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ORIGINAL PAPER

A Simple and Neutral Receptor Acting as a Sensitive and Switch-on Fluorescent Chemosensor for $H_2PO_4^-$

Weiwei Huang · Hongyan Su · Sikai Yao · Hai Lin · Zunsheng Cai · Huakuan Lin

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Abstracts A novel artificial anion chemosensor **1** based on 2, 2′-di (4-nitrophenylurea-β-*N*-yl) -1, 1′-binaphthyl is designed and synthesized for sensing anions including halide ions and oxoanions. The fluorescent emission of the binaphthyl of receptor **1**, forming the hydrogen bonding with anions as the sensing mechanism, is monitored in DMSO for detecting anions. In brief, while most of the anion chemosensors are switch-off fluorescent chemosensor, or non-fluorescent sensor, receptor **1** exhibits obviously the switch-on emission during the complexation with $H_2PO_4^-$.

Keywords Anion recognition · Hydrogen-bonding · Fluorescent · Switch-on

Introduction

Numerous efforts have been devoted to the development of chemosensor for anions such as dihydrogenphosphate, fluoride, acetate, and iodine due to their fundamental role in a wide range of chemical and biological process [1–4]. From the supramolecular chemistry concept, a chemosensor molecule is mostly composed by a component selected for a particular analyte and a signaling unit capable of translating the changes induced by analyte-binding into an output signal [5]. In fact, the output signal may include the changes in either color or fluorescence in the presence of a certain guest. In addition, the changes in electrochemical properties such as the oxidation potential of redox active groups have also been widely used [6–9]. However, it is noteworthy that fluorescence detection has been widely used in analytical chemistry, biochemistry, and cell biology because of its high sensibility and other principal advantage over other light-based methods [10]. In this article, we have reported a binaphthyl and urea-based receptor as efficient fluorescent sensor for selective recognition of dihydrogenphosphate [11].

The 1, 1 ′-binaphthyl unit is expected to act as spectroscopic signaling subunit which is able to transduce the coordination event into changes in fluorescence behavior. However, as far as we know, few anion receptors based on 1, 1′-binaphthyl have been reported before. This urges us to synthesis an anion receptor which composes 1, 1′-binaphthyl and two urea groups at 2- and 2′- positions, since it is the way that follows the approach of the covalent attachment of signaling subunits and binding site [12]. Furthermore, in order to increase the number of binding site and make the bonding stronger, we choose the 4-nitrophenylisocyanate unit as the component in our experiment. With this information, we have designed and synthesized receptor **1** containing four binding sites (see Scheme 1).

Experimental

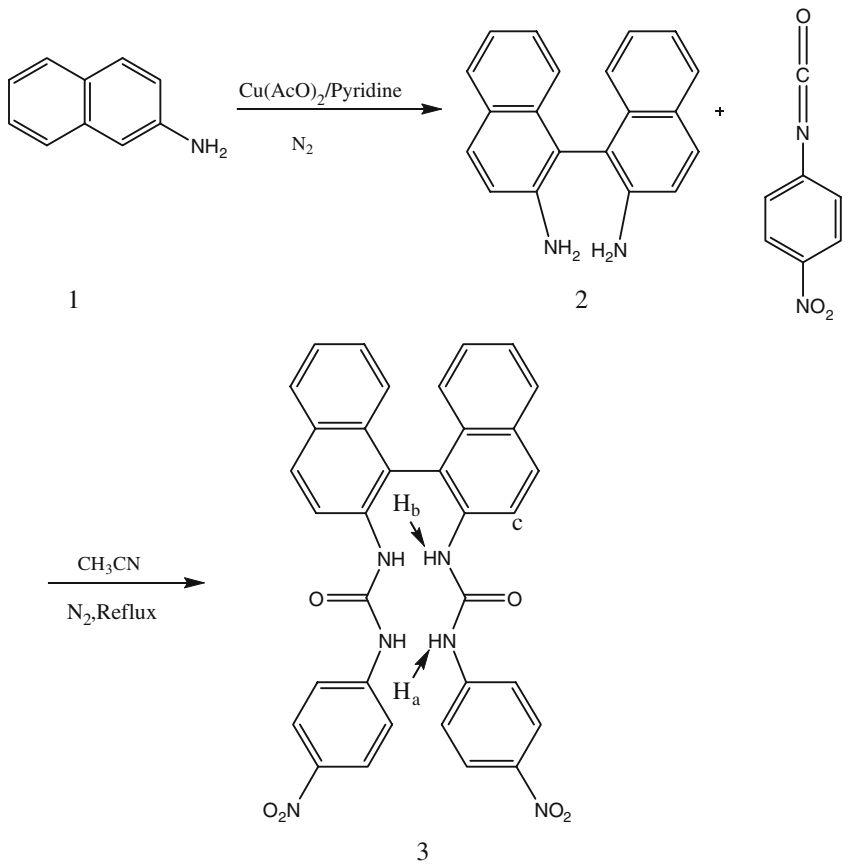
Materials

All reagents for synthesis obtained commercially were used without further purification. In the titration experi-

W. Huang · H. Su · S. Yao · Z. Cai · H. Lin (✉)
Department of Chemistry, Nankai University,
Tianjin 300071, People's Republic of China
e-mail: hklin@nankai.edu.cn

H. Lin
Key Laboratory of Functional Polymer Materials of Ministry of Education, Nankai University,
Tianjin 300071, People's Republic of China

Scheme 1 The synthetic procedures of receptor 1



ments, all the anions were added in the form of tetrabutylammonium (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.

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, N elemental analyses were made on an elementar vario EL. UV−vis spectra were recorded on a Shimadzu UV-2450 Spectrophotometer with a quartz cuvette (path length=1 cm) at 298.2±0.1 K and the width of the slits used is 5 nm. Fluorescent spectra were recorded on a FP-750 fluorescence spectrometer at 298.2± 0.1 K and the width of the slits used is 10 nm.

General Method

All experiments were carried out at 298.2±0.1 K, unless otherwise mentioned. UV−vis spectra were measured using an ultraviolet−visible spectrophotometer, UV-2450 (Shimadzu 2.1 Apparatus Corp., Kyoto, Japan). Fluorescence spectra were recorded on a FP-750 fluorescence spectrometer with the excitation and emission slits of 10 nm width at 298.2±0.1 K.

A 2.0×10^{-3} M solution of the receptor 1 in DMSO was prepared and stored in the dry atmosphere. Solutions of 1.0×10^{-2} and 1.0×10^{-1} M tetrabutylammonium salt of the respective anion were prepared in dried and distilled DMSO and were stored under a dry atmosphere.

^{1}H NMR titration experiments were carried out in the DMSO-d_6 solution (TMS as an internal standard). Certain amount of the receptor 1 solution in the DMSO-d_6 was prepared with a concentration of 0.01 M. ^{1}H NMR of the host-guest system was recorded by adding increasing amount of dihydrogenphosphate anions (1.0 M in DMSO-d_6) into the receptor 1 solution.

Synthesis of 2, 2′-Di (4-Nitrophenylurea-β-*N*-yl) -1, 1′-Binaphthyl

4-nitrophenylisocyanate (0.0952 g, 0.8 mmol) in dry CH_3CN was added dropwise to a refluxing solution of 2,

2′-diamino-1, 1′-binaphthyl (0.1136 g, 0.4 mmol) (2), which was prepared from 2-aminonaphthalene (3) according to the literature [13] (see Scheme 1). Then the reaction mixture was stirred and refluxed under atmosphere for 8 h. After cooling to the room temperature, The formed precipitate was filtered and washed with CH_3CN. (yield: 0.0979 g, 40%). ^{1}H NMR (DMSO-d_6) δ_H : 9.59 (s, 2 H, N-H), 8.39 (m, 2 H, N-H), 8.14 (t, 6 H, binaphthyl-H), 8.02 (dd, 2 H, Ph-H), 7.66 (s, 2 H, Ph-H), 7.43 (dd, 6 H, binaphthyl-H), 7.27 (t, 2 H, Ph-H), 6.81 (t, 2 H, Ph-H). ESI-mass: m/z (negative ion mode) 611.20 ($M\text{-}H^+$) Elemental analysis calcd for $C_{34}H_{24}N_6O_6$ (612.20): C, 66.67; H, 3.92 N, 13.73; found: C, 66.63; H, 4.13; N, 13.88.

Results and Discussions

Fluorescence Spectrum

Fluorescence experiment was performed to investigate properties of receptor **1** towards various anions in DMSO. With the aim of evaluating the stoichiometry for the binding interaction, 20 molar equivalent anions, i.e. $H_2PO_4^-$, AcO^-, F^-, Cl^-, Br^- and I^- as their tetrabutylammonium salts (TBA^+), were added to the solution of receptor **1** (2×10^{-5} M). Then, a strong emission band centered at 396 nm was observed when excited at λ= 358 nm (see Fig. 1).

In the literature published before, most of the anion chemosensors, especially the urea-and thiourea-based sensors, are switch-off fluorescent chemosensors, or non-fluorescent sensors. This may be interpreted by the photo-induced electron transfer (PET) quenching mechanism [14, 15] or the heavy atom effect of the sulfur atom. But considering the sensitivity of chemosensing, a switch-on, rather than a switch-off fluorescent sensor would be more preferred [16].

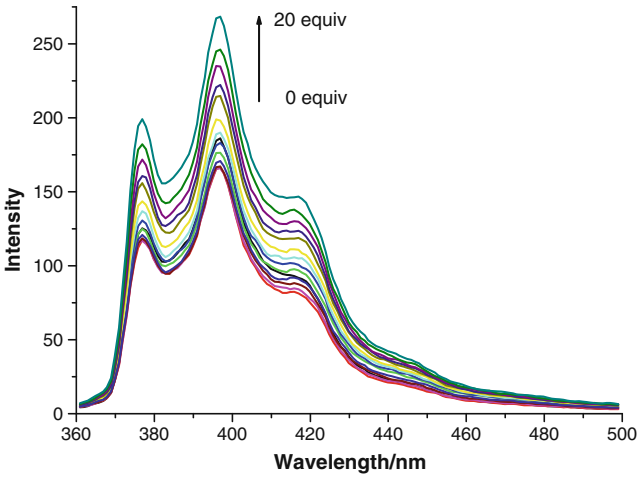


Fig. 1 The fluorescence spectral changes of receptor 1 (2×10^{-5} M) observed upon addition of 20 equiv. of $H_2PO_4^-$, respectively. λ_{ex}= 358 nm

It is evident from Fig. 1, the chemosensor of receptor **1** displays the switch-on reaction towards $H_2PO_4^-$, F^- and AcO^-, but not towards Cl^-, Br^- and I^-. This phenomenon may be due to binding-induced rigidity of the host molecule [17, 18]. Upon complexation with $H_2PO_4^-$ ion, the host molecule **1** was rigidified, which gave birth to a large increase in emission intensity because of inhibition vibrational and totational relaxation modes of nonradiative decay. Similarly, the addition of F^- and AcO^- resulted in similar fluorescent changes as $H_2PO_4^-$. On the other hand, receptor **1** was found to be insensitive to the addition of Cl^-, Br^- and I^-, even in abundance. The fitted affinity constants of receptor **1** towards anions are listed in Table 1 and the differences on the ability of switch-on the fluorescence spectrum in Fig. 2. From these results, it is clearly demonstrated that the cleft of the molecule is more preferred by $H_2PO_4^-$ and receptor **1** may be regarded as the anion-selective sensor for $H_2PO_4^-$.

UV–Vis Experiments

To gain an insight on the binding and sensing properties of receptor **1** towards various anions, we carried out UV–vis experiment in DMSO. As it is shown in Fig. 3, upon addition 20 equiv of $H_2PO_4^-$, a bathochromic shift can be observed passing through the isosbestic point at 358 nm (form 349 nm to 364 nm). The same behavior can also be observed in the case of the AcO^- and F^- . The changes of absorbance constituted evidence for hydrogen bonding interaction between receptor **1** and the given anions.

Determination of the Binding Constant and Stoichiometry

First, the total fluorescence signal intensity F can be expressed by the following Eq. 1 [19]**:**

$$F = \frac{[G]^n F_{max} + 10^{-B} F_{min}}{10^{-B} + [G]^n} \quad (1)$$

In the spectrofluorometry of this work, F_{min}, F_{max} and F are the emission intensities of the solution at wavelength 396 nm in the absence of guest, presence of the saturated guest, and after addition of a given amount of guest to certain concentration, respectively. [G] is the concentration of guest, n is the number of G bound per receptor 1. Once

Table 1 Affinity constants of receptor **1** with various anions in DMSO

Anions	$H_2PO_4^-$	F^-	AcO^-	Cl^-	Br^-	I^-
lgK_{ass} [a]	3.6978±0.11	3.0±0.04	2.58±0.12	ND[d]	ND	ND
lgK_{ass} [b]	3.6335±0.10	3.19±0.06	2.49±0.03	ND	ND	ND
R[c]	0.9758	0.9891	0.9759	ND	ND	ND

[a] the affinity constants determined by fluorescence in DMSO

[b] the affinity constants determined by UV–vis in DMSO

[c] Correlation coefficient (R) determined by non-linear fitting analyses

[d] *ND* cannot determined

the fluorescence experiments were done, the sigmoidal curve was obtained and the total binding constant $logK_{ass}$ was deduced as follows:

Firstly, the equation can be linearised in the form of Hill polt and the Hill coefficient (n) can be obtained from Eq. 2 [20–23] (see Fig. 4).

$$\log\frac{F-F_{\min}}{F_{\max}-F} = n\log[G] + B \tag{2}$$

Then, the binding constant of compound 1 to $H_2PO_4^-$, $logK_{ass}$ is determined by fitting Eq. 2 and is 3.6978. Also, the Hill coefficient (n) is obtained to be 1.0889, indicating that receptor **1** binds the $H_2PO_4^-$ anion guest with a ratio of 1:1, which is consistent with the Job's plot. Job's plot was obtained according to the method reported by K.A. Connors [24]. Job's plot of receptor **1** and F^- in DMSO shows the maximum at a molar fraction of 0.5, which indicates that the receptor **1** binds F^- guest at a 1:1 ratio. (see Fig. 3)

At same time, we also treated the data from UV–vis anion titration in another way as show below.

For a complex of 1:1 stoichiometry, the relation in Eq. 3 could be derived easily, where X is the absorption intensity, and C_H or C_G is the concentration of the host or the anion guest correspondingly, K_{ass} is the affinity constant of host-guest complexation [25].

$$X = X_0 + (X_{\lim} - X_0)\{C_H + C_G + 1/K_{ass} - [(C_H + C_G + 1/K_{ass})^2 - 4C_H C_G]^{1/2}\}/2C_H \tag{3}$$

The constants of receptor **1** binding to other anions were also calculated (see Table 1). The results drawn from the data of fluorescence spectrum are qualitatively matched with that from the UV–vis spectral titrations, and show that K_{ass} of receptor **1** toward dihydrogenphosphate ($H_2PO_4^-$) is larger than other anions, which maybe due to the following two reasons: the first, $H_2PO_4^-$ bears four oxygen atoms which favors the formation of the strongest receptor **1**-

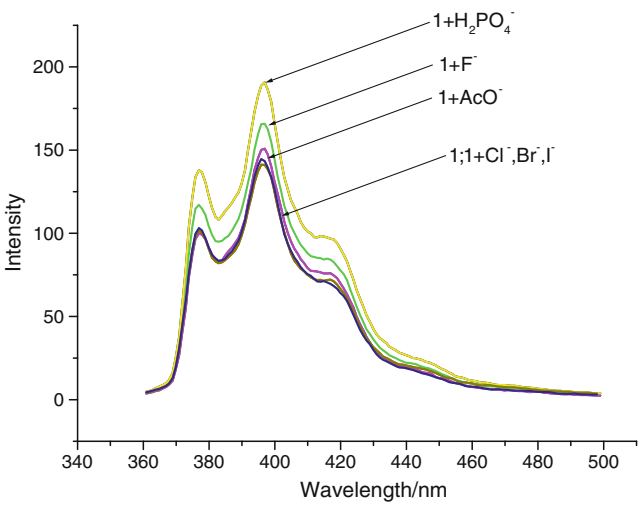


Fig. 2 The fluorescence titration of receptor 1 (2×10^{-5} M) with 20 equiv. $H_2PO_4^-$, F^- and AcO^-, respectively. λ_{ex}=358 nm

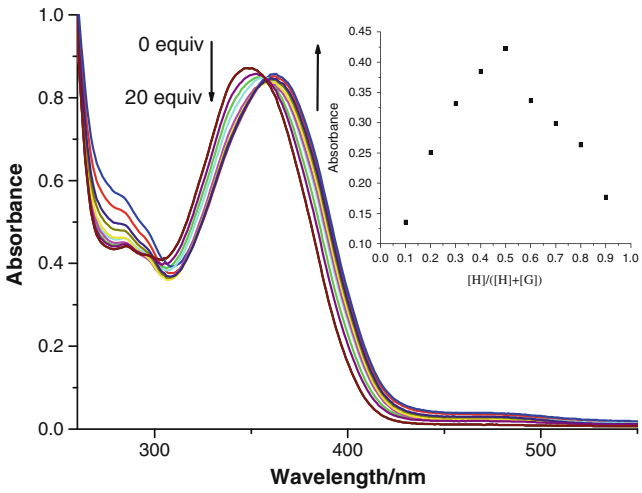


Fig. 3 Evolution of the UV–vis spectra of receptor 1 (2.0×10^{-5} M) during the titration with 20 equiv. $H_2PO_4^-$. Inset: Job's plot for complexation of receptor 1 with $H_2PO_4^-$ in DMSO, [host]+[guest]= 2.0×10^{-5} M

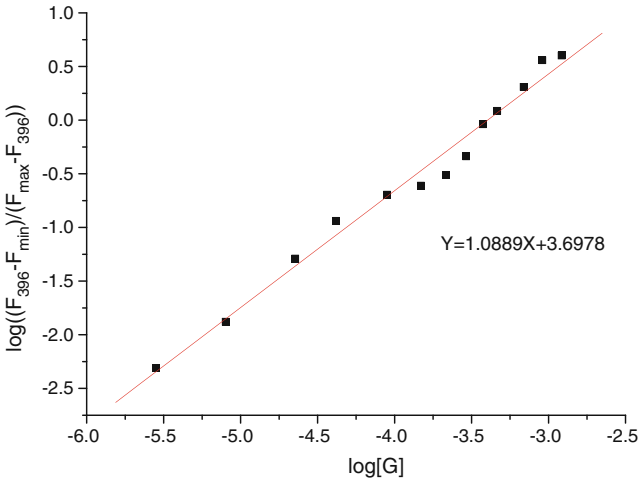


Fig. 4 Fluorescence intensity at 396 nm (F_{369}) of receptor 1 (2×10^{-5} M) versus increasing concentration of log[G]

anion complex via multiple hydrogen-bonding interactions and the second, the cleft of the complex may be more fitted for tetrahedral dihydrogenphosphate.

^{1}H NMR Titrations

To further investigate the binding properties of receptor **1** towards these given anions, detailed ^{1}H NMR titrations of **1** in DMSO-d_6 were carried out to observe the chemical shift signal changes in two urea and the aromatic protons upon the action of recognition of anions. The stack plot of the ^{1}H NMR spectra was obtained upon addition of $H_2PO_4^-$ as its TBA^+ salt to the DMSO-d_6 solution of receptor **1** (1×10^{-2} M) (see Fig. 5). Obviously, the proton signals at 9.59 ppm and 8.39 ppm that have been assigned to H_a and H_b (marked in Scheme 2) experienced significant downfield shifts (δ=0.418 ppm and δ=0.331 ppm), which have been

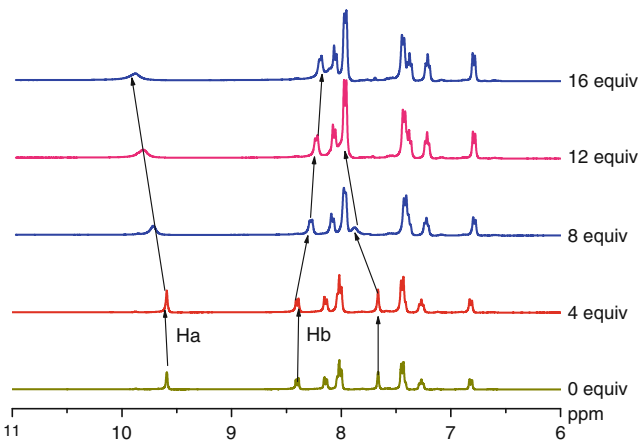
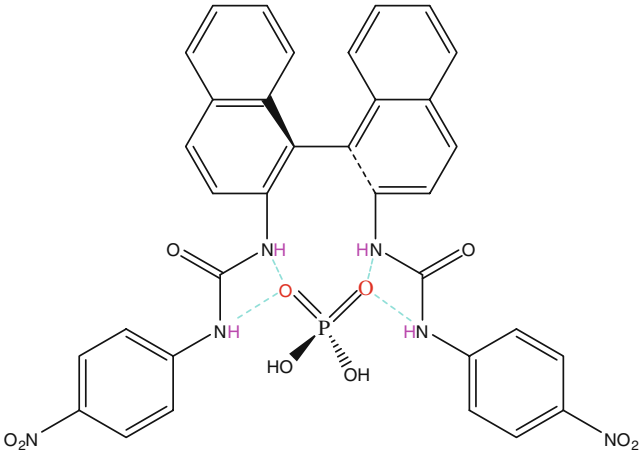


Fig. 5 ^{1}H NMR titration of receptor 1 (1.0×10^{-3} M) in DMSO-d_6 with $[Bu_4N]$ H_2PO_4



Scheme 2 The proposed mechanism of receptor 1 towards $H_2PO_4^-$

previously reported for those receptors based on diaryl urea and thiourea [26–28], indicating the formation of a host-guest hydrogen-bonding complex. So we can reasonably presume that the urea protons (H_a and H_b) function as anion-binding moieties and participate in the formation of hydrogen bonds with dihydrogenphosphate ions [29, 30]. The increase of electron density in the aromatic rings causes a shielding effect and should promote an upfield shift, which is expected to come through the formed hydrogen bond [31]. Accordingly, the proposed binding mode of receptor **1** with $H_2PO_4^-$ in solution can be demonstrated in Scheme 2.

Analytical Application

Experimental result is given to show the performance of receptor **1**: it has high selectivity for the $H_2PO_4^-$. The changes of fluorescence and UV differential spectra were observed obviously, upon addition of only 20 equiv of $H_2PO_4^-$ to the solution of **1** (2.0×10^{-5} M). However, no detectable spectral responses were observed when adding other anions. When the concentration of receptor **1** is 2×10^{-5} M in DMSO, the limit of [$H_2PO_4^-$] detection (LOD) is 2×10^{-5} M, so we hope receptor **1** may be applied in detection of biologically important anions such as the $H_2PO_4^-$ ion.

Conclusions

In conclusion, we synthesized an easily prepared anion chemosensor based on binaphthyl, which could recognize $H_2PO_4^-$ among the anions investigated. It is expected to be applied for detection of $H_2PO_4^-$ in analytical chemistry for its easy synthesis and highly selective sensing ability.

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