

Synthesis of Highly Sensitive Fluorescent Probe Based on Tetrasubstituted Imidazole and Its Application for Selective Detection of Ag⁺ Ion in Aqueous Media

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Abstract A small molecule fluorescent probe, 4-[2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazol-1-yl]aniline(L) for detecting Ag⁺ ion was gently synthesized *via* one-pot multi-component reaction catalyzed by H₃[PW₁₂O₄₀] under solvent-free microwave irradiation. When the concentration of Ag⁺ ion changed from 0 to 8.0×10⁻⁶ mol/L in the solution of H₂O/CH₃OH(19:1, volume ratio), the fluorescence emission spectrum was blue-shifted and accompanied by a gradual increase in fluorescence intensity with a low detection limit of 3.0×10⁻¹¹ mol/L. Moreover, UV-Vis absorption titration experiment demonstrated a 1:1 stoichiometric ratio and an association constant of (9.95±0.44)×10⁵ L/mol between probe L and Ag⁺ ion, and thus their complexation mechanism was also proposed and verified. More importantly, this fluorescent probe was remarkably specific for Ag⁺ ion under the interference of other metal ions and exhibited a wide pH application range of 4.0—8.0. Additionally, preliminary application of this probe was also carried out and satisfactory results were shown.

Keywords Fluorescent probe; Imidazole; Ag⁺ ion; Microwave irradiation

1 Introduction

The design and synthesis of fluorescent probes with high selectivity and sensitivity for heavy and transition metal ions have attracted much attention owing to their affection to people's daily life and health^[1,2]. Heavy metal ions, especially Ag⁺ ion, are often used as antimicrobial agents in curative and preventive health care^[3]. However, excessive existence of Ag⁺ ion either in human body or the surroundings can endanger human health and environment. It is reported that thousands of tons of waste silver is annually released to the environment^[4]. Traditionally, methods including atomic absorption spectroscopy, atomic emission spectroscopy, inductively coupled plasma-mass spectroscopy, stripping voltammetry, ultrasound irradiated and small gold-nanoclusters based detector, etc. have been applied to detecting Ag⁺ ion^[5-7]. Although these methods might meet the requirements of fast measurement and good sensitivity, most of them are suffering from one or more limitations, such as expensive apparatus, complex pretreatment procedures of the sample, high solvent consumption, restricted detection limit, etc., which constrain their practical application. Accordingly, highly sensitive and selective probes obtained by facile methods, which enable professionals to monitor environmental silver ions simply and conveniently are entirely justified.

Fluorescent sensors can transfer molecular recognition events into fluorescent signals and offer distinct advantages in terms of their sensitivity, selectivity and *in situ* observation

property. Monitoring in real-time, real-space and the level of analytes is of great interest to many scientists^[8-10]. Especially, chemosensors targeting heavy and transition metal cations, such as Hg²⁺, Pb²⁺, Ag⁺, Fe³⁺ and Cu²⁺, etc., are particularly challenging and have drawn much attention. In most cases, these ions generally act as quenchers *via* the electron transfer or facilitated intersystem crossing processes, which are often accompanied by a red or blue shift of wavelength after the addition of the under-determination metal ions^[11-14]. A number of satisfactory chemosensors for detecting Ag⁺ ion have been reported^[15,16] and most of the probes possess high sensitivity and selectivity, but simultaneously expose some disadvantages: complex synthesis steps consuming large amounts of organic solvents being environment unfriendly and costly; rigorous detecting conditions, *e.g.*, organic solvents or buffer solutions, making the application of the probes limited^[17].

Organic small molecules, such as imidazole derivatives have received considerable attention as sensing probes owing to their nature properties of π -conjugated chromophore backbones^[18]. Importantly, they can be facilely synthesized in one pot from the condensation of cheap raw materials by microwave irradiation. Classically, microwave irradiation as a dielectric heating is the process, in which organic compound consumes electromagnetic energy, which can accelerate the reaction rate hundreds or thousands of times in comparison with the conventional heating^[19]. Thus, the use of microwave irradiation indicates the shorter reaction time, less solvent and catalyst consumption^[20], in other words, more efficient and

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Received December 25, 2017; accepted March 6, 2018.

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eco-friendly. Further, imidazole possesses two nitrogen atoms, which represents a robust and stable heterocyclic compound, and can be further functionalized at positions of C2, C4, C5 and N1(Fig.1)^[21]. With these excellent properties in mind, we aimed at utilizing imidazole derivative to develop a cheap, simple and environmental friendly probe to realize on-site tracking of Ag⁺ ion sensitively and selectively in aqueous solution.

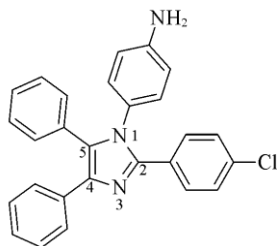


Fig.1 Molecular structure of probe L

Herein, a fluorescent probe, 4-[2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazol-1-yl]aniline(L)(Fig.1) was gently synthesized *via* one-pot multi-component reaction catalyzed by H₃[PW₁₂O₄₀] under the condition of solvent-free microwave irradiation. Characterizations including FTIR spectrum, ¹H and ¹³C NMR spectra, HPLC-MS spectrum and elemental analysis were utilized to confirm the chemical structure of probe L. Fluorescent emission and UV-Vis absorption titration experiments were conducted to explore the detection limit and selectivity of the probe, as well as the stoichiometric ratio and association constant between probe L and Ag⁺ ion. Moreover, probable complexation mechanism between probe L and Ag⁺ ion was proposed and proved by ¹H NMR and ESI-MS spectra.

2 Experimental

2.1 Materials and Characterization

All the reagents obtained from commercial companies (Tianjin Fuyu Chemical Reagent Co., China and Aladdin-reagent Co., China) were analytical reagents and used without further purification. Deionized water was used throughout the experiments. For selectivity experiment of probe L, all the metal salts were in the form of their corresponding nitrates, such as NaNO₃, Fe(NO₃)₂, Fe(NO₃)₃, etc., to exclude the interference of different anions to fluorescence titration experiments. An MCL-3-type microwave reactor(Sichuan University, China) was used for the synthesis of probe L. Melting point was determined on an XT-4 melting point apparatus and the result was not corrected. High resolution liquid chromatography-mass spectrometry(HPLC-MS) and electrospray ionization mass spectrometry(ESI-MS) tests were conducted on an Agilent 1290-microTOF Q II spectrometer. ¹H and ¹³C NMR spectra were obtained on a Bruker AVANCE-500 NMR spectrometer with TMS as the internal standard and DMSO-d₆ as the solvent. FTIR spectrum was obtained on a Shimadzu IRAffinity-1 instrument at a resolution of 4 cm⁻¹ in the range of 500—3500 cm⁻¹ using KBr as pellets. Fluorescent emission spectra titration experiment was conducted on an Edinburgh Instrument FLS920 spectrofluorimeter and the excitation wavelength was 315 nm with slit widths at 3 nm. The UV-Vis absorption spectra

titration experiment was performed on a Perkinelmer equipment in the wavelength range of 200—800 nm with slit widths at 2 nm.

2.2 Synthesis of Probe L

A mixture of *p*-phenylenediamine(1 mmol), benzil(1 mmol), *p*-chlorobenzaldehyde(1 mmol), ammonium acetate(4 mmol), silica-gel(1 g) and H₃[PW₁₂O₄₀](0.0043 g) was fully ground in a mortar, and then transferred to a 50 mL dried round-bottomed flask and heated under microwave irradiation for 15 min at 130 °C. The reaction progress was monitored by TLC on GF254 silica gel plates. After the reaction, the residue was cooled to room temperature and directly purified by column chromatography on 200—300 mesh silica gel [*V*(petroleum ether):*V*(ethyl acetate)=3:1] to obtain light yellow solid powders, yield 66.7%. m.p. 238—239 °C. Fluorescence quantum yield 0.265[detected in 0.05 mol/L H₂SO₄ aqueous solution against quinine sulfate in 0.05 mol/L H₂SO₄(Φ_F=0.55)]. IR(KBr), $\tilde{\nu}/\text{cm}^{-1}$: 3484, 3382(N—H), 3053, 3017(Ar—H), 1624, 1600, 1597, 1518, 1477(C=C, C=N), 1458, 1416, 1290, 1272, 1168, 1119, 1014, 961, 831, 755, 729, 698. ¹H NMR(500 MHz, DMSO-d₆), δ : 7.46(dt, *J*=11.1, 3.0 Hz, 4H), 7.40—7.37(m, 2H), 7.33—7.29(m, 3H), 7.25—7.20(m, 4H), 7.18—7.14(m, 1H), 6.87(d, *J*=8.6 Hz, 2H), 6.43(d, *J*=8.6 Hz, 2H), which were ascribed to protons on benzene rings. 5.34(s, —NH₂, 2H). ¹³C NMR(75 MHz, DMSO-d₆), δ : 148.92 (1-phenyl-C4), 144.93(imidazole-C2), 136.70(2-phenyl-C1), 134.55(imidazole-C5), 132.86(4-phenyl-C1), 132.06 (5-phenyl-C1), 131.11(imidazole-C4), 130.68, 129.62, 128.98, 128.34, 128.17, 128.09(ascribed to non-quaternary carbon of 2-phenyl, 4-phenyl and 5-phenyl.), 126.36(1-phenyl-C3, C5), 124.33 (1-phenyl-C1), 113.75(1-phenyl-C2, C6). HPLC-MS, *m/z*: [M+2]⁺ calcd. for C₂₇H₂₀ClN₃: 423.1346; found: 423.1353.

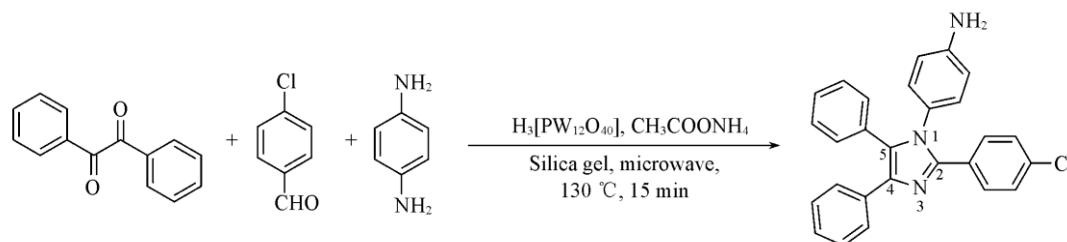
2.3 Preparation of Solutions for Fluorescent Emission and UV-Vis Absorption Spectra Titration Experiments

For solutions of fluorescence titration experiment, a stock solution of probe L(2.0×10⁻⁵ mol/L) was prepared by dissolving probe L in methanol. And a standard stock solution of Ag⁺ ion(2.0×10⁻⁴ mol/L) was obtained by dissolving silver nitrate into deionized water, and the standard stock solution of Ag⁺ ion was continuous diluted with deionized water to different concentrations. The preparation of a solution of probe L(1.0×10⁻⁶ mol/L) and Ag⁺(1.0×10⁻⁶ mol/L) was utilized as a representative to describe the detailed steps: 5.0 mL of stock solution of probe L and 0.5 mL of stock solution of Ag⁺ ion were mixed in a 100 mL volumetric flask, and then 90.5 mL of deionized water and 4.5 mL of methanol were added to the volumetric flask to obtain a homogeneous aqueous solution(H₂O/CH₃OH volume ratio: 19:1), the volumetric flask was gently shaken and left for 10 min prior to test. The other solutions for fluorescent emission and UV-Vis absorption titration experiment were prepared in a similar manner. For each titration solution, 2.0 mL of titration solution was transferred to a quartz cuvette for testing.

3 Results and Discussion

3.1 Synthesis and Characterization of Probe L

As shown in Scheme 1, probe L was synthesized by the solvent-free microwave irradiation, using Keggin- $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ and SiO_2 as the catalyst and dispersing agent, respectively. It can be demonstrated that the absence and presence of 0.5% (molar fraction) Keggin- $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ lead to the yields of probe L at 43.3% and 66.7%, respectively, indicating that Keggin- $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ is an efficient catalyst. Characterizations including FTIR, ^1H NMR, ^{13}C NMR, HRLC-MS spectra and elemental analysis were used to confirm the chemical structure



Scheme 1 Synthetic route of probe L

3.2 Fluorescence Titration Experiment

Fluorescence titration experiment was utilized to assess the sensitivity of probe L to Ag^+ ion at 25 °C. As shown in Fig.2(A), with the concentration of Ag^+ ion varying from 0 to 8.0×10^{-6} mol/L, the fluorescence emission band of probe L (1.0×10^{-6} mol/L) is blue-shifted from 450 nm to 405 nm, and

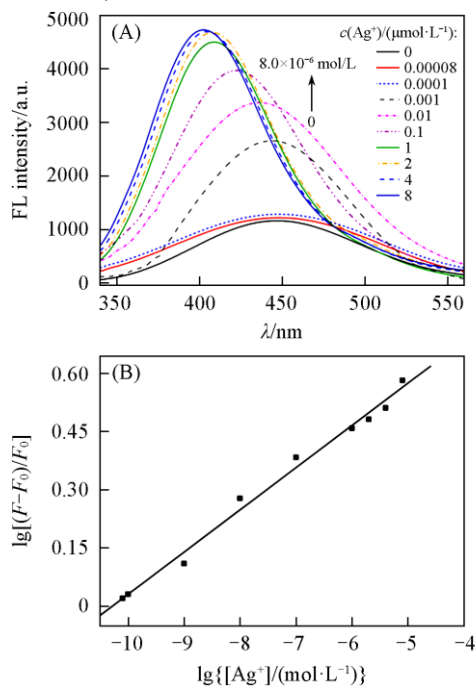


Fig.2 Fluorescence emission spectra of probe L (1.0×10^{-6} mol/L) in the presence of Ag^+ ion ($0-8.0 \times 10^{-6}$ mol/L) (A) and plot of $\lg[(F-F_0)/F_0]$ as a function of the $\lg[\text{Ag}^+]$ (B)

F_0 was the fluorescence intensity at 450 nm in the absence of Ag^+ ion, F was the maximum fluorescence intensity at the corresponding concentration of Ag^+ ion and $[\text{Ag}^+]$ was the concentration of Ag^+ ion.

of probe L. As shown in Fig.S1 (see the Electronic Supplementary Material of this paper), characteristic absorption peaks near $3500-3342 \text{ cm}^{-1}$ (N—H stretching), 1628 cm^{-1} and 1610 cm^{-1} (N—H bending) demonstrate the presence of $-\text{NH}_2$. Moreover, as can be seen in the ^1H NMR spectrum in Fig.S2 (see the Electronic Supplementary Material of this paper), the proton resonance at δ 5.34 illustrates the existence of $-\text{NH}_2$, which is consistent with the FTIR result. All the other protons and carbon atoms (Fig.S3, see the Electronic Supplementary Material of this paper) were also unambiguously assigned. Additionally, the results of HRLC-MS spectrum and elemental analysis are well consistent with the theoretical ones.

accompanied by a gradual increase in fluorescence intensity. Such a blue shift could be attributed to the polarization of the nitrogen atom, the dipole moment in the excited state is larger than that in the ground state, in other words, the excited state is more destabilized by Ag^+ ion than the ground state, which may lead to a blue shift of the emission spectrum^[22,23]. Besides, the gradually enhanced fluorescence intensity might be attributed to that the interaction of Ag^+ ion with probe L may restrict the electron transfer from the imidazole ring to its adjacent substituents^[24,25]. Additionally, the fluorescent emission response of probe L toward Ag^+ ion was calculated to cover a linear range [Fig.2(B)] when the concentration of Ag^+ ion ranged from 8.0×10^{-11} mol/L to 4.0×10^{-6} mol/L, with a detection limit of 3.0×10^{-11} mol/L (based on $S/N=3$)^[14]. The linear regression equation was $\lg[(F-F_0)/F_0]=0.109\lg[\text{Ag}^+]+1.12$ (correlation coefficient $R^2=0.995$)^[14]. Such a detection limit of probe L is far lower than that of the standard solution (4.62×10^{-7} mol/L, 0.05 mg/L) defined by US Environmental Protection Agency (EPA) for drinking water and is comparable to some of the reported detection limits^[26-28], indicating a high sensitivity of probe L to Ag^+ ion.

3.3 UV-Vis Absorption Titration Experiment and Possible Complexation Mechanism Between Probe L and Ag^+ Ion

To obtain the stoichiometric ratio and association constant between probe L and Ag^+ ion, UV-Vis absorption titration experiment was carried out with the concentration of probe L and Ag^+ ion at 1.0×10^{-6} mol/L and $0-2.5 \times 10^{-5}$ mol/L, respectively. As shown in Fig.3, two absorption bands of probe L center at 259 and 282 nm, respectively. As the concentration of Ag^+ ion increases from 0 to 2.5×10^{-5} mol/L, the absorbance gradually increases at 259 nm but decreases at 282 nm with an isosbestic point at 274 nm, which might be induced by the changes of the

molecular orbitals and the intramolecular transfer charge resulted from the complexation of Ag^+ ion and probe L^[29].

Based on the linear Benesi-Hildebrand expression^[30,31], $1/(A-A_0)$ at 282 nm presents a linear function relation with $1/[\text{Ag}^+]$ ($R^2=0.9975$), suggesting that the stoichiometric ratio between Ag^+ ion to probe L is 1:1. Moreover, the association constant of probe L with Ag^+ ion in the solution of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (19:1, volume ratio) was calculated to be $(9.95\pm 0.44)\times 10^5$ L/mol(see the Electronic Supplementary Material of this paper), indicating that probe L and Ag^+ ion generated a stable complex in the solution of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (19:1, volume ratio)^[31].

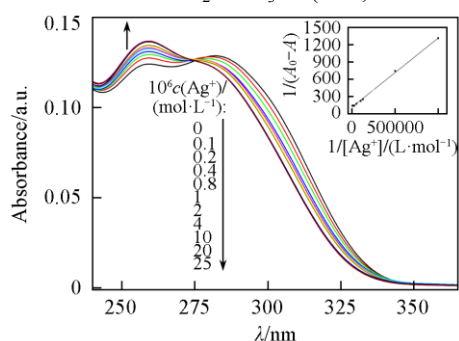


Fig.3 UV-Vis absorption spectra of probe L(1.0×10^{-6} mol/L) upon increasing the concentration of Ag^+ ion from 0 to 2.5×10^{-5} mol/L

Inset: Benesi-Hildebrand plot of $1/(A-A_0)$ vs. $1/[\text{Ag}^+]$.

$$\frac{1}{A-A_0} = \frac{a}{a-b} \left(\frac{1}{K[M]} + 1 \right)$$

Further, Job's method and ESI-MS were utilized to verify 1:1 stoichiometric ratio and the results are shown in Fig.4(A)

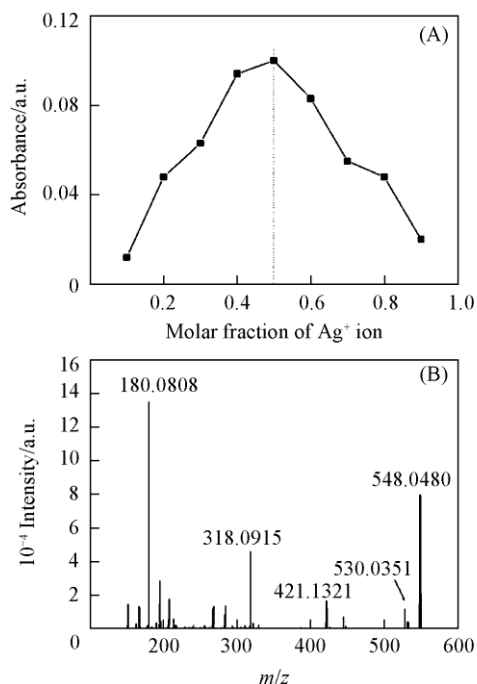
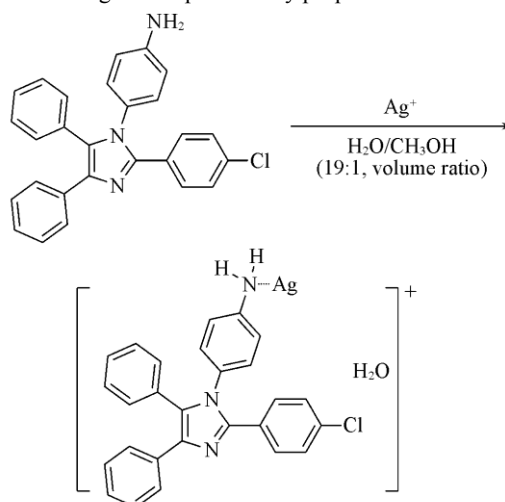


Fig.4 Job's plot for determining the stoichiometric ratio between Ag^+ ion and probe L in a total concentration of 1.0×10^{-6} mol/L, where the integrated absorbance was plotted against the molar fraction of Ag^+ ion ($[\text{Ag}^+]/([\text{Ag}^+]+[\text{L}])$ (A) and ESI-MS of Ag^+ ion and probe L in a solution of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (19:1, volume ratio)(B)

and (B), respectively. In Fig.4(A), with the molar fraction of Ag^+ ion varying from 0 to 1, the absorbance value goes through a maximum at a molar fraction of 0.5, demonstrating a 1:1 stoichiometric ratio between Ag^+ ion and probe L; in Fig.4(B), mass to charge ratio (m/z) of 530.0351 and 421.1321 can be attributed to the molecular ion peak of $[\text{L}]^+$ and $[\text{L}+\text{Ag}^+2]^+$, respectively, which further provides a solid evidence of 1:1 stoichiometric ratio between Ag^+ ion and probe L, and the mass to charge ratio (m/z) of 548.0480 can be ascribed to $[\text{L}+\text{Ag}^+\text{H}_2\text{O}+2]^+$, consequently, a possible complexation mechanism of L- Ag^+ ion is presumed in Scheme 2.



Scheme 2 Presumed complex mechanism between Ag^+ ion and probe L

To further confirm the complexation of probe L and Ag^+ ion, equimolar quantities of anhydrous silver nitrate and probe L were dissolved in DMSO-d_6 for ^1H NMR spectrum characterization(Fig.5). As a result, the resonances of the protons in $-\text{NH}_2$ change from δ 5.34 for probe L to δ 5.47 for $\text{L}+\text{Ag}^+$ ion, accompanied by a sharply decrease in the intensity of

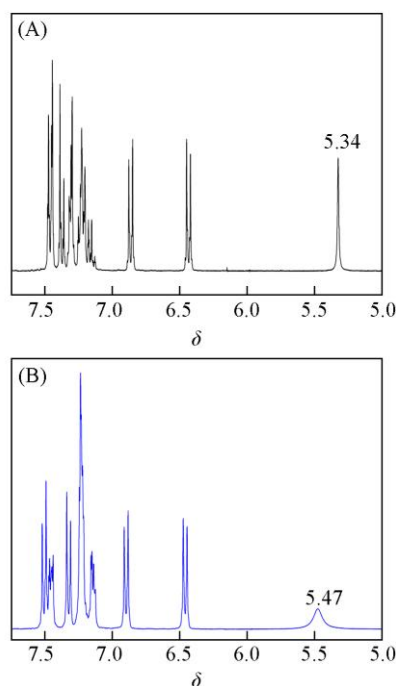


Fig.5 ^1H NMR spectra of probe L(A) and $\text{L}+\text{Ag}^+$ ion(B)

probe L. Nevertheless, almost no change can be found for other protons, illustrating the complexation between probe L and Ag^+ ion.

3.4 Selectivity of Probe L

As selectivity is also an integrant parameter of a probe, the fluorescence detection of probe L to Ag^+ ion was carried out under the interference of a number of common metal ions. As displayed in Fig.6(A), the fluorescent emission intensity of probe L in the presence of Ag^+ ion can be obviously enhanced, accompanied by the blue shift of the emission wavelength. Compared with the fluorescence response of probe L to Ag^+ ion, the fluorescent intensity or shift changes of probe L to other interference ions are slightly changed despite that these ions possess 10 times concentration that of Ag^+ ion, which could be probably attributed to their low affinity with probe L^[5]. Additionally, the fluorescence-enhancing degrees (F/F_0-1) of probe L at 405 nm in the presence of different metal ions are presented in Fig.6(B). It can be found that the loading of Fe^{3+} , Cu^{2+} , Co^{2+} , Ba^{2+} , Mn^{2+} and Mg^{2+} slightly changes the fluorescence intensity, not interfering the identification of probe L to Ag^+ ion.

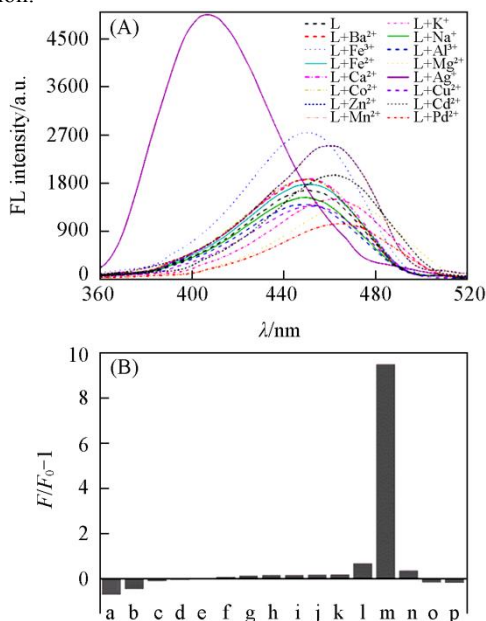


Fig.6 Fluorescence responses of probe L in the presence of various metal ions(A) and fluorescence-enhancing degrees of probe L in the presence of other ions at 405 nm(B)

(A) All the cations were presented in the form of their nitrate; (B) a. Mg^{2+} ; b. K^+ ; c. Al^{3+} ; d. Na^+ ; e. probe L; f. Fe^{2+} ; g. Ca^{2+} ; h. Zn^{2+} ; i. Mn^{2+} ; j. Ba^{2+} ; k. Co^{2+} ; l. Fe^{3+} ; m. Ag^+ ; n. Cu^{2+} ; o. Cd^{2+} ; p. Pd^{2+} .

3.5 Applied pH Range of Probe L

To find out the proper applied pH range of the probe, two series of solutions of probe L (1.0×10^{-6} mol/L) and $\text{L}+\text{Ag}^+$ ion (1.0×10^{-6} mol/L) were adjusted to different pH using nitric acid and anhydrous sodium hydroxide. The responses of the fluorescence emission intensity at different pH are shown in Fig.7. Apparently, as pH varies from 2.5 to 9.0, the fluorescence intensity of probe L is basically invariable; however, the

fluorescence intensity of $\text{L}+\text{Ag}^+$ ion initially increases rapidly (pH=2.0—4.0), which can probably be attributed to the deprotonated nitrogen in $-\text{NH}_2$, thus leading to a gradual binding between probe L and Ag^+ ion, and drastically decreases (pH=8.0—9.0), which can be due to the formation of silver hydroxide^[32,33]. The proper applied range of pH could be evaluated at 4.0—8.0 due to the higher and approximately unchanged fluorescence intensity.

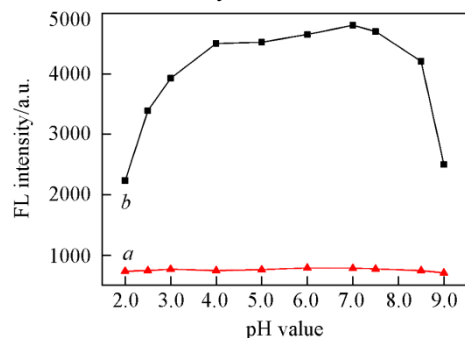


Fig.7 Fluorescence emission intensity of probe L(a, 1.0×10^{-6} mol/L) and $\text{L}+\text{Ag}^+$ ion(b, 1.0×10^{-6} mol/L) at 405 nm obtained at different pH values

3.6 Preliminary Analytical Application and Comparison of Different Detection Methods

Table 1 shows the applicability of the proposed fluorescent probe in practical samples. Three detection samples (tap water, south lake water, waste water) derived from different places of Changchun, China were simply filtrated with $0.22 \mu\text{m}$ infiltration head. Each water sample was divided into two parts, one spiked with standard Ag^+ ion solution to obtain an added concentration of 4.0×10^{-8} mol/L and the other did not do any treatment. To calculate the Ag^+ content of each sample, a new calibration curve ($R^2=0.997$) was drawn (Fig.S4, see the Electronic Supplementary Material of this paper). It can be found that the determined recovery values of Ag^+ ion in different water samples are 101.0% (tap water), 99.5% (south lake water) and 100.2% (waste water), respectively (Table 1), which illustrates that the developed method could accurately detect and distinguish the concentration of Ag^+ ion in different water samples. Also, a comparison of the developed probe with the reported ones in the detection limit and the linear range is shown in Table 2. As can be found, the linear range and sensitivity of probe L are quite comparable to those of the reported ones.

Table 1 [Ag^+] determination in environmental water samples ($n=3$)

Sample	$10^8 [\text{Ag}^+] \text{ added/}$ (mol·L ⁻¹)	$10^8 [\text{Ag}^+] \text{ founded/}$ (mol·L ⁻¹)	Recovery (%)
Tap water ^a	—	N.D. ^d	—
	4.00	4.04(±0.03)	101.0
South lake water ^b	—	N.D.	—
	4.00	3.98(±0.02)	99.5
Waste water ^c	—	0.13(±0.02)	—
	4.00	4.14(±0.04)	100.2

a. Indoor tap water, Changchun, China; b. south lake water, Changchun, China; c. waste water from sewage treatment plant, Changchun, China; d. not detected.

Table 2 Comparison of different methods in detecting Ag⁺ ion

Method	10 ⁶ Detection limit/ (mol·L ⁻¹)	10 ⁶ Linear range / (mol·L ⁻¹)	Association constant	Reference
ICT fluorescent probe based on 4-(dimethylamino)-benzamide	0.8	—	1.8×10 ⁸ L ² ·mol ⁻²	[34]
Optical chemosensor based on 2(4-hydroxypent-3-en-2-ylideneamine)phenol	7.0×10 ⁻²	0.4—500	—	[32]
Graphene-based fluorescent nanoprobe	5.0×10 ⁻³	<0.1	1.2×10 ⁷ L/mol	[26]
Fluorescent probe based on 4-[2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazol-1-yl]aniline	8.0×10 ⁻⁵	0.001—6	(9.95±0.44)×10 ⁵ L/mol	This work

4 Conclusions

A green and convenient method was developed for synthesizing a fluorescent probe of Ag⁺ ion, 4-[2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazol-1-yl]aniline(L) by the method of solvent-free microwave irradiation using H₃[PW₁₂O₄₀] as catalyst and SiO₂ as dispersing agent. With the increased concentration of Ag⁺ ion in the solution of H₂O/CH₃OH(19/1, volume ratio), the fluorescence intensity of probe L was enhanced markedly and the emission wavelength was blue-shifted from 450 nm to 405 nm with a lower detection limit of 3.0×10⁻¹¹ mol/L, illustrating a high sensitivity. Further, the UV-Vis absorption titration experiment demonstrated a 1:1 stoichiometric ratio and an association constant of (9.95±0.44)×10⁵ L/mol between probe L and Ag⁺ ion, and thus their possible complexation mechanism was proposed and verified by the characterization of ¹H NMR and ESI-MS spectra. More importantly, this probe exhibited a high selectivity for Ag⁺ ion in spite of the existence of higher concentration of other heavy and transition metal ions and a wide pH usage range of 4.0—8.0. Additionally, the probe was also used for the detection of Ag⁺ ions in tap water, lake water and waste water and showed satisfactory practical application results. It was no doubt that probe L not only could be simply synthesized, conveniently used but also had a high selectivity and sensitivity to Ag⁺ ion detection, which could meet the requirements of environmental monitoring application.

Acknowledgements

We are grateful to Dr. WANG Chunyu(Jilin University) for NMR spectra test, Dr. WEI Zhonglin(Jilin University) for MS spectra test and Dr. DAO Jungang(Jilin University) for fluorescent emission spectra test.

Electronic Supplementary Material

Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s40242-018-7426-5>.

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