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A Colorimetric Receptor Based on Schiff-Base Bearing Azo-Phenolic Hydroxy Group

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A novel N-(2-hydroxy-5-chlorodibenzophenone)-N′-[2-hydroxy-5-azophenyl-benzaldehyde]-1,2-diaminobenzene receptor has been synthesized by simple steps with good yields. The anion recognition properties were studied by ultraviolet-visible spectroscopy. The results showed that the receptor had a higher affinity to F^-, AcO^-, and $H_2PO_4^-$, but no evident binding with Cl^-, Br^-, and I^-. Upon addition of the three former anions to the receptors in DMSO, the solution exhibited an obvious color change from colorless to yellow, which 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 stoichiometric complex is formed through hydrogen bonding interactions between receptor and anions.

Key words: Schiff-base, Synthesis, Supramolecular chemistry, Hydrogen bonding, UV-visible titration

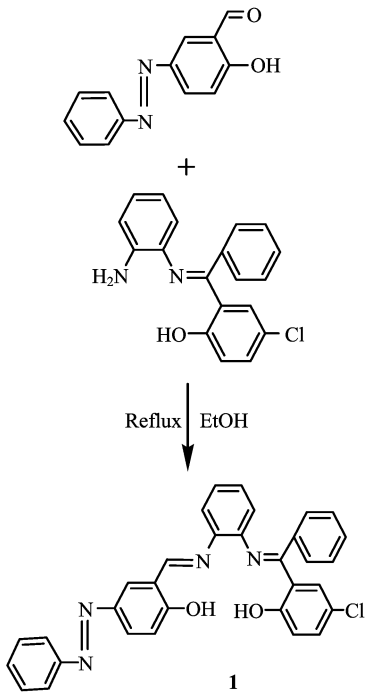
I. INTRODUCTION

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]. Particularly, colorimetric anion sensing is useful because visual detection can give immediate qualitative information [13−15]. It is also important to design and synthesize sensitive receptors for certain biologically important anions like fluoride, acetate, dihydrogen-phosphate, chloride, bromine and iodine [16]. The receptors containing urea [17], thiourea [18], amide [19], pyrrole [20], imidazole [21], and phenol [22] subunits have been well investigated and present excellent selectivity, which is a kind of neutral receptor. Of particular interest in this regard is that Azo-phenolic exhibits such an obvious color change when anion is added that one can use naked-eye detection without resorting to spectroscopic instrumentation. In this work, we designed and synthesized the receptor **1** (Scheme 1). The investigation of the receptor showed that it is an excellent sensor for F^-, AcO^-, and $H_2PO_4^-$.

II. EXPERIMENTS

A. Apparatus

^{1}H NMR spectra were obtained on a Varian UNITY Plus-400 MHz spectrometer. ESI-MS was performed with a MARINER apparatus. C, H, and N elemental analyses were made on an elementar vario EL. UV-Vis spectra were recorded on a TU-1810 spectrophotometer made by Beijing Puxi Tongyong apparatus company with quartz cuvette (path length=1 nm).



Scheme 1 Synthetic route for the receptor **1**.

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B. Chemicals

All reagents for synthesis obtained commercially were used without further purification. In the titration experiments, all the anions were added in the form of tetrabutylammonium (TBA) salts, which were purchased from Alfa Aesar Chemical, stored in a vacuum desiccator containing self-indicating silica and dried fully before using. DMSO was dried with CaH_2 and distilled in reduced pressure.

C. General method

All experiments were carried out at 298.2±0.1 K, unless otherwise mentioned. A 0.5 mmol/L solution of the compound **1** in DMSO was prepared and stored in dry atmosphere. This solution was used for all spectroscopic studies after appropriate dilution. Then, given amount of the solution of **1** was added to the quartz cuvette and the increased amount of tested anions (0.2 mmol/L in DMSO) was added to the above-mentioned solution, absorbance spectra were tested immediately.

^{1}H NMR titration experiments were carried out in the DMSO-d_6 solution (TMS as an internal standard). A 0.1 mmol/L solution of the compound **1** in DMSO-d_6 was prepared. Then, the increased amount of F^-(0.1 mol/L in DMSO-d_6) was added to the solution above-mentioned and ^{1}H NMR of the host-guest system was tested.

D. Synthesis of receptor 1

To a solution of N-(2-hydroxy-5-chlorodibenzophenone)-1,2-diaminobenzene [23] (1 mmol) in ethanol (20 mL) was added 2-hydroxy-5-azophenylbenzaldehyde (1 mmol) [24]. The mixture was stirred and heated to reflux for 2 h. Then the reaction mixture was cooled to room temperature. Precipitate was filtered and washed with ethanol and gained 0.42 g. Yield=77%. ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 14.47 (s, 1H, OH), 13.98 (s, 1H, OH), 9.13 (s, 1H, N=CH), 8.27 (d, J=13.5, 1H, ArH), 7.97 (m, 1H, ArH), 7.86 (m, 2H, ArH), 7.74 (s, 1H, ArH), 7.55 (m, 6H, ArH), 7.36 (s, 1H, ArH), 7.12 (m, 5H, ArH), 6.85 (m, 3H, ArH); ESI-MS (electrospray ionization-mass spectrometry): $C_{32}H_{23}ClN_4O_2$, m/z= 529.1 $[M]^-$; Anal. for ($C_{32}H_{23}ClN_4O_2$), Calc. C, 72.38; H, 4.37; N, 10.55; Found: C, 72.62; H, 4.85; N, 10.93.

III. RESULTS AND DISCUSSION

A. UV-Vis spectral responses of the receptor 1

In dry DMSO solution, receptor **1** could interact with anions such as F^-, AcO^-, and $H_2PO_4^-$ through hydrogen bonds, and naked-eye color changes were observed from colorless to yellow upon addition of F^-, AcO^-, and $H_2PO_4^-$ (Fig.1). The binding ability of

FIG. 1 Color changes observed in receptor **1** (0.05 mmol/L, DMSO) in the presence of 10 equivalence of anions (from left to right: **1** only, **1**+AcO^-, **1**+F^-, **1**+$H_2PO_4^-$, **1**+Cl^-, Br^-, and I^-). For clarity of the color change in this figure legend, the reader can refer to the web version of this article.

TABLE I Association constants K_{ass} between receptor **1** and anions in DMSO. The association constants of Cl^-, Br^-, and I^- could not be determined.

	K_{ass}/(mol/L)	R^2
AcO^-	1.01×10^5	0.9913
F^-	1.14×10^5	0.9959
$H_2PO_4^-$	5.71×10^3	0.9963

anions was investigated by UV-Vis titration of the receptor in DMSO solution using standard tetrabutylammonium salts of F^-, AcO^-, and $H_2PO_4^-$. As shown in Fig.2(a), compound **1** exhibited strong absorption at 350 nm, which was assigned to the charge transfer of the azo moiety. As the concentration of AcO^- was increased, the absorption intensity at 350 nm gradually decreased and a new absorption peak appeared at 469 nm. The increase in intensity of 469 nm and the obvious color changes could be attributed to fluoride-induced deprotonation of the hydroxy protons [25]. In addition, similar effects were observed in the UV-Vis spectra of the receptor **1** upon the addition of AcO^- and $H_2PO_4^-$ ions (Fig.2 (b) and (c)). But addition of excess equivalent weak basic ions such as Cl^-, Br^-, and I^- resulted in slight changes in the UV-Vis spectrum of **1** (see Fig.3).

B. Determination of association constants

To determine the stoichiometry of the host-guest complex, job plots were obtained according to the method reported by Connors [26]. As an example (F^-), Fig.4 demonstrates the formation of 1:1 stoichiometry host-guest complex. The association constants of host **1** for anionic species, which are shown in Table I, were determined by nonlinear fitting analyses of the titration curves according to Eq.(1), 1:1 host-guest complexation [27],

$$A = A_0 + \frac{A - A_0}{2c_H}\left\{c_H + c_G + \frac{1}{K_{ass}} - \left[\left(c_H + c_G + \frac{1}{K_{ass}}\right)^2 - 4c_H c_G\right]^{1/2}\right\} \quad (1)$$

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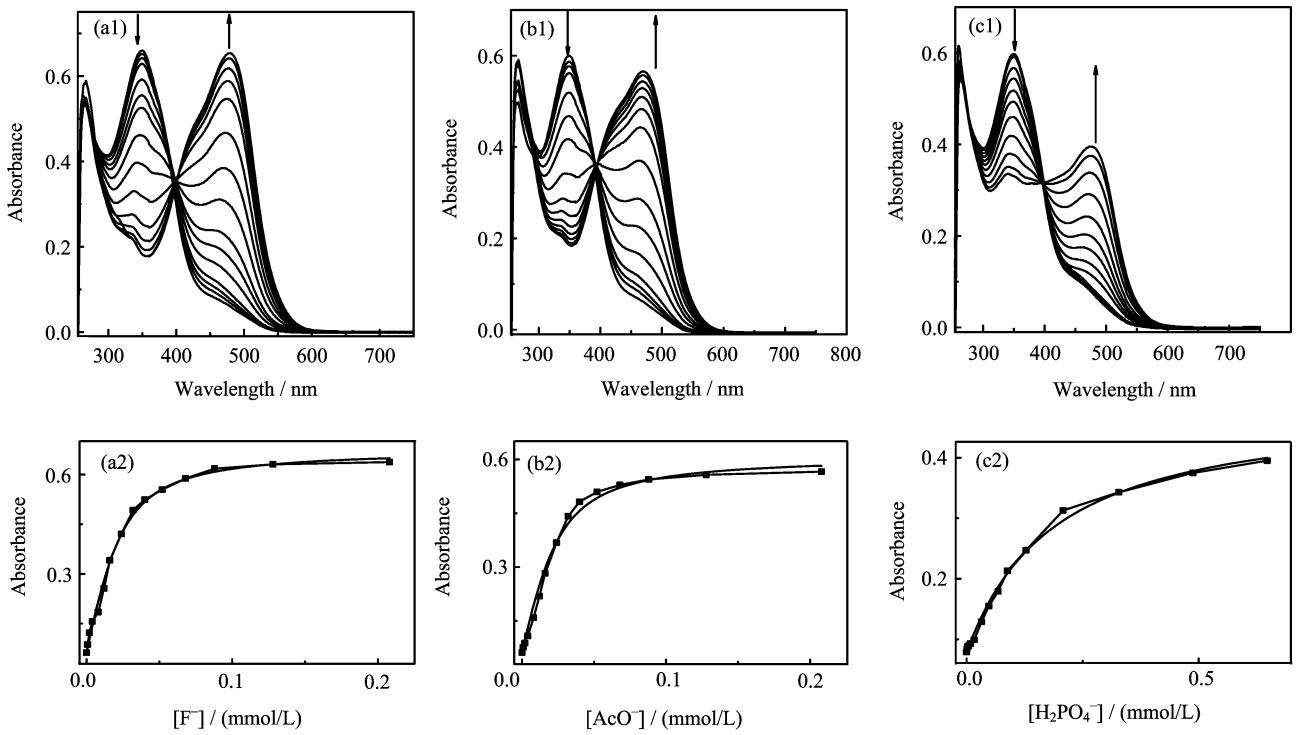

FIG. 2 UV-Vis spectra ((a1), (b1), and (c1)) and the plot of the UV-Vis absorbance ((a2), (b2), and (c2)) at 477 nm of **1** (0.02 mmol/L) in DMSO after the addition of F^- (a), AcO^- (b), and $H_2PO_4{}^-$ (c) (arrow direction: 0−10 equivalence).

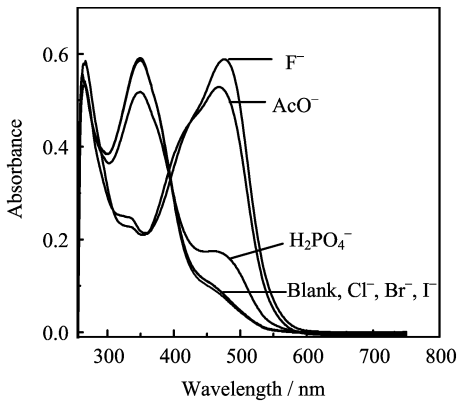

FIG. 3 UV-Vis spectra of the receptor **1** (0.02 mmol/L) in DMSO in the presence of 10 equivalence of AcO^- , F^-, $H_2PO_4{}^-$, Cl^-, Br^-, and I^-.

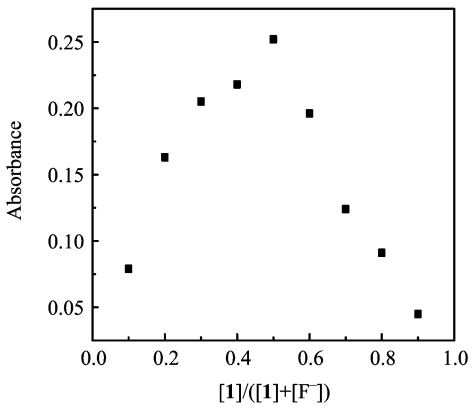

FIG. 4 The stoichiometry analysis of complex **1**+F^- by job plot analysis.

where c_G and c_H are the concentration of guest and host, respectively, A is the intensity of absorbance at certain concentration of host and guest. A_0 is the intensity of absorbance of host only, K_{ass} is the affinity constant of host-guest complexation. For receptor **1**, the association constant for F^- was larger than that for AcO^- and $H_2PO_4{}^-$, which may be due to probably selective recognition of the fouride anion related to the structure of the fluoride matching with the receptor **1** (Scheme 2) and the basicity of the anion. Because the acetate anion is spherical, the distance between two oxygen atoms was just matching with the host molecule receptor **1**, and furthermore the alkalescence of fluoride anion was stronger than that of the other anions. So, the association constant K_{ass} for fluoride was maximal. Table I illustrates that the receptor can bind anions in the order F^->AcO^->$H_2PO_4{}^-$≫Cl^-∼Br^-∼I^-.

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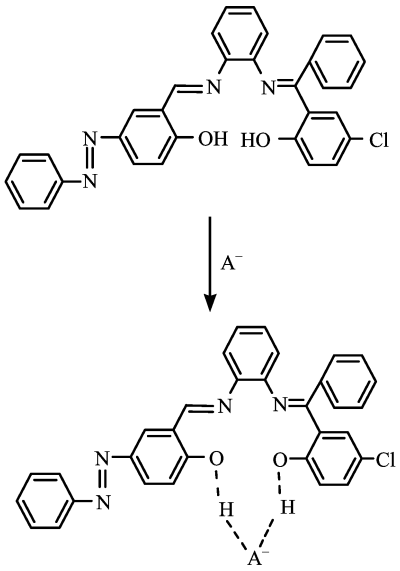

Scheme 2 The proposed binding mode of receptor **1** and A^-. A^- denotes anions such as AcO^-, F^-, and $H_2PO_4{}^-$.

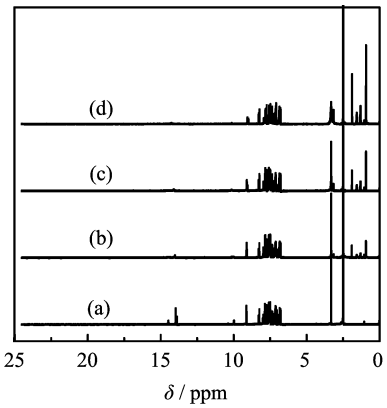

FIG. 5 ^{1}H NMR spectra of receptor **1** and in the presence of different equivalence F^- in DMSO-d_6. (a) 0, (b) 0.5, (c) 1, and (d) 2.

C. ^{1}H NMR titration

To further elucidate the nature of the intermolecular interactions between anions and the receptor **1**, as an example, ^{1}H NMR spectral changes upon addition of F^- as its tetrabutylammonium salt to the DMSO-d_6 solution of 1 (10 mmol/L) were investigated. As the concentration of fluoride salt was increased, the signal of O−H at 13.98 ppm shifted downfield (see Fig.5), a supramolecular complexe was formed by hydrogen-bonding interactions with F^- [28, 29]. Upon addition of 0.5 equivalence F^-, the signal of O−H at 14.47 ppm disappeared, which implied deprotonation of O−H. The signals of the phenylprotons exhibited slight upfield shifts, through-bond effects, which increase the electron density of the phenyl ring and promote an upfield shift [30]. In addition, the results of ^{1}H NMR titration also further corroborated the above supposition of the interactions between the host and fluoride ion during fluorescence titrations. According to the results from UV-Vis spectral titration, and ^{1}H NMR titration, the proposed host-guest binding mode in solution was depicted in Scheme 2.

IV. CONCLUSION

A N-(2-hydroxy-5-chlorodibenzophenone)-N′-[2-hydroxy-5-azophenylbenzalde-hyde]-1,2-diaminobenzene was used as a colorimetric anion receptor to detect F^-, AcO^-, and $H_2PO_4{}^-$. The solution color changed obviously after addition of F^-, AcO^-, and $H_2PO_4{}^-$. Such a naked-eye observation method is fast, simple, and convenient. The recognition for F^-, AcO^- and $H_2PO_4{}^-$ can be owed to the formation of multi-hydrogen bonds between the receptor **1** and anionic substrates. The UV-Vis data indicates that a 1:1 stoichiometry complex formed through hydrogen bonding interactions between receptor and anions.

V. ACKNOWLEDGMENTS

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