Design, Synthesis of Nitrogen-Rich Triazine Derivatives and its Application in Water Sample, Vegetables and Oil Product

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Abstract A triazine nitrogen-rich derivative fluorescent probe, 1,1'-(6-chloro-1,3,5-triazine-2,4-diyl)bis(1H-benzo[d][1,2,3]triazole)(**L**), has been synthesized and successfully achieved for the efficient detection for Fe^{3+}, $Cr_2O_7^{2-}$, nitrobenzene as a turn-off chemosensor in DMF/H_2O. The quenching constant(K_{sv}) and detection of limit for Fe^{3+}, $Cr_2O_7^{2-}$, nitrobenzene on fluorescence response of the sensor can be as low as 470.00 M^{-1}, 359.94 M^{-1}, 3.62*10^3 mL^{-1}, 2.10*10^{-5} M, 5.73*10^{-5} M, 1.24*10^{-5} mL, respectively. On the contrary, It is applied to detected for toluene and xylene as a turn-on chemosensor in DMF. The quenching constant and detection of limit for toluene and xylene on fluorescence response of the sensor can be as low as -11.05 mL^{-1}, -6.23 mL^{-1}, 9.30*10^{-4} mL, 7.35*10^{-3} mL, respectively. The application of water sample and vegetables showed that the **L** had high sensitive detection for Fe^{3+} ions. Meanwhile the application of gasoline, diesel and engine oil showed that the **L** had high sensitive detection for toluene and xylene.

Keywords: Triazine nitrogen-rich derivative; Multiple fluorescence sensor; Fe^{3+}, $Cr_2O_7^{2-}$ ions; Toluene, xylene and nitrobenzene

1 | INTRODUCTION

Environmental pollution has become an urgent global concern and the detection of toxic contaminants present in water has attracted significant research attention, it is very significant to effectively identify and remove the remaining pollutants from wastewater[1]. There are lots of ways for water pollution, the most common is heavy-metal pollution. Heavy metal ions in natural water can easily enter the body of living organisms and animals. Ultimately, accumulation of heavy metals in the body of animals induces various diseases[2]. The fluctuation of Fe^{3+} concentration also concerns with many health problems, including anemia, diabetes, even cancer. Therefore, Fe^{3+} detection is in great need due to the identification and diagnosis of the related diseases[3]. The

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hexavalent chromate anions ($Cr_2O_7^{2-}$) in aqueous solution are highly carcinogenic to human and harmful to living conditions, even with a relative low concentration[4-7]. Upon skin contact, $Cr_2O_7^{2-}$ can cause genetic defects and allergic reactions[8]. World Health Organization has identified these ions as a Group "A" carcinogen[9]. Aromatic compounds are also a source of water pollution, especially toluene, xylene and nitrobenzene. These volatile toxic organic compounds can cause irritation symptoms in the respiratory tract, skin, eyes, and cause fatigue, headache and dizziness, and serious health problems such as heart arrhythmia, central nervous system disorders, and so on[10-12].

Up to the present, the detection methods cover electrochemical atomic absorption/emission spectroscopy, voltammetry, inductively coupled plasma mass spectrometry, and potentiometry and inductively coupled plasma mass spectrometry[13-15]. However, above methods require sophisticated instrumentation, complicated samples preparation, expensive reagents, time-consuming, cumbersome pre-treatments such as solvent extraction, solid-phase extraction as well as precipitation in order to achieve higher sensitivity. Fortunately, fluorescent probes have attracted much attention due to their high sensitivity, good selectivity, short response time, and easy monitoring[16,17]. Various types of fluorescence chemosensors for detecting Fe^{3+} ions have been reported, such as Schiff bases[18], benzothiazole[19], imidazole derivative[20], coumarin derivatives[21], oxadiazole derivatives[22], tetraphenylethylene-rhodamine[23], cucurbit derivative[24] and lots of MOFs[25,26]. Many MOFs fluorescent probes can also be used to detect $Cr_2O_7^{2-}$ions, such as Ba-MOFs[27], Co-MOFs[28], Cd-MOFs[29,30], Re-MOFs(Re=Eu,Tb)[31-34]. For toluene and xylene fluorescence detection is relatively small. Only multifunctional nitrogen and sulfur doped fluorescence carbon dots (N, S-CDs)[35] can be used to detect toluene in aqueous solution, the detection limit was low as 0.03μM. As for nitrobenzene, the common fluorescent sensors are Eu^{3+}@SOF-1[36], Zn-MOFs[37], Cd-MOFs[38,39], UiO-66-NH_2[40], etc. All of the above fluorescent sensors have the advantages of high sensitivity, good selectivity, short response time and easy

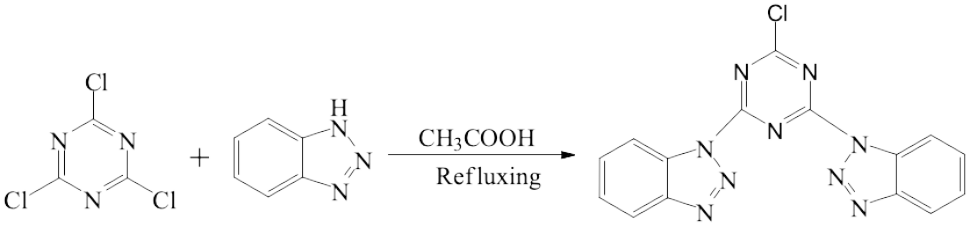
monitoring. However, single detection, complex synthesis and high price limit the application of these fluorescent sensors.

In this work, a new complex, triazine nitrogen-rich derivative fluorescent probe, 1,1'-(6-chloro-1,3,5-triazine-2,4-diyl)bis(1H-benzo[d][1,2,3]triazole)(**L**), has been prepared by reaction of cyanuric chloride and 1,2,3-benzotriazole in glacial acetic acid. The compound **L** was investigated for multiple fluorescence response to Fe^{3+}, $Cr_2O_7^{2-}$ ions, toluene, xylene and nitrobenzene. especially it is first reported that the fluorescence intensity of compound **L** is enhanced when toluene and xylene are added in DMF/H_2O, respectively.

2| EXPERIMENTAL SECTION

2.1| Synthesis fluorescent probe compound L

1 mmol(0.1844 g) cyanuric chloride and 20 mL glacial acetic acid were added to a 50 mL round bottom flask to dissolve it. And then 2 mmol(0.2663 g) 1,2,3-benzotriazole was added. The mixture was stirred and refluxed immediately at 120 °C for 20 minutes, generating lots of white soild. Then, the suspension was filtered and the product was washed several times with boiling water and ethanol, and then dried in vacuum dryer at 80 °C for one day. The 0.3752 g white powder was collected in 99.3% yield; 1,1'-(6-chloro-1,3,5-triazine-2,4-diyl)bis(1H-benzo[d][1,2,3]triazole) (**L**): m.p. ≥330℃(dec.); IR (KBr, cm^{-1}): 1598, 1537, 1485, 1462, 1333, 1295, 1233, 990, 753, 671; ^{1}HNMR (DMSO-d_6, 500 MHz): δ 8.75 (d, J = 5.0 Hz, 2H, ArH), 8.31 (d, 3H, J = 10.0 Hz, ArH), 7.88-7.91 (m, 2H, ArH), 7.64-7.67 (m, 2H, ArH); ^{13}C NMR (DMSO-d_6, 125MHz) δ: 163.2, 146.6, 131.7, 131.0, 126.8, 120.7, 115.89, 79.7, 79.5, 79.2 cm^{-1}; Anal. calcd for $C_{15}H_8ClN_9$(Mr = 349.74): C 51.51, N 36.04, H 2.31; found C 51.39, N 36.19, H 2.92.



Scheme 1 The synthetic route of compound **L**

2.2| Fluorescence sensing experiments

2.2.1| Cations sensing

Because of the excellent fluorescence property of compound **L**, we were strongly interested to explore the application of compound **L** for sensing metal ions in DMF/H_2O. A powder sample of compound **L** was dissolved with sonification in 500 mL DMF/H_2O[V(DMF):V(H_2O)=24:1] to form a solution of $1.3*10^{-3}$ mol/L. Add 0.1mL 20 different metal chloride ($2.5*10^{-3}$ mol/L) to 2.9 mL the solution of compound **L** at room temperature respectively. After full mixing for 10 s, the resultant suspensions were then monitored by fluorescence spectroscopy and the fluorescence data were collected under an excitation wavelength of 350 nm. Additionally, to confirm its selective identification ability of Fe^{3+} among other ions, equal amounts of Fe^{3+} ($1*10^{-3}$ M)solution was added to the suspensions of compound **L** pretreated with other ions, respectively. and then the fluorescence measurements were carried out. Respectively, different amounts of Fe^{3+} solution was added into compound **L** aqueous to determine the relationship between the fluorescence intensity and the concentration of compound **L**.

2.2.2| Anions sensing

Based on strong fluorescence properties of compound **L**, the fluorescence recognition anions were further discussed. Add 0.1mL 27 different sodium salts ($1*10^{-3}$ mol/L) to 2.9 mL the solution of compound **L** at room temperature, respectively. After full mixing for 10 s, the resultant suspensions were then monitored by fluorescence spectroscopy and the fluorescence data were collected under an excitation wavelength of 350 nm. And then, to confirm its selective identification ability of $Cr_2O_7^{2-}$ among other anions, equal amounts of $Cr_2O_7^{2-}$($1*10^{-3}$ M)solution was added to the suspensions of compound **L** pretreated with other anions, respectively. and then the fluorescence measurements were carried out. Respectively different amounts of $Cr_2O_7^{2-}$ solution were added into compound **L** aqueous to determine the relationship between the fluorescence intensity and the concentration of compound **L**.

2.2.3|Organic solvent sensing

The effect of organic solvents on the fluorescence intensity of compound **L** were also studied. Add 0.1 mL 21 different organic solvents to 2.9 mL solution of compound **L** at room temperature, respectively. After full mixing for 10 s, the resultant suspensions were then monitored by fluorescence spectroscopy and the fluorescence data were collected under an excitation wavelength of 350 nm. After that, to confirm its selective identification ability of toluene, xylene and nitrobenzene among other organic solvents, equal amounts of toluene, xylene and nitrobenzene solution were added to the suspensions of compound **L** pretreated with other organic solvents, respectively.

2.2.4| pH sensing

The effect of pH on the fluorescence of compound **L** solution was also investigated. Add 0.1mL different pH values aqueous solution to 2.9 mL solution of compound **L** at room temperature, respectively. After full mixing for 10 s, the resultant suspensions were then monitored by fluorescence spectroscopy and the fluorescence data which were collected under an excitation wavelength of 350 nm.

3| RESULTS AND DISCUSSION

3.1| Complexation ratio of compound L to Fe^{3+}

The Fe^{3+} ions exhibit superior fluorescence quenching effect on compound **L**. To explore the detection effects of compound **L** in DMF/H_2O[V(DMF):V(H_2O)=24:1](1*10^{-4} M) as the fluorescence probe of Fe^{3+}ions, concentration-dependent experiments were further taken (Figure1a). The fluorescence intensity of compound **L** gradually reduced with the increasing the proportion of Fe^{3+} ions. The fluorescence intensity reaches the maximum when the ratio of compound **L** to Fe^{3+} is 9:1, and then decreases with the increase of the ratio of Fe^{3+} ions. The Job's curve was given according to the fluorescence concentration curve of compound **L** and Fe^{3+} ions (Figure 1b). The results showed that the molar fraction of [Fe^{3+}]/[L+Fe^{3+}] was 0.1 when the curve has inflection point, demonstrating 2:1 binding stoichiometry ration for **L**+Fe^{3+}.

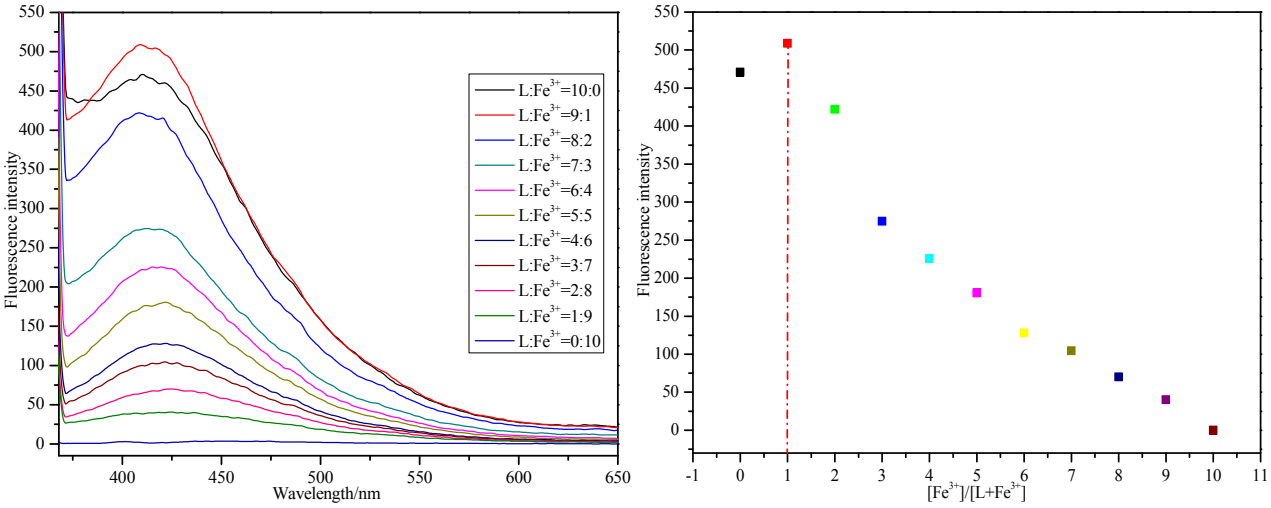


FIGURE 1 (a)Fluorescence spectra of different proportions of **L** and Fe^{3+} ions at the same concentration (λex=350 nm, slit = 10 nm), [**L**] =1*10^{-3} M, [Fe^{3+}] =1*10^{-3} M; (b) The Job's plot of **L** with Fe^{3+} ions.

3.2| Selective sensing of Fe^{3+} ions

As shown in Figure 2, the fluorescence intensity of compound **L** at 409 nm reduced obviously when metal ions(Li^{+}, Na^{+}, K^{+}, Cu^{+}, Mg^{2+}, Zn^{2+}, Ba^{2+}, Ca^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Sn^{2+}, Hg^{2+}, Cd^{2+}, Sb^{3+}, Sr^{3+}, Cr^{3+} and Fe^{3+} ions) were added, respectively. Compared with other metal ions, after addition of Fe^{3+} ions, the fluorescence intensity at 409 nm was quenched with a quenching ratio of 42%, which enabled the "turn-off" detection of Fe^{3+} ions.

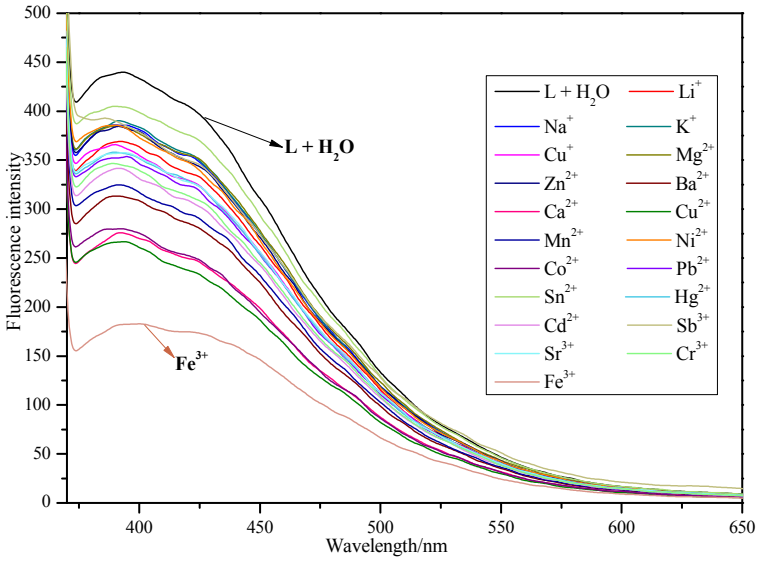


FIGURE 2 Fluorescence change of **L** (DMF/H_2O) in different metal chloride aqueous solution, **L** = 2.9 mL, 1.3*10^{-3} M, metal chloride = 0.1mL, 2.5*10^{-3} mol/L, λ_{ex} = 350 nm, slit = 10 nm.

The experiment of Fe^{3+} ions concentration showed that the fluorescence intensity of compound **L** reduced with the increase of the concentration of Fe^{3+} ions(Figure 3a). The fluorescence intensity

of compound **L** shows a highly broad linear relationship with the concentration of Fe^{3+} ion from $2*10^{-4}$ to $9*10^{-4}$ M expressed as an equation of $y = 1.324*10^{5}\ x - 2.783$ and $R^2 = 0.9995$. where y is the ratio of $(F-F_0)$ and x is the concentration of Fe^{3+} ions. According to the fluorescence intensity of compound **L**, different concentration of Fe^{3+} ions, Benesi-Hildebrand equation, the detection limit of Fe^{3+}ions in compound **L**(DMF/H_2O) is calculated to be $2.10*10^{-5}$ mol/L(Figure3b). In addition, the quenching efficiency can be rationalized by the Stern−Volmer(SV) equation, $F_0/F = 1+K_{SV}[M]$, where F_0 and F are the relative fluorescence intensity before and after adding Fe^{3+} ions, [M] is the molar concentration of the Fe^{3+} ions, and K_{SV} (M^{-1}) is the Stern−Volmer quenching constant. The $K_{SV}(Fe^{3+})$ value is calculated as 470.00 M^{-1} which indicated that Fe^{3+} have a strong enhancement effect on the fluorescence of compound **L**. Under the same conditions, the quenching constants of other metals are shown(Table S1).

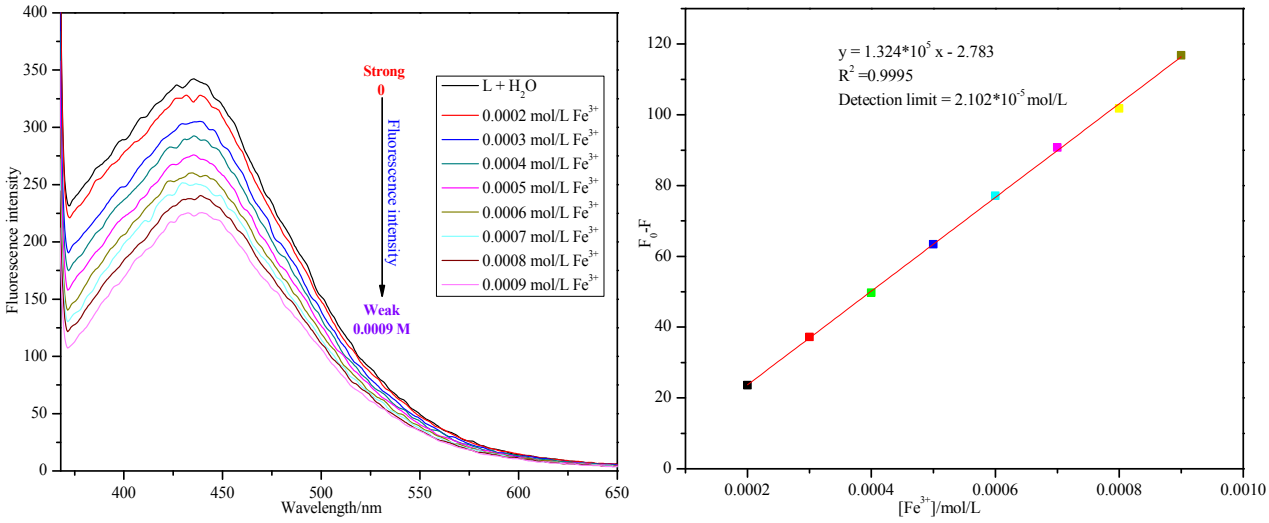
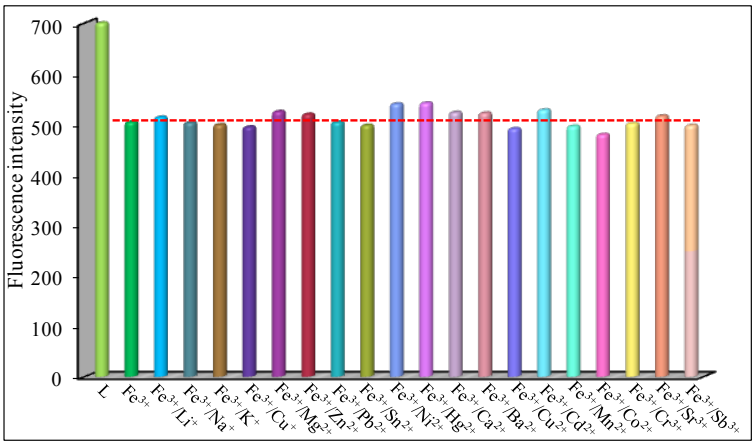


FIGURE 3 (a)Fluorescence change of **L** (DMF/H_2O) in different concentrations of Fe^{3+} ions, **L** = 2.9 mL, $1.3*10^{-3}$ mol/L, $[Fe^{3+}]$ = 0.1mL, $2*10^{-4}$~$9*10^{-4}$ mol/L, λ_{ex}=350 nm, slit = 10nm; (b) Detection limit of Fe^{3+}ions.

The interference of other metal ions on Fe^{3+} ions was also investigated, respectively(Figure 4). For Fe^{3+} ions, most metal ions have little interference with Fe^{3+} in the DMF/H_2O of compound **L**. Therefore, compound **L** exhibited selectivity and specificity for detection of Fe^{3+} in the presence of these other metal ions.



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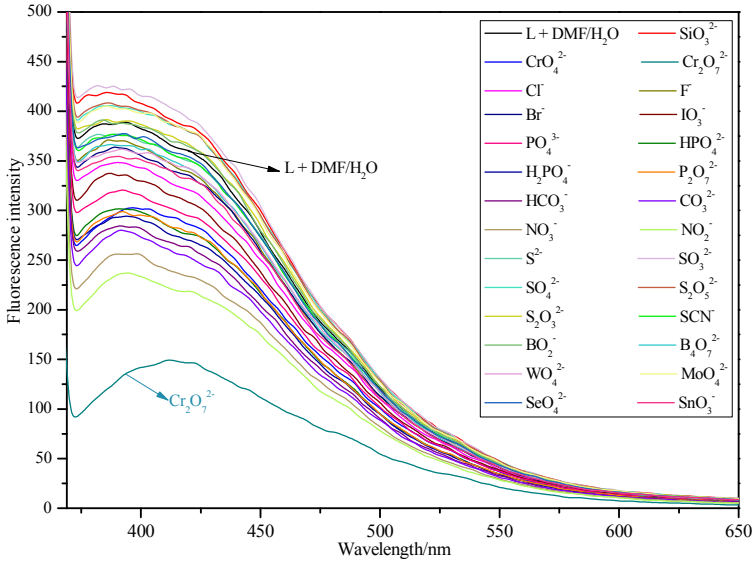
160 **FIGURE 4** The influence of metal ions interference on the fluorescence recognition of Fe^{3+} by compound
161 **L**(DMF/H_2O), **L** = 2.8 mL, 1.3*10^{-3} mol/L, metal ions = 0.1mL, 1*10^{-3} mol/L, λ_{ex}=350nm, slit =10 nm.

162 **3.3| Selective sensing of $Cr_2O_7^{2-}$ ions**

163 The fluorescence properties are recorded and listed in Figure 5(λ_{ex}=350 nm). The fluorescence
164 intensity changed slightly when 26 anions (F^-, Cl^-, Br^-, IO_3^-, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, $P_2O_7^{2-}$, HCO_3^-,
165 CO_3^{2-}, NO_2^-, NO_3^-, S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, SO_4^{2-}, $S_2O_5^{2-}$, BO_2^-, $B_4O_7^{2-}$, SCN^-, CrO_4^{2-}, MnO_4^-, SnO_3^-, SeO_4^{2-},
166 MoO_4^{2-} and WO_4^{2-}) were added, respectively. Apparently, the fluorescence intensity of compound **L**
167 was reduced at 414 nm obviously only by adding $Cr_2O_7^{2-}$ ions, which enabled the "turn-off"
168 detection of $Cr_2O_7^{2-}$ ions.



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170 **FIGURE 5** Fluorescence change of **L**(DMF/H_2O) in different anions solution, **L** = 1.3*10^{-3} mol/L, anions =
171 0.1mL, 1*10^{-3} mol/L, λ_{ex}=350 nm, slit =10 nm.

172 The results show that with the addition of different concentrations $Cr_2O_7^{2-}$ ions, the
173 fluorescence intensity of compound **L** gradually reduces and shows a highly broad linear

relationship with the concentration of $Cr_2O_7^{2-}$ ions from $1*10^{-4}$ to $7*10^{-4}$ M expressed as an equation of y = 79464 x + 6.571 and R^2 = 0.9990, where y is the ratio of F_0-F and x is the concentration of $Cr_2O_7^{2-}$ ions(Figure 6a). According to the fluorescence intensity of compound **L**, different concentration of $Cr_2O_7^{2-}$ ions and Benesi-Hildebrand equation, the detection limit of $Cr_2O_7^{2-}$ ions in compound **L**(DMF/H_2O) is calculated to be 5.73×10^{-5} mol/L(Figure 6b). Further, the quenching efficiency can be rationalized by the Stern−Volmer(SV) equation, $F_0/F = 1+K_{SV}[M]$, where F_0 and F are the relative fluorescence intensity before and after adding $Cr_2O_7^{2-}$ ions, [M] is the molar concentration of the $Cr_2O_7^{2-}$ ions, and K_{SV} (M^{-1}) is the Stern−Volmer quenching constant. The $K_{SV}(Cr_2O_7^{2-})$ value is calculated as 359.94 M^{-1}, suggesting a strong quenching effect on fluorescence. Under the same conditions, the quenching constants of other anions are shown(Table S2).

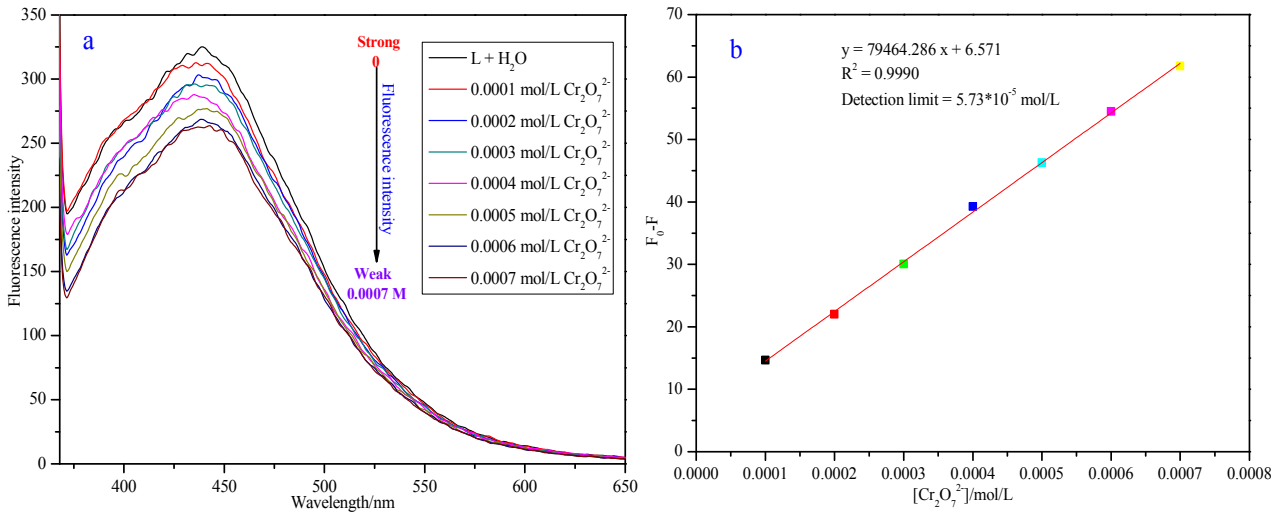


FIGURE6 (a)Fluorescence change of **L** (DMF/H_2O) in different concentrations of $Cr_2O_7^{2-}$ ions, **L** = 2.9 mL, $1.3*10^{-3}$ mol/L, $[Cr_2O_7^{2-}]$ = 0.1mL, $1*10^{-4}$ ~$7*10^{-4}$ mol/L, λ_{ex}=350 nm, slit = 10nm; (b) Detection limit of $Cr_2O_7^{2-}$ ions.

The interference of other anions on $Cr_2O_7^{2-}$ ions was also discussed, respectively. The interference of 25 anions on the $Cr_2O_7^{2-}$ ions are shown in Figure 7. These anions did not induce a significant decrease in the fluorescence of $Cr_2O_7^{2-}$ ions in compound **L**(DMF/H_2O). Only a few anions cause a slight decrease in the fluorescence intensity of $Cr_2O_7^{2-}$ ions in compound **L** from the histogram analysis. However the whole fluorescence intensity is lower than without adding any anions. It demonstrated that compound **L** can detect $Cr_2O_7^{2-}$ ions in the presence of these other

anions respectively.

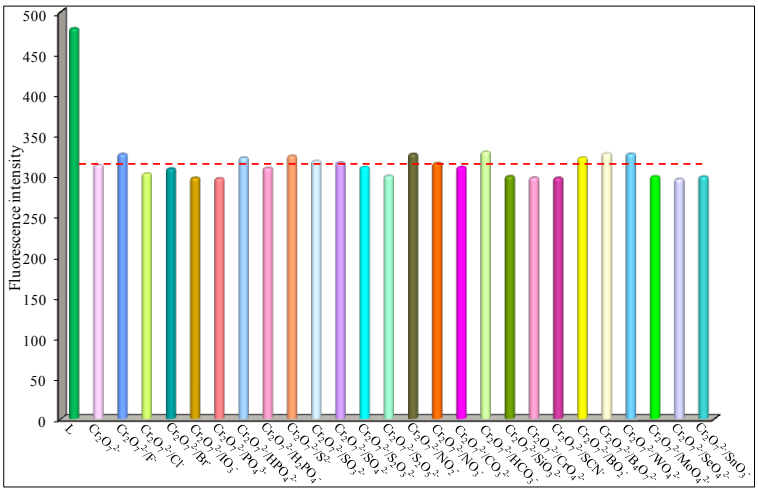


FIGURE 7 The influence of anions interference on the fluorescence recognition of $Cr_2O_7^{2-}$ ions by compound **L**(DMF/H_2O), **L** = 2.8 mL, 1.3*10^{-3} mol/L, anions = 0.1mL, 1*10^{-3} mol/L, λ_{ex}=350nm, slit =10 nm.

3.4| Selective sensing of toluene, xylene and nitrobenzene

The fluorescence properties are recorded and listed in Figure 8a (λ_{ex}=350 nm). The fluorescence intensity of compound **L** were decreased and enhanced at 410 nm when 21 organic solvents(CH_3OH, EtOH, CH_2Cl_2, $CHCl_3$, CCl_4,THF, DMSO, Diox, CH_3CN, CH_3COOH, acetone, benzol, toluene, xylene, trimethylbenzene, ethylbenzene, n-propanol, isopropanol, ethyl acetate, bromobenzene and nitrobenzene) were added, respectively. Compared with other solvents, the fluorescence intensity of compound **L** were obviously enhanced when toluene and xylene were added, respectively. The fluorescence enhancement are 2.5 and 3 times that of compound **L**, respectively, which enabled the “turn-on” detection of toluene and xylene. Interestingly, only toluene, xylene and ethylbenzene can enhance the fluorescence of compounds **L** in the series of benzene, toluene, xylene, trimethylbenzene and ethylbenzene homologues, especially toluene and xylene(Figure 8b). On the contrary, the fluorescence intensity of compound **L** was quenched with a quenching ratio of 99%, which enabled the “turn-off” detection of nitrobenzene.

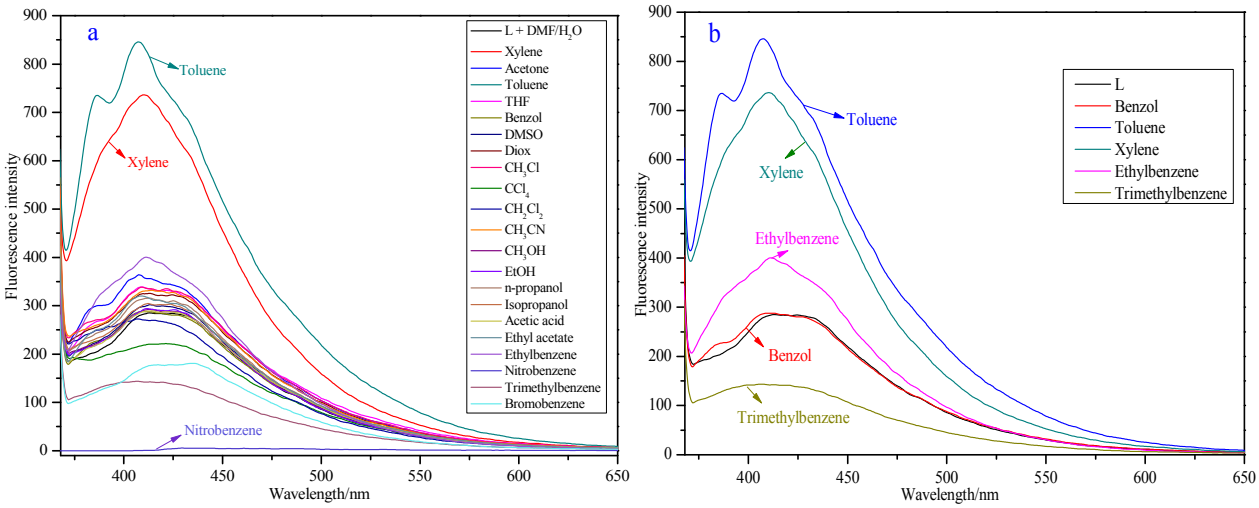
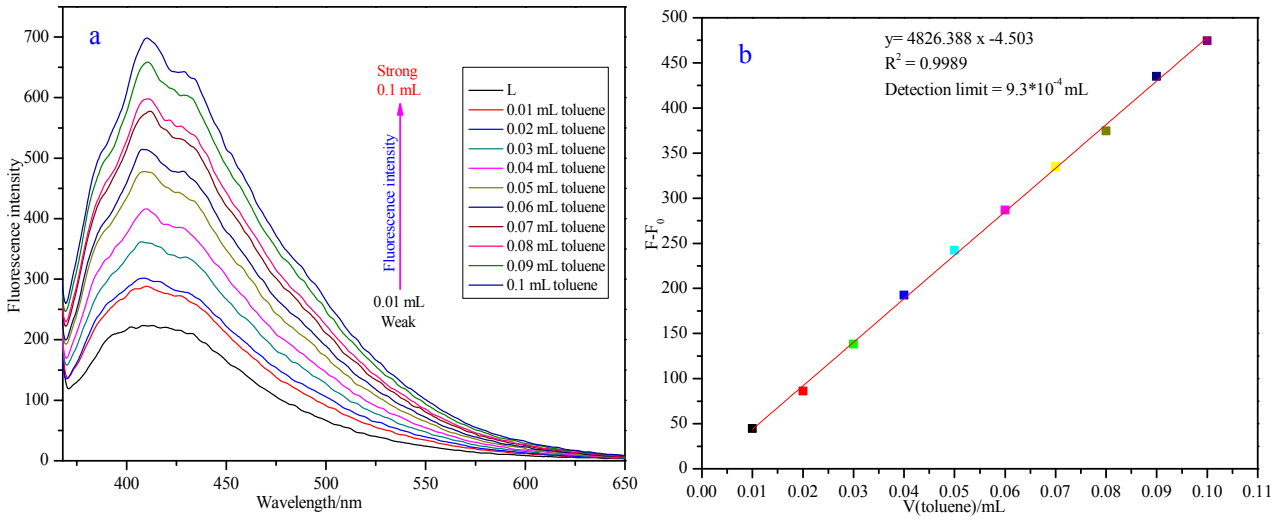
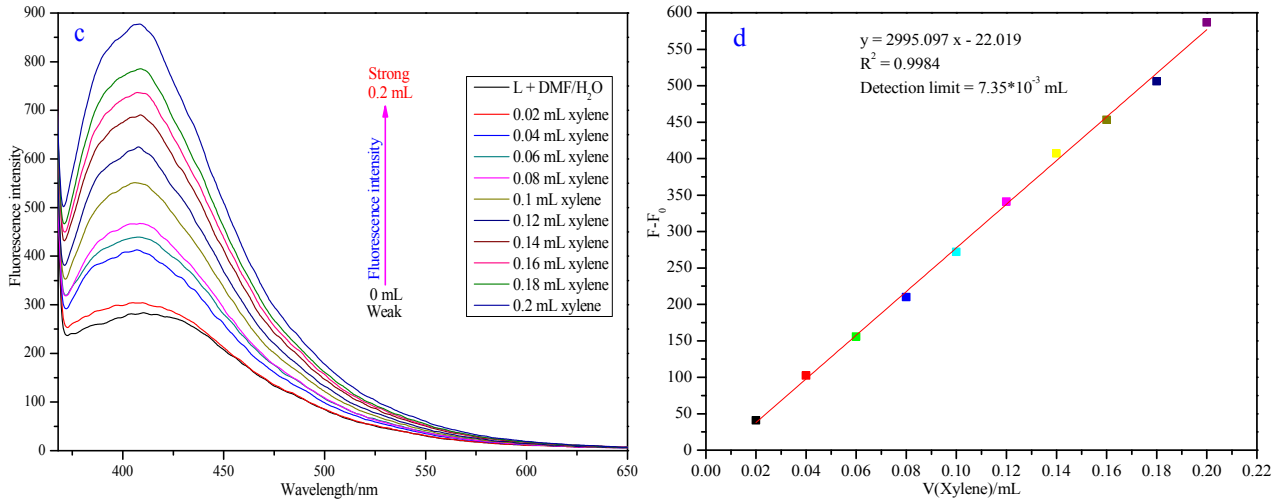


FIGURE 8(a) Fluorescence changes of compound **L** in different organic solvents, **L** = 2.9 mL, $1.3*10^{-3}$ mol/L, organic solvents = 0.1mL, λ_{ex}=350 nm, slit = 10 nm;(b) Fluorescence changes of benzene homologues in compound **L** in DMF/H_2O.

The experimental resulted show that with the addition of different volumes of toluene and xylene, respectively(Figure 9a,c). the fluorescence intensity of compound **L** gradually enhances and shows a highly broad linear relationship with the volume of toluene from 0.01 to 0.1 mL expressed as an equation of y = 4826.388 x – 4.503 and R^2 = 0.9989, and linear relationship with the volume of xylene from 0.02 to 0.2 mL expressed as an equation of y = 2995.097 x – 22.019 and R^2 = 0.9984, where y is the ratio of F-F_0 and x is the volume of xylene(Figure 9b,d). According to the fluorescence intensity of compound **L**, different volumes of toluene, xylene and Benesi-Hildebrand equation, the detection limit of toluene in compound **L** solution are calculated to be $9.3*10^{-4}$ mL and $7.35*10^{-3}$ mL. Further, the quenching efficiency can be rationalized by the Stern−Volmer(SV) equation, $F_0/F = 1+K_{SV}[V]$, where F_0 and F are the relative fluorescence intensity before and after adding toluene(xylene), [V] is the volume of the toluene(xylene), and K_{SV} (V^{-1}) is the Stern−Volmer quenching constant. The K_{SV}(toluene, xylene) value are calculated as -11.05 mL^{-1} and -6.23 mL^{-1}, suggesting a strong enhancing effect on fluorescence. On the contrary, the fluorescence intensity of compound **L** gradually decreases and shows a highly broad linear relationship with the volume of nitrobenzene from 0.00003 to 0.0001 mL expressed as an equation of $y = 1.388*10^6$ x – 17.217 and R^2 = 0.9991, where y is the ratio of F-F_0 and x is the volume of nitrobenzene (Fig.9f). According to the fluorescence intensity of compound **L**, different volumes of nitrobenzene and Benesi-

Hildebrand equation, the detection limit of nitrobenzene in compound **L** solution are calculated to be $1.24*10^{-5}$ mL. The K_{SV}(nitrobenzene) value are calculated as $3.62*10^{3}$ mL^{-1}, suggesting a strong quenching effect on fluorescence.Under the same conditions, the quenching constants of other organic solvents are shown(Table S3).





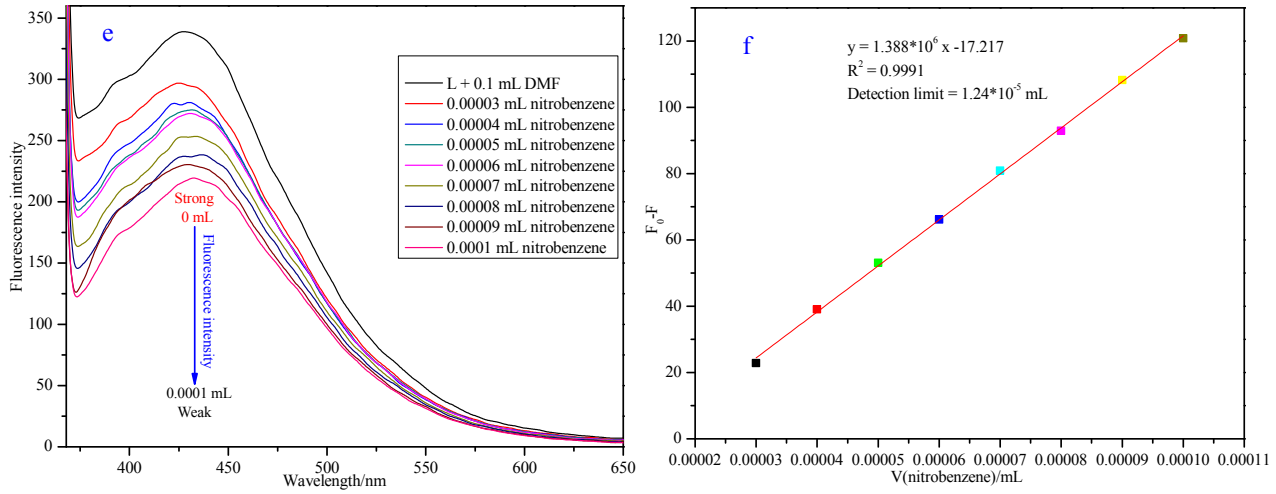
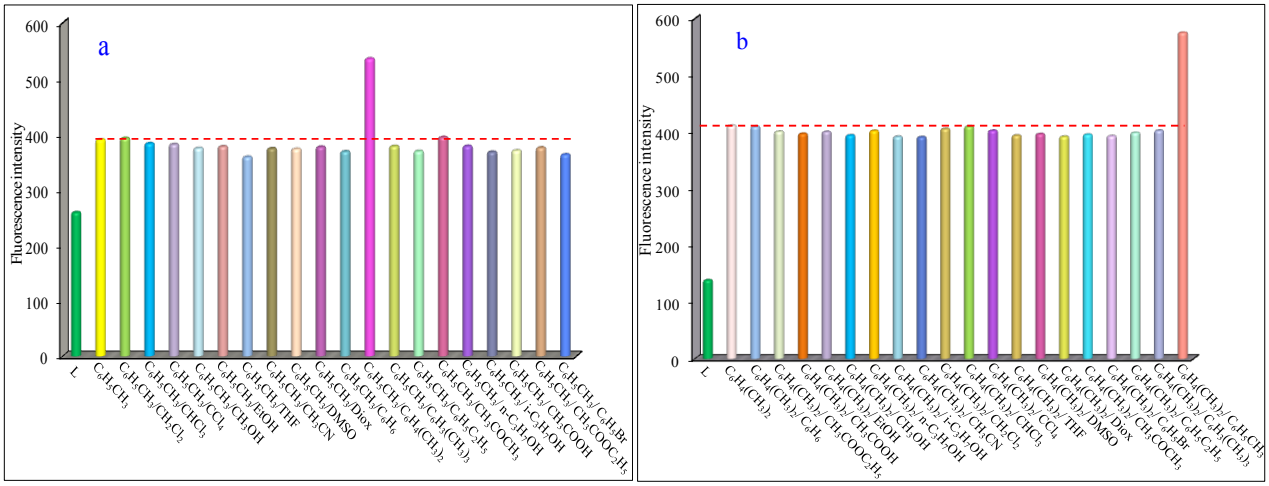


FIGURE 9 (a) Fluorescence changes of compound **L** in different volumes of toluene, **L** = 2.9 mL, $1.3*10^{-3}$

mol/L, V(toluene) = 0.01-0.1mL, λ_{ex}=350 nm, slit = 10 nm; (b) Detection limit of toluene; (c) Fluorescence changes of compound **L** in different volumes of xylene, **L** = 2.9 mL, 1.3*10^{-3} mol/L, V(xylene) = 0.02-0.2mL, λ_{ex}=350 nm, slit = 10 nm; (d) Detection limit of xylene; (e) Fluorescence changes of compound **L** in different volumes of nitrobenzene, **L** = 2.9 mL, 1.3*10^{-3} mol/L, V(nitrobenzene) = 0.00003-0.0001 mL, λ_{ex}=350 nm, slit = 10 nm;(f) Detection limit of nitrobenzene.

The interference of other organic solvents on toluene, xylene and nitrobenzene was also discussed, respectively. The interference of 20 organic solvents on the toluene and xylene are shown in Figure10a,b. The interference of 21 organic solvents on the nitrobenzene are shown in Figure10c. These organic solvents did not induce a significant decrease in the fluorescence of toluene and xylene in compound **L**(DMF/H_2O). the whole fluorescence intensity is higher than without adding any organic solvents. It is worth noting that the fluorescence of compound **L** was enhanced when the toluene coexists with xylene in compound **L**(DMF/H_2O). It demonstrated that compound **L** can detect toluene and xylene in the presence of these other organic solvents, respectively. In addition, for nitrobenzene, the quenching effect of nitrobenzene on compound **L** was almost unchanged when the volume of nitrobenzene was 1/10 of that of other organic solvents. It demonstrated that compound **L** can detect nitrobenzene in the presence of these other organic solvents, respectively.



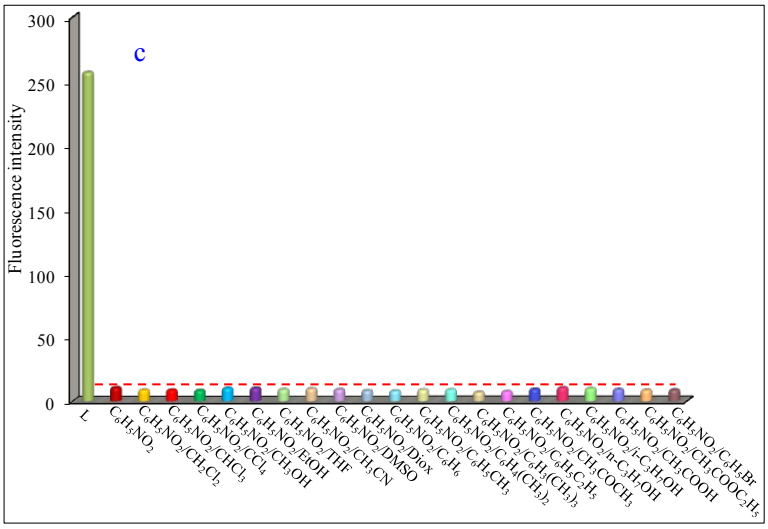


FIGURE 10 (a)The influence of organic solvents interference on the fluorescence recognition of toluene by compound **L**(DMF/H_2O), **L** = 2.8 mL, 1.3*10^{-3} mol/L, organic solvents = 0.1mL, λ_{ex}=350nm, slit =10 nm; (b)The influence of organic solvents interference on the fluorescence recognition of xylene by compound **L**(DMF/H_2O), **L** = 2.8 mL, 1.3*10^{-3} mol/L, organic solvents = 0.1mL, λ_{ex}=350nm, slit =10 nm; (b)The influence of organic solvents interference on the fluorescence recognition of nitrobenzene by compound **L**(DMF/H_2O), **L** = 2.8 mL, 1.3*10^{-3} mol/L, organic solvents = 0.1mL, nitrobenzene = 0.01 mL, λ_{ex}=350nm, slit =10 nm.

3.5| pH sensing

The fluorescence properties are recorded and listed in Figure11a (λ_{ex}=350 nm). The fluorescence intensity of compound **L** is influenced by the pH value, which is basically symmetrically distributed with pH = 7(Figure11b). At the same time, it is not difficult to find that H^+ and OH^- can quench the fluorescence of compound **L**, especially strong acid and strong base. Therefore, the fluorescence of compound **L** is sensitive to acid and base, and the acidity and basicity of the solution must be considered in practical application.

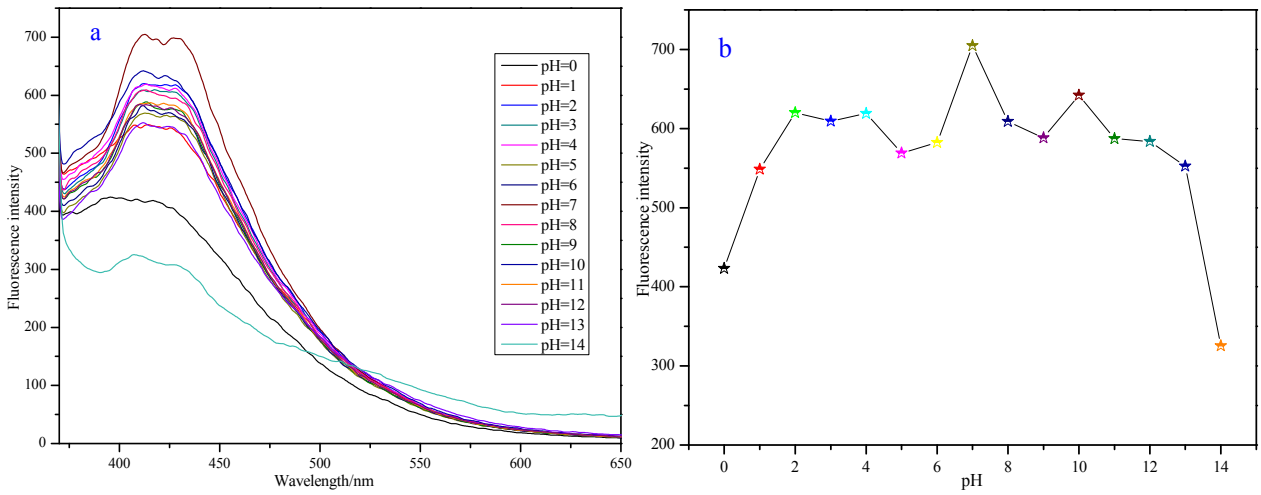


FIGURE 11 (a)Fluorescence change of compound **L** (DMF/H_2O) in different pH, L = 2.9 mL, 1.3*10^{-3} mol/L, pH =1-14, λ_{ex}=350 nm, slit = 10 nm;(b) The curves of compound **L** (DMF/H_2O) at different pH values.

3.6| Mechanism of sening

The competition between absorption and emission spectra is one of the causes of fluorescence quenching[41]. For Fe^{3+} and $Cr_2O_7^{2-}$ ions, there are partial overlap between the absorption spectrum of Fe^{3+} and $Cr_2O_7^{2-}$ ions with the emission spectrum of **L**, which were competitive adsorption between Fe^{3+}, $Cr_2O_7^{2-}$ ions and **L**(Figure S4). According to Fe^{3+} and $Cr_2O_7^{2-}$ ions fluorescence experiments, the fluorescence of compound **L** was not completely quenched when 0.1mL $Fe^{3+}$and $Cr_2O_7^{2-}$ ions(1×10^{-3} mol/L) were added, respectively. In addition, there is a larger overlap between the absorption spectra of nitrobenzene and the emission spectra of compound **L** from 350nm to 427 nm. In the competition, the absorption of nitrobenzene is obviously stronger than the emission of compound **L**. Therefore, the nitrobenzene has a strong fluorescence quenching effect on compound **L**. In contrast, the toluene and xylene have no absorption peaks at 350-500nm in the UV spectrum. There is not evidence for competitive adsorption between toluene, xylene and compound **L**, respectively. It could be inferred that the toluene and xylene could induce the aggregation of compound **L** in DMF solution, thus resulting in an enhanced fluorescence intensity.

3.7|Application to the determination of Fe^{3+} in water samples, vegetables and the determination of toluene and xylene in gasoline

The samples were taken from the Yellow River, the Park Lake and the tap water. The Yellow River and the Park Lake must be be purified by centrifugation for 10 minutes at 5000 rpm to remove solid impurities. The tap water is boiled for 5 minutes to remove the HClO from the water. Fresh vegetables are bought from the vegetable market and are ground, nitrated, filtered, centrifuged and pH adjusted to neutral. Add 0.1 mL samples directly to compound **L** DMF/H_2O solution without any other treatment before test analysis. The concentration of Fe^{3+} ions in samples were calculated by Stern−Volmer(SV) equation and $y = 1.324*10^5 x - 2.783$ were shown in Table 1. The error range of Fe^{3+} ions in water samples and vegetables were about 0.11-0.42 by calculation. The standard solutin to the error is found to be less than 0.11 by solving two curve equations. In general, the iron mass in cabbage, potato and spinach are 0~5mg, 0~1mg and 0-2.5 mg/100 g, respectively. According to the analysis and calculation, the mass of iron is 1.7-2.1 mg, 1.3-1.7 mg and 1.0-1.3

mg, respectively. In a sense, the compound **L** can be used as a fluorescence probe to measure the molarity of Fe^{3+} ion conveniently.

Table 1 Detection of Fe^{3+} ion concentration in water samples and vegetables by fluorescence of compound **L**[a]

Samples	F_0	F	$[Fe^{3+}]/10^{-4}$ mol/L		Error
			F_0/F[b]	Y[c]	
Standard Solution	342.30	275.86	5.12	5.23	±0.11
Yellow River	342.30	323.57	1.23	1.62	±0.39
Park Lake	342.30	324.08	1.20	1.59	±0.39
Tap Water	342.30	320.70	1.43	1.84	±0.41
Cabbage	342.30	315.23	1.83	2.25	±0.42
Potatoes	342.30	321.52	1.37	1.77	±0.40
Spinach	342.30	326.46	1.03	1.41	±0.38

[a](L =2.9 mL, $1.3*10^{-3}$ mol/L; sample = 0.1 mL; λex=350 nm, slit =10 nm); [b]$F_0/F=1+K_{SV}[Fe^{3+}]$; [c]$Y = 1.324*10^5$ x – 2.783.

The gasoline(92#), diesel(0#) and engine oil are purchased from gas stations. Add different volumes samples directly to compound **L** DMF/H_2O solution without any other treatment before test analysis. It found that toluene or xylene can be distinguished from gasoline, diesel and engine oil by the fluorescence curve of compound **L**(Figure S5). The results show that toluene is one of the aromaticity found in gasoline(92#), and there are isomers of xylene (except ethylbenzene) in diesel oil and engine oil. In addition, The volume of toluene and xylene in samples were calculated by Stern−Volmer(SV) equation and y(toluene) = 4826.388 x – 4.503, y(xylene) =2995.097 x -22.019 were shown in Table 2. The standard solutin to the error is found to be less than 0.001 by solving two curve equations, the error range of samples were about 0.022 and 0.010-0.011 by calculation. In a sense, the compound **L** can be used as a fluorescence probe conveniently to toluene and xylene in gasoline, diesel and engine oil.

Table 2 Detection of toluene and xylene volume in gasoline, diesel and engine oil by fluorescence of compound **L**[a]

Samples	F_0	F	$V_{toluene}$/mL		V_{xylene}/mL		Error
			F_0/F[b]	Y[c]	F_0/F[d]	Y[e]	
toluene	283.40	416.14	0.029	0.028	–	–	±0.001
xylene	283.40	412.81	–	–	0.050	0.051	±0.001
gasoline(92#)	283.40	569.34	–	–	0.081	0.103	±0.022
diesel(0#)	283.40	533.95	0.042	0.052	–	–	±0.010

Engine oil	283.40	547.37	0.044	0.055	−	−	±0.011

[a](L =2.9 mL, 1.3*10^{-3} mol/L; sample = 0.1 mL; λex=350 nm, slit =10 nm); [b]$F_0/F=1+K_{SV}$ $V_{toluene}$; [c]Y = 4826.388 x – 4.503; [d]$F_0/F=1+K_{SV}$ V_{xylene}; [e]Y = 2995.09 x – 22.019.

4| Conclusions

In conclusion, A multiple fluorescent sensor was developed for the sensitive and selective detection of Fe^{3+}, $Cr_2O_7^{2-}$ ions in aqueous solution, and probe detection of toluene, xylene and nitrobenzene in DMF solution. Compared with the reported chemical fluorescence sensors, the compound **L** is able to detect toluene and xylene, which are due to the enhancement of fluorescence of the compound **L** by toluene and xylene. The chemical fluorescence sensors for the detection of toluene and xylene are rarely reported. The compound **L** has been applied to the detection of Fe^{3+} in water samples and vegetables, and the good results have been obtained. Of course, the compound **L** is also used as a chemical fluorescent sensor to detect toluene and xylene in gasoline, diesel and engine oil, and the good results have been obtained.

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