

## Electronic supplementary information

### Amplified fluorescent assay of potassium ions using graphene oxide and a conjugated cationic polymer

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## Experimental Section

### 1. Materials and Reagents.

Graphite powder, sulfuric acid, potassium persulfate, phosphorus pentoxide, hydrogen peroxide, and potassium permanganate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 2,7-dibromo-9,9-bis (6'-bromohexyl)-fluorene, 1,4-phenyldiboronic acid, and Pd(dppf)Cl<sub>2</sub> were purchased from Synwit Technology Co., Ltd. (Beijing, China). All chemicals were of analytical grade or of the highest purity available. The oligonucleotides were purchased from Sangon Biological Engineering Technology & Services Co., Ltd. (Shanghai, China) and purified using high performance liquid chromatography. The sequence of the G-quadruplex used in the study is: 5'-GGTTGGTGTGGTTGG-3'.

### 2. Apparatus

A Hitachi F-4600 fluorescence spectrophotometer (Hitachi Company, Tokyo, Japan) was used to record the fluorescence spectra and measure the fluorescence intensity. The <sup>1</sup>H NMR spectra were recorded on Mercury VX 300MHz spectrometer (Varian, USA). The chemical structure of PFP was confirmed using a Fourier transform infrared microspectrometer (FT-IR) (Nicolet-5700, USA). The number and molecular weight of polymer were characterized by gel permeation chromatography (GPC) equipped with a Waters 2690D separations module and Waters 2410 refractive index detector. Tetrahydrofuran (THF) was used as eluent and polystyrene standards as calibration.

### 3. Synthesis of Graphene Oxide

Graphite oxide was synthesized from natural graphitic powder according to Hummer's method with some modification.<sup>1</sup> Briefly, a mixture of natural graphite (3.0 g), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2.5 g), P<sub>2</sub>O<sub>5</sub> (2.5 g), and H<sub>2</sub>SO<sub>4</sub> (12 mL) was vigorously stirred at 80 °C and then diluted with deionized water (0.5 L). After treating the above mixture via filtering and washing, the initial product was re-dispersed into concentrated H<sub>2</sub>SO<sub>4</sub> (120 mL). Then, KMnO<sub>4</sub> (15 g) was slowly added at 0 °C. Successively, the mixed solution was stirred at 35 °C for 2 h, followed by dilution with deionized water (250 mL). After continuously stirring for another 2 h, additional deionized water (0.7 L) and 30% H<sub>2</sub>O<sub>2</sub> (20 mL) were added to the mixture drop by drop. The resulting mixture was filtered and washed with 10% HCl aqueous solution and deionized water. Finally, the as-synthesized product was purified by dialysis for one week, dried in a desiccator and then dispersed in water under sonication for 5 h.

#### **4. Synthesis of poly [(9, 9-bis (6'-N, N, N-trimethylammonium) hexyl)-fluorenylene phenylene dibromide] (PFP)**

Poly [(9, 9-bis (6'-N, N, N-trimethylammonium) hexyl)-fluorenylene phenylene dibromide] was synthesized using a previously reported method *via* the Suzuki reaction.<sup>2</sup> A mixture of 2,7-dibromo-9,9-bis(6'-bromo-hexyl)fluorene (325 mg, 0.5 mmol), 1,4-phenyldiboronic acid (82.9 mg, 0.5 mmol), Pd(dppf)Cl<sub>2</sub> (7 mg) and potassium carbonate (830 mg, 6 mmol) in water (3 mL) and THF (6 mL) was vigorously stirred at 85 °C for 24 h under nitrogen atmosphere. Cooled and methanol was added, the resulting precipitate was filtered and washed with methanol and acetone, and then dried under vacuum to afford the neutral polymer as a yellow solid

(200 mg, 70.9%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.8 (m, 5H), 7.7-7.6 (m, 4H), 7.5 (m, 1H), 3.3 (t, 4H), 2.1 (m, 4H), 1.7 (m, 4H), 1.3-1.2 (m, 8H), 0.8 (m, 4H). FT-IR (KBr disk,  $\text{cm}^{-1}$ ): 3448, 3025, 2961, 2929, 2853, 1461, 1261, 1096, 1022, 809, 758, 698, 642, 561. GPC (THF, polystyrene standard),  $M_w$ : 37,449 kg/mol;  $M_n$ : 12,833 kg/mol; PDI: 2.9.

The final water solution of PFP (polymer 2, Figure S1) was obtained by treating the neutral polymer with condensed trimethylamine. Briefly, 30% trimethylamine (2 mL) was added dropwise to a solution of polymer 1 (60 mg) in THF (10 mL) at  $-78\text{ }^\circ\text{C}$  and then the mixture was allowed to warm to room temperature. The precipitate was re-dissolved by the addition of water (10 mL). After the mixture was cooled down to  $-78\text{ }^\circ\text{C}$ , extra 30% trimethylamine (2 mL) was added, and the mixture was stirred at room temperature for 24 h. After removing the solvent, acetone was added to precipitate PFP as a yellow powder (60 mg, 74.2%).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ , ppm):  $\delta$  7.9-7.8 (m, 10H), 3.2 (t, 4H), 3.0 (s, 18H), 2.3 (br, 4H), 1.6 (br, 4H), 1.2 (br, 8H), 0.8 (br, 4H). FT-IR (KBr disk,  $\text{cm}^{-1}$ ): 3409, 3022, 2928, 2856, 1606, 1462, 1259, 1095, 965, 908, 817, 744, and 599.

## 5. $\text{K}^+$ Assay

All experiments were performed in 10 mM Tris (pH 7.4) containing 100 mM  $\text{MgCl}_2$ . For  $\text{K}^+$  assay, a solution containing 80 nM of P and different concentrations of  $\text{K}^+$  was incubated for 20 min at room temperature, then 10.0  $\mu\text{L}$  of 500  $\mu\text{g}/\text{mL}$  GO was added into the solution. After the mixture was incubated for 10 min at room temperature, 30.0  $\mu\text{L}$  of 28.63  $\mu\text{M}$  PFP in repeat units was added and incubated for 20

min at 4 °C. Then the fluorescence emission spectra were recorded immediately. The same procedures were repeated in the presence of other metal ions instead of K<sup>+</sup> to assess the selectivity.

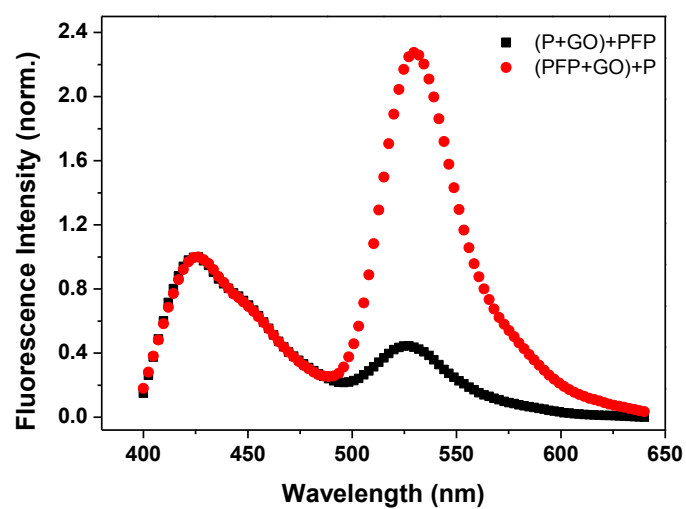


Figure S1. Normalized fluorescence spectra of P-GO-PFP system under different addition order. Black: addition PFP into P/GO complex; Red: addition P into PFP/GO complex. Excitation: 370 nm.

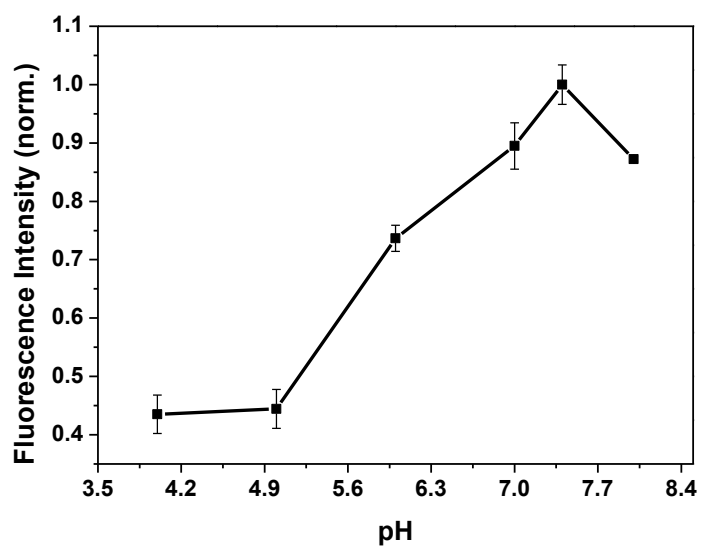


Figure S2. Normalized fluorescence intensities of P-GO-PFP system under different pH. Excitation: 370 nm.

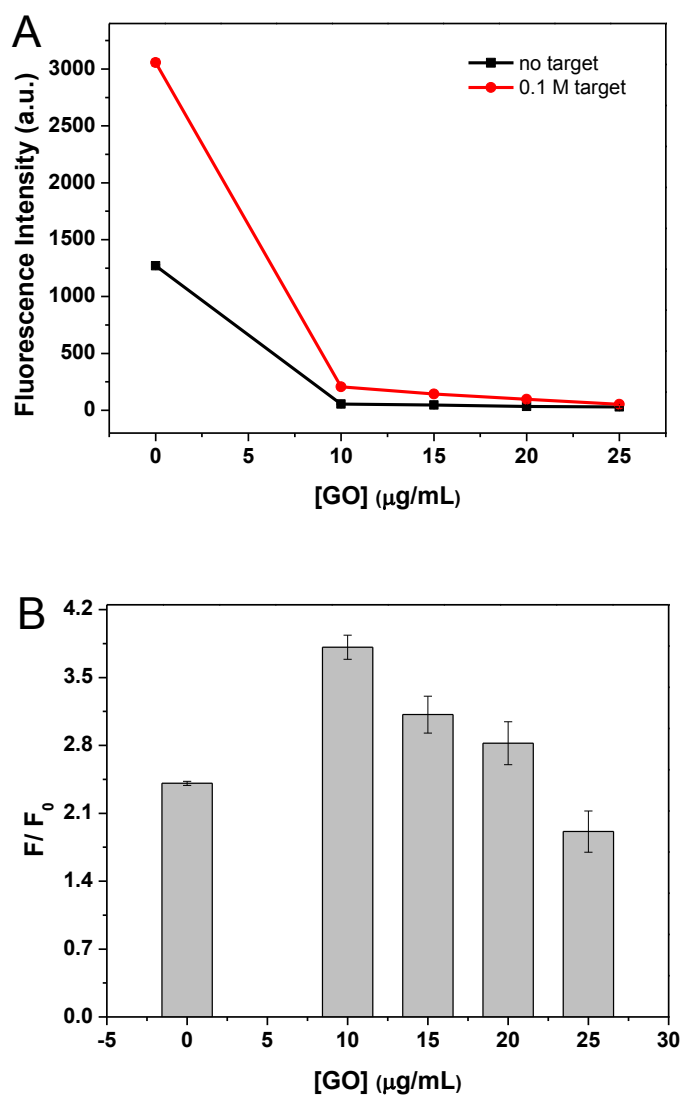


Figure S3. (A) Effect of GO concentration on the fluorescence intensity of P without and with target. (B) The fluorescence enhancement of P by 0.1 M  $K^+$  as a function of GO concentration. P, 80.0 nM. Excitation: 480 nm.



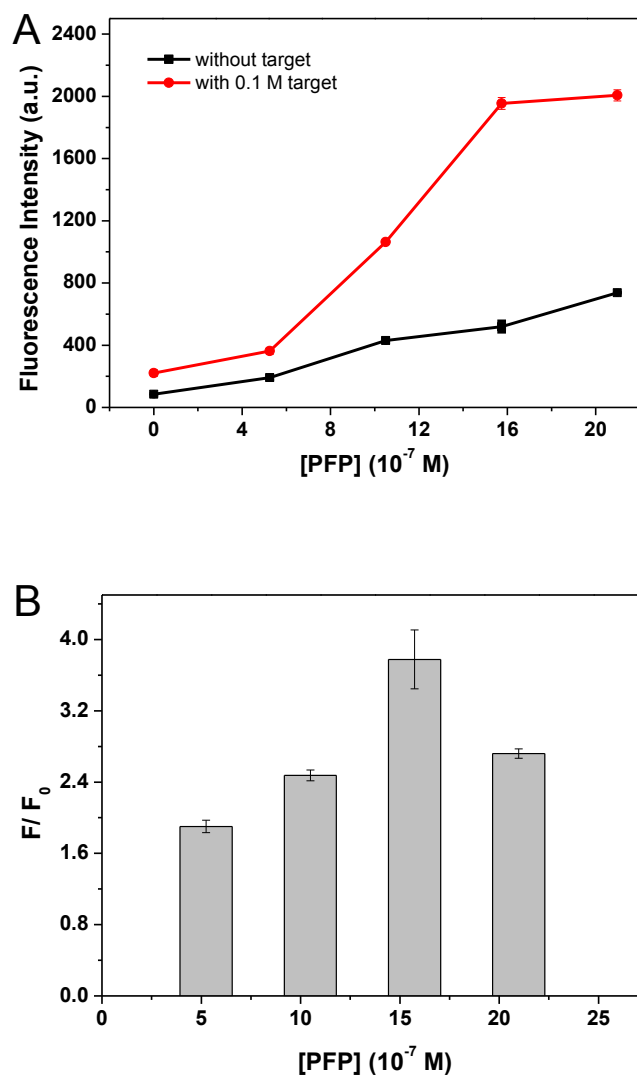
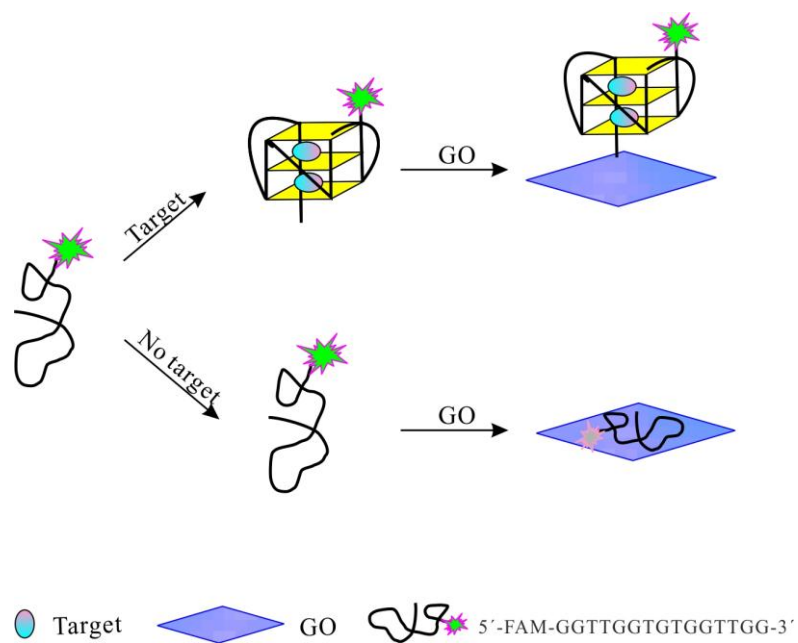


Figure S4. (A) Effect of PFP concentration on the FRET induced fluorescence intensity at 525 nm without and with target. (B) The fluorescence enhancement of the assay system by 0.1 M  $K^+$  as a function of PFP concentration. P, 80.0 nM; GO, 10.0  $\mu$ M. Excitation: 370 nm.



Scheme S1. Schematic representation of GO-based platform without PFP for the detection of  $K^+$ .

**Table S1.** The fluorescence intensity of GO-based platform without PFP.

<b>[K<sup>+</sup>] (mM)</b>	<b><i>F</i> (a.u.)</b>	<b><i>Relative error</i> (%)</b>
0	30.86	2.8434
0.2	34.94	5.8387
0.6	24.38	5.4077
1	36.30	5.7369
2	33.34	0.4267
4	30.74	0.2836
6	39.61	3.1444
10	54.78	2.5904
20	63.68	3.4356
30	82.16	5.1051
40	114.63	2.1814

**Table S2.** Comparison of detection limit between the proposed method with other reported indicator dyes based methods for K<sup>+</sup>.

Indicator dye	Linear range	LOD	References
Benzofuran isophthalate	7-305 mM	1.2 mM	3
Polydiacetylene (PDA) liposome	Not given	0.5 mM.	4
4-acrylamidobenzo-18-crown-6 residues	Not given	3.6 μM	5
TPE-(B15C5)4	Not given	1.0 μM	6
3,6-bis(dimethylamino)xanthylum	0-50 mM	Not given	7

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