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Synthesis of novel colorimetric probe molecules and their application in anion recognition based on strong hydrogen bond

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ABSTRACT

A novel pair of ferrocene-containing azobenzene-based probe molecules, which behave as a selective probe for sensing fluoride and dihydrogen phosphate in colorimetric systems (even by naked eye), were designed. The probe 2 (*N*,*N*′-bisamideazophenyl-ferrocene) showed a high selectivity toward F^- and $H_2PO_4^-$ with a color change from yellow to salmon pink without any interference from other ions. Meanwhile, the probe 1 (4-amideferrocenylazobenzene) showed only high selectivity for F^- with a color change from yellow to salmon pink without any interference from other ions.

1. Introduction

The keen interest in the recognition and sensing of anions lies in their major concern with environmental chemistry and biological science [1–3]. In particular, fluoride (F^-) and dihydrogen phosphate ($H_2PO_4^-$) anions' sensing have attracted a growing attention in the past decades, due to their close relationship with the people's health and the environmental protection. For example, the dental fluorosis and skeletal fluorosis [4–10], reported in different countries around the world, have been believed to be associated with the presence of high concentration of F^- in drinking water. Recently, F^- was accused of being a main reason for osteosarcoma [11,12], and intelligence growing problems by injuring the brain, especially for the children. Moreover, $H_2PO_4^-$ is involved in the hydrolysis process of adenosine triphosphate, which is essential for organisms [13,14]. World Health Organization published Guidelines for Drinking-Water Quality in 2004 [15,16], in which the value of F^- in drinking water should be 1–5 mg/L, and the optimal concentration is 1.5 mg/L; meanwhile, the concentration of $H_2PO_4^-$ should not be more than 5 mg/L. During the past few decades, various chemosensors were developed for the recognition of F^- and $H_2PO_4^-$ ions', including F^- (or $H_2PO_4^-$)-selective electrodes [4–10,17–21], probes utilizing hydrogen-bonding interactions [22–29], receptors based on Lewis acid–base interactions [30–36] and so forth. Most of these chemosensors focused on high sensitivity with the lack of a good selectivity. Some of synthesized chemosensors had a low detection limit of about 1×10^{-5} M and some others showed lower sensing concentration. Miguel Vzquez and co-workers synthesized thiourea-containing receptors for the selective sensing of F^- up to 1×10^{-3} M [17–21]. Suning Wang and co-workers designed a series of sensors which had excellent selectivity and sensitivity (lower than 1×10^{-5} M), but the disadvantage is that the sensing process took place in non-polar solvents [17–21]. Jong Seung Kim and co-workers investigated a series of F^- receptors which possessed high sensitivity in high-polar solvents, but the major handicap is the interfered with other ions like acetate and $H_2PO_4^-$. However, few sensors can combined the selectivity and low detection limit in polar solvents, even in water.

Herein, we report a novel pair of ferrocene-containing azobenzene-based colorimetric probe molecules (Scheme 1) for the selective sensing of F^- and $H_2PO_4^-$ ions in polar solvents. The most interesting finding was that this pair of sensors allowed the naked-eye detection of F^- and $H_2PO_4^-$ ions around the guideline value reported by the World Health Organization for Drinking-Water Quality.

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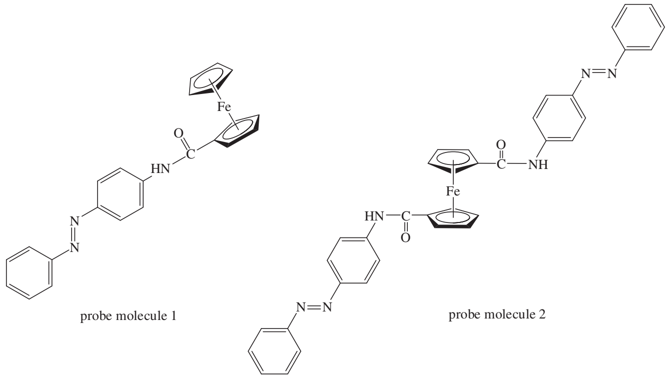


Scheme 1. Structures of probe molecule 1 and 2.

2. Experimental section

2.1. Materials

Dichloromethane (CH_2Cl_2, AR) and triethylamine (Et_3N, AR) were distilled over calcium hydride, while dimethyl sulfoxide (DMSO, AR) was dried under molecule sieves (4A), and all other chemicals were used as received. 4-Aminoazobenzene (98%) was supplied from TCI. Ferrocene carbonate acid was supplied by China National Pharmaceutical Group Chemical Co. Ltd.

2.2. Synthesis process

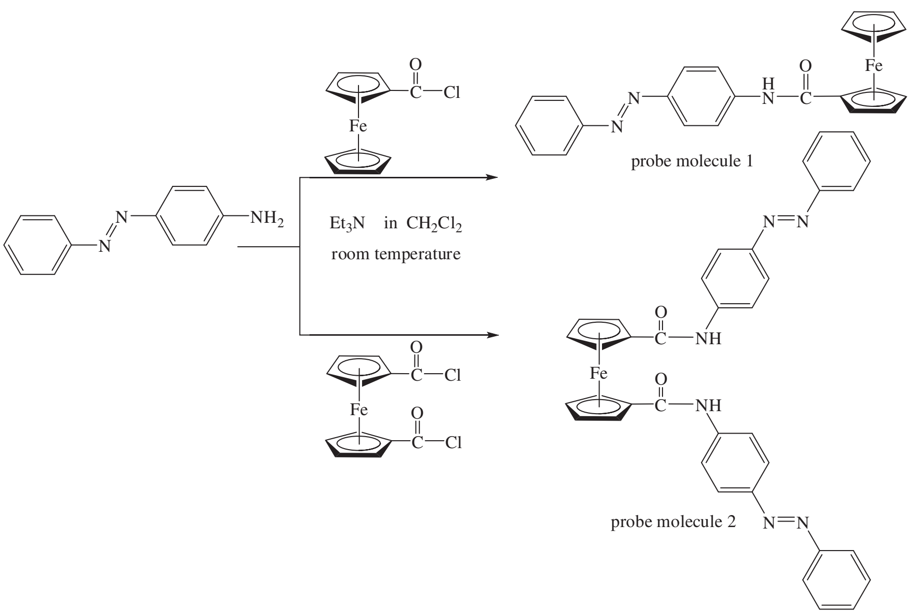
Chlorocarbonyl-ferrocene and 1,1′-dichloro-carbonylferrocene were synthesized as reference [37].

2.2.1. Synthesis of 4-amideazophenylferrocene (probe molecule 1)

As shown in Scheme 2, 0.789 g (4 mmol) 4-aminoazobenzene was dissolved in 20 mL CH_2Cl_2 in a flask and 0.4 mL triethylamine was added as catalyst. Afterward, 30 mL refluxed CH_2Cl_2, containing 1.950 g (7.8 mmol) chlorocarbonyl-ferrocene was added dropwise into the system. The reaction mixture was stirred at room temperature for 10 h and then filtered the mixture solution to remove the precipitated salt, meanwhile the filtrate was recrystallized to get the pure product chemosensor 1 as a yellow powder. Yield: 0.98 g (59.8%).

2.2.2. Synthesis of N,N′-bisamideazophenylferrocene (probe molecule 2)

As shown in Scheme 2, 3.548 g (18 mmol) 4-aminoazobenzene was dissolved in 30 mL CH_2Cl_2 in a flask and 0.8 mL triethylamine



Scheme 2. Synthetic procedure of probe molecule 1 and 2.

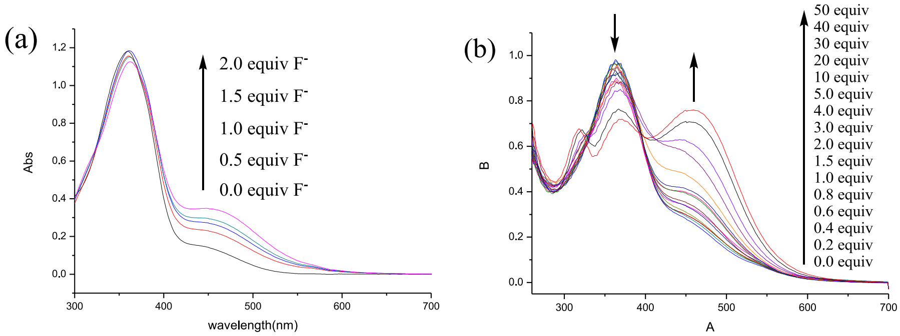


Fig. 1. UV–vis absorption spectral changes of probe molecule 1 (5×10^{-5} M in DMSO) (a) and probe molecule 2 (2.5×10^{-5} M in DMSO) (b) upon addition of F^-.

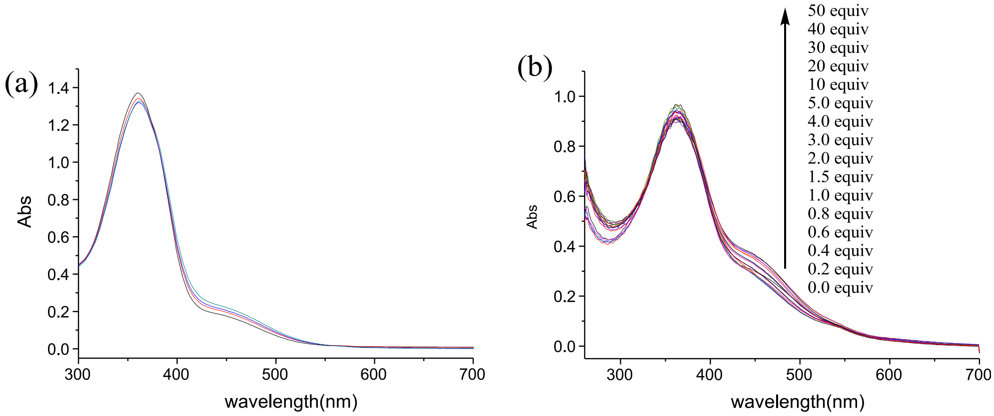


Fig. 2. UV–vis absorption spectral changes of probe molecule 1 (5×10^{-5} M in DMSO) (a) and probe molecule 2 (2.5×10^{-5} M in DMSO) (b) upon addition of $H_2PO_4^-$.

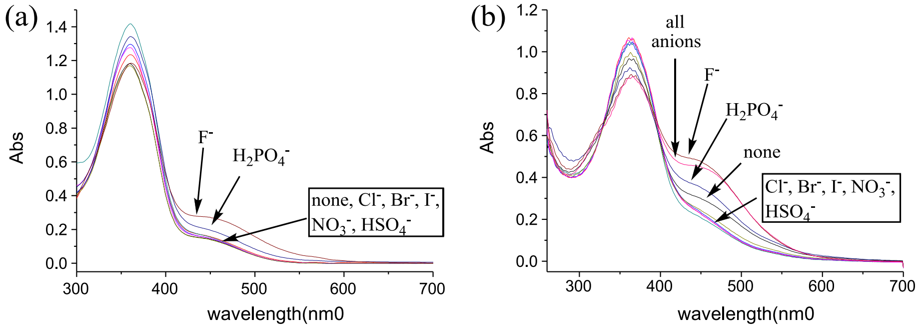


Fig. 3. UV–vis absorption spectra of probe molecule 1 (5×10^{-5} M in DMSO) (a) and probe molecule 2 (2.5×10^{-5} M in DMSO) (b) upon the addition of different anions (none, F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, NO_3^- or mixture).

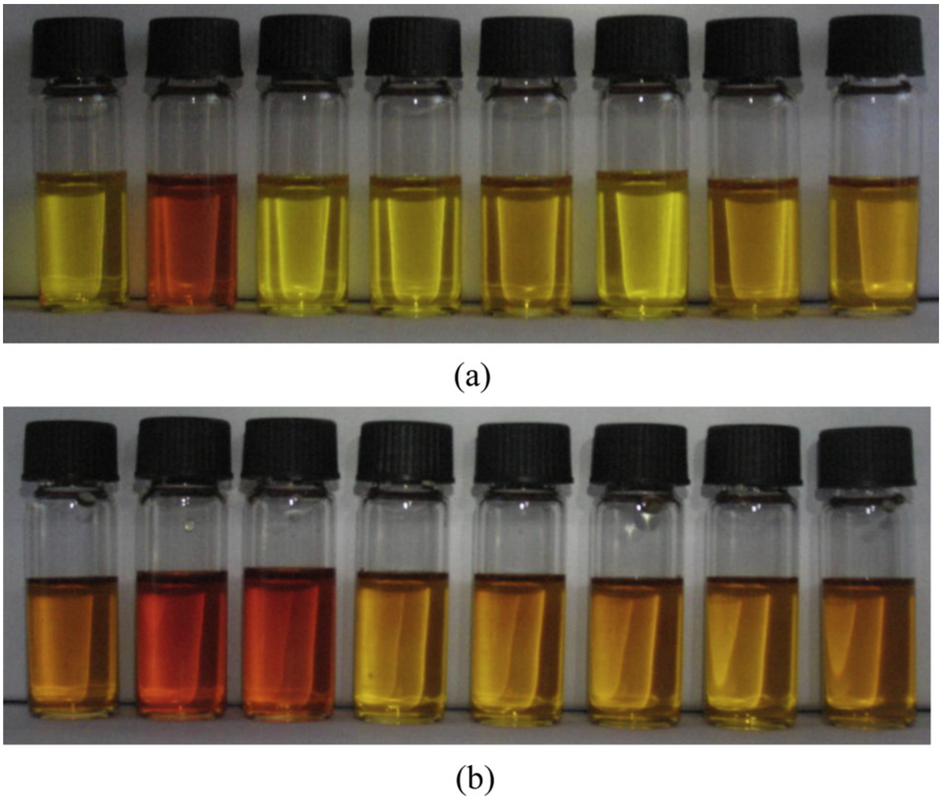


Fig. 4. (a) Colorimetric changes of probe molecule 1 upon different anions in DMSO(from left to right: 1 (2.63×10^{-4} M); 1 + F^- (1 equiv); 1 + $H_2PO_4^-$ (10 equiv); 1 + Cl^- (10 equiv); 1 + Br^- (10 equiv); 1 + I^- (10 equiv); 1 + HSO_4^- (10 equiv); 1 + NO_3^- (10 equiv)), (b) colorimetric changes of probe molecule 2 upon different anions in DMSO (from left to right: 1 (2.63×10^{-4} M); 1 + F^- (1 equiv); 1 + $H_2PO_4^-$ (1 equiv); 1 + Cl^- (10 equiv); 1 + Br^- (10 equiv); 1 + I^- (10 equiv); 1 + HSO_4^- (10 equiv); 1 + NO_3^- (10 equiv)).

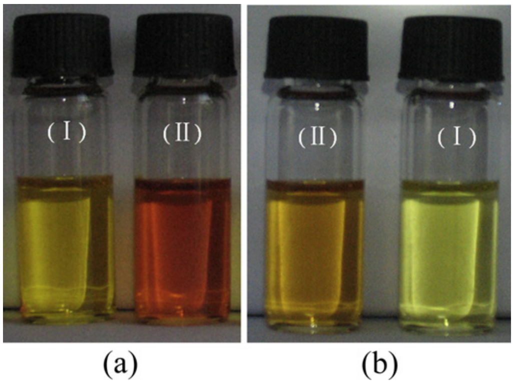


Fig. 5. Colorimetric changes of probe molecule 1 with(II) or without(I) F^- in DMSO under different concentration of probe molecule 1: (a) 2.63×10^{-4} M; (b) 5.3×10^{-5} M.

was added as catalyst. Then 20 mL refluxed CH_2Cl_2, containing 1.870 g (6 mmol) 1,1′-dichloro-carbonylferrocene was added dropwise into the system. The reaction mixture was stirred at room temperature for 10 h, filtered and the precipitate was washed with ethanol three times to get pure product chemosensor 2 as a yellow powder. Yield: 2.56 g (67.4%).

2.3. Characterization

^{1}H NMR spectra of the probe molecules 1, 2 and their F^- ($H_2PO_4^-$) titration were recorded on a 400 MHz AVANCE DMX spectrometer instrument using deuterated chloroform ($CDCl_3$-d_6) or dimethyl sulfoxide (DMSO-d_6) as solvents. UV–vis absorption spectra of the probe molecules 1, 2 and their anions titration were obtained on a UNIC 3802 UV–vis spectrophotometer.

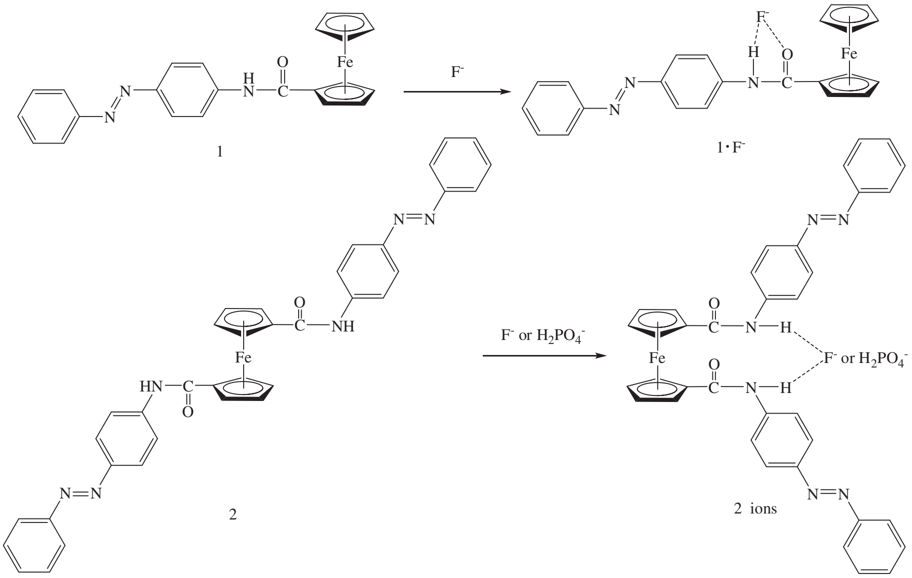
3. Results and discussion

The ^{1}H NMR spectra of the probe molecules 1 and 2 were shown in the Supporting information (ESI).

The probe molecules 1 and 2 were titrated with F^- in DMSO under room temperature, and the UV–vis absorption spectra were recorded as shown in Fig. 1. In Fig. 1(a), a significant phenomenon was detected that as the concentration of F^- increased, the absorption band of the probe molecule 1 around 465 nm increased with a slight decrease in the absorption band around 360 nm. The same spectral change was observed fro the probe molecule 2 in Fig. 1(b). However, the absorption band 360 nm decreased obviously when adding more than 30 equiv F^-. The same titration experiments were done using $H_2PO_4^-$ as a titrant for the probe molecules 1 and 2, and the UV–vis spectra were recorded as shown in Fig. 2(a) and (b). The probe molecules 1 and 2 had different phenomenons upon addition of $H_2PO_4^-$. The UV–vis spectrum of the probe molecule 1 was not affected by the addition of $H_2PO_4^-$, while probe molecule 2's changed obviously, as shown in Fig. 2.

Fig. 3 showed the UV–vis absorption spectral changes of the probe molecules 1 and 2 in DMSO upon the addition of 10 equiv anions (F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^- or NO_3^-) and 10 equiv anions' mixture. As shown in Fig. 3(a), only F^- increased the absorption peak around 465 nm for the probe molecule 1. On the other hand, $H_2PO_4^-$ lead to a slightly different absorption band around 465 nm, but the other anions did not result in any difference of absorption spectra. Meanwhile, as shown in Fig. 3(b) both F^- and $H_2PO_4^-$ led to absorption spectra changes around 465 nm for the probe molecule 2, and little difference could be discriminated between the ions mixture and the F^- anion solution.

The probe molecules 1 and 2's colorimetric recognition and their sensing of F^- or $H_2PO_4^-$ ions were demonstrated as shown in Fig. 4, in which the concentration of probe molecules 1 and 2 were 2.63×10^{-5} M. In Fig. 4(a), the solution color changed from yellow to salmon pink upon the addition of F^-. In contrast, the addition of the other anions did not induce any color change. From above, it can be deduced that probe molecule 1 can serve as a selective F^- sensor without interference from any other ions. From Fig. 4(b), 1 equiv F^- and 10 equiv $H_2PO_4^-$ lead the probe molecule 2's solution color change from yellow to salmon pink. Therefore, the probe molecule 2 can serve as a selective sensors for F^- and $H_2PO_4^-$ without interference from any other ions. More importantly, the concentration of F^- added into the probe molecule 1's solution is 2.63×10^{-4} M that equals to 5 mg/L which is the largest amount of



Scheme 3. Schematic representation of sensing F^- and $H_2PO_4^-$ processes.

F^- concentration that can exist in drinking water. Furthermore, it was found that the colorimetric change is highly dependent on the concentrations of the probe molecule 1 and F^-, as shown in Fig. 5. Inspiringly, the concentration of probe molecule 1 and F^- in Fig. 5(b) is 5.3×10^{-5} mol/L, that equals to 1 mg/L, which is the lowest concentration of F^- in drinking water.

From above, a possible mechanism was proposed to illustrate the sensing F^- and $H_2PO_4^-$ process by the probe molecules 1 and 2. For probe molecule 1, one amide group would only bind with F^- tightly in DMSO, which can be demonstrated by Figure S5 and Figure S7. Meanwhile, the probe molecule 2 could provide two amide groups at the same side to bind with F^- or $H_2PO_4^-$ via hydrogen bonding. In Figure S5, we can see clearly that the peak belonging to proton from amide group (red arrow) was shifted to the upfield, after the addition of F^- or $H_2PO_4^-$. In Figure S6, the situation was similar. In which the peak at 9.81 ppm (red arrow) was shifted to the upfield around 4.40–4.50 ppm, after the addition of F^- or $H_2PO_4^-$, and also the peak at 9.81 ppm, which belonged to the diproton of amide group, disappeared. Therefore, we supposed that the free rotation of the two cyclopentadienyl rings of the ferrocene moiety is restricted via the addition of F^- or $H_2PO_4^-$, which brings the two arms of the ferrocene moiety together in one direction. The proposed mechanisms were shown in Scheme 3.

4. Conclusions

We successfully prepared a novel pair of ferrocene-containing azobenzene-based probe molecules, which behave as a selective probe for sensing fluoride and dihydrogen phosphate ions in colorimetric systems (even by the naked eye). The sensing properties were examined by UV–vis spectra, photo image, ^1H NMR and J-plot. Based on the results, a sensing mechanism was proposed as shown in Scheme 3.

Acknowledgments

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Appendix A. Supporting information

Synthesis and characterization of probe molecules, UV–vis spectra of probe molecules with different ions, and J-plot of two chemosensors'ion-titration.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.12.012.

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