Supporting Information

Fluorescent Graphene Quantum Dots with Boronic Acid Appended Bipyridinium Salts to Sense monosaccharide in Aqueous Solution

Ya-Hua Li, Li Zhang, Jing Huang, Ru-Ping Liang and Jian-Ding Qiu*

Department of Chemistry, Nanchang University, Nanchang 330031, China.

E-mail: jdqiu@ncu.edu.cn.

Experimental Section

Apparatus. The fluorescence and the absorption spectra were recorded with a Hitachi F-7000 fluorescence spectrophotometer (Tokyo, Japan) and a Shimadzu UV-2450 spectrophotometer (Tokyo, Japan), respectively. The morphology of GQDs was observed on a JEOL Ltd JEM-2010 transmission electron microscope (TEM) (Japan) and a Bruker MultiMode8 atomic force microscope (AFM) (Germany). The ^{1}H NMR of BBV was measured on a Bruker AVANCE III (600 MHz) spectrometer with chemical shifts reported in ppm (TMS as an internal standard). Infrared spectrum (IR) was taken on a Nicolet 5700 IR spectrophotometer (Nicolet). Zeta potential was measured on a PSA Nano 2590 zeta-potential analyzer (Malvern, UK). The FL lifetime measurements were performed on a Horiba Jobin Yvon FL-TCSPC fluorescence spectrophotometer (France). The GQDs was prepared using a Nanjing University Instrument Plant TOL1200 Tube Furnace (Nanjing, China). A Leici pHS-3C digital pH meter (Shanghai, China) was used to measure the pH values of the aqueous solutions.

Reagents. BBV and GQDs were prepared according to literature procedures.[1,2]

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. Graphite flake (99.8%, 325 mesh) was provided by Alfa (Tianjin, China), 2-(Bromomethyl)phenylboronic acid and 4,4'-Dipyridyl were purchased from J&K Scientific (Shanghai, China). Ultra-pure water (18.2 MΩ, Milli-Q Integral) was used throughout the experiment.

Preparation of N, N'-4, 4'-bis(benzyl-2-boronic acid)bi-pyridinium dibromide (BBV). To a solution of 0.87g (4.1 mmol) 2-bromomethylphenylboronic acid in 7.5 mL DMF was added with 0.25 g (1.6 mmol) 4,4'-bipyridyl, and the reaction was stirred at 70 °C for 48 h under nitrogen. After the mixture was cooled to room temperature, the yellow precipitate was collected by centrifugation, washed with DMF, acetone and then diethyl ether and dried under a stream of nitrogen to yield BBV.[1] The data of ^{1}H NMR (D_2O, 600 MHz) and Fourier transform infrared (FTIR) spectrograms are as follows, ^{1}H NMR: δ 9.01 (d, J = 7.2, 4H), 8.42 (d, J = 7.2 Hz, 4H), 7.75 (d, J = 6.6Hz 2H), 7.57 (t, J = 6.0 Hz, 2H), 7.52 (m, 4H), 6.04 (s, 4H) (Fig. S1); IR (KBr) cm^{-1}: 3402, 3019, 2937, 2852, 1639, 1597, 1504, 1450, 1324 (Fig. S2). These spectral data are in accordance with the literature and confirm the molecular structure of BBV.[1]

Synthesis of GO. GO was synthesized from graphitic powder according to Hummer's method. In brief, 0.5 g of graphite powder, 0.5 g of $NaNO_3$ and 23 mL of H_2SO_4 were added into a three-necked flask with stirring in an ice bath. Then, 3 g of $KMnO_4$ was slowly added to make sure the temperature below 20 °C. After mixed together, the flask was transferred to 35 ± 5 °C water bath for 1 h with stirring, forming a brown

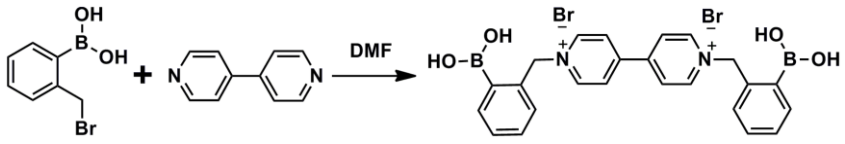
paste. Next, 40 mL of distilled water was added, and the solution was stirred for 30 min. Another 100 mL of distilled water was added. Last, dropwise addtion of 3 mL H_2O_2 (wt 30 %) changed the color of the solution to bright yellow. The warm GO solution was filtered and washed with distilled water until pH to 7. The precipitates were dried in a vacuum drying oven at 50 °C.

Preparation of fluorescent graphene quantum dots (GQDs). GQDs were prepared from graphene sheets (GSs) by a hydrothermal approach as literature procedure.[2] GSs were produced by thermal deoxidization of GO sheets in a tube furnace at 200 °C for 2 h with a heating rate of 5 °C·min^{-1} in a nitrogen atmosphere. 0.05 g of GSs was oxidized with concentrated H_2SO_4 and HNO_3 (volume ratio 1:3) for 17 h under mild ultrasonication. The mixture was diluted with 250 mL ultrapure water and then filtered through a 0.22-μm microporous membrane to remove the acids. The product was dried at ambient temperature over 5~6 hours. Purified oxidized GSs were re-dispersed in 20 mL ultrapure water and the pH was tuned to 8 with NaOH solution. The suspension was transferred to a poly(tetrafluoroethylene) (Teflon)-lined autoclave and heated at 200 °C for 11.5 h. After cooling to room temperature, the resulting black suspension was filtered through a 0.22-μm microporous membrane to remove the large tracts of GSs. The brown filtrate was dialyzed in a dialysis bag (retained molecular weight: 3500 Da) for 24 h and the GQDs showed strong blue fluorescence.

Detection Procedure. For the sensing of glucose, to a 1.5 mL centrifugal tube was sequentially added 20 μL of 0.5 mM GQDs solution, 10 μL of 20 mM BBV solution to obtain a quencher/GQDs ratio of 20:1, different amount of glucose solution, and

then diluted with 100 mM phosphate buffer solution (pH 7.4) to a final volume of 400 μL. After the solution was shaken for 60 s, the FL spectra of the resulting solution were recorded at the F-7000 spectrophotometer by fitting the excitation wavelengths at 310.0 nm, during which the slit widths were kept at 5.0 nm. The FL intensity was measured at 445.0 nm.

Ionic strength-dependent quenching studies. For the quenching experiments, to a 1.5 mL centrifugal tube was sequentially added 20 μL of 0.5 mM GQDs solution, various amounts of BBV and then diluted with phosphate buffer solution (pH 7.4) containing 0 or 0.5 M KCl to a final volume of 400 μL. After the solution was shaken for 60 s, the FL spectra of the resulting solution were recorded at the F-7000 spectrophotometer by fitting the excitation wavelengths at 310.0 nm, during which the slit widths were kept at 5.0 nm. The FL intensity was measured at 445.0 nm. We observed that the quenching efficiency decreased with increasing ionic concentration (Fig. S3). As ion concentration is increased, more cations adsorb to the negatively charged GQDs, gradually neutralizing the surface charge, hence, suppressing the electrostatic attraction between GQDs and BBV, and then reduced the quenching efficiency of GQDs.



Scheme S1 The synthetic scheme of BBV

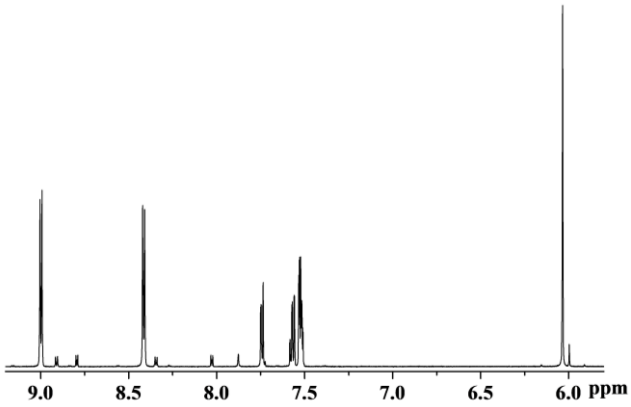


Fig. S1 ^{1}H NMR spectrum of BBV

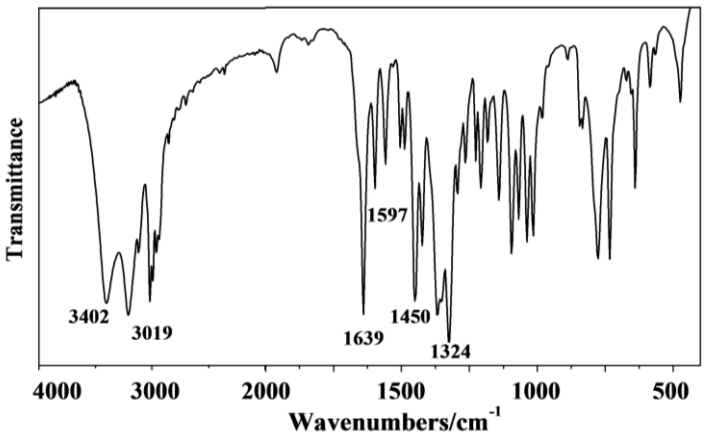


Fig. S2 FT-IR spectrum of BBV.

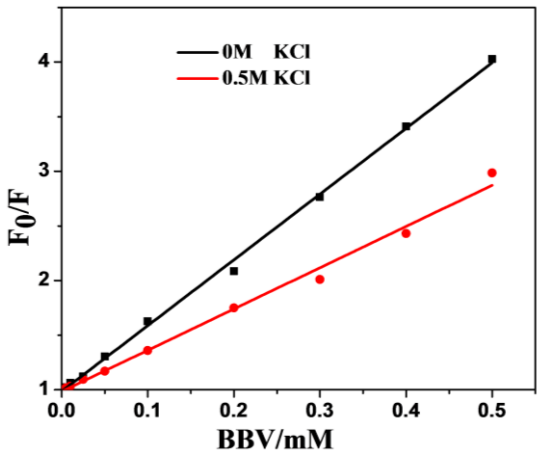


Fig. S3 The effect of ionic strength on the quenching degree of the GQDs caused by BBV.

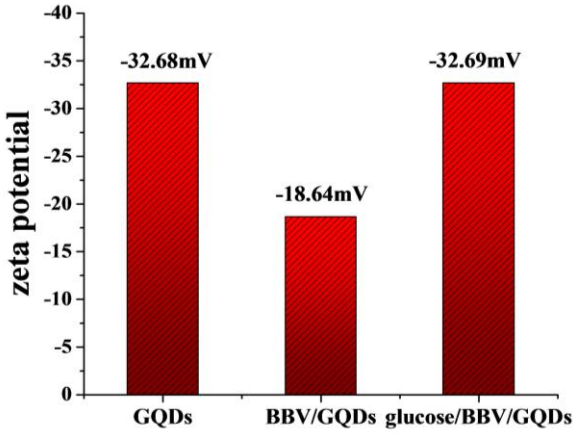


Fig. S4 Zeta potential histogram of GQDs, BBV/GQDs and glucose/BBV/GQDs determined by zeta-potential analyzer.

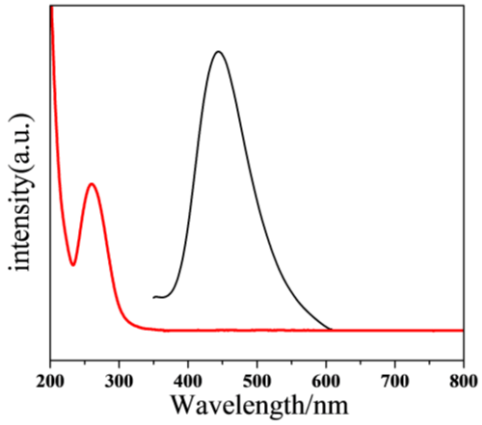


Fig. S5 The emission spectrum of the GQDs (λ_{em} = 310 nm) (black curve), and UV-vis spectrum of BBV (red curve).

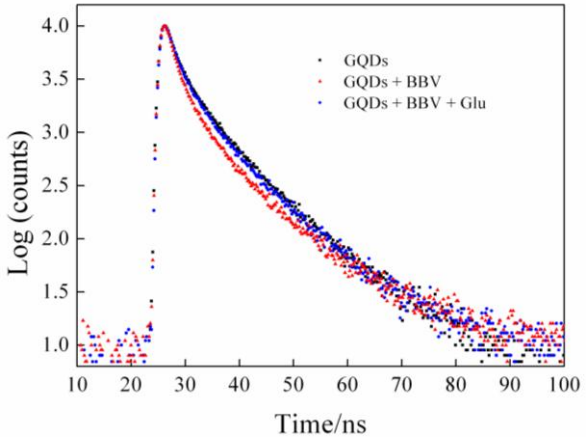


Fig. S6 Time-resolved fluorescence decay of the GQDs alone (black curve), GQDs+BBV (red curve), and GQDs+BBV+glucose (blue curve).

Table S1 Fluorescence lifetimes obtained with three-exponential fit of the fluorescence decay curves of the GQDs alone, GQDs-BBV, and GQDs-BBV-glucose, respectively

Sample	τ_1/ns(%)	τ_2/ns(%)	τ_3/ns(%)
GQDs	4.97(46.31)	1.11(28.98)	11.58(24.71)
GQDs+BBV	4.32(39.45)	1.05(39.64)	12.16(20.91)
GQDs+BBV+Glucose	4.27(41.54)	1.02(29.09)	10.56(29.37)

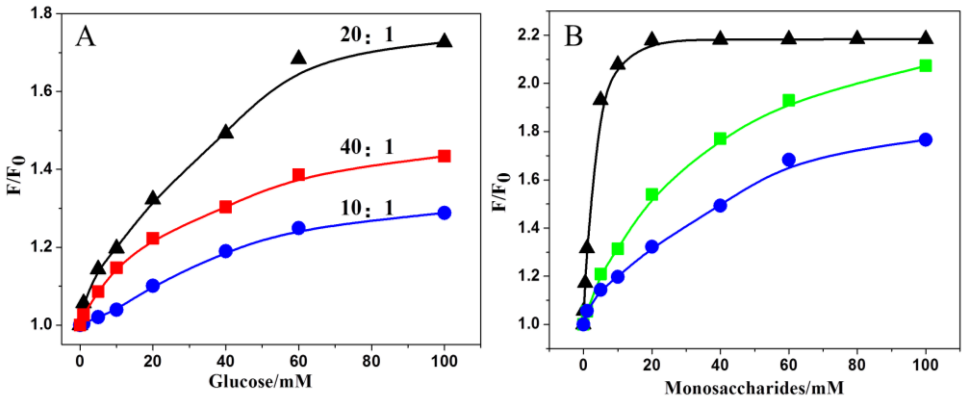


Fig. S7 (A) Glucose response curves obtained from BBV/GQDs system in different mole ratios (Q/F). (▲, Q/F=20:1; ■, Q/F=40:1; ●, Q/F=10:1). (B) Relative FL recovery of GQDs (25 μM) in the presence of the quencher BBV (0.5 mM) and upon the addition of different monosaccharides. (▲, fructose; ■, galactose; ●, glucose).

Supporting References

1. L. Feng, F. Liang, Y. Wang, M. Xu and X. Wang, *Org. Biomol. Chem.*, 2011, **9**, 2938.

2. D. Pan, J. Zhang, Z. Li and M. Wu, *Adv. Mater.*, 2010, **22**, 734.