Abstract  By replacing the hydrogen of the 4-amino group of a 4-amino-1,8-naphthalimide derivative with an N-acryloyxethyl group, the fluorophore has been covalently immobilized on an optical sensor surface by UV photopolymerization. The optical sensor obtained can be used for the determination of picric acid. The linear range and detection limit of the sensor are $9.80 \times 10^{-7}$ –$1.96 \times 10^{-4}$ mol L$^{-1}$ and $7.1 \times 10^{-7}$ mol L$^{-1}$, respectively. Leaching of the fluorophore from the membrane is effectively prevented by covalent immobilization, resulting in a sensor with a relatively long lifetime. The response time of the sensor is short, and the reproducibility and reversibility are good. The sensor has been used for the indirect determination of the chloroquine content of pharmaceutical tablets.

Keywords  Optical fiber sensor · Aminonaphthalimide · Covalent immobilization · Fluorescence quenching

Introduction

Naphthalimides are luminophores with high stability and quantum yield which have been used as fluorescent brightening agents and laser dyes [1, 2]. Stewart [3] reported the synthesis of sulfonated aminonaphthalimides as highly fluorescent water-soluble compounds which were useful as biological tracers. Yan et al. [4] synthesized co-polymeric aminonaphthalimide derivatives as potentially useful industrial colorants. The introduction of the amino group at the 4-position greatly enhances the fluorescence of the molecule. This group of compounds seems quite promising as fluorescent carriers in the preparation of optical fiber sensors. By replacing one hydrogen of the amino group it is possible to introduce into the molecule a carbon chain with double bonds capable of copolymerization with a monomer on a modified sensor surface. Covalent immobilization [5, 6, 7, 8, 9, 10, 11, 12] effectively prevents leakage of the carrier dye from the sensor membrane, a phenomenon that shortens the lifetime of ordinary optical sensors. An attempt was therefore made to synthesize an aminonaphthalimide derivative $N$-propyl-4-(N-acryloxyethyl)amino-1,8-naphthalimide (PAEAN) and covalently immobilize it on the surface of a glass plate by photopolymerization. It has been observed experimentally that the sensor prepared has strong fluorescence which is quenched by picric acid, making it possible to use the sensor for determination of picric acid.

Picric acid, 2,4,6-trinitrophenol, is an organic acid used as an explosive and an antiseptic. The compound is an important analytical reagent used in the determination of organic bases such as chloroquine, a drug effective against malaria. Optical sensors for picric acid have been the subject of a number of investigations [13, 14]. The optical sensors reported so far employ a cellulose triacetate or PVC membrane with the fluorescent carrier dissolved in a solvent mediator; this might result in a leakage problem. The search for a new method of immobilization to circumvent this problem is of considerable interest. PAEAN was synthesized from 4-bromo-1,8-naphthalic anhydride as starting material. Under UV radiation it was photo-copolymerized with 2-hydroxypropyl methacrylate (HPMA) on a sensor surface treated with a silanizing agent. The spectral characteristics and the analytical performance of the optical sensor for the determination of picric acid were investigated.

Experimental

Materials and apparatus

4-Bromo-1,8-naphthalic anhydride, purchased from Taizhou Chemicals (Zhejiang, China), was recrystallized twice from chlorobenzene (mp 218–220°C). 3-(Trimethoxysilyl)propyl methacrylate (TSPM: Acros, Sweden) and 2,4,6-trinitrophenol of analytical...
reagent grade were used as received. Methacryl chloride was synthesized according to a method described elsewhere [15] (bp 95–96 °C). An aqueous stock solution of 2,4,6-trinitrophenol of ca. 2×10⁻² mol L⁻¹ was prepared, and the actual concentration of picric acid was determined by titration with sodium hydroxide standard solution. The working solutions of picric acid were prepared by serial dilution with Britton–Robinson (B–R) buffer solution. B–R buffer solutions of different pH were prepared by mixing appropriate amounts of phosphoric acid, acetic acid, and boric acid and adjusting to the desired pH with 0.2 mol L⁻¹ sodium hydroxide. Other chemicals were of analytical-reagent grade and used without further purification. All solutions were prepared with redistilled water.

All fluorescence measurements were conducted with a Hitachi F4500 fluorescence spectrometer. Solution pH was measured with a PHS-3C pH meter (Shanghai Analytical Instruments, China).

Synthesis of PAEAN

The general scheme of the synthesis is shown in Fig. 1.

### Synthesis of N-propyl-4-bromo-1,8-naphthalimide (II)

Crayshan et al. [16] synthesized N-(2-hydroxymethyl)-4-bromo-1,8-naphthalimide by reaction of an acid anhydride with ethanolamine to form a hydroxyethyl imido-group. Compound II was synthesized by a similar method with some modifications. Instead of ethanolamine, n-propylamine (2.2 mL) was reacted with compound I (2.50 g) by heating under reflux for 2 h in 80 mL of ethanol. The reaction mixture was filtered, and the solid was washed with doubly distilled water and dried in an oven at 120 °C to give 2.71 g of pale yellow product, compound II, with a nominal yield of 94.0%.

### Synthesis of N-propyl-4-(ethoxy) amino-1,8-naphthalimide (III)

Compound III was synthesized by a method similar to the synthesis of N-(2,4′-dimethyl)phenyl-4-((hydroxyethyl)amino)-1,8-naphthalimide (IV) [4]. Instead of N-(2,4′-dimethyl)phenyl-4-bromo-1,8-naphthalimide used for synthesis of IV, compound II obtained in the previous step was used as the starting compound. Compound II (2.24 g), which was shown by TLC to be of sufficient purity, was mixed with 10 mL ethanolamine and 0.6 g of CuSO₄·5H₂O and heated under reflux for 2 h in 50 mL ethylene glycol monomethyl ether. The reaction mixture was cooled, poured into 200 mL water, and filtered. The solid was washed with doubly distilled water and dried in an oven at 120 °C to give 1.96 g of yellow solid, compound III, with a nominal yield of 93.3%.

### Synthesis of PAEAN

Compound III (1.80 g) was dissolved in 60 mL anhydrous tetrahydrofuran (THF) and 0.80 mL triethylamine was added. Methacryl chloride (0.60 mL) was then added slowly to the vigorously stirred solution. The mixture was stirred continuously at room temperature for 4 h. Filtration, then removal of the THF under reduced pressure, gave the brown yellow crude product. Column chromatography (2-butanol–trichloromethane=3:4 (v/v), silica) then gave the required product, PAEAN, as a yellow solid (1.60 g, 72.6%). Mp 156–157 °C, ms: base peak 182, M⁺ 366.

Silanization of the glass surface

Conventional glass plates (13 mm diameter) were immersed successively in 3% HF and 10% H₂O₂ for 5–10 min each and then washed thoroughly with redistilled water. A solution of TSPM was prepared by mixing 0.2 mL TSPM, 2 mL of 0.2 mol L⁻¹ HAc–NaAc buffer solution, pH 3.6, and 8 mL distilled water. The glass plates were submerged in this solution and soaked for 2 h, then rinsed with water and dried at room temperature.

Preparation of the sensing membrane

2-Hydroxypropyl methacrylate (2.9 mL), PAEAN (10 mg), benzoil ethyl ether (90 mg), diphenyl diketone (0.12 g), and triethanolamine (0.2 mL) were mixed and cast on to a cleaned poly(tetrafluoroethylene) (PTFE) plate. Silanized glass plates were placed over the droplets, and UV radiation (254 nm) was directed from 10 cm on to the glass plates for ~4 h. After UV irradiation the glass plates were washed with water and methanol to remove any unreacted species until no leaching of the PAEAN was observed.

Fluorescence measurements

Fluorescence measurements were performed with the Hitachi F-4500 spectrophotometer with the slits set at 5 nm and 2.5 nm for excitation and emission, respectively. The fluorescence of the membrane was measured at the wavelength of maximum emission of 522 nm and a wavelength of maximum excitation of 457 nm. A home-made poly(tetrafluoroethylene) flow-cell (Fig. 2) and a bifurcated optical fiber (30+30 quartz fibers, diameter 8 mm and length 1 m) were used for picric acid-sensing measurements. The excitation light was carried to the cell through one arm of the bifurcated optical fiber and the emission light was collected through the other. A glass plate (diameter 13 mm) with the covalently-imobilized sensing membrane was fixed on the top of the flow chamber by means of the mounting screw nut with the membrane.