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Reaction based colorimetric and fluorescence probes for selective detection of hydrazine

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ABSTRACT

Development of simple and selective methods for the detection of hydrazine has attracted much attention, because hydrazine is harmful to human organs and is a probable human carcinogen. As presented in this work, two new colorimetric and fluorescent probes (**HP1** and **HP2**) for hydrazine based on dipyrromethene boron difluoride (BODIPY) fluorophore were synthesized and characterized, which showed different reactivity with hydrazine through Gabriel reaction mechanism. In the case of **HP1**, the hydrazinelysis occurred completely and lead to an enhanced fluorescence that is due to the released N-protecting group. However, the hydrazinelysis of **HP2** did not reach its completion, where the additioned hydrazine group caused efficient PET quenching, resulting in a decreased fluorescence. Both probes displayed good sensitivity and selectivity to hydrazine in aqueous medium.

1. Introduction

In the past few decades, optical based detecting techniques (the fluorescence spectroscopic methods especially) have been attracted much attention [1,2], especially, well-developed and wide application in the detections of various analysts, such as heavy metal ions [3–6], anions [7,8], neutral molecules [9,10], and enzymes [11]. Benefits from these methods are attributed to their outstanding advantages including high sensitivity and selectivity, simple operation, and real-time monitoring. Hydrazine, as a basic synthetic reactant, is widely used in the synthesis of pharmaceuticals, pesticides, and other various fine chemicals [12]. As a volatile and toxic compound, hydrazine is very easy to be inhaled by chemists or industrial workers, resulting in possible damages to human body. Several research indicated that hydrazine is harmful for the central nervous system, lungs, liver and kidneys and could cause serious diseases [13,14]. The US Environmental Protection Agency (USEPA) also set up a threshold limit value (TLV) of 10 ppb because hydrazine is a probable human carcinogen [15]. Therefore, exploration of a practical method to detect hydrazine is significantly important for human healthy.

So far, a large number of methods for detecting hydrazine, including chromatography mass spectrometric [16] and electrochemical sensor [17], have been developed. Recently, several fluorescent probes as hydrazine detectors were also reported, and some of them showed good selectivity and reactivity with hydrazine [18–39]. Herein, we chose BODIPY as the fluorophore because of its high light and thermal stability, high fluorescence quantum yield and easy to be modified [40–42]. The probes were easily synthesized as outlined in Scheme 1. In this work, we synthesized two fluorescent probes for detection of hydrazine, which displayed different reactivity with hydrazine through the Gabriel reaction.

2. Experimental

2.1. Chemicals and instruments

All reagents and solvents were purchased from commercial sources and used without further purification. NMR spectra were measured on a Bruker DRX-400 spectrometer. Mass spectra were measured on an Agilent 6410B LC-MS spectrometer. Fluorescent

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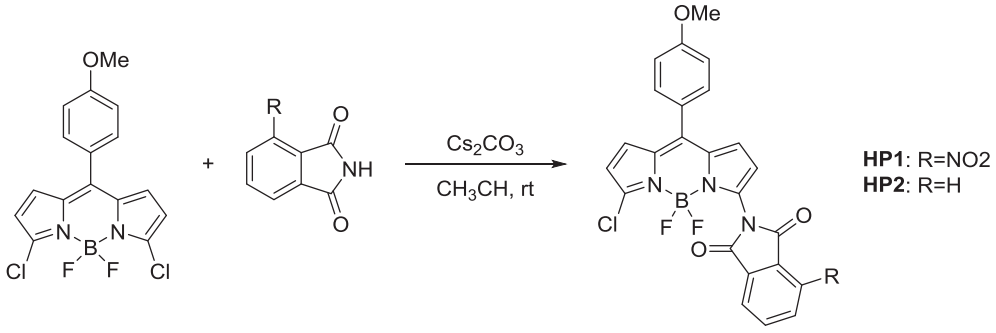

Scheme 1. Synthesis of **HP1** and **HP2**.

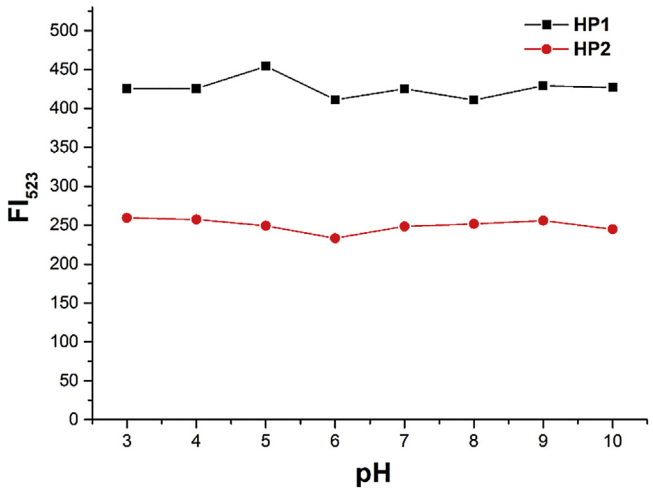

Fig. 1. Influence of pH on fluorescence intensity of **HP1** and **HP2**.

spectra were determined on a Hitachi Fluorescence Spectrophotometer F-7000.

2.2. Synthesis of *HP1* and *HP2*

1 [43] (500 μmol) and **2** (500 μmol) were dissolved in acetonitrile (50 mL), then Cs_2CO_3 (204 mg, 625 μmol) was added in above solution. The resulting mixture was stirring overnight at room temperature under an inert atmosphere. After the reaction completed, the solvent was removed under vacuum and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 3/1, v/v).

HP1, red solid, 93 mg, 36% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 7.5 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.01 (t, J = 7.8 Hz, 1H), 7.54 (d, J = 8.7 Hz, 2H), 7.09 (d, J = 8.7 Hz, 2H), 7.05 (d, J = 4.6 Hz, 1H), 7.01 (d, J = 4.3 Hz, 1H), 6.56 (d, J = 4.2 Hz, 1H), 6.50 (d, J = 4.6 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 147.7, 146.8, 145.6, 135.8, 134.1, 134.0, 132.6, 129.8, 129.2, 129.2, 128.0, 128.0, 124.8, 120.2, 117.3, 114.4, 55.6; HRMS (ESI) m/z Calcd for $C_{24}H_{14}BClF_2N_4NaO_5$ $[M+Na]^+$, 545.0610, found 545.0612.

HP2, red solid, 107 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–7.94 (m, 2H), 7.87–7.77 (m, 2H), 7.54 (d, J = 8.7 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 4.4 Hz, 2H), 6.56 (d, J = 4.2 Hz, 1H), 6.47 (d, J = 4.4 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 162.4, 134.5, 134.5, 133.4, 132.6, 132.1, 130.2, 125.0, 124.3, 119.8, 117.6, 117.6, 114.3, 55.6; HRMS (ESI) m/z Calcd for $C_{24}H_{15}BClF_2N_3NaO_3$ $[M+Na]^+$, 500.0760, found 500.0756.

2.3. Synthesis of *HP1-H* and *HP2-H*

HP1 or **HP2** (60 μmol) was dissolved in acetonitrile (10 mL), then hydrazine hydrate (3.1 μL, 60 μmol) was added in above solution. The resulting mixture was stirring at room temperature for 2 h under an inert atmosphere. Then the solvent was removed under vacuum and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 3/1, v/v).

HP1-H, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 4.8 Hz, 1H), 6.55–6.48 (m, 1H), 6.39–6.33 (m, 1H), 6.09 (d, J = 4.9 Hz, 1H), 5.76 (s, 2H), 3.90 (s, 3H); HRMS (ESI) m/z Calcd for $C_{16}H_{13}BClF_2N_3NaO$ $[M+Na]^+$, 370.0703, found 370.0701.

HP2-H, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–7.93 (m, 2H),

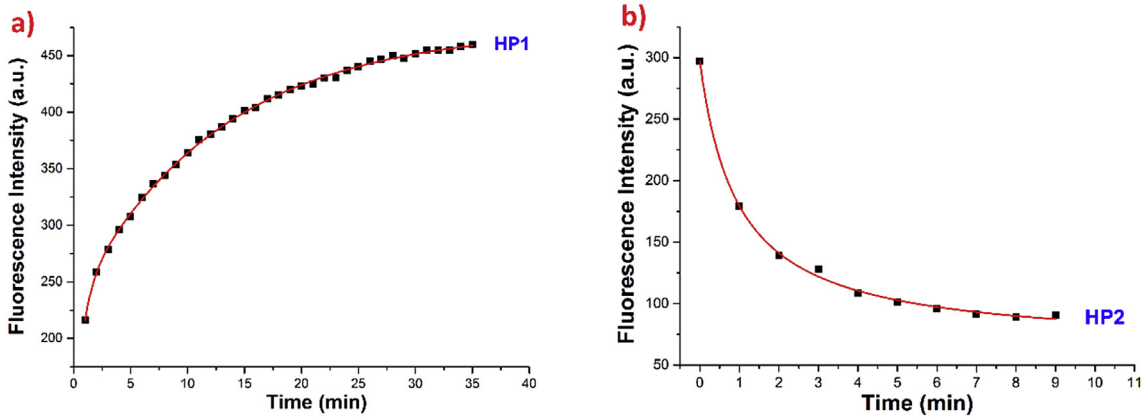

Fig. 2. The time course of the fluorescence intensity of a) **HP1** and b) **HP2** (5 μM) at 523 nm to hydrazine (50 μM).