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Fluorometric and naked-eye detectable dual signaling chemodosimeter for hypochlorite

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ABSTRACT

Phenanthroline dialdehyde appended sensor (PDS) has been designed and synthesized which displays an excellent selectivity as hypochlorite sensor in mixed aqueous medium. Its selectivity and sensitivity is established through hypochlorite promoted de-diaminomaleonitrile reaction causing naked eye recognizable color change from yellow to colorless as well as remarkable fluorescence turn on by the disrupted intra-molecular charge transfer mechanism but in presence of different analytes like H_2O_2, HS^-, NO_3^-, NO_2^-, hydrazine, CN^-, F^-, and Cl^-, no such characteristic change is observed.

1. Introduction

Molecular oxygen (O_2) is biologically significant to all aerobic organisms including humans. During wide variety of physiological processes, the body produces a number of species derived from oxygen. One class of these species, referred to as 'reactive oxygen species (ROS)', includes the superoxide, hydroxyl and peroxyl radical, hydrogen peroxide, singlet oxygen ($^1O_2$) and hypochlorous acid/hypochlorite. The ROS are produced endogenously from oxygen mainly through the mitochondrial respiration process [1]. An important member of ROS hypochlorous acid, which is approximately half dissociated into its conjugate base (ClO^-) at physiological condition, are strong oxidizing agents employed in various organic syntheses [2] and used as disinfectant and household bleach [3]. Endogenous HOCl, which are produced from the myeloperoxidase (MPO)-mediated peroxidation of chloride ions in activated phagocytic leukocytes including neutrophils, monocytes, and macrophages, play important roles in the human immune defence system, and contribute to the destruction of invading bacteria and pathogens [4]. Although HOCl contributes to the destruction of bacteria in living organisms, the overproduced HOCl causes oxidative stress through the oxidation of bio-molecules, such as lipids, proteins and DNA, and numerous disorders such as inflammatory diseases, atherosclerosis, respiratory distress, cardiovascular diseases, rheumatoid arthritis, cancer and renal disease [5–8]. Owing to its significance in human health and disease, the elucidation of the biological functions of hypochlorite has become an important area of research. One of the major obstacles to understand the roles that these species play is the lack of suitable methods for detecting ROS *in vivo* that is caused by their very short lifetimes and the presence of various antioxidants in cells. Synthetic fluorescent probes are the most powerful tools for the detection of this ClO^-, owing to their inherent advantages including greater sensitivity, fast response time and simplicity of implementation, offering application methods not only for *in vitro* assays but also for *in vivo* imaging studies. These probes also have the advantage of facile visualization of intracellular dynamics and high-resolution localization of bio-molecules of interest. Thus biological relevant findings inspire us to develop sensitive and specific probes for detecting HOCl in both water samples and living systems.

Most fluorescent probes are abiotic supramolecular systems that commonly bind analytes by non-covalent interactions, such as hydrogen bonding, electrostatic attractions and coordination phenomena. Recent continuing demands for improving sensitivity and selectivity have inspired us toward fascinating chemodosimeter that has been designed using chemical events. Few fluorescent probes for hypochlorite have been developed recently, based upon the strong oxidation property [9–17]. Although these reported chemosensors have demonstrated reasonable selectivity for HOCl

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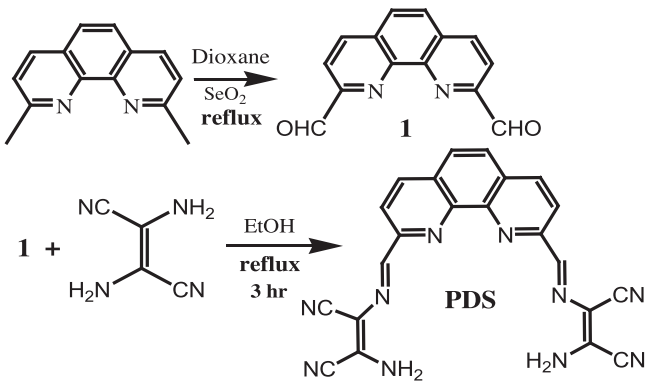

Scheme 1. Synthetic route to PDS.

over other ROS, easily synthesizable fluorescent probes of better sensitivity and reactivity for HOCl are still required for the biological imaging applications.

Herein, we report a dual-signaling chemodosimeter which can combine the sensitivity of fluorescence with the convenience and esthetic appeal of a colorimetric assay for hypochlorite. It is well known that photoluminescence of a fluorophore can be partially or completely quenched through intramolecular charge transfer (ICT), when an electron donating group remains conjugated with it. Sometimes fluoro-ionophore is designed in such a way that after being bound to cation the electron donating group loses its electron donating ability, hence ICT ceases making the ionophore highly fluorescent [18]. But here, instead of suppressing ICT, we have such a way designed our present sensor where the electron donating group has been detached, through certain chemical reaction promoted by specific analytes from parent fluorophoric moiety to rejuvenate its original fluorescence intensity. In this context we have designed phenanthroline diimine appended sensor (PDS) (Scheme 1).

2. Experimental

The chemicals and solvents were purchased from Sigma–Aldrich Chemicals Private Limited and were used without further purification. ^{1}H NMR spectra were recorded on Brucker 400 MHz instruments. NMR titration was carried out in d_6-DMSO solvent on 400 MHz instrument. For NMR spectra, d_6-DMSO was used as solvent with TMS as an internal standard. Chemical shifts are expressed in δ units and ^{1}H–^{1}H and ^{1}H–C coupling constants in Hz. UV–Vis titration was performed on a JASCO UV-V530 spectrophotometer and fluorescence titration was done using PerkinElmer LS 55 fluorescence spectrophotometer with a fluorescence cell of 10 mm path.

2.1. Synthesis of PDS

(a) 1,10-Phenanthroline-2,9-dicarbaldehyde was prepared through oxidation of 2,9-dimethyl-1,10-phenanthroline by SeO_2 in refluxing dioxane in presence of 2 drops of water for 12 h.

(b) PDS was then prepared through simple Schiff's base condensation reaction between 1,10-phenanthroline-2,9-dicarbaldehyde and diaminomaleonitrile in refluxing ethanol in presence of two drops of acetic acid as 70% yield. The PDS was characterized by ^{1}H NMR and HRMS.

^{1}H NMR (d_6-DMSO, 400 MHz): δ (ppm): 8.72 (d, 2H, J = 8.20 Hz), 8.54 (d, 2H, J = 8.30 Hz), 8.47 (s, 2H), 8.37 (s, 4H), 8.03 (d, 2H, J = 6.10 Hz).

HRMS $(M + Na)^+$: calcd for 439.1702, found 439.1785.

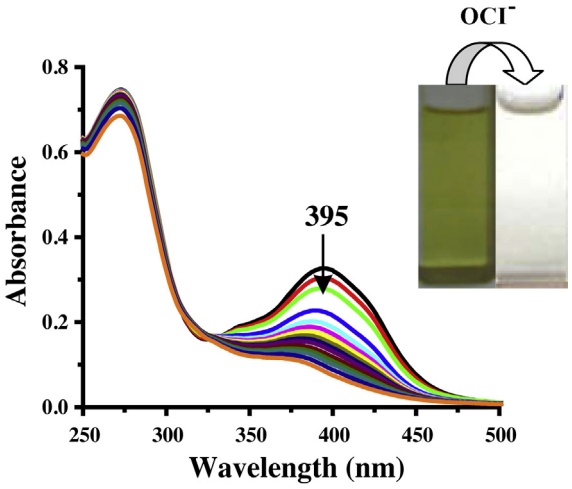

Fig. 1. UV–Vis absorption spectra of PDS upon titration with NaOCl in CH_3CN—H_2O (6:4 v/v, 10 mM HEPES, pH 7.4).

Anal calcd for $C_{22}H_{12}N_{10}$: 63.30% C, 3.14% H, 33.56% N; found: 63.41% C, 3.26% H, 33.51% N.

2.2. Spectroscopic measurements

For UV–Vis and fluorescence titrations, stock solution of the sensor PDS was prepared in DMSO and diluted with CH_3CN—H_2O (6:4 v/v, 10 mM HEPES, pH 7.4) to get $C = 2 \times 10^{-5}$ M solution. The solution of the guest anion like NaOCl was prepared (2×10^{-4} ml^{-1}) in pure water or CH_3CN. The original volume of the PDS solution was 2 ml. Solutions of the sensor of various concentrations and increasing concentrations of anions were prepared separately. The spectra of these solutions were recorded by means of UV–Vis methods and fluorescence method.

3. Results and discussion

The sensing properties of PDS ($C = 2 \times 10^{-5}$ M) were investigated by means of UV–Vis and fluorescence titration in CH_3CN—H_2O solution (6:4 v/v, 10 mM HEPES, pH 7.4). The absorption spectra of PDS show the absorption band centered at 395 nm (Fig. 1). Upon addition of sodium hypochlorite ($C = 2 \times 10^{-4}$ M) as the source of OCl^-, the absorption band of PDS which by itself peaked at 395 nm gradually weakened accompanied by the visually detectable distinct color change from yellow to colorless.

To have some idea about the selectivity of PDS toward OCl^- we had carried out the absorption titration with different analytes like

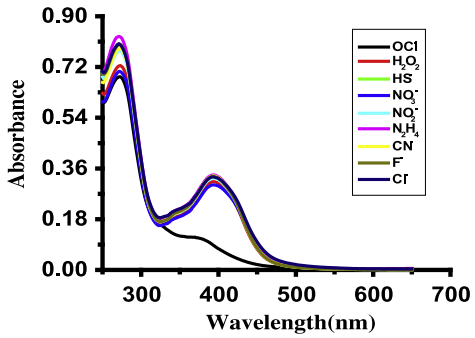

Fig. 2. UV–Vis spectra of PDS upon addition of different analytes (5 equiv.) in CH_3CN—H_2O(6:4 v/v, 10 mM HEPES, pH 7.4).