



Dual signaling of water contents of biofuel-relevant ethanol and butanol by pyranines



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ABSTRACT

Novel optical sensors for measuring the water contents of biofuel-relevant ethanol and 1-butanol based on the pyranine fluorophore were investigated. The diethylsulfonamide derivative of pyranine showed a pronounced absorption and fluorescent signaling in response to changes in the water content of ethanol and 1-butanol. This signaling was based on the increased dissociation of the acidic hydroxy group of pyranine in response to the increasing water content of the alcohol solutions. The signaling behavior of the sensors was readily analyzed by ratiometric measurements using the absorption and fluorescence characteristics of the undissociated and dissociated forms. Upon the derivatization to diethylsulfonamide, the signaling became more sensitive than that for its parent pyranine. The detection limits of the pyranine and diethylsulfonamide derivative for the measurement of the water content in ethanol were 1.9% and 0.03%, respectively. On the other hand, the detection limit of the diethylsulfonamide derivative for the determination of the water content in 1-butanol was 0.01%, whereas underivatized pyranine was not useful because of the limited solubility of the sensor. The practical application of this method for measuring the water content in ethanol and 1-butanol using a smartphone as an easy-to-use signal capturing device was also explored.

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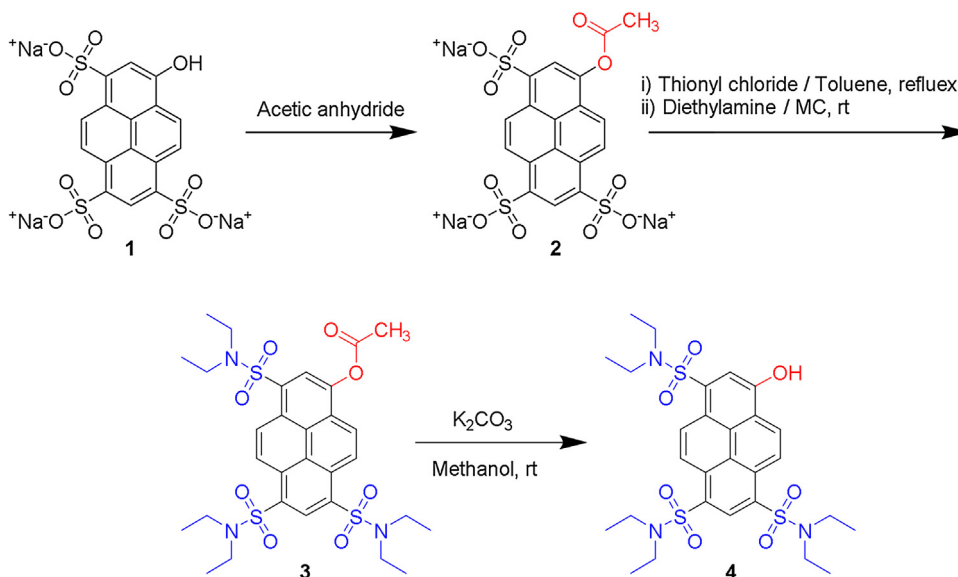
1. Introduction

Bioethanol is considered one of the most important alternatives to gasoline and diesel because its use leads to substantial reductions in the consumption of fossil fuels and the emission of greenhouse gases [1,2]. Numerous studies have been conducted to investigate the practical application of this environmentally important topic, particularly from the socio-economic point of view [3–5]. In routine use, bioethanol is blended with gasoline. However, it is highly hygroscopic, and thus, water can be introduced into the ethanol fuel during its production, distribution, and storage [6]. An increase in the water content of the fuel results in increased corrosion in engines and fuel tanks [7]. Furthermore, if the water content in ethanol-blended gasoline exceeds a certain level, phase separation can occur, which causes serious problems in vehicles and other engine systems [8]. To prevent this critical problem, the water content in bioethanol fuels should be carefully monitored. In fact, the water content in bioethanol fuels has been regulated to less than 1.0% in the United States [9].

The water content in ethanol can be determined using standard instrumental methods such as Karl Fischer titration [10,11], gas chromatography [12], infrared spectroscopy [13,14], conductometry [15], and quartz crystal microbalance measurements [16]. However, optical probes with colorimetric and/or fluorescent behaviors are more desirable because they frequently enable the naked-eye visualization of the target and allow for a quantitative assay with a simple and rapid device. Based on this viewpoint, numerous optical sensors have been designed to the efficient sensing of the water content in various organic solvents such as acetonitrile, THF, and alcohols (Table S1, Supplementary data) [17–26]. In particular, to optically measure the water content in ethanol, a number of elaborate systems such as glass slides chemically modified with the fluorescent dye 10-allyl-acridine orange [27], luminescent optical fibers based on Ru(II)-bisphenanthroline-dipyridophenazine immobilized in Nafion [28], and optode membranes composed of europium ion fluorescent chelates on silanized glass slides [29] have been developed. More recently, an interesting colorimetric and fluorescent dual-mode sensor for detecting the alcoholic strength of spirit samples using stimuli-responsive coordination polymers based on the Zn²⁺ complex of 1,4-bis(imidazol-1-ylmethyl)benzene has been developed [30].

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Scheme 1. Preparation of pyranine diethylsulfonamide sensor **4**.

Pyranine (8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt) exhibits an interesting environment-sensitive fluorescence behavior and is used as a versatile molecular probe in a variety of chemical, biological, and medical applications. Its photoacidic characteristics, fluorescence shift, and UV–vis absorption changes are exploited for these purposes [31]. For instance, pyranine has been used to study biological properties such as the binding of carbon monoxide to hemoglobin [32] and the pH of endocytic vesicles [33]. It has also been used for determining fundamental chemical species such as carbon dioxide [34], ammonia [35], and Cu^+ ions [36]. Other applications with more practical purposes such as monitoring the monomer conversion during free-radical copolymerization [37], the simultaneous measurement of pH and temperature [38], detection of the water content changes in SiO_2 gels [39], and a non-destructive alternative for measuring the acidity of paper [40] have also been reported.

In this paper, we report an easily synthesizable optical sensor for measuring the water content in biofuel-relevant alcohols based on the prominent spectral changes resulting from the water-induced deprotonation of pyranine dyes. A sulfonamide derivative of pyranine showed a pronounced signaling behavior even with small changes in the water content of ethanol and 1-butanol, which could be useful for practical applications to biofuel samples. The use of a smartphone as a convenient screening tool for the determination of water content in ethanol is also reported.

2. Experimental section

2.1. General

Pyranine was purchased from Tokyo Chemical Industry Co, Ltd. Acetic anhydride, thionyl chloride, and diethylamine were obtained from Aldrich Chemical Co. All of the other chemicals and solvents were purchased from commercial sources and used as received. The ^1H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were measured with a Varian VNS NMR spectrometer, using residual solvent signals as internal standards. The UV–vis spectra were recorded on a Scinco S-3100 spectrophotometer equipped with a Peltier temperature controller. The fluorescence spectra were measured using a PTI QuantaMaster steady-state spectrofluorometer. The mass spectra were obtained using a Micromass Autospec mass spectrometer. Column chromatography was carried out with silica gel (Merck,

240 mesh). A standard drying method was used to dry commercially available absolute ethanol and spectroscopic 1-butanol by storage over activated 3 Å molecular sieves (10% m/v) for 24 h [41]. The water contents of the anhydrous ethanol, aqueous ethanol, and 1-butanol solutions were determined using a Karl Fischer titrator (870 KF Titrino plus, Metrohm, Switzerland). Pyranine acetate **2** was prepared by the acetylation of pyranine following a reported procedure [42].

2.1.1. Preparation of pyranine diethylsulfonamide acetate **3**

A dispersed solution of pyranine acetate **2** (0.57 g, 1.0 mmol) in toluene (50 mL) was placed in a 100 mL round-bottom flask equipped with a Dean-Stark trap for the removal of water. The solution was refluxed for 3 h to dry the reaction mixture. The mixture was then cooled, and thionyl chloride (10 mL) was added. The resulting mixture was heated under reflux for 8 h. The precipitate formed was removed by filtration, and the filtrate was evaporated under reduced pressure. The residue was dissolved in dichloromethane (2 mL), and the resulting solution was slowly added to a solution of diethylamine (1.0 mL, 10.0 mmol) in dry dichloromethane (30 mL). The reaction mixture was stirred for 8 h, and was then washed with 1N HCl and distilled water. The organic phase was collected, and the solvent was removed under reduced pressure. After purification by column chromatography (silica gel, CH_2Cl_2), the desired acetate derivative of pyranine, diethylsulfonamide **3**, was obtained as a greenish-yellow powder. Because the partial hydrolysis of the acetate group was observed during the acidic work-up procedure, the diethylsulfonamide **3** was used for the next step without any further purification or identification.

2.1.2. Preparation of pyranine diethylsulfonamide **4**

A mixture of pyranine diethylsulfonamide acetate **3** (0.67 g, 1.0 mmol) and potassium carbonate (0.28 g, 2.0 mmol) in methanol (10 mL) was stirred at room temperature. After completion of the reaction, the residual potassium carbonate was removed, and the solution was evaporated and dissolved in dichloromethane. The resulting solution was washed with distilled water and evaporated. After purification by column chromatography (silica gel, dichloromethane/methanol 19:1, v/v), the desired pyranine diethylsulfonamide **4** was obtained as a yellow powder (0.53 g, 85%). ^1H NMR (600 MHz, CDCl_3) δ 9.18 (s, 1H), 9.13 (d, $J=9.9$ Hz, 1H), 9.01 (dd, $J=9.6, 3.9$ Hz, 1H), 8.94 (dd, $J=9.8, 3.5$ Hz, 1H), 8.79 (d,

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