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# HCHO-reactive molecule with dual-emission-enhancement property for quantitatively detecting HCHO in near 100% water solution

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ABSTRACT

A dual-model fluorescent probe for formaldehyde has been developed. With excitation at 365 and 400 nm respectively and upon addition of formaldehyde, the fluorescent probe displays off-on fluorescence responses at 415 and 505 nm. Formaldehyde can be detected quantitatively in the concentration range from 0 to $2.7 \times 10^{-2}$ M and the detection limit on fluorescence response of the probe can be as low as 6 μM. The proposed method was successfully employed for preliminary application in several commercially available foods.



## 1. Introduction

As an important industrial commodity chemical, millions of tons of formaldehyde are produced every year and are widely used to manufacture building materials and numerous household products [1,2]. As a result, formaldehyde has become one of the most important air pollutants in residential and industrial occupational environments. Besides, it is also used in many other fields such as chemical synthesis, medicinal applications and present in food items like fruits, vegetables, fish [3,4] and meat. However, if the concentration of formaldehyde in food items is high enough, there will be a reduction in food quality and even result in a pernicious effect on consumers' health [5]. As well known, formaldehyde has serious effects on human health, and in 2004, the International Agency for Research on Cancer (IARC) reclassified it as a human carcinogen [6,7] and the US Environmental Protection Agency (EPA) has classified formaldehyde as a probable human carcinogen [8]. A formaldehyde concentration of 0.04 ppm from 7 to 180 days was established as the permitted maximum concentration by the National Aeronautic Space Agency.

To ensure that residual formaldehyde has no harmful effect on human health, early detection is critical to control the formaldehyde level. Although there are many types of formaldehyde detection methods, including piezoelectric sensors [9], electrochemical biosensors [10], quartz crystal microbalance [11,12], Raman spectroscopy [13], gas chromatography [14,15], liquid chromatography [16,17], X-ray diffraction (XRD), transmission electron microscopy (TEM) [18] and biosensor methods [19–21]. Novel sensor technologies are needed to enable real time, in situ detection of formaldehyde in a compact and reusable manner [22,23]. Due to simplicity, high sensitivity, and instantaneous response [24], rapid progress has been made in the development of fluorescent probes for metal ions, biomolecules and anions. Comparison to semiconductor sensors based on gas-sensitive films [25–28], fluorescent sensors have advantages in the sensitivity [29]. However, whether for gas HCHO or for aqueous HCHO, very few fluorescent sensors have been reported [30–32]. Therefore, it is significant to develop fluorescent probe for HCHO.

In our previous work, we have developed a fluorescent dye 2-amino-3-(1H-benzo[d]imidazol)pyridine, which has strong dual-emission fluorescence property. The dual emissions have been attributed to the excited normal (N*) and tautomer (T*) forms which result from an ESIPT (N*→T*) process. Using such fluorescence property, we have successfully applied this compound

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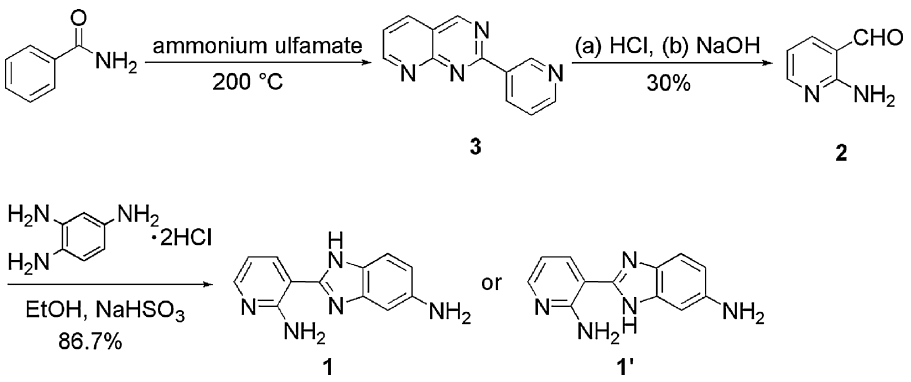


**Scheme 1.** Synthetic route of compound **1**.

in the detection of $Al^{3+}$/$Cu^{2+}$ and $F^-$ [33]. If we introduce an amino group in the benzene ring, such as 2-amidyl-3-(3-amidly-1H-benzo[d]imidazolyl)-pyridine (compound **1**, Scheme 1), what change will happen to the fluorescence property? As we know, formaldehyde can react easily with amine derivatives, what influence will the reaction between compound **1** and formaldehyde bring on the fluorescence property of compound **1**? Based on such thoughts, in this paper, we synthesized a highly sensitive and stable fluorescent dye compound **1**, which also has dual-emission property. Compound **1** can quantitatively detect formaldehyde with dramatically enhanced fluorescence in aqueous solution. The detection limit on fluorescence response of the probe can be as low as 6 μM.

## 2. Experiment

### 2.1. Materials and reagents

All commercial grade chemicals and solvents were purchased and were used without further purification. The 2-amidyl-3-(3-amidly-1H-benzo[d]imidazolyl)-pyridine (**1**) was synthesized according to Scheme 1 and following our recently reported method [33,34].

### 2.2. Synthesis of 2-amidyl-3-(3-amidly-1H-benzo[d]imidazolyl)-pyridine (*1*)

The ethanol solution of 1,2,4-triaminobenzene dihydrochloride was slowly added to the ethanol solution of compound **2** (0.3615 g, 0.003 mol) and $NaHSO_3$ (0.8669 g, 0.008 mol), after the pH of the ethanol solution containing 1,2,4-triaminobenzene dihydrochloride (0.5870 g, 0.003 mol) was adjusted to 7 with 1 mol/L NaOH ethanol solution. Under argon atmosphere, the above mixture was refluxed for 5 h, cooled to room temperature, and filtered. The crude product was obtained from the concentration of the filtrate in vacuum. The final product (0.5860 g) was obtained by column chromatography over silica gel column using ethyl acetate/triethylamine (100:1) as eluent. The yield was 86.7%. Characterization of compound **1** or **1**′: HRMS (EI) calcd. for $C_{12}H_{12}N_5$ [M+1], 226.1093; found, 226.1091. $^1$H NMR: $\delta_H$ (400 MHz, DMSO-$d_6$, $Me_4Si$): 5.04 (s, 2H), 6.54 (d, 1H), 6.68 (m, 2H), 7.33 (d, 1H), 7.80 (s, 2H), 8.01 (d, 1H), 8.08 (d, 1H), and 12.27 (s, 1H). $^{13}$C NMR: $\delta_C$ (100 MHz, DMSO-$d_6$): 94.41, 107.18, 111.87, 111.96, 119.08, 134.31, 135.40, 135.69, 146.02, 148.17, 148.88, and 157.31.

### 2.3. Instruments

Mass spectra were obtained on high resolution mass spectrometer (IonSpec4.7 Tesla FTMS-MALDI/DHB). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 400 NMR spectrometer. Chemical shifts are reported in parts per million using tetramethylsilane (TMS) as the internal standard.

All spectral characterizations were carried out in HPLC-grade solvents at 20 °C within a 10 mm quartz cell. Fluorescence spectroscopy was determined on a Hitachi F-4500 spectrometer. The fluorescence quantum yields were measured at 20 °C with quinine bisulfate in 1 M $H_2SO_4$ ($\Phi_{fl}$ = 0.546) selected as the reference [35]. Time-resolved fluorescence spectra were measured on a LifeSpec picosecond TRF spectrometer (Edinburgh Instruments Ltd.). The sample concentration was set to $1.0 \times 10^{-5}$ M.

### 2.4. DFT calculations

DFT calculations using the Becke three-parameter exchange/Lee–Yang–Parr correlation hybrid functional (B3LYP) with 6-31G(d, p) basis sets as implemented in the Gaussian 09 suite of programs were carried out for the geometry optimizations of **1**, **1**′. The energies of **1** and the product from the reaction of **1** and HCHO were obtained using time-dependent DFT (TD-DFT) with the same basis sets.

## 3. Results and discussion

### 3.1. Synthesis of compound *1* or *1*′

In this work, compound **1** was prepared in a yield of 86.7% from nicotinamide by a three-step synthetic procedure. The chemical structure was confirmed by HRMS, $^1$H, and $^{13}$C NMR.

### 3.2. Structure determination of compound *1* or *1*′

The HRMS, $^1$H, and $^{13}$C NMR data of product from reaction between 1,2,4-triaminobenzene dihydrochloride and compound **2** indicate that there is only one product, suggesting no isomers exist. It is too difficult to determine the exact structure of the final step of reaction with the current characterization methods.

To further analyze structures of the final reaction, theoretical calculations were performed on compounds **1** and **1**′. From Fig. 1, it is obvious that the ground state energy of **1** (−737.714) is less than that of **1**′ (−737.710). Such little difference of the ground state energies of **1** and **1**′ indicates that **1** possibly is more stable than **1**′.

### 3.3. Dual-emission fluorescent properties of compound *1*

Upon excitation at 365 nm, very weak fluorescence emission at 409 and 515 nm with $\Phi_{fl}$ = 0.016 (Fig. S1) was obtained in the emission spectrum of compound **1**, indicating a dual-emission behavior, which was similar to that of our previous reported dye