Near Infra-Red emitting Ru(II) complexes of tridentate ligands: electrochemical and photophysical consequences of strong donor ligand with large bite angles

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Electronic Supporting Information

Materials and Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded in CD_3CN at room temperatutre (r.t.) on Bruker AV400 (400 MHz) and Bruker AV700 (700 MHz) spectrometers for ^1H NMR and at 100 and 175 MHz for ^{13}C NMR respectively, as mentioned in the experimental. Chemical shifts are reported in part per million (ppm) relative to residual solvent protons (1.94 ppm for CD_3CN, 7.26 ppm for $CDCl_3$) and the carbon resonance (118.69 ppm for CD_3CN, 77.00 ppm for $CDCl_3$) of the solvent.

Absorption spectra were measured in deaerated acetonitrile at r.t. on a Cary 500i UV-Vis-NIR Spectrophotometer. Corrected fluorescence emission spectra (450 W Xe lamp) in the IR range were obtained with a modular UV-VIS-NIR spectrofluorimeter Edinburgh Instrument, equipped with an Edinburgh Instruments Ge detector (for the 800–1600 nm spectral range). Corrections for instrumental response, inner filter effects and phototube sensitivity were performed. The luminescence quantum yield of **1** and **2** were calculated[1] by optical dilution method recording the emission spectra of the degassed solution in acetonitrile and of a solution of cyanine IR-125 in dimethylsulfoxide (Φ = 0.23)[2] as the reference. Luminescence lifetimes were determined by time-correlated single-photon-counting (TCSPC) with an Edinburgh EPL-405 spectrometer (light pulse: picosecond pulse diode laser, pulse width 500 ps at 405 nm). Due to poor spectrometer response and weak signal to noise ratio at 77 K the excited-state lifetime measurements of complexes **1**-**4** were not possible.

Electrochemical measurements were carried out in argon-purged purified acetonitrile at room temperature with a BAS CV50W multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon electrode. The counter electrode was a Pt wire, and the pseudo-

reference electrode was a silver wire. The reference was set using an internal 1 mM ferrocene/ferrocinium sample at 395 mV *vs.* SCE in acetonitrile. The concentration of the compounds was about 1 mM. Tetrabutylammonium hexafluorophosphate (TBAP) was used as supporting electrolyte and its concentration was 0.10 M. Cyclic voltammograms were obtained at scan rates of 100 mV/s. The criteria for reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. Experimental uncertainties are as follows: absorption maxima, ±2 nm; molar absorption coefficient, 10%; redox potentials, ± 10 mV.

Hydrated ruthenium trichloride, 1,3,4,6,7,8-Hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, 2-bromopyridine, 2,6-dibromopyridine and potassium hexafluorophosphate were purchased from Aldrich Chemicals. The ligands Ph-tpy, Tolyl-tpy and the complexes [Ru(Ph-tpy)Cl_3], [Ru(*p*-Tolyl-tpy)Cl_3], [Ru(Br-Ph-trz)Cl_3], [Ru(^{t}Bu-Ph-trz)Cl_3] starting materials were synthesized following similar literature procedures.[3,4a]

2,4-dipyrid-2′-yl-6-(p-tert-butyl)-1,3,5-triazine (**L2**)

The ligand 2,4-dipyrid-2′-yl-6-(*p-tert*-butyl)-1,3,5-triazine was synthesized using a modified literature procedure.[4b,c] To a stirred solution of $HNMe_2$ (2 M in THF, 8.37 mL, 16.59 mmol) in anhydrous Et_2O (150 mL) was added *n*-BuLi (1.6 M in hexanes, 10.41 mL, 16.59 mmol), dropwise, under an inert atmosphere. The mixture was stirred for 30 min until a white suspension formed and *p-tert*-butylbenzonitrile (2.4 g, 15.08 mmol) was added. Stirring was continued for 1 h at room temperature followed by the addition of 2-cyanopyridine (3.14 g, 30.16 mmol). Stirring was continued for 16 h after which time the reaction was diluted with a 5 : 1 mixture of

water–EtOH (250 mL : 50 mL, v/v) and the solution was heated to remove the Et_2O. The white precipitate thus formed was collected by filtration and washed with EtOH (10 mL) and Et_2O (2x25 mL) and dried under vacuum to afford **L2** as a white powder. The compound was crystallized from EtOH-H_2O. Yield = 3.6 g (65%). ^{1}H NMR (DMSO-d_6, 400 MHz); 1.37 (s, 9H), 7.64-7.76 (m, 4H), 8.13 (td, J^{td} = 8.0, 2.0 Hz, 2H), 8.65 (d, J^d = 8.0 Hz, 2H), 8.74 (d, J^d = 8.0 Hz, 2H), 8.91 (d, J^d = 4.0 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz); 171.7, 171.1, 156.3, 152.9, 150.1, 137.4, 132.4, 128.7, 126.7, 125.8, 124.7, 34.8, 30.8. HRMS (ESI), m/z: 184.59777 $[M+2H^+]^{2+}$ ($C_{23}H_{23}N_5$ requires 184.59712), 368.18809 $[M+H^+]^+$ ($C_{23}H_{22}N_5$ requires 368.18697), 390.16982 $[M+Na^+]^+$ ($C_{23}H_{21}N_5Na$ requires 390.16892). Anal. Calc for $C_{23}H_{21}N_5$: C, 75.18; H, 5.76; N, 19.06. Found: C, 74.96; H, 5.81; N, 18.94.

*[Ru(p-Tolyl-tpy)(**L1**)](PF$_6$)$_2$* (**2**)

A mixture of [Ru(*p*-Tolyl-tpy)Cl_3] (100 mg, 0.188 mmol) and 4-ethylmorpholine (10 drops) in nitrogen-degassed *n*-butanol (60 mL) was heated at 80 °C for half an hour to give a dark brown-red suspension. After cooling the mixture to ambient temperature, **L1** (70 mg, 0.197 mmol) was added to the suspension and the resulting mixture was refluxed for 16 h under a nitrogen atmosphere. After 16 h, the dark purple mixture was cooled to ambient temperature and was evaporated to dryness. The resulting solid was purified by chromatography on silica using a mixture of 7/1 (v/v) acetonitrile/saturated aq. KNO_3 to afford the pure complex **2** as a purple solid. The nitrate salt was metathesized to the PF_6 salt by addition of saturated aqueous KPF_6 solution to the aquous solution of the compound. Crystals suitable for X-ray crystallography were grown by diffusion of diethyl ether into a moderately concentrated solution of the complex in acetone. Yield = 120 mg (60%). ^{1}H NMR (CD_3CN, 700 MHz); 8.67 (s, 2H) 8.54 (d, J^d = 8.0 Hz, 2H), 8.14 (t, J^t = 8.0 Hz, 1H), 8.04 (d, J^d = 6.0 Hz, 2H), 7.98 (m, 4H), 7.46 (m, 6H), 4.03 (m,

2H), 3.19 (m, 2H), 3.04 (m, 4H), 2.76 (m, 3H), 2.46 (s, 3H), 2.31 (m, 2H), 2.09 (m, 2H), 1.67 (m, 2H), 1.44 (m, 2H), 1.19 (m, 3H), 0.84 (m, 2H). ^{13}C NMR (CD_3CN, 175 MHz); 159.8, 158.7, 155.9, 154.1, 153.8, 143.7, 140.9, 140.8, 137.1, 135.3, 130.9, 128.0, 126.8, 123.9, 120.5, 112.8, 49.6, 48.8, 48.4, 43.8, 23.3, 23.1, 21.2. HRMS (ESI), m/z: 923.24348 $[M\text{-}PF_6]^+$ ($C_{41}H_{44}N_{10}RuPF_6$ requires 923.24302), 389.14029 $[M\text{-}2PF_6]^{2+}$ ($C_{41}H_{44}N_{10}Ru$ requires 389.13915). Anal. Calc for $C_{41}H_{44}N_{10}RuP_2F_{12}$: C, 46.11; H, 4.15; N, 13.12. Found: C, 46.13; H, 4.11; N, 13.01.

*[Ru(Br-Ph-dpt)(**L1**)](PF$_6$)$_2$* (**3**)

A mixture of Ru(Br-Ph-dpt)Cl_3 (100 mg, 0.167 mmol) and 4-ethylmorpholine (10 drops) in nitrogen-degassed *n*-butanol (60 mL) was heated at 80 °C for half an hour to give a dark brown-red suspension. After cooling of the mixture to ambient temperature, **L1** (62 mg, 0.175 mmol) was added to the suspension and the resulting mixture was refluxed for 16 h under a nitrogen atmosphere. After 14 h, the dark purple mixture was cooled to ambient temperature and was evaporated to dryness. The resulting solid was purified by chromatography on silica using a mixture of 7/1 (v/v) acetonitrile/saturated aq. KNO_3 to afford the pure complex **3** as a purple solid. The nitrate salt was metathesized to the PF_6 salt by addition of saturated aqueous KPF_6 solution to the aqueous solution of the compound. Crystals suitable for X-ray crystallography were grown by diffusion of diethyl ether into a moderately concentrated solution of the complex in acetone. Yield = 90 mg (47%). ^{1}H NMR (CD_3CN, 700 MHz); 9.04 (d, J^d = 7.0 Hz, 2H), 8.49 (d, J^d = 8.0 Hz, 2H), 8.23 (m, 3H), 8.20 (t, J^t = 7.0 Hz, 2H), 7.89 (d, J^d = 8.0 Hz, 2H), 7.73 (t, J^t = 7.0 Hz, 2H), 7.58 (d, J^d = 8.0 Hz, 2H), 4.12 (d, J^d = 14.0 Hz, 2H), 3.22 (m, 2H), 3.08 (t, J^t = 13.0 Hz, 2H), 3.01 (m, 2H), 2.73 (m, 4H), 2.34 (m, 2H), 2.12 (m, 2H), 1.47 (m, 2H), 1.18 (m, 4H), 0.78 (m, 2H). ^{13}C NMR (CD_3CN, 175 MHz); 172.9, 162.3, 155.6, 155.4, 155.3, 154.3,

141.7, 137.9, 135.8, 133.4, 131.2, 129.9, 127.9, 127.6, 113.0, 49.4, 48.9, 48.2, 44.0, 23.2, 23.1. HRMS (ESI), m/z: 989.12744 $[M\text{-}PF_6]^+$ ($C_{38}H_{39}N_{12}BrRuPF_6$ requires 989.12838), 422.08339 $[M\text{-}2PF_6]^{2+}$ ($C_{38}H_{39}N_{12}BrRu$ requires 422.08183). Anal. Calc for $C_{38}H_{39}N_{12}BrRuP_2F_{12}$: C, 40.22; H, 3.46; N, 14.81. Found: C, 40.08; H, 3.45; N, 14.54.

*[Ru(^{t}Bu-Ph-dpt)(**L1**)](PF$_6$)$_2$* (**4**)

A mixture of Ru(^{t}Bu-Ph-dpt)Cl_3 (100 mg, 0.174 mmol) and 4-ethylmorpholine (10 drops) in nitrogen-degassed *n*-butanol (60 mL) was heated at 80 °C for half an hour to give a dark brown-red suspension. After cooling of the mixture to ambient temperature, **L1** (65 mg, 084 mmol) was added to the suspension and the resulting mixture was refluxed for 16 h under a nitrogen atmosphere. After 16 h, the dark purple mixture was cooled to ambient temperature and was evaporated to dryness. The resulting solid was purified by chromatography on silica using a mixture of 7/1 (v/v) acetonitrile/saturated aq. KNO_3 to afford the pure complex **4** as a purple solid. The nitrate salt was metathesized to the PF_6 salt by addition of saturated aqueous KPF_6 solution to the aquous solution of the compound. Crystals suitable for X-ray crystallography were grown by diffusion of diethyl ether into a moderately concentrated solution of the complex in acetone. Yield = 110 mg (60%). ^{1}H NMR (CD_3CN, 700 MHz); 9.02 (d, J^d = 8.0 Hz, 2H), 8.85 (d, J^d = 8.0 Hz, 2H), 8.22 (t, J^t = 8.0 Hz, 1H), 8.17 (m, 4H), 7.77 (d, J^d = 8.0 Hz, 2H), 7.72 (t, J^t = 6.0 Hz, 2H), 7.56 (d, J^d = 8.0 Hz, 2H), 4.11 (d, J^d = 16.0 Hz, 2H) 3.13-2.76 (m, 8H), 2.34 (m, 2H), 2.12 (m, 2H), 1.50 (m, 2H), 1.44 (s, 9H), 1.21 (m, 6H), 0.81 (m, 2H). ^{13}C NMR (CD_3CN, 175 MHz); 172.9, 163.8, 157.8, 155.8, 155.6, 155.5, 154.3, 141.6, 137.8, 133.8, 129.8, 129.6, 127.5, 127.2, 118.2, 113.0, 49.5, 48.9, 48.30, 44.0, 35.8, 31.2, 23.2, 23.1. HRMS (ESI), m/z: 967.27643 $[M\text{-}PF_6]^+$ ($C_{42}H_{48}N_{12}Ru\ PF_6$ requires 967.28047), 411.15951 $[M\text{-}2PF_6]^{2+}$

($C_{42}H_{48}N_{12}Ru$ requires 411.15787). Anal. Calc for $C_{42}H_{48}N_{12}Ru_1P_2F_{12}$: C, 45.37; H, 4.35; N, 15.12. Found: C, 45.38; H, 4.38; N, 15.04.

Crystallographic Section

Diffraction data were collected on a Bruker SMART 6000 with Montel 200 monochromator, equipped with a rotating anode source for Cu Kα radiation. The diffraction quality of the crystals were checked, revealing in some cases poor diffraction with a large amount of diffuse scattering, signaling extensive crystal disorder. Cell refinement and data reduction were done using APEX2.[5] Absorption corrections were applied using SADABS.[6] Structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL97.[7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropic on calculated positions using a riding model. For complexes **1** and **4**, during the refinement of the structure, electron density peaks were located and were believed to be six severely disordered solvated acetone molecules, and a total of one disordered water and eight disordered acetone molecules, respectively (by counting the number of electrons suppressed). All the attempts made to model the solvent molecules were not successful and they were removed using the SQUEEZE routine from PLATON,[8] which resulted in a significant improvement of R1 factor by ~3.5% in all the squeezed structures. For compound **1**, the highest difference peak is located 1.09 Å from atom F4 and the deepest hole is 0.51 Å from atom F1A. In addition, three peaks of density ~2 to 1 e/Å^3 were present essentially due to the quality of the crystal employed, which was the best available, and is believed due to the frequent discrete positional disorder of the freely rotating anions (see .cif file for more details). The structure of **2** and **4** also showed that the guanidine moiety is positionally disordered over two positions. The disorder was modelled as two components [~0.58:0.42 for **2** and ~0.60:0.40 for **4**] and refined anisotropically. In complexes **1**

and **4** positional disorders in anion or solvent molecules were observed, and they were resolved in the aforesaid way. Some atomic displacement restraints were applied among the disorder components to model the anion positions in **1** but not applicable for the cation structure.

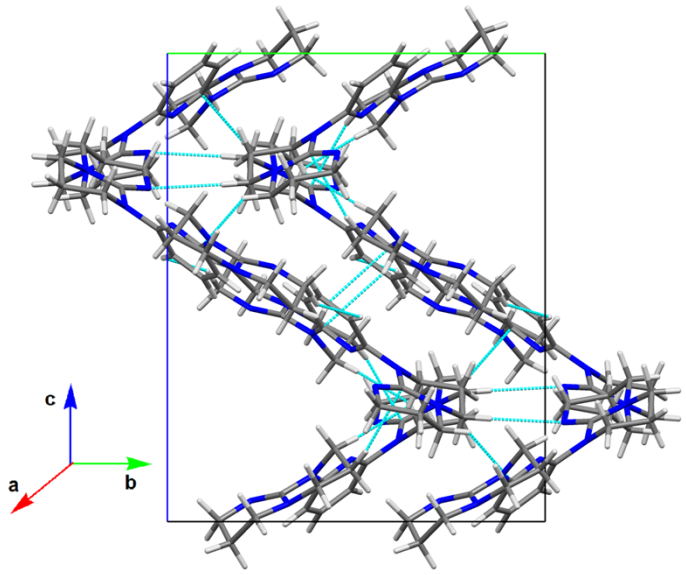


Figure S1. Packing diagram of ligand **L1** along crystallographic *a*-axis. Colour code: carbon: grey, nitrogen: slate blue; C-H and N-H intermolecular interactions: cyan dashed.

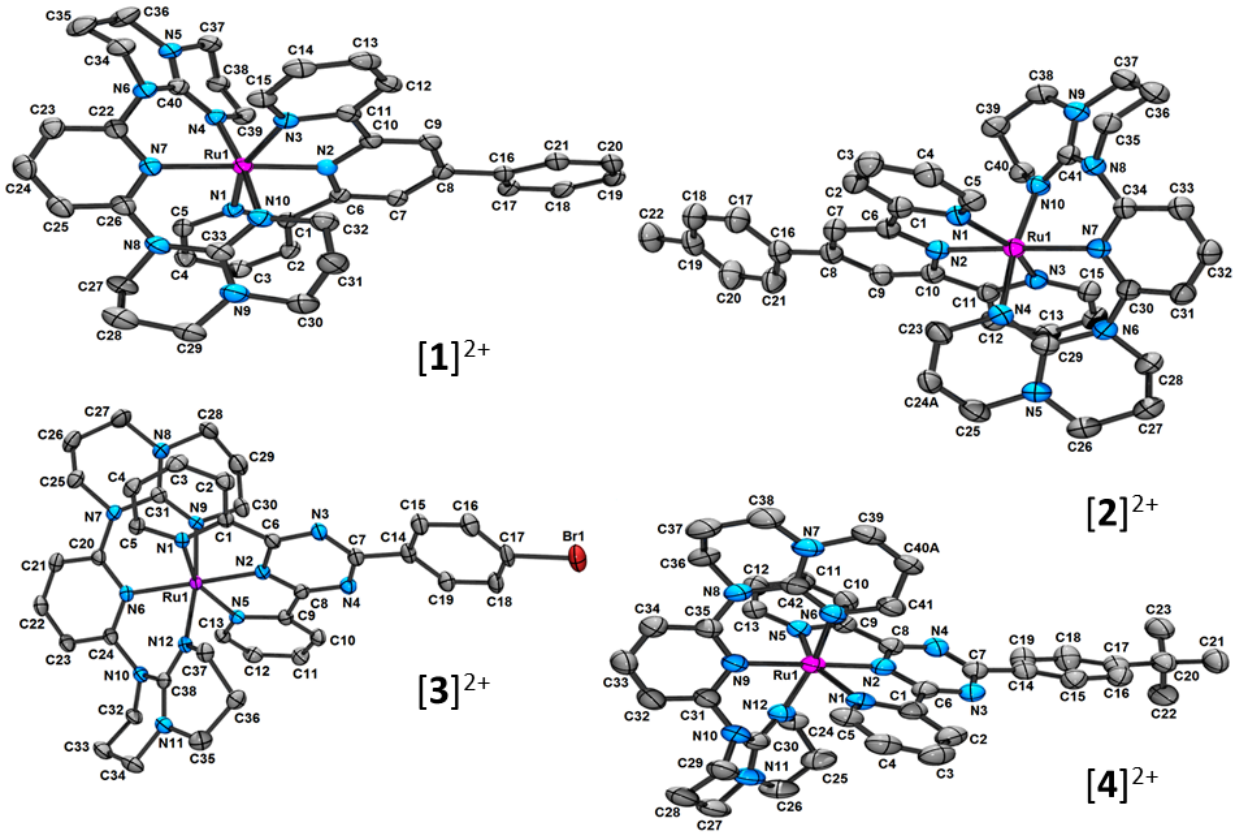


Figure S2. Perspective views of complexes **1**−**4**, as cations only, with complete labeling. Ellipsoids correspond to a 50% probability level. Hydrogen atoms, anions, solvent molecules and disordered components of **2** and **4** are omitted for clarity.

Table S1. Comparison of bond distances and angles in **1–4** from X-ray and DFT studies

Compound	Bond Length			Angle		
1		Obs. (X-ray)	Calc. (DFT)		Obs. (X-ray)	Calc. (DFT)
	N1-Ru1	2.0646 (0.0024)	2.12887	N1-Ru1-N3	159.28 (0.10)	157.256
	N2-Ru1	1.9462 (0.0024)	1.98758	N4-Ru1-N10	173.83 (0.10)	172.513
	N3-Ru1	2.0761 (0.0025)	2.12874			
	N4-Ru1	2.0711 (0.0025)	2.13996			
	N7-Ru1	2.0720 (0.0025)	2.11279			
	N10-Ru1	2.0919 (0.0026)	2.13997			
	N4-C40	1.3050 (0.0039)	1.31063			
	N5-C40	1.3498 (0.0043)	1.36487			
	N6-C40	1.4072 (0.0040)	1.40913			
	N10-C33	1.3102 (0.0043)	1.31062			
	N9-C33	1.3430 (0.0045)	1.36485			
	N8-C33	1.3998 (0.0043)	1.40917			
2	N1-Ru1	2.0859 (0.0019)	2.12784	N1-Ru1-N3	158.89 (0.08)	157.238
	N2-Ru1	1.9307 (0.0018)	1.98638	N4-Ru1-N10	172.68 (0.07)	171.592
	N3-Ru1	2.0722 (0.0019)	2.12795			
	N4-Ru1	2.0947 (0.0019)	2.13422			
	N7-Ru1	2.0707 (0.0018)	2.11501			
	N10-Ru1	2.0639 (0.0018)	2.13415			
	N4-C29	1.3080 (0.0030)	1.31024			
	N5-C29	1.3502 (0.0030)	1.36492			
	N6-C29	1.3842 (0.0030)	1.40789			
	N10-C41	1.3042 (0.0029)	1.31024			
	N9-C41	1.3434 (0.0029)	1.36494			

	N8-C41	1.4044 (0.0028)	1.40794			
3	N1-Ru1	2.0789 (0.0029)	2.10617	N1-Ru1-N5	157.19 (0.15)	157.189
	N2-Ru1	1.9247 (0.0028)	1.91497	N9-Ru1-N12	171.51 (0.13)	171.637
	N5-Ru1	2.0876 (0.0027)	2.07686			
	N6-Ru1	2.0688 (0.0028)	2.06985			
	N9-Ru1	2.0874 (0.0029)	2.09241			
	N12-Ru1	2.0628 (0.0029)	2.06290			
	N9-C31	1.3082 (0.0058)	1.31015			
	N8-C31	1.3563 (0.0060)	1.34625			
	N7-C31	1.3778 (0.0059)	1.38473			
	N12-C38	1.3040 (0.0054)	1.30261			
	N11-C38	1.3433 (0.0055)	1.34104			
	N10-C38	1.4041 (0.0052)	1.40823			
4	N1-Ru1	2.0897 (0.0020)	2.15308	N1-Ru1-N5	156.29 (0.09)	154.942
	N2-Ru1	1.9297 (0.0022)	1.97508	N6-Ru1-N12	171.02 (0.08)	171.488
	N5-Ru1	2.1074 (0.0020)	2.15333			
	N6-Ru1	2.0784 (0.0020)	2.13339			
	N9-Ru1	2.0857 (0.0021)	2.11261			
	N12-Ru1	2.0888 (0.0020)	2.13352			
	N12-C30	1.3075 (0.0032)	1.31100			
	N11-C30	1.3396 (0.0031)	1.36403			
	N10-C30	1.3945 (0.0032)	1.40833			
	N6-C42	1.2966 (0.0032)	1.31096			
	N7-C42	1.3481 (0.0032)	1.36409			
	N8-C42	1.3988 (0.0032)	1.40847			

Table S2. Spectroscopic and photophysical data in CH_3CN solutions for Ligands **L1**, **L2** and complexes **1**−**4**.

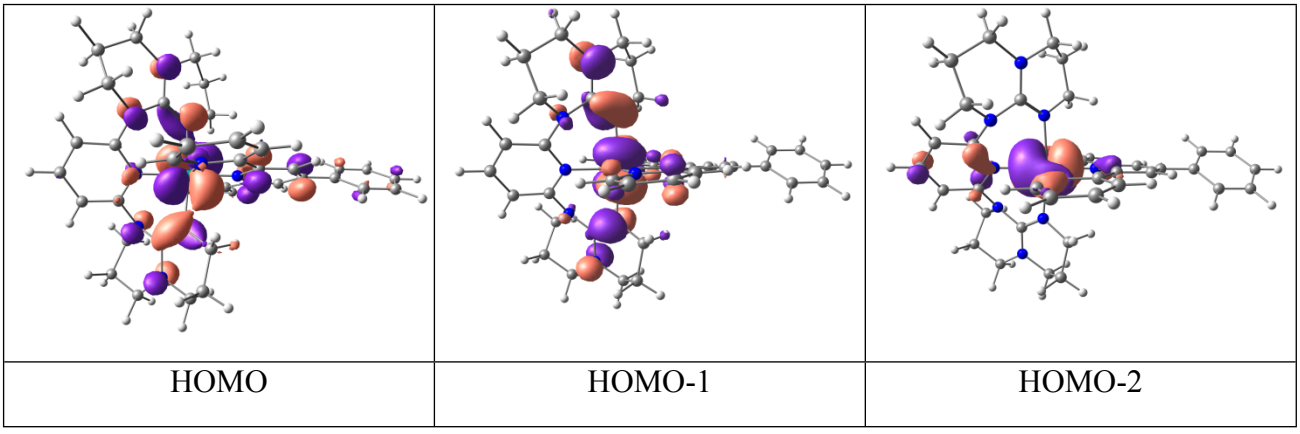
Compounds	λ_{max}, nm (ε x 10^3, $M^{-1}cm^{-1}$)						
L1	228(29.0)	311(12.8)					
L2	245(9.7)	285(20.9)					
1	225(44.7)	244(39.3)	289(45.9)	317(23.1)	379(10.5)	541(8.8)	622(5.6)
2	225(44.8)	247(39.7)	288(45.1)	313(27.9)	383(11.3)	538(9.4)	620(6.2)
3	244(33.3)	291(35.3)	380(7.0)	411(8.6)	560(11.8)	740(3.8)	
4	243(29.1)	288(27.8)	373(6.7)	405(7.0)	558(9.3)	740(3.0)	
$[Ru(tpy)_2]^{2+}$		270(40.9)	307(66.7)	475(15.3)[a]			
[Ru(Br-Ph-dpt)(tpy)]$^{2+}$		282(53.5)	301(59.6)	476(21.7)[b]			
$[Ru(Br\text{-}Ph\text{-}dpt)_2]^{2+}$		279(50.9)	295(50.6)	491(27.5)[b]			

[a]from ref 9, [b]from ref 10

DFT Calculations:

Table S3. MO composition of $[\mathbf{1}]^{2+}$ in singlet (*S*=0) ground state (b3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

MO	Energy (eV)	Approximate Composition (%)		
		Ru	Ph-tpy	hpp
LUMO+5	-0.99	1	1	98
LUMO+4	-1.25	3	95	2
LUMO+3	-1.36	1	99	0
LUMO+2	-1.43	4	2	94
LUMO+1	-2.27	2	98	0
LUMO	**-2.46**	**9**	**88**	**2**
HOMO	**-5.37**	**57**	**18**	**25**
HOMO-1	-5.37	61	10	29
HOMO-2	-5.86	84	10	6
HOMO-3	-6.56	2	1	97
HOMO-4	-6.69	5	26	70
HOMO-5	-6.85	13	22	66



HOMO | HOMO-1 | HOMO-2

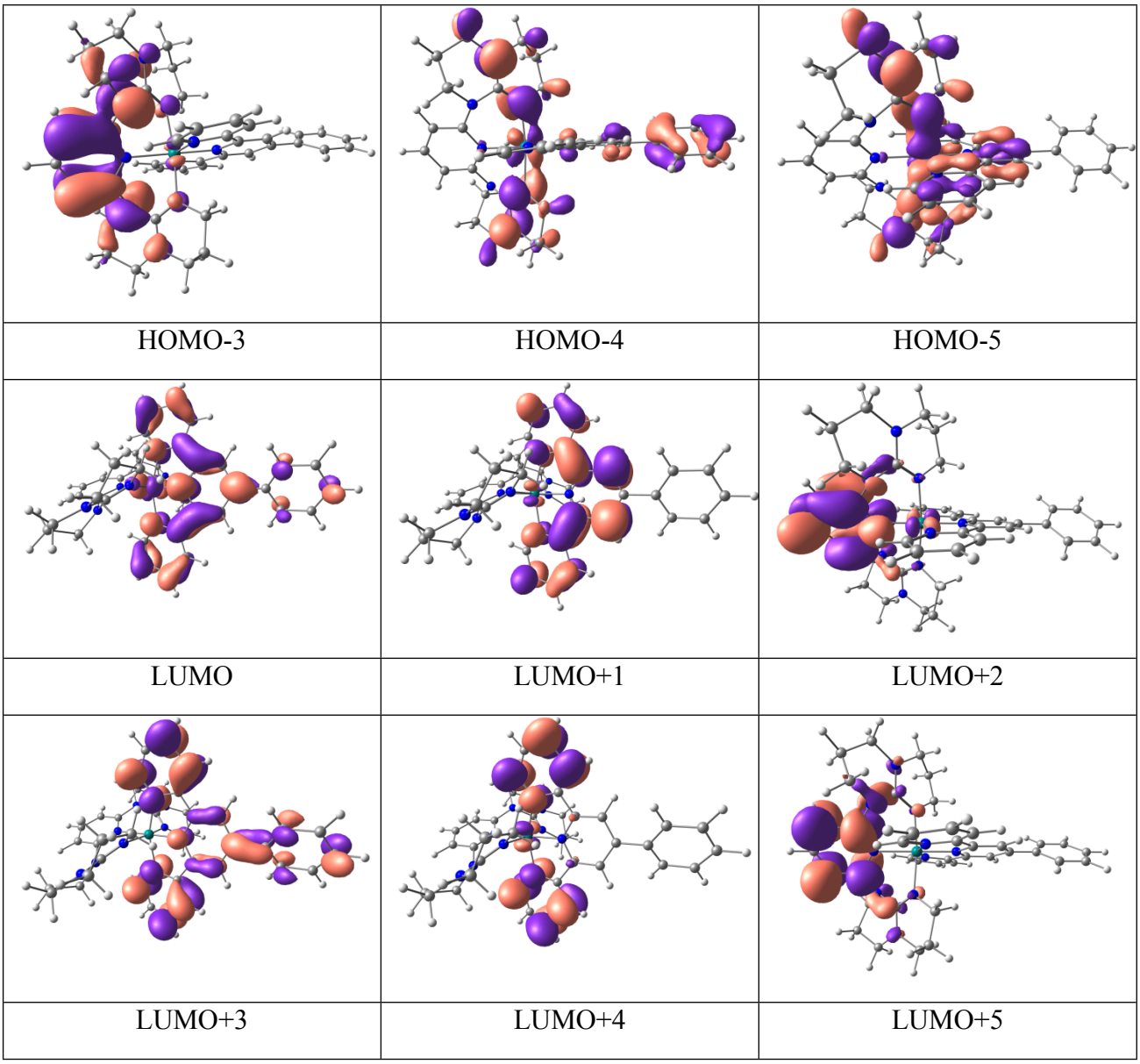


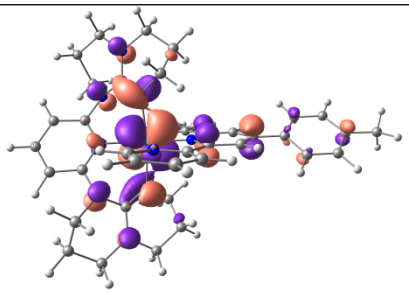
Figure S3. Kohn-Sham molecular orbital sketches for $[\mathbf{1}]^{2+}$ in (*S=0*) ground state

Table S4. Selected transitions from TD-DFT calculations of $[\mathbf{1}]^{2+}$ in the singlet ground state (b3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N], CPCM (CH_3CN)).

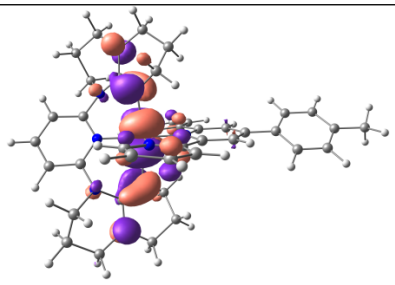
state	energy (eV)	λ/nm	λ/nm (ε x10^3 $M^{-1}cm^{-1}$) [expt.]	f	Major transition(s)	Character
58	5.03	246	244 (39.3)	0.2525	H-3->L+5 (68%)	Hpp (n/π) to Hpp (n/π*)
41	4.44	279	289 (45.9)	0.3477	H-7->L+1 (61%), H-8->L+1 (13%)	Ph-tpy(π) to Ph-tpy(π*)
29	4.02	308	317 (23.1)	0.2449	H-7->L (51%)	Ph-tpy(π) to Ph-tpy(π*)
11	3.34	371	379 (10.5)	0.0632	H-1->L+3 (92%)	Ru(dπ) to Ph-tpy(π*) (major) + hpp(n/π) to Ph-tpy(π*) (minor)
2	2.20	562	541 (8.8)	0.0444	H->L (64%), H-1->L+1 (20%), H-2->L (10%)	Ru(dπ) to Ph-tpy(π*) + (major) + hpp(n/π) to Ph-tpy(π*) (minor)
1	2.01	616	622 (5.6)	0.0117	H-1->L (94%)	Ru(dπ) to Ph-tpy(π*) + (major) + hpp(n/π) to Ph-tpy(π*) (minor)

Table S5. MO composition of [**2**]$^{2+}$ in singlet (*S*=0) ground state (b3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

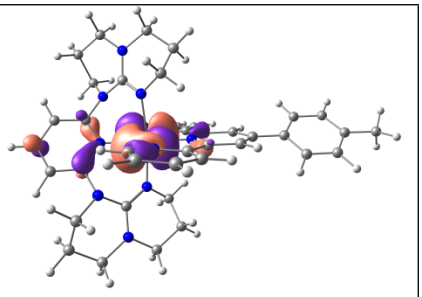
MO	Energy (eV)	Approximate Composition (%)		
		Ru	Tolyl-tpy	hpp
LUMO+5	-1.01	1	1	99
LUMO+4	-1.22	3	95	1
LUMO+3	-1.35	1	98	1
LUMO+2	-1.44	3	2	95
LUMO+1	-2.26	2	97	1
LUMO	**-2.45**	**9**	**88**	**3**
HOMO	**-5.34**	**57**	**19**	**24**
HOMO-1	-5.35	62	10	28
HOMO-2	-5.85	83	11	6
HOMO-3	-6.58	4	3	93
HOMO-4	-6.61	1	63	36
HOMO-5	-6.88	9	29	63



HOMO



HOMO-1



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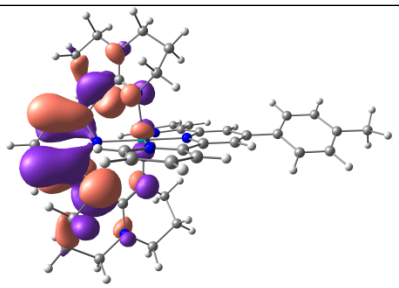

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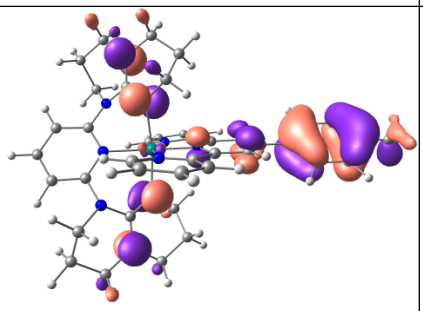
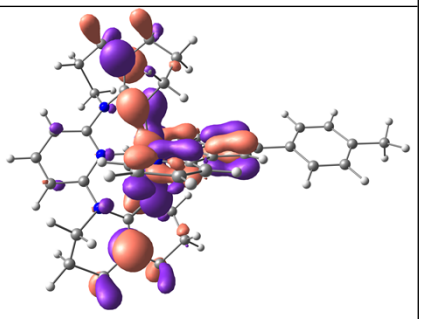


HOMO-4



HOMO-5

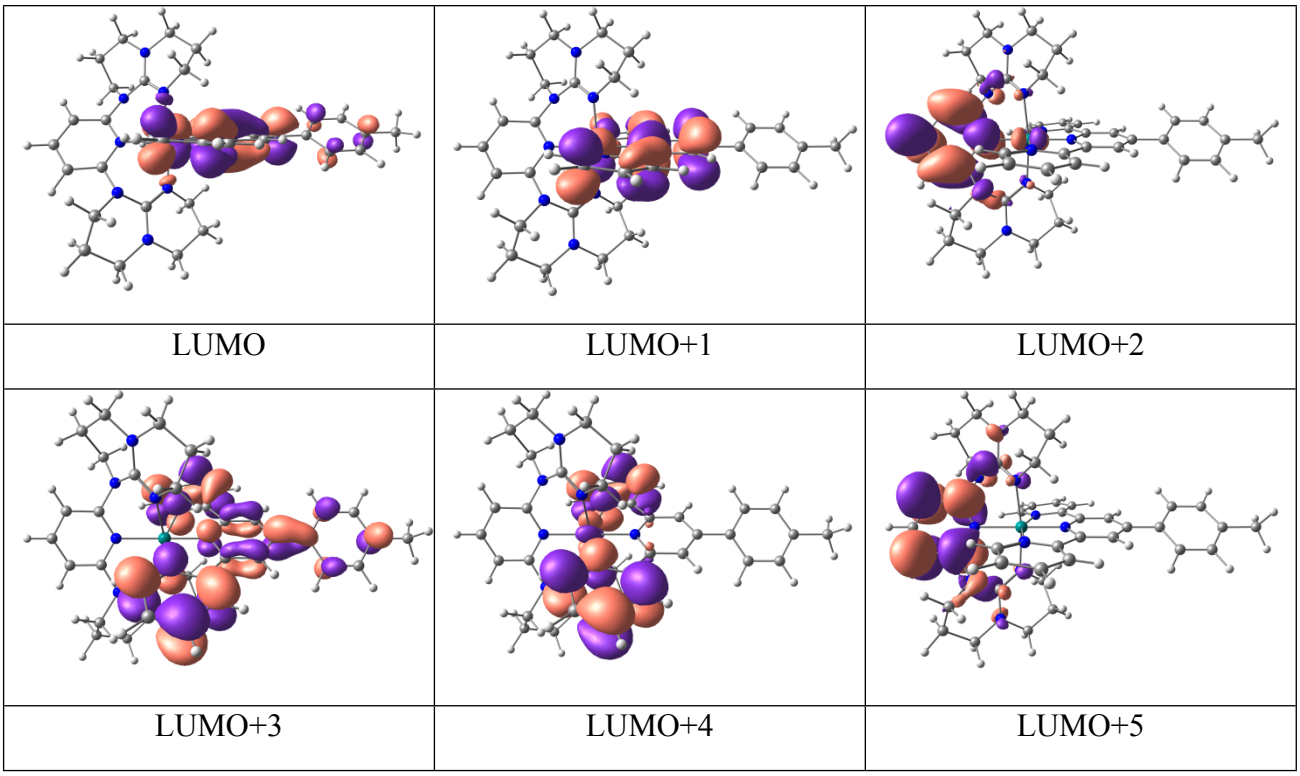


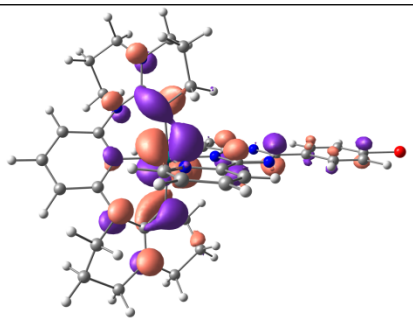
Figure S4. Kohn-Sham molecular orbital sketches for [**2**]$^{2+}$ in (*S=0*) ground state

Table S6. Selected transitions from TD-DFT calculations of $[\mathbf{2}]^{2+}$ in the singlet ground state (b3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N], CPCM (CH_3CN)).

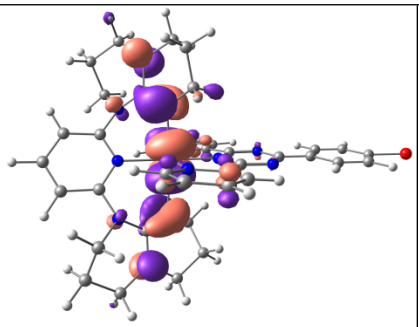
state	energy (eV)	λ/nm	λ/nm (ε x10^3 $M^{-1}cm^{-1}$) [expt.]	f	Major transition(s)	Character
59	5.04	246	247 (39.7)	0.2134	H-10->L+1 (46%) H-5->L+3 (24%)	Tolyl-tpy(π) to Tolyl-tpy(π*) (major) + hpp (n/π) to Tolyl-tpy(π*) (minor)
41	4.44	279	288 (45.1)	0.3339	H-8->L+1 (41%), H-7->L+1 (19%), H-9->L (16%)	Tolyl-tpy(π) to Tolyl-tpy(π*) (major) + hpp (n/π) to Tolyl-tpy(π*) (minor)
32	4.06	305	313 (27.9)	0.1566	H-7->L (34%), H-6->L+1 (33%), H-8->L (20%)	Tolyl-tpy(π) to Tolyl-tpy(π*) (major) + hpp (n/π) to Tolyl-tpy(π*) (minor)
10	3.31	375	383 (11.3)	0.0631	H->L+3 (93%)	Ru(dπ) to Tolyl-tpy(π*) (major) + hpp(n/π) to Tolyl-tpy(π*) (minor)
2	2.19	565	538 (9.4)	0.0485	H->L (63%), H-1->L+1 (22%)	Ru(dπ) to Tolyl-tpy(π*) (major) + hpp(n/π) to Tolyl-tpy(π*) (minor)
1	2.00	620	620 (6.2)	0.0119	H-1->L (94%)	Ru(dπ) to Tolyl-tpy(π*) (major) + hpp(n/π) to Tolyl-tpy(π*) (minor)

Table S7. MO composition of [**3**]$^{2+}$ in singlet (*S*=0) ground state (b3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N,Br]).

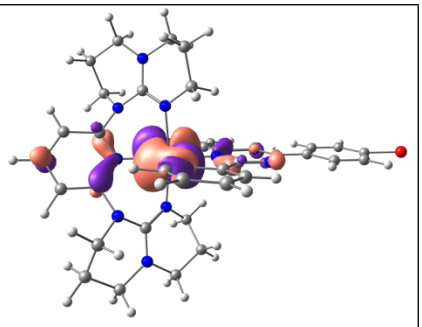
MO	Energy (eV)	Approximate Composition (%)		
		Ru	Br-Ph-dpt	hpp
LUMO+5	-1.31	1	96	3
LUMO+4	-1.44	3	96	1
LUMO+3	-1.52	1	3	94
LUMO+2	-1.80	1	99	0
LUMO+1	-2.90	10	87	3
LUMO	**-2.99**	**2**	**97**	**1**
HOMO	**-5.58**	**53**	**19**	**28**
HOMO-1	-5.62	57	9	34
HOMO-2	-6.09	81	13	6
HOMO-3	-6.66	2	1	97
HOMO-4	-6.81	5	33	62
HOMO-5	-7.05	20	17	63



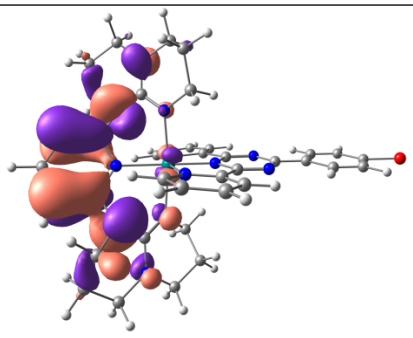
HOMO



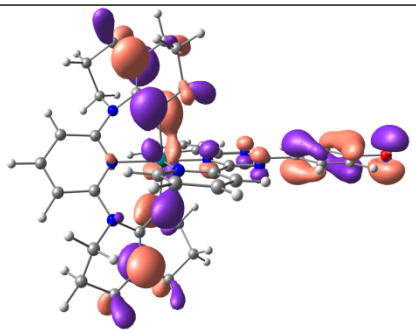
HOMO-1



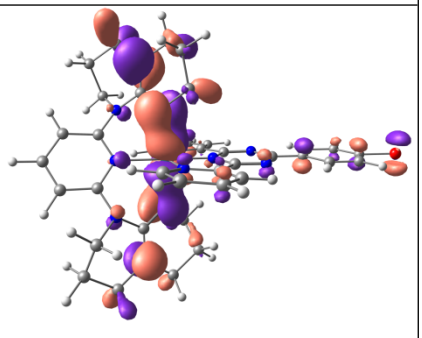
HOMO-2



HOMO-3



HOMO-4



HOMO-5

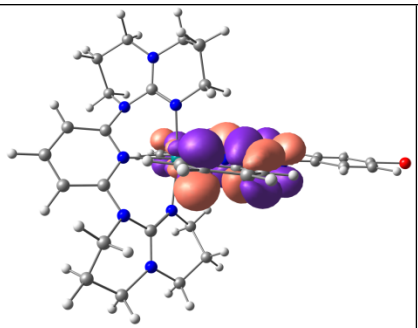
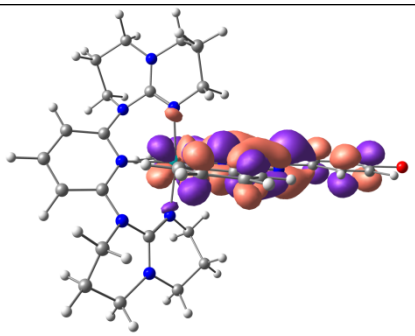
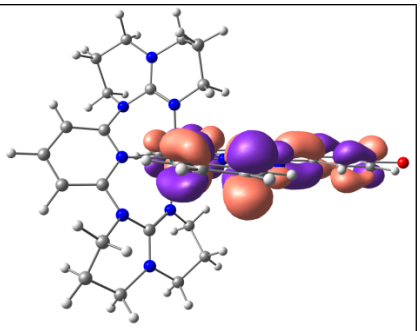
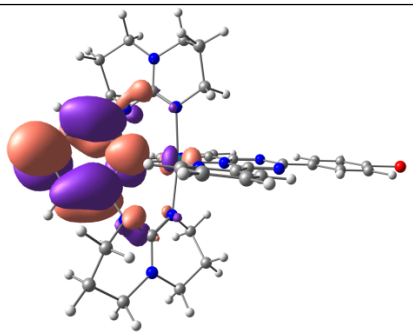
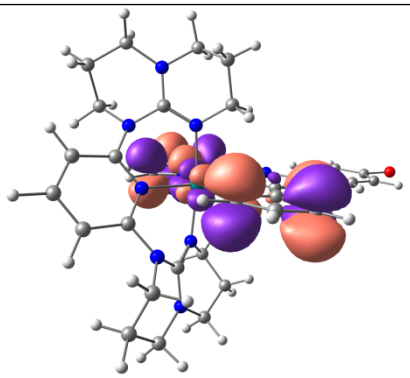
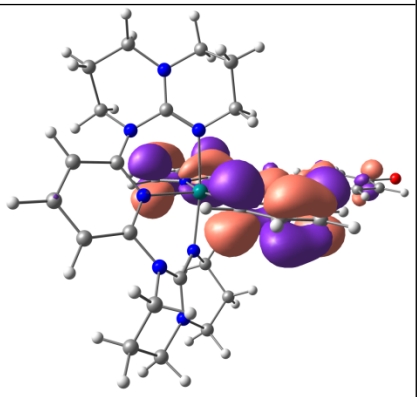
		
LUMO	LUMO+1	LUMO+2
		
LUMO+3	LUMO+4	LUMO+5

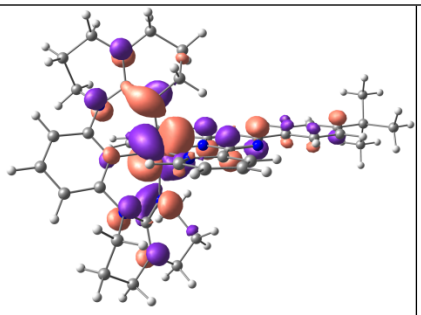
Figure S5. Kohn-Sham molecular orbital sketches for [**3**]$^{2+}$ in (*S=0*) ground state

Table S8. Selected transitions from TD-DFT calculations of [**3**]$^{2+}$ in the singlet ground state (b3lyp/LanL2DZ(f)[Ru], 6-31G**[C,H,N,Br], CPCM (CH_3CN)).

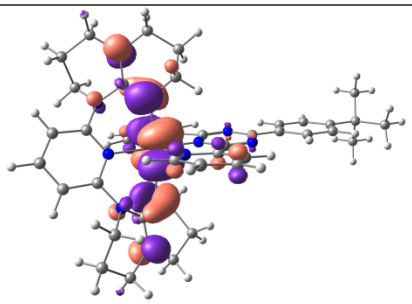
state	energy (eV)	λ/nm	λ/nm (ε x10^3 M^{-1}cm^{-1}) [expt.]	f	Major transition(s)	Character
67	5.02	247	244 (33.3)	0.0715	H-1->L+12 (61%)	hpp (n/π) to hpp (n/π*)
46	4.49	276	291 (35.3)	0.2777	H-11->L (49%), H-10->L (17%)	Br-Ph-dpt(π) to Br-Ph-dpt (π*)
22	3.57	347	380 (7.0)	0.3221	H-2->L+2 (28%), H-1->L+4 (34%)	Ru(dπ) to Br-Ph-dpt (π*)(major) + hpp(n/π) to Br-Ph-dpt(π*)(minor)
8	3.15	394	411 (8.6)	0.0985	H->L+2 (93%)	Ru(dπ) to Br-Ph-dpt (π*)(major) + hpp(n/π) to Br-Ph-dpt(π*)(minor)
6	2.38	520	560 (11.8)	0.2337	H-2->L+1 (44%), H->L+1 (32%)	Ru(dπ) to Br-Ph-dpt (π*)(major) + hpp(n/π) to Br-Ph-dpt(π*)(minor)
1	1.84	675	740 (3.8)	0.0017	H-1->L+1 (47%), H->L(44%)	Ru(dπ) to Br-Ph-dpt (π*)(major) + hpp(n/π) to Br-Ph-dpt(π*)(minor)

Table S9. MO composition of [**4**]$^{2+}$ in singlet (*S*=0) ground state (b3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

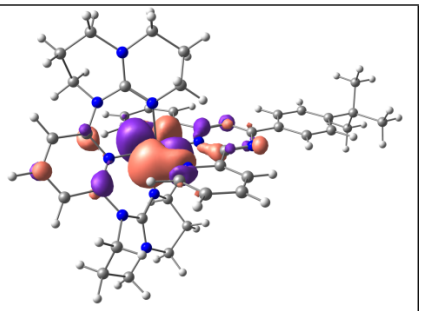
MO	Energy (eV)	Approximate Composition (%)		
		Ru	*t*Bu-Ph-Trz	hpp
LUMO+5	-1.23	1	97	1
LUMO+4	-1.38	3	96	1
LUMO+3	-1.51	3	2	95
LUMO+2	-1.71	1	99	1
LUMO+1	-2.85	12	86	3
LUMO	**-2.98**	**3**	**97**	**1**
HOMO	**-5.5**	**54**	**20**	**25**
HOMO-1	-5.53	59	9	32
HOMO-2	-5.99	81	13	6
HOMO-3	-6.69	3	1	96
HOMO-4	-6.79	4	33	64
HOMO-5	-7.04	19	8	72



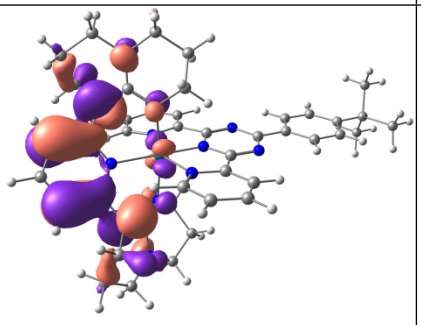
HOMO



HOMO-1



HOMO-2



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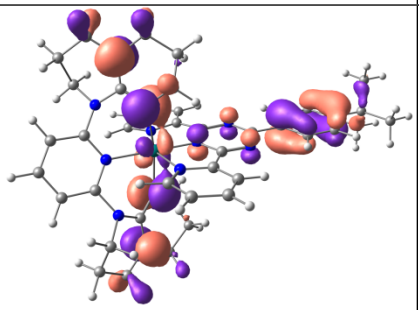

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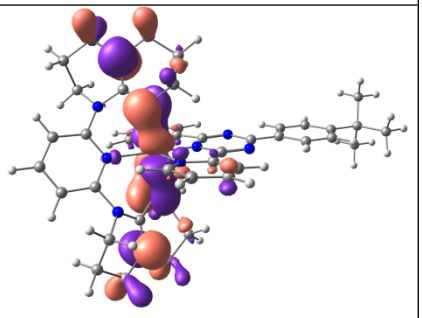

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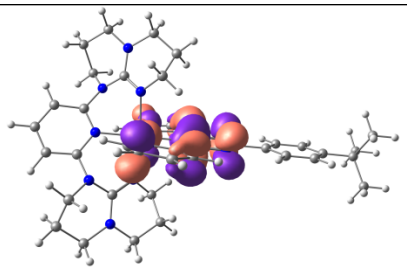
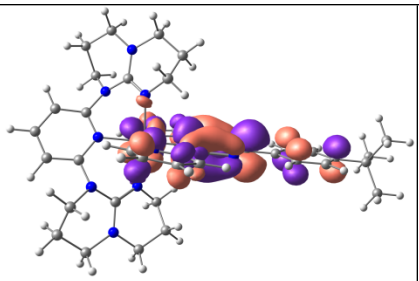
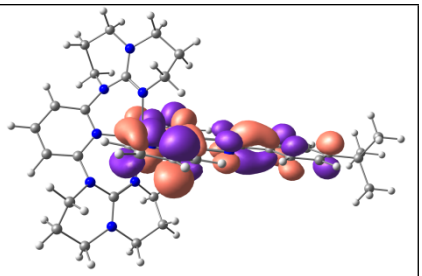
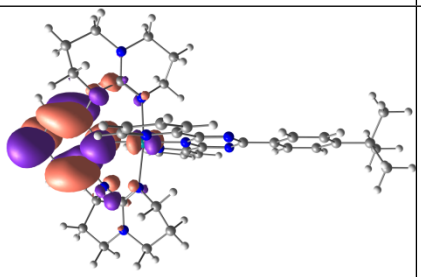
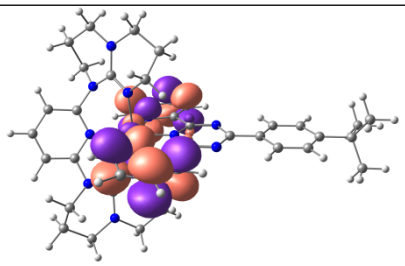
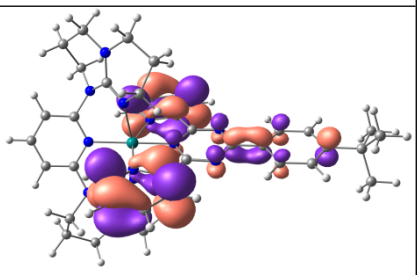
		
LUMO	LUMO+1	LUMO+2
		
LUMO+3	LUMO+4	LUMO+5

Figure S6. Kohn-Sham molecular orbital sketches for [**4**]$^{2+}$ in (*S=0*) ground state

Table S10. Selected transitions from TD-DFT calculations of [**4**]$^{2+}$ in the singlet ground state (b3lyp/LanL2DZ(f)[Ru], 6-31G**[C,H,N], CPCM (CH_3CN)).

state	energy (eV)	λ/nm	λ/nm (ε x10^3 $M^{-1}cm^{-1}$) [expt.]	f	Major transition(s)	Character
72	5.16	240	243 (29.1)	0.1502	H-4->L+6 (65%)	hpp (n/π) to hpp (π*) (major) + ^{t}Bu-Ph-dpt(π) to hpp (π*) (minor)
47	4.56	271	288 (27.8)	0.2940	H-11->L (76%)	^{t}Bu-Ph-dpt(π) to ^{t}Bu-Ph-dpt(π∗)
21	3.54	350	373 (6.7)	0.3102	H-2->L+2 (27%), H-1->L+4 (27%), H-2->L+3 (18%)	Ru(dπ) to ^{t}Bu-Ph-dpt(π∗) (major) + hpp(n/π) to ^{t}Bu-Ph-dpt(π) (minor)
8	3.14	394	405 (7.0)	0.1027	H->L+2 (92%)	Ru(dπ) to ^{t}Bu-Ph-dpt(π∗) (major) + hpp(n/π) to ^{t}Bu-Ph-dpt(π) (minor)
6	2.37	523	558 (9.3)	0.2879	H->L+1 (37%), H-2->L+1 (34%)	Ru(dπ) to ^{t}Bu-Ph-dpt(π∗) (major) + hpp(n/π) to ^{t}Bu-Ph-dpt(π) (minor)
3	1.84	674	740 (3.0)	0.0419	H->L(53%), H-1->L+1(41%)	Ru(dπ) to ^{t}Bu-Ph-dpt(π∗) (major) + hpp(n/π) to ^{t}Bu-Ph-dpt(π) (minor)

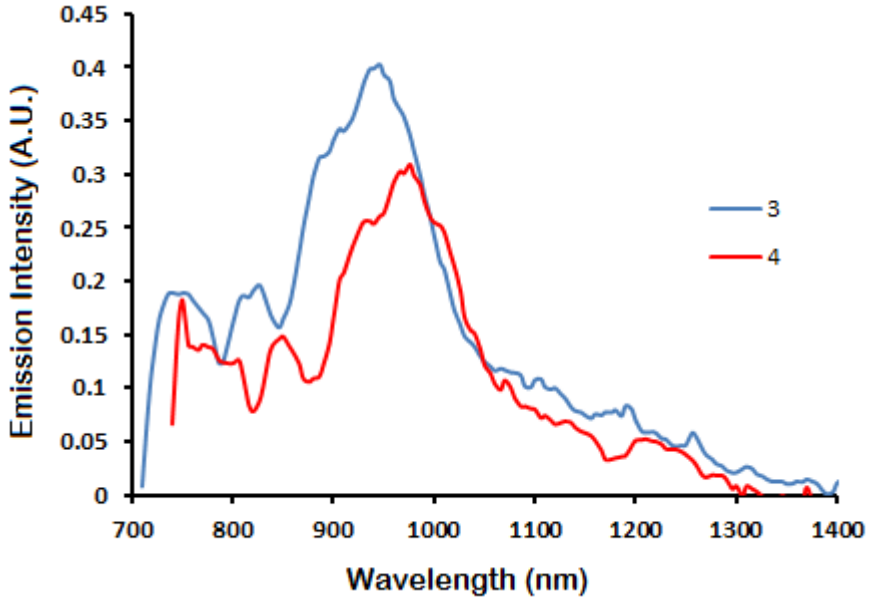


Figure S7. Corrected emission spectra of complexes **3** and **4** at 77 K in rigid butyronitrile matrix.

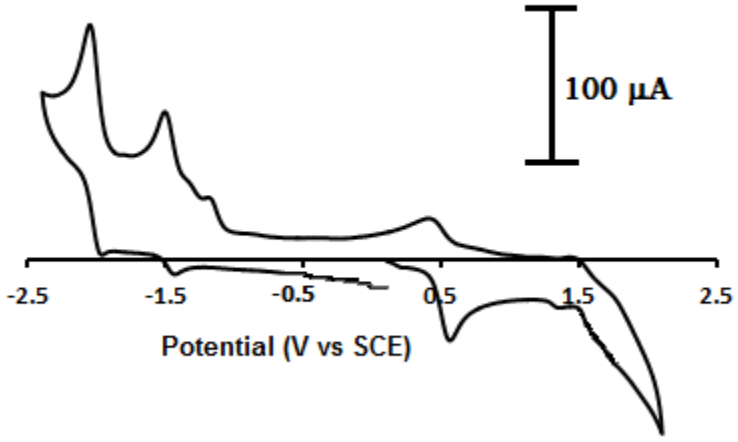


Figure S8. Cyclic voltammogram of the complex **1** in dry, degassed acetonitrile.

Table S11. Optimized Atomic coordinates obtained from DFT for [**1**]$^{2+}$ in singlet ground state (b3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.545664	0.000015	0.000029
2	7	0	-0.125997	-0.992801	-1.835809
3	7	0	1.441919	-0.000293	0.000095
4	7	0	-0.125823	0.992635	1.835781
5	7	0	-0.685039	1.879629	-1.013404
6	7	0	-1.557872	4.078253	-1.035268
7	7	0	-2.632296	2.381660	0.198591
8	7	0	-2.658451	0.000291	-0.000208
9	7	0	-2.632879	-2.381065	-0.198906
10	7	0	-1.559575	-4.077736	1.035804
11	7	0	-0.685736	-1.879521	1.013545
12	6	0	1.215531	-1.205606	-2.029274
13	6	0	1.683070	-1.874469	-3.164219
14	1	0	2.745061	-2.044867	-3.295426
15	6	0	0.783095	-2.310952	-4.132485
16	1	0	1.137914	-2.829022	-5.017247
17	6	0	-0.575421	-2.054084	-3.949415
18	1	0	-1.311835	-2.352853	-4.687259
19	6	0	-0.981762	-1.397838	-2.791368
20	1	0	-2.026384	-1.177505	-2.609378
21	6	0	2.107587	-0.628445	-1.001251
22	6	0	3.500601	-0.648214	-1.013787
23	1	0	4.033544	-1.176265	-1.794746
24	6	0	4.232029	-0.000458	0.000019
25	6	0	3.500739	0.647372	1.013878
26	1	0	4.033778	1.175389	1.794796
27	6	0	2.107723	0.627761	1.001416
28	6	0	1.215752	1.205071	2.029420
29	6	0	1.683342	1.873669	3.164492
30	1	0	2.745375	2.043705	3.295850
31	6	0	0.783382	2.310310	4.132703
32	1	0	1.138248	2.828196	5.017553
33	6	0	-0.575185	2.053844	3.949446
34	1	0	-1.311602	2.352737	4.687237
35	6	0	-0.981583	1.397818	2.791295
36	1	0	-2.026237	1.177782	2.609166
37	6	0	5.710344	-0.000517	-0.000054
38	6	0	6.427415	0.049301	-1.209224
39	1	0	5.896264	0.124435	-2.153750
40	6	0	7.820229	0.052787	-1.207627
41	1	0	8.359749	0.105880	-2.147907
42	6	0	8.520394	-0.000641	-0.000197
43	1	0	9.605732	-0.000690	-0.000255
44	6	0	7.820349	-0.054003	1.207305

45	1	0	8.359957	-0.107143	2.147531
46	6	0	6.427534	-0.050395	1.209041
47	1	0	5.896471	-0.125471	2.153621
48	6	0	-3.348245	1.170337	0.050467
49	6	0	-4.747245	1.198068	0.013790
50	1	0	-5.279232	2.138914	-0.009551
51	6	0	-5.449020	0.000742	-0.001062
52	1	0	-6.534046	0.000896	-0.001430
53	6	0	-4.747612	-1.196815	-0.015457
54	1	0	-5.279963	-2.137458	0.007572
55	6	0	-3.348583	-1.169566	-0.051243
56	6	0	-3.271660	-3.476228	-0.959430
57	1	0	-2.518399	-3.898114	-1.636251
58	1	0	-4.058349	-3.050662	-1.581165
59	6	0	-3.784006	-4.545603	-0.004833
60	1	0	-4.512594	-4.112064	0.687692
61	1	0	-4.283864	-5.355724	-0.543260
62	6	0	-2.583733	-5.099862	0.752223
63	1	0	-2.893187	-5.553467	1.700507
64	1	0	-2.102096	-5.888222	0.159208
65	6	0	-0.391239	-4.570924	1.779657
66	1	0	0.423413	-4.814073	1.083522
67	1	0	-0.683072	-5.496891	2.279690
68	6	0	0.040204	-3.511660	2.781920
69	1	0	-0.760307	-3.359666	3.514395
70	1	0	0.930867	-3.833960	3.328886
71	6	0	0.331589	-2.222815	2.021853
72	1	0	0.414511	-1.386817	2.720554
73	1	0	1.299327	-2.306988	1.512104
74	6	0	-1.584556	-2.765697	0.660654
75	6	0	-3.271059	3.476777	0.959209
76	1	0	-2.518006	3.898102	1.636619
77	1	0	-4.058266	3.051268	1.580322
78	6	0	-3.782431	4.546739	0.004756
79	1	0	-4.282251	5.356848	0.543233
80	1	0	-4.510812	4.113789	-0.688361
81	6	0	-2.581520	5.100802	-0.751417
82	1	0	-2.890331	5.555206	-1.699527
83	1	0	-2.099683	5.888518	-0.157691
84	6	0	-0.389181	4.571063	-1.778811
85	1	0	0.425486	4.813658	-1.082502
86	1	0	-0.680501	5.497293	-2.278662
87	6	0	0.041902	3.511833	-2.781274
88	1	0	-0.758605	3.360364	-3.513858
89	1	0	0.932764	3.833862	-3.328076
90	6	0	0.332619	2.222704	-2.021441
91	1	0	0.415327	1.386798	-2.720289
92	1	0	1.300305	2.306385	-1.511509
93	6	0	-1.583561	2.766106	-0.660472

Table S12. Optimized Atomic coordinates obtained from DFT for $[\mathbf{2}]^{2+}$ in singlet ground state (b3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-0.773882	-0.000117	-0.000185
2	7	0	-0.353309	1.045790	-1.804878
3	7	0	1.212502	-0.000742	0.000247
4	7	0	-0.354649	-1.046556	1.804631
5	7	0	-0.930902	-1.820646	-1.102864
6	7	0	-1.765263	-4.027989	-1.185942
7	7	0	-2.863072	-2.389806	0.106542
8	7	0	-2.888895	0.000857	-0.000872
9	7	0	-2.860725	2.391500	-0.107928
10	7	0	-1.763712	4.027834	1.187598
11	7	0	-0.929779	1.820369	1.102590
12	6	0	0.988375	1.255556	-1.997969
13	6	0	1.456820	1.940963	-3.122848
14	1	0	2.519565	2.105878	-3.254841
15	6	0	0.556830	2.399774	-4.080312
16	1	0	0.912178	2.930095	-4.957574
17	6	0	-0.802991	2.150107	-3.896221
18	1	0	-1.540007	2.468223	-4.625317
19	6	0	-1.209580	1.475090	-2.749492
20	1	0	-2.255237	1.259865	-2.567370
21	6	0	1.880313	0.660004	-0.979374
22	6	0	3.273095	0.673983	-0.994832
23	1	0	3.805360	1.175366	-1.793459
24	6	0	4.006324	-0.000490	0.001486
25	6	0	3.272375	-0.675225	0.997068
26	1	0	3.803925	-1.176270	1.796364
27	6	0	1.879570	-0.661469	0.980353
28	6	0	0.986853	-1.256936	1.998333
29	6	0	1.454450	-1.942898	3.123226
30	1	0	2.517053	-2.108367	3.255659
31	6	0	0.553794	-2.401611	4.080114
32	1	0	0.908487	-2.932341	4.957395
33	6	0	-0.805832	-2.151346	3.895410
34	1	0	-1.543344	-2.469381	4.624037
35	6	0	-1.211568	-1.475835	2.748664
36	1	0	-2.257051	-1.260187	2.566042
37	6	0	5.481594	0.000008	0.001769
38	6	0	6.205040	1.113056	-0.463481
39	1	0	5.680143	2.004407	-0.795455
40	6	0	7.595759	1.112925	-0.454418
41	1	0	8.130408	1.992723	-0.801054
42	6	0	8.320880	0.003373	0.006225
43	6	0	7.596793	-1.106374	0.468847
44	1	0	8.132579	-1.981420	0.825841

45	6	0	6.206298	-1.110764	0.471117
46	1	0	5.682418	-2.000836	0.808083
47	6	0	9.827812	-0.006635	-0.017133
48	1	0	10.196953	-0.431961	-0.958499
49	1	0	10.237693	-0.612499	0.795453
50	1	0	10.237157	1.003462	0.066522
51	6	0	0.016728	-2.196546	-2.160827
52	1	0	0.814547	-1.457387	-2.192127
53	1	0	-0.485588	-2.171279	-3.138343
54	6	0	0.576047	-3.590952	-1.894803
55	1	0	1.296597	-3.886591	-2.662673
56	1	0	1.097816	-3.594226	-0.931640
57	6	0	-0.584373	-4.574456	-1.882151
58	1	0	-0.304718	-5.512157	-1.387604
59	1	0	-0.883440	-4.827745	-2.907350
60	6	0	-2.839823	-5.028115	-1.044947
61	1	0	-2.403986	-5.891521	-0.526788
62	1	0	-3.133048	-5.370857	-2.044679
63	6	0	-4.041781	-4.511827	-0.261207
64	1	0	-4.563182	-5.351721	0.206444
65	1	0	-4.754394	-4.012789	-0.925058
66	6	0	-3.521302	-3.528395	0.780244
67	1	0	-4.304586	-3.141588	1.430803
68	1	0	-2.776433	-4.012338	1.423131
69	6	0	-1.812142	-2.730000	-0.766373
70	6	0	-3.579072	-1.170789	0.007742
71	6	0	-4.978255	-1.195712	-0.027071
72	1	0	-5.513725	-2.132873	-0.080945
73	6	0	-5.678451	0.002086	-0.003343
74	1	0	-6.763459	0.002575	-0.004325
75	6	0	-4.977240	1.199255	0.021691
76	1	0	-5.512037	2.136847	0.074634
77	6	0	-3.577993	1.173136	-0.010573
78	6	0	-3.517080	3.531128	-0.781678
79	1	0	-4.299534	3.145479	-1.433925
80	1	0	-2.770797	4.015124	-1.422871
81	6	0	-4.038573	4.513985	0.259807
82	1	0	-4.558586	5.354691	-0.207932
83	1	0	-4.752636	4.014886	0.922042
84	6	0	-2.837515	5.028690	1.045974
85	1	0	-2.400354	5.892391	0.529417
86	1	0	-3.132091	5.370554	2.045608
87	6	0	-0.583543	4.573108	1.885947
88	1	0	-0.883669	4.824863	2.911213
89	1	0	-0.303262	5.511538	1.393144
90	6	0	0.576756	3.589491	1.898240
91	1	0	1.296609	3.883908	2.667230
92	1	0	1.099444	3.594182	0.935581
93	6	0	0.017166	2.194738	2.161743
94	1	0	0.814989	1.455572	2.192443
95	1	0	-0.485796	2.167973	3.138885
96	6	0	-1.810482	2.730351	0.766411

Table S13. Optimized Atomic coordinates obtained from DFT for $[\mathbf{3}]^{2+}$ in singlet ground state (b3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-8.898623	0.103425	-0.209417
2	44	0	1.308804	0.055589	0.023965
3	7	0	0.882670	1.153329	1.770456
4	7	0	-0.601138	-0.063705	0.097415
5	7	0	-2.634610	0.526029	1.129263
6	7	0	-2.603097	-0.967413	-0.746190
7	7	0	0.913819	-1.113919	-1.646515
8	7	0	3.376583	0.133682	-0.029054
9	7	0	3.417803	-2.244492	-0.152888
10	7	0	2.233499	-3.933336	0.936518
11	7	0	1.568613	-1.695710	1.139283
12	7	0	3.273680	2.495388	-0.009990
13	7	0	2.126387	3.953522	-1.425759
14	7	0	1.348826	1.767836	-1.126022
15	6	0	-0.392048	-1.561817	-1.682270
16	6	0	-0.805765	-2.555992	-2.557942
17	1	0	-1.683897	-2.868187	-2.545668
18	6	0	0.119719	-3.071196	-3.450438
19	1	0	-0.119827	-3.769065	-4.019013
20	6	0	1.394721	-2.551415	-3.496755
21	1	0	2.005189	-2.857575	-4.129235
22	6	0	1.752690	-1.571090	-2.591401
23	1	0	2.611157	-1.211696	-2.638342
24	6	0	-1.281810	-0.877530	-0.747135
25	6	0	-3.242679	-0.228328	0.189115
26	6	0	-1.313427	0.587166	1.057634
27	6	0	-0.459122	1.289945	2.004005
28	6	0	-0.961387	1.978024	3.106358
29	1	0	-1.880153	2.070517	3.229003
30	6	0	-0.072303	2.516716	4.012757
31	1	0	-0.380702	2.993310	4.751368
32	6	0	1.278356	2.338686	3.808242
33	1	0	1.892288	2.664164	4.428773
34	6	0	1.714461	1.679232	2.681047
35	1	0	2.632773	1.593008	2.544834
36	6	0	-4.704502	-0.195703	0.142200
37	6	0	-5.394090	-0.833951	-0.865662
38	1	0	-4.930391	-1.351959	-1.485478
39	6	0	-6.753920	-0.703831	-0.949398
40	1	0	-7.234669	-1.106479	-1.635366
41	6	0	-7.381296	0.007593	-0.042830
42	6	0	-6.788352	0.638762	0.946402

43	1	0	-7.291626	1.135531	1.549012
44	6	0	-5.422445	0.548208	1.065132
45	1	0	-4.978551	0.980010	1.759044
46	6	0	0.615913	-2.086949	2.178216
47	1	0	0.643216	-1.409637	2.873944
48	1	0	-0.271833	-2.060527	1.789506
49	6	0	0.777927	-3.336172	2.792611
50	1	0	-0.019002	-3.568444	3.297181
51	1	0	1.533614	-3.315012	3.402444
52	6	0	1.031747	-4.417178	1.631963
53	1	0	1.182985	-5.300170	2.007859
54	1	0	0.275857	-4.457485	1.025356
55	6	0	3.371903	-4.885711	0.805409
56	1	0	3.735819	-5.052968	1.690045
57	1	0	3.027596	-5.729725	0.468396
58	6	0	4.445308	-4.454260	-0.055251
59	1	0	4.718580	-5.202272	-0.610627
60	1	0	5.204367	-4.203051	0.495060
61	6	0	4.090638	-3.305011	-0.937045
62	1	0	4.894572	-2.947000	-1.344664
63	1	0	3.500087	-3.608767	-1.645966
64	6	0	2.371378	-2.620085	0.672773
65	6	0	4.097865	-1.010613	-0.001865
66	6	0	5.474016	-1.009657	0.138306
67	1	0	5.943378	-1.811247	0.191160
68	6	0	6.139175	0.191518	0.198975
69	1	0	7.062839	0.211559	0.305555
70	6	0	5.421719	1.372523	0.100376
71	1	0	5.862218	2.192269	0.105531
72	6	0	4.040633	1.317942	-0.005215
73	6	0	3.886122	3.729815	0.508128
74	1	0	4.612791	3.507235	1.111351
75	1	0	3.226557	4.242746	1.001915
76	6	0	4.411137	4.548745	-0.649710
77	1	0	4.840791	5.354889	-0.319833
78	1	0	5.065774	4.036561	-1.151758
79	6	0	3.244073	4.908674	-1.532926
80	1	0	2.926347	5.793330	-1.292678
81	1	0	3.543994	4.941326	-2.455385
82	6	0	0.914620	4.411969	-2.102965
83	1	0	1.113883	4.568367	-3.040205
84	1	0	0.632595	5.255287	-1.713711
85	6	0	-0.212133	3.415079	-1.995121
86	1	0	-0.881419	3.594172	-2.674871
87	1	0	-0.633614	3.483152	-1.123428
88	6	0	0.367941	2.029819	-2.186858
89	1	0	-0.341468	1.366937	-2.151511
90	1	0	0.797807	1.969682	-3.055355
91	6	0	2.207093	2.721563	-0.901318

Table S14. Optimized Atomic coordinates obtained from DFT for $[\mathbf{4}]^{2+}$ in singlet ground state (b3lyp/LanL2DZ(f)[Ru]6-31G**[C,H,N]).

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	44	0	-1.348493	0.000183	0.000581
2	7	0	-0.888845	-1.079414	1.805836
3	7	0	0.626580	-0.004275	0.005955
4	7	0	-0.873940	1.077575	-1.802426
5	7	0	-1.505872	1.810089	1.118981
6	7	0	-2.335143	4.018621	1.212590
7	7	0	-3.422842	2.394636	-0.107689
8	7	0	-3.461086	0.005110	-0.006121
9	7	0	-3.435034	-2.384529	0.096563
10	7	0	-2.342875	-4.015666	-1.211278
11	7	0	-1.507773	-1.809496	-1.118164
12	6	0	0.458186	-1.271899	1.986673
13	6	0	0.976348	-1.950228	3.088527
14	1	0	2.051122	-2.066425	3.168695
15	6	0	0.102336	-2.441409	4.055672
16	1	0	0.480175	-2.971399	4.923658
17	6	0	-1.265623	-2.222552	3.890473
18	1	0	-1.982946	-2.568064	4.627080
19	6	0	-1.715504	-1.543035	2.759110
20	1	0	-2.770423	-1.354499	2.601701
21	6	0	1.325554	-0.653542	0.964003
22	7	0	2.644104	-0.686729	0.998612
23	6	0	3.299855	-0.010804	0.013147
24	7	0	2.652683	0.668238	-0.975731
25	6	0	1.333671	0.641458	-0.948197
26	6	0	0.474959	1.263890	-1.975632
27	6	0	1.002479	1.939866	-3.074487
28	1	0	2.078211	2.051091	-3.148553
29	6	0	0.136213	2.435057	-4.046529
30	1	0	0.521357	2.963396	-4.912308
31	6	0	-1.233637	2.222351	-3.889159
32	1	0	-1.945177	2.571121	-4.629827
33	6	0	-1.693040	1.544845	-2.760414
34	1	0	-2.749695	1.361035	-2.609097
35	6	0	4.756211	-0.013801	0.016509
36	6	0	5.473891	-0.695710	1.016920
37	1	0	4.932934	-1.224165	1.793151
38	6	0	6.863208	-0.694925	1.015749
39	1	0	7.380241	-1.230364	1.802273
40	6	0	7.598935	-0.019935	0.025162
41	6	0	6.866833	0.659104	-0.971739
42	1	0	7.395571	1.192362	-1.754305
43	6	0	5.482097	0.667230	-0.983168
44	1	0	4.946587	1.197577	-1.761743

45	6	0	9.133435	-0.000104	-0.004300
46	6	0	9.753916	-0.790021	1.163408
47	1	0	9.470620	-1.847476	1.140516
48	1	0	9.470523	-0.375419	2.136445
49	1	0	10.844453	-0.743896	1.095332
50	6	0	9.621733	-0.627504	-1.334174
51	1	0	10.715623	-0.616684	-1.368716
52	1	0	9.258479	-0.078030	-2.207625
53	1	0	9.291054	-1.666942	-1.426656
54	6	0	9.622284	1.467496	0.082643
55	1	0	10.716167	1.495622	0.059159
56	1	0	9.292093	1.939533	1.013471
57	1	0	9.258506	2.074037	-0.751937
58	6	0	-0.565648	-2.179163	-2.183230
59	1	0	0.231381	-1.438930	-2.216750
60	1	0	-1.072855	-2.147802	-3.157978
61	6	0	-0.004025	-3.574763	-1.928654
62	1	0	0.712211	-3.865296	-2.702377
63	1	0	0.523660	-3.585269	-0.968711
64	6	0	-1.164398	-4.558335	-1.915695
65	1	0	-1.468636	-4.806458	-2.940531
66	1	0	-0.882290	-5.498192	-1.426931
67	6	0	-3.416331	-5.017349	-1.070426
68	1	0	-2.979194	-5.881188	-0.554163
69	1	0	-3.709858	-5.358254	-2.070598
70	6	0	-4.617797	-4.502878	-0.285209
71	1	0	-5.141147	-5.344267	0.177499
72	1	0	-5.328851	-3.999096	-0.947135
73	6	0	-4.096264	-3.526342	0.762267
74	1	0	-4.879126	-3.141826	1.414776
75	1	0	-3.352694	-4.015928	1.402370
76	6	0	-2.388154	-2.721339	-0.783205
77	6	0	-4.152183	-1.165367	-0.000988
78	6	0	-5.551069	-1.187947	-0.039609
79	1	0	-6.088501	-2.123948	-0.094044
80	6	0	-6.248702	0.011611	-0.019727
81	1	0	-7.333692	0.014176	-0.025108
82	6	0	-5.545705	1.207886	0.007169
83	1	0	-6.079430	2.146284	0.056353
84	6	0	-4.146580	1.178886	-0.017596
85	6	0	-4.073027	3.540753	-0.776799
86	1	0	-4.851230	3.161242	-1.437771
87	1	0	-3.321293	4.028720	-1.408513
88	6	0	-4.600318	4.516985	0.268073
89	1	0	-5.115546	5.361778	-0.197540
90	1	0	-5.319890	4.014750	0.921893
91	6	0	-3.404194	5.024250	1.066141
92	1	0	-2.959489	5.888671	0.557374
93	1	0	-3.705610	5.362164	2.064988
94	6	0	-1.161256	4.555027	1.929246
95	1	0	-0.873526	5.496998	1.447916
96	1	0	-1.472816	4.798082	2.953115

97	6	0	-0.003089	3.569073	1.945415
98	1	0	0.708904	3.854901	2.724783
99	1	0	0.530575	3.582512	0.988815
100	6	0	-0.568986	2.173621	2.190870
101	1	0	0.226526	1.431812	2.225655
102	1	0	-1.081620	2.139057	3.162652
103	6	0	-2.381189	2.725520	0.780721

References:

1. (a) Parker, C. A. and Rees, W. T. *Analyst* 1960, **85**, 587, (b) Crosby, G. A.; Demas, J. N. *J. Phys. Chem.* 1971, **75**, 991.
2. Würth, C.; Grabolle, M.; Pauli, J.; Spieles, M.; Resch-Genger, U. *Nat. Protocol* 2013, **8**, 1535.
3. Wang, J.; Hanan, G. S. *Synlett*, 2005, **8**, 1251.
4. a) Santoni, M.-P.; Pal, A. K.; Hanan, G. S.; Proust, A.; Hasenknopf, B. *Inorg. Chem. Commun.* 2011, **14**, 399; b) M. I. J. Polson, E. A. Medlycott, G. S. Hanan, L. Mikelsons, N. J. Taylor, M. Watanabe, Y. Tanaka, F. Loiseau, R. Passalacqua, S. Campagna, *Chem. Eur. J.*, 2004, **10**, 3640; c) E. A. Medlycott, K. A. Udachin, G. S. Hanan, *Dalton Trans.*, 2007, 430.
5. *APEX2 (2007) version 2.4-0; Bruker Molecular Analysis Research Tool.* Bruker AXS Inc., Madison, WI 53719-1173.
6. Sheldrick, G. M. (1996). *SADABS*, Bruker Area Detector Absorption Corrections. Bruker AXS Inc., Madison, WI 53719-1173.
7. *SHELXTL (2001) version 6.12*; Bruker Analytical X-ray Systems Inc., Madison, WI 53719-1173.
8. Platon (A. L. SPEK, 2003).

9. Siemeling, U.; Bruggen, J. V. der; Vorfeld, U.; Neumann, B.; Stammler, A.; Stammler, H.-G.; Brockhinke, A.; Plessow, R.; Zanello, P.; Laschi, F.; Biani, F. F. de; Fontani, M.; Steenken, S.; Stapper, M. and Gurzadyan G. *Chem. Eur. J.*, 2003, **9**, 2819.
10. Medlycott, E. A.; Hanan, G. S.; Loiseau, F.; Campagna, S. *Chem. Eur. J.* 2007, **13**, 2837.