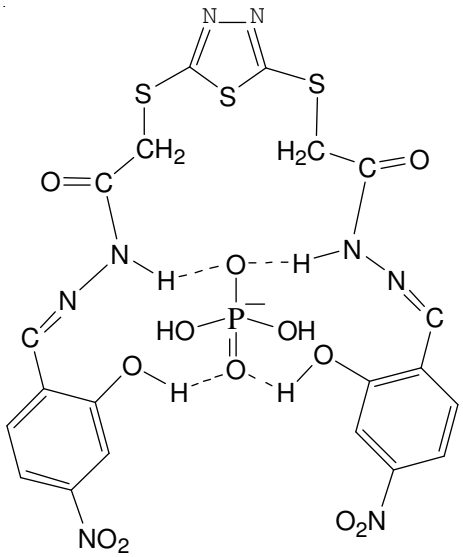


Fig. 5. Proposed recognition mechanism of receptor **2** with $H_2PO_4^-$

^{1}H NMR spectral study: The binding ability of **2** for anions (as tetrabutylammonium salts) was investigated by ^{1}H NMR spectroscopy. The downfield shift of acylhydrozone NH resonance (> 0.5 ppm) was detected upon complexation with $H_2PO_4^-$. Broadening of the phenolic OH resonance was also observed, indicating its participation in hydrogen-bonding interaction[15] (Fig. 6).

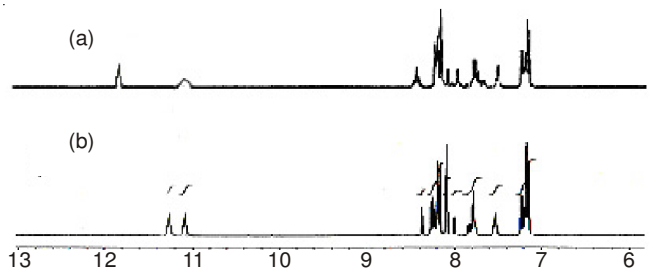


Fig. 6. ^{1}H NMR spectra of receptor **2** in DMSO-d_6; a) receptor **2** in the presence of $H_2PO_4^-$, b) receptor **2**

Conclusion

In summary, we have synthesized three receptors by simple method and studied their properties of anion recognition by UV-visible spectroscopy. The results showed that receptors **1**, **2** and **3** formed 1:1 complex with anions such as $H_2PO_4^-$, CH_3COO^- by multiple hydrogen bonding interactions and formed 1:2 complex with F^- ions. Concerning the anion recognition difference from the receptors containing auxochrome and chromophore, respectively. This study is helpful in designing a new colourimetric receptor for certain anion in polar solvent. Extensive efforts are being directed toward this end.

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