

基于 2,4-二硝基苯腙的比色法阴离子探针

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摘要: 本文设计合成了 4 个双臂 2,4-二硝基苯腙衍生物作为 F^- 和 $H_2PO_4^-$ 阴离子的比色法检测用探针主体, 并得到其中一个主体的单晶结构。4 种受体可以通过溶液颜色的变化选择性识别 F^- 和 $H_2PO_4^-$ 。UV-Vis 和 1H NMR 光谱研究表明受体与 F^- 和 $H_2PO_4^-$ 的作用都形成氢键, 与 F^- 作用还伴随一个脱氢过程。

关键词: 比色法; 探针; 阴离子

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Development of 2,4-Dinitrophenylhydrazones as New Generation of Colorimetric Anion Sensors

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Abstract: Four of two branched bis-2,4-dinitrophenylhydrazones were prepared as colorimetric anion receptors, which recognize F^- and $H_2PO_4^-$ selectively in solution of DMSO through hydrogen binding. Single crystal of one of the compounds was obtained (CCDC: 298951). The UV-Vis titration with F^- or $H_2PO_4^-$ revealed that new intense absorption bands for all of receptors accompanied by dramatic color changes with the association constants in the range of $10^4 \sim 10^5 L \cdot mol^{-1}$. The UV-Vis and 1H NMR investigation indicated that the hydrogen bonds were formed between F^- or $H_2PO_4^-$ and receptors, and there was also a deprotonation of binding fragment during the hydrogen bond formation in the case of F^- .

Key words: colorimetric; sensor; anion

0 Introduction

The importance of anions in nature, as agricultural fertilizers and industrial raw materials and the corresponding environmental concerns necessitate the development of highly sensitive anion sensors^[1,2]. So far, the focus has been mainly on the supramolecular chemistry of a receptor^[3]. This approach, however, suffers from shortcomings such as the high cost of synthesis and the loss of the real-time response^[4]. Therefore, for anion-sensing applications, in particular, the

challenge faced by chemists goes beyond the achievement of strong and highly selective anion binding and becomes one of detecting and amplifying an anion binding event to produce a measurable output^[5,6]. Of particular interest in this regard are colorimetric anion sensors, species that would allow the so-called naked-eye detection of anions without resort to any spectroscopic instrumentation. While the utility of these approaches are becoming increasingly appreciated in terms of both qualitative and quantitative analyses^[7,8], the number of colorimetric sensor available at

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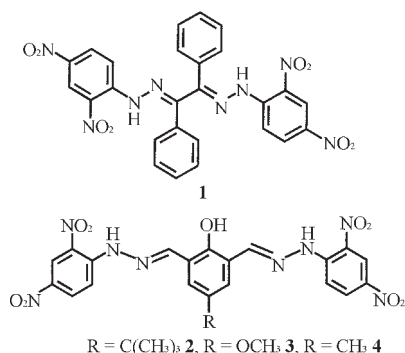
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present for anions remains quite limited.

Recently, Wu et al reported that nitrophenyl-hydrazone compounds could be used as colourimetric sensors for fluoride and their derivatives were very easy to be synthesized in high yield^[9]. Here we report the two branched receptors derived from 2,4-dinitrophenylhydrazine (Scheme 1) and benzil or substituted 1,3-benzaldidehyde. It is expected that chelating effects of the multiple hydrogen binding between anion and receptor made the host-guest complexes exhibiting higher stability than the single nitrophenylhydrazones.



Scheme 1 Chemical structure of the receptors

1 Experimental

1.1 Materials and Characterization

Benzil and 2,4-dinitrophenylhydrazine used were obtained from Sigma. Other reagents were purchased from commercial source. ¹H NMR spectra were recorded on a Bruker spectrometer using d₆-DMSO with TMS as an internal standard. UV-Vis absorption spectra were recorded on a Perkin Elmer Lambda 35 spectrometer. The elemental analyses were carried on Perkin-Elmer 240C.

1.2 Preparation of 2,4-dinitrophenylhydrazone derivatives 1~4

Preparation of **1** was according to literature^[10]. The substituted 1,3-benzaldidehydes were synthesized, following reference^[11]. Compounds **2~4** were obtained by simply mixing the corresponding carbonyl compound with 2,4-dinitrophenylhydrazine (molar ratio=1:2) in phosphoric acid/ethanol solution. Anal. calcd for compound **2** C₂₄H₂₂N₈O₉ (%):C, 50.89; H, 3.91; N, 19.78. Found(%): C, 50.86; H, 3.93; N, 19.72. ¹H NMR (d₆-DMSO) δ=7.94 (s, 1H), 8.08 (d, 2H), 8.65

(d, 2H), 9.08 (s, 1H), 9.20 (s, 2H), 10.68 (d, 1H), 11.82 (s, 2H). Anal.calcd for compound **3** C₂₁H₁₆N₈O₁₀·C₂H₅OH (%): C, 47.10; H, 3.78; N, 19.11. Found (%): C, 47.16; H 3.30; N 18.53. ¹H NMR (d₆-DMSO) δ=7.52 (s, 1H), 8.09 (d, 2H), 8.48 (d, 2H), 8.90 (s, 1H), 9.02 (s, 2H), 10.12 (s, 1H), 11.80 (s, 2H). Anal.calcd for compound **4** C₂₁H₁₆N₈O₉(%):C, 48.10; H, 3.08; N, 21.37. Found(%): C, 48.22; H, 3.18; N, 21.14. ¹H NMR (d₆-DMSO) δ=7.71 (s, 1H), 8.02 (d, 2H), 8.50 (d, 2H), 8.82 (s, 1H), 9.01 (s, 2H), 10.48 (s, 1H), 11.80 (s, 2H).

1.3 Crystallography

Crystals of **1** suitable for X-ray structure analyses were obtained by slow evaporating a nitrile solution in air. Crystal data for **1**, C₂₆H₁₈N₈O₈, *M_r*=570.48, Orthorhombic, space group, *Pnam*, *a*=1.968 5(5) nm, *b*=0.671 51(1) nm, *c*=1.978 1(5) nm, *V*=2.614 7(1) nm³. ρ_{calc}=1.449 g·cm⁻³, *T*=293(2) K, μ=0.090 9 mm⁻¹, *R*₁=0.077 6, *wR*₂=0.172 4 for 4 158 reflection observed reflection with *I*≤2σ(*I*). Intensities of the compound **1** were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo *K*α radiation (λ=0.071 073 nm) using SMART and SAINT program^[12]. The structure was solved by direct methods and refined on *F*² using full-matrix least-squares methods of SHELXTL version 5.1^[13]. Non-hydrogen

Table 1 Single crystal diffraction parameters for compound **1**

Chemical formula	C ₂₆ H ₁₈ N ₈ O ₈
Formula weight	570.48
Crystal system	Orthorhombic
Space group	<i>Pnam</i>
λ(Mo <i>K</i> α) / cm ⁻¹	0.710 73
<i>a</i> / nm	1.968 5(5)
<i>b</i> / nm	0.671 51(1)
<i>c</i> / nm	1.978 1(5)
<i>V</i> / nm ³	2.614 7(1)
<i>Z</i>	4
<i>T</i> / K	293(2)
<i>R</i> _{int}	0.090 9
<i>R</i> , <i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.077 6, 0.172 4
<i>R</i> , <i>wR</i> ₂ (all data)	0.280 5, 0.202 9
Reflections: Collected	11 830
Independent	4 158

atoms were refined anisotropically with hydrogen atoms localized in their calculated positions and re-fined using a riding model.

CCDC: 298951.

Table 2 Selected bond lengths (nm) and angles (°) for **1**

C(1)-N(3)	0.133 1(1)	N(5)-N(6)	0.136 8(9)
N(3)-N(4)	0.136 6(9)	N(6)-C(17)	0.137 5(1)
N(4)-C(7)	0.141 6(1)	C(7)-C(8)	0.154 4(1)
C(7)-C(12)	0.136 8(9)	N(5)-C(12)	0.127 4(1)
N(3)-C(1)-C(2)	123.1(1)	C(7)-N(4)-N(3)	116.1(8)
N(3)-C(1)-C(6)	120.9(1)	N(4)-C(7)-C(12)	116.6(1)
C(1)-N(3)-N(4)	123.2(8)	C(12)-N(5)-N(6)	115.4(8)

2 Results and discussion

2.1 Crystal structure of **1**

As shown in Fig.1, two 2,4-dinitrophenylhydrazine moieties were found positioned on opposite sides of the N(4)-C(7)-C(12)-N(5) fragment, giving rise to planar skeleton and lying on the special position. An intramolecular hydrogen bond is formed between the N(3)-H(3B) group and the adjacent nitro group. This is a common feature of o-nitrophenylhydrazine^[14]. The N(3)-C(1) bond distance of 0.133 1(1) nm indicates partial double-bond character. It should be noted that, within the dinitrophenyl ring attached to N(3), both the C(1)-C(2) bond 0.140 0(1) nm and the C(1)-C(6) bond 0.141 3(1) nm are significantly longer than the average distance of 0.137 5(3) nm for the other four C-C bonds. This is presumably due to the fact that the non-bonding orbital of nitrogen can overlap with the orbitals of the arene, thus contributing to the iminocyclohexadiene resonance structure. The N(3)-N(4) bond distance of 0.136 6(9) nm is shorter than that found in free 2,4-dinitrophenylhydrazine^[15], while the N(4)-C(7) bond distance of 0.130 3(1) nm is longer than the typical N=C bond distance. These values suggest a delocalized double bond in the hydrazone moiety, also involving C(7)-C(8) [0.154 4(1) nm]. The bond distance of C(7)-C(12) is 0.141 6(1) nm indicating a double bond character. Thus the whole molecule is a big electrons delocation system. A slight interaction with the molecule can induce significantly rearrangement of

electrons and the change of spectra. Such sensitive property can satisfy detecting anions by hydrogen bonding interaction. It can be speculated that the conjugate bonds characterization of **2~4** were similar as **1**.

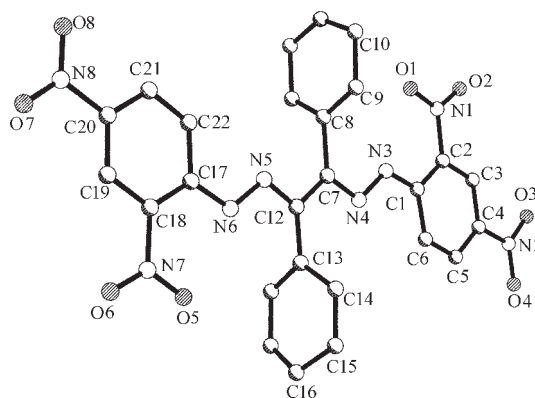


Fig.1 Molecular structure of **1** with the atomic-numbering scheme, hydrogen atoms and solvent molecules were omitted for clarity

2.2 Evaluation of **1~4** as colorimetric anion sensor

In DMSO solution, compounds **1~4** can form hydrogen bond with F^- and $H_2PO_4^-$ anion respectively, and the color of solution changed obviously (Fig.2). The formation was investigated by UV-vis titration of the compound in DMSO solution using standard tetrabutylammonium salts of $H_2PO_4^-$ and F^- . As shown in Fig.3, the addition of $H_2PO_4^-$ to **1** will result in decrease at 446 nm and increase at 599 nm. The bathochromic shift of optical spectra was due to the hydrogen bond formed by -NH fragment with anions. As the N(3)-N(4) bond having partial double bond character, the increased electron density on each -NH fragment would induce the double bond character of N(3)-N(4). Thus delocation electron of the N(3)-N(4) fragment and phenyl groups came into being a more stable structure and the optical spectra bathochromic shifted. The electrons rearranged in the whole molecule. An isosbestic point was seen clearly and a 1:1 stoichiometry complexation was found. For both of F^- and $H_2PO_4^-$ anion, when interacting with **1**, the bathochromic of (max was the same with new band at 599 nm, resulting in the same color change. Each of compounds **2~4** exhibited a strong absorption band at about 420 nm, which was decreased with the addition

of F^- or $H_2PO_4^-$. The color of the solution changed from yellow to violet as shown in Fig.2. As seen from Fig.4, in the solution of **2**, the addition of the fluoride anion would produce a new band at 533 nm, while the addition of $H_2PO_4^-$ showed a new band at 509 nm, both with obvious isosbestic points. That is, receptor **2**

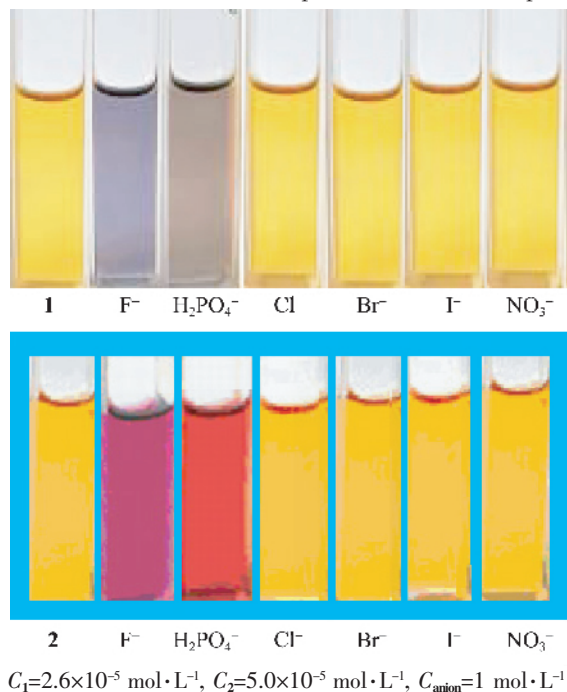


Fig.2 Color changes of **1** (upper) and **2** (lower) in DMSO solution

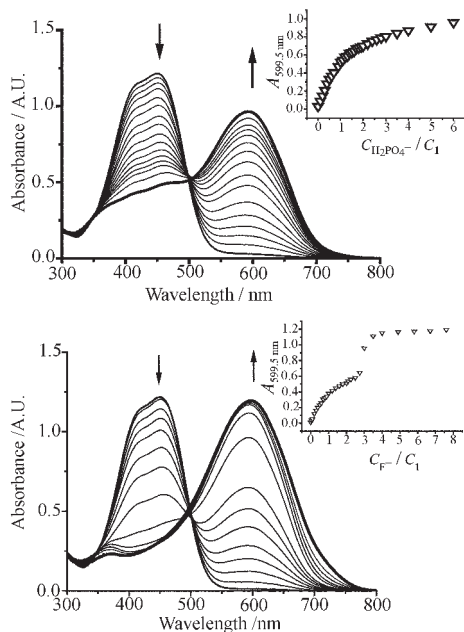


Fig.3 Family of spectra taken in the course of the titration of a $2.6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ DMSO solution of **1** with standard solution of $[Bu_4N]H_2PO_4$ (upper) and $[Bu_4N]F$ (lower)

can distinguish F^- from $H_2PO_4^-$, while **1** can not. Compound **3** and **4** showed very similar behaviors as **2**. Another notable point was that the bathochromic of λ_{\max} of **1** was higher than that of **2~4**. The difference of **2~4** from **1** was that there was no influence of phenol group in **1**. Though the opposite position of phenol in **2~4** was different, the bathochromic of λ_{\max} was almost the same. Detail data were given in table 3. The association constant K_1 was calculated by non-linear least square regression method^[16]. For **1**, the association constant for F^- was larger than that of $H_2PO_4^-$. However, the opposite was true for **2~4**.

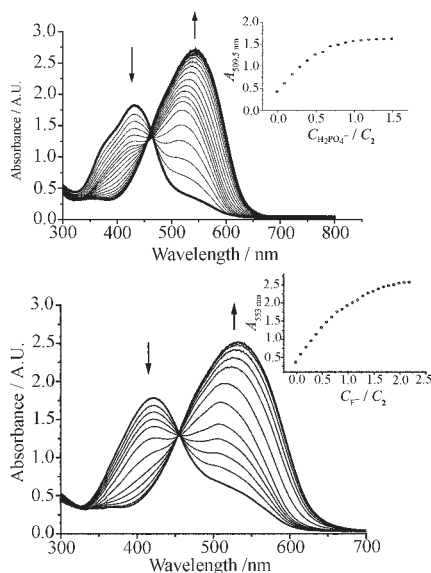


Fig.4 Family of spectra taken in the course of the titration of a $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ DMSO solution of **2** with standard solution of $[Bu_4N]H_2PO_4$ (upper) and $[Bu_4N]F$ (lower)

Table 3 Anion affinity constants (K_1) for **1~4** determined by UV-Vis spectrometric method

Compound	anion	$K_1 / (\text{L} \cdot \text{mol}^{-1})$	$\Delta\lambda_{\max} / \text{nm}$
1	F^-	$1.48(\pm 0.19) \times 10^5$	153
	$H_2PO_4^-$	$4.93(\pm 0.27) \times 10^4$	153
2	F^-	$6.30(\pm 0.20) \times 10^4$	113
	$H_2PO_4^-$	$4.68(\pm 0.12) \times 10^5$	89.5
3	F^-	$1.11(\pm 0.03) \times 10^5$	113.5
	$H_2PO_4^-$	$1.95(\pm 0.03) \times 10^5$	90
4	F^-	$1.09(\pm 0.02) \times 10^4$	111.5
	$H_2PO_4^-$	$2.37(\pm 0.05) \times 10^5$	89.5

1H NMR titration confirmed the host-guest interactions. The 1H NMR titration of **1** with F^- was

showed in Fig.5. After the addition of F^- or $H_2PO_4^-$, the $-NH$ signal of **1~4** shifted downfield and was broadened. The hydrogen signals of phenyl group all shifted to upfield. The upfield shift of hydrogen signals of phenyl group is because of the increased electronegative charge-transfer from the $-NH$ fragment to the dinitrophenyl group with a through-bond propagation. It is interesting that after the addition of 2 equiv. of F^- , a broad signal at about 16 ppm appeared. It indicates the formation of HF_2^- . Continuous addition of excess equiv. of F^- would result in a broad triplet signal at about 17 ppm. The facts suggest that the compound interacts with F^- firstly through hydrogen bonding below 1 equiv, forming 1:1 complexation $[LH-F]^-$ by hydrogen bonding. The second F^- induces the deprotonation of one $-NH$ fragment with formation of the $[HF_2]^-$ ion. Such deprotonation by F^- was also reported^[17,18]. The dimer $[HF_2]^-$ is particularly stable^[19]. However, $H_2PO_4^-$ does not induce the deprotonation of $-NH$ hydrogen. It interacted with the compound merely by hydrogen bonding. The interaction with phenol group (for **2~4**) was also observed that the signal of OH turned broad and downfield. The UV-Vis and 1H NMR spectrum do not change even when adding Cl^- , Br^- , I^- and NO_3^- in a high equivalence.

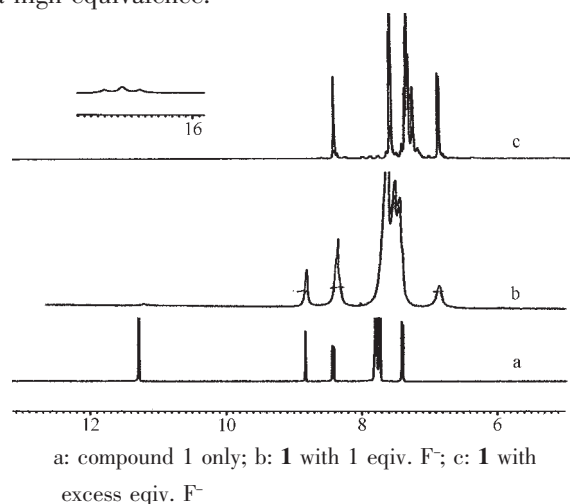


Fig.5 1H NMR titration of a d_6 -DMSO solution of **1** with standard d_6 -DMSO solution of $[Bu_4N]F$

3 Conclusions

A series of two branched dinitrophenylhydrazones

were used as colormetric anion sensors to detect F^- and $H_2PO_4^-$. The solution color changed obviously after the addition of F^- and $H_2PO_4^-$. A deprotonation course happened when interaction with F^- . The receptors with phenol at center showed the different color changes for F^- and $H_2PO_4^-$, thus usefulness in distinguishing these two anions. Such naked-eye observation method is fast, simple and convenient.

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