Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

A DFT-D Study on the Electrochromic Mechanism of Ruthenium Sulfoxide Complexes

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Benchmark Calculations

All calculations were performed using the Gaussian 09 package.[13] For the aim to find a better theoretical method for our study, molecular structure of the S-linked [Ru(bpy)(tpy)(dmso)]$^{2+}$ in the ground state was optimized with different functionals, including B3LYP,[14-16] ωB97X-D,[17] PBE0[18], M062X[19] and B2PLYPD[20], which were used in previous studies for ruthenium or other transition metal based complexes.[11a,11c,21] Two basis set systems were employed for calculations here: one basis set was made of a double-ζ quality basis set LANL2DZ and corresponding effective core potential for ruthenium[22], all-electron 6-31G(d,p) basis sets for carbon, nitrogen, hydrogen, oxygen and sulfur atoms[23]. In another basis set, usual 6-31G(d,p) for nonmetal atoms and SDD for ruthenium [24].

It is known that Ru–S is weak interaction and the bond length is overestimated by current density functional theory, as shown in previous report.[9b] Now, Dispersion effects that are missing in DFT functionals have been accounted for according to Grimme's correction scheme (DFT-D3).[25] The accuracy and reliability of the dispersion corrected density functional theory (DFT-D) approach for the description of weak interactions have been proved in recent studies.[25-28] Thereby, in optimization calculations, the empirical dispersion correction introduced by Grimme[25] was added to the DFT functional with Becke's and Johnson's rational damping function,[29] and dubbed this variant DFT-D3(BJ).

In addition, considering crystals suitable for structural determination were obtained by slow evaporation of saturated acetonitrile/ethanol solutions in experimental studies,[7a] solvent may play an important roles in geometry determination. Thus, for comparison, conductor-like polarizable continuum model (CPCM)[30] with solvent acetonitrile (ε=35.688) was also considered to optimize the involved geometries. Harmonic vibrational frequencies were calculated analytically at the same level to confirm that each stationary point was a minimum on the potential energy surface.

Optimized geometry parameters of the *S*-[Ru(bpy)(tpy)(dmso)]$^{2+}$ complex with different computational methods were collected in Table 1. Experimental determined

crystal structures were also listed in the table for comparison. It is found that Ru–S bond length obtained at the PBE0-D3(BJ)/[SDD/6-31G(d,p)] level (2.290 Å) is very close to that from experimental crystal structure (2.282 Å).

MOs and Spin Density Distributions

The percentage of ruthenium or ligand character in some of the occupied (canonical) molecular orbitals (MOs) in the complexes was calculated from a full population analysis, using

$$\%\, Ru(Ligand)\ Character = \frac{\sum {\phi_{Ru(ligand)}}^2}{\sum {\phi_{all}}^2} \times 100\%$$

Where $\sum {\phi_i}^2$ is the sum of the squares of the eigenvalues associated with the ruthenium atomic orbital (AO) (or all AOs involved in one ligand) and all of the AOs in a particular MO, respectively. Similar calculation was used for the percentage of ruthenium or ligand character in some of the occupied (canonical) spin density distributions in the complexes associated with the radical ion state.

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Table S1. Main geometrical parameters for the *S*-[Ru(bpy)(tpy)(dmso)]$^{2+}$.

	B3LYP /BS1[a]	B3LYP -D3(BJ) /BS1	M062X /BS1	ωB97X-D /BS1	B2PLYPD /BS1	PBE0 /BS1	PBE0 -D3(BJ) /BS1	PBE0 -D3(BJ) /BS2[b]	PBE0 -D3(BJ) /BS2(CPCM)	Exptl.
bond lengths										
Ru-S	2.406	2.385	2.371	2.351	2.340	2.346	2.324	2.290	2.288	2.282
S-O	1.505	1.509	1.496	1.492	1.505	1.496	1.495	1.496	1.505	1.467
Ru-N_t'	2.140	2.114	2.155	2.123	2.107	2.107	2.094	2.082	2.081	2.079
Ru-N_t''	2.014	2.003	2.026	2.006	1.998	1.992	1.986	1.978	1.979	1.975
Ru-N_t'''	2.131	2.109	2.144	2.118	2.104	2.101	2.088	2.078	2.075	2.073
Ru-N_b'	2.167	2.140	2.174	2.148	2.138	2.136	2.122	2.112	2.103	2.100
Ru-N_b''	2.118	2.102	2.130	2.112	2.099	2.096	2.087	2.086	2.080	2.084
angles										
O-S-Ru	112.83	114.22	113.10	114.37	114.91	113.46	114.08	114.84	115.62	115.70
S-Ru-N_t'	93.02	92.23	92.04	92.36	92.40	92.82	92.50	92.66	92.53	91.30
S-Ru-N_t'	87.55	87.10	86.56	87.69	87.69	87.40	87.04	88.10	89.12	90.31
S-Ru-N_b'	95.35	96.04	96.43	96.44	96.59	95.54	95.87	96.01	96.17	96.89
dihedral angles										
***d*(O-S-Ru-N_t''')**	-61.92	-61.70	-62.27	-64.03	-64.07	-61.24	-60.89	-60.49	-58.51	-58.39
***d*(O-S-Ru-N_b'')**	38.54	38.39	38.45	36.29	36.33	39.13	39.27	39.81	42.08	42.55

[a] Basis set 1 (BS1) was made of a double-ζ quality basis set LANL2DZ and corresponding effective core potential for Ru, all-electron 6-31G(d,p) basis sets for carbon, nitrogen, hydrogen, oxygen and sulfur atoms.

[b] In basis set 2 (BS2), usual 6-31G(d,p) for nonmetal atoms and SDD for Ru.

Table S2. The frontier MOs energies, ionization potentials as well as electron affinities for the ground state of [Ru(bpy)(tpy)(dmso)]$^{2+}$ complexes.

	HOMO	LUMO	IP	EA
***S*-[Ru(bpy)(tpy)(dmso)]$^{2+}$**	-6.8	-2.8	6.1	-3.3
***O*-[Ru(bpy)(tpy)(dmso)]$^{2+}$**	-6.1	-2.6	5.4	-3.1

Table S3. Main distributions of the frontier MOs as well as spin densities in the [Ru(bpy)(tpy)(dmso)]$^{2+}$ complexes.

	***S*-[Ru(bpy)(tpy)(dmso)]$^{2+}$**				***O*-[Ru(bpy)(tpy)(dmso)]$^{2+}$**			
	Ru(II)		Ru(III)	Ru(I)	Ru(II)		Ru(III)	Ru(I)
	HOMO	LUMO	Spin	Spin	HOMO	LUMO	Spin	Spin
Ru	77.1	9.5	95.0	3.7	74.5	9.4	91.2	5.0
dmso	1.0	4.5	0	0	6.4	3.5	6.2	1.1
bpy	8.8	2.2	1.7	0	6.4	2.5	0	0
tpy	13.2	83.8	4.4	96.5	12.7	84.7	3.1	94.0

Table S4 Vertical absorption energies (in eV), dominated orbital excitations, oscillator strength (*f*) obtained from TD-DFT calculations. The absorption (emission) energies are based on the S0 (T1) state equilibrium geometry.

	Abs.	dominated orbitals	E	*f*	Exptl.(λ_{max})
***S*-[Ru(bpy)(tpy)(dmso)]$^{2+}$**	$S_0 \rightarrow S_1$	HOMO→LUMO(98%)	2.64	0.00	
	$S_0 \rightarrow S_2$	HOMO-1→LUMO(96%)	2.83	0.03	
	$S_0 \rightarrow S_3$	HOMO→LUMO+1(96%)	3.07	0.00	
	$S_0 \rightarrow S_4$	HOMO-2→LUMO(59%)	3.17	0.01	
	$S_0 \rightarrow S_5$	HOMO→LUMO+2(79%)	3.29	0.04	
	$S_0 \rightarrow S_6$	HOMO-1→LUMO+2(42%)	3.37	0.05	412nm(3.01)[a]
***O*-[Ru(bpy)(tpy)(dmso)]$^{2+}$**	$S_0 \rightarrow S_1$	HOMO→LUMO(95%)	2.27	0.01	
	$S_0 \rightarrow S_2$	HOMO-1→LUMO(94%)	2.52	0.00	
	$S_0 \rightarrow S_3$	HOMO→LUMO+1(55%)	2.68	0.00	
	$S_0 \rightarrow S_4$	HOMO→LUMO+2(83%)	2.77	0.01	
	$S_0 \rightarrow S_5$	HOMO-1→LUMO+1(32%)	2.93	0.04	490nm(2.53)[a]
	$S_0 \rightarrow S_6$	HOMO-1→LUMO+2(52%)	2.99	0.04	

[a] Ref. 20.

Table S5. Optimized Cartesian coordinates and energies of the *S*-[Ru(bpy)(tpy)(dmso)]$^{2+}$ at PBE0-D3(BJ)/[SDD/6-31G(d,p)] level. Optimizations are conducted in acetonitrile by using the CPCM model. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Energies (a.u.)	
Sum of electronic and zero-point Energies	-1883.721227
Sum of electronic and thermal Enthalpies	-1883.691107
Sum of electronic and thermal Free Energies	-1883.780051

C	-2.59455100	-0.58952800	0.71632000
C	-2.09254400	1.69977200	0.37094500
C	-3.87219500	-0.26799500	1.16489200
C	-3.36156200	2.06992000	0.80742600
C	-4.25024700	1.07149900	1.19691700
H	-4.56058100	-1.03851400	1.48952600
H	-3.65442200	3.11145200	0.85304500
H	-5.24256900	1.34079600	1.54071200
C	-0.99416000	2.59701500	-0.03242200
C	1.22531000	2.71951100	-0.73727200
C	-1.09826500	3.98259900	-0.03924500
C	1.18391900	4.10755400	-0.75982000
H	2.12308400	2.17331200	-1.00447600
C	0.00210900	4.74785300	-0.40988700
H	-0.06652600	5.83001200	-0.41996700
N	-1.76356000	0.39458600	0.32004500
C	2.66528300	-0.97203000	-1.69234700
C	2.88428900	-0.40788900	0.54875200
C	4.02922300	-1.18994300	-1.81616500
H	1.98792500	-1.14725200	-2.52114800
C	4.26085200	-0.60935900	0.48791900
C	4.84565500	-0.99563500	-0.70942700
H	4.43143500	-1.50904800	-2.77066900
H	4.87362700	-0.47043900	1.36932600
H	5.91720200	-1.15125900	-0.77000400
C	0.12117700	0.39706500	2.76271800
C	2.18445000	-0.03737600	1.78420900
C	0.69672800	0.58816200	4.00873000
H	-0.94898000	0.48810500	2.62867800
C	2.82452300	0.14916900	3.00756800
C	2.07561800	0.46698900	4.13140100
H	2.56403300	0.61468200	5.08834000

N	2.09492300	-0.57065200	-0.54395500
Ru	0.06807800	-0.09600600	-0.24667100
N	0.84215000	0.09627000	1.67406600
H	0.06762600	0.82930900	4.85729300
H	3.89923900	0.04651500	3.08578100
H	-2.02745600	4.46183300	0.24463000
H	2.06725100	4.66467700	-1.04888600
N	0.16725400	1.97776700	-0.39305300
S	-0.57292400	-0.38040700	-2.42435700
O	0.01024300	-1.57888300	-3.12309200
C	-0.22564900	1.05287800	-3.44541200
H	-0.74470500	1.92637500	-3.04748100
H	0.85325700	1.21285400	-3.42498800
H	-0.55715600	0.82892700	-4.46105600
C	-2.35142500	-0.48005700	-2.64155700
H	-2.70114600	-1.36222400	-2.10363800
H	-2.82941900	0.42177200	-2.25609300
H	-2.54431300	-0.59489800	-3.70961800
C	-1.99490800	-1.93388400	0.63032700
C	-2.67131800	-3.10115900	0.96235000
C	-0.07924600	-3.14825200	0.08568700
C	-2.01745000	-4.32337600	0.84898500
H	-3.69861200	-3.05976100	1.30347700
C	-0.70146800	-4.34824500	0.40570200
H	0.94433000	-3.11166200	-0.26849200
H	-2.53409500	-5.24202100	1.10420900
H	-0.15465700	-5.27823900	0.30375400
N	-0.70360200	-1.97154600	0.19174700

Table S6. Optimized Cartesian coordinates and energies of the η^2-[Ru(bpy)(tpy)(dmso)]$^{2+}$ at PBE0-D3(BJ)/[SDD/6-31G(d,p)] level. Optimizations are conducted in acetonitrile by using the CPCM model. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Imaginary frequency	-226.7
IR Inten	26.3

Energies (a.u.)	
Sum of electronic and zero-point Energies	-1883.680479
Sum of electronic and thermal Enthalpies	-1883.649889
Sum of electronic and thermal Free Energies	-1883.741381

C	-2.49607900	-0.86569700	0.80876800
C	-2.26765500	1.46270800	0.43637500
C	-3.82885100	-0.70294900	1.17564200
C	-3.59566200	1.67574100	0.79485700
C	-4.37036500	0.57990000	1.16581700
H	-4.43756900	-1.55235800	1.46051200
H	-4.02402100	2.67047000	0.78608000
H	-5.40688200	0.72669300	1.44801800
C	-1.28224600	2.47770700	0.02113600
C	0.91333500	2.85779200	-0.66568300
C	-1.56401800	3.83669400	-0.04914000
C	0.69334000	4.22640000	-0.75213500
H	1.87700600	2.42122200	-0.90248400
C	-0.56647600	4.72246400	-0.44152300
H	-0.77440300	5.78515900	-0.50048000
N	-1.76768300	0.21223800	0.45899400
C	2.61295300	-0.61462300	-1.78173000
C	2.95471300	-0.20184400	0.48342300
C	3.97517300	-0.75854000	-1.99944000
H	1.87628300	-0.73895200	-2.56815700
C	4.33209800	-0.33470200	0.32996100
C	4.84976500	-0.61230200	-0.92773400
H	4.33542300	-0.98354800	-2.99662500
H	4.99403100	-0.22495400	1.17989000
H	5.92035500	-0.71735900	-1.06552200
C	0.23343700	0.39765300	2.81627200
C	2.28881600	0.07369700	1.75769100
C	0.84583900	0.56236400	4.04708400
H	-0.84177100	0.45872000	2.71334300

C	2.95482800	0.23473200	2.96948800
C	2.23150100	0.48120700	4.12708000
H	2.74261000	0.60769100	5.07495100
N	2.11111000	-0.33397200	-0.56930100
Ru	0.10853500	-0.05944700	-0.10632500
N	0.93201900	0.15811400	1.69370600
H	0.23486100	0.75282900	4.92145900
H	4.03491800	0.16616000	3.00659000
H	-2.55254100	4.20245300	0.20160200
H	1.50095700	4.88013300	-1.05997400
N	-0.04324700	1.99984800	-0.29469000
S	-1.13704100	0.04767500	-2.65397300
O	-0.25233800	-1.20297900	-2.67382800
C	-0.67000700	1.06512600	-4.05582700
H	-1.34793800	1.91940200	-4.11474100
H	0.34864100	1.41125900	-3.87458100
H	-0.71397700	0.46205300	-4.96609800
C	-2.77860700	-0.44665100	-3.18465500
H	-3.18181300	-1.10695100	-2.41541800
H	-3.40389700	0.44417900	-3.27588600
H	-2.70052100	-0.97439800	-4.13846100
C	-1.73797500	-2.12868600	0.73610400
C	-2.27589700	-3.36862900	1.05825600
C	0.30495000	-3.10793000	0.18951800
C	-1.48460500	-4.50602000	0.93956000
H	-3.30158300	-3.44689900	1.39823500
C	-0.17422500	-4.37485000	0.49686200
H	1.31790300	-2.95121600	-0.16318400
H	-1.89080700	-5.48010000	1.18915600
H	0.47614800	-5.23481200	0.38790300
N	-0.44965100	-2.01128300	0.30578100

Table S7. Optimized Cartesian coordinates and energies of the *O*-[Ru(bpy)(tpy)(dmso)]$^{2+}$ at PBE0-D3(BJ)/[SDD/6-31G(d,p)] level. Optimizations are conducted in acetonitrile by using the CPCM model. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Energies (a.u.)	
Sum of electronic and zero-point Energies	-1883.716475
Sum of electronic and thermal Enthalpies	-1883.685505
Sum of electronic and thermal Free Energies	-1883.778217

C	2.14643600	-0.48422300	-1.48209700
C	1.93718200	1.76431500	-0.77043100
C	3.32946900	-0.18972300	-2.15261100
C	3.11765300	2.10623900	-1.42406000
C	3.80859500	1.11733000	-2.11880400
H	3.87430200	-0.95877300	-2.68670300
H	3.49701900	3.12047300	-1.39496800
H	4.72919100	1.36606700	-2.63472200
C	1.06037700	2.65385300	0.00909400
C	-0.89565800	2.79739600	1.26791500
C	1.30870900	4.00899900	0.19690200
C	-0.70333300	4.15466100	1.48895900
H	-1.75253300	2.27118100	1.67326900
C	0.41796600	4.76979700	0.94485000
H	0.59983300	5.82790200	1.09819400
N	1.48827700	0.49374700	-0.82563300
C	-2.06212700	-0.82584300	2.35318600
C	-3.04936200	-0.34366600	0.29810100
C	-3.28852400	-1.14746400	2.91347700
H	-1.13283400	-0.87053800	2.91118100
C	-4.31020800	-0.65476600	0.80212200
C	-4.43180300	-1.06145200	2.12374000
H	-3.33934400	-1.45945100	3.95025200
H	-5.18786200	-0.58302300	0.17158100
H	-5.40656800	-1.30759600	2.53057200
C	-1.14912400	0.73339700	-2.60471800
C	-2.78887700	0.09592000	-1.07696600
C	-2.09023300	0.92205000	-3.60367800
H	-0.09487800	0.90606400	-2.78358200
C	-3.77968300	0.27096000	-2.03984400
C	-3.43088500	0.68789400	-3.31650200
H	-4.19460000	0.82753100	-4.07363700

N	-1.94285600	-0.43447300	1.07584100
Ru	-0.16171300	0.03755400	0.14572000
N	-1.48158000	0.33111600	-1.36786200
H	-1.76772500	1.24845600	-4.58551000
H	-4.81762300	0.08409400	-1.79322400
H	2.18930900	4.46707600	-0.23753500
H	-1.42424100	4.70888300	2.07866800
N	-0.04274000	2.05901700	0.54860300
S	2.26750100	-1.03630900	1.93933500
O	0.90841100	-0.26799400	1.95768400
C	3.29908200	-0.06150000	3.02931700
H	4.24033000	-0.59146800	3.19002200
H	3.48720800	0.88615600	2.52261900
H	2.77226600	0.10147200	3.97170600
C	1.97414800	-2.46620900	2.97830900
H	1.28524200	-3.11714200	2.43770400
H	2.92302200	-2.98281800	3.13859800
H	1.53687500	-2.14176300	3.92493100
C	1.48915000	-1.79723000	-1.37178100
C	1.96761200	-2.95348700	-1.97706500
C	-0.29542600	-2.97612000	-0.44146900
C	1.28402200	-4.15069200	-1.80002400
H	2.86586200	-2.91973200	-2.58187000
C	0.13383900	-4.16300500	-1.01934900
H	-1.18555400	-2.93186400	0.17615400
H	1.64703900	-5.05969700	-2.26701600
H	-0.43006100	-5.07376100	-0.85480400
N	0.35896000	-1.81938000	-0.60578200

Table S8. Optimized Cartesian coordinates and energies of *S*-[Ru(bpy)(tpy)(dmso)]$^{3+}$ at PBE0-D3(BJ)/[SDD/6-31G(d,p)] level. Optimizations are conducted in acetonitrile by using the CPCM model. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Energies (a.u.)	
Sum of electronic and zero-point Energies	-1883.496732
Sum of electronic and thermal Enthalpies	-1883.466611
Sum of electronic and thermal Free Energies	-1883.555606

C	-2.55114400	-0.83689700	0.70507300
C	-2.25433300	1.49936200	0.50073600
C	-3.85980300	-0.65933700	1.14038900
C	-3.55733300	1.72880700	0.92838500
C	-4.36074900	0.63509800	1.23559900
H	-4.47525600	-1.50873300	1.40822500
H	-3.93660100	2.73740900	1.03310300
H	-5.37964100	0.79357100	1.56967400
C	-1.23783200	2.51087600	0.19075600
C	1.00877900	2.82900000	-0.38801600
C	-1.44120600	3.88075000	0.26085500
C	0.86222100	4.20748800	-0.33143300
H	1.95467500	2.36810600	-0.64632300
C	-0.37959700	4.73886900	-0.00820700
H	-0.52428700	5.81210200	0.04213300
N	-1.80417900	0.23575800	0.37879500
C	2.61815900	-0.62448400	-1.90704200
C	2.94604600	-0.23745800	0.37815100
C	3.98062500	-0.72949400	-2.12463100
H	1.90447500	-0.78475200	-2.70722900
C	4.32172000	-0.32929700	0.21420600
C	4.84659700	-0.56847200	-1.04979500
H	4.34454300	-0.93697100	-3.12352800
H	4.98309200	-0.22018800	1.06357000
H	5.91995500	-0.63876100	-1.18660400
C	0.24858500	0.19624900	2.76635500
C	2.29559000	-0.02535000	1.67288500
C	0.87127300	0.30793800	3.99948200
H	-0.82962700	0.23707200	2.68331600
C	2.97809900	0.08608400	2.87980700
C	2.25835300	0.25581300	4.05498200
H	2.77840800	0.34341400	5.00233000

N	2.10576700	-0.36537600	-0.68824000
Ru	0.09842300	-0.06415700	-0.25643500
N	0.94451400	0.03616800	1.63424200
H	0.26862100	0.43475500	4.89054200
H	4.05897100	0.03850500	2.90797700
H	-2.41463300	4.27474300	0.52551300
H	1.71603500	4.84036800	-0.54054800
N	-0.02078900	2.00595100	-0.14994800
S	-0.71026900	-0.24330400	-2.46785200
O	-0.08704700	-1.39792700	-3.18783000
C	-0.41326000	1.25949100	-3.39304000
H	-0.93923500	2.09514500	-2.92823200
H	0.66296500	1.43842200	-3.39653400
H	-0.77148900	1.09011100	-4.41052100
C	-2.48676100	-0.39491200	-2.59987400
H	-2.78253200	-1.31628500	-2.09750100
H	-2.97732900	0.47352100	-2.15885200
H	-2.71494700	-0.46509500	-3.66513700
C	-1.82877800	-2.10770200	0.57901200
C	-2.37113300	-3.35602800	0.84331200
C	0.25460700	-3.06352600	0.09721400
C	-1.56553200	-4.48433000	0.72112400
H	-3.40733900	-3.44986800	1.14335100
C	-0.23616400	-4.33713200	0.34786500
H	1.28274700	-2.89612100	-0.19903600
H	-1.97644000	-5.46706100	0.92300900
H	0.42521900	-5.18919900	0.24892000
N	-0.52852000	-1.98299600	0.19727900

Table S9. Optimized Cartesian coordinates and energies of η^2-[Ru(bpy)(tpy)(dmso)]$^{3+}$ at PBE0-D3(BJ)/[SDD/6-31G(d,p)] level. Optimizations are conducted in acetonitrile by using the CPCM model. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Imaginary frequency	-209.7
IR Inten	19.7

Energies (a.u.)	
Sum of electronic and zero-point Energies	-1883.477428
Sum of electronic and thermal Enthalpies	-1883.447225
Sum of electronic and thermal Free Energies	-1883.537173

C	-2.58520400	-0.84062900	0.75495100
C	-2.28664000	1.48861500	0.41857100
C	-3.90034200	-0.64032400	1.16550000
C	-3.59376300	1.73800900	0.82112400
C	-4.39771600	0.65899300	1.18288500
H	-4.52179500	-1.47177900	1.47329900
H	-3.98258400	2.74755200	0.86297200
H	-5.41972600	0.83636600	1.49787000
C	-1.26672800	2.48621800	0.04626400
C	0.95971900	2.81456500	-0.59390700
C	-1.49523100	3.85414900	0.03827200
C	0.78990500	4.19244600	-0.61596400
H	1.90889700	2.35534300	-0.84223500
C	-0.45536400	4.71670300	-0.29803600
H	-0.62234400	5.78799900	-0.30664200
N	-1.84414100	0.21795100	0.37838400
C	2.57028200	-0.58618300	-1.93064900
C	2.89671900	-0.10764800	0.32273200
C	3.93706500	-0.62598600	-2.16016800
H	1.85503800	-0.79834800	-2.71386700
C	4.27727400	-0.12714600	0.15613900
C	4.80449100	-0.38177400	-1.10270600
H	4.30223200	-0.84753700	-3.15583800
H	4.93588800	0.04853300	0.99678200
H	5.87857800	-0.39860600	-1.24968500
C	0.16563600	0.18264500	2.70680900
C	2.23125700	0.09999200	1.60761800
C	0.77946800	0.36850900	3.93249300
H	-0.91131000	0.13768700	2.62556400

C	2.89646800	0.29214000	2.81343400
C	2.16711400	0.43090500	3.98569100
H	2.67884900	0.58117700	4.92966900
N	2.05759600	-0.31654600	-0.72170300
Ru	0.02740300	-0.10400200	-0.25027900
N	0.87402300	0.05812900	1.57298100
H	0.16824100	0.46418400	4.82146700
H	3.97792800	0.32855500	2.83795700
H	-2.47136700	4.24770900	0.29350100
H	1.62557500	4.82914700	-0.87991500
N	-0.04011500	1.98601700	-0.27794100
S	-0.99149500	-0.00839900	-2.56879000
O	-0.26261400	-1.34670400	-2.34118500
C	-0.36621500	0.77794500	-4.04276800
H	-0.96044200	1.67640700	-4.22067200
H	0.67284100	1.04974100	-3.85429700
H	-0.44820900	0.07264200	-4.87271400
C	-2.69519800	-0.34433100	-2.97588700
H	-3.13140600	-0.87288300	-2.12783400
H	-3.20348100	0.60897300	-3.13354400
H	-2.72043600	-0.96560400	-3.87372100
C	-1.84713700	-2.11198800	0.71474500
C	-2.39141800	-3.33963900	1.06559100
C	0.22704500	-3.10063200	0.28523400
C	-1.58756800	-4.47405400	1.02091400
H	-3.42775800	-3.41121400	1.37193200
C	-0.26023100	-4.35440800	0.62939600
H	1.25110100	-2.95453600	-0.03706500
H	-1.99837000	-5.44011000	1.29237500
H	0.39783600	-5.21367800	0.58342500
N	-0.54692200	-2.01342800	0.32398900

Table S10. Optimized Cartesian coordinates and energies of *O*-[Ru(bpy)(tpy)(dmso)]$^{3+}$ at PBE0-D3(BJ)/[SDD/6-31G(d,p)] level. Optimizations are conducted in acetonitrile by using the CPCM model. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Energies (a.u.)	
Sum of electronic and zero-point Energies	-1883.518063
Sum of electronic and thermal Enthalpies	-1883.487170
Sum of electronic and thermal Free Energies	-1883.579517

C	2.15137500	-0.92297600	-1.31534300
C	2.00539700	1.43057200	-1.10533500
C	3.35469800	-0.81416900	-2.00491700
C	3.20709200	1.59295500	-1.78696100
C	3.87928800	0.45591500	-2.22777800
H	3.87463300	-1.69343200	-2.36394700
H	3.61322000	2.57858800	-1.97721000
H	4.81757400	0.56159100	-2.76037700
C	1.12523400	2.49065400	-0.58852600
C	-0.89848500	2.93937600	0.50212000
C	1.38904300	3.84682500	-0.70893700
C	-0.68536300	4.30735000	0.41204200
H	-1.78572700	2.53047300	0.97083600
C	0.47472200	4.76459200	-0.20043700
H	0.66978600	5.82765600	-0.28822400
N	1.53417700	0.19089200	-0.88380100
C	-2.03194500	-0.29706100	2.53683500
C	-3.04846200	-0.18325700	0.43569200
C	-3.26151700	-0.40994200	3.16677500
H	-1.09407900	-0.29195800	3.08131600
C	-4.30993600	-0.29433000	1.01078500
C	-4.41591500	-0.40880200	2.39109800
H	-3.30363800	-0.49702300	4.24585900
H	-5.19958700	-0.29187600	0.39396900
H	-5.39260400	-0.49604600	2.85410600
C	-1.16073200	0.14407400	-2.65812700
C	-2.80165200	-0.05701700	-1.00369400
C	-2.11495800	0.17233100	-3.66067900
H	-0.10389000	0.21144600	-2.88399100
C	-3.80300300	-0.03089700	-1.96828500
C	-3.45732400	0.08497100	-3.30793800
H	-4.23073800	0.10578100	-4.06772100

N	-1.93181700	-0.18733100	1.20519900
Ru	-0.14668400	-0.00630500	0.17501800
N	-1.49554200	0.03441800	-1.36428500
H	-1.80191400	0.26228900	-4.69374300
H	-4.84367100	-0.10059000	-1.67844100
H	2.29510200	4.18666200	-1.19503500
H	-1.42195500	4.99079200	0.81663800
N	-0.01467400	2.05667300	0.02277300
S	2.42932800	-0.22043300	2.09613500
O	0.84905700	-0.11825500	1.93138500
C	2.76614800	1.10948900	3.24046900
H	3.81353200	1.03603300	3.54184300
H	2.59807300	2.04494200	2.70532500
H	2.09897800	1.02149100	4.09971500
C	2.58982800	-1.64569600	3.16141900
H	2.31190700	-2.52139400	2.57308300
H	3.63582600	-1.72082400	3.46746800
H	1.93081800	-1.52599500	4.02309900
C	1.42009900	-2.15677600	-0.98896100
C	1.85325800	-3.43098200	-1.32555600
C	-0.51133500	-3.03210500	0.00665000
C	1.07217800	-4.52829700	-0.97611300
H	2.78862800	-3.56910000	-1.85375600
C	-0.12632700	-4.32866200	-0.30228700
H	-1.43349200	-2.82112300	0.53490500
H	1.40055600	-5.52950800	-1.23235700
H	-0.76164100	-5.15747700	-0.01443600
N	0.24332100	-1.97748400	-0.32174600

Table S11. Optimized Cartesian coordinates and energies of *S*-[Ru(bpy)(tpy)(dmso)]$^{+}$ at PBE0-D3(BJ)/[SDD/6-31G(d,p)] level. Optimizations are conducted in acetonitrile by using the CPCM model. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Energies (a.u.)	
Sum of electronic and zero-point Energies	-1883.844212
Sum of electronic and thermal Enthalpies	-1883.813585
Sum of electronic and thermal Free Energies	-1883.904086

C	2.47212700	0.95212100	0.65355300
C	2.21066100	-1.44087100	0.58806800
C	3.73981100	0.83110900	1.18835800
C	3.49803100	-1.58690000	1.12327800
C	4.25964300	-0.46358000	1.40571700
H	4.32149800	1.70587900	1.45408100
H	3.89264900	-2.57560000	1.33237300
H	5.25394000	-0.57782700	1.82296400
C	1.24769000	-2.46391100	0.29946500
C	-0.93401100	-2.92473600	-0.46686300
C	1.47623600	-3.84768500	0.45335300
C	-0.75648600	-4.28565500	-0.32649500
H	-1.86925200	-2.50999600	-0.83036600
C	0.48847000	-4.75306300	0.14437200
H	0.66731400	-5.81683600	0.26316600
N	1.76549300	-0.16373600	0.32511700
C	-2.78464500	0.36521800	-1.81145600
C	-2.93025700	0.22993400	0.50147300
C	-4.16268700	0.46645900	-1.93413300
H	-2.12512300	0.37836700	-2.67497900
C	-4.31945100	0.32436100	0.44331200
C	-4.94787300	0.44163600	-0.78769700
H	-4.60293500	0.56130500	-2.92035900
H	-4.90854600	0.30673900	1.35170700
H	-6.02849700	0.51452700	-0.84666300
C	-0.08417400	-0.05042600	2.73679800
C	-2.18803300	0.11977600	1.76253000
C	-0.62329000	-0.07055000	4.01359900
H	0.98493200	-0.10935400	2.57620500
C	-2.79220000	0.10467500	3.01900000
C	-2.00408400	0.00740000	4.15652600
H	-2.46339900	-0.00591500	5.13902700

N	-2.16901000	0.24268400	-0.62312900
Ru	-0.10231500	0.03938600	-0.30567500
N	-0.84345600	0.04064300	1.63645100
H	0.03388700	-0.14653900	4.87198700
H	-3.86891300	0.16967000	3.11122700
H	2.43953500	-4.18945300	0.81657000
H	-1.56203400	-4.96544500	-0.57762200
N	0.02084600	-2.02381800	-0.17931700
S	0.61704900	0.01665200	-2.46134100
O	-0.35358200	0.27341800	-3.58875800
C	1.46391500	-1.51592700	-2.86028800
H	2.26418700	-1.68478400	-2.13703700
H	0.72941600	-2.31925900	-2.79809300
H	1.85832400	-1.42976400	-3.87432200
C	1.98349200	1.15456500	-2.71867500
H	1.60351300	2.16420200	-2.55947900
H	2.78305500	0.93267800	-2.00960500
H	2.32895000	1.03543000	-3.74700600
C	1.73113100	2.19086200	0.41026200
C	2.24763900	3.46893400	0.63378400
C	-0.29540100	3.11758800	-0.30740300
C	1.46630100	4.58310500	0.37844300
H	3.25929800	3.58162500	1.00617800
C	0.16482400	4.40536600	-0.09902500
H	-1.29527300	2.92265900	-0.67999600
H	1.86188000	5.57857100	0.54942300
H	-0.48291100	5.24861800	-0.30891300
N	0.45726500	2.03064700	-0.07174900

Table S12. Optimized Cartesian coordinates and energies of η^2-[Ru(bpy)(tpy)(dmso)]$^+$ at PBE0-D3(BJ)/[SDD/6-31G(d,p)] level. Optimizations are conducted in acetonitrile by using the CPCM model. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Imaginary frequency	-36.2
IR Inten.	5.7

Energies (a.u.)	
Sum of electronic and zero-point Energies	-1883.800391
Sum of electronic and thermal Enthalpies	-1883.774334
Sum of electronic and thermal Free Energies	-1883.869306

C	-0.28491700	0.76182600	-0.29257400
C	-0.06767100	-1.61458500	-0.15931000
C	-0.76518700	0.65711700	-1.59393000
C	-0.54115900	-1.74815100	-1.45734900
C	-0.88862400	-0.60250900	-2.17852600
H	-1.04656400	1.54490200	-2.14936300
H	-0.65070100	-2.72918800	-1.90602500
H	-1.26352000	-0.69435600	-3.19170200
C	0.30910400	-2.67682100	0.76033600
C	1.01140500	-3.17498700	2.93817700
C	0.33215100	-4.03520800	0.43218900
C	1.04856300	-4.52817600	2.66557600
H	1.27575300	-2.78457600	3.91526400
C	0.69979700	-4.96974200	1.38368200
H	0.72053700	-6.02561700	1.13609800
N	0.05522500	-0.37123600	0.39321600
C	0.33868600	0.03200700	5.23944300
C	2.54636900	0.04228200	4.49001300
C	0.74965700	0.14676600	6.55876300
H	-0.70864100	-0.01081300	4.94477100
C	3.02125000	0.15645400	5.79520300
C	2.11263400	0.20659600	6.84278400
H	0.00770800	0.18871900	7.34825300
H	4.08595900	0.20778700	5.98991200
H	2.46287700	0.29472300	7.86561100
C	3.37077300	-0.13068300	0.96311100
C	3.38783800	-0.00414900	3.29406000
C	4.75313400	-0.07835400	0.90964900
H	2.76364700	-0.20303200	0.06818600

C	4.78026800	0.04884300	3.29994900
C	5.47303500	0.01120200	2.09904000
H	6.55668600	0.05208000	2.09053000
N	1.21781400	-0.02502200	4.22466700
Ru	0.69262400	-0.20375700	2.23397100
N	2.69649100	-0.09632100	2.12615300
H	5.25043700	-0.10868600	-0.05305500
H	5.31604200	0.11996700	4.23908700
H	0.06606400	-4.34827800	-0.57120600
H	1.34475200	-5.22386800	3.44245200
N	0.64675900	-2.25280900	2.02468100
S	-2.72247900	0.47573700	2.36498600
O	-2.55322100	-0.02062600	3.79584000
C	-4.35251300	-0.07688500	1.82798300
H	-4.56996800	0.35093600	0.84641800
H	-4.31559200	-1.16512100	1.75338500
H	-5.10418200	0.22653100	2.56100300
C	-3.09367600	2.23585200	2.46412400
H	-2.19875800	2.73641800	2.83774800
H	-3.32821200	2.60856800	1.46433200
H	-3.93119300	2.39656700	3.14761100
C	-0.10069700	1.97089500	0.48842600
C	-0.34573900	3.26562400	0.01594600
C	0.55117200	2.84243500	2.56607000
C	-0.14239100	4.35455200	0.84210200
H	-0.69430700	3.40667000	-1.00108200
C	0.32140800	4.13714300	2.14750600
H	0.90724800	2.62383100	3.56715600
H	-0.33509400	5.35961500	0.48274200
H	0.49849300	4.96071900	2.82983100
N	0.33911700	1.76664500	1.77869600

Table S13. Optimized Cartesian coordinates and energies of *O*-[Ru(bpy)(tpy)(dmso)]$^{+}$ at PBE0-D3(BJ)/[SDD/6-31G(d,p)] level. Optimizations are conducted in acetonitrile by using the CPCM model. Thermochemical data are given at T = 298.15 K and P = 1Atm.

Energies (a.u.)	
Sum of electronic and zero-point Energies	-1883.830678
Sum of electronic and thermal Enthalpies	-1883.799326
Sum of electronic and thermal Free Energies	-1883.893477

C	2.16584600	-0.37114700	-1.45182000
C	1.83233200	1.89667200	-0.73990600
C	3.32920200	0.02791500	-2.13694800
C	2.97411300	2.31631700	-1.39795900
C	3.72454100	1.35169800	-2.10802200
H	3.91758600	-0.70229500	-2.68279000
H	3.28975000	3.35249600	-1.37629500
H	4.62225900	1.65629700	-2.63567000
C	0.90318900	2.73122500	0.03364500
C	-1.06646200	2.76435300	1.28836300
C	1.05848400	4.10446000	0.21714100
C	-0.96420200	4.12907000	1.50067800
H	-1.89031600	2.18684800	1.69414400
C	0.12201400	4.81313500	0.95507800
H	0.23555900	5.88191100	1.10202400
N	1.45477200	0.59867900	-0.78022600
C	-2.09566800	-0.91801000	2.33540500
C	-3.04326400	-0.50642600	0.24783400
C	-3.31805200	-1.30290400	2.86153200
H	-1.18213900	-0.91048600	2.92130800
C	-4.30074100	-0.88429900	0.71719100
C	-4.44173400	-1.28755400	2.03709400
H	-3.38316300	-1.60988400	3.89929900
H	-5.16087100	-0.86471600	0.05871800
H	-5.41316900	-1.58509300	2.41692700
C	-1.11383700	0.67113300	-2.59404500
C	-2.76587400	-0.05936200	-1.11933000
C	-2.02894100	0.79364900	-3.62586500
H	-0.06417000	0.90295100	-2.72907400
C	-3.73081300	0.04779600	-2.11949900
C	-3.36407000	0.47825800	-3.38589400
H	-4.10666300	0.56479800	-4.17158000

N	-1.95378000	-0.52957000	1.05750100
Ru	-0.18520300	0.03940000	0.17206900
N	-1.46377600	0.25639000	-1.36356800
H	-1.69275400	1.13153200	-4.59953600
H	-4.76293800	-0.20468300	-1.90782300
H	1.91085400	4.61176400	-0.21996400
H	-1.72166500	4.64037400	2.08387400
N	-0.16447100	2.06865900	0.57722700
S	2.36683700	-0.80496500	1.89393900
O	0.91388900	-0.25119500	1.99654900
C	3.14631600	-0.14135900	3.36431600
H	4.14312000	-0.57643400	3.46363000
H	3.22453500	0.93777900	3.22463900
H	2.52872300	-0.37220000	4.23496700
C	2.24744500	-2.52828500	2.38560800
H	1.72208900	-3.05517600	1.58718200
H	3.25759200	-2.93043300	2.49365400
H	1.69390600	-2.60049100	3.32452400
C	1.61552300	-1.68214400	-1.32312600
C	2.16860800	-2.85283400	-1.89309100
C	-0.11000800	-2.98854700	-0.37367500
C	1.57605400	-4.07471400	-1.69012500
H	3.07055200	-2.77399800	-2.49141700
C	0.39813500	-4.15372100	-0.90816300
H	-1.01074000	-2.99154500	0.23367100
H	2.00719200	-4.97019300	-2.12634300
H	-0.10322700	-5.09729600	-0.72738500
N	0.45978700	-1.78168200	-0.54459700

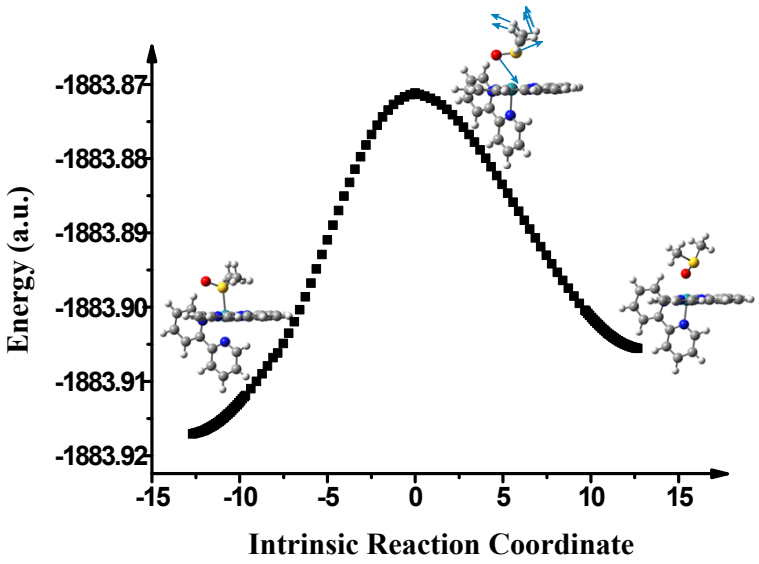

Figure S1. Intrinsic reaction coordinate (IRC) for intramolecular isomerization in $[Ru(bpy)(tpy)(dmso)]^{2+}$ performed at the PBE0-D3(BJ)/[SDD/6-31G(d,p)] level. Optimized structures (Tables S5-S7 for Cartesian coordinates and transition vector are shown).

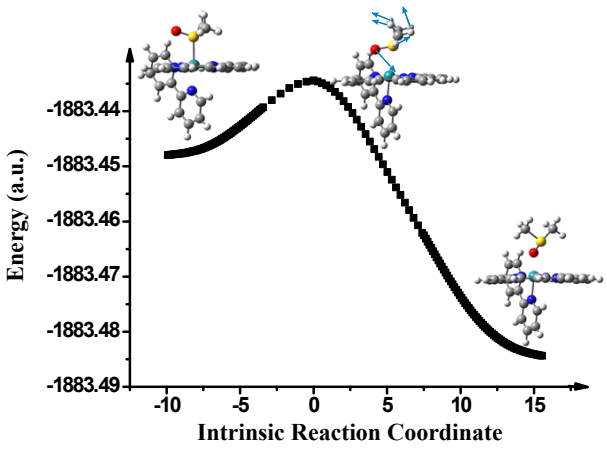

Figure S2. Intrinsic reaction coordinate (IRC) for intramolecular isomerization in $[Ru(bpy)(tpy)(dmso)]^{3+}$ performed at the PBE0-D3(BJ)/[SDD/6-31G(d,p)] level. Optimized structures (Tables S8-S10 for Cartesian coordinates and transition vector are shown).

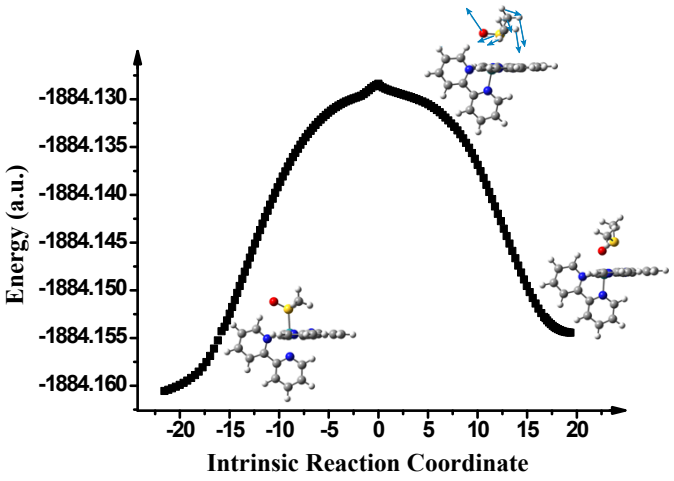

Figure S3. Intrinsic reaction coordinate (IRC) for intramolecular isomerization in $[Ru(bpy)(tpy)(dmso)]^+$ performed at the PBE0-D3(BJ)/[SDD/6-31G(d,p)] level. Optimized structures (Tables S11-S13 for Cartesian coordinates and transition vector are shown).