Spectrochimica Acta Part A 79 (2011) 1352–1355

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

A novel fluoride ion colorimetric chemosensor based on coumarin

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ARTICLE INFO

Article history:
Received 22 March 2011
Received in revised form 15 April 2011
Accepted 27 April 2011

Keywords:
Colorimetric chemosensor
Anion recognition
Fluoride sensing
Coumarin
Schiff base

ABSTRACT

A novel visible colorimetric sensor (**L_1**) with high selectivity for fluoride ion based on coumarin has been synthesized by a simple modification of our earlier report. The chemosensor **L_1** shows an obvious color change from yellow to blue upon addition of fluoride ion with a large red shift of 145 nm in acetonitrile, and without interference of other anions such as Cl^-, Br^-, I^-, NO_3^-, $H_2PO_4^-$, HSO_4^-, and AcO^-. The investigation of ^1H NMR spectrum titration indicates the proposed mechanism is that F^- first establishes a hydrogen bonding interaction with **L_1**, and then the formation of $[F–H–F]^-$ induces deprotonation.

1. Introduction

Anion recognition is an important issue in supramolecular chemistry as anions play a significant role in chemistry industry, biochemistry, and environmental science [1,2]. As the first anion in the periodic table of elements, fluoride ion has unique biology and chemistry properties. It is an essential trace element in human and shortage of fluoride results in dental caries and osteoporosis. In many countries, fluoride has been added to water widespread to prevent tooth decay. However, high dose or chronic ingestion of lower doses of fluoride may result in fluorosis, and lead to nephrotoxic changes and urolithiasis in humans [3–8]. In addition, with the development of industry and the increase in the number and the scale of enterprises on fluorine products, the contamination of fluorine becomes more serious. For these reasons, selective recognition of fluorine ion is of realistic significance.

In recent years, many analytical methods have been developed for fluoride ion detection. Among all the analysis methods, colorimetry, known as naked eye detection, has attracted much attention due to its rather straightforward and fast measurement protocols and no need of valuable instruments [9,10,2,11–13]. These methods are mostly based on N–H proton transfer from the donor unit to fluoride ion, which induced π-electron delocalization, or N–H deprotonation [14]. The hydrogen donator includes amine [15], amide [16], pyrrole [17,18], and urea [19–21]. However, highly basic anions such as $CH_3CO_2^-$ or $H_2PO_4^-$ can also act as an acceptor, and cause similar spectral changes with fluoride ion [22,23]. Therefore, there is a great challenge to construct the colorimetric sensor with specific receptor for the fluoride ion and suitable chromophore for obvious color change. Up to now, the colorimetric sensors based on N–H proton transfer that satisfy the above conditions are rarely reported.

Present study is a part of our current research interest towards chemosensors based on coumarin with Schiff base (–C=N–) as bridge [24–26]. The present chemoreceptor in this work is a simple structural modification of one of our earlier report [27]. This modification was worthwhile to modulate the acidity of N–H proton by decreasing the numbers of nitro-group, so that the new receptor can be able to discriminate between anions of high and comparable basicity like fluoride and dihydrogen phosphate. Compound **L_1** was designed and synthesized by the condensation of 7-N,N-diethyl-aminocoumarin and 4-nitrophenylhydrazine (Scheme 1). The result shows that the fluoride ion could be detected by naked eyes without interference from other anions. The details of anion binding characteristics of the compound **L_1** have been investigated by UV–vis and ^1H NMR titrations. The maximum of absorption of **L_1** shifts 145 nm in the presence of the fluoride ion in CH_3CN solution due to the N–H deprotonation and formation of the particularly stable $[F–H–F]^-$ dimer.

2. Experimental

2.1. Reagents and instruments

7-(Diethylamino)-2-oxo-2H-chromene-3-carbaldehyde was synthesized according to reported methods [24]. 4-nitrophenylhydrazine hydrochloride and all anions were purchased from Sigma Aldrich and used without any further

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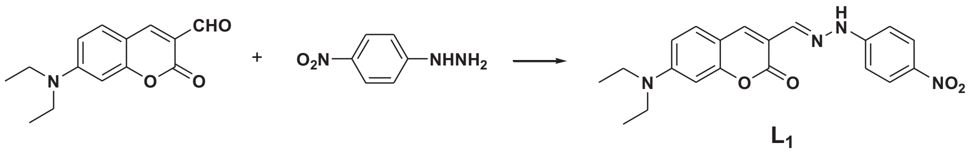
doi:10.1016/j.saa.2011.04.068



Scheme 1. Preparation of $\mathbf{L_1}$.

purification. N,N-dimethyl formamide was dried with calcium hydride and distilled at reduced pressure prior to use. Acetonitrile was chromatographical grade, and other chemicals were analytical grade.

All UV–vis spectra in this work were recorded using Hitachi U3010 spectrometer. NMR spectra were recorded on Varian Gemin-400 NMR instrument (400 MHz), and MS spectra were performed on Finnigan 4021C and APEXII FT-ICR.

2.2. *Synthesis*

7-(Diethylamino)-2-oxo-2H-chromene-3-carbaldehyde (245 mg, 1 mmol) and 4-nitrophenylhydrazine hydrochloride (189 mg, 1 mmol) was added in ethanol (40 mL) (Scheme 1). The mixed solution was refluxed for 6 h, cooled to room temperature. Then the solvent was concentrated to half and garnet crystals were precipitated, washed with hot ethanol for several times to yield $\mathbf{L_1}$ 198 mg (yield 52.1%). 1H NMR (DMSO-d6) δ 1.13 (6H, t, J = 7.0 Hz), 3.45 (4H, q, J = 7.1 Hz), 6.57 (1H, d), 6.74 (1H, dd), 7.15 (1H, d), 7.58 (1H, d), 8.07 (1H, s), 8.11 (2H, m), 8.37 (1H, s), 11.39 (1H, s). TOF-HRMS found [M]+: *m*/*z*, 380.1254, Calcd. 380.15.

2.3. *General spectroscopic procedures*

Stock solutions of $\mathbf{L_1}$ was prepared by dissolving $\mathbf{L_1}$ in acetonitrile to the concentration of 1.0×10^{-3} M and stored at −25 °C in the dark. Then the stock solution was diluted with acetonitrile to a final concentration of 5 μM for spectra analysis. All anion stock solutions were prepared by dissolving corresponding tetra-n-butyl ammonium salts into acetonitrile. Each time 2 mL of $\mathbf{L_1}$ solution was filled in a quartz cell of 1 cm optical path length, and different stock solutions of anions were added into the quartz cell gradually using a pipette. The volume of anion stock solution added was less than 100 mL to keep the total volume of testing solution without obvious change. The temperature of analysis was 25 °C.

3. Results and discussion

The interactions between $\mathbf{L_1}$ and anions were investigated by UV–vis spectroscopy. The maximum absorption of $\mathbf{L_1}$ is 475 nm and the molar absorption coefficient is 5.0×10^5 in acetonitrile. Fig. 1 shows the absorption spectra of $\mathbf{L_1}$ in the presence of several anions. On the addition of 20 equiv of F^-, the color of $\mathbf{L_1}$ turned from yellow to blue (Fig. 2). (For interpretation of the references to color in this text, the reader is referred to the web version of the article.) A new peak appears at 620 nm with a shoulder peak at 650 nm, indicating a red shift of 145 nm. However, $\mathbf{L_1}$ has no color change in the presence of 20 equiv Cl^-, Br^-, I^-, $NO_3{}^-$, $H_2PO_4{}^-$, $HSO_4{}^-$, and AcO^-. This result shows that L_1 exhibits highly selective recognition of F^-.

It deserves to be specially noted that the presence of other anions do not interfere the color reaction of $\mathbf{L_1}$ with F^- except for $HSO_4{}^-$, as shown in Fig. 3. On the addition of 20 equiv of F^-, red shift occurs in the absorption spectra in the presence of 20 equiv Cl^-, Br^-, I^-, $NO_3{}^-$, $H_2PO_4{}^-$, $HSO_4{}^-$, and AcO^-, which indicates that the hydrogen bonding interaction between $\mathbf{L_1}$ and F^- is stronger than other anions. This is mainly because the ion radius of F^- is smaller and the charge density is higher compared to other anions.

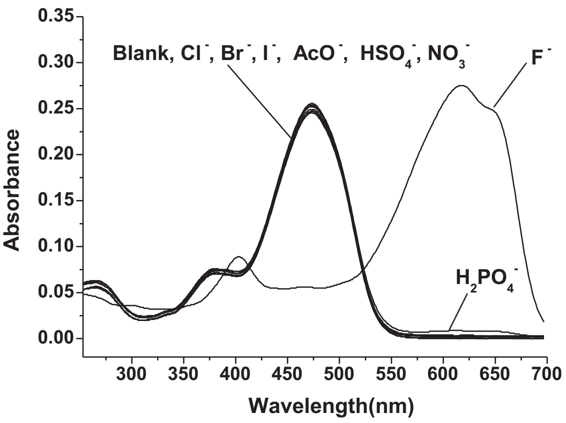


Fig. 1. Absorption spectra changes of $\mathbf{L_1}$ (5 μM in MeCN) upon addition of different anions (20 equiv).

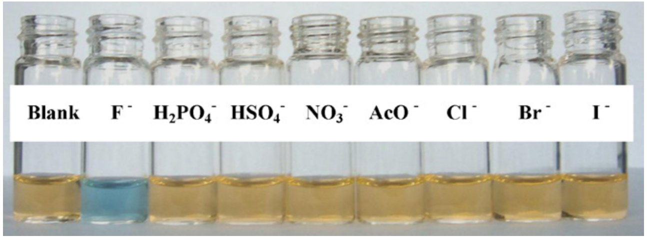


Fig. 2. Color changes upon addition of 20 equiv different anions in 10 μM MeCN solution of $\mathbf{L_1}$.

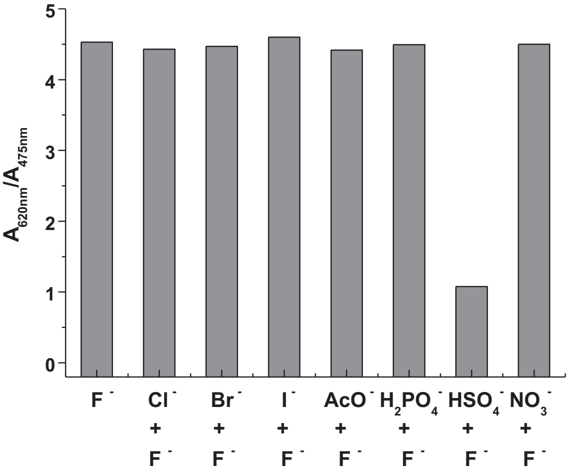
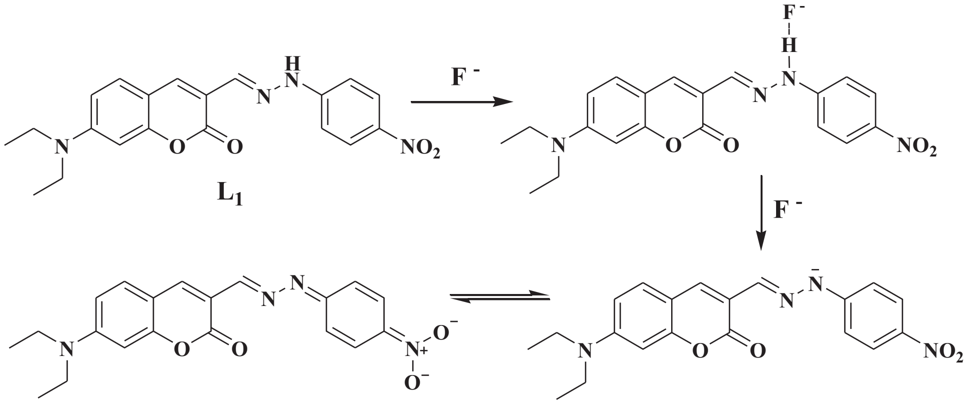


Fig. 3. Variation of absorption spectra of $\mathbf{L_1}$ (5 μM in MeCN) in the presence of 20 equiv F^- with coexisting competitive anions (20 equiv).

To evaluate the effect of the concentration of F^- on UV–vis spectrum, the UV–vis titration experiment of $\mathbf{L_1}$ was carried out in acetonitrile. Upon the addition of F^-, the absorption peak at



Scheme 2. Proposed mechanism for $\mathbf{L_1}$ with F^-.

475 nm was decreasing, whereas new absorption peaks at 620 nm and 650 nm were observed and gradually increased (Fig. 4a). As shown in titration curves at 475 nm and 620 nm (Fig. 4b), when the addition of F^- is less than 2 equiv, there are no significant changes in spectra. When more than 2 equiv F^- is added, the spectra significantly change. These changes indicate the reaction takes place in steps and the first step shows little influence on absorption spectra [28]. The appearance of new absorption peaks at 620 nm and 650 nm may indicate the existence of similar structures or similar conjugate structures in the reaction system.

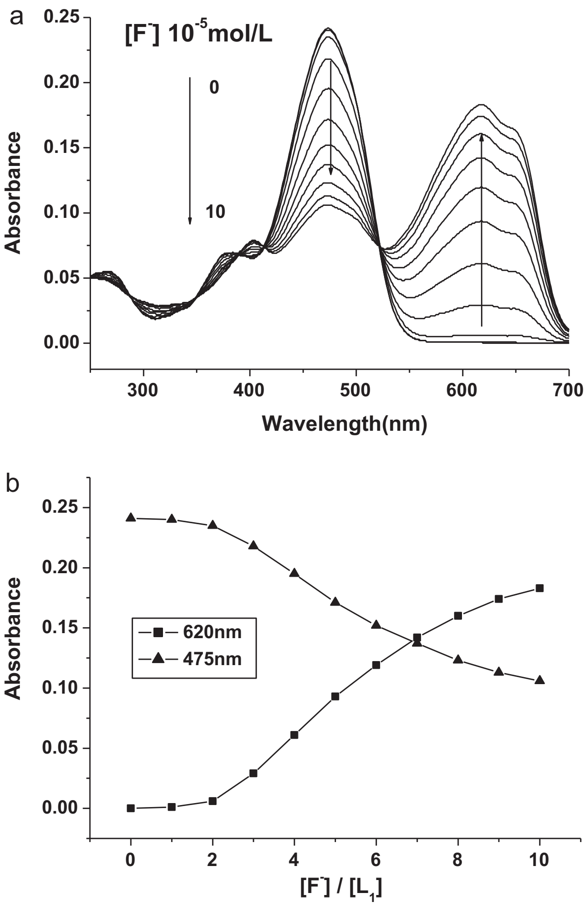


Fig. 4. (a) Absorption spectra changes of $\mathbf{L_1}$ (5 μM in MeCN) in the course of the titration of F^- (0–50 μM). (b) The absorbance was measured at 475 nm and 620 nm, respectively with titration of F^- (0–50 μM).

In order to clarify the function mechanism of the interaction of $\mathbf{L_1}$ with F^-, ^{1}H NMR spectroscopy was investigated. In particular, a DMSO-d_6 solution in $\mathbf{L_1}$ was titrated with F^-, which was added stepwise up to 5 equiv. Fig. 5 shows different ^{1}H NMR spectra obtained in the course of the titration. After the addition of 5 equiv of F^-, the –NH proton (11.39 ppm) disappeared, while a typical triplet influenced by F^- was appeared at 16.14 ppm which indicated the formation of $[F–H–F]^-$. The mechanism is that –NH interacts with F^- through hydrogen bonding at first, and then more F^- participate in the interaction inducing the proton transfer reaction [29]. As shown in Scheme 2, when –NH is deprotonated, the electron density is increased. This leads to the intramolecular charge transfer in the whole system and the red shift of absorption spectrum. Meanwhile, the electron density of nitroaromatic ring is greatly increased and the hydrogens on aromatic ring shift upfield significantly. This explains the changes in the UV–vis titration of $\mathbf{L_1}$ with F^-. The absorption spectra shift little when the hydrogen bond complex is formed in the first step. But when the deprotonation reaction undergoes further, the absorption spectra shift dramatically. Besides, we also performed UV–vis titration of $\mathbf{L_1}$ with 20 equiv F^- in proton polarity solvent methanol. The absorption peaks at 620 nm and 650 nm were decreasing and showed a blue shift, while the absorption peak at 475 nm was increasing. At last, the titration spectrum overlapped with the absorption spectrum of $\mathbf{L_1}$. This indicates that

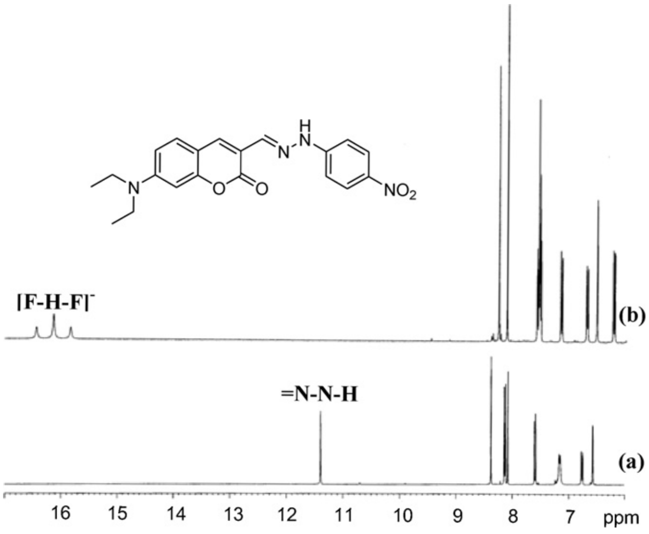


Fig. 5. ^{1}H NMR spectra of (a) $\mathbf{L_1}$ in DMSO-d_6 and (b) $\mathbf{L_1}$ in DMSO-d_6 upon addition of 5 equiv F^-.

N^- or C^- in $\mathbf{L_1}$ suffered a protonation process in the presence of methanol.

4. Conclusion

In summary, a new colorimetric chemosensor $\mathbf{L_1}$ based on coumarin with –NH as hydrogen donator and –C=N as bridge has been synthesized by a simple modification of our earlier report. When treated with F^-, a dramatic color change from yellow to blue is observed. The study of UV–vis absorption spectroscopy indicates that $\mathbf{L_1}$ exhibits highly selective recognition of F^- without interference from other anions, which results a 145 nm red shift of the maximum absorption. The study of ^{1}H NMR spectroscopy indicates the mechanism is that the proton transfer reaction between $\mathbf{L_1}$ and F^- leads to the delocalization of electron in the system, which increases the intermolecular charge transfer and makes the absorption spectra red shift significantly. Thus, $\mathbf{L_1}$ can be applied as a highly selective naked-eye colorimetric chemosensor for F^-.

Acknowledgements

This project was supported by the Main Direction Program of Knowledge Innovation of Chinese Academy of Sciences, the NNSF of China (Nos. 21073213, 20673132), the Research Grants Council of the Hong Kong SAR (No. CityU 123607), and “863” Program (No. 2009AA03Z318).

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