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# Fluorescent and colorimetric detection of pH by a rhodamine-based probe

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ABSTRACT

Described here is a rhodamine-based derivative (**1**) that acts as a colorimetric and fluorescent "off-on" probe for the detection of pH. The design tactics for the probe is based on the change in structure between spirocyclic (non-fluorescent) and quinoid-type (fluorescent) forms of rhodamine dyes. The tetrahydrofuran/Tris(hydroxymethyl)aminomethane-HCl (4:6, v:v, pH 7.5) buffer solution of **1** is colorless and nonfluorescent, whereas ring-opening of the corresponding spirolactam to a conjugated quinoid form induced by $H^+$ gives rise to strong absorption and fluorescence emission as well as a pink color. The fluorescence change of **1** is reversible and takes place mainly within the pH range from 1.1 to 4.0, which is valuable for the detection of strong acidic environment.



## 1. Introduction

In recent years, the highly sensitive and selective detection of pH becomes extremely important because it usually plays a key role in a variety of systems [1–7]. Many detection methods such as acid–base indicator titration [8–10] and potentiometric titration [11,12] have been used for measurement of pH values. Although much success has been achieved for the detection of $H^+$ using these excellent analytical techniques [13–15], there is still a strong demand to design and develop low-cost, selective and real-time monitoring systems for the detection of $H^+$.

Fluorescent probes [16] are treated as significant detection systems because of their particular performance. The hydrogen ion induced changes in fluorescence appeared to be an active research area due to its convenient operation, high selectivity and sensitivity [17–20]. To date, a number of efforts have been made to the development of efficient fluorescent chemosensors for the detection of pH in environmental samples [21–23]. It still remains great challenging to design useful probes for monitoring pH level especially in strong acidic environment.

Rhodamine derivatives [24–29] are prized for their relatively high photostability, high quantum yield in aqueous solutions and to be excitable at long wavelength and have been widely used for detection of various metal ions [30–45]. Serious of this kind of fluorescent probes have been prepared and attained considerable effect, while pH-sensitive systems relying on rhodamine derivatives as pH fluorescence probes are less common.

We envisioned that the proton-promoted ring-opening reaction of rhodamine Schiff bases could be utilized to detect pH level [46]. Herein, an efficient method for the detection of pH using rhodamine 6G hydrazide derivative **1** as a sensitive and selective probe is described. The method is based on the $H^+$ induced structure change of **1** from spirocyclic to quinoid form (Fig. 1), the formation of conjugated system results in the increase intensity of UV absorbance and fluorescence emission, and a color change from colorless to pink. Based on this phenomenon, a new fluorescent probe for pH was developed and showed excellent sensitivity and selectivity in aqueous solutions (pH < 4.0).

## 2. Experimental

### 2.1. Chemicals and apparatus

All the reagents were of analytical-reagent grade and were used without further purification unless otherwise mentioned. Doubly distilled water was used throughout the experiment. All reactions were magnetically stirred and monitored by thin layer chromatography (TLC). Solutions of metal ions were all prepared from their chloride salts. A 0.06 M of tetrahydrofuran (THF)/Tris-HCl (4:6, v:v, pH 7.5) buffer solution was prepared. Different pH (1.1, 2.0, 3.1, 4.0,

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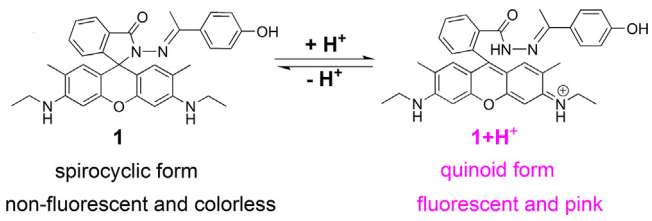



**Fig. 1.** Chemical structure of **1** and **1**+**H**$^+$.

5.1, 6.1, 6.9, 8.1, 9.0, 10.0, 11.0, 12.1 and 12.9) buffer solutions were also prepared.

Absorption spectra were recorded on an UV-2550 spectrophotometer. Fluorescence spectra were performed on Varian Cary Eclipse fluorescence spectrometer. $^1$H NMR and $^{13}$C NMR were measured on a Varian Unity-plus spectrometer with TMS as an internal standard and $d_6$-DMSO as solvent. Electro spray ionization mass spectra (ESI-MS) were obtained on a LCQ Advantage MAX system. The pH values were measured with a PHS-3C pH meter (Shanghai, China). Data of the single crystals were collected on a Bruker Apex CCD diffract meter at 173 ± 0.2 K. IR spectra were recorded on a Nicolet FT-IR200 spectrometer.

### 2.2. Synthesis of probe *1*

The synthetic route of **1** is shown in Scheme 1, rhodamine 6G hydrazide (**2**) was synthesized firstly. **2** was synthesized from the literature methods [47] by a one-step reaction of rhodamine 6G with hydrazine hydrate (80%) in ethanol. Probe **1** was prepared by following procedures. To a 100 mL round-bottomed flask, rhodamine 6G hydrazide attained above (**2**, 0.900 g, 2.10 mmol) and *p*-hydroxyacetophenone (0.286 g, 2.10 mmol) were dissolved in 20 mL methanol with 0.15 mL acetic acid and refluxed for 6 h. The solvent was removed under reduced pressure, then put the mixture to cooled water and filtered. The solid product was dried in vacuum. The crude product was purified via silica gel column chromatograph (petroleum ether/ethyl acetate 5:3, v:v) to afford the corresponding rhodamine 6G derivative **1** as a light yellow solid (0.96 g) in a moderate to good yield about 83.62%. Mp: 234 °C. $^1$H NMR ($d_6$-DMSO, 400 MHz) $\delta$ (ppm): 1.192 (6H, t, 2NHCH$_2$CH$_3$), 1.866 (6H, s, Xanthene–2CH$_3$), 2.058 (3H, s, CNCH$_3$), 3.101 (4H, q, 2NHCH$_2$CH$_3$), 3.472 (1H, s, OH), 5.018 (2H, s, 2NH), 6.223 (4H, s, Xanthene–4H), 6.708 (2H, d, $J$ = 8.4 Hz, Ar–H), 7.052 (1H, S, Ar–H), 7.413 (2H, d, $J$ = 8.4 Hz, Ar–H), 7.542 (2H, s, Ar–H), 7.823 (1H, s, Ar–H). $^{13}$C NMR ($d_6$-DMSO, 101 MHz) $\delta$ (ppm): 14.654, 17.521, 18.027, 37.956, 40.019, 55.389, 62.028, 66.622, 96.112, 106.097, 115.527, 118.200, 123.002, 124.145, 127.993, 128.989, 130.822, 132.986, 147.870, 151.782, 160.077, 160.414, 168.592. IR (KBr pellet, cm$^{-1}$): 3397, 2966, 2923, 2858, 1657, 1609, 1517, 1359, 1270, 1206, 839, 732. HRMS (ESI): $m/z$, calculated for $C_{34}H_{34}N_4O_3$ [M+H]$^+$ 546.3; found 547.3.

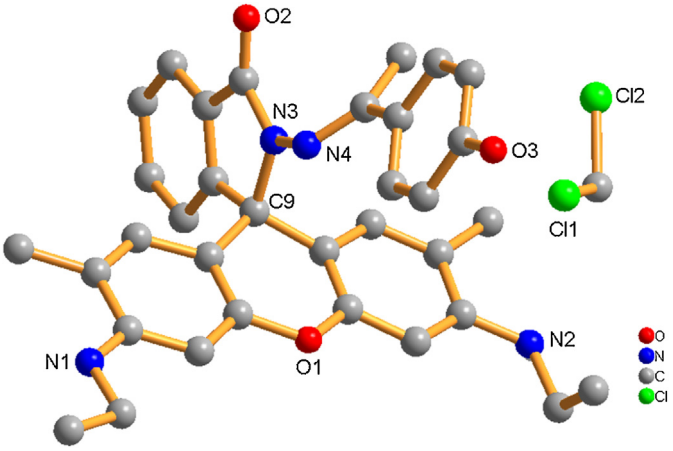



**Fig. 2.** View of the crystal structure of **1** with all hydrogen atoms omitted for clarity.

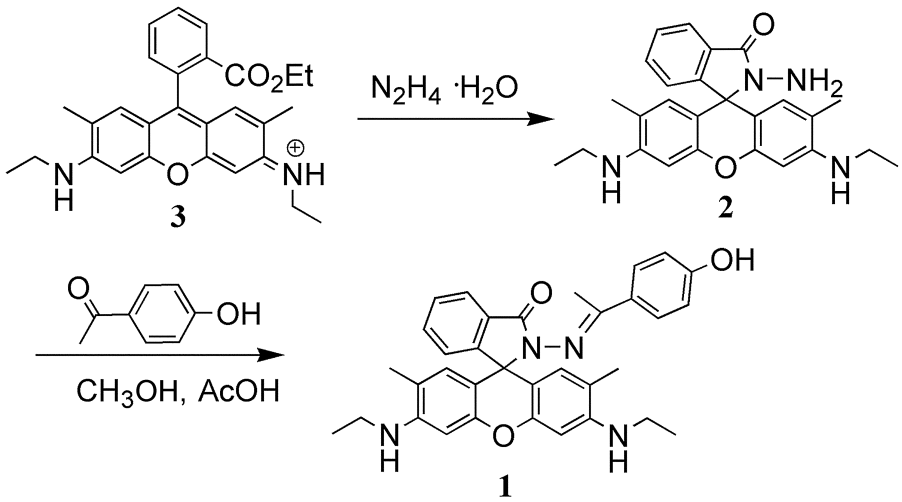
### 2.3. Single crystal growth

**1** was highly purified. A light yellow single crystal of **1** was grown from a saturated CH$_3$OH–CH$_2$Cl$_2$ (1:5, v:v) solution at room temperature (25 °C) after 2 days and was characterized by X-ray crystallography.

## 3. Results and discussion

### 3.1. The single crystal structure of *1*

The spirolactam-ring skeleton of **1** is clearly observed from the crystal structure, which revealed two planes of a xanthene ring and a spirolactam ring are coordinated mutually vertical (Fig. 2). The contents of the unit cell also include a dichloromethane molecule.




**Scheme 1.** Synthetic route of probe **1**.