

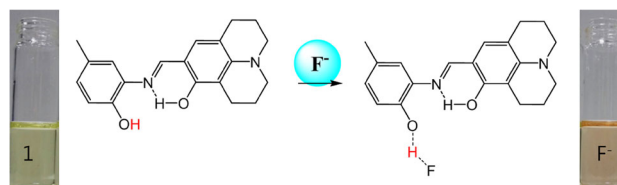
# A colorimetric F<sup>-</sup> chemosensor with high selectivity: experimental and theoretical studies

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**Abstract** A new and simple colorimetric receptor **1**, based on the combination of 2-amino-4-methylphenol moiety and julolidine moiety, has been designed and synthesized. **1** showed a selective colorimetric sensing ability toward F<sup>-</sup> ion by changing color from yellow to orange, and could be utilized to monitor F<sup>-</sup> without any inhibition by competitive anions such as CH<sub>3</sub>COO<sup>-</sup> and CN<sup>-</sup>. Based on Job plot, ESI-mass spectrometry and the <sup>1</sup>H NMR titration, the binding mode of **1** for F<sup>-</sup> was proposed to be 1:1. Moreover, the sensing mechanism for F<sup>-</sup> was theoretically supported by DFT and TD-DFT calculations.

## Graphical Abstract



**Keywords** Colorimetric chemosensor · Fluoride · Deprotonation · Theoretical calculations

## Introduction

Recognition and detection of various anions have been consistently paid much attention, due to their important roles in chemical sciences, biological, medical and environmental [1–3]. Among the various anions, especially, fluoride is most concerned, because it is very useful in a wide range of biological, medical, chemical processes, and etc. [4–7]. Also, intake of suitable amount of fluoride can prevent dental disease and osteoporosis [8]. Despite the advantages of fluoride, however, chronic intake of fluoride can cause accumulation in our body [9]. Such hyper-ingestion of fluoride can bring many problems due to its toxicity, such as gastric and kidney disorders, dental and skeletal fluorosis, urolithiasis, or even death [10–15]. These various effects of fluoride drove many scientists to develop chemosensors for fluoride recognition in the specific concentration range [16–18]. Nevertheless, many chemosensors are still unable to distinguish fluoride effectively from anions such as CH<sub>3</sub>COO<sup>-</sup> and CN<sup>-</sup> because they have similar basicity to F<sup>-</sup> and easily form hydrogen bonds [19].

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Therefore, it is still an important challenge to develop a chemosensor for highly selective detection of fluoride.

Several methods, such as inductively coupled-plasma atomic emission spectrometry [20], atomic absorption spectroscopy [21], electrochemical methods [22] and so on, have been developed to detect anions. Among the methods, the most attractive one may be colorimetric sensors, which can detect targets via naked-eye of the color change. In addition, colorimetric materials have advantages such as low cost, rapid response rate, easy detection, no requirement of a specific equipment and high selectivity [23–29].

Schiff bases have been utilized to develop novel chemosensors with selectivity and sensitivity toward anions. In particular, Schiff bases containing phenolic groups are known as one of strategies of designing sensor for anions because of the ability of the phenolic-OH group to interact with anions through hydrogen bonding [30, 31]. In addition, the julolidine moiety is one of the well-known chromophores [32, 33]. Moreover, we expected that the combination of the methylphenol moiety having the electron-donor methyl group and the julolidine moiety may show interesting electronic and sensing properties toward anions.

Herein, we report a highly selective chemosensor **1** for  $F^-$ , which was synthesized in one step by the condensation reaction of 2-amino-4-methylphenol with 8-hydroxyjulolidine-9-carboxaldehyde (Scheme 1). Chemosensor **1** can selectively detect  $F^-$  by color change from yellow to orange via the ‘naked-eye’. Also, it was able to distinguish  $F^-$  from competitive anions such as  $CH_3COO^-$  and  $CN^-$ . Moreover, a deprotonation mechanism for sensing of  $F^-$  was proposed, which was supported by the DFT/TD-DFT calculation method.

## Results and discussion

The colorimetric chemosensor **1** for fluoride was synthesized by condensing 2-amino-4-methylphenol with 8-hydroxyjulolidine-9-carboxaldehyde (Scheme 1) and characterized by  $^1H$  NMR and  $^{13}C$  NMR, ESI-mass spectrometry, and elemental analysis. The binding abilities of **1** were investigated by UV–vis,  $^1H$  NMR spectroscopy and the DFT/TD-DFT studies.

### UV–vis study of **1**- $F^-$

The sensing abilities of **1** were observed by “naked-eye” and confirmed by UV–vis spectroscopy. The absorption response of **1** toward the tetraethylammonium (TEA) salts ( $F^-$ ,  $CN^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ) or tetrabutylammonium (TBA) salts ( $AcO^-$ ,  $H_2PO_4^-$ ,  $BzO^-$ ,  $N_3^-$ ,  $SCN^-$ ) was carried out in a mixture of bis–tris buffer/DMSO (3:97, v/v, 10 mM

bis–tris, pH 7.0) (Fig. 1a). Upon the addition of each anion to **1**, only  $F^-$  induced a clear spectral change while other anions showed either no or a little change in the absorption spectra relative to the spectra of **1**. In addition, only  $F^-$  showed a color change from yellow to orange by the ‘naked-eye’ (Fig. 1b). By contrast, other anions did not cause any color change of solution. This observation suggested that the receptor **1** can serve as a potential candidate of a “naked-eye” chemosensor for  $F^-$ .

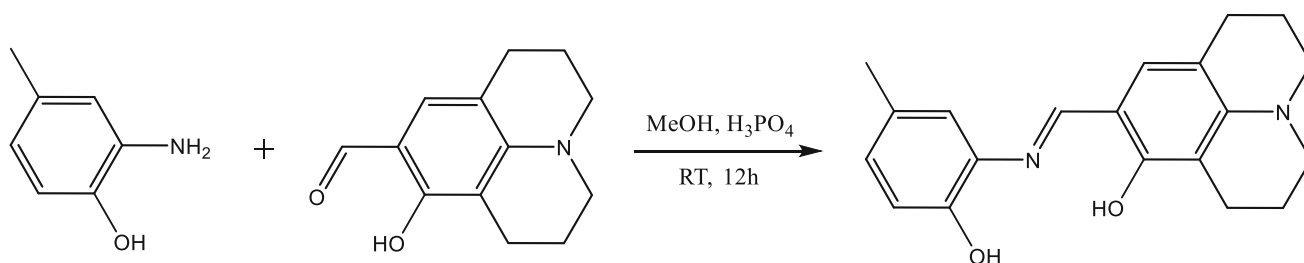
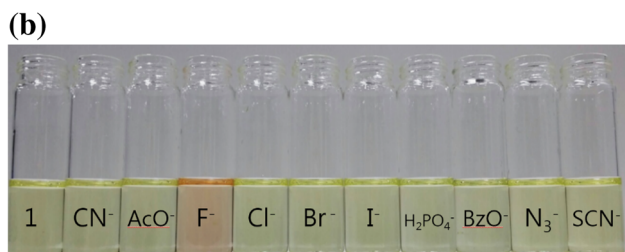
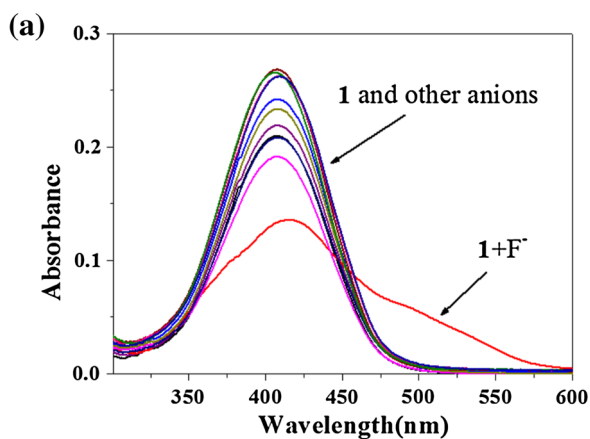
The binding properties of **1** with  $F^-$  were studied by UV–vis titration experiments (Fig. 2). Upon the gradual addition of  $F^-$  into a solution of **1**, a new band at 500 nm appeared and the absorption band at 403 nm gradually decreased, resulting in a color change from yellow to orange. Simultaneously, two clear isosbestic points were observed at 358 and 442 nm, indicating the formation of the only one species between **1** and  $F^-$ . This bathochromic shift indicates that the proton of phenol in 4-methylphenol might be deprotonated by  $F^-$ , which leads to the formation of phenolate. The phenolate donates the electron density into the  $\pi$ -system, thus resulting in formation of extended  $\pi$ -conjugated system [34, 35]. On the other hand, the increase of an amount of the bis–tris buffer rendered **1** lose the sensing property toward  $F^-$ . This might be due to the inhibition of deprotonation of **1** by water.

The binding mode between **1** and  $F^-$  was identified to be a 1:1 stoichiometry through Job plot analysis (Fig. 3), which was also confirmed by ESI-mass spectrometry analysis (Fig. 4). The positive ion mass spectrum of ESI-mass showed that a peak at  $m/z = 581.20$  was assignable to  $[1-H^+ + 2TEA]^+$  [calcd,  $m/z$ : 581.48], which supports the deprotonation mechanism of **1** by fluoride. From the UV–vis titration data, the association constant for **1** with  $F^-$  was determined as  $6.15 \times 10^2 M^{-1}$  on the basis of Benesi-Hildebrand equation (Fig. S1) [36]. The detection limit ( $3\sigma/k$ ) of receptor **1** for the analysis of  $F^-$  ions was calculated to be 31.4  $\mu M$  (Fig. S2) [37].

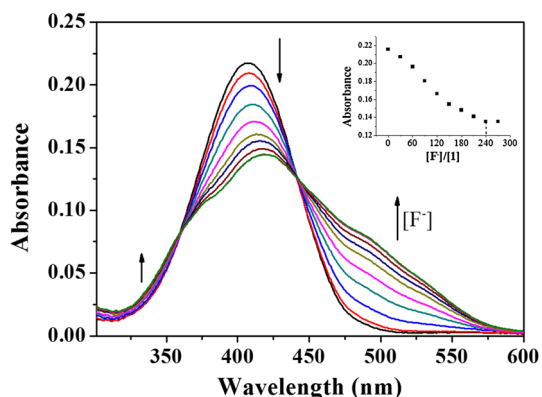
An important feature to develop a practical sensor is its high selectivity toward other competitive species. To confirm the properties of **1** as the practical sensor, the selectivity of **1** was studied in the presence of various competing anions. The receptor **1** was treated with 240 equiv of  $F^-$  in the presence of 240 equiv of other anions (Fig. 5). There was no interference for the detection of  $F^-$  toward other anions. This observation suggested that **1** could be an excellent sensor for detecting  $F^-$  in the presence of all the competing anions.

### $^1H$ NMR study of **1**- $F^-$

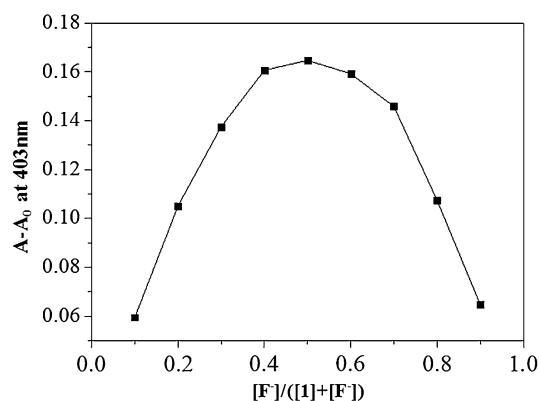
$^1H$  NMR titration experiments were performed to understand the interaction between **1** and fluoride at room temperature (Fig. 6). In absence of fluoride, the hydroxyl

Scheme 1 Synthetic procedure of **1**

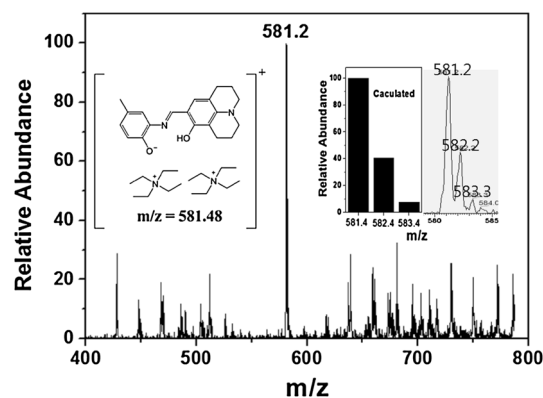
**Fig. 1** **a** Absorption spectral change of **1** (10  $\mu\text{M}$ ) in the presence of 240 equiv of various anions in a mixture of DMSO/bis-tris buffer (97:3, v/v, 10 mM bis-tris, pH 7.0). **b** Color change of receptor **1** (10  $\mu\text{M}$ ) in the presence of 240 equiv of various anions in a mixture of DMSO/bis-tris buffer (97:3, v/v, 10 mM bis-tris, pH 7.0)



**Fig. 2** UV-vis spectral changes of **1** (10  $\mu\text{M}$ ) upon addition of  $\text{F}^-$  (up to 270 equiv)

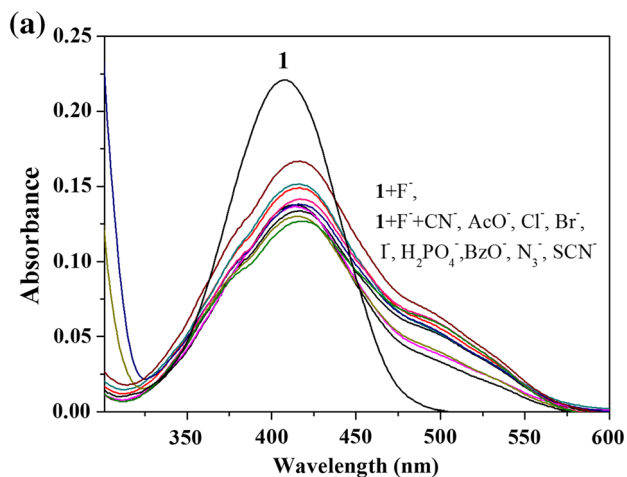


**Fig. 3** Job plot of receptor **1** and  $\text{F}^-$ . The total concentration of  $\text{F}^-$  ions with receptor **1** was  $3.0 \times 10^{-5}$  M



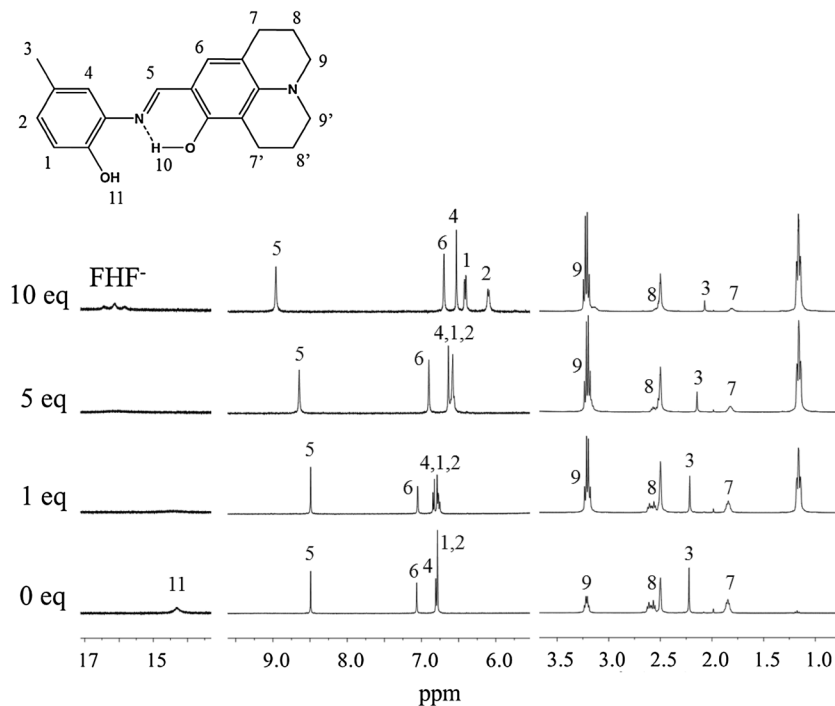
**Fig. 4** Positive-ion electrospray ionization mass spectrum of **1** (10  $\mu\text{M}$ ) upon addition of  $\text{F}^-$  (1 equiv)

proton ( $\text{H}_{10}$ ) of the julolidine moiety was not observed maybe due to hydrogen bonding, while the hydroxyl proton ( $\text{H}_{11}$ ) of methylphenol moiety appeared as a singlet at 14.37 ppm, and the aromatic protons ( $\text{H}_1$ ,  $\text{H}_2$ ,  $\text{H}_4$ , and  $\text{H}_6$ ) were resonated in the range of 7.09–6.79 ppm. Upon addition of  $\text{F}^-$  (1 equiv), the  $\text{H}_{11}$  at 14.37 ppm disappeared immediately. The further addition of  $\text{F}^-$  (1–10 equiv) rendered all aromatic protons to shift upfield. In contrast,  $\text{H}_5$  moved to down-field, suggesting that the electron density of the imine moiety decreased due to the hydrogen



**Fig. 5** **a** Competitive selectivity of **1** (10  $\mu\text{M}$ ) toward  $\text{F}^-$  (240 equiv) in the presence of other anions (240 equiv). **b** The color changes of **1** (10  $\mu\text{M}$ ) in the presence of  $\text{F}^-$  (240 equiv) and other anions (240 equiv)

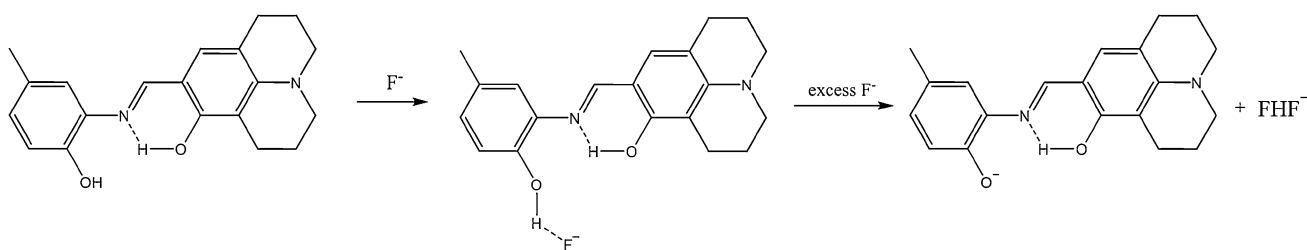
**Fig. 6**  $^1\text{H}$  NMR titration of **1** (2 mM) with  $\text{F}^-$  (0, 2, 10 and 20 mM)



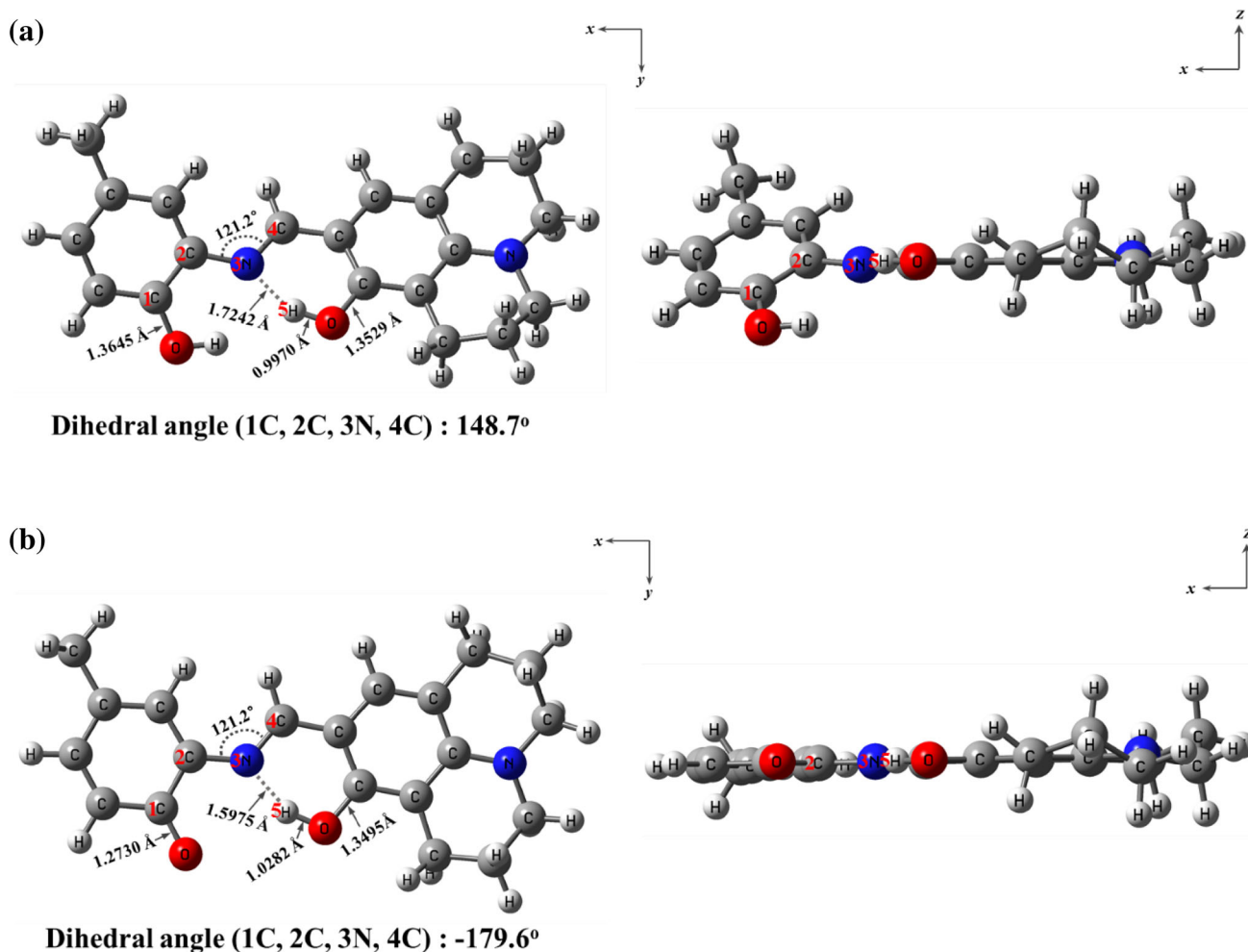
bonding between N atom and -OH group. Then, a new peak at 16 ppm appeared, indicating the formation of  $[\text{FHF}^-]$  species [38]. These results indicate that the negative charge originated from deprotonation of **1** by  $\text{F}^-$  might be delocalized through the receptor molecule [39]. Therefore, the  $^1\text{H}$  NMR titration would support the proposal that the binding mechanism of **1** for fluoride might occur by the deprotonation pathway, resulting in color change [40]. Based on Job plot, ESI-mass spectrometry and  $^1\text{H}$  NMR titration, we proposed the mechanism of  $\text{1-F}^-$  binding pathway as shown in Scheme 2.

### Density function theory (DFT) studies

To understand the sensing mechanisms of **1** with  $\text{F}^-$ , theoretical calculations were performed in parallel to the experimental studies. As it was proposed that the hydroxyl proton of 4-methylphenol group in **1** was deprotonated by  $\text{F}^-$ , based on ESI-mass spectrometry analysis and  $^1\text{H}$  NMR titrations,  $\text{1}^-$  species was optimized by DFT/B3LYP/6-31G\*\*/DMSO level. The significant structural properties of the energy-minimized structures for **1** and  $\text{1}^-$  were shown in Fig. 7. The energy-minimized structure of **1** indicated a skew structure between 4-methylphenol and 8-hydroxy-9-iminomethyljulolidine [dihedral angle (1C, 2C, 3N, 4C) =  $148.7^\circ$ ], and the hydrogen bond was observed between 3N and 5H (Fig. 7a).  $\text{1}^-$  showed a planar



**Scheme 2** Proposed sensing mechanism of fluoride by **1**



**Fig. 7** The energy-minimized structures of **a 1** and **b 1<sup>-</sup>**

structure [dihedral angle (1C, 2C, 3N, 4C) =  $-179.6^\circ$ ], and the hydrogen bond was also observed between 3N and 5H (Fig. 7b).

To further gain an insight into colorimetric sensing mechanism of **1** toward  $F^-$ , time-dependent density functional theory (TD-DFT) calculations were carried out at the optimized geometries (Figs. S3 and S4). In order to clearly understand the absorption energies, the UV–vis spectra of **1**

and  $1^-$  were compared to their TD-DFT calculations (B3LYP/6-31G\*\*/DMSO) [Figs. S(3a) and S(4a)]. In case of **1**, the main molecular orbital (MO) contribution of the first lowest excited state was determined for HOMO  $\rightarrow$  LUMO transition with oscillator strength of 1.1019 [390.34 nm, Fig. S(3b)]. The main MO contribution of the first excited state of  $1^-$  was determined for HOMO  $\rightarrow$  LUMO with oscillator strength of 0.754 [483.86 nm,



**Fig. 8** Frontier molecular orbitals and their energies involved in the UV-vis absorption of **1** and **1<sup>-</sup>**

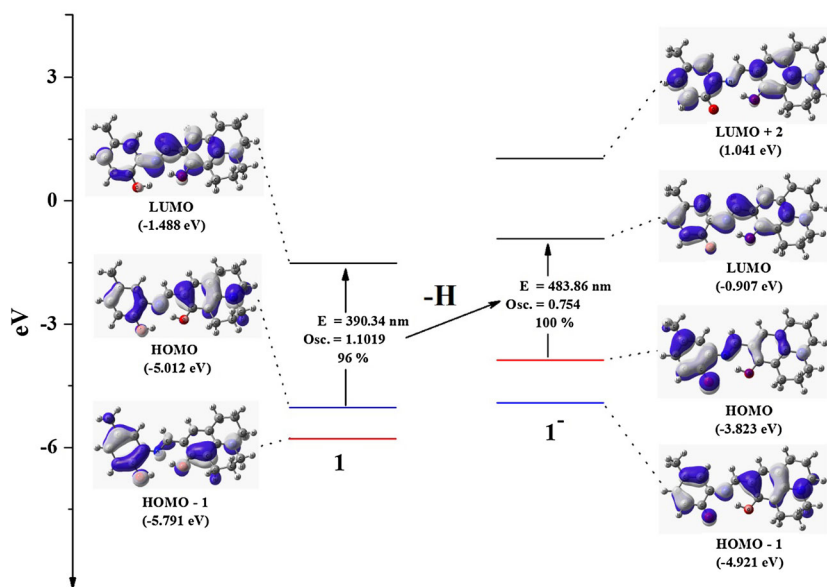


Fig. S(4b)]. As shown in Fig. 8, the deprotonation of 4-methylphenol group in **1** showed mainly that HOMO-1 ( $-5.791$  eV) of **1** destabilized to HOMO ( $-3.823$  eV) of **1<sup>-</sup>** by  $+1.968$  eV, whereas LUMO of **1** ( $-1.488$  eV) destabilized to LUMO ( $-0.907$  eV) of **1<sup>-</sup>** by  $+0.581$  eV. The difference of the destabilization energy induced the red shifted spectrum, resulting in the color change from yellow to orange.

## Conclusion

We have presented a simple imine-based naked-eye chemosensor **1** for the detection of  $F^-$ . The receptor **1** obviously showed selectivity toward  $F^-$  through color change (yellow to orange), which was explained by theoretical calculations. Based on the Job plot,  $^1H$  NMR titration and ESI-mass spectrometry analysis, we suggested that the receptor **1** interacted with  $F^-$  in a 1:1 stoichiometric manner. Moreover, the receptor **1** could distinguish  $F^-$  in the presence of other anions. Therefore, we believe that this type of easy-to-synthesized naked-eye chemosensor **1** could contribute to developing a new ‘fluoride sensor’.

## Experiment

### General information

Unless otherwise specified, all the solvents and reagents (analytical grade and spectroscopic grade) were obtained commercially and used without further purification.  $^1H$

NMR and  $^{13}C$  NMR measurements were performed on a Varian 400 and 100 MHz spectrometer and chemical shifts were recorded in ppm. Absorption spectra were recorded using a Perkin Elmer model Lambda 25 UV-Vis spectrometer at room temperature. Electrospray ionization mass spectra (ESI-mass) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQ<sup>TM</sup> Advantage MAX quadrupole ion trap instrument. The spray voltage was set at 4.2 kV, and the capillary temperature was set at 80 °C. 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 receptor **1**

To a solution of 2-amino-4-methylphenol (0.12 g, 1 mmol) in methanol (10 mL), 8-hydroxyjulolidine-9-carboxaldehyde (0.22 g, 1 mmol) was added, followed by addition of three drops of phosphoric acid into the reaction mixture. The reaction mixture was stirred for 3 h at room temperature, whereupon the red-brown powder was produced. The powder was collected by filtration, washed with ethyl acetate, and air-dried. The yield was 93 % and the melting point 150 °C.  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 14.33 (s, 1H), 8.49 (s, 1H), 7.07 (s, 1H), 6.79 (m, 3H), 3.21 (m, 4H), 2.57 (m, 4H), 2.23 (s, 3H), 1.85 (m, 4H);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ , ppm): 162.01, 157.56, 147.70, 147.14, 133.83, 129.83, 128.45, 126.43, 118.69, 116.18, 112.80, 108.59, 105.73, 49.66, 49.30, 27.00, 21.82, 20.85, 20.52, 20.29 ppm. ESI-MS  $m/z$  [**1**- $H^+$ ] $^-$ : calcd, 321.4;

found, 321.4. Anal. Calcd for  $C_{20}H_{22}N_2O_2$ : C, 74.51; H, 6.88; N, 8.69 %. Found: C, 74.85; H, 6.43; N, 8.92 %.

### UV–vis study of **1** with various anions

Receptor **1** (3.22 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 3  $\mu$ L of the receptor **1** (10 mM) was diluted with 2.997 mL DMSO/bis–tris buffer (97:3, v/v) to make the final concentration of 10  $\mu$ M. Stock solutions (100 mM) of tetraethylammonium salts ( $F^-$ ,  $Br^-$ ,  $Cl^-$ ,  $I^-$ , and  $CN^-$ ) or tetrabutylammonium salts ( $SCN^-$ ,  $BzO^-$ ,  $N_3^-$ ,  $AcO^-$  and  $H_2PO_4^-$ ) were separately prepared in DMSO. 75  $\mu$ L of the stock solution (100 mM) of each anion was transferred to 3 mL of receptor **1** solution (10  $\mu$ M) prepared above. After mixing them for a few seconds, UV–vis spectra of **1** were taken at room temperature.

### UV–vis titration of **1**

The receptor **1** (3.22 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 3  $\mu$ L of the receptor **1** (10 mM) was diluted to 2.997 mL of DMSO-buffer solution (97:3, v/v, 10 mM bis–tris, pH 7.0) to make the concentration of 10  $\mu$ M. Tetraethylammonium fluoride ((TEA)F, 26.1 mg, 0.1 mmol) was also dissolved in DMSO (1 mL) and 1.5–75  $\mu$ L of the  $F^-$  solution (100 mM) was transferred to the solution of **1** (10  $\mu$ M, 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** (3.22 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 0.09 mL of the solution was diluted to 29.91 mL of DMSO-buffer solution (97:3, v/v, 10 mM bis–tris, pH 7.0) to make the concentration of 30  $\mu$ M. 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. In the same way, (TEA)F (2.61 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 0.09 mL the (TEA)F solution was diluted to 29.91 mL of DMSO-buffer solution (97:3, v/v, 10 mM bis–tris, pH 7.0) to make the concentration of 30  $\mu$ M. 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 diluted **1** solution. Each vial had a total volume of 5 mL. After shaking them for a few seconds, UV–vis spectra were taken at room temperature.

### Competition with other anions

The receptor **1** (3.22 mg, 0.01 mmol) was dissolved in DMSO (1 mL). Tetraethylammonium salts ( $F^-$ ,  $Br^-$ ,  $Cl^-$ ,  $I^-$ , and  $CN^-$ ; 0.1 mmol) or tetrabutylammonium salts

( $SCN^-$ ,  $BzO^-$ ,  $N_3^-$ ,  $AcO^-$  and  $H_2PO_4^-$ ; 0.1 mmol) were separately dissolved in DMSO (1 mL). 75  $\mu$ L of each anion solution (100 mM) was diluted to 2.847 mL of DMSO-buffer solution (97:3, v/v, 10 mM bis–tris, pH 7.0). 75  $\mu$ L of the  $F^-$  solution (100 mM) was taken and added to the solutions prepared above. Then, 3  $\mu$ L of the **1** (10 mM) was taken and added to the mixed solutions. Each vial had a total volume of 3 mL. After shaking them for a few seconds, UV–vis spectra were taken at room temperature.

### $^1H$ NMR titration of **1** with $F^-$

Four NMR tubes of **1** (0.644 mg, 0.002 mmol) dissolved in DMSO- $d_6$  (0.7 mL) were prepared, and four different equiv (0, 1, 5 and 10 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  $^1H$  NMR spectra were taken.

### Theoretical calculation methods

All theoretical calculations were performed by DFT method with the hybrid exchange–correlation functional B3LYP [41, 42] applying the 6-31G\*\* [43, 44] basis set without any symmetry restrictions. The energy-minimized structure of **1** was obtained in various geometric forms. In case of **1**- $F^-$ , as the proton of the hydroxyl group in 4-methylphenol was deprotonated, **1** $^{1-}$  species was optimized by the same level of **1**. In vibrational frequency calculations, there was no imaginary frequency for the optimized geometries of **1** and **1** $^{1-}$ , suggesting that these geometries represented local minima. For all calculations, the solvent effect of DMSO was considered by using the Cossi and Barone's CPCM (conductor-like polarizable continuum model) [45, 46]. In order to investigate the transition energies for the optimized structures of **1** and **1** $^{1-}$ , we calculated the lowest 20 singlet–singlet transition using their ground state geometry ( $S_0$ ) with TD-DFT (B3LYP) method. The GaussSum 2.1 was used to calculate the contribution of molecular orbital in electronic transitions [47]. All the calculations were performed with Gaussian 03 suite [48].

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