A guanosine-based 2-formylphenylborate ester hydrogel with high selectivity to K⁺ ions

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Contents

General procedure for G-2FPB-K⁺ hydrogel preparation.......................................................................................................................S2
Rheology Procedure..................................................................................................................................................................................S2
Morphological Assay.............................................................................................................................................................................S2
Powder X-ray Diffraction (PXRD) Assay...............................................................................................................................................S2
Circular Dichroism (CD) Assay...............................................................................................................................................................S2
FTIR Spectroscopy Assay........................................................................................................................................................................S2
VT ¹H NMR and VT ¹¹B NMR Assay of Diluted G-2FPB-K⁺ Assembly Solution..................................................................................S2
Procedure for Diffusion-Ordered Spectroscopy Measurements.......................................................................................................S3
Fluorescence assay.............................................................................................................................................................................S3
UV-Vis assay.....................................................................................................................................................................................S3

Fig. S1. The CD spectra of G-2FPB-M⁺ solution with various concentration.........................................................................................S4
Fig. S2. FTIR spectra of G-2FPB-Na⁺ and G-2FPB-K⁺..........................................................................................................................S4
Fig. S3. ¹H NMR spectra of G-2FPB-K⁺ hydrogel and 2-formylphenylboronic acid..................................................................................S5
Fig. S4. DOSY spectrum of G-2FPB-K⁺ hydrogel...............................................................................................................................S5
Fig. S5. The contents of guanosine 2-formylphenylborate ester 3 in 50 mM G-2FPB-M⁺ at different temperature...........................S6
Fig. S6. UV-Vis spectra of the G-2FPB-K⁺ hydrogel with different concentration of berberine ...............................................................S6
Fig. S7. The fluorescence spectra of G-2FPB-Na⁺/BBR anti-ion interference assays...........................................................................S7
Fig. S8. The ISE reports of the China-Japan Friendship Hospital.....................................................................................................S7
**General procedure for G-2FPB-K⁺ hydrogel preparation**

283.0 mg of guanosine (1, 1.0 mmol, 1 equiv) and 150.0 mg of 2-formylphenylboronic acid (2, 1.0 mmol, 1 equiv) was added to a 50 mL round bottom flask. Then 56.0 mg of KOH solids (1.0 mmol, 1 equiv) and 20 mL of ultrapure water were added. The suspension was stirred and heated to 95 °C in an oil bath until all the substances were dissolved and the solution became clear. When the solution was cooled to room temperature, a transparent and stable supramolecular G-2FPB-K⁺ hydrogel (50 mM) was formed. The G-2FPB-M⁺ solution with other alkali metal ions (Li⁺, Na⁺, Rb⁺, and Cs⁺) were prepared similarly.

**Rheology Procedure**

Gels were prepared at 50 mM G-2FPB-K⁺, following the general gel procedure. All rheological data was collected using an AR2000ex stress-controlled rheometer from TA instruments. Rheological experiments were performed at 20 °C using parallel plate geometry (40 mm diameter) and a solvent trap to minimize sample drying during measurements. The gel samples were allowed to equilibrate on the plate for 10 min. Frequency sweeps were performed at 1% strain. Stress sweeps were performed at 10 rad/sec by ramping the stress from 0.5 to 1000 Pa.

**Morphological Assay**

Transmission electron microscopy (TEM) images were obtained on a JEM 1200EX, operating at accelerating voltages of 100 kV. Ten μL of a freshly prepared solution of G-2FPB-K⁺ assembly (5 mM or 10 mM) was cast onto carbon-coated copper grids (300 mesh) for 3 min. The sample was dried under an ambient temperature.

Atomic force microscopy (AFM) images were performed on freshly cleaved fluorophlogopite mica (1 cm × 1 cm). A total of 5 μL of the freshly prepared solution of the G-2FPB-K⁺ assembly (5 mM) was spincoated for 30 s, and the mica was briefly dried under a stream of N₂ (g). AFM imaging was performed with a Nanoscope IIIa (Digital Instruments) in tapping mode in air, using Si tips. The probes were commercially available silicon tips with a spring constant of 42 N m⁻¹.

**Powder X-ray Diffraction (PXRD) Assay**

A 50 mM G-2FPB-K⁺ hydrogel was prepared and lyophilized to form a white powder. X-ray powder diffraction measurements were performed with a Cu radiation source at 20 °C using a LabX PXRD-6000 with a LynxEye detector.

**Circular Dichroism (CD) Assay**

All experiments were performed with a Jasco J-815 spectropolarimeter. CD spectroscopy of various assemblies solution was measured with a 0.01 mm cell. Three scans were accumulated and averaged by the computer. All experiments were carried out at 25 °C. A hot G-2FPB-M⁺ solution with various concentration was added in cell. The samples were used directly to test when they cooled down to room temperature.

**FTIR Spectroscopy Assay**

FTIR spectra were recorded on a Nicolet FTIR spectrometer (Nicolet iS5, USA). A 50 mM G-2FPB-M⁺ system was lyophilized and mixed with dry potassium bromide (KBr). The spectra were recorded from 400 to 4000 cm⁻¹.

**VT ¹H NMR and VT ¹¹B NMR Assay of Diluted G-2FPB-K⁺ Assembly Solution**

All VT NMR spectra of G-2FPB-K⁺ hydrogel were recorded on a Bruker AV-400 nuclear magnetic resonance spectrooscope in D₂O and the temperature was controlled from 5 to 85°C. BF₃·(CH₂CO₂)₂ was used as an external standard for VT ¹¹B NMR and 2,2,3,3-(d₄)-3-(trimethylsilyl) propionic acid sodium salt (0.31 mM) was used as an
internal standard for VT $^1$H NMR. A total of 600 $\mu$L of the 50 mM G-2FPB-K$^+$ hydrogel containing an internal standard or external standard was added to the NMR sample tube as the sample of VT $^1$H NMR or VT $^{11}$B NMR.

**Procedure for Diffusion-Ordered Spectroscopy Measurements**

A 50 mM G-2FPB-Na$^+$ solution (1, 2, and NaOH 50 mM each) was prepared in D$_2$O according to the general preparation procedure. The warm gel (600 $\mu$L) was then transferred into a NMR tube, and the gel was allowed to cool overnight. Diffusion experiments were performed on a Bruker AVIII-600, using a Stimulated Echo Pulse Gradient sequence in FT mode. Experiments consisted of 32 points at 100 scans with a delay of 5 s, a gradient pulse length of 1.65 ms, and $\Delta$ value of 60.0 ms. The temperature was controlled at 25.0 °C, and the measurements were repeated at least 3 times.

**Fluorescence assay**

Fluorescence Spectra were recorded on HITACHI F-7000 Fluorescence spectrophotometer. Standard quartz cuvettes with a 1 cm light path were used for all fluorescent spectra measurements. All the fluorescent experiments were repeated three times and were carried out at 25 °C. Other parameter: excitation wavelength: 371 nm; emission wavelength: 523 nm; EX Slit: 5.0 nm; EM Slit: 5.0 nm; PMT Voltage: 400 V

**UV-Vis assay**

A 5 $\mu$L (or 10 $\mu$L) of solution of berberine hydrochloride (3.1 mM) was added in a 1 mL of G-2FPB-K$^+$ thermal solution (50 mM), and then cooled room temperature. UV–vis titration spectra were recorded on HITACHI UHS300 spectrophotometer. A path length cell of 0.01 mm was used and all experiments were performed at room temperature.

**G-2FPB-Na$^+$/BBR anti-ion interference assay**

A total of 2000 $\mu$L of the 100 mM G-2FPB-Na$^+$ PB buffer solution (pH=7.4) containing 3.1 mM berberine was added to the standard quartz cuvettes. 20 $\mu$L of the corresponding M$^{n+}$ solutions (20 mM, 200 mM or 2000 mM) were added to obtain a fluorescence spectra. Then 20 $\mu$L of 20 mM KCl solution was added to obtain another fluorescence spectra. See Figure S3 for details.

**The detection assays of human blood serum samples**

A total of 1800 $\mu$L of the 111 mM G-2FPB-Na$^+$ PB buffer solution (pH=7.4) containing 3.44 mM berberine was added to the standard quartz cuvettes. 200 $\mu$L of the corresponding blood serum samples were added to obtain a fluorescence spectra.
Fig. S1. The CD spectra of G-2FPB-M⁺ solution with various concentration. (A) Li⁺, (B) Na⁺, (C) Rb⁺, (D) Cs⁺. (guanosine 1.0 equiv, 2-formylphenylboronic acid 1.0 equiv, LiOH, NaOH, RbOH or CsOH 1.0 equiv)

Fig. S2. FTIR spectra of G-2FPB-Na⁺ (black line) and G-2FPB-K⁺ (red line).
Fig. S3. $^1$H NMR spectra of a 50 mM G-2FPB-K$^+$ hydrogel and 2-formylphenylboronic acid in KOH at 25 ºC.

Fig. S4. (A) DOSY spectrum of a 50 mM G-2FPB-K$^+$ hydrogel at 25 ºC. (B) The possible visible species in hydrogel. (C) The diffusion coefficients of various species.
Fig. S5. The contents of guanosine 2-formylphenylborate ester 3 in 50 mM G-2FPB-M⁺ (Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺) at different temperature.

Fig. S6. UV-Vis spectra of the G-2FPB-K⁺ hydrogel with different concentration of berberine at 25 °C.
**Fig. S7.** The fluorescence spectra of G-2FPB-Na\(^+\)/BBR anti-ion interference assays. (A) 100 equiv Li\(^+\); (B) 100 equiv Na\(^+\); (C) 1 equiv Rb\(^+\); (D) 100 equiv Cs\(^+\); (E) 10 equiv NH\(_4^+\); (F) 1 equiv Ca\(^{2+}\); (G) 10 equiv Mg\(^{2+}\); (H) 1 equiv Zn\(^{2+}\); (I) 1 equiv Cu\(^{2+}\); (J) 1 equiv Mn\(^{2+}\); (K) 1 equiv Fe\(^{3+}\).
| item name | value | range |
|-----------|-------|-------|
| Cysc      | 1.08  | 0.50–1.03 |
| CR        | 44.1  | 35–106 |
| GLU       | 7.26  | 3.61–6.11 |
| CO2       | 26.9  | 4.35 |
| CL        | 97.7  | 90–110 |
| IP        | 1.12  | 0.81–1.78 |
| eGFR      | 116.4 | ml/min/1.73m² |

| item name | value | range |
|-----------|-------|-------|
| Urea      | 3.16  | 2.78–7.85 |
| UA        | 310   | 150–420 |
| GA        | 17.4  | 11.0–16.0 |
| Clq       | 197   | 150–233 |
| Na        | 134   | 135–145 |
| Ca        | 1.94  | 2.00–2.75 |
| B2-MG     | 1.98  | 1.00–2.75 |

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| item name | value | range |
|-----------|-------|-------|
| ALB       | 26.1  | 35.0–55.0 |
| Pre-A      | 30.71 | 200–200 |
| TP        | 5.90  | 4.00–5.50 |
| A/G       | 1.02  | 1.30–2.50 |
| GGT       | 1.10  | 0–1.00 |
| MAO       | 9.20  | <12 |
| ADA       | 9.20  | <12 |
| CHE       | 4855.84 | 150–1200 |
| SOD       | 82.00 | 120–216 |
| Urea      | 3.14  | 2.78–7.65 |
| UA        | 106.0 | 50–200 |
| GA        | 35.9  | 11.0–16.0 |
| Clq       | 211   | 150–253 |
| Na        | 134   | 135–145 |
| Ca        | 1.90  | 2.00–2.75 |
| B2-MG     | 3.41  | 1.00–1.78 |
| eGFR      | 116.4 | ml/min/1.73m² |

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| item name | value | range |
|-----------|-------|-------|
| AST       | 13    | 0–42  |
| ALP       | 4.27  | 0.00–7.00 |
| Pre-A      | 30.71 | 200–200 |
| TP        | 5.90  | 4.00–5.50 |
| A/G       | 1.02  | 1.30–2.50 |
| GGT       | 1.10  | 0–1.00 |
| MAO       | 9.20  | <12 |
| ADA       | 9.20  | <12 |
| CHE       | 4855.84 | 150–1200 |
| SOD       | 82.00 | 120–216 |
| Urea      | 3.14  | 2.78–7.65 |
| UA        | 106.0 | 50–200 |
| GA        | 35.9  | 11.0–16.0 |
| Clq       | 211   | 150–253 |
| Na        | 134   | 135–145 |
| Ca        | 1.90  | 2.00–2.75 |
| B2-MG     | 3.41  | 1.00–1.78 |
| eGFR      | 116.4 | ml/min/1.73m² |
### Clinical Test Report

**Serum**

| Item       | Name                      | Value         | Range      |
|------------|---------------------------|---------------|------------|
| ALT        | 谷丙转氨酶               | 29 IU/L       | 0-40       |
| TBIL       | 总胆红素                 | 13.09 μmol/L  | 0-20       |
| TP         | 总蛋白定量               | 62.6 g/L      | 50-80      |
| A/G        | 白球比                   | 1.25          | 0.8-2.0    |
| GGT        | 谷丙转氨酶                | 17.0 IU/L     | 0-52       |
| TBA        | 血清总胆汁酸             | 1.4 μmol/L    | 0-10       |
| MAO        | 单胺氧化酶               | 7.5 IU/L      | <12        |
| ADA        | 凝血酶                  | 113.84 IU/L   | 129-216    |
| CHE        | 血清碱性磷酸酶           | 6.19 μmol/L   | 35-106     |
| SOD        | 血清超氧化物歧化酶     | 2294.24 IU/L  | 5400-12000 |
| CR         | 氯化物                  | 4.38 mmol/L   | 3.5-5.5    |
| GLU        | 葡萄糖                  | 5.38 mmol/L   | 3.6-6.1    |
| CL         | 钙                     | 4.12 mmol/L   | 3.5-5.5    |
| TP         | 胆红素                  | 1.23 mmol/L   | 0.81-1.78  |

**Emergency Department**

| Item       | Name                      | Value         | Range      |
|------------|---------------------------|---------------|------------|
| AST        | 丙氨酸氨基转移酶         | 28 IU/L       | 0-40       |
| DBIL       | 直接胆红素                | 8.71 μmol/L   | 0-20       |
| ALB        | 白蛋白                    | 26.1 g/L      | 40-55      |
| Pre-Alb     | 前白蛋白                  | 46.9 μg/mL    | 1500-4000  |
| ALP        | 碱性磷酸酶                | 150 IU/L      | 40-150     |
| GG         | 卵磷脂酰胆碱             | 0.1 μmol/L    | <2.7       |
| AFU        | α-淀粉酶                 | 27 IU/L       | 5-40       |
| LAP        | 谷氨酸脱氢酶            | 57 IU/L       | 38-75      |
| TPS        | 血清总蛋白               | 120 mg/dl     | 44-75      |
| Urea       | 尿素                     | 8.20 mmol/L   | 2.78-7.85  |
| UA         | 尿酸                     | 243 μmol/L    | 150-420    |
| CO2        | 二氧化碳                  | 22.07 mmol/L  | 21-35      |
| Na         | 钠                       | 139 mmol/L    | 155-154    |
| Ca         | 钙                       | 2.05 mmol/L   | 2.00-2.75  |
| eGFR       | 算肾小球滤过率           | 96.41 ml/min/1| 1.75       |
Fig. S8. The laboratory reports of the China-Japan Friendship Hospital using the ion selective electrode method to test the potassium concentration: (A) sample 1; (B) sample 2; (C) sample 3; (D) sample 4; (E) sample 5.