Electronic Supplementary Material (ESI)
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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

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 fluorphlogopite 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 N_2 (*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 $N \cdot m^{-1}$.

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 ^{1}H NMR and VT ^{11}B 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 spectroscope in D_2O and the temperature was controlled from 5 to 85°C. $BF_3 \cdot O(C_2H_5)_2$ was used as an external standard for VT ^{11}B NMR and 2,2,3,3-(d_4)-3-(trimethylsilyl) propionic acid sodium salt (0.31 mM) was used as an

internal standard for VT ^{1}H NMR. A total of 600 μL 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_2O according to the general preparation procedure. The warm gel (600 μL) 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 Δ 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; emissiom wavelength: 523 nm; EX Slit: 5.0 nm; EM Slit: 5.0 nm; PMT Votage: 400 V

UV-Vis assay

A 5 μL (or 10 μL) 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 UH5300 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 μL 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 μL of the corresponding M^{n+} solutions (20 mM, 200 mM or 2000 mM) were added to obtain a fluorescence spectra. Then 20 μL 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 μL 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 μL of the corresponding blood serum samples were added to obtain a fluorescence spectra.

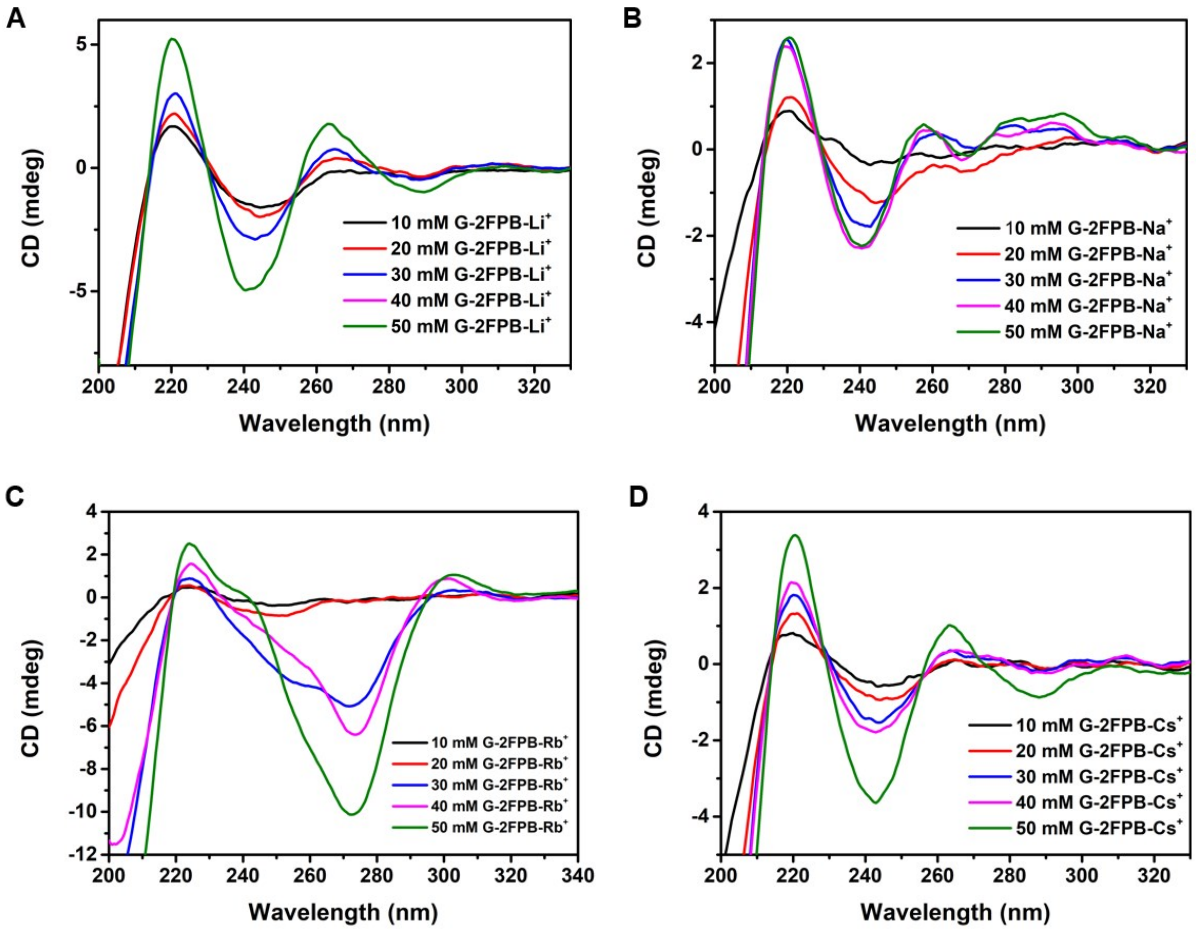


Fig. S1. The CD spectra of **G-2FPB-M⁺** solution with various concentration. (A) Li^+, (B) Na^+, (C) Rb^+, (D) Cs^+.(guanosine 1.0 equiv, 2-formylphenylboronic acid 1.0 equiv, LiOH, NaOH, RbOH or CsOH 1.0 equiv)

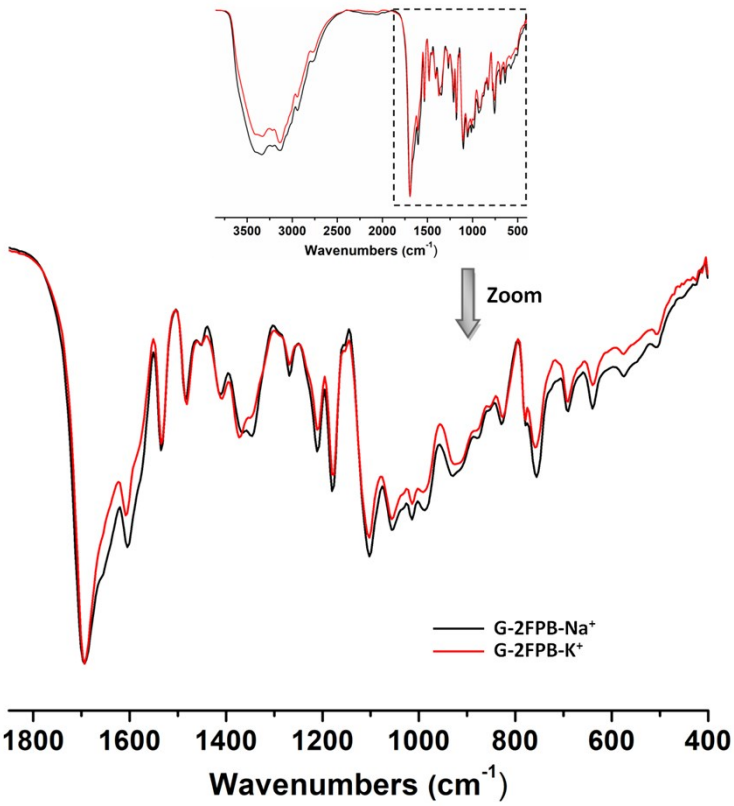


Fig. S2. FTIR spectra of **G-2FPB-Na⁺** (black line) **and G-2FPB-K⁺** (red line).

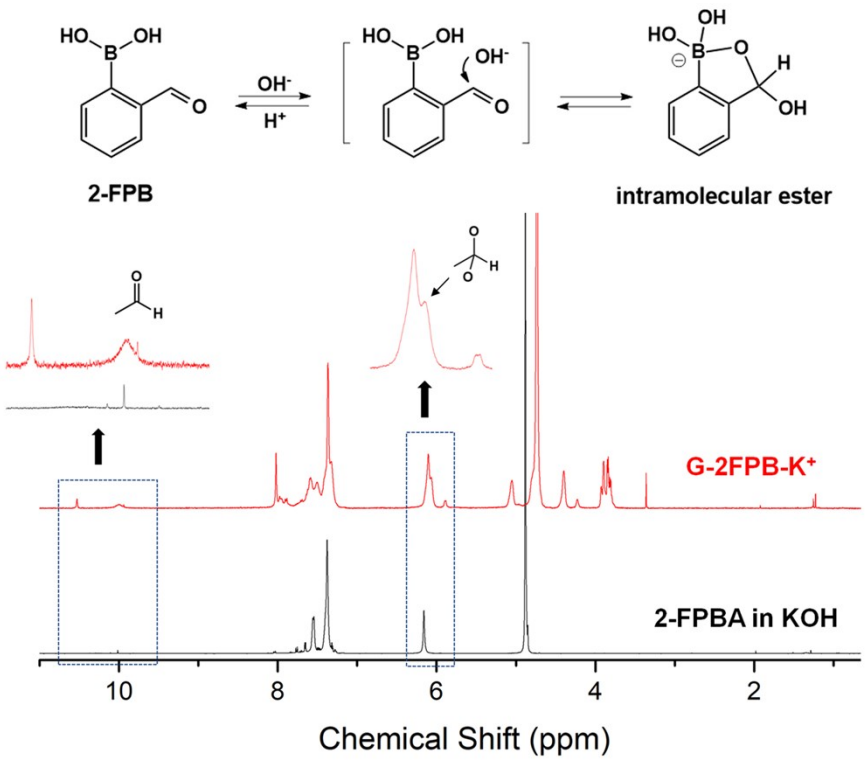
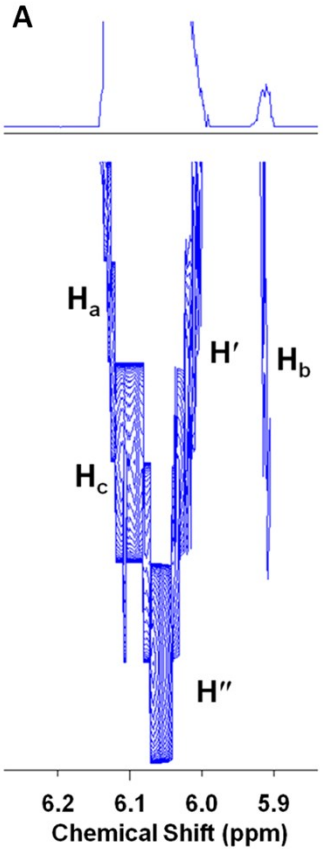
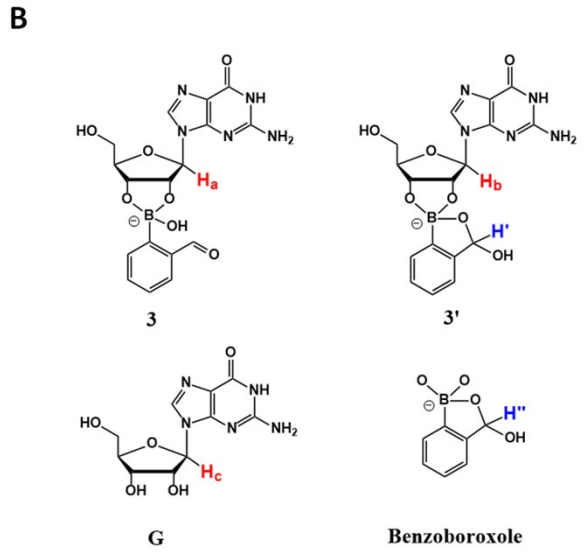


Fig. S3. ^{1}H NMR spectra of a 50 mM **G-2FPB-K⁺** hydrogel and 2-formylphenylboronic acid in KOH at 25 ºC.





C

Species	Protons	δ (ppm)	Log (m²/s)	D (×10⁻¹⁰ m²s⁻¹)
3	H_a	6.115	-9.411	3.882
3'	H_b	5.894	-9.411	3.882
	H′	6.006	-9.411	3.882
G	H_c	6.091	-9.256	5.546
benzoboroxole	H″	6.055	-9.072	8.472

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.

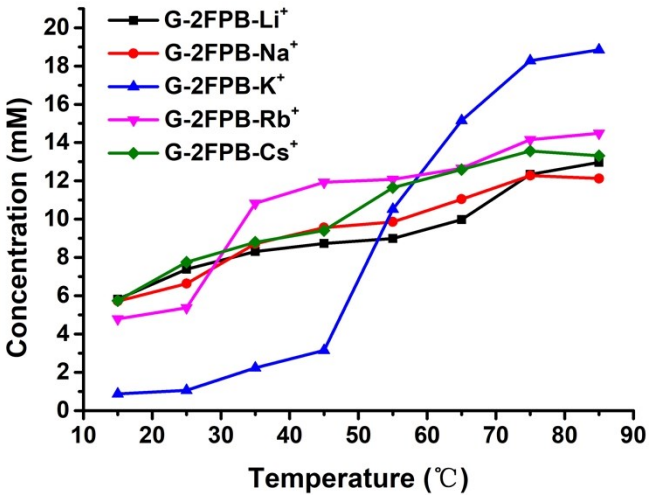


Fig. S5. The contents of guanosine 2-formylphenylborate ester **3** in 50 mM **G-2FPB-M⁺** (Li^+, Na^+, K^+, Rb^+, and Cs^+) at different temperature.

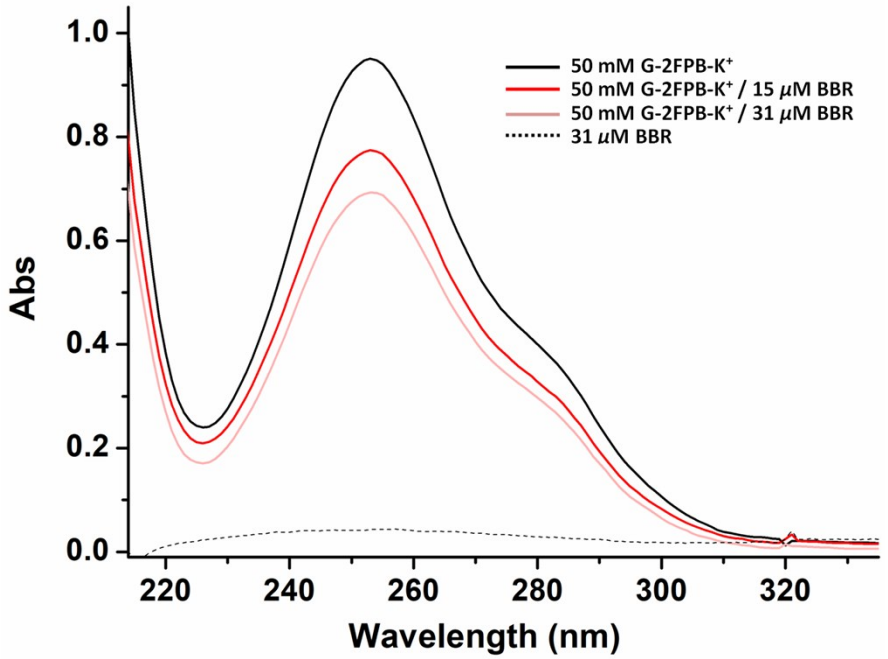


Fig. S6. UV-Vis spectra of the **G-2FPB-K⁺** hydrogel with different concentration of berberine at 25 ºC.

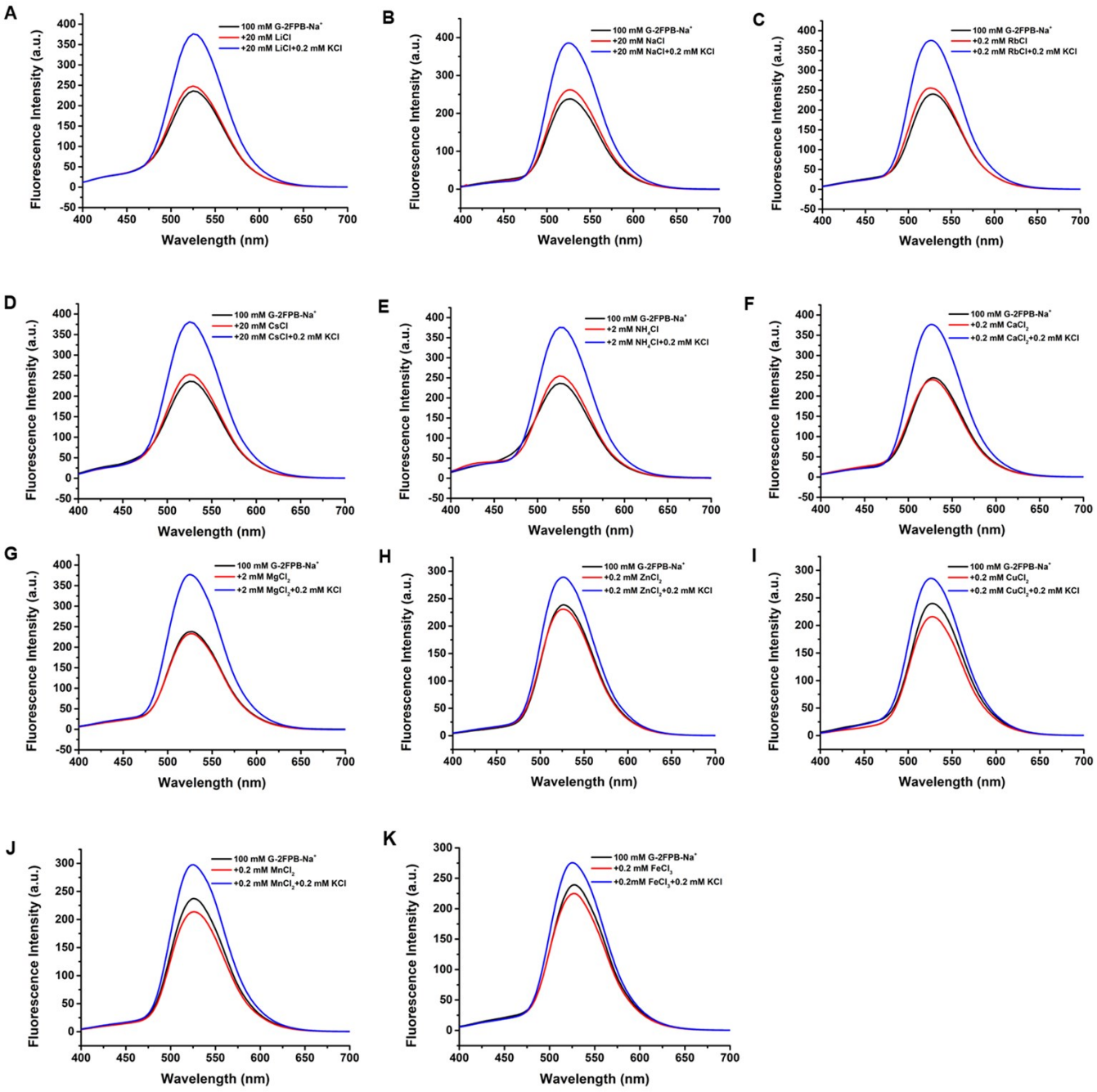
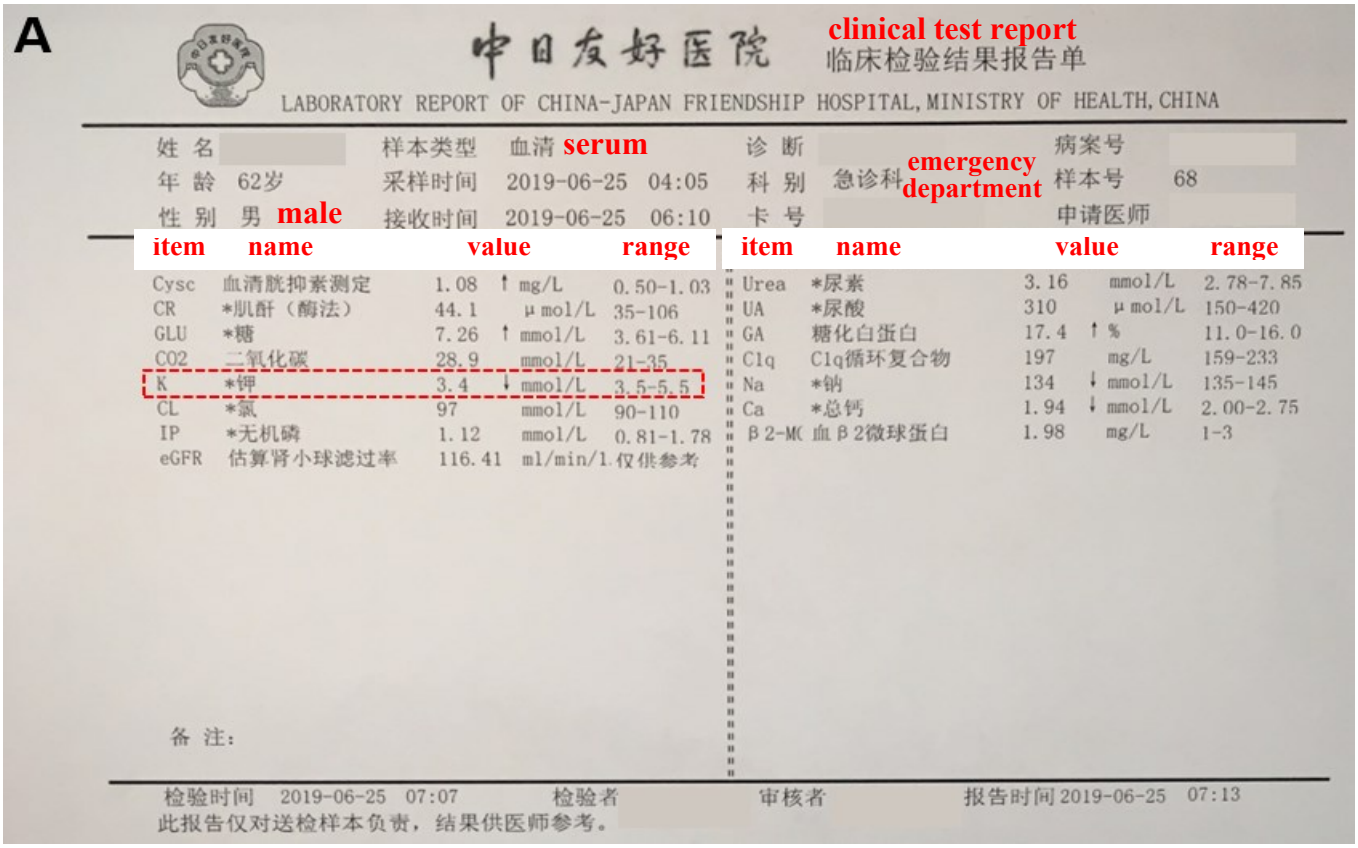


Fig. S7. The fluorescence spectra of **G-2FPB-Na$^+$**/BBR anti-ion interference assays. (A) 100 equiv Li^+ ; (B) 100 equiv Na^+ ; (C) 1 equiv Rb^+ ; (D) 100 equiv Cs^+ ; (E) 10 equiv NH_4^+ ; (F) 1 equiv Ca^{2+} ; (G) 10 equiv Mg^{2+} ; (H) 1 equiv Zn^{2+} ; (I) 1 equiv Cu^{2+} ; (J) 1 equiv Mn^{2+} ; (K) 1 equiv Fe^{3+}.



A

中日友好医院 clinical test report 临床检验结果报告单

LABORATORY REPORT OF CHINA-JAPAN FRIENDSHIP HOSPITAL, MINISTRY OF HEALTH, CHINA

姓 名 | 样本类型 血清 serum | 诊 断 | 病案号

年 龄 62岁 | 采样时间 2019-06-25 04:05 | 科 别 急诊科 emergency department | 样本号 68

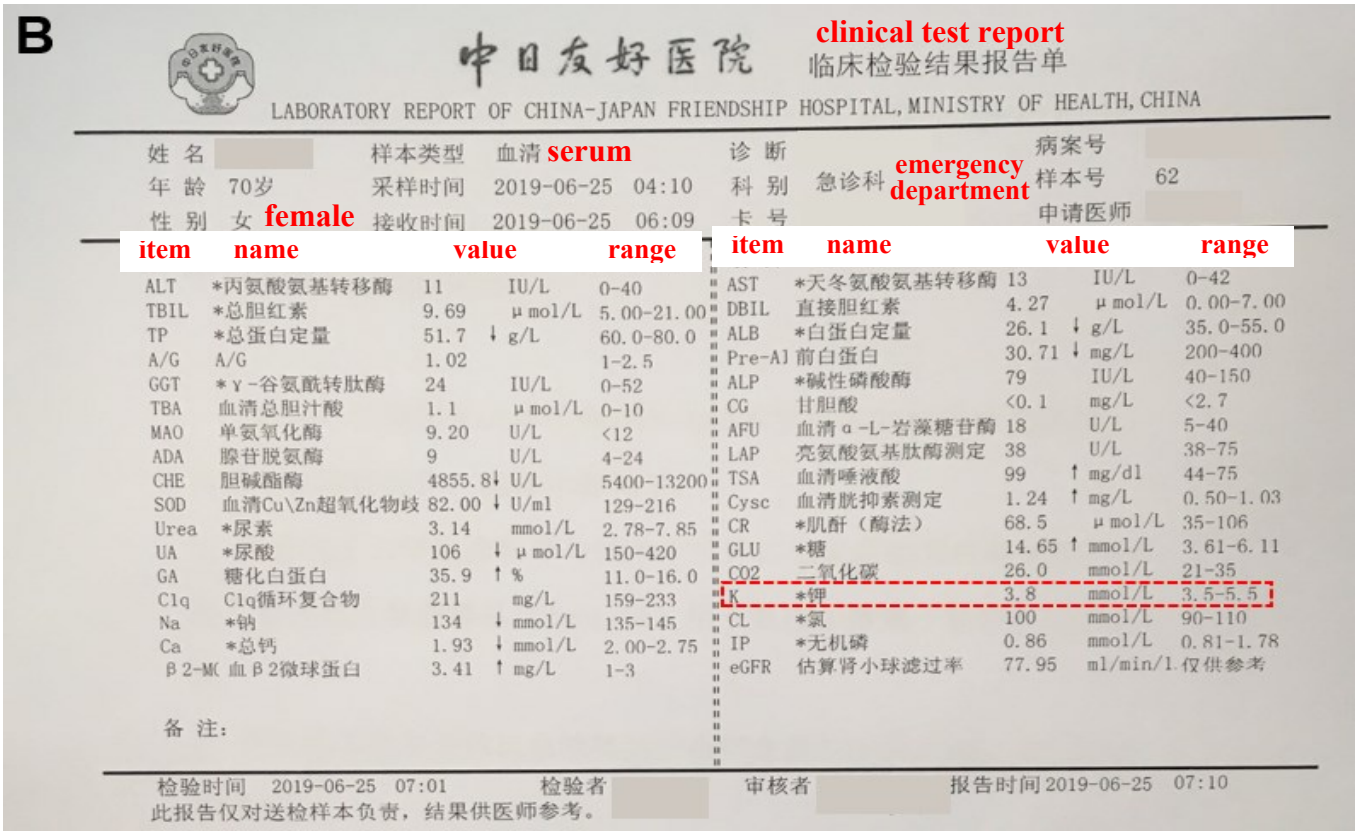
性 别 男 male | 接收时间 2019-06-25 06:10 | 卡 号 | 申请医师

item	name	value		range	item	name	value		range
Cysc	血清胱抑素测定	1.08	↑ mg/L	0.50-1.03	Urea	*尿素	3.16	mmol/L	2.78-7.85
CR	*肌酐（酶法）	44.1	μmol/L	35-106	UA	*尿酸	310	μmol/L	150-420
GLU	*糖	7.26	↑ mmol/L	3.61-6.11	GA	糖化白蛋白	17.4	↑ %	11.0-16.0
CO2	二氧化碳	28.9	mmol/L	21-35	C1q	C1q循环复合物	197	mg/L	159-233
K	*钾	3.4	↓ mmol/L	3.5-5.5	Na	*钠	134	↓ mmol/L	135-145
CL	*氯	97	mmol/L	90-110	Ca	*总钙	1.94	↓ mmol/L	2.00-2.75
IP	*无机磷	1.12	mmol/L	0.81-1.78	β2-MG	血β2微球蛋白	1.98	mg/L	1-3
eGFR	估算肾小球滤过率	116.41	ml/min/1.	仅供参考					

备 注：

检验时间 2019-06-25 07:07 检验者 审核者 报告时间 2019-06-25 07:13

此报告仅对送检样本负责，结果供医师参考。



B

中日友好医院 clinical test report 临床检验结果报告单

LABORATORY REPORT OF CHINA-JAPAN FRIENDSHIP HOSPITAL, MINISTRY OF HEALTH, CHINA

姓 名 | 样本类型 血清 serum | 诊 断 | 病案号

年 龄 70岁 | 采样时间 2019-06-25 04:10 | 科 别 急诊科 emergency department | 样本号 62

性 别 女 female | 接收时间 2019-06-25 06:09 | 卡 号 | 申请医师

item	name	value		range	item	name	value		range
ALT	*丙氨酸氨基转移酶	11	IU/L	0-40	AST	*天冬氨酸氨基转移酶	13	IU/L	0-42
TBIL	*总胆红素	9.69	μmol/L	5.00-21.00	DBIL	直接胆红素	4.27	μmol/L	0.00-7.00
TP	*总蛋白定量	51.7	↓ g/L	60.0-80.0	ALB	*白蛋白定量	26.1	↓ g/L	35.0-55.0
A/G	A/G	1.02		1-2.5	Pre-Al	前白蛋白	30.71	↓ mg/L	200-400
GGT	*γ-谷氨酰转肽酶	24	IU/L	0-52	ALP	*碱性磷酸酶	79	IU/L	40-150
TBA	血清总胆汁酸	1.1	μmol/L	0-10	CG	甘胆酸	<0.1	mg/L	<2.7
MAO	单氨氧化酶	9.20	U/L	<12	AFU	血清α-L-岩藻糖苷酶	18	U/L	5-40
ADA	腺苷脱氨酶	9	U/L	4-24	LAP	亮氨酸氨基肽酶测定	38	U/L	38-75
CHE	胆碱酯酶	4855.8	↓ U/L	5400-13200	TSA	血清唾液酸	99	↑ mg/dl	44-75
SOD	血清Cu\Zn超氧化物歧	82.00	↓ U/ml	129-216	Cysc	血清胱抑素测定	1.24	↑ mg/L	0.50-1.03
Urea	*尿素	3.14	mmol/L	2.78-7.85	CR	*肌酐（酶法）	68.5	μmol/L	35-106
UA	*尿酸	106	↓ μmol/L	150-420	GLU	*糖	14.65	↑ mmol/L	3.61-6.11
GA	糖化白蛋白	35.9	↑ %	11.0-16.0	CO2	二氧化碳	26.0	mmol/L	21-35
C1q	C1q循环复合物	211	mg/L	159-233	K	*钾	3.8	mmol/L	3.5-5.5
Na	*钠	134	↓ mmol/L	135-145	CL	*氯	100	mmol/L	90-110
Ca	*总钙	1.93	↓ mmol/L	2.00-2.75	IP	*无机磷	0.86	mmol/L	0.81-1.78
β2-MG	血β2微球蛋白	3.41	↑ mg/L	1-3	eGFR	估算肾小球滤过率	77.95	ml/min/1.	仅供参考

备 注：

检验时间 2019-06-25 07:01 检验者 审核者 报告时间 2019-06-25 07:10

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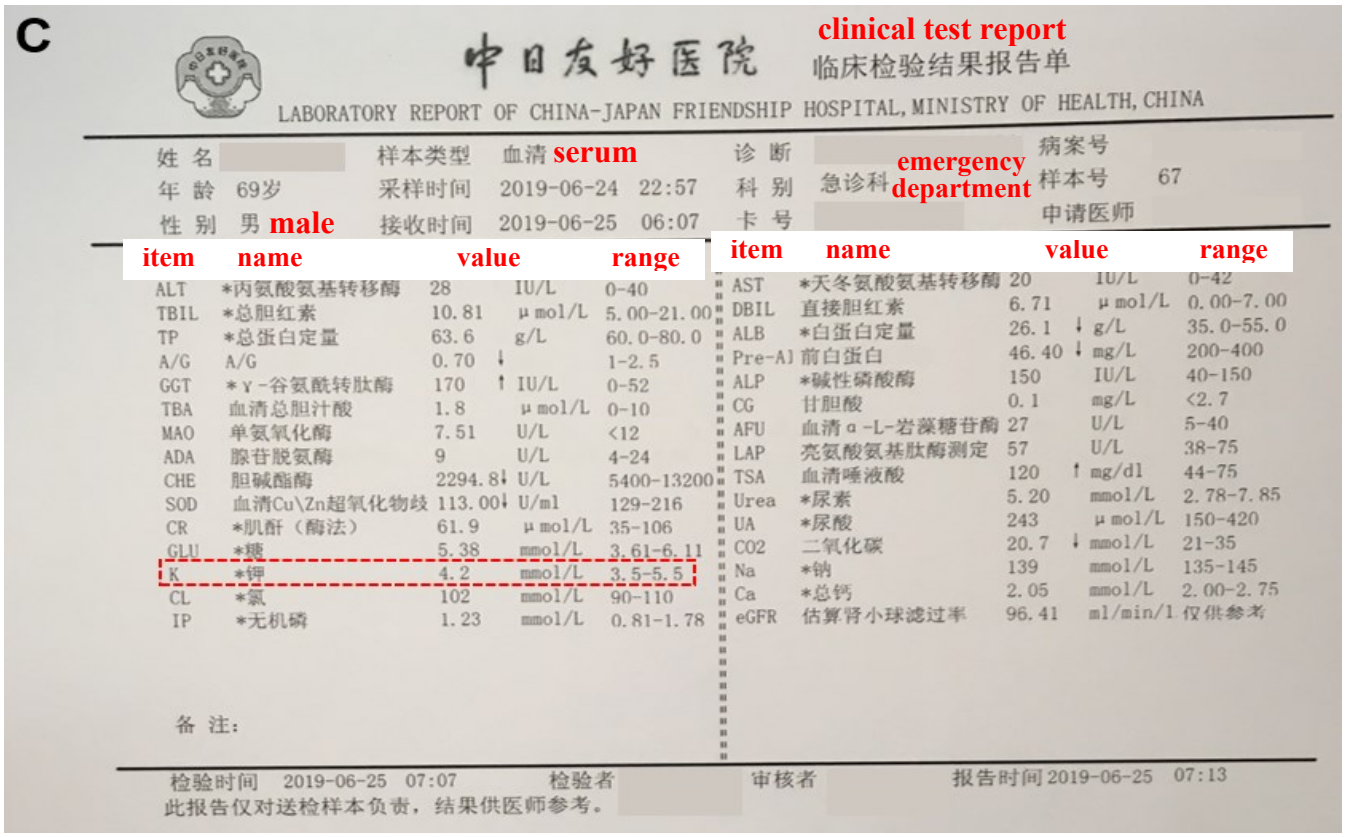
C
中日友好医院
clinical test report
临床检验结果报告单
LABORATORY REPORT OF CHINA-JAPAN FRIENDSHIP HOSPITAL, MINISTRY OF HEALTH, CHINA
姓 名
样本类型 血清 serum
诊 断
病案号
年 龄 69岁
采样时间 2019-06-24 22:57
科 别 急诊科 emergency department
样本号 67
性 别 男 male
接收时间 2019-06-25 06:07
卡 号
申请医师
item name value range
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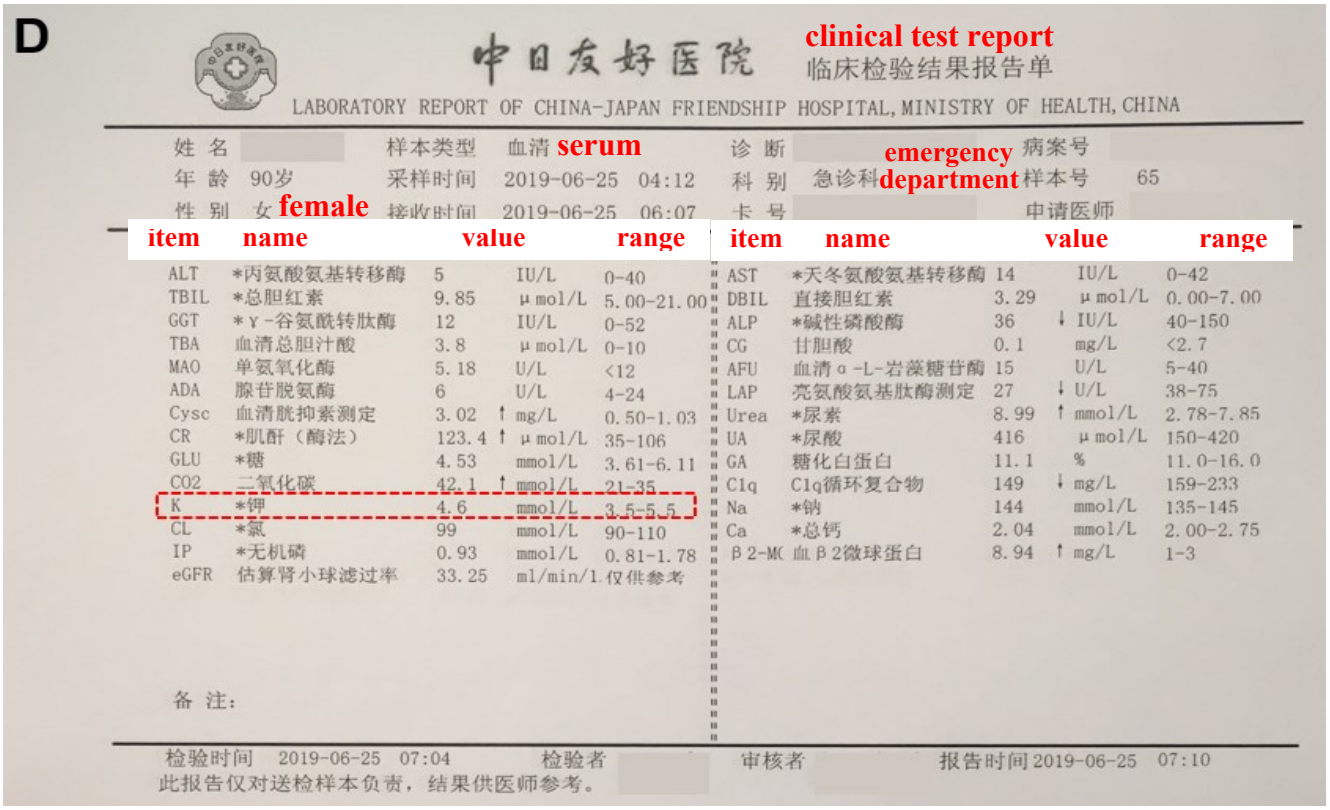
TBIL *总胆红素 10.81 μmol/L 5.00-21.00
TP *总蛋白定量 63.6 g/L 60.0-80.0
A/G A/G 0.70 ↓ 1-2.5
GGT *γ-谷氨酰转肽酶 170 ↑ IU/L 0-52
TBA 血清总胆汁酸 1.8 μmol/L 0-10
MAO 单氨氧化酶 7.51 U/L <12
ADA 腺苷脱氨酶 9 U/L 4-24
CHE 胆碱酯酶 2294.8 ↓ U/L 5400-13200
SOD 血清Cu\Zn超氧化物歧 113.00 ↓ U/ml 129-216
CR *肌酐（酶法） 61.9 μmol/L 35-106
GLU *糖 5.38 mmol/L 3.61-6.11
K *钾 4.2 mmol/L 3.5-5.5
CL *氯 102 mmol/L 90-110
IP *无机磷 1.23 mmol/L 0.81-1.78
item name value range
AST *天冬氨酸氨基转移酶 20 IU/L 0-42
DBIL 直接胆红素 6.71 μmol/L 0.00-7.00
ALB *白蛋白定量 26.1 ↓ g/L 35.0-55.0
Pre-Al 前白蛋白 46.40 ↓ mg/L 200-400
ALP *碱性磷酸酶 150 IU/L 40-150
CG 甘胆酸 0.1 mg/L <2.7
AFU 血清α-L-岩藻糖苷酶 27 U/L 5-40
LAP 亮氨酸氨基肽酶测定 57 U/L 38-75
TSA 血清唾液酸 120 ↑ mg/dl 44-75
Urea *尿素 5.20 mmol/L 2.78-7.85
UA *尿酸 243 μmol/L 150-420
CO2 二氧化碳 20.7 ↓ mmol/L 21-35
Na *钠 139 mmol/L 135-145
Ca *总钙 2.05 mmol/L 2.00-2.75
eGFR 估算肾小球滤过率 96.41 ml/min/1 仅供参考
备 注：
检验时间 2019-06-25 07:07 检验者 审核者 报告时间 2019-06-25 07:13
此报告仅对送检样本负责，结果供医师参考。


D
中日友好医院
clinical test report
临床检验结果报告单
LABORATORY REPORT OF CHINA-JAPAN FRIENDSHIP HOSPITAL, MINISTRY OF HEALTH, CHINA
姓 名
样本类型 血清 serum
诊 断
病案号
年 龄 90岁
采样时间 2019-06-25 04:12
科 别 急诊科 emergency department
样本号 65
性 别 女 female
接收时间 2019-06-25 06:07
卡 号
申请医师
item name value range
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TBIL *总胆红素 9.85 μmol/L 5.00-21.00
GGT *γ-谷氨酰转肽酶 12 IU/L 0-52
TBA 血清总胆汁酸 3.8 μmol/L 0-10
MAO 单氨氧化酶 5.18 U/L <12
ADA 腺苷脱氨酶 6 U/L 4-24
Cysc 血清胱抑素测定 3.02 ↑ mg/L 0.50-1.03
CR *肌酐（酶法） 123.4 ↑ μmol/L 35-106
GLU *糖 4.53 mmol/L 3.61-6.11
CO2 二氧化碳 42.1 ↑ mmol/L 21-35
K *钾 4.6 mmol/L 3.5-5.5
CL *氯 99 mmol/L 90-110
IP *无机磷 0.93 mmol/L 0.81-1.78
eGFR 估算肾小球滤过率 33.25 ml/min/1.仅供参考
item name value range
AST *天冬氨酸氨基转移酶 14 IU/L 0-42
DBIL 直接胆红素 3.29 μmol/L 0.00-7.00
ALP *碱性磷酸酶 36 ↓ IU/L 40-150
CG 甘胆酸 0.1 mg/L <2.7
AFU 血清α-L-岩藻糖苷酶 15 U/L 5-40
LAP 亮氨酸氨基肽酶测定 27 ↓ U/L 38-75
Urea *尿素 8.99 ↑ mmol/L 2.78-7.85
UA *尿酸 416 μmol/L 150-420
GA 糖化白蛋白 11.1 % 11.0-16.0
C1q C1q循环复合物 149 ↓ mg/L 159-233
Na *钠 144 mmol/L 135-145
Ca *总钙 2.04 mmol/L 2.00-2.75
β2-MC 血β2微球蛋白 8.94 ↑ mg/L 1-3
备 注：
检验时间 2019-06-25 07:04 检验者 审核者 报告时间 2019-06-25 07:10
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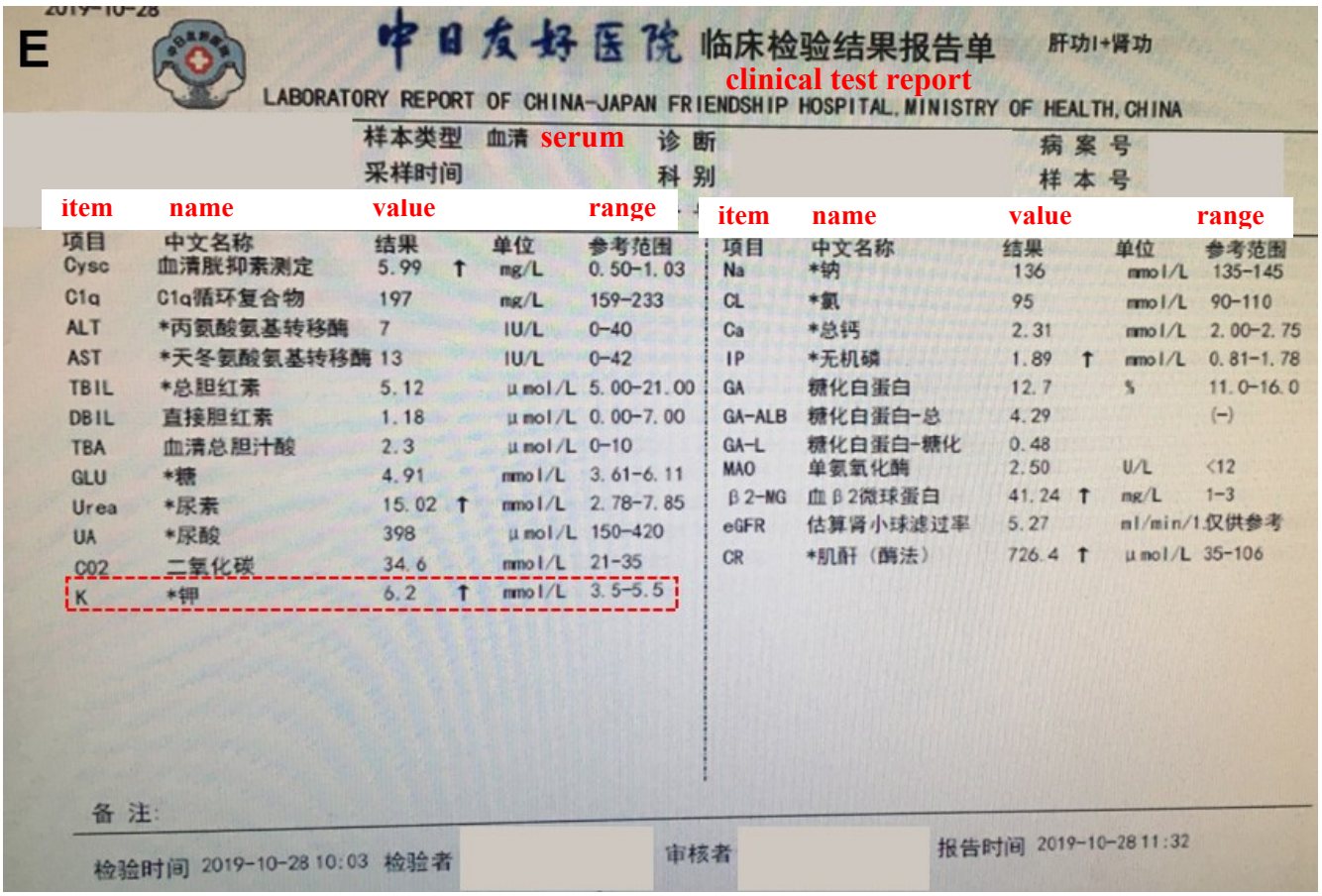

Fig. S8. The laboratory reports of the China-Japan Friendship Hospital using the ion selective electrode method to test the potassium concentration: (A) sample 1 ; (B) sample 2 ; (C) sample 3 ; (D) sample 4 ; (E) sample 5.