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Electronic supplementary information (ESI)

A Combined Computational and Experimental Study on DNA-Photocleavage of Ru(II) Polypyridyl Complexes $[Ru(bpy)_2(L)]^{2+}$ (L=pip, *o*-mopip and *p*-mopip)

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Table S1 Natural Charge Populations (unit: |e|) of $[Ru(bpy)_2(L)]^{3+}$ **(1~3)** Calculated at the Level of UHF/LanL2DZ.

Atom	Ru	N_1	C_2	C_3	C_4	N_5	C_6	C_7	C_8	$-OCH_3$	main	co-ligand
1	1.4533	–0.6236	0.2116	–0.0671	0.16187	–0.6500	0.5902	–0.1549	–0.1385		0.5233	1.0233
2	1.4533	–0.6214	0.2090	–0.06591	0.1575	–0.6480	0.5841	–0.2046	0.4427	–0.2827	0.5297	1.0170
3	1.4529	–0.6201	0.2122	–0.0693	0.1573	–0.6543	0.5923	–0.1940	–0.1323	–0.2280	0.5259	1.0212

Table S2 Calculated Thermochemical Data in Gas and the Free Energies in Aqoues Solution for All Complexes $[Ru(bpy)_2(L)]^{n+}$ (n=1~3) and Excited Complex $[Ru(bpy)_2(L)]^{2+}$(**1~3**)[a,b,c]

L=pip	G^0_{gas}	S^0_{tot}(g)	G_{corr}(g)	H_{corr}(g)	ε_{ZPE}	ΔE_{tot}	ε^0_{scf}(g)	G_{aq}[d]
$[Ru(bpy)_2(L)]^{2+}$	-2033.829475	220.192	0.532802	0.637422	0.601001	0.636478	-2034.36227729	-2034.528053
$[Ru(bpy)_2(L)]^{3+}$	-2033.413576	221.633	0.531361	0.636666	0.600055	0.635722	-2033.944937	-2034.314033
$[Ru(bpy)_2(L)]^{1+}$	-2034.070981	223.310	0.527203	0.633305	0.596581	0.632360	-2034.598184	-2034.633940
$[Ru(bpy)_2(L)]^{2+}(T_1)$							-2034.29243041	-2034.450107
L=*o*-mopip								
$[Ru(bpy)_2(L)]^{2+}$	-2148.321367	230.394	0.563024	0.672492	0.633588	0.671547	-2148.88439059	-2149.030975
$[Ru(bpy)_2(L)]^{3+}$	-2147.916547	232.349	0.561442	0.671838	0.632718	0.670894	-2148.4779894	-2148.815238
$[Ru(bpy)_2(L)]^{1+}$	-2148.558959	233.236	0.557725	0.668543	0.629345	0.667599	-2149.1166843	-2149.136539
$[Ru(bpy)_2(L)]^{2+}(T_1)$							-2148.81099723	-2148.950288
L=*p*-ompip								
$[Ru(bpy)_2(L)]^{2+}$	-2148.31220	232.781	0.561640	0.672242	0.633109	0.671297	-2148.87383885	-2149.034093
$[Ru(bpy)_2(L)]^{3+}$	-2147.91875	234.610	0.560525	0.671996	0.632671	0.671051	-2148.47927534	-2148.822058
$[Ru(bpy)_2(L)]^{1+}$	-2148.55167	236.066	0.556030	0.668193	0.628764	0.667249	-2149.10769591	-2149.140102
$[Ru(bpy)_2(L)]^{2+}(T_1)$							-2148.80296997	-2148.953937

a) All energies values in Hartrees/particle and S^0_{tot}(g) in $CalM^{-1}K^{-1}$, [b]all values were calculated at the level of UB3LYP/LanL2DZ [c] the values for the excited $[Ru(bpy)_2(L)]^{2+}$ (T_1)(**1-3**) were obtained via the single point calculation with U3lYP/LanL2DZ based on the optimized geometies of the lowest triplet excited state (T_1) [d] G_{aq} were not corrected with ZPE and thermal correction, and were directly obtained via the single point calculation with U3lYP/LanL2DZ and CPCM model.