Electronic Supplementary Material (ESI) for Dalton Transactions


# Studies on characterization, telomerase inhibitory properties and G-quadruplex binding of $\eta^6$-arene ruthenium complexes with 1,10-phenanthroline-derived ligands

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Eq. (1)

$$(\varepsilon_a-\varepsilon_f)/(\varepsilon_a-\varepsilon_f) = (b-(b^2-2K_b^2C_t[DNA]/s)^{1/2})/\ 2K_bC_t \quad (1a)$$

$$b = 1+K_bC_t+K_b[DNA]/\ 2s \quad (1b)$$

where [DNA] is the concentration of DNA in nucleotides, $\varepsilon_a$ is the molar absorption coefficient ($A_{abs}$/[M]) of the MLCT absorption band at a given DNA concentration, $\varepsilon_f$ and $\varepsilon_b$ are the molar absorption coefficients of the free $Ru^{II}$ complex and the molar absorption coefficient of the $Ru^{II}$ complex in the fully bound form, respectively. $K_b$ is the equilibrium binding constant in $M^{-1}$, Ct is the total $Ru^{II}$ complex concentration, and s is the binding site size. Eq. (1) has been applied to titration data for noncooperative metallointercalator binding to DNA.

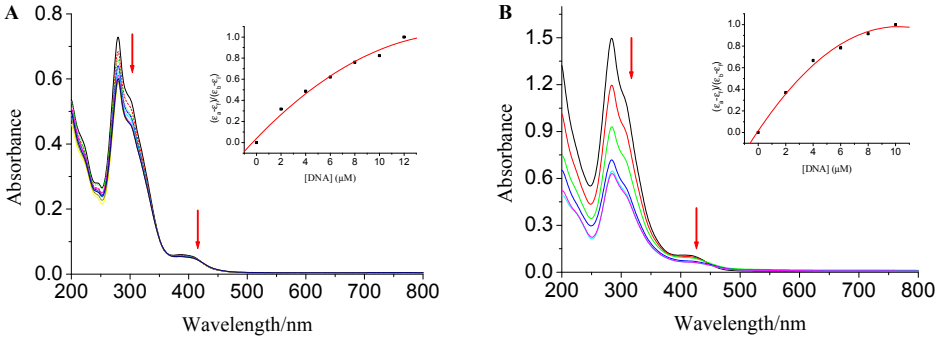


Figure S1. Absorption spectra of complexes **1** (A) and **2** (B) in buffer with increasing amounts of G-quadruplex. [Ru] = 10.0 or 20 μM, [CT-DNA] = 0-12 μM from top to bottom. Arrows refer to the change in absorbance upon increasing the DNA concentration.

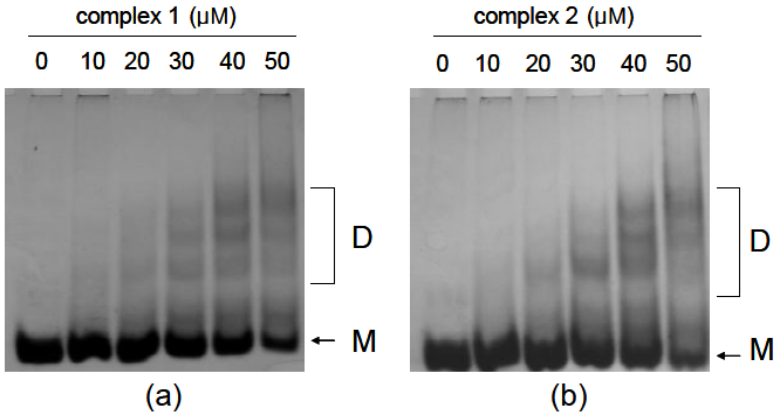


Figure S2. Effect of complex **1** (a) and **2** (b) on the assembly of the HTG21 structure illustrated by native PAGE analysis . Ruthenium complexes at the indicated concentration were incubated with HTG21 (10 μM) at 20 °C in a buffer containing 10 mM Tris, 1 mM EDTA, 100 mM KCl, pH 8.0. Major bands were identified as monomer (M), dimer (D).

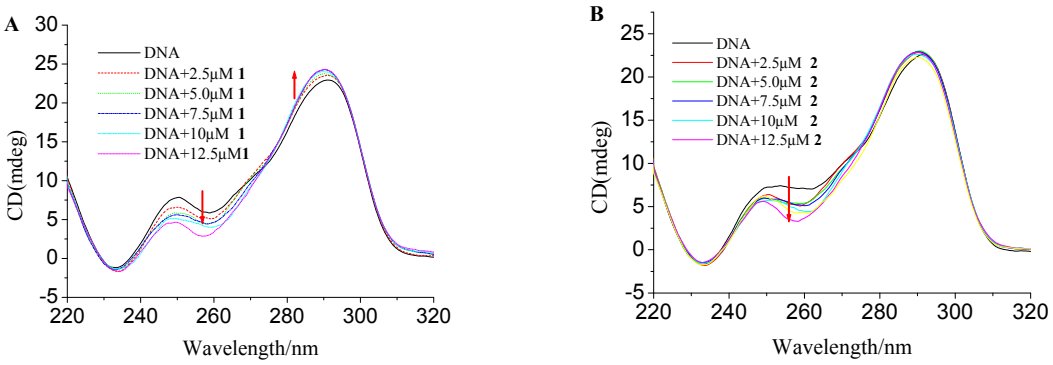


Figure S3. CD spectra of HTG21 acquired at 20 °C in the absence or presence of different concentrations of 1 (A) and 2 (B). All experiments were carried out in 10 mM Tris-HCl, 100 mM KCl, pH 7.4. The HTG21 concentration is 2 μM.

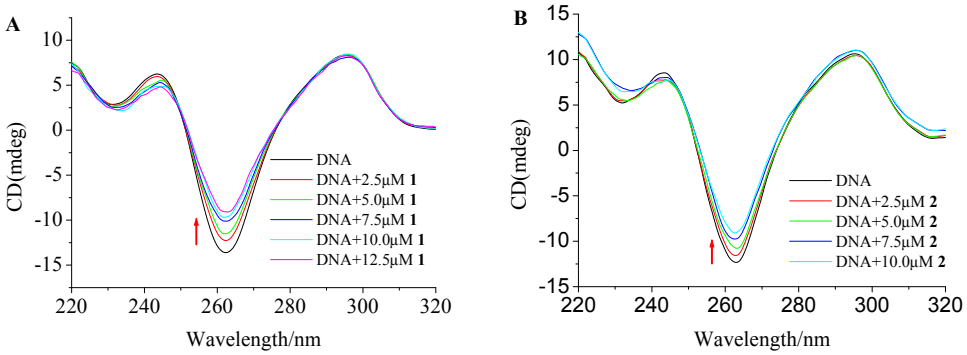


Figure S4. CD spectra of HTG21 acquired at 20 °C in the absence or presence of different concentrations of 1 (A) and 2 (B). All experiments were carried out in 10 mM Tris-HCl, 100 mM NaCl, pH 7.4. The HTG21 concentration is 2 μM.

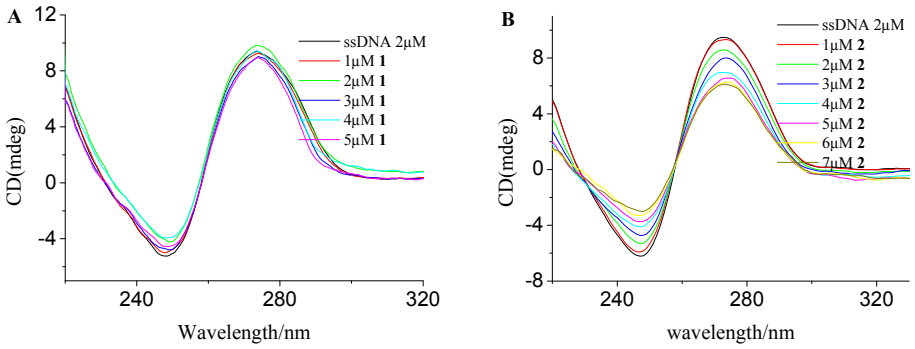


Figure S5. CD spectra of ssDNA acquired at 20 °C in the absence or presence of different concentrations of **1**(A) and **2**(B). All experiments were carried out in 10 mM Tris-HCl, pH 7.4. The HTG21 concentration is 2 μM.

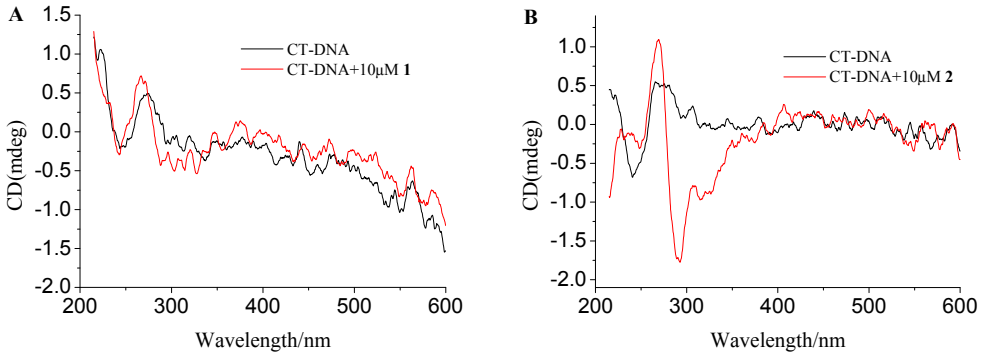


Figure S6. CD spectra of CT-DNA(10uM) in 10 mM Tris-HCl, 100 mM KCl, pH = 7.5 buffer at 25 °C in the presence of increasing amounts of **1** (A) and **2** (B), [Ru]/[DNA] = 1:1.

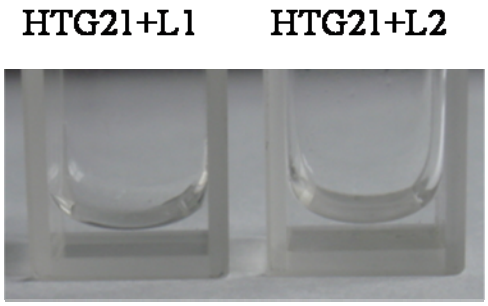


Figure S7. Characterizations of the DNAzyme functions of HTG21 DNA in the presence of 500 nM L1 and 500 nM L2 in the TMB-$H_2O_2$ system. Conditions: TMB, 266 mM in Tris-MES buffer (25 mM MES, pH = 5.10); $H_2O_2$, 794 mM; DNA, 500 nM; hemin, 500 nM. (L1 = p–MOPIP, L2 = p–CFPIP)

Table S1. Absorption spectra (λmax/nm) and DNA-binding constants $K_b$ ($\times 10^5$ $M^{-1}$) of complexes **1** and **2**.

| complex | DNA | $\lambda_{max}$(free) | $\lambda_{max}$(bound) | △λ/nm | *H%* | $K_b/10^5$ $M^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | HTG21 | 279 | 281 | 2 | 29.3 | |
| | | 425 | 425 | 0 | 19.2 | 3.87 |
| | CT-DNA | 282 | 282 | 0 | 17.5 | |
| | | 425 | 425 | 0 | 12.5 | 1.04 |
| 2 | HTG21 | 279 | 277 | -2 | 26.8 | |
| | | 425 | 425 | 0 | 18.5 | 2.14 |
| | CT-DNA | 282 | 280 | -2 | 57.8 | |

Table S2. $IC_{50}$ Values of Tested Compounds towards Different Cell Lines[a]

| | $IC_{50}$(μM) | | | | |
|---|---|---|---|---|---|
| Complexes | HepG2 | HeLa | A549 | SW620 | NIH/3T3 |
| 1 | 24.35 ± 3.3 | 8.70 ± 2.2 | 35.72 ± 2.5 | 17.48 ± 2.4 | >100 |
| 2 | 28.56 ± 3.7 | 14.50 ± 3.5 | 46.41 ± 4.2 | 26.63 ± 2.3 | 48.37 ± 4.7 |
| Cisplatin | 13.63 ± 1.1 | 7.51 ± 1.2 | 3.16 ± 0.2 | 29.98 ± 1.8 | 19.72 ± 1.5 |

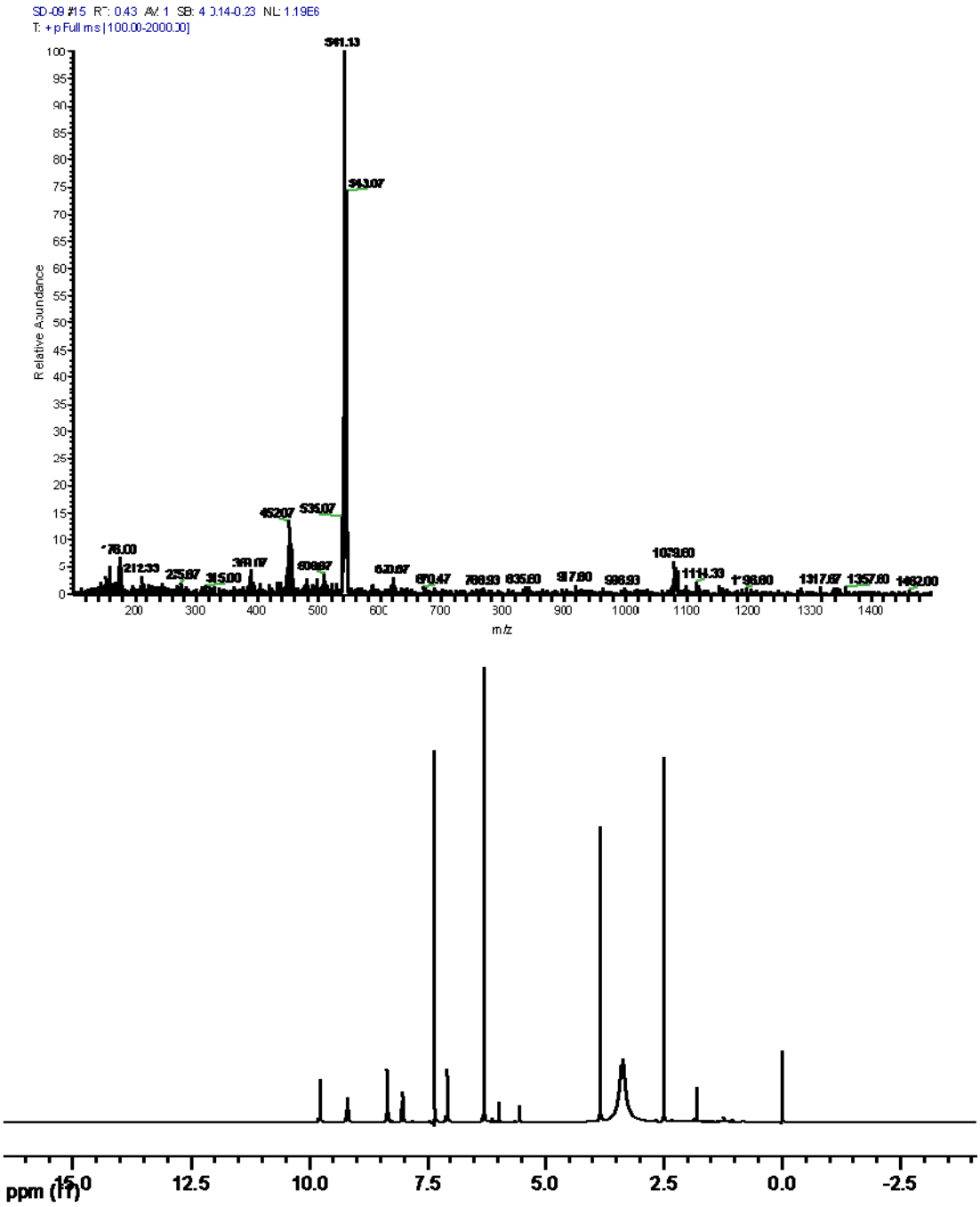


Figure S8. ESI-MS and $^{1}$H NMR spectra of complex **1**.

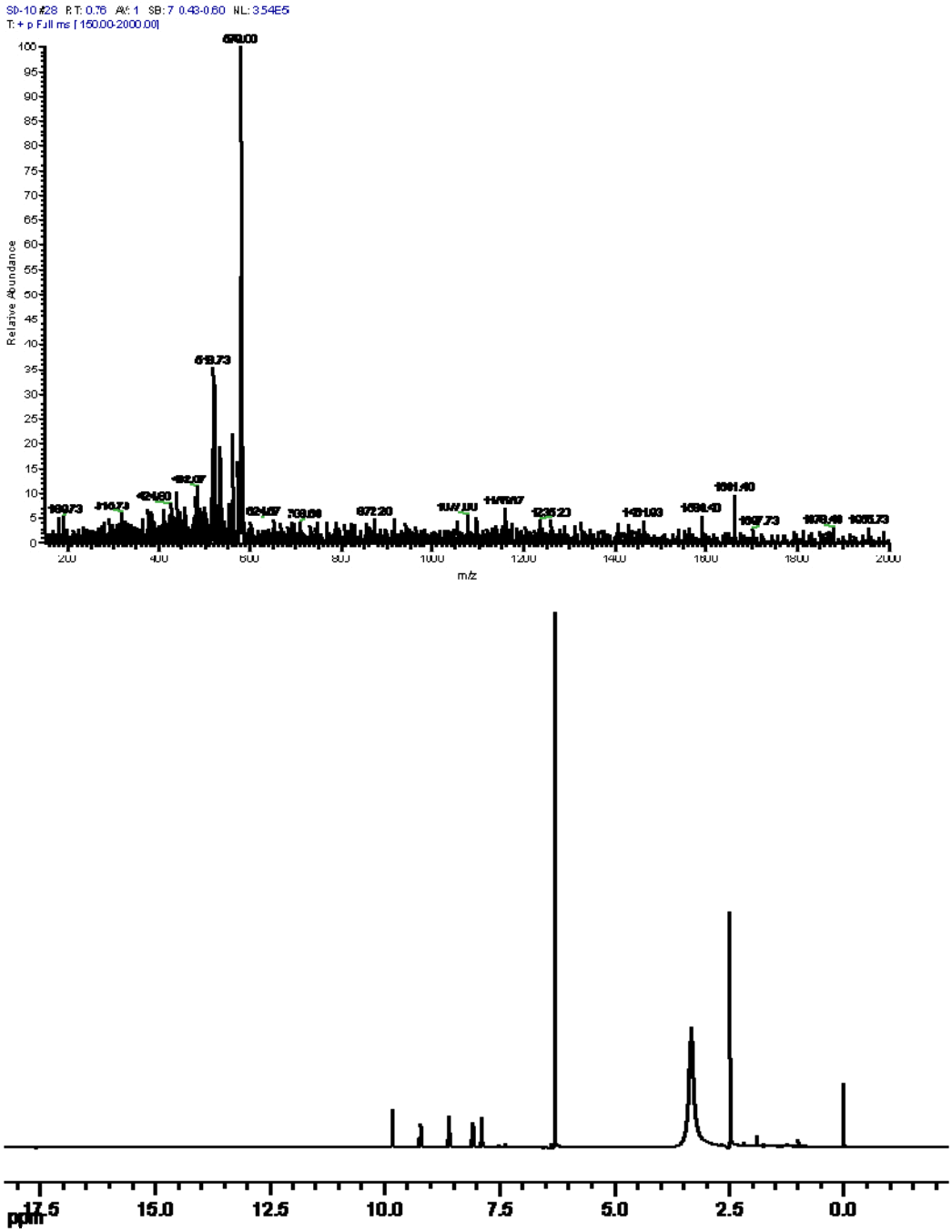


Figure S9. ESI-MS and $^{1}$H NMR spectra of complex **2**.