Supporting Information

Label-free Dual Assay of DNA Sequences and Potassium Ions Using an Aptamer Probe and a Molecular Light Switch Complex

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Experimental Section

Materials and Instrumentation. Water was purified with a MilliQ purification system. *rac*-$Ru(phen)_2(dppz)^{2+}$ (**1**) was prepared as described elsewhere[1]. All oligonucleotides were purchased from JenoTec Inc. (Deajeon, Korea) and were purified by HPLC using a Thermo hypersyl gold column (0.46 x 25 cm). Other chemicals were purchased from Aldrich. Oligonucleotide concentrations were determined spectrophotometrically monitoring the absorbance at 260 nm, ε = 6600 M^{-1} cm^{-1} on a Hewlett-Packard 8452A diode-array spectrometer. Once single-stranded DNA concentrations were known, equal molar amounts of target DNA were mixed, annealed at 90 °C for 10 min, and then allowed to slowly cool to room temperature to prepare the double-stranded DNA. The G-quadruplex form of **P** was prepared with 0.4 μM **P** in the presence of 1.6 mM K^+. The mixed solution of **P** and K^+ was warmed to 70 °C for 30 min and cooled down to form the G-quadruplex form.

Optical rotations were determined at ambient temperature using a JASCO J-810 polarimeter. Emission spectra were collected on a Perkin-Elmer LS 55 luminescence spectrophotometer and the temperature held constant by a water thermostat.

DNA sequence analysis and mismatch detection. In a typical experiment, a sample containing the G-quadruplex form of 0.4 μM **P** and 1.6 mM potassium ions dissolved in buffered aqueous solution containing 5 mM Tris-HCl buffer (pH = 7.4) was mixed with 0.4 μM matched or mismatched oligonucleotides (**T1-T5**) for 5 min at room temperature. Then, $Ru(phen)_2(dppz)^{2+}$ (4 μM) was added and then emission spectra were taken after 1 min. Each target was suspended in the buffer so that the composition of the buffer did not change in the final solution.

Time-dependent fluorescence measurement. The vials containing the G-quadruplex form of 0.4 μM **P** was prepared in 5 mM Tris-HCl buffer (pH = 7.4) at 4 °C. **T1** (0.4 μM) was treated to all vials at the same time, and then $Ru(phen)_2(dppz)^{2+}$ (4 μM) was mixed 1 min

before the fluorescence emission measurement of the solution in each vial at a specific time. The data points were obtained from the average of three independent measurements.

Detection of potassium ions. The solution of **P**/**T1** (0.4 μM) mixed with a certain amount of potassium or other metal ions was heated to 70 °C for 30 min and cooled down quickly by placing it in a ice bath. Then, the emission fluorescence of **1** was taken right after the solution was warmed to room temperature. The data points were obtained from the average of three independent measurements.

References

[1] (a) A. E. Friedman, J.-C. Chambron, J. P. Sauvage, N. J. Turro, J. K. Barton, *J. Am. Chem. Soc.* **1990**, *112*, 4960. (b) Y. Jenkins, A. E. Friedman, N. J. Turro, J. K. Barton, *Biochemistry*, **1992**, *31*, 10809.

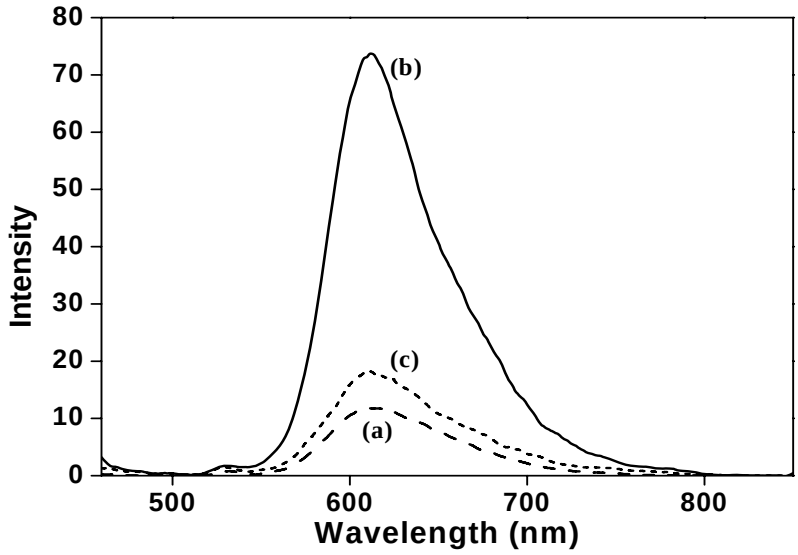
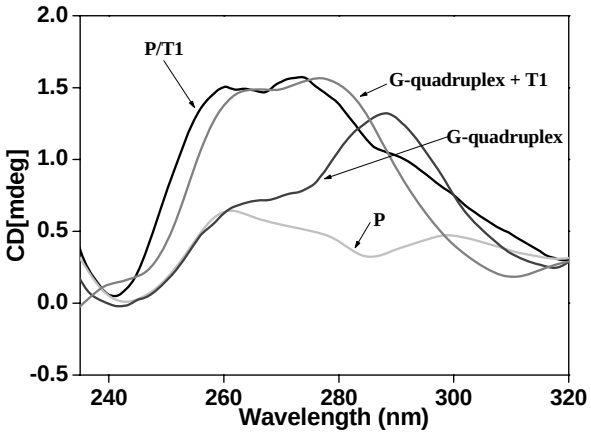


Figure S1. Comparison of fluorescence emission observed for 4 μM solution of **1** in the presence of (a) 0.4 μM **P**, (b) the double-stranded **P/T1**, and (c) the quadruplex generated with **P** and 1.6 mM K^+. Solution: 5 mM Tris-HCl (pH 7.4); excitation wavelength: 450 nm. The fluorescence intensities are plotted in arbitrary units (au).

a)



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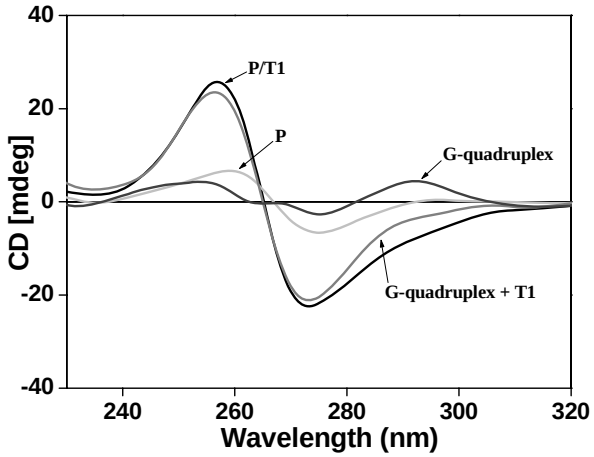

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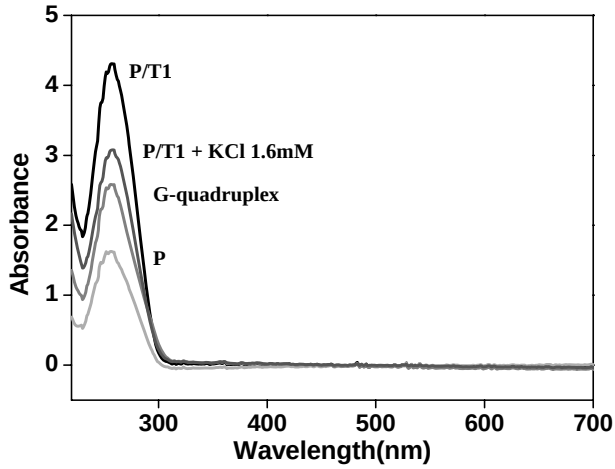

Figure S2. (a)(b) CD spectra and (c) UV-vis spectra of the solutions of **P** (0.4 μM), **P**/**T1**, the G-quadruplex of **P** formed in the presence of 1.6 mM K^+, and the G-quadruplex form treated with **T1** at room temperature in 5 mM Tris-HCl buffer at pH 7.4. In the case of (b), all four samples were measured in the presence of **1**.

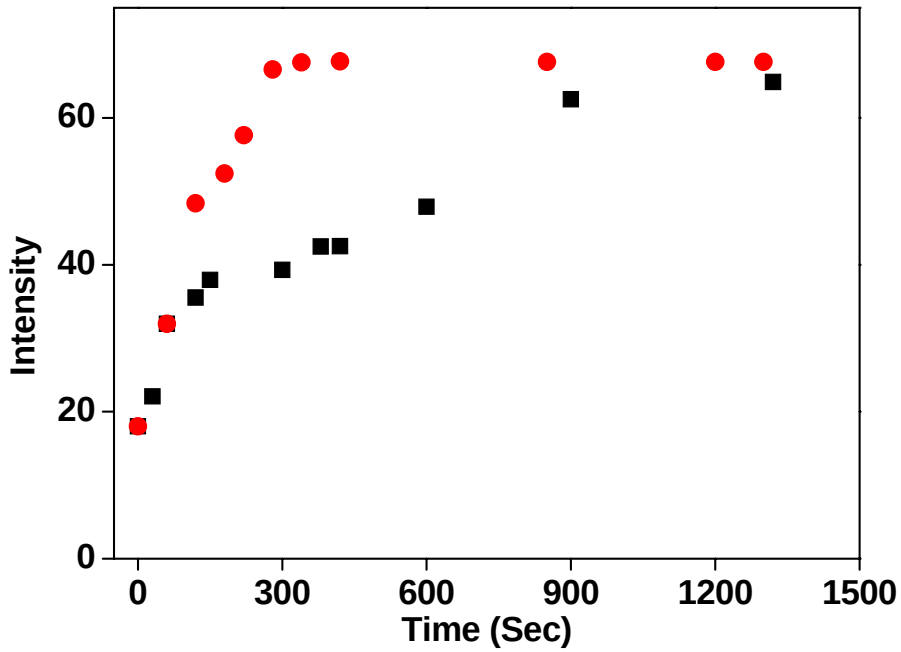

Figure S3. Time-dependent change of fluorescence intensities of the solutions after adding **T1** to **P** (each 0.4 μM, ●) and the G-quadruplex structure of **P** (prepared with 1.6 mM K^+, ■) at 610 nm at 4 °C.

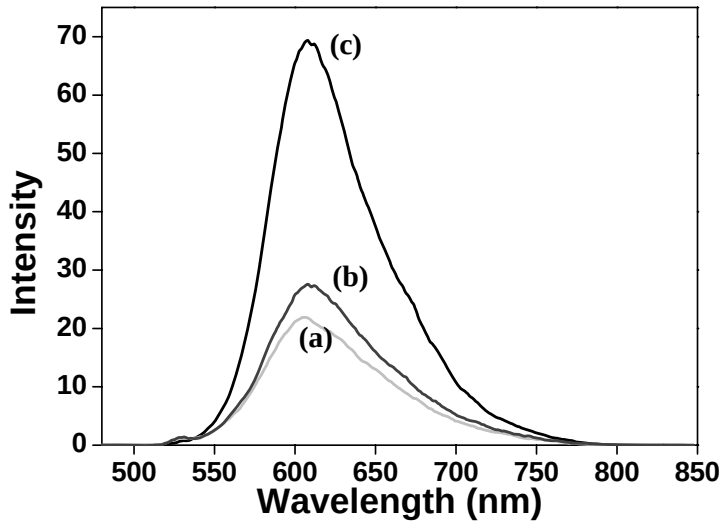

Figure S4. Fluorescence emission spectra of 4 μM **1** in the solutions containing (a) the G-quadruplex form of **P** (0.4 μM) prepared with 1.6 mM K^+, (b) the G-quadruplex form treated with **T2** (0.4 μM) for 5 min at room temperature, and (c) the G-quadruplex form treated with **T2** (0.4 μM) for 5 min and then **T1** (0.4 μM) for 10 min.

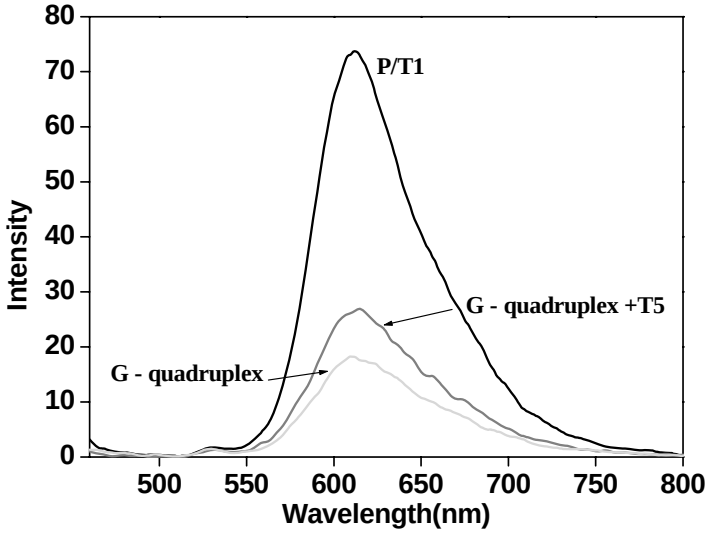

Figure S5. Fluorescence emission spectra of the solutions containing the double-stranded **P**/**T1** (0.4 μM), the G-quadruplex form of **P** (0.4 μM), and the G-quadruplex form of **P** treated with **T5** (0.4 μM).

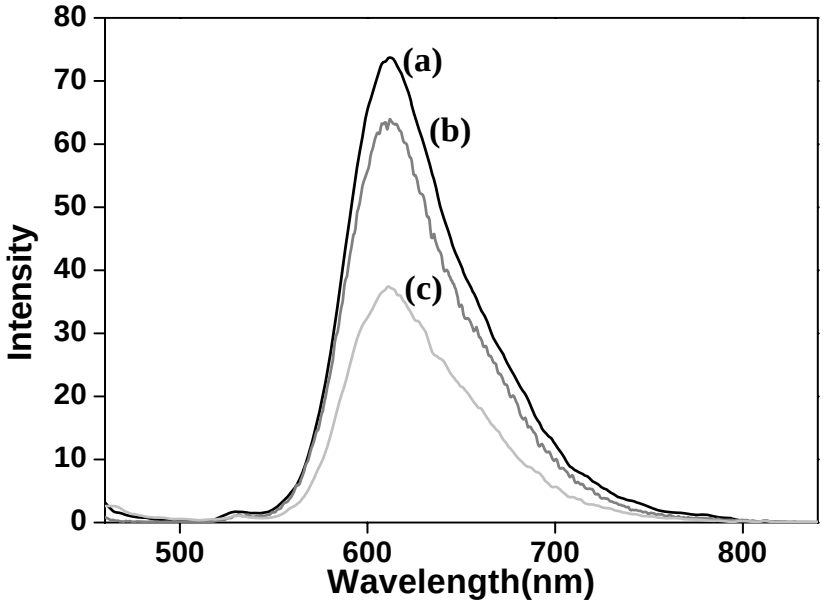

Figure S6. Fluorescence spectra acquired using λ_{ex} = 450 nm: (a) 0.4 μ M **P**/**T1**, (b) **P**/**T1** mixed with 1.6 mM K^+ at room temperature, and (c) **P**/**T1** treated by heating and fast cooling in the presence of 1.6 mM K^+.

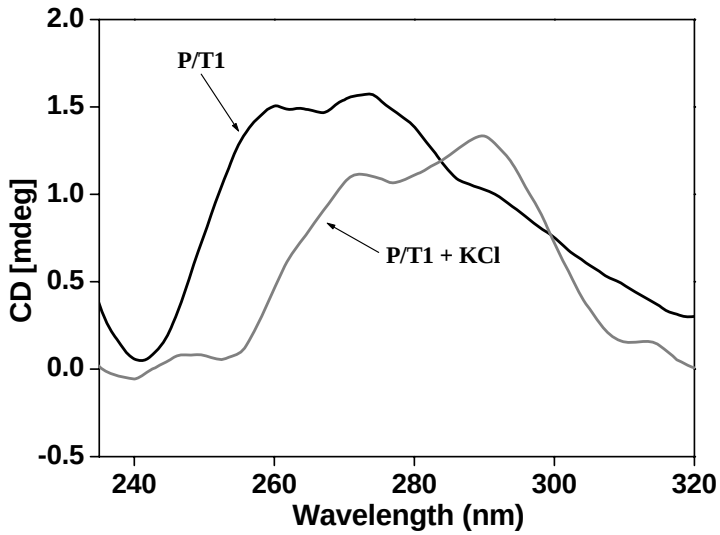

Figure S7. CD spectra of **P**/**T1** (0.4 μM), and **P**/**T1** and 1.6 mM K^+ prepared by the treatment of heating and fast-cooling in 5 mM Tris-HCl buffer at pH 7.4.

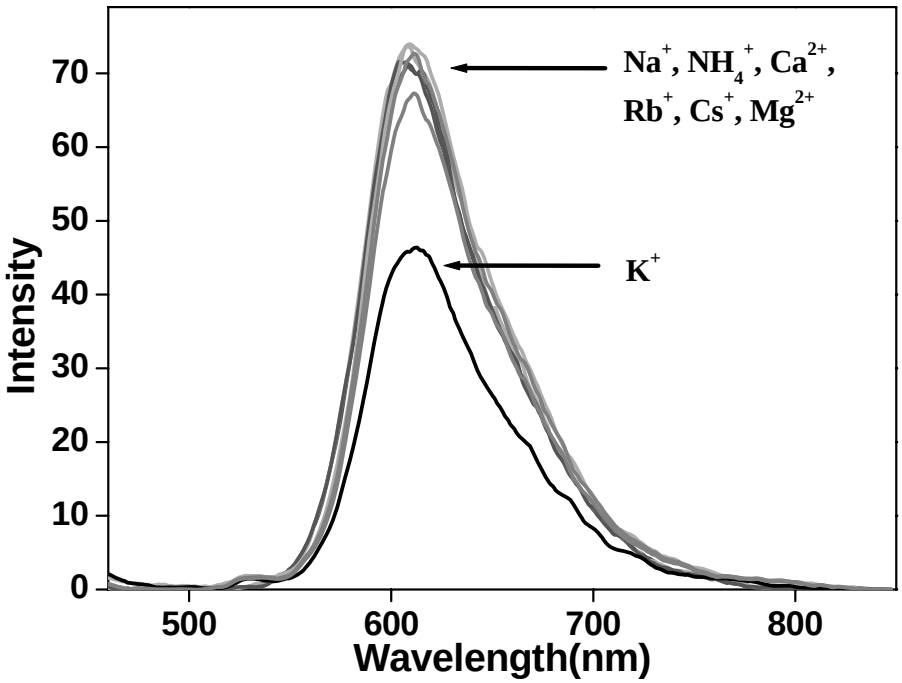

Figure S8. Fluorescence spectra of the solutions of 0.4 μM **P/T1** duplex after the treatment of heating and fast-cooling in the presence of selected cations (0.48 mM), in 5 mM Tris-HCl buffer, pH 7.4, excitation at 450 nm.

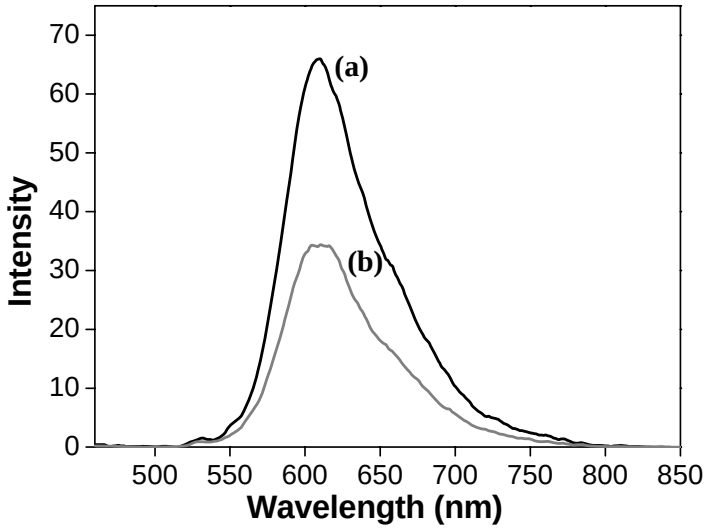

Figure S9. Fluorescence spectra of the solutions of 0.4 μM **P/T1** duplex after the treatment of heating and fast-cooling in the presence of (a) 50 mM Na^+ and (b) 1.6 mM K^+ and 50 mM Na^+, in 5 mM Tris-HCl buffer, pH 7.4, excitation at 450 nm.