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Construction and application of a facile chemosensor for monosaccharides detection in blood and urine

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ABSTRACT

A highly sensitive ensemble for monosaccharides was constructed by an anionic dye (HPTS) and a cationic quencher/receptor (*S*-BINOLPB). In the ensemble, HPTS is a signal reporting group and its fluorescence is modulated by electron transfer from HPTS to *S*-BINOLPB. The cationic pyridine salt *S*-BINOLPB acts as both a quencher and a receptor. Compared with previously reported BBVs/HPTS ensembles, the sensitivity of the ensemble for monosaccharides is higher about 10-fold. The high sensitivity depends on the matched space of hydroxyl groups (monosaccharides) and boron acid groups (*S*-BINOLPB), and then efficient charge transfer from B^- to N^+ on the same ring when *S*-BINOLPB bonded with monosaccharides. Noticeably, the probe may be applied to detect saccharides in blood and urine samples. The type ensemble will be a potential application in diabetes detection and biomedicine fields.

1. Introduction

Fluorescence spectroscopy is nowadays indispensable tool in various fields of modern science and medicine, including clinical diagnostics, biotechnology, molecular biology materials science and environmental chemistry. Chemosensor based on fluorescence technology has many advantages such as high sensitivity, real-time analysis, remote detection capabilities and multiple sensing modes [1–5]. Many researches indicate that well-designed probes are crucial of obtaining high sensitivity and selectivity to analytes [6–8]. Saccharides not only play important roles in biological systems but also lead to some diseases such as renal glycosuria, cystic fibrosis, diabetes and cancers because of the breakdown of their transport in human body [9–12]. However, due to many saccharides with only one kind of functional group (hydroxyl) and many variable configurations in aqueous solution, it is rather difficult to obtain highly sensitive and selective recognition receptor for saccharide [13,14]. Therefore, designed and synthesized novel fluorescence compounds with high sensitivity and practicality for sensing saccharides is desired for biological, material and chemical scientists.

To date, besides many reported and applied one-component probe for monosaccharides, another promising probe is two-component ensemble which was proposed by Singaram and his coworkers [15–23]. A typical two-component probe is comprised by a water-soluble anionic fluorescent dye and a boronic acid functionalized benzyl viologen (BBV, Scheme 1). In the probe, the anionic fluorescence dye is an optic signal reporter section and its fluorescence is modulated by electron transfer from dye to BBV. Cationic viologen BBV is both a quencher and a receptor. It is reasonably believed that the two-component approach to molecular recognition can provide considerable flexibility in choosing the quencher/receptor and luminophor components depending on the particular requirements of the sensing application. Based on the fundamental sensing principle, our group also developed many ensembles for sensing saccharides [24–29]. However, it is a pity that despite the progress has been made great efforts, the current two-component probes based on viologen quenchers display lower sensitivity for monosaccharides sensing. Especially, the detection of monosaccharide for the lower concentrations is restricted, and which will limit the practical application of the probe.

As part of our efforts aimed at the challenging problem of highly sensitive and practical probe for saccharides, we think that a feasible way to realize the goal is depended on providing the matched bonding-space to improve efficient charge transfer of the receptor and saccharides. Therefore, it is fatal for designing and synthesizing suitable compounds and constructing facile ensembles. Here, based on the strategy, we developed a facile quencher/receptor

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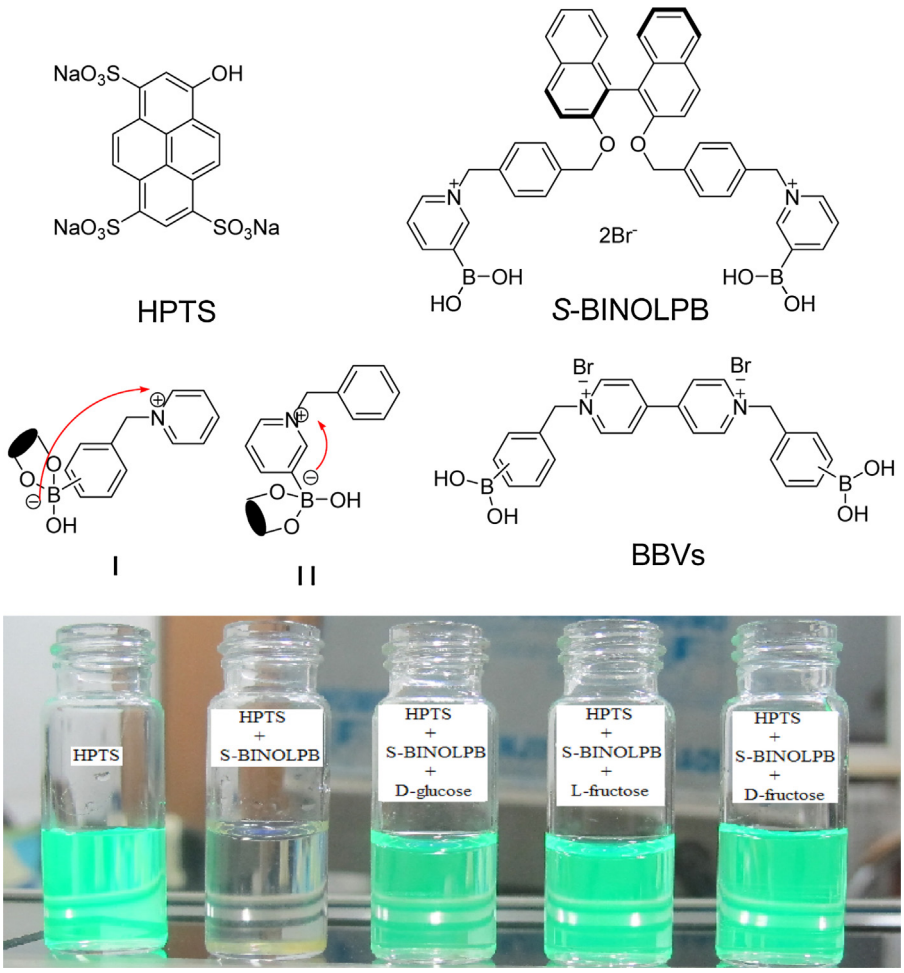

Scheme 1. The structures of HPTS, BBVs, *S*-BINOLPB and the binding ways of the two class quenchers with monosaccharides, according, the color changes of HPTS fluorescent dye (4.0×10^{-6} M) solution by introduction of *S*-BINOLPB quencher (1.6×10^{-5} M) followed by 5.0 mM of monosaccharides in pH 7.4 phosphate buffer solution, respectively. The solutions were irradiated by λ_{365} nm UV–vis light and daylight lamp.

with boronic acid directly bonding to pyridine ring as a receptor (*S*-BINOLPB). The developed probe (Scheme 1) is comprised of an anionic fluorescence dye, 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS), and a cationic boronic acid directly substituted pyridine salt quencher/receptor (*S*-BINOLPB). Similarly, the HPTS is a signal reporting group and its fluorescence is modulated by electron transfer from HPTS to the quencher. The cationic pyridine salt is both a quencher and a receptor in the probe. Compared with BBVs quencher/receptors, the prominent benefit of *S*-BINOLPB quencher lies in more stable intra-complex to efficient change transfer of *S*-BINOLPB with monosaccharides than of BBVs with saccharides. High sensitivity of the probe for monosaccharides is crucial for practical applications. Due to shorter distance and efficient charge transfer of N^+ and B^- in the same conjugated ring (Scheme 1), the intramolecular complex of *S*-BINOLPB and monosaccharide is rather stable, which will a large extent even completely destroy the electrostatic action between HPTS and *S*-BINOLPB. Obviously, the ensemble probe is worth looking forward to sensing monosaccharides with high sensitivity and detecting the saccharides in blood and urine of diabetes.

2. Experimental

2.1. Materials and instruments

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. Solvents used were purified and dried by standard methods prior to use. 8-Hydroxy-pyrene-1,3,6-trisulfonic acid trisodium salt (HPTS), bis-(pinacolato)diboron, (*S*)-2,2′-dihydroxy-l,l′-dinaphthyl were purchased from Aldrich (Steinheim, Germany). 1,4-Bis(bromomethyl)benzene and 3-boronic acid-pyridine were obtained form Creasyn Finechem (Tianjin, China). D-monosaccharides were provided from Alfa Aesar (Tianjin, China). The blood and urine samples of diabetic persons came from the affiliated hospital of Shanxi Medical University. pH Measurements were carried out on a Mettler Toledo MP 220 pH meter, ^{11}B NMR spectra were recorded on a Bruker at 80 MHz and are reported in ppm with respect to $BF_3{\cdot}OEt_2$ ($\delta = 0$). ^{1}H NMR and ^{13}C NMR were measured on a Bruker ARX400 spectrometer with chemical shifts reported as ppm (TMS as an internal standard). Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). High-resolution mass spectra (HRMS) were acquired on an Agilent 6510 Q-TOF LC/MS instrument (Agilent Technologies, Palo Alto, CA) equipped with an electrospray ionization (ESI) source.

2.2. Fluorescence measurements for quenching and sensing studies

All experiments of water were redistilled water. All of the working solutions were buffered at pH 7.4 ± 0.1 using a phosphate (the mixture system of Na_2HPO_4 (0.2 M, 61.0 mL) and NaH_2PO_4 (0.2 M,