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# A novel pyridyl triphenylamine–BODIPY aldoxime: Naked-eye visible and fluorometric chemodosimeter for hypochlorite

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ABSTRACT

An aldoxime containing fluorescent probe based on vinylpydine-appended triphenylamine–BODIPY has been designed and used for hypochlorite detection. OX-PPA-BODIPY was developed by introducing an aldoxime group into the 2-position of BODIPY, which can be used for the detection of hypochlorite with a sharp color change from pink to green. The attachment of 4-vinylpyridine moiety to triphenylamine–BODIPY constructs a fluorogen with desirable conjugated system. The probe, which displays extremely weak fluorescence owing to the C═N isomerization mechanism at 2-position of BODIPY, responds to HClO/$ClO^-$ through a dramatic enhancement of its fluorescence intensity. This new probe, a naked-eye visible and fluorometric chemodosimeter, exhibits high selectivity and sensitivity toward hypochlorite over other reactive oxygen species (ROS) and anions. The detection is accompanied by a 20-fold increase in fluorescent intensity ($\Phi_F$ from 0.02 to 0.43). The detection limit of the probe for hypochlorite is $7.37 \times 10^{-7}$ M. Moreover, OX-PPA-BODIPY can be used to detect hypochlorite in real water samples.



## 1. Introduction

Hypochlorous acid (HClO)/hypochlorite ($ClO^-$) is known to be a kind of biologically important reactive oxygen species (ROS) [1]. In living organisms, hypochlorous acid is produced predominantly from hydrogen peroxide and chloride ions in a chemical reaction catalyzed by the heme enzyme myeloperoxidase (MPO), which plays a pivotal role in the immune defense against microorganisms and in inflammation [2–5]. However, excessive amounts of hypochlorous acid/hypochlorite in the physiological and pathological processes can lead to various diseases, such as atherosclerosis, osteoarthritis, rheumatoid arthritis and even cancers [6–10]. Thus, monitoring HClO/$ClO^-$ in living organisms is highly demanded for the research in biology and medicine.

Fluorescent probes have been evaluated as powerful tools to detect biological agents in recent years, due to their high sensitivity and selectivity, real-time detection and easiness of manipulating [11–13]. In recent years, a number of fluorescent probes for HClO/$ClO^-$ based on unique reaction mechanisms have been developed, including oxidation of p-methoxyphenol to benzoquinone [14], selenide to selenoxide [15–17], oxime to aldehyde [18], and others [19]. Most of them are based on different fluorophores that included rhodamine [20], boradiazaindacene (BODIPY) [21], fluorescein [22], naphthalimide [23] and so on [24]. Chen et al. [25] developed a highly selective turn-on fluorescent probe for hypochlorous acid based on hypochlorous acid-induced oxidative intramolecular cyclization of boron dipyrromethene-hydrazone. Cheng [26] and his coworkers have demonstrated a highly sensitive and selective hypochlorite fluorescent probe based on oxidation of hydrazine via free radical mechanism. Mulay's group [27] constructed two closely related phenyl selenyl based boron-dipyrromethene turn-on fluorescent probes for the detection of hypochlorous acid (HClO). Sun [28] and his group developed a probe for hypochlorous acid based on the cleavage of carbon-carbon double bonds. Liu [29] synthesized a highly sensitive and selective hypochlorite fluorescent probe based on oxidation of hydrazine via free radical mechanism. Recently, BODIPY dyes has attracted more and more attention because of its exceptional photophysical properties such as long emission wavelengths, high molar absorption coefficients and fluorescence quantum yield [30–33]. In addition, BODIPY, a group of luminogenic molecules, is easy to modify to obtain desirable performance. According to the previous work, the reports on the probe for HClO/$ClO^-$ based on BODIPY are still limited. A number of BODIPY-based HClO/$ClO^-$ probes have been reported, however, emission band of these probes majorly falled into the region of 500–520 nm. Therefore, the development of fluorescent probes for HClO/$ClO^-$ based on BODIPY is in urgent demand.

In our work, a naked-eye visible and fluorometric chemodosimeter based on the HClO/$ClO^-$-promoted oxidation of aldoxime for hypochlorite was designed by combining pyridyl triphenylamine and BODIPY. Based on the deoximation reaction some fluorescent probes were designed. Compared with the previous reported sensors [34–36], the structure of dye moiety is novel and used for the first time to sense hypochlorite. As we know, triphenylamine-BODIPY derivatives with their emissions are tunable from green to red exhibit highly efficient and stable photophysical properties [37]. Therefore, triphenylamine–BODIPY

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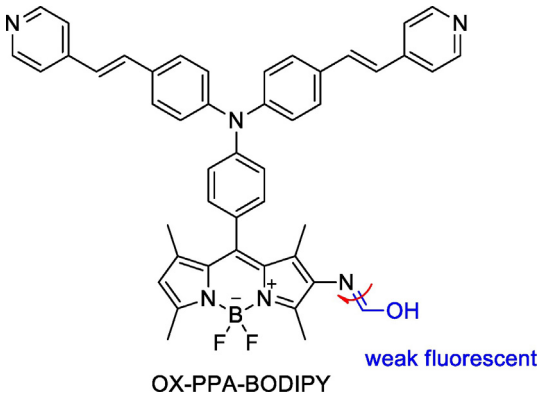



**Scheme 1.** Chemical structures of pyridyl triphenylamine–BODIPY aldoxime.

was adopted as fluorogenic moiety. The attachment of 4-vinylpyridine moiety to triphenylamine–BODIPY can successfully build a new fluorogen and extend the conjugation system. In this probe, an aldoxime group was employed as hypochlorite-responsive moiety. As shown in Scheme 1, due to C═N isomerization, the probe is weak fluorescent. OX-PPA-BODIPY could react rapidly with HClO/$ClO^-$, while HClO/$ClO^-$ mediated removal of the aldoxime group restores the fluorescence of the BODIPY fluorogenic moiety.

## 2. Experiment

### 2.1. Chemicals and Instruments

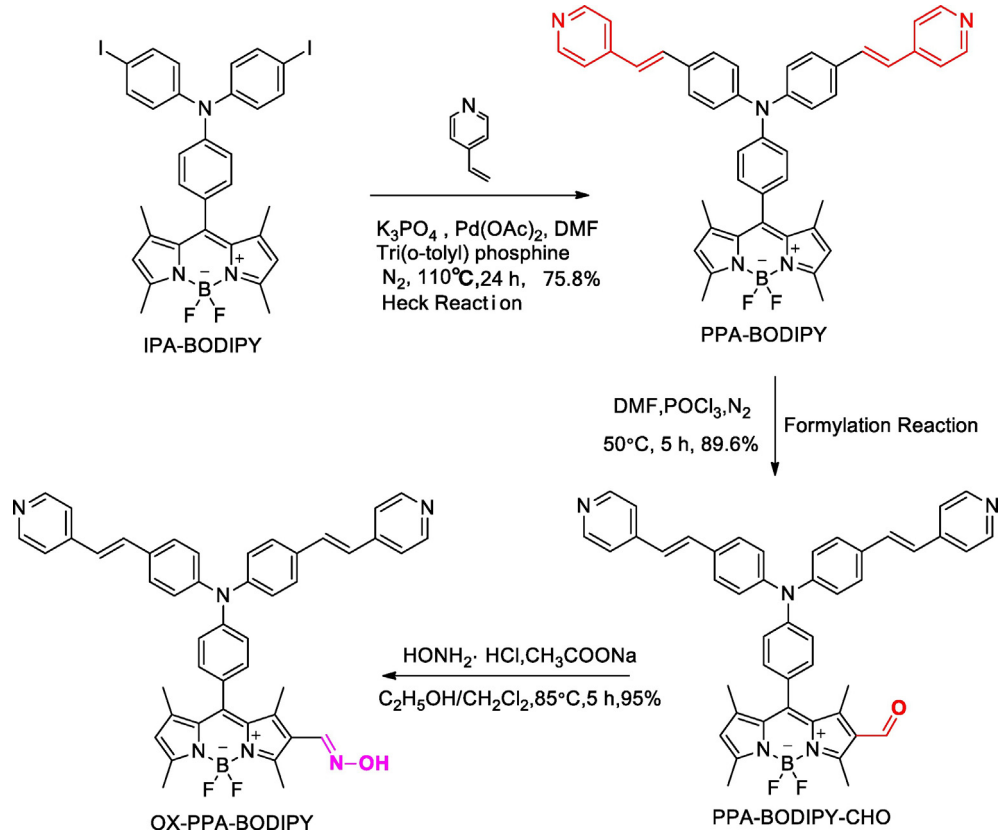
Chemical structures were confirmed by NMR analysis and mass spectrometry. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker 300 MHz spectrometer and a Bruker 300 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Chemical shifts are given in parts per million (ppm). Mass spectra were recorded on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. UV–visible absorption spectra were determined on a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were measured on a HORIBA FL-4 Max spectrometer. 1 × 1 × 3 cm quartz cuvettes were used for absorption and emission spectral titration.

All reagents used were purchased and used without further purification. All solvents used in spectroscopic measurements were of analytical grade. Reactions were monitored by thin layer chromatography using Merck TLC Silica gel 60 F254. Silica gel column chromatography was performed over Merck Silica gel 60.

### 2.2. Synthesis

The synthetic routes are presented in Scheme 2. 2,4-dimethyl-pyrrole, *N*,*N*-di (4-iodophenyl) aminobenzaldehyde, and other important intermediates were synthesized according to literature procedures [38–39]. All chemical structures were confirmed by $^1$H NMR, $^{13}$C NMR and mass spectrometry.

8-{4-{*N*,*N*-bis{4-[2-(4-pyridyl)ethenyl]phenyl}amino}phenyl}-1,3,5,7-tetramethyl-4,4′-difluoro-4-bora-3a,4a-diaza-s-indacene(PPA-BODIPY). A mixture of IPA-BODIPY (0.50 g, 0.67 mmol), 4-vinylpyridine (0.17 g, 1.62 mmol), $Pd(OAc)_2$ (4.53 mg, 0.02 mmol), $K_3PO_4$ (0.21 g, 1.01 mmol) and Tri(o-tolyl)phosphine (0.02 g, 0.07 mmol) in DMF (6 mL)was stirred for 24 h at the temperature of 130 °C in nitrogen atmosphere. Then, the reaction mixture was brought to room temperature, washed with water and extracted by filtration method. The residue was purified by column chromatography on silica gel to obtain the pure product PPA-BODIPY as an orange powder in 75.8% yield. $^1$H NMR (300 MHz, $CDCl_3$) δ: 8.57 (d, *J* = 3.00 Hz, 4H), 7.48 (d, *J* = 9.00 Hz, 4H), 7.35 (d, *J* = 6.00 Hz, 4H), 7.27 (m, 4H),7.19 (d, *J* = 9.00 Hz, 2H), 7.13 (d, *J* = 9.00 Hz, 4H), 6.94 (d, *J* = 15.00 Hz, 2H),




**Scheme 2.** Synthesis of pyridyl triphenylamine-BODIPY derivative.