Supporting Information

Efficient DNA photocleavage by $[Ru(bpy)_2(dppn)]^{2+}$ with visible light

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Synthesis and characterization

Dppn was synthesized according to a modified method.[S1] 1,10-Phenthroline-5,6-dione (0.210 g) and 2,3-naphthalenediamine (0.158 g) were refluxed in 10 ml $CHCl_3$ under N_2 for 2 h. Dppn was precipitated by cooling the solution, was then filtered and washed with ether, and dried under vacuum. Yield: 0. 211 g (64%). ^{1}H NMR (400 MHz, *CDCl$_3$*) δ (ppm): 9.63 (dd, *J* = 8.08, 1.75 Hz, 1H), 9.24 (dd, *J* = 4.39, 1.62 Hz, 1H), 8.93 (s, 1H), 8.19 (dd, *J* = 6.50, 3.27 Hz, 1H), 7.77 (dd, *J* = 8.07, 4.46 Hz, 1H), 7.62 (m, 1H).

$[Ru(bpy)_2(dppn)](PF_6)_2$, [**3**]$(PF_6)_2$, was synthesized by the direct coordination of dppn (0. 020 g) to $Ru(bpy)_2Cl_2$ (0.028 g) in refluxing 15 ml ethylene glycol under N_2 for 8 h. The cool mixture was filtered through Celite to remove free dppn ligand. An equal volume of a saturated NH_4PF_6 solution was added to the filtrate to precipitate the red product, followed by filtration. The powder was washed with water and ether, and was dried under vacuum. Yield: 0.035 g (63 %).[1] ^{1}H NMR (400 MHz, *CD$_3$CN*) δ (ppm): 9.66 (dd, *J* = 8.20, 1.29 Hz, 2H), 9.13 (s, 2H), 8.53 (dd, *J* = 11.30, 8.14 Hz, 4H), 8.37 (dd, *J* = 6.54, 3.25 Hz, 2H), 8.19-8.06 (m, 4H), 8.02 (dt, *J* = 8.07, 8.07, 1.45 Hz, 2H), 7.93-7.81 (m, 4H), 7.80-7.72 (m, 4H), 7.46 (ddd, *J* = 7.57, 5.62, 1.29 Hz, 2H), 7.28 (m, 2H). MALDI/MS, $[Ru(bpy)_2(dppn)]^+$, 746.327.

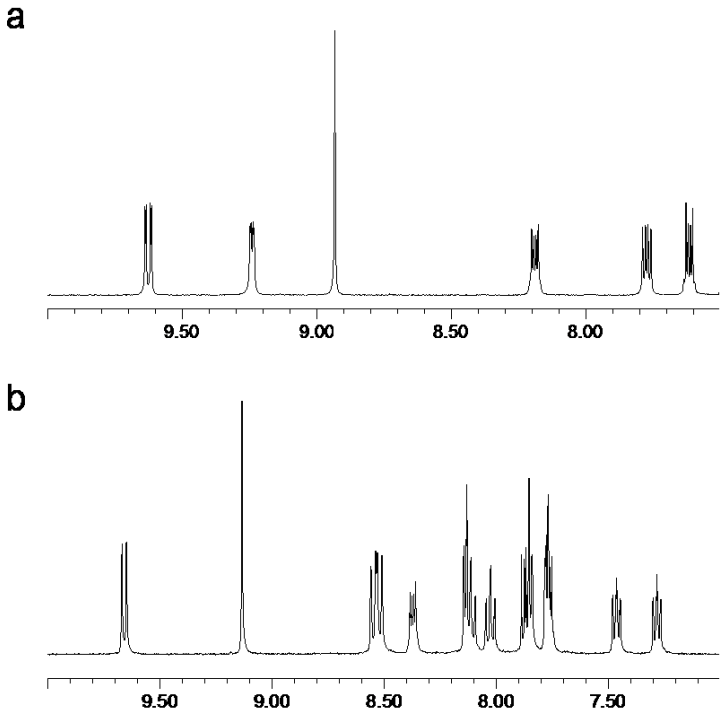


Fig. S1 ^{1}H NMR spectrum of (a) dppn in $CDCl_3$ and (b) [**3**]$(PF_6)_2$ in CD_3CN.

$[Ru(bpy)_3](PF_6)_2$ ([**1**]$(PF_6)_2$) and $Ru(bpy)_2(dppz)](PF_6)_2$ ([**2**]$(PF_6)_2$) were synthesized by a similar method as that described $[Ru(bpy)_2(dppn)](PF_6)_2$. The chloride salts $[Ru(bpy)_2L]Cl_2$ (L = bpy, dppz, and dppn) were precipitated by the addition of a saturated Bu_4NCl acetone solution to the corresponding $[Ru(bpy)_2L](PF_6)_2$ complex in acetone. The solid was filtered, washed with acetone, diethyl ether, and dried under vacuum. Column chromatography using Sephadex G-15 solid phase was employed to obtain samples of high purity for luminescence studies.

Electronic absorption and emission spectra

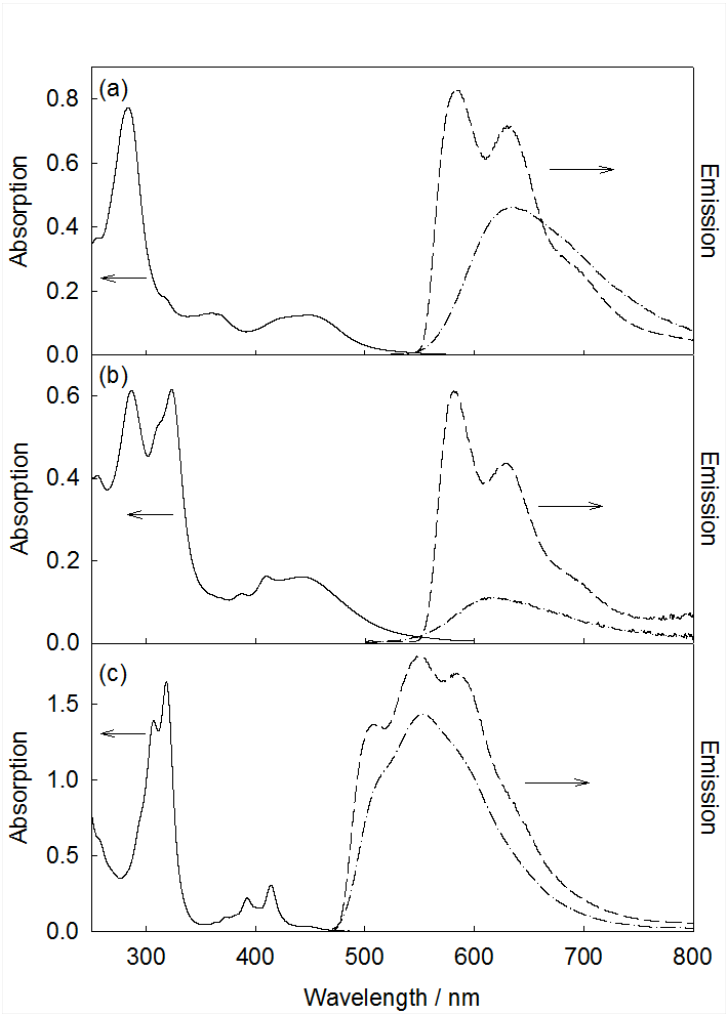


Fig. S2 Absorption (solid) and emission spectra at room temperature (dotted-dash) and at 77 K (dash) in ethanol/methanol (v/v: 4/1) of (a) [**2**]$(PF_6)_2$, (b) [**3**]$(PF_6)_2$, and (c) dppn. The room temperature absorption spectra of **2** and **3** were obtained in CH_3CN, and that of dppn was in $CHCl_3$.

^{1}H NMR spectra as a function of concentration

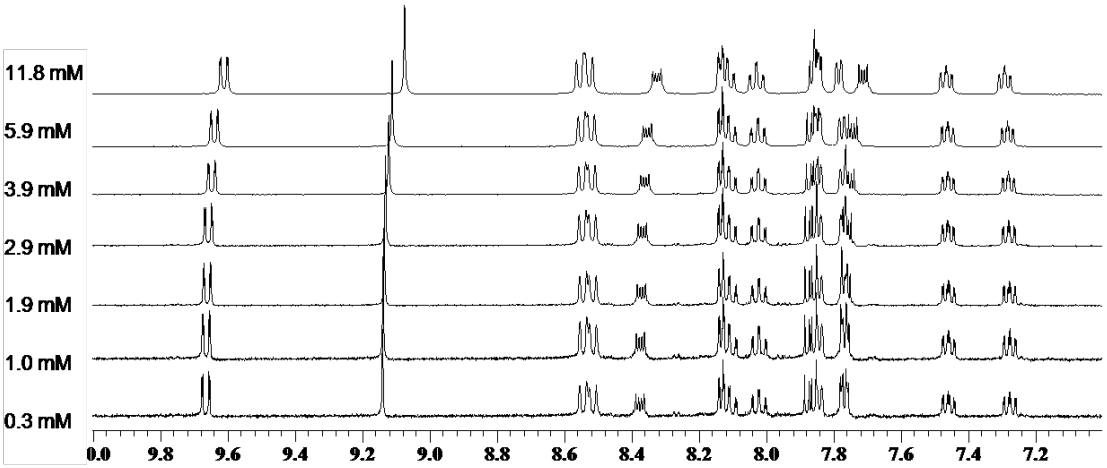


Fig. S3 ^{1}H NMR spectra of [**3**](PF$_6$)$_2$ in CD$_3$CN as function of its concentration.

Nanosecond - microsecond transient absorption spectra

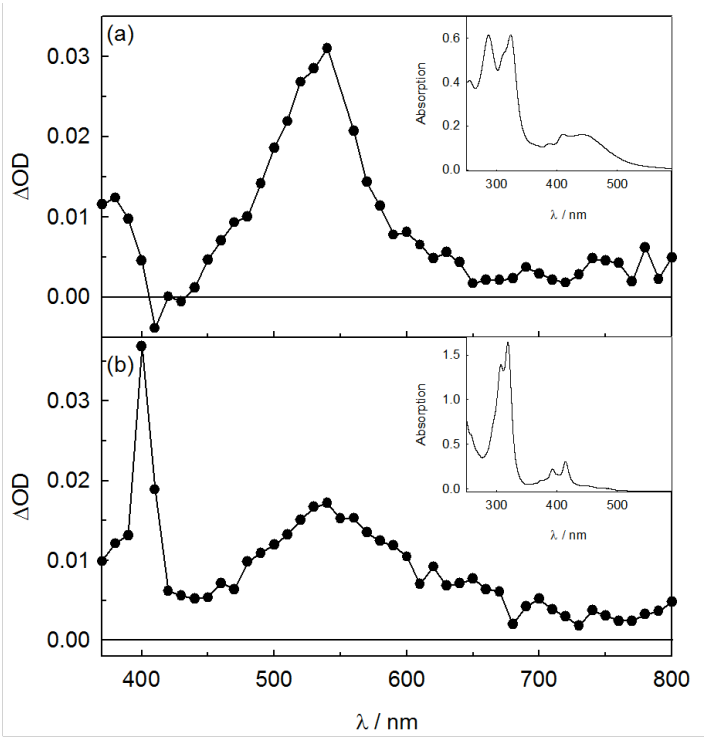
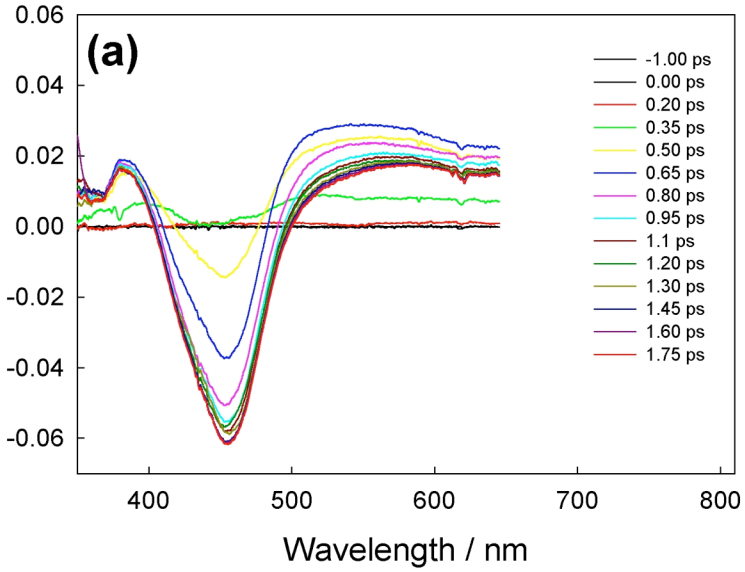


Fig. S4 Transient absorption spectra of (a) [**3**](PF$_6$)$_2$ (43 μM) in deaerated CH$_3$CN collected at 0.6 μs and (b) dppn (25 μM) in deaerated CHCl$_3$ collected at 0.6 μs after the laser pulse (λ_{ex} = 355 nm, fwhm ~ 8 ns). Insets: corresponding ground state absorption spectra.

Ultrafast data for 2



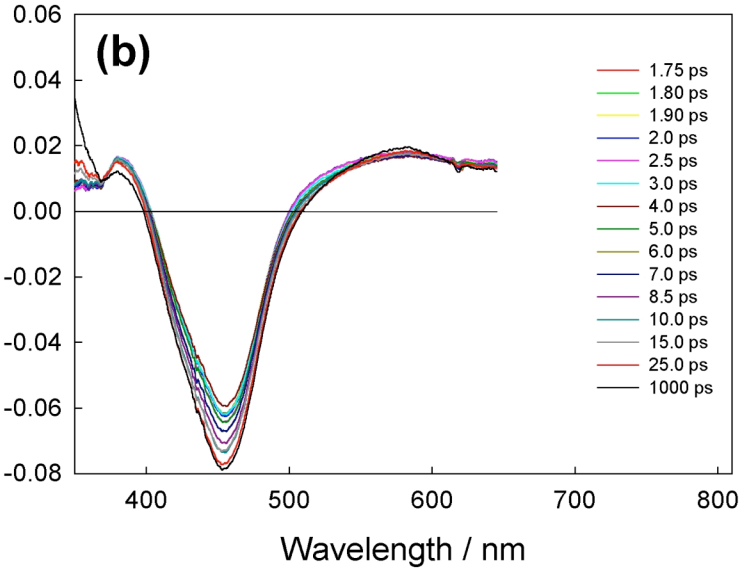


Fig. S5 Transient absorption spectra of 73 μM [**2**]$(PF_6)_2$ in CH_3CN collected (a) 0 - 1.75 ps and (b) 1.75 to 1000 ps after excitation pulse (λ_{exc} = 290 nm, fwhm = 300 ps).

Relative viscosity plot

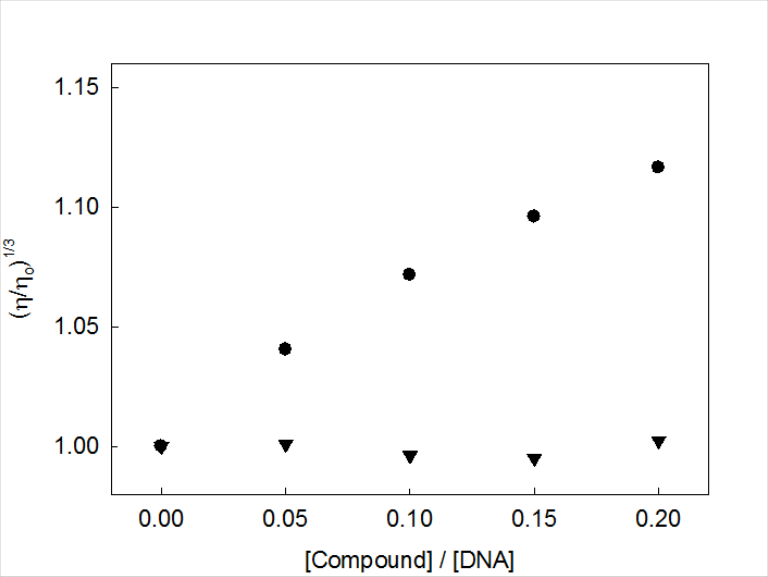


Fig. S6 Relative viscosity plot of $(\eta/\eta_o)^{1/3}$ vs [Compound]/[DNA] for complexes $[1]Cl_2$ (▼) and $[3]Cl_2$ (●) at 24 ± 1 °C in 5 mM Tris (50 mM NaCl, pH = 7.5).

Wavelength dependence of irradiation light for DNA photocleavage by 3

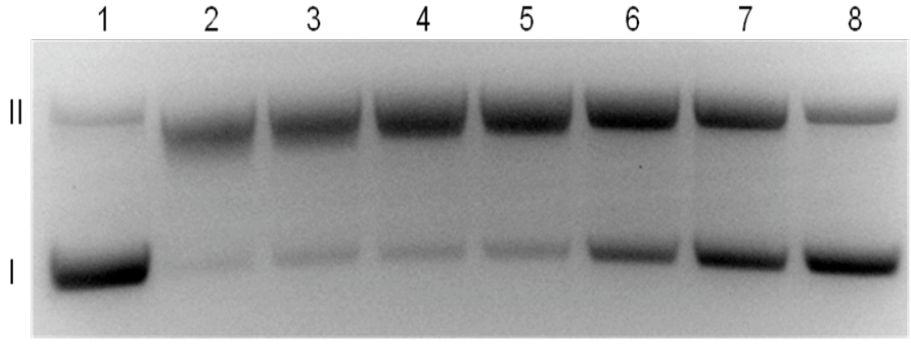


Fig. S7 Ethidium bromide stained agarose gel of the photocleavage of 100 μM pUC18 plasmid by 20 μM [**3**]Cl_2 in air (t_{irr} = 5 min, 5 mM Tris, pH = 7.5, 50 mM NaCl) at various irradiation wavelengths: lane 1, dark; lane 2, λ ≥ 475 nm; lane 3, λ ≥ 495 nm; lane 4, λ ≥ 515 nm ; lane 5, λ ≥ 530 nm ; lane 6, λ ≥ 550 nm; lane 7, λ ≥ 570 nm; lane 8, λ ≥ 590 nm.

Emission quenching by GMP

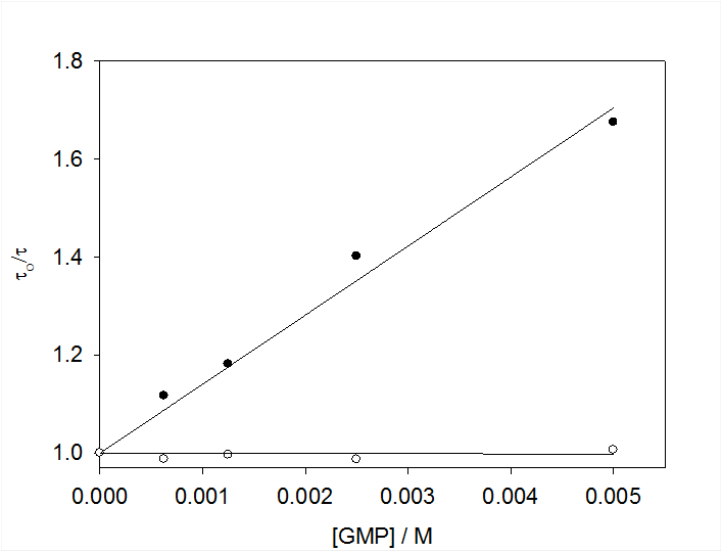


Fig. S8 Stern-Volmer plot obtained from the luminescence lifetimes of 20 μM [**1**]Cl_2 (○) and 20 μM [**3**]Cl_2 (●) with addition of GMP in deaerated 50 mM Tris buffer (50 mM NaCl, pH = 7.5).

References

S1 Z. B. Zhang, W. P. Yan and M. G. Fan, *Chin. J. App. Chem.*, 2005, **22**, 103-104.