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A highly sensitive and selective hypochlorite fluorescent probe based on oxidation of hydrazine via free radical mechanism

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ABSTRACT

Developing fluorescent probes for selective and sensitive detection of hypochlorite has received much attention, because hypochlorite is closely related to human health. In this work, a new fluorescent probe based on dipyrromethene boron difluoride (BODIPY) fluorophore using hydrazine as detecting group for hypochlorite was synthesized and fully characterized. The reaction of the probe with sodium hypochlorite is complete within 1 min in phosphate-buffered saline, and the fluorescence of the system significantly enhanced. The probe also exhibits admirable sensitivity and selectivity as well. The results of nuclear magnetic resonance monitoring and high-performance liquid chromatography analysis indicate that the detection process plausibly involves a free radical oxidation mechanism.

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1. Introduction

Reactive oxygen species (ROS) and reactive nitrogen species (RNS) are well-known and of scientific interest, since they play a prominent role in biological systems such as aging and immunity [1,2]. They are also involved in a number of diseases, because deregulation of ROS or RNS production or elimination may cause pathophysiological consequences [3–5]. Endogenous hypochlorous acid, an important member of ROS, generated from reaction of chloride ion and hydrogen peroxide catalyzed by enzyme of myeloperoxidase (MPO) in leukocytes in response to inflammatory stimuli [6,7], plays an essential role in innate immune system. Regulated generation of hypochlorous acid maintains normal physiological activity, while abnormal amount of hypochlorous acid causes several diseases such as cardiovascular disease and inflammatory disease [8–11]. Accordingly, it is extremely significant to develop facile approach enabling professionals to detect or image hypochlorite quickly and sensitively.

Fluorescence is a powerful method possessing outstanding properties such as simple operation and high sensitivity [12–21]. Therefore, fluorescent probe for hypochlorite or hypochlorous acid has attracted considerable attention, and several outstanding fluorescent probes [22–38] have been developed. Most of these fluorescent probes utilize the strong oxidation property of the hypochlorite, for example, oxidation of selenium, phenol, pyrrole, and so on. San Filippo and co-workers [40] found that arylhydrazine can be initially oxidized by superoxide to an aryldiazene, which is rapidly autoxidized by a radical chain reaction to an aryl radical. Then a hydrogen atom transfer from aryldiazene carries out followed by the unimolecular decomposition of the resulting arylazo radical to aryl radical and nitrogen (Scheme 1). Due to the high reactivity and quick reaction rate of the free radical reaction, this process offers a potential possibility to design fluorescent probes for superoxide. In addition, dipyrromethene boron difluoride (BODIPY) is an eminent fluorophore possessing remarkable properties, including sharp absorption and emission peaks, high thermostability and photostability, and high fluorescence quantum yield [41–48]. Together both, in this work, we design a BODIPY-

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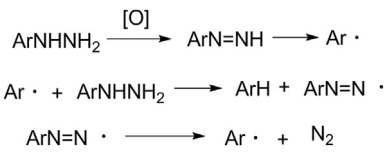


Scheme 1. Oxidation of arylhydrazine.

based fluorescent probe with a hydrazine as detecting group for hypochlorite, finding that the probe displays high sensitivity and selectivity for sodium hypochlorite in aqueous solution.

2. Experimental

2.1. Chemicals and instruments

All reagents and solvents were purchased from commercial sources and used without further purification. ROS solutions were prepared as previously reported [30]. NMR spectra were measured on a Bruker DRX-400 spectrometer. Mass spectra were measured on an Agilent 6410B LC-MS spectrometer. Fluorescent spectra were determined on a Hitachi Fluorescence Spectrophotometer F-7000.

2.2. Synthesis of **2**

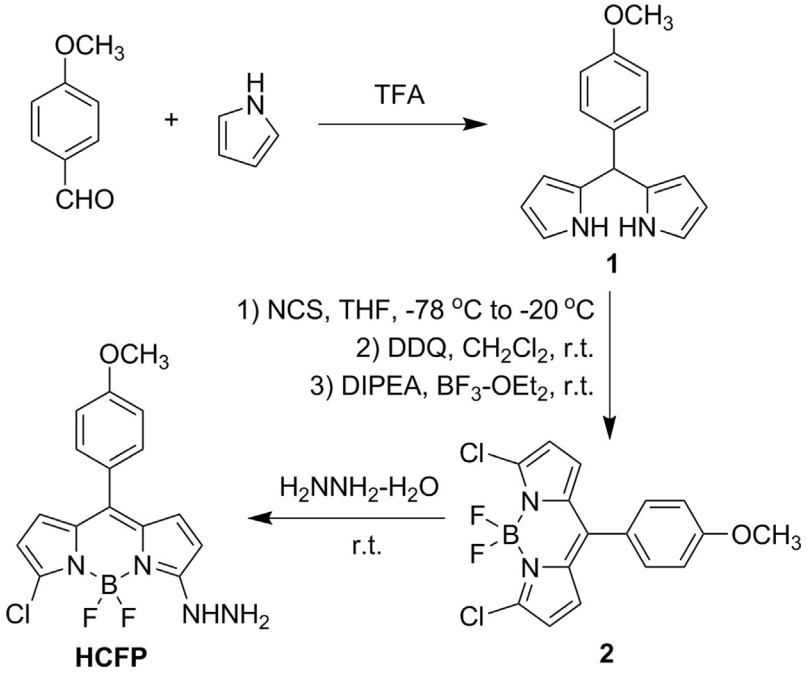
1 [49] (3.96 mmol, 1.0 g) was dissolved in 30 mL of dry THF, and N-chlorosuccinimide (7.93 mmol, 1.06 g) in dry THF (70 mL) was added to above solution under nitrogen at −78 °C. Then the mixture was stirred for 1 h at −78 °C and for another 3 h at −20 °C. After completion of the reaction, the solvent was distilled under vacuum. The residue was dissolved in 100 mL of CH_2Cl_2, which was washed with water twice. The organic layer was dehydrated with anhydrous Na_2SO_4. After the evaporation of CH_2Cl_2, the residue was dissolved in 50 mL of CH_2Cl_2, and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 4.76 mmol, 1.08 g) in CH_2Cl_2 (150 mL) was added into the solution. The mixture was stirred at room temperature for 2 h. Then N,N-diisopropylethylamine (10 mL) and 46% BF_3—OEt_2 (10 mL) were added to the mixture, which was stirred for another 1 h. After completion of the reaction, 200 mL water was added to the mixture, which was extracted CH_2Cl_2 by (3 × 150 mL). The combined organic layer was dehydrated with anhydrous Na_2SO_4. After the evaporation of CH_2Cl_2, the residue was purified by silica gel column chromatography (petroleum ether/CH_2Cl_2, 3/1, v/v). The product **2** was obtained as red solid (0.45 g, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 4.1 Hz, 2H), 6.44 (d, J = 4.3 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 144.4, 133.9, 132.5, 131.7, 125.0, 118.8, 114.4, 55.8. HRMS (ESI) m/z Calcd for $C_{16}H_{11}BCl_2F_2N_2O$ $[M + H]^+$, 367.0385, found 367.0387.

2.3. Synthesis of ***HCFP***

2 (0.54 mmol, 200 mg) was suspended in 40 mL of 85% hydrazine hydrate, and the mixture was stirred under nitrogen at room temperature for 3 h. After completion of the reaction, 100 mL water was added to the mixture, which was extracted CH_2Cl_2 by (3 × 100 mL). The combined organic layer was washed with water twice and dehydrated with anhydrous Na_2SO_4. After the evaporation of CH_2Cl_2, the residue was purified by silica gel column chromatography (petroleum ether/CH_2Cl_2, 1/10, v/v). The product **HCFP** was obtained as red solid (130 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.38 (d, J = 8.7 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 4.9 Hz, 1H), 6.58 (d, J = 4.9 Hz, 1H), 6.37 (d, J = 3.8 Hz, 1H), 6.18 (d, J = 3.8 Hz, 1H), 4.15 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.2, 160.5, 135.6, 134.8, 132.2, 132.0, 130.3, 127.4, 126.4, 125.5, 117.0, 115.9, 114.6, 112.0, 55.9. HRMS (ESI) m/z Calcd for $C_{16}H_{114}BCl_2F_2N_2O$ $[M-H]^-$, 361.0848, found 361.0849.

2.4. Synthesis of ***HFP***

HFP was synthesized according to reported method [50]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.53 (d, J = 8.7 Hz, 2H), 7.07



Scheme 2. Synthesis of **HCFP**.

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