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A selective colorimetric chemosensor with an electron-withdrawing group for muti-analytes CN^- and F^-

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Abstract

A new colorimetric chemosensor with an electron-withdrawing group ($-NO_2$) **1** for the detection of CN^- and F^- has been simply developed. Receptor **1** showed selectively colorimetric responses to CN^- in aqueous solution and F^- in acetonitrile, respectively. An obvious color change of **1** from yellow to colorless was observed for CN^- through a nucleophilic addition mechanism, while F^- was detected through deprotonating mechanism with a distinct color change from pale yellow to orange. The binding modes of receptor **1** with two analytes (CN^- and F^-) were proposed to be 1:1, based on Job plot, ^1H NMR titration, and ESI-mass spectrometry analysis.

Keywords: Cyanide, Fluoride, Colorimetric, Multi-analytes, Nucleophilic addition, Deprotonation

1. Introduction

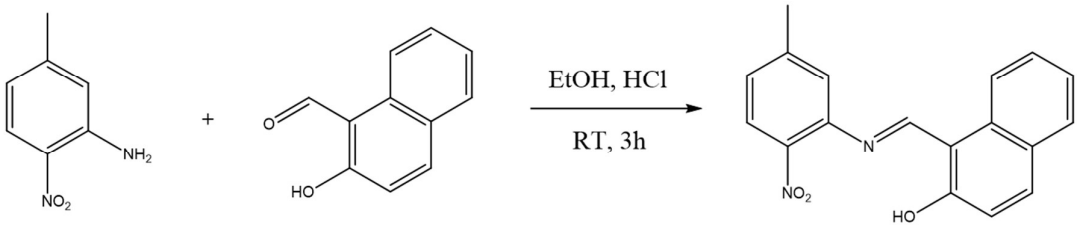
Anion recognition and sensing via artificial receptors are of key interest in analytical and environmental chemistry because of their major role in chemical, biological and environmental assays.[1-5] Among various approaches such as fluorescence techniques and electrochemical methods for the detection of anions, the most attractive approach focuses on novel colorimetric anion sensors, which allow naked-eye detection of the color change without resorting to the use of expensive instruments.[6-9] Colorimetric materials have good points like low cost, rapid response rate, easy method and high selectivity.[10-15] Therefore, colorimetric sensors that are capable of recognizing anions have to be developed.

Among the anions, in particular, the cyanide and fluoride play an important role, exhibiting specific biochemical behaviors in enzymes, antidotes, critical components of numerous metabolic processes and in a broad range of industrial and pharmaceutical products.[16] Cyanide is among the most toxic inorganic anions for even a small amount being a serious threat to human health.[17] Its toxicity results from its propensity to bind to the iron in cytochrome *c* oxidase, interfering with electron transport and resulting in hypoxia.[18-26] Cyanide could be absorbed through lungs, gastrointestinal track and skin, leading to vomiting, convulsion, loss of consciousness, and eventual death.[27-29] Despite its toxicity, its application in various areas as raw materials for synthetic fibers, resins, herbicides, and the gold-extraction process is inevitable,[30-32] which releases cyanide into the environment as a toxic contaminant.

The monitoring of fluoride, the smallest anion with a high charge density, is of particular interest due to their fundamental role. The fluoride is widely used in a number of applications such as dental care,[33] treatment of osteoporosis,[34,35] fluoridation of water supplies,[36] and even in chemical and nuclear warfare agents.[37,38] Fluoride is also relevant in industrial applications, in particular, in the steel and aluminum industries, and widely employed as a well-established reagent in organic synthesis.[39,40] However, fluoride is absorbed easily by the body and excreted slowly from the body.[41] Therefore, the presence of excess fluoride resulted in dental and skeletal fluorosis, bone diseases, mottling of teeth, lesions of the thyroid, liver and other organs.[42-50] Thus, detecting and monitoring fluoride anion is very important for environment

and human health care.

For these reasons, therefore, considerable effort has been devoted to the development of novel methods for the detection of cyanide and fluoride in the past decade. For examples, various chemosensors containing acidic NH and OH groups have been developed to detect fluoride because it can form strong hydrogen bonds. Meanwhile, the detection of cyanide has been accomplished through various approaches such as transition metals,[51] the displacement approach,[52] hydrogen-bonding interactions,[53] deprotonation[54] and nucleophilic addition reactions.[55-61] Based on the previous sensing mechanisms and the structures of various chemosensors, we planned to attach electron-withdrawing groups such as $-NO_2$ to a chemosensor, which might enhance both the deprotonation process and nucleophilic addition reaction by each anion. Hence, we designed and synthesized a single molecular sensor **1** with the electron-withdrawing group ($-NO_2$) (Scheme 1).



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

Herein, we reported a new receptor **1**, which was synthesized in one step by coupling 5-methyl-2-nitroaniline with 2-hydroxy-1-naphthaldehyde. The receptor **1** showed a selective colorimetric sensing ability for cyanide by a distinct color change via a nucleophilic addition mechanism in aqueous solution. Additionally, **1** could also recognize F^- by an intense color change from pale yellow to orange via a deprotonation mechanism.

2. Experimental

2.1. Materials and Instrumentation

All the solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma-Aldrich and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 400 MHz and 100 MHz spectrometer. Chemical shifts (δ) are reported in ppm, relative to tetramethylsilane $Si(CH_3)_4$. Absorption spectra were recorded at room temperature using a Perkin Elmer model Lambda 2S UV/Vis spectrometer. 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 1

5-Methyl-2-nitroaniline (0.16 g, 1 mmol) and 2-hydroxy-1-naphthaldehyde (0.18 g, 1 mmol) were dissolved in 5 mL of ethanol. Then, three drops of hydrochloric acid were added into the reaction mixture, which was stirred for 5 h at room temperature. The orange powder was produced. The orange solid was collected by filtration, washed with diethyl ether and air-dried. Yield: 50%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.93 (s, 1H), 9.61 (s, 1H), 8.54 (d, J = 8 Hz, 1H), 8.08 (d, J = 8 Hz, 1H), 8.00 (d, J = 12 Hz, 1H), 7.93 (s, 1H), 7.82 (d, J = 12 Hz, 1H), 7.58 (t, , J = 8 Hz, 1H), 7.40 (t, J = 8 Hz, 1H), 7.32 (d, J = 12 Hz, 1H), 7.02 (d, J = 8 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.68, 156.76, 147.06, 139.85, 139.57, 138.83, 133.74, 129.82, 129.05, 127.66, 127.49, 126.04, 124.78, 122.83, 121.83, 121.51, 110.25, 21.85 ppm. Anal. calcd for $C_{18}H_{14}N_2O_3$ (306.10): C, 70.58; H, 4.61; N, 9.15 %. Found: C, 70.23; H, 4.68; N, 8.79%. ESI-MS m/z ($M+H^+$): calcd, 307.10; found, 307.38.

2.3. UV-vis titrations of 1 with CN^- and F^-

For CN^-, **1** (3.1 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 9 μL of it (10 mM) were diluted to 2.991 mL with DMSO/bis-tris Buffer (1:5, v/v) to make a final concentration of 30 μM. Tetraethylammonium cyanide (TEACN, 0.1 mmol) was dissolved in DMSO (1 mL) and 0-63 μL of the CN^- solution (100 mM) were transferred to the solution of **1** (30 μM) prepared above. After mixing them for a few seconds, UV-vis spectra were obtained at room

temperature.

For F^-, **1** (3.1 mg, 0.01 mmol) was dissolved in CH_3CN (1 mL) and 6 μL of it (10 mM) were diluted to 2.994 mL with CH_3CN to make a final concentration of 20 μM. Tetraethylammonium fluoride (TEAF, 0.1 mmol) was dissolved in CH_3CN (1 mL) and 0-48 μL of the F^- solution (100 mM) were transferred to the solution of **1** (20 μM) prepared above. After mixing them for a few seconds, UV-vis spectra were obtained at room temperature.

2.4. Job plot measurements

For CN^-, **1** (3.1 mg, 0.01 mmol) and TEACN (1.56 mg, 0.01 mmol) were dissolved in DMSO (1 mL), respectively. 0.15 mL of the receptor **1** solution were diluted to 29.85 mL of DMSO/bis-tris buffer (1:5, v/v) to make the concentration of 50 μM. The CN^- solution was diluted in the same way. 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.5, 1, 0.5 and 0 mL of the receptor **1** solution were taken and transferred to vials. 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 mL of the CN^- solution were added to each receptor solution separately. Each vial had a total volume of 5 mL. After shaking the vials for a few minutes, UV-vis spectra were taken at room temperature.

For F^-, **1** (3.1 mg, 0.01 mmol) and TEAF (1.49 mg, 0.01 mmol) were dissolved in CH_3CN (1 mL), respectively. 0.15 mL of the receptor **1** solution were diluted to 29.85 mL of CH_3CN to make the concentration of 50 μM. The TEAF solution was diluted in the same way. 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.5, 1, 0.5 and 0 mL of the receptor **1** solution were taken and transferred to vials. 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 mL of the F^- solution were added to each receptor solution separately. Each vial had a total volume of 5 mL. After shaking the vials for a few minutes, UV-vis spectra were taken at room temperature.

2.5. Competition of 1 toward anions

For CN^-, **1** (3.1 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 9 μL of this solution (10 mM) were diluted to 2.991 mL with DMSO/bis-tris buffer (1:5, v/v) to make the final concentration of 30 μM. Stock solutions (100 mM) of the tetraethylammonium salts of F^-, CN^-, Cl^-, Br^- and I^-, the tetrabutylammonium salts of AcO^-, $H_2PO_4^-$, BzO^-, N_3^- and SCN^-, and

the sodium salts of HS^- and S^{2-} anions were prepared in DMSO. 63 μL of each anion solution (100 mM) were taken and added to 2.937 mL of the solution of receptor **1** (30 μM) to give 70 equiv of anions. Then, 63 μL of TEACN solution (100 mM) were added to the mixed solution of each anion and **1** to make 70 equiv. After mixing them for a few seconds, UV-vis spectra were obtained at room temperature.

For F^-, **1** (3.1 mg, 0.01 mmol) was dissolved in CH_3CN (1 mL) and 6 μL of this solution (10 mM) were diluted with 2.994 mL of CH_3CN to make the final concentration of 20 μM. Stock solutions (100 mM) of the tetraethylammonium salts of F^-, CN^-, Cl^-, Br^- and I^-, the tetrabutylammonium salts of AcO^-, $H_2PO_4^-$, BzO^-, N_3^- and SCN^-, and the sodium salts of HS^- and S^{2-} anions were prepared in DMSO. 48 μL of each anion solution (100 mM) were taken and added to 2.952 mL of the solution of receptor **1** (20 μM) to give 80 equiv of anions. Then, 48 μL of TEACN solution (100 mM) were added to the mixed solution of each anion and **1** to make 80 equiv. After mixing them for a few seconds, UV-vis spectra were obtained at room temperature.

2.6. pH effect test

A series of buffers with pH values ranging from 2 to 12 was prepared by mixing sodium hydroxide solution and hydrochloric acid in bis-tris buffer. After the solution with a desired pH was achieved, receptor **1** (3.1 mg, 0.01 mmol) was dissolved in DMSO (1 mL), and then 9 μL solution of the receptor **1** (10 mM) were diluted to 2.991 mL with DMSO/bis-tris buffer (1:5, v/v) to make the final concentration of 30 μM. TEACN (0.1 mmol) was dissolved in bis-tris buffer (1 mL, pH 7.0). 63 μL of the CN^- solution (100 mM) were transferred to each receptor **1** solution (30 μL) prepared above. After mixing them for a few seconds, UV-vis spectra were taken at room temperature.

2.7. ^{1}H NMR titrations

For CN^-, three NMR tubes of receptor **1** (3.1 mg, 0.01 mmol) dissolved in DMSO-d_6 (700 μL) were prepared and then three different concentrations (0, 1 and 2 equiv) of tetraethylammonium cyanide dissolved in DMSO-d_6 were added to each solution of receptor **1**. After shaking them for a minute, ^{1}H NMR spectra were obtained at room temperature.

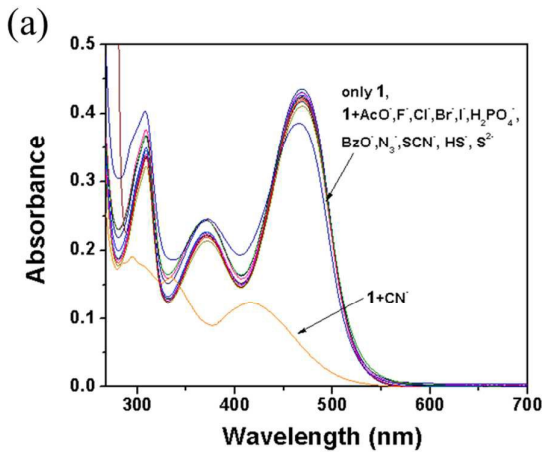
For F^-, four NMR tubes of receptor **1** (3.1 mg, 0.01 mmol) dissolved in DMSO-d_6 (700 μL) were prepared and then four different concentrations (0, 0.5, 1 and 5 equiv) of tetraethylammonium fluoride dissolved in DMSO-d_6 were added to each solution of receptor **1**. After shaking them for a minute, ^{1}H NMR spectra were obtained at room temperature.

3. Results and discussion

The colorimetric chemosensor **1** for cyanide and fluoride was synthesized by combination of 5-methyl-2-nitroaniline and 2-hydroxy-1-naphthaldehyde (Scheme 1), and characterized by ^{1}H NMR, ^{13}C NMR and elemental analysis.

3.1. Colorimetric sensing of 1 toward CN^-

The colorimetric selective sensing abilities of receptor **1** with various anions in a mixture of DMSO/bis-tris buffer (1:5, v/v) were monitored by UV-vis absorption spectra (Fig. 1a). 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^-, SCN^-, HS^- and S^{2-} did not induce any spectral changes. Consistent with the change of UV-vis spectrum, the solution of **1** resulted in an immediate color change (less than one second) from yellow to colorless with cyanide ion (Fig. 1b). The fast reaction of **1** with CN^- is connected with the electronic effect of the strong electron-withdrawing group $-NO_2$. Therefore, these results indicate that receptor **1** can serve as a fast 'naked-eye' cyanide indicator in aqueous solution.



(b)

Figure 1. (a) Absorption spectral change of **1** (30 μM) in the presence of 70 equiv of various anions in a mixture of DMSO/bis-tris buffer (1:5, v/v). (b) Color change of receptor **1** (30 μM) in the presence of 70 equiv of various anions in a mixture of DMSO/bis-tris buffer (1:5, v/v).

To further investigate the interaction between receptor **1** and CN^-, UV-vis absorption spectral variation of **1** was monitored during titration with different concentrations of CN^-. As shown in Fig. 2, a sharp decrease in the UV-vis absorption at 469 nm was observed after adding of CN^-, and then the absorption at 285 nm increased gradually. This phenomenon indicated that the conjugated electron network was lessened and the intramolecular charge transfer (ICT) efficiency decreased, which results in color change from yellow to colorless. The isosbestic point at 295 nm was clearly observed with increasing concentrations of CN^-, indicating the formation of a single species between the receptor **1** and the cyanide.

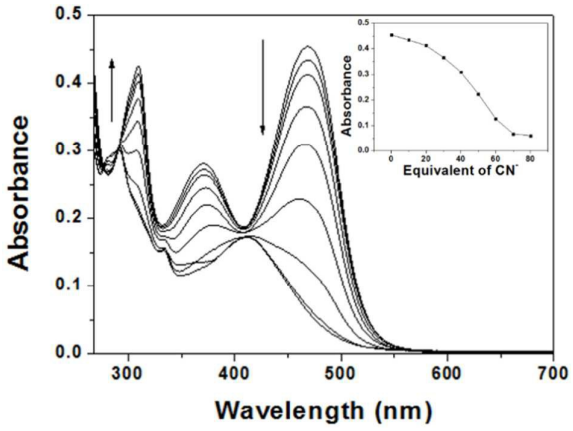
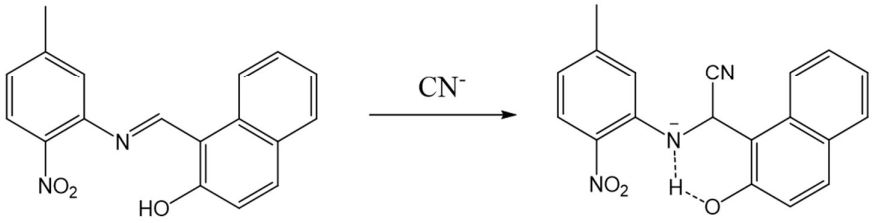


Figure 2. Absorption spectra of receptor **1** (30 μM) upon the addition of CN^- in a mixture of DMSO/bis-tris buffer (1:5, v/v). Inset: Absorbance at 469 nm versus the number of equiv of CN^- added.

The Job plot indicated a 1:1 binding interaction between the receptor **1** and CN^- (Fig. S1), which was further confirmed by ESI-mass spectrometry analysis (Fig. S2). The negative ion mass spectrum of ESI-mass indicated that a peak at *m*/*z* = 551.00 was assignable to **1**-$2H^+$+CN^-+TEA+$5H_2O$ [calcd, *m*/*z*: 551.31]. Based on Job plot and ESI-mass spectrometry analysis, we propose the sensing mechanism of CN^- by **1** as shown in Scheme 2.



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

Based on UV-vis titration, the apparent association constant (K) of **1** with the CN^- ion was calculated using the Benesi-Hildebrand equation (Fig. S3).[62] The K value turned out to be 4.1 x 10^2 M^{-1}, which is within the values (10-10^5) previously reported for CN^- chemosensors.[63] The detection limit (3∂/k) of receptor **1** for the analysis of CN^- ions was calculated to be 105 μM (Fig. S4).[64]

To explore the ability of **1** as a colorimetric sensor for CN^- in the presence of competing anions, inhibition experiments were performed in the presence of CN^- mixed with various anions (Fig. 3). No significant change in the absorbance was found when comparing the results with other anions. 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.

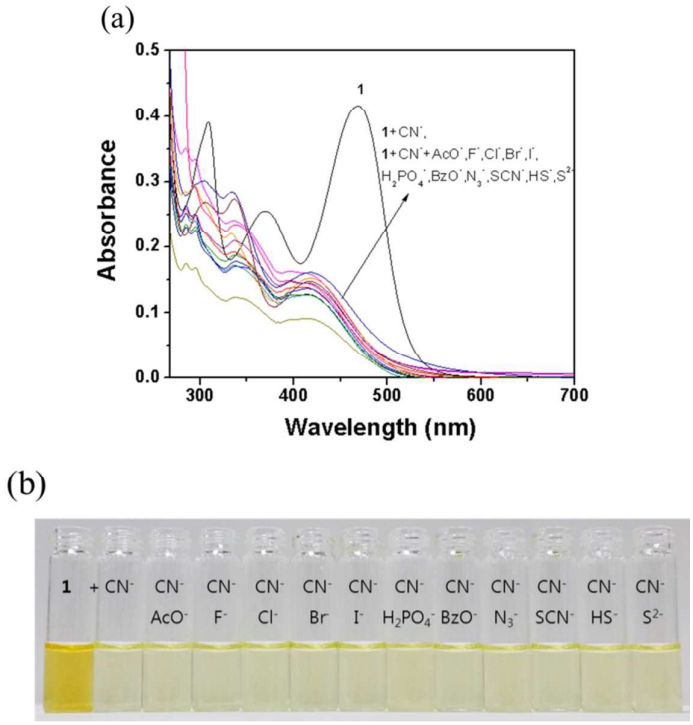


Figure 3. (a) Competitive selectivity of **1** (30 μM) toward CN^- (70 equiv) in the presence of other anions (70 equiv) in a mixture of DMSO/bis-tris buffer (1:5, v/v). (b) Colorimetric competitive experiment of **1** (30 μM) in the presence of CN^- (70 equiv) and other anions (70 equiv) in a mixture of DMSO/bis-tris buffer (1:5, v/v).

To gain a fuller understanding of the interaction between **1** and cyanide, ^{1}H NMR titrations of **1** were performed in the absence and presence of different equiv of the cyanide as the TEA salt (Fig. 4). In absence of cyanide ion, the C=N proton (H_a) and the OH proton (H_{11}) appeared, respectively, as a singlet at 9.6 ppm and 14.9 ppm, and the aromatic protons of the sensor **1** were resonated in the 9.0-6.0 ppm region. Upon gradual addition of cyanide, the H_a at 9.6 ppm disappeared and a new peak ($H_{a'}$) at 6.5 ppm appeared, indicating that the cyanide anion functioned as a nucleophile. The H_a disappeared eventually and the aromatic protons were shifted to upfield, which suggests that the negative charge developed by the attack of CN^- was delocalized through the whole receptor molecule. The ^{1}H NMR titration experiments further supported the structure of **1**-CN^- species proposed in Scheme 2.

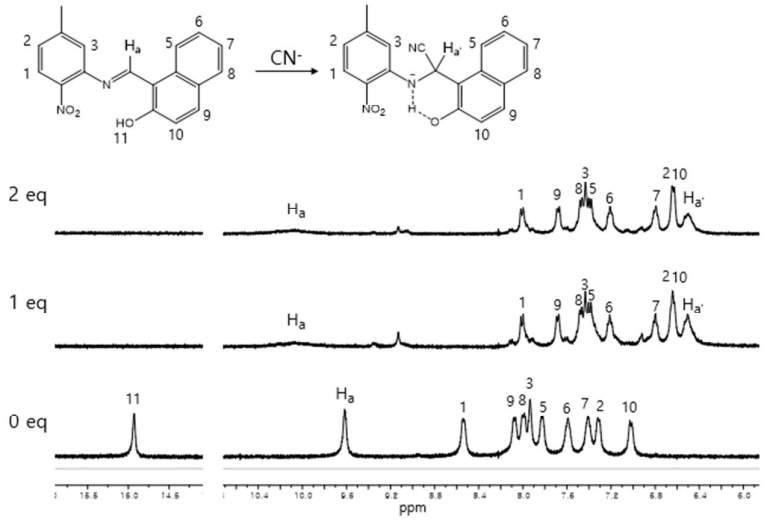


Figure 4. ^{1}H NMR titration of receptor **1** with CN^- in DMSO-d_6.

We investigated the effect of pH on the absorption response of receptor **1** to CN^- in a series of buffers with pH values ranging from 2 to 12 (Fig. 5). The color of the **1** remained in the yellow region between pH 5 and 10, while the color of **1**-CN^- remained to colorless at pH 2-12. These results indicate that CN^- could be clearly detected by the naked eye or UV-vis absorption measurements using **1** over the wide pH range of 5-10.

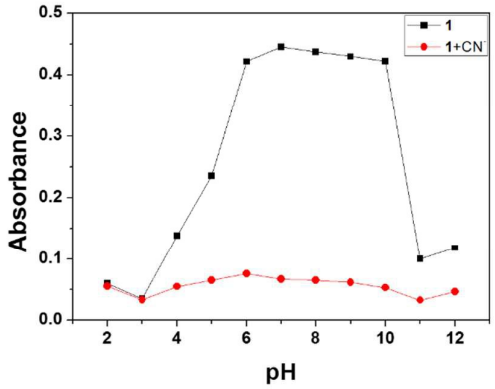


Figure 5. Absorbance of **1** and **1**-CN^- species (469 nm) at different pH values (2-12) in a mixture of DMSO/bis-tris buffer (1:5, v/v).

3.2. Colorimetric sensing of 1 toward F^-

We also investigated the sensing properties of **1** toward various anions in various solvents. While **1** showed no selectivity toward various anions in most of organic solvents, only F^- was sensed by **1** in CH_3CN. Therefore, the absorption response of **1** toward the tetraethylammonium (TEA) or tetrabutylammonium (TBA) or sodium salts of F^-, CN^-, AcO^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, BzO^-, N_3^-, SCN^-, HS^- and S^{2-} was carried out in CH_3CN (Fig. 6). Upon addition of 80 equiv of each anion, F^- induced a noticeable spectral change, while other anions showed either no or slight change in the absorption spectra relative to the free receptor **1** except for CN^- (Fig. 6a). Interestingly, the solution color of **1** with fluoride changed from pale yellow to orange with fast response time (less than one second), while the other anions showed no color change (Fig. 6b). These results also demonstrate that receptor **1** can serve as a fast "naked-eye" indicator for F^-, as observed with CN^-.

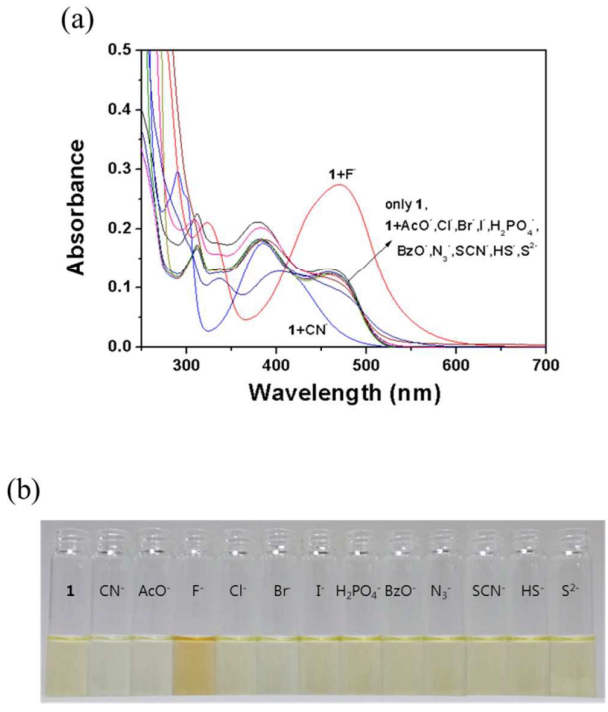


Figure 6. (a) Absorption spectral change of **1** (20 μM) in the presence of 80 equiv of various anions in CH_3CN. (b) Color change of receptor **1** (20 μM) in the presence of 80 equiv of

various anions in CH_3CN.

The recognition properties of **1** with F^- were further studied by UV-vis titration experiments. As shown in Fig. 7, the decrease in the absorption band at 379 nm was observed after adding of F^-, and then the absorption bands at 458 nm gradually reached maxima at 80 equiv of F^-. The isosbestic point at 410 nm was clearly observed, indicating the formation of a single species between the receptor **1** and the fluoride. The red-shift of **1**-F^- species led us to propose that the electron density in **1** might increase because of the deprotonation of phenol of **1** by F^-. The resulting negative charge on the phenolate oxygen would be associated with the enhancement of the push-pull effect of the ICT transition,[65] which is highly visible to the naked eye with a change in color from pale yellow to orange. The Job plot for the binding between **1** and F^- exhibited a 1:1 stoichiometry (Fig. S5). The positive ion mass spectrum of ESI-mass showed that a peak at m/z = 583.90 was assignable to $[\mathbf{1}\text{-}H^+ + 2TEA + H_2O]^+$ [calcd, m/z = 583.42], which is corresponding to the receptor $\mathbf{1}^-$ deprotonated by fluoride (Fig. S6). From the UV-vis titration data, the apparent association constant (K) for **1** and fluoride was determined as 1.7 x 10^3 using the nonlinear-fitting analysis of the change in the absorbance at 458 nm (R^2=0.9952, Fig. S7).[67] The detection limit (3∂/k) of receptor **1** for the analysis of F^- ions was calculated to be 60 μM (Fig. S8).[64]

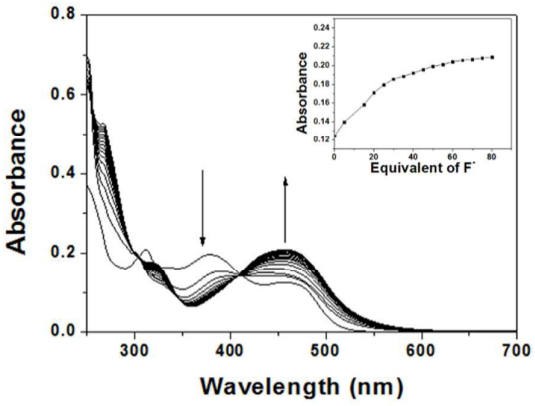


Figure 7. Absorption spectra of receptor **1** (20 μM) upon the addition of F^- in CH_3CN. Inset: Absorbance at 458 nm versus the number of equiv of F^- added.

To explore the ability of **1** as a colorimetric sensor for F^- in the presence of competing anions, inhibition experiments were performed in the presence of F^- mixed with various anions (Fig. 8). The coexistent anions had a small and negligible influence on the absorbance of the sensing except for $H_2PO_4^-$. These results indicate that receptor **1** shows a good selectivity for fluoride anion in the presence of other anions.

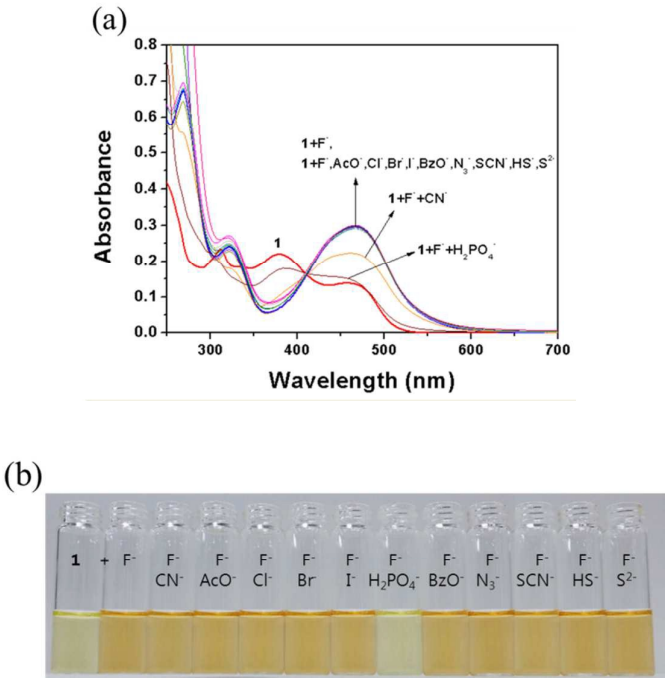


Figure 8. (a) Competitive selectivity of **1** (20 μM) toward F^- (80 equiv) in the presence of other anions (80 equiv) in CH_3CN. (b) Colorimetric competitive experiment of **1** (20 μM) in the presence of F^- (80 equiv) and other anions (80 equiv) in CH_3CN.

The sensing mechanism of **1** was further investigated by ^1H NMR titration experiments at room temperature (Fig. 9). In absence of fluoride ion, the phenolic OH proton (H_{11}) and the imine proton (H_4) appeared, respectively, as a singlet at 14.9 ppm and 9.6 ppm. Upon the addition of F^- (0.5 equiv), the singlet of H_{11} almost disappeared by hydrogen bonding with fluoride and H_4 was shifted to upfield. After the further addition of F^- (1 equiv), the H_{11} disappeared completely. With the increasing of the fluoride concentration, the up-field shifts

of the H_4 and the rest protons were also observed except for H_1, and a new peak at 16 ppm appeared, indicating the formation of [HF_2^-] species.[66] Based on ^{1}H NMR titrations, Job plot, and ESI-mass spectrometry analysis, we proposed the sensing mechanism of F^- by **1**, as shown in Scheme 3.

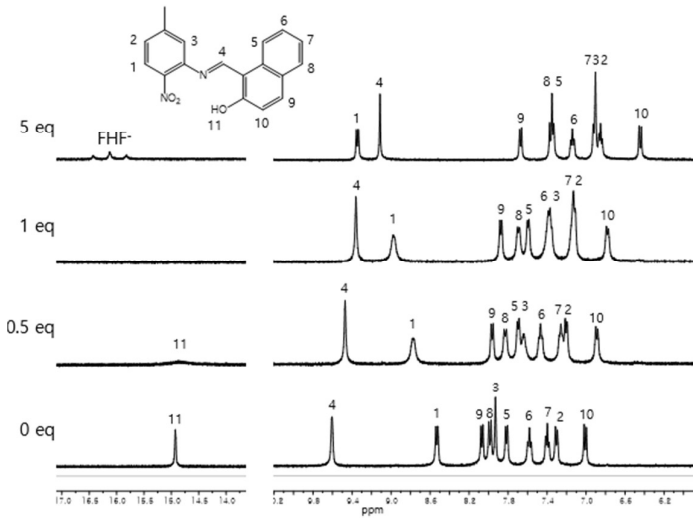
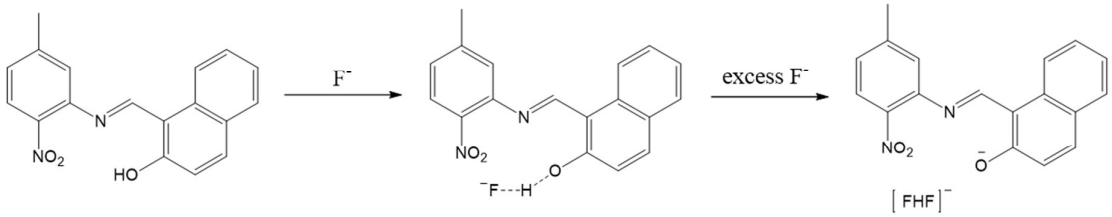


Figure 9. ^{1}H NMR titration of receptor **1** with F^- in DMSO-d_6.



Scheme 3. Proposed sensing mechanism of **1** for fluoride.

4. Conclusion

A new multifunctional colorimetric chemosensor **1** with the electron-withdrawing group (-NO_2) was synthesized and found to be sensitive to cyanide and fluoride with color changes

through different sensing mechanism. **1** can distinguish CN^- by the nucleophilic addition mechanism in the presence of other anions such as CH_3COO^- and F^-. Moreover, the receptor **1** recognized F^- selectively with a colorimetric change from pale yellow to orange by deprotonation. The binding modes of receptor **1** with two analytes (CN^- and F^-) were proposed to be 1:1, based on Job plot, ^1H NMR titration, and ESI-mass spectrometry analysis. Importantly, it has been found that **1** with the strong electron-withdrawing group NO_2 showed the fast detection processes by the electronic effects toward multi-analytes CN^- and F^-. These results suggest that receptor **1** with the electron-withdrawing group will offer an important guidance to the development of a new type of receptors for recognizing both CN^- and F^-.

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Appendix A. Supplementary Material

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

References

1 (a) P. A. Gale, T. Gunnlaugsson, *Chem. Soc. Rev.*, 2010, **39**, 3595-3596; (b) P. A. Gale, *Chem. Soc. Rev.*, 2010, **39**, 3746-3771.

2 Q. Wang, Y. Xie, Y. Ding, X. Li, W. Zhu, *Chem. Commun.*, 2010, **46**, 3669-3671.

3 T. Gunnlaugsson, M. Glynn, G. M. Tocci, P. E. Kruger, F. M. Pfeffer, *Coord. Chem. Rev.*, 2006, **250**, 3094-3117.

4 J. W. Steed, *Chem. Soc. Rev.*, 2010, **39**, 3686-3699.

5 A. F. Li, J. H. Wang, F. Wang, Y. B. Jiang, *Chem. Soc. Rev.*, 2010, **39**, 3729-3745.

6 K. B. Kim, H. Kim, E. J. Song, S. Kim, I. Noh, C. Kim, *Dalton Trans.*, 2013, **42**, 16569-16577.

7 J. P. Anzenbacher, A. C. Try, H. Miyaji, K. Jursikova, V. M. Lynch, M. Marquez, J. L. Sessler, *J. Am. Chem. Soc.*, 2000, **122**, 10268-10269.

8 H. Miyaji, W. Sato, J. L. Sessler, *Angew. Chem. Int. Ed.*, 2000, **39**, 1777-1780.

9 L. Zhou, H. Sun, H. Li, H. Wang, X. Zhang, S. Wu, S. Lee, *Org. Lett.*, 2004, **6**, 1071-1074.

10 J. Yoshino, N. Kano, T. Kawashima, *J. Org. Chem.*, 2009, **74**, 7496-7498.

11 K. P. Divya, S. Sreejith, B. Balakrishna, P. Jayamurthy, P. Anees, A. Ajayaghosh, *Chem. Commun.*, 2010, **46**, 6069-6071.

12 H. B. Yu, M. Y. Fu, Y. Xiao, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7386-7386.

13 X. Lv, J. Liu, Y. L. Liu, Y. Zhao, M. L. Chen, P. Wang, W. Guo, *Sens. Actuators B*, 2011, **158**, 405-406.

14 (a) J. Y. Noh, G. J. Park, Y. J. Na, H. Y. Jo, S. A. Lee, C. Kim, *Dalton Trans.*, 2014, **43**, 5652-5656; (b) H. Y. Jo, G. J. Park, Y. J. Na, Y. W. Choi, G. R. You, C. Kim, *Dyes. Pigments*, 2014, **109**, 127-134; (c) Y. J. Na, G. J. Park, H. Y. Jo, S. Ah Lee, C. Kim, *New J. Chem.*, 2014, **38**, 5769-5776.

15 Y. Ding, T. Li, W. Zhu, Y. Xie, *Org. Biomol. Chem.*, 2012, **10**, 4201-4207.

16 G. J. Park, H. Y. Jo, K. Y. Ryu, C. Kim, *RSC Adv.*, 2014, **4**, 63882-63890.

17 (a) K. W. Kulig, B. Ballantyne, Cyanide toxicity, *US Department of Health & Human Services: Atlanta*, GA, 1991; (b) Z. Lin, Y. Ma, X. Zheng, L. Huang, E. Yang, C. Wu, T. J. Chow, *Dyes. Pigments*, 2015, **113**, 129-137; (c) Y. Ding, Y. Tang, W. Zhua, Y. Xie, *Chem. Soc. Rev.*, 2015, **44**, 1101-1112.

18 B. Vennesland, E. E. Comm, C. J. Knownles, J. Westly, F. Wissing, Cyanide in biology, *Academic Press*, London, 1981.

19 J. Y. Noh, I. H. Hwang, H. Kim, E. J. Song, K. B. Kim, C. Kim, *B. Kor. Chem. Soc.*, 2013, **34**, 1985-1989.

20 G. J. Park , I. H. Hwang , E. J. Song , H. Kim, C. Kim, *Tetrahedron*, 2014, **70**, 2822-2828.

21 L. Tang, P. Zhou, K. Zhong, S. Hou, *Sens. Actuators B*, 2013, **182**, 439-445.

22 R. Yang, W. Wu, W. Wang, Z. Li, J. Qin, *Macromol. Chem. Physic.*, 2010, **211**, 18-26.

23 (a) B. Chen, Y. Ding, X. Li, W. Zhu, J. P. Hill, K. Arigac, Y. Xie, *Chem. Commun.*, 2013, **49**, 10136-10138; (b) Y. Xie, Y. Ding, X. Li, C. Wang, J. P. Hill, K. Ariga, W. Zhanga, W. Zhu, *Chem. Commun.*, 2012, **48**, 11513-11515.

24 X. Chen, S. Nam, G. Kim, N. Song, Y. Jeong, I. Shin, S. K. Kim, J. Kim, S. Park, J. Yoon, *Chem. Commun.*, 2010, **46**, 8953-8955.

25 Y. Qua, B. Jin, Y. Liu, Y. Wub, L. Yang, J. Wua, J. Hua, *Tetrahedron Lett.*, 2013, **54**, 4942-4944.

26 (a) S. Sumiya, T. Doi, Y. Shiraishi, T. Hirai, *Tetrahedron*, 2012, **68**, 690-696; (b) V. K. Gupta, A. K. Singh, N. Gupta, *Sens. Actuators B*, 2014, **204**, 125-135; (c) S. S. Razi, R. Ali, P. Srivastava, A. Misra, *Tetrahedron Lett.*, 2014, **55**, 2936-2941; (d) M. Kumar, R, Kumar, V. Bhalla, *Tetrahedron Lett.*, 2013, **54**, 1524-1527.

27 G. J. Park, Y. W. Choi, D. Lee, C. Kim, *Spectrochim. Acta A*, 2014, **132**, 771-775.

28 S. L. Baskin, T. G. Brewer, in: F.R. Sidell, E.T. Takafuji, D.R. Franz (Eds.), Medical aspects of chemical and biological warfare, *TMM Publications*, Washington, DC, 1997, pp. 271-286.

29 C. Baird, M. Cann, Environmental chemistry, *Freeman*, New York, 2005.

30 G. C. Miller, C. A. Pritsos, Cyanide, social, industrial and economic aspects, *the Proceedings of the TMS Annual Meeting*, 2001, pp. 73-81.

31 S. A. Lee, G. R. You, Y. W. Choi, H. Y. Jo, A. R. Kim, I. Noh, S. Kim, Y. Kim, C. Kim, *Dalton Trans.*, 2014, **43**, 6650-6659.

32 C. Young, L. Tidwell, C. Anderson, Cyanide : Social, Industrial and Economic Aspects: Minerals, Metals, and Materials Society, *Warrendale*, 2001.

33 (a) K. L. Kirk. Biochemistry of the elemental halogens and inorganic halides, *New York: Plenum Press*, 1991; (b) H. Wang, P. Fan, B. Tong, Y. Dong, X. Ou, F. Li, X. Zhang, *Adv. Funct. Mater.*, 2015, DOI: 10.1002/adfm.201401632.

34 D. Briancon, *Rev. Rheum. Engl. Ed.*, 1997, **64**, 78-81.

45 M. Kleerekoper, *Endocrinol. Metab. Clin. North Am.*, 1998, **27**, 441-452.

46 R. H. Dreisbuch, Handbook of poisoning, *Los Altos: Lange Medical Publishers*, 1980.

47 H. Sohn, S. L etant, M. J. Sailor, W. C. Trogler, *J. Am. Chem. Soc.*, 2000, **122**, 5399-5400.

48 S. W. Zhang, T. M. Swager, *J. Am. Chem. Soc.*, 2003, **125**, 3420-3421.

49 J. H. Clark, *Chem. Rev.*, 1980, **80**, 429-452.

40 H. Y. Kim, H. G. Im, S. Chang, *Dyes. Pigments*, 2015, **112**, 170-175.

41 N. M. Mattiwala, R. Kamal, S. K. Sahoo, *Res. Chem. Intermed.*, 2013, 1-10.

42 P. G. Sutariya, N. R. Modi, A. Pandya, B. K. Joshi, K. V. Joshia, S. K. Menon, *Analyst*, 2012, **137**, 5491-5494.

43 S. Velmathi, V. Reena, S. Suganya, S. Anandan, *J. Fluoresc.*, 2012, **22**, 155-162.

44 D. Sharma, S. K. Sahoo, R. K. Bera, R. Kamal, *J. Fluoresc.*, 2013, **23**, 387-392.

45 R. Sivakumar, V. Reena, N. Ananthi, M. Babu, S. Anandan, S. Velmathi, *Spectrochim. Acta A*, 2010, **75**, 1146-1151.

46 L. Zang, D. Wei, S. Wang, S. Jiang, *Tetrahedron*, 2012, **68**, 636-641.

47 C. Wang, G. Li, Q. Zhang, *Tetrahedron Lett.*, 2013, **54**, 2633-2636.

48 S. Sharma, M. S. Hundal, G. Hundal, *Tetrahedron Lett.*, 2013, **54**, 2423-2427.

49 H. S. Jung, H. J. Kim, J. Vicens, J. S. Kim, *Tetrahedron Lett.* 2009, **50**, 983-987.

50 J. J. Lee, G. J. Park, Y. W. Choi, G. R. You, Y. S. Kim, S. Y. Lee, C. Kim, *Sens. Actuators B*, 2015, **207**, 123-132.

51 (a) Y. H. Kim, J. I. Hong, *Chem. Commun.*, 2002, **5**, 512-513; (b) H. Liu, X. B. Shao, M. X. Jia, X. K. Jiang, Z. T. Li, G. J. Chen, *Tetrahedron*, 2005, **61**, 8095-8100; (c) C. F. Chow, M. H. W. Lamand, W. Y. Wong, *Inorg. Chem.*, 2004, **43**, 8387-8393; (d) F. H. Zelder, *Inorg. Chem.*, 2008, **47**, 1264-1266; (e) Q. Zeng, P. Cai, Z. Li, J. Qin, B. Z. Tang, *Chem. Commun.*, 2008, **9**, 1094-1096.

52 Y. Chung, H. Lee, K. H. Ahn, *J. Org. Chem.*, 2006, **71**, 9470-9474.

53 H. Miyaji, J. L. Sessler, *Angew. Chem. Int. Ed.*, 2001, **40**, 154-157.

54 (a) N. Gimeno, X. Li, J. R. Durrant, R. Vilar, *Chem. Eur. J.*, 2008, 14, 3006-3012; (b) Y. J. Na, Y. W. Choi, J. Y. Yun, K. Park, P. Chang, C. Kim, *Spectrochim. Acta A*, 2015, **136**, 1649-1657.

55 (a) Y. K. Kim, Y. H. Lee, H. Y. Lee, M. K. Kim, G. S. Cha, K. H. Ahn, *Org. Lett.*, 2003, **5**, 4003-4006; (b) Y. K. Yang, J. Tae, *Org. Lett.*, 2006, **8**, 5721-5723; (c) M. Tomasulo, S. Sortino, A. J. P. White, F. M. Raymo, *J. Org. Chem.*, 2006, **71**, 744-753; (d) C. L. Chen, Y. H. Chen, C. Y. Chen, S. S. Sun, *Org. Lett.*, 2006, **8**, 5053-5056; (e) K. S. Lee, J. T. Lee, J. I. Hong, H. J. Kim, *Chem. Lett.*, 2007, **36**, 816-817; (f) K. S. Lee, H. J. Kim, G. H. Kim, I. Shin,

J. I. Hong, *Org. Lett.*, 2008, **10**, 49-51; (g) Z. Ekmekci, D. Yilmaz, E. U. Akkya, *Org. Lett.*, 2008, **10**, 461-464.

56 M. Tomasulo, F. M. Raymo, *Org. Lett.* 2005, **7**, 4633-4636.

57 G. R. You, G. J. Park, S. A. Lee, Y. W. Choi, Y. S. Kim, J. J. Lee, C. Kim, *Sens. Actuators B*, 2014, **202**, 645-655.

58 F. García, J. M. García, B. García-Acosta, R. Martínez-Má˜ nez, F. Sancenón, J. Soto, *Chem. Commun.*, 2005, **22**, 2790-2792.

59 J. V. Ros-Lis, R. Martínez-Má˜ nez, J. Soto, *Chem. Commun.*, 2002, **19**, 2248-2249.

60 H. Lee, Y. M. Chung, K. H. Ahn, *Tetrahedron Lett.*, 2008, **49**, 5544-5547.

61 H. Miyaji, D. Kim, B. Chang, E. Park, S. Park, K. H. Ahn, *Chem. Commun.*, 2008, **6**, 753-755.

62 H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703-2707.

63 (a) W. Gong, Q. Zhang, L. Shang, B. Gao, G. Ning, *Sens. Actuators B*, 2013, **177**, 322-326; (b) Y. M. Hijji , B. Barare, Y. Zhang, *Sens. Actuators B*, 2012, **16**, 106-112; (c) H. Tavallali, G. Deilamy-Rad, A. Parhami, S. Kiyani, *Spectrochim. Acta A*, 2014, **121**, 139-146; (d) D. Kim, Y. Chung, M. Jun, K. H. Ahn, *J. Org. Chem.*, 2009, **74**, 4849-4854.

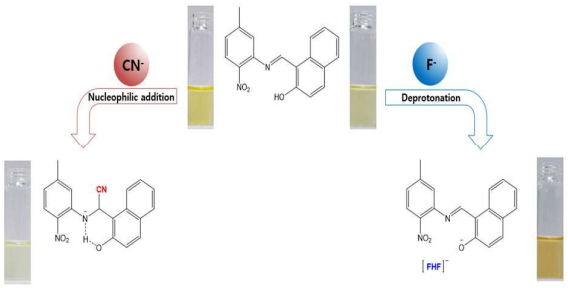
64 Y. Tsui, S. Devaraj, Y. Yen, *Sens. Actuators B*, 2012, **161**, 510-519.

65 (a) M. A. Kaloo, J. Sankar, *Analyst*, 2013, **138**, 4760-4763; (b) R. Sheng, P. Wang, Y. Gao, Y. Wu, W. Liu, J. Ma, H. Li, S. Wu, *Org. lett.*, 2008, **10**, 5015-5018.

66 I. G. Shenderovich, H. Limbach, S. N. Smirnov, P. M. Tolstoy, G. S. Denisov, N. S. Golubev, *Phys. Chem. Chem. Phys.*, 2002, **4**, 5488-5497.

67 P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305-1323.

Graphical abstract



A colorimetric chemosensor with an electron-withdrawing group (-NO_2) **1** for the detection of CN^- and F^- was developed.