

Glucose-responsive vesicular sensor based on boronic acid–glucose recognition in the ARS/PBA/DBBTAB covesicles

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Abstract

The amphiphile, 4-(4-dodecyloxybiphenyl-4-yloxy) butyl trimethylammonium bromide (DBBTAB), has a cationic group with quaternary ammonium salt, which can self-organize into vesicles in dilute aqueous solutions. The alizarin red S (ARS) with a negatively charged group is attracted electrostatically to the positively charged surface on the DBBTAB vesicles to form covesicles. By taking advantages of the features, a vesicular fluorescent sensor was prepared based on phenylboronic acid (PBA)–glucose recognition in the aqueous ARS/PBA/DBBTAB covesicles. The sensor was constructed with three constituents: PBA, DBBTAB amphiphile and ARS which served as the detector. The vesicular sensor enhanced the sensitivity to glucose by about seven- to eight-fold, compared with the same aqueous PBA/ARS solution, which was ascribed to the increased local concentrations of glucose on the surface of vesicles. The vesicular sensor may be available for detection of saccharides in biological systems. © 2006 Elsevier B.V. All rights reserved.

Keywords: Vesicular sensor; Glucose; Phenylboronic acid; Alizarin red S; Amphiphile

1. Introduction

The design and synthesis of effective fluorescent chemosensors for biologically relevant analytes are of paramount interest in supramolecular chemistry [1]. Saccharides are of great importance in biological systems [2]. It is therefore unsurprising that receptors with the capacity to detect chosen saccharides selectively and signal this presence by altering their optical signature have attracted considerable interest in recent years [3–6]. To date, a wide variety of methods have been reported for glucose analysis in research literature, including electrochemistry [7], near infrared spectroscopy [8], optical rotation [9], colorimetric [10] and fluorescence detection [11]. The most commonly used technology for blood glucose determination is an enzyme-based method [12], which requires frequent collection of blood samples. Although frequent “finger pricking” with a small needle to obtain the blood sample is a relatively painless process, this method does suffer from a few practical problems. The first one is inconvenience, which affects compliance by patients.

Second, this is not a continuous monitoring method. Recently, there is a great deal of interest in the development of continuous glucose monitoring systems, which would be able to provide patients with instantaneous feedback and should help to improve the management of proper glucose concentration in diabetic patients [13,14]. To develop a continuous monitoring system, it would be ideal to use an implantable device that is in constant contact with the biological fluid to give a continuous reading of glucose concentration. It is unlikely that the currently used enzyme-based method could be developed as an implantable device due to the instability issues associated with protein-based products [15]. Chemical sensors do offer the advantage of higher stability and relatively easy manufacturing. Such a concept has already been put into test by companies such as Sensors for Medicine and Science [16]. To develop a chemical sensor-based continuous monitoring device, one needs to develop glucose sensors that show high sensitivity and selectivity. Along this line, we are interested in the development of fluorescent sensors for glucose in the vesicular system.

Following the pioneering works of Yoon and Czarnik [17] and later Sandanayake and Shinkai [18], boronic acid derivatives have been used in the recognition and sensing of vicinal

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diols, carbohydrates, and catechols for the past two decades, with many successful examples emerging during this time period [19, and references within]. Boronic acids are known to bind with compounds containing diol moieties with a high affinity through reversible ester formation [20]. Such tight bonding allows boronic acids to be used as the recognition moieties in the construction of sensors for saccharides [21, and references within]. However, the boronic acid compounds are not fluorescent and are only weakly chromophoric. Under such a circumstance, spectroscopic determination relying on the intrinsic spectroscopic property changes upon binding becomes very difficult. Springsteen and Wang [22] has developed a two component competitive assay containing the fluorescent compound alizarin red S (ARS) in the phenylboronic acid (PBA)/ARS system, in which ARS was used as a general fluorescent reading agent for studying the binding events between boronic acids and compounds containing diol moieties with a high affinity.

It is known that the amphiphile, 4-(4-dodecyloxybiphenyl-4-yloxy) butyl trimethylammonium bromide (DBBTAB), has a cationic group with quaternary ammonium salt, which can self-organize into vesicles in dilute aqueous solution [23,24]. The vesicles composed of bilayer structure may be used as membrane models [25]. The ARS with a negatively charged group can be attracted electrostatically to the positively charged surface of the DBBTAB vesicles to form covesicles. Herein, we have developed a novel vesicular sensor composed of three tunable components: PBA receptor, ARS “read-out” units and DBBTAB vesicular carrier, in which the DBBTAB vesicles were used as a novel carrier of device to bind to the ARS component. This fluorescence sensor designed is mainly based upon self-organization of DBBTAB amphiphile and vesicular functionalization as mimetic membranes.

2. Experimental

2.1. Materials

The DBBTAB amphiphile was synthesized by this group previously [26]. Alizarin red S (Xinzhong Chemical Factory, A.R. grade), phenylboronic acid (Tianjin Taida Chemical Factory, A.R. grade), D (+)-glucose (Beijing Chemical Factory, A.R. grade) were used without further purification. Water was doubly distilled after passing through an ion-exchange resin column. Phosphate buffer was purchased from Shanghai Weiye Instrument Plant. The structure of the DBBTAB amphiphile and ARS is shown in Fig. 1.

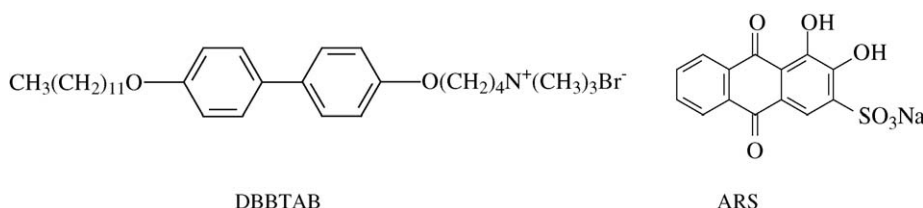


Fig. 1. The structure of 4-(4-dodecyloxybiphenyl-4-yloxy) butyl trimethylammonium bromide (DBBTAB) and alizarin red S (ARS).

2.2. Preparation of the DBBTAB-ARS-PBA covesicles [27]

The DBBTAB and ARS were combined with spectroscopic grade CHCl_3 in a 50 ml beaker. Solvent was removed under N_2 flow, followed by evacuation at high vacuum for 2 h. The resulting amphiphilic film in the beaker was then covered with a pH 6.8 phosphate buffer solution, which was an ideal situation because we were most interested in searching for a sensor that was functional at physiological pH values. The concentrations of DBBTAB amphiphile and ARS were fixed at 4×10^{-3} M and 5×10^{-5} M, respectively. A clear solution was obtained by sonication (Bransonic 12 Ultrasonicator, water-bath type) for 4 h at about 50°C . The covesicles were stable for weeks in the aqueous solution in a pH range of 4–10.

2.3. Instrumentation

Steady-state fluorescence spectra were recorded on a RF-5301PC spectrophotometer. UV spectra were measured with a Shimadzu UV-3100 spectrophotometer. Since N_2 -bubbled and air-saturated solutions gave the same results, the data presented here are all for air-saturated solutions. An aqueous solution was dripped on a silica plate which was then dried in a desiccator at room temperature. Scanning electron microscopy (SEM) was collected on a JEOL JSM-6700F electron microscope. The phase transition from crystal to liquid crystal (T_c) of the covesicles (ca. 5 wt.%) was determined by means of differential scanning calorimetry (Netzsch DSC 204).

3. Results and discussion

Stable aqueous vesicular morphologies were determined by SEM. The typical SEM image from a mixture solution containing 4×10^{-3} M of DBBTAB amphiphile, 5×10^{-5} M of ARS and 5.2×10^{-4} M of PBA is shown in Fig. 2. The diameter of the vesicles was estimated about 150–500 nm from Fig. 2. The phase transition from crystal to liquid crystal (T_c) determined by means of differential scanning calorimetry was located at 45°C . These results confirmed that the system of ARS/PBA/DBBTAB formed covesicles [24].

A typical fluorescence spectrum is shown in Fig. 3 when a PBA buffer solution was dropwise added into an aqueous DBBTAB-ARS vesicular solution. It is obvious that the fluorescent intensities of ARS bound on the surfaces of DBBTAB vesicles centred at 560 nm increase dramatically with increasing the concentration of PBA from 0 M to 5.2×10^{-4} M, suggesting that the boronic acid formed a boronate ester with ARS [22].

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