†Electronic supplementary information (ESI)

N-(aryl)pyrrole-2-aldimine complexes of ruthenium: Synthesis, structure and, spectral and electrochemical properties†

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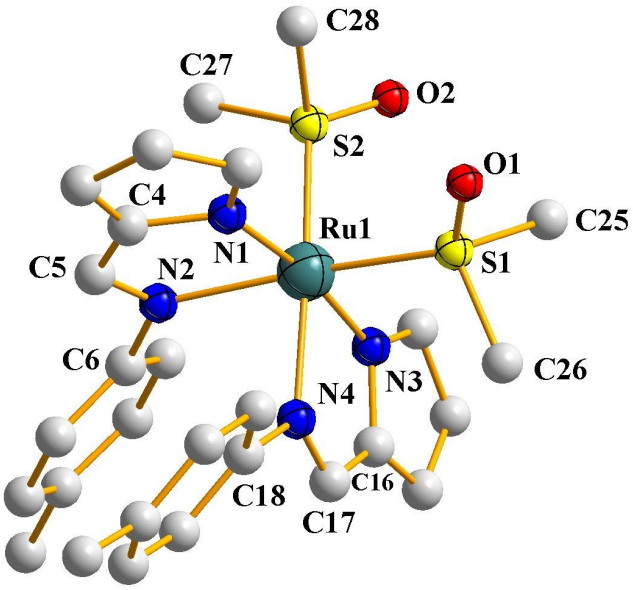


Fig. S1. Crystal structure of the [Ru(L-CH_3)$_2$(dmso)$_2$] complex.

Table S1. Selected bond distances and bond angles for [Ru(L-CH_3)$_2$(dmso)$_2$].

Bond distances (Å)			
Ru1-N1	2.0774(19)	N3-C16	1.385(3)
Ru1-N2	2.1576(18)	C16-C17	1.408(3)
Ru1-N3	2.0812(19)	N4-C17	1.308(3)
Ru1-N4	2.1422(18)	N4-C18	1.421(3)
Ru1-S1	2.2492(6)	S1-O1	1.474(2)
Ru1-S2	2.2419(7)	S1-C25	1.781(3)
N1-C4	1.378(3)	S1-C26	1.784(3)
C4-C5	1.402(4)	S2-O2	1.467(2)
N2-C5	1.313(3)	S2-C27	1.778(4)
N2-C6	1.428(3)	S2-C28	1.778(3)
Bond angles (°)			
N1-Ru1-N3	171.43(8)	N1-Ru1-N2	77.94(8)
S1-Ru1-N2	171.34(5)	N3-Ru1-N4	78.11(7)
S2-Ru1-N4	172.62(5)		

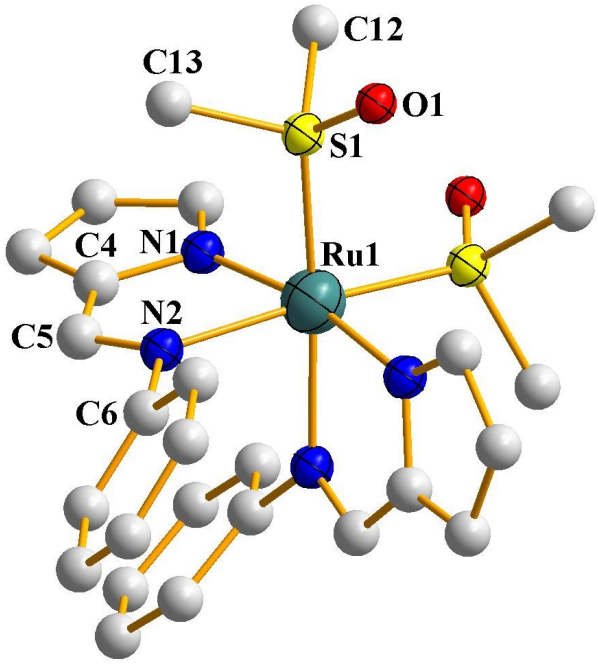


Fig. S2. Crystal structure of the $[Ru(L\text{-}H)_2(dmso)_2]$ complex.

Table S2. Selected bond distances and bond angles for $[Ru(L\text{-}H)_2(dmso)_2]$.

Bond distances (Å)			
Ru1-N1	2.082(2)	C5-N2	1.312(4)
Ru1-N2	2.148(2)	C6-N2	1.416(4)
Ru1-S1	2.2459(8)	S1-O1	1.484(2)
C4-N1	1.387(4)	C12-S1	1.789(4)
C4-C5	1.406(4)	C13-S1	1.789(3)
Bond angles (°)			
N1-Ru1-N1a	169.21(13)	N1-Ru1-N2	78.10(9)
S1-Ru1-N2a	173.54(7)		

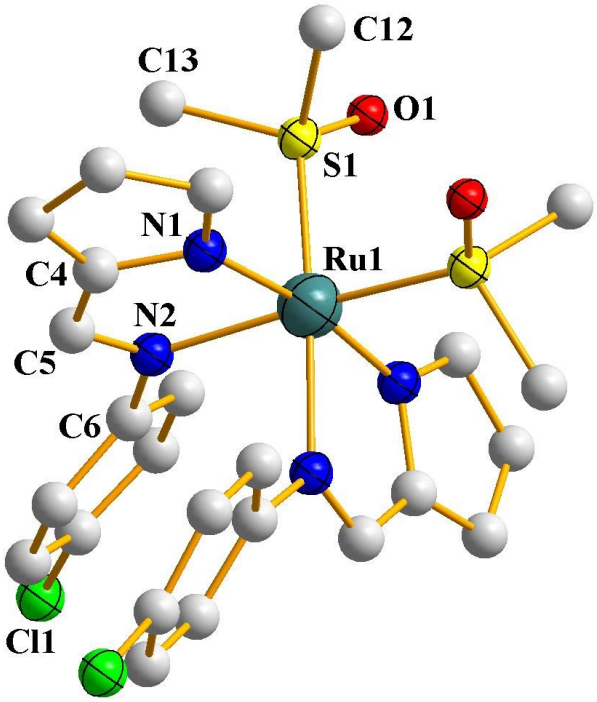


Fig. S3. Crystal structure of the $[Ru(L\text{-}Cl)_2(dmso)_2]$ complex.

Table S3. Selected bond distances and bond angles for $[Ru(L\text{-}Cl)_2(dmso)_2]$.

Bond distances (Å)			
Ru1-N1	2.0806(13)	C5-N2	1.309(3)
Ru1-N2	2.1415(17)	C6-N2	1.422(3)
Ru1-S1	2.2504(5)	S1-O1	1.4853(15)
C4-N1	1.380(2)	C12-S1	1.790(2)
C4-C5	1.405(2)	C13-S1	1.782(2)
Bond angles (°)			
N1-Ru1-N1a	171.30(10)	N1-Ru1-N2	77.61(7)
S1-Ru1-N2	172.24(5)		

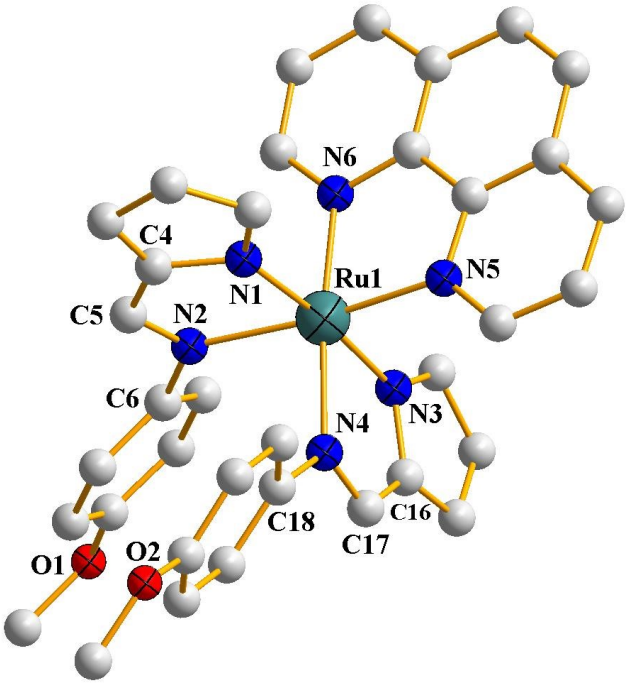


Fig. S4. DFT-optimized structure of the [Ru(L-OCH_3)$_2$(phen)] complex.

Table S4. Some computed bond distances and bond angles for [Ru(L-OCH_3)$_2$(phen)].

Bond distances (Å)			
Ru1-N1	2.1148	C4-C5	1.4087
Ru1-N2	2.1762	N2-C5	1.3190
Ru1-N3	2.1148	N2-C6	1.4167
Ru1-N4	2.1762	N3-C16	1.3849
Ru1-N5	2.0764	C16-C17	1.4087
Ru1-N6	2.0764	N4-C17	1.3190
N1-C4	1.3849	N4-C18	1.4167
Bond angles (°)			
N1-Ru1-N3	174.15	N1-Ru1-N2	77.56
N2-Ru1-N5	173.18	N3-Ru1-N4	77.56
N4-Ru1-N6	173.18	N5-Ru1-N6	79.35

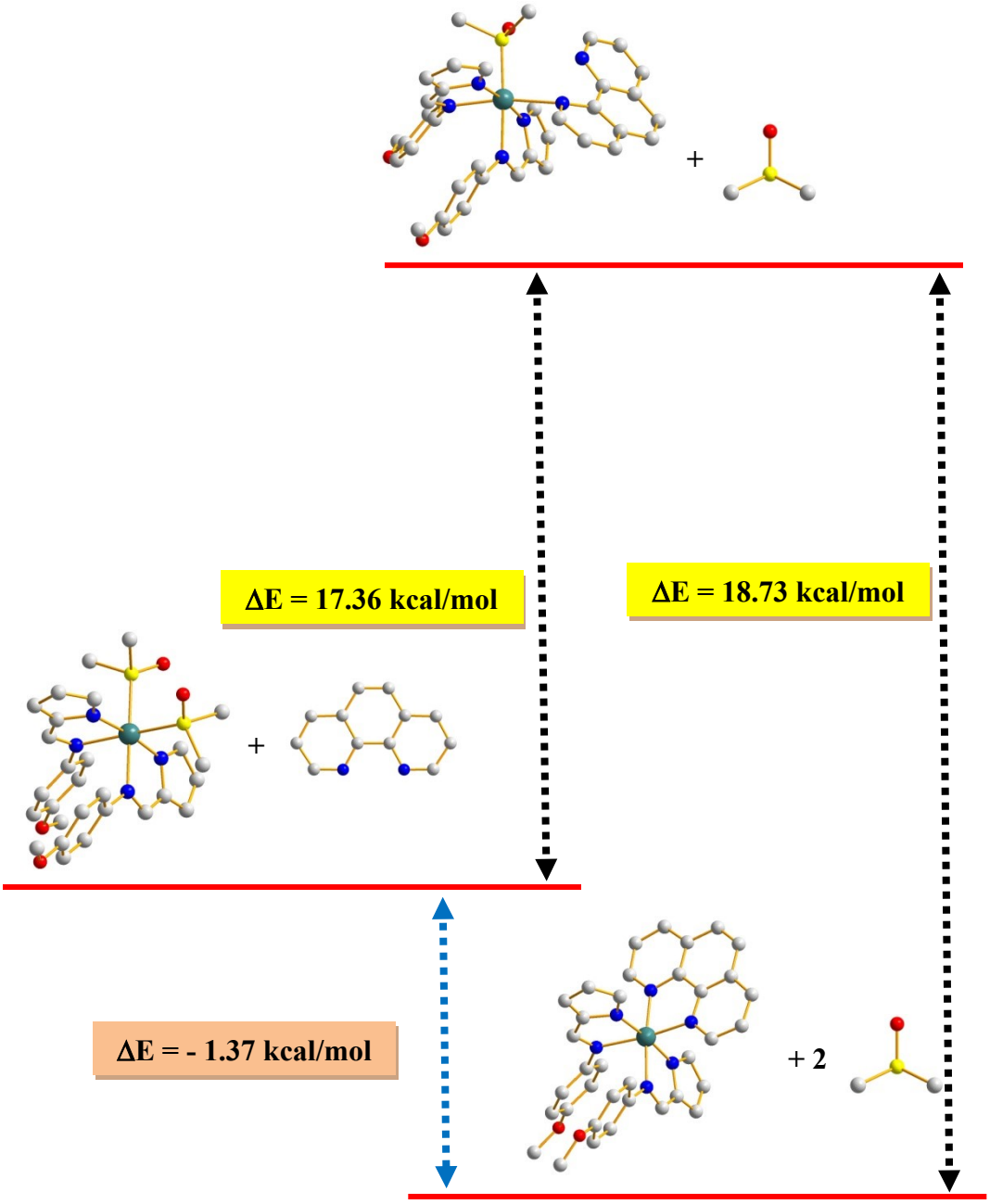


Fig. S5. Energy difference (ΔE) between the reactants, intermediates and products for the phen reaction.

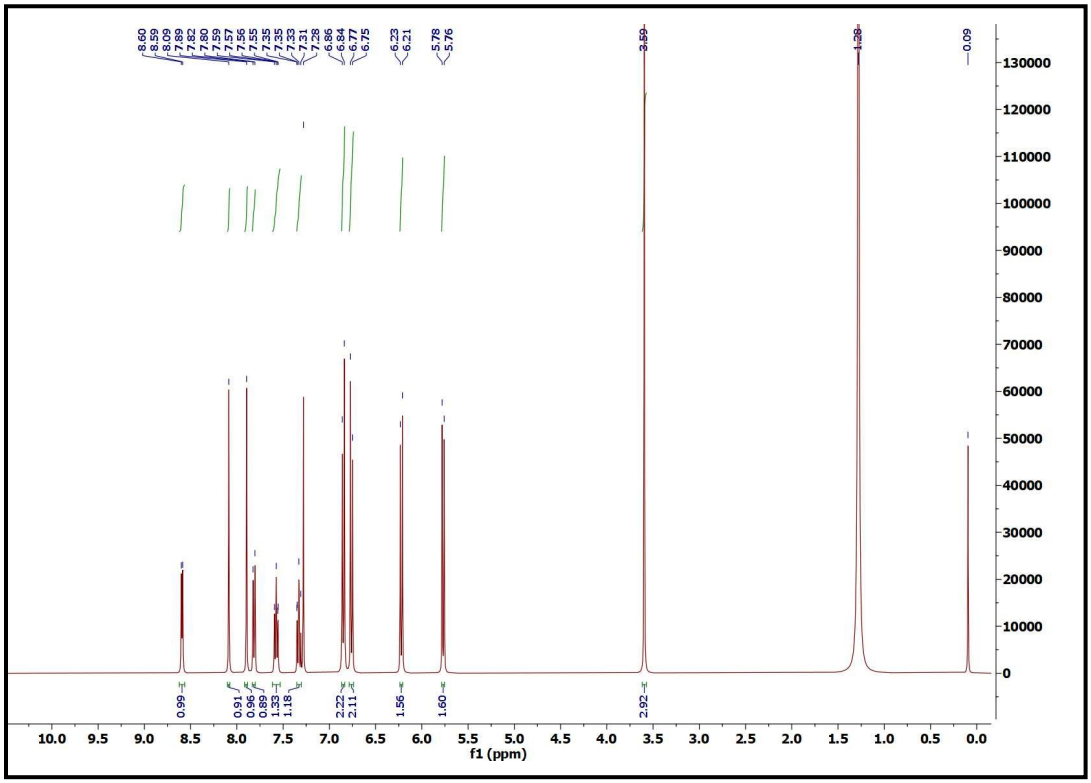


Fig. S6. ^{1}H NMR spectrum of [Ru(L-OCH_3)$_2$(bpy)] in $CDCl_3$ solution.

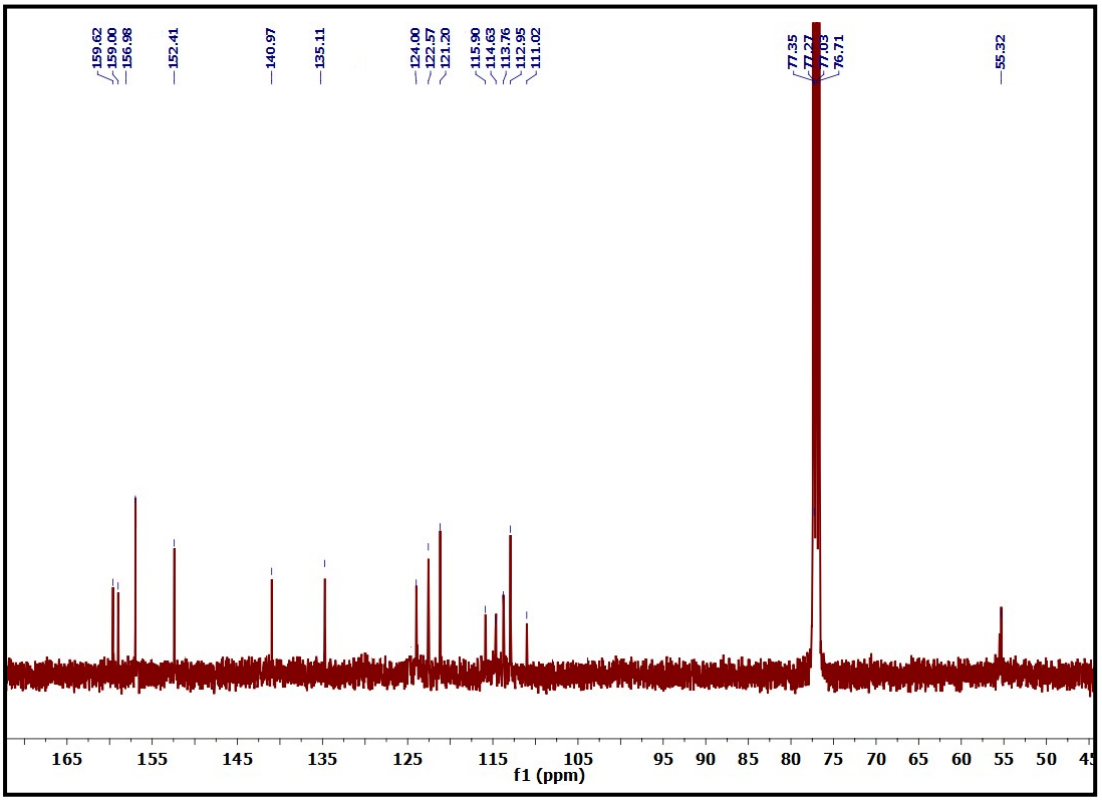


Fig. S7. ^{13}C NMR spectrum of [Ru(L-OCH_3)$_2$(bpy)] in $CDCl_3$ solution.

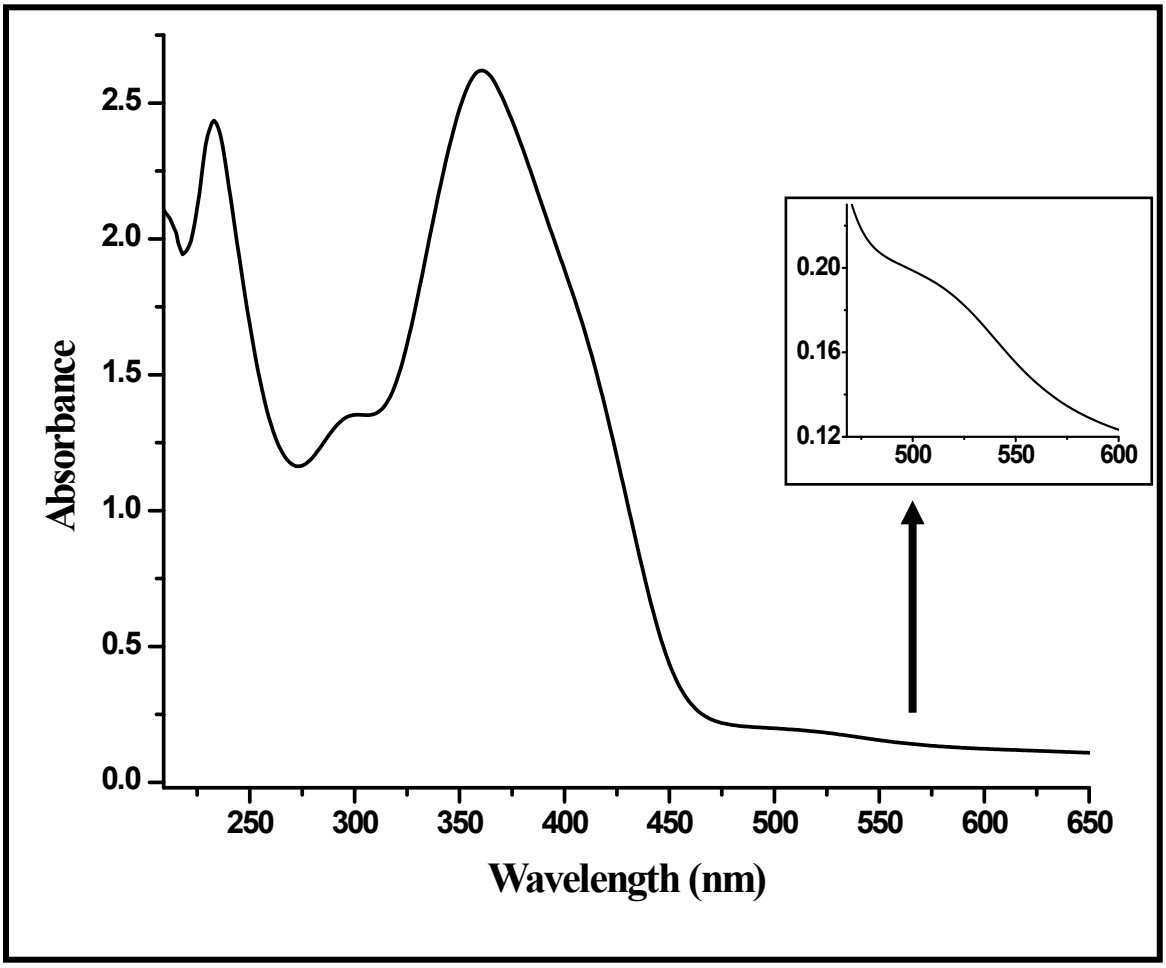


Fig. S8. Electronic spectrum of $[Ru(L\text{-}OCH_3)_2(dmso)_2]$ in dichloromethane solution.

Table S5. Computed parameters from TDDFT calculations on $[Ru(L\text{-}OCH_3)_2(dmso)_2]$ for electronic spectral properties in dichloromethane solution.

Excited State	Composition	CI value	E (eV)	Oscillator strength (f)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
9	H-3 → L H-3 → L+2 H-2 → L+1 H-2 → L+5 H → L+1	0.52215 0.12248 0.40210 0.10548 0.11512	3.4745	0.0182	356.85	MLCT/LLCT LLCT/LMCT MLCT/ILCT ILCT/LMCT/LLCT MLCT/ILCT	361
18	H-6 → L H-4 → L H-1 → L+3	0.12636 0.24950 0.62639	4.2299	0.0748	293.11	MLCT/ LLCT ILCT/MLCT/LLCT ILCT/LMCT	298
45	H-2 → L+7 H-1 → L+6 H → L+7 H → L+8	0.10803 0.15783 0.64427 0.13006	5.1320	0.0198	241.59	LLCT/LMCT LLCT/LMCT LMCT/LLCT LMCT/LLCT	233

Table S6. Compositions of selected molecular orbitals of $[Ru(L\text{-}OCH_3)_2(dmso)_2]$ associated with the electronic spectral transitions.

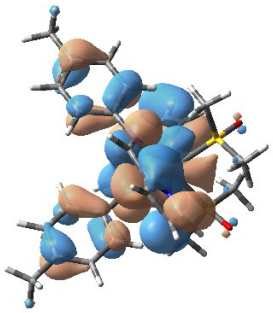
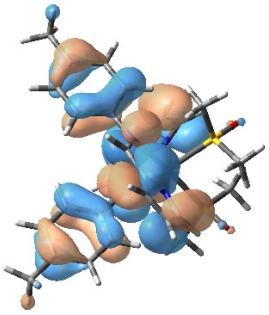
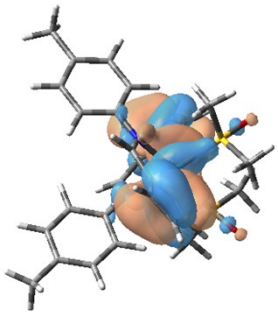
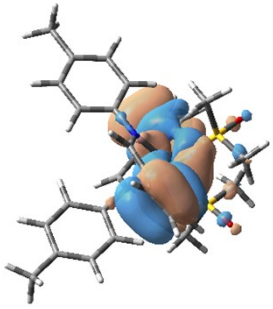
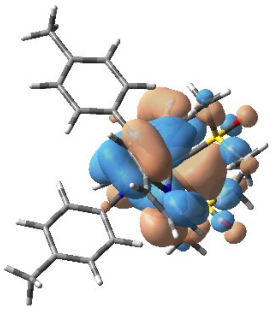
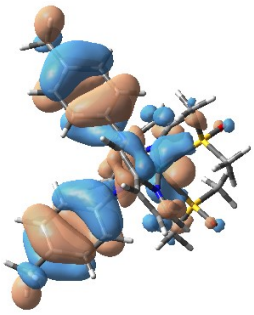
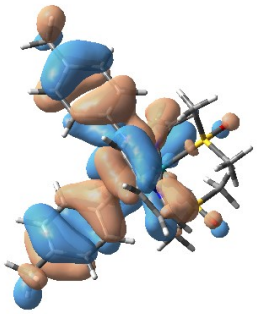
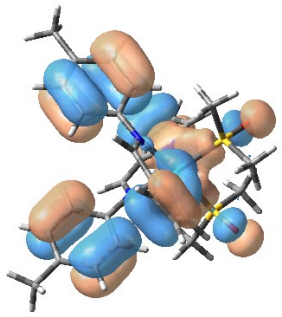
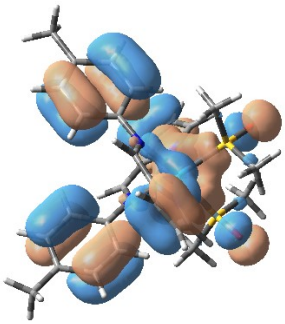
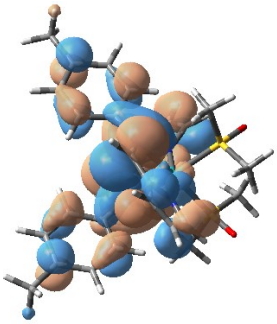
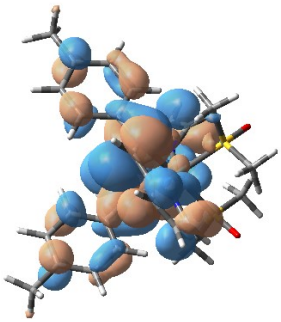
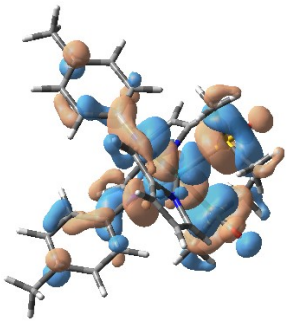
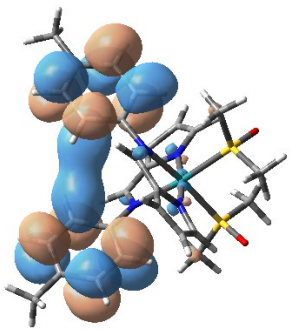
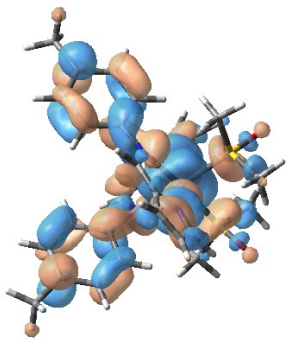
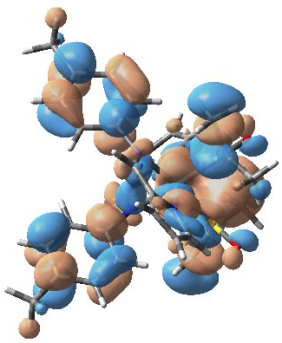
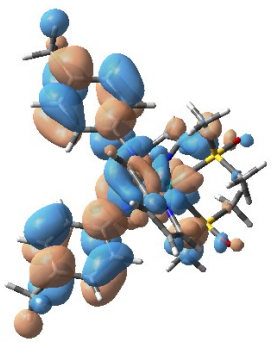
% Contribution of fragments to	Fragments				
	Ru	L-OCH_3 (1)	L-OCH_3 (2)	DMSO (1)	DMSO (2)
HOMO (H)	13	43	42	1	1
H-1	0	48	50	1	1
H-2	46	26	26	1	1
H-3	52	23	23	1	1
H-4	6	46	46	1	1
H-6	65	14	13	4	4
LUMO (L)	4	50	46	0	0
L+1	3	46	49	1	1
L+2	55	12	12	10	11
L+3	2	48	48	1	1
L+5	52	20	20	4	4
L+6	18	13	13	28	28
L+7	59	2	2	19	18
L+8	19	38	37	3	3

Table S7. Computed parameters from TDDFT calculations on $[Ru(L\text{-}CH_3)_2(dmso)_2]$ for electronic spectral properties in dichloromethane solution.

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
10	H-3 → L	0.35155	3.5790	0.0649	346.42	MLCT/LLCT	362
	H-2 → L+1	0.45932				MLCT	
	H-1 → L	0.29312				LMCT/LLCT	
	H → L+1	0.25131				MLCT	
17	H-6 → L+1	0.11733	4.3474	0.0791	285.19	LMCT	296
	H-5 → L	0.29040				MLCT/ILCT	
	H-4 → L	0.53986				MLCT/LLCT	
	H-4 → L+2	0.22434				LLCT/LMCT	
	H-1 → L+3	0.10327				LMCT/ILCT/LLCT	
	H-1 → L+5	0.10910				LMCT/LLCT	
	H → L+2	0.12302				LMCT/LLCT	
47	H-10 → L+2	0.22300	5.1785	0.0049	239.42	LMCT/LLCT	232
	H-9 → L+2	0.17687				LMCT/LLCT	
	H-3 → L+5	0.13899				ILCT/MLCT	
	H-3 → L+6	0.37084				MLCT/ILCT	
	H-3 → L+8	0.20246				LLCT/LMCT	
	H-2 → L+2	0.10090				ILCT/LLCT/LMCT	
	H-2 → L+7	0.10274				MLCT/ILCT	
	H → L+9	0.37242				LLCT/LMCT	

Table S8. Compositions of selected molecular orbitals of $[Ru(L\text{-}CH_3)_2(dmso)_2]$ associated with the electronic spectral transitions.

% Contribution of fragments to	Fragments				
	Ru	L-OCH_3 (1)	L-OCH_3 (2)	DMSO (1)	DMSO (2)
HOMO (H)	16	41	41	1	1
H-1	0	49	50	1	0
H-2	46	26	26	1	1
H-3	52	23	23	1	1
H-4	56	18	18	4	4
H-5	14	42	42	1	1
H-6	2	48	48	1	1
H-9	16	36	36	6	6
H-10	14	35	35	8	8
LUMO (L)	4	48	48	0	0
L+1	3	48	47	1	1
L+2	54	13	13	10	10
L+3	1	49	48	1	1
L+5	44	25	25	3	3
L+6	21	24	24	16	15
L+7	7	43	43	4	3
L+8	62	2	2	17	17
L+9	20	13	13	27	27

HOMO (H)	H-1	H-2	H-3
			
H-4	H-5	H-6	H-9
			
H-10	LUMO (L)	L+1	L+2
			
L+3	L+5	L+6	L+7
			

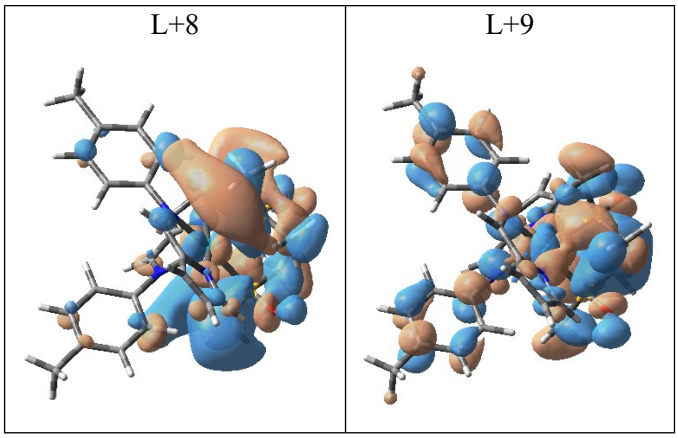


Fig. S9. Contour plots of the molecular orbitals of $[Ru(L\text{-}CH_3)_2(dmso)_2]$, which are associated with the electronic spectral transitions (See **Table S7**).

Table S9. Computed parameters from TDDFT calculations on $[Ru(L\text{-}H)_2(dmso)_2]$ for electronic spectral properties in dichloromethane solution.

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
10	H-3 → L	0.33033	3.5831	0.0618	346.42	MLCT/LLCT	362
	H-2 → L+1	0.44927				MLCT/ILCT	
	H-1 → L	0.32134				LMCT/ILCT	
	H → L+1	0.26103				MLCT	
18	H-5 → L	0.16605	4.3719	0.0630	283.59	MLCT/LLCT	294
	H-4 → L	0.53796				MLCT/LLCT	
	H-4 → L+2	0.29483				LLCT/MLCT	
	H-1 → L+3	0.14986				ILCT/LMCT	
	H → L+2	0.16599				LMCT/LLCT	
48	H-11 → L+1	0.14411	5.2263	0.0112	237.23	LLCT/MLCT	234
	H-6 → L+2	0.23293				LMCT/LLCT	
	H-2 → L+5	0.15005				ILCT/LLCT/LMCT	
	H-2 → L+6	0.28472				MLCT/ILCT/LLCT	
	H-1 → L+7	0.26006				LMCT/ LLCT	
	H → L+8	0.44984				LMCT /LLCT	

Table S10. Compositions of selected molecular orbitals of $[Ru(L\text{-}H)_2(dmso)_2]$ associated with the electronic spectral transitions.

% Contribution of fragments to	Fragments				
	Ru	L-OCH_3 (1)	L-OCH_3 (2)	DMSO (1)	DMSO (2)
HOMO (H)	17	40	41	1	1
H-1	0	50	49	1	0
H-2	45	26	27	1	1
H-3	52	23	23	1	1
H-4	61	15	15	5	4
H-5	10	43	43	2	2
H-6	30	27	27	8	8
H-11	16	15	15	27	27
LUMO (L)	4	48	47	1	0
L+1	3	47	48	1	1
L+2	54	13	13	10	10
L+3	2	48	48	1	1
L+5	43	25	26	3	3
L+6	21	24	25	15	15
L+7	8	43	43	3	3
L+8	57	2	2	20	19

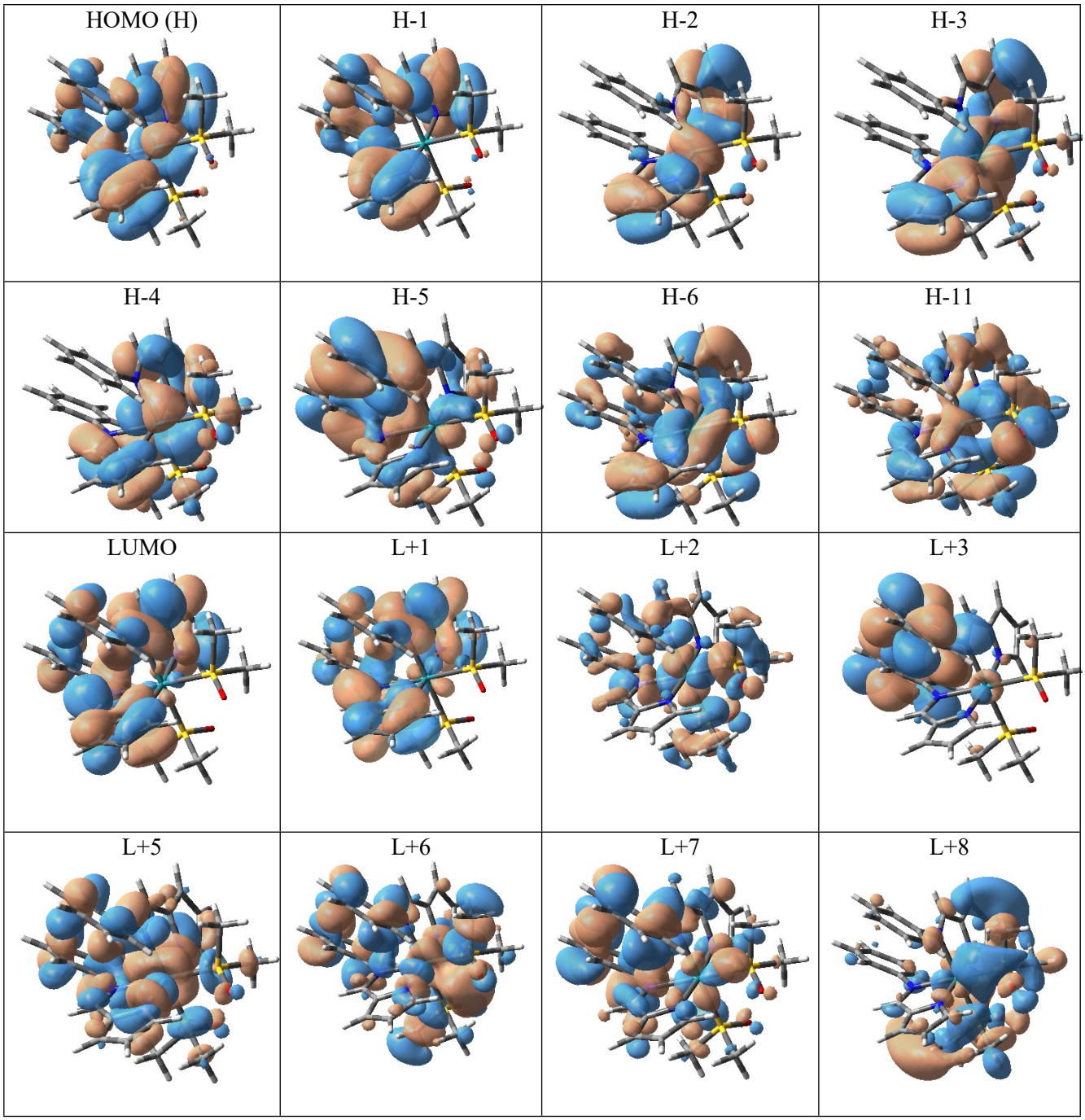


Fig. S10. Contour plots of the molecular orbitals of $[Ru(L\text{-}H)_2(dmso)_2]$, which are associated with the electronic spectral transitions (See **Table S9**).

Table S11. Computed parameters from TDDFT calculations on $[Ru(L\text{-}Cl)_2(dmso)_2]$ for electronic spectral properties in dichloromethane solution.

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
10	H-3 → L	0.31217	3.5191	0.0812	352.32	MLCT/LLCT	368
	H-2 → L+1	0.47843				MLCT/LLCT	
	H-1 → L	0.29867				LMCT	
	H → L+1	0.25777				MLCT/LLCT	
21	H-5 → L	0.16977	4.3393	0.0783	285.72	MLCT/LLCT	301
	H-5 → L+2	0.10364				LMCT/LLCT	
	H-4 → L	0.44230				MLCT/LLCT	
	H-4 → L+2	0.37961				MLCT/LLCT	
	H → L+2	0.21509				LMCT/LLCT	
	H → L+4	0.20806				MLCT	
48	H-11 → L	0.35133	5.1433	0.0145	241.06	LLCT/MLCT	224
	H-8 → L+2	0.17869				LMCT/ILCT	
	H-5 → L+2	0.10853				LMCT/LLCT	
	H-3 → L+5	0.18709				MLCT/LLCT	
	H-3 → L+6	0.30032				MLCT/ LLCT	
	H-2 → L+2	0.10998				LLCT /LMCT/ILCT	
	H-2 → L+7	0.36800				MLCT/LLCT	
	H-2 → L+8	0.13372				LLCT/LMCT/ILCT	

Table S12. Compositions of selected molecular orbitals of $[Ru(L\text{-}Cl)_2(dmso)_2]$ associated with the electronic spectral transitions.

% Contribution of fragments to	Fragments				
	Ru	L-OCH_3 (1)	L-OCH_3 (2)	DMSO (1)	DMSO (2)
HOMO (H)	17	41	40	1	1
H-1	0	49	49	1	1
H-2	45	26	27	1	1
H-3	52	23	23	1	1
H-4	60	16	16	4	4
H-5	11	43	44	1	1
H-8	28	20	20	16	16
H-11	18	17	17	24	24
LUMO (L)	4	48	48	0	0
L+1	3	48	48	1	0
L+2	52	14	14	10	10
L+4	2	48	48	1	1
L+5	35	30	30	3	2
L+6	29	26	26	10	10
L+7	8	43	43	3	3
L+8	50	12	12	13	13

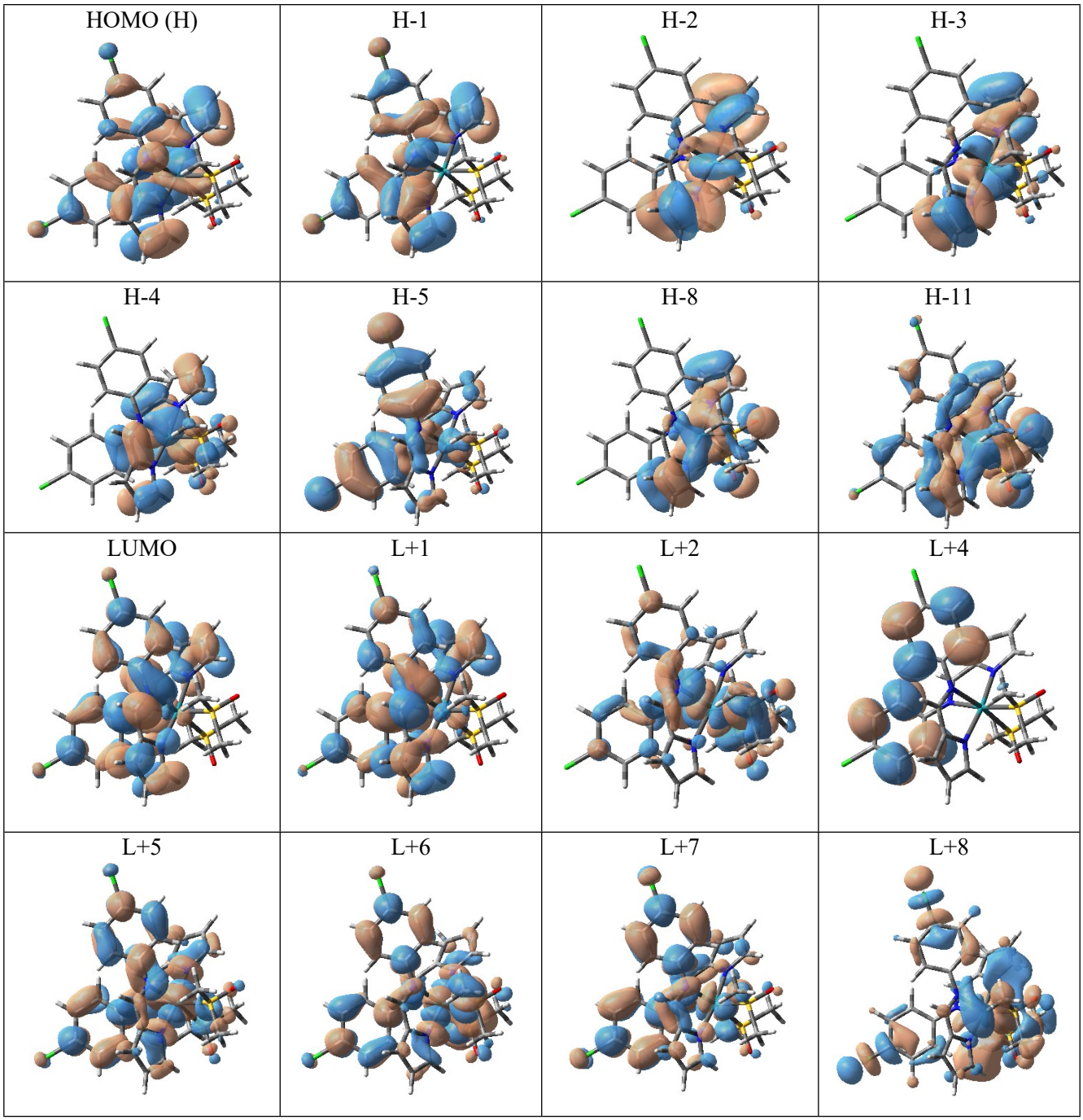


Fig. S11. Contour plots of the molecular orbitals of $[Ru(L\text{-}Cl)_2(dmso)_2]$, which are associated with the electronic spectral transitions (See **Table S11**).

Table S13. Computed parameters from TDDFT calculations on [Ru(L-OCH_3)$_2$(bpy)] for electronic spectral properties in dichloromethane solution.

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
3	H-3 → L H-2 → L	0.39991 0.55631	2.3083	0.0758	537.11	MLCT/LLCT MLCT/LLCT	585
14	H-3 → L+3 H-3 → L+4 H-2 → L+3 H-1 → L+2 H → L+2	0.43733 0.14873 0.27789 0.40105 0.11966	3.1573	0.1032	392.70	MLCT/ LLCT MLCT/LLCT MLCT/LLCT LLCT/LMCT MLCT/LLCT	428
27	H-8 → L	0.69257	3.7463	0.0036	330.95	LLCT/MLCT	336
52	H-7 → L+2 H-6 → L+1 H-6 → L+2 H-5 → L+3 H-5 → L+4 H-3 → L+8 H-2 → L+8	0.10258 0.34118 0.23555 0.31180 0.15936 0.28652 0.27896	4.5465	0.0358	272.70	LLCT/ MLCT LLCT/LMCT LLCT/LMCT ILCT/LMCT ILCT/LMCT MLCT/ILCT MLCT/LLCT	266
155	H-10 → L+6 H-5 → L+10 H-1 → L+16	0.13321 0.12661 0.62420	6.4047	0.0771	193.58	LMCT/LLCT LMCT/LLCT LLCT/LMCT	234

Table S14. Compositions of selected molecular orbitals of [Ru(L-OCH_3)$_2$(bpy)] associated with the electronic spectral transitions.

% Contribution of fragments to	Fragments			
	Ru	L-OCH_3 (1)	L-OCH_3 (2)	bpy
HOMO (H)	37	30	30	3
H-1	1	50	49	0
H-2	55	21	21	3
H-3	54	17	17	12
H-5	3	49	48	0
H-6	1	49	50	0
H-7	23	35	35	7
H-8	23	36	36	5
H-10	0	50	50	0
LUMO (L)	7	1	1	91
L+1	4	1	1	94
L+2	3	0	0	97
L+3	4	48	48	0
L+4	4	48	47	1
L+6	7	46	46	1
L+8	46	20	19	15
L+10	73	13	13	1
L+16	2	35	35	28

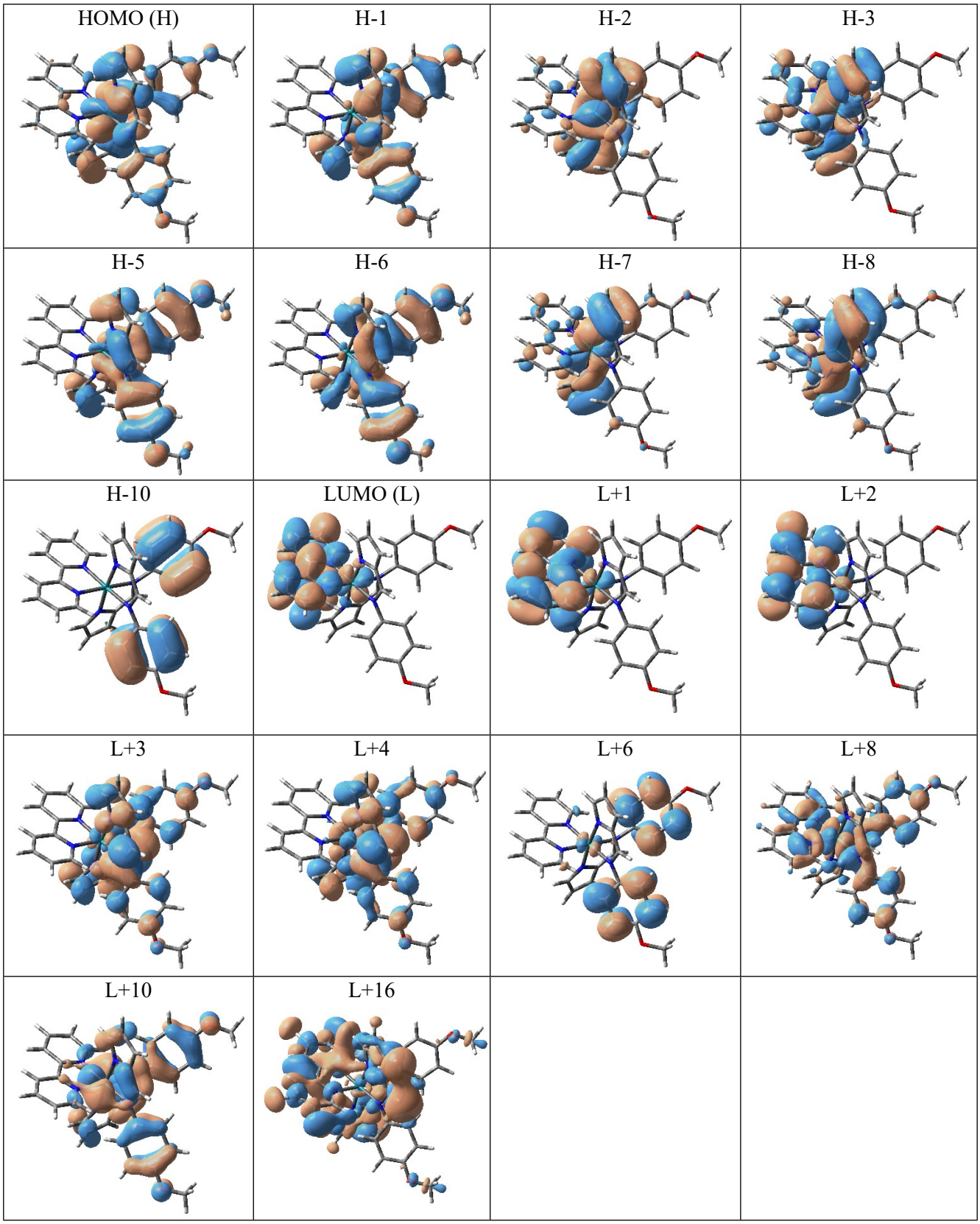


Fig. S12. Contour plots of the molecular orbitals of [Ru(L-OCH_3)$_2$(bpy)] which are associated with the electronic spectral transitions (See **Table S13**).

Table S15. Computed parameters from TDDFT calculations on [Ru(L-OCH_3)$_2$(phen)] for electronic spectral properties in dichloromethane solution.

Excited State	Composition	CI value	*E* (eV)	Oscillator strength (*f*)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
7	H-3 → L H-2 → L H-1 → L+1 H → L+1	0.46170 0.41324 0.28254 0.13857	2.4477	0.1421	506.54	MLCT/LLCT MLCT/LLCT LLCT/LMCT LLCT/MLCT	563
16	H-3 → L+2 H-2 → L+2 H-2 → L+4 H-1 → L+3 H → L+3	0.37172 0.18283 0.10159 0.50468 0.17454	3.2560	0.0082	380.79	MLCT/ LLCT MLCT/LLCT MLCT/LLCT LLCT/LMCT MLCT	405
30	H-8 → L H-6 → L+1	0.62869 0.29257	3.7849	0.0025	327.58	LLCT/MLCT LLCT/LMCT	334
70	H-12 → L H-12 → L+4 H-11 → L+1 H-9 → L+1 H-8 → L+4 H-7 → L+1	0.54547 0.12438 0.26289 0.14407 0.17899 0.12295	4.8252	0.6994	256.95	ILCT LLCT/LMCT LMCT/LLCT LLCT /LMCT MLCT/LLCT LLCT/MLCT	266
157	H-10 → L+6 H-9 → L+5	0.31295 0.59951	6.2786	0.1044	197.47	ILCT LLCT/LMCT	231

Table S16. Compositions of selected molecular orbitals of [Ru(L-OCH_3)$_2$(phen)] associated with the electronic spectral transitions.

% Contribution of fragments to	Fragments			
	Ru	L-OCH_3 (1)	L-OCH_3 (2)	phen
HOMO (H)	36	31	31	2
H-1	1	49	49	1
H-2	55	21	21	3
H-3	55	17	17	11
H-6	1	50	49	0
H-7	21	35	35	9
H-8	23	36	36	5
H-9	0	50	49	1
H-10	0	50	50	0
H-11	4	4	3	89
H-12	1	1	0	98
LUMO (L)	2	0	0	98
L+1	8	1	1	90
L+2	3	10	10	77
L+3	5	38	38	19
L+4	4	47	48	1
L+5	1	1	0	98
L+6	1	49	49	1

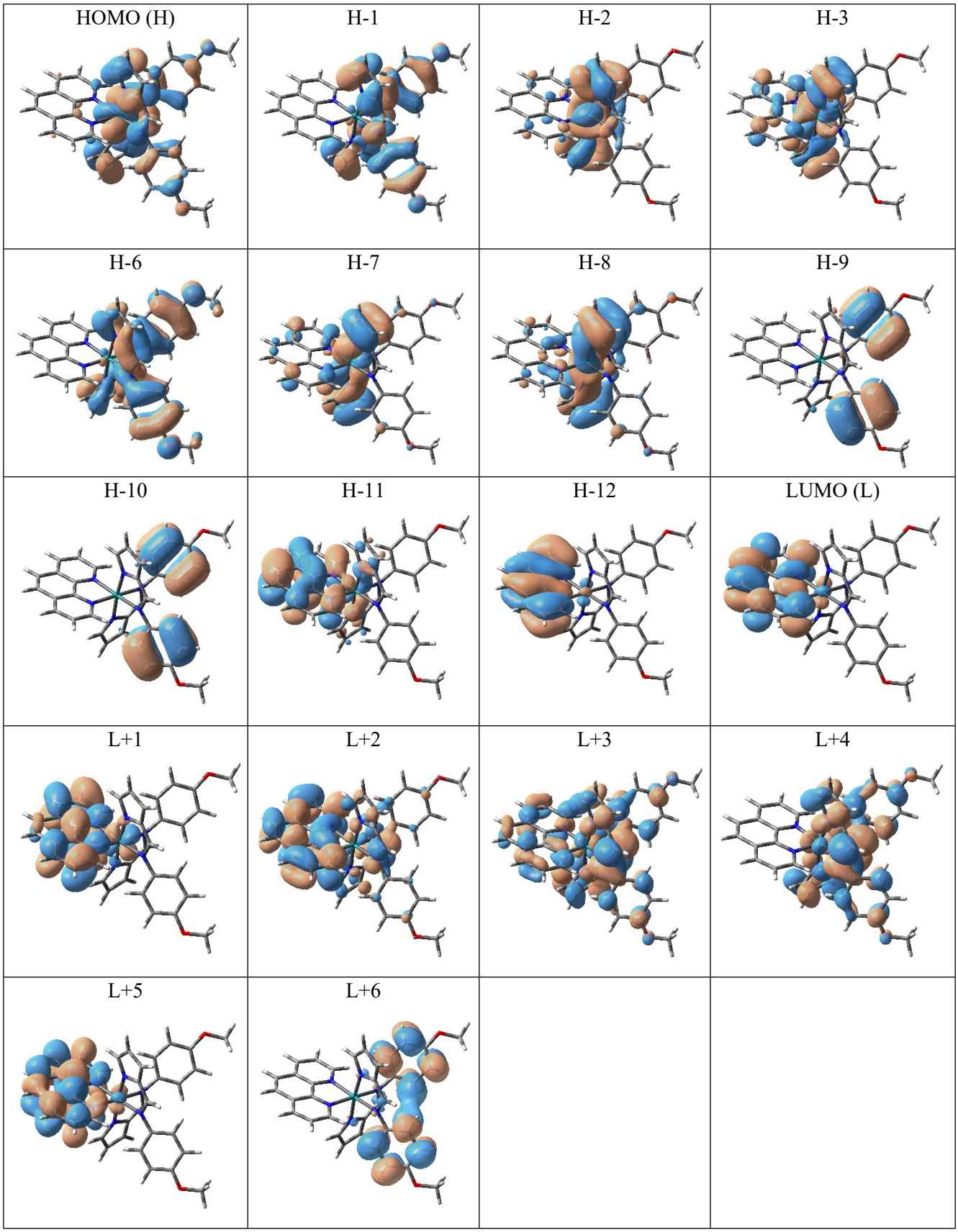


Fig. S13. Contour plots of the molecular orbitals of [Ru(L-OCH_3)$_2$(phen)] which are associated with the electronic spectral transitions (See **Table S15**).

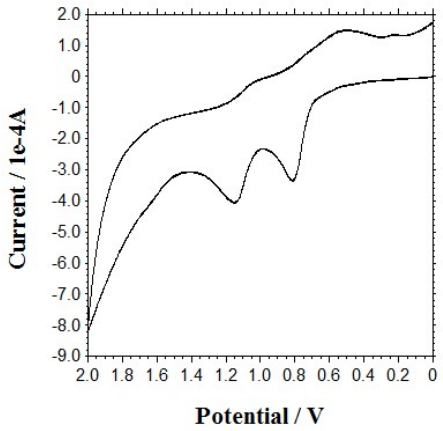


Fig. S14. Cyclic voltammogram of $[Ru(L\text{-}CH_3)_2(dmso)_2]$ in acetonitrile solution (0.1 M TBHP) at a scan rate of 100 mVs^{-1}.

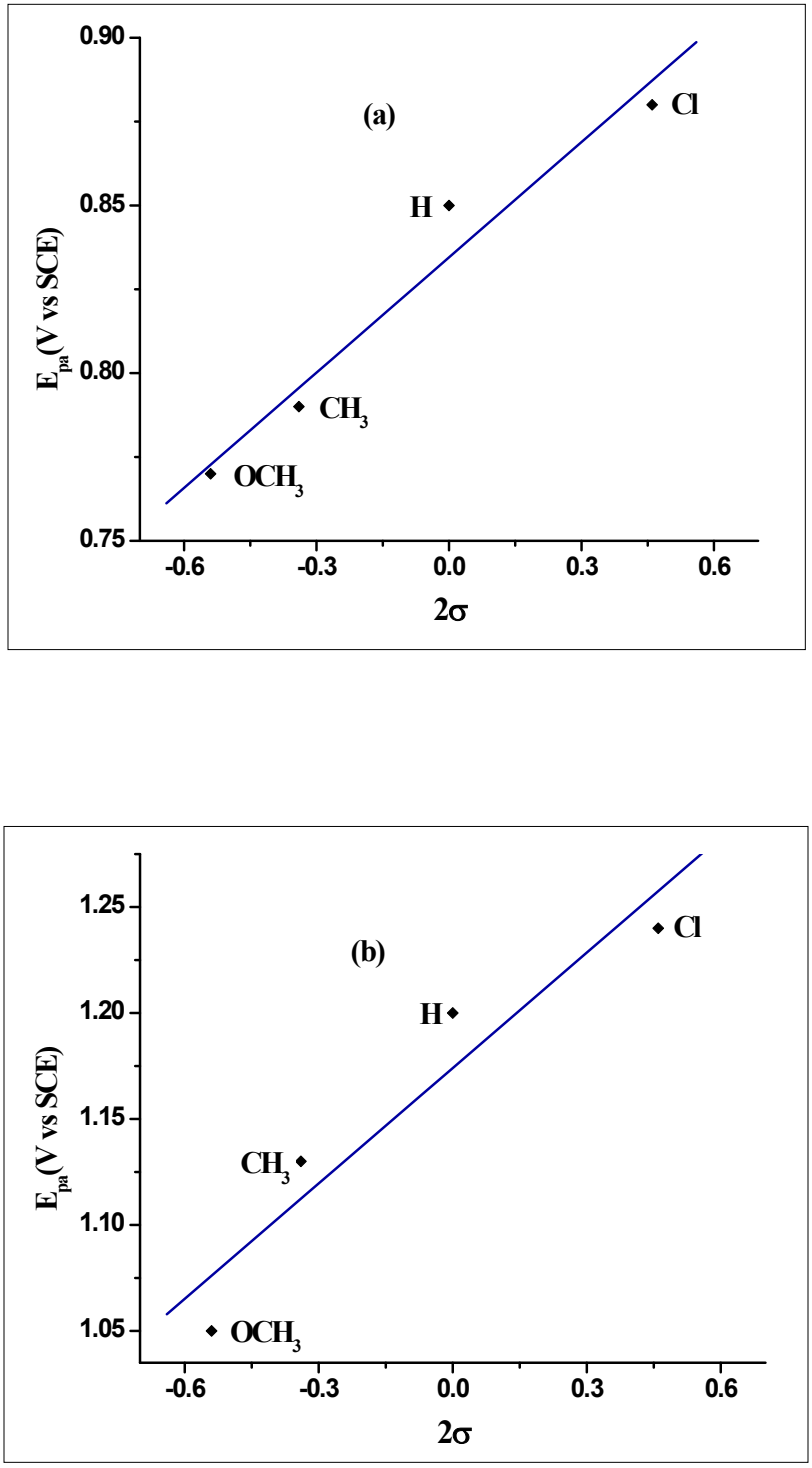


Fig. S15. Least squares plot of E_{pa} values of (a) Ru(II)-Ru(III) oxidation vs 2σ and (b) Ru(III)-Ru(IV) oxidation vs 2σ.

Table S17. Crystallographic data for $[Ru(L\text{-}OCH_3)_2(dmso)_2]$ and $[Ru(L\text{-}CH_3)_2(dmso)_2]$.

complex	$[Ru(L\text{-}OCH_3)_2(dmso)_2]$	$[Ru(L\text{-}CH_3)_2(dmso)_2]$
empirical formula	$C_{28}H_{34}N_4O_4RuS_2$	$C_{28}H_{34}N_4O_2RuS_2$
formula weight	655.78	623.78
crystal system	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	11.261(6)	9.9413(11)
b (Å)	14.816(8)	21.144(2)
c (Å)	17.804(9)	13.6997(14)
α (◦)	90	90
β (◦)	105.319(15)	101.252(3)
γ (◦)	90	90
V (Å^3)	2865(3)	2824.3(5)
Z	4	4
D_{calcd} /g cm^{-3}	1.520	1.467
F (000)	1352	1288
crystal size (mm)	0.28 × 0.32 × 0.36	0.24 × 0.38 × 0.42
T (K)	293	273
μ (mm^{-1})	0.734	0.735
R1[a]	0.0501	0.0298
wR2[b]	0.1453	0.0829
GOF[c]	1.148	1.084

[a] $R1 = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o|$.

[b] $wR2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)\}]^{1/2}$.

[c] $GOF = [\Sigma(w(F_o^2-F_c^2)^2)/(M-N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

Table S18. Crystallographic data for $[Ru(L\text{-}H)_2(dmso)_2]$ and $[Ru(L\text{-}Cl)_2(dmso)_2]$.

complex	$[Ru(L\text{-}H)_2(dmso)_2]$	$[Ru(L\text{-}Cl)_2(dmso)_2]$
empirical formula	$C_{26}H_{30}N_4O_2RuS_2$	$C_{26}H_{28}Cl_2N_4O_2RuS_2$
formula weight	595.73	664.63
crystal system	Monoclinic	Monoclinic
space group	C2/c	C2
a (Å)	14.9301(12)	16.0714(13)
b (Å)	12.2534(10)	10.2764(8)
c (Å)	14.5416(12)	8.3434(7)
α (◦)	90	90
β (◦)	97.136(2)	95.284(2)
γ (◦)	90	90
V (Å^3)	2639.7(4)	1372.11(19)
Z	4	2
D_{calcd} /mg m^{-3}	1.499	1.609
F (000)	1224	676
crystal size (mm)	0.11 × 0.22 × 0.31	0.20 × 0.24 × 0.32
T (K)	273	273
μ (mm^{-1})	0.783	0.950
R1[a]	0.0355	0.0137
wR2[b]	0.0932	0.0362
GOF[c]	1.105	1.029

[a] $R1 = \Sigma \, || F_o | - | F_c || / \Sigma \, | F_o |$.

[b] $wR2 = [\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)\}]^{1/2}$.

[c] $GOF = [\Sigma(w(F_o^2-F_c^2)^2)/(M-N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

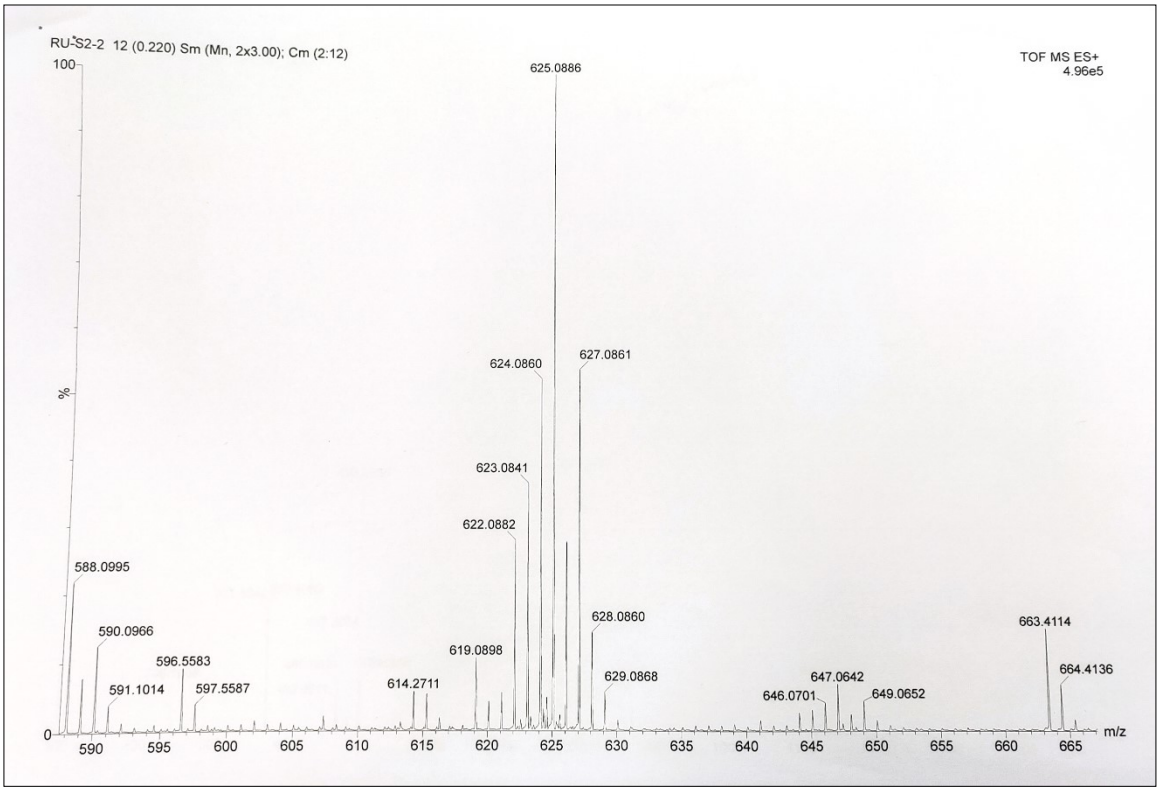


Fig. S16. Mass spectrum of $[Ru(L\text{-}CH_3)_2(dmso)_2]$.