#### **ORIGINAL ARTICLE**



# A Versatile Aggregation-induced Emission Fluorescent Probe for Visible Detection of pH

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#### Abstract

By tactfully structuring a luminescent molecule as an accurate pH probe with aggregation-induced emission (AIE) feature, it is significant to overcome aggregation-caused quenching of emitted light in practice. Herein, we present a simple AIE-active fluorescence probe for pH detection on the basis of intramolecular charge transfer (ICT) with wide response range and high sensitivity reaction. The donor-acceptor-donor (D-A-D) style probe utilized a conjugated structural hybrid of the electron-withdrawing nitrile group and electron-donating hydroxyl as well as dimethylamino groups for fluorescent platform. The AIE-active probe possesses good fluorescence under water fraction up to 90% in mixed MeOH/water system. Furthermore, it can be used in profiling and visualization of pH detection in MeOH/water system at  $f_w = 90\%$  under UV 365 nm lamp. What's more, the probe can be employed to be a broad range test paper of pH detection, paving the way for low-cost practical applications.

Keywords  $\alpha$ -cyanostilbene · Aggregation-induced emission · Intramolecular charge transfer · pH probe · Fluorescence

# Introduction

Since its inception coined by Tang in 2001 [1], aggregationinduced emission (AIE) luminogens, which depend on the availability of strong fluorescence emission in the aggregated states or solid states, have been exceedingly explored in versatile fields such as high-performance emissive materials [2, 3], electroluminescence [4, 5], photovoltaic devices [6-9], sensors [10-12], hydrogels [13], liquid crystals [14-16], fluorescence imaging [17–20], pathogen identification [21], photosensitizers [22, 23], drug delivery [24], and cancer cell ablation [25]. In view of the manifestation and augmentation of radiative excited states for organic molecular systems, a series of AIE-active organic luminogens have been exploited so far, including tetraarylethenes [5, 10, 11, 15, 26, 27], phenanthroimidazole [6, 28], carbazole [9, 29], triphenylamine [30–32], fluorenone [33], phenanthrenequinone [34], BODIPY [35], thieno[3,2-b]thiophene S,S-dioxide [36], terpyridine [37], salicylaldazine [38], triazatruxene [39], cyanostilbenes [14, 16, 20, 40-46] derivatives and so on. Among them,  $\alpha$ -cyanostilbene derivatives have

received considerable attention because of the stilbenic  $\pi$ conjugated backbone equipped with cyano-group, which can display a lacking electron character. Affixing electron-donating substituents at the positions of aryl groups in the  $\alpha$ -cyanostilbene unit, significantly influences the electron density distribution (band gap) of  $\pi$ -conjugated system (i.e. the emission properties in solid and solution states) via intramolecular charge transfer (ICT) [46].

Accurate and reliable measurement of pH plays a great importance in a wide range of chemical, environmental, biological and industrial applications. In recent years, although numerous highly sensitive, flexible, real-time, reversible and reliable pH sensors have been fabricated with self-healing polymer [47], hydrogel [48], electrochemical reaction [49, 50], fluorescent molecular [51-53], and so forth, the biocompatibility and aggregation are still the main limitations in the use of fluorescent signals. Considering that the colorimetric fluorescent molecular for pH detection is still vastly superior due to its high sensitivity, simple operation and dynamic monitoring, especially the AIE-active pH sensors are proved to be more advantageous than the dyes having the fluorescence quenching effect in the aggregated or solid states [17, 54–60], Therefore, It is well accepted that development of a versatile AIE fluorescent probe for detecting real-time changes of pH in both solution and solid states has important significance.

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In this work, we explored a colorimetric AIE-active fluorescent probe for pH detection in mixed MeOH/water system. The probe was constructed using a conjugated structural system in which dimethylamino and hydroxyl groups appeared to interact significantly with acid and base, respectively. With changing the pH from 7.4 to 1.8 under acidic conditions, the emission peak of the probe gradually declined and generated blue shift from 547 nm to 484 nm, and the color of solution changed from bright orange-yellow to blue under UV 365 nm light. Under alkaline conditions, as the pH gradually increased, a new fluorescence peak emerged and enhanced at 589 nm with a 42 nm red-shift, and the yellow color of the solution significantly enhanced under UV 365 nm light. Furthermore, the probe had high sensitivity and selectivity. Finally, the probe was developed as a pH test strip for a broad range of pH detection in practical application.

## Experimental

## **Materials and Equipments**

Unless indicated otherwise, all chemicals acquired commercially were used without further purification. Metal ions were all nitrates salts, and anions were all sodium salt. Thin-layer chromatography (TLC) was performed on glass plates precoated with silica gel. Chemical structures were identified by hydrogen nuclear magnetic resonance (<sup>1</sup>H NMR) spectra, which were obtained with a Bruker-ARX 400 spectrometer in CD<sub>3</sub>OD solvent, and calibrated using tetramethylsilane (TMS,  $\delta = 0$  ppm) as internal standard. Chemical shifts are quoted in parts per million (ppm), and coupling constants are made out as J-values in Hz. MALDI mass spectrum was determined on a Bruker MALDI-Mass spectrometer. Elemental analysis (C, H and N) was performed on a PerkinElmer 2400 CHN Analyzer. Emission and absorbance spectra were recorded in quartz cuvettes at room temperature on a UV-visible absorption spectrophotometer (Shimadzu, UV-2550) and a fluorescence spectrophotometer (Shimadzu, RF-5301PC), respectively. The fluorescence absolute quantum yields  $(\Phi_F)$  were measured on an Edinburgh Instruments FLS920 fluorescence spectrometer with a calibrated integrating sphere. The pH value of solution was measured and controlled with a PHS-3C pH meter (Shanghai LeiCi Device Works, China). Density functional theory (DFT) (B3LYP/6-31G (d) level of theory) was utilized to model the structure geometry and electronic properties of relevant molecular.

#### Synthesis of Probe 1

Under a nitrogen atmosphere, 4-hydroxybenzene acetonitrile (2.663 g, 20 mmol), *p*-dimethylaminobenzaldehyde (2.984 g, 20 mmol) and sodium hydroxide (0.8 g, 20 mmol) were

dissolved in ethyl alcohol (50 mL), stirred and refluxed for 6 h. Reaction progress was monitored by TLC. As the completion of the reaction, the mixture was cooled to ambient temperature, the excess solvent was evaporated under reduced pressure. After admixing with 30 mL of HCl solution (1 M), the precipitate was formed in resulting mixture, filtered, and purified with recrystallization in methyl alcohol/water (1/1, v/v) to obtain compound 1 as a saffron yellow powder. Compound 1: Yield 87%; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD)  $\delta_{\text{ppm}}$ : 7.75 (d, J=9.0 Hz, 2H, Ar-H), 7.41 (d, J=9.0 Hz, 2H, Ar-H), 7.37 (s, 1H, CH3), 6.78 (d, J=9.0 Hz, 2H, Ar-H), 6.72 (d, J = 8.5 Hz, 2H, Ar-H), 2.95 (m, 6H, N(CH<sub>3</sub>)<sub>2</sub>); anal. Calcd for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O: C, 77.25; H, 6.10; N, 10.60; O, 6.05. Found: C, 77.91; H, 6.02; N, 11.18; O, 6.35. MALDI-MS (C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O) [M]<sup>+</sup>: calcd: m/z = 264.13. found: m/z =264.04.

## Fluorescence and UV-Vis Measurements

For absorption or fluorescence measurements, probe 1 was dissolved in CH<sub>3</sub>OH to obtain stock solutions  $(1.0 \times 10^{-3})$ mol/L). The stock solutions of ions  $(1.0 \times 10^{-2} \text{ mol/L})$  were prepared in deionized water by dissolving a pre-determined amount of their salts. The pH meter was adjusted by using standard solution of potassium hydrogen phthalate (pH = 4.00) and mixed phosphate (pH = 6.86). The pH-dependent spectral characteristics of probe 1 were adjusted by HCl and NaOH. In the interfering experiment, the pH = 4.00 buffer solution was prepared by dissolving potassium hydrogen phthalate in deionized water, and the pH = 9.18 buffer solution was prepared by dissolving sodium tetrabrate in deionized water. The emission spectra of the samples were recorded with  $\Delta \lambda_{ex} = 5$  nm and  $\Delta \lambda_{em} = 10$  nm, respectively. For the absorbance and the fluorescence of probe in solid state, 50 mg of probe 1 was dissolved in 10 mL methanol, and then the solution was dropwise added on guartz cuvettes, followed by natural evaporation at room temperature.

#### Calculation of pKa

The pKa value can be analyzed using the well-known Henderson-Hasselbach type equation:  $pKa = pH \log((F_{max} F)/(F F_{min}))$ , where  $F_{max}$  and  $F_{min}$  are maximal and minimal fluorescence intensity at detection range, respectively. F is the fluorescence intensity of probe 1 under corresponding pH, whereas the eventual pKa refers to the average estimated value for a succession of pKa under acidic or basic pHs, respectively [61].

## **Preparation of Test Paper Strips**

The test paper strips were obtained by cutting filter paper with the size of  $10 \times 20$  mm. Prepared filter paper was placed in methyl alcohol solution of the probe **1** ( $2.0 \times 10^{-3}$  mol/L), and

dried in the air. Then 50 mL HCl and NaOH solutions with different pH were dripped into the filter paper. After placing the test paper 30 mm above the solvent of hydrochloric acid and ethylenedi-amine respectively and keeping it for 30 s, the color changes of the test paper strips were observed under UV 365 nm lamps.

# **Result and Discussion**

## Synthesis and Characterization

The chemical structure and synthetic route of probe 1 is shown in Scheme 1. Probe 1 was obtained by a simple one-step reaction between 4-hydroxybenzene acetonitrile and dimethylaminobenzaldehyde, having a favourable yield (87%). The chemical structure of probe 1 was characterized by various characterization techniques (NMR, MALDI-MS and elemental analysis), and the results fitted well to the expected structure. <sup>1</sup>H NMR spectrum and the details of other characterization spectra are given in Supplementary Information. Probe 1 exhibited good solubility in common organic solvents such as methyl alcohol, ethyl alcohol, tetrahydrofuran, dichloromethane, acetonitrile, and so on, but insoluble in water.

#### Photophysical Properties of Probe 1

The photographs of probe 1 in MeOH solution (10  $\mu$ M) and solid state under natural light and UV 365 nm lamp were presented in Fig. 1b. The probe 1 in MeOH solution is golden colour under natural light and shows barely fluorescence under UV 365 nm lamp, respectively. Moreover, the solid state of probe 1 is pale yellow solid under natural light and presents brick-red fluorescence under UV 365 nm lamp, respectively. To evaluate the photophysical properties of probe 1 in a single-molecule and agminated states, the UV-vis absorption and fluorescence spectra of probe 1 were recorded in MeOH solution and solid state, respectively (Fig. 1a). The corresponding data was summarized in Table 1. In MeOH solution, the well-structured probe 1 exhibits a broad absorption band in the range of 300-500 nm due to the conjugated skeleton, a main maximum absorption peak is located at 378 nm. Under an excitation wavelength of 380 nm, there is a weak fluorescence emission peak at about 490 nm with a fluorescence quantum yield ( $\Phi_{\rm F}$ ) of 0.13, a large stokes shift is about 112 nm. Compared with the spectra in MeOH solution, the absorption and emission peaks of probe 1 in solid are severely bathochromic shifted to 415 nm and 550 nm, respectively. A stokes shift reaches up to 187 nm, the  $\Phi_F$  is of 0.34. Additionally, the absorption and fluorescence spectra of probe 1 in both MeOH solution and solid state keep unchanged after being left to natural light for 10 days, indicating its high photostability.

#### Aggregation-induced Emission

Investigation of the AIE behaviour of probe 1 was carried out in MeOH /water system through the fluorescence spectra. As shown in Fig. 2a, the probe 1 has a weak fluorescence signal at 490 nm in pure MeOH solution. The fluorescence intensity maintains at low level with the increase of the  $f_w$  from 0 to 40% in MeOH /water system. However, on increasing  $f_w$  from 40 to 90%, the fluorescence intensity begins to enhance and reaches the summit with 7-fold enhancement at  $f_{\rm w} = 90\%$ , highlighting the contribution of the molecular aggregation state, which limites the free rotation of aryl groups and reduces the nonradiative transition. The fluorescence spectra of probe 1 exhibit a remarkably red-shift from 490 nm in pure MeOH solution to 547 nm at  $f_w = 90\%$  in MeOH/water system, originating from intramolecular charge transfer (ICT) state along with an increase of solvent polarity, which depends mainly on the electron-withdrawing nitrile group and electron-donating hydroxyl as well as dimethylamino groups. Meanwhile, the  $\Phi_{\rm F}$  of probe 1 is 0.31 at  $f_{\rm w}$  = 90%, which is higher than that in pure MeOH solution ( $\Phi_{\rm F} = 0.13$ ). While the emission intensity begin to quench when the fraction of water continue to increase to  $f_{\rm w} = 95\%$  (Fig. 2b), mainly due to the production of more compact nanoaggregate. Since probe 1 possesses an excellent AIE property and shows the fluorescence maximum emission in MeOH /water system at  $f_w = 90\%$ , we mainly focused on this solution system to further explore the pH sensor.

## Optical Response of the Probe 1 to pH

The pH-dependent sensing performances of probe **1** in the mixed solution of MeOH/water (10  $\mu$ M, 1/9, v/v) were further explored by utilizing UV absorption and fluorescence emission spectra in detail. As observed in Fig. 3a, probe **1** shows a strong absorption peak at 446 nm in original solution (pH = 7.4) before H<sup>+</sup>-triggered titration process. There is a drastic



Scheme 1 Synthesis of AIE-active pH probe 1: anhydrous EtOH, NaOH, refluxing, 6 h, yield: 87%



**Fig. 1** a the UV absorption and fluorescence emission spectra of probe 1 in MeOH solution (10  $\mu M$ ,  $\lambda_{ex} = 380$  nm) and solid ( $\lambda_{ex} = 420$  nm). **b** The photographs of probe 1 (10  $\mu M$ ) in MeOH solution and solid under natural light and UV 365 nm lamp

attenuation of absorption band at 446 nm caused by the variation of pH from 7.4 to 1.8, whereas a new peak emerges and strengthens at 358 nm with an well-defined isosbestic point at 398 nm, reflecting that the protonation of dimethylamino moiety was the solely acting factor under the circumstances. The obvious blue shift (~88 nm) of the absorption spectra from 446 nm to 398 nm means that the electron-donating ability of dimethylamino group was weakened and the conjugation of N atom and aromatic core was breaked due to the protonation of dimethylamino moiety. Simultaneously, an intuitive colour change of the aforementioned effect was given in Supplementary Information (Fig. S3(a)), the solution colour of probe 1 is from light yellow to colourless upon decreasing pH from 7.4 to 1.8 under natural light. Additionally, the pHdependent changes in fluorescence emission spectra of probe 1 were demonstrated in Fig. 3b. On decreasing the solution pH from 7.4 to 1.8, an intense emission band located at 547 nm  $(\Phi_{\rm F}=3.15)$  in original solution is declined gradually and moved to 484 nm ( $\Phi_{\rm F}$  = 1.27) with a blue shift of 63 nm under the solution pH of 1.8 ( $\lambda_{ex}$  = 380 nm), indicating that the protonation of dimethylamino group can reduce the rigidity of probe molecule, make a dent in ICT effect in molecule. As expected, the luminescence colour of the probe 1 solution changes from bright orange-yellow to blue as the pH value decreases from 7.4 to 1.8 under UV<sub>365nm</sub> light irradiation (Fig. S3(b)). What's more, the sigmoidal fitting of the relative emission intensity ratio (I/I<sub>max</sub>) and pH value gives a pKa (average pKa of protonated dimethylamino unites under acidic pHs) of 4.23 (Fig. 3c), and a good linear relationship ( $R^2 = 0.99668$ )

between the fluorescent intensity and pH values is obtained in the pH range of 3.9-5.9 (Fig. 3d), the linear regression equation is y = 357.04819x-677.91114.

Under alkaline conditions, the absorption spectra of probe 1 displayed in Fig. 4a have a gradual enhancement and the relevant absorption bands become stronger when the pH increase from 7.4 to 12.0, implying that the structure of probe 1 was altered at a higher pH. The peak shifted from 446 nm to a higher wavelength around 487 nm at pH = 12.0, generating a conspicuous red-shift (41 nm) as compared to that at pH = 7.4. Moreover, the fluorescence titration reveals a tendency similar to that of the UV spectra (Fig. 4b). As the pH jump from 7.4 to 12.0, a new fluorescence peak emerges and heightens at 589 nm ( $\Phi_{\rm F}$  = 3.49), along with a 42 nm red-shift. Because the deprotonation of the phenolic hydroxyl group of probe 1 is taken into account in the OH-triggered process, the above observations could be explained by the electron-donating and p- $\pi$  conjugate effects of O atom with a negative charge under alkaline conditions. What's more, the sigmoidal fitting of the relative emission intensity ratio (I/I<sub>max</sub>) and pH value affords a pKa (average pKa of deprotonated phenolic hydroxyl groups under basic pHs) of 10.87 (Fig. S4(a)). A good linear relationship ( $R^2 = 0.99196$ ) between the fluorescent intensity and pH values is achieved in range of pH values of 10.0-11.3 (Fig. S4(b)), and the linear regression equation is y =293.36032x-1314.22267. Of note, this OH-triggered titration process makes an apparent effect on luminescence colour of the probe 1 solution, which changes from bright orange-yellow to yellow as the pH jump from 7.4 to 12.0 under  $UV_{365nm}$  light irradiation (Fig. S5). As a result, probe 1 is capable of sensing

Table 1	The photophysical data
of probe	1

Compound	states	$\lambda_{abs} \ (nm)$	$\lambda_{em} \ (nm)$	Stokes shift (nm)	$\Phi_{\rm F}$
1	in MeOH solution	378	490 <sup>[a]</sup>	112	0.13
	in solid	415	550 <sup>[b]</sup>	135	0.34

[a]  $\lambda_{ex} = 380$  nm;

[b]  $\lambda_{ex} = 420 \text{ nm}$ 



Fig. 2 a Fluorescence emission spectra of probe 1 in MeOH/water system with different water fractions (10  $\mu M$ ,  $\lambda_{ex} = 380$  nm). b Plot of the fluorescence intensities of probe 1 in MeOH/water system with different water fractions (Inset: fluorescence images)

extreme pH values over two wide pH windows (pH = 3.9-5.9 and 10.0-11.4). This result indicates that this probe has potential application value for the quantitative determination of acidic pH values by the fluorescence methods.

## **Reversibility, Interference and Time Course Test**

A good reversibility of the probe is the prerequisite for practical application, the emission intensities of probe 1 were monitored repeatedly through regulating and controlling pH values between 1.8 and 7.4, 7.4 and 12.0 several times in the mixed solution of MeOH/water (10  $\mu$ M, 1/9, v/v). As shown in Fig. 5a and b, the probe enables to restore the fluorescence intensity at pH = 1.8 and pH = 12.00 after six cycles, hinting the probe with a favourable reversibility.

In addition, an estimation of the fluorescent time-response of probe 1 (10  $\mu$ M) to the solution of pH = 1.8 and pH = 12.00 was carried out, respectively. The sensing process is very





**Fig. 3** a The absorption spectra of probe 1 (10  $\mu$ M) in MeOH/water system with decreasing pH from 7.4 to 1.8. b The fluorescent emission spectra of probe 1 in MeOH/water system with decreasing pH from 7.4 to 1.8 (10  $\mu$ M,  $\lambda_{ex} = 380$  nm). c The sigmoidal fitting of fluorescence

intensity ratios I/I<sub>max</sub> of probe l in MeOH/water system at various pH values. **d** A good linear plot of fluorescence intensity I<sub>max</sub> in the pH range of 3.9-5.9



Fig. 4 a The absorption spectra of probe 1 (10  $\mu$ M) in MeOH/water system with decreasing pH from 7.4 to 12.0. b The fluorescent emission spectra of probe 1 in MeOH/water system with decreasing pH from 7.4 to 12.0 (10  $\mu$ M,  $\lambda_{ex} = 380$  nm)

quick after probe **1** mixed with pH solution for 1 min, and the fluorescence intensity remains stable over a period of 2 h (Fig. 5c). That means the probe **1** can be used as a high-efficiency fluorescence sensor for pH detection.

In fact, there may be a deal of ion species to disturb the sensing process in actual application. To evaluate the high selectivity of probe 1 towards  $H^+$  and  $OH^-$  over other potential competitive ion species, the interference experiments of probe

1 (10  $\mu$ *M*) for pH detection were measured the in the media (pH = 5.9 and pH = 10.5) mixed with other ion species (5.0 equiv.), including K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ba<sup>2+</sup>, Al<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Cr<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, S<sup>2-</sup>, CH<sub>3</sub>COO<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>. As shown in Fig. 5d, the fluorescence intensities examined for other metal ions in the solution of pH = 5.9 is similar to that induced by H<sup>+</sup> alone.





**Fig. 5** The reversible fluorescence emission intensities of probe 1 at 484 nm between pH 1.8 and 7.4 (**a**) and at 589 nm between pH 7.4 and 12.0 (**b**) in the mixed solution of MeOH/water ( $\lambda_{ex} = 380 \text{ nm}, 10 \,\mu M, 1/9$ , v/v). (**c**) Time-dependent fluorescence intensity changes of probe 1 at pH = 1.8 ( $\lambda_{em} = 484 \text{ nm}$ ) and at pH = 12.0 ( $\lambda_{em} = 589 \text{ nm}$ ). (**d**) Change in emission intensity of probe 1 in the mixed solution of MeOH/water ( $\lambda_{ex} = 380 \text{ nm}, 10 \,\mu M, 1/9, v/v$ ) at pH = 5.9 ( $\lambda_{em} = 546 \text{ nm}$ ) and at pH =

10.5 ( $\lambda_{em}$  = 585 nm) upon addition of various ions (5.0 equiv.), respectively. 1, blank; 2, K<sup>+</sup>; 3, Na<sup>+</sup>; 4, Ca<sup>2+</sup>; 5, Mg<sup>2+</sup>; 6, Zn<sup>2+</sup>; 7, Fe<sup>2+</sup>; 8, Fe<sup>3+</sup>; 9, Cu<sup>2+</sup>; 10, Ba<sup>2+</sup>; 11, Al<sup>3+</sup>; 12. Co<sup>2+</sup>; 13, Ni<sup>2+</sup>; 14, Cd<sup>2+</sup>; 15, Cr<sup>2+</sup>; 16, Pb<sup>2+</sup>; 17, Mn<sup>2+</sup>; 18, F<sup>-</sup>; 19, Cl<sup>-</sup>; 20, Br<sup>-</sup>; 21, l<sup>-</sup>; 22, CO<sub>3</sub><sup>2-</sup>; 23, NO<sub>3</sub><sup>-</sup>; 24, NO<sub>2</sub><sup>-</sup>; 25, SO<sub>4</sub><sup>2-</sup>; 26, SO<sub>3</sub><sup>2-</sup>; 27, S<sup>2-</sup>; 28, CH<sub>3</sub>COO<sup>-</sup>; 29, ClO<sub>4</sub><sup>-</sup>; 30, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>; 31, HPO<sub>4</sub><sup>2-</sup>; black bar: pH = 5.9; red bar: pH = 10.5

In the solution with pH = 10.5, most of the competitive ions have negligible impact on the pH detection, whereas the presence of Cu<sup>2+</sup> leads to minor fluorescence enhancement by about 15%. These results suggest that the probe **1** has excellent anti-interference ability against the aforementioned additives for fluorescent pH detection.

## Proposed Mechanism and Theoretical Calculations

In the light of the above, the pH-dependent photophysical properties of probe **1** with proposed change and adjustment of the structure are demonstrated in Fig. 6a. To support this mechanism, <sup>1</sup>H NMR titrations of the probe **1** in acid and alkali conditions were performed in CD<sub>3</sub>OD/D<sub>2</sub>O (1/1, v/v). As depicted in Fig. 6c, the aromatic resonance signals of phenolic ring exhibit two double peaks at 6.72 ppm (a) and 7.41 ppm (b), one cuspidal singlet located at 7.37 ppm (c) is characteristic signal of CH group, and the aromatic protons of dimethylaniline ring have two double peaks at 7.75 ppm (d) and 6.78 ppm (e) in neutral media. However, the chemical shifts of resonance signals (a ~ e) of probe **1** display an obvious downfield shift by  $\Delta\delta$  0.13 ~ 0.79 ppm under acidic condition, which derives from the enhanced electron-withdrawing effect and the decreased electron density of the conjugation system due to the protonation of the



Fig. 6 (a) The proposed action mechanism of probe 1 for the pH-dependent sensing under  $UV_{365nm}$  light irradiation. <sup>1</sup>H NMR titrations of the probe 1 in (b) acid, (c) neutral and (d) alkali conditions, respectively





dimethylamino group (Fig. 6b). Under alkali condition, the deprotonation of the phenolic hydroxyl group of probe 1 improve the electron-donating and p- $\pi$  conjugate effect, which would impact considerably on the electron cloud distribution in molecule. The proton signals of phenolic ring and CH group produce a slight upfield shift at 6.71 ppm (a"), 7.37 ppm (b") and 7.34 ppm (c''), respectively. While the protons of dimethylaniline ring are shifted downfield by  $\Delta \delta$  0.06 ppm (Fig. 6d). To gain insight into the electronic structures of probe 1 under different conditions, the density functional theory (DFT) calculations were carried out at the B3LYP/6-31G\* level as basic set with the Gaussian 09 program, and viewed from Fig. S6. In water (neutral media), the electron cloud of LUMO and HOMO is delocalized on the whole molecular, which indicates that the complete charge separation could transport on the whole molecule. Except for HOMO electron cloud in acid condition, others in acid and alkali conditions possess the similar electron cloud distributions to that of probe 1 in water. It means that the protonation of the dimethylamino group eliminates the p- $\pi$  conjugate system of N atom and aromatic core. The energy band gaps of probe 1 in water, acid and alkali conditions were calculated as 3.32 eV, 3.53 eV and 2.67 eV, respectively. It is seen that the energy gap of probe 1 in alkali media is lower than that in neutral media, contributing to the additional  $\pi$ -electron conjugated structure from the deprotonation of the phenolic hydroxyl group. Additionally, a trend of decreasing band gaps (3.53 eV, 3.32 eV and 2.67 eV) suggests that the optical behaviour of probe 1 had a gradual red-shift on increasing the pH values. The analysis of <sup>1</sup>H NMR experiment results and theoretical calculations confirms that the proposed mechanism agrees well with the electronic structure and optical properties.

#### Test Paper Strips of Probe 1 for pH Detection

In consideration of visible pH sensing performance of probe 1 at different wavelength with the same excitation wavelength, test paper strips of probe 1 for pH detection were developed and demonstrated in Fig. 7. It is obvious that the color of the strips is nattier blue under  $UV_{365nm}$  light irradiation while the strips of

probe **1** were treated by the acidic solution. After immersing the strips into the alkaline solutions containing probe **1**, the paper strips turns to yellow color under  $UV_{365nm}$  light irradiation. With regards to the paper strips soaked by the solutions with increased pH, the color of the paper strips shows the deepened yellow fluorescence under  $UV_{365nm}$  light irradiation. Besides, the test paper strips could be used to detect volatilized solvent such as hydrochloric acid and ethylenedi-amine. Due to the gas from the solvent interacted with probe **1**, the color of test paper above hydrochloric acid and ethylenediamine changed to cyan and yellow under UV 365 nm lamp respectively.

# Conclusions

In summary, we have described a conjugated structural AIEactive pH probe 1, which could respond to pH via intramolecular charge transfer. Probe 1 could respond to a broad pH range from 1.8 to 12.0, exhibiting different fluorescence emissions (blue/ orange yellow at pH  $1.8 \sim 7.4$ , and orange yellow/yellow at pH  $7.4 \sim 12.0$ ). Probe 1 was not susceptible to common potentially competing ions in the pH sensing process. In particular, the protonation and deprotonation mechanism of probe 1 was confirmed by <sup>1</sup>H NMR titrations and the density functional theory (DFT) calculations in the pH sensing process. What's more, the application of probe 1 as a pH test strip for a broad range of pH detection was successfully achieved, providing a promising candidate for pH detection in other fields.

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s10895-020-02669-x.

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**Data Availability** All the data and materials from this manuscript will be made available on request.

## **Compliance with Ethical Standards**

**Competing Interests** No potential conflict of interest was reported by the authors.

Ethical Approval Not applicable.

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