

A novel, simple, colorimetric receptor based on 2',4'-dinitrophenylhydrazone for acetate ion in organic medium

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Abstract A novel 1,3-di(2',4'-dinitrophenylhydrazone)-5-nitrobenzene receptor has been synthesized by simple steps with good yields. The anion recognition properties were studied by ultraviolet-visible (UV-Vis) spectroscopy. The results showed that the receptor had a higher affinity to F^- , CH_3COO^- and $H_2PO_4^-$, but no evident binding with Cl^- , Br^- , and I^- . Upon addition of the three former anions to the receptors in dimethyl sulphoxide (DMSO) at 298.2 ± 0.1 K, the solution exhibited an obvious color change from yellow to mauve that could be observed by the naked eye, thus the receptor could act as a fluoride ion sensor even in the presence of other halide ions. The UV-Vis data indicates that a 1:1 stoichiometry complex formed through hydrogen-bonding interactions between receptor and anions. The hydrogen bond between phenylhydrazone $-NH$ and acetate or fluoride anion was determined on the basis of 1H nuclear magnetic resonance (NMR) experiments.

Keywords Anion receptor · Colorimetric · Supramolecular chemistry · Phenylhydrazone · UV-Vis titration

Introduction

The development of chromogenic receptors for anion sensing is a relatively new area of research [1–5], since

anions play an important role in a wide range of environmental and chemical processes [6–9] and in biology [10–12]; for example, the switching activity of enzymes involves phosphorylation and dephosphorylation on a protein surface [13]. In recent years, colorimetric anion sensing is particularly useful because visual detection can give immediate qualitative information [14–16]. However, the design and synthesis of receptors capable of binding anionic guests is of considerable interest in the context of sensing and removal of environmental contaminants such as nitrate [17] or radioactive pertechnetate produced in the nuclear fuel cycle [18]. Synthetic receptors for anions are usually based on macrocyclic ammonium/guanidinium [19, 20], amides [21, 22], urea/thiourea [23, 24], functionalized calixarenes [25, 26], and particularly phenylhydrazone [27, 28], which is a kind of neutral receptor and has a simple synthetic method. Of particular interest in this regard is that phenylhydrazone exhibits such an obvious color change when anion is added that one can use naked-eye detection without resorting to spectroscopic instrumentation.

In the present work, we designed and synthesized 1,3-di(2',4'-dinitrophenylhydrazone)-5-nitrobenzene. The receptor has the merit which we referred to. We believe that the receptor has a potential application in the future.

Experimental

Reagents

Unless otherwise specified, all reagents for synthesis were obtained commercially and were used without further purification. In the titration experiments, all the anions were added in the form of tetra-*n*-butylammonium (TBA) salts, which were purchased from Sigma-Aldrich

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Chemical, stored in a vacuum desiccator containing self-indicating silica, and fully dried before use. DMSO was dried with CaH_2 and then distilled at reduced pressure.

General methods

Unless otherwise specified, all of the UV-Vis titration experiments were carried out at 298.2 ± 0.1 K. The ^1H NMR spectra were recorded on a Varian UNITY-plus 400-MHz spectrometer using tetramethylsilane (TMS) as an internal standard. UV-Vis spectra were recorded on a Shimadzu UV-2450 PC spectrophotometer.

The binding ability of receptor for CH_3CO_2^- , H_2PO_4^- , and halide anions (as tetrabutylammonium salts) was investigated by UV-Vis spectroscopy in DMSO solution using a constant host concentration (2.0×10^{-5} M) and increasing concentrations of anions. The change in absorbance at 517 nm for receptor was plotted against anion concentration and fitted by the equation as described by Connors [29].

^1H NMR titration of the receptor 1 (5.0×10^{-3} M in $\text{DMSO}-d_6$) with acetate anions (tetrabutylammonium salt) was carried out in $\text{DMSO}-d_6$ by addition of excess anion.

Synthesis of 1,3-di(2',4'-dinitrophenylhydrazone)-5-nitrobenzene

A solution of 5-nitrobenzene-1,3-dialdehyde (4 mmol) in ethanol (20 ml) was added dropwise to a solution of 2,4-dinitrophenylhydrazine (8 mmol) in ethanol (60 ml) with stirring at reflux. After stirring for 6 h, the solvent was removed by evaporation. Recrystallization (ethanol) yielded red crystals. δ_{H} (400 MHz; $\text{DMSO}-d_6$; Me_4Si): 11.73 (s, 2H, -NH), 8.85 (s, 2H, Ar-H), 8.79 (d, 2H, Ar-H), 8.40 (d, 2H, N=C-H), 8.12 (d, 2H, Ar-H), 7.97 (s, 2H, Ar-H), 7.64 (s, 1H, Ar-H). Anal. calcd. for $\text{C}_{20}\text{H}_{13}\text{N}_9\text{O}_{10}$: C 44.54%, H 2.43%, N 23.37%; found C 44.63%, H 2.17%, N 23.55%.

Results and discussion

UV-Vis titration

In dry DMSO solution, receptor 1 could interact with anions such as AcO^- , F^- and H_2PO_4^- through hydrogen bonds, and naked-eye color changes were observed from yellow to mauve upon addition of AcO^- (Fig. 1). The binding ability of anions was investigated by UV-Vis titration of the receptor in DMSO solution using standard tetrabutylammonium salts of AcO^- , F^- , and H_2PO_4^- . As shown in Fig. 2, addition of AcO^- resulted in decrease at 395 nm and increase at 517 nm. The significant bathochromic shift

($\Delta = 122$ nm) in the optical spectra was due to the hydrogen bond forming between the -NH fragment and anions added. The N(3)-N(4) bond (Scheme 1) has partial double-bond character [30] and the increased electron density on each -NH fragment would induce the double-bond character of N(3)-N(4) when anion combined with receptor. Thus, the delocalized electron of the N(3)-N(4) fragment and phenyl groups came into being a more stable structure. The electrons rearranged in the whole molecule and therefore bathochromic shift along with color change was seen. There was a well-defined isosbestic point at 441 nm, implying a 1:1 stoichiometry adduct, which was supported by Job plots (Fig. 3). In the case of H_2PO_4^- anion, when interacting with receptor 1, the bathochromic effect (maximum absorbance band at 517 nm) resulted in the same color change. The sensor 1 exhibited a strong absorption band at about 395 nm, which decreased with gradual addition of H_2PO_4^- (Fig. 4). Similarly, the addition of F^-

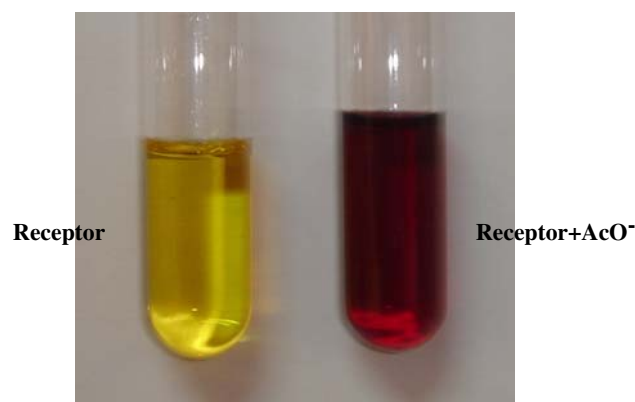


Fig. 1 Color changes from receptor to receptor + AcO^- in DMSO

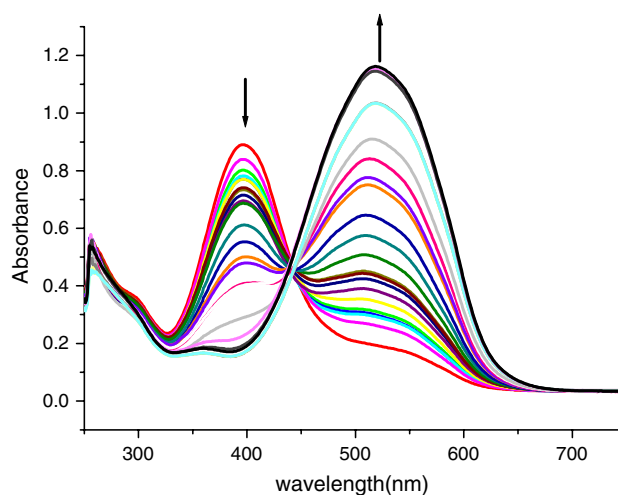
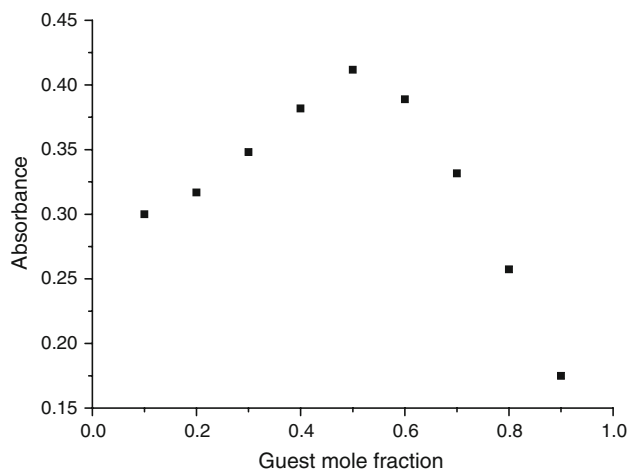
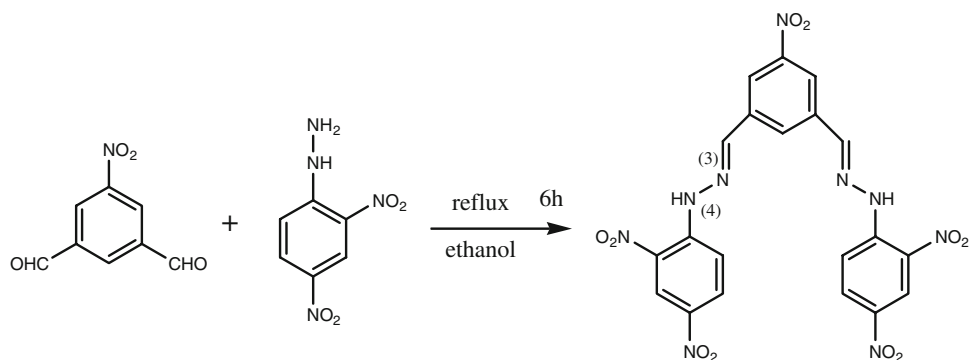
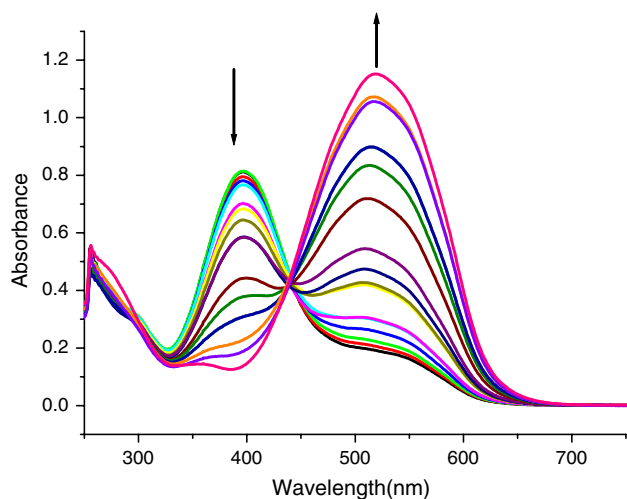


Fig. 2 UV-Vis spectra of receptor (2×10^{-5} M) in DMSO solution during the titration with tetrabutylammonium (TBA) acetate (0, 0.08, 0.2, 0.46, 0.52, 0.6, 0.68, 0.8, 1, 1.2, 1.4, 1.6, 1.8, 2, 2.8, 3.5, 4, 6, 8 equivalents) at 298.2 ± 0.1 K

Scheme 1 Synthesis procedure for the anion receptor**Fig. 3** Job plot of receptor ($[Host] + [Guest] = 4 \times 10^{-5} M$) with tetrabutylammonium fluoride at $298.2 \pm 0.1 K$ **Fig. 4** UV-Vis spectra of receptor ($2 \times 10^{-5} M$) in DMSO solution during the titration with tetrabutylammonium (TBA) dihydrogenphosphate (0, 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8, 2, 4, 6, 8, 12, 15, 25 equivalents) at $298.2 \pm 0.1 K$

led to similar color changes, but when Cl^- , Br^- , and I^- were titrated with the receptor, the color hardly changed even with excessive anion.

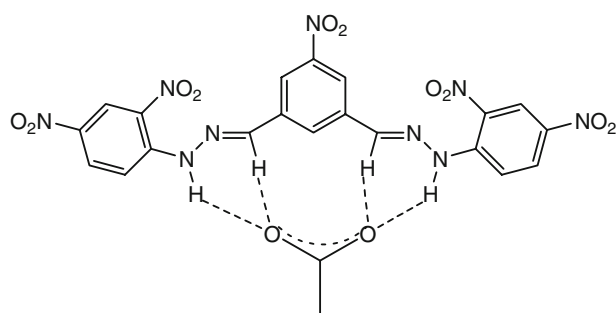
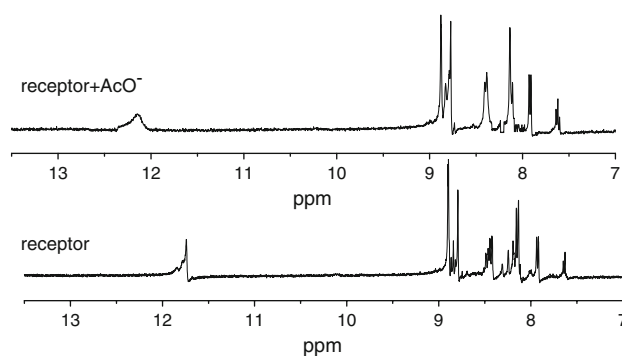
Table 1 Association constants K_{ass} of the receptors $1 (2 \times 10^{-5} M)$ with anions in DMSO at $298.2 \pm 0.1 K$

Anion ^a	AcO^-	F^-	$H_2PO_4^-$	Cl^-	Br^-	I^-
$K_{ass} (M^{-1})^b$	6.53×10^4	2.75×10^4	1.23×10^4	ND ^c	ND	ND

^a Anions were added as their tetrabutylammonium salts

^b All errors are $\pm 10\%$

^c Association constant could not be determined

**Scheme 2** Structure of the proposed binding mode of the receptor with AcO^- **Fig. 5** 1H NMR titration of a DMSO- d_6 solution ($5 \times 10^{-3} mol L^{-1}$) of receptor with excess of AcO^- at $298.2 \pm 0.1 K$

Determination of association constants

The association constant K_{ass} was calculated by nonlinear least-square regression method and is given in Table 1

[29]. For receptor, the association constant for AcO^- was larger than that for F^- and H_2PO_4^- . The reason for this was probably selective recognition of the acetate anion related to the structure of the acetate matching with the receptor (Scheme 2) and the basicity of the anion. Because the acetate anion is in a plane, the angle of $\text{O}-\text{C}-\text{O}$ was about 120° , the distance between two oxygen atoms was just matching with the host molecule 1, and furthermore the alkalinescence of acetate anion was stronger than that of the other anions. So, the association constant K_{ass} for acetate was maximal. Table 1 illustrates that the receptor can bind anions in the order $\text{AcO}^- > \text{F}^- > \text{H}_2\text{PO}_4^- > \text{Cl}^- \sim \text{Br}^- \sim \text{I}^-$.

^1H NMR titration

To further elucidate the nature of the intermolecular interactions between anions and the receptor 1, as an example, ^1H NMR spectral changes upon addition of AcO^- as its tetrabutylammonium salt to the $\text{DMSO}-d_6$ solution of 1 ($5 \times 10^{-3} \text{ mol L}^{-1}$) were investigated. As shown in Fig. 5, the peak at 11.73 ppm, which was assigned to $-\text{NH}$, exhibited a downfield shift to 12.26 ppm upon addition of excess AcO^- ion, indicating that NH participated in hydrogen-bonding interactions with AcO^- [31, 32]. In addition, the signals of binding sites did not disappear and the signals of the benzene ring protons had a neglectable chemical shift, which demonstrates that addition of AcO^- ion did not induce deprotonation of the sensor 1 and that a supramolecular chemistry system was formed. As described, the proposed anion recognition process in solution is shown in Scheme 2, which was supported by Corey-Pauling-Koltun (CPK) models.

Furthermore, proton NMR titration experiments of the receptor was carried out with AcO^- , but the discrepancy between stability constants calculated from proton NMR titration experiments and from UV-Vis was large. This is because the binding constants calculated by UV-Vis are for the whole affinity ability of multiple binding sites whereas that by NMR titration experiments (324.3 by AcO^-) is for a single binding site [33].

Conclusion

A 1,3-di(2',4'-dinitrophenylhydrazon)-5-nitrobenzene was used as a colorimetric anion receptor to detect AcO^- , F^- , and H_2PO_4^- . The solution color changed obviously after addition of AcO^- , F^- , and H_2PO_4^- . Thus it is useful in distinguishing these anions. In particular, the receptor can recognize acetate and fluoride anions with higher affinity than other halide anions. Such a naked-eye observation method is fast, simple, and convenient.

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