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A ditopic colorimetric sensor for fluoride ion based on thiourea mercury complex

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Abstract

A novel ditopic chromogenic receptor, *N*-5-(8-hydroxy)quinoline-*N*′-4′-nitro-phenyl thiourea (**1**), was synthesized. The metal complex **1**-Hg^{2+} showed sensitive and highly selective responses to F^- over other anions such as $CH_3CO_2^-$, $H_2PO_4^-$, HSO_4^- and Cl^-. **1**-Hg^{2+}–F^- complex formed, which promoted the intramolecular charge transfer and led to a dramatic spectral change. The color of **1**-Hg^{2+} solution changed from colorless to red upon addition of F^-. Thus, a colorimetric assay of F^- was developed in acetonitrile by naked-eye detection. F^- behaved linearly in the 8.0×10^{-6} to 2.0×10^{-5} mol L^{-1} concentration range with LOD as 1.4×10^{-6} mol L^{-1}.

Keywords: Ditopic chromogenic receptor; *N*-5-(8-Hydroxy)quinoline-*N*′-4′-nitro-phenyl thiourea; Fluoride ion; Colorimetric assay

1. Introduction

Because anions play important roles in many biological and chemical processes, there is an increasing interest in the design and development of receptors for sensing and recognizing anions selectively [1–7]. Chromogenic receptors that undergo a vivid color change upon complexation are an important class of optical devices for naked-eye detection [8–10]. Most of them only respond to anions [11–14] or cations separately [15–17]. An expanded area of anion recognition was the simultaneous binding of cationic and anionic guests as an ion pair [18–30]. The binding moieties of the ditopic receptors for cations usually are cyclic compounds such as crown ether [19,23,25] porphyrin [24] and calyx[4]arene [27] or calix[4]pyrrole, [30] while the binding moieties for anions include pyrrol, amide and guanidyl [5]. Here, we report a new and simple structured chromoionophore, *N*-5-[8-hydroxy-quinoline]-*N*′-4′-nitro phenyl thiourea (**1**) (shown in Scheme 1). Hg^{2+} bound to the thiourea moiety while the anion bound to the 8-hydroxy-quinoline moiety via hydrogen bond. The binding of **1**-Hg^{2+} with trace amount of F^- triggered intense color change from colorless to red as the result of the intramolecular charge transfer.

2. Experimental

Absorption spectra were recorded on Shimadzu-2501 UV–vis spectrophotometer (Japan) using 1 cm quartz cell. ^1H NMR spectra were carried out in DMSO-d_6 on a Bruker Avance 400 MHz NMR spectrometer using TMS as the internal standard. ESI mass spectra were recorded using a Waters ZQ4000/2695 LC–MS spectrometer. Infrared spectra were obtained as KBr pellets on a Nicolet 5700 FTIR spectrometer.

Receptor **1** was easily obtained by one-step reaction of 5-amino-8-hydroxyquinoline dihydrochloride (Sigma–Aldrich Corp.) with *p*-nitrobenzyl-isothiocyanate (Sigma–Aldrich Corp.) in ethanol (Shanghai Chemical Corp.) and purified by repeated washing with ethanol. Control compound **2** was prepared in the similar way [31]. The compounds were characterized by IR, ^1H NMR and ESI mass data, which were consistent with the proposed formulation. **1**: ^1H NMR (DMSO-d_6): δ(ppm) 7.42 (d, $J = 8.88$ Hz, 1H, QH), 7.54–7.58 (m, 1H, QH), 7.98–8.02 (t, 3H, QH, ArH), 8.22 (d, $J = 9.00$Hz, 2H, QH), 8.34 (d, $J = 7.56$Hz, 1H, QH), 8.87 (d, $J = 3.00$ Hz, 2H, ArH), 9.92 (s, NH), 10.59 (s, NH), 11.62 (s, OH); SI mass: *m*/*e* calcd. for $C_{16}H_{12}N_4O_3S$ $[M+H^+]$ 341.06, found $[M+H^+]$ 341.00; **2**: ^1H NMR(DMSO-d_6): δ(ppm) 7.56–7.62 (m, 4H), 7.90–8.01 (m, 5H), 8.22 (d, $J = 9.00$ Hz, 2H), 10.30 (s, NH), 10.41 (s, NH); ESI mass: *m*/*e* calcd. for $C_{17}H_{13}N_3O_2S$ $[M+H^+]$ 324.07, found

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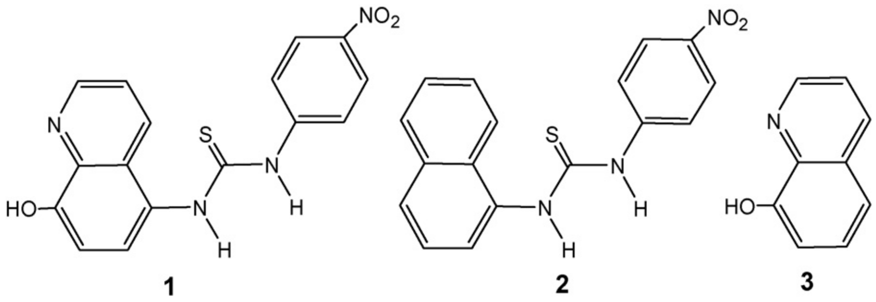

Scheme 1. Structures of receptors **1**–**3**.

[M+H$^+$] 324.00. Control compound **3** was purchased from Shanghai Chemical Corp. The tetrabutylammonium salts of the tested anions and the perchlorate of the tested cations were Sigma–Aldrich Corp. products. Acetonitrile (Merck. Corp.) was HPLC grade and was not purified before use.

3. Results and discussion

Metal complexes between **1** and different metal ions were investigated by absorption spectroscopy. The presence of Al^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+} could not lead to distinct spectral changes. But upon addition of Cu^{2+} or Hg^{2+} the spectrum of **1** underwent obvious changes which implied that **1** was a good ligand for Cu^{2+} and Hg^{2+}(seen in Fig. S1). Furthermore **1**-Hg^{2+} complex can selectively sensed fluoride ion.

Fig. 1 showed the spectral changes of **1**-Hg^{2+} upon addition of various anions. Upon addition of 10 equiv. of anions such as F^-, $CH_3CO_2^-$ or $H_2PO_4^-$, the spectrum of **1**-Hg^{2+} only underwent dramatic change for F^-. A new absorption peak at long wavelength of 490 nm appeared and the solution turned from colorless to red. However, the addition of $CH_3CO_2^-$ or $H_2PO_4^-$ merely produced slight spectral change and no obvious color change was observed (seen in Fig. S2). The presence of 20 equiv. of other anions such as HSO_4^-, Cl^-, Br^-, NO_3^- and ClO_4^- induced neither spectral profile nor solution color change. Obviously, **1**-Hg^{2+} exhibited the most sensitive and selective response to F^-.

To make a comparison, the interaction between **1** and anions was also investigated. Fig. 2 displayed the spectral change of **1** in the presence and absence of anions in acetonitrile. The presence of F^-, $CH_3CO_2^-$ and $H_2PO_4^-$ all led to red shift of the spectra along with the color change from colorless to yellow. The addition of other anions such as HSO_4^-, Cl^-, Br^-, NO_3^- and ClO_4^- induced little changes because of the weak anionic basicity. Although the sensitivity for F^- was higher than that for $CH_3CO_2^-$ or $H_2PO_4^-$, the selectivity was poor. It is obvious that **1**-Hg^{2+} and **1** have different mechanisms of binding anions. The existence of Hg^{2+} in **1**-Hg^{2+} promoted the intramolecular charge transfer when the metal complex bound with anions, which induced the large red shift of the spectra and the color change. It was noted that the selectivity of **1**-Hg^{2+} for F^- was greatly improved.

The absorption titration of **1**-Hg^{2+} with F^- was performed and the result was presented in Fig. 3. In the absence of F^-, the solution of **1**-Hg^{2+} was colorless and the maximal wave-

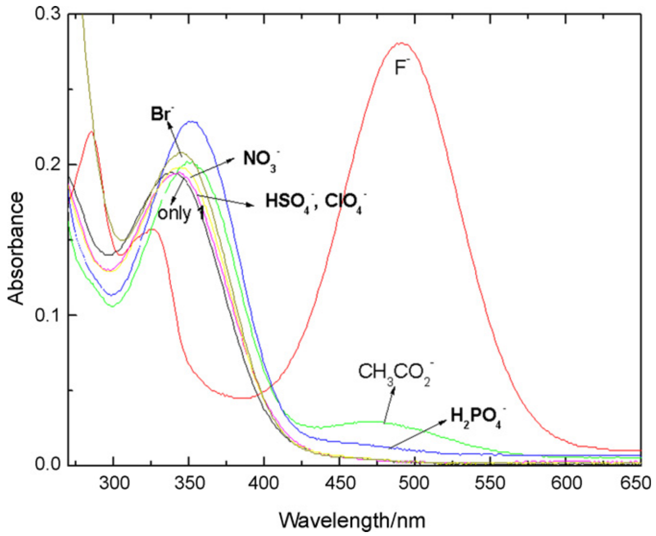

Fig. 1. Absorption of **1**-Hg^{2+} (8.0×10^{-6} mol L^{-1}) complex in the presence and absence of the anion in acetonitrile. The concentrations were 8.0×10^{-5} mol L^{-1} for F^-, $CH_3CO_2^-$ and $H_2PO_4^-$, respectively. The concentrations of other anions were 1.6×10^{-4} mol L^{-1}, respectively.

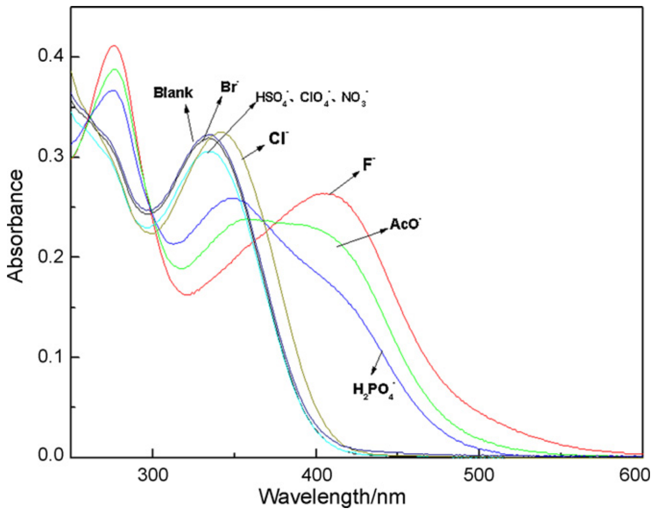

Fig. 2. Absorption spectra of **1** (1.6×10^{-5} mol L^{-1}) in the presence and absence of anions in acetonitrile. The concentrations were 8.0×10^{-5} mol L^{-1} for F^-, $CH_3CO_2^-$ and $H_2PO_4^-$, respectively, and the concentrations of other anions were 3.2×10^{-4} mol L^{-1}, respectively.

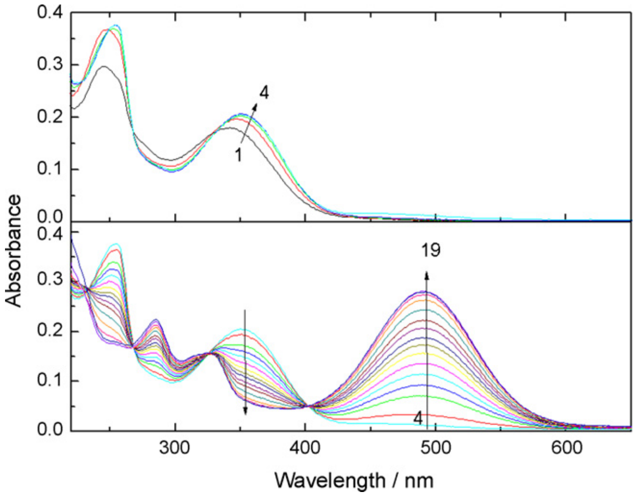

Fig. 3. Absorption spectra of **1**-Hg^{2+} (8.0×10^{-6} mol L^{-1}) in acetonitrile with increasing amounts of F^-. The concentrations of curves 1–4 were 0, 0.2, 0.6, and 0.8×10^{-5} mol L^{-1}, respectively. The concentrations of curves 4–19 were 0.8, 1.0, 1.2, 1.28, 1.36, 1.44, 1.52, 1.6, 1.68, 1.8, 1.92, 2.2, 2.8, 4.0, 8.0, and 20×10^{-5} mol L^{-1}, respectively.

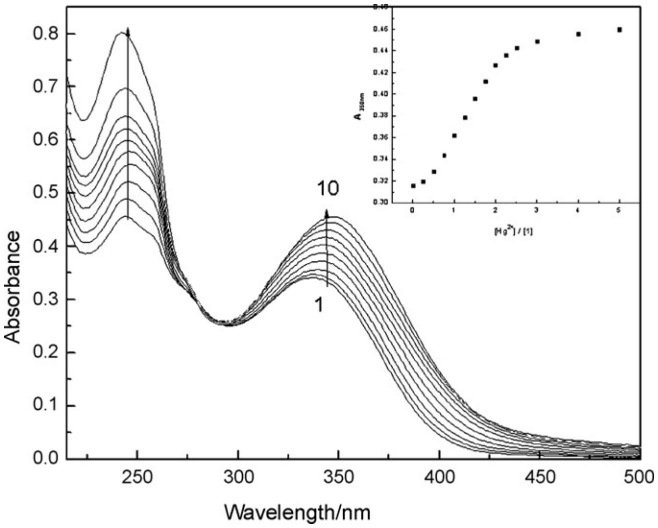

Fig. 4. Absorption spectra of **1** (1.6×10^{-5} mol L^{-1}) in the absence and presence of Hg^{2+} in acetonitrile. The concentrations for curves 1–10 were 0, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 4.0, and 8.0×10^{-5} mol L^{-1}, respectively.

length of absorption spectrum centered at 339 nm, whereas upon addition of F^-, the spectra underwent dramatic change in two steps. When the concentration of F^- was lower than 1.0 equiv. of **1**-Hg^{2+} the spectra slightly red shifted and the absorbance increase. While the concentration increased to more than 1.0 equiv., the absorbance at 339 nm decreased remarkably and a new peak at 490 nm appeared along with the absorbance increase. Clear isosbetic points were observed at 326 and 401 nm. The spectral change kept constant after the addition of 10 equiv. F^-. The color of the solution turned to red which was easily observed via naked eyes. It was assumed that ternary complex of **1**-Hg^{2+}-F^- was formed. F^- behaved linearly in the 8.0×10^{-6} to 2.0×10^{-5} mol L^{-1} concentration range with LOD as 1.4×10^{-6} mol L^{-1}.

In order to explain the interaction between **1**-Hg^{2+} and F^-, the effects of Hg^{2+} or anions on the spectra of **1**–**3** were also investigated, respectively. Fig. 4 showed the titration of **1** with Hg^{2+}. Upon addition of Hg^{2+}, the spectrum of **1** red shifted from 339 to 349 nm and a clear isosbetic point at 294 nm appeared which implied a stometric complex formation. Inset plot of Fig. 4 displayed the absorbance change vs. the concentration ratio of **1** and Hg^{2+}. It confirmed 1:2 (**1**:Hg^{2+}) stoichiometric complex formation. The similar experiment was also performed on **2**, the molar ratio displayed 1:1 complex formation (shown in Fig. S3). However, **3** showed weak affinity to Hg^{2+}. It was explained that Hg^{2+} bound to the thiourea moiety and the hydroxyquinoline moiety of **1** simultaneously. Meanwhile, the binding ability of thiourea moiety with Hg^{2+} was stronger than that of 8-hydroxy quinoline moiety. The binding affinity of **2** to anions followed the order of $CH_3CO_2^- > F^- > H_2PO_4^-$ [31] which was in agreement with the order of anionic basicity. It is because that thiourea is a good hydrogen bond donor which provides two hydrogen atoms to bind with $CH_3CO_2^-$. However, for **1** the order was $F^- > CH_3CO_2^- > H_2PO_4^-$. Job-plot experiments exhibited the binding ratios between **1** and anions such as F^- and $CH_3CO_2^-$ were both 1:1 (seen in Figs. S4 and S5). Thus, it is supposed that F^- bound the hydroxyquinoline moiety instead of the thiourea moiety of **1**. Then we tried to explain the above two-step phenomenon when titrating **1**-Hg^{2+} with F^-. At the beginning, HgF_2 was formed with Hg^{2+} displaced from 8-hydroxy quinoline moiety of **1**-Hg^{2+}. However, with higher concentration of F^-, it formed hydrogen bond with **1**-Hg^{2+} at the hydroxy moiety. Hg^{2+} bound thiourea moiety acting as electron acceptor and F^- serving as electron donor, thus the intramolecular charge transfer was promoted with a new peak at 490 nm appeared.

The effect of the addition order on the spectral change was also studied (seen in Fig. S6). Upon addition of Hg^{2+} into the mixture of **1** and F^-, the new peak at 490 nm was also observed implicating the ternary complex formation. However, when the amount of Hg^{2+} was increased the absorbance at long wavelength decreased and the spectral changed to that of **1**-Hg^{2+} complex. It was assumed that HgF_2 was formed and the rest Hg^{2+} bound hydroxyquinoline moiety.

To further confirm the mechanism, F^- or $CH_3CO_2^-$ was added into the solution of **2**-Hg^{2+}, the spectrum underwent slight change (shown in Fig. S7). Although the competing binding between anions and Hg^{2+} for the thiourea group occurred, no obvious spectral changes were observed since the absorption spectral profile and peak's location of **2**-Hg^{2+} and those of **2**-anion were similar. The results implied that ternary complex could not form because of the absence of simultaneous binding sites for Hg^{2+} and the anion. It also confirmed the binding action of **1** involved both the thiourea group and the hydroxyquinoline group.

We also studied the interaction between **1**-Cu^{2+} and anions (shown in Fig. 5). The results showed the similar spectral change as **1**-Hg^{2+}. However, **1**-Cu^{2+} was sensitive to anions such as F^- and $CH_3CO_2^-$, which indicated that the selectivity of **1**-Cu^{2+} for F^- was poor.

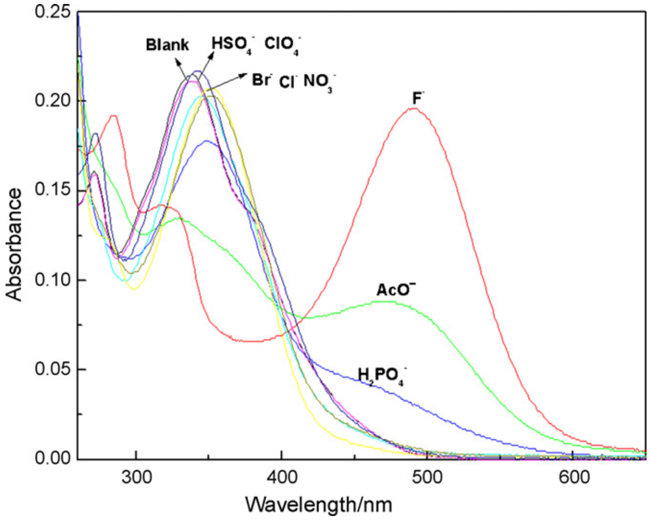

Fig. 5. Absorption spectra of **1**-Cu^{2+} (8.0×10^{-6} mol L^{-1}) complex in the presence and absence of the anion in acetonitrile. The concentrations were 1.2×10^{-4} mol L^{-1} for F^-, $CH_3CO_2{}^-$ and $H_2PO_4{}^-$, respectively. The concentrations of other anions were 2.4×10^{-4} mol L^{-1}, respectively.

4. Conclusion

A novel and ditopic compound, *N*-5-[8-hydroxy-quinoline]-*N*′-4′-nitro phenyl thiourea, was synthesized. Its Hg^{2+} complex sensed F^- by hydrogen bond formation. Intramolecular charge transfer of **1**-Hg^{2+}-F^- led to the red shift of the absorption peak with a vivid color change from colorless to red.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2008.02.024.

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