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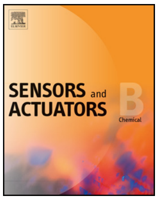

Discriminating detection between F⁻ and CN⁻ by naked eye from Schiff base sensor

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ABSTRACT

A simple colorimetric and turn-on fluorescence receptor **1** was prepared and its cations and anions sensing properties were investigated in CH_3CN solution. Receptor **1** can selectively sense F^- and CN^- based on distinct color changes among a series of ions. Receptor **1** displayed a highly selective colorimetric response to fluoride anions based on a hydrogen bonding interaction process and fluorescent with colorimetric response to cyanide anions based on a generation of a cyanide adduct. The detection limit of receptor **1** toward F^- and CN^- ion was determined to be 0.28 ppm and 0.41 ppm, respectively. The two detection limit values were sufficiently low to detect submicromolar concentration of the F^- and CN^-.

1. Introduction

In recent years, the search of colorimetric fluorescent sensors for various chemically or biologically significant ions has emerged as an area of great interest because of their potential applications in clinical biochemistry and in environmental research [1–7]. Among various important analytes, fluoride ions (F^-) are significant due to their role in dental care and treatment of osteoporosis [8]. In addition, high concentration of F^- after a certain level is toxic, leads to severe health risks. F^- usually forms the strongest H-bond interaction with NH or OH fragment of an artificial receptor, and further the interaction should likely arouse an advanced stage of the proton transfer reactions. Such features have been observed in few amide-, phenol-, and urea-based receptors containing electron-withdrawing chromogenic substituents. Indeed, the colorimetric sensor based on the deprotonation of the binding moiety by anions is very efficient and highly sensitive. Although some of colorimetric type receptors for F^- detection have been developed [9–20], most of them usually require complicated syntheses involving severe reaction conditions and expensive chemicals. Thus, for practical applications, it is necessary to develop the F^- sensor that can be easily prepared, and possess selective and sensitive signaling mechanisms.

On the other hand, CN^- is one of the most toxic anions and harmful to environment or human health. However, CN^- is still widely used in gold mining, plastics production and other industrial activities [21]. Widespread use of CN^- leads to the deterioration in the environment. Thus, great efforts have been devoted to the development of sensors for the recognition of CN^- [22–31]. However, many of the reported CN^- sensors suffer from disturbance by anions such as F^- and AcO^-. Therefore, reliable and efficient ways of detecting the presence of CN^- are desirable.

Development of new receptors for the detection of different analytes simultaneously is emerging as an area of great interest [32], since such system would lead to faster analytical processing and potential cost reductions. However most of the reported sensors are effective only in selective recognition of a particular analyte. Since the recognition units of sensors are distinctive in sensing cations or anions behavior, thus developing such sensors with multiple analyte recognition capability is a challenging task. Jiang et al. reported a simple sensor, which displayed a highly selective colorimetric response to fluoride anions based on a deprotonation process and fluorescent response to cyanide anions based on a cyclization process [33]. Up to now, there are only few reports where sensors could allow selective detection of F^- and CN^- simultaneously by distinct color changes [34–37]. Herein, we reported a colorimetric sensor (receptor **1**), which could selectively detect F^- and CN^- based on the distinct color changes among a series of ions. More importantly, receptor **1** can be readily prepared by a simple Schiff-base reaction of 1-aminopyrene with 8-hydroxy-2-quinolinecarboxaldehyde, as shown in Scheme 1. The structure of receptor **1** was confirmed by NMR spectra and mass data (Figs. S1 and S2).

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2. Experimental

2.1. General procedure

All reagents were obtained from commercial suppliers and were used without further purification. DCM was distilled over CaH_2. MeOH was distilled over magnesium and iodine. Analytical thin-layer chromatography was performed using silica gel 60 F254 plates (Merck). The ^1H and ^{13}C NMR spectra were recorded with a Bruker AM 300 spectrometer. Chemical shifts were given in ppm with residual DMSO as reference. Mass spectra were recorded under electron impact (EI) or electron spray interface (ESI) conditions. UV–vis spectra were recorded by using Jasco V630 spectrophotometer with a diode array detector, and the resolution was set at 1 nm. Fluorescence spectra were recorded on a Jasco FP-8300 fluorescence spectrophotometer.

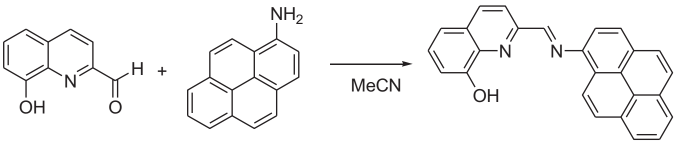
2.2. Synthesis of 8-hydroxy-2-quinoline-1-aminopyrene

8-Hydroxy-2-quinolinecarboxaldehyde (0.50 g, 2.89 mmol) was added to a stirring solution of 1-aminopyrene (0.63 g, 2.89 mmol) in dry CH_3CN (50 mL). The reaction mixture was stirred at room temperature for 12 h. The resulting canary yellow precipitate was filtered and washed with cold ethanol. The resulting residue was dried under vacuum to give yellow solid product **1** (0.75 g, 69%). m.p. 212.5–213.5 °C; ^1H NMR (300 MHz, DMSO-*d6*) δ: 10.14 (br, 1H), 9.11 (s, 1H), 8.80 (d, $J = 9.0$ Hz, 1H), 8.62 (d, $J = 8.4$ Hz, 1H), 8.53 (d, $J = 8.7$ Hz, 1H), 8.40 (d, $J = 8.1$ Hz, 1H), 8.32–8.07 (m, 7H), 7.59–7.49 (m, 2H),7.2 (q, $J = 8.7$ Hz, 1H); ^{13}C NMR (75 MHz, DMSO-*d6*) δ: 161.61, 154.38, 152.94, 143.94, 138.80, 137.37, 131.41, 131.24, 130.32, 129.99, 129.61, 127.92, 127.72, 127.56, 127.01, 126.47, 125.26, 125.77, 124.84, 124.35, 123.28, 119.14, 118.26, 116.05, 112.69; HRMS (EI): Calcd for $C_{26}H_{16}N_2O$ $[M]^+$, *m*/*z* 372.1263, found *m*/*z* 372.1260.

3. Results and discussion

3.1. Fluorescence and absorption studies of receptor 1 toward various anions

The UV–vis and fluorescence spectra of receptor **1** were studied in presence of various anions (as TBA salts): (F^-, Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, $H_2PO_4^-$, AcO^-, CN^-, N_3^-). Addition of F^- and CN^- to the solution of receptor **1**, respectively, resulted in a prominent change in the UV–visible absorption spectra, as shown in Fig. 1. However, other anions such as Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, $H_2PO_4^-$, AcO^- and N_3^- did not cause any significant changes in their UV–visible absorption spectra. Upon addition of F^-, the absorption band at 385 nm disappeared and displayed a new absorption band at 525 nm. This is presumably due to the hydrogen bond interaction between F^- with receptor **1**. Meanwhile, the solution of receptor **1** showed a dramatic color change from yellow to red which could easily be detected by the naked-eye (Fig. 2). Upon addition of CN^- to the solution of receptor **1,** the absorption maximum at 385 nm exhibited a hypochromic and red shift accompanied a new absorption band at 616 nm. The solution of receptor **1** showed a dramatic color change from yellow to green which could easily be detected by the naked-eye. These results indicated that receptor **1** can be used for selective sensing of F^- and CN^- based on the distinct color changes.



Scheme 1. Synthesis of receptor **1**.

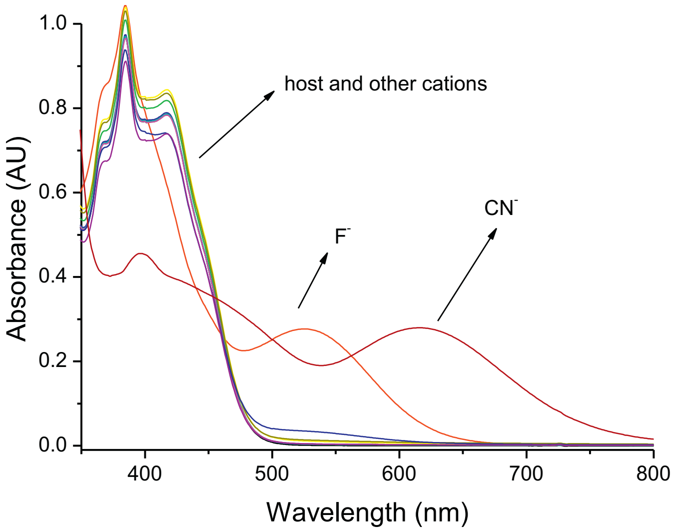


Fig. 1. UV/vis spectra of **1** (40 μM) recorded in CH_3CN after addition of 10.0 equiv. of various anions.

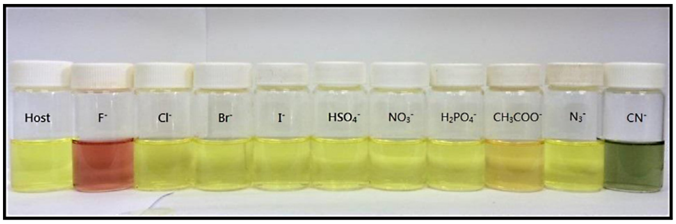


Fig. 2. The color changes observed by naked eye of receptor **1** (40 μM) upon addition of 10.0 equiv. of various metal ions in CH_3CN.

The sensing phenomena were also monitored by fluorescence spectroscopy. As shown in Fig. 3, receptor **1** alone and other anions all displayed weak fluorescence emission bands except for CN^-. Upon addition of CN^-, receptor **1** exhibited a prominent fluorescence enhancement and accompanied by a new major band at 425 nm with two shoulder bands at 490 nm and 527 nm, respectively. The fluorescent enhancement efficiency observed at 425 nm

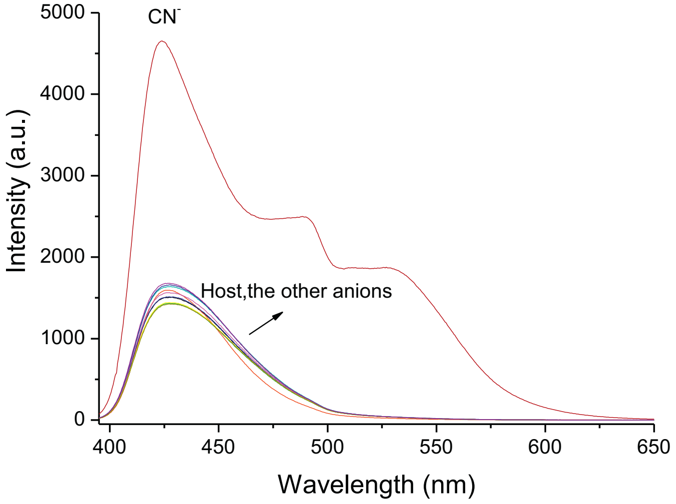


Fig. 3. Fluorescence emission spectra ($\lambda_{ex} = 385$ nm) of receptor **1** (40 μM) in the presence of 10.0 equiv. of various metal ions in CH_3CN.