Supporting Information for

DNA Photocleavage in anaerobic conditions by a Ru(II) polypyridyl complex

with long wavelength MLCT absorption

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1. The photostability of $[Ru(bpy)_2(dpb)]^{2+}$

Figure S1 and Figure S2 show the UV-vis absorption spectra and ^1H NMR spectra before and after irradiation with the light above 470 nm for 1 hour, a condition similar to the DNA cleavage experiments. No spectrum changes were found after irradiation, suggesting that $[Ru(bpy)_2(dpb)]^{2+}$ is stable enough at least under the employed conditions. Notably, the absorption spectrum of $[Ru(bpy)_2(dpb)]^{2+}$ undergoes remarkable bathochromic shift in PBS buffer (pH = 7.4) than in acetonitrile, which is favorable for PDT application.

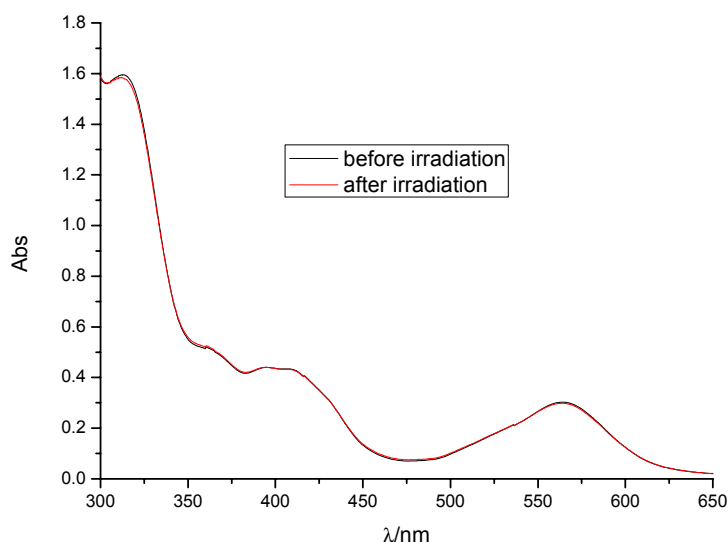**Figure S1**. UV-vis absorption spectra of $[Ru(bpy)_2(dpb)]^{2+}$ in PBS buffer (pH = 7.4) before and after irradiation (> 470 nm) for an hour.
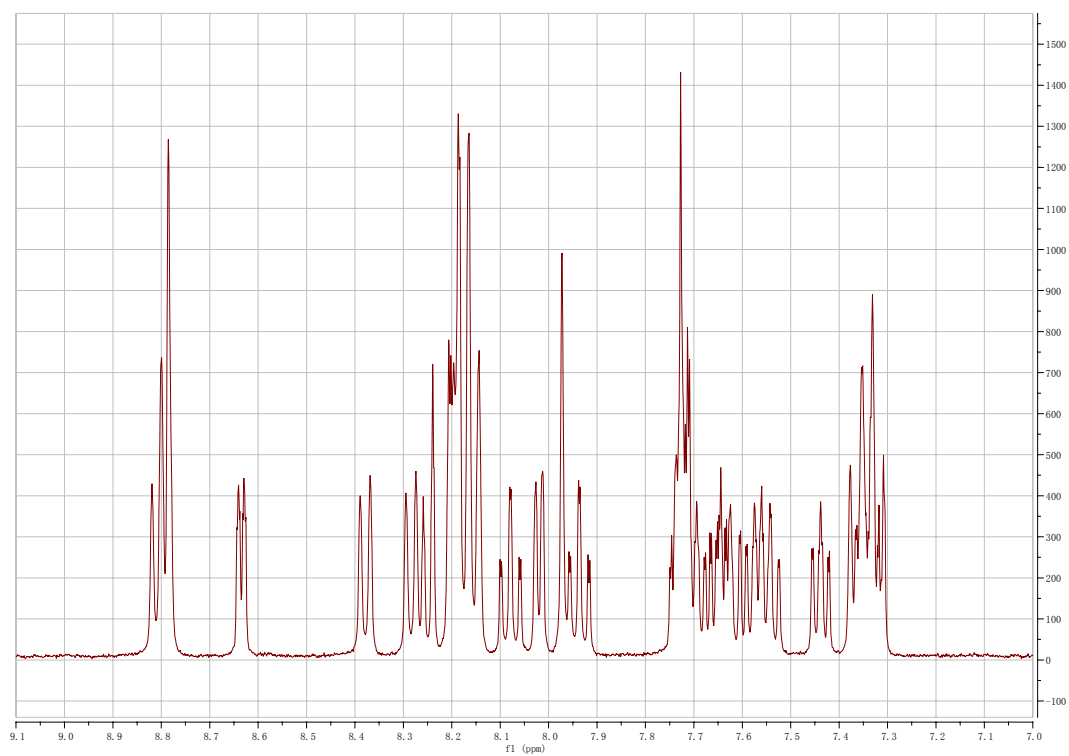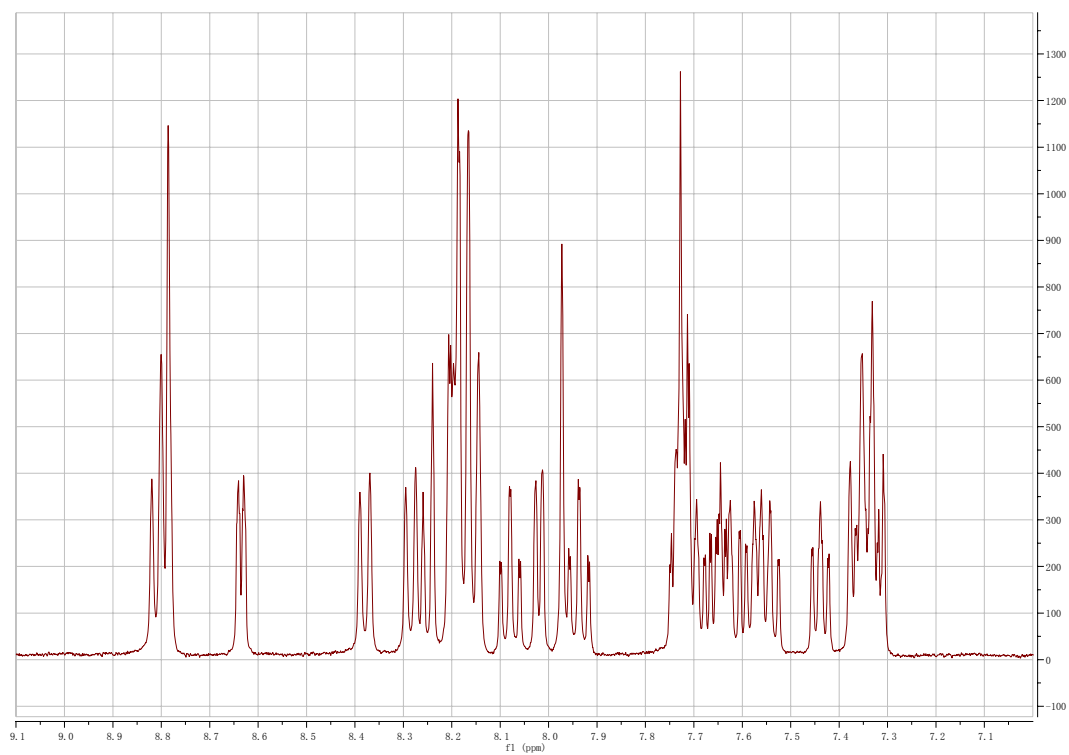
Figure S2. ^{1}H NMR spectra of **1** before (top) and after (bottom) irradiation (> 470 nm) for 1 h. All samples are in D_2O/d_6-DMSO (1/1).

2. Oxidation potential of [Ru(bpy)$_2$(dpb)]$^{2+}$

The half-wave oxidation potential of [Ru(bpy)$_2$(dpb)]$^{2+}$ in acetonitrile was measured to be 1.40 V vs SCE (1.64 V vs NHE) using cyclic voltammetry method (Figure S3).
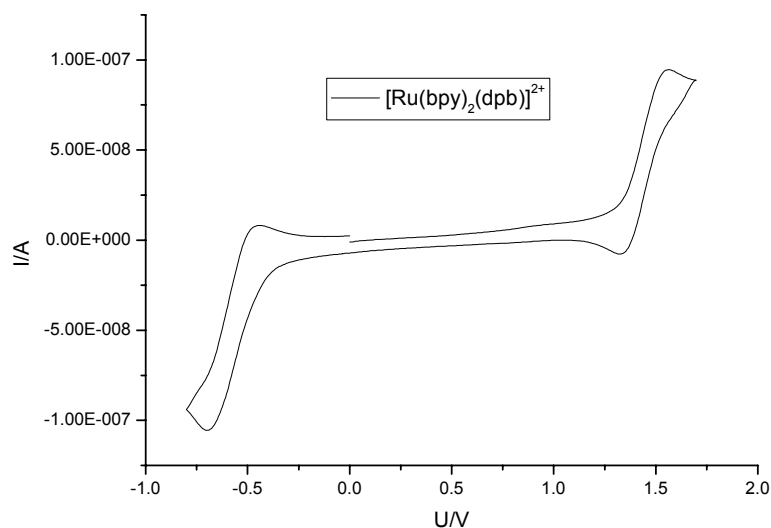

Figure S3. Cyclic voltammogram of [Ru(bpy)$_2$(dpb)]$^{2+}$ (100 μM) in acetonitrile vs SCE. Scan rate: 150 mV/s.

3. Reduction potential of [Co(NH$_3$)$_5$Cl]$^{2+}$

The reduction of [Co(NH$_3$)$_5$Cl]$^{2+}$ is a chemically irreversible process due to the lability of Co(II) complex.[1] Thus the reduction turn-on potential, which was measured to be 0.064 V vs SCE (0.31 V vs NHE), was applied for the calculation of Rehm-Weller equation.
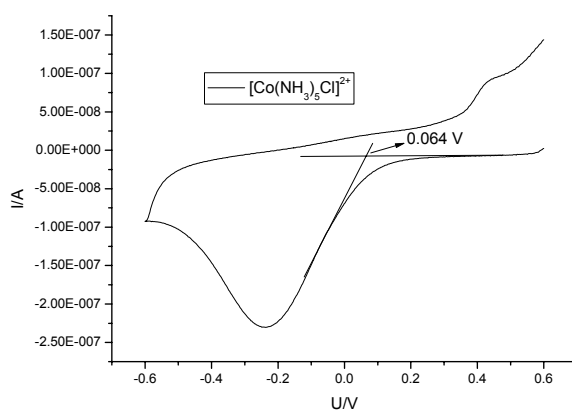

Figure S4. Cyclic voltammogram of [Co(NH$_3$)$_5$Cl]$^{2+}$ in PBS buffer (pH = 7.4) vs SCE. Scan rate: 150 mv/s.

4. 0-0 transition energy of the ^{3}MLCT state of [Ru(bpy)$_2$(dpb)]$^{2+}$

In many cases, the ^{3}MLCT 0-0 transition energy of a Ru complex may be estimated from the ^{3}MLCT emission maximum measured in glass matrix at 77K. Generally, ^{3}MLCT emission of a Ru complex will undergo a remarkable blue shift (about 40 nm)[2] in glass matrix at 77K than in the same solution but at room temperature. Thus, on the basis of the ^{3}MLCT emission maxima of 926 nm at room temperature, the ^{3}MLCT 0-0 transition energy of [Ru(bpy)$_2$(dpb)]$^{2+}$ was estimated to be 1.4 eV, equivalent to 886 nm (obtained by subtracting 40 nm from 926 nm).

[1] E. D. A. Stemp, M. R. Arkin, J. K. Barton, *J. Am. Chem. Soc.* 1997, **119**, 2921.

[2] (a) Y. Liu, R. Hammitt, D. A. Lutterman, R. P. Thummel, C. Turro, *Inorg. Chem.* 2007, **46**, 6011. (b) Y. Liu, R. Hammitt, D. A. Lutterman, R. P. Thummel, C. Turro, *Inorg. Chem.* 2009, **48**, 375