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Spectrochimica Acta Part A 70 (2008) 682–685
SPECTROCHIMICA ACTA PART A
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A simple and efficient colorimetric anion receptor for $H_2PO_4^-$

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Received 6 July 2007; received in revised form 24 August 2007; accepted 27 August 2007

Abstract

A novel and neutral anion sensor bearing a urea group as binding sites and 2,4-di nitrophenylhydrazine unit as a molecular architecture and a chromophore was synthesized and the visible color changes, the UV–vis and ^{1}H NMR spectral responses toward anions were assessed.

Keywords: Colorimetric; Receptor; Supramolecular chemistry

1. Introduction

The recognition and sensing of anionic analytes is currently an expanding area within the field of supramolecular chemistry [1–3]. Anions play a major function in the environment, industry and especially in biology where phosphate, carbonate and chloride are the most commonly found. In particular, organic or inorganic phosphates are key substrates or intermediates for many biochemical reactions, and are main components of biomolecules such as DNA and RNA. Accordingly, a significant amount of work has been devoted to obtain specific chemosensors [4–7] that are able to change one or several macroscopic properties, upon complexation with the target guests. In response to the molecular coordination events, the changes in color, which are used in the development of optical chemosensors, are the most applicable output signals among the changes in the fluorescence, absorbance, and cyclic voltammetry, etc. In this regard, the colorimetric anion sensors would allow 'naked-eye' detection of anions without resort to any spectroscopic instrumentation. In general, such sensor systems are mainly composed of two parts: one is the anion binding part (receptor), which is typically hydrogen-bonding donors such as pyrrole [8], urea/thiourea [9], amine [10] or phenol [11] moieties, and the other is a chromophore, which converts binding induced changes into an optical signal such as the appearance of color. These two parts are either directly linked [12] or intramolecularly associated [13]. In the past, a lot of studies [14–15] have showed that urea is a good H-bond donor and excellent receptor for tetrahedral anions and Y-shaped anions through the formation of multitopic H-bonds. Therefore, we attempted to integrate the urea group as bonding sites into 2,4-dinitrophenylhydrazine unit (a chromophore) and obtained a simple and efficient colorimetric $H_2PO_4^-$ sensor, which was synthesized by only one single-step procedure. Large numbers of receptors [16–18] for $H_2PO_4^-$ have been reported in the literature, but most of them [14,16,17] cannot act as the colorimetric receptors and require complicated and rigorous synthesis methods. In this paper, an easy-to-prepare receptor 1 is proved by the naked-eye experiment, the UV–vis titration and ^{1}H NMR titration methods to be a highly sensitive to $H_2PO_4^-$ anion.

2. Experimental

2.1. General procedures and materials

All reagents for synthesis were obtained commercially except CH_3CN, which was dried with P_2O_5 (0.5–1:100, v/v) stirring at room temperature overnight and then distilled, and were used without further purification. ^{1}H NMR spectra were obtained on a Varian UNITY Plus-400 MHz Spectrometer. ESI-MS was performed with a MARINER apparatus. C, H, N elemental analyses were made on a elementar vario EL. UV–vis spectra were recorded on a Shimadzu UV2450 Spectrophotometer with a quartz cuvette (path length = 1 cm) at 298.2 ± 0.1 K. In the UV–vis titration experiment, all the anions were added in

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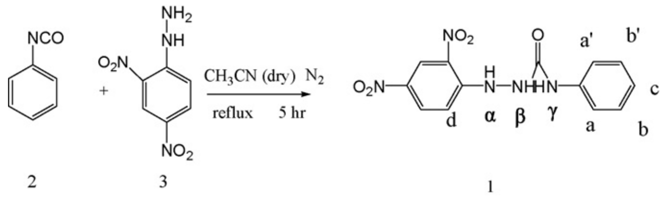
doi:10.1016/j.saa.2007.08.018



Scheme 1. General synthetic routes to the target compound 1.

the form of tetra-*n*-butylammonium (TBA) salts, which were purchased from Sigma–Aldrich Chemical, stored in a vacuum desiccator containing self-indicating silica and dried fully before using. DMSO was dried with CaH_2 and then distilled in reduced pressure.

2.2. Synthesis of β-N-(2,4-dinitroanilin-N-yl)-phenylurea (*1*)

The synthesis of the receptor 1 was summarized in Scheme 1. 2,4-Dinitrophenyl-hydrazine (0.198 g, 1 mmol) was dissolved in dry 30 ml CH_3CN. To this solution was added phenylisocyanate (0.1119 g, 1 mmol) dropwise slowly and stirred under inert atmosphere refluxing for 8 h. Then the reaction mixture was cooled to room temperature. Precipitate formed was filtered and washed with CH_3CN and obtained 0.24 g. Yield = 75%. ^{1}H NMR (DMSO-d_6) δH 10.127 (s, 1H), 8.975 (s, 1H), 8.885 (d, 1H, $J = 2.4$), 8.741 (s, 1H), 8.389 (m, 1H, $J = 12.4$), 7.47 (d, 2H, $J = 8$), 7.416 (d, 1H, $J = 10.4$), 7.28 (t, 2H, $J = 14$), 7.003 (t, 1H). ESI-mass: *m/z* (negative ion mode) 316.10 ($M - H^+$). Elemental analysis calcd. for $C_{13}H_{11}N_5O_5$ ($M = 317.08$): C, 49.22; H, 3.49; N, 22.07, found: C, 49.01; H, 3.62; N, 21.82.

3. Results and discussion

The recognition properties of the host molecular 1 toward different anions were studied by the several methods such as the naked-eye experiment, the UV–vis titration and ^{1}H NMR titration. Firstly, in the naked-eye experiments, the receptor 1 (4×10^{-5} M in DMSO) gave birth to dramatic color changes from light yellow to light purple in the presence of 5 equiv. of $H_2PO_4^-$, F^- and CH_3COO^- (see Fig. 1). However, addition of a large excess of Cl^-, Br^- and I^- could not result in any color changes of the receptor 1 at all. Furthermore, the color changes of the host molecular 1 would disappear upon addition of a small quantity of water. It has been very clear [21] that the protic solvent such as H_2O would compete with the anionic guests for the bonding sites of hosts and therefore, could disturb hydrogen bonding interactions between hosts and guests. So the results observed indicated that visible color changes were most probably due to hydrogen bond interactions between the NH groups and anions tested.

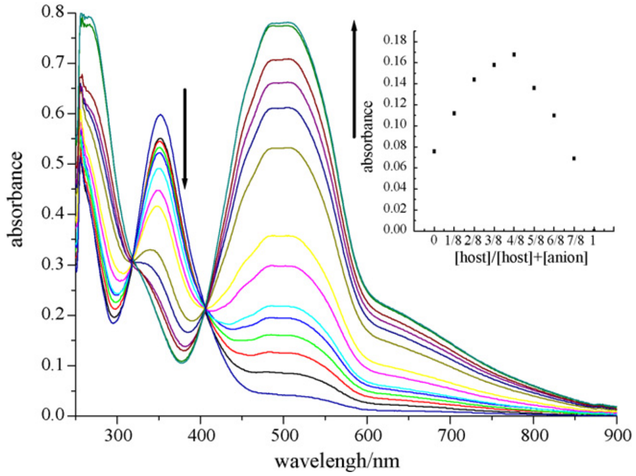


Fig. 2. UV–vis titration curves of 1 (4×10^{-5} M) in DMSO upon addition of different concentrations of $H_2PO_4^-$ and inset: Job's plot of 1 vs. $H_2PO_4^-$.

Secondly, the binding ability of the receptor 1 with a variety of anions in dry DMSO was investigated by UV–vis spectroscopy at room temperature. The UV–vis titrations were carried out in DMSO at a concentration level of 4×10^{-5} M upon addition of $H_2PO_4^-$ as tetrabutylammonium and the spectra were shown in Fig. 2. The receptor 1 exhibited two main bands centered at 264 and 351 nm and the peak at 264 nm increased gradually and the peak at 351 nm decreased slowly upon additions of $H_2PO_4^-$ anion. And simultaneously, a new broad peak centered at 500 nm, which corroborated well with the color changes observed in the naked-eye experiment, was observed and increased with the increase of concentration of $H_2PO_4^-$ anion. The big bathochromic shift (from 351 to 500 nm) could be explained on the basis of internal charge-transfer between the anion-bond urea unit and the electron-deficient $-NO_2$ moiety. In addition, there were two well-defined isosbestic points at 319 and 407 nm, which indicated that two species were present at equilibrium: 1 and $1H_2PO_4^-$ adduct. And 1:1 stoichiometry of the complex was also confirmed by the Job's plot as shown in Fig. 2 (inset). On the basis of 1:1 stoichiometry, the binding constant (K_{ass}) was calculated to be 8658 M^{-1}, which was shown in Table 1, based on the UV–vis titration data. As for

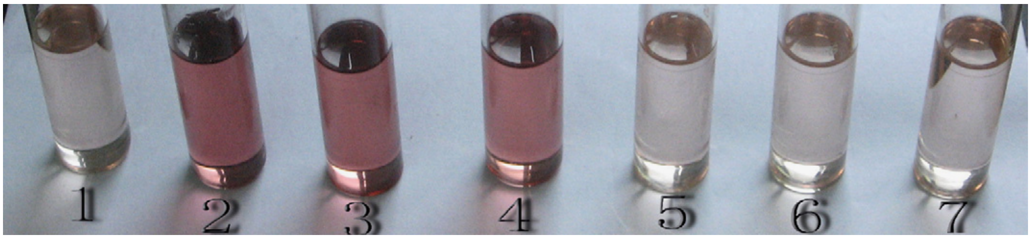


Fig. 1. The visible color changes of the receptor 1 in DMSO (4×10^{-5} M) upon additions of 5 equiv. of different anions (1: host only, 2: host + $H_2PO_4^-$, 3: host + F^-, 4: host + CH_3COO^-, 5: host + Cl^-, 6: host + Br^-, 7: host + I^-).

Table 1
Association constants for various anions toward receptor 1

Anion[a]	K_{ass} (M^{-1})
$H_2PO_4^-$	$(8.66 \pm 0.31) \times 10^3$
F^-	$(4.49 \pm 0.34) \times 10^3$
AcO^-	$(2.33 \pm 0.34) \times 10^3$
Cl^-	ND[b]
Br^-	ND
I^-	ND

[a] The anions were added as their tetrabutylammonium salts.
[b] The affinity constant cannot be determined by the spectra.

the other anions, the additions of F^- and CH_3COO^- induced similar changes (see Supplementary data) in the UV–vis spectrum with $H_2PO_4^-$, but additions of Cl^-, Br^- and I^- did not result in significant absorbance spectral changes (see S1 in the Supplementary data). Obviously shown in Table 1, the selectivity trends of binding affinities of anions for 1 were determined to be $H_2PO_4^- > F^- > AcO^- \sim Cl^- \sim Br^- \sim I^-$. However, a full understanding of the principles that govern anion recognition has not been achieved. It became clear early on that multiple hydrogen-bonding interactions are necessary in high-affinity anion binding sites. Charge and shape complementarity [19] between the host and the anionic guests are also extremely important. As expected from the basicity of anions, $H_2PO_4^-$, F^-, and AcO^- gave stronger complexes than other anions. However, $H_2PO_4^-$ anion with four oxygens could form the strongest 1·anion complex via multitopic hydrogen-bonding interactions with 1 [20] among the rest anions tested (see Scheme 2). That was why $H_2PO_4^-$ could be recognized selectively from the other anions.

Thirdly, further insights to the nature of 1-$H_2PO_4^-$ interactions were investigated by ^1H NMR titration experiment in DMSO-d_6. Fig. 3 displayed the spectra recorded when a 1×10^{-2} M DMSO-d_6 solution of 1 was titrated with $[Bu_4N]H_2PO_4^-$. Upon addition of $H_2PO_4^-$, the peaks at 10.127, 8.975 and 8.741 ppm, which were assigned to the N–H protons, shifted downfield and finally disappear, indicating the formation of a host-guest hydrogen-bonding complex between 1 and $H_2PO_4^-$. In addition, the slight down-field shifts of the aromatic proton signals (H_a) were also found, demonstrating that potential C–H···$H_2PO_4^-$ hydrogen bonding existed in the complex and cooperated with the N–H···$H_2PO_4^-$ hydrogen bonds. ^1H NMR spectra of 1 with F^-, which was similar with Fig. 3, was shown in Fig. 4. Obviously seen from Fig. 4, the proton signals (H_d and H_a) firstly shifted downfield before addition of the first equivalent of fluoride and then shifted upfield upon further equivalent of fluoride. On the other hand, the N–H signals shifted downfield and finally disappear. The results observed suggested that, in the first step, the fluoride established a hydrogen-bonding interaction with a urea subunit of the receptor. In this situation, an effective electrostatic effect was exerted on the nearby protons, including significant deshielding and a downfield shift, by the H-bond anion. Then, on addition of the second fluoride ion,

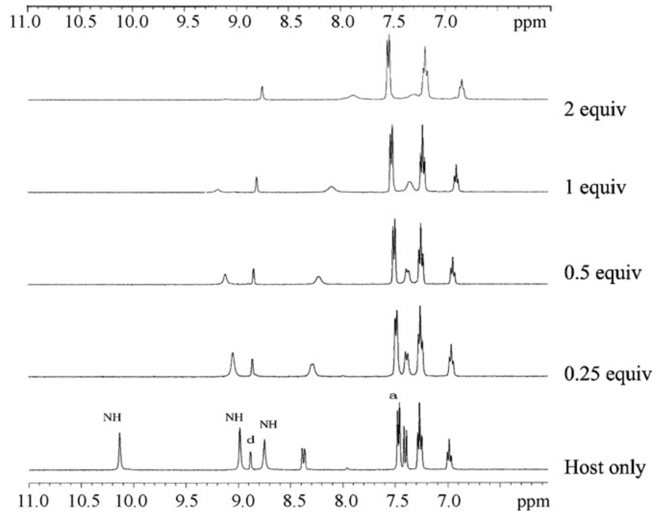


Fig. 3. Plots of ^1H NMR spectra of 1 (1×10^{-2} M) on addition of F^- in DMSO-d_6.

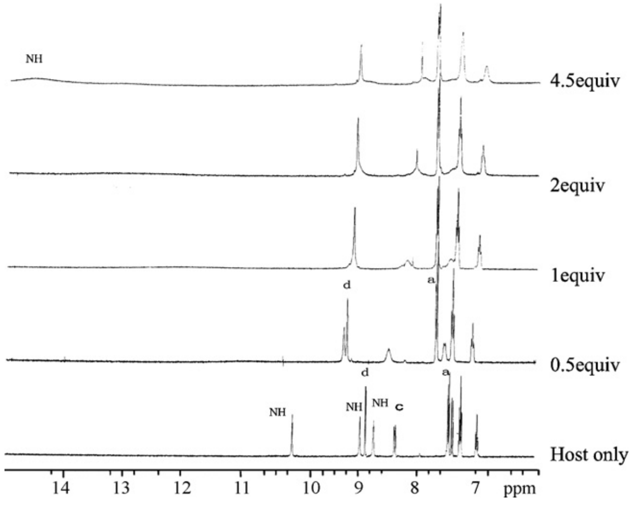
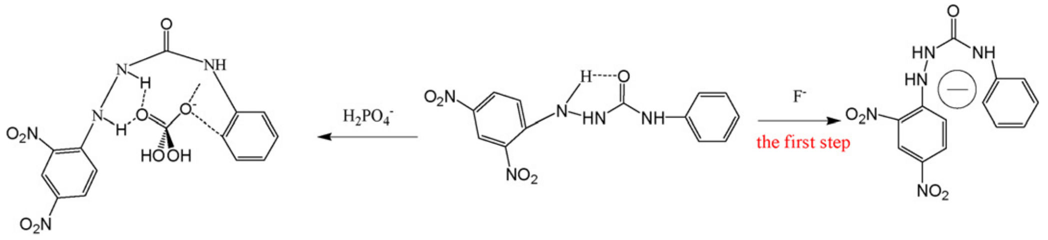


Fig. 4. Plots of ^1H NMR spectra of 1 (1×10^{-2} M) on addition of F^- in DMSO-d_6.



Scheme 2. The proposed host-guest binding mode in solution.

an HF molecular was released from the H-bond complex, with the formation of the deprotonated receptor [22]. As mentioned above, the proposed binding mode was shown in Scheme 2.

4. Conclusion

In summary, a highly sensitive colorimetric sensor bearing urea unit as bonding sites for $H_2PO_4^-$ has been successfully presented. A small quantity of $H_2PO_4^-$ anion (only 5 equiv.) can result in remarkable changes not only in the UV–vis and ^1H NMR spectra but also in the visible colors of the receptor 1 in DMSO solution. The recognition for $H_2PO_4^-$ can be owed to the formation of multi-hydrogen bonds between the receptor 1 and anionic substrates.

Acknowledgments

This project was supported by the National Natural Science Foundation of China (20371028, 20671052). The authors also thank the reviewers for giving advice on the paper.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2007.08.018.

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