Electronic Supplementary Information (ESI)

Photocytotoxic Kinetically Stable Ruthenium(II)-N,N-donor Polypyridyl Complexes of Oxalate for Anticancer Activity Against HepG2 Liver Cancer Cells

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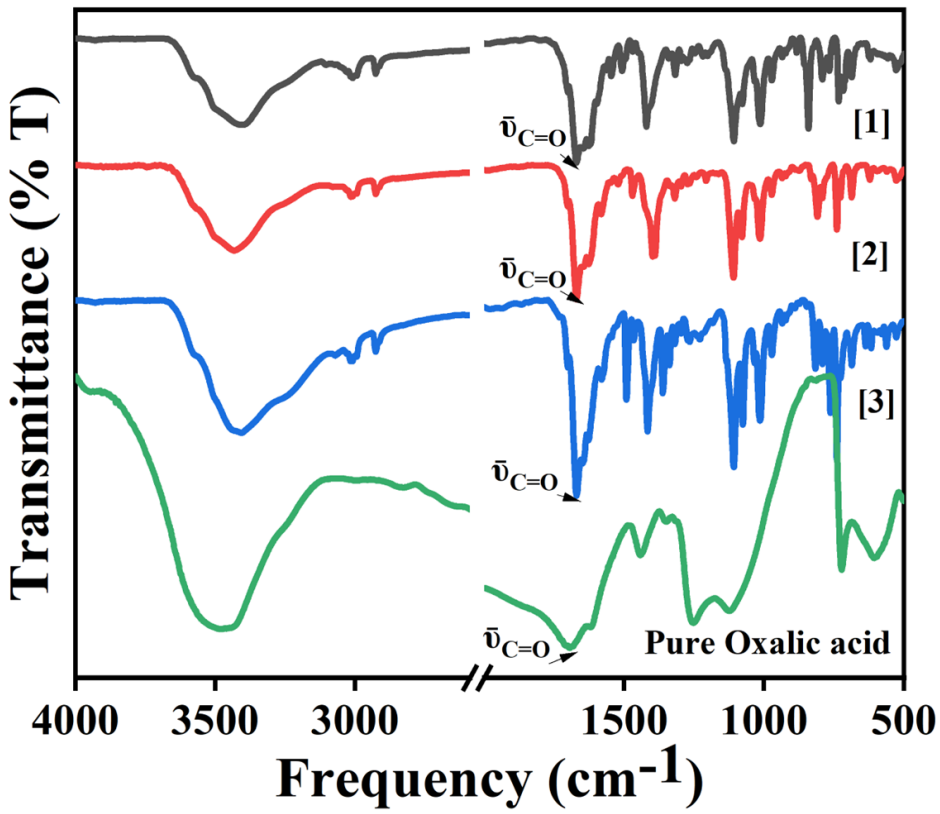

Figure S1. An overlay of the solid-state FT-IR spectra of the complexes **1**, **2**, **3** and oxalic acid in KBr pellet.

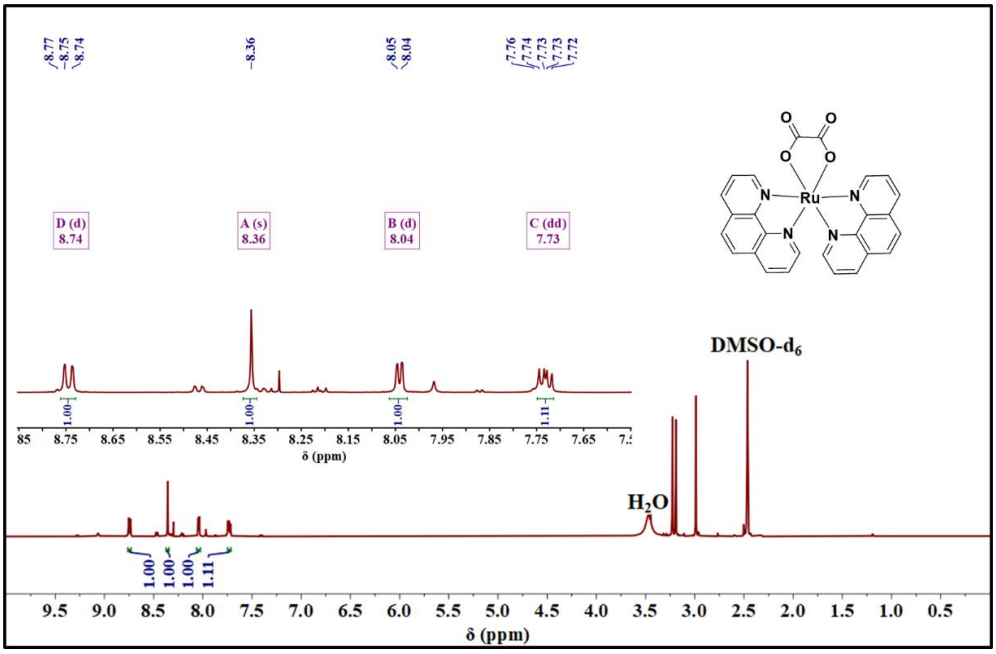

Figure S2. ^{1}H NMR spectrum of complex $[Ru^{II}(phen)_2(ox)]$ (**1**) (400 MHz, DMSO-d_6).

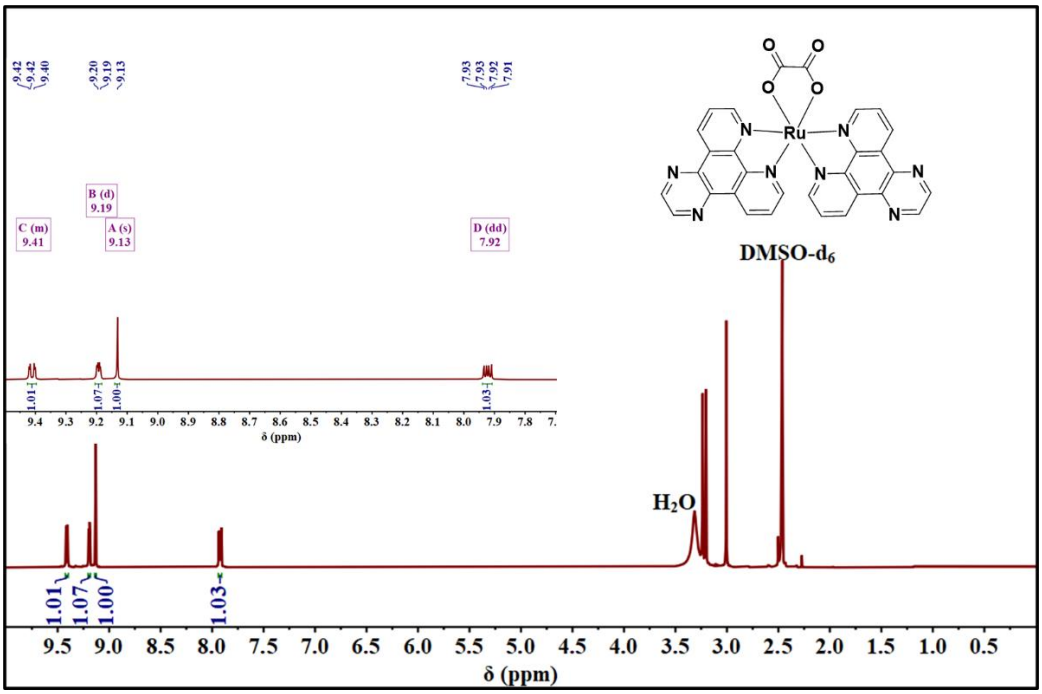

Figure S3. ^{1}H NMR spectrum of complex $[Ru^{II}(dpq)_2(ox)]$ (**2**) (400 MHz, DMSO-d_6).

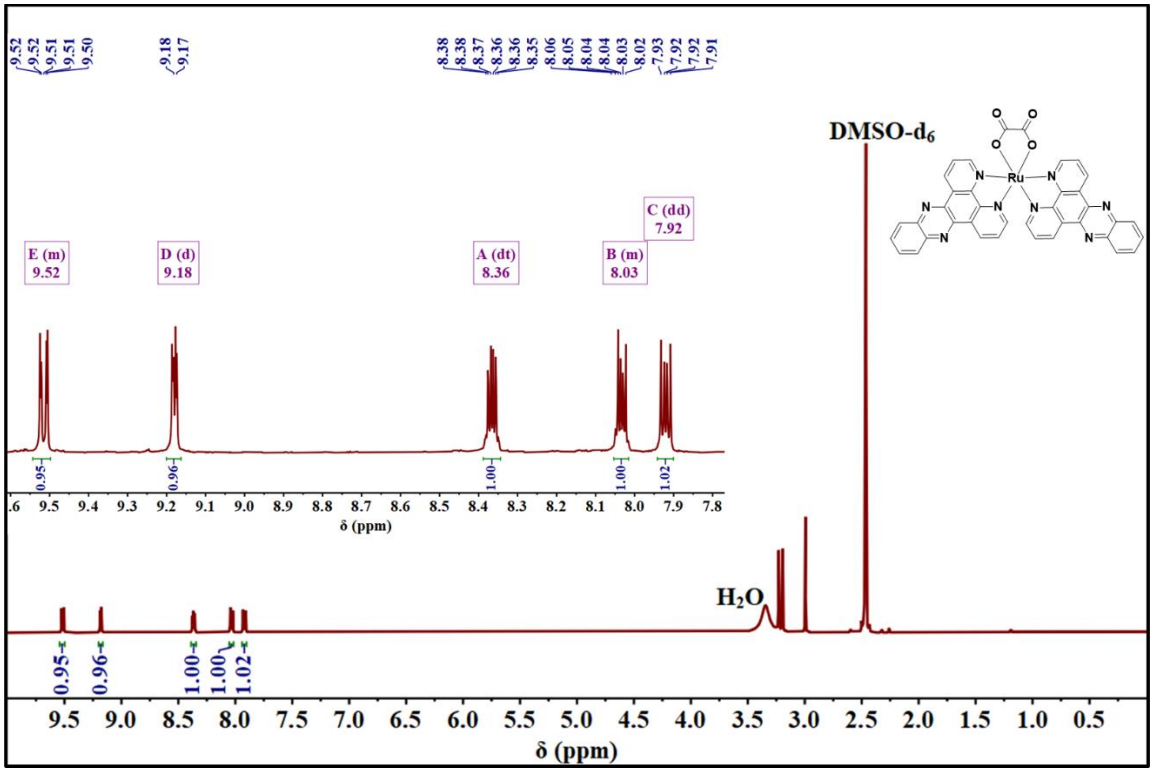

Figure S4. ^{1}H NMR spectrum of complex [$Ru^{II}(dppz)_2(ox)$] (**3**) (400 MHz, DMSO-d_6).

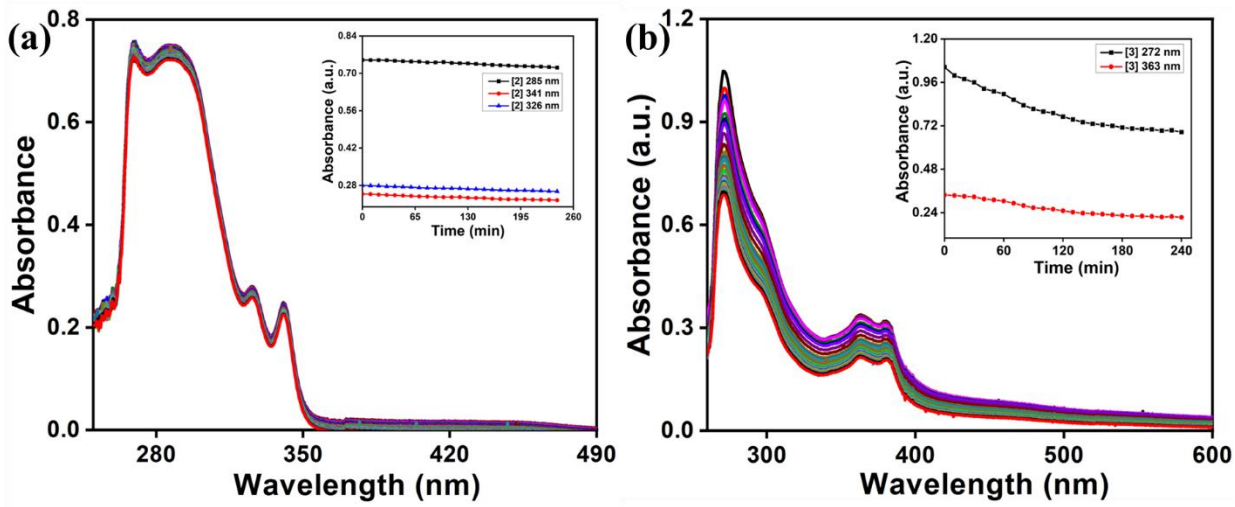

Figure S5. The electronic absorption changes of the complex **2** (a) and **3** (b) (48 µM) upon solvation for 240 min in the dark in 5% (v/v) DMF-5 mM Tris-HCl/NaCl buffer (pH = 7.2) mixture. Inset: Changes in $A_{272\ nm}$ and $A_{363\ nm}$ for complexes **2** and **3**.

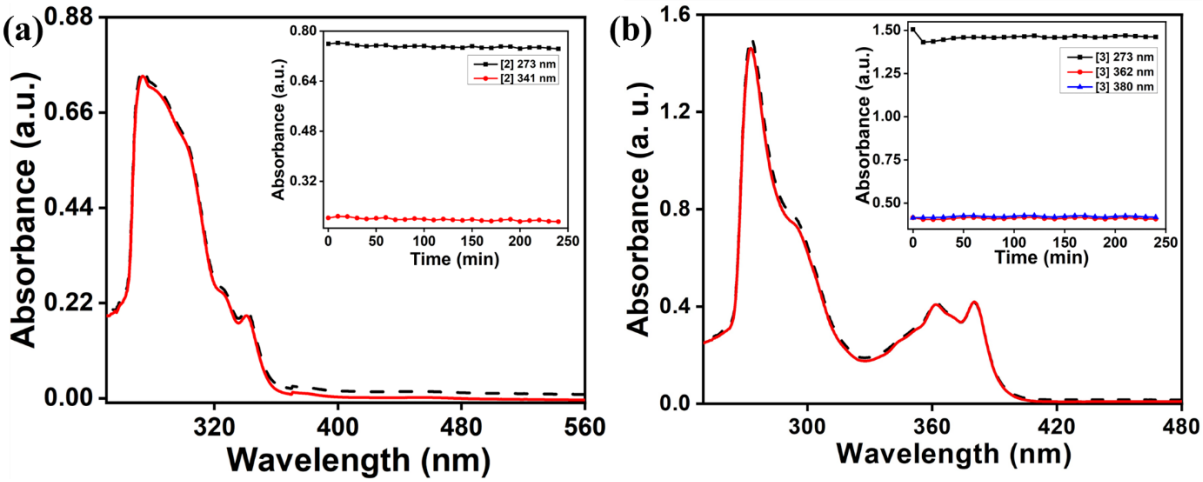

Figure S6. The electronic absorption changes of the complexes (48 μM) **2** (a) and **3** (b) upon solvation for 0–240 min in the dark in DMF. Inset: Changes in A_λ for complexes **2** and **3**.

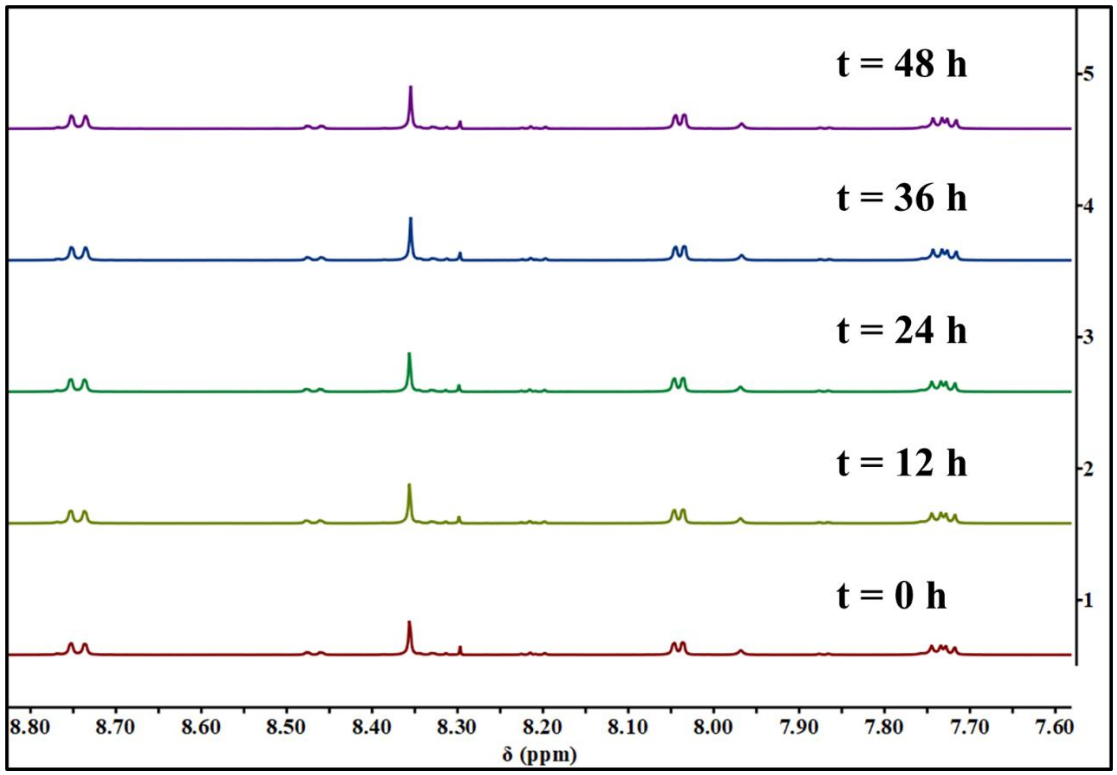

Figure S7. Time-dependent ^{1}H-NMR spectra of the complex **1** (DMSO-d_6, 500 MHz). (a) Overlay of the region 7.50-8.50 ppm.

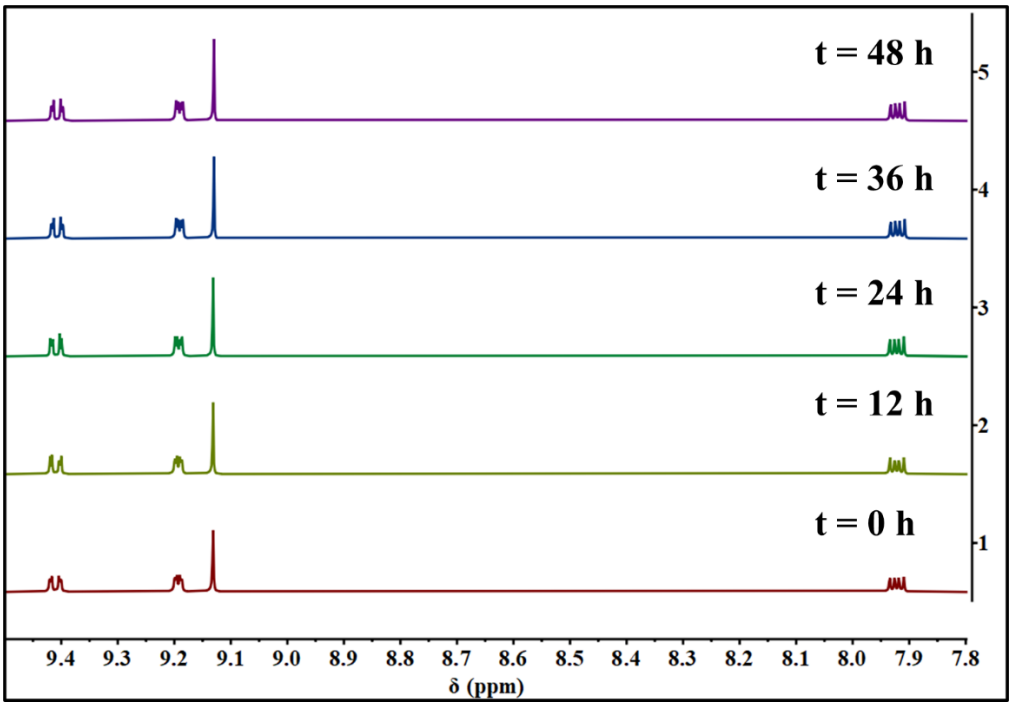

Figure S8. Time-dependent ^{1}H-NMR spectra of the complex **2** (DMSO-d6, 500 MHz). (a) Overlay of the region 7.50-9.50 ppm.

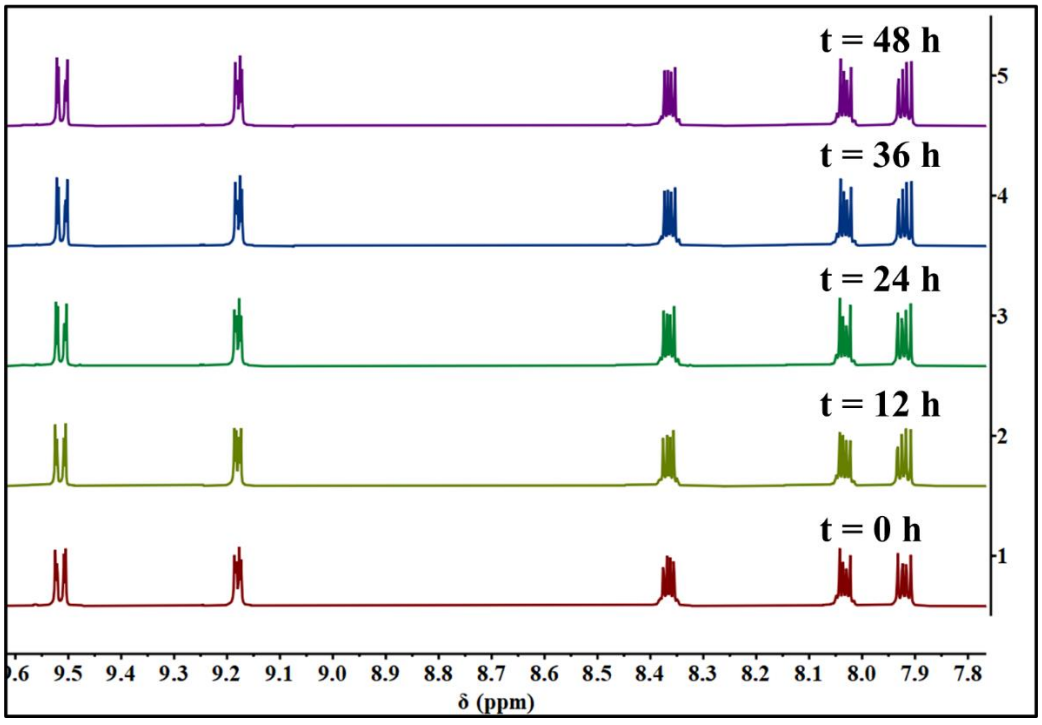

Figure S9. Time-dependent ^{1}H-NMR spectra of the complex **3** (DMSO-d_6, 500 MHz). (a) Overlay of the region 7.50-9.60 ppm.

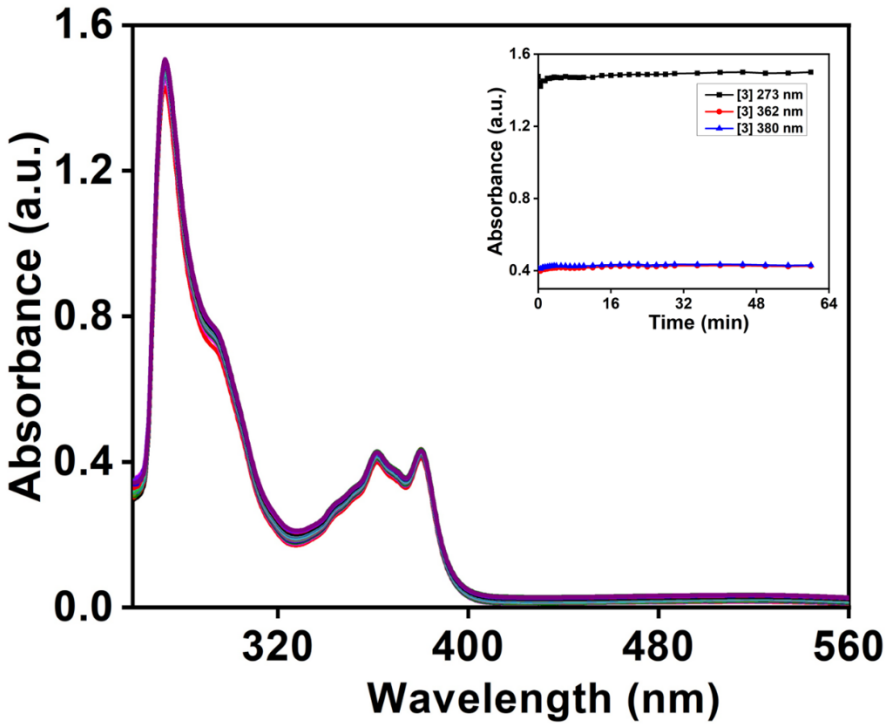

Figure S10. The green light (λ_{irrad} = 530 nm) LED (3 V, 158 lm@700 mA) induced spectral changes observed for the complexes **3** in DMF. Absorption spectral traces of complex **3** (24 µM) for the 0-60 min. Inset: Changes in $A_{273\ nm}$, $A_{362\ nm}$ and $A_{380\ nm}$ of complex **3** with photoirradiation time.

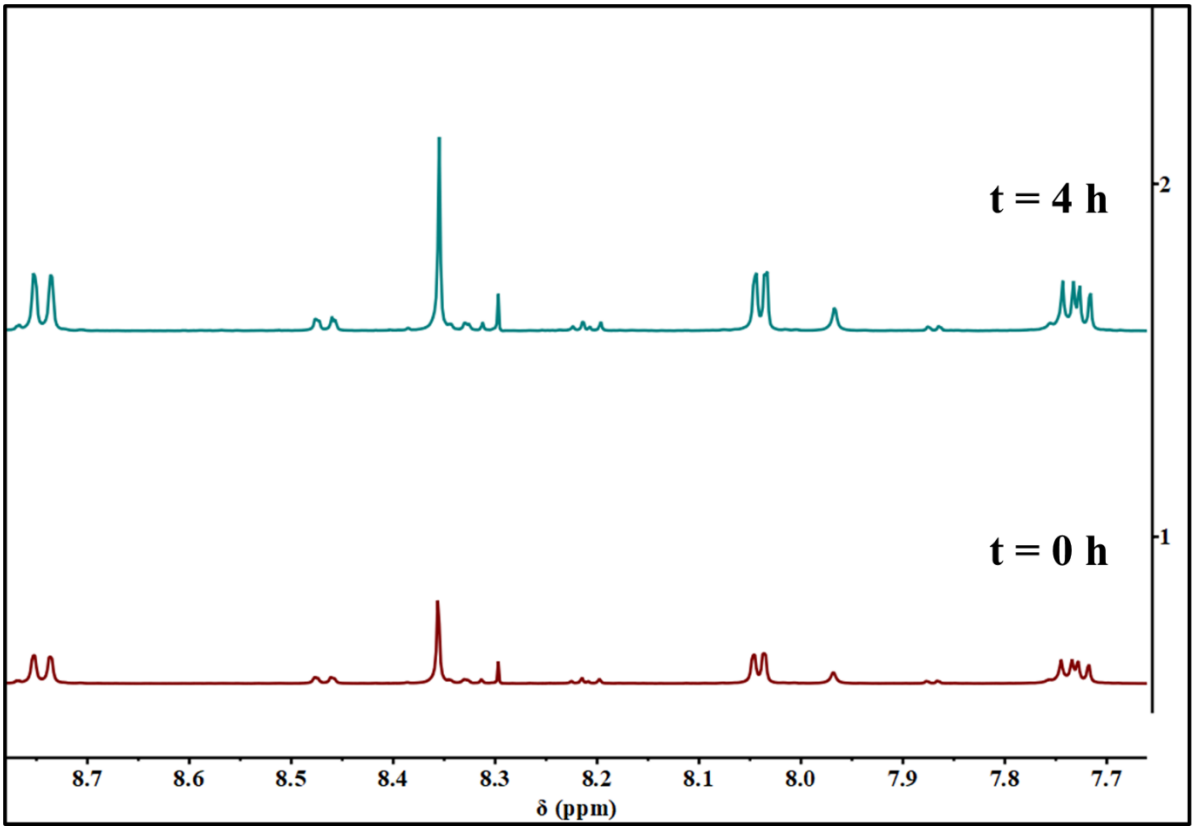

Figure S11. Green light (λ_{irr} =530 nm) irradiated Time-dependent ^{1}H-NMR spectra of the complex **1** (DMSO-d_6, 500 MHz). (a) Overlay of the region 7.50-9.60 ppm. Maroon trace (0 h) and green trace (4 h).

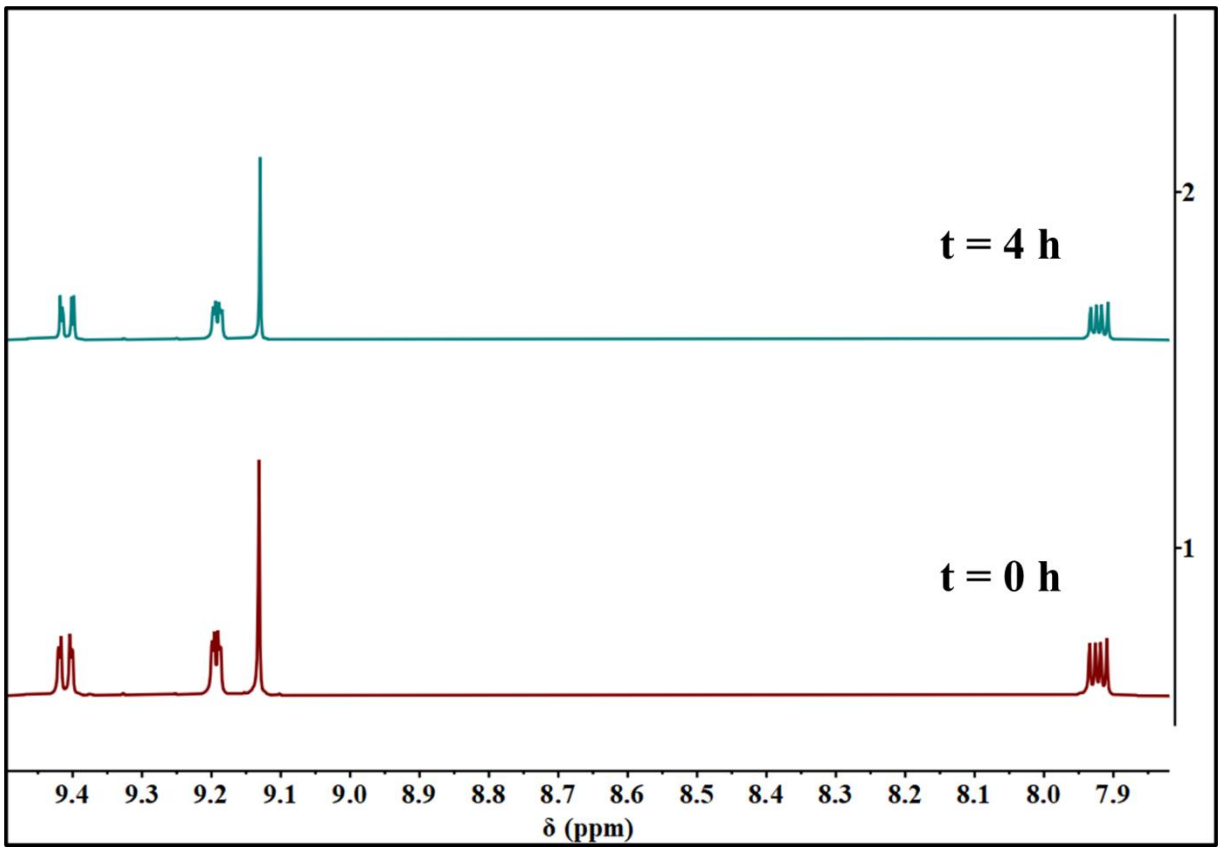

Figure S12. Green light (λ_{irr} =530 nm) irradiated time-dependent ^{1}H-NMR spectra of the complex **2** (DMSO-d_6, 500 MHz). (a) Overlay of the region 7.50-9.60 ppm. Maroon trace (0 h) and green trace (4 h).

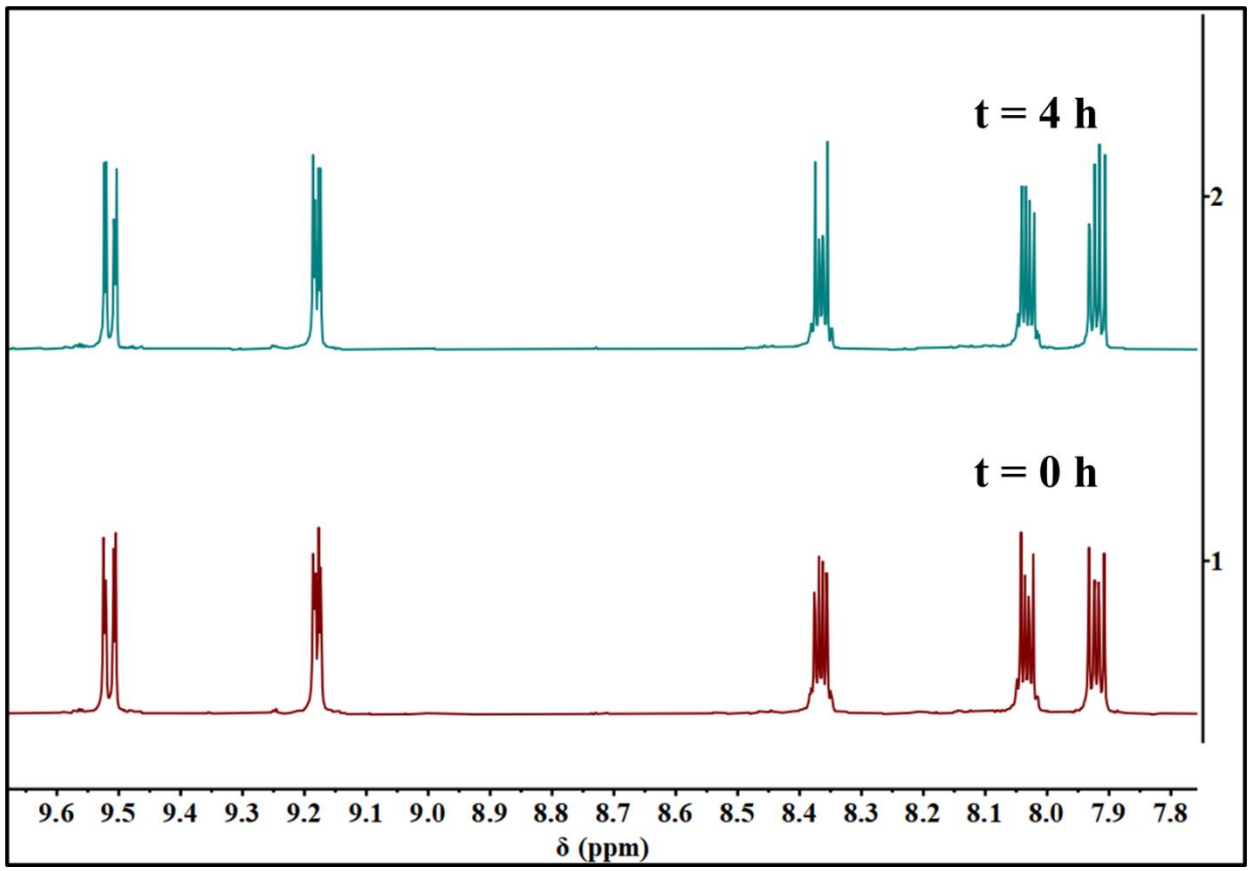

Figure S13. Greenlight (λ_{irr} =530 nm) irradiated Time-dependent ^{1}H-NMR spectra of the complex **3** (DMSO-d_6, 500 MHz). (a) Overlay of the region 7.50-9.60 ppm. Maroon trace (0 h) and green trace (4 h).

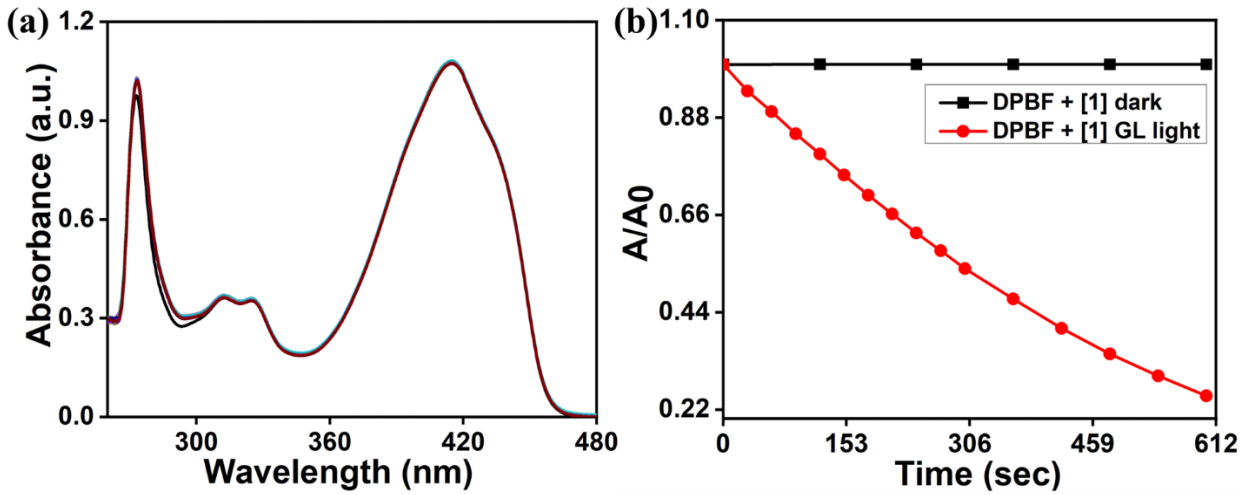

Figure S14. The absorption spectral profile of DPBF (50 µM) with **1** (10 µM) in the dark for 10 min shows the dark stability (a). Overlay of A/A_0 at 414 nm for complex **1** with DPBF in the dark and green-light LED (λ_{irr} = 530 nm, 3V, 158 lm@700mA) for 0–10 min (b). Spectra were recorded at 298 K in DMF solution.

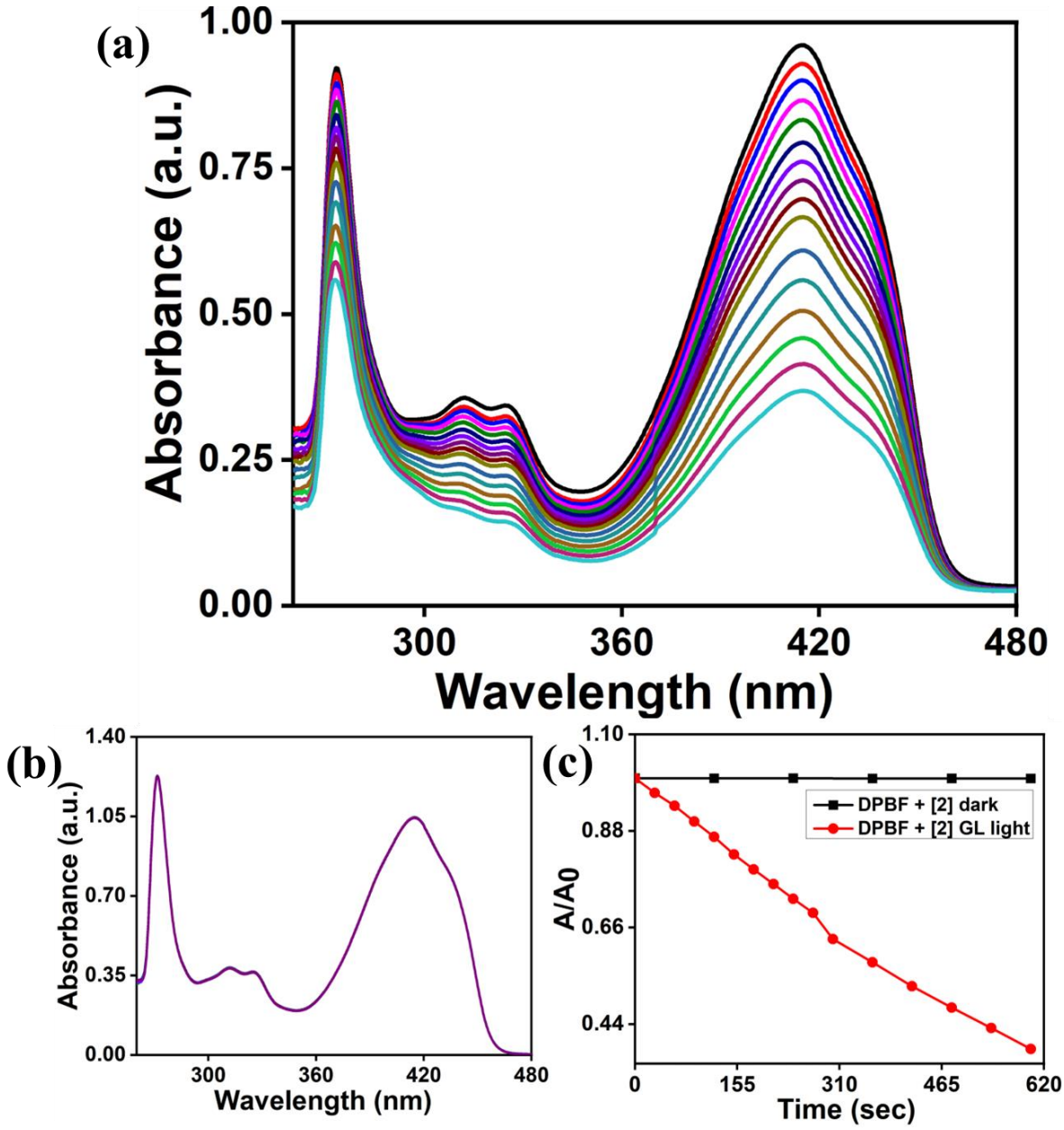

Figure S15. Absorption spectral profile of DPBF (50 µM) with **2** (10 µM) upon green light irradiation (λ_{irr}=530 nm) for 10 min shows the $^1O_2$ generation (a) and, in the dark for 10 min shows the dark stability (b). Overlay of A/A_0 at 414 nm for complex **2** with DPBF in the dark and green-light LED (λ_{irr} = 530 nm, 3V 158 lm@700mA) for 0–10 min (c). Spectra were recorded at 298 K in DMF solution.

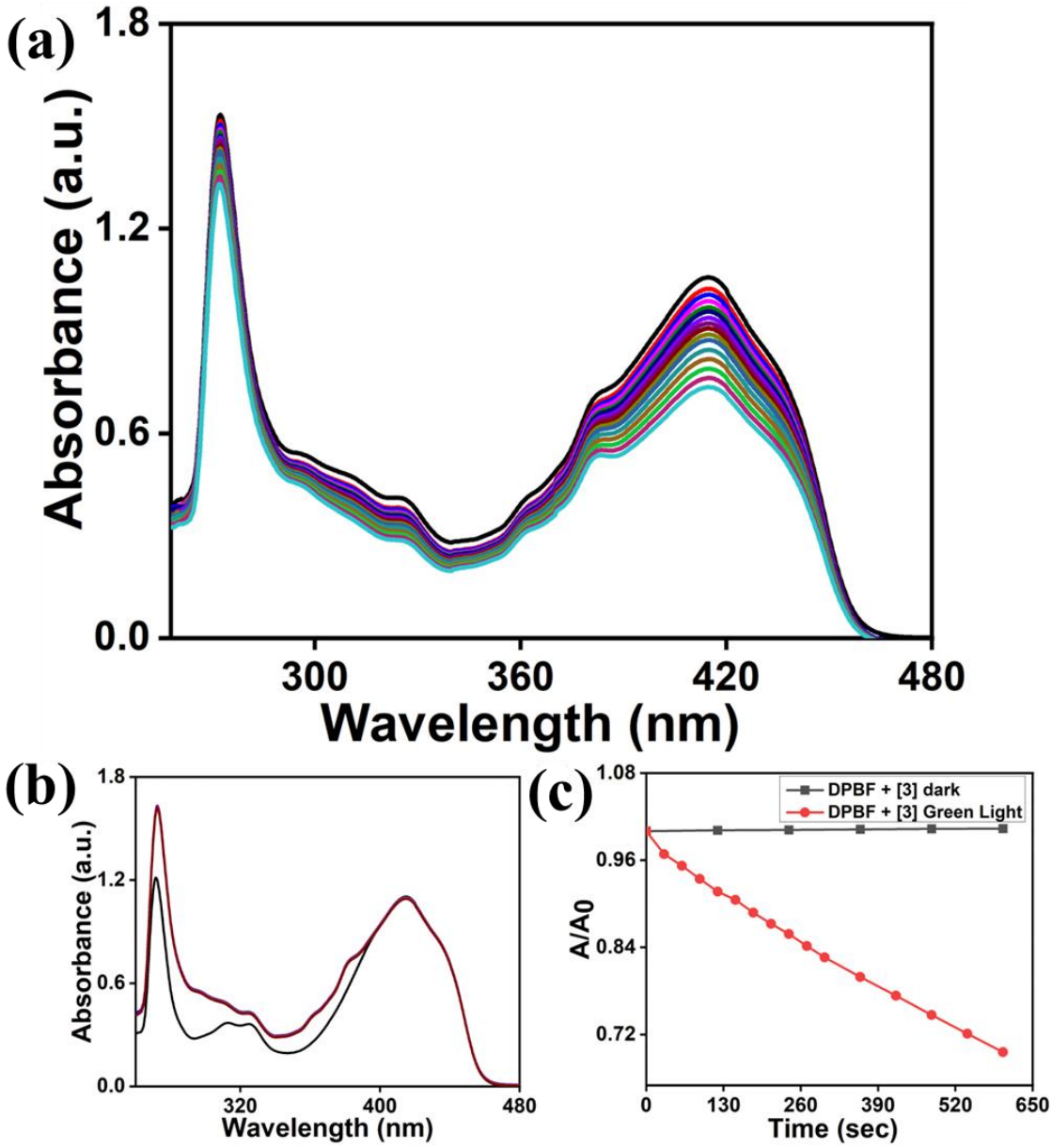

Figure S16. Absorption spectral profile of DPBF (50 μM) with **3** (10 μM) upon green light irradiation (λ_{irr} = 530 nm) for 10 min shows the $^1O_2$ generation (a) and, in the dark for 10 min shows the dark stability (b). Overlay of A/A_0 at 414 nm for complex **3** with DPBF in the dark and green-light LED (λ_{irr} = 530 nm, 3V, 158 lm@700 mA) for 0–10 min (c). Spectra were recorded at 298 K in DMF solution.

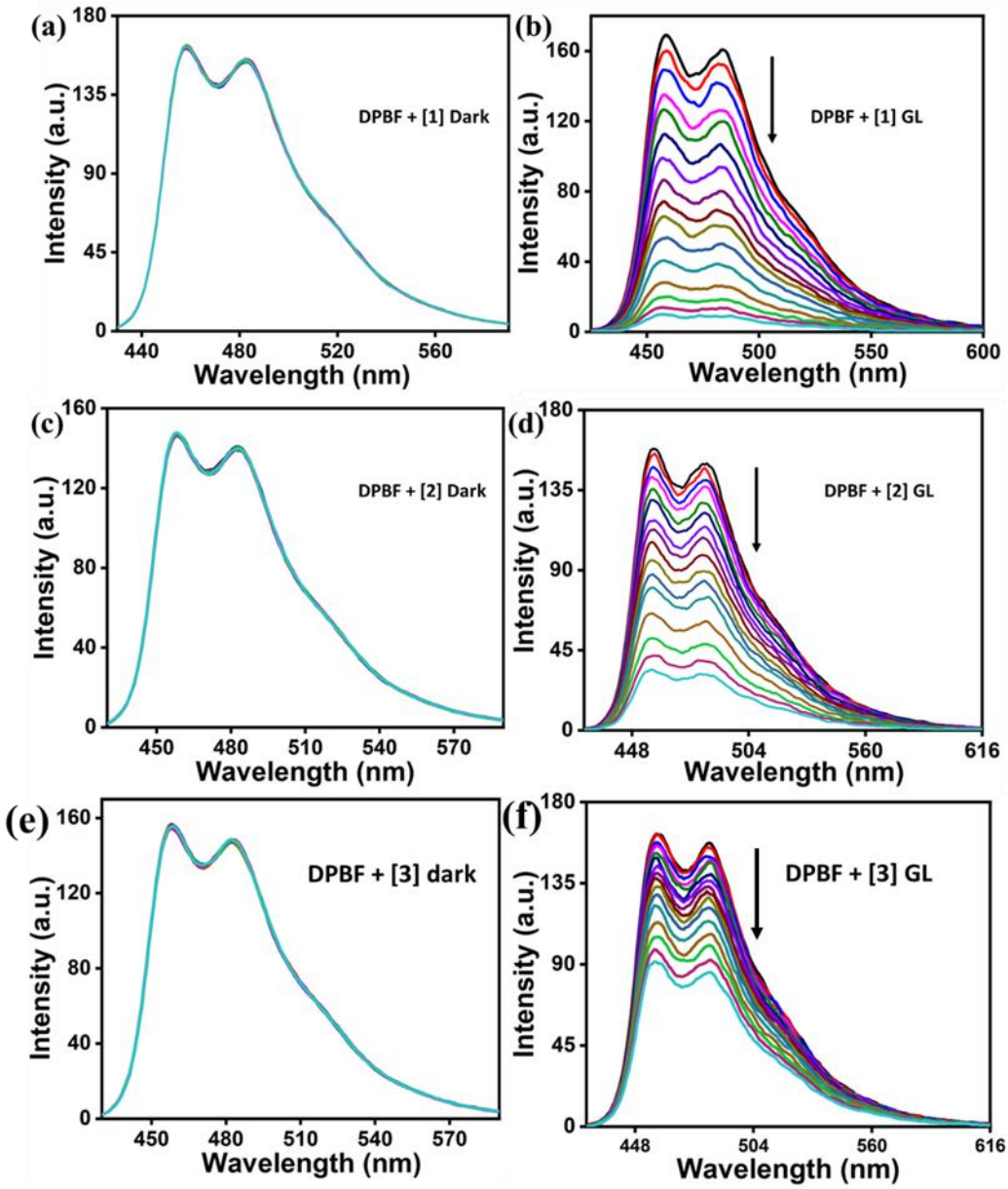

Figure S17. The emission spectral profile of DPBF (50 µM) with complexes **1**, **2** and **3** (5 µM) upon green light irradiation (λ_{Irr} = 530 nm) for 10 min shows the $^1O_2$ generation (b, d, f) and, in the dark for 10 min shows the dark stability (a, c, e), Green-light LED (λ_{irr} = 530 nm, 3V, 158 lm@700 mA) for 0–10 min (c). Spectra were recorded at 298 K in DMF solution, λ_{exc}=415 nm, λ_{em}=460 nm.

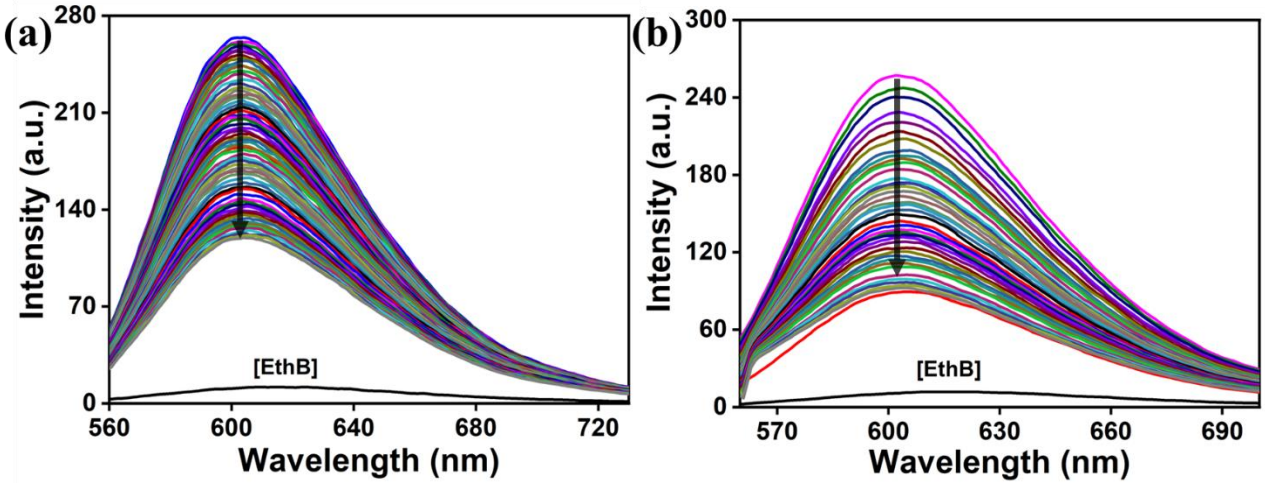

Figure S18. Emission spectrum of ethidium bromide (EB)-bound to DNA in the presence of complexes **2** (a) and **3** (b). ([EB] = 12.5 µM, [DNA] = 15 µM, [**2**] = 0-102 µM, [**3**] = 0-45 µM, λ_{ex} = 546 nm, Ex. and Em. slit width = 10 nm. The arrow shows the intensity change upon increasing complex concentration.

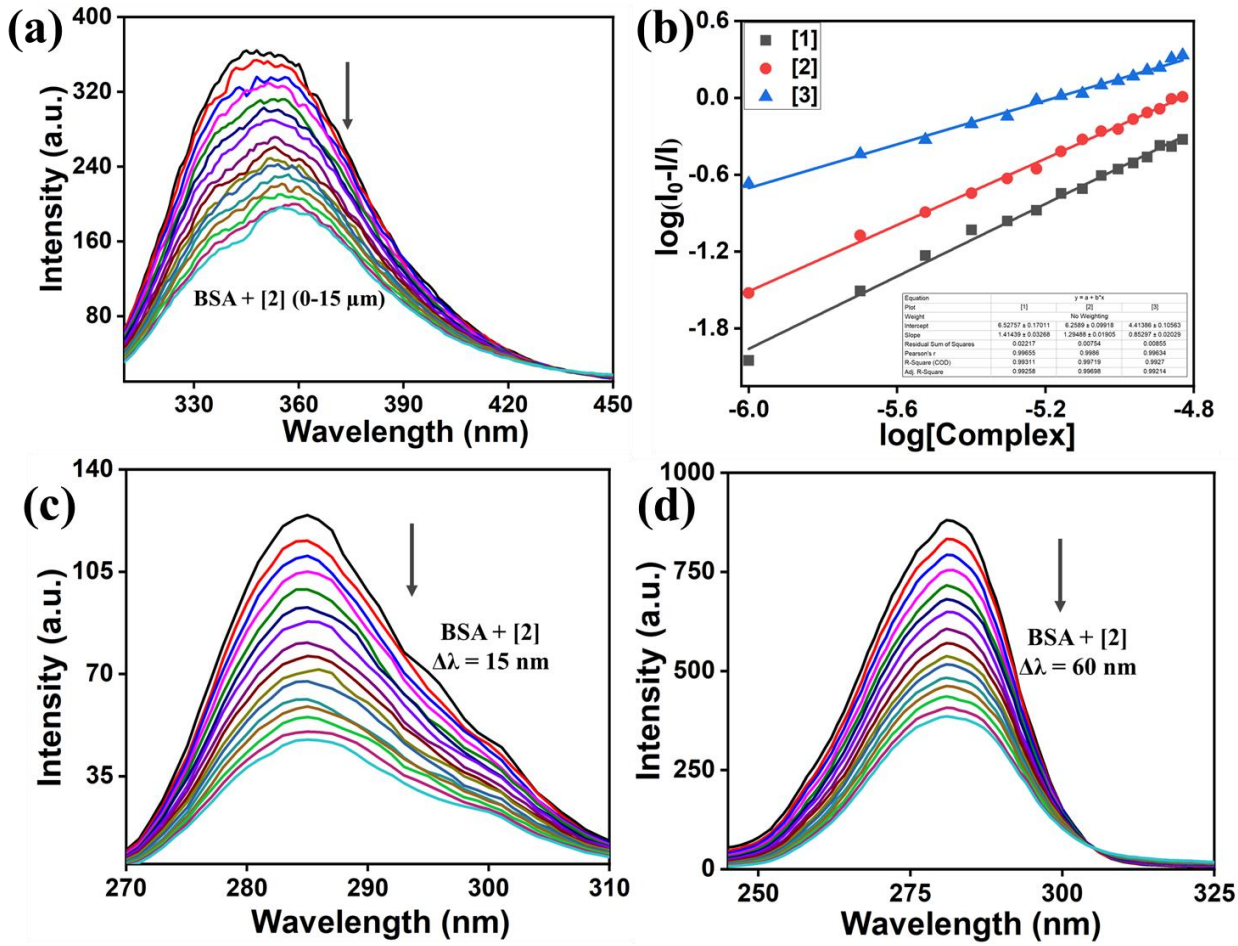

Figure S19. (a) The BSA (2 µM) binding of the complex **2** (0-15 µM) in 0.7% (v/v) DMF-5 mM Tris-HCl/NaCl buffer (pH = 7.2) at 298 K, $\lambda_{ex/em}$ = 295/345 nm and slit width = 10/5. (b) The Scatchard plot for the determination of the static equilibrium binding constant from the intercept and number of binding sites available (*n*) from the slope of the plot. (c) The tyrosine fluorescence emission quenching of BSA upon increasing concentration of complex **2** using synchronous fluorescence studies. (d) The tryptophan fluorescence emission quenching of BSA upon increasing concentration of complex **2** using synchronous fluorescence studies.

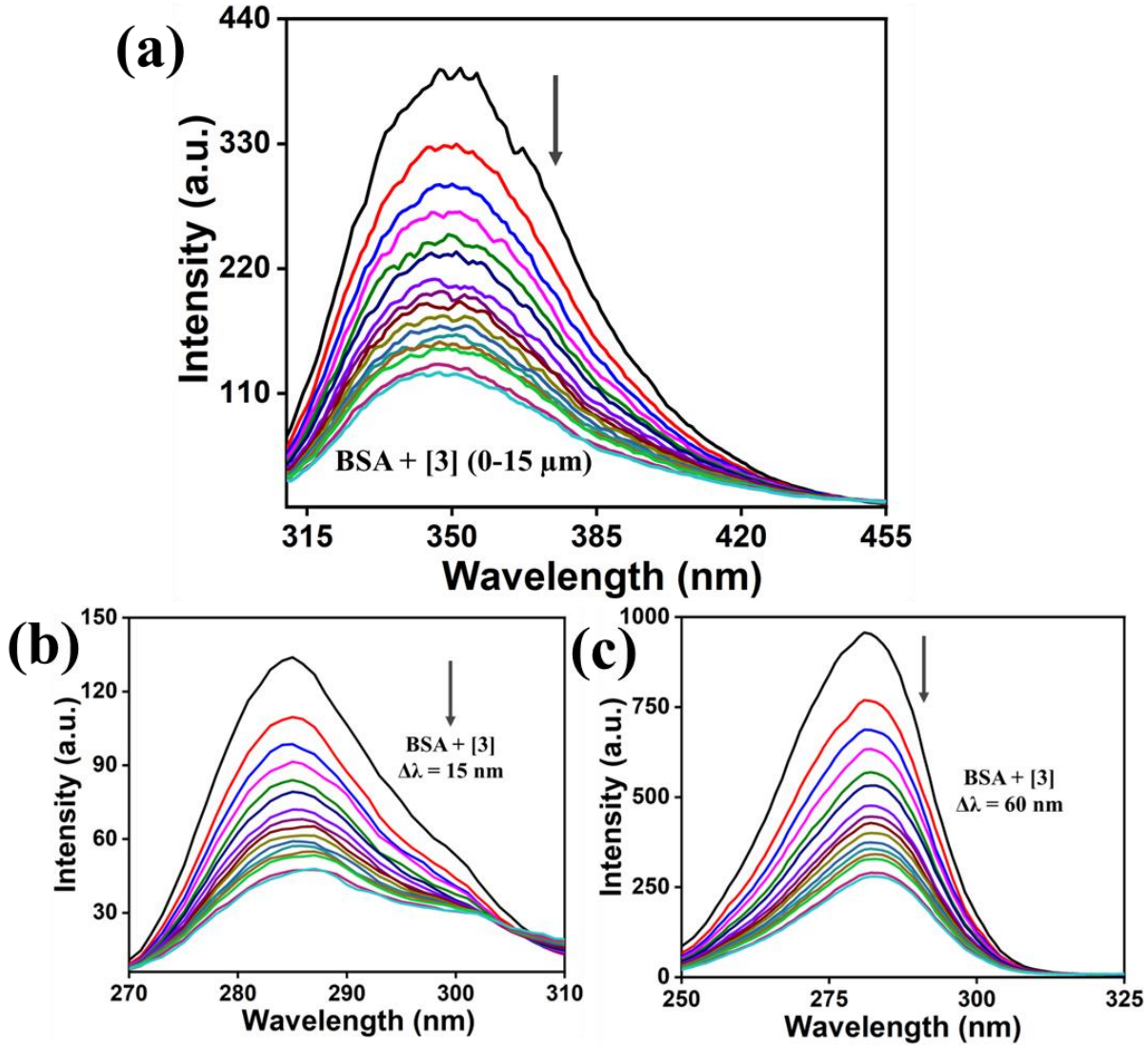

Figure S20. (a) The BSA (2 µM) binding of the complex **3** (0-15 µM) in 0.7% (v/v) DMF-5mM Tris-HCl/NaCl buffer (pH=7.2) at 298 K, $\lambda_{ex/em}$ = 295/345 nm and Ex./Em. slit widths= 10/5 nm. (b) The tyrosine fluorescence emission quenching of BSA upon increasing concentration of complex **3** using synchronous fluorescence studies. (d) The tryptophan fluorescence emission quenching of BSA upon increasing concentration of complex **3** using synchronous fluorescence studies.