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SHORT COMMUNICATION

A Sensitive Fluorescent Sensor for Highly Sensitive Detection of Water in Organic Solvents Based on Substituted Imidazole

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Abstract

A novel substituted imidazole derivative 1a with carboxyl and quinoline structure has been designed and synthesized. And our initial discovery is that this compound can effectively detect water in ethanol. And the metal in solution couldn't affect the absorption and fluorescence Spectra of 1a. With the addition of water, the energy band appears a red-shift from 330nm to 355nm in the absorption spectra. And the emission spectrum undergoes an important change in its fluorescent effect in the presence of water. Furthermore, absorption peak of 1a displays a red-shift with increasing pH from 2.31 to 10.72. All available data (absorption and emission) strongly support the possible mechanism. Due to the pronounced fluorescence changing property, the substituted imidazole derivative 1a could be utilized as fluorescent probes for detecting water in ethanol.

Keywords Substituted imidazole · Carboxyl and quinoline · A little amount of water · No affected by metal ion · Aggregation

Introduction

Although water is the most important liquid for human beings and the living being in the world. As the most common contaminant in organic solvents, water is often adverse in many organic synthetic reactions and industrial production processes, which negatively affected not only the yield of chemicals but also their activities. [1–5] Therefore the detection of trace water in organic solvents is very important for organic synthetic reactions and industrial productions. Normally, Karl-Fisher titration has been widely employed to detect trace water in organic solvents. [6–8] However, strict sample manipulation, the use of toxic reagents and the need for special equipment are unavoidable defects of this method. Nowadays, fluorescent sensors have been widely employed to detect trace water in organic solvents caused by their high sensitivity, inexpensive, quick and easy. [9–12] Although several fluorescence water probes based on dyes, which have disadvantages such as difficulty in synthesis, long preparation period, certain toxicity of the dye itself and environmental pollution, have been reported, it is still an urgent need to develop a novel sensor which is easily synthesized, fast-response and highly sensitive.

Imidazole, especially multi-substituted imidazole, has been found in the core fragment of many kinds of anti-inflammatory and analgesic drugs. [13–15] In addition, due to the optical activity of imidazole derivatives, they are also used in many fields such as fluorescent labeling agents, photoluminescence materials, biological imaging reagents, etc. [16, 17] In recent years, due to the wide application of imidazole derivatives in biology, industry and synthesis, several synthesis methods of imidazole compounds have been reported, such as heterocyclic rearrangement, four component condensation, phosphoric acid, acetic acid, sulfuric acid or dimethyl sulfoxide (DMSO) catalytic reaction. [18–25] Besides this, the π-π interaction can cause the organic compounds possessing such structures to form molecular aggregates with close intermolecular spacing and strong coupling. And H-aggregation denotes the aggregation showing a blue-shifted band the molecular absorption band. [26, 27] In this paper, a novel multiaryl-substituted imidazole compound has been synthesized for detecting water in ethanol by using disaggregation.

Experiment

Reagents

Benzoin, 2-quinolinecarboxaldehyde, ammonium acetate, 6-aminocaproic acid and Iodine were obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd. All of the reagents are analytical grade, which can be used without further

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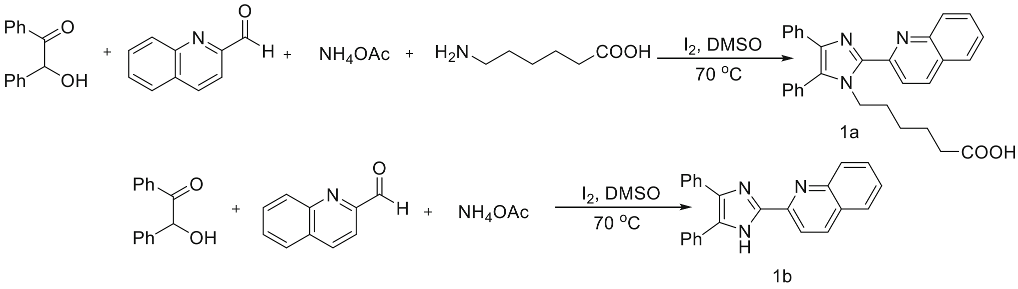
purification. All solvents were obtained commercially and used as received without further purification. Double-distilled water was used throughout the experiments. The metal ion solutions were prepared from NaCl, KCl, $Mg(ClO_4)_2$, $Ca(NO_3)_2$, $Cr(NO_3)_3$, $FeSO_4$, $CoSO_4$, $NiSO_4$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, $AgNO_3$, $CdSO_4$, $HgCl_2$, $Pb(NO_3)_2$, $AlCl_3$ in distilled water with a concentration of 0.05 M. All spectroscopic experiments were carried out at room temperature.

Apparatus

^{1} H NMR and ^{13} C NMR spectra were recorded on a Bruker AVANCE-600 spectrometer and referenced to internal tetramethylsilane. Infrared spectral data were measured with Nicolet Avatar-370. Mass spectra were obtained on a Waters Xevo G2-S QT. Melting points were measured using an X-6 microscopic melting point apparatus (Beijing, China). The UV–vis spectra were measured on a Puxi TU-1901 (Beijing, China) spectrophotometer. Fluorescence measurements were made on a Hitachi F-7000 (Tokyo, Japan). The samples were excited by the light with wavelength of 350 nm, and the emission spectrum was recorded in the range of 360 to 690 nm. The excitation and emission slit widths were kept at 1.0 and 2.5 nm, respectively.

Preparation of the Substituted Imidazole



6-(4,5-diphenyl-2-(quinolin-2-yl)-1 H-imidazol-1-yl)hexanoic acid was synthesized by a modified procedure, benzoin 0.212 g (1.00 mmol), 2-quinolinecarboxaldehyde 0.157 g (1.00 mmol), ammonium acetate 0.077 g (1.00 mmol), 6-aminocaproic acid 0.131 g (1.00 mmol) and Iodine 0.025 g (0.10 mmol) were mixed in DMSO (5 mL), then the resulting mixture was allowed to stir 4 h at 70 . After the reactant was consumed, as monitored by TLC, water (10 mL) was added to the mixture, which was then extracted with EtOAc (3 × 10 mL). The extract was washed with 10 % $Na_2S_2O_3$ solution (w/w), dried with anhydrous Na_2SO_4, and evaporated. The residue was purified by chromatography on a silica gel column (Hexane/EtOAc = 1:1) to give the desired product 1a as a light yellow solid (96.8 mg, 21 % yield).

2-(4,5-diphenyl-1 H-imidazol-2-yl)quinoline was synthesized by a modified procedure, benzoin 0.212 g (1.00 mmol), 2-quinolinecarboxaldehyde 0.157 g (1.00 mmol), ammonium acetate 0.231 g (3.00 mmol) and Iodine 0.025 g (0.10 mmol) were mixed in DMSO (5 mL), then the resulting mixture was allowed to stir 4 h at 70 . After the reactant was consumed, as monitored by TLC, water (10 mL) was added to the mixture, which was then extracted with EtOAc (3 × 10 mL). The extract was washed with 10 % $Na_2S_2O_3$ solution (w/w), dried with anhydrous Na_2SO_4, and evaporated. The residue was purified by chromatography on a silica gel column (Hexane/EtOAc = 1:1) to give the desired product 1b as a light yellow solid (138.8 mg, 40 % yield).

Results and Discussion

Absorption and Fluorescence Spectra of the 1a in Different Solvents

Initially, UV and fluorescence spectra of sensor 1a were obtained in different solvents. As shown in Fig. 1a, the maximum absorption wavelengths of the compound 1a were at 340–360 nm in common organic solvent, such as acetone, dimethylsulfoxide, acetonitrile, tetrahydrofuran, dichloromethane, ethyl acetate, methanol, ethanol, glycol, isopropanol. But nearly no absorption could be found in water. The same phenomenon could be seen from Fig. 1b, nearly no fluorescence could be found in water. But maximum emission wavelength around 455 nm could be found in common organic solvent. All these suggested that 1a could well be dissolved in most solvents except water.

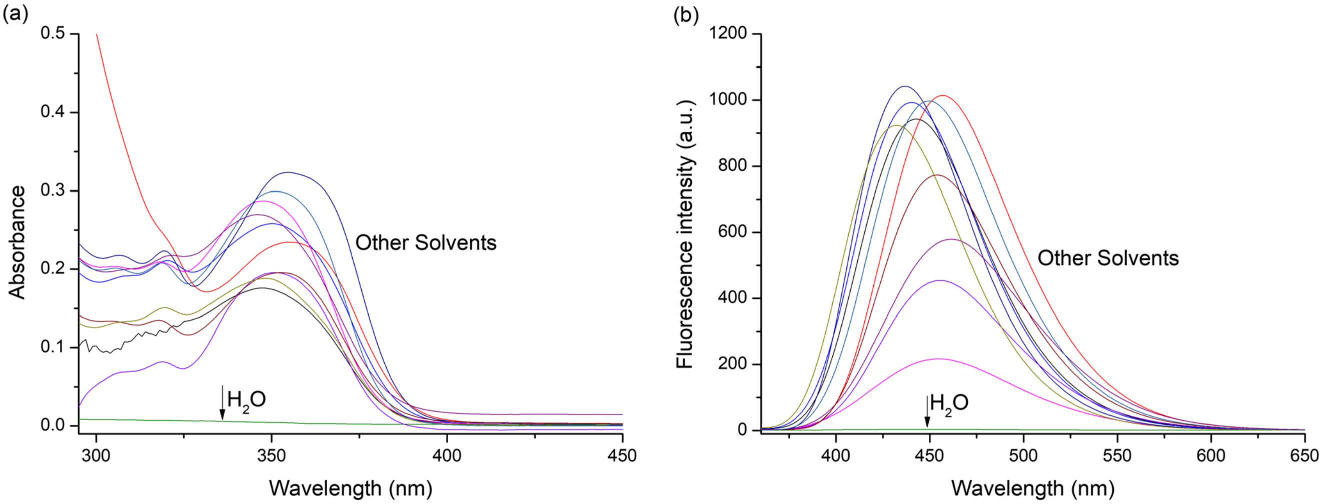


Fig. 1 **a** Absorption spectra of 1a (10 μM) in different solvents. **b** Fluorescence spectra of 1a (10 μM) in different solvents. Acetone, dimethylsulfoxide, acetonitrile, tetrahydrofuran, dichloromethane, ethyl acetate, methanol, ethanol, glycol, isopropanol, water

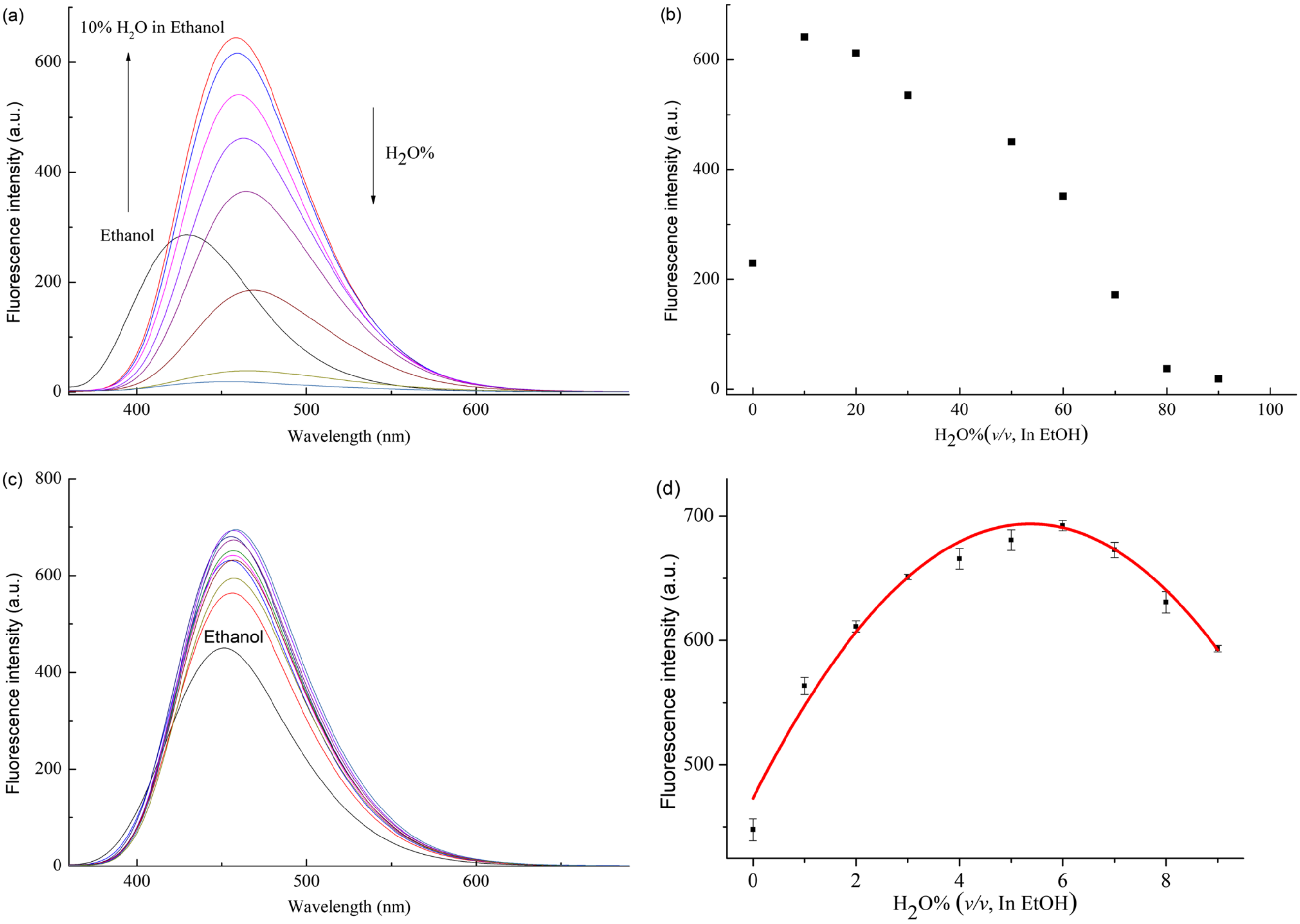


Fig. 2 **a** Fluorescence spectra of 1a (10 μM) in ethanol with different concentration of H_2O (0, 10, 20, 30, 50, 60, 70, 80, 90 v/v, %). **b** Fluorescence intensity of 1a (10 μM) at 455 nm in ethanol with different concentration of H_2O (0, 10, 20, 30, 50, 60, 70, 80, 90 v/v, %). **c** Fluorescence spectra of 1a (10 μM) in ethanol with different concentration of H_2O (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 v/v, %). **d** Fluorescence intensity of 1a (10 μM) at 455 nm in ethanol with different concentration of H_2O (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 v/v, %)

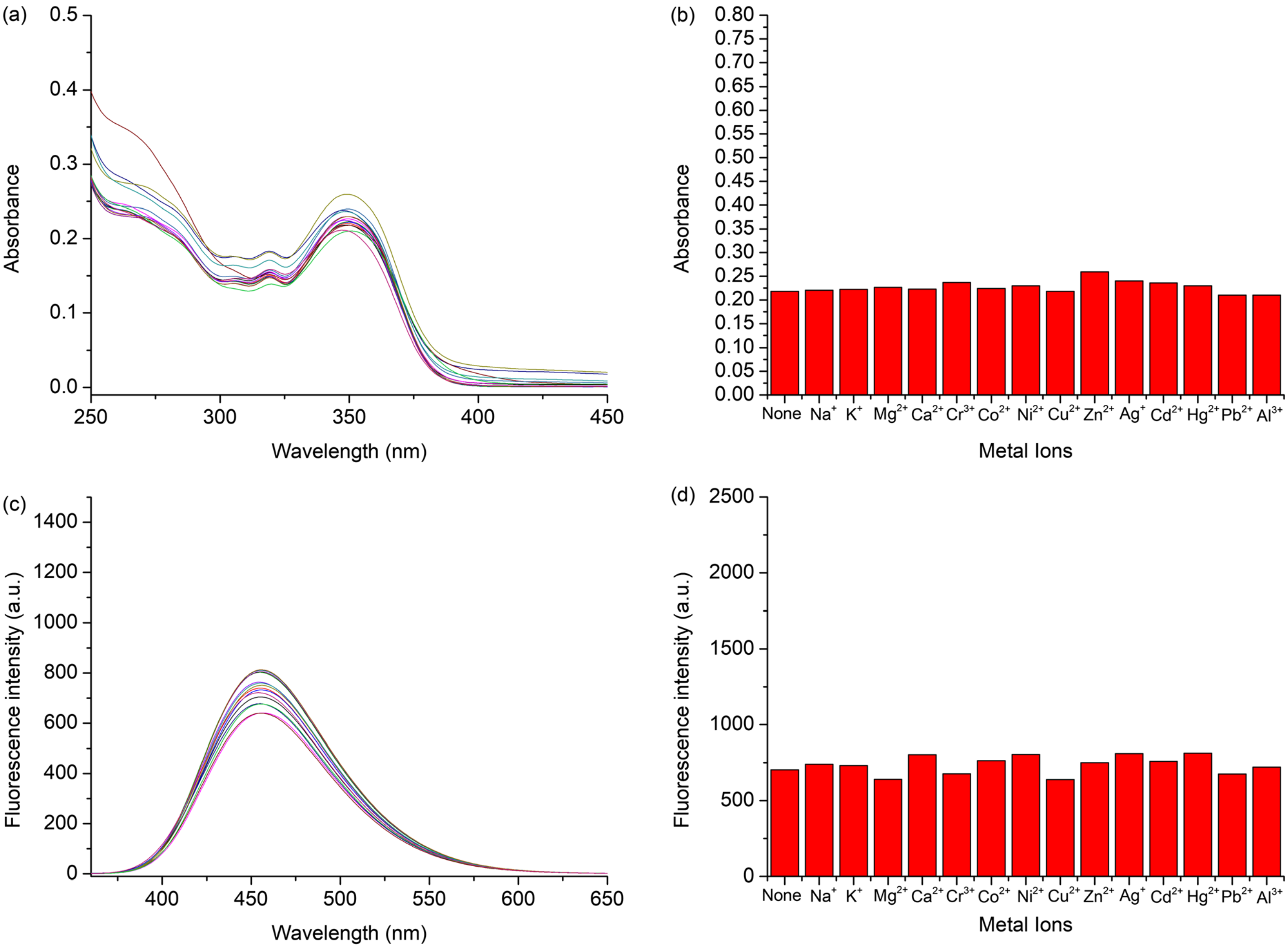


Fig. 3 **a** Absorption spectra of 1a (10 μM) with different metal ions (50 μM) including Na^+, K^+, Mg^{2+}, Ca^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Pb^{2+}, Al^{3+} in EtOH:H_2O = 94:6. **b** Absorption intensity of 1a (10 μM) at 350 nm with different metal ions (50 μM) in EtOH:H_2O = 94:6. **c** Fluorescence spectra of 1a (10 μM) with different metal ions (50 μM) in EtOH:H_2O = 94:6. **d** Fluorescence intensity of 1a (10 μM) at 455 nm with different metal ions (50 μM) in EtOH:H_2O = 94:6

Fluorescence Determination of Water Content in Ethanol

Water exists in all kinds of organic solvents and is the most common impurity in organic solvents. As the most common contaminant in organic solvents, water is often adverse in many organic synthetic reactions and industrial production processes, which negatively affected not only the yield of chemicals but also their activities. Therefore, the determination of the water content in the organic solvent is one of the most important and most commonly encountered analytical problems.

In order to explore the possibility for application of the synthesized sensor in the detection of water content in organic solvents, the fluorescence emission spectra excited by the light of 350 nm of 1a dispersed in ethanol were further examined. As shown in Fig. 2a, when the ethanol solution of 1a changed to 10 % water in ethanol, the fluorescent intensity increased significantly. This indicates that 1a can be used as fluorescent probes to quickly detect water content in organic solvents. Figure 2a and b shows the fluorescence intensity of 1a changed in ethanol with different concentration of H_2O (0, 10, 20, 30, 50, 60, 70, 80, 90 v/v, %). It can be seen that with the increase of water content, the fluorescence intensity decreases gradually and the emission peak get a red shift. In order to get more details, Fig. 2c and d shows the fluorescence intensity of 1a changed in ethanol with different concentration of H_2O (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 v/v, %). It can be seen that with the increase of water content, the fluorescence intensity increased firstly then decreased. The maximum fluorescence intensity could be detected in 6 % water in ethanol. The limit of detection was as low as 0.22 % based on five times the standard deviation rule.

Absorption and Fluorescence Spectra of the Sensor 1a with Metal Ion

The absorption and fluorescence spectra of sensor 1a were examined following the treatment with different metal ions

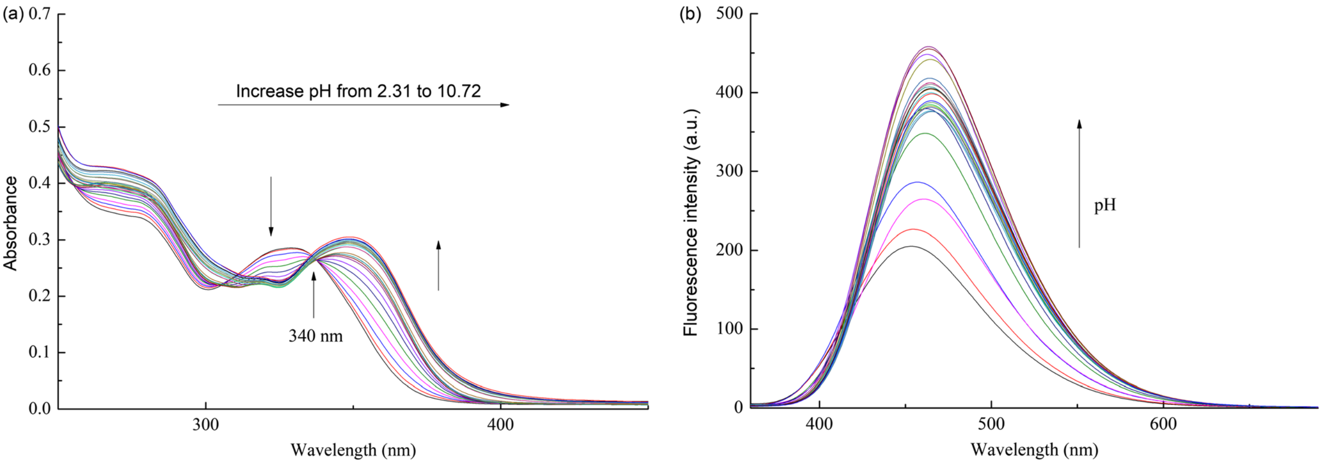


Fig. 4 **a** Absorption spectra of 1a (10 μM) with different pH from2.31 to 10.72 in EtOH:H_2O = 1:1. **c** Fluorescence spectra of 1a (10 μM) with different pH from 2.31 to 10.72 in EtOH:H_2O = 1:1

(5.0 eq.) in 6 % water in ethanol solutions. As shown in Fig. 3, after adding Na^+, K^+, Mg^{2+}, Ca^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, Hg^{2+}, Pb^{2+}, Al^{3+}, the absorption intensity (I_{350} nm) and fluorescence intensity (I_{455} nm) of 1a basically no changed. All these suggested that 1a couldn't recognize any metal ion, and the metal in solution couldn't affect the interaction of 1a with water.

Absorption and Fluorescence Spectra of 1a in Acidic and Basic Solutions

Since the compound 1a comprise both acidic (-COOH) and basic (Ar-N) groups, their properties can be very different under acidic or basic conditions, and this was next evaluated. Aqueous/ethanol (1:1 v/v) solutions were used, ensuring complete dissolution of the fluorophores, and the observed pH of the solutions adjusted by aqueous/ethanol (1:1 v/v) NaOH/HCl solutions. As shown in Fig. 4a, fluorophore 1a showed highly varied absorption peaks in different acidic and basic solutions. Absorption peak of 1a displayed a red-shift with increasing pH from 2.31 to 10.72. Then fluorescence spectra of 1a in acidic and basic solutions could be observed. As shown in Fig. 4b, fluorophore 1a showed highly varied fluorescence in different acidic and basic solutions. The fluorophore 1a showed strong emission under basic conditions while being weakly emissive in acidic solutions, similar to azo chromophores. [28] In general, azo chromophores can take H-aggregation as the typical aggregation manner under different conditions. [29–32] And H-aggregation denotes the aggregation showing a blue-shifted band to the molecular absorption band. All these suggested that compound 1a could take H-aggregation with pH decreasing and disaggregate with pH increasing.

The Possible Mechanism for Water Detection in Organic Solvents

In order to explore the mechanism for the detection of water content in organic solvents, compound 1b was synthesized. The absorption and fluorescence spectra of 1b dispersed in different organic solvents (dichloromethane, H_2O, acetonitrile, tetrahydrofuran, ethanol) were further examined. As shown in Fig. S5 and S6, the maximum emission wavelength of 1b dispersed in dichloromethane, tetrahydrofuran and acetonitrile was around 455 nm. But nearly no fluorescence could be found in water and ethanol. All these suggested that the long carboxyl chain in 1a could increase the solubility in ethanol and denote to increase the fluorescent intensity with the addition of water.

Figure 5a shows the absorption spectra of 1a changed in ethanol with different concentration of H_2O (0, 10, 20, 30, 40, 50, 60, 70 v/v, %). It can be seen that with the increase of water content, the absorption intensity decreases gradually and the absorption peak get a red shift. Figure 5b shows the absorption spectra of 1a at 350 nm in ethanol with different concentration of H_2O (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 v/v, %). It can be seen that with the increase of water content, the absorption intensity first increase and then decrease.

All these indicate that the presence of hydroxyl in water will lead to the red-shift effect for the absorption peak and change of absorption intensity. Combined with the results of Fig. 4a, H-aggregation of 1a could disaggregate with addition of water, and 1a could precipitate with the increase of water. Because the electron density around N is higher, this atom serves as a stronger acceptor of hydrogen bonds, which decreases the possibility of molecular aggregation caused by π-π interaction in the presence of water. In a word, the change of absorption and fluorescence of compound 1a is attributed to the aggregation and disaggregate caused by addition of water

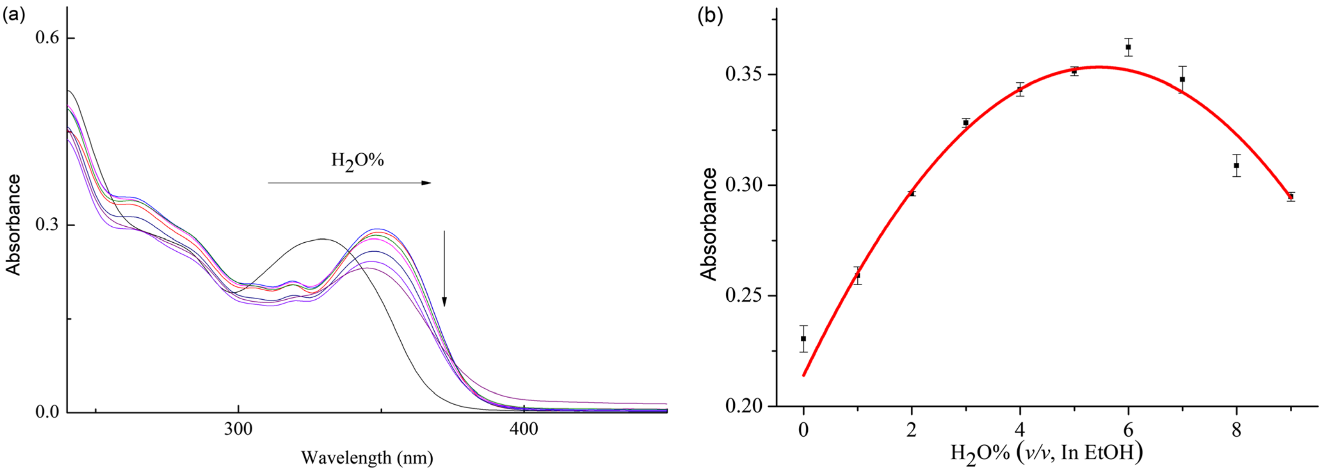


Fig. 5 **a** Absorption spectra of 1a (10 μM) in ethanol with different concentration of H_2O (0, 10, 20, 30, 40, 50, 60, 70 v/v, %). **b** Absorption spectra of 1a (10 μM) at 350 nm in ethanol with different concentration of H_2O (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 v/v, %)

and partially to the increase in polarity of the solvent caused by the addition of water (Fig. 6).

Conclusions

Novel substituted imidazole derivative 1a containing carboxyl and quinoline group has been successfully developed. The emission of 1a was highly sensitive to solvents. Significantly, the change of 1a in fluorescence intensity and wavelength was suitable for the qualitative detection of water in ethanol. And the metal in solution couldn't affect the interaction of 1a with water. Furthermore, this is the first time that substituted imidazole was adopted as the water sensing fluorescent probe. This work makes the 1a a promising material used without any modification in the detection of water in organic solvents and with immense potential for applications in quality management of the solvent products. The possible mechanism for water detection in organic solvents is attributed to the aggregation and disaggregate of 1a caused by addition of water. Further work for developing substituted imidazole-based advanced functional materials utilizing this molecular design concept for potential applications is ongoing.

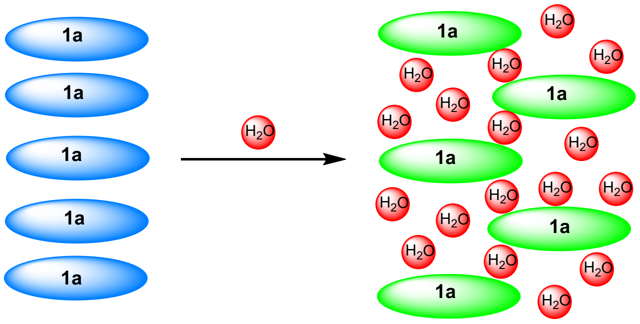


Fig. 6 The possible mechanism

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10895-021-02729-w.

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Author Contributions Weijian Xue contributed to the conception of the study and wrote the manuscript;

Huiqian Li performed the experiment;

Jinping Wang contributed significantly to analysis;

Jie Ma performed the data analyses and manuscript preparation;

Bing Zhao helped perform the analysis with constructive discussions;

Xiangfeng Guo helped perform the analysis with constructive discussions.

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Data Availability All data generated or analyzed during this study are included in this published article.

Declarations

Confict of Interest Huiqian Li declares that she has no confict of interest. Weijian Xue declares that he has no confict of interest. Jinping Wang declares that she has no confict of interest. Jie Ma declares that she has no confict of interest. Bing Zhao declares that she has no confict of interest. Xiangfeng Guo declares that he has no confict of interest.

Ethical Approval This article does not contain any studies with human or animal subjects.

Informed Consent A statement regarding informed consent is not applicable.

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