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ORIGINAL ARTICLE

New Fluorescent and Colorimetric Chemosensor for Detection of Cyanide with High Selectivity and Sensitivity in Aqueous Media

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Abstract A fluorescent and colorimetric chemosensor for detection of cyanide ion based on a styryl quinoline derivative has been designed and synthesized. The chemosensor (*E*)-2-(4-mercaptostyryl)quinolin-8-ol **L** showed high selectivity for detection of cyanide over other anions such as F^-, Cl^-, Br^-, I^-, NO_3^-, SCN^-, N_3^-, ClO_4^-, $H_2PO_4^-$, AcO^-, HCO_3^-, SO_4^{2-} and HSO_4^-in aqueous solution. The chemosensor **L** displayed an immediate visible and fluorescence changes from nearly colorless to orange and greenish-blue to brick-red upon addition of cyanide ion respectively. It is more likely, these distinct changes can be attributed to hydrogen bonding interaction between phenol group and cyanide anion leading to a 1:1 binding stoichiometry following with deprotonation of phenol group. The detection limit for chemosensor **L** toward CN^- was 2.73×10^{-8} M. Thus, the chemosensor can be used efficiently and selectively for detection and monitoring of small amounts of cyanide ion in aqueous media.

Keywords Fluorescence · Chemosensor · Colorimetric · Cyanide ion

Introduction

Due to important role of anions in environmental, chemical, clinical, and biological processes [1–7], detection of anions such as cyanide has been of great interest in supramolecular chemistry. Cyanide is one of the most toxic anions because of its effects on numerous body functions such as inhibit oxygen utilization by cells and binding to the active site of cytochrome oxidase [8]. Therefore, central nervous systems and heart that requiring more oxygen compared with other body organs, are strictly affected by cyanide poisoning. Cyanide could be absorbed through the skin, gastrointestinal track, and the lungs and approximately 0.5–3.5 mg of cyanide per kg of body weight is fatal for human [9]. Despite its high toxicity, cyanide is used in many industrial processes (1.5 million tons per year), such as electroplating of metals, plastics manufacturing, in the recovery of gold and silver from ores, and metallurgy [10–12]. Thus, it is necessary to develop an efficient sensing system for selective detection of cyanide ion. Among the various approaches for the detection of cyanide such as chromatographic [13], flow injection [14, 15] and electrochemical analyses [16–19],fluorescence and colorimetric detections due to their high sensitivity, rapid response rate, easy detection, and low cost are the most convenient methods in this regard. To date, numerous fluorescent sensors for detection of cyanide ion have been developed based on various mechanisms including metal ion coordination of CN^- [20–22], deprotonation reactions [23–26],nucleophilic addition reactions [27–31],and hydrogen bonding interactions [32–35]. Meanwhile, many of these sensors suffer from low selectivity and interference with other anions [36–39].

After our previous work in development of a fluorescence and colorimetric chemosensor for detection of Zn^{2+} and Sn^{2+} [40], herein, we report synthesis of a new simple styryl quinoline based chemosensor **L** and investigation of its application for highly selective detection of CN^- which is one of the most important issues in the environmental chemistry.

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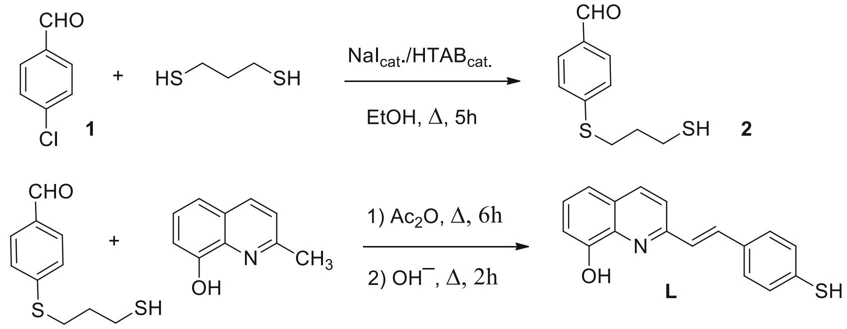

Scheme 1 Synthesis of chemosensor **L** starting from 4-chlorobenzaldehyde

Experimental Section

Materials and Instrumentations

All chemical reagents and solvents used were obtained commercially from Merck (Germany) at analytical grade and used without further purification. NMR spectra were recorded on Bruker Avance NMR spectrometer (Germany) at an operating frequency of 400 MHz for ^{1}HNMR and 100 MHz for ^{13}CNMR. UV/visible absorption spectra were recorded by using the Shimadzu UV-160 (Japan). Fluorescence spectra were measured on a Shimadzu RF-5000 Spectrofluorometer.

Synthesis of (*E*)-2-(4-Mercaptostyryl)Quinolin-8-Ol L

A) In a 25 mL flask a mixture of 4-chlorobenzaldehyde (10 mmol, 1.41 g), 1,3-propanedithiol (11 mmol, 1.19 g), hexadecyltrimethylammonium bromide (HTAB, 20 mg), and NaI (20 mg) were dissolved in EtOH (10 mL) and refluxed for 5 h. Then, the reaction mixture was triturated in EtOAc-H$_2$O (50:50, 30 mL) and the organic phase was separated and dried. After removal of the solvent, the residue was chromatographed on silica gel using EtOAc-hexane (1:5) as eluent to obtain pure 4-((3-mercaptopropyl)thio)benzaldehyde as a creamy-white solid having a characteristic odor (1.17 g, 55%).

4-((3-mercaptopropyl)thio)benzaldehyde: mp: 35 °C (uncorrected); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.92 (qui, 2 H, J = 7.2 Hz), 2.61 (t, 2H, J = 7.2 Hz), 3.08 (t, 2H, J = 7.2 Hz), 7.30 (d, 2H, J = 8.4 Hz), 7.70 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ: 27.1, 29.5, 30.0, 125.5, 127.2, 127.8, 129.0, 190.1; IR (KBr); 2835, 2736(=CH), 2566(S-H), 1694(C = O), 2918, 1590, 1489, 1088, 836.

B) In a 10 mL round bottom flask equipped with a reflux condenser, a mixture of 4-((3-mercaptopropyl)thio)benzaldehyde (5 mmol, 1.06 g) and 8-hydroxyquinaldine (5 mmol, 0.80 g) were dissolved in acetic anhydride (4 mL) and heated under reflux condition for 6 h. After cooling, the reaction mixture was poured in a mixture of ice-water to deposit a crude gummy solid. Then the precipitated solid was added to a solution of NaOH in EtOH (2.5 M, 15 mL) and heated under reflux temperature for 2 h. The reaction mixture was cooled, neutralized with HCl (1 M), and extracted with EtOAc. Then, the organic phase was remove under reduced pressure and the residue was subjected to column chromatography using EtOAc-hexane (1:4) as eluent to afford the pure (*E*)-2-(4-mercaptostyryl)quinolin-8-ol **L** as a yellow powder (0.45 g, 32%).

(*E*)-2-(4-mercaptostyryl)quinolin-8-ol: mp: 87–89 °C (uncorrected);^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.09

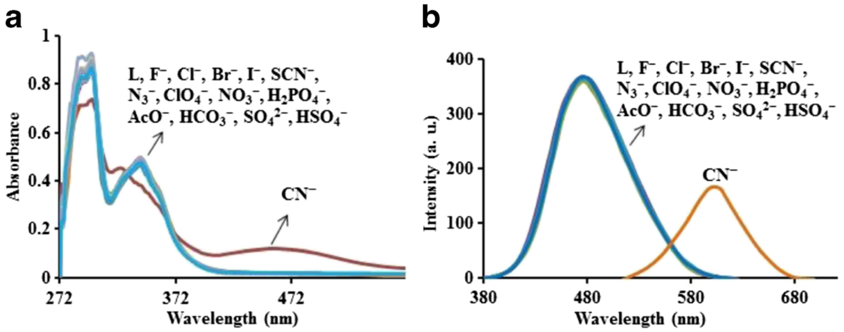

Fig. 1 **a** UV-vis absorption spectra of **L** (3.5 × 10^{-5} M) in DMSO/H$_2$O (50/50 *v*/v) in the presence of F$^-$, Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, SCN$^-$, N$_3^-$, ClO$_4^-$, H$_2$PO$_4^-$, AcO$^-$, HCO$_3^-$, SO$_4^{2-}$, HSO$_4^-$ and CN$^-$ [A^{n-}] 100 μM. (**b**) Fluorescence spectra of **L** (1 μM) with various anions in DMSO/H$_2$O (50/50, *v*/v) [A^{n-}] = 10 μM

Fig. 2 Visible (**a**) and fluorescence changes (**b**) upon addition of various anions ($[A^{n-}] = 5 \times 10^{-5}$ M) to **L**(5×10^{-5} M) in DMSO/H_2O (50/50, *v*/v)

(dd,J_1 = 7.2 Hz, J_2 = 2.0 Hz,1H), 7.35–7.41(m, 2H), 7.47–7.51(m, 3H), 7.72–7.77(m, 3H), 8.12 (d, J = 16 Hz, 1H), 8.29 (J = 8.8 Hz, 1H), 9.56 (s, 1H).^{13}C NMR(100 MHz, DMSO-d_6) δ:110.3, 117.7, 120.4, 127.5, 128.4, 128.5, 129.1, 133.0, 134.5, 134.8, 136.6, 137.9, 152.0, 153.2; Anal. Calcd. for $C_{17}H_{13}NOS$: C, 73.09; H, 4.69; N, 5.01; S, 11.48 Found: C, 73.13; H, 4.67; N, 5.05; S, 11.45.

Results and Discussion

The chemosensor (*E*)-2-(4-mercaptostyryl)quinolin-8-ol **L** was synthesized in three simple steps starting from 4-chlorobenzaldehyde as a readily available compound. (Scheme 1). First, 4-chlorobenzaldehyde**1** was reacted with 1,3-propanedithiol to produce 4-((3-mercaptopropyl)thio)benzaldehyde**2**. After that, compound **2** was condensed with 8-hydroxyquinaldine in the presence of acetic anhydride following with base catalyzed hydrolysis with ethanolic NaOH to afford (*E*)-2-(4-mercaptostyryl)quinolin-8-ol **L** as a yellow solid (scheme 1).

The anion sensing of **L** was first investigated by UV/visible absorption spectra. Figure 1 shows the absorbance change of **L** upon addition of various anions including F^-, Cl^-, Br^-, I^-, NO_3^-, SCN^-, N_3^-, ClO_4^-, $H_2PO_4^-$, AcO^-, HCO_3^-, SO_4^{2-}, HSO_4^- and CN^- (in DMSO/H_2O, 50/50 *v*/v). As shown in the Fig. 1, the chemosensor **L** displayed only a distinct response to CN^- and other anions had no obvious effect in UV/visible absorption spectra. It was found that, bare chemosensor **L** showed intense absorption bands at 298 nm (ε = 23,314 M^{-1} cm^{-1}) and 341 nm (ε = 13,514 M^{-1} cm^{-1}). When CN^- ion was added to the solution of **L**, intensity of signal at 298 nm was decreased with no shift and the intensity of signal at 341 nm was also suppressed alongside with a small blue-shift and subsequently a new broad peak was appeared in 460 nm. As shown in Fig. 1b, an emission band at 475 nm for the fluorescence spectra of the bare chemosensor **L** was observed and upon addition of CN^- a big red-shift to 602 nm was detected and the fluorescence intensity was notably declined.

Fortunately, both colorimetric and the fluorescence response of **L** to CN^- can be traced visually. During addition a 50 μM solution of CN^- to also a 50 μM colorless solution of **L** a vivid orange color was appeared instantly while, the fluorescence emission was changed from a greenish-blue to a brick-red under illumination with a 365 nm UV lamp (Fig. 2). These clear changes indicate that compound **L** can be used as a selective, sensitive, and fast chemosensor for detection of cyanide anion.

The fluorescence intensity of **L** in the presence of various concentration of CN^- in DMSO/H_2O (50/50, *v*/v) is presented in Fig. 3. As it is obvious from Fig. 3a, the fluorescence intensity at 602 nm was increased with increasing the

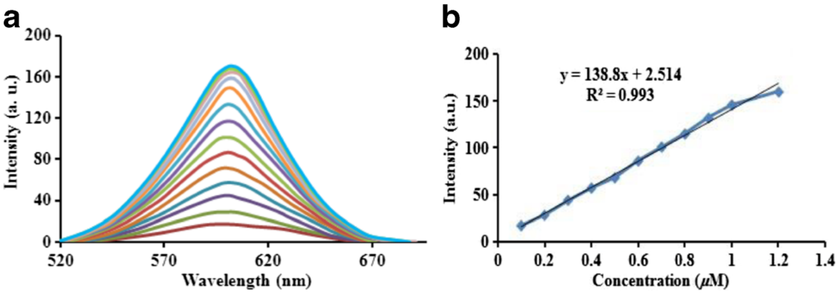

Fig. 3 **a** Fluorescence emission spectra of **L** (1 μM) in the presence of different concentrations of CN^- (0.1–10 μM); (**b**) linear relationship between the fluorescence intensity at 602 nm and in the concentration range of 0.1–1.2 μM of CN^-

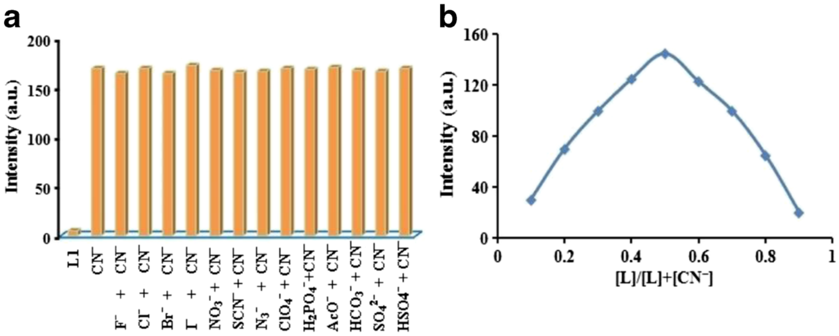

Fig. 4 **a** Fluorescence intensity changes at 620 nm of **L** (1 μM in DMSO/H_2O 50/50, *v*/v) upon addition of CN^- (10 μM) and different anions $[A^{n-}]$ = 100 μM; (**b**) Job's plot diagram of sensor **L** for CN^- indicating a 1:1 interaction (the total concentrations of **L** and CN^- were 2 μM)

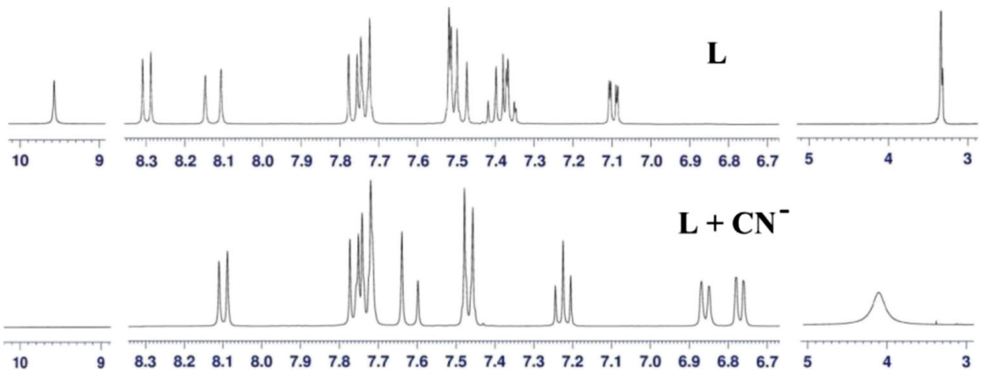

Fig. 5 ^{1}HNMR spectra changes of **L** in a solution (DMSO-d_6), upon the addition of CN^- anion

concentration of cyanide ion. The calibration curve of the fluorescence emission at 602 nm is shown in Fig. 3b which indicate that, there is a good linear relationship between cyanide concentration and the fluorescence intensity in the range of 0.1–1.2 μM ($R = 0.993$). Various solvents such as CH_3CN, EtOH, dioxane, and DMF in different H_2O percentages were examined for the evaluation of chemosensory role of **L**. We practically found that the optimal solvent mixture was DMSO/H_2O (50/50, *v*/v). The detection limit of **L** for CN^- in DMSO/H_2O (50/50, *v*/v) was measured to be 2.73×10^{-8} M which is far lower than the World Health Organization (WHO) guideline value for cyanide ion (1.9 μM).

To evaluate the selectivity of chemosensor **L** for detection of cyanide anion, competitive experiments were conducted in the presence of 100 equiv. of other anions in the solution of DMSO/H_2O. Figure 4a indicates that, except CN^-, other anions have no observable effect on fluorescence emission of **L** at 602 nm. These findings confirm the high selectivity and anti-interference of chemosensor **L** for detection of cyanide anion.

The stoichiometric ratio between the **L** and CN^- was determined by Job's plots method. As shown in Fig. 4b, a 1:1 stoichiometry was observed for the interaction of **L** with CN^- ion.

As well known, a long response time is a serious problem that chemosensors often encounter. In our study, the colorimetric and the fluorescence response time of chemosensor **L** to CN^- was very fast and in the order of a few seconds (<5 s) and conservative (Fig. 4 in Supporting Information).

The interaction mode and the detection mechanism of sensor **L** for detection of CN^- was further analyzed by ^{1}HNMR spectroscopy through adding an equiv. amount of a solution

Table 1 Comparison of other researches with our work

Fluorescent and colorimetric sensors	Advantage/Disadvantage
Lee M, Jo S, Lee D, Xu Z, Yoon J (2015) Dyes Pigm 120:288–292.	Interference with other anions
Chen Y, Shi W, Hui Y, Sun X, Xu L, Feng L, Xie Z (2015) Talanta137:38–42.	Low fluorescence color change
Singh Y, Ghosh T (2016) Talanta 148:257–263.	Low color change
Kim GJ, Kim HJ (2010) Tetrahedron Lett. 51:2914–2916.	Long detection time
Lin YD, Peng YS, Su W, Tu CH, Sun CH, Chow TJ (2012) Tetrahedron 68:2523–2526.	High detection limit
This work	No Interference with other anions, high color and fluorescence change, short detection time and low detection limit.

NaCN in DMSO-d_6 to a solution of chemosensor **L** also in DMSO-d_6. Probably, upon addition of cyanide ion, a hydrogen bonding interaction between phenol group and cyanide ion is established and it is more likely following that, deprotonation of hydroxyl group is occurred. This fact was approved by disappearance of phenolic proton signal at 9.56 ppm and occurrence a noticeable downfield shift for H_2O signal residue at 3.34 ppm. Furthermore, aromatic and vinylic protons were also displayed substantial upfield shifts as shown in the Fig. 5.

A comparison of other works with our study was shown in Table 1.

As shown in Table 1, high color and fluorescence change, short detection time, low detection limit, and no interference with other anions are the salient features of our chemosensor.

Conclusions

In summary, a new colorimetric and fluorescent chemosensor for rapid, highly selective and sensitive detection of cyanide anion was designed and synthesized. Upon addition of CN^- to a solution of **L**, a significant color change was observed under visible light from colorless to orange and from greenish-blue to brick-red under UV illumination with a large red-shift. The detection mechanism was confirmed by ^{1}HNMR and Job's plot and indicated that, there was a 1:1 stoichiometric ratio between the **L** and CN^- and following the establishment of a hydrogen bonding interaction between the CN^- and phenolic group, deprotonation of hydroxyl group was occurred. The detection limit was measured to be 2.73×10^{-8} M, which explicitly demonstrate that chemosensor **L** can be used as an efficient sensor for the rapid detection of CN^- in aqueous media.

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