Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

pH luminescence switch, DNA binding and photocleavage, and cytotoxicity of a dinuclear ruthenium complex

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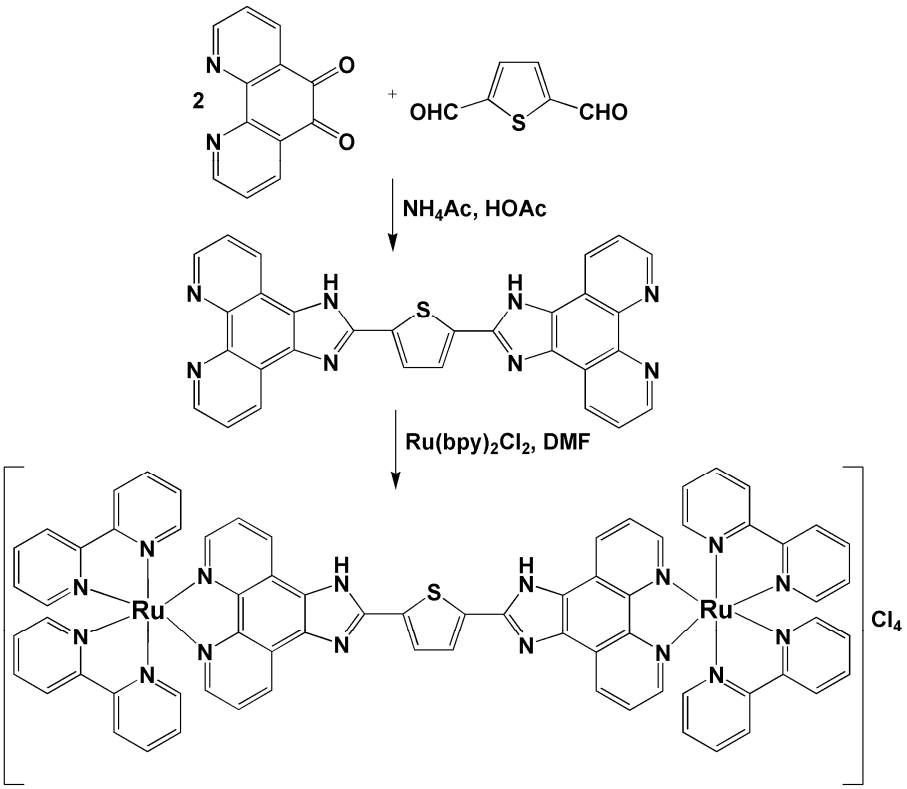

Scheme S1.The synthetic route to **1**Cl_4

1. Synthesis of 2-(5-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)thiophen-2-yl)-1*H*-imidazo[4,5-*f*][1,10]phenanthroline (H_2bipt)

To a solution of 1,10-phenanthroline-5,6-dione (0.42 g, 2.0 mmol) and ammonium acetate (3.0 g, 40 mmol) in 40 mL glacial acetic acid were added thiophene-2,5-dicarbaldehyde (0.14 g, 1.0 mmol). The reaction mixture was refluxed at 80 ℃ for 1 h under the protection of nitrogen. After cooling, the solution was neutralized to pH = 7 with concentrated NH_3 solution and filtered. The yellow precipitate was collected, washed with distilled water and diethyl ether, and dried in vacco, giving yield of 67%. The H_2bipt ligand is sparingly soluble in common organic solvents, so it was not characterized by ^{1}H NMR.

2. Synthesis of $[Ru_2(bpy)_4(H_2bipt)]Cl_4$ **1**Cl_4

A mixture of *cis*-$Ru(bpy)_2Cl_2$•$2H_2O$ (0.104 g, 0.2 mmol) and H_2bipt (0.052 g, 0.1 mmol) in 8 mL DMF was refluxed at 110 ℃ for 12 h under nitrogen. After cooling to room temperature, the solution was filtrated and the filtrate was collected. The purification was carried out by column chromatography on Al_2O_3 followed by recrystallized from CH_3CN-diethyl ether, giving **1**Cl_4 as a red solid with yield of 46%. ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 9.06 (s, 4H), 8.90 (dd, J_1 = 8 Hz, J_2 = 15 Hz, 8H), 8.21 (t, J = 8 Hz, 4H), 8.10 (t, J = 8 Hz, 4H), 7.95 (s, 2H), 7.88 (d, J = 5 Hz, 6H), 7.83 (d, J = 6 Hz, 6H), 7.61 (dd, J_1 = 5 Hz, J_2 = 10 Hz, 8H), 7.37 (t, J = 6 Hz, 4H). Anal. Found: C, 48.71; N, 13.76; H, 5.00. Calc. for $C_{70}H_{48}N_{16}C_{l4}Ru_2$·4.3$HCON(CH_3)_2$·$13H_2O$: C, 48.83; N, 13.90; H, 5.10. Anal. Calc. for MALDI-TOF MS: *m/z* 336.8 ($[M-4Cl]^{4+}$); Found : *m/z* 336.9 ($[M-4Cl]^{4+}$). IR (KBr, cm^{-1}): 3427, 3072, 1602, 1444, 1384, 1191, 809, 768, 725.

Some equations used in this paper.

$1/T_m^0 - 1/T_m = (R/\Delta H_m)\ln(1 + KL)^{1/s}$ (1)

T_m^0 and T_m are the melting temperatures of DNA, in the absence and the presence of the ruthenium complex, respectively. ΔH_m is the enthalpy of DNA melting (per base pair) taken as 6.9 kcal mol^{-1}, R is the gas constant, K is the DNA binding constant at T_m, L is the free complex concentration (approximated by the total complex concentration at T_m, and s is the binding site size.

$\ln(K_1/K_2) = (\Delta H^0/R)[(T_1 - T_2)/T_1T_2]$ (2)

$\Delta G_T^0 = -RT\ln K$ (3)

$\Delta G_T^0 = \Delta H^0 - T\Delta S^0$ (4)

K_1 and K_2 are the DNA-binding constants of the complex at temperatures T_1 and T_2, respectively. ΔG_T^0, ΔH^0, and ΔS^0 are the changes of the standard free energy, standard enthalpy, and standard entropy of binding of the complex to DNA, respectively.

The $^1O_2$ generation quantum yields (Φ_Δ) of the complexes were calculated according to following Eqs. (5) and (6).

$-\Delta[DPBF]/t = (I_0 - I_t)/t = I_{in}\Phi_{ab}\Phi_\Delta\Phi_r$ (5)

$k/k_s = \Phi_{ab}\Phi_\Delta/\Phi_{ab}^s\Phi_\Delta^s$ (6)

I_{in} is the incident monochromatic light intensity, Φ_{ab} is the light absorbing efficiency of the photosensitizer, Φ_r is the reaction quantum yield of $^1O_2$ with DPBF, t is the irradiation time, I_0 and I_t are the luminescence intensity of DPBF before and after irradiation, k is the slope and superscript s stands for the standard complex $[Ru(bpy)_3]^{2+}$.

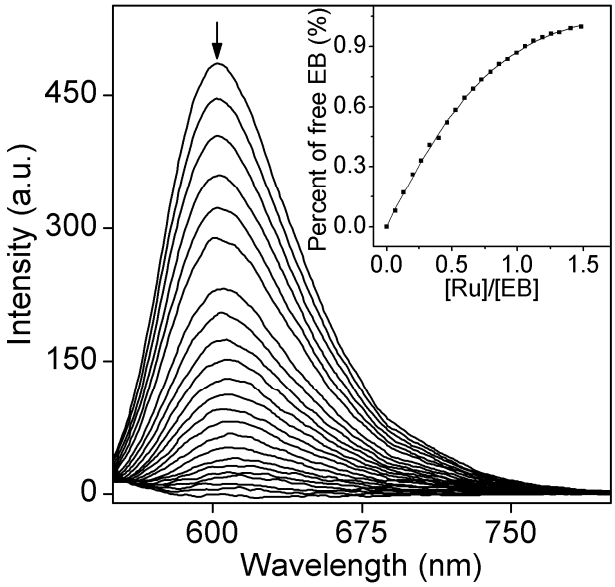

Fig. S1 Changes in emission spectra (λ_{ex} = 537 nm) of EB (10 μM) bound to DNA (50 μM) in the presence of **1**Cl_4. Inset: plot of percentage of free EB vs. [Ru]/[EB].

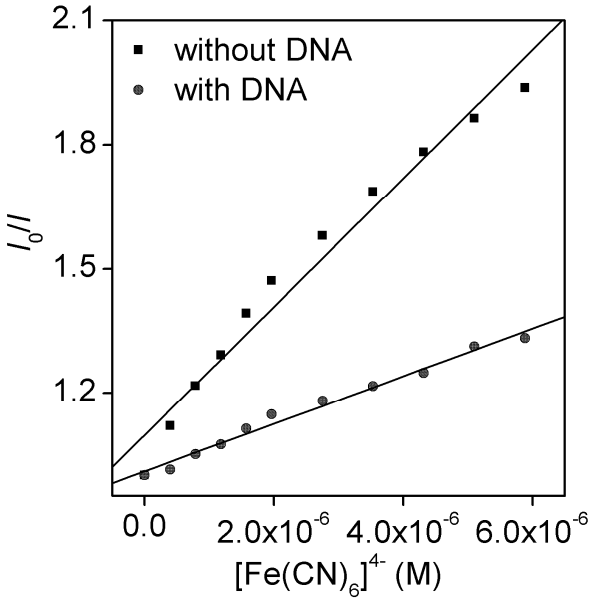

Fig. S2 Emission quenching of **1**Cl_4 (5 μM) upon increasing concentraions of $[Fe(CN)_6]^{4-}$ in the absence and the presence of DNA (50 μM).

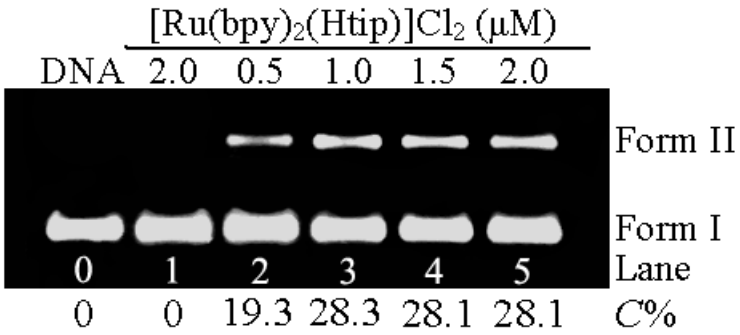

Fig. S3 Photoactivated cleavage of pUC 18 DNA in the presence of different concentrations of $[Ru(bpy)_2(Htip)]Cl_2$ **9**Cl_2 after irradiation at 360 nm (16 mW/cm^2) for 2 h.

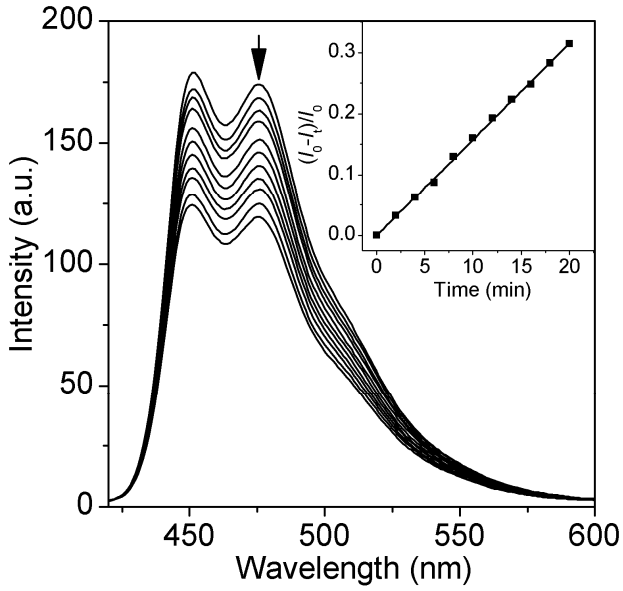

Fig. S4 The emission spectra changes of DPBF (20 μM)–$[Ru(bpy)_3]^{2+}$ (5 μM) system upon irradiation at 480 nm. Inset: the DPBF consumption percentage as a function of irradiation time in the air-equilibrated methanol solution of $[Ru(bpy)_3]^{2+}$.

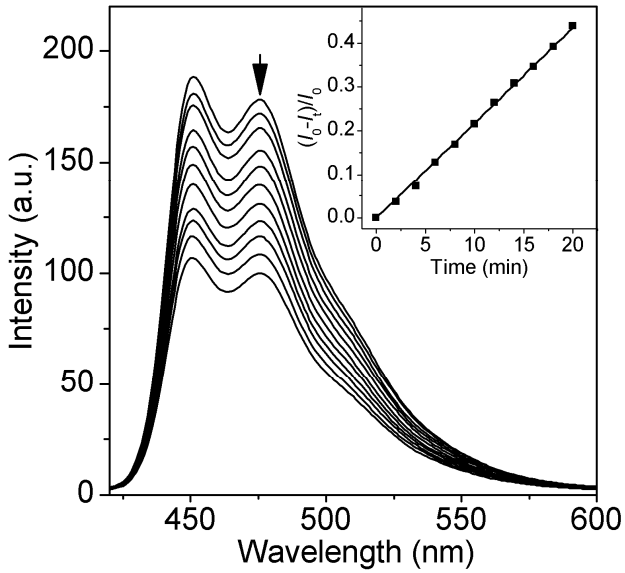

Fig. S5 The emission spectra changes of DPBF (20 μM)–**9**Cl_2 (5 μM) system upon irradiation at 480 nm. Inset: the DPBF consumption percentage as a function of irradiation time in the air-equilibrated methanol solution of **9**Cl_2.

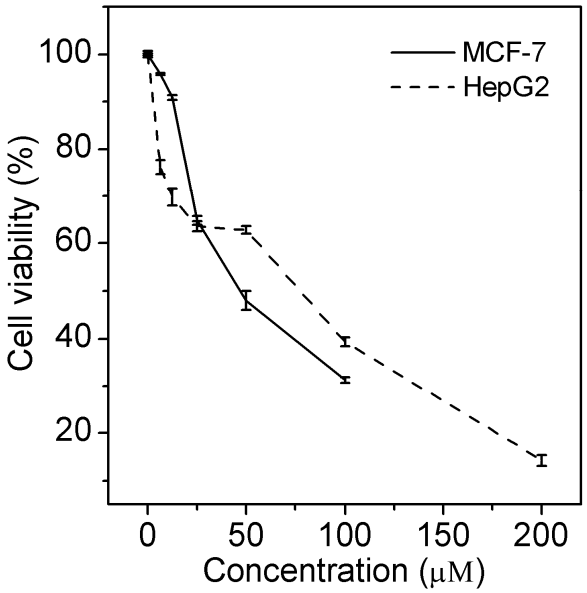

Fig. S6 Cell viability of **1**Cl_4 on tumor (MCF-7 and HepG2) cell proliferation in vitro.

Table S1 Computated selective bond lengths (nm), bond angles A_m and A_{co} (°)*, dihedral angles and some frontier molecular orbital energies (a.u.)

Complex	Ru-N_m	Ru-N_{co}	C-C(N)$_m$	C-C(N)$_{co}$	A_m	A_{co}	Dihedral angles	Frontier molecular orbital energies	Ref.
9	0.2124	0.2115	0.1397	0.1389	78.46	77.70	179.88	-0.255(LUMO+2)	Z.S. Li, H.X. Yang, A.G. Zhang, H. Luo, K.Z. Wang, *Inorg. Chim. Acta*, 2011, **370**, 132.
1	0.2127	0.2118	0.1393	0.1389	78.10	77.66	179.42(N1-C2-C3-S4) 179.40(S4-C5-C6-N7)	-0.327(LUMO)	This work

*Subscript "m" stands for the main ligands of Hip, Htip and H_2bipt, and "co" represents for the co-ligand of bpy.