

# A selective optical chemical sensor for 2,6-dinitrophenol based on fluorescence quenching of a novel functional polymer

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## Abstract

A bifurcated optical fiber based chemical sensor for continuous monitoring of 2,6-dinitrophenol (2,6-DNP) has been proposed based on the reversible chemical reaction between a novel functional poly(vinyl chloride) (PVC) as the sensing material and the analytes. The functional PVC (FPVC), containing a fluorescent curcumin moiety, was synthesized by the nucleophilic substitution of a fraction of the chlorine atoms bound to the PVC backbone by curcumin. When plasticized in a membrane of 5  $\mu\text{m}$  thickness, FPVC extracts 2,6-DNP from aqueous solution into the bulk membrane phase and reacts with the analyte to form a complex with low fluorescence efficiency through hydrogen bonding. Formation of the complex gave a significant fluorescence quenching which is suitable for signalling the occurrence of the host–guest interaction. At pH 3.50, the sensor exhibits a dynamic detection range from  $2.5 \times 10^{-6}$  to  $7.0 \times 10^{-3}$   $\text{mol L}^{-1}$  with a limit of detection of  $1.0 \times 10^{-6}$   $\text{mol L}^{-1}$ . As 2,6-DNP can provide an optimal space geometry matches to the formation of hydrogen bonds, the sensor shows excellent selectivity for 2,6-DNP over other nitrophenols. The forward and reverse response time ( $t_{95}$ ) of the sensor both was within 1 min. The repeatability, reproducibility, and lifetime of the sensor were also satisfied. The sensor was applied to determine 2,6-DNP in water samples successfully.

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**Keywords:** Optical chemical sensor; 2,6-Dinitrophenol; Fluorescence quenching; Functional polymer

## 1. Introduction

In recent years, the ever-increasing number of organic toxic compounds being detected in human environment has risen concern about the contamination of environment resources. Among various toxic compounds, nitrophenols are widely presented and persistent in the environment, especially in waters [1,2]. They have great potential toxicities of carcinogenesis, teratogenesis, and mutagenesis such that are considered to be hazardous wastes and priority toxic pollutants by U.S. Environmental Protection Agency (EPA) [3]. 2,6-Dinitrophenol (2,6-DNP) is one of the six possible dinitro phenol forms used in the synthesis of dyes, picric acid, picramic acid, wood preservatives, diaminophenoldihydrochloride (a photographic developer), explosives, and insecticides [4]. A few literatures about the determination of 2,6-DNP are focused on conventional chromatographic meth-

ods [5–7], which suffer from various disadvantages such as discontinuity, time consumption, analyte destruction, and high running cost. Thus there is still a significant demanding for the fabrication of a new optical fiber chemical sensor for 2,6-DNP, since the user-friendly optochemical sensors can offer advantages in terms of no sample pretreatment, small size, low cost, and quick signal transmission. The determination using an optical sensor can be performed through immobilizing the sensing materials on a solid-state support to form a chemically recognized membrane which was connected with a transducer device. Since nitrophenols are known to be good electron acceptors and quenchers, the quenching effect of nitrophenols on some fluorescent substances have been used to fabricate optical sensors for nitrophenols [8–10].

In the recent years, polymers have gained tremendous recognition in the field of artificial sensor in the goal of gaining better selectivity and fast measurement [11,12]. But as one of the most widely used polymers, PVC was mainly used as the plasticized matrices for the dispersion of sensing molecules within it and the modified PVC was rarely used to behave a sensing substance.

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Fortunately, the studies on the functionalization of PVC through nucleophilic substitution have been carried out [13–15]. These functional PVC (FPVC) have been successfully applied to prepare surfactant-selective electrode [13], reduce plasticizer migration [14], and construct novel biomaterials [15].

This paper describes our efforts focused on developing a solid-state chemical sensor for 2,6-DNP in water using a novel FPVC as the sensing substance. The FPVC was synthesized by the nucleophilic substitution reaction on PVC backbone with curcumin. The design of the approach consists of electron-donating curcumin moiety as a 2,6-DNP-bonding site as well as a fluorescence site, where the hydrogen bonding is responsible for the quenching of the fluorescence emission of curcumin moiety. The sensing characteristics of the proposed sensor were investigated. The steric effect or spatial matching occurred between host and guest was proved to be the primary factor that dominated the complex formation. FPVC was readily used as the sensing substance in an optic fiber based chemical sensor for 2,6-DNP. Compared with the physically embedded curcumin membrane with PVC as the matrixes, the proposed FPVC-based membrane showed markedly better sensing performance in terms of sensitivity, selectivity, response time, and lifetime. The proposed sensor was used to determine 2,6-DNP in water samples satisfactorily. To our best knowledge, the functionally substituted polymer based fluorescence sensor was rarely reported.

## 2. Experimental

### 2.1. Apparatus

$^1\text{H}$  NMR spectra were recorded on an ARX-400 (Bruker, 400 MHz, Germany) spectrometer in DMSO- $d_6$  with tetramethylsilane as internal standard. Infrared spectra were obtained from a NEXUS 670-FT-IR (Thermo Nicolet Corporation, Massachusetts, USA) spectrophotometer with KBr disk. Elemental analysis was performed on a Flash EA 1112 elemental analyzer (Thermoquest, Italy). A Dektak 8 surface profiler (Digital Instruments, California, USA) was used to determine the film thickness by scanning the edge of a small scratch that was applied to the sensing membrane that was coated to a circular quartz plate. UV–visible measurements were performed on a Shimadzu UV-2401 UV–visible spectrophotometer (Shimadzu, Kyoto, Japan). All fluorescence measurements were carried out on a Hitachi F-2500 fluorescence spectrometer (Hitachi, Tokyo, Japan) with excitation and emission slits set at 5 and 10 nm, respectively. A homemade PTFE flow cell and a bifurcated optical fiber (50 + 50 quartz fibers, diameter 6 mm and length 1.2 m) were used for the sensing measurements (Fig. 1). The quartz plate with the sensing membrane on it was mounted in the flow cell. The membrane side is facing the cell chamber with the circulating sample solution sweeping over the membrane driven by a peristaltic pump (Lange Instruments, Baoding, China). The opposite side of the quartz plate tightly matching the common end of the optical fiber. Data processing was performed on a Pentium III computer with software of Sigma plot. For pH measurements, an Orion Model 828 pH meter (Massachusetts, USA) was used. A spin-on device [12] was used to prepare the membrane.

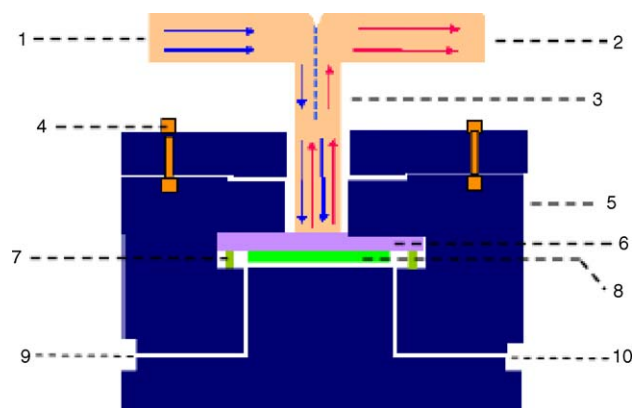


Fig. 1. Schematic diagram of the flow cell arrangement: (1) excitation light, (2) signal light, (3) bifurcated optical fiber, (4) screw cap, (5) cell body, (6) quartz glass slide, (7) O silicon ring, (8) sensing membrane, (9) sample inlet, and (10) sample outlet.

### 2.2. Chemicals

Analytical reagent grade chemicals were used unless indicated otherwise. The following reagents were used for FPVC synthesis and membrane preparation: high molecular weight PVC was purchased from Sigma (St. Louis, USA). Curcumin was from Shanghai Chemical Factory (Shanghai, China). Hexadecyltrimethyl ammonium bromide (CTAB), tetrahydrofuran (THF), tributyl phosphate (TBP), diisooctyl sebacate (DOS), and dioctyl phthalate (DOP) were obtained from Beijing Chemical Factory (Beijing, China).

2,6-DNP, *o*-nitrophenol (*o*-NP), *m*-nitrophenol (*m*-NP), *p*-nitrophenol (*p*-NP), 2,4-dinitrophenol (2,4-DNP), 2,4,6-trinitrophenol (2,4,6-TNP), and other phenols used were from Beijing Chemical Factory (Beijing, China). The stock solutions of nitrophenols were prepared by dissolving the appropriate amount of each sample in methanol. Working solutions were prepared by successive dilution of the stock solutions with 0.1 M sodium acetate–hydrochloric acid buffer solution of pH 3.50. The ultra high purity deionized water used in the experiment was obtained from Easypure water purification system with a 0.2  $\mu\text{m}$  fiber filter (Barnstead, USA).

### 2.3. Substitution reaction of PVC with curcumin

0.5 g curcumin (1.36 mmol) was added to a 40 mL sodium carbonate–sodium bicarbonate buffer solution (0.1 mol L $^{-1}$ , pH 10.0) at room temperature and stirred for 20 min. Then a 50 mL THF solution of PVC resin (2 g, 0.01 mmol) was added. The resulting red brown solution was heated and stirred for 30 min at 50  $^{\circ}\text{C}$ , after which, calculated amount (0.1 g, 0.27 mmol) of CTAB as phase-transfer catalyst was added dropwise. After stirring the mixture at 80  $^{\circ}\text{C}$  for 5 h, THF was removed under reduced pressure. A brown color precipitate developed immediately. The products were collected by filtration, subjected to mild sonication in a bath type sonicator for 3 min to remove any surface adhering reactants, and then dried in an air oven at 80  $^{\circ}\text{C}$  to constant weight. Product:  $^1\text{H}$  NMR [16,17] (400 MHz, DMSO- $d_6$ ) 2.23–2.34 ppm (br m, 20H, methylene protons of

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