Supporting Information for

Theoretical Studies on the Photoisomerization Mechanism of Osmium(II) Sulfoxide Complexes

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Benchmark Calculations

For the aim to find a better functional and basis functions for our study, geometries of the S,S-linked $[Os(bpy)_2(dmso)_2]^{2+}$ in the ground state were optimized with four different functionals, including B3LYP,[1-2] ωB97X-D,[3] M062X[5,6] and PBE0[7], which were used in previous study of the transition metal-based complexes.[8-12] Four basis set systems (BS1, BS2, BS3, and BS4) were employed for calculations here: In BS1, a double-ζ quality basis set SDD and corresponding effective core potential[13,14] for osmium, and usual 6-31G(d,p) basis sets were used for carbon, nitrogen, hydrogen, oxygen and sulfur atoms. In BS2, SDD basis set was used for osmium, and 6-311++G(d,p) basis sets were used for carbon, nitrogen, hydrogen, oxygen and sulfur atoms. BS3 is made of SDD for Ru, a correlation-consistent polarized double-ζ basis set (cc-pVDZ)[15] for H atoms, and a correlation-consistent polarized triple-ζ basis set (cc-pVTZ)[15] for C, N, O and S atoms. BS4 is made of pseudopotential-based augmented correlation-consistent basis set (aug-cc-pVDZ-pp)[16] for osmium and aug-cc-pVDZ for non-metal atoms.

The Os-S linkage mode is a weak interaction and the bond length was overestimated by current density functional theory, as shown in previous report.[8] Now, Dispersion effects that are missing in DFT functional have been accounted for according to Grimme's correction scheme (DFT-D3)[17] and the accuracy and reliability of the DFT-D approach for the description of weak interactions have been proved in recent studies.[18-21] Thereby, in optimization calculations, the empirical dispersion correction introduced by Grimme[17] was added to the DFT functional with Becke's and Johnson's rational damping function[22-24] and dubbed this variant DFT-D3(BJ). Considering solvent may play an important role in geometry determination, polarizable continuum model[25] with solvent acetonitrile (ε=35.688) was also considered to optimize the involved geometries.

Optimized geometry parameters of the *S,S*-$[Os(bpy)_2(dmso)_2]^{2+}$ in the ground state with different computational methods were collected in Table S1. Experimental determined crystal structures were also listed in for comparison. From our calculation

results, it is found that the PBE0, M062X and ωB97X-D functionals are outperformed the standard B3LYP functional. Moreover, dispersion correction plays an important role in correctly describing weak interactions. Thereby, there is a much better description of the Os-S bond length with PBE0-D3(BJ) compared with those from PBE0. Moreover, it is observed that solvent effect appreciably improve the computed structures.

All calculations were performed using the Gaussian 09 package.[26]

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Table S1. Main geometrical parameters of *S,S*-$[Os(bpy)_2(dmso)_2]^{2+}$ in the ground state (S_0). The atom numbering scheme is shown in Fig. 1.

	B3LYP /BS1	B97X-D /BS1	B97X-D /BS1	M062X /BS1	PBE1PBE /BS1	PBE0-D3(BJ) /BS1	PBE0-D3(BJ) /BS1(CPCM)	PBE0-D3(BJ) /BS2(CPCM)	PBE0-D3(BJ) /BS3(CPCM)	PBE0-D3(BJ) /BS4(CPCM)	Exptl.[a]
Os-S_1	2.371	2.325	2.325	2.316	2.325	2.310	2.301	2.305	2.298	2.286	2.276
S_1-O_1	1.510	1.515	1.515	1.498	1.501	1.500	1.507	1.505	1.492	1.494	1.471
Os-S_2	2.371	2.325	2.325	2.316	2.325	2.310	2.301	2.305	2.298	2.286	2.268
S_2-O_2	1.510	1.515	1.515	1.498	1.501	1.500	1.507	1.505	1.492	1.494	1.477
Os-N_{b1}	2.144	2.112	2.112	2.139	2.116	2.106	2.101	2.102	2.103	2.009	2.100
Os-N_{b1}'	2.131	2.110	2.110	2.135	2.109	2.100	2.097	2.099	2.100	2.101	2.091
Os-N_{b2}	2.131	2.110	2.110	2.135	2.109	2.100	2.097	2.099	2.100	2.101	2.097
Os-N_{b2}'	2.144	2.112	2.112	2.139	2.116	2.106	2.101	2.102	2.103	2.009	2.094
α(O_1-S_1-Os)	114.4	116.2	116.2	114.7	115.1	115.6	116.0	116.0	116.1	116.0	115.8
α(S_1-Os-Nb_1)	98.2	98.5	98.5	98.6	98.3	98.5	98.1	98.5	98.1	98.0	97.8
α(O_2-S_2-Os)	114.4	116.2	116.2	114.7	115.1	115.6	116.0	116.0	116.1	116.3	116.0

[a] Ref. 26.

Table S2. Vertical absorption and emission energies (in eV), dominated orbital excitations, oscillator strength (*f*) and squares of the transition dipole moments μ^2_{ge} (D) obtained from TD-DFT calculations at the PBE0-D3(BJ)/[SDD-ECP/cc-pVTZ] level of theory. The absorption (emission) energies are based on the S_0 (T_1) state equilibrium geometry.

	Excitation	$\lambda_{abs.}$ (nm)	$\lambda_{max.}$ (nm)[a]	*f*	Dominated Orbitals
S,S-bonded	$S_0 \rightarrow S_1$	401		0.004	HOMO-1→LUMO (92%)
	$S_0 \rightarrow S_2$	399		0.001	HOMO→LUMO（65%）
	$S_0 \rightarrow S_3$	396		0.002	HOMO-1→LUMO+1（65%）
	$S_0 \rightarrow S_4$	395		0.009	HOMO→LUMO+1（88%）
	$S_0 \rightarrow S_5$	366	355	0.086	HOMO-2→LUMO（94%）
	$S_0 \rightarrow S_6$	350		0.041	HOMO-2→LUMO+1（90%）
O,S-bonded	$S_0 \rightarrow S_1$	495		0.004	HOMO→LUMO (84%)
	$S_0 \rightarrow S_2$	471		0.002	HOMO→LUMO+1（83%）
	$S_0 \rightarrow S_3$	463		0.019	HOMO-1→LUMO（77%）
	$S_0 \rightarrow S_4$	420	403	0.075	HOMO-1→LUMO+1（78%）
	$S_0 \rightarrow S_5$	400		0.032	HOMO-2→LUMO（69%）
	$S_0 \rightarrow S_6$	387		0.030	HOMO-2→LUMO+1（59%）
	Emission	$\lambda_{em.}$ (nm)			
S,S-bonded	$T_1 \rightarrow S_0$	493			
O,S-bonded	$T_1 \rightarrow S_0$	660			

[a] Ref. 26.

Table S3. Optimized Cartesian coordinates of the *S,S*-$[Os(bpy)_2(dmso)_2]^{2+}$ in the lowest triplet state ($^3MLCT_S$) obtained at PBE0-D3(BJ)/[SDD/cc-pVTZ] level. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Os	-0.01572300	-0.29459800	-0.00267300
S	-0.70720500	-1.97341000	1.54581300
S	0.55467400	-2.01085600	-1.50018600
O	0.34763300	-2.97716400	1.83740600
O	-0.47244600	-3.07377700	-1.67108000
N	2.02478500	-0.12229300	0.54763600
N	0.68352100	1.25242400	-1.23796900
N	-0.59087400	1.25323600	1.26041700
N	-1.93591400	-0.04823900	-0.58874200
C	2.64182200	-0.88165700	1.46181900
H	2.06669200	-1.69880600	1.87648300
C	3.94416000	-0.64709200	1.85281100
H	4.39402400	-1.28724300	2.59799200
C	4.64047100	0.39928500	1.27479200
H	5.66359900	0.60828000	1.55628000
C	4.00929900	1.17660000	0.32173200
H	4.53611000	1.99348400	-0.14726900
C	2.69807200	0.90062100	-0.02637500
C	1.95312000	1.65945900	-1.02837300
C	2.48144700	2.72509200	-1.73805900
H	3.49872000	3.04183400	-1.56607900
C	1.69738700	3.38095700	-2.66840400
H	2.10064400	4.21384800	-3.22814700
C	0.39579900	2.95573900	-2.86907400
H	-0.25683800	3.43534600	-3.58415600
C	-0.07736400	1.88971500	-2.13377000
H	-1.08464700	1.52380600	-2.26094600
C	0.17502900	1.85014700	2.18570300
H	1.15937700	1.43152800	2.33946100
C	-0.25135300	2.92253900	2.92407700
H	0.40606400	3.35775400	3.66217800
C	-1.54763300	3.42132800	2.69655000
H	-1.91591200	4.26541500	3.26453500
C	-2.33965000	2.83133500	1.75506800
H	-3.33733600	3.20210400	1.57164100
C	-1.86085900	1.72743600	1.01428900
C	-2.58673400	1.04694000	0.02144000
C	-3.89654500	1.37708400	-0.38164800
H	-4.38836600	2.22411200	0.07458800
C	-4.53824100	0.64406000	-1.33111300
H	-5.54246500	0.90563900	-1.63628700

C	-3.87950400	-0.47890300	-1.91297900
H	-4.36559700	-1.09387000	-2.65592000
C	-2.61840700	-0.77889700	-1.51762400
H	-2.09099700	-1.63456900	-1.91520900
C	-2.17513000	-2.82817900	1.01556700
H	-1.94626700	-3.26925100	0.04799000
H	-3.00356900	-2.12660300	0.95170700
H	-2.35759600	-3.59115300	1.77152400
C	-1.25566900	-1.26383400	3.08649800
H	-1.59696200	-2.09008800	3.70802500
H	-2.06034000	-0.55709100	2.89188200
H	-0.40449300	-0.76440800	3.54275600
C	2.07940100	-2.83649700	-1.08947600
H	1.94404500	-3.25833200	-0.09551400
H	2.91148900	-2.13693300	-1.11763600
H	2.20479900	-3.62377800	-1.83119100
C	0.94452300	-1.37445100	-3.12135700
H	1.20683400	-2.22869800	-3.74328200
H	1.77146000	-0.67066400	-3.05187300
H	0.05021200	-0.88530100	-3.50296900

Table S4. Optimized Cartesian coordinates of the η^2-$[Os(bpy)_2(dmso)_2]^{2+}$ in the lowest triplet state ($^3MLCT_{SO}$) obtained at PBE0-D3(BJ)/[SDD/cc-pVTZ] level. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Os	-0.00589600	-0.18086900	-0.27655000
S	-1.59439300	-2.27646700	0.79153400
S	0.41383500	-1.64804800	-2.02449800
O	-0.88434400	-3.59541900	0.85369800
O	-0.79036800	-2.33573300	-2.57516700
N	1.75679800	-0.87566200	0.71604600
N	1.47304700	1.29722600	-0.69521700
N	-0.59778900	1.02370100	1.31927100
N	-1.78441200	0.55819500	-0.94213500
C	1.83063000	-2.02445500	1.39959400
H	0.95143900	-2.65752100	1.39012900
C	2.97182300	-2.40876100	2.07355000
H	2.97570100	-3.34494500	2.61328700
C	4.08498300	-1.58782900	2.03229400
H	4.99787200	-1.86360000	2.54258800
C	4.01494300	-0.40450800	1.32132500
H	4.87225200	0.24948200	1.26750200
C	2.83770600	-0.06348700	0.67605300
C	2.66374800	1.17335300	-0.08394800
C	3.61775200	2.17452600	-0.18577500
H	4.56773800	2.07838700	0.31830200
C	3.33624700	3.30257600	-0.93300100
H	4.07134500	4.09095400	-1.02249600
C	2.10334100	3.41290900	-1.55671400
H	1.84215400	4.27795600	-2.14934200
C	1.18979900	2.39081500	-1.40659100
H	0.21023600	2.43638200	-1.86397500
C	0.05631200	1.15010500	2.48571000
H	0.90968200	0.50506500	2.63311600
C	-0.33669100	2.03329100	3.45983700
H	0.21649700	2.08256500	4.38675000
C	-1.44781000	2.84409700	3.22592600
H	-1.78138100	3.55147900	3.97318000
C	-2.11843700	2.72955700	2.03213800
H	-2.98311100	3.34499200	1.83178400
C	-1.68522400	1.80492600	1.08057800
C	-2.31841200	1.58259800	-0.18978000
C	-3.39183000	2.32926500	-0.66626000
H	-3.78847400	3.13422200	-0.06520700
C	-3.93710200	2.05103500	-1.89736100
H	-4.77113600	2.62976000	-2.27002600

C	-3.39395900	1.00597700	-2.65351500
H	-3.79725800	0.74016600	-3.62032600
C	-2.33935100	0.29507900	-2.15356100
H	-1.91683400	-0.54487900	-2.68592900
C	-3.08360600	-2.48793900	-0.17142300
H	-2.75970200	-2.69812900	-1.18858000
H	-3.66325800	-1.56718500	-0.13173500
H	-3.63949500	-3.32318500	0.25273800
C	-2.29447700	-1.93932600	2.40413400
H	-2.90370400	-2.79328100	2.69827600
H	-2.89117500	-1.03008700	2.34508200
H	-1.46201200	-1.80134200	3.09136200
C	1.59255300	-2.93432300	-1.65721600
H	1.16149300	-3.53142700	-0.85596700
H	2.54729900	-2.50250300	-1.36738300
H	1.68884900	-3.52557100	-2.56630400
C	1.23709200	-0.83889800	-3.38830000
H	1.37773000	-1.57840100	-4.17504800
H	2.19040700	-0.43963400	-3.04669600
H	0.58509500	-0.03613700	-3.72718800

Table S5. Optimized Cartesian coordinates of the *O,S*-$[Os(bpy)_2(dmso)_2]^{2+}$ in the lowest triplet state ($^3MLCT_O$) obtained at PBE0-D3(BJ)/[SDD/cc-pVTZ] level. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Os	0.04226400	-0.15268700	-0.23031000
S	-2.27772100	-2.04934600	0.91208900
S	0.80339500	-1.15706900	-2.20779900
O	-0.88052500	-1.94821900	0.18781400
O	-0.10817200	-1.12949700	-3.38251800
N	1.81679300	-0.79550600	0.63993500
N	1.22130200	1.50559600	-0.46390600
N	-0.67295400	0.75124700	1.50420400
N	-1.74066300	0.71693800	-0.88387500
C	2.02480600	-2.00229000	1.19726900
H	1.19363300	-2.69185200	1.14108200
C	3.20158700	-2.34451100	1.80383200
H	3.31382600	-3.32657000	2.23919700
C	4.23993300	-1.38747300	1.84558800
H	5.18443100	-1.62622200	2.31670600
C	4.04333900	-0.15638600	1.29231200
H	4.82766500	0.58656100	1.32296400
C	2.81226800	0.16424800	0.67791100
C	2.49317400	1.40004300	0.07898600
C	3.35815800	2.51297800	-0.00038500
H	4.35184900	2.43716100	0.41788000
C	2.94946000	3.66954400	-0.59541900
H	3.61965700	4.51720300	-0.65273200
C	1.64392500	3.75452600	-1.13007400
H	1.27962000	4.65277100	-1.60626700
C	0.82835700	2.66356000	-1.03092500
H	-0.17688100	2.68399500	-1.42709000
C	-0.04526200	0.70671300	2.68325900
H	0.86954400	0.13361800	2.71986900
C	-0.53972300	1.34979900	3.79862000
H	-0.00045700	1.28421600	4.73264200
C	-1.71938400	2.06703200	3.68844700
H	-2.13430000	2.58313600	4.54369000
C	-2.36495900	2.11887000	2.46731400
H	-3.28446900	2.67437000	2.36160500
C	-1.82070300	1.45122500	1.38200700
C	-2.41881500	1.43047300	0.05086300
C	-3.60082400	2.07701400	-0.26511900
H	-4.12977200	2.64213800	0.48732600
C	-4.10025500	1.99397800	-1.55209300
H	-5.02244600	2.49724600	-1.80984600

C	-3.40458000	1.25964100	-2.49676600
H	-3.75773500	1.16558300	-3.51372000
C	-2.23114700	0.63451900	-2.12891300
H	-1.64604400	0.04698700	-2.82550700
C	-3.17836800	-3.13735900	-0.16925200
H	-3.37482100	-2.58685700	-1.08649600
H	-4.11656000	-3.38730600	0.32552900
H	-2.57681600	-4.02474600	-0.35786200
C	-1.92538700	-3.14361200	2.26998100
H	-1.43623200	-4.03794500	1.88810100
H	-2.87275300	-3.38293600	2.75192300
H	-1.28219900	-2.60099100	2.95960900
C	1.24918300	-2.85913200	-1.92659900
H	0.36621300	-3.35658100	-1.53188700
H	2.07178500	-2.90990500	-1.21691300
H	1.53495700	-3.26826800	-2.89410000
C	2.36481700	-0.46332400	-2.71229600
H	2.69404000	-1.01481600	-3.59126800
H	3.07729500	-0.55198400	-1.89455700
H	2.18474600	0.58220600	-2.95314900

Table S6. Optimized Cartesian coordinates of the transition state *O,S*-$[Os(bpy)_2(dmso)_2]^{2+}$-TS from the $^3MLCT_O$ to the ^3LF_O state obtained at PBE0-D3(BJ)/[SDD/cc-pVTZ] level. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Os	0.01371600	0.04141600	-0.24801000
S	-2.29272900	-2.43221900	0.66459700
S	0.41395900	-1.49938500	-1.90058300
O	-1.10155800	-1.61173600	1.18786700
O	-0.63307800	-2.54350600	-2.09174600
N	1.75465000	-0.67430600	0.82692300
N	1.59723300	1.33180500	-0.80774900
N	-0.53331200	1.34861900	1.27346300
N	-1.92348600	0.42352800	-0.71611900
C	1.73686500	-1.72489000	1.65259500
H	0.77666100	-2.20608500	1.77127300
C	2.87041400	-2.15915100	2.31106600
H	2.80556900	-3.01545000	2.96729200
C	4.06375300	-1.48736700	2.11087900
H	4.97036200	-1.80529200	2.60789600
C	4.08156000	-0.39569300	1.26286200
H	4.99873600	0.14751000	1.09144100
C	2.91084500	-0.00642300	0.63260000
C	2.81689800	1.13679300	-0.27300000
C	3.86921500	1.98836800	-0.57282900
H	4.84416300	1.82352600	-0.13881000
C	3.65698600	3.05315100	-1.42718000
H	4.46851400	3.72559400	-1.67008500
C	2.39266300	3.24891500	-1.95940400
H	2.17841200	4.07165200	-2.62641000
C	1.38535600	2.36902700	-1.62394700
H	0.38276900	2.48407300	-2.01383800
C	0.25654400	1.73564200	2.28517300
H	1.24919900	1.31165300	2.31154700
C	-0.15896700	2.61885200	3.25187000
H	0.51620000	2.89109200	4.05044500
C	-1.44983900	3.13844000	3.17457600
H	-1.81040000	3.83339800	3.92117400
C	-2.26348600	2.75529700	2.13424600
H	-3.26752100	3.14577400	2.05608600
C	-1.78972300	1.85279900	1.18144500
C	-2.54322600	1.39004500	0.04690200
C	-3.79957400	1.87719100	-0.29905000
H	-4.25684400	2.64330800	0.31011400
C	-4.45017400	1.39825700	-1.41230400

H	-5.42587800	1.77651000	-1.68462200
C	-3.82182200	0.40831400	-2.17735900
H	-4.29833100	-0.01895100	-3.04856200
C	-2.59013900	-0.04829800	-1.80443100
H	-2.11103900	-0.85466200	-2.33938200
C	-1.71688700	-4.12385900	0.64137000
H	-0.96851800	-4.17434800	-0.14678500
H	-2.56003800	-4.77068100	0.40044600
H	-1.29367500	-4.37333100	1.61345300
C	-3.39961400	-2.51409400	2.06553700
H	-2.85294900	-2.87618900	2.93492100
H	-4.22695200	-3.17689400	1.81367100
H	-3.76882200	-1.50375900	2.23163600
C	1.97138100	-2.36133100	-1.74199900
H	1.91440400	-2.97181700	-0.84403600
H	2.78935900	-1.64673100	-1.67317300
H	2.07546500	-2.99043000	-2.62397800
C	0.67353200	-0.71039400	-3.48571400
H	0.82218900	-1.49539000	-4.22541600
H	1.54187700	-0.05636000	-3.42689300
H	-0.21973700	-0.13099000	-3.71036700

Table S7. Optimized Cartesian coordinates of the *O,S*-$[Os(bpy)_2(dmso)_2]^{2+}$ in the metal-centered ligand field excited state (^3LF_O) obtained at PBE0-D3(BJ)/[SDD/cc-pVTZ] level. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Os	0.11447400	0.01156200	-0.25871100
S	-3.17229700	-1.22818100	1.08504500
S	0.18673900	-2.01402600	-1.34255900
O	-1.69224800	-1.40155500	1.40490600
O	-0.98059200	-2.42281600	-2.18191700
N	1.57532100	-0.71383900	1.14167100
N	2.15658000	0.69628700	-0.97903900
N	-0.13655100	1.78547400	0.81780800
N	-1.64606700	0.75292200	-1.04048900
C	1.18370700	-1.33801400	2.25987500
H	0.11874700	-1.50253000	2.35912600
C	2.08220000	-1.75184200	3.22193400
H	1.71678000	-2.25258100	4.10721700
C	3.43223000	-1.51623100	3.02496500
H	4.16341500	-1.83075900	3.75742600
C	3.83504600	-0.86039800	1.87696900
H	4.88056500	-0.64881800	1.70974200
C	2.88692800	-0.46042900	0.94811000
C	3.21607500	0.28284900	-0.27252500
C	4.51009400	0.56225500	-0.68936300
H	5.36080200	0.21535400	-0.12172700
C	4.69689600	1.28776100	-1.85163300
H	5.69770900	1.51282100	-2.19538500
C	3.59097000	1.72085900	-2.56602200
H	3.69441100	2.29469300	-3.47617600
C	2.33215400	1.40214000	-2.09392500
H	1.43608200	1.71103000	-2.61745800
C	0.71759600	2.25661800	1.73317800
H	1.61313900	1.67894000	1.90414500
C	0.48280100	3.41817300	2.43701600
H	1.20586700	3.75154300	3.16780100
C	-0.68012000	4.12902800	2.18653200
H	-0.89779400	5.04289900	2.72263800
C	-1.55922300	3.65468100	1.23337300
H	-2.46678900	4.19725800	1.01484300
C	-1.26512800	2.47969200	0.55678400
C	-2.10561200	1.90705300	-0.48479400
C	-3.29073000	2.48360100	-0.90935000
H	-3.64402100	3.39251800	-0.44627800
C	-4.01612600	1.89476000	-1.92760300
H	-4.94444400	2.33745100	-2.26282900

C	-3.52729800	0.73590800	-2.50788300
H	-4.05179700	0.23967100	-3.31220200
C	-2.34874000	0.19599400	-2.04203200
H	-1.94612800	-0.72574800	-2.44026200
C	-3.63104400	-2.68439300	0.14802300
H	-3.05118300	-2.65302400	-0.77409000
H	-4.69757700	-2.63825500	-0.06999500
H	-3.38432200	-3.57432300	0.72644700
C	-4.03724700	-1.60048000	2.60756300
H	-3.68951000	-2.56076900	2.98685800
H	-5.10728700	-1.62102800	2.40279500
H	-3.80694000	-0.80063400	3.30864400
C	0.44820100	-3.36875600	-0.20631800
H	-0.34968100	-3.30529300	0.53109200
H	1.42316100	-3.28798200	0.26819100
H	0.37412900	-4.28176300	-0.79443500
C	1.62691100	-2.18270600	-2.38990400
H	1.61291000	-3.18666700	-2.81063700
H	2.53218300	-2.01247400	-1.81032200
H	1.53094900	-1.43462100	-3.17427300

Table S8. Optimized Cartesian coordinates of the *S,S*-$[Os(bpy)_2(dmso)_2]^{2+}$ in the metal-centered ligand field excited state (^3LF_S) obtained at PBE0-D3(BJ)/[SDD/cc-pVTZ] level. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Os	0.12982700	0.07561600	-0.28232900
S	-3.05225800	-1.54747800	1.12121700
S	0.10063600	-1.72302600	-1.72143000
O	-1.98270900	-2.57959300	1.42287000
O	-1.09591900	-1.90778300	-2.59670000
N	1.47933600	-0.98756000	0.97667100
N	2.20076400	0.76242100	-0.82159600
N	-0.03238000	1.64714000	1.08880400
N	-1.55568500	1.07351000	-0.95178400
C	1.00982800	-1.80182100	1.93222400
H	-0.06497500	-1.96338200	1.94368200
C	1.84922300	-2.42139600	2.83606300
H	1.42677800	-3.06814300	3.59189400
C	3.21343500	-2.20296500	2.74798500
H	3.89705400	-2.67679900	3.43954400
C	3.69454700	-1.36152600	1.76245200
H	4.75336000	-1.16647800	1.68168300
C	2.80647000	-0.75566300	0.88806200
C	3.21355000	0.18868800	-0.15614400
C	4.53274200	0.49957000	-0.45380500
H	5.34438900	0.02734500	0.07948400
C	4.79679700	1.42108000	-1.45038700
H	5.81904400	1.67311500	-1.69908800
C	3.74000000	2.01584200	-2.12076800
H	3.90285500	2.74475700	-2.90202900
C	2.45153300	1.65876600	-1.77416900
H	1.59231400	2.09178900	-2.26993600
C	0.82697000	1.88724900	2.08493700
H	1.67119900	1.22074200	2.17234000
C	0.66031300	2.92844900	2.97231700
H	1.38573500	3.07581200	3.75962900
C	-0.43842400	3.76029400	2.82861400
H	-0.60160000	4.58619400	3.50772800
C	-1.32465500	3.52204000	1.79650600
H	-2.18300200	4.16193900	1.65883100
C	-1.09981500	2.45863400	0.93431400
C	-1.95233700	2.13681400	-0.20159000
C	-3.08832700	2.85764700	-0.52669300
H	-3.39588700	3.68984200	0.08838400
C	-3.82637900	2.51145900	-1.64257500
H	-4.71648700	3.06875600	-1.90190600

C	-3.40124400	1.44528700	-2.41690600
H	-3.93897600	1.13754900	-3.30250500
C	-2.27080600	0.75161000	-2.04281600
H	-1.92042200	-0.11079000	-2.59304100
C	-3.84269700	-2.09098200	-0.39484200
H	-3.09050500	-2.03243700	-1.18102100
H	-4.67571000	-1.42477700	-0.61819700
H	-4.18338900	-3.11812500	-0.26493000
C	-4.40530100	-1.89788400	2.24684100
H	-4.66649200	-2.95287100	2.16742700
H	-5.25171000	-1.26136200	1.98992100
H	-4.05405900	-1.66269400	3.24989600
C	0.31749200	-3.27818400	-0.87233500
H	-0.48077800	-3.33644000	-0.13171500
H	1.29710800	-3.31652200	-0.40134500
H	0.21932500	-4.05484000	-1.62905800
C	1.52165800	-1.74602900	-2.80616900
H	1.44814700	-2.64141900	-3.42105900
H	2.43486600	-1.75130300	-2.21425100
H	1.46827900	-0.84964900	-3.42067500

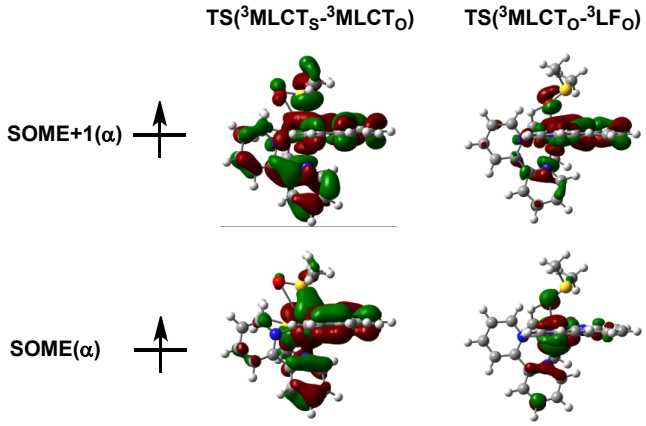

Figure S1. Electron configuration for the singly occupied molecular orbitals of the transition state in excited states of $[Os(bpy)_2(dmso)_2]^+$.

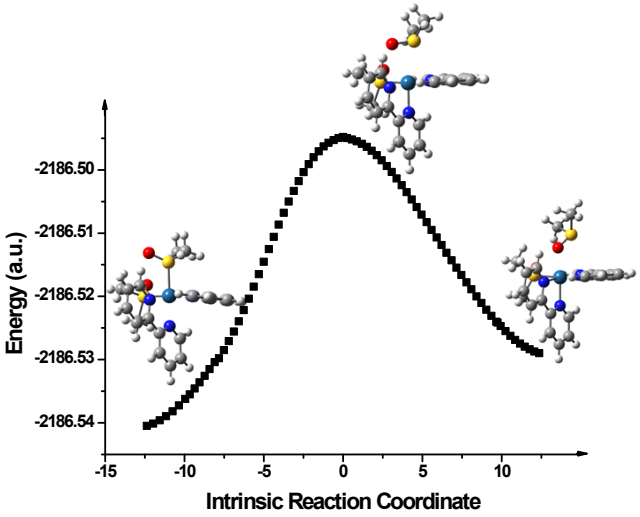

Figure S2. IRC analysis results for the intramolecular isomerization in the ground state of $[Os(bpy)_2(dmso)_2]^{2+}$.

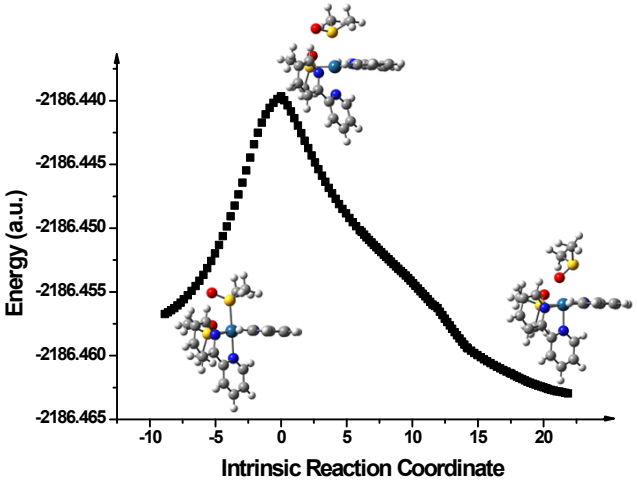

Figure S3. IRC analysis results for the intramolecular isomerization in the lowest ^{3}MLCT excited state of $[Os(bpy)_2(dmso)_2]^{2+}$.

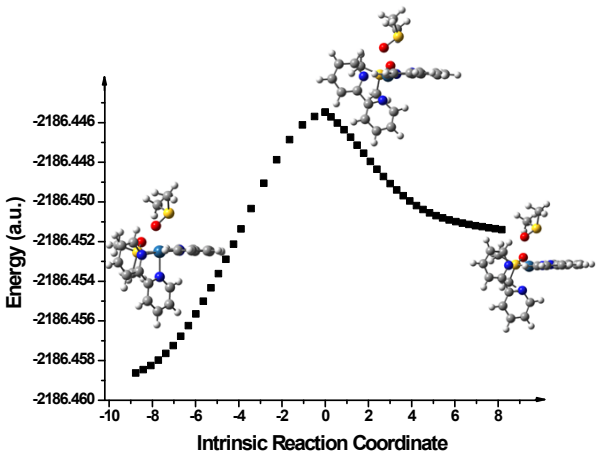

Figure S4. IRC analysis results for the Ru-O bond breaking from the lowest ^{3}MLCT to the ^{3}LF excited state in $[Os(bpy)_2(dmso)_2]^{2+}$.