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A new multifunctional Schiff base as fluorescence sensor for Al^{3+} and colorimetric sensor for CN^- in aqueous media: an application to bioimaging

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A multifunctional fluorescent and colorimetric receptor **1** ((E)-N'-((8-hydroxy-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-9-yl)methylene)benzohydrazide) for the detection of both Al^{3+} and CN^- in aqueous solution has been developed. Receptor **1** exhibited an excellent selective fluorescence response toward Al^{3+}. The sensitivity of fluorescent based assay (0.193 μM) for Al^{3+} is far below the World Health Organization (WHO) guideline of the drinking water (7.41 μM). In addition, receptor **1** showed excellent detection ability at a wide pH range of 4-10 and also in living cells. Moreover, the receptor **1** showed a highly selective colorimetric response to CN^- by changing its color from colorless to yellow immediately without any interference by other anions.

Introduction

Aluminum is the most prevalent (8.3% by weight) metallic element and the third most abundant of all elements (after oxygen and silicon) in the earth's crust.[1] However, excess aluminum can cause damages to certain human tissues and cells, resulting in health problems such as Alzheimer's disease and Parkinson's disease.[2] Therefore, the World Health Organization (WHO) listed excess aluminum as one of the food pollutants and restricted the aluminum concentration to 200 μg L^{-1} (7.41 μM) in drinking water.[3] Additionally, solubility of aluminum minerals in water increases under acidic conditions and any such increased amount of Al^{3+} is fatal to plants and fish.[4,5,6] Hence, it is highly desirable to develop a more sensitive and selective receptor which can detect Al^{3+} below the limit that is recommended by WHO within a wide range of pH.[7]

Cyanide is well known as one of the most rapidly acting and fatal poisons, and its toxicity results from its propensity to bind to the iron in cytochrome c oxidase, interfering with electron transport and resulting in hypoxia. Several researchers also reported that cyanide occasionally plays a significant role in many fire related deaths.[8] Despite these toxicities, the use of cyanides as raw materials for synthetic fibers, resins, herbicides, and the gold-extraction process is inevitable.[9] Therefore, reliable and efficient ways of detecting the presence of cyanide are quite necessary. In recent years, a number of efforts have been devoted to design various chemo-sensors targeting the detection of cyanides.[10] The most attractive approach focuses on novel colorimetric cyanide receptors, which allow a naked-eye detection by a simple color change without the intervention of any expensive instruments.[11] However, many receptors for cyanide reported so far have several limitations such as poor selectivity over F^- or OAc^-, or utilization of expensive instruments, complicated synthesis, and working only in organic media.[12,13] Therefore, the search for an effective and selective cyanide-sensing system in aqueous environments is still a great challenge.

The development of a chemo-sensor, which is capable of recognizing a metal ion and an anion simultaneously, is one of the most significant tasks because of its important potential applications in biological industry and environmental processes.[14] In addition, the detection of multiple targets with a single receptor would be more efficient and at the same time less expensive than a one-to-one analysis method and thereby, would attract more attention.[15] Among various approaches for the detection of both metal ions and anions, especially the fluorimetric and colorimetric methods are more popular because of their high sensitivities, easy operations, rapid response rates, and relative low costs.[16]

The 8-hydroxyjulolidine-9-carboxaldehyde is a well-known chromophore used in a fluorescence chemosensor[17] and chemosensors with the julolidine moiety are usually soluble in aqueous solutions.[18] On the other hand, benzhydrazide, containing an amide group, demonstrates an anion recognition ability by linking the anions with its amide group via a

hydrogen bond.[19] Therefore, we designed to synthesize a structurally simple chemosensor **1** integrating julolidine chromophore and activated amide functionality for detection of both cations and anions in aqueous solution, and tested its sensing properties towards various metal ions and anions.

Herein, we report a chemo-sensor **1** based on the combination of julolidine and benzhydrazide for a simultaneous selective detection of Al^{3+} and CN- in aqueous media. The chemo-sensor **1** demonstrated the presence of the cation, Al^{3+} by a fluorescence enhancement and that of the anion, CN- by an instant change of color from colorless to yellow. It is expected that **1** would have potential practical applications, such as in bio-imaging, through mapping of Al^{3+} levels in cells.

Experimental section

General information

All the solvents and reagents (analytical and spectroscopic grade) were purchased from Sigma-Aldrich. ^1H and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer and chemical shifts are recorded in ppm. Electro spray ionization mass spectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQ_{TM} Advantage MAX quadrupole ion trap instrument by infusing samples directly into the source using a manual method. Spray voltage was set at 4.2 kV, and the capillary temperature was at 80 ^oC. Absorption spectra were recorded at room temperature using a Perkin Elmer model Lambda 2S UV/Vis spectrometer. Emission spectra were recorded on a Perkin-Elmer LS45 fluorescence spectrometer. Elemental analysis for carbon, nitrogen, and hydrogen was carried out using a Flash EA 1112 elemental analyzer (thermo) at the Organic Chemistry Research Center of Sogang University, Korea.

Synthesis of receptor 1

An ethanolic solution of 8-hydroxyjulolidine-9-carboxaldehyde (0.23 g, 1 mmol) was added to benzhydrazide (0.14 g , 1 mmol) in absolute ethanol (3 mL). Two drops of HCl were added into the reaction solution and it was stirred for 30 min at room temperature. A yellow precipitate was filtered and washed several times with ethanol and dried in vacuum to obtain the pure yellowish solid.

Yield 0.17 g (51%); Anal. Calc. for C20H21N3O2: C, 71.62; H, 6.31; N, 12.53; Found: C, 71.45; H, 6.45; N, 12.39; 1H NMR (400 MHz DMSO-d6, ppm): δ 11.79 (s, 1H), 11.78 (s, 1H), 8.31 (s, 1H), 7.91 (d, 2H), 7.59 (t, 1H), 7.52 (t, 2H), 6.72 (s, 1H), 3.18 (m, 4H), 2.62 (m, 4H), 1.86 (m, 4H); 13C NMR (400 MHz DMSO-d6, ppm): 162.78, 155.37, 151.58, 145.90, 133.83, 132.31, 129.14, 128.96, 128.15, 113.10, 106.96, 106.45, 50.00, 49.54, 27.21, 22.20, 21.38, 20.91. ESI-MS m/z (M + H+): calcd, 335.16; found, 335.23;

X-ray data collection and structure determination

A dark color needle-type crystal, approximate dimensions 0.20 mm x 0.02 mm x 0.01 mm, was used for the X-ray crystallographic analysis. The diffraction data for the compound 1 were collected on a Bruker SMART APEX diffractometer equipped with a monochromator in the Mo Ka (k = 0.71073 Å) incident beam. The crystal was mounted on a glass fiber. The CCD data were integrated and scaled using the BRUKER-SAINT software package, and the structure was solved and refined using SHEXTL V6.12. All hydrogen atoms except amide hydrogen atom were located in the calculated positions. The crystallographic data are listed in Table 1. The bond lengths and angles are listed in Table S1. Structural information was deposited at the Cambridge Crystallographic Data Center (CCDC 972999).

Table 1 Crystal data and structure refinement for receptor **1**.

Empirical formula	$C_{20}H_{21}N_3O_2$	
Formula weight	335.40	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 12.835(3) Å	α = 90.00°
	b = 9.3810(19)Å	β = 90.00°
	c = 28.713(6) Å	γ = 90.00°
Volume	3457.2(12) Å	
Z	8	
Density (calculated)	1.289 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
Crystal size	0.20 x 0.02 x 0.01 mm^3	
Reflections collected	18350	
Independent reflections	3394 [R(int) = 0.1756]	
Data / restraints / parameters	3394 / 2 / 231	
Goodness-of-fit on F^2	0.769	
Final R indices [I>2σ(I)]	R1 = 0.0607, wR_2 = 0.1328	
R indices (all data)	R1 = 0.1587, wR_2 = 0.1596	
Extinction coefficient	0.0146(11)	
Largest diff. peak and hole	0.248 and -0.250 e•$Å^{-3}$	

Fluorescence titration

1 (1.01 mg, 0.003 mmol) was dissolved in methanol (1 mL) and 10 μL of this solution (3 mM) were diluted with 2.97 mL of 10 mM bis-tris buffer to make the final concentration of 10 μM. $Al(NO_3)_3$ (0.10 mmol) was dissolved in methanol (5 mL) and 1.5-28.5 μL of this Al^{3+} solution (20 mM) were transferred to each receptor solution (10 μM) to give 1-19 equiv. After mixing them for a few seconds, fluorescence spectra were taken at room temperature.

UV-vis titrations

For Al^{3+}; **1** (1.01 mg, 0.003 mmol) was dissolved in methanol (1 mL) and 10 μL (3mM) of it were diluted to 2.99 mL with bis-tris buffer/methanol (999/1, v/v) to make a final concentration of 10 μM. $Al(NO_3)_3$ (0.10 mmol) was dissolved in bis-tris buffer (5 mL) and 3-27 μL of the Al^{3+} ion solution (10 mM) were transferred to the solution of **1** (10 μM) prepared

above. After mixing them for a few seconds, UV-vis spectra were taken at room temperature.

For CN^-; **1** (1.01 mg, 0.003 mmol) was dissolved in methanol (1 mL) and 30 μL (3mM) of it were diluted to 2.97 mL with bis-tris buffer/methanol (7/3, v/v) to make a final concentration of 30 μM. Tetraethylammonium cyanide (TEACN) (0.3 mmol) was dissolved in bis-tris buffer (5 mL) and 4.5-90 μL of the CN^- solution (300 mM) were transferred to the solution of **1** (10 μM) prepared above. After mixing them for a few seconds, UV-vis spectra were taken at room temperature.

Job plot measurements

For Al^{3+}; **1** (1.01 mg, 0.003 mmol) was dissolved in methanol (1 mL). 100, 90, 80, 70, 60, 50, 40, 30, 20, 10 and 0 μL of the **1** solution were taken and transferred to vials. Each vial was diluted with bis-tris buffer to make a total volume of 2.9 mL. $Al(NO_3)_3$ (0.003 mmol) was dissolved in bis-tris buffer (1 mL). 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 μL of the Al^{3+} solution were added to each diluted **1** solution. Each vial had a total volume of 3 mL. After shaking them for a minute, UV-vis spectra were taken at room temperature.

Competition with other metal ions or anions

For Al^{3+}; **1** (1.01 mg, 0.003 mmol) was dissolved in methanol (1 mL) and 10 μL of this solution (3 mM) were diluted with 2.99 mL of 10 mM bis-tris buffer to make the final concentration of 10 μM. MNO_3 (M = Na, K, 0.20 mmol) or $M(NO_3)_2$ (M = Mn, Co, Ni, Cu, Zn, Cd, Mg, Ca, Pb, 0.20 mmol) or $M(NO_3)_3$ (M = Fe, Cr, Ga, In, 0.20 mmol) or $M(ClO_4)_2$ (M = Fe, 0.20 mmol) were dissolved in methanol (5 mL). 27 μL of each metal solution (20 mM) were taken and added to 3 mL of the solution of receptor **1** (10 μM) to give 19 equiv of metal ions. Then, 29 μL of Al^{3+} solution (20 mM) were added into the mixed solution of each metal ion and **1** to make 19 equiv. After mixing them for a few seconds, fluorescence spectra were taken at room temperature.

For CN^-; **1** (1.01 mg, 0.003 mmol) was dissolved in methanol (1 mL) and 30 μL of this solution (3 mM) were diluted with 2.88 mL of bis-tris buffer/methanol (7/3, v/v) to make the final concentration of 30 μM. Tetraethylammonium salts of F^-, Cl^-, Br^-, and I^-, and tetrabutylammonium salts of $H_2PO_4^-$ and OAc^-, and sodium salts of SO_4^{2-} and N_3^- (0.20 mmol) were dissolved in bis-tris buffer (1 mL). 90 μL of each anion solution (200 mM) were taken and added to 2.91 mL of the solution of receptor **1** (10 μM) to give 200 equiv of anions. Then, 90 μL of tetraethylammonium cyanide solution (200 mM) were added into the mixed solution of each anion and **1** to make 200 equiv. After mixing them for a few seconds, UV-vis spectra were taken at room temperature.

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** (1.01 mg, 0.003 mmol) was dissolved in methanol (1mL), and then 10 μL of the methanolic solution of the receptor **1** (3 mM) were diluted with 2.97 mL buffers to make the final concentration of 10 μM.
$Al(NO_3)_3 \cdot 9H_2O$ (11.3 mg, 0.03 mmol) was dissolved in bis-tris buffer (1 mL, pH 7.00). 10 μL of the Al^{3+} solution (30 mM) were transferred to each receptor solution (10 μM) prepared above. After mixing them for a few seconds, fluorescence spectra were taken at room temperature.

^{1}H NMR titrations

For ^{1}H NMR titrations of receptor **1** with cyanide, four NMR tubes of receptor **1** (3.35 mg, 0.01 mmol) dissolved in DMSO-d_6 (700 μL) were prepared and then four different concentrations (0, 0.005, 0.01, 0.02, and 0.05 mmol) 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 taken at room temperature. In order to check the influence of water on binding property, the same ^{1}H NMR titrations of receptor **1** with cyanide were carried out in a mixture of DMSO-d_6/D_2O (9/1, v/v).

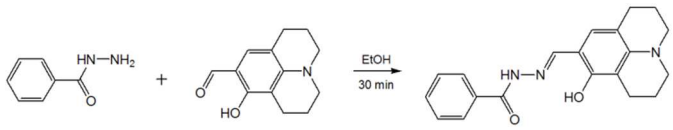
Methods for cell imaging

The cell imaging test was carried out by the same method as our previous study.[20] Human dermal fibroblast cells in low passage were cultured in FGM-2 medium (Lonza, Switzerland) supplemented with 10% fetal bovine serum, 1% penicillin/streptomycin in the *in vitro* incubator with 5% CO_2 at 37°C. Cells were seeded onto a 12 well plate (SPL Lifesciences, Korea) at a density of 2×10^5 cells per well and then incubated at 37 ºC for 4 h after the addition of various concentrations (0 ~ 100 μM) of $Al(NO_3)_3$. After washing with phosphate buffered saline (PBS) two times to remove the remaining $Al(NO_3)_3$, the cells were incubated with **1** (20 μM) for 30 min at room temperature. The cells were observed by using a microscope (Olympus, Japan). The fluorescent images of the cells were obtained by using a fluorescence microscope (Leica DMLB, Germany) at the excitation wavelength of 515-560 nm.

Results and discussion

Synthesis and X-ray crystal structure of 1

Receptor **1** was obtained by the coupling reaction of 8-hydroxyjulolidine-9-carboxaldehyde and benzhydrazide with 51% yield in ethanol (Scheme 1), and characterized by ^{1}H NMR and ^{13}C NMR, elemental analysis, ESI-mass spectrometry analysis, and X-ray crystallography. Crystals of **1** were obtained by slow evaporation in methanol and its structure is shown Fig. 1.



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

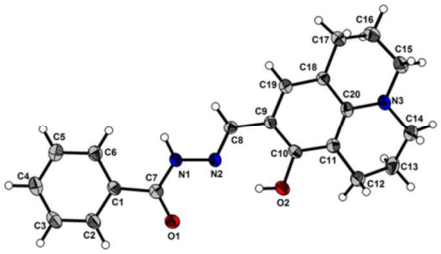
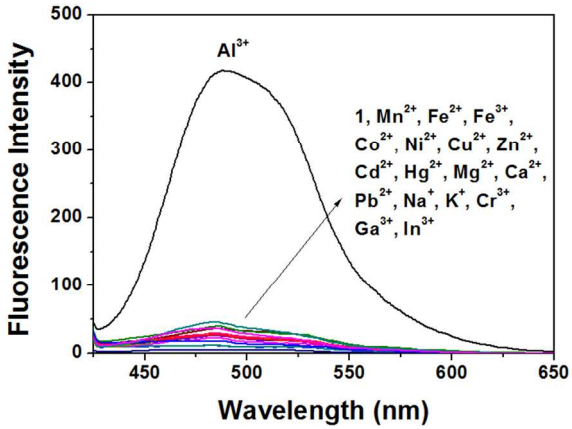


Fig. 1 Crystal structure of receptor **1**. Displacement ellipsoids are shown at the 50% probability level.

Fluorescence and absorption studies of 1 toward different metal cations

The selectivity of receptor **1** toward various metal cations, viz., Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Cr^{3+}, Hg^{2+}, Pb^{2+}, Ga^{3+}, In^{3+}, Pb^{2+} and Fe^{3+}, were primarily studied by fluorescence in bis-tris buffer/methanol (999/1,v/v).

(a)



(b)

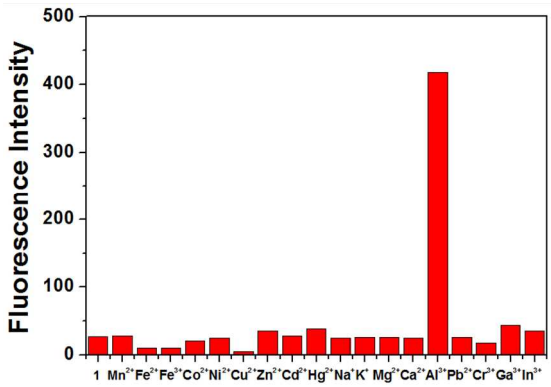
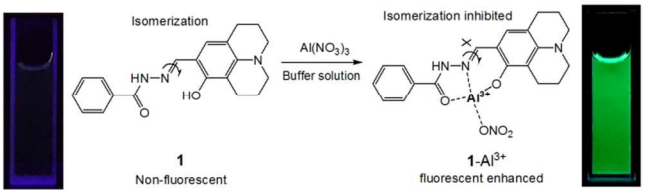


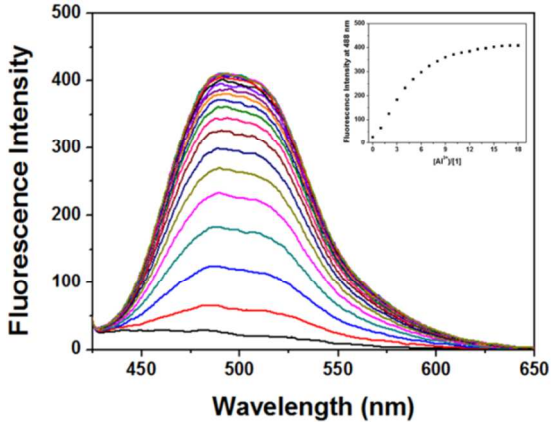
Fig. 2 (a) Fluorescence spectra of **1** (10 μM) before and after addition of various metal ions (200 μM) of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Al^{3+}, Pb^{2+} Cr^{3+}, Ga^{3+}, In^{3+} and Fe^{2+} in bis-tris buffer/methanol (999/1, v/v). (b) Bar graph shows the relative emission intensity of **1** at 483 nm upon treatment.



Scheme 2 Fluorescent enhancement mechanism of **1**-Al^{3+} complex.

As shown in Fig. 2a, receptor **1** exhibits a little emission with a low fluorescence quantum yield (Φ = 0.035) upon excitation at 410 nm. Upon the addition of 20 equiv of the afore-mentioned metal ions into the solution of **1**, only Al^{3+} caused a remarkable enhancement of fluorescence intensity with a high quantum yield (Φ = 0.502).). This fluorescence enhancement could be explained by an excited state intramolecular proton transfer (ESIPT) mechanism, C=N isomerization, and chelation enhanced fluorescence (CHEF) (Scheme 2). When **1** exists as an unbound form, the excited state intramolecular proton transfer[21] and C=N isomerization of the imine double bond in receptor **1** are responsible for nonradiative deactivation, showing a very low fluorescence intensity.[22] By contrast, upon addition of Al^{3+} to **1**, a stable chelation of **1** with Al^{3+} prevents both the C=N isomerization and ESIPT in **1**, resulting in a strong fluorescence intensity. In conjunction, stable chelate complexation of Al^{3+} with **1** possibly induce rigidity in the resulting complex, thereby, generating efficient chelation enhanced fluorescence.[23] The selectivity of receptor **1** for Al^{3+} has been plotted as a bar graph in Fig. 2b. On the other hand, Cr^{3+} and Fe^{3+}, considered as a strong Lewis acid, did not show any fluorescence enhancements. This might be due to their paramagnetic properties which promote dissipation of the excited state energy in a non-radiative process as a result of spin-orbital coupling.[24]

Fig. 3 Fluorescence spectra of **1** (10 μM, λex = 410 nm) after addition of



increasing amounts of Al^{3+} (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 and 20 equiv) in bis-tris buffer/methanol (999/1, v/v) at room temperature. Inset: Intensity at 488 nm versus the number of equiv of Al^{3+} added.

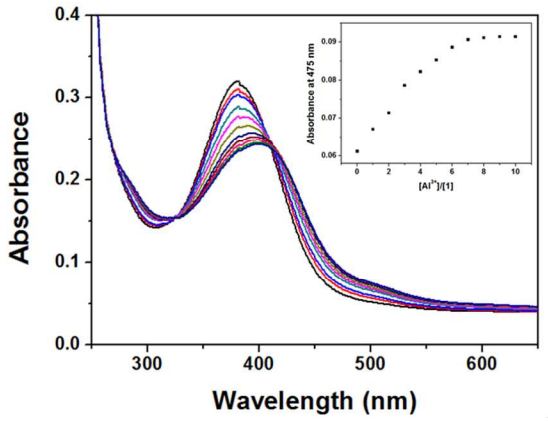


Fig. 4 Absorption spectra changes of **1** (10 μM) after addition of the gradual amounts of Al^{3+} (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 equiv) in bis-tris buffer/methanol (999/1, v/v) at room temperature. Inset: Absorption at 475 nm versus the number of equiv of Al^{3+} added.

A quantitative investigation of the binding affinity of **1** with Al^{3+} was performed by a fluorescence titration (Fig. 3). The fluorescence intensity increased up to 19 equiv of Al^{3+} and, no further change was observed. A UV-visible spectrometric titration of **1** with Al^{3+} solution revealed that the absorption band at 380 nm decreased and two new bands at 290 nm and 450 nm emerged and increased gradually to maxima at 19 equiv of Al^{3+} (Fig. 4). In addition, an isosbestic point was observed at 326 nm, indicating that only one product was generated from **1** upon binding to Al^{3+}.

The Job plot analysis showed a 1:1 stoichiometry for the **1**-Al^{3+} complex (Fig. S1), which was further confirmed by a positive-ion ESI-mass spectrometry (Fig.5). The mass spectrum showed a peak at m/z 423.60 that corresponds to the complex, $[\mathbf{1}+Al+NO_3]^+$, and demonstrates a 1:1 binding of the Al^{3+} to **1**.

Based on the Job plot, ESI-mass spectrometry analysis, and the crystal structures reported in the literatures,[25] we propose the structure of a 1:1 complex of 1 and Al^{3+} as shown in Scheme 2.

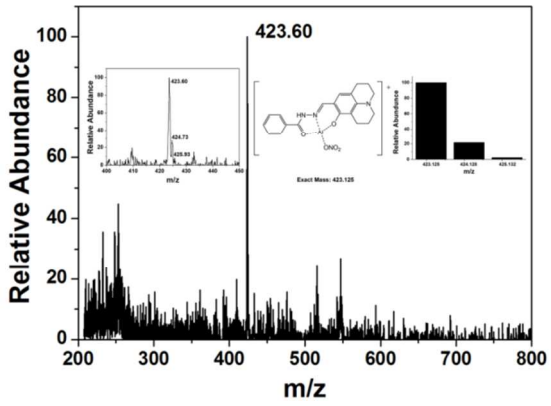


Fig. 5 Positive-ion electrospray ionization mass spectrum of **1** upon addition of 19 equiv of Al^{3+} in methanol.

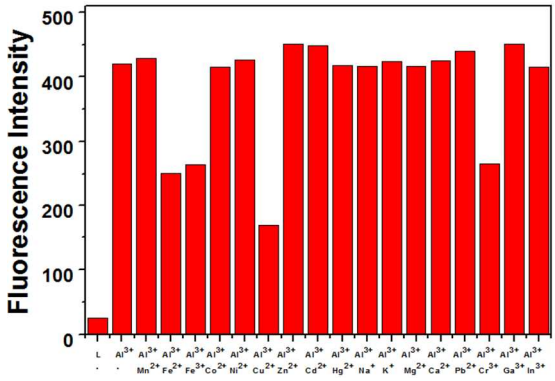


Fig. 6 Relative fluorescence of **1** and its complexation with Al^{3+} in the presence of various metal ions. Response of **1** was included as controls. **1** alone, **1**+Al^{3+}, **1**+Al^{3+}+Mn^{2+}, **1**+Al^{3+}+Fe^{2+}, etc. (Left to right) Conditions: **1**, 10 μM; Al^{3+}, 19 equiv; other metal ions, 19 equiv (λ_{ex} = 410 nm).

The binding constant K_a of **1** with Al^{3+} has been determined as 1.8 x 10^3 M^{-1} on the basis of Li analysis (Fig. S2).[25a,26] This value is within those (10^3~10^7) previously reported for Al^{3+}-binding chemosensors.[27] The detection limit for **1**- Al^{3+} complex was determined to be 0.193 μM on basis of 3σ/K (Fig. S4).[28] Importantly, the detection limit of **1** is much lower than the WHO limit (*vide supra*),[3] and suggests that **1** could be an effective sensor for the detection of aluminum in the drinking water.

To further check the practical applicability of receptor **1** as an Al^{3+}-selective fluorescence receptor, we carried out a competitive experiment with different metal ions in an aqueous solution (Fig. 6). It was found that most of the metal ions did not interfere with the detection of Al^{3+} by **1**. However, Fe^{2+}, Fe^{3+}, Cu^{2+} and Cr^{3+} quenched about 39, 37, 58 and 38% of the fluorescence obtained with Al^{3+} alone, respectively. Nevertheless, **1** still had sufficient "turn-on" ratios for the detection of Al^{3+} in the presence of Fe^{2+}, Fe^{3+}, Cu^{2+} and Cr^{3+}. These results indicate that **1** could be a good sensor for Al^{3+} over competing metal ions.

For biological applications, the pH dependence of the **1**-Al^{3+} complex was examined. Over the pH range tested, the fluorescence intensity of **1**-Al^{3+} displayed strong pH dependence (Fig. 7). An intense and stable fluorescence of **1**-Al^{3+} found in the pH range of 4.0-10.0 warrants its application under physiological conditions, without any change in detection results.

Based on the pH dependence experiment, further experiments were conducted to test whether intracellular Al^{3+} could be monitored by fluorimetry. Adult human dermal fibroblasts were first incubated with various concentrations of Al^{3+} (0, 10, 20, 40, 70 90 and 100 μM) for 4 h and then exposed to **1** (20 μM) for 40 min before imaging, so that **1** could permeate easily through the living cells without any harm. The

fibroblasts that were cultured with both Al^{3+} and **1** exhibited fluorescence (Fig. 8), whereas the cells cultured without Al^{3+} or

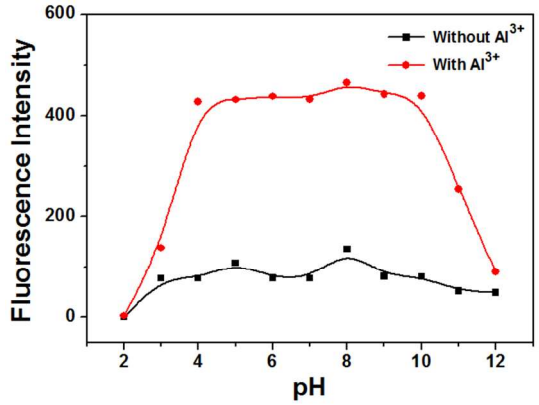


Fig. 7 Fluorescence intensity of **1**-Al^{3+} (**1**, 10 μM) after addition of 19 equiv of Al^{3+} at various range of pH in bis-tris buffer/methanol (999/1, v/v) at room temperature. Inset: Intensity at 483 nm.

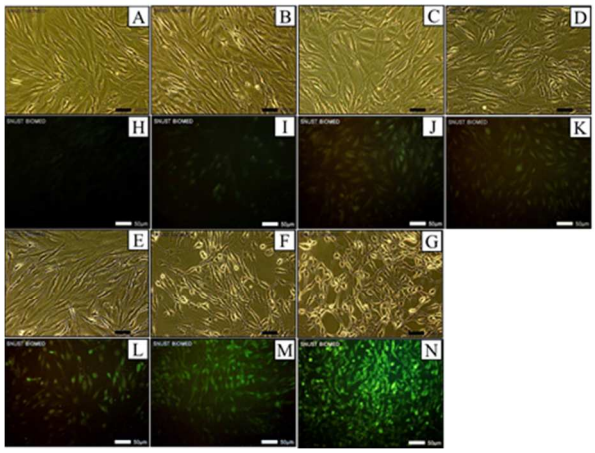


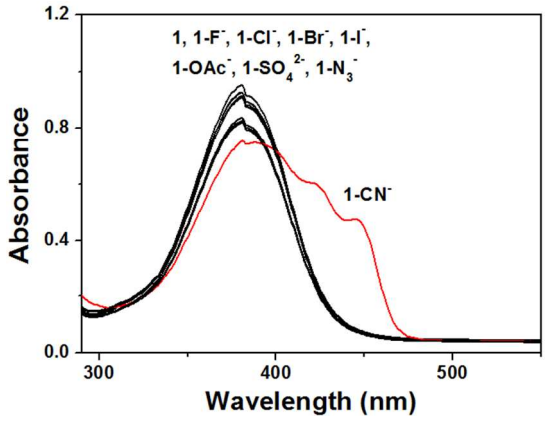
Fig. 8 Fluorescence images of fibroblasts cultured with Al^{3+} and **1**. Cells were exposed to 0 (A and H), 10 (B and I), 20 (C and J), 40 (D and K), 70 (E and L), 90 (F and M) and 100 μM (G and N) $Al(NO_3)_3$ for four hours and then later with **1** (20 μM) for 30 min. The top images (A–G) were observed with the light microscope and the bottom images were taken with a fluorescence microscope. The scale bar is 50 μm.

1 did not exhibit respondence. The intensity and region of the fluorescence within the cell containing **1** gradually increased with an increase in the Al^{3+} concentration from 10 to 100 μM. In addition, the fluorescence intensity of the cells persisted even after 5 h from exposure to **1** at 20 μM. These results show that the new receptor **1** is efficient to image Al^{3+} in cells, and could be useful in the determination of the exposure level of cells to Al^{3+}.

Colorimetric and spectral response of 1 toward CN^-

Receptor **1** was treated with a variety of anions to investigate the selectivity in bis-tris buffer/methanol mixtures (7/3, v/v). As shown in Fig. 9, the addition of CN^- to **1** caused a significant bathochromic shift in absorption spectra (Fig. 9a) and showed a color change from colorless to yellow instantly (Fig. 9b).

(a)



(b)

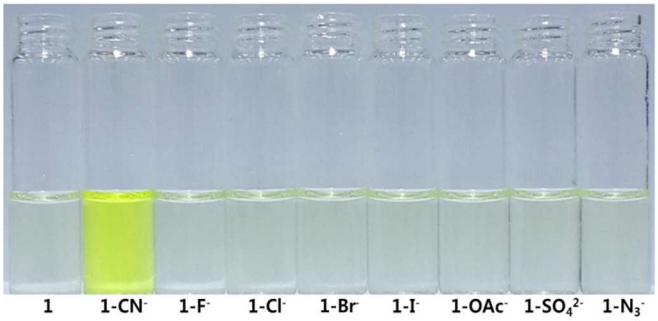


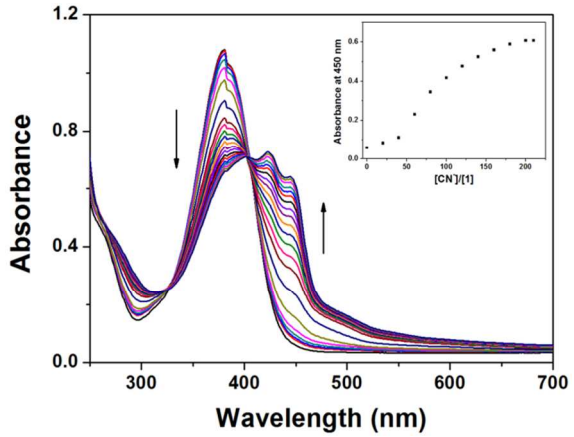
Fig. 9 (a) Absorption spectra changes of **1** (30 μM) in the presence of 200 equiv of different anions (b) The color changes of **1** (30 μM) upon addition of various anions (200 equiv) in bis-tris buffer/methanol (7/3, v/v).

However, other species such as F^-, Cl^-, Br^-, I^-, OAc^-, SO_4^{2-} and N_3^- demonstrated almost no change in the UV-visible spectra under identical conditions.

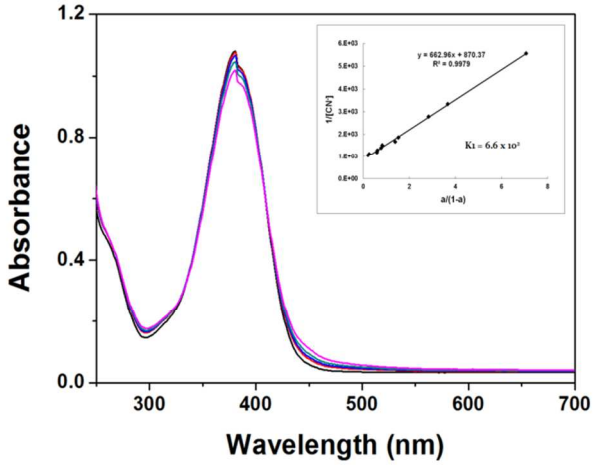
The binding properties of **1** with CN^- were further studied by UV-visible titration experiments (Fig. 10). Once one looks carefully into the UV-visible titration and inset in Fig. 10a, there is the two-step change of the absorption bands. The first step up to 40 equiv of CN^- shows that the absorption band at 478 nm gradually decreased and two new band at 350 nm and 400 nm appeared with two clear isosbestic points at 337 and 408 nm (Fig. 10b). The second step up to 200 equiv of CN^- shows that the absorption peak at 370 nm decreased obviously, whereas two new prominent bands at 290 nm and 450 nm was developed with well-defined isosbestic points at 324 and 403 nm (Fig. 10c). Based on this two-step UV-vis process, we propose that the first and second steps are the deprotonation of phenolic OH and NH of amide, respectively. Moreover, the bathochromic shift of the absorption bands led us to propose the transition of intramolecular charge transfer (ICT) band through the deprotonation of the chemosensor **1** by the CN^-, based on

Bhattacharya's proposal.[29,30] To identify the ICT property of **1**, we have checked the change of its absorption spectra in both polar and non-polar solvents such as bis-tris buffer, dimethylsu-

(a)



(b)



(c)

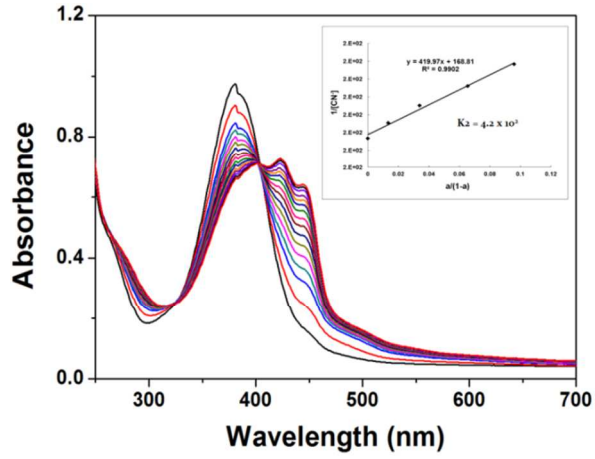


Fig. 10 (a) Absorption spectra changes of **1** (30 μM) after addition of increasing amounts of CN^- (10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190 and 200 equiv) in 10 mM bis-tris buffer/methanol (7/3, v/v) at room temperature. Inset: Absorption at 450 nm versus the number of equiv of CN^- added. (b) Absorption spectra changes of **1** in the range of 0-40 equiv of CN^- in Fig. 10(a). (c) Absorption spectra changes of **1** in the range of 50-200 equiv of CN^- in Fig. 10(a).

Table 2. Absorption properties of **1** in various solvents.

Solvent	λ_{abs} [nm] (log ε)
Buffer [a]	386 (3.93)
DMSO	384 (4.18)
MeOH	382 (4.10)
Toluene	378 (4.12)

[a] 10mM bis-tris, pH 7.0.

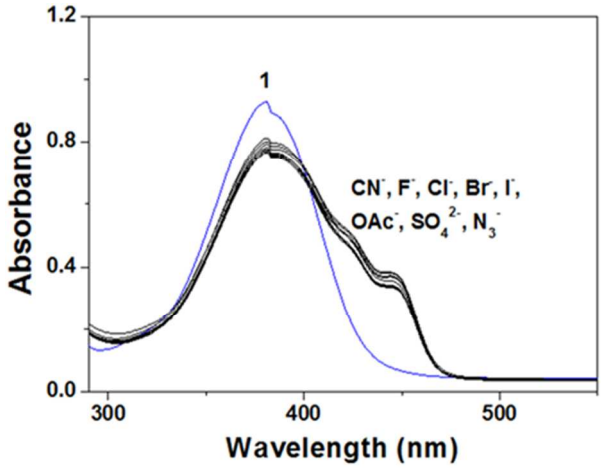
-lfoxide, methanol, and toluene, because it has been reported that the solvent dipole can relax the ICT excited by polar solvents.[31,] As shown in Fig. S4 and summarized in Table 2, the absorption spectra of **1** featured a marginal red-shift of absorption maxima ($\Delta\lambda_{abs}$=8 nm), indicating an apparent solvent dependence of the absorption band. Therefore, this solvatochromic behavior demonstrates the occurrence of ICT transition in receptor **1**.[14,31] In order to confirm whether the color change originated from the transition of ICT through a deprotonation mechanism, the interaction between **1** and OH^- was conducted. UV-visible spectral change of **1** upon addition of OH^- was almost identical to that of **1** upon addition of CN^-, demonstrating the deprotonation mechanism between **1** and CN^- (Fig. S5). Based on the UV-vis titrations, the binding constant of each step of receptor **1** and CN^- was determined using Li's equition. As shown in the insets of Fig. 10b and Fig. 10c, K_1 and K_2 were determined to be 6.6 x 10^2 (0~40 equiv) and 4.2 x 10^2 (50~200 equiv), respectively.

The preferential selectivity of **1** as a colorimetric chemosensor for the detection of CN^- was studied in the presence of various competing anions. For competition tests, receptor **1** was treated with 200 equiv of CN^- in the presence of 200 equiv of other anions. No interference was observed in the detection of CN^- in the presence of other anions (Fig. 11). This result suggests that **1** could be an excellent sensor for selectively detecting CN^- in the presence of the competing anions.

To further elucidate the binding interaction of receptor **1** with CN^-, ^{1}H NMR titration experiments were carried out in DMSO-d_6 (Fig. 12). Upon addition of 2 equiv of the CN^- to the receptor **1**, the proton signals of -OH and -NH at 11.85 ppm and 11.69 ppm disappeared completely. These results indicate that the cyanide participates in the deprotonation of the -OH and -NH protons. The aromatic protons, 3, 4, 5 and 9 shifted to upfield, which suggests that the negative charges developed from deprotonation of **1** by CN^- are delocalized through the whole receptor molecule.[11] To check the influence of water on

binding property, ^{1}H NMR titration experiments of **1** with CN^- were also carried out in a mixture of DMSO-d_6/ D_2O (9:1, v/v) (Fig. S6). Almost identical results were observed, indicating that water did not affect the binding interaction of receptor **1** with CN^-.

(a)



(b)

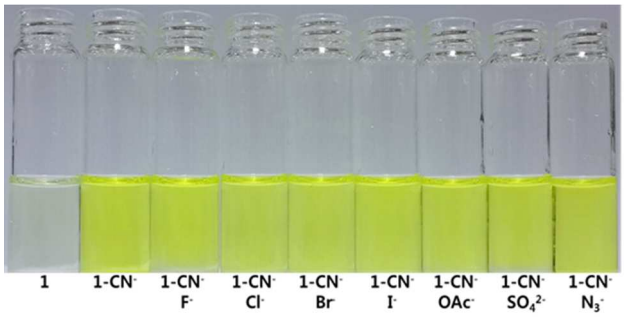


Fig. 11 (a) Absorption spectra of **1** and its complexation with CN^- in the presence of various anions. Response of **1** was included as controls. **1** alone, **1**-CN^-, **1**-F^-, **1**-Cl^-, **1**-Br^-, **1**-I^-, **1**-OAc^-, **1**-SO_4^{2-}, **1**-N_3^- (b) The color changes of **1** and its complexation with CN^- in the presence of various anions in bis-tris buffer/methanol (7/3, v/v). Conditions: **1**, 30 μM; CN^-, 200 equiv; other metal ions, 200 equiv.

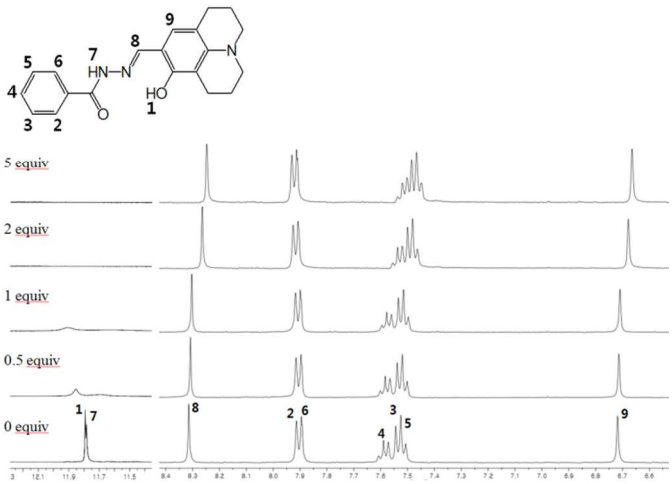


Fig. 12 ^{1}H NMR titration of **1** with CN^- in DMSO-d_6.

Conclusion

We have successfully designed and synthesized a simple, fluorescent and colorimetric chemosensor **1**, capable of recognizing both cations and anions in aqueous solution. **1** exhibited an excellent selectivity and sensitivity towards Al^{3+} by fluorescent intensity enhancement and CN^- by inducing a rapid color change from colorless to yellow. The detection limit of **1** for Al^{3+} (0.193 μM) was much lower than the guideline of the WHO (7.41 μM). Moreover, **1** could operate at a wide range of pH and can be successfully applied to living cell for detecting Al^{3+}. On the basis of the results, we believe that receptor **1** will offer an important guidance to the development of single receptors for recognizing both cations and anions both *in vivo* and *in vitro*.

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Supplementary Information

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

Notes and references

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†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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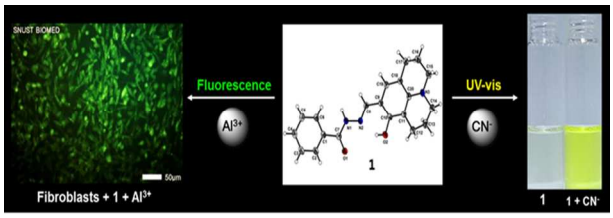
Graphical Abstract TOC



A new multifunctional Schiff-base receptor **1** which exhibits an excellent cell-permeable fluorescence for Al^{3+} and color change for CN^- in aqueous media was prepared