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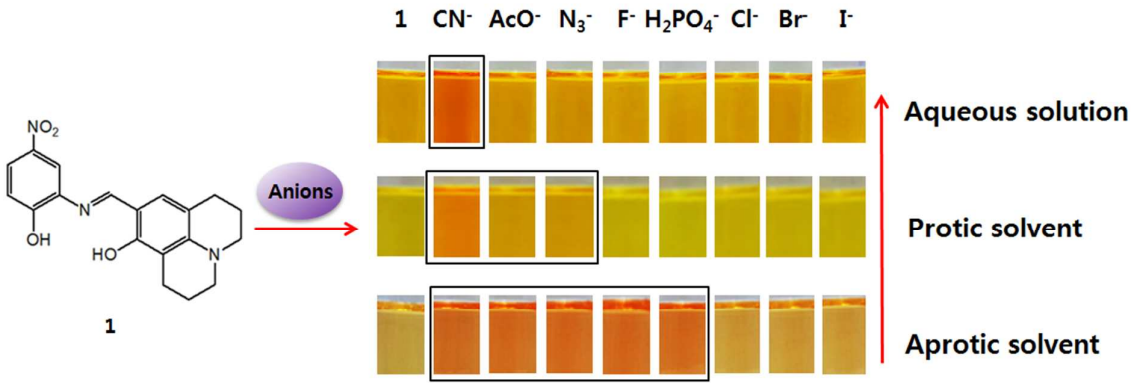

A new highly selective colorimetric chemosensor **1** shows exclusive response toward cyanide by a color change in aqueous solution.

Colorimetric chemosensor based on a Schiff base for highly selective sensing of cyanide in aqueous solution: Influence of solvents

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Abstract

A new highly selective colorimetric chemosensor **1** (E)-9-(((2-hydroxy-5-nitrophenyl)imino)methyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-8-ol for CN^- was developed. Receptor **1** showed exclusive response toward cyanide by a color change in aqueous solution. However, in aprotic solvents and methanol, the unique selectivity of **1** for CN^- disappeared, and its nonselective color change was observed for other anions. This phenomenon could be possibly explained by the combination of the basicity and the hydrogen bonding ability of the anions. Moreover, **1** could be used as a practical, visible colorimetric test kits in aqueous environment.

Keywords: deprotonation, cyanide, colorimetric, solvent effect

1. Introduction

The development of molecular sensors for anions has been a subject of intense research interest, because anions play important roles in a wide range of environmental, clinical chemicals, and biological applications.[1-8] 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.[9-17] Cyanide could be absorbed through lungs, gastrointestinal track and skin, leading to vomiting, convulsion, loss of consciousness, and eventual death.[18-20] Despite its toxicity, its application in various areas as raw materials for synthetic fibers, resins, herbicides, and the gold-extraction process is inevitable,[21-23] which releases cyanide into the environment as a toxic contaminant. Thus, there is a need for an efficient sensing system to monitor cyanide concentration from contaminant sources. Among various approaches such as fluorescence techniques and electrochemical methods for the detection of cyanide, the most attractive approach focuses on novel colorimetric cyanide sensors, which allow naked-eye detection of the color change without resorting to the use of expensive instruments.[24-27] Colorimetric materials have good points like low cost, rapid response rate, easy method and high selectivity.[28-32] Therefore, colorimetric sensors that are capable of recognizing cyanide in aqueous environment have to be developed.

Over the past decades, many efforts have been devoted to design various chemosensors to detect cyanide, including the formation of cyanide complexes with transition metals,[33] nucleophilic addition reactions to carbonyl groups,[34] the displacement approach,[35] hydrogen-bonding interactions[36] and deprotonation.[37] However, many receptors for cyanide reported to date have several limitations as follows[38-41]: (i) poor selectivity, especially in the presence of fluoride or acetate, (ii) requiring specific conditions, such as high temperature or basic media, (iii) not instantaneously registering the addition of cyanide, (iv) requiring the use of instruments such as luminoscopes, or UV light, (v) only working in an organic environment, and (vi) complicated synthesis. To overcome these limitations, we synthesized a new colorimetric sensor capable of detecting CN^- with color change by ICT transition in aqueous environment.

Herein, we report a new chemosensor **1** for CN^-, which was synthesized in one step by condensation reaction of 2-amino-4-nitrophenol and julolidine (scheme 1). Receptor **1** can detect cyanide by color change from yellow to orange via the 'naked-eye' with high selectivity in aqueous environment. In contrast, the unique selectivity for CN^- disappeared and nonselective color changes were observed in methanol and aprotic solvents. These results are possibly explained by the combination of the basicity and the hydrogen bonding ability of the anions.

2. Experimental

2.1. Reagent and apparatus

All the solvents and reagents (analytical grade and spectroscopic grade) were obtained commercially and used as received. ^{1}H NMR and ^{13}C NMR measurements were performed on a Varian 400 MHz spectrometer and chemical shifts are recorded in ppm. Absorption spectra were recorded using a Perkin Elmer model Lambda 2S UV-Vis spectrometer at room temperature. Electrospray ionization mass spectra (ESI-mass) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument. Elemental analysis for carbon, nitrogen, and hydrogen was carried out by using a Flash EA 1112 elemental analyzer (thermo) in Organic Chemistry Research Center of Sogang University, Korea.

2.2. Synthesis of receptor 1

2-Amino-4-nitrophenol (0.71 g, 2 mmol) and 8-Hydroxyjulolidine-9-carboxaldehyde (0.45 g, 2 mmol) were dissolved in 5 mL of ethanol. Then, three drops of hydrochloric acid was added into the reaction mixture, which was stirred for 3 hour at room temperature. The orange powder was produced. The orange solid was collected by filtration, washed with diethyl ether and air-dried. Yield: 0.075 g (20.0 %). mp : 230-232 ^{o}C. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 13.94 (s, 1H), 11.17 (s, 1H), 8.70 (s, 1H), 8.14 (s, 1H), 7.96 (d, J=8 Hz, 1H), 7.07 (d, J=8 Hz, 1H), 6.93 (s, 1H), 3.24 (m, 4H), 2.60 (m, 4H), 1.85 (m, 4H) ppm. ^{13}C NMR (DMSO-d_6, 400 MHz) δ 161.66, 160.53, 157.73, 147.90, 140.76, 136.66, 130.91, 122.45,

116.54, 114.45, 113.58, 108.97, 105.95, 50.15, 49.75, 27.40, 22.16, 21.19, 20.62 ppm. LRMS (ESI): m/z calcd for $C_{19}H_{19}N_3O_4$ ([M-H^+]), 352.13; found, 352.27. Anal. calcd for $C_{19}H_{19}N_3O_4$ (353.14): C, 64.58; H, 5.42; N, 11.89. Found: C, 65.01; H, 5.90; N, 11.72 %.

2.3. UV-vis measurements

Receptor **1** (3.35 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 6 μL of the **1** (10 mM) were diluted with 2.994 mL methanol/H_2O (2:1, v/v) to make the final concentration of 20 μM. Tetraethylammonium cyanide (TEACN, 15.6 mg, 0.1 mmol) was dissolved in a mixture of methanol/H_2O (2:1; v/v, 1 mL). 6-114 μL of the CN^- solution (100 mM) were transferred to each receptor solution (20 μM) prepared above. After shaking the vials for a few minutes, UV-vis spectra were taken at room temperature.

2.4. Competition with other anions

Receptor **1** (3.35 mg, 0.01 mmol) was dissolved in DMSO and 6 μL of the **1** (10 mM) were diluted with 2.994 mL methanol/H_2O (2:1, v/v) to make the final concentration of 20 μM. Tetraethylammonium (TEA) salt (F^-, Br^-, Cl^-, I^- and CN^-; 0.1 mmol) or tetrabutylammonium (TBA) salt (AcO^-, $H_2PO_4^-$ and N_3^-; 0.1 mmol) were dissolved in a mixture of methanol/bis-tris buffer (2:1; v/v, 1 mL), respectively. 24 μL of each anion solution (100 mM) were taken and added into 3 mL of each **1** solution (20 μM) prepared above to make 40 equiv. Then, 24 μL of CN^- solution (100 mM) were added into the mixed solution of each metal ion and **1** to make 40 equiv. After shaking the vials for a few minutes, UV-vis spectra were taken at room temperature.

2.5. Job plot measurement

Receptor **1** (3.35 mg, 0.01 mmol) was dissolved in a mixture of methanol/H_2O (2:1; v/v, 1 mL). 12, 10.8, 9.6, 8.4, 7.2, 6.0, 4.8, 3.6, 2.4, and 1.2 μL of the **1** solution were taken and transferred to vials. Each vial was diluted with a mixture of methanol/H_2O (2:1, v/v) to make a total volume of 2.988 mL. TEACN (1.56 mg, 0.01 mmol) was dissolved in a mixture of methanol/H_2O (2:1; v/v, 1 mL). 0, 1.2, 2.4, 3.6, 4.8, 6.0, 7.2, 8.4, 9.6, 10.8, and 12 μL of the CN^- solution were added to each diluted **1** solution. Each vial had a total volume of 3 mL. After shaking the vials for a few minutes, UV-vis spectra were taken at room temperature.

2.6. ^{1}H NMR titration of 1 with CN^-

Four NMR tubes of **1** (0.76 mg, 0.002 mmol) dissolved in a mixture of DMSO-d_6/CD_3OD/D_2O (5:2:1; v/v/v, 0.7 mL) were prepared, and four different equiv (0, 0.5, 2, 5 equiv) of tetraethylammonium cyanide dissolved in the mixture of DMSO-d_6/CD_3OD/D_2O (5:2:1; v/v/v, 0.7 mL) were added to **1** solution separately. After shaking them for a minute, their ^{1}H NMR spectra were taken at room temperature.

2.7. Colorimetric test kit

Receptor **1** (3.35 mg, 0.01 mmol) was dissolved in a mixture of methanol/DMSO (8:2; v/v, 1 mL). Receptor **1**-test kits were prepared by immersing filter papers into receptor **1** solution (5 mM), and then dried in air. Tetraethylammonium salt (F^-, Br^-, Cl^-, I^- and CN^-; 0.002 mmol) or tetrabutylammonium salt (AcO^-, $H_2PO_4^-$ and N_3^-; 0.002 mmol) were dissolved in bis-tris buffer (1 mL), respectively. The test kits prepared above were added into different anion solutions (1 mL), and then dried at room temperature.

3. Results and discussion

The colorimetric chemosensor **1** for cyanide was synthesized by condensing of 2-amino-4-nitrophenol with julolidine (Scheme 1), and characterized by ^{1}H and ^{13}C NMR, ESI-mass spectrometry, and elemental analysis.

3.1. Sensing properties of 1 toward anions in aqueous solution

The colorimetric selective sensing abilities of receptor **1** with various anions in a mixture of methanol/H_2O (2:1, v/v) were monitored by UV-vis absorption spectra (Fig. 1a). Only the addition of CN^- induced distinct spectral changes while other anions such as F^-, AcO^-, Cl^-, Br^-, I^- , $H_2PO_4^-$ and N_3^- did not induce any spectral changes. Consistent with the change of UV-vis spectra, the solution of **1** resulted in an immediate color change from yellow to orange with cyanide ion (Fig. 1b), indicating that receptor **1** can serve as a ‘naked-eye’ cyanide indicator in aqueous solution.

UV-vis absorption spectral variation of sensor **1** was monitored during titration with different concentrations of CN^-. As shown in Fig. 2, the decrease in the absorption bands at 310 nm and 442 nm was observed after adding of CN^-, and then the absorption bands at 360 nm and 500 nm gradually reached maxima at 40 equivalent of CN^-. The isosbestic points at 278 nm, 333 nm, 394 nm and 472 nm were clearly observed, indicating the formation of a single species between the receptor **1** and the cyanide. The orange color of the solution observed upon addition of cyanide to receptor **1** might be attributed to the intramolecular charge transfer (ICT) transition from the phenolate to the electron deficient nitrophenyl group.[42-44] To clarify the ICT properties of **1**, we have checked the change of the emission spectra in polar and non-polar solvents such as DMSO, MeOH, EtOH and chloroform, because the solvent dipoles can relax the ICT excited state in response to the charge separation, thus expecting red-shifted fluorescence induced by polar solvents.[45-47] As shown in Table 1, the fluorescence spectra of **1** were red-shifted with increase of the solvent polarity. This solvatochromic behavior demonstrates the occurrence of ICT in receptor **1**.[45-47] In the presence of cyanide, then, the energy gap of ICT band decreases, being responsible for the increase of the band at 500 nm and for the development of the orange color (Scheme. 2). The Job plot indicated a 1:1 binding interaction between the receptor **1** and cyanide (Fig. S3). The negative ion mass spectrum of ESI-mass indicated that a peak at m/z = 352.27 is assignable to **1**-H^+ [calcd, m/z = 352.13], which is corresponding to the receptor **1** deprotonated by cyanide ion (Fig. S4). From the Benesi-Hildebrand equation,[48] the association constant was found to be 1.7(±0.2) x 10^2 M^{-1} for the CN^- recognition of receptor **1** (Fig. S5). This value is within the range of those (1.0 ~ 1.0 x 10^5) reported for CN^- sensing chemosensors.[49-53] The detection limit (3∂/k) of receptor **1** for the analysis of CN^- ions was calculated to be 105 μM (Fig. S6).[54]

To gain a fuller understanding of the host-guest interaction between **1** and cyanide, ^1H NMR titrations of **1** were performed in the absence and presence of different equiv of the cyanide as the TEA salt (Fig. S7). The receptor **1** gave a singlet at 8.6 ppm corresponding to the CH=N proton while the aromatic protons of the sensor were resonated in the 8.2-6.8 ppm region. Upon gradual addition of cyanide, the imine and aromatic protons were shifted to upfield. Especially, the pronounced upfield shift was observed for H(2). This large upfield

shift could be explained that the nitrophenolic OH was deprotonated by CN^- and the resulting deprotonation increased a negative charge on the 2-position of the nitrophenyl ring, as shown in Scheme 2. Therefore, H(2) showed the large upfield shift. In addition, no new peak was observed in the range of 5-6 ppm, which indicates exclusion for the nucleophilic addition of cyanide to the imine moiety.

To further confirm the sensing mechanism between **1** and CN^-, the interaction between **1** and OH^- was also investigated. UV-vis spectral change of **1** upon addition of OH^- was similar with that of **1** obtained from the addition of CN^-, which indicated the deprotonation between **1** and CN^- (Fig. S8).

To understand reversibility between **1** and CN^-, HCl-addition experiments were conducted in the mixture of methanol/H_2O (2:1, v/v) (Fig. S9). After adding 40 equiv of HCl to **1**-CN^- solution, the color changed from orange to yellow and the absorbance at 500 nm completely changed. Upon addition of CN^- into the solution again, the color and the absorbance were recovered. The color change and absorbance were almost reversible even after several cycles with the sequentially alternative addition of CN^- and HCl.

To explore the ability of **1** as a colorimetric sensor for CN^- in the presence of competing anions, competition experiments were performed in the presence of CN^- mixed with various anions (Fig. 3). The coexistent anions had no influence on the color change of CN^-. These results indicate that receptor **1** shows an excellent selectivity for cyanide anion in the presence of other anions, making it very useful in practical applications

For the practical application of receptor **1**, test kits were prepared by immersing filter papers in a methanol solution of **1** (5 mM) and then drying in air. These test kits were utilized to sense CN^- among different anions. As shown in Fig. 4, when the test kits coated with **1** were added to different anion solutions, the obvious color change was observed only with CN^- in methanol/H_2O solution (2:1, v/v). Therefore, the test kits coated with the receptor **1** solution would be convenient for detecting CN^-. These results showed that receptor **1** could be a valuable practical sensor for environmental analyses of CN^-.

3.2. Sensing properties of 1 toward anions in a protic solvent methanol

We also investigated the sensing properties of **1** toward various anions in a protic solvent methanol. Receptor **1** displayed a deep color change with CN^- and pale color changes with AcO^- and N_3^-, whereas other anions showed no effect (Fig. 5). Consistent with the color change of the three anions, UV-vis spectral changes were also observed to large extent with CN^- and to small extent with AcO^- and N_3^- (Fig. 5). This phenomenon could be possibly explained by the combination of the basicity and the hydrogen bonding ability of the anions. The basicity of anions is known to be in order of $CN^- > AcO^- > N_3^- > F^- > H_2PO_4^- > Cl^- > Br^- > I^-$ [55] and their hydrogen bonding ability is assumed to be in order of $F^- > AcO^- > H_2PO_4^- > N_3^- \sim CN^-$, based on their electro-negativity. In water, therefore, water molecules form strong hydrogen bonding with the anions having a strong hydrogen bonding character such as F^-, AcO^-, and $H_2PO_4^-$. Therefore, those anions are not able to deprotonate the phenolic proton of **1**, thus showing no color change. In contrast, CN^- with the most basic and least hydrogen bonding character might deprotonate the phenolic proton instead of forming the hydrogen bonding with water molecules, thus resulting in the color change.

In the protic solvent methanol, F^- and $H_2PO_4^-$ with a strong hydrogen bonding character could still form hydrogen bonding with a less polar solvent methanol. Therefore, they are not able to deprotonate the phenolic proton of **1**. In contrast, CN^-, AcO^-, and N_3^- with a strong basicity and less hydrogen bonding character might deprotonate the phenolic proton of **1** instead of forming the hydrogen bonding with methanol molecules, and then, showing color change. In addition, the basicity of CN^- is greater than those of AcO^-, and N_3^-. Therefore, CN^- with a strong deprotonation ability showed a deep color change with **1**, and AcO^- and N_3^- with less deprotonation ability did pale color changes with it, as shown in Fig. 7.

In order to further understand the binding character between **1** and CN^-, the UV-vis titration experiments of **1** with CN^- were carried out in MeOH (Fig. 6). Increase in the absorption bands at 342 nm and 428 nm was observed after adding of CN^-, and then the absorption bands at 300 nm and 310 nm decreased gradually until the amount of CN^- reached 22.5 equiv. The spectra showed the clear isosbestic points at 267 nm, 318 nm, 375 nm and 453 nm, indicating the formation of the only one species between **1** and CN^-. The Job plot indicated a 1:1 binding interaction between the receptor **1** and cyanide (Fig. S10a). Both acetate and azide also showed similar results (Fig. S10b and c). From the Benesi-Hildebrand

equation,[48] the association constants for the anions with **1** were found to be 5.0(±2) x 10^3 M^{-1} for CN^-, 6.3(±2) x 10^2 M^{-1} for AcO^- and 3.5(±2) x 10^2 for N_3^-, respectively (Fig. S11), which match well the basicity order of the three anions. In addition, these results demonstrate that **1** showed stronger binding property toward the anions in methanol than in water, because water molecules with a good hydrogen-bonding character interfere with the interaction between **1** and the anions except for CN^-. The detection limit (3∂/k) of receptor **1** for the analysis of CN^-, AcO^-, and N_3^- were calculated to be 32(±10) μM, 840(±20) μM and 840(±20) μM, respectively (Fig. S12).[54]

3.3. Sensing properties of 1 toward anions in aprotic solvents

We further investigated the sensing properties of **1** toward anions in various aprotic solvents such as DMSO, DMF, and CH_3CN. In DMSO, receptor **1** displayed an absorption band at 424 nm, and the addition of **1** into CN^-, AcO^-, N_3^-, F^-, and $H_2PO_4^-$ showed dramatic color change from yellow to orange, whereas other anions showed no color change (Fig. 7a and b). The dramatic color changes were consistent with UV-vis spectral changes. Nearly identical results were also observed in aprotic solvents such as DMF and CH_3CN (Fig. S13). These results could be also explained by the combination of the basicity and the hydrogen bonding ability of the anions. The basic anions such as CN^-, AcO^-, N_3^-, F^-, and $H_2PO_4^-$ are able to deprotonate the phenolic proton of **1** in the aprotic solvents, because the solvents cannot form the hydrogen bonding with the anions. Therefore, the anions could change color from yellow to orange due to deprotonation. As a result, the selectivity of **1** towards CN^- is not observed in aprotic solvents.

Fig. 8 shows the family of spectra obtained over the course of the titration of solution **1** with CN^- in DMSO. As cyanide ions were added to the 20 μM solution of **1**, maximum of **1** moved from 416 nm to 500 nm and the spectra showed the clear isosbestic points at 275 nm, 331 nm, 354 nm and 439 nm. The presence of the clear isosbestic points also indicates that only two species were present at equilibrium over the course of the titration experiment. Other basic anions such as F^-, AcO^-, $H_2PO_4^-$, and N_3^- showed almost the same phenomena. The Job plots of CN^-, AcO^-, N_3^-, F^-, and $H_2PO_4^-$ with **1** indicated a 1:1 binding interaction (Fig. S14). From the Benesi-Hildebrand equation,[48] the association constants for all CN^-,

AcO^-, $H_2PO_4^-$, and F^- were found to be 5.0(±2) x 10^4 M^{-1} (Fig. S15), while the association constant for N_3^- with **1** was found to be 1.6(±0.2) x 10^3 M^{-1}. The association constants of selective anions depending on solvents were summarized in Table 2. As one can see, the association constants decrease according to the change of the solvent systems from aprotic to protic to aqueous solution. These results are consistent with our early explanation, based on by the combination of the basicity and the hydrogen bonding ability of the anions towards receptor **1** and solvent systems. The detection limits (3∂/k) of receptor **1** were calculated to be 1.2(±0.2) μM for the CN^- and AcO^-, and 1.6(±0.2) μM for F^- and $H_2PO_4^-$, and 70(±14) μM for N_3^-, respectively (Fig. S16).[54]

In summary, the receptor **1** showed different anion selectivity in various solvent systems (e.g.; CN^- in aqueous solvent; CN^-, AcO^-, and N_3^- in protic solvents such as methanol; CN^-, AcO^-, N_3^-, F^-, and $H_2PO_4^-$ in aprotic solvent), while most anion receptors reported to date detected a single anion in a single solvent system.[17,56] These results were understood by the modulation of the basicity and the hydrogen bonding ability of the anions.

4. Conclusion

We developed a simple imine-based colorimetric chemodosimeter **1**, which displays high selectivity for detection of cyanide in aqueous solution. The receptor **1** bound to cyanide ions in a 1:1 stoichiometric manner, which induces a fast color change from yellow to orange for CN^- over other anions. In contrast, poor selectivity for cyanide was observed due to non-selective deprotonation by basic anions in protic and aprotic solvent. These results could be possibly explained by the combination of the basicity and the hydrogen bonding ability of the anions. There are several advantages associated with **1** for cyanide detection: such as (i) a simple synthesis of the receptor **1**; (ii) showing high selectivity over other competing anions such as, AcO^-, N_3^-, F^-, and $H_2PO_4^-$ in aqueous solution and (iii) a practical application of **1** by using test kits. Therefore, receptor **1** may constitute a simple and inexpensive chemodosimeter which demonstrates a highly viable and useful application for the detection of CN^- in aqueous environment.

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Supplementary Information.

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

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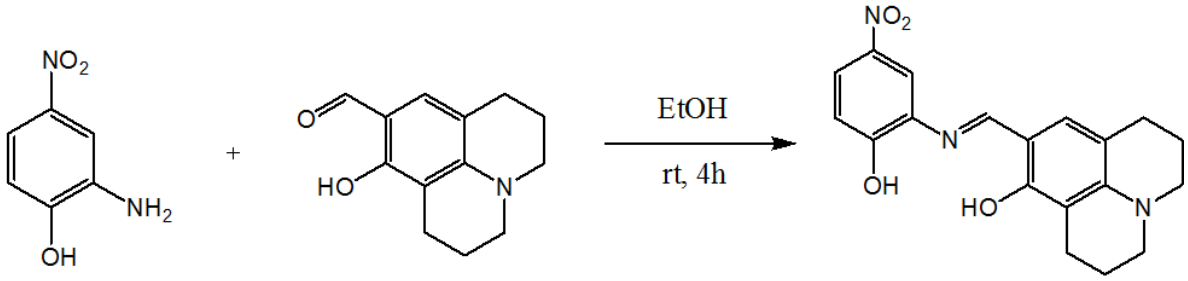
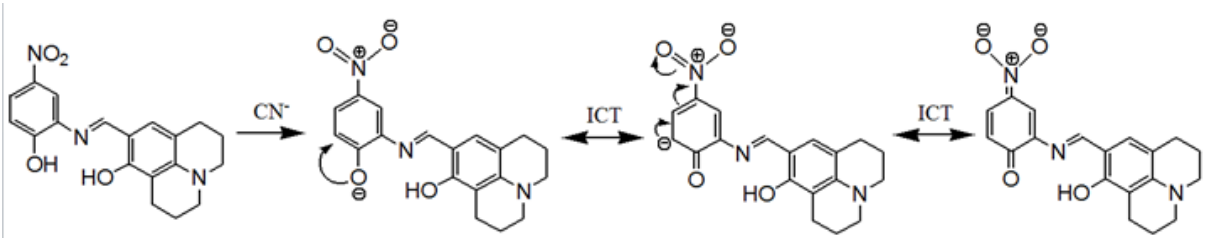


Scheme 1. Synthetic procedure of **1**



Scheme 2. Proposed sensing mechanism of **1** for cyanide in a mixture of methanol/H_2O (2:1, v/v)

Table 1. Emission properties of **1** in various solvents.

Solvent	λ_{ex}	λ_{em}
DMSO	360	588
MeOH	360	570
EtOH	360	562
$CHCl_3$	360	520

Table 2. Binding constants for **1** with anions in various solvents.

	$K(M^{-1}, CN^-)$	$K(M^{-1}, AcO^-)$	$K(M^{-1}, N_3^-)$	$K(M^{-1}, F^-)$	$K(M^{-1}, H_2PO_4^-)$
Methanol/H_2O (2:1, v/v)	$1.7(\pm0.2)x10^2$	-	-	-	-
Methanol	$5.0(\pm2)x10^3$	$6.3(\pm2)x10^2$	$3.5(\pm2)x10^2$	-	-
DMSO	$5.0(\pm2)x10^4$	$5.0(\pm2)x10^4$	$1.6(\pm0.2)x10^3$	$5.0(\pm2)x10^4$	$5.0(\pm2)x10^4$

Figure captions

Figure 1. (a) UV-vis spectral changes of **1** (20 μM) upon the addition of various anions (40 equiv) in a mixture of methanol/H_2O (2:1, v/v). (b) The color changes of **1** (20 μM) upon addition of various anions (40 equiv) in a mixture of methanol/H_2O (2:1, v/v).

Figure 2. UV-vis spectral changes of **1** (20 μM) upon addition of CN^- (up to 60 equiv) in a mixture of methanol/H_2O (2:1, v/v). Inset: Absorbance at 500 nm versus the number of equiv of CN^- added.

Figure 3. Competitive selectivity of **1** (20 μM) towards CN^- in the presence of other anions (40 equiv).

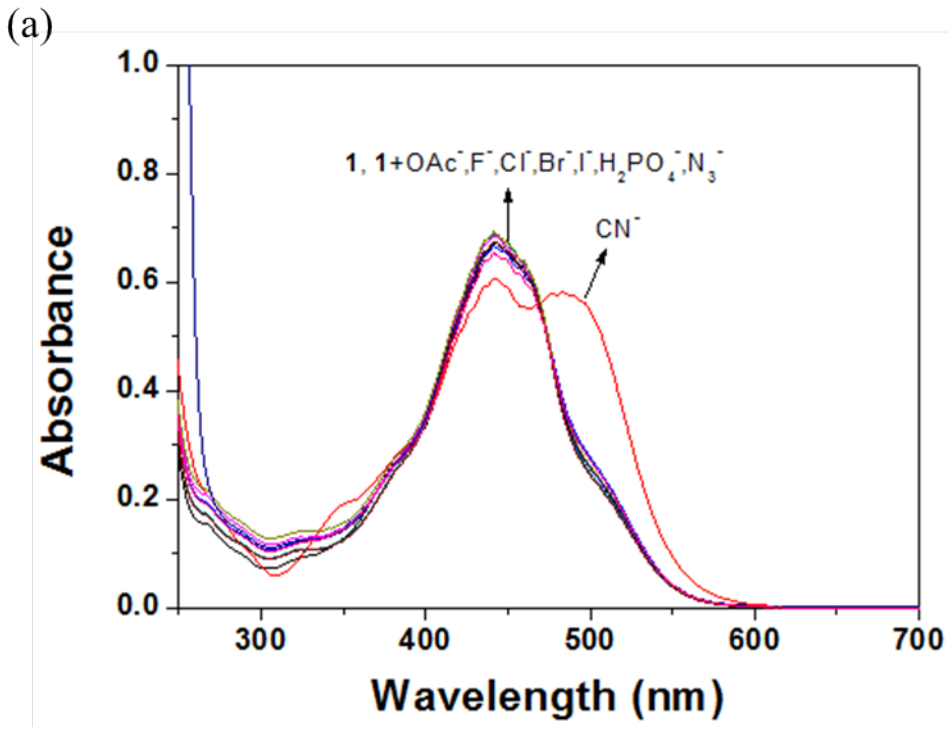
Figure 4. Photographs of the test kits with **1** (5 mM) for detecting cyanide ion in neutral aqueous solution with other anions.

Figure 5. UV-vis spectral changes of **1** (20 μM) upon the addition of various anions (22.5 equiv) in methanol. Inset: The color changes of **1** (40 μM) upon addition of various anions (22.5 equiv).

Figure 6. UV-vis spectral changes of **1** (20 μM) upon addition of CN^- (up to 22.5 equiv) in methanol. Inset: Absorbance at 500 nm versus the number of 22.5 equiv of CN^- added.

Figure 7. (a) UV-vis spectral changes of **1** (20 μM) upon the addition of various anions (1 equiv) in DMSO. (b) The color changes of **1** (40 μM) upon addition of various anions (1 equiv) in DMSO.

Figure 8. UV-vis spectral changes of **1** (20 μM) upon addition of CN^- (up to 1 equiv) in DMSO. Inset: Absorbance at 500 nm versus the number of equiv of CN^- added.



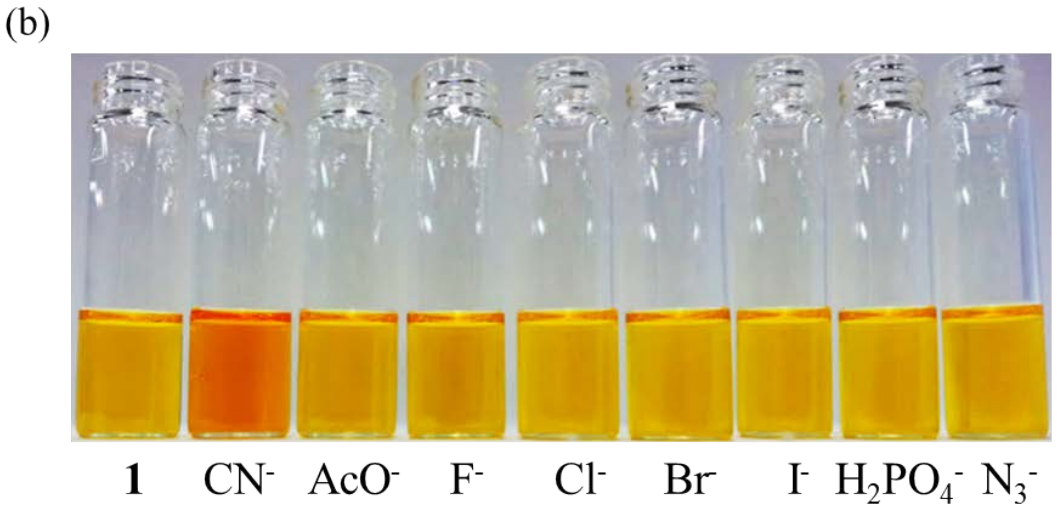


Fig. 1

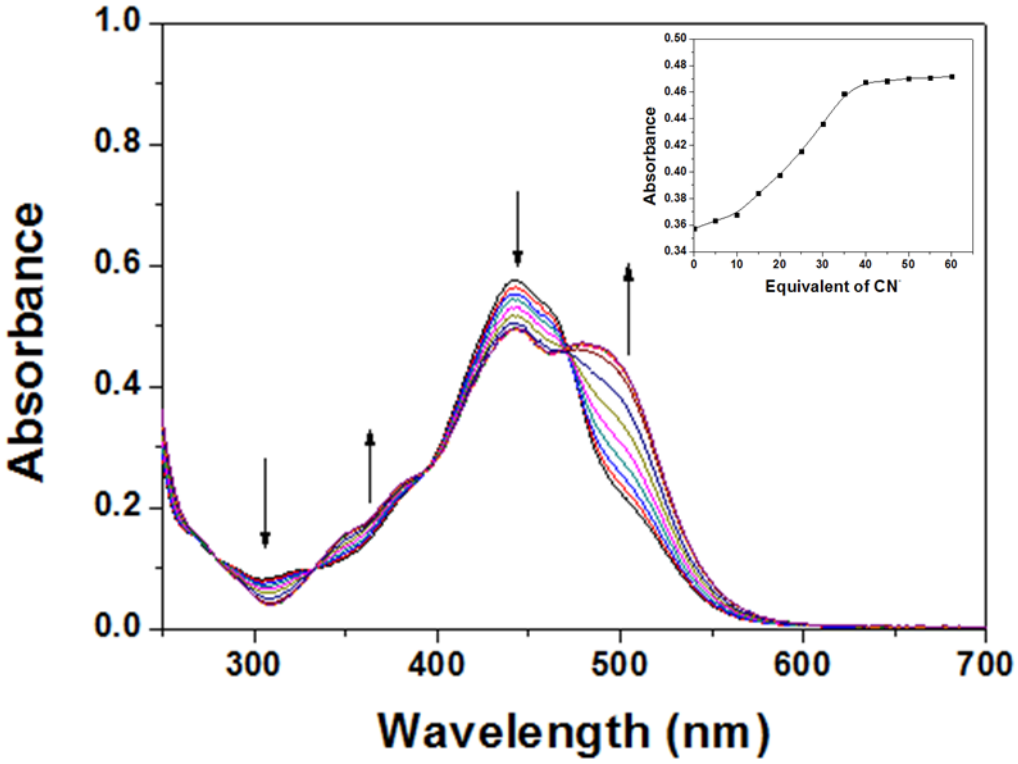
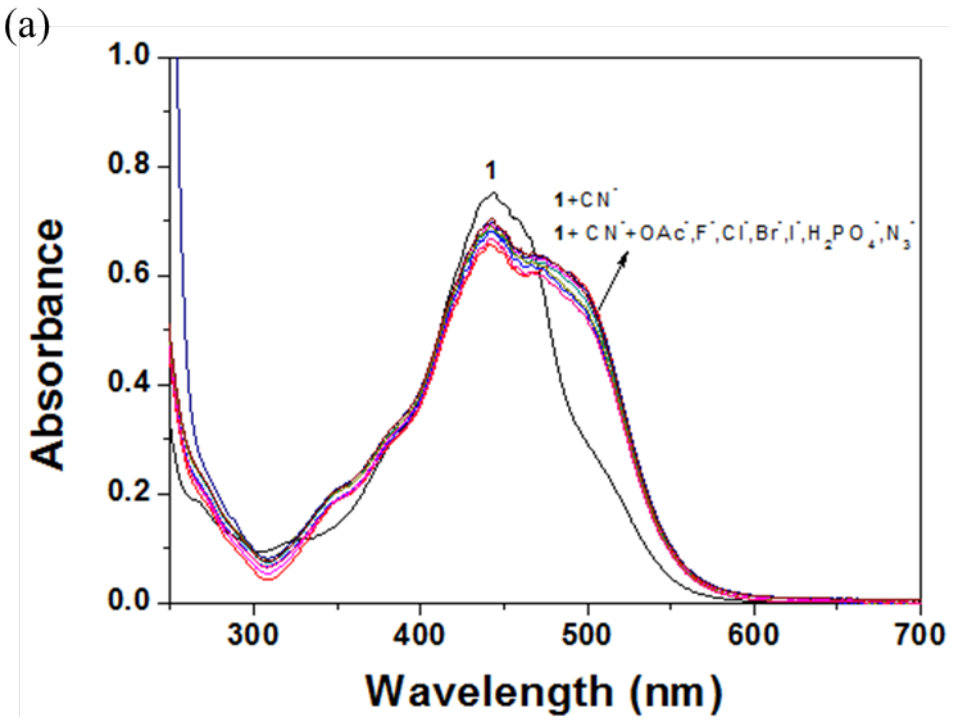


Fig. 2



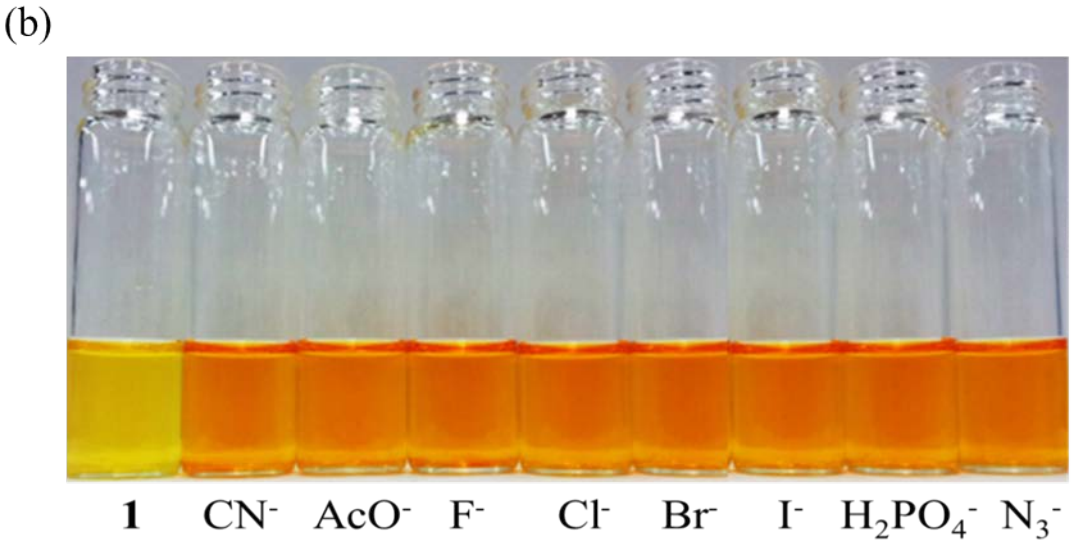


Fig. 3

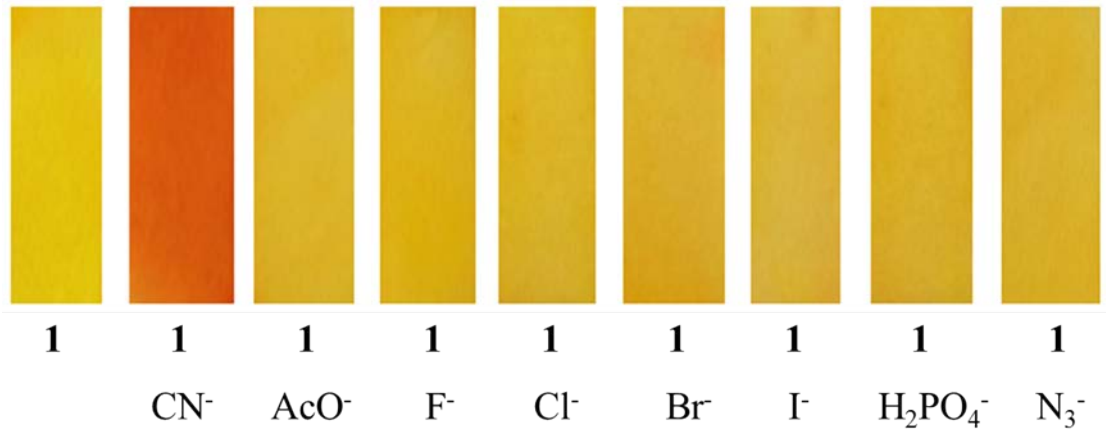


Fig. 4

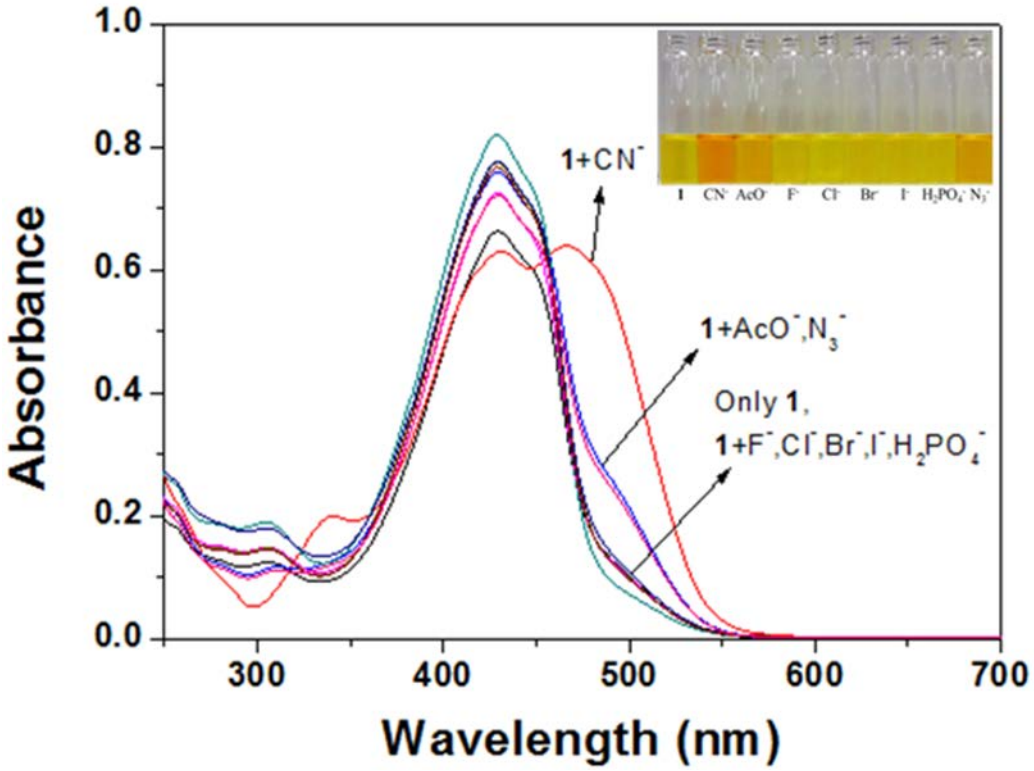


Fig. 5

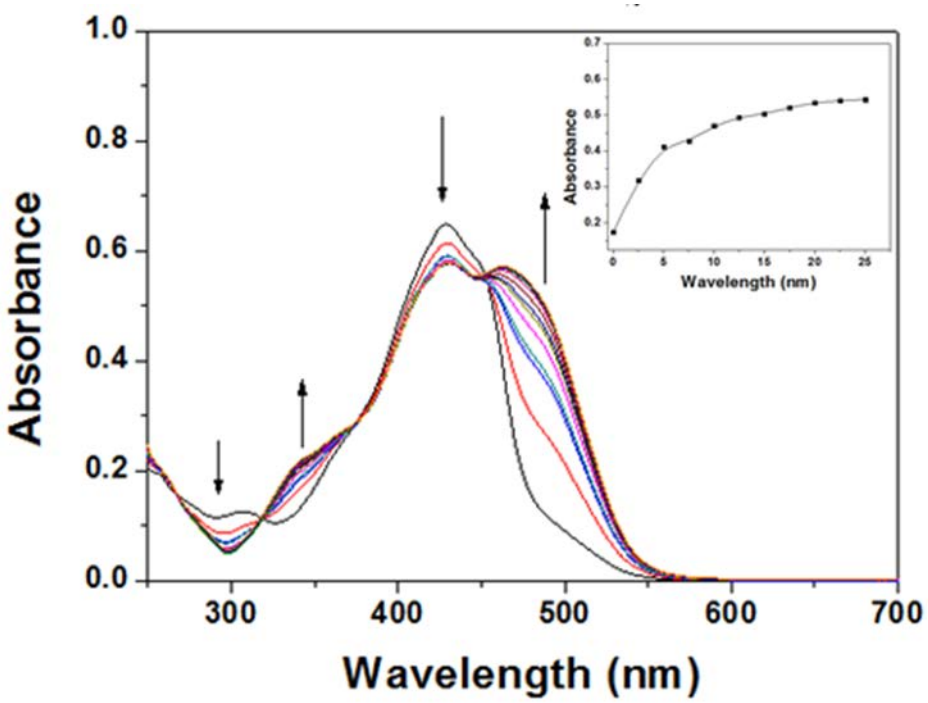


Fig. 6

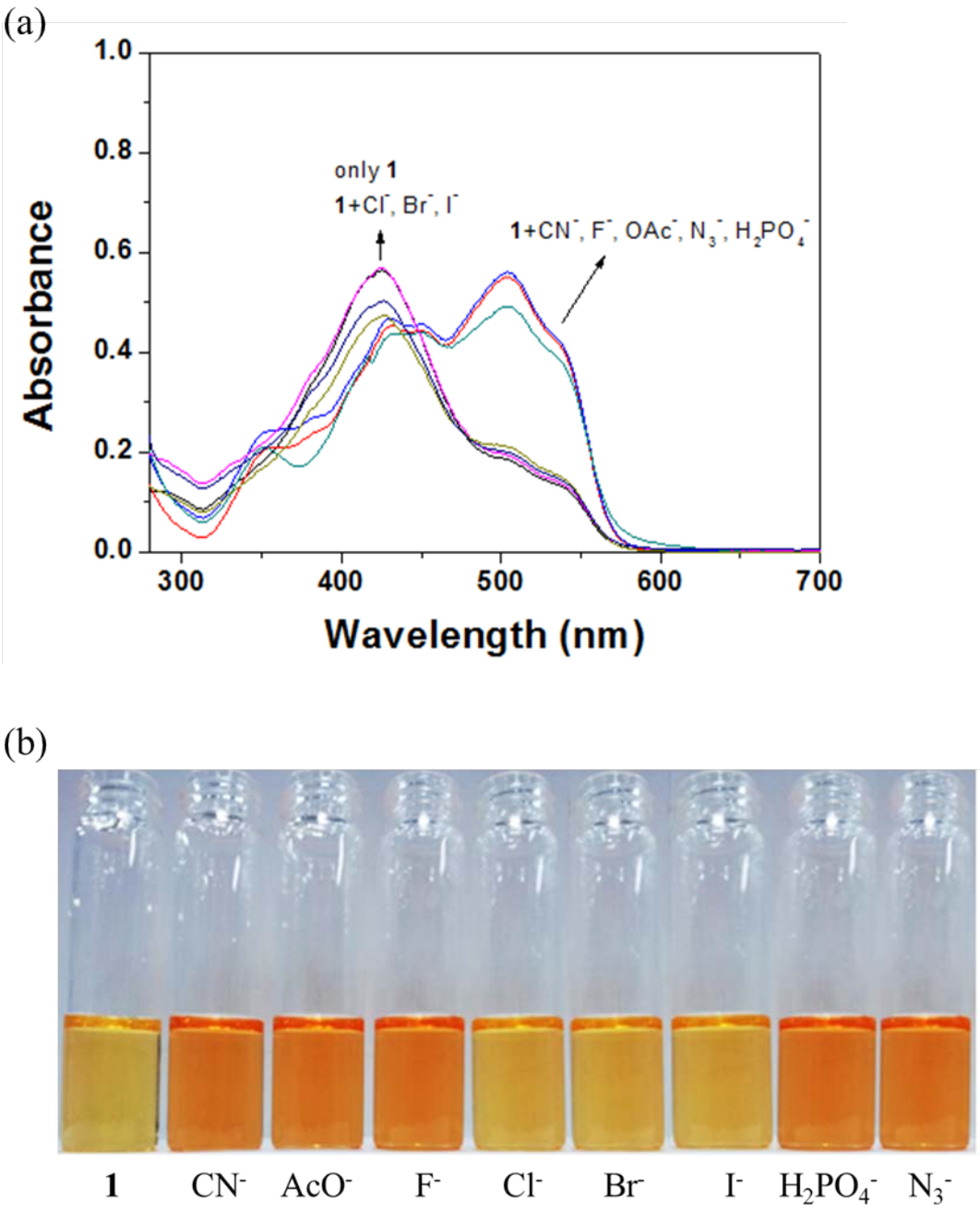


Fig. 7

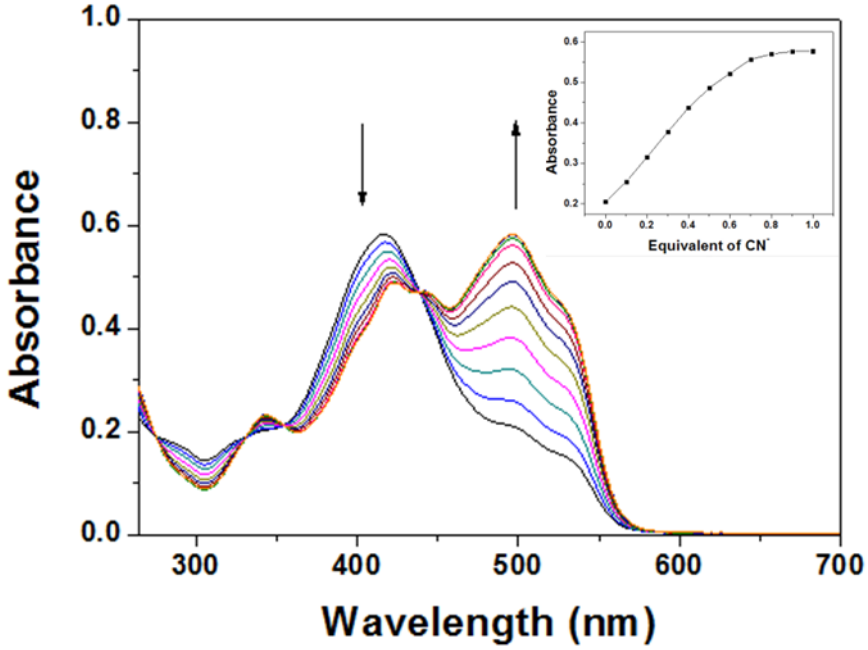


Fig. 8