RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

A new coumarin-based chromogenic chemosensor for the detection of dual analytes Al^{3+} and F^-

Gyeong Jin Park, Hyun Yong Jo, Ka Young Ryu, Cheal Kim*

[a]Department of Fine Chemistry and Department of Interdisciplinary Bio IT Materials, Seoul National University of Science and Technology, Seoul 139-743, Korea. Fax: +82-2-973-9149; Tel: +82-2-970-6693; E-mail: chealkim@seoultech.ac.kr

Abstract

A multifunctional colorimetric receptor **1** (2-(3-nitro-2-oxo-2H-chromen-4-ylamino)-3-aminomaleonitrile) for the detection of both Al^{3+} and F^- has been developed. The receptor **1** showed a significant color change in the presence of Al^{3+} over most other competitive metal ions including Ga^{3+} and In^{3+} in aqueous solution. The selectivity mechanism of **1** for Al^{3+} might be attributed to the enhancement of intramolecular charge transfer band. Interestingly, it could be recyclable simply through treatment with a proper reagent such as ethylenediaminetetraacedtic acid. Moreover, the **1** showed a highly selective colorimetric response to F^- due to the decrease in intramolecular charge transfer band by a deprotonation process without any interference from other anions. Therefore, **1** can serve as 'single sensor for dual targets'.

Keywords : Aluminum ion; Fluoride; Colorimetric; Intramolecular charge transfer; Deprotonation

Introduction

Both cations and anions play critical roles in many biological, chemical and environmental systems. Therefore, the environmental and health problems associated with these ions have received a considerable attention.[1] As the third most abundant element in the earth's crust, aluminum is extensively used in modern society such as the water purification, food additives, pharmaceuticals and the production of light alloy.[2] Due to these widespread uses, a significant amount of aluminum ions exceed the human body's excretory capacity, and the excess is deposited in various tissues. The unregulated amounts of aluminum in the brain may lead to the malfunction of the central nervous system such as Parkinson and Alzheimer diseases.[3] Thus, detection of Al^{3+} is crucial in controlling its concentration level in environment and its direct impact in human health.[4]

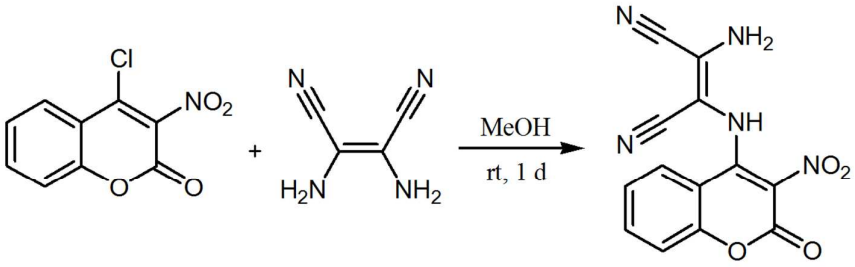
Among the biologically important anions, fluoride plays an important role in biological, medical and chemical processes.[5] Proper ingestion of fluoride can prevent and cure dental problems and osteoporosis. Hence, it is necessary to add fluoride to toothpaste and drinking water.[6] However, fluoride is absorbed easily by the body and excreted slowly from the body.[7] Therefore, excess intake of F^- may cause many diseases due to its toxicity, such as gastric and kidney disorders, dental and skeletal fluorosis, urolithiasis, or even death.[8] Thus, it is of fundamental importance to develop some analytical methods for detecting and controlling the concentration levels of fluoride in the environment and the human body.[9]

Many sensing methods for detecting cations and anions have been described, including colorimetric chemosensors, fluorescent chemosensors, and electrochemical methods. Colorimetric sensors among them are the most promising because of the simplicity of the assay. Colorimetric assays also have a significantly lower capital cost than other methods such as fluorescent sensors, in which spectrophotometric equipment and a UV light source are both required.[10] Among the different available chemosensors, colorimetric/chromogenic chemosensors are especially attractive, because analyte determination can be carried out by the naked eye under visible light, and because the use of expensive equipment can be avoided.[11] Colorimetric/chromogenic sensors have therefore attracted considerable attention regarding the detection of metal ions or anions.[12]

2,3-Diaminomaleonitrile represents a class of organic π-conjugated compound with electronic donor ($-NH_2$ groups) and acceptor (-C≡N groups) parts with high electron affinity

connected by single and double bonds, which features a strong intramolecular charge transfer (ICT) character with broad and intense absorption bands in the visible spectral range as previously reported ICT compounds with the 2,3-diaminomaleonitrile moiety behaved.[13] In addition, 4-chloro-3-nitrocoumarin with an electron acceptor part (-NO_2 group) has been frequently used in recent years as the chromogenic dye in chemosensors.[14] Therefore, we designed and synthesized a new chemosensor **1** based on the combination of the maleonitrile and the coumarin moieties, and tested its sensing properties towards various metal ions and anions.

Herein, we reported a new receptor **1** with such an ICT character, which was synthesized in one step by coupling 2,3-diaminomaleonitrile with 4-chloro-3-nitrocoumarin (Scheme 1). The receptor **1** showed a remarkably blue-shifted absorption spectrum with the distinct color change in the presence of Al^{3+} in aqueous solution. Additionally, **1** could also recognize F^- through an intense color change from yellow to pink with red-shifted absorption spectrum.



Scheme 1. The synthetic procedure for receptor **1**

Experimental Section

Materials and Instrumentation

All the solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma-Aldrich and used as received. NMR spectra were recorded on a Varian 400 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.

Synthesis of 1

To a solution of 4-chloro-3-nitrocoumarin (0.23 g, 1 mmol) in absolute methanol (10 mL), 2,3-diaminomaleonitrile (0.32 g, 3 mmol) was slowly added. The mixture was stirred for one day. After evaporating the solution, it was recrystallized by ice methanol. A yellow precipitate was filtered off, washed with diethyl ether, and dried in vacuum to obtain the desired compound. Yield 0.25 g (84 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.62 (s, 1H, -NH), 8.23 (d, J = 8 Hz, 1H, Ar-H), 8.07 (s, 2H, -NH_2), 7.79 (t, J = 7.8 Hz, 1H, Ar-H), 7.51 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): 155.15, 151.00, 144.28, 134.13, 124.78, 124.61, 117.31, 116.07, 112.78. ESI-MS m/z [M-H]$^-$: calcd, 296.05; found, 296.13. Anal. Calcd for $C_{13}H_7N_5O_4$: C, 52.53; H, 2.37; N, 23.56 %. Found: C, 52.85; H, 2.43; N, 23.12 %.

Chromogenic Al^{3+} Sensing

UV-vis titration. The receptor **1** (3.0 mg, 0.01 mmol) was dissolved in MeOH (1 mL) and 9 μL of the **1** (10 mM) were dilluted to 2.991 mL of MeOH-buffer solution (9:1, v/v, 10 mM bis-tris, pH 7.0) to make the concentraiton of 30 μM. $Al(NO_3)_2$ (3.8 mg, 0.03 mmol) was dissolved in MeOH (1 mL). 3-30 μL of the Al^{3+} solution (30 mM) were transferred to the receptor solution (30 μM, 3 mL) prepared above. After mixing them for a few seconds, UV-vis spectra were taken at room temperature.

Job plot measurement. The receptor **1** (3.0 mg, 0.01 mmol) and $Al(NO_3)_3$ (3.8 mg, 0.01 mmol) were dissolved in MeOH (1 mL), respectively. 0.09 mL of the receptor **1** solution were diluted to 29.91 mL of MeOH-buffer solution (9:1, v/v, 10 mM bis-tris, pH 7.0) to make the concentraiton of 30 μM. The $Al(NO_3)_3$ solution was diluted in the same way. 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5 and 0 mL of the receptor **1** solution were taken and transferred to vials. 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 mL of the Al^{3+} solution were added to each receptor solution seperately. Each vial had a total volume of 5 mL. After shaking the

vials for a few seconds, UV-vis spectra were taken at room temperature.

Competitive experiments. The receptor **1** (3.0 mg, 0.01 mmol) was dissolved in MeOH (1 mL). MNO_3 (M = Na and K, 0.03 mmol) or $M(NO_3)_2$ (M = Mn, Co, Ni, Cu, Zn, Cd, Mg, Ca, Hg and Pb; 0.03 mmol) or $M(NO_3)_3$ (M = Al, Ga, In, Fe and Cr; 0.03 mmol) or $M(ClO_4)_2$ (M = Fe, 0.03 mmol) were dissolved in MeOH (1 mL), respectively. 24 μL of each metal solution (30 mM) were dilluted to 2.943 mL of MeOH-buffer solution (9:1, v/v, 10 mM bis-tris, pH 7.0), separately. 24 μL of the Al^{3+} solution (30 mM) were taken and added to the solutions prepared above. Then, 9 μL (1 mM) of the **1** were taken and added to the mixed solutions. Each vial had a total volume of 3 mL. After shaking the vials for a few seconds, UV-vis spectra were taken at room temperature.

NMR titration. Four NMR tubes of **1** (0.6 mg, 0.002 mmol) dissolved in CD_3OD (0.7 mL) were prepared, and four different equiv (0, 0.2, 0.5 and 1 equiv) of the $Al(NO_3)_3$ dissolved in CD_3OD (0.3 mL) were added to the **1** solution, respectively. After shaking them for a minute, their ^1H NMR spectra were taken.

Chromogenic F^- Sensing

UV-vis titration. The receptor **1** (3.0 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 9 μL of the **1** (10 mM) were dilluted to 2.991 mL of DMSO to make the concentraiton of 30 μM. Tetraethylammonium fluoride ((TEA)F, 0.03 mmol) was also dissolved in DMSO (1 mL) and 30-660 μL of the F^- solution (30 mM) were transferred to the solution of **1** (30 μM, 3 mL) prepared above. After mixing them for a few seconds, fluorescence spectra were taken at room temperature.

Job plot measurement. The receptor **1** (3.0 mg, 0.01 mmol) and (TEA)F (0.01 mmol) were dissolved in DMSO (1 mL), respectively. 0.09 mL of the receptor **1** solution were diluted to 29.91 mL of DMSO to make the concentraiton of 30 μM. The (TEA)F solution was diluted in the same way. 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5 and 0 mL of the receptor **1** solution

were taken and transferred to vials. 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 mL of the F^- solution were added to each receptor solution seperately. Each vial had a total volume of 5 mL. After shaking the vials for a few seconds, UV-vis spectra were taken at room temperature.

Competitive experiments. The receptor **1** (3.0 mg, 0.01 mmol) was dissolved in DMSO (1 mL). Tetraethylammonium salt (F^-, Br^-, Cl^-, I^-, and CN^-; 0.03 mmol) or tetrabutylammonium salt (SCN^-, BzO^-, N_3^-, AcO^- and $H_2PO_4^-$; 0.03 mmol) were dissolved in DMSO (1 mL), respectively. 600 μL of each anion solution (10 mM) were dilluted to 1.791 mL of DMSO, separately. 600 μL of the F^- solution (30 mM) were taken and added to the solutions prepared above. Then, 9 μL of the **1** (10 mM) were taken and added to the mixed solutions. Each vial had a total volume of 3 mL. After shaking the vials for a few seconds, fluorescence spectra were taken at room temperature.

NMR titration with F^- ion. Three NMR tubes of **1** (0.6 mg, 0.002 mmol) dissolved in DMSO-d_6 (0.7 mL) were prepared, and three different equiv (0, 0.5 and 1 equiv) of the (TEA)F dissolved in DMSO-d_6 (0.3 mL) were added to the **1** solution, respectively. After shaking them for a minute, their ^{1}H NMR spectra were taken.

Results and discussion

Synthesis of 1

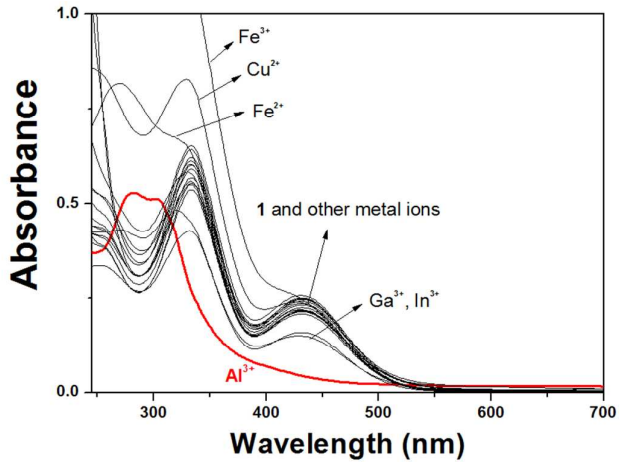
A new receptor **1** was obtained by coupling 4-chloro-3-nitrocoumarin with 2,3-diaminomaleonitrile with an 84 % yield in methanol (Scheme 1), and characterized by ^{1}H NMR (Fig. S1), ^{13}C NMR (Fig. S2), ESI-mass spectrometry analysis, and elemental analysis.

Chromogenic sensing for Al^{3+}

The colorimetric sensing ability of **1** was examined with various metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} in MeOH-buffer solution (9:1, v/v, 10 mM bis-tris, pH 7.0) at room temperature.

Upon the addition of 8 equiv of each cation, the **1** showed almost no change in absorption peak in the presence of Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}, while the presence of Ga^{3+}, and In^{3+} led to a small decrease in the absorption maxima to different extents (Fig. 1a). Most importantly, only Al^{3+} showed a distinct spectral change (Fig. 1a) and a color change from yellow to colorless (Fig. 1b). Moreover, **1** can distinguish Al^{3+} from Ga^{3+} and In^{3+}, whereas their discrimination is still a challenge as they are in the same group of the Periodic table and have similar properties. Therefore, this result indicates that receptor **1** can serve as a potential candidate of a "naked-eye" chemosensor for Al^{3+} in aqueous solution.

(a)



(b)

Figure 1. (a) Absorption spectra changes of **1** (30 μM) in the presence of various metal ions (8 equiv) in MeOH-buffer solution (10 mM bis-tris, pH 7.0, 9:1, v/v). (b) Color changes of receptor **1** (30 μM) in the presence of 8 equiv of metal ion in MeOH-buffer solution (10 mM bis-tris, pH 7.0, 9:1, v/v).

To further investigate the chemosensing properties of **1**, UV-vis titration of **1** with Al^{3+} was performed (Fig. 2). Upon the addition of Al^{3+} to a solution of **1**, the absorbance peaks at 250, 334 and 432 nm gradually decreased and a new absorbance at 302 nm appeared concomitantly, resulting in a color change from a yellow to colorless. This color change could be explained by one of two possibilities: one is that such colorless phenomenon might be originated from blue shift generated by the decrease in the push-pull effect of the ICT transition. The weak push-pull electronic effect was induced by binding of Al^{3+} ion to the -NH_2 and -NH groups in the receptor **1** with the electron-donating groups (-NH_2 and -NH) and the electron-withdrawing one (-C≡N group). The other is that decomposition phenomenon would occur when binding the receptor **1** to Al^{3+}.

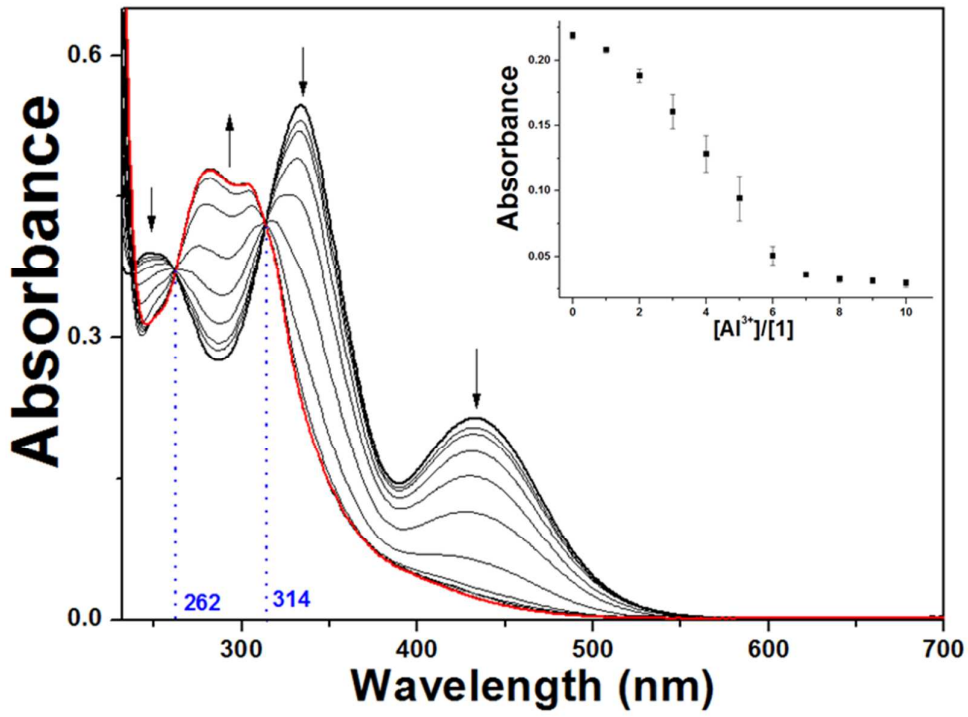


Figure 2. UV-vis spectra of receptor **1** (30 μM) upon the addition of Al^{3+}. Inset: The ratio of absorbance (432 nm) of **1** as a function of Al^{3+} equiv.

To determine the correct reason, ^1H NMR titration was conducted (Fig. 3). Upon addition of Al^{3+} to sensor **1**, the protons H_2, H_3, and H_4 showed downfield shift by 0.002, 0.003 and 0.011 ppm, while up-field shift was observed for H_1 by 0.005 ppm. There was no shift in the

position of proton signals on further addition of Al^{3+} (>1.0 equiv), which indicates that the **1** did not decompose when binding to Al^{3+}. Therefore, the chemosensing properties of **1** might be attributed to the decrease in the push-pull effect of the ICT transition. Also, these chemical shifts suggest that the two nitrogen atoms of the -NH_2 and -NH moieties might coordinate to Al^{3+} ion.

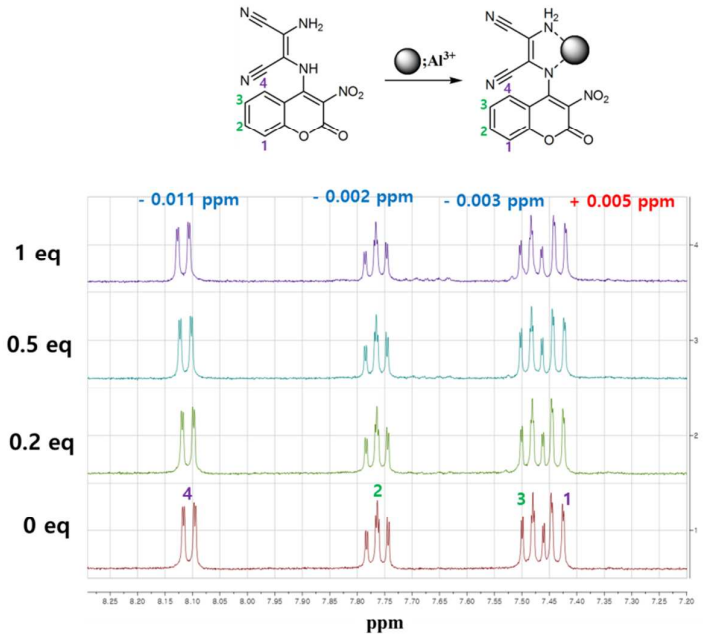


Figure 3. ^{1}H NMR titration of receptor **1** with Al^{3+}.

Job plot analysis exhibited a 1:1 complexation stoichiometry for **1**-Al^{3+} complex formation (Fig. S3), which was further confirmed by ESI-mass spectrometry analysis (Fig. 4). The positive-ion mass spectrum indicated that a peak at m/z= 470.73 was assignable to [**1**-H^++Al^{3+}+NO_3^-+3H_2O+MeOH]$^+$ [calcd, m/z: 471.07]. Based on Job plot, ESI-mass spectrometry analysis and the ^{1}H NMR titration, we propose the structure of **1**-Al^{3+} complex (Scheme 2).

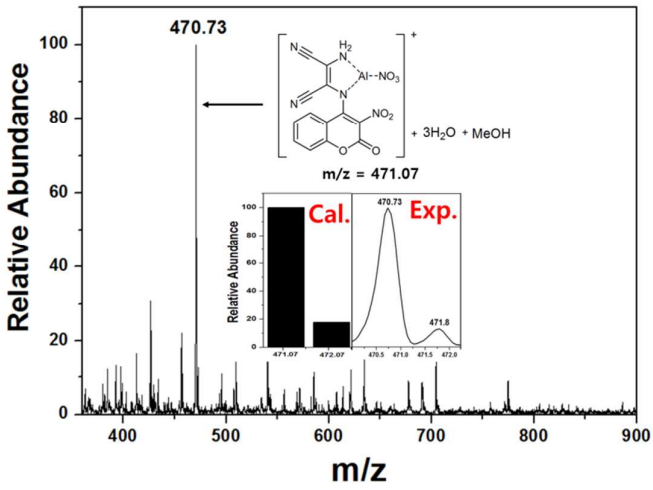
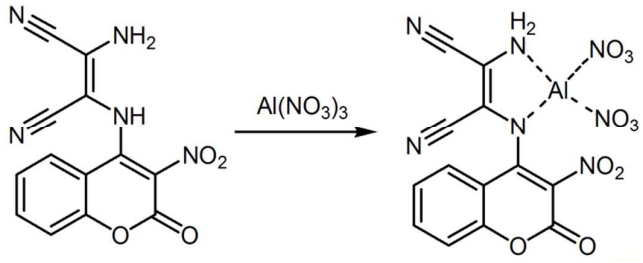


Figure 4. Positive-ion electrospray ionization mass spectrum of **1** (0.1 mM) upon addition of Al^{3+} (1 equiv).



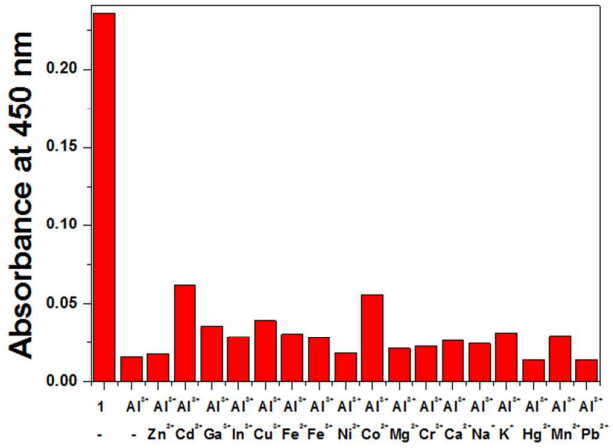
Scheme 2. The proposed structure for a **1**-Al^{3+} complex.

The association constant for the **1**-Al^{3+} complexation was determined as 4.7 x 10^3 M^{-1} through Benesi-Hildebrand equation (Fig. S4). This value is in the range of those (10^3 ~ 10^9) reported for Al^{3+} binding chemosensor.[15] Based on the result of UV-vis titration, the detection limit (3σ/k) of the receptor **1** for the analysis of Al^{3+} ion was calculated to be 38.2 μM (Fig. S5).

To check the practical applicability of **1** as a selective colorimetric sensor for Al^{3+}, the competition experiments were conducted in the presence of Al^{3+} mixed with other relevant metal ions, such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ga^{3+}, In^{3+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}. When **1** was treated with 8 equiv of Al^{3+} in the presence of the same concentration of other metal ions (Fig. 5), the coexistent metal ions had a small and

negligible effect on naked-eye detection of Al^{3+} by the receptor **1**, while Cd^{2+} and Co^{2+} did interfere to small extent. Therefore, these results suggest that **1** could be a selective colorimetric sensor for detecting Al^{3+} in the presence of competing metal ions.

(a)



(b)

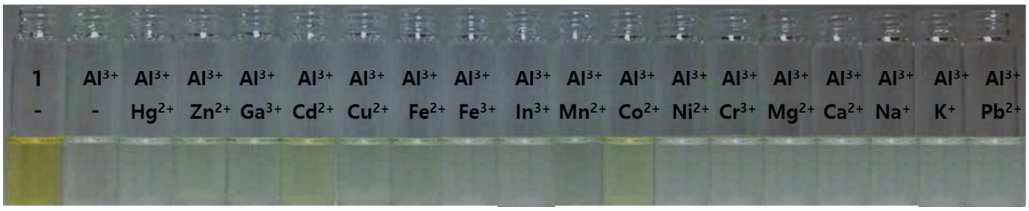


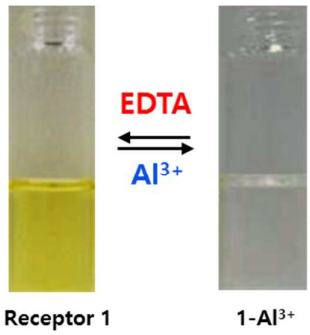
Figure 5. (a) Competitive bar graph of absorbance **1** (30 μM) towards Al^{3+} (8 equiv) in the presence of other metal ions (8 equiv). (b) Colorimetric competitive experiment of **1** (30 μM) in the presence of Al^{3+} (8 equiv) and other metal ions (8 equiv).

The effect of pH on the absorption response of receptor **1** to Al^{3+} ions was investigated in the pH range of 2 to 11 (Fig. S6). The absorbance and color of the **1**-Al^{3+} complex remained between pH 7 and 11, which warrant that Al^{3+} could be clearly detected by the naked eye or UV-vis absorption measurements using receptor **1** over a wide pH range of 7-11.

To examine the reversibility of receptor **1** toward Al^{3+}, ethylenediaminetetraacetic acid (EDTA) (8 equiv) was added to the complexed solution of receptor **1** and Al^{3+}. As shown in Fig. 6, the addition of EDTA to a mixture of **1** and Al^{3+} resulted in return of the absorbance

with colorless at 450 nm, which indicates the regeneration of the free **1**. This result further supports that the response of **1** in the presence of Al^{3+} is not due to decomposition process. Upon addition of Al^{3+} into the solution again, the color and the absorbance were recovered. The color change (Fig. 6a) and absorbance (Fig. 6b) were almost reversible even after several cycles with the sequentially alternative addition of Al^{3+} and EDTA, which indicate that the receptor **1** could be used as a reversible colorimetric chemosenor in aqueous solution.

(a)



(b)

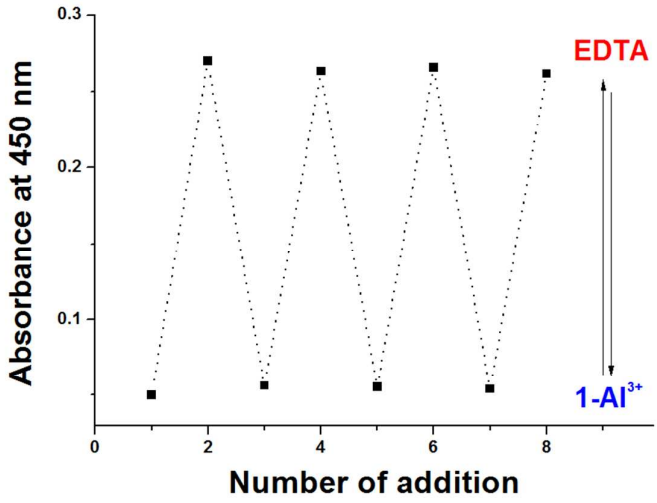
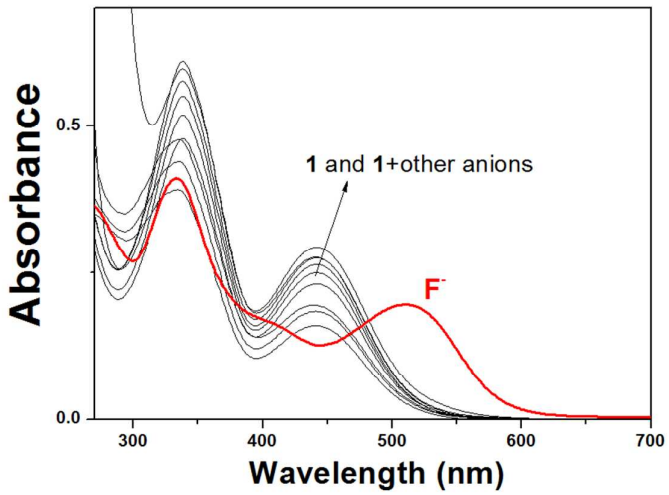


Figure 6. (a) Colorimetric changes of **1** (30 μM) after the sequential addition of Al^{3+} and EDTA. (b) Reversible changes in absorbance of **1** (30 μM) at 450 nm after the sequential addition of Al^{3+} and EDTA.

Chromogenic sensing for F^-

The colorimetric sensing abilities of **1** were also investigated towards various anions (F^-, Cl^-, Br^-, I^-, AcO^-, BzO^-, $H_2PO_4^-$, N_3^-, SCN^- and CN^-) in DMSO as shown in Fig.7. Upon the addition of 200 equiv of each anion, the solution of **1** exhibited no or small absorption change except F^-. In the presence of F^-, the receptor **1** showed a distinct spectral change (Fig. 7a) and a color change from yellow to pink (Fig. 7b), indicating that receptor **1** can serve as a potential candidate of "naked-eye" chemosensor for F^-.

(a)



(b)

Figure 7. (a) UV-vis spectra changes of **1** (30 μM) upon addition of various anions (200 equiv). (b) Colorimetric changes of **1** (30 μM) upon the addition of various anions (200 equiv).

The recognition properties of **1** with F^- were further studied by UV-vis titration experiments. On treatment with F^- of a solution of **1**, the absorption bands at 338 and 441 nm gradually decreased, and a new band at 510 nm reached maxima at 200 equivalent of F^- (Fig. 8).

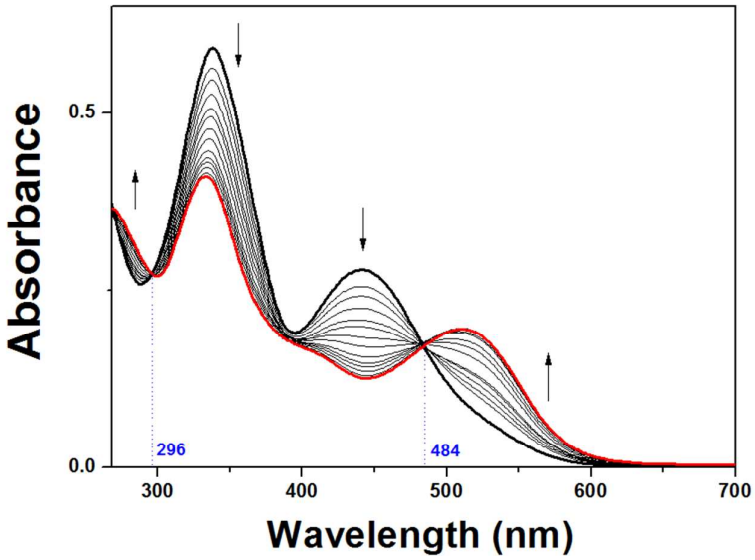
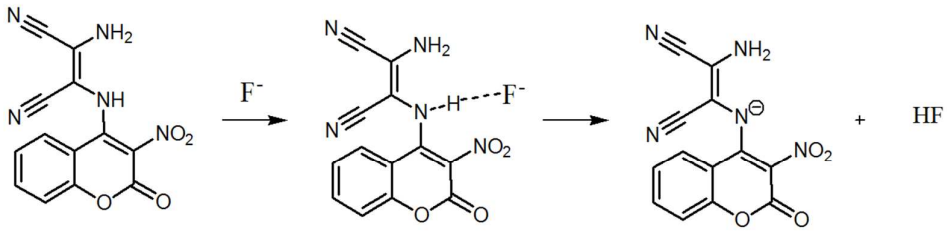


Figure 8. UV-vis spectra of receptor **1** (30 μM) upon the addition of F^-.

Meanwhile, two clear isosbestic points were observed at 296 and 484 nm, indicating the formation of the only one species between **1** and F^-. The pink color of the solution may be due to the deprotonation of receptor **1** by F^-. The deprotonation through the hydrogen-bond donor interaction of amine hydrogen (N-H) with F^- might be coupled with an intermolecular proton transfer from **1** to the fluoride ion (Scheme 3).[16]



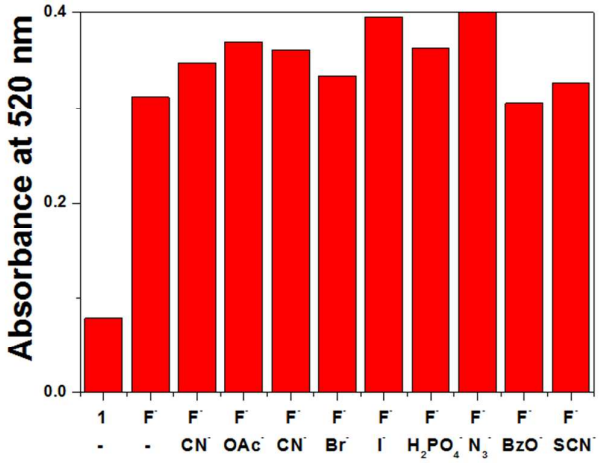
Scheme 3. Proposed sensing mechanism of **1** for fluoride

The resulting negative charge on the amine moiety would lead to the enhancement of the push-pull effect of the ICT transition,[13a] which is highly visible to the naked eye with a change in color from yellow to pink. From the UV-vis titration data, the association constant

for **1** with F^- was determined as 1.3 x 10^2 M^{-1} using the nonlinear-fitting analysis of the change in the absorbance at 520 nm (R^2= 0.9883, Fig. S7).[17] The detection limit (3σ/k) of receptor **1** for the analysis of F^- ions was calculated to be 2.1 x 10^{-3} M (Fig. S8).

The Job plot showed a 1:1 stoichiometry between **1** and F^- (Fig. S9), which was further confirmed by ESI-mass spectrometry analysis (Fig. S10). The positive-ion mass spectrum of **1** upon addition of 1 equiv of F^- showed the formation of the $\mathbf{1}^-$+2TEA [m/z: 556.13; calcd, 556.36]. The preferential selectivity of **1** as a naked eye chemosensor for the detection of F^- was studied in the presence of various competing anions. For competition studies, receptor **1** was treated with 200 equiv of F^- in the presence of the same concentration of other anions, as indicated in Fig. 9. There was no interference for the detection of F^- in the presence of Cl^-, Br^-, I^-, AcO^-, BzO^-, $H_2PO_4^-$, N_3^-, SCN^- and CN^-. Thus, **1** could be used as a selective colorimetric sensor for F^- in the presence of the competing anions.

(a)



(b)

Figure 9. (a) Competitive bar graph of the relative absorbance of **1** (30 μM) towards F^- (200 equiv) in the presence of other anions (200 equiv). (b) Colorimetric competitive experiment

of **1** (30 μM) in the presence of F^- (200 equiv) and other anions (200 equiv).

To further understand the nature of interaction between sensor **1** and the fluoride, ^{1}H NMR study was initiated in DMSO-d_6 (Fig. 10). Before the addition of F^-, chemical shifts of the -NH and -NH_2 protons (H_5 and H_6) on **1** appeared at 9.96 and 8.07 ppm. With the continuous addition of F^- up to 1 equiv, the signal of -NH proton (H_5) disappeared gradually. Meanwhile, all aromatic protons were shifted to upfield, and the signal of the -NH_2 proton (H_6) was most shifted to upfield (6.25 ppm), which suggests that the negative charge generated from the deprotonation of **1** by F^- was delocalized over the whole receptor molecule. These results suggest that the -NH proton (H_5) might form a -N-H···F^- hydrogen bond, and subsequently undergo a deprotonation process as shown in Fig. 10. No shift in the position of proton signals was observed on any further addition of F^- (> 1.0 equiv). Based on Job plot, ESI-mass spectrometry analysis, and ^{1}H NMR study, we propose that the sensing ability of receptor **1** might be due to the deprotonation process by F^-, as shown in Scheme 3.

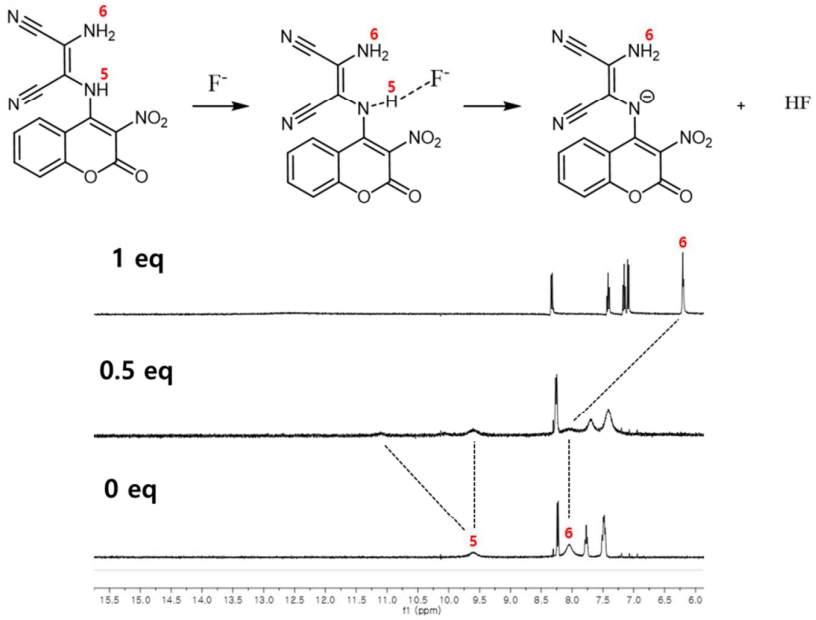


Figure 10. ^{1}H NMR titration of receptor **1** with F^-.

Conclusion

We have developed a new colorimetric sensor **1**, based on the combination of coumarin and maleonitrile moieties. It distinguished Al^{3+} ion from other metal ions, especially Ga^{3+} and In^{3+}, by color change in aqueous media without expensive equipment. Moreover, the addition of EDTA to the **1**-Al^{3+} complex regenerated the free **1**, indicating that the sensor **1** could be recyclable simply through treatment with a proper reagent such as EDTA. The receptor **1** also detected F^- selectively, which induced an obvious color change from yellow to pink. Such selectivity results from the increase in the push-pull effect of the ICT transition by deprotonation between **1** and F^-. This type of highly selective naked-eye chemosensor will be useful for development of new chemosensors for multiple targets such as cations and anions.

Acknowledgements

Financial support from Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012001725 and 2012008875) are gratefully acknowledged.

Supplementary Material

Additional experimental data are available. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2013.??.??.

References

1 (a) M. Kumar, N. Kumar, V. Bhalla, *Dalton Trans.*, 2012, **41**, 10189-10193; (b) D. Karak, S. Lohar, A. Banerjee, A. Sahana, I. Hauli, S. K. Mukhopadhyay, J. S. Matalobos, D. Das, *RSC Adv.*, 2012, **2**, 12447-12454; (c) Y. J. Lee, D. Seo, J. Y. Kwon, G. Son, M. S. Park, Y. Choi, J. H. Soh, H. N. Lee, K. D. Lee, J. Yoon, *Tetrahedron*, 2006, **62**, 12340-12344; (d) 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; (e) V. Bhalla, S. Pramanik, M. Kumar, *Chem. Comm.,* 2013, **49**, 895-897; (f) J. Kang, S. P. Jang, Y. Kim, J. H. Lee, E. B. Park, H. G. Lee, J. H. Kim, Y. Kim, S. Kim, C. Kim, *Tetrahedron Lett*., 2010, **51**, 6658-6662.

2 (a) J. R. J. Sorenson, I. R. Campbell, L. B. Tepper, R. D. Lingg, *Environ. Health Perspect*, 1974, **8**, 3-95; (b) D. Wang, Y. Ke, H. Guo, J. Chen, W. Weng, *Spectrochim. Acta Part A*, 2014, **122**, 268-272; (c) Y. J. Jang, Y. H. Yeon, H. Y. Yang, J. Y. Noh, I. H. Hwang, C. Kim, *Inorg. Chem. Commun.*, 2013, **33**, 48-51; (d) K. B. Kim, D. M. You, J. H. Jeon, Y. H. Yeon, J. H. Kim, C. Kim, *Tetrahedron Lett.*, 2014, **55**, 1347-1352; (e) S. Das, M. Dutta, D. Das, *Anal. Methods*, 2013, **5**, 6262-6285; (f) H.S. Jung, P.S. Kwon, J.W. Lee, J.I. Kim, C.S. Hong, J.W. Kim, S. Yan, J.Y. Lee, J.H. Lee, T. Joo, J.S. Kim, *J. Am. Chem. Soc.*, 2009, **131**, 2008-2012; (g) J. You, H. Hu, J. Zhou, L. Zhang, Y. Zhang, T. Kondo, *Langmuir*, 2013, **29**, 5085-5092; (h) Z. Li, Q. Hu, C. Li, J. Dou, J. Cao, W. Chen, Q. Zhu, *Tetrahedron Lett.*, 2014, **55**, 1258-1262; (i) S. Malkondu, *Tetrahedron*, 2014, **70**, 5580-5584.

3 (a) L, Elečková, M. Alexovič, J. Kuchár, I. S. Balogh, V. Andruch, *Talanta*, http://dx.doi.org/10.1016/j.talanta.2014.04.064; (b) G. D. Fasman, *Coord. Chem. Rev*., 1996, **149**, 125-165; (c) P. Nayak, *Environ. Res.,* 2002, **89**, 101-115; (d) 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; (e) S. Kim, J. Y. Noh, S. J. Park, Y. J. Na, I. H. Hwang, J. Min, C. Kim, J. Kim, *RSC Adv.*, 2014, **4**, 18094-9; (f) S. Goswami, S. Paul, A. Manna, *RSC Adv.*, 2013, **3**, 25079-25085; (g) J.Y. Kwon, Y.J. Jang, Y.J. Lee, K.M. Kim, M.S. Seo, W. Nam, J. Yoon, *J. Am. Chem. Soc.*, 2005, **127**, 10107-10111; (h) Z. Zheng, Z. Duan, Y. Ma, K. Wang, *Inorg. Chem.*, 2013, **52**, 2306-2316; (i) L. Fan, X. Jiang, B. Wang, Z. Yang, *Sens. Actuators B*, 2014, **205**, 249-254.

4 (a) C. S. Cronan, W. J. Walker, P. R. Bloom, *Nature*, 1986, **324**, 140-143; (b) G. Berthon, *Coord. Chem. Rev.*, 2002, **228**, 319-341; (c) D. R. Burwen, S. M. Olsen, L. A. Bland, M. J. Arduino, M. H. Reid, W. R. Jarvis, *Kidney Int.*, 1995, **48**, 469-474; (d) J. Y. Noh, S. Kim, I.

H. Hwang, G. Y. Lee, J. Kang, S. H. Kim, J. Min, S. Park, C. Kim, J. Kim, *Dyes Pigm.*, 2013, **99**, 1016-1021; (e) C. Li, Y. Zhou, Y. Li, C. Zou, X. Kong, *Sens. Actuators B*, 2013, **186**, 360-366; (f) S. Sen, T. Mukherjee, B. Chattopadhyay, A. Moirangthem, A. Basu, J. Marek, P. Chattopadhyay, *Analyst*, 2012, **137**, 3975-3981; (g) S. Kim, J.Y. Noh, K.Y. Kim, J.H. Kim, H.K. Kang, S. Nam, S.H. Kim, S. Park, C. Kim, J. Kim, *Inorg. Chem.*, 2012, **51**, 3597-3602; (h) S. Goswami, K. Aich, S. Das, A. K. Das, D. Sarkar, S. Panja, T. K. Mondal, S. Mukhopadhyay, *Chem. Comm.*, 2013, **49**, 10739-10741; (i) S. Basurto, O. Riant, D. Moreno, J. Rojo, T. Torroba, *J. Org. Chem.*, 2007, **72**, 4673-4688.

5 (a) H. Miyaji, W. Sato, J. L. Sessler, *Angew. Chem. Int. Ed.*, 2000, **39**, 1777-1780; (b) S. K. Kim, J. L. Sessler, *Chem. Soc. Rev.*, 2010, **39**, 3784-3809; (c) J. Aaseth, M. Shimshi, J. L. Gabrilove, G. S. Birketvedt, *Trace Elem. Exp. Med.*, 2004, **17**, 83-92; (d) J. Chen, P. Zhou, L. Zhao, T. Chu, *RSC Adv.*, 2014, **4**, 254-259.

6 J. Chen, P. Zhou, G. Li, T. Chu, G. He, *J. Phys. Chem. B*, 2013, **117**, 5212-5221.

7 N. M. Mattiwala, R. Kamal, S. K. Sahoo, *Res. Chem. Intermed.*, http://dx.doi.org/10.1007/s11164-013-1200-6.

8 (a) Y. Kim, F. P. Gabbaï, *J. Am. Chem. Soc.*, 2009, **131**, 3363-3369; (b) A. E. J. Broomsgrove, D. A. Addy, A. D. Paolo, I. R. Morgan, C. Bresner, V. Chislett, I. A. Fallis, A. L. Thompson, D. Vidovic, S. Aldridge, *Inorg. Chem.*, 2010, **49**, 157-173; (c) S. Madhu, M. Ravikanth, *Inorg. Chem.*, 2014, **53**, 1646-1653; (d) K. Tayade, S.K. Sahoo, A. Singh, N. Singh, P. Mahulikar, S. Attarde, A. Kuwar, *Sens. Actuators B*, 2014, **202**, 1333-1337; (e) L. Wang, G. Fang, D. Cao, *J. Fluoresc.*, 2014, http://dx.doi.org/10.1007/s10895-014-1464-2; (f) A. Bamesberger, C. Schwartz, Q. Song, W. Han, Z. Wang, H. Cao, *New J. Chem.*, 2014, **38**, 884-888.

9 (a) K. Ghosh, D. Kar, R. Fröhlich, A. P. Chattopadhyay, A. Samaddera, A. R. Khuda-Bukhsh, *Analyst*, 2013, **138**, 3038-3045; (b) V. Luxami, S. Kumar, *Tetrahedron Lett.*, 2007, **48**, 3083-3087; (c) H. G. Im, H. Y. Kim, M. G. Choi, S. Chang, *Org. Biomol. Chem.*, 2013, **11**, 2966-2971; (d) E. J. Song, H. Kim, I. H. Hwang, K. B. Kim, A. R. Kim, I. Noh, C. Kim, *Sens. Actuators B*, 2014, **195**, 36-43; (e) J. Kang, Y. J. Lee, S. K. Lee, J. H. Lee, J. J. Park, Y. Kim, S. Kim, C. Kim, *Supramol. Chem.*, 2010, **22**, 267-273 ; (f) Y. Jo, N. Chidalla, D. Cho, *J. Org. Chem.*, 2014, **79**, 9418-9422; (g) X. Cheng, H. Jia, J. Feng, J. Qin, Z. Li, *Sens. Actuators B*, 2014, **199**, 54-61; (h) I.S. Turan, E.U. Akkaya, *Org. Lett.*, 2014, **16**, 1680-1683.

10 (a) D. Wang, Y. Ke, H. Guo, J. Chen, W. Weng, *Spectrochim. Acta Part A*, 2014, **122**,

268-272; (b) R. Sheng, P. Wang, W. Liu, X. Wu, S. Wu, *Sens. Actuators B*, 2008, **128**, 507-511.

11 A. P. Silva, H. N. Q. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515-1566.

12 (a) K. Yoosaf, B. I. Ipe, C. H. Suresh, K. G. Thomas, *J. Phys. Chem. C*, 2007, **111**, 12839-12847; (b) H. M. Yeo, B. J. Ryu, K. C. Nam, *Org. Lett.,* 2008, **10**, 2931-2934.

13 (a) M. A. Kaloo, J. Sankar, *Analyst*, 2013, **138**, 4760-4763; (b) M. A. Kaloo, J. Sankar, New. J. Chem., 2014, **38**, 923-926; (c) W. Xi, Y. Gong, B. Mei, X. Zhang, Y. Zhang, B. Chen, J. Wu, Y. Tian, H. Zhou, *Sens. Actuators B*, 2014, DOI: 10.1016/j.snb.2014.08.068.

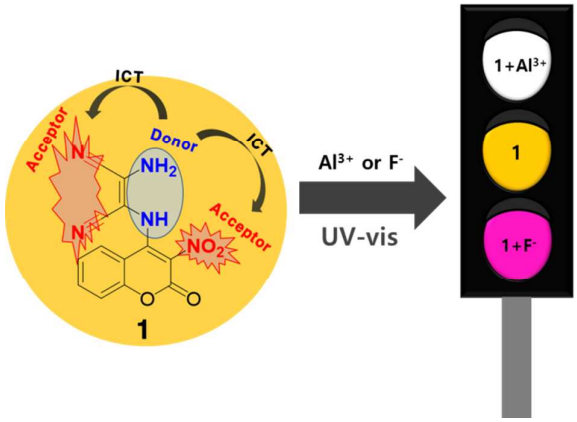
14 H. Y. Jo, G. J. Park, Y. J. Na, Y. W. Choi, G. R. You, C. Kim, *Dyes Pigm.*, 2014, **109**, 127-134.

15 (a) H. M. Park, B. N. Oh, J. H. Kim, W. Qiong, I. H. Hwang, K. Jung, C. Kim, J. Kim, *Tetrahedron Lett.*, 2011, **52**, 5581-5584; (b) D. Maity, T. Govindaraju, *Chem. Commun.*, 2010, **46**, 4499-4501; (c) Y. Wang, M. Yu, Y. Yu, Z. Bai, Z. Shen, F. Li, *Tetrahedron Lett.*, 2009, **50**, 6169-6172; (d) S. H. Kim, H. S. Choi, J. Kim, S. J. Lee, D. T. Quang, J. S. Kim, *Org. Lett.*, 2010, **12**, 560-563;

16 X. Peng, Y. Xu, J. Fan, M. Tian, K. Han, *J. Org. Chem.*, 2005, **70**, 10524-10531.

17 B. Valeur, J. Pouget, J. Bourson, M. Kaschke, N. P. Ernsting, *J. Phys. Chem.*, 1992, **96**, 6545-6549.

Graphical Abstract



A simple and easy-to-make colorimetric sensor for Al^{3+} and F^- was designed and synthesized.