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Spectroscopy and a theoretical study of colorimetric sensing of fluoride ions by salicylidene based Schiff base derivatives



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ABSTRACT

Three colorimetric anion sensors based on salicylidene Schiff bases (salicylaldehyde-o-aminophenol **[SA1**], 3,5-dimethyl-salicylaldehyde-o-aminophenol **[SA2**], and 3,5-dichloro-salicylaldehyde-o-aminophenol **[SA3**] were comprehensively studied based on experimental methods combined with theoretical calculations. All derivatives showed high sensitivity for colorimetric detection of fluoride ions (F^-) with a binding stoichiometry of 1:1 in acetonitrile solutions. The color of the sensor solutions visibly changed from light yellow to orange red in the presence of F^- . From the experimental results, **SA1** and **SA2** showed higher potential as F^- sensors than **SA3** due to their higher selectivity with a limit of detection (LOD) as low as 8×10^{-5} , 21×10^{-5} and 7×10^{-5} M, respectively. The optimized structure and electronic transitions were confirmed by DFT and TDDFT studies. In this study, F^- detection mechanism is proposed based on experimental and the density functional theory (DFT) calculation.

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1. Introduction

Fluoride is a mineral present in water and soil and plays a crucial role in biological and chemical applications [1-3]. Fluoride is commonly added to toothpaste and drinking water at limited concentrations recommended by the World Health Organization (WHO) (≤ 2 mg/L) to reduce dental cavities [4, 5] and for clinical treatment of osteoporosis [6]. High fluoride levels can cause skeletal and dental fluorosis, resulting in bleaching or a brownish discoloration of teeth and bones [7-8]. Furthermore, excess fluoride exposure causes human health impacts such as decreased thyroid function, Type II diabetes, attention deficit hyperactivity disorder (ADHD), and neurotoxicity [4,5,9]. Fluoride can also be an environmental pollutant [8,10]. Therefore, detection of fluoride levels in drinking water, food, and the environment is crucial and necessary.

In recent years, high sensitivity and selectivity of colorimetric sensors for fluoride ion (F^-) detection have been developed based on chemical interactions such as Lewis acids-based interactions [11], hydrogen-bonding interactions [12,13], reaction-based interac-

* Corresponding author. E-mail address: fsciswsm@ku.ac.th (S. Suramitr). tions [14], polymer-based interactions [15], quantum dots and gold nanoparticles-based interactions [16], and mesoporous silica or silica particle-based interactions [17]. In many cases, the binding unit is primarily composed of F⁻ anion which interacts with hydrogen donors, called chemosensors, through hydrogen bonding in a sensing system. Various types of chemosensors have been introduced for this purpose, including urea or thiourea groups, amides, porphyrin, and phenols [18]. Among these chemosensors, salicylidene Schiff bases have received widespread interest due to their photochromic and thermochromic properties caused by tautomerism of two different forms (enol and keto forms) [19-21]. These properties depend on the molecular planarity, nature of crystal packing, effect of substituent, and nature of the solvent [22], which can be visible colorimetric chemosensors for anion detection via naked eye.

However, development of sensors which exhibit high selectivity and sensitivity in the visible region of the spectrum remains challenging because traditional methods to detect F^- such as highperformance electrochemical sensors are difficult and expensive [23]. Here the researchers report on high selective and sensitive optical chemosensors based on salicylidene Schiff bases for F^- anion detection. Three anion sensors, salicylaldehyde-o-aminophenol



Fig. 1. Structure and synthetic route of salicylidene Schiff base derivatives (SA1, SA2 and SA3).

(SA1), 3,5-dimethyl-salicylaldehyde-o-aminophenol (SA2), and 3,5dichloro-salicylaldehyde-o-aminophenol (SA3), are designed, synthesized, and characterized using several methods. The sensor molecules were modified by substitution of aromatic proton (H) (in SA1) with electron donating groups (methyl for SA2) and electron withdrawing group (chlorine for SA3) (Fig. 1). The photophysical properties of the compounds were studied followed by an evaluation of their fluoride sensing performance. The structural geometries and proton transfers processes of all molecules were investigated and F^- detection mechanism was also proposed using quantum chemical calculations. It shown that the developed salicylidene Schiff base sensors exhibited high sensitivity and selectivity which can clearly be seen with the naked eye when detecting fluoride anions.

2. Experimental

2.1. Materials and equipment

All materials for synthesis were purchased from Sigma Aldrich and used without further purification. Solvents and reagents used in spectroscopic studies were of analytical grade. Nuclear Magnetic Resonance analyses were recorded on an INNOVA UNITYVARIN spectrometer operated at 400.00 MHz for ¹H-NMR in deuterated dimethyl sulfoxide-d₆ (DMSO-d₆) and tetramethylsilane (TMS) was used as an internal reference. UV-vis absorption spectra were taken using Jasco V-670 UV/VIS/NIR spectrophotometer in the wavelength range of 200-700 nm. The experiments were carried out using a 2 nm slit width in 1 cm quartz cells at room temperature. In the titration experiments, the stock solutions of sensor molecules (SA1, SA2 and SA3) $(1.0 \times 10^{-4} \text{ mol } L^{-1})$ were prepared in acetonitrile (CH₃CN) solution. All anions (F⁻, Cl⁻, Br⁻, I⁻, AcO⁻ and H₂PO₄⁻) used in this study were prepared by dissolving the anions, which were presented in the form of tetrabutylammonium (TBA) salts in acetonitrile to reach a concentration of 0.004 mol L⁻¹. Equilibrium constants of the sensors and anions were calculated following the method reported previously [24].

2.2. Synthesis of salicylidene Schiff base derivatives (SA1, SA2 and SA3)

Sensor molecules were prepared using condensation of 2amino-phenol (5 mmol) with 0.5 ml of salicylaldehyde, 3,5dimethylsalicylaldehyde, and 3,5-dichlorosalicylaldehyde to produce **SA1, SA2,** and **SA3**, respectively. The chemicals were mixed in 10 ml glycerol, stirred, and refluxed for 2 hours at 80°C. The reaction was monitored using thin-layer chromatography (TLC). Disappearance of starting compounds on the TLC indicated that the

Table 1

Summary of absorption and emission spectral data and molar absorptivity of SA1, SA2 and SA3 in different solvents.

Compounds	Solvents	λ_{abs} (nm)	Molar absorptivity (cm ⁻¹ M ⁻¹)	λ_{em} (nm)
SA1	Chloroform	354	8,585	525
	Ethanol	350	11,675	519
	Acetonitrile	348	11,602	529
SA2	Chloroform	366	8,177	564
	Ethanol	353	5,101	555
	Acetonitrile	341	10,340	559
SA3	Chloroform	367	16,628	553
	Ethanol	358	20,135	549
	Acetonitrile	357	27,893	554

Table 2

The association constants of **SA1**, **SA2** and **SA3** with F⁻, AcO⁻, H₂PO₄⁻ in CH₃CN as determined from UV-vis absorption titrations.

	Association constant (K_a in M^{-1})				
Sensors	F-	AcO-	H_2PO_4 -		
SA1	3.92×10^3	-	-		
SA2	$1.38 imes 10^3$	-	-		
SA3	8.30×10^3	14.10×10^3	5.28×10^3		

reaction was completed. After that, the synthesized compound was washed with DI water.

Salicylaldehyde-o-aminophenol, (SA1) was obtained as an orange powder with a yield of 82% and melting point in the range of 181-182°C. ¹H NMR (DMSO-d₆, δ ppm): 13.77 s 1H (OH); 9.73 s 1H (OH); 8.96 s 1H (CH=N); 7.79-6.45 m 8H (Aromatic). UV-vis (CH₃CN) λ _{max}: 348 nm.

3,5-dimethyl-salicylaldehyde-o-aminophenol, (SA2) was obtained as a brown powder with a yield of 81% and melting point in the range 164-165°C. ¹H NMR (DMSO-d₆, δ ppm): 13.89 s 1H (OH); 9.74 s 1H (OH); 8.87 s 1H (CH=N); 7.70-6.38 m 6H (Aromatic); 2.38-1.69 m 6H (CH). UV-vis (CH₃CN) λ_{max} : 341 nm.

3,5-dichloro-salicylaldehyde-o-aminophenol, (SA3) was obtained as an orange powder with a yield of 75% and melting point in the range 237-238°C. ¹H NMR (DMSO-d₆, δ ppm): 10.22 s 1H (OH); 9.08 s 1H (CH=N); 7.95-6.58 m 5H (Aromatic). UV-vis (CH₃CN) λ_{max} : 359 nm.

2.3. Computational details

Theoretical calculations were performed with the Gaussian 09 package [25]. The geometries of the electronic ground state (S_0) of the three sensors (**SA1, SA2** and **SA3**) are shown in Fig. 1 which were calculated using the density functional theory (DFT) method.



(c)

Fig. 2. UV-visible absorption spectra of (a) SA1, (b) SA2 and (c) SA3 in CH₃CN (1×10^{-4} M) in the presence of various anions (4×10^{-3} M) (F^- , CI^- , Br^- , I^- , AcO⁻, and H₂PO₄⁻)

The long-range corrected version of B3LYP using the Coulombattenuating method CAM-B3LYP functional, which contains 65% long-range HF exchange [25,26] and the 6-31G(d,p) basis set was chosen for all atoms. Frequency calculations were also conducted at the same level to ensure that the optimized structure was the minimum on the potential energy surface (PES). Absorption spectra were also studied using the Time-dependent DFT method with the 6-311G(d,p) basis set and the Coulomb-attenuating method (CAM) with a long-range corrected version of B3LYP (TD-CAM-B3LYP/6-311G(d,p)) calculations under the S₀ and S₁ minimum structures



(c)

Fig. 3. UV-visible absorption titration spectra of (a) SA1, (b) SA2 and (c) SA3 recorded in CH₃CN (1 × 10⁻⁴ M) after addition of TBAF (0-8 equivalent).

[27-30]. The integral equation formalism variant of the polarizable continuum model (PCM) [31] was employed using acetonitrile as a solvent throughout the whole theoretical calculations. Furthermore, complexes consisting of the three sensors and F^- ion were optimized at the same theoretical levels as above with the consideration of the BSSE correction using the counterpoise method [32].

3. Results and discussion

3.1. Photophysical properties

3.1.1. Absorption and fluorescence properties

Three salicylidene Schiff base derivatives, **SA1**, **SA2**, and **SA3**, were synthesized followed by structural characterizations using ¹H-NMR and FT-IR techniques. The results obtained from ¹H-NMR measurements in dimethyl sulfoxide (DMSO-d₆) detailed in the Supporting Information (SI) (**Fig. S1**) confirmed the formation of

Schiff base structures of all compounds. Photophysical properties including absorption, emission, and molar absorptivity of the salicylidene derivatives were investigated in three solvents with different polarities, as shown in Table 1. The solvents were chloroform (CHCl₃, dielectric constant = 4.81), ethanol (C₂H₆O, dielectric constant = 24.5), and acetonitrile (CH₃CN, dielectric constant = 37.5). The absorption spectra of the derivatives in all solvents showed maximum wavelengths of absorption (λ_{abs}) in the range of 340-370 nm. With increased solvent polarity, the λ_{abs} of all derivatives slightly shifted to a longer wavelength (blue-shift). This is potentially caused by increasing of the interaction stabilization between hydroxyl group of the solvents and phenol group of the salicylidene enabling high delocalization of electron cloud on the aromatic system.

For maximum wavelengths of emission (λ_{em}) (See in Supporting Information, **Fig. S2**) of all compounds, emission wavelengths



Fig. 4. Partial ¹H NMR spectra of SA1 (7 mM in DMSO-d₆) with addition of different equivalent (0.0, 1.0 and 2.0) of TBAF.



Fig. 5. ESP molecular surfaces of the sensors (SA1, SA2 and SA3). Positive and negative ESP surfaces are represented in blue and red regions, respectively. Only positive values presented on the ESP surfaces are shown.

at a large Stokes shift in a range of 525-560 nm were observed when using non-polar solvent (CHCl₃) and aprotic solvent (CH₃CN). The emission is normally caused by an excitation of enol isomer to produce keto isomer, and this resulted in the presence of ESIPT process in the system. In the case of using protic solvent (EtOH), the short wavelength emission bands (< 450 nm) disappeared and only the emission bands in a large Stokes shift range (519-555 nm) were observed. This phenomenon is caused by the presence of intermolecular hydrogen bonding of the derivatives with solvent molecules leading to stabilization of the solvated keto isomers and prevention of the ESIPT process [30].



Fig. 6. Geometry structures of (a) SA1_{enol}, (b) SA1_{keto} and (c) SA1_{keto}-F⁻ complex. Only the intramolecular H-bond distances (in Å) are shown. The colors of various atoms within the molecules are grey for carbon, white for hydrogen, red for oxygen, blue for nitrogen, green for chlorine, and indigo blue for fluoride.

3.1.2. UV-Visible absorption of anion sensing

The interactions between the salicylidene Schiff base derivatives (**SA1, SA2**, and **SA3**) and various types of anions (F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, and H₂PO₄⁻) were investigated in CH₃CN solutions through colorimetric analysis. UV-vis absorption spectra of the salicylidene Schiff base derivatives solutions (1×10^{-4} M) after adding different anions (4×10^{-3} M) were recorded after three minutes, as shown in Fig. 2. It was found that the color of **SA1** and **SA2** solutions changed from light yellow (340-350 nm) to orange red (400-425

nm) in the presence of F⁻, while no apparent color change was observed as treatment with the other anions (Cl⁻, Br⁻, I⁻, AcO⁻, and $H_2PO_4^{-}$). In the case of **SA3**, the solution color changed from light yellow to orange red (420 nm) after treatment with three anions, which were F⁻, AcO⁻, and $H_2PO_4^{-}$. No noticeable change in color was found when **SA3** was treated with Cl⁻, Br⁻, and I⁻. These findings indicate that all derivative compounds had colorimetric sensitivity to F⁻ in CH₃CN solution. However, **SA1** and **SA2** could be potentially utilized as sensors because they showed higher selectivity toward the F⁻ detection than **SA3**.

Binding affinities between the derivatives and F⁻ ions were examined using titration experiments. The titrations were carried out by adding tetrabutylammonium fluoride (TBAF) solution, which contained F⁻ ions, into the derivative solutions $(1 \times 10^{-4} \text{ M})$ prepared in CH₃CN and monitored using UV-visible spectroscopy. Absorption titration spectra of all compounds with increasing F⁻ concentrations are shown in Fig. 3. Before F⁻ addition, the spectra of SA1, SA2, and SA3 showed λ_{abs} peaks at 348, 341 and 359 nm, respectively, which corresponded to enol structure of the compounds [30]. Obviously, weak absorption bands at 440 and 470 nm were detected in SA1 and SA3 spectra, respectively, which are presumably caused by the presence of both enol and keto forms in the solutions. After increasing F⁻ concentrations, new peaks at 406, 425, and 420 nm for SA1, SA2, and SA3, respectively, were visibly detected. The formation of these peaks is likely caused by either hydrogen bonding between F⁻ and Ar-OH or deprotonation of Ar-OH protons [33].

Binding stoichiometry of the SA1, SA2, and SA3 with F^- can be calculated using the Benesi-Hildebrand equation [34] as follows:

$$1/(A-A_0)=1/(A_{\infty}-A_0)[1/K[F^-]_0+1]$$

where, A_0 is an absorbance of free sensor, A_{∞} is an absorbance measured with excess amount of F⁻, A is an absorbance measured with a specific amount of F⁻, K_a is the association constant (M⁻¹), and [F⁻]₀ is a concentration of F⁻ added (M).

The plot of $1/(A-A_0)$ versus $1/[F^-]_0$ of **SA1, SA2**, and **SA3** showed a linear relationship with R² of 0.9855, 0.9912, and 0.9923, respectively. This indicates that all sensors and fluoride ions formed a 1:1 binding stoichiometry. The association constants (K_a) between the sensors and F⁻ were calculated from the ratio of intercept/slope and summarized in Table 2. The K_a values revealed that the fluoride affinities of all sensors are in an order of SA2 < SA1 < **SA3**. This implies that proton substitution by electron withdrawing group (Cl in SA3) in the sensor molecule could lead to higher fluoride affinity than that by electron donating groups (CH₃ for SA2) and higher than the molecule without substitution (H for SA1). Limit of detections (LOD) for all sensors could be calculated from $3\sigma/m$, where σ is the standard deviation of the blank solution and m is the slope of the calibration curve [35]. The calculated values were 8×10^{-5} , 21×10^{-5} , and 7×10^{-5} M for **SA1**, **SA2**, and **SA3**, respectively.

To further understand the interaction between the fluoride ion and the developed sensors, ¹H NMR titration experiments were conducted in DMSO-d₆ solution, as shown in Fig. 4. Before treatment **SA1** with F⁻, the chemical shifts of OH protons were s 13.77 and s 9.73 ppm and of -HC=N proton combined with aromatic protons was s 8.87 ppm. After addition of one equivalent of F⁻, the OH peaks disappeared indicating the formation of hydrogenbond interactions between the **SA1** and the fluoride ions. The remaining peaks presented at s 9.73 and s 8.96 ppm could be mainly attributed to aromatic protons in the **SA1** molecule. As increase F⁻ concentration to be 2 equivalent of F⁻, these peaks were slightly shifted to larger value, which is likely caused by deprotonation of the **SA1** at high concentration of F⁻. Similar phenomenon was also observed for **SA2** and **SA3**. (See in Supporting Information, **Fig. S1**).



Scheme 1. Potential mechanism for F⁻ detection of all sensors.

3.2. Theoretical calculation

To investigate the active site of **SA1, SA2**, and **SA3** molecules for F^- detection, theoretical calculations were conducted. Electrostatic potential (ESP) analysis was undertaken using the Gauss View 5.0 program. The ESP molecular surfaces of the sensor molecules are presented in Fig. 5. For all sensing compounds, it is revealed that the H atom of the OH moieties gave a positive ESP surface, while the aromatic unit showed a negative ESP surface. This resulted in the preference of F^- anions to close to the positively charged H atoms rather than to the negatively charged aromatic units. In conclusion, detection of the sensor compounds can be performed via interaction between F^- anion and H atom of the OH moieties of the sensors.

Structures of the SA_{enol}, SA_{keto}, and SA_{keto}-F⁻ intermediate and the deprotonated form were optimized separately (Fig. 6) in DFT formalism with 6-311 G(d,p) basis set and the CAM-B3LYP functional. At each optimized structure, lowest few electronic transitions of the molecules (SA_{enol}, SA_{keto}, and SA_{keto}-F⁻) were examined with TDDFT formalism. All calculations were carried out in acetonitrile as solvent, treated in Onsager's SCRF formalism, with polarisable continuum (PCM) approximation. A single imaginary frequency confirmed the obtained structure as the desired transition state.

The optimized structure of the SA_{enol}, SA_{keto}, and SA_{keto}-F⁻ form confirmed the mechanism of fluoride binding (Scheme 1) through hydrogen bond formation between the O-H and N-H with F⁻. Some geometrical parameters were shown in Fig. 6. The lengths of O-H of SA1_{enol}, SA1_{keto}, and SA1_{keto}-F⁻ were increased to 0.991 Å, 1.561 Å and 1.998 Å, respectively, while the N-H lengths were decreased to 1.741 Å, 1.063 Å and 1.034 Å, respectively. Moreover, this study revealed that the NH-O and N-HO hydrogen bonds in Figs. 6 and S2 are involved in NH and OH tautomers from which it could be inferred that F⁻ binding occurs through the SA_{keto}-F⁻ form, followed by deprotonation of the ligand, formation of hydrogen bond between deprotonated oxygen, and -NH and release of HF. In addition to, the frequency calculations were performed on each optimized structure. Similar phenomenon was also observed for **SA2** and **SA3** (See in Supporting Information, **Fig. S3**).

Frequency calculations were carried out on each optimized structure, and their IR spectra were discussed. Fig. 7 showed the simulated infrared (IR) spectra for the SA-enol, SA-keto and SA-keto+ F^- , where the intensity was plotted against the harmonic vibrational frequencies. For the complexity of vibrational modes, it was difficult to attribute all bands, so we have only analyzed some H–X (X = O and N) vibrational frequencies [36-38] in the SA1enol,

SA1keto and SA1keto-F⁻ complexes. For the SA1-enol and SA1-keto, it shown that the O-H stretching vibrations of the SA1-enol appeared at 3760 cm⁻¹ and 3322 cm⁻¹, while SA1keto's O-H and N-H stretching vibrations appeared at 3777 cm⁻¹ and 2493 cm⁻¹, respectively. Compared to SA-keto+F⁻ complex, the N-H stretching vibration of complex appeared at 3260 cm⁻¹, indicating large redshifts. All calculation in Fig. 8 indicated that there were strong interactions in the O•••H-X (X = N and F) hydrogen bond and there were large red-shifts for H-X stretching vibrational frequencies in the SA-enol, SA-keto and SA-keto+F⁻ complexes.

The interaction energies with BSSE corrections for complexes (SA1-keto+F⁻, SA2-keto+F⁻ and SA3-keto+F⁻) are listed in Table 3. All the values of the adsorption energies being negative, it is implied that the adsorption structures are stable, and the process is exothermic. It is clear that the BSSE-corrected interaction energy (ΔE_{BSSE}) of complex SA1-keto+F⁻, SA2-keto+F⁻ and SA3-keto+F⁻ are favorable for the distinct selectivity of F⁻. These calculation results are in good agreement with the reported experimental observations that intermolecular proton transfer (IPT) between chemosensor substrate SA1, SA2 and SA3. Thus, one can conclude that the host chemosensors have a much stronger affinity to F⁻ ion through intermolecular proton transfer, which leads to the formation of chemosensor anions by F⁻.

To simulate the absorption spectra of the molecules, vertical excitation energies of the SA_{enol} , SA_{keto} , and SA_{keto} -F⁻ for **SA1**, **SA2**, and **SA3** were calculated based on the time-dependent density functional theory (TD-DFT) method using their ground-state optimized structures. The calculated electronic transitions energies and corresponding transition oscillator strengths for transition from the ground state (S₀) to the excited state (S₁) of the sensor molecules as well as the experimental UV-vis absorption data are summarized in Table 4.

From the DFT/TDDFT studies, it was observed that the theoretical absorption peak (λ_{abs}) of SA1, SA2, and SA3 at 321, 327, and 329 nm of the enol form were caused due to H \rightarrow L transition which was compared with experimental values (λ_{expt}) at 334, 343, and 349 nm, respectively. The theoretical absorption peaks of the keto form, at 368, 382, and 383 nm may be compared with the experimental values at 380, 398, and 400 nm, respectively. It is found that all the calculated wavelengths (λ_{cal}) showed a slight blue shift compared to that obtained from the experiments with an underestimated error of ~3-7%, which was in an acceptable range. The absorption of the probable intermediate (**SA_{keto}-F**⁻) were obtained theoretically at 378, 386, and 395 nm which is very close to the experimental value of keto at 380, 398, and 400 nm, respectively. The



Fig. 7. IR spectra of SA1enol, SA1keto and SA1keto $+F^-$ complexes.



Fig. 8. IR spectra of SA1, SA2 and SA3 and F⁻ complexes.

Table 3

The interaction energies with BSSE corrections ΔE_{BSSE} (in kcal/mol) of complexes, bond length of O -H/N -H hydrogen bonds (in Å) of SA_{keto} -F $^-$ interaction at the CAM-B3LYP/6-311G(d,p) level.

Complexes	O-H bond length (Å)	N-H bond length (Å)	ΔE_{BSSE} (kcal/mol)
SA1 _{keto} -F ⁻	1.998	1.034	-59.67
SA2 _{keto} -F ⁻	2.001	1.033	-58.69
SA3 _{keto} -F ⁻	2.052	1.039	-56.62

Table 4

Excitation energies (E_{ex}), maximum absorption wavelengths (λ_{max}) and oscillator strengths (f) of enol (SA_{enol}) and keto (SA_{keto}) form, and intermediate (SA1_{keto}-F⁻) calculated in acetonitrile medium by the TDDFT method.

States	Transition	E_{ex} (eV)	λ _{cal} (nm)	f	Transition composition	λ_{Expt} (nm)
SA1						-
SAenol	$S_0 \rightarrow S_1$	3.87	321	0.563	HOMO→LUMO (91%)	334
SAketo	$S_0 \rightarrow S_1$	3.36	368	0.395	HOMO→LUMO (97%)	380
SA _{keto} -F ⁻	$S_0 \rightarrow S_1$	3.27	378	0.498	HOMO→LUMO (91%)	-
SA2						
SAenol	$S_0 \rightarrow S_1$	3.79	327	0.502	HOMO→LUMO (94%)	343
SA _{keto}	$S_0 \rightarrow S_1$	3.24	382	0.365	HOMO→LUMO (98%)	398
SA _{keto} -F ⁻	$S_0 \rightarrow S_1$	3.21	386	0.486	HOMO→LUMO (95%)	-
SA3						
SAenol	$S_0 \rightarrow S_1$	3.77	329	0.521	HOMO→LUMO (89%)	349
SAketo	$S_0 \rightarrow S_1$	3.23	383	0.392	HOMO→LUMO (97%)	400
SA _{keto} -F ⁻	$S_0 \rightarrow S_1$	3.14	395	0.508	HOMO→LUMO (89%)	-



Fig. 9. Molecular orbital characteristics of SA1, SA2 and SA3 in keto-form.

theoretical values confirmed the probable deprotonation via hydrogen bonding.

The calculated results showed that the $S_0 \rightarrow S_1$ states of all sensor molecules were mainly derived from an electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (by $\geq 89\%$). This indicated that all molecules exhibited a π - π * type character. From molecular orbital studies of all the sensor molecules (in Fig. 9), it is revealed that both of HOMO and LUMO were mainly contributed by phenol and imine. This confirmed the presence of intramolecular charge transfer character of the transitions from HOMO to LUMO

of all compounds. It was also evident that the atomic orbitals of the N atom in the sensor molecules took more proportion in LUMO than in HOMO. This led to an increased electron density of the N6 upon excitation to the S₁ state. Consequently, the N–H bond length in the sensor was shortened in the S₁ state resulting in the occurrence of ESPT process in each sensor molecule.

4. Conclusions

In summary, the present paper has reported anion chemosensors based on salicylidene Schiff bases, salicylaldehyde-oaminophenol (SA1), 3,5-dimethyl-salicylaldehyde-o-aminophenol (SA2), and 3,5-dichloro-salicylaldehyde-o-aminophenol (SA3), for colorimetric detection of fluoride ions. The sensing mechanisms were also investigated based on experimental methods combined with theoretical calculations. The salicylidene derivatives showed maximum absorption (λ_{abs}) and emission (λ_{em}) at wavelengths ranges of 341-357 nm and 407-427 nm, respectively. All compounds showed high sensitivity in colorimetric detection of Fin CH₃CN solutions with a binding stoichiometry of one F⁻ ion per sensor molecule. Although SA3 showed maximum F⁻ binding affinity $(8.30 \times 10^3 \text{ M}^{-1})$ and highest stability in keto-form, it provided lowest selectivity in F^- detection. Therefore, $\boldsymbol{SA1}$ and SA2 are selected as promising F- sensors due to their high selectivity with a low detection limit (LOD). Theoretical calculations confirmed the presence of intramolecular charge transfer character of the transitions from HOMO to LUMO of all compounds. Based on DFT and ESP calculations, it is revealed that F⁻ detection could occur through the interaction between F⁻ anion and H atom of the OH moieties of the sensor molecules.

Author statement

Buchitar Nakwanich: Conceptualization, Methodology, Data curation, Writing - original draft. Amonchat Koonwong: Data curation, Writing- Original draft preparation, Investigation

Anwaraporn Suramitr: Writing- Reviewing. Panida Prompinit: Investigation. Rungtiva P. Poo-arporn: Investigation. Supa Hannongbua: Software, Investigation. Songwut Suramitr: Supervision, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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References

- [1] J. Du, M. Hu, J. Fan, X. Peng, Fluorescent chemodosimeters using "mild" chemical events for the detection of small anions and cations in biological and environmental media, Chem. Soc. Rev. 41 (12) (2012) 4511–4535.
- [2] V. Amendola, D. Esteban-Gómez, L. Fabbrizzi, M. Licchelli, What anions do to N- H-containing receptors, Acc. Chem. Res. 39 (5) (2006) 343-353.
- [3] Z.Q. Liu, M. Shi, F.Y. Li, Q. Fang, Z.H. Chen, T. Yi, et al., Highly selective two-photon chemosensors for fluoride derived from organic boranes, Org. Lett. 7 (24) (2005) 5481–5484.

- [4] H.S. Horowitz, The 2001 CDC recommendations for using fluoride to prevent and control dental caries in the United States, J. Public Health Dent. 63 (1) (2003) 3–8.
- [5] R.J. Carton, Review of the 2006 United States National Research Council report: fluoride in drinking water, Fluoride 39 (3) (2006) 163–172.
- [6] K.L. Kirk, Biochemistry of inorganic fluoride, in: Biochemistry of the Elemental Halogens and Inorganic Halides, Springer, 1991, pp. 19–68.
- [7] V. Kumar, M. Kaushik, A. Srivastava, A. Pratap, V. Thiruvenkatam, T.G. Row, Thiourea based novel chromogenic sensor for selective detection of fluoride and cyanide anions in organic and aqueous media, Anal. Chim. Acta 663 (1) (2010) 77–84.
- [8] P. Singh, M. Barjatiya, S. Dhing, R. Bhatnagar, S. Kothari, V. Dhar, Evidence suggesting that high intake of fluoride provokes nephrolithiasis in tribal populations, Urol. Res. 29 (4) (2001) 238–244.
- [9] A.J. Malin, C. Till, Exposure to fluoridated water and attention deficit hyperactivity disorder prevalence among children and adolescents in the United States: an ecological association, J. Environ. Health 14 (1) (2015) 17.
- [10] Y. Michigami, Y. Kuroda, K. Ueda, Y. Yamamoto, Determination of urinary fluoride by ion chromatography, Anal. Chim. Acta 274 (2) (1993) 299–302.
- [11] M. Melaimi, F.P. Gabbaï, A heteronuclear bidentate Lewis acid as a phosphorescent fluoride sensor, J. Am. Chem. Soc. 127 (27) (2005) 9680–9681.
- [12] Z.J. Chen, L.M. Wang, G. Zou, L. Zhang, G.J. Zhang, X.F. Cai, et al., Colorimetric and ratiometric fluorescent chemosensor for fluoride ion based on perylene diimide derivatives, Dyes Pigm. 94 (3) (2012) 410–415.
- [13] M. Lee, S. Jo, D. Lee, Z. Xu, J. Yoon, A new naphthalimide derivative as a selective fluorescent and colorimetric sensor for fluoride, cyanide and CO2, Dyes Pigments 120 (2015) 288–292.
- [14] J.M. Eun, B. Roy, A.K. Han, Turn-on" fluorescent sensing with "reactive" probes, Chem. Commun. 47 (27) (2011) 7583–7601.
- [15] T.H. Kim, T.M. Swager, A fluorescent self-amplifying wavelength-responsive sensory polymer for fluoride ions, Angew. Chem. Int. Ed. 42 (39) (2003) 4803–4806.
- [16] A.M. Alkilany, S.E. Lohse, C.J. Murphy, The gold standard: gold nanoparticle libraries to understand the nano-bio interface, Accounts Chem. Res. 46 (3) (2013) 650–661.
- [17] Y. Zhou, J.F. Zhang, J. Yoon, Fluorescence and colorimetric chemosensors for fluoride-ion detection, Chem. Rev. 114 (10) (2014) 5511–5571.
- [18] C.B. Da Silva, T. Kroetz, F.S. Santos, F.S. Rodembusch, Synthesis and photophysical characterization of proton transfer-based thiourea derivatives: Potential application as colorimetric naked-eye chemosensor for fluoride detection in solution, J. Braz. Chem. Soc. 28 (9) (2017) 1830–1841.
- [19] E. Hadjoudis, I.M. Mavridis, Photochromism and thermochromism of Schiff bases in the solid state: structural aspects, Chem. Soc. Rev. 33 (9) (2004) 579–588.
- [20] G.Y. Li, D. Liu, H. Zhang, W.W. Li, F. Wang, Y.H. Liang, TDDFT study on the sensing mechanism of a fluorescent sensor for fluoride anion: inhibition of the ESPT process, Spectrochimica Acta Part A: Mol. Biomol. Spectrosc. 149 (2015) 17–22.
- [21] Y.M. Hijji, B. Barare, A.P. Kennedy, R. Butcher, Synthesis and photophysical characterization of a Schiff base as anion sensor, Sens. Actuat. B: Chem. 136 (2) (2009) 297–302.
- [22] S. Maity, M. Shyamal, P. Mazumdar, G.P. Sahoo, R. Maity, G. Salgado-Morán, et al., Solvatochromism and turn-off fluorescence sensing property of N, N'-bis (3-pentyl) perylene-3, 4, 9, 10-bis (dicarboximide) towards nitroaromatics and photophysical study of its microstructures, J. Mol. Liq. 224 (2016) 255–264.
- [23] R. Hein, P.D. Beer, J.J. Davis, Electrochemical anion sensing: Supramolecular approaches, Chem. Rev. 120 (2020) 1888–1935.
- [24] C. Qinghui, D.A. Medvetz, P. Yi, A polymeric colorimetric sensor with excited-state intramolecular proton transfer for anionic species, Chem. Mater. 19 (26) (2007) 6421–6429.
- [25] Gaussian09 RA. 1, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, GA Petersson et al., Gaussian. Inc, Wallingford CT. 2009.
- [26] Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao, A long-range-corrected time-dependent density functional theory, J. Chem. Phys. 120 (2004) 8425–8433.
- [27] T. Yanai, D.P. Tew, N.C. Handy, A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP), Chem. Phys. Lett. 393 (2004) 51–57.
- [28] W.J. Hehre, R. Ditchfield, J.A. Pople, Self-consistent molecular orbital methods. XII. Further extensions of gaussian-type basis sets for use in molecular orbital studies of organic molecules, J. Chem. Phys. 56 (5) (1972) 2257–2261.
- [29] C. Van Caillie, R.D. Amos, Geometric derivatives of density functional theory excitation energies using gradient-corrected functionals, Chem. Phys. Lett. 317 (1) (2000) 159–164.
- [30] N. Klinhom, N. Saengsuwan, S. Sriyab, P. Prompinit, S. Hannongbua, S. Suramitr, Photophysical properties for excited-state intramolecular proton transfer (ESIPT) reaction of N-salicylidene-o-aminophenol: experimental and DFT based approaches, Spectrochim. Acta A Mol. Biomol. Spectrosc. 206 (2019) 359–366.
- [31] A. Pedone, Role of solvent on charge transfer in 7-aminocoumarin dyes: new hints from TD-CAM-B3LYP and state specific PCM calculations, J. Chem. Theory Comput. 9 (9) (2013) 4087–4096.
- [32] S. Simon, M. Duran, J.J. Dannenberg, How does basis set superposition error change the potential surfaces for hydrogen-bonded dimers? J. Chem. Phys. 105 (1996) 11024–11031.

- [33] A. Costela, I. Garcia-Moreno, R. Mallavia, F. Amat-Guerri, J. Barroso, R. Sastre, Proton-transfer lasers based on solid copolymers of modified 2-(2'-hydroxyphenyl) benzimidazoles with methacrylate monomers, Opt. Commun. 152 (1-3) (1998) 89–95.
 [34] Q. Lin, B. Sun, Q.P. Yang, Y.P. Fu, X. Zhu, T.B. Wei, et al., Double metal
- [34] Q. Lin, B. Sun, Q.P. Yang, Y.P. Fu, X. Zhu, T.B. Wei, et al., Double metal ions competitively control the guest-sensing process: a facile approach to stimuli-responsive supramolecular gels, Chem. Eur. J. 20 (36) (2014) 11457– 11462.
- [35] J. Wu, G. Lai, Z. Li, Y. Lu, T. Leng, Y. Shen, et al., Novel 2, 1, 3-benzothiadiazole derivatives used as selective fluorescent and colorimetric sensors for fluoride ion, Dyes Pigm. 124 (2016) 268–276.
- [36] Y.L. Leng, J.H. Zhang, Q. Li, Y.M. Zhang, Q. Lin, H. Yao, et al., An easy prepared dual-channel chemosensor for selective and instant detection of fluoride based on double Schiff-base, Spectrochim. Acta A Mol. Biomol. Spectrosc. 167 (2016) 116–121.
- [37] S. Sriyab, M.P. Gleeson, S. Hannongbua, S. Suramitr, Photophysical properties and computational investigation on substituent effects on the structural and electronic properties of 3, 6-di (thiophene-2-yl)-carbazole-based derivatives, J. Mol. Struct. 1125 (2016) 532–539.
- [38] Y.X. Tan, Z.J. Zhang, Y. Liu, J.X. Yu, X.M. Zhu, D.Z. Kuang, et al., Synthesis, crystal structure and biological activity of the Schiff base organotin (IV) complexes based on salicylaldehyde-o-aminophenol, J. Mol. Struct. 1149 (2017) 874–881.