Electronic Supplementary Information (ESI)

Ternary Eu(III) and Tb(III) β-diketonate Complexes Containing Chalcones: Photophysical Studies and Biological outlook

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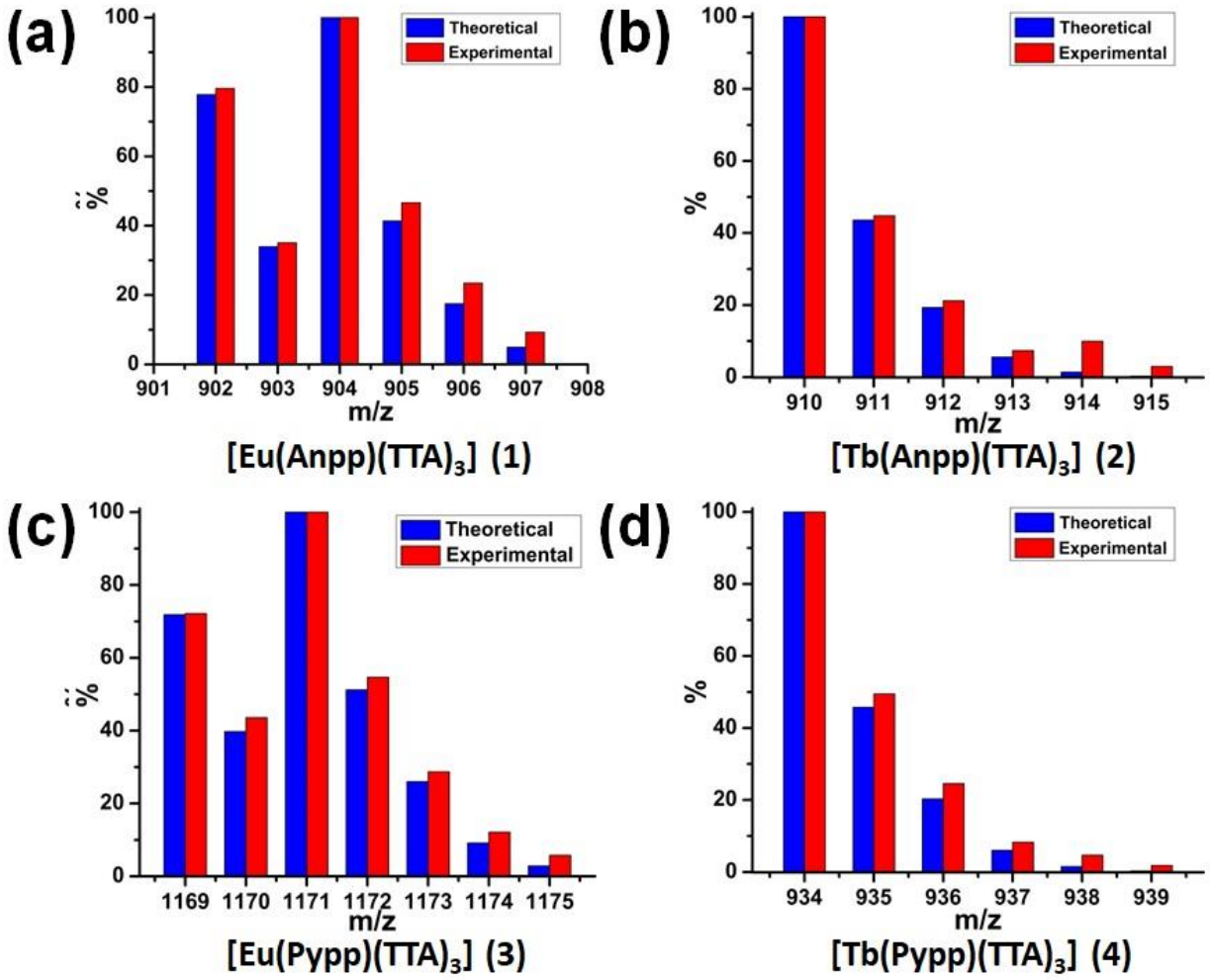

Figure S1. ESI-MS spectra with isotopic distribution for the parent ion peak of (a) Complex **1**, (b) Complex **2**, (c) Complex **3** and (d) Complex **4** in DMF.

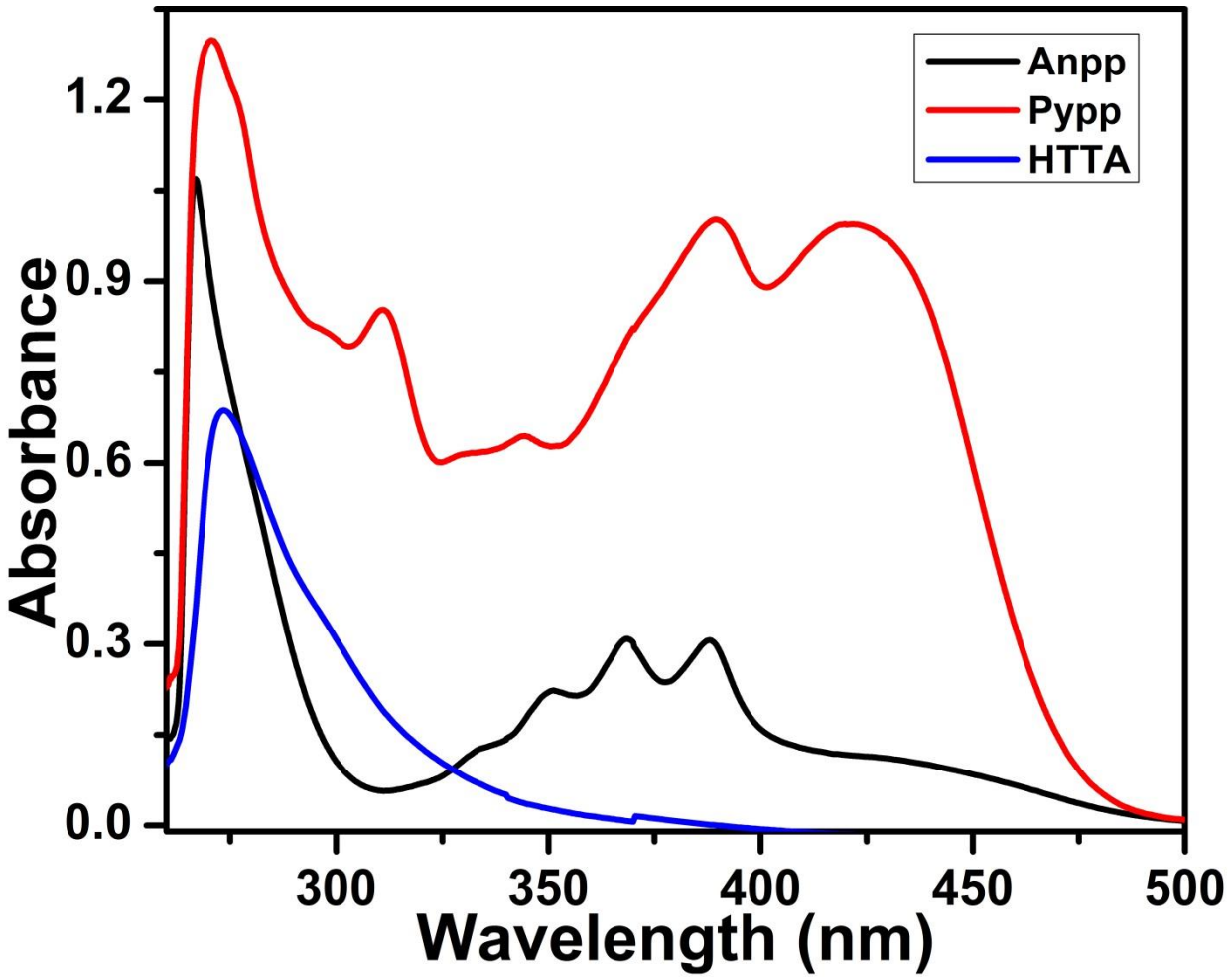

Figure S2. UV-Vis absorption spectral traces of chalcones and TTA ligands in DMF at 298 K.

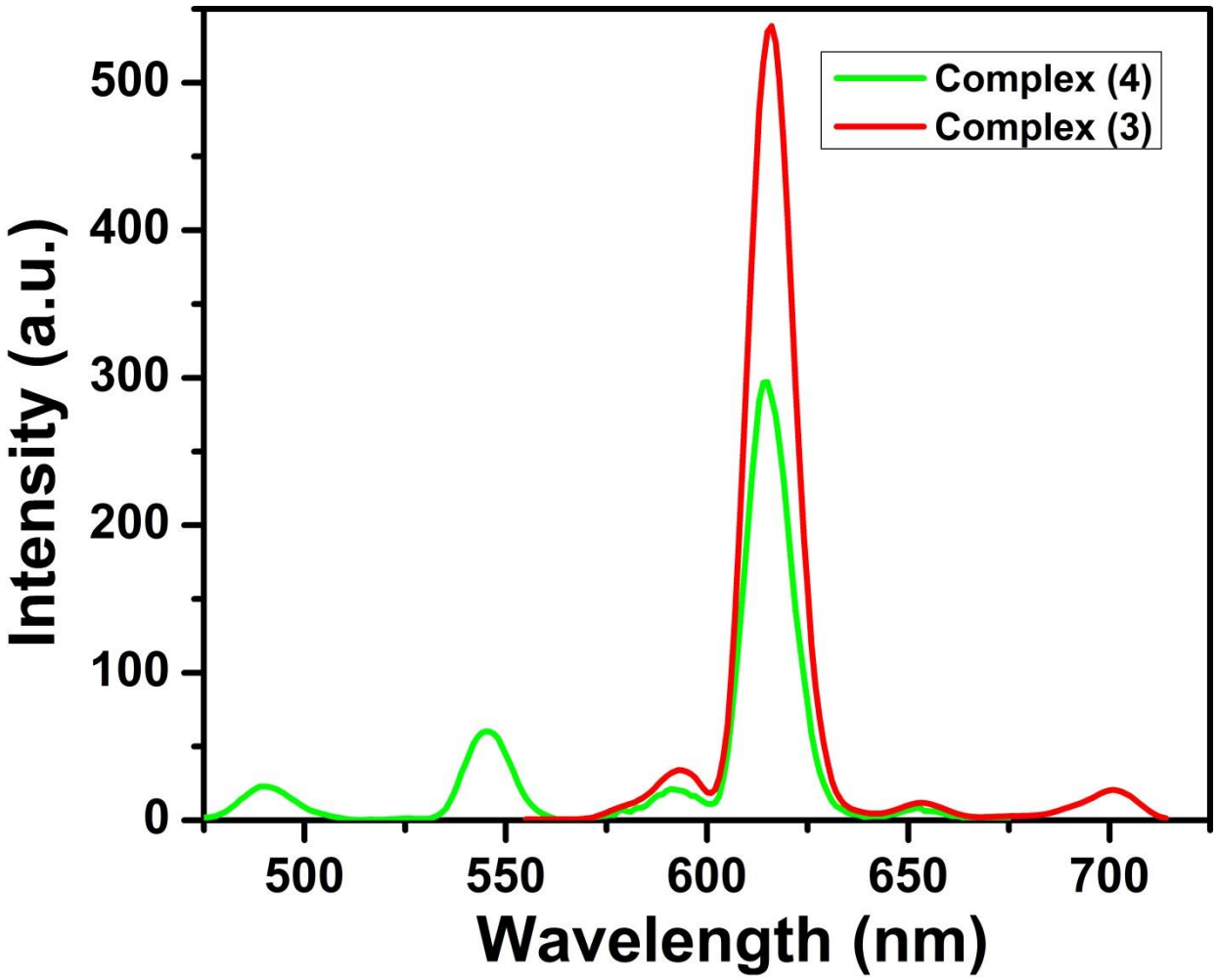

Figure S3. Time-delayed luminescence spectra for complexes **3** and **4** (20 μM each) in DMF at 298 K [delay time = 0.1 ms, gate time =0.1 ms, λ_{ex} = 340 nm, slit width = 10 nm].

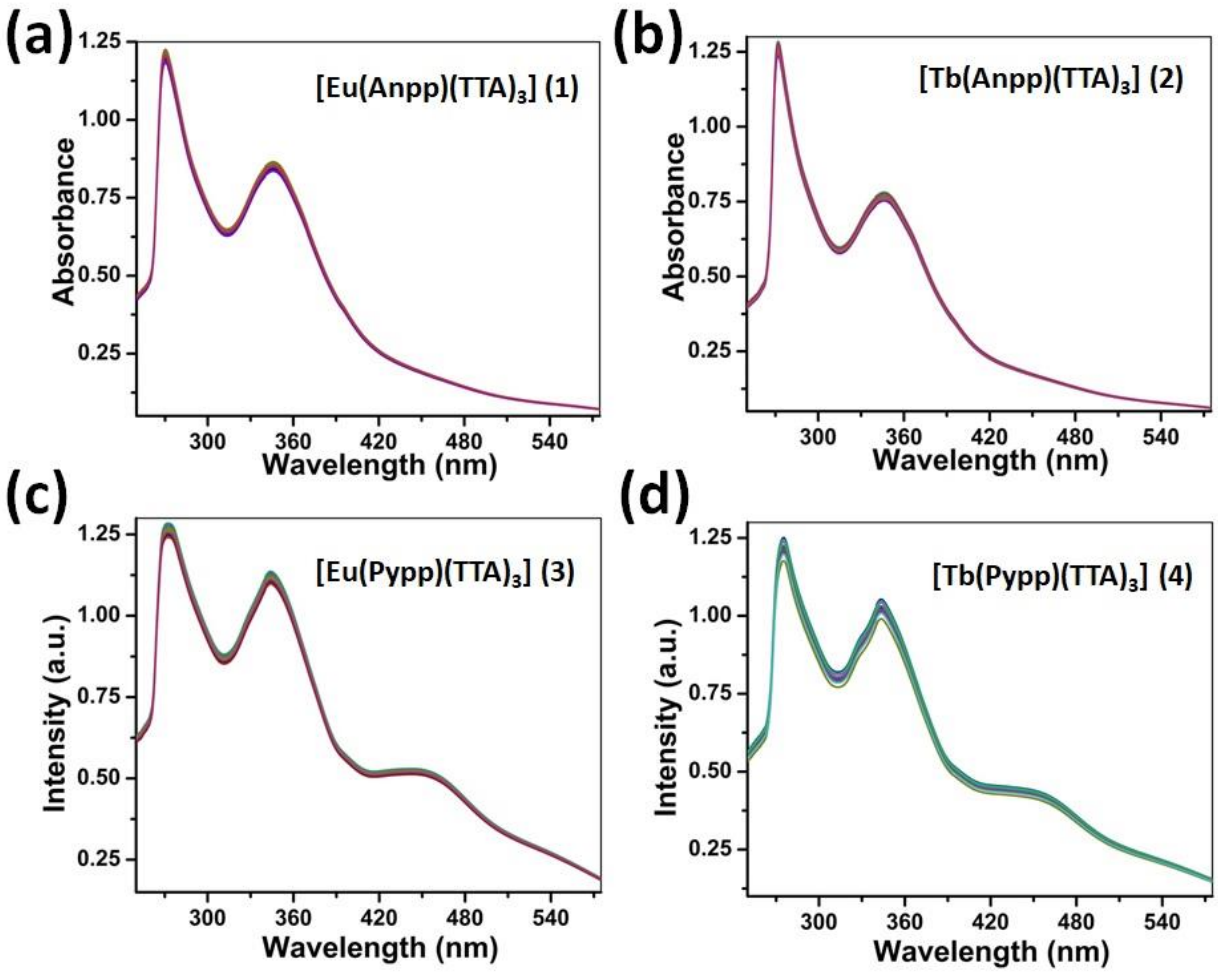

Figure S4. Time-dependent absorption spectral traces of (a) complex **1**, (b) Complex **2**, Complex **3** and Complex **4** recorded for 4 h in DMF at 298 K to access the stability of the complexes in solution.

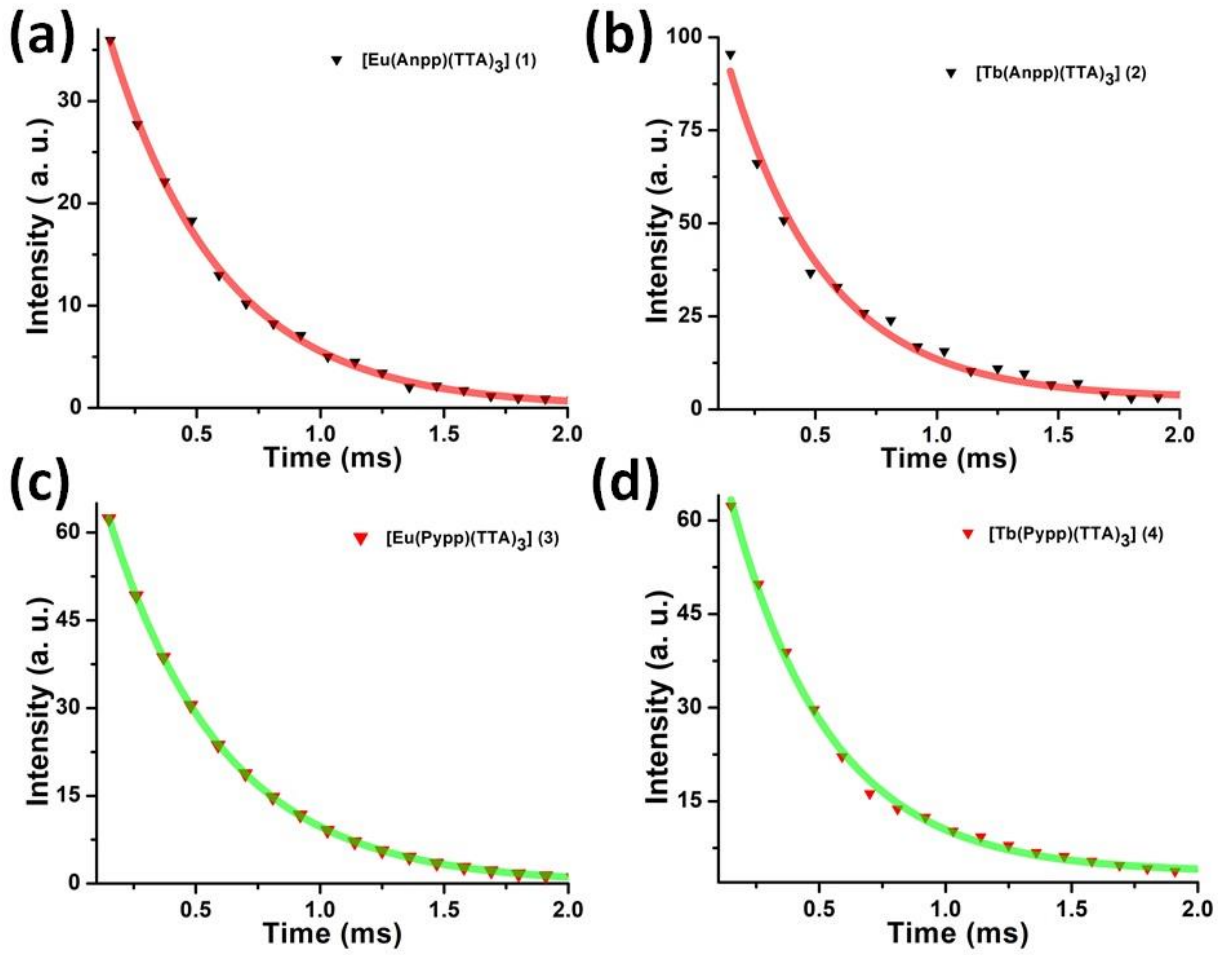

Figure S5. Luminescence decay profile from $^5D_0$ and $^5D_4$ states and lifetime measurement at 616 nm and 545 nm for Eu^{3+} and Tb^{3+} in complexes **1** (a)**, 2** (b), **3** (c) and **4** (d) respectively in DMF under ambient condition at 298 K. λ_{ex} = 340 nm, delay time and gate time = 0.1 ms, total decay time = 3.0 ms, slit width = 10 nm.

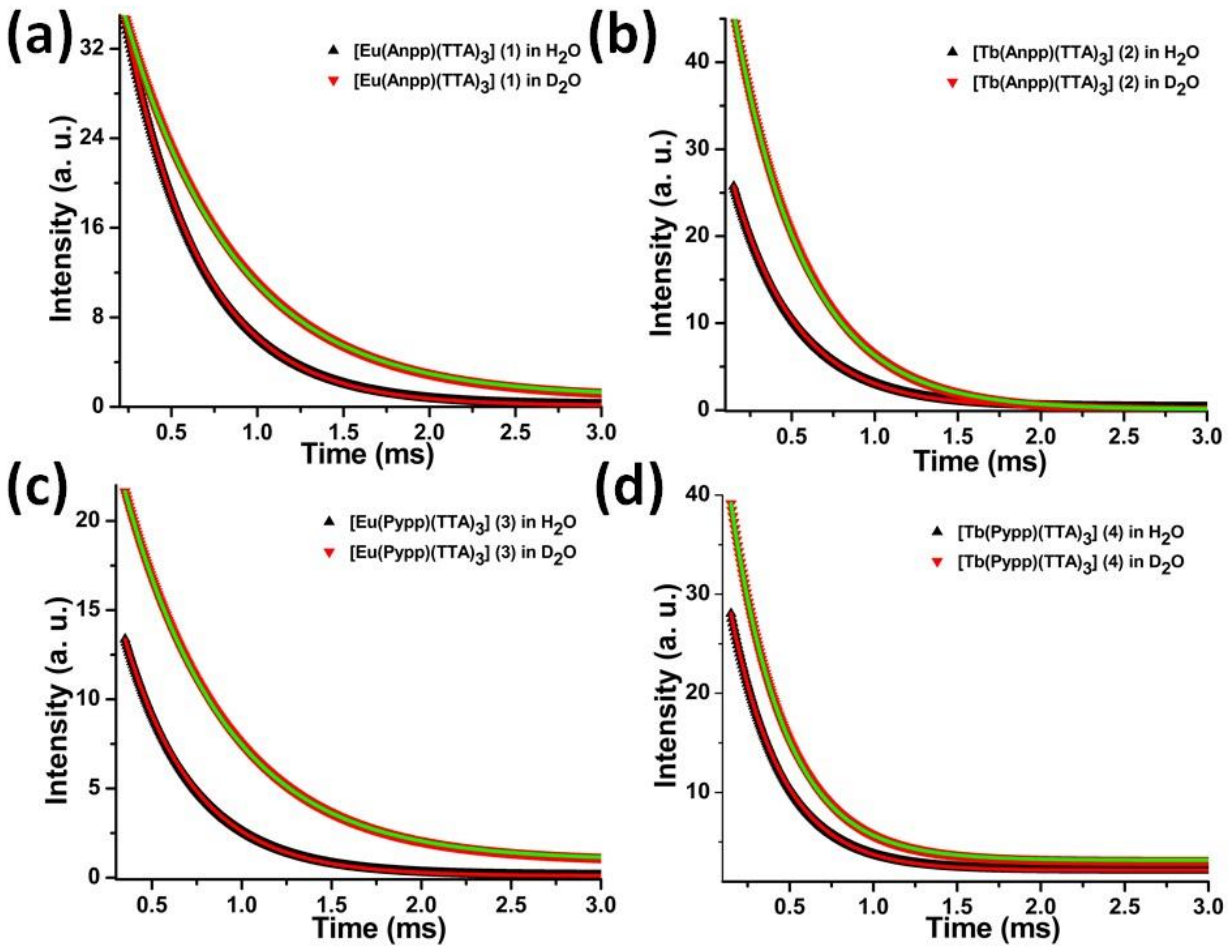

Figure S6. Luminescence lifetime measurements from the decay profile of $^5D_0$ and $^5D_4$ excited states at 616 nm and 545 nm for complexes **1** (a), **2** (b), **3** (c) and **4** (d) respectively in H_2O and D_2O under ambient condition at 298 K. The solid lines are mono exponential fittings in H_2O and D_2O respectively. λ_{ex} = 340 nm, delay time = 0.1 ms and gate time = 0.1 ms, slit width = 10 nm, total decay time = 3 ms.

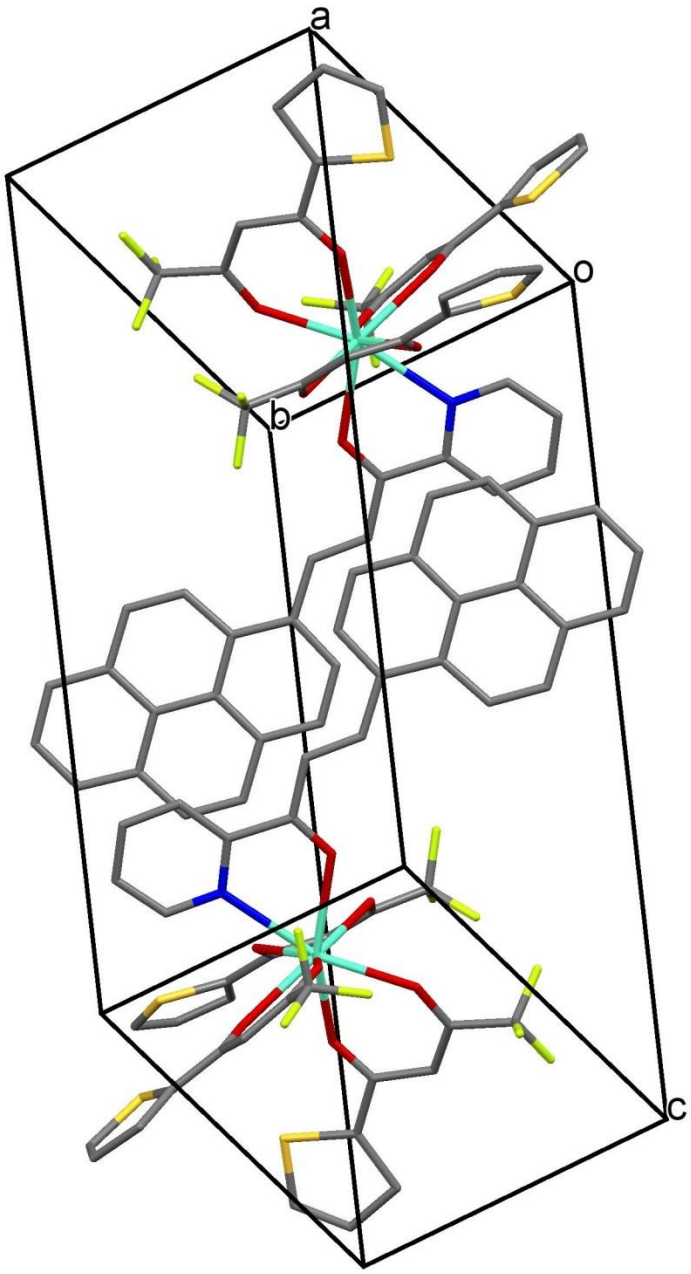

Figure S7. Unit cell packing diagram of complex **3** viewed along b-axis.

Table S1: Selected bond lengths (Å) and bond angles (deg) for [Eu(Pypp)(TTA)3] (**3**).

Bond length (Å)	
Eu(1)-N(1)	2.608(6)
Eu(1)-O(1)	2.453(5)
Eu(1)-O(2)	2.356(6)
Eu(1)-O(3)	2.357(5)
Eu(1)-O(4)	2.375(6)
Eu(1)-O(5)	2.360(5)
Eu(1)-O(6)	2.357(5)
Eu(1)-O(7)	2.349(5)
Bond angle (deg)	
O(1)-Eu(1)-N(1)	62.43(18)
O(2)-Eu(1)-N(1)	81.4(2)
O(3)-Eu(1)-N(1)	74.44(19)
O(4)-Eu(1)-N(1)	154.2(2)
O(5)-Eu(1)-N(1)	133.86(19)
O(6)-Eu(1)-N(1)	107.94(19)
O(7)-Eu(1)-N(1)	72.06(19)
O(2)-Eu(1)-O(1)	76.34(18)
O(3)-Eu(1)-O(1)	129.02(18)
O(4)-Eu(1)-O(1)	95.94(19)
O(5)-Eu(1)-O(1)	158.25(19)
O(6)-Eu(1)-O(1)	72.44(18)
O(7)-Eu(1)-O(1)	107.64(18)
O(3)-Eu(1)-O(2)	71.36(18)
O(4)-Eu(1)-O(2)	79.7(2)
O(5)-Eu(1)-O(2)	116.6(2)
O(6)-Eu(1)-O(2)	137.44(19)
O(7)-Eu(1)-O(2)	146.39(19)
O(4)-Eu(1)-O(3)	115.29(19)
O(5)-Eu(1)-O(3)	72.73(19)
O(6)-Eu(1)-O(3)	151.04(19)
O(7)-Eu(1)-O(3)	81.72(19)
O(5)-Eu(1)-O(4)	71.02(19)
O(6)-Eu(1)-O(4)	75.6(2)
O(7)-Eu(1)-O(4)	131.3(2)
O(6)-Eu(1)-O(5)	87.18(19)
O(7)-Eu(1)-O(5)	71.90(19)
O(7)-Eu(1)-O(6)	72.15(19)

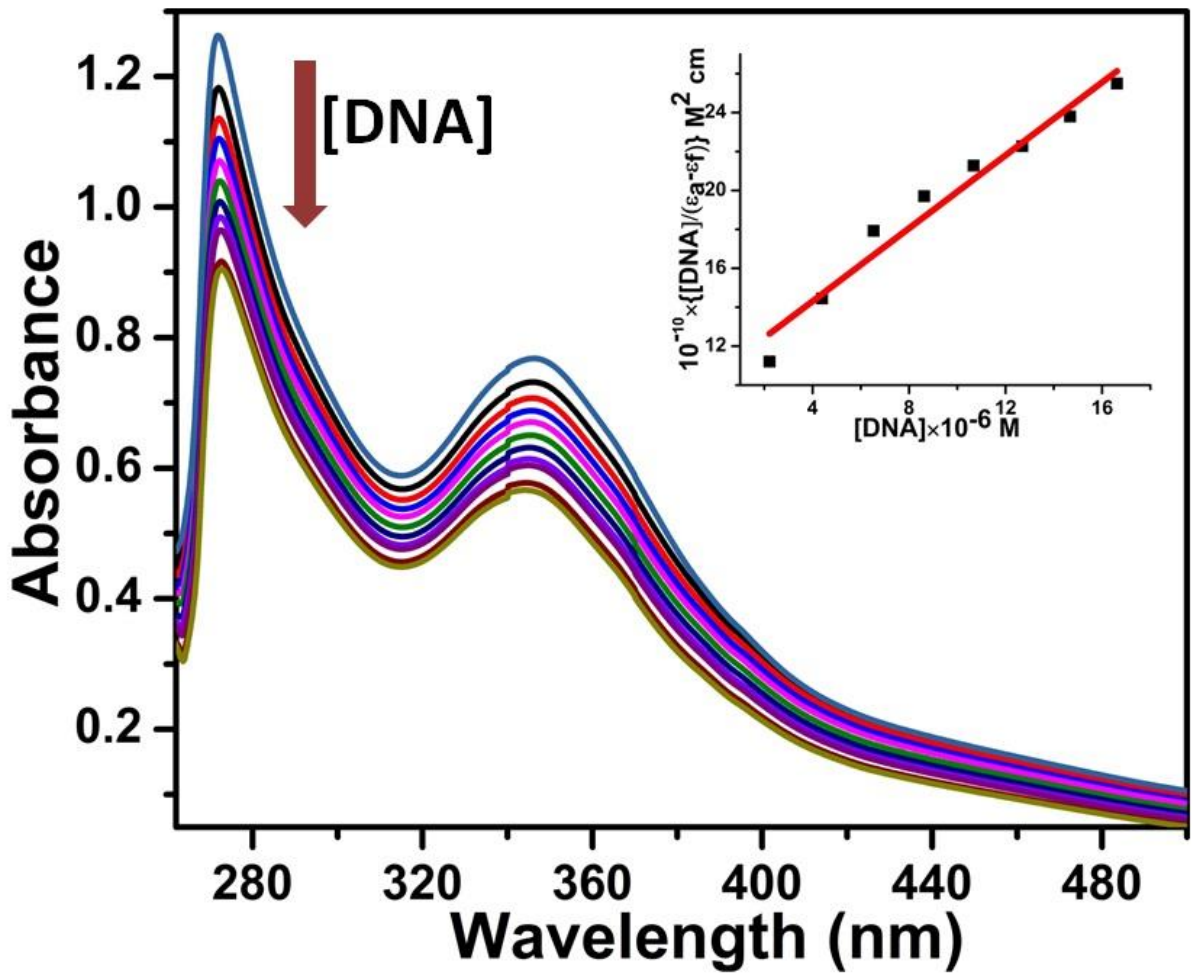

Figure S8. UV/Vis traces for complex **2** (20 μM) in 5 mM Tris buffer (pH 7.2) with increasing [CT-DNA] at 298 K; Inset: $[DNA]/\Delta\varepsilon_{af}$ versus [DNA] plot for complex **2**.

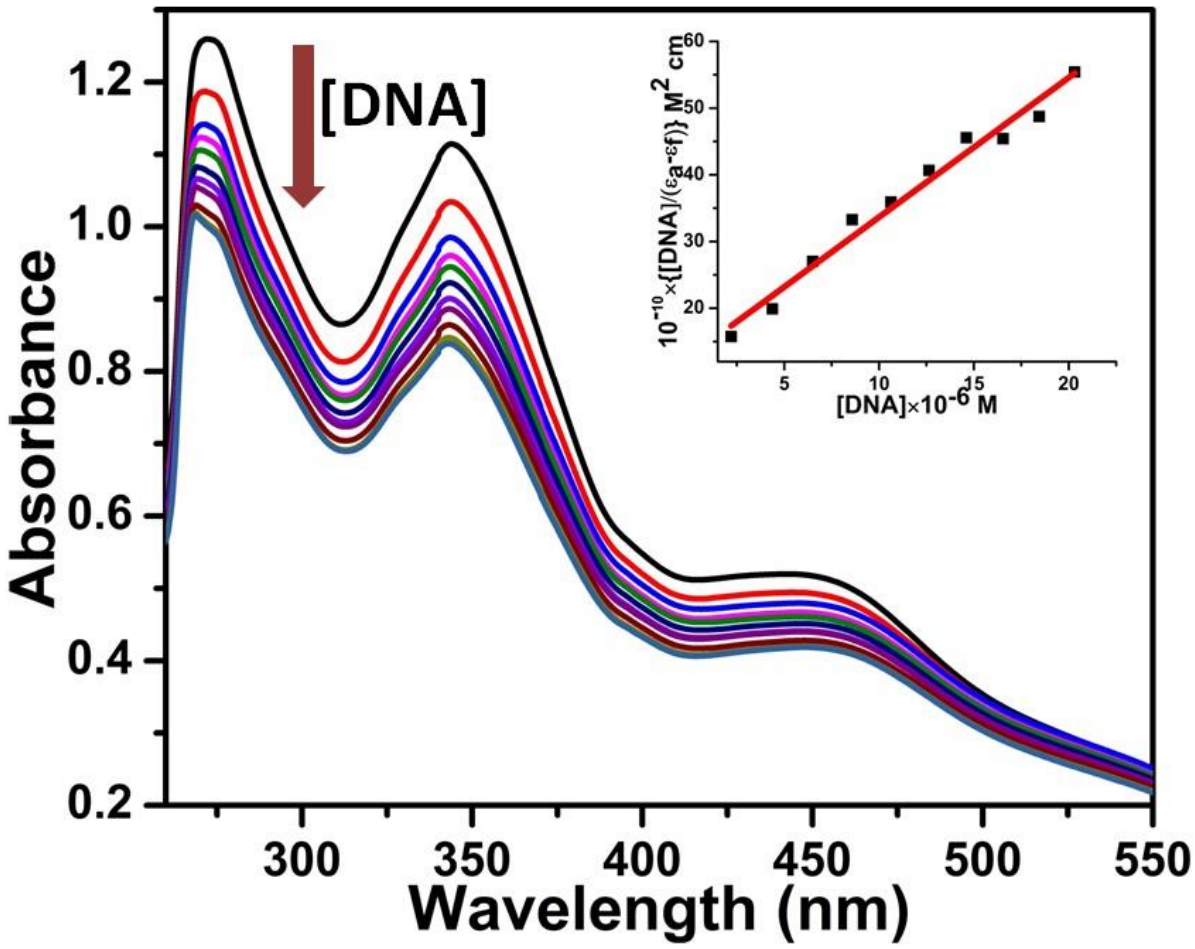

Figure S9. UV/Vis traces for complex **3** (20 μM) in 5 mM Tris buffer (pH 7.2) with increasing [CT-DNA] at 298 K; Inset: [DNA]/$\Delta\varepsilon_{af}$ versus [DNA] plot for complex **3**.

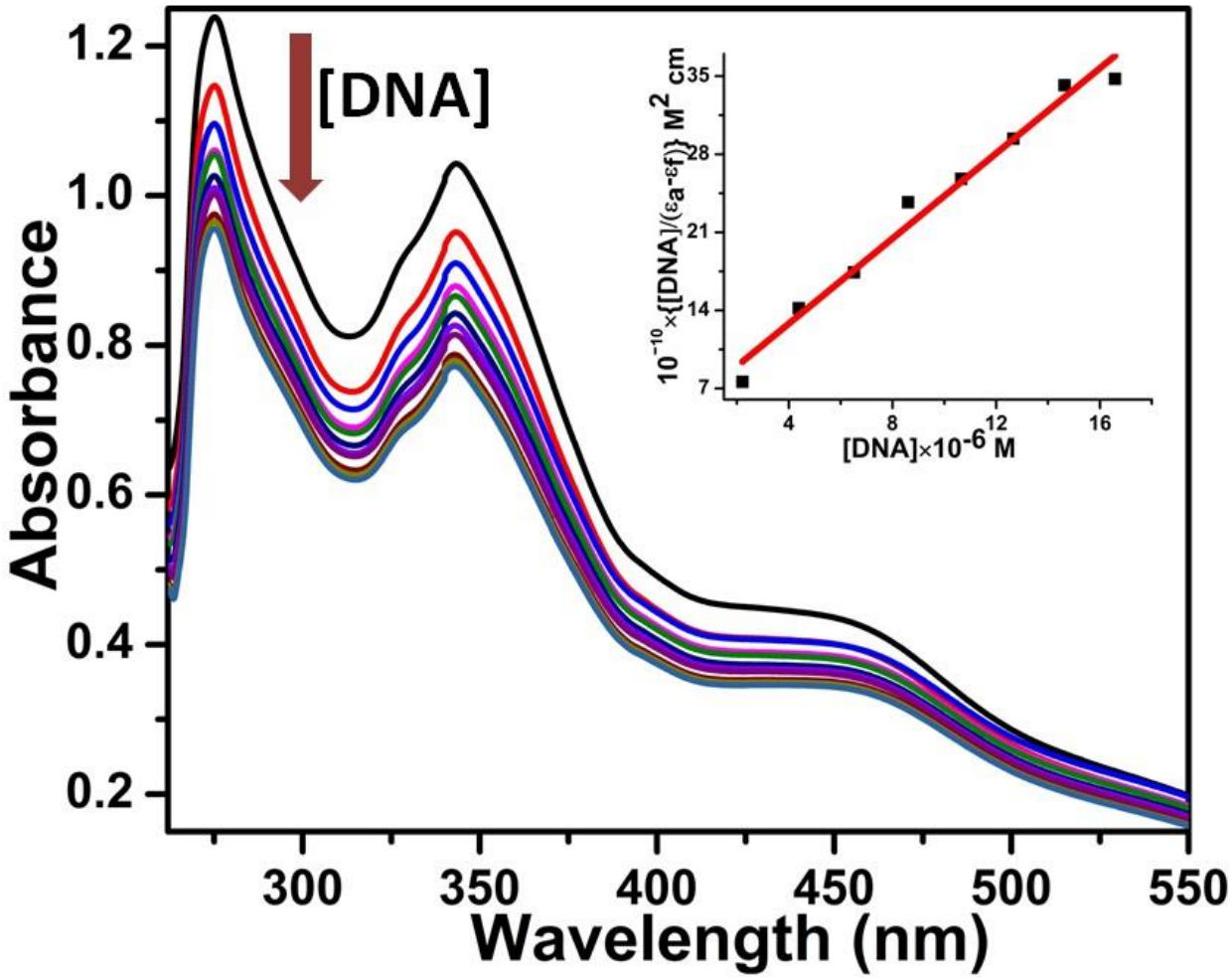

Figure S10. UV/Vis traces for complex **4** (20 μM) in 5 mM Tris buffer (pH 7.2) with increasing [CT-DNA] at 298 K; Inset: $[DNA]/\Delta\varepsilon_{af}$ versus [DNA] plot for complex **4**.

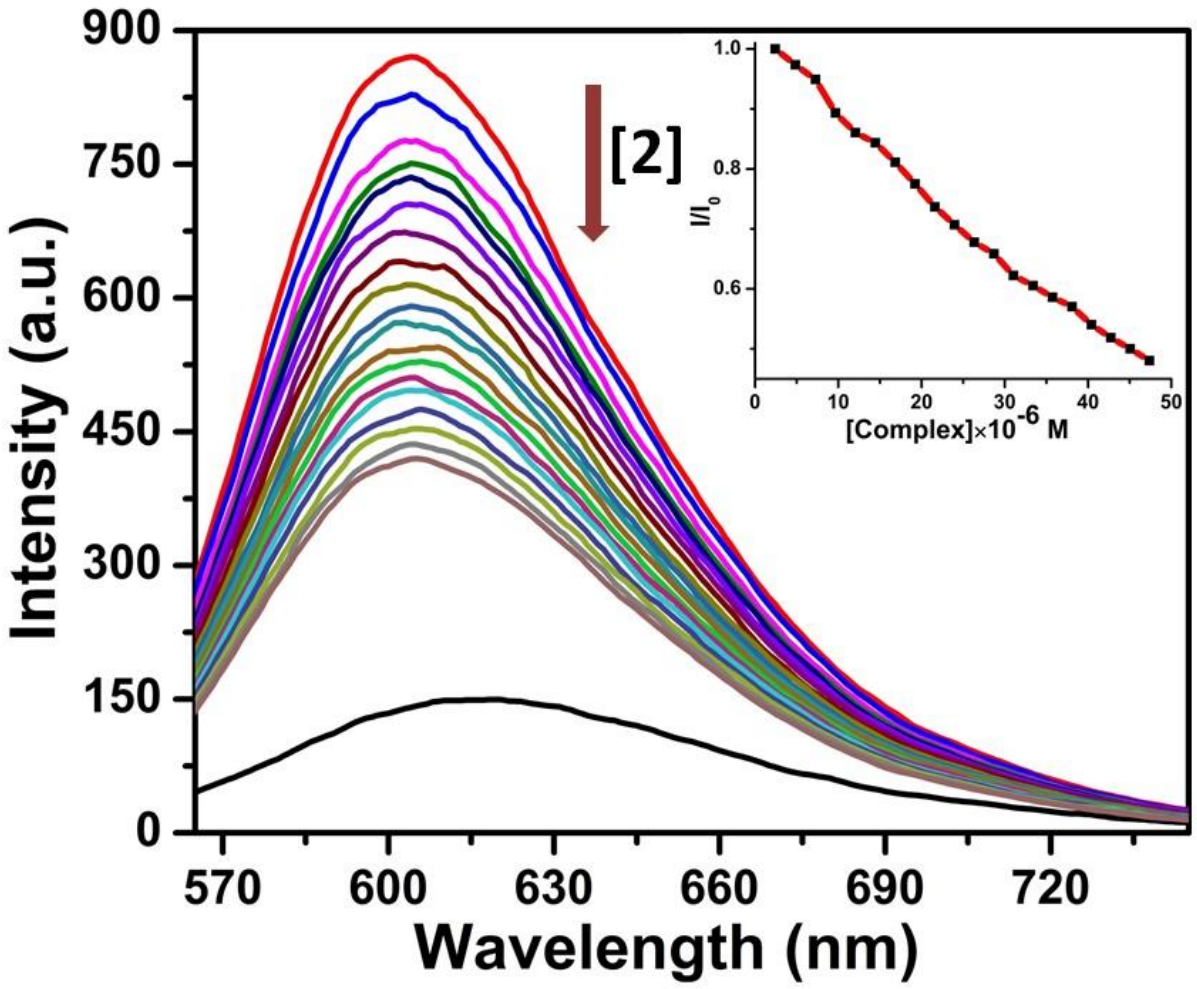

Figure S11. Emission spectral traces for EB-bound CT-DNA with increasing concentration of complex **2** in 5 mM Tris buffer (pH 7.2) at 298 K; λ_{ex} = 546 nm, λ_{em} = 603 nm, [DNA] = 212 μM, [EB] = 12 μM; Inset: a plot of I/I_0 versus [complex **2**].

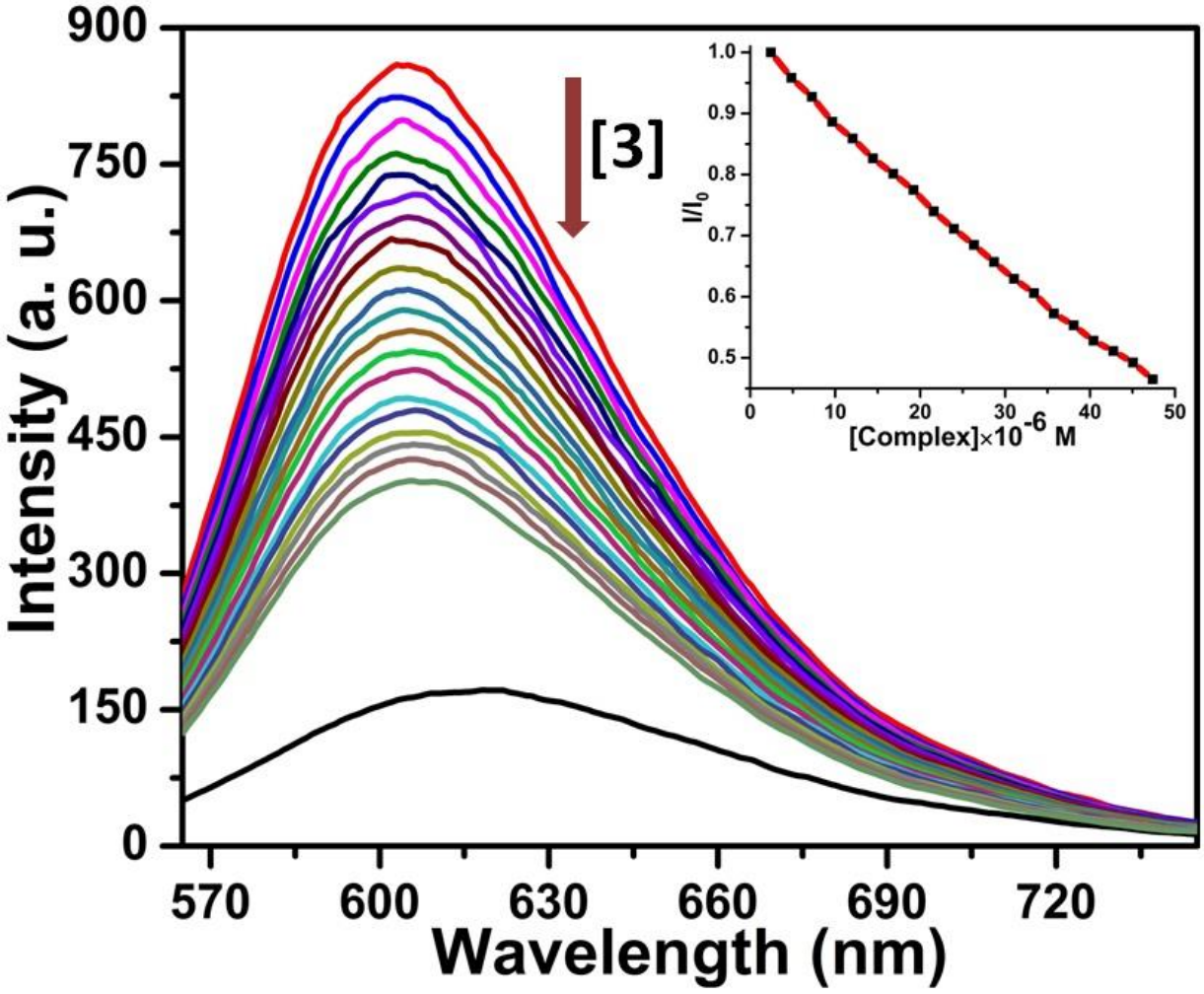

Figure S12. Emission spectral traces for EB-bound CT-DNA with increasing concentration of complex **3** in 5 mM Tris buffer (pH 7.2) at 298 K; λ_{ex} = 546 nm, λ_{em}=603 nm, [DNA] = 212 μM, [EB] = 12 μM; Inset: a plot of I/I_0 versus [complex **3**].

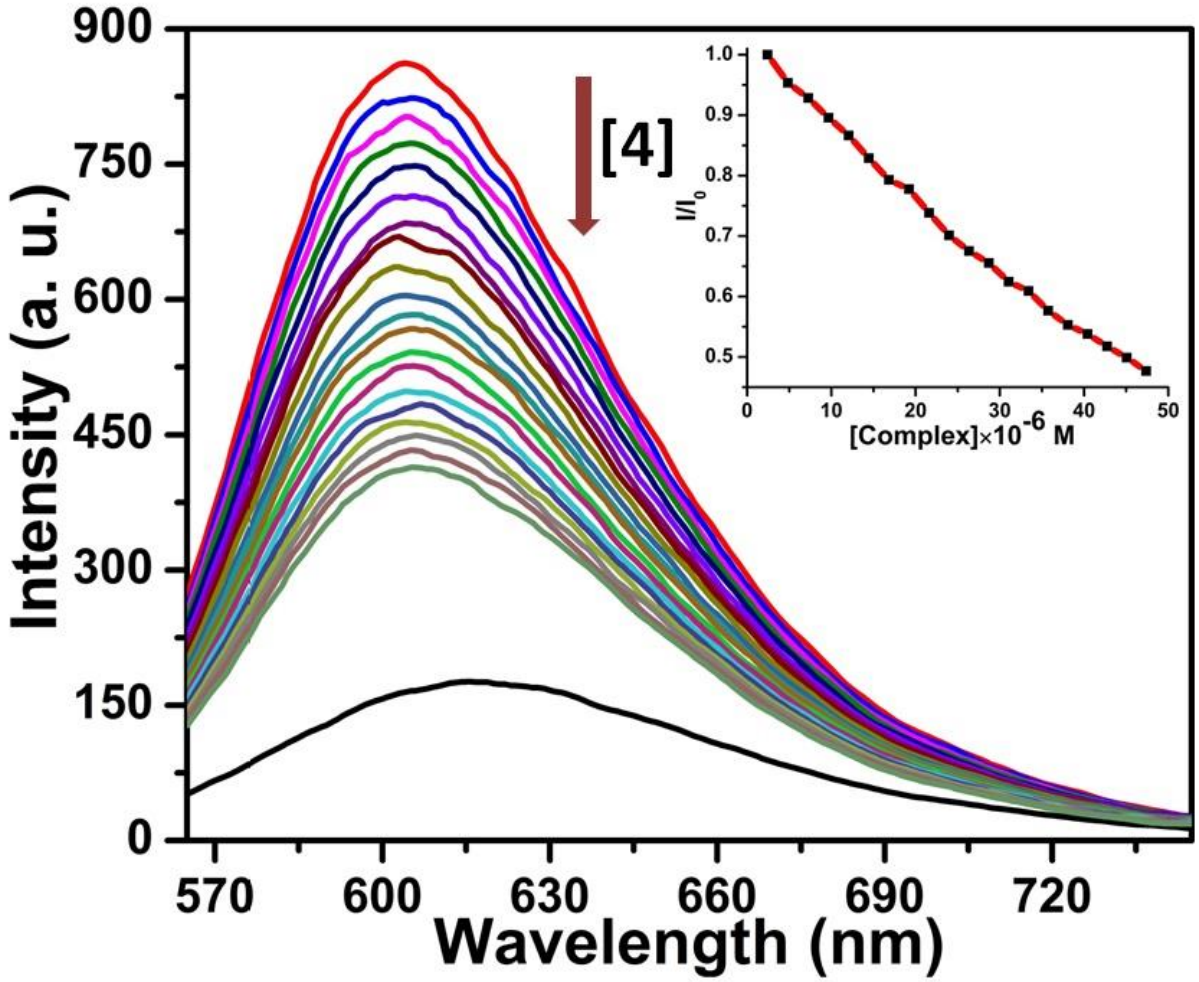

Figure S13. Emission spectral traces for EB-bound CT-DNA with increasing concentration of complex **4** in 5 mM Tris buffer (pH 7.2) at 298 K; λ_{ex} = 546 nm, λ_{em} = 603 nm, [DNA] = 212 μM, [EB] = 12 μM; Inset: a plot of I/I_0 versus [complex **4**].

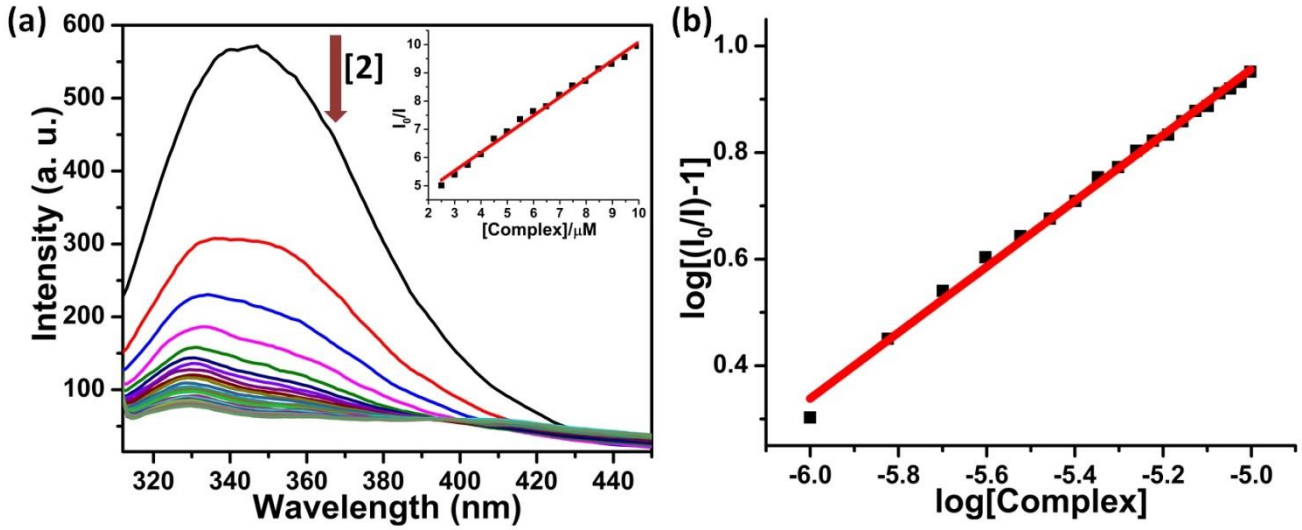

Figure S14. (a) The emission quenching of HSA addition of complex **2** in 5 mM Tris buffer (pH 7.2) at 298 K; Inset: a plot of I_0/I versus [complex] for **2**; λ_{ex} = 295 nm, λ_{em} = 345 nm, [HSA] = 5 μM. **(b)** Scatchard plot: log[(I_0-I)/I] vs. log[Complex] for HSA in the presence of complex **2**.

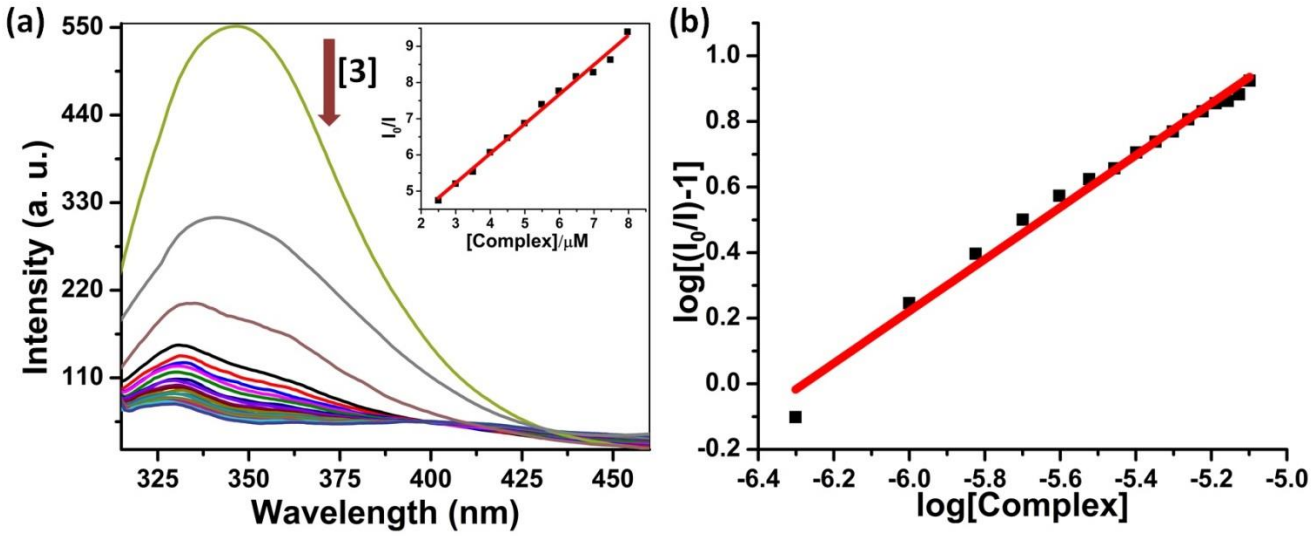

Figure S15. (a) The emission quenching of HSA addition of complex **3** in 5 mM Tris buffer (pH 7.2) at 298 K; Inset: a plot of I_0/I versus [complex] for **3**; λ_{ex} = 295 nm, λ_{em} = 345 nm, [HSA] = 5 μM. **(b)** Scatchard plot: log[(I_0-I)/I] vs. log[Complex] for HSA in the presence of complex **3**.

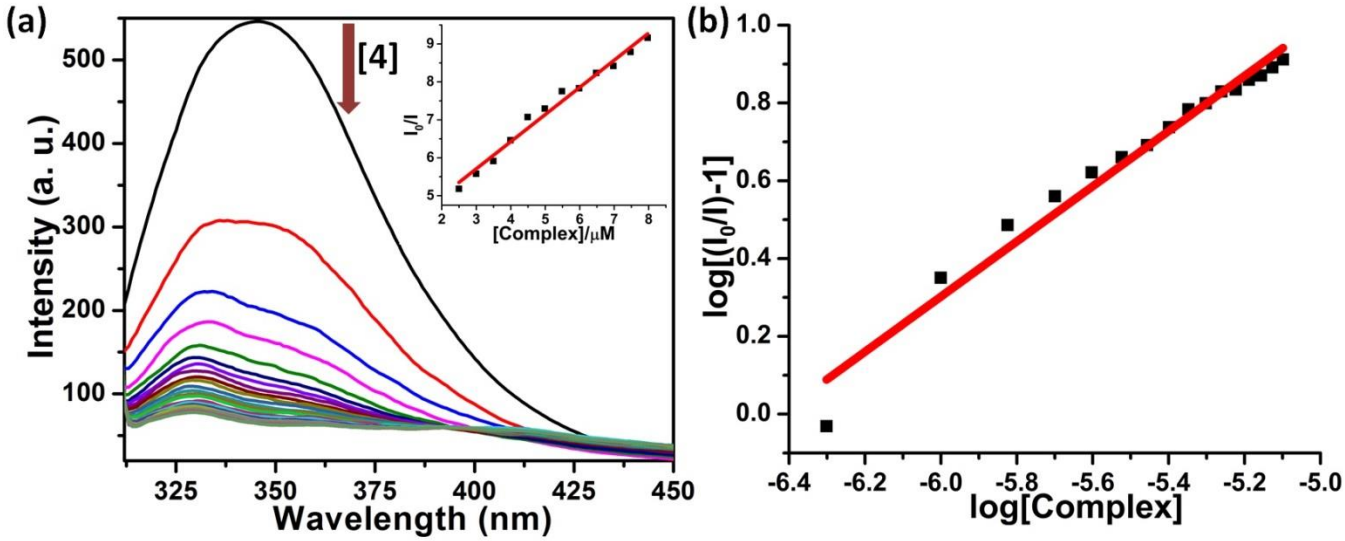

Figure S16. (a) The emission quenching of HSA addition of complex **4** in 5 mM Tris buffer (pH 7.2) at 298 K; Inset: a plot of I_0/I versus [complex] for **4**; λ_{ex} = 295 nm, λ_{em} = 345 nm, [HSA] = 5 μM. **(b)** Scatchard plot: log[(I_0-I)/I] vs. log[Complex] for HSA in the presence of complex **4**.

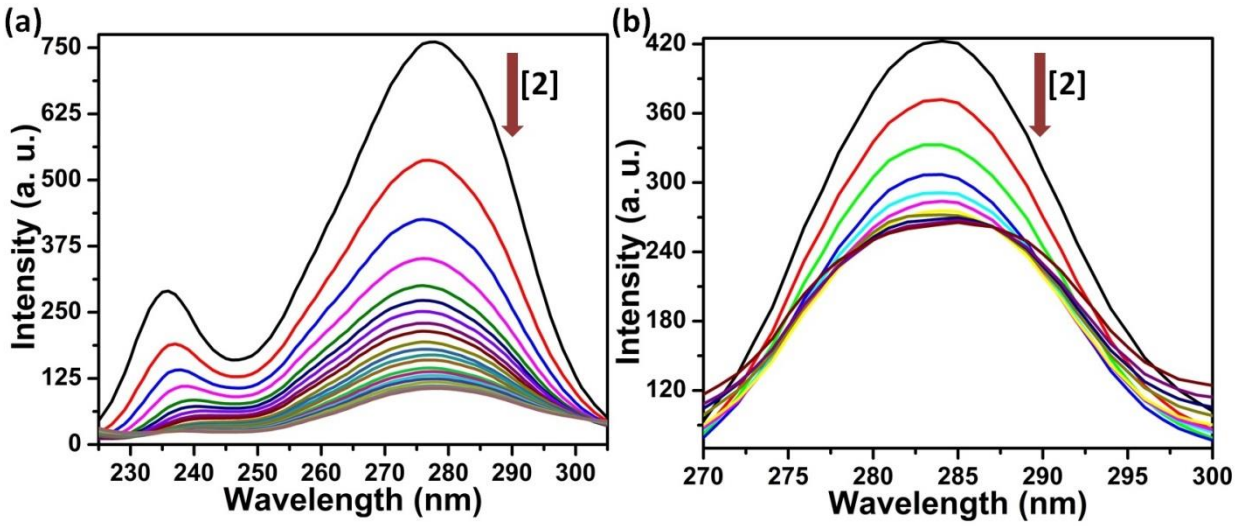

Figure S17. Synchronous emission spectra of HSA (5 μM) showing effect of increasing concentration of complex **2 (a)** with $\Delta\lambda$ = 60 nm and **(b)** with $\Delta\lambda$ = 15 nm at 298 K in Tris buffer (pH = 7.2).

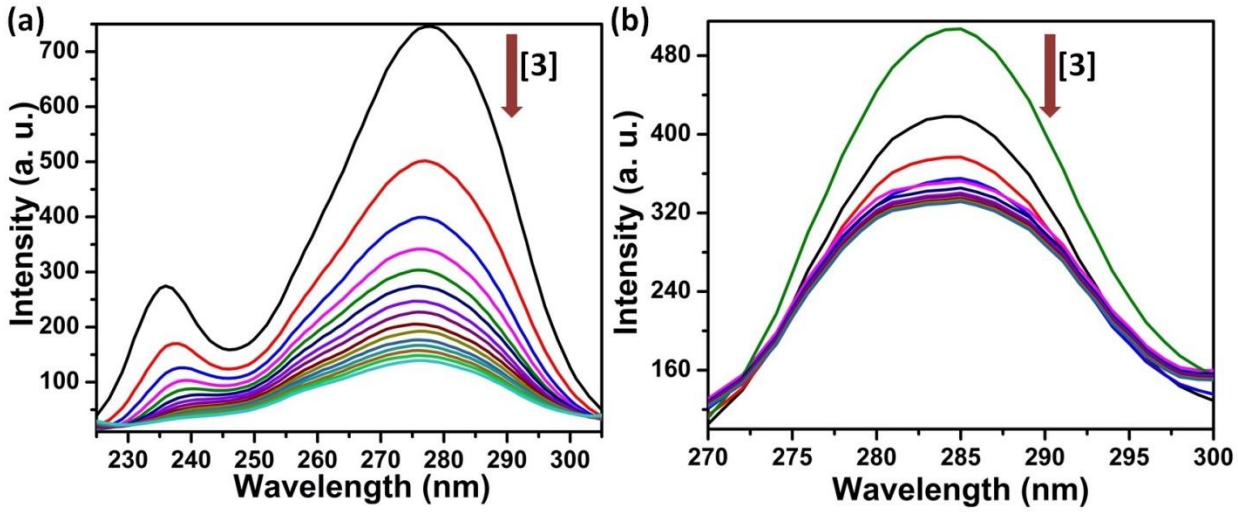

Figure S18. Synchronous emission spectra of HSA (5 μM) showing effect of increasing concentration of complex **3 (a)** with $\Delta\lambda$ = 60 nm and **(b)** with $\Delta\lambda$ = 15 nm at 298 K in Tris buffer (pH = 7.2).

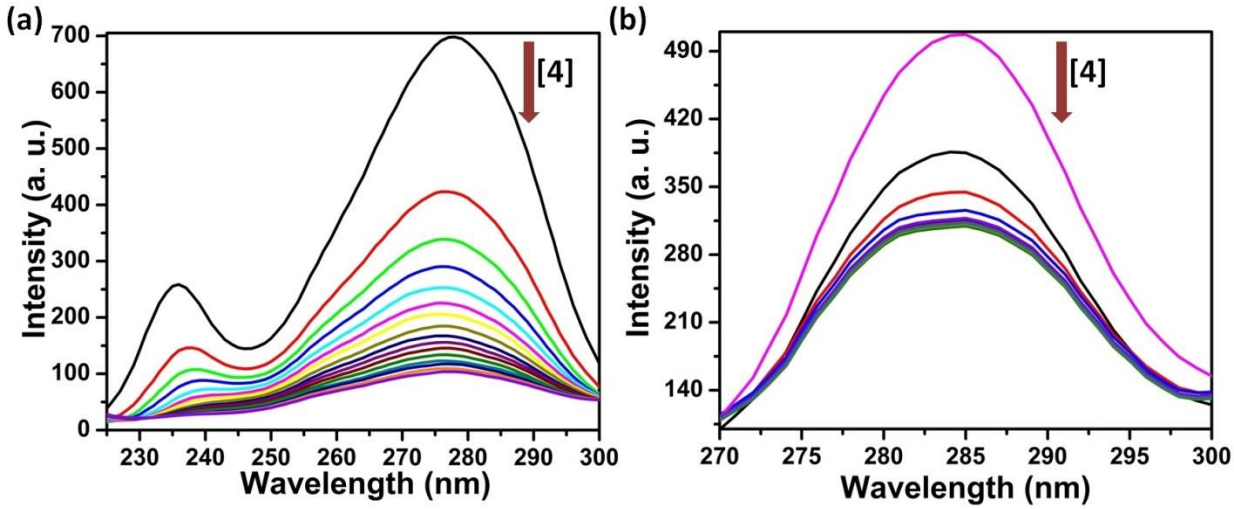

Figure S19. Synchronous emission spectra of HSA (5 μM) showing effect of increasing concentration of complex **4 (a)** with $\Delta\lambda$ = 60 nm and **(b)** with $\Delta\lambda$ = 15 nm at 298 K in Tris buffer (pH = 7.2).

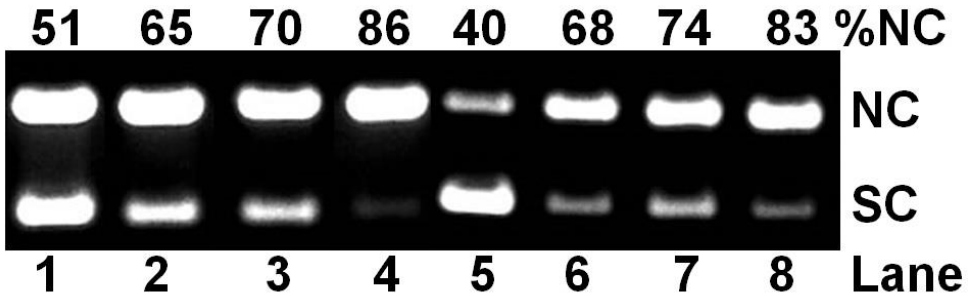

Figure S20. Gel electrophoresis diagram showing the cleavage of SC pUC19 DNA (30 μM, 0.2 μg) incubated with complexes **1** and **2** (60 μM) in 50 mM Tris-HCl/NaCl buffer (pH, 7.2) at 37 °C for 1.5 h on irradiation with UV-A light of 365 nm (6 W) for various exposure time. Detailed conditions are given below in a tabular form.

Lane No.	**Reaction Condition**	**λ/nm**	**Exposure time (t/min)**	**%NC**
1	DNA+ **1**	365	30	51
2	DNA+ **1**	365	60	65
3	DNA+ **1**	365	90	70
4	DNA+ **1**	365	120	86
5	DNA+ **2**	365	30	40
6	DNA+ **2**	365	60	68
7	DNA+ **2**	365	90	74
8	DNA+ **2**	365	120	83

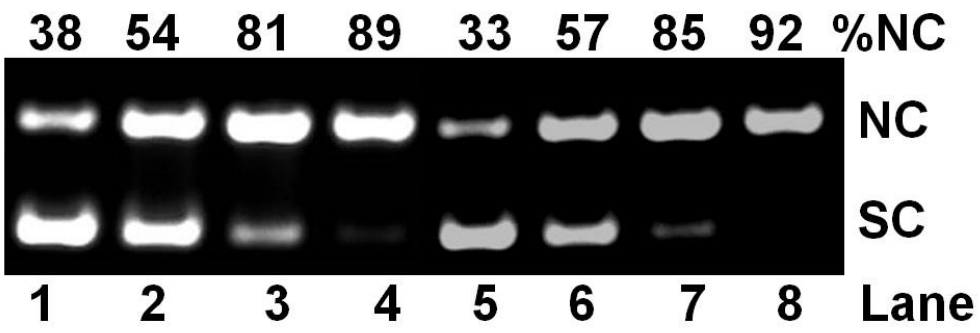

Figure S21. Gel electrophoresis diagram showing the cleavage of SC pUC19 DNA (30 μM, 0.2 μg) incubated with complexes **3** and **4** (60 μM) in 50 mM Tris-HCl/NaCl buffer (pH, 7.2) at 37 °C for 1 h on irradiation with UV-A light of 365 nm (6 W) for various exposure time. Detailed conditions are given below in a tabular form.

Lane No.	**Reaction Condition**	**λ/nm**	**Exposure time (t/min)**	**%NC**
1	DNA+ **3**	365	30	38
2	DNA+ **3**	365	60	54
3	DNA+ **3**	365	90	81
4	DNA+ **3**	365	120	89
5	DNA+ **4**	365	30	33
6	DNA+ **4**	365	60	57
7	DNA+ **4**	365	90	85
8	DNA+ **4**	365	120	92

Figure S22. Gel electrophoresis diagram showing the cleavage of SC pUC19 DNA (30 μM, 0.20 μg μL^{-1}) incubated with complexes **1** and controls in 50 mM Tris-HCl/NaCl buffer (pH, 7.2) at 37 °C for 2 h on irradiation with UV-A light of 365 nm (6 W) for 1 h: lane 1, DNA control; lane 2, DNA + HTTA (60 μM); lane 3, DNA + Anpp (60 μM); lane 4, DNA + Pypp (60 μM); lane 5, $EuCl_3 \cdot xH_2O$ control (60 μM); lane 6, DNA + **1** (60 μM); Lane 7, DNA + **1** (60 μM) + DMSO (4 μL); Lane 8, DNA + **1** (60 μM) + KI (400 μM); Lane 9, DNA + **1** (60 μM) + NaN_3 (400 μM); Lane 10, DNA + **1** (60 μM) + L-Histidine (400 μM); Lane 11, DNA + **1** (60 μM) + D_2O (16 μL); Lane 12, DNA + catalase (4 unit**) + 1** (60 μM).

Figure S23. Gel electrophoresis diagram showing the cleavage of SC pUC19 DNA (30 μM, 0.20 μg μL^{-1}) incubated with complexes **2** and controls in 50 mM Tris-HCl/NaCl buffer (pH, 7.2) at 37 °C for 2 h on irradiation with UV-A light of 365 nm (6 W) for 1 h: lane 1, DNA control; lane 2, DNA + HTTA (60 μM); lane 3, DNA + Anpp (60 μM); lane 4, DNA + Pypp (60 μM); lane 5, $TbCl_3 \cdot xH_2O$ control (60 μM); lane 6, DNA + **2** (60 μM); Lane 7, DNA + **2** (60 μM) + DMSO (4 μL); Lane 8, DNA + **2**(60 μM) + KI (400 μM); Lane 9, DNA + **2** (60 μM) + NaN_3 (400 μM); Lane 10, DNA + **2** (60 μM) + L-Histidine (400 μM); Lane 11, DNA + **2** (60 μM) + D_2O (16 μL); Lane 12, DNA + catalase (4 unit**) + 2** (60 μM).

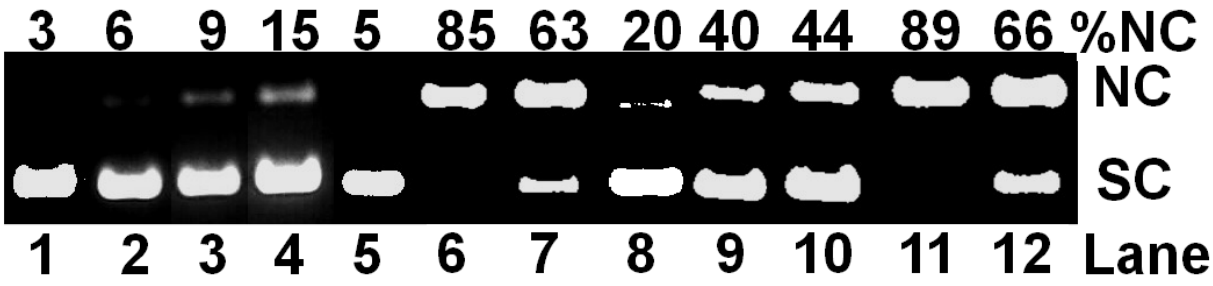

Figure S24. Gel electrophoresis diagram showing the cleavage of SC pUC19 DNA (30 μM, 0.20 μg μL^{-1}) incubated with complexes **3** and controls in 50 mM Tris-HCl/NaCl buffer (pH, 7.2) at 37 °C for 2 h on irradiation with UV-A light of 365 nm (6 W) for 1 h: lane 1, DNA control; lane 2, DNA + HTTA (60 μM); lane 3, DNA + Anpp (60 μM); lane 4, DNA + Pypp (60 μM); lane 5, $EuCl_3 \cdot xH_2O$ control (60 μM); lane 6, DNA + **3** (60 μM); Lane 7, DNA + **3** (60 μM) + DMSO (4 μL); Lane 8, DNA + **3** (60 μM) + KI (400 μM); Lane 9, DNA + **3** (60 μM) + NaN_3 (400 μM); Lane 10, DNA + **3** (60 μM) + L-Histidine (400 μM); Lane 11, DNA + **3** (60 μM) + D_2O (16 μL); Lane 12, DNA + catalase (4 unit**) + 3** (60 μM).

Figure S25. Gel electrophoresis diagram showing the cleavage of SC pUC19 DNA (30 μM, 0.20 μg μL^{-1}) incubated with complexes **2** and controls in 50 mM Tris-HCl/NaCl buffer (pH, 7.2) at 37 °C for 2 h on irradiation with UV-A light of 365 nm (6 W) for 1 h: lane 1, DNA control; lane 2, DNA + HTTA (60 μM); lane 3, DNA + Anpp (60 μM); lane 4, DNA + Pypp (60 μM); lane 5, $TbCl_3 \cdot xH_2O$ control (60 μM); lane 6, DNA + **4** (60 μM); Lane 7, DNA + **4** (60 μM) + DMSO (4 μL); Lane 8, DNA + **4** (60 μM) + KI (400 μM); Lane 9, DNA + **4** (60 μM) + NaN_3 (400 μM); Lane 10, DNA + **4** (60 μM) + L-Histidine (400 μM); Lane 11, DNA + **4** (60 μM) + D_2O (16 μL); Lane 12, DNA + catalase (4 unit**) + 4** (60 μM).

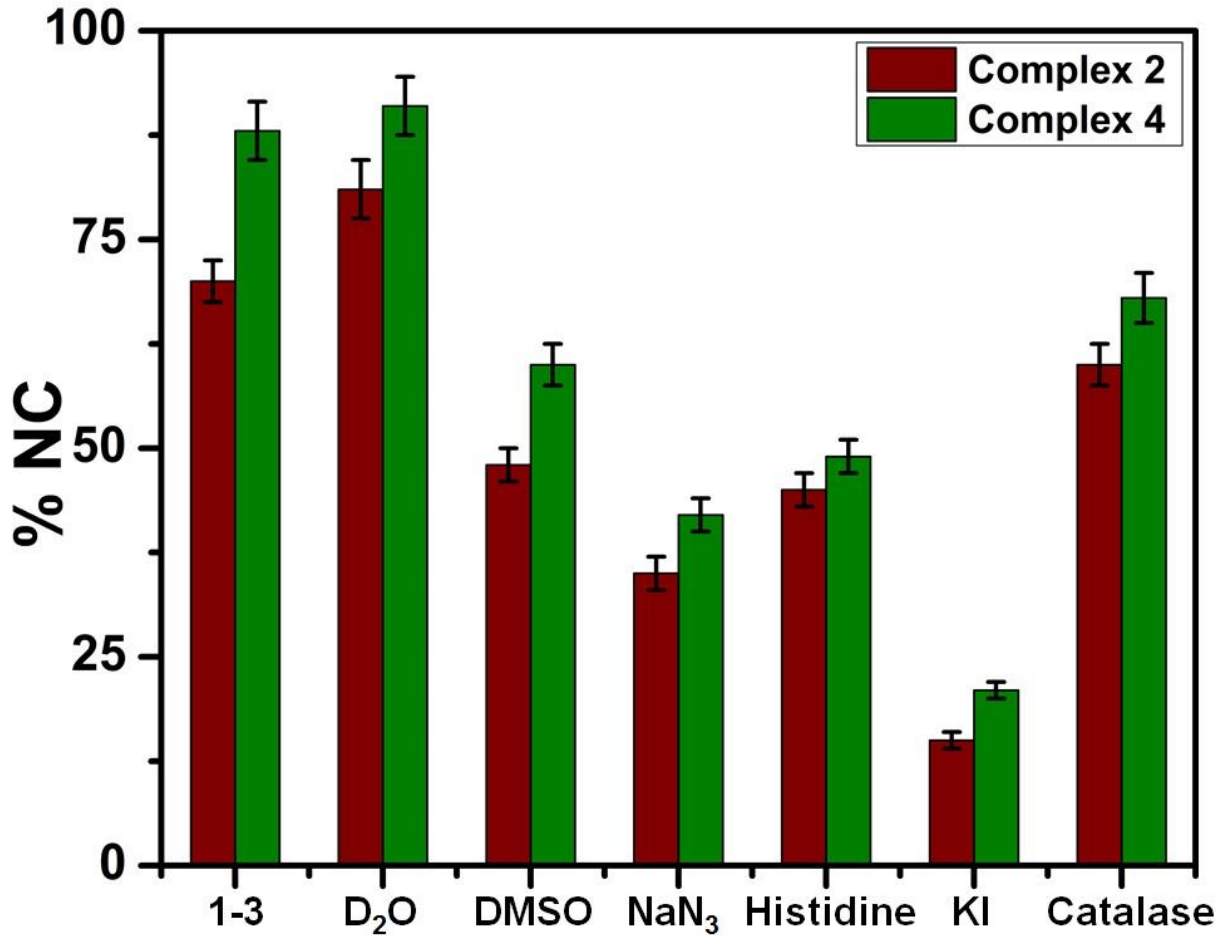

Figure S26. Cleavage of SC pUC19 DNA (30 μM, 0.2 μg) by complexes **2** and **4** (60 μM) (Wine) and (Olive) on photo-exposure at 365 nm (6 W) for 1.5 h in the presence of various additives in Tris-HCl/NaCl buffer. NaN_3, 0.4 mM; KI, 0.4 mM; D_2O, 16 μL; L-histidine, 0.4 mM; DMSO, 4 μL; catalase, 4 U.

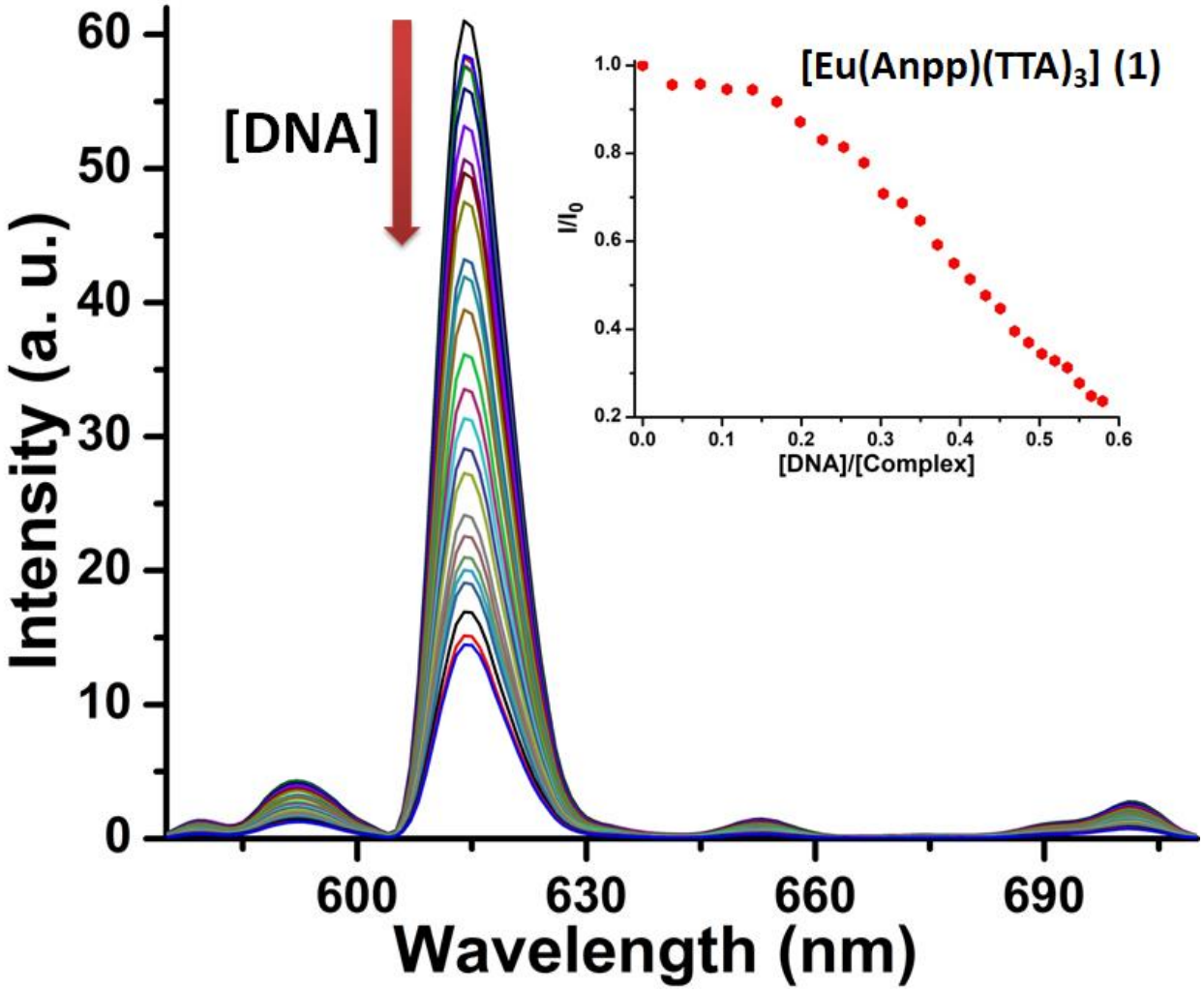

Figure S27. Time delayed luminescence spectra of [Eu(Anpp)(TTA)$_3$] (**1**) showing quenching of luminescence intensity with increasing the concentration of CT-DNA in 5 mM Tris buffer (pH=7.2) at 298 K [delay time = gate time = 0.1 ms, λ_{ex} = 340 nm, slit width = 5 nm].