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Supporting Information

Photo-Oxidizing Ruthenium(II) Complexes with Enhanced Visible-Light Absorption and G-quadruplex DNA Binding Abilities

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Figure S1. ¹H NMR spectrum of bpph (*Benzo[a]pyrazino[2,3-h]phenazine*) (300 MHz, CDCl₃)



Figure S2. ¹H NMR spectrum of [Ru(phen)₂bpph]²⁺ (300 MHz, CD₃CN)





2. High-Resolution Mass Spectrometry



Elemental Composition Results

m/z	Formula	Score	Delta ppm	OriginalFormula
283.09773	C ₁₈ H ₁₁ N ₄	100.00	-0.33	C18H11N4

Table S1. HRMS data for *bpph* benzo[*a*]pyrazino[2,3-*h*]phenazine



Elemental Composition Results

m/z	Formula	Score	Delta ppm	OriginalFormula	Theo. Mass
883.09951	$C_{42}H_{26}N_8F_6P^{96}Ru$	96.10	0.27	C42H26N8F6P[96]Ru	883.09927

Table S2. HRMS data for [Ru(phen)₂bpph]²⁺



Table S3. HRMS data for [Ru(TAP)₂dph]²⁺

3. G4 DNA Model



Figure S5: Biomolecular model used for bio-layer interferometry studies wtTel23 intramolecular Gquadruplex structure.

4. DNA Titrations



Figure S 6: Absorption and emission spectra of complex 1 in the presence of 0 to 50 base pair equivalents of CT-DNA. Measurements were performed using 1 μ M of complex in Tris·HCl buffer 5 mM, NaCl 50 mM at pH 7.5 under ambient air conditions.



Figure S 7: Absorption and emission spectra of complex 2 in the presence of 0 to 50 base pair equivalents of CT-DNA. Measurements were performed using 1 μ M of complex in Tris·HCl buffer 5 mM, NaCl 50 mM at pH 7.5 under ambient air conditions.



Figure S 8: Absorption and emission spectra of complex 3 in the presence of 0 to 50 base pair equivalents of CT-DNA. Measurements were performed using 1 μ M of complex in Tris·HCl buffer 5 mM, NaCl 50 mM at pH 7.5 under ambient air conditions.



Figure S 9: Absorption and emission spectra of complex 4 in the presence of 0 to 50 base pair equivalents of CT-DNA. Measurements were performed using 1 μ M of complex in Tris·HCl buffer 5 mM, NaCl 50 mM at pH 7.5 under ambient air conditions.

5. Fitting via a McGhee-von Hippel type equation

Titrations with the duplex CT-DNA or G-quadruplexes wtTel23 DNA were used to estimate the binding affinity of the complex for double stranded DNA and G4 sites. In order to evaluate this binding affinity, we used a McGhee-von Hippel type equation.

 $C + Site \rightleftharpoons [C_Site]$ (eq.1) $K_{ass} = \frac{[C_Site]}{[C][Site]}$ (eq.2)

where K_{ass} describes the binding equilibrium between the complex, *C*, and the site of interaction, *Site*, either a base pair stack in ds-DNA or a G-quartet motif in G-quadruplex DNA. The total concentration of complex as C_c ; this is kept constant throughout the titration. We can then define the various molar fractions for the complex as follows:

$$f = \frac{[C]}{c_c}$$
, the molar fraction of free complex.
 $b = \frac{[C_site]}{c_c}$, the molar fraction of complex bound to DNA.

Additionally, we express the total concentration of hairpin as C_{DNA} ; this value increased throughout the titration. The variable *R* is introduced as being equal to the ratio C_{DNA}/C_C , and in our titration the luminescence of the complex is measured as a function of this ratio *R*. The ratio of luminescence intensity, I/I_0 , can be expressed as a function of *R* as follows:

$$I/I_0 = f + \alpha b \tag{eq.3}$$

where α is equal to the relative emissivity of complex associated with *DNA*, compared to the emission of the complex free in solution.

Another parameter is defined: p, the occupational factor which takes into account (*i*) for ds-DNA the possible inhibition of intercalation of two complexes in close vicinity of each other's; the actual *Site* with which the complex can interact is thus: p. [*Site*], with $p \ge 1$. (*ii*) for G4, this same factor is used to take into account that more than one complex could interact with the G4 site (and thus $p \le 1$).

$$[Site] = C_{DNA} - p [Site] = C_{DNA} - p b C_C$$
(eq.4)

Thus, $\frac{[Site]}{c_{c}} = R - p b$ The binding equilibrium equations are thus rewritten as: $K_{ass} = \frac{b}{f c_{c}(R-p b)}$ The expression of *b* as functions of *f* can thus be obtained: $K_{ass} f C_{c}(R - p b) - b = 0 \qquad (eq.5)$ $b = \frac{K_{ass} f C_{c} R}{1 + p K_{ass} f C_{c}}$ (eq.6)

With

$$1 = f + b$$
(eq.7)
$$0 = f - 1 + \frac{K_{ass} f C_C R}{1 + p K_{ass} f C_C}$$
(eq.8)

The expression of the ratio of the intensity of luminescence, I/I_0 , can be expressed as follows: $I/I_0 = f + \alpha \frac{K_{ass} f C_C R}{1 + p K_{ass} f C_C}$ (eq.9)

The fitting process using eq.9 is performed by an iterative solving to the expression of f using the eq.8. The factor p is modified manually and we selected the best fit values; for ds-DNA, the best results are obtained with p=1, *i.e.* the complex interact with one equivalent of base pair, and p=3 for G4 quartets, indicating that only one complex interact with a G4 structure (3 quartets).

6. Bio-layer interferometry sensograms



Figure S 10: BLI sensorgrams for the interaction of complex 1 with A) G4 DNA and B) duplex DNA hairpin. The complex concentrations were 5, 10, 20, 30 and 40 μ M.



Figure S 11: BLI sensorgrams for the interaction of complex **2** with A) G4 DNA and B) duplex DNA hairpin. The complex concentrations were 5, 10, 20, 30 and 40 μM.



Figure S 12: BLI sensorgrams for the interaction of complex 3 with A) G4 DNA and B) duplex DNA hairpin. The complex concentrations were 5, 10, 20, 30 and 40 μ M.



Figure S 13: BLI sensorgrams for the interaction of complex 4 with A) G4 DNA and B) duplex DNA hairpin. The complex concentrations were 5, 10, 20, 30 and 40 μ M.