

A highly sensitive water-soluble system to sense glucose in aqueous solution†

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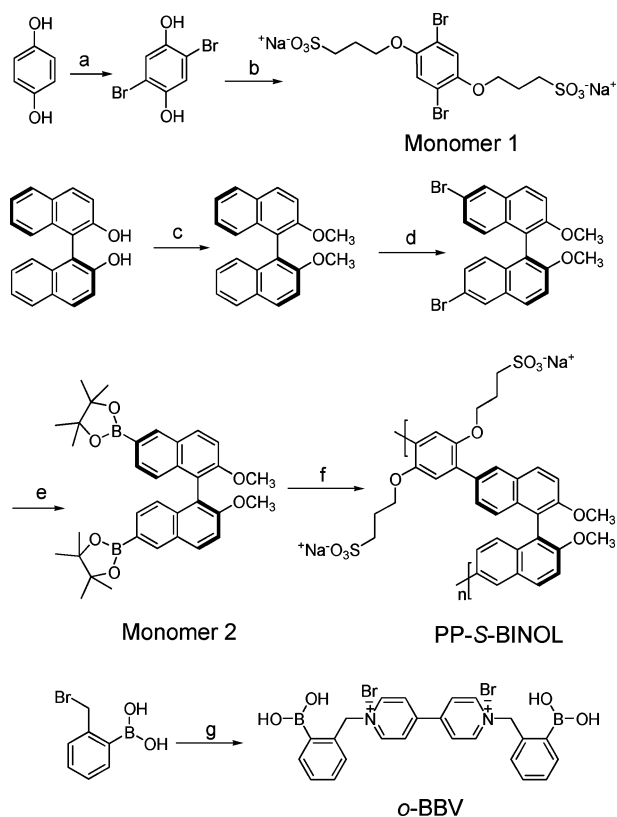
A glucose sensing switch is formed by water soluble conjugated polymer (PP-S-BINOL) and boronic acid-functionalized benzyl viologen (*o*-BBV). The two-component system shows a high sensitivity for glucose sensing with a 17-fold increase in the fluorescence intensity in the presence of 100 mM glucose.

Introduction

Molecular sensing of biological analytes with a metabolic function in living organisms has attracted extensive attention and well-designed recognition systems are crucial for high sensitivities.¹ Much research has indicated that renal glycosuria, cystic fibrosis, diabetes and some cancers are correlated with the breakdown of glucose transport in the human body.² However, due to glucose having only one kind of functional group (hydroxyl), producing a higher sensitivity of sensing systems for glucose is rather different than that for ions. 1,1'-bi-2-naphthol (BINOL) and its derivatives have been extensively used in asymmetric synthesis and molecular recognition because of their stable chiral configuration and excellent luminosity.³ However, it is a pity that previous studies into BINOL derivatives mainly focused on their asymmetric properties. Their photoelectric properties have been seriously overlooked. Despite the large and diverse number of sensing systems for glucose,⁴ no method for glucose detection utilizing a water soluble conjugated BINOL polymer has been reported.⁵ BINOL derivatives, which are currently applied in molecular recognition, are mainly monomeric receptors and their measurement media is limited to organic or organic/water mixed solvents.⁶ Given the extended π -electronic structures and high electron densities of conjugated polymers,⁷ the development of a high sensitivity system for glucose sensing based on the water soluble polymer BINOL is desirable for chemists, biologists and medical scientists.⁸

Fortunately, boronic acid-functionalized benzyl viologens for monosaccharide sensing have been reported by Singaram and coworkers⁹ which provides us with the fundamental principles and showed the feasibility for glucose recognition. Consequently, we now introduce a new way for BINOL derivatives to sense glucose. This glucose sensing system is comprised of a water-soluble anionic polymer (PP-S-BINOL) and boronic acid-functionalized

benzyl viologen (*o*-BBV) (Scheme 1). The anionic conjugated polymer PP-S-BINOL is the reporting group and its fluorescence is modulated by electron transfer from PP-S-BINOL to *o*-BBV. The cationic viologen *o*-BBV is both the quencher and the receptor in the system. Due to the flexibility and the special spatial



Scheme 1 The synthesis routes of PP-S-BINOL and *o*-BBV. a) CH_3COOH , Br_2 , room temperature 24 h, 45.8%; b) 1,3-propanesultone, NaOH , dioxane/ H_2O , N_2 , room temperature 12 h, then 80–100 °C 3 h, 68.4%; c) CH_3I , K_2CO_3 , acetone, reflux 36 h, N_2 , 89.2%; d) Br_2 , CH_2Cl_2 , 0 °C, 5 h, 92.3%; e) bis(pinacolato)diboron, $\text{Pd}(\text{dppf})\text{Cl}_2$, KOAc , DMSO , 80 °C 6 h, N_2 , 51.4%; f) $\text{Pd}(\text{PPh}_3)_4$, 1,4-dibromo-2,5-bis(3-sulfonatopropoxy)benzene, Na_2CO_3 , $\text{DMF}/\text{H}_2\text{O}$, 80 °C 48 h, N_2 , 51.6%; g) 4,4'-bipyridine, DMF , 80 °C 48 h, 78.3%.

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structure of the polymer chain, the efficient interaction between PP-S-BINOL and *o*-BBV through the formation of a neutral hole-complex can give an appropriate microenvironment and provide multidimensional reactive groups to catch a glucose molecule. The reversible formation of boronate by *o*-BBV and glucose through electrostatic interactions will weaken the interaction between *o*-BBV and PP-S-BINOL and result in the fluorescence recovery of PP-S-BINOL. The results display that the two-component system showed a high sensitivity for glucose sensing with a 17-fold increase in fluorescence intensity in the presence of 100 mM glucose. Even at a practical clinical range of glucose concentrations (2.5–20.0 mM), there was still high sensitivity and a good superlinear relationship for glucose detection.

Results and discussion

The polymer PP-S-BINOL was synthesized in six steps from the commercially available *p*-hydroquinone and (*S*)-2,2'-di-methoxy-1,1'-dinaphthyl (*S*-BINOL).¹⁰ A water soluble monomer **1**, 1,4-dibromo-2,5-bis(3-sulfonatopropoxy)benzene, was obtained by bromination of *p*-hydroquinone and then treatment with 1,3-propanesultone in a strongly alkali solution. Monomer **2**, (*S*)-2,2'-dimethoxy-6,6'-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-1,1'-naphthalene, was prepared through etherification, bromination and then boric acid esterification under Pd(dppf)Cl₂ catalysis. Then monomer **1** and monomer **2** reacted through a Suzuki coupling gave polymer PP-S-BINOL with a 51.6% yield. *N,N'*-4,4'-bis(benzyl-2-boronic acid)bi-pyridinium dibromide (*o*-BBV) was synthesized by quaternization of commercially available 2-(bromomethyl)-phenylboronic acid and 4,4'-dipyridyl with a 78.3% yield.¹¹

Firstly, the characteristics of fluorescence quenching for the binding of *o*-BBV to polymer PP-S-BINOL were investigated in an aqueous solution at pH 7.4. (Fig. 1) As expected, a reduction of about 130-fold in the PP-S-BINOL fluorescence intensity was observed in the presence of only 20 times *o*-BBV (8.0×10^{-5} M) at physiological pH (pH 7.4). By comparison, the quenching efficiency of the PP-S-BINOL/*o*-BBV system gave a 50-fold reduction in the fluorescence intensity compared to the previously

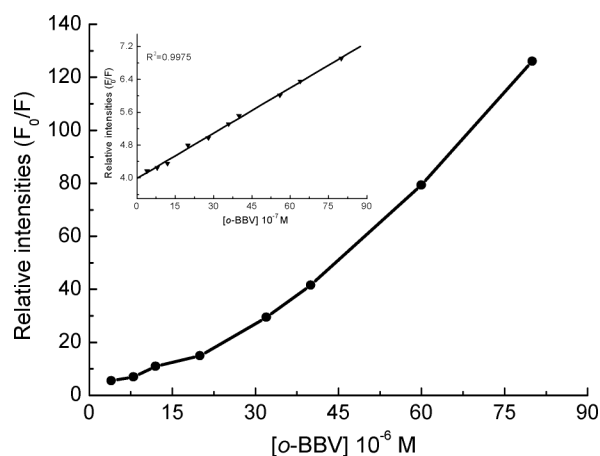


Fig. 1 The relative fluorescence quenching intensities (F_0/F) of PP-S-BINOL (4.0×10^{-6} M) with *o*-BBV viologen quencher in different pH phosphate buffer solutions. The molarity of PP-S-BINOL was calculated according to the minimum structural unit of the polymer.

reported two-component glucose sensing system (*o*-BBV and monomeric 8-hydroxyprone-1,3,6-tri-sulfonic acid trisodium salt (HPTS)). At lower quencher concentrations, the Stern–Volmer plot was linear and the linearly dependent coefficient (R^2) was 0.9975. At higher quencher concentrations, the Stern–Volmer plot curved upwards, which indicated a large sphere of static quenching had been produced by the electrostatic interaction between the polymer and the quencher. The effectiveness of the static quenching through forming a complex between polymer and quencher was very helpful for development of a highly sensitive glucose sensor.

The sensitivity of the glucose sensing ensemble composed of PP-S-BINOL and *o*-BBV was determined by fluorescence spectroscopy in phosphate buffer (pH 7.4) at ambient temperature (Fig. 2). Obviously, a ground-state complex between the anionic polymer PP-S-BINOL and the cationic *o*-BBV was formed by electron transfer from PP-S-BINOL to *o*-BBV, resulting in a great reduction of PP-S-BINOL fluorescence intensity. Upon the introduction of glucose to the ground-state complex, an apparent recovery of the fluorescence was observed by the formation of a negatively charged borate ester between *o*-BBV and glucose. The fluorescence recovery of PP-S-BINOL was dependent on the glucose concentration. The 17-fold increase in the fluorescence intensity was observed when 100 mM glucose was added to the PP-S-BINOL/*o*-BBV (1/10) system. To the best of our knowledge, we estimated that the PP-S-BINOL/*o*-BBV glucose sensing system was more sensitive (with about a 10-fold increase in sensitivity) than the previously reported glucose sensor.¹¹ Moreover, the high sensitivity of the ensemble for glucose had also been confirmed by the large reduction in the quenching efficiency of *o*-BBV to PP-S-BINOL in the presence of 100 mM glucose (see Fig. S1†). Interestingly, the Stern–Volmer plot had good linearity and the linearly dependent coefficient (R^2) was 0.9944.

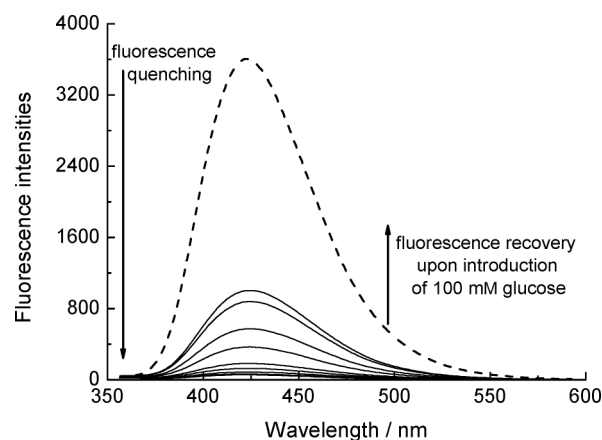


Fig. 2 The characteristic fluorescence response due to introduction of the quencher followed by glucose to the PP-S-BINOL solution (4.0×10^{-6} M) at pH 7.4. The *o*-BBV/PP-S-BINOL ratio for this data was 10/1 and the final glucose concentration was 100 mM. The dashed line indicates unquenched fluorescence, the bold line indicates the fluorescence after the introduction of the quencher *o*-BBV. The molarity of PP-S-BINOL was calculated according to the minimum structural unit of the polymer.

It is well known that boronic acids can form a covalent and reversible interaction with many 1,2-diols or saccharides in water. Fig. 3 shows the sigmoidal curves of PP-S-BINOL/*o*-BBV against

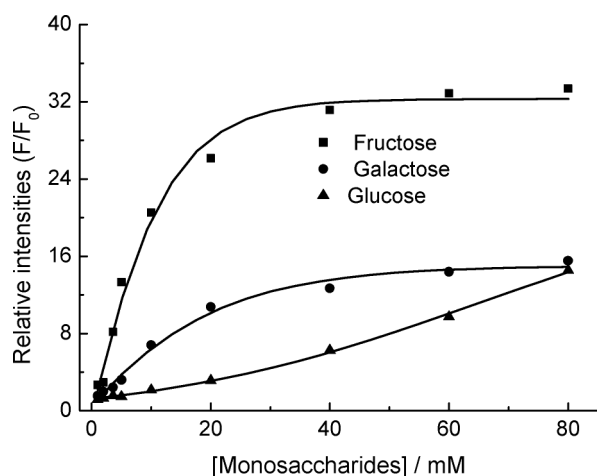


Fig. 3 The sigmoidal curves against monosaccharides for the PP-S-BINOL (4.0×10^{-6} M)/*o*-BBV (4.0×10^{-5} M) system, measured in pH 7.4 phosphate buffer solution.

three monosaccharides. The obvious response order was fructose > galactose > glucose. Remarkably, we found a desirable superlinear response of the PP-S-BINOL/*o*-BBV sensing ensemble for a practical clinical range of glucose concentrations at pH 7.4 (Fig. S2†). The results indicated that the two-component glucose sensing system of *o*-BBV/PP-S-BINOL ($Q/F = 10/1$) has a potential application in biochemical and biological research.

The ground-state complex formation (PP-S-BINOL/*o*-BBV) and the return to the uncomplexed (PP-S-BINOL) led to a colour change of the solution under 365 nm UV-vis light (Fig. S3†). The blue solution of PP-S-BINOL turned into a black solution upon the addition of *o*-BBV, revealing the ground-state complex formation (low fluorescence). When glucose was added to the black solution, the black solution changed to a dark blue solution, which demonstrated that the complex was less stable and had been largely dissociated with considerable recovery of the original PP-S-BINOL.

For a two-component glucose sensing system, it is crucial to choose an appropriate quencher/fluorochrome (Q/F) ratio, especially for the detection of low concentrations of glucose (<10.0 mM). So we carried out a series of tests for glucose response at quencher/fluorochrome ratios of 5/1, 10/1 and 20/1 (Fig. 4). From the binding lines, we observed a considerable degree of recovery of the initial fluorescence intensity due to the introduction of glucose at a 10/1 (Q/F) ratio. The Stern–Volmer plots of the glucose response were superlinear. The optimal result was clearly a Q/F of 10/1.

Conclusions

In summary, we firstly developed a water soluble BINOL polymer (PP-S-BINOL), which can be applied to sense glucose in a two-component system with boronic acid-functionalized benzyl viologen (*o*-BBV). This flexible sensing system for glucose is the most sensitive and promising compared to previously reported glucose sensors. The 17-fold increase in the fluorescence intensity to glucose response can be observed. Moreover, even at low concentrations of glucose, there was still a high sensitivity and a rare superlinear relationship for glucose. We believe that these

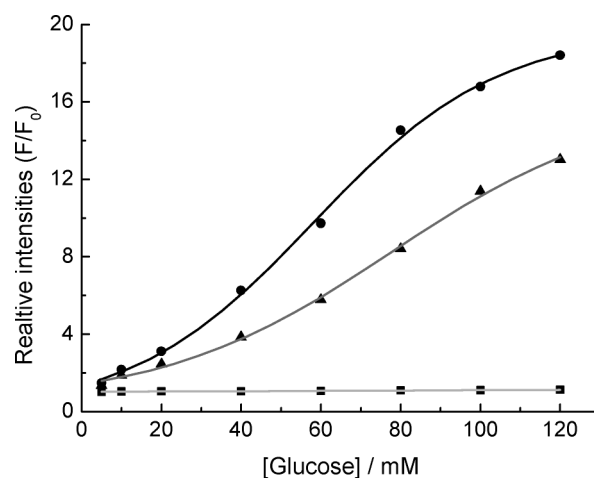


Fig. 4 The glucose response for the PP-S-BINOL (4.0×10^{-6} M)/*o*-BBV system in different mole ratios at pH 7.4. ■ $Q/F = 5/1$, ● $Q/F = 10/1$, ▲ $Q/F = 20/1$.

results will offer a new strategy for the development of BINOL derivatives and carbohydrate sensors. Further studies on the PP-S-BINOL/*o*-BBV sensing system are currently under way.

Experimental section

Materials and instruments

(*S*)-2,2'-dimethoxy-1,1'-dinaphthyl,^{10a} (*S*)-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthyl^{10a} and 2,5-dibromobenzene-1,4-diol,^{10b} were prepared by literature procedures. Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. The solvents used were purified and dried by standard methods prior to use. pH measurements were carried out on a Mettler Toledo MP 220 pH meter, ¹H NMR and ¹³C NMR were measured on a Bruker ARX400 spectrometer with chemical shifts reported in ppm (TMS as an internal standard). ¹¹B NMR spectra were recorded on a Bruker spectrometer at 80 MHz and are reported in ppm with respect to BF₃·OEt₂ ($\delta = 0$). The IR spectra were determined on a PE-1700 IR spectrophotometer by dispersing samples in KBr discs. 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.

Synthesis of PP-S-BINOL and *o*-BBV

1,4-dibromo-2,5-bis(3-sulfonatopropoxy)benzene (monomer 1). A solution of 6.35 g (20.0 mmol) 2,5-dibromobenzene-1,4-diol, 2.0 g (50.0 mmol) sodium hydroxide and 200 mL water in a Erlenmeyer flask was stirred under nitrogen. Then, a solution of 6.1 g (50.0 mmol) 1,3-propanesultone in 40 mL dioxane was added to the former solution at once. The resulting mixture was then stirred at room temperature overnight, during which time a thick pink slurry formed. The reaction mixture was then stirred at 80–100 °C for another 30 min and then cooled in a water/ice bath. The suspension obtained was vacuum filtered, and the retained solid was washed with cold water followed by acetone. The crude

products were purified by recrystallization twice from water to yield the product as a white powder (7.61 g, yield 68.4%). ^1H NMR (D_2O , 400 MHz) δ 7.16 (s, 1H), 4.03 (dd, $J = 6.0$, 6.0 Hz, 4H), 3.05 (dd, $J = 4.4$, 5.6 Hz, 4H), 2.21 (m, 4H); ^{13}C NMR (D_2O , 100 MHz) δ 24.24, 47.91, 68.97, 111.03, 119.19, 149.42; IR (KBr) cm^{-1} : 2965, 2922, 2871, 1614, 1479, 1444, 1417, 1392, 1353, 1262, 1144, 1051, 1032, 937, 835, 736, 634, 576; Elemental analysis for $\text{C}_{12}\text{H}_{14}\text{Br}_2\text{Na}_2\text{O}_8\text{S}_2$ ($M_w = 556.15$) calcd: C 25.92; H 2.54; Br 28.73; S 11.53, found: C 25.89; H 2.57; Br 28.69; S 11.58; HRMS-ESI for $\text{C}_{12}\text{H}_{14}\text{Br}_2\text{Na}_2\text{O}_8\text{S}_2$ (m/z) 533 [M-23].

(S)-2,2'-dimethoxy-6,6'-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-1,1'-naphthalene (monomer 2). A mixture with 9.44 g (20.0 mmol) (S)-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthyl, 11.18 g (44.0 mmol) bis-(pinacolato)diboron, 0.58 g (8 mol %) Pd(dppf)Cl₂ and 11.78 g (0.12 mol) potassium acetate in 60 mL DMSO was stirred at 80 °C for 6 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, poured into 200 mL ice water, filtrated and then purified by column chromatography on silica gel with ethyl acetate : petroleum ether (60–90 °C) (1 : 15) as the eluent to afford a white powder (5.82 g, 51.4%). ^1H NMR (CDCl_3 , 400 MHz) δ 8.42 (s, 2H), 8.05 (d, $J = 9.2$ Hz, 2H), 7.58 (d, $J = 8.8$ Hz, 2H), 7.45 (d, $J = 8.8$ Hz, 2H), 7.10 (d, $J = 8.8$ Hz, 2H), 3.76 (s, 6H), 1.38 (s, 24H); ^{13}C NMR (DMSO, 100 MHz) δ 24.89, 56.71, 83.70, 113.94, 119.31, 124.32, 128.60, 130.34, 130.85, 135.73, 136.52, 155.94; IR (KBr) cm^{-1} : 3002, 2973, 2849, 1654, 1529, 1496, 1424, 1392, 1381, 1208, 1164, 1051, 1043, 937, 846, 738, 673; Elemental analysis for $\text{C}_{34}\text{H}_{40}\text{B}_2\text{O}_6$ ($M_w = 566.30$) calcd: C 72.11, H 7.12, O 16.95, found: C 72.28, H 7.09, O 16.69; HRMS-ESI for $\text{C}_{34}\text{H}_{40}\text{B}_2\text{O}_6$ (m/z) 567 [M + 1], 566 [M], 565 [M - 1].

PP-S-BINOL. To a 100 mL three-neck flask, equipped with a mechanical stirrer, was added 3.336 g (6.0 mmol) 1,4-dibromo-2,5-bis(3-sulfonatopropoxy)benzene, 3.396 g (6.0 mmol) 2,2'-dimethoxy-6,6'-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-1,1'-naphthalene, 60 mL dried DMF and 0.224 g (0.18 mol) Pd(PPh₃)₄ under nitrogen. The mixture was stirred under nitrogen for 30 min, and then a 20 mL aqueous solution with 3.816 g (36.0 mmol) sodium carbonate was added using a dropping funnel. The reaction was heated at 80 °C for 48 h. The reaction turned black as Pd(0) particles were liberated. The tan-violet filtrate was collected, precipitated into 1 L of acetone, and redissolved in deionized water. The polymer was dialyzed using a membrane with a 3500 cut-off for 3 days. The final product, a dark yellow polymer, was obtained after drying *in vacuo* at 110 °C for 24 h, yielding 2.21 g (51.6%) after dialysis: ^1H NMR (*d*-DMSO, 400 MHz) δ 8.22 (s, 2H), 8.15 (d, $J = 7.6$ Hz, 2H), 7.64 (d, $J = 7.6$ Hz, 2H), 7.55 (d, $J = 7.6$ Hz, 2H), 7.16 (s, 2H), 7.04 (d, $J = 7.2$ Hz, 2H), 4.12 (broad, 4H), 3.77 (s, 6H), 2.58 (broad, 4H), 1.97 (broad, 4H); ^{13}C NMR (*d*-DMSO, 100 MHz) δ 25.82, 48.47, 56.74, 68.32, 114.82, 116.23, 118.64, 129.11, 129.87, 130.26, 132.80, 133.35, 150.24, 153.20, 155.25; IR (KBr) cm^{-1} : 3008, 2924, 2866, 1634, 1504, 1455, 1427, 1384, 1323, 1254, 1244, 1041, 1035, 945, 846, 724, 653; Elemental analysis for $\text{C}_{34}\text{H}_{30}\text{Na}_2\text{O}_{10}\text{S}_2$ (M_w monomeric unit: 708.72) calcd: C 57.62; H 4.27; S 9.04; Na 6.49, found: C 57.58; H 4.31; S 9.09; Na 6.55.

***N,N'*-4,4'-bis(benzyl-2-boronic acid)-bipyridinium dibromide (*o*-BBV).** To a solution of 1.74 g (8.1 mmol) 2-(bromomethyl)-

phenylboronic acid in 15 mL DMF was added with 0.5 g (3.2 mmol) 4,4'-dipyridyl, and the reaction mixture was stirred at 70 °C for 48 h under nitrogen. The orange precipitate was collected by filtration, washed with DMF, acetone, then diethyl ether and dried under a stream of nitrogen to yield *o*-BBV (1.47 g, 78.3% yield). ^1H NMR (CD_3OD , 400 MHz) δ 9.08 (d, $J = 6.0$, 4H), 8.69 (d, $J = 5.6$ Hz, 4H), 7.68–7.49 (m, 8H), 6.14 (s, 4H); ^{13}C NMR (CD_3OD , 100 MHz) δ 64.65, 122.21, 126.61, 129.17, 130.85, 131.52, 135.97, 145.59, 149.88, 150.39; IR (KBr) cm^{-1} : 3409, 3054, 2961, 2876, 1637, 1603, 1555, 1498, 1359, 1276, 1182, 1087, 934, 835, 722, 685; ^{11}B NMR (80 MHz, D_2O) δ 28.6; HRMS-ESI for $\text{C}_{24}\text{H}_{24}\text{B}_2\text{Br}_2\text{N}_2\text{O}_4$ (m/z) HRMS-ESI (m/z) 426 [M - 2Br].

Procedures of glucose sensing

All experiments requiring water used commercially available pure water. All of the working solutions were buffered at pH 7.4 \pm 0.1 using a phosphate buffer solution (a mixture system of Na₂HPO₄ (0.2 M, 61.0 mL) and NaH₂PO₄ (0.2 M, 39.0 mL) . The stock solution (4.0×10^{-3} M) of PP-S-BINOL was diluted in a 1.0 L measuring flask with pH 7.4 buffer solution to afford the working solution (4.0×10^{-6} M), the concentration was calculated by the minimum structural unit of the polymer. The stock solution (0.04 M) of *o*-BBV was prepared with 0.2343 g *o*-BBV in a 10 mL measuring flask. The stock solution (1.0 M) of glucose was prepared with 1.80 g glucose in a 10 mL measuring flask. The standard stock solutions of lower concentration were prepared by suitable dilution of the stock solution with pH 7.4 buffer solution. All spectral analysis studies were carried out using a pH = 7.4 buffer solution and the working solutions were placed in a quartz cuvette with a 1 cm path. The total volume of the working solutions was 2 mL. The studies into fluorescence quenching and sensing glucose used titration experiments and the volume added did not exceed 3% of the total. After the mixture solution was shaken for 30 s, the new spectra were measured. The fluorescence spectra were acquired with a Hitachi F-4500 fluorescence spectrophotometer and the excitation and emission slit widths were 5 nm and 10 nm respectively. The excitation wavelength was set to 320 nm according to experimental requirements. All of the experiments were performed at atmospheric pressure and room temperature.

Acknowledgements

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