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A facile channel for D-glucose detection in aqueous solution

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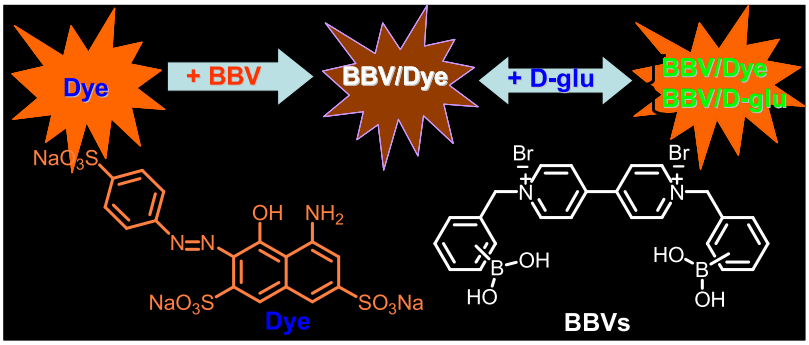
HIGHLIGHTS

- Three new ensembles for D-glucose detection are constructed.
- These sensing ensembles are comprised of dye NAHBDS and quenchers BBVs.
- Fluorescence reversible signals for D-glucose sensing are observed.
- These ensembles show highly sensitive for D-glucose detection.
- This research can provide a new strategy for molecular recognition.

GRAPHICAL ABSTRACT



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ABSTRACT

Three facile ensembles for sensing D-glucose are designed and constructed. The ensembles are comprised of fluorescent dye (NAHBDS) and boronic acid substituted viologens (BBVs) quenchers/receptors. The sensing processes of three ensembles (NAHBDS/*o*-BBV, NAHBDS/*m*-BBV and NAHBDS/*p*-BBV) to D-glucose were determined by fluorescence spectra at pH 7.4 buffer solution. The results show that NAHBDS/*o*-BBV and NAHBDS/*m*-BBV ensembles embody higher sensitivity for D-glucose with reversible "on–off" fluorescence response. More importantly, the recovery of relative intensity has good linear relation to low concentration of D-glucose. The action between the ensemble with D-glucose is dynamically reversible equilibrium process. The research results provide a new mode to design highly selective probe.

Introduction

D-glucose and its derivatives play important roles in biological systems. However, due to the breakdown of D-glucose transport in human body, many diseases have been initiated such as diabetes, renal glycosuria, cystic fibrosis and cancers in the past few decades [1–4]. To date, enzyme-based method for determining D-glucose is firstly and mainly used in diagnostic analysis, process control of food industries and so on because it has high selectivity for D-glucose among the mixture of isomers and even in the biological fluids such as blood and urine [5,6]. As the dilemma of enzyme-based method, obtaining the standard quality enzymes and maintaining the catalytic activity of enzymes are rather difficult for enzyme sensors. Owing to the fluorescence-based method with high sensitivity, real-time analysis, remote detection capabilities and multiple sensing modes detection, developing novel fluorescent receptor to sensing D-glucose is promising for replacing enzyme-based method [7–11]. However, it is well known that D-glucose only has one kind functional group (hydroxyl) and exists many configurations in water solution. Therefore, the detection of D-glucose with high sensitivity is different by fluorescent probe,

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especially, for low concentration detection of D-glucose [12,13]. Well-designed and synthesized facile receptors or ensembles are crucial for highly sensitive sensing D-glucose [14].

Besides many reported one-component fluorescent probes for D-glucose, two-component probe is another promising sensing ensemble for D-glucose, which is proposed and developed by Singaram and co-workers [15–23]. In the probe, anionic fluorescent dye is an optic signal reported section and its fluorescence is modulated by electron transfer from dye to BBVs. Cationic viologen BBV acts as quenchers and receptors. It is reasonably believed that the two-component approach to molecular sensing can provide considerable flexibility in choosing the quencher/receptor and luminophor components depending on the particular requirements of the sensing application. Three boronic acid substituted viologens BBVs (*o*-BBV, *m*-BBV and *p*-BBV) are firstly used in sensing monosaccharide ensembles as quenchers/receptors [15,16]. In order to expand and obtain high sensitivity and selectivity ensembles for monosaccharides, our group [24–29] also developed some two-component ensembles for monosaccharide by using polyelectrolyte or fluorescent quantum dots as optic signal reported section, and polymer BBV, different boric acid substituted BBVs, different charge BBVs as quenchers/receptors. Despite the progress has been made great efforts, the sensing ensembles based on BBVs quenchers/receptors with high sensitivity for low concentration D-glucose (<10.0 mM) is poor. In the paper, our aim is to realize highly sensitive detection for D-glucose in water solution based on BBVs quenchers/receptors. The design idea lies in employing simple ensemble and easy preparation method to obtain highly efficient probes. Azo dye, 2,7-naphthalenedisulfonic acid-5-amino-4-hydroxy-3-[p-sodium benzenesulfonate)-diazenyl]-sodium salt (NAHBDS), is long wavelength emission fluorescence material, which can avoid the interference of D-glucose and other species in blood samples. In the ensembles, cationic viologen BBVs are both quenchers and receptors. Anionic fluorescent dye NAHBDS is an optic signal reported section. The efficient interactions of NAHBDS and BBVs through forming neutral hole-complex can give an appropriate microenvironment and provide multidimensional reactive groups to catch D-glucose molecule.

Experimental

Materials and instruments

Solvents used were purified and dried by standard methods prior to use. Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. 4-Aminobenzenesulfonic acid and 5-amino-4-hydroxy-7-sulfonaphthalene-2-sulfonate were purchased from Aohe Finechem (Beijing, China). *o*-(Bromomethyl)-phenylboronic acid, *m*-(bromomethyl)-phenylboronic acid, *p*-(bromomethyl)-phenylboronic acid and 4,4′-dipyridyl were obtained by from Aldrich (Steinheim, Germany). ^{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). 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 were reported in ppm with respect to $BF_3{\cdot}OEt_2$ ($\delta = 0$). 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.

Solution preparation and fluorescence measurements

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 ensemble of Na_2HPO_4 (0.2 M, 61.0 mL) and NaH_2PO_4 (0.2 M, 39.0 mL)) buffer solution. The stock solution (5.0×10^{-3} M) of NAHBDS was diluted in 100 mL volumetric flask with pH 7.4 buffer solution to afford the working solution (5.0×10^{-5} M). The stock solutions of BBVs all were 0.04 M. The stock solutions of monosaccharides all were 1.0 M in 10 mL measuring flask. The standard stock solutions of lower concentration were prepared by suitable dilution of the stock solutions with pH 7.4 buffer solution. All spectra detections were carried out at pH = 7.4 buffer solution and the working solutions were placed in a quartz cuvette with 1 cm path. The total volume of working solution was 2 mL. The added volume of all titration experiments did not exceed 3% of the total. Fluorescence spectra were monitored with a Perkin–Elmer LS50B luminescence spectrometer, the excitation and emission slit widths were 15 nm and 20 nm respectively. The Uv–vis absorption spectra were recorded on a Varian Cary 300 absorption spectrometer. All of the experiments were performed at room temperature.

Synthesis of NAHBDS, o-BBV, m-BBV and p-BBV

NAHBDS and BBVs were synthesized according to previously reported methods [29,19]. The structures were showed in Fig. 1. The detailed synthetic procedures can be seen supplementary data.

Results and discussion

The formation of preliminary quenching ensembles

Based on the sensing way to D-glucose, the quenching efficiency of BBVs to NAHBDS dye is crucial for obtaining highly selective D-glucose detection. Firstly, the Uv–vis and fluorescent emission spectra of dye NAHBDS were determined in pH 7.4 buffer solutions (Fig. 2). It can be seen from Fig. 2, the maximum wavelengths of Uv–vis and fluorescent emission spectra of NAHBDS are 526 nm and 590 nm, respectively. The longer wavelength of NAHBDS (590 nm) is desired for D-glucose detection because it can avoid the interference of D-glucose itself absorption in 400–500 nm. Next, the interactions of NAHBDS and BBVs were observed by titration experiments in pH 7.4 buffer solution (Figs. 3, S1 and S2). The results indicate that the fluorescence of NAHBDS all is quenched by three BBVs quenchers and form stable ground-state complexes. The fluorescent intensities of NAHBDS are reduced and new long wavelength emission peaks can be observed in Figs. 4 and S3. The quenching order of three BBVs to NAHBDS is *m*-BBV > *o*-BBV > *p*-BBV at different pH buffer solutions. The quenching actions of NAHBDS and BBVs in pH 7.4 buffer solution are stronger than that in pH 2.6 and 10.0. The results may come from the lower efficiency of charge transfer from dye to quencher in pH 2.6 and 10.0 than that of pH 7.4. The charge transfer of the ensembles may be restrained by relative excess ions (H^+ or OH^-) in pH 2.6 and 10.0.

The sensing processes of three sensing ensembles to D-glucose

The sensing processes of the sensing ensembles to D-glucose were investigated by fluorescent spectra in pH 7.4 buffer solutions (Figs. 4 and S3). Upon introducing D-glucose to the NAHBDS/*m*-BBV sensing ensemble (fluorescent "on–off" state), an apparent recovery of the NAHBDS fluorescence (590 nm) is observed by forming negatively charged borate ester between *m*-BBV and D-glucose. The recovery extent of NAHBDS fluorescence is dependent on the D-glucose concentration. The 7.5-fold recovery of NAHBDS/*m*-BBV fluorescent intensity "off-state" is observed only in the present of 10.0 mM D-glucose (Fig. 5). Compared with previously reported D-glucose sensing probes, the ensemble has higher sensitivity for D-glucose. It is worth notice that the relative fluorescent intensities

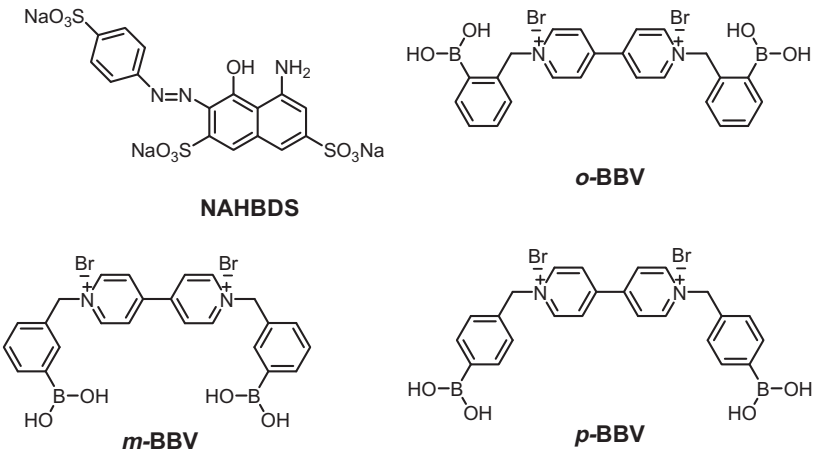

Fig. 1. The structures of NAHBDS, *o*-BBV, *m*-BBV and *p*-BBV.

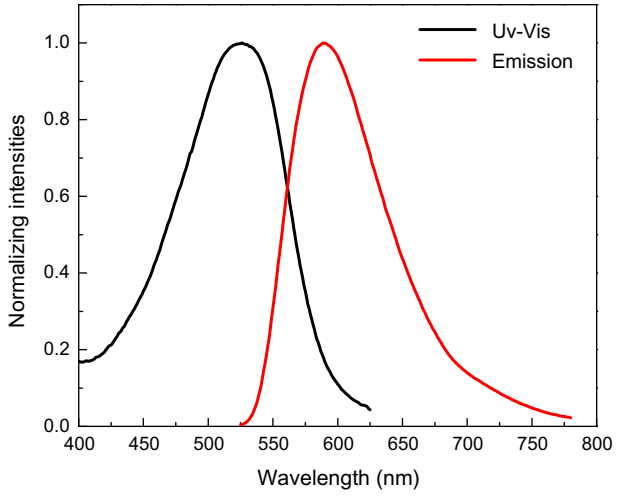

Fig. 2. Uv–vis and fluorescence emission spectra of NAHBDS (5.0×10^{-5} M) in pH 7.4 buffer solutions.

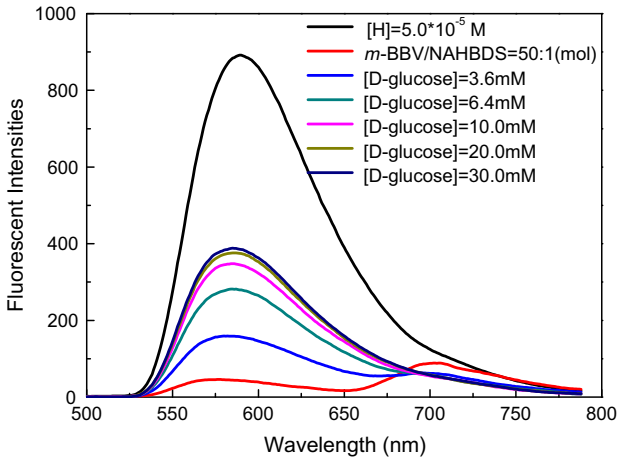

Fig. 4. Characteristic fluorescence responses upon introduction quencher *m*-BBV (2.5×10^{-3} M) followed by D-glucose to NAHBDS (5.0×10^{-5} M) at pH 7.4 buffer solution.

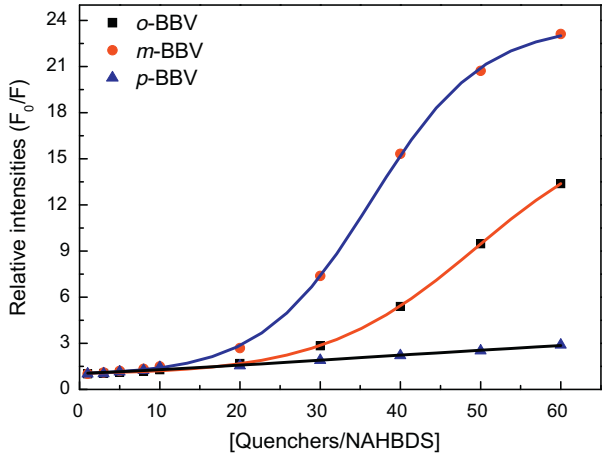

Fig. 3. Sigmoidal fit curves for Relative fluorescent intensities of NAHBDS (5.0×10^{-5} M) with increasing of *o*-BBV, *m*-BBV and *p*-BBV concentrations at pH 7.4 buffer solutions.

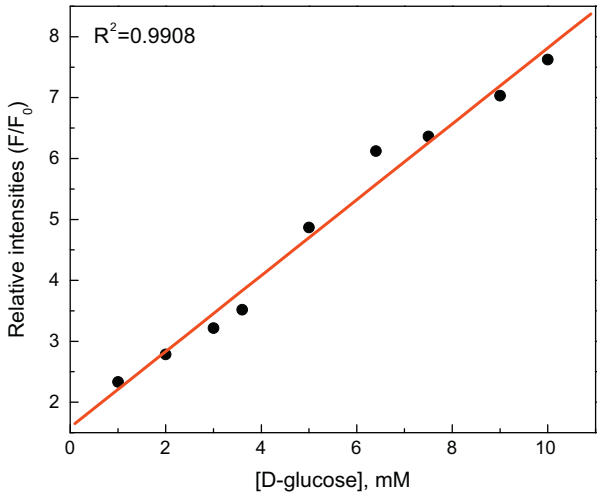

Fig. 5. Linear fit line of relative fluorescent intensities to low D-glucose concentrations in *m*-BBV (2.5×10^{-3} M) and NAHBDS (5.0×10^{-5} M) at pH 7.4 buffer solution.

to the concentrations of D-glucose (<10.0 mM) have a good linear relation and the linearly dependent coefficient (R^2) is 0.9908 (Fig. 5). The result provides a facile method to detect D-glucose for practical samples of the biochemical and biological research. Similarly, the reversible "on–off" fluorescence response to

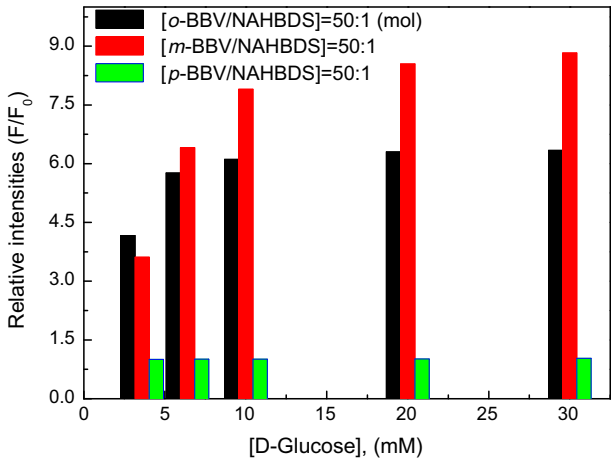

Fig. 6. Bar graph of relative fluorescence intensities of three BBVs/NAHBDS ensembles to D-glucose at pH 7.4 buffer solution, the concentration of NAHBDS is 5.0×10^{-5} M.

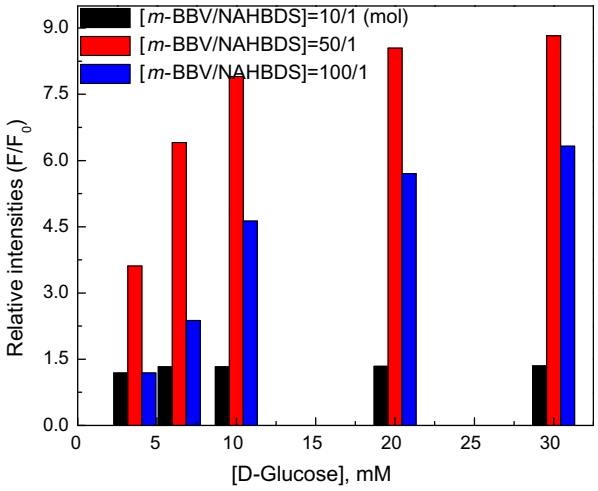

Fig. 7. Bar graph of relative fluorescence intensities of *m*-BBV/NAHBDS different ratios ensemble to D-glucose at pH 7.4 buffer solution, the concentration of NAHBDS is 5.0×10^{-5} M.

D-glucose can also be observed for NAHBDS/*o*-BBV (Fig. S3). As expected, introducing D-glucose to the *p*-BBV/NAHBDS ensemble, the ensemble took place a little fluorescence recovery. It may be due to the weaker quenching action and unsuitable binding space of *p*-BBV/NAHBDS ensemble for D-glucose. The order of sensitivity of three ensembles to D-glucose is *m*-BBV/NAHBDS > *o*-BBV/NAHBDS > *p*-BBV/NAHBDS (Fig. 6). In addition, the sensing ensembles are easy to reach saturation states for D-glucose. The fluorescent recoveries of NAHBDS have only a little change upon 20.0 mM D-glucose (Fig. S4).

The choice of appropriate quencher and reported group ratios

For the two-component ensembles, another considerable benefit is the ability of varying the quantities of quencher and reporting group to optimize the magnitude of the sensing response. So, a series of tests for D-glucose responses at different ensembles were carried out (Figs. 7, S5 and S6). From the bonding bar graphs, the best sensing ensembles of the three probes to D-glucose were obtained as follows: NAHBDS (5.0×10^{-5} mol/L) with *o*-BBV (2.5×10^{-3} mol/L), *m*-BBV (2.5×10^{-3} mol/L) and *p*-BBV (5.0×10^{-4} mol/L),

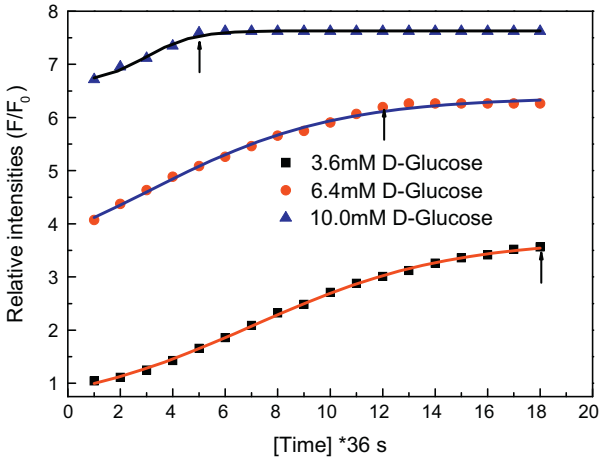

Fig. 8. Sigmoidal fit curves for relative fluorescent intensities of *m*-BBV/NAHBDS in different D-glucose concentrations with the change of action time at pH 7.4 buffer solutions. The concentration of NAHBDS is 5.0×10^{-5} M and the concentration of *m*-BBV is 2.5×10^{-3} M.

respectively. The considerable recoveries of the initial fluorescence intensities are observed upon introduction of D-glucose at the best sensing ensembles of the three probes.

The dynamic reversible equilibriums of the ensembles with D-glucose

It is well known that the bonding way of boric acid group with glucose is to form reversible borate and it is a dynamic reversible equilibrium. In the work, the dynamic reversible bonding ways of *m*-BBV/NAHBDS and *o*-BBV/NAHBDS ensembles with D-glucose were observed by fluorescent spectra (Figs. 8 and S7). The relative fluorescent intensities of the ensembles will increase with the interaction time on certain D-glucose concentrations. The balance time is shortened with the increase of D-glucose concentrations. Based on the research results, dynamic reversible time is easy to be obtained, which is important and useful for diabetes sample detection in practical application.

Conclusion

In summary, we successfully developed highly selective D-glucose ensembles that contain long wavelength emission dye and BBVs quencher/receptors. Among three BBVs/NAHBDS sensing ensembles, NAHBDS/*m*-BBV and NAHBDS/*o*-BBV sensing ensembles display high sensitivity for D-glucose in pH 7.4 buffer solution. It should be noted that the present sensing ensembles for D-glucose has the following advantages: (1) the detection can be carried out in aqueous solution; (2) they have higher sensitivity for low concentration D-glucose (<10.0 mM); (3) the components of the ensembles are easily synthesized. Further studies of the sensing ensembles for detecting D-glucose in practical samples are currently underway.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.05.089.

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