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ORIGINAL PAPER

# A Selective Spectrofluorometric Determination of Micromolar Level of Cyanide in Water Using Naphthoquinone Imidazole Boronic-Based Sensors and a Surfactant Cationic CTAB Micellar System

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**Abstract** We developed a new spectrofluorometric method for qualitative and quantitative determination of cyanide in water using the incorporation of naphthoquinone imidazole boronic-based sensors (***m*-NQB** and ***p*-NQB**) and a cationic surfactant, certyltrimethyl ammonium bromide (CTAB). This micellar system exhibited great selectivity for cyanide detection with an assistance of the cationic surface of micelle. The interaction of boronic acid of the sensor toward cyanide in CTAB micellar media gave a quantitative measure of cyanide concentration in the micromolar level. Under the optimal condition, fluorescence intensity at 460 nm of ***m*-NQB** and ***p*-NQB** provided two sets of linear ranges, 0.5–15 $\mu$M and 20–40 $\mu$M and the limit of cyanide detection of 1.4 $\mu$M. Hence, both sensors in CTAB aqueous micellar system offered a considerably promising cyanide detection with 1000–fold enhancement of the detection limit compared to those studied in DMSO: $H_2O$. The proposed sensors could also be used to determine cyanide in water with good analytical characteristics.

**Keywords** Naphthoquninone imdazole · Boronic acid · Micromolar cyanide detection · CTAB · Micellar system

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## Introduction

Cyanide ion is extremely toxic substance due to metabolic asphyxiation. The World Health Organization (WHO) has suggested that an acceptable cyanide concentration for drinking water is 0.07 mg/L [1]. Recently, cyanide level in blood for fire victim has been reported to be *ca.* 20 $\mu$M [2]. Any potential cyanide determination methods should offer the detection limit in micromolar concentration level. As described in previous reports, low concentration cyanide detection in water can be accomplished by various instrumental methods such as voltammetry [3], ion selective potentiometry [4], indirect atomic absorption spectrometry [5], spectrofluorimetry in flow systems [6, 7]. However cyanide determination by spectrofluorimetry methods often needed complicated separation steps such as liquid chromatography [8, 9]. In the field of supramolecular chemistry, the development of cyanide sensors has been widely considered due to its simple procedure and reasonable cost with high selectivity and sensitivity [10–26]. During the past decade, synthetic cyanide chemosensors utilized H-bonding interactions [10], metal coordination [11–14] and nucleophilic substitution of cyanide [15–24] for cyanide recognition events have been reported. However, most of them showed excellent characteristic of cyanide probes in organic solvents [10–12, 15–18, 20–22, 24] especially, in the cases of non-covalent based sensors. Regarding to the remarkable nucleophillic properties of cyanide, many organic reagents were used to serve as cyanide probes for low concentration of cyanide detection in water [15, 22–28]. Recently, boronic acid probes have shown an excellent characteristic of

fluorometric probes for detecting micromolar concentration of cyanide in water [25–29].

In our previous work [29], we successfully synthesized new acceptor-donor-acceptor (A-D-A) type of fluorescence sensors for cyanide (Scheme 1) possessing naphthoimidazolediones as a main donor site and boronic acid as an acceptor site. The results showed that ***m*-NQB** and ***p*-NQB** offered a good characteristic of fluorescence probes for cyanide in terms of selectivity and sensitivity in the mixture of DMSO and water (1:1).

Upon interacting with cyanide, fluorescence spectra of these sensors showed a new emission band at 460 nm due to the intramolecular change transfer (ICT) mechanism. The alternation of the boron center from the electron deficient $sp^2$ boron, R-B$(OH)_2$, to the electron rich $sp^3$ boron, R-B$(CN)_3^-$, resulted in the switching on of the ICT band at 460 nm with a large Stoke shift ($\Delta\lambda_{ex\text{-}emiss}$=120 nm) as well as a large blue shift of *ca*. 100 nm. Unfortunately, this approach gave a low detection limit, a slow rate of cyanide-substitution on the boron center and a poor solubility in water. It is very challenging to improve the efficiency of neutral boronic acid based receptors, ***o*-NQB, *m*-NQB** and ***p*-NQB,** for micromolar detection of cyanide in water without any synthetic modification. Previously, a number of the micellar systems were used to improve the efficiency of the synthetic chemosensors for detecting cations [30–35] but anion detections were rarely studied [36–39]. The incorporation of our sensors into a micellar system was expected to not only increase solubility of sensors in water but also enhance the cyanide complexation ability of sensors.

Herein, we describe a protocol for optimum micellar system in detecting micromolar concentration of cyanide in water by the incorporation of the synthesized receptors (***o*-NQB, *m*-NQB** and ***p*-NQB)** into a cationic surfactant (CTAB). We evaluate the stability constants of the *tri*-substitution of cyanide on the boron centers of ***m*-NQB** or ***p*-NQB** in the CTAB micellar system, while such a stability constant of this approach could not be obtained in DMSO:$H_2O$. The validation of our sensing approach has also been carried out to determine cyanide in drinking water samples.

## Experimental

### Apparatus

All of fluorescence spectra were recorded on a Varian Cary Eclipse spectrophotometer (Australia) with excitation and emission slits at 10.0 nm, $\lambda_{ex}$=344 nm and scan rate 120 nm/min.

### Reagent and Materials

Analytical grade surfactants, certyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), sodium dodecyl sulfate (SDS), and Triton X-100 (TX-100) were purchased from Merck (Germany). Spectroscopic grade ethanol was purchased from Merck (Germany). Water used for the experiment was purified with a Milli-Q filtration system (Millipore). Sensors, ***m*-NQB**, ***p*-NQB,** and ***o*-NQB** were prepared according to the literature [29].

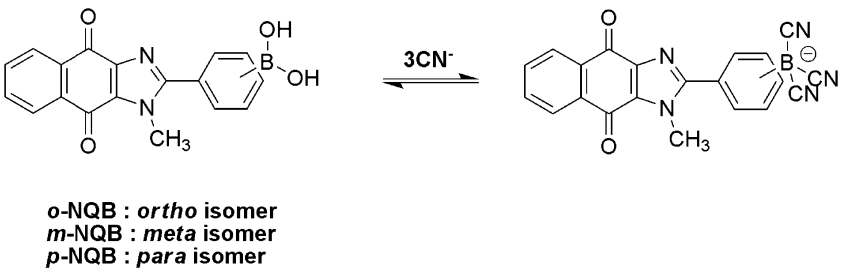
### Stock Solutions

A sensor stock solution of ***m*-NQB**, ***p*-NQB,** and ***o*-NQB** ($2.5\times10^{-4}$ mol/L) was prepared in spectroscopic grade ethanol. A surfactant stock solution CTAB, DTAB, TTAB, TX-100 and SDS ($1.25\times10^{-2}$ mol/L) was prepared in Milli-Q water. A $2.5\times10^{-3}$ mol/L standard stock solution of potassium salts of anions including KCN, KF, KAcO, KBzO, $KH_2PO_4$, $KNO_3$, $KClO_4$, KCl, KBr, KSCN, and KI was prepared in Milli-Q water.

### Procedure

#### *Construction of Calibration Graphs*

In a 5.0 mL volumetric flask, 1.0 mL of stock solution of a sensor was mixed with 2.0 mL of stock solution of CTAB. Aliquots of the stock solution of KCN were then added to the mixture to give the final concentration of $CN^-$ in the range of 0–250 $\mu$M upon the volume adjustment with Milli-Q water. After standing at room temperature for




***o*-NQB : *ortho* isomer**
***m*-NQB : *meta* isomer**
***p*-NQB : *para* isomer**

**Scheme 1** Equilibrium involved in the interaction between naphthoimidazolediol and boronic acid based sensors, ***o*-NQB**, ***m*-NQB** and ***p*-NQB** and cyanide

30 min, the sample mixture was transferred to a 10.0 mm width quartz cell and then fluorescence spectra were recorded with excitation wavelength at 344 nm. Calibration graphs were obtained by the plot of fluorescence intensity at 460 nm and KCN concentrations.

*Cyanide Sensing with Various Surfactants*

Into a 5.0 mL volumetric flask, 1.0 mL of stock solution of a sensor was mixed with a stock solution of surfactants (CTAB, SDS, TX-100) and 0.1 mL of stock solution of KCN to give a final concentration of $5\times10^{-5}$ mol/L cyanide ion, $5\times10^{-5}$ mol/L sensor and $5\times10^{-3}$ mol/L surfactant with Milli-Q water. After standing at room temperature for 30 min, the sample mixture was transferred to a 10.0 mm width quartz cell and then fluorescence spectra were recorded with the excitation wavelength at 344 nm.

*Anion Sensing with Excess Anions in the CTAB Micellar System*

In a 5.0 mL volumetric flask, 1.0 mL of stock solution of a sensor was mixed with 2.0 mL of stock solution of CTAB. Then, 0.10 mL of stock solution of potassium salts of anions was added to the mixtures. Upon the volume adjustment with Milli-Q water, the final concentration of the anion, the sensor and the surfactant are $5\times10^{-5}$ mol/L, $5\times10^{-5}$ mol/L and $5\times10^{-3}$ mol/L, respectively. After standing at room temperature for 30 min, the sample mixture was transferred to a 10.0 mm width quartz cell and then fluorescence spectra were recorded with the excitation wavelength at 344 nm.

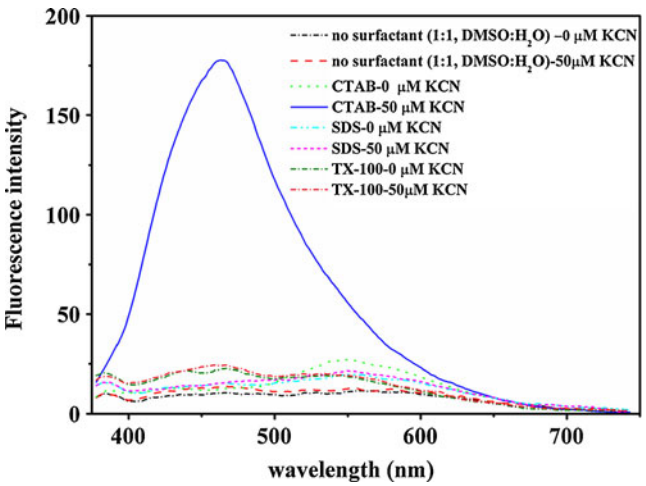



**Fig. 1** Fluorescence spectra of ***m*-NQB** and ***m*-NQB** + 50 M KCN with various types of surfactants ($5.0\times10^{-5}$ mol/L of ***m*-NQB**, $5.0\times10^{-3}$ mol/L of surfactant in 1:4 ethanol:$H_2O$)

**Table 1** Fluorescence enhancement ($I/I_0$ at 460 nm) in different media of ***m*-NQB**

| Medium | $I/I_0$ at 460 nm |
|---|---|
| 1:1 DMSO-$H_2O$ | 1.30 |
| $5.0\times10^{-3}$ mol/L of CTAB | 14.74 |
| $5.0\times10^{-3}$ mol/L of TX-100 | 1.02 |
| $5.0\times10^{-3}$ mol/L of SDS | 1.12 |

*Fluorescence Titrations with $CN^-$ in Optimum Conditions of the Micellar System*

In a 5.0 mL volumetric flask, 1.0 mL of ethanol solution of the sensors was mixed with 2.0 mL of the stock solution of CTAB. Then, the mixture was added with portions of the stock solution of KCN to give final concentrations of $CN^-$ ranging from 0 to 250 $\mu$M after the volume adjustment with MilliQ water. After standing at room temperature for 30 min, the sample mixture was transferred to a 10.0 mm width quartz cell and then fluorescence spectra were recorded with the excitation wavelength at 344 nm.

*Effect of Interference Anions on Cyanide Sensing under Optimum Condition of Micellar System*

In a 5.0 mL volumetric flask, 1.0 mL of ethanol solution of the sensors and 2.0 mL of the stock solution of CTAB was mixed with 0.10 mL of stock solution of KCN to give the final concentration of 1.3 $\mu$g/mL of $CN^-$. Then, the mixture was added with portions of the stock solution of interference anion salts after the volume adjustment with MilliQ water. After standing at room temperature for 30 min, the sample mixture was transferred to a 10.0 mm width quartz cell and then fluorescent spectra were recorded with excitation wavelength at 344 nm.

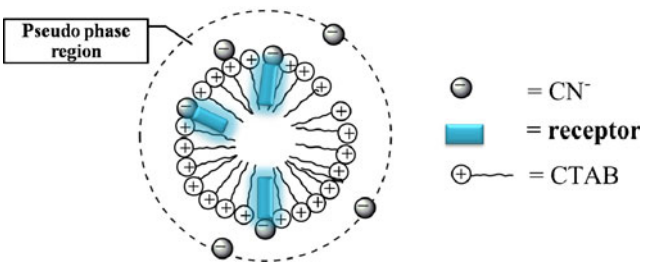



**Fig. 2** The proposed model of the reaction of receptors and cyanide in the CTAB micellar system

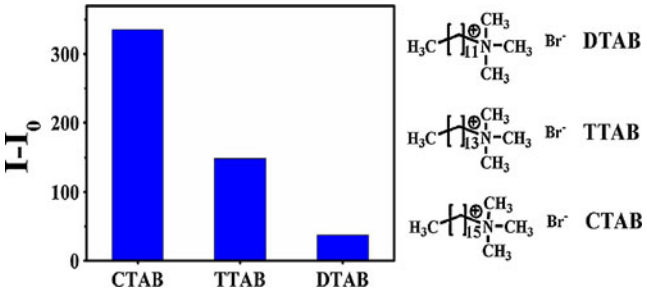



**Fig. 3** Fluorescence responses (I-$I_0$ at 460 nm) of ***m*-NQB** and ***m*-NQB** + 50 $\mu$M KCN with various types of cationic surfactants ($5.0\times10^{-5}$ mol/L of ***m*-NQB**, $5.0\times10^{-3}$ mol/L of surfactant in 1:4 ethanol:$H_2O$)

*Cyanide Detection of Drinking Water Sample*

In a 5.0 mL volumetric flask, 1.0 mL of stock solution of a sensor and 2.0 mL of stock solution of CTAB. Then the commercially drinking water sample was used for the volume adjustment to give the final concentration of 40%(V/V) of the sample. The portion of KCN stock solution was spiked to the mixture to give the final concentration of 5–40 $\mu$M of $CN^-$. After standing at room temperature for 30 min, the sample mixture was transferred to a 10.0 mm width quartz cell and then fluorescent spectra were recorded with excitation wavelength at 344 nm.

## Results and Discussion

Effect of Surfactant Types

Three types of surfactants, neutral (TX-100), anionic (SDS) and cationic (CTAB) surfactants were first examined for fluorescence response in the presence of 50 $\mu$M cyanide ion (50 $\mu$M of a sensor in 5 mM of surfactant

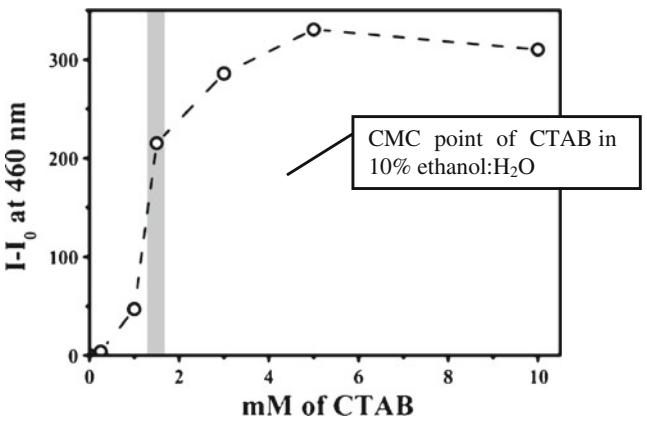



**Fig. 4** Fluorescence response (I-$I_0$ at 460 nm) of ***m*-NQB** ($5.0\times10^{-5}$ mol/L) + 50 $\mu$M KCN in various concentrations of CTAB and CMC of CTAB in 10% ethanol:$H_2O$ shown as gray area [43]

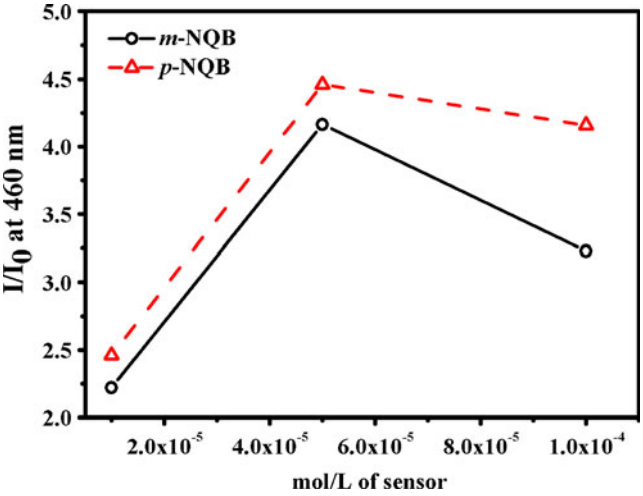



**Fig. 5** Fluorescence response of ***m*-NQB** + 25 $\mu$M KCN and ***p*-NQB** + 25 $\mu$M KCN with various concentrations of sensors (100 equivalents of CTAB compared to sensors in 1:4 ethanol:$H_2O$)

in 1:4 ethanol:$H_2O$). Due to the sustainable pH under micromolar concentration of the cyanide (50 $\mu$M) in water, the pH control using buffer was not required in these studies.

All types of surfactants, cationic, anionic, and neutral surfactants were able to improve the solubility of the sensors, ***o*-NQB**, ***m*-NQB** and ***p*-NQB,** in water. Emission spectra of free sensors in three micellar systems exhibited similar features with emission maxima at 560 nm. Fluorescence spectra of ***m*-NQB** in different media are shown in Fig. 1. The fluorescence spectra showed that the characteristic of $sp^3$ band of ***m*-NQB** upon binding with $CN^-$ at 460 nm was remarkably affected in the CTAB system while

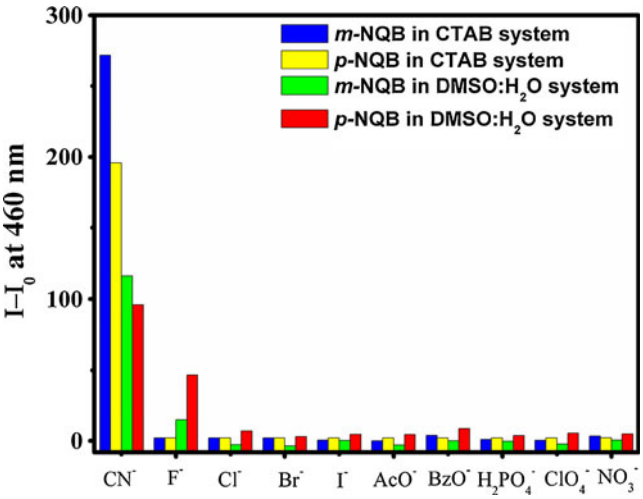



**Fig. 6** Fluorescence responses (I-$I_0$ at 460 nm) of ***m*-NQB** and ***p*-NQB** in the CTAB micellar system in the presence of 50 $\mu$M (1 equiv.) of various anions ($5.0\times10^{-5}$ mol/L of sensors, $5.0\times10^{-3}$ mol/L of CTAB in 1:4 ethanol:$H_2O$) and fluorescence responses (I-$I_0$ at 460 nm) of ***m*-NQB** and ***p*-NQB** in DMSO:$H_2O$ system with 25 mM (500 equiv.) of various anions ($5.0\times10^{-5}$ mol/L of sensor in 0.1 mol/L of NaCl in 50% DMSO: HEPES pH 7.4)

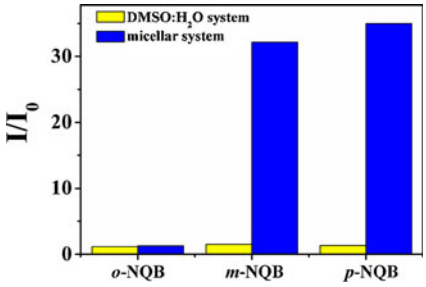



**Fig. 7** Fluorescence responses ($I/I_0$ at 460 nm) of ***o*-NQB**, ***m*-NQB** and ***p*-NQB** with 0.25 mM of cyanide for 30 min of DMSO:$H_2O$ system ($5.0\times10^{-5}$ mol/L of sensor in 0.1 mol/L of NaCl in 50% DMSO:HEPES pH 7.4) and micellar system ($5.0\times10^{-5}$ mol/L of sensors, $5.0\times10^{-3}$ mol/L of CTAB in 1:4 ethanol:$H_2O$)

in other types of the media including TX-100, SDS and DMSO-$H_2O$ showed slightly response of this emission band upon the addition of 50 $\mu$M $CN^-$. As illustrated in Table 1, the fluorescence enhancement of the band at 460 nm ($I/I_0$) revealed that CTAB micellar system could improve the complexation ability of the sensor with $CN^-$. In the case of SDS anionic micelle, the fluorescence response of the ICT band (460 nm) remained unchanged in both sensors suggesting that interactions between sensors and cyanide did not occur in this system. This result implied that the complexation ability of sensors toward cyanide was interrupted by the electrostatic repulsion between the anionic micellar surface and cyanide. Therefore, neutral and anionic surfactants improved only the solubility of the sensors in water but did not promote the cyanide-substitution on the boron center.

According to the previous literature, the model of the reaction between sensors and cyanide in the micellar system was proposed in Fig. 2 [34, 40–42]. The improvement of cyanide complexation ability in CTAB probably stemmed from electrostatic interactions between the cationic surface of the CTAB micelle and the negative charge of cyanide. In the psudo-phase region of the micelle surface, the local concentrations of the sensors and cyanide increased resulting in the enhancing of interactions between both species. Subsequently, the boronic acid sensor was easily converted to the cyanide-adduct species. The anionic R-$B(CN)_3^-$species produced fluorescence enhancement at 460 nm as described previously. Additionally, this method improved the emission properties of R-$B(CN)_3^-$due to a good distribution of the sensors in hydrophobic region of the micellar system. This distribution could prevent the solvation of sensors by water and polar solvents, which probably caused a low quantum yield of the fluorophore in aqueous system due to non-emissive relaxation by polar solvents.

The effect of the chain length of cationic surfactants was also explored. Figure 3 showed the fluorescence responses ($I-I_0$ at 460 nm) of ***m*-NQB** and ***m*-NQB** + 50 $\mu$M KCN in

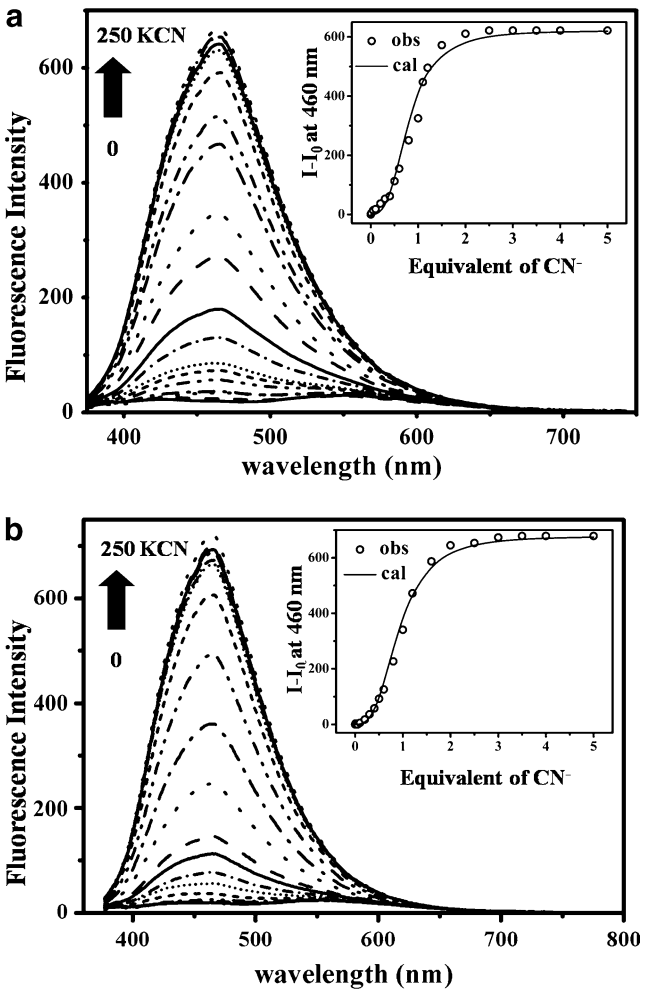



**Fig. 8** **a** Fluorescence titration spectra of ***m*-NQB** and **b** fluorescence titration spectra of ***p*-NQB** upon the addition of cyanide ion in CTAB micellar system ($5.0\times10^{-5}$ mol/L of sensors, $5.0\times10^{-3}$ mol/L of CTAB in 1:4 ethanol:$H_2O$)

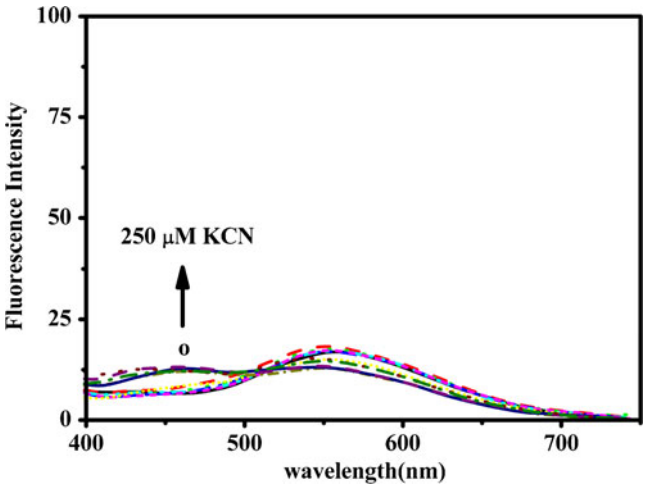



**Fig. 9** **a** Fluorescence titration spectra of ***o*-NQB** upon the addition of cyanide ion in the CTAB micellar system ($5.0\times10^{-5}$ mol/L of ***o*-NQB**, $5.0\times10^{-3}$ mol/L of CTAB in 1:4 ethanol:$H_2O$)

**Table 2** Effect of interference anions on the determination of $CN^-$ ($C_{CN}$=1.3 μg/mL)

| Interference ions | Tolerance limit (μg/mL) | |
|---|---|---|
| | *m*-NQB | *p*-NQB |
| $F^-$ | 0.48 | 1.90 |
| $Cl^-$ | 1.78 | 3.55 |
| $Br^-$ | 11.99 | 5.99 |
| $OAc^-$ | 8.85 | 4.43 |
| $NO_3^-$ | 3.10 | 3.10 |

DTAB, TTAB and CTAB. It was clearly seen that incorporated sensors in a longer chain micelles, CTAB, gave remarkable cyanide sensing properties compared to that in shorter chain micelles. Regarding to the high CMC point of a shorter chain cationic surfactant, DTAB could not be aggregated in a micellar form at $5.0\times10^{-3}$ mol/L in 1:4 ethanol:$H_2O$. Thus, the improvement of cyanide sensing could not occur in this condition for DTAB [42]. On the other hand, the longer chain CTAB presumably gave a larger surface area than DTAB did. Therefore, CTAB offered a higher concentration of the sensor and the cyanide at the psuedo-phase region resulting in a strong fluorescence response [42]. The results shown in Fig. 3 also agreed well with the proposed model in Fig. 2.

## Effect of CTAB Concentrations

The effect of CTAB concentrations was also studied as shown in Fig. 4. The concentration of CTAB at $1.5\times10^{-3}$ mol/L showed a large change of fluorescence response of ***m*-NQB** and ***p*-NQB**. These results agreed well with critical micelle concentration (CMC) of CTAB reported in the literature (the CMC of CTAB is 1.5 mM in 10% of ethanol in water) [43]. However, the concentration of CTAB at $5.0\times10^{-3}$ mol/L provided the highest response. Therefore, this concentration of CTAB was used in all preparations of the micellar system. (100 equivalents of CTAB compared to the sensor)

## Effect of Sensor Concentrations

The effect of sensor concentrations was also examined in the presence of 100 equivalents of CTAB compared to the sensor concentration and 25 $\mu$M of KCN. Fluorescence responses of ***m*-NQB** and ***p*-NQB** were displayed in Fig. 5. $I/I_0$ of the detection system showed the highest response at $5.0\times10^{-5}$ mol/L of sensors and $5.0\times10^{-3}$ mol/L of CTAB. At low concentration of the sensor, the accessibility of the molecular probes toward cyanide was disturbed by the competitive interaction between CTAB and cyanide. At high concentration of the sensor ($1.0\times10^{-4}$ mol/L), fluorescence responses were slightly decreased probably due to a low amount of cyanide and an excessive amount of the sensor incorporated in the micelle. Therefore, the optimum condition selected for the cyanide detection was $5.0\times10^{-5}$ mol/L of the sensor and $5.0\times10^{-3}$ mol/L of CTAB.

## Selectivity and Sensitivity of Sensors in the Micellar System

The selectivity of sensors, ***m*-NQB** and ***p*-NQB**, with various anions was evaluated under the optimum conditions as shown in Fig. 6. Both sensors in the CTAB micellar system exhibited a dramatically selective response at 460 nm for $CN^-$ while other anions gave slight changes in fluorescence enhancement. In addition, the micellar system can improve much greater selectivity than the DMSO: $H_2O$ (1:1) system [29].

To compare the sensitivity of ***m*-NQB** and ***p*-NQB** for cyanide detection in the micellar system and in the solution of DMSO:$H_2O$ in the same period of time (30 min), the fluorescence responses (shown in Fig. 7) of ***m*-NQB** and ***p*-NQB** with 0.25 mM $CN^-$ in the micellar system showed remarkably higher sensitivity than that in the solution of the mixed DMSO: $H_2O$. As described in our previous work, the sensors in DMSO:$H_2O$ system showed responses in a millimolar level of $CN^-$ while in the micellar system, the sensors exhibited the working range in a micromolar level of $CN^-$ [29]. Furthermore, the sensors in the CTAB micellar system showed the complete emission change

**Table 3** Analytical characteristics of ***m*-NQB** and ***p*-NQB** sensors in the optimal condition of CTAB micellar system (50 $\mu$M of ***m*-NQB**, $5.0\times10^{-3}$ mol/L of surfactant in 1:4 of ethanol:$H_2O$)

| Sensor | Linear range (μM) | Linear regression equation (μM) | Correlation coefficient (R) | Detection limit[a](μM) |
|---|---|---|---|---|
| ***m*-NQB** | 2.5–15 | $I=3.15C_{CN}+25.47$ | 0.9956 | 1.4 |
| | 20–40 | $I=11.22C_{CN}-135.12$ | 0.9920 | |
| ***p*-NQB** | 2.5–15 | $I=2.37C_{CN}+15.09$ | 0.9970 | 1.4 |
| | 20–40 | $I=6.84C_{CN}-72.46$ | 0.9963 | |

**a** Detection limits were calculated from the concentration at which the fluorescence intensity is 3 times of standard deviation of the blank ($n$=10) [45]

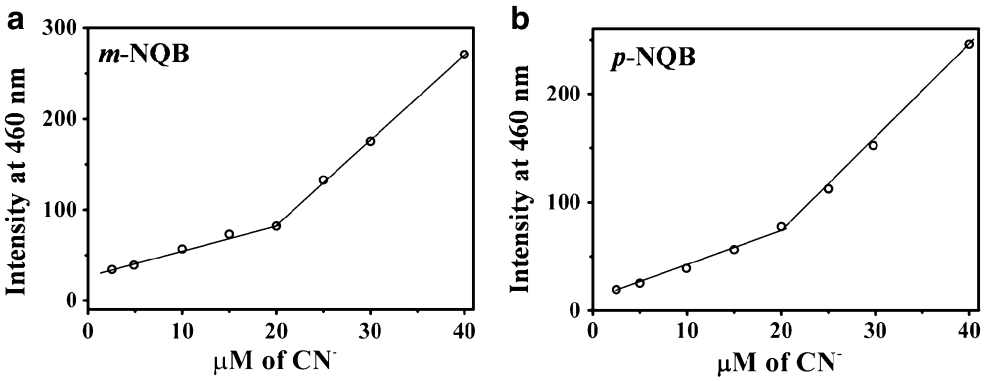



**Fig. 10** Calibration graphs of cyanide 2.5–40.0 $\mu$M for **a *m*-NQB** and **b *p*-NQB** in optimum condition ($5.0\times10^{-5}$ mol/L of sensors, $5.0\times10^{-3}$ mol/L of CTAB in 1:4 ethanol in $H_2O$)

upon the addition of 0.25 mM of $CN^-$ whereas the sensors in DMSO:$H_2O$ gave insignificant response ($I/I_0=1$).

Stability Constants for Sensor-Cyanide Adducts

Fluorescence titration was carried out to elucidate the cyanide binding properties of the sensors in the cationic micellar optimum condition. From our attempts in the previous work, binding constants of sensor-cyanide adducts in DMSO:HEPES (pH 7.4) system could not be obtained. This disadvantage was possibly stemmed from the interference of hydroxide ion which was generated by a very high concentration of cyanide in the solution of 50% DMSO: HEPES (pH 7.4). Regarding the micellar system, the fluorescence titration was performed at low concentration of cyanide (0–250 $\mu$M) without any buffer because the pH of solution remained at pH 7 even adding excess cyanide. Therefore, the interference from hydroxide ion could be neglected. As illustrated in Fig. 8, the emission intensity at 460 nm progressively increased upon the increment of the cyanide concentration. Interestingly, the fluorescence intensity was saturated at 3 equivalents (150 $\mu$M) of KCN. It was indicative of the *tri*-substitution of cyanide on the boron center as described in previous report [27]. The overall stability constants ($\beta_3$) of *tri*-cyanide complexes of sensors, ***m*-NQB** or ***p*-NQB**, in the CTAB micellar media ($5\times10^{-5}$ mol/L of sensors, $5\times10^{-3}$ mol/L of CTAB in 1:4 ethanol:$H_2O$) were evaluated by fitting the titration curves using equations 1 and 2, where $n$=3. The intensities $I_{min}$ and $I_{max}$ are the initial and the final fluorescence intensities of the titration curves, respectively [44].

$$I = \frac{I_0 + I_\infty \beta_n [CN^-]^n}{1 + \beta_n [CN^-]^n} \quad (1)$$

$$\beta_n = \frac{\left[RB(OH)_{3-n}(CN)_n^-\right]}{\left[RB(OH)_2\right][CN^-]^n} \quad (2)$$

Overall stability constants of the *tri*-cyano substituted complex (log $\beta_3$) of ***m*-NQB** and ***p*-NQB** obtained from the best fit of the curves were 4.16±0.09 and 3.99±0.05, respectively. These results showed that *meta* and *para* isomers possessed similar binding abilities towards cyanide in the CTAB micellar system. Therefore, the position of the boronic acids at *meta* and *para* does not give a different influence on cyanide substitution on the boron center.

Sensitivity of the *ortho* isomer, ***o*-NQB**, was also measured in the CTAB micellar system. However, in the mixture of DMSO:$H_2O$, ***o*-NQB** showed insignificant fluorescence response toward cyanide substitution due to steric hindrance [27]. As shown in Fig. 9, ***o*-NQB** also showed a poor response toward cyanide in the optimal CTAB micellar system. It indicated that the steric hindrance between hydroxyl groups of boronic acid played an important factor for cyanide substitution on this isomer

**Table 4** Analysis of $CN^-$ in drinking water

| Added $CN^-$ ($\mu$M) | *m*-NQB | | *p*-NQB | |
|---|---|---|---|---|
| | Found ($\mu$M) | % Recovery | Found ($\mu$M) | % Recovery |
| 5 | 5.32 | 106 | 5.08 | 102 |
| 10 | 10.19 | 102 | 10.48 | 105 |
| 15 | 14.82 | 99 | 15.53 | 104 |
| 25 | 25.09 | 100 | 24.91 | 100 |
| 30 | 33.12 | 110 | 30.52 | 102 |
| 40 | 40.61 | 102 | 39.50 | 99 |

resulting in a poor photophysical changes upon the addition of cyanide in both systems [29].

### Effect of Interference Anions

The effect of interference anions was evaluated in the determination of 1.3 $\mu$g/mL of $CN^-$. The tolerance amounts of five common anions were considered at less than 5% relative error compared to the fluorescence intensity at 460 nm in the presence of 1.3 $\mu$g/mL of $CN^-$. As listed in Table 2, the tolerance limit of various anions revealed that most common anions did not affect the cyanide detection in this system for both sensors especially, ***p*-NQB** (Table 2).

### Calibration Curves and the Limit of Detection

Under optimum condition of the CTAB micellar system, the calibration curves of cyanide detection were obtained from plots between fluorescence intensity at 460 nm and $CN^-$ concentration. At below 50 $\mu$M cyanide concentration corresponding to the level in practical application for high toxic substance as cyanide, the emission intensities at 460 nm of ***m*-NQB** and ***p*-NQB** versus the cyanide concentration provided two well linear ranges of cyanide detections, 2.5–15 $\mu$M and 20–40 $\mu$M. As illustrated in Fig. 10, the analytical data (Table 3) of both sensors clearly demonstrated that both sensors in CTAB micellar media gave excellent limits of detection of cyanide at 1.4 $\mu$M.

The proposed spectrofluorometric method was applied to determine $CN^-$ in commercial drinking water, and results were shown in Table 4. Average%recoveries of the spike samples of ***m*-NQB** and ***p*-NQB**, were 103 and 102, respectively. Our method thus gave good analytical characteristics of cyanide detection.

## Conclusion

In summary, we have successfully developed a new effective determination system for cyanide by the incorporating naphthoquinone boronic based sensors, ***m*-NQB** and ***p*-NQB**, into a cationic surfactant (CTAB). The optimized condition used in this proposed method is $5.0\times10^{-5}$ mol/L of sensors and $5.0\times10^{-3}$ mol/L of CTAB in 1:4 ethanol: $H_2O$. Compared to the cyanide detection studied in the 1:1 DMSO:$H_2O$ solution, the cationic micellar system provided significant improvement in sensitivity and selectivity resulting in 1000-fold enhancement of the detection ability. The proposed sensing system could also be used to determine cyanide in drinking water with good analytical characteristics.

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## References

1. Guidelines for Drinking-Water Quality. World Health Organization, Geneva, (1996)
2. Ishii A, Watanabe-Suzuki H, Suzuki O, Kumazawa T (1998) Determination of cyanide in whole blood by capillary gas chromatography with cryogenic oven trapping. Anal Chem 70:4873–4876
3. González LaFuente JM, Fernández Martínez E, Vicente Pérez JA, Fernández Fernández S, Miranda Ordiores AJ, Sánchez Uría JE, Fernández Sánchez ML, Sanz-Medel A (2000) Differential-pulse voltammetric determination of low $\mu gl^{-1}$ cyanide levels using EDTA, Cu(II) and a hanging mercury drop electrode. Anal Chim Acta 410:135–142
4. Vallejo-Pecharromán B, Luque de Castro MD (2002) Determination of cyanide by a pervaporation–UV photodissociation–potentiometric detection approach. Analyst 127:267–270
5. López Gómez AV, Martínez Calatayud J (1998) Determination of cyanide by a flow injection analysis-atomic absorption spectrometric method. Analyst 123:2103–2107
6. Miralles E, Prat D, Compañó R, Granados M (1997) Assessment of different fluorimetric reactions for cyanide determination in flow systems. Analyst 122:553–558
7. Recalde-Ruiz DL, Andrés-García E, Díaz-García ME (2000) Fluorimetric flow injection and flow-through sensing systems for cyanide control in waste water. Analyst 125:2100–2105
8. Miralles E, Compañó R, Granados M, Prat MD (2000) Determination of metal-cyanide complexes by ion-interaction chromatography with fluorimetric detection. Anal Chim Acta 403:197–204
9. Gamoh K, Imamichi S (1991) Postcolumn liquid chromatographic method for the determination of cyanide with fluorimetric detection. Anal Chim Acta 251:255–259
10. Miyaji H, Sessler JL (2001) Off-the-shelf colorimetric anion sensors. Angrew Chem Int Ed 40:154–157
11. Jr Anzenbacher P, Tyson DS, Jursíková K, Castellano FN (2002) Luminescence lifetime-based sensor for cyanide and related anions. J Am Chem Soc 124:6232–6233
12. Kim Y-H, Hong J-I (2002) Ion pair recognition by Zn–porphyrin/crown ether conjugates: visible sensing of sodium cyanide. Chem Commun 512–513
13. Chow C-F, Lam MHW, Wong W-Y (2004) A heterobimetallic ruthenium(II)-copper(II) Donor-acceptor complex as a chemodosimetric ensemble for selective cyanide detection. Inorg Chem 43:8387–8393
14. Chung S-Y, Nam S-W, Lim J, Park S, Yoon J (2009) A highly selective cyanide sensing in water via fluorescence change and its application to in vivo imaging. Chem Commun 2866–2868
15. Chung Y, Lee H, Ahn KH (2006) N-acyl triazenes as tunable and selective chemodosimeters toward cyanide Io. J Org Chem 71:9470–9474
16. Chen C-L, Chen Y-H, Chen C-Y, Sun S-S (2006) Dipyrrole carboxamide derived selective ratiometric probes for cyanide ion. Org Lett 8:5053–5056

17. Tomosulo M, Sortino S, White AJP, Raymo FM (2006) Chromogenic oxazines for cyanide detection. J Org Chem 71:744–753
18. Lee K-S, Kim H-J, Shin I, Hong J-I (2008) Fluorescence chemodosimeter for selective detection of cyanide in water. Org Lett 10:49–51
19. Ekmekci Z, Yilmaz MD, Akkaya EU (2008) A monostyryl-boradiazaindacene (BODIPY) derivative as colorimetric and fluorescence probe for cyanide ions. Org Lett 10:461–464
20. Yang Y-K, Tae J (2006) Acridinium salt based fluorescence and colorimetric chemosensor for the detection of cyanide in water. Org Lett 8:5721–5723
21. Ros-Lis JV, Matinez-Manez R, Soto J (2002) A selective chromogenic reagent for cyanide determination. Chem Commun 2248–2249
22. Hudnall TW, Gabbaï FP (2007) Ammonium boranes for the selective complexation of cyanide or fluoride ions in water. J Am Chem Soc 129:11978–11986
23. Sun Y, Wang G, Guo W (2009) Colorimetric detection of cyanide with N-nitrophenyl benzamide derivatives. Tetrahedron 65:3480–3485
24. Huh JO, Do Y, Lee MH (2008) A BODIPY-Borane dyad for the selective complexation of cyanide ion. Organometallics 27:1022–1025
25. Badugu R, Lakowicz JR, Geddes CD (2005) Anion sensing using quinolinium based boronic acid probes. Curr Anal Chem 1:157–170
26. Badugu R, Lakowicz JR, Geddes CD (2005) Cyanide-sensitive fluorescence probes. Dyes Pigments 64:49–55
27. Badugu R, Lakowicz JR, Geddes CD (2005) Enhanced fluorescence cyanide detection at physiologically lethal levels: reduced ICT-based signal transduction. J Am Chem Soc 127:3635–3641
28. Badugu R, Lakowicz JR, Geddes CD (2004) Fluorescence intensity and lifetime-based cyanide sensitive probes for physiological safeguard. Anal Chem Acta 522:9–17
29. Jamkratoke M, Ruangpornvisuti V, Tumcharern G, Tuntulani T, Tomapatanaget B (2009) A-D-A sensors based on naphthoimidazoledione and boronic acid as Turn-On cyanide probes in water. J Org Chem 74:3919–3922
30. Fernandez YD, Gramateges AP, Amendola V, Foti F, Mangano C, Pallavicini P, Patroni S (2004) Using micelles for a new approach to fluorescence sensors for metal cations. Chem Commun 1650–1651
31. Nakahara Y, Kida T, Nakatsuji Y, Akashi M (2004) A novel fluorescence indicator for $Ba^{2+}$ in aqueous micellar solutions. Chem Commun 224–225
32. Nakahara Y, Kida T, Nakatsuji Y, Akashi M (2005) Fluorometric sensing of alkali metal and alkaline earth metal cations by novel photosensitive monoazacryptand derivatives in aqueous micellar solutions. Org Biomol Chem 3:1787–1794
33. Vargas LV, Sand J, Brãno TAS, Fiedler HD, Quina FH (2005) Determination of environmentally important metal ions by fluorescence quenching in anionic micellar solution. Analyst 130:242–246
34. Mallick A, Mandal MC, Haldar B, Charabarty A, Das P, Chattopadhyay N (2006) Surfactant-induced modulation of fluorosensor activity: a simple way to maximize the sensor efficiency. J Am Chem Soc 126:3126–3127
35. Pallavicini P, Dias-Fernandez YA, Foti F, Mangano C, Patroni S (2007) Fluorescence sensors for $Hg^{2+}$ in micelles: a new approach that transforms an ON–OFF into an OFF–ON response as a function of the lipophilicity of the receptor. Chem Eur J 13:178–187
36. Cuccovia IM, Chaimovich H (1982) Determination of micromolar concentrations of iodine with aqueous mice1lar hexadecyltrimethylammonium bromide. Anal Chem 54:789–791
37. Kunda S, Ghosh SK, Manadal M, Pal T (2002) Micelle bound redox dye marker for nanogram level arsenic detection promoted by nanoparticles. New J Chem 26:1081–1084
38. Hayakawa K, Kanda M, Satake I (1979) The determination of formation constant of triiodide ion in micellar solution of dodecyltrimethyammonium choloride. Bull Chem Jpn Soc 52:3171–3175
39. Grosh SK, Kundu S, Mandal M, Pal T (2002) Silver and gold nanocluster catalyzed reduction of methylene blue by arsine in a micellar medium. Langmuir 18:8756–8760
40. Button CA, Nome F, Quina FH, Romsted LS (1991) Ion binding and reactivity at charged aqueous interfaces. Acc Chem Res 24:357–364
41. Mallick K, Jewraka S, Pradhan N, Pal T (2001) Micelle-catalysed redox reaction. Curr Sci 80:1408–1412
42. Matizinger S, Hussey DM, Fayer MD (1998) Fluorescence probes solubilization in the headgroup and core regions of micelles: fluorescence lifetime and orientational relaxation measurement. J Phy Chem B 102:7216–7224
43. Wei L, Ming Z, Jinli Z, Yongcai H (2006) Self-assembly of cetyl trimethylammonium bromide in ethanol-water mixtures. Front Chem China 4:438–442
44. Cooper CR, Spencer N, James TD (1998) Selective fluorescence detection of fluoride using boronic acids. Chem Commun 1365–1366
45. Ingle JD Jr, Wilson RL (1976) Difficulties with determining the detection limit with nonlinear calibration curves in spectrometry. Anal Chem 48:1641–1642