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 μm 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 2.5×10^{-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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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

^1H NMR spectra were recorded on an ARX-400 (Bruker, 400 MHz, Germany) spectrometer in $\text{DMSO}-d_6$ 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 μm 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: ^1H NMR [16,17] (400 MHz, $\text{DMSO}-d_6$) 2.23–2.34 ppm (br m, 20H, methylene protons of

–[CH₂–CHCl]_n–), 4.34–4.45 ppm (br m, 10H, methyne protons of –[CH₂–CHCl]_n–), 9.65 ppm (s, 2H, hydroxy H of benzene ring), 7.14–7.56 ppm (m, 6H, *ortho*- and *meta*-H of the substituted benzene ring), 6.74–6.83 ppm (m, 4H, –HC=CH– double bond H), 6.06 ppm (s, 1H, hydroxy H of enol form of curcumin moiety), 3.82 ppm (s, 6H, methoxy-H); FT-IR (KBr disk) 2910, 2850, 1430, 1250, 964, 768, 690, 636, 611 cm^{–1} (C–C and C–H stretching vibrations of PVC), 611, 636, 690, 768 cm^{–1} (stretching vibrations of C–Cl) [18,19], 845 cm^{–1} (adjoining hydrogens at benzene ring), 1590 cm^{–1} (benzene ring skeleton vibration), 1620 cm^{–1} (–C=C– stretching vibration of benzene ring), 3640 cm^{–1} (C–O–H stretching vibration); UV spectra λ_{max} (THF): 426 nm.

2.4. Preparation of sensing membrane

The sensing membrane solution was prepared by dissolving a mixture of 50 mg of FPVC and 200 mg of TBP in 2 mL of freshly distilled THF. A circular quartz plate of 25 mm diameter was mounted on the spin-on device and then rotated at a frequency of 800 rpm. Using a syringe, 0.2 mL of the membrane solution was sprayed to the center of the plate. After a spinning time of 4 s, a membrane of 5 μm thickness, which was determined by the surface profiler [20], was then coated on the quartz plate. The membrane was stored in buffer solution when not used.

2.5. Measurement procedure

Two arms of the bifurcated optical fiber were fixed in the detecting chamber of the spectrofluorimeter to carry the excitation and emission light. The fluorescence measurements were carried out at the maximum excitation wavelength of 460 nm and the maximum emission wavelength of 503 nm. The sample solution was fed through the detecting chamber of the flow cell by the peristaltic pump at a rate of 2.0 mL min^{–1}. After each measurement, the flow cell was washed with blank buffer solution until the fluorescence intensity of the sensor reached the original blank value.

3. Results and discussion

3.1. Elemental analysis

The elemental analysis presents us the C% of PVC and FPVC with 38.57% and 39.82%, respectively, from which a 1:120 number ratio of curcumin molecules to –[CH₂CHCl]– units in FPVC was calculated, which corresponds to about 4.5% covalently bound curcumin in 1 g of FPVC. According to the molar absorptivity of curcumin at 423 nm (151.8 cm^{–1} mg^{–1} mL) in THF, 1 g of the novel polymer contains 4.0 % of curcumin [21].

3.2. pK_a determination

In order to testify the formation of FPVC, the absorption spectra at various acidities of the polymer were studied and its pK_a was determined according to reported method [22]. The pK_a of FPVC, characterized by a difference of those two values of curcumin reported (8.05 ± 0.05, 10.41 ± 0.05) [23], has only

Scheme 1. The molecular structure of novel FPVC.

one value and was calculated to be 10.72. The results indicated that PVC was nucleophilic attacked by one hydroxyl group of curcumin and curcumin was attached to the backbone of the polymer, which was consistent with the conclusion obtained from ¹H NMR spectra, FT-IR spectra and elemental analysis. Thus the molecular structure of FPVC was drawn and shown in Scheme 1.

Since FPVC was found to show excellent membrane formability with plasticizers, there was no need to use PVC as matrixes in the fabrication of sensing membrane.

3.3. Optical properties of FPVC

The absorption spectra (not shown here) of FPVC (λ_{max} = 426 nm) in sensing membrane redshifted 3 nm compared with curcumin in tributyl phosphate plasticized PVC membrane (λ_{max} = 423 nm). The reason for this perhaps was the electron-donating effect experienced by curcumin moiety produced through adjacent electron-offering alkyl backbone of the polymer, which decreased the electronic energy level of curcumin.

Fig. 2 shows the fluorescence spectra of the sensing membrane exposed to a solution containing different concentrations of 2,6-DNP, which are recorded at λ_{ex} = 460 nm, λ_{em} = 503 nm. Owing to the conjugated double bond system and the high mobility of its π-electrons, curcumin moiety exhibits fluorescence emission at 503 nm when excited by 460 nm radiation. From Fig. 2, one can see that the fluorescence intensities of the sensing membrane decrease with increase of the concentration of 2,6-DNP, which constitutes the basis for the determination of 2,6-DNP with the optical fiber sensor proposed in this paper.

3.4. Optimization of membrane compositions

Since plasticization can increase the mobility of polymer segments to improve the rate of guest extraction into and diffusion

Fig. 2. Fluorescence spectra of the sensing membrane in the presence of different concentrations of 2,6-DNP at pH 3.50: (1) 0; (2) 1.0×10^{-6} ; (3) 5.0×10^{-6} ; (4) 1.0×10^{-5} ; (5) 5.0×10^{-5} ; (6) 1.0×10^{-4} ; (7) 5.0×10^{-4} ; (8) 1.0×10^{-3} ; (9) 5.0×10^{-3} ; (10) 8.0×10^{-3} mol L⁻¹ ($\lambda_{\text{ex}} = 460$ nm, $\lambda_{\text{em}} = 503$ nm).

throughout the film [24], as well as increase the workability, flexibility, and distensibility of the film, several membrane compositions were investigated by selecting appropriate plasticizers and varying the ratio of plasticizers to FPVC. A sensing membrane made of different plasticizers, such as tributyl phosphate (TBP), diisooctyl sebacate (DOS), and dioctyl phthalate (DOP) were prepared. Membranes consisting of TBP show the best response to 2,6-DNP and the longest lifetime. When the amount of FPVC for immobilizing was 50 mg, the optimal amount of TBP was found to be 200 mg (Table 1).

3.5. Characteristics of the optical membrane

3.5.1. Determination of the complex ratio and the equilibrium constant

Based on an operation principle reported [25], the relationship between response parameter, α , and 2,6-DNP concentration [G_{aq}] can be represented as

$$\frac{\alpha^n}{1 - \alpha} = \frac{1}{nKC_{\text{H}}^{n-1}[G_{\text{aq}}]^m} \quad (1)$$

where m and n are the complexing number of 2,6-DNP and FPVC, respectively. C_{H} and K refer to the total amount of

Fig. 3. Response parameter values (α) at 460/503 nm as a function of the logarithm of 2,6-DNP concentration at pH 3.50. Theoretical response of 2,6-DNP as predicted by Eq. (1). The experimental data were fitted to the equation with the different complex ratios and equilibrium constant: (1) $n:m = 1:2$, $K = 7.7 \times 10^5$; (2) $n:m = 2:2$, $K = 1.2 \times 10^6$; (3) $n:m = 1:1$, $K = 2.0 \times 10^3$ (best fit); (4) $n:m = 2:1$, $K = 2.2 \times 10^6$ (●●) experimentally observed data points).

FPVC in membrane and the overall equilibrium constant, respectively. Eq. (1) is the basis of the quantitative determination of 2,6-DNP in aqueous solution by using the proposed sensor. The experimental data were fitted to Eq. (1) by changing the ratio of n to m and adjusting the overall equilibrium constant, K . Fig. 3 shows the fitted curves that represents the experimental data for 2,6-DNP. The curve referring to the 1:1 complex ratio and $K = 2.0 \times 10^3$ is the best one fitted to the experimental data (Fig. 3, solid line 3). The best-fitting curve can serve as the calibration curve for the determination of 2,6-DNP.

3.5.2. Effect of pH and flow rate

The effect of solution pH and flow rate on α and response time, t , was investigated over a wide pH range from 2.0 to 12.0 and flow rate range from 0.5 to 4.5 mL min⁻¹ in the presence of 5.0×10^{-5} mol L⁻¹ 2,6-DNP. The blank fluorescence of the sensing membrane itself was found to be independent of pH from 2.0 to 10.5. Solutions at pH > 10.8 caused FPVC to be dissolved

Table 1

Composition of the membrane cocktail and the response behavior of the sensing membrane at pH 3.50^a

Membrane number	Plasticizer (mg)	Working range (mol L ⁻¹)	Detection limit ^b (mol L ⁻¹)	Lifetime ^c (times)
1	DOS, 200	7.8×10^{-5} to 3.7×10^{-3}	2.5×10^{-5}	80
2	DOP, 200	9.8×10^{-5} to 1.1×10^{-3}	3.6×10^{-5}	100
3	TBP, 100	3.4×10^{-6} to 8.5×10^{-3}	2.0×10^{-6}	100
4	TBP, 200	2.5×10^{-6} to 7.0×10^{-3}	1.0×10^{-6}	>250
5	TBP, 300	4.0×10^{-6} to 4.0×10^{-3}	1.3×10^{-6}	150

^a Each membrane cocktail contains 50 mg of FPVC and the listed amount of plasticizer, which were diluted to 2 mL with fresh distilled THF.

^b The detection limit was defined as $\alpha = 0.99$.

^c The lifetime was defined as the usage times of the sensing membrane that produced fluorescence signal changes less than 5% [31].

out from the PVC membrane because of its pK_a of 10.72. Since the pK_a of 2,6-DNP is approximately 3.68 [26], the ionization of 2,6-DNP was inhibited at $pH < 4.2$ and α remained a constant. The extent of 2,6-DNP ionization was increased at $pH > 4.2$ so that the ability to form complex with FPVC was weakened and α gradually increased. In the tested pH range, t increased only from 46 to 48 s with increasing pH. So 0.1 mol L^{-1} sodium acetate–hydrochloric acid buffer solution was used to adjust solution pH at 3.50. The flow rate had almost no effect on α and α remained a constant with variation of the flow rate. The response time t was apparently influenced by the flow rate with a variation from 53 to 45 s when the flow rate was increased from 0.5 to 4.5 mL min^{-1} , which was resulted from increasing of the renew rate of the sensing membrane interface and will strengthen the migration process of 2,6-DNP from the aqueous solution to the membrane phase. In order to avoid the leakage of the sensing substance in the membrane at high flow rate, a flow rate of 2.0 mL min^{-1} was finally selected as a compromise among response time and membrane stability.

3.5.3. Dynamic response behavior

With the optimum conditions, the sensor exhibits a dynamic detection range from 2.5×10^{-6} to $7.0 \times 10^{-3} \text{ mol L}^{-1}$ ($0.05 < \alpha < 0.95$) [27] and limit of detection of $1.0 \times 10^{-6} \text{ mol L}^{-1}$. The response behavior of the sensor to 2,6-DNP was shown in Fig. 4. As can be seen, under the optimum conditions, the forward response time (going from lower to higher 2,6-DNP concentrations), t_{95} (time needed for 95% of the total signal change to occur) was within 1 min, whereas the time for the reverse response was in the range of 1 min over the entire concentration range. Thus the proposed sensor was independent of the order of concentration change, and it was quite reversible and no noticeable hysteresis effect was observed, which indicated that the migration rate of the analyte in the dynamic process was fast [28].

Clearly, both the polymer cavity size and the binding strength can affect the diffusion rate of analytes in a polymer film

Fig. 4. The time-dependent response of the sensor. The sensor is alternatively exposed to (b) 2.5×10^{-6} , (c) 1.0×10^{-4} , (d) 1.0×10^{-3} , and (e) $8.0 \times 10^{-3} \text{ mol L}^{-1}$ 2,6-DNP solutions with (a) blank solution in between.

[29]. Larger cavities and weaker polymer–analyte interactions will result in faster diffusion. Linking curcumin moieties to the backbone of polymer made the cavities generated between adjacent polymers are sufficiently large enough to allow rapid and facile diffusion of small analyte molecules, to the entity of polymer, and simultaneously, the supramolecular recognition interaction between the electron-rich polymer and the electron-deficient analyte was quiet reversible, all of which were responsible for the distinctly fast response of the sensing membrane.

3.5.4. Repeatability and reproducibility

The sensor repeatability and reproducibility were calculated according to the definition by Alabbas et al. [30]. The R.S.D. for repeatability of the sensor for the measurement of 2,6-DNP concentration of $5.0 \times 10^{-5} \text{ mol L}^{-1}$ and $5.0 \times 10^{-6} \text{ mol L}^{-1}$ was calculated to be 1.2% and 1.1%, respectively. On the other hand, the reproducibility was found to have a R.S.D. value of 3.0% for 2,6-DNP concentration of $5.0 \times 10^{-5} \text{ mol L}^{-1}$ and 4.1% for 2,6-DNP concentration of $5.0 \times 10^{-6} \text{ mol L}^{-1}$.

3.5.5. Lifetime

The stability of the sensor was tested by recording the fluorescence intensity of $5.0 \times 10^{-5} \text{ mol L}^{-1}$ 2,6-DNP over a period of 8 h for 50 measurements. A relative standard deviation of the fluorescence reading of 1.0% was recorded. No decrease of the fluorescence intensity of the membrane was observed after a continuous 150 measurement. The sensing membrane exhibited neither bleaching of the fluorophore, chemical decomposition, nor peeling-off of the polymer layer from the glass support for a period of longer than 5 months when stored in buffer solution in the dark at room temperature. The increase of the stability and lifetime of the sensor was resulted from its effective protection from backbone of PVC.

3.5.6. Selectivity

To define the response of the sensor to other nitrophenols, different concentrations of 2,6-DNP, *o*-NP, *m*-NP, *p*-NP, 2,4-DNP, and 2,4,6-TNP solutions were pumped to the flow cell separately and the fluorescence intensity was recorded. In Fig. 5, the response parameter, α , at pH 3.50, are plotted as functions of the concentrations logarithms of 2,6-DNP and other nitrophenols. The curve fittings for the experimental points were calculated by assuming a 1:1 complex ratio. The optical selectivity coefficients, $\log K^{\text{opt}}$ values [31] are summarized in Table 2. From Fig. 5 and Table 2, we can see that the response of the sensor toward nitrophenols decreases in the order of $2,6\text{-DNP} \gg 2,4\text{-DNP} > p\text{-NP} > m\text{-NP} > o\text{-NP} > 2,4,6\text{-TNP}$.

The effects of other potential interferences such as phenols except for nitrophenols, amines, organic acids, alcohols, and some ions were tested for their possible co-occurrences in environmental or industrial samples with 2,6-DNP. The tolerance limit is set as the concentration of interferences that produces a relative error of less than $\pm 5\%$ in the apparent recovery of $5.0 \times 10^{-5} \text{ mol L}^{-1}$ 2,6-DNP. The results are summarized in

Fig. 5. Response function of the sensing membrane on exposure to various aqueous solutions of nitrophenols measured at pH 3.50 and at an excitation wavelength of 460 nm and an emission wavelength of 503 nm: (a) 2,6-DNP; (b) 2,4-DNP; (c) *p*-NP; (d) *m*-NP; (e) *o*-NP; (f) 2,4,6-TNP. The solid lines were calculated according to Eq. (1).

Table 3. As can be seen, many possibly coexisting substances in environmental water showed no remarkable interference for the determination of 2,6-DNP even at high concentration. The limiting water solubility of the tested phenols precluded their higher concentration interference determination. The most serious interference come from $\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^- , which were anionic oxidants with color and can be eliminated through a column packed with anionic-exchange resins.

In order to clarify the specific sensing properties of the proposed sensor, the comparison of the sensing characteristics in determining 2,6-DNP between the proposed curcumin substituted PVC sensor and a curcumin embedded sensor was carried out under the same experimental conditions, even though the latter was reported to show high selectivity to *o*-nitrophenol [10]. The results were shown in Table 4. As can be seen, the proposed sensor exhibited apparent advantages over the embedded sensor in terms of sensitivity, selectivity, response time, and lifetime, which almost covers the whole scope of sensor characteristics. The results also reconfirmed the nucleophilic substitution of PVC by curcumin and the distinct sensing ability of FPVC.

Table 2

Association constants (K) and selectivity coefficients ($\log K^{\text{opt}}$) of the sensing membrane for other nitrophenols in comparison to 2,6-DNP at pH 3.50

Interfering agent	K (mol L^{-1})	$\log K^{\text{opt}}$
2,6-DNP	2.0×10^3	0
2,4-DNP	7.3×10^2	−1.14
<i>p</i> -NP	4.4×10^2	−1.23
<i>m</i> -NP	3.1×10^2	−1.61
<i>o</i> -NP	1.9×10^2	−1.81
2,4,6-TNP	0.42×10^2	−1.92

Table 3

Effect of different phenols and possible interference on the determination of 0.05 mM 2,6-DNP in pH 3.50 buffer solution

Interference	Tolerance limit (molar ratio)	Fluorescence variation
Phenols		
Pyrocatechol, resorcinol	300	+
<i>m</i> -Cresol, 2,6-xyleneol	250	+
Phenol, <i>o</i> -cresol, hydroquinone	200	+
<i>p</i> -Cresol	180	+
2,4-Xyleneol, 2-naphthol, pyrogallol	150	+
2,4,6-Trinitrophenol		—
<i>p</i> -Chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 1-naphthol	120	+
2,4,6-Trichlorophenol		—
Salicylic acid	100	—
<i>o</i> -Nitrophenol	80	—
<i>m</i> -Nitrophenol, <i>p</i> -nitrophenol	60	—
2,4-Dinitrophenol	50	—
Cationic ions		
Na^+ , K^+ , NH_4^+ , Ag^+ , Mn^{2+} , Ni^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Zn^{2+} , Fe^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , Al^{3+} , Fe^{3+}	1000	a
Co^{2+} , Cl^{3+}	200	—
Anionic ions		
F^- , Cl^- , Br^- , I^- , NO_3^- , NO_2^- , ClO_3^- , BrO_3^- , HCOO^- , CH_3COO^- , IO_4^- , S^{2-} , SO_4^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, SiO_3^{2-} , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, MoO_4^{2-} , PO_4^{3-} , AsO_4^{3-}	1000	a
$\text{Cr}_2\text{O}_7^{2-}$	15	—
MnO_4^-	8	—
Organic acids		
Formic acid, propionic acid, <i>n</i> -butyric acid, succinic acid, tartaric acid, citric acid, lactic acid, <i>p</i> -toluenesulfonic acid, <i>p</i> -phthalic acid, DL-malic acid	1000	a
Others		
Glucose, boric acid, urea	1000	a
Aniline, humic acid	100	—

—, Fluorescence decrease; +, fluorescence increase.

^a No interference.

Table 4

Comparison of sensing characteristics between the two sensors for 2,6-DNP determination

Sensors	The proposed sensor	The curcumin embedded sensor
Membrane matrices	No matrices	PVC
Sensing substances	Curcumin substituted PVC	Curcumin
Dynamic range (mol L^{-1})	2.5×10^{-6} to 7.0×10^{-3}	8.0×10^{-4} to 1.0×10^{-3}
Detection limit (mol L^{-1})	1.0×10^{-6}	6.0×10^{-4}
Response time (t_{95}) (s)	50	100
Lifetime ^a (%)	0	20

^a Fluorescence intensity decrease percent after a continuous 200 measurements.

3.6. Sensing mechanism

Suppose that the curcumin moiety in FPVC remains the keto–enol tautomeric equilibrium of curcumin molecule [32], i.e.,

So it is possible for hydroxyl or carbonyl groups to form associated complexes by the means of hydrogen bond with some compounds containing hydroxyl or nitro group.

As the stoichiometric ratio of the tested nitrophenols to FPVC was proved to be 1:1 and 2,6-DNP exists mainly in the molecular form at pH 3.50, it seems that the hydroxyl and nitro-groups in 2,6-DNP simultaneously associate with the carbonyl and hydroxyl groups of enol form of FPVC through hydrogen bond to form non-fluorescent ground state complex, i.e.,

The formation of the cyclic structure III causes the fluorescence quenching of FPVC.

The 2,6-DNP selectivity of this sensing membrane was based on the ability difference between 2,6-DNP and other nitrophenols in forming the cyclic non-fluorescent complex with FPVC through hydrogen bonding. Two factors, including the steric hindrance and acidity of nitrophenols, must be considered. The steric hindrance, or spatial matching effect, was predominated by the cavity size of polymer and the molecular structure of the analyte. The ionisation constant ($\text{p}K_{\text{a}}$) was the indicator for acidity of nitrophenols, which was summarized in Table 5. As can be seen from Table 5, under the experimental pH, the tested nitrophenols were all in their molecular form except 2,4,6-TNP. The solution pH of 3.50 deprotonated its phenolic hydroxy group and it is mainly in the anion form such that inclined to stay in the solution and not to diffuse into the membrane phase. In addition, the steric hindrance experienced by 2,4,6-TNP because of its three-dimensional molecular structure [35] may also block its migration into the membrane phase and react with the sensing materials. So FPVC showed the smallest response to 2,4,6-TNP. *o*-NP was very much more intramolecularly hydrogen bonded than other nitrophenols [36], which may form a unfavorable molecular structure for its effective interaction with FPVC to

Table 5

Ionisation constant ($\text{p}K_{\text{a}}$) of tested nitrophenols

Nitrophenols	$\text{p}K_{\text{a}}$
<i>o</i> -NP	7.23 ^a
<i>m</i> -NP	8.39 ^a
<i>p</i> -NP	7.15 ^a
2,4-DNP	4.09 ^a
2,6-DNP	3.68 ^b
2,4,6-TNP	0.71 ^c

^a Data taken from [33].

^b Data taken from [26].

^c Data taken from [34].

form the non-fluorescent complex. The similar phenomenon also occurred to 2,4-DNP, i.e.,

It is apparent that the 3- and 4-position nitro groups in *m*- and *p*-NP may offer disadvantageous configuration for their effective interaction with FPVC through hydrogen bond and their response was relatively small.

It can be seen that the spatial adaptability between the analytes and sensing substance showed the dominating effect on their effective interaction in the proposed chemical sensor. 2,6-DNP possesses a most spatially matching structure for its migra-

Table 6
Analytical results for 2,6-DNP in water samples ($n=5$)

Sample	Nitrophenols added (10^{-5} mol L $^{-1}$)	2,6-DNP found (10^{-5} mol L $^{-1}$)		Recovery (%)	
		Proposed sensor	HPLC method [7]	Proposed sensor	HPLC method [7]
Tap water 1	<i>o</i> -NP, 0.2; <i>m</i> -NP, 0.15; <i>p</i> -NP, 0.3; 2,4-DNP, 0.15; 2,6-DNP, 0.2; 2,4,6-TNP, 0.1	0.21 ± 0.01	0.20 ± 0.01	105	100
Tap water 2	<i>o</i> -NP, 0.3; <i>m</i> -NP, 0.15; <i>p</i> -NP, 0.3; 2,4-DNP, 0.15; 2,6-DNP, 0.3; 2,4,6-TNP, 0.1	0.32 ± 0.02	0.31 ± 0.01	107	103
River water 1	<i>o</i> -NP, 1.0; <i>m</i> -NP, 1.5; <i>p</i> -NP, 1.0; 2,4-DNP, 1.5; 2,6-DNP, 5.0; 2,4,6-TNP, 1.5	4.7 ± 0.2	4.8 ± 0.1	94	96
River water 2	<i>o</i> -NP, 1.0; <i>m</i> -NP, 1.0; <i>p</i> -NP, 0.8; 2,4-DNP, 1.2; 2,6-DNP, 1.0; 2,4,6-TNP, 0.8	1.1 ± 0.2	1.1 ± 0.2	110	110

tion through the polymer cavity and approach the fluorophore to form a supramolecular complex.

3.7. Preliminary analytical application

The proposed sensor was applied to the determination of 2,6-DNP in tap and river water samples in the presence of other nitrophenols. River water samples were first acidified by sulphuric acid to pH 3.50, then filtered through a 0.45- μ m filter membrane (Ya Dong Nuclear Grade Resins Co. Ltd., Shanghai Institute of Pharmaceutical Industry, Shanghai, China) and a column packed with anionic-exchange resin (Amberlite IRA-400, USA), successively. Tap water samples were acidified to pH 3.50 and analyzed without any pretreatment. All the water samples were spiked with nitrophenols at different concentration levels and then analyzed. The results obtained for 2,6-DNP determination were also compared with those obtained by HPLC method [7] and were shown in Table 6. We can see that the results were satisfactory. The present sensor may be useful for the determination of 2,6-DNP in real samples.

4. Conclusions

A novel functional polymer has been successfully synthesized by the nucleophilic substitution of a fraction of the chlorine atoms bound to the PVC backbone by curcumin. The polymer was applied to fabricate an optical fiber chemical sensor for the determination of 2,6-DNP simply, quickly, and selectively. The fluorescence signal variation was very reversible and was proportional to 2,6-DNP concentration. As 2,6-DNP can provide an optimal space geometry matches to the formation of a cyclic complex with low fluorescence efficiency, the sensor shows excellent selectivity for 2,6-DNP. The response time, repeatability, and lifetime of the sensor were also satisfied. The study results enabled better understanding of the interaction between functional polymer and the analytes and prove useful in the future development of high-quality chemical sensors for on line environmental monitoring.

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