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ORIGINAL ARTICLE

Furan and Julolidine-Based "Turn-on" Fluorescence Chemosensor for Detection of F⁻ in a Near-Perfect Aqueous Solution

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Abstract A new fluorescent sensor **1**, containing furan and julolidine moieties linked through a Schiff-base, has been synthesized. Distinct "turn-on" fluorescence enhancement of **1** was observed upon the addition of F⁻ in a near-perfect aqueous solution. The binding capabilities of **1** with F⁻ were studied by using fluorescent spectroscopic techniques, ESI-mass analysis and NMR titration measurements. The detection limit for the analysis of F⁻ was found to be 10.02 μM, which is below the WHO guideline (79 μM) for drinking water. Practically, the sensing ability of **1** for F⁻ was successfully applied in real water samples. The sensing mechanism for F⁻ was proposed to be the ICT mechanism via the hydrogen bonding, which was well explained by theoretical calculations.

Keywords Fluoride · Fluorometric · Furan · Julolidine · Theoretical calculations

Introduction

To the design and development of chemosensor for detecting target anions have been paid much attention, due to their important roles in a wide range of chemical, biological, medical and environmental processes [1–6]. Among various anions, the smallest anion F⁻ with a high charge density is of special attention due to its role in dental and osteoporosis treatments [7, 8]. Proper intake of fluoride helps to prevent tooth loss and demineralization of tooth enamel, but its high concentration or ingestion of even low concentration for a prolong period causes skeletal fluorosis, depression of thyroid activity, bone disorders and adverse effect on the immune system [9–13]. The World Health Organization (WHO) has set 79 μM as the maximum contaminant level of fluoride in drinking water [14]. Therefore, it is of importance to develop a chemosensor for highly sensitive detection of fluoride [15–22].

Several conventional methods such as inductively coupled-plasma atomic emission spectrometry, atomic absorption spectroscopy, and electrochemical methods, have been applied to detect various anions [23–25]. However, most of these methods require sophisticated equipment, tedious sample preparation procedures, and trained operators. In contrast, fluorometric methods are especially attractive because of their advantages, such as low cost, facile sample preparation, the simplicity and high sensitivity. Therefore, the fluorescent signaling methods have been widely applied in biology and environment [26–36].

Furan moieties have been widely used as a fluorescence signaling agent [37–39], and juloilidine is a well-known chromophore with a hydrophilic character and acts as an electron donor site [40, 41]. In addition, Schiff-bases have been widely used in development of chemosensors toward various anions. In particular, Schiff bases containing phenolic groups are known to be efficient sensors for anions, because the phenol group can interact with anions through hydrogen bonding [42–45]. Therefore, we expected that the chemosensor having the furan and julolidine moieties linked with Schiff-base would show a unique fluorescent property toward a specific anion.

Herein, we report a chemosensor **1** based on one-step condensation of julolidine and furan moieties connected via Schiff-base. Sensor **1** showed a turn-on fluorescence in the presence of

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F⁻ in a near-perfect aqueous solution. The sensing mechanism of **1** toward F⁻ was proposed to be the ICT mechanism via hydrogen bonding, which was well explained by theoretical calculations.
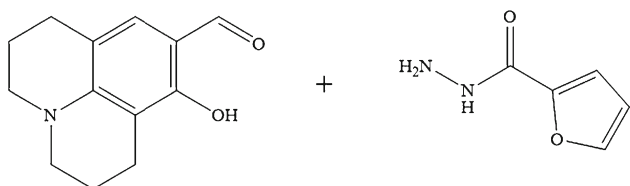
Experimental

Materials and Equipment

All the solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma-Aldrich and used as received. ^{1}H NMR and ^{13}C NMR measurements were performed on a Varian 400 MHz and 100 MHz spectrometer, and chemical shifts were recorded in ppm. Electrospray ionization mass spectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument. Absorption spectra were recorded at room temperature using a Perkin Elmer model Lambda 25 UV/Vis spectrometer. The emission spectra were recorded on a Perkin-Elmer LS45 fluorescence spectrometer. Elemental analysis for carbon, nitrogen and hydrogen was carried out by using a Vario micro cube elemental analyzer (ELEMENTAR) in laboratory center of Seoul National University of Science and Technology, Korea. FT-IR spectrum was collected on an Agilent Cary 670 FTIR spectrometer.

Synthesis of Sensor 1

Sensor **1** was prepared by the reaction of 8-hydroxyjulolidine-9-carboxaldehyde (0.22 μL, 1.0 mmol) and furan-2-carbohydrazide (0.13 g, 1.0 mmol) in ethanol. Two drops of HCl were added into the reaction solution, which was stirred for 2 days at room temperature. A yellow precipitate was filtered, washed several times with cold ethanol, and dried in vacuum. Yield: 0.29 g (89%). The ^{1}H NMR spectra were recorded in DMSO-d_6, and the descriptions of the signals include: s = singlet, d = doublet, t = triplet and m = multiplet (400 MHz, 25 °C): δ = 11.82 (s, 1H), 11.66 (s, 1H), 8.29 (s, 1H), 7.91 (d, 1H), 7.22 (d, 1H), 6.68 (d, 2H), 3.16 (m, 4H), 2.48 (m, 4H), 1.84 (m, 4H); ^{13}C NMR (100 MHz, CD$_3$CN, 25 °C): δ = 154.91, 153.72, 151.35, 145.75, 128.56, 115.23, 112.31, 106.07, 49.61, 26.82, 21.23. IR (KBr, ν cm^{-1}) = 3209 (m), 2938 (m), 2839 (m), 2361 (m), 2160 (m), 1627 (m), 1590 (s), 1507 (s), 1461 (m), 1349 (m), 1292 (s), 1174 (s), 1086 (m), 1013 (m), 968 (m), 844 (m), 744 (s), 662 (s). Anal. calcd for C$_{18}$H$_{19}$N$_3$O$_3$: C, 66.45; H, 5.89; N, 12.91%. Found: C, 66.27; H, 5.94; N, 12.83%.

Fluorescence Titration

A stock solution (5 mM) of sensor **1** was prepared in DMSO and 6 μL of the sensor **1** (5 mM) was diluted to 2.994 mL bis-tris buffer solution to make final concentration of 10 μM. Then, 3–72 μL of the stock solution of tetraethylammonium fluoride (TEAF, 100 mM) were added to **1** solution (10 μM). After mixing them for a few seconds, fluorescence spectra were taken at room temperature.

UV-vis Titration

A stock solution (5 mM) of sensor **1** was prepared in DMSO and 6 μL of the sensor **1** (5 mM) was diluted to 2.994 mL bis-tris to make final concentration of 10 μM. Then, 3–39 μL of the stock solution of TEAF (100 mM) were added to **1** solution (10 μM). After mixing them for a few seconds, UV-vis spectra were taken at room temperature.
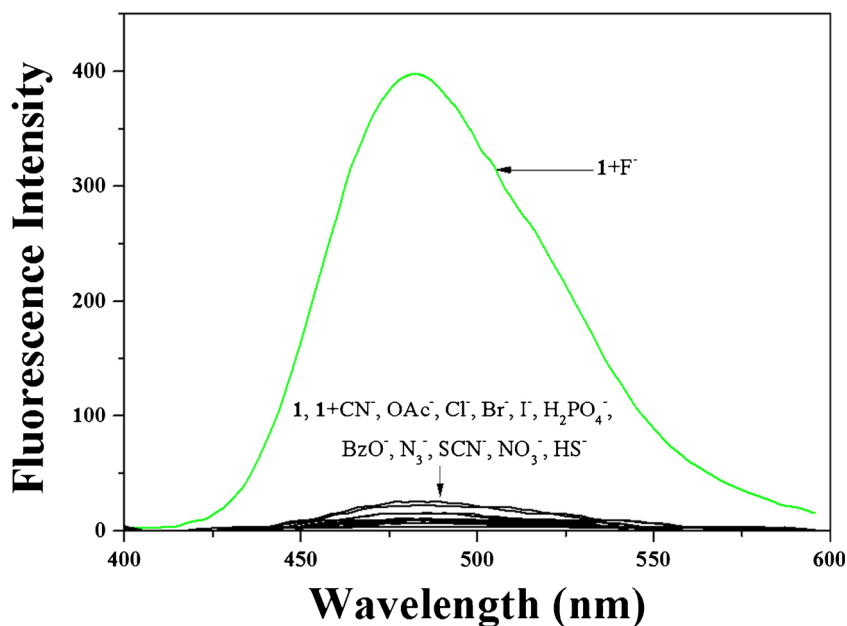
Job Plot Measurement

A series of solutions containing sensor **1** (70 μM) and TEAF (70 μM) were prepared in such a manner that the total volumes of sensor **1** and anion remained constant (3 mL), and bis-tris buffer was used as a solvent. After mixing them for a few seconds, UV-vis spectra were taken at room temperature. Job plot was drawn by plotted against the molar fraction of sensor **1** under the constant total concentration.

Competition Experiment

A stock solution of sensor **1** (5 mM) was prepared in DMSO and 6.0 μL of this solution was diluted to 2.994 mL of bis-tris buffer to make final concentration of 10 μM. Stock solutions (100 mM) of various anions such as CN⁻, Cl⁻, Br⁻, I⁻, H$_2$PO$_4$⁻, BzO⁻, OAc⁻, SCN⁻, N$_3$⁻, NO$_2$⁻ and HS⁻ were prepared and 63 μL of each anion solution was taken and added to 3 mL of the solution of sensor **1** (10 μM) to give 210 equiv. of anions. Then, 63 μL of F⁻ solution (100 mM) was added

Scheme 1 Synthesis of **1**

into the mixed solution of each anion and **1** to make 210 equiv. After mixing them for a few seconds, fluorescence spectra were taken at room temperature.

pH Effect Test

A series of buffers with pH values ranging from 2 to 12 were prepared by mixing sodium hydroxide solution and hydrochloric acid in bis-tris buffer. After the solution with a desired pH was achieved, a stock solution (5 mM) of sensor **1** was prepared in DMSO and 6.0 μL of this solution was diluted to 3 mL of bis-tris buffer to make final concentration of 10 μM. Stock solutions (100 mM) of F^- were prepared at different pH

and 63 μL of each stock solution was taken and added to the each pH solution (2–12) of sensor **1** (5 μM) to give 210 equiv. of anions. After stirring them for a few seconds, fluorescence spectra were taken at room temperature.

^{1}H NMR Titration

Four NMR tubes of sensor **1** (1.62 mg, 0.005 mmol) dissolved in DMSO-d_6 (700 μL) were prepared and then four different concentrations (0, 0.0025, 0.005 and 0.025 mmol) of TEAF dissolved in DMSO-d_6 were added to each solution of sensor **1**. After shaking them for 1 min, ^{1}H NMR spectra were obtained at room temperature.
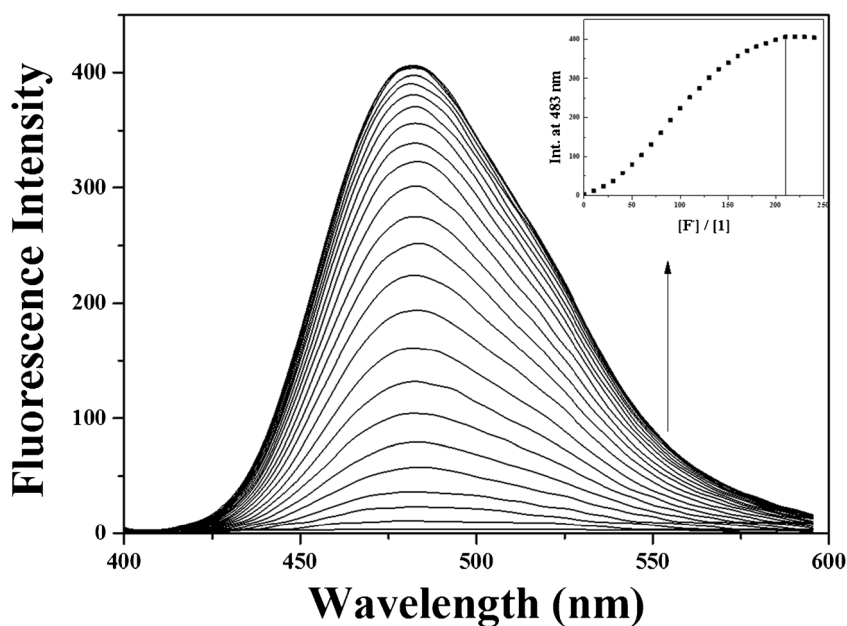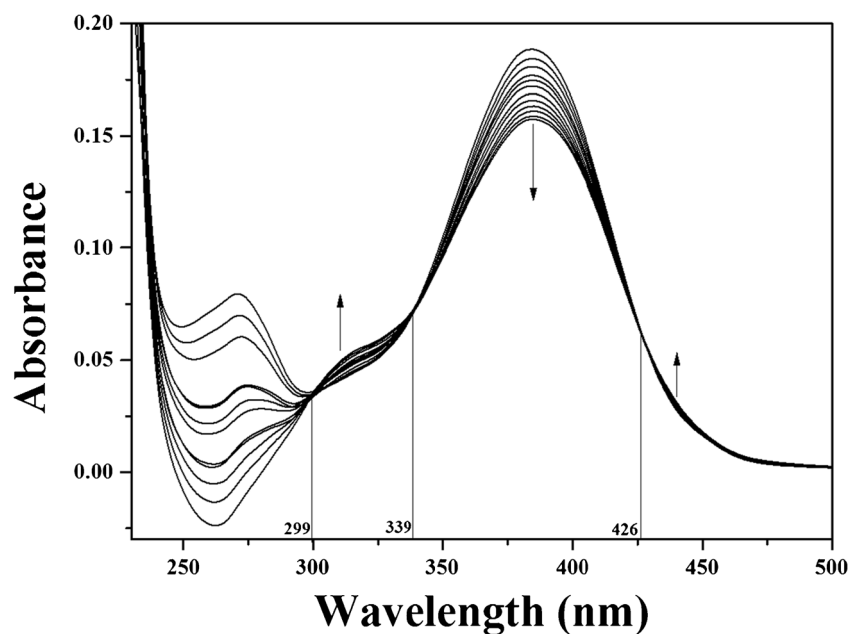
Fig. 3 Absorption spectral changes of **1** (10 μM) in the presence of different concentrations of F⁻ in bis-tris buffer at room temperature

Theoretical Calculation Methods

All DFT/TDDFT calculations based on the hybrid exchange correlation functional B3LYP [46, 47] were carried out using Gaussian 03 program [48]. The 6-31G** basis set [49, 50] was used for the main group elements. In vibrational frequency calculations, there was no imaginary frequency for the optimized geometries of **1** and **1**-F⁻, suggesting that these geometries represented local minima. For all calculations, the solvent effect of water was considered by using the Cossi and Barone's CPCM (conductor-like polarizable continuum model) [51, 52]. To investigate the electronic properties of singlet excited states, time-dependent DFT (TDDFT) was performed in the ground state geometries of **1** and **1**-F⁻. The 25 singlet-singlet excitations were calculated and analyzed. The GaussSum 2.1 [53] was used to calculate the contributions of molecular orbitals in electronic transitions.

Results and Discussion

Sensor **1** was synthesized by direct condensation of 8-hydroxyjulolidine-9-carboxaldehyde and furan-2-carbohydrazide with 89% yield in ethanol (Scheme 1), and characterized by ¹H NMR, ¹³C NMR, FT-IR spectrometry and elemental analyses.

Fluorescence Studies of 1 toward F⁻

To study the sensing ability, sensor **1** was treated with various anions such as CN⁻, F⁻, Cl⁻, Br⁻, I⁻, $H_2PO_4^-$, BzO⁻, OAc⁻, SCN⁻, N_3^-, NO_2^- and HS⁻ in bis-tris buffer (10 mM, pH 7.0). Compared to the other anions examined, the prominent fluorescence change of **1** was observed in the presence of F⁻ with a visual color change from colorless to green (Fig. 1). In contrast, sensor **1** showed no or weak fluorescence with other anions. The fluorescence titration experiments were performed by
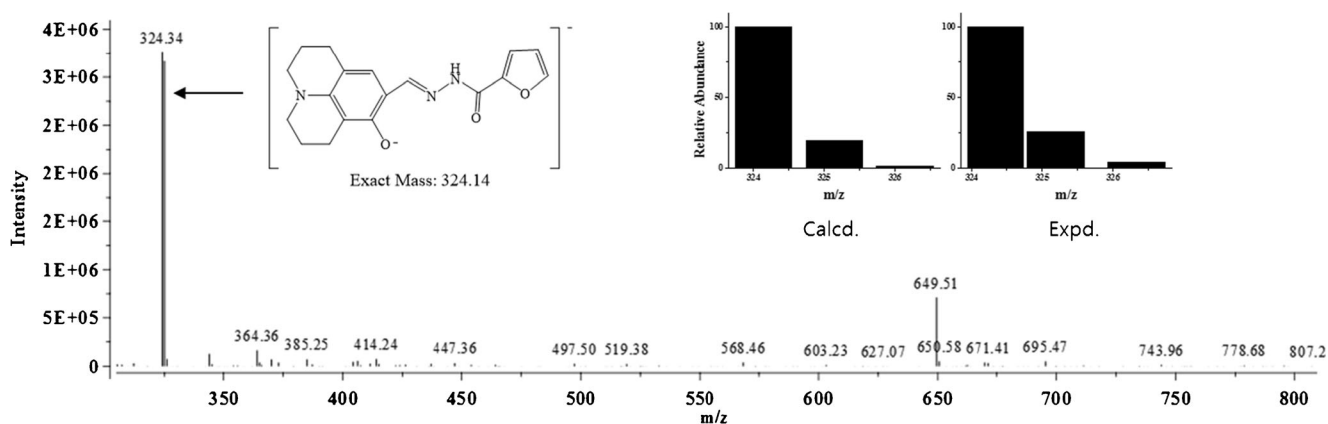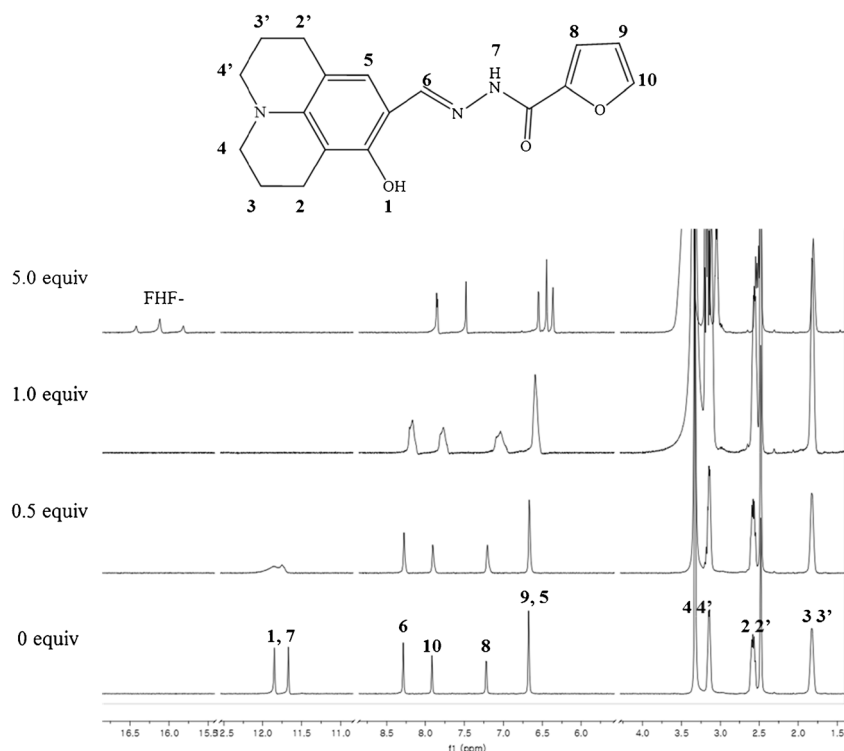

Fig. 4 Negative-ion electrospray ionization mass spectrum of **1** (100 μM) upon addition of TEAF (1.0 equiv)

Fig. 5 ^{1}H NMR titration of **1** with F$^-$

increasing concentration of F$^-$ into a solution of **1**. As shown in Fig. 2, the fluorescence intensity at 483 nm increased about 400 folds ($\lambda_{ex} = 384$ nm). The corresponding UV-vis spectral changes were also investigated (Fig. 3). The UV-vis titration of **1** with F$^-$ solution revealed that the absorption bands at 250 nm and 375 nm decreased, and new bands at 325 nm and 450 nm increased slightly. Clear isosbestic points emerged at 299 nm, 339 nm and 426 nm during the UV-vis titration,

which indicated that the only one species was formed between **1** and F$^-$.

The stoichiometry of **1** with F$^-$ was determined by Job plot analysis using emission titration experiments in the presence of various molar fractions of F$^-$ [54]. The Job plot for the binding between **1** and F$^-$ exhibited a 1:1 stoichiometry (Fig. S1). In addition, the formation of the 1:1 species between **1** and F$^-$ was further confirmed by the appearance of a peak at
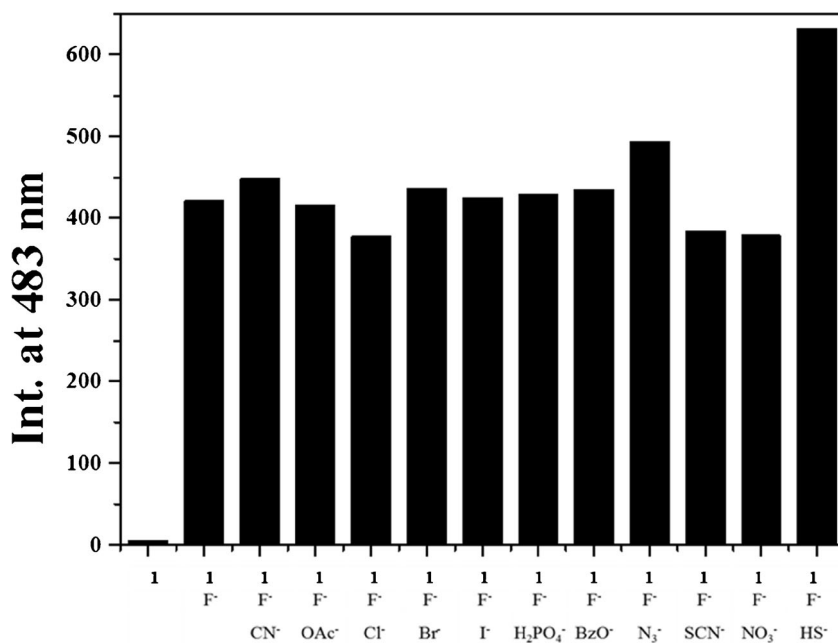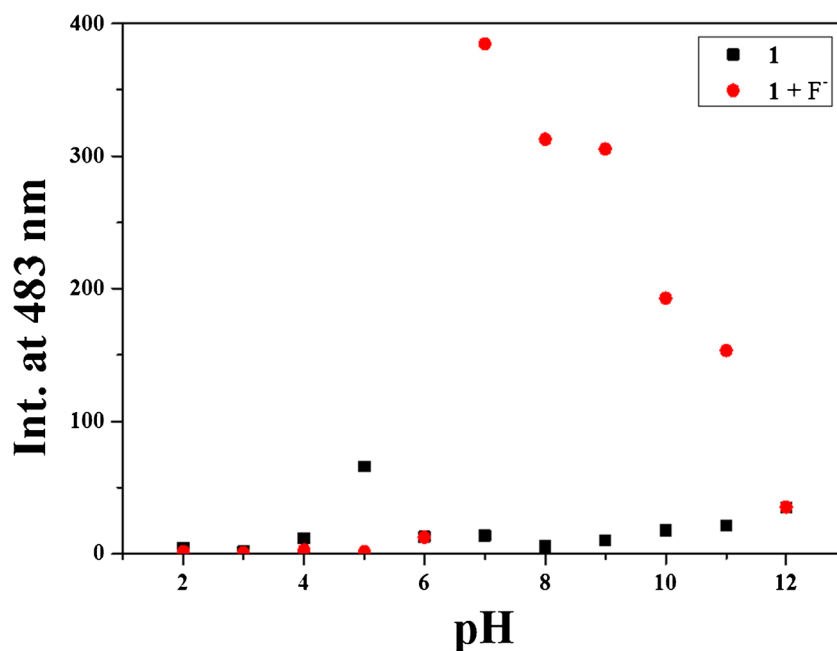
Fig. 6 Competitive selectivity of **1** (10 μM) toward F$^-$ (210 equiv) in the presence of other anions (210 equiv)

Fig. 7 Fluorescence spectra (483 nm) of **1** (10 μM) and **1**-F⁻, respectively, at pH 2–12 in bis-tris buffer at room temperature

m/z 324.34, assignable to [**1** - H⁺]⁻ (calcd: 324.14) in the ESI-mass analysis (Fig. 4). The evidence for the reaction between **1** and F⁻ was further provided by ^{1}H NMR titration (Fig. 5). Upon the addition of 1.0 equiv. of F⁻, the signals of -OH- and -NH- completely disappeared, which may be ascribed to the strong hydrogen bonding interaction between F⁻ and the -OH- and -NH- units of **1**. On excess addition of F⁻ (5.0 equiv) to **1** solution, a new peak at 16.11 ppm appeared, indicating the formation of FHF⁻ species. At the same time, most of aromatic protons were shifted to upfield, which indicates that the negative charge generated from deprotonation of **1** by F⁻ might be delocalized through the whole molecule. There was no shift in the position of the proton signals on further addition of F⁻ (>5.0 equiv).
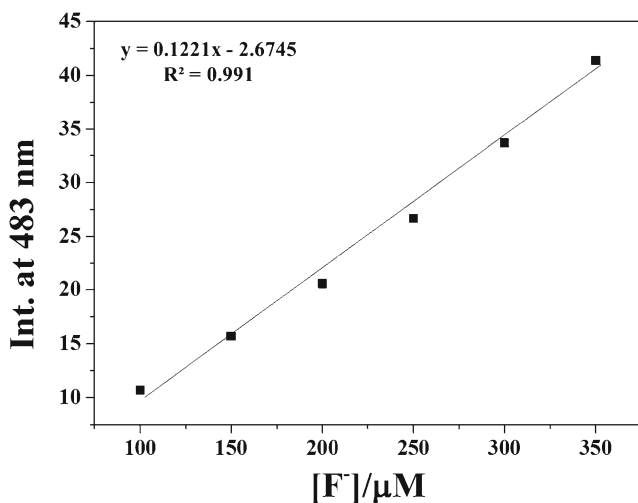
The association constant was calculated to be 7.5×10^2 M⁻¹ from a Benesi-Hildebrand plot using emission changes at 483 nm (Fig. S2) [55]. This value is within the range of those (10^1–10^6) reported for F⁻ sensors. The detection limit (DL) of sensor **1** for F⁻ detection was determined from a plot of fluorescence intensity as a function of F⁻ concentration (Fig. S3) [56]. The DL was found to be 10.02 μM, which is lower than the maximum allowable level (79 μM) of F⁻ regulated by WHO in drinking water.

To further examine the fluorescence response of sensor **1** toward F⁻ in the presence of preferentially competing species, competition experiments with various anions were conducted (Fig. 6). Upon addition of 210 equiv. of F⁻ in the presence of other anions (210 equiv), such as CN⁻, OAc⁻, Cl⁻, Br⁻, I⁻, $H_2PO_4^-$, BzO⁻, N_3^-, SCN⁻, NO_2^- and HS⁻, there was no interference in the detection of F⁻ from other anions.

In order to apply to the environmental systems, the pH dependence of **1** in the absence and presence of F⁻ was conducted at various pH (Fig. 7). The increase of intensity caused by addition of F⁻ was observed between pH 7.0 and 11.0. This

Fig. 8 Emission intensity (483 nm) of 1 as a function of F⁻ concentration. [**1**] = 10 μmol/L and [F⁻] = 100–350 μmol/L in bis-tris buffer

y = 0.1221x - 2.6745
R² = 0.991

Table 1 Determination of F⁻ in water samples [a]

Sample	F⁻ added (μmol/L)	F⁻ found (μmol/L)	Recovery (%)	R.S.D. (n = 3) (%)
Drinking water	0.0	0.0		1.22
	100	98.97	98.97	2.46
Tap water	0.0	48.67		1.26
	100	150.81	101.44	3.43

[a] Conditions: [**1**] = 10 μmol L⁻¹ in 10 mM bis-tris buffer solution (pH 7.0)

Fig. 9 The energy-minimized structures of (a) **1** and (b) **1**-F⁻

Dihedral angle (1C, 2C, 3N, 4C) : -3.946°

F-6H : 1.4678 Å
F-7H : 1.6962 Å
5O-6H : 1.0398 Å
3N-7H : 1.0454 Å

Dihedral angle (1C, 2C, 3N, 4C) : 54.427°
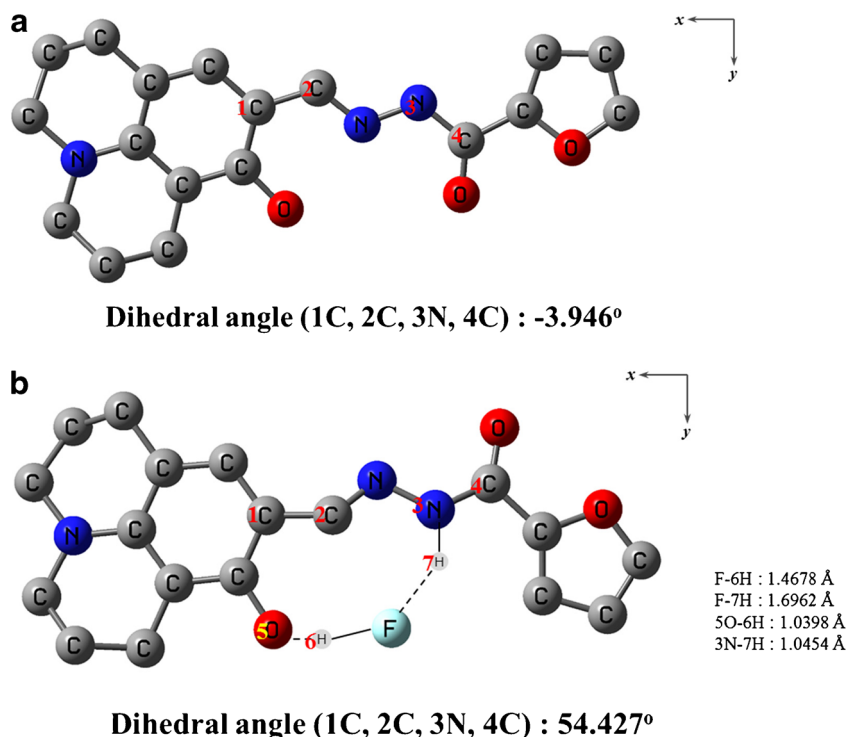
result warranted its application under physiological conditions, without any change in detection F⁻.

For practical application, we constructed a calibration curve for the determination of F⁻ by **1** (Fig. 8). A good linear relationship was observed for **1**-F⁻ species with a correlation coefficient of $R^2 = 0.991$ ($n = 3$). To evaluate the practical abilities of **1** with F⁻, drinking and tap water samples were selected and each sample was analyzed with three replicates. As shown in Table 1, satisfactory recoveries and suitable R.S.D. values for F⁻ were obtained. These results suggested that chemosensor **1** could be useful for the measurements of F⁻ in chemical and environmental applications.
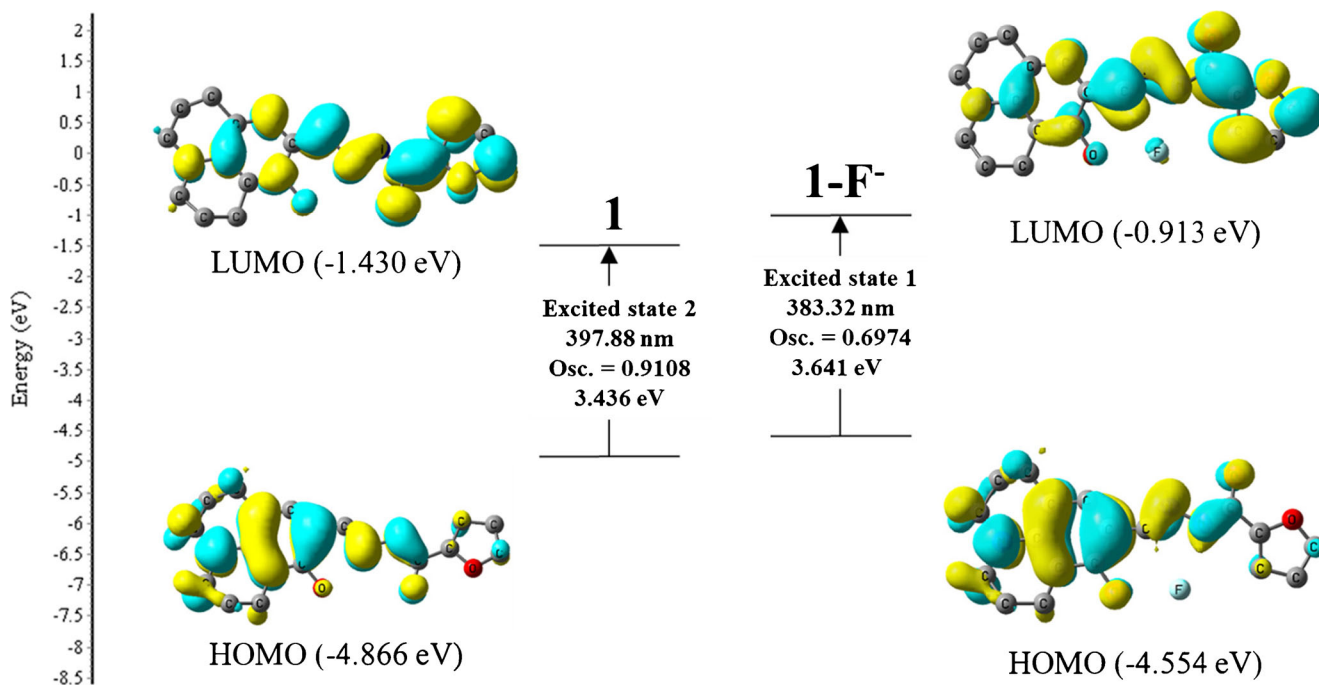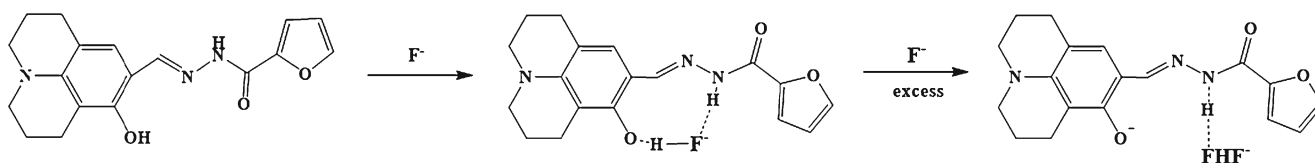

Fig. 10 Molecular orbital diagrams and excitation energies of **1** and **1**-F⁻

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

Theoretical Studies

In order to understand fluorescence sensing mechanism of **1** to F$^-$, electronic properties were calculated by using the Gaussian 03 program. The density functional theory (DFT) and time dependent-density functional theory (TD-DFT) calculations were conducted with the B3LYP/6-31G(d, p) method basis set. To evaluate the solvent effect, water was used as a solvent by using the CPCM method. The optimized geometry structures of **1** and **1**-F$^-$ species are shown in Fig. 9. The energy-minimized structure of **1** showed a nearly planar structure with the dihedral angle of 1C, 2C, 3 N, 4C = −3.946^o (Fig. 9a). For **1**-F$^-$, F$^-$ hydrogen bonded with 6H and 7H of **1** with dihedral angle of 1C, 2C, 3 N, 4C = 54.427 ^{o} (Fig. 9b). The transition energies and oscillator strengths of **1** and **1**-F$^-$ were obtained from TD-SCF calculation. In the case of **1**, the main molecular orbital (MO) contribution of the 2nd lowest excited state was determined for the HOMO → LUMO transition (397.88 nm, Fig. S4). The HOMO orbital mainly lied in the julolidine moiety, and the LUMO orbital did in the furan one. These results indicated ICT from the julolidine to the furan. For **1**-F$^-$, the 1st excited state was found to be relevant to the 'turn-on' fluorescence showing predominant ICT band (383.32 nm, Fig. S5). The HOMO was localized in electron-donor parts of the julolidine moiety, while the LUMO was located in electron-acceptor sites of the furan one. These transitions indicated the ICT band from the julolidine to the furan. MO diagrams and excitation energies of **1** and **1**-F$^-$ are shown in Fig. 10. Thus, these results suggested that the "turn-on" sensing mechanism of **1** toward F$^-$ may be due to the ICT process. Based on Job plot, ^{1}H NMR titration and theoretical calculations, the sensing mechanism of F$^-$ by **1** is depicted in Scheme 2.

Conclusion

We have successfully synthesized and characterized a new chemosensor **1** for selective detection of F$^-$ in a near-perfect aqueous solution. The binding properties of the sensor **1** toward F$^-$ have been studied by spectroscopic techniques, ESI-mass analysis and ^{1}H NMR titration. Sensor **1** showed high sensitivity to F$^-$ with a detection limit of 10.02 μM and excellent selectivity avoiding the interference from other anions. The sensing mechanism for F$^-$ was proposed to be the ICT mechanism via hydrogen bonding with DFT and TD-DFT

studies. For practical application, **1** could be used to detect and quantify F$^-$ levels in real water samples.

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