



Lawsonone (2-hydroxy-1,4-naphthoquinone) as a sensitive cyanide and acetate sensor

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ARTICLE INFO

Article history:

Received 13 September 2011

Received in revised form 15 March 2012

Accepted 23 March 2012

Available online 1 April 2012

Keywords:

Lawsonone

Cyanide sensors

Acetate sensors

Colorimetric sensors

Electrochemical sensors

ABSTRACT

Lawsonone (2-hydroxy-1,4-naphthoquinone), the essential component of henna, is used as a sensitive colorimetric and electrochemical sensor for anions such as cyanide, acetate, fluoride and dihydrogen phosphate (DHP) in acetonitrile. These anions cause a color change in Lawsonone's solution from yellow to orange-red. Other anions, such as chloride, bromide, iodide, perchlorate, do not show a significant change. Cyanide changes the color of Lawsonone in water:acetonitrile (95:5) solution significantly while acetate causes a slight color change. On the other hand, hydrogen sulfate anion fades the yellow color of the solution. Job's plots show a 1:1 host:guest complex in acetonitrile for cyanide, acetate and fluorides and 1:2 for DHP. In water/acetonitrile the stoichiometry is 1:1 for host:anion. The binding constants show strong binding with cyanide and acetate in both solvent systems.

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1. Introduction

Anion sensing is of great significance and consequence in the industry, the environment, and in biological systems. Among the anions, cyanide is a very notorious toxic chemical that gets into the environment from industrial waste like gold mining, metal electroplating, nitrile manufacturing, herbicide production and acrylic plastic industries which are associated with cyanide contaminations. Cyanide fishing [1] also contributes to pollution of waters in areas used for fishing exotic fish such as the coral reefs areas. Cyanide is a component of the tabun, the chemical warfare agent [2]. Biological sources of cyanide include bacteria, fungi and algae, which produce this ion as part of their nitrogen metabolic pathways. Vegetables containing cyanogenic glycosides are sources of cyanide ingestion in humans and animals. Dietary foodstuffs that contain moderate to high levels of cyanogenic glycosides include cassava [3], as well as other common foods such as lima beans, sorghum, linseed, kernels of fruits, bamboo shoots and bitter almonds. The maximum contaminant level (MCL) for cyanide in drinking water is set by the United States Environmental Protection Agency (EPA) at 0.1 ppm. Due to these health effects of cyanide, developing selective, sensitive sensors for its monitoring is of paramount importance.

There have been numerous studies on the development of cyanide sensors [4]. The mechanism of action is either based on

(i) hydrogen bonding, for those sensors with functionality capable of hydrogen bonding, such as amides [5], ureas [6], thiourea [7,8], Schiff bases [9], imides [10], and hydrazones [11]. Most of these sensors are synthetic and usually used in organic solvents. (ii) Metal coordination complexes where displacement strategy of ligands from copper [12] and cobalt [13] was used for sensing cyanide. (iii) Chemodosimeters and nucleophilic addition of cyanide to ketones [14,15], aldehydes [16,17] or amides [18]. Electrochemical methods are also utilized in cyanide sensing [19].

Dyes [20,21] and their derivatives have been used as cyanide sensors as well as the natural spice derivatives of curcumin [22].

Henna plant (*Lawsonia inermis*) contains (1.0–1.4%) the well-known ancient red-orange dye hennotannic acid named 2-hydroxy-1,4-naphthoquinone (HNQ; Lawsonone). Humans have used henna extracts containing Lawsonone as hair and skin pigments for more than 5000 years. HNQ reacts chemically with the protein keratin in skin and hair via Michael addition, resulting in a strong permanent stain that lasts until the skin or hair is shed [23].

Inspection of the structure of HNQ shows the presence of keto-enol group that may be suited for hydrogen bonding with electronegative anions and a substrate for conjugate addition of strong nucleophiles such as cyanide which makes it a reasonable candidate as anion receptor, while the presence of naphthoquinone unit could be used as a signaling unit. Naphthoquinone is also redox active, suggesting that HNQ may be used as an electrochemical receptor for anions.

Here, we report for the first time the use of Lawsonone, a natural dye, for anion sensing.

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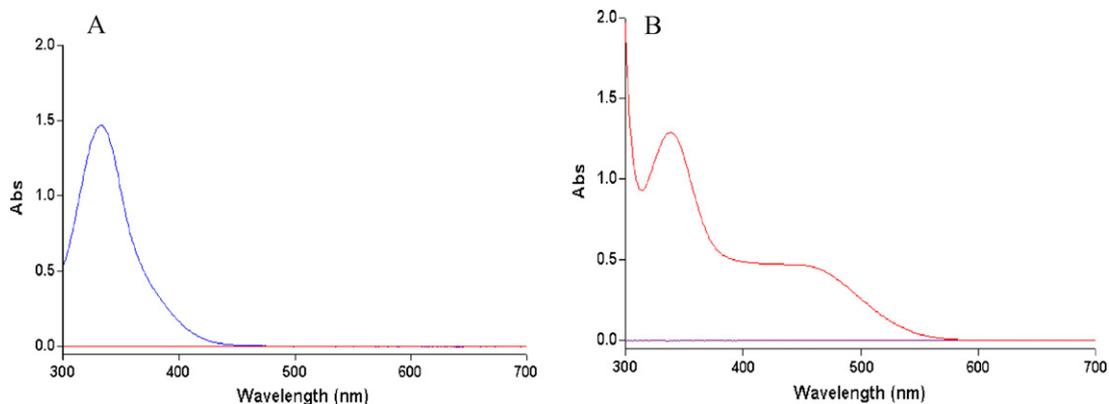


Fig. 1. UV-vis spectrum of HNQ in (A) acetonitrile and (B) water/acetonitrile mixture (95:5).

2. Experimental

2.1. Materials

2-Hydroxy-1,4-naphthoquinone (HNQ), acetonitrile (CHROMASOLV® Plus grade) were purchased from Sigma–Aldrich (St. Louis, MO) and was used as received. Tetrabutylammonium perchlorate (electrochemical grade), tetrabutylammonium cyanide, tetrabutylammonium fluoride, tetrabutylammonium acetate, tetrabutylammonium phosphate and all other chemicals were purchased from Sigma–Aldrich (St. Louis, MO) and were used without further purification.

2.2. Electrochemical measurement

All electrochemical measurements were performed using a CHI 660C Electrochemical Workstation (CH Instruments, Austin, TX), connected to a conventional three-electrode cell with a 3-mm glassy carbon electrode (CHI 104, CH Instruments, Inc., Austin, TX) as the working electrode, a “no-leak” Ag/AgCl electrode (EE009, Cypress Systems, Chelmsford, MA) or a miniature Ag/AgCl electrode (EE008, Cypress Systems, Chelmsford, MA) as the reference electrode, and a Pt wire as the counter electrode. All experiments were carried out at room temperature. In non-aqueous experiments acetonitrile was used as the solvent and 30 mM tetrabutylammonium perchlorate was used as the supporting electrolyte. In aqueous experiments 10 mM NaCl was used as the supporting electrolyte.

3. Results and discussion

3.1. Characterization of HNQ

HNQ possesses the criteria of an anion sensor. (i) It is capable of hydrogen bonding to anions due to the hydroxyl of the enol. (ii) It contains conjugated ketone suitable for conjugate or nucleophilic addition of strong nucleophiles such as cyanide. (iii) It contains a naphthoquinone chromophore as a signaling unit. (iv) It is soluble in organic solvents as well as in water (2.0 g/L), therefore, detection can be done in both aqueous and non-aqueous media. In addition, HNQ is natural, commercially available, and commonly used, so does not pose health problems; it also has shown antimicrobial and antioxidant activities.

3.1.1. UV-vis absorption

With all of this information in mind, we were encouraged to investigate the interaction of HNQ with various anions in acetonitrile and water. Initially, the solubility and solvent effect on HNQ were investigated. Solutions of HNQ in acetonitrile are very pale

yellow, and give an absorption band in UV-vis at 333 nm (Fig. 1), but they get intense yellow color upon addition of water which indicates the dissociation in protic solvents as presented in Scheme 1.

The presence of the dissociated species is indicated by the orange color, and the appearance of an absorption band at 478 nm in the UV-vis spectrum of HNQ in aqueous solution (Fig. 1).

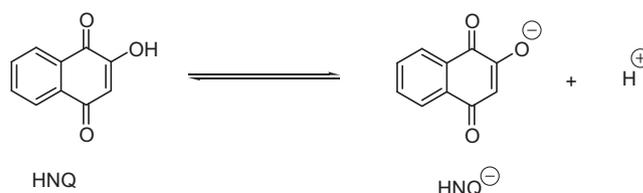
3.1.2. NMR

H-NMR studies on the effect of solvent on HNQ are presented in Figs. 2 and S-9–S1-4 which show the change of chemical shifts of the aromatic protons as solvent changes from CDCl₃ to CD₃CN to D₂O. The chemical shifts changed to lower values probably due to shielding in the protic polar solvents after dissociation. The chemical shift changes varied for different protons as seen in the spectra Fig. 2.

3.1.3. Electrochemistry

The electrochemistry of HNQ has been studied extensively [24–27]. Depending on the solvent and other conditions HNQ may experience 2 successive 1-electron reductions or a 2-electron reduction which may or may not be accompanied by transfer of protons (Scheme 2):

Fig. 3A is the cyclic voltammogram of HNQ in acetonitrile, where the reduction of HNQ is not accompanied by proton transfer from the solvent. An irreversible reduction peak is observed in the potential window corresponding to the one-electron reduction of HNQ to the radical anion. The lack of oxidation peak can be explained by a fast self-protonation following the electrochemical reduction of HNQ—a process where the produced radical anion is consumed by proton transfer from another HNQ molecule, thus eliminates the reverse electrochemical oxidation process of the radical anion [27]. Fig. 3B is the cyclic voltammogram of HNQ in an aqueous solution which is accompanied by transfer of protons. A quasi-reversible redox wave is observed, and the pH-dependent redox potential is in good agreement with the literature values [24,25,28].



Scheme 1. Dissociation of Lawsone in water.

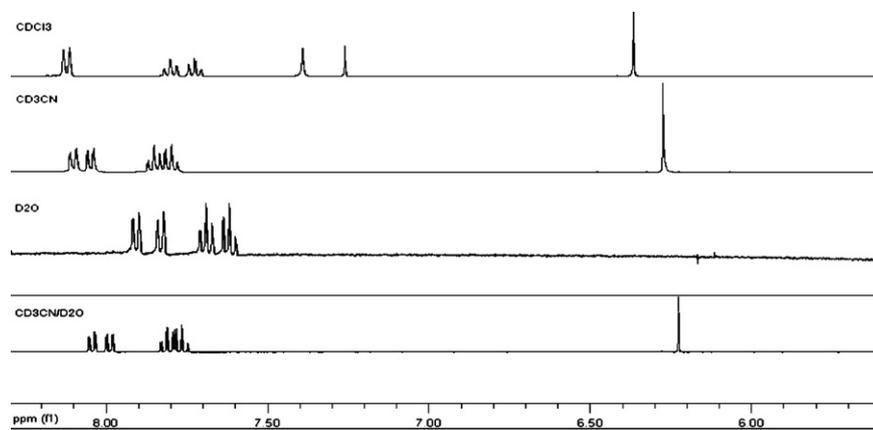


Fig. 2. 400 MHz ^1H NMR spectra of HNQ in different solvents.

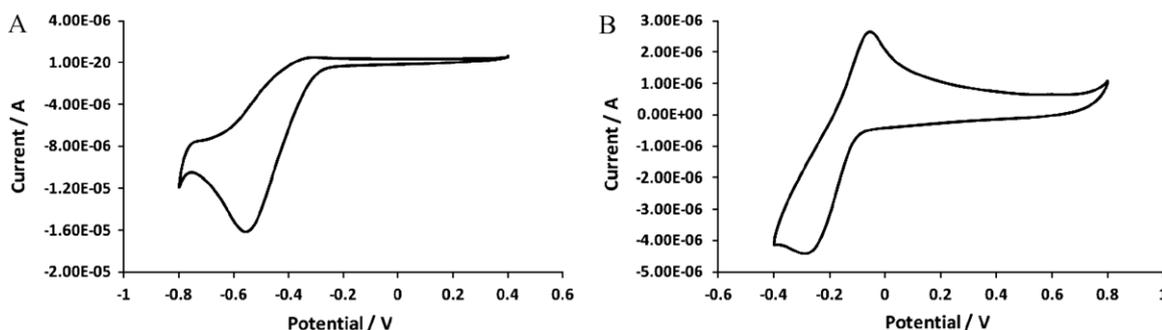


Fig. 3. Cyclic voltammograms of (A) 1 mM HNQ in acetonitrile containing 30 mM tetrabutylammonium perchlorate, and (B) 1 mM HNQ in water containing 10 mM NaCl. Reference: Ag/AgCl. Scan rate: 50 mV s^{-1} .

3.2. Titrations of HNQ with various anions

The impact of various anions on the optical and electrochemical properties of HNQ was investigated through optical and electrochemical methods.

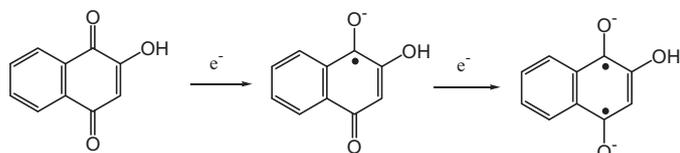
3.2.1. UV–vis absorption in acetonitrile

The effect of various anions on HNQ is presented in Figs. 4 and 5. Addition of two equivalents of tetrabutyl ammonium salts of CN^- , AcO^- , F^- , H_2PO_4^- , Cl^- , Br^- , I^- , N_3^- , ClO_4^- , SCN^- , and HSO_4^- to solutions of $5.0 \times 10^{-4}\text{ M}$ HNQ in acetonitrile caused a dramatic change in color from yellow to red, and dramatic spectral changes when CN^- , AcO^- , F^- , H_2PO_4^- solutions were added, while the other anions caused no significant change. The change is demonstrated

by the appearance of a new maximum at 478 nm and the decrease in the absorption at 333 nm.

The interacting anions can cause strong hydrogen bonding or deprotonation depending on their basicity, while cyanide might interact by hydrogen bonding or addition to the carbonyl. Less basic or less electronegative anions are unable to cause H-bonding. Cyanide, acetate, and fluoride showed comparable interaction while dihydrogen phosphate was less effective as it is less basic.

Upon addition of increasing amounts of tetrabutylammonium salts of cyanide (Fig. 6), acetate (Fig. S-1), fluoride (Fig. S-2), and dihydrogen phosphate (Fig. S-3) to the acetonitrile solutions of receptor HNQ, the absorption band at 333 nm decreased while a new band was formed at 478 nm. A clear isosbestic point was formed at 385 nm indicating the formation of a stable new species



(A) Successive 1-electron reduction without proton transfer.

(B) 2-electron reduction accompanied by proton transfer.

Scheme 2. Reduction of HNQ.

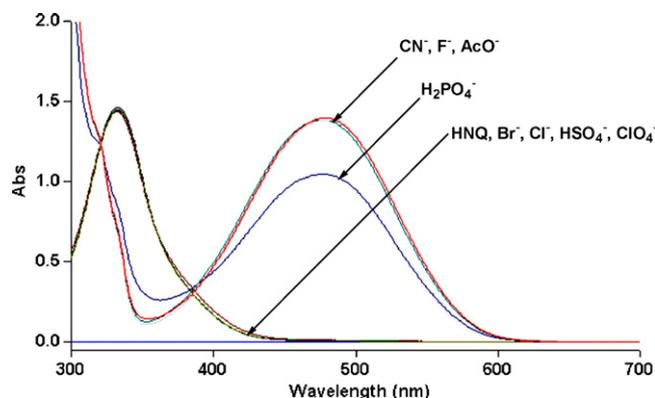


Fig. 4. UV–vis absorption spectra of HNQ ($5 \times 10^{-4}\text{ M}$) in CH_3CN in the presence of 2.0 equiv. of each tetrabutylammonium salts.

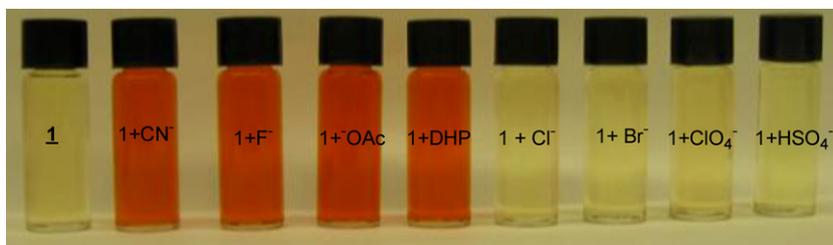


Fig. 5. Color changes of HNQ (5×10^{-4} M) upon addition of 1.0 equiv. of each anion in CH_3CN .

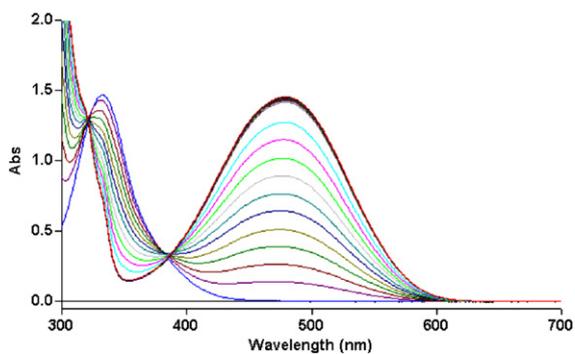


Fig. 6. UV/vis spectral changes of HNQ (5×10^{-4} M) in CH_3CN upon addition of 0.0–2.0 equiv. of CN^- .

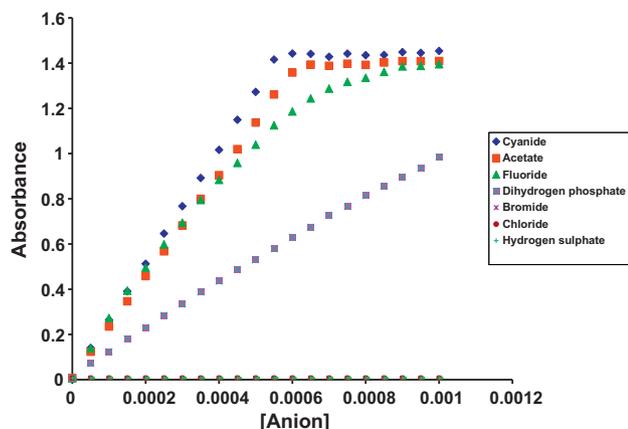


Fig. 7. Plots of absorbance of HNQ (5×10^{-4} M, 478 nm) as a function of anion concentration in acetonitrile.

with unique spectroscopic properties as a result of the interaction between HNQ and the selected anions. There was no observable change in the UV/vis absorption band after the addition of more than 1.1 equiv. (5.5×10^{-4} M) CN^- , 1.7 equiv. (8.5×10^{-4} M) F^- , 1.2 equiv. (6.0×10^{-4} M) AcO^- , and 2.8 equiv. (1.4×10^{-3} M) H_2PO_4^- .

The dependence of the change at 478 nm on anion concentrations is presented in Fig. 7. The binding constants of selective anions were calculated according to The Benesi–Hildebrand method and shown in Table 1.

As observed, HNQ showed higher selectivity towards the more basic anions, CN^- , F^- , AcO^- , hydroxide and H_2PO_4^- as compared to the less basic anions Cl^- , Br^- , HSO_4^- , and ClO_4^- .

Table 1
Binding constants for HNQ with selective anions in acetonitrile.

Anion	CN^-	ACO^-	F^-	H_2PO_4^-
K (M^{-1})	$2.56 \times 10^2 \pm 43$	$2.65 \times 10^2 \pm 49$	$1.141 \times 10^3 \pm 44$	$5.50 \times 10^2 \pm 58$

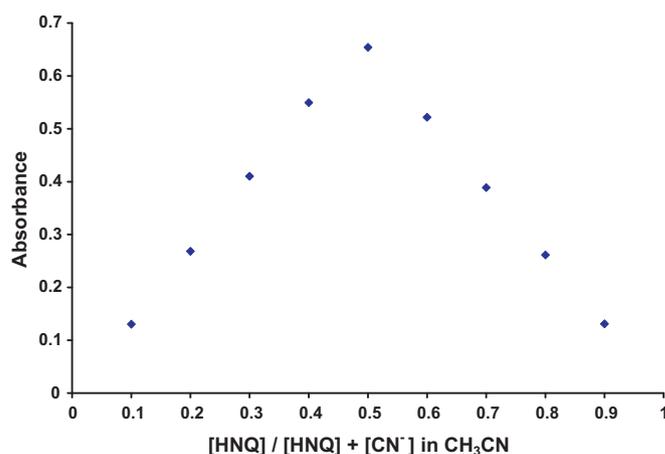


Fig. 8. Job's plot between HNQ and CN^- (5×10^{-4} M) in CH_3CN .

In acetonitrile, Job's plots demonstrated that the stoichiometry of HNQ to CN^- (Fig. 8) and AcO^- (Fig. S-4) and F^- (Fig. S-5) is a 1:1 stoichiometry while H_2PO_4^- (Fig. S-6) demonstrated a 1:2 stoichiometry. The ratio 1:2 for HNQ and DHP may be explained by the formation of the stable anion $\text{H}_3\text{P}_2\text{O}_7^-$ [29].

The binding between host and guest may be attributed to possible strong hydrogen bonding of HNQ with selective anions (CN^- , F^- , AcO^- , H_2PO_4^-).

3.2.2. Titration of HNQ in water/acetonitrile 95:5(v:v)

In water:acetonitrile mixture (95:5, v/v), addition of 2 equiv. of the various anions to HNQ (5×10^{-4} M) solution resulted in a significant color and spectral changes. Cyanide caused a significant change while acetate showed a lower effect with a minimal effect for fluoride. Fig. 9 shows the UV–vis spectra in the presence of the anions tested. The color change is depicted in Fig. 10. The absorbance change at 454 nm is presented in Fig. 10 which shows the significant increase for cyanide > hydroxide > acetate > fluoride

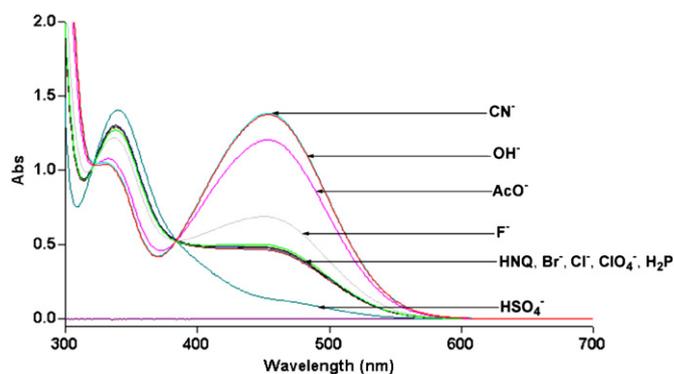


Fig. 9. UV–vis absorption spectra of HNQ (5×10^{-4} M) in water: CH_3CN (95:5, v:v) in the presence of 1.0 equiv. of each tetrabutylammonium salts at 478 nm.

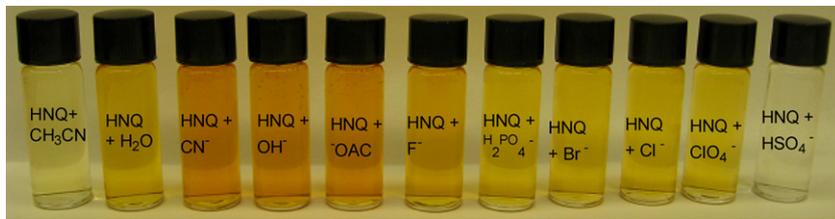


Fig. 10. Color changes of HNQ (5×10^{-4} M) upon addition of 2.0 equiv. of each anion in water/acetonitrile (95:5, v/v).

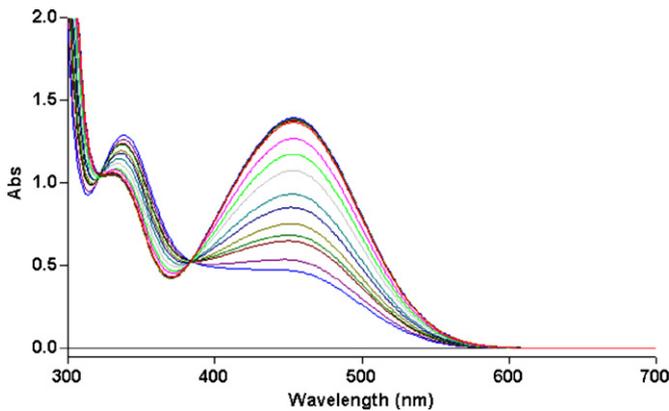


Fig. 11. UV/vis spectral changes of HNQ (5×10^{-4} M) water/acetonitrile (95:5, v/v) upon addition of 0.0–2.0 equiv. of CN^- .

and insignificant change for others. On the other hand hydrogen sulfate caused discoloring, elimination of the absorption at 454 nm and intensity increase of the band at 338 nm. This is believed to be due to the protonation of the dissociated enol with the acidic hydrogen sulfate.

Titration of HNQ (5×10^{-4} M) solution in water:acetonitrile mixture (95:5) with sodium salts of various anions resulted in a gradual increase of the absorption band at 454 and the decrease of the band at 338 nm, and the appearance of two isosbestic points at 385 nm and 322 nm. Titration with sodium cyanide (0.0–2.0 equiv.) gave the spectra shown in Fig. 11 and for acetate is presented in Fig. S-7. The stoichiometry of cyanide and acetate to HNQ is 1:1 as deduced from the job plots Figs. 12 and S-8 respectively. The binding constants are presented in Table 2.

The use of 95:5 water/acetonitrile mixture is significant, as it represents water solution. The solution can be done totally in water but the use of acetonitrile is to enhance the solubility to a higher

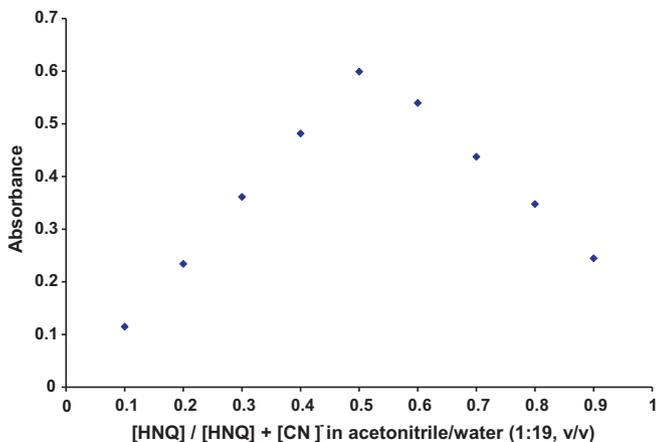


Fig. 12. Job's plot between HNQ and CN^- (5×10^{-4} M) in acetonitrile/water (1:19, v/v).

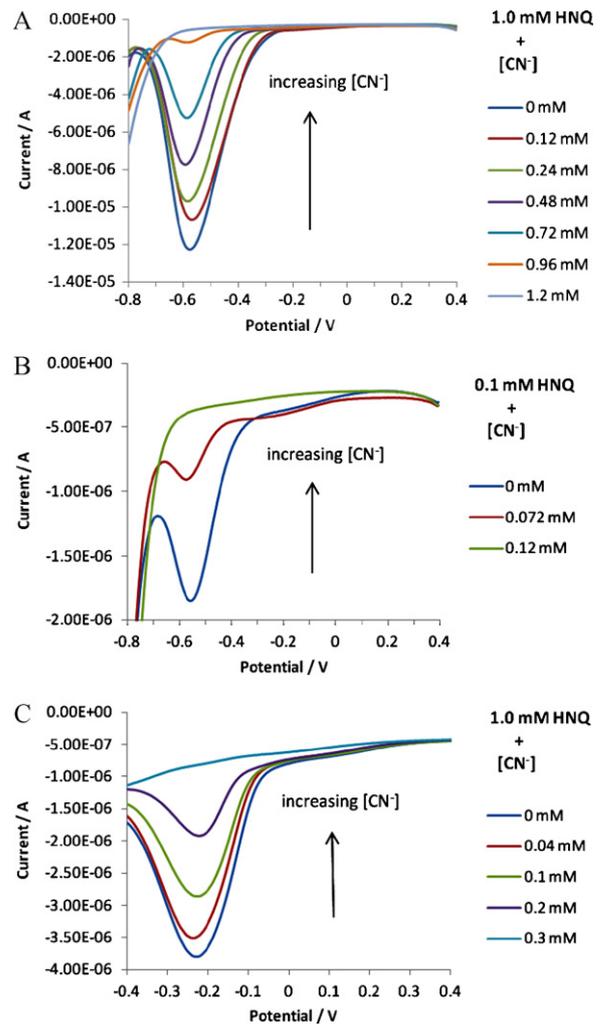


Fig. 13. Square wave voltammograms of HNQ with increasing concentration of CN^- . (A) 1.0 mM HNQ in acetonitrile, (B) 0.1 mM HNQ in acetonitrile, and (C) 1.0 mM HNQ in water. Initial potential: 0.4 V. Increment potential: 4 mV. Square wave amplitude: 15 mV. Square wave frequency: 15 Hz. Reference: Ag/AgCl.

level for HNQ initial solutions. The purely aqueous solution can be achieved if the stock solution is made at higher dilutions. The use of mostly water is significant as it represents the actual media that real samples are in aqueous media. Such systems show high selectivity for cyanide over other interacting anions. Hydroxide, a strong base,

Table 2

Binding constants for sensor HNQ with selective anions in water/acetonitrile (95:5, v/v).

Anion	Cyanide	Acetate	Hydroxide
$K(\text{M}^{-1})$	$4.50 \times 10^2 \pm 16$	$4.91 \times 10^2 \pm 13$	$5.31 \times 10^2 \pm 9$

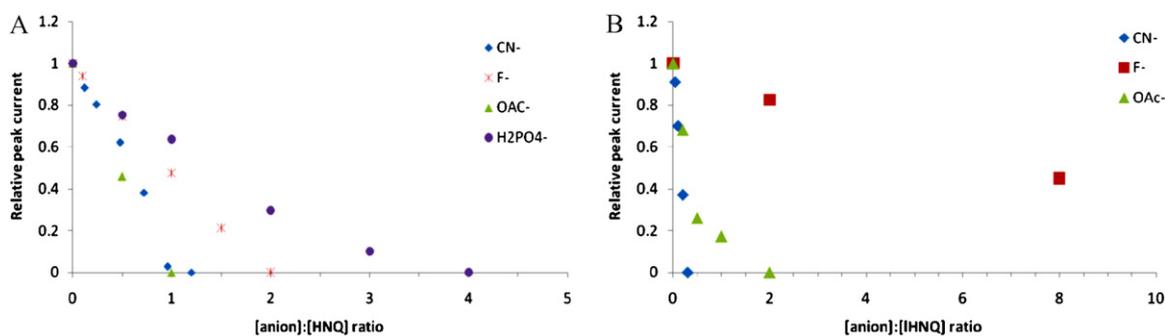


Fig. 14. Quenching of the SWV peak current of 1.0 mM HNQ in (A) acetonitrile and (B) water by increasing the anion concentrations.

deprotonates the phenol to produce similar spectra as those from the strongly basic anions.

3.3. Electrochemistry of titration of HNQ

The redox property of HNQ is strongly and sensitively affected by the presence of anions, in both organic and aqueous solutions. As shown in Fig. 13A, in acetonitrile, the square wave voltammogram (SWV) of HNQ shows a reduction peak similar to that in its CV; addition of CN^- effectively diminishes the intensity of this peak, and addition of about 1 equiv. of CN^- completely quenches the peak. Interestingly, the quenching of the reduction peak of HNQ depends on the CN^- -to-HNQ mole ratio, as evidenced in Fig. 13 B, where a 10-fold more dilute HNQ solution requires the same CN^- -to-HNQ ratio to completely diminish the peak intensity.

Fig. 13C shows the SWV of HNQ in aqueous solutions with increasing $[\text{CN}^-]$. Addition of CN^- diminishes the peak intensity even more effectively than in acetonitrile, and the total quenching of the intensity occurs at $\sim 0.3:1$ anion-to-HNQ ratio.

Hence, the intensity of the SWV peak current of HNQ can be used to quantitatively detect the presence of anions. As shown in Fig. 14A, CN^- , F^- , AcO^- , and H_2PO_4^- all have the ability to diminish the peak intensity of HNQ in acetonitrile. With CN^- and AcO^- the total quenching occurs at a 1:1 anion-to-HNQ mole ratio, while F^- completely diminishes the HNQ peak at a 2:1 anion-to-HNQ ratio; H_2PO_4^- has the lowest quenching ability with the total quenching occurring at a 4:1 ratio. CN^- , F^- , AcO^- all show linear responses.

As discussed in the previous section, some of the anions interact strongly with HNQ through hydrogen bonding or deprotonation of the hydroxy group which may cause structural changes of HNQ leading to diminished intensity of the reduction peak of HNQ.

In aqueous solutions, however, the HNQ reduction peak shows different sensitivities and selectivities towards various anions (Fig. 14B). CN^- again has the highest sensitivity, with the total quenching occurring at $\sim 0.3:1$ anion-to-HNQ ratio. AcO^- becomes less sensitive, and the total quenching occurs at a 2:1 ratio compared to 1:1 in acetonitrile; with a 2:1 F^- -to-HNQ ratio which normally completely diminishes the peak intensity in acetonitrile, $>80\%$ of the HNQ peak intensity remains, and $\sim 50\%$ remains at a 8:1 ratio; and the HNQ reduction peak is not sensitive to the presence of H_2PO_4^- at all. In aqueous solutions hydrogen bonding exists extensively between the anions and water as well as between HNQ and water which may weaken the interactions between the anions and HNQ, leading to diminished sensitivity of HNQ towards these anions. On the other hand, CN^- may interact strongly with HNQ through addition to the carbonyl of HNQ which may explain why HNQ remains very sensitive toward CN^- . In fact, HNQ is more sensitive toward CN^- in aqueous solution than in acetonitrile (total quenching occurring at $\sim 0.3:1$ anion-to-HNQ ratio), and the reason is still unknown.

In other words, while HNQ shows comparable sensitivities for CN^- , F^- , AcO^- and is less sensitive to H_2PO_4^- in organic solutions, it has ~ 3 times the sensitivity for CN^- in aqueous solutions; and more importantly, because it is less sensitive for the other anions in aqueous solutions, it becomes quite selective in detecting CN^- in aqueous solutions. This is in line with the results from the UV-vis studies.

4. Conclusions

We have established that HNQ can be a sensitive colorimetric and electrochemical sensor for cyanide in both water and acetonitrile. It is also sensitive to acetate, fluoride and DHP in acetonitrile as well. The selectivity for cyanide over other strongly basic anions is enhanced in aqueous media. The stoichiometry seems to be 1:1 anion:sensor but 2:1 for DHP, due to dimerization of DHP in acetonitrile.

Acknowledgements

Y.M.H. would like to thank United Negro College Fund Special Programs (UNCFSP) for NASA Astrobiology Program–Minority Institutions Research Support (NAP–MIRS) summer fellowship and Dr. Paul Mahaffy (Goddard Space Flight Center) for collaboration. Partial support from Homeland security grant DHS 2008–ST–062–000011 is appreciated. Y.Z. would like to thank the National Science Foundation (NSF–HRD 0627276) for part of the support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.snb.2012.03.067>.

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