Scientific paper

Anthracene Derivative Covalently Immobilized on Sensing Membrane as a Fluorescent Carrier for Water Assay

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Abstract

This article describes an optical chemical sensor based on a fluorescent dye 1-allyloxy-4-hydroxyanthracene-9, 10-dione (AHD) with terminal double bond, which is covalently bonded to quartz glass plate surface treated with a silanizing agent to prevent its leakage. The purpose of this work was to characterize and optimize the sensor for determining the water content in the acetone organic solvent. The sensor is resistant to swelling; the membrane possesses relatively long lifetime, short response and recovering time. The reversibility and reproducibility of the sensor are adequate for practical measurements.

Keywords: Fluorescent sensor, Water content, 1-allyloxy-4-hydroxyanthracene-9, 10-dione

1. Introduction

The key element in an optical sensor is the indicator, a chemical substance that displays changes in its optical properties, which include the absorbance intensity, the fluorescence intensity, maximal absorption wavelength, emission wavelength, fluorescence lifetime and fluorescence quantum yield et al upon interacting chemically or physically with the analyte of interest. Sensors based on fluorescence quenching of organic dyes belong to the type of most widely used devices of this category, though the scope of useful fluorescent carriers remains limited to a few groups of compounds.[1–10] Searching for sensing agents with excellent reversibility, selectivity and sensitivity is of considerable interest.

Owing to its specific solvent-polarity-sensitive features, 1, 4-dihydroxyanthraquinone (HAQ) could be referred to as solvatchromic dyes, some of which have been reported to detect water in alcohol[11–13]. It is interesting to explore the possibility of using HAQ as a fluorescent carrier for optical chemo-sensing. However, due to the hydrophilic character, this compound itself doesn't meet the requirement to be treated as a fluorescent carrier for optical sensor. We hypothesized that introduce of a terminal double bond to 1, 4-dihydroxyanthraquinone may be capable to copolymerize with a monomer on the sensor surface. It was reported that 1,4-dihydroxyanthraquinone reacted with bromopropylene to form 1-allyloxy-4-hydroxyanthracene-9,10-dione (AHD).[14] Under UV radiation AHD could be photocopolymerized on the modified quartz glass surface treated with a silanizing agent and it prevented the leakage of the dye.[15–16]

A water sensor is of interest in numerous applications. For example, in the petroleum industry, on-line determination of the water content of oil-in-water emulsion is an important issue for crude oil processing and oil transportation. In synthetic chemistry, dehydration procedures are performed to ensure experimental reproducibility when water-sensitive reagents such as acetone are used. Therefore, it is of importance to develop water sensor for the measurement of water in organic solvents, which is generally the most common impurity in organic solvents owing to water's ubiquity, solubility, and propensity to physisorb on reaction vessel surfaces. Traditional method for the quantitative measurement of water in the organic solvents is the Karl Fisher titration. Although this approach has several useful characteristics, some disadvantages such as the requirement of skilled personnel and specialized equipment, the complex of sample manipulations and interference from other co-existing species limit its wider application. Several novel methods have been reported for the determination of water in organic solvents.[13,17–24] In particular, Niu et al reported the naphthalimide derivative fluorescent probe for detection of water in organic solvents dioxane, acetonitrile and ethanol.[21] Sun et al developed convenient 19F-NMR-based aquametry methods to measure the trace water contamination in alcohols and polar aprotic solvents (Dimethylformamide, Acetonitrile, Dimethyl sulfoxide, Benzene, Toluene, Ether, Tetrahydrofuran, Pyridine).[22] Samadi-Maybodi et al found a highly efficient fluorescent sensor 2, 3 biphenyl quinoxaline 6-amine in the presence of bis-(2, 4, 6-trichlorophenyl) oxalate (TCPO) and Zn(2+) to detect trace water in ethanol and methanol.[23]

However, the methods related to determination of water in acetone are limited. Chang et al[24] reported a fluorescence lifetime-based water sensor based on the solvent-polarity-sensitive fluorescent metal-ligand compound, which showed reliable response of water in acetone with content from 0% to 20%. Therefore, an alternative, more robust and accurate analytical procedure would be desirable. In the study, the fluorescent sensor based on AHD through covalent immobilization, a simple and sensitive tool for water in acetone solvent assay from 0% to 80%, is reported. The assay is simple, applicable, and straightforward and the mechanism is also discussed.

2. Experimental

2. 1. Chemicals and Solutions

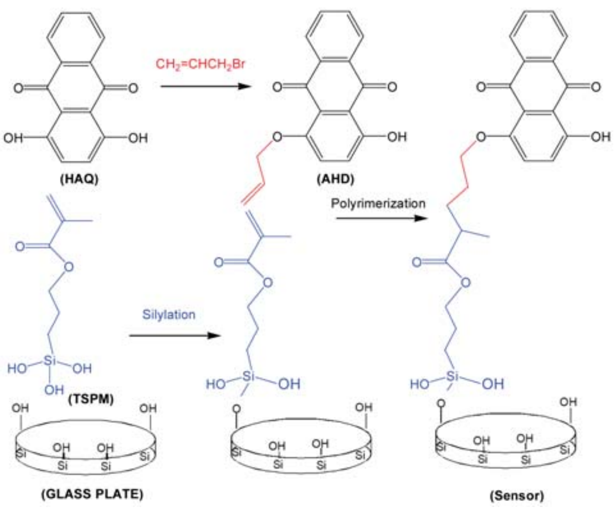
Twice-distilled water was used throughout all experiments. 1,4-dihydroxyanthraquinone was obtained from Suzhou pharmaceuticals (Jiangsu, China). Bromopropylene was prepared and purified in this laboratory. Benzoin ethyl ether used as a polymerization initiator was purchased from Shanghai Reagents. The silanizing agent 3-(trimethoxysilyi)propyl-methacrylate(TSPM) was from ACROS (Sweden). Acetone solution used in this work was distilled to eliminate any water residue. The buffer solutions used in the various experiments were obtained by serial dilution with Britton – Robinson (B-R) buffer solution. The B-R buffer solution of different pH were prepared by mixing appropriate amounts of phosphoric acid, acetic acid, and boric acid and adjusting to desired pH with sodium hydroxide. All other reagents and solvents were of analytical regent grade unless otherwise stated. The organic synthesis experimental procedures were performed in the fume hood to prevent inhalation of organic and inorganic vapors. Goggles, rubber gloves and lab coats are needed when dealing with chemicals and volatile organic solvents.

2. 2. Apparatus

The fluorescence measurements were carried out on a Hitachi F-4500 spectrofluorimeter with excitation and emission slits set at both 10 nm controlled by a computer data processing unit. The light source is a 150 W Xe lamp and the detector is a R928F red-sensitive photomultiplier tube. By using a specially designed flow-through cell and pumping the sample solutions at a flow rate of 2.0 ml min^{-1} using a peristaltic pump (Guokang Instruments, Zhejiang). The glass slide (diameter 25 mm) with the sensing membrane fabricated on it by a photo-polymerization procedure (vide infra) was mounted in the flow-through cell. The membrane side is facing the cell chamber with the circulating sample sweeping over the membrane and the opposite side of the glass disc tightly matching vs. light source. UV-vis spectra were measured by a Multispec-1501 UV-vis spectrophotometer (SHIMAOZU) by using a 5 cm quartz cell at 25 °C. A PHS-3C pH meter (Shanghai Analytical Instruments, Shanghai) was used for pH values measurements. The fluorescence measurements were made under ambient temperature at 25 °C. Mass spectra were obtained on a GC-17A, QP-5000 (SHIMADZU) spectrometer.

2. 3. Preparation of AHD[14]

1-Allyloxy-4-hydroxyanthracene-9, 10-dione (AHD) was synthesized (Scheme 1) using a procedure similar to that reported by Hauser et al.[15] Powdered anhydrous potassium carbonate (5.5 g, 40 mM) was added in small portions to a magnetically stirred solution of 1,4-dihydroxyanthraquinone (9.6 g, 40 mM) in dry dimethylformamide (DMF) (200 ml) under nitrogen. The thick slurry of potassium salt that formed over 15~30 min was thinned with additional DMF (200 ml). The mixture was heated to 55–60 °C for 0.5 h, and then bromopropylene (18 ml) was added. The mixture was heated at 65–70 °C for 40 h and then cooled (5 °C) and acidified with HCl (1 M, 80 ml), water (300 ml) and CH_2Cl_2 (300 ml) were added, and the mixture was stirred thoroughly. The phases were separated, and the aqueous layer was extracted with additional CH_2Cl_2 (3 × 300 ml). The combined organic extracts were washed successively with water (400 ml) and saturated sodium chloride solution and then dried ($MgSO_4$), filtered, and evaporated to give 11 g of crude material, which



Scheme 1. Synthesis of AHD and the sensor

went through the silica gel chromatography to yield 6.17 g AHD, with mass, m/z equals to 280 (M^+).

2. 4. Preparation of the Sensing Membrane

Glass slides were dipped for 3 h in chromic acid, washed thoroughly with distilled water and allowed to dry. The glass surface was silanized according to following steps. The conventional glass plates (diameter = 25 mm) were immersed in 3% hydrofluoric acid (HF) and 10% H_2O_2 for 30min each and washed with water. The glass plates were submerged in a solution containing 0.6 ml silanizing agent 3-(trimethoxysilyl)propyl methacrylate (TSPM), 6 ml of 0.2 mol L^{-1} HOAc-NaOAc buffer solution (pH 3.6) and 24 ml of double-distilled water for 2 h. The quartz glass plates were washed with water and dried at room temperature. The AHD polymer membrane was prepared according to the following procedure. Acrylamide (400 mg), benzoine ethyl ether (90 mg), benzophenone (60 mg), 2-hydroxypropyl methacrylate (2.0 ml), triethanolamine (0.2 ml) and AHD (10 mg) were mixed and a red transparent cocktail was observed under ultrasonic agitation. Many drops of above cocktail were put onto a poly(tetrafluoroethylene) plate, then a glass plate treated as above was covered onto the cocktail drop. After put in the UV radiation (254 nm) for about 5 h, the glass plates with the membrane formed were washed with double-distilled water and methanol to remove any non-reacted species until no leaking of the AHD was detected, then dried and storied for use.

2. 5. Procedure of Detection of Water in Acetone

Home-made flow-cell was fixed at special position in the detecting chamber of the Hitachi F-4500 spectrofluorimeter to carry the excitation and emission light. A sensing membrane prepared as described was fixed on the home-made flow-cell by the mounting screw nut with the membrane contacted with the sample solution. The sample solution was driven through the flow-cell by a peristaltic pump at a flow rate of 2.0 ml min^{-1}. The sensor membrane was equilibrated with the sample solution for obtaining a stable fluorescence signal. The excitation and emission fluorescence spectra of AHD are recorded with the emission and excitation wavelengths fixed at 561 and 462 nm, respectively. After each measurement, the fluorescence intensity of the sensing membrane was recovered by pumping the blank solution (organic solvents such as acetone) through the cell prior to the next measurement.

3. Results and Discussion

3. 1. Spectral Characteristics

UV-vis spectra of AHD show no obvious change of either the intensity or the maximal wavelength with various contents of water/acetone solutions (Figure not shown). Figure.1 shows the fluorescence spectra of the AHD (1.0×10^{-5} mol L^{-1}) membrane in acetone solutions containing various content of water (20%–100% v/v). With increasing of the content of water in acetone, the fluorescence intensity of AHD optode gradually enhanced. Due to the solvatochromism of AHD, the maximal excitation wavelength about 462 nm didn't change in different content of water, but the maximal emission wavelength changed from 561 nm (in acetone) to 591 nm (20%–80% water in acetone). The dominant electronic transition of AHD to the first excited state should be of $\pi \rightarrow \pi^*$ character. The electronic charge distribution of $\pi \rightarrow \pi^*$ excited state is more extended than the ground state and the excited state is more polarizable. Changing from a non-polar (acetone) to a polar solvent (acetone and water) increases the solvent interaction and moves the emission spectra to longer wavelengths (red shifted).[22] Usually, the addition of small amounts of water to nonaqueous solvents decreases the fluorescence.[25] However, for this specific AHD copolymer membrane, increasing water strongly enhanced its fluorescence intensity owing to the formation of hydrogen bonding between water and the carbonylic oxygens of AHD, which decreased the change in dipole moment on excitation which resulted in a fluorescence quantum yield remarkably enhanced as the solvent polarity increased[26].

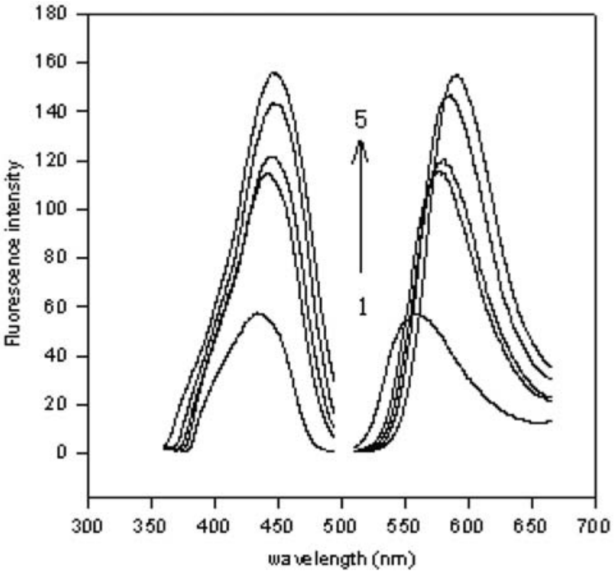


Figure 1: Fluorescence excitation (left) and emission spectra (right) of the sensing membrane contacted with different water content in acetone solutions (v/v%): (1) 0; (2) 20.00; (3) 40.0; (4) 60.0; (5) 80.0.

3. 2. Effect of pH

Hydroxyl and carbonyl groups in AHD are capable to protonation, which is sensitive to acidity of solutions. The fluorescence behavior of the AHD sensor was exami-

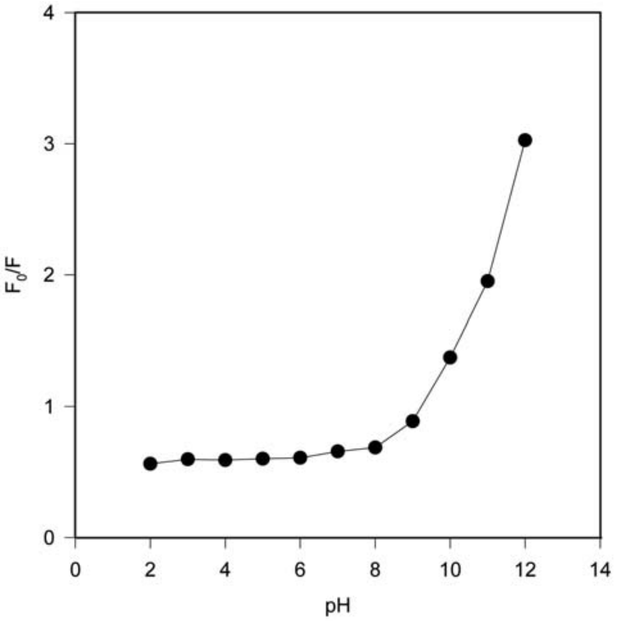


Figure 2: The effect of pH on the relative fluorescence intensity F_0/F values recorded with 10 % water content in acetone solutions of different pH.

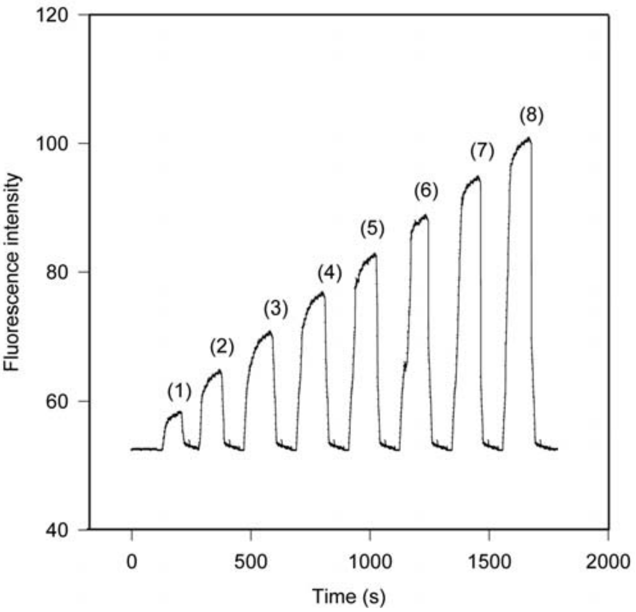


Figure 3: The time response curve for flowing system with fed samples of different water content in acetone solutions (v/v%): (1),2; (2), 4; (3), 6; (4), 8; (5), 10; (6), 12; (7),14; (8), 16.

ned at different pH conditions (Figure 2). There is a noticeable influence of pH on fluorescence intensity under conditions of high alkalinity. A pH of 7.0 B-R buffer solutions was used in subsequent experiments.

3. 3. Repeatability, Reversibility and Response Time

The repeatability and reversibility of the sensor were evaluated by exposing into acetone solutions containing various content of water (0, 2%, 4%, 6%, 8%, 10%, 12%, 14%, 16%, 18%, 20% V/V) of pH 7.0. Figure 3 presents the fluorescence intensity change upon switching form one solution to another. The response time of the sensor and the recovering time was 35 s.

3. 4. Short-time Stability and Lifetime

In order to examine the short-time stability of the sensor, the sensor is exposed to the blank buffer solution in a period of 10 h. The fluorescence intensity was recorded at interval of 30 min. The fluorescence response remains stable even after one month's usage. The carrier immobilized on quartz glass plates by covalent bonding effectively prevented the leakage of carrier. A newly prepared sensor can be used at least two months.

3. 5. Quantitative Determination, Measurement Range

The AHD sensor designed in this study was successfully used to determinate the water content in acetone. The change of fluorescence intensity of optode with different water content in acetone(0–20%) was examined. The F_0/F values show a quasi-linear relationship with the water content in acetone in the concentration range of 0–20% with the regression equations of the form $F_0/F = 0.92711–0.02541\ [H_2O]$ (r = 0.9504)

4. Conclusions

AHD, which contains a terminal double bond, is possible to covalently immobilize on the surface of the modified quartz glass. The sensor prepared using AHD containing membrane shows excellent analytical characteristics including fast response, sufficient repeatability and selectivity. The solvent-polarity-sensitive indicator of AHD can be utilized for water content assay in acetone. The life time of the sensor is guaranteed due to the prevention of carrier leakage by covalent immobilization. The anthraquinone derivatives possessing excellent fluorescent characteristics provide a promising group of optical chemical sensor fluorophore for various chemical species, which deserves further investigation.

5. Acknowlegement

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6. References

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Povzetek

Članek opisuje optični kemični senzor, osnovan na fluorescentnem barvilu 1-aliloksi-4-hidroksiantracen-9,10-dion (AHD) s terminalno dvojno vezjo, ki je kovalentno vezano na površino plošče iz kvarčnega stekla, ki je silanizirana, da preprečimo odtekanje senzorja. Namen raziskave je bil karakterizirati in optimizirati senzor za določitev vsebnosti vode v organskem topilu acetonu. Senzor je odporen na nabrekanje; membrana ima relativno dolgo življenjsko dobo, hiter odgovor in hiter regeneracijski čas. Reverzibilnost in reproducibilnost senzorja zadostujeta za praktične meritve.