Supporting Information

Materials. All of the following oligonucleotides were purchased from Invitrogen Technology (Shanghai, China). The sequences were as following: G4TTA (5'-TTAGGG TTAGGG TTAGGG TTAGGG-3'); ss-DNA (5'-CCCTAA CCCTAA CCCTAA CCCTAA-3'); bcl2 (5'-GGGCGC GGGAGG AATTGG GCGGG-3'); Pu18 (5'-AGGGTGGGGAGGGTGGGG-3'); c-kit (5'-GGGCGGGCGCGAGGGAGGGG-3'); vegf (5'-GGGCGG GCCGGG GGCGGG-3'). F21T (*FAM*-$G_3[TTAG_3]_3$-*Tamra*, *FAM*: 6-carboxyfluorescein, *Tamra*: 6-carboxytetramehtylrhodamine) was purchased from TaKaRa, Dalian, China, which was used in FRET melting experiment.

Fluorescent Experiments. Samples for fluorescent detection are prepared as following: The solutions (10 mM tris-HCl, pH 7.4, 100 mM KCl) with DNA and Ru-complex compound were maintained at 37 °C for about 2 h to achieve the equilibrium, whereafter iodide ions (50 mM NaI with 0.1 mM $Na_2S_2O_3$ which can prevent iodide ions being oxidized) were added before detection. Fluorescent spectra were detected by F900 (Combinal Steady-stata and Lifetime Spectrometer) at room temperature with excitation wavelength 468 nm, Exslit 5.00 nm, and Emslit 1.50 nm.

Circular Dichroic Studies. CD experiments utilizing a Jasco-810 spectropolarimeter (Jasco, Easton, MD, USA) were measured at room temperature using a quartz cell with a 1 cm path length; CD spectra were collected from 220 to 320 nm and with a scanning speed of 200 nm/min. The bandwidth was 5 nm, and the response time was 2 s. All CD spectra were baseline-corrected for signal contributions due to the buffer.

Colorimetric Experiments. 250 nM Ru-complex and different concentration of oligonucleotides were incubated in 37 °C for 2 h in Tris-HCl, pH 7.4 and 100 mM KCl. The concentrations of ssDNA, dsDNA, CT-DNA (per basepair for CT-DNA) and G4TTA were the same as Ru-complex, namely, 250 nM, and the concentrations of other four sequences, pu18, ckit, bcl2 and vegf, were half of Ru-complex, namely, 125 nM. The total volume of every sample was 1 mL. After incubation, all the samples were treated by adding NaI (the final concentration of iodide ions was 50 mM) and photographed under irradiation of UV light (Vilber Lourmat, Bio-Print, VL).

FRET melting Assay.[1] It is performed with a real-time PCR machine (Rotor-Gene 2000, Corbett, Australia), using a total reaction volume of 20 μL, with 0.5 μM of labelled oligonucleotide and different concentrations of Ru-complex in a buffer containing 10 mM Cacodylate Lithium, pH 7.4 and 100 mM KCl. After non-Ru-complexe samples were boiled at 95°C for 5 minutes first and then cooling down to room temperature to form G-quadruplex structures, we added the different concentrations of Ru-complex into different samples. Then we lay them at 25°C for 30 minutes. Following experiments should keep the temperature procedure in real-time PCR and procedure was finished as following: 30°C for 5 minutes, then a stepwise increase of 1°C every minute from 30°C to reach 95°C. During the procedures, we measured the FAM after each stepwise.

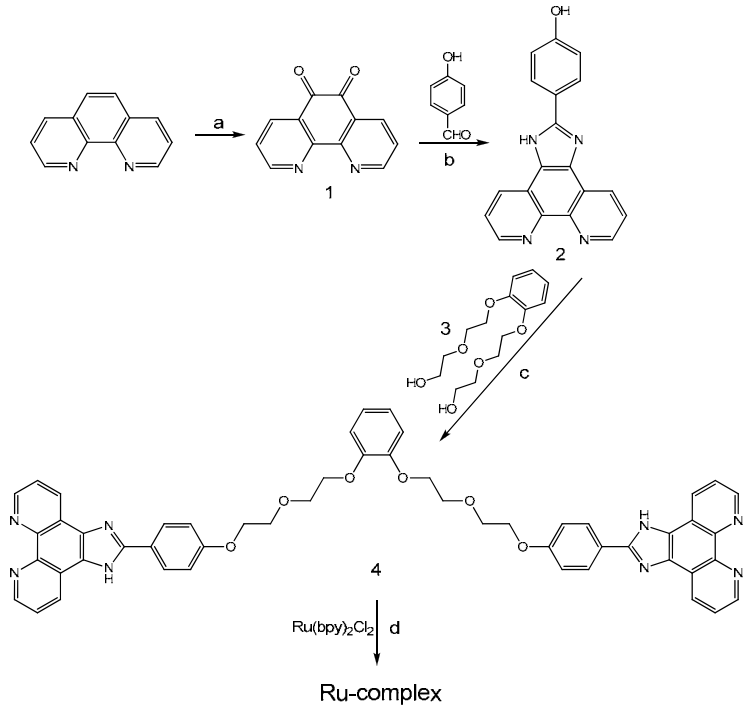
SPR experiments. The measurements were finished by using BIAcore 3000 optical biosensor system (BIAcore AB, Uppsala, Sweden) using a CM5 sensor chip covered streptavidin by an Amine Coupling Kit. Experimental procedures were described in the reported papers.[2]

References:

1. P. Yang, A. De Cian, M.-P. Teulade-fichou, J.-L. Mergny, D. Monchaud, *Angew. Chem. Int. Ed.*, **2009**, 48, 2188-2191.

2. a) Z. A. E. Waller, P. S. Shirude, R. Rodriguez, S. Balasubramanian. *Chem. Commun.*, **2008**, 1467-1469; b) H. Ma, M. Zhang, D. Zhang, R. Huang, Y. Zhao, H. Yang, Y. Liu, X. C. Weng, Y. Y. Zhou, M. G. Deng, L. Xu, and X. Zhou, *Chem. Asian. J.* **2009**, accepted for publication

Synthesis of Ru-complex.



The Compound **1**, **2** and **3** are synthesized with reported methods.[1-3]

Synthesis of compound **4**. A mixture of compound 2 (297 mg, 0.5 mmol), 3 (343 mg, 1.1 mmol) and K_2CO_3 (500 mg) in dry DMF (20 mL) was heated at 120 °C under N_2 for 24 h. The reaction mixture was filtered and then concentrated under reduced pressure. The crude product purified by column chromatography over silica gel (eluent: 9/1 $CHCl_3/CH_3OH$ and then 7/1) to afford 2 (107 mg, yield 24.5%) as a brown solid.

^{1}H NMR (300 MHz, [D6] DMSO) δ = 3.92-3.96 (m, 8H), 4.21-4.26 (m, 8H), 6.97 (br, 2H), 7.07 (br, 2H), 7.20 (br, 4H), 7.83 (br, 4H), 8.22 (br, 4H), 8.90-9.03 (m, 8H), 13.60 (br, 2H) ppm.

ESI-MS: *m/z*: 875.5 ($M+H^+$).

HRMS(ESI): *m/z*: calculated for: 875.3306 ($M+H^+$); found: 875.3308 ($M+H^+$).

Synthesis of Ru-complex. Compound **4** (21.9 mg, 0.025 mmol) and $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (26 mg, 0.05 mmol) was dissolved into 30 mL methanol. The mixture was refluxed for 4 h, then filtered and concentrated under reduced pressure. The crude product purified by column chromatography over neutral Al_2O_3 (eluent: 10/1 $CHCl_3/CH_3OH$), and then recrystallized with methanol and Et_2O to afford pure 1 (38 mg, yield 82.6%) as a red solid.

^{1}H NMR (600 MHz, [D6] DMSO) δ = 3.84(br, 4H), 3.88 (br, 4H), 4.15(br, 4H), 4.19 (br, 4H), 6.89-6.91 (m, 2H), 7.01-7.02 (m, 2H), 7.08 (br, 4H), 7.34-7.36 (m, 4H), 7.57-7.59 (m, 8H), 7.60 (br, 4H), 7.86-7.88 (m, 8H), 8.08-8.10 (m, 4H), 8.18-8.22 (m, 4H), 8.38 (br, 4H), 8.85 (br, 4H), 8.88-8.90 (m, 4H), 9.17 (br, 4H) ppm.

HRMS(ESI): *m/z*: calculated for: 425.6011 ([M-4Cl$^-$]/4); found: 425.6028 ([M-4Cl$^-$]/4).

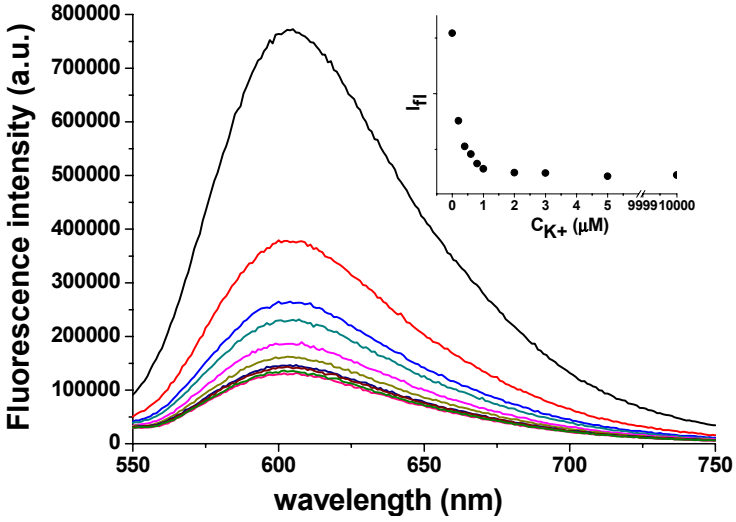
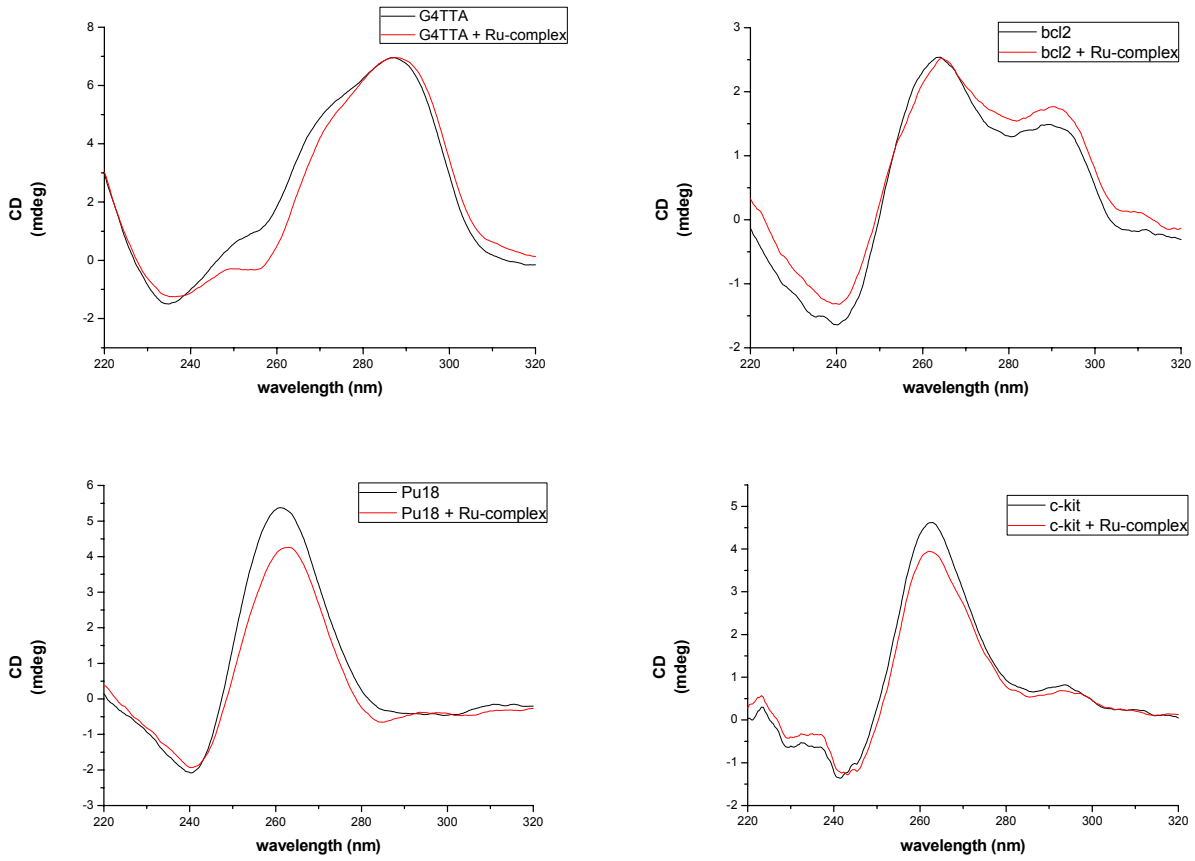


Figure S1. Fluorescence spectra of Ru-complex at 1 μM by adding K+ from 0.2 μM to 10 mM in water. The inset shows the fluorescence intensity at 604 nm during the titration.



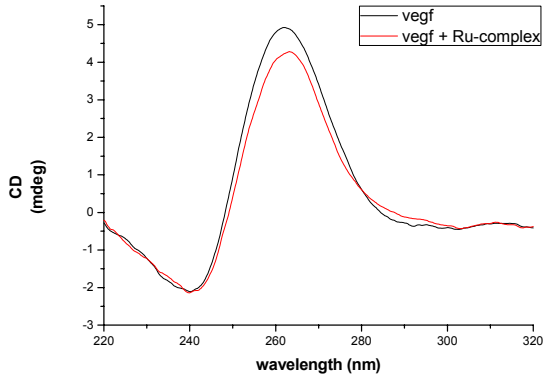


Figure S2. CD spectra of these G-quadruplxes. All of CD spectra were detected under this condition: Tris-HCl 10mM, pH 7.4, KCl 100mM.

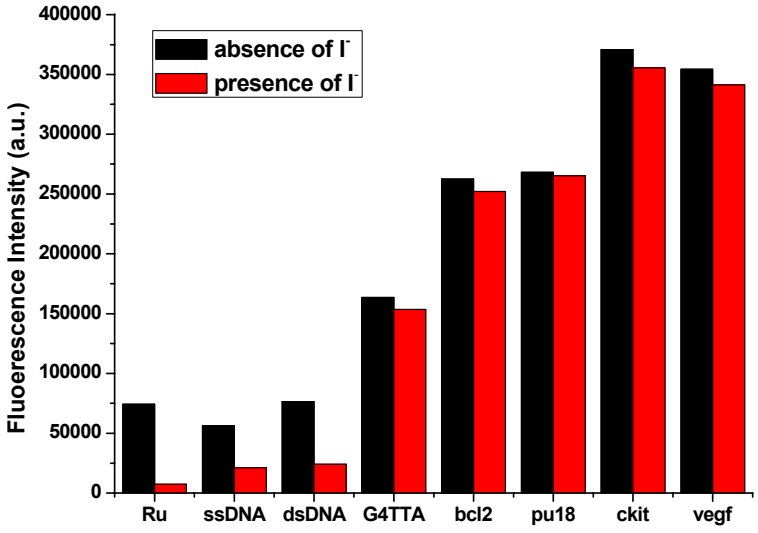


Figure S3. Influence of iodide ions. The black bar diagrams refer to iodide-absent systems. The red bar diagrams refer to iodide-present systems ([NaI] = 50 mM). Conditions: Tris-HCl 10mM, KCl 100mM, [Ru-complex] = 0.5 μM; the concentrations of all DNA are 1μM.

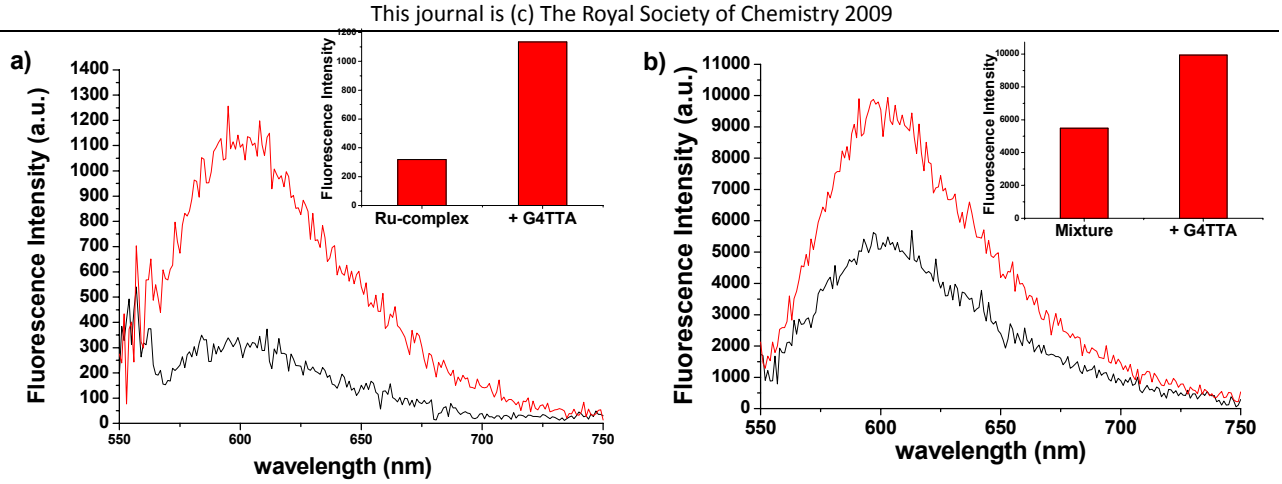


Figure S4. Detection limit of telomeric quadruplex DNA. (a) Fluorescence spectra of Ru-complex (15 nm) before addition of 20 nM G4TTA (black curve) and after addition of 20 nM G4TTA (red curve). The inset shows comparison of fluorescent intensity at 603 nm. (b) Fluorescence spectra of Ru-complex (50 nm) in the mixture with 1 μM dsDNA in the absence of 50 nM G4TTA (black curve) and presence of 50 nM G4TTA (red curve). The inset shows comparison of fluorescent intensity at 603 nm. Even 20 nM G-quadruplex structure in this system can be revealed by 15nM Ru-complex. This high sensitivity can also be observed in the mixture of G-quadruplex and duplex structures. In the solution within 1uM duplex DNA, 50nM quadruplex can be detected by Ru-complex.

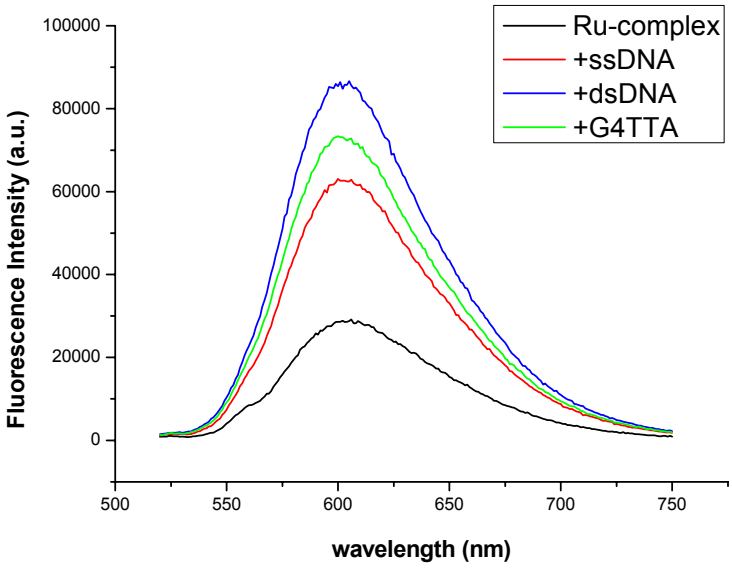


Figure S5. Fluorescence behavior of Ru-complex with non-quadruplex telomeric DNA. Conditions: Tris-HCl 10mM, LiI 100mM.

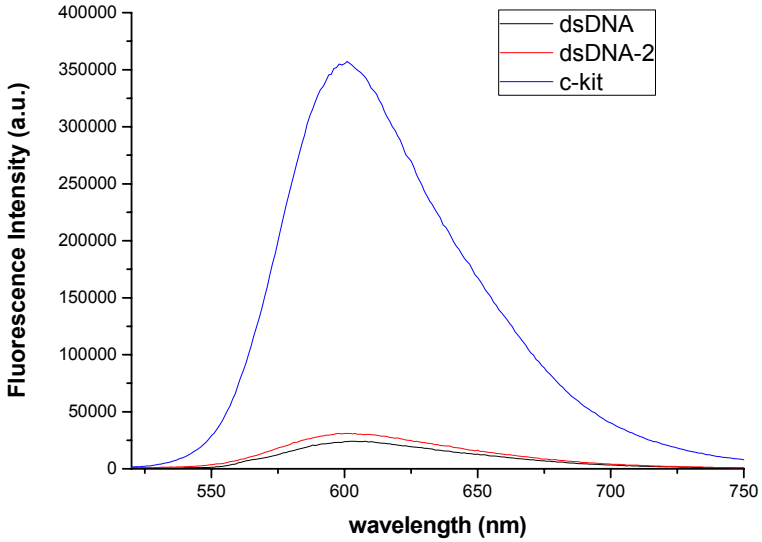
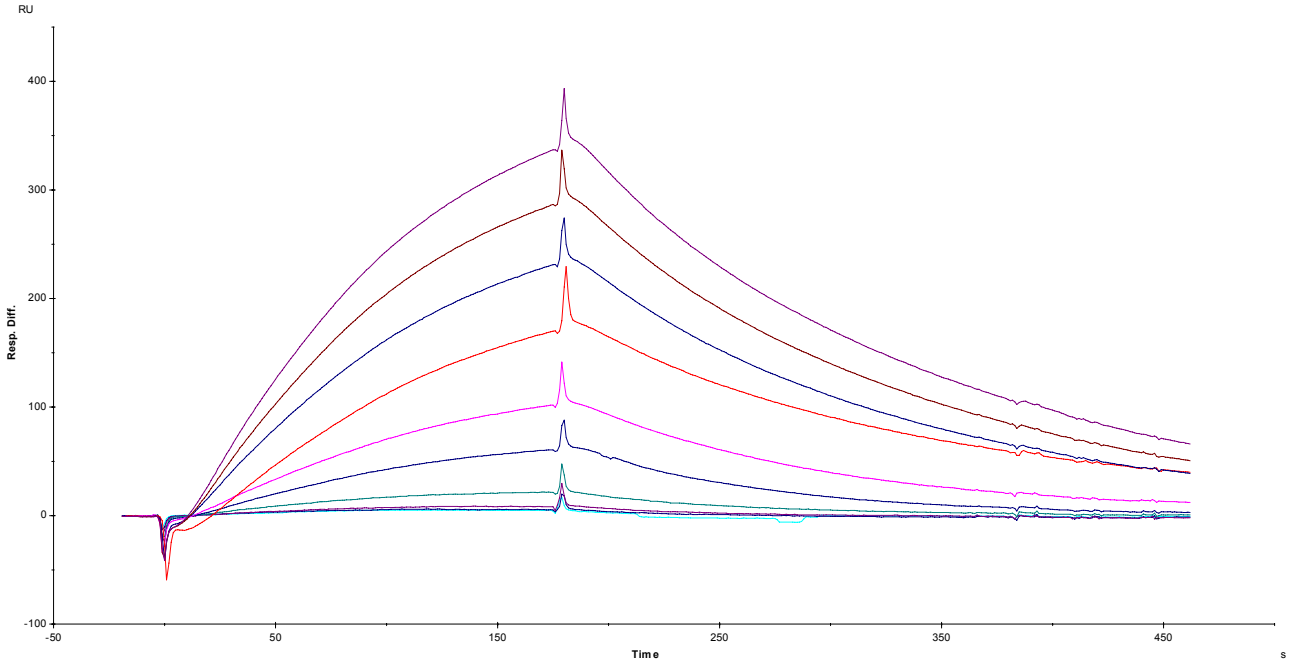


Figure S6. Fluorescence behavior of Ru-complex (0.5 μM) with another duplex DNA (dsDNA-2). dsDNA-2 is the duplex formed by the sequence 5'-TTAGGGTTAGGGTTAGAATTAGGG-3' and its complimentary sequence. The concentrations of DNA are all 1 μM.



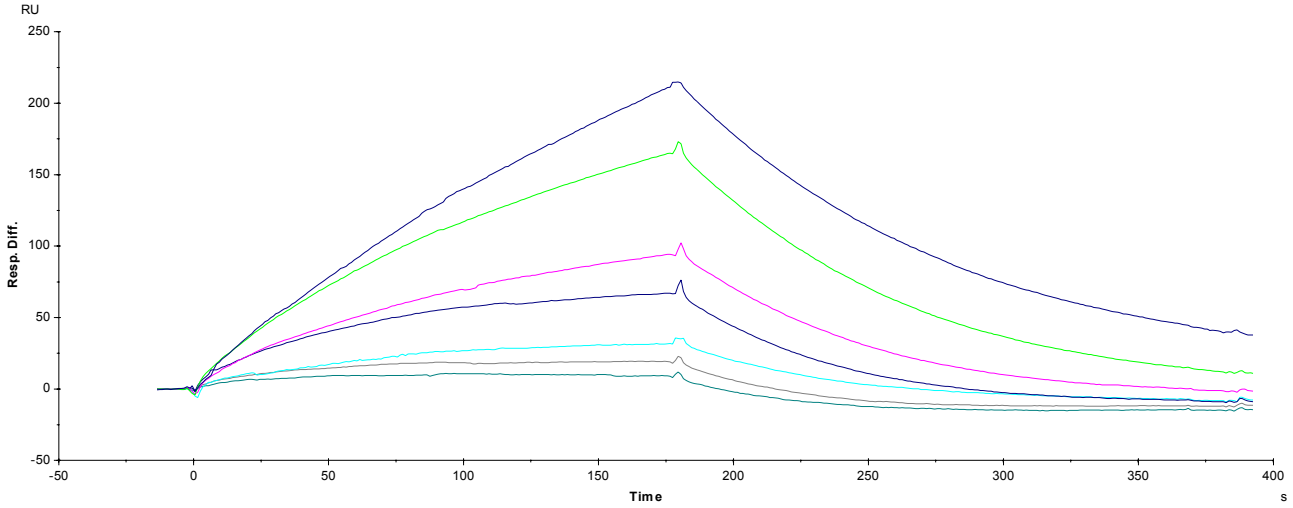


Figure S7. SPR sensorgram overlay for binding of Ru-complex to G-quadruplex (above) and duplex (below) at 25 °C. The unbound ligand concentrations in the flow solution were 10, 20, 40, 60, 80, 100, 120, 140, 160, 180 nM from the lowest curve to the top curve for G-quadruplex, and the unbound ligand concentrations in the flow solution were 20, 30, 40, 50, 60, 80, 100 nM from the lowest curve to the top curve for duplex.

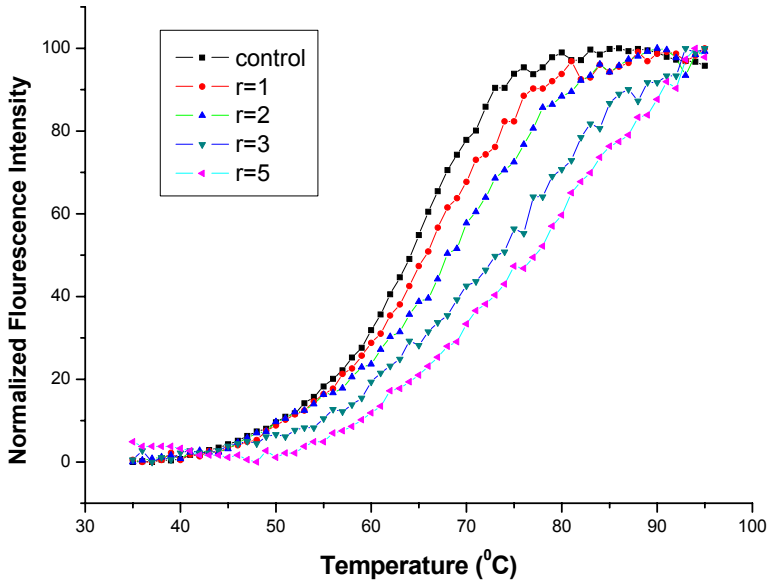


Figure S8. FRET melting curves for experiments carried out with F21T (0.5μM) in 10 mM Tris-HCl buffer, 100 mM KCl with Ru-complex. r: [Ru-complex]/[DNA].

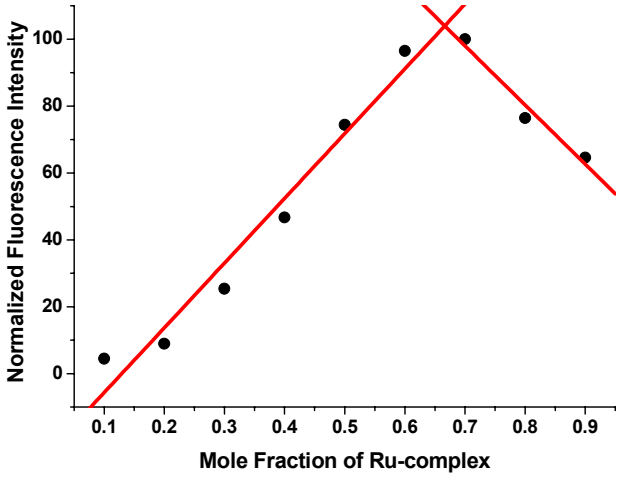


Figure S9. Job Plot of Ru-complex with telomeric quadruplex DNA. Total concentration was maintained at 1μM.

References:

1 J.-Z. Wu, L. Li, T.-X. Zeng, L.-N. Ji, J.-Y. Zhou, T. Luo, and R.-H. Li, *Polyhedron,* **1997**, *16*, 103-107.

2 E. A. Steck, and A. R. Day, *J. Am. Chem. Soc.* **1943**, *65*, 452–456.

3 I. Satoshi, K. Kazuya, F. Katsuhiko, K. Naohiro, I. Tsukasa, O. Toru, and H. Kazuhisa, *Tetrahedron Letters* **2006**, *47,* 8563–8566.