



Hydrogen bond induced fluorescence recovery of coumarin-based sensor system [☆]

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ABSTRACT

Two coumarin-type fluorescent sensors were synthesized and their fluorescence response to pH value was investigated. The fluorescence intensity of sensor **3** and sensor **4** is obviously enhanced along with the increase of pH from 7 to 12 and the reduction of pH value from 8 to 1, respectively. Possible mechanism for these fluorescence recovery systems is proposed. Intramolecular hydrogen bond could be formed under different condition, which blocks electron transferring route from nitrogen atom to fluorophore. The blue fluorescence color change of the two sensory systems could be directly detected by naked eyes under UV-lamp for pH values.

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Hydrogen bond is a kind of nonbonded interaction that widely exists in natural world. Its significance has been identified by chemists, biologists, and physical scientists.¹ Hydrogen bond participates in numbers of functional activities such as spatial structure of protein and helical conformation of DNA.² It also shows its positive help in new drug design, crystal engineering, and functional material synthesis.³ Hydrogen bond is so attractive and important that IUPAC published an article in which a novel definition was recommended for this term in 2011.⁴

Fluorescence technology has been widely used in chemistry and biology during the last few years. Because of its sensitivity, selectivity, rapid response, and high spatial resolution via microscopic imaging,⁵ chemical sensors that can cause fluorescent change response are intensively investigated to monitor metal ions and pH in cell and animal body.⁶ There are several reports on hydrogen bond assisted fluorescent sensors in neutral circumstance.⁷ But so far there have been very few works on hydrogen bond induced fluorescence recovery of sensory system.⁸ In this Letter, a fluorescent sensory system was developed via intramolecular hydrogen bond formation under alkaline condition.

Coumarin is one of the most used fluorophores in the designing of fluorescent sensors due to its easy accessibility and high quantum yield in aqueous media. Coumarin-based fluorescence sensor has been developed for detection of Al³⁺, Mg²⁺, Hg²⁺, Cu²⁺, Zn²⁺, DNA, and saccharides in the past few years.⁹ Recently, our group designed and synthesized several coumarin-based sensors that could exhibit unique fluorescence response features for the detection of Mg²⁺.¹⁰ In order to further explore its potentiality in sensor design, herein we synthesized two novel fluorescent pH sensors based on hydrogen bond induced fluorescence recovery.

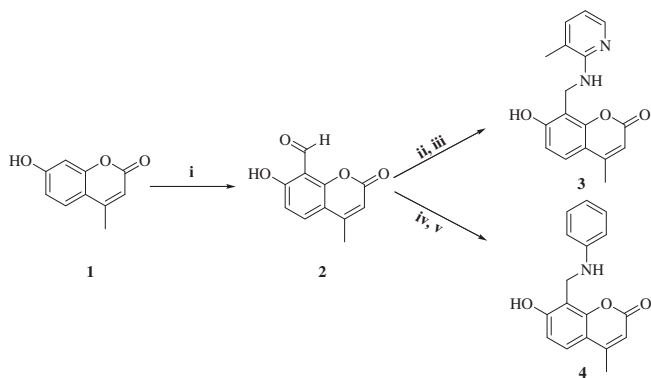
Compound **2** was prepared according to reported procedures (Scheme 1).¹¹ 7-Hydroxy-8-((6-methylpyridin-2-ylimino)methyl)-4-methylcoumarin could be synthesized via nucleophilic addition–elimination reaction of compound **2** and 2-amino-6-methylpyridine in EtOH, which was immediately reduced by sodium borohydride to afford 7-hydroxy-8-((6-methylpyridin-2-ylamino)methyl)-4-methylcoumarin (compound **3**) in a two-step yield of 78.5%. Compound **4** was obtained following the similar procedures of compound **3**.

As shown in Figure 1a, the UV–vis spectra of sensor **3** (10 μM, MeOH/water = 1:1) exhibited a maximal absorption at 319 nm under neutral condition. As the pH value gradually increased from 7 to 12 in the solution, the maximal absorption peak made an obvious reduction, and a new peak situated at 374 nm arose simultaneously. The maximal absorption showed 55 nm red shift when pH value changed from 7 to 12 with an isosbestic point at 343.5 nm, which could be attributed to the ionization and isomerization of sensor **3**. Figure 1b is the UV–vis spectra of sensor **4**,

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Scheme 1. Synthesis procedures for sensors **3** and **4**. Reagents and conditions: (i) hexamine, HCl, water, 70–80 °C; (ii) 2-amino-6-methylpyridine, EtOH, reflux; (iii) NaBH₄, THF, 0 °C; (iv) aniline, EtOH, reflux; (v) NaBH₄, THF, 0 °C.

which exhibits a main maximum absorption peak at 321 nm and shows no obvious change with decreasing of pH value from 6 to 1.

Quantum yields of sensors **3** and **4** are determined to be 5% and 7% using the quinine sulfate solution in 0.5 mol/L⁻¹ H₂SO₄ ($\Phi_f = 55\%$) as a standard, respectively. The low quantum yields of these two sensors should be attributed to a typical photoinduced electron transfer (PET) process, herein, the NH group with lone pair

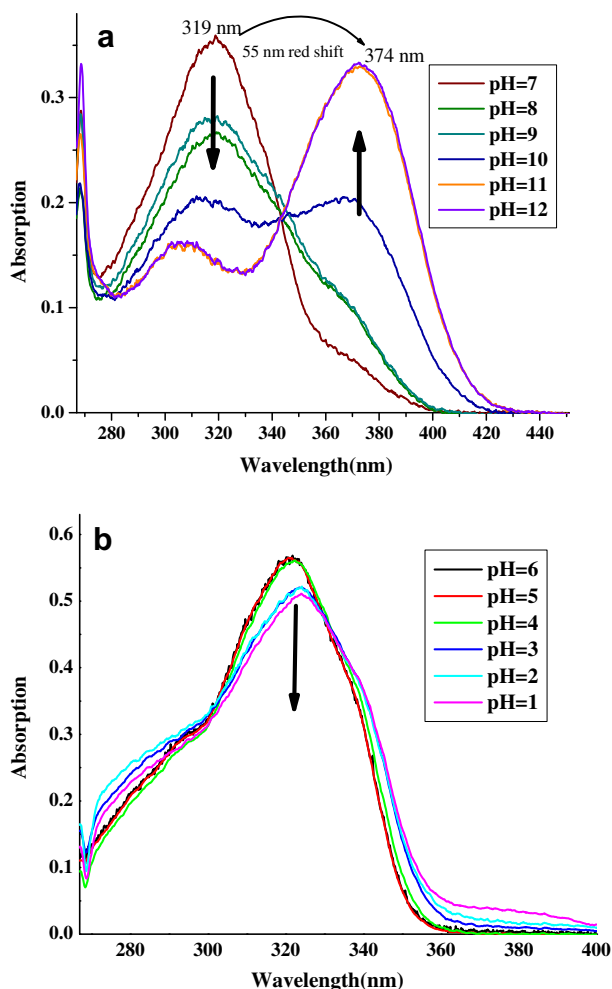


Figure 1. UV-vis spectra of sensor **3** (a, pH 7–12) and sensor **4** (b, from pH 6 to 1) on H⁺.

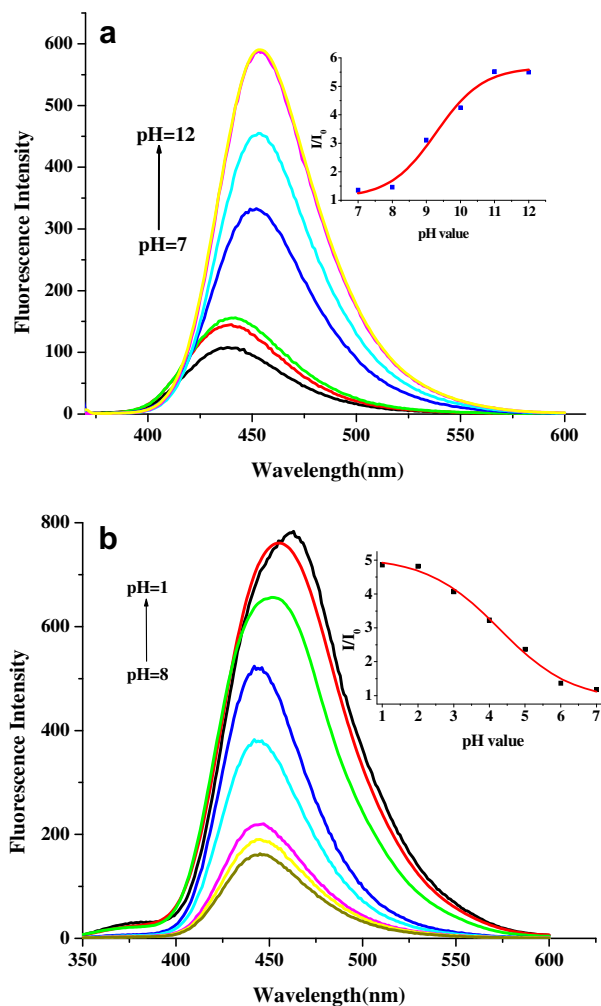


Figure 2. (a) The fluorescence change with increased pH value of sensor **3** (from pH 7–12; $\lambda_{ex} = 365$ nm, $\lambda_{em} = 453$ nm), inset: sigmoidal fitting plot of I/I_0 versus pH value. (b) The fluorescence change with decreased pH value of sensor **4** (from pH 8 to 1; $\lambda_{ex} = 327$ nm, $\lambda_{em} = 463$ nm), inset: sigmoidal fitting plot of I/I_0 versus pH value.

of electrons quenches the fluorescence of these systems.¹² The fluorescence response of sensor **3** to pH value was investigated. As shown in Figure 2a, sensor **3** (10 μ M in MeOH/water, 1:1) showed a relatively weak peak at pH 7, which was centered at 437 nm. The fluorescence intensity was obviously enhanced as high as 5.5-fold with the increased pH value from 7 to 12. Moreover, the maximal emission wavelength displayed a red shift from 437 nm to 453 nm in the fluorescence spectra. We also found that a distinct fluorescent color change of sensor **3** occurred from pale blue to deep sky blue upon the change of pH value, indicating that the fluorescence changing could be detected by naked eyes (Fig. 3). The possible mechanism of this pH responsive sensory system is shown in Figure 3. Structure **3A** is obtained in alkaline solution, then intramolecular hydrogen bond could be formed with the help of one water molecule, which confines the electron transfer from N atom of the N–H group to the fluorophore of the coumarin group; another reason is that there exists a dynamic resonance balance between **3A** and **3B** and the balance makes intramolecular hydrogen bond much more stable than its normal style. Figure 2b shows the fluorescence intensity of sensor **4** is enhanced with the decreasing of pH value from 8 to 1 and the maximum emission wavelength shifts from 442 to 463 nm. As shown in Figure 3, under acidic conditions, the N–H group of sensor **3** is protonated and the

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