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Zoualou Arvel Consty, Yanxia Zhang, Yuankang Xu

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A simple sensor based on imidazo[2,1-*b*]thiazole for recognition and differentiation of Al³⁺, F⁻ and PPi

Zoualou Arvel Consty, Yanxia Zhang* and Yuankang Xu*

School of chemistry and chemical engineering, University of Jinan, Jinan 250022, China.

***Corresponding author**: Yanxia Zhang, E-mail address: chm_zhangyx@ujn.edu.cn. Yuankang Xu, E-mail address: chem_xuyk@hotmail.com.



Graphical abstract



- A new simple fluorescence sensor (**X**) was designed and synthesized based on 2,3dihydroxybenzaldehyde.
- X could be used as multifunctional sensor for sequential detection of Al³⁺, F⁻ and PPi.
- The detection limits for Al³⁺, F⁻ and PPi were calculated to be 3.57×10^{-8} M, 9.24×10^{-9} M and 3.14×10^{-8} M, respectively.
- The binding details and sensing mechanism for Al³⁺, F⁻ and PPi were proposed and proved by theoretical calculation.
- X was proved to have practical application potential by real water sample experiment and test paper strip experiment.

Abstract

Based on imidazo[2,1-*b*]thiazole and 2,3-dihydroxybenzaldehyde, a simple sensor, (E)-N'-(2,3dihydroxybenzylidene)imidazo[2,1-b]thiazole-6-carbohydrazide (**X**), was designed and synthesized and its fluorescence responses to various ions were explored in DMF/H₂O buffer solution (v:v = 1:1, tris = 10 mM, pH = 7.4). The **X** could be used as "turn on" sensor to detect Al³⁺. The resultant complex **X**[Al³⁺] could be used as a new multifunctional sensor to recognition of F⁻ through the further enhancement of fluorescence intensity and to detection of PPi by the fluorescence quenching. The detection limits for Al³⁺, F⁻ and PPi were calculated to be 3.57×10^{-8} M, 9.49×10^{-9} M and 3.24×10^{-8} M, respectively. According to ESI-MS studies, the binding ratio for Al³⁺ and F⁻ were determined both as 1:1. Otherwise, the binding details and sensing mechanism for Al³⁺, F⁻ and PPi were proposed and proved by theoretical calculation. The application experiments proved that **X** could be made into test paper strips for Al³⁺, F⁻ and PPi and could be used as a sensor to recognition of Al³⁺, F⁻ and PPi in tap water.

Keywords: Schiff base, Al³⁺, F⁻, PPi, Gaussian calculations, Practical application.

1. Introduction

As is known to all, metal ions are important to both human health and plant growth, which also play an essential role in medicine, chemistry, industry and other fields [1]. For instance, aluminum is one of the most abundant metal elements in the earth's, accounting for about 8 percent, and is extensively used in various aspects, such as daily necessities, manufacturing industry, medicine and so on [2, 3]. Sometimes, aluminum could be inevitable ingested by the body even in excess of the normal daily intake of 3-10 milligrams because it is widely used in food flavoring agents, aluminum based pharmaceuticals and cooking utensils [4]. However, excessive accumulation of aluminum in the body could cause damage to the nervous system and increase the risk of various diseases, including Alzheimer's disease, Parkinson's disease, amyotrophic lateral sclerosis, etc [5-7].

Moreover, the increase of aluminum concentration in soil will also restrict the growth and development of plants [8-10]. So, it is imperative to quantitatively and efficiently detect aluminum in organisms and environments.

In addition, anions also play a fundamental role in human physiological processes, especially fluoride and pyrophosphate [11, 12]. Fluoride is the smallest anions with the strongest electronegativity, which mainly distributed in natural water and the tissues of human body [13]. Proper levels of fluoride are necessary for human body and could enhance the structural stability of bones and teeth, helping to prevent tooth decay and osteoporosis [14, 15]. However, excessive intake of fluoride could lead to various serious diseases, including dental and skeletal fluorosis and immune system disruption, while the deficiency of aluminum is also a major factor to stomach illness, tooth decay, osteoporosis, etc [16-18]. As another important anion in the human body, pyrophosphate ($P_2O_7^4$, PPi), is high in body fluids and is involved in many vital activities, such as RNA and DNA replication, metabolism processes, ATP hydrolysis, the synthesis of protein and other physiological processes [19-21]. Moreover, pyrophosphate is an important index in the diagnosis of arthritis, chondrocalcinosis, calcium pyrophosphate deposition, rheumatism, etc [22-24]. For these reasons, the detection of fluoride and pyrophosphate is particularly important and valuable.

Recently, fluorescence sensor for metal ions and anions has become one of the hot research fields, which mainly due its simple operation, high selectivity and sensitivity, real-time detection and functional diversity [25, 26]. Nowadays, a number of sensors that could identify metal ions and subsequently anions have been reported, such as Al³⁺/F⁻ and Al³⁺/PPi [27, 28]. However, aluminum is a kind of metal ion which is difficult to detect because of its strong hydration ability and poor coordination ability [29]. Therefore, most sensors for aluminum are designed and synthesized with N and O complexation sites to improve the ability of recognition [30]. After binding with aluminum, the fluorescence signal of sensor is changed under the excited state, thus realizing the specific recognition of metal ions [31-35]. In addition, fluoride and pyrophosphate could restore the sensor' original optical properties, realizing the cycle of optical properties, because they could extract aluminum from the complex of sensor-aluminum to free the sensor [28, 36]. Moreover, some sensors containing -OH and -NH groups have been developed to detection of fluoride by forming hydrogen bonds because fluoride is the most electronegative anion [37-40]. However, these reported sensors could only identify a single ion or two ions in sequence. As a result, it is still full of challenge and

charm to design new sensors that have multiple recognition capabilities for aluminum, fluoride and pyrophosphate.

Up to now, Schiff base synthesized based on a variety of aldehydes could be used as a kind of fluorescent sensor with simple synthesis and strong recognition ability [41, 42]. Recently, in our group, some Schiff base were designed and synthesized by different aldehydes, including salicylaldehyde, 2-hydroxy-1-naphthaldehyde and 3-ethoxy-2-hydroxybenzaldehyde, which could be used as a sensor for detection of various ions [43-46]. Similarly, these sensors could form a cavity near three sites that the oxygen atom on the hydroxy group and the nitrogen atoms on the C=N bond and the imidazo group for complexing metal ions. However, these sensors contain only one hydroxyl group in their structure, which results in their single performance that could only achieve the selective recognition of one ion. In this study, a new fluorescent sensor (X) based on imidazo[2,1-*b*]thiazole and 2,3-dihydroxybenzaldehyde was designed and synthesized. imidazo[2,1-*b*]thiazole with two conjugated rings was a potential fluorescent compound and had been used in the synthesis of fluorescent sensors for many times [45-47]. 2,3-dihydroxybenzaldehyde differed from other aldehydes in that it contains two hydroxyl groups, making it more soluble and able to recognize ions than aldehydes with one hydroxyl group.

As expected, **X** could be used as a multifunctional sensor for sequential detection of aluminum, fluoride and pyrophosphate in DMF/H₂O (v/v = 9/1, tris = 10 mM, pH = 7.4) buffer solution. The fluorescence intensity of the sensor was very weak and increased after binding with aluminum due to the formation of the complex **X**[Al³⁺]. Moreover, fluoride could further enhance the fluorescence intensity of the above system, while pyrophosphate could make the optical properties of system above disappear, displaying different fluorescence behaviors.

2. Results and discussion

As shown in scheme 1, **X** was designed and synthesized by the reaction of imidazo[2,1b]thiazole-6-carbohydrazide and 2,3-dihydroxybenzaldehyde with 53.9 % yield according to the synthetic route [46]. Moreover, the structure of **X** was characterized by ¹H NMR (Fig. S1), ¹³C NMR (Fig. S2), FTIR (Fig. S3), ESI-MS (Fig. S4).



Scheme 1. Synthesis routes of **X**. Conditions: (a) THF/ethanol, r.t./refluxed, 20 h/4 h; (b) ethanol, r.t., overnight; (c) ethanol, r.t., 12 h.

2.1. The sensing behavior of X to Al³⁺

Primarily, the time effect on the fluorescence intensity of **X** (1×10^{-5} M) in the presence of Al³⁺ (10 equiv.) were explored in DMF/H₂O buffer solution (v:v = 1:1, tris 10 mM, pH = 7.4). As illustrated in Fig. S5, in the presence of Al³⁺, the fluorescence intensity of **X** was gradually increased with the time from 0 to 12 minutes and remained unchanged for the next 4 minutes. Obviously, the recognition time of **X** for Al³⁺ was about 12 minutes, which was lower than many reported sensors. So, in order to ensure the accuracy of test results, 15 minutes complexation time should be applied in all subsequent tests.

The sensing behavior and recognition ability of **X** toward various metal ions (Al³⁺, Zn²⁺, Ga³⁺, Cd²⁺, Ag⁺, Hg²⁺, Mg²⁺, K⁺, Mn²⁺, In³⁺, Li⁺, Cu²⁺, Fe³⁺, Cr³⁺, Ni²⁺ and Co²⁺) were roundly explored by fluorescence spectral and UV-vis spectral in DMF/H₂O buffer solution (v:v = 1:1, tris 10 mM, pH = 7.4). As shown in Fig. 1a, **X** with a concentration of 1 ×10⁻⁵ M displayed no fluorescence, which may be caused by the PET mechanism. When various metal ions (10 equiv.) were respective added to **X**, there was a significant fluorescence enhancement at 497 nm caused only by the addition of Al³⁺, about 24 times (Fig. 1b). Meanwhile, the other metal ions could lead to a little or no change in fluorescence intensity, such as Zn²⁺ and Co²⁺. Moreover, as shown in Fig. S6, the fluorescence response of **X** to Al³⁺ was explored in the presence of other metal ions. As a result, the fluorescence intensity of **X** in the presence of other metal ions displayed varying degrees of enhancement after addition of Al³⁺. So, **X** could be used as a selective sensor for Al³⁺ even in the presence of some other competitive metal ions. The UV-vis spectral of **X** was also investigated in the absence and

presence of various metal ions (10 equiv.). As shown in Fig. S7, the free **X** exhibited an absorbance band at 305 nm. Obviously, there was many metal ions could cause change in the UV absorption spectrum, including Al^{3+} , Cu^{2+} , Co^{2+} , etc, indicating that **X** could not only form fluorescent complexes (**X**[Al^{3+}]) with Al^{3+} but also form complexes without fluorescence properties with other metal ions. Evidently, **X** could be used as a specific sensor for Al^{3+} .



Fig. 1. (a) fluorescence spectra of X in the presence of various metal ions (10 equiv.); (b) the changes (I / I_0) in fluorescence intensity caused by the addition of various metal ions.

Next, the fluorescence titration and ultraviolet titration were further carried out in DMF/H₂O buffer solution to investigate the sensing behavior of **X** toward Al³⁺ in details. As shown in Fig. 2a, the fluorescence intensity at 497 nm increased gradually with the accumulation of Al³⁺ from 0 to 8 equivalents and reached a plateau with no enhancement upon further addition of Al³⁺, accompanying with color change from colorless to yellow-green. The fluorescence quantum yield of **X** increased from 0.001 to 0.105 when addition of Al³⁺. displaying an obvious fluorescence turn-on behavior. Meanwhile, as shown in Fig. S8, as the gradual addition of Al³⁺ from 0 to 10 equiv., the UV absorption intensity of **X** decreased gradually at 305 nm and increased gradually at 323 nm and 384 nm accompanied by a distinct isosbestic point at 320 nm, indicating that a stable complex **X**[Al³⁺] was formed between **X** and Al³⁺. In addition, based on the fluorescence titration, the detection limit and complexation constant of **X** for Al³⁺ were calculated to be 3.57×10^{-8} M (Formula 2, Y = 2.77X + 18.95, R² = 0.9987, Fig. 2b) and 5.09×10^4 M⁻¹ (Equation 3, Y = 4.14×10⁻⁸X - 0.00151, R² = 0.9929, Fig. S9), respectively.



Fig. 2. (a) Fluorescence spectra of **X** with the addition of Al^{3+} (0 - 11 equiv.); (b) Fluorescence intensity of **X** at 497 nm with the addition of Al^{3+} (0 - 6 × 10⁻⁷ M).

2.2. The sensing behavior of X[Al³⁺] to F⁻ and PPi

Furthermore, the reversibility was another important index to measure the properties of sensor. So, the fluorescence intensity of $\mathbf{X}[Al^{3+}]$ was measured after treatment with various anions, including F⁻, PPi, Cl⁻, Br⁻, I⁻, CrO₄²⁻, NO₂⁻, HCO₃⁻, S²⁻, S₂O₃⁻, SO₄²⁻, NO₃⁻, HSO₃⁻ and BF₄⁻. As shown in Fig. 3, the fluorescence intensity of $\mathbf{X}[Al^{3+}]$ exhibited medium fluorescence in DMF/H₂O buffer solution (1:1, tris 10 mM, pH = 7.4) under excitation wavelength of 340 nm. Upon addition of various anions, the fluorescence intensity of $\mathbf{X}[Al^{3+}]$ was further enhanced by the addition of F⁻ and completely disappeared in the presence of PPi, display different fluorescence emission behaviors. However, the further change in the fluorescence intensity of $\mathbf{X}[Al^{3+}]$ caused by other anions were not significant, whether it was increased or decreased. Therefore, the complex $\mathbf{X}[Al^{3+}]$ could be further used as a new sensor for the multiple detection of F⁻ and PPi, which was different from the traditional sensors that sequential detection Al^{3+} and F⁻/PPi.



Fig. 3. Fluorescence spectra of $X[Al^{3+}]$ with the addition of 10 equiv. various anions in DMF/H₂O buffer solution (1:1, tris 10 mM, pH = 7.4).

Analogously, the time effect on the fluorescence intensity of $\mathbf{X}[Al^{3+}]$ in the presence of F⁻ (10 equiv.) were also explored in Fig. S5. In the presence of Al^{3+} , the fluorescence intensity of \mathbf{X} was gradually increased with the time from 0 to 5 minutes and reached a platform after 5 minutes. So, 10 minutes complexation time was used in all subsequent experiments related to F⁻.

As shown in Fig. 4a, F⁻ could cause the fluorescence intensity of $X[A]^{3+}]$ to be further enhanced regardless of the presence or absence of other anions, indicating that the complex $X[A]^{3+}]$ showed excellent selectivity for F⁻ even in the presence of other interference anions. As shown in Fig. 4b, the fluorescence intensity at 497 nm gradually increased with the incremental addition of F⁻ from 0 to 15 equiv., after that the intensity remained stable. At the same time, the fluorescence quantum yield was increased to 0.173 after addition of F⁻, corresponding to the fluorescence became bright and visible. Moreover, on the basic of the fluorescence titration experiment, the detection limit and complexation constant of $X[A]^{3+}]$ for F⁻ were calculated to be 9.49×10^{-9} M (Formula 2, Y = 10.43X + 495.58, R² = 0.9898, Fig. 4c) and 1.76×10^4 M⁻¹ (Equation 3, Y = 0.02548X + 8.89E-5, R² = 0.9871, Fig. 4d), respectively.



Fig. 4. (a) Competitive selectivity of $\mathbf{X}[Al^{3+}]$ toward F⁻ in the presence of other anions ions (10 equiv.); (b) Fluorescence spectra titration of $\mathbf{X}[Al^{3+}]$ with the gradual addition of F- (0 - 15 equiv.); (c) Fluorescence intensity of **X** at 497 nm with the addition of Al^{3+} (1 × 10⁻⁷ M - 8 × 10⁻⁷ M); (d) Benesi-Hildebrand plot for determination of binding constant of **X** with F⁻.

As shown in Fig. 5a, it could be found that the decrease in fluorescence intensity caused by PPi in the presence of other anions was similar to that caused by PPi alone, indicating that the complex $\mathbf{X}[Al^{3+}]$ had a good selectivity to PPi even in the presence of other co-existing anions. As shown in Fig. 5b, the fluorescence intensity at 497 nm gradually decreased with the incremental addition of PPi from 0 to 3 equiv. and almost completely disappeared when the concentration of PPi was added to 5×10^{-5} M. Moreover, As shown in Fig. 5c, a good linear relationship ($R^2 = 0.9893$) was obtained between the I₀ - I and low concentrations of PPi (1×10^{-7} M - 1×10^{-6} M), where I and I₀ were the fluorescence intensity of $\mathbf{X}[Al^{3+}]$ with and without PPi. The detection limit of $\mathbf{X}[Al^{3+}]$ for PPi were calculated to be 3.24×10^{-8} M according to the formula 2. And, the complexation constant of $\mathbf{X}[Al^{3+}]$ for PPi was also calculated to be 1.06×10^{5} M⁻¹ (Equation 3, $\mathbf{Y} = 0.01988\mathbf{X} + 0.00556$, $R^2 = 0.9891$, Fig. 5d).



Fig. 5. (a) Competitive selectivity of $X[A]^{3+}$ toward PPi in the presence of other anions ions (10

equiv.); (b) Fluorescence spectra titration of X[Al³⁺] with the gradual addition of PPi (0 - 5 equiv.);
(c) Fluorescence intensity of X[Al³⁺] at 497 nm with the addition of PPi (1 × 10⁻⁷ M - 1 × 10⁻⁶ M);
(d) Benesi-Hildebrand plot for determination of binding constant of X[Al³⁺] with PPi.

Some multifunctional sensors for sequential detection of AI^{3+} and F^{-} or AI^{3+} and PPi were listed in Table 1, which could only identify one metal ion and an anion sequentially. In this work, **X** could be used as a primary sensor for detection of AI^{3+} and the resultant **X**[AI^{3+}] could also be used as a secondary sensor for F^{-} and PPi, which was one of its advantages. Moreover, the detection limits for AI^{3+} , F^{-} and PPi were calculated to be 3.57×10^{-8} M, 9.49×10^{-9} M and 3.24×10^{-8} M, respectively, which was obviously better than the reported sensors. Obviously, **X** had some advantages in functional diversity and sensitivity over other sensors.

Table 1. Comparison to some published sensors.

Solvent system	Primary sensor	Secondary sensor	Ref.
MeOH	Al ³⁺ (turn on, 9.24×10^{-7} M)	F ⁻ (turn off, 1.4×10^{-5} M)	[36]
DMF/H ₂ O (1:1)	Al^{3+} (turn on, $1.1 \times 10^{-7} M$)	F ⁻ (turn off, 1.47×10^{-6} M)	[27]
EtOH/H ₂ O (3:7)	Al ³⁺ (turn on, 5.36×10^{-6} M)	F- (turn off, 8.05×10^{-6} M)	[49]
DMSO	Al ³⁺ (turn on, 3.38×10^{-8} M)	F- (turn off, 2.62×10^{-7} M)	[50]
H ₂ O	Al ³⁺ (turn on, 6.2×10^{-8} M)	$F^{\text{-}}$ (turn off, $3.26\times 10^{\text{-7}}$ M)	[51]
EtOH/H ₂ O (1:99)	Al ³⁺ (turn on, 2.94×10^{-8} M)	PPi (turn off, 2.74×10^{-7} M)	[48]
DMF/H ₂ O (5:1)	Al ³⁺ (turn on, 4.96×10^{-7} M)	PPi (turn off, 5.70×10^{-7} M)	[28]
DMF/H ₂ O (4:1)	Al ³⁺ (turn on, 3.9×10^{-7} M)	PPi (turn off, 7.5×10^{-7} M)	[33]
MeOH/H ₂ O (7:3)	Al ³⁺ (turn on, 8.6×10^{-7} M)	PPi (turn off, 2.19×10^{-6} M)	[52]
MeOH/H ₂ O (1:1)	Al ³⁺ (turn on, 7.7×10^{-8} M)	PPi (turn off, 1.71×10^{-6} M)	[53]
DMF/H ₂ O (1:1)	Al ³⁺ (turn on, 3.57×10^{-8} M)	F ⁻ (turn on, 9.49×10^{-9} M)	This
		PPi (turn off, 3.24×10^{-8} M)	work

2.3. The effect of pH

In addition, it is important for recognition of ions by the sensor to determine the pH response range. As shown in Fig. S14, the fluorescence intensity of **X**, **X**[Al³⁺], **X**[Al³⁺ + PPi] and **X**[Al³⁺ + F⁻] were monitored at various pH values (2 - 12) in DMF/H₂O buffer solution (v/v = 1:1, tris = 10 mM). **X** exhibited weak and stable fluorescence in the pH range of 2 to 12 under the excitation

wavelength of 340 nm. The fluorescence intensity of $\mathbf{X}[Al^{3+}]$ decreased gradually with the increased of pH from 2 to 12. At the high pH (> 5.6), the formation of the complex $\mathbf{X}[Al^{3+}]$ was affected by the high concentration of OH⁻. Moreover, PPi could quench the fluorescence of the $\mathbf{X}[Al^{3+}]$ in a pH range of 2 to 10. In addition, the resultant $\mathbf{X}[Al^{3+}]$ could efficiently detection of F⁻ at a pH of 7.4. The results of pH experiments indicated that \mathbf{X} could be used as a multifunctional sensor for sequential detection of Al³⁺, F⁻ and PPi at a pH of 7.4, indicating that \mathbf{X} had potential for the practical application.

2.4. The binding mode and theoretical calculations

The complexation ratio between sensor and ions was investigated by mass spectrometric titration. As shown in Fig. S11, a molecular ion peak m/z at 362.97 corresponded to the molecular weight of $[X - H^+ + AI^{3+} + CI^-]^+$ (m/z calculated 362.99), which proved that **X** could form stable complex with AI^{3+} at a stoichiometric ratio of 1:1. Furthermore, the Fig. S12 showed the ESI mass spectra of **X** in the presence of AI^{3+} After addition of F⁻. Obviously, a new molecular ion peak was appeared at 347.02 m/z, which could be attributed to the species of $[X - H^+ + AI^{3+} + F^-]^+$ (m/z calculated 362.99), indicating that **X**[AI³⁺] and F⁻ complexed with a 1:1 stoichiometry. Meanwhile, the 1:1 stoichiometry between **X**[AI³⁺] and PPi could also be demonstrated by the Benesi-Hildebrand equation with a good linear relationship (R² = 0.9891) between 1 / (I_0 - I) and 1 / PPi. Therefore, the complexation ratio of sensor to AI³⁺, F⁻ and PPi were all 1:1.

Based on all of the above experiments, the possible binding mode of **X** with Al^{3+} , F^{-} and PPi were illustrated in Scheme 2. **X** could form a moderate fluorescence complex with Al^{3+} and Cl⁻. When addition of PPi to the **X**[Al³⁺], PPi could extract Al^{3+} from the complex to free the sensor, resulting in fluorescence quenching of the system. As shown in Fig. S13, after addition of F⁻, the absorbance peaks of **X**[Al³⁺] at 325 nm and 384 nm were increased without wavelength shift. In addition, the isosbestic point at 320 nm was not affected by the addition of F⁻ at all. The results showed that, different from PPi, F⁻ could replace Cl⁻ to form more stable ternary compounds with **X** and Al^{3+} , which corresponded to the result of ESI-mass. Moreover, F⁻ with highly electronegative could also form hydrogen bond with the free hydroxyl next to it.



Scheme 2. The possible binding mode for X, $X[A1^{3+}]$ and $X[A1^{3+}][F^{-}]$.

The optimal structures and energy levels of **X**, **X**[Al³⁺] and **X**[Al³⁺][F⁻] were investigated using the Gaussian 09 program with the basis set of B3LYP/6-31 G(d) to verify the feasibility of the structures of **X**, **X**[Al³⁺] and **X**[Al³⁺][F⁻] and explore the sensing mechanism for ions. The optimal structures of **X**, **X**[Al³⁺] and **X**[Al³⁺][F⁻] were shown in Fig. 6. For free **X**, the whole molecule was in the same plane, showing good planarity. After binding with Al³⁺ and Cl⁻, a 144.4-degree angle was maintained between the imidazo[2,1-*b*]thiazole part and 2,3-dihydroxybenzaldehyde part of molecular. After further addition of F⁻, a ternary complex with good planarity and stability was form between **X**, Al³⁺ and F⁻. Obviously, the structure of **X**[Al³⁺][F⁻] was more stable and more similar to the **X**'s than **X**[Al³⁺]'s. The results showed that the proposed structures of complex **X**[Al³⁺] and **X**[Al³⁺][F⁻] were feasible, which proved that the binding mode of the sensor to Al³⁺ and F⁻ was possible.



Fig. 6. The optimized molecular structure of **X**, $\mathbf{X}[Al^{3+}]$ and $\mathbf{X}[Al^{3+}][F^{-}]$, where light-gray, blue, white, pink, cyan and green spheres denote C, O, N, H, Al, F and Cl atom, respectively.

Moreover, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were also shown in Fig. 7. For free **X**, most of the electrons in HOMO orbital were localized on the benzene ring, while the electrons in the LUMO orbital were distributed throughout the whole molecule. Based on the PET mechanism, **X** exhibited very weak fluorescence due to the partial electron transfer when excited. For **X**[Al³⁺] and **X**[Al³⁺][F⁻], the HOMO was still concentrated near the benzene ring, while the LUMO was distributed near the benzene ring and metal ions, indicating that electron transfer was partially inhibited under excitation. So after binding ions, **X**[Al³⁺] and **X**[Al³⁺][F⁻] exhibited the appropriate fluorescence. In contrast, **X**[Al³⁺][F⁻] showed stronger fluorescence than **X**[Al³⁺] because of its better planarity and conjugation. Meanwhile, the energy gaps between HOMO and LUMO of **X**, **X**[Al³⁺] and **X**[Al³⁺][F⁻] were calculated to be 3.98 eV, 3.24eV and 3.06eV, respectively. The results showed that the sensor could identify Al³⁺ and F⁻ based on photoinduced electron transfer (PET) and the chelation enhanced fluorescence mechanism (CHEF). The calculation results were highly consistent with the experimental results.



Fig. 7. HOMO and LUMO of **X**, **X**[A1³⁺] and **X**[A1³⁺][F⁻].

2.5. Application of X in real water sample

In order to explore the practical application ability of sensor, the sensor was applied to detect Al³⁺, F⁻ and PPi in real water samples, and satisfactory results were obtained. The sample solutions of Al³⁺, F⁻ and PPi were prepared from laboratory tap water. The recover experiments were carried

out by adding different concentrations of Al^{3+} , F^{-} and PPi to the sensor. The calculated results were shown in Table 2, the recoveries for Al^{3+} , F^{-} and PPi were within the range of 99.8% - 101.1%, 93.7% - 107.2 and 91.6% - 106.7, respectively. Moreover, the relative standard deviation (RSD) of three measurements was less than 3.47%, which proved that the experimental data was credible and usable. These results indicated that **X** had good selectivity to Al^{3+} , and that **X**[Al^{3+}] could also efficiently detect F^{-} and PPi. Therefore, **X** had potential for practical application in real water system.

Ion	Sample	Ion added (M)	Ion recovered (M)	Recovery (%)	RSD (%)
A1 ³⁺	1	$1.0 imes 10^{-5}$	$9.98 imes10^{-6}$	99.8	1.61
	2	$2.0 imes 10^{-5}$	$2.02 imes 10^{-5}$	101.1	2.18
F	1	$1.0 imes 10^{-5}$	$1.07 imes 10^{-5}$	107.2	3.47
	2	$2.0 imes 10^{-5}$	$1.87 imes 10^{-5}$	93.7	1.48
PPi	1	$1.0 imes 10^{-5}$	$9.16 imes 10^{-6}$	91.6	2.25
	2	$2.0 imes 10^{-5}$	$2.13 imes 10^{-5}$	106.7	3.32

Table 2. Determination of	of Al ³⁺ , F ⁻	and PPi in t	ap samples
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2.6. Practical application on test strips

According to the reported literature [38], the paper test was conducted to check the practicality of the sensor and was shown in Fig. 8. Firstly, filter paper strips were immersed in DMF/H₂O solution of the **X** for 5minutes and then dried in the air. Then the water solution of Al^{3+} , F⁻ and PPi was sequentially added dropwise to the above test paper. In this process, the significant changes in fluorescence could be observed under the UV lamp. Therefore, **X** could be made into test paper strips for qualitative and convenient detection of Al^{3+} , F⁻ and PPi.



Fig. 8. The changes in the color of test paper under the UV lamp (a) \mathbf{X} ; (b) $\mathbf{X} + Al^{3+}$; (c) $\mathbf{X} + Al^{3+}$ + F⁻; (d) $\mathbf{X} + Al^{3+} + PPi$.

Conclusions

In summary, a new simple sensor, X, was synthesized based on imidazo[2,1-b]thiazole and 2,3-

dihydroxybenzaldehyde and was characterized by ¹H NMR, ¹³C NMR, FTIR, ESI-MS. In DMF/H₂O (v/v = 1/1, tris = 10 mM, pH = 7.4) buffer solution, **X** could be used as a "turn-on" sensor for Al³⁺ with good selectivity and sensitivity. Furthermore, F⁻ could further enhance the fluorescence intensity of the above system, while PPi could make the optical properties of system above disappear, displaying different fluorescence behaviors. In addition, the binding model and sensing mechanism for Al³⁺, F⁻ and PPi were proposed by experimental method and proved by theoretical calculation. Otherwise, the application experiments proved that **X** had the potential of practical application. Meanwhile, **X** had been successfully developed as a multifunctional sensor for detecting Al³⁺, F⁻ and PPi, which provided reference and guidance for the design and research of multi-target sensor in the future.

Author statement

Zoualou Arvel Consty is studying for master degree in Department of Chemistry at University of Jinan.

Yanxia Zhang is a teacher in Department of Chemical Engineering, University of Jinan, China.

Yuankang Xu is studying for master degree in Department of Chemistry at University of Jinan.

All authors contribute equally.

Declaration of interests

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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