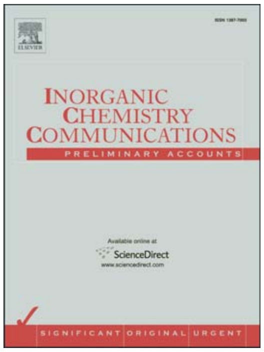

A colorimetric Schiff base chemosensor for CN^- by naked-eye in aqueous solution

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A colorimetric Schiff base chemosensor for CN^- by naked-eye in aqueous solution

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Abstract

A highly selective colorimetric chemosensor 6,6'-((1E,1'E)-hydrazine-1,2-diylidenebis(methanylylidene))bis(2,4-dichlorophenol) (**1**) based on the combination of hydrazine and 3,5-dichloro-2-hydroxybenzaldehyde was designed and synthesized. Receptor **1** showed exclusive response toward cyanide by a color change from colorless to yellow in aqueous solution. The binding mode of **1**-CN^- species was determined to be a 1:1 stoichiometry through Job plot, ^{1}H NMR titration, and ESI-mass spectrometry analysis. Also, the sensor **1** could be recyclable simply through treatment with a proper reagent such as hydrochloric acid.

Keywords: deprotonation, cyanide, colorimetric, Schiff base, reversible

Development of anion sensors is of great interest in supramolecular chemistry due to their chemical and biological importance [1]. Among the various anions, cyanide is one of the most concerned, because it is known as one of the most rapidly acting and powerful poisons. Its toxicity results from its propensity to bind to the iron in cytochrome c oxidase, interfering with electron transport and resulting in hypoxia [2-9]. Cyanide could be absorbed through lungs, gastrointestinal track and skin, leading to vomiting, convulsion, loss of consciousness, and eventual death [10-13]. Nevertheless, it has been produced in large quantities and used in various industrial processes, which has led to environmental contamination as well [14]. Thus, it is absolutely necessary to develop selective and sensitive methods for CN^- detection in aqueous solution.

Several methods to detect CN^- have been developed using various experimental protocols and detection techniques, such as chromatography, spectrophotography electrochemical methods and flow injection analysis technique [15]. However, most of these methods require sophisticated equipment, tedious sample preparation procedures, and trained operators. In contrast, colorimetric methods can conveniently and easily monitor target ions with the naked eye [16-19]. Colorimetric methods have therefore attracted considerable attention in the detection of toxic anions including CN^-. However, many anion sensors are not capable of distinguishing cyanide effectively from anions such as F^- and AcO^-, because they possess similar basicity to CN^- and easily form hydrogen bonds. To overcome these limitations, we synthesized a new chemosensor capable of exclusively detecting CN^- by naked-eye.

Herein we report on the synthesis, characterization and sensing properties of a new colorimetric receptor **1**, based on the combination of hydrazine and 3,5-dichloro-2-hydroxybenzaldehyde. Receptor **1** can detect cyanide by color change from colorless to yellow via the ‘naked-eye’ in aqueous environment. In particular, it can distinguish cyanide effectively from anions such as F^- and AcO^-.

The colorimetric chemosensor **1** was synthesized by condensing hydrazine with 3,5-dichloro-2-hydroxybenzaldehyde (Scheme 1) and characterized by ^{1}H NMR, ^{13}C NMR, ESI-mass spectrometry, and elemental analysis.

The chromogenic sensing ability of receptor **1** with various anions in a mixture of CH_3CN/bis-tris buffer (v/v, 3:7, 10 mM) was monitored by UV-vis absorption spectra (Fig. 1(a)). The best selectivity was observed in the mixture of CH_3CN/bis-tris buffer (v/v, 3:7) among various organic solvent systems. Only the addition of CN^- induced a distinct spectral change while other anions such as F^-, AcO^-, Cl^-, Br^-, I^- , $H_2PO_4^-$, BzO^-, N_3^- and SCN^- did not induce any spectral changes. Consistent with the change of UV-vis spectrum, the solution of **1** resulted in an immediate color change from colorless to yellow with cyanide (Fig. 1(b)), indicating that receptor **1** can serve as a ‘naked-eye’ cyanide indicator in aqueous solution.

To further investigate the chemosensing properties of **1**, UV-vis titration of **1** with the CN^- ion was performed (Fig. 2). On gradual addition of CN^- to a solution of **1**, the absorption band at 300 nm decreased and a new band at 440 nm emerged and gradually increased to maxima at 120 equiv with a distinct isosbestic point at 490 nm, indicating the formation of the only one species between **1** and CN^-. This bathochromic shift led us to propose the transition of intramolecular charge transfer (ICT) band through the deprotonation of the chemosensor **1** by CN^-, based on Bhattacharya’s proposal [20,21].

The binding mode between **1** and CN^- was determined through Job plot analysis. The Job plot exhibited a 1:1 binding interaction (Fig. 3), which was confirmed by ESI-mass spectrometry analysis (Fig. 4). The positive-ion mass spectrum of **1** upon addition of CN^- showed the formation of [**1**-H^+ + 2TEA]$^+$ binding mode [m/z: 636.87; calcd: 637.24]. To elucidate in more details the binding interaction of receptor **1** with CN^-, ^1H NMR titration experiments were carried out in DMSO-d_6 (Fig. 5). Upon addition of 1 equiv of the CN^- to the receptor **1**, the proton signals of -OH at 11.81 ppm disappeared completely and the imine and aromatic protons were shifted to upfield. This result indicates that the cyanide participates in the deprotonation of the -OH protons. In addition, no new peak was observed in the range of 5-6 ppm, which shows that the nucleophilic addition of cyanide to the imine moiety did not occur.

To further confirm whether the color change originated from the transition of ICT through the deprotonation mechanism, the interaction between **1** and OH^- was also conducted. UV-vis spectral change of **1** upon addition of OH^- was nearly identical to that of **1** upon addition of CN^-, which supports the deprotonation mechanism of **1** by CN^- (Fig. S1).

From the Benesi-Hildebrand equation [22], the association constant was found to be 4 x 10^2 M^{-1} for the CN^- recognition of receptor **1** (Fig. S2). This value is within the range of those (1.0 ~ 1.0 x 10^5) reported for CN^- sensing chemosensors [23-27]. The detection limit ($3\partial/k$) of receptor **1** for the analysis of CN^- ions was calculated to be 210 μM (Fig. S3) [28].

The preferential selectivity of **1** as a colorimetric chemosensor for the detection of CN^- was studied in the presence of various competing anions. For competition tests, receptor **1** was treated with 120 equiv of CN^- in the presence of 120 equiv of other anions. No interference was observed for the detection of CN^- in the presence of other anions, while H_2PO_4 did interfere completely (Fig. 6). This result suggests that **1** could be an excellent sensor for selectively detecting CN^- in the presence of most of the competing anions.

To examine the reversibility of receptor **1** toward CN^- in a mixture of CH_3CN/bis-tris buffer (v/v, 3:7, 10 mM) solution, hydrochloride acid (HCl) (120 equiv) was added to the **1**-CN^- solution. As shown in Fig. 7, the solution color changed from yellow to colorless and the absorbance at 440 nm completely disappeared. Upon addition of CN^- into the solution again, the color and the absorbance were recovered. The color changes were almost reversible even after several cycles with the sequentially alternative addition of CN^- and HCl. These results indicate that receptor **1** could be recyclable simply through treatment with a proper reagent such as HCl, and further confirm that **1** would detect CN^- by the deprotonation mechanism.

In summary, we have reported a simple imine-based naked-eye chemo-sensor **1** for the detection of CN^- in aqueous solution. The receptor **1** showed high selectivity toward CN^- ions in a 1:1 stoichiometric manner, which induced a fast color change from colorless to yellow. Moreover, the addition of hydrochloric acid (HCl) to the **1**-CN^- solution regenerated the free **1**, indicating that the sensor **1** could be recyclable easily through treatment with a proper reagent such as hydochloric acid (HCl). Therefore, this type of a simple, easy-to-synthesize chemo-sensor **1** will contribute to potential use for detecting and monitoring cyanide in aqueous environment.

Acknowledgements

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Supplementary Information.

Supplementary material associated with this article can be found, in the online version.

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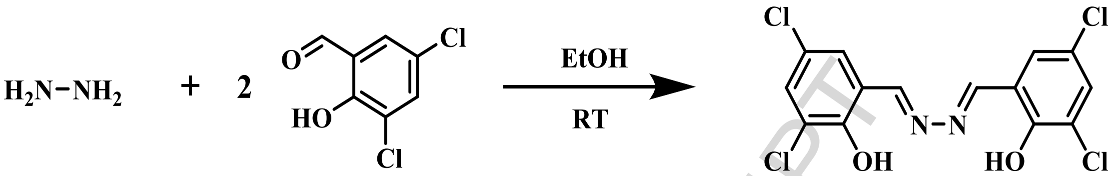
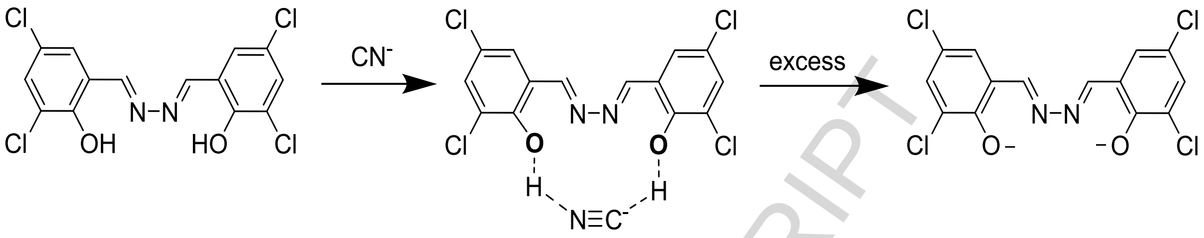


Scheme 1. Synthetic procedure of **1**.



Scheme 2. Proposed sensing mechanism of **1** for cyanide.

Figure captions

Figure 1. (a) UV-vis spectral changes of **1** (20 µM) upon the addition of various anions (120 equiv) in a mixture of CH_3CN/bis-tris buffer solution (v/v, 3:7). (b) The color changes of **1** (20 µM) upon addition of various anions (120 equiv).

Figure 2. UV-vis spectral changes of **1** (20 µM) upon addition of CN^- (up to 120 equiv).

Figure 3. Job plot of receptor **1** and cyanide. The total concentration of CN^- ions with receptor **1** was 1.0×10^{-5} M.

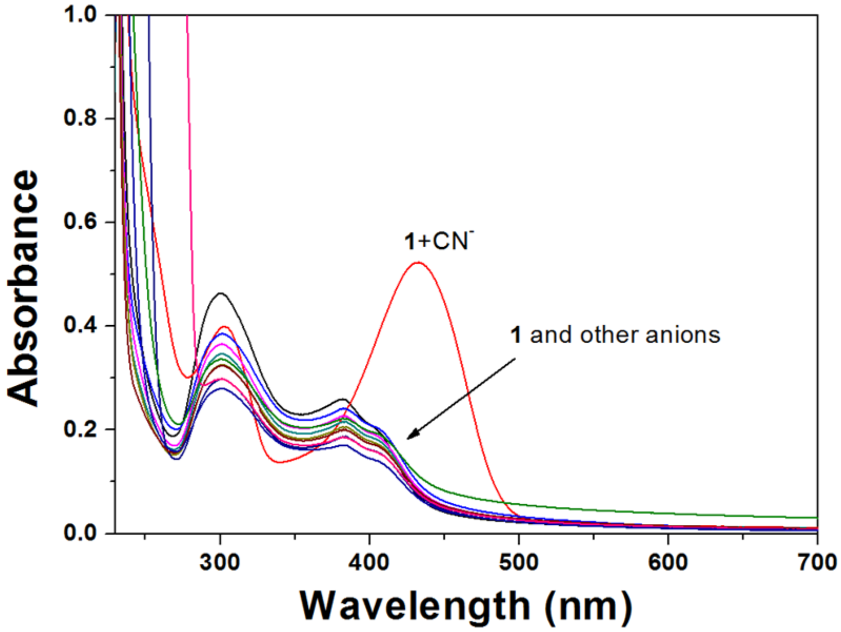
Figure 4. Positive-ion electrospray ionization mass spectrum of **1** (20 µM) upon addition of CN^- (1 equiv).

Figure 5. ^1H NMR titration of **1** (10 mM) with CN^-.

Figure 6. (a) Competitive selectivity of **1** (20 µM) towards CN^- (120 equiv) in the presence of other anions (120 equiv). (b) The color changes of **1** (20 µM) in the presence of CN^- (120 equiv) and other anions (120 equiv).

Figure 7. (a) UV-vis spectral changes of **1** (20 µM) after the sequential addition of CN^- and HCl. **(**b) The color changes of **1** (20 µM) after the sequential addition of CN^- and HCl.

(a)


1.0
0.8
0.6
0.4
0.2
0.0
Absorbance
300
400
500
600
700
Wavelength (nm)
1+CN-
1 and other anions

(b)

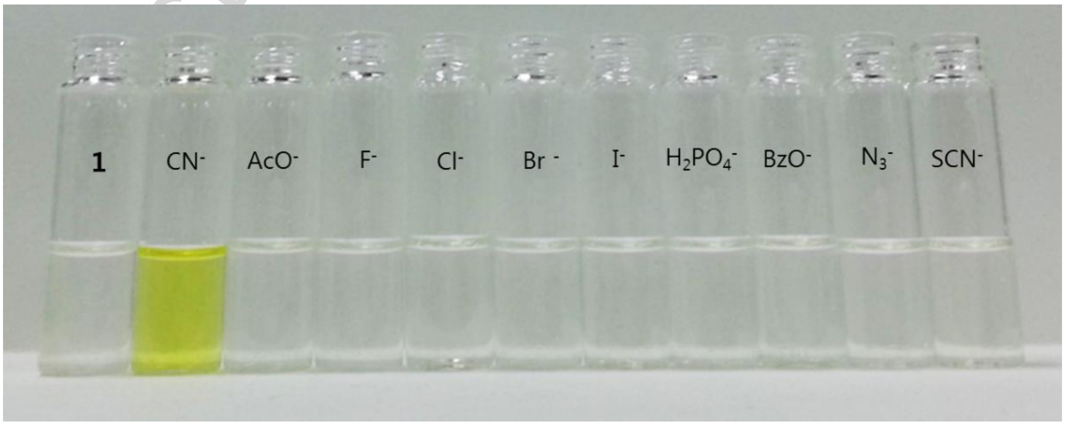

1
CN-
AcO-
F-
Cl-
Br -
I-
H2PO4-
BzO-
N3-
SCN-

Fig. 1

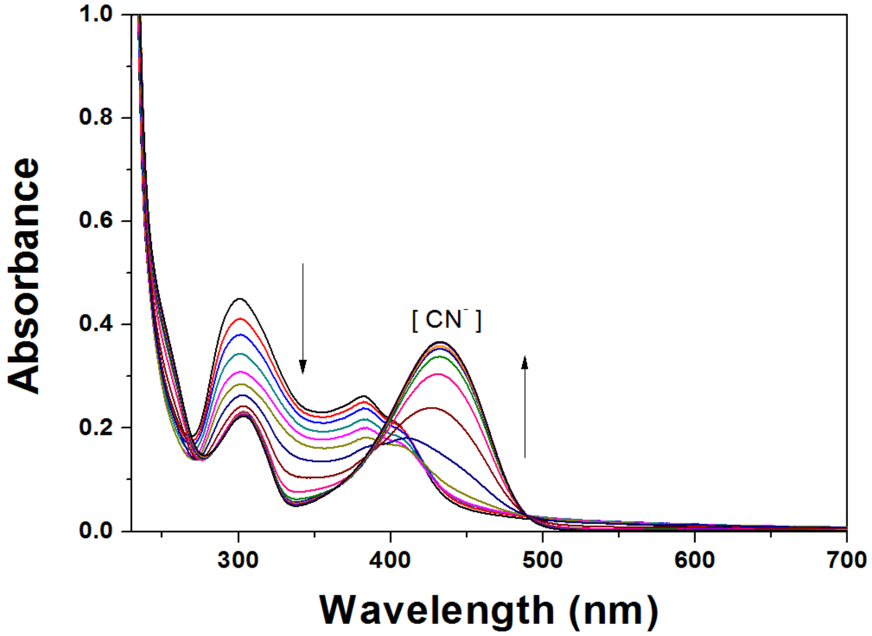

1.0
0.8
0.6
0.4
0.2
0.0
Absorbance
300
400
500
600
700
Wavelength (nm)
[CN⁻]

Fig. 2

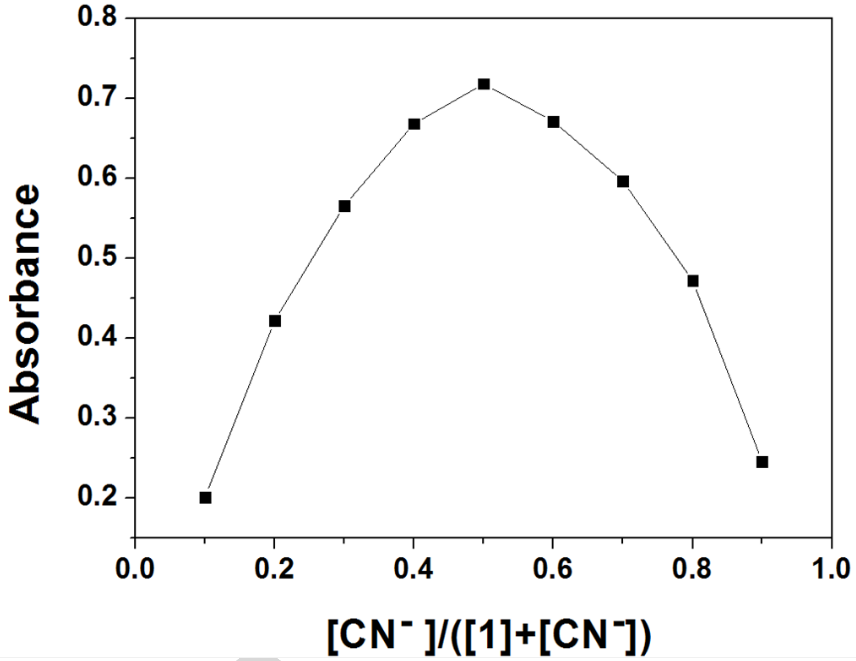


Fig. 3

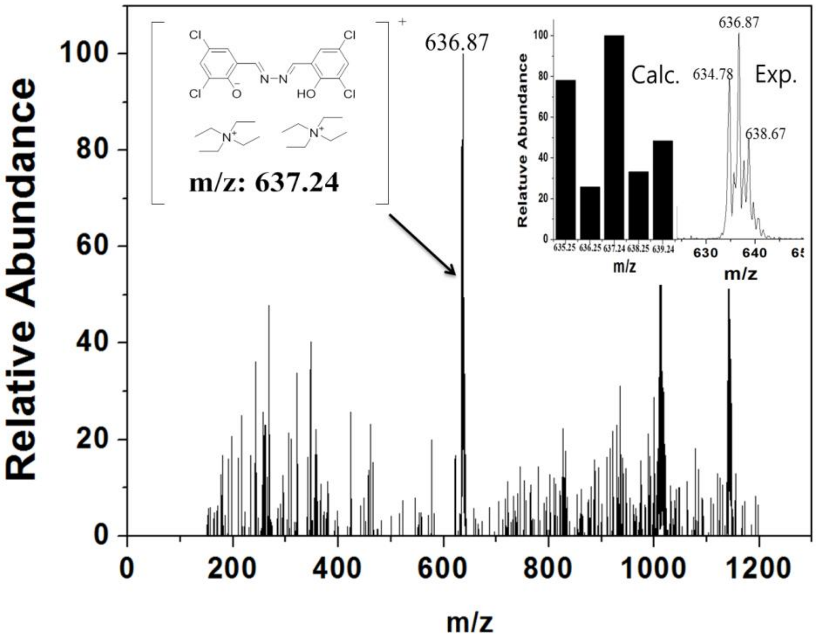

Relative Abundance
m/z
0
20
40
60
80
100
0
200
400
600
800
1000
1200
636.87
m/z: 637.24
Cl
O
N–N
HO
N+
Calc.
Exp.
634.78
638.67
Relatuve Abundance
635.25
636.25
637.24
638.25
639.24
630
640

Fig. 4

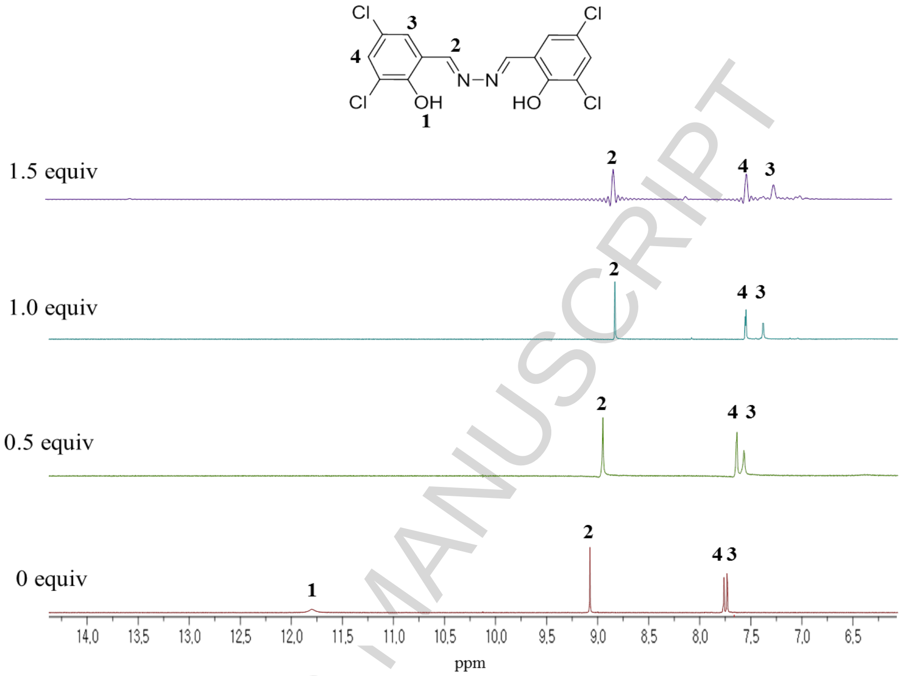
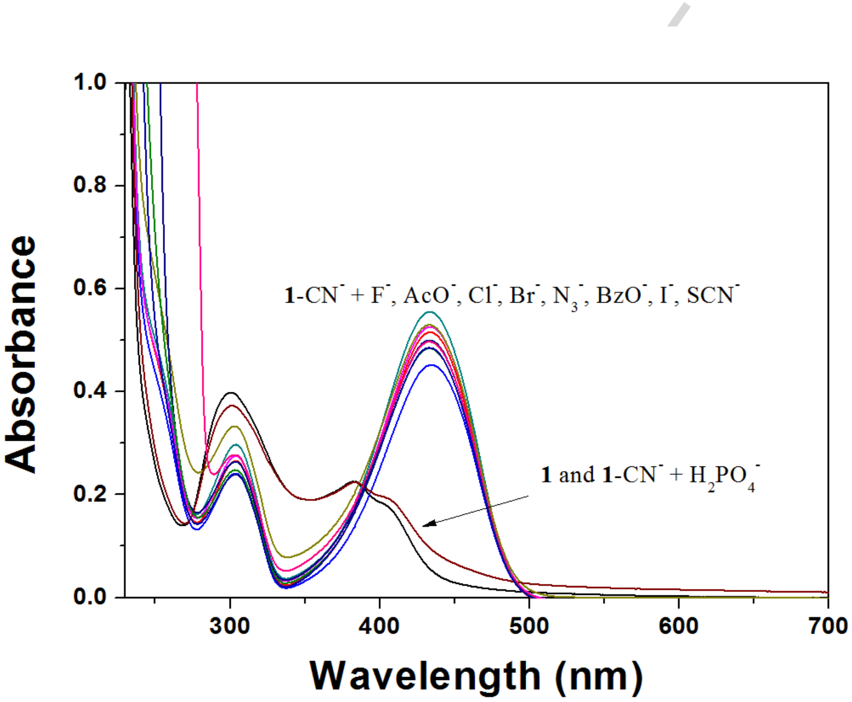

Cl
3
2
4
Cl
OH
1
N
N
HO
Cl
Cl
1.5 equiv
2
4
3
1.0 equiv
2
4 3
0.5 equiv
2
4 3
0 equiv
1
2
4 3
14,0
13,5
13,0
12,5
12,0
11,5
11,0
10,5
10,0
9,5
9,0
8,5
8,0
7,5
7,0
6,5
ppm

Fig. 5

(a)


Absorbance
0.0
0.2
0.4
0.6
0.8
1.0
300
400
500
600
700
Wavelength (nm)
1-CN$^-$ + F$^-$, AcO$^-$, Cl$^-$, Br$^-$, N$_3^-$, BzO$^-$, I$^-$, SCN$^-$
1 and **1**-CN$^-$ + H$_2$PO$_4^-$

(b)

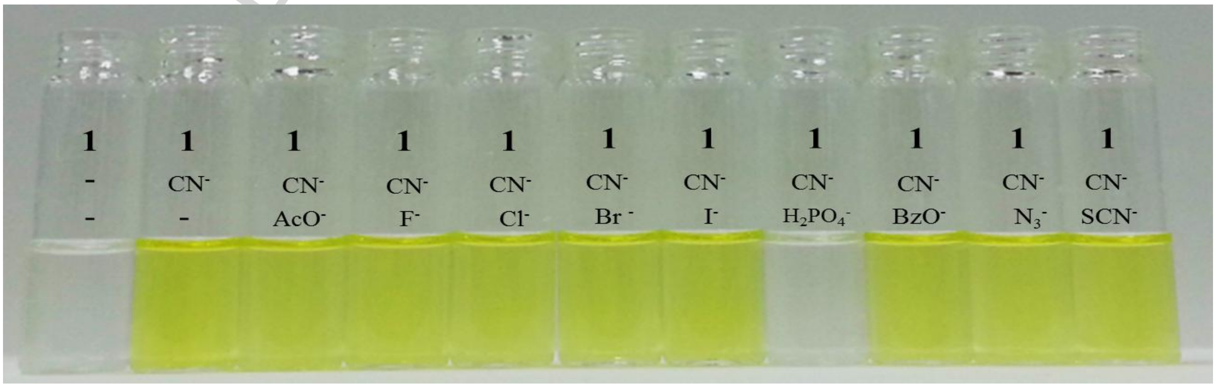
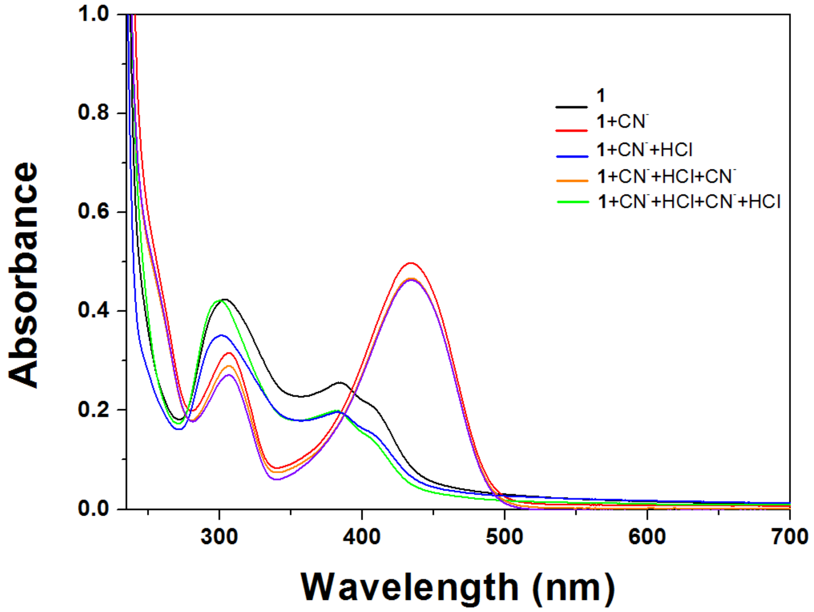

1 - -
1 CN$^-$ -
1 CN$^-$ AcO$^-$
1 CN$^-$ F$^-$
1 CN$^-$ Cl$^-$
1 CN$^-$ Br$^-$
1 CN$^-$ I$^-$
1 CN$^-$ H$_2$PO$_4^-$
1 CN$^-$ BzO$^-$
1 CN$^-$ N$_3^-$
1 CN$^-$ SCN$^-$

Fig. 6

(a)


1.0
0.8
0.6
0.4
0.2
0.0
Absorbance
300
400
500
600
700
Wavelength (nm)
1
1+CN-
1+CN-+HCl
1+CN-+HCl+CN-
1+CN-+HCl+CN-+HCl

(b)

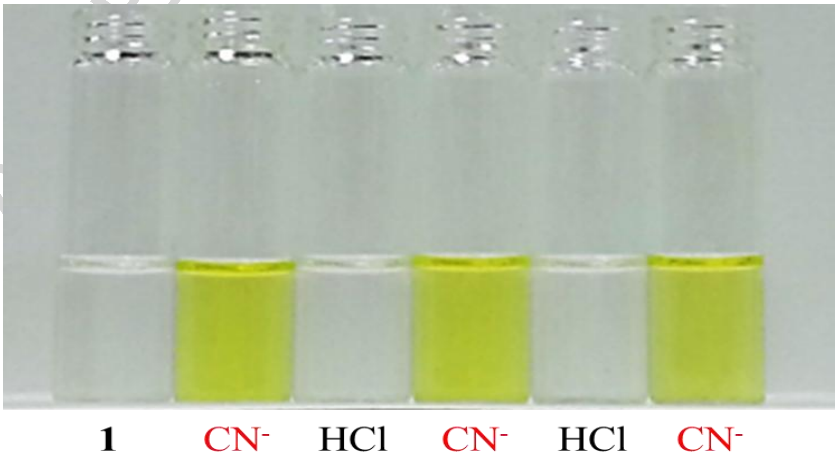
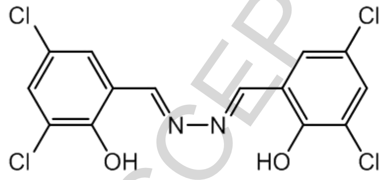

1
CN-
HCl
CN-
HCl
CN-

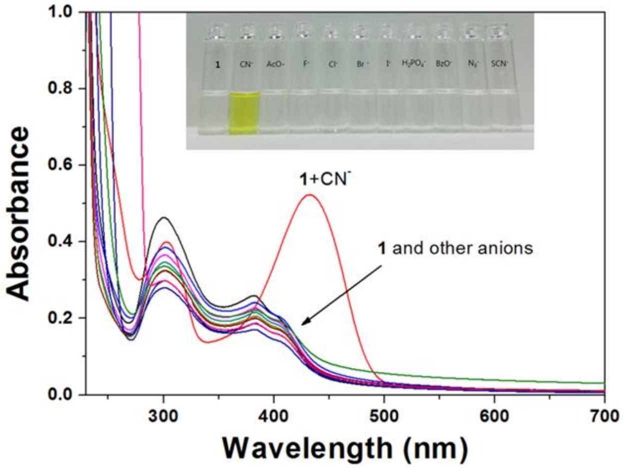
Fig. 7

Graphical abstract

A highly selective colorimetric chemosensor (**1**) based on the combination of hydrazine and 3,5-dichloro-2-hydroxybenzaldehyde was designed and synthesized. Receptor **1** showed exclusive response toward cyanide by a color change from colorless to yellow in aqueous solution. The binding mode of **1**-CN^- species was determined to be a 1:1 stoichiometry through Job plot, ^{1}H NMR titration, and ESI-mass spectrometry analysis.



1



Highlights

► A colorimetric Schiff base chemosensor **1** was synthesized.

► CN^- resulted in an immediate color change from colorless to yellow.

► Receptor **1** could be recyclable simply through treatment HCl.